Supporting Information

Eleganketal A, a Highly Oxygenated Dibenzospiroketal from the Marine Derived Fungus *Spicaria elegans* KLA03

Yepeng Luan, † Hongjuan Wei,† Zhenpei Zhang,† Qian Che,† Yankai Liu,† Tianjiao Zhu,† Attila Mándi,‡ Tibor Kurtán,‡ Qianqun Gu,† and Dehai Li†*

†Key Laboratory of Marine Drugs, Chinese Ministry of Education, School of Medicine and Pharmacy, Ocean University of China, Qingdao 266003, People's Republic of China.

‡Department of Organic Chemistry, University of Debrecen, POB 20, H-4010 Debrecen, Hungary.

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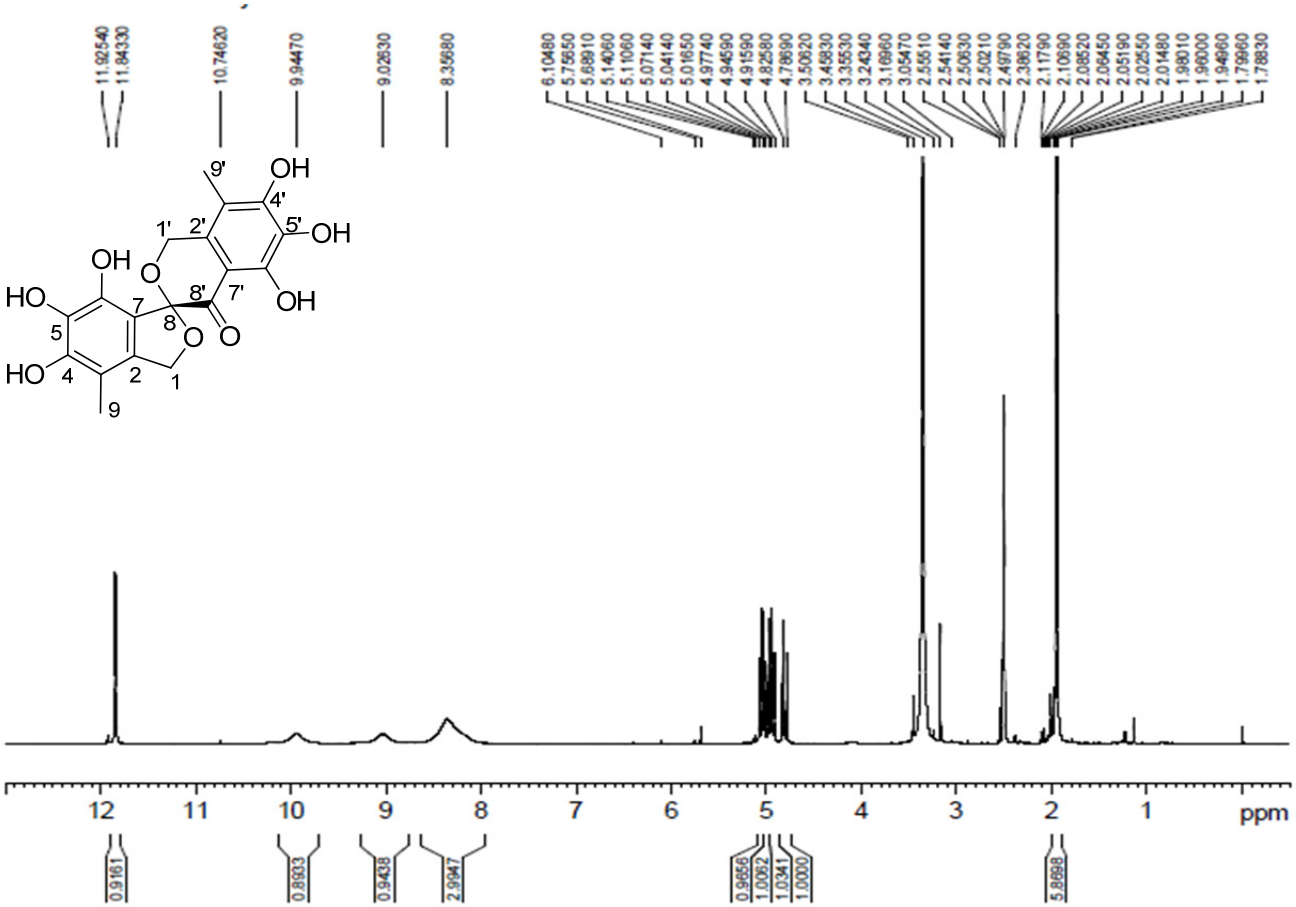


