

SUPPLEMENTARY MATERIAL

Investigation of the Enzymatic and Non-enzymatic Cope Rearrangement of Carboprephenate to Carbochorismate

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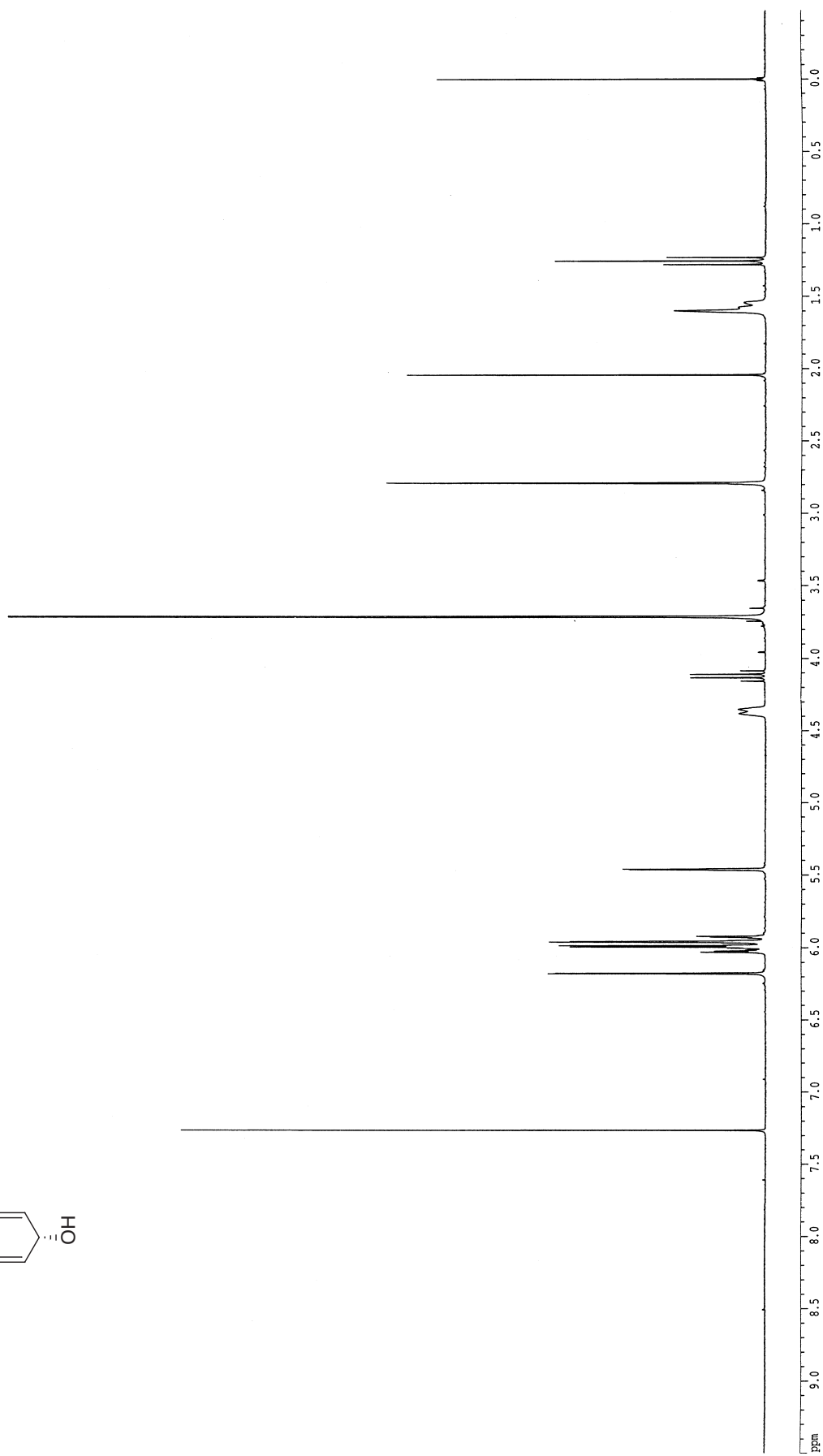
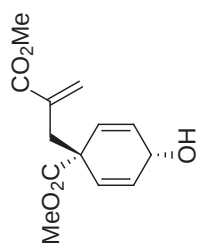
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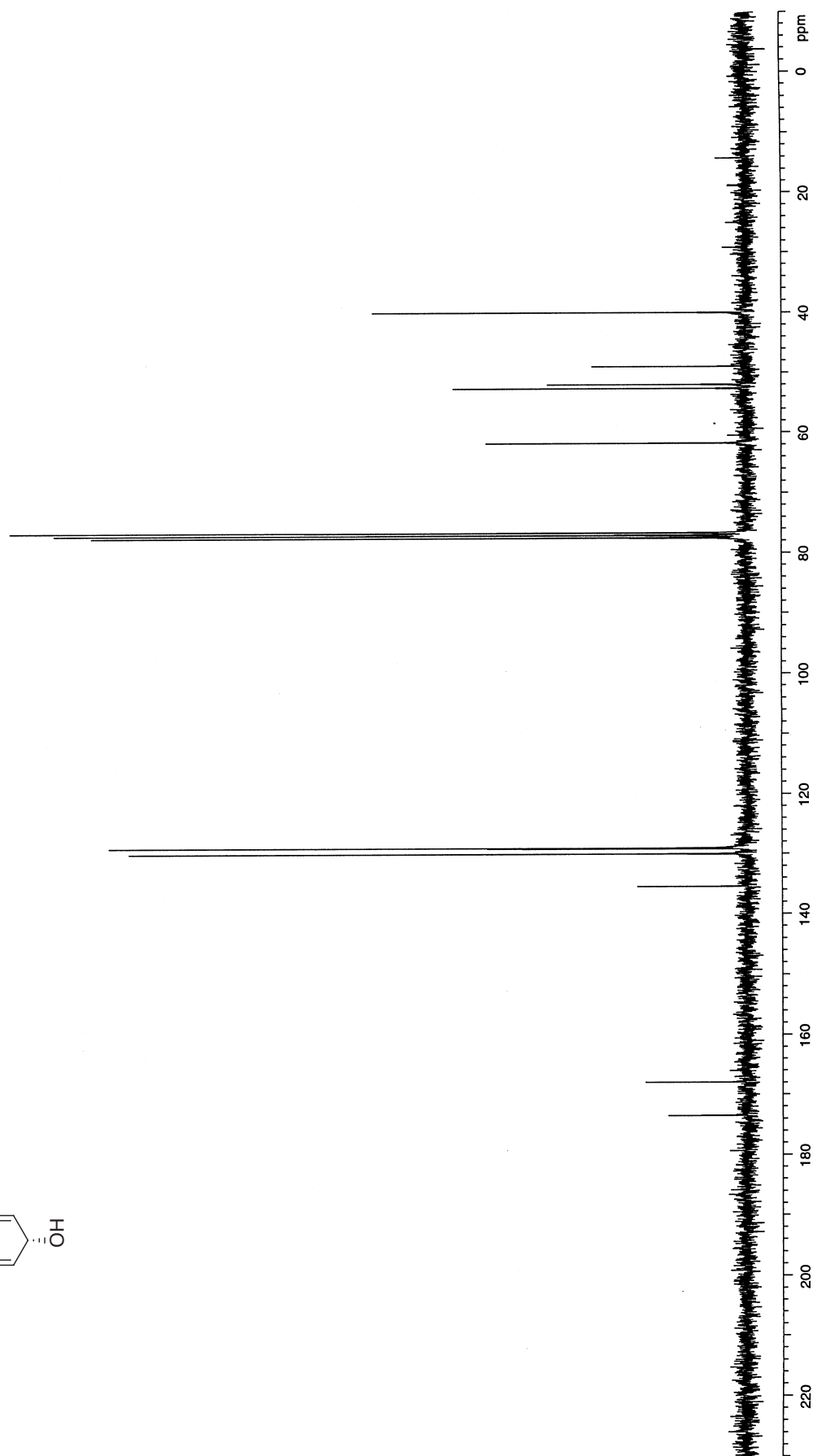
