Supplementary Information

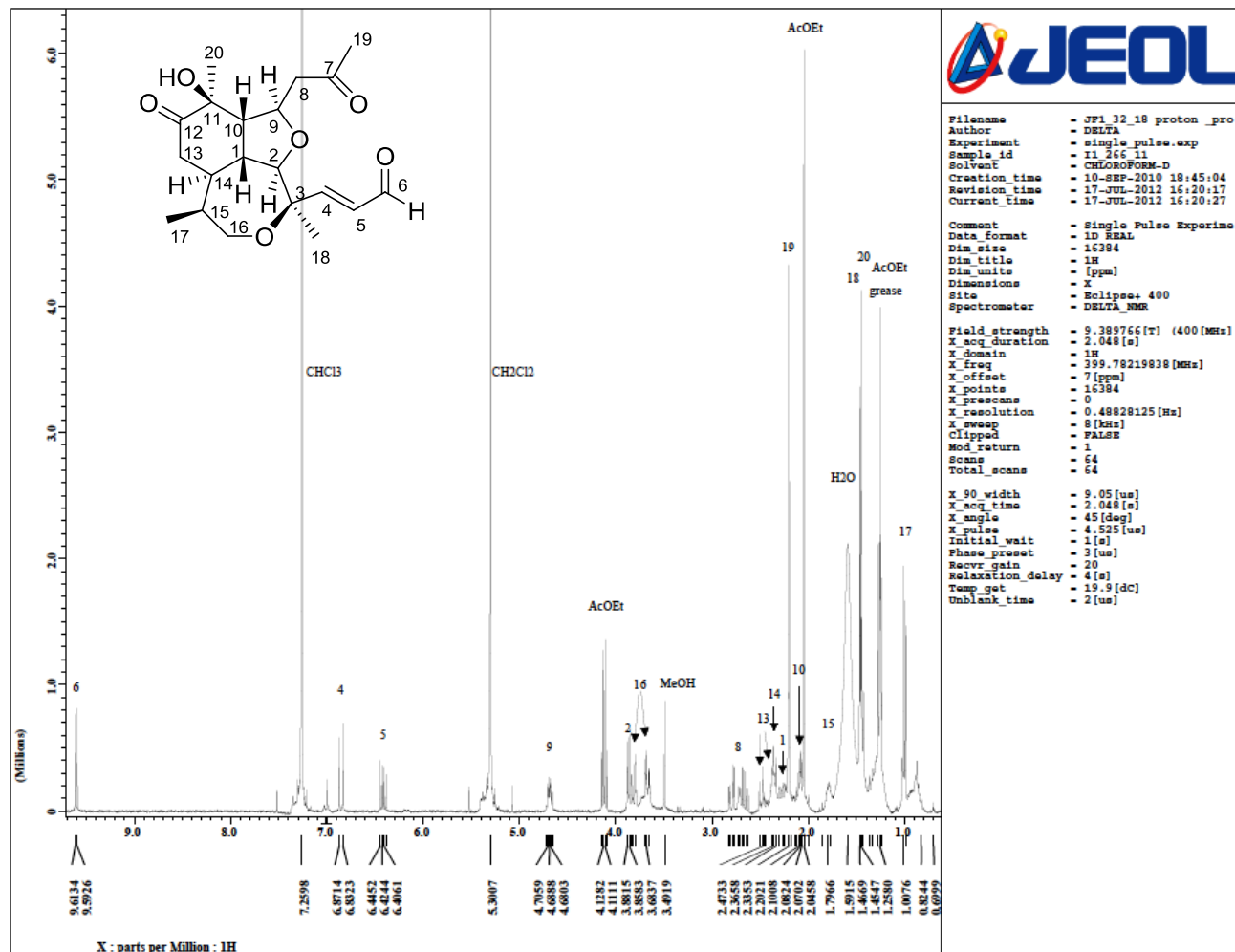**Figure S1.** *seco*-Briarellinone, ^{1}H NMR spectrum.

