[2+2] Photocycloaddition Studies on Complex Tetronic Acid Esters Related to the Synthesis of Cembranoid Diterpenes

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1. General

All reactions involving water-sensitive chemicals were carried out in flame-dried glassware under positive pressure of argon with magnetic stirring. Tetrahydrofuran (THF) was purified using a SPS-800 solvent purification system (M. Braun). Triethylamine was distilled over calcium hydride. All other chemicals were either commercially available or prepared according to the cited references. For photochemical reactions, the reaction mixture was degassed by purging with argon in an ultrasonicating bath. Subsequently, the solution was transferred into quartz tubes (diameter: 1 cm, volume: 10 mL) and irradiated in a Rayonet RPR100 reactor, equipped with 16 Rayonet RPR2537 Å (λ = 254 nm) lamps. The reactor was cooled with an internal fan, the operating temperature for photochemical reactions was ca. 35 °C. Thin layer chromatography (TLC) was performed on silica coated glass plates (silica gel 60 F254) with detection by UV (λ = 254 nm) or KMnO₄ (0.5% in water) with subsequent heating. Flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh) with the indicated eluent. Common solvents for chromatography [pentane (P), ethyl acetate (EtOAc), diethyl ether (Et₂O), ethanol (EtOH), methanol (MeOH)] were distilled prior to use. IR spectra were recorded on a JASCO IR-4100 (ATR) or Perkin-Elmer 1600 FT/IR, MS / HRMS-measurements were performed on a Finnigan MAT 8200 (EI) / Finnigan MAT 95S (HR-EI). \(^1\)H and \(^{13}\)C NMR were recorded in CDCl₃ at 303 K on a Bruker AV-250, Bruker AV-360, Bruker AV-500. Chemical shifts are reported relative to CHCl₃ (δ = 7.26 ppm). Apparent multiplets that occur as a result of the accidental equality of coupling constants to those of magnetically non-equivalent protons are market as virtual (virt.). The multiplicities of the \(^{13}\)C NMR signal were determined by DEPT experiments, assignments are based on COSY, HMBC and HMQC experiments.
2. Substrate Synthesis

\((2S,3R,4'S)-4'-\text{Benzyl-3'}-(3\text{-hydroxy-2-vinylhept-6-enoxy})\text{oxazolidin-2'}-\text{one (2)}\)

To a solution of \((S,E)-4\text{-benzyl-3-(but-2-enoxy)}\text{oxazolidin-2-one (1)}\) (1.25 g, 5.09 mmol) in CH₂Cl₂ (30 mL) was added subsequently di-\(n\)-butylboryltriflate (5.60 mL, 5.60 mmol, 1 M in CH₂Cl₂) and NEt₃ (0.99 mL, 0.72 g, 7.13 mmol) dropwise at −78 °C. The mixture was stirred at −78 °C for 1 h and further 20 min at 0 °C. After cooling to −78 °C a solution of pent-4-en-1-al (772 mg, 7.64 mmol) in CH₂Cl₂ (8 mL) was added dropwise. The reaction was kept at −78 °C over night and at 0 °C for 1 h before it was quenched by addition of phosphate-buffer (8 mL, pH = 7) followed by MeOH (30 mL). After 5 min, H₂O₂ (8 mL, 35%) was added at 0 °C and the mixture was stirred for 1 h. Most of the solvent was removed in vacuo and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with HCl (30 mL, 1 M), NaHCO₃ solution (30 mL, 5%), brine (30 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/\text{EtOAc} = 4/1 → 2/1) to afford 1.22 g (3.72 mmol, 71%) 2 as a colorless oil.

**DC:** \(R_f = 0.35\) (P/\text{EtOAc} = 7/3).

\([\alpha]_D^{20} = + 4.1\) (c = 1.00, CHCl₃).

**IR (ATR):** \(\tilde{\nu} (\text{cm}^{-1}) = 3405\) (OH), 3060 (C=CH), 2969 (CH), 1775 (CO), 1692 (CO).

**\(^1\text{H-NMR}\) (360 MHz, CDCl₃):** \(\delta\) (ppm) = 1.50-1.72 (m, 2 H, C4-H), 2.11-2.33 (m, 2 H, C5-H), 2.78 (dd, \(^2J = 13.4\) Hz, \(^3J = 9.4\) Hz, 1 H, PhCH/H), 3.03 (br s, 1 H, OH), 3.26 (dd, \(^2J = 13.4\) Hz, \(^3J = 3.3\) Hz, 1 H, PhCH/H), 4.03-4.06 (m, 1 H, C2-H), 4.18-4.27 (m, 2 H, C5′-H), 4.57-4.60 (m, 1 H, C3-H), 4.75 (ddt, \(^3J = 9.4\) Hz, \(^2J = 7.6\) Hz, \(^3J = 3.3\) Hz, 1 H, C4′-H), 4.97-5.10 (m, 1 H, C7-Hcis), 5.08 (virt. td, \(^2J ≈ 4J = 1.6\) Hz, \(^3J = 17.1\) Hz, 1 H, C7-Htrans), 5.41-5.51 (m, 2 H, C2″-H), 5.84 (ddt, \(^3J = 17.1\) Hz, \(^2J = 10.2\) Hz, \(^3J = 6.7\) Hz, 1 H, C6-H), 6.06 (ddd, \(^3J = 17.1\) Hz, \(^2J = 10.2\) Hz, \(^3J = 9.0\) Hz , 1 H, C1″-H), 7.20-7.36 (m, 5 H, Ph).
$^{13}$C-NMR (90.6 MHz, CDCl$_3$): δ (ppm) = 29.9 (t, C-5), 33.2 (t, C-4), 37.6 (t, PhCH$_2$), 52.1 (d, C-2), 55.1 (d, C-4'), 66.0 (t, C-5'), 71.0 (d, C-3), 115.0 (t, C-7), 121.6 (t, C-2''), 127.4 (d, C-4''), 129.0 (d, C-3'''), 129.4 (d, C-2''''), 131.0 (s, C-1'''), 134.9 (d, C-1'''), 138.1 (d, C-6), 152.9 (s, C-2''), 174.2 (s, C-1).

MS (EI, 70 eV): $m/z$ (%) = 329 (1) [M$^+$], 244 (33) [(C$_{14}$H$_{14}$NO$_3$)$^+$], 230 (20), 154 (35) [(C$_9$H$_{13}$O$_2$)$^+$], 91 (67), 86 (20), [(C$_5$H$_3$O)$^+$], 69 (100) [(C$_4$H$_4$O$_2$)$^+$].

HRMS (EI): calcd. C$_{19}$H$_{23}$NO$_4^+$ [M$^+$]: 329.1622; found: 396.1614.

(4$'$S,1$'$S,6$'$R)-4$'$-Benzy1-3$'$-(6-hydroxy-cyclohex-2-encarbonyl)oxazolidin-2$'$-one (20)

To a solution of Grubbs-I catalyst (157 mg, 185 μmol, 3 mol-%) in degassed CH$_2$Cl$_2$ (150 mL) was added a solution of alcohol 2 (2.03 mg, 6.16 mmol) in degassed CH$_2$Cl$_2$ (100 mL) at ambient temperature dropwise. The mixture was stirred for 24 h and concentrated in vacuo. The crude product was purified by flash chromatography (P/EtOAc = 1/1) to afford 1.62 g (5.38 mmol, 87%) 20 as a colorless oil.

**TLC:** $R_f = 0.21 \text{ (P/EtOAc} = 1/1).$

$[α]_D^{20} = +169 \text{ (c = 0.10, CHCl}_3).$

**IR** (ATR): $\tilde{ν}$ (cm$^{-1}$) = 3424 (OH), 3030 (C=CH), 2973 (CH), 1775 (CO), 1700 (CO).

$^1$H-NMR (360 MHz, CDCl$_3$): δ (ppm) = 1.87-1.93 (m, 1 H, C4-HH), 2.01-2.23 (m, 2 H, C4-HH/C5-HH), 2.27-2.42 (m, 1 H, C5-HH), 2.69-2.75 (m, 1 H, C1-H), 2.82 (dd, $^2$J = 13.3 Hz, $^3$J = 9.4 Hz, 1 H, PhCH/H), 3.03 (dd, $^2$J = 13.3 Hz, $^3$J = 3.3 Hz, 1 H, PhCH/H), 4.19-4.30 (m, 2 H, C5'-H), 4.56-4.70 (m, 1 H, C6-H), 4.78 (ddt, $^3$J = 9.4 Hz, $^3$J = 7.6 Hz, $^3$J = 3.3 Hz, 1 H, C4'-H), 5.68 (ddt, $^3$J = 9.8 Hz, $^3$J = 4.3 Hz, $^4$J = 2.0 Hz 1 H, C2-H), 6.01 (ddd, $^3$J = 9.8 Hz, $^3$J = 6.1 Hz, $^3$J = 3.7 Hz, 1 H, C3-H), 7.21-7.39 (m, 5 H, Ph).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): δ (ppm) = 22.4 (t, C-4), 27.5 (t, C-5), 37.9 (t, PhCH$_2$), 45.6 (d, C-1), 55.4 (d, C-4'), 66.3 (t, C-5'), 67.1 (d, C-6), 121.4 (d, C-2), 127.4 (s, C-1''), 129.0 (d, C-3''), 129.4 (d, C-2'''), 130.3 (d, C-4''), 135.1 (d, C-3), 153.6 (s, C-2''), 173.1 (s, CO).
**MS (EI, 70 eV):** $m/z$ (%) = 301 (1) [M$^+$], 178 (37) [(C$_{10}$H$_{10}$NO$_2$)$^+$], 92 (100) [(C$_7$H$_8$)$^+$], 91 (83) [(C$_7$H$_7$)$^+$], 86 (77) [(C$_3$H$_3$NO$_2$)$^+$].

**HRMS (EI):** calcd. for C$_{17}$H$_{19}$NO$_4$ $^+$ [M$^+$]: 301.1309, found: 301.1300.

(1S,4′S,6R)-4′-Benzyl-3′-{6-[tert-butyldimethylsilyl]oxy}cyclohex-2-encarbonyl-oxazolidin-2′-one (21)

![Chemical Structure of 21](image)

To a solution of alcohol 20 (0.92 g, 3.07 mmol) and 2,6-lutidine (0.79 mL, 0.73 g, 7.76 mmol) in CH$_2$Cl$_2$ (25 mL), TBSOTf (1.41 mL, 1.63 g, 6.15 mmol) was added dropwise at $-10$ °C. The mixture was warmed up to ambient temperature over 1.5 h and stirred for further 3 h, prior to dilution with Et$_2$O (25 mL) followed by hydrolysis with H$_2$O (25 mL). The aqueous layer was separated and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with HCl (20 mL, 0.5 m) and sat. NaHCO$_3$ solution (20 mL), dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (P/EtOAc = 95/5) to afford 1.27 g (3.05 mmol, 94%) 21 as a colorless oil.

**TLC:** $R_t = 0.72$ (P/EtOAc = 1/1).

$[a]_D^{20} = +149$ (c = 0.14, CHCl$_3$).

**IR (ATR):** $\tilde{\nu}$ (cm$^{-1}$) = 3030 (C=C), 2927 (CH), 2856 (CH), 1779 (CO), 1704 (CO).

**$^1$H-NMR (360 MHz, CDCl$_3$):** $\delta$ (ppm) = 0.03 (s, 3 H, SiCH$_3$), 0.07 (s, 3 H, SiCH$_3$), 0.86 [s, 9 H, SiC(CH$_3$)$_3$], 1.72-1.81 (m, 1 H, C4-HH), 2.04-2.16 (m, 2 H, C4-HH/C5-HH), 2.27-2.41 (m, 1 H, C5-HH), 2.79 (dd, $^2J = 13.3$ Hz, $^3J = 9.8$ Hz, 1 H, PhCH$_2$H), 3.36 (dd, $^2J = 13.3$ Hz, $^3J = 3.3$ Hz, 1 H, PhCH$_2$H), 4.11-4.20 (m, 2 H, C5′-H), 4.26 (ddd, $^3J = 8.7$ Hz, $^3J = 4.3$ Hz, $^4J = 2.1$ Hz, 1 H, C1-H), 4.66 (dd, $^3J = 9.8$ Hz, $^3J = 7.4$ Hz, $^3J = 3.3$ Hz, 1 H, C4′-H), 4.82-4.87 (m, 1 H, C6-H), 5.63 (ddd, $^3J = 9.8$ Hz, $^3J = 4.3$ Hz, $^4J = 2.0$ Hz, 1 H, C2-H), 5.98 (ddd, $^3J = 9.8$ Hz, $^3J = 3.4$ Hz, $^4J = 2.1$ Hz, 1 H, C3-H), 7.24-7.37 (m, 5 H, Ph).
$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = −5.1 (q, SiCH$_3$), −4.7 (q, SiCH$_3$), 17.9 [s, SiC(CH$_3$)$_3$], 23.1 (t, C-4), 25.7 [q, SiC(CH$_3$)$_3$], 28.0 (t, C-5), 37.9 (t, PhCH$_2$), 45.0 (d, C-1), 56.0 (d, C-4'), 65.8 (t, C-5'), 68.4 (d, C-6), 122.0 (d, C-2), 127.3 (s, C-1’’), 128.9 (d, C-3’’), 129.5 (d, C-2’’), 130.0 (d, C-3), 135.5 (d, C-4’’), 153.4 (s, C-2’'), 172.3 (s, CO).

**MS** (EI, 70 eV): $m/z$ (%) = 415 (1) [M$^+$], 400 (2) [(M–CH$_3$)$^+$], 358 (57) [(M–C$_4$H$_9$)$^+$], 75 (100) [(C$_2$H$_7$OSi)$^+$].

**HRMS** (ESI): calcd. for C$_{23}$H$_{34}$NO$_4$Si$^+$ [(M+H)$^+$]: 416.22523, found: 416.22516.

(1R,6R)-6-[(tert-Butyldimethylsilyl)cyclohex-2-en-1-yl]methanol (3)

To a solution of amide 21 (306 mg, 0.74 mmol) and methanol (72.1 $\mu$L, 57.0 mg, 1.78 mmol) in THF (15 mL), LiBH$_4$ (0.45 mL, 1.78 mmol, 4 M in THF) was added dropwise at $-10$ °C via syringe pump. The mixture was stirred for 24 h, increasing the temperature to 0 °C. The reaction was quenched by addition of NaOH (10 mL, 1 M) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/EtOAc = 6/1 → 2/1) to afford 129 mg (0.53 mmol, 72%) primary alcohol 3 as a colorless oil.

**TLC:** $R_f$ = 0.15 (P/Et$_2$O = 8/1).

[α]$_D^{20}$ = +64.2 (c = 1.00, CHCl$_3$).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3418 (OH), 3023 (C=CH), 2923 (CH), 2854 (CH), 1469 (C=C).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.13 (s, 3 H, SiCH$_3$), 0.14 (s, 3 H, SiCH$_3$), 0.93 [s, 9 H, SiC(CH$_3$)$_3$], 1.69-1.76 (m, 1 H, C4-HH), 1.80-1.90 (m, 1 H, C4-HH), 2.03-2.21 (m, 2 H, C5-H), 2.53-2.62 (m, 1 H, C1-H), 3.35 (br s, 1 H, OH), 3.59 (dd, $^3J$ = 11.3 Hz, $^1J$ = 3.3 Hz, 1 H, CHHOH), 3.83 (dd, $^2J$ = 11.3 Hz, $^3J$ = 8.5 Hz, 1 H, CH/OH), 4.20 (ddd, $^3J$ = 10.2 Hz, $^2J$ = 5.2 Hz, $^3J$ = 3.5 Hz, $^1J$ = 3.5 Hz, 1 H, C6-H), 5.47 (ddtt, $^3J$ = 9.8 Hz, $^2J$ = 4.3 Hz, $^4J$ = 2.0 Hz, 1 H, C2-H), 5.71 (ddddd, $^3J$ = 9.8 Hz, $^4J$ = 6.1 Hz, $^3J$ = 3.7 Hz, $^4J$ = 1.7 Hz, 1 H, C3-H).

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\(^{13}\)C-NMR (90.6 MHz, CDCl\(_3\)): \(\delta\) (ppm) = −5.1 (q, SiCH\(_3\)), −4.6 (q, SiCH\(_3\)), 18.0 [s, SiC(CH\(_3\))\(_3\)], 24.3 (t, C-4), 25.8 [q, SiC(CH\(_3\))\(_3\)], 27.5 (t, C-5), 42.6 (d, C-1), 64.1 (d, C-6), 72.2 (t, CH\(_2\)OH), 125.4 (d, C-2), 128.4 (d, C-3).

GC-MS [STD]: \(t_R = 12.4\) min.

MS (EI, 70 eV): \(m/z\) (%) = 242 [M\(^{+}\)], 227 (2) [(M–CH\(_3\))\(^{+}\)], 185 (75) [(M–C\(_4\)H\(_9\))\(^{+}\)], 75 (100) [(C\(_2\)H\(_7\)OSi\(^{+}\)].

HRMS (ESI): calcd. for C\(_{13}\)H\(_{27}\)O\(_2\)Si\(^{+}\) [(M+H\(^{+}\)]: 243.17766, found: 243.17748.

\((2R,5R)\)-5-(But-3ʹ-en-1ʹ-yl)-2-(tert-butyl)-5-methyl-1,3-dioxolan-4-one (22)

To a solution of freshly distilled diisopropylamine (4.04 mL, 2.89 g, 28.6 mmol) in THF (100 mL) at −78 °C was added n-BuLi (10.5 mL, 26.4 mmol, 2.5 M in hexane) and the mixture was stirred at −78 °C for 1 h, then the dioxolanone 4 (3.48 g, 22.0 mmol) in THF (45 mL) was added dropwise and the mixture stirred for 45 min. 4-Iodobutene (2.00 g, 11.0 mmol) in THF (33 mL) was added, the reaction mixture warmed up slowly to −10 °C and stirred at this temperature for 1 h more. The reaction was quenched with NH\(_4\)Cl (40 mL), and the aqueous phase extracted with Et\(_2\)O (3 × 100 mL). The combined organic layers were washed with NaHCO\(_3\) (40 mL), brine (40 mL), dried over MgSO\(_4\), filtered and concentrated \(\text{in vacuo}\). The crude product was purified by flash chromatography (P/CH\(_2\)Cl\(_2\) = 9/1) to afford 2.03 g (9.54 mmol, 86%) dioxolanone 22 as single diastereoisomer.

TLC: \(R_f = 0.71\) (P/EtOAc = 3/1).

[\(\alpha\)]\(_D\)\(^{20}\) = +33.9 (c = 1.00, CHCl\(_3\)).

IR (ATR): \(\tilde{\nu}\) (cm\(^{-1}\)) = 2977 (w, CH), 2963 (w, CH), 1792 (s, CO), 1486 (m, CH).

