Synthetic studies towards naturally occurring $\gamma$-(Z)/(E)-alkylidenebutenolides through bimetallic cascade cyclization and an adventitious photoisomerization method

Shrestha Chatterjee, Ranjan Kumar Acharyya, Pratik Pal, and Samik Nanda*

Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur, 721302, India

Contents

Experimental procedures for few known compounds 2-4

$^1$H/$^13$C and DEPT-135 NMR spectra for selected compounds 5-55 & 57-104

UV-Vis spectra for few $\gamma$-(Z)-alkylidenebutenolides 56
Synthesis of enantiopure aldehyde 17: The aldehyde 17 was prepared according to a known procedure as described below.

(R)-Methyl 2-hydroxy-2-phenylacetate (A1): A mixture of (R)-mandelic acid (2.28 g, 15 mmol), 2,2-dimethoxypropane (1.85 mL, 15 mmol), concentrated H$_2$SO$_4$ (150 μL) and MeOH (15 mL) were refluxed for 5 h. The mixture was concentrated and the residual oil was dissolved in diethyl ether (20 mL) and washed with 5% NaHCO$_3$. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and evaporated under reduced pressure. The crude ester was purified by flash column chromatography (EtOAc:hexane = 1:20) to afford the compound A1 (2.19 g, 13.2 mmol) in 88% yield as a white solid. $\alpha_{D}^{25} = -110.7$ (c 1.0, CHCl$_3$).

(R)-methyl 2-(tert-butyldiphenylsilyloxy)-2-phenylacetate (18): To a stirred solution of A1 (1.8 g, 10.8 mmol) in dry DCM (40 mL), imidazole (884 mg, 13 mmol) was added at 0 °C and stirred for 10 min. TBDPS-Cl (4.2 mL, 16.2 mmol) was then added to the solution at the same temperature and the reaction was allowed to warm at room temperature. After that the reaction mixture was stirred for 4 h and it was then quenched with water and extracted with DCM. The aqueous layer was washed with DCM (30 mL x 2). Organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was then purified by flash column chromatography (EtOAc:hexane = 1:50) to afford the compound 18 (4 g, 9.9 mmol) in 92% yield as white solid. $\alpha_{D}^{25} = -38.9$ (c 1.5, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 – 7.69 (m, 2H), 7.53 – 7.47 (m, 2H), 7.43 (d, $J = 7.0$ Hz, 3H), 7.38 (t, $J = 7.1$ Hz, 3H), 7.35 – 7.25 (m, 5H), 5.14 (s, 1H), 3.47 (s, 3H), 1.11 (d, $J = 1.7$ Hz, 10H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.2, 138.9, 135.9, 135.7, 132.9, 132.7, 129.9, 129.8, 128.4, 128.2, 127.7, 127.6, 126.6, 74.8, 51.9, 26.8, 19.4 HRMS (ESI) m/z: for C$_{25}$H$_{28}$O$_3$SiNa[M + Na]$^+$, calculated: 427.1705; found: 427.1709.

(R)-2-(tert-butyldiphenylsilyloxy)-2-phenylethanol (17): To a stirred solution of compound 18 (3 g, 7.4 mmol) in dry DCM (30 mL) at -78 °C, DIBAI-H (15.6 mL, 1 M in cyclohexane) was added drop-wise for 10 min and stirred at the same temperature for 2 h. After completion of the reaction, it was quenched with a saturated solution of Rochelle salt (4 mL) at -78 °C. The reaction solution was allowed to warm at room temperature and stirred for another 1 h. The reaction mixture was then filtered through a celite pad and washed with DCM. The filtrate was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude aldehyde was immediately used for the next step without any further purification. $\alpha_{D}^{25} = -32.8$ (c .5, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.50 (d, $J = 1.9$ Hz, 1H), 7.70 – 7.66 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.42 (m, 1H), 7.39 (d, $J = 7.4$ Hz, 2H), 7.35
(d, \( J = 4.7 \) Hz, 5H), 7.32 – 7.25 (m, 3H), 5.0 (d, 1.9 Hz, 1H) 1.13 (s, 9H). HRMS (ESI) \( m/z \): for \( C_{24}H_{26}O_2SiNa[M + Na]^+ \), calculated: 397.1600; found: 397.1609.