Figure S2. *seco*-Briarellinone, 13C NMR spectrum. The inset shows the total view of spectrum.
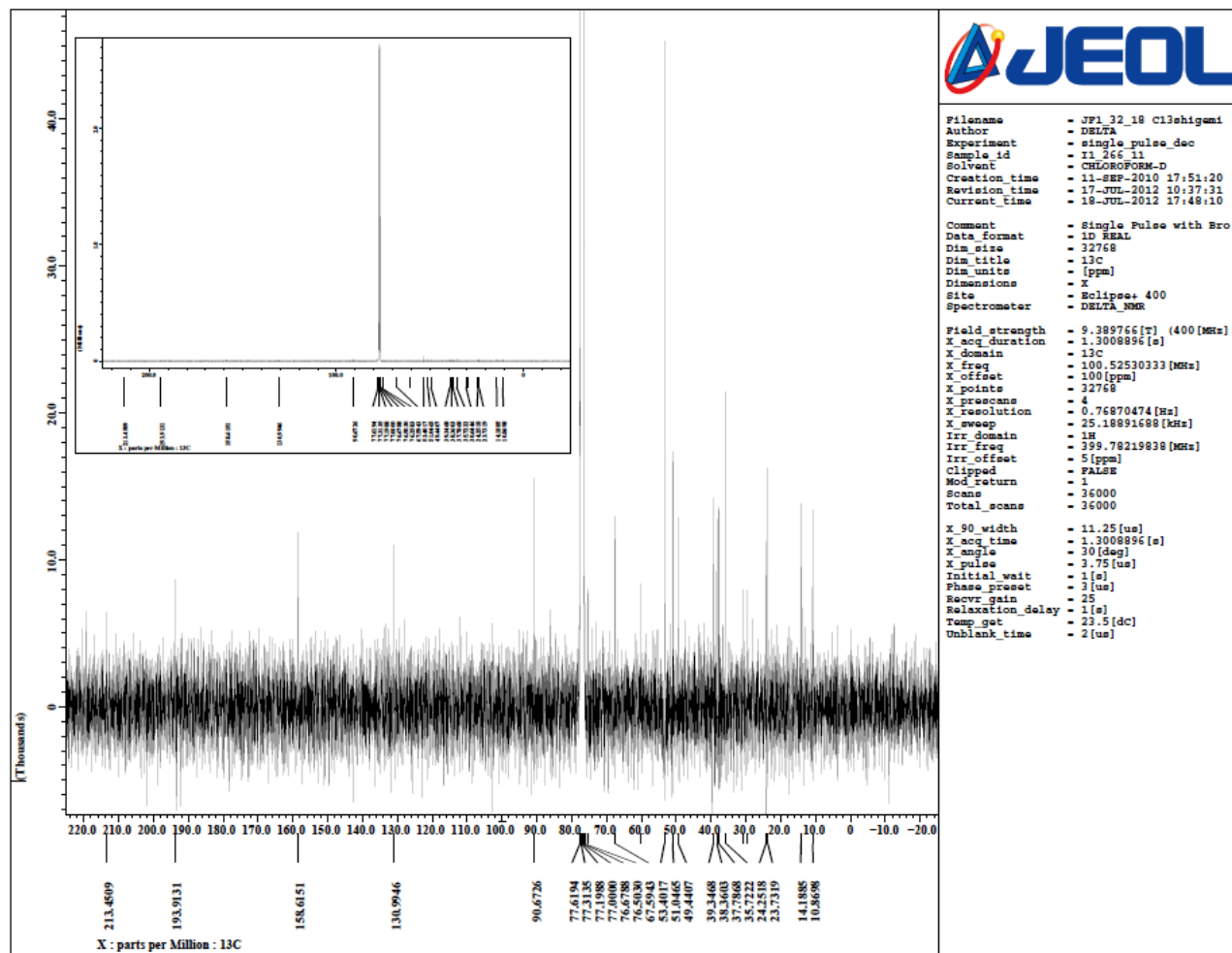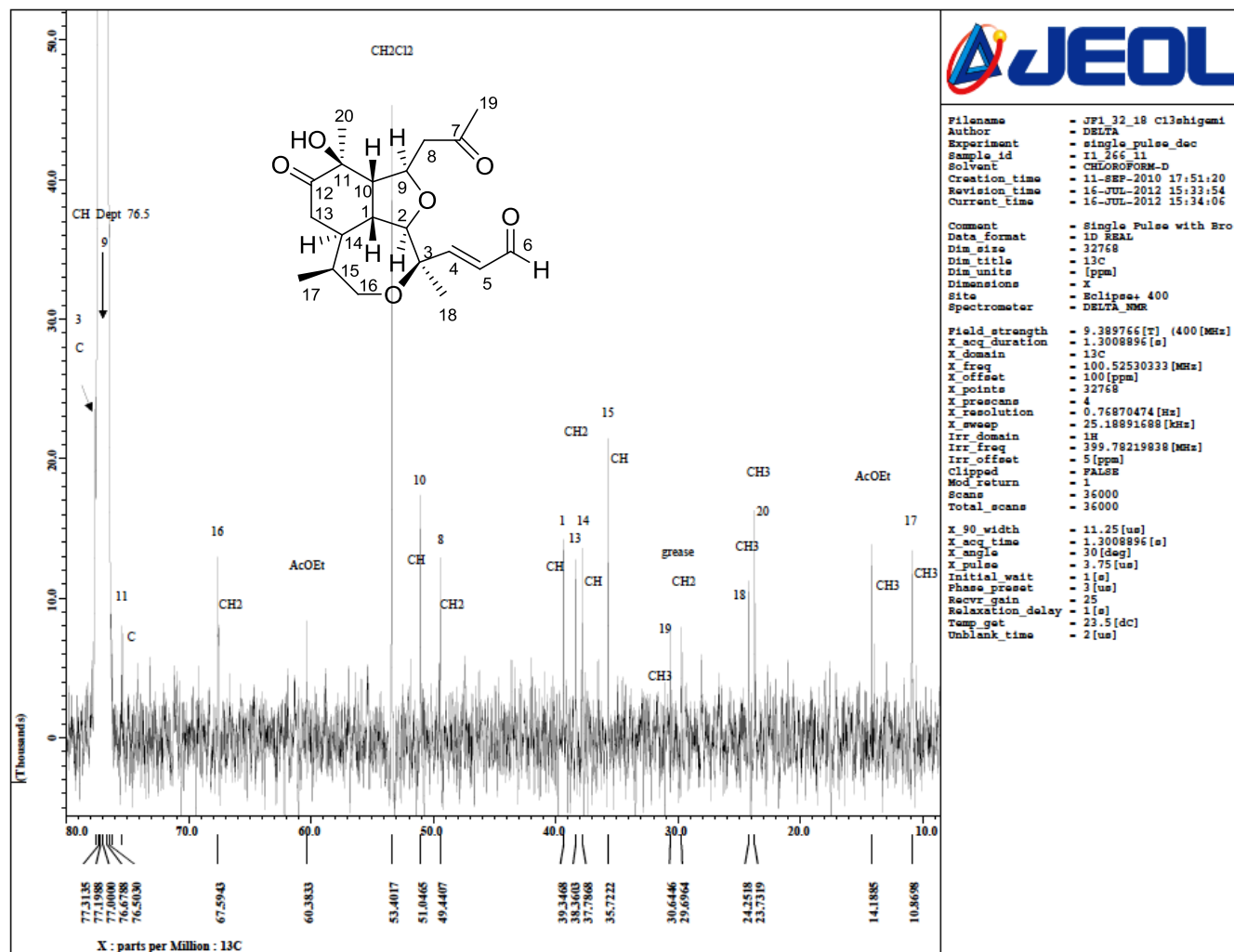
Figure S3. *seco*-Briarellinone, expanded view of the 13C NMR spectrum (9–80 ppm).
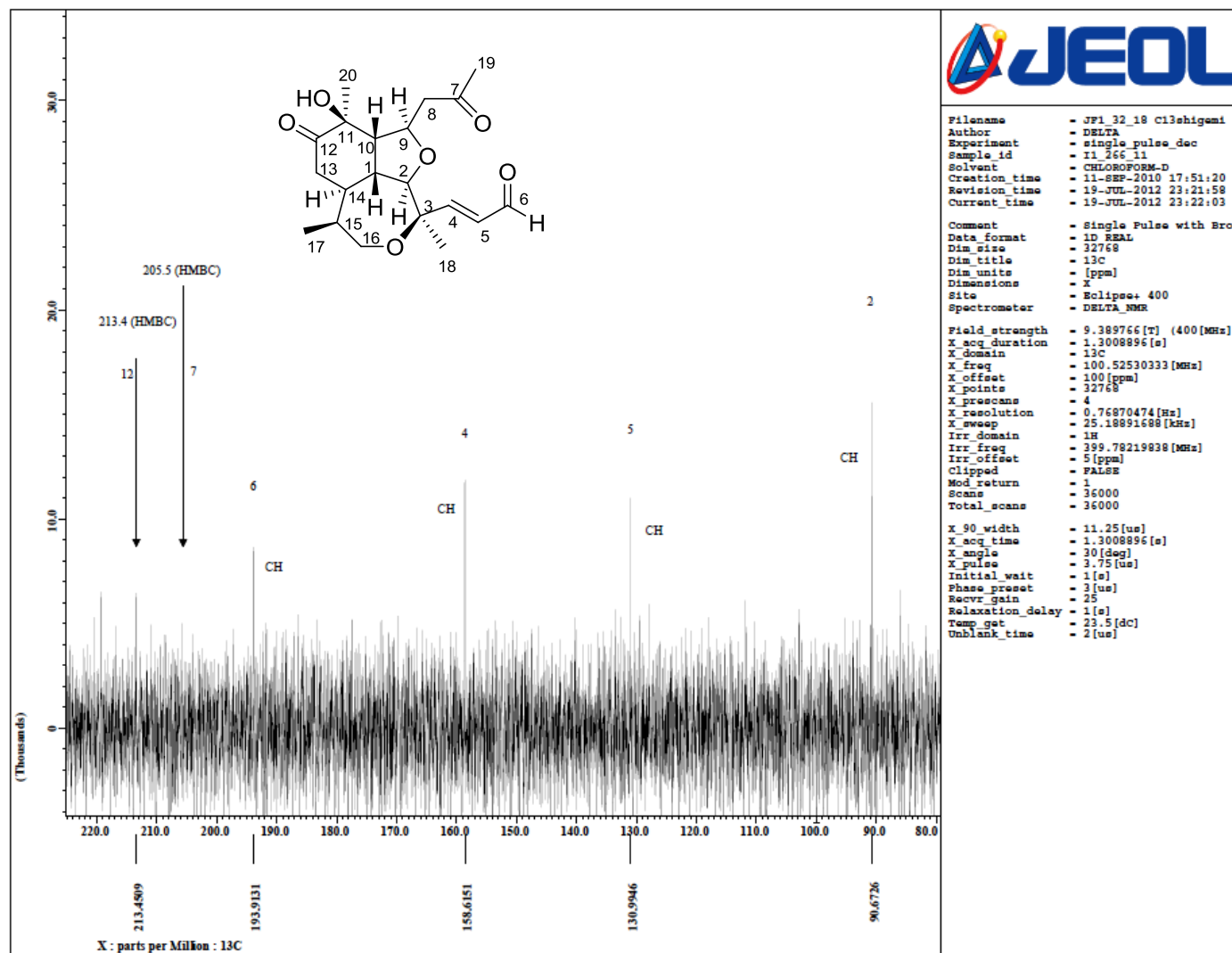
Figure S4. *seco*-Briarellinone, expanded view of the 13C NMR spectrum (80–225 ppm).
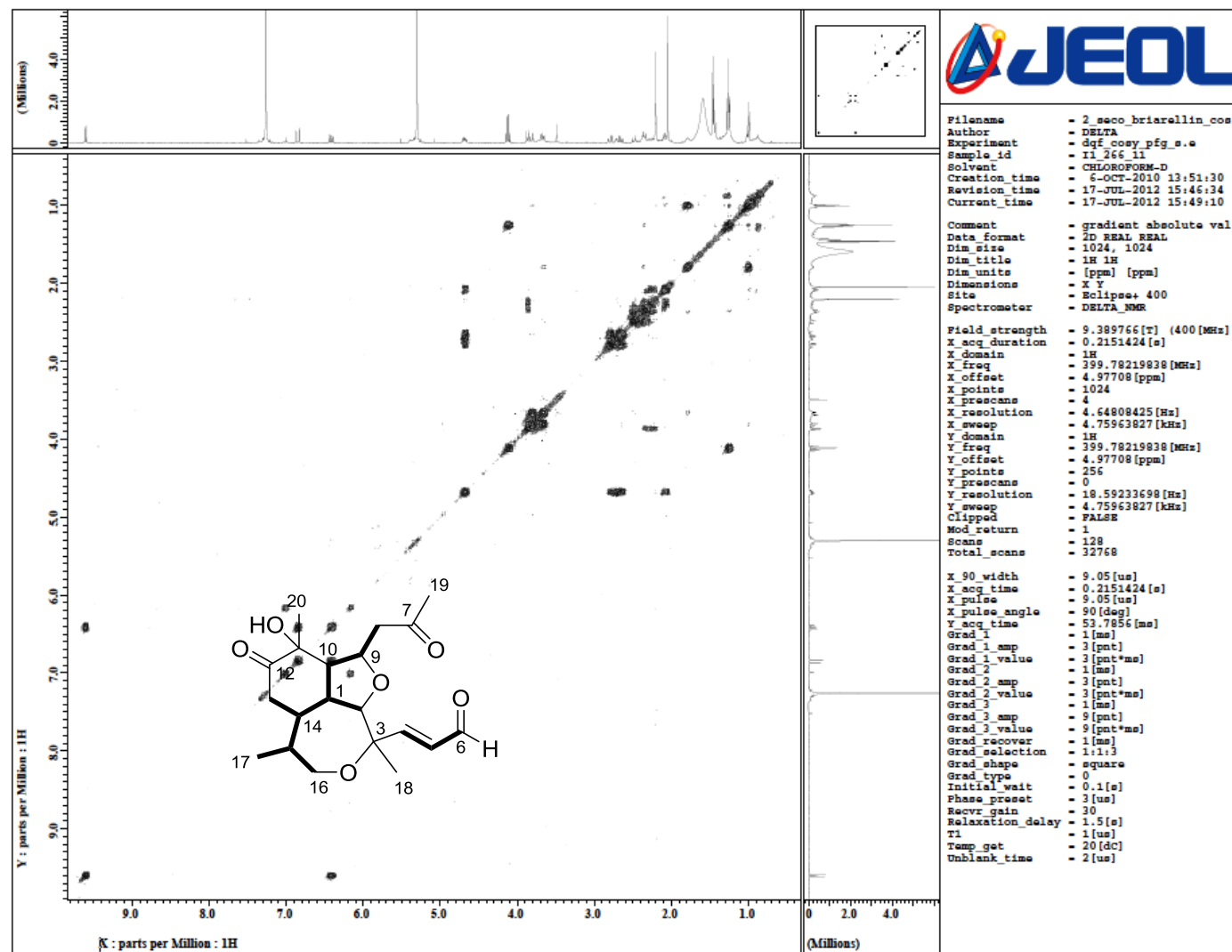
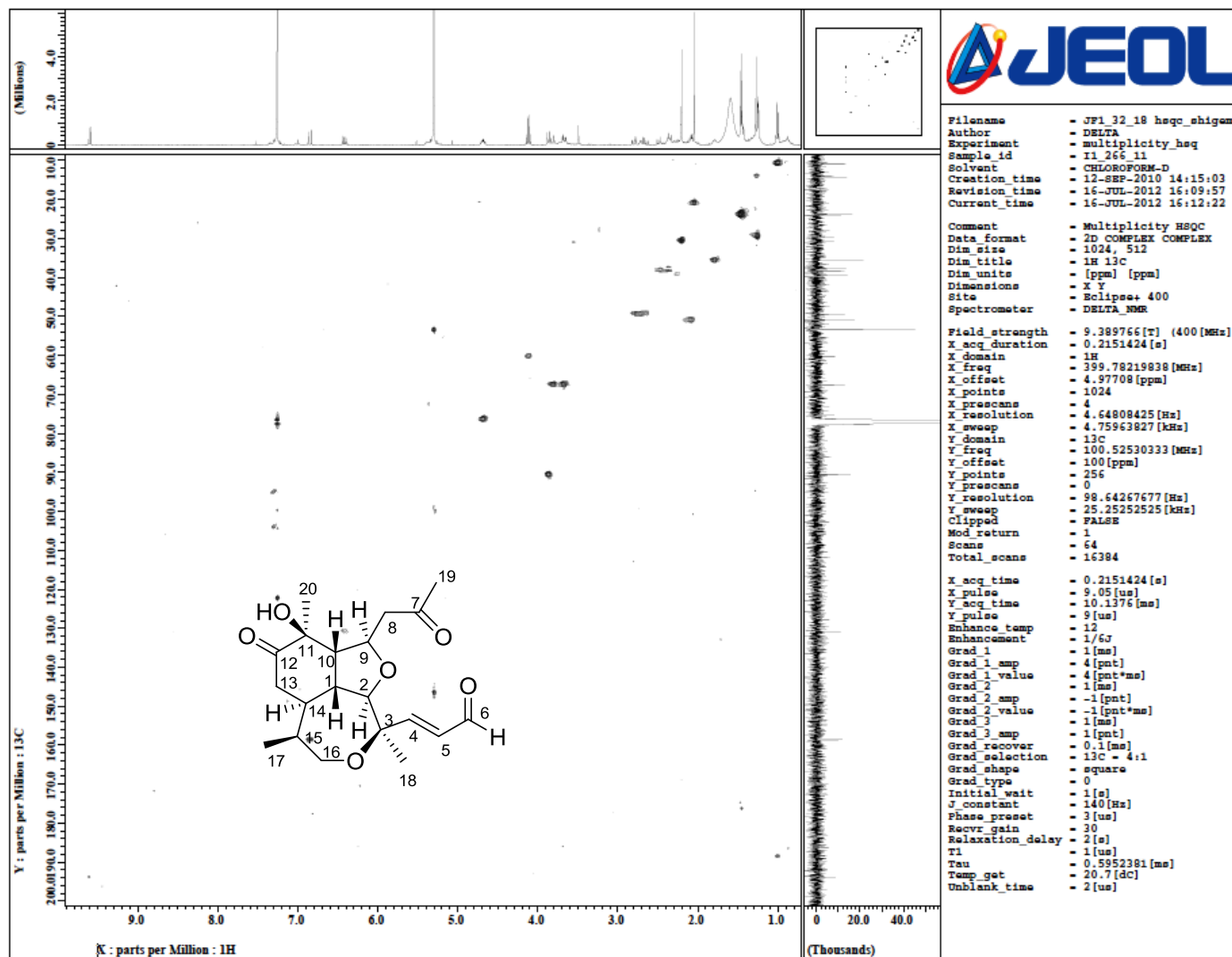**Figure S5.** *seco*-Briarellinone, COSY spectrum.
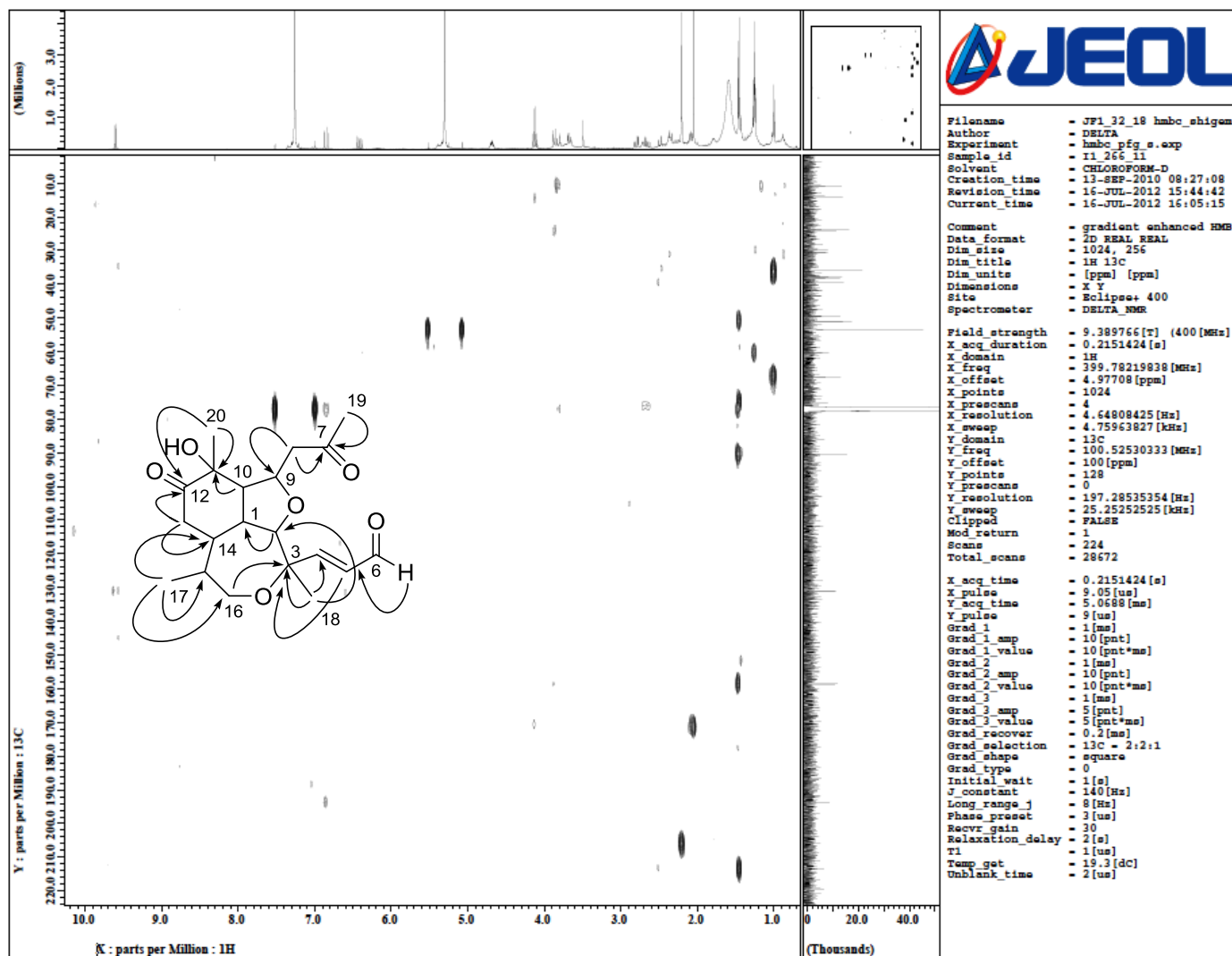
Figure S6. *seco*-Briarellinone, HSQC spectrum.

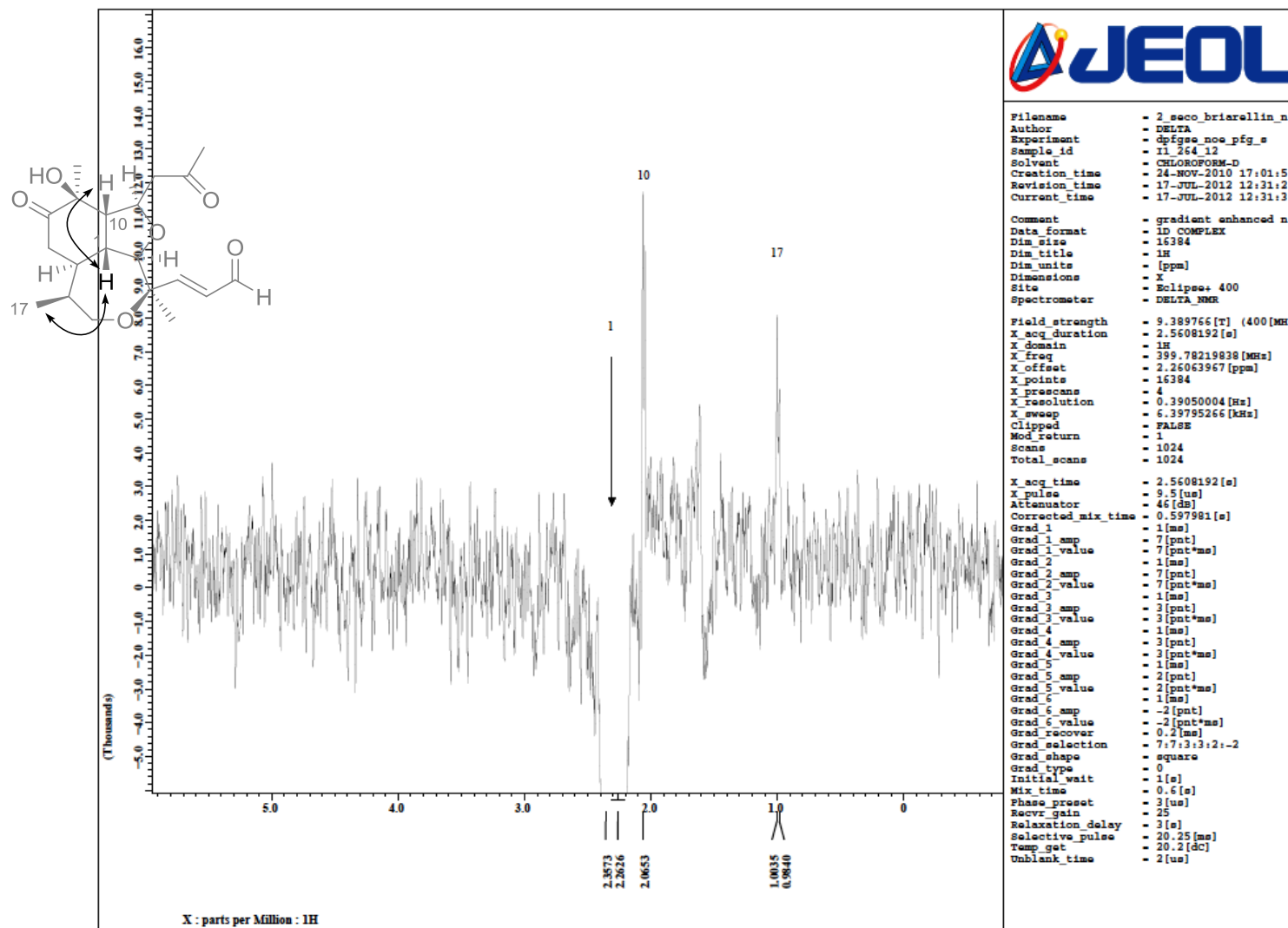**Figure S7.** *seco*-Briarellinone, HMBC spectrum.

