

Supporting Information

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

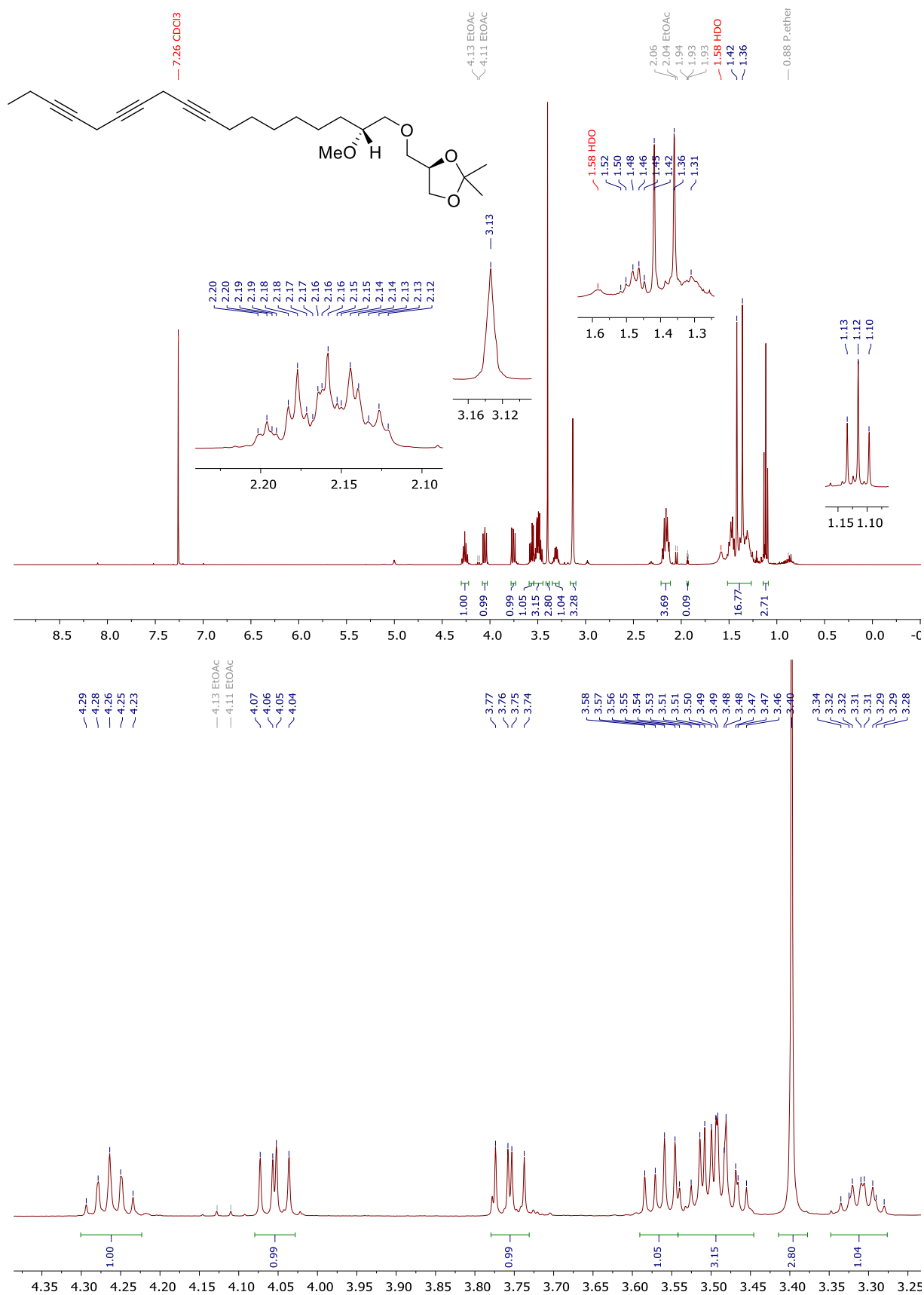
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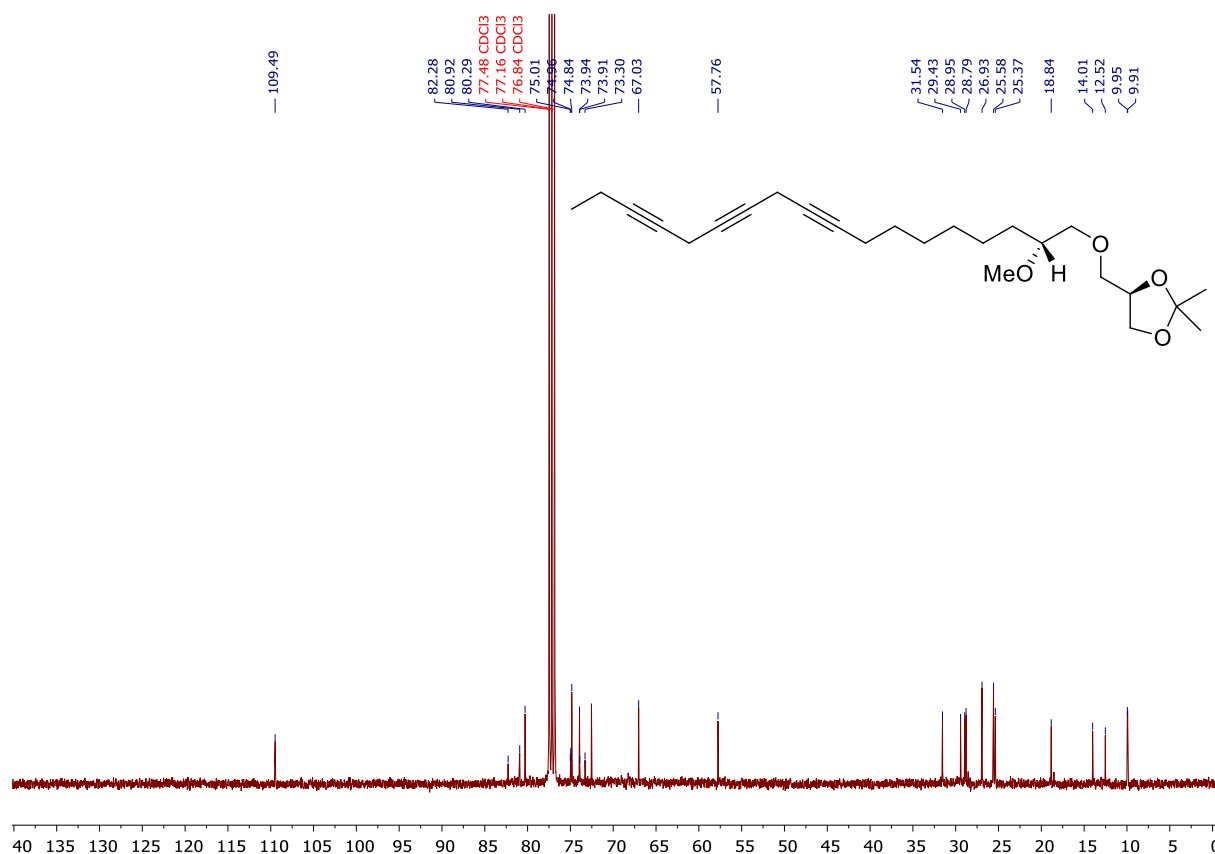
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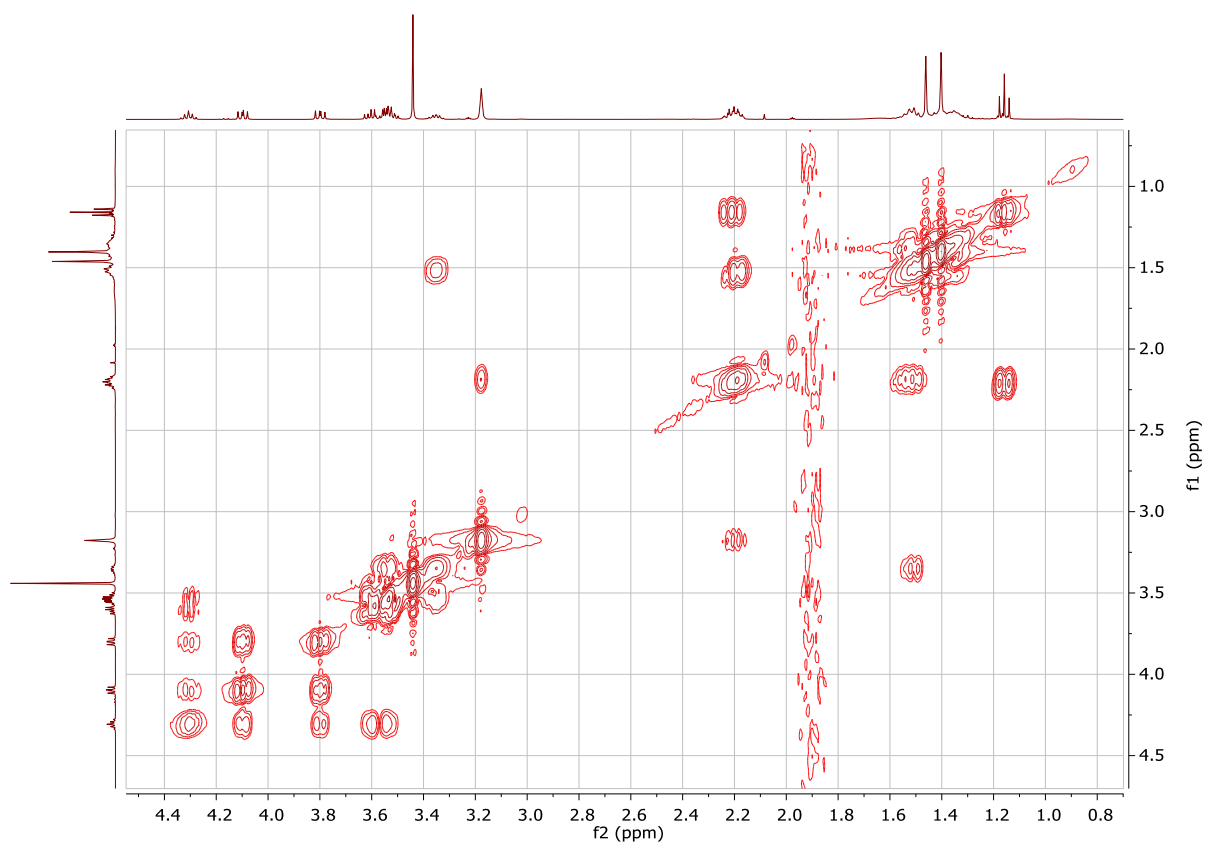
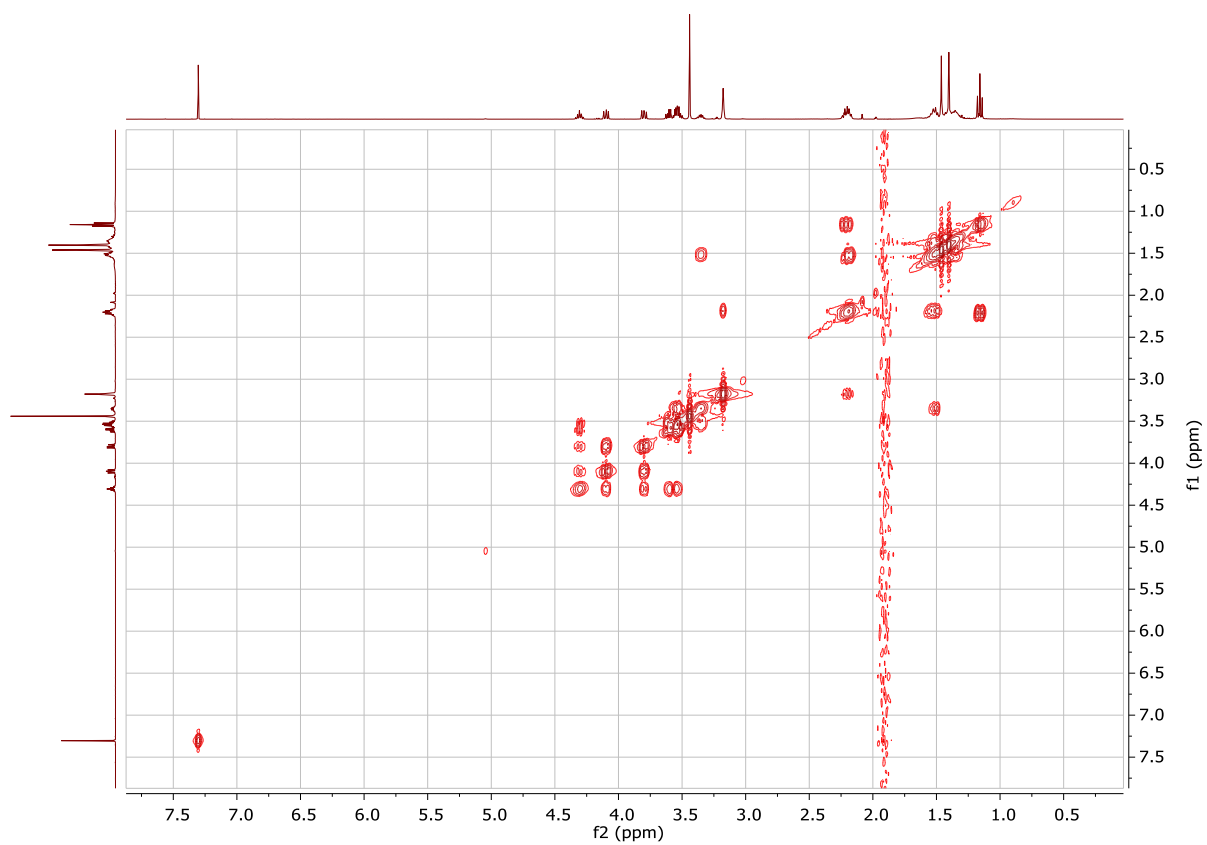
^1H NMR (400 MHz, CDCl_3) of compound **12**



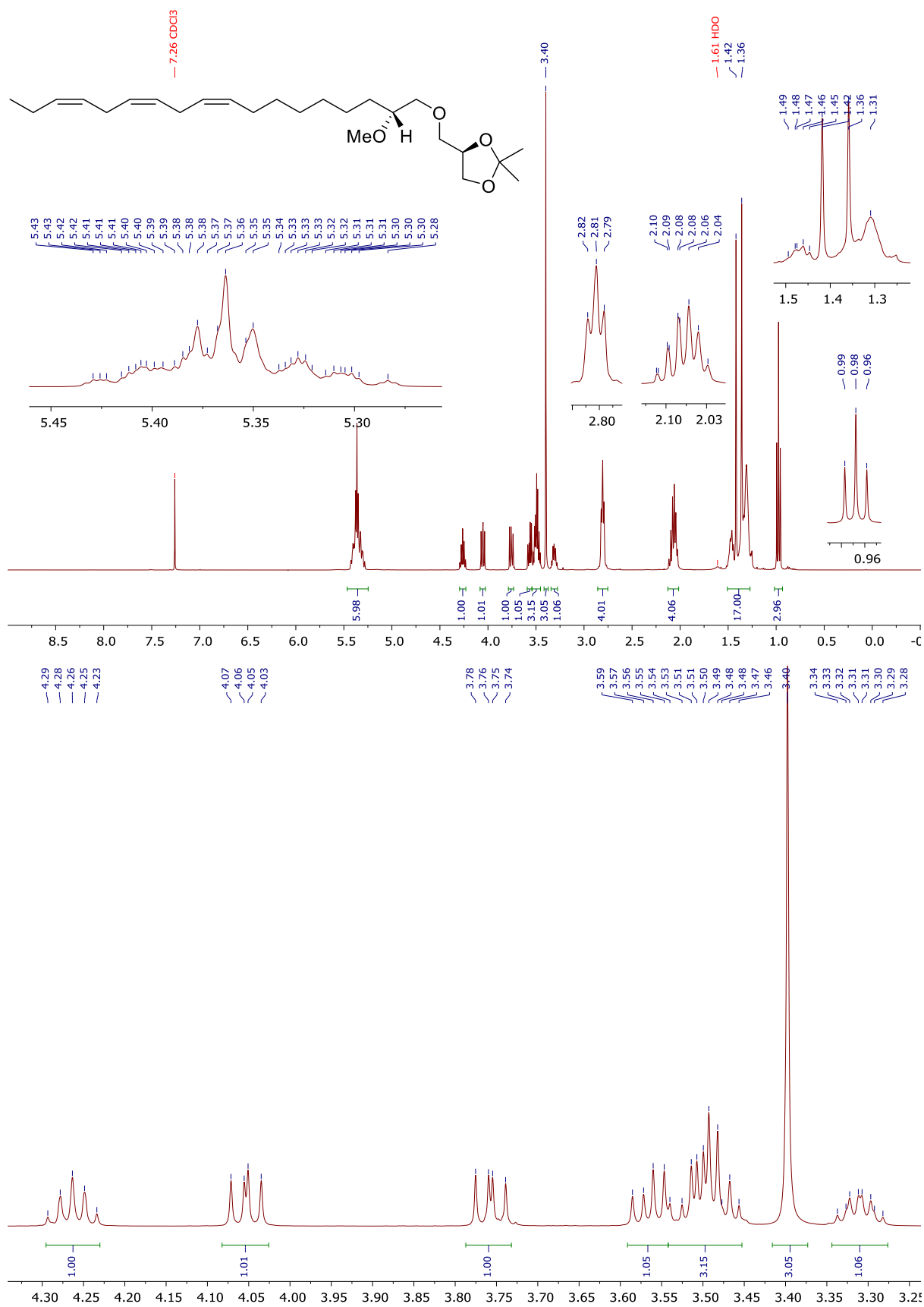
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **12**



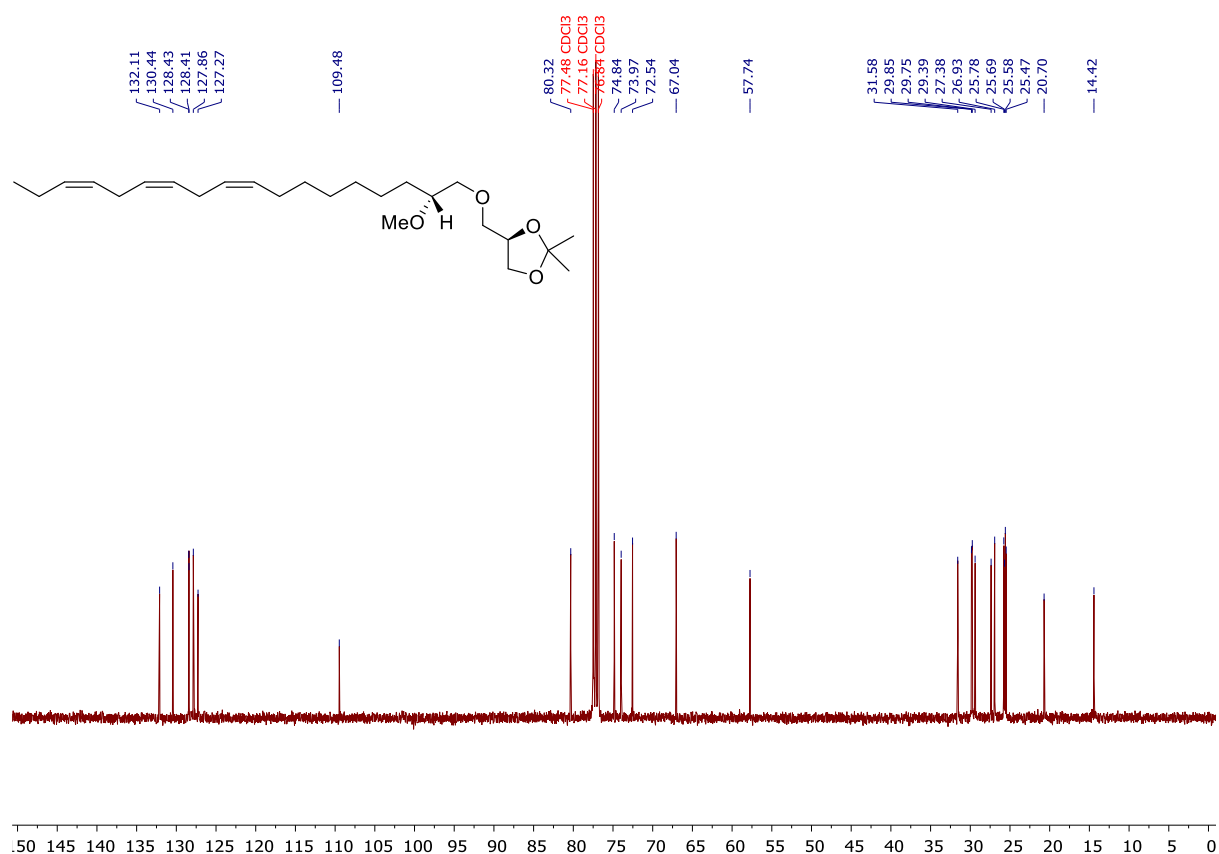
^1H - ^1H COSY spectrum of compound **12**



