# Supporting Information

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## Longiflorol, a bergenin $\alpha$-D-apioside from the stem bark of *Diospyros longiflora*, and its antioxidant activity

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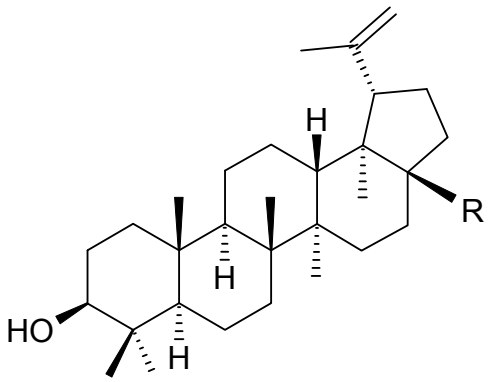
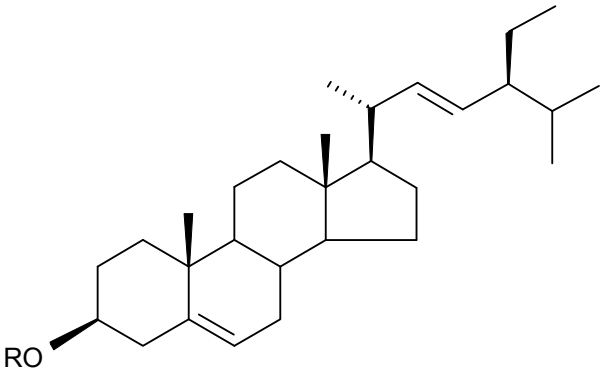
**Abstract:** Phytochemical investigation of the stem bark of *Diospyros longiflora* yielded longiflorol (**1**), a new bergenin $\alpha$-D-apioside, together with bergenin (**2**) and five known compounds, lupeol (**S1**), betulin (**S2**), betulinic acid (**S3**), stigmasterol (**S4**), and stigmasterol glucoside (**S5**). Their structures were determined by 1D and 2D NMR experiments along with

high resolution electrospray ionisation mass spectrometry (ESI-HRMS) and extended DFT calculations of chiroptical properties. Longiflorol (**1**) and bergenin (**2**) were evaluated for their DPPH (2,2-diphenyl-1-picrylhydrazyl) antioxidant activity, with the crude extract for comparison and ascorbic acid as standard. Results showed that the extract and **2** had good antioxidant activity, whereas **1** showed only moderate activity at high concentration (>2 mg $mL^{-1}$).

**Keywords**: Longiflorol*; Diospyros longiflora; Ebenaceae*; antioxidant activity; ECD calculations

# Content




**S1** : R = $CH_3$, Lupeol
**S2** : R = $CH_2OH$, Betulin
**S3** : R = COOH, Betulinic acid
**S4** : R = H, Stigmasterol
**S5** : R = Glc, Stigmasterol glucoside

**Figure S1:** Known compounds isolated from *Diospyros longiflora*

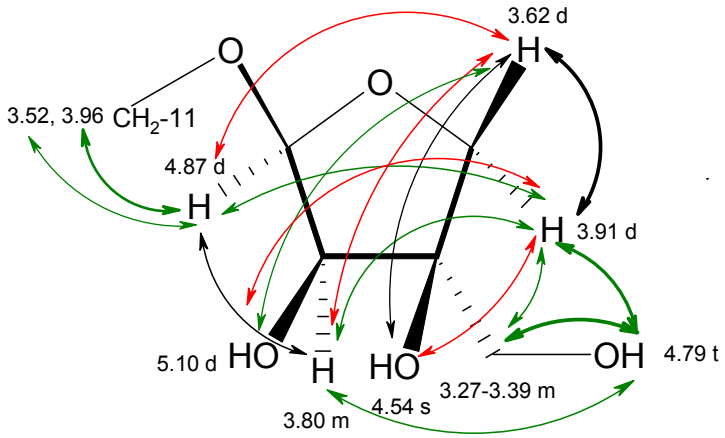



**Figure S2:** NOESY correlations in the D-apio-$\alpha$-D-furanose part of longiflorol (**1**).
Color of correlation arrows: black = trivial; green = visible and expected; red = not visible and unexpected for **1**. The line strength reflects the correlation intensity.

