

Supporting Information

Asymmetric synthesis of methoxylated ether lipids: Total synthesis of polyunsaturated C18:3 omega-3 and omega-6 MEL triene derivatives

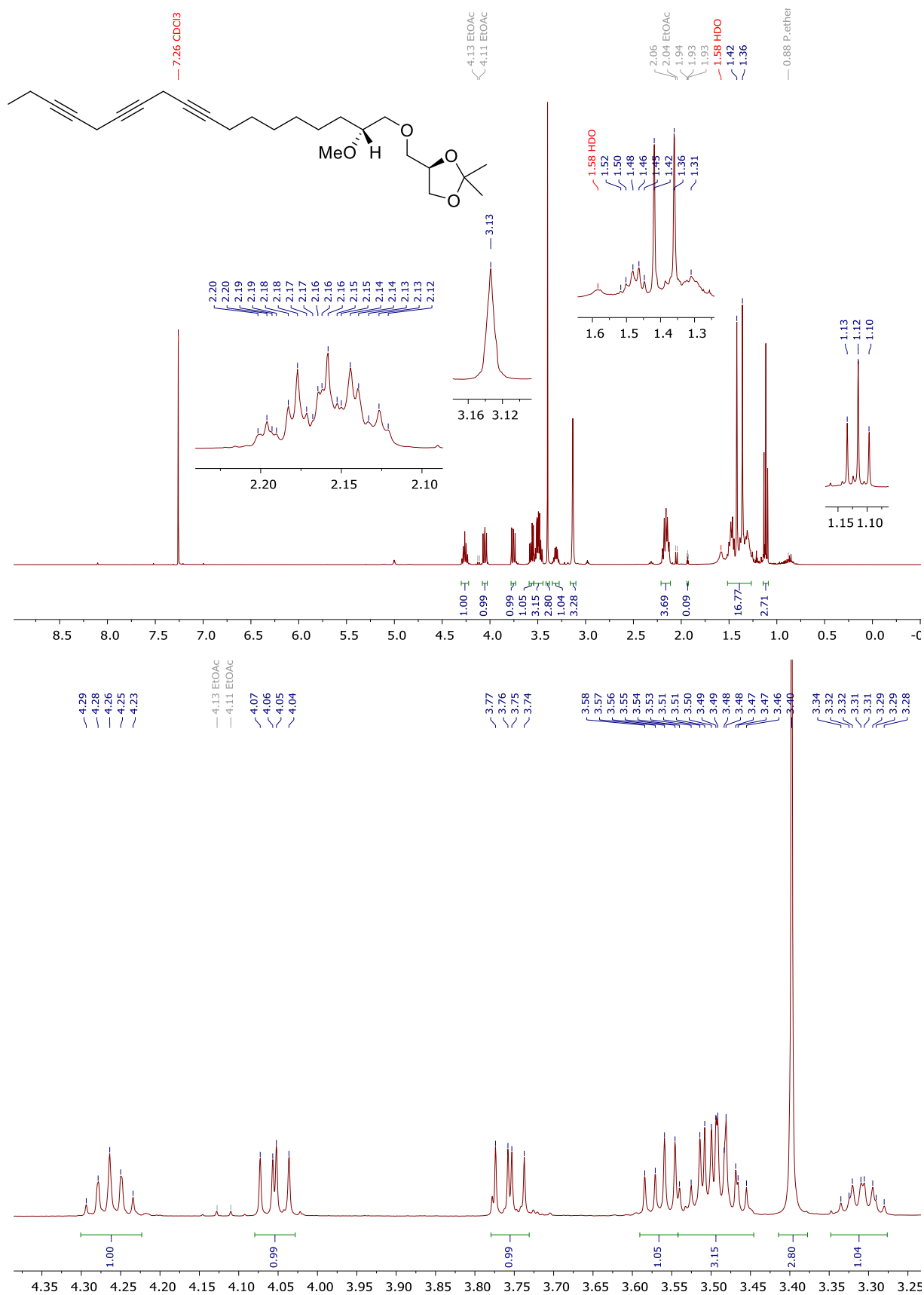
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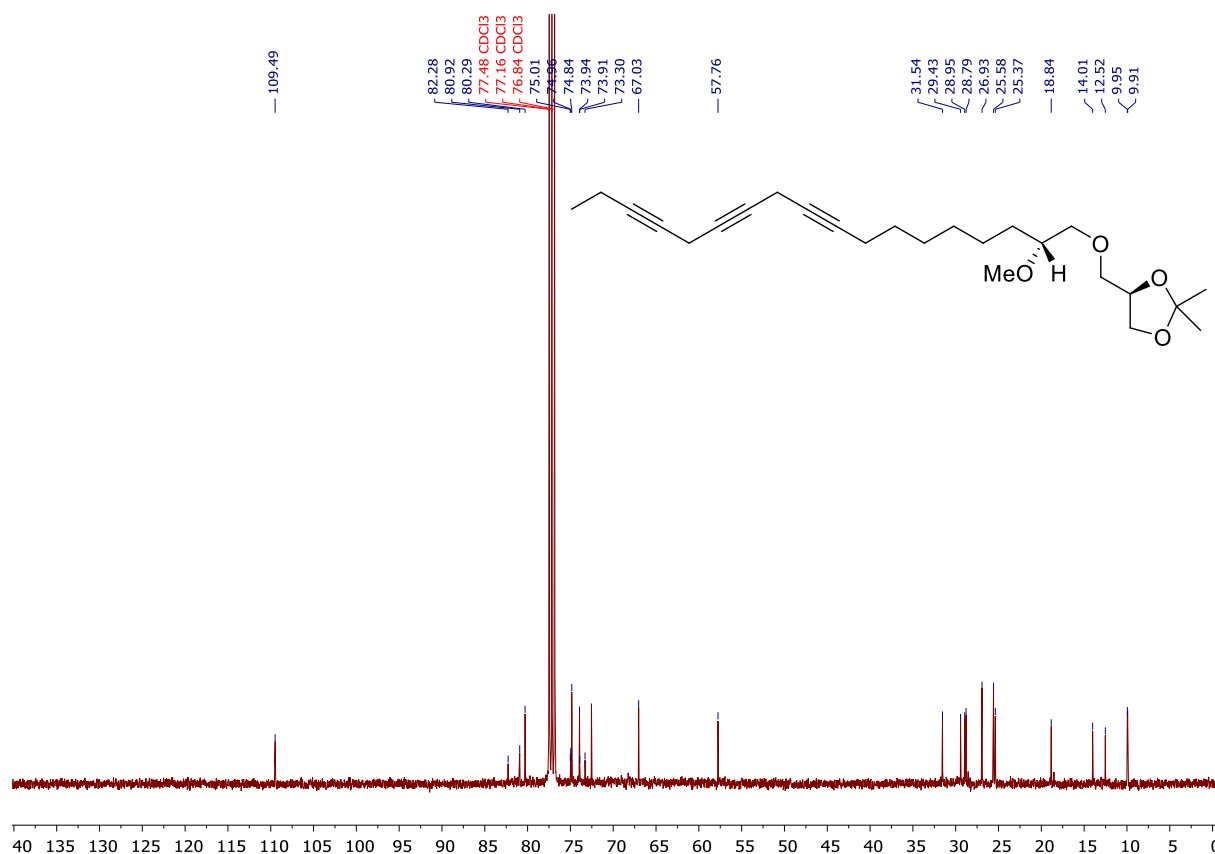
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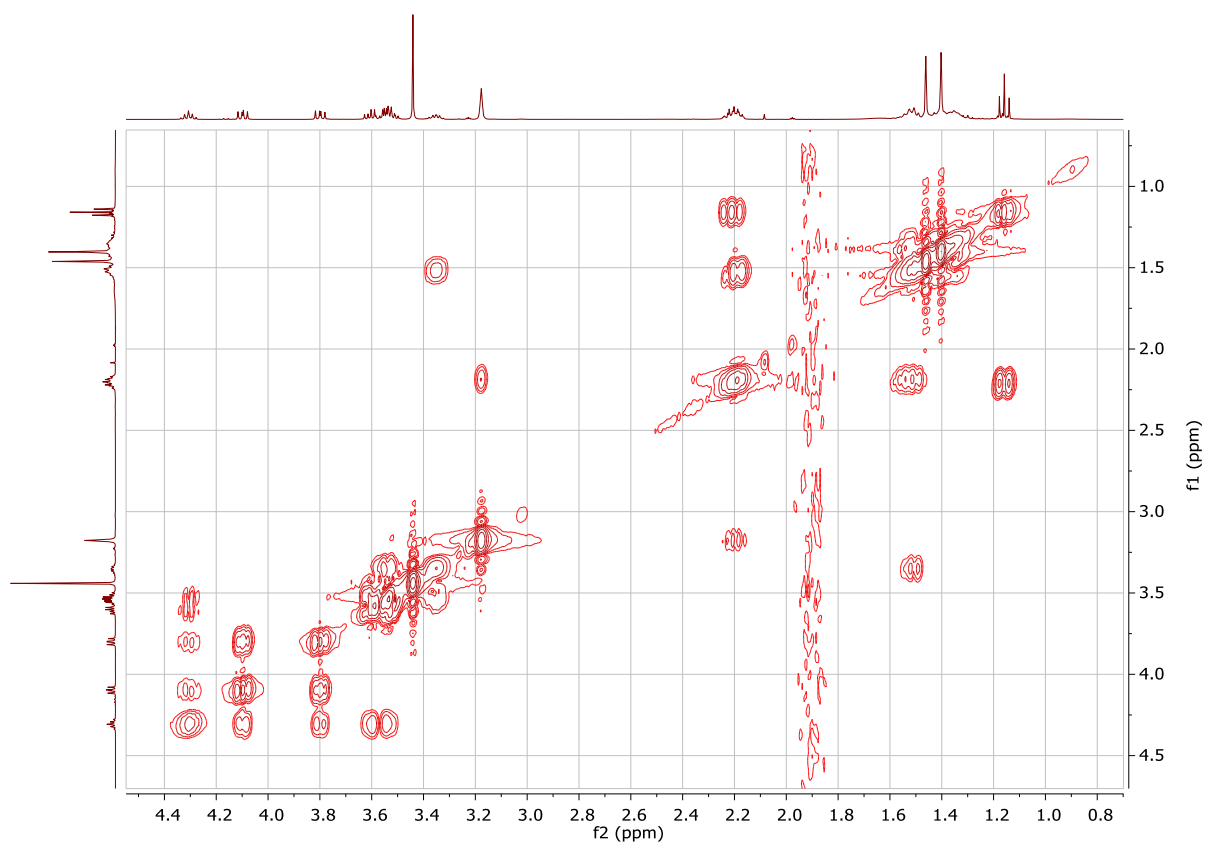
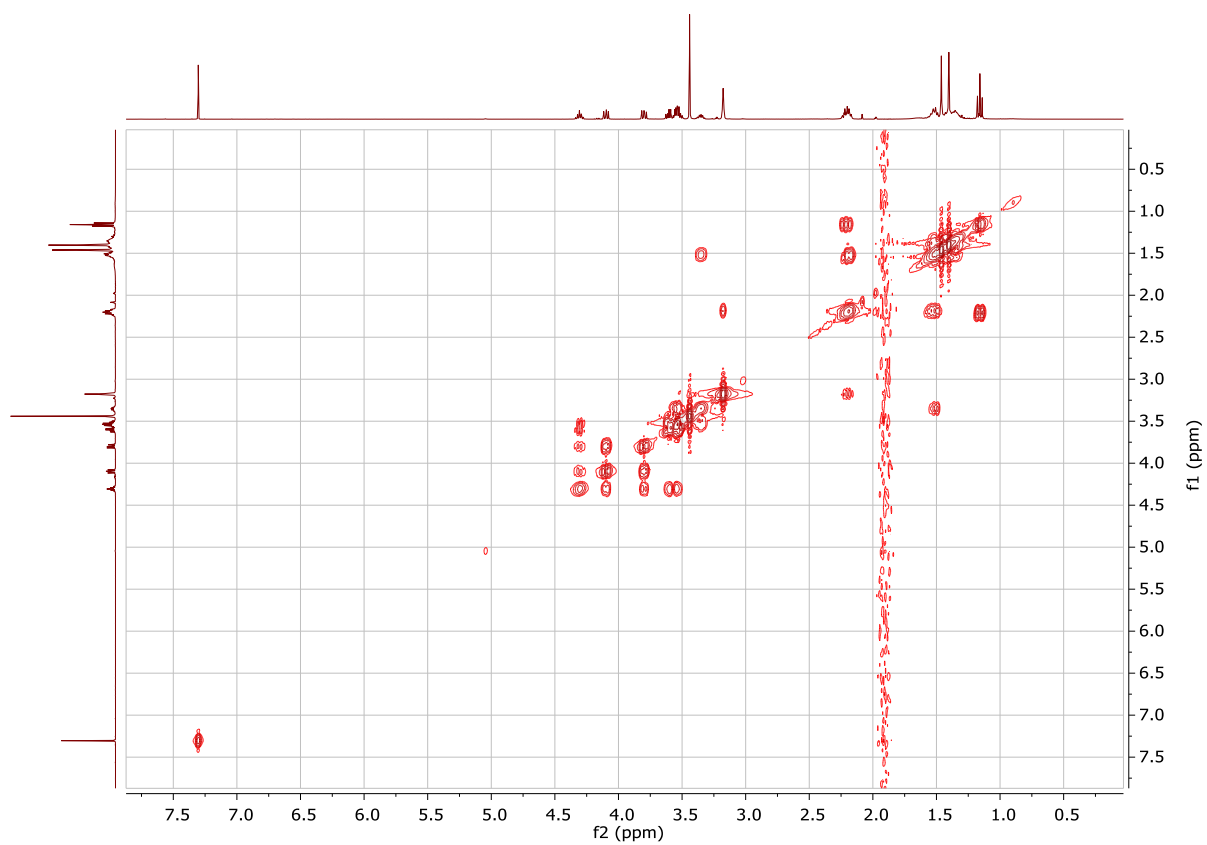
^1H NMR (400 MHz, CDCl_3) of compound **12**



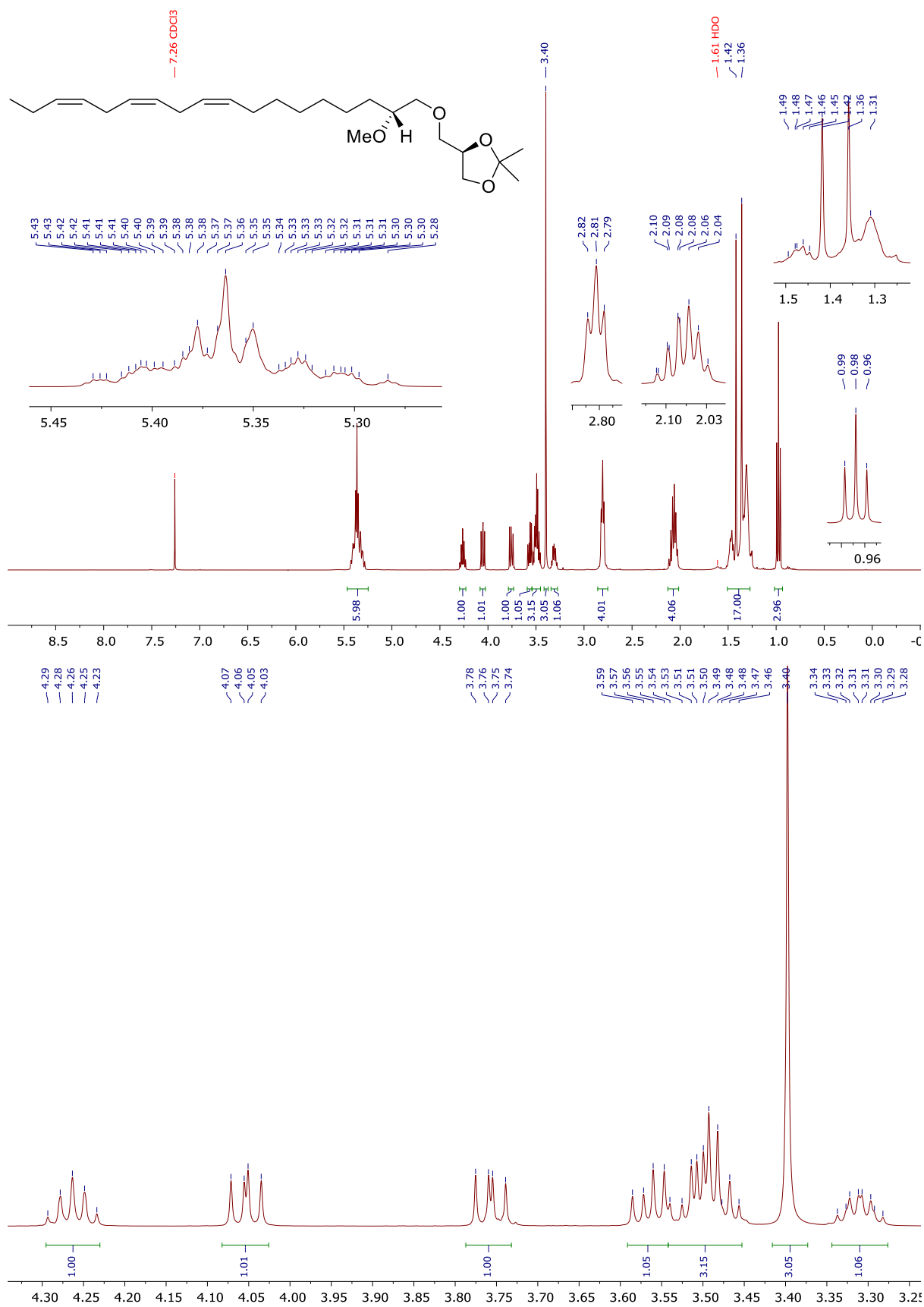
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **12**



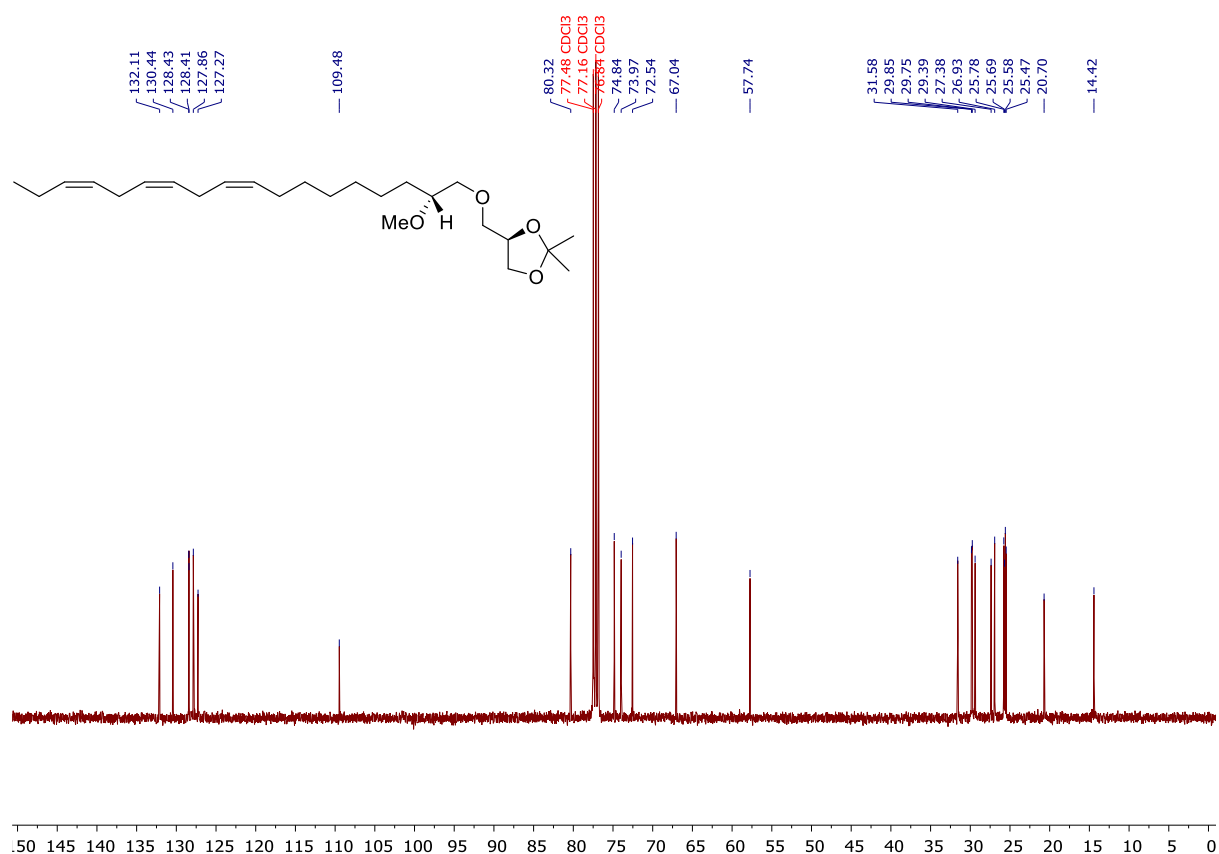
^1H - ^1H COSY spectrum of compound **12**