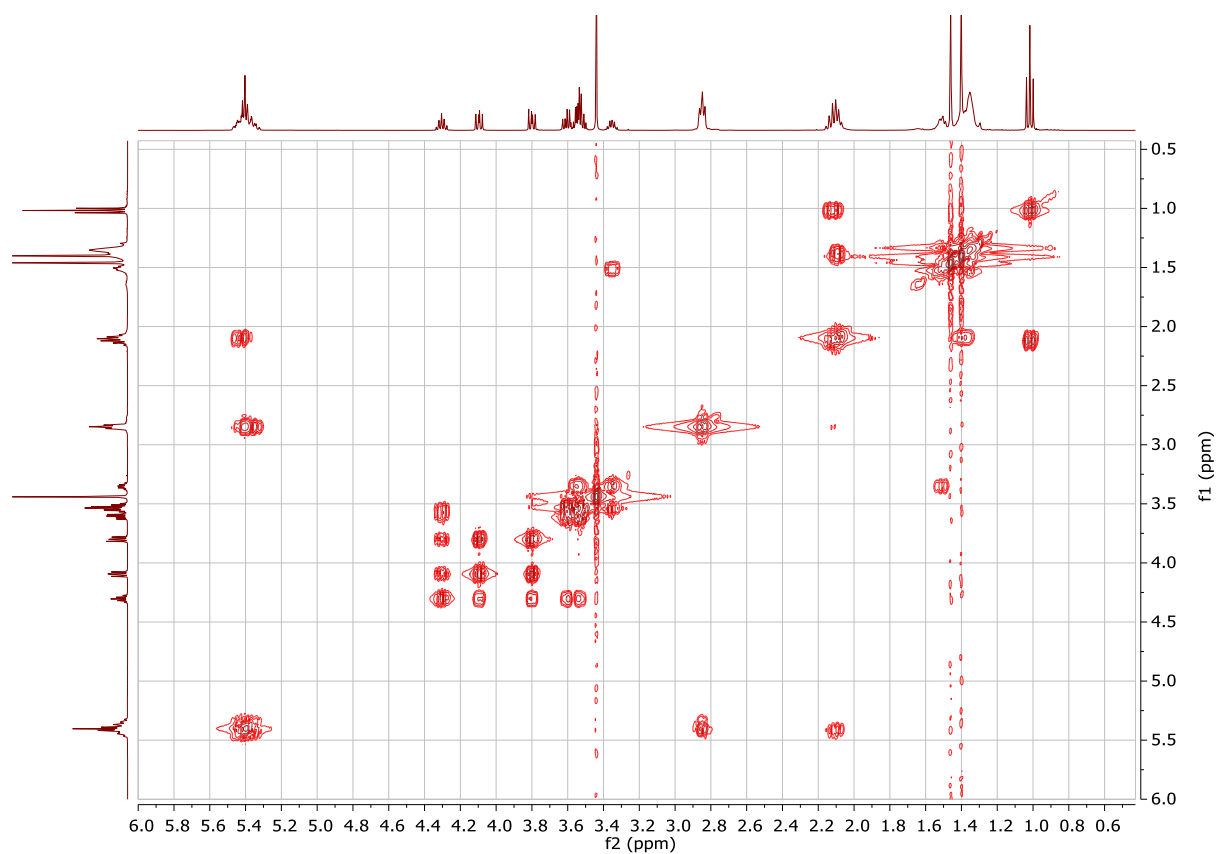
^1H NMR (400 MHz, CDCl_3) of compound **13**



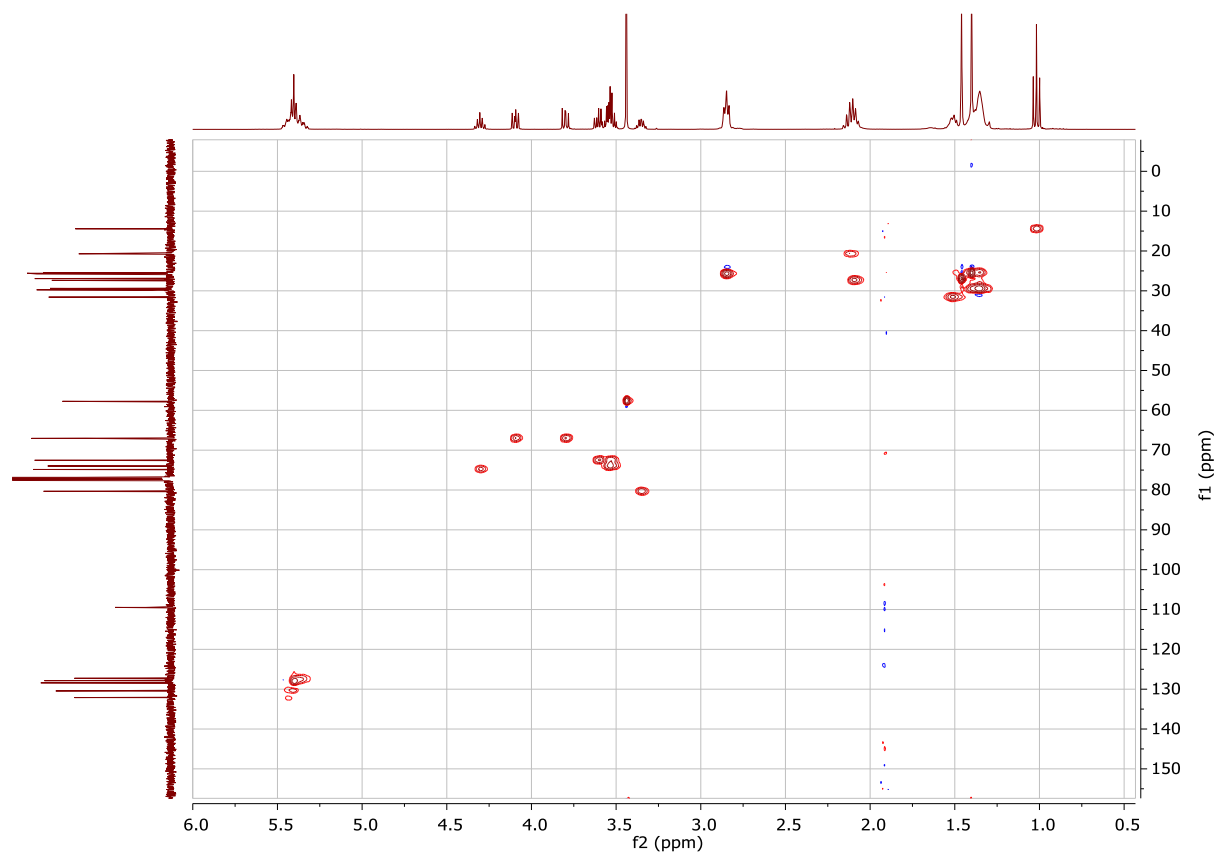
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **13**



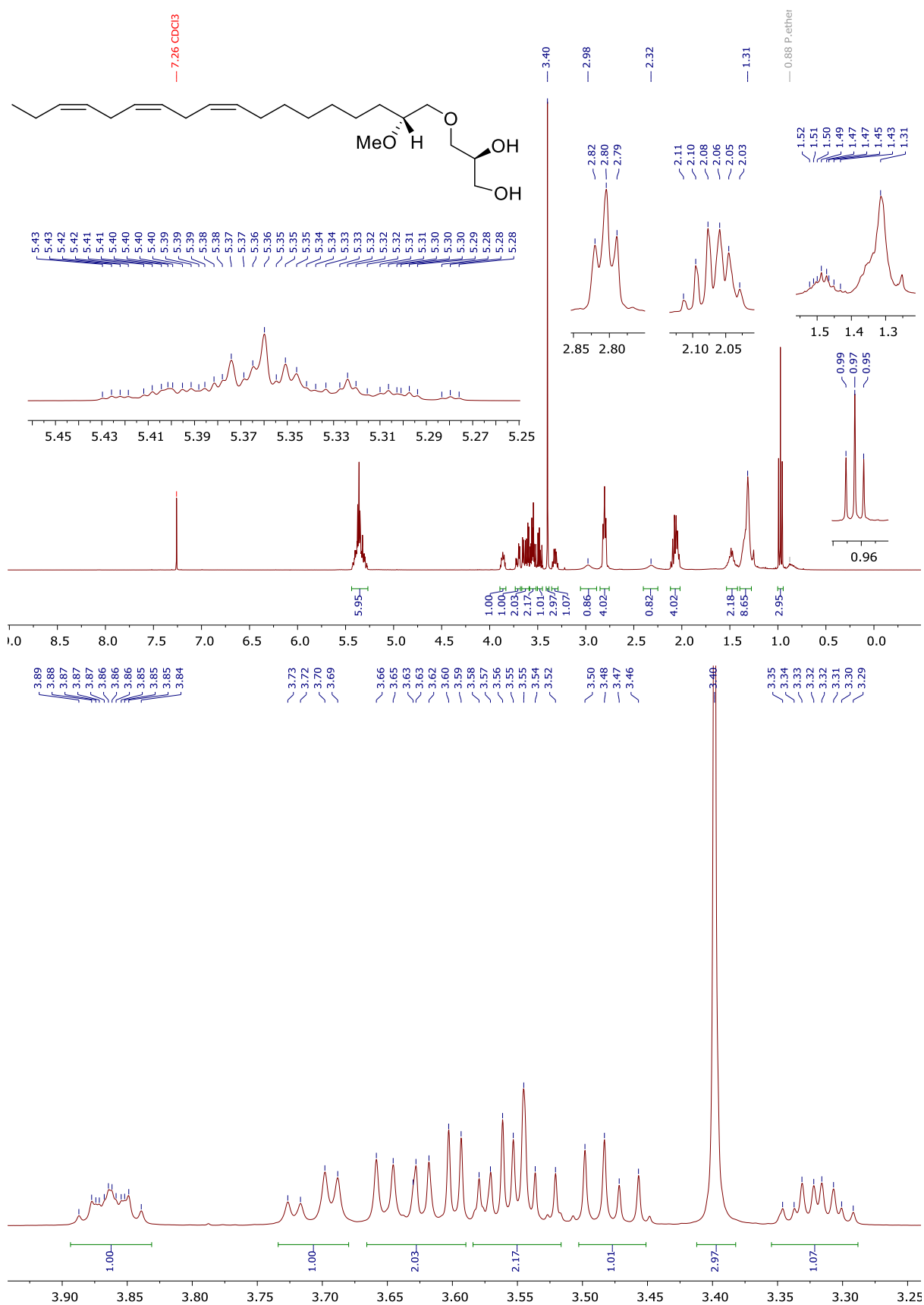
^1H - ^1H COSY spectrum of compound **13**



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



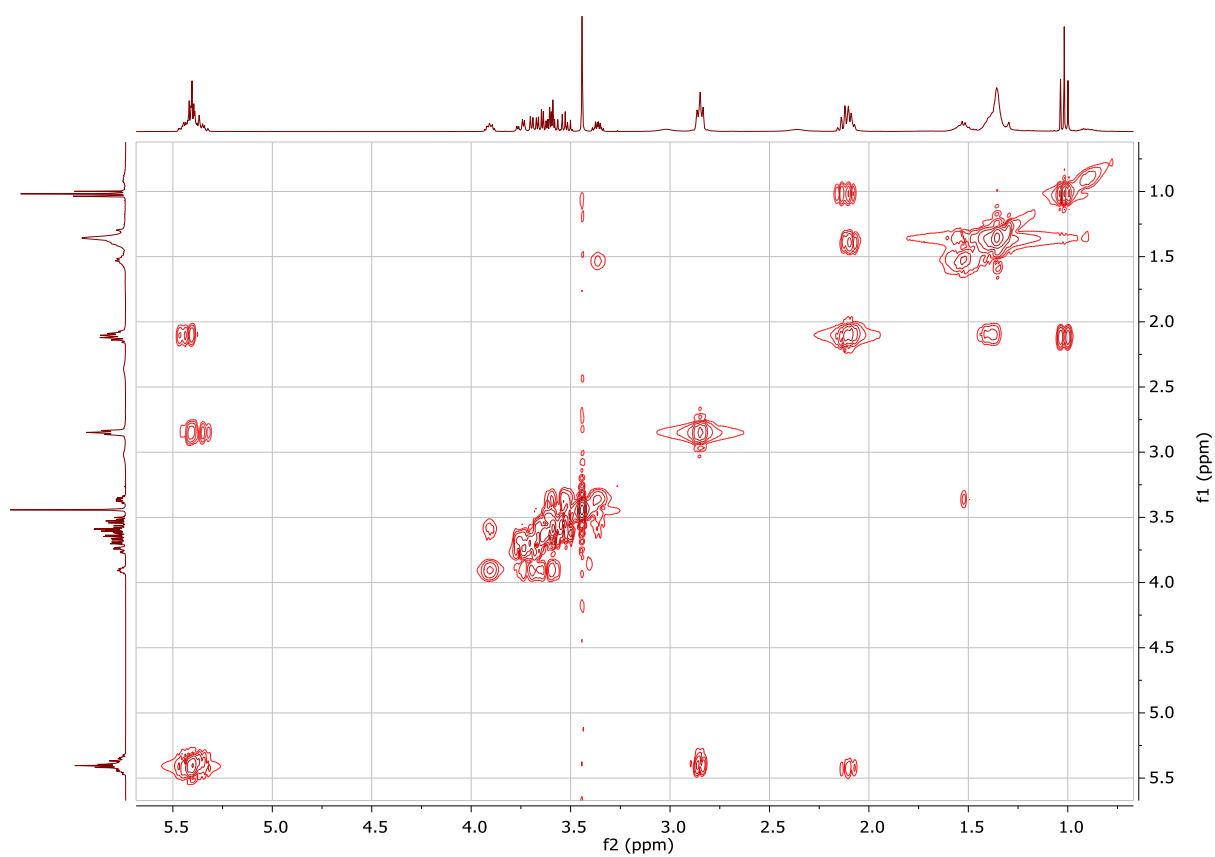
^1H NMR (400 MHz, CDCl_3) of MEL **5**



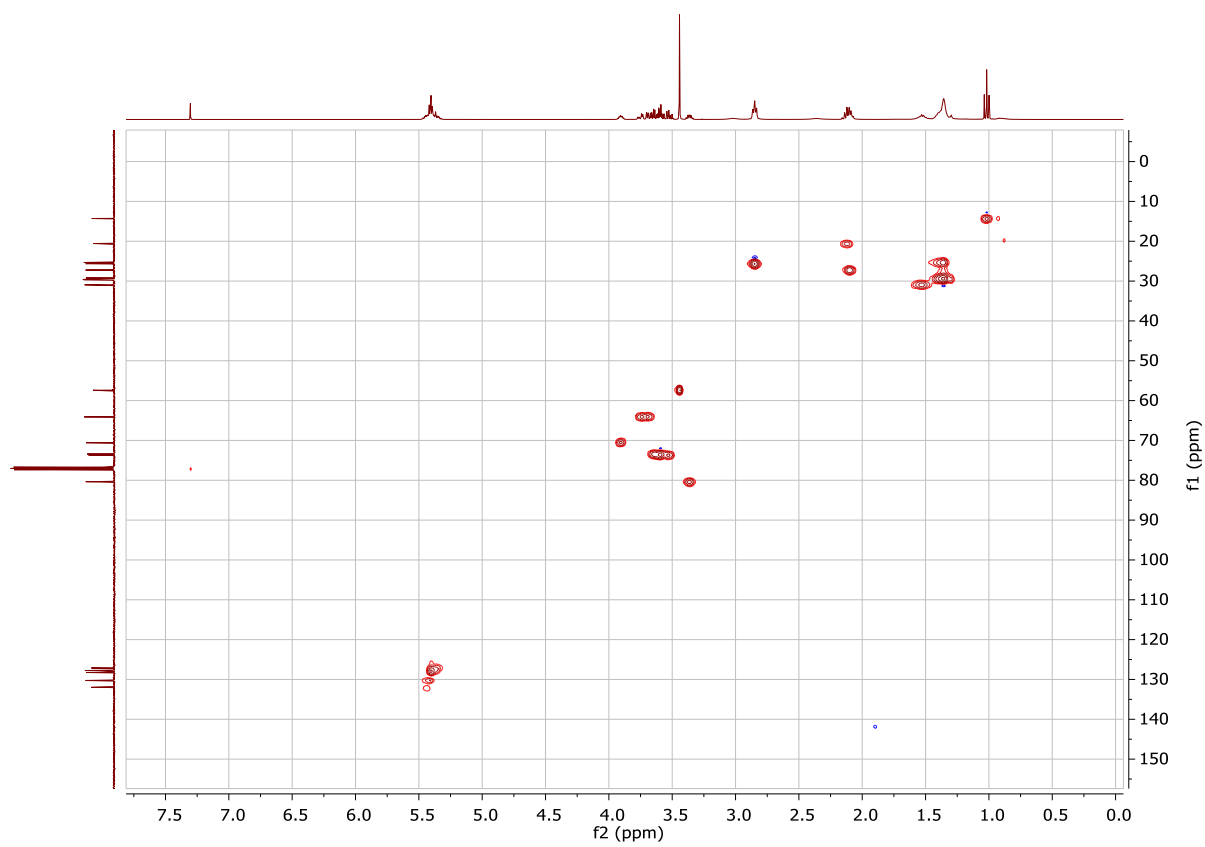
Chemical structure of (E)-12-((S)-2,3-dihydroxypropyl)-12-methoxyundec-5,7,9-triene is shown above the ^{13}C NMR spectrum. The structure includes a long chain with three conjugated double bonds (5,7,9-triene) and a side chain containing a methoxy group (MeO), a hydrogen atom (H), and a 2,3-dihydroxypropyl group (CH(OH)CH₂OH).

The ^{13}C NMR spectrum displays peaks corresponding to the following chemical shifts (ppm):

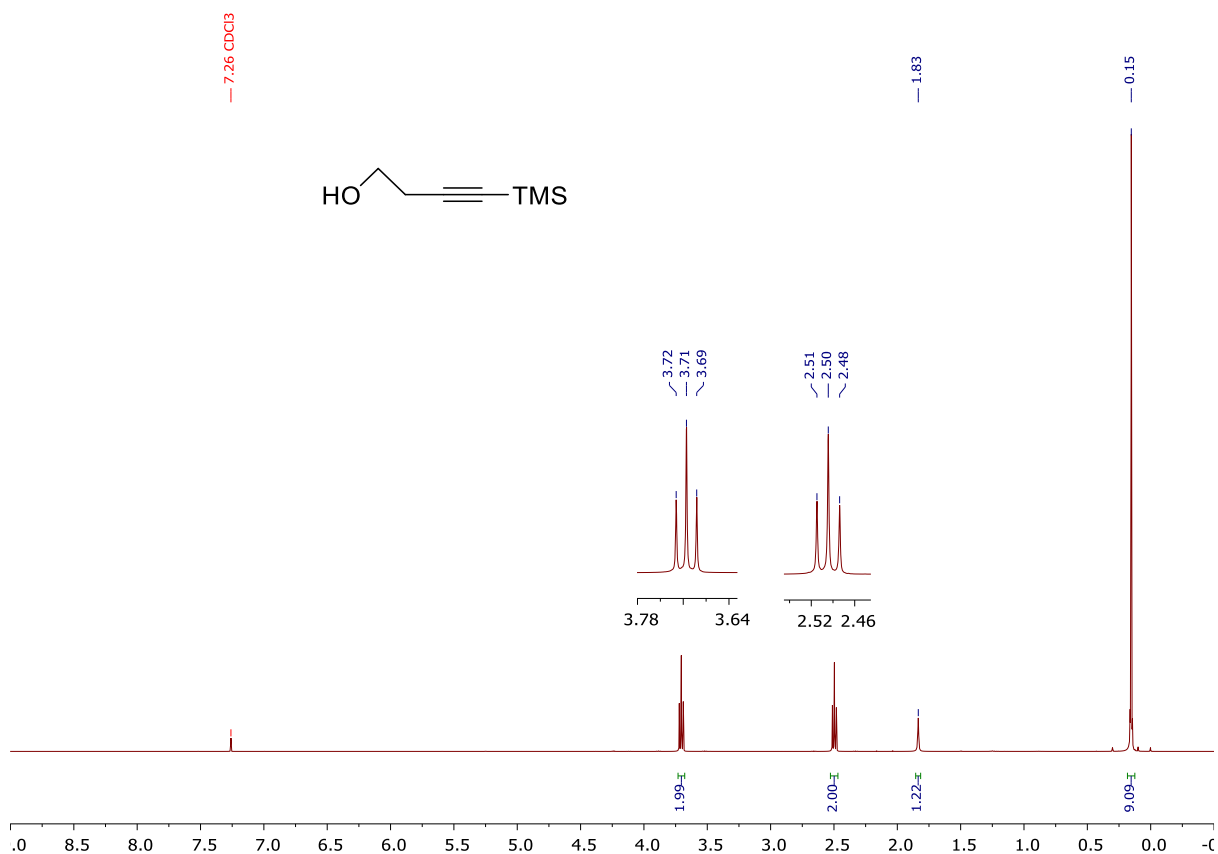
- 132.11
- 130.39
- 128.44
- 128.39
- 127.90
- 127.25
- 80.49
- 77.48 CDCl₃
- 77.16 CDCl₃
- 76.84 CDCl₃
- 73.79
- 73.54
- 70.71
- 64.22
- 57.53
- 31.07
- 29.84
- 29.72
- 29.36
- 27.36
- 25.77
- 25.68
- 25.46
- 20.70
- 14.42



