3. RESULTS AND DISCUSSION

Chemical investigation of *Garcinia* plants was divided into two parts. The first part involved isolation, purification and structural elucidation of the constituents from the fruits of *Garcinia scortechinii*. The fruits were extracted with methanol and the methanol extract was then subjected to various chromatography to obtain ten new compounds: four caged-tetraprenylated xanthones (**GF8**, **GF9**, **GF15** and **GF18**), four rearranged xanthones (**GF19**, **GF20**, **GF21** and **GF22**) and two sesquiterpenes (**GF1** and **GF2**), along with fourteen known compounds: eleven caged-polyprenylated xanthones (**GF3**, **GF4**, **GF5**, **GF6**, **GF10**, **GF11**, **GF12**, **GF13**, **GF14**, **GF16** and **GF17**), two biflavonoids (**GF23** and **GF24**) and one sesquiterpene (**GF7**). The second part dealt with the compounds isolated from the fruits of *Garcinia hanburyi*. Chromatographic separation of the crude methanol extract of its fruits afforded one new caged-tetraprenylated xanthone (**GF27**) together with four known caged-tetraprenylated xanthones (**GF25**, **GF26**, **GF28** and **GF29**). Their structures were elucidated by analysis of 1D and 2D NMR spectroscopic data. The ^{1}H and ^{13}C NMR signals were assigned from DEPT, HMQC and HMBC spectra. For known compounds, their ^{1}H NMR data and optical rotation were compared with those reported in the literatures.

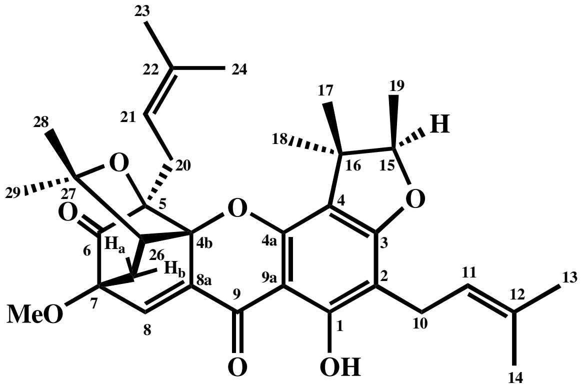
3.1 Characteristic spectroscopic data of caged-polyprenylated xanthones isolated from *G. scortechinii*

Caged-polyprenylated xanthones isolated from the twigs (Rukachaisirikul, 2000), latex (Rukachaisirikul, 2003b) and stem bark (Rukachaisirikul, 2005) of *G. scortechinii* were 7-methoxy caged-polyprenylated xanthones with a 2,3,3-trimethyldihydrofuran unit attached at C-3 and C-4 by forming an ether linkage at C-3. They were divided into three types: the ones with and without a C8/C8a double bond and a degraded caged-tetraprenylated xanthone. They were primarily distinguished by UV absorption bands. The caged-polyprenylated xanthones with the

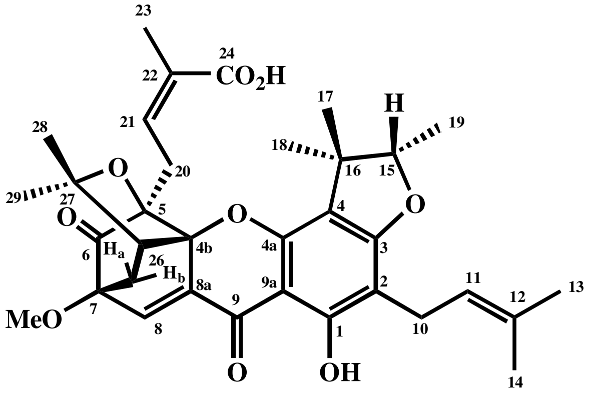
C8/C8a double bond and the degraded caged-tetraprenylated xanthone showed a typical UV absorption band in the range of 360-368 nm due to a conjugated carbonyl chromophore while the ones lacking the C8/C8a double bond gave a characteristic absorption band at shorter wavelength (λ_{max} 304 nm). The IR spectrum exhibited absorption bands of a hydroxyl group of a carboxylic acid (in the range of 3600-2500 cm^{-1}), an unconjugated carbonyl group (approximately at 1746 cm^{-1}) and a chelated *ortho*-hydroxyl carbonyl group (approximately at 1636 cm^{-1}).

Caged-polyprenylated xanthones with the C8/C8a double bond and the degraded caged-tetraprenylated xanthone showed signals for a chelated hydroxy proton (δ_H 13.00, 1-OH), an olefinic proton of an α, β-unsaturated carbonyl moiety at δ_H 7.58 (H-8) and characteristic signals for $-OC(Me)_2-CHCH_2-C-$ unit of a caged-prenylated moiety at δ_H 2.55 (*d*, *J* = 9.6 Hz, 1H, H-26), 2.33 (*dd*, *J* = 12.8 and 1.4 Hz, 1H, H_a-25), 1.65 (*dd*, *J* = 12.8 and 9.6 Hz, 1H, H_b-25), 1.71 (*s*, 3H, Me-28) and 1.29 (*s*, 3H, Me-29) in the ^1H NMR spectrum [see scortechinone A (**1**) (Rukachaisirikul, 2000)]. This moiety was assigned to be located on C-4b, C-5 and C-7 due to the HMBC correlations of the olefinic proton, H-8, with C-25, the methylene protons, H_a-25 and H_b-25, with C-4b, C-6, C-7 and C-8 and the methine proton, H-26, with C-4b, C-5 and C-7. The chemical shift values of Me-28 and Me-29 were assigned by the NOEDIFF data observed between Me-28 and H-26 and between Me-29 and H_a-25 as well as the methoxy protons ($7-OCH_3$). The ^1H NMR spectrum of caged-prenylated xanthones also showed characteristic signals for a 2,3,3-trimethylhydrofuran unit: the *quartet* signal of the methine proton (δ_H 4.37, *J* = 6.6 Hz, H-15), the *doublet* signal of the methyl protons (δ_H 1.41, *J* = 6.6 Hz, Me-19) together with two *singlets* of two *gem*-dimethyl groups [δ_H 1.16 (Me-17) and 1.58 (Me-18)]. This unit was fused to the aromatic ring by linkage of its *gem*-dimethyl carbon and ring oxygen atom with C-4 and C-3, respectively, according to the HMBC correlations of Me-17 and Me-18 with C-4 together with the chemical shift values of C-3 and C-4. The relative stereochemistry of the methine proton, H-15, of the dihydrofuran unit in all caged-polyprenylated xanthones was assigned by NOEDIFF data (Rukachaisirikul, 2003b). The spatial arrangement at either α- or β-position was further supported by the ^1H and ^{13}C chemical shift values of the *gem*-dimethyl groups of the dihydrofuran unit. In the case of the dihydrofurans with the *β*-methine proton, such as scortechinone B (**2**), the *gem*-dimethyl groups appeared at similar δ_H values, but distinctly different δ_C values ($\Delta\delta_C$ ca 8 ppm). In contrast, the *gem*-dimethyl groups of the dihydrofurans with the *α*-methine proton, such as scortechinone A (**1**), gave differences in both ^{1}H and ^{13}C signals with approximately 0.4 and 3 ppm, respectively.

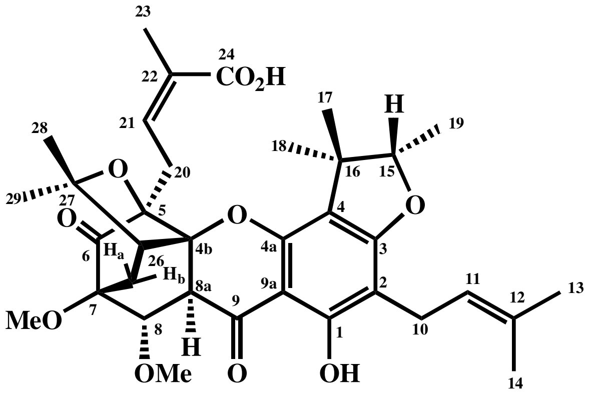
Caged-polyprenylated xanthones lacking the C8/C8a double bond displayed two additional methine-proton signals at δ_H 4.46 (*s*, 1H, H-8) and 3.16 (*s*, 1H, H-8a) and one additional methoxy-proton signal at δ_H 3.36 (*s*, 3H, 8-OCH$_3$) in the ^{1}H NMR spectrum [see scortechinone I (**3**) (Rukachaisirikul, 2003b)]. The methoxyl group was assigned to be at C-8 due to a HMBC correlation between the methoxy protons (8-OCH$_3$) and C-8. The relative stereochemistry of H-8 and H-8a was determined by NOEDIFF data. Irradiation of the methylene protons, H$_b$-25, enhanced the signals of the oxymethine proton, H-8, but did not affect the signals of the methoxy protons (8-OCH$_3$) while irradiation of H-8a enhanced the signals of H-8, 8-OCH$_3$ and H-21 of the C-5 3-carboxybut-2-enyl unit. These results indicated that H-8 and H-8a were *trans* and located at *β*- and *α*-position, respectively.



1: scortechinone A



2: scortechinone B

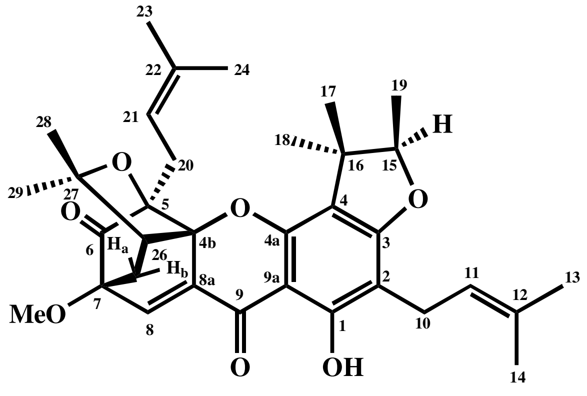


3: scortechinone I

3.2 Structural determination of compounds isolated from the fruits of *G. scortechinii*

3.2.1 Compound GF3

Compound **GF3** was isolated as a yellow gum. The UV spectrum (**Figure 3**) (λ_{max} 361 nm) indicated the presence of a caged-polyprenylated xanthone nucleus with the C8/C8a double bond while its IR spectrum (**Figure 4**) exhibited absorption bands at 3648 (a hydroxyl group), 1746 (an unconjugated carbonyl group) and 1635 cm^{-1} (a chelated *ortho*-hydroxyl carbonyl group). **GF3** was identified as scortechinone A (**1**), which was previously isolated from the twigs (Rukachaisirikul, 2000), latex (Rukachaisirikul, 2003b) and stem bark (Rukachaisirikul, 2005) of *G. scortechinii*, by comparison of its ^{1}H NMR data (**Figure 5**) (**Table 93**) and silica gel TLC analysis with those of scortechinone A (**1**).



1

Table 93 The ^{1}H NMR data of scortechinone A and **GF3**

Position	Scortechinone A δ_H (*mult.*, J_{Hz})[a]	**GF3** δ_H (*mult.*, J_{Hz})[b]
1-OH	13.15 (*s*)	13.16 (*s*)
7-OCH$_3$	3.62 (*s*)	3.62 (*s*)
H-8	7.49 (*d*, 1.4)	7.49 (*d*, 1.0)
H-10	3.22 (*dm*, 7.2)	3.21 (*d*, 7.0)
H-11	5.22 (*th*, 7.2, 1.4)	5.21 (*tm*, 7.0)
Me-13	1.68 (*brd*, 1.2)	1.67 (*s*)
Me-14	1.75 (*brd*, 1.2)	1.75 (*s*)
H-15	4.37 (*q*, 6.4)	4.36 (*q*, 6.5)
Me-17	1.16 (*s*)	1.16 (*s*)
Me-18	1.58 (*s*)	1.58 (*s*)
Me-19	1.41 (*d*, 6.4)	1.41 (*d*, 6.5)
H$_a$-20	2.69 (*ddh*, 14.4, 4.5, 1.5)	2.68 (*dm*, 14.0)
H$_b$-20	2.55 (*dd*, 14.4, 10.5)	2.55 (*dd*, 14.0, 10.0)
H-21	4.39 (*m*)	4.37 (*m*)
Me-23	1.36 (*brt*, 1.5)	1.36 (*s*)
Me-24	1.07 (*brt*, 1.4)	1.06 (*s*)
H$_a$-25	2.33 (*dd*, 12.8, 1.4)	2.33 (*d*, 13.5)
H$_b$-25	1.65 (*dd*, 12.8, 9.6)	1.65 (*dd*, 13.5, 9.5)

