Supporting Information

Electrochemical Methoxymethylation of Alcohols – A New Green and Safe Approach for the Preparation of MOM Ethers and Other Acetals

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1. General Experimental Section

Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for $^1$H and 75 MHz for $^{13}$C. Chemical shifts (δ) are reported in ppm from CDCl$_3$ (δ = 7.27 ppm) or DMSO-$d_6$ (δ = 2.50 ppm) for $^1$H NMR and relative to CDCl$_3$ (δ = 77.2 ppm) or DMSO-$d_6$ (δ = 39.5 ppm) for $^{13}$C NMR. Column chromatography was performed over ROCC Silica gel 60 (40-63μ mesh) eluting with ethyl acetate (or diethyl ether) and petroleum ether. Mass spectra were recorded using Varian Matt 44S and Finnigan-Matt TSQ-70 spectrometer. High-resolution mass data were obtained with a Kratos MS50TC instrument. Infrared spectra were recorded on a SHIMADZU-FTIR-8400S spectrometer and recorded in cm$^{-1}$. The electrolysis were carried out using a Thurlby/Thandar PL320QMT 30V coupled to a 2A Quad Mode Triple Output DC Power Supply or using an Electrasyn 2.0 equipped with graphite electrodes.

2. Procedure for the Synthesis of α-alkoxy Carboxylic Acids

All starting materials were purchased from commercial suppliers and used without further purification.

Procedure: A flame dried 250 mL three-necked flask was equipped with a
magnetic stir bar and a reflux condenser. Sodium hydride (1.20 g, 60% dispersion in mineral oil, 30 mmol) was then suspended in dry THF (20 mL) at 0 °C under argon. Alcohol 1 (10 mmol), dissolved in dry THF (30 mL), was then added slowly. After 30 min, bromoacetic acid 2 (10 mmol), dissolved in dry THF (30 mL), was added dropwise. The mixture was heated to reflux, and the progress of the reaction was monitored by TLC. Upon completion of the reaction, as shown by TLC, the mixture was cooled down to room temperature and diluted with water (60 mL). The mixture was extracted with hexane (2 x 30 mL), the aqueous layer was acidified with HCl (2 M) until pH 2 was reached and extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over MgSO₄, the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography on silica gel (petroleum ether / ethyl acetate) to give the pure α-alkoxy carboxylic acids 3.

2-(octyloxy)acetic acid (3a)

![Chemical structure](attachment:image)

Pale yellow oil, 95% yield; **¹H NMR** (CDCl₃, 300 MHz) δ 10.09 (s, 1H), 4.12 (s, 2H), 3.55 (t, J = 6.7 Hz, 2H), 1.68-1.58 (m, 2H), 1.37-1.22 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H); **¹³C NMR** (CDCl₃, 75 MHz) δ 175.4, 72.3, 67.9, 31.9, 29.6, 29.5, 29.3, 26.0, 22.8, 14.2; **IR** (neat) ν 3507, 2923, 1728, 1465, 1242, 1124; **MS** (Cl) m/z (%): 189.2 (30), 143.2 (20), 113.2 (45), 77.0 (100).
2-(but-3-en-1-yloxy)acetic acid (3b)

\[ \text{\begin{tikzpicture} 
\node (o) at (0,0) {\text{\textup{O}}}; 
\node (c) at (1,0) {\text{\textup{COOH}}}; 
\end{tikzpicture}} \]

Pale yellow liquid, 87% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 11.27 (s, 1H), 5.88-5.75 (m, 1H), 5.16-5.04 (m, 2H), 4.14 (s, 2H), 3.62 (t, $J = 6.7$ Hz, 2H), 2.39 (qt, $J = 6.7, 1.3$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 175.9, 134.6, 117.1, 71.3, 67.9, 34.0; IR (neat) $\nu$ 3506, 2914, 2873, 1728, 1641, 1431, 1220, 1119, 997, 914; MS (Cl) $m/z$ (%): 131.0 (17), 76.9 (23), 55.0 (100).

