

## Supporting Information

# The unprecedented iridal lactone and adducts of spiroiridal and isoflavonoid from *Belamcanda chinensis*

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**Figure S1. The UV spectrum of belamcandinin A (1)**

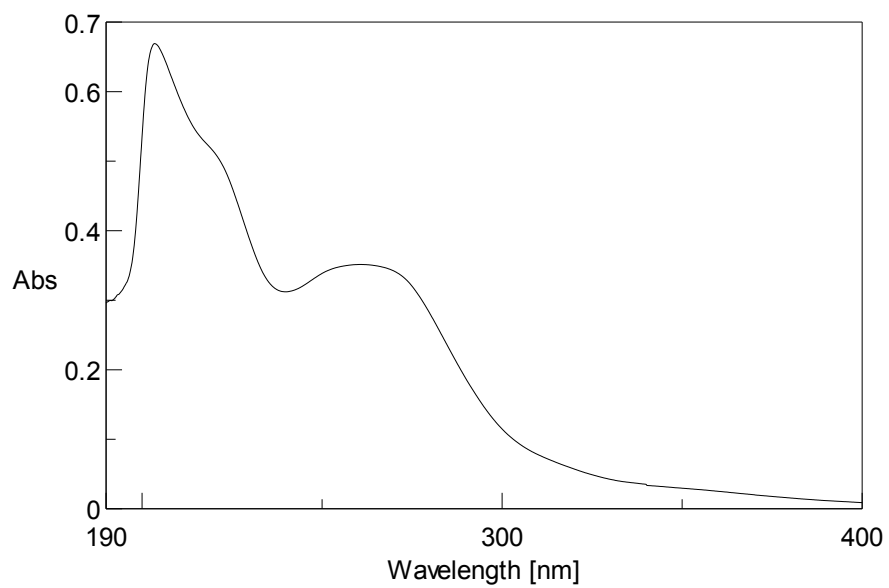
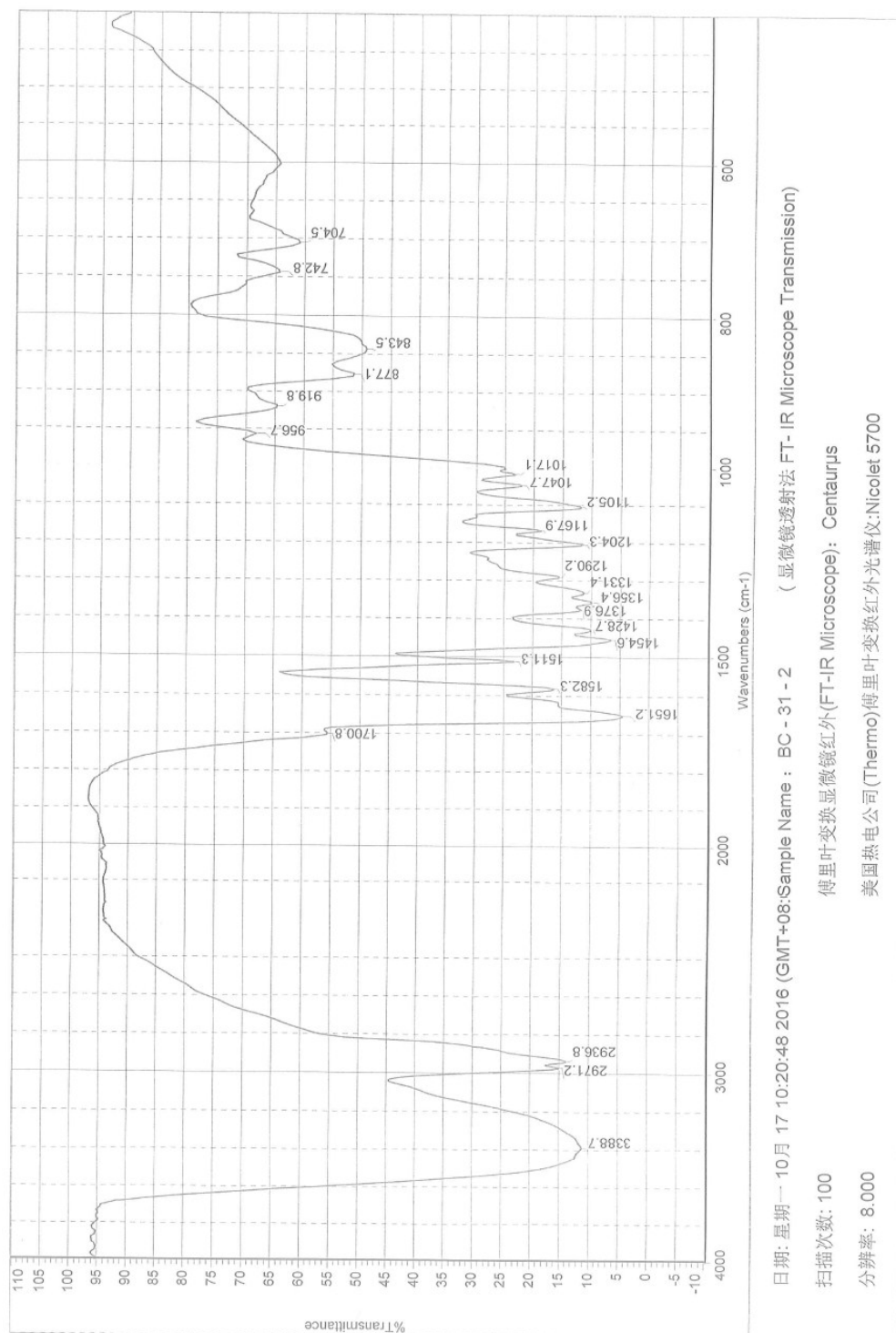
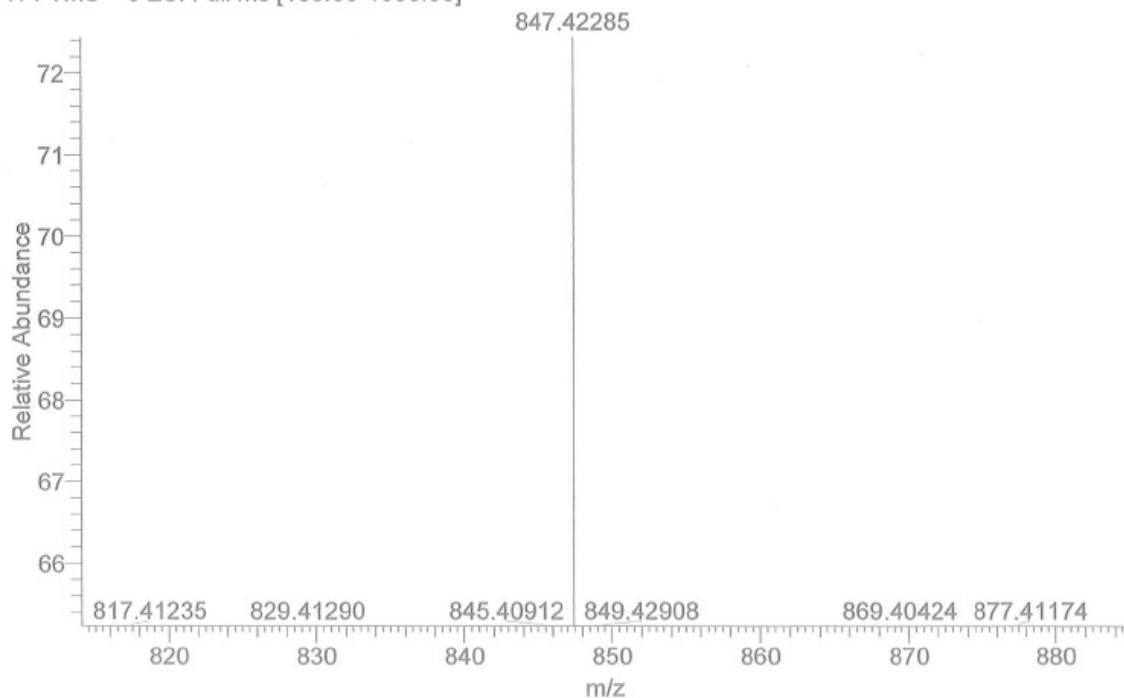


Figure S2. The IR spectrum of belamcandanin A (1)



**Figure S3. The HRESI spectrum of belamcandanin A (1)**

BC-31-2 #1997 RT: 5.27 AV: 1 NL: 1.62E7  
 T: FTMS + c ESI Full ms [100.00-1000.00]



Elemental composition search on mass 847.42

m/z= 842.42-852.42

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
847.42285	847.42045	2.84	26.5	C <sub>55</sub> H <sub>59</sub> O <sub>8</sub>
	847.42632	-4.09	17.5	C <sub>48</sub> H <sub>63</sub> O <sub>13</sub>
	847.43219	-11.02	8.5	C <sub>41</sub> H <sub>67</sub> O <sub>18</sub>
	847.41106	13.91	13.5	C <sub>44</sub> H <sub>63</sub> O <sub>16</sub>
	847.43570	-15.17	30.5	C <sub>59</sub> H <sub>59</sub> O <sub>5</sub>
	847.40519	20.84	22.5	C <sub>51</sub> H <sub>59</sub> O <sub>11</sub>
	847.44157	-22.10	21.5	C <sub>52</sub> H <sub>63</sub> O <sub>10</sub>
	847.39932	27.77	31.5	C <sub>58</sub> H <sub>55</sub> O <sub>6</sub>
	847.44745	-29.03	12.5	C <sub>45</sub> H <sub>67</sub> O <sub>15</sub>
	847.39581	31.91	9.5	C <sub>40</sub> H <sub>63</sub> O <sub>19</sub>

Figure S4. The  $^1\text{H}$  NMR spectrum of belamcandinin A (1)

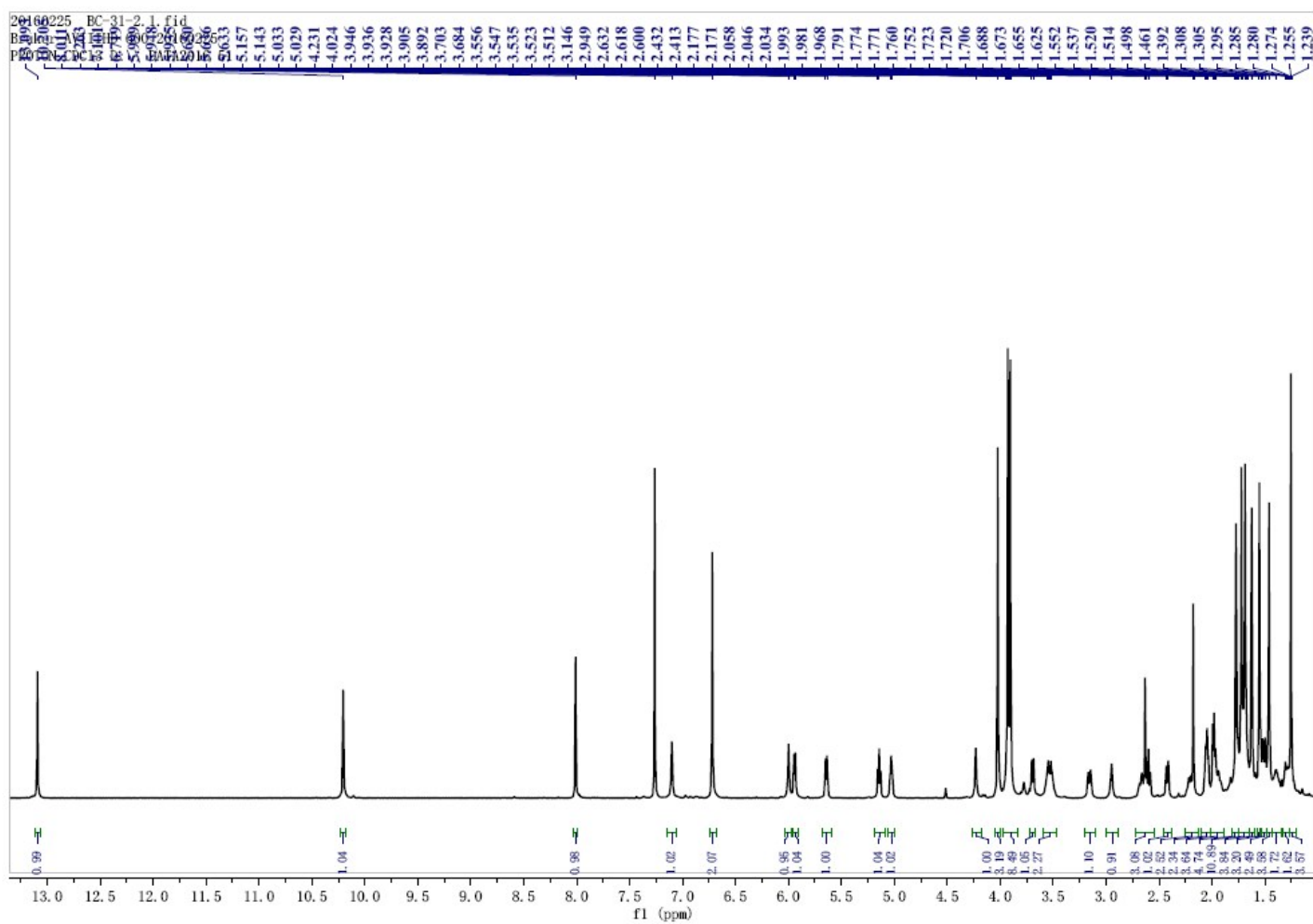


Figure S5. The  $^{13}\text{C}$  NMR spectrum of belamcandanin A (1)

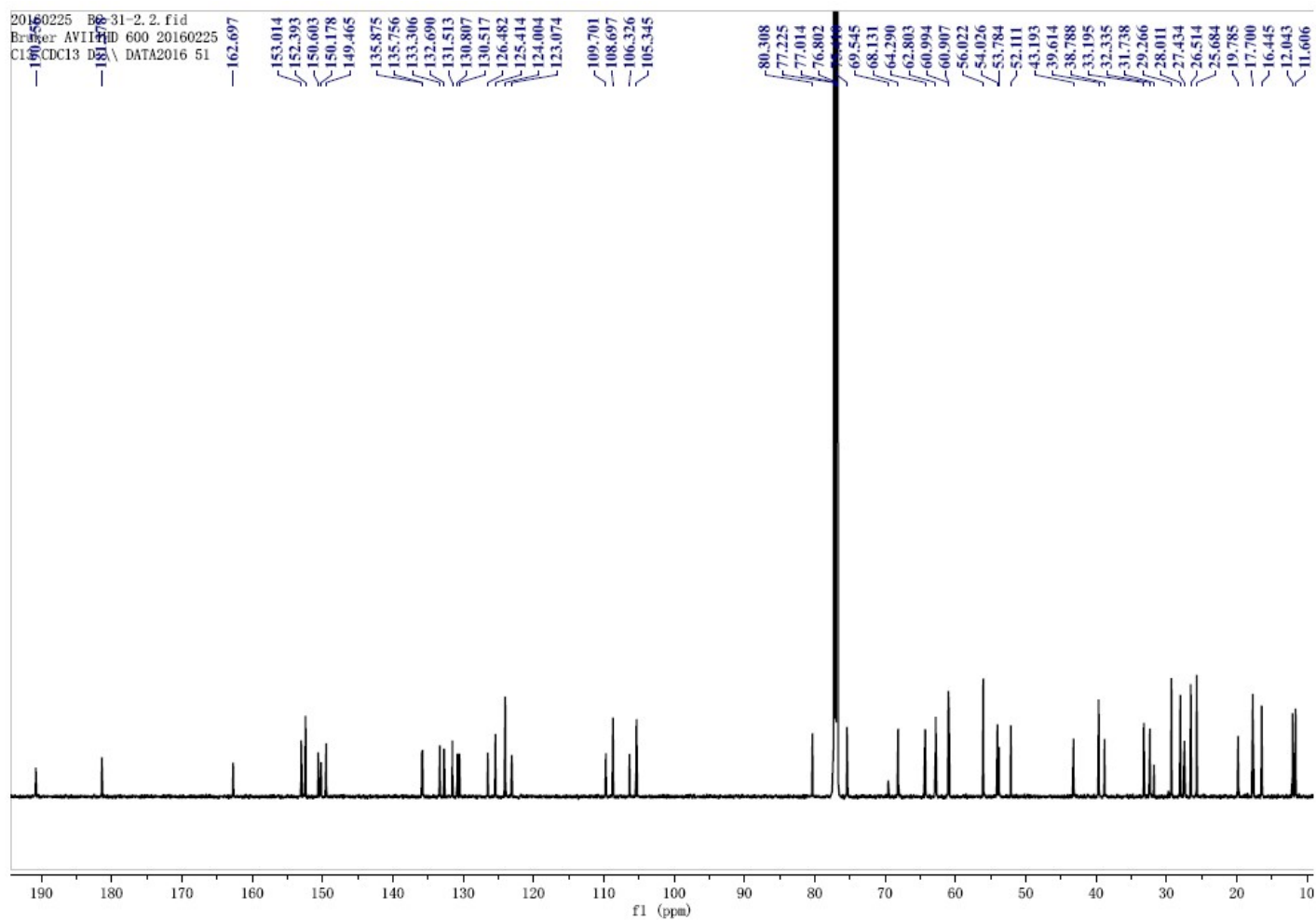




Figure S6. The DEPT spectrum of belamcandanin A (1)