\(^1\)H-NMR (360 MHz, CDCl\(_3\)): \(\delta\) (ppm) = 0.98 [s, 9 H, C(CH\(_3\))\(_3\)], 1.47 (s, 3 H, CH\(_3\)), 1.78-1.91 (m, 2 H, C2ʹ-H), 2.08-2.30 (m, 2 H, C1ʹ-H), 4.99 (dd, \(^2\)J = 1.6 Hz, \(^3\)J = 10.2 Hz, 1 H, C4ʹ-H\(_{\text{cis}}\)), 5.06 (dd, \(^2\)J = 1.6 Hz, \(^3\)J = 17.1 Hz, 1 H, C4ʹ-H\(_{\text{trans}}\)), 5.19 (s, 1 H, C2-H), 5.82 (ddt, \(^3\)J = 17.1 Hz, \(^2\)J = 10.2 Hz, \(^3\)J = 6.4 Hz, 1 H, C3ʹ-H).
\[ ^{13}\text{C-NMR} \ (90.6 \text{ MHz, CDCl}_3): \ \delta (\text{ppm}) = 22.8 \ (\text{t, C-2'}), \ 23.3 \ [\text{q, C(CH}_3)_3], \ 27.8 \ (\text{q, CH}_3), \ 34.6 \ [\text{s, C(CH}_3)_3], \ 35.5 \ (\text{t, C-1'}), \ 79.6 \ (\text{s, C-5}), \ 108.5 \ (\text{d, C-2}), \ 115.3 \ (\text{t, C-4'}), \ 137.0 \ (\text{d, C-3'}), \ 175.6 \ (\text{s, C-4}). \]

\[ \text{MS (El, 70 eV): } m/z \ (%) = 155 \ (15) \ [(\text{M–C}_4\text{H}_9)], \ 43 \ (100) \ [(\text{C}_2\text{H}_3\text{O})^+]. \]

\[ \text{HRMS (El): calcd. for C}_8\text{H}_{11}\text{O}_3 \ [(\text{M–C}_4\text{H}_9)^+]: 155.0703; \text{ found: 155.0701.} \]

\[ (2\text{R})\text{-Methyl 2-hydroxy-2-methylhex-5-enoate (23)} \]

\[ \text{Methanol (4.00 mL) was slowly added to sodium (350 mg, 15.2 mmol) at 0 °C and the mixture was stirred until complete dissolution of sodium. Then this solution was added to a stirred solution of dioxolanone 22 (1.90 g, 8.95 mmol) in MeOH (25 mL) at 0 °C and the reaction mixture was stirred at this temperature for 2 h. The reaction was quenched with cold water (20 mL) and the aqueous phase was extracted with EtOAc (3 × 70 mL). The combined organic layers were washed with brine (20 mL), dried over Na}_2\text{SO}_4, \text{ filtered and concentrated}\ in\ vacuo. \text{ The crude product was purified by flash chromatography (P/Et}_2\text{O = 3/1) to afford 1.30 g (8.19 mmol, 92%) methyl ester 23 as a colorless oil.} \]

\[ \text{TLC: } R_f = 0.57 \ (\text{P/Et}_2\text{O = 2/1).} \]

\[ [\alpha]_D^{20} = -12.3 \ (c = 0.50, \text{ CHCl}_3). \]

\[ \text{IR (ATR): } \tilde{\nu} (\text{cm}^{-1}) = 3524 \ (\text{br. w, OH}), 3076 \ (\text{w, C=C}), 2978 \ (\text{w, CH}), 2952 \ (\text{w, CH}), 1729 \ (\text{s, CO}), 1554 \ (\text{m, C=C}). \]

\[ ^1\text{H-NMR} \ (360 \text{ MHz, CDCl}_3): \ \delta (\text{ppm}) = 1.42 \ (\text{s, 3 H, CH}_3), 1.73-1.97 \ (\text{m, 3 H, C3-HH/C4-H}), 2.16-2.26 \ (\text{m, 1 H, C3-HH}), 3.14 \ (\text{br s, 1 H, OH}), 3.81 \ (\text{s, 3 H, OCH}_3), 4.98 \ (\text{dd, }^2J = 1.6 \text{ Hz, }^3J = 10.2 \text{ Hz, 1 H, C6-Hcis}), 5.04 \ (\text{dd, }^2J = 1.6 \text{ Hz, }^3J = 17.1 \text{ Hz, 1 H, C6-Htrans}), 5.79 \ (\text{ddt, }^3J = 17.1 \text{ Hz, }^3J = 10.2 \text{ Hz, }^3J = 6.4 \text{ Hz, 1 H, C5-H}). \]

\[ ^{13}\text{C-NMR} \ (90.6 \text{ MHz, CDCl}_3): \ \delta (\text{ppm}) = 26.2 \ (\text{q, CH}_3), 28.1 \ (\text{t, C-4}), 39.1 \ (\text{t, C-3}), 52.7 \ (\text{q, OCH}_3), 74.3 \ (\text{s, C-2}), 114.9 \ (\text{t, C-6}), 137.8 \ (\text{d, C-5}), 177.5 \ (\text{s, C-1}). \]

\[ \text{GC-MS [STD]: } t_R = 7.11 \text{ min.} \]

\[ \text{MS (El, 70 eV): } m/z \ (%) = 158 \ (45) \ [\text{M}^+], \ 43 \ (100) \ [(\text{C}_2\text{H}_3\text{O})^+]. \]

\[ \text{HRMS (El): calcd. for C}_8\text{H}_{14}\text{O}_3 \ [\text{M}^+]: 158.0937; \text{ found: 158.0933.} \]
(2R)-Methyl 2-acetoxy-2-methylhex-5-enoate (5a)

To solution of methyl ester 23 (500 mg, 3.16 mmol) in toluene (16 mL) was added pyridine (0.51 mL, 0.50 g, 6.32 mmol), acetic anhydride (0.50 mL, 0.54 g, 6.32 mmol), DMAP (77.0 mg, 0.63 mmol) and the mixture was stirred at 80 °C overnight. The reaction mixture was cooled to ambient temperature and concentrated in vacuo. The crude product was purified by flash chromatography (P/Et₂O = 9/1) to afford 500 mg (2.50 mmol, 79%) acetate 5a as a colorless oil.

TLC: \( R_f = 0.69 \) (P/EtOAc = 2/1).

\([\alpha]_D^{20} = +21.3 \) (c = 0.20, CHCl₃).

IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3076 (w, C=C), 2975 (w, CH), 2956 (w, CH), 1739 (s, CO).

\(^1\)H-NMR (360 MHz, CDCl₃): \( \delta \) (ppm) = 1.60 (s, 3 H, CH₃), 1.85-1.93 (m, 1 H, C3-HH), 2.00-2.05 (m, 1 H, C3-HH), 2.08 (s, 3 H, COCH₃), 2.07-2.17 (m, 2 H, C4-H), 3.74 (s, 3 H, OCH₃) 5.00 (ddd, \( ^2\)J = 1.6 Hz, \( ^3\)J = 10.2 Hz, \( ^4\)J = 1.4 Hz, 1 H, C6-H cis), 5.04 (ddd, \( ^2\)J = 1.6 Hz, \( ^3\)J = 17.1 Hz, \( ^4\)J = 1.3 Hz, 1 H, C6-H trans), 5.81 (ddt, \( ^3\)J = 17.1 Hz, \( ^3\)J = 10.2 Hz, \( ^3\)J = 6.4 Hz, 1 H, C5-H).

\(^1\)C-NMR (90.6 MHz, CDCl₃): \( \delta \) (ppm) = 21.2 (q, COCH₃), 21.4 (q, CH₃), 27.5 (t, C-4), 37.3 (t, C-3), 52.3 (q, OCH₃), 80.4 (s, C-2), 115.1 (t, C-6), 137.3 (d, C-5), 170.0 (s, COCH₃), 172.6 (s, C-1).

MS (EI, 70 eV): \( m/z \) (%) = 141 (24) [(M–C₂H₅O₂)^+], 55 (3) [(C₄H₇]^+), 43 (100) [(C₂H₃O)^+].

HRMS (EI): calcd. for C₈H₁₃O₂^+ [(M–C₂H₅O₂)^+]: 141.0910; found: 141.0907.

(5R)-5-(But-3’-en-1’-yl)-5-methylfuran-2(5H)-one (6a)

(5R)-5-(But-3’-en-1’-yl)-5-methylfuran-2(5H)-one (6a)

S10
To a solution of lithium hexamethyldisilazane (6.60 mL, 6.60 mmol, 1 M in THF) in THF (6 mL) was added a solution of acetate 5a (600 mg, 3.00 mmol) in THF (3 mL) at −78 °C and the mixture was stirred for 2 h. The reaction was quenched with water (10 mL) and warmed up to ambient temperature. The mixture was acidified with concentrated HCl (pH = 1) and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo to afford 502 mg (2.99 mmol, >99%) tetronic acid 6a.

**TLC:** $R_f = 0.10$ (CHCl₃/iPrOH = 5/1).

$[\alpha]_D^{20} = +34.7$ ($c = 0.10$, CHCl₃).

**IR** (ATR): $\tilde{\nu}$ (cm⁻¹) = 3408 (br m, OH), 2980 (w, CH), 2918 (w, CH), 1737 (s, CO).

**¹H-NMR** (360 MHz, DMSO-d₆): $\delta$ (ppm) = 1.38 (s, 3 H, CH₃), 1.70-2.01 (m, 4 H, C₁'-H/C₂'-H), 4.89 (s, 1 H, C₃-H), 4.99 (dd, $J = 1.6$ Hz, $J = 10.2$ Hz, 1 H, C₄'-Hcis), 5.05 (dd, $J = 1.6$ Hz, $J = 5.4$ Hz, 1 H, C₄'-Htrans), 5.79 (ddt, $J = 17.1$ Hz, $J = 10.2$ Hz, $J = 6.4$ Hz, 1 H, C₃'-H), 12.6 (br s, 1 H, OH).

**¹³C-NMR** (90.6 MHz, DMSO-d₆): $\delta$ (ppm) = 23.1 (q, CH₃), 27.0 (t, C-2'), 34.9 (t, C-1'), 83.1 (s, C-5), 87.3 (d, C-3), 115.0 (t, C-4'), 137.5 (d, C-3'), 172.0 (s, C-2), 183.7 (s, C-4).

**MS** (EI, 70 eV): $m/z$ (%) = 168 (1) [M⁺], [(M–C₄H₇)⁺], 55 (25) [(C₄H₇)⁺], 43 (100).

**HRMS** (EI): calcd. for C₅H₅O₃⁺ [(M–C₄H₇)⁺]: 113.0311; found: 113.0307.

(2R)-Ethyl 1'-[(methoxy-2-methyl-1-oxohex-5-en-2-yl)malonate (5b)

![Chemical structure of 23](image1)

![Chemical structure of 5b](image2)

To a solution of Methylester 23 (500 mg, 3.16 mmol) in CH₂Cl₂ (40 mL) was added mono-ethylmalonate (0.75 mL, 0.84 g, 6.32 mmol) and DMAP (70.9 mg, 0.63 mmol). The mixture was cooled to 0 °C and DCC (7.59 mL, 7.59 mmol, 1 M in CH₂Cl₂) was added dropwise. The solution was stirred overnight, filtered and concentrated in vacuo. The residue was dissolved in Et₂O (40 mL), filtered and washed with NH₄Cl (20 mL). The aqueous layer is separated and extracted with Et₂O (3 × 50 mL). The combined organic layers were washed with brine,
dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/CH₂Cl₂ = 5/4) to afford 674 mg (2.47 mmol, 69%) ester 5b as a yellow oil.

**TLC:** $R_f = 0.61$ (P/EtOAc = 2/1).

$[\alpha]_D^{20} = -3.0$ ($c = 0.17$, CHCl₃).

**IR** (ATR): $\tilde{\nu}$ (cm⁻¹) = 2981 (w, CH), 1746 (s, CO), 1736 (s, CO), 1730 (s, CO).

**1H-NMR** (360 MHz, CDCl₃): $\delta$ (ppm) = 1.30 (t, $^3J = 7.1$ Hz, 3 H, OCH₂CH₃), 1.63 (s, 3 H, CH₃), 1.87-2.21 (m, 4 H, C₃-H/C₄-H), 3.38 (d, $^2J = 17.5$ Hz, 1 H, C₂'-HH), 3.38 (d, $^2J = 17.5$ Hz, 1 H, C₂'-HH), 3.75 (s, 3 H, OCH₃), 4.23 (q, $^3J = 7.1$ Hz, 2 H, OCH₂CH₃), 5.00 (dd, $^2J = 1.6$ Hz, $^3J = 10.2$ Hz, 1 H, C₆-Hcis), 5.04 (dd, $^2J = 1.6$ Hz, $^3J = 17.1$ Hz, 1 H, C₆-Htrans), 5.79 (ddt, $^3J = 17.1$ Hz, $^3J = 10.2$ Hz, $^3J = 6.4$ Hz, 1 H, C₅-H).

**13C-NMR** (90.6 MHz, CDCl₃): $\delta$ (ppm) = 14.1 (q, OCH₂CH₃), 21.3 (q, CH₃), 27.4 (t, C-4), 37.2 (t, C-3), 41.8 (t, C-2'), 52.4 (q, OCH₃), 61.5 (t, OCH₂CH₃), 81.6 (s, C-2), 115.2 (t, C-6), 137.2 (d, C-5), 165.3 (s, C-1), 166.2 (s, C-3'), 172.0 (s, C-2').

**MS** (EI, 70 eV): $m/z$ (%) = 227 (15) [(M–OC₂H₅)+], 141 (30) [(C₈H₁₅O₂)+], 125 (100) [(C₅H₇O₃)+].

**HRMS** (EI): calcd. for C₁₁H₁₅O₅⁺ [(M–OC₂H₅)+]: 227.0914; found: 227.0920.

(5R)-5-(But-3'-en-1'-yl)-3-ethoxycarbonyl-5-methylfuran-2(5H)-one (6b)

![Chemical structure of 6b](attachment:structure.png)

To a solution of lithium hexamethyldisilazane (0.35 mL, 0.35 mmol, 1 M in THF) in THF (2 mL) was added a solution of ester 5b (47.0 mg, 0.17 mmol) in THF (2 mL) at −78 °C and the mixture was stirred for 2 h. The reaction was quenched with water (5 mL) and warmed up to ambient temperature. The mixture was acidified with concentrated HCl (pH = 1) and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo to afford 23.8 mg (0.99 mmol, 57%) tetronic acid 6b.

**TLC:** $R_f = 0.61$ [CH₂Cl₂/MeOH(1% HCOOH) = 9/1].

$[\alpha]_D^{20} = +83.6$ ($c = 0.15$, CHCl₃).
IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3240 (br. w, OH), 3076 (w, C=C), 2979 (w, CH), 2932 (m, CH), 1749 (s, CO), 1623 (s, CO).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 1.42 (t, $^3$J = 7.1 Hz, 3 H, OCH$_2$CH$_3$), 1.57 (s, 3 H, CH$_3$), 1.89-2.20 (m, 4 H, C1'-H/C2'-H), 4.44 (q, $^3$J = 7.1 Hz, 2 H, OCH$_2$CH$_3$), 4.98-5.07 (m, 2 H, C4'-H), 5.69-5.83 (m, 1 H, C3'-H). OH-proton was not visible.

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 14.2 (q, OCH$_2$CH$_3$), 22.9 (q, CH$_3$), 27.3 (t, C-2'), 35.7 (t, C-1'), 62.0 (t, OCH$_2$CH$_3$), 82.5 (s, C-3), 82.8 (s, C-5), 115.7 (t, C-4'), 136.5 (d, C-3'), 166.6 (s, CO), 168.3 (s, C-2), 193.8 (s, C-4).

MS (EI, 70 eV): $m/z$ (%) = 195 (1) [(M–OC$_2$H$_5$)$^+$], 186 (46) [(M–C$_4$H$_7$)$^+$], 140 (95) [(M–C$_6$H$_{12}$O)$^+$], 55 (25) [(C$_4$H$_7$)$^+$], 43 (100).

HRMS (EI): calcd. for C$_8$H$_9$O$_5^+$ [(M–C$_4$H$_7$)$^+$]: 185.0523; found: 185.0520.

(2R,5R)-5-(But-3′-yn-1′-yl)-2-(tert-butyl)-5-methyl-1,3-dioxolan-4-one (24)

To a solution of freshly distilled diisopropylamine (0.31 mL, 222 mg, 3.12 mmol) in THF (6 mL) at $-78$ °C was added $n$-BuLi (1.15 mL, 2.88 mmol, 2.5 M in hexane) and the mixture was stirred at $-78$ °C for 1 h, then dioxolanone 4 (380 mg, 2.40 mmol) in THF (2 mL) was added dropwise and the mixture stirred for 45 min. 1-Iodobut-3-yn (216 mg, 1.20 mmol) in THF (2 mL) was added, the reaction mixture warmed up slowly to $-10$ °C and stirred at this temperature for 1 h more. The reaction was quenched with NH$_4$Cl (10 mL), and the aqueous phase extracted with Et$_2$O (3 × 30 mL). The combined organic extracts were washed with NaHCO$_3$ (10 mL), brine (10 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/Et$_2$O = 98/2) to afford 319 mg (1.52 mmol, 63%) dioxolanone 24 as single diastereoisomer.

TLC: $R_f$ = 0.59 (P/EtOAc = 9/1).

$[\alpha]_{D}^{20}$ = +25.6 (c = 0.45, CHCl$_3$).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3295 (w, C≡CH), 2963 (m, CH), 2875 (w, CH), 1796 (s, CO), 1485 (w, CH).
$^1$H-NMR (360 MHz, CDCl$_3$): δ (ppm) 0.96 [s, 9 H, C(CH$_3$)$_3$], 1.45 (s, 3 H, CH$_3$), 1.90-2.02 (m, 1 H, C1'-H), 2.00 (t, $^4$J = 2.4 Hz, 1 H, C4'-H), 2.08 (ddd, $^2$J = 14.1 Hz, $^3$J = 9.1 Hz, $^3$J = 6.5 Hz, 1 H, C1'-H), 3.21-3.40 (m, 2 H, C2'-H), 5.22 (s, 1 H, C2-H).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): δ (ppm) = 13.4 (t, C-2'), 22.7 (q, CH$_3$), 23.5 [q, C(CH$_3$)$_3$], 34.7 (t, C-1'), 34.9 [s, C(CH$_3$)$_3$], 69.3 (d, C-4'), 79.1 (s, C-3'), 82.8 (s, C-5), 108.7 (d, C-2), 175.2 (s, C-4).

MS (EI, 70 eV): m/z (%) = 153 (39) [(M–C$_4$H$_9$)$_3$], 125 (24) [(C$_7$H$_9$O$_2$)$^+$], 57 (30) [(C$_4$H$_9$)$_3$], 43 (100).

HRMS (EI): calcd. for C$_8$H$_{10}$O$_3$ $^+$ [(M–C$_4$H$_9$)$_3$]: 153.0546; found: 153.0553.