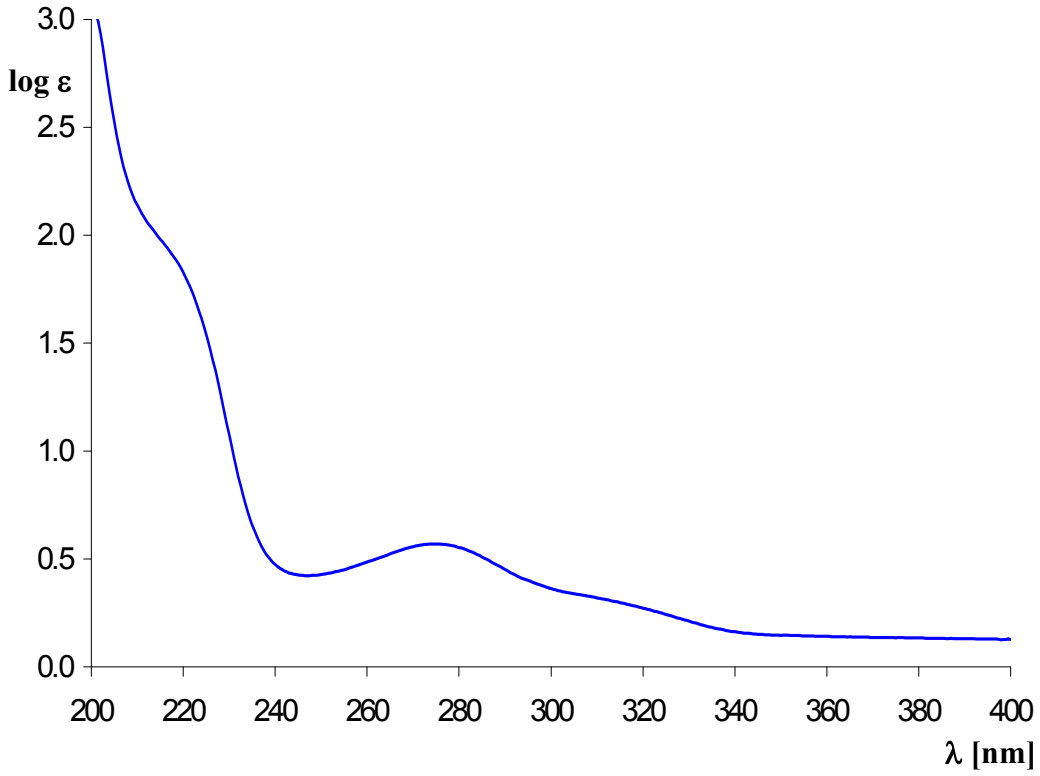



**Figure S3**: UV/Vis spectrum of longiflorol (**1**) in methanol

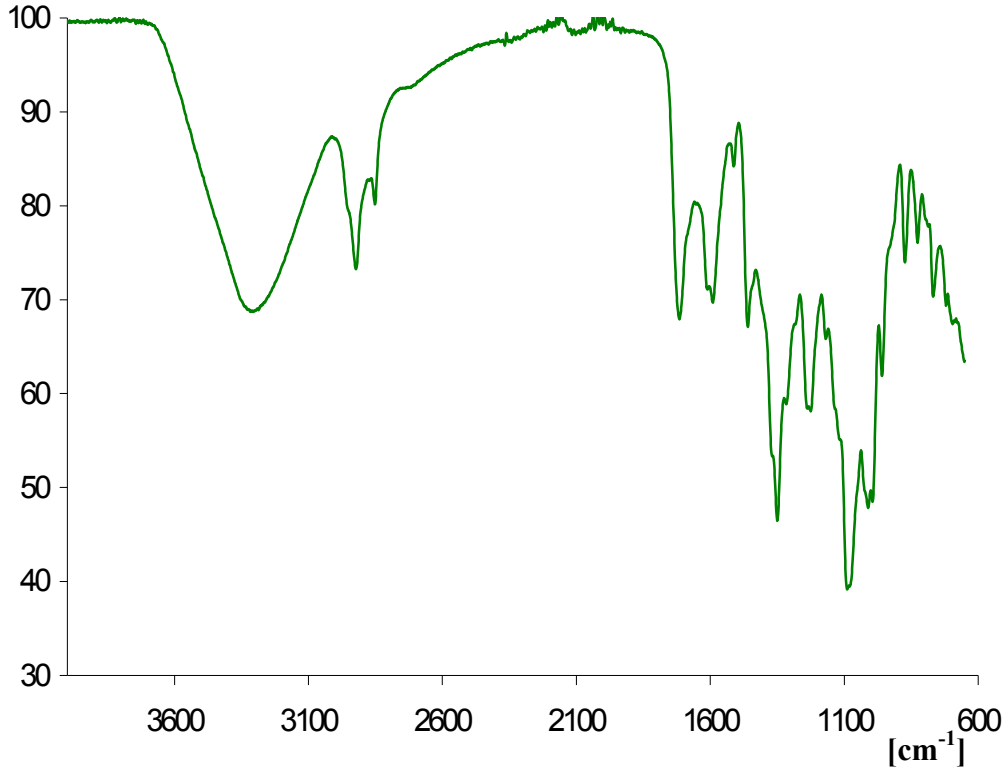



**Figure S4:** IR spectrum (neat, on diamond) of longiflorol (**1**)

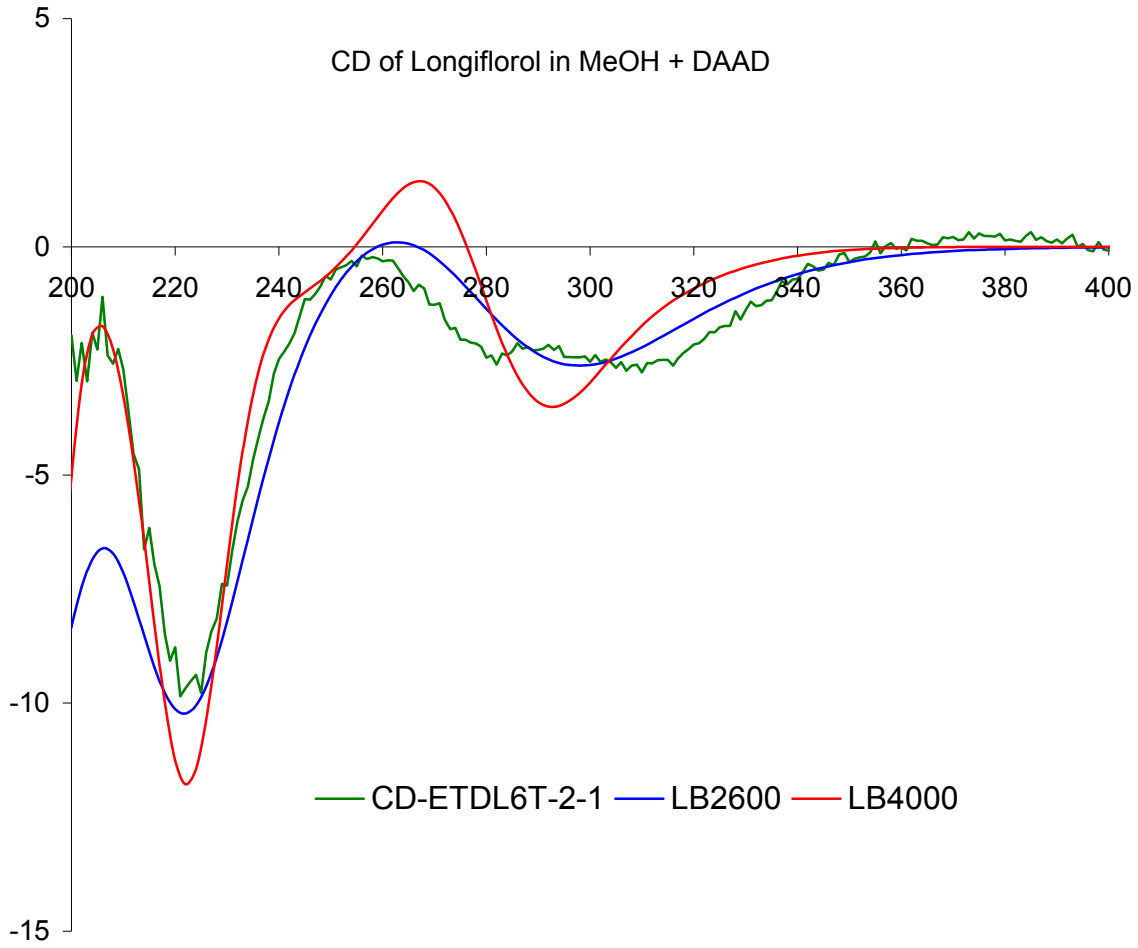



**Figure S5:** Experimental CD spectrum of **1** (green), in comparison with the calculated spectrum (blue, red) of D-apio-$\alpha$-D-furanosyl)-bergenin, DAAD); LB = line broadness [$cm^{-1}$]. Calcd. OR (589 nm) = –228.4°.