Figure S8. *seco*-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-1.
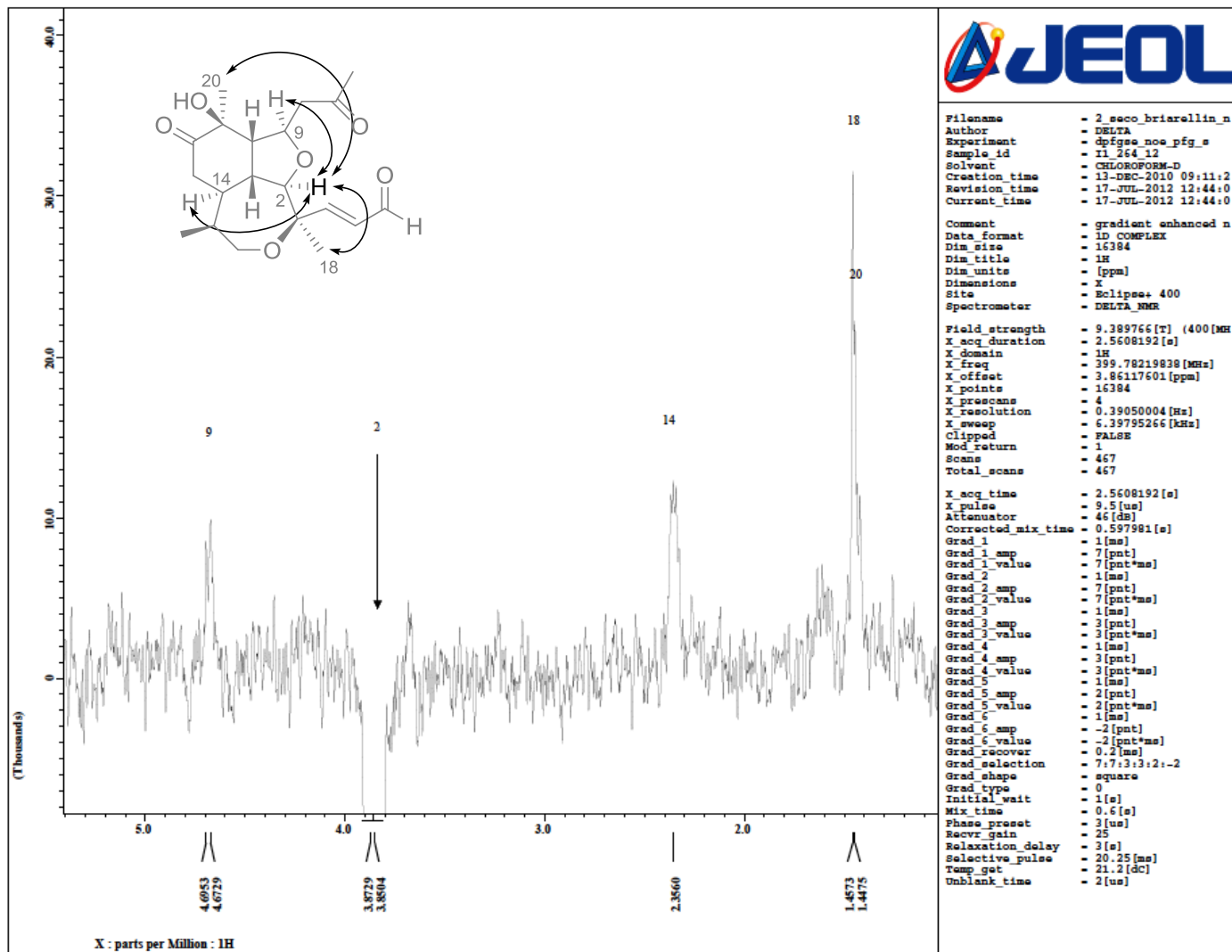

X : parts per Million : 1H

Figure S9. *seco*-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-2.
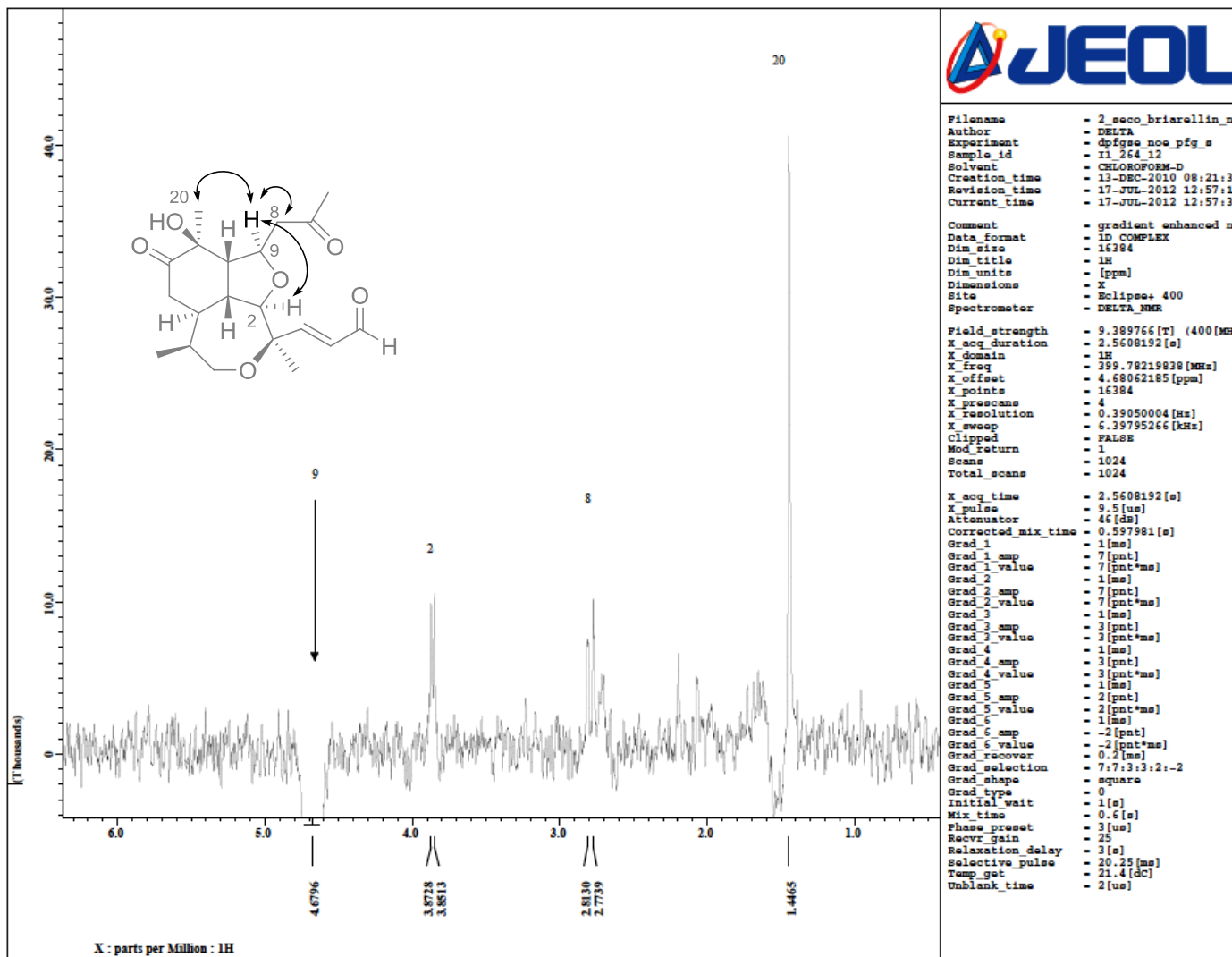
Figure S10. *seco*-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-9.
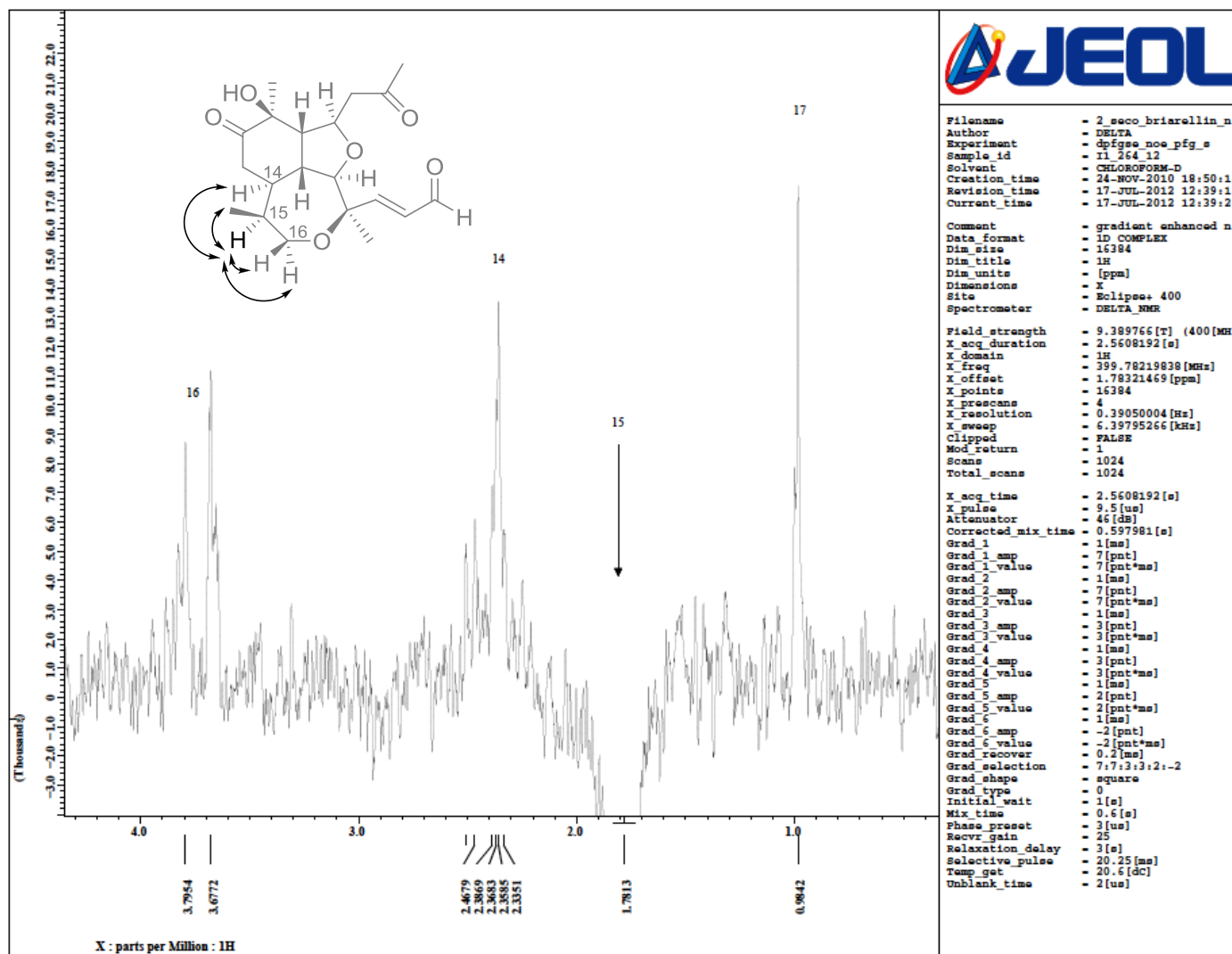
Figure S11. *seco*-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-15.
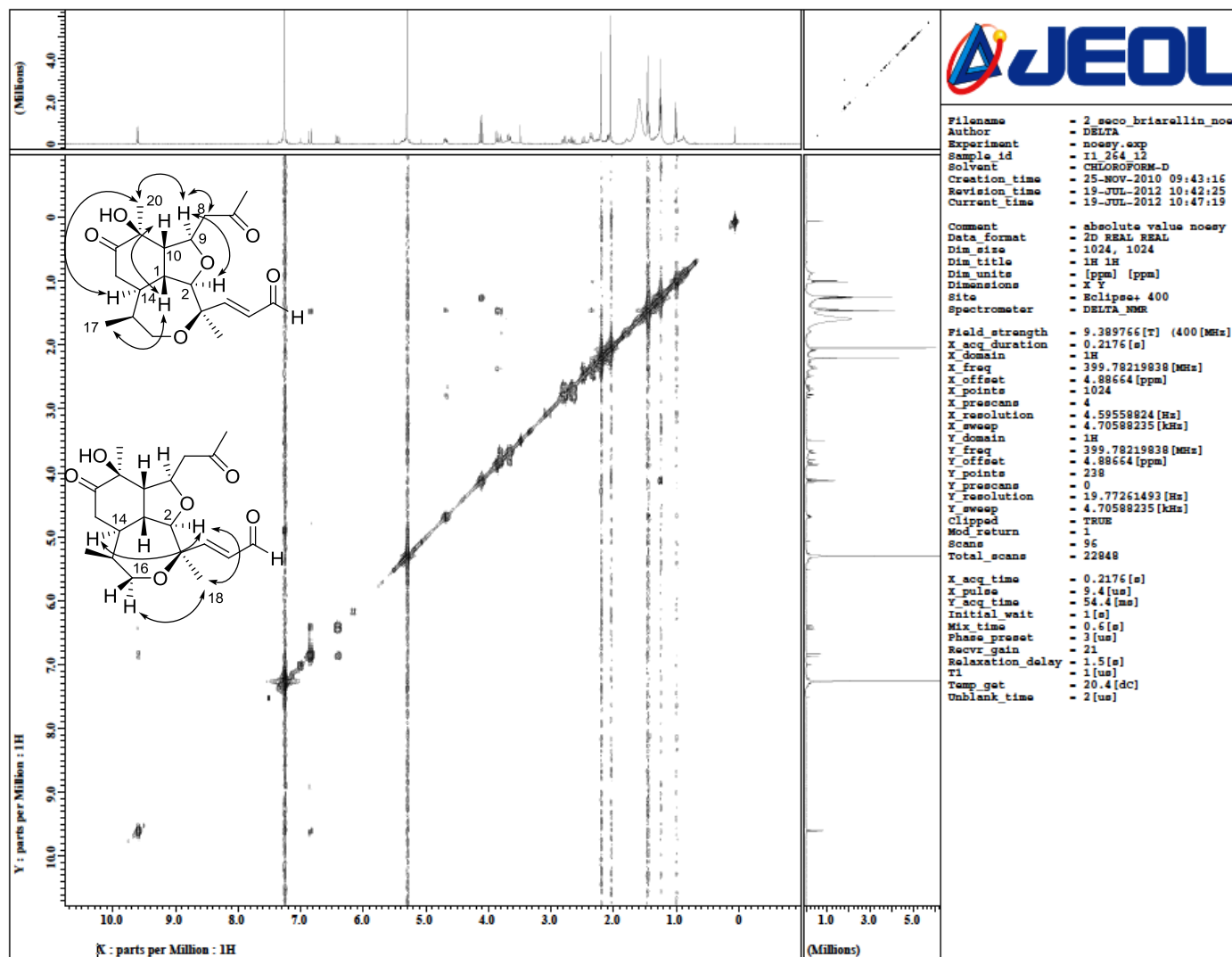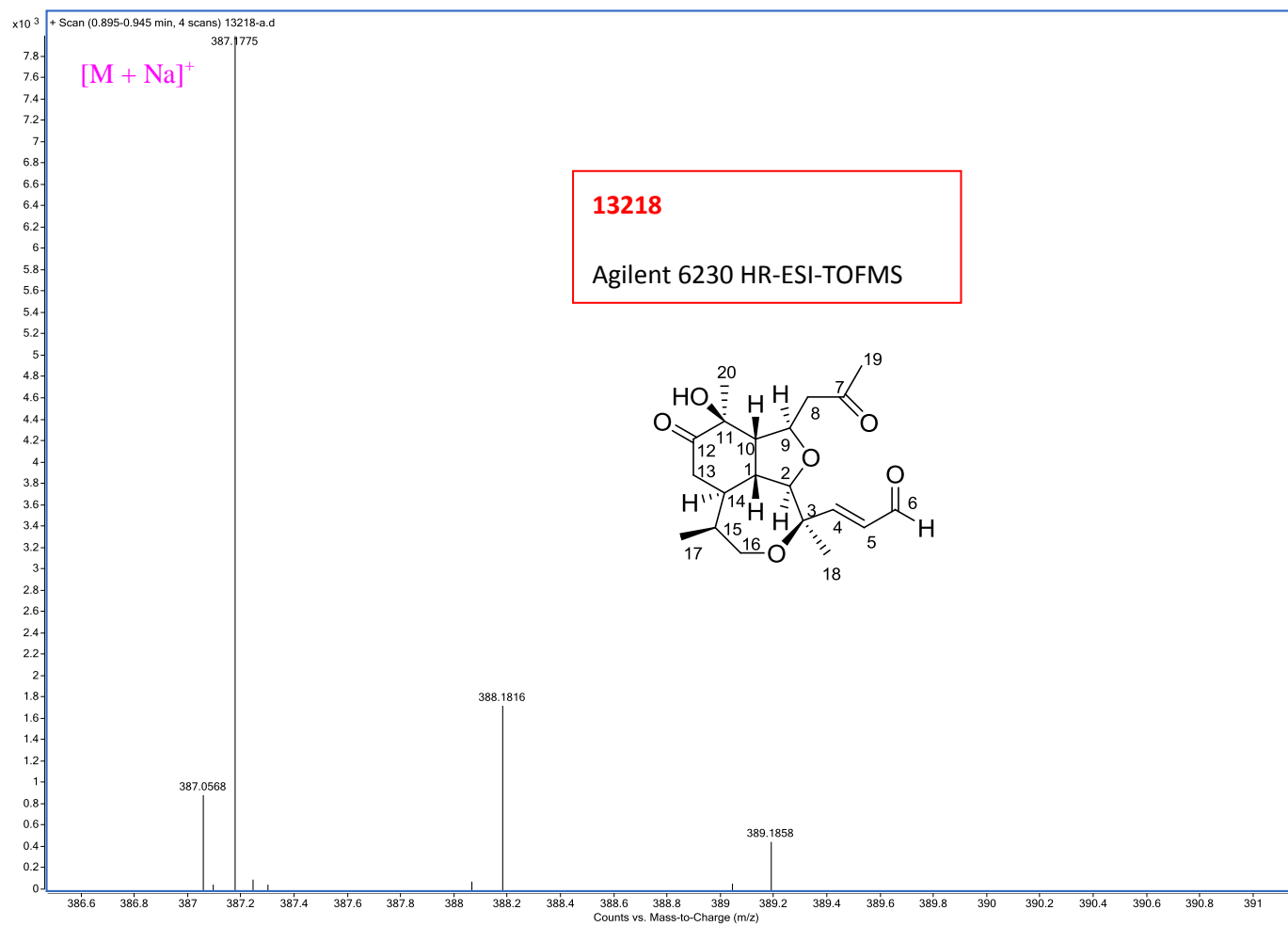
Figure S12. *seco*-Briarellinone, NOESY spectrum.

