S. Vedachalam et al.  

Supporting Information

NHC catalyzed enantioselective Coates-Claisen rearrangement: A rapid access to the dihydropyran core for Oleuropein based Secoiridoids

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Supporting Information

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I. General methods:

**General:** All the reactions were carried out in a flame or oven dried glassware under an argon or nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (0.010–0.063 nm). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using base solution of potassium permanganate. Technical grade solvents were used for chromatography and were distilled prior to use. NMR spectra were recorded at room temperature on 300 MHz Bruker ACF 300, 400 MHz Bruker DPX 400, 500 MHz Bruker AMX 500, and 400 MHz JEOL ECA 400 NMR spectrometers. The residual solvent signals were taken as the reference (7.26 ppm for $^1$H NMR spectra and 77.0 ppm for $^{13}$C NMR spectra in CDCl$_3$, 2.5 ppm for $^1$H NMR spectra and 39.5 ppm for $^{13}$C NMR spectra in DMSO-$d_6$). Sometimes the TMS signal at 0.0 ppm was used an internal standard for $^1$H NMR spectra. Chemical shift ($\delta$) is reported in ppm, coupling constants ($J$) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal. HR-MS (ESI) spectra were recorded on a Waters Q-Tof premier™ mass spectrometer.

**Materials:** All solvents were distilled under argon from the following drying agents immediately before use: tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl; dichloromethane was distilled from calcium hydride. All the starting materials were purchased from commercial suppliers and used without further purification. All the NHC catalyses were purchased from commercial suppliers and catalyst G and H was prepared from standard literature procedure.$^1$
Experimental Sections

Synthesis of Propargyl fragment 2:

But-3-yn-1-yloxy)(tert-butyl)dimethylsilane:

To a solution of 3-butyn-1-ol (9.26 g, 132.1 mmol) and imidazole (21.59 g, 317.1 mmol) in tetrahydrofuran (200 mL) was added tert-butyl-dimethyl-silyl chloride (TBSCl) (23.90 g, 158.5 mmol). After stirring at ambient temperature for 3 h, the reaction mixture was filtered through a pad of silica and concentrated under reduced pressure. Gradient flash chromatography (Petroleum ether/Ethyl acetate, 100:0 → 95:5) afforded the alkyne (23.62 g, 98%) as a clear colorless oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.74 (t, $J$ = 7.1 Hz, 2 H), 2.40 (dt, $J_1$ = 7.1, $J_2$ = 2.6 Hz, 2H), 1.95 (t, $J$ = 2.6 Hz, 1 H), 0.89 (s, 9 H), 0.07 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 81.5, 69.2, 61.7, 25.8, 22.8, 18.3; HRMS (ESI) m/z [M+H]$^+$: calcd. for C$_{10}$H$_{21}$OSi: 185.1330, found: 185.1324.

5-((Tert-butyldimethylsilyl)oxy)pent-2-ynal (2):

The alkyne (5 g, 27.0 mmol) was dissolved in dry THF (50 mL) and the solution was cooled to −40 °C under nitrogen. n-Butyl lithium (2 M in cyclohexane, 14.2 mL, 28.3 mmol) was added dropwise over 2 minutes maintaining the temperature between −35 and −40 °C. After completion of the addition, anhydrous DMF (4.16 mL, 54.0 mmol, 2 equiv) was added in one portion and the cold bath was removed. The reaction mixture was allowed to warm to room temperature and aged for 30 minutes. The THF solution was poured into a vigorously stirred biphasic solution prepared from a 10% aqueous solution of KH$_2$PO$_4$ (150
mL, 100 mmol) and methyl tert-butyl ether (MTBE) (150 mL) cooled over ice to +5 °C. Layers were separated and the organic extract was washed with water (2x200 mL). Combined aqueous layers were back extracted with MTBE (150 mL). Combined organic layers were dried over MgSO₄, filtered and concentrated to give the crude acetylenic aldehyde as oil which was purified by column chromatography. 