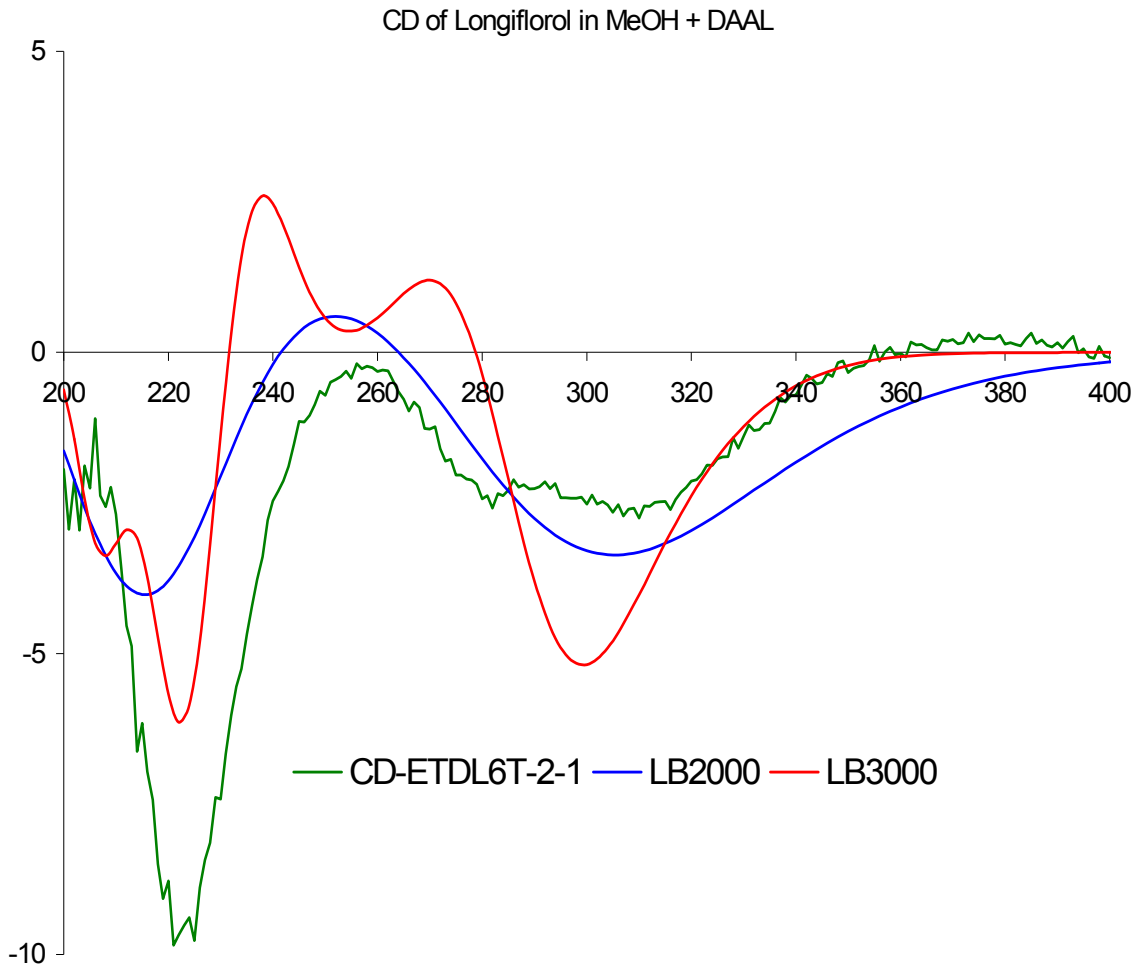



**Figure S6:** Experimental CD spectrum of **1** (green), in comparison with the calculated spectrum (blue, red) of D-apio-$\alpha$-L-furanosyl)-bergenin (DAAL); LB = line broadness [$cm^{-1}$]; Calcd. OR (589 nm) = –190.5°.

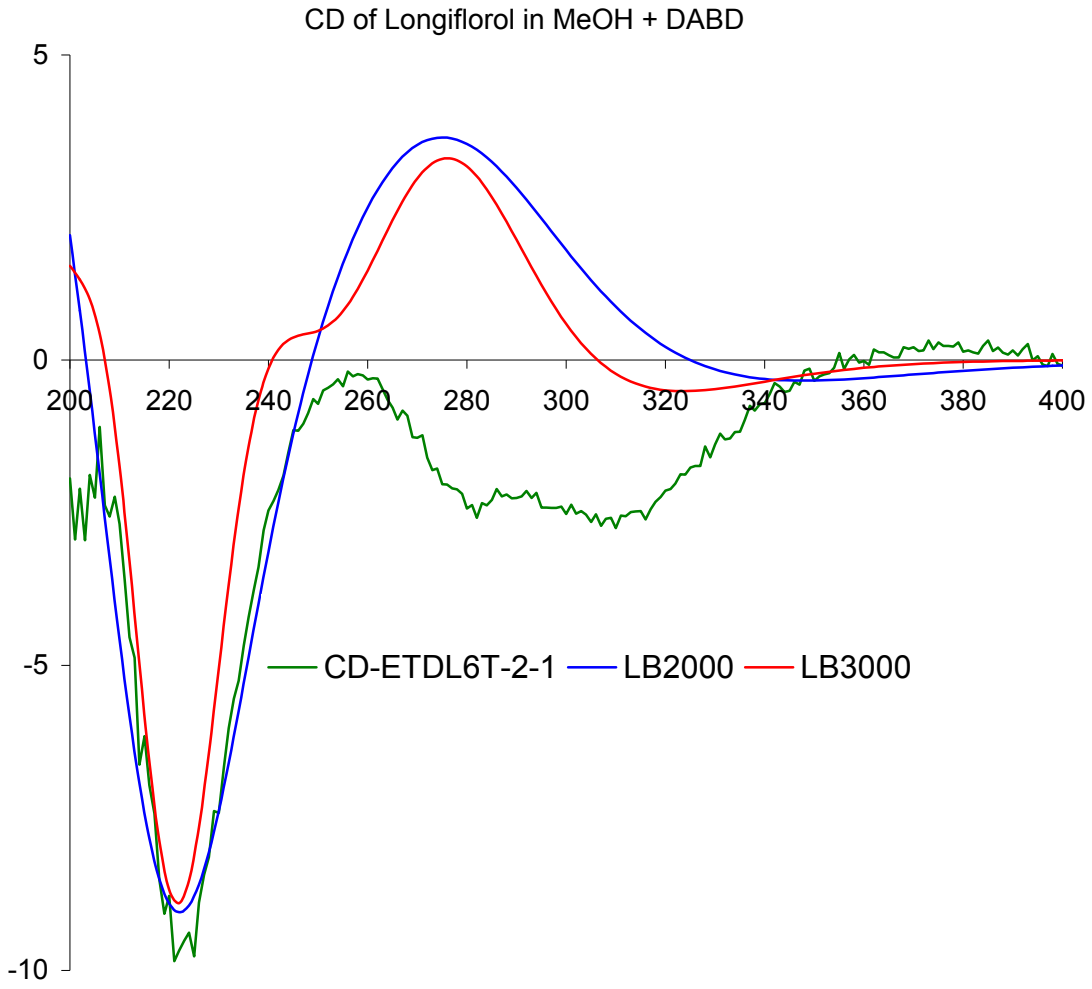



**Figure S7:** Experimental CD spectrum of **1** (green), in comparison with the calculated spectrum (blue, red) of D-apio-*β*-D-furanosyl)-bergenin (DABD); LB = line broadness [$cm^{-1}$]; Calcd. OR (589 nm) = +39.3°.

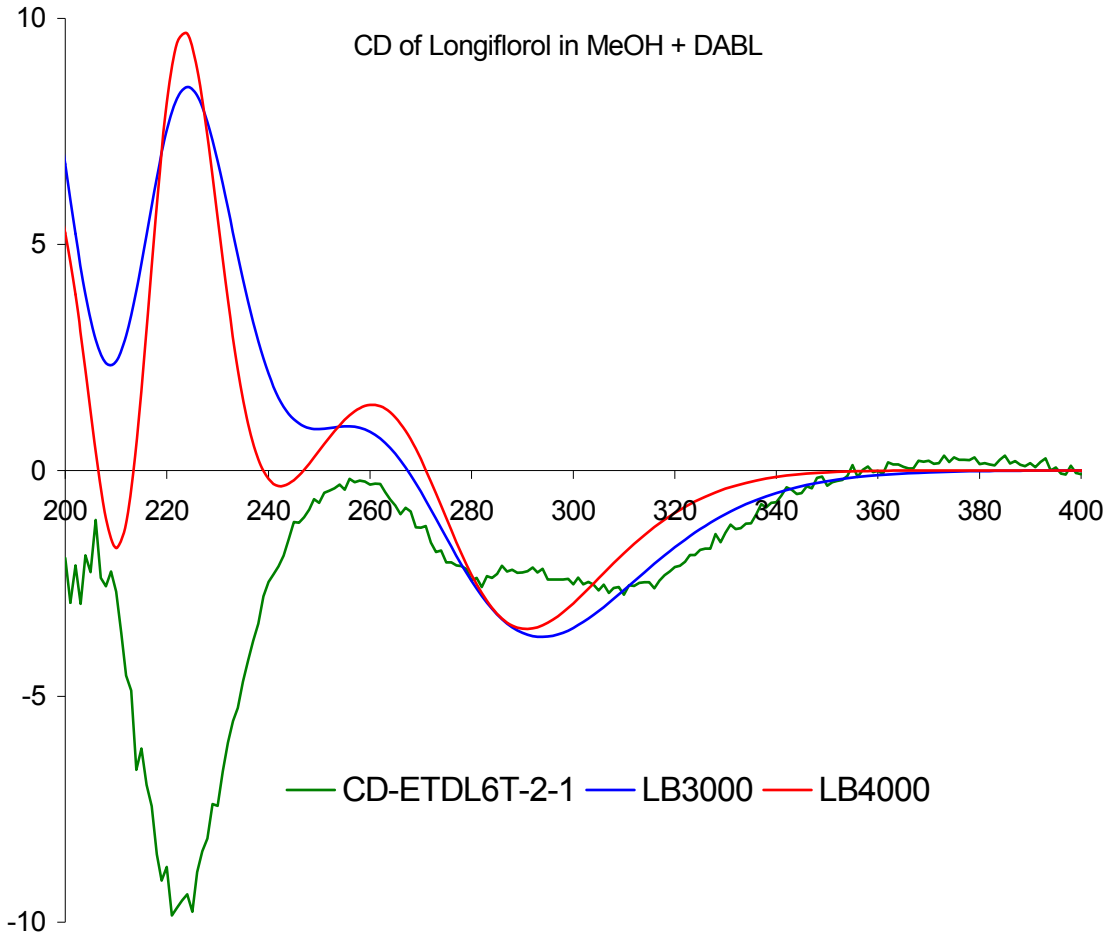



Figure S8: Experimental CD spectrum of **1** (green), in comparison with the calculated spectrum (blue, red) of D-apio-*β*-L-furanosyl)-bergenin (DABL); LB = line broadness [$cm^{-1}$]; Calcd. OR (589 nm) = –190.5°; Calcd. OR (589 nm) = +166.8°.