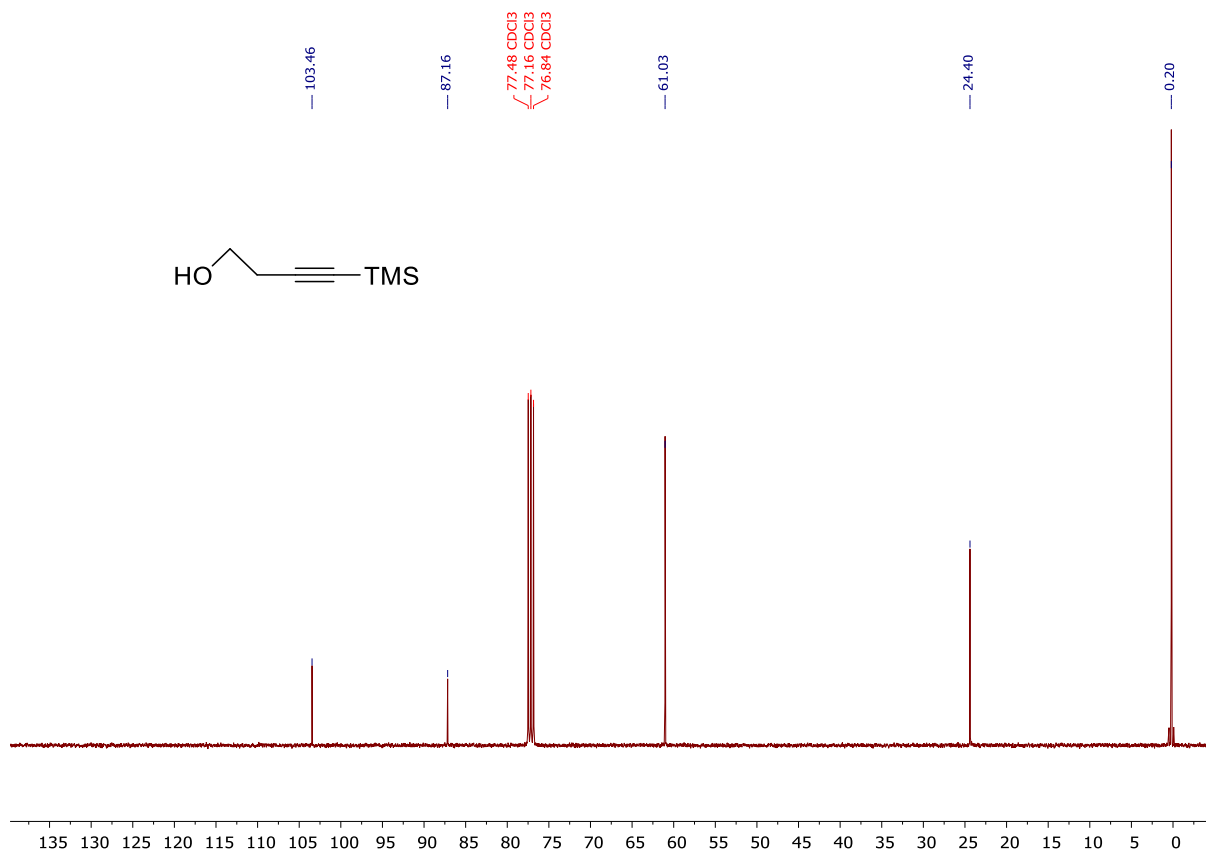
^{13}C - ^1H HSQC spectrum of MEL 5



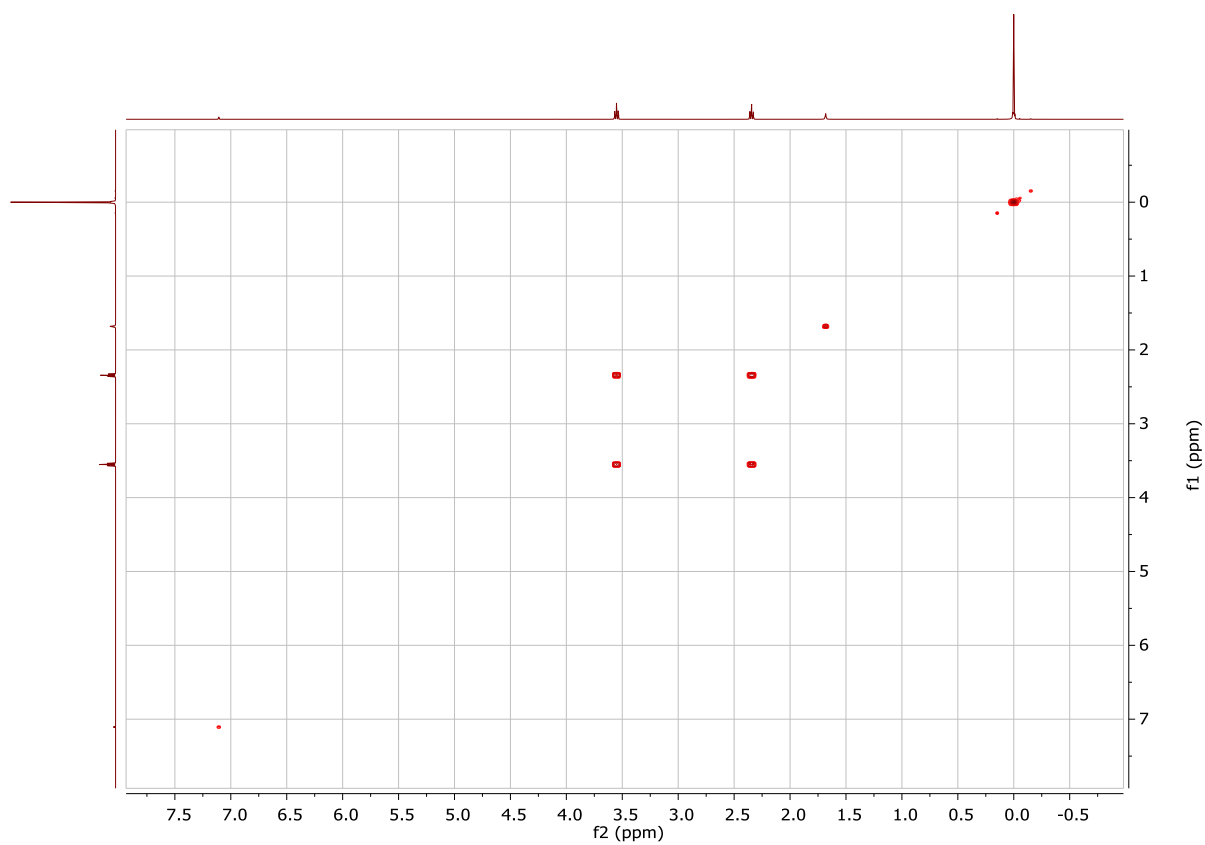
^1H NMR (400 MHz, CDCl_3) of compound **14**



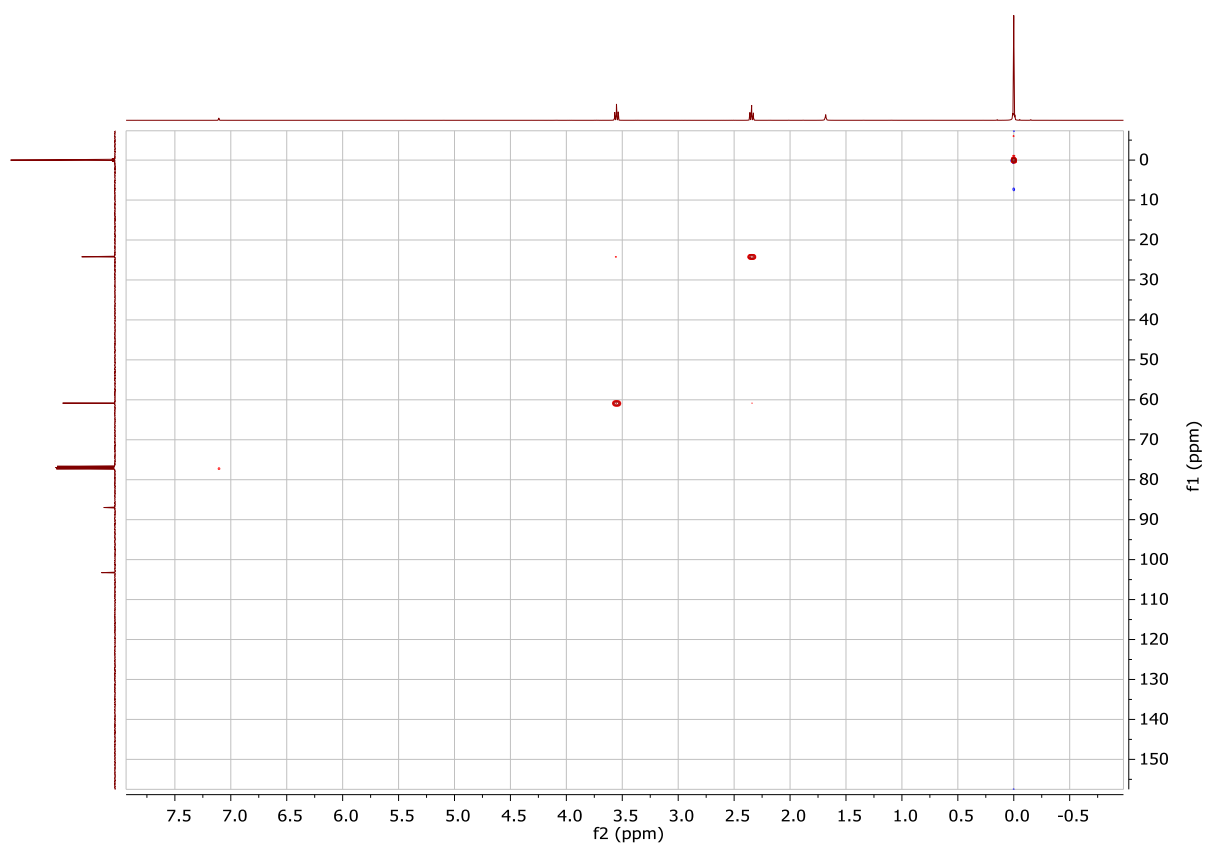
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **14**



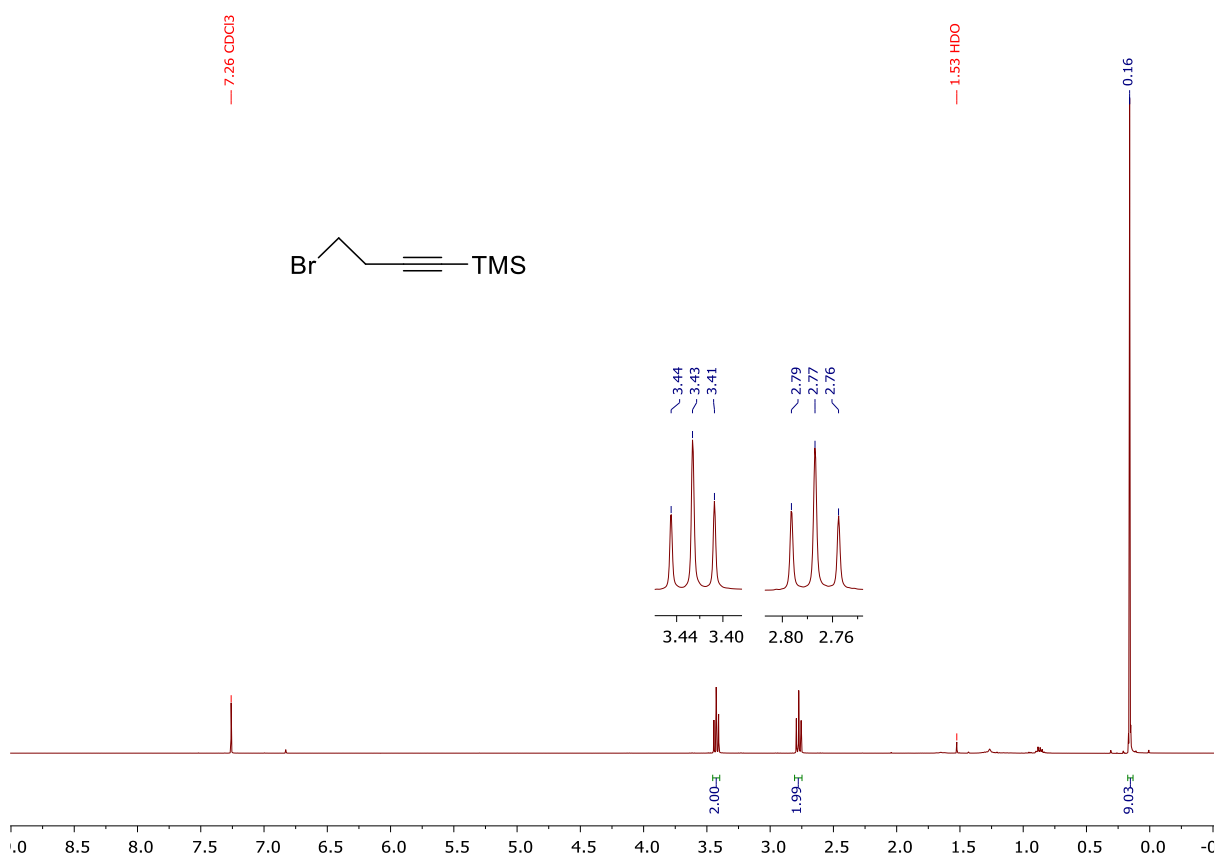
^1H - ^1H COSY spectrum of compound **14**



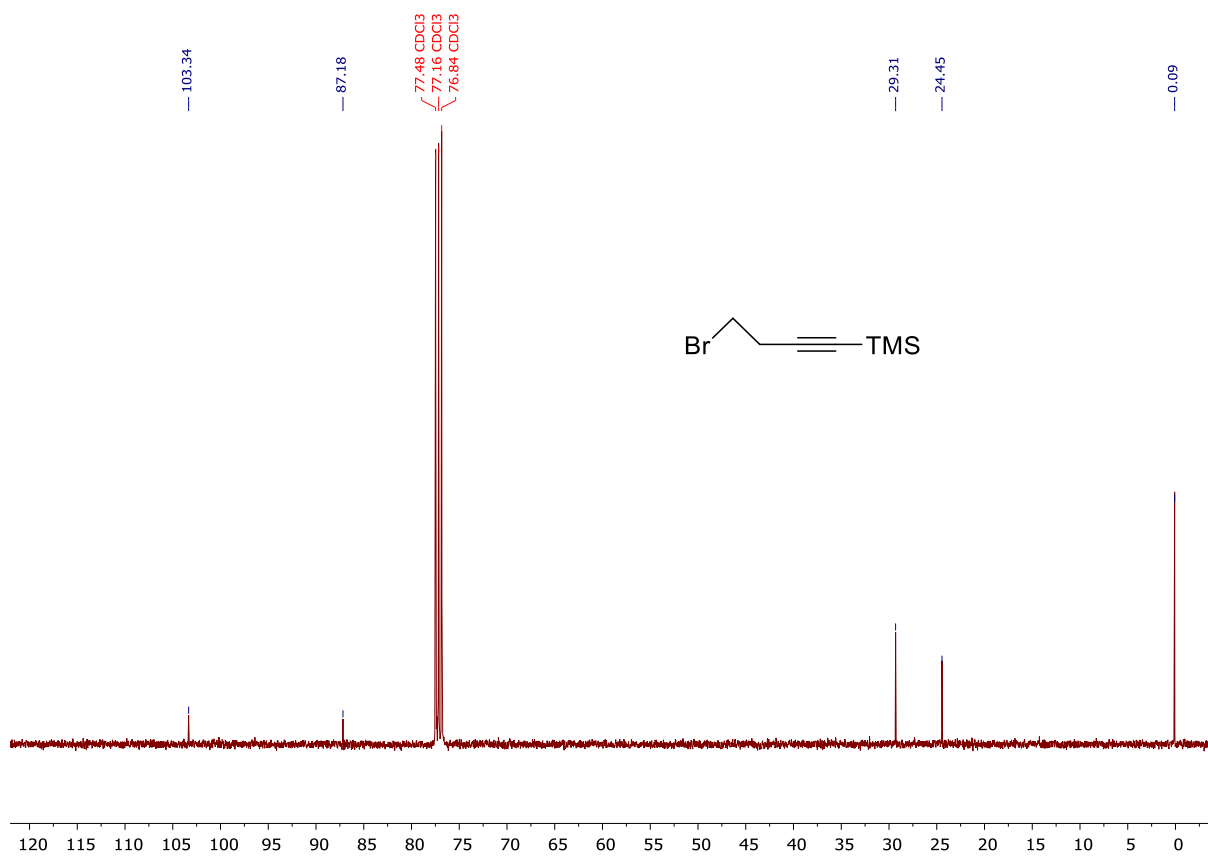
^{13}C - ^1H HSQC spectrum of compound **14**



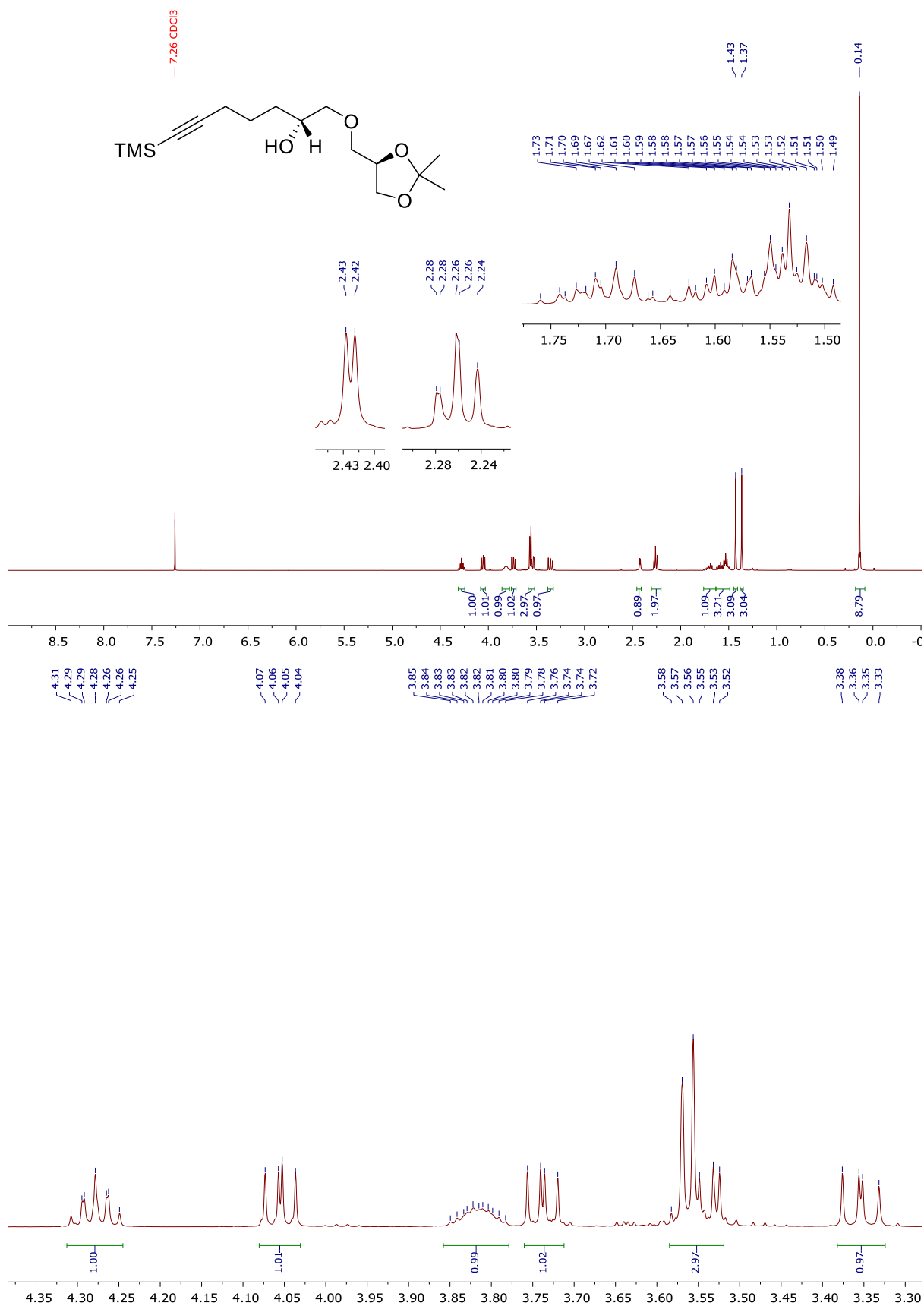
^1H NMR (400 MHz, CDCl_3) of compound **15**



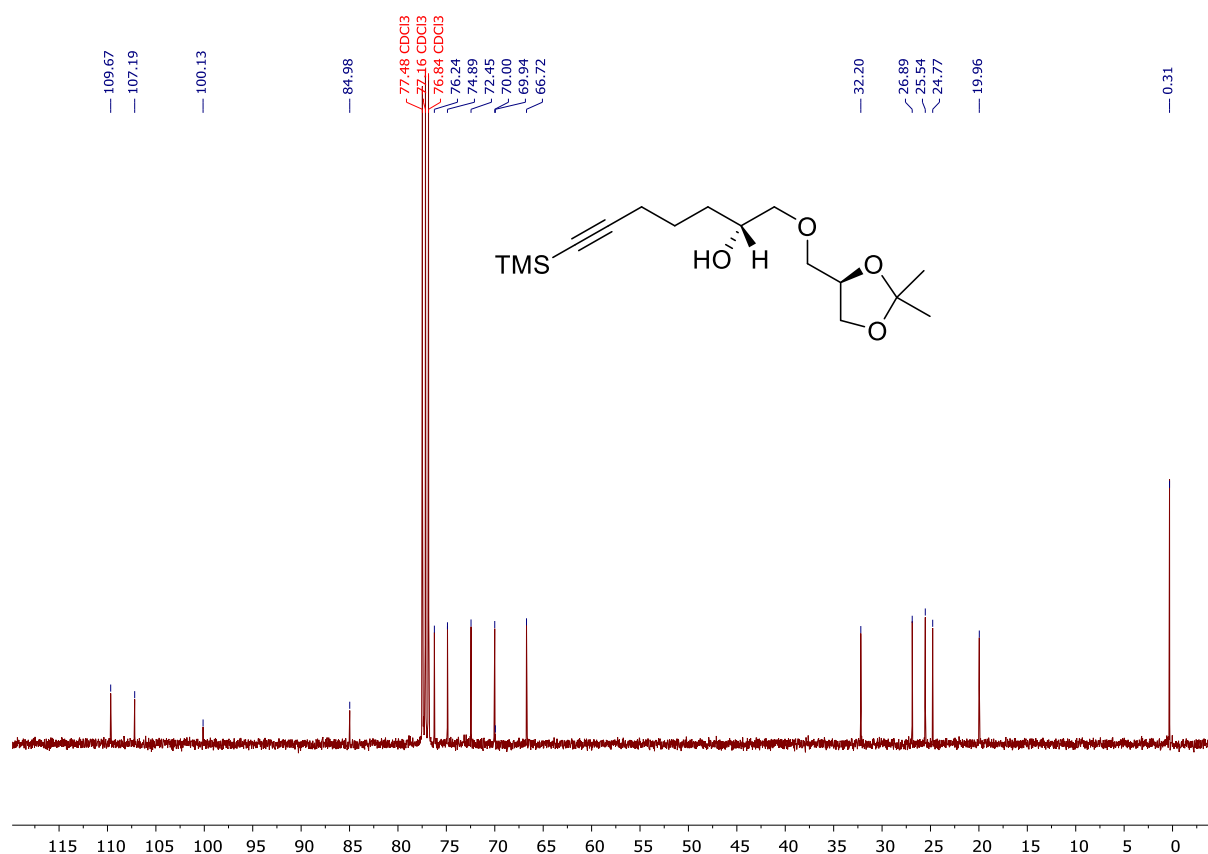
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **15**