**Synthesis of compound 43:** Compound 43 was synthesized according to known procedure starting from C2-symmetric L-DET.²

(4R,5R)-diethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (B1): To a stirred solution of diethyl L-tartrate in dry toluene, fitted with Dean-Stark apparatus, 2,2-DMP and PTSA were added. The reaction was then heated to reflux for 12 h. After completion of the reaction, it was quenched with a saturated solution of NaHCO₃. The mixture was then extracted with ethyl acetate (30 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was then purified with flash column chromatography to afford compound B1 as a colorless liquid in a 95% yield. The spectral data of B1 matches well with the previous literature report.² \([\alpha]_{D}^{25} = -41.4 \) (c 1.0, CHCl₃).

((4S,5S)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanol (B2): To a stirred suspension of lithium aluminum hydride (LAH) in dry THF, a solution of compound B1 in dry THF was added drop-wise at 0 °C. The reaction was warmed at room temperature and stirred for 2 h at the same temperature. After completion of the reaction, it was cooled to 0 °C and a saturated solution of Na₂SO₄ was added to the reaction mixture drop-wise till a white precipitate appears. The precipitate was then filtered through a celite bed and washes with ethyl acetate. The combined filtrate was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the compound B2 as a colorless liquid in 90% yield. The spectral data of B2 matches well with the previous literature report.² \([\alpha]_{D}^{25} = -24.2 \) (c 1.0, MeOH).

((4S,5S)-5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl-4-methylbenzenesulfonate (B3): To a stirred solution of compound B2, in dry DCM, Et₃N was added at 0 °C and stirred for 5 min. Freshly recrystallized tosyl chloride and DMAP were added to the reaction mixture at 0 °C and stirred for 6 h. After the complete disappearance of the starting material, the reaction was quenched with water and extracted with DCM. The organic layer was washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude reaction mixture was then purified with flash column chromatography to afford compound B3 as a colorless liquid in 85% yield. \([\alpha]_{D}^{25} = -15.2 \) (c 1.0, CHCl₃).¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.75 (m, 2H), 7.33 (d, \( J = 8.1 \) Hz, 2H), 4.12 (t, \( J = 4.5 \) Hz, 2H), 4.10 – 4.04 (m, 1H), 3.94 (dt, \( J = 7.8, 4.0 \) Hz, 1H), 3.79 – 3.70 (m, 1H), 3.61 (dd, \( J = 12.0, 4.2 \) Hz, 1H), 2.43 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H).¹³C NMR (101
MHZ, CDCl$_3$) δ 145.1, 132.5, 129.9, 128.0, 110.0, 78.0, 74.5, 68.9, 61.7, 27.0, 26.7, 21.6.
HRMS (ESI) m/z: for C$_{14}$H$_{20}$O$_6$SNa[M + Na]$^+$, calculated: 339.0878; found: 339.0885.

((4S,5S)-2,2,5-trimethyl-1,3-dioxolan-4-yl)methanol (43): To a suspension of LAH in dry THF, a solution of compound B3 in dry THF was added drop-wise at 0 °C. The reaction was then warmed at room temperature and stirred for 12 h. After complete consumption of the starting material, the reaction solution was cooled to 0 °C and a saturated solution of Na$_2$SO$_4$ was added to it drop-wise till a white precipitate appears. The precipitate was then filtered through a celite bed and washed with ethyl acetate. The combined filtrate was dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was then purified by flash column chromatography to furnish compound 43 as a colorless liquid in 80% yield. [α]$_D^{25}$ = +2.3 (c 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 4.02 (dq, $J$ = 8.3, 6.0 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.70 – 3.56 (m, 2H), 1.42 (d, $J$ = 10.0 Hz, 6H), 1.30 (d, $J$ = 6.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 108.4, 82.7, 72.7, 61.3, 27.3, 26.9, 17.6. HRMS (ESI) m/z: for C$_7$H$_{14}$O$_3$Na[M + Na]$^+$, calculated: 169.0841; found: 169.0847.

