

# Supporting Information

## Total Synthesis of (+)-Chinensiolid B via Tandem Allylboration/Lactonization

*Tim G. Elford and Dennis G. Hall\**

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

## Table of Contents

<b>1) GENERAL INFORMATION .....</b>	<b>3</b>
<b>2) EXPERIMENTAL PROCEDURES.....</b>	<b>3</b>
(Z)-Methyl 6-(( <i>tert</i> -butyldiphenylsilyl)oxy)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hex-2-enoate (Z-5).....	3
(2 <i>S</i> ,3 <i>R</i> ,5 <i>S</i> )-3-(( <i>tert</i> -Butyldimethylsilyl)oxy)-2-chloro-2-methyl-5-(prop-1-en-2-yl) cyclohexanone (SI-12).....	4
(1 <i>R</i> ,2 <i>S</i> ,3 <i>R</i> ,5 <i>R</i> )-Methyl 3-(( <i>tert</i> -butyldimethylsilyl)oxy)-2-methyl-5-(prop-1-en-2-yl) cyclopentanecarboxylate (7) .....	4
((1 <i>R</i> ,2 <i>S</i> ,3 <i>S</i> ,5 <i>R</i> )-3-(( <i>tert</i> -Butyldimethylsilyl)oxy)-2-methyl-5-(prop-1-en-2-yl) cyclopentyl) methanol (SI-13).....	5
(1 <i>R</i> ,2 <i>S</i> ,3 <i>R</i> ,5 <i>R</i> )-3-(( <i>tert</i> -Butyldimethylsilyl)oxy)-2-methyl-5-(prop-1-en-2-yl) cyclopentanecarbaldehyde (4).....	6
(4 <i>S</i> ,5 <i>S</i> )-5-((1' <i>R</i> ,2' <i>S</i> ,3' <i>R</i> ,5' <i>R</i> )-3'-(( <i>tert</i> -Butyldimethylsilyl)oxy)-2'-methyl-5'-(prop-1-en-2-yl) cyclopentyl)-4-(3-(( <i>tert</i> -butyldiphenylsilyl)oxy)propyl)-3-methylenedihydrofuran-2(3 <i>H</i> )-one (3).....	6
(4 <i>S</i> ,5 <i>S</i> )-5-((1' <i>R</i> ,2' <i>S</i> ,3' <i>R</i> ,5' <i>R</i> )-3'-(( <i>tert</i> -Butyldimethylsilyl)oxy)-2'-methyl-5'-(prop-1-en-2-yl) cyclopentyl)-4-(3-hydroxypropyl)-3-methylenedihydrofuran-2(3 <i>H</i> )-one (SI-14) .....	7
(4 <i>S</i> ,5 <i>S</i> )-4-allyl-5-((1 <i>R</i> ,2 <i>S</i> ,3 <i>S</i> ,5 <i>R</i> )-3-(( <i>tert</i> -Butyldimethylsilyl)oxy)-2-methyl-5-(prop-1-en-2-yl)cyclopentyl)-3-methylenedihydrofuran-2(3 <i>H</i> )-one (9) .....	8
(3 <i>S</i> ,4 <i>S</i> ,5 <i>S</i> )-5-((1' <i>R</i> ,2' <i>S</i> ,3' <i>S</i> ,5' <i>R</i> )-3'-( <i>t</i> -Butyl(dimethyl)siloxy)-2'-methyl-5'-(prop-1-en-2-yl)cyclopentyl)-5-cyanomethyl-4-(prop-2-en-1-yl)tetrahydrofuran-2-one (8).....	8
(3 <i>aS</i> ,6 <i>aR</i> ,8 <i>R</i> ,9 <i>S</i> ,9 <i>aR</i> ,9 <i>bR</i> )-8-(( <i>tert</i> -Butyldimethylsilyl)oxy)-6,9-dimethyl-3-methylene-3 <i>a</i> ,4,6 <i>a</i> ,7,8,9 <i>a</i> ,9 <i>b</i> -octahydroazuleno[4,5- <i>b</i> ]furan-2(3 <i>H</i> )-one (10).....	9
(1 <i>S</i> ,2 <i>R</i> ,3 <i>aR</i> ,3 <i>bS</i> ,4 <i>aR</i> ,5 <i>aS</i> ,8 <i>aR</i> ,8 <i>bS</i> )-2-(( <i>tert</i> -Butyldimethylsilyl)oxy)-1,3 <i>b</i> -dimethyl-6-methylenedecahydrooxireno[2',3':7,8]azuleno[4,5- <i>b</i> ]furan-7(2 <i>H</i> )-one (2) .....	10
(3 <i>aS</i> ,6 <i>R</i> ,6 <i>aR</i> ,8 <i>R</i> ,9 <i>S</i> ,9 <i>aS</i> ,9 <i>bR</i> )-8-(( <i>tert</i> -Butyldimethylsilyl)oxy)-6-hydroxy-6,9-dimethyl-3-methylenedecahydroazuleno[4,5- <i>b</i> ]furan-2(9 <i>bH</i> )-one (11).....	11
(3 <i>aS</i> ,6 <i>R</i> ,6 <i>aR</i> ,9 <i>S</i> ,9 <i>aR</i> ,9 <i>bR</i> )-6-Hydroxy-6,9-dimethyl-3-methyleneoctahydroazuleno[4,5- <i>b</i> ]furan-2,8(3 <i>H</i> ,9 <i>bH</i> )-dione (1).....	11
<b>3) COMPARISON OF <sup>13</sup>C-NMR DATA FOR 1.....</b>	<b>13</b>
<b>4) CRYSTALLOGRAPHIC DATA FOR 8 .....</b>	<b>14</b>
<b>5) COPIES OF NMR SPECTRA.....</b>	<b>22</b>
<b>6) REFERENCES.....</b>	<b>36</b>

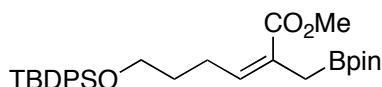
## 1) General information

Unless otherwise noted, all reactions were performed under an argon atmosphere. Toluene, HMPA, CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> were distilled over CaH<sub>2</sub>. THF was distilled over sodium/benzophenone ketyl. NH<sub>4</sub>Cl(aq) and NaHCO<sub>3</sub>(aq) refer to saturated aqueous solutions. All other chemicals were used as received from commercial sources. Thin layer chromatography (TLC) was performed on Macherey-Nagel Polygram Sil G/UV<sub>254</sub> plates and was visualized with UV light, potassium permanganate stain or Seebach's stain. NMR spectra were recorded on 300, 400, 500 or 600 MHz instruments as indicated in procedures. The residual solvent protons (<sup>1</sup>H) or the solvent carbons (<sup>13</sup>C) were used as internal standards. <sup>1</sup>H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, integration, coupling constant). The following abbreviations are used in reporting NMR data: br, broad; app, apparent; s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; ddd, doublet of doublet of doublets; dddd, doublet of doublet of doublet of doublets; p, pentet; qt, quartet of triplets; m, multiplet. High-resolution mass spectra were recorded by the University of Alberta Mass Spectrometry Services Laboratory using either electron impact (EI) or electrospray (ES) ionization techniques. Infrared spectra and optical rotations were recorded by the University of Alberta Spectral Services Laboratory.

### Full authorship for reference 3:

Zhang, S.; Zhao, M.; Bai, L.; Hasegawa, T.; Wang, J.; Wang, L.; Xue, H.; Deng, Q.; Xing, F.; Bai, Y.; Sakai, J.; Bai, J.; Koyanagi, R.; Tsukumo, Y.; Kataoka, T.; Nagai, K.; Hirose, K.; Ando, M. *J. Nat. Prod.* **2006**, *69*, 1425-1428.

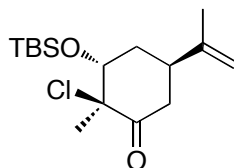
## 2) Experimental procedures



### (Z)-Methyl 6-((tert-butyldiphenylsilyl)oxy)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hex-2-enoate (Z-5)

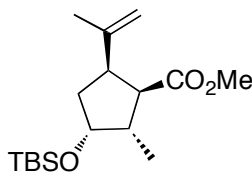
To a solution of HMPA (10.0 ml, 6.0 equiv) in toluene (100 ml) under argon at 0 °C was added DIBALH (10.0 ml, 1.5 M solution in toluene, 1.5 equiv). This mixture was left to stir for 1 h, at which point, known propiolic ester derivative<sup>1</sup> (3.81 g, 1.0 equiv) was added. The mixture was stirred for 5 h at 0 °C, then freshly distilled chloromethylpinacolboronate<sup>2</sup> was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 1M HCl and extracted with ether (x4). The combined organics were washed with 1M HCl (x3), NaHCO<sub>3</sub>(aq) (x2), water and brine. The organics were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude product was then purified by flash chromatography (3% ethyl acetate in dichloromethane) to provide allylboronate **5** as a mixture of alkene isomers (3.92 g, 68% yield). The major isomer was the desired one and was often obtained in a ratio >3.5:1. The mixture of isomers was used for the next step as separation on

large scale was difficult and the minor isomer does not react in the next step of the synthesis.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70-7.63 (m, 4H), 7.45-7.33 (m, 6H), 5.92 (t, 1H,  $J = 7.6$  Hz), 3.69 (s, 3H), 3.68 (t, 2H,  $J = 6.5$  Hz), 2.60 (q, 2H,  $J = 7.8$  Hz), 1.82 (br s, 2H), 1.68 (app p, 2H,  $J = 7.3$  Hz), 1.23 (s, 12H), 1.05 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.3, 142.9, 135.6, 134.1, 129.5, 128.1, 127.6, 83.3, 63.6, 51.2, 32.5, 26.9, 26.4, 24.8, 19.3.  $^{11}\text{B}$ -NMR (160 MHz,  $\text{CDCl}_3$ ):  $\delta$  33.1. IR ( $\text{CDCl}_3$ , cast film,  $\text{cm}^{-1}$ ): 3071, 2932, 1722. HRMS (EI,  $m/z$ ) Calcd for  $\text{C}_{26}\text{H}_{34}\text{O}_5\text{Si}^{35}\text{B}^{11} [\text{M}-\text{C}_4\text{H}_9]^+$ : 465.22687. Found: 465.22809.



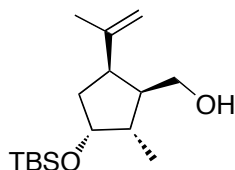
**(2*S*,3*R*,5*S*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-chloro-2-methyl-5-(prop-1-en-2-yl)cyclohexanone (SI-12)**

Known alcohol **6**<sup>3</sup> (127.8 mmol, 1.00 equiv) was dissolved in 150 ml acetonitrile and cooled to 0 °C under argon. To this stirred solution was added pyridine (12.4 ml, 1.20 equiv) followed by *tert*-butyldimethylsilyltrifluoromethane sulfonate (32.3 ml, 1.10 equiv). The reaction solution was then warmed to room temperature and allowed to stir overnight. The reaction was then quenched by the addition of  $\text{NH}_4\text{Cl}$ (aq) and the mixture was extracted with ethyl acetate (x3). The organic layers were combined, washed with water and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. Crude product **SI-12** was obtained as a colorless oil and was pure enough by  $^1\text{H}$ -NMR to be used without further purification (39.5 g, 97% yield).  $[\alpha]_D = +60.5$  ( $c$  0.34,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.80 (br s, 1H), 4.76 (br s, 1H), 4.19 (dd, 1H,  $J = 3.5$ , 1.9 Hz), 3.04 (dd, 1H,  $J = 14.0$ , 14.0 Hz), 2.83 (app tt, 1H,  $J = 12.5$ , 3.4 Hz), 2.42 (ddd, 1H,  $J = 14.3$ , 12.6, 2.0 Hz), 2.35 (ddd, 1H, 13.5, 3.7, 2.2 Hz), 1.84-1.73 (m, 1H), 1.75 (s, 3H), 1.60 (s, 3H), 0.87 (s, 9H), 0.09 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.5, 146.7, 110.4, 77.9, 68.2, 41.1, 39.2, 33.7, 25.7, 23.0, 20.4, 18.0, -4.5, -4.9. IR ( $\text{CDCl}_3$ , cast film,  $\text{cm}^{-1}$ ): 2957, 2936, 1729. HRMS (EI,  $m/z$ ) Calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_2\text{Si}^{35}\text{Cl} [\text{M}-\text{C}_4\text{H}_9]^+$ : 259.09210. Found: 259.09199.



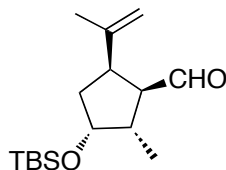
**(1*R*,2*S*,3*R*,5*R*)-Methyl 3-((*tert*-butyldimethylsilyl)oxy)-2-methyl-5-(prop-1-en-2-yl)cyclopentanecarboxylate (7)**

Sodium hydride (3.23 g, 1.50 equiv, 60 wt% in oil) was washed with pentane and then suspended in 60 ml dry methanol at 0 °C under argon. Crude TBS-protected alcohol **SI-12** (53.9 mmol) was dissolved in dry ether at 0 °C under argon, and to this solution was added the sodium methoxide/methanol solution by cannula. The reaction was left to stir at 0 °C for 1.5 h, then quenched with 30 ml NH<sub>4</sub>Cl(aq) and 10 ml water. The reaction was warmed to room temperature and stirred vigorously for 1 h. The mixture was then extracted with ether (x3) and the combined organics were washed with brine. The organics were dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. THF (100 ml) was added to help removed methanol during concentration. Crude product **7** was obtained as an orange oil and was essentially pure by <sup>1</sup>H-NMR and could be used without further purification (14.34 g, 85% yield). [ $\alpha$ ]<sub>D</sub> = –20.5 (*c* 1.00, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.78 (br s, 1H), 4.70 (br s, 1H), 4.17 (dd, 1H, *J* = 3.9, 3.9 Hz), 3.60 (s, 3H), 3.20 (ddd, 1H, *J* = 10.5, 10.5, 7.0 Hz), 2.82 (dd, 1H, *J* = 10.1, 9.3 Hz), 2.48-2.34 (m, 1H), 2.01-1.90 (m, 1H), 1.78-1.68 (m, 1H), 1.73 (s, 3H), 0.98 (d, 3H, *J* = 7.3 Hz), 0.89 (s, 9H), 0.05 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  175.2, 145.5, 111.2, 75.5, 53.3, 51.1, 46.5, 43.2, 40.1, 25.8, 22.5, 18.1, 14.3, –4.7, –5.0. IR (CDCl<sub>3</sub>, cast film, cm<sup>–1</sup>): 2956, 2931, 1738. HRMS (ESI, *m/z*) Calcd for C<sub>17</sub>H<sub>33</sub>O<sub>3</sub>Si<sup>35</sup> [M+H]<sup>+</sup>: 313.21935. Found: 313.21904.



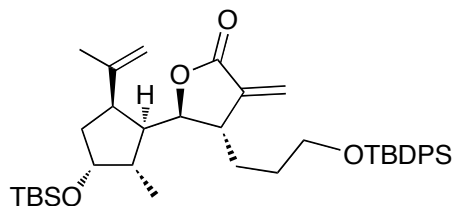
**((1R,2S,3S,5R)-3-((*tert*-Butyldimethylsilyl)oxy)-2-methyl-5-(prop-1-en-2-yl) cyclopentyl) methanol (SI-13)**

Crude ester **7** (45.9 mmol) was dissolved in 150 ml THF and cooled to 0 °C under argon. LiAlH<sub>4</sub> (1.82 g, 1.00 equiv) was added slowly to the reaction mixture. The reaction was stirred at 0 °C for 1 h, then warmed to room temperature and stirred for an additional 1 h. The reaction was quenched by slowly adding water and ethyl acetate until all the bubbling stopped. The reaction mixture was then filtered through a pad of celite and concentrated *in vacuo*. THF was used to help coevaporate the water in the mixture. This provided the crude product as a white solid that was pure enough by <sup>1</sup>H-NMR to be used without further purification (10.11 g, 77% yield). [ $\alpha$ ]<sub>D</sub> = –17.5 (*c* 1.00, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.90 (br s, 1H), 4.81 (br s, 1H), 4.12 (dd, 1H, *J* = 3.6, 3.6 Hz), 3.56 (dd, 1H, *J* = 11.6, 4.8), 3.49 (dd, 1H, *J* = 11.6, 5.9 Hz), 3.09-2.98 (m, 1H), 2.02-1.84 (m, 2H), 1.86 (s, 3H), 1.80 (dd, 1H, *J* = 11.9, 3.6 Hz), 1.66 (ddd, 1H, *J* = 12.7, 6.7, 1.3 Hz), 1.00 (d, 3H, *J* = 7.0 Hz), 0.89 (s, 9H), 0.05 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  147.9, 110.4, 75.0, 63.9, 48.3, 44.8, 42.1, 39.7, 25.8, 24.0, 18.2, 14.6, –4.6, –5.0. IR (CDCl<sub>3</sub>, cast film, cm<sup>–1</sup>): 3353, 2957, 2929. HRMS (EI, *m/z*) Calcd for C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>Si: 284.21716. Found: 284.21731.



