Supporting Information
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Supporting Information

Radical Zinc-Atom Transfer Based Multicomponent Approaches to 3-Alkylidene-Substituted Tetrahydrofurans

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PART I: GENERAL INFORMATION

Experiments involving organometallic compounds were carried out in dried glassware under a positive pressure of dry Ar. All solvents were distilled to remove stabilizers and dried with a Mbraun Solvent Purification System SPS-800. ZnBr$_2$ (98%) was melted under dry N$_2$ and, immediately after cooling to r.t., was dissolved in Et$_2$O. Bu$_2$Zn (Fluka, ~1N in heptane), Et$_2$Zn (Aldrich, 1.0M in hexanes), Me$_2$Zn (Aldrich, 1.0 M in heptane) and all other reagents were of commercial quality and were used without purification. $^1$H NMR, $^{13}$C NMR spectra were recorded with Brucker AVANCE 400 spectrometer fitted with BBFO probe with Z gradient. Chemical shifts are reported in δ relative to an internal standard of residual chloroform (δ = 7.27 for $^1$H NMR and 77.16 for $^{13}$C NMR). IR spectra were recorded with an ATR diamond spectrophotometer. High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95.
PART II: EXPERIMENTAL PROCEDURES AND COMPOUND CHARACTERIZATION DATA

II.1 Preparation of \(\beta\)-(propargyloxy)enoates from propargylic alcohols

II.1.A Preparation of \(\beta\)-(propargyloxy)enoates bearing pendant alkynes

Enoates 1a-h were prepared by reaction between the corresponding known propargylic alcohols and bromomethyl acrylic acid methyl ester following our previously described procedure.\(^1\)

II.1.B Preparation of \(\beta\)-(propargyloxy)enoates bearing pendant ynamides

\[ \text{TBSO} \quad = \quad \text{N} \quad \text{R}^1 \quad \text{R}^2 \quad \quad \text{TBAF, THF} \quad = \quad \text{HO} \quad \text{N} \quad \text{R}^1 \quad \text{R}^2 \quad \quad \text{Et}_3\text{N, NaI} \quad = \quad \text{CO}_2\text{Me} \]

II.1.B.1 Experimental procedures

General procedure 1 – Preparation of ynamide derived propargylic alcohols:
To a stirred solution of TBS-protected ynamine derived propargylic alcohol (1 mmol) in THF (3 mL) cooled to 0 °C, was added TBAF (1 M in THF, 1.5 mL, 1.5 mmol). The mixture was stirred for 2 h and then water (3 mL) was added. The aqueous layer was extracted 3 times with EtOAc. The combined organic layers were washed with brine, dried over MgSO\(_4\) and concentrated under reduced pressure.

General procedure 2 – Preparation of enoates 1i-k containing pendant ynamides:
To a stirred solution of bromomethyl acrylic acid methyl ester (3.6 mmol) in CH\(_2\)Cl\(_2\) (10 mL) at 0 °C was added successively Et\(_3\)N (0.75 mL, 5.4 mmol), alcohol (1.8 mmol), and NaI (0.150 g, 1 mmol). The mixture was heated in a sealed tube at 80 °C for 12 to 24 h. The mixture was cooled to room temperature and diluted with CH\(_2\)Cl\(_2\) (30 mL). HCl (1 M, 15 mL) was added and the layers separated, the aqueous one being extracted once with CH\(_2\)Cl\(_2\) (15

mL). The combined organics were washed with brine, dried over MgSO₄ and the crude material "solid loaded" on a silica gel column.

**II.1.B.2 Product characterization data**

![Chemical structure](image)

**N-Benzyl-N-(3-hydroxyprop-1-ynyl)-p-toluenesulfonamide**: Prepared according to general procedure 1 from the parent TBS-protected propargylic alcohol² (376 mg, 0.89 mmol). Purification by chromatography using cyclohexane/ethyl acetate (50:50) as eluent gave the title compound (160 mg, 57%).

IR (neat) : 2959, 2245, 1360, 1168, 1090, 1019, 814, 704, 656 cm⁻¹.

¹H NMR (400 MHz, CDCl₃) : δ = 7.74 (d, J = 8.1 Hz, 2H), 7.30 (m, 7H), 4.50 (s, 2H), 4.28 (d, J = 6.0 Hz, 2H), 2.44 (s, 3H), 1.56 (t, J = 6.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) : δ = 144.9, 135.0, 134.7, 130.0, 128.9, 128.8, 128.5, 127.9, 79.6, 70.5, 55.6, 51.3, 21.6.


**3-(3-Hydroxyprop-1-ynyl)oxazolidin-2-one**: Prepared according to general procedure 1 from the parent TBS-protected propargylic alcohol² (859 mg, 3.36 mmol). Purification by chromatography using cyclohexane/ethyl acetate (gradient) as eluent gave the title compound (253 mg, 53%).

¹H NMR (400 MHz, CDCl₃) : δ = 4.47-4.40 (m, 4H), 3.94-3.90 (m, 2H), 2.56 (s, 1H).

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(S)-4-Benzyl-3-(3-hydroxyprop-1-ynyl)oxazolidin-2-one: Prepared according to general procedure 1 from the parent TBS-protected propargylic alcohol \(^2\) (815 mg, 2.36 mmol). Purification by chromatography using cyclohexane/ethyl acetate (gradient) as eluent gave the title compound (503 mg, 92%).

IR (neat): 3389, 2258, 1753, 1403, 1211, 1183, 1111, 1013, 750, 702, 640, 594 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.36-7.31\) (m, 2H), 7.30-7.28 (m, 1H), 7.22-7.18 (m, 2H), 4.44 (s, 2H), 4.33 (m, 1H), 4.30-4.22 (m, 1H), 4.15-4.10 (m, 1H), 3.22 (dd, \(J = 14.1, 4.2\) Hz, 1H), 2.92 (dd, \(J = 14.1, 8.3\) Hz, 1H), 2.30 (s, 1H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 156.2, 134.3, 129.5, 129.0, 127.5, 74.4, 72.7, 67.6, 58.1, 50.8, 37.8\).

**Methyl 2-((3-(N-benzyl-p-toluenesulfonamido)prop-2-ynyloxy)methyl)acrylate (1i):** Prepared according to general procedure 2 from the parent propargylic alcohol (140 mg, 0.4 mmol). Purification by chromatography using cyclohexane/ethyl acetate (50:50) as eluent gave the title compound (110 mg, 67%).

IR (neat): 2951, 2244, 1721, 1439, 1360, 1310, 1168, 815, 704, 658 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.75\) (d, \(J = 7.7\) Hz, 2H), 7.32-7.26 (m, 7H), 6.26 (s, 1H), 5.75 (s, 1H), 4.50 (s, 2H), 4.23 (s, 2H), 4.07 (s, 2H), 3.76 (s, 3H), 2.43 (s, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 166.3, 144.8, 136.7, 134.8, 134.6, 129.9, 128.8, 128.6, 128.4, 127.8, 126.7, 80.3, 67.8, 67.3, 58.2, 55.5, 52.0, 21.6\).