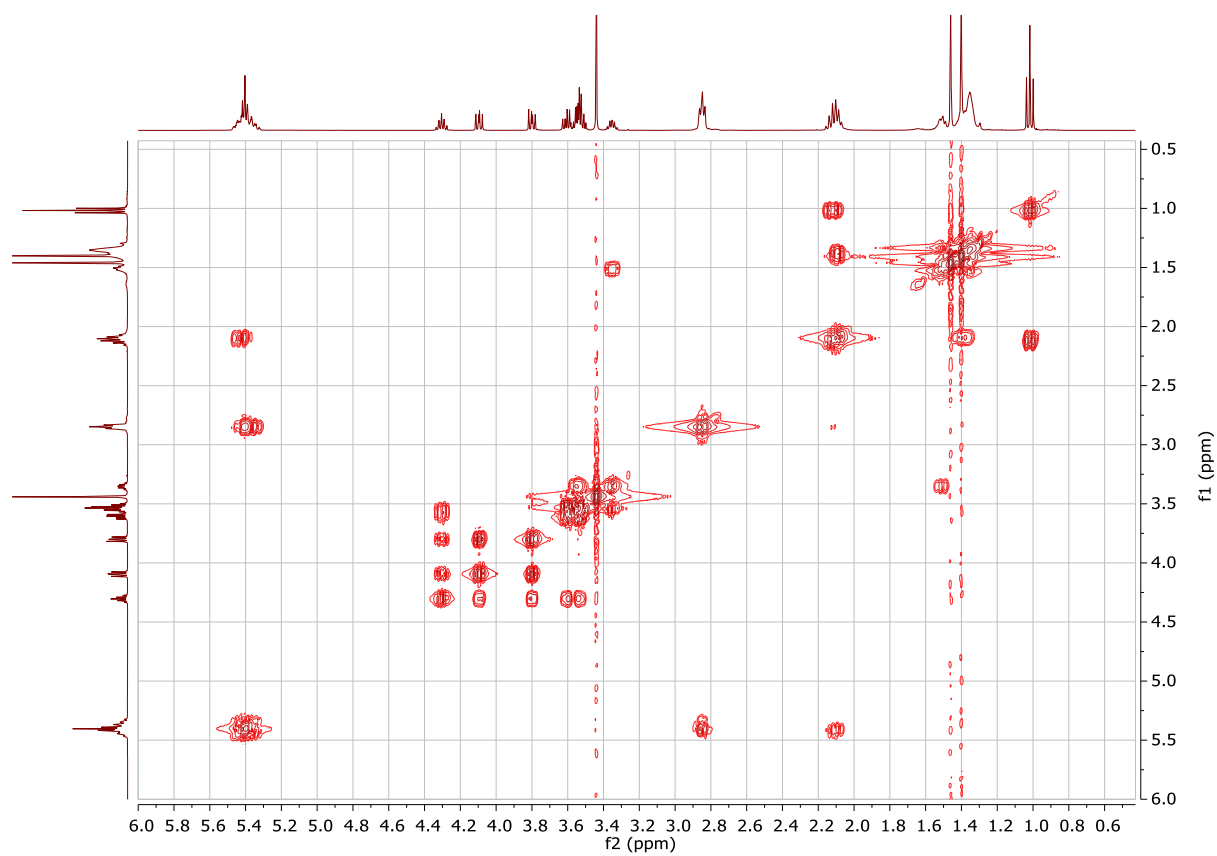
¹H NMR (400 MHz, CDCl₃) of compound **13**



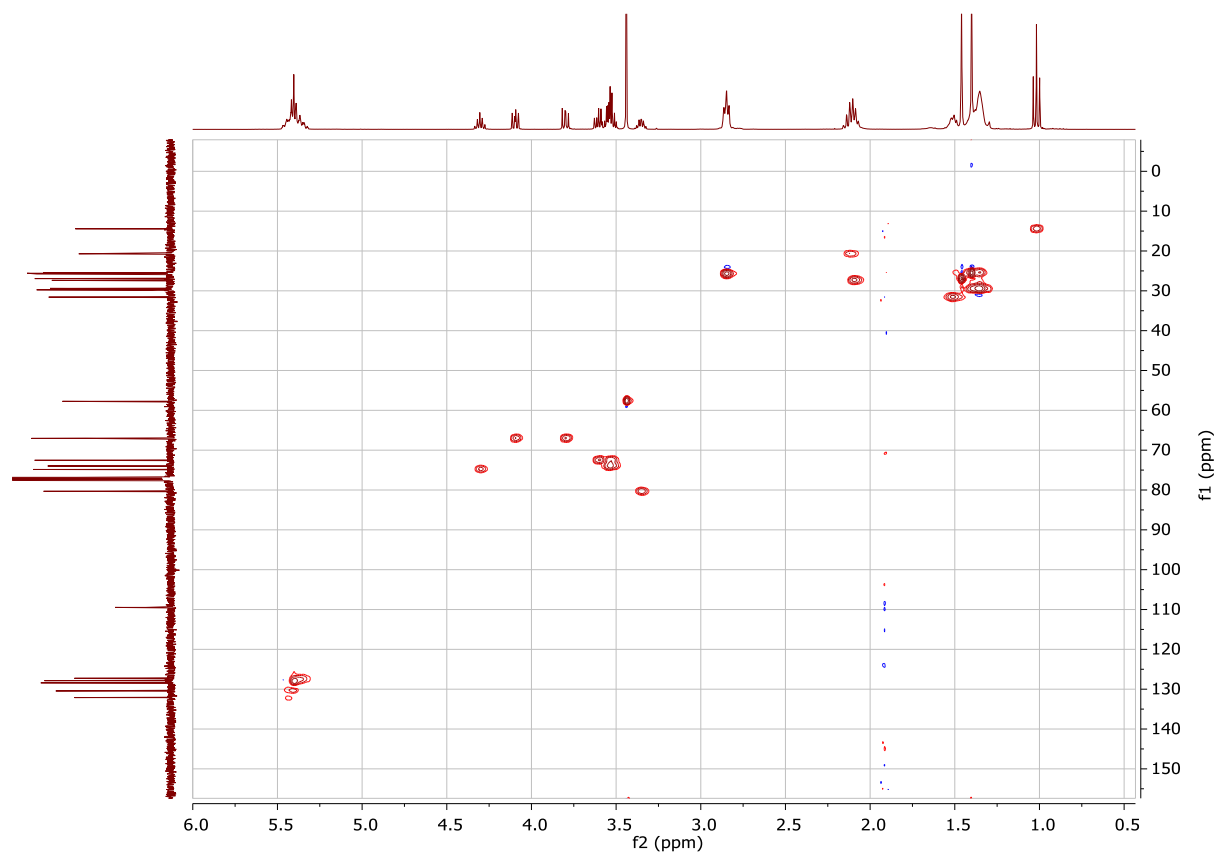
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **13**



^1H - ^1H COSY spectrum of compound **13**



^{13}C - ^1H HSQC spectrum of compound **13**



Chemical structure of (S)-1,2-dihydroxy-1-methoxy-10-undecene is shown. The structure is a long chain with a terminal double bond, a methoxy group, and two hydroxyl groups. The stereochemistry at the chiral center is (S).

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 6 ppm. The spectrum is characterized by a large peak at 3.40 ppm (integration 2.97) and a smaller peak at 3.35 ppm (integration 1.07). Other peaks are visible in the 1.3-2.1 ppm range (integration 1.01) and the 3.8-4.0 ppm range (integration 1.00). A list of peak chemical shifts is provided on the right side of the spectrum.

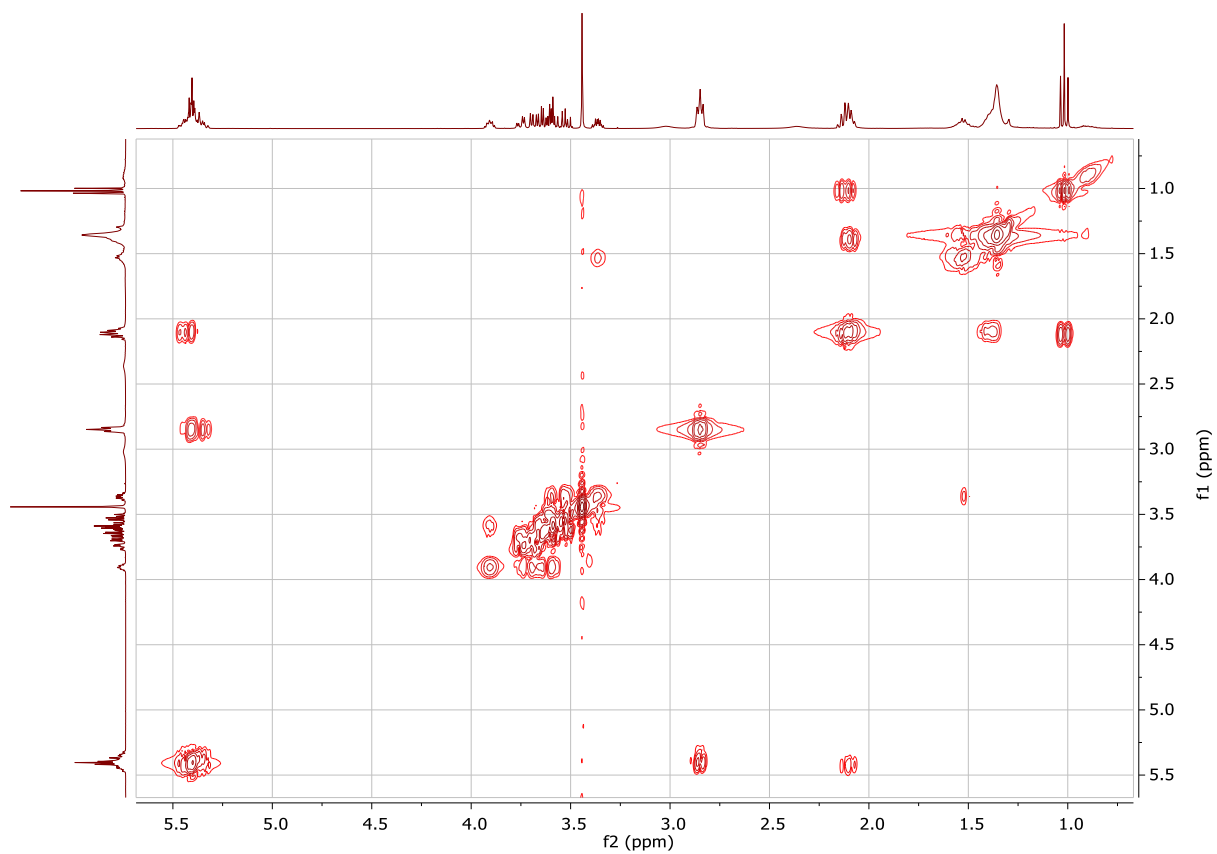
Peak chemical shifts (ppm): 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.73, 3.72, 3.70, 3.69, 3.66, 3.65, 3.63, 3.62, 3.60, 3.58, 3.57, 3.56, 3.55, 3.54, 3.52, 3.50, 3.48, 3.47, 3.46, 3.40, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 2.82, 2.80, 2.79, 2.11, 2.10, 2.08, 2.06, 2.05, 2.03, 1.52, 1.51, 1.50, 1.49, 1.47, 1.45, 1.43, 1.31, 0.99, 0.97, 0.95.

Integration values: 1.00, 1.00, 2.03, 2.17, 1.01, 2.97, 1.07.

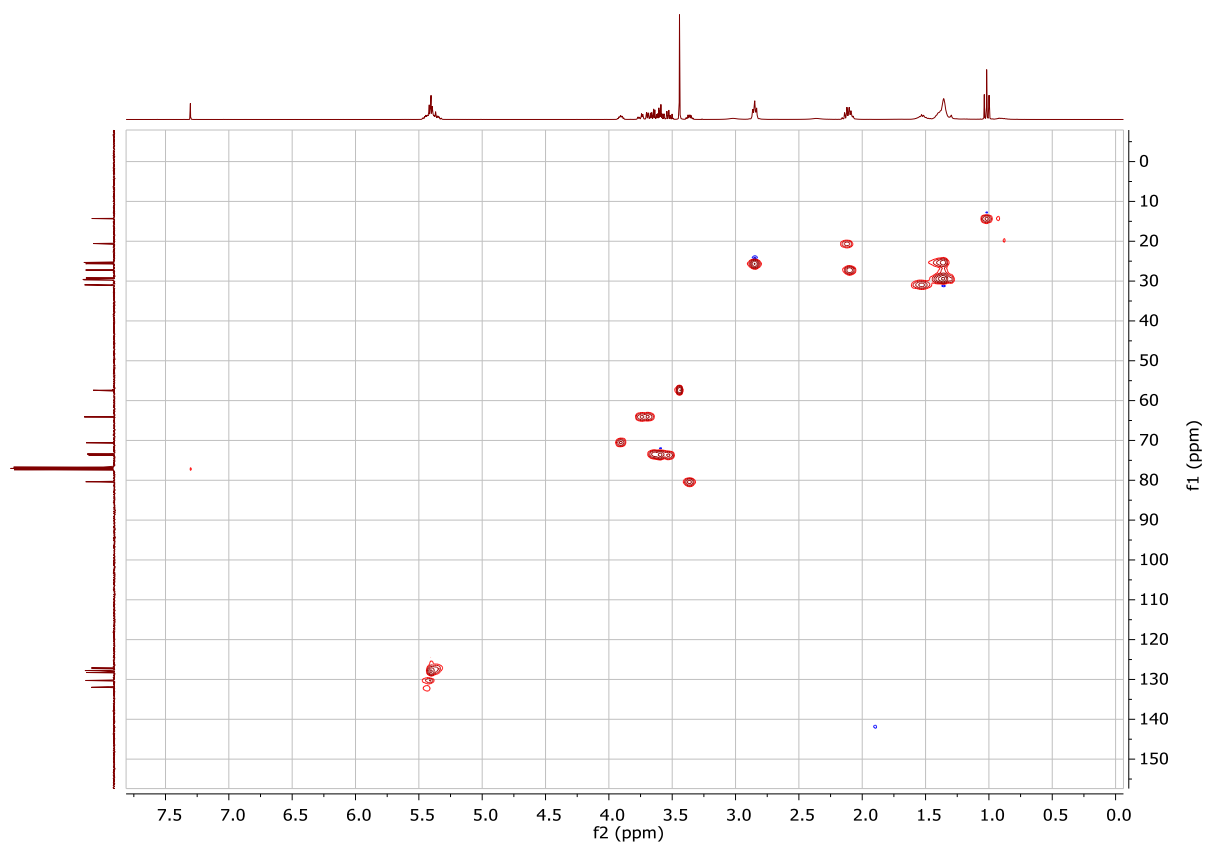
Chemical structure of (E)-12-((S)-2,3-dihydroxypropyl)undec-5-en-1-yl methyl ether is shown above the spectrum. The structure is a long-chain molecule with a terminal methyl ether group, a double bond, and a terminal dihydroxypropyl group.

The ^{13}C NMR spectrum (CDCl₃) shows the following chemical shifts (ppm):

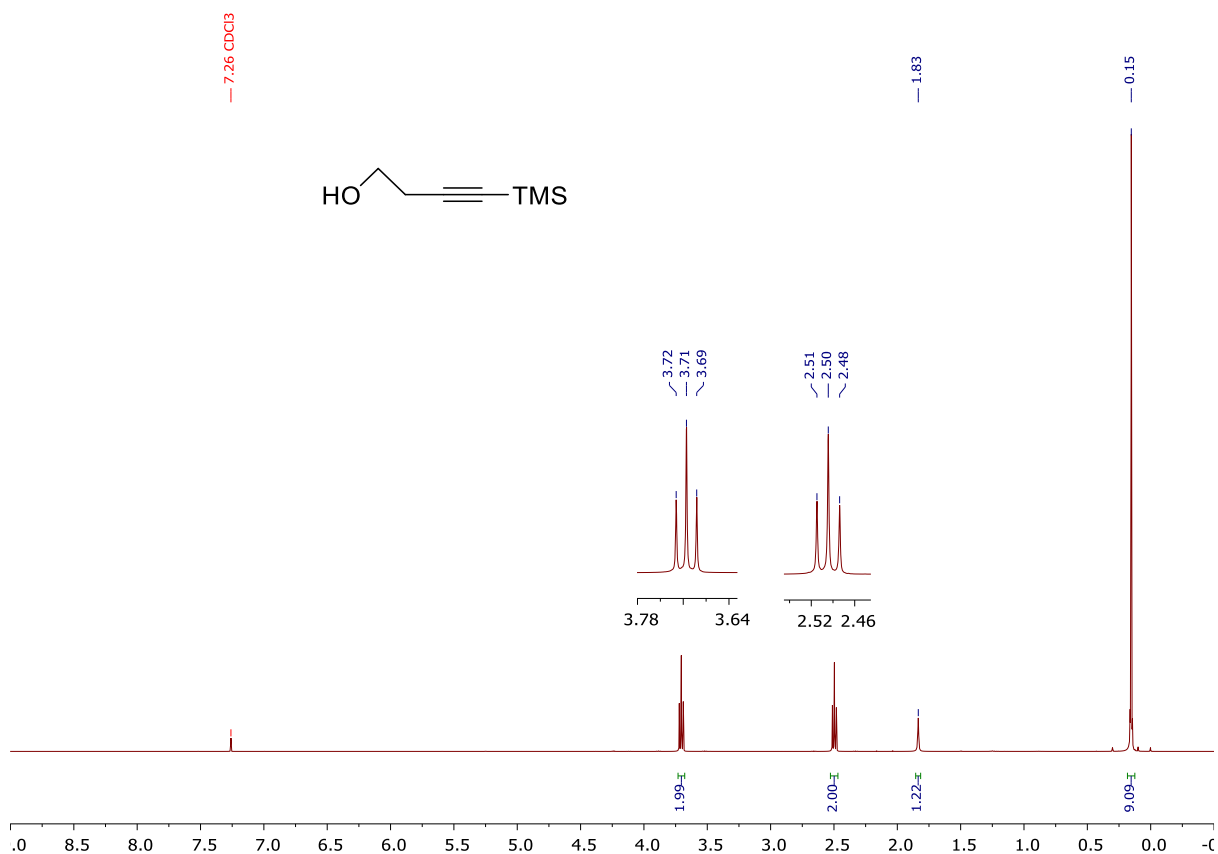
- 132.11
- 130.39
- 128.44
- 127.90
- 127.25
- 80.49
- 77.48 CDCl₃
- 77.16 CDCl₃
- 76.84 CDCl₃
- 73.79
- 73.54
- 70.71
- 64.22
- 57.53
- 31.07
- 29.84
- 29.72
- 29.36
- 27.36
- 25.77
- 25.68
- 25.46
- 20.70
- 14.42



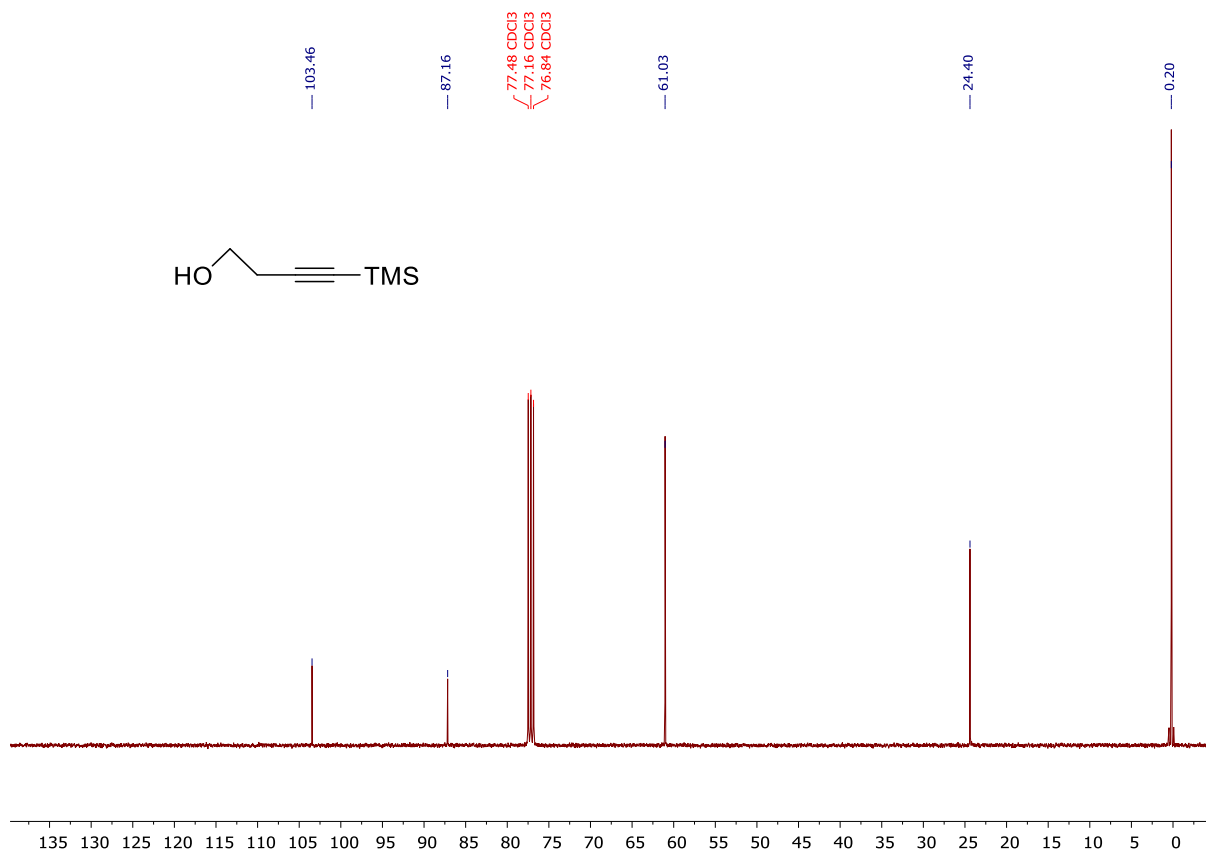
^{13}C - ^1H HSQC spectrum of MEL 5



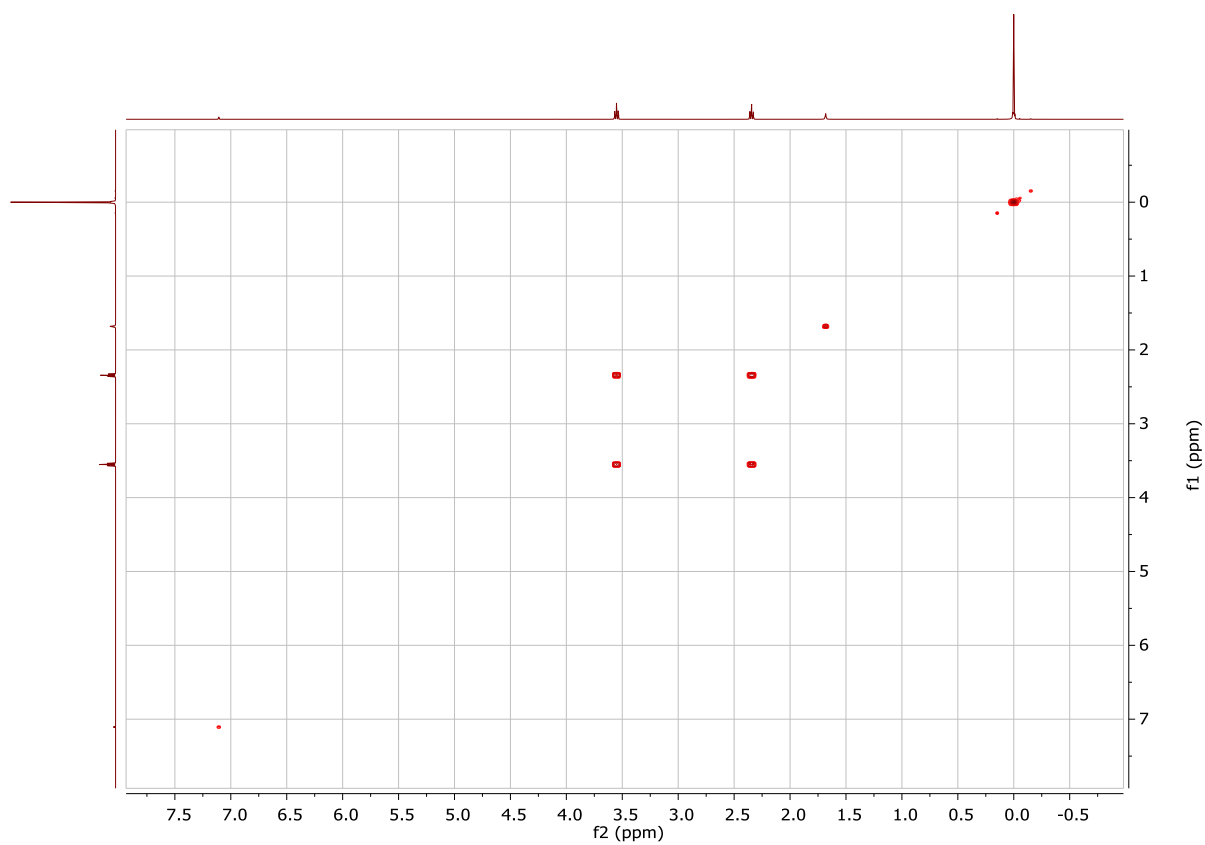
^1H NMR (400 MHz, CDCl_3) of compound **14**