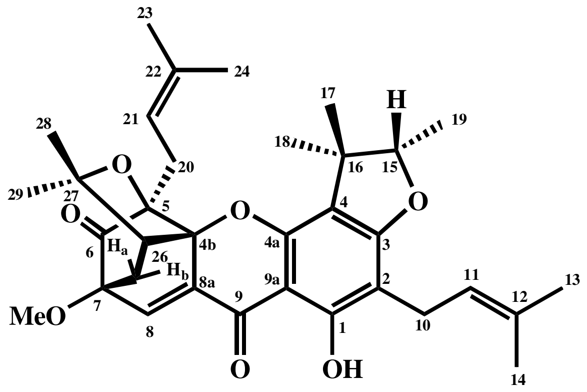
Table 93 (continued)

Position	Scortechinone A δ_H (*mult.*, J_{Hz})[a]	**GF3** δ_H (*mult.*, J_{Hz})[b]
H-26	2.55 (*d*, 9.6)	2.55 (*d*, 9.5)
Me-28	1.71 (*s*)	1.71 (*s*)
Me-29	1.29 (*s*)	1.28 (*s*)

[a]400 MHz ^{1}H NMR spectrum in $CDCl_3$, [b]500 MHz ^{1}H NMR spectrum in $CDCl_3$

3.2.2 Compound GF4

Compound **GF4**, a yellow gum, was found to have a molecular formula of $C_{34}H_{42}O_7$ by EIMS (*m/z* 562, $[M]^+$) (**Figure 6**). Its IR (**Figure 8**) and UV (**Figure 7**) spectral data were similar to those of **GF3** (scortechinone A) with the C8/C8a double bond. Their NMR spectral data (**Figure 9**) (**Table 94**) were different only in chemical-shift values of ^{1}H and ^{13}C signals of a 2,3,3-trimethylhydrofuran unit. The attachment of all substituents was found to be identical to **GF3**, according to HMBC data (**Figure 15**) (**Table 94**). The NOE enhancement observed between the methine proton (δ_H 4.55, H-15) and the methyl protons (δ_H 1.42, Me-17) (**Figure 13**) and between the methyl protons (δ_H 1.49, Me-18) and the methylene proton (δ_H 2.54, H_b-20) of the C-5 prenyl group (**Figure 12**) suggested that H-15 was at *β*-position. Therefore, **GF4** (**4**) was the C-15 epimer of **GF3**, previously reported as scortechinone L.



4

Table 94 The NMR data of compound **GF4**

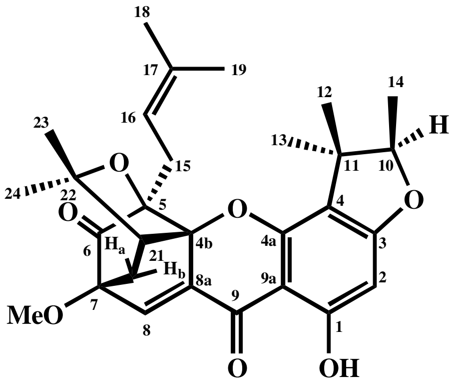
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
1-OH	13.24 (*s*)	163.27 (C)	C-1, C-2, C-9a
2		105.79 (C)	
3		166.54 (C)	
4		111.91 (C)	
4a		154.32 (C)	
4b		89.30 (C)	
5		84.36 (C)	
6		202.28 (C=O)	
7		84.88 (C)	
7-OCH$_3$	3.64 (*s*)	53.91 (CH$_3$)	C-7
8	7.51 (*d*, 1.5)	133.91 (CH)	C-4b, C-6, C-7, C-8a, C-9
8a		132.42 (C)	
9		178.11 (C=O)	
9a		101.36 (C)	
10	3.22 (*d*, 7.0)	21.34 (CH$_2$)	C-1, C-2, C-3, C-11, C-12
11	5.23 (*tm*, 7.0)	121.62 (CH)	C-10, C-13, C-14
12		132.01 (C)	
13	1.68 (*s*)	25.69 (CH$_3$)	C-2, C-11, C-12, C-14
14	1.76 (*s*)	17.79 (CH$_3$)	C-11, C-12, C-13
15	4.55 (*q*, 6.5)	91.24 (CH)	C-3, C-4
16		43.70 (C)	
17	1.42 (*s*)	28.17 (CH$_3$)	C-4, C-15, C-16, C-18
18	1.49 (*s*)	20.11 (CH$_3$)	C-4, C-15, C-16, C-17
19	1.30 (*d*, 6.5)	16.35 (CH$_3$)	C-15, C-16
20	a: 2.67 (*dm*, 14.5)	28.92 (CH$_2$)	C-5, C-21
	b: 2.54 (*dd*, 14.5, 10.0)		C-5, C-6, C-21, C-22
21	4.36 (*dm*, 10.0)	117.08 (CH)	
22		135.49 (C)	
23	1.36 (*s*)	25.44 (CH$_3$)	C-21, C-22, C-24
24	1.02 (*s*)	16.66 (CH$_3$)	C-21, C-22, C-23
25	a: 2.34 (*d*, 13.5)	30.69 (CH$_2$)	C-4b, C-7, C-8, C-27
	b: 1.67 (*dd*, 13.5, 9.5)		C-5, C-6, C-27
26	2.58 (*d*, 9.5)	49.95 (CH)	C-4b, C-5, C-6, C-7
27		83.18 (C)	

Table 94 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
28	1.72 (*s*)	30.94 (CH_3)	C-20, C-26, C-27
29	1.29 (*s*)	28.98 (CH_3)	C-26, C-27, C-28

3.2.3 Compound GF5

Compound **GF5** was obtained as a yellow gum. The UV spectrum (**Figure 16**) (λ_{max} 358 nm) showed the presence of a caged-polyprenylated xanthone chromophore. Its IR spectrum (**Figure 17**) exhibited absorption bands at 1746 (an unconjugated carbonyl group) and 1641 cm^{-1} (a chelated *ortho*-hydroxyl carbonyl group). Comparison of its ^{1}H NMR data (**Figure 18**) (**Table 95**) and silica gel TLC analysis with those of scortechinone D, previously isolated from latex (Rukachaisirikul, 2003b) and stem bark (Rukachaisirikul, 2005) of *G. scortechinii* indicated that **GF5** was scortechinone D (**5**).



5

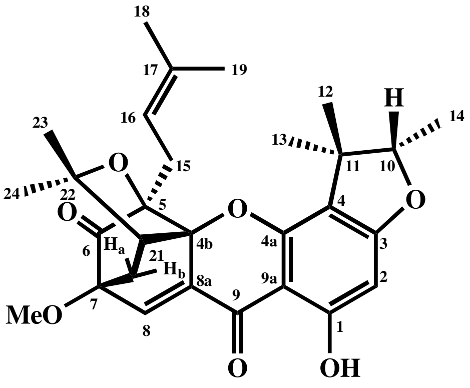
Table 95 The ^{1}H NMR data of scortechinone D and **GF5**

Position	Scortechinone D δ_H (*mult.*, J_{Hz})^a	**GF5** δ_H (*mult.*, J_{Hz})^b
1-OH	13.03 (*s*)	13.03 (*s*)
7-OCH_3	3.64 (*s*)	3.64 (*s*)
H-2	6.04 (*s*)	6.04 (*s*)
H-8	7.52 (*d*, 1.5)	7.52 (*d*, 1.5)
H-10	4.40 (*q*, 6.5)	4.39 (*q*, 6.5)
Me-12	1.17 (*s*)	1.17 (*s*)
Me-13	1.59 (*s*)	1.59 (*s*)
Me-14	1.41 (*d*, 6.5)	1.41 (*d*, 6.5)
H_a-15	2.71 (*dm*, 14.5)	2.71 (*dm*, 14.5)
H_b-15	2.58 (*dd*, 14.5, 10.5)	2.58 (*dd*, 14.5, 10.5)
H-16	4.38 (*dm*, 10.5)	4.38 (*dm*, 10.5)
Me-18	1.38 (*brs*)	1.37 (*t*, 1.5)
Me-19	1.09 (*brs*)	1.09 (*s*)
H_a-20	2.36 (*d*, 13.0)	2.36 (*d*, 13.0)
H_b-20	1.66 (*dd*, 13.0, 9.5)	1.66 (*dd*, 13.0, 9.5)
H-21	2.59 (*d*, 9.5)	2.59 (*d*, 9.5)
Me-23	1.72 (*s*)	1.72 (*s*)
Me-24	1.30 (*s*)	1.30 (*s*)

[a, b]500 MHz ^{1}H NMR spectrum in $CDCl_3$

3.2.4 Compound GF6

Compound **GF6** was obtained as a yellow gum. The caged-polyprenylated xanthone chromophore was evident by its UV (**Figure 19**) absorption band at λ_{max} 359 nm. The unconjugated carbonyl and chelated *ortho*-hydroxyl carbonyl stretching frequencies were found at 1745 and 1640 cm^{-1}, respectively, in the IR spectrum (**Figure 20**). **GF6** was identified as scortechinone E (**6**) by direct comparison of its ^{1}H NMR data (**Figure 21**) (**Table 96**) and TLC chromatogram with those of scortechinone E that was obtained from the latex of *G. scortechinii* (Rukachaisirikul, 2003b).



6

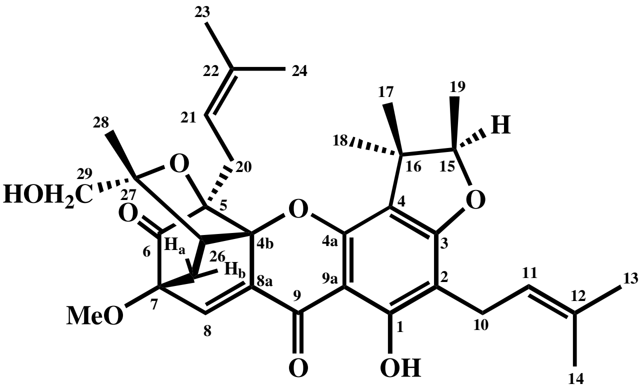
Table 96 The ^{1}H NMR data of scortechinone E and **GF6**

Position	Scortechinone E δ_{H} (*mult.*, J_{Hz})[a]	**GF6** δ_{H} (*mult.*, J_{Hz})[b]
1-OH	13.09 (*s*)	13.09 (*s*)
7-OCH$_3$	3.64 (*s*)	3.64 (*s*)
H-2	6.03 (*s*)	6.04 (*s*)
H-8	7.52 (*d*, 1.0)	7.52 (*d*, 1.0)
H-10	4.55 (*q*, 6.5)	4.55 (*q*, 6.5)
Me-12	1.42 (*s*)	1.42 (*s*)
Me-13	1.49 (*s*)	1.49 (*s*)
Me-14	1.30 (*d*, 6.5)	1.31 (*d*, 6.5)
H$_a$-15	2.68 (*dm*, 14.5)	2.69 (*dm*, 14.0)
H$_b$-15	2.55 (*dd*, 14.5, 11.0)	2.55 (*dd*, 14.0, 10.5)
H-16	4.36 (*dm*, 11.0)	4.36 (*dm*, 10.5)
Me-18	1.38 (*brs*)	1.38 (*t*, 1.5)
Me-19	1.07 (*brs*)	1.07 (*brs*)
H$_a$-20	2.36 (*dd*, 13.0, 1.0)	2.36 (*dd*, 13.0, 1.5)
H$_b$-20	1.67 (*dd*, 13.0, 9.5)	1.67 (*dd*, 13.0, 9.5)
H-21	2.61 (*d*, 9.5)	2.61 (*d*, 9.5)
Me-23	1.72 (*s*)	1.72 (*s*)
Me-24	1.29 (*s*)	1.30 (*s*)

[a, b] 500 MHz ^{1}H NMR spectrum in CDCl$_3$

3.2.5 Compound GF8

Compound **GF8**, a yellow gum, was found to have a molecular formula of $C_{34}H_{42}O_8$ by EIMS (*m/z* 578, $[M]^+$) (**Figure 22**). Its IR (**Figure 24**) and UV (**Figure 23**) spectral data were similar to those of **GF3** (scortechinone A) with the C8/C8a double bond. Their ^1H NMR spectra (**Figure 25**) (**Table 97**) were also similar except for the fact that one *singlet* methyl signal was replaced by separated methylene signals of a hydroxymethyl group (δ_H 3.56 and 3.65 both as *doublet*, J = 11.5 Hz). The presence of the hydroxymethyl group was confirmed by a signal of an oxymethylene carbon at δ_C 67.88 in the ^{13}C NMR spectrum (**Figure 26**) (**Table 97**). The ^{13}C NMR, DEPT (**Figure 27**) and HMQC (**Figure 29**) spectra showed resonances for 16 quaternary, 5 methine, 4 methylene and 9 methyl carbons. The location of the hydroxymethyl group was assigned to be at C-27 (δ_C 85.16) due to the HMBC correlations between the oxymethylene protons ($H_{a,b}$-29) and C-26 (δ_C 41.36), C-27 and C-28 (δ_C 25.13). Irradiation of H_a-25 (δ_H 2.84, *d*, J = 12.5 Hz) (**Figure 28**), in a NOEDIFF experiment, enhanced signal intensity of H_b-25 (δ_H 1.76, *dd*, J = 12.5 and 10.0 Hz) and $H_{a,b}$-29, not H-26 (δ_H 2.57, *d*, J = 10.0 Hz), suggesting that the hydroxymethyl substituent was located at α-position. The attachment of other substituents and relative stereochemistry were identical to those of **GF3**, based on HMBC correlations (**Figure 30**) (**Table 97**) and NOEDIFF data (**Table 97**), respectively. The position of H-15 (δ_H 4.50, *q*, J = 6.5 Hz) of the dihydrofuran ring at α-position was further confirmed by the ^1H and ^{13}C chemical shift values of Me-17 (δ_H 1.19, *s* and δ_C 21.11) and Me-18 (δ_H 1.55, *s* and δ_C 25.24). Therefore, **GF8** had the structure **7**, a new caged-tetraprenylated xanthone which had an α-hydroxymethyl substituent at C-27.