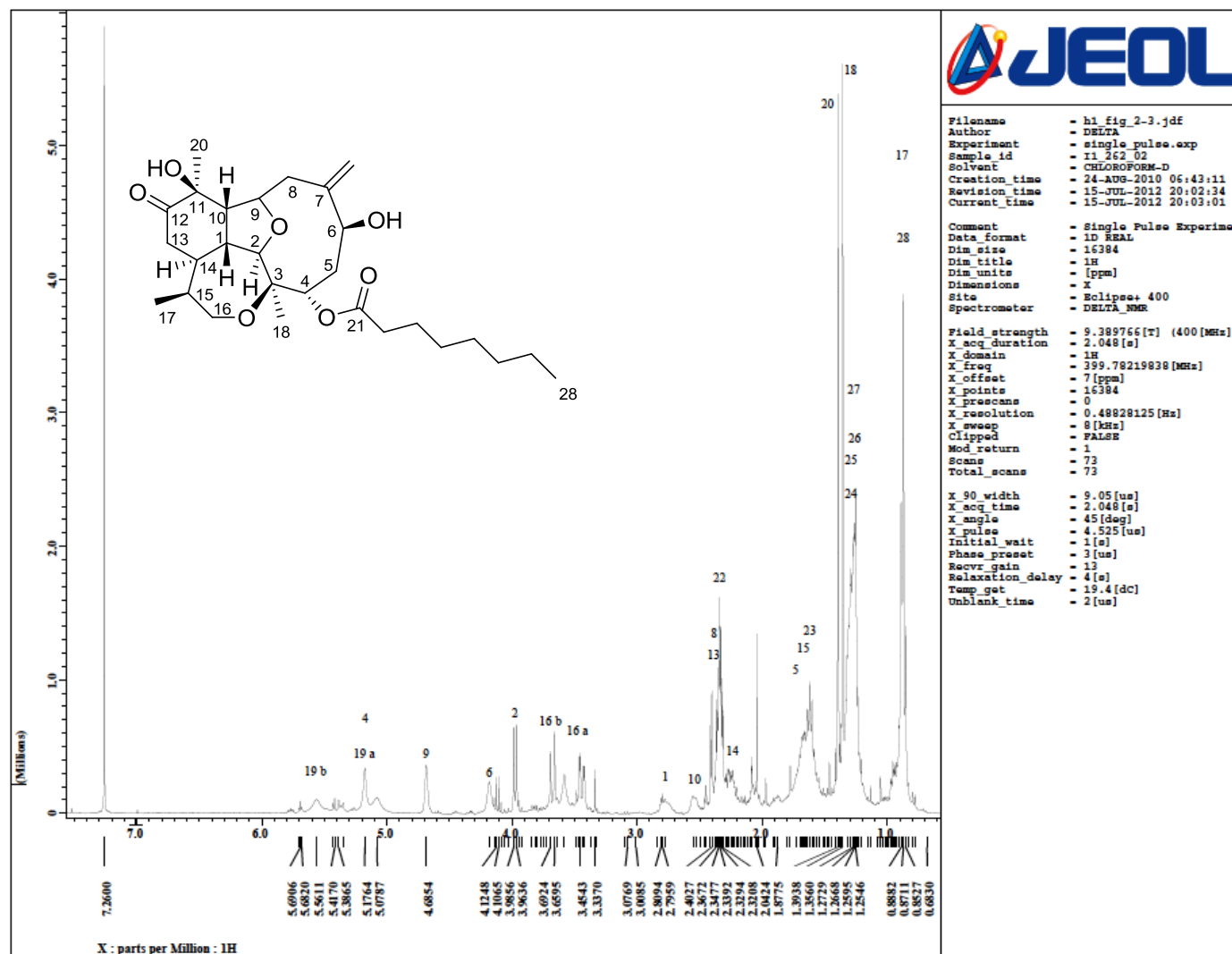**Figure S13.** *seco*-Briarellinone, HRMS-ESI-TOF spectrum.
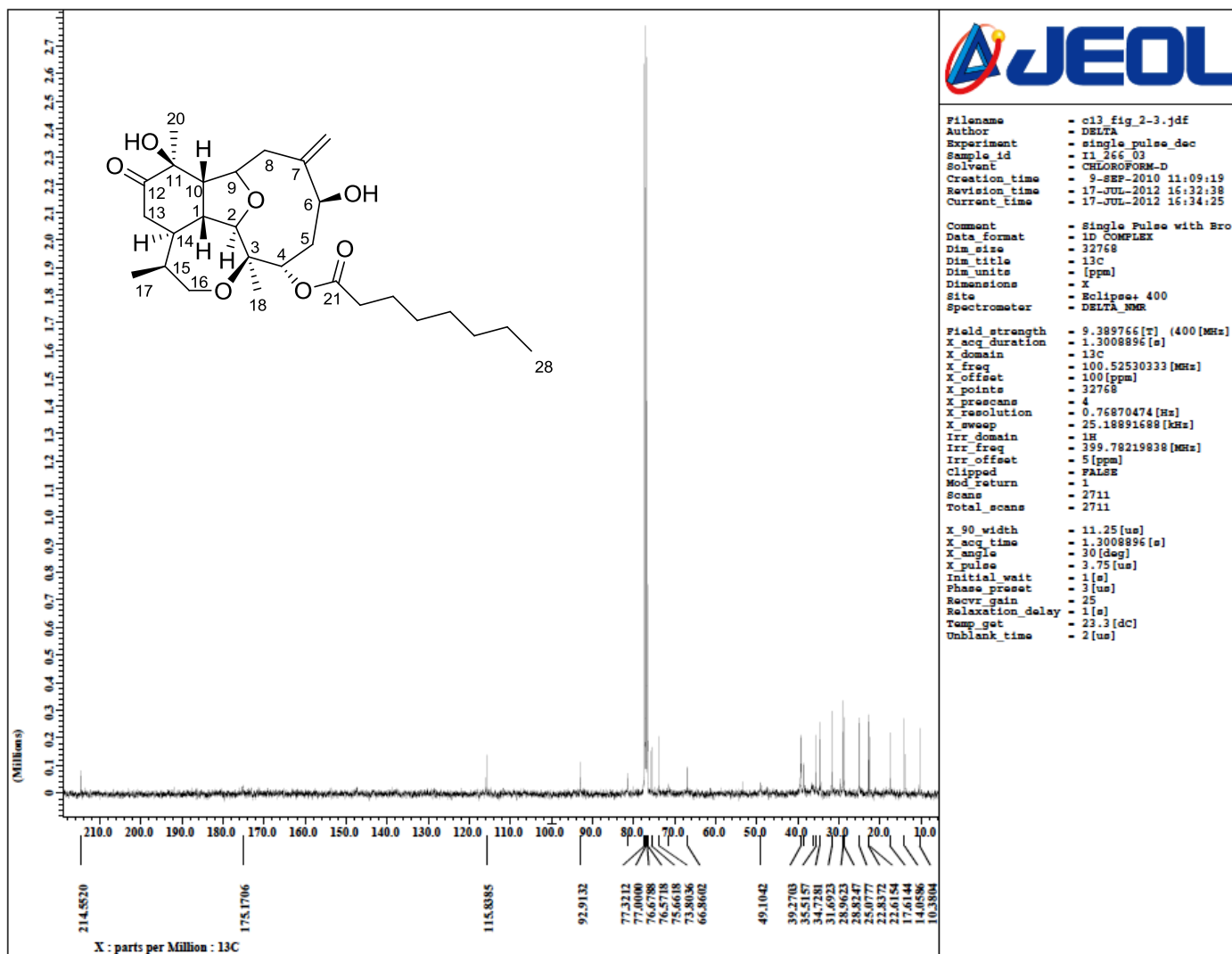
Figure S14. Briarellin S, 1H NMR spectrum.

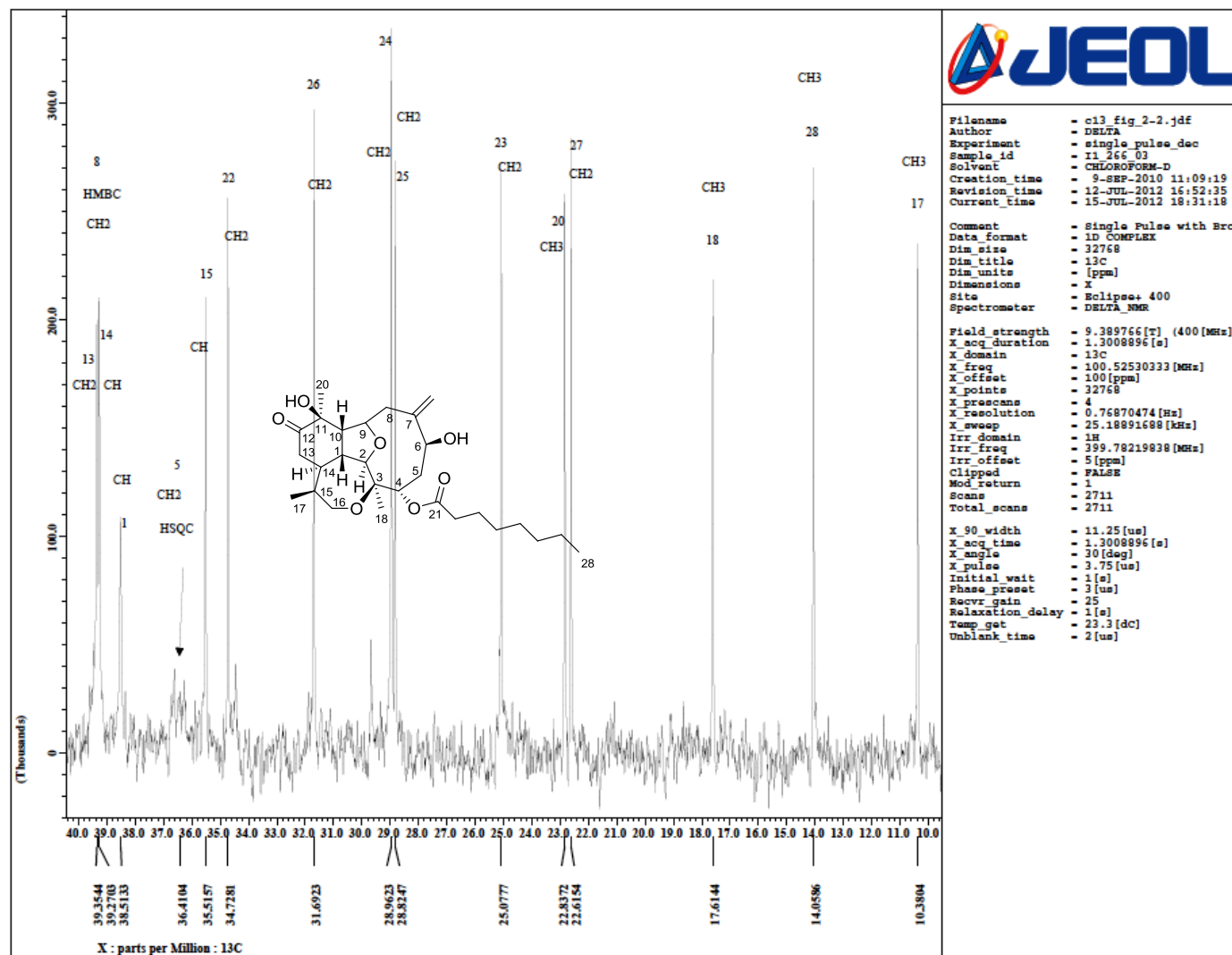**Figure S15.** Briarellin S, 13C NMR spectrum.