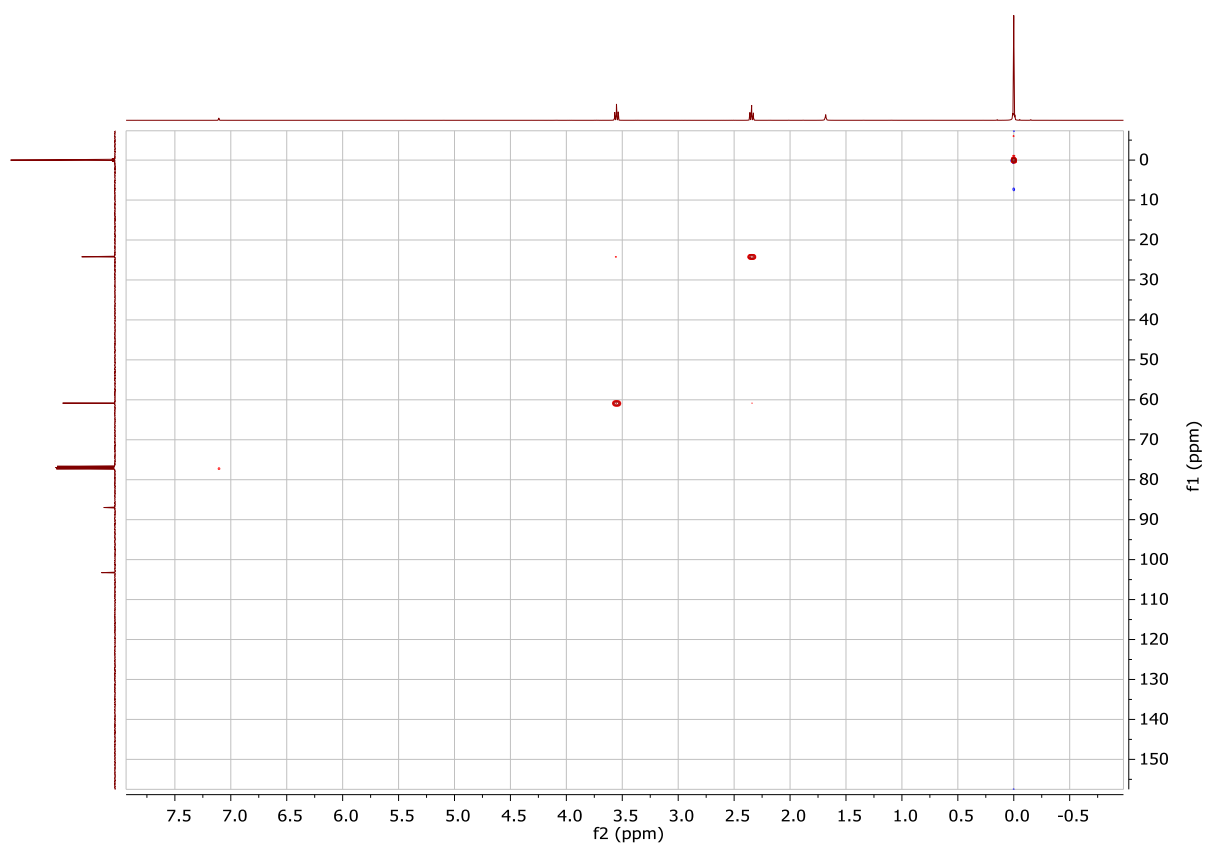
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **14**



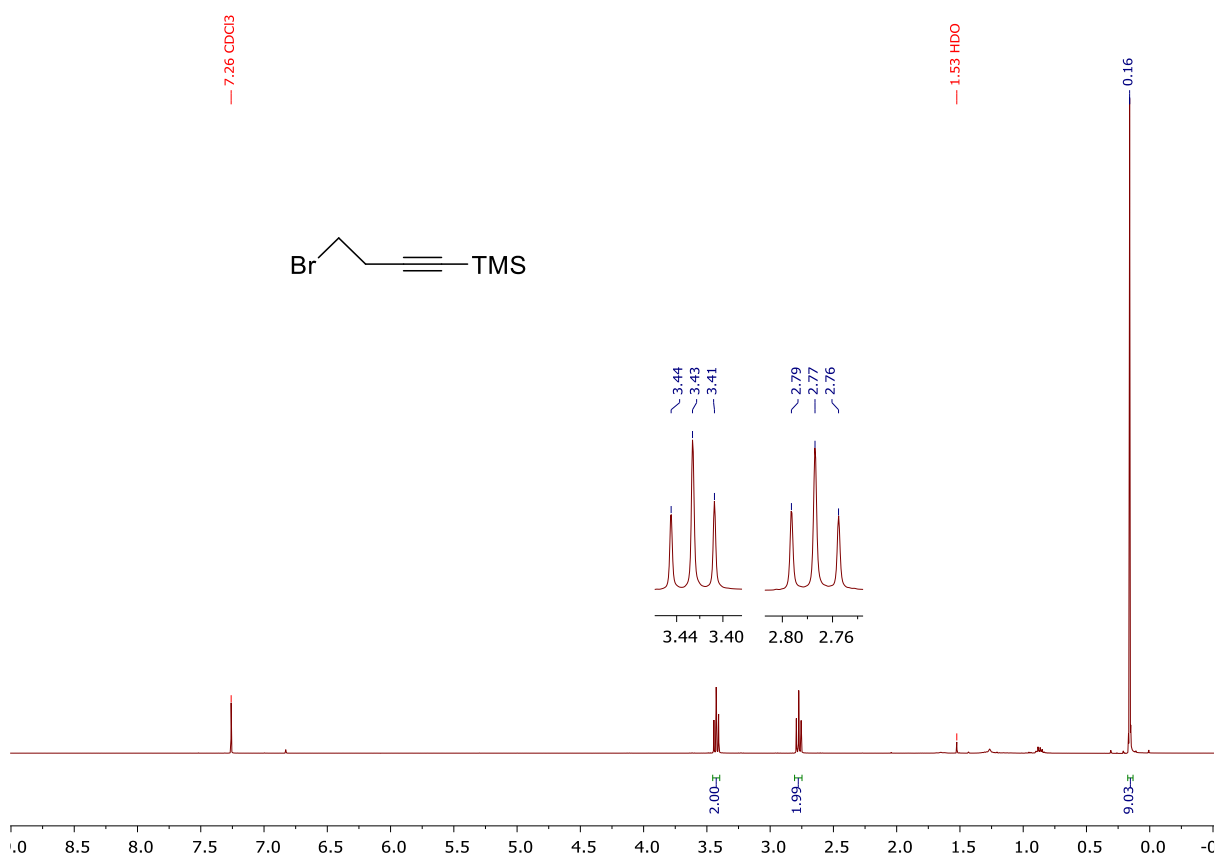
^1H - ^1H COSY spectrum of compound **14**



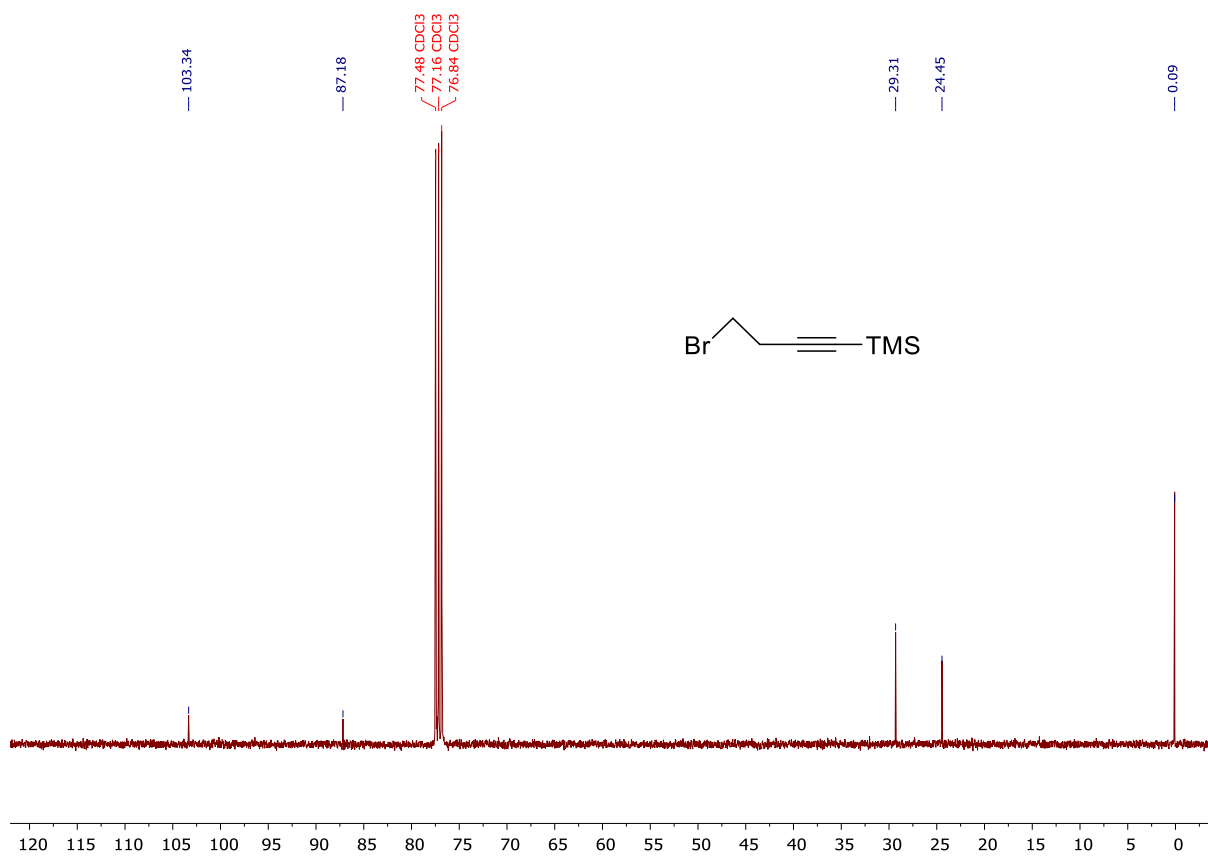
^{13}C - ^1H HSQC spectrum of compound **14**



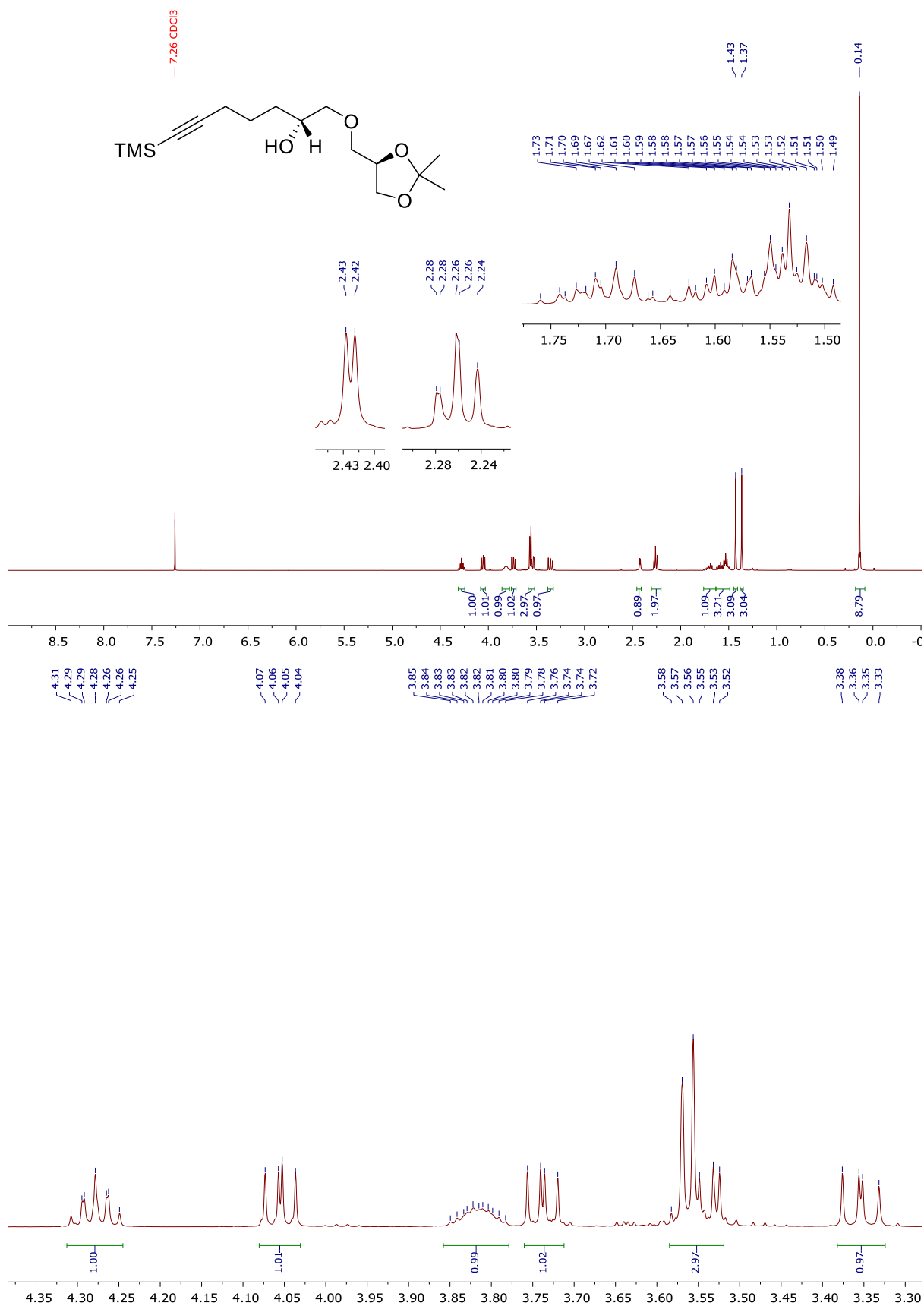
^1H NMR (400 MHz, CDCl_3) of compound **15**



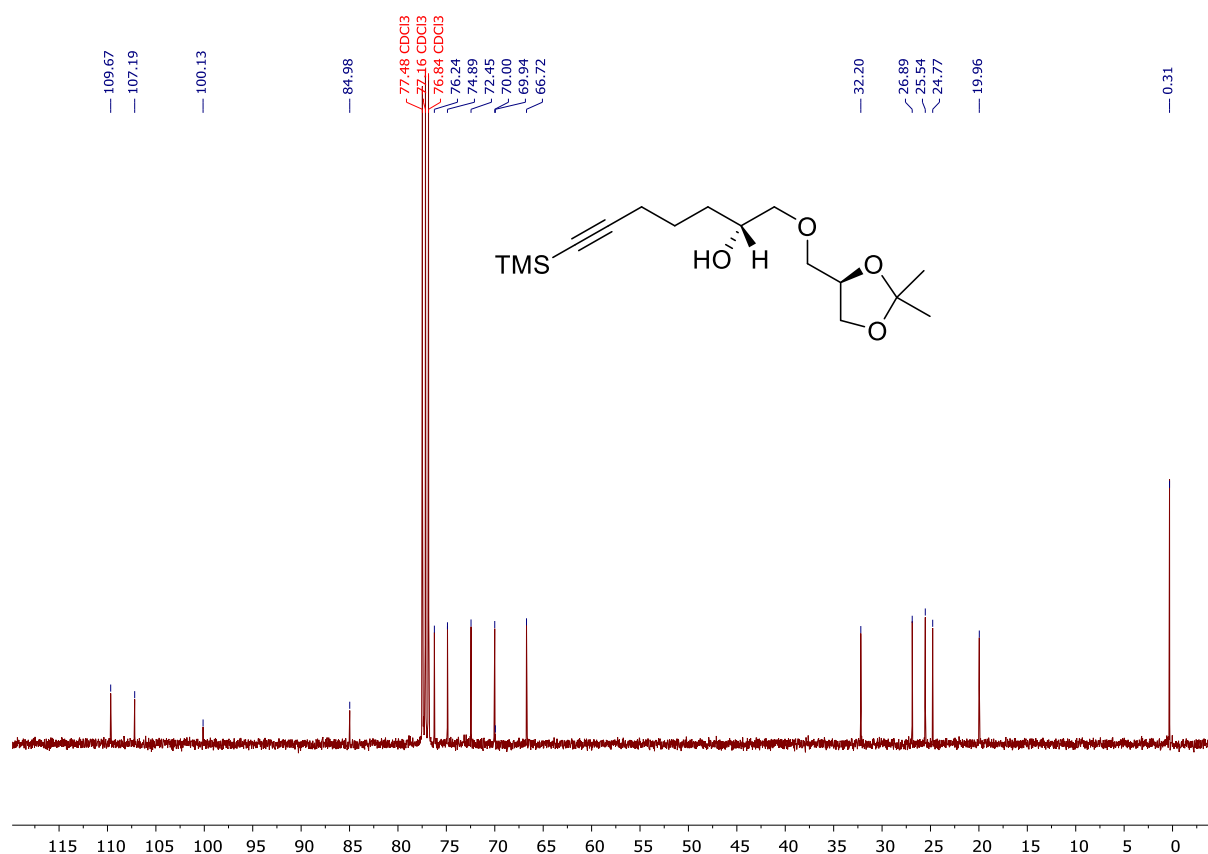
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **15**



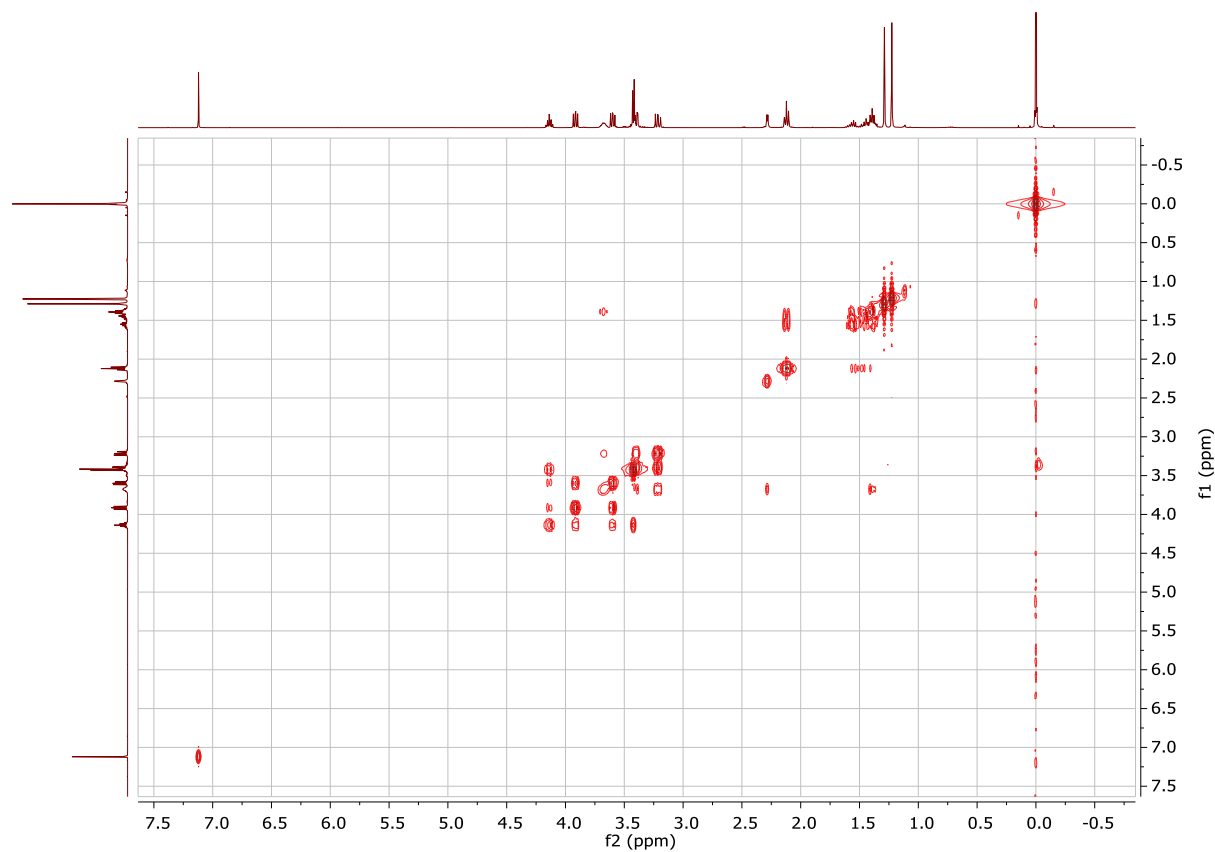
^1H NMR (400 MHz, CDCl_3) of compound **16**