Figure S1.^{1}H NMR spectrum (400 MHz) of eleganketal A (**1**) in DMSO-d_6

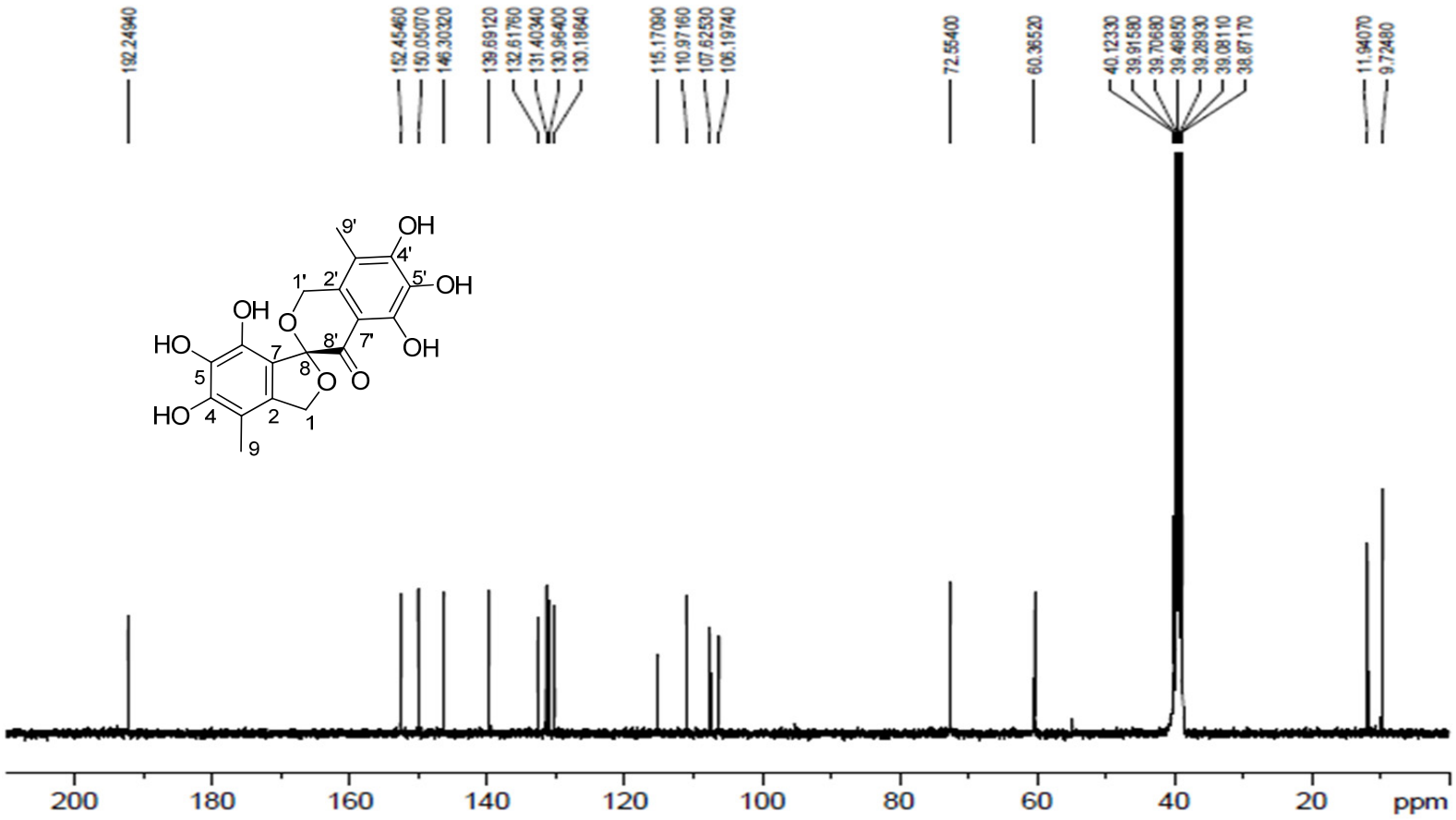


Figure S2. ^{13}C NMR spectrum (100 MHz) of eleganketal A (**1**) in DMSO-d_6

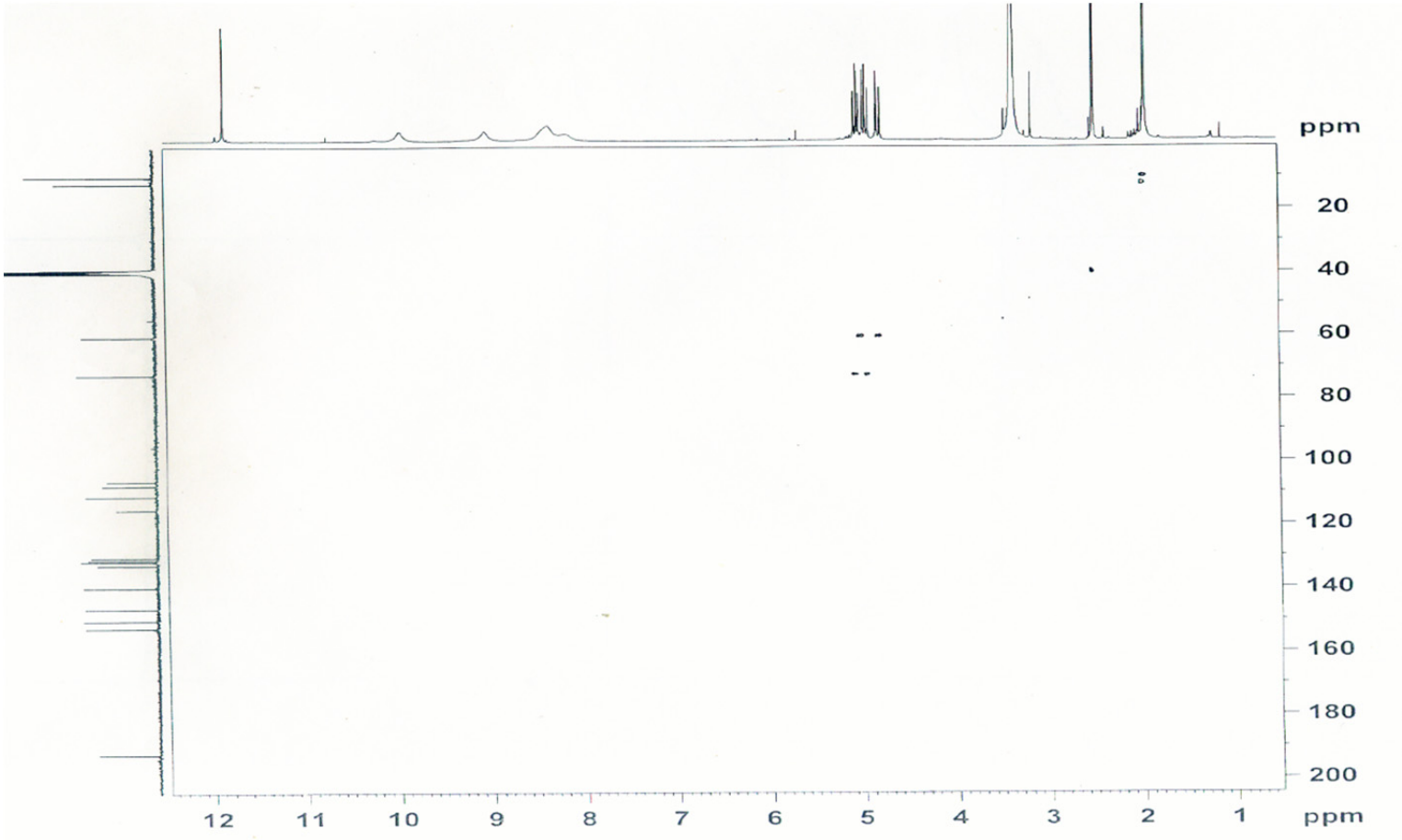


Figure S3. HMQC spectrum of eleganketal A (**1**) in DMSO-d_6

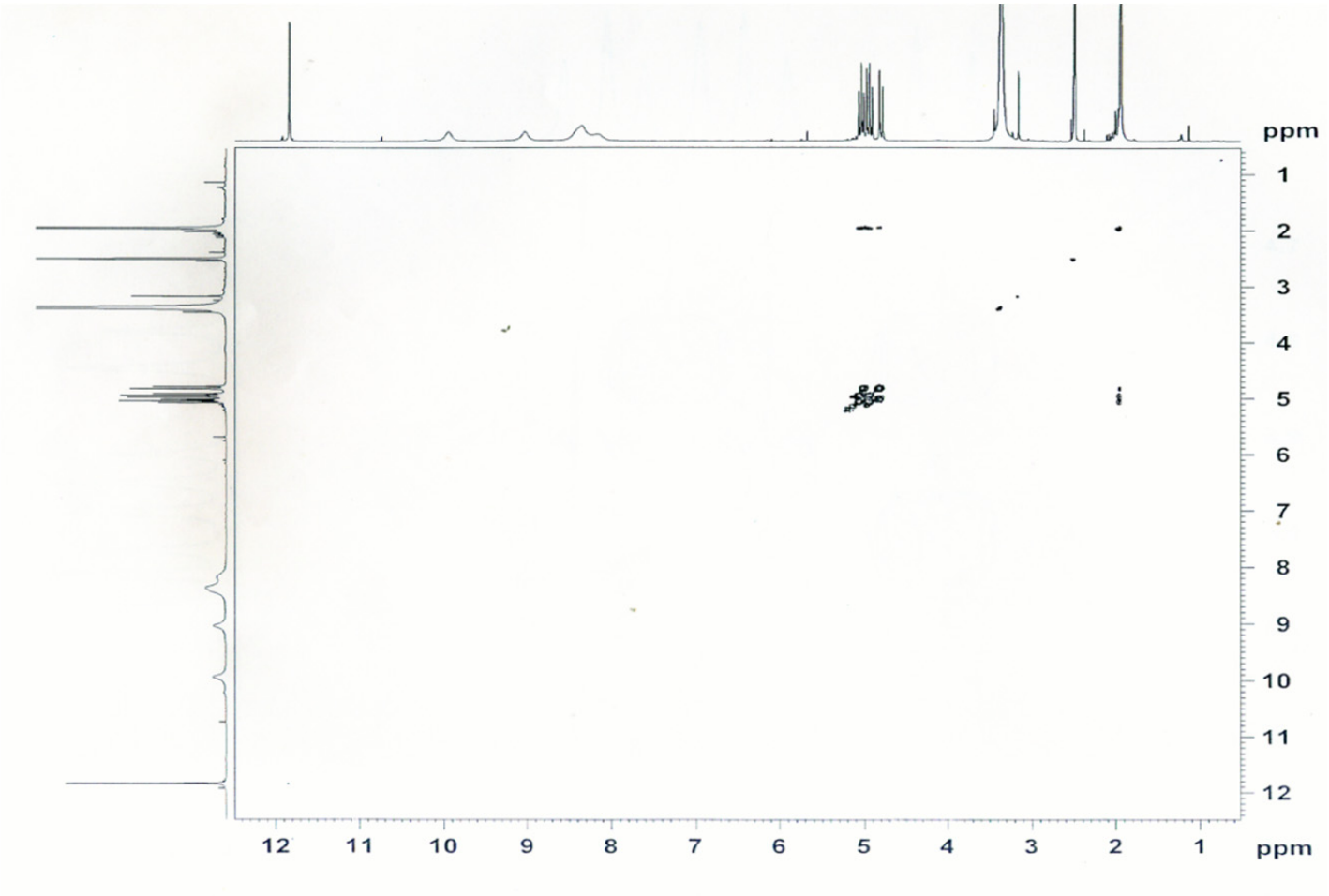


Figure S4. ^{1}H-^{1}H COSY spectrum of eleganketal A (**1**) in DMSO-d_6

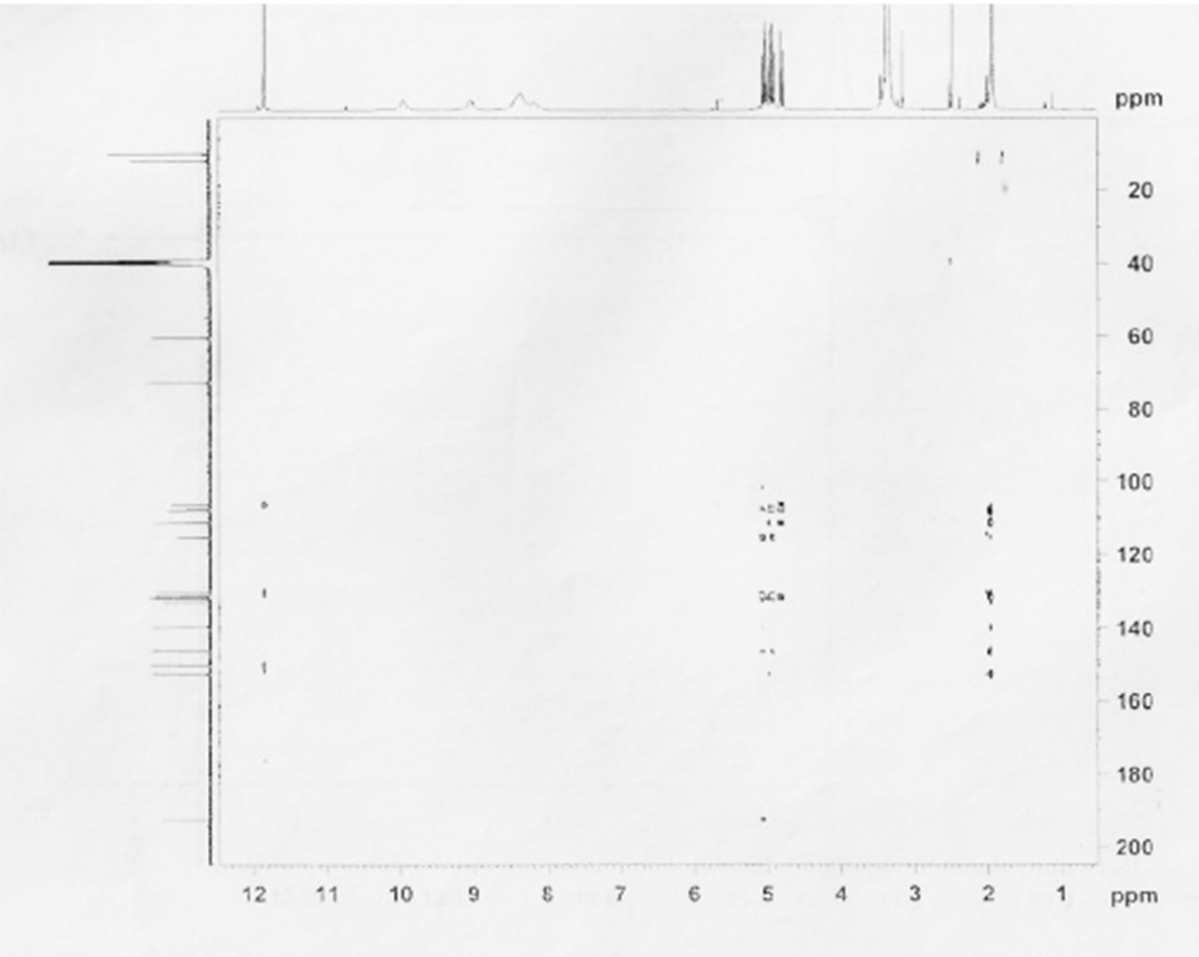
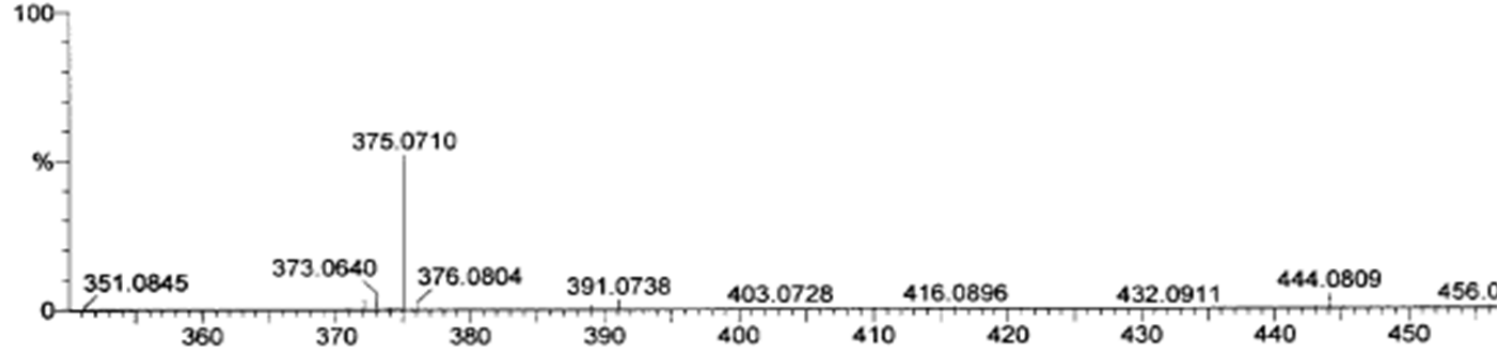


Figure S5. HMBC spectrum of eleganketal A (**1**) in DMSO-d_6

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

WHJ-N-11
20090508-WHJ-N-11-2 192 (1.978) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (160:192)



Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
375.0710	375.0716	-0.6	-1.6	11.5	1	C18 H15 O9

Figure S6. HRESIMS spectrum of eleganketal A (**1**).

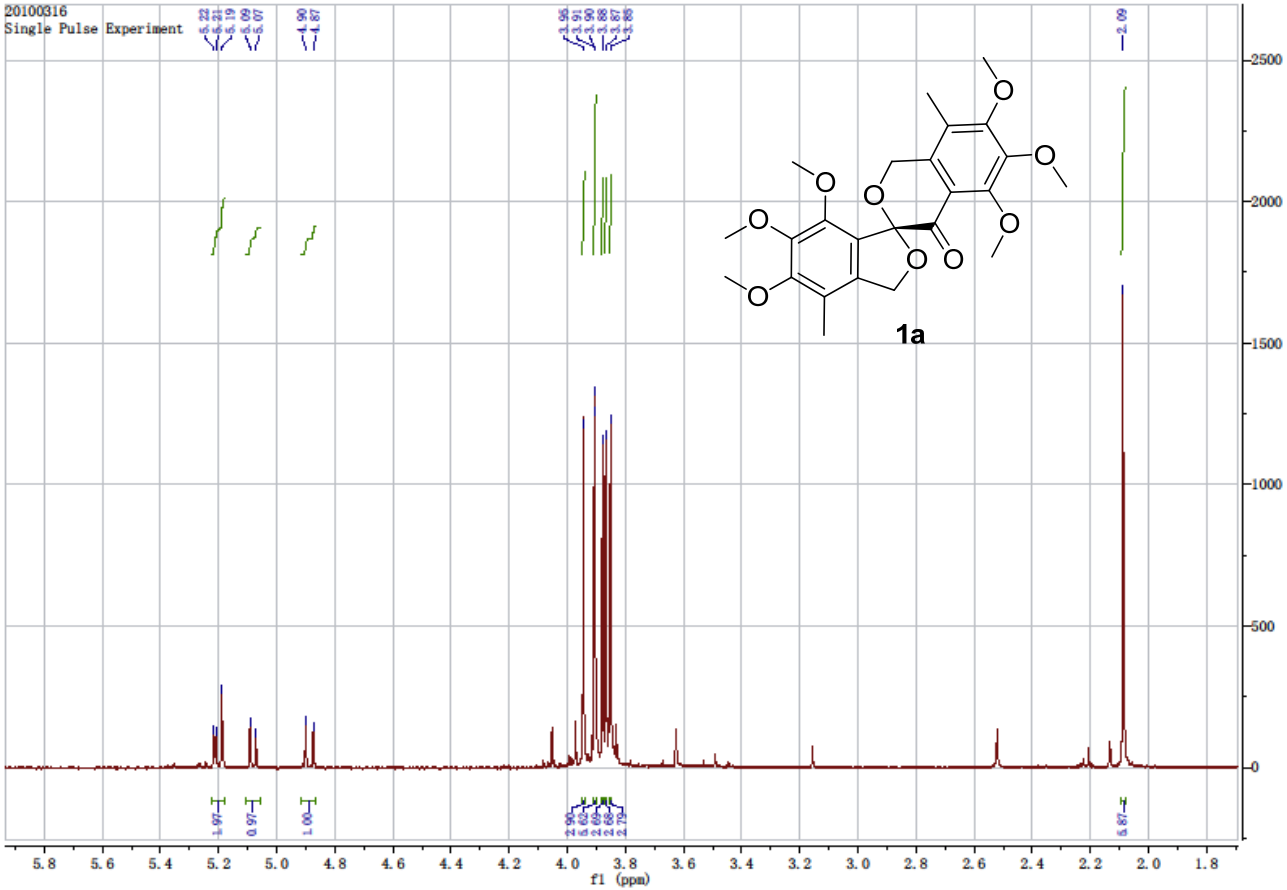


Figure S7. ^{1}H NMR spectrum (400 MHz) of natural methylated product **1a** in DMSO-d_6

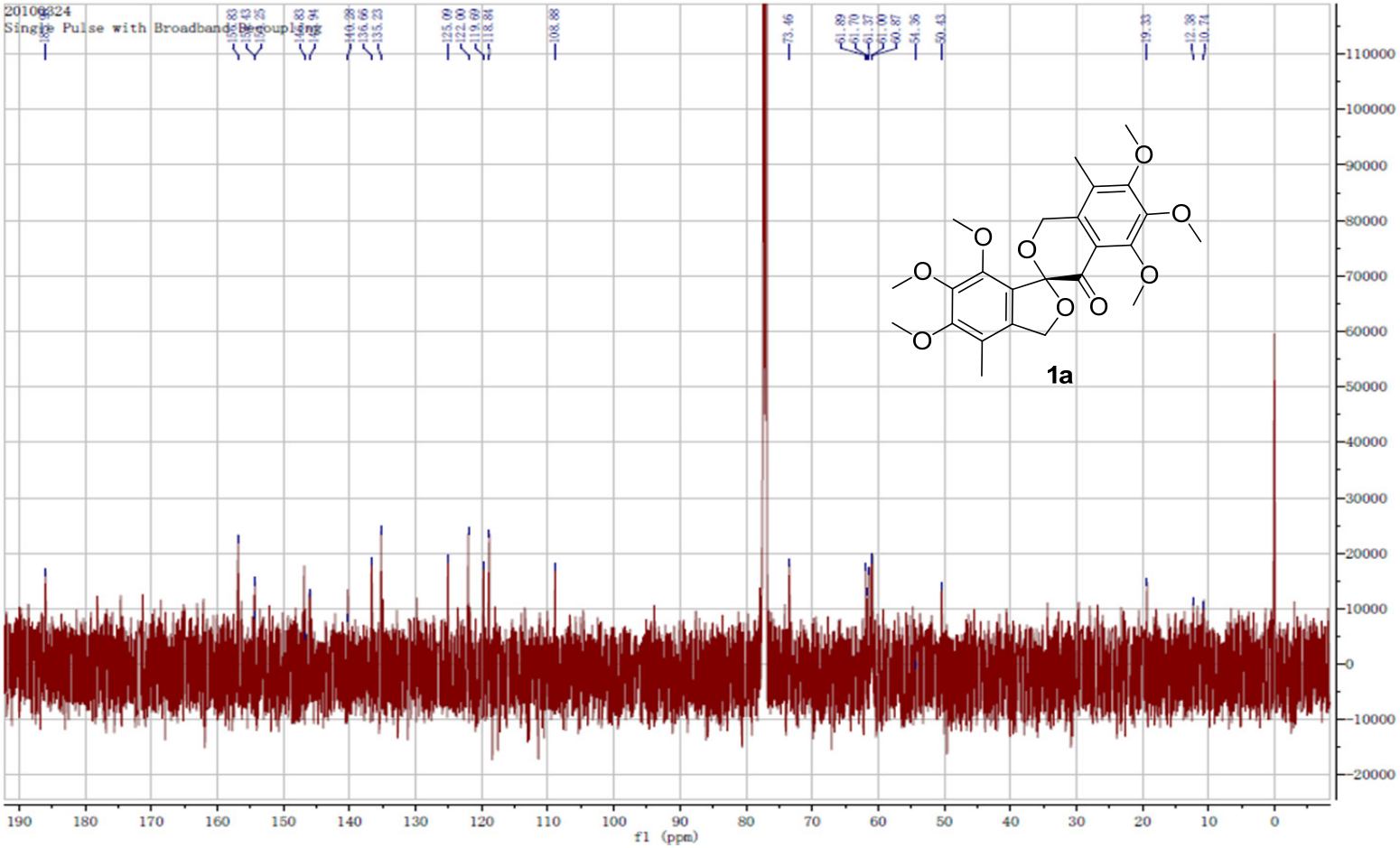


Figure S8. ^{13}C NMR spectrum (100 MHz) of natural methylated product **1a** in DMSO-d_6