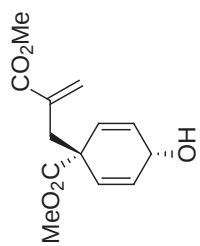
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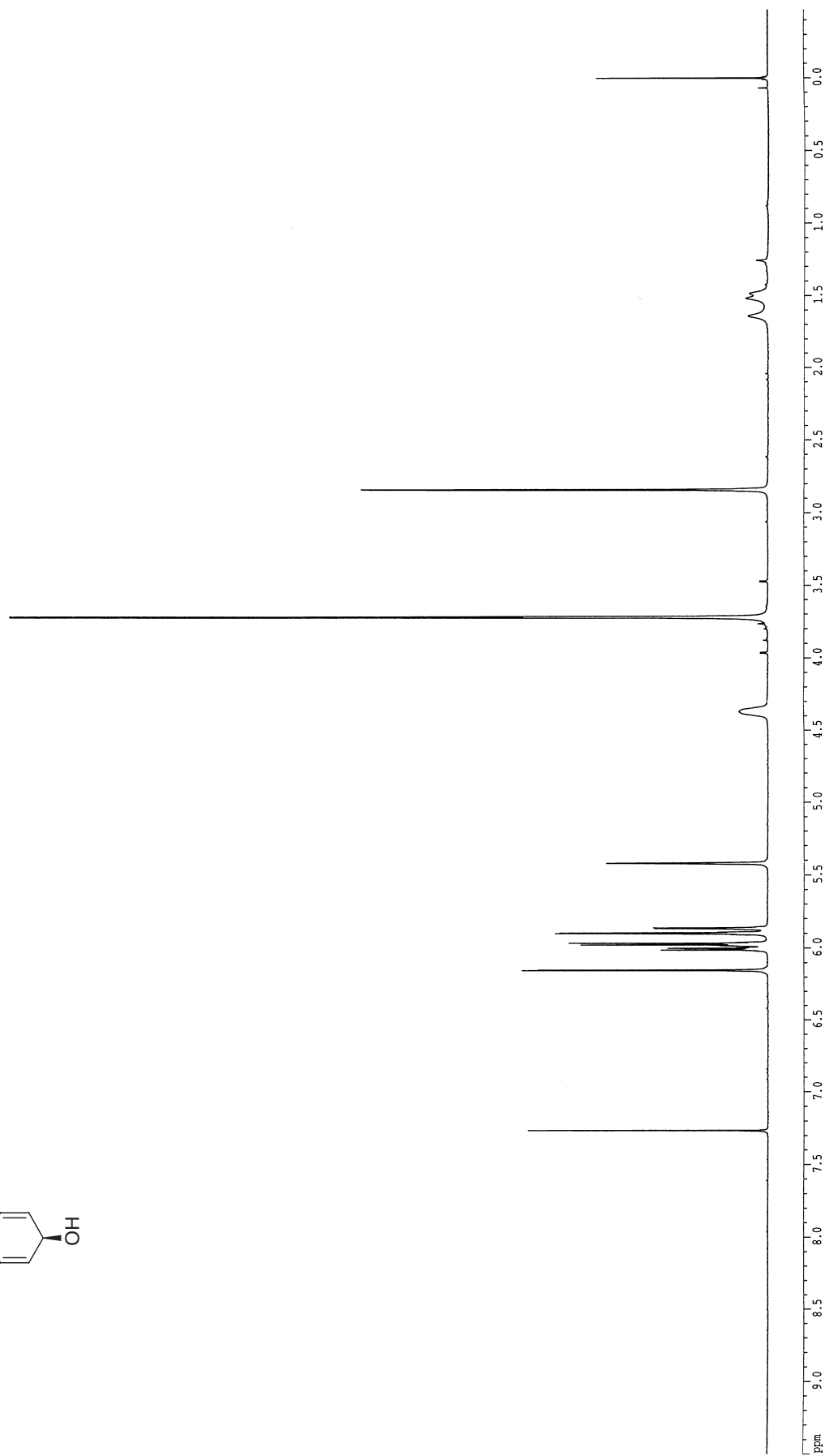
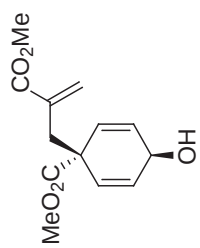
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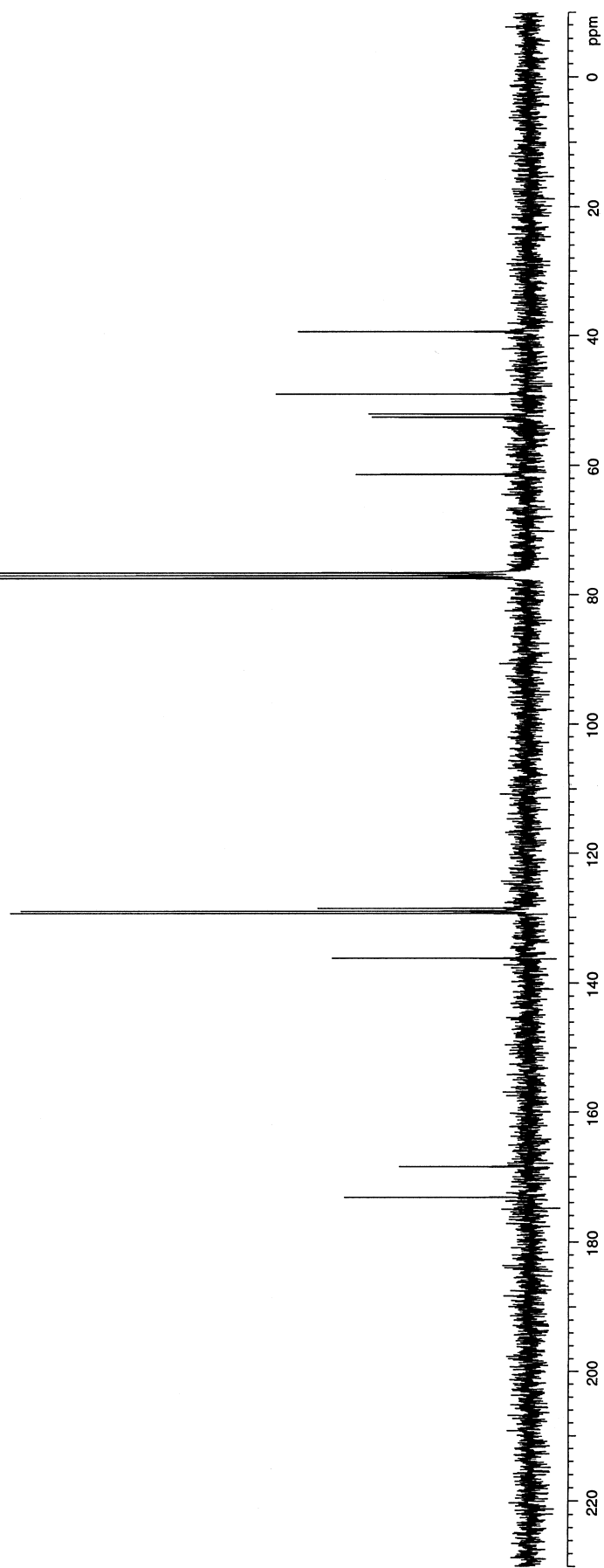
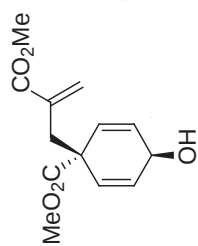