Figure S16. Briarellin S, expanded view of the 13C NMR spectrum (10–40 ppm).
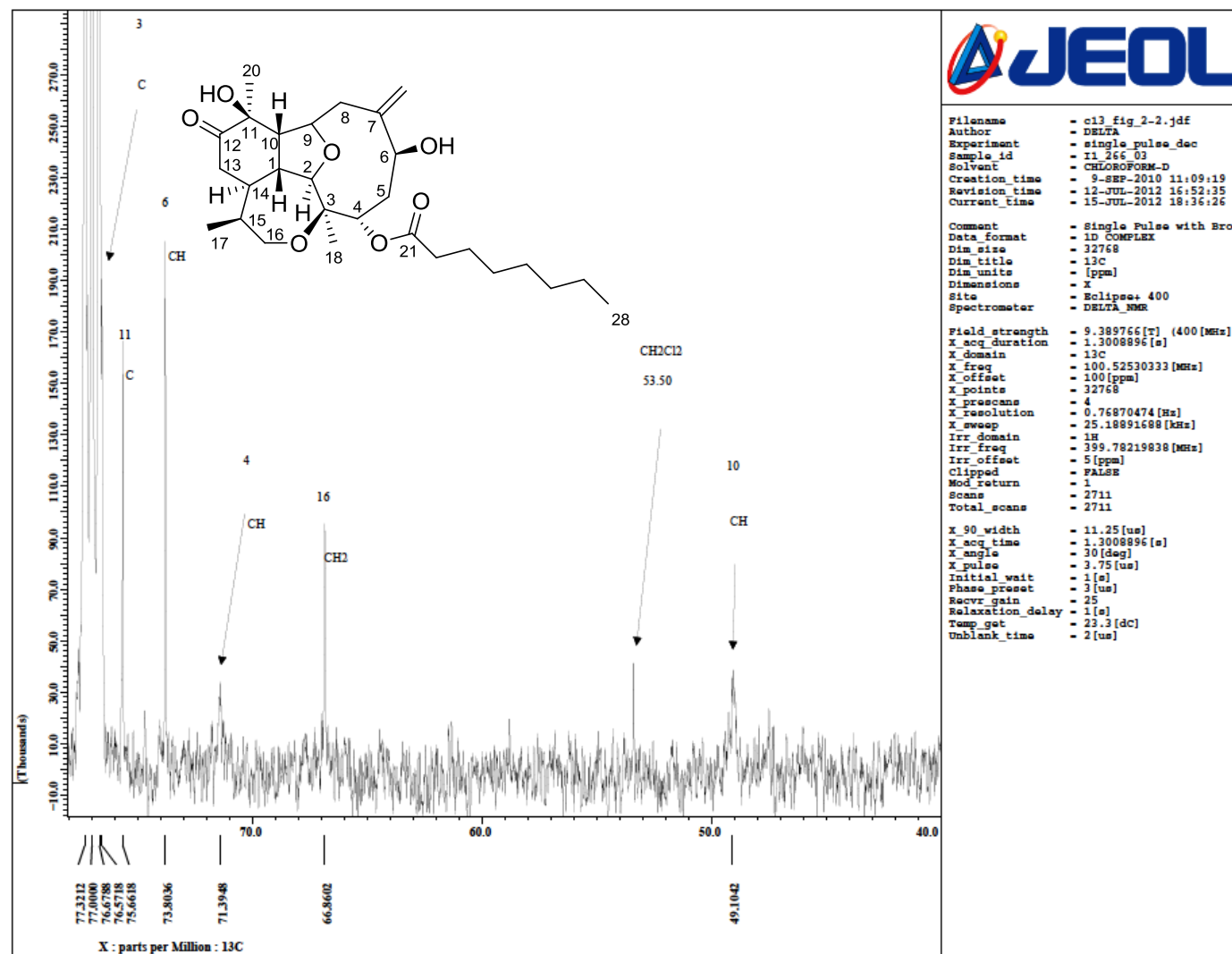
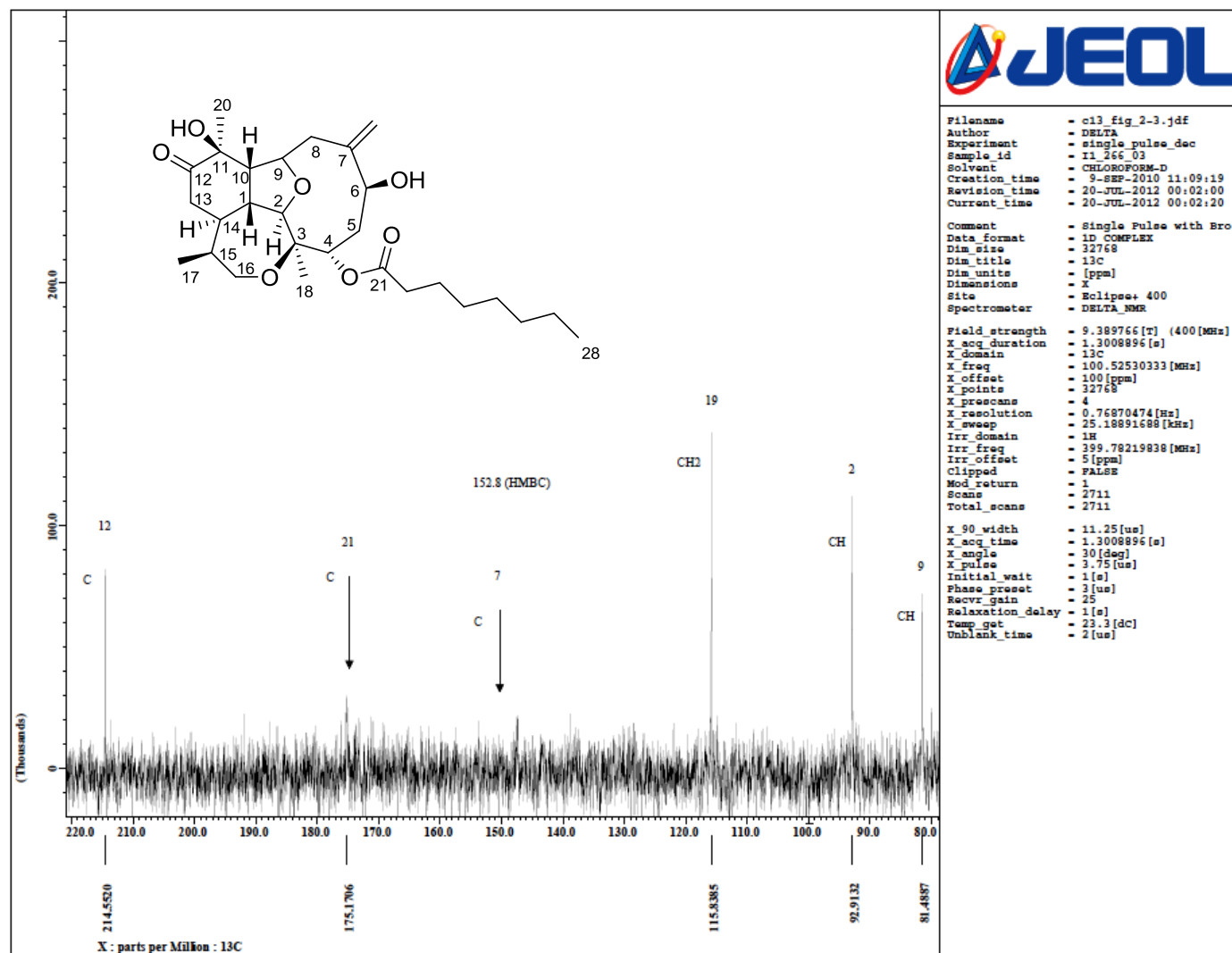**Figure S17.** Briarellin S, expanded view of the 13C NMR spectrum (40–80 ppm).

Figure S18. Briarellin S, expanded view of the 13C NMR spectrum (78–220 ppm).

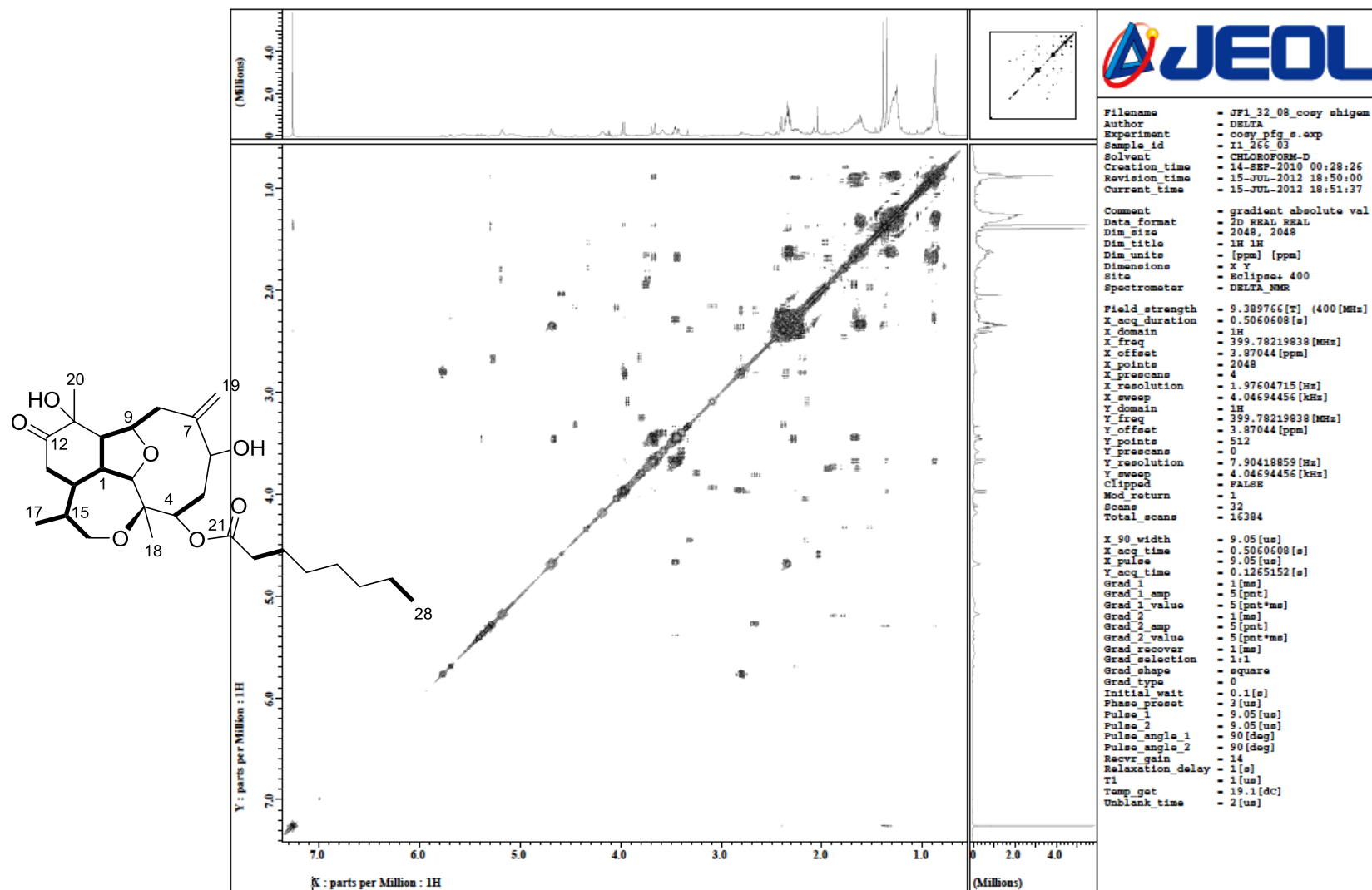**Figure S19.** Briarellin S, COSY spectrum.