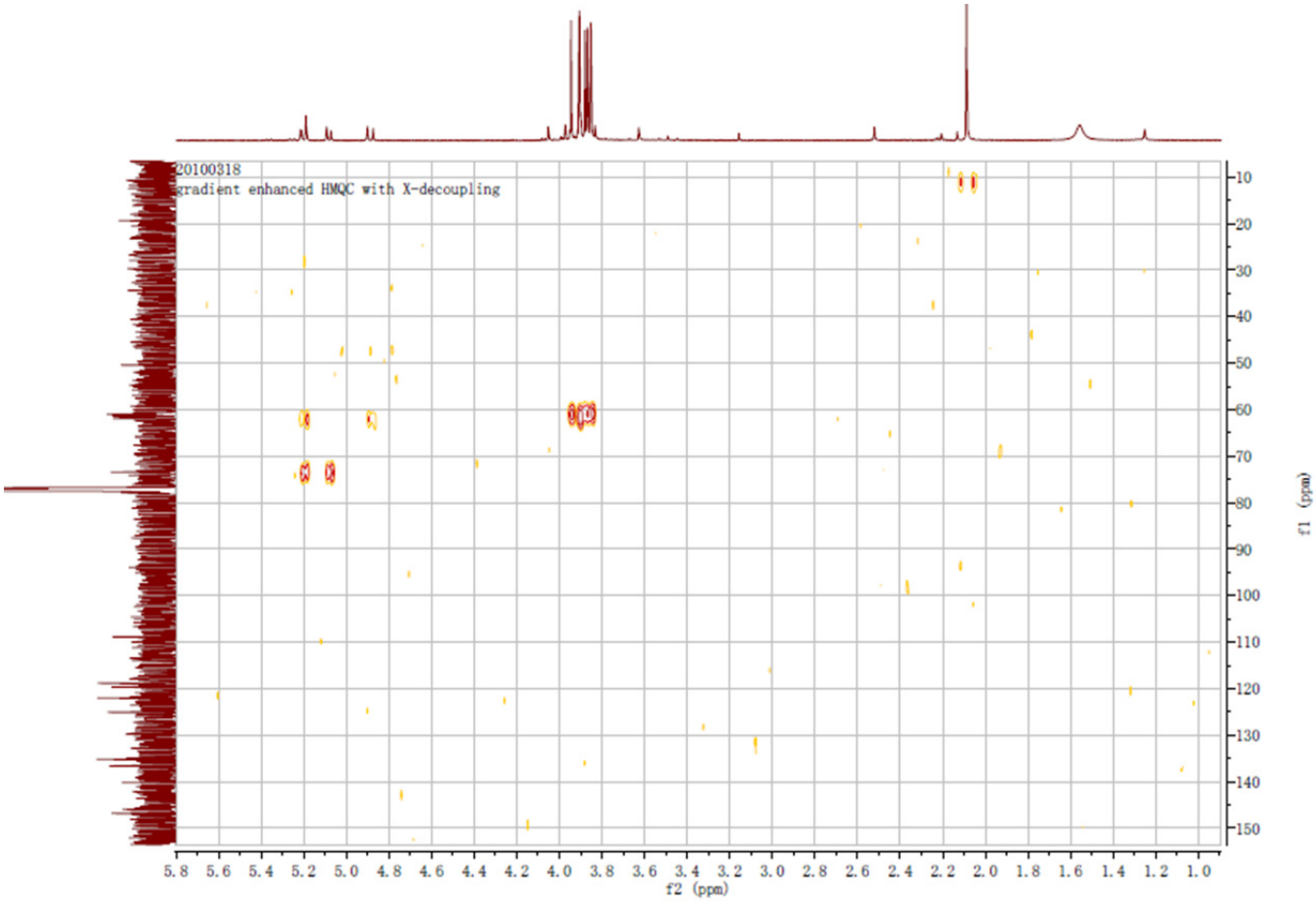


Figure S9. HMQC spectrum of natural methylated product **1a** in DMSO-d_6

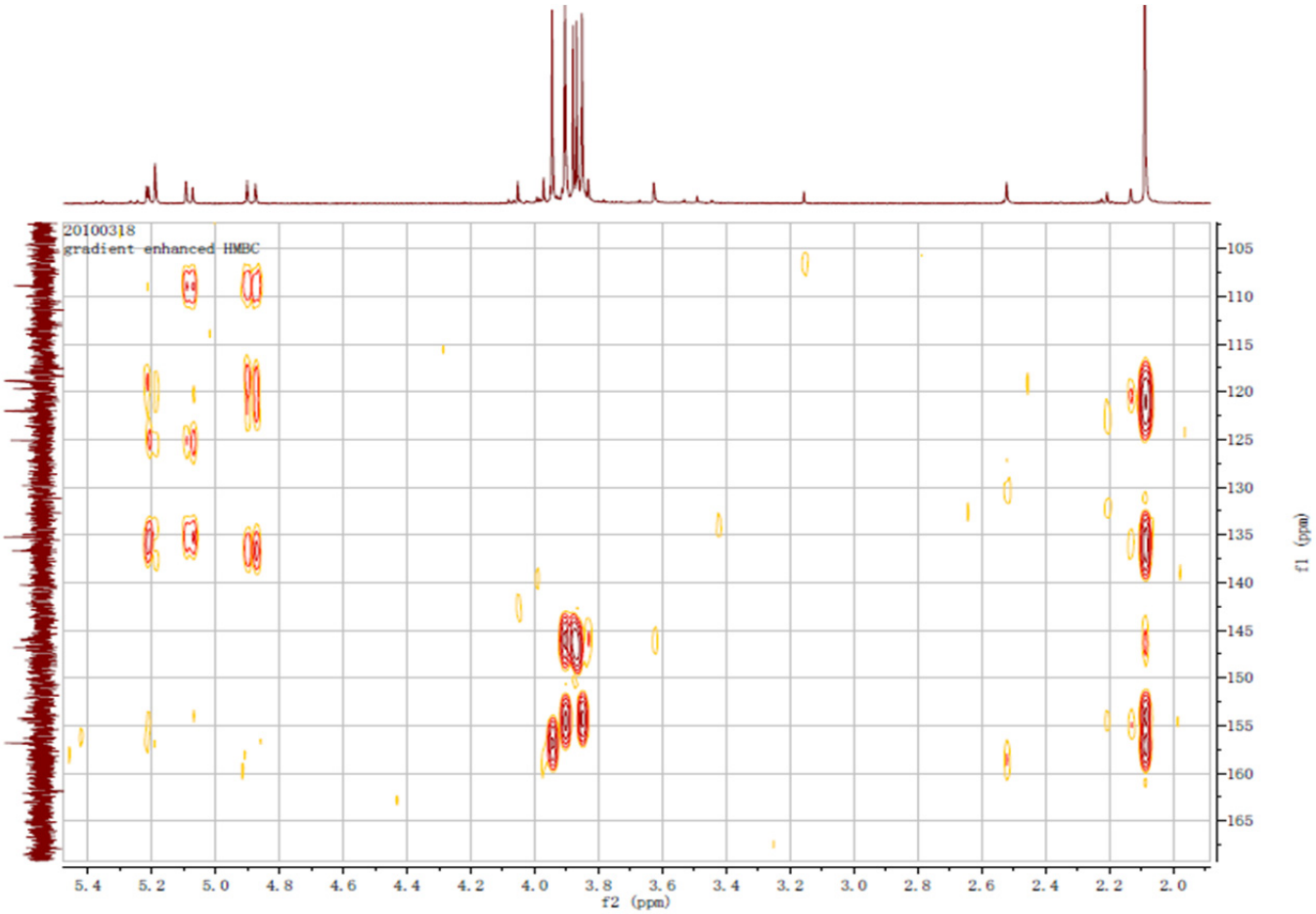


Figure S10. HMBC spectrum of natural methylated product **1a** in DMSO-d_6

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Enhanced Resolution	Scan Begin	100 m/z	Scan End	2000 m/z
Capillary Exit	140.0 V	n/a	n/a	Trap Drive	56.6
Accumulation Time	13 µs	Averages	3 Spectra	Auto MS/MS	off

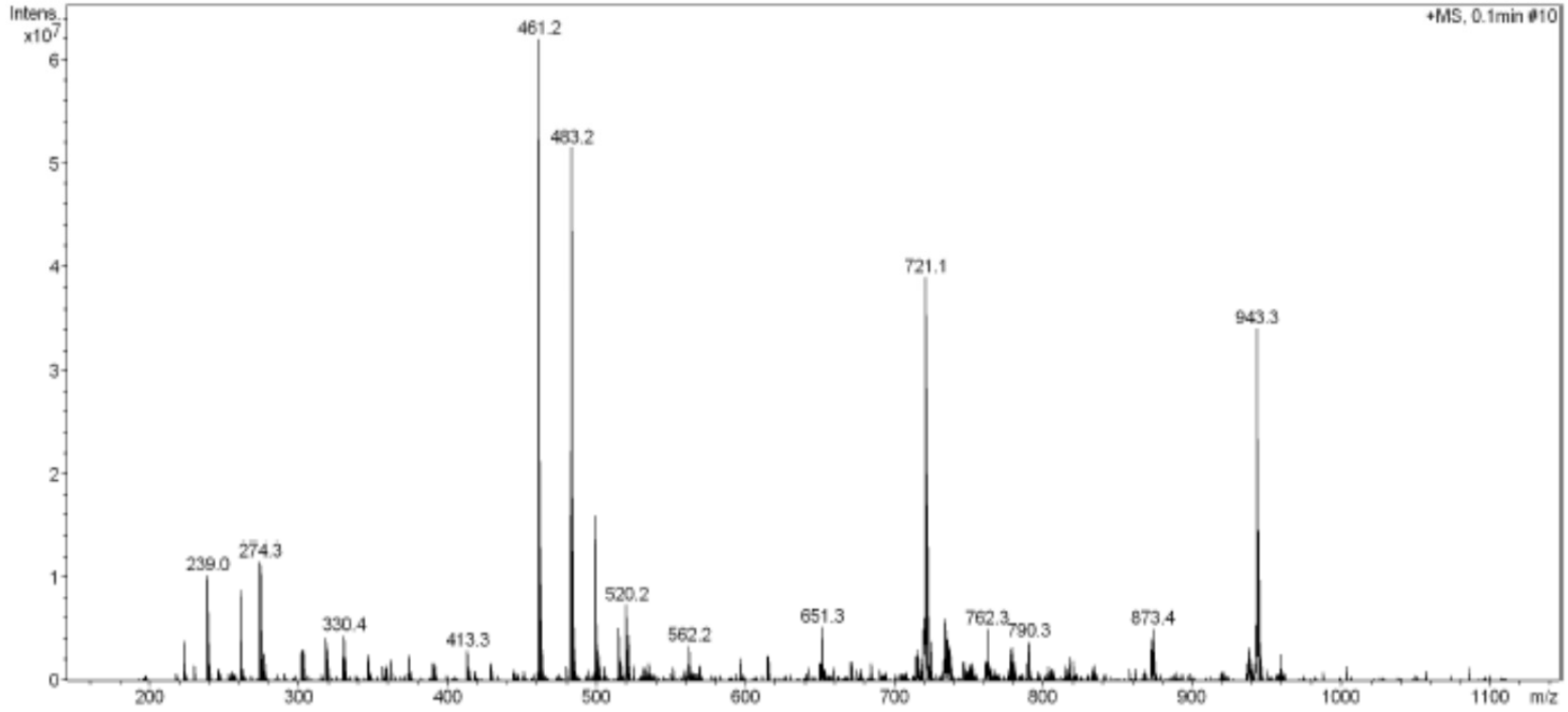


Figure S11. LRESIMS spectrum of natural methylated product **1a.**

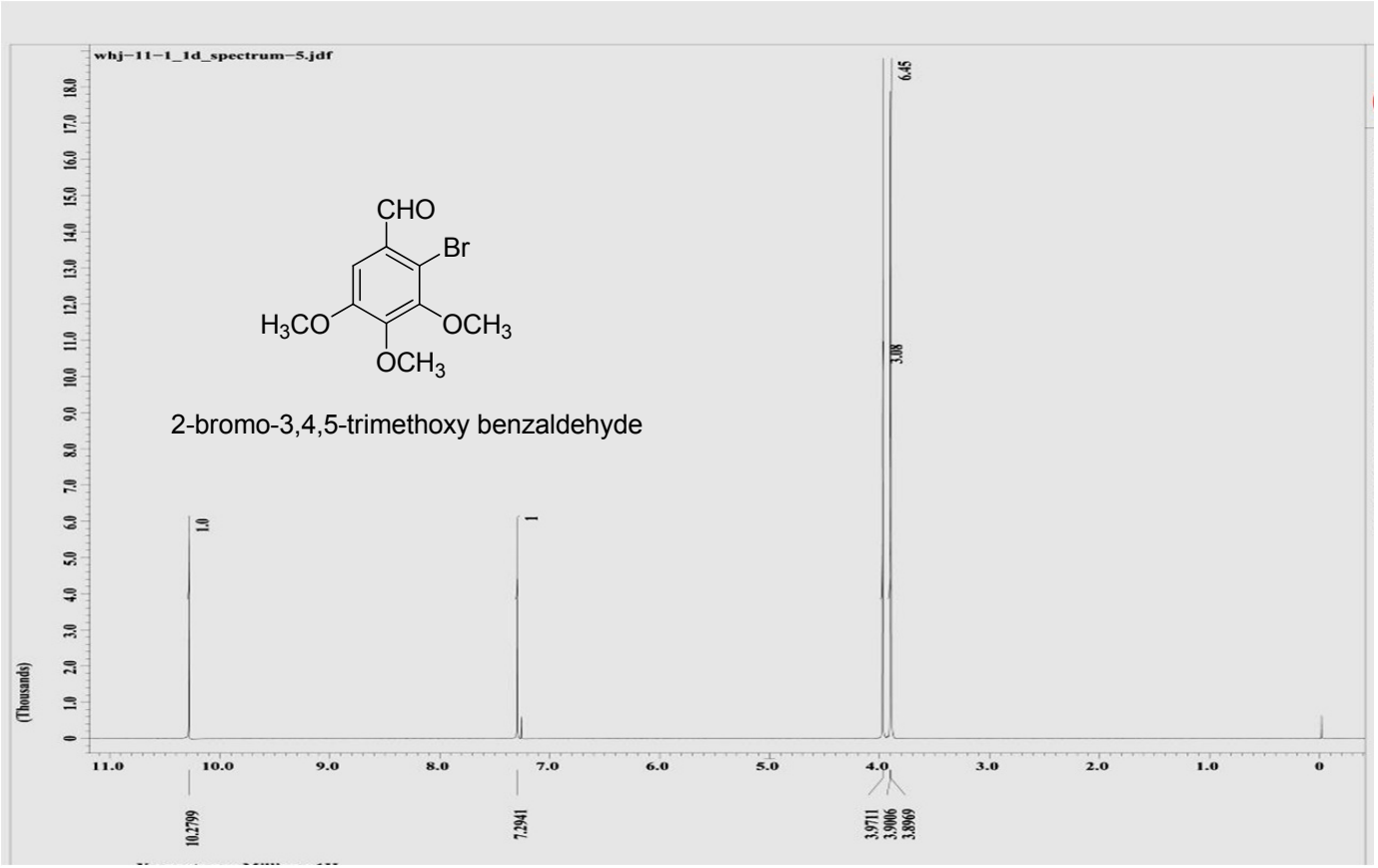


Figure S12. ^{1}H NMR spectrum (600 MHz) of 2-bromo-3,4,5-trimethoxy benzaldehyde in $CDCl_3$.