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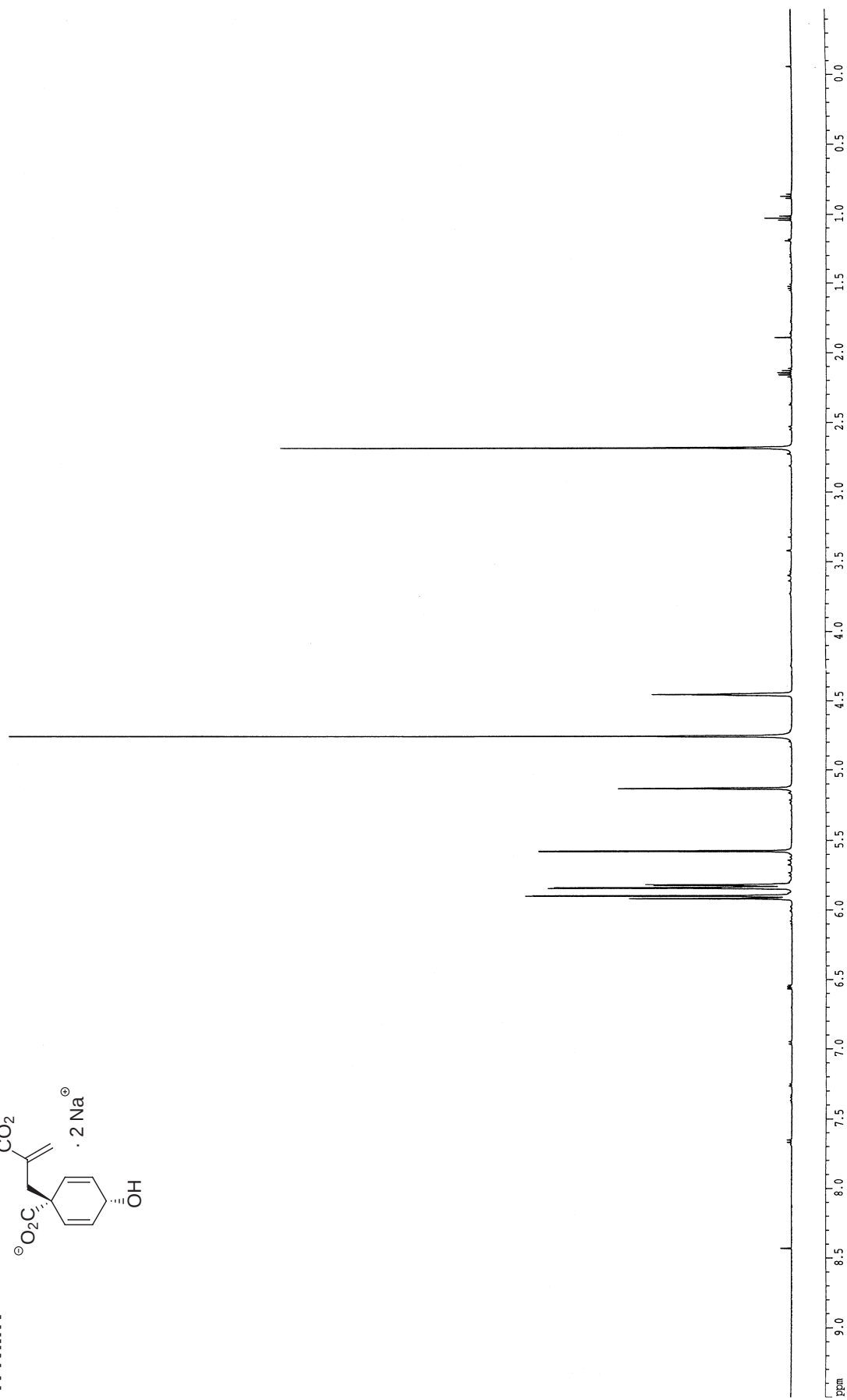
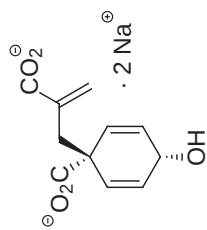
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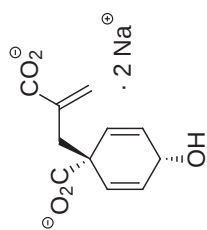
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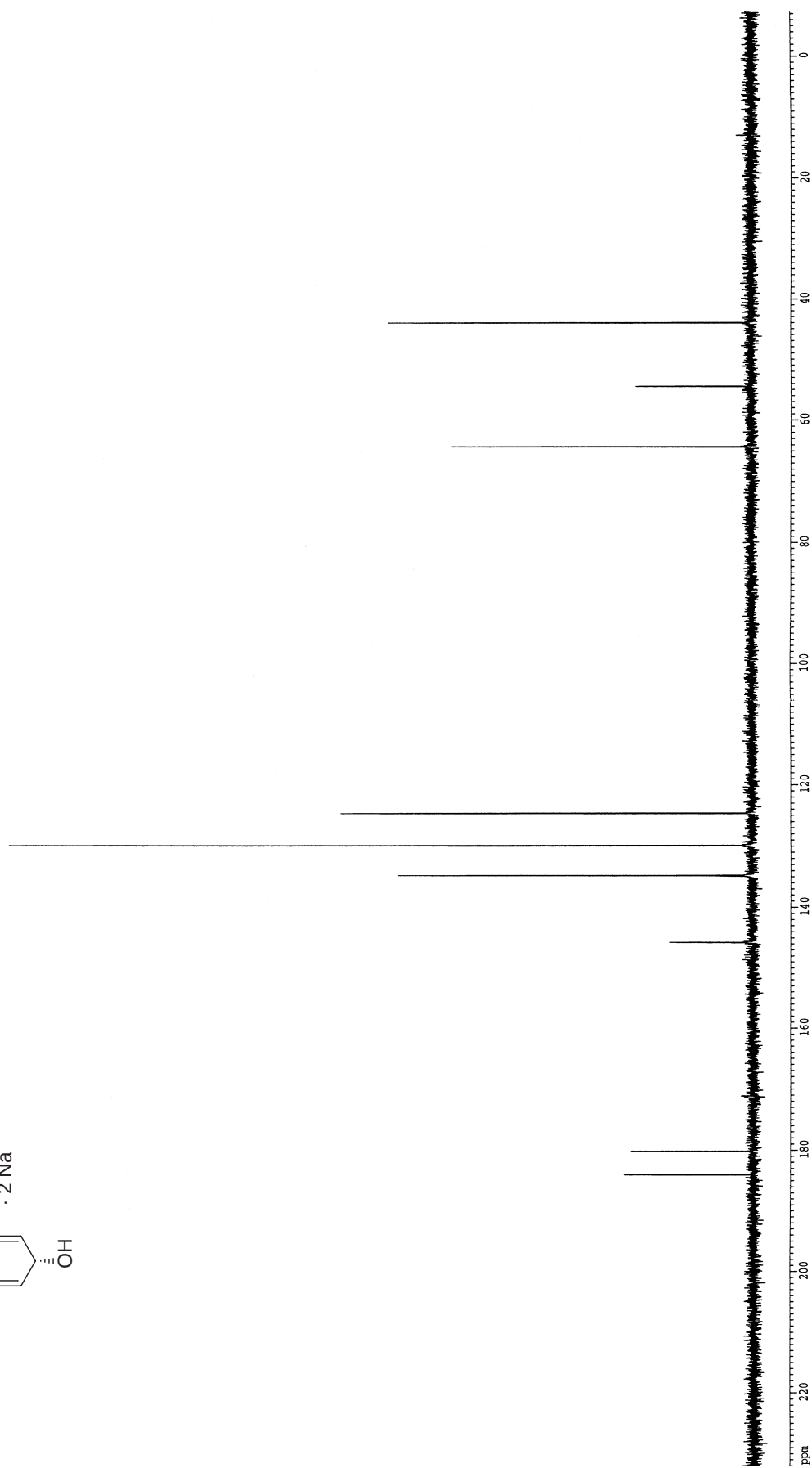