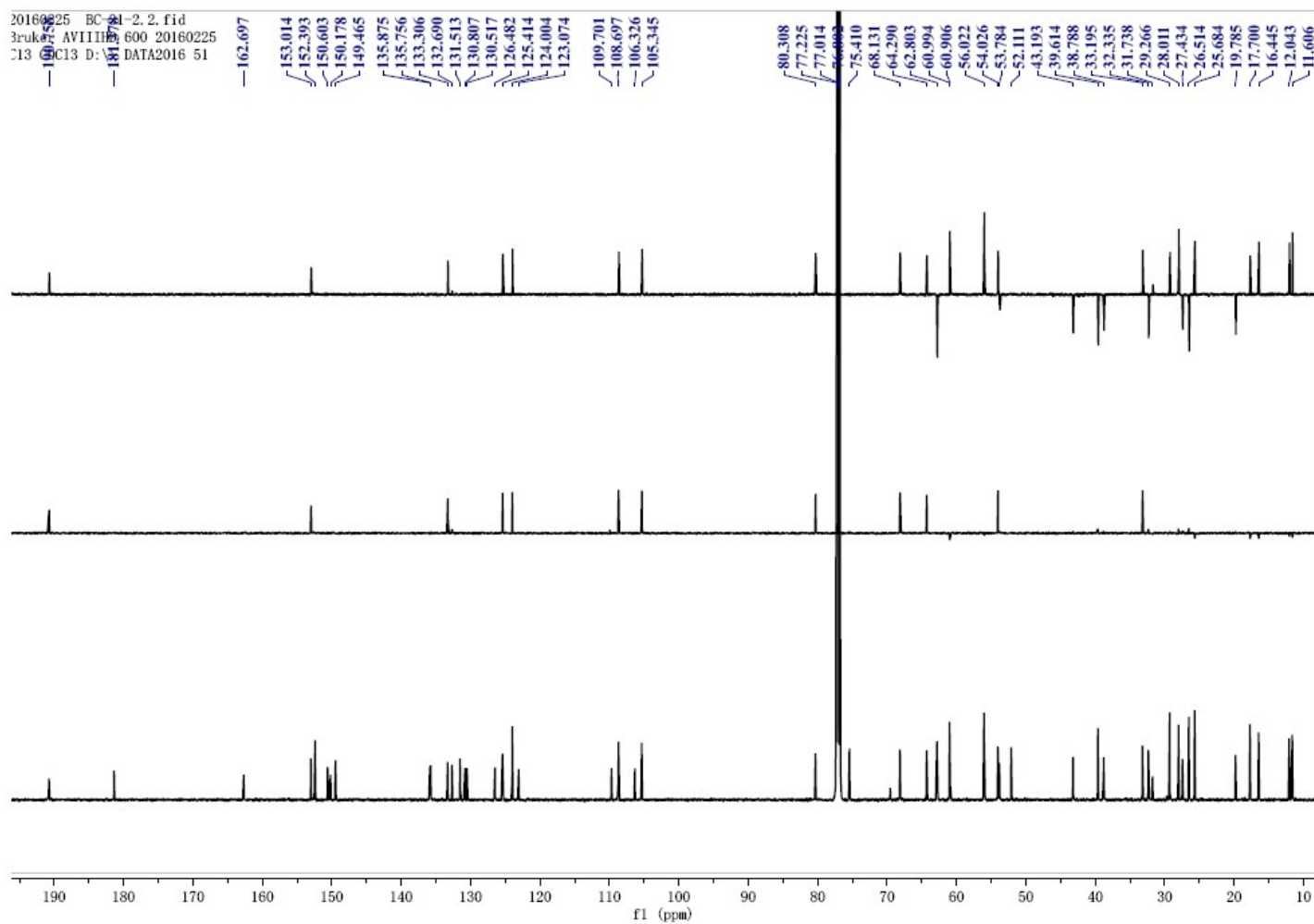
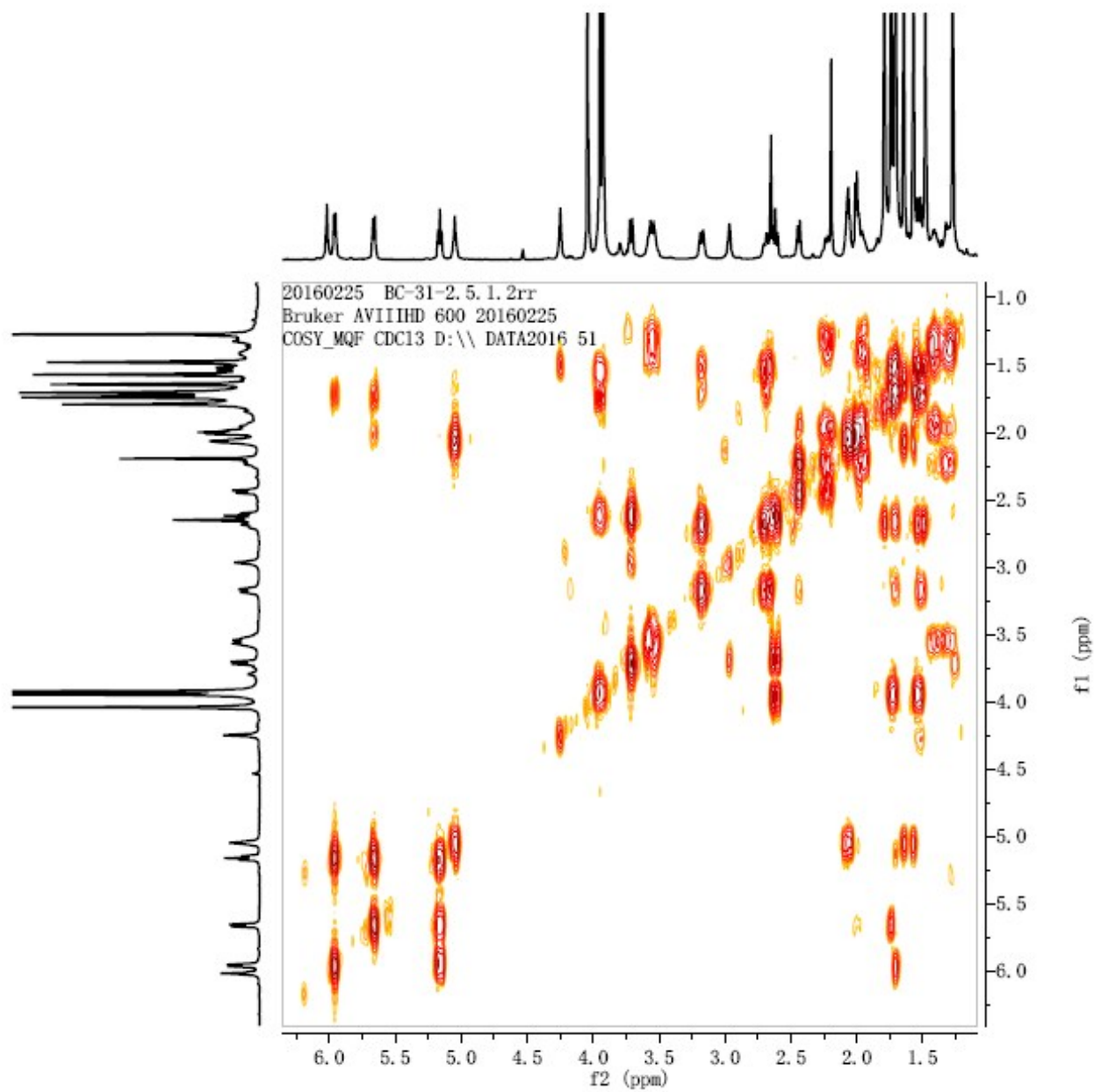
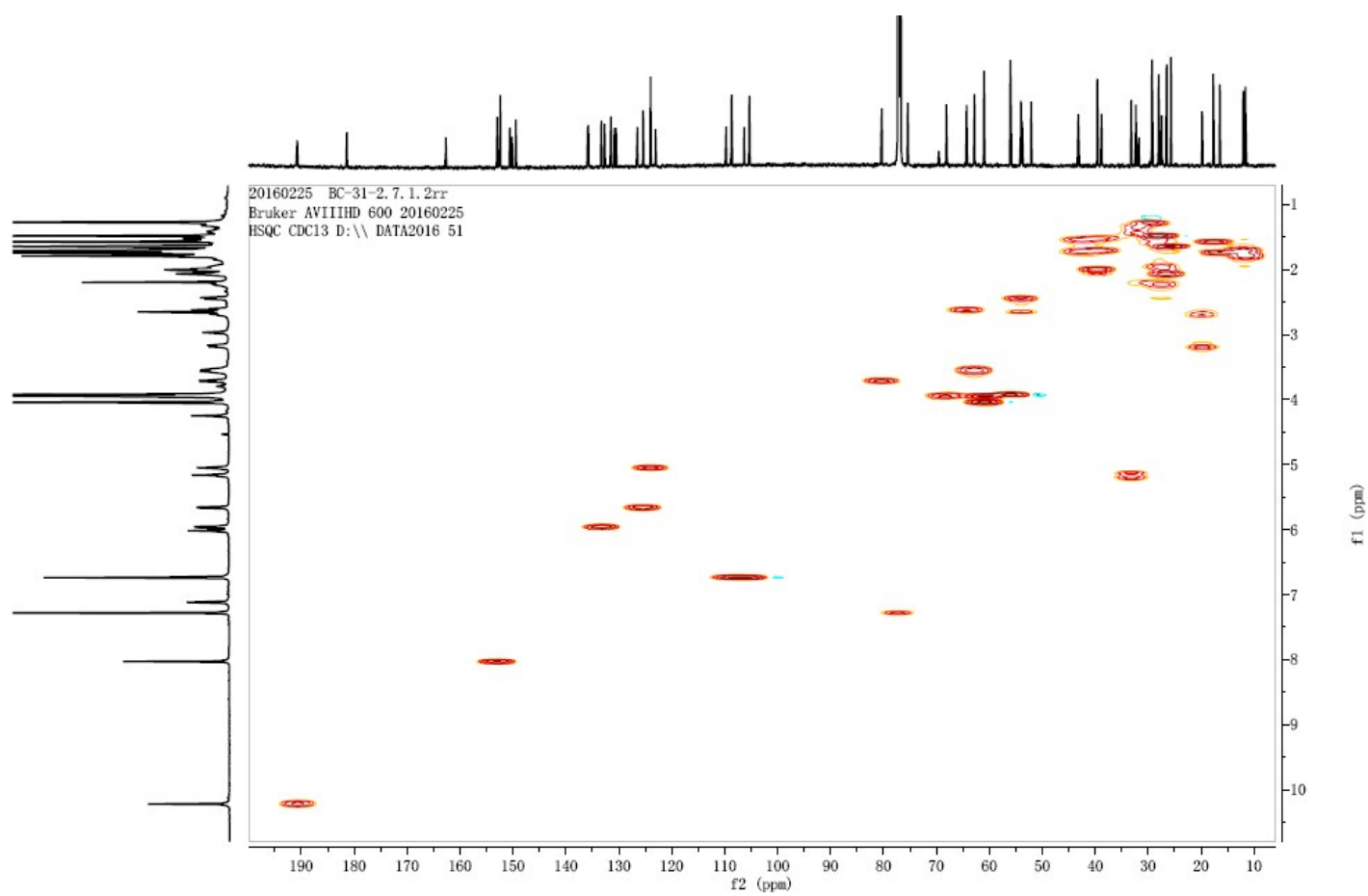


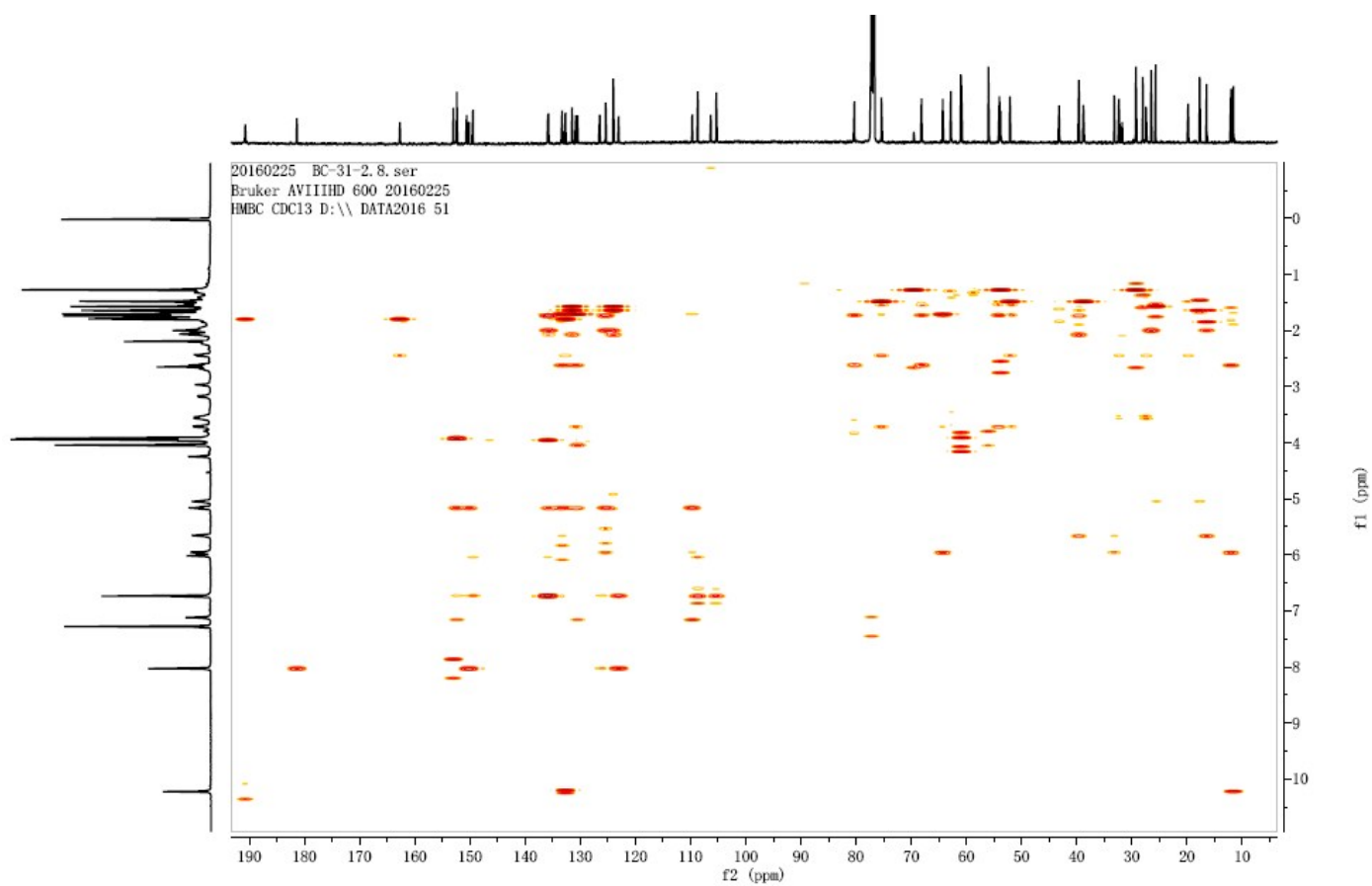
Figure S7. The  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of belamcandanin A (1)



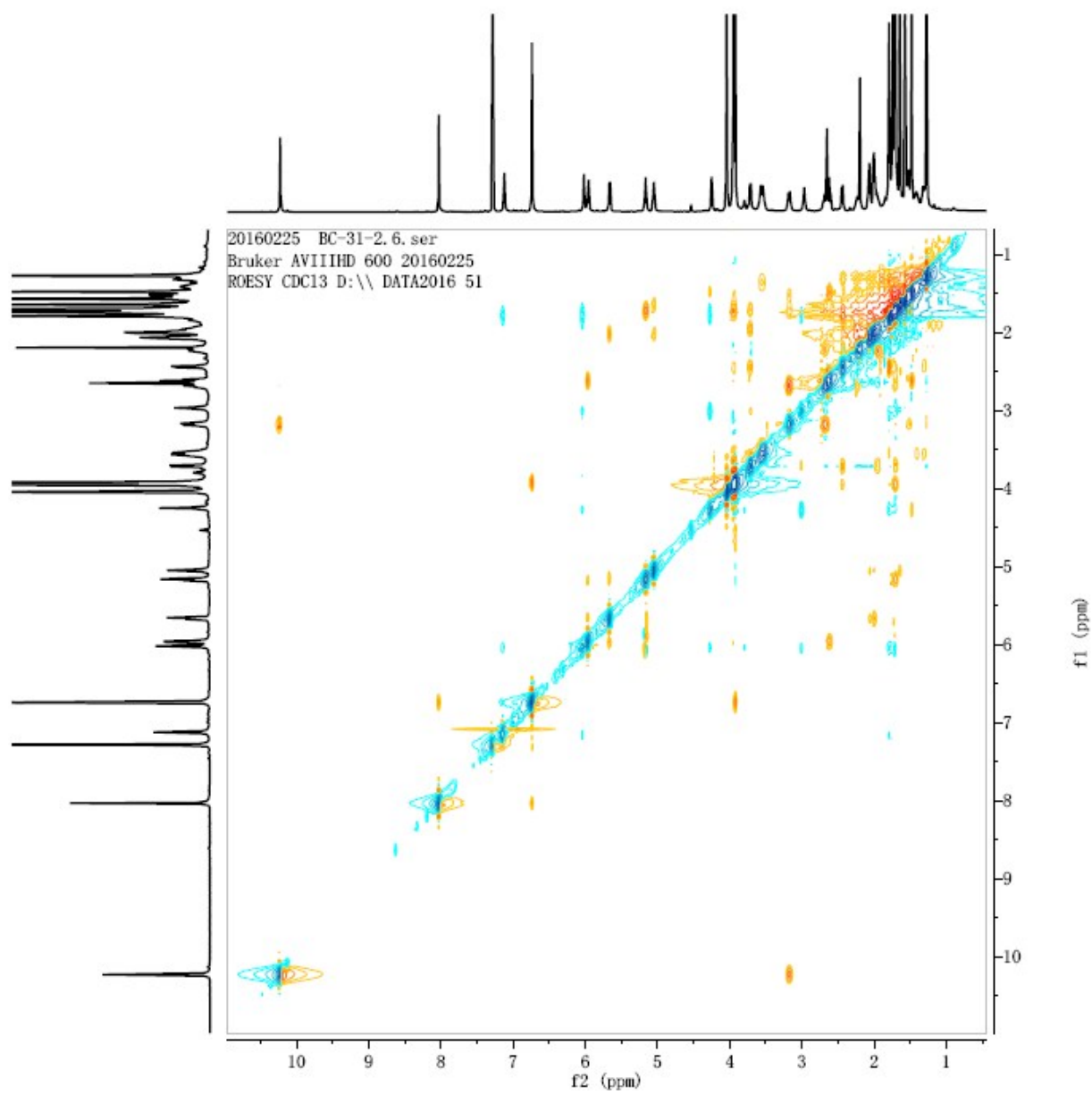
**Figure S8. The HMQC spectrum of belamcandanin A (1)**



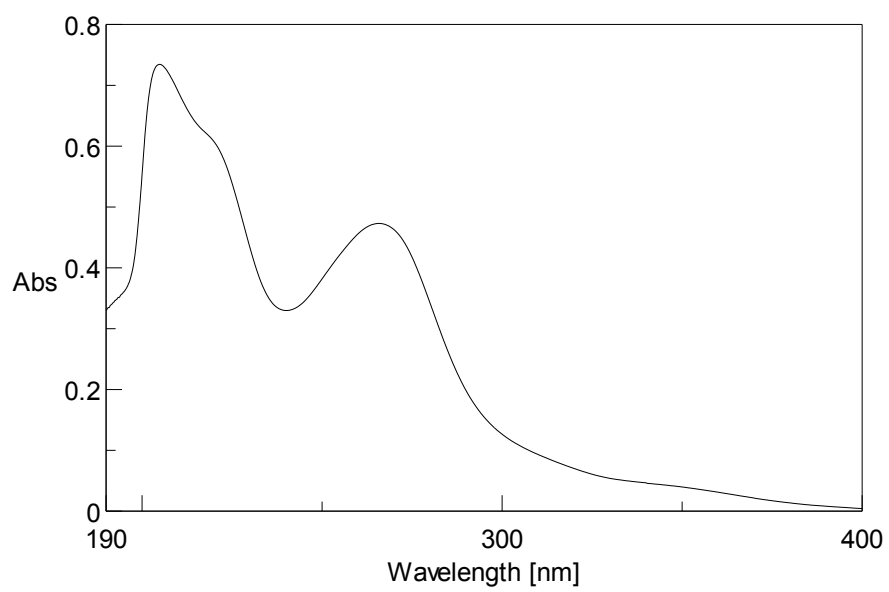
**Figure S9. The HMBC spectrum of belamcandanin A (1)**



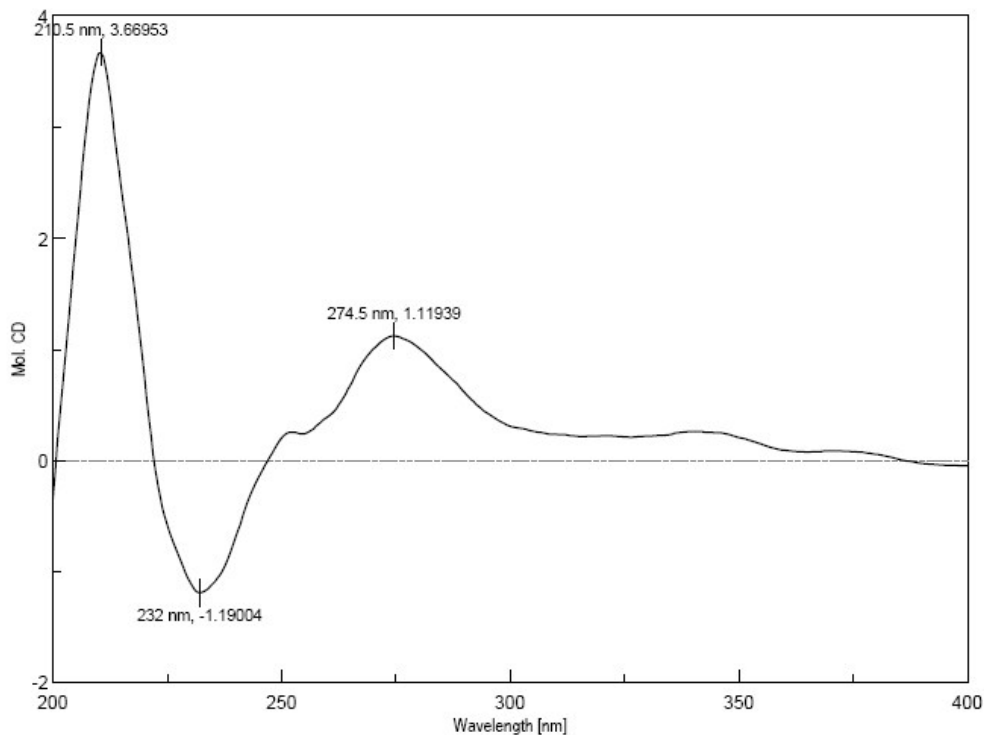
**Figure S10. The ROESY spectrum of belamcandanin A (1)**



**Figure S11. The UV spectrum of belamcandinin B (2)**



**Figure S12. The CD spectrum of belamcandanin B (2)**



[Measurement Information]