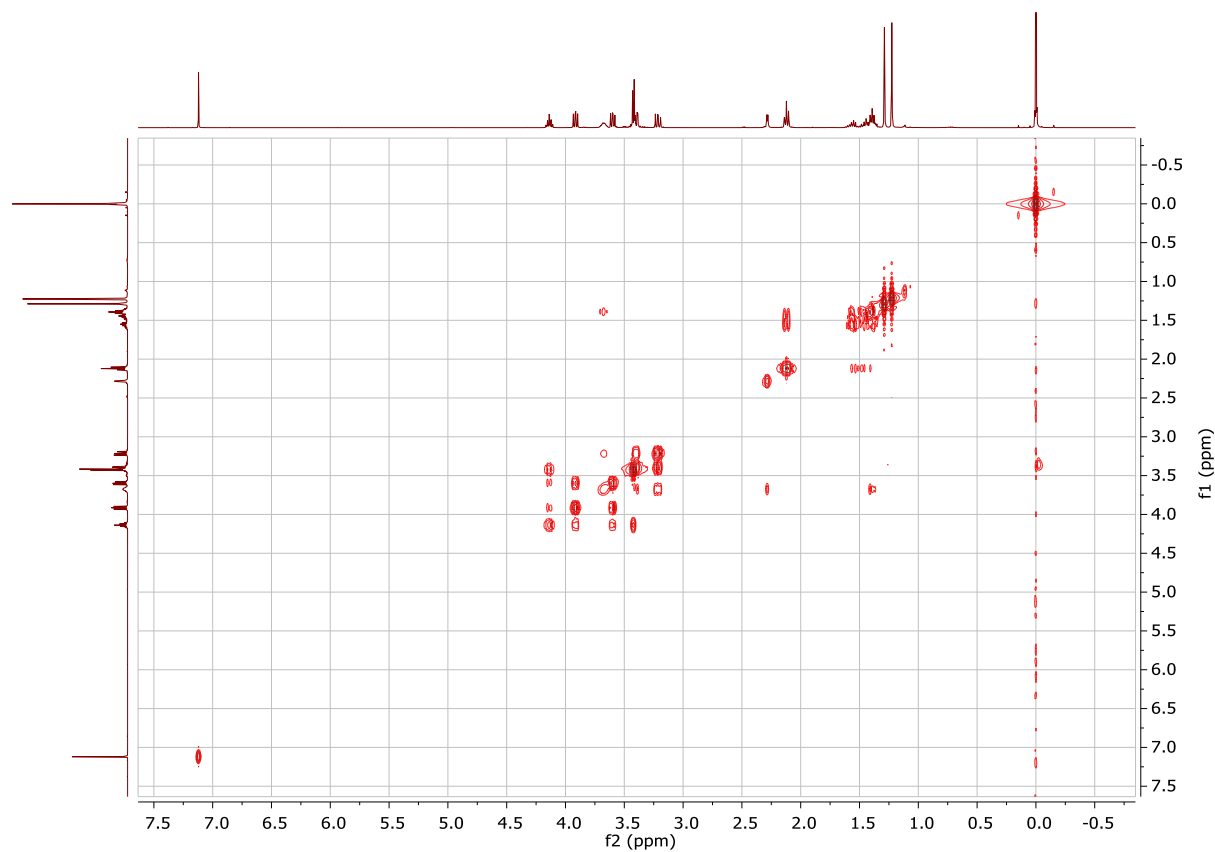
^1H NMR (400 MHz, CDCl_3) of compound **16**

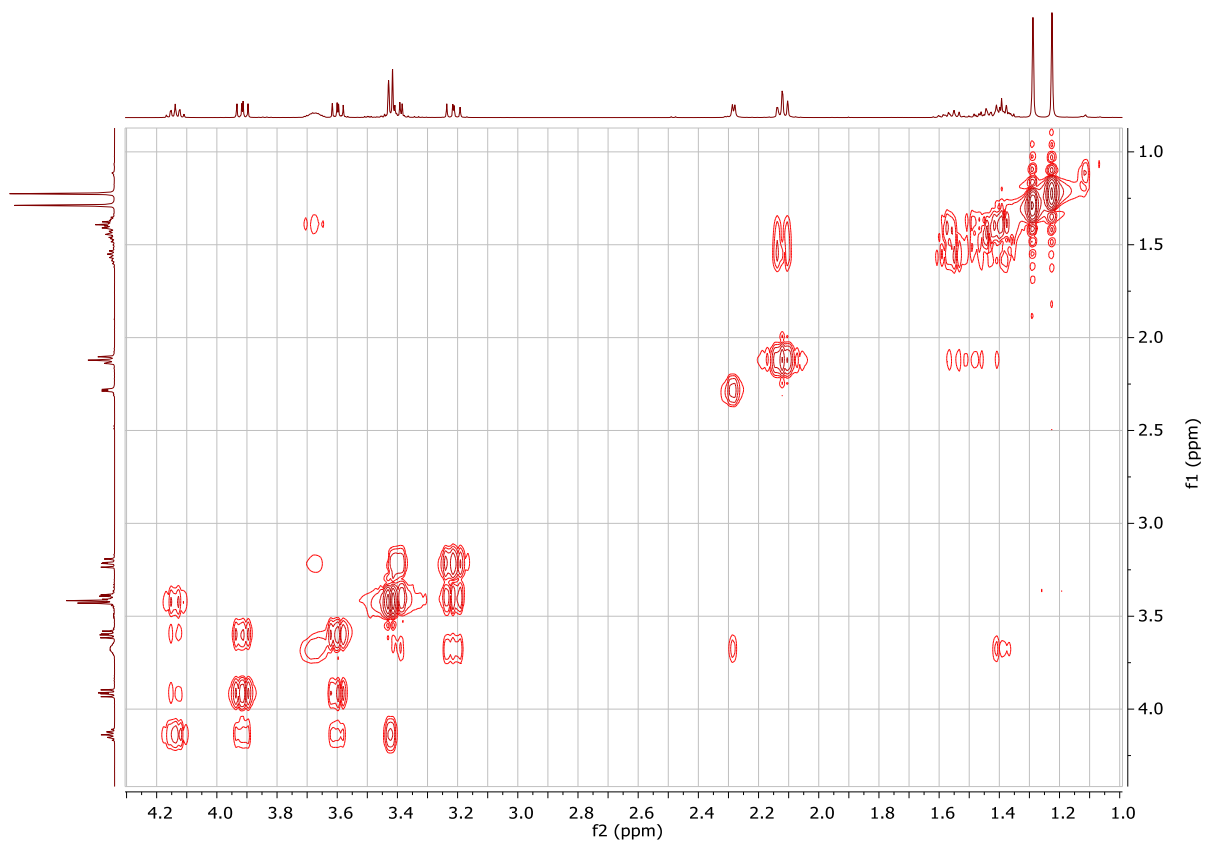


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **16**

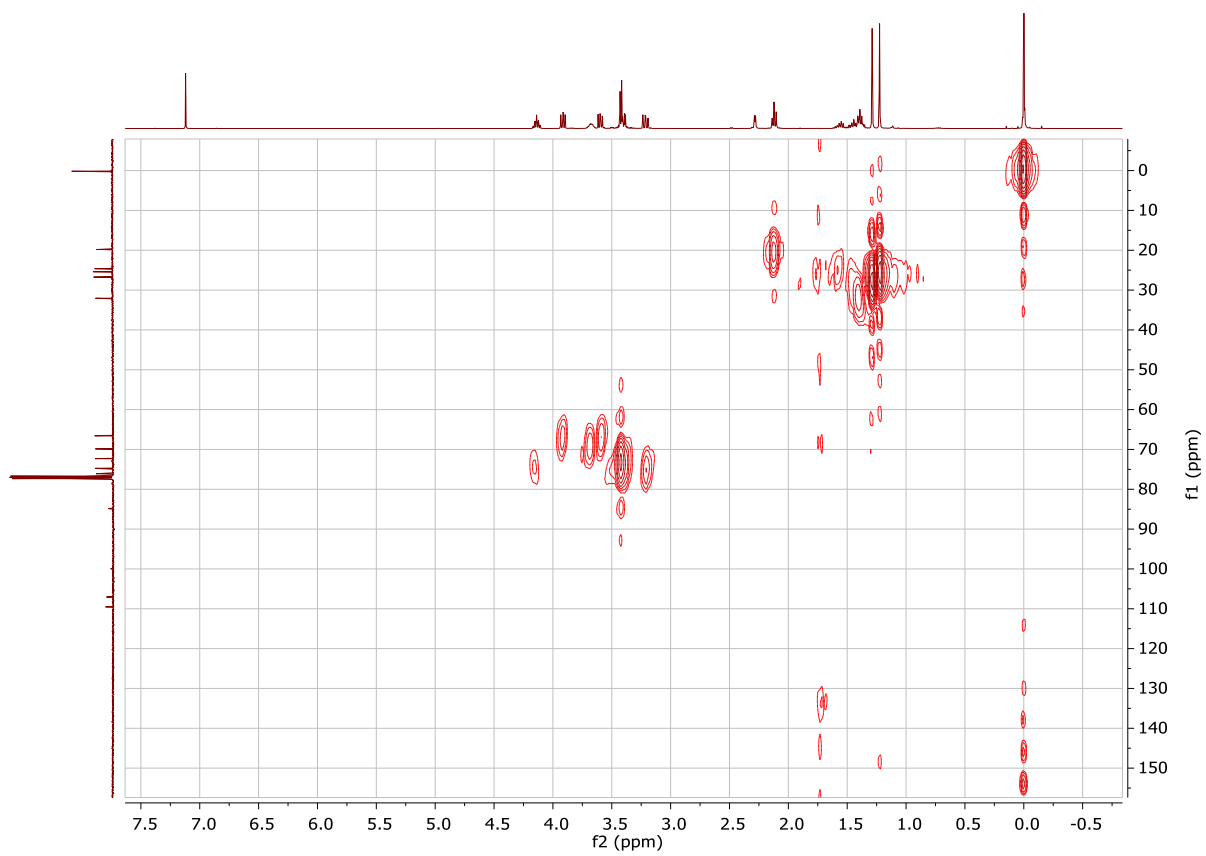


^1H - ^1H COSY spectrum of compound **16**

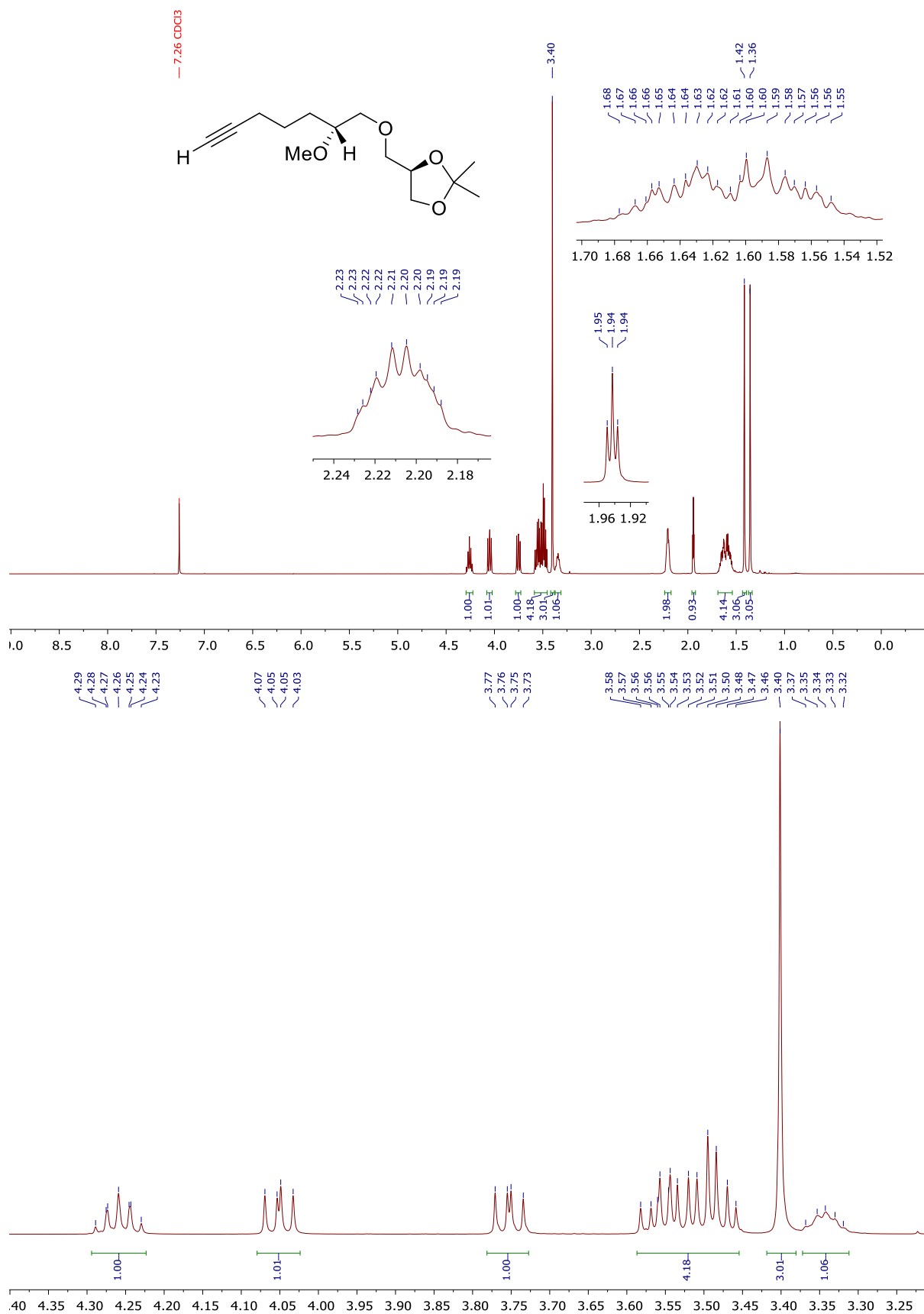




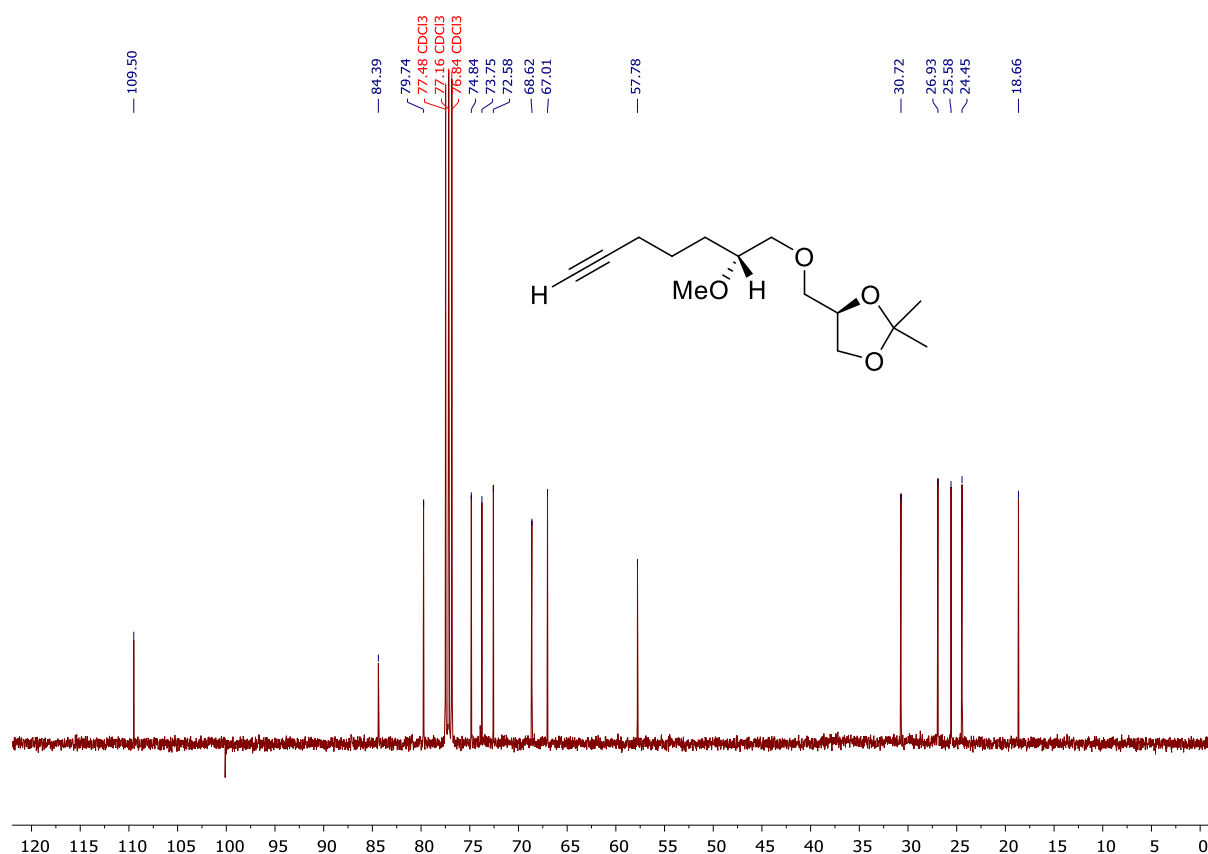
^{13}C - ^1H HSQC spectrum of compound **16**



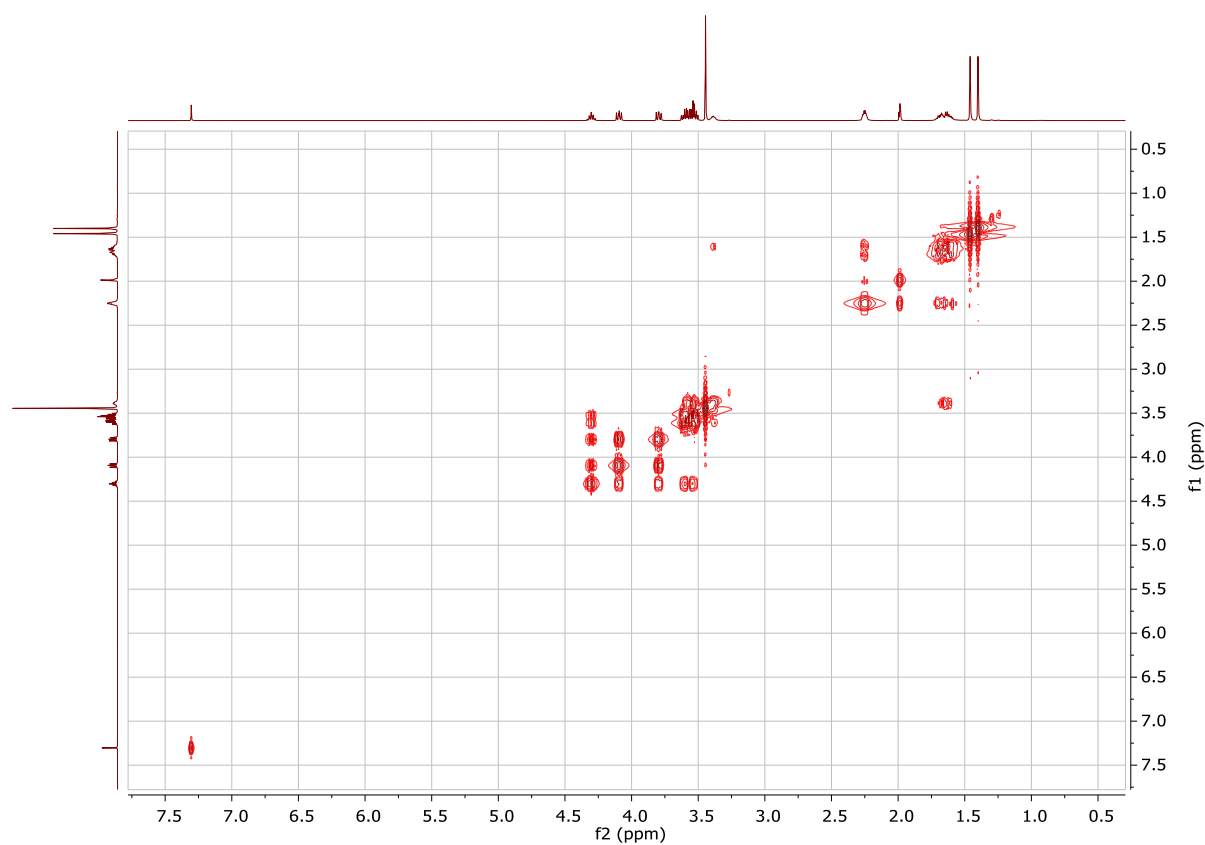
^1H NMR (400 MHz, CDCl_3) of compound **17**