7

Table 97 The NMR data of compound **GF8**

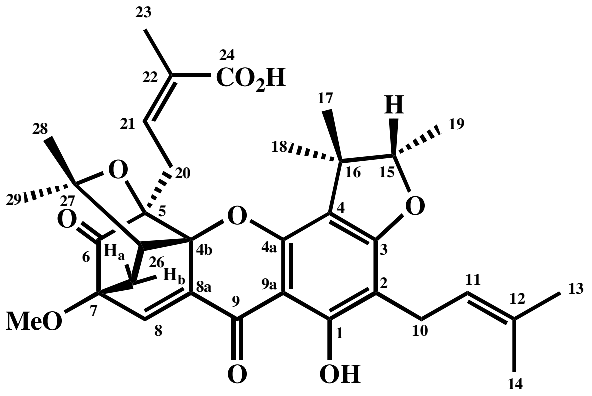
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1-OH	12.87 (*s*)	162.96 (C)	C-1, C-2, C-9a	
2		105.35 (C)		
3		166.92 (C)		
4		113.71 (C)		
4a		154.28 (C)		
4b		83.73 (C)		
5		84.86 (C)		
6		198.88 (C=O)		
7		87.96 (C)		
7-OCH$_3$	3.50 (*s*)	51.83 (CH$_3$)	C-7	H-8, Me-28
8	7.08 (*d*, 1.0)	134.92 (CH)	C-4b, C-6, C-8a, C-9	7-OCH$_3$
8a		131.49 (C)		
9		176.47 (C=O)		
9a		101.91 (C)		
10	3.20 (*d*, 7.0)	21.40 (CH$_2$)	C-1, C-2, C-3, C-11, C-12	Me-14
11	5.25 (*tm*, 7.0)	121.71 (CH)	C-10, C-13, C-14	H-10, Me-13
12		132.03 (C)		
13	1.69 (*s*)	25.80 (CH$_3$)	C-11, C-12, C-14	H-11
14	1.75 (*s*)	17.73 (CH$_3$)	C-11, C-12, C-13	H-10
15	4.50 (*q*, 6.5)	90.94 (CH)	C-18	Me-18, Me-19
16		43.74 (C)		

Table 97 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
17	1.19 (*s*)	21.11 (CH_3)	C-4, C-15, C-16, C-18	Me-18
18	1.55 (*s*)	25.24 (CH_3)	C-4, C-15, C-16, C-17	H-15, $H_{a,b}$-20, Me-17
19	1.38 (*d*, 6.5)	14.53 (CH_3)	C-15, C-16	H-15, Me-17
20	a: 2.66 (*dd*, 13.5, 10.0)	28.12 (CH_2)	C-5, C-6, C-21, C-22	H-21
	b: 2.62 (*dm*, 13.5)		C-5, C-6, C-21, C-22	H-21
21	4.48 (*m*)	117.84 (CH)	C-24	Me-23
22		136.45 (C)		
23	1.59 (*s*)	25.76 (CH_3)	C-21, C-22, C-24	H-21, $H_{a,b}$-29
24	1.61 (*s*)	17.86 (CH_3)	C-22	H_b-20, $H_{a,b}$-29
25	a: 2.84 (*d*, 12.5)	33.80 (CH_2)	C-4b, C-7, C-27	H_b-25, $H_{a,b}$-29
	b: 1.76 (*dd*, 12.5, 10.0)		C-4b, C-7, C-27	H_a-25, H-26
26	2.57 (*d*, 10.0)	41.36 (CH)	C-4b, C-7, C-25, C-28	H_b-25
27		85.16 (C)		
28	1.41 (*s*)	25.13 (CH_3)	C-26, C-27	H-26, $H_{a,b}$-29, 7-OCH_3
29	a: 3.65 (*d*, 11.5)	67.88 (CH_2)	C-26, C-27, C-28	H_a-25, H_b-29, Me-28
	b: 3.56 (*d*, 11.5)		C-26, C-27, C-28	H_a-29, Me-24, Me-28

3.2.6 Compound GF16

Compound **GF16** was isolated as a yellow gum. An UV absorption band (**Figure 31**) at λ_{max} 363 nm indicated the presence of a caged-polyprenylated xanthone nucleus with the C8/C8a double bond while its IR spectrum (**Figure 32**) exhibited absorption bands at 3500-2500 (a hydroxyl group of a carboxylic acid), 1744 (an unconjugated carbonyl group), 1689 (an α,β-unsaturated carboxyl group) and 1633 cm^{-1} (a chelated *ortho*-hydroxyl carbonyl group). **GF16** was identified as scortechinone B (**2**), which was previously isolated from the twigs (Rukachaisirikul, 2000), latex (Rukachaisirikul, 2003b) and stem bark (Rukachaisirikul, 2005) of *G. scortechinii*, by comparison of its ^{1}H NMR data (**Figure 33**) (**Table 98**) and silica gel TLC analysis with those of scortechinone B (**2**).



2

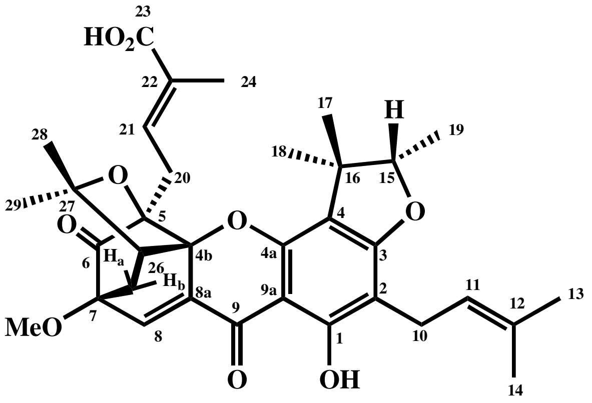
Table 98 The ^{1}H NMR data of scortechinone B and **GF16**

Position	Scortechinone B δ_H (*mult.*, J_{Hz})[a]	**GF16** δ_H (*mult.*, J_{Hz})[b]
1-OH	13.10 (*s*)	13.14 (*s*)
7-OCH$_3$	3.52 (*s*)	3.63 (*s*)
H-8	7.56 (*d*, 1.2)	7.57 (*d*, 1.0)
H$_a$-10	3.17 (*ddm*, 14.4, 7.2)	3.18 (*d*, 7.0)
H$_b$-10	3.11 (*ddm*, 14.4, 7.2)	
H-11	5.20 (*th*, 7.2, 1.5)	5.25 (*tm*, 7.0)
Me-13	1.65 (*q*, 1.5)	1.68 (*s*)
Me-14	1.72 (*brs*)	1.72 (*s*)
H-15	4.46 (*q*, 6.6)	4.52 (*q*, 6.5)
Me-17	1.37 (*s*)	1.38 (*s*)
Me-18	1.37 (*s*)	1.38 (*s*)
Me-19	1.23 (*d*, 6.6)	1.30 (*d*, 6.5)
H$_a$-20	3.27 (*brdd*, 16.0, 9.6)	3.26 (*dd*, 16.0, 10.0)
H$_b$-20	2.83 (*ddq*, 16.0, 4.5, 2.0)	2.82 (*dm*, 16.0)
H-21	5.67 (*ddq*, 9.6, 4.5, 1.5)	5.65 (*ddq*, 10.0, 5.0, 1.5)
Me-23	1.72 (*s*)	1.75 (*s*)
H$_a$-25	2.33 (*dd*, 13.2, 1.2)	2.33 (*d*, 13.0)
H$_b$-25	1.68 (*dd*, 13.2, 9.2)	1.69 (*dd*, 13.0, 9.0)
H-26	2.60 (*d*, 9.2)	2.61 (*d*, 9.0)
Me-28	1.72 (*s*)	1.72 (*s*)
Me-29	1.28 (*s*)	1.29 (*s*)

[a]400 MHz ^{1}H NMR spectrum in CDCl$_3$, [b]500 MHz ^{1}H NMR spectrum in CDCl$_3$

3.2.7 Compound GF13

Compound **GF13** was isolated as a yellow gum. In the UV spectrum (**Figure 34**), the long wavelength absorption band at λ_{max} 361 nm indicated the presence of a caged-polyprenylated xanthone nucleus with a C8/C8a double bond. The IR spectrum (**Figure 35**) exhibited absorption bands at 3500-2500, 1745, 1693 and 1633 cm^{-1} for hydroxyl, unconjugated carbonyl, α,β-unsaturated carboxyl and chelated *ortho*-hydroxyl carbonyl functionalities, respectively. **GF13** was identified as scortechinone F (**8**) by direct comparison of its ^1H NMR spectrum (**Figure 36**) (**Table 99**) and TLC chromatogram with those of scortechinone F, previously isolated from the latex (Rukachaisirikul, 2003b) and stem bark (Rukachaisirikul, 2005) of *G. scortechinii.*



8

Table 99 The ^1H NMR data of scortechinone F and **GF13**

Position	Scortechinone F δ_H (*mult.*, J_{Hz})^a	**GF13** δ_H (*mult.*, J_{Hz})^b
1-OH	13.10 (*s*)	13.09 (*s*)
7-OCH_3	3.63 (*s*)	3.63 (*s*)
H-8	7.61 (*d*, 1.0)	7.60 (*brs*)
H_a-10	3.20 (*d*, 7.0)	3.21 (*m*)
H-11	5.22 (*tm*, 7.0)	5.21 (*tm*, 7.0)
Me-13	1.67 (*s*)	1.68 (*s*)
Me-14	1.74 (*s*)	1.74 (*s*)

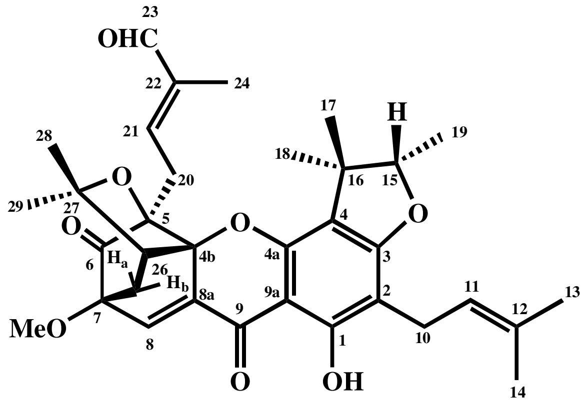
Table 99 (continued)

Position	Scortechinone F δ_H (*mult.*, J_{Hz})[a]	**GF13** δ_H (*mult.*, J_{Hz})[b]
H-15	4.54 (*q*, 6.5)	4.55 (*q*, 6.5)
Me-17	1.41 (*s*)	1.41 (*s*)
Me-18	1.46 (*s*)	1.47 (*s*)
Me-19	1.30 (*d*, 6.5)	1.30 (*d*, 6.5)
H_a-20	2.79 (*ddm*, 15.0, 5.5)	2.80 (*ddm*, 15.0, 5.5)
H_b-20	2.56 (*dd*, 15.0, 10.0)	2.56 (*dd*, 15.0, 10.0)
H-21	6.41 (*ddq*, 10.0, 5.5, 1.5)	6.38 (*ddq*, 10.0, 5.5, 1.5)
Me-24	1.38 (*s*)	1.38 (*s*)
H_a-25	2.33 (*d*, 13.0)	2.34 (*d*, 13.0)
H_b-25	1.69 (*dd*, 13.0, 9.5)	1.69 (*dd*, 13.0, 9.5)
H-26	2.61 (*d*, 9.5)	2.61 (*d*, 9.5)
Me-28	1.72 (*s*)	1.72 (*s*)
Me-29	1.29 (*s*)	1.29 (*s*)

[a, b] 500 MHz ^{1}H NMR spectrum in $CDCl_3$

3.2.8 Compound GF10

Compound **GF10** was isolated as a yellow gum. Its UV (**Figure 37**) and IR (**Figure 38**) spectral data were similar to those of **GF13** (scortechinone F). The ^{1}H NMR spectrum (**Figure 39**) (**Table 100**) was similar to that of **GF13** except for an additional signal of an aldehyde proton at δ_H 9.23. Comparison of its ^{1}H NMR data and silica gel TLC analysis with scortechinone H (**9**), structurally differing from **GF13** in the functional group of C-23, indicated that **GF10** had the same structure as scortechinone H (**9**), previously isolated from latex of *G. scortechinii* (Rukachaisirikul, 2003b).