**(1*R*,2*S*,3*R*,5*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-methyl-5-(prop-1-en-2-yl)cyclopentanecarbaldehyde (4)**

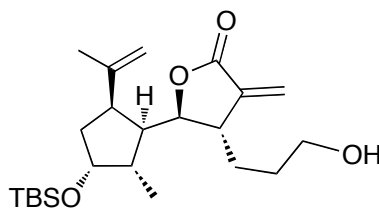
Oxalyl chloride (2.0 ml, 1.3 equiv) was dissolved in 30 ml DCM under argon at  $-78^{\circ}\text{C}$ . To this stirred solution was slowly added a solution of DMSO (2.75 ml, 2.2 equiv) in 3 ml DCM. The reaction mixture was stirred for 15 minutes, then a solution of crude alcohol **SI-13** (17.6 mmol) dissolved in 10 ml DCM was added. The reaction mixture was stirred for 15 minutes, then triethylamine (12.0 ml, 5.0 equiv) was added. The reaction was then allowed to warm to room temperature over 1 h. The reaction was quenched with water and extracted with DCM (x3). The organic layers were combined, washed with brine, dried over  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. The crude mixture was purified via flash chromatography (5% ethyl acetate in hexanes) to provide **4** as a colorless oil (4.89 g, 99% yield). There was a trace amount of a contaminant in the final product that could not be removed despite several attempts. This contaminant was not characterized and did not affect subsequent reactions.  $[\alpha]_{\text{D}} = -21.6$  ( $c$  1.00,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.53 (d, 1H,  $J = 4.0$  Hz), 4.86 (br s, 1H), 4.83 (br s, 1H), 4.19 (dd, 1H,  $J = 3.8, 3.8$  Hz), 3.31 (ddd, 1H,  $J = 10.7, 10.7, 6.9$ ), 2.62 (ddd, 1H,  $J = 10.7, 8.6, 3.9$  Hz), 2.32-2.25 (m, 1H), 1.87 (ddd, 1H,  $J = 12.8, 12.8, 3.4$  Hz), 1.80 (ddd, 1H,  $J = 12.8, 6.8, 1.0$  Hz), 1.73 (s, 3H), 0.99 (d, 3H,  $J = 6.9$  Hz), 0.90 (s, 9H), 0.07 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.2, 144.1, 111.8, 75.6, 58.1, 46.0, 40.6, 40.0, 25.9, 22.9, 18.2, 14.1,  $-4.6$ . IR ( $\text{CDCl}_3$ , cast film,  $\text{cm}^{-1}$ ): 2957, 2930, 1721. HRMS (EI,  $m/z$ ) Calcd for  $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$ : 282.20151. Found: 282.20131.



**(4*S*,5*S*)-5-((1'*R*,2'*S*,3'*R*,5'*R*)-3'-((*tert*-Butyldimethylsilyl)oxy)-2'-methyl-5'-(prop-1-en-2-yl)cyclopentyl)-4-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-3-methylenedihydrofuran-2(3*H*)-one (3)**

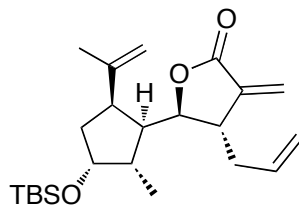
Allylboronate **5** (6.2 mmol, 1.0 equiv) and aldehyde **4** (6.2 mmol, 1.0 equiv) were dissolved in toluene under argon and cooled to  $0^{\circ}\text{C}$ . To this stirred solution was added  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (20  $\mu\text{l}$ , 0.025 equiv) and the reaction was stirred for 48 h. Crude  $^1\text{H}$ -NMR at this point showed complete consumption of *Z*-**5**, a significant amount of *E*-**5** still remaining, and a small amount of unreacted aldehyde **4**. The reaction was quenched with a solution of 9:1  $\text{NH}_4\text{Cl}(\text{aq})$ : $\text{NH}_4\text{OH}$  and extracted with ethyl acetate (x3). The organics were dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (5% ethyl acetate in hexanes) to

provide **3** as a colorless oil (3.49 g, 87% yield).  $[\alpha]_D = +1.3$  ( $c$  1.00,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69-7.62 (m, 4H), 7.47-7.34 (m, 6H), 6.22 (d, 1H,  $J = 2.6$  Hz), 5.51 (d, 1H,  $J = 2.4$  Hz), 4.92 (br s, 1H), 4.85 (br s, 1H), 4.19-4.12 (m, 2H), 3.75-3.61 (m, 2H), 3.04 (ddd, 1H,  $J = 13.7, 8.9, 6.0$  Hz), 2.77-2.67 (m, 1H), 2.07-1.88 (m, 3H), 1.77 (s, 3H), 1.73-1.54 (m, 5H), 1.06 (s, 9H), 1.01 (d, 3H,  $J = 6.8$  Hz), 0.89 (s, 9H), 0.04 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.0, 144.3, 139.6, 135.8, 134.0, 129.9, 127.9, 121.7, 112.8, 83.6, 74.8, 63.6, 50.4, 46.2, 42.8, 40.0, 38.7, 30.0, 29.6, 27.1, 26.1, 23.7, 19.5, 18.4, 17.4, -4.4, -4.8. IR ( $\text{CDCl}_3$ , cast film,  $\text{cm}^{-1}$ ): 3072, 2956, 2931, 1767. HRMS (ESI,  $m/z$ ) Calcd for  $\text{C}_{39}\text{H}_{58}\text{O}_4\text{Si}_2\text{Na}$   $[\text{M}+\text{Na}]^+$ : 669.37658. Found: 669.37507.



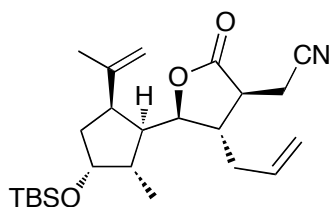
**(4*S*,5*S*)-5-((1'*R*,2'*S*,3'*R*,5'*R*)-3'-((*tert*-Butyldimethylsilyl)oxy)-2'-methyl-5'-(prop-1-en-2-yl)cyclopentyl)-4-(3-hydroxypropyl)-3-methylenedihydrofuran-2(3*H*)-one (SI-14)**

A solution of tetrabutylammonium fluoride (2.6 ml, 1.0 M solution in THF, 1.5 equiv) and glacial acetic acid (146  $\mu\text{l}$ , 1.50 equiv) was stirred in 10 ml DMF for 30 minutes under argon. This mixture was then cannulated into a solution of **3** in 10 ml DMF at room temperature. The reaction mixture was stirred and monitored by TLC (20% ethyl acetate in hexanes) until consumption of **3** was complete (typically 3 to 4 hours). The reaction was quenched with water and extracted with ether (x3). The organics were washed with water and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. The crude mixture was purified by flash chromatography (20 to 30% ethyl acetate in hexanes) to provide alcohol **SI-14** as a colorless oil (487 mg, 70% yield).  $[\alpha]_D = +14.2$  ( $c$  0.84,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.24 (d, 1H,  $J = 3.1$  Hz), 5.58 (d, 1H,  $J = 2.4$  Hz), 4.93 (br s, 1H), 4.85 (br s, 1H), 4.19 (dd, 1H,  $J = 5.3, 2.8$  Hz), 4.14 (dd, 1H,  $J = 4.8, 4.8$  Hz), 3.70-3.65 (m, 2H), 3.05 (ddd, 1H,  $J = 12.7, 9.0, 6.1$  Hz), 2.80-2.73 (m, 1H), 2.05-1.91 (m, 3H), 1.79 (s, 3H), 1.70-1.51 (m, 6H), 1.03 (d, 3H,  $J = 6.5$  Hz), 0.88 (s, 9H), 0.03 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.7, 144.1, 139.2, 121.7, 112.6, 83.4, 74.5, 62.4, 50.3, 45.9, 42.6, 39.8, 38.5, 29.8, 29.3, 25.8, 23.4, 18.1, 17.1, -4.7, -5.0. IR ( $\text{CDCl}_3$ , cast film,  $\text{cm}^{-1}$ ): 3433, 2956, 2930, 1764. HRMS (ESI,  $m/z$ ) Calcd for  $\text{C}_{23}\text{H}_{44}\text{O}_4\text{SiNa}$   $[\text{M}+\text{Na}]^+$ : 432.25881. Found: 431.25961.



**(4*S*,5*S*)-4-allyl-5-((1'*R*,2'*S*,3'*S*,5'*R*)-3'-((*tert*-Butyldimethylsilyl)oxy)-2'-methyl-5'-(prop-1-en-2-yl)cyclopentyl)-3-methylenedihydrofuran-2(3*H*)-one (9)**

Alcohol **SI-14** (1.05 g, 2.57 mmol) was dissolved in 24 ml of THF under argon at room temperature. To this was added 2-nitrophenylselenium cyanate (583 mg, 2.57 mmol) and the dark red reaction mixture was cooled down to 0 °C. Once cooled, tributylphosphine (0.63 ml, 2.57 mmol) was added to create a black solution, which was stirred at 0 °C for 3 h and eventually became a orange/brown, transparent solution. The reaction was quenched with NH<sub>4</sub>Cl(aq) and extracted with ethyl acetate (x3). The organics were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude mixture was the redissolved in 24 ml of THF, put under argon and cooled to 0 °C. Hydrogen peroxide (2.6 ml, 1.0 ml/mmol substrate) was added and the mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with saturated NaHSO<sub>3</sub> and extracted with ethyl acetate (x3). The organics were washed with water and brine, dried over MgSO<sub>4</sub>, filtered and concentrated. Flash chromatography (3-5% ethyl acetate:hexanes) provided **9** as a pale yellow oil (602 mg, 60% yield).  $[\alpha]_D = -1.1$  (*c* 0.07, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.25 (d, 1H, *J* = 3.0 Hz), 5.74 (dddd, 1H, *J* = 16.8, 10.8, 7.3, 7.3), 5.59 (d, 1H, *J* = 2.6 Hz), 5.15 (m, 1H), 5.12 (m, 1H), 4.92 (br s, 1H), 4.85 (br s, 1H), 4.19 (dd, 1H, *J* = 6.2, 2.7 Hz), 4.15 (dd, 1H, *J* = 4.6, 4.6 Hz), 3.02 (ddd, 1H, *J* = 13.8, 9.0, 5.9 Hz), 2.85-2.79 (m, 1H), 2.41-2.34 (m, 1H), 2.34-2.26 (m, 1H), 2.06-1.93 (m, 3H), 1.76 (s, 3H), 1.59 (dd, 1H, *J* = 12.7, 6.0 Hz), 1.03 (d, 3H, *J* = 6.9 Hz), 0.88 (s, 9H), 0.03 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.6, 144.0, 138.7, 134.0, 121.7, 118.3, 112.3, 82.8, 74.5, 49.6, 45.9, 42.0, 39.8, 38.3, 37.5, 25.9, 23.4, 18.2, 17.2, -4.7, -5.0. IR (CDCl<sub>3</sub>, cast film, cm<sup>-1</sup>): 2957, 2930, 1767. HRMS (EI, *m/z*) Calcd for C<sub>19</sub>H<sub>29</sub>O<sub>3</sub>Si [M-C<sub>4</sub>H<sub>9</sub>]<sup>+</sup>: 333.18860. Found: 333.18994.

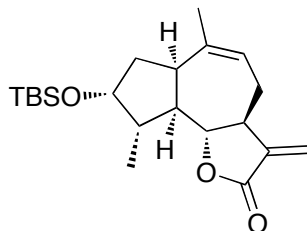


**(3*S*,4*S*,5*S*)-5-((1'*R*,2'*S*,3'*S*,5'*R*)-3'-(*t*-Butyl(dimethyl)siloxy)-2'-methyl-5'-(prop-1-en-2-yl)cyclopentyl)-5-cyanomethyl-4-(prop-2-en-1-yl)tetrahydrofuran-2-one (8)**

Obtained during the purification of **9** in an amount of 325 mg (30% yield) and was recrystallized from diethyl ether. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.83-5.73 (m, 1H), 5.24-5.21 (m, 1H), 5.20 (br s, 1H), 4.91 (br s, 1H), 4.82 (br s, 1H), 3.10-3.03 (m, 1H), 4.17 (br dd, 1H, *J* = 4.9, 4.9 Hz), 4.14 (br d, 1H, *J* = 9.1 Hz), 3.10-3.03 (m, 1H), 2.81 (dd, 1H, *J* = 17.2, 5.4 Hz), 2.76 (dd, 1H, *J* =

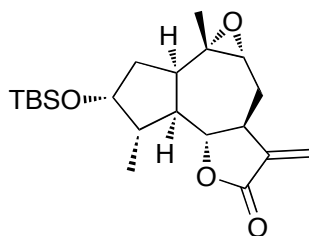


17.1, 5.0 Hz), 2.53 (ddd, 1H,  $J = 11.0, 5.1, 5.1$  Hz), 2.46-2.29 (m, 3H), 2.13-2.03 (m, 2H), 1.97 (ddd, 1H,  $J = 13.2, 13.2, 4.7$  Hz), 1.75 (s, 3H), 1.58 (dd, 1H,  $J = 12.5, 5.4$  Hz), 1.09 (d, 3H,  $J = 7.1$  Hz), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  174.9, 143.8, 133.3, 119.5, 116.7, 112.3, 82.8, 74.4, 46.9, 45.9, 42.9, 41.7, 39.6, 37.8, 34.5, 25.9, 23.5, 18.2, 17.7, 17.3, -4.6, -4.9. IR ( $\text{CDCl}_3$  cast film,  $\text{cm}^{-1}$ ): 3083, 2957, 2930, 2857, 2251, 1776. HRMS (EI,  $m/z$ ) Calcd for  $\text{C}_{20}\text{H}_{30}\text{NO}_3\text{Si}$   $[\text{M}-\text{C}_4\text{H}_9]^+$ : 360.19949. Found: 360.19935. This product was also analyzed by X-ray analysis. See Section 4 for crystallographic data.



**(3a*S*,6a*R*,8*R*,9*S*,9a*R*,9b*R*)-8-((*tert*-Butyldimethylsilyl)oxy)-6,9-dimethyl-3-methylene-3a,4,6a,7,8,9,9a,9b-octahydroazuleno[4,5-*b*]furan-2(3*H*)-one (10)**

$\gamma$ -Lactone **9** (300 mg, 0.77 mmol, 1.0 equiv) was dissolved in 150 ml DCM under argon. Grubbs second generation catalyst (32 mg, 0.038 mmol, 0.05 equiv) was added and the reaction was heated to 40 °C for 12 h. The solvent was removed and the crude mixture was purified by flash chromatography (10% ethyl acetate:hexanes) to provide **10** as a light beige solid (259 mg, 93% yield).  $[\alpha]_{\text{D}} = -42.8$  ( $c$  0.50,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.20 (d, 1H,  $J = 3.5$  Hz), 5.47 (d, 1H,  $J = 3.2$  Hz), 5.44 (br s, 1H), 4.11 (br. t, 1H,  $J = 4.4$  Hz), 3.92 (dd, 1H,  $J = 11.3, 8.9$  Hz), 3.19-3.07 (m, 1H), 2.74-2.67 (m, 1H), 2.64-2.56 (m, 1H), 2.29-2.17 (m, 1H), 2.08-2.03 (m, 1H), 2.03-1.95 (m, 1H), 1.91, (ddd, 1H,  $J = 11.2, 8.6, 5.4$  Hz), 1.78 (s, 3H), 1.54 (ddd, 1H,  $J = 12.5, 12.5, 3.9$  Hz), 1.10 (d, 3H,  $J = 7.0$  Hz), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.4, 140.3, 137.0, 120.1, 119.9, 87.3, 73.6, 52.3, 45.3, 44.7, 42.7, 42.3, 30.7, 28.5, 25.9, 18.2, 15.8, -4.6, -4.9. IR (cast film microscope,  $\text{cm}^{-1}$ ): 2957, 2930, 1771. HRMS (EI,  $m/z$ ) Calcd for  $\text{C}_{21}\text{H}_{34}\text{O}_3\text{Si}$ : 362.22772. Found: 362.22799.