References:

^1H NMR of compound 3a (600 MHz, CDCl$_3$)

^13C NMR of compound 3a (150 MHz, CDCl$_3$)
$^1$H NMR of compound 4a (600 MHz, CDCl$_3$)

$^{13}$C NMR of compound 4a (150 MHz, CDCl$_3$)
$^1$H NMR of compound 3b (600 MHz, CDCl$_3$)

$^{13}$C NMR of compound 3b (150 MHz, CDCl$_3$)
$^1$H NMR of compound 4b (600 MHz, CDCl$_3$)

$^{13}$C NMR of compound 4b (150 MHz, CDCl$_3$)
$^1$H NMR of compound 3c (600 MHz, CDCl$_3$)

$^{13}$C NMR of compound 3c (150 MHz, CDCl$_3$)
$^1$H NMR of compound 4c (600 MHz, CDCl$_3$)

13C NMR of compound 4c (150 MHz, CDCl$_3$)
2D NOESY OF COMPOUND 3C:
$^1$H NMR (400 MHz, CDCl$_3$) of compound 3d
$^{13}$C NMR of compound 3d (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4d
$^{13}$C NMR of compound 4d (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3e
$^{13}$C NMR of compound 3e (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4e

![NMR Spectrum](image_url)
$^{13}$C NMR of compound 4e (100 MHz, CDCl$_3$)
$^1$H NMR (600 MHz, CDCl$_3$) of compound 3f
$^{13}$C NMR of compound 3f (150 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4f
$^{13}$C NMR of compound 4f (100 MHz, CDCl$_3$)
$^1$H NMR (600 MHz, CDCl$_3$) of compound 3g

![H NMR spectrum of compound 3g](image)
$^{13}$C NMR of compound 3g (125 MHz, CDCl$_3$)
$^1$H NMR (600 MHz, CDCl$_3$) of compound 4g
$^{13}$C NMR of compound 4g (125 MHz, CDCl$_3$)
$^1$H NMR (600 MHz, CDCl$_3$) of compound 3h
$^{13}$C NMR of compound 3h (150 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$) of compound 4h
$^{13}$C NMR of compound 4h (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3i
$^{13}$C NMR of compound 3i (125 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4i
$^{13}$C NMR of compound 4i (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3j
$^{13}$C NMR of compound 3j (125 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$) of compound 4j
$^{13}$C NMR of compound 4j (100 MHz, CDCl$_3$)
2D NOESY OF COMPOUND 3j:
$^1$H NMR of compound 3k (400 MHz, CDCl$_3$)

13C NMR of compound 3k (100 MHz, CDCl$_3$)
DEPT NMR of compound 3k (100 MHz, CDCl₃)

1H NMR of compound 4k (400 MHz, CDCl₃)
$^{13}$C NMR of compound 4k (100 MHz, CDCl$_3$)

DEPT NMR of compound 4k (100 MHz, CDCl$_3$)
$^1$H NMR of compound 3l (400 MHz; CDCl$_3$)

$^{13}$C NMR of compound 3l (100 MHz, CDCl$_3$)
DEPT NMR of compound 3l (100 MHz, CDCl₃)

1H NMR of compound 4l (400 MHz, CDCl₃)
$^{13}$C NMR of compound 4l (100 MHz, CDCl$_3$)

DEPT NMR of compound 4l (100 MHz, CDCl$_3$)
$^1$H NMR of compound 3m (400 MHz, CDCl$_3$)

13C NMR of compound 3m (100 MHz, CDCl$_3$)
DEPT NMR of compound 3m (100 MHz, CDCl₃)

\[
\begin{align*}
&\text{O} \\
&\text{HO} \\
&\text{O} \\
&\text{HO}
\end{align*}
\]

1H NMR of compound 4m (400 MHz, CDCl₃)

\[
\begin{align*}
&\text{O} \\
&\text{O} \\
&\text{HO} \\
&\text{HO}
\end{align*}
\]
$^{13}$C NMR of compound 4m (100 MHz, CDCl$_3$)

DEPT NMR of compound 4m (100 MHz, CDCl$_3$)
$^{1}$H NMR of compound 3n (400 MHz, CDCl$_3$)

$^{13}$C NMR of compound 3n (100 MHz, CDCl$_3$)
DEPT NMR of compound 3n (100 MHz, CDCl₃)

1H NMR of compound 4n (400 MHz, CDCl₃)
$^{13}$C NMR of compound 4n (100 MHz, CDCl$_3$)

DEPT NMR of compound 4n (100 MHz, CDCl$_3$)
$^1$H NMR of compound 3o (600 MHz, CDCl$_3$)

$^{13}$C NMR of compound 3o (150 MHz, CDCl$_3$)
DEPT-135 NMR of compound 3o (150 MHz, CDCl₃)

{Chemical structure diagram}

1H NMR of compound 4o (600 MHz, CDCl₃)

{Chemical structure diagram}
$^{13}$C NMR of compound 4o (150 MHz, CDCl$_3$)