Table S1: Experimental $^{13}C$ NMR shifts (125 MHz, DMSO-$d_6$) of longiflorol (**1**) in comparison with shifts calculated for DAAD = D-*apio*-$\alpha$-D-furanosyl)-bergenin = **1** and three further diastereomers: DAAL = D-*apio*-$\alpha$-L-furanosyl)-bergenin; DABD = D-*apio*-$\beta$-D-furanosyl)-bergenin, and DABL = D-*apio*-$\beta$-L-furanosyl)-bergenin; $\Delta\delta$ = sum of abs. values of (experimental – calculated) $^{13}C$ shifts.

| atom no. | $\delta_C$ exp | $\delta$ DAAD | $\Delta\delta$ | $\delta$ DAAL | $\Delta\delta$ | $\delta$ DABD | $\Delta\delta$ | $\delta$ DABL | $\Delta\delta$ |
|---|---|---|---|---|---|---|---|---|---|
| 2 | **79.0** | 79.57 | 0.57 | 78.10 | 0.90 | 79.34 | 0.34 | 78.98 | 0.02 |
| 3 | **70.7** | 67.85 | 2.85 | 69.21 | 1.49 | 72.63 | 1.93 | 71.25 | 0.55 |
| 4 | **73.5** | 74.85 | 1.35 | 75.23 | 1.73 | 76.48 | 2.98 | 75.92 | 2.42 |
| 4a | **79.2** | 78.20 | 1.00 | 78.95 | 0.25 | 79.08 | 0.12 | 78.51 | 0.69 |
| 6 | **163.3** | 162.37 | 0.93 | 161.75 | 1.55 | 161.64 | 1.66 | 161.59 | 1.71 |
| 6a | **118.0** | 120.35 | 2.35 | 118.22 | 0.22 | 119.72 | 1.72 | 119.39 | 1.39 |
| 7 | **109.4** | 109.39 | 0.01 | 110.32 | 0.92 | 110.69 | 1.29 | 110.84 | 1.44 |
| 8 | **151.0** | 153.15 | 2.15 | 152.43 | 1.43 | 153.06 | 2.06 | 153.49 | 2.49 |
| 9 | **140.5** | 136.70 | 3.80 | 138.26 | 2.24 | 136.96 | 3.54 | 136.94 | 3.56 |
| 10 | **148.0** | 152.68 | 4.68 | 146.91 | 1.09 | 148.55 | 0.55 | 149.13 | 1.13 |
| 10a | **115.7** | 114.79 | 0.91 | 112.05 | 3.65 | 112.50 | 3.20 | 111.23 | 4.47 |
| 10b | **72.0** | 72.74 | 0.74 | 73.45 | 1.45 | 73.61 | 1.61 | 73.84 | 1.84 |
| 11 | **67.8** | 69.11 | 1.31 | 60.27 | 7.53 | 68.04 | 0.24 | 67.39 | 0.41 |
| 12-OMe | **59.8** | 59.52 | 0.28 | 61.17 | 1.37 | 58.89 | 0.91 | 58.31 | 1.49 |
| 1' | **109.1** | 112.22 | 3.12 | 106.49 | 2.61 | 110.97 | 1.87 | 104.23 | 4.87 |
| 2' | **75.9** | 75.25 | 0.65 | 83.48 | 7.58 | 79.67 | 3.77 | 83.51 | 7.61 |
| 3' | **78.7** | 77.82 | 0.88 | 83.26 | 4.56 | 79.35 | 0.65 | 77.49 | 1.21 |
| 4' | **73.4** | 74.03 | 0.63 | 75.97 | 2.57 | 74.17 | 0.77 | 73.80 | 0.40 |
| 5' | **62.9** | 67.00 | 4.10 | 65.77 | 2.87 | 65.83 | 2.93 | 68.60 | 5.70 |
| | | **$\Sigma\lvert\Delta\delta\rvert$ =** | **32.31** | | **46.01** | | **32.13** | | **43.37** |