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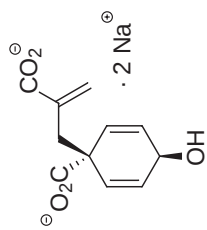
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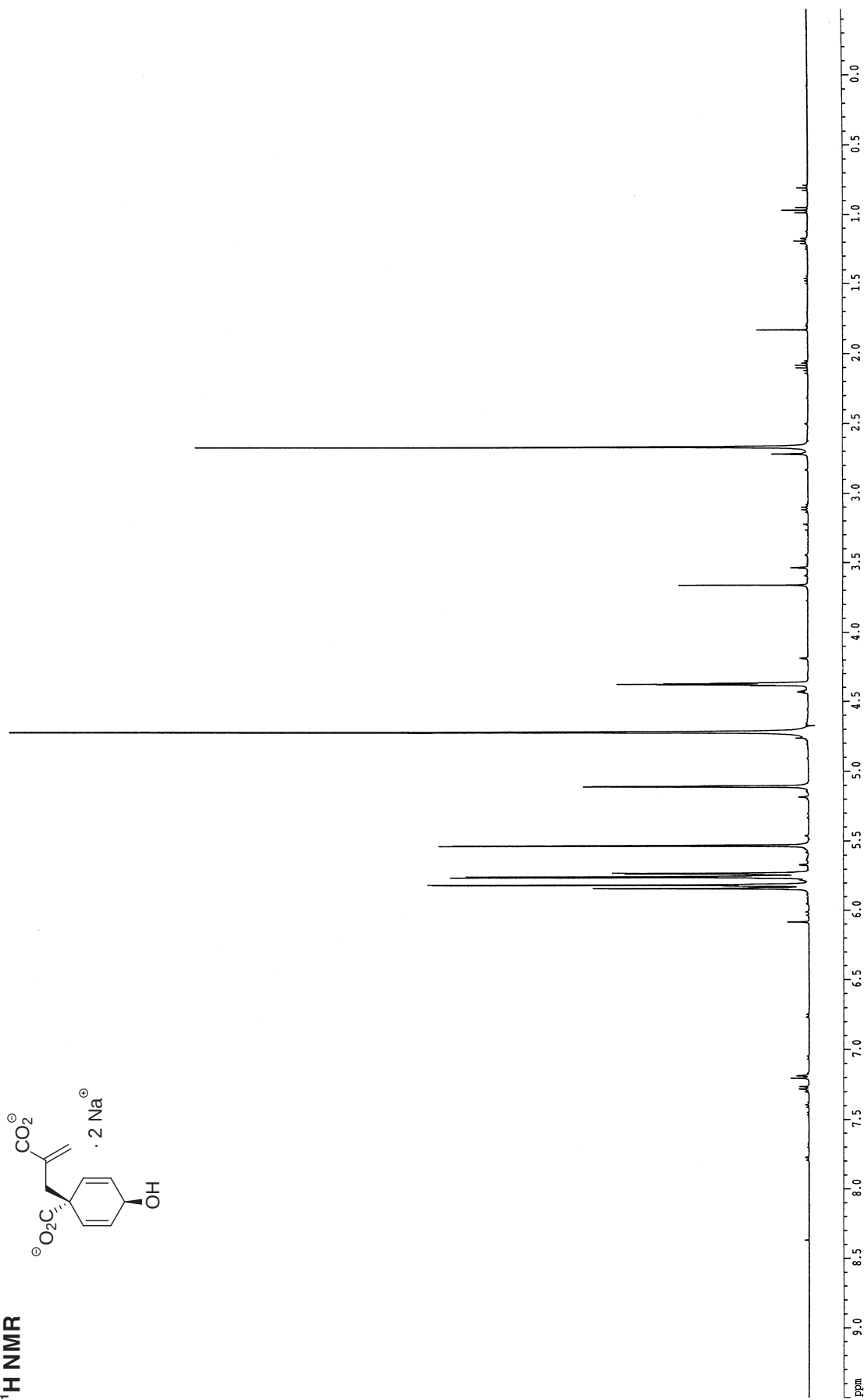
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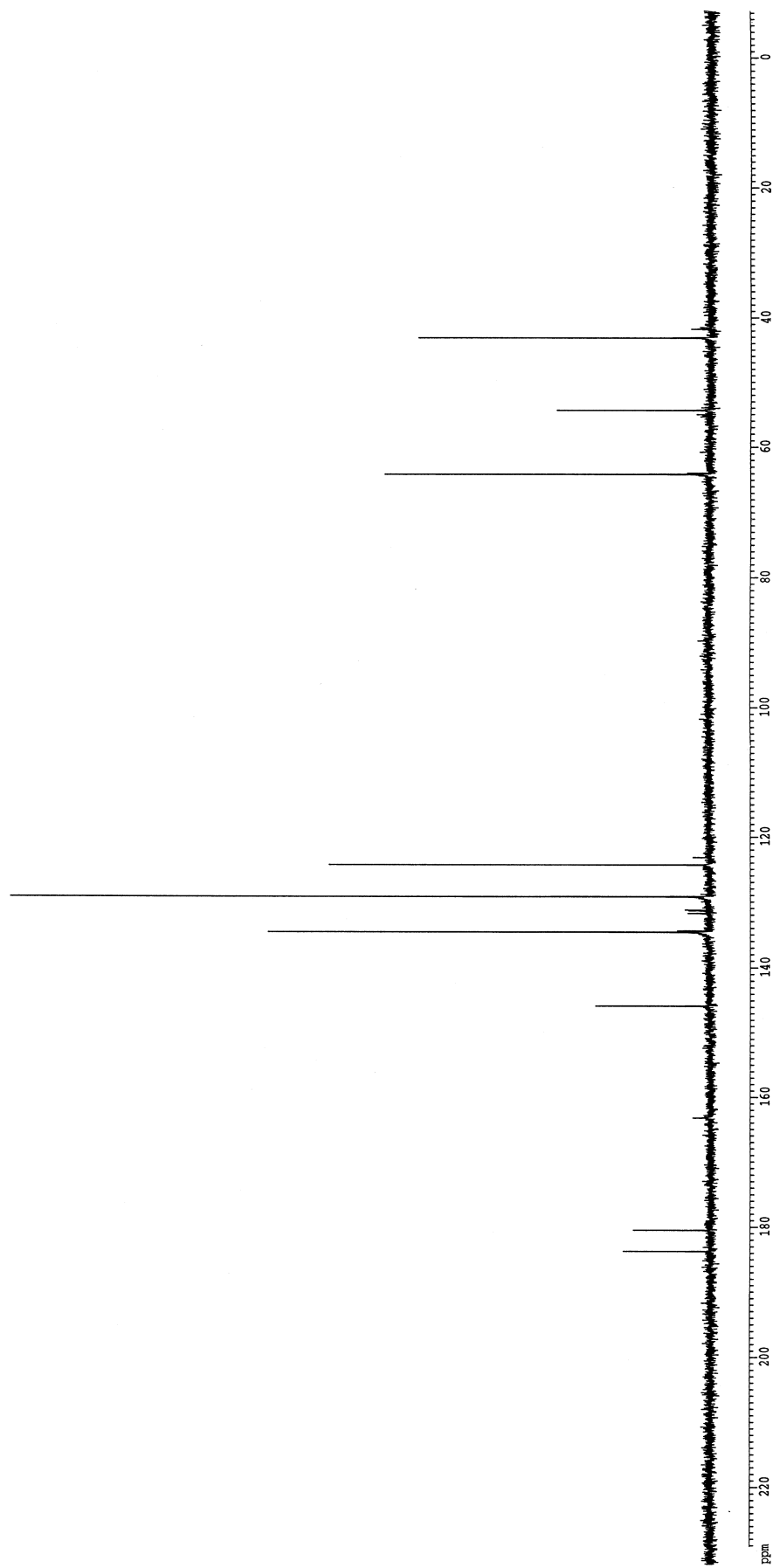
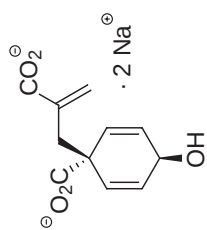
¹H NMR