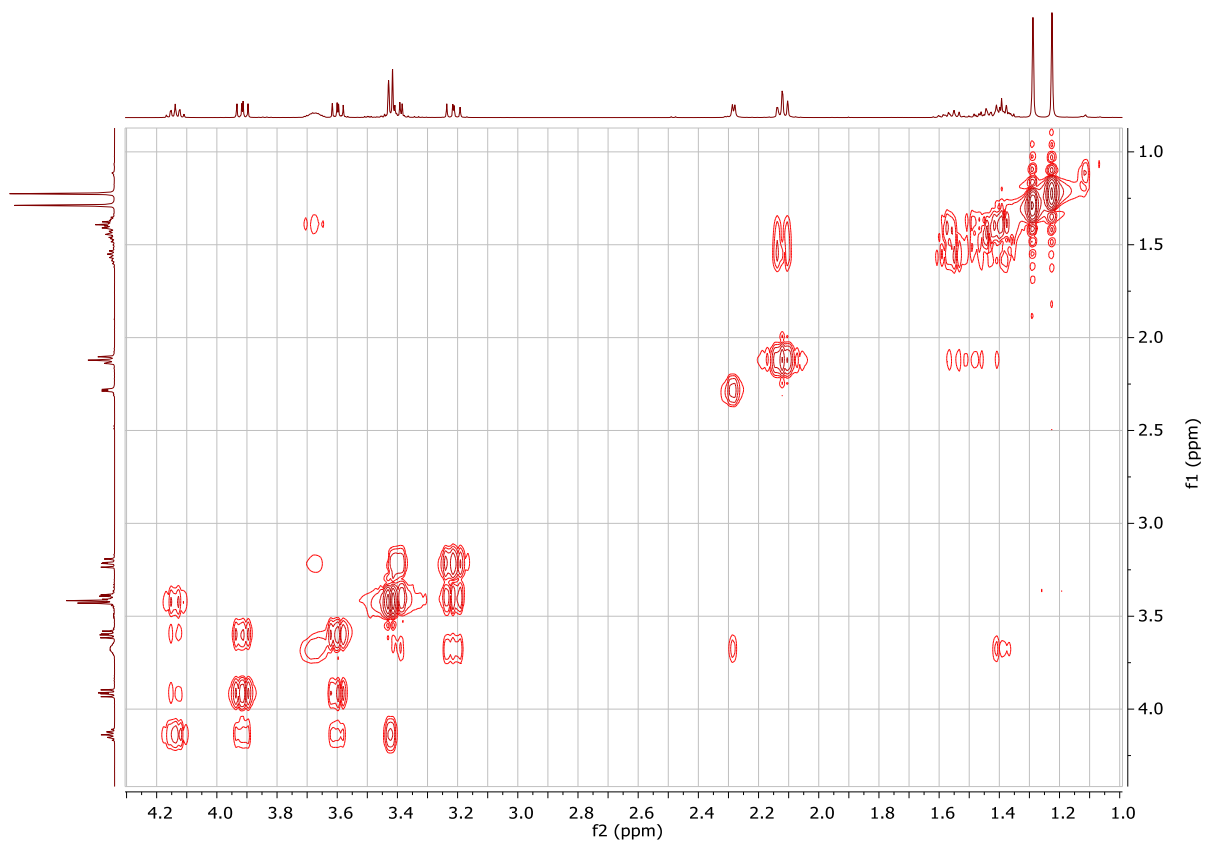


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **16**

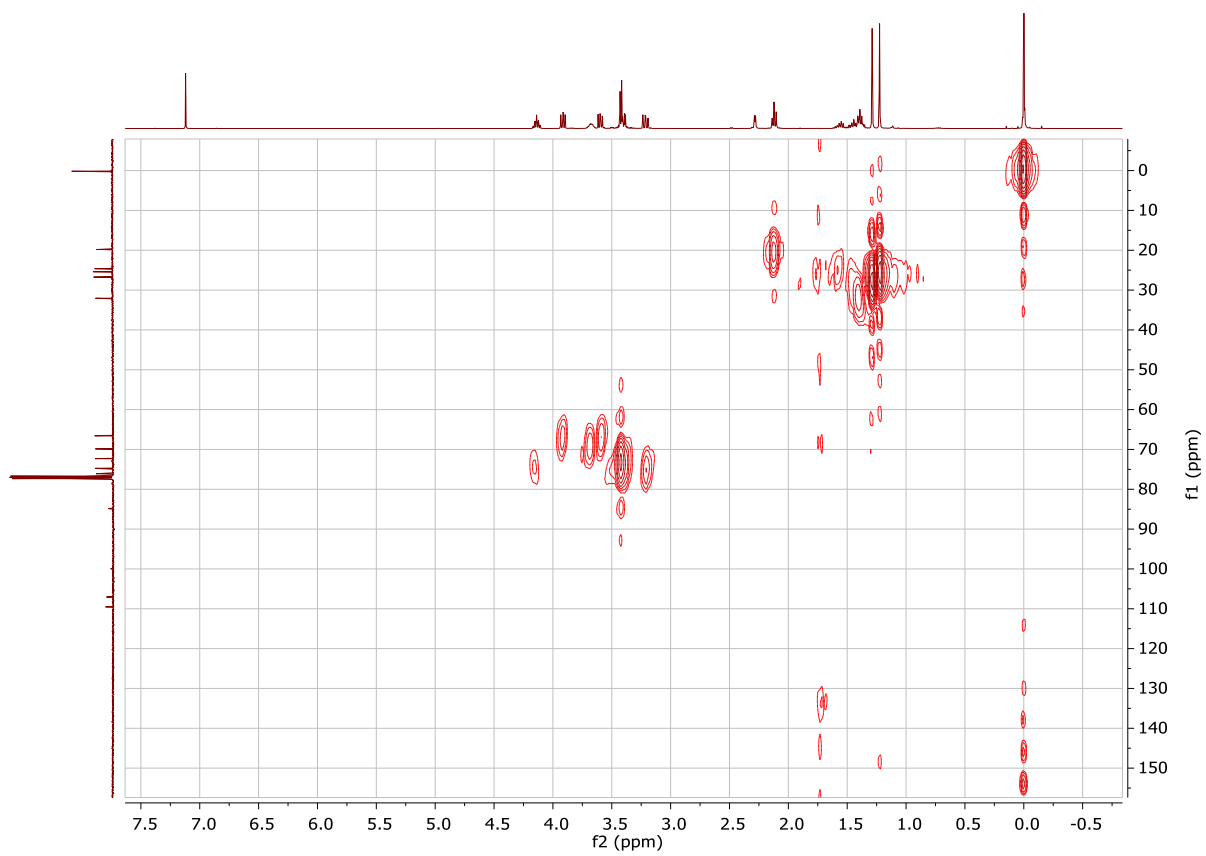


^1H - ^1H COSY spectrum of compound **16**

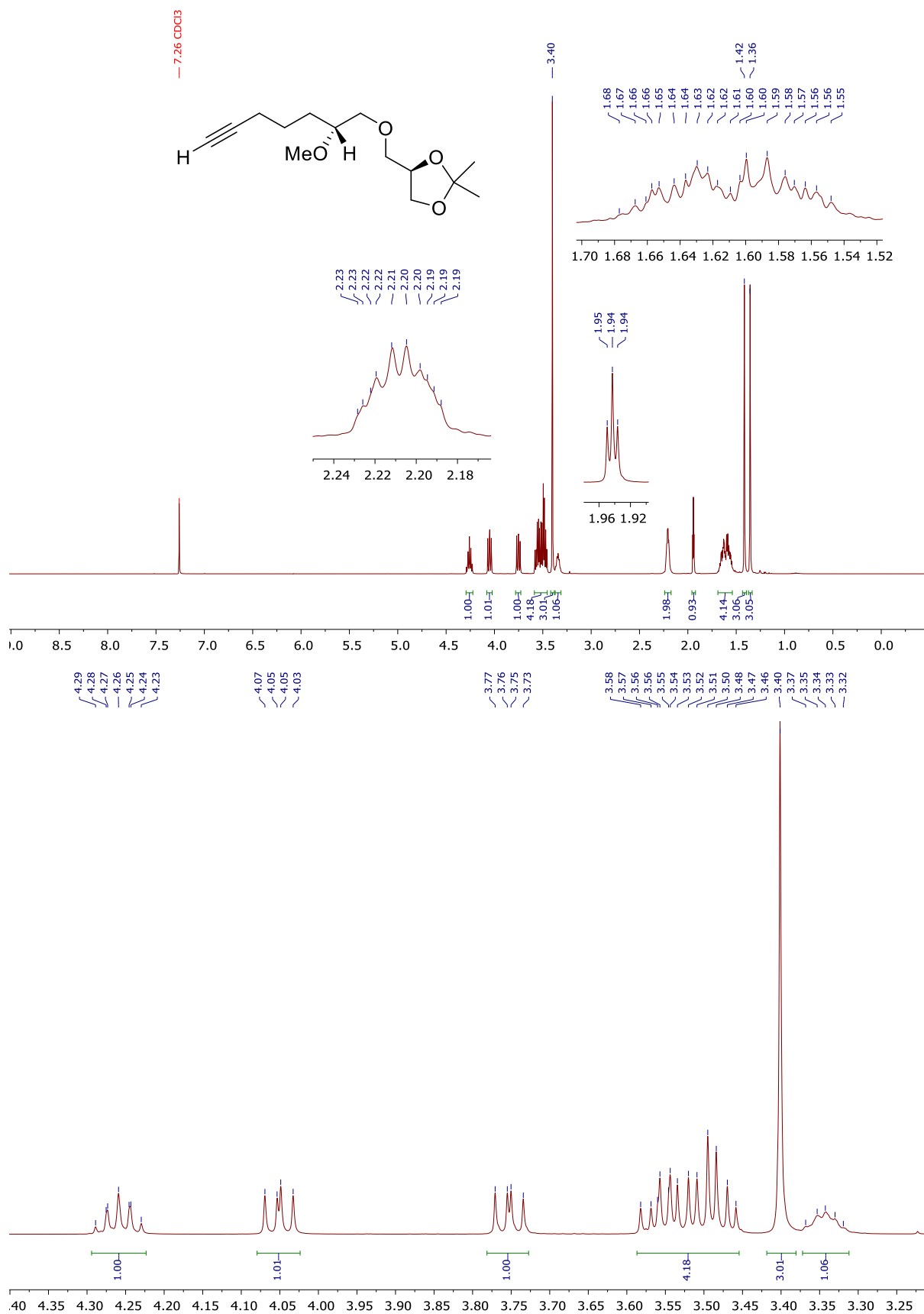




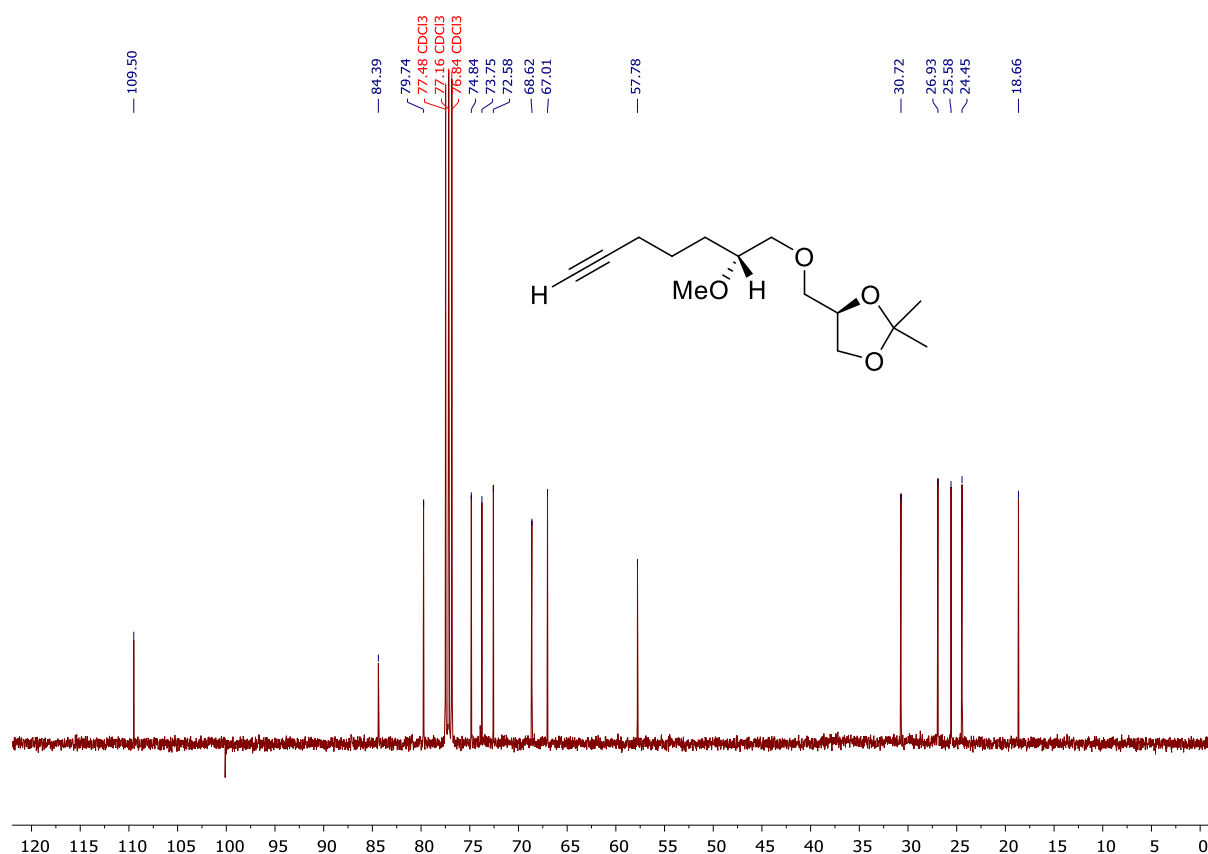
^{13}C - ^1H HSQC spectrum of compound **16**



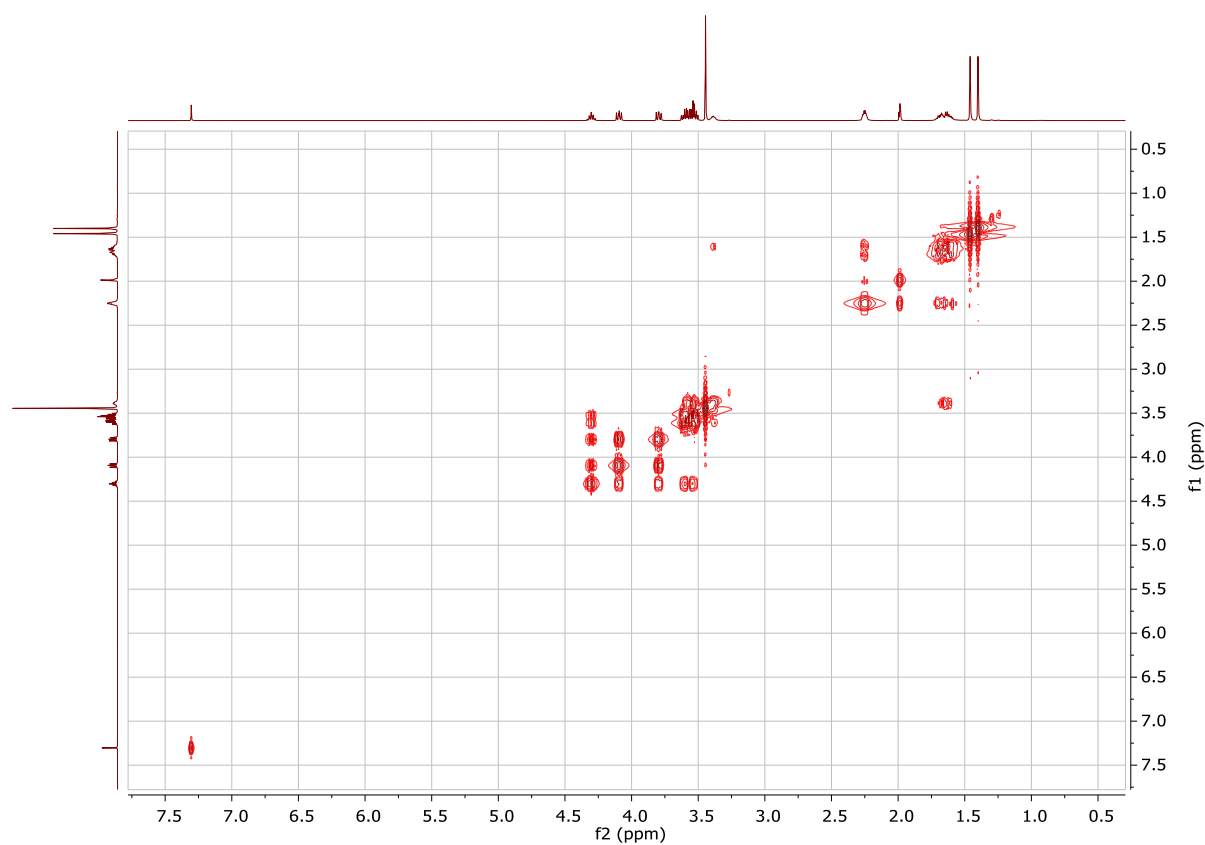
^1H NMR (400 MHz, CDCl_3) of compound **17**