$(2R)$-Methyl 2-hydroxy-2-methylhex-5-ynoate (25)

![Chemical Structure](image)

MeOH (2.3 mL) was slowly added to sodium 179 mg (7.80 mmol) at 0 °C and the mixture was stirred until complete dissolution of sodium. Then this solution was added to a stirred solution of dioxolanone 24 (1.10 g, 5.20 mmol) in MeOH (20 mL) at 0 °C and the reaction mixture was stirred at this temperature for 2 h. The reaction was quenched with cold water (15 mL) and the aqueous phase was extracted with EtOAc (3 × 70 mL). The combined organic layers were washed with brine (15 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/Et$_2$O = 5/1) to afford 688 g (4.41 mmol, 85%) methyl ester 25 as a colorless oil.

TLC: $R_f$ = 0.63 (P/Et$_2$O = 3/1).

$[\alpha]_D^{20}$ = −23.4 (c = 0.18, CHCl$_3$).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3524 (br. w, OH), 3295 (w, C=CH), 2960 (m, CH), 1739 (s, CO).

$^1$H-NMR (360 MHz, CDCl$_3$): δ (ppm) = 1.42 (s, 3 H, CH$_3$), 1.88-1.95 (m, 1 H, C3-H), 2.19 (dddd, $^2$J = 16.8 Hz, $^3$J = 9.0 Hz, $^3$J = 6.5 Hz, $^4$J = 2.6 Hz, 1 H, C4-H), 2.36 (ddddd, $^2$J = 16.8 Hz, $^3$J = 9.1 Hz, $^3$J = 5.6 Hz, $^4$J = 2.6 Hz, 1 H, C4-H), 3.26 (br s, 1 H, OH), 3.79 (s, 3 H, OCH$_3$).
$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 13.2 (t, C-4), 26.4 (q, CH$_3$), 38.5 (t, C-3), 52.8 (q, OCH$_3$), 68.5 (d, C-6), 73.7 (s, C-2), 83.5 (s, C-5), 177.1 (s, C-1).

**MS** (EI, 70 eV): $m/z$ (%) = 156 (5) [M$^+$], 97 (100) [(C$_6$H$_9$O)$_2$].

**HRMS** (EI): calcd. for C$_8$H$_{12}$O$_3$ $^+$ [M$^+$]: 156.0781; found: 156.0778.

(2R)-Methyl 2-acetoxy-2-methylhex-5-ynoate (5c)

To a solution of methyl ester 25 (250 mg, 1.60 mmol) in toluene (30 mL) was added pyridine (0.26 mL, 0.25 g, 3.20 mmol), acetic anhydride (0.30 mL, 0.32 g, 3.20 mmol), DMAP (39.1 mg, 0.32 mmol) and the mixture was stirred at 80 °C overnight. The reaction mixture was cooled to ambient temperature and concentrated *in vacuo*. The crude product was purified by flash chromatography (P/Et$_2$O = 6/1) to afford 254 mg (1.28 mmol, 80%) acetate 5c as a colorless oil.

**TLC:** $R_f = 0.43$ (P/Et$_2$O = 6/1).

$[\alpha]_D^{20}$ = +17.2 (c = 0.50, CHCl$_3$).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3288 (w, C=CH), 2952 (w, CH), 2868 (w, CH), 1739 (s, CO), 1440 (m, C=C).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 1.61 (s, 3 H, CH$_3$), 1.97 (t, $^4J = 2.6$ Hz, 1 H, C6-H), 2.08 (s, 3 H, COCH$_3$), 2.15-2.37 (m, 4 H, C3-H/C4-H), 3.75 (s, 3 H, OCH$_3$).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 13.0 (t, C-4), 21.1 (q, COCH$_3$), 21.6 (q, CH$_3$), 36.8 (t, C-3), 52.4 (q, OCH$_3$), 68.6 (d, C-6), 79.8 (s, C-2), 83.2 (s, C-5), 169.8 (s, C-1), 172.0 (s, COCH$_3$).

**MS** (EI, 70 eV): $m/z$ (%) = 139 (65) [(M–C$_2$H$_3$O$_2$)$^+$], 43 (100) [(C$_2$H$_3$O)$^+$].

**HRMS** (EI): calcd. for C$_8$H$_{11}$O$_2$ $^+$ [(M–C$_2$H$_3$O$_2$)$^+$]: 139.0754; found: 139.0754.
(2R)-Ethyl 1’-(methoxy-2-methyl-1-oxohex-5-yn-2-yl)malonate (5d)

To a solution of methylester 25 (400 mg, 2.56 mmol) in CH$_2$Cl$_2$ (40 mL) was added monoethylmalonate (0.94 mL, 1.06 g, 7.70 mmol) and DMAP (94.0 mg, 0.78 mmol). The mixture was cooled to 0 °C and DCC (7.70 mL, 7.70 mmol, 1 m in CH$_2$Cl$_2$) was added dropwse. The solution was stirred overnight, filtered and concentrated in vacuo. The residue was dissolved in Et$_2$O (40 mL), filtered and washed with NH$_4$Cl (20 mL). The aqueous layer was separated and extracted with Et$_2$O (3 × 50 mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/CH$_2$Cl$_2$/EtOAc = 7/2/1) to afford 416 mg (1.54 mmol, 60%) ester 5d as a yellow oil.

**TLC:** $R_f = 0.38$ (P/CH$_2$Cl$_2$/EtOAc = 7/2/1).

$[\alpha]_{D}^{20} = -4.5$ ($c = 0.30$, CHCl$_3$).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3284 (s, C≡CH), 2988 (m, CH), 2952 (m, CH), 1732 (br. s, CO), 1443 (w, CH).

**$^1$H-NMR** (360 MHz, CDCl$_3$): $\delta$ (ppm) = 1.31 (t, $^3J = 7.1$ Hz, 3 H, OCH$_2$CH$_3$), 1.65 (s, 3 H, CH$_3$), 1.97 (t, $^4J = 2.6$ Hz, 1 H, C6-H), 2.06-2.35 (m, 4 H, C3-H/C4-H), 3.38 (d, $^2J = 17.6$ Hz, 1 H, C2’-H), 3.41 (d, $^2J = 17.6$ Hz, 1 H, C2’-H), 3.76 (s, 3 H, OCH$_3$), 4.23 (q, $^3J = 7.1$ Hz, 2 H, OCH$_2$CH$_3$).

**$^{13}$C-NMR** (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 12.9 (t, C-4), 14.1 (q, OCH$_2$CH$_3$), 21.4 (q, CH$_3$), 36.7 (t, C-3), 41.7 (t, C-2’), 52.6 (q, OCH$_3$), 61.6 (t, OCH$_2$CH$_3$), 68.7 (d, C-6), 80.9 (s, C-2), 83.0 (s, C-5), 165.2 (s, C-3’), 166.1 (s, C-1’), 171.4 (s, CO).

**MS** (EI, 70 eV): $m/z$ (%) = 293 (100) [(M+Na)$^+$], 288 (21) [(M+NH$_4$)$^+$], 271 (95) [(M+H)$^+$].

**HRMS** (EI): calcd. for C$_{13}$H$_{19}$O$_6^+$ [(M+H)$^+$]: 271.11761; found: 271.11756.
(2R,5R)-5-(But-2’-yn-1’-yl)-2-(tert-butyl)-5-methyl-1,3-dioxolan-4-one (28)

To a solution of freshly distilled diisopropylamine (6.12 mL, 4.38 g, 43.3 mmol) in THF (130 mL) at −78 °C was added n-BuLi (16.0 mL, 40.0 mmol, 2.5 M in hexane) and the mixture was stirred at −78 °C for 1 h, then dioxolanone 4 (5.27 g, 33.3 mmol) in THF (20 mL) was added dropwise and the mixture was stirred for 45 min. 1-Iodobut-2-yn (3.00 g, 16.7 mmol) in THF (5 mL) was added, the reaction mixture warmed up slowly to −10 °C and stirred at this temperature for 1 h more. The reaction was quenched with NH₄Cl (25 mL), and the aqueous phase was extracted with Et₂O (3 × 100 mL). The combined organic extracts were washed with NaHCO₃ (20 mL) and brine (20 mL), dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/Et₂O = 98/2) to afford 2.88 g (13.7 mmol, 82%) dioxolanone 28 as single diastereoisomer.

**TLC:** \( R_f = 0.60 \) (P/EtOAc = 9/1).

\[\alpha\]D\text{20} = +13.5 (c = 0.45, CHCl₃).

**IR** (ATR): \( \tilde{\nu} \) (cm⁻¹) = 2963 (m, CH), 2907 (w, CH), 1796 (s, CO), 1482 (w, CH).

**¹H-NMR** (360 MHz, CDCl₃): δ (ppm) = 0.98 [s, 9 H, C(CH₃)₃], 1.48 (s, 3 H, CH₃), 1.80 (t, \( ^5J = 2.6 \) Hz, 3 H, C4’-H), 2.57 (dq, \( ^2J = 16.9 \) Hz, \( ^5J = 2.6 \) Hz, 1 H, C1’-H), 2.64 (dq, \( ^2J = 16.9 \) Hz, \( ^5J = 2.6 \) Hz, 1 H, C1’-HH), 5.42 (s, 1 H, C2-H).

**¹³C-NMR** (90.6 MHz, CDCl₃): δ (ppm) = 3.5 (q, C-4’), 23.0 (q, CH₃), 23.3 [q, C(CH₃)₃], 27.7 (t, C-1’), 34.6 [s, C(CH₃)₃], 72.8 (s, C-3’), 78.9 (s, C-2’), 79.7 (s, C-5), 109.5 (d, C-2), 174.7 (s, C-4).

**MS** (EI, 70 eV): \( m/z \) (%) = 157 (99) [\( \text{M} – \text{C}_4\text{H}_5\)^+], 57 (71) [\( \text{C}_4\text{H}_9\)^+], 43 (100) [\( \text{C}_2\text{H}_3\text{O}\)^+].

**HRMS** (EI): calcd. for C₈H₁₃O₃⁺ [\( \text{M} – \text{C}_4\text{H}_5\)^+]: 157.0859, found: 157.0855.
(2R)-Methyl 2-hydroxy-2-methylhex-4-ynoate (29)

MeOH (5.9 mL) was added slowly to sodium 469 mg (20.5 mmol) at 0 °C and the mixture was stirred until complete dissolution of sodium. Then this solution was added to a stirred solution of dioxolanone 28 (2.87 g, 13.7 mmol) in MeOH (80 mL) at 0 °C and the reaction mixture was stirred at this temperature for 2 h. The reaction was quenched with cold water (30 mL) and the aqueous layer was extracted with EtOAc (3 × 130 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (P/Et₂O = 5/1) to afford 1.91 g (12.2 mmol, 89%) methyl ester 29 as a colorless oil.

**TLC:** \( R_f = 0.65 \) (P/Et₂O = 3/1).

\[ [\alpha]_D^{20} = -14.3 \ (c = 0.18, \ \text{CHCl}_3). \]

**IR** (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3506 (br w, OH), 2980 (m, CH), 1737 (s, CO), 1447 (w, CH).

**\( ^1H\)-NMR** (360 MHz, CDCl₃): \( \delta \) (ppm) = 1.46 (s, 3 H, CH₃), 1.80 (t, \( ^5J = 2.6 \) Hz, 3 H, C6-H), 2.51 (dq, \( ^2J = 16.4 \) Hz, \( ^5J = 2.6 \) Hz, 1 H, C3-H/H), 2.64 (dq, \( ^2J = 16.4 \) Hz, \( ^5J = 2.6 \) Hz, 1 H, C3-H/H), 3.30 (br s, 1 H, OH), 3.82 (s, 3 H, OCH₃).

**\( ^{13}C\)-NMR** (90.6 MHz, CDCl₃): \( \delta \) (ppm) = 3.5 (q, C-6), 24.8 (q, CH₃), 31.4 (t, C-3), 52.9 (q, OCH₃), 73.3 (s, C-5), 74.1 (s, C-2), 79.2 (s, C-4), 175.9 (s, C-1).

**MS** (EI, 70 eV): \( m/z \ (%) = 156 \ (5 \ [\text{M}^+]), 43 \ (100) \ [(\text{C}_2\text{H}_3\text{O})^+]. \)

**HRMS** (EI): calcd. for \( \text{C}_8\text{H}_{12}\text{O}_3^+ \ [\text{M}^+] \): 156.0781, found: 156.0779.

(2R)-Methyl 2-acetoxy-2-methylhex-4-ynoate (5e)
To a solution of methyl ester 29 (1.00 mg, 6.40 mmol) in toluene (80 mL) was added pyridine (1.03 mL, 1.01 g, 12.8 mmol), acetic anhydride (1.21 mL, 1.31 g, 12.8 mmol), DMAP (156 mg, 1.28 mmol) and the mixture was stirred at 80 °C overnight. The reaction mixture was cooled to ambient temperature and concentrated in vacuo. The crude product was purified by flash chromatography (P/Et₂O = 6/1) to afford 741 mg (3.74 mmol, 58%) acetate 5e as a colorless oil.

**TLC:** \(R_f = 0.47\) (P/Et₂O = 6/1).

\([\alpha]_D^{20} = +40.2\ (c = 0.50, \text{CHCl}_3)\).

**IR** (ATR): \(\tilde{\nu}\ (\text{cm}^{-1}) = 2995 \ (\text{w, CH}), 2956 \ (\text{w, CH}), 1737 \ (\text{s, CO}), 1433 \ (\text{w, C=C})\).

**\(^{1}\text{H-NMR}\)** (360 MHz, CDCl₃): \(\delta\) (ppm) = 1.64 (s, 3 H, CH₃), 1.81 (t, \(^5J = 2.6\) Hz, 3 H, C₆-H), 2.10 (s, 3 H, COCH₃), 2.69 (dq, \(^2J = 16.9\) Hz, \(^5J = 2.6\) Hz, 2 H, C₃-HH), 2.96 (dq, \(^2J = 16.9\) Hz, \(^5J = 2.6\) Hz, 2 H, C₃-HH), 3.75 (s, 3 H, OCH₃).

**\(^{13}\text{C-NMR}\)** (90.6 MHz, CDCl₃): \(\delta\) (ppm) = 3.5 (q, C-6), 21.0 (q, COCH₃), 21.9 (q, CH₃), 27.8 (t, C-3), 52.5 (q, OCH₃), 72.5 (s, C-5), 79.0 (s, C-2), 79.0 (s, C-4), 169.9 (s, C-1), 171.9 (s, COCH₃).

**MS** (EI, 70 eV): \(m/z\) (%): 145 (9) [(M–C₄H₅)⁺], 139 (15) [(M–C₂H₅O₂)⁺], 97 (20), 43 (100).

**HRMS** (EI): calcd. for C₆H₉O₄⁺ [(M–C₄H₅)⁺]: 145.0495, found: 145.0498.

**General procedure 1 for Mitsunobu reactions with tetronic acids.** The tetronic acid (10.0 mmol) was dissolved in THF (100 ml) followed by addition of the primary alcohol (11.0 mmol). The mixture was cooled to 0 °C, triphenylphosphine (11.0 mmol) or tris(chlorophenyl)phosphine (11.0 mmol) were added and di-iso-propyl azodicarboxylate (11.0 mmol) or di-ethyl azodicarboxylate (11.0 mmol) were slowly dropped into the solution. The mixture was allowed to warm up to ambient temperature overnight. The solvent was removed under reduced pressure, and the residue was purified by column chromatography.

\((1′RS,5R)-5-(\text{But}-3′′-\text{en}-1′′-\text{yl})-4-(\text{cyclohex}-2′-\text{en}-1′-\text{ylmethoxy})-5\text{-methyl-2-oxo-2,5-dihydrofuran} \ (8a)\).
Following the general procedure 1, reaction of tetronic acid 6a (70.0 mg, 0.42 mmol) and cyclohexene-2-methanol (7a) (0.05 mL, 51.6 mg, 0.46 mmol) with triphenylphosphine and diisopropyl azodicarboxylate in 4 mL THF yielded after purification by flash chromatography (P/Et2O = 5/1) tetronic acid ester 8a (69.7 mg, 0.27 mmol, 64%) as a yellow oil. Mixture of two diastereoisomers (d.r. = 50/50).

TLC: R<sub>f</sub> = 0.19 (P/EtOAc = 3/2).

IR (ATR): ν̃<sub>cm<sup>−1</sup></sub> = 2977 (CH), 2832 (CH), 1745 (CO), 1619 (C=CO), 1446 (CH).

<sup>1</sup>H-NMR (360 MHz, CDCl<sub>3</sub>): δ (ppm) = 1.40-1.45 (m, 1 H, C6'<H/H), 1.48 (s, 3 H, CH<sub>3</sub>), 1.54-1.66 (m, 1 H, C5'-HH), 1.73-1.96 (m, 5 H, C5'-HH/C6'-HH/C2''-H/C1''-HH), 2.01-2.16 (m, 3 H, C1'''-HH/C4'-H), 2.61-2.64 (m, 1 H, C1'-H), 3.81-3.91 (m, 2 H, OCH<sub>2</sub>), 4.95-5.04 (m, 3 H, C4'''-H/C3-H), 5.54-5.58 (m, 1 H, C2'-H), 5.70-5.83 (m, 1 H, C3''-H), 5.87 (dt, 3<sup>3</sup>J = 9.8 Hz, 3<sup>3</sup>J = 3.4 Hz, 4<sup>3</sup>J = 2.0 Hz, 1 H, C3'-H).

<sup>13</sup>C-NMR (90.6 MHz, CDCl<sub>3</sub>): δ (ppm) = 20.4 (t, C-5'), 23.5 (q, CH<sub>3</sub>), 25.1 (t, C-4'), 25.5 (t, C-6'), 27.5 (t, C-2''), 34.8 (d, C-1'), 35.9 (t, C-1''), 76.2 (t, OCH<sub>2</sub>), 84.2 (s, C-5), 88.1 (d, C-3), 115.2 (t, C-4''), 125.7 (d, C-2''), 130.5 (d, C-3''), 137.2 (d, C-3''), 172.0 (s, C-2), 183.7 (s, C-4).

Two signal sets for each peak due to the existence of two diastereoisomers.

MS (EI, 70 eV): m/z (%) = 262 (1) [M<sup>+</sup>], 168 (12), 112 (14), 95 (100) [(C<sub>7</sub>H<sub>11</sub>)+], 79 (13), 55 (7) [(C<sub>4</sub>H<sub>7</sub>)+].

HRMS: (EI, 70 eV): calcd. for C<sub>16</sub>H<sub>22</sub>O<sub>3</sub> <sup>+</sup> [M<sup>+</sup>]: 262.1563, found: 262.1562.