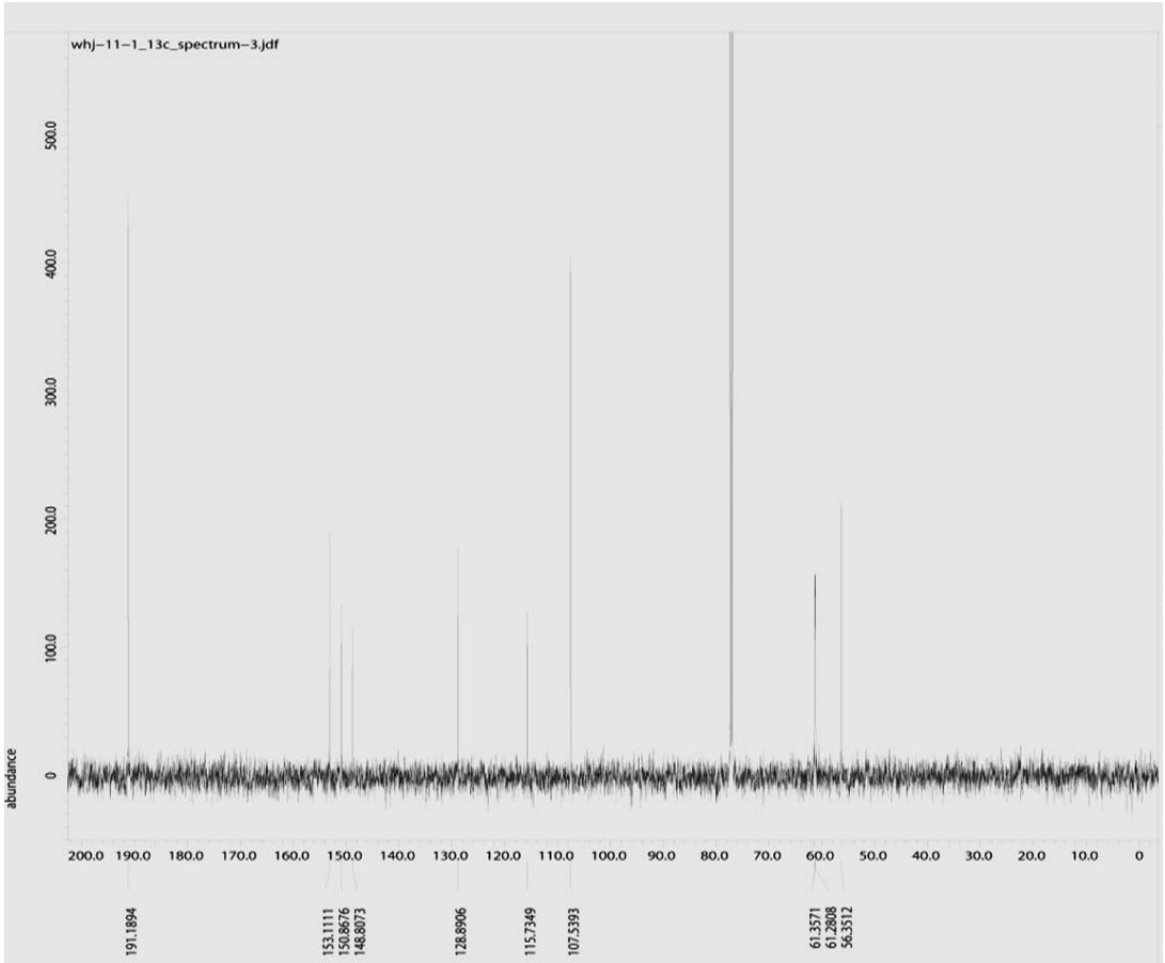


Figure S13. ^{13}C NMR spectrum (150 MHz) of 2-bromo-3,4,5-trimethoxy benzaldehyde in $CDCl_3$.

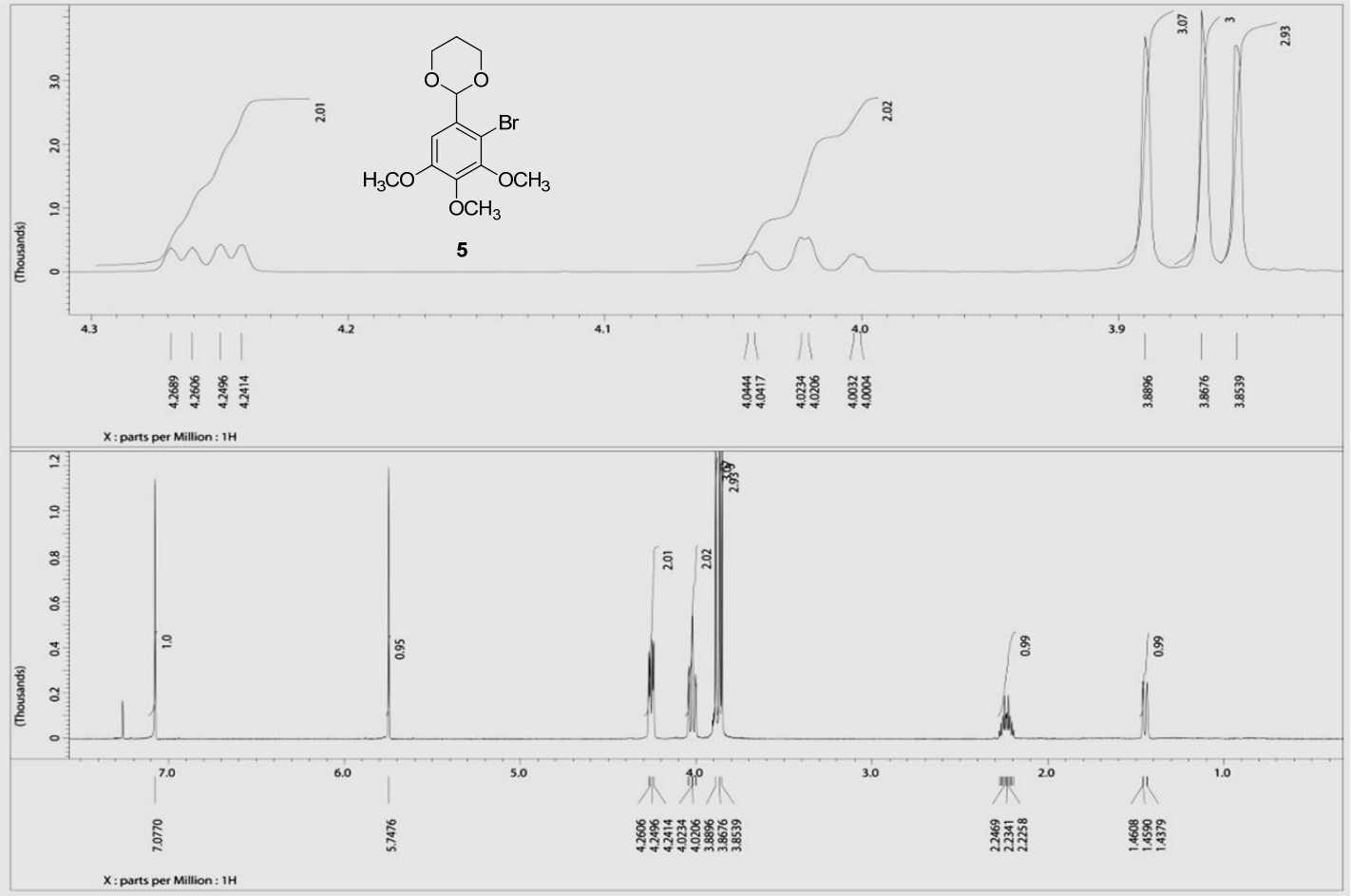


Figure S14. ^{1}H NMR spectrum (600 MHz) of **5** in $CDCl_3$.

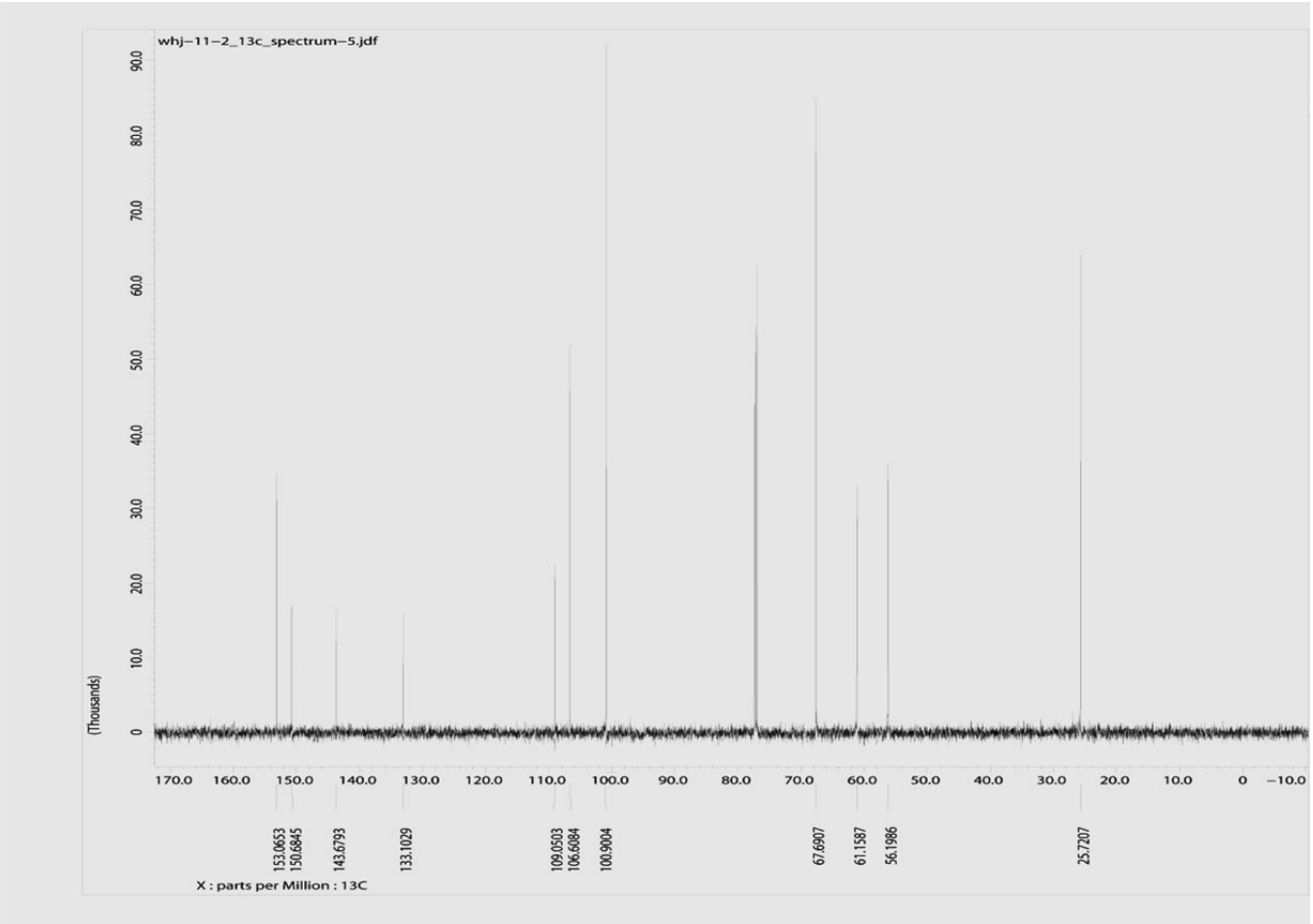


Figure S15. ^{13}C NMR spectrum (150 MHz) of **5** in $CDCl_3$.

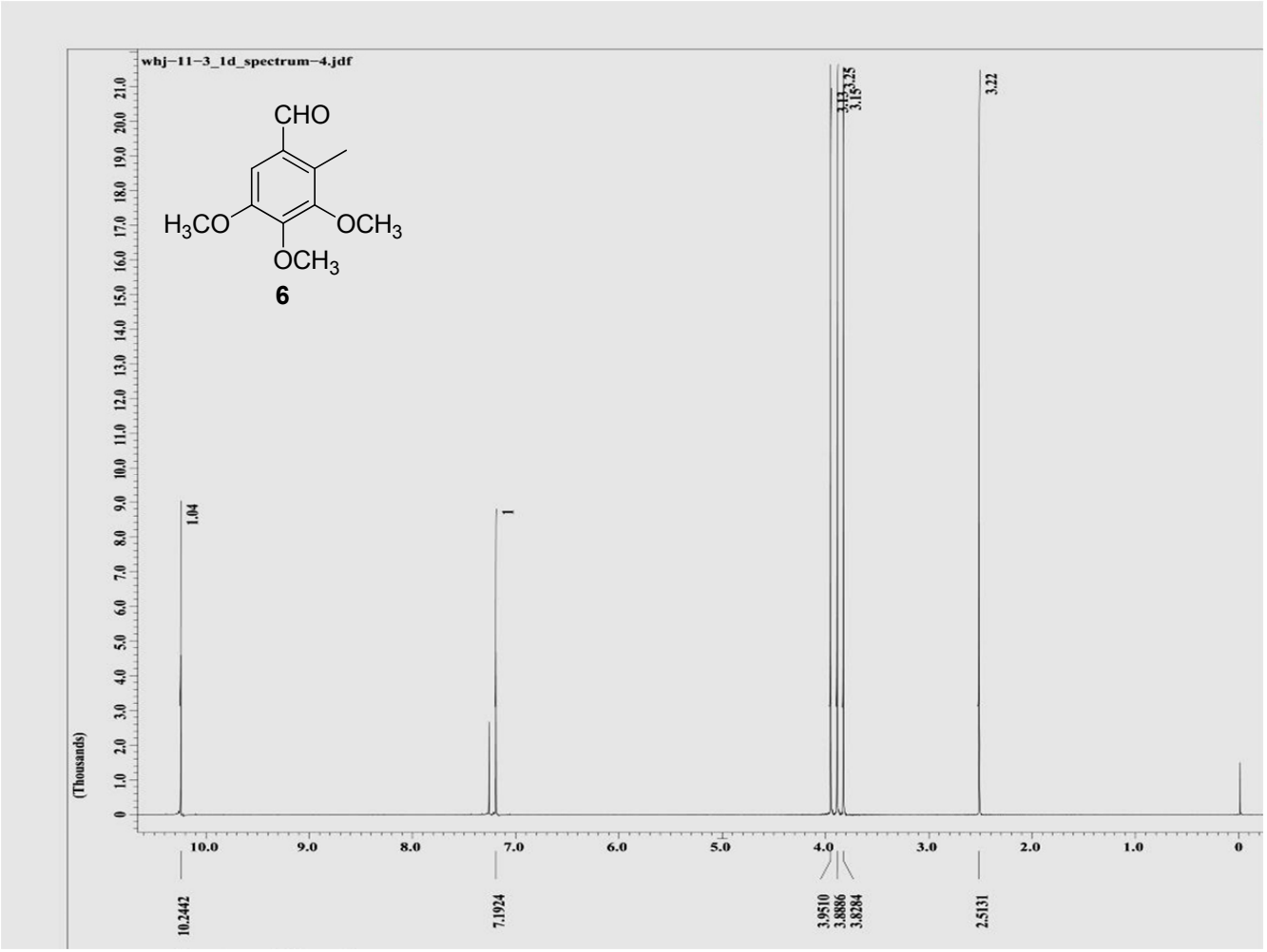


Figure S16. ^{1}H NMR spectrum (600 MHz) of **6** in $CDCl_3$.