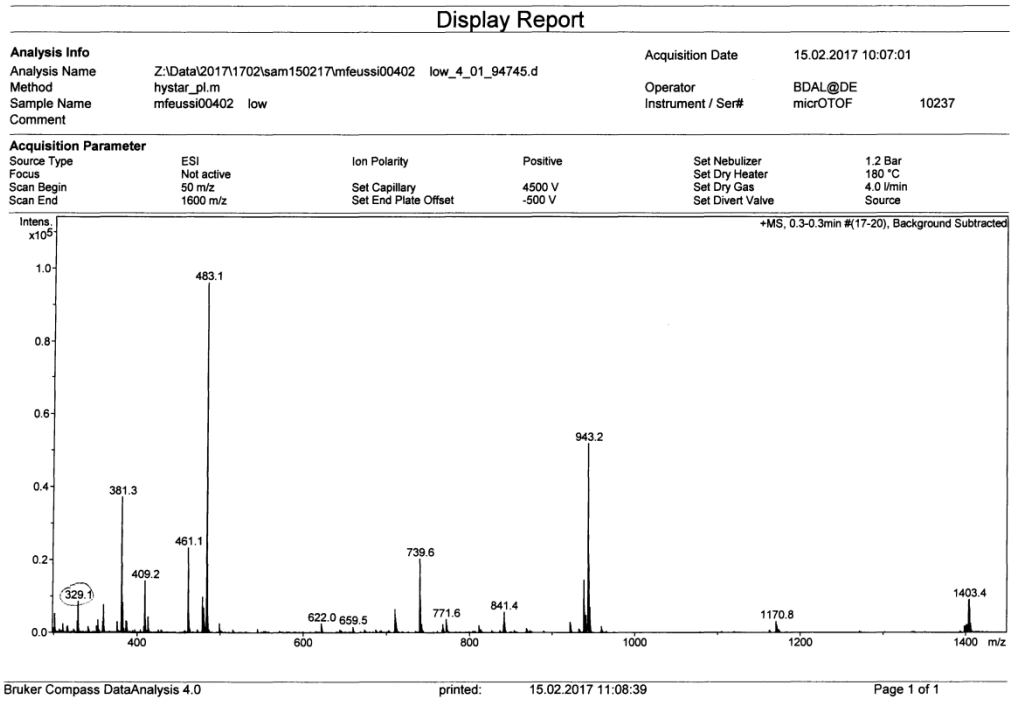



**Figure S9:** (+)-ESI mass spectrum of longiflorol (**1**)

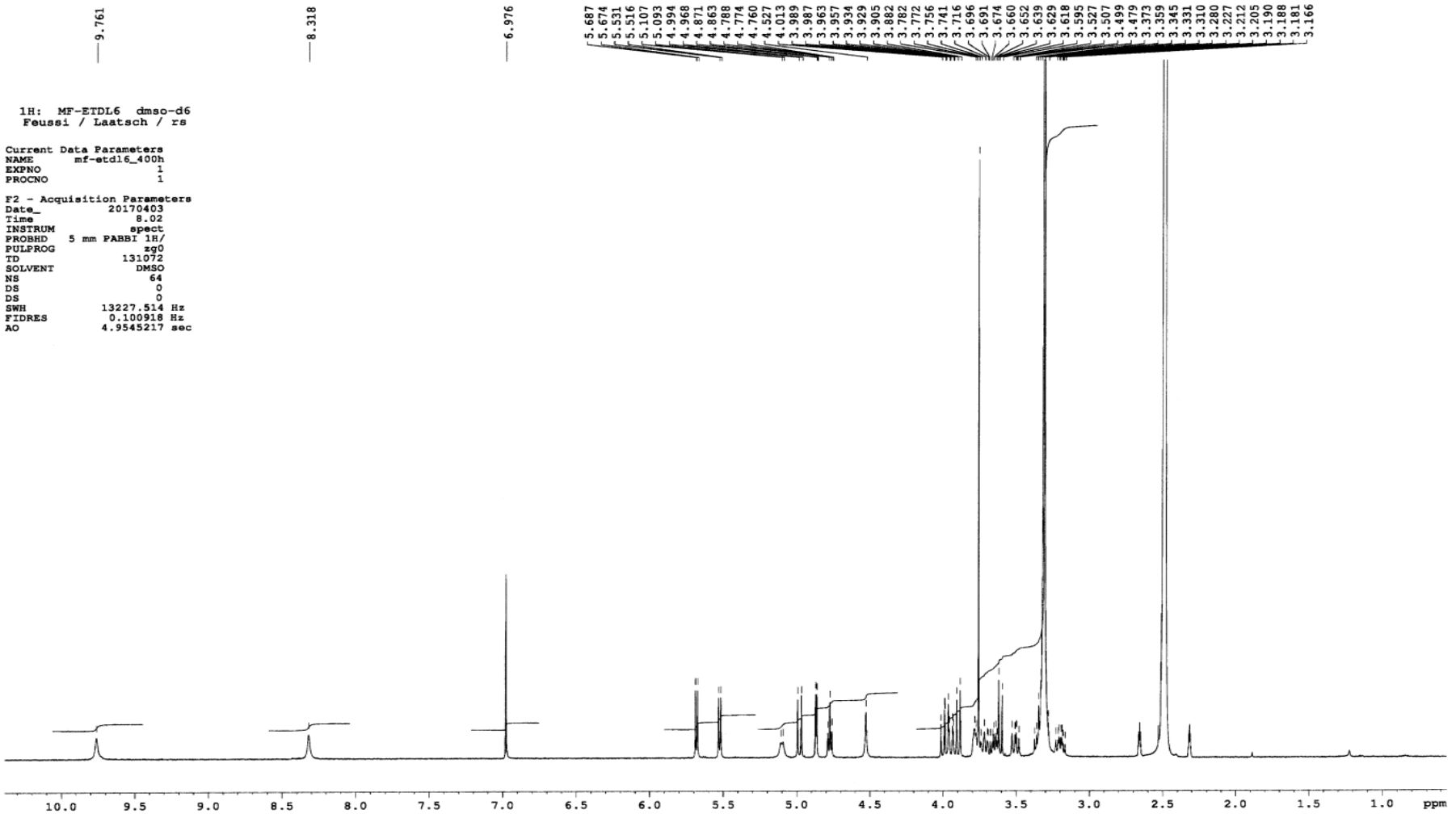



**Figure S10:** $^{1}$H NMR spectrum of longiflorol (**1**) in DMSO-$d_6$ at 400 MHz

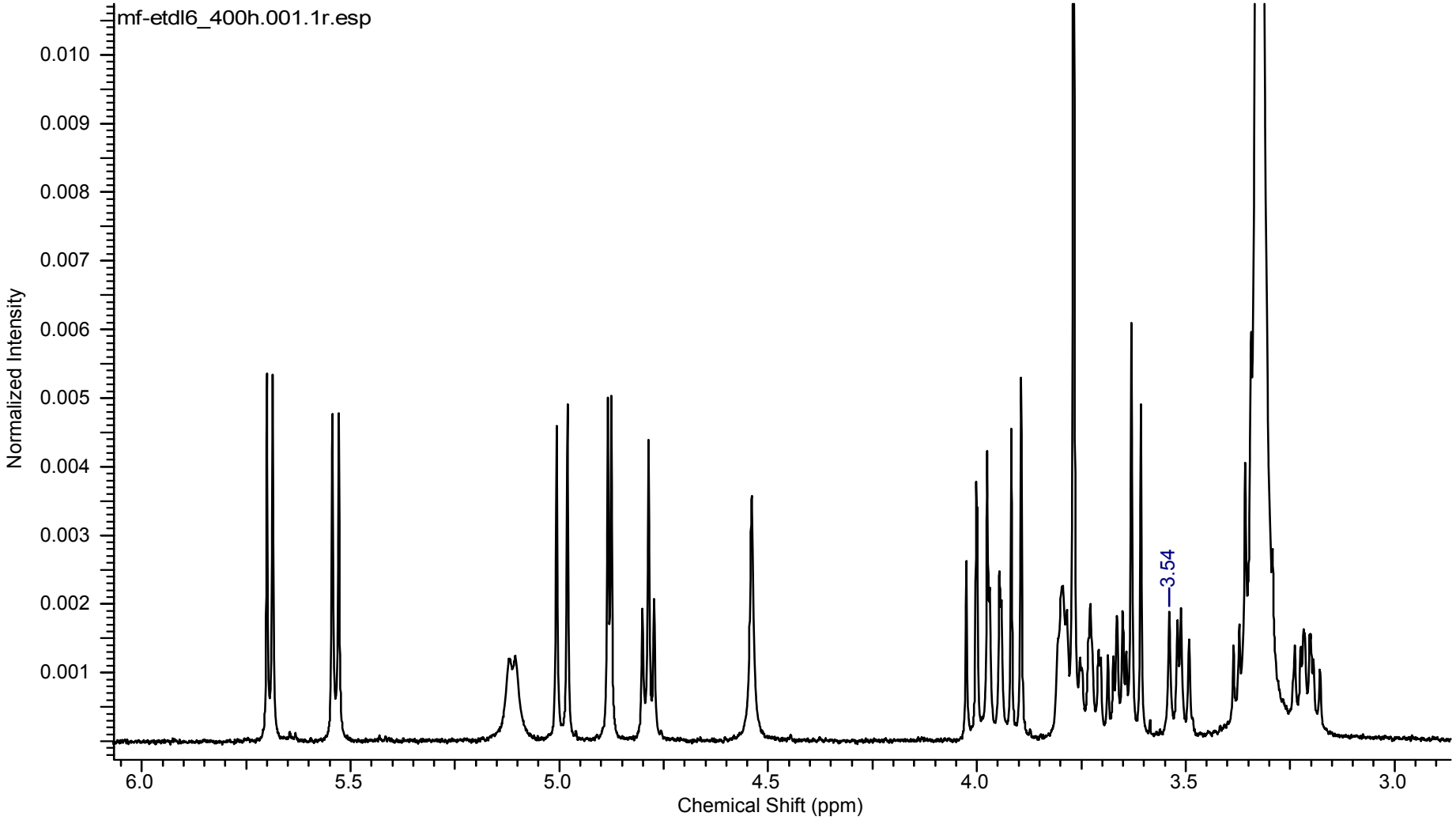