Instrument Name IMM-CD  
Model Name J-815  
Serial No. A024461168

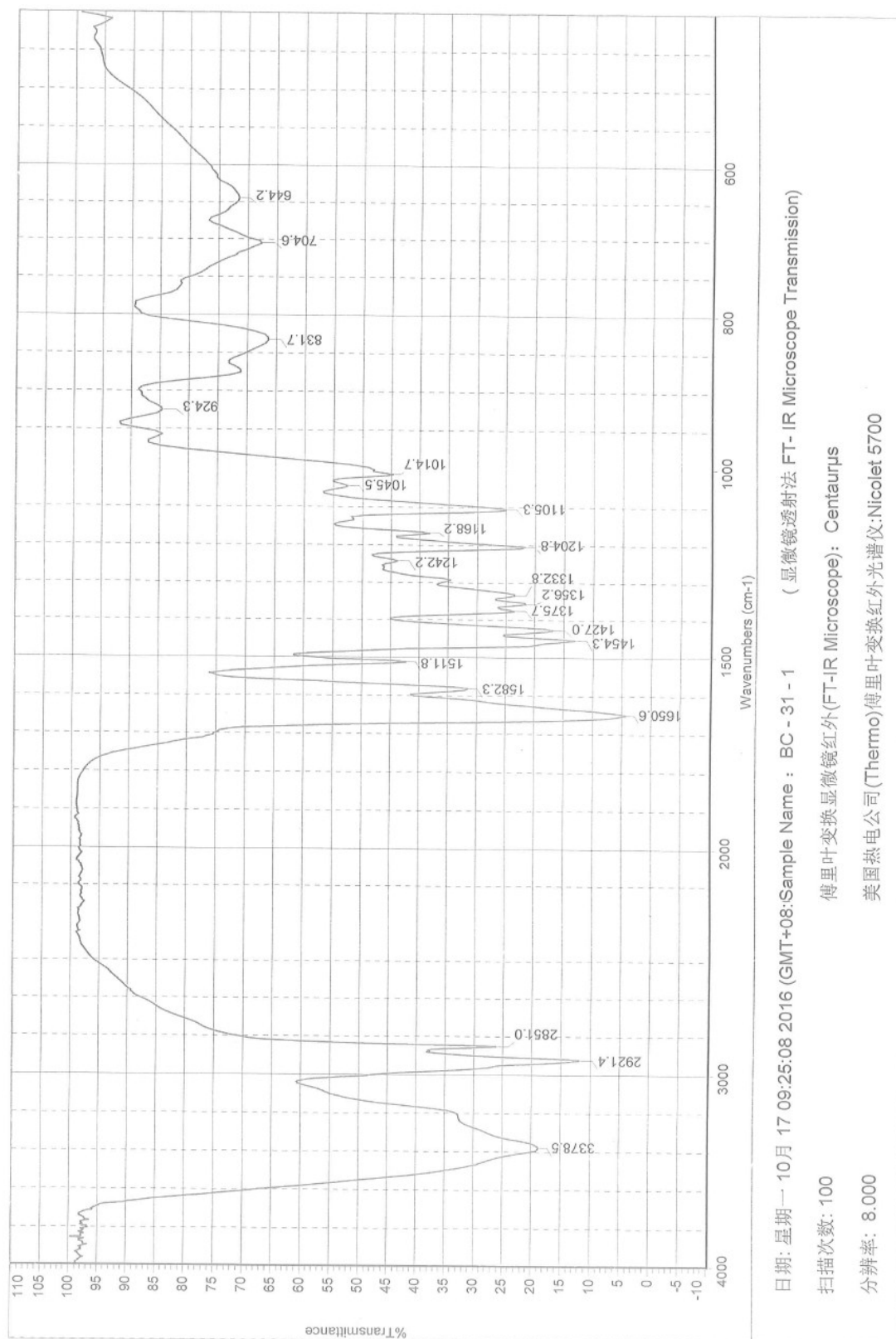
Accessory Standard  
Accessory S/N A024461168  
Cell Length 0.1 mm

Measurement date 2016/10/20 10:31

Photometric Mode CD, HT, Abs  
Measure Range 400 - 200 nm  
Data pitch 0.5 nm  
Sensitivity Standard  
D.I.T. 1 sec  
Bandwidth 2.00 nm  
Start Mode Immediately  
Scanning Speed 100 nm/min  
Baseline Correction Baseline  
Shutter Control Auto  
CD Detector PMT  
PMT Voltage Auto  
Accumulations 2  
Solvent MEOH  
Concentration 0.265 (w/v)%

BC-40-1-2-s-m.jws

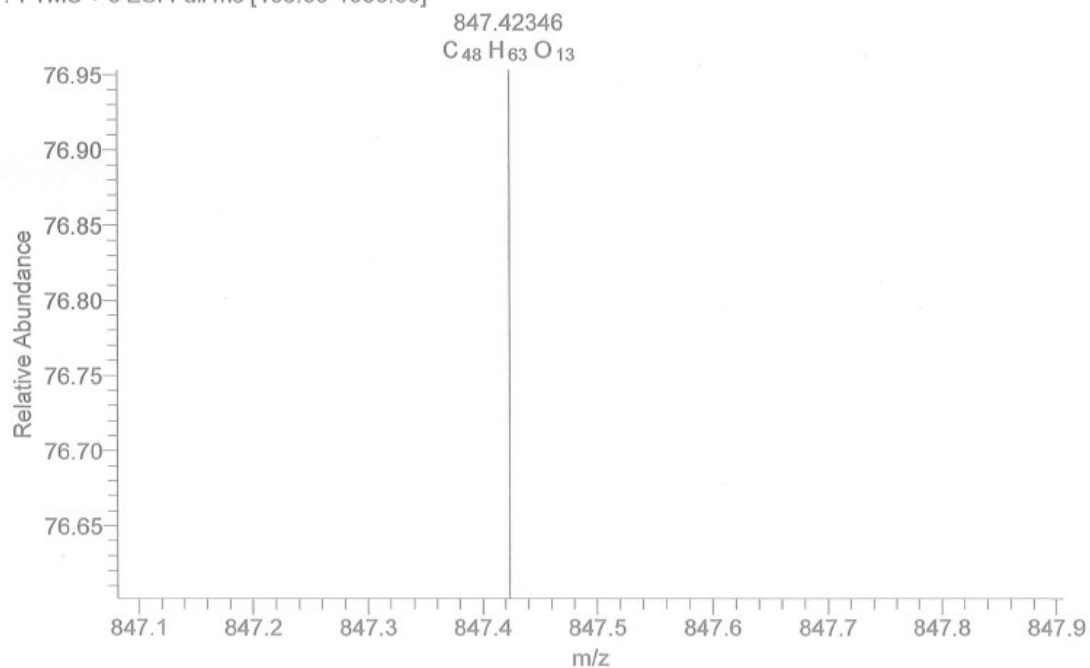
Figure S13. The IR spectrum of belamcandanin B (2)





**Figure S14. The HRESI spectrum of belamcandanin B (2)**

BC-40-1 #1324 RT: 4.77 AV: 1 NL: 5.06E5  
T: FTMS + c ESI Full ms [100.00-1000.00]



Elemental composition search on mass 847.42

m/z= 842.42-852.42

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
847.42346	847.42632	-3.37	17.5	C <sub>48</sub> H <sub>63</sub> O <sub>13</sub>
	847.29603	150.37	25.5	C <sub>48</sub> H <sub>47</sub> O <sub>14</sub>
	847.55660	-157.12	9.5	C <sub>48</sub> H <sub>79</sub> O <sub>12</sub>

Figure S15. The <sup>1</sup>H NMR spectrum of belamcandinin B (2)

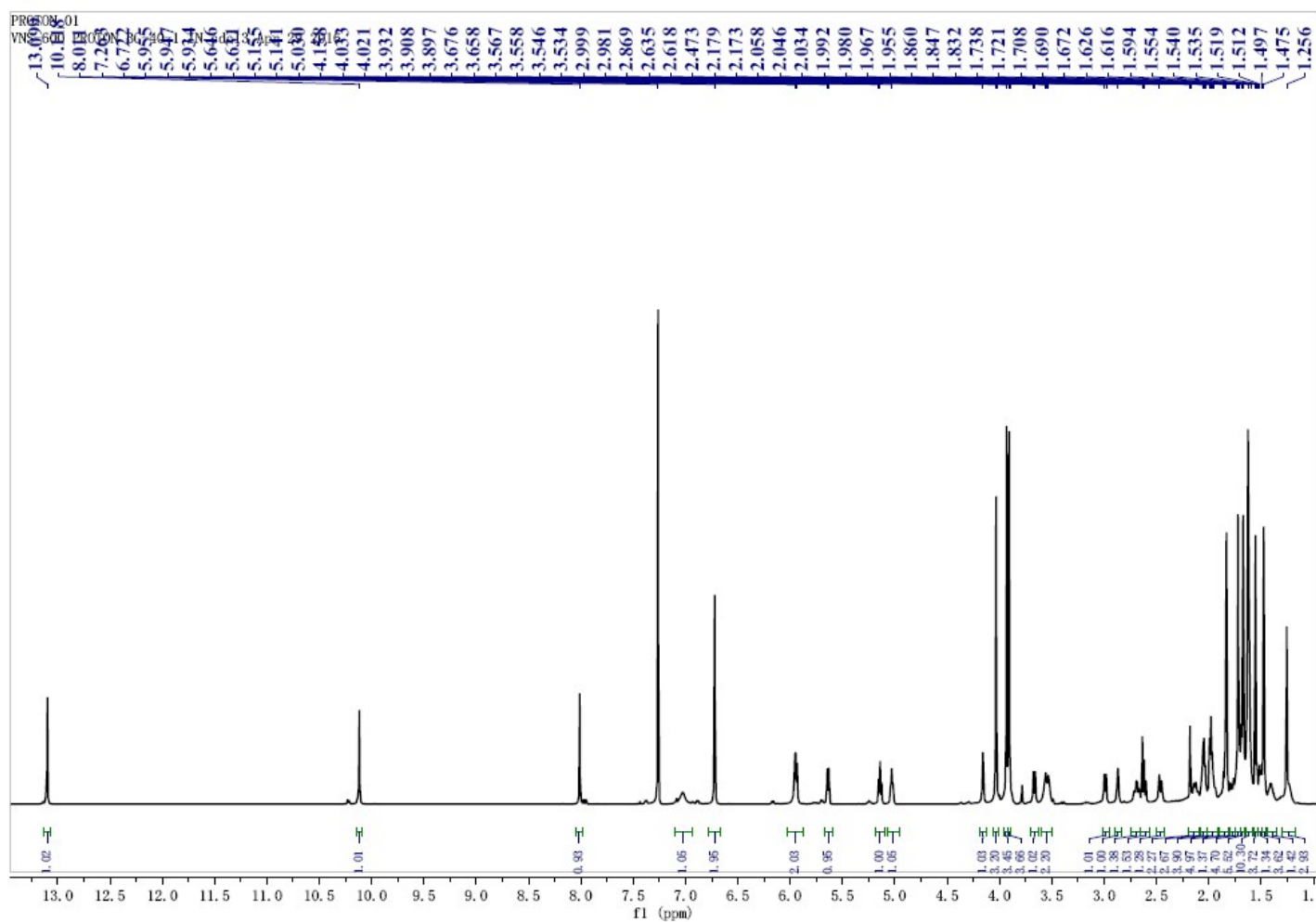


Figure S16. The  $^{13}\text{C}$  NMR spectrum of belamcandinin B (2)

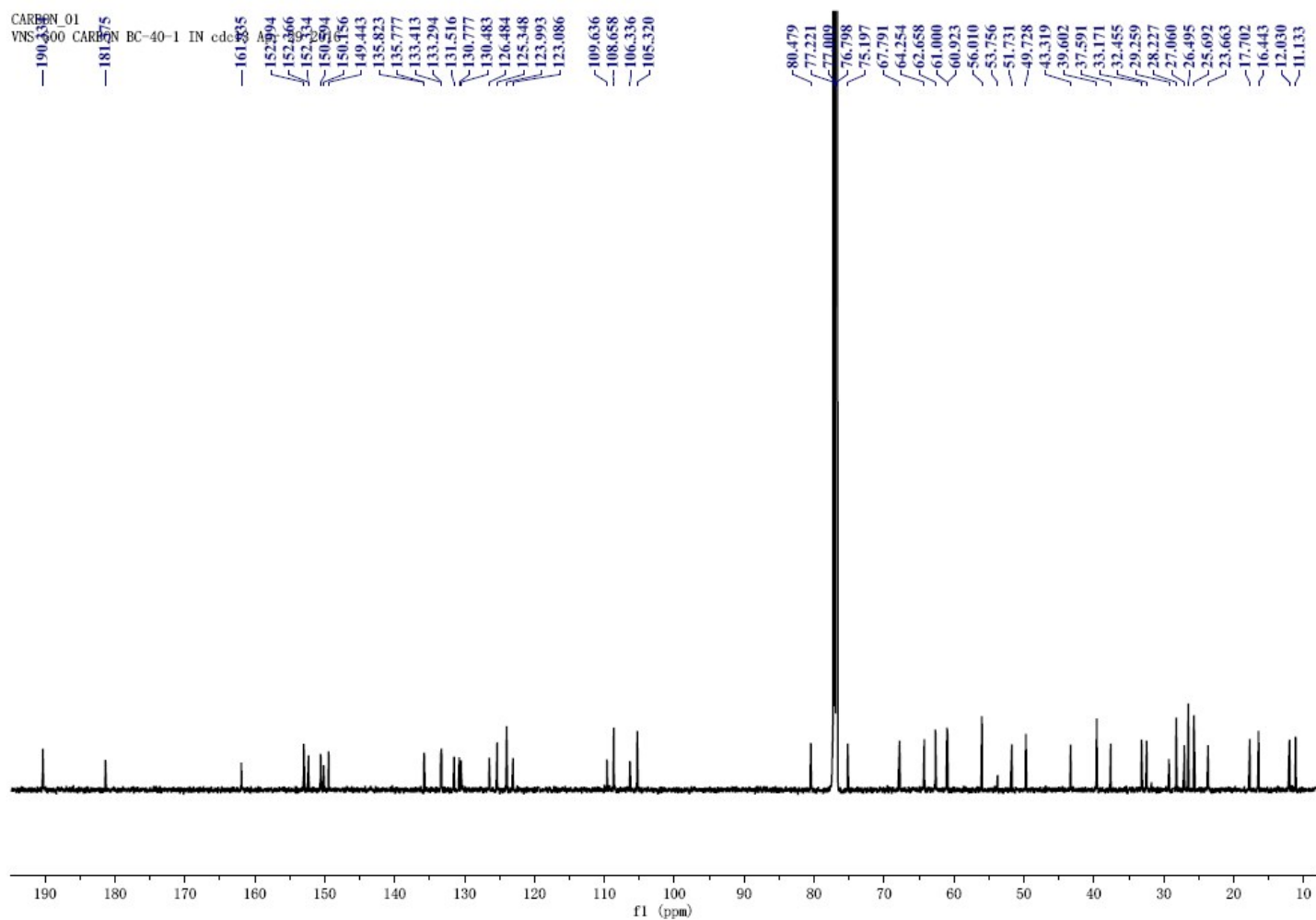


Figure S17. The HMQC spectrum of belamcandanin B (2)

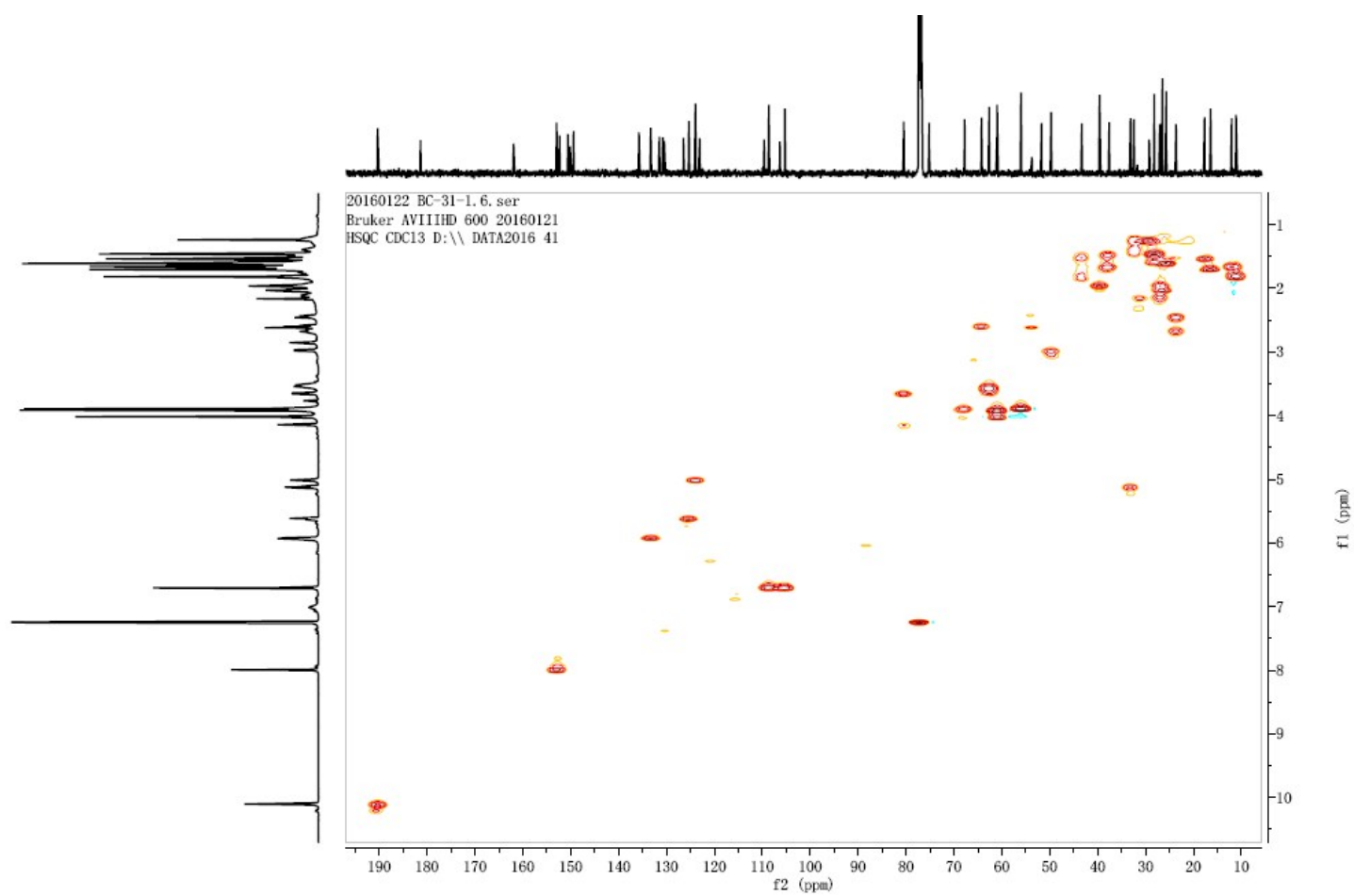


Figure S18. The HMBC spectrum of belamcandanin B (2)