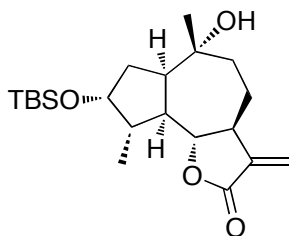
**(1*S*,2*R*,3*aR*,3*bS*,4*aR*,5*aS*,8*aR*,8*bS*)-2-((*tert*-Butyldimethylsilyl)oxy)-1,3*b*-dimethyl-6-methylenedecahydrooxireno[2',3':7,8]azuleno[4,5-*b*]furan-7(2*H*)-one (2)**

$\gamma$ -Lactone **10** (90 mg, 0.25 mmol, 1.0 equiv) was dissolved in 5 ml DCM under argon and cooled to 0 °C. *m*-CPBA (111 mg, 0.50 mmol, 2.0 equiv) was added and the reaction was stirred at 0 °C for 1 h. The reaction mixture was quenched with water and diluted with ethyl acetate. The water layer was extracted with ethyl acetate (x3), then the organics were washed with 1N NaOH (x2) and brine, dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude mixture was purified by flash chromatography (20% ethyl acetate:hexanes) to provide **2** as an inseparable mixture of diastereomers (85 mg, 90% yield). The major diastereomer was the desired one and was obtained in a ratio ranging from 3.5:1 to 4.5:1, depending on the batch.

Major diastereomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.18 (d, 1H, *J* = 3.6 Hz), 5.48 (d, 1H, *J* = 3.2 Hz), 4.23 (td, 1H, *J* = 5.8, 2.4 Hz), 3.60 (dd, 1H, *J* = 11.7, 9.3 Hz), 3.11 (dt, 1H, *J* = 13.9, 7.5 Hz), 3.06 (d, 1H, *J* = 5.0 Hz), 2.89-2.76 (m, 1H), 2.67 (ddd, 1H, *J* = 15.4, 5.0, 3.6 Hz), 2.43 (pd, 1H, *J* = 7.2, 2.5 Hz), 1.98 (dd, 1H, *J* = 8.8, 2.9 Hz), 1.96-1.73 (m, 3H), 1.35 (s, 3H), 1.02 (d, 3H, *J* = 6.8 Hz), 0.90 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

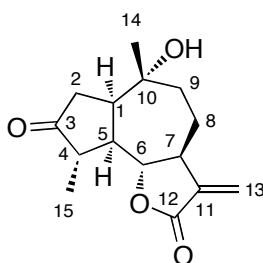
Minor diastereomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.20 (d, 1H, *J* = 3.6 Hz), 5.47 (d, 1H, *J* = 3.3 Hz), 4.42 (dd, 1H, *J* = 10.3, 8.9 Hz), 4.09-4.06 (m, 1H), 3.05 (d, 1H, *J* = 3.9), 3.01-2.93 (m, 1H), 2.89-2.76 (m, 1H), 2.57 (ddd, 1H, *J* = 15.4, 5.0, 5.0 Hz), 2.14 (dd, 1H, *J* = 16.0, 11.9 Hz), 2.09-2.02 (m, 1H), 1.96-1.73 (m, 3H), 1.29 (s, 3H), 1.09 (d, 3H, *J* = 6.8 Hz), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H).

Mixture of diastereomers: <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  169.8, 139.9, 139.6, 120.0, 119.5, 85.4, 83.5, 75.2, 72.1, 64.9, 64.7, 63.6, 62.3, 60.4, 51.8, 51.0, 45.7, 42.9, 41.9, 41.5, 40.5, 40.2, 40.1, 39.4, 29.3, 29.0, 27.2, 25.8, 25.8, 24.9, 18.1, 15.4, 14.9, 14.2, 11.9, -4.6, -4.8, -5.0. IR (microscope, cm<sup>-1</sup>): 2957, 2929, 1769. HRMS (EI, *m/z*) Calcd for C<sub>21</sub>H<sub>34</sub>O<sub>4</sub>Si: 378.22263. Found: 378.22250.



**(3a*S*,6*R*,6a*R*,8*R*,9*S*,9a*S*,9b*R*)-8-((*tert*-Butyldimethylsilyl)oxy)-6-hydroxy-6,9-dimethyl-3-methylenedecahydroazuleno[4,5-*b*]furan-2(9b*H*)-one (11)**

Epoxide **2** (30 mg, 0.08 mmol, 1.0 equiv) was dissolved in THF under argon and cooled to  $-78^{\circ}\text{C}$ . To this mixture was added DIBALH (0.19 ml, 0.28 mmol, 3.5 equiv) as a 1.5 M solution in toluene. The reaction mixture was stirred for 2 h, then  $\text{LiEt}_3\text{BH}$  (87  $\mu\text{l}$ , 87  $\mu\text{mol}$ , 1.1 equiv) was added and the reaction was allowed to warm to rt over 30 min. The reaction was quenched with a 30% solution of NaKtartrate and extracted with ethyl acetate ( $\times 4$ ). The organics were dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The crude residue was dissolved in 15 ml DCM and to this was added powdered 90%  $\text{MnO}_2$  ( $\sim 20$  equiv). The reaction was stirred overnight at rt, then filtered through celite, washed with DCM and the solvent was removed. Flash chromatography (20 to 50% ethyl acetate:hexanes) provided **11** as a colorless oil (15 mg, 50% yield).  $[\alpha]_{\text{D}} = -22.2$  ( $c$  0.48,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.19 (d, 1H,  $J = 3.5$  Hz), 5.47 (d, 1H,  $J = 3.2$  Hz), 4.11-4.04 (m, 2H), 2.88-2.77 (m, 1H), 2.25-2.12 (m, 2H), 2.00-1.87 (m, 2H), 1.87-1.81 (m, 2H), 1.78-1.68 (m, 1H), 1.51-1.39 (m, 1H), 1.19 (s, 3H), 1.11 (d, 3H,  $J = 7.2$  Hz), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.3, 140.1, 119.5, 85.9, 75.5, 75.0, 49.8, 46.4, 45.6, 41.6, 37.8, 29.8, 25.9, 25.3, 18.2, 15.0,  $-4.6$ ,  $-4.8$ . IR (microscope,  $\text{cm}^{-1}$ ): 3474, 2955, 2928, 1762. HRMS (EI,  $m/z$ ) Calcd for  $\text{C}_{17}\text{H}_{27}\text{O}_4\text{Si}$   $[\text{M}-\text{C}_4\text{H}_9]^+$ : 323.16788. Found: 323.16800.



**(3a*S*,6*R*,6a*R*,9*S*,9a*R*,9b*R*)-6-Hydroxy-6,9-dimethyl-3-methyleneoctahydroazuleno[4,5-*b*]furan-2,8(3*H*,9b*H*)-dione (1)**

To a suspension of PDC (15 mg, 1.5 equiv) in 0.5 ml DCM under argon at  $0^{\circ}\text{C}$  was added  $\text{TMSCl}$  (12  $\mu\text{l}$ , 3.5 equiv). After stirring this mixture for 5 min,  $\gamma$ -lactone **11** (10 mg, 1.0 equiv) was dissolved in 0.5 ml DCM and added to the reaction mixture. This mixture was stirred at  $0^{\circ}\text{C}$  for 4 h, then quenched by the addition of moist silica gel. The resulting suspension was filtered through a short pad of silica with DCM and ethyl acetate. Purification of the reaction mixture

was done via flash chromatography (20% ethyl acetate:hexanes) to provide pure **1** as a crystalline solid (5 mg, 71% yield).

The initial isolation<sup>4</sup> of chinensiolid B indicates that the NMR spectra were obtained using CDCl<sub>3</sub> as the solvent. However, upon consultation with the corresponding author (Professor Masayoshi Ando), it was found that the NMR spectra were actually recorded in deuterated pyridine. Upon running NMR analyses of the synthetic sample of **1** in deuterated pyridine, the spectral properties (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were identical to those provided by Professor Ando.

At this point, it was also noticed that the <sup>1</sup>H NMR data listed in the isolation paper did not match the spectrum provided by Professor Ando. The peak listed at 2.27 ppm in the <sup>1</sup>H NMR data in the paper was observed at 2.76 ppm in the actual spectrum. Also, the peak listed at 1.36 ppm was observed at 1.84 ppm in the actual spectrum. These errors must have been made in describing the chemical shifts for these two protons in the isolation paper, as the actual spectrum of natural chinensiolid B is different from that listed in the isolation paper.

After these corrections and errors are taken into account, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of synthetic **1** was identical to that of natural **1**. Other analyses (IR, HRMS and [ $\alpha$ ]<sub>D</sub><sup>20</sup>) were consistent with that reported in the original isolation paper.<sup>4</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.24 (d, 1H,  $J$  = 3.5 Hz), 5.52 (d, 1H,  $J$  = 3.1 Hz), 4.11 (dd, 1H,  $J$  = 9.9, 9.9 Hz), 3.12-3.02 (m, 1H), 2.66-2.57 (m, 2H), 2.51-2.34 (m, 3H), 2.32-2.22 (m, 1H), 1.99 (d, 1H,  $J$  = 14.5, 6.1, 6.1 Hz), 1.78 (ddd, 1H,  $J$  = 14.3, 8.3, 5.8 Hz), 1.57-1.47 (m, 1H), 1.25 (d, 3H,  $J$  = 7.2 Hz), 1.22 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  219.0, 169.7, 139.8, 120.5, 85.0, 74.2, 50.5, 48.0, 46.0, 44.3, 39.8, 39.8, 28.0, 25.3, 15.9.

<sup>1</sup>H NMR (400 MHz, Pyr-D<sub>5</sub>):  $\delta$  6.24 (d, 1H,  $J$  = 3.7 Hz), 6.22 (br s, 1H), 5.44 (d, 1H,  $J$  = 3.2 Hz), 4.12 (dd, 1H,  $J$  = 9.9 Hz), 3.09-2.96 (m, 2H), 2.79 (m, 1H), 2.54-2.44 (m, 2H), 2.34 (ddd, 1H,  $J$  = 10.0, 8.4, 8.4 Hz), 2.18-2.03 (m, 2H), 1.88-1.81 (m, 1H), 1.39-1.29 (m, 1H), 1.27 (s, 3H), 1.24 (d, 3H,  $J$  = 7.2 Hz). <sup>13</sup>C NMR (100 MHz, Pyr-D<sub>5</sub>):  $\delta$  219.7, 170.1, 141.2, 119.6, 86.0, 73.3, 50.5, 48.3, 46.4, 44.5, 40.4, 27.1, 25.8, 15.8.

IR (microscope, cm<sup>-1</sup>): 3459, 2968, 2932, 1761, 1738. HRMS (EI, m/z) Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>: 264.13617. Found: 264.13638. [ $\alpha$ ]<sub>D</sub> = +4.8 (*c* 0.12, CHCl<sub>3</sub>). Literature<sup>4</sup> = +2.6 (*c* 0.469, CHCl<sub>3</sub>).

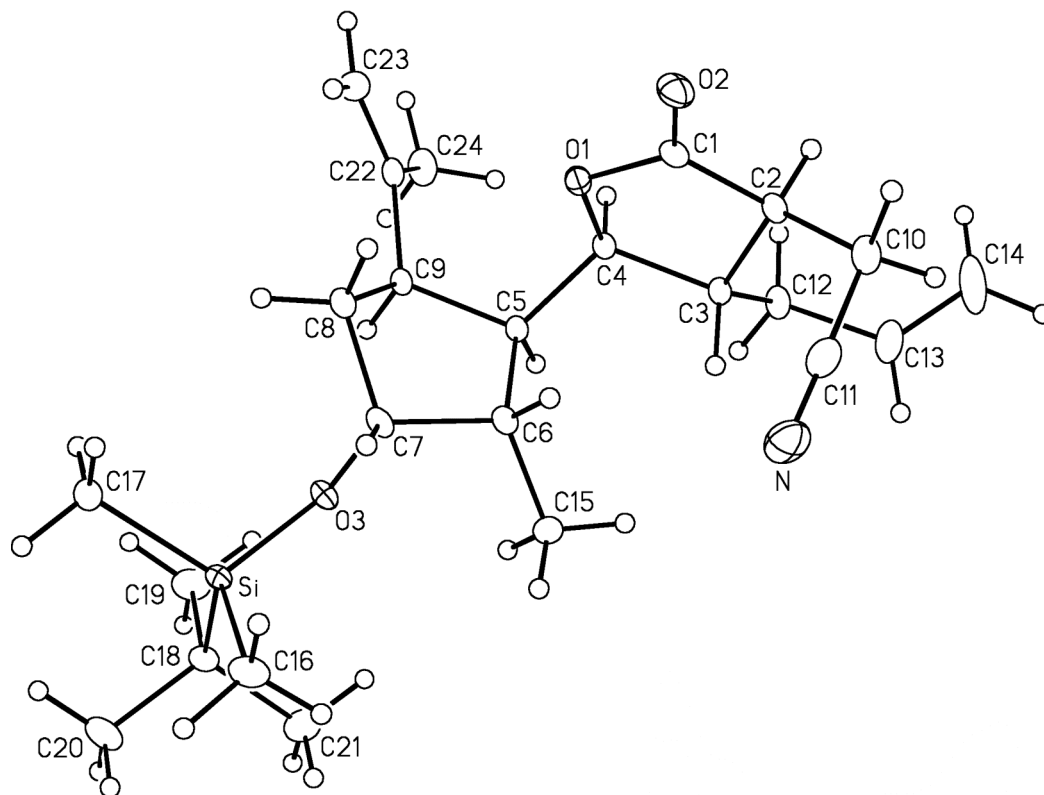
### **3) Comparison of $^{13}\text{C}$ -NMR data for 1**

Carbon	Natural product <sup>4</sup> in Pyr-D <sub>5</sub> (ppm)	Synthetic product in Pyr-D <sub>5</sub> (ppm)	Synthetic product in CDCl <sub>3</sub> (ppm)
1	46.5	46.4	46.0
2	40.3	40.4	39.8
3	219.3	219.7	219.0
4	48.3	48.3	48.0
5	50.5	50.5	50.5
6	85.8	86.0	85.0
7	44.5	44.5	44.3
8	25.9	25.8	25.3
9	40.6	-- <sup>a</sup>	39.8
10	73.1	73.3	74.2
11	141.3	141.2	139.8
12	169.9	170.1	169.7
13	119.4	119.6	120.5
14	27.3	27.1	28.0
15	15.9	15.8	15.9

<sup>a</sup> Due to conformational flexibility in the seven-member ring, the carbon peaks for C9 and C14 appear as very broad peaks. The peak for C9 in the  $^{13}\text{C}$  NMR is sometimes not observed due to overlap with the C2 peak. This issue was mentioned and discussed in the original isolation paper.<sup>4</sup>

#### 4) Crystallographic data for **8**

ORTEP diagram of crystal structure



**Table 1.** Crystallographic Experimental Details

##### A. Crystal Data

formula	C <sub>24</sub> H <sub>39</sub> NO <sub>3</sub> Si
formula weight	417.65
crystal dimensions (mm)	0.47 × 0.25 × 0.12
crystal system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> (No. 4)
unit cell parameters <sup>a</sup>	
<i>a</i> (Å)	10.9585 (4)
<i>b</i> (Å)	7.9293 (3)
<i>c</i> (Å)	15.5064 (6)
β (deg)	107.7359 (4)
<i>V</i> (Å <sup>3</sup> )	1283.36 (8)
<i>Z</i>	2
ρ <sub>calcd</sub> (g cm <sup>-3</sup> )	1.081
μ (mm <sup>-1</sup> )	0.113

### B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD <sup>b</sup>
radiation ( $\lambda$ [Å])	graphite-monochromated Mo K $\alpha$ (0.71073)
temperature (°C)	−100
scan type	$\omega$ scans (0.3°) (20 s exposures)
data collection $2\theta$ limit (deg)	55.00
total data collected	11315 ( $-14 \leq h \leq 14$ , $-10 \leq k \leq 10$ , $-20 \leq l \leq 19$ )
independent reflections	5820 ( $R_{\text{int}} = 0.0160$ )
number of observed reflections (NO)	5554 [ $F_o^2 \geq 2\sigma(F_o^2)$ ]
structure solution method	direct methods (SHELXD <sup>c</sup> )
refinement method	full-matrix least-squares on $F^2$ (SHELXL-97 <sup>d</sup> )
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9867–0.9482
data/restraints/parameters	5820 [ $F_o^2 \geq -3\sigma(F_o^2)$ ] / 0 / 263
Flack absolute structure parameter <sup>e</sup>	0.04(7)
goodness-of-fit ( $S$ ) <sup>f</sup>	1.045 [ $F_o^2 \geq -3\sigma(F_o^2)$ ]
final $R$ indices <sup>g</sup>	
$R_1$ [ $F_o^2 \geq 2\sigma(F_o^2)$ ]	0.0319
$wR_2$ [ $F_o^2 \geq -3\sigma(F_o^2)$ ]	0.0868
largest difference peak and hole	0.388 and −0.159 e Å <sup>−3</sup>

<sup>a</sup>Obtained from least-squares refinement of 9952 reflections with  $5.42^\circ < 2\theta < 54.90^\circ$ .