HRMS: \(m/z\) [M + Na\(^+\)] calcd for C\(_{23}\)H\(_{23}\)O\(_3\)NNaS: 436.11891; found: 436.11896.
Methyl 2-((3-(2-oxooxazolidin-3-yl)prop-2-ynyloxy)methyl)acrylate (1j): Prepared according to general procedure 2 from the parent propargylic alcohol (253 mg, 1.79 mmol). Purification by chromatography using cyclohexane/ethyl acetate (50:50) as eluent gave the title compound (323 mg, 75%).

IR (neat): 2260, 1768, 1718, 1636, 1418, 1197, 1162, 1088, 1034, 750 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 6.31 (m, 1H), 5.89 (m, 1H), 4.46 (t, J = 7.9 Hz, 2H), 4.35 (s, 2H), 4.26 (s, 2H), 3.92 (t, J = 7.9 Hz, 2H), 3.76 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 166.4, 156.3, 136.7, 126.7, 77.4, 76.7, 67.9, 63.2, 58.3, 52.1, 46.9.

HRMS: m/z [M + Na]⁺ calcd for C₁₁H₁₃O₅NNa: 262.06859; found: 262.06846.

(S)-Methyl 2-((3-(4-benzyl-2-oxooxazolidin-3-yl)prop-2-ynyloxy)methyl)acrylate (1k): Prepared according to general procedure 2 from the parent propargylic alcohol (210 mg, 0.91 mmol). Purification by chromatography using cyclohexane/ethyl acetate (50:50) as eluent gave the title compound (273 mg, 91%).

[α]D²⁰ + 67.3 (c 1.0, CHCl₃).

IR (neat): 2953, 2256, 1768, 1719, 1413, 1191, 1086, 1030, 955, 817, 751, 703 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.30 (m, 2H), 7.28 (m, 1H), 7.20 (m, 2H), 6.33 (s, 1H), 5.91 (s, 1H), 4.40 (s, 2H), 4.34-4.24 (m, 4H), 4.12 (m, 1H), 3.76 (s, 3H), 3.22 (dd, J = 13.9, 3.8 Hz, 1H), 2.93 (dd, J = 13.9, 8.1 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ = 166.3, 155.8, 136.7, 134.2, 129.5, 129.1, 127.7, 126.9, 75.7, 69.8, 67.9, 67.6, 58.3, 58.2, 52.0, 37.9.

II.2 Tandem 1,4-addition / cyclization reactions starting from β-(propargyloxy)enoates

II.2.A Experimental procedures

General procedure 3. Reaction of \(n\text{Bu}_2\text{Zn}\) and \(\text{Et}_2\text{Zn}\) with β-(propargyloxy)enoates:
Under argon, to a stirred solution of β-(propargyloxy)-enoate (0.2 mmol) in \(\text{Et}_2\text{O}\) (5 mL) was added dialkylzinc reagent \(R_2\text{Zn}\) (~1N in heptane or hexane, 0.6 mmol) at room temperature. The reaction mixture was stirred at room temperature for 16 h. The reaction was hydrolyzed with an aqueous solution of HCl (1M). The layers were separated, the aqueous one being extracted twice with ether. The combined organic layers were washed with brine, dried over MgSO₄ and the solvents evaporated under reduced pressure. The product was purified by flash chromatography on silica gel.

General procedure 4. Reaction of \(\text{Me}_2\text{Zn}\) with β-(propargyloxy)enoates:
Under argon, to a stirred solution of β-(propargyloxy)enoate (0.2 mmol) in 1,2-dichloroethane (1 mL) at 0 °C was added \(\text{Me}_2\text{Zn}\) (1.2 mL, 1.0 M in heptane, 1.2 mmol). Air (20 mL) was slowly introduced over 1h into the solution via a syringe pump using a syringe fitted with a CaCl₂ guard. The reaction mixture was then stirred at 0 °C for 1h. \(\text{CH}_2\text{Cl}_2\) (5 mL) was the added and the reaction was hydrolyzed with an aqueous solution of HCl (1M, 5 mL). The layers were separated, the aqueous one being extracted with \(\text{CH}_2\text{Cl}_2\) (3×10 mL). The combined organic layers were washed with brine, dried over MgSO₄ and the solvents evaporated under reduced pressure. The product was purified by flash chromatography on silica gel.

General procedure 5. Reaction of \(\text{RZnBr-LiBr}\) with β-(propargyloxy)enoates:
Under argon, to stirred \(\text{ZnBr}_2\) (1M in \(\text{Et}_2\text{O}\), 1.0 mL, 1.0 mmol) was added drop wise \(n\text{BuLi}\) (2.2 M in hexane, 0.45 mL, 0.99 mmol) at –60 °C. After 5 min, the initial slurry gave place to a colourless solution. The mixture was further stirred for 15 min at room temperature before being cooled again to –30 °C. \(\text{Et}_2\text{O}\) (2 mL), and a solution of β-(propargyloxy)enoate (0.5 mmol) in \(\text{Et}_2\text{O}\) (2 mL) was added. The reaction mixture was stirred at room temperature for 20 h. The reaction was hydrolyzed with an aqueous solution of HCl (1M, 10 mL). The layers were separated, the aqueous one being extracted with \(\text{Et}_2\text{O}\) (2×15 mL). The combined organic
layers were washed with brine, dried over MgSO₄ and the solvents evaporated under reduced pressure. The product was purified by flash chromatography on silica gel.

**General procedure 6. Me₂Zn-mediated reaction of alkyl iodides with β-(propargyloxy)enoates :**

Under argon, to a stirred solution of β-(propargyloxy)enoate (0.2 mmol) and alkyl iodide (1 mmol) in CH₂Cl₂ (1 mL) at 0 °C was added Me₂Zn (0.6 mL, 1.0 M in heptane, 0.6 mmol). Air (20 mL) was slowly introduced over 1 h into the solution via a syringe pump using a syringe fitted with a CaCl₂ guard. The reaction mixture was then stirred at 0 °C for 1 h. CH₂Cl₂ (5 mL) was then added and the reaction was hydrolyzed with an aqueous solution of HCl (1 M, 5 mL). The layers were separated, the aqueous one being extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were washed with brine, dried over MgSO₄ and the solvents evaporated under reduced pressure. The product was purified by flash chromatography.