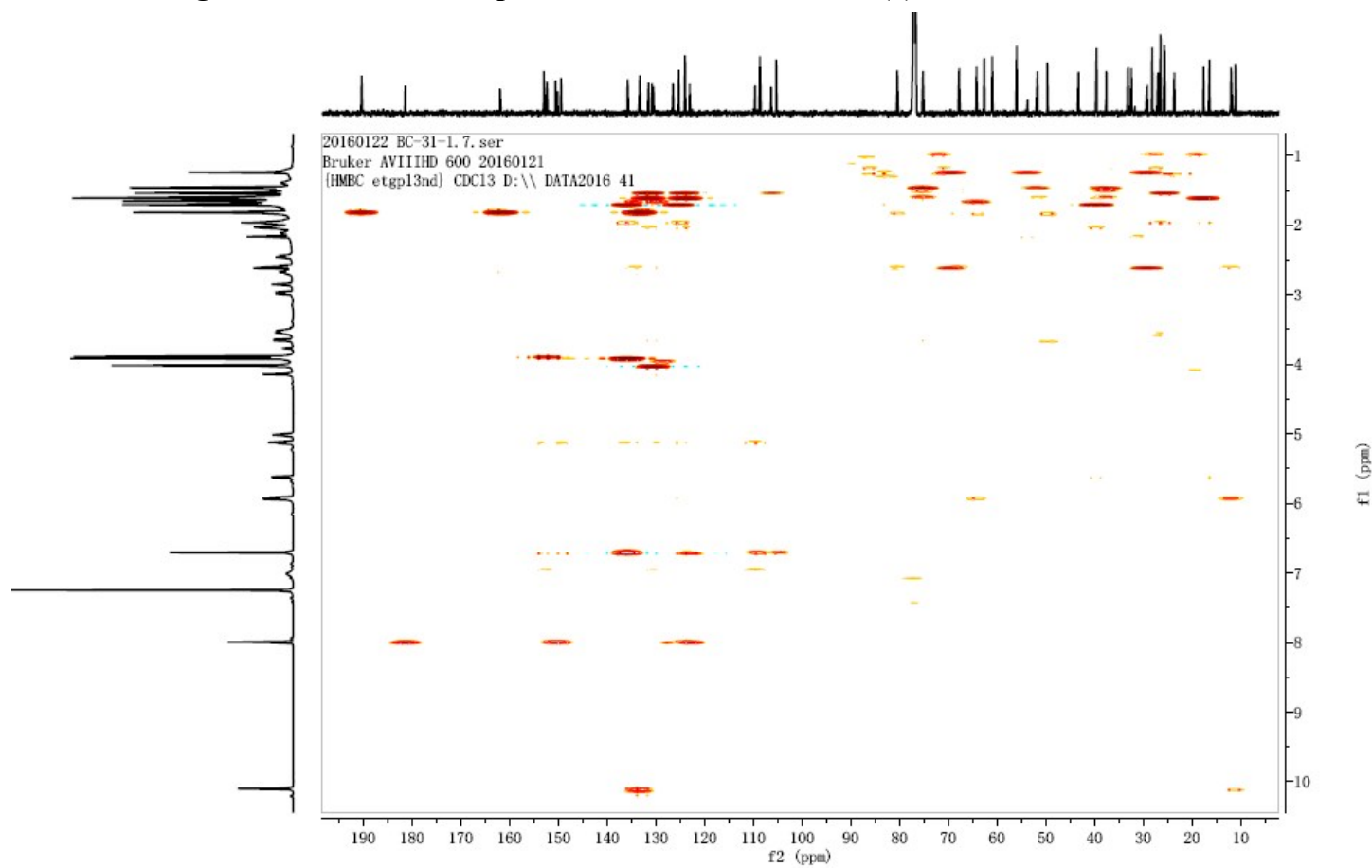
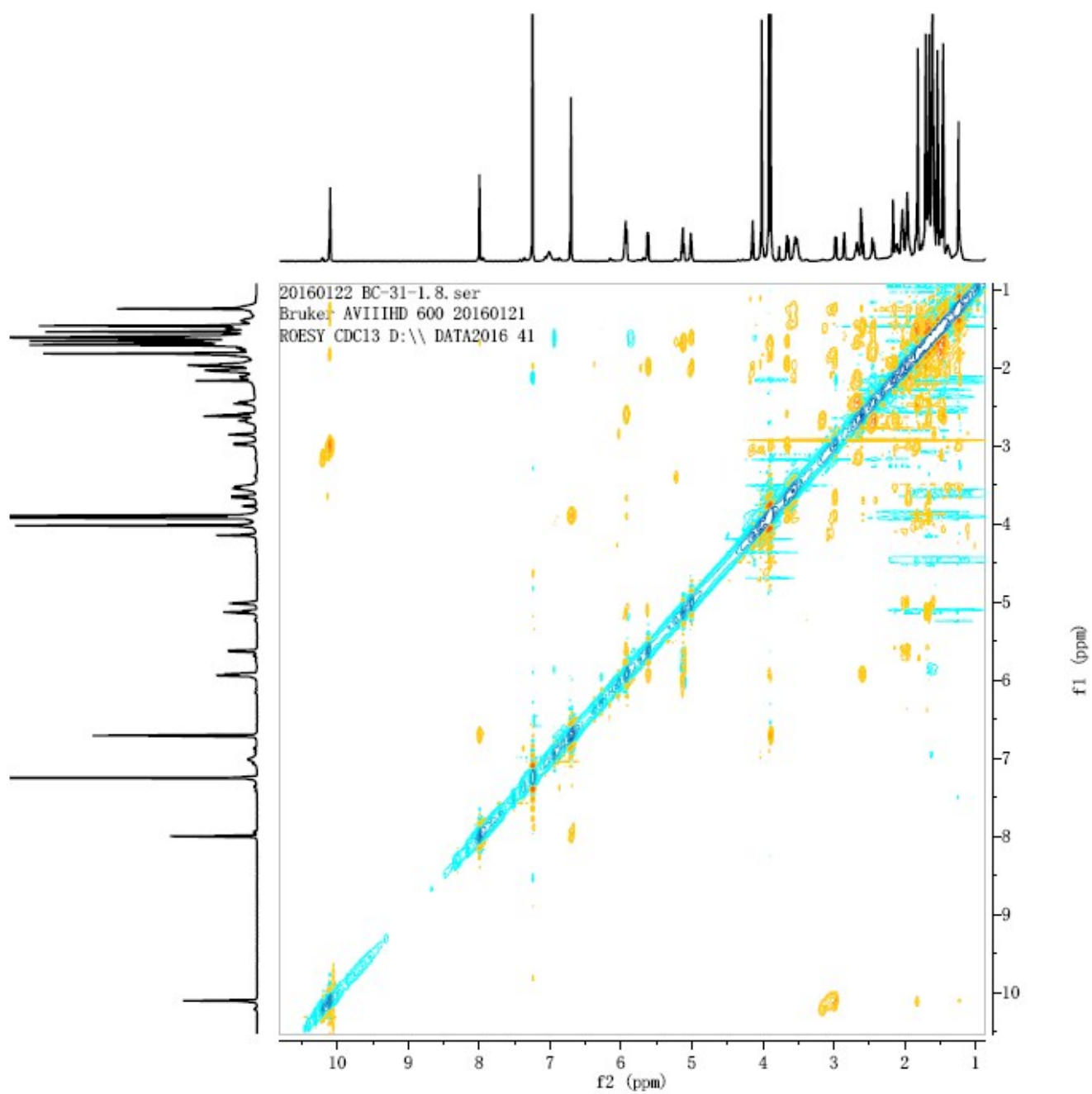
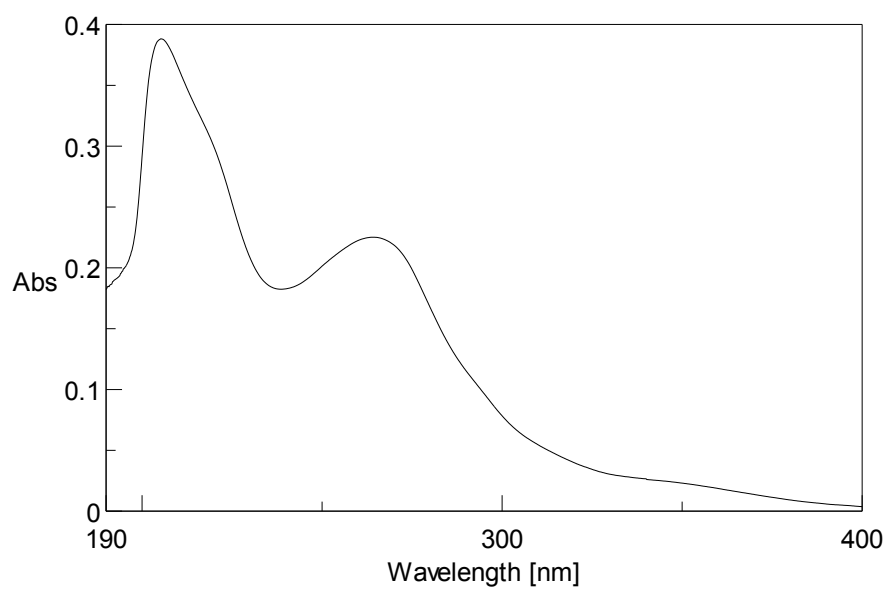


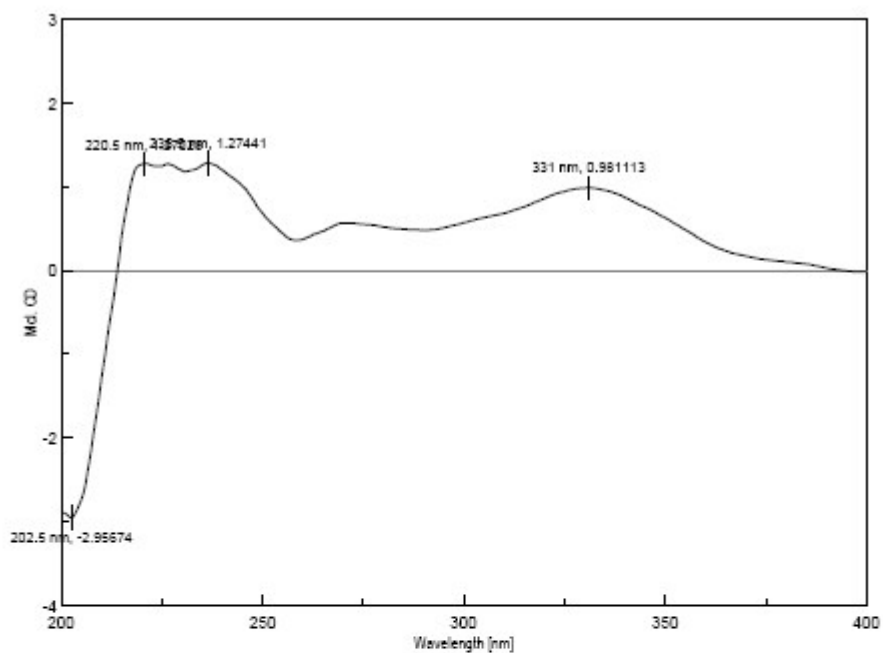
Figure S19. The ROESY spectrum of belamcandanin B (2)



**Figure S20. The UV spectrum of belamcandinin C (3)**



**Figure S21. The CD spectrum of belamcandanin C (3)**



[Measurement Information]

Instrument Name IMM-CD  
 Model Name J-815  
 Serial No. A024461168

Accessory Standard  
 Accessory S/N A024461168  
 Cell Length 0.1 mm

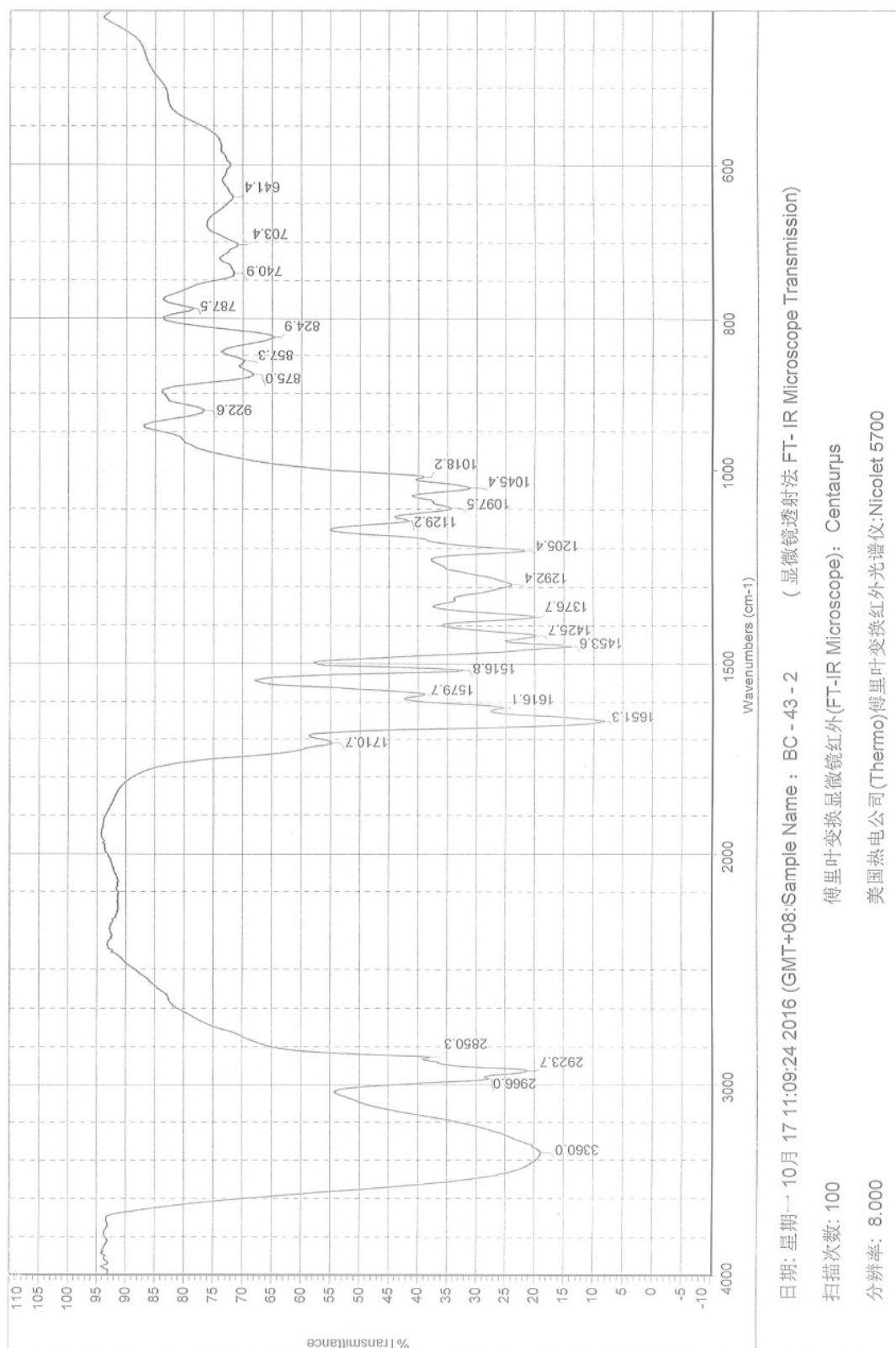
Measurement date 2016/10/20 10:17

Photometric Mode CD, HT, Abs  
 Measure Range 400 - 200 nm  
 Data pitch 0.5 nm  
 Sensitivity Standard  
 D.I.T. 1 sec  
 Bandwidth 2.00 nm  
 Start Mode Immediately  
 Scanning Speed 100 nm/min  
 Baseline Correction Baseline  
 Shutter Control Auto  
 CD Detector PMT  
 PMT Voltage Auto  
 Accumulations 2  
 Solvent MEOH  
 Concentration 0.2613 (w/v)%

BC-43-2-3-s-m.jws



Figure S22. The IR spectrum of belamcandinin C (3)



日期: 星期一 10月 17 11:09:24 2016 (GMT+08:Sample Name : BC - 43 - 2 (显微镜透射法 FT- IR Microscope Transmission)

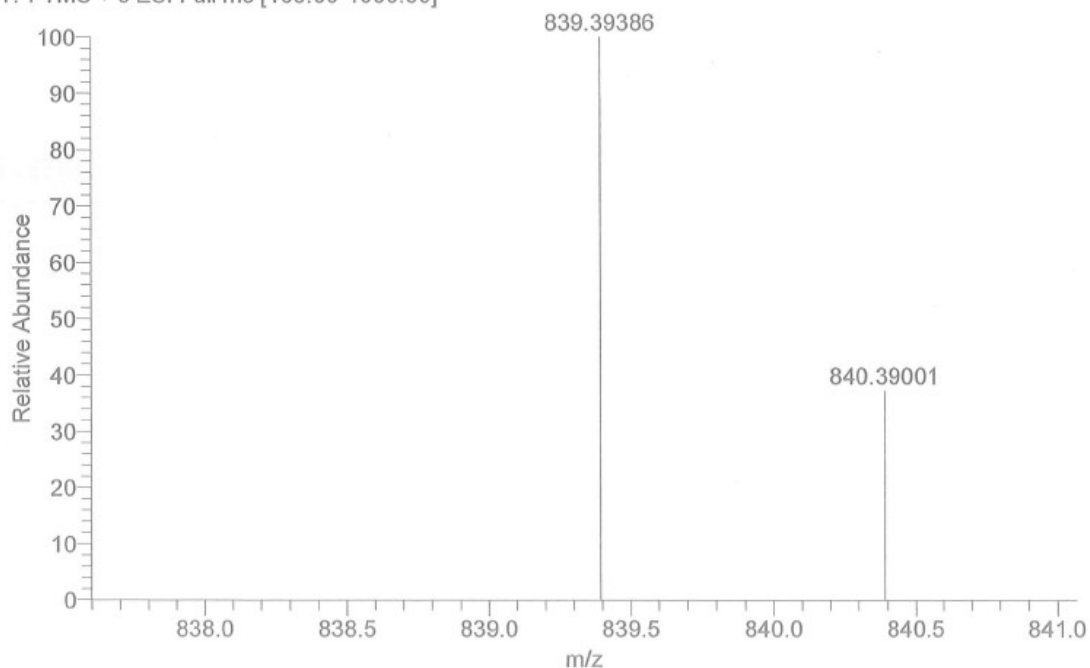
傅里叶变换显微镜红外(FT-IR Microscope): Centaurus

扫描次数: 100 美国热电公司(Thermo)傅里叶变换红外光谱仪:Nicolet 5700

分辨率: 8.000

**Figure S23. The HRESI spectrum of belamcandanin C (3)**

BC-43-2 #1558 RT: 4.94 AV: 1 NL: 4.51E4  
 T: FTMS + c ESI Full ms [100.00-1000.00]



Elemental composition search on mass 839.39

m/z= 834.39-844.39

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
839.39386	839.39423	-0.44	29.5	C <sub>56</sub> H <sub>55</sub> O <sub>7</sub>
	839.39183	2.42	26.5	C <sub>54</sub> H <sub>56</sub> O <sub>7</sub> Na
	839.39072	3.74	7.5	C <sub>38</sub> H <sub>63</sub> O <sub>20</sub>
	839.39770	-4.57	17.5	C <sub>47</sub> H <sub>60</sub> O <sub>12</sub> Na
	839.38832	6.61	4.5	C <sub>36</sub> H <sub>64</sub> O <sub>20</sub> Na
	839.40010	-7.44	20.5	C <sub>49</sub> H <sub>59</sub> O <sub>12</sub>
	839.38485	10.74	16.5	C <sub>45</sub> H <sub>59</sub> O <sub>15</sub>
	839.40357	-11.57	8.5	C <sub>40</sub> H <sub>64</sub> O <sub>17</sub> Na
	839.38244	13.60	13.5	C <sub>43</sub> H <sub>60</sub> O <sub>15</sub> Na
	839.40598	-14.44	11.5	C <sub>42</sub> H <sub>63</sub> O <sub>17</sub>

Figure S24. The  $^1\text{H}$  NMR spectrum of belamcandarin C (3)

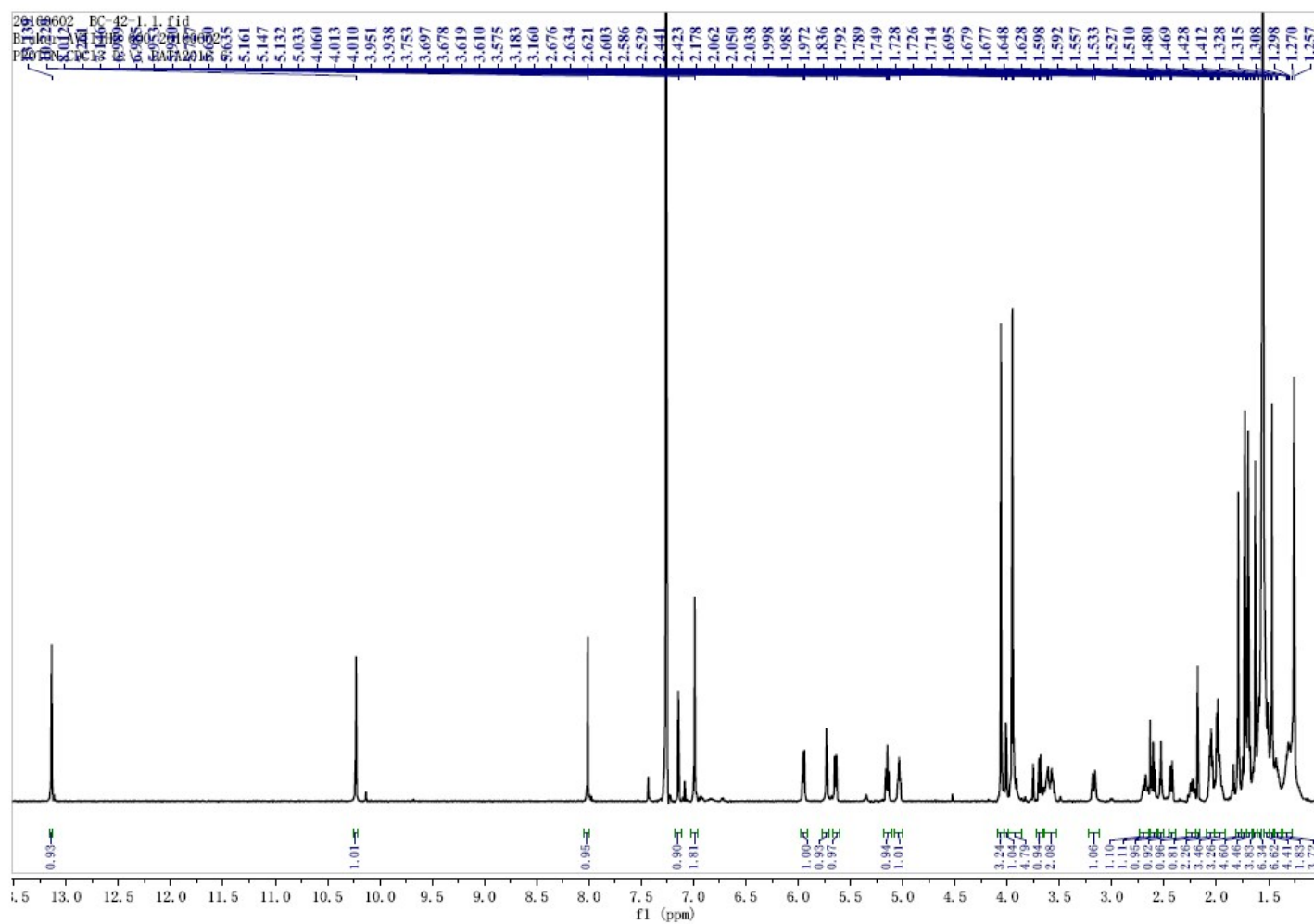


Figure S25. The  $^{13}\text{C}$  NMR spectrum of belamcandinin C (3)