**¹H NMR** (400 MHz, CDCl₃) δ 9.1 (s, 1 H), 3.80 (t, \(J = 6.7 \text{ Hz}, 2 \text{ H}\)), 2.62 (dt, \(J_1 = 6.7, J_2 = 0.7 \text{ Hz}, 2 \text{ H}\)), 0.89 (s, 1 H), 0.08 (s, 9 H); 

**¹³C NMR** (100 MHz, CDCl₃): δ 177.0, 96.2, 82.2, 60.5, 25.7, 23.7, 23.5, 18.2; 

**HRMS** (ESI) m/z [M+H]⁺: calcd. for C₁₁H₂₁O₂Si: 213.1388, found: 213.1331. Spectra consistent with known data.

**Synthesis of fragment 3:**

![Synthesis of fragment 3](image)

**5-(methoxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione:**

A mixture of Meldrum's acid (15 g, 104.1 mmol) and 50 g. of CH(OMe)₃ was heated for 3 h at 85–95 °C. After complete conversion of starting material by checking the TLC, CH(OMe)₃ was removed and through rotavap. The light brown oil was diluted with 100 mL of 5 % CH₂Cl₂ in hexane and scratch the sides using spatula to obtained yellow solid which is filtered through Buchner to obtained (Methoxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione. The product was obtained as yellow solid; (17.6 g, 91 % yield); 

**¹H NMR** (400 MHz, CDCl₃): δ 8.17 (s, 1H), 4.29 (s, 3H), 1.74 (s, 6H); 

**¹³C NMR** (100 MHz, CDCl₃): δ 175.0, 163.2, 158.6, 104.8, 96.8, 66.3, 27.3; 

2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-carbaldehyde.\(^4\)

\[
\begin{align*}
\text{(Methoxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione} & \quad \text{(10 g, 53.7 mmol)} \\
\text{which upon treatment with 2N HCl (30 mL) for 2 h obtained hydrolyzed product.} \\
\text{The reaction mixture was diluted with ethyl acetate (200 mL) and separated} \\
\text{through separating funnel. The aqueous layer again extracted with (2x50 mL) of ethyl acetate.} \\
\text{The combined organic layer was dried over Na}_2\text{SO}_4, \text{filtered and concentrated to obtained} \\
\text{light brown solid; (8.13 g, 88 % yield);} \\
\text{\(^1\)H NMR (400 MHz, CDCl}_3\): } \delta 8.56 \text{ (s, 1H), 1.77 (s, 6H);} \\
\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\): } \delta 177.0, 168.0, 160.6, 107.1, 95.4, 27.2; \text{ HRMS (ESI) m/z [M+H]^+: calcd. for C}_7\text{H}_9\text{O}_5: 173.0450, \text{ found: 173.0457. Spectra consistent with known data.} \\
\end{align*}
\]

\text{t-Butyl formylacetate (3):}\(^4\)

\[
\begin{align*}
\text{A solution of formyl Meldrum’s acid} & \quad \text{(10 g, 58.1 mmol) and tert-butylalcohol} \\
\text{(6.6 mL, 69.7 mmol) in dry benzene (100 mL) was refluxed for 90 min. The} \\
\text{solvent was evaporated in vacuo at room temperature. Distillation of the residue in 35-60 °C} \\
\text{in 11 torr obtained colourless oil which was immediately stored in –78°C fridge. (5.8 g, 70 %} \\
\text{yield);} \\
\text{\(^1\)H NMR (400 MHz, CDCl}_3\): mixture of Keto-enol tautomers } \delta 11.5 \text{ (d, J=12.5, 1H,} \\
\text{–OH), 9.87 (t, J = 2.4, 1H, –CHO), 7.46 (dd, J\textsubscript{1} = 7.6 Hz, J\textsubscript{2} = 1.6 Hz, 1H), 1.77 (s, 6H);} \\
\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\): } \delta 177.0, 168.0, 160.6, 107.1, 95.4, 27.2; \text{ HRMS (ESI) m/z [M+Na]^+: calcd. for C}_7\text{H}_5\text{O}_3\text{Na: 167.0684, found: 167.0681. Spectra consistent with known data.} \\
\end{align*}
\]