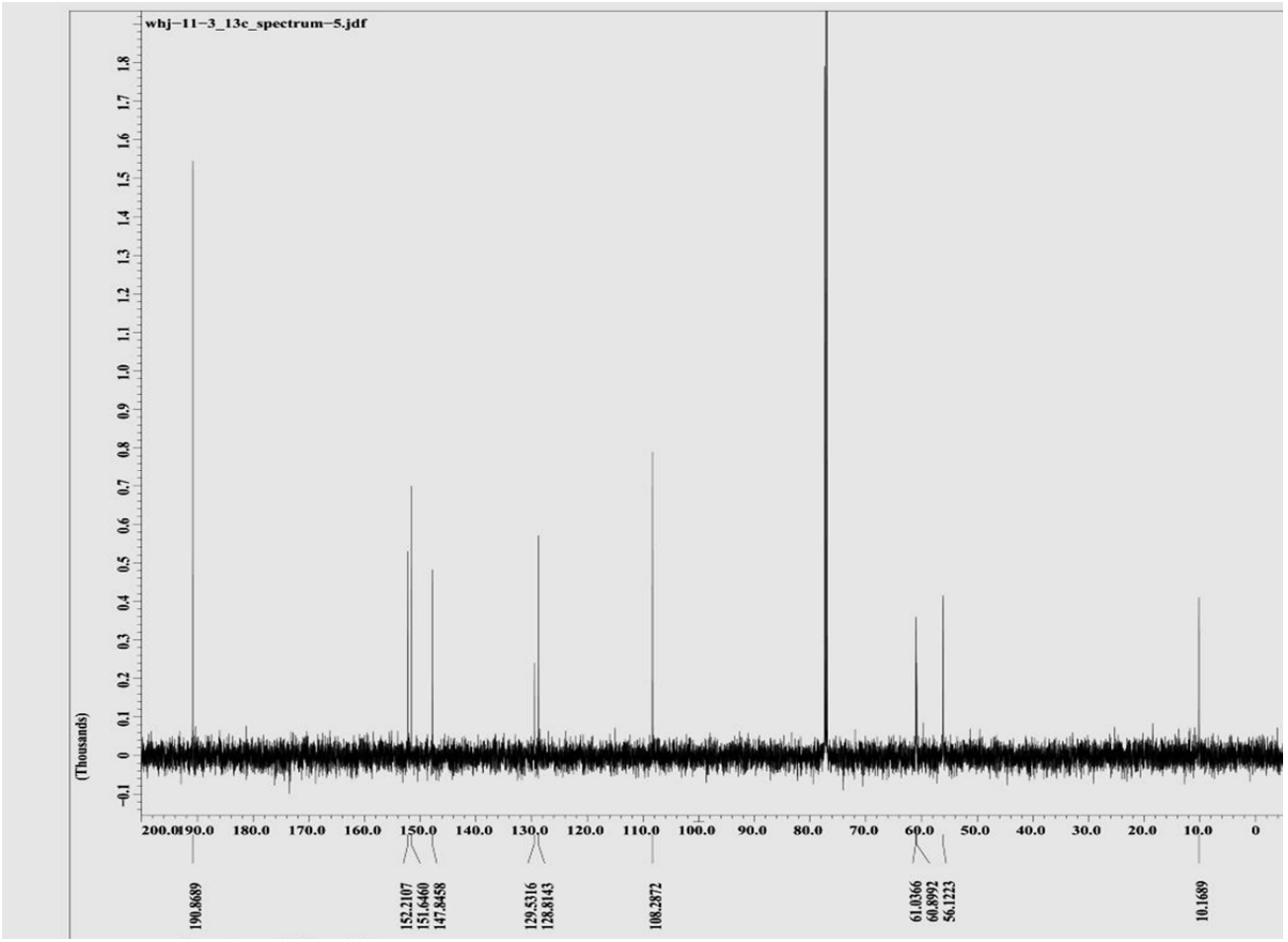


Figure S17. ^{13}C NMR spectrum (150 MHz) of **6** in $CDCl_3$.

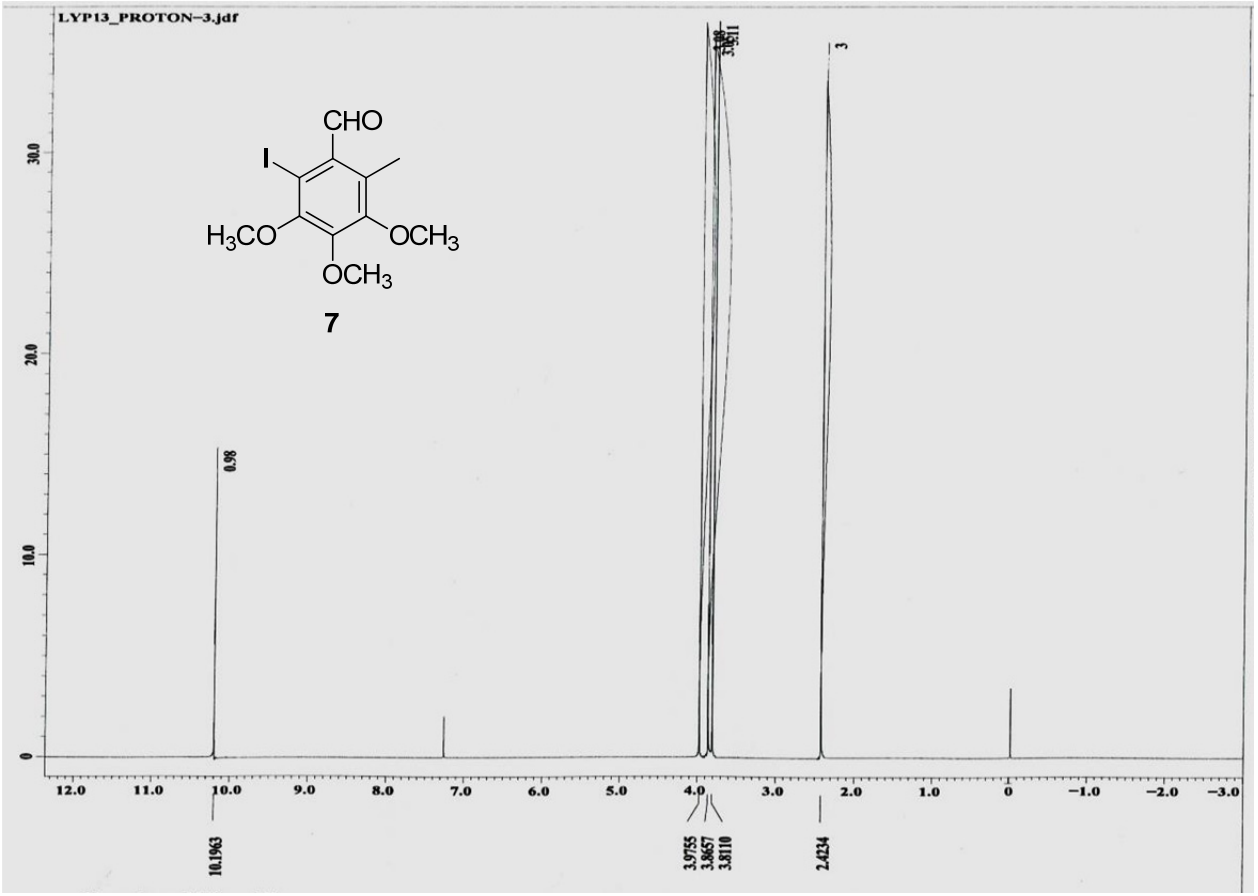


Figure S18. ^{1}H NMR spectrum (600 MHz) of **7** in $CDCl_3$.

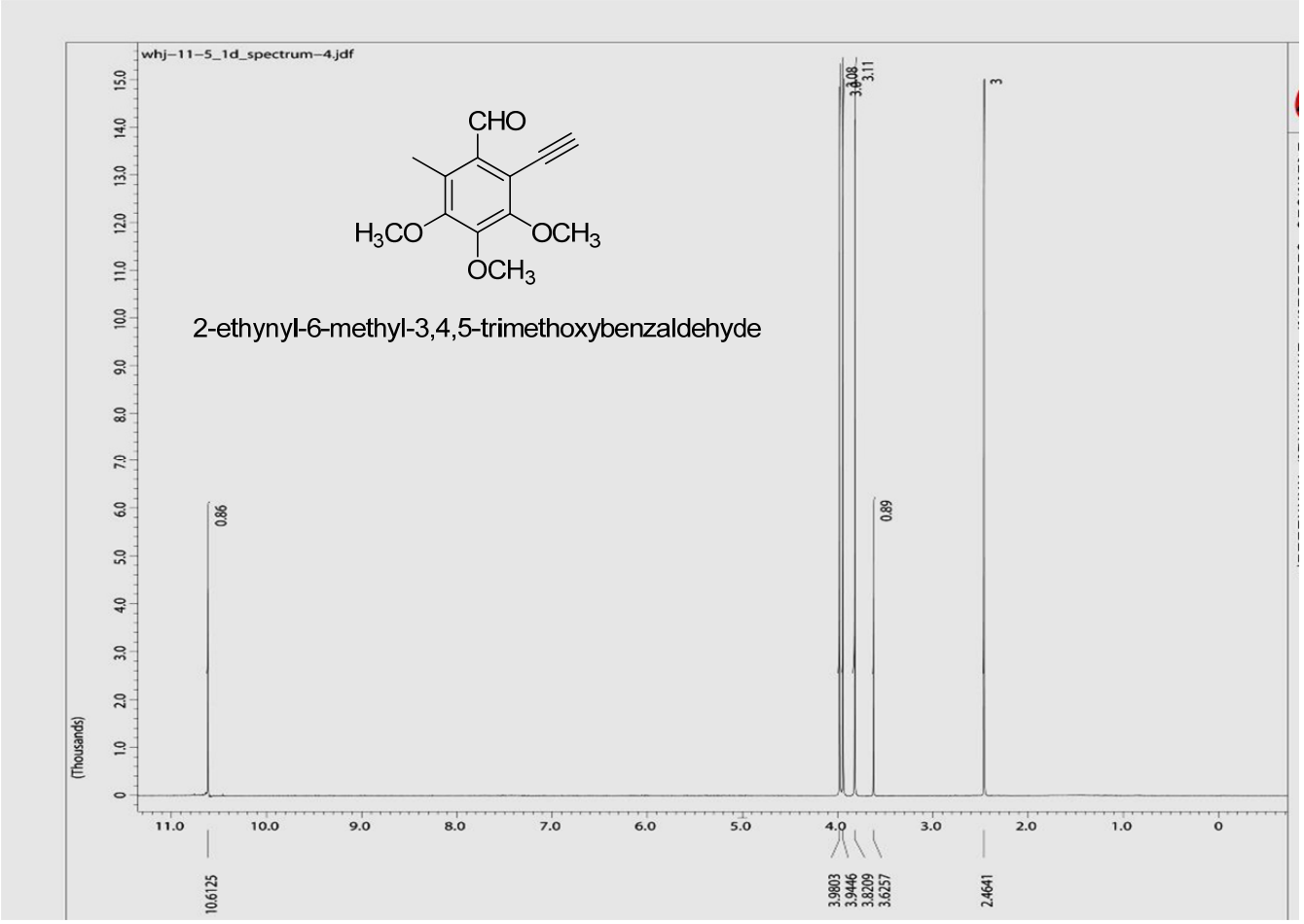


Figure S19. ^{1}H NMR spectrum (600 MHz) of 2-ethynyl-6-methyl-3,4,5-trimethoxybenzaldehyde in $CDCl_3$.

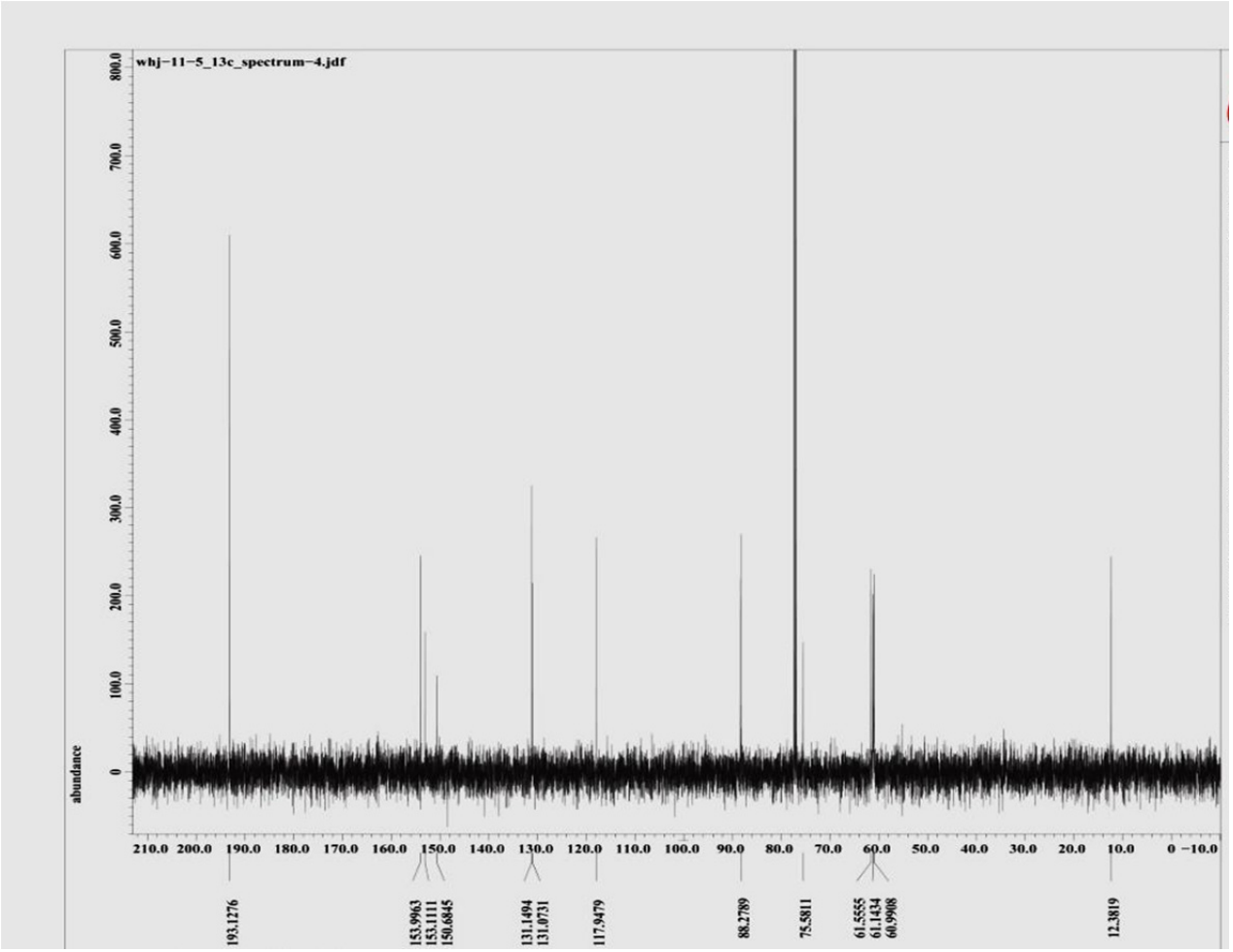


Figure S20. ^{13}C NMR spectrum (150 MHz) of 2-ethynyl-6-methyl-3,4,5-trimethoxybenzaldehyde in $CDCl_3$.

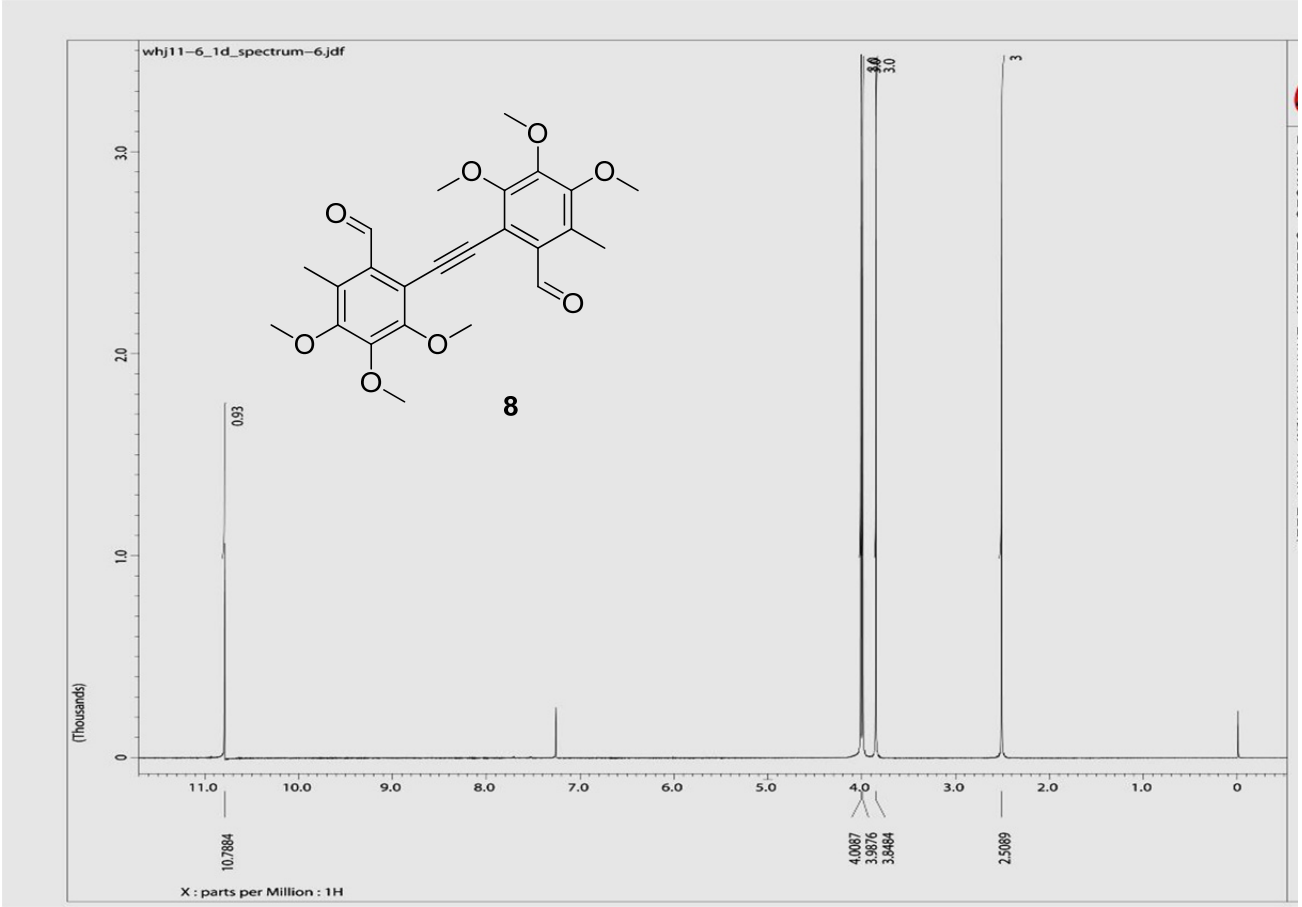


Figure S21. ^{1}H NMR spectrum (600 MHz) of **8** in $CDCl_3$.

