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

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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 OH H<sub>2</sub>SO<sub>4</sub> (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 Ph CO<sub>2</sub>Me mL) and washed with 5% NaHCO3. The organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, 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.  $R_f = 0.5$  (EtOAc:hexane =1:15). Spectral data matches well with previously reported compound.<sup>1</sup>  $[\alpha]_D^{25} = -110.7$  (c 1.0, CHCl<sub>3</sub>).

(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<sub>2</sub>SO<sub>4</sub> 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.  $R_f = 0.5$  (EtOAc:hexane =1:40).  $[\alpha]_{D}^{25} = -38.9$  (c 1.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 138.9, 135.9, 135.7, 132.9, 132.8, 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<sub>25</sub>H<sub>28</sub>O<sub>3</sub>SiNa[M + Na]<sup>+</sup>, 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<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude aldehyde was immediately used for the next step without any further purification.  $R_f=0.5$  (EtOAc:hexane =1:20).  $[\alpha]_D^{25}$  = -32.8 (c .5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>24</sub>H<sub>26</sub>O<sub>2</sub>SiNa[M + Na]<sup>+</sup>, calculated: 397.1600; found: 397.1609.

**Synthesis of compound 43:** Compound **43** was synthesized according to known procedure starting from C<sub>2</sub>-symmetric L-DET.<sup>2</sup>



(4R,5R)-diethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (B1): To a stirred solution

CO<sub>2</sub>Et

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 NaHCO<sub>3</sub>. The mixture was then extracted with ethyl acetate

(30 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, 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.<sup>2</sup>  $[\alpha]_D^{25} = -41.4$  (c 1.0, CHCl<sub>3</sub>).

((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 Na<sub>2</sub>SO<sub>4</sub> 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 Na<sub>2</sub>SO<sub>4</sub> 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.<sup>2</sup>  $[\alpha]_D^{25} = -24.2$  (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,  $Et_3N$  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 Na<sub>2</sub>SO<sub>4</sub>, 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, CHCl<sub>3</sub>).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101

MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>14</sub>H<sub>20</sub>O<sub>6</sub>SNa[M + Na]<sup>+</sup>, 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<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> 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.  $[\alpha]_D^{25} = +2.3$  (c 1.0, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  108.4, 82.7, 72.7, 61.3, 27.3, 26.9, 17.6. HRMS (ESI) *m/z*: for C<sub>7</sub>H<sub>14</sub>O<sub>3</sub>Na[M + Na]<sup>+</sup>, calculated: 169.0841; found: 169.0847.

#### **References:**

- (a)Y. Sun, X. Wan, J. Wang, Q. Meng, H. Zhang, L. Jiang, and Z. Zhang, Org. Lett. 2005, 7, 5425-5427. (b) T. Peňaška, P. Koukal, and M. Kotora, Eur. J. Org. Chem. 2018, 147–149.
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#### <sup>1</sup>H NMR of compound 3a (600 MHz, CDCl<sub>3</sub>)



### <sup>1</sup>H NMR of compound 4a (600 MHz, CDCl<sub>3</sub>)



#### <sup>13</sup>C NMR of compound 4a (150 MHz, CDCl<sub>3</sub>)



### <sup>1</sup>H NMR of compound 3b (600 MHz, CDCl<sub>3</sub>)



### <sup>1</sup>H NMR of compound 4b (600 MHz, CDCl<sub>3</sub>)

C 236 C 236 C 236 C 237 C 238 C





#### <sup>13</sup>C NMR of compound 4b (150 MHz, CDCl<sub>3</sub>)



### <sup>1</sup>H NMR of compound 3c (600 MHz, CDCl<sub>3</sub>)





#### <sup>13</sup>C NMR of compound 3c (150 MHz, CDCl<sub>3</sub>)



### <sup>1</sup>H NMR of compound 4c (600 MHz, CDCl<sub>3</sub>)

 $\left\{\begin{array}{c} 8.31\\ 8.31\\ 8.30\\ 8.30\\ 8.30\\ 8.30\\ 7.55\\ 7.756\\ 7.756\\ 7.756\\ 7.756\\ 7.756\\ 7.28\\ 6.69\\ 6.49\\ 6.49\end{array}\right.$ 





#### <sup>13</sup>C NMR of compound 4c (150 MHz, CDCl<sub>3</sub>)



### 2D NOESY OF COMPOUND 3C:



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound 3d



# <sup>13</sup>C NMR of compound 3d (125 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound 4d



# <sup>13</sup>C NMR of compound 4d (125 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound 3e



# <sup>13</sup>C NMR of compound 3e (125 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound 4e



### <sup>13</sup>C NMR of compound 4e (100 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of compound 3f



# <sup>13</sup>C NMR of compound 3f (150 MHz, CDCl<sub>3</sub>)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 fl (ppm)