DEPT-135 NMR of compound 4o (150 MHz, CDCl$_3$)
UV-Vis spectrum of few γ-Z-alkylidenebutenolides

\[ R = p{-}\text{Cl}, p{-}\text{NO}_2, p{-}\text{OMe}, o{-}\text{NO}_2 \text{ and } p{-}\text{Ph} \]
$^1$H (600 MHz) NMR of compound 12 in CDCl$_3$

$^{13}$C (150 MHz) NMR of compound 12 in CDCl$_3$
DEPT (150 MHz) NMR of compound 12 in CDCl₃
$^1$H (600 MHz) NMR of compound 7 in CDCl$_3$

$^{13}$C (150 MHz) NMR of compound 7 in CDCl$_3$
DEPT (150 MHz) NMR of compound 7 in CDCl₃
$^1\text{H} \ (400 \text{ MHz}) \ \text{NMR of compound 13 in CDCl}_3$

$^{13}\text{C} \ (100 \text{ MHz}) \ \text{NMR of compound 13 in CDCl}_3$
DEPT (100 MHz) NMR of compound 13 in CDCl₃
$^1$H NMR of versicolactone A (6) (600 MHz, DMSO-$d_6$)

\[ \text{\(f_1\) (ppm)} \]

\[
\begin{align*}
7.0 & \quad 2.76 \\
6.4 & \quad 1.07 \\
6.0 & \quad 1.03 \\
5.6 & \quad 1.00 \\
5.2 & \quad 0.92 \\
4.6 & \quad 1.01 \\
4.3 & \quad 1.03 \\
4.0 & \quad 1.04 \\
3.7 & \quad 2.50 \\
3.4 & \quad 2.50 \\
3.1 & \quad 2.51 \\
2.8 & \quad 2.51 \\
2.5 & \quad 3.59 \\
2.2 & \quad 3.60 \\
2.0 & \quad 3.61 \\
1.8 & \quad 3.61 \\
1.6 & \quad 3.62 \\
1.4 & \quad 3.63 \\
1.2 & \quad 3.63 \\
1.0 & \quad 4.26 \\
0.7 & \quad 4.27 \\
0.5 & \quad 4.28 \\
0.3 & \quad 4.29 \\
0.1 & \quad 5.48 \\
0.0 & \quad 5.49 \\
1.0 & \quad 6.43 \\
1.5 & \quad 7.87 \\
2.0 & \quad 7.88 \\
\end{align*}
\]

$^{13}$C NMR of versicolactone A (6) (150 MHz, DMSO-$d_6$)

\[ \text{\(f_1\) (ppm)} \]

\[
\begin{align*}
170.1 & \quad 19.62 \\
146.6 & \quad 39.68 \\
146.0 & \quad 39.82 \\
119.8 & \quad 39.95 \\
117.8 & \quad 40.09 \\
146.0 & \quad 40.23 \\
69.9 & \quad 69.89 \\
51.9 & \quad 70.49 \\
170.2 & \quad 70.54 \\
69.8 & \quad 117.33 \\
40.2 & \quad 119.86 \\
39.8 & \quad 146.01 \\
39.5 & \quad 146.65 \\
39.2 & \quad 150.17 \\
39.0 & \quad 150.17 \\
38.8 & \quad 150.17 \\
38.6 & \quad 150.17 \\
38.4 & \quad 150.17 \\
38.2 & \quad 150.17 \\
38.0 & \quad 150.17 \\
210 & \quad 150.17 \\
200 & \quad 150.17 \\
190 & \quad 150.17 \\
180 & \quad 150.17 \\
170 & \quad 150.17 \\
160 & \quad 150.17 \\
150 & \quad 150.17 \\
140 & \quad 150.17 \\
130 & \quad 150.17 \\
120 & \quad 150.17 \\
110 & \quad 150.17 \\
100 & \quad 150.17 \\
90 & \quad 150.17 \\
80 & \quad 150.17 \\
70 & \quad 150.17 \\
60 & \quad 150.17 \\
50 & \quad 150.17 \\
40 & \quad 150.17 \\
30 & \quad 150.17 \\
20 & \quad 150.17 \\
10 & \quad 150.17 \\
0 & \quad 150.17 \\
-10 & \quad 150.17 \\
\end{align*}
\]
DEPT-135- NMR of versicolactone A (6) (150 MHz, DMSO-D$_6$)

\[
\begin{array}{c}
\text{OH} \\
\text{HO-} \\
\text{O}
\end{array}
\]