9

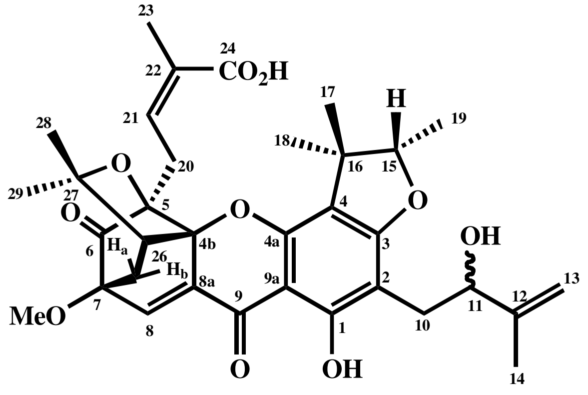
Table 100 The ^{1}H NMR data of scortechinone H and **GF10**

Position	Scortechinone H δ_H (*mult.*, J_{Hz})	**GF10** δ_H (*mult.*, J_{Hz})
1-OH	13.08 (*s*)	13.03 (*s*)
7-OCH_3	3.63 (*s*)	3.63 (*s*)
H-8	7.60 (*brs*)	7.59 (*s*)
H-10	3.20 (*d*, 6.5)	3.20 (*m*)
H-11	5.21 (*t*, 6.5)	5.21 (*t*, 6.4)
Me-13	1.69 (*s*)	1.69 (*s*)
Me-14	1.75 (*s*)	1.75 (*s*)
H-15	4.56 (*q*, 6.5)	4.39 (*q*, 6.5)
Me-17	1.42 (*s*)	1.41 (*s*)
Me-18	1.45 (*s*)	1.42 (*s*)
Me-19	1.30 (*d*, 6.5)	1.30 (*d*, 6.5)
H_a-20	2.89 (*dd*, 15.5, 5.5)	2.90 (*dd*, 14.8, 5.2)
H_b-20	2.62 (*dd*, 15.5, 8.0)	2.61 (*dd*, 14.8, 8.4)
H-21	6.23 (*ddm*, 8.0, 5.5)	6.29 (*ddm*, 8.4, 6.8)
H-23	9.23 (*s*)	9.23 (*s*)
Me-24	1.36 (*s*)	1.40 (*s*)
H_a-25	2.38 (*d*, 13.0)	2.37 (*d*, 13.0)
H_b-25	1.69 (*dd*, 13.0, 9.5)	1.68 (*dd*, 13.0, 9.2)
H-26	2.66 (*d*, 9.5)	2.64 (*d*, 9.2)
Me-28	1.74 (*s*)	1.74 (*s*)
Me-29	1.31 (*s*)	1.31 (*s*)

$^{a,\,b}$500 MHz ^{1}H NMR spectrum in $CDCl_3$

3.2.9 Compound GF14

Compound **GF14** was obtained as a yellow gum. The caged-polyprenylated xanthone chromophore was evident by its UV (**Figure 40**) absorption band at λ_{max} 364 nm. The hydroxyl, unconjugated carbonyl, α,β-unsaturated carbonyl and chelated *ortho*-hydroxyl carbonyl stretching frequencies were found in the region of 3500-2500, 1744, 1693 and 1633 cm^{-1}, respectively, in the IR spectrum (**Figure 41**). Comparison of its ^1H NMR data (**Figure 42**) (**Table 101**), TLC chromatogram (R_f = 0.35, 2% $MeOH/CHCl_3$) and optical rotation ($[\alpha]_D^{29}$ -154°, c = 0.16, CH_3OH) with the previously reported data of scortechinone C ($[\alpha]_D^{29}$ -107°, c = 0.01, CH_3OH) (Rukachaisirikul, 2000), indicating that **GF14** was scortechinone C (**10**).



10

Table 101 The ^1H NMR data of scortechinone C and **GF14**

Position	Scortechinone C δ_H (*mult.*, J_{Hz})[a]	**GF14** δ_H (*mult.*, J_{Hz})[b]
1-OH	13.15 (*s*)	13.14 (*s*)
7-OCH_3	3.65 (*s*)	3.65 (*s*)
H-8	7.51 (*d*, 1.4)	7.54 (*d*, 1.0)
H_a-10	2.98 (*dd*, 14.0, 3.4)	2.98 (*dd*, 14.0, 3.5)
H_b-10	2.64 (*dd*, 14.0, 11.1)	2.65 (*dd*, 14.0, 11.0)
H-11	4.32 (*brdd*, 11.1, 3.4)	4.32 (*dm*, 11.0)
H-13	5.07 (*m*), 4.92 (*m*)	5.08 (*brs*), 4.92 (*brs*)

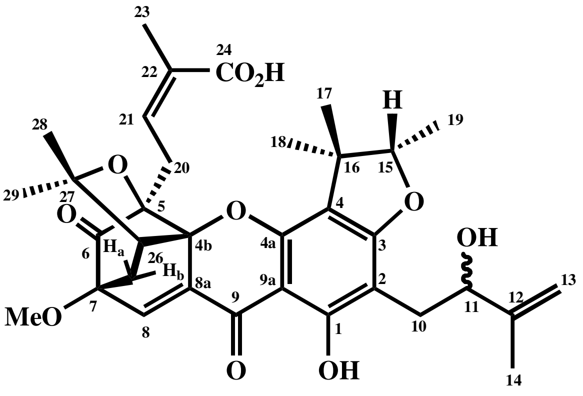
Table 101 (continued)

Position	Scortechinone C δ_H (*mult.*, J_{Hz})[a]	**GF14** δ_H (*mult.*, J_{Hz})[b]
Me-14	1.87 (*m*)	1.87 (*s*)
H-15	4.56 (*q*, 6.6)	4.57 (*q*, 7.0)
Me-17	1.56 (*s*)	1.56 (*s*)
Me-18	1.37 (*s*)	1.38 (*s*)
Me-19	1.45 (*d*, 6.6)	1.44 (*d*, 7.0)
H_a-20	3.81 (*dd*, 15.2, 11.8)	3.82 (*dd*, 15.0, 11.5)
H_b-20	2.73 (*ddq*, 15.2, 3.4, 2.5)	2.71 (*dm*, 15.0)
H-21	5.20 (*ddq*, 11.4, 3.4, 1.4)	5.20 (*dm*, 11.5)
Me-23	1.65 (*dd*, 2.5, 1.4)	1.63 (*m*)
H_a-25	2.35 (*dd*, 13.0, 1.4)	2.34 (*d*, 13.0)
H_b-25	1.70 (*dd*, 13.0, 9.3)	1.72 (*dd*, 13.0, 9.5)
H-26	2.64 (*d*, 9.3)	2.64 (*d*, 9.5)
Me-28	1.71 (*s*)	1.71 (*s*)
Me-29	1.29 (*s*)	1.29 (*s*)

[a] 400 MHz ^{1}H NMR spectrum in $CDCl_3$, [b] 500 MHz ^{1}H NMR spectrum in $CDCl_3$

3.2.10 Compound GF12

Compound **GF12** was obtained as a yellow gum. Its UV spectrum (**Figure 43**) (λ_{max} 364 nm) indicated the presence of a caged-polyprenylated xanthone nucleus. Its IR spectrum (**Figure 44**) showed absorption bands at 3600-2500 (a hydroxyl group of carboxylic acid), 1744 (an unconjugated carbonyl group), 1689 (an α, β-unsaturated carboxyl group) and 1633 cm^{-1} (a chelated *ortho*-hydroxyl carbonyl group). Comparison of its ^{1}H NMR data (**Figure 45**) (**Table 102**), silica gel TLC analysis (R_f = 0.27, 2% MeOH/$CHCl_3$) and optical rotation ($[\alpha]_D^{29}$ -376°, c = 0.15, CH_3OH) with those of scortechinone M (**11**) ($[\alpha]_D^{29}$ -353°, c = 0.02, CH_3OH), previously isolated from the stem bark of *G. scortechinii* (Rukachaisirikul, 2005), indicated that **GF12** had the same structure as scortechinone M (**11**) which differed from scortechinone C in the stereochemistry of C-11.



11

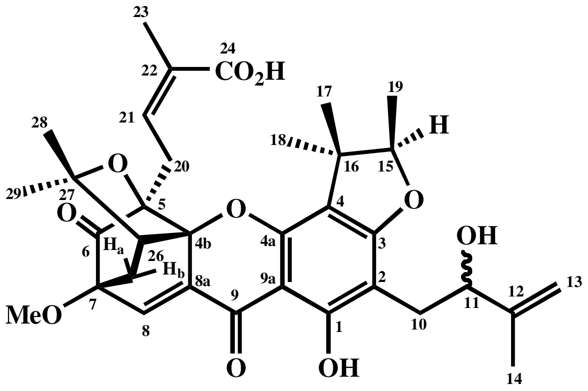
Table 102 The ^{1}H NMR data of scortechinone M and **GF12**

Position	Scortechinone M δ_H (*mult.*, J_{Hz})^a	**GF12** δ_H (*mult.*, J_{Hz})^b
1-OH	13.28 (*s*)	13.26 (*s*)
7-OCH$_3$	3.63 (*s*)	3.63 (*s*)
H-8	7.52 (*s*)	7.51 (*brs*)
H$_a$-10	2.92 (*dd*, 14.3, 10.8)	2.96 (*dd*, 14.4, 10.8)
H$_b$-10	2.68 (*dd*, 14.3, 3.0)	2.71 (*m*)
H-11	4.50 (*dd*, 10.8, 3.0)	4.51 (*d*, 10.8)
H$_a$-13	5.03 (*brs*)	5.06 (*brs*)
H$_b$-13	4.88 (*brs*)	4.90 (*brs*)
Me-14	1.84 (*s*)	1.86 (*s*)
H-15	4.55 (*q*, 6.6)	4.55 (*q*, 6.4)
Me-17	1.39 (*s*)	1.40 (*s*)
Me-18	1.46 (*s*)	1.49 (*s*)
Me-19	1.37 (*d*, 6.6)	1.39 (*d*, 6.4)
H$_a$-20	3.51 (*dd*, 15.6, 10.4)	3.57 (*dd*, 15.0, 11.5)
H$_b$-20	2.75 (*d brd*, 15.6, 4.2)	2.73 (*m*)
H-21	5.43 (*ddq*, 10.4, 4.2, 1.5)	5.37 (*dm*, 9.0)
Me-23	1.67 (*brs*)	1.67 (*s*)
H$_a$-25	2.32 (*d*, 13.6)	2.31 (*d*, 13.0)
H$_b$-25	1.72 (*dd*, 13.6, 9.5)	1.72 (*m*)
H-26	2.63 (*d*, 9.5)	2.63 (*d*, 9.6)
Me-28	1.72 (*s*)	1.72 (*s*)
Me-29	1.28 (*s*)	1.28 (*s*)

^{a}500 MHz ^{1}H NMR spectrum in CDCl$_3$, ^{b}400 MHz ^{1}H NMR spectrum in CDCl$_3$

3.2.11 Compound GF15

Compound **GF15**, with a molecular formula of $C_{34}H_{40}O_{10}$ determined by EIMS (*m/z* 608, $[M]^+$) (**Figure 46**), was isolated as a yellow gum. Its IR (**Figure 48**) and UV (**Figure 47**) spectral data were similar to those of scortechinone M. Its ^1H NMR spectrum (**Figure 49**) (**Table 103**) indicated that **GF15** contained identical substituents to scortechinone M: one chelated hydroxyl group (δ_H 13.26, *s*), one methoxyl group (δ_H 3.64, *s*), one 3-carboxybut-2-enyl group [δ_H 5.40 (*dm*, *J* = 11.0 Hz, 1H), 3.57 (*dd*, *J* = 15.5 and 11.0 Hz, 1H), 2.78 (*dm*, *J* = 15.5 Hz, 1H) and 1.67 (*t*, *J* = 1.5 Hz, 3H)], one 2-hydroxy-3-methylbut-3-enyl group [δ_H 5.06 (*brs*, 1H), 4.89 (*brs*, 1H), 4.51 (*dd*, *J* = 10.5 and 3.5 Hz, 1H), 2.93 (*dd*, *J* = 14.5 and 10.5 Hz, 1H), 2.71 (*dd*, *J* = 14.5 and 3.5 Hz, 1H) and 1.85 (*s*, 3H)], and one 2,3,3-trimethyldihydrofuran ring [δ_H 4.53 (*q*, *J* = 6.5 Hz, 1H), 1.57 (*s*, 3H), 1.39 (*d*, *J* = 6.5 Hz, 3H) and 1.15 (*s*, 3H)]. The minor differences were the ^1H and ^{13}C chemical shift values of the *gem*-dimethyl groups of the hydrofuran unit which indicated that in **GF15** the methine proton (δ_H 4.53, H-15) had the α-stereochemistry. The following NOEDIFF results confirmed the α-configuration of H-15. Irradiation of the methylene proton (δ_H 3.57, H_a-20) of the α-C-5-carboxybutenyl unit and H-15 enhanced signal of Me-18 (δ_H 1.57) (**Figures 52 and 53**). The location of all substituents and relative stereochemistry were supported by HMBC correlations (**Figure 55**) (**Table 103**) and NOEDIFF data (**Table 103**), respectively. Therefore, **GF15** was assigned to have the structure **12**, a new naturally occurring caged-tetraprenylated xanthone of which the structure differed from scortechinones M (Rukachaisirikul, 2005) and C (Rukachaisirikul, 2000) in the stereochemistry of C-15.