# <sup>13</sup>C NMR of compound 4f (100 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of compound 3g

7.70
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 7.70
 7.90
 7.49
 7.49
 7.49
 7.49
 7.49
 6.88
 6.87
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# <sup>13</sup>C NMR of compound 3g (125 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of compound 4g



# <sup>13</sup>C NMR of compound 4g (125 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of compound 3h



# <sup>13</sup>C NMR of compound 3h (150 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound 4h

7.82
7.81
7.52
7.51
7.54
7.44
7.44
7.44
7.44
7.44
7.44
7.44
7.623
6.05





# <sup>13</sup>C NMR of compound 4h (125 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound 3i



# <sup>13</sup>C NMR of compound 3i (125 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound 4i



## <sup>13</sup>C NMR of compound 4i (125 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound 3j




# <sup>13</sup>C NMR of compound 3j (125 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound 4j







# <sup>13</sup>C NMR of compound 4j (100 MHz, CDCl<sub>3</sub>)





# <sup>1</sup>H NMR of compound 3k (400 MHz, CDCl<sub>3</sub>)



# DEPT NMR of compound 3k (100 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of compound 4k (100 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of compound 3l (400 MHz; CDCl<sub>3</sub>)



# DEPT NMR of compound 3l (100 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of compound 4l (100 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR of compound 3m (400 MHz, CDCl<sub>3</sub>)



# DEPT NMR of compound 3m (100 MHz, CDCl<sub>3</sub>)



# <sup>13</sup>C NMR of compound 4m (100 MHz, CDCl<sub>3</sub>)



f1 (ppm) 

### <sup>1</sup>H NMR of compound 3n (400 MHz, CDCl<sub>3</sub>)





### <sup>13</sup>C NMR of compound 3n (100 MHz, CDCl<sub>3</sub>)

169.33	148.84 143.86 138.46	128.37 127.67 127.55 120.33 118.24	77.36 CDCI3 77.04 CDCI3 76.72 CDCI3 72.92 70.10 66.85	36.75	29.42	21.92
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# DEPT NMR of compound 3n (100 MHz, CDCl<sub>3</sub>)



### <sup>13</sup>C NMR of compound 4n (100 MHz, CDCl<sub>3</sub>)



### <sup>1</sup>H NMR of compound 30 (600 MHz, CDCl<sub>3</sub>)





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# UV-Vis spectrum of few $\gamma$ -Z-alkylidenebutenolides



# <sup>1</sup>H (600 MHz) NMR of compound 12 in CDCl<sub>3</sub>



<sup>13</sup>C (150 MHz) NMR of compound 12 in CDCl<sub>3</sub>



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200	190	180	170	160	150	140	130	120	110	100 f1 (	90 (ppm)	80	70	60	50	40	30	20	10	0	-10

### DEPT (150 MHz) NMR of compound 12 in CDCl<sub>3</sub>





# <sup>1</sup>H (600 MHz) NMR of compound 7 in CDCl<sub>3</sub>



<sup>13</sup>C (150 MHz) NMR of compound 7 in CDCl<sub>3</sub>



DEPT (150 MHz) NMR of compound 7 in CDCl<sub>3</sub>





# <sup>1</sup>H (400 MHz) NMR of compound 13 in CDCl<sub>3</sub>



<sup>13</sup>C (100 MHz) NMR of compound 13 in CDCl<sub>3</sub>



DEPT (100 MHz) NMR of compound 13 in CDCl<sub>3</sub>



# <sup>1</sup>H NMR of versicolactone A (6) (600 MHz, DMSO-D<sub>6</sub>)



### DEPT-135- NMR of versicolactone A (6) (150 MHz, DMSO-D<sub>6</sub>)



# <sup>13</sup>C NMR of versicolactone B (5) (150 MHz, DMSO-D<sub>6</sub>)



<sup>1</sup>H (400 MHz) NMR of compound 18 in CDCl<sub>3</sub>



# <sup>13</sup>C (100 MHz) NMR of compound 18 in CDCl<sub>3</sub>





### DEPT (100 MHz) NMR of compound 18 in CDCl<sub>3</sub>





### DEPT (100 MHz) NMR of compound 20 in CDCl<sub>3</sub>





# <sup>13</sup>C (100 MHz) NMR of compound 16 in CDCl<sub>3</sub>



# <sup>1</sup>H NMR of goniobutenolide A (15) (400 MHz, CDCl<sub>3</sub>)

6.11 6.15 





### <sup>13</sup>C NMR of goniobutenolide A(15) (100 MHz, CDCl<sub>3</sub>)







<sup>13</sup>C NMR of goniobutenolide B (14) (150 MHz, CDCl<sub>3</sub>)