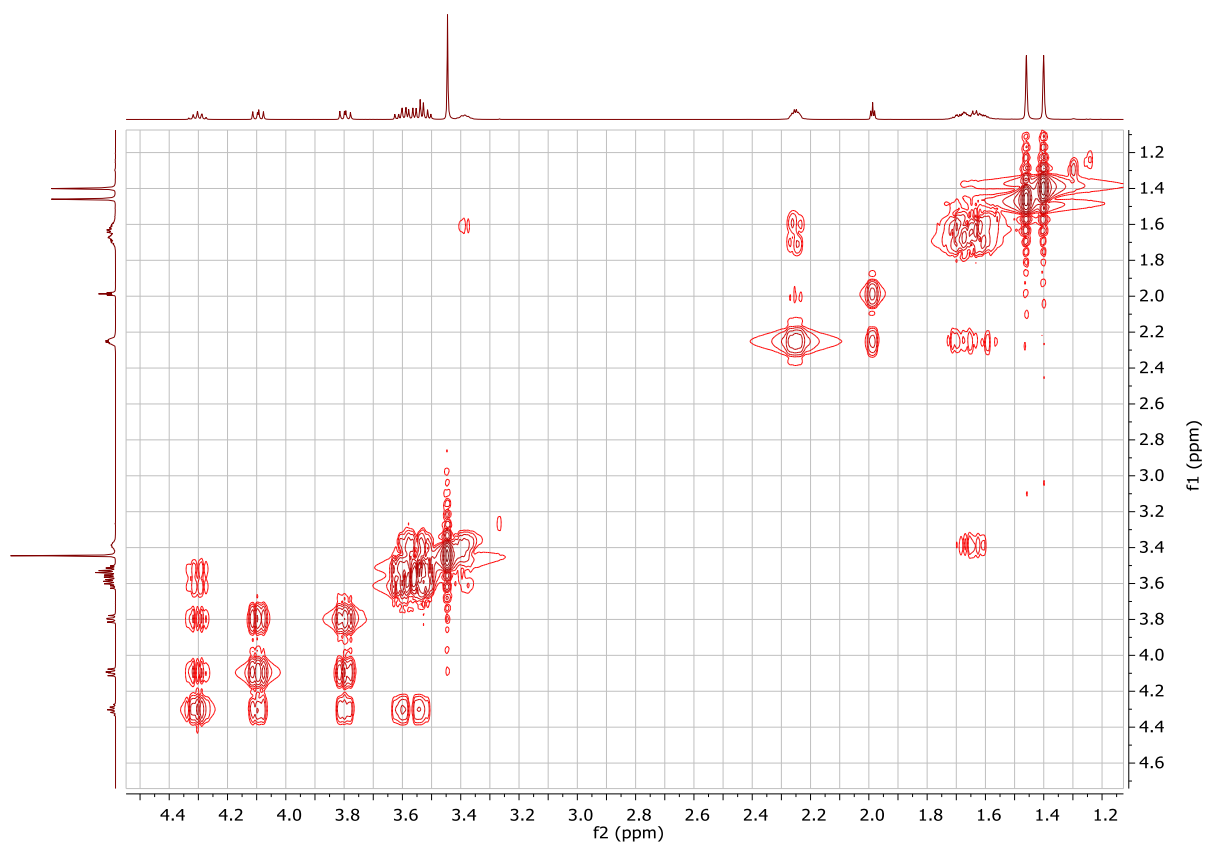


$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **17**

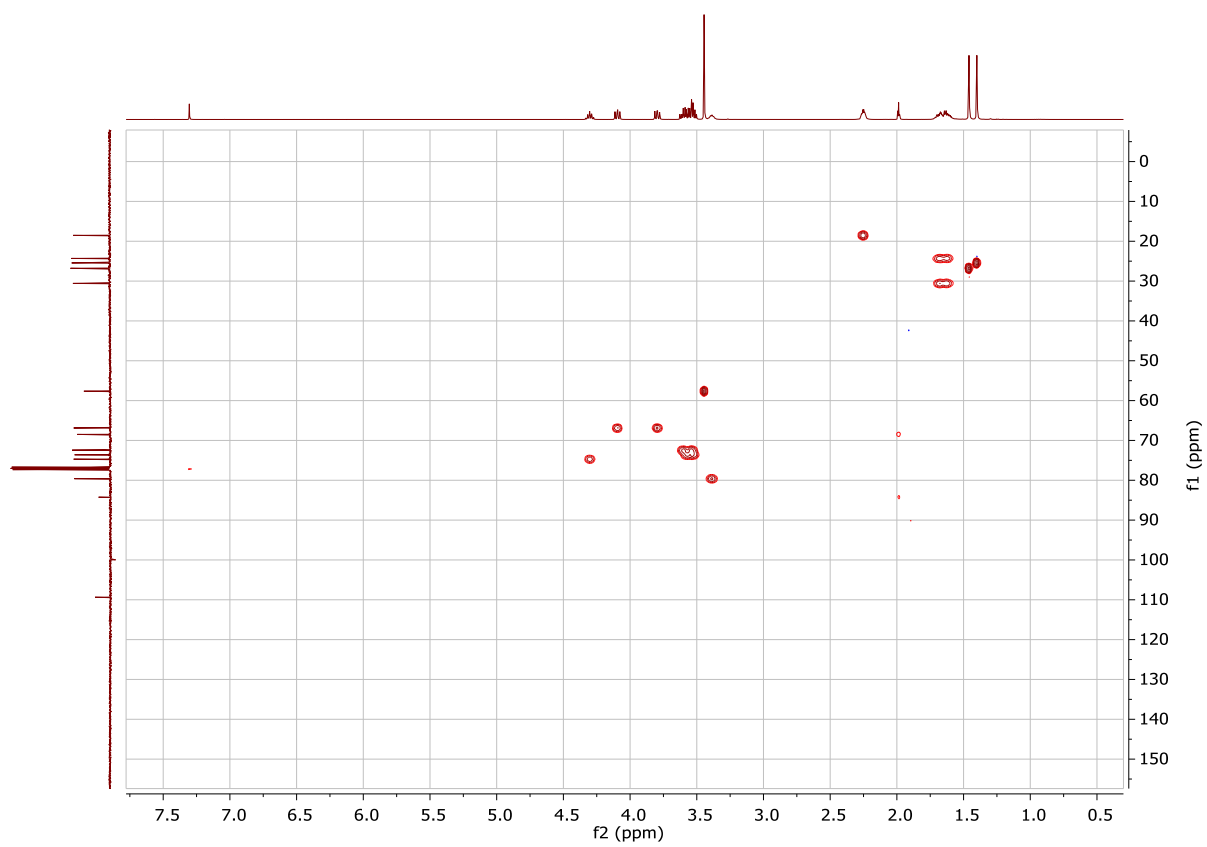


^1H - ^1H COSY spectrum of compound **17**

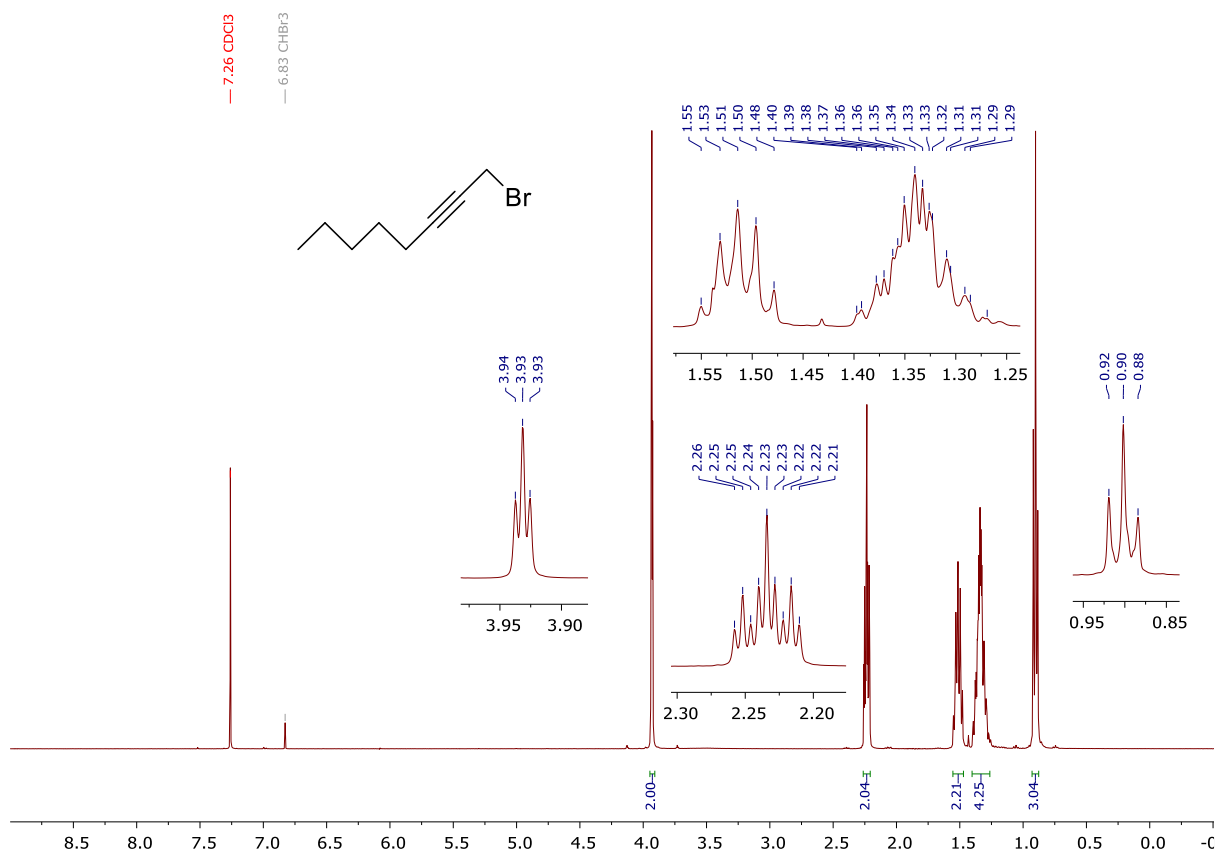




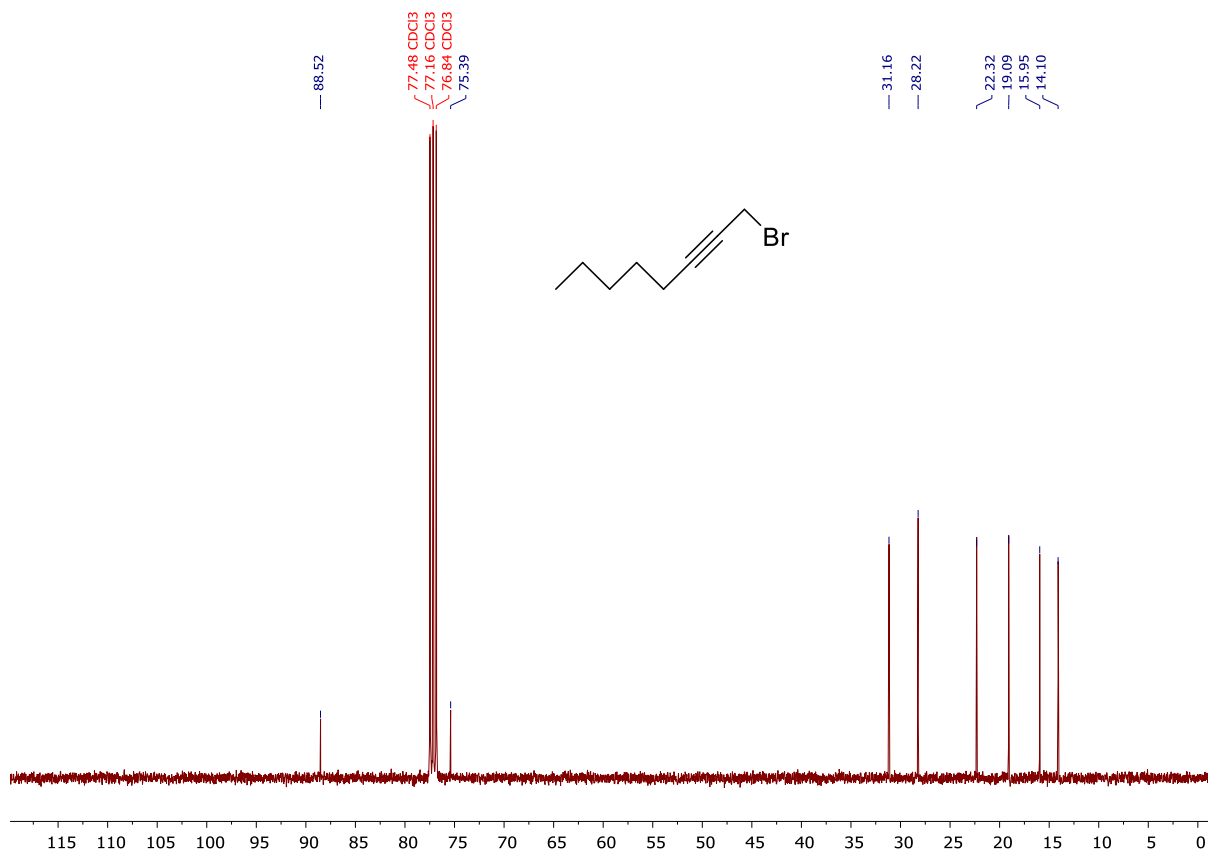
^{13}C - ^1H HSQC spectrum of compound **17**



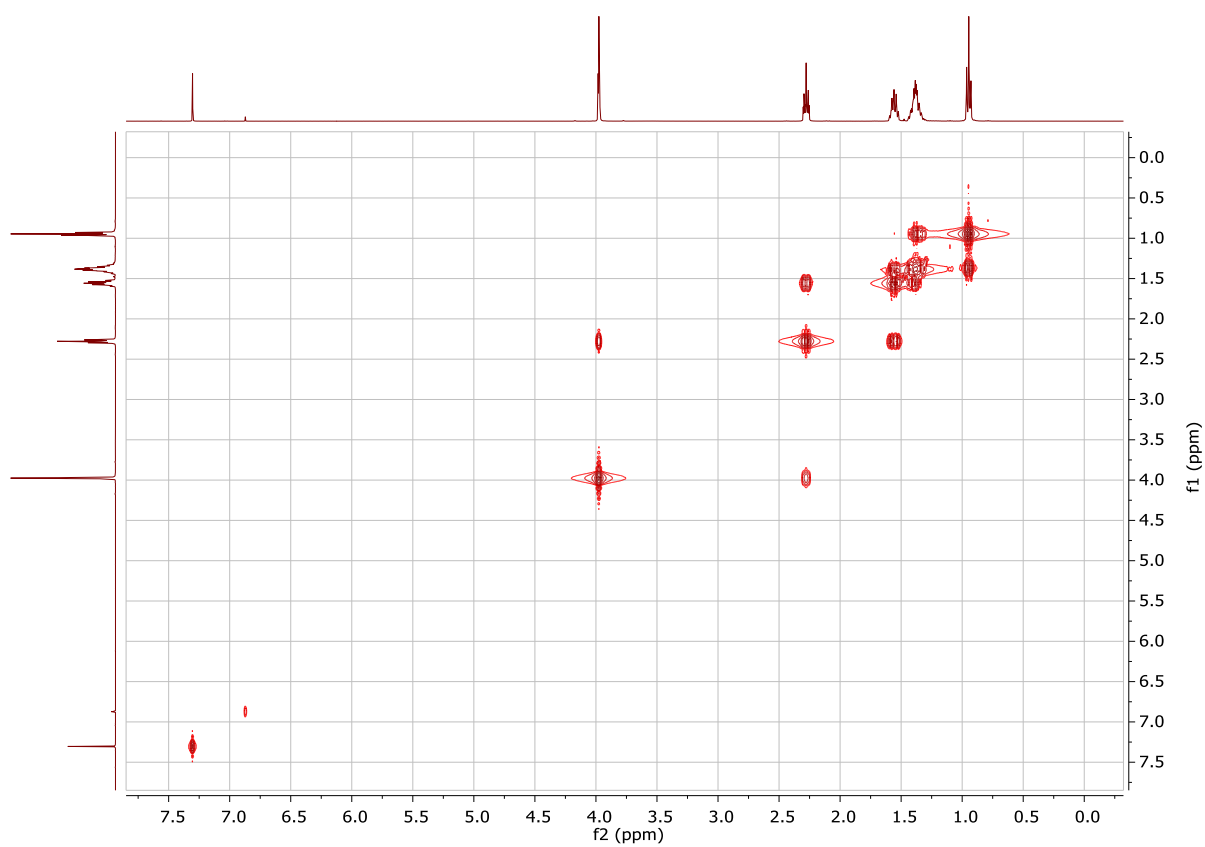
^1H NMR (400 MHz, CDCl_3) of compound **18**



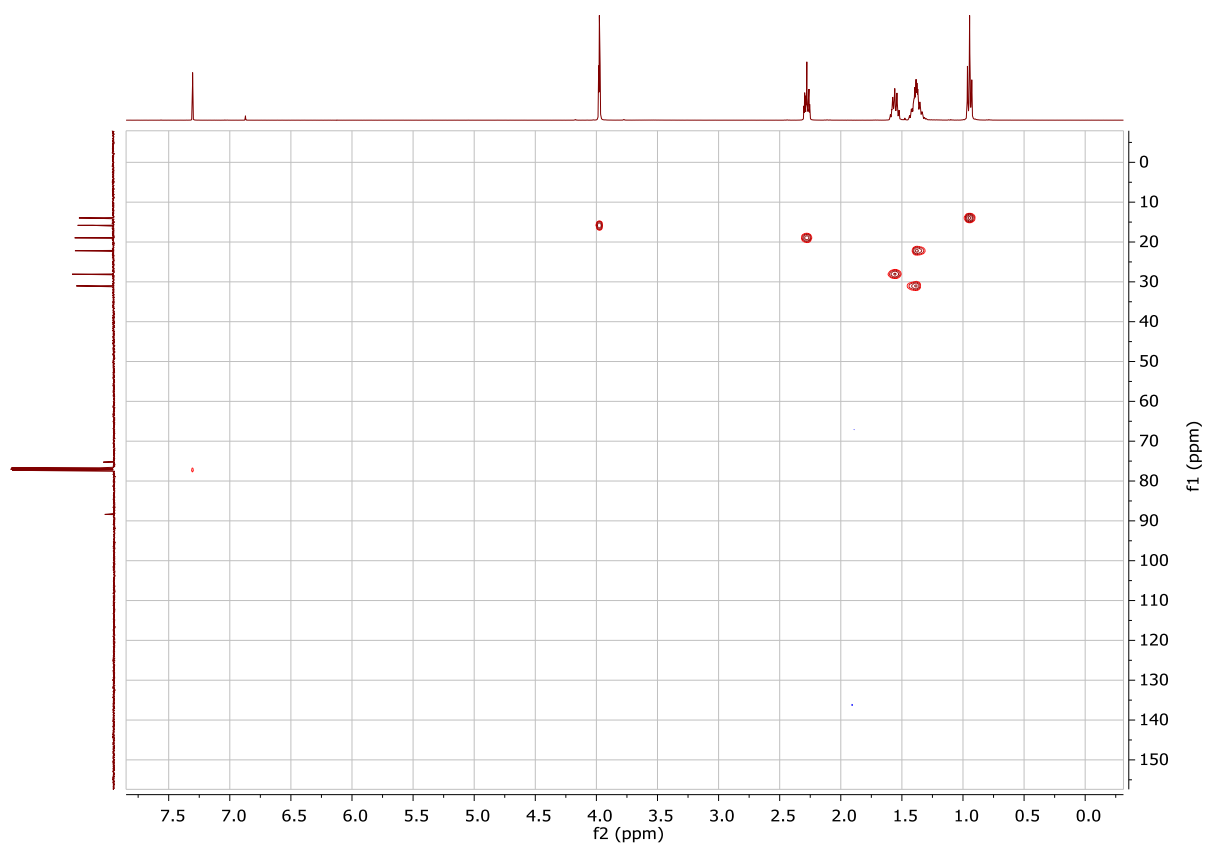
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **18**



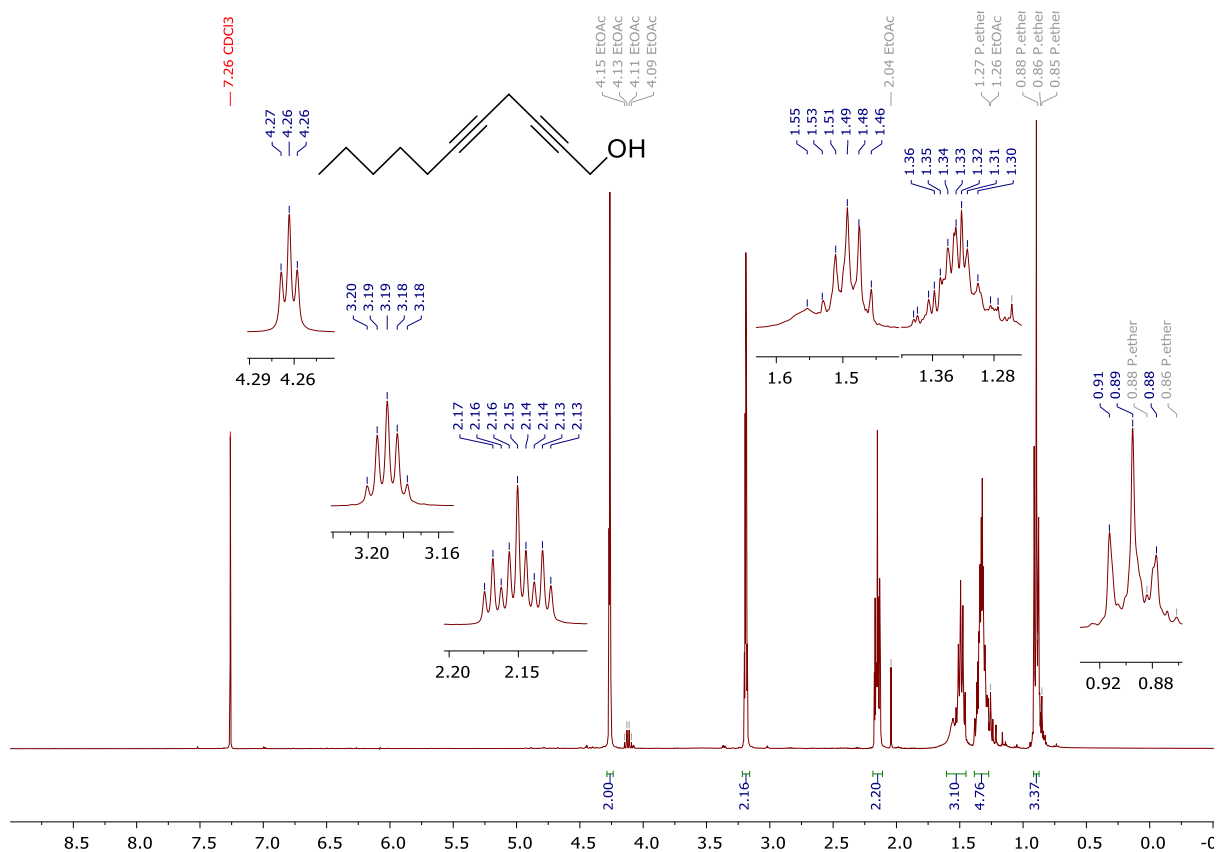
^1H - ^1H COSY spectrum of compound **18**



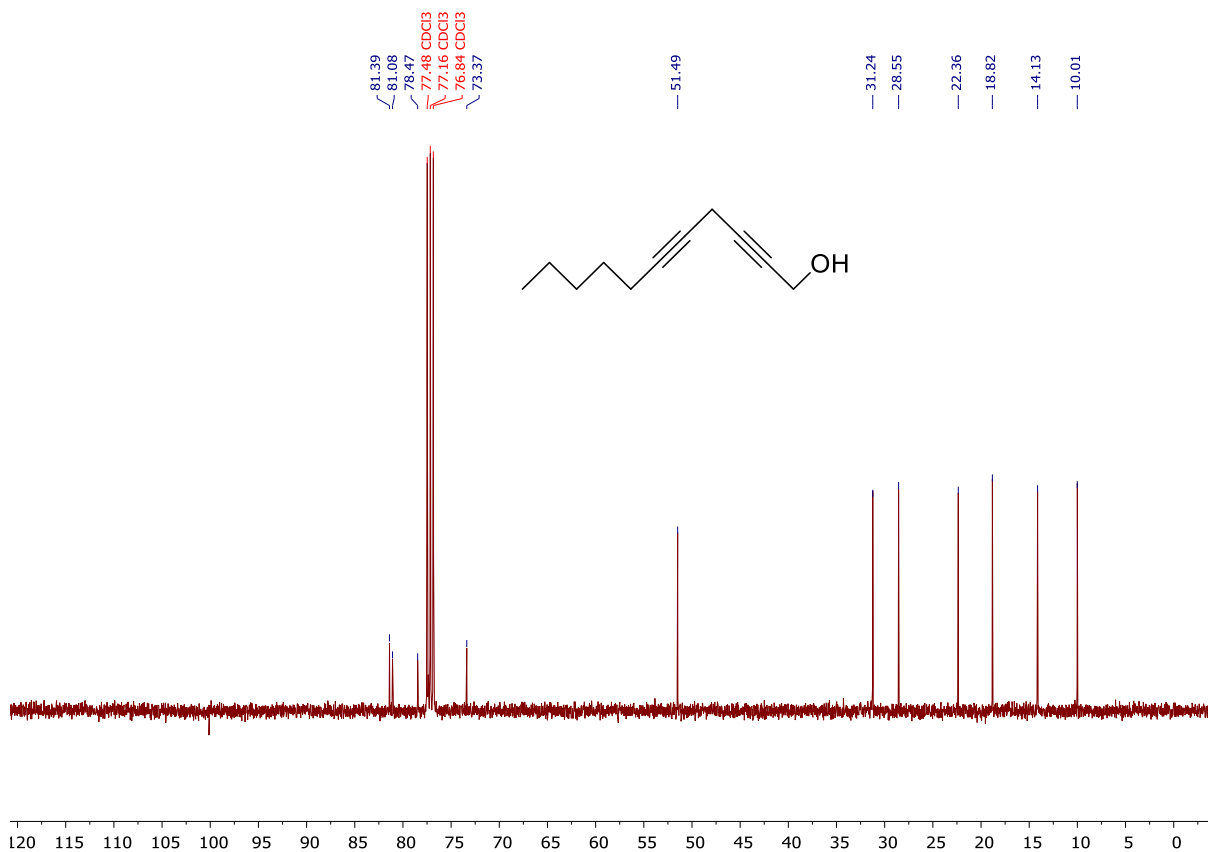
^{13}C - ^1H HSQC spectrum of compound **18**