**General procedure 7. Me₂Zn-mediated reaction of alkyl iodides with β-(propargyloxy)enoates followed by iodine quench:**

Under argon, to a stirred solution of β-(propargyloxy)enoate (0.2 mmol) and alkyl iodide (1 mmol) in CH₂Cl₂ (1 mL) at 0 °C was added Me₂Zn (0.6 mL, 1.0 M in heptane, 0.6 mmol). Air (20 mL) was slowly introduced over 1 h into the solution via a syringe pump using a syringe fitted with a CaCl₂ guard. The reaction mixture was then stirred at 0 °C for 1 h. A solution of I₂ (343 mg, 1.4 mmol) in THF (2.5 mL) was then added at the same temperature and the mixture was stirred for 1 h. CH₂Cl₂ (10 mL) followed by an aqueous solution of Na₂S₂O₃ (10%) were added. The layers were separated, the aqueous one being extracted with CH₂Cl₂ (2 × 10 mL). The combined organic layers were washed with HCl (1 M) (10 mL), brine (10 mL), dried over MgSO₄, and the solvents evaporated under reduced pressure. The product was purified by flash chromatography.
II.2.B Product characterization data

The preparation and characterization data of compounds 5aa, 5ab, 5da, 5ea, 5eb, 5ec, 5ga, 5gb following general procedure 3 has been previously described.3

**Methyl tetrahydro-4-methylene-3-pentylfuran-3-carboxylate (5aa)**: Prepared according to general procedure 5 from enoate 1a (76 mg, 0.50 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (49 mg, 46%). The product characterization data obtained are the same as those previously reported using general procedure 3.

IR (neat): 2954, 2928, 2859, 1731, 1379 cm⁻¹

¹H NMR (CDCl₃, 400 MHz): δ 5.22 (t, J = 2.4 Hz, 1H), 5.07 (t, J = 2.1 Hz, 1H), 4.37-4.43 (m, 2H), 4.34 (dt, J = 13.1, 2.2 Hz, 1H), 3.74 (d, J = 9.0 Hz, 1H), 3.73 (s, 3H), 1.96 (m, 1H), 1.61 (m, 1H), 1.20-1.32 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 173.5, 150.4, 106.2, 75.0, 71.7, 56.8, 52.3, 37.1, 32.0, 25.2, 22.4, 13.9.


**Methyl tetrahydro-3-(2-methylbutyl)-4-methylenefuran-3-carboxylate (5af)**: Prepared according to general procedure 5 from enoate 1a (76 mg, 0.50 mmol) using s-BuLi (1.3 M in cyclohexane/hexane, 0.76 mL, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (43 mg, 41%, d.r. = 50:50).

¹H NMR (CDCl₃, 400 MHz): δ 5.27 (t, J = 2.4 Hz, 1H), 5.08 (t, J = 2.0 Hz, 1H), 4.53 (d, J = 9.0 Hz, 1H), 4.50 (J = 9.0 Hz, 1H), 2.12 (dd, J = 13.6, 4.6 Hz, 1H), 1.95 (dd, J = 14.0,

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8.4 Hz, 1H isomer 2 or 1), 1.64 (dd, J = 14.0, 4.4 Hz, 1H isomer 2 or 1), 1.47-1.09 (m, 5H+1H isomer 1 or 2), 0.86-0.80 (m, 6H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) : δ 172.8, 172.6, 150.1, 149.7, 105.7, 105.4, 74.4, 73.5, 70.3, 70.2, 55.7, 55.2, 51.3, 51.2, 43.0, 42.7, 31.20, 31.16, 29.7, 29.1, 19.1, 18.1, 10.23, 10.20.

**Methyl tetrahydro-4-methylene-3-neopentylfuran-3-carboxylate (5ag)** : Prepared according to general procedure 5 from enoate 1a (75 mg, 0.50 mmol) using t-BuLi (1.6 M in pentane, 0.62 mL, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (42 mg, 41 %).

$^1$H NMR (CDCl$_3$, 400 MHz) : δ 5.30 (t, J = 2.5 Hz, 1H), 5.10 (t, J = 2.1 Hz, 1H), 4.76 (d, J = 9.0 Hz, 1H), 4.39 (dt, J = 13.2, 2.2, 1H), 4.19 (m, 1H), 3.70 (s, 3H), 3.59 (d, J = 9.0 Hz, 1H), 2.32 (d, J = 14.5 Hz, 1H), 1.52 (d, J = 14.5 Hz, 1H), 0.91 (s, 9H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) : δ 173.7, 151.8, 107.2, 75.0, 70.4, 56.2, 52.2, 50.5, 31.7, 30.5.

Selected nOe signals :

\[ \begin{align*}
&\text{nOe} \\
&\text{H}_{\text{cis}} (5.10 \text{ ppm}) \\
&\text{H}_{\text{trans}} (5.30 \text{ ppm}) \\
&\text{nOe} \\
&^4J(\text{H}_{\text{cis}}\text{-H}_3) = 2.1 \text{ Hz} \\
&^4J(\text{H}_{\text{trans}}\text{-H}_3) = 2.5 \text{ Hz}
\end{align*} \]

**Methyl tetrahydro-4-methylene-3,5-dipentylfuran-3-carboxylate (5ba)** : Prepared according to general procedure 3 from enoate 1b (224 mg, 1.0 mmol) and Bu$_2$Zn. Purification by chromatography using cyclohexane/ethylacetate (gradient) as eluent gave the title compound (169 mg, 60 %, d.r.=75:25).

$^1$H NMR (CDCl$_3$, 400 MHz) : δ 5.22 (d, J = 2.5 Hz, 1H), 5.00 (d, J = 2.0 Hz, 1H minor), 4.97 (d, J = 2.3 Hz, 1H major), 4.53 (d, J = 9.1 Hz, 1H minor), 4.30-4.35 (m, 1H), 4.23 (d, J = 9.1 Hz, 1H minor), 4.18 (dd, J = 14.0, 4.4 Hz, 1H minor), 1.47-1.09 (m, 5H+1H major), 0.86-0.80 (m, 6H).
Hz, 1Hmajor), 3.87 (d, J = 9.1 Hz, 1Hmajor), 3.73 (s, 3Hmajor), 3.72 (s, 3Hminor), 3.56 (d, J = 9.1 Hz, 1Hminor), 2.04 (1Hminor), 1.2-1.9 (m, 15H + 1Hmajor), 0.87-0.90 (m, 6H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 173.7, 173.6, 154.2, 106.5, 106.0, 81.4, 81.3, 73.2, 72.2, 69.3, 57.4, 57.3, 52.4, 52.1, 37.6, 37.4, 35.5, 34.7, 32.0, 31.9, 31.8, 31.4, 25.4, 25.2, 25.0, 24.8, 22.6, 22.5, 22.4, 22.3, 14.0, 13.9.