(1'R,5R,6'R)-5-(But-3''-en-1''-yl)-4-{[(6'-tert-butyldimethylsilyl)oxy]cyclohex-2'-en-1''-ylmethoxy}-5-methyl-2-oxo-2,5-dihydrofuran (8b)

Following the general procedure 1, reaction of tetronic acid 6a (76.3 mg, 0.45 mmol) and alcohol 3 (50.0 mg, 0.21 mmol) with triphenylphosphine and diisopropyl azodicarboxylate in 5 mL THF yielded after purification by flash chromatography (P/Et2O = 2/1) tetronic acid ester 8b (42.0 mg, 0.11 mmol, 52%) as a yellow oil.
TLC: $R_f = 0.27$ (P/EtO = 3/1).

$[\alpha]_D^{20} = +37.1$ (c = 0.50, CHCl$_3$).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2951 (CH), 2928 (CH), 2855 (CH), 1754 (CO), 1628 (C=CO), 1461 (CH).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.08 (s, 3 H, SiCH$_3$), 0.10 (s, 3 H, SiCH$_3$), 0.91 [s, 9 H, SiC(CH$_3$)$_3$], 1.49 (s, 3 H, CH$_3$), 1.65-1.98 (m, 4 H, C1ʹʹ-H/C2ʹʹ-H), 2.01-2.30 (m, 4 H, C5ʹ-H/C4ʹ-H), 2.65-2.69 (m, 1 H, C1ʹ-H), 3.97 (dd, $^3$$J$ = 9.5 Hz, $^3$$J$ = 7.7 Hz, 1 H, OCH/H), 4.12 (ddd, $^3$$J$ = 7.6 Hz, $^3$$J$ = 4.2 Hz, $^3$$J$ = 2.7 Hz, 1 H, C6ʹ-H), 4.21 (dd, $^2$$J$ = 9.5 Hz, $^3$$J$ = 5.7 Hz, 1 H, OCH/H), 4.97-5.05 (m, 2 H, C4ʹʺ-H), 4.99 (s, 1 H, C3-H), 5.52 (ddt, $^3$$J$ = 9.8 Hz, $^3$$J$ = 4.1 Hz, $^4$$J$ = 1.9 Hz, 1 H, C2ʹ-H), 5.74-5.81 (m, 1 H, C3ʹ-H), 5.84 (ddt, $^3$$J$ = 9.8 Hz, $^3$$J$ = 3.7 Hz, $^4$$J$ = 1.9 Hz, 1 H, C3ʹ-H).

$^1$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = -5.0 (q, SiCH$_3$), -4.4 (q, SiCH$_3$), 18.1 [s, SiC(CH$_3$)$_3$], 22.5 (t, C-2ʹʺ), 23.4 (q, CH$_3$), 25.8 [q, SiC(CH$_3$)$_3$], 27.4 (t, C-4ʹ), 28.8 (t, C-5ʹ), 36.0 (t, C-1ʹʺ), 40.4 (d, C-1ʹ), 67.2 (d, C-6ʹ), 73.9 (t, OCH$_2$), 84.1 (s, C-5), 88.0 (d, C-3), 115.1 (t, C-4ʹʺ), 124.0 (d, C-2ʹʺ), 129.2 (d, C-3ʹ), 137.2 (d, C-3ʹʺ), 172.0 (s, C-2), 184.1 (s, C-4).

MS (ESI): $m/z$ (%) = 1199 (6) [(3M+Na)$^+$], 807 (13) [(2M+Na)$^+$], 785 (100), [(2M+H)$^+$], 393 (27) [(M+H)$^+$], 335 (14) [(M–C$_4$H$_9$)$^+$].

HRMS: (ESI): calcd. for C$_{22}$H$_{37}$O$_4$Si$^+$ [(M+H)$^+$]: 393.24556, found: 393.24575.

(5R)-5-(But-3ʺ-en-1ʹʺ-yl)-4-(3ʹ-methylbut-3ʹ-en-1ʹ-yl-oxy)-5-methyl-2-oxo-2,5-dihydrofuran (8c).

Following the general procedure 1, reaction of tetronic acid 6a (70.0 mg, 0.42 mmol) and 3-methylbut-3-en-1-ol (7c) (48.0 μL, 39.6 mg, 0.46 mmol) with triphenylphosphine and diisopropyl azodicarboxylate in 2 mL THF yielded after purification by flash chromatography (P/EtOAc = 2/1) tetronic acid ester 8c (81.4 mg, 0.34 mmol, 82%) as a yellow oil.

TLC: $R_f = 0.39$ (P/EtOAc = 1/1).

$[\alpha]_D^{20} = +24.0$ (c = 0.50, CHCl$_3$).
**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2977 (CH), 2933 (CH), 1746 (CO), 1620 (C=CO), 1456 (C-H).

**$^1$H-NMR** (360 MHz, CDCl$_3$): $\delta$ (ppm) = 1.47 (s, 3 H, CH$_3$), 1.75-1.80 (m, 1 H, C1''-H/H), 1.81 (s, 3 H, CH$_3$), 1.84-1.99 (m, 2 H, C1''-H/C2''-H), 2.05-2.16 (m, 1 H, C2''-H), 2.50 (t, $^3J = 6.5$ Hz, 2 H, C2'-H), 4.06-4.16 (m, 2 H, C1'-H), 4.75-4.79 (m, 1 H, C4'-H), 4.86-4.98 (m, 1 H, C4''-H), 4.98 (s, 1 H, C3-H), 5.75 (ddt, $^3J = 17.1$ Hz, $^3J = 10.2$ Hz, $^3J = 6.4$ Hz, 1 H, C3''-H).

**$^{13}$C-NMR** (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 22.5 (q, CH$_3$), 23.5 (q, CH$_3$), 27.4 (t, C-2''), 28.2 (t, C-1''), 35.9 (t, C-2'), 70.8 (t, C-1'), 84.2 (s, C-5), 88.1 (d, C-3), 113.0 (t, C-4'), 115.2 (t, C-4''), 137.2 (d, C-3''), 140.5 (s, C-3'), 171.9 (s, C-2), 183.5 (s, C-4).

**MS** (EI, 70 eV): $m/z$ (%) = 236 (1) [M$^+$], 181 (5) [(C$_4$H$_7$)$^+$], 113 (10), 69 (100) [(C$_3$H$_9$)$^+$].

**HRMS**: (EI, 70 eV): calcd. for C$_{14}$H$_{20}$O$_3$ $^+$ [M$^+$]: 236.1407, found: 236.1409.

(1'RS,5'R)-5-(But-3''-en-1''-yl)-3-(ethoxycarbonyl)-4-(cyclohex-2'-en-1'-ylmethoxy)-5-methyl-2-oxo-2,5-dihydrofuran (8d)

Following the general procedure 1, reaction of tetrone acid 6b (108.6 mg, 0.45 mmol) and cyclohexenyl-2-methanol (7a) (60.0 µL, 55.7 mg, 0.50 mmol) with triphenylphosphine and di-isopropyl azodicarboxylate in 4 mL THF yielded after purification by flash chromatography (CH$_2$Cl$_2$/EtOAc = 95/5) tetrone acid ester 8d (59.7 mg, 178 µmol, 36%) as a yellow oil. Mixture of two diastereoisomers (d.r. = 50/50).

**TLC**: $R_f = 0.57$ (CH$_2$Cl$_2$/EtOAc = 9/1).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3020 (C=CH), 2980 (CH), 2928 (CH), 1767 (CO), 1715 (CO), 1641 (s, C=CCO).
$^{13}$C-NMR (90.6 MHz, CDCl$_3$): δ (ppm) = 14.2 (q, OCH$_2$CH$_3$), 20.5 (t, C-5'), 23.6 (q, CH$_3$), 25.1 (t, C-4'), 27.4 (t, C-6'), 31.0 (t, C-2''), 35.4 (d, C-1''), 36.2 (t, C-1''), 61.8 (t, OCH$_2$CH$_3$), 78.4 (t, OCH$_2$), 83.3 (s, C-5), 97.0 (s, C-3), 115.5 (t, C-4''), 125.4 (d, C-2'), 130.7 (d, C-3''), 136.8 (d, C-3''), 162.2 (s, CO), 168.1 (s, C-2), 181.8 (s, C-4). Two signal sets for each peak due to the existence of two diastereoisomers.

**MS** (ESI): m/z (%) = 335 (100) [M+], 241 (99), 213 (3).

**HRMS** (ESI): calcd. for C$_{19}$H$_{27}$O$_5$+ [(M+H)$^+$]: 335.18530, found: 335.18496.

(5$R$,1'$R$,6'R)-5-(But-3''-en-1''-yl)-3-ethoxycarbonyl-4-[[6'-tert-butyldimethylsilyl]oxy]cyclohex-2''-en-1''-ylmethoxy]-5-methyl-2-oxo-2,5-dihydrofuran (8e)

Following the general procedure 1, reaction of tetronic acid 6b (56.6 mg, 0.24 mmol) and alcohol 3 (19.1 mg, 79.3 μmol) with triphenylphosphine and diisopropyl azodicarboxylate in 2.5 mL THF yielded after purification by flash chromatography (P/Et$_2$O = 6/1) tetronic acid ester 8e (19.2 mg, 41.0 μmol, 53%) as a yellow oil.

**TLC:** R$_f$ = 0.33 (P/Et$_2$O = 3/1).

[a]$^\text{D}_{20}$ = +31.0 (c = 0.50, CHCl$_3$).

**IR** (ATR): ν (cm$^{-1}$) = 2980 (CH), 2931 (CH), 1720 (CO), 1466 (CH).

**1H-NMR** (360 MHz, CDCl$_3$): δ (ppm) = 0.09 (s, 3 H, SiCH$_3$), 0.10 (s, 3 H, SiCH$_3$), 0.91 [s, 9 H, SiC(CH$_3$)$_3$], 1.37 (t, $^3$J = 7.1 Hz, 3 H, OCH$_2$CH$_3$), 1.51 (s, 3 H, CH$_3$), 1.69 (dtd, $^2$J = 13.3 Hz, $^3$J = 6.8 Hz, $^3$J = 3.4 Hz, 1 H, C4''-HH), 1.74-1.85 (m, 2 H, C1''-HH/C4'-HH), 1.90 (dt, $^2$J = 10.6 Hz, $^3$J = 5.0 Hz, 1 H, C1''-HH), 1.96-2.02 (m, 1 H, C2''-HH), 2.04-2.17 (m, 2 H, C5''-HH/C2''-HH), 2.20-2.28 (m, 1 H, C5'-HH), 2.61-2.65 (m, 1 H, C1'-H), 4.11 (ddd, $^3$J = 7.8 Hz, $^3$J = 4.8 Hz, $^3$J = 2.9 Hz, 1 H, C6'-H), 4.33 (q, $^3$J = 7.1 Hz, 2 H, OCH$_2$CH$_3$), 4.37 (dd, $^2$J = 9.5 Hz, $^3$J = 6.9 Hz, 1 H, OCH(H), 4.63 (dd, $^2$J = 9.5 Hz, $^3$J = 5.7 Hz, 1 H, OCHH), 4.94-4.98 (m, 1 H, C4''-H$_\text{cis}$), 5.03 (dd, $^2$J = 1.6 Hz, $^3$J = 17.1 Hz, 1 H, C4''-H$_\text{trans}$), 5.49-5.52 (m, 1 H, C2'-
H), 5.74 (ddt, 3$J$ = 17.1 Hz, 3$J$ = 10.2 Hz, 3$J$ = 6.3 Hz, 1 H, C3'-H), 5.83 (dtd, 3$J$ = 9.8 Hz, 3$J$ = 3.4 Hz, 4$J$ = 1.9 Hz, 1 H, C3'-H).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = -5.0 (q, SiCH$_3$), -4.4 (q, SiCH$_3$), 14.1 (q, OCH$_2$CH$_3$), 18.0 [s, SiC(CH$_3$)$_3$], 22.7 (t, C-2''), 23.5 (q, CH$_3$), 25.8 [q, SiC(CH$_3$)$_3$], 27.3 (t, C-4'), 28.8 (t, C-5'), 36.2 (t, C-1''), 41.1 (d, C-1'), 61.7 (t, OCH$_2$CH$_3$), 67.1 (d, C-6'), 76.0 (t, OCH$_2$), 83.2 (s, C-5), 97.1 (s, C-3), 115.4 (t, C-4''), 123.8 (d, C-2'), 129.4 (d, C-3'), 136.9 (d, C-3''), 162.1 (s, CO), 168.1 (s, C-2), 181.7 (s, C-4).

MS (ESI): $m/z$ (%) = 951 (21) [(2M+Na)$^+$], 946 (23) [(2M+NH$_4$)$^+$], 465 (100) [(M+H)$^+$], 243 (18) [(C$_{13}$H$_{27}$O$_2$Si)$^+$].

HRMS (ESI): calcd. for C$_{25}$H$_{41}$O$_6$Si$^+$ [(M+H)$^+$]: 465.26669, found: 465.26673

(5R)-5-(But-3''-en-1''-yl)-4-(but-3'-en-1'-yloxy)-5-methyl-2-oxo-2,5-di-hydrofuran (8f)

Following the general procedure 1, reaction of tetronic acid 6a (70.0 mg, 0.42 mmol) and but-3-en-1-ol (7b) (40.0 $\mu$L, 33.0 mg, 0.46 mmol) with triphenylphosphine and diisopropyl azodicarboxylate in 5 mL THF yielded after purification by flash chromatography (P/CH$_2$Cl$_2$/Et$_2$O = 4/1/1) tetronic acid ester 8f (67.0 mg, 30.1 $\mu$mol, 72%) as a yellow oil.

TLC: $R_f$ = 0.27 (P/CH$_2$Cl$_2$/Et$_2$O = 4/1/1).

[\alpha]$_D^{20}$ = +16.1 (c = 0.10, CHCl$_3$).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3080 (C=CH), 2980 (CH), 2935 (CH), 1750 (CO), 1623 (C=CCO).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 1.46 (s, 3 H, CH$_3$), 1.75-1.82 (m, 1 H, C2'-H), 1.85-1.99 (m, 2 H, C2''-HH/C1''-HH), 2.05-2.17 (m, 1 H, C1''-HH), 2.50-2.57 (m, 2 H, C2'-H), 4.03 (dt, 3$J$ = 10.2 Hz, 3$J$ = 6.5 Hz, 1 H, C1'-H), 4.07 (dt, 3$J$ = 10.2 Hz, 3$J$ = 6.6 Hz, 1 H, C1'-HH), 4.94-5.03 (m, 2 H, C4'-H), 4.97 (s, 1 H, C3-H), 5.13-5.15 (m, 1 H, C4''-H$_{trans}$), 5.17 (dd, 3$J$ = 9.8 Hz, 3$J$ = 9.8 Hz, 1 H, C4''-H$_{cis}$), 5.71-5.84 (m, 2 H, C3'-H/C3''-H).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 23.7 (q, CH$_3$), 27.6 (t, C-2'), 32.9 (t, C-1'), 36.0 (t, C-2''), 71.8 (t, C-1''), 84.3 (s, C-5), 88.4 (d, C-3), 115.3 (t, C-4''), 118.3 (t, C-4'), 132.9 (d, C-3'), 137.3 (d, C-3''), 172.0 (s, C-2), 183.7 (s, C-4).
MS (El, 70 eV): \( m/z (\%) = 167 (13) [(M−C_4H_7)^+] \), 55 (100) [(C_4H_7)^+].


(5R)-5-(But-3''-en-1''-yl)-3-ethoxycarbonyl-4-(but-3'-en-1'-yloxy)-5-methyl-2-oxo-2,5-dihydrofuran (8g)

Following the **general procedure 1**, reaction of tetronic acid 6b (35.0 mg, 0.15 mmol) and but-3-en-1-ol (7b) (30.0 \( \mu L \), 23.1 mg, 0.32 mmol) with triphenylphosphine and diisopropyl azodicarboxylate in 4 mL THF yielded after purification by flash chromatography (P/Et_2O = 4/1) tetronic acid ester 8g (16.1 mg, 56.0 \( \mu \)mol, 76%) as a yellow oil.

**TLC:** \( R_f = 0.21 \) (P/Et_2O = 3/1).

\( [\alpha]_D^{20} = +13.3 \) (c = 0.50, CHCl_3).

**IR (ATR):** \( \tilde{\nu} (\text{cm}^{-1}) = 2993 \) (C=CH), 2928 (CH), 2856 (CH), 1755 (CO), 1624 (C=CCO).

**1H-NMR** (360 MHz, CDCl_3): \( \delta (\text{ppm}) = 1.37 \) (t, \( J = 7.1 \) Hz, 3 H, OCH_2CH_3), 1.48 (s, 3 H, CH_3), 1.79-2.00 (m, 3 H, C1''-HH/C2''-H), 2.05-2.17 (m, 1 H, C1''-HH), 2.49-2.55 (m, 2 H, C2'-H), 4.34 (q, \( J = 7.1 \) Hz, 2 H, OCH_2CH_3), 4.46 (dt, \( J = 9.8 \) Hz, \( J = 6.4 \) Hz, 1 H, C1'-HH), 4.52 (dt, \( J = 9.8 \) Hz, \( J = 6.3 \) Hz, 1 H, C1'-HH), 4.97-5.05 (m, 2 H, C4''-H), 5.14-5.20 (m, 2 H, C4'-H), 5.71-5.83 (m, 2 H, C3'-H/C3''-H).

**13C-NMR** (90.6 MHz, CDCl_3): \( \delta (\text{ppm}) = 14.1 \) (q, OCH_2CH_3), 23.5 (q, CH_3), 27.3 (t, C-1''), 33.4 (t, C-2'), 36.1 (t, C-2''), 61.8 (t, OCH_2CH_3), 73.9 (t, C-1'), 83.2 (s, C-5), 97.1 (s, C-3), 115.4 (t, C-4''), 118.3 (t, C-4'), 132.7 (d, C-3''), 136.9 (d, C-3'), 162.2 (s, CO), 167.9 (s, C-2), 181.7 (s, C-4).

**MS** (ESI): \( m/z (\%) = 317 (4) [(M+Na)^+] \), 312 (5) [(M+NH_4)^+], 295 (100) [(M+H)^+].

**HRMS** (ESI): calcd. for C_{16}H_{23}O_5^+ [(M+H)^+]: 295.15400, found: 295.15415.
To a solution of acetate 5d (150 mg, 0.57 mmol) in DMF (10 mL) was added KOtBu (174 mg, 1.43 mmol) at 0 °C and the mixture was stirred overnight. The solution was concentrated in vacuo, the residue dissolved in NaOH/Et₂O (15 mL, 1/1) and extracted with Et₂O (10 mL). The aqueous layer was acidified with HCl (2 M, pH = 2) and extracted with CHCl₃/iPrOH (3 × 20 mL, 5/1). The combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo, to afford 91.7 mg (0.39 mmol, 67%) tetronic acid 27, which was used without further purification. Following the general procedure 1, reaction of tetronic acid 27 (78.6 mg, 0.33 mmol) and alcohol 3 (90.0 mg, 0.37 mmol) with tris(chlorophenyl)phosphine and diiso-ethylazodicarboxylate in 4 mL THF yielded after purification by flash chromatography (P/Et₂O = 4/1) tetronic acid ester 8h (85.5 mg, 185 μmol, 56%) as a yellow oil.