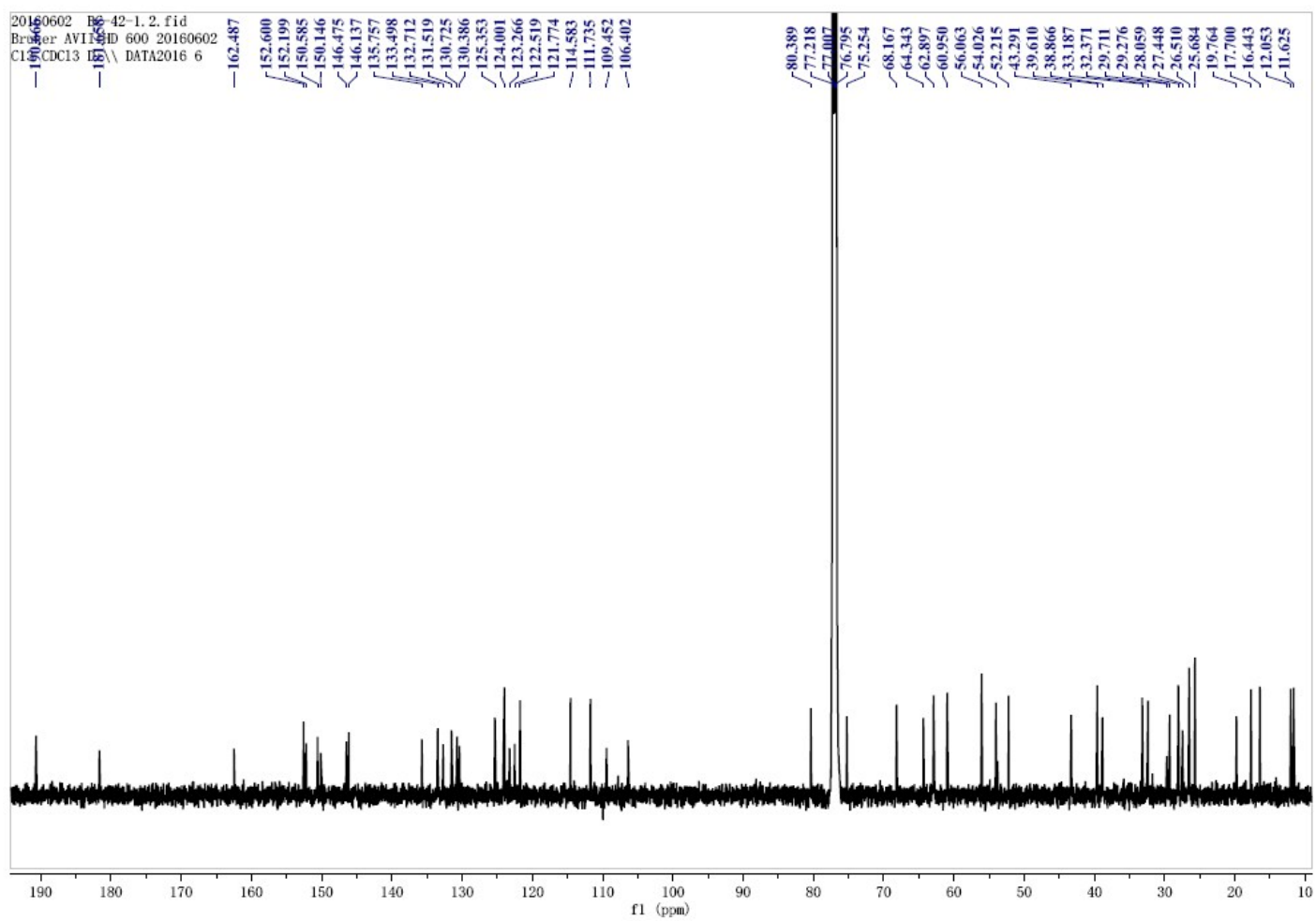


Figure S26. The HMQC spectrum of belamcandanin C (3)

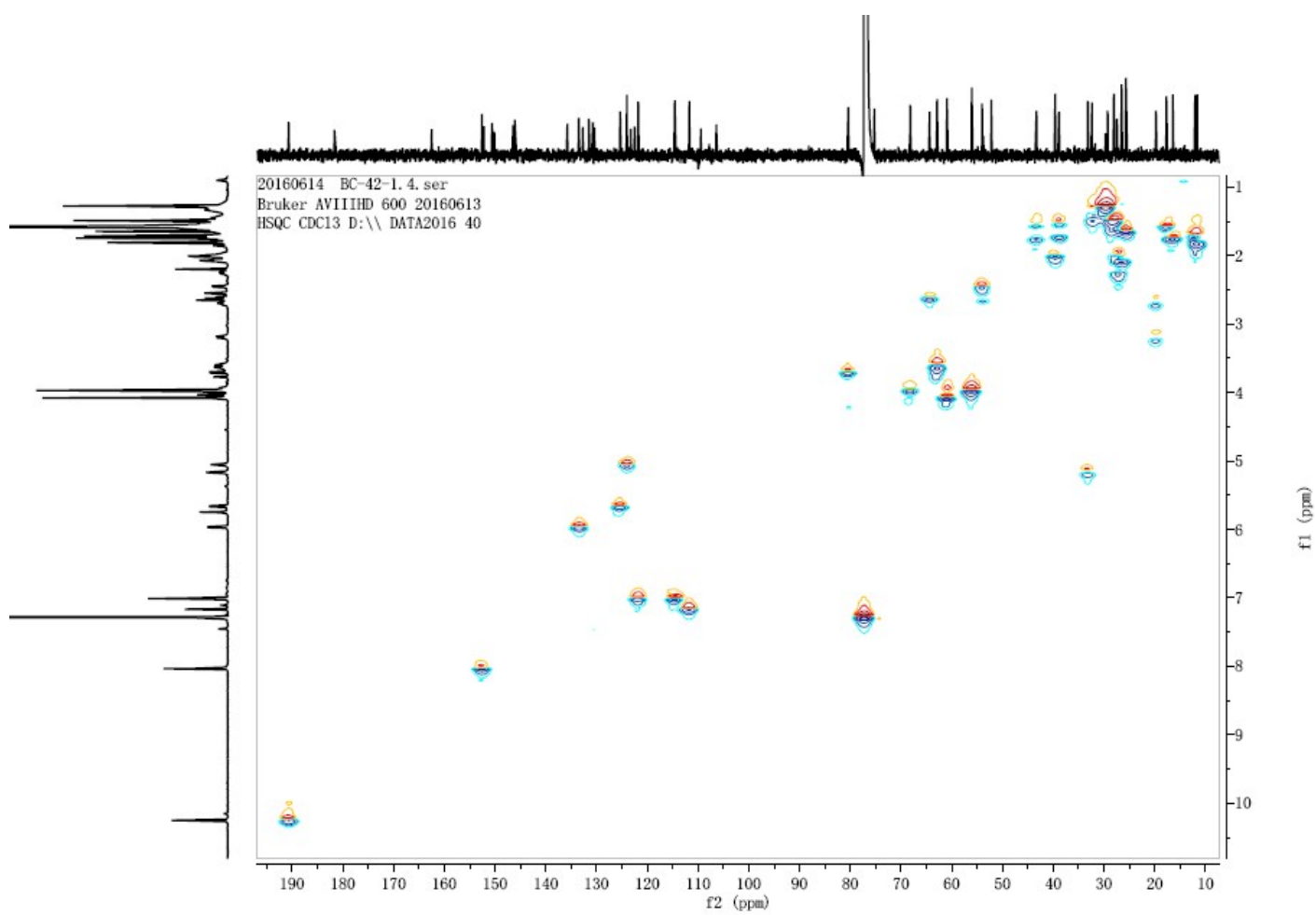


Figure S27. The HMBC spectrum of belamcandanin C (3)

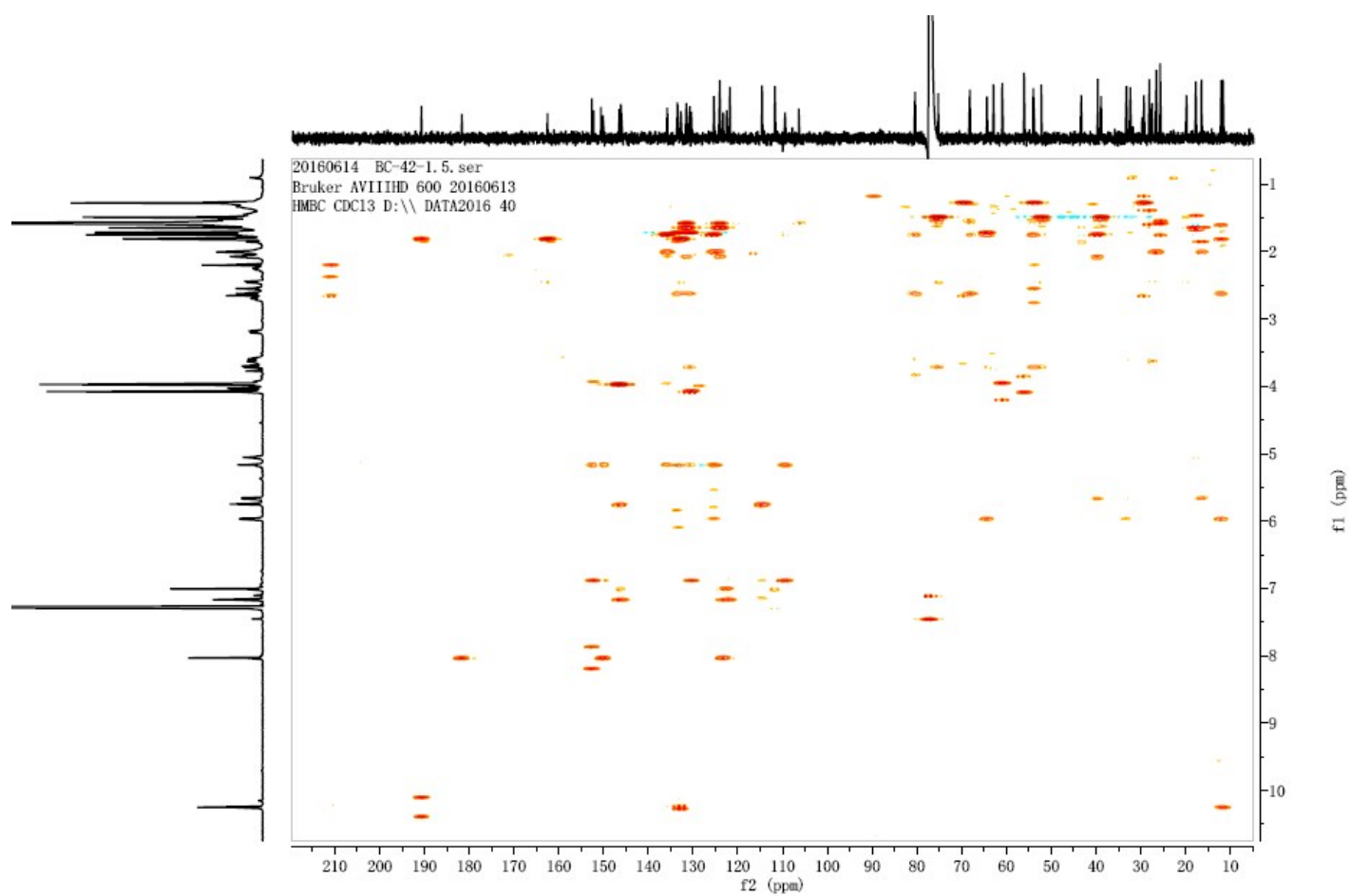
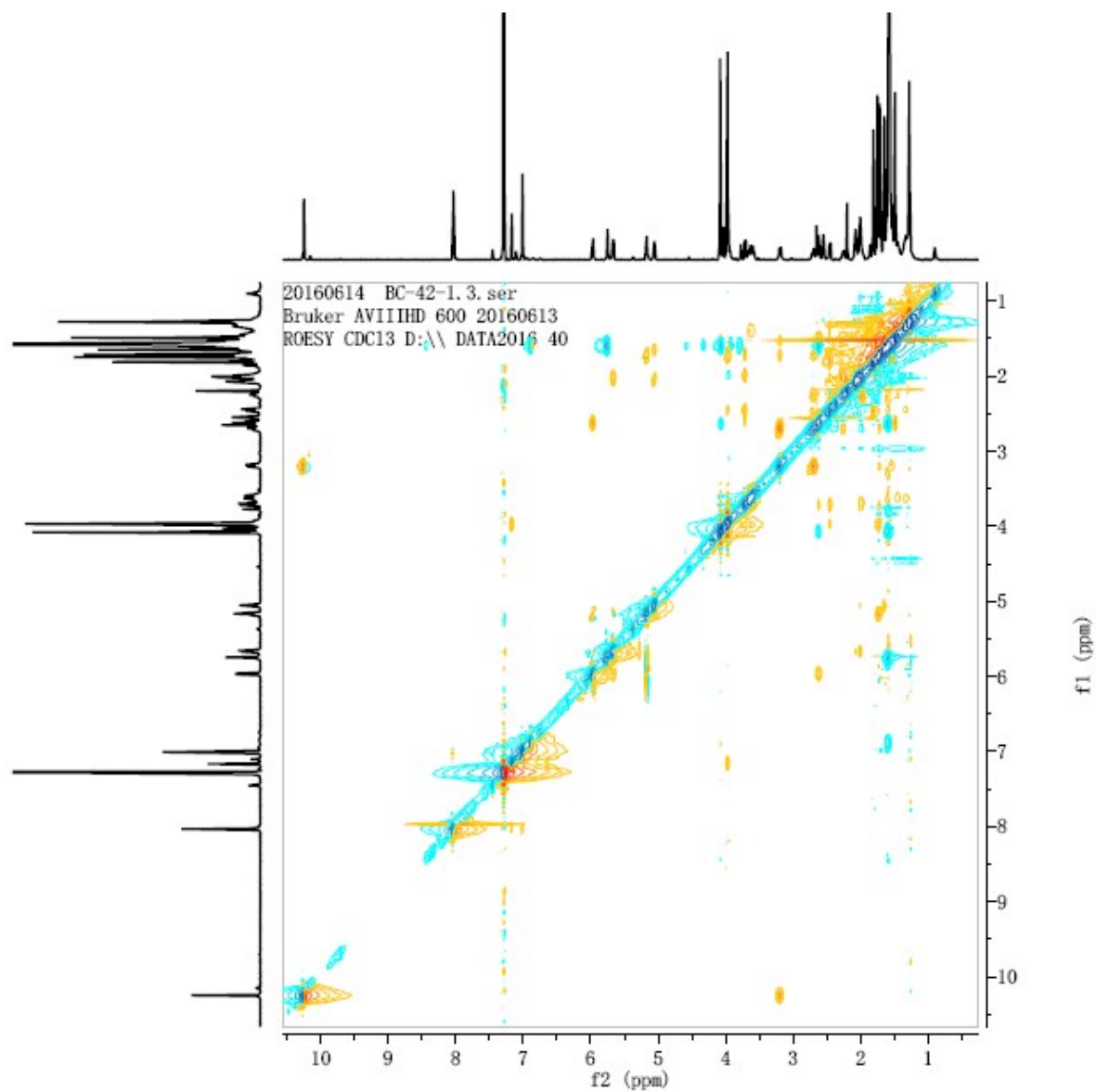
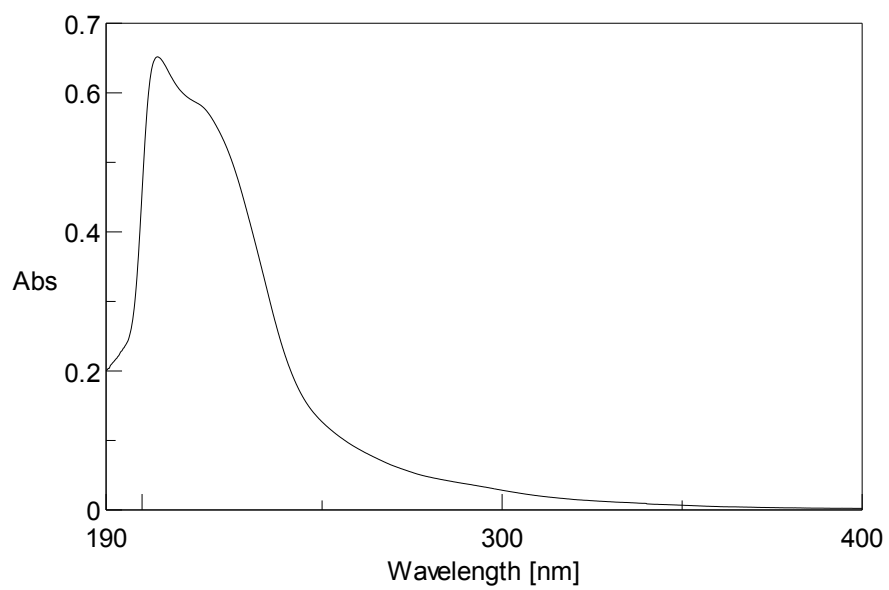


Figure S28. The ROESY spectrum of belamcandarin C (3)

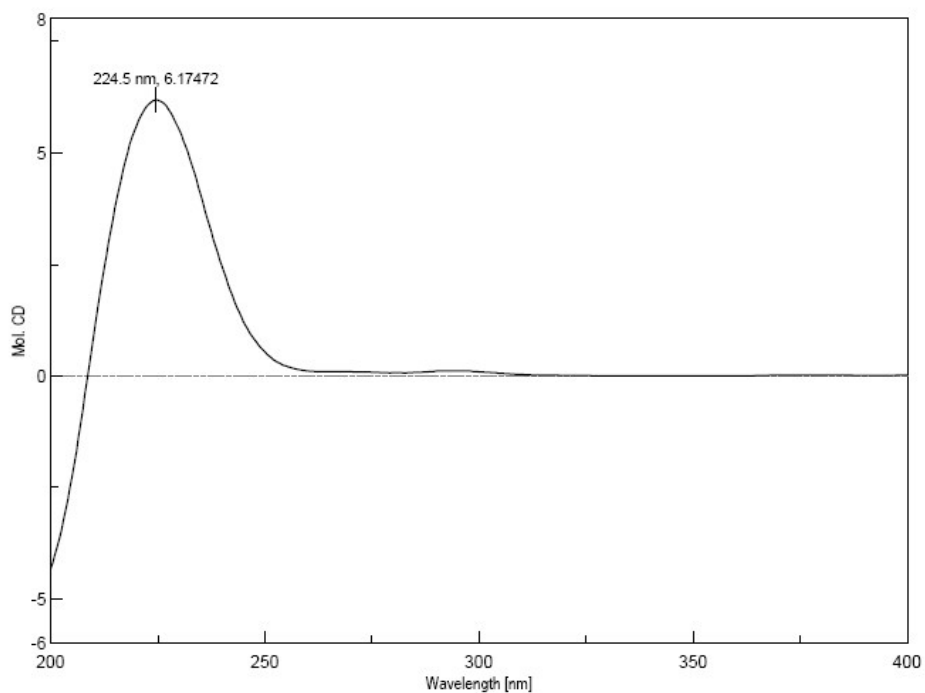


**Figure S29. The UV spectrum of belamcanolide A (4) in MeOH**





**Figure S30. The CD spectrum of belamcanolide A (4) in MeOH**



[Measurement Information]