Methyl tetrahydro-4-methylene-3-pentyl-5-phenylfuran-3-carboxylate (5ca): Prepared according to general procedure 3 from enoate 1c (85 mg, 0.4 mmol) and Bu$_2$Zn. Purification by chromatography using cyclohexane/ethylacetate (90/10) as eluent gave the title compound (64 mg, 59 %, d.r.=70:30).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.30-7.35 (m, 5H), 5.32 (m, 1H), 5.28 (t, J = 2.3 Hz, 1Hmajor), 5.24 (t, J = 2.3 Hz, 1Hminor), 4.82 (d, J = 2.0 Hz, 1Hminor), 4.78 (d, J = 2.3 Hz, 1Hmajor), 4.75 (d, J = 9.1 Hz, 1Hminor), 4.43 (d, J = 9.4 Hz, 1Hmajor), 4.19 (d, J = 9.4 Hz, 1Hmajor), 3.78 (m, 3Hmajor), 3.75 (s, 3Hminor), 3.73 (d, J = 9.1 Hz, 1Hminor), 2.15 (m, 1Hminor), 1.96 (m, 1Hmajor), 1.79-1.65 (m, 1H), 1.40-1.20 (m, 6H), 0.93-0.90 (m, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 173.5, 154.4, 154.1, 140.5, 140.0, 128.4, 128.1, 127.5, 109.7, 109.3, 84.1, 77.3, 74.2, 73.0, 57.5, 57.2, 52.4, 37.8, 37.5, 32.0, 25.3, 22.4, 14.0.

Methyl tetrahydro-3-pentyl-4-propylidenefuran-3-carboxylate (5da): Prepared according to general procedure 3 from enoate 1d (36 mg, 0.2 mmol) and Bu$_2$Zn. Purification by chromatography using ether/pentane (gradient) as eluent gave the title compound (30 mg, 64 %, Z:E = 64:36).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 5.49 (tt, J = 7.2, 2.4 Hz, 1H-(Z)), 5.33 (tt, J = 7.7, 1.9 Hz, 1H-(E)), 4.28-4.40 (m, 2H + 1H-(Z)), 4.21 (d, J = 8.8 Hz, 1H-(E)), 3.84 (d, J = 8.8 Hz, 1H-
(E)), 3.72 (s, 3H), 3.68 (d, J = 9.0 Hz, 1H-(Z)), 2.05 (m, 2H-(E)), 1.90-2.00 (m, 3H-(Z) + 1H-(E)), 1.80 (m, 1H-(E)), 1.58 (m, 1H-(Z)), 1.18-1.40 (m, 6H), 0.98 (t, J = 7.5 Hz, 3H-(Z)), 0.94 (t, J = 7.5 Hz, 3H-(E)), 0.88 (m, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) : δ 174.8, 174.0, 140.4, 139.5, 124.4, 124.2, 77.9, 74.9, 73.5, 69.4, 52.2 (2C), 56.4, 55.4, 37.2, 34.7, 32.3, 32.1, 25.2, 24.4, 22.9, 22.5, 22.4, 21.6, 14.0, 13.9, 13.8, 13.7.


Stereochemical assignment:

Stereochemical (Z) / (E) assignment was deduced from nOe experiments performed on unsubstituted product 5ag which showed that: (1) vinylic protons syn to the carbomethoxy moiety are less shielded than vinylic protons anti to the carbomethoxy group and, (2) the $^4J$ coupling constant of the vinylic proton with the two H3 protons is also diagnostic as this constant is higher for the trans vinylic proton (2.4 Hz) than for the cis vinylic proton (2.1 Hz).

(Z)-Methyl tetrahydro-3-isobutyl-4-propyldenefuran-3-carboxylate (5dc) : Prepared according to general procedure 6 from enoate 1d (36 mg, 0.20 mmol) and iPrI (0.1 mL, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave a mixture of compounds 5dc, 5dd and 15dc (37 mg, 72 %, 5dc/5dd/15dc=71:15:14). Further purification by flash chromatography provided an analytically pure sample of 5dc.
IR (neat) : 2956, 1730 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta \) 5.52 (tt, 1H, \(J = 9.7, 2.4 \) Hz, 1H), 4.50 (d, \(J = 9.0 \) Hz, 1H), 4.38 (dd, \(J = 13.2, 2.4 \) Hz, 1H), 4.28 (dd, \(J = 13.2, 2.4 \) Hz, 1H), 3.69 (s, 3H), 3.64 (d, \(J = 9.0 \) Hz, 1H), 2.02 (m, 1H), 1.92 (m, 2H), 1.60 (m, 1H), 1.48 (m, 1H), 0.97 (t, \(J = 7.5 \) Hz, 3H), 0.87 (dd, \(J = 13.2 \) Hz, 3H), 0.86 (dd, \(J = 13.2 \) Hz, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) : \(\delta \) 174.4, 141.0, 124.8, 75.0, 69.1, 56.1, 52.3, 46.1, 26.1, 24.1, 23.1, 23.0 13.8.

(Z)-Methyl 3-ethyl-tetrahydro-4-propylidenefuran-3-carboxylate (5dd) : Prepared according to general procedure 4 from enoate 1d (36 mg, 0.20 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (22 mg, 56%).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta \) 5.49 (tt, \(J = 7.3, 2.4 \) Hz, 1H), 4.38 (m, 3H), 3.73 (d, \(J = 9.0 \) Hz, 1H), 3.72 (s, 3H), 1.97 (m, 3H), 1.65 (m, 1H), 0.99 (t, \(J = 7.5 \) Hz, 3H), 0.88 (t, \(J = 7.5 \) Hz, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) : \(\delta \) 173.9, 140.2, 124.3, 74.6, 69.5, 56.9, 52.2, 30.1, 22.9, 13.7, 9.9.

(Z)-Methyl 3-ethyl-tetrahydro-4-((trimethylsilyl)methylene)furan-3-carboxylate (5ed) : Prepared according to general procedure 4 from enoate 1e (45 mg, 0.20 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (37 mg, 76%).

IR (neat) : 2953, 2360, 1731, 1627, 837 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta \) 5.67 (t, \(J = 2.3 \) Hz, 1H), 4.38 (d, \(J = 7.2 \) Hz, 1H), 4.38 (dd, \(J = 13.6, 2.3 \) Hz, 1H), 4.32 (dd, \(J = 13.6, 2.3 \) Hz, 1H), 3.74 (dd, \(J = 7.2 \) Hz, 1H), 3.70 (s, 3H), 1.98 (m, 1H), 1.64 (m, 1H), 0.86 (t, \(J = 7.4 \) Hz, 3H), 0.08 (s, 9H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) : \(\delta \) 173.5, 158.0, 120.1, 73.9, 71.1, 59.9, 52.4, 30.2, 10.0, 0.7.
HRMS: $m/z$ [M + Na]$^+$ calcld for $\text{C}_{12}\text{H}_{22}\text{O}_3\text{NaSi}$: 265.12304; found: 265.12251.

\((Z)\)-Methyl tetrahydro-4-(((trimethylsilyl)methylene)-3-neopentylfuran-3-carboxylate \((5\text{eg})\): Prepared according to general procedure 6 from enoate \(1\text{e} \) (45 mg, 0.20 mmol) and \(\text{tBuI} \) (0.14 mL, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave a mixture of compounds \(5\text{eg} \) and \(15\text{eg} \) (46 mg, 77 \%, \(5\text{eg}/15\text{eg}=91:9\)).