<sup>b</sup>Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

<sup>c</sup>Schneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, D58, 1772–1779.

<sup>d</sup>Sheldrick, G. M. *Acta Crystallogr.* **2008**, A64, 112–122.

<sup>e</sup>Flack, H. D. *Acta Crystallogr.* **1983**, A39, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, A55, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, 33, 1143–1148. Ideally, the Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration. In this case, the relatively large standard uncertainty indicates that the structural data alone should not be used to confirm absolute stereochemistry. The conformation of the model presented herein is based upon the established stereochemistry of the precursor compound (specifically the configurations of the stereogenic centers of the 3-*t*-butyl(dimethyl)siloxy)-2-methyl-5-(prop-1-en-2-yl)cyclopentyl group).

$fS = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$  ( $n$  = number of data;  $p$  = number of parameters varied;  $w = [\sigma^2(F_o^2) + (0.0570P)^2 + 0.0794P]^{-1}$  where  $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ ).

$gR_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ;  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$ .

**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}, \text{\AA}^2$
Si	-0.17321(3)	0.52206(4)	0.04847(2)	0.02365(8)*
O1	0.34611(8)	0.55436(13)	0.38211(6)	0.0317(2)*
O2	0.47670(10)	0.76824(15)	0.44097(8)	0.0418(3)*
O3	-0.07215(8)	0.46586(12)	0.14665(6)	0.0287(2)*
N	0.14210(17)	0.9668(2)	0.46920(13)	0.0605(4)*
C1	0.40153(12)	0.66359(19)	0.44880(9)	0.0301(3)*
C2	0.35633(13)	0.63258(18)	0.53070(9)	0.0281(3)*
C3	0.23970(11)	0.51706(18)	0.49444(8)	0.0256(2)*
C4	0.26391(12)	0.43460(17)	0.41129(8)	0.0251(3)*
C5	0.14563(12)	0.39474(16)	0.33250(8)	0.0235(2)*
C6	0.05835(12)	0.55107(17)	0.29753(8)	0.0290(3)*
C7	0.03885(12)	0.56094(17)	0.19503(8)	0.0286(3)*
C8	0.15888(13)	0.47833(19)	0.18460(9)	0.0320(3)*
C9	0.17337(12)	0.32347(17)	0.24605(8)	0.0265(3)*
C10	0.33532(16)	0.80013(19)	0.57389(10)	0.0378(3)*
C11	0.22748(17)	0.8951(2)	0.51583(12)	0.0419(4)*
C12	0.22169(15)	0.38815(19)	0.56324(9)	0.0337(3)*
C13	0.2031(2)	0.4701(2)	0.64526(11)	0.0487(4)*
C14	0.2859(3)	0.4598(3)	0.72698(12)	0.0747(7)*
C15	-0.06660(14)	0.5473(3)	0.32158(10)	0.0450(4)*
C16	-0.22779(14)	0.74276(18)	0.05361(12)	0.0387(3)*
C17	-0.09707(13)	0.5053(2)	-0.04333(9)	0.0393(3)*
C18	-0.31049(13)	0.36902(17)	0.02907(10)	0.0295(3)*
C19	-0.26065(16)	0.18782(19)	0.03268(13)	0.0435(4)*
C20	-0.40858(15)	0.4003(2)	-0.06451(12)	0.0456(4)*
C21	-0.37666(16)	0.3914(2)	0.10211(12)	0.0459(4)*
C22	0.29202(14)	0.2170(2)	0.25999(9)	0.0361(3)*
C23	0.39190(15)	0.2661(3)	0.23399(11)	0.0494(4)*
C24	0.28853(19)	0.0474(2)	0.30016(11)	0.0520(4)*

Anisotropically-refined atoms are marked with an asterisk (\*). The form of the anisotropic displacement parameter is:  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$ .



**Table 3.** Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Si	O3	1.6479(9)	C5	C6	1.5587(17)
Si	C16	1.8589(14)	C5	C9	1.5675(17)
Si	C17	1.8610(14)	C6	C7	1.5397(18)
Si	C18	1.8843(14)	C6	C15	1.5252(19)
O1	C1	1.3438(17)	C7	C8	1.5215(19)
O1	C4	1.4718(16)	C8	C9	1.5326(19)
O2	C1	1.2012(18)	C9	C22	1.5095(19)
O3	C7	1.4335(15)	C10	C11	1.458(2)
N	C11	1.144(2)	C12	C13	1.497(2)
C1	C2	1.517(2)	C13	C14	1.317(3)
C2	C3	1.5332(18)	C18	C19	1.532(2)
C2	C10	1.536(2)	C18	C20	1.540(2)
C3	C4	1.5391(16)	C18	C21	1.530(2)
C3	C12	1.5330(19)	C22	C23	1.335(2)
C4	C5	1.5191(16)	C22	C24	1.487(3)

**Table 4.** Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
O3	Si	C16	110.45(6)	C5	C6	C7	106.09(10)
O3	Si	C17	110.83(6)	C5	C6	C15	113.62(12)
O3	Si	C18	104.62(5)	C7	C6	C15	113.63(11)
C16	Si	C17	108.98(8)	O3	C7	C6	110.02(10)
C16	Si	C18	111.18(7)	O3	C7	C8	109.95(11)
C17	Si	C18	110.73(7)	C6	C7	C8	103.60(10)
C1	O1	C4	110.78(10)	C7	C8	C9	102.01(10)
Si	O3	C7	124.44(8)	C5	C9	C8	103.44(11)
O1	C1	O2	122.04(13)	C5	C9	C22	117.52(10)
O1	C1	C2	110.70(11)	C8	C9	C22	117.30(12)
O2	C1	C2	127.26(13)	C2	C10	C11	112.24(12)
C1	C2	C3	103.78(10)	N	C11	C10	178.59(19)
C1	C2	C10	110.81(12)	C3	C12	C13	112.43(13)
C3	C2	C10	117.23(12)	C12	C13	C14	123.9(2)
C2	C3	C4	102.94(10)	Si	C18	C19	109.86(10)
C2	C3	C12	114.38(10)	Si	C18	C20	109.92(10)
C4	C3	C12	113.03(12)	Si	C18	C21	110.03(10)
O1	C4	C3	105.14(10)	C19	C18	C20	108.92(14)
O1	C4	C5	109.82(10)	C19	C18	C21	109.01(14)
C3	C4	C5	116.08(10)	C20	C18	C21	109.06(13)
C4	C5	C6	113.40(10)	C9	C22	C23	122.92(16)
C4	C5	C9	115.00(10)	C9	C22	C24	115.76(14)
C6	C5	C9	104.33(10)	C23	C22	C24	121.23(16)

**Table 5.** Torsional Angles (deg)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C16	Si	O3	C7	-51.38(12)	C12	C3	C4	O1	-149.14(11)
C17	Si	O3	C7	69.50(12)	C12	C3	C4	C5	89.29(14)
C18	Si	O3	C7	-171.11(10)	C2	C3	C12	C13	60.50(17)
O3	Si	C18	C19	-56.30(13)	C4	C3	C12	C13	177.88(13)
O3	Si	C18	C20	-176.15(10)	O1	C4	C5	C6	-63.40(13)
O3	Si	C18	C21	63.72(11)	O1	C4	C5	C9	56.56(14)
C16	Si	C18	C19	-175.54(12)	C3	C4	C5	C6	55.65(15)
C16	Si	C18	C20	64.62(13)	C3	C4	C5	C9	175.61(11)
C16	Si	C18	C21	-55.51(13)	C4	C5	C6	C7	126.60(11)
C17	Si	C18	C19	63.15(13)	C4	C5	C6	C15	-107.86(13)
C17	Si	C18	C20	-56.69(12)	C9	C5	C6	C7	0.74(13)
C17	Si	C18	C21	-176.82(11)	C9	C5	C6	C15	126.28(12)
C4	O1	C1	O2	176.92(13)	C4	C5	C9	C8	-98.91(12)
C4	O1	C1	C2	-2.61(15)	C4	C5	C9	C22	32.11(17)
C1	O1	C4	C3	17.99(13)	C6	C5	C9	C8	25.94(12)
C1	O1	C4	C5	143.56(11)	C6	C5	C9	C22	156.96(12)
Si	O3	C7	C6	142.74(9)	C5	C6	C7	O3	90.12(12)
Si	O3	C7	C8	-103.78(11)	C5	C6	C7	C8	-27.38(13)
O1	C1	C2	C3	-13.82(15)	C15	C6	C7	O3	-35.42(17)
O1	C1	C2	C10	-140.49(12)	C15	C6	C7	C8	-152.92(13)
O2	C1	C2	C3	166.68(14)	O3	C7	C8	C9	-73.81(12)
O2	C1	C2	C10	40.01(19)	C6	C7	C8	C9	43.74(13)
C1	C2	C3	C4	23.33(13)	C7	C8	C9	C5	-43.19(12)
C1	C2	C3	C12	146.34(11)	C7	C8	C9	C22	-174.33(11)
C10	C2	C3	C4	145.84(12)	C5	C9	C22	C23	-113.14(16)
C10	C2	C3	C12	-91.14(15)	C5	C9	C22	C24	70.28(16)
C1	C2	C10	C11	67.93(16)	C8	C9	C22	C23	11.2(2)
C3	C2	C10	C11	-50.89(17)	C8	C9	C22	C24	-165.39(12)
C2	C3	C4	O1	-25.22(12)	C2	C10	C11	N	13(8)
C2	C3	C4	C5	-146.80(11)	C3	C12	C13	C14	-113.09(19)

**Table 6.** Anisotropic Displacement Parameters ( $U_{ij}$ , Å<sup>2</sup>)

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Si	0.02151(15)	0.02406(16)	0.02326(16)	0.00321(13)	0.00365(11)	0.00183(13)
O1	0.0272(4)	0.0439(6)	0.0235(4)	-0.0025(4)	0.0067(3)	-0.0050(4)
O2	0.0328(5)	0.0503(7)	0.0400(6)	0.0016(5)	0.0076(4)	-0.0128(5)
O3	0.0270(4)	0.0306(5)	0.0237(4)	0.0037(4)	0.0004(3)	-0.0017(4)
N	0.0679(10)	0.0501(9)	0.0678(10)	0.0031(8)	0.0269(9)	0.0196(8)
C1	0.0225(6)	0.0372(7)	0.0272(7)	0.0007(5)	0.0024(5)	-0.0003(5)
C2	0.0285(6)	0.0301(6)	0.0222(6)	-0.0024(5)	0.0025(5)	-0.0020(5)
C3	0.0271(5)	0.0281(5)	0.0201(5)	-0.0028(5)	0.0052(4)	-0.0005(5)
C4	0.0251(6)	0.0288(6)	0.0203(6)	-0.0007(5)	0.0053(5)	0.0005(5)
C5	0.0249(6)	0.0256(6)	0.0189(5)	0.0000(5)	0.0051(5)	-0.0001(5)
C6	0.0289(6)	0.0306(7)	0.0235(6)	-0.0009(5)	0.0021(5)	0.0042(5)
C7	0.0280(6)	0.0295(7)	0.0227(6)	0.0041(5)	-0.0004(5)	-0.0022(5)
C8	0.0294(6)	0.0434(8)	0.0216(6)	0.0050(5)	0.0053(5)	-0.0019(5)
C9	0.0273(6)	0.0321(7)	0.0182(5)	-0.0020(5)	0.0040(5)	0.0020(5)
C10	0.0469(8)	0.0329(7)	0.0331(7)	-0.0086(6)	0.0112(6)	-0.0077(6)
C11	0.0536(9)	0.0323(7)	0.0458(9)	-0.0058(7)	0.0237(8)	0.0010(7)
C12	0.0419(8)	0.0350(7)	0.0243(6)	-0.0019(6)	0.0104(6)	-0.0077(6)
C13	0.0693(11)	0.0501(10)	0.0345(8)	-0.0068(7)	0.0274(8)	-0.0183(8)
C14	0.1220(19)	0.0741(14)	0.0273(8)	-0.0092(9)	0.0215(10)	-0.0426(14)
C15	0.0335(7)	0.0681(12)	0.0329(7)	-0.0016(8)	0.0093(6)	0.0156(8)
C16	0.0342(7)	0.0240(6)	0.0530(9)	0.0041(6)	0.0062(7)	0.0045(6)
C17	0.0334(7)	0.0568(10)	0.0279(6)	0.0073(7)	0.0096(5)	0.0015(7)
C18	0.0246(6)	0.0272(6)	0.0345(7)	0.0021(5)	0.0058(5)	0.0006(5)
C19	0.0406(8)	0.0257(7)	0.0617(11)	-0.0015(7)	0.0116(8)	-0.0010(6)
C20	0.0307(7)	0.0481(9)	0.0467(9)	0.0045(8)	-0.0050(6)	-0.0068(7)
C21	0.0375(8)	0.0478(9)	0.0578(10)	-0.0014(8)	0.0227(8)	-0.0090(7)
C22	0.0353(7)	0.0490(9)	0.0198(6)	-0.0072(6)	0.0024(5)	0.0124(6)
C23	0.0346(8)	0.0721(12)	0.0398(8)	-0.0126(8)	0.0087(7)	0.0110(8)
C24	0.0664(10)	0.0505(10)	0.0348(8)	0.0023(7)	0.0090(7)	0.0247(9)

The form of the anisotropic displacement parameter is:

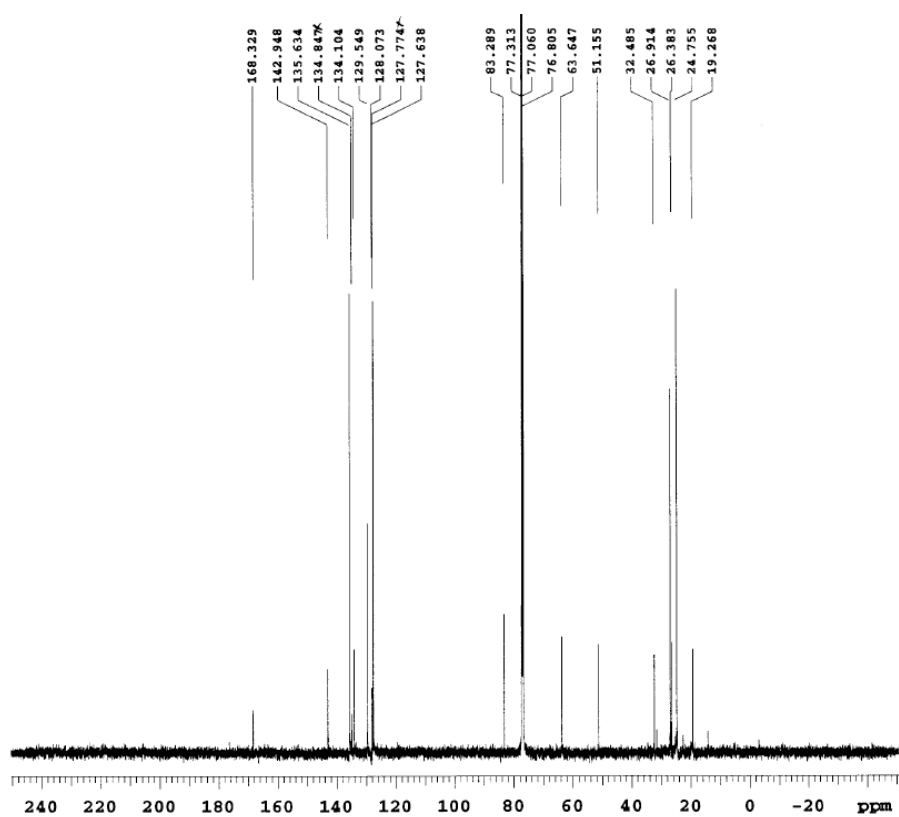
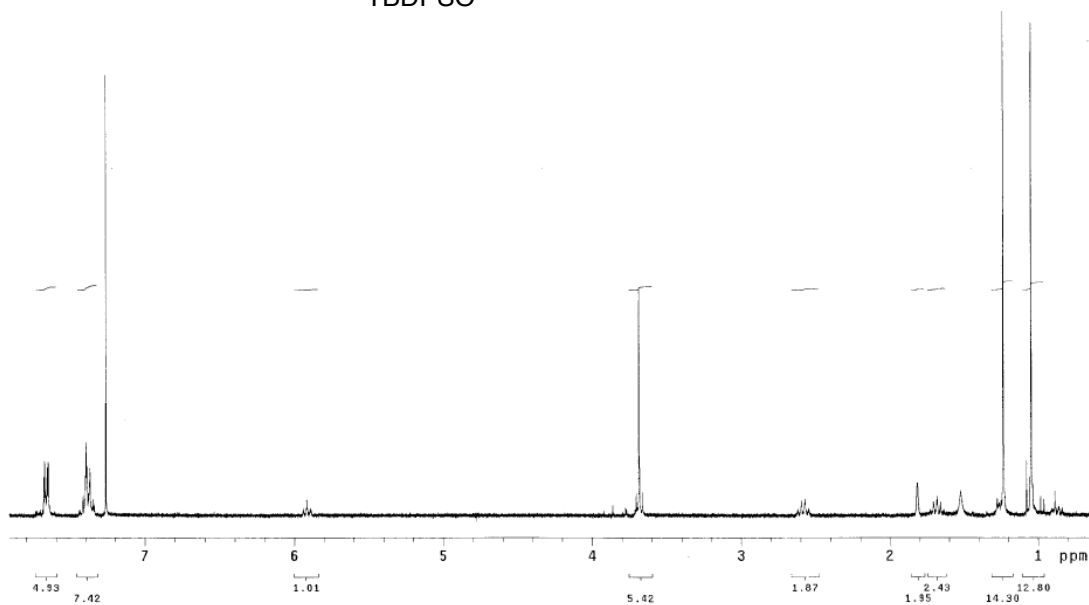
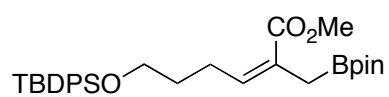
$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

**Table 7.** Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

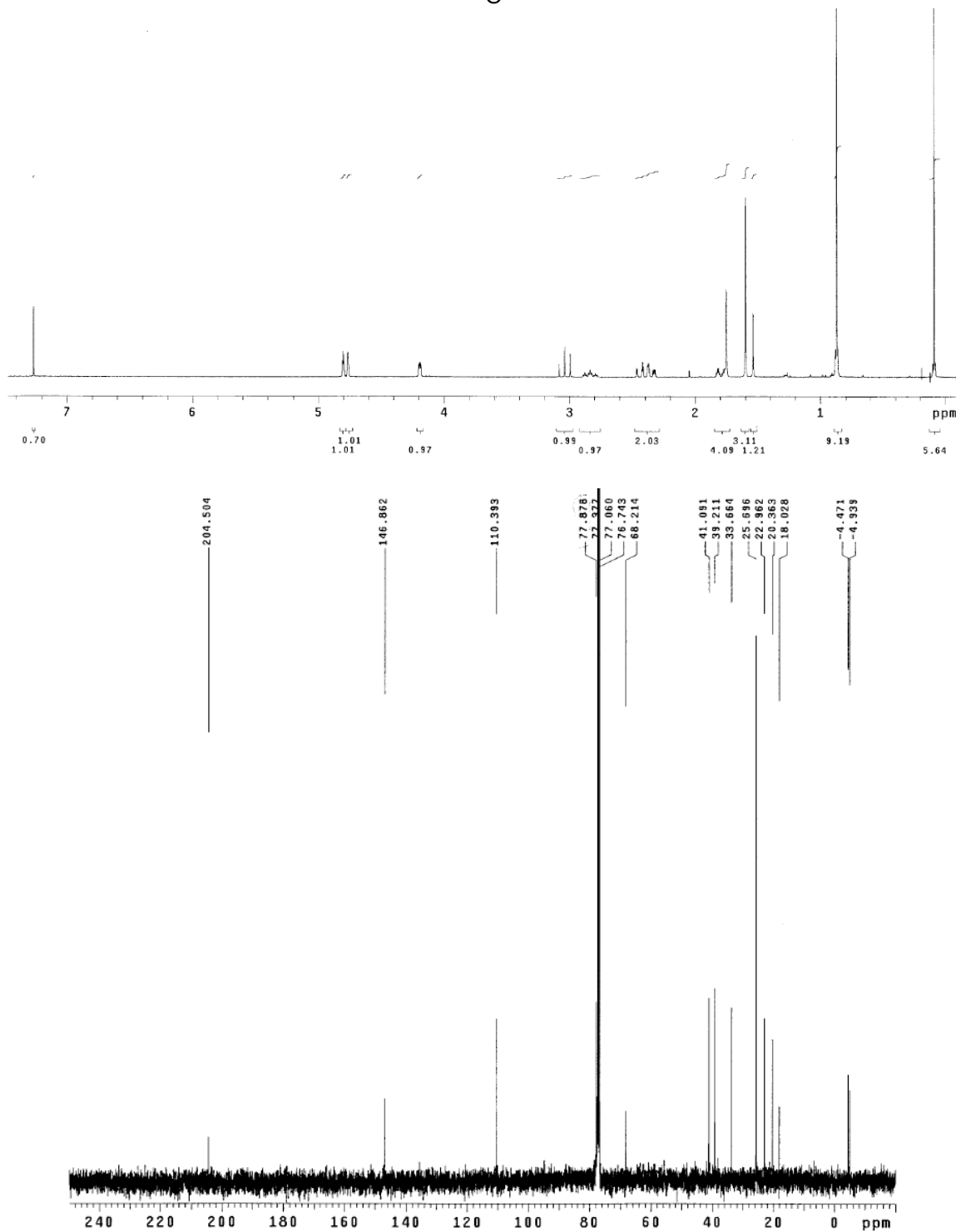
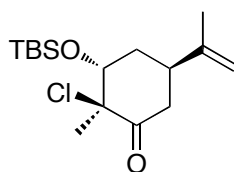
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> , Å <sup>2</sup>
H2	0.4245	0.5680	0.5764	0.034
H3	0.1609	0.5885	0.4736	0.031
H4	0.3130	0.3278	0.4310	0.030
H5	0.0942	0.3088	0.3535	0.028
H6	0.1071	0.6537	0.3262	0.035
H7	0.0317	0.6807	0.1739	0.034
H8A	0.2340	0.5540	0.2054	0.038
H8B	0.1470	0.4453	0.1210	0.038
H9	0.0994	0.2482	0.2160	0.032
H10A	0.3197	0.7768	0.6324	0.045
H10B	0.4140	0.8694	0.5864	0.045
H12A	0.1463	0.3169	0.5339	0.040
H12B	0.2978	0.3138	0.5821	0.040
H13	0.1270	0.5334	0.6380	0.058
H14A	0.3629	0.3975	0.7364	0.090
H14B	0.2686	0.5148	0.7764	0.090
H15A	-0.1166	0.6488	0.2980	0.054
H15B	-0.0475	0.5434	0.3875	0.054
H15C	-0.1160	0.4471	0.2947	0.054
H16B	-0.2652	0.7536	0.1033	0.046
H16A	-0.2924	0.7716	-0.0037	0.046
H16C	-0.1546	0.8195	0.0640	0.046
H17A	-0.0263	0.5860	-0.0322	0.047
H17B	-0.1607	0.5303	-0.1017	0.047
H17C	-0.0642	0.3906	-0.0445	0.047
H19B	-0.1993	0.1661	0.0924	0.052
H19C	-0.2182	0.1725	-0.0140	0.052
H19A	-0.3326	0.1089	0.0219	0.052
H20A	-0.4793	0.3198	-0.0743	0.055
H20B	-0.3669	0.3857	-0.1117	0.055
H20C	-0.4420	0.5155	-0.0671	0.055
H21A	-0.4477	0.3111	0.0916	0.055
H21B	-0.4098	0.5066	0.0997	0.055
H21C	-0.3149	0.3708	0.1618	0.055
H23A	0.4625	0.1923	0.2410	0.059
H23B	0.3924	0.3749	0.2085	0.059
H24A	0.3640	-0.0172	0.2986	0.062
H24B	0.2108	-0.0121	0.2653	0.062
H24C	0.2885	0.0599	0.3630	0.062

## 5) Copies of NMR spectra

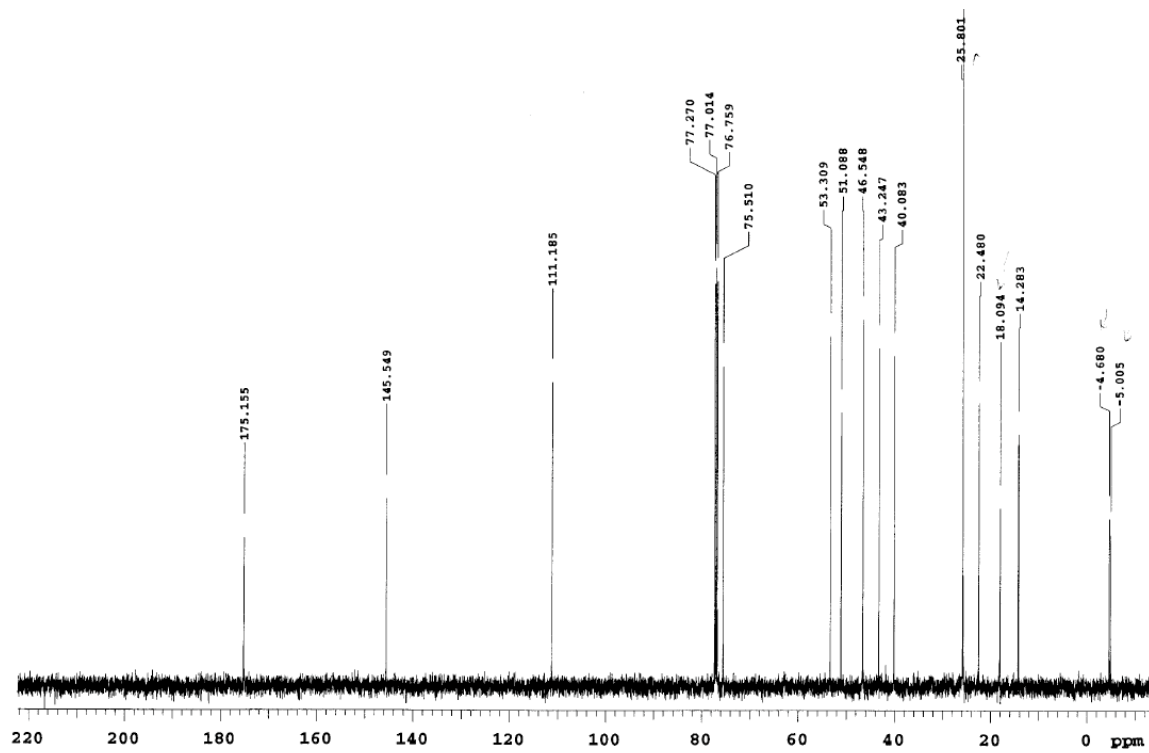
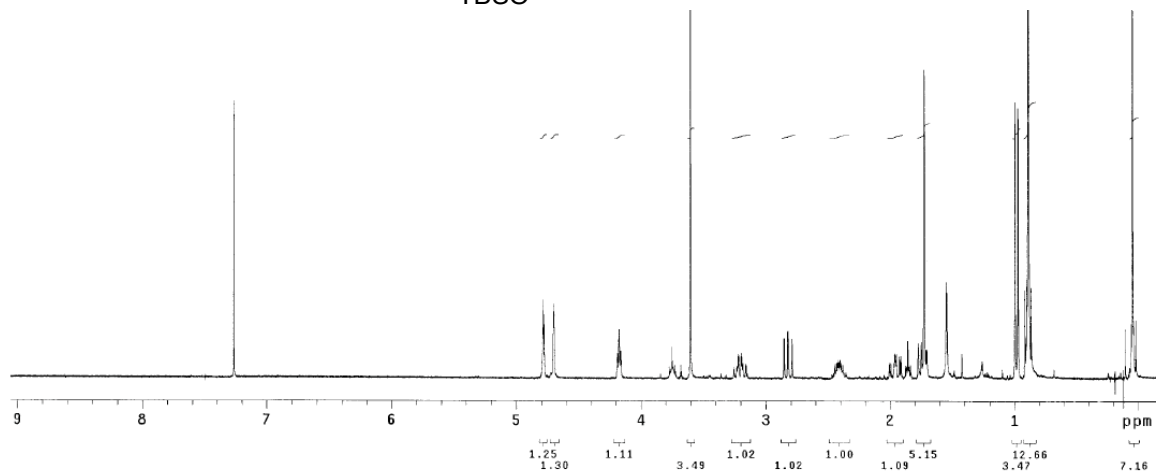
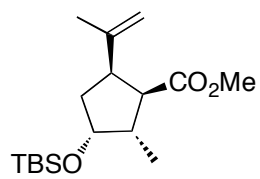
Compound **Z-5** in CDCl<sub>3</sub>



Compound **SI-12** in CDCl<sub>3</sub>

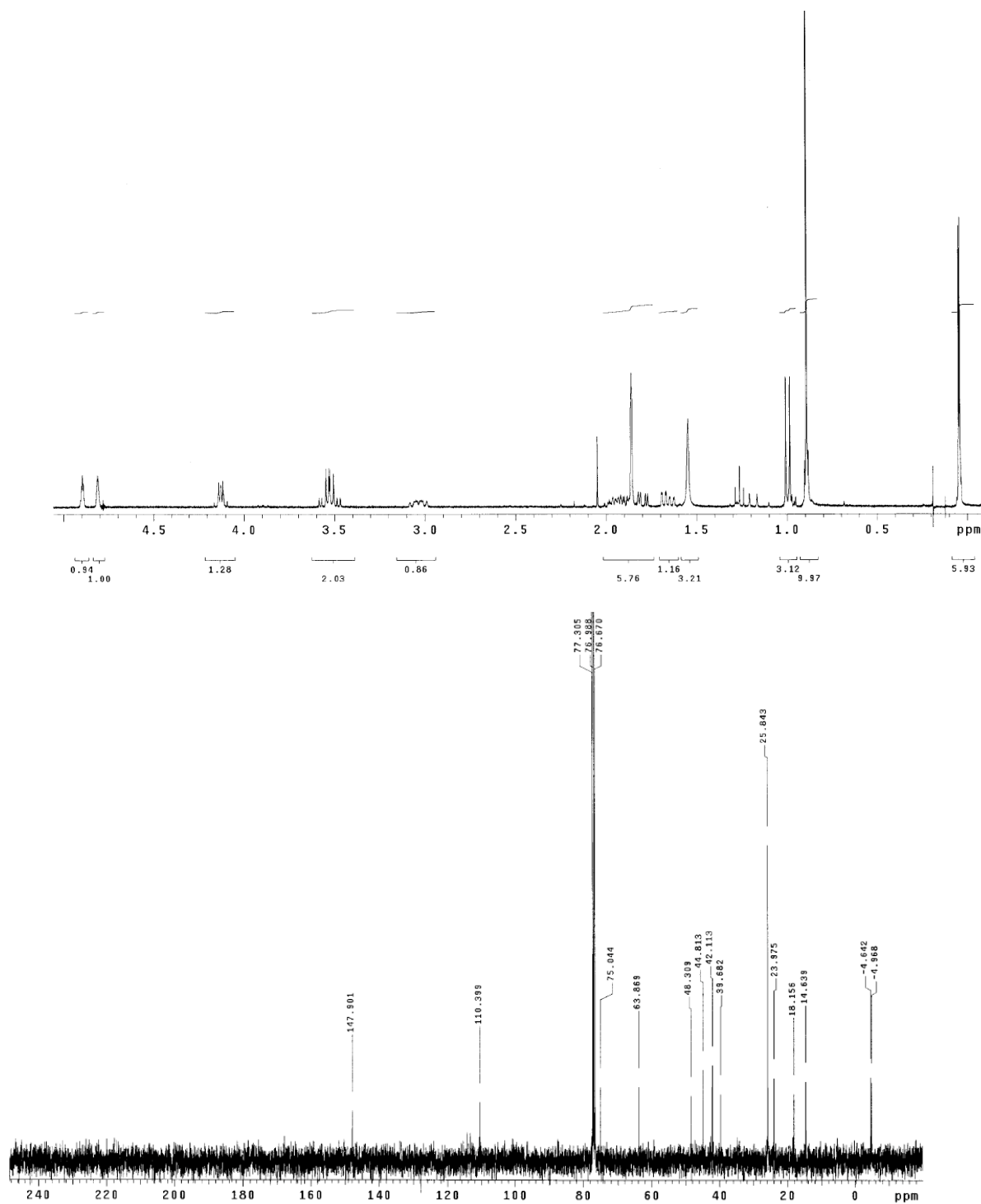
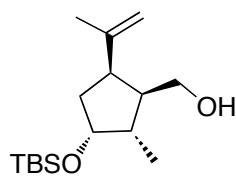