S8



¹³C NMR



Structural assignment of compound **10a**

The structure of the rearrangement product derived from compound **6a** was elucidated by 500 MHz ^1H - and 125 MHz ^{13}C -NMR spectroscopy. Due to the tricyclic nature of the rearrangement product and the concomitant presence of several long-range H-C couplings over more than three bonds, the analysis of the 2D NMR data, in particular of the HMBC spectrum, did not lead to a single structure proposal but to a set of four possible structures (I-IV in Figure 1). In order to distinguish between structures I, II, and III, which contain a four-membered or a three-membered ring, and structure IV, which contains only larger rings, the $^1J_{\text{CH}}$ coupling constants were measured by non-decoupled high resolution HSQC. The resulting one-bond H-C couplings for the two methylene carbons at 30.0 and 37.5 ppm are 132 and 140 Hz, respectively, which is consistent with the carbon resonating at 37.5 ppm being in a four-membered but not in a three- or a five-membered ring. This allowed structures III and IV to be ruled out. Structure II could be ruled out on the basis of the NOEs (Figure 2) observed by 1D NOE difference spectroscopy. The latter not only confirmed structure I (= **10a**) but also allowed assignment of the relative configuration at the center bearing the hydroxyl group as shown in **10a**. This assignment unambiguously establishes that the minor isomer of the selenoxide elimination of compound **5** is dimethyl carboprephenate (**6a**). Analogous experiments confirm that **6b** is dimethyl 4-*epi*-carboprephenate.

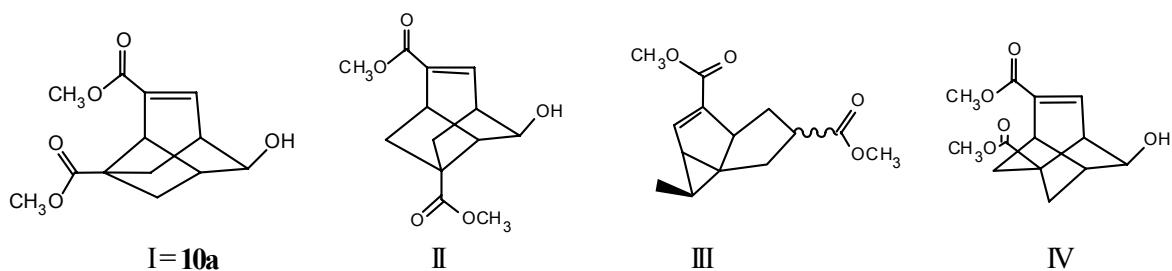


Figure 1. Structures compatible with the COSY and HMBC spectra of the final rearrangement product from the minor isomer **6a**.