Instrument Name IMM-CD  
Model Name J-815  
Serial No. A024461168

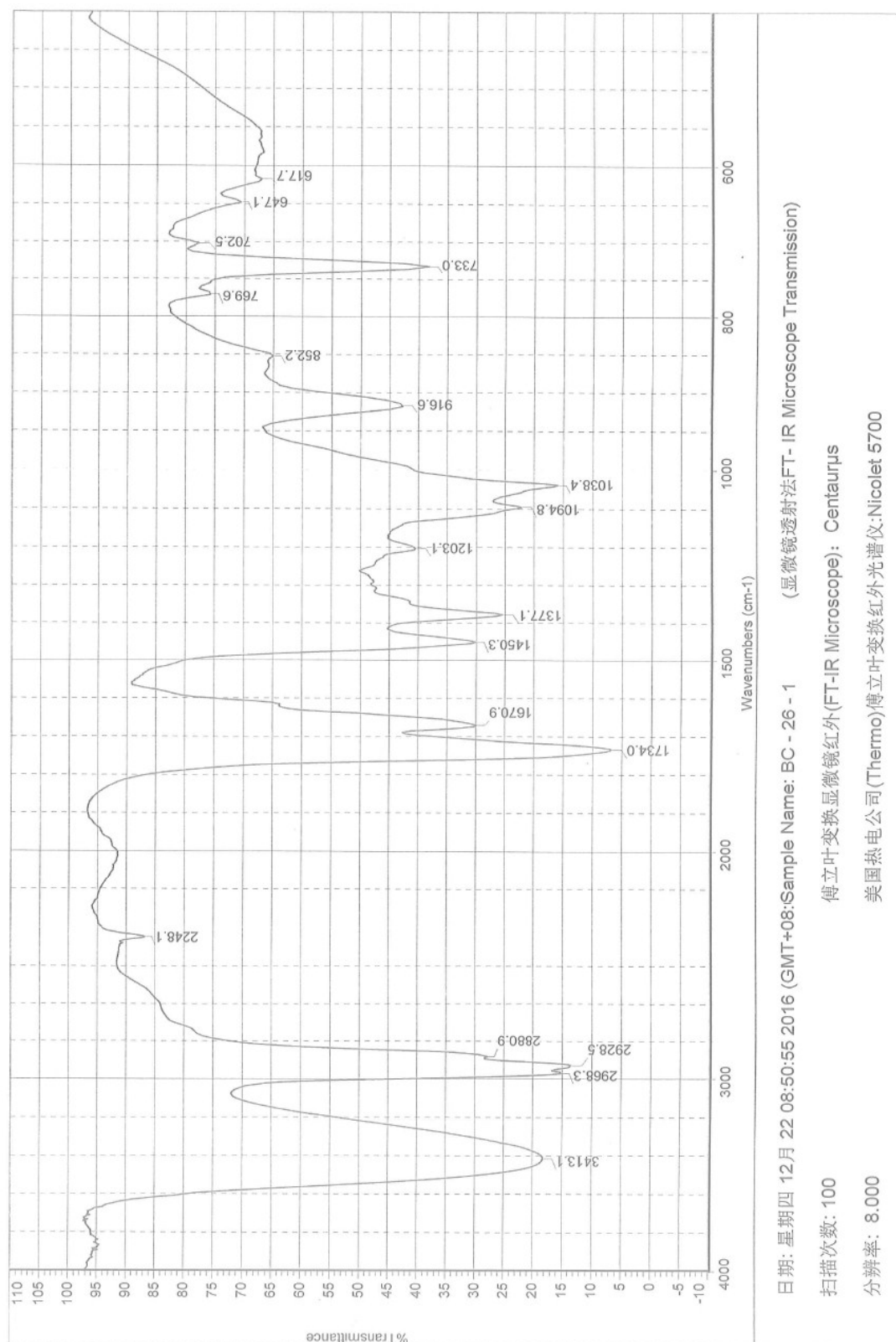
Accessory Standard  
Accessory S/N A024461168  
Cell Length 0.1 mm

Measurement date 2016/10/20 8:46

Photometric Mode CD, HT, Abs  
Measure Range 400 - 200 nm  
Data pitch 0.5 nm  
Sensitivity Standard  
D.I.T. 1 sec  
Bandwidth 2.00 nm  
Start Mode Immediately  
Scanning Speed 100 nm/min  
Baseline Correction Baseline  
Shutter Control Auto  
CD Detector PMT  
PMT Voltage Auto  
Accumulations 2  
Solvent MEOH  
Concentration 0.55 (w/v)%

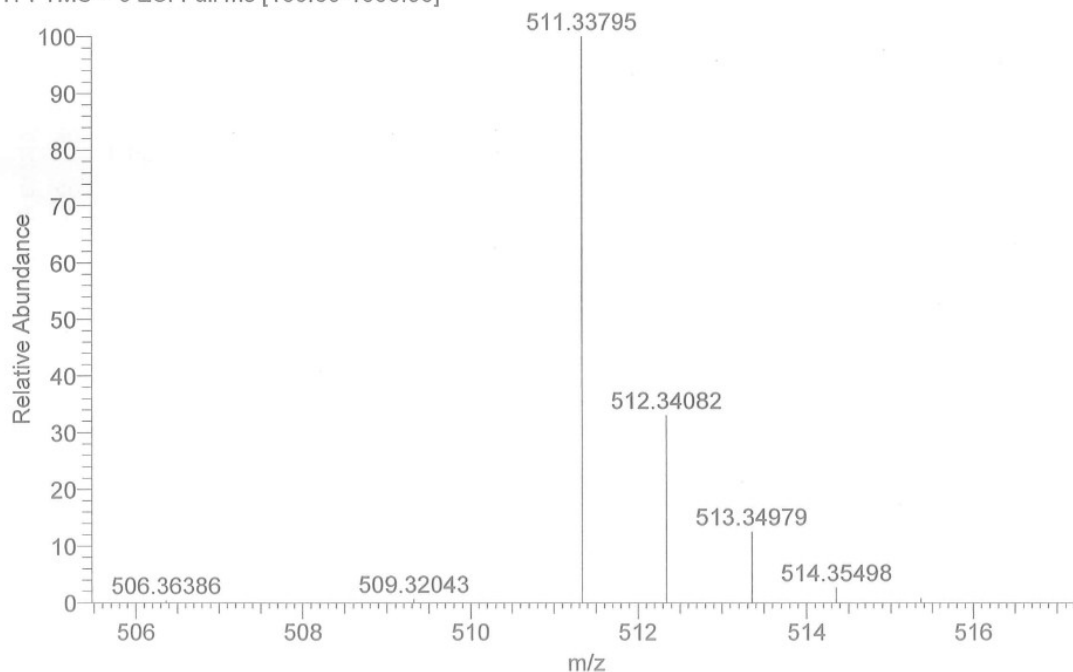
BC-26-1-1-s-m.jws

Figure S31. The IR spectrum of belamcanolide A (4)



**Figure S32. The HRESI spectrum of belamcanolide A (4)**

BC-26-1 #1502 RT: 4.63 AV: 1 NL: 1.92E6  
 T: FTMS + c ESI Full ms [100.00-1000.00]



Elemental composition search on mass 511.34

m/z= 506.34-516.34

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
511.33795	511.33940	-2.83	6.5	C <sub>30</sub> H <sub>48</sub> O <sub>5</sub> Na
	511.32886	17.77	4.5	C <sub>30</sub> H <sub>50</sub> OKNa <sub>2</sub>
	511.34984	-23.26	4.5	C <sub>30</sub> H <sub>50</sub> O <sub>2</sub> Na <sub>3</sub>
	511.31842	38.20	6.5	C <sub>30</sub> H <sub>48</sub> O <sub>4</sub> K
	511.28992	93.93	7.5	C <sub>30</sub> H <sub>43</sub> ONa <sub>4</sub>
	511.27948	114.36	9.5	C <sub>30</sub> H <sub>41</sub> O <sub>4</sub> Na <sub>2</sub>
	511.25850	155.38	9.5	C <sub>30</sub> H <sub>41</sub> O <sub>3</sub> KNa
	511.23752	196.40	9.5	C <sub>30</sub> H <sub>41</sub> O <sub>2</sub> K <sub>2</sub>
	511.21956	231.54	12.5	C <sub>30</sub> H <sub>34</sub> O <sub>3</sub> Na <sub>3</sub>
	511.19858	272.56	12.5	C <sub>30</sub> H <sub>34</sub> O <sub>2</sub> KNa <sub>2</sub>

Figure S33. The  $^1\text{H}$  NMR spectrum of belamcanolide A (4) in  $\text{CDCl}_3$

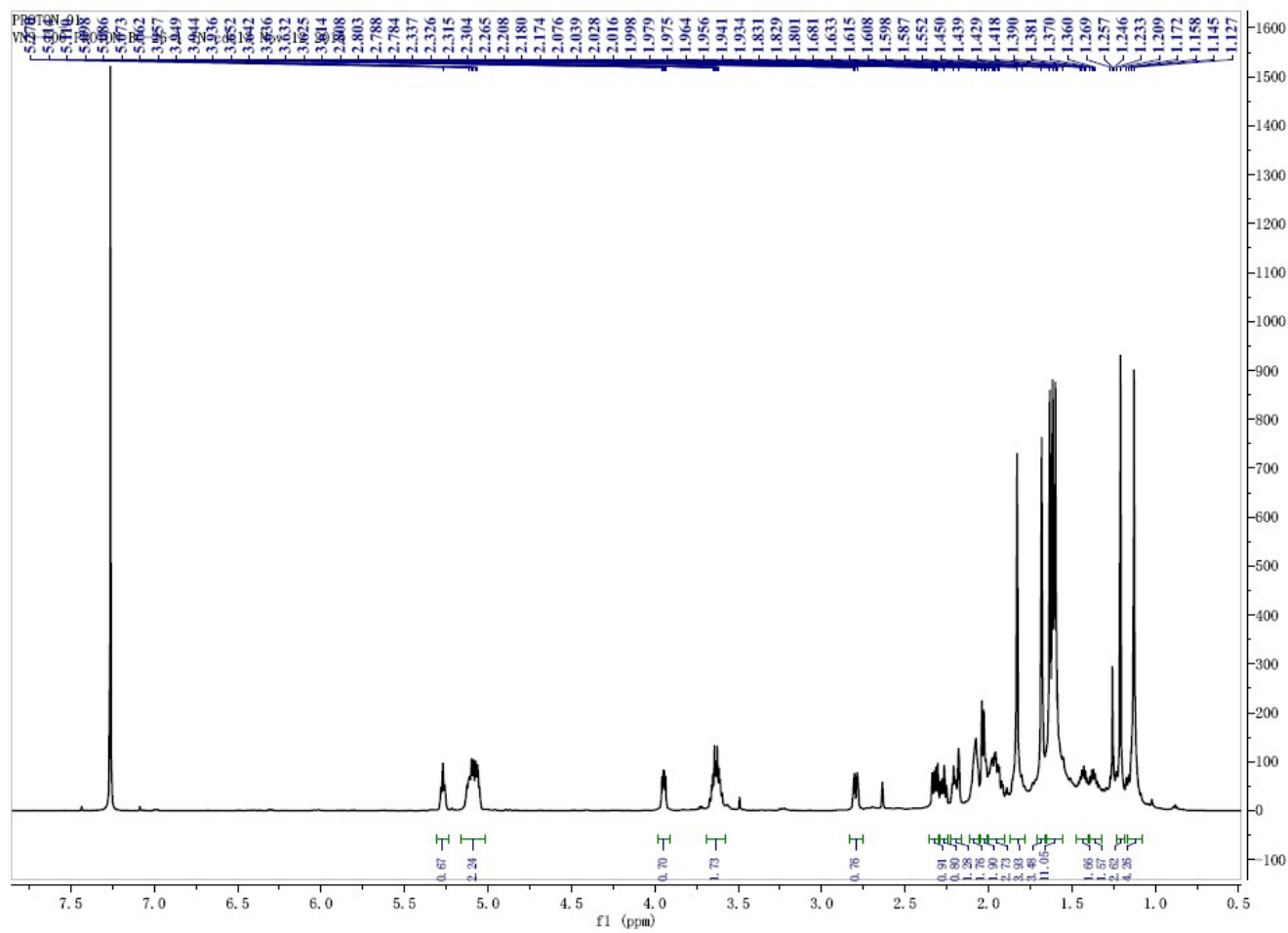


Figure S34. The  $^{13}\text{C}$  NMR spectrum of belamcanolide A (4) in  $\text{CDCl}_3$