$^1\text{H}$ NMR \((\text{CDCl}_3, 400 \text{ MHz})\): $\delta$ 5.80 (t, $J = 2.4 \text{ Hz}$, 1H), 4.72 (d, $J = 9.0 \text{ Hz}$, 1H), 4.39 (dd, $J = 13.5, 2.4 \text{ Hz}$, 1H), 4.14 (dd, $J = 13.5, 2.4 \text{ Hz}$, 1H), 3.66 (s, 3H), 3.53 (d, $J = 9.0 \text{ Hz}$, 1H), 2.28 (d, $J = 14.4 \text{ Hz}$, 1H), 1.42 (d, $J = 14.4 \text{ Hz}$, 1H), 0.89 (s, 9H), 0.07 (s, 9H).

$^{13}\text{C}$ NMR \((\text{CDCl}_3, 100 \text{ MHz})\): $\delta$ 174.3, 159.5, 121.9, 75.1, 70.6, 58.4, 53.0, 51.4, 32.4, 31.3, 0.00.

\((Z)\)-Methyl 3-(cyclohexylmethyl)-tetrahydro-4-(((trimethylsilyl)methylene)furan-3-carboxylate \((5\text{eh})\): Prepared according to general procedure 6 from enoate \(1\text{e} \) (45 mg, 0.20 mmol) and cyclohexyl iodide (422 mg, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave a mixture of compounds \(5\text{eh} \) and \(5\text{ed} \) (35 mg, 56 \%, \(5\text{eh}/5\text{ed}=76:24\)).

$^1\text{H}$ NMR \((\text{CDCl}_3, 400 \text{ MHz})\): $\delta$ 5.72 (t, $J = 2.5 \text{ Hz}$, 1H), 4.49 (d, $J = 9.0 \text{ Hz}$, 1H), 4.39 (dd, $J = 13.6, 2.4 \text{ Hz}$, 1H), 4.27 (m, 1H), 3.68 (s, 3H), 3.65 (d, $J = 9.0 \text{ Hz}$, 1H), 1.98 (dd, $J = 14.2, 7.0 \text{ Hz}$, 1H), 1.70-1.50 (m, 5H), 1.42 (dd, $J = 14.2, 5.8 \text{ Hz}$, 1H), 1.30-1.00 (m, 4H), 0.96-0.80 (m, 2H), 0.07 (s, 9H).

$^{13}\text{C}$ NMR \((\text{CDCl}_3, 100 \text{ MHz})\): $\delta$ 173.8, 158.6, 120.4, 74.3, 70.7, 58.0, 52.4, 44.7, 35.6, 34.6, 33.5, 26.4(2C), 26.3, 0.6.

SI-15
(Z)-Methyl 4-benzylidene-tetrahydro-3-isobutylfuran-3-carboxylate (5gc) : Prepared according to general procedure 6 from enoate 1g (46 mg, 0.20 mmol) and iPrI (0.1 mL, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (32 mg, 58 %) contaminated with 5gd (5gc/5gd=85:15).

IR (neat) : 2953, 2251, 1728 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) : δ 7.35 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.4 Hz, 2H), 6.41 (t, J = 2.5 Hz, 1H), 4.70 (dd, J = 13.8, 6.3 Hz, 1H), 4.61 (dd, J = 13.8, 6.3 Hz, 1H), 4.57 (d, J = 9.1 Hz, 1H), 3.74 (d, J = 9.1 Hz, 1H), 3.74 (s, 3H), 2.13 (m, 1H), 1.65 (m, 2H), 0.92 (d, J = 10.7 Hz, 3H), 0.90 (d, J = 10.7 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) : δ 174.0, 143.8, 137.0, 128.8, 128.5, 127.2, 123.3, 74.1, 70.4, 57.5, 52.5, 46.2, 26.2, 24.2, 23.0.


(Z)-Methyl 4-benzylidene-3-ethyl-tetrahydrofuran-3-carboxylate (5gd) : Prepared in CH₂Cl₂ (1 mL) according to general procedure 4 from enoate 1g (46 mg, 0.20 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (28 mg, 57%).

IR (neat) : 2951, 1727 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) : δ 7.35 (t, J = 7.3 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 7.3 Hz, 2H), 6.55 (t, J = 2.5 Hz, 1H), 4.72 (dd, J = 13.9, 2.5 Hz, 1H), 4.66 (dd, J = 13.9, 2.5 Hz, 1H), 4.44 (d, J = 9 Hz, 1H), 3.79 (d, J = 9 Hz, 1H), 3.75 (s, 3H), 2.12 (m, 1H), 1.77 (m, 1H), 0.93 (t, J = 7.4 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) : δ 173.7, 143.2, 136.2, 128.7, 128.4, 127.2, 122.9, 73.9, 71.0, 58.5, 52.5, 30.4, 10.1.

(Z)-Methyl 4-benzylidene-tetrahydro-3-neopentylfuran-3-carboxylate (5gg) : Prepared according to general procedure 6 from enoate 1g (46 mg, 0.20 mmol) and tBuI (0.14 mL, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave a mixture of compounds 5gg and (Z)-15gg (58 mg, 80 %, 5gg/(Z)-15gg=81:19).

IR (neat) : 2950, 2251, 1729 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta\) 7.35 (t, \(J = 7.6\) Hz, 2H), 7.24 (t, \(J = 7.6\) Hz, 1H), 7.16 (d, \(J = 7.6\) Hz, 2H), 6.56 (t, \(J = 2.3\) Hz, 1H), 4.78 (d, \(J = 9.0\) Hz, 1H), 4.69 (dd, \(J = 13.9, 2.3\) Hz, 1H), 4.50 (dd, \(J = 13.9, 2.3\) Hz, 1H), 3.72 (s, 3H), 3.63 (d, \(J = 9.0\) Hz, 1H), 2.43 (d, \(J = 14.4\) Hz, 1H), 1.63 (d, \(J = 14.4\) Hz, 1H), 0.95 (s, 9H).

\(^13\)C NMR (CDCl\(_3\), 100 MHz) : \(\delta\) 174.0, 144.6, 137.0, 128.7, 128.4, 127.3, 124.1, 74.4, 69.7, 57.3, 52.5, 51.0, 32.0, 30.7.

Methyl-4-(2-(methoxycarbonyl)benzylidene)-tetrahydro-3-pentylfuran-3-carboxylate (5ha) : Prepared according to general procedure 3 from enoate 1h (57 mg, 0.2 mmol) and nBu\(_2\)Zn. Purification by chromatography using pentane/ether (50/50) as eluent gave two fractions containing the title compound as a mixture of diastereoisomers : fraction 1 (32 mg, 45%, Z/E=80:20), fraction 2 (18 mg, 26%, Z/E=20:80).