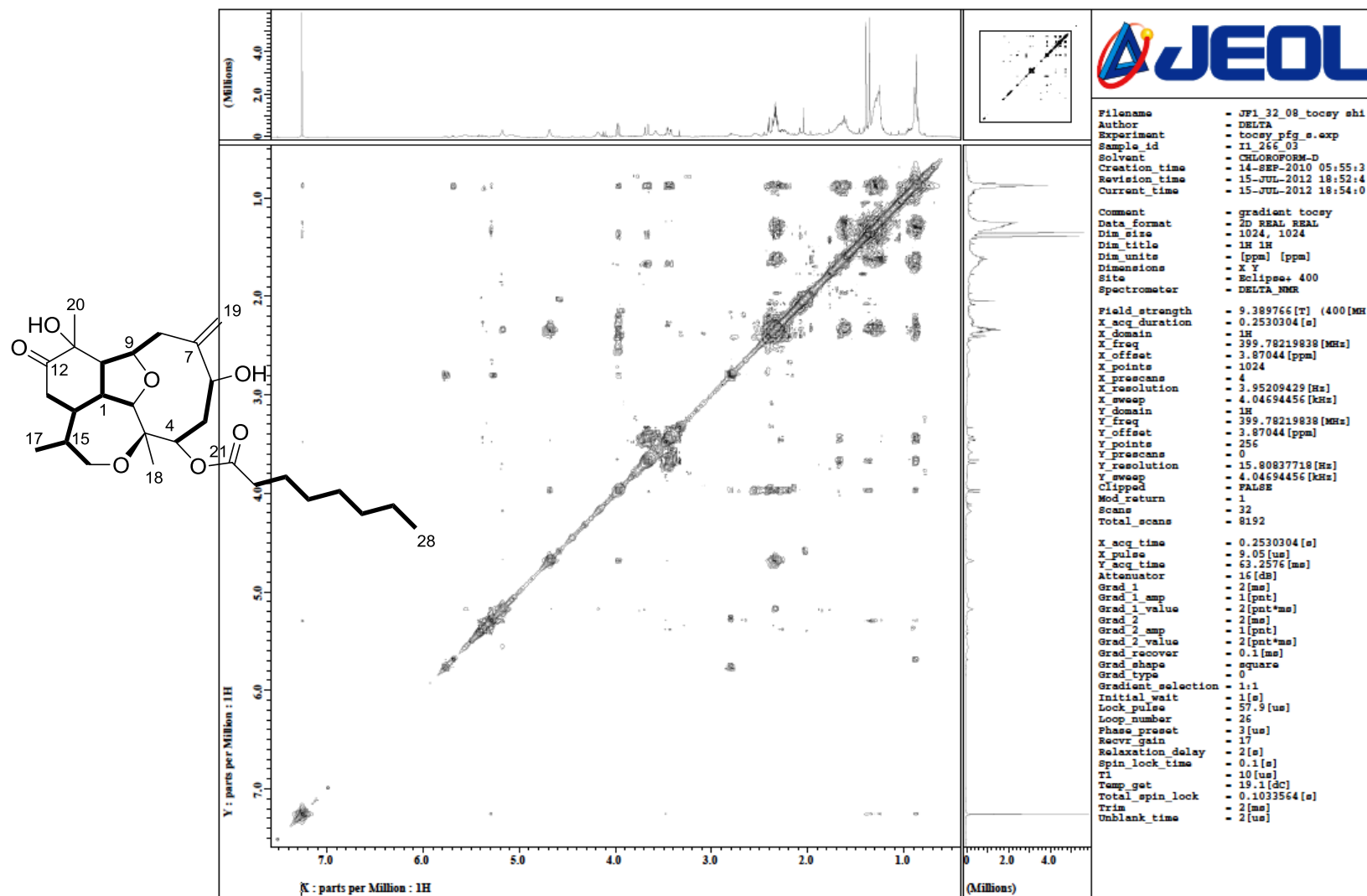**Figure S20.** Briarellin S, TOCSY spectrum.
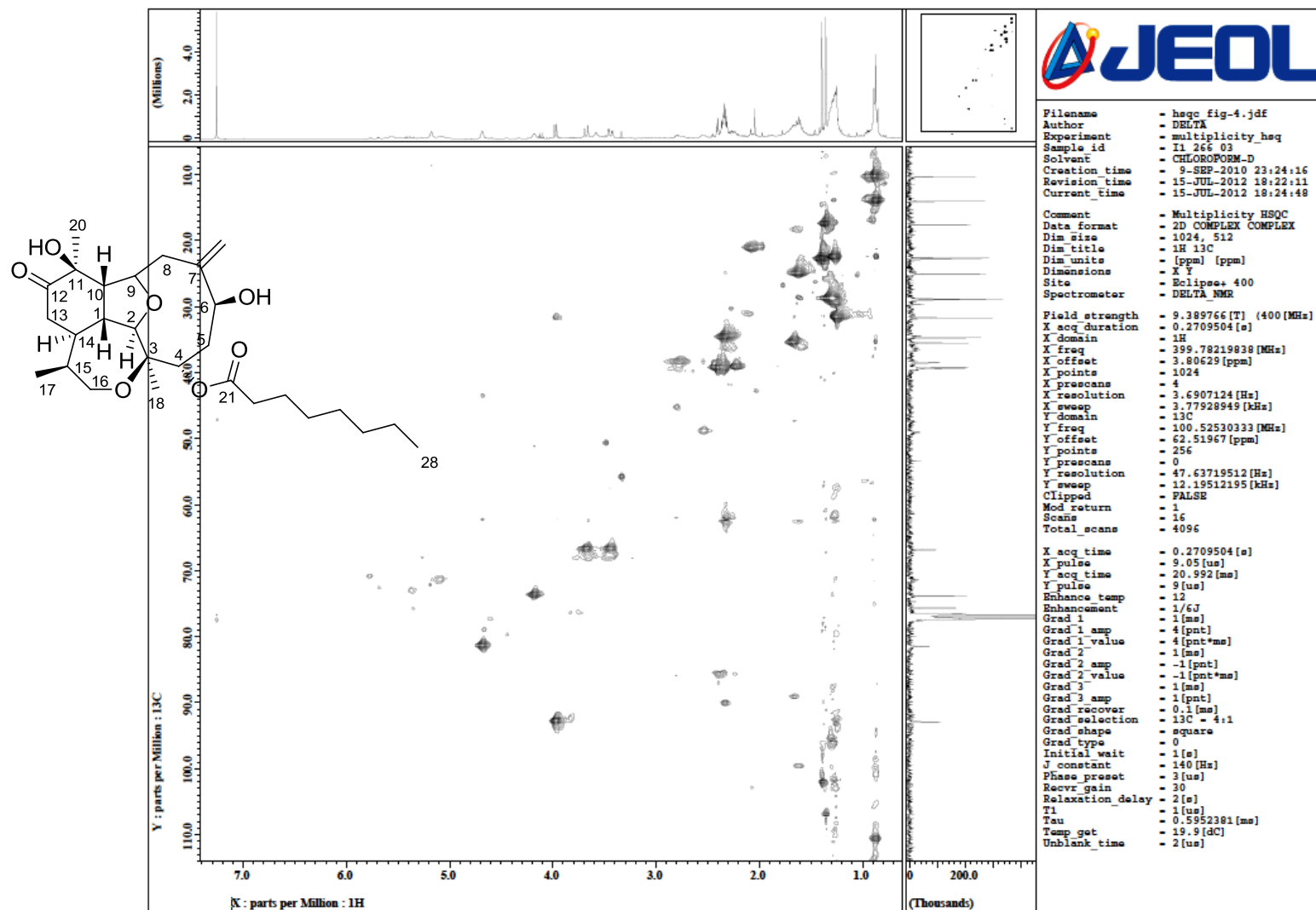
Figure S21. Briarellin S, HSQC spectrum.

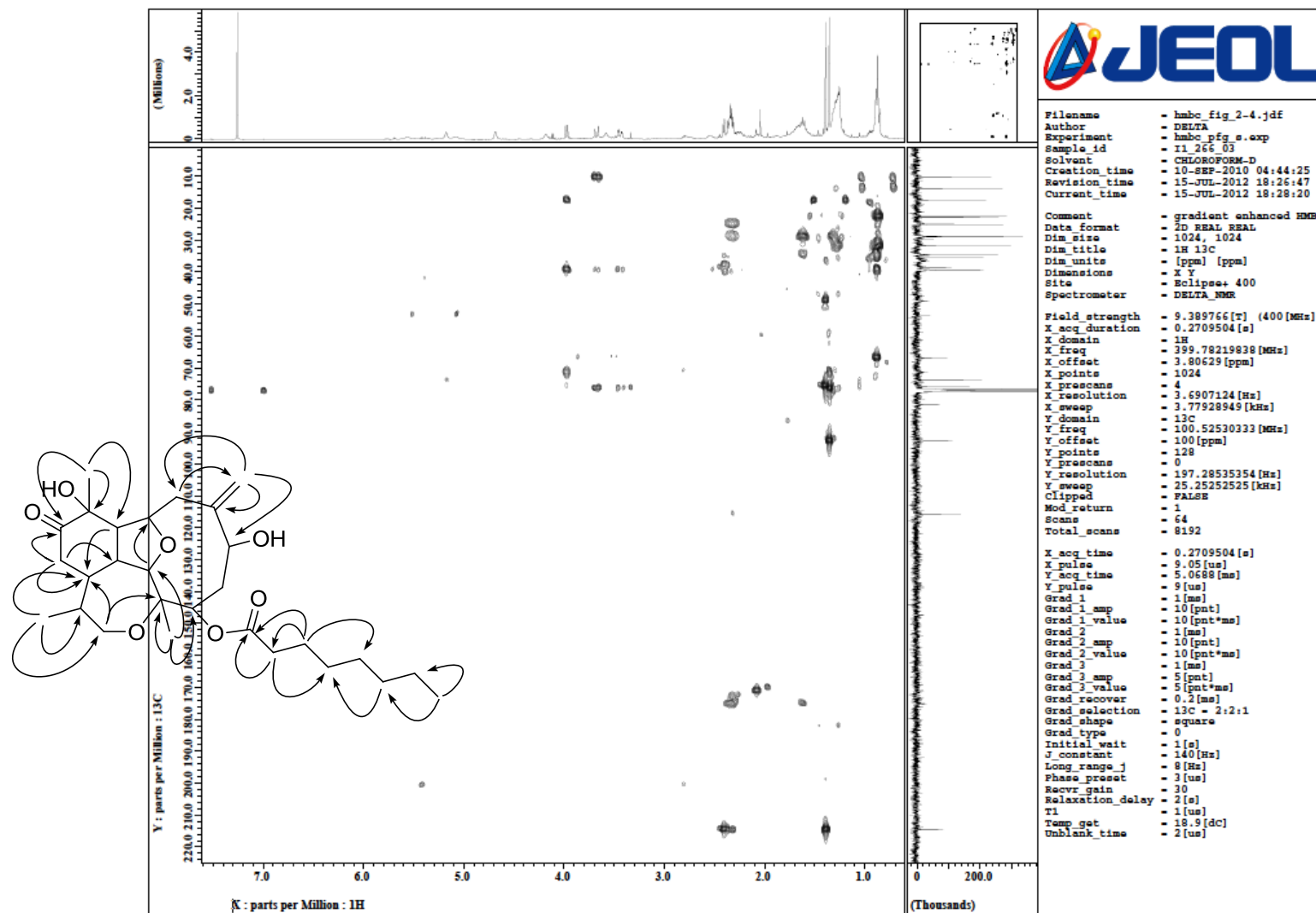**Figure S22.** Briarellin S, HMBC spectrum.

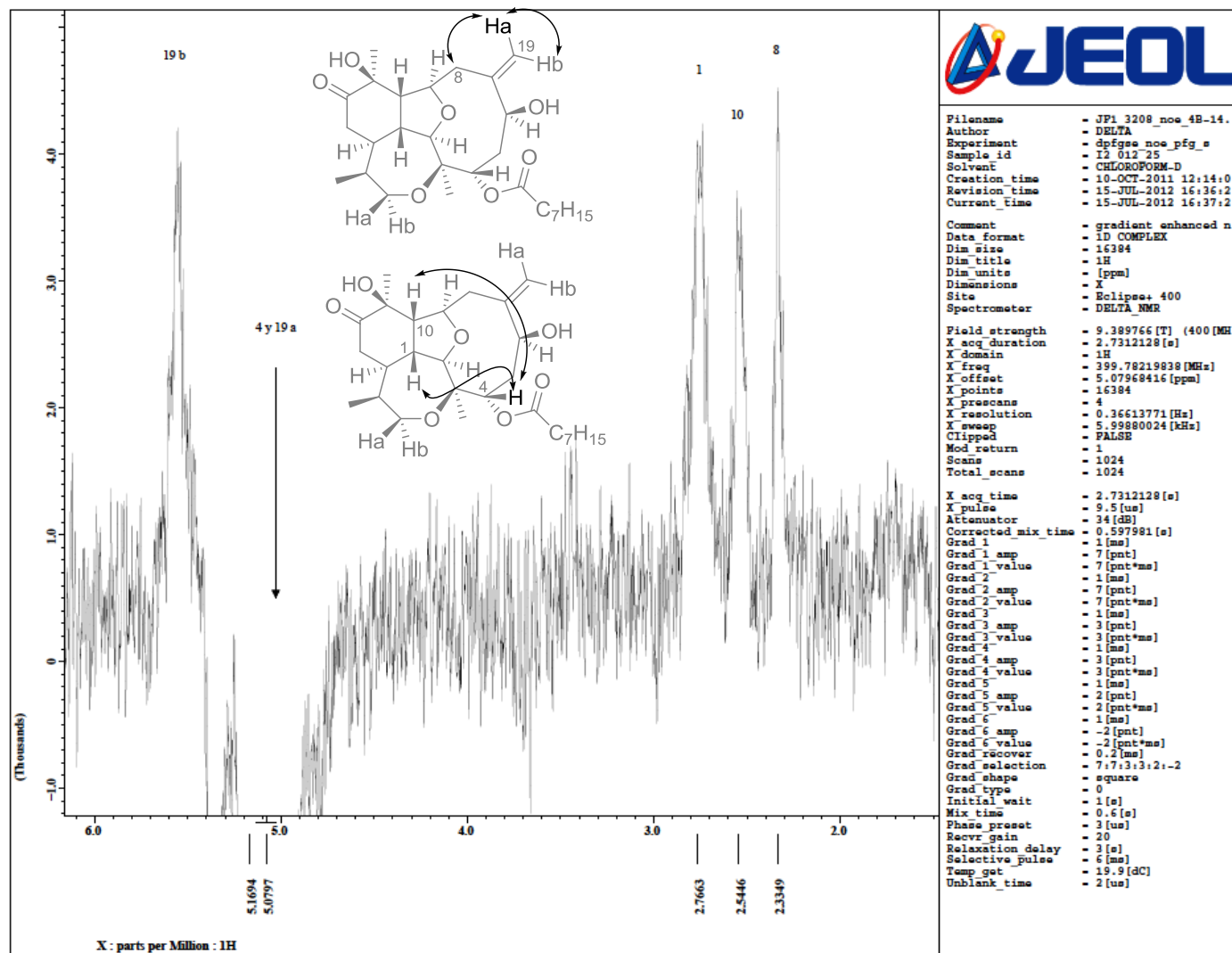**Figure S23.** Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-4 and H-19a.