12

Table 103 The NMR data of compound **GF15**

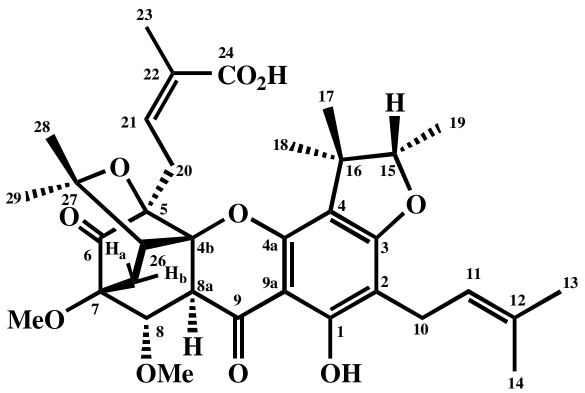
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1-OH	13.26 (*s*)	164.06 (C)	C-1, C-2, C-9a	
2		102.31 (C)		
3		168.29 (C)		
4		113.78 (C)		
4a		154.42 (C)		
4b		89.08 (C)		
5		84.03 (C)		
6		203.15 (C=O)		
7		85.11 (C)		
7-OCH_3	3.64 (*s*)	53.88 (CH_3)	C-7	H-8, H_a-25
8	7.52 (*d*, 1.0)	134.75 (CH)	C-4b, C-8a, C-9	7-OCH_3
8a		132.42 (C)		
9		177.91 (C=O)		
9a		101.33 (C)		
10	a: 2.93 (*dd*, 14.5, 10.5)	28.31 (CH_2)	C-1, C-2, C-3, C-11	H_b-10, H-11, Me-14
	b: 2.71 (*dd*, 14.5, 3.5)		C-1, C-2, C-3	H_a-10
11	4.51 (*dd*, 10.5, 3.5)	74.82 (CH)	C-10, C-13, C-14	H_b-10, H_a-13, Me-14
12		147.12 (C)		
13	a: 5.06 (*brs*)	110.62 (CH_2)	C-11, C-14	H-11, H_b-13
	b: 4.89 (*brs*)		C-11, C-14	H_a-13, Me-14
14	1.85 (*s*)	18.33 (CH_3)	C-11, C-12, C-13	$H_{a,b}$-10, H-11, H_b-13
15	4.53 (*q*, 6.5)	91.07 (CH)	C-17, C-18	Me-18, Me-19
16		43.12 (C)		

Table 103 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
17	1.15 (*s*)	21.13 (CH_3)	C-4, C-15, C-16, C-18	Me-17, Me-19, Me-28
18	1.57 (*s*)	23.63 (CH_3)	C-4, C-15, C-16, C-17	H-15, Me-17
19	1.39 (*d*, 6.5)	13.70 (CH_3)	C-15, C-16	H-15, Me-17
20	a: 3.57 (*dd*, 15.5, 11.0)	28.91 (CH_2)	C-6, C-21	H_b-20, H-21, Me-18
	b: 2.78 (*dm*, 15.5)		C-5, C-6, C-21, C-22	H_a-20
21	5.40 (*dm*, 11.0)	135.69 (CH)	C-24	$H_{a,b}$-20, Me-23
22		129.43 (C)		
23	1.67 (*t*, 1.5)	21.23 (CH_3)	C-21, C-22, C-24	H-21
24		167.85 (C=O)		
25	a: 2.32 (*d*, 13.5)	30.56 (CH_2)	C-4b, C-7, C-8, C-27	H_b-25, Me-29, 7-OCH_3
	b: 1.72 (*dd*, 13.5, 9.5)		C-6, C-26, C-27	H-8, H_a-25, H-26
26	2.62 (*d*, 9.5)	49.62 (CH)	C-4b, C-7, C-28	H_b-25
27		83.62 (C)		
28	1.71 (*s*)	30.72 (CH_3)	C-26, C-27, C-29	H-26, Me-29, 7-OCH_3
29	1.29 (*s*)	28.72 (CH_3)	C-26, C-27, C-28	H_a-25, Me-28

3.2.12 Compound GF11

Compound **GF11** was obtained as a yellow gum. It exhibited IR (**Figure 57**) absorption bands similar to those of **GF12** (scortechinone M). However, the UV spectrum (**Figure 56**) showed absorption band at λ_{max} 303 nm, suggesting that **GF11** had a caged-polyprenylated xanthone chromophore without the C8/C8a double bond. Comparison of its ^1H NMR data (**Figure 58**) (**Table 104**) and TLC chromatogram with those of scortechinone I (**3**), previously isolated from latex (Rukachaisirikul, 2003b) and stem bark (Rukachaisirikul, 2005) of *G. scortechinii*, indicated that **GF11** had the same structure as scortechinone I (**3**).



3

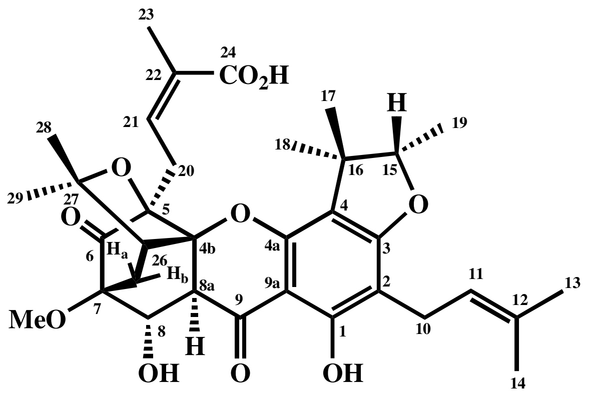
Table 104 The ^{1}H NMR data of scortechinone I and **GF11**

Position	Scortechinone I δ_H (*mult.*, J_{Hz})^a	**GF11** δ_H (*mult.*, J_{Hz})^b
1-OH	12.08 (*s*)	12.07 (*s*)
7-OCH$_3$	3.50 (*s*)	3.50 (*s*)
H-8	4.46 (*s*)	4.47 (*d*, 1.0)
8-OCH$_3$	3.36 (*s*)	3.37 (*s*)
H-8a	3.16 (*s*)	3.16 (*s*)
H$_a$-10	3.21 (*m*)	3.21 (*m*)
H-11	5.25 (*tm*, 7.0)	5.23 (*tm*, 7.5)
Me-13	1.69 (*s*)	1.68 (*s*)
Me-14	1.76 (*s*)	1.76 (*s*)
H-15	4.40 (*q*, 6.8)	4.40 (*q*, 6.5)
Me-17	1.43 (*s*)	1.44 (*s*)
Me-18	1.10 (*s*)	1.11 (*s*)
Me-19	1.34 (*d*, 6.8)	1.34 (*d*, 6.5)
H$_a$-20	3.23 (*m*)	3.21 (*ddm*, 17.5, 7.0)
H$_b$-20	3.23 (*m*)	3.11 (*ddm*, 17.5, 7.0)
H-21	6.62 (*tq*, 6.8, 1.5)	6.59 (*tm*, 7.0)
Me-23	1.98 (*d*, 1.5)	1.97 (*s*)
H$_a$-25	2.02 (*d*, 14.2)	2.01 (*d*, 14.0)
H$_b$-25	1.63 (*dd*, 14.2, 8.8)	1.63 (*dd*, 14.0, 9.0)
H-26	2.70 (*d*, 8.8)	2.70 (*d*, 9.0)
Me-28	1.41 (*s*)	1.42 (*s*)
Me-29	1.20 (*s*)	1.21 (*s*)

$^{a,\,b}$500 MHz ^{1}H NMR spectrum in CDCl$_3$

3.2.13 Compound GF17

Compound **GF17** was isolated as a yellow gum. Its IR (**Figure 60**) and UV (**Figure 59**) spectra were almost identical to those of caged-polyprenylated xanthones, lacking a C8/C8a double bond. The ^{1}H NMR data (**Figure 61**) (**Table 105**) of **GF17** were well compared with those of scortechinone P (**13**), which was isolated from the stem bark of *G. scortechinii* (Rukachaisirikul, 2005), indicating that **GF17** had the same structure as scortechinone P (**13**).



13

Table 105 The ^{1}H NMR data of scortechinone P and **GF17**

Position	Scortechinone P δ_H (*mult.*, J_{Hz})^a	**GF17** δ_H (*mult.*, J_{Hz})^b
1-OH	12.08 (*s*)	12.08 (*s*)
7-OCH$_3$	3.48 (*s*)	3.48 (*s*)
H-8	4.82 (*s*)	4.82 (*s*)
H-8a	3.19 (*s*)	3.19 (*s*)
H-10	3.26-3.13 (*m*)	3.19 (*m*)
H-11	5.23 (*t sept*, 7.0, 1.0)	5.21 (*tm*, 7.0)
Me-13	1.69 (*d*, 1.0)	1.69 (*s*)
Me-14	1.76 (*d*, 1.0)	1.76 (*s*)
H-15	4.40 (*q*, 6.5)	4.40 (*q*, 6.6)
Me-17	1.43 (*s*)	1.43 (*s*)
Me-18	1.10 (*s*)	1.10 (*s*)

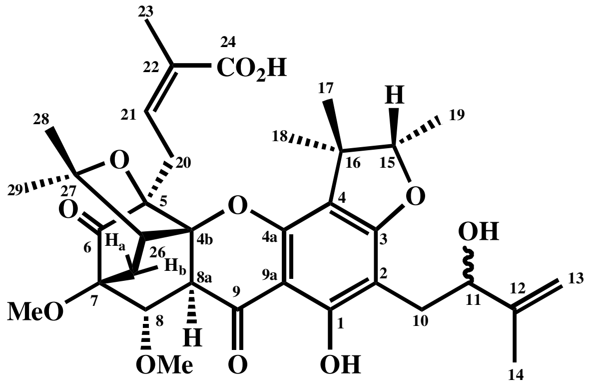
Table 105 (continued)

Position	Scortechinone P δ_H (*mult.*, J_{Hz})[a]	**GF17** δ_H (*mult.*, J_{Hz})[b]
Me-19	1.34 (*d*, 6.5)	1.34 (*d*, 6.6)
H-20	3.24-3.17 (*m*)	3.20 (*m*)
H-21	6.64 (*tq*, 7.0, 1.2)	6.64 (*tm*, 7.5)
Me-23	1.97 (*d*, 1.2)	1.97 (*s*)
H_a-25	2.08 (*d*, 14.0)	2.08 (*d*, 14.4)
H_b-25	1.57 (*dd*, 14.0, 8.5)	1.57 (*dd*, 14.4, 8.4)
H-26	2.72 (*d*, 8.5)	2.71 (*d*, 8.4)
Me-28	1.42 (*s*)	1.43 (*s*)
Me-29	1.22 (*s*)	1.22 (*s*)

[a]500 MHz ^{1}H NMR spectrum in $CDCl_3$, [b]300 MHz ^{1}H NMR spectrum in $CDCl_3$