2-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)acetic acid (3c)

\[ \text{\begin{tikzpicture} 
\node (o) at (0,0) {\text{\textup{O}}}; 
\node (e) at (1,0) {\text{\textup{O}}}; 
\node (c) at (2,0) {\text{\textup{COOH}}}; 
\end{tikzpicture}} \]

Pale yellow oil, 85% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 5.55 (d, $J = 5.0$ Hz, 1H), 4.66 (dd, $J = 7.9, 2.5$ Hz, 1H), 4.37 (dd, $J = 5.0, 2.6$ Hz, 1H), 4.31 (dd, $J = 7.9, 2.1$ Hz, 1H), 4.26-4.13 (m, 2H), 4.07-4.03 (m, 1H), 3.79-3.68 (m, 2H), 1.54 (s, 3H), 1.47 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 172.0, 110.0, 109.1, 96.3, 71.2, 71.0, 70.7, 70.5, 68.9, 66.3, 26.1, 26.0, 25.0, 24.6; IR (neat) $\nu$ 3501, 3215, 2987, 2935, 1738, 1456, 1371, 1253, 1213, 1164, 1064, 1003, 891; ESI-HRMS: $m/z$ calcd for C$_{14}$H$_{24}$O$_8$ [M+H]$^+$: 319.1387; found: 319.1388.

2-(pent-3-yn-1-yloxy)acetic acid (3d)

\[ \text{\begin{tikzpicture} 
\node (o) at (0,0) {\text{\textup{O}}}; 
\node (c) at (1,0) {\text{\textup{COOH}}}; 
\end{tikzpicture}} \]

Pale yellow liquid, 81% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 4.18 (s, 2H), 3.66 (t, $J = 6.7$ Hz, 2H), 2.50-2.44 (m, 2H), 1.79 (t, $J = 2.5$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 174.3, 77.6, 75.4, 70.7, 68.1, 20.2, 3.6; IR (neat) $\nu$ 3517, 3479, 2922, 2565, 2538, 1732, 1429, 1429, 1221, 1124, 957.
ESI-HRMS: m/z calcd for C$_7$H$_{11}$O$_3$ [M+H]$^+$: 143.0703; found: 143.0703.

2-(cyclohexyloxy)acetic acid (3e)

![Structural formula](image)

Colorless liquid, 82% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.83 (s, 1H), 4.14 (s, 2H), 3.53-3.35 (m, 1H), 1.96-1.92 (m, 2H), 1.77-1.75 (m, 2H), 1.56-1.53 (m, 1H), 1.41-1.19 (m, 5H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 174.1, 79.2, 65.2, 32.0, 25.6, 24.0; IR (neat) $\nu$ 3064, 2932, 2856, 1728, 1448, 1358, 1217, 1113, 933, 887.

2-(cyclopentyloxy)acetic acid (3f)

![Structural formula](image)

Colorless liquid, 80% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 9.04 (s, 1H), 4.08 (s, 2H), 4.07-4.02 (m, 1H), 1.79-1.66 (m, 6H), 1.64-1.51 (m, 2H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 174.3, 83.0, 66.0, 32.2, 23.5; IR (neat) $\nu$ 3110, 2949, 2874, 1728, 1435, 1348, 1221, 1121, 982, 960.

2-((3-methylpentan-3-yl)oxy)acetic acid (3g)

![Structural formula](image)

Colorless liquid, 82% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.94 (s, 1H), 3.96 (s, 2H), 1.52 (q, $J$ = 7.4 Hz, 4H), 1.14 (s, 3H), 0.86 (t, $J$ = 7.5 Hz, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 173.0, 80.0, 59.5, 29.9, 22.1, 8.0; IR (neat) $\nu$ 3105, 2970, 2941, 1728, 1435, 1375, 1209, 1117, 879; ESI-HRMS: m/z calcd for C$_8$H$_{16}$O$_3$Na [M+Na]$^+$: 183.0992; found: 183.0992.

(E)-2-(hex-2-en-1-yloxy)acetic acid (3h)
Pale yellow oil, 89% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 10.17 (s, 1H), 5.80-5.70 (m, 1H), 5.60-5.50 (m, 1H), 4.11 (s, 2H), 4.06 (d, $J=6.4$, 2H), 2.04 (q, $J=6.9$, 2H), 1.48-1.35 (m, 2H), 0.90 (t, $J=7.4$, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 175.7, 136.9, 125.0, 72.4, 66.2, 34.4, 22.2, 13.8; IR (neat) $\nu$ 2956, 1728, 1426, 1207, 1114, 1038, 971.