**Figure S11:** Expanded $^{1}$H NMR spectrum of longiflorol (**1**) in DMSO-$d_6$ at 400 MHz

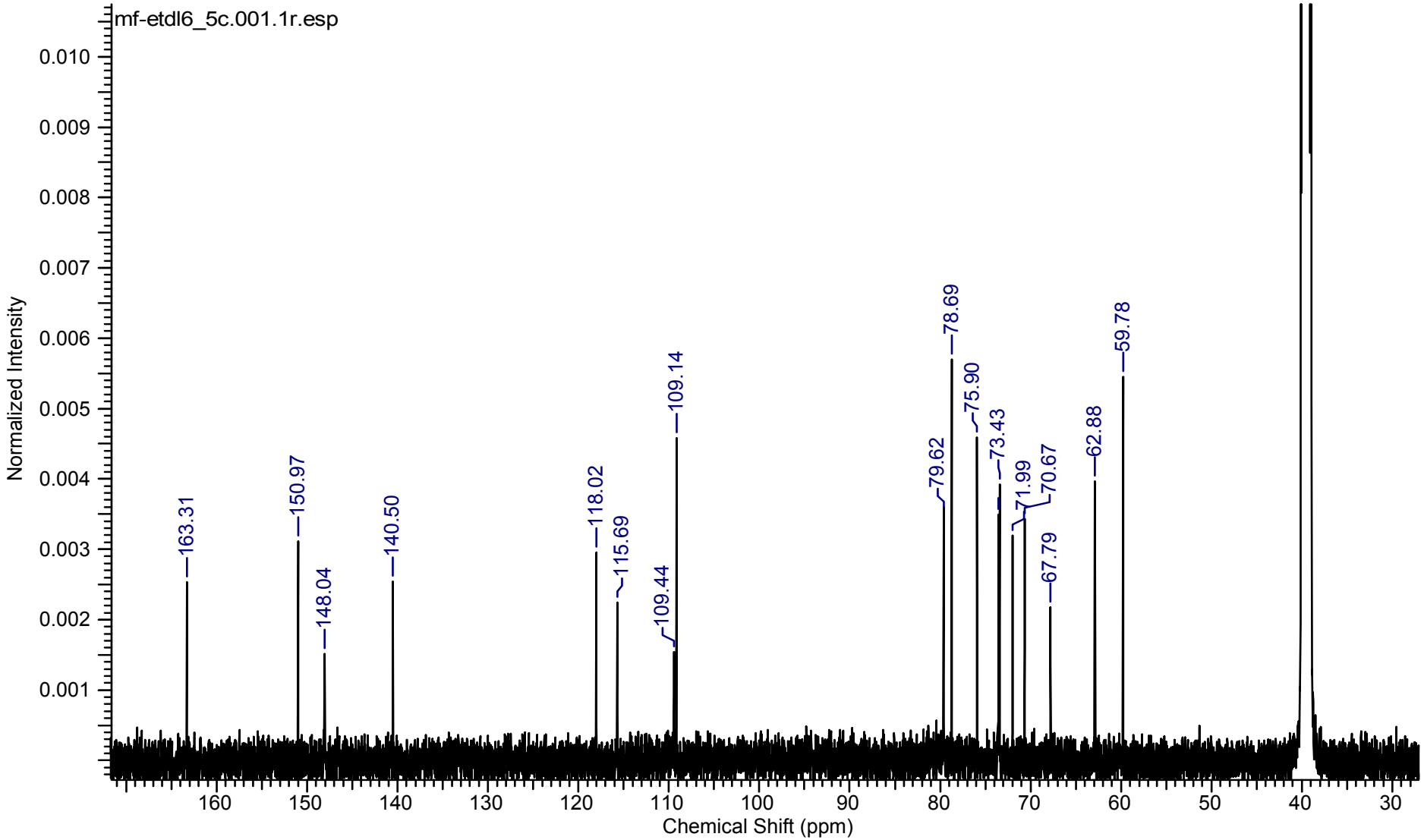



**Figure S12:** $^{13}$C NMR spectrum of longiflorol (**1**) in DMSO-$d_6$ at 125 MHz

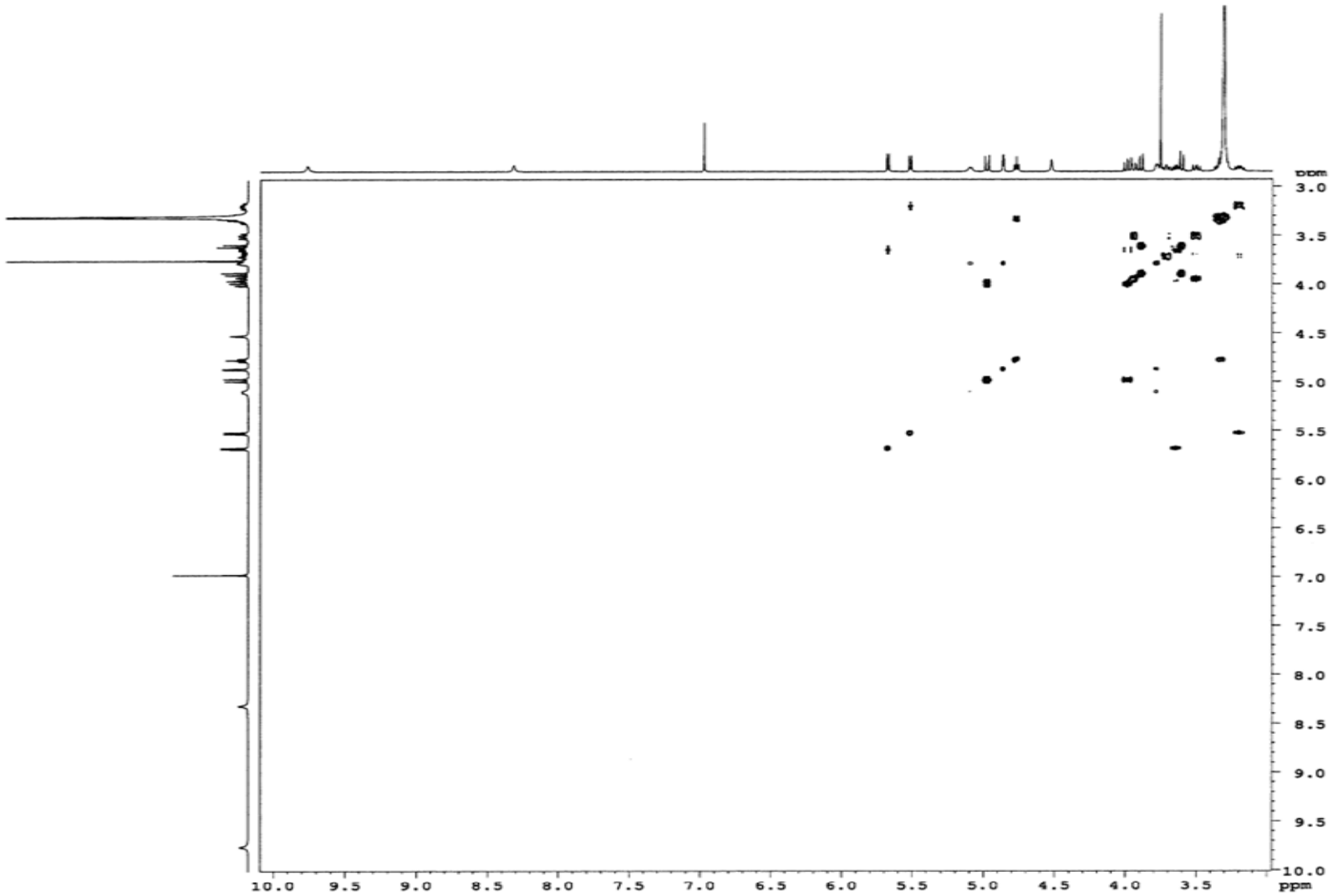



**Figure S13:** COSY NMR spectrum of longiflorol (**1**) in