3.2.14 Compound GF18

Compound **GF18** was obtained as a yellow gum with a molecular formula of $C_{35}H_{44}O_{11}$ determined by EIMS (*m/z* 608, [M-MeOH]$^+$) (**Figure 62**). Its IR (**Figure 64**) and UV (**Figure 63**) spectral data were similar to those of **GF11** (scortechinone I), lacking the C8/C8a double bond. The ^{1}H (**Figure 65**) and ^{13}C NMR (**Figure 66**) (**Table 106**) data were similar to those of **GF11** except that **GF18** contained none of signals for a 3-methylbut-2-enyl group. These signals were replaced by signals which could be ascribed to a 2-hydroxy-3-methylbut-3-enyl group [δ_H 4.99 (*s*, 1H), 4.84 (*s*, 1H), 4.27 (*dd*, J = 9.0 and 4.0 Hz, 1H), 2.90 (*dd*, J = 14.0 and 4.0 Hz, 1H), 2.77 (*dd*, J = 14.0 and 9.0 Hz, 1H) and 1.84 (*s*, 3H)]. This substituent was assigned to be at C-2 (δ_C 102.37) by ^3J HMBC correlations of the methylene protons [$H_{a,b}$-10, δ_H 2.90 (*dd*, J = 14.0 and 4.0 Hz) and 2.77 (*dd*, J = 14.0 and 9.0 Hz)] with C-1 (δ_C 162.00) and C-3 (δ_C 167.37). The attachment of other substituents was identical to **GF11**, based on HMBC data (**Figure 69**) (**Table 106**). The NOEDIFF data (**Table 106**) confirmed the α-configuration of H-8a (δ_H 3.20, *s*), the β-configurations of H-8 (δ_H 4.46, *s*) and H-15 (δ_H 4.41, *q*, J = 6.3 Hz), and the *Z* configuration of the C21/C22 double bond which were identical to those of **GF11**. From these results, **GF18** had the structure **14**, the fourth new caged-tetraprenylated xanthone, lacking a C8/C8a double bond isolated from *G. scortechinii.*



14

Table 106 The NMR data of compound **GF18**

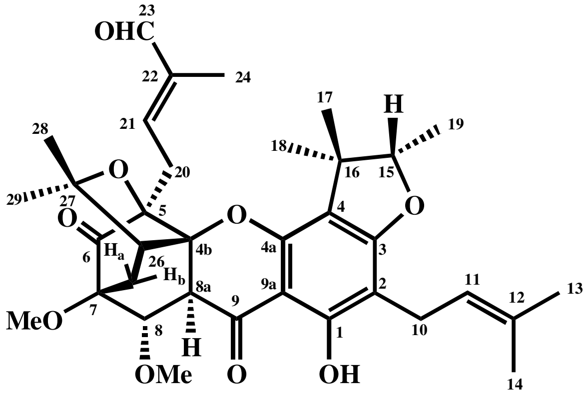
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1-OH	12.27 (*s*)	162.00 (C)	C-1, C-2, C-9a	
2		102.37 (C)		
3		167.37 (C)		
4		113.90 (C)		
4a		152.71 (C)		
4b		87.14 (C)		
5		86.46 (C)		
6		205.37 (C=O)		
7		81.43 (C)		
7-OCH_3	3.49 (*s*)	52.42 (CH_3)	C-7	H-8, H_a-25
8	4.46 (*s*)	75.12 (CH)	C-4b, C-6, C-7, C-8a, C-9, C-25, 8-OCH_3	H-8a, H_b-25, 7-OCH_3, 8-OCH_3
8-OCH_3	3.39 (*s*)	57.51 (CH_3)	C-8	H-8, H-8a
8a	3.20 (*s*)	48.94 (CH)	C-4b, C-7, C-8, C-9, C-26	H-8, H-21, 8-OCH_3
9		192.19 (C=O)		
9a		102.62 (C)		
10	a: 2.90 (*dd*, 14.0, 4.0)	29.13 (CH_2)	C-1, C-2, C-3, C-11	H_b-10, H-11, Me-14
	b: 2.77 (*dd*, 14.0, 9.0)		C-1, C-2, C-3, C-12	H_a-10

Table 106 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
11	4.27 (*dd*, 9.0, 4.0)	75.48 (CH)	C-10	H$_{a,b}$-10, H$_a$-13, Me-14
12		147.36 (C)		
13	a: 4.99 (*s*)	110.37 (CH$_2$)	C-11, C-12, C-14	H-11, H$_b$-13
	b: 4.84 (*s*)		C-11, C-12, C-14	H$_a$-13, Me-14
14	1.84 (*s*)	18.15 (CH$_3$)	C-11, C-12, C-13	H$_{a,b}$-10, H-11, H$_b$-13
15	4.41 (*q*, 6.3)	90.56 (CH)	C-17, C-18	Me-17, Me-19
16		44.01 (C)		
17	1.44 (*s*)	26.10 (CH$_3$)	C-4, C-15, C-16, C-18	H-15, H-26, Me-18
18	1.12 (*s*)	22.07 (CH$_3$)	C-4, C-15, C-16, C-17	H$_{a,b}$-20, H-21, Me-17
19	1.34 (*d*, 6.3)	13.89 (CH$_3$)	C-15, C-16	H-15, Me-18
20	a: 3.24 (*ddm*, 16.0, 7.0)	28.39 (CH$_2$)	C-6, C-21	H$_b$-20, H-21
	b: 3.12 (*ddm*,16.0, 7.0)		C-5, C-6, C-21, C-22	H$_a$-20
21	6.59 (*tm*, 7.0)	137.29 (CH)	C-5, C-23, C-24	H$_{a,b}$-20, Me-23
22		128.39 (C)		
23	1.97 (*d*, 1.5)	20.91 (CH$_3$)	C-21, C-22, C-24	H-21
24		170.39 (C=O)		
25	a: 2.04 (*d*, 14.0)	23.88 (CH$_2$)	C-4b, C-7, C-8, C-27	H$_b$-25, Me-29, 7-OCH$_3$
	b: 1.64 (*dd*, 14.0, 8.5)		C-6, C-26, C-27	H-8, H$_a$-25, H-26
26	2.72 (*d*, 8.5)	45.28 (CH)	C-4b, C-7, C-25, C-28	H$_b$-25
27		82.81 (C)		
28	1.43 (*s*)	30.46 (CH$_3$)	C-26, C-27, C-29	H-15, H-26, Me-29
29	1.22 (*s*)	27.17 (CH$_3$)	C-26, C-27, C-28	H$_a$-25, Me-28, 7-OCH$_3$

3.2.15 Compound GF9

Compound **GF9**, a yellow gum, was found to have a molecular formula of $C_{35}H_{44}O_9$ by EIMS (*m/z* 608, $[M]^+$) (**Figure 70**). Its IR (**Figure 72**) and UV (**Figure 71**) spectral data were similar to those of **GF11**. The ^{1}H NMR spectrum (**Figure 73**) (**Table 107**) was almost identical to that of **GF11** with an additional *singlet* of an aldehyde proton at δ_H 9.48. Furthermore, the DEPT spectrum (**Figure 75**) revealed that a carbon signal at δ_C 195.05 was an aldehyde carbonyl carbon. The HMBC correlations (**Figure 78**) (**Table 107**) between the aldehyde H-23 and C-22 (δ_C 139.79) and C-24 (δ_C 9.38) suggested that the C-5 3-carboxybut-2-enyl substituent in **GF11** was replaced by a 2-butenyl-3-carboxaldehyde unit in **GF9**. A NOE enhancement of the olefinic H-21 (δ_H 7.01, *t*, J = 6.5 Hz) after irradiation of the aldehyde H-23 (**Figure 76**) established an *E* configuration for the C21/22 double bond. This was in agreement with the observed proton signal of H-21 which was shifted to much lower field than that found in **GF11**. The ^3J HMBC data between the methylene protons [$H_{a,b}$-20, δ_H 3.04 (*dd*, J = 16.5 and 6.5 Hz) and 2.96 (*dd*, J = 16.5 and 6.5 Hz)] of the 2-butenyl-3-carboxaldehyde group and C-4b (δ_C 86.08) and C-6 (δ_C 205.41) confirmed the attachment of the 2-butenyl-3-carboxaldehyde substituent at C-5 (δ_C 87.07). Furthermore, the location of other substituents was identical to those of **GF11**, based on HMBC data (**Table 107**). The relative stereochemistry of H-8 (δ_H 4.48, *s*), H-8a (δ_H 3.09, *s*) and H-15 (δ_H 4.42, *q*, J = 6.5 Hz) was proved to be identical to those of **GF11** by the NOEDIFF data (**Table 107**). Thus, the structure of **GF9** was assigned as **15**, a new caged-tetraprenylated xanthone which had a C-5 2-butenyl-3-carboxaldehyde unit.



15

Table 107 The NMR data of compound **GF9**

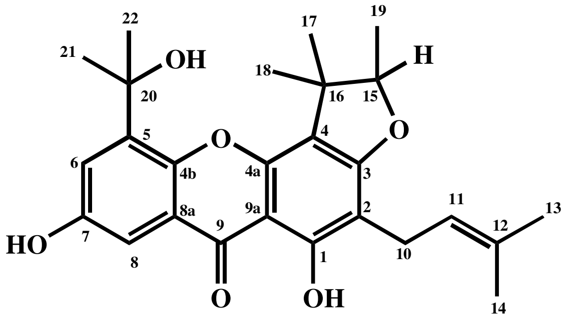
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1-OH	12.08 (*s*)	161.72 (C)	C-1, C-2, C-9a	
2		105.61 (C)		
3		166.88 (C)		
4		113.60 (C)		
4a		152.01 (C)		
4b		86.08 (C)		
5		87.07 (C)		
6		205.41 (C=O)		
7		81.67 (C)		
7-OCH_3	3.52 (*s*)	52.32 (CH_3)	C-7	H-8, H_a-25
8	4.48 (*s*)	75.32 (CH)	C-6, C-7, C-8a, C-9, 8-OMe	H-8a, H_b-25, 7-OCH_3, 8-OCH_3
8-OCH_3	3.40 (*s*)	57.72 (CH_3)	C-8	H-8, H-8a, H-23
8a	3.09 (*s*)	49.34 (CH)	C-5, C-8, C-9, C-26	H-8, H-21, 8-OCH_3
9		191.68 (C=O)		
9a		102.37 (C)		
10	3.21 (*m*)	21.44 (CH_2)	C-1, C-2, C-3, C-11, C-12	H-11, Me-14
11	5.24 (*tm*, 7.0)	121.45 (CH)	C-13, C-14	$H_{a,b}$-10, Me-13
12		132.96 (C)		
13	1.69 (*s*)	25.79 (CH_3)	C-11, C-12, C-14	H-11
14	1.76 (*s*)	17.74 (CH_3)	C-11, C-12, C-13	$H_{a,b}$-10
15	4.42 (*q*, 6.5)	90.15 (CH)	C-17, C-18	Me-17, Me-19
16		43.92 (C)		
17	1.45 (*s*)	26.24 (CH_3)	C-4, C-15, C-16, C-18	H-15, H-26, Me-18
18	1.09 (*s*)	22.35 (CH_3)	C-4, C-15, C-16, C-17	H_a-20, H-21, Me-17
19	1.35 (*d*, 6.5)	13.84 (CH_3)	C-15, C-16	H-15, Me-18
20	a: 3.04 (*dd*, 16.5, 6.5)	27.89 (CH_2)	C-4b, C-6, C-21, C-22	H_b-20, H-21, Me-18, Me-24
	b: 2.96 (*dd*, 16.5, 6.5)		C-4b, C-6, C-21, C-22	H_a-20
21	7.01 (*t*, 6.5)	148.64 (CH)	C-23, C-24	H-8a, $H_{a,b}$-20, H-23

Table 107 (continued)

Position	δ_H (*mult*., J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
22		139.79 (C)		
23	9.48 (*s*)	195.05 (CH)	C-22, C-24	H-21
24	1.76 (*s*)	9.38 (CH_3)	C-21, C-22, C-23	H_b-20
25	a: 2.07 (*d*, 14.5)	23.77 (CH_2)	C-8, C-26	H_b-25, Me-29, 7-OCH_3
	b: 1.64 (*dd*, 14.5, 8.5)		C-8, C-26, C-27	H-8, H_a-25, H-26
26	2.73 (*d*, 8.5)	45.26 (CH)	C-5, C-7, C-25, C-28	H_a-25, Me-28
27		82.21 (C)		
28	1.42 (*s*)	30.54 (CH_3)	C-26, C-27, C-29	H-15, H-26, Me-29
29	1.22 (*s*)	27.26 (CH_3)	C-26, C-27, C-28	H_a-25, Me-28, 7-OCH_3