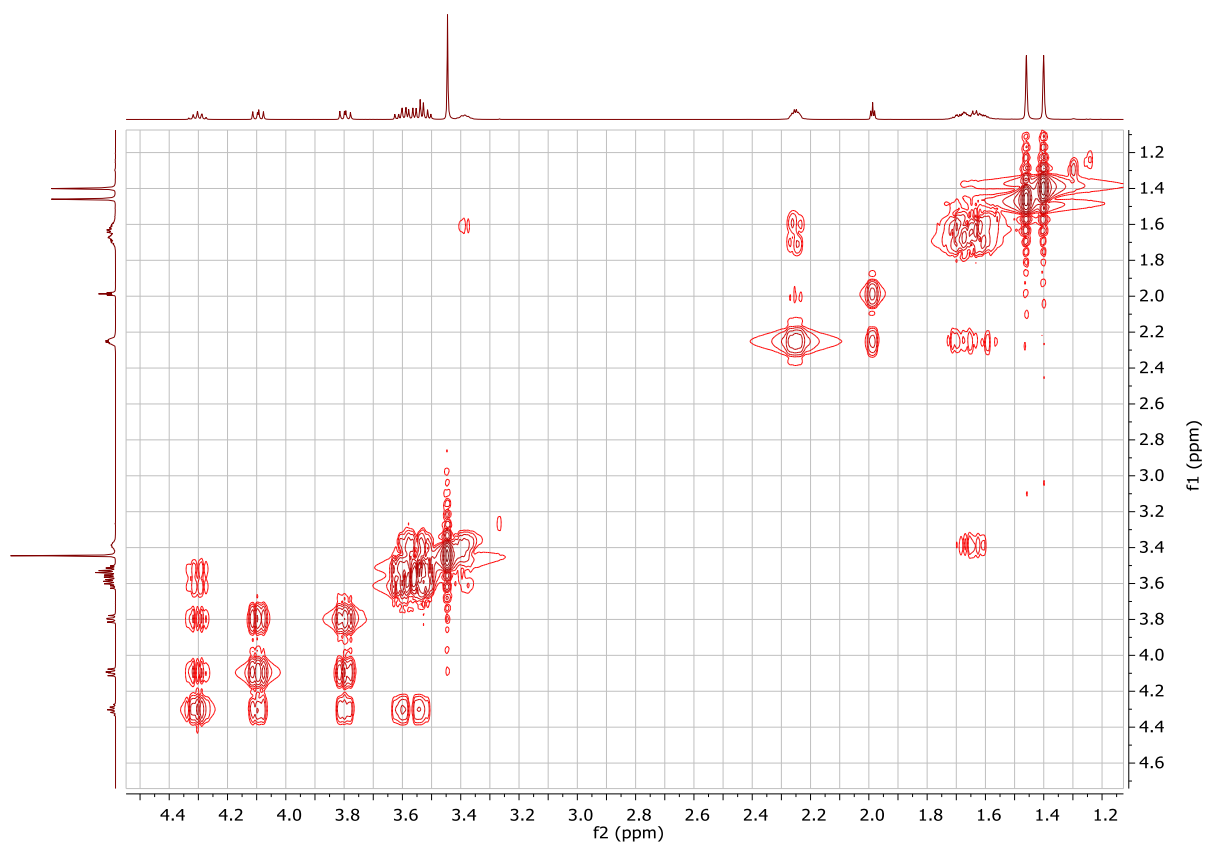


$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **17**

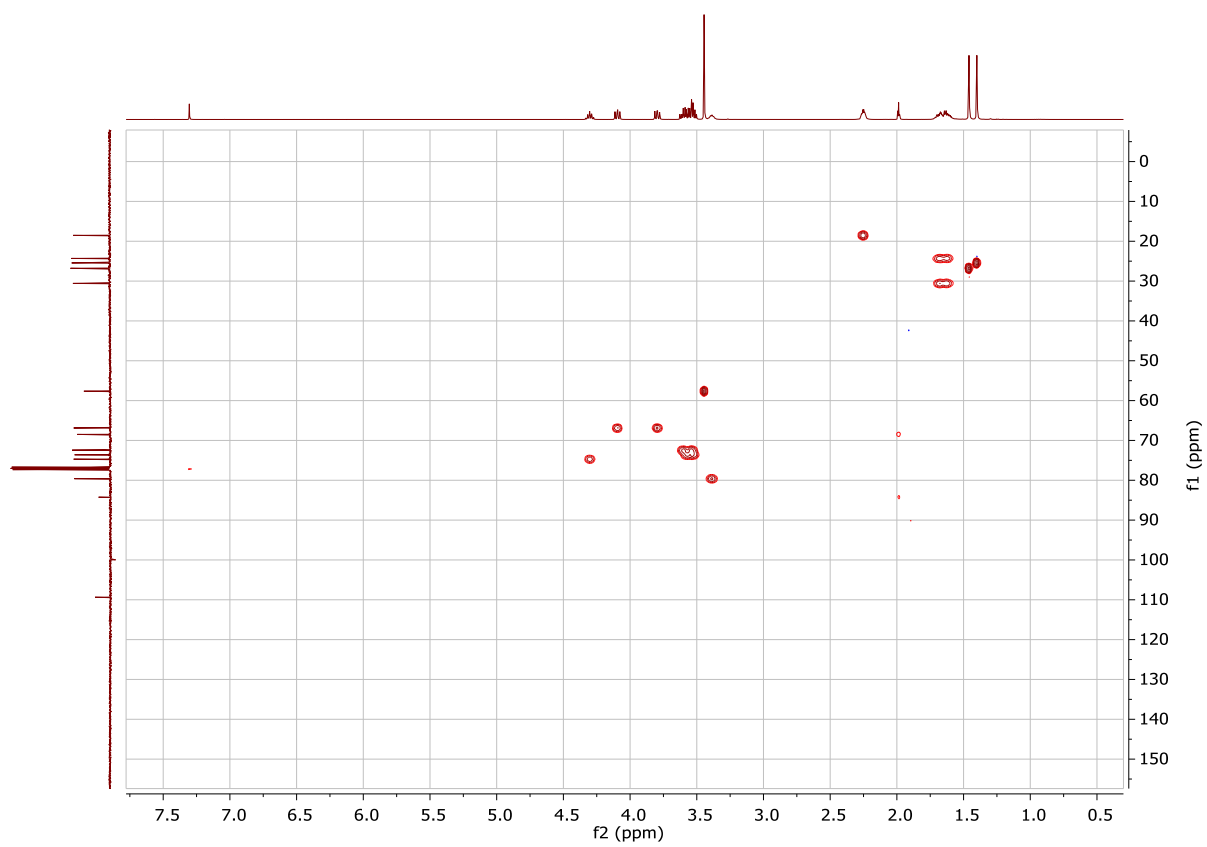


^1H - ^1H COSY spectrum of compound **17**

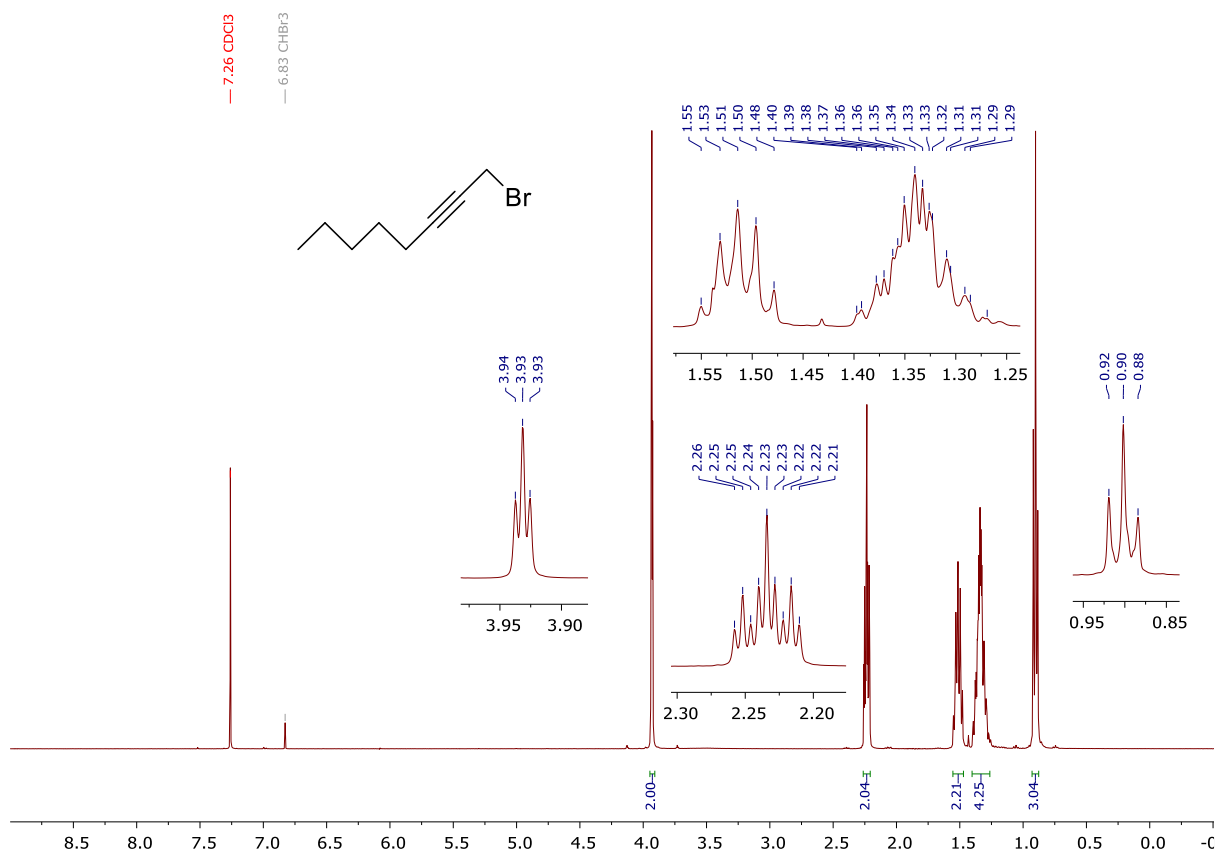




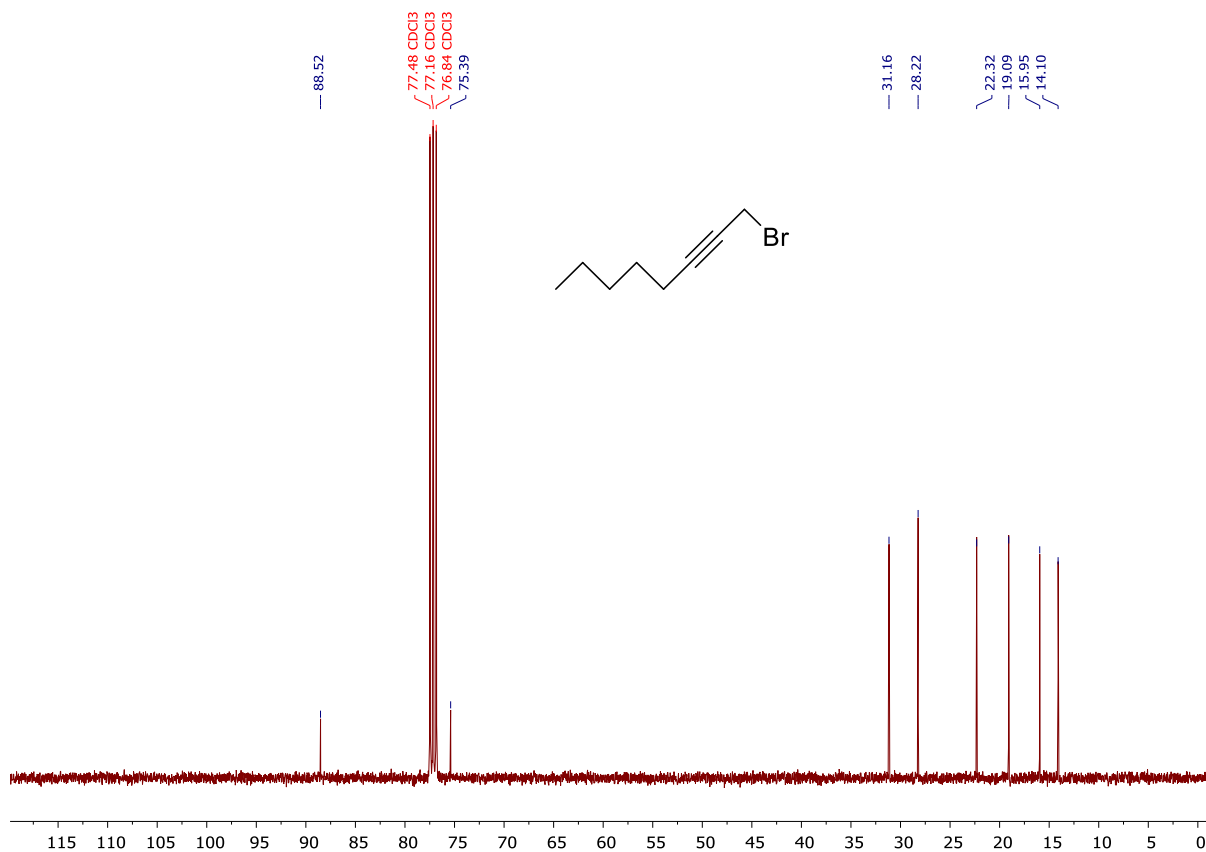
^{13}C - ^1H HSQC spectrum of compound **17**



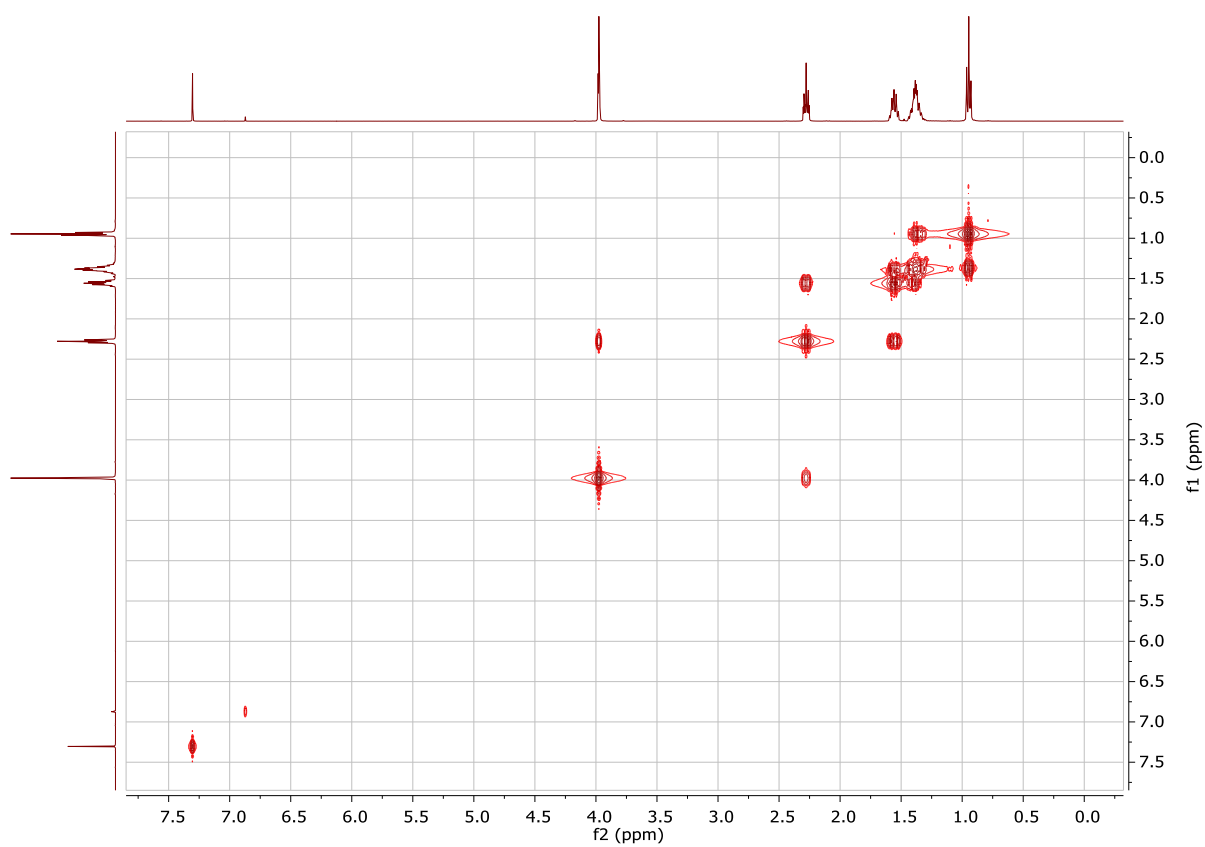
^1H NMR (400 MHz, CDCl_3) of compound **18**



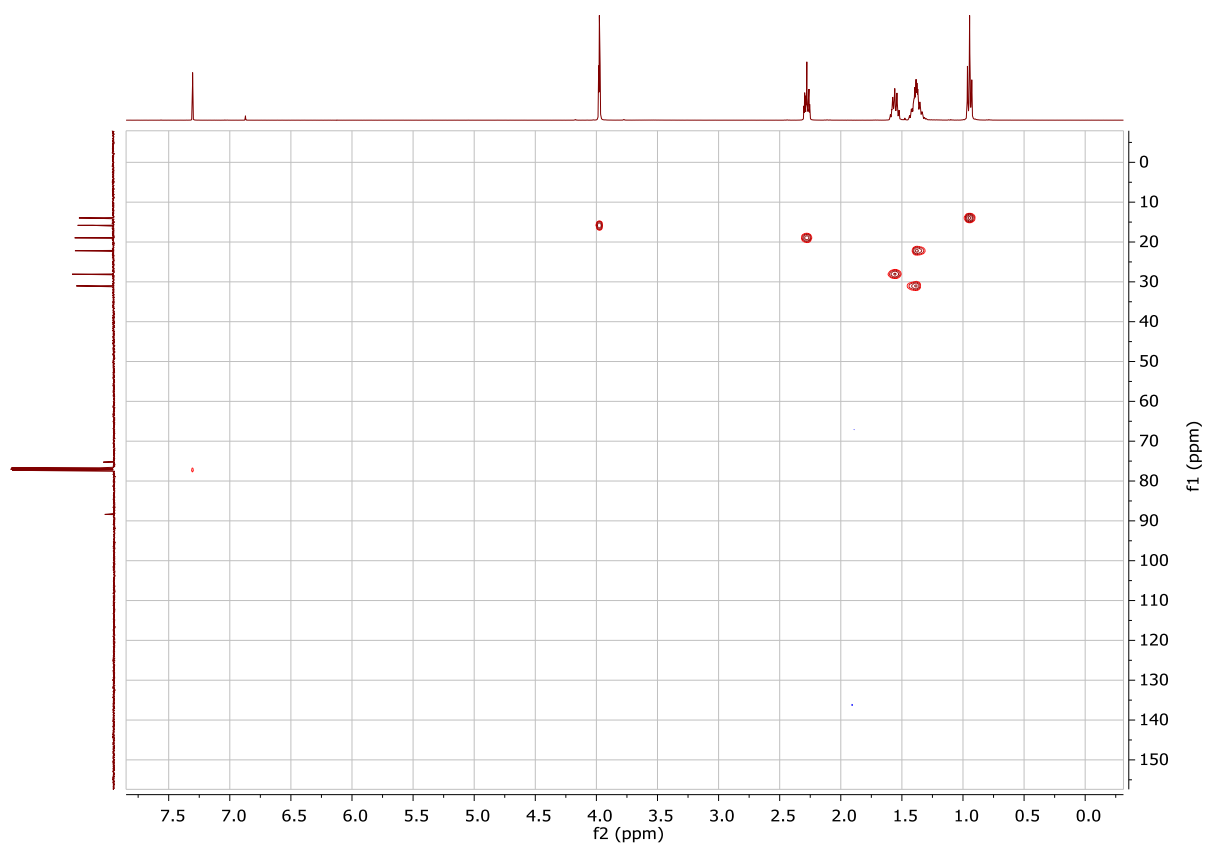
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **18**



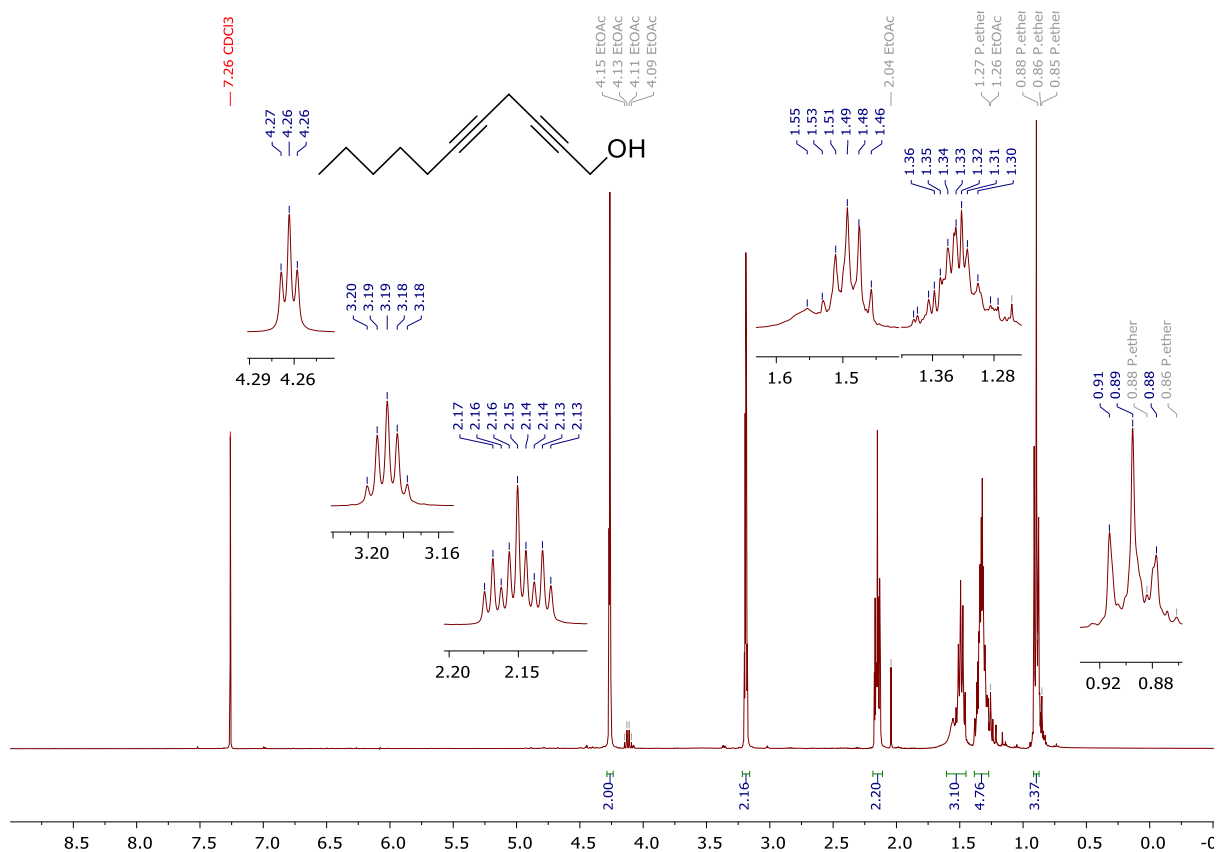
^1H - ^1H COSY spectrum of compound **18**