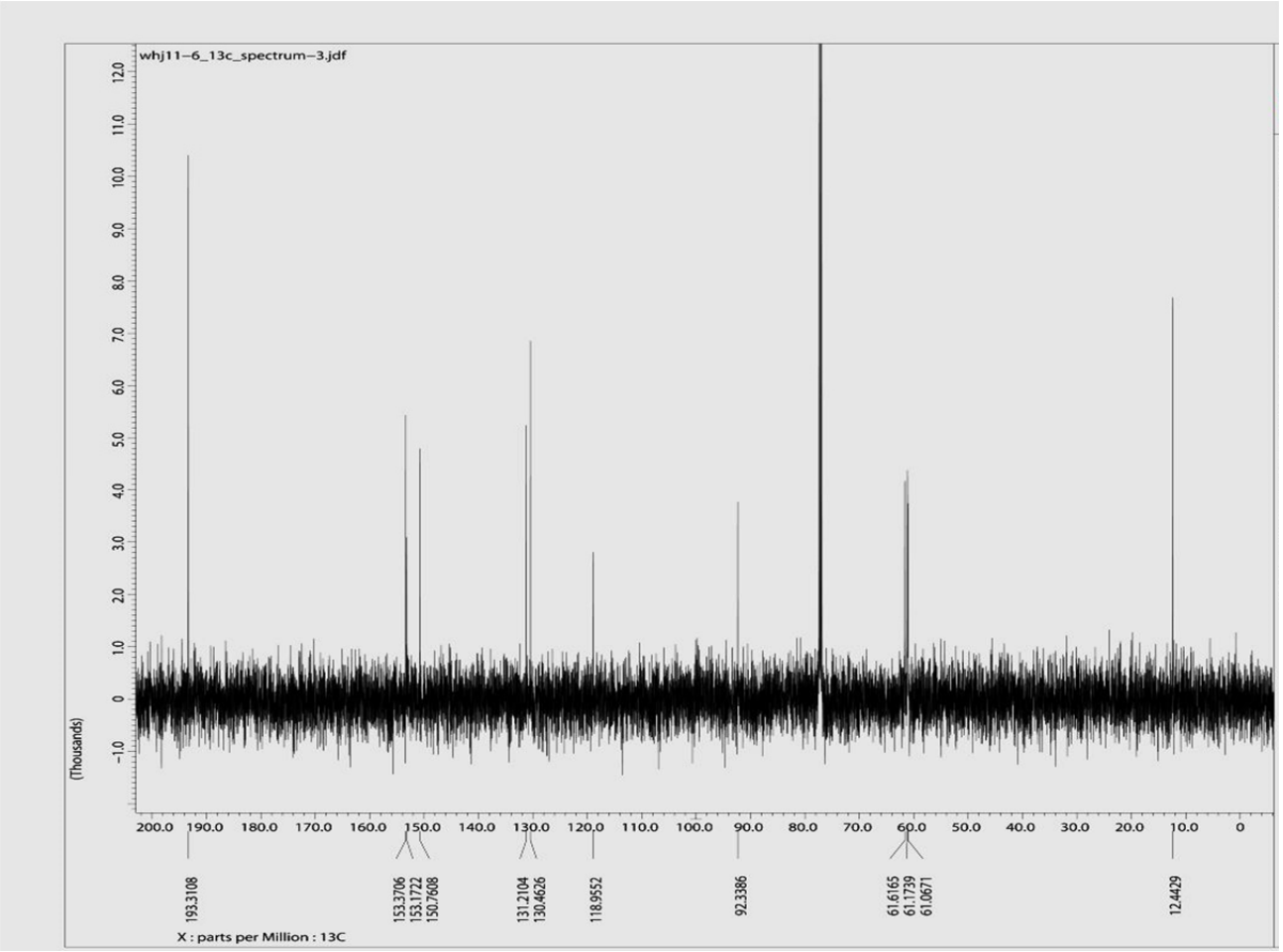


Figure S22. ^{13}C NMR spectrum (150 MHz) of **8** in $CDCl_3$.

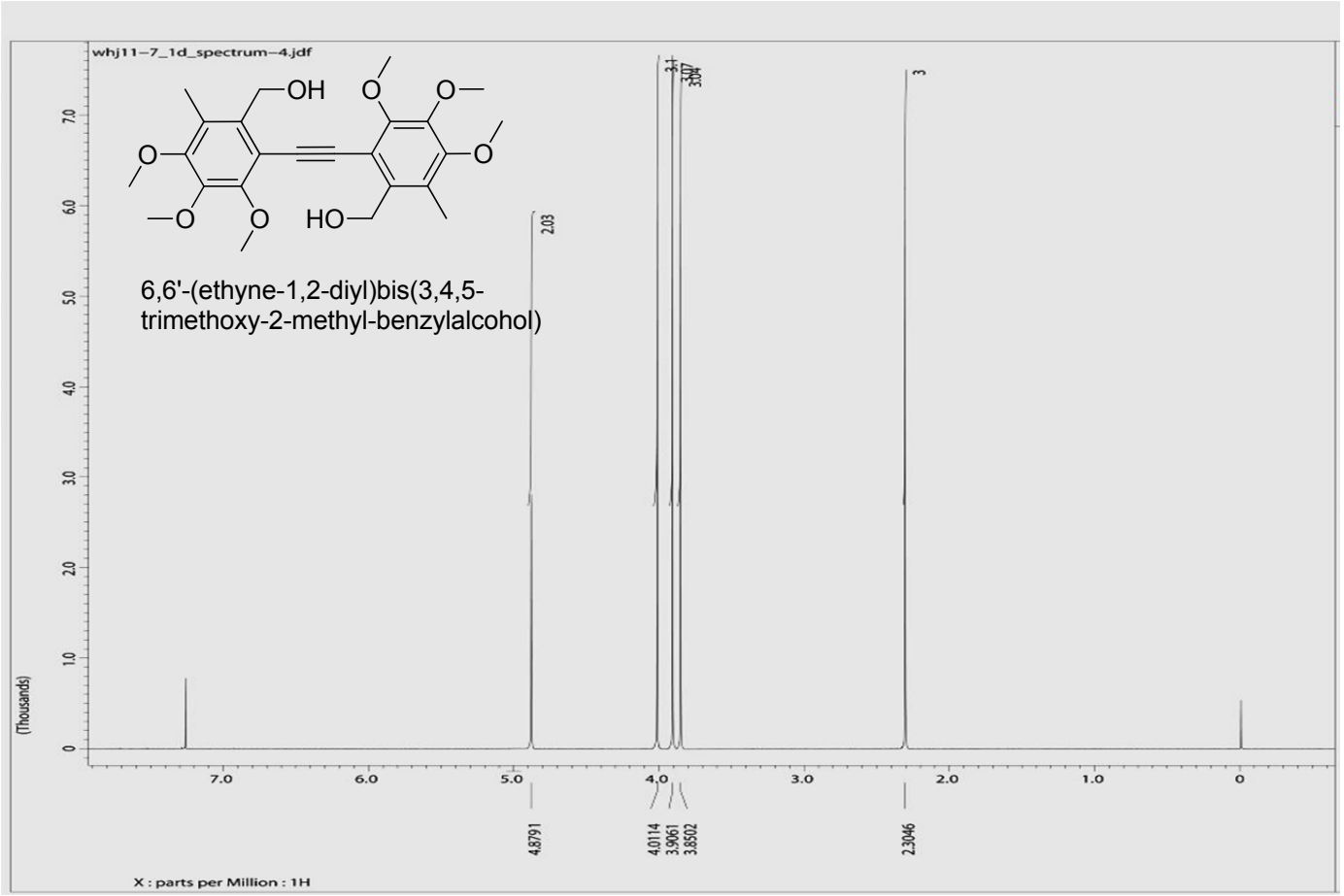


Figure S23. ^{1}H NMR spectrum (600 MHz) of 6,6'-(ethyne-1,2-diyl)bis(3,4,5-trimethoxy-2-methyl-benzylalcohol) in $CDCl_3$.

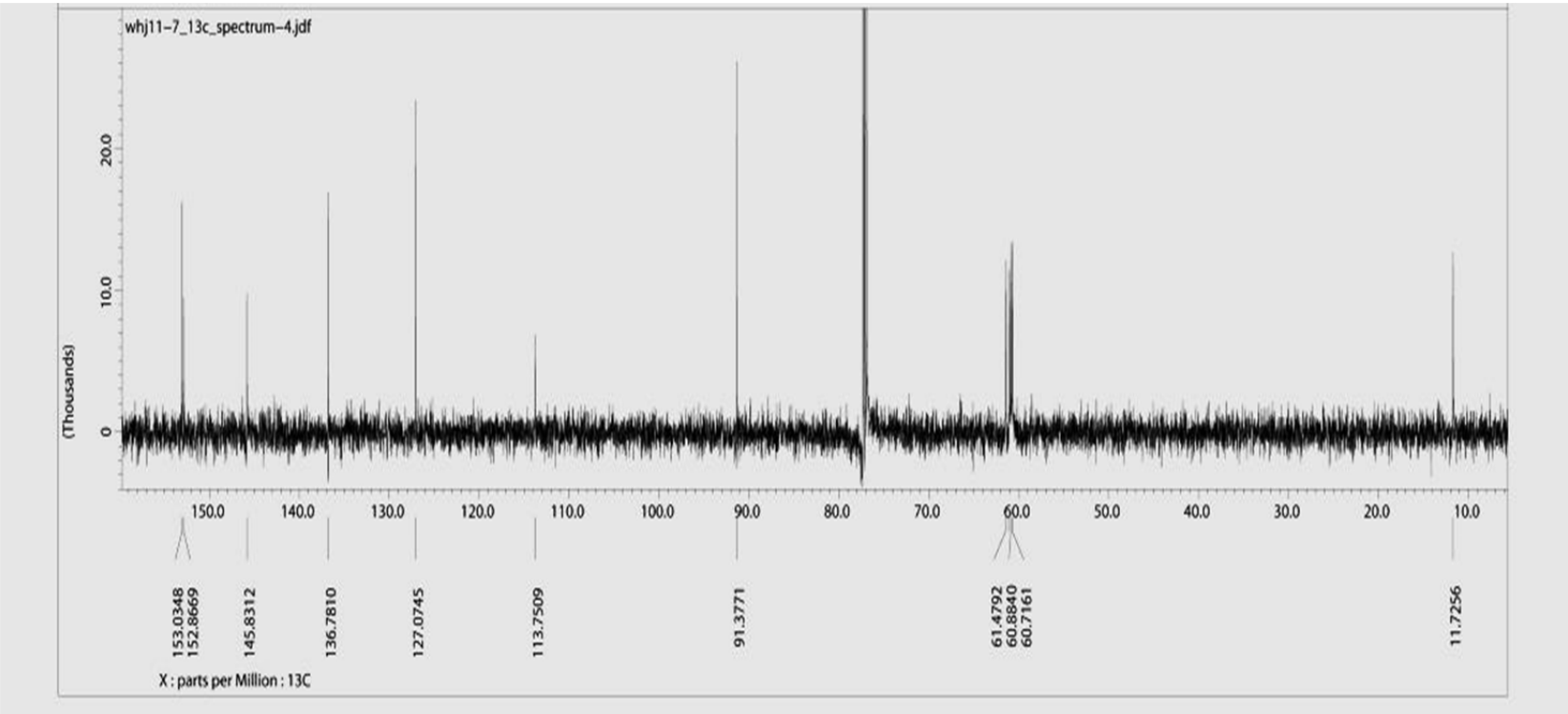


Figure S24. ^{13}C NMR spectrum (150 MHz) of 6,6'-(ethyne-1,2-diyl)bis(3,4,5-trimethoxy-2-methyl-benzylalcohol) in $CDCl_3$.

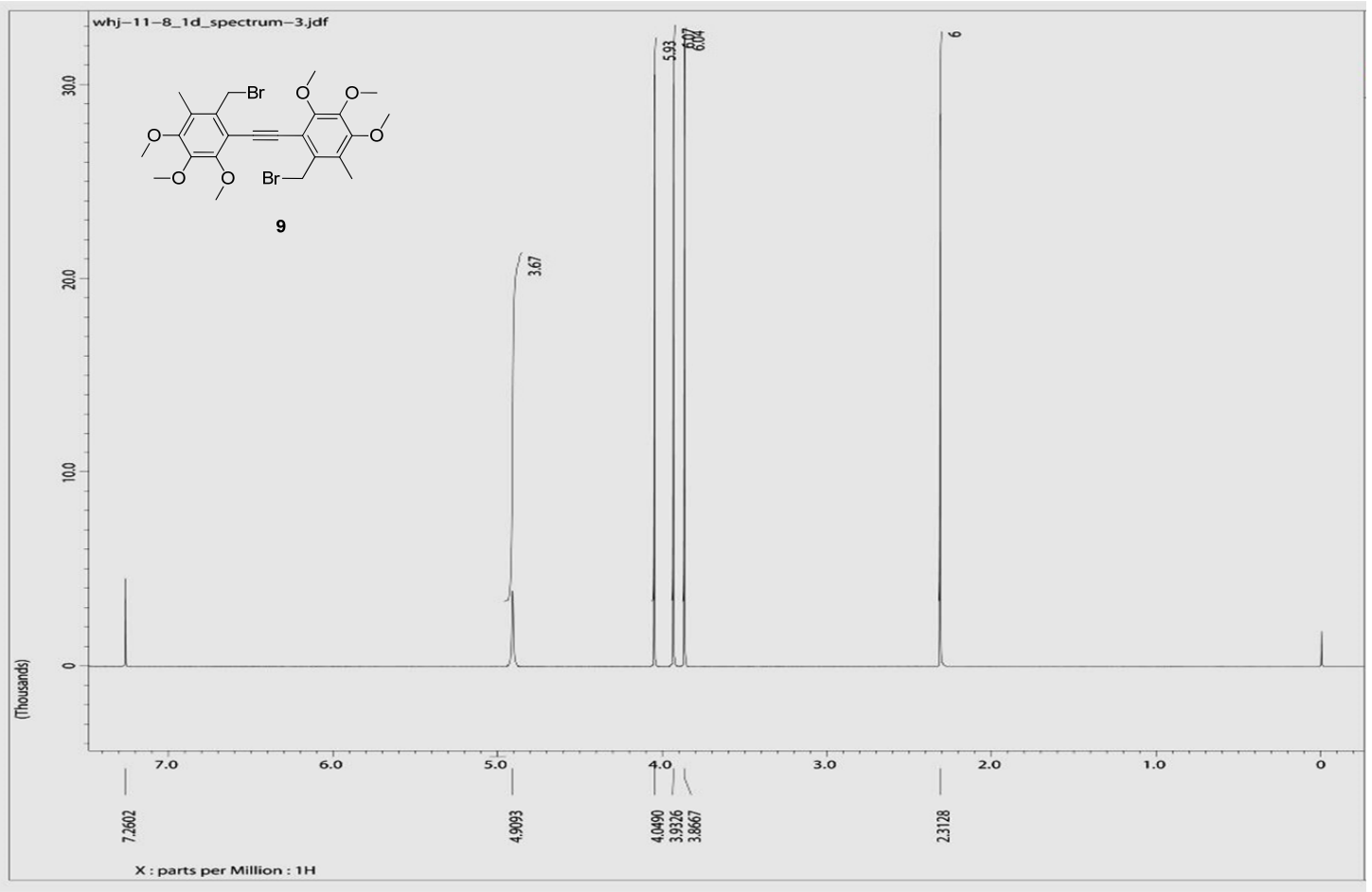


Figure S25. ^{1}H NMR spectrum (600 MHz) of **9** in $CDCl_3$.