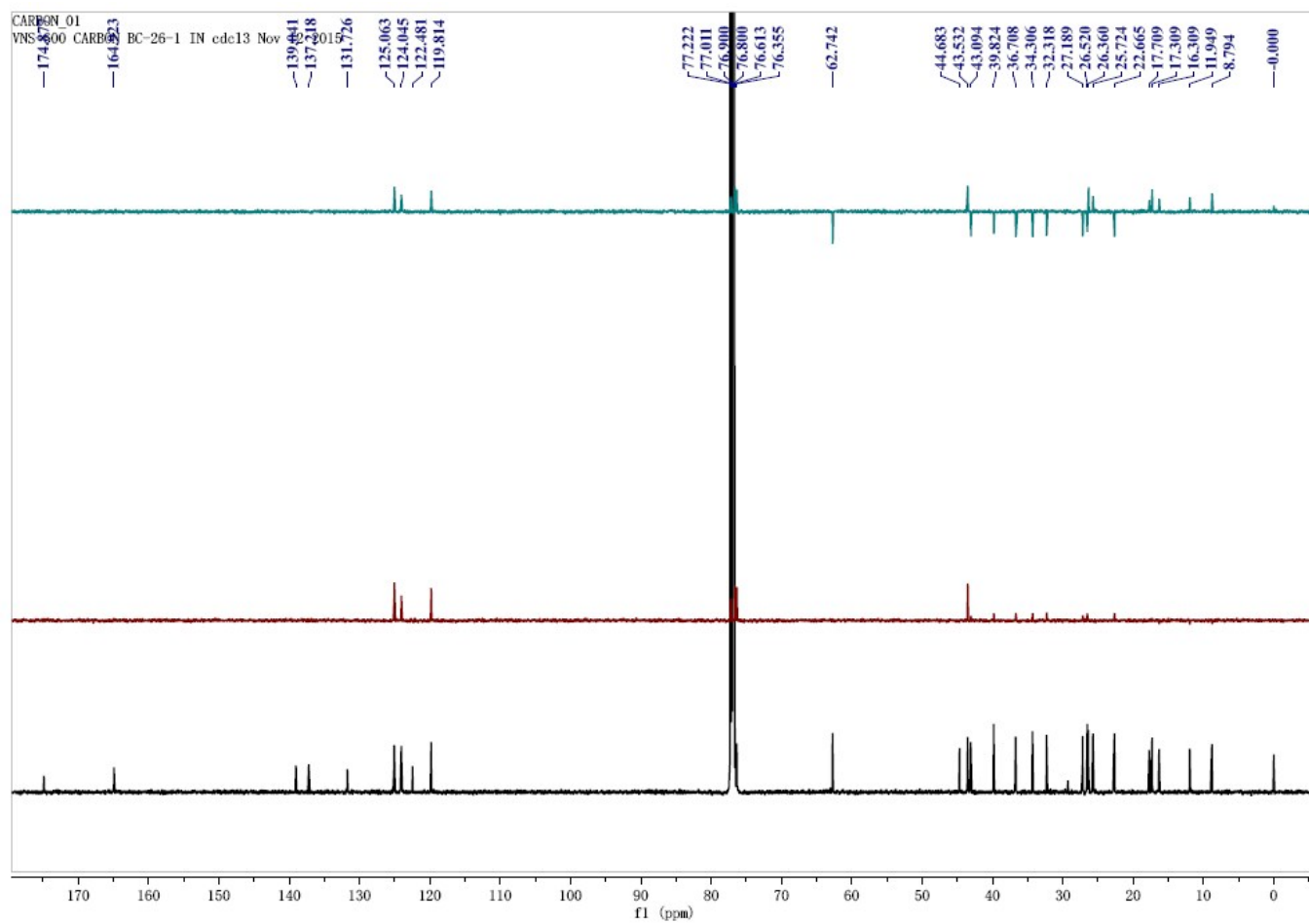


Figure S35. The COSY spectrum of belamcanolide A (4) in CDCl<sub>3</sub>

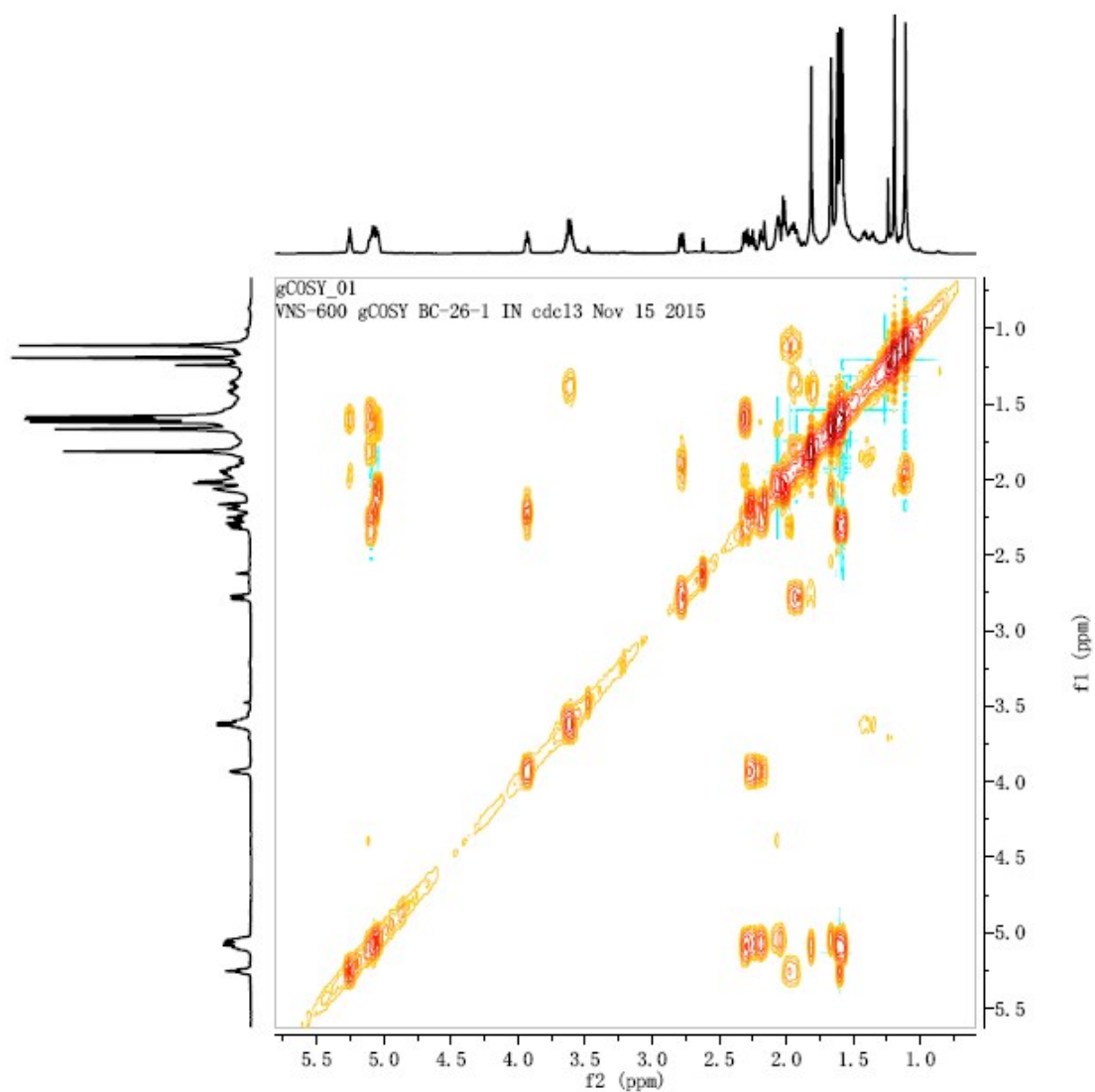


Figure S36. The HMQC spectrum of belamcanolide A (4) in CDCl<sub>3</sub>

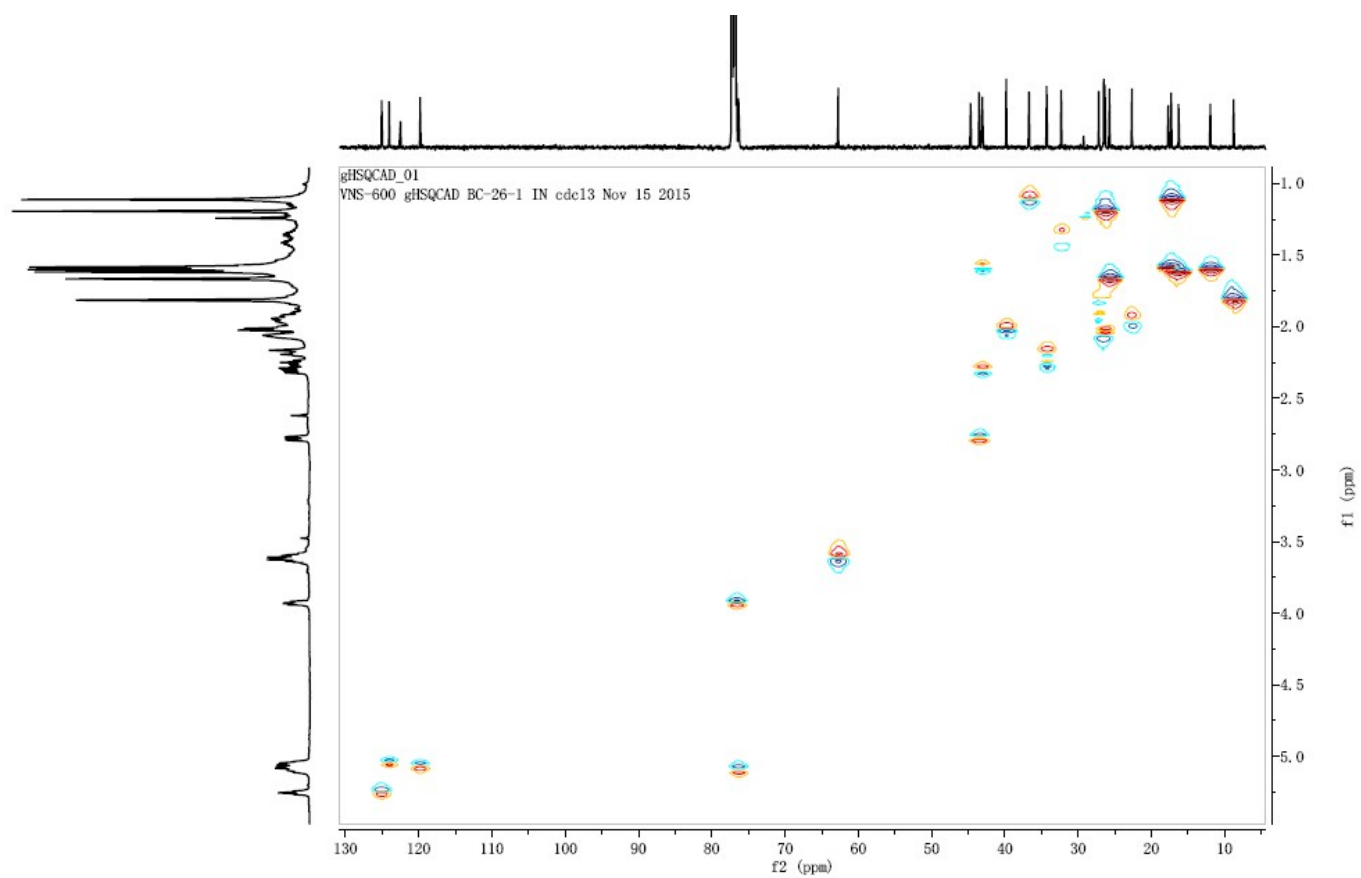


Figure S37. The HMBC spectrum of belamcanolide A (4) in CDCl<sub>3</sub>

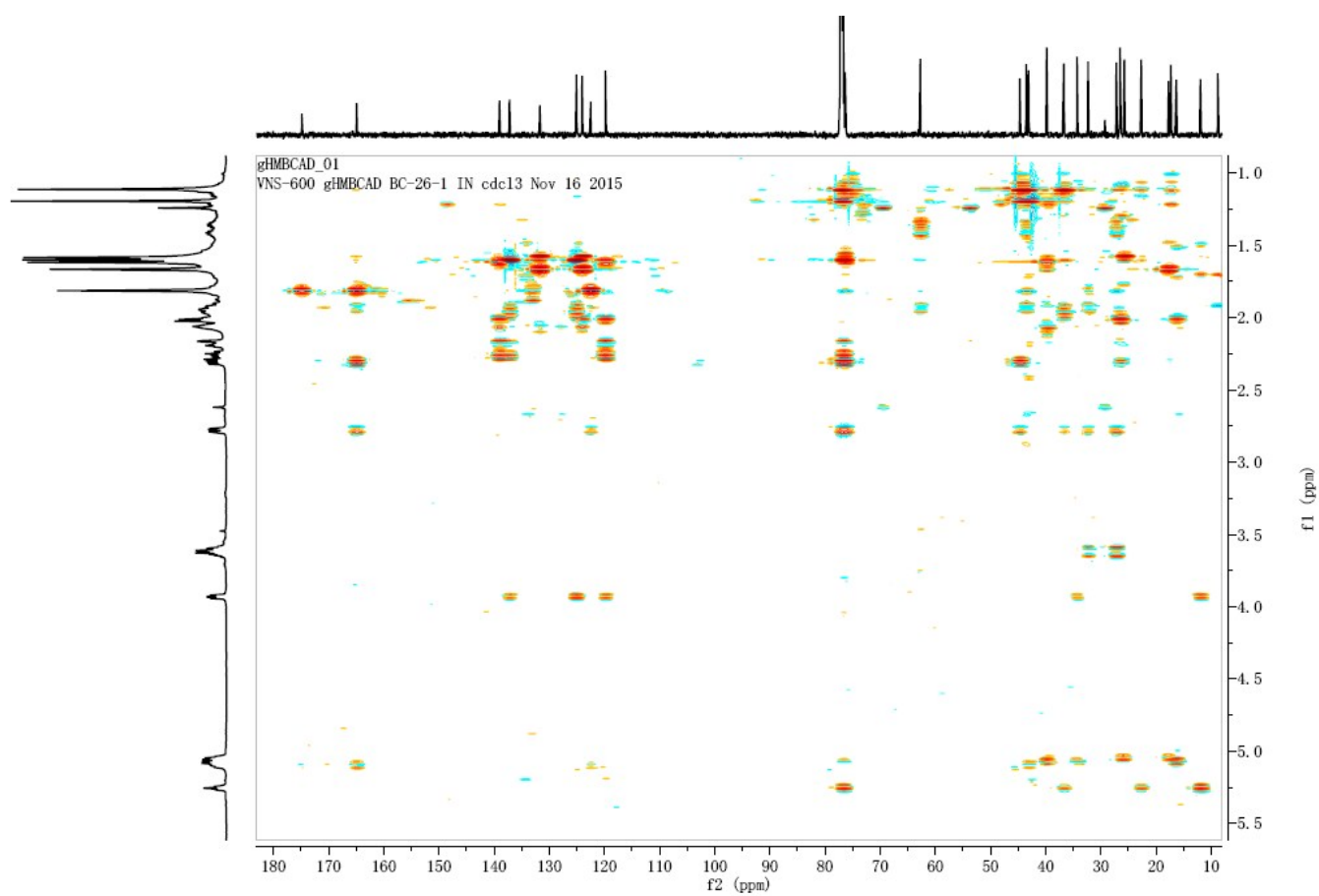
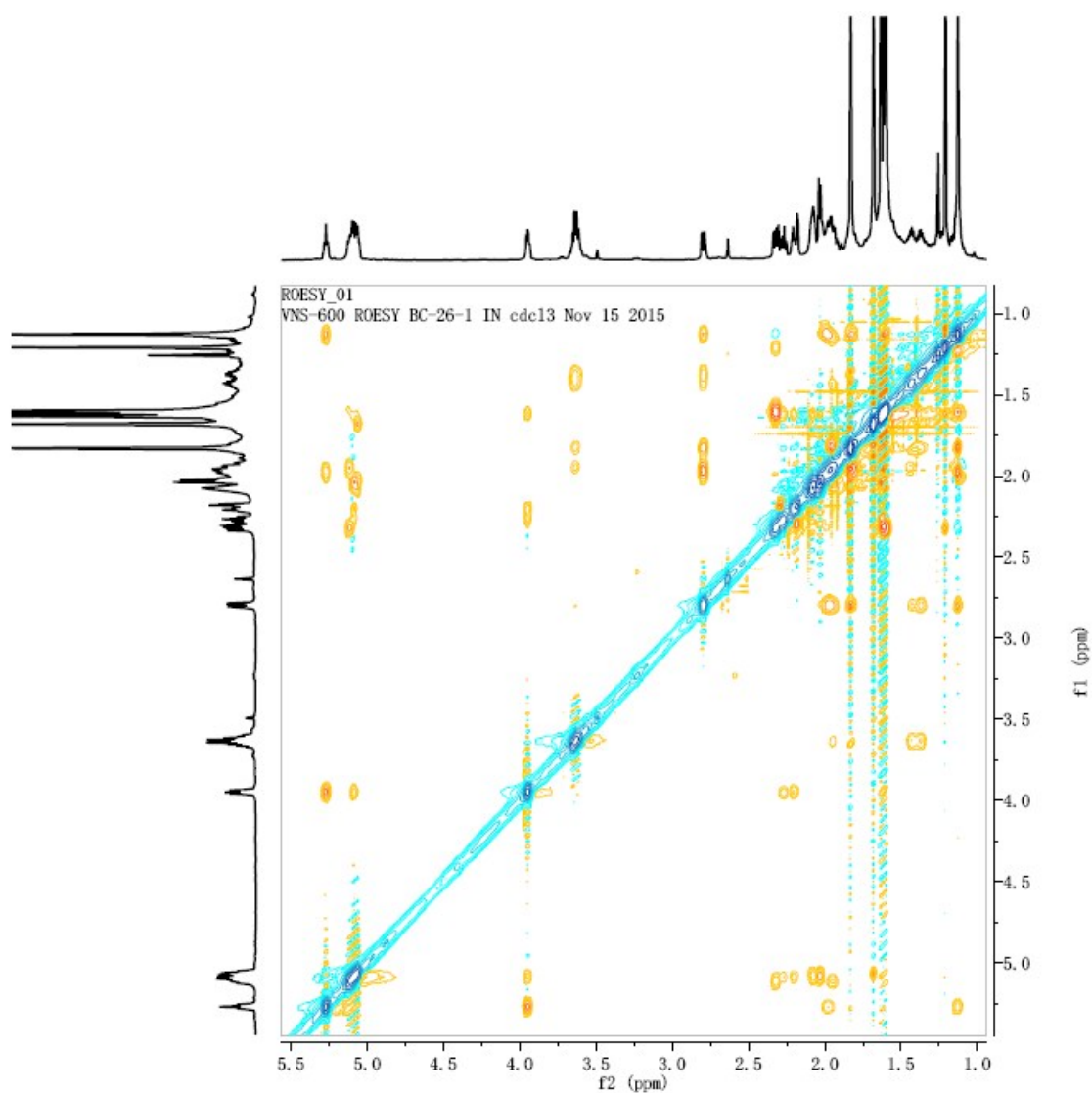
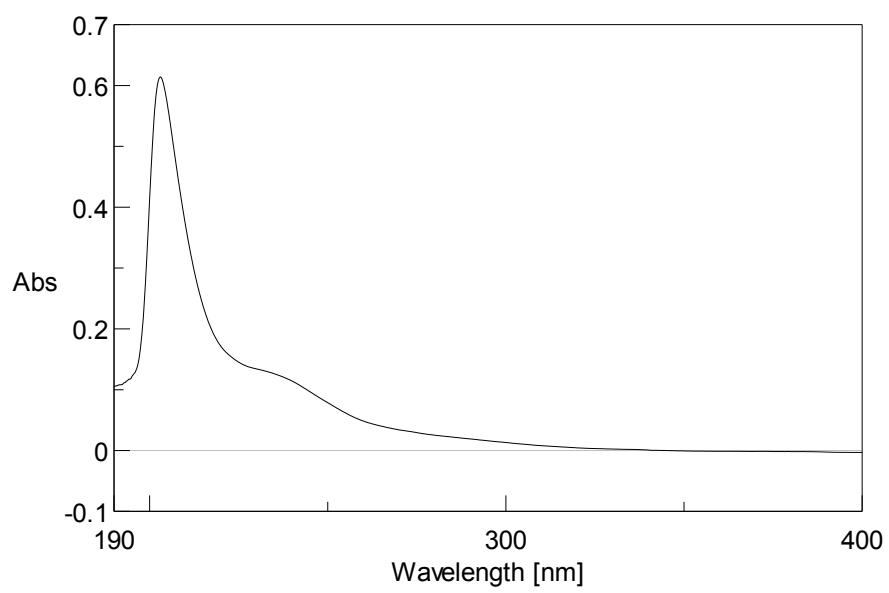




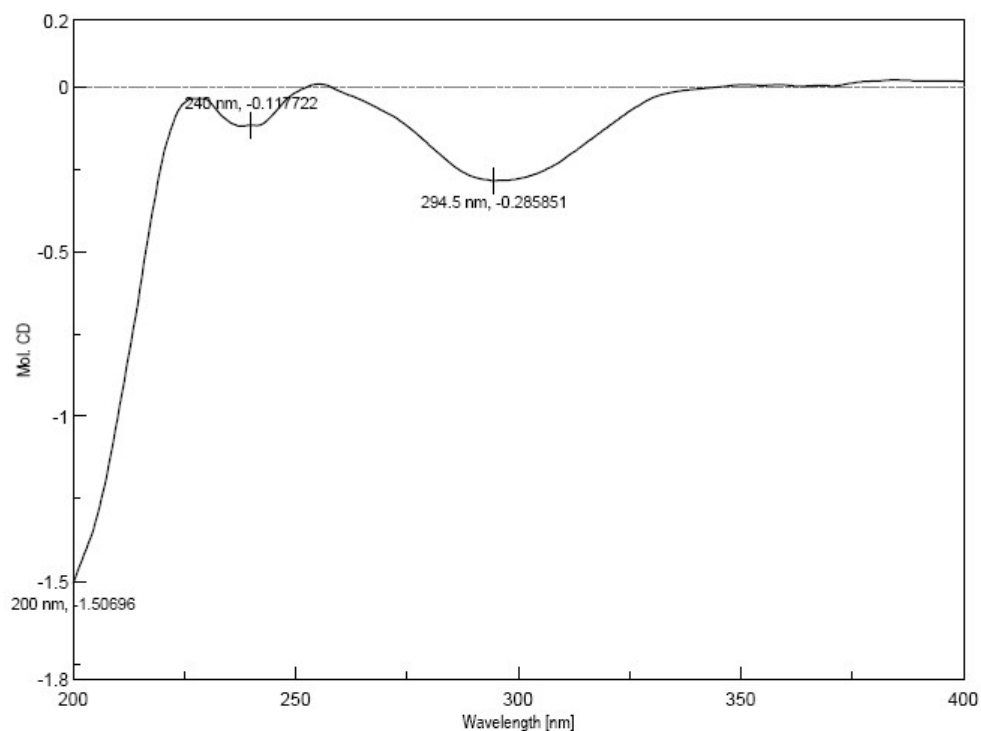
Figure S38. The HMBC spectrum of belamcanolide A (4) in CDCl<sub>3</sub>



**Figure S39. The UV spectrum of belamcanoxide A (5)**



**Figure S40. The CD spectrum of belamcanoxide A (5)**



[Measurement Information]

Instrument Name IMM-CD  
Model Name J-815  
Serial No. A024461168

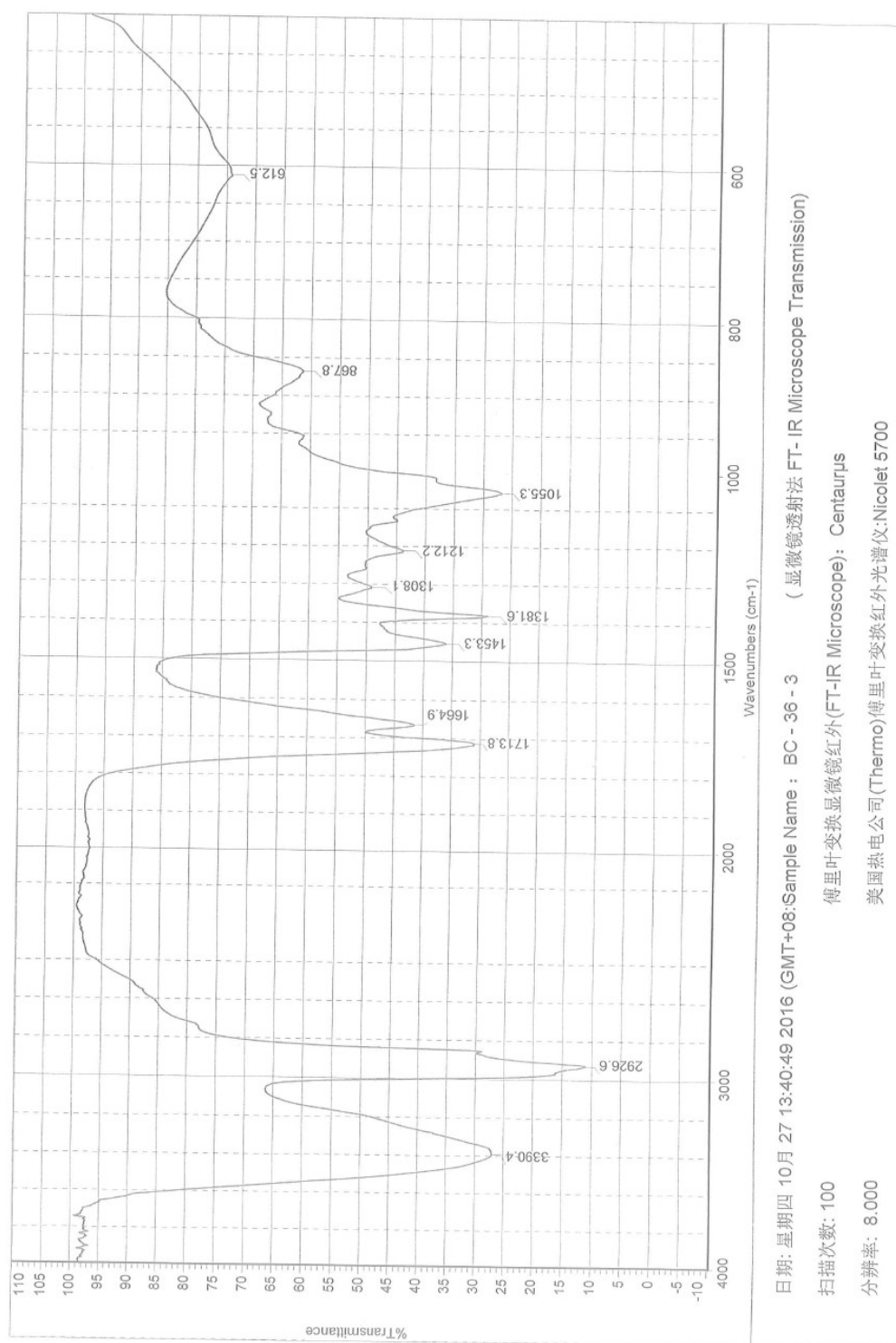
Accessory Standard  
Accessory S/N A024461168  
Cell Length 0.1 mm

Measurement date 2016/10/21 15:34

Photometric Mode CD, HT, Abs  
Measure Range 400 - 200 nm  
Data pitch 0.5 nm  
Sensitivity Standard  
D.I.T. 1 sec  
Bandwidth 2.00 nm  
Start Mode Immediately  
Scanning Speed 100 nm/min  
Baseline Correction Baseline  
Shutter Control Auto  
CD Detector PMT  
PMT Voltage Auto  
Accumulations 2  
Solvent MEOH  
Concentration 0.9 (w/v)%

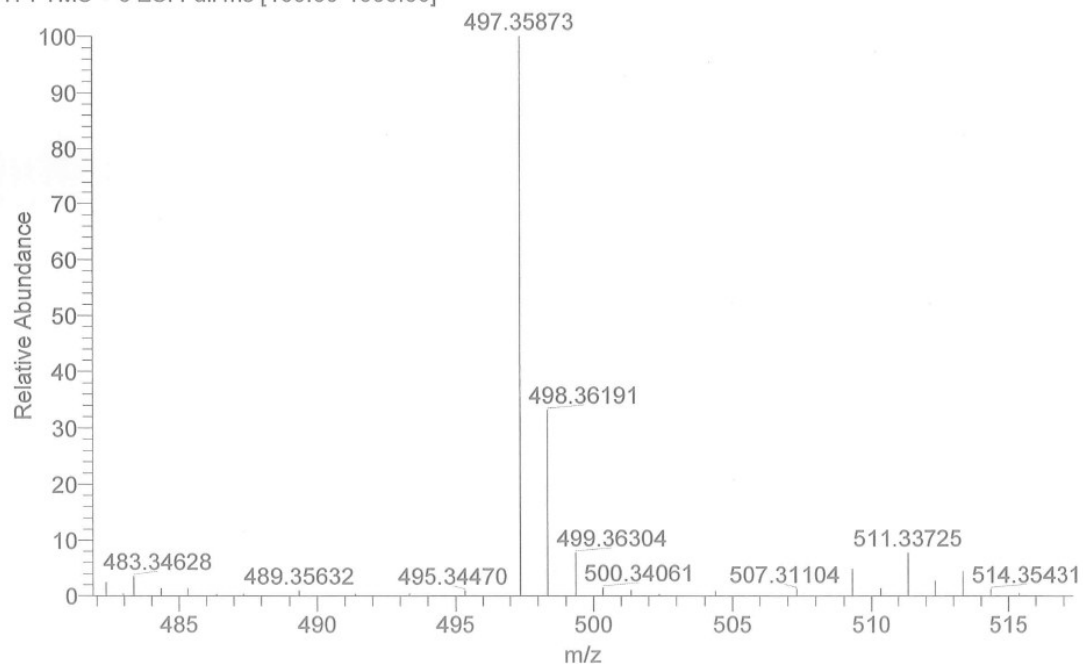
BC-36-2-3-s-m.jws

Figure S41. The IR spectrum of belamcanoxide A (5)