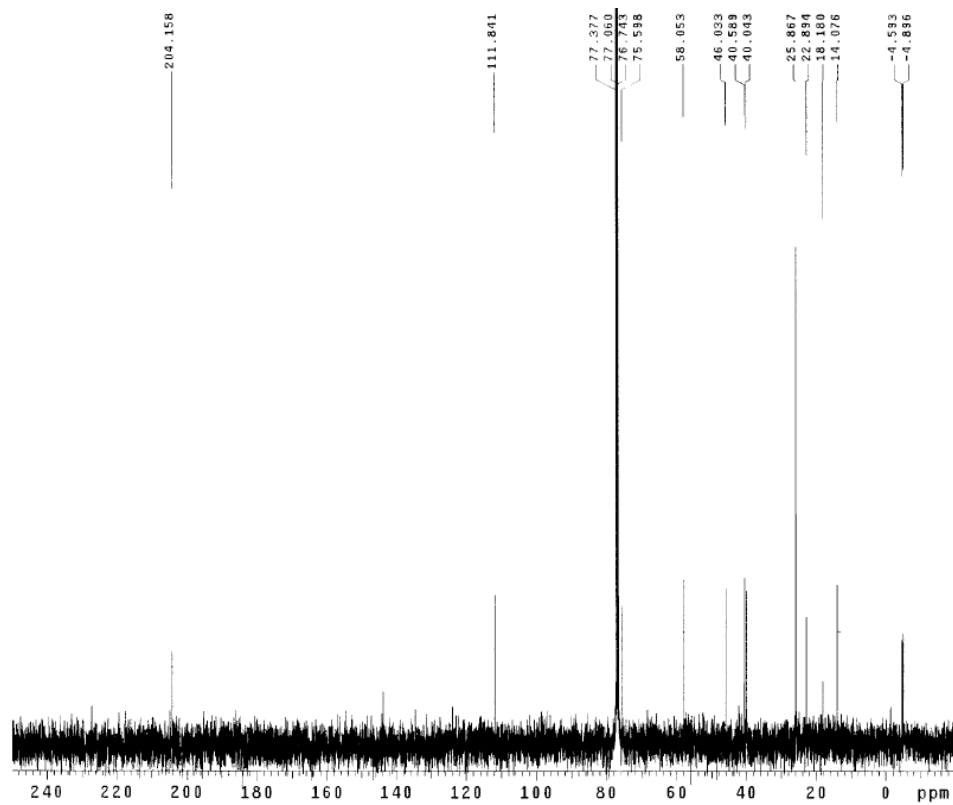
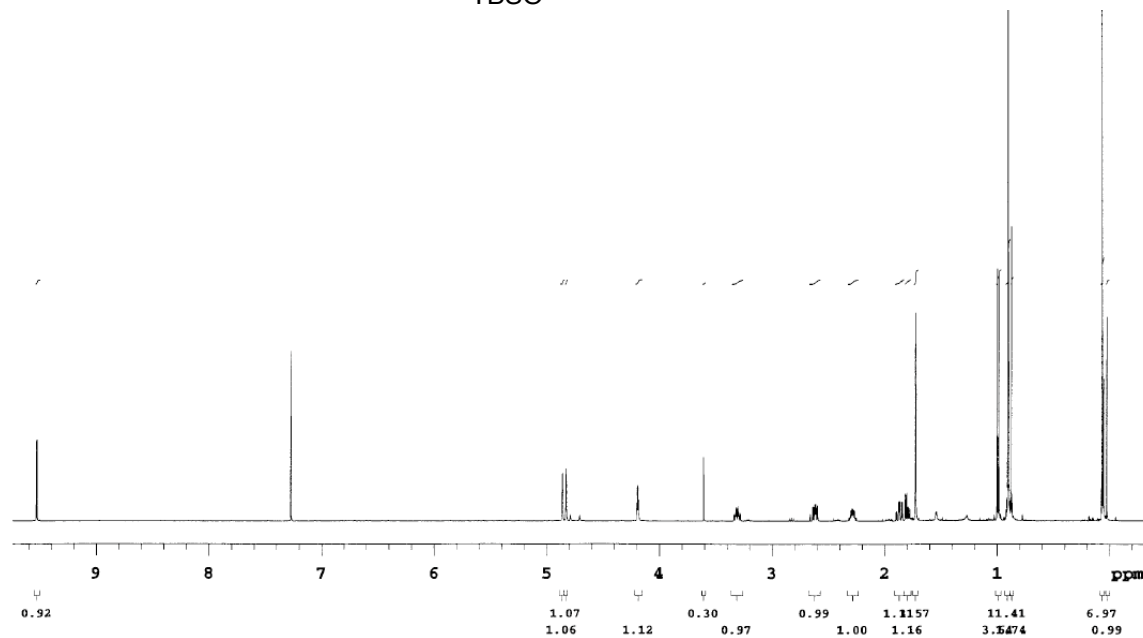
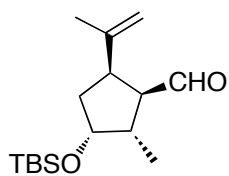
Compound **7** in CDCl<sub>3</sub>

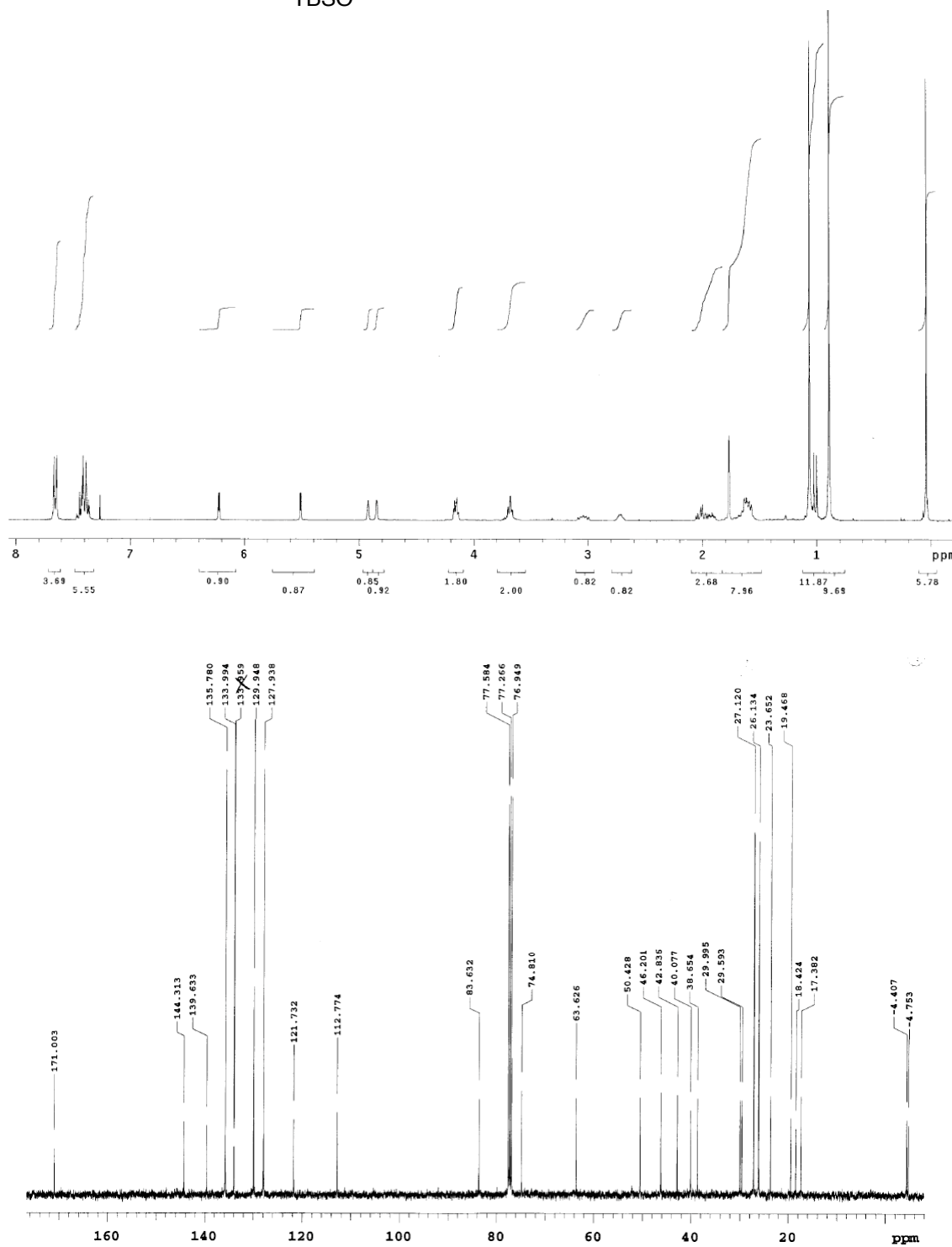
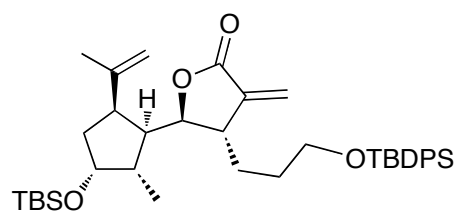


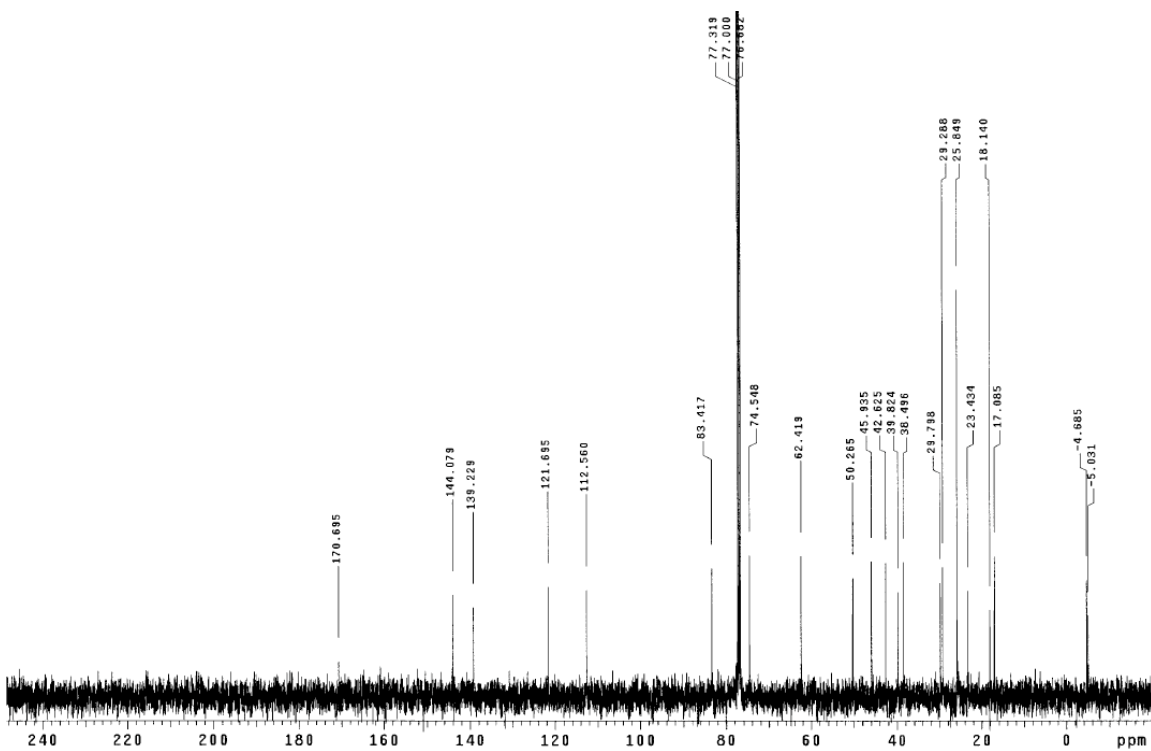
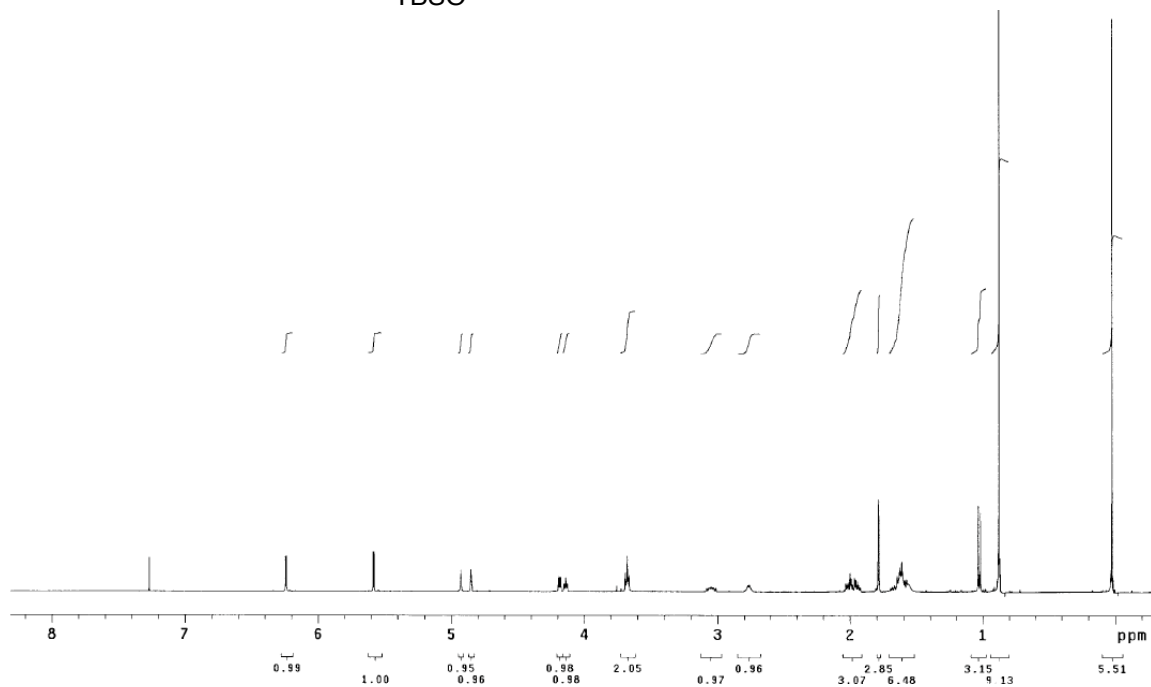
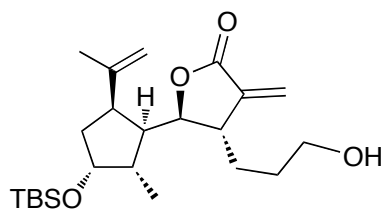