2-phenoxyacetic acid (3i)

White solid, 83% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 9.59 (s, 1H), 7.34-7.26 (m, 2H), 7.02 (t, $J=7.3$ Hz, 1H), 6.93 (d, $J=7.9$ Hz, 2H), 4.68 (s, 2H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 174.7, 157.5, 129.9, 122.3, 114.8, 65.0; IR (neat) $\nu$ 3421, 3036, 2575, 2005, 1957, 1907, 1866, 1732, 1697, 1596, 1583, 1496, 1487, 1434, 1373, 1265, 1091, 835.

$3j'$ was synthesised following the general procedure for the preparation of $\alpha$-alkoxy carboxylic acids and used for the next step without further purification.

In a 250 three-necked flask, $3j'$ (1.86 g, 9.2 mmol) was dissolved in dichloromethane (100 mL). The mixture was cooled to -78 °C and a gentle flux of ozone was passed through the solution until a persisting deep blue colour appeared. The excess of ozone was removed by passing a flow of dry air through the solution and then triphenylphosphine (2.66 g, 10.12 mmol) was
added. The solution was refluxed overnight and then washed with 0.5 M sulfuric acid (50 mL) and extracted with DCM (2 x 20 mL), the organic layer was dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The crude mixture was then purified on silica gel by chromatography. The excess of phosphine and the formed phosphine oxide were eluted using a mixture of ethyl acetate / dichloromethane / triethylamine (2 : 2 : 1) and the ammonium salt of 3j was eluted using pure methanol. The methanol was removed under reduced pressure and the residue was dissolved into dichloromethane and 1 M HCl (50 mL). The aqueous layer was extracted with dichloromethane, the organic layers were collected, dried over MgSO₄ and concentrated under reduced pressure to give 3j as pale yellow oil.

2-(3-oxobutoxy)hexanoic acid (3j)

Yellowish oil, 92% yield; ¹H NMR (CDCl₃, 300 MHz) δ 9.33 (s, 1H), 3.81 (ddd, J = 17.9, 8.5, 4.0 Hz, 2H), 3.60 (dt, J = 9.2, 4.6 Hz, 1H), 2.92-2.70 (m, 2H), 2.23 (s, 3H), 1.86-1.64 (m, 2H), 1.42-1.26 (m, 4H), 0.91-0.86 (m, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 208.8, 175.9, 79.3, 65.2, 43.0, 32.7, 30.3, 27.4, 22.4, 14.0; IR (neat) ν 3508, 2929, 1743, 1714, 1651, 1467, 1359, 1193, 1123; MS (Cl) m/z (%): 203.4 (100), 157.3 (66), 87.4 (50).

2-(but-3-en-1-yloxy)hexanoic acid (3k)

Yellowish oil, 90% yield; ¹H NMR (CDCl₃, 300 MHz) δ 11.02 (s,
1H), 5.90-5.76 (m, 1H), 5.16-5.05 (m, 2H), 3.88 (dd, J = 7.1, 5.2 Hz, 1H), 3.67 (dt, J = 9.0, 6.7 Hz, 1H), 3.48 (dt, J = 9.0, 6.7 Hz, 1H), 2.42-2.35 (m, 2H), 1.85-1.69 (m, 2H), 1.49-1.26 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 178.0, 134.8, 117.1, 78.9, 70.3, 34.2, 32.4, 27.3, 22.5, 14.0; IR (neat) ν 3447, 2957, 2930, 1717, 1643, 1124, 1101, 914; MS (Cl) m/z (%): 187.1 (100), 172.3 (65), 158.2 (15), 144.9 (12), 141.2 (45).