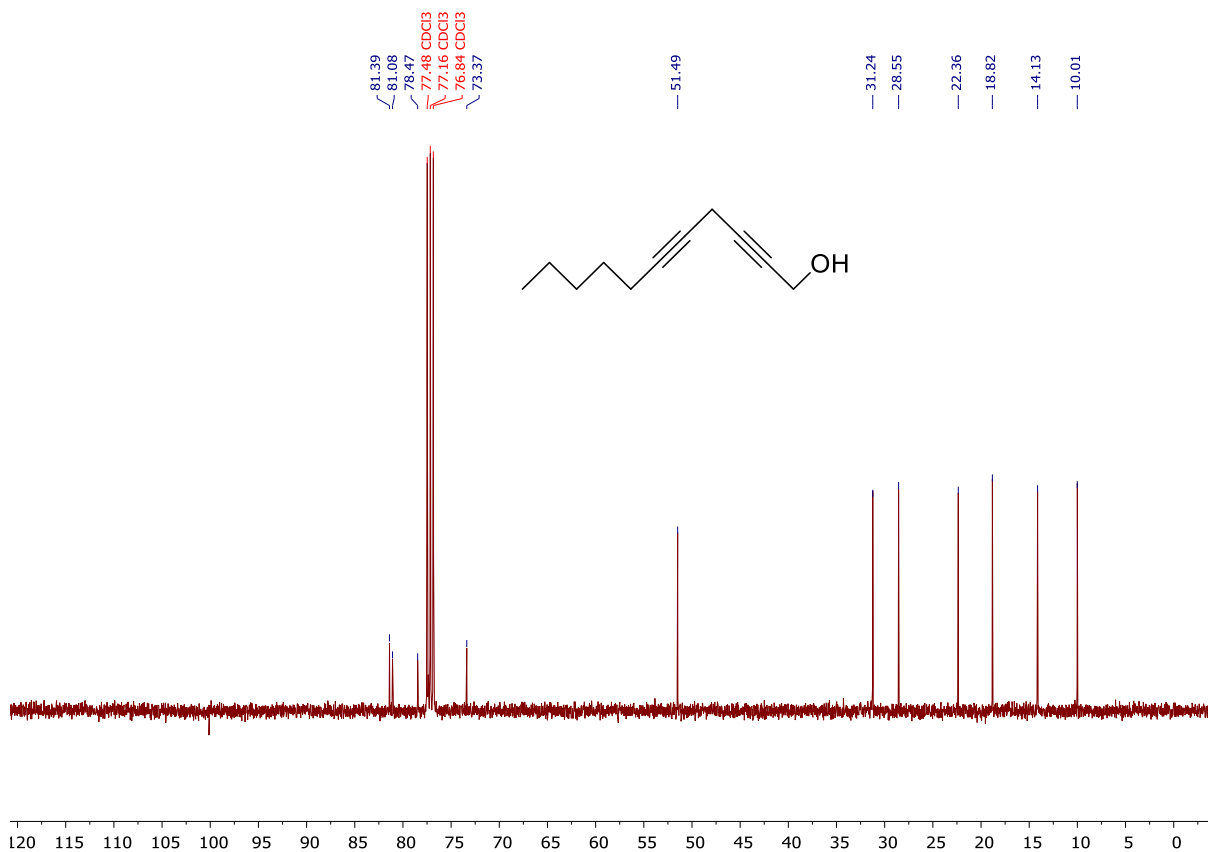
^{13}C - ^1H HSQC spectrum of compound **18**



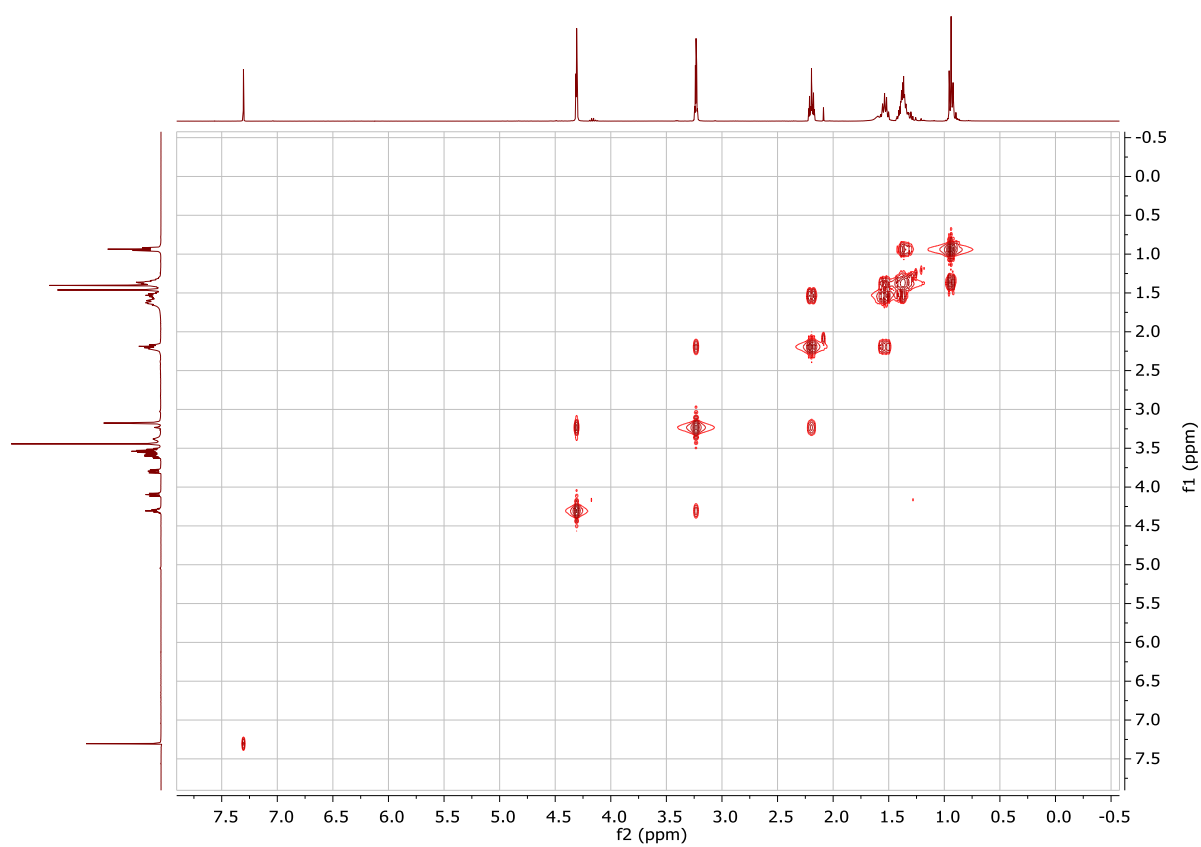
^1H NMR (400 MHz, CDCl_3) of compound **19**



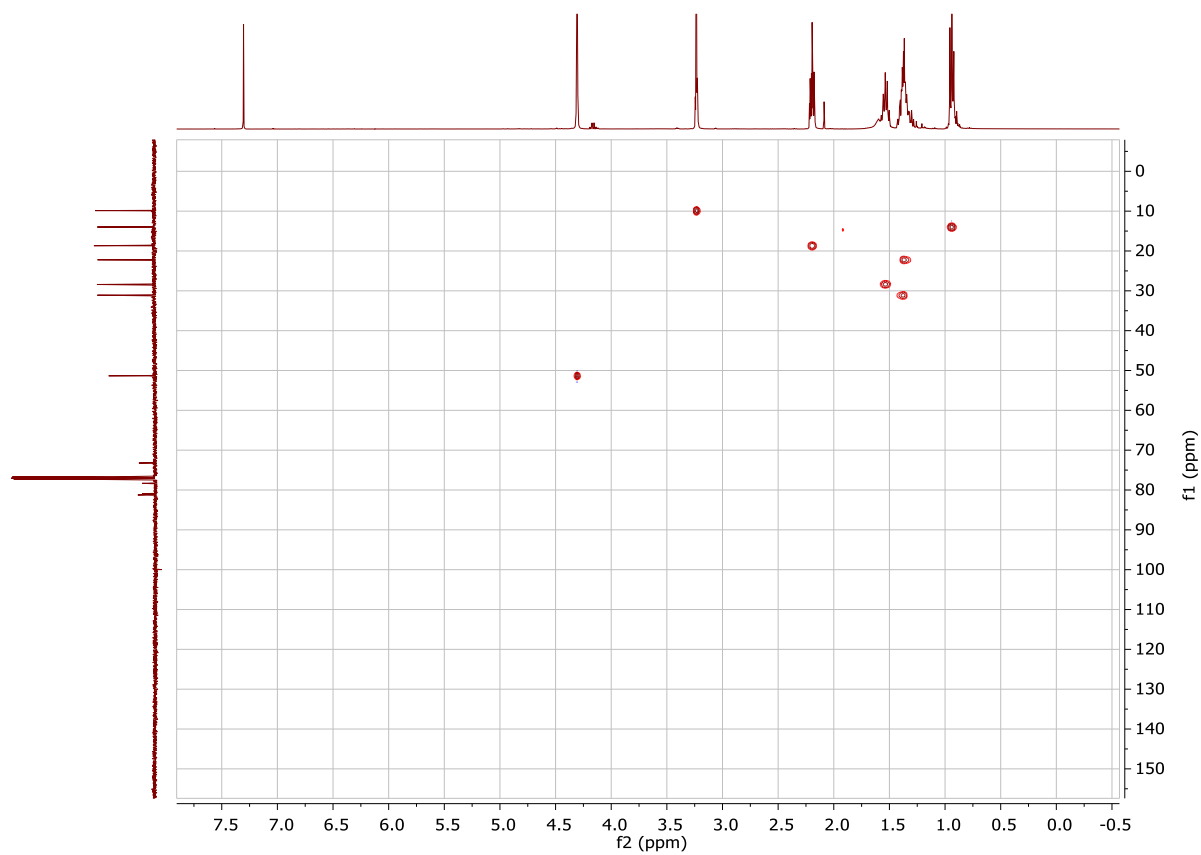
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **19**



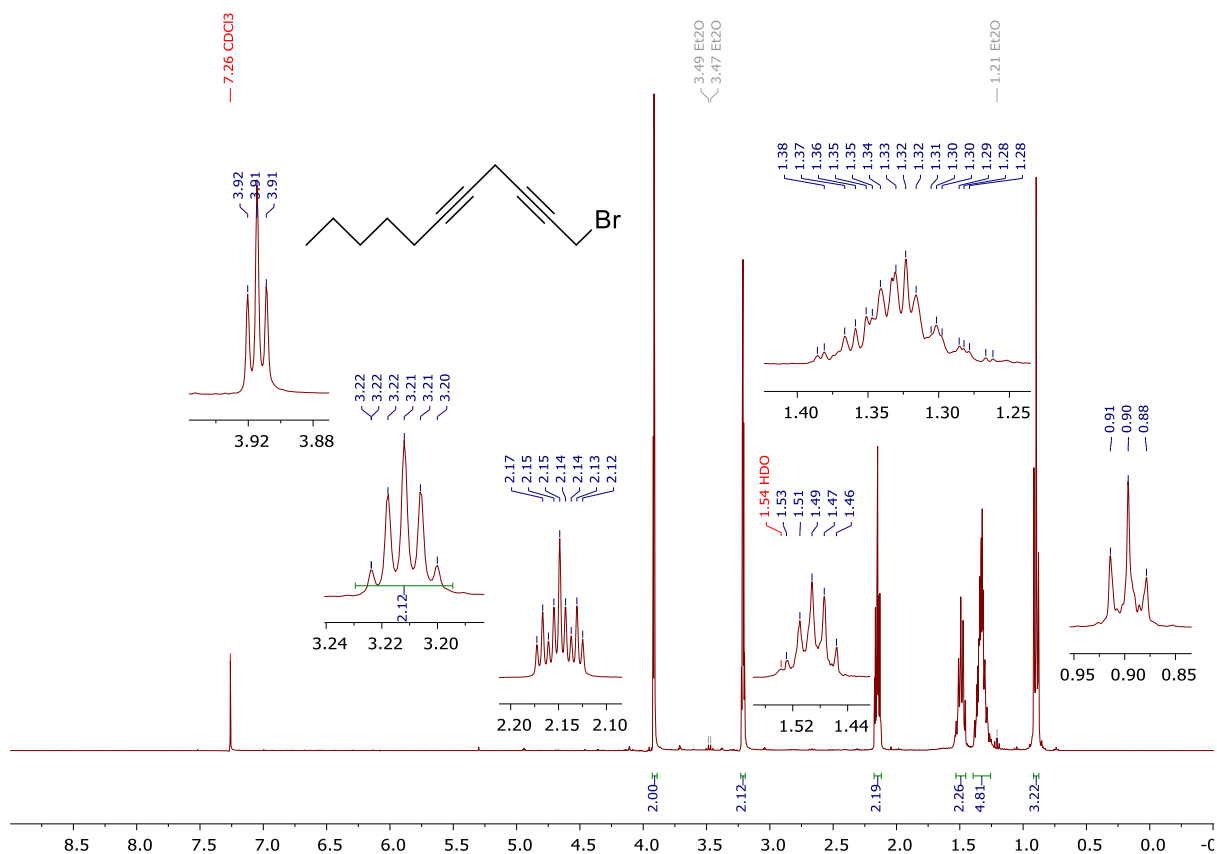
^1H - ^1H COSY spectrum of compound **19**



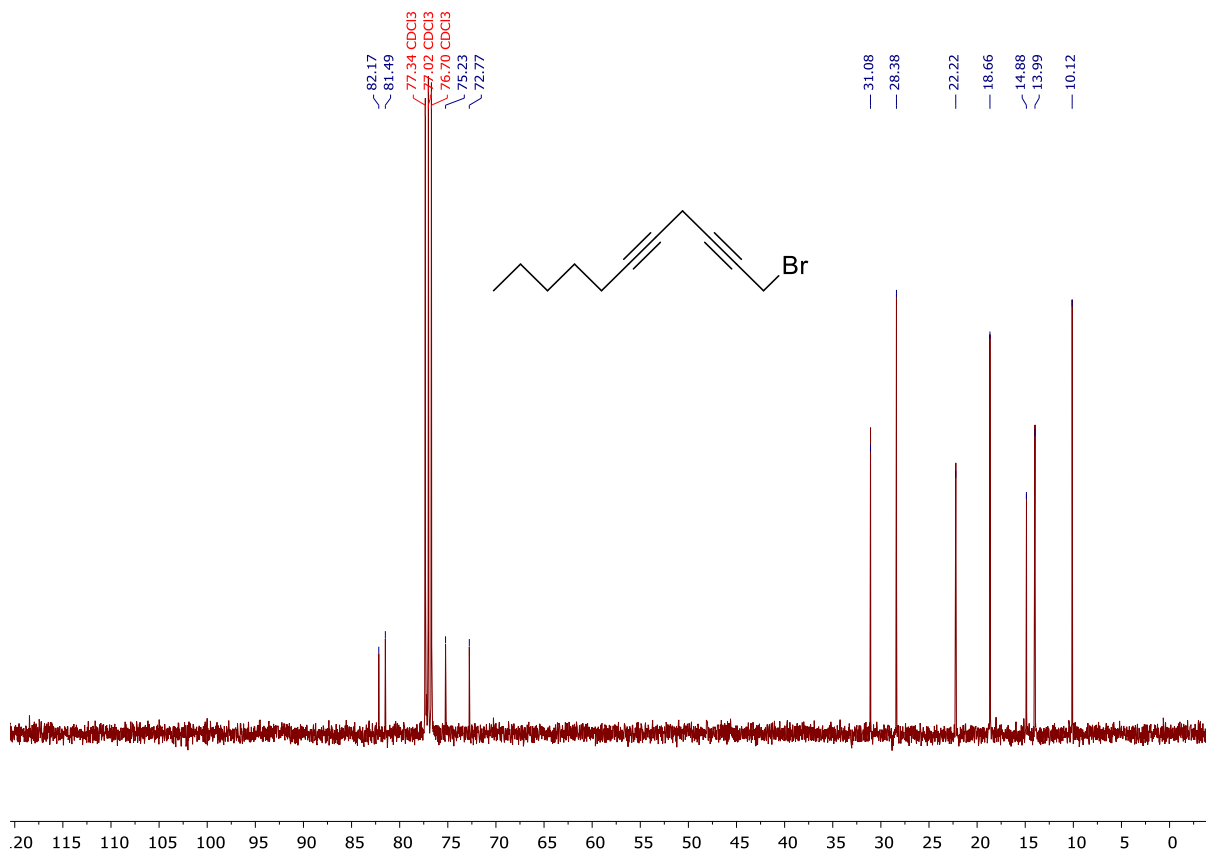
^{13}C - ^1H HSQC spectrum of compound **19**



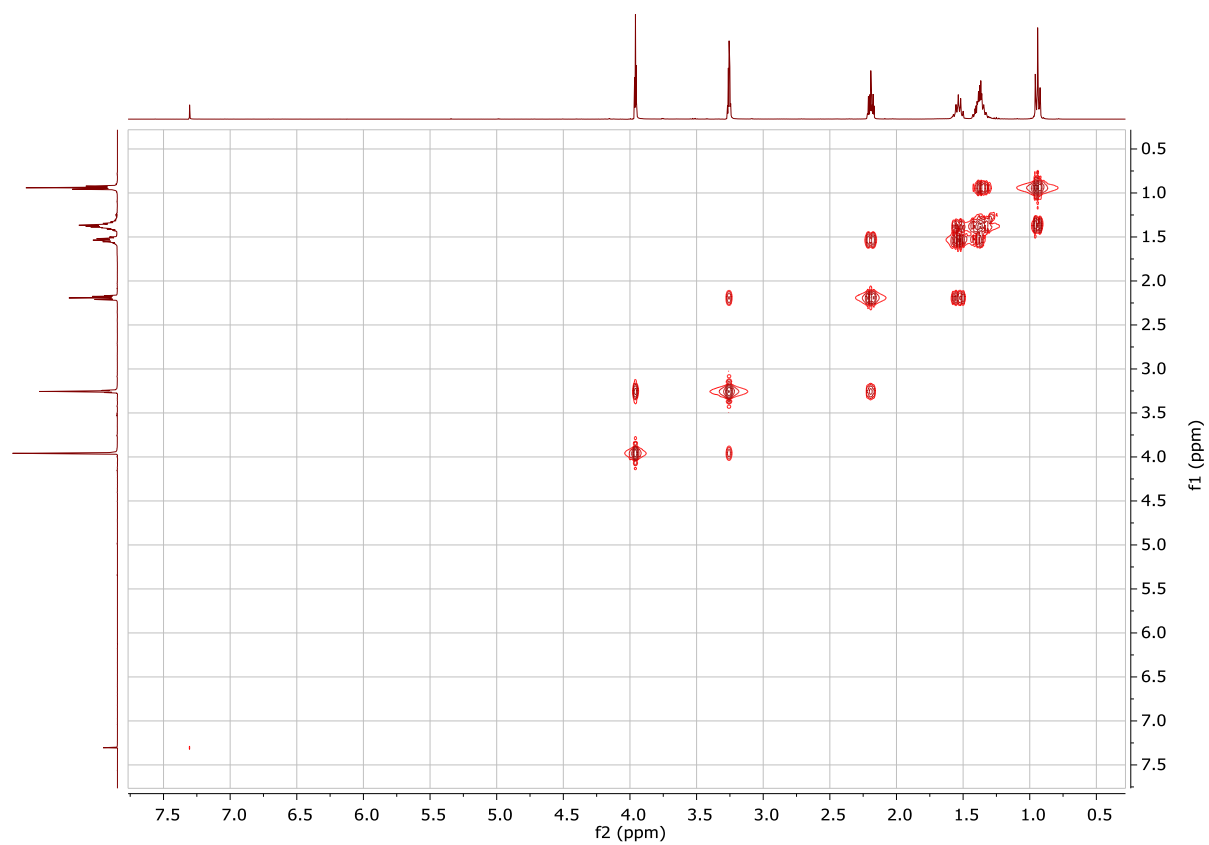
^1H NMR (400 MHz, CDCl_3) of compound **20**