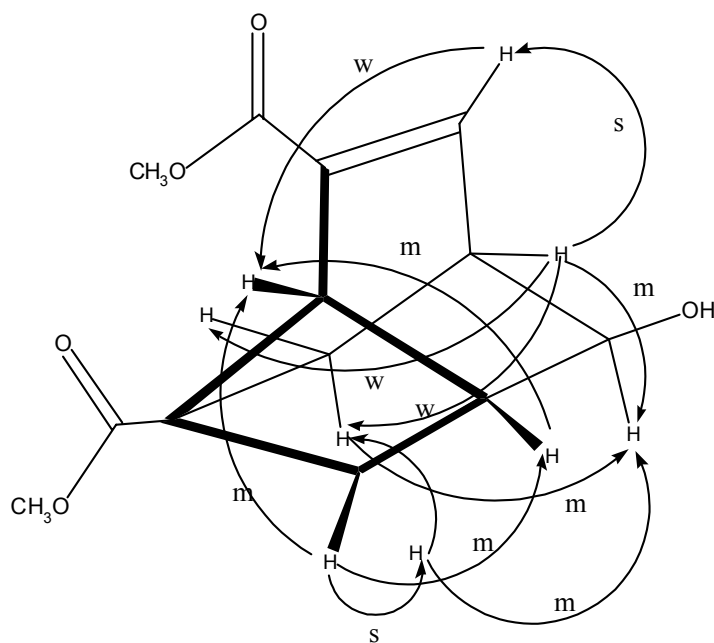
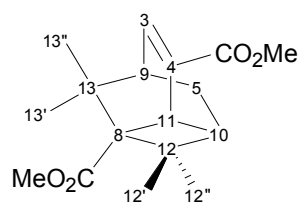


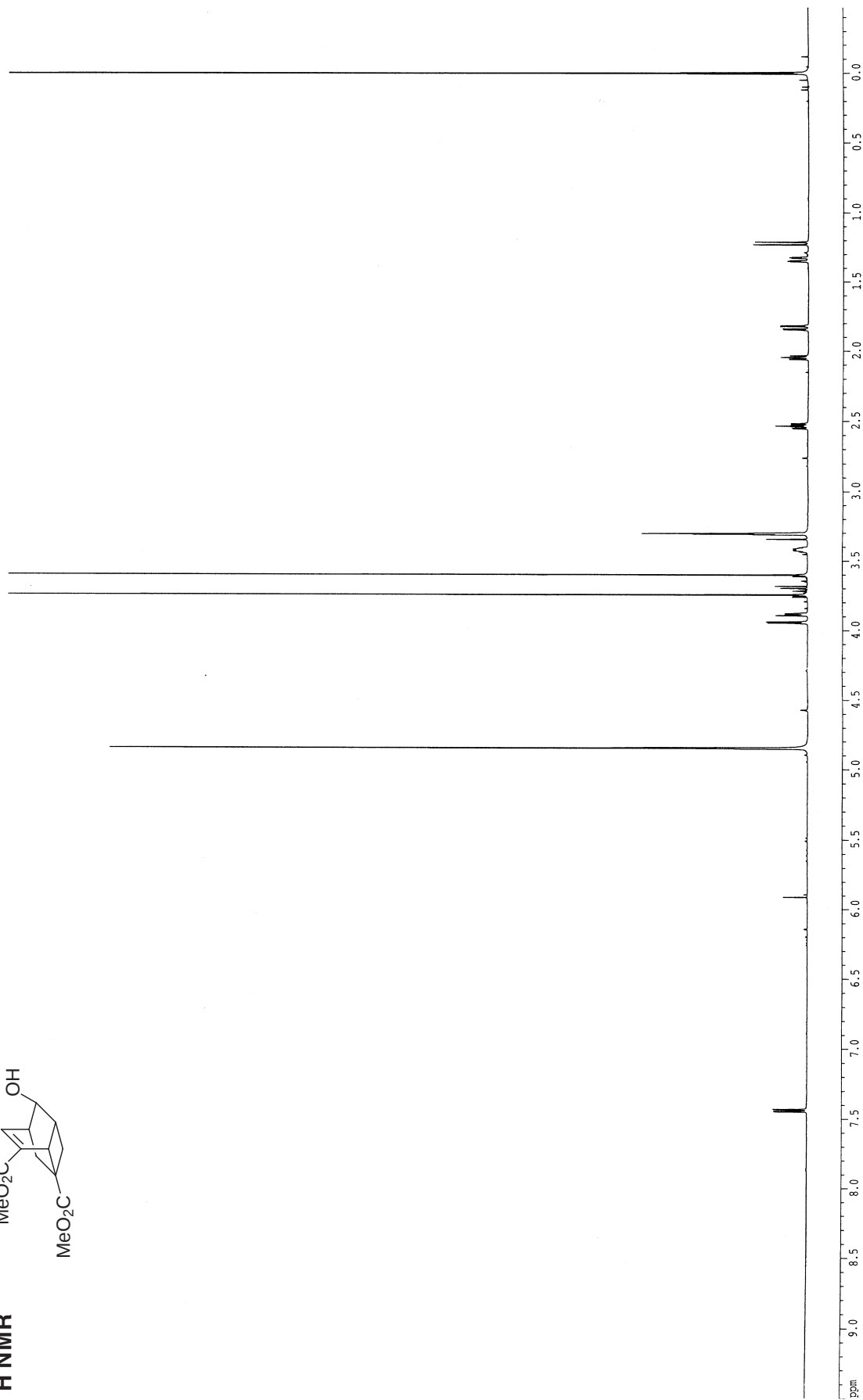
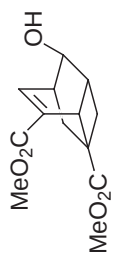
Figure 2. NOEs observed for the rearrangement product derived from compound **6a** (i.e. **10a**) by 1D NOE difference spectroscopy.

NMR Shift Assignment for 10a

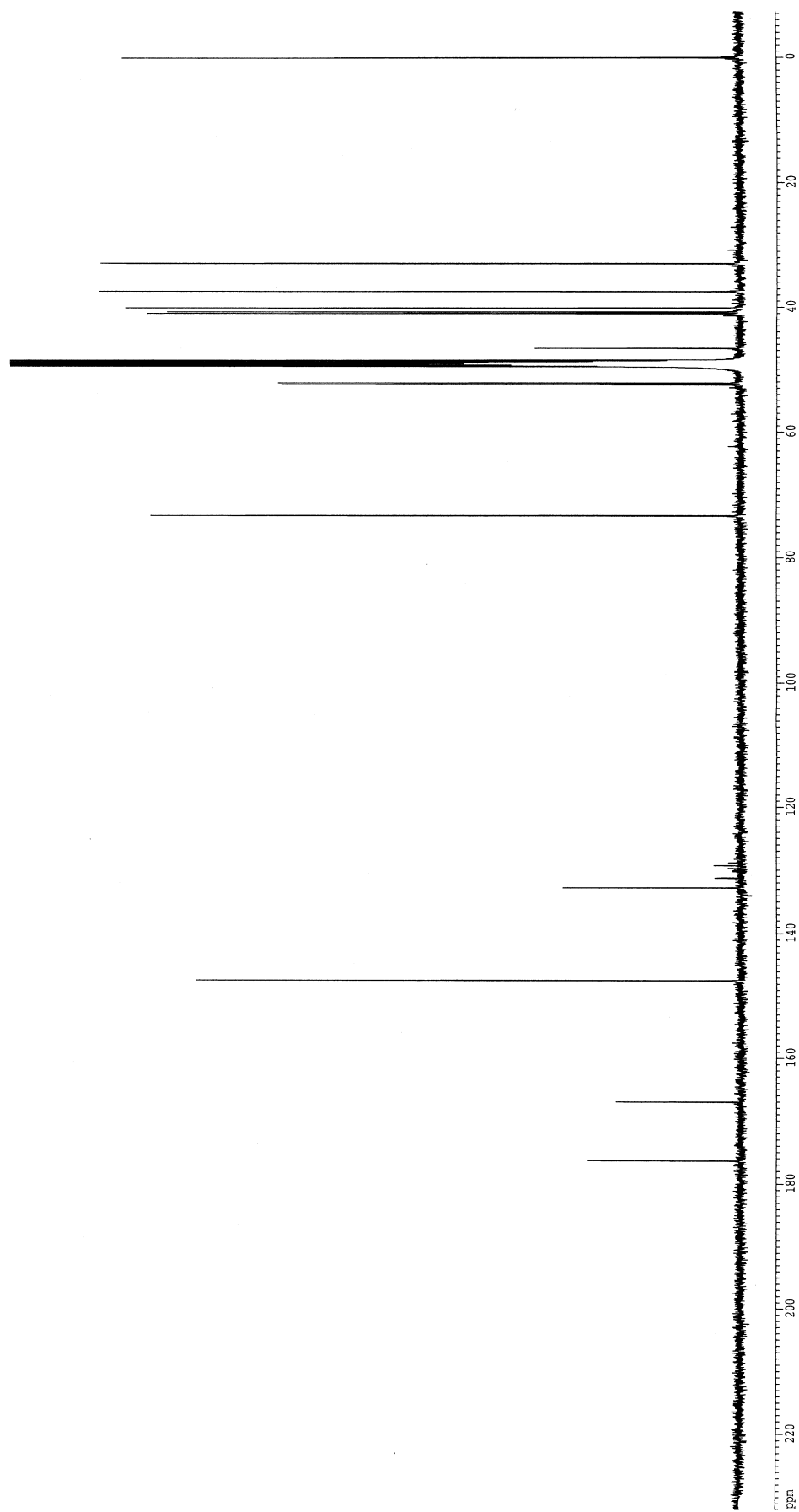
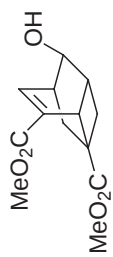