3. Procedure for the Electrolysis of Carboxylic Acids

![Chemical Reaction Diagram]

**General Electrolysis Procedure:** In an undivided beaker-type cell (100 mL) equipped with two graphite electrodes (2 cm × 3 cm), or in an Electrasyn 2.0, $\alpha$-alkoxy carboxylic acid 3 (1.87 mmol) was dissolved in MeOH (50 mL). The acid was then partially neutralised with NaOMe (0.46 mmol) and a current density of 100 mA.cm$^{-2}$ was applied. The reaction was monitored by TLC. Upon completion of the reaction, as shown by TLC, the solvent was carefully removed under reduced pressure and then water (10 mL) was added (in the case the solution was not basic, 5 mL of 1 M KOH were added). The aqueous mixture was then extracted with diethylether (3 x 15 mL). The organic layers were collected, dried over Na$_2$CO$_3$, and concentrated under reduced pressure to yield the clean product 4 without the need for any further purifications.
1-(methoxymethoxy)octane (4a)

\[
\begin{align*}
\text{Colorless liquid, 90% yield; }^1\text{H NMR (CDCl}_3, \text{ 300 MHz) } &\text{ δ 4.62} \\
&\text{(s, 2H), 3.51 (t, } J = 6.6 \text{ Hz, 2H), 3.36 (s, 3H), 1.63-1.54 (m, 2H), 1.37-1.27 (m, 10H), 0.88 (t, } J = 6.7 \text{ Hz, 3H); }^1^3\text{C NMR (CDCl}_3, \text{ 75 MHz) } &\text{ δ 96.5, 68.0, 55.2,} \\
&\text{32.0, 29.9, 29.5, 29.4, 26.4, 22.8, 14.2; IR (neat) } &\text{ ν 2925, 2854, 1737, 1465,} \\
&\text{1151, 1110, 1039, 919; MS (EI) } &\text{m/z (%): } 175.2 (11) , 159.1 (1), 143.2 (100), \\
&\text{129.2 (15), 71 (46), 57 (27).}
\end{align*}
\]

4-(methoxymethoxy)but-1-ene (4b)

\[
\begin{align*}
\text{Colorless liquid, 75% yield; }^1\text{H NMR (CDCl}_3, \text{ 300 MHz) } &\text{ δ 5.90-5.77 (m, 1H), 5.15-5.03 (m, 2H), 4.63 (s, 2H), 3.59 (t, } J = 6.7 \text{ Hz, 2H),} \\
&\text{3.36 (s, 3H), 2.36 (qt, } J = 6.7, 1.4 \text{ Hz, 2H); }^1^3\text{C NMR (CDCl}_3, \text{ 75 MHz) } &\text{ δ 135.4,} \\
&\text{116.6, 96.5, 67.1, 55.3, 34.3; IR (neat) } &\text{ ν 2954, 2929, 1641, 1191, 1107, 1049,} \\
&\text{914; MS (Cl) } &\text{m/z (%): } 115.2 (25), 101.2 (14), 85.2 (2), 75.1 (1.5), 55.1 (4).
\end{align*}
\]

(3aR,5R,5aS,8aS,8bR)-5-((methoxymethoxy)methyl)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (4c)

\[
\begin{align*}
\text{Colorless oil, 90% yield; }^1\text{H NMR (CDCl}_3, \text{ 300 MHz) } &\text{ δ 5.55} \\
&\text{(d, } J = 4.9 \text{ Hz, 1H), 4.67 (s, 2H), 4.61 (dt, } J = 7.9, 2.7 \text{ Hz,} \\
&\text{1H), 4.34-4.31 (m, 1H), 4.26 (dt, } J = 7.9, 2.7 \text{ Hz, 1H), 3.99 (t, } J = 6.1 \text{ Hz,} \\
&\text{1H), 3.78-3.65 (m, 2H), 3.38 (s, 3H), 1.55 (s, 3H), 1.45 (s, 3H), 1.34 (s, 6H); }^1^3\text{C NMR (CDCl}_3, \text{ 75 MHz) } &\text{ δ 109.5, 108.7, 96.9, 96.5, 71.3, 70.8, 70.6, 67.0, 66.7,} \\
&\text{55.4, 26.2, 26.1, 25.1, 24.6; IR (neat) } &\text{ ν 2987, 2935, 1737, 1716, 1456, 1371,}
\end{align*}
\]
1253, 1211, 1166, 1108, 1070, 1039, 999, 918, 889, 865; **ESI-HRMS**: m/z calcd for C_{14}H_{24}O_{7}Na [M+Na]^+: 327.1414; found: 327.1415.