(Z)-5ha :

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta\) 7.93 (dd, \(J = 7.7, 1.3\) Hz, 1H), 7.46 (t, \(J = 7.7, 1.3\) Hz, 1H), 7.30 (td, \(J = 7.7, 1.3\) Hz, 1H), 7.14 (d\(_{app}\), \(J = 7.7\) Hz, 1H), 7.13 (t, \(J = 1.5\) Hz, 1H), 4.51 (dd, \(J = 13.7, 2.4\) Hz, 1H), 4.46 (d, \(J = 9.0\) Hz, 1H), 4.44 (dd, \(J = 13.7, 2.4\) Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.78 (d, \(J = 9.0\) Hz, 1H), 2.12 (m, 1H), 1.78 (m, 1H), 1.29 (m, 6H), 0.90 (t, \(J = 1.9\) Hz, 3H).
$^{13}$C NMR (CDCl$_3$, 100 MHz) : $\delta$ 173.8, 167.6, 143.7, 138.3, 132.0, 130.9, 129.21, 129.16, 127.3, 122.6, 74.7, 70.2, 57.6, 52.6, 52.1, 37.4, 32.3, 25.4, 22.6, 14.1.

HRMS : $m/z$ [M + Na]$^+$ calcd for C$_{20}$H$_{26}$O$_5$Na: 369.16725 ; found: 369.16748.

(E)-5ha :

$^1$H NMR (CDCl$_3$, 400 MHz) : $\delta$ 7.96 (d$_{app}$, $J$ = 7.8 Hz, 1H), 7.44 (t$_{app}$, $J$ = 7.8 Hz, 1H), 7.34 (t, $J$ = 7.8 Hz, 1H), 7.18 (d$_{app}$, $J$ = 7.8 Hz, 1H), 6.90 (s$_{app}$, 1H), 4.65 (d, $J$ = 12.6, 1.8 Hz, 1H), 4.56 (dd, $J$ = 12.6, 1.8 Hz, 1H), 4.17 (d, $J$ = 8.8 Hz, 1H), 3.87 (d, $J$ = 8.8 Hz, 1H), 3.86 (s, 3H), 3.59 (s, 3H), 1.56 (m, 2H), 1.30 (m, 6H), 0.78 (t, $J$ = 1.9 Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) : $\delta$ 175.0, 167.2, 141.3, 138.2, 131.9, 130.6, 130.3, 129.0, 127.5, 122.5, 77.8, 74.6, 55.8, 52.3, 52.0, 33.2, 32.4, 24.0, 22.5, 14.1.

HRMS : $m/z$ [M + Na]$^+$ calcd for C$_{20}$H$_{26}$O$_5$Na: 369.16725 ; found: 369.16764.

Stereochemical assignment :

Stereochemical (Z) / (E) assignment was deduced from nOe experiments performed on unsubstituted product 5ag which showed that the $^4J$ coupling constant of the vinylic proton with the two H3 protons is higher for the trans vinylic proton (2.4 Hz) than for the cis vinylic proton (1.8 Hz).

(Z)-Methyl 4-(2-(methoxycarbonyl)benzylidene)-tetrahydro-3-isobutylfuran-3-carboxylate (5hc) : Prepared according to general procedure 6 from enoate 1h (57 mg, 0.20 mmol) and iPrI (0.1 mL, 1 mmol). Purification by chromatography using ether/pentane.
(90:10) as eluent gave the title compound (33 mg, 50 %) contaminated with 5hd (5hc/5hd=84:16).

IR (neat) : 2953, 1717 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) : δ 7.92 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 1.5 Hz, 1H), 4.58 (d, J = 9.0 Hz, 1H), 4.49 (dd, J = 13.7, 2.5 Hz, 1H), 4.40 (dd, J = 13.7, 2.5 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.75 (d, J = 9.0 Hz, 1H), 2.21 (m, 1H), 1.68 (m, 2H), 0.93 (d, J = 9.7 Hz, 3H), 0.91 (d, J = 9.7 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) : δ 173.9, 167.6, 144.2, 138.3, 132.0, 130.9, 129.2, 129.1, 127.3, 123.0, 74.4, 69.6, 57.1, 52.5, 46.0, 26.2, 24.1, 22.5.


(Z)-Methyl 4-(2-(methoxycarbonyl)benzylidene)-3-ethyl-tetrahydrofuran-3-carboxylate (5hd) : Prepared in CH₂Cl₂ (1 mL) according to general procedure 4 from enoate 1h (58 mg, 0.20 mmol). Purification by chromatography using ether/pentane (50:50) as eluent gave the title compound (16 mg, 27%).

IR (neat) : 2953, 2361, 1716 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) : δ 7.93 (dd, J = 7.9, 1.4 Hz, 1H), 7.47 (td, J = 7.6, 1.4 Hz, 1H), 7.36 (td, J = 7.7, 1.4 Hz, 1H), 7.14 (d, J = 7.9 Hz, 1H), 7.12 (t, J = 2.4 Hz, 1H), 4.54 (dd, J =13.6, 2.5 Hz, 1H), 4.45 (d, J = 9.2 Hz, 1H), 4.44 (dd, J =13.6, 2.5 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.81 (d, J = 9.2 Hz, 1H), 2.16 (m, 1H), 1.82 (m, 1H), 0.96 (t, J = 7.4 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) : δ 173.7, 167.6, 148.9, 143.5, 138.3, 132.1, 130.9, 129.1, 127.3, 122.7, 74.2, 70.2, 58.1, 52.5, 52.0, 30.0, 9.9.

HRMS : m/z [M + Na⁺] calcd for C₁₇H₂₀O₅Na: 327.12029 ; found: 327.11981.
**Methyl 4-((N-benzyl-N-tosylamino)methylene)-3-propyl-tetrahydrofuran-3-carboxylate (5ib)**: Prepared according to general procedure 3 from enoate i (50 mg, 0.12 mmol) and Et₂Zn. Purification by chromatography using cyclohexane/ethyl acetate (80/20) as eluent gave two fractions containing the title compound: fraction 1 Z-isomer (13 mg, 24%), fraction 2 E-isomer (12 mg, 23%).

**(Z)-5ib**:

IR (neat) : 2960, 1730, 1349, 1165, 774, 658 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ 7.69 (m, 2H), 7.36 (m, 2H), 7.32-7.19 (m, 5H), 5.32 (t, J = 2.5 Hz, 1H), 4.31 (s, 2H), 4.25 (d, J = 13.2 Hz, 1H), 4.19 (d, J = 9.1 Hz, 1H), 4.08 (d, J = 13.2 Hz, 1H), 3.62 (s, 3H), 3.61 (d, J = 9.1 Hz, 1H), 2.47 (s, 3H), 1.23-1.03 (m, 2H), 1.02-0.85 (m, 2H), 0.80 (t, J = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 173.2, 148.3, 144.1, 135.6, 134.5, 129.9, 129.0, 128.6, 128.2, 128.0, 120.3, 74.9, 70.8, 56.3, 54.9, 52.4, 39.7, 21.7, 18.4, 14.4.