**TLC:** Rₜ = 0.29 (P/Et₂O = 3/1).

[α]D^20 = +81.1 (c = 0.18, CHCl₃).

**IR (ATR):** \( \tilde{\nu} \) (cm\(^{-1}\)) = 3285 (C≡CH), 2956 (CH), 2931 (CH), 2857 (CH), 1767 (CO), 1715 (CO), 1644 (C=CO), 1458 (CH).

**¹H-NMR (360 MHz, CDCl₃):** \( \delta \) (ppm) = 0.07 (s, 3 H, SiCH₃), 0.09 (s, 3 H, SiCH₃), 0.90 [s, 9 H, SiC(CH₃)₃], 1.36 (t, \( ^3J = 7.1 \) Hz, 3 H, OCH₂CH₃), 1.51 (s, 3 H, CH₃), 1.64-1.72 (m, 1 H, C₂′′-H), 1.73-1.80 (m, 1 H, C₂′-H/H), 1.94 (t, \( ^4J = 2.6 \) Hz, 1 H, C⁴′′-H), 1.98-2.19 (m, 4 H, C₄′-H/C₅′-H/C₁′′-H/C₂′′-H), 2.20-2.32 (m, 2 H, C₄′-HH/C₅′-HH/C₁′′-H), 2.61-2.65 (m, 1 H, C₁′-H), 4.10 (ddd, \( ^3J = 8.0 \) Hz, \( ^3J = 4.9 \) Hz, \( ^3J = 2.9 \) Hz, 1 H, C₆′-H), 4.32 (q, \( ^3J = 7.1 \) Hz, 2 H, OCH₂CH₃), 4.37 (dd, \( ^2J = 9.8 \) Hz, \( ^3J = 7.4 \) Hz, 1 H, OCHH), 4.63 (dd, \( ^2J = 9.8 \) Hz, \( ^3J = 5.8 \) Hz, 1 H, OCHH), 5.49 (ddt, \( ^3J = 9.8 \) Hz, \( ^3J = 4.1 \) Hz, \( ^4J = 1.9 \) Hz, 1 H, C₂′-H), 5.83 (ddd, \( ^3J = 9.8 \) Hz, \( ^3J = 3.6 \) Hz, \( ^4J = 2.1 \) Hz, 1 H, C₃′-H).
\[ ^{13} \text{C-NMR} \ (90.6 \text{ MHz, CDCl}_3): \delta \ (\text{ppm}) = -5.0 \ (\text{q, SiCH}_3), -4.4 \ (\text{q, SiCH}_3), 12.9 \ (\text{t, C-2''}), 14.1 \ (\text{q, OCH}_2\text{CH}_3), 18.0 \ [\text{s, SiC(CH}_3)_3], 22.8 \ (\text{t, C-4'}), 23.3 \ (\text{q, CH}_3), 25.8 \ [\text{q, SiC(CH}_3)_3], 28.8 \ (\text{t, C-5'}), 36.0 \ (\text{t, C-1''}), 41.1 \ (\text{d, C-1'}), 61.7 \ (\text{t, OCH}_2\text{CH}_3), 67.2 \ (\text{d, C-6'}), 69.1 \ (\text{d, C-4''}), 76.1 \ (\text{t, OCH}_2), 82.5 \ (\text{s, C-3''}), 82.5 \ (\text{s, C-5}), 97.1 \ (\text{s, C-3)}, 123.8 \ (\text{d, C-2'}), 129.5 \ (\text{d, C-3'}), 161.9 \ (\text{s, CO}), 167.7 \ (\text{s, C-2}), 181.0 \ (\text{s, C-4}). \]

**MS** (ESI): \[ m/z \ (\%) = 947 \ (51) \ [(2M+Na)^+], 485 \ (15) \ [(M+Na)^+], 463 \ (100) \ [(M+H)^+]. \]

**HRMS** (ESI): calcd. for C\(_{25}\)H\(_{39}\)O\(_6\)Si\(^+\) [(M+H)^+]: 463.25104, found: 463.25083.

\((5R,1'R,6'R)-5-(\text{But-3''-yn-1''-yl})-4\cdot[(6'-\text{tert-butyldimethylsilyl})\text{oxy}]\text{cyclohex-2'-en-1'ylmethoxy}]\)-5-methyl-2-oxo-2,5-dihydrofuran \((8i)\)

![Reaction Scheme](image)

To a solution of acetate \(5c\) (100 mg, 0.51 mmol) in DMF (7 mL) was added KO\(^t\)Bu (92.1 mg, 0.82 mmol) at 0 °C and the mixture was stirred overnight. The solution was concentrated in vacuo, the residue dissolved in NaOH/Et\(_2\)O (10 mL, 1/1) and extracted with Et\(_2\)O (5 mL). The aqueous layer was acidified with HCl (2 M, pH = 2) and extracted with CHCl\(_3\)/iPrOH (3 × 10 mL, 5/1). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtered and concentrated in vacuo, to afford 68.4 (0.41 mmol, 81%) tetronic acid \(26\), which was used without further purification. Following the general procedure \(1\), reaction of tetronic acid \(26\) (55.4 mg, 0.33 mmol) and alcohol \(3\) (89.0 mg, 0.37 mmol) with tris(chlorophenyl)phosphine and diiso-ethylazodicarboxylate in 4 mL THF yielded after purification by flash chromatography (P/Et\(_2\)O = 4/1) tetronic acid ester \(8i\) (52.3 mg, 134 \(\mu\)mol, 40%) as a yellow oil.

**TLC:** \(R_f = 0.43\) (P/Et\(_2\)O = 3/1).

\([\alpha]_D^{20} = +79.1 \ (c = 0.50, \text{CHCl}_3).\)

**IR** (ATR): \(\tilde{\nu} \ (\text{cm}^{-1}) = 3309 \ (\text{C=CH}), 2956 \ (\text{CH}), 2928 \ (\text{CH}), 2854 \ (\text{CH}), 1757 \ (\text{CO}), 1630 \ (\text{C=CO}).\)
$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.08 (s, 3 H, SiCH$_3$), 0.10 (s, 3 H, SiCH$_3$), 0.91 (s, 9 H, SiC(CH$_3$)$_3$), 1.48 (s, 3 H, CH$_3$), 1.64-1.83 (m, 2 H, C2′′-H), 1.94 (t, $^4$J = 2.6 Hz, 1 H, C4′′-H), 1.95-2.05 (m, 2 H, C1′′-H), 2.06-2.31 (m, 4 H, C4′-H/C5′-H), 2.65-2.69 (m, 1 H, C1′-H), 3.97 (virt $^2$J $\approx$ $^3$J = 9.3 Hz, 1 H, OCH$_2$), 4.11-4.12 (m, 1 H, C6′-H), 4.21 (dd, $^3$J = 9.3 Hz, $^3$J = 6.0 Hz, 1 H, OCH$_2$/J), 4.97 (s, 1 H, C3-H), 5.45-5.55 (m, 1 H, C2′-H), 5.84 (ddt, $^3$J = 9.8 Hz, $^3$J = 3.4 Hz, $^4$J = 1.9 Hz, 1 H, C3′-H).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = −5.0 (q, SiCH$_3$), −4.3 (q, SiCH$_3$), 12.9 (t, C-2″), 18.1 [s, SiC(CH$_3$)$_3$], 22.5 (t, C-4′), 23.3 (q, CH$_3$), 25.8 [q, SiC(CH$_3$)$_3$], 28.8 (t, C-5′), 35.7 (t, C-1″), 40.3 (d, C-1′), 67.1 (d, C-6′), 68.8 (d, C-4″), 74.1 (t, OCH$_2$), 83.0 (s, C-3″), 83.4 (s, C-5), 88.2 (d, C-3), 123.9 (d, C-2′), 129.3 (d, C-3′), 171.7 (s, C-2), 183.4 (s, C-4).

MS (EI, 70 eV): m/z (%) = 333 (6) [(M–C$_4$H$_9$)+], 57 (100) [(C$_4$H$_9$)$_2^+$].

HRMS (EI): calcd. for C$_{18}$H$_{25}$O$_4$Si$: [(M–C$_4$H$_9$)+]: 333.1517, found: 333.1512.

(5$R$,1′$R$,6′$R$)-5-(But-2′′-yn-1″-yl)-3-ethoxycarbonyl-4-{[(6′-tert-butyldimethylsilyl)oxy]cyclohex-2′-en-1′-ylmethoxy}-5-methyl-2-oxo-2,5-dihydrofuran (8j)

To a solution of acetate 5d (380 mg, 1.41 mmol) in DMF (40 mL) was added KO$_2$Bu (258 mg, 2.11 mmol) at 0 °C and the mixture was stirred overnight. The solution was concentrated in vacuo, the residue dissolved in NaOH/Et$_2$O (30 mL, 1/1), stirred for 1 h to complete the alkyne isomerisation and extracted with Et$_2$O (30 mL). The aqueous layer was acidified with HCl (2 M, pH = 2) and extracted with CHCl$_3$/iPrOH (3 × 50 mL, 5/1). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated in vacuo, to afford 265 mg (1.11 mmol, 83%) tetronic acid 31, which was used without further purification.

Following the general procedure 1, reaction of tetronic acid 31 (11.0 mg, 46.0 μmol) and alcohol 3 (14.0 mg, 57.2 μmol) with tris(chlorophenyl)-phosphine and di$iso$ethyl azodicarboxylate yielded after purification by flash chromatography (P/Et$_2$O = 4/1) tetronic acid ester 8j (12.5 mg, 27.0 μmol, 59%) as a yellow oil.
TLC: $R_f = 0.39$ (P/Et$_2$O = 3/1).
$[\alpha]_D^{20} = +84.6$ (c = 0.11, CHCl$_3$).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2960 (CH), 2924 (CH), 2857 (CH), 1765 (CO), 1641 (CH).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.08 (s, 3 H, SiCH$_3$), 0.09 (s, 3 H, SiCH$_3$), 0.90 [s, 9 H, SiC(CH$_3$)$_3$], 1.36 (t, $^3J = 7.1$ Hz, 3 H, OCH$_2$CH$_3$), 1.54 (s, 3 H, CH$_3$), 1.60-1.74 (m, 2 H, C4'-H), 1.76 (t, $^5J = 2.6$ Hz, 3 H, C4''-H), 1.99-2.11 (m, 1 H, C5'-HH), 2.15-2.29 (m, 1 H, C5'-HH), 2.54-2.69 (m, 3 H, C1'-H/C1''-H), 4.11 (ddd, $^3J = 7.8$ Hz, $^3J = 4.8$ Hz, $^3J = 2.9$ Hz, 1 H, OCH$_2$), 4.29-4.39 (m, 3 H, OCH$_2$CH$_3$/OCH$_2$H), 4.62 (dd, $^2J = 9.8$ Hz, $^2J = 6.3$ Hz, 1 H, OCH$_2$H), 5.48-5.51 (m, 1 H, C2'-H), 5.82 (ddt, $^3J = 9.8$ Hz, $^3J = 3.4$ Hz, $^4J = 1.9$ Hz, 1 H, C3'-H).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = -5.1 (q, SiCH$_3$), -4.5 (q, SiCH$_3$), 3.4 (q, C-4''), 14.1 (q, OCH$_2$CH$_3$), 18.0 [s, SiC(CH$_3$)$_3$], 22.2 (t, C-4''), 22.5 (q, CH$_3$), 25.8 [q, SiC(CH$_3$)$_3$], 28.8 (t, C-1''), 28.8 (t, C-5''), 41.1 (d, C-1'), 61.7 (t, OCH$_2$CH$_3$), 66.9 (d, C-6'), 71.6 (s, C-3''), 76.3 (t, CH$_2$O), 80.0 (s, C-2''), 82.0 (s, C-5), 97.4 (s, C-3), 123.8 (d, C-2''), 129.2 (d, C-3''), 162.0 (s, CO), 167.7 (s, C-2), 180.6 (s, C-4).

ESI-MS [C$_4$, 20-95%, 5 min]: $t_R = 3.45$ min.
MS (ESI): $m/z$ (%) = 947 (13) [(2M+Na)$^+$], 485 (6) [(M+Na)$^+$], 463 (100), [(M+H)$^+$].
HRMS (ESI): calcd. for C$_{22}$H$_{34}$O$_5$Si$^+$ [(M+H)$^+$]: 463.25104, found: 463.25135.

(5R,1'R,6'R)-5-(But-2''-yn-1''-yl)-4-[[6''-tert-butyldimethylsilyl]oxy]cyclohex-2'-en-1''-ylmethoxy]-5-methyl-2-oxo-2,5-dihydrofuran (8k)

To a solution of acetate 5e (450 mg, 2.27 mmol) in DMF (60 mL) was added KO'Bu (417 mg, 3.41 mmol) at 0 °C and the mixture was stirred overnight. The solution was concentrated in vacuo, the residue dissolved in NaOH/Et$_2$O (30 mL, 1/1) and extracted with Et$_2$O (30 mL). The aqueous layer was acidified with HCl (2 M, pH = 2) and extracted with CHCl$_3$/iPrOH (3 × 50 mL, 5/1). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated in vacuo, to afford 315 mg (1.89 mmol, 83%) tetronic acid 30, which was used without
further purification. Following the general procedure 1, reaction of tetronic acid 30 (69.3 mg, 0.42 mmol) and alcohol 3 (72.3 mg, 0.30 mmol) with tris(chlorophenyl)phosphine and diisooethyl azodicarboxylate yielded after purification by flash chromatography (P/Et$_2$O = 4/1) tetronic acid ester 8k (45.4 mg, 0.12 mmol, 39%) as a yellow oil.

**TLC:** $R_f = 0.36$ (P/Et$_2$O = 3/1).

$[\alpha]_D^{20} = +72.3$ ($c = 0.10$, CHCl$_3$).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3027 (C=CH), 2952 (CH), 2928 (CH), 2854 (CH), 1757 (CO), 1630 (C=CO), 1461 (C-H).

**$^1$H-NMR** (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.08 (s, 3 H, SiCH$_3$), 0.10 (s, 3 H, SiCH$_3$), 0.90 [s, 9 H, SiC(CH$_3$)$_3$], 1.51 (s, 3 H, CH$_3$), 1.62-1.68 (m, 1 H, C4'-HH), 1.75 (t, $^5$J = 2.6 Hz, 3 H, C4''-H), 1.75-1.80 (m, 1 H, C4'-HH), 2.01-2.09 (m, 1 H, C5'-HH), 2.19-2.27 (m, 1 H, C5'-HH), 2.55 (dq, $^2$J = 16.9 Hz, $^5$J = 2.6 Hz, 1 H, C1''-HH), 2.67 (dq, $^2$J = 16.9 Hz, $^5$J = 2.6 Hz, 1 H, C1''-HH), 2.66-2.72 (m, 1 H, C1'-H), 3.94 (dd, $^2$J = 9.5 Hz, $^3$J = 7.7 Hz, 1 H, OCH/H), 4.11 (dd, $^3$J = 7.5 Hz, $^3$J = 4.6 Hz, $^3$J = 2.6 Hz, 1 H, C6'-H), 4.21 (dd, $^2$J = 9.5 Hz, $^3$J = 6.1 Hz, 1 H, OCH/H), 5.48 (s, 1 H, C3-H), 5.48-5.53 (m, 1 H, C2'-H), 5.83 (dt, $^3$J = 9.8 Hz, $^4$J = 3.4 Hz, $^4$J = 1.9 Hz, 1 H, C3'-H).

**$^{13}$C-NMR** (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = -5.0 (q, SiCH$_3$), -4.4 (q, SiCH$_3$), 3.5 (q, C-4''), 18.1 [s, SiC(CH$_3$)$_3$], 22.3 (t, C-4'), 22.4 (q, CH$_3$), 25.8 [q, SiC(CH$_3$)$_3$], 28.5 (t, C1'''), 30.3 (t, C-5'), 40.3 (d, C-1''), 67.0 (d, C-6'), 72.1 (s, C-3''), 74.1 (t, CH$_2$O), 79.3 (s, C-2''), 82.8 (s, C-5), 88.3 (d, C-3), 124.0 (d, C-2'), 129.1 (d, C-3'), 171.6 (s, C-2), 183.0 (s, C-4).

**MS** (ESI): $m/z$ (%) = 803 (22) [(2M+Na)$^+$], 781 (85) [(2M+H)$^+$], 413 (12) [(M+Na)$^+$], 391 (100) [(M+H)$^+$].

**HRMS** (ESI): calcd. for C$_{22}$H$_{35}$O$_4$Si$^+$ [(M+H)$^+$]: 391.22991, found: 391.22997.

(5R)-5-(But-2''-yn-1'-yl)-3-ethoxycarbonyl-4-(but-3''-en-1'-yloxy)-5-methyl-2-oxo-2,5-dihydrofuran (8l)
To a solution of acetate 5d (380 mg, 1.41 mmol) in DMF (40 mL) was added KOtBu (258 mg, 2.11 mmol) at 0 °C and the mixture was stirred overnight. The solution was concentrated \textit{in vacuo}, the residue dissolved in NaOH/Et₂O (30 mL, 1/1), stirred for 1 h to complete the alkyne isomerisation and extracted with Et₂O (30 mL). The aqueous layer was acidified with HCl (2 M, pH = 2) and extracted with CHCl₃/iPrOH (3 × 50 mL, 5/1). The combined organic layers were dried over Na₂SO₄, filtered and concentrated \textit{in vacuo}, to afford 265 mg (1.11 mmol, 83%) tetrionic acid 31, which was used without further purification. Following the \textbf{general procedure 1}, reaction of tetrionic acid 31 (78.6 mg, 0.33 mmol) and but-3-en-1-ol (7b) (60.0 μL, 46.4 mg, 0.63 mmol) with triphenylphosphine and diisoethyl azodicarboxylate yielded after purification by flash chromatography (P/Et₂O/CH₂Cl₂ = 4/1/1) tetrionic acid ester 8l (49.8 mg, 0.17 mmol, 51%) as a yellow oil.

\textbf{DC}: \textit{R}ᵣ = 0.45 (P/Et₂O/CH₂Cl₂ = 4/1/1).

\([\alpha]_{D}^{20} = +12.4 \ (c = 0.21, \text{CHCl}_3)\).

\textbf{IR} (ATR): \tilde{\nu} (\text{cm}^{-1}) = 2963 (\text{CH}), 2910 (\text{CH}), 1767 (\text{CO}), 1715 (\text{CO}), 1641 (\text{C=CO}), 1415 (\text{CH}).