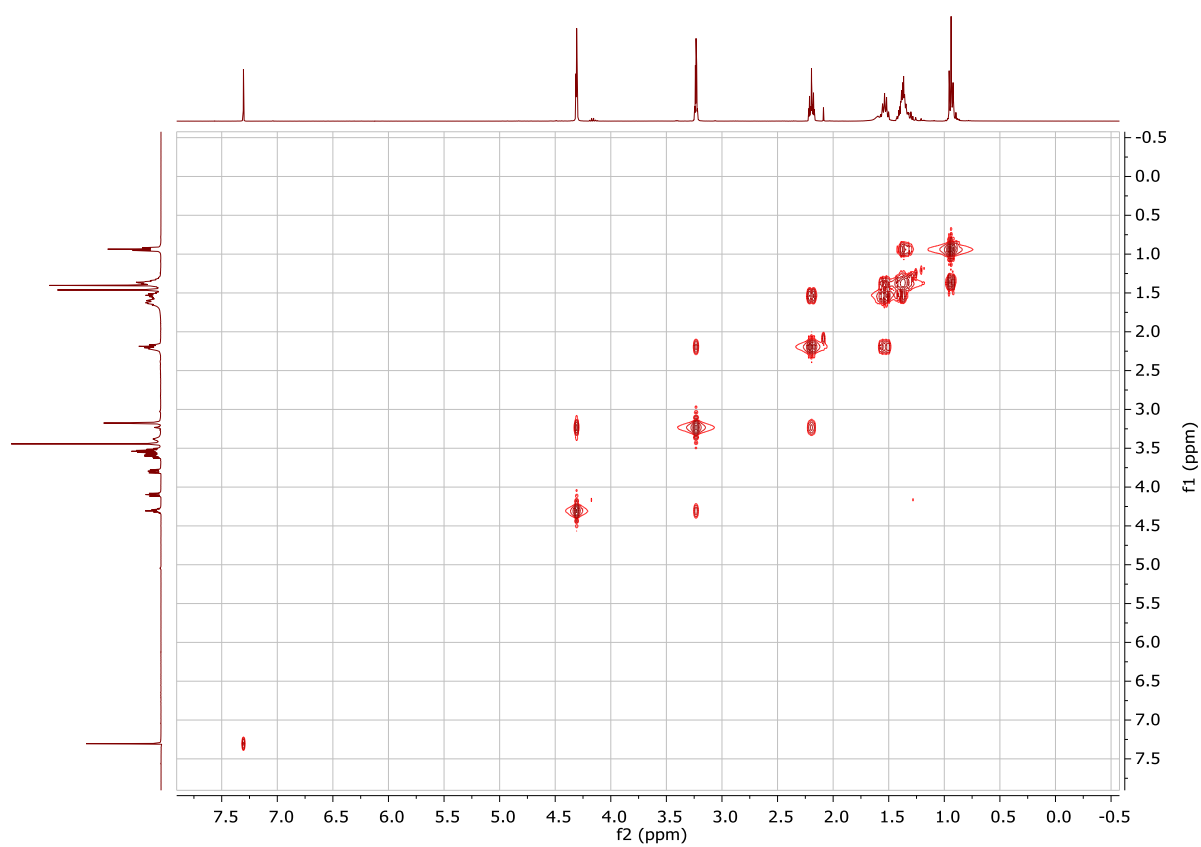
^1H NMR (400 MHz, CDCl_3) of compound **19**



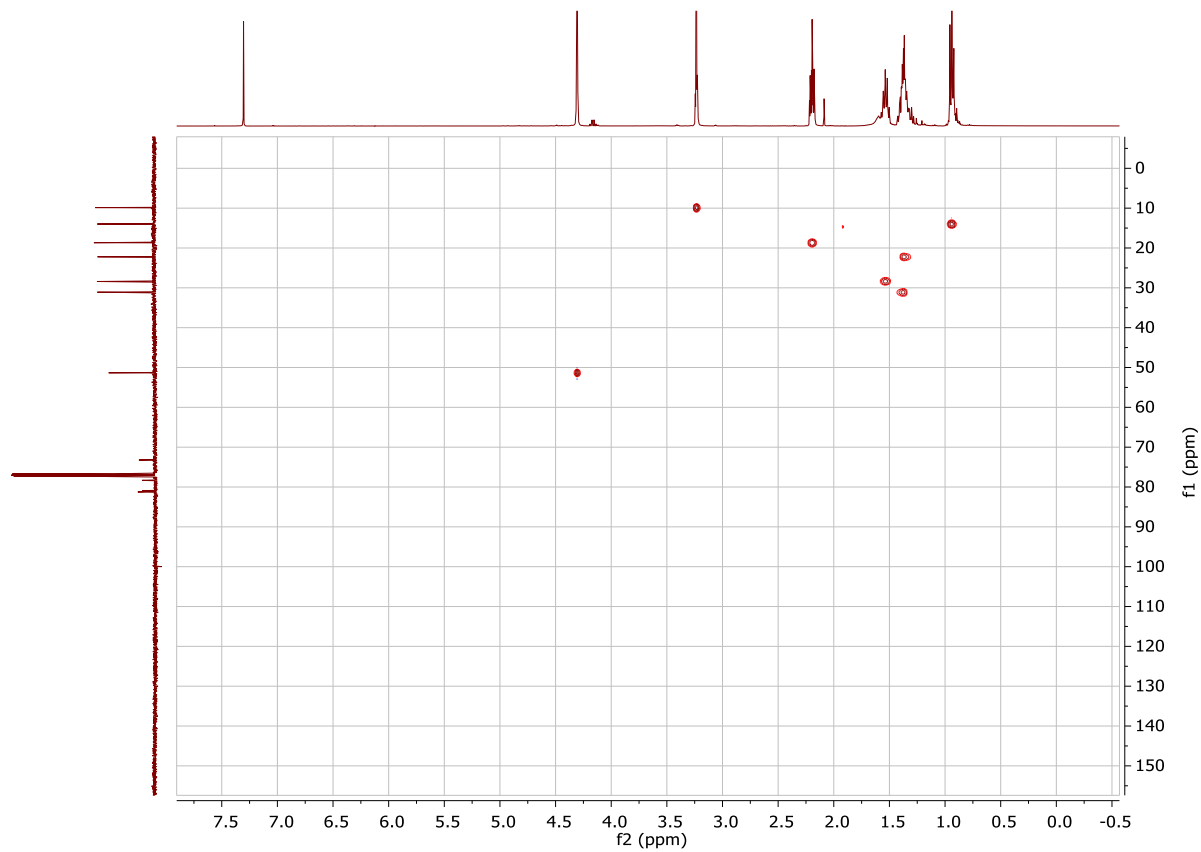
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **19**



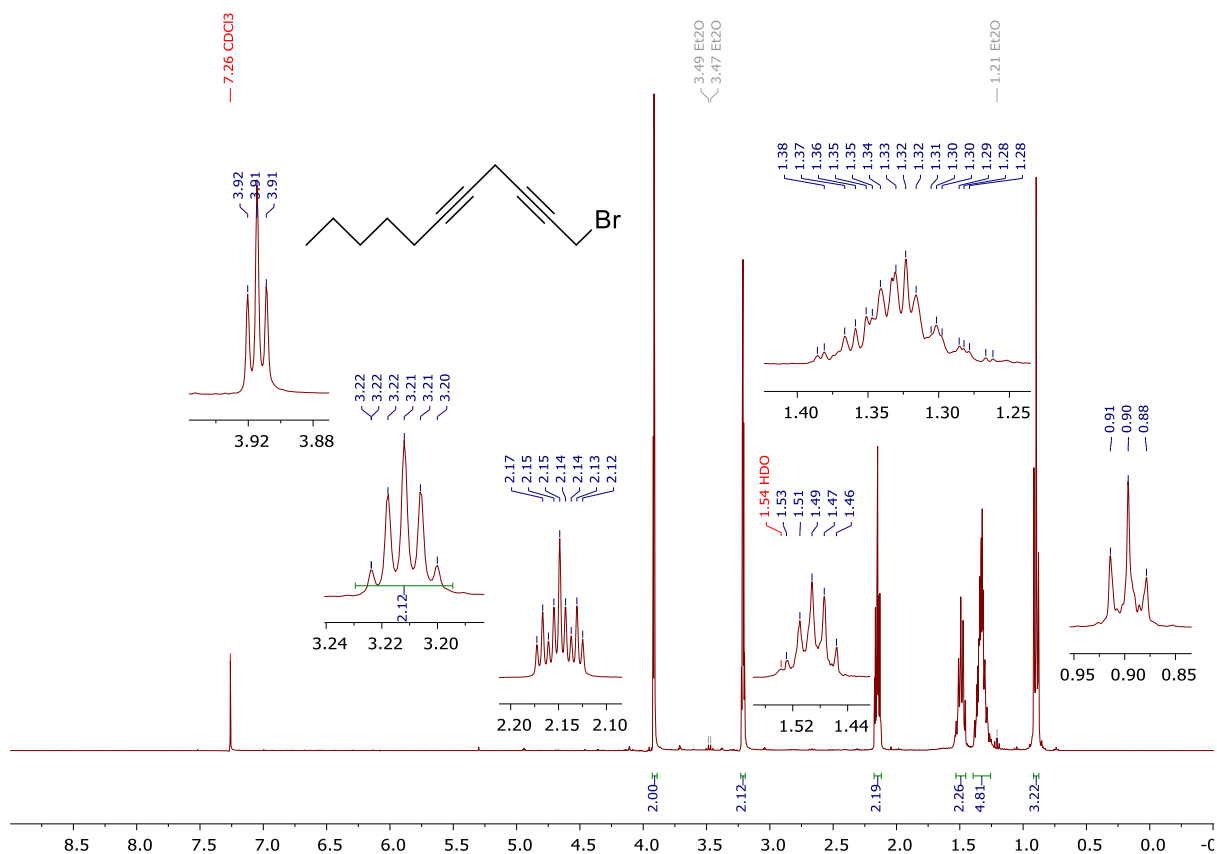
^1H - ^1H COSY spectrum of compound **19**



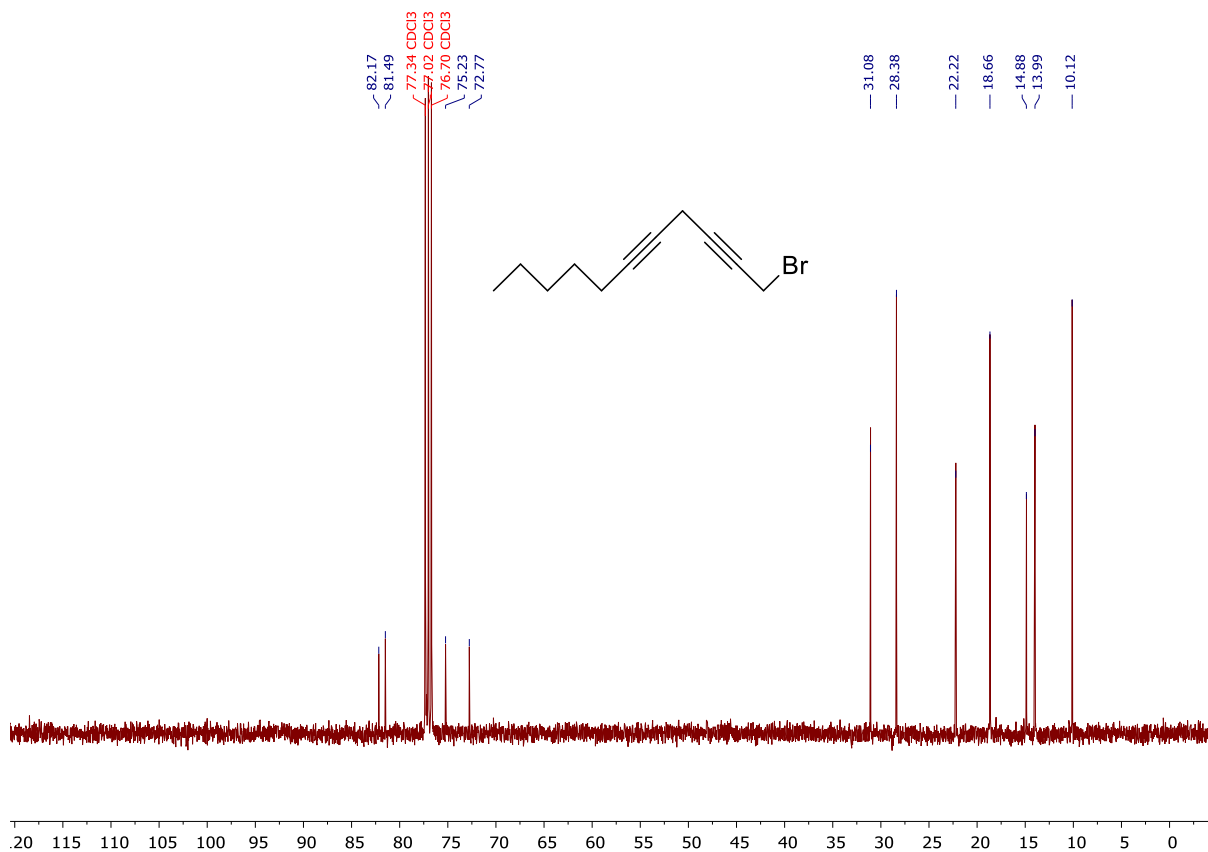
^{13}C - ^1H HSQC spectrum of compound **19**



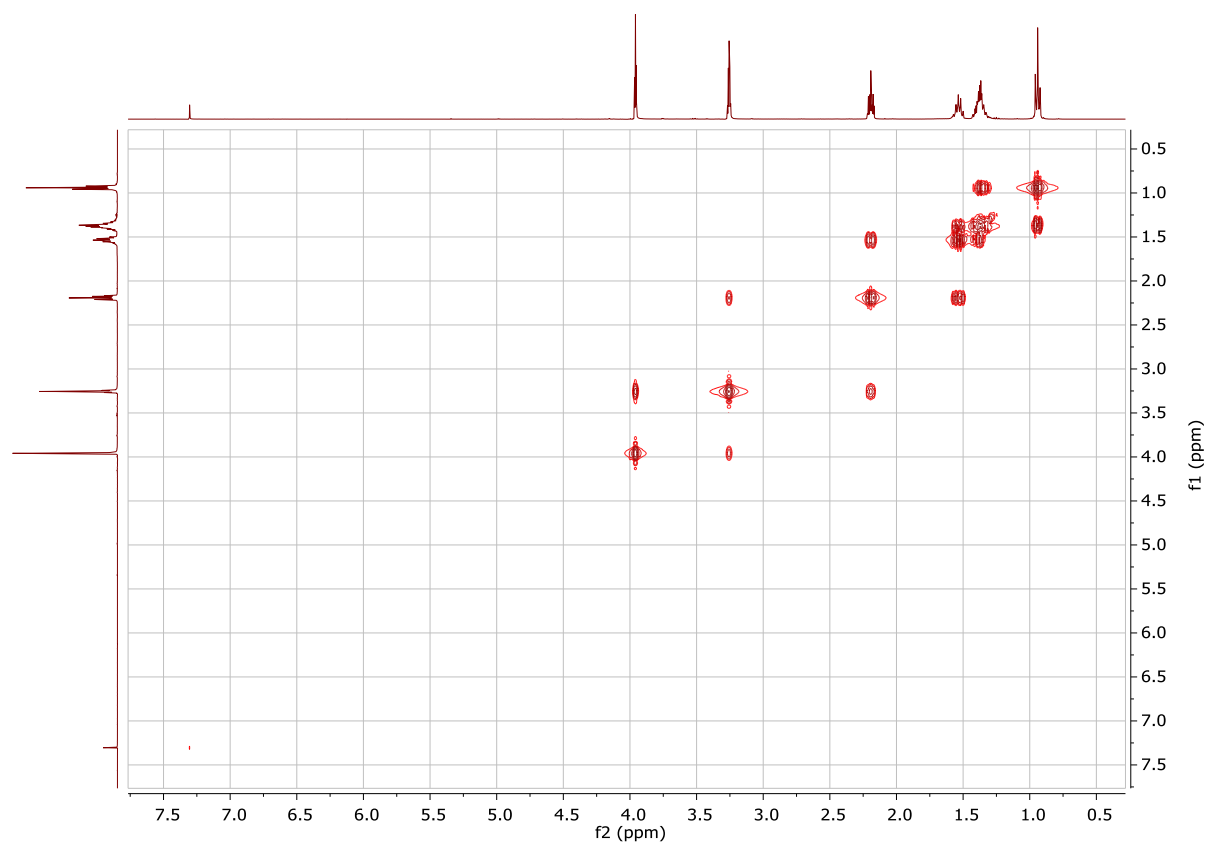
^1H NMR (400 MHz, CDCl_3) of compound **20**



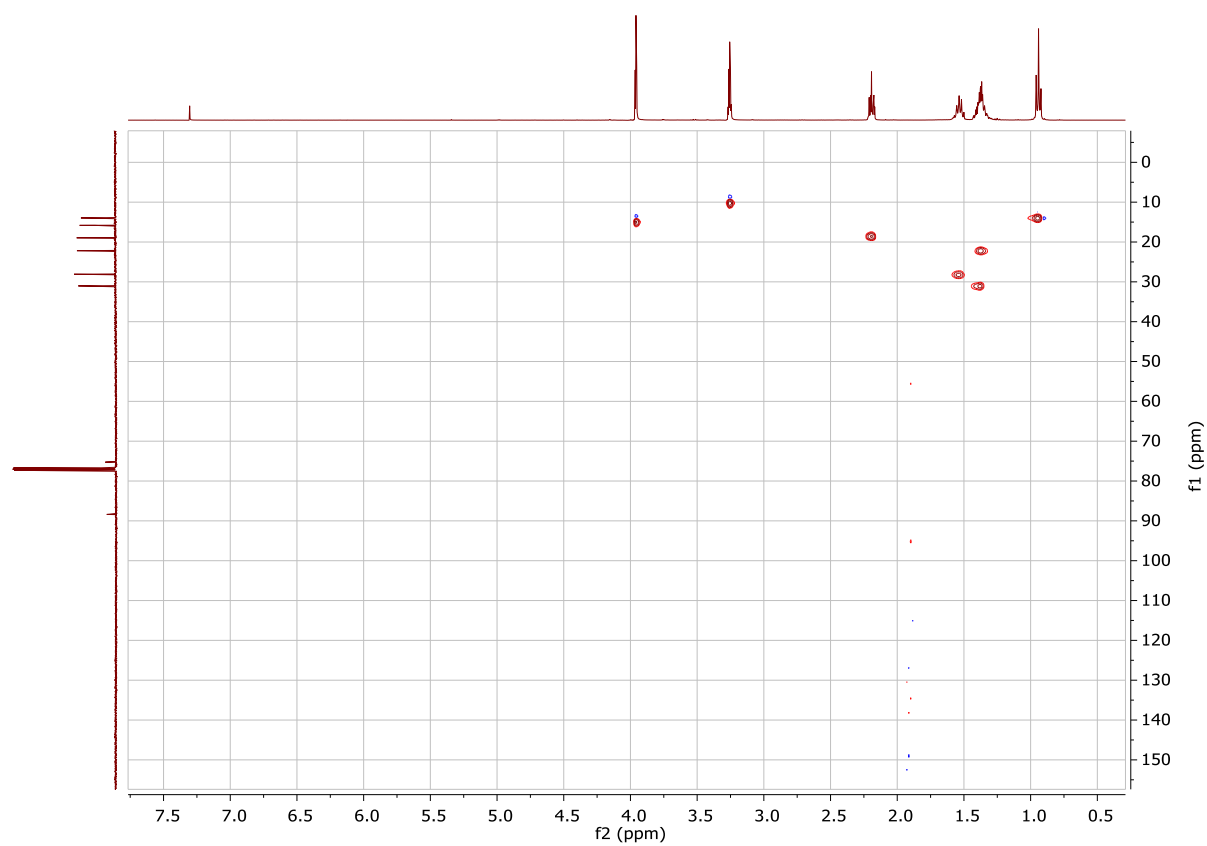
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **20**



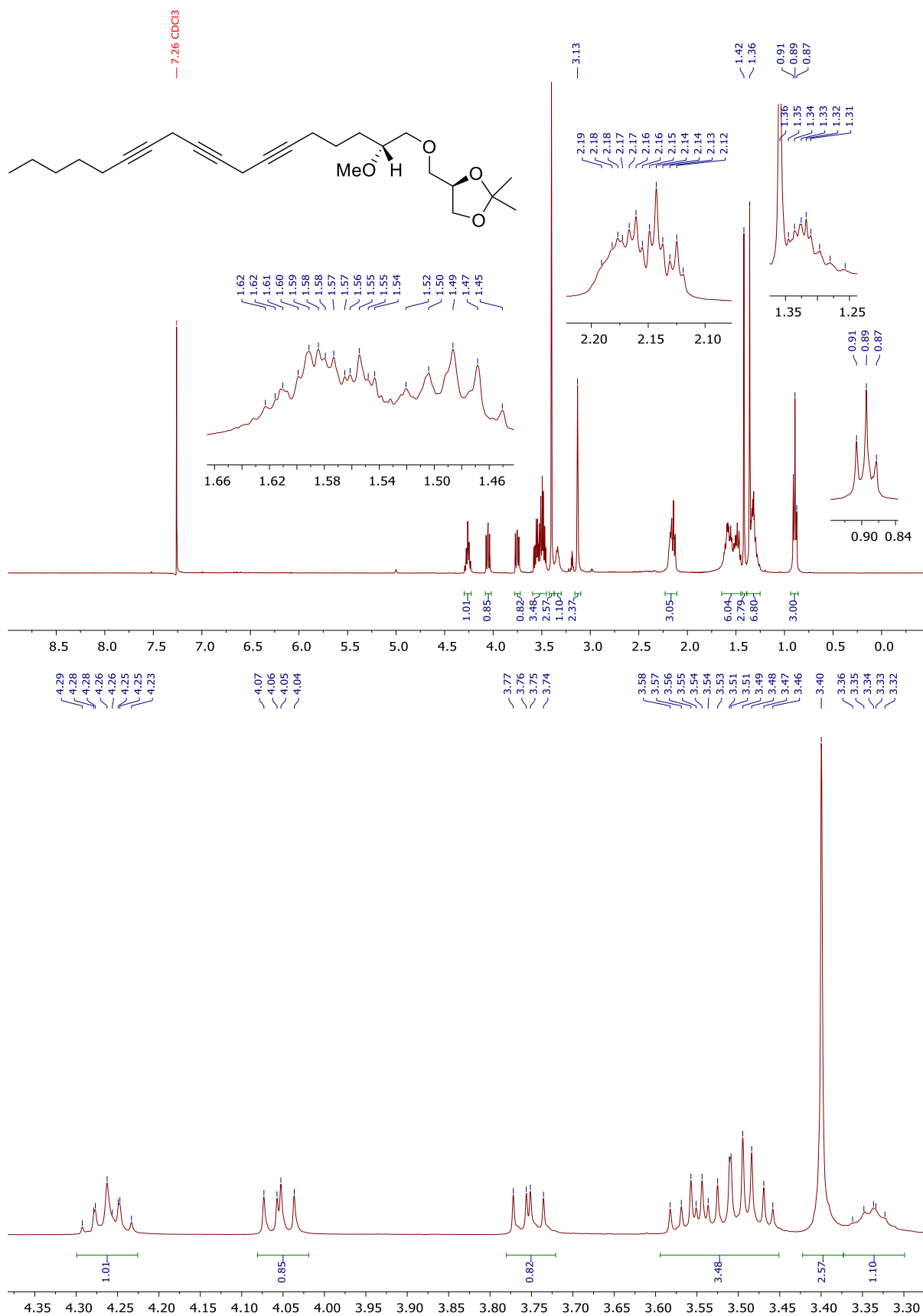
^1H - ^1H COSY spectrum of compound **20**