HRMS: m/z [M + Na]⁺ calcd for C₂₄H₂₉O₅NNaS: 466.16586; found: 466.16538.

**(E)-5ib**:

IR (neat) : 2956, 1729, 1351, 1163, 1090, 700, 660, 610 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ 7.63 (m, 2H), 7.39-7.10 (m, 7H), 5.42 (t, J = 2 Hz, 1H), 4.74 (d, J = 14.3 Hz, 1H), 4.50 (dd, J = 12.7, 2.3 Hz, 1H), 4.32 (dd, J = 12.7, 1.7 Hz, 1H), 4.18 (d, J = 9.0 Hz, 1H), 3.77 (d, J = 14.3 Hz, 1H), 3.75 (d, J = 9.0 Hz, 1H), 3.71 (s, 3H), 2.43 (s, 3H), 1.27-1.13 (m, 2H), 0.99-0.84 (m, 2H), 0.72 (t, J = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 173.1, 146.0, 144.0, 135.0, 129.8, 129.6, 128.5, 128.1, 128.0, 127.3, 118.9, 77.4, 72.7, 55.9, 52.5, 34.6, 21.7, 18.3, 14.8.

HRMS: m/z [M + Na]⁺ calcd for C₂₄H₂₉O₅NNaS: 466.16586; found: 466.16538.

Selected nOe signals:
(E)-Methyl tetrahydro-4-((2-oxooxazolidin-3-yl)methylene)-3-pentylfuran-3-carboxylate (5ja) : Prepared according to general procedure 3 from enoate 1j (30 mg, 0.12 mmol) and nBu₂Zn. Purification by chromatography using cyclohexane/ethyl acetate (50/50) as eluent gave the title compound (10 mg, 27%, E/Z = 90:10).

$^1$H NMR (CDCl$_3$, 400 MHz) (Major isomer – (E)) : $\delta$ 6.29 (t, $J$ = 1.7 Hz, 1H), 4.53 (dd, $J$ = 12.3, 1.7 Hz, 1H), 4.47 (dd, $J$ = 12.3, 1.7 Hz, 1H), 4.42-4.36 (m, 2H), 4.20 (d, $J$ = 8.8 Hz, 1H), 3.95 (d, $J$ = 8.8 Hz, 1H), 3.80-3.66 (m, 2H), 3.75 (s, 3H), 2.01-1.92 (m, 1H), 1.82-1.76 (m, 1H), 1.51-1.2 (m, 6H), 0.91 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) (Major isomer – (E)) : $\delta$ 174.5, 157.3, 133.4, 117.0, 78.2, 73.3, 62.3, 55.3, 52.6, 46.3, 34.1, 32.3, 24.1, 22.4, 14.0.

Selected nOe signals:
(E)-Methyl 4-((2-oxooxazolidin-3-yl)methylene)-3-propyl-tetrahydrofuran-3-carboxylate (5jb) : Prepared according to general procedure 3 from enoate 1j (48 mg, 0.20 mmol) and Et₂Zn. Purification by chromatography using cyclohexane/ethyl acetate (50/50) as eluent gave the title compound (15 mg, 28%, E/Z = 82:18).

IR (neat) : 2958, 1751, 1724, 1228, 1122, 1074, 1038, 761, 695 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) (Major isomer – (E)) : δ 6.25 (t, J = 1.8 Hz, 1H), 4.47 (m, 2H), 4.36 (t, J = 7.3 Hz, 2H), 4.17 (d, J = 8.8 Hz, 1H), 3.92 (d, J = 8.8 Hz, 1H), 3.78-3.69 (m, 2H), 3.72 (s, 3H), 2.01-1.92 (m, 1H), 1.82-1.72 (m, 1H), 1.51-1.38 (m, 1H), 1.36-1.21 (m, 1H), 0.93 (t, J = 6.8 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) (Major isomer – (E)) : δ 174.6, 157.5, 133.6, 117.2, 78.3, 73.4, 62.5, 55.5, 52.7, 46.5, 36.6, 18.0, 14.8.


Selected nOe signals :

(E)-Methyl 4-(((S)-4-benzyl-2-oxooxazolidin-3-yl)methylene)-3-propyl-tetrahydrofuran-3-carboxylate (5kb) : Prepared according to general procedure 3 from enoate 1k (66 mg, 0.20 mmol) and Et₂Zn. Purification by chromatography using cyclohexane/ethyl acetate (50/50) as eluent gave the title compound (36 mg, 52%, d.r. = 55:45:0:0).
IR (neat) : 2874, 1760, 1730, 1455, 1215, 1139, 1072, 746, 704 cm⁻¹.

**1H NMR** (CDCl₃, 400 MHz) : δ 7.34-7.26 (m, 3H), 7.19-7.13 (m, 2H), 6.12 (t, J = 1.8 Hz, 1Hmajor), 5.96 (t, J = 1.9 Hz, 1Hminor), 4.55-4.45 (m, 2H), 4.25-4.21 (m, 3H), 4.02 (d, J = 8.8 Hz, 1Hminor), 3.91 (d, J = 9.0 Hz, 1Hmajor), 3.77-3.74 (m, 1H), 3.76 (s, 3Hmajor), 3.63 (s, 3Hminor), 3.05 (m, 1H), 2.62 (m, 1H), 2.01-1.90 (m, 1H), 1.88-1.78 (m, 1H), 1.51-1.10 (m, 2H), 0.98 (t, J = 7.3 Hz, 3Hminor), 0.92 (t, J = 7.3 Hz, 3Hmajor).

**13C NMR** (CDCl₃, 100 MHz) : δ 173.9, 173.0, 157.0, 156.8, 143.5, 139.8, 135.6, 135.5, 129.3, 129.2, 129.1, 129.0, 127.5, 127.4, 116.1, 115.3, 77.4, 76.7, 72.9, 71.2, 66.5, 66.4, 60.3, 59.2, 56.2, 55.8, 52.7, 52.6, 37.8, 35.6, 34.4, 27.0, 18.2, 18.0, 14.8, 14.7.

**HRMS** : m/z [M + Na]+ calcd for C₂₀H₂₅O₅NNa: 382.16249 ; found: 382.16245.

(E)-Methyl tetrahydro-4-(1-iodopropylidene)-3-isobutylfuran-3-carboxylate (E)-15dc : Prepared according to general procedure 7 from enoate 1d (36 mg, 0.20 mmol) and iPrI (0.1 mL, 1 mmol). Purification by chromatography using pentane/ether (90:10) as eluent gave a mixture of compounds (E)-15dc, 5dc, (E)-15dd, and (Z)-15dc (64 mg, 86 %, (E)-15dc/5dc/(E)-15dd/(Z)-15dc=62:12:12:14). Further purification by flash chromatography provided a pure sample of (E)-15dc.