Compound **SI-13** in CDCl<sub>3</sub>

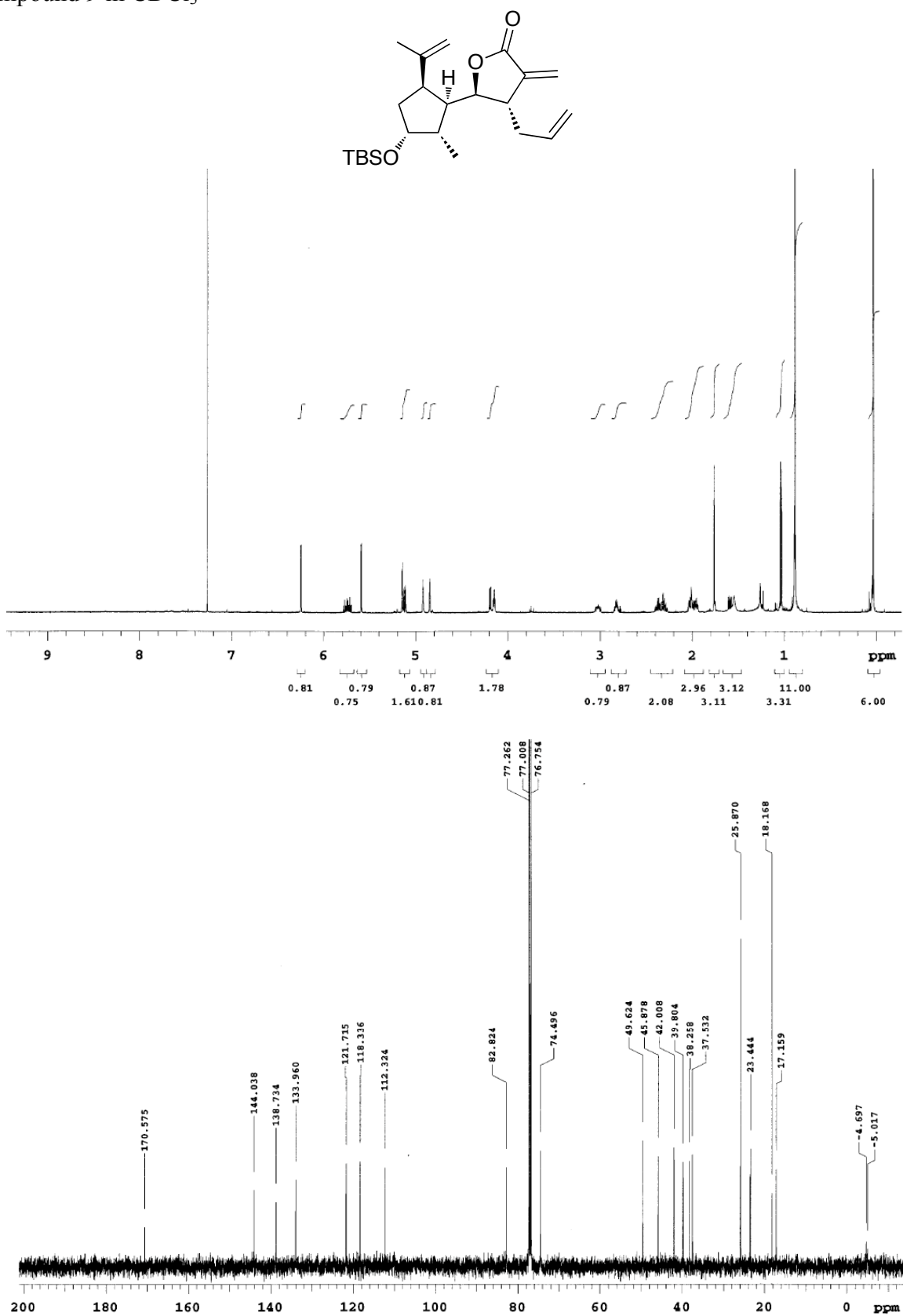


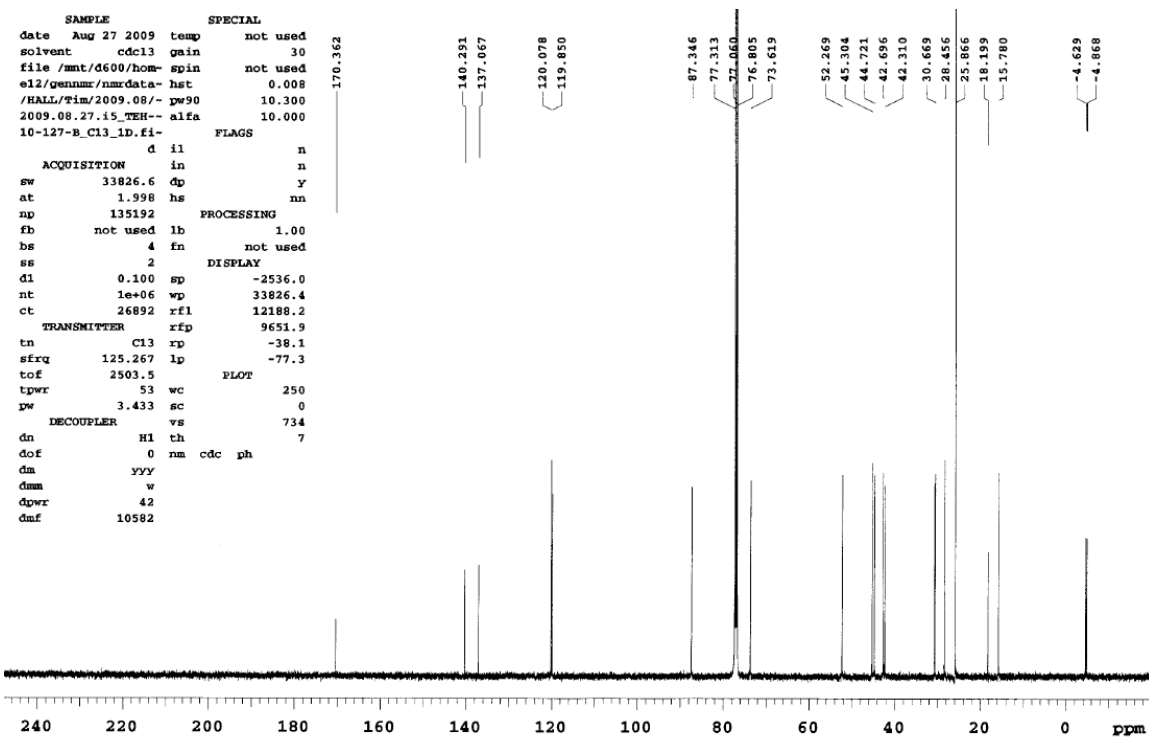
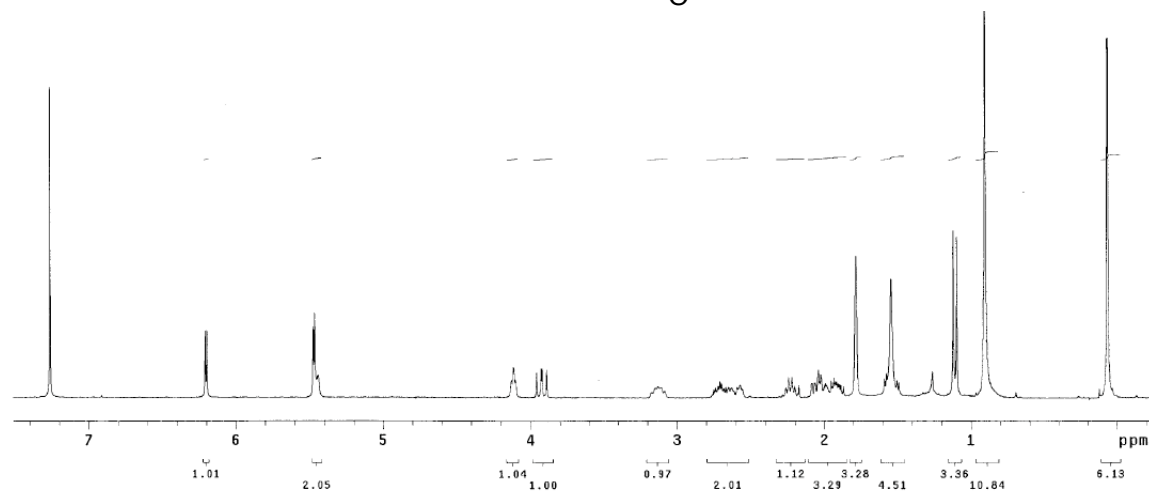
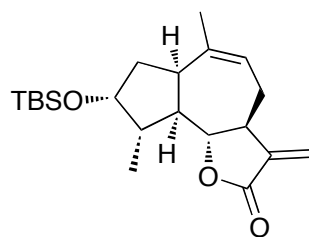
Compound **4** in CDCl<sub>3</sub>

Compound **3** in CDCl<sub>3</sub>

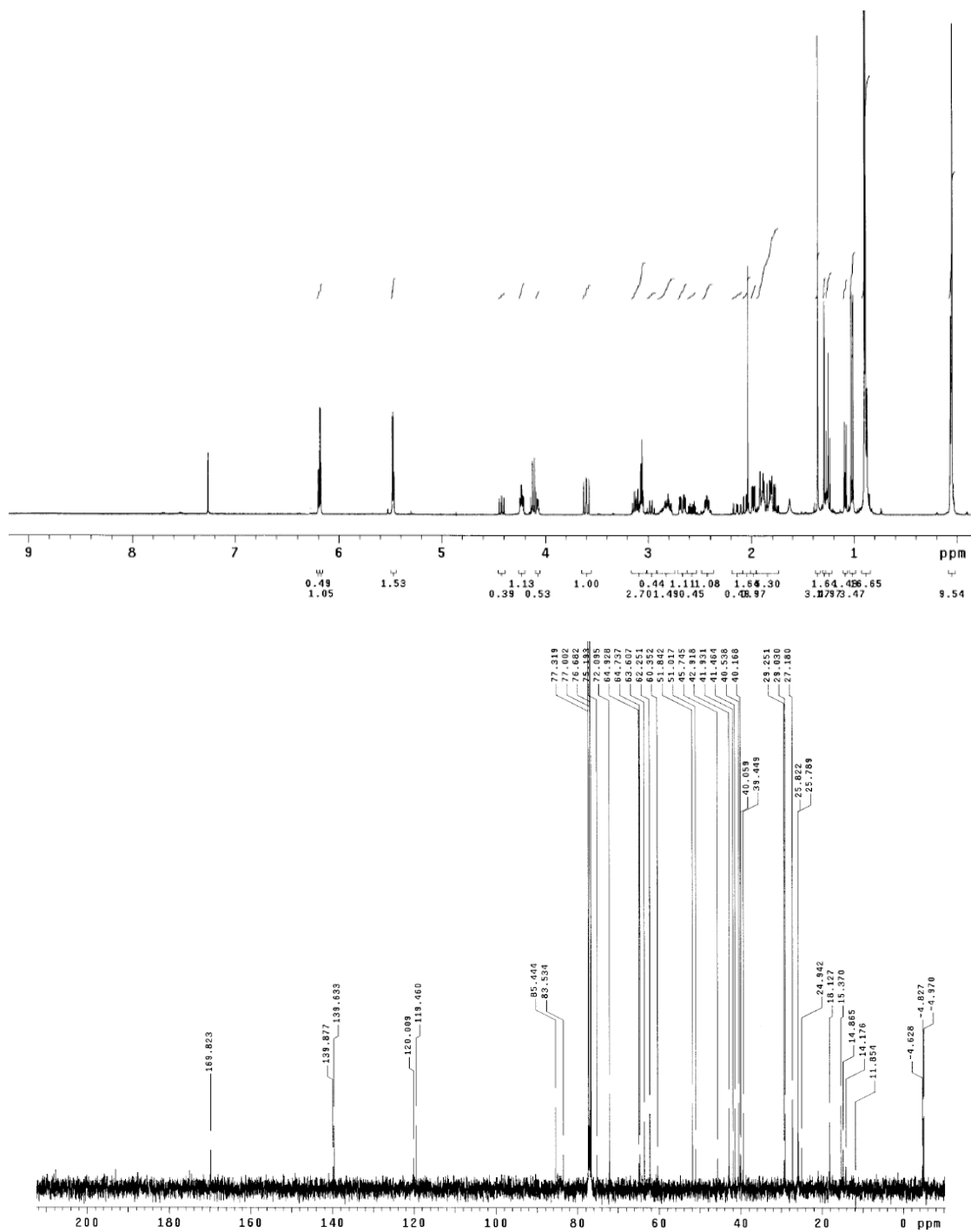
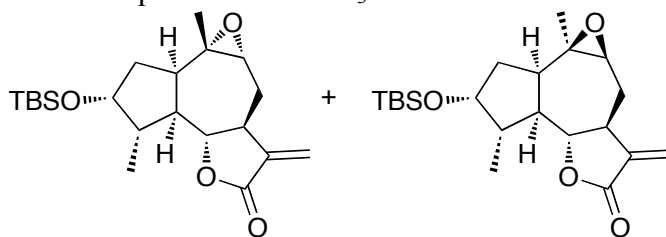
Compound **SI-14** in CDCl<sub>3</sub>

Compound **9** in CDCl<sub>3</sub>

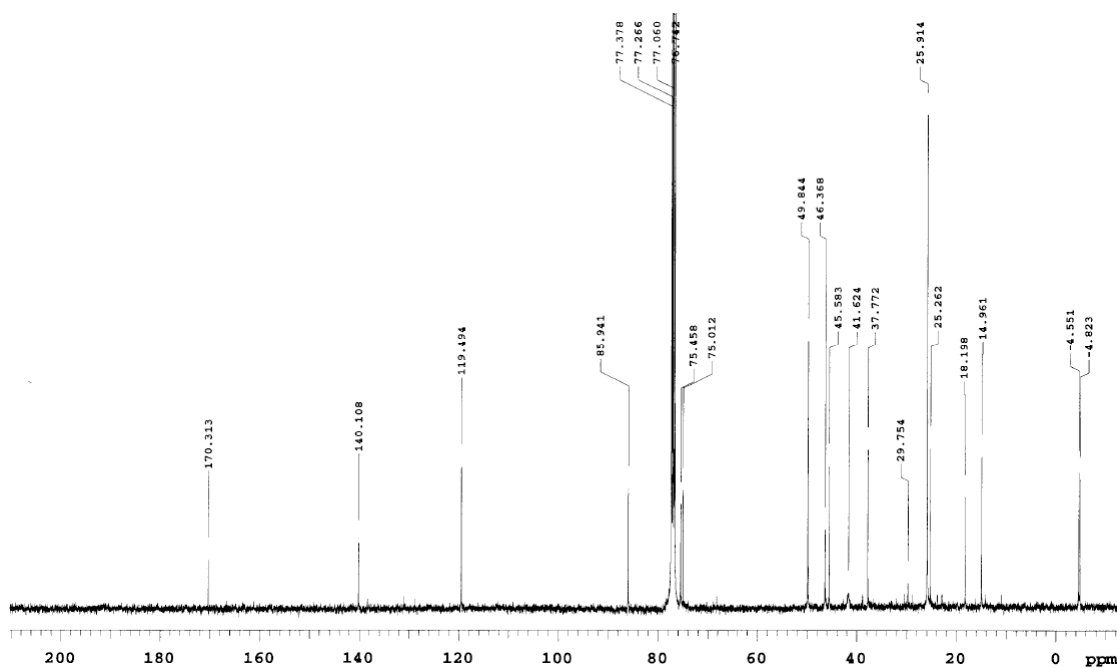
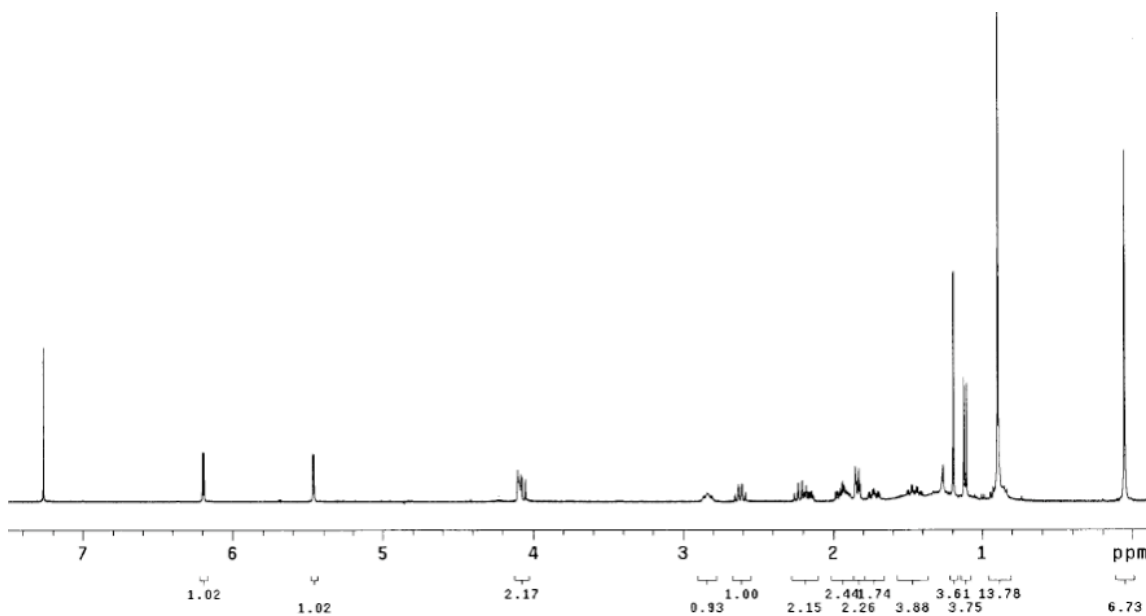
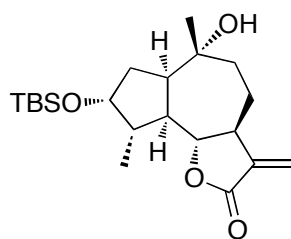