3.2.16 Compound GF19

Compound **GF19** with a molecular formula of $C_{26}H_{30}O_6$ by EIMS (*m/z* 438, $[M]^+$) (**Figure 79**) was isolated as a yellow solid, melting at 148.8-150.0 ^{o}C. The xanthone chromophore was evident by its UV (**Figure 80**) absorption bands at 241, 267 and 322 nm while the hydroxyl and conjugated carbonyl absorption bands were found at 3427 and 1640 cm^{-1}, respectively, in the IR spectrum (**Figure 81**). Its ^{1}H NMR spectrum (**Figure 82**) (**Table 108**) contained signals of one chelated hydroxyl group (δ_H 13.90, *s*), two *meta*-coupled aromatic protons [δ_H 7.75 (*d*, J = 3.5 Hz, 1H) and 7.56 (*d*, J = 3.5 Hz, 1H)], one prenyl unit [δ_H 5.28 (*tm*, J = 7.0 Hz, 1H), 3.30 (*d*, J = 7.0 Hz, 2H), 1.78 (*s*, 3H) and 1.66 (*s*, 3H)], one unit of a 2,3,3-trimethyldihydrofuran ring [δ_H 4.55 (*q*, J = 6.5 Hz, 1H), 1.66 (*s*, 3H), 1.44 (*d*, J = 6.5 Hz, 3H) and 1.33 (*s*, 3H)], one unit of a 2-hydroxyisopropyl group [δ_H 1.87 (*s*, 3H) and 1.79 (*s*, 3H)] and two hydroxyl groups [δ_H 9.12 (*brs*) and 4.63 (*brs*)]. The ^{13}C NMR spectral data (**Figure 83**) (**Table 108**) deduced from DEPT (**Figure 84**) and HMQC (**Figure 88**) spectra showed 14 quaternary, 4 methine, 1 methylene and 7 methyl carbons. The location of all subunits was established by HMBC data (**Figure 89**) (**Table 108**). The chelated hydroxyl group at C-1 (δ_C 161.81), a *peri*-position of the xanthone carbonyl group, gave ^3J cross peaks with C-2 (δ_C 107.24) and C-9a (δ_C 103.72). HMBC correlations between the methylene protons [H-10, (δ_H 3.30)] of the prenyl group and C-1, C-2 and C-3 (δ_C 165.60) established the attachment of the prenyl group at C-2, *ortho* to the chelated hydroxyl group. Two *meta* aromatic protons (δ_H 7.75 and 7.56) were attributed to H-6 and H-8, respectively, according to the values of the chemical shift and the HMBC correlations of H-6/C-4b (δ_C 147.50), C-7 (δ_C 154.12) and C-8 (δ_C 108.00) and those of H-8/C-4b and C-6 (δ_C 122.33). According to the chemical shift value of C-7, C-7 carried a hydroxyl substituent. The hydroxyisopropyl group was assigned to be at C-5 (δ_C 140.62), *ortho* to H-6, by a ^3J correlation of H-6/C-20 (δ_C 71.52) and those of the *gem*-dimethyl protons [Me-21 (δ_H 1.79) and Me-22 (δ_H 1.87)]/C-5. NOE enhancement of Me-21 and Me-22, upon irradiation of H-6 (**Figure 87**), supported above assignment. From these results, the remaining dihydrofuran unit was placed at C-3 and C-4 (δ_C 112.77) of the right-handed ring. *Gem*-dimethyl protons [Me-17 (δ_H 1.33) and Me-18 (δ_H 1.66)] of the 2,3,3-trimethyldihydrofuran ring showed HMBC correlations with C-4, not with C-3, supported the attachment of the hydrofuran ring at C-3 and C-4 of the xanthone nucleus with an ether linkage at C-3. Signal enhancement of Me-22, upon irradiation of Me-17 (**Figure 85**), confirmed that the hydroxyisopropyl side chain and the dihydrofuran unit were located at the same side of the xanthone skeleton. Me-17 was found to have *trans* relationship with H-15 (δ_H 4.55) since irradiation of H-15 enhanced the signals of Me-18 and Me-19, not Me-17 (**Figure 86**). Thus, **GF19** was determined as 1,7-dihydroxy-5-(2′-hydroxyisopropyl)-2-(3-methylbut-2-enyl)-4″,4″,5″-trimethylfurano(2″,3″:3,4)xanthone (**16**), a new xanthone isolated from *G. scortechinii*.



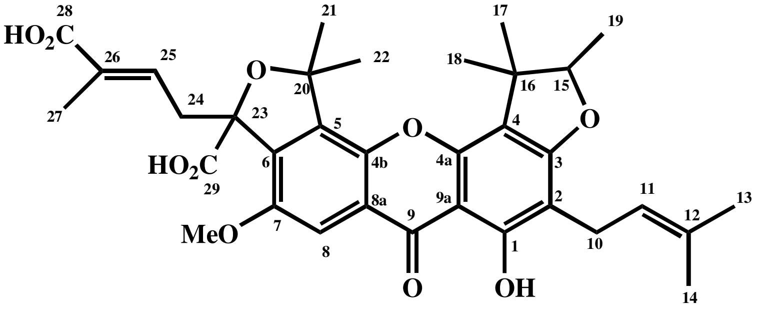
16

Table 108 The NMR data of compound **GF19**

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1-OH	13.90 (*s*)	161.81 (C)	C-1, C-2, C-9a	
2		107.24 (C)		
3		165.60 (C)		
4		112.77 (C)		
4a		151.64 (C)		
4b		147.50 (C)		
5		140.62 (C)		
6	7.75 (*d*, 3.5)	122.33 (CH)	C-4b, C-7, C-8, C-20	20-OH, Me-21, Me-22
7-OH	9.12 (*brs*)	154.12 (C)		
8	7.56 (*d*, 3.5)	108.00 (CH)	C-4b, C-6	
8a		122.54 (C)		
9		181.37 (C=O)		
9a		103.72 (C)		
10	3.30 (*d*, 7.0)	22.19 (CH_2)	C-1, C-2, C-3, C-11, C-12	H-11, Me-14
11	5.28 (*tm*, 7.0)	122.58 (CH)	C-10, C-13, C-14	H-10, Me-13
12		132.01 (C)		
13	1.66 (*s*)	25.79 (CH_3)	C-11, C-12, C-14	H-11
14	1.78 (*s*)	17.79 (CH_3)	C-11, C-12, C-13	H-10
15	4.55 (*q*, 6.5)	90.89 (CH)	C-17, C-18	Me-18, Me-19
16		44.69 (C)		
17	1.33 (*s*)	22.00 (CH_3)	C-4, C-15, C-16	Me-18, Me-19, Me-22
18	1.66 (*s*)	25.95 (CH_3)	C-4, C-15, C-16	H-15, Me-17, Me-21, Me-22
19	1.44 (*d*, 6.5)	14.16 (CH_3)	C-15, C-16	H-15, Me-18
20-OH	4.63 (*brs*)	71.52 (C)		
21	1.79 (*s*)	30.55 (CH_3)	C-5, C-20, C-22	H-6
22	1.87 (*s*)	30.18 (CH_3)	C-5, C-20, C-21	H-6, Me-17

3.2.17 Compound GF21

Compound **GF21** with a molecular formula of $C_{34}H_{38}O_{10}$ determined by EIMS (*m/z* 562 $[M–CO_2]^+$) (**Figure 90**) was isolated as a yellow solid, decomposed at 210 °C. Its UV (**Figure 91**) and IR (**Figure 92**) spectral data were similar to those of **GF19**. Additional IR absorption bands at 3600-2500 (a hydroxyl group of a carboxylic group) and 1694 (a carbonyl group of a carboxylic group) cm^{-1} indicated the presence of a carboxylic acid functional group. The presence of the carboxyl groups was confirmed by the carbon signals in the ^{13}C NMR spectrum (**Figure 94**) (**Table 109**) at δ_C 171.99 and 168.94. The ^1H NMR spectrum (**Figure 93**) (**Table 109**) showed a chelated hydroxy proton at δ 13.15 (*s*), characteristic signals of a prenyl group [δ_H 5.26 (*tm*, J = 7.5 Hz, 1H), 3.28 (*d*, J = 7.5 Hz, 2H), 1.75 (*s*, 3H) and 1.64 (*s*, 3H)], and one unit of a 2,3,3-trimethyldihydrofuran ring [δ_H 4.64 (*q*, J = 6.5 Hz, 1H), 1.61 (*s*, 3H), 1.43 (*d*, J = 6.5 Hz, 3H) and 1.33 (*s*, 3H)]. These data together with identical HMBC data (**Figure 99**) (**Table 109**) to those of **GF19** indicated that **GF19** and **GF21** had the same structure of the right-handed ring. In addition, the ^1H NMR spectrum exhibited the *singlet* aromatic proton at δ_H 7.44, a *singlet* signal of a methoxyl group at δ_H 4.10, characteristic signals of a 3-carboxybut-2-enyl group [δ_H 6.59 (*tm*, J = 7.5 Hz, 1H), 3.54 (*dd*, J = 15.0 and 7.5 Hz, 1H), 3.28 (*dd*, J = 15.0 and 7.5 Hz, 1H) and 1.70 (*d*, J = 1.5 Hz, 3H)] and two *gem*-dimethyl signals of an oxyisopropyl group at δ_H 1.61 (*s*, 3H) and 1.53 (*s*, 3H). The location of these substituents on the left-handed ring of the xanthone nucleus was established by the following HMBC data (**Table 109**). The *singlet* aromatic proton, which was attributed to H-8, according to the value of chemical shift, showed ^2J cross peaks with C-7 (δ_C 150.76) and C-8a (δ_C 117.01) and ^3J cross peaks with C-4b (δ_C 147.17) and C-6 (δ_C 128.19). A HMBC correlation between the methoxy protons and the C-7 established the attachment of the methoxyl group at C-7. In addition, HMBC spectrum showed correlations between one of methylene protons, H_b-24 (δ_H 3.28), of the 3-carboxybut-2-enyl group with C-6, C-23 (δ_C 91.62) and C-29 (δ_C 171.99) of the carboxyl group and that between the olefinic H-25 (δ_H 6.59) with C-23. These data established the attachment of the carboxyl group and the 3-carboxybut-2-enyl group on the same oxyquaternary carbon, C-23, which further linked with C-6 of the xanthone moiety. The *gem*-dimethyl protons [Me-21 (δ_H 1.61) and Me-22 (δ_H 1.53)] of the oxyisopropyl group gave cross peaks with the remaining aromatic carbon at C-5 (δ_C 145.07) and an oxyquaternary carbon at C-20 (δ_C 87.15), indicating the presence of the oxyisopropyl group at C-5. Based on the above molecular formula, a dihydrofuran unit was constructed by forming an ether linkage between two oxyquaternary carbons, C-20 and C-23. Irradiation of H-25 (**Figure 97**) enhanced the signal intensity of Me-21, not Me-27 (δ_H 1.70), indicating that the 3-carboxybut-2-enyl unit had *E* configuration and *cis*-relationship to Me-21. Signal enhancement of the oxymethine H-15 (δ_H 4.64) and the olefinic proton, H-25, upon irradiation of Me-18 and Me-21 which appeared at the same chemical shift (**Figure 96**), indicated that Me-18 and Me-21 was *cis* to H-15 and the C-23 3-carboxybut-2-enyl unit, respectively. The relative stereochemistry (C-15 and C-23) was not assigned. Therefore, **GF21** was identified as 1-hydroxy-7-methoxy-2′,2′-dimethyl-5′-carboxy-5′-(3-carboxybut-2-enyl)furano(3′,4′:5,6)-2-(3-methylbut-2-enyl)-4″,4″,5″-trimethylfurano(2″,3″:3,4)xanthone (**17**), a new highly-rearranged xanthone.