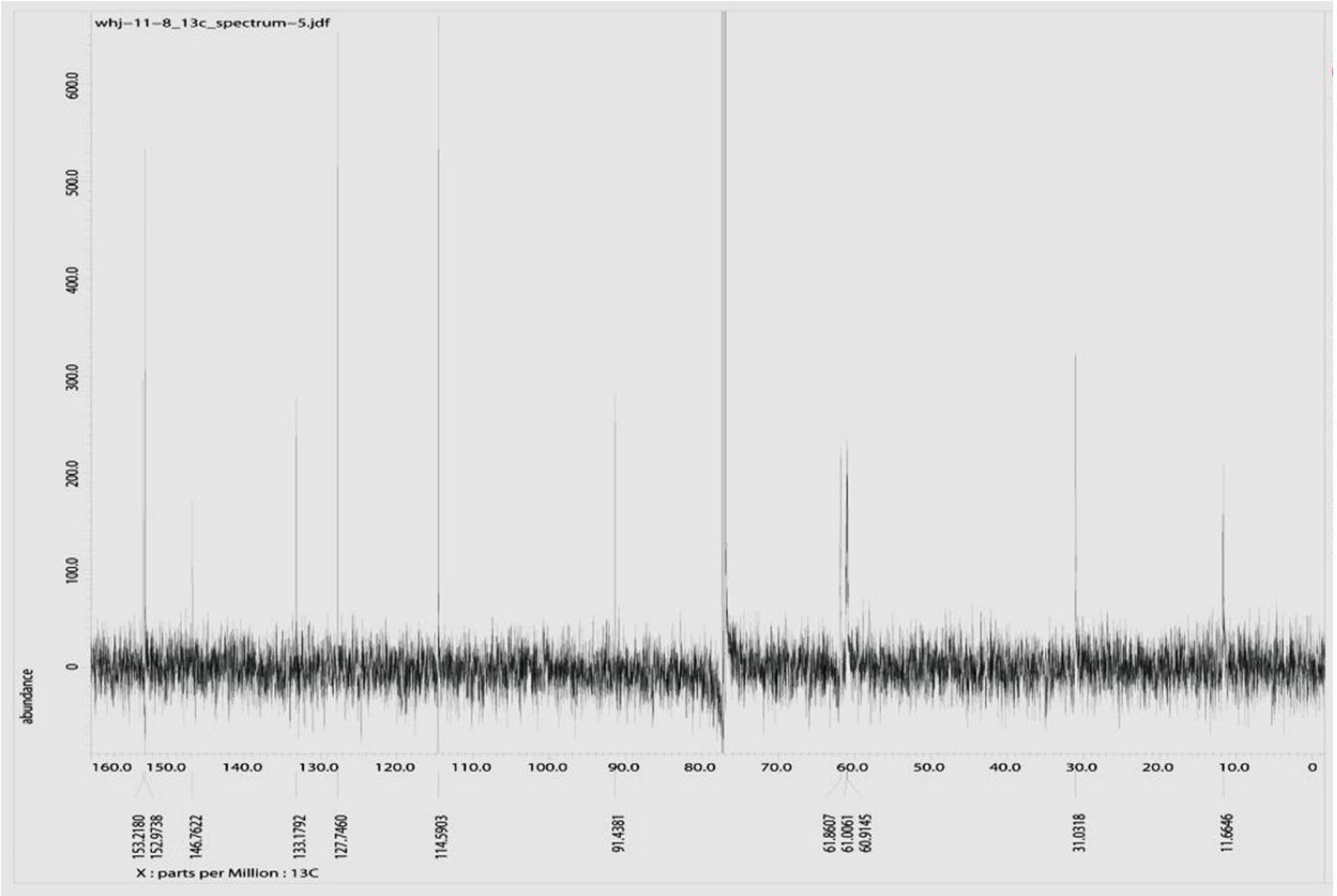


Figure S26. ^{13}C NMR spectrum (150 MHz) of **9** in $CDCl_3$.

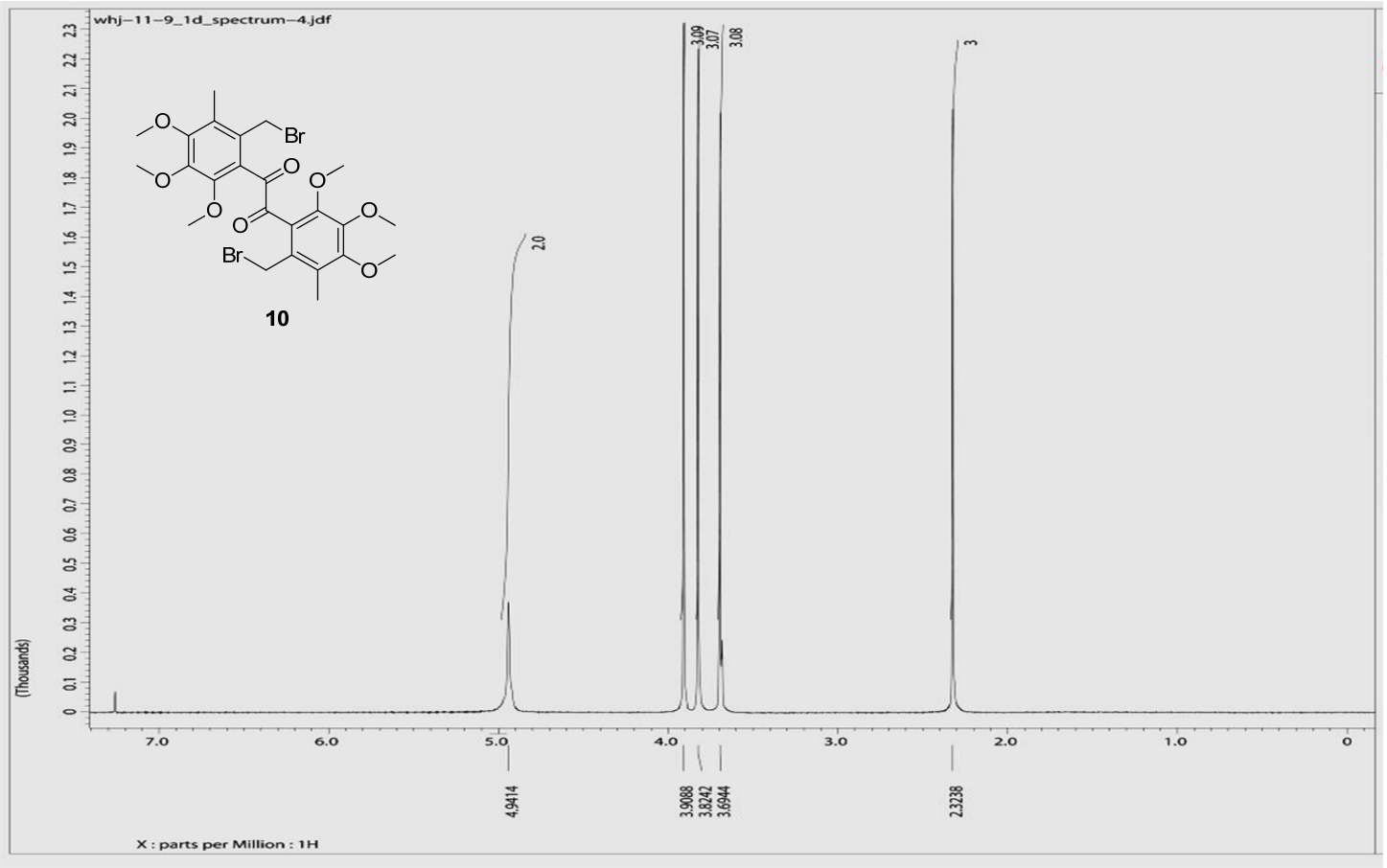


Figure S27. ^{1}H NMR spectrum (600 MHz) of **10** in $CDCl_3$.

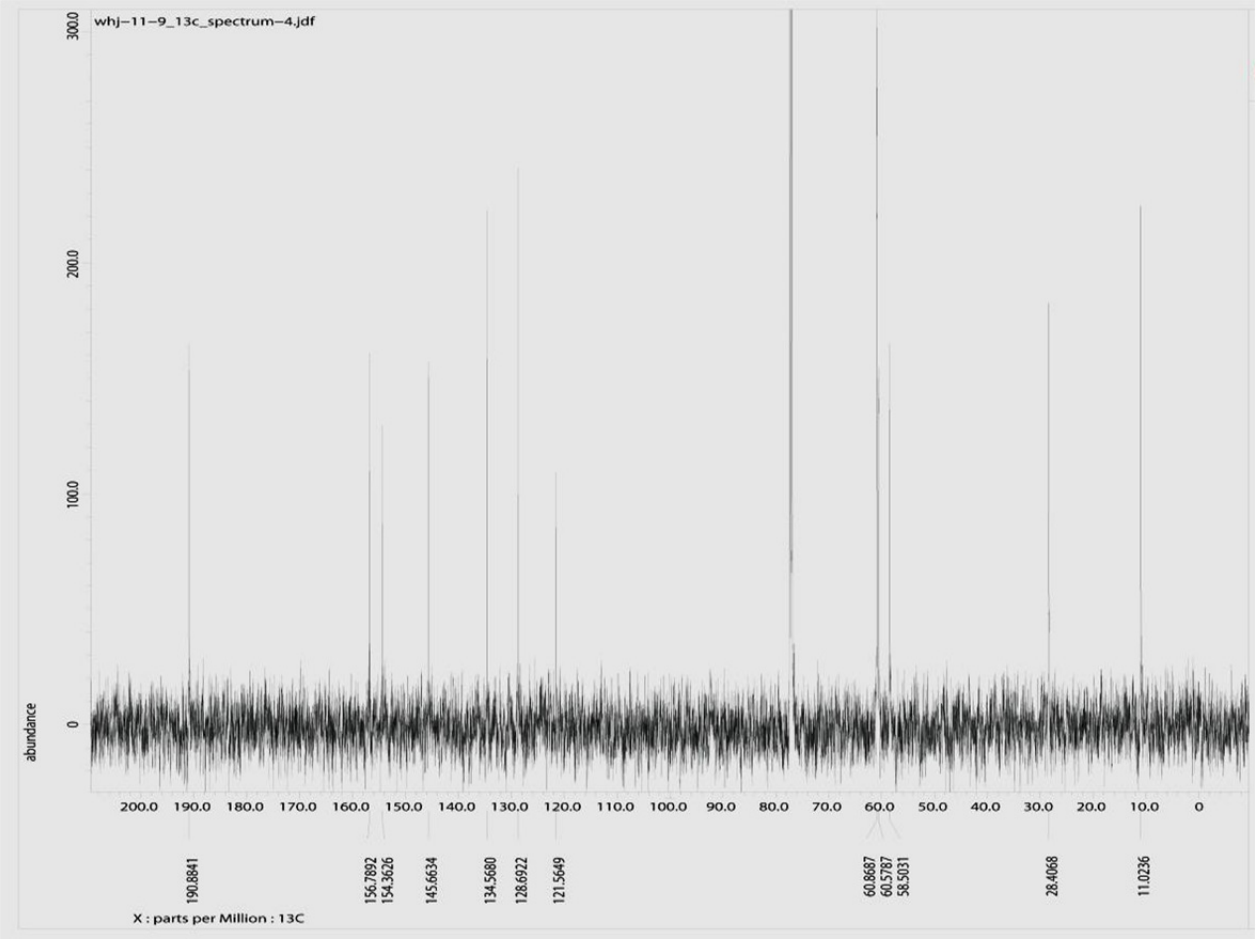


Figure S28. ^{13}C NMR spectrum (150 MHz) of **10** in $CDCl_3$.

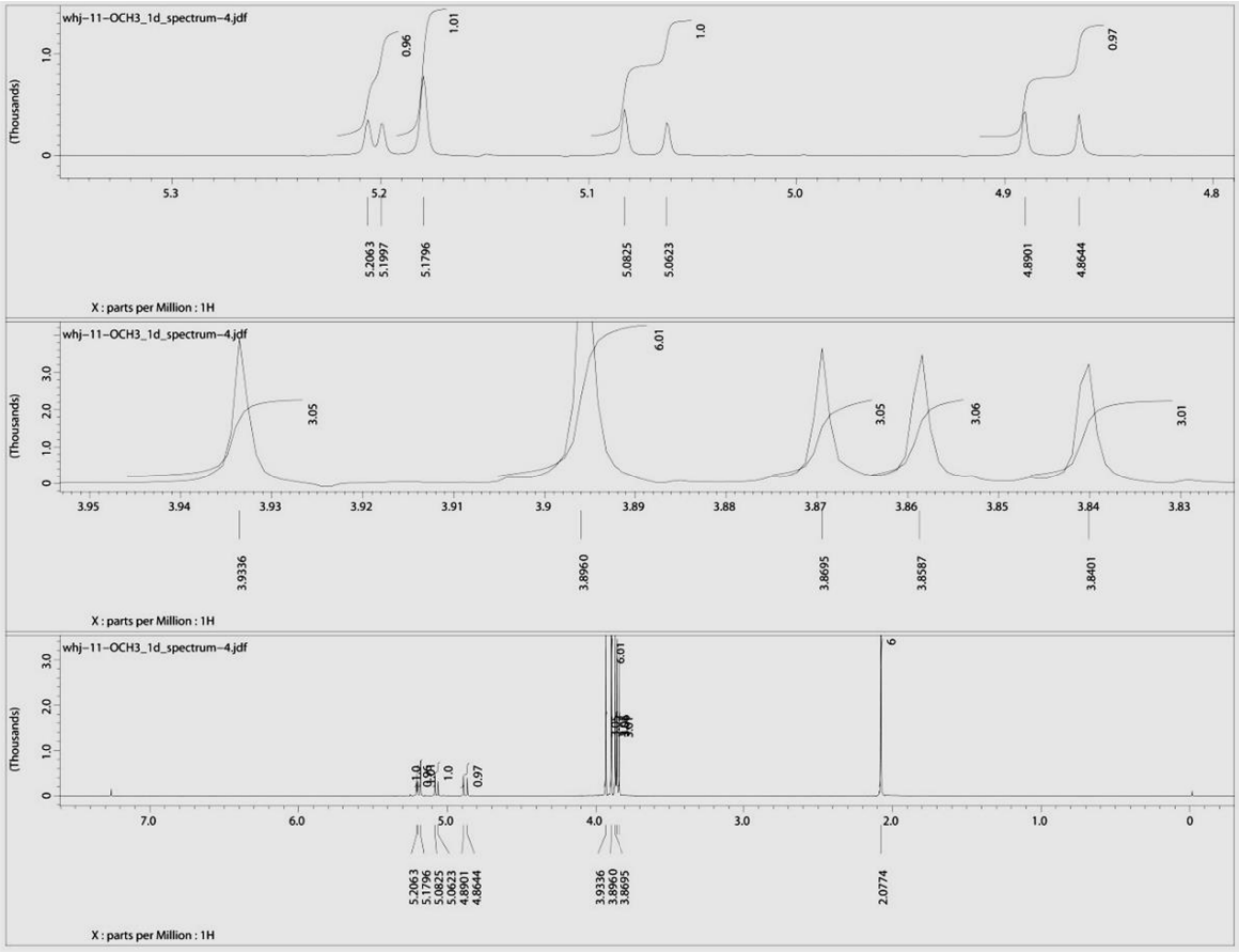


Figure S29. ^{1}H NMR spectrum (600 MHz) of the synthesized (±)**-1a** in $CDCl_3$.