$^{13}N$MR of versicolactone B (5) (600 MHz, DMSO-D$_6$)

\[
\begin{array}{c}
\text{OH} \\
\text{HO-} \\
\text{O}
\end{array}
\]
$^{13}$C NMR of versicolactone B (5) (150 MHz, DMSO-$D_6$)

$^1$H (400 MHz) NMR of compound 18 in CDCl$_3$
\(\text{\textsuperscript{13}C (100 MHz) NMR of compound 18 in CDCl}_3\)
DEPT (100 MHz) NMR of compound 18 in CDCl₃

$\text{OTBDPS}$
$\text{Ph} \text{CO}_2\text{Me}$

$^1\text{H} (400 MHz) \text{ NMR of compound 17 in CDCl}_3$

$\text{OTBDPS}$
$\text{Ph} \text{CHO}$
$^1$H (400 MHz) NMR of compound 20 in CDCl$_3$

[Diagram of $^1$H NMR spectrum]

$^{13}$C (100 MHz) NMR of compound 20 in CDCl$_3$

[Diagram of $^{13}$C NMR spectrum]
DEPT (100 MHz) NMR of compound 20 in CDCl$_3$

1H (400 MHz) NMR of compound 16 in CDCl$_3$
$^{13}$C (100 MHz) NMR of compound 16 in CDCl$_3$

DEPT (100 MHz) NMR of compound 16 in CDCl$_3$
$^1$H NMR of goniobutenolide A (15) (400 MHz, CDCl$_3$)

$^{13}$C NMR of goniobutenolide A(15) (100 MHz, CDCl$_3$)
$^1$H NMR of goniobutenolide B (14) (400 MHz, CDCl$_3$)

$^{13}$C NMR of goniobutenolide B (14) (150 MHz, CDCl$_3$)
DEPT (150 MHz) NMR of goniobutenolide B (14) in CDCl₃

\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{O} & \quad \text{OH} \\
\text{O} & \quad \text{O}
\end{align*}
\]

\[\begin{array}{c}
72.32 \\
77.06 \\
112.14 \\
121.19 \\
126.56 \\
128.51 \\
128.66 \\
140.57 \\
\end{array}\]

\[f_1 (\text{ppm})
\]

\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{O} & \quad \text{OH} \\
\text{O} & \quad \text{O}
\end{align*}
\]

\[\begin{array}{c}
72.32 \\
77.06 \\
112.14 \\
121.19 \\
126.56 \\
128.51 \\
128.66 \\
140.57 \\
\end{array}\]

\[f_1 (\text{ppm})
\]

\[1^H (400 MHz) \text{ NMR of compound 26 in CDCl}_3\]
$^{13}$C (100 MHz) NMR of compound 26 in CDCl$_3$
DEPT (100 MHz) NMR of compound 26 in CDCl$_3$

$\text{Ph}$

$\text{O}$

$\text{O}$

$\text{CHO}$

$^1$H (400 MHz) NMR of compound 27 in CDCl$_3$
$^{13}$C (100 MHz) NMR of compound 27 in CDCl$_3$
DEPT (100 MHz) NMR of compound 27 in CDCl$_3$

$\text{Ph} \ O \ O \ H$

$\text{O} \ \text{TMS}$

$^1$H (400 MHz) NMR of compound (S)-25 in CDCl$_3$
$^{13}$C (100 MHz) NMR of compound (S)-25 in CDCl$_3$
DEPT (100 MHz) NMR of compound (S)-25 in CDCl₃

[Chemical structure image]

$^1$H NMR of Z-melorinol (24) (400 MHz, CDCl₃)
13C NMR of Z-melodorinol (24) (100 MHz, CDCl$_3$)

DEPT-135- NMR of Z-melodorinol (24) (100 MHz, CDCl$_3$)
$^1$H NMR of $E$-melodorinol (23) (400 MHz, CDCl$_3$)

$^{13}$C NMR of $E$-melodorinol (23) (100 MHz, CDCl$_3$)
DEPT-135- NMR of *E*-melodorinol (23) (100 MHz, CDCl$_3$)

$^1$H NMR of *Z*-acetylmelodorinol (28) (400 MHz, CDCl$_3$)
13C NMR of Z-acetylmelodorinol (28) (100 MHz, CDCl₃)

DEPT-135- NMR of Z-acetylmelodorinol (28) (100 MHz, CDCl₃)
$^1$H NMR of $E$-acetylmelodorinol (22) (400 MHz, CDCl$_3$)