\textbf{1H-NMR} (360 MHz, CDCl₃): δ (ppm) = 1.36 (t, \(3J = 7.1 \text{ Hz} \), 3 H, OCH₂C₃H₃), 1.50 (s, 3 H, CH₃), 1.75 (t, \(5J = 2.6 \text{ Hz} \), 3 H, C⁴″-H), 2.46-2.58 (m, 3 H, C²'-H/C¹″-H/H), 2.65 (dq, \(2J = 16.7 \text{ Hz}, 5J = 2.6 \text{ Hz}, 1 \text{ H}, \text{C¹″-H/H})), 4.33 (q, \(3J = 7.1 \text{ Hz} \), 2 H, OCH₂CH₃), 4.47 (dt, \(2J = 10.1 \text{ Hz}, 3J = 6.5 \text{ Hz} \), 1 H, C¹'-HH), 5.12-5.18 (m, 2 H, C⁴'-H), 5.79 (ddt, \(3J = 17.0 \text{ Hz} \), \(3J = 10.2 \text{ Hz} \), \(3J = 6.7 \text{ Hz} \), 1 H, C³'-H).

\textbf{13C-NMR} (90.6 MHz, CDCl₃): δ (ppm) = 3.4 (q, C-⁴″), 14.1 (q, OCH₂CH₃), 22.2 (q, CH₃), 28.7 (t, C-1″), 33.4 (t, C-2″), 61.7 (t, OCH₂CH₃), 71.6 (s, C-3″), 74.0 (t, C-1′), 80.0 (s, C-2″), 82.0 (s, C-5), 97.5 (s, C-3), 118.1 (t, C-4″), 132.7 (d, C-3″), 162.1 (s, CO), 167.5 (s, C-2), 180.7 (s, C-4) .

\textbf{MS} (ESI): \textit{m/z} (%) = 315 (6) [(M+Na)⁺], 293 (100) [(M+H)⁺].

\textbf{HRMS} (ESI): calcd. for C₁₆H₂₁O₅⁺ [(M+H)⁺]: 293.13820, found: 293.13820.
3. [2+2] Photocycloaddition

**General procedure 2 for [2+2] photocycladdition.** The tetronate (0.10 mmol) was dissolved in t-BuOH (20 mL, 5mM), degassed by purging with Ar in an ultrasonicator for 15 min and irradiated in a Rayonet RPR 100 merry-go-round reactor, equipped with 16 Rayonet RPR 2537 Å lamps (λ = 254 nm). Unless otherwise stated, the reaction was stopped when the starting material was fully consumed according to TLC analysis. Then the solvent was removed and the residue was purified by flash chromatography.

(1R,1'SR,4S,6R,9S)-9-(Cyclohex-2'-en-1'-ylmethoxy)-1-methyl-2-oxatricyclo[4,2,1,04,9]-non-3-one (9a)

Following the **general procedure 2**, reaction of tetronic acid ester 8a (20.0 mg, 76.2 μmol) in t-BuOH (15 mL) for 2 h yielded after purification by flash chromatography (P/Et₂O = 3/1) straight-photocycloaddition product 9a (16.2 mg, 62.0 μmol, 81%) as a colorless amorphous solid. Mixture of two diastereoisomers (d.r. = 50/50).

**TLC:** $R_f = 0.81$ (P/Et₂O = 1/1).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2931 (CH), 2861 (CH), 1774 (CO), 1447 (CH).

**1H-NMR** (360 MHz, CDCl$_3$): $\delta$ (ppm) = 1.30-1.40 (m, 1 H, C6'-H/H), 1.45 (s, 3 H, CH$_3$), 1.54-1.62 (m, 2 H, C5'-HH/C5-H/H), 1.66-1.75 (m, 2 H, C5'-HH/C7-H/H), 1.80-1.82 (m, 1 H, C6'-H/H), 1.94 (vrt. dt, $^2J = 14.1$ Hz, $^3J \approx ^3J = 7.9$ Hz, 1 H, C8-H/H), 1.99-2.05 (m, 2 H, C4'-H), 2.12 (vrt. dtd, $^2J = 13.7$ Hz, $^3J \approx ^3J = 7.9$ Hz, $^3J = 6.1$ Hz, 1 H, C7-H/H), 2.25 (ddd, $^2J = 14.1$ Hz, $^3J = 7.9$ Hz, $^3J = 4.0$ Hz, 1 H, C8-H/H), 2.34-2.44 (m, 1 H, C1'-H), 2.62-2.69 (m, 1 H, C5-H/H), 2.95-3.04 (m, 1 H, C6-H), 3.16-3.21 (m, 1 H, C4-H), 3.37-3.42 (m, 2 H, OCH$_2$), 3.50 (ddt, $^3J = 9.8$ Hz, $^3J = 4.3$ Hz, $^4J = 1.9$ Hz, 1 H, C2'-H), 5.80 (dt, $^3J = 9.8$ Hz, $^3J = 3.4$ Hz, $^4J = 2.0$ Hz, 1 H, C3'-H).

**13C-NMR** (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 20.0 (q, CH$_3$), 20.7 (t, C-5'), 24.8 (t, C-6'), 25.3 (t, C-5), 25.9 (t, C-4'), 29.9 (t, C-7), 36.0 (d, C-1'), 38.5 (d, C-6), 39.5 (d, C-4), 40.0 (t, C-8),
69.9 (t, OCH₂), 90.8 (s, C-9), 96.1 (s, C-1), 127.6 (d, C-2'), 129.1 (d, C-3'), 177.4 (s, C-3).

Two signal sets for each peak due to the existence of two diastereoisomers.

**MS** (EI, 70 eV): \( m/z \) (%) = 262 (1) [M⁺], 168 (5) [(C₈H₁₂O₂)⁺], 95 (100).

**HRMS** (EI): calcd. for C₁₆H₂₂O₃⁺ [M⁺]: 262.1563, found: 262.1554.

**NOE**

(1R,1'R,4S,6R,6'R,9S)-9-[(6'-tert-Butyldimethylsilyl)-oxy]cyclohex-2'-en-1'-ylmethoxy]-1-methyl-2-oxatricyclo[4,2,1,0⁴,⁹]-non-3-one (9b)

Following the **general procedure 2**, reaction of tetronic acid ester 8b (30.7 mg, 78.0 μmol) in 'BuOH (16 mL) for 2 h yielded after purification by flash chromatography (P/Et₂O = 5/1) **straight-photocycloaddition** product 9b (23.9 mg, 60.8 μmol, 78%) as a colorless amorphous solid.

**TLC**: \( R_f = 0.42 \) (P/Et₂O = 3/1).

\([\alpha]_{D}^{20} = +87.2 \) (c = 0.20, CHCl₃).

**IR** (ATR): \( \tilde{\nu} \) (cm⁻¹) = 2952 (CH), 2928 (CH), 2884 (CH), 1765 (CO), 1463 (CH).

**¹H-NMR** (500 MHz, CDCl₃): \( \delta \) (ppm) = 0.07 (s, 3 H, SiCH₃), 0.09 (s, 3 H, SiCH₃), 0.91 [s, 9 H, Si(CH₃)₃], 1.44 (s, 3 H, CH₃), 1.58-1.73 (m, 3 H, C5'-HH/C7-HH/C5-HH), 1.75-1.84 (m, 1 H, C5'-HH), 1.92 (virt. dt, \( ^2J = 13.9 \) Hz, \( ^3J \approx ^2J = 7.9 \) Hz, 1 H, C8-HH), 1.99-2.29 (m, 4 H, C8-HH/C7-HH/C4'-H), 2.41-2.48 (m, 1 H, C1'-H), 2.64 (ddd, \( ^2J = 12.8 \) Hz, \( ^3J = 11.3 \) Hz, \( ^3J = 2.2 \) Hz, 1 H, C5-HH), 2.98-3.06 (m, 1 H, C6-H), 3.22 (ddd, \( ^3J = 11.2 \) Hz, \( ^3J = 3.7 \) Hz, \( ^4J = 2.2 \) Hz, 1 H, C4-HH), 3.40 (virt. t, \( ^2J \approx ^3J = 8.4 \) Hz, 1 H, OCHH), 3.74 (dd, \( ^2J = 8.4 \) Hz, \( ^3J = 8.4 \) Hz, \( ^3J = 8.4 \) Hz, \( ^3J = 8.4 \) Hz, 1 H, C4'-H), 3.84 (ddd, 1 H, C7'HH)
6.0 Hz, 1 H, OCH\textsubscript{3}), 4.07-4.10 (m, 1 H, C6'-H), 5.45 (ddt, \(^3J = 9.8\) Hz, \(^3J = 4.3\) Hz, \(^4J = 1.9\) Hz, 1 H, C2'-H), 5.76 (ddt, \(^3J = 9.7\) Hz, \(^3J = 3.6\) Hz, \(^4J = 2.2\) Hz, C3'-H)

\(^{13}\text{C-NMR}\) (90.6 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = -5.0 (q, SiCH\textsubscript{3}), -4.4 (q, SiCH\textsubscript{3}), 18.1 [s, SiC(CH\textsubscript{3})\textsubscript{3}], 20.0 (q, CH\textsubscript{3}), 22.6 (t, C-4'), 25.1 (t, C-5), 25.8 [q, SiC(CH\textsubscript{3})\textsubscript{3}], 28.9 (t, C-5'), 30.0 (t, C-7), 38.6 (d, C-6), 39.6 (d, C-4), 40.0 (t, C-8), 41.6 (d, C-1'), 66.8 (t, OCH\textsubscript{2}), 67.4 (d, C-6'), 91.1 (s, C-9), 96.1 (s, C-1), 125.6 (d, C-2'), 127.9 (d, C-3'), 177.4 (s, C-3).

**MS** (ESI): \(m/z\) (%) = 1199 (6) [(3M+Na\textsuperscript{+}), 785 (100) [(2M+H\textsuperscript{+})], 415 (8) [(M+Na\textsuperscript{+})], 410 (22) [(M+NH\textsubscript{4}\textsuperscript{+})], 393 (70) [(M+H\textsuperscript{+})].

**HRMS** (ESI): calcd. for C\textsubscript{22}H\textsubscript{37}O\textsubscript{4}Si\textsuperscript{+} [(M+H\textsuperscript{+})]: 393.24556, found: 393.24570.

**NOE**

(1R,4S,6R,9R)-9-(3'-Methylbut-3'-en-1'-yloxy)-1-methyl-2-oxatricyclo[4,2,1,0\textsuperscript{4,9}]-non-3-one (9c)

Following the **general procedure 2**, reaction of tetronic acid ester 8c (25.6 mg, 108 \(\mu\)mol) in \(^t\text{BuOH}\) (22 mL) for 2 h yielded after purification by flash chromatography (P/Et\textsubscript{2}O = 5/1) straight-photocycloaddition product 9c (14.4 mg, 61.0 \(\mu\)mol, 56%) as a colorless amorphous solid.

**TLC:** \(R_f = 0.45\) (P/Et\textsubscript{2}O = 3/1).

\([\alpha]\)\textsubscript{D}\textsuperscript{20} = +11.4 (c = 0.25, CHCl\textsubscript{3}).

**IR** (ATR): \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 2956 (CH), 2939 (CH), 1761 (CO), 1447 (CH).

**\(^1\text{H-NMR}\) (360 MHz, CDCl\textsubscript{3}):** \(\delta\) (ppm) = 1.41 (s, 3 H, CH\textsubscript{3}), 1.58 (virt. dt, \(^2J = 12.8\) Hz, \(^3J \approx 3.7\) Hz, 1 H, C5-HH), 1.67 (virt. dtd, \(^2J = 13.6\) Hz, \(^3J \approx 7.9\) Hz, \(^3J = 4.0\) Hz, 1 H, C7-HH), 1.75 (s, 3 H, CH\textsubscript{3}), 1.91 (virt. dt, \(^2J = 14.1\) Hz, \(^3J \approx 7.9\) Hz, 1 H, C8-HH), 2.09 (virt. dtd, \(^2J = 13.6\) Hz, \(^3J \approx 7.9\) Hz, \(^3J = 6.1\) Hz, 1 H, C7-HH), 2.17-2.28 (m, 1 H, C8-HH), 2.63-2.88 (d, 1 H, C4-HH), 3.27-3.53 (m, 1 H, C5-HH), 3.55-3.74 (m, 1 H, C6-HH), 3.74-3.92 (m, 1 H, C1-HH), 4.21-4.33 (m, 1 H, C2-HH), 4.36-4.44 (m, 1 H, C3-HH), 4.47-4.55 (m, 1 H, C4-HH).
2.30 (t, 3\( J = 6.7 \) Hz, 2 H, C2'-H), 2.64 (ddd, 2\( J = 12.8 \) Hz, 3\( J = 11.3 \) Hz, 3\( J = 2.2 \) Hz, 1 H, C5-HH), 2.95-3.02 (m, 1 H, C6-H), 3.18 (ddd, 3\( J = 11.2 \) Hz, 3\( J = 3.7 \) Hz, 4\( J = 2.2 \) Hz, 1 H, C4-H), 3.56-3.60 (m, 2 H, C1'-H), 4.71-4.73 (m, 1 H, C4'-HH), 4.79-4.80 (m, 1 H, C4'-HH).

\( ^{13}\text{C-NMR} \) (90.6 MHz, CDCl3): \( \delta \) (ppm) = 20.0 (q, CH3), 22.9 (q, C-5'), 24.8 (t, C-5), 29.9 (t, C-7), 38.1 (t, C-2'), 38.5 (d, C-6), 39.4 (d, C-4), 40.1 (t, C-8), 64.7 (t, C-1'), 90.9 (s, C-1), 96.1 (s, C-9), 112.0 (t, C-4'), 142.4 (s, C-3'), 177.3 (s, C-3).

MS (EI, 70 eV): \( m/z \) (%) = 236 (1) [M⁺], 69 (100) [(C5H9)+].


\( ^{13}\text{C-NMR} \) (90.6 MHz, CDCl3): \( \delta \) (ppm) = 20.0 (q, CH3), 22.9 (q, C-5'), 24.8 (t, C-5), 29.9 (t, C-7), 38.1 (t, C-2'), 38.5 (d, C-6), 39.4 (d, C-4), 40.1 (t, C-8), 64.7 (t, C-1'), 90.9 (s, C-1), 96.1 (s, C-9), 112.0 (t, C-4'), 142.4 (s, C-3'), 177.3 (s, C-3).

MS (EI, 70 eV): \( m/z \) (%) = 236 (1) [M⁺], 69 (100) [(C5H9)+].


**1H,4S,6R,9R-9-(But-3'-en-1'-yloxy)-1-methyl-2-oxatricyclo[4,2,1,0^4,9]-non-3-one (9d)**

Following the general procedure 2, reaction of tetronic acid ester 8f (20.0 mg, 90.0 \( \mu \)mol) in \(^{t}\text{BuOH} \) (18 mL) for 2 h yielded after purification by flash chromatography (P/Et2O = 3/1) straight-photocycloaddition product 9d (13.2 mg, 59.3 \( \mu \)mol, 66%) as colorless amorphous solid and straight-photocycloaddition 9e (3.50 mg, 15.8 \( \mu \)mol, 18%) as mixture with 9d.

TLC: \( R_f = 0.55 \) (P/Et2O = 3/1).

\([\alpha]_D^{20} = +14.6 \) (c = 0.39, CHCl3).

IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2999 (CH), 2871 (CH), 1761 (CO), 1447 (CH).

\( ^1\text{H-NMR} \) (360 MHz, CDCl3): \( \delta \) (ppm) = 1.44 (s, 3 H, CH3), 1.60 (virt. dt, 2\( J = 12.8 \) Hz, 3\( J \approx 3 J  = 3.7 \) Hz, 1 H, C5-HH), 1.69 (virt. dt, 2\( J = 13.6 \) Hz, 3\( J \approx 3 J = 7.9 \) Hz, 3\( J = 4.0 \) Hz, 1 H, C7-HH), 1.93 (virt. dt, 2\( J = 14.1 \) Hz, 3\( J \approx 3 J = 7.9 \) Hz, 1 H, C8-IH), 2.02-2.18 (m, 1 H, C7-HH), 2.18-2.28 (m, 1 H, C8-HH), 2.31-2.39 (m, 2 H, C2'-H), 2.66 (ddd, 2\( J = 12.8 \) Hz, 3\( J = 11.3 \) Hz, 3\( J = 2.2 \) Hz, 1 H, C5-HH), 2.90-3.03 (m, 1 H, C6-H), 3.19 (ddd, 3\( J = 11.2 \) Hz, 3\( J = 3.7 \) Hz, 4\( J = 2.2 \) Hz, 1 H, C4-H), 3.47-3.58 (m, 2 H, C1'-H), 5.06-5.10 (m, 1 H, C4'-Hcis), 5.12 (dd, 2\( J = 1.7 \) Hz, 3\( J = 17.1 \) Hz, 1 H, C4'-Htrans), 5.83 (ddt, 3\( J = 17.1 \) Hz, 3\( J = 10.2 \) Hz, 3\( J = 6.4 \) Hz, 1 H, C3'-H). The second photocycloaddition product 9e could only be isolated as mixture with 9d.

An unambiguous structure determination was not possible.
$^{13}$C-NMR (90.6 MHz, CDCl$_3$): δ (ppm) = 20.0 (q, CH$_3$), 24.8 (t, C-5), 29.9 (t, C-7), 34.4 (t, C-2'), 38.5 (d, C-6), 39.4 (d, C-4), 40.1 (t, C-8), 65.3 (t, C-1'), 90.9 (s, C-1), 96.1 (s, C-9), 117.0 (t, C-4'), 134.6 (s, C-3'), 177.3 (s, C-3).

MS (EI, 70 eV): $m/z$ (%) = 222 (1) [M$^+$], 167 (15) [(M–C$_4$H$_7$)$^+$], 55 (100) [(C$_4$H$_7$)$^+$].

HRMS (EI): calcd. for C$_{13}$H$_{18}$O$_3$$^+$ [M$^+$]: 222.1250, found: 222.1252.

(1$R$,4$S$,6$R$,9$R$)-9-(But-3$′$-enyloxy)-4-ethoxycarbonyl-1-methyl-2-oxatricyclo-[4,2,1,0$^{4,9}$]-non-3-one (9f)

Following the general procedure 2, reaction of tetronic acid ester 8g 15.0 mg (51.0 μmol) in tBuOH (10 mL) for 45 min yielded after purification by flash chromatography (P/Et$_2$O = 3/1) straight-photocycloaddition product 9f (10.5 mg, 35.7 μmol, 70%) as colorless amorphous solid and straight-photocycloaddition product 9g (3.0 mg, 10.2 μmol, 20%) as mixture with 9f.

TLC: $R_f = 0.27$ (P/Et$_2$O = 3/1).

[α]$_D^{20}$ = +61.0 (c = 0.50, CHCl$_3$).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3076 (C=CH), 2980 (CH), 2940 (CH), 1767 (CO), 1733 (CO).