Figure S24. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-6.
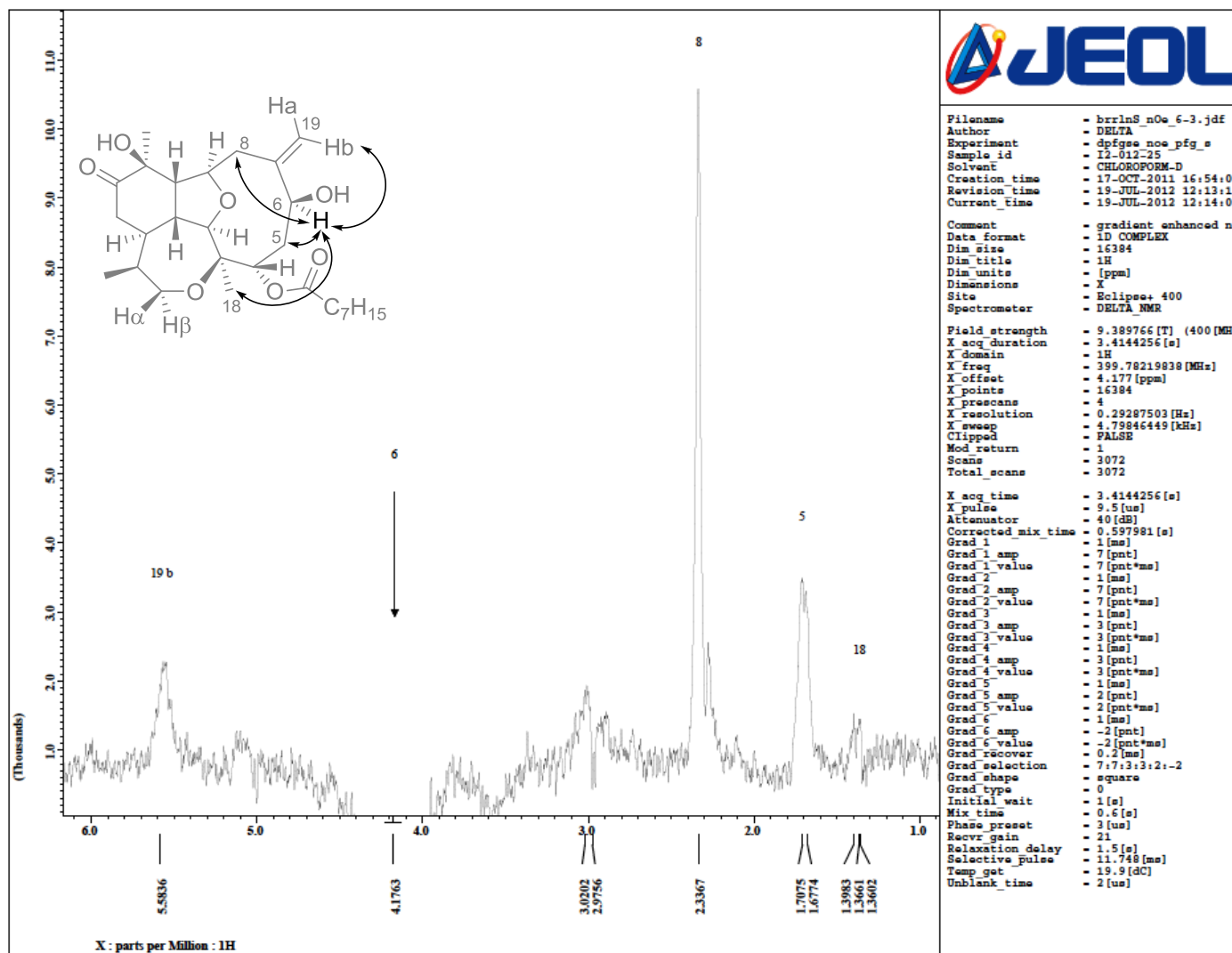
Figure S25. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-17 and H-28.
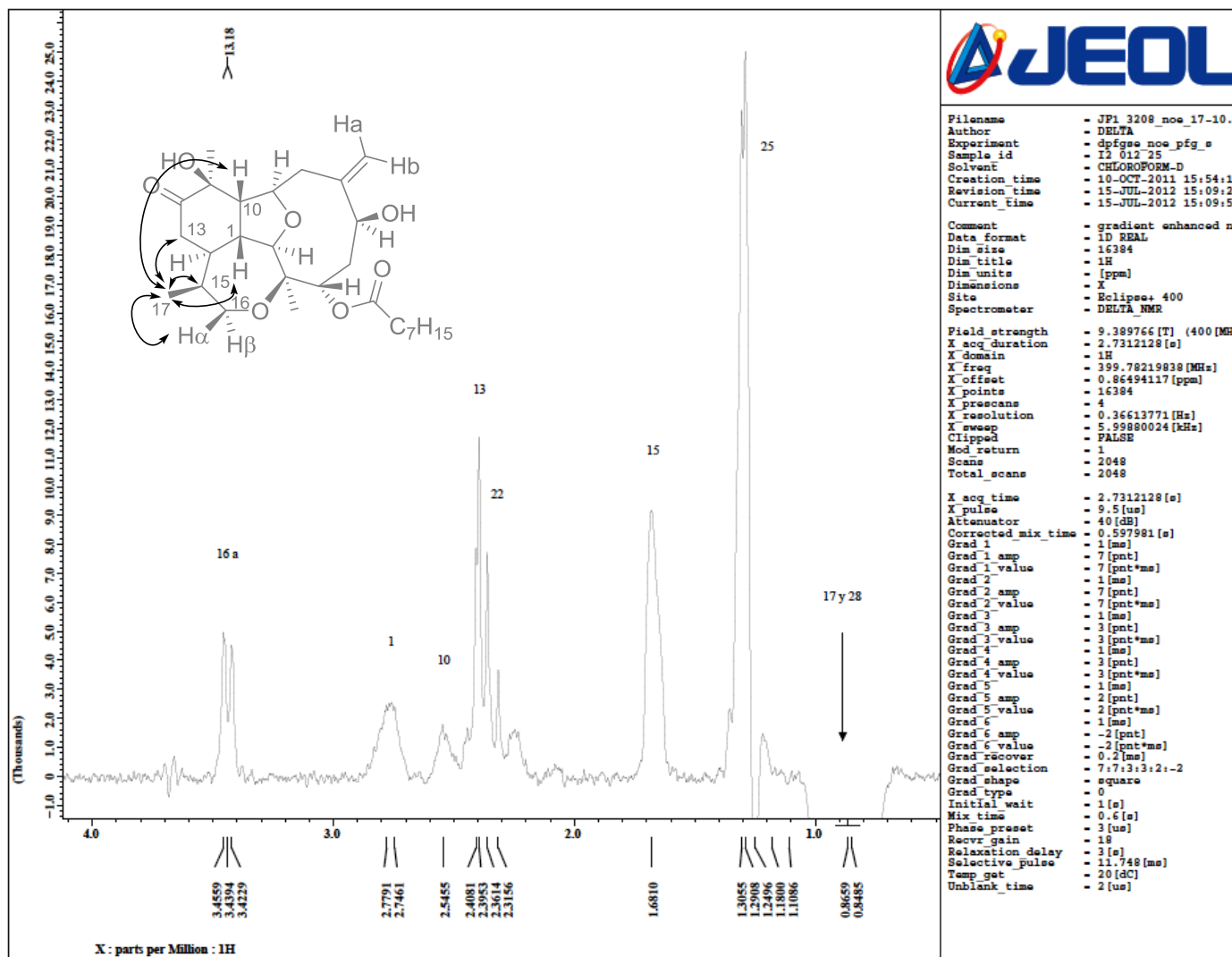
Figure S26. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-18.
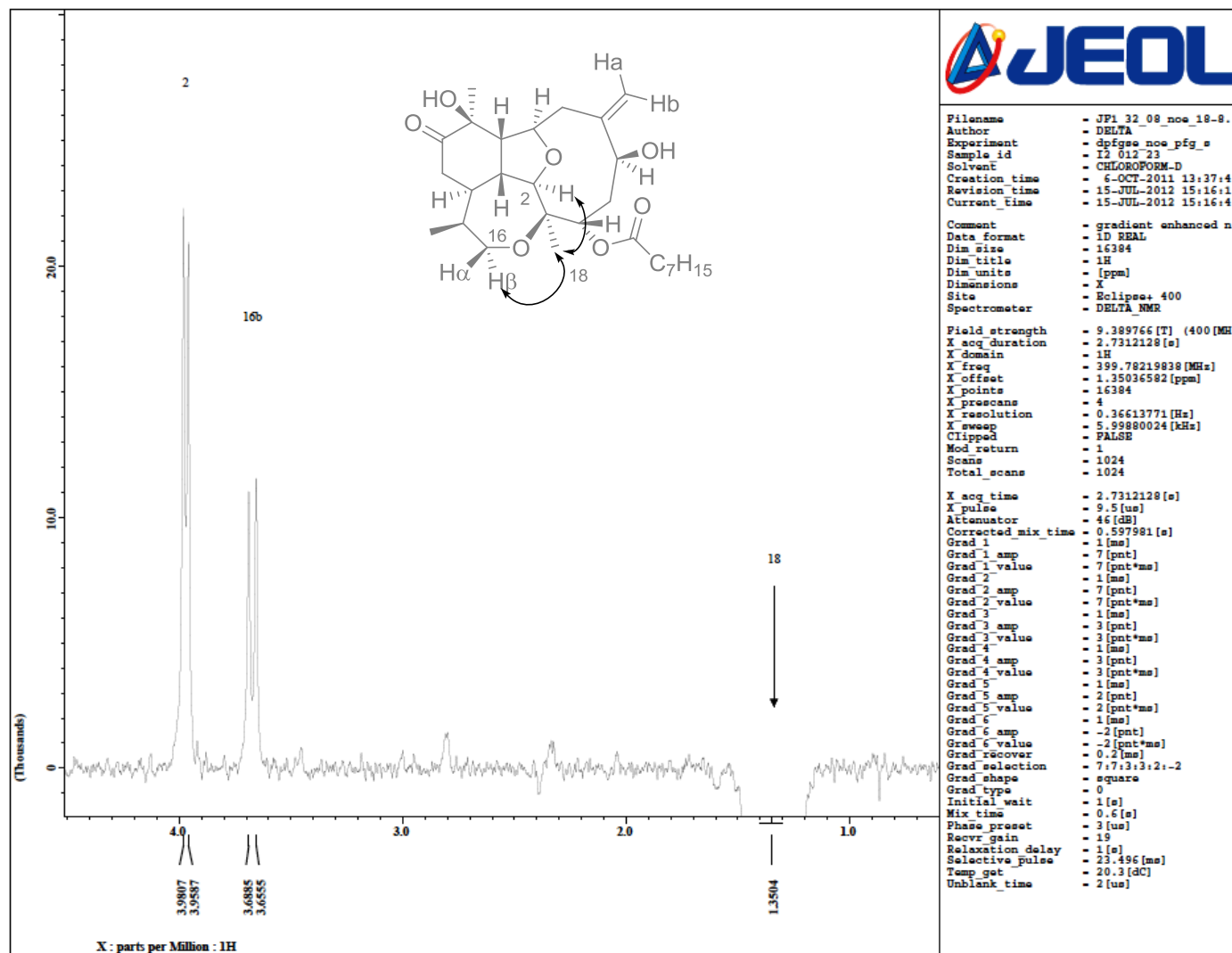
Figure S27. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-20.
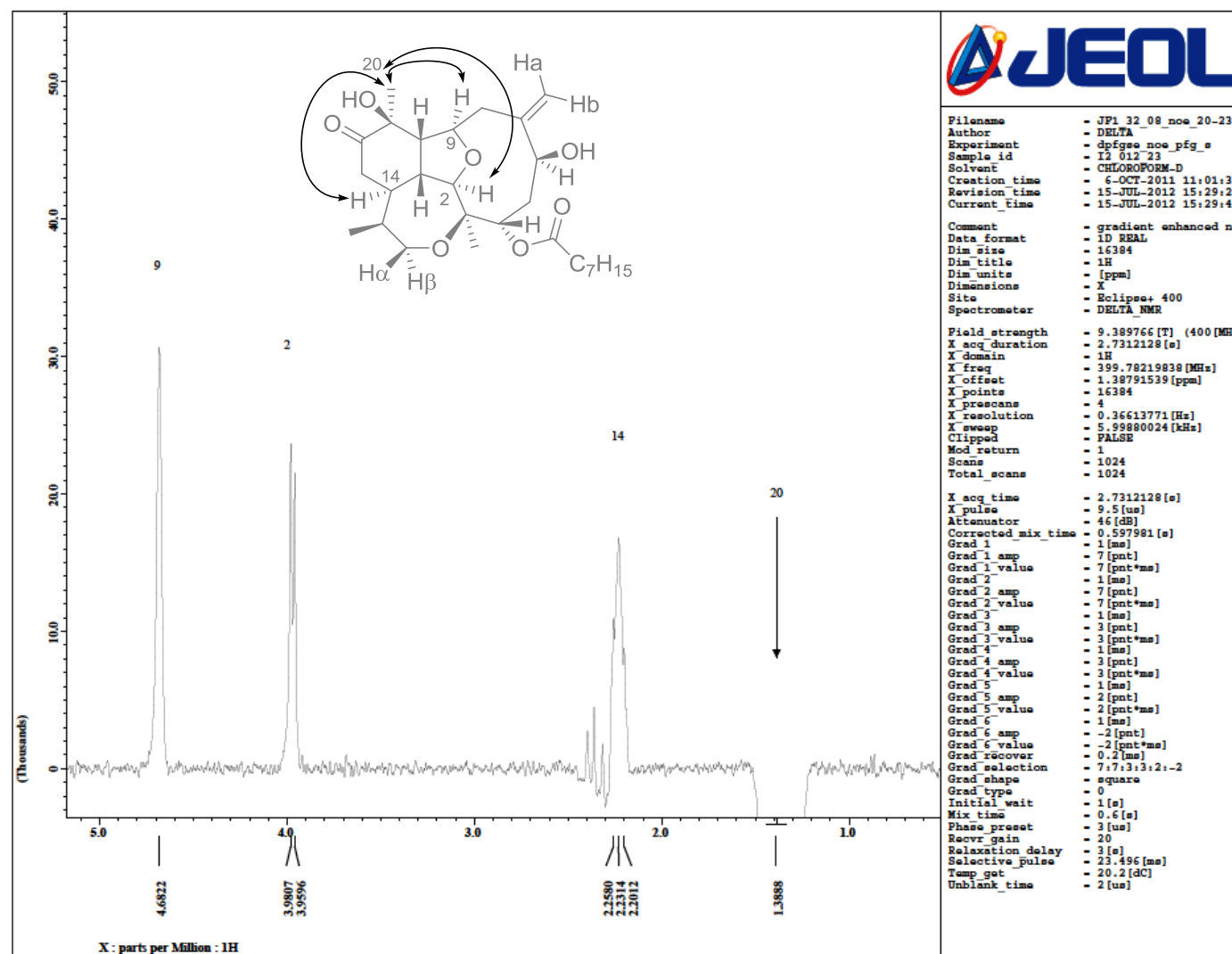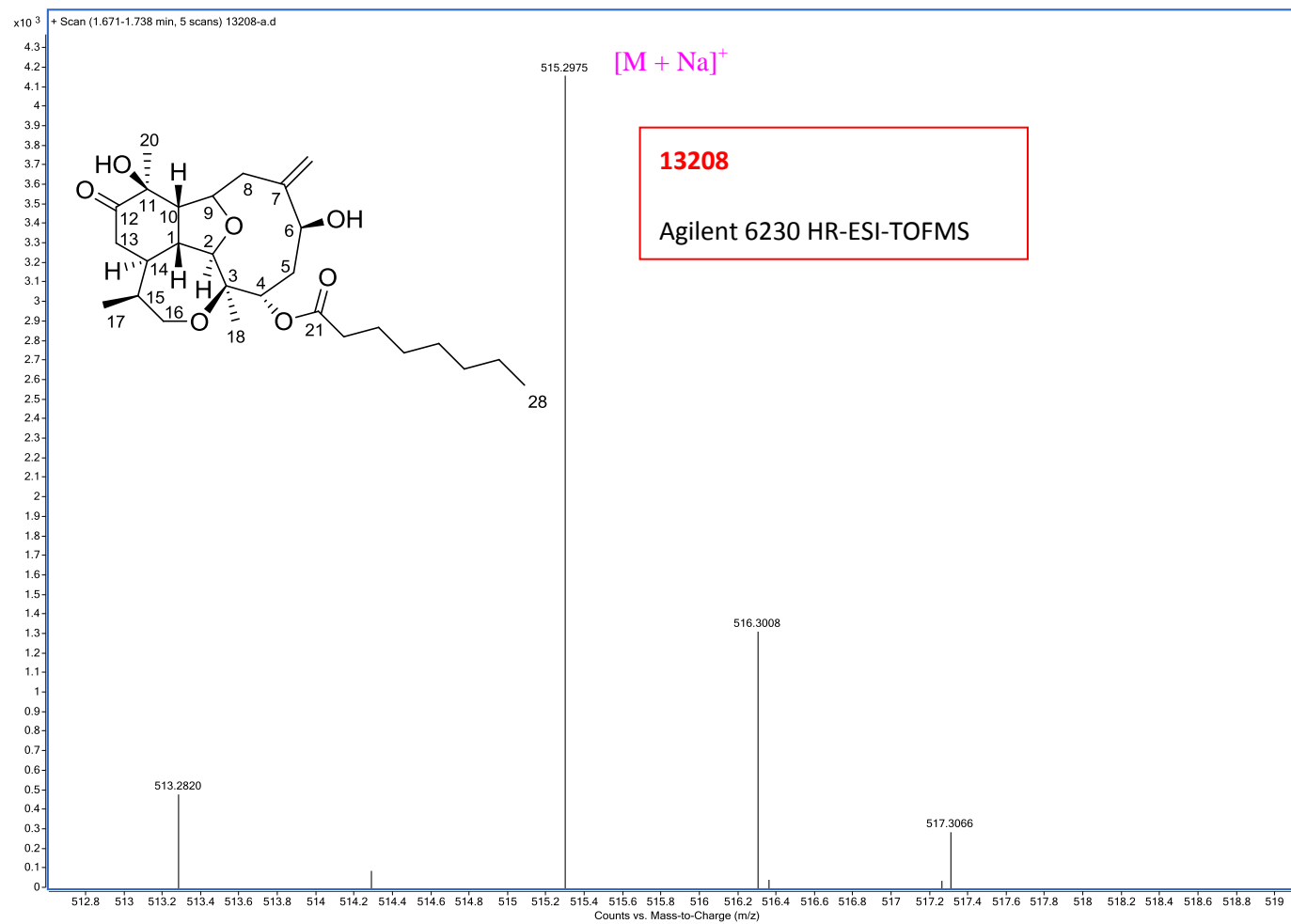
Figure S28. Briarellin S, HRMS-ESI-TOF spectrum. HSQC and HMBC correlations of the olefinic protons at C-19.