$^{13}$C NMR of $E$-acetylmelodorinol (22) (100 MHz, CDCl$_3$)
DEPT-135- NMR of E-acetylmelodorinol (22) (100 MHz, CDCl₃)

¹H (400 MHz) NMR of compound 32 in CDCl₃
$^{13}$C (100 MHz) NMR of compound 32 in CDCl$_3$
DEPT (100 MHz) NMR of compound 32 in CDCl$_3$

$^1$H (400 MHz) NMR of compound 31 in CDCl$_3$
$^{13}$C (100 MHz) NMR of compound 31 in CDCl$_3$
DEPT (100 MHz) NMR of compound 31 in CDCl\textsubscript{3}

\begin{align*}
\text{H} \quad \text{f1} (\text{ppm})
\end{align*}

\begin{align*}
14.10 & \quad 22.68 \\
25.01 & \quad 29.23 \\
29.34 & \quad 29.51 \\
29.54 & \quad 29.63 \\
31.91 & \quad 37.68 \\
62.37 & \quad \\
\end{align*}

\begin{align*}
1^H (600 MHz) \text{ NMR of compound 34 in CDCl}_3
\end{align*}
$^{13}$C (150 MHz) NMR of compound 34 in CDCl$_3$

DEPT (100 MHz) NMR of compound 34 in CDCl$_3$
$^{1}H$ NMR of hygrophorone G (30) (400 MHz, CDCl$_3$)

$^{13}C$ NMR of hygrophorone G (30) (100 MHz, CDCl$_3$)
DEPT-135- NMR of hygrophorone G (30) (100 MHz, CDCl₃)

1H NMR of hygrophorone F (29) (600 MHz, CDCl₃)
$^{13}$C NMR of hygrophorone F (29) (150 MHz, CDCl$_3$)

$^1$H (600 MHz) NMR of compound 37 in CDCl$_3$
$^{13}$C (150 MHz) NMR of compound 37 in CDCl$_3$
DEPT (100 MHz) NMR of compound 37 in CDCl₃

1H (600 MHz) NMR of compound 38 in CDCl₃
$^{13}C$ (150 MHz) NMR of compound 38 in CDCl$_3$

$^1$H NMR of compound 36 (600 MHz, C$_6$D$_6$)
$^{13}$C NMR of compound 36 (100 MHz, C$_6$D$_6$)

DEPT-135- NMR of compound 36 (100 MHz, C$_6$D$_6$)
$^{1}H$ NMR of ramariolide D (35) (600 MHz, C$_6$D$_6$)

$^{13}C$ NMR of ramariolide D (35) (150 MHz, C$_6$D$_6$)
DEPT-135- NMR of ramariolide D (35) (150 MHz, C₆D₆)

¹H (400 MHz) NMR of compound B3 in CDCl₃
$^{13}$C (100 MHz) NMR of compound B3 in CDCl$_3$

DEPT (100 MHz) NMR of compound B3 in CDCl$_3$
$^1$H (400 MHz) NMR of compound 43 in CDCl$_3$
$^{13}$C (100 MHz) NMR of compound 43 in CDCl$_3$

DEPT (100 MHz) NMR of compound 43 in CDCl$_3$
$^1$H (400 MHz) NMR of compound 42 in CDCl$_3$
$^{13}$C (100 MHz) NMR of compound 42 in CDCl$_3$

DEPT (100 MHz) NMR of compound 42 in CDCl$_3$
$^1$H (400 MHz) NMR of compound 45 in CDCl$_3$

$^{13}$C (100 MHz) NMR of compound 45 in CDCl$_3$
DEPT (100 MHz) NMR of compound 45 in CDCl$_3$
$^{1}$H (400 MHz) NMR of compound 41 in CDCl$_3$ 

$^{13}$C (100 MHz) NMR of compound 41 in CDCl$_3$
DEPT (100 MHz) NMR of compound 41 in CDCl$_3$

1H (600 MHz) NMR of compound 46 in CDCl$_3$
$^{13}$C (150 MHz) NMR of compound 46 in CDCl$_3$

$^1$H (400 MHz) NMR of phomopsolidone C (40) in CDCl$_3$
$^{13}$C (150 MHz) NMR of compound phomopsolidone C (40) in CDCl$_3$

$^1$H (500 MHz) NMR of phomopsolidone D (39) in CDCl$_3$
$^{13}$C (125 MHz) NMR of phomopsolidone D (39) in CDCl$_3$