$^1$H-NMR (360 MHz, CDCl$_3$): δ (ppm) = 1.31 (t, $^3$J = 7.1 Hz, 3 H, OCH$_2$CH$_3$), 1.48 (s, 3 H, CH$_3$), 1.65-1.90 (m, 3 H, C5-HH/C7-HH/C8-HH), 2.19-2.34 (m, 4 H, C7-HH/C8-HH/C2'-H), 3.03-3.08 (m, 1 H, C6-H), 3.17 (dd, $^2$J = 12.8 Hz, $^3$J = 10.2 Hz, 1 H, C5-HH), 3.47 (dt, $^2$J = 8.5 Hz, $^3$J = 6.5 Hz, 1 H, C5'-HH), 3.52 (dt, $^2$J = 8.5 Hz, $^3$J = 6.6 Hz, 1 H, C1'-HH), 4.16-4.35 (m, 2 H, OCH$_2$CH$_3$), 5.05 (dd, $^2$J = 1.6 Hz, $^3$J = 10.2 Hz, 1 H, C4'-H$_{cis}$), 5.08 (dd, $^2$J = 1.6 Hz, $^3$J = 17.1 Hz, 1 H, C4'-H$_{trans}$), 5.79 (ddt, $^3$J = 17.1 Hz, $^3$J = 10.2 Hz, $^3$J = 6.4 Hz, 1 H, C3'-H).

The second photocycloaddition product 9g could only be isolated as mixture with 9f. An unambiguous structure determination was not possible.

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): δ (ppm) = 14.1 (q, OCH$_2$CH$_3$), 19.4 (q, CH$_3$), 29.2 (t, C-5), 29.9 (t, C-7), 34.4 (t, C-2'), 35.4 (d, C-6), 40.0 (t, C-8), 55.3 (s, C-4), 61.9 (t, OCH$_2$CH$_3$), 65.2 (t, C-1'), 94.1 (s, C-1), 95.6 (s, C-9), 117.0 (t, C-4'), 134.3 (d, C-3'), 166.6 (s, CO), 173.6 (s, C-3).
MS (ESI): m/z (%) = 589 (11) [(2M+H)+], 317 (23) [(M+Na)+], 312 (100) [(M+NH4)+], 295 (74) [(M+H)+].


(1R,1′RS,4S,6R,9S)-Ethyl 9-(cyclohex-2′-en-1′-ylmethoxy)-4-ethoxycarbonyl-1-methyl-2-oxatricyclo[4.2.1.02,9]-non-3-on-4-carbonate (9h) and (1S,2S,3R,6S,7R,8RS)-3-(But-3′-en-1′-yl)-6-ethoxycarbonyl-3-methyl-2,8-oxathano-4-oxatricyclo[5.4.0.02,6]-undecan-5-one (9i)

Following the general procedure 2, reaction of tetronic acid ester 8d (10.0 mg, 29.9 μmol) in tBuOH (6 mL) for 1 h yielded after purification by flash chromatography (P/Et2O = 3/1) straight-photocycloaddition product 9h (6.5 mg, 19.3 μmol, 65%) and crossed-photocycloaddition product 9i (1.0 mg, 3.1 μmol, 10%) as colorless amorphous solids.

straight-photocycloaddition product 9h: Mixture of two diastereoisomers (d.r. = 50/50).

TLC: Rf = 0.36 (P/Et2O = 3/1).

IR (ATR): \(\tilde{\nu} (cm^{-1}) = 2928 \text{ (CH)}, 2850 \text{ (CH)}, 1765 \text{ (CO)}, 1718 \text{ (CO)}\).

\(^1\text{H-NMR} (360 MHz, CDCl}_3\): \(\delta \text{ (ppm)} = 1.31 \text{ (t, }^3J = 7.1 \text{ Hz, 3 H, OCH}_2\text{CCH}_3\)}, 1.26-1.39 \text{ (m, 2 H, C6′-H)}, 1.49 \text{ (s, 3 H, CH}_3\)}, 1.64-1.82 \text{ (m, 5 H, C5-HH/C7-H/C5′-H)}, 1.98-2.02 \text{ (m, 2 H, C4′-H)}, 2.19-2.37 \text{ (m, 4 H, C8-H/C3′-H/ C5-HH)}, 3.01-3.13 \text{ (m, 1 H, C6-H)}, 3.14-3.20 \text{ (m, 1 H, OCH)}, 3.29-3.36 \text{ (m, 1 H, OCHHH)}, 4.18-4.32 (m, 2 H, OCH2CH3), 5.55 (ddt, \(^3J = 9.8 \text{ Hz, }^3J = 4.3 \text{ Hz, }^4J = 1.9 \text{ Hz, 1 H, C2′-H}), 5.77 \text{ (ddt, }^3J = 9.8 \text{ Hz, }^3J = 3.5 \text{ Hz, }^4J = 1.8 \text{ Hz, 1 H, C3′-H)}\).

\(^13\text{C-NMR} (90.6 MHz, CDCl}_3\): \(\delta \text{ (ppm)} = 14.1 \text{ (q, OCH}_2\text{CH}_3\)}, 19.5 \text{ (q, CH}_3\)}, 20.7 \text{ (t, C-5′), 25.3 (t, C-4′), 25.6 (t, C-6′), 29.2 (t, C-5), 29.9 (t, C-7), 31.9 (d, C-1′), 36.0 (d, C-6), 40.0 (t, C-8), 55.4 (s, C-4), 61.9 (t, OCHCHCH3), 69.7 (t, OCH2), 94.0 (s, C-1), 95.7 (s, C-9), 127.4 (d, C-2′), 129.2 (d, C-3′), 166.6 (s, CO), 173.8 (s, C-3). Two signal sets for each peak due to the existence of two diastereoisomers.

MS (EI, 70 eV): m/z (%) = 334 (1) [M+], 186 (100), 95 (26) [(C7H11)+].
HRMS (EI): calcd. for C_{19}H_{26}O_{5}^{+} [M^{+}]: 334.1775, found: 334.1767.

crossed-Photocycloadditionsprodukt 9i: Mixture of two diastereoisomers (d.r. ca. 75/25).

TLC: $R_f = 0.58$ (P/Et$_2$O = 3/1)

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 2935 (CH), 2831 (CH), 1760 (CO), 1718 (CO).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 1.33 (t, $^3J = 7.1$ Hz, 3 H, OCH$_2$CH$_3$), 1.47-1.54 (m, 3 H, C10-H/C9-H), 1.68-2.39 (m, 8 H, C1-H/C10-HH/C11-H/C1'-H/C2'-H), 2.65-2.72 (m, 1 H, C8-H), 2.92-2.95 (m, 1 H, C7-H), 3.81-3.87 (m, 1 H, C12-HH), 4.05-4.11 (m, 1 H C12-HH), 4.22-4.34 (m, 2 H, OCH$_2$CH$_3$), 5.01 (dd, $^2J = 1.6$ Hz, $^3J = 10.2$ Hz, 1 H, C4'-Hcis), 5.06 (dd, $^3J = 1.6$ Hz, $^3J = 17.1$ Hz, 1 H, C4'-Htrans), 5.77-5.89 (m, 1 H, C3'-H).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = 13.9 (q, OCH$_2$CH$_3$), 17.3 (t, C-10), 18.3 (q, CH$_3$), 20.1 (t, C-11), 20.7 (t, C-9), 28.2 (t, C-2'), 32.7 (t, C-8), 34.5 (t, C-1'), 36.2 (d, C-1), 40.0 (d, C-7), 59.8 (s, C-6), 62.1 (t, OCH$_2$CH$_3$), 70.2 (t, C-12), 88.3 (s, C-3), 96.0 (s, C-2), 115.0 (t, C-4'), 137.5 (d, C-3'), 166.7 (s, CO), 171.8 (s, C-5). Two signal sets for each peak due to the existence of two diastereoisomers.

MS (EI, 70 eV): $m/z$ (%) = 334 (1) [M$^+$], 186 (100), 95 (26) [(C$_7$H$_{11}$)$_+$].

HRMS (EI): calcd. for C$_{19}$H$_{26}$O$_5$ [M$^+$]: 334.1775, found: 334.1767.

(1R,1'R,4S,6R,6'R,9S)-9-[(6'-tert-Butyldimethylsilyl)oxy]-cyclohex-2'-en-1'-ylmethoxy]-4-ethoxycarbonyl-1-methyl-2-oxatricyclo[4,2,1,0$^{4,9}$]-non-3-one (9j) and (1S,2S,3R,6S,7R,8R,9R)-9-[(tert-Butyldimethylsilyl)oxy]-3-(but-3'-en-1'-yl)-6-ethoxycarbonyl-3-methyl-2,8-oxathano-4-oxatricyclo[5.4.0.0$^{2,6}$]-undecan-5-one (9k)

Following the general procedure 2, reaction of tetronic acid ester 8e 12.0 mg (25.8 $\mu$mol) in tBuOH (5 mL) for 45 min yielded after purification by flash chromatography (P/Et$_2$O = 3/1 $straight$-photocycloaddition product 9j (5.6 mg, 12.1 $\mu$mol, 47%) and crossed-photocycloaddition product 9k (2.2 mg, 4.73 $\mu$mol, 18%) as colorless amorphous solids.
straight-photocycloaddition product 9j:

**TLC:** $R_f = 0.41$ (P/EtO = 3/1).

$[\alpha]D^{20} = +65.4$ ($c = 0.50$, CHCl$_3$).

**IR (ATR):** $\tilde{\nu}$ (cm$^{-1}$) = 2980 (CH), 2924 (CH), 2857 (CH), 1771 (CO), 1729 (CO).

**$^1H$-NMR (360 MHz, CDCl$_3$):** $\delta$ (ppm) = 0.06 (s, 3 H, SiCH$_3$), 0.08 (s, 3 H, SiCH$_3$), 0.98 [s, 9 H, SiC(CH$_3$)$_3$], 1.30 (t, $^3J = 7.1$ Hz, 3 H, OCH$_2$CH$_3$), 1.50 (s, 3 H, CH$_3$), 1.62-1.81 (m, 5 H, C5-H/C7-H/C4'-H), 1.95-2.06 (m, 1 H, C8-H/H/H/C5'-H), 2.13-2.31 (m, 3 H, C8-H/H/H/C5'-H), 2.35-2.39 (m, 1 H, C1'-H), 3.04-3.09 (m, 1 H, C6-H), 3.17 (dd, $^2J = 12.8$ Hz, $^3J = 10.2$ Hz, 1 H, C8-H/H/H/C5'-H), 3.36 (virt. t, $^2J \approx ^3J = 8.4$ Hz, 1 H, OCH$_2$CH$_3$), 3.68 (dd, $^2J = 8.4$ Hz, $^3J = 5.8$ Hz, 1 H, OCH$_2$CH$_3$), 4.05 (ddd, $^3J = 7.1$ Hz, 2 H, OCH$_2$CH$_3$), 5.52 (ddt, $^3J = 9.8$ Hz, $^3J = 4.3$ Hz, $^4J = 1.9$ Hz, 1 H, C2'-H), 5.73 (ddt, $^3J = 9.8$ Hz, $^3J = 3.4$ Hz, $^4J = 1.9$ Hz, 1 H, C3'-H).

**$^{13}$C-NMR (90.6 MHz, CDCl$_3$):** $\delta$ (ppm) = -5.0 (q, SiCH$_3$), -4.4 (q, SiCH$_3$), 14.0 (q, OCH$_2$CH$_3$), 18.1 [s, SiC(CH$_3$)$_3$], 19.4 (q, CH$_3$), 22.6 (t, C-4'), 25.8 [q, SiC(CH$_3$)$_3$], 28.9 (t, C-5'), 29.4 (t, C-5), 29.9 (t, C-7), 35.4 (d, C-6), 40.0 (t, C-8), 41.7 (d, C-1'), 55.3 (s, C-4), 61.9 (t, OCH$_2$CH$_3$), 66.9 (t, OCH$_2$CH$_3$), 67.4 (d, C-6'), 94.4 (s, C-5), 95.5 (s, C-1), 125.6 (d, C-2'), 127.7 (q, C-3'), 166.4 (s, CO), 173.7 (s, C-3).

**MS (ESI):** $m/z$ (%) = 951 (67) [(2M+Na)$^+$], 946 (66) [(2M+NH$_4$)$^+$], 487 (7) [(M+Na)$^+$], 482 (6) [(M+NH$_4$)$^+$], 465 (100) [(M+H)$^+$].

**HRMS (ESI):** calcd. for C$_{25}$H$_{41}$O$_6$Si$^+$ [(M+H)$^+$]: 465.26669, found: 465.26654.

crossed-photocycloaddition product 9k:

**TLC:** $R_f = 0.58$ (P/EtO = 3/1).

$[\alpha]D^{20} = +44.3$ ($c = 0.50$, CHCl$_3$).

**IR (ATR):** $\tilde{\nu}$ (cm$^{-1}$) = 2980 (CH), 2928 (CH), 2861 (CH), 1771 (CO), 1729 (CO).

**$^1H$-NMR (360 MHz, CDCl$_3$):** $\delta$ (ppm) = 0.06 (s, 3 H, SiCH$_3$), 0.08 (s, 3 H, SiCH$_3$), 0.89 [s, 9 H, SiC(CH$_3$)$_3$], 1.34 (t, $^3J = 7.1$ Hz, 3 H, OCH$_2$CH$_3$), 1.65 (s, 3 H, CH$_3$), 1.68-1.84 (m, 5 H, C10-H/C11-H/C2'-H), 1.95 (dt, $^2J = 11.6$ Hz, $^3J = 6.1$ Hz, 1 H, C1'-H/H), 2.16-2.20 (m, 2 H, C2'-H/C1'-H/H/H), 2.24-2.27 (m, 1 H, C1-H), 2.53-2.57 (m, 1 H, C8-H), 3.05 (virt. t, $^3J \approx ^3J = 5.4$ Hz, 1 H, C7-H), 3.77-3.80 (m, 1 H, C9-H), 3.86 (ddd, $^2J = 12.4$ Hz, $^3J = 5.8$ Hz, $^4J = 1.2$ Hz, 1 H, C12-H/H), 4.25-4.35 (m, 3 H, OCH$_2$CH$_3$/C12-H/H), 5.00 (dd, $^2J = 1.6$ Hz, $^3J = 10.2$ Hz, 1 H, C4'-H$_{cis}$), 5.06 (dd, $^3J = 1.6$ Hz, $^3J = 17.1$ Hz, 1 H, C4'-H$_{trans}$), 5.82 (ddt, $^3J = 17.1$ Hz, $^3J = 10.2$ Hz, $^3J = 6.4$ Hz, 1 H, C3'-H).
$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = −4.7 (q, SiCH$_3$), −4.5 (q, SiCH$_3$), 13.8 (q, OCH$_2$CH$_3$), 18.0 [s, SiC(CH$_3$)$_3$], 18.2 (q, CH$_3$), 20.9 (t, C-10), 25.7 [q, 3 C, SiC(CH$_3$)$_3$], 27.5 (t, C-11), 28.1 (t, C-2'), 34.6 (t, C-1'), 35.5 (d, C-1), 40.5 (d, C-7), 41.6 (d, C-8), 59.6 (s, C-6), 62.2 (t, OCH$_2$CH$_3$), 64.9 (d, C-9), 69.8 (t, C-12), 88.4 (s, C-3), 96.2 (s, C-2), 115.0 (t, C-4'), 137.4 (d, C-3'), 166.5 (s, CO), 171.5 (s, C-5).

MS (ESI): m/z (%) = 951 (75) [(2M+Na)$^+$], 946 (60) [(2M+NH$_4$)$^+$], 482 (6) [(M+NH$_4$)$^+$], 465 (100) [(M+H)$^+$].

HRMS (ESI): calcd. for C$_{25}$H$_{41}$O$_6$Si$^+$ [(M+H)$^+$]: 465.26669, found: 465.26673.

(1S,2R,5R,6R,9R,10R,13S)-10-[(tert-Butyldimethylsilyl)oxy]-5-(but-3′-yn-1′-yl)-5-methyl-4,7-dioxatetra-cyclo[7.3.1.0$^2$6.0$^6$13]tridecan-3-one (10)

Following the general procedure 2, reaction of tetronic acid ester 8i (4.0 mg, 10.2 $\mu$mol) in tBuOH (2 mL) for 2 h yielded after purification by flash chromatography (P/Et$_2$O = 5/1 $\rightarrow$ 4/1) straight-photocycloaddition product 10 (3.5 mg, 9.0 $\mu$mol, 88%) as a colorless amorphous solid.

TLC: $R_f = 0.37$ (P/Et$_2$O = 3/1).

[α]$^D_{20} = +8.6$ (c = 0.50, CHCl$_3$).

IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3312 (C≡CH), 2956 (CH), 2925 (CH), 2854 (CH), 1767 (CO).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.07 (s, 3 H, SiCH$_3$), 0.07 (s, 3 H, SiCH$_3$), 0.89 [s, 9 H, SiC(CH$_3$)$_3$], 1.30-1.36 (m, 1 H, C11-H/H), 1.48 (s, 3 H, CH$_3$), 1.65-1.71 (m, 1 H, C11-H/H), 1.76-1.83 (m, 1 H, C2′-H/H), 1.87-1.93 (m, 1 H, C2′-H/H), 1.97 (t, $^4$J = 2.6 Hz, 1 H, C4′-H), 1.99-2.11 (m, 2 H, C1′-H), 2.26-2.30 (m, 1 H, C1-H), 2.33 (dddd, $^2$J = 10.8 Hz, $^3$J = 7.8 Hz, $^3$J = 5.1 Hz, $^3$J = 2.2 Hz, 1 H, C12-H/H), 2.42 (dddd, $^2$J = 10.8 Hz, $^3$J = 16.2 Hz, $^3$J = 5.3 Hz, $^3$J = 2.7 Hz, 1 H, C12-H/H), 2.69-2.76 (m, 1 H, C9-H), 2.94 (d, $^3$J = 6.6 Hz, 1 H, C2-H), 3.04 (virt. t, $^3$J ≈ $^3$J = 9.6 Hz, 1 H, C13-H), 3.94 (ddd, $^3$J = 10.7 Hz, $^3$J = 5.9 Hz, $^3$J = 4.3 Hz, 1 H, C10-
(1S,2R,5R,6R,10R,13S)-10-[(tert-Butyldimethylsilyl)oxy]-5-(but-3′-yn-1′-yl)-5-methyl-2-ethoxycarbonyl-4,7-dioxatetracyclo[7.3.1.0²,6.0⁶,13]tridecan-3-one (11) and
(1S,2S,3R,6S,7R,8R,9R)-9-[(tert-Butyldimethylsilyl)oxy]-3-(but-3′-yn-1′-yl)-6-ethoxycarbonyl-3-methyl-2,8-oxathano-4-oxatricyclo[5.4.0.0²,6]undecan-5-one (12)

Following the **general procedure 2**, reaction of tetronic acid ester 8h 12.0 mg (26.4 μmol) in tBuOH (5 mL) for 40 min yielded after purification by flash chromatography (P/Et₂O = 5/1) **straight-photocycloaddition product** 11 (3.2 mg, 6.9 μmol, 26%) and **crossed-photocycloaddition product** 12 (3.8 mg, 8.2 μmol, 31%) as colorless amorphous solids.
\textit{straight}-photocycloaddition product 11:

**TLC:** $R_f = 0.31$ (P/Et$_2$O = 3/1).

$[\alpha]_D^{20} = +8.5$ (c = 0.10, CHCl$_3$).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3270 (C=CH), 2952 (CH), 2931 (CH), 2854 (CH), 1765 (CO), 1733 (CO), 1461 (CH).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.05 (s, 3 H, SiCH$_3$), 0.06 (s, 3 H, SiCH$_3$), 0.87 [s, 9 H, SiC(CH$_3$)$_3$], 1.31 (t, $^3J = 7.1$ Hz, 3 H, OCH$_2$CH$_3$), 1.40 (s, 3 H, CH$_3$), 1.65-1.76 (m, 2 H, C11-HH/C2'-HHH), 1.95 (t, $^4J = 2.6$ Hz, 1 H, C4'-H), 2.03-2.08 (m, 2 H, C11-HH/C2'-HHH), 2.23-2.29 (m, 1 H, C1'-HH), 2.35-2.47 (m, 2 H, C12-HH/C1'-HHH), 2.49-2.52 (m, 2 H, C1-H/C12-HH), 2.71-2.76 (m, 1 H, C9-H), 3.20 (dd, $^3J = 10.2$ Hz, $^3J = 9.2$ Hz, 1 H, C13-H), 3.96 (virt. td, $^3J \approx 3J = 10.7$ Hz, $^3J = 5.0$ Hz, 1 H, C10-H), 4.10 (virt. t, $^2J \approx 3J = 9.2$ Hz, 1 H, C8-HH), 4.18 (virt. t, $^2J \approx 3J = 9.2$ Hz, 1 H, C8-HH), 4.26-4.33 (m, 2 H, OCCH$_2$CH$_3$).