**1H NMR** (CDCl₃, 400 MHz) : δ 4.57 (d, J = 12.8 Hz, 1H), 4.51 (d, J = 12.8 Hz, 1H), 4.10 (d, J = 8.8 Hz, 1H), 4.04 (m, 1H), 3.74 (s, 3H), 2.40 (m, 2H), 2.21 (m, 1H), 1.90-1.78 (m, 2H), 1.06 (t, J = 7.5 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H).

**13C NMR** (CDCl₃, 100 MHz) : δ 173.8, 145.5, 98.5, 78.4, 72.3, 60.3, 52.5, 40.7, 37.1, 25.0, 24.6, 24.3, 13.4.

**Methyl tetrahydro-4-(iodo(phenyl)methylene)-3-neopentylfuran-3-carboxylate (15gg)** : Prepared according to general procedure 7 from enoate 1g (46 mg, 0.20 mmol) and tBuI (0.14
mL, 1 mmol). Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound as a mixture of diastereoisomers (70 mg, 85 %, (E)-15gg/(Z)-15gg =73:27).

(E)-15gg :

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta\) 7.34-7.18 (m, 5H), 4.32 (s, 2H), 4.26 (d, \(J = 9.0\) Hz, 1H), 4.07 (d, \(J = 9.0\) Hz, 1H), 3.81 (s, 3H), 2.60 (d, \(J = 15.0\) Hz, 1H), 2.08 (d, \(J = 15.0\) Hz, 1H), 1.09 (s, 9H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz) : \(\delta\) 174.0, 149.6, 144.9, 128.7, 128.3, 126.9, 88.5, 78.0, 73.6, 60.6, 53.0, 43.7, 32.0, 31.2.

(Z)-15gg :

\(^1\)H NMR (CDCl\(_3\), 400 MHz) : \(\delta\) 7.30-7.18 (m, 5H), 4.71 (d, \(J = 8.9\) Hz, 1H), 4.48 (d, \(J = 14.3\) Hz, 1H), 4.40 (d, \(J = 14.3\) Hz, 1H), 3.97 (d, \(J = 8.9\) Hz, 1H), 3.57 (s, 3H), 1.78 (d, \(J = 14.8\) Hz, 1H), 1.35 (d, \(J = 14.8\) Hz, 1H), 0.76 (s, 9H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz) : \(\delta\) 172.8, 148.1, 143.2, 128.6, 128.25, 127.7, 93.0, 80.4, 77.7, 59.6, 52.2, 47.3, 31.5, 30.7.
II.3 Tandem 1,4-addition / cyclization reactions starting from malonate derived enoates

Trimethyl 7-(trimethylsilyl)hept-1-en-6-yn-2,4,4-tricarboxylate (16a) : To a stirred solution of bromomethyl acrylic acid methyl ester (0.432 g, 2.44 mmol) in CH₂Cl₂ (8 mL) at 0 °C was added successively Et₃N (0.36 mL, 2.52 mmol), dimethyl 2-(3-(trimethylsilyl)prop-2-ynyl)malonate (0.404 g, 1.68 mmol), and NaI (0.063 g, 0.42 mmol). The mixture was heated in a sealed tube at 75 °C for 24 h. The mixture was cooled to room temperature and diluted with CH₂Cl₂ (30 mL). HCl (1 M, 15 mL) was added and the layers separated, the aqueous one being extracted once with CH₂Cl₂ (15 mL). The combined organics were washed with brine, dried over MgSO₄ and the crude material "solid loaded" on a silica gel column. Purification by chromatography using pentane/ether (90:10) as eluent gave the title compound (389 mg, 68%).

¹H NMR (CDCl₃, 400 MHz) : δ 6.33 (d, J = 1.5 Hz, 1H), 5.85 (s, 1H), 3.72 (s, 6H), 3.71 (s, 3H), 3.12 (s, 2H), 2.77 (s, 2H), 0.14 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz) : δ 170.3, 167.2, 135.3, 130.3, 101.6, 89.1, 56.7, 52.9, 52.1, 33.8, 24.3, 0.07.

(E)-Trimethyl 5-((trimethylsilyl)methylene)-1-propylcyclopentane-1,3,3-tricarboxylate (17ab) : Prepared according to general procedure 3 from enoate 16a (67 mg, 0.2 mmol) and Et₂Zn. Purification by chromatography using pentane/ether (85/15) as eluent gave the title compound (50 mg, 70%).

IR (neat) : 2953, 1732, 1615, 1434, 1250, 1203, 1149, 1086, 840, 750, 692 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) : δ 5.65 (t, J = 2.0 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H), 3.20 (d, J = 16.5 Hz, 1H), 2.99 (d, J = 14.0 Hz, 1H), 2.76 (dd, J = 16.5, 2.0 Hz, 1H), 2.44
(d, J = 14.0 Hz, 1H), 1.97 (td, J = 12.3, 4.2 Hz, 1H), 1.40-1.10 (m, 3H), 0.90 (t, J = 7.5 Hz, 3H), 0.11 (s, 9H).

$^{13}\text{C NMR}$ (CDCl$_3$, 100 MHz) : $\delta$ 174.5, 172.2, 171.8, 158.7, 123.0, 58.4, 58.1, 52.9, 52.8, 52.3, 41.8, 40.3, 40.2, 18.9, 14.5, -0.5.

HRMS : $m/z$ [M + Na]$^+$ calcd for C$_{18}$H$_{30}$O$_6$NaSi: 393.17039 ; found: 393.17019.

![Chemical Structure](image)

$(E)$-Trimethyl 1-ethyl-5-((trimethylsilyl)methylene)cyclopentane-1,3,3-tricarboxylate (17ad) : Prepared according to general procedure 4 from enoate 16a (66 mg, 0.20 mmol).

Purification by chromatography using ether/pentane (90:10) as eluent gave the title compound (38 mg, 53%) contaminated with 8% of the product resulting from the addition of the dichloromethyl radical (R=CHCl$_2$).

$^1\text{H NMR}$ (CDCl$_3$, 400 MHz) : $\delta$ 5.62 (t, J = 2.0 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.62 (s, 3H), 3.20 (dl, J = 16.5 Hz, 1H), 2.97 (d, J = 14.2 Hz, 1H), 2.78 (dl, J = 16.5 Hz, 1H), 2.43 (d, J = 14.2 Hz, 1H), 2.00 (m, 1H), 1.40 (m, 1H), 0.84 (t, J = 7.3 Hz, 3H), 0.10 (s, 9H).

$^{13}\text{C NMR}$ (CDCl$_3$, 100 MHz) : $\delta$ 175.0, 172.8, 172.3, 159.1, 123.6, 59.2, 58.9, 53.4, 53.3, 52.8, 40.3, 39.8, 32.6, 10.4, 0.00.

HRMS : $m/z$ [M + Na]$^+$ calcd for C$_{17}$H$_{28}$O$_6$NaSi: 379.15474 ; found: 379.15479.