**5-(methoxymethoxy)pent-2-yne (4d)**

\[\text{\hspace{1cm}}\textcolor{red}{\text{\Huge 5}}\text{-(methoxymethoxy)pent-2-yne (4d)}\]

Colorless liquid, 93% yield; **\text{^1H NMR}** (CDCl\textsubscript{3}, 300 MHz) \( \delta \) 4.64 (s, 2H), 3.60 (t, \( J = 6.8 \) Hz, 2H), 3.36 (s, 3H), 2.45-2.38 (m, 2H), 1.77 (t, \( J = 2.5 \) Hz, 3H); **\text{^{13}C NMR}** (CDCl\textsubscript{3}, 75 MHz) \( \delta \) 96.5, 76.7, 76.0, 66.5, 55.3, 20.3, 3.6; **\text{IR}** (neat) \( \nu \) 2937, 1442, 1379, 1274, 1149, 1108, 1041, 918, 763; **ESI-HRMS**: m/z calcd for C_{7}H_{13}O_{2} [M+H]^+: 129.0910; found: 129.0911.

**\text{(methoxymethoxy)cyclohexane (4e)}**

\[\text{\hspace{1cm}}\textcolor{red}{\text{\Huge (}}\text{methoxymethoxy)\text{cyclohexane (4e)}\]

Colorless liquid, 88% yield; **\text{^1H NMR}** (CDCl\textsubscript{3}, 300 MHz) \( \delta \) 4.66 (s, 2H), 3.53-3.44 (m, 1H), 3.35 (s, 3H), 1.91-1.83 (m, 2H), 1.73-1.69 (m, 2H), 1.53-1.49 (m, 1H), 1.32-1.21 (m, 5H); **\text{^{13}C NMR}** (CDCl\textsubscript{3}, 75 MHz) \( \delta \) 94.5, 75.2, 55.2, 32.9, 25.8, 24.3; **\text{IR}** (neat) \( \nu \) 3496, 2925, 2854, 1448, 1365, 1269, 1217, 1091.

**\text{(methoxymethoxy)cyclopentane (4f)}**

\[\text{\hspace{1cm}}\textcolor{red}{\text{\Huge (}}\text{methoxymethoxy)\text{cyclopentane (4f)}\]

Colorless liquid, 84% yield; **\text{^1H NMR}** (CDCl\textsubscript{3}, 300 MHz) \( \delta \) 4.63 (s, 2H), 4.18-4.12 (m, 1H), 3.36 (s, 3H), 1.78-1.64 (m, 6H), 1.57-1.52 (m, 2H); **\text{^{13}C NMR}** (CDCl\textsubscript{3}, 75 MHz) \( \delta \) 95.2, 78.9, 55.3, 32.8, 23.5; **\text{IR}** (neat) \( \nu \) 2927, 1456, 1261, 1091.

**3-(methoxymethoxy)-3-methylpentane (4g)**
Colorless liquid, 83% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 4.68 (s, 2H), 3.38 (s, 3H), 1.52 (q, $J = 7.4$ Hz, 4H), 1.15 (s, 3H), 0.86 (t, $J = 7.5$ Hz, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 90.8, 78.9, 55.4, 31.1, 23.0, 8.2; IR (neat) $\nu$ 2925, 1442, 1365, 1271, 1217, 1091, 1041, 918; ESI-HRMS: m/z calcd for C$_8$H$_{18}$O$_2$Na [M+Na]$^+$: 169.1199; found: 169.1199.

**(E)-1-(methoxymethoxy)hex-2-ene (4h)**

Colorless liquid, 91% yield; $^1$H NMR (DMSO-d$_6$, 300 MHz) $\delta$ 5.71-5.61 (m, 1H), 5.55-5.46 (m, 1H), 4.54 (s, 2H), 3.93 (dd, $J = 5.9$, 1.0 Hz, 2H), 3.24 (s, 3H), 1.99 (q, $J = 7.2$ Hz, 2H), 1.36 (dd, $J = 14.7$, 7.3 Hz, 2H), 0.87 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (DMSO-d$_6$, 75 MHz) $\delta$ 133.3, 126.5, 94.8, 67.2, 54.5, 33.7, 21.8, 13.5; IR (neat) $\nu$ 2937, 1664, 1563, 1492, 1456, 1440, 1228, 1197, 1078; MS (Cl) m/z (%): 139.3 (20), 123.4 (25.), 107.2 (100), 94.2 (27), 61.2 (3).