$^{13}$C-NMR (90.6 MHz, CDCl$_3$): $\delta$ (ppm) = -4.6 (q, SiCH$_3$), -4.9 (q, SiCH$_3$), 13.1 (t, C-2'), 14.1 (q, OCH$_2$CH$_3$), 18.0 [s, SiC(CH$_3$)$_3$], 18.8 (q, CH$_3$), 23.6 (t, C-11), 25.7 [q, SiC(CH$_3$)$_3$], 26.4 (t, C-12), 32.3 (t, C-1'), 34.1 (d, C-1), 35.6 (d, C-13), 41.7 (d, C-9), 56.9 (s, C-2), 61.7 (t, OCH$_2$CH$_3$), 68.4 (d, C-4'), 68.6 (d, C-10), 71.1 (t, C-8), 84.0 (s, C-3'), 85.8 (s, C-5), 93.9 (s, C-6), 164.9 (s, CO), 173.2 (s, C-3).

**MS** (ESI): $m/z$ (%) = 1409 (5) [(2M+Na)$^+$], 947 (25) [(2M+Na)$^+$], 925 (25) [(2M+H)$^+$], 485 (100) [(M+Na)$^+$], 463 (93) [(M+H)$^+$].

**HRMS** (ESI): calcd. for C$_{25}$H$_{39}$O$_6$Si$^+$ [(M+H)$^+$]: 463.15104, found: 463.15176.

crossed-photocycloaddition product 12:

**TLC:** $R_f = 0.41$ (P/Et$_2$O = 3/1).

$[\alpha]_D^{20} = +94.8$ (c = 0.25, CHCl$_3$).

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3284 (C=CH), 2953 (CH), 2931 (CH), 2857 (CH), 1771 (CO), 1726 (CO), 1461 (CH).

$^1$H-NMR (360 MHz, CDCl$_3$): $\delta$ (ppm) = 0.04 (s, 3 H, SiCH$_3$), 0.07 (s, 3 H, SiCH$_3$), 0.86 [s, 9 H, SiC(CH$_3$)$_3$], 1.31 (t, $^3J = 7.1$ Hz, 3 H, OCH$_2$CH$_3$), 1.68-1.78 (m, 2 H, C11-HH/C2'-HHH), 1.84-1.90 (m, 2 H, C10-HH/C2'-HHH), 1.94-1.99 (m, 2 H, C10-HH/C11-HH), 2.00 (t, $^4J = 2.6$ Hz, 1 H, C4'-H), 2.23-2.27 (m, 1 H, C1-H), 2.31-2.35 (m, 2 H, C1'-H), 2.53-2.57 (m, 1 H, C8-H), 3.03 (virt. t, $^3J \approx 3J = 5.0$ Hz, 1 H, C7-H), 3.76-3.81 (m, 1 H, C9-H), 3.82 (dd, $^2J = 12.5$ Hz, $^3J = 5.9$ Hz, 1 H, C12-HH), 4.22-4.30 (m, 3 H, OCH$_2$CH$_3$/C12-HH).
\[ ^{13}\text{C-NMR} \text{ (90.6 MHz, CDCl}_3\)): \delta \text{ (ppm)} = -4.7 \text{ (q, SiCH}_3\), -4.5 \text{ (q, SiCH}_3\), 13.6 \text{ (t, C-2\text{'})}, 13.8 \text{ (q, OCH}_2\text{CH}_3\), 17.9 \text{ [s, SiC(CH}_3)_3\], 18.0 \text{ (q, CH}_3\), 20.8 \text{ (t, C-10), 25.7 \text{ [q, 3 C, SiC(CH}_3)_3\], 27.5 \text{ (t, C-11), 34.6 \text{ (t, C-1'), 35.5 \text{ (d, C-1), 40.5 \text{ (d, C-7), 41.6 \text{ (d, C-8), 59.5 \text{ (s, C-6), 62.2 \text{ (t, OCH}_2\text{CH}_3\), 65.0 \text{ (d, C-9), 68.8 \text{ (d, C-4'), 69.8 \text{ (t, C-12), 83.2 \text{ (s, C-3'), 87.4 \text{ (s, C-3), 95.9 \text{ (s, C-2), 166.3 \text{ (s, CO), 171.2 \text{ (s, C-5).}}}}}}}}}

\text{MS (ESI): m/z (%) = 947 (100) [(2M+Na)+], 485 (78) [(M+Na)+], 480 (27) [(M+NH}_4\text{)+], 463 (96) [(M+H)+].}

\text{HRMS (ESI): calcd. for C}_{25}\text{H}_{39}\text{O}_6\text{Si}^+ [(M+H)+]: 463.15204, found: 463.15180.}

\text{(1R,3S,7R,8R)-8-(But-2'-yn-1'-yl)-1-ethoxycarbonyl-8-methyl-6,9-dioxatricyclo[5.3.1.0^3,7]non-10-one (13)}

\[
\begin{align*}
\text{hv (}\lambda\text{ = 254 nm)} & \quad \text{EtO}_2\text{C} \quad \text{EtO}_2\text{C} \\
\text{(}^8\text{BuOH)} & \quad \text{5 mM} \quad \text{72%} \\
\text{8I} & \quad \text{13}
\end{align*}
\]

Following the \textbf{general procedure 2}, reaction of tetronic acid ester \textit{8I} (10.0 mg, 34.2 \text{µmol}) in \textit{^8}\text{BuOH (7 mL) for 45 min yielded after purification by flash chromatography (P/Et}_2\text{O = 4/1} \rightarrow \text{4/1) straight-photocycloaddition product 13 (7.2 mg, 24.6 \text{µmol, 72%) as a colorless solid.}}

\text{TLC: R}_f = 0.39 \text{ (P/Et}_2\text{O = 3/1).}

\[\alpha\]_D\text{ }^{20} = +6.8 \text{ (c = 0.32, CHCl}_3\).\]

\text{IR (ATR): }\tilde{\nu} \text{ (cm}^{-1}) = 2956 \text{ (CH), 2925 (CH), 2855 (CH), 1775 (CO), 1733 (CO), 1454 (CH).}

\text{\textit{^1}\text{H-NMR} \text{ (360 MHz, CDCl}_3\)): \delta \text{ (ppm)} = 1.30 \text{ (t, }^3\text{J = 7.1 Hz, 3 H, OCH}_2\text{CH}_3\), 1.45 \text{ (s, 3 H, CH}_3\), 1.81 \text{ (t, }^5\text{J = 2.6 Hz, 3 H, C4'-H), 1.79-1.90 \text{ (m, 2 H, C4-H), 2.31 \text{ (dd, }^2\text{J = 13.3 Hz, }^3\text{J = 8.6 Hz, 1 H, C2-H/H), 2.49 \text{ (dd, }^2\text{J = 13.3 Hz, }^3\text{J = 13 Hz, 4 H, C2-H/H), 2.50-2.57 \text{ (m, 1 H, C1'-H), 2.81-2.86 \text{ (m, 1 H, C1'-H), 3.15-3.21 \text{ (m, 1 H, C3-H), 4.09-4.16 \text{ (m, 1 H, C5-H/H), 4.20-4.32 \text{ (m, 3 H, C5-H/H/OCH}_2\text{CH}_3\).}}}}}}

\text{\textit{^13}\text{C-NMR} \text{ (90.6 MHz, CDCl}_3\)): \delta \text{ (ppm)} = 3.7 \text{ (q, C-4'), 14.1 \text{ (q, OCH}_2\text{CH}_3\), 18.0 \text{ (q, CH}_3\), 26.6 \text{ (t, C-1'), 26.8 \text{ (t, C-2), 30.7 \text{ (t, C-4), 37.7 \text{ (d, C-3), 53.3 \text{ (s, C-1), 62.2 \text{ (t, OCH}_2\text{CH}_3\), 70.4 \text{ (s, C-3'), 73.6 \text{ (t, C-5), 78.3 \text{ (s, C-2'), 85.0 \text{ (s, C-8), 94.4 \text{ (s, C-7), 166.0 \text{ (s, CO), 172.8 \text{ (s, C-10).}}}}}}}}

S43
**MS** (ESI): $m/z$ (%) = 315 (12) [(M+Na)$^+$], 293 (100) [(M+H)$^+$].

**HRMS** (ESI): calcd. for $\text{C}_{16}\text{H}_{21}\text{O}_5^+$ [(M+H)$^+$]: 293.13835, found: 293.13818.
4. $^1$H- and $^{13}$C NMR Spectra

(2S,3R,4'S)-4'-Benzyl-3'-(3-hydroxy-2-vinylhept-6-enoyl)oxazolidin-2'-one (2)
(4'S,1'S,6'R)-4'-Benzyl-3'-(6-hydroxy-cyclohex-2-encarbonyl)oxazolidin-2'-one (20)
(1S,4′S,6R)-4′-Benzyl-3′-{6-[(tert-butyldimethylsilyl)oxy]cyclohex-2-encarbonyl}-oxazolidin-2′-one (21)
(1R,6R)-6-[(tert-Butyldimethylsilyl)cyclohex-2-en-1-yl]methanol (3)
(2S,5R)-5-(But-3-en-1-yl)-2-(tert-butyl)-5-methyl-1,3-dioxolan-4-one (22)
(2R)-Methyl 2-hydroxy-2-methylhex-5-enoate (23)
(2R)-Methyl 2-acetoxy-2-methylhex-5-enoate (5a)
(5R)-5-(But-3'-en-1'-yl)-4-hydroxy-5-methylfuran-2(5H)-one (6a)
Ethyl (2R)-1-(methoxy-2-methyl-1-oxohex-5-en-2-yl)malonate (5b)
(5R)-5-(But-3′-en-1′-yl)-3-ethoxycarbonyl-4-hydroxy-5-methylfuran-2(5H)-one (6b)
(2R,5R)-5-(But-3'-yn-1'-yl)-2-(tert-butyl)-5-methyl-1,3-dioxolan-4-one (24)
(2R)-Methyl 2-hydroxy-2-methylhex-5-ynoate (25)
(2R)-Methyl 2-acetoxy-2-methylhex-5-ynoate (5c)
(2R)-Ethyl 1’-(methoxy-2-methyl-1-oxohex-5-yn-2-yl)malonate (5d)
(2R,5R)-5-(But-2′-yn-1′-yl)-2-(tert-butyl)-5-methyl-1,3-dioxolan-4-one (28)
(2R)-Methyl 2-hydroxy-2-methylhex-4-ynoate (29)
(2R)-Methyl 2-acetoxy-2-methylhex-4-ynoate (5e)
(1'RS,5R)-5-(But-3''-en-1''-yl)-4-(cyclohex-2'-en-1'-ylmethoxy)-5-methyl-2-oxo-2,5-dihydrofuran (8a)
(5R)-5-(But-3"-en-1"-yl)-4-(3'-methylbut-3'-en-1'-yloxy)-5-methyl-2-oxo-2,5-dihydrofuran (8c)
(1'R,5R,6'R)-5-(But-3''-en-1''-yl)-4-{{(6''-tert-butyldimethylsilyl)oxy}cyclohex-2''-en-1''-ylmethoxy}-5-methyl-2-oxo-2,5-dihydrofuran (8b)
(5R)-5-(But-3''-en-1''-yl)-4-(but-3'-'en-1'-yloxy)-5-methyl-2-oxo-2,5-di-hydrofuran (8f)
(1’RS,5R)-5-(But-3’”-en-1”-yl)-3-(ethoxycarbonyl)-4-(cyclohex-2’-en-1’-ylmethoxy)-5-methyl-2-oxo-2,5-dihydrofuran (8d)
(5R,1"R,6"R)-5-(But-3'-en-1'-yl)-3-ethoxycarbonyl-4-\{[(6-\text{tert-butyldimethylsilyl})oxy]cyclohex-2''-en-1''-ylmethoxy\}-5-methyl-2-oxo-2,5-dihydrofuran (8e)
(5R)-5-(But-3''-en-1''-yl)-3-ethoxycarbonyl-4-(but-3’-en-1’-yloxy)-5-methyl-2-oxo-2,5-dihydro-furan (8g)
$(5R,1'R,6'R)-5\text{-}(\text{But-3''-yn-1''-yl})-4\text{-}[[6\text{-}tert\text{-butyldimethylsilyl}]oxy]\text{cyclohex-2'-en-1'-ylmethoxy}-5\text{-}methyl-2\text{-}oxo-2,5\text{-}dihydrofuran (8i)$
(5R,1'R,6'R)-5-(But-3''′-yn-1''′-yl)-3-ethoxycarbonyl-4-[(6'-tert-butyldimethylsilyl)oxy]cyclohex-2'-en-1''′-ylmethoxy)-5-methyl-2-oxo-2,5-dihydrofuran (8h)
(5R,1′R,6′R)-5-(But-2’-yn-1’-yl)-4-[(6′-tert-butyldimethylsilyl)oxy]cyclohex-2′-en-1′-ylmethoxy]-5-methyl-2-oxo-2,5-dihydrofuran (8k)
(5R,1'R,6'R)-5-((But-2''-yn-1''-yl)-3-ethoxycarbonyl-4-[(6''-tert-butyldimethylsilyl)oxy]cyclohex-2''-en-1''-ylmethoxy)-5-methyl-2-oxo-2,5-dihydrofuran (8j)
(5R)-5-(But-2''-yn-1''-yl)-3-ethoxycarbonyl-4-(but-3’-en-1’-yloxy)-5-methyl-2-oxo-2,5-dihydrofuran (8I)
(1R,1'SR,4S,6R,9S)-9-(Cyclohex-2'-en-1'-ylmethoxy)-1-methyl-2-oxatricyclo[4,2,1,0^{4,9}]-non-3-one (9a)
(1R,4S,6R,9R)-9-(3′-Methylbut-3′-en-1′-yloxy)-1-methyl-2-oxatricyclo[4,2,1,0^{4,9}]-non-3-one (9c)

9c
(1R,1'R,4S,6R,6'R,9S)-9-\{[(6'-\text{tert-Butyldimethylsilyl})-oxy]cyclohex-2'-en-1'-ylmethoxy\}-1-methyl-2-oxatricyclo[4,2,1,0^{4,9}]-non-3-one (9b)
(1R,4S,6R,9R)-9-(But-3'-en-1'-yloxy)-1-methyl-2-oxatricyclo[4,2,1,0^4,9]-non-3-one (9d)
(1R,1RS,4S,6R,9S)-Ethyl 9-(cyclohex-2′-en-1′-ylmethoxy)-4-ethoxycarbonyl-1-methyl-2-oxatricyclo[4,2,1,0^{4,9}]-non-3-on-4-carbonate (9h)
(1S,2S,3R,6S,7R,8RS)-3-(But-3’-en-1’-yl)-6-ethoxycarbonyl-3-methyl-2,8-oxathano-4-oxatricyclo[5.4.0.0^{2,6}]-undecan-5-one (9i)
(1R,1'R,4S,6R,6'R,9S)-9-\{[(6'-tert-Butyldimethyl-silyl)oxy]-cyclohex-2'-en-1'-ylmethoxy\}-4-ethoxycarbonyl-1-methyl-2-oxatricyclo[4,2,1,0^{4,9}]-non-3-one (9j)
(1\text{S},2\text{S},3\text{R},6\text{S},7\text{R},8\text{R},9\text{R})-9-[(\text{tert-Butyldimethylsilyl})\text{oxy}]\cdot 3-(\text{but-3'-en-1'-yl})\cdot 6\text{-ethoxycarbonyl} \cdot 3\text{-methyl} \cdot 2,8\text{-oxathano} \cdot 4\text{-oxatricyclo}[5.4.0.0^{2,6}]\cdot \text{undecan-5-one} (9\text{k})
(1R,4S,6R,9R)-9-(But-3′-en-1′-yloxy)-4-ethoxycarbonyl-1-methyl-2-oxatricyclo-[4,2,1,0^{4,9}]-non-3-one (9f)
(1S,2R,5R,6R,9R,10R,13S)-10-[(tert-Butyldimethylsilyl)oxy]-5-(but-3′-yn-1′-yl)-5-methyl-4,7-dioxatetra-cyclo[7.3.1.0²,6.0⁶,13]tridecan-3-one (10)
(1S,2S,3R,6S,7R,8R,9R)-9-((tert-Butyldimethylsilyl)oxy)-3-(but-3′-yn-1′-yl)-6-ethoxycarbonyl-3-methyl-2,8-oxathano-4-oxatricyclo[5.4.0.02,6]undecan-5-one (12)
(1S,2R,5R,6R,6R,10R,13S)-10-[(tert-Butyldimethylsilyl)oxy]-5-(but-3′-yn-1′-yl)-5-methyl-2-ethoxycarbonyl-4,7-dioxatetracyclo[7.3.1.0²,6.0⁶,13]tridecan-3-one (11)
(1R,3S,7R,8R)-8-(But-2'-yn-1'-yl)-1-ethoxycarbonyl-8-methyl-6,9-dioxatricyclo[5.3.1.0^3,7]non-10-one (13)