DMSO-$d_6$

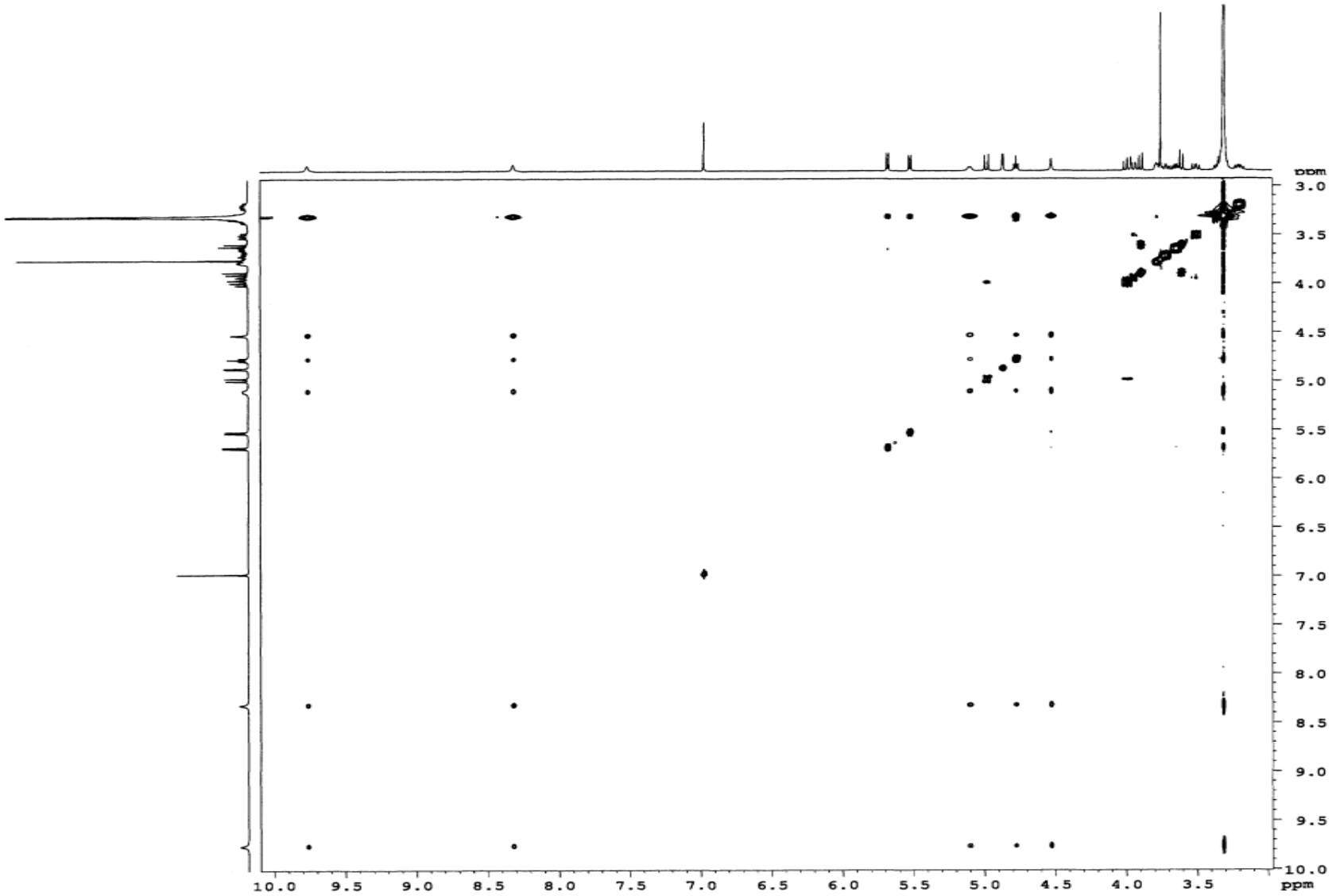



**Figure S14:** NOESY spectrum of longiflorol (**1**) in DMSO-$d_6$

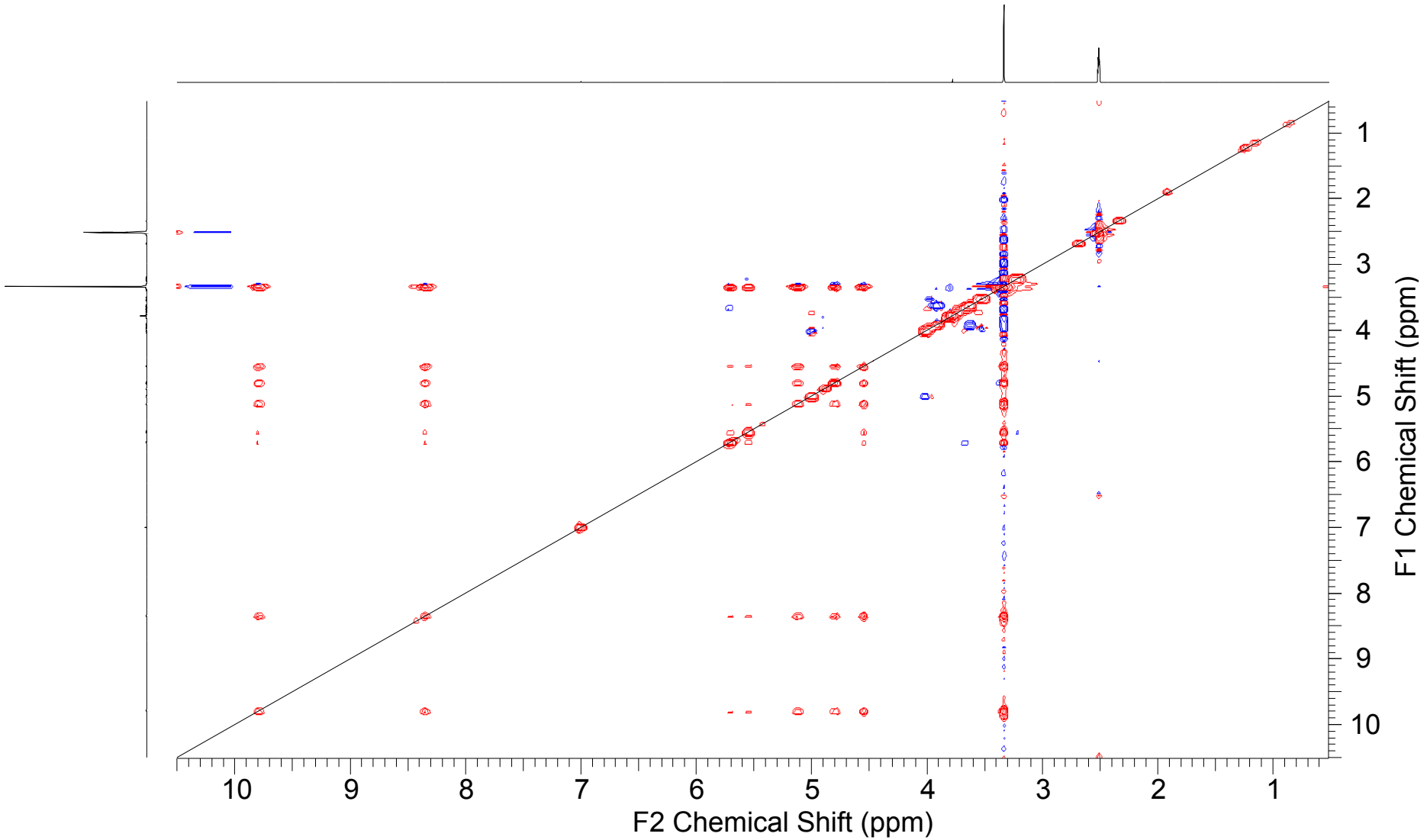



**Figure S15:** NOESY spectrum of longiflorol (**1**) in DMSO-$d_6$; ref spots = OH/OH and H,H correlations, blue spots = H/OH correlations