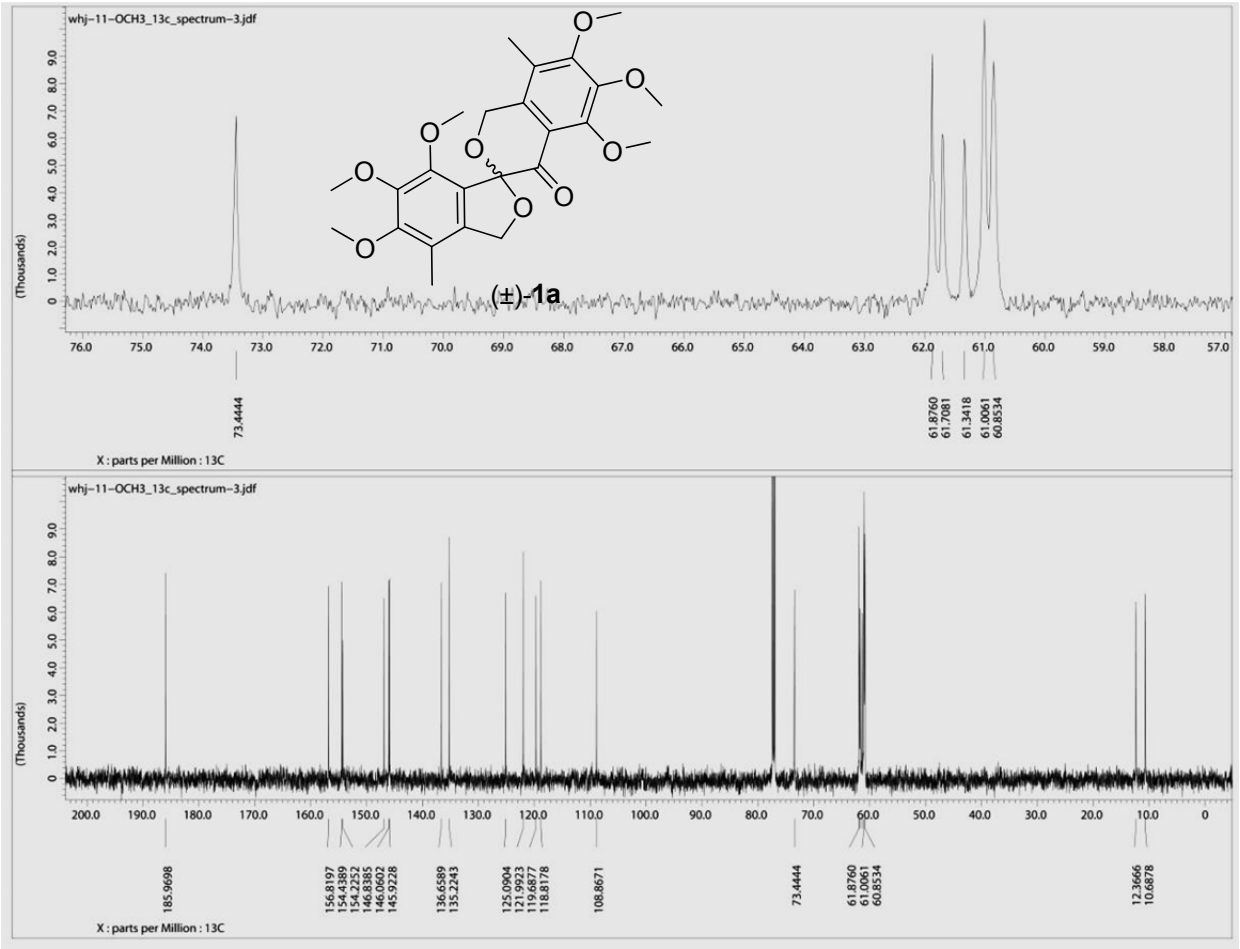


Figure S30. ^{13}H NMR spectrum (150 MHz) of the synthesized (±)-**1a** in $CDCl_3$.

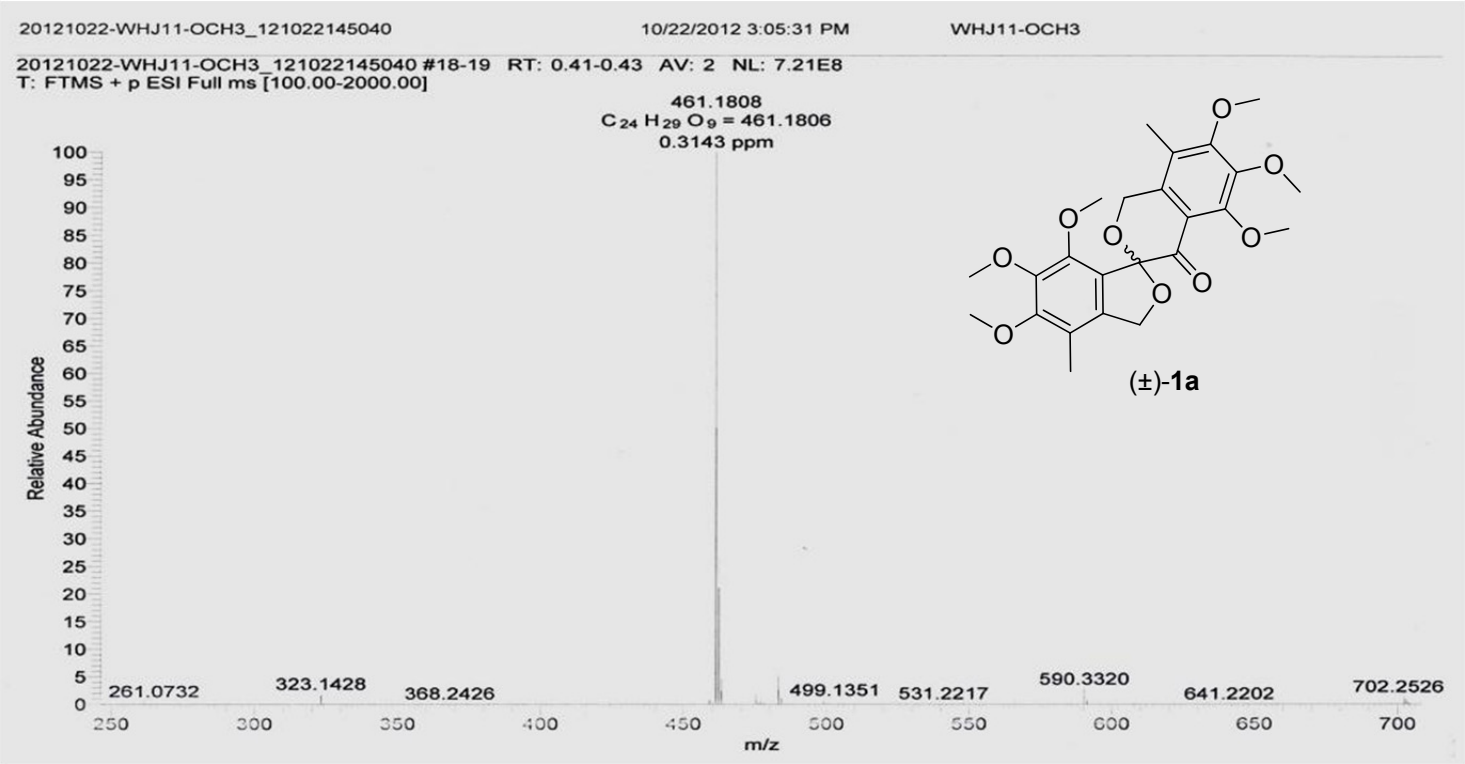


Figure S31.HRESI-MS spectrum of the synthesized (±)-**1a**.

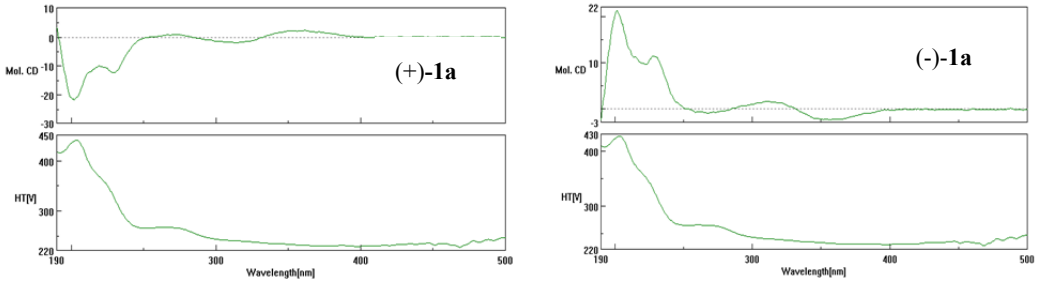


Figure S32. The experimental ECD spectra for the first-eluting enantiomer [(+)-**1a**, 8*S*] and the second-eluting enantiomer [(-)-**1a**, 8*R*]

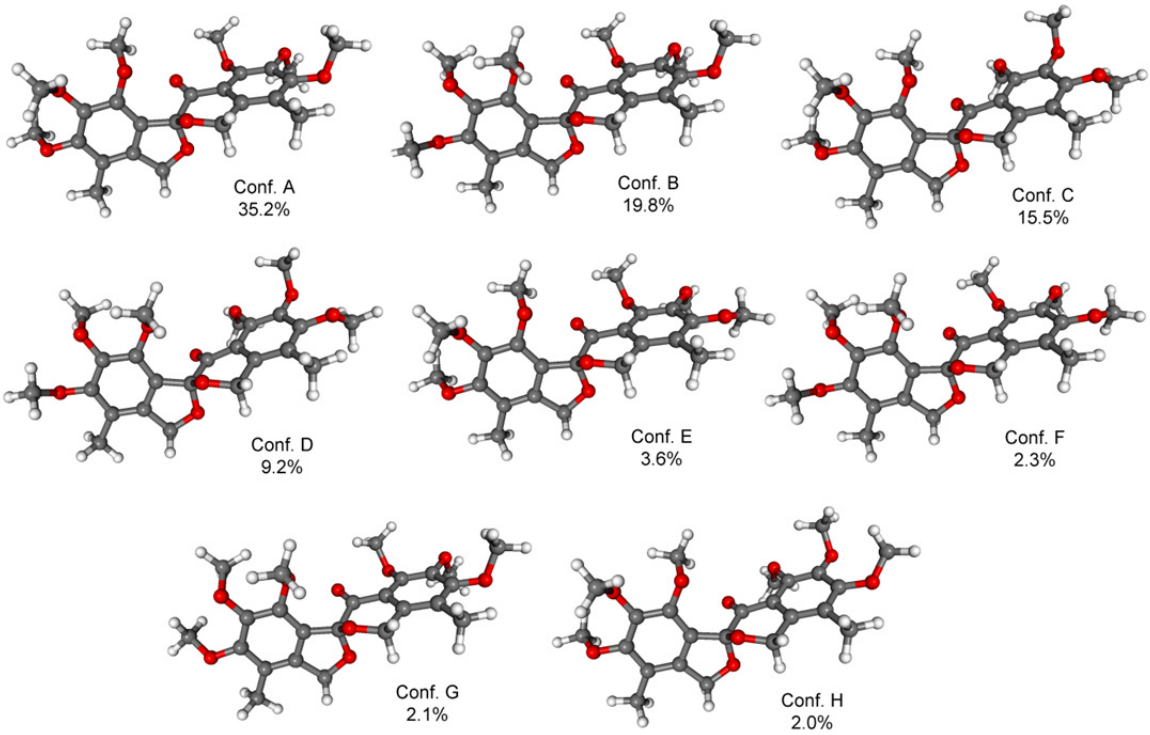


Figure S33. Low-energy conformers (> 2%) of (8*S*)-**1a** calculated at B3LYP/6-31G(d) level of theory in vacuo.

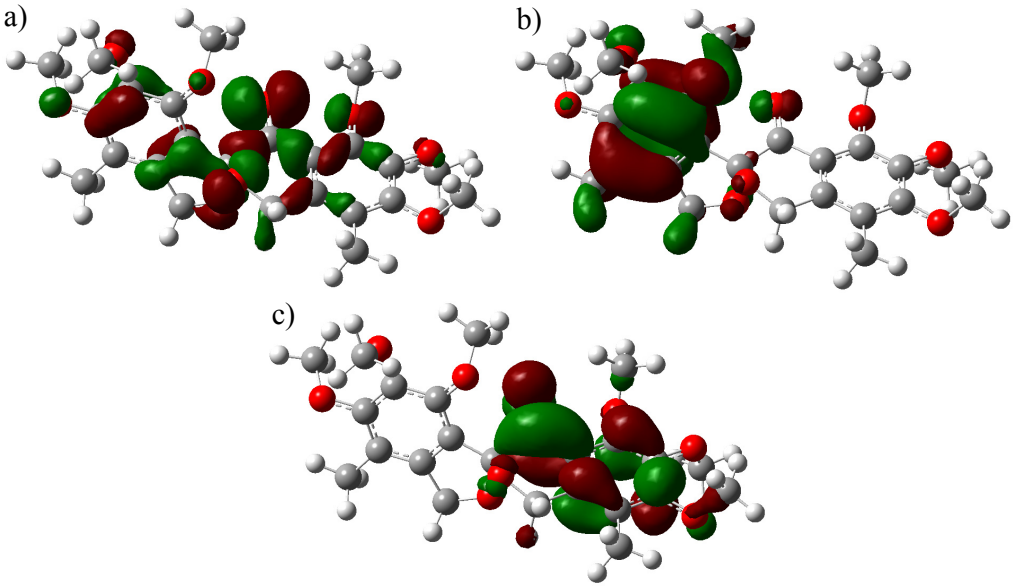


Figure S34. Kohn-Sham orbitals of (8*S*)-**1a** attributed to the 358 nm n–π* [a) n orbital, c) π*] and the 312 nm π–π* [b) π orbital c) π*] ECD transitions extracted from the PBE0/TZVP calculation of the lowest-energy conformer and plotted with an isovalue of 0.032.