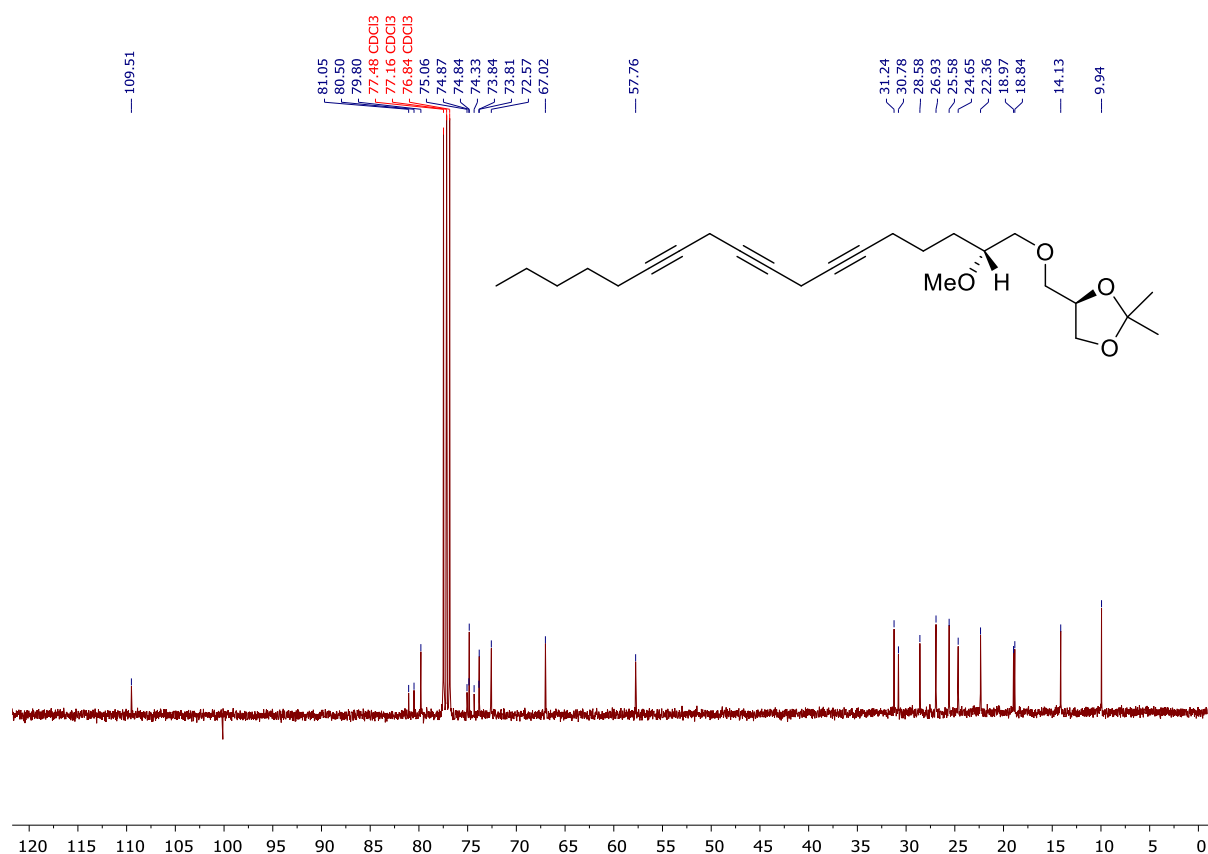
^{13}C - ^1H HSQC spectrum of compound **20**



^1H NMR (400 MHz, CDCl_3) of compound **21**

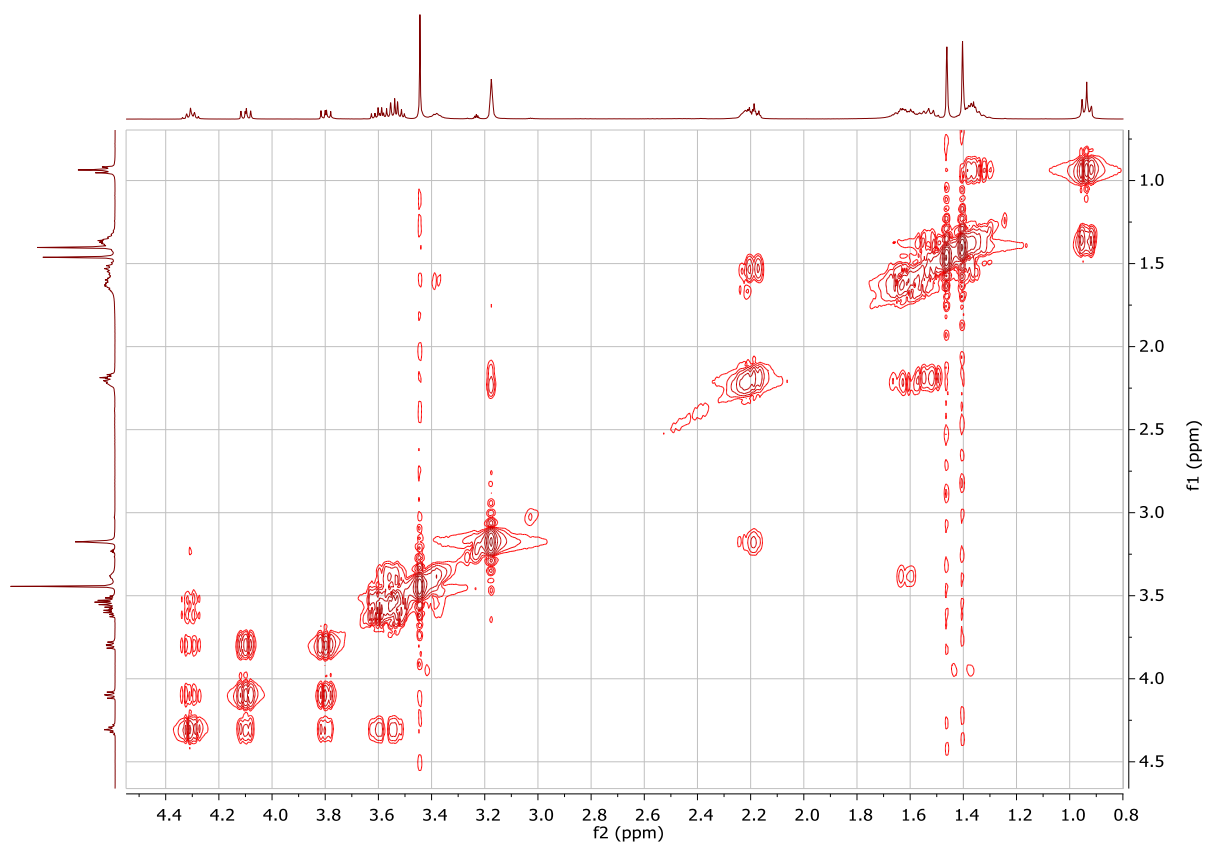


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **21**

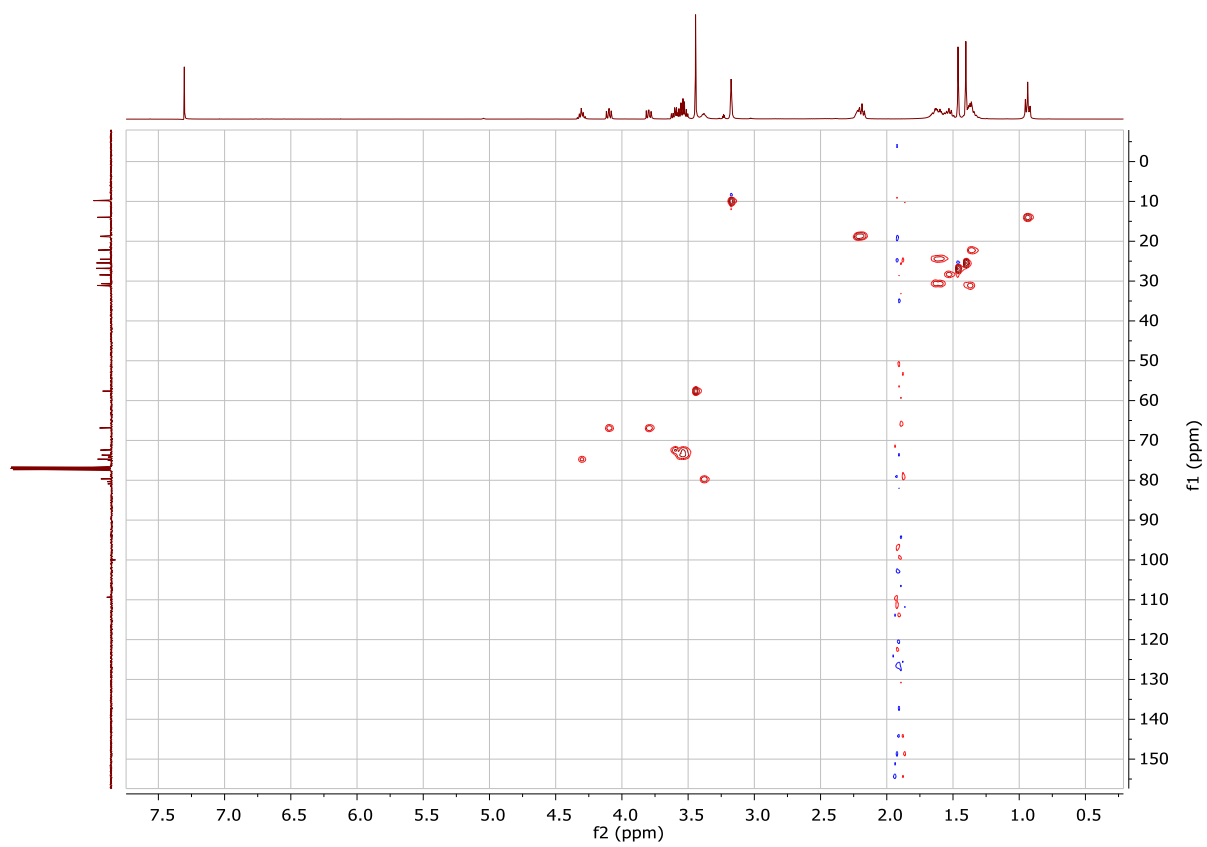


^1H - ^1H COSY spectrum of compound **21**

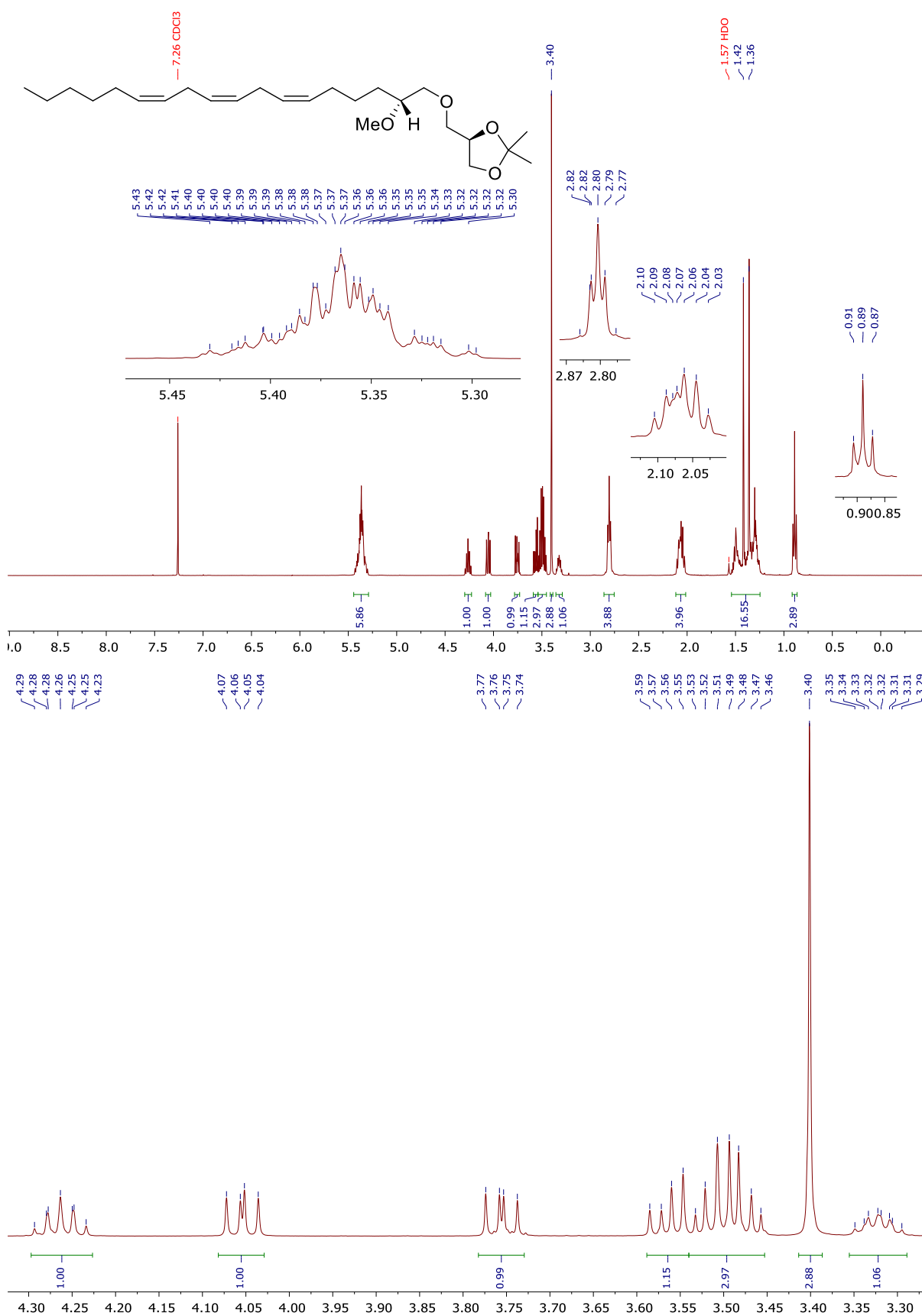




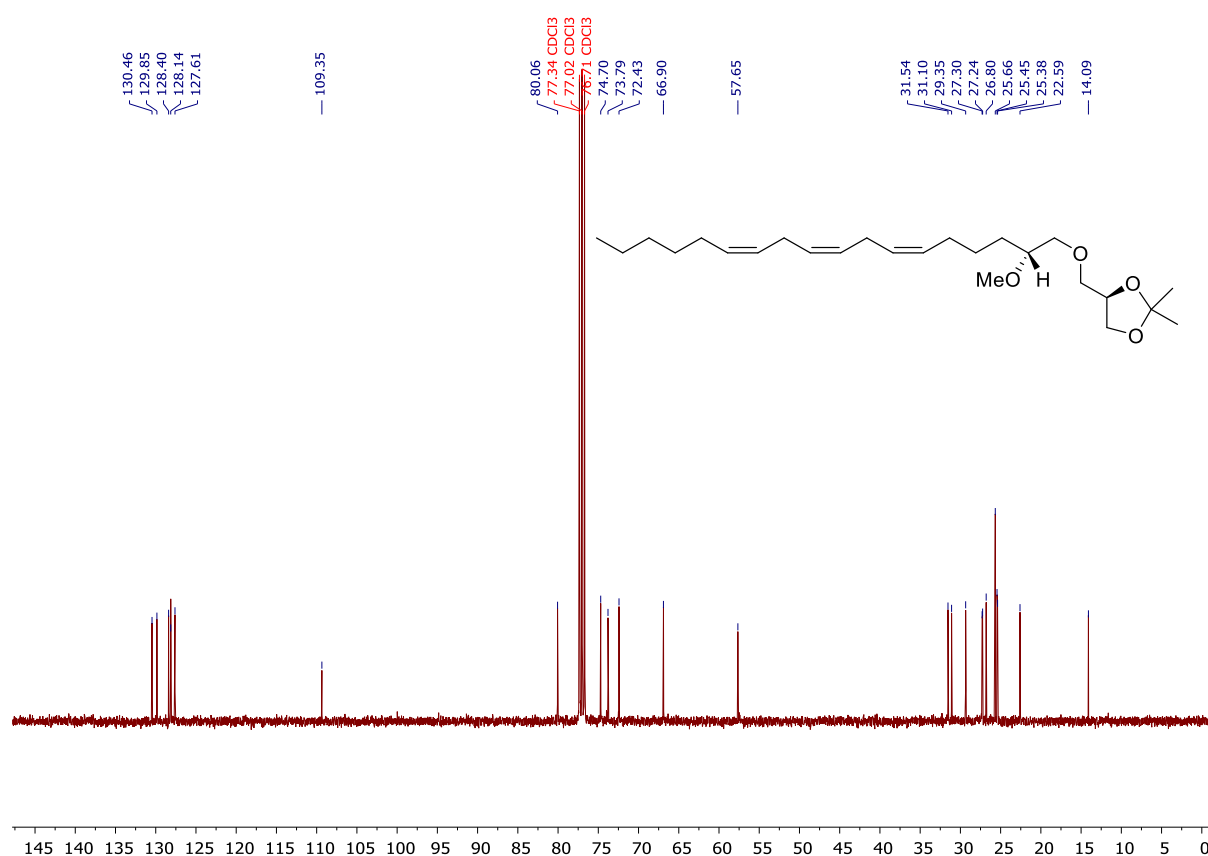
^{13}C - ^1H HSQC spectrum of compound **21**



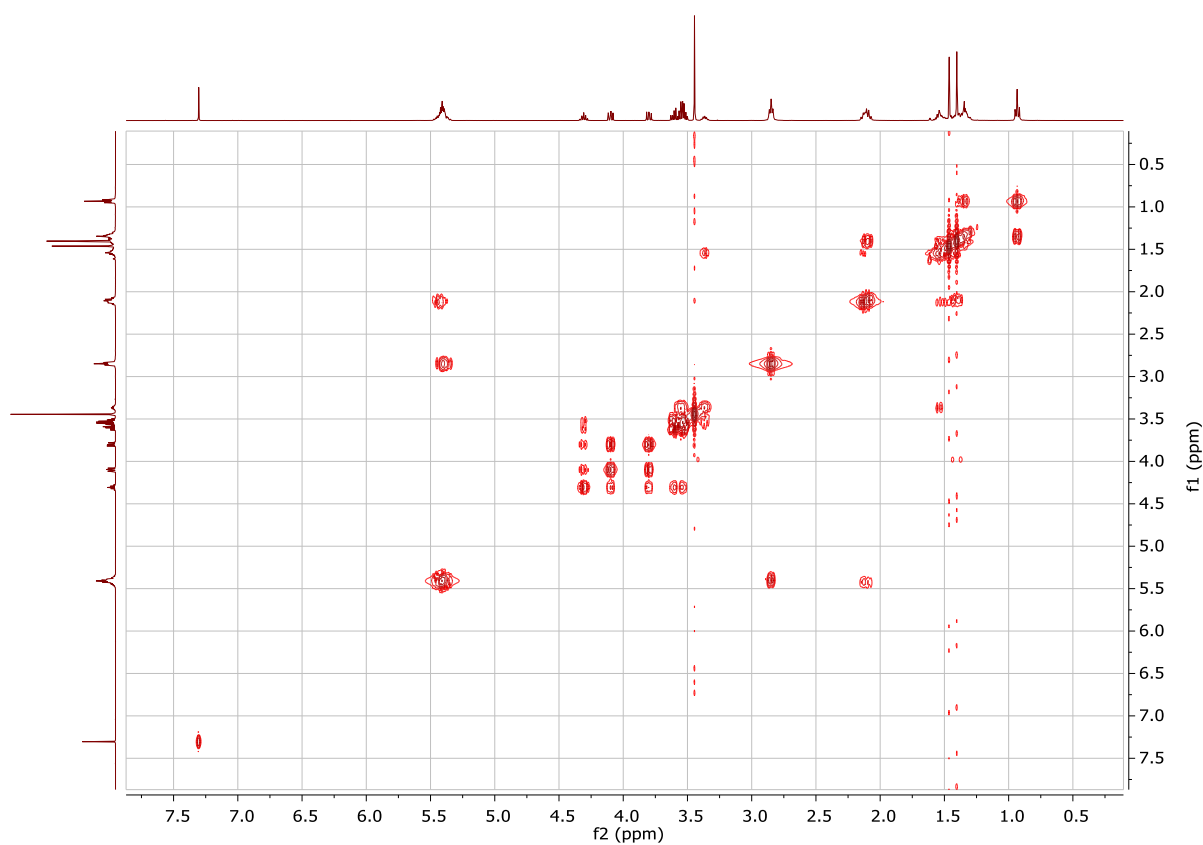
^1H NMR (400 MHz, CDCl_3) of compound **22**