**Figure S42. The HRESI spectrum of belamcanoxide A (5)**

BC-36-2\_161014151703 #1659 RT: 5.51 AV: 1 NL: 3.21E6  
 T: FTMS + c ESI Full ms [100.00-1000.00]



Elemental composition search on mass 497.36

m/z= 492.36-502.36

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
497.35873	497.36013	-2.82	5.5	C <sub>30</sub> H <sub>50</sub> O <sub>4</sub> Na
	497.36254	-7.65	8.5	C <sub>32</sub> H <sub>49</sub> O <sub>4</sub>
	497.37539	-33.49	9.5	C <sub>34</sub> H <sub>50</sub> O <sub>4</sub> Na
	497.34141	34.83	13.5	C <sub>35</sub> H <sub>45</sub> O <sub>2</sub>
	497.37779	-38.33	12.5	C <sub>36</sub> H <sub>49</sub> O

Figure S43. The  $^1\text{H}$  NMR spectrum of belamcanoxide A (5)

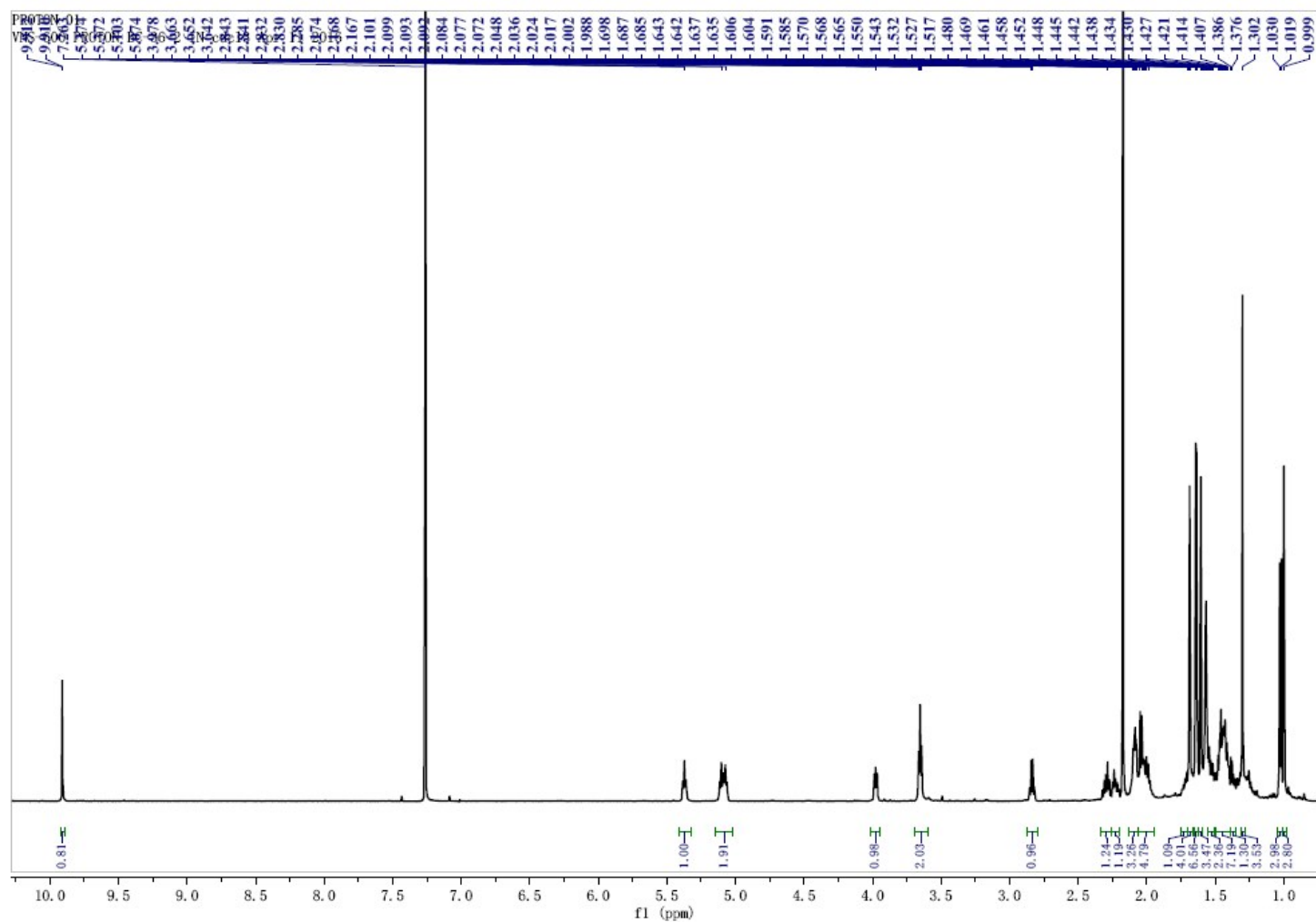


Figure S44. The  $^{13}\text{C}$  NMR spectrum of belamcanoxide A (5)

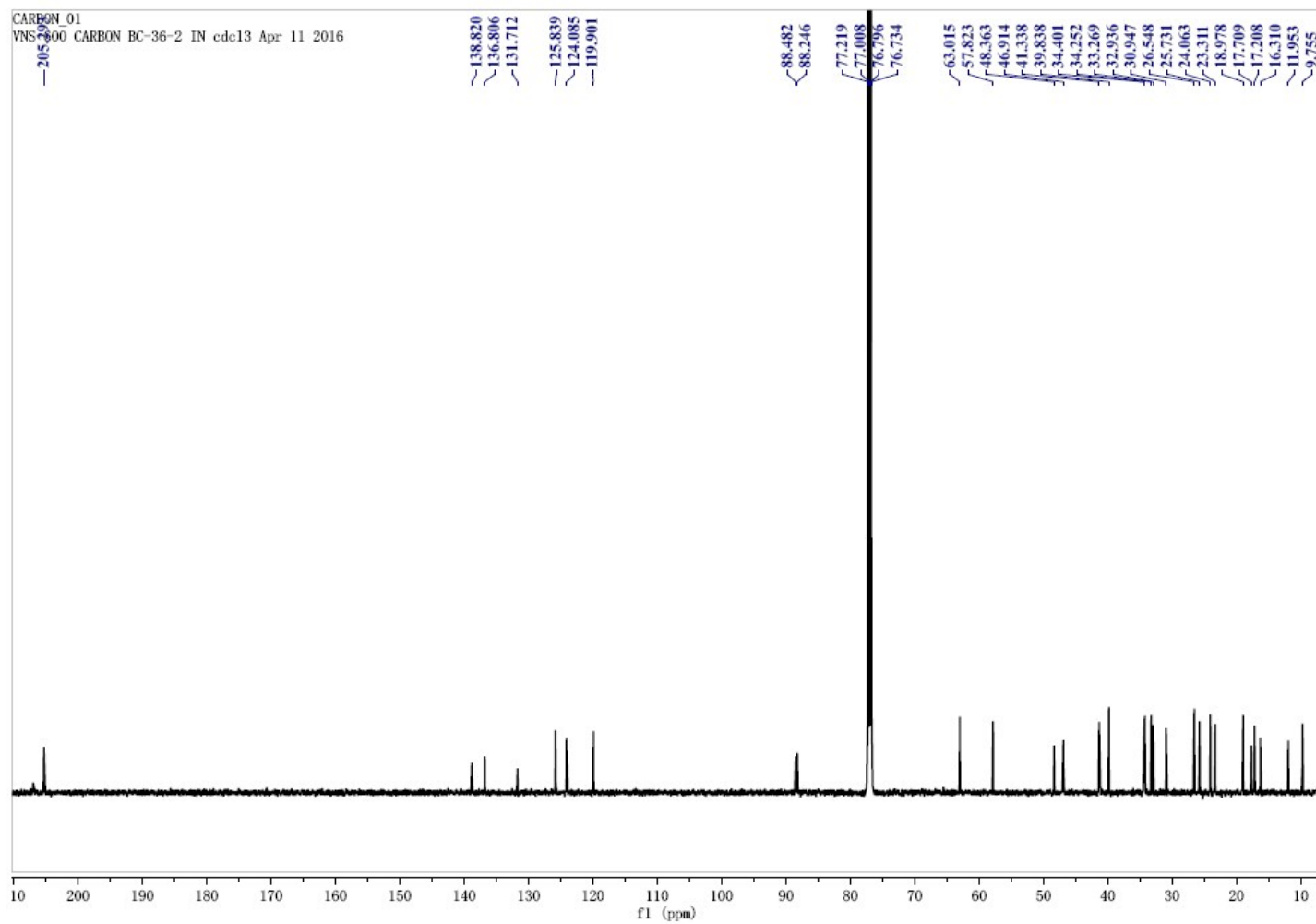


Figure S45. The DEPT NMR spectrum of belamcanoxide A (5)

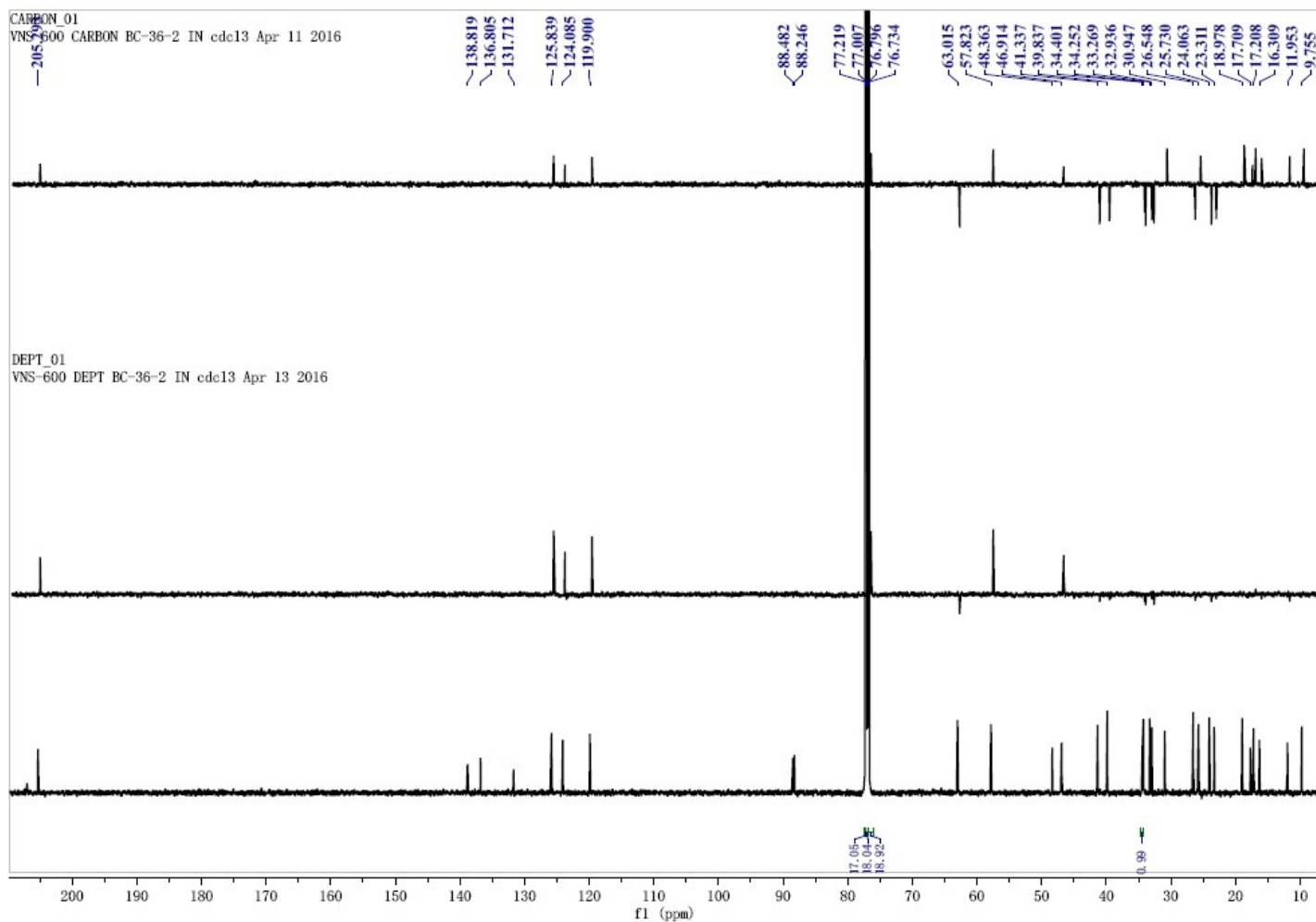
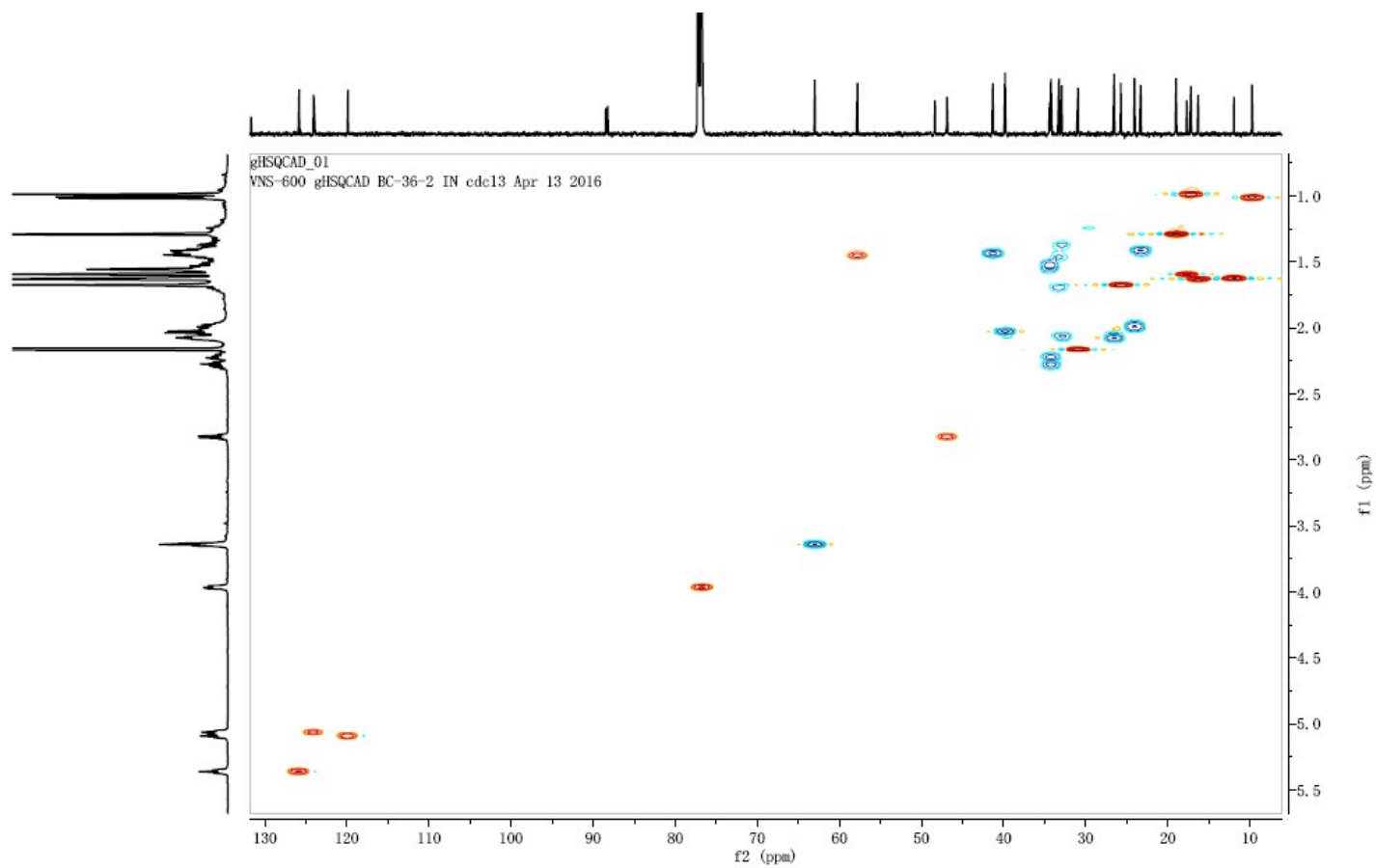
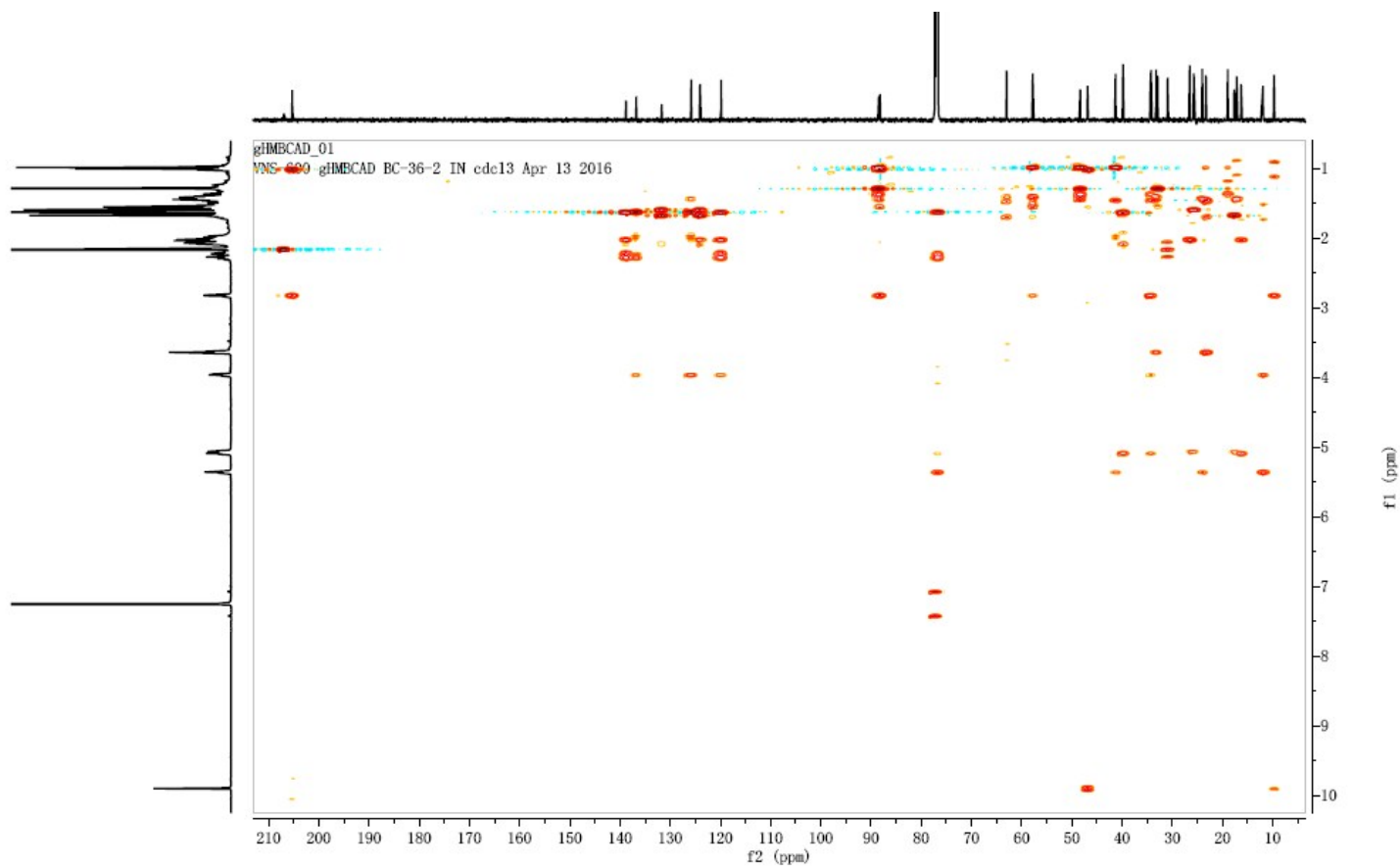




Figure S46. The HMQC spectrum of belamcanoxide A (5)



### S47. The HMBC spectrum of belamcanoxide A (5)



S48. The ROESY spectrum of belamcanoxide A (5)