Figure S29. Briarellin S, HSQC correlation of H-19 (HSQC spectrum with a low peak threshold level).
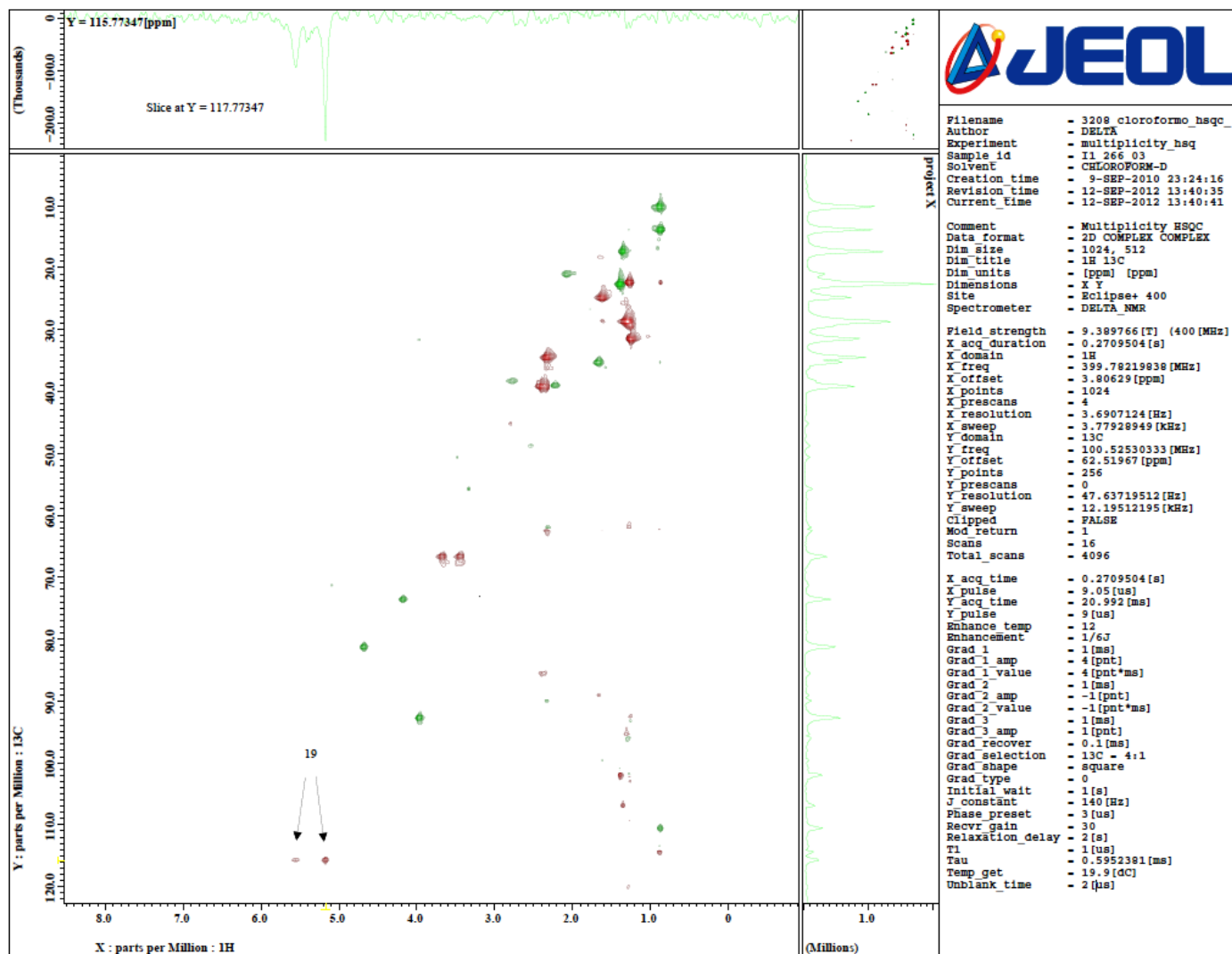
Figure S30. Briarellin S, HMBC correlations of H-19 (HMBC spectrum with a low peak threshold level).
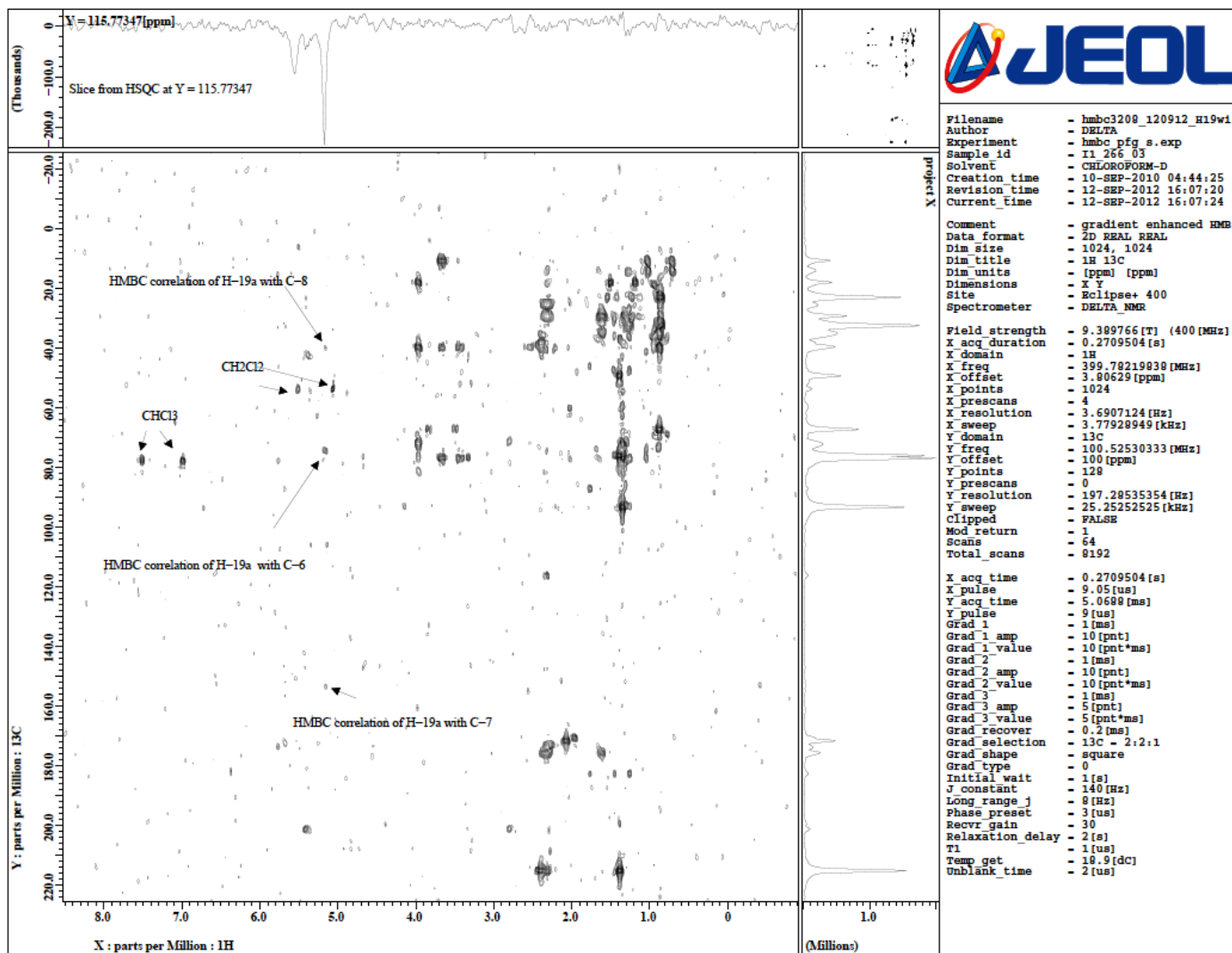
Figure S31. Briarellin S, HMBC correlations of H-19 (slice at *X* = 5.16).
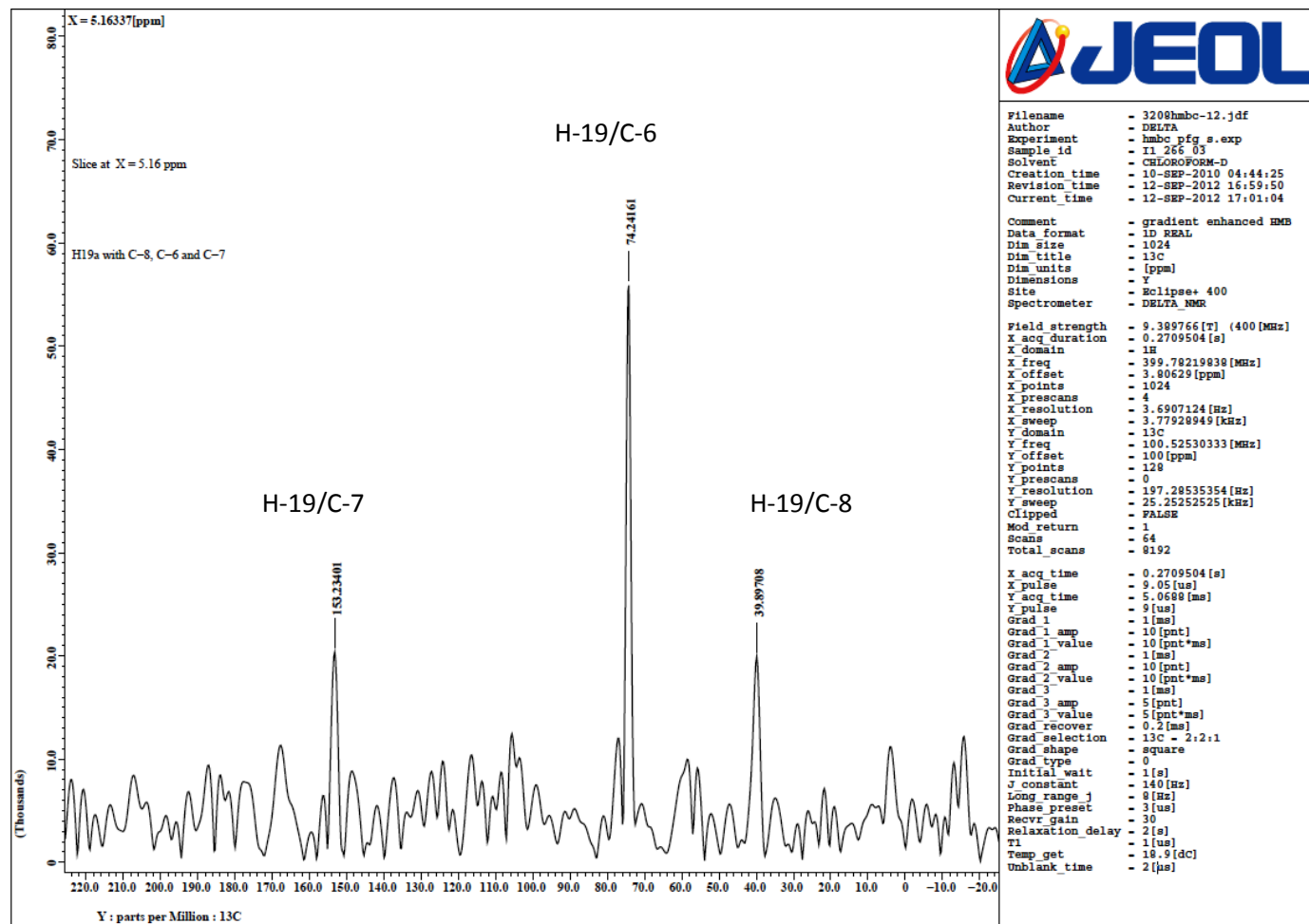
Figure S32. Briarellin S, HMBC correlations of H-19 (slices at *Y* = 39.90, *Y* = 74.49 and *Y* = 153.23).