\text{Sugar fragment:}\(^5\)
Perchloric acid was added dropwise to a suspension of 0.5 g of glucose in acetic anhydride (36 mL) at 0 °C. Additional glucose (9.5 g, 55.5 mmol) was added portion wise then the solution was warmed to room temperature and stirred for additional 3 h. Quench and hydrolyzed the excess acetic anhydride by 2 N HCl (100 mL). The reaction mixture was extracted with ethylacetate (250 mL) and washed with water (3x100 mL), ammonium chloride (50 mL) and sodium chloride (50 mL). The organic layer was dried using Na₂SO₄, filtered and concentrated to obtained petaacetyl glucose as white solid which is used for further steps (17.3 g, 80 %).

Methyl amine in THF (1M) was added drop wise to a suspension of pentaacetyl glucose (3 g, 7.69 mmol), in dry THF (15 mL) to obtained tetraacetyl glucose at 0 °C. Additionally the reaction mixture was stirred for 3 h. Evaporate the solvent and the residue was purified by column chromatography obtained. tetraacetyl glucose which is immediately used for next steps (2.32 g, 85 %).

**l-O-(Trimethylsilyl)-2,3,4,6-tetra-O-acetyl-β-D-glucopyranose:**

To a stirred solution of tetraacetyl glucose (2 g, 5.7 mmol) in dichloromethane (15 mL) containing triethylamine (0.89 mL, 6.8 mmol) was added chlorotrimethylsilane (0.73 mL, 6.8 mmol) dropwise at room temperature. After being stirred for 2 h, the mixture was filtered through a pad of Celite and worked up to afford a residue that was crystallized to afford silyl derivative of tetraacetyl glucose in 85 % yield as a single anomer: mp 104−105 °C. **¹H NMR** (400 MHz, CDCl₃): δ 5.17 (t, J = 9.2 Hz, 1H), 5.04 (t, J = 9.6 Hz, 1H), 4.90 (dd, J₁ = 9.6 Hz, J₂ = 7.6 Hz, 1H), 4.73 (d, J = 7.6 Hz, 1H), 4.20−4.09 (m, 2H), 3.72−3.67 (m, 1H), 2.15 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 0.13 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.6, 170.3, 169.4, 169.3,
95.5, 73.2, 72.7, 71.8, 68.6, 62.2, 20.6 (3C), –0.02 (3C); HRMS (ESI) m/z [M+Na]^+: calcd. for C_{17}H_{28}O_{10}SiNa: 443.1349, found: 443.1359. Spectra consistent with known data.

Methyl [3,4-Bis(tert-butyldimethylsilyloxy)phenyl]acetate:\(^7\)

At 0 °C acetyl chloride (6 mL) was added dropwise to the solution of (3,4-dihydroxyphenyl)acetic acid (6.51 g, 38.7 mmol) in MeOH (250 mL). After 1 h, the mixture was allowed to warm to room temperature. The progress of the reaction was monitor by TLC which tells complete conversion after 2 h. The reaction mixture was concentrated to dryness, and the residue was redissolved in dry DMF (60 mL). From the reaction mixture, TBDMSCl (14 g, 92.8 mmol) and imidazole (3.8 g, 57 mmol) were added and the mixture was stirred for 2 h. After complete conversion by TLC the reaction mixture was diluted with diethyl ether (200 mL) and washed with water (3x100 mL). The organic layer was dried over Na\(_2\)SO\(_4\) and concentrated to obtained crude oil which upon column chromatography to form TBS protected ester. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 6.78–6.76 (m, 1H), 6.74 (s, 1H), 6.69 (dd, \(J_1 = 8.2\) Hz, \(J_2 = 2.1\) Hz, 1H), 3.67 (s, 3H), 3.49 (s, 3H), 0.98 (s, 18H), 0.19 (s, 12H), 0.13 (s, 9H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): δ 172.1, 146.6, 145.9, 126.8, 122.0, 51.8, 40.4, 25.8; Spectra consistent with known data.