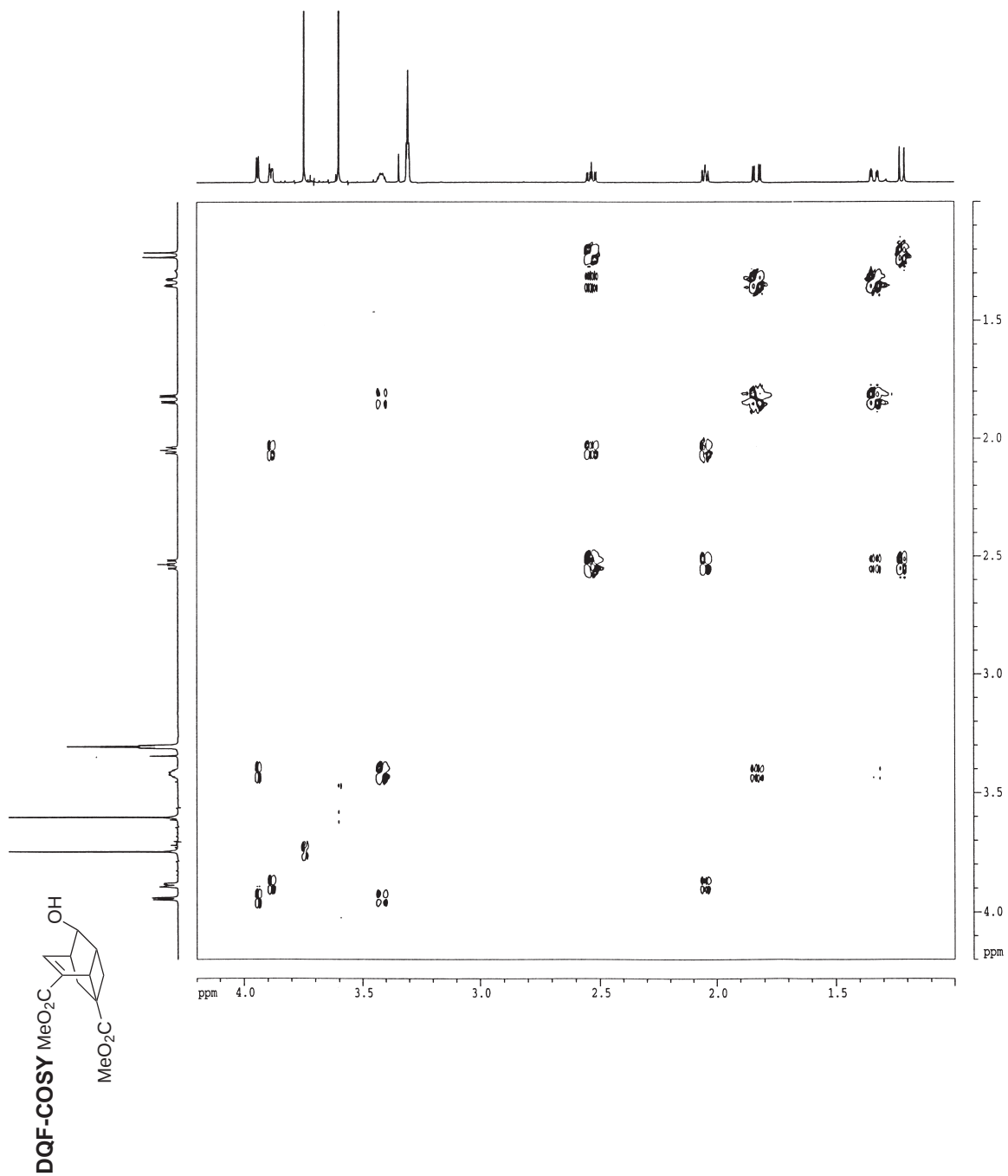
500 MHz ¹ H NMR	Position	125 MHz ¹³ C NMR	Position
7.44	3	176.34	<u>COOMe</u>
3.94	5	167.02	<u>COOMe</u>
3.89	11	147.45	3
3.75	<u>COOMe</u>	132.78	4
3.60	<u>COOMe</u>	73.31	5
3.40	9	52.41	<u>COOMe</u>
2.53	12'	52.14	<u>COOMe</u>
2.05	10	46.64	8
1.83	13'	41.00	9
1.35-1.32	13''	40.74	10
1.22	12''	40.10	11
		37.36	12
		32.98	13