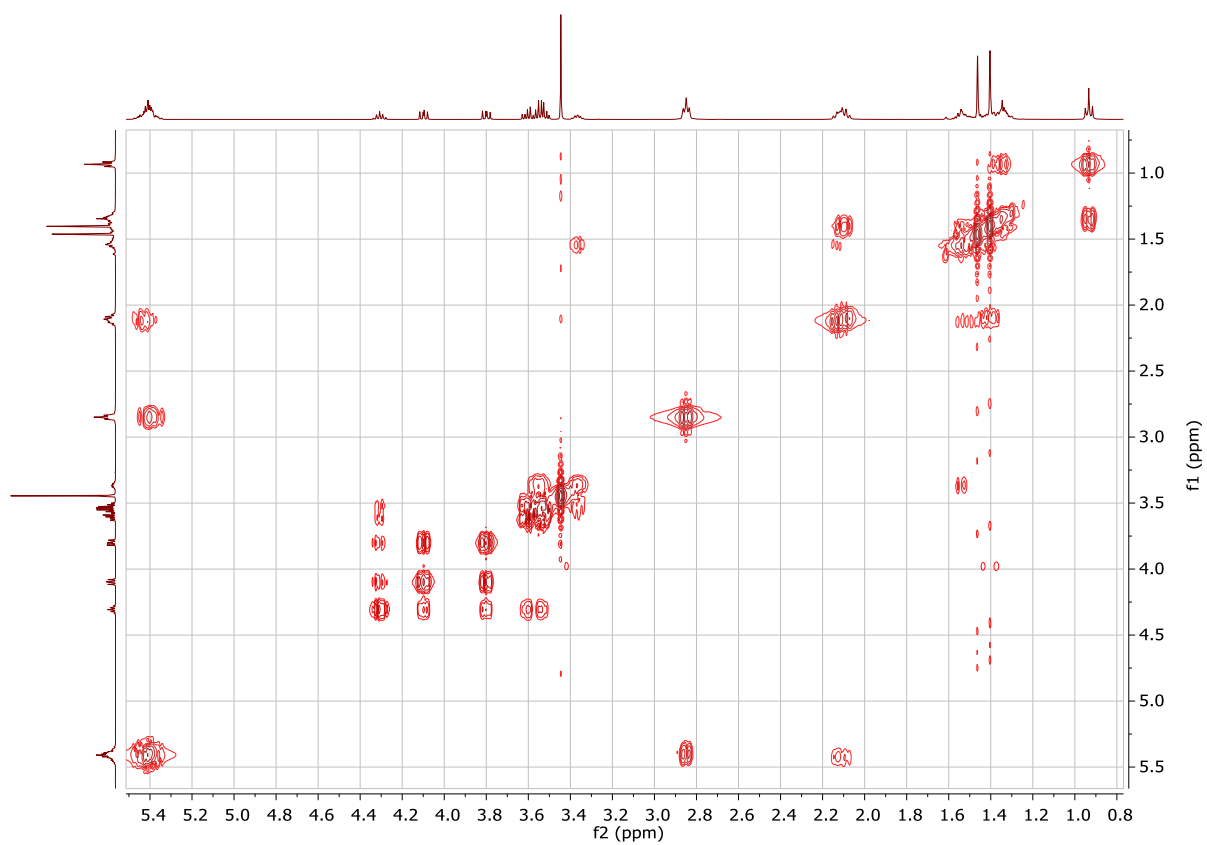


$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **22**

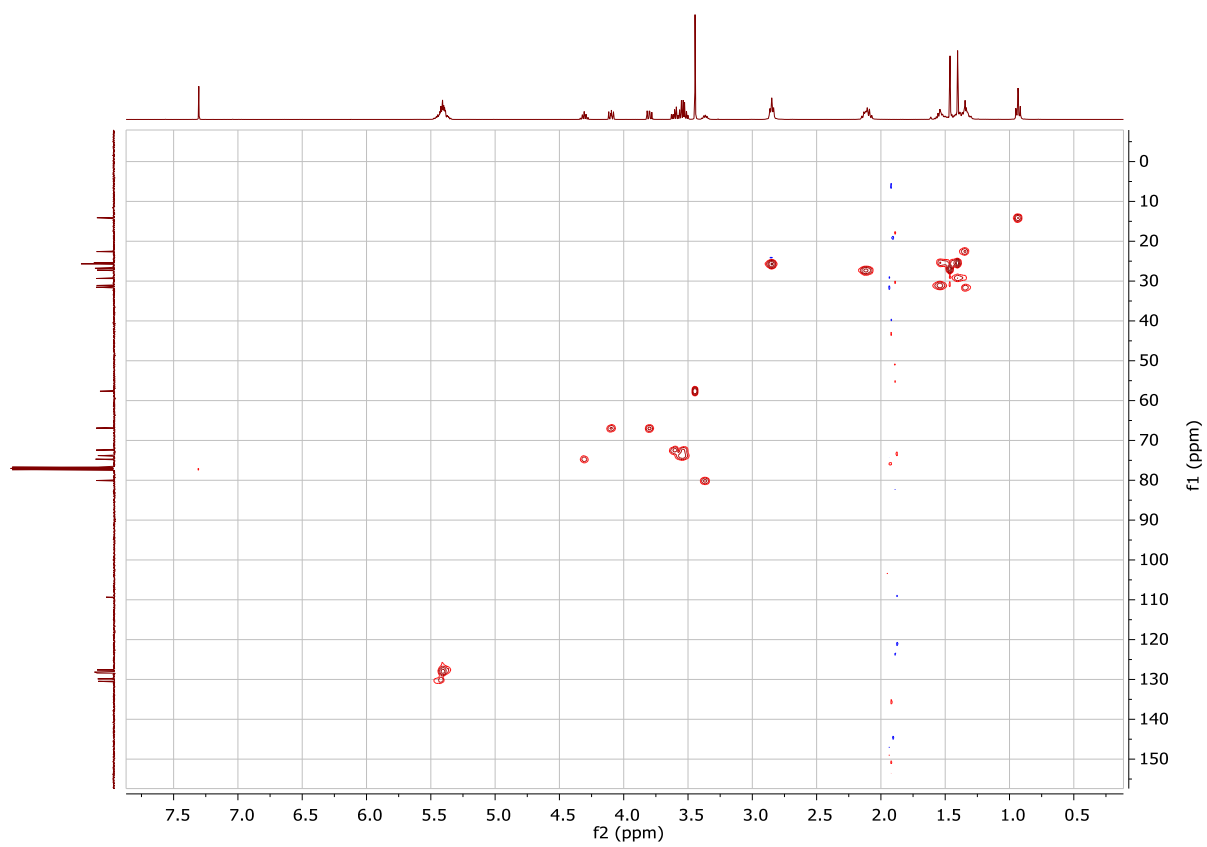


^1H - ^1H COSY spectrum of compound **22**

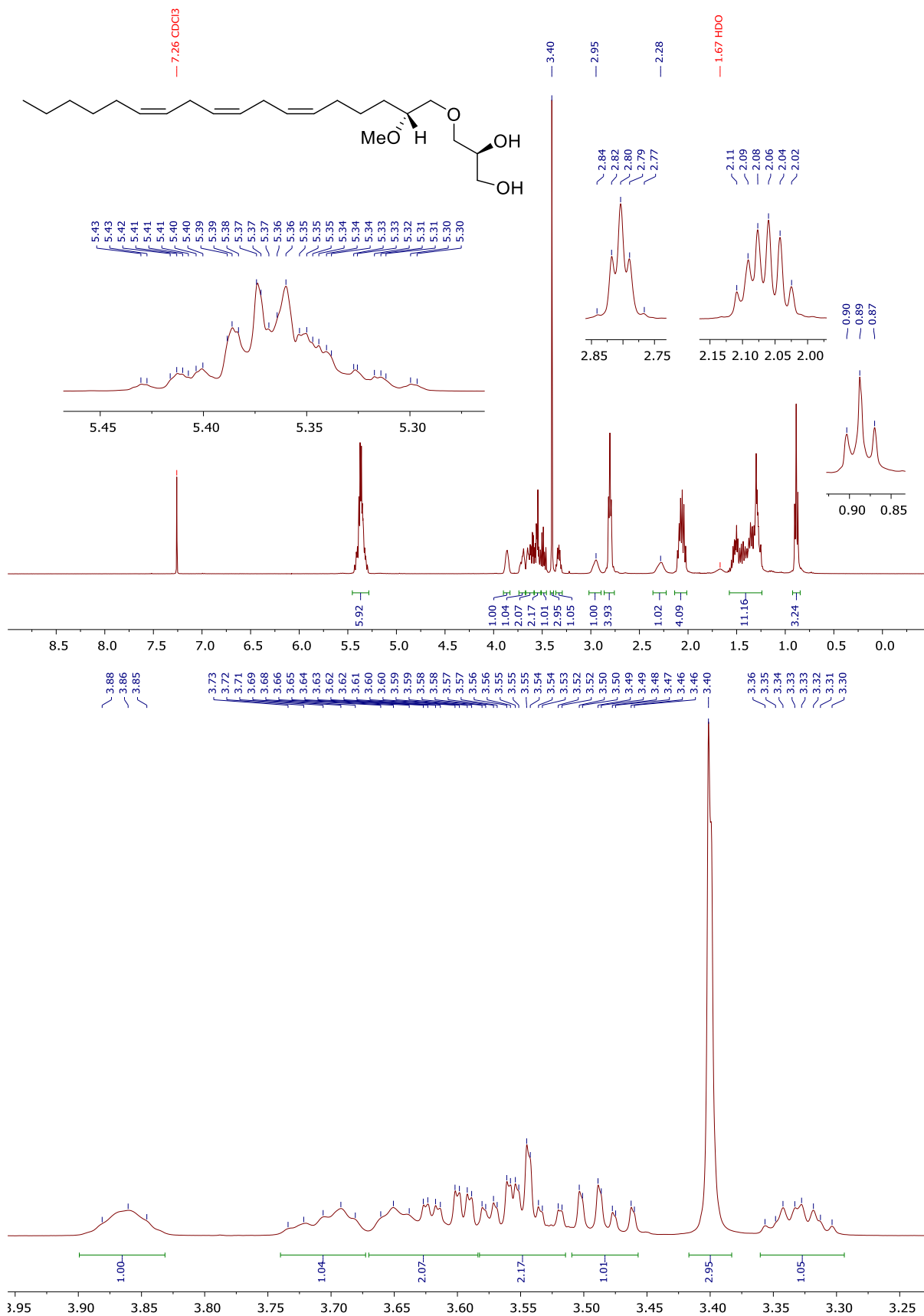




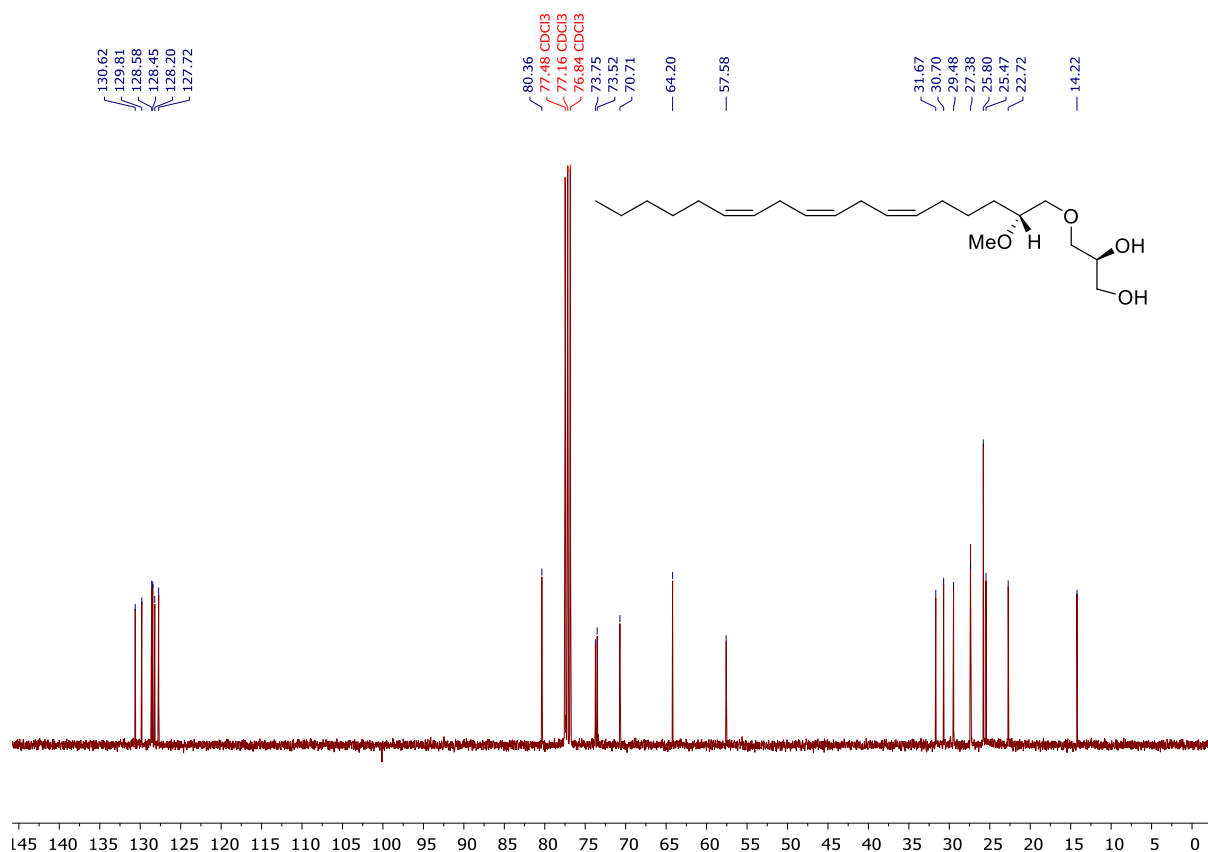
^{13}C - ^1H HSQC spectrum of compound **22**



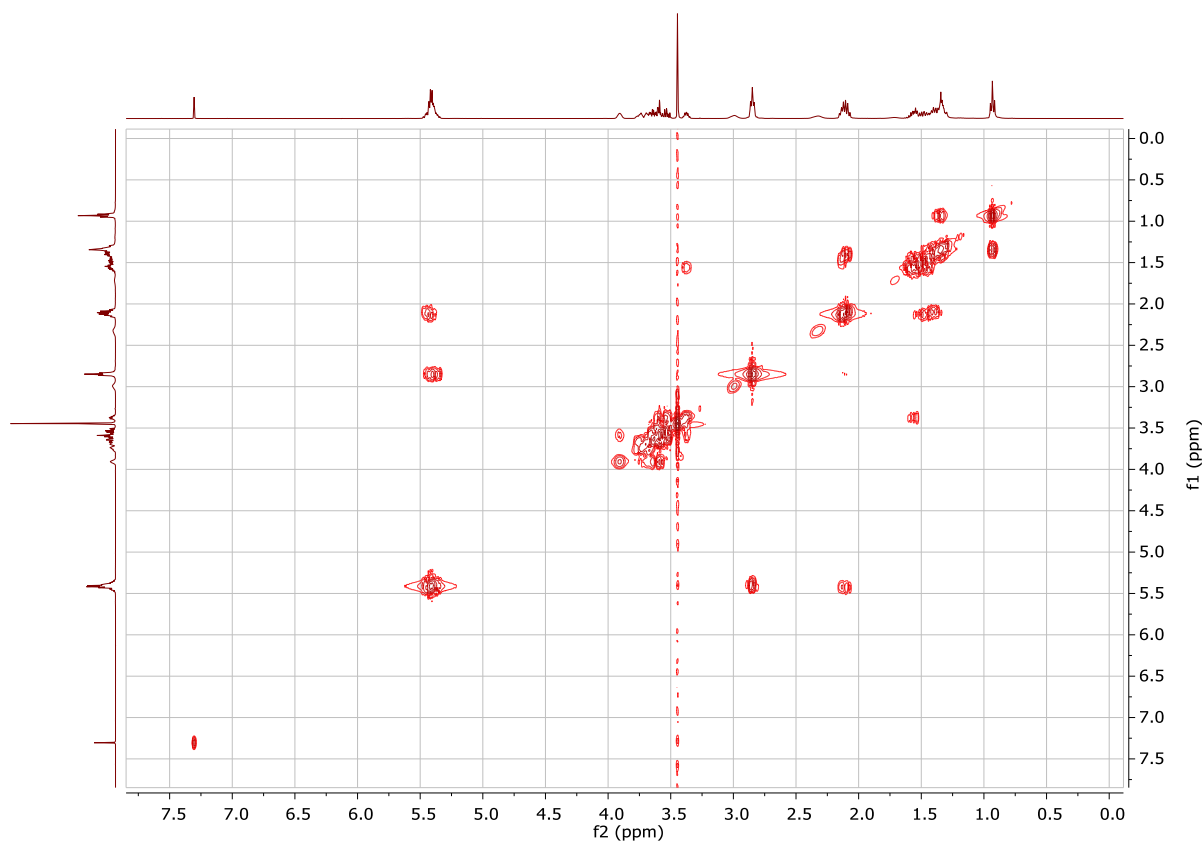
^1H NMR (400 MHz, CDCl_3) of MEL **6**



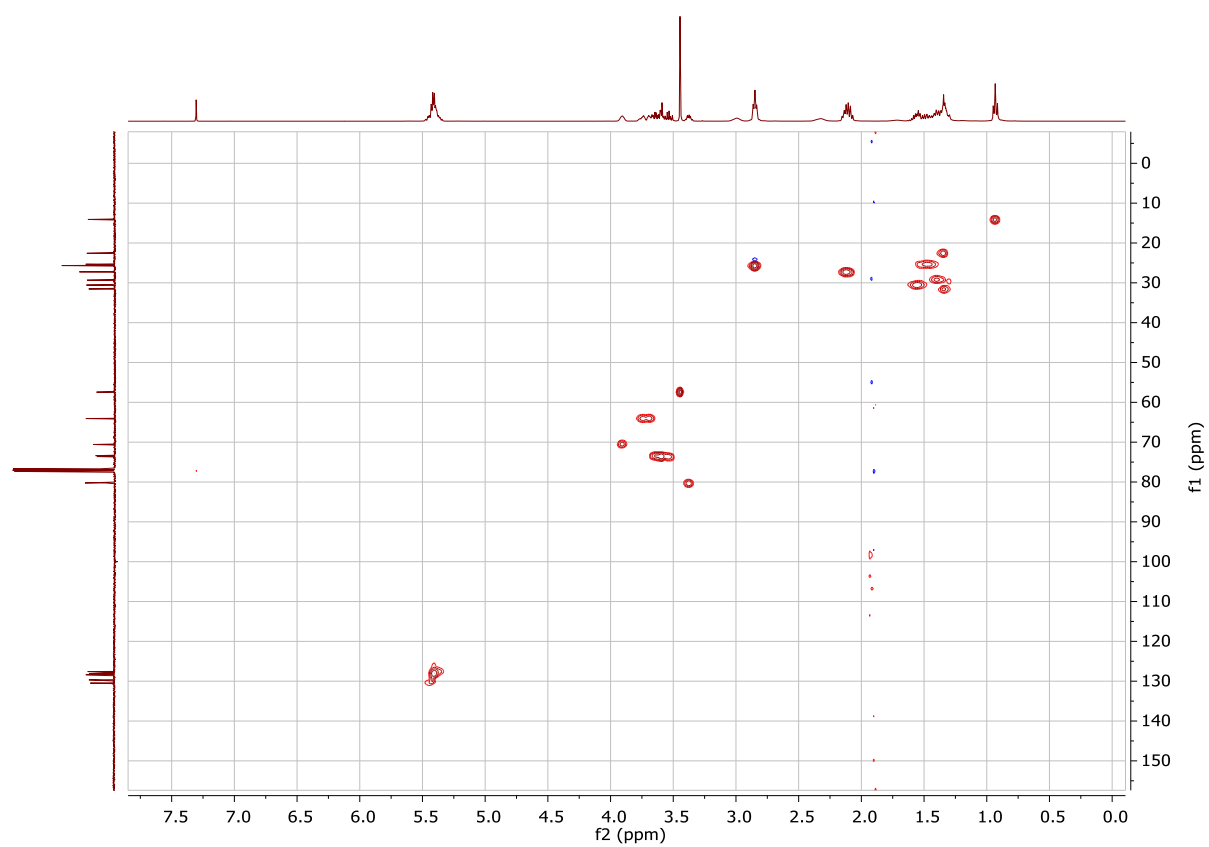
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of MEL 6



^1H - ^1H COSY spectrum of MEL 6



^{13}C - ^1H HSQC spectrum of MEL 6



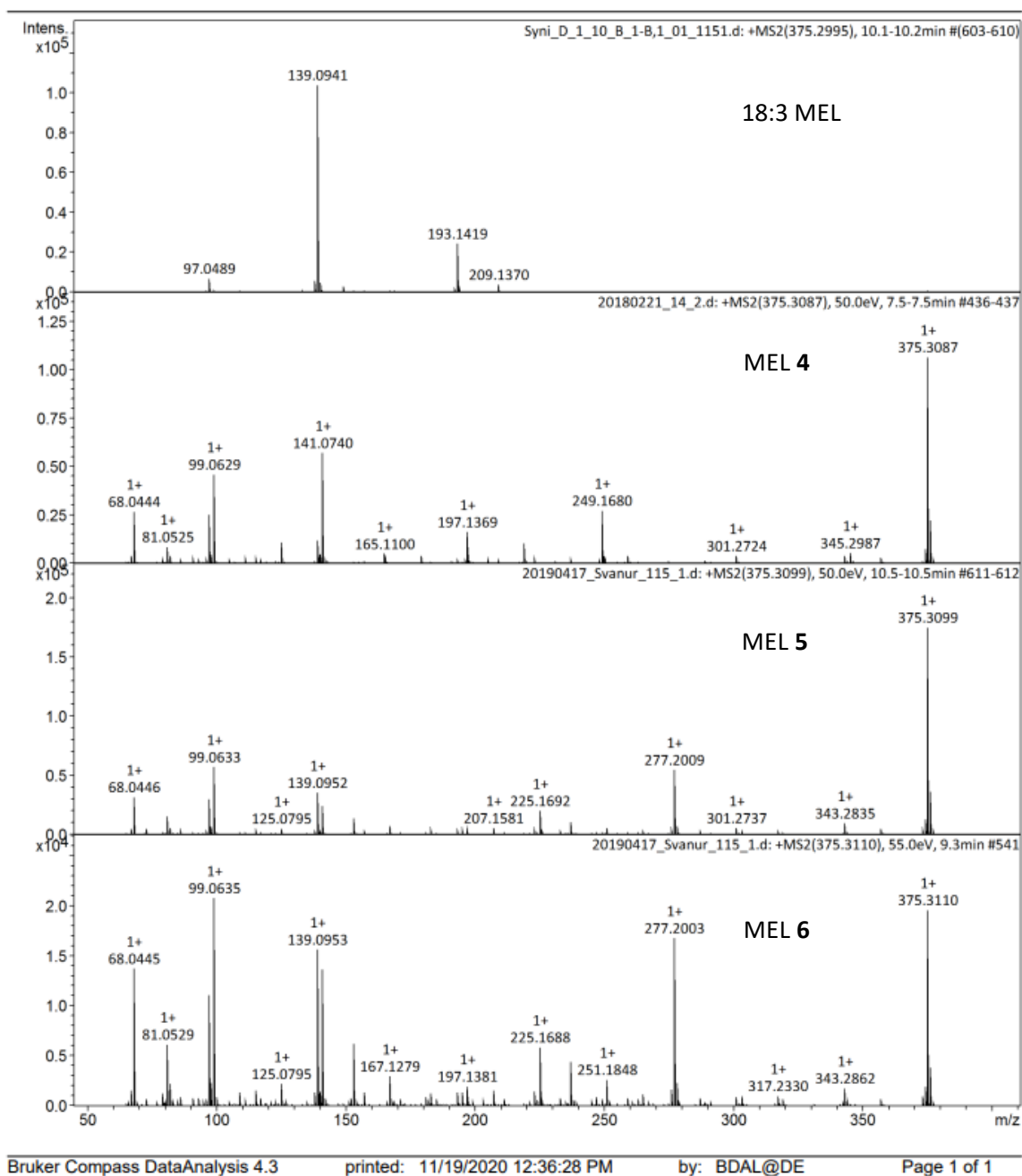


Figure S1. Comparison of the $[M+Li]^+$ MS/MS fragmentation spectra of the synthesized MELs **4**, **5**, **6** and the 18:3 MEL found in the shark and dogfish liver oil sample (top).