2-[3,4-Bis(tert-butyldimethylsilyloxy)phenyl]ethanol:\(^7\)

Methyl[3,4-bis(tert-butyldimethylsilyloxy)phenyl]acetate (4.13 g, 10.03 mmol) in dry THF (25 mL) was added dropwise to a cooled (0 °C) suspension of LiAlH\(_4\) (400 mg, 10.5 mmol) in THF (25 mL) and stirred for 15 min. TLC analysis revealed complete disappearance of the starting material in this time period. The
reaction was quenched by dropwise addition of methanol and diluted with diethyl ether and subsequently washed with water. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to obtained residual oil which is purified through silica gel column chromatography. 

**¹H NMR** (400 MHz, CDCl₃): δ 6.76 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.63 (dd, J₁ = 8.0 Hz, J₂ = 2.0 Hz, 1H), 3.78 (q, J = 4.2 Hz, 1H), 2.73 (t, J = 6.5 Hz, 1H), 1.45 (s, 1H), 0.98 (s, 18H), 0.19 (s, 12H); 

**¹³C NMR** (100 MHz, CDCl₃): δ 146.7, 145.4, 131.2, 121.8, 121.8, 121.0, 63.8, 38.4, 25.9, 18.4, −4.0; 


**Stereo chemical prediction based on Literature report:**

Supporting reaction:

- **a) DIBAL-H reduction of 5:**

- **b) Acetyl deprotection of 15:**

n-2018 400MHz, CDCl3, bbf4 ol, otbs formyl alkyne

S-9
BBOP01, 400Hz, CDCl3, tbs homo prop aldehyde
### Elemental Composition Report

**Single Mass Analysis**

- Tolerance = 5.0 PPM
- DBE: min = -1.5, max = 50.0
- Element prediction: Off
- Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

169 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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C11H20O2Si

SNV-2-10 3 (0.082) Cm (3.9)

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1: TOF MS ES+ 7.58e+002
n=1194 BBFO1, CDCl3, merlene trimethyl ortho format-II
n-1192 BBF01, CDCl3, merline trimethyl ortho format

[Chemical structure image]

[Graph of 1H NMR spectrum with ppm scale]

S-13
n-1158 1H, BBOF01, 400Hz, CDCl3, formyl merlam acid
n-11745, BBF01, CDC13 formyl mantric acid
n-1234, cdcl3, 1h, n-1229 tertbutyl formyl 4 th batch

400M

11.52725
11.5412
9.7839
9.7778
9.7715
7.2599
7.0715
7.0564
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7.0251
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4.9600
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3.2933
1.4832

S-16
Elemental Composition Report

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
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Elements Used:
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C7H12O3
SNV-2-13 9 (0.220)

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**Elemental Composition Report**

**Single Mass Analysis**
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Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
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SNV-2-21 7 (0.156)

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Method File Name: IPA2%-30min254nm-5.lcm
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Report File Name: Default.lcr
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![Chromatogram Image]

Detector A Ch1 254 nm

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Shimadzu LCsolution Analysis Report

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[Image of chromatogram]

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n-2027 400MHz, CDCl3, bbf4 ol,lihmds acetaldehyde first spot prepara

HO

CTBS

CO\text{$_2$}Bu

two major diastereomers
n-2028 400MHz, CDCl3, bbf4 ol, lhmds acetaldehyde second spot prepara

two major diastereomers
n-2033 400MHz, CDCl3, bbf4 ol, lihmds aldol pure isomer

two major diastereomers
n-2034 400MHz, CDCl₃, bbf4 ol, trans alkene pure
n-2034 400MHz, CDCl3, bbf4 ol, trans alkene pure

\[
\text{OTBS}
\]

\[
\text{CO}_2\text{tBu}
\]