Compound **10** in CDCl<sub>3</sub>

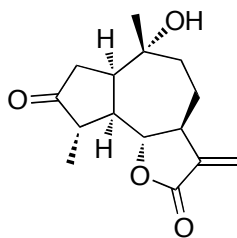
Mixture of diastereomers of compound **2** in CDCl<sub>3</sub>



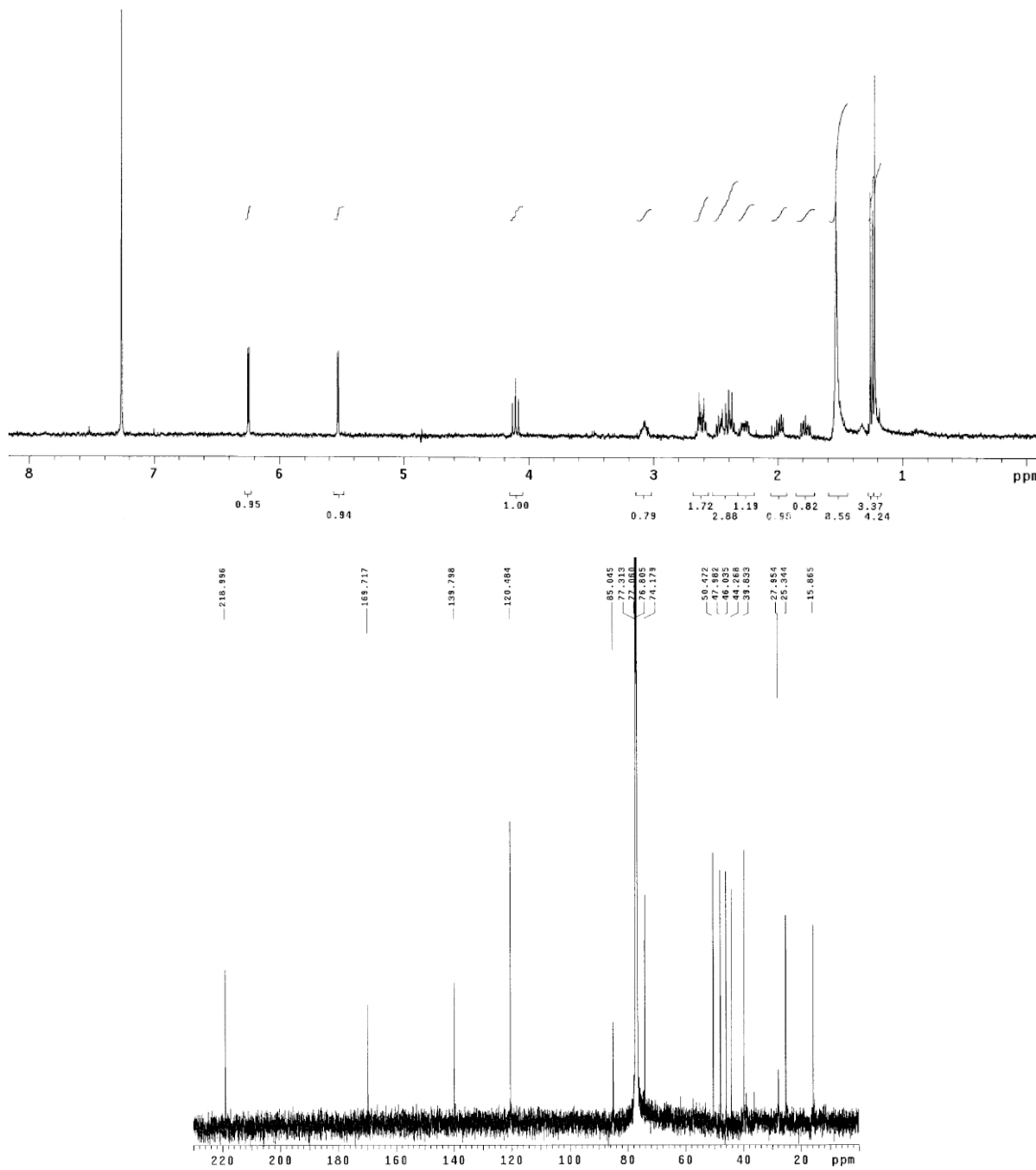
Compound **11** in CDCl<sub>3</sub>



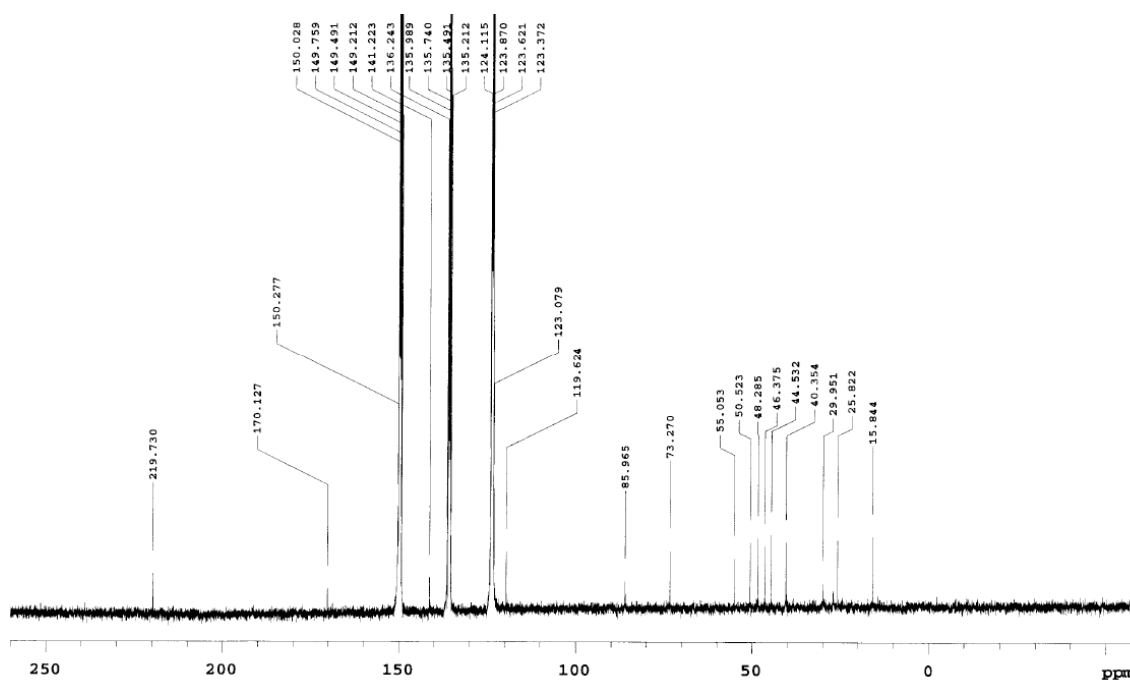
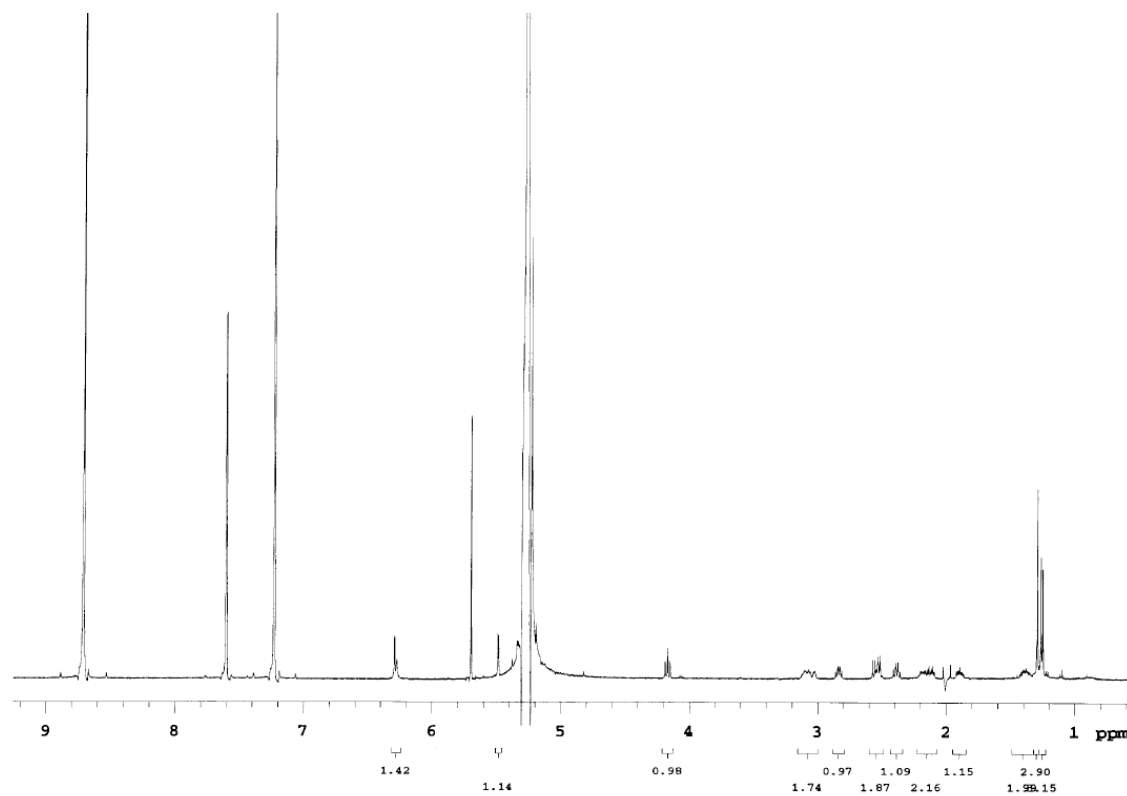


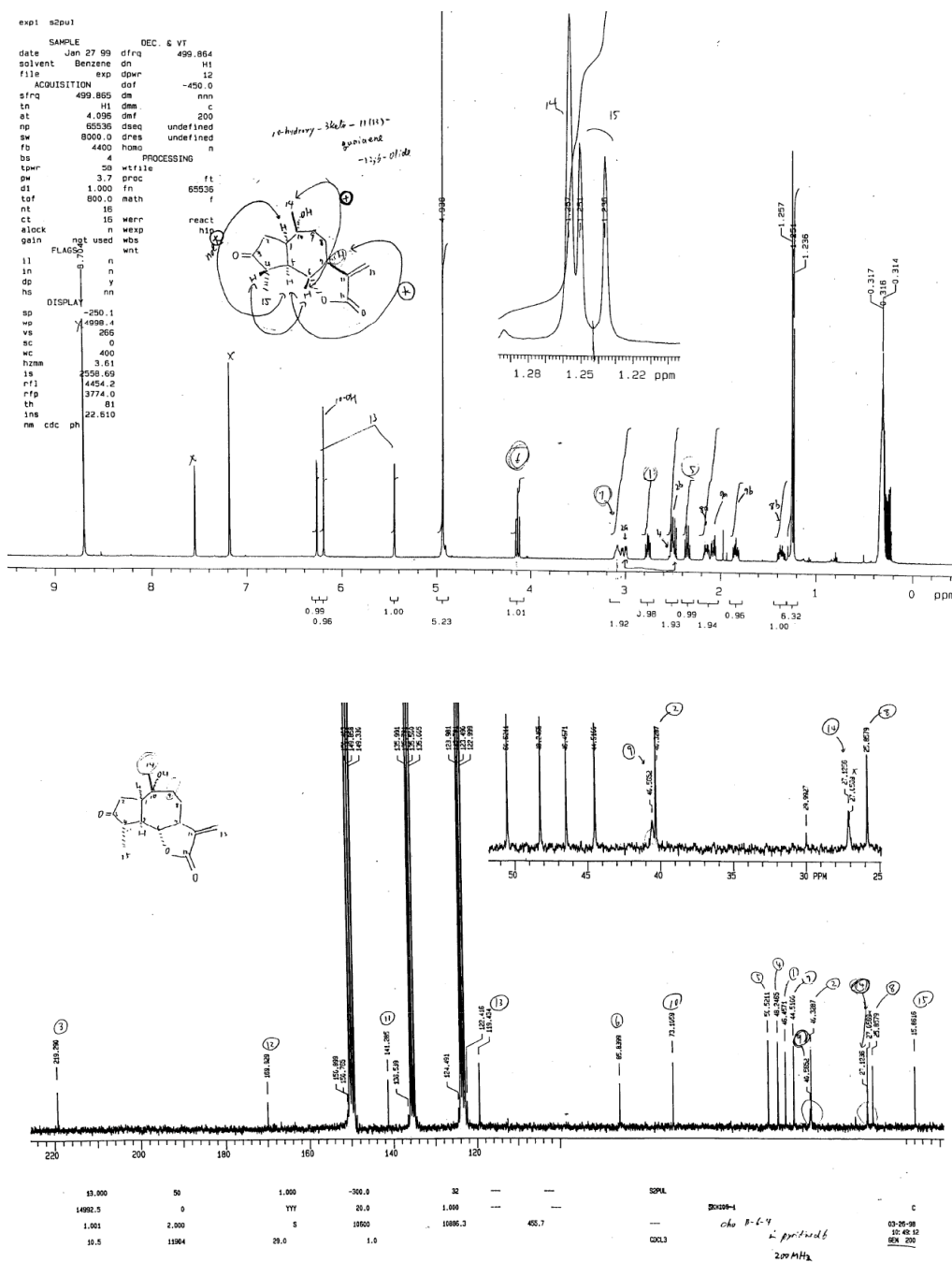


NMR spectra for synthetic **1** in CDCl<sub>3</sub>:



NMR spectra for synthetic **1** in pyridine-D<sub>5</sub>:





## 6) References

---

<sup>1</sup> Hall, D.G.; Deslongchamps, P. *J. Org. Chem.* **1995**, *60*, 7796-7814.

<sup>2</sup> Whiting, A. *Tetrahedron Lett.* **1991**, *32*, 1503-1506.

<sup>3</sup> Andrews, S.P.; Ball, M.; Wierschem, F.; Cleator, E.; Oliver, S.; Hogenauer, K.; Simic, O.; Antonello, A.; Hunger, U.; Smith, M.D.; Ley, S.V. *Chem. Eur. J.* **2007**, *13*, 5688-5712.

<sup>4</sup> Zhang, S.; Wang, J.; Xue, H.; Deng, Q.; Xing, F.; Ando, M. *J. Nat. Prod.* **2002**, *65*, 1927-1929.

### Full authorship for reference 3:

Zhang, S.; Zhao, M.; Bai, L.; Hasegawa, T.; Wang, J.; Wang, L.; Xue, H.; Deng, Q.; Xing, F.; Bai, Y.; Sakai, J.; Bai, J.; Koyanagi, R.; Tsukumo, Y.; Kataoka, T.; Nagai, K.; Hirose, K.; Ando, M. *J. Nat. Prod.* **2006**, *69*, 1425-1428.