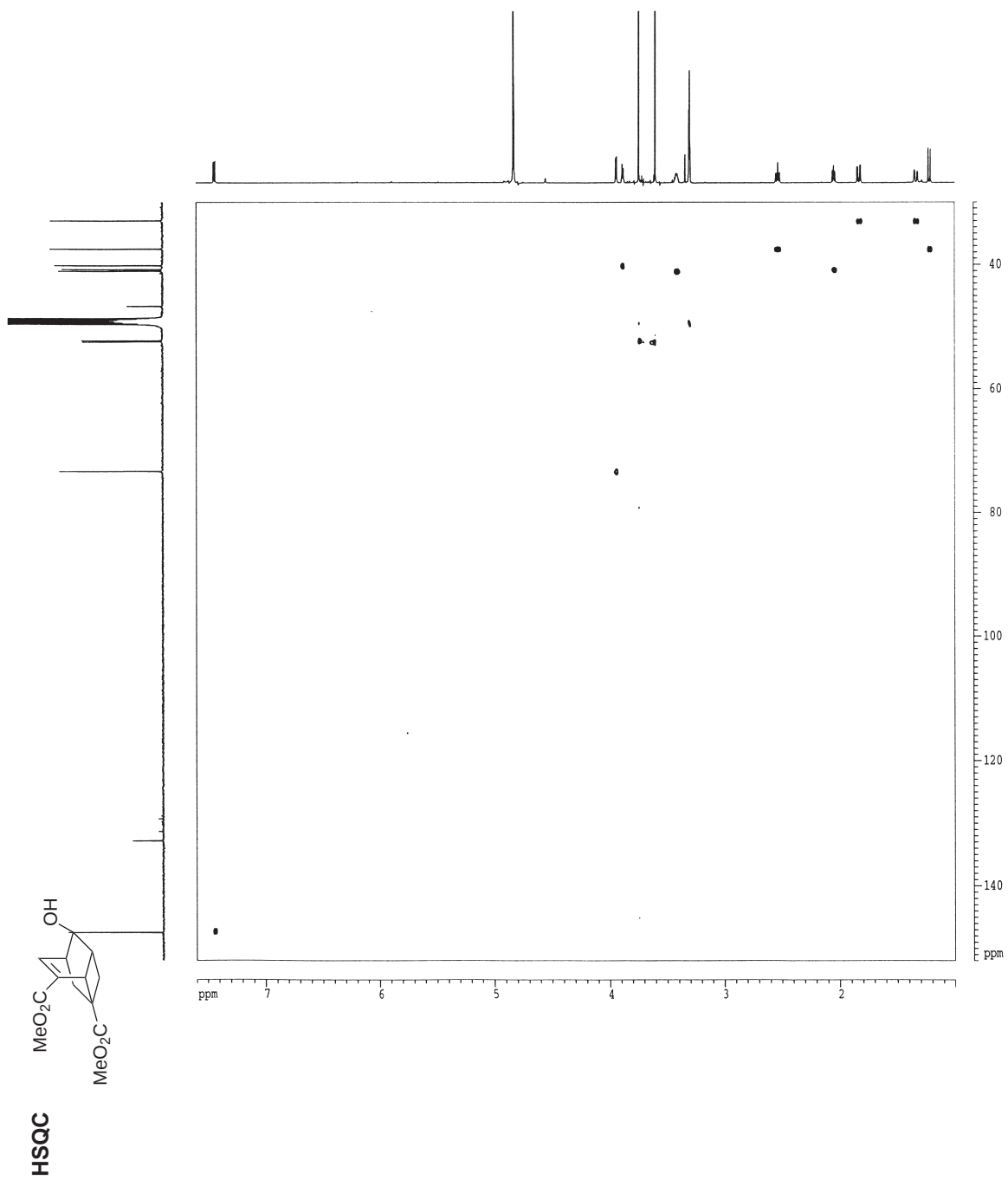
¹H NMR



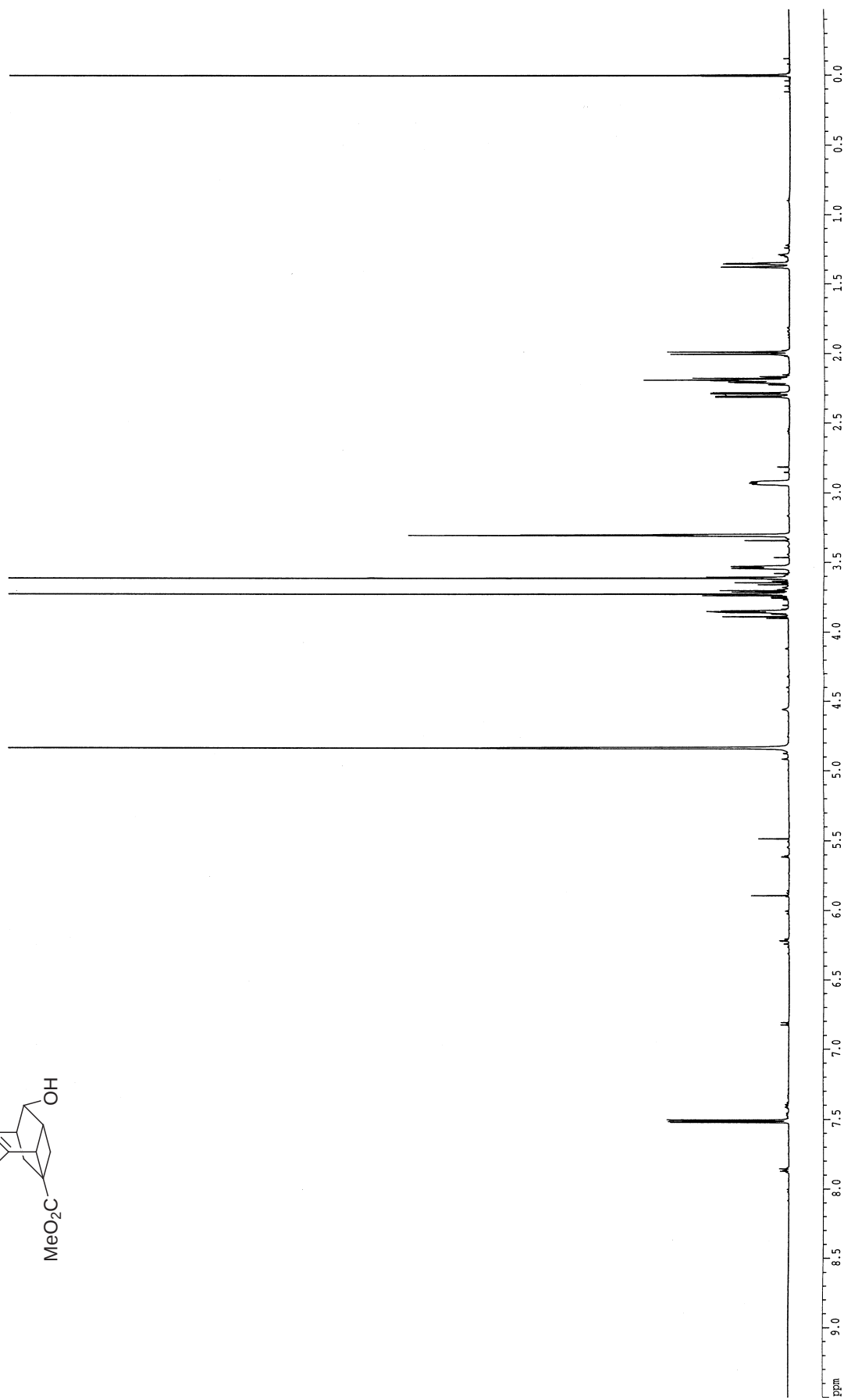
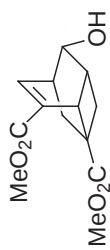
^{13}C NMR







¹H NMR



¹³C NMR