S-30
n-2034  400MHz, CDCl3, bbf4 ol, trans alkene pure
n-2035 400MHz, CDCl3, brb4 ol,cis alkene pure
n-2036 400MHz, CDCl3, bbf4 ol, cis alkene pure, 135 dept
## Elemental Composition Report

### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
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Elements Used:
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C20H34O5Si
SNV-2-17 4 (0.101)

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Minimum:

Maximum:

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n-2074, 1H, AV400MHz cdcl3, cis alkene
n-2074,13c, AV400MHz cdcl3, cis alkene
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
167 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
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SNV-2-18 3 (0.082) Cm (3:12)

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S-37
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n-2105, 1H AV400MHz CDC13, 1 eq diBn h first spot primary alcoho
n-2057, BBFO1 400MHz, CDCl3, dicalcolum pure marjor spot

7
Elemental Composition Report

Single Mass Analysis
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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
330 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:

C24H42O7Si
SNV-5-1 3 (0.082) Cm (3.8)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>493.2608</td>
<td>493.2598</td>
<td>1.0</td>
<td>2.0</td>
<td>4.5</td>
<td>29.0</td>
<td>0.0</td>
<td>C24 H42 O7 Si Na</td>
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</tbody>
</table>

1: TOF MS ES+
5.38e+002
n-2106, 1H AV400MHz CDC13, 1 eq dibal h second spot primary alcoho

$\text{OTBS}$

$\text{t-BuO}_2\text{C}$

$\text{8}$
n-2106, 1H AV400MHz CDCl3, 1 eq dibal h second spot primary alcoho
n-2106, 1H AV400MHz CDCl3, 1 eq dibal h second spot primary alcohol
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM  /  DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
176 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-40   H: 0-43   O: 0-7   Na: 0-1   Si: 0-2
C22H38O6Si
SNV-5-2 3 (0.082) Cm (3.9)

<table>
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<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
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<tbody>
<tr>
<td>449.2233</td>
<td>449.2245</td>
<td>-1.2</td>
<td>-2.7</td>
<td>18.5</td>
<td>12.9</td>
<td>0.0</td>
<td>C33 H30 Na</td>
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</tbody>
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8

1: TOF MS ES+ 4.05e+000
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
90 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-30  H: 0-45  O: 0-7  Na: 0-1  Si: 0-2
C24H40O7Si
SNV-5 3 4 (0.101)

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<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
</tr>
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<tbody>
<tr>
<td>495.2719</td>
<td>495.2723</td>
<td>-0.4</td>
<td>-0.8</td>
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<td>13.1</td>
<td>0.6</td>
<td>C28 H40 O6 Na</td>
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<tr>
<td>495.2727</td>
<td>495.2727</td>
<td>-0.8</td>
<td>-1.6</td>
<td>7.5</td>
<td>13.3</td>
<td>0.8</td>
<td>C27 H44 O3 Na Si2</td>
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</tbody>
</table>
n-2058, 1H, AV400MHz CDCl3, diacetyl tbs deprotection

10

S-49
n-2058, 1H, AV400MHz CDC13, diacetyl tbs deprotection

1.1273  2.1250  1.0000  2.0145

5.7261  4.7142  4.1807  3.6429
5.7102  4.6830  4.5807  3.6268
5.6847  4.6122  4.1408  3.6018

S-50
n-2058, 1H, AV400MHz CDCl3, diacetyl tbs deprotection

S-51
n-2061,1H, AV400MHz CDCl3, diacetyl tbs deprotection

<table>
<thead>
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<th>ppm</th>
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<tbody>
<tr>
<td>166.458</td>
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<td>144.186</td>
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<td>135.013</td>
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<td>128.385</td>
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<td>119.589</td>
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<td>81.492</td>
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<td>77.335</td>
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<td>77.017</td>
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<tr>
<td>76.700</td>
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<td>28.123</td>
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<tr>
<td>21.154</td>
</tr>
<tr>
<td>20.720</td>
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<tr>
<td>13.513</td>
</tr>
</tbody>
</table>