## DEPT (150 MHz) NMR of goniobutenolide B (14) in CDCl<sub>3</sub>



<sup>1</sup>H (400 MHz) NMR of compound 26 in CDCl<sub>3</sub>





## <sup>13</sup>C (100 MHz) NMR of compound 26 in CDCl<sub>3</sub>



## DEPT (100 MHz) NMR of compound 26 in CDCl<sub>3</sub>



<sup>1</sup>H (400 MHz) NMR of compound 27 in CDCl<sub>3</sub>



## <sup>13</sup>C (100 MHz) NMR of compound 27 in CDCl<sub>3</sub>



## DEPT (100 MHz) NMR of compound 27 in CDCl<sub>3</sub>



<sup>1</sup>H (400 MHz) NMR of compound (S)-25 in CDCl<sub>3</sub>

#### 25:55 25



<sup>13</sup>C (100 MHz) NMR of compound (S)-25 in CDCl<sub>3</sub>



## DEPT (100 MHz) NMR of compound (S)-25 in CDCl<sub>3</sub>



<sup>1</sup>H NMR of Z-melodorinol (24) (400 MHz, CDCl<sub>3</sub>)

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<sup>13</sup>C NMR of Z-melodorinol (24) (100 MHz, CDCl<sub>3</sub>)



DEPT-135- NMR of Z-melodorinol (24) (100 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of *E*-melodorinol (23) (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of Z-acetylmelodorinol (28) (400 MHz, CDCl<sub>3</sub>)



DEPT-135- NMR of Z-acetylmelodorinol (28) (100 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR of *E*-acetylmelodorinol (22) (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of *E*-acetylmelodorinol (22) (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H (400 MHz) NMR of compound 32 in CDCl<sub>3</sub>



## <sup>13</sup>C (100 MHz) NMR of compound 32 in CDCl<sub>3</sub>



## DEPT (100 MHz) NMR of compound 32 in CDCl<sub>3</sub>



<sup>1</sup>H (400 MHz) NMR of compound 31 in CDCl<sub>3</sub>



## DEPT (100 MHz) NMR of compound 31 in CDCl<sub>3</sub>



<sup>1</sup>H (600 MHz) NMR of compound 34 in CDCl<sub>3</sub>



DEPT (100 MHz) NMR of compound 34 in CDCl<sub>3</sub>



<sup>13</sup>C NMR of hygrophorone G (30) (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of hygrophorone F (29) (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of hygrophorone F (29) (150 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H (600 MHz) NMR of compound 37 in CDCl<sub>3</sub>

# 



## <sup>13</sup>C (150 MHz) NMR of compound 37 in CDCl<sub>3</sub>



## DEPT (100 MHz) NMR of compound 37 in CDCl<sub>3</sub>



<sup>1</sup>H (600 MHz) NMR of compound 38 in CDCl<sub>3</sub>



<sup>1</sup>H NMR of compound 36 (600 MHz, C<sub>6</sub>D<sub>6</sub>)





DEPT-135- NMR of compound 36 (100 MHz, C<sub>6</sub>D<sub>6</sub>)





<sup>13</sup>C NMR of ramariolide D (35) (150 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>1</sup>H (400 MHz) NMR of compound B3 in CDCl<sub>3</sub>



DEPT (100 MHz) NMR of compound B3 in CDCl<sub>3</sub>



## <sup>13</sup>C (100 MHz) NMR of compound 43 in CDCl<sub>3</sub>



DEPT (100 MHz) NMR of compound 43 in CDCl<sub>3</sub>





#### <sup>1</sup>H (400 MHz) NMR of compound 42 in CDCl<sub>3</sub>



## <sup>13</sup>C (100 MHz) NMR of compound 42 in CDCl<sub>3</sub>



DEPT (100 MHz) NMR of compound 42 in CDCl<sub>3</sub>





## <sup>1</sup>H (400 MHz) NMR of compound 45 in CDCl<sub>3</sub>



<sup>13</sup>C (100 MHz) NMR of compound 45 in CDCl<sub>3</sub>



<sup>30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -7</sup> f1 (ppm)

## <sup>1</sup>H (400 MHz) NMR of compound 41 in CDCl<sub>3</sub>



## DEPT (100 MHz) NMR of compound 41 in CDCl<sub>3</sub>


## <sup>13</sup>C (150 MHz) NMR of compound 46 in CDCl<sub>3</sub>











## <sup>13</sup>C (125 MHz) NMR of phomopsolidone D (39) in CDCl<sub>3</sub>