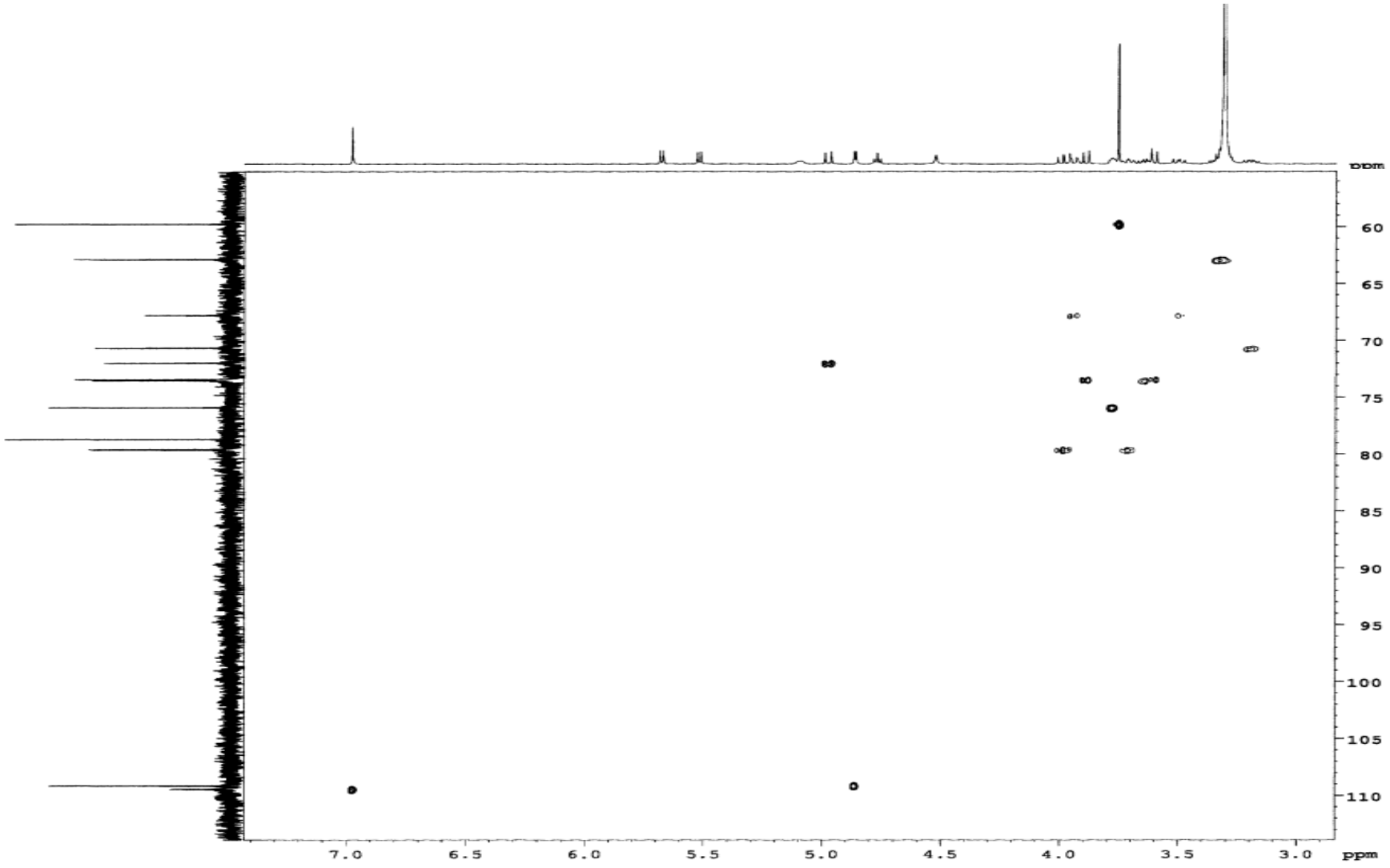



**Figure S16:** HSQC spectrum of longiflorol (**1**) in DMSO-$d_6$

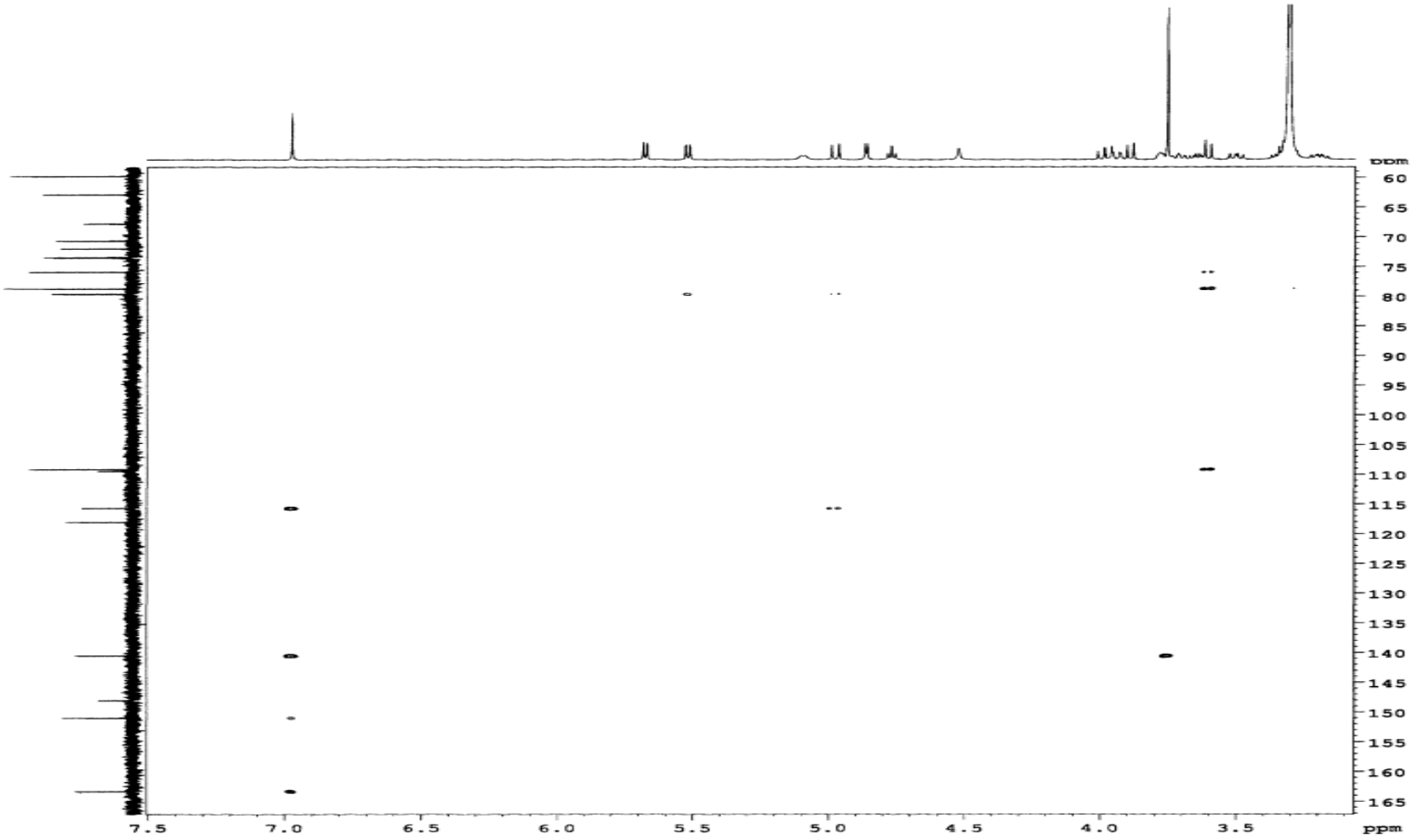



**Figure S17:** HMBC spectrum of longiflorol (**1**) in DMSO-$d_6$