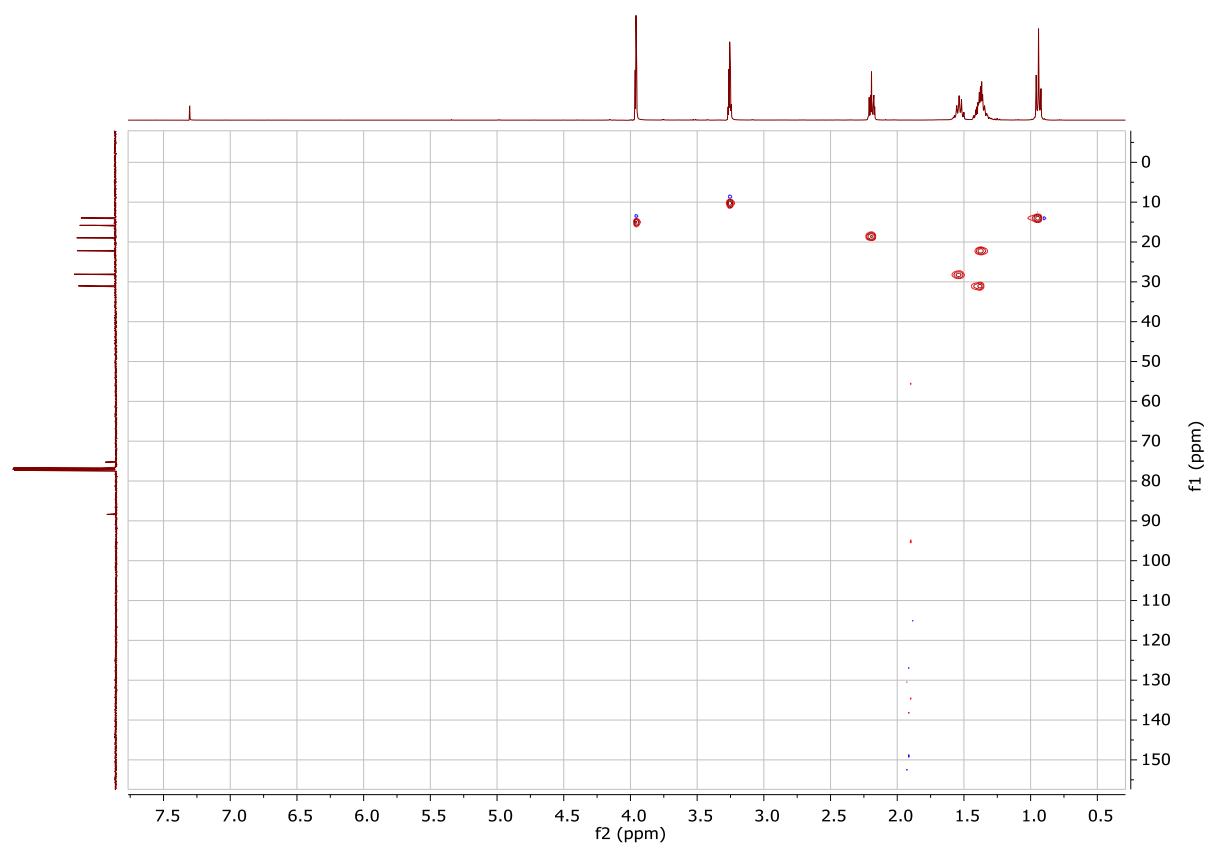
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **20**



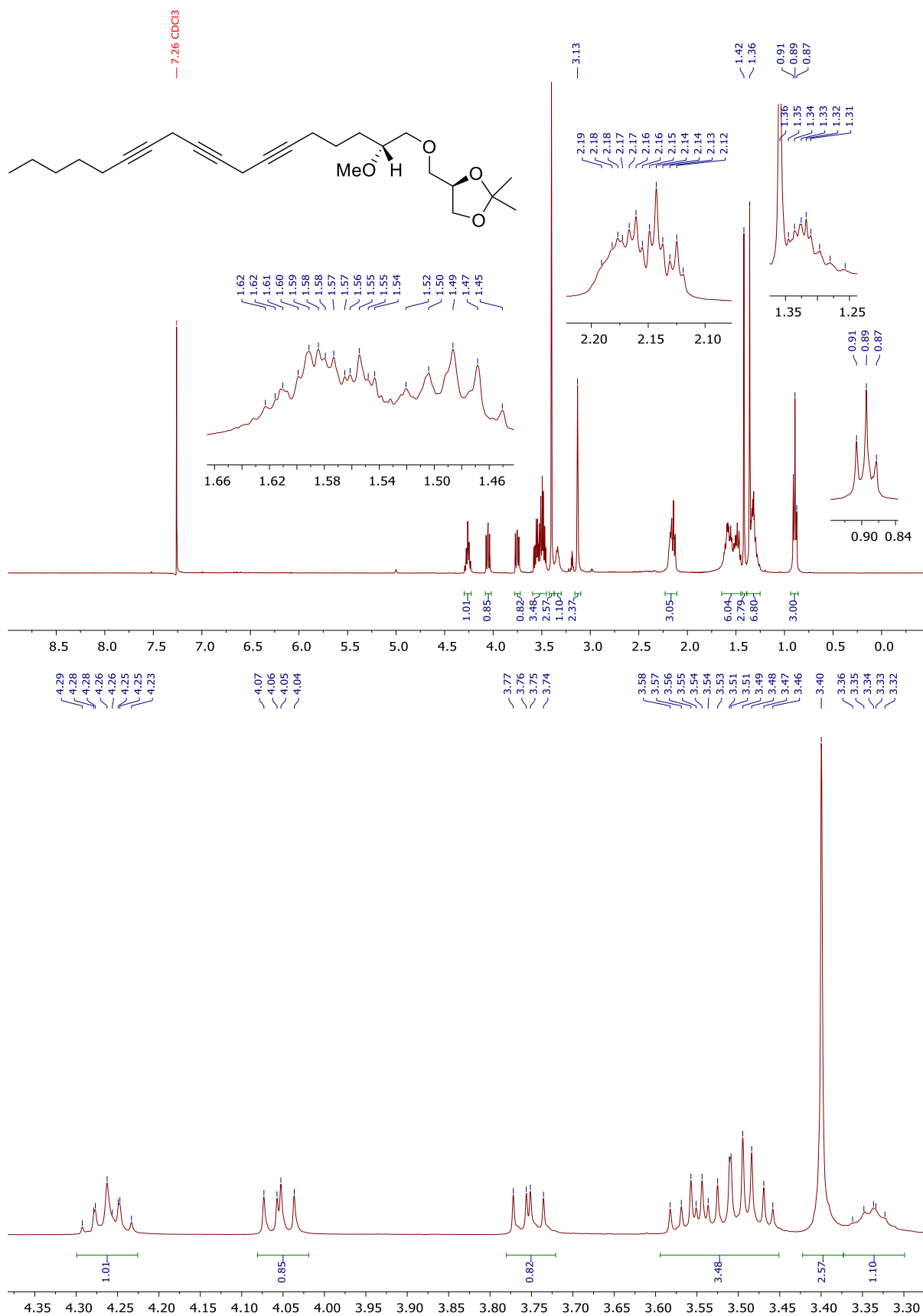
^1H - ^1H COSY spectrum of compound **20**



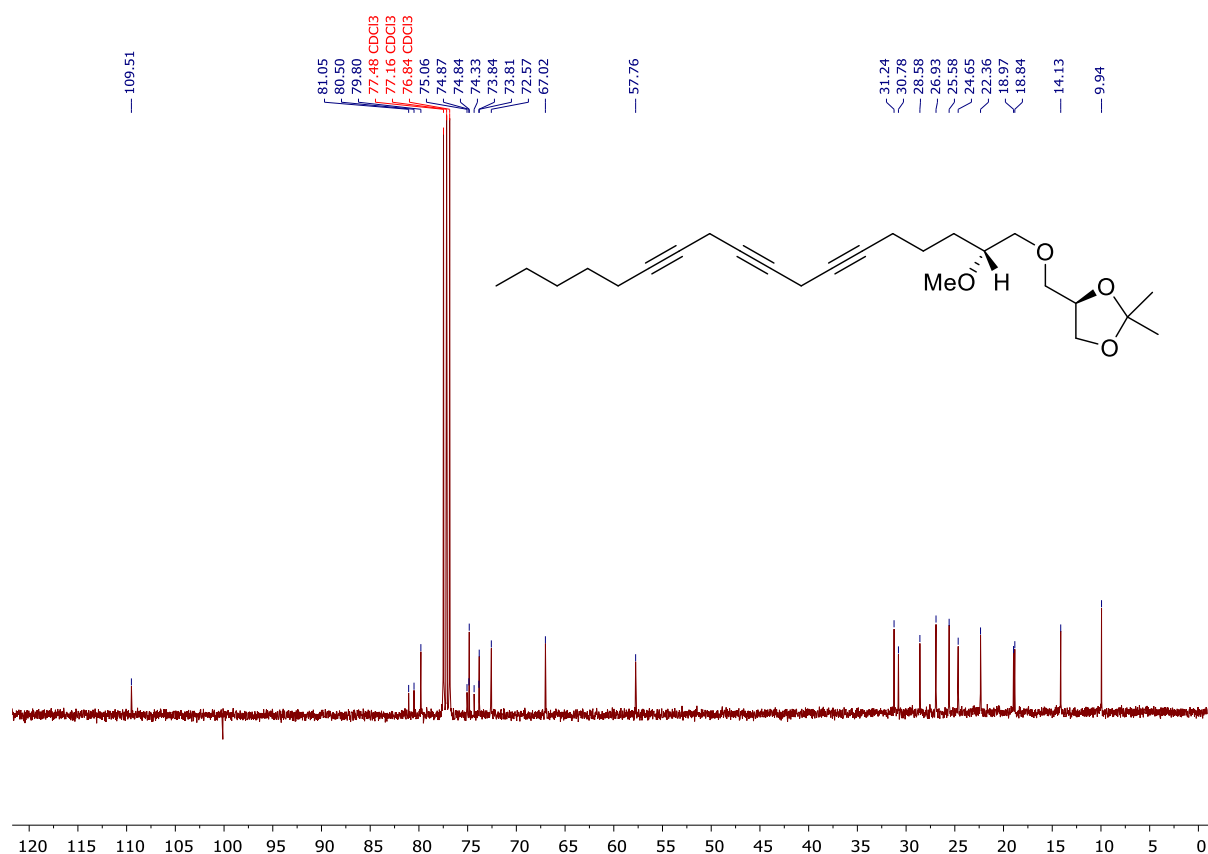
^{13}C - ^1H HSQC spectrum of compound **20**



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

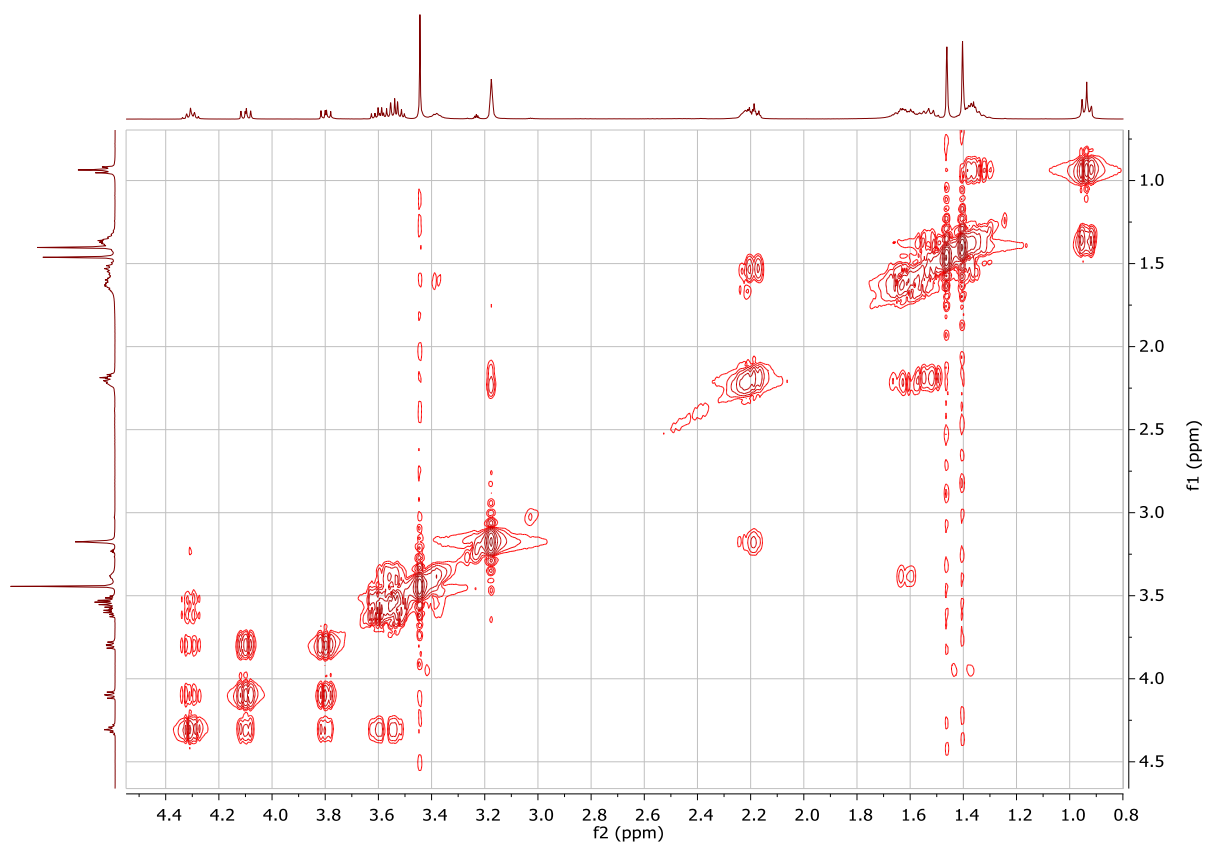


$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **21**

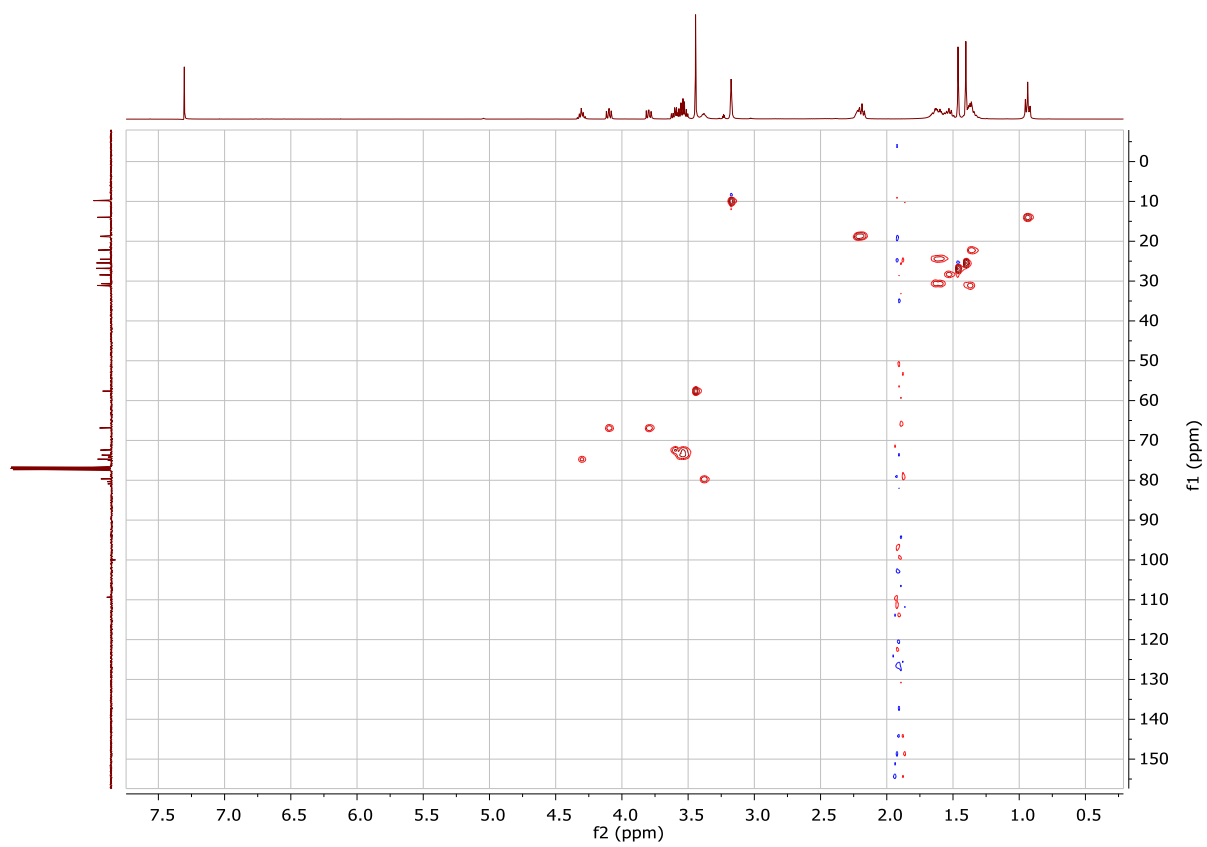


^1H - ^1H COSY spectrum of compound **21**

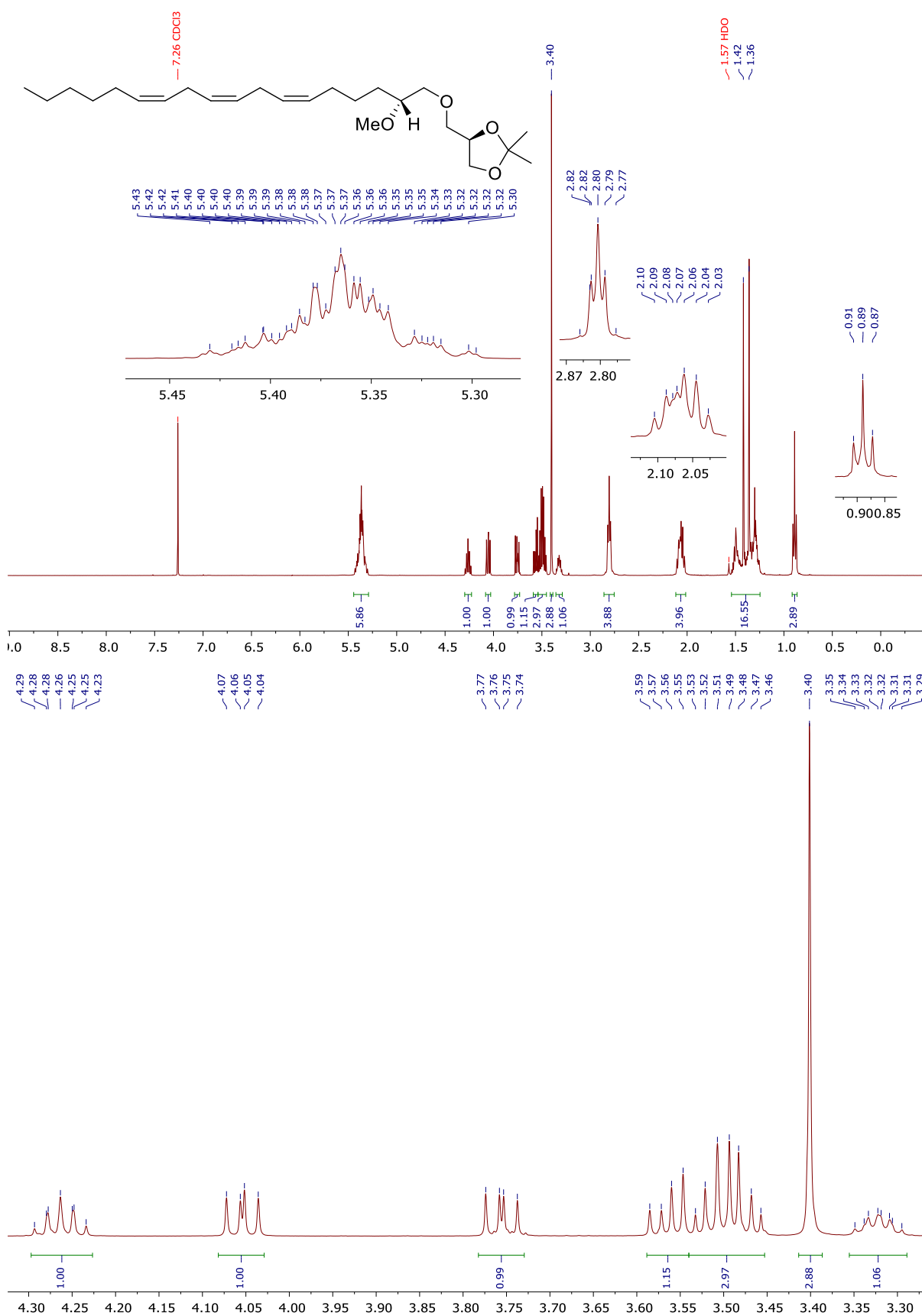




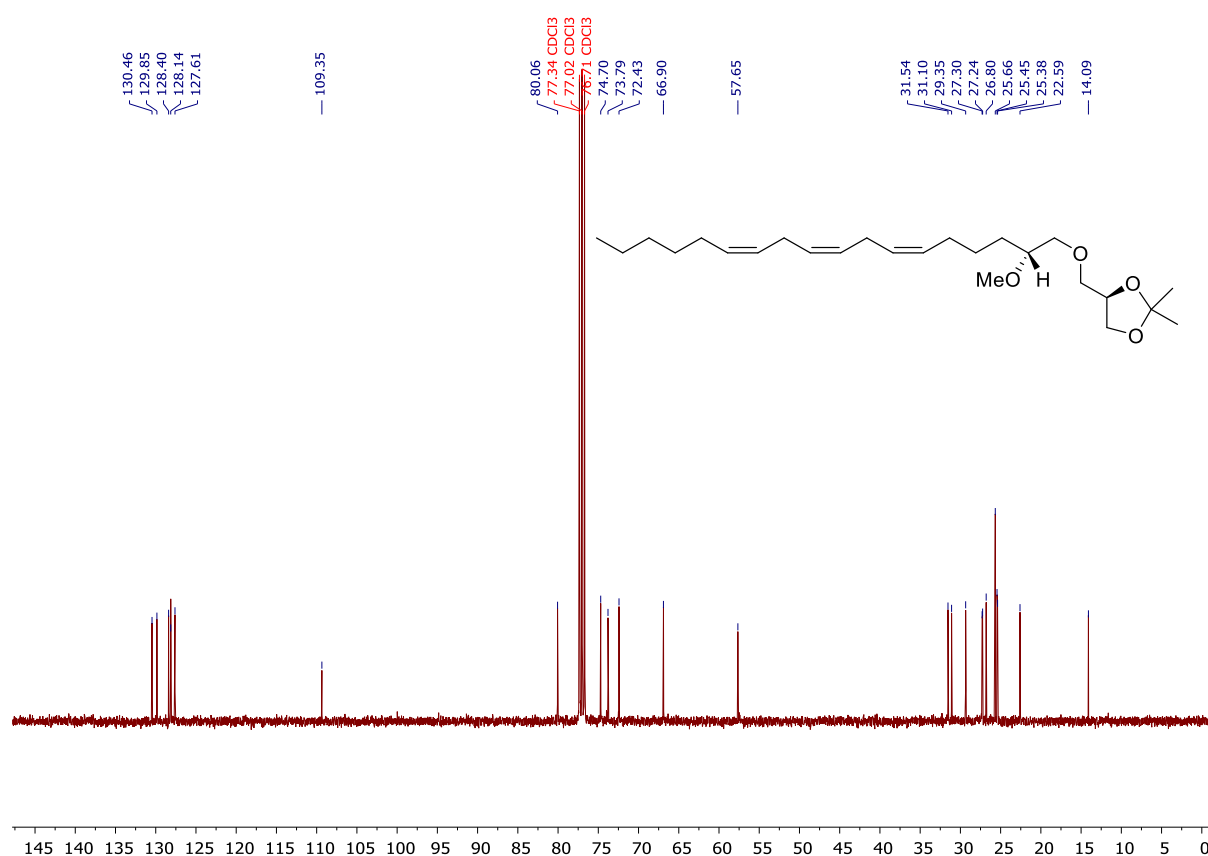
^{13}C - ^1H HSQC spectrum of compound **21**