$^{t-\text{BuO}_2\text{C}}$OH

S-52
Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18   H: 0-28   O: 0-7   Na: 0-1
C18H28O7
SNV-1001 (0.045)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>379.1716</td>
<td>379.1733</td>
<td>-1.7</td>
<td>-4.5</td>
<td>4.5</td>
<td>12.2</td>
<td>0.0</td>
<td>C18 H28 O7 Na</td>
</tr>
</tbody>
</table>
N-2333(Av 400), cdcl3 esmartin aldehyde

S-54
N-2333(Av 400), cdcl3 desmartin aldehyde

S-55
Elemental Composition Report

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-18  H: 0-27  O: 0-7  Na: 0-1
C18H26O7
SNV-101 7 (0.156) Cm (7:9)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
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<td>355.1757</td>
<td>355.1757</td>
<td>0.0</td>
<td>0.0</td>
<td>5.5</td>
<td>13.9</td>
<td>0.0</td>
<td>C18 H27 O7</td>
</tr>
</tbody>
</table>
n-2072, 1H, AV400MHz cdcl3, oxidation acid
n-2072, 1H, AV400MHz cdcl3, oxidation acid
n-2072,13c, AV400MHz cdcl3, oxidation acid
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
C: 0-26   H: 0-28   O: 0-10
C18H26O8
snv-102 5 (0.119)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>371.1706</td>
<td>371.1706</td>
<td>0.0</td>
<td>0.0</td>
<td>5.5</td>
<td>12.6</td>
<td>0.0</td>
<td>C18 H27 O8</td>
</tr>
</tbody>
</table>

Minimum: -1.5
Maximum: 5.0 5.0 50.0

1: TOF MS ES+ 5.49e+000
nm-2408, AV 400MHz, 1H, CDCl3, intra lactone 1st spot req
n-2408, AV 400MHz, 1H, CDCl3, intra lactone 1st spot req

S-63
n-2408, AV 400MHz, 1H, CDCl3, intra lactone 1st spot req
n-2408, AV 400MHz, 13c, CDCl3, intra lactone 1st spot req
n-2408 AV 400MHz, 1H, CDCl3, intra lactone 1st spot req

13

S-66
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
29 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-26   H: 0-28   O: 0-10
C16H22O6
snv-103 215 (4.702)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>311.1502</td>
<td>311.1495</td>
<td>0.7</td>
<td>2.2</td>
<td>5.5</td>
<td>14.8</td>
<td>0.0</td>
<td>C16 H23 O6</td>
</tr>
</tbody>
</table>

Minimum: 5.0 5.0 -1.5
Maximum: 5.0 5.0 50.0
N-2394 (Av 400), CF3COOH deprotection in tta lactone

[Diagram showing chemical structure with peaks labeled: 4.4576, 4.4399, 4.3601, 4.1534, 5.8485, 5.8313, 1.0727, 1.0751, 1.0196]
n-2410 AV 400MHz, 1H, CDCl3, intralacotne methyl ester pure
n-2410 AV 400MHz, 1H,CDCl3, intralacotne methyl ester pure
n-2410 400MHz, 1H, CDCl3, intralactone methyl ester pure
n-2410 AV 400MHz, 13c, CDCl3, intralacotne methyl ester pure
Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
26 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-26  H: 0-28  O: 0-10
C13H16O6
svx-104 13 (0.294)

<table>
<thead>
<tr>
<th>Mass</th>
<th>Calc. Mass</th>
<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>269.1019</td>
<td>269.1025</td>
<td>-0.6</td>
<td>-2.2</td>
<td>5.5</td>
<td>14.7</td>
<td>0.0</td>
<td>C13 H17 O6</td>
</tr>
</tbody>
</table>

Minimum: 5.0  Maximum: 50.0
N-2398(Av 400), acetyl deprotoention napuproduc intermed-1 spot
N-2398 (Av 400), acetyl deprotection natuproduc intermed-1 spot
N-2398 (Av 400), acetyl deprotection nuproduct intermed-l spot

S-77