**(methoxymethoxy)benzene (4i)**

Colorless liquid, 89% yield; $^1$H NMR (DMSO-d$_6$, 300 MHz) $\delta$ 7.32-7.26 (m, 2H), 7.06-7.00 (m, 3H), 5.18 (s, 2H), 3.37 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 75 MHz) $\delta$ 156.8, 129.5, 121.6, 116.1, 93.8, 55.5; IR (neat) $\nu$ 2921, 1737, 1596, 1492, 1456, 1440, 1228, 1197, 1149, 1078; MS (Cl) m/z (%): 139.3 (20), 123.4 (25.), 107.2 (100), 94.2 (27), 61.2 (3).

**4-((1-methoxypentyl)oxy)butan-2-one (4j)**

Colorless liquid, 87% yield; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 4.40 (t, $J = 5.7$ Hz, 1H), 3.86-3.79 (m, 1H), 3.73-3.65 (m, 1H), 3.30 (s, 3H), 2.67 (t, $J = 6.2$ Hz, 2H), 2.18 (s, 3H), 1.58-1.54 (m, 2H), 1.32-1.28 (m, 4H),...
0.89 (t, J = 6.9 Hz, 3H); **13C NMR** (CDCl$_3$, 75 MHz) $\delta$ 207.3, 104.3, 60.8, 52.9, 43.8, 32.7, 30.6, 26.8, 22.6, 14.1; **IR** (neat) $\nu$ 2927, 1716, 1361, 1193, 1051; **MS** (Cl) $m/z$ (%): 173.4 (5), 157.3 (100), 131.3 (25), 101.2 (91), 87.7 (25), 71.1 (54).

**1-(but-3-en-1-yloxy)-1-methoxypentane (4k)**

Colorless liquid, 92% yield; **1H NMR** (DMSO-d$_6$, 300 MHz) $\delta$ 5.88-5.74 (m, 1H), 5.11-5.00 (m, 2H), 4.39 (t, J = 5.7 Hz, 1H), 3.54 (dt, J = 9.4, 6.87 Hz, 1H), 3.44-3.33 (m, 1H), 3.20 (s, 3H), 2.25 (q, J = 6.6 Hz, 2H), 1.53-1.46 (m, 2H), 1.31-1.24 (m, 4H), 0.86 (t, J = 6.7 Hz, 3H); **13C NMR** (DMSO-d$_6$, 75 MHz) $\delta$ 135.7, 116.4, 103.1, 64.5, 52.1, 33.9, 32.2, 26.4, 22.0, 13.9; **IR** (neat) $\nu$ 2955, 2932, 1641, 1465, 1193, 1110; **MS** (Cl) $m/z$ (%): 171.5 (1), 141.5 (2), 115.3 (5), 101.1 (63), 70.9 (100), 56.8 (81).

**4. Synthesis of tetrahydro-2H-pyran from acetal (5)**

**Procedure**: In a flame dried round bottom flask, at 0 °C, titanium (IV) chloride (1.161 mmol) was dissolved in dichloromethane (4.8 mL). Then the acetal 4k (100 mg, 0.581 mmol), dissolved in dichloromethane (5 mL), was added dropwise. The reaction was stirred for 15 min and then quenched by adding methanol (1 mL) followed by 2M HCl (8 mL) saturated with NaCl. The reaction mixture was then extracted with DCM (2 x 20 mL), the organic layers
were then collected and dried over MgSO₄. The pure product was purified by distillation at atmospheric pressure.

2-butyl-4-chlorotetrahydro-2H-pyran (5)

Pale yellow oil, 84% yield; ¹H NMR (CDCl₃, 300 MHz) δ 4.00-3.86 (m, 2H), 3.48-3.27 (m, 2H), 2.28-1.69 (m, 3H), 1.52-1.21 (m, 7H), 0.85-0.81 (m, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 77.6, 67.0, 56.0, 42.8, 37.1, 35.6, 27.5, 22.6, 14.1; IR (neat) ν 2956, 2929, 1149.
5. NMR spectra