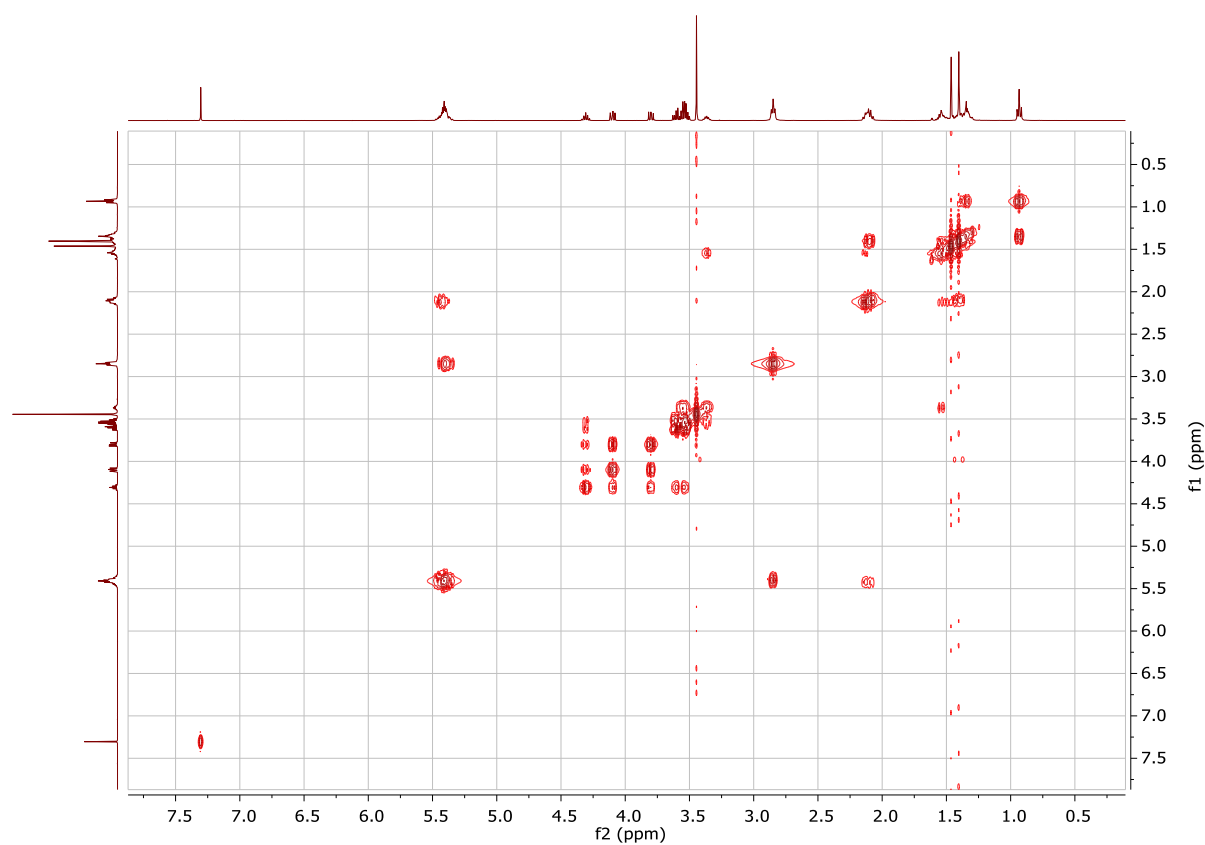
¹H NMR (400 MHz, CDCl₃) of compound **22**

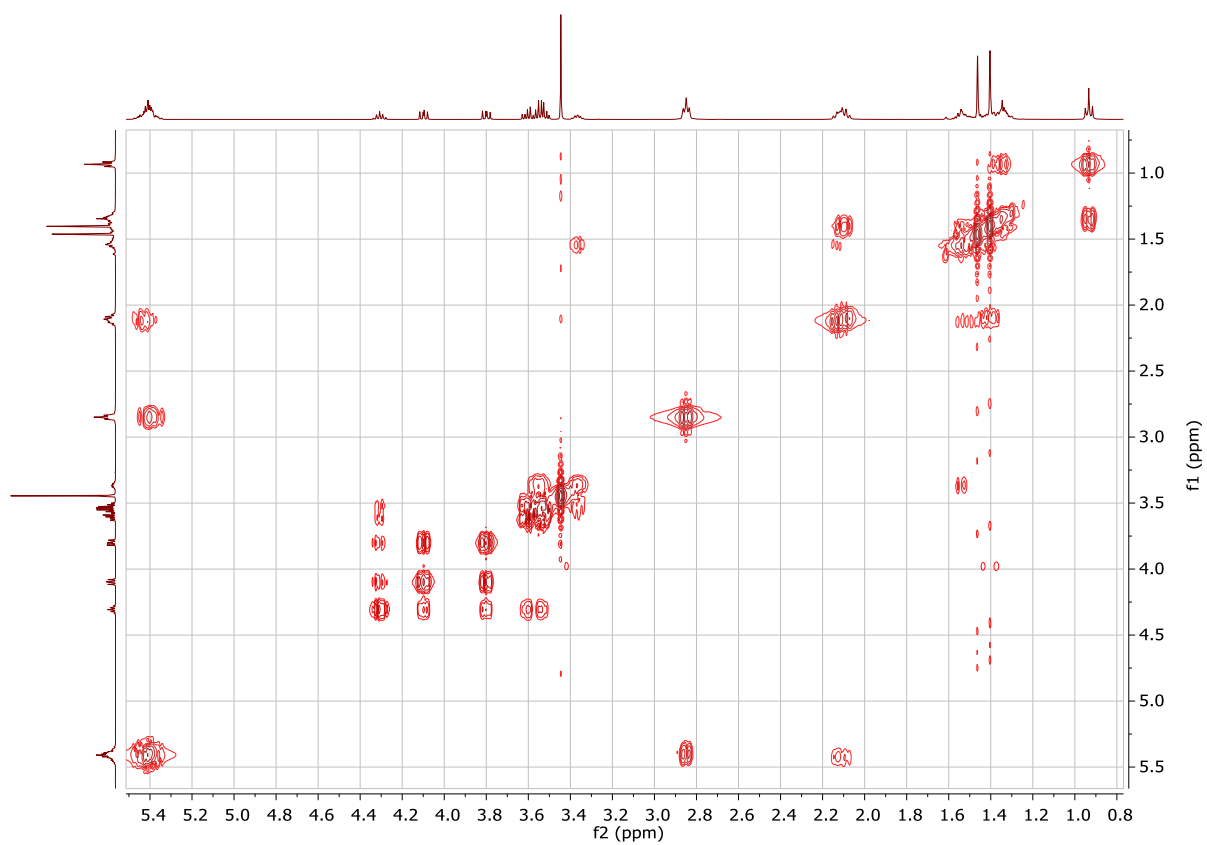


$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) of compound **22**

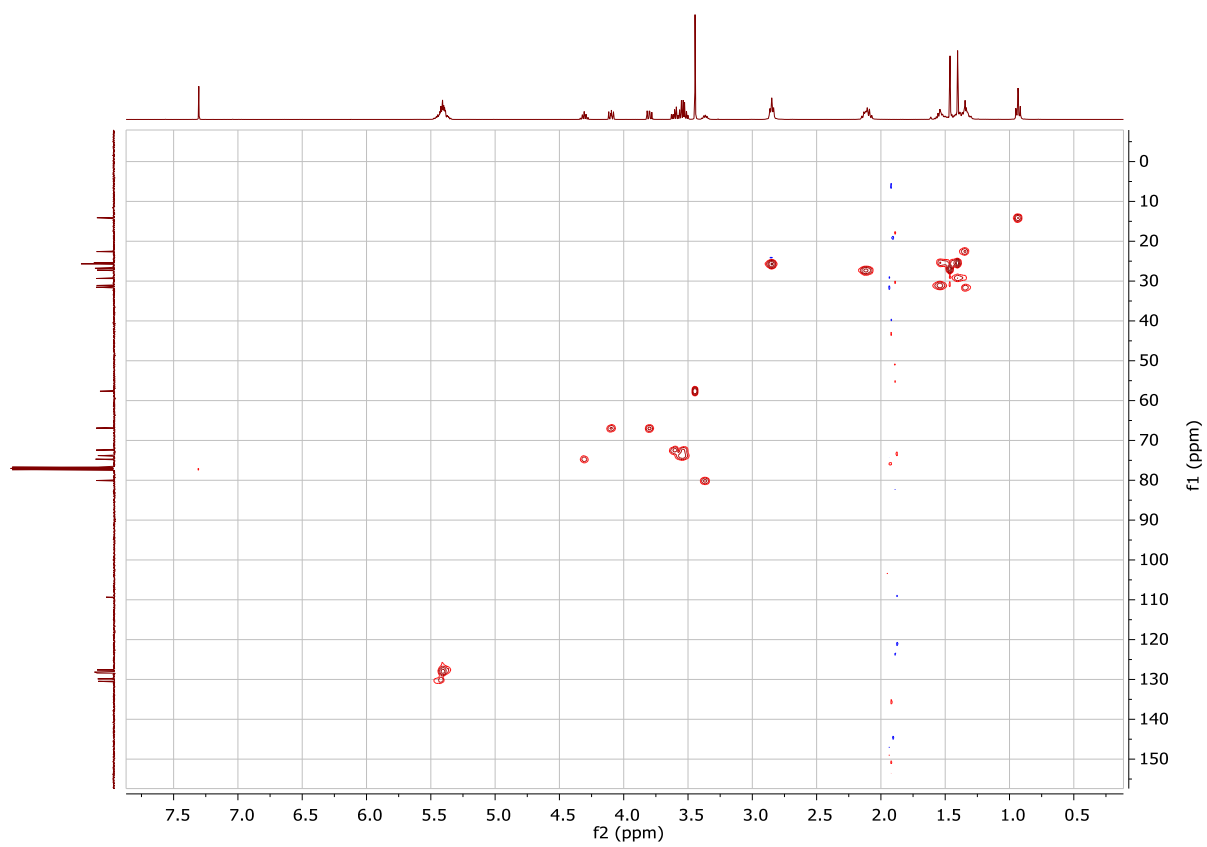


^1H - ^1H COSY spectrum of compound **22**





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



Chemical structure: CCCCC/C=C\CCCC[C@H](CO)CO

¹H NMR spectrum (CDCl₃) showing peaks from 0.8 to 5.5 ppm. The spectrum includes an inset of the 5.3-5.5 ppm region and zoomed-in views of the 2.8-3.0 ppm and 0.85-0.90 ppm regions.

Integration values (from left to right): 1.00, 1.04, 2.07, 2.17, 1.01, 2.95, 1.05.

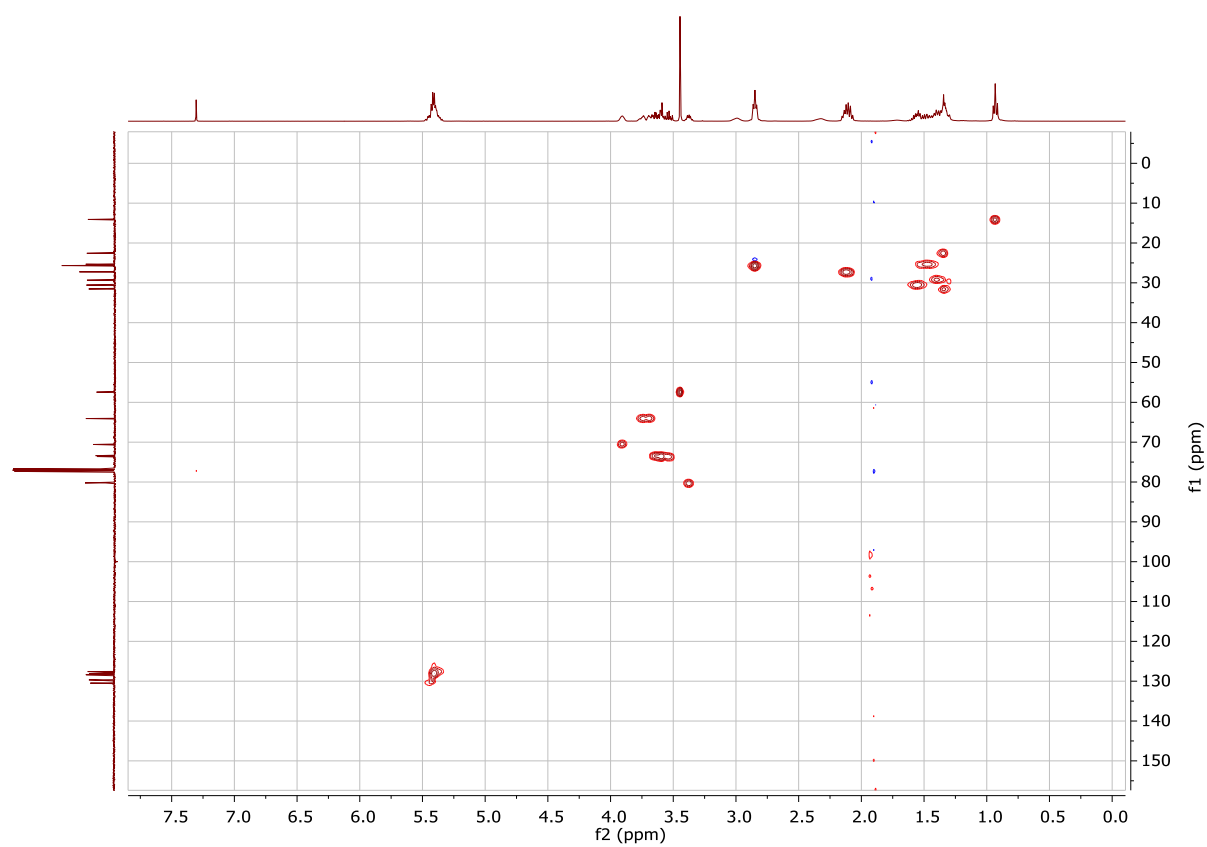
Peak labels (from left to right): 3.88, 3.86, 3.85, 3.73, 3.72, 3.71, 3.69, 3.68, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25, 1.24, 1.23, 1.22, 1.21, 1.20, 1.19, 1.18, 1.17, 1.16, 1.15, 1.14, 1.13, 1.12, 1.11, 1.10, 1.09, 1.08, 1.07, 1.06, 1.05, 1.04, 1.03, 1.02, 1.01, 1.00, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85, 0.84, 0.83, 0.82, 0.81, 0.80, 0.79, 0.78, 0.77, 0.76, 0.75, 0.74, 0.73, 0.72, 0.71, 0.70, 0.69, 0.68, 0.67, 0.66, 0.65, 0.64, 0.63, 0.62, 0.61, 0.60, 0.59, 0.58, 0.57, 0.56, 0.55, 0.54, 0.53, 0.52, 0.51, 0.50, 0.49, 0.48, 0.47, 0.46, 0.45, 0.44, 0.43, 0.42, 0.41, 0.40, 0.39, 0.38, 0.37, 0.36, 0.35, 0.34, 0.33, 0.32, 0.31, 0.30, 0.29, 0.28, 0.27, 0.26, 0.25, 0.24, 0.23, 0.22, 0.21, 0.20, 0.19, 0.18, 0.17, 0.16, 0.15, 0.14, 0.13, 0.12, 0.11, 0.10, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.00.

Chemical structure: COC[C@H](CO)OCC/C=C/C/C=C/C/C=C/C/C=C/C/C=C/C

¹³C NMR peaks (ppm):

- 130.62, 129.81, 128.58, 128.45, 128.20, 127.72
- 80.36, 77.48 CDCl₃, 77.16 CDCl₃, 76.84 CDCl₃, 73.75, 73.52, 70.71
- 64.20, 57.58
- 31.67, 30.70, 29.48, 27.38, 25.80, 25.47, 22.72
- 14.22

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



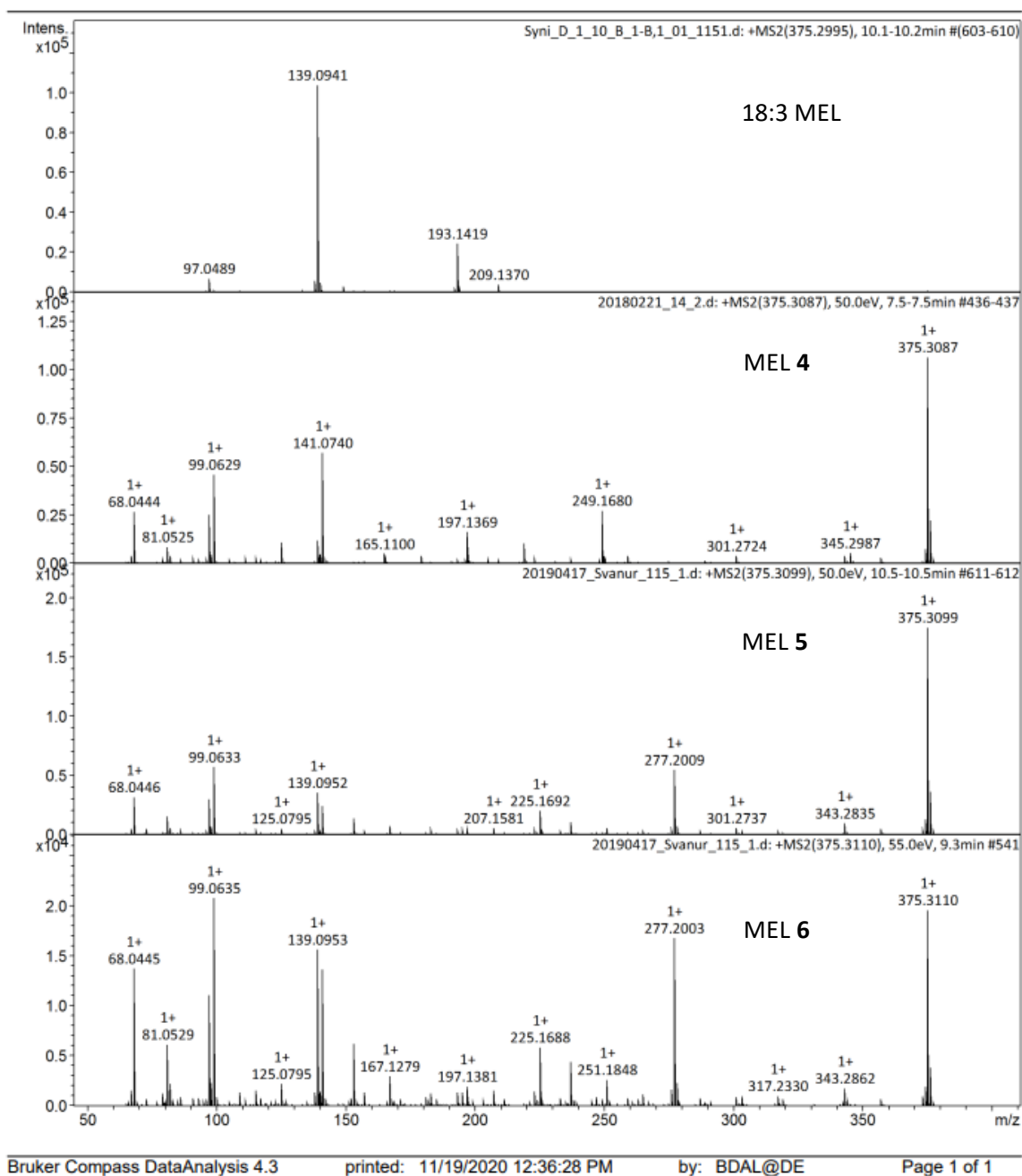


Figure 1S. Comparison of the $[M+Li]^+$ MS/MS fragmentation spectra of the synthesized MELs **4**, **5**, **6** and the 18:3 MEL found in the shark and dogfish liver oil sample (top).