17

Table 109 The NMR data of compound **GF21**

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1-OH	13.15 (*s*, OH)	161.40 (C)	C-1, C-2, C-9a	
2		107.56 (C)		
3		165.50 (C)		

Table 109 (continued)

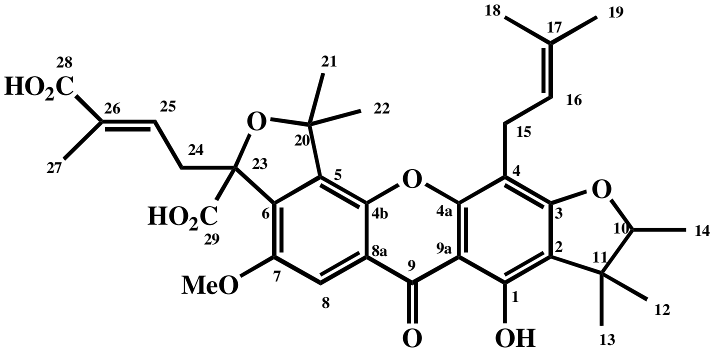
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
4		113.20 (C)		
4a		151.26 (C)		
4b		147.17 (C)		
5		145.07 (C)		
6		128.19 (C)		
7		150.76 (C)		
7-OCH_3	4.10 (*s*)	57.29 (CH_3)	C-7	H-8
8	7.44 (*s*)	109.38 (CH)	C-4b, C-6, C-7, C-8a	7-OCH_3
8a		117.01 (C)		
9		181.43 (C=O)		
9a		104.47 (C)		
10	3.28 (*d*, 7.5)	22.22 (CH_2)	C-1, C-2, C-3, C-11, C-12	H-11, Me-14
11	5.26 (*tm*, 7.5)	122.38 (CH)	C-10, C-13, C-14	H-10, Me-13
12		132.23 (C)		
13	1.64 (*s*)	25.79 (CH_3)	C-11, C-12, C-14	H-11
14	1.75 (*s*)	17.78 (CH_3)	C-11, C-12, C-13	H-10
15	4.64 (*q*, 6.5)	91.73 (CH)	C-16, C-17, C-18	Me-18, Me-19
16		44.74 (C)		
17	1.33 (*s*)	21.44 (CH_3)	C-4, C-15, C-16	Me-18, Me-19
18	1.61 (*s*)	25.98 (CH_3)	C-4, C-15, C-16, C-17	H-15, H-25, Me-17
19	1.43 (*d*, 6.5)	14.75 (CH_3)	C-15, C-16	H-15
20		87.15 (C)		
21	1.61 (*s*)	28.84 (CH_3)	C-5, C-20, C-22	H-8, H-25
22	1.53 (*s*)	30.25 (CH_3)	C-5, C-20, C-21	H-8
23		91.62 (C)		
24	a : 3.54 (*dd*, 15.0, 7.5)	36.03 (CH_2)	C-23, C-25, C-26, C-29	H-25, Me-27
	b : 3.28 (*dd*, 15.0, 7.5)		C-6, C-23, C-25, C-26, C-29	H_a-24, H-25
25	6.59 (*tm*, 7.5)	139.34 (CH)	C-23, C-24, C-26, C-27, C-28	$H_{a,b}$-24, Me-18, Me-21
26		129.86 (C)		

Table 109 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
27	1.70 (*d*, 1.5)	12.77 (CH_3)	C-25, C-26, C-28	H_a-24
28		168.94 (C=O)		
29		171.99 (C=O)		

3.2.18 Compound GF20

Compound **GF20** with a molecular formula of $C_{34}H_{38}O_{10}$ from EIMS (*m/z* 562, $[M–CO_2]^+$) (**Figure 100**) was isolated as a yellow solid, melting at 213-215 °C. It displayed UV (**Figure 101**) and IR (**Figure 102**) absorption bands similar to those of **GF21**. The ^1H (**Figure 103**), ^{13}C NMR (**Figure 104**) (**Table 110**) and HMBC data (**Figure 109**) (**Table 110**) of the left-handed aromatic ring revealed that **GF20** and **GF21** had identical structure of the left-handed ring. In addition, the ^1H NMR spectrum showed characteristic signals of a chelated hydroxy proton (δ_H 12.87, *s*), a 2,3,3-trimethyldihydrofuran ring [δ_H 4.58 (*q*, J = 6.5 Hz, 1H), 1.49 (*s*, 3H), 1.41 (*d*, J = 6.5 Hz, 3H) and 1.24 (*s*, 3H)] and a prenyl unit [δ_H 5.34 (*tm*, J = 7.5 Hz, 1H), 3.47 (*d*, J = 7.5 Hz, 2H), 1.84 (*s*, 3H) and 1.64 (*s*, 3H)]. The location of these substituents on the right-handed aromatic ring was established by the following HMBC data (**Table 110**). The chelated hydroxy proton, at C-1 (δ_C 157.03), showed ^3J cross peaks with C-2 (δ_C 117.43) and C-9a (δ_C 105.11). The 2,3,3-trimethyldihydrofuran ring was fused in a linear fashion at C-2 with an ether linkage at C-3 (δ_C 165.34), according to ^3J HMBC correlations between Me-12 (δ_H 1.49) and Me-13 (δ_H 1.24) with C-2. The remaining prenyl unit was attached at C-4 (δ_C 103.49), according to the ^3J correlations of H-15 (δ_H 3.47)/C-3 and C-4a (δ_C 154.98). The chemical shifts of the *gem*-dimethyl groups of both dihydrofuran rings were established by the following NOEDIFF data. Irradiation of H-25 (δ_H 6.58) of the 3-carboxybut-2-enyl unit enhanced the signal of Me-21 (δ_H 1.61) (**Figure 107**), indicating their *cis*-relationship. The oxymethine H-10 (δ_H 4.58) was *cis* to Me-12 (δ_H 1.49) because of the signal enhancement of Me-12 upon irradiation of H-10 (**Figure 106**). However, the NOEDIFF results could not determine the relative stereochemistry of both dihydrofuran units. Attempts to recrystallize **GF20** in various solvent systems were unsuccessful. Thus, **GF20** was assigned as 1-hydroxy-7-methoxy-2′,2′-dimethyl-5′-carboxy-5′-(3-carboxybut-2-enyl)furano(3′,4′:5,6)-4-(3-methylbut-2-enyl)-4″,4″,5″-trimethylfurano(2″,3″:3,2)-xanthone (**18**).



18

Table 110 The NMR data of compound **GF20**

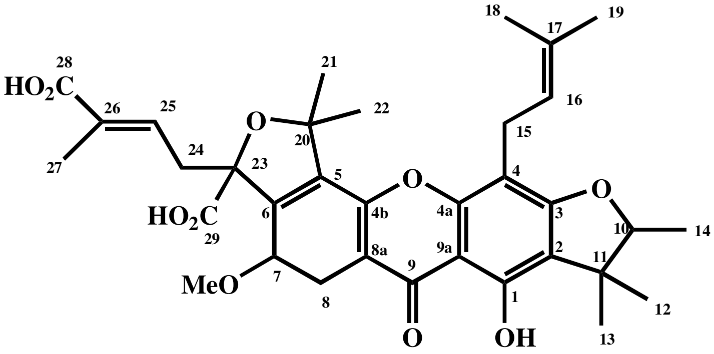
Position	δ_{H} (*mult.*, J_{Hz})	δ_{C} (C-type)	HMBC correlations	NOE
1-OH	12.87 (*s*, OH)	157.03 (C)	C-1, C-2, C-9a	
2		117.43 (C)		
3		165.34 (C)		
4		103.49 (C)		
4a		154.98 (C)		
4b		147.47 (C)		
5		145.10 (C)		
6		127.95 (C)		
7		150.75 (C)		
7-OCH_3	4.09 (*s*)	57.07 (CH_3)	C-7	H-8
8	7.44 (*s*)	109.26 (CH)	C-4b, C-6, C-7, C-8a	7-OCH_3
8a		116.82 (C)		
9		182.03 (C=O)		
9a		105.11 (C)		
10	4.58 (*q*, 6.5)	91.60 (CH)	C-12, C-13	Me-12, Me-14

Table 110 (continued)

Position	δ_{H} (*mult.*, J_{Hz})	δ_{C} (C-type)	HMBC correlations	NOE
11		44.38 (C)		
12	1.49 (*s*)	25.44 (CH_3)	C-2, C-10, C-11, C-13	H-10, Me-13
13	1.24 (*s*)	20.81 (CH_3)	C-2, C-10, C-11, C-12	Me-12, Me-14
14	1.41 (*d*, 6.5)	14.61 (CH_3)	C-10, C-11	H-10, Me-13
15	3.47 (*d*, 7.5)	22.28 (CH_2)	C-3, C-4, C-4a, C-16, C-17	Me-18, Me-21
16	5.34 (*tm*, 7.5)	122.43 (CH)	C-15, C-18, C-19	H-15, Me-19
17		132.48 (C)		
18	1.84 (*s*)	17.74 (CH_3)	C-16, C-17	H-15, Me-19, Me-22, 7-OMe
19	1.64 (*d*, 6.5)	25.87 (CH_3)	C-16	H-16, Me-18
20		87.17 (C)		
21	1.61 (*s*)	28.85 (CH_3)	C-5, C-20, C-22	H-8, H-25
22	1.53 (*s*)	30.21 (CH_3)	C-5, C-20, C-21	H-8
23		91.71 (C)		
24	a : 3.54 (*dd*, 15.0, 7.5)	35.98 (CH_2)	C-23, C-25, C-26, C-29	H_b-24, H-25, Me-27
	b : 3.26 (*dd*, 15.0, 7.5)		C-6, C-23, C-25, C-26, C-29	H_a-24, H-25
25	6.58 (*tm*, 7.5)	139.31 (CH)	C-23, C-26, C-27, C-28	$H_{a,b}$-24, Me-21
26		129.87 (C)		
27	1.69 (*d*, 1.0)	12.76 (CH_3)	C-25, C-26, C-28	$H_{a,b}$-24
28		168.92 (C=O)		
29		171.98 (C=O)		

3.2.19 Compound GF22

Compound **GF22**, a yellow gum, was found to have a molecular formula of $C_{34}H_{40}O_{10}$ by EIMS (*m/z* 608, $[M]^+$) (**Figure 110**). The IR (**Figure 112**) absorption bands at 3600-2500, 1697 and 1651 cm^{-1} for a hydroxyl group of a carboxylic group, acid carbonyl and conjugated carbonyl groups, respectively. The UV spectrum (**Figure 111**) displayed absorption band at 278 nm, shorter wavelength than those found in **GF20** and **GF21**. The ^{1}H NMR spectrum (**Figure 113**) (**Table 111**) was similar to that of **GF20** except for the fact that a *singlet* aromatic proton (δ_H 7.44, H-8) was replaced by the signals of an oxymethine proton at δ_H 4.50 (*t*, *J* = 8.5 Hz) and methylene protons at δ_H 2.70 (*dd*, *J* = 18.0 and 8.0 Hz) and δ_H 2.59 (*dd*, *J* = 18.0 and 8.0 Hz). These indicated that **GF22** had the same structure of the right-handed ring as that of **GF20**. The HMBC and NOEDIFF data (**Table 111**) confirmed these assignments. The oxymethine proton (δ_H 4.50) and methylene protons (δ_H 2.70 and 2.59) were attributed to H-7 and H-8, respectively, since H-7 showed ^3J correlations in the HMBC spectrum (**Figure 117**) with C-5 (δ_C 140.43) and C-8a (δ_C 111.55) while both methylene protons, H-8, gave ^3J correlations with C-4b (δ_C 163.16) and C-6 (δ_C 122.80). A methoxyl group (δ_H 3.54) was assigned to be at C-7 (δ_C 74.76) due to a HMBC correlation between the methoxy protons and C-7. Furthermore, the location of other substituents on the left-handed ring was identical to that of **GF20**, based on HMBC data (**Table 111**). The relative stereochemistry of this molecule (C-7, C-10 and C-23) was not assigned. Therefore, **GF22** (**19**) was determined as the first naturally occurring 7,8-dihydroxanthone.



19

Table 111 The NMR data of compound **GF22**

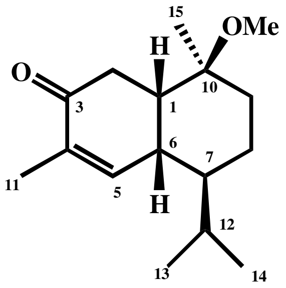
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1-OH	12.36 (*s*, OH)	155.44 (C)	C-1, C-2, C-9a	
2		118.05 (C)		
3		163.29 (C)		
4		102.78 (C)		
4a		154.20 (C)		
4b		163.16 (C)		
5		140.43 (C)		
6		122.80 (C)		
7	4.50 (*t*, 8.0)	74.76 (CH)	C-5, C-8, C-8a, 7-OCH_3	H_b-8, 7-OMe
7-OMe	3.54 (*s*)	58.03 (CH_3)	C-7	H-7
8	a: 2.70 (*d*, 18.0, 8.0) b: 2.59 (*d*, 18.0, 8.0)	27.11 (CH_2)	C-4b, C-6, C-7	7-OCH_3
8a		111.55 (C)		
9		178.73 (C=O)		
9a		105.87 (C)		
10	4.47 (*q*, 6.5)	90.63 (CH)	C-2, C-11, C-12, C-13, C-14	Me-12, Me-14
11		43.76 (C)		
12	1.46 (*s*)	25.09 (CH_3)	C-2, C-10, C-11, C-13	H-10
13	1.21 (*s*)	20.46 (CH_3)	C-2, C-10, C-11, C-12	Me-14
14	1.37 (*d*, 6.5)	14.36 (CH_3)	C-10, C-11	
15	3.37 (*m*)	21.92 (CH_2)	C-3, C-4, C-4a, C-16, C-17	
16	5.22 (*tm*, 7.0)	121.56 (CH)	C-15, C-18, C-19	Me-19, 7-OCH_3
17		132.34 (C)		
18	1.77 (*s*)	17.79 (CH_3)	C-16, C-17	H-15
19	1.67 (*s*)	25.69 (CH_3)	C-16	H-16, 7-OCH_3
20		88.01 (C)		
21	1.38 (*s*)	26.71 (CH_3)	C-5, C-20, C-22	
22	1.38 (*s*)	26.58 (CH_3)	C-5, C-20, C-21	
23		91.03 (C)		

Table 111 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
24	a : 3.31 (*dd*, 16.0, 8.0)	35.64 (CH_2)	C-23, C-25, C-26, C-29	H-25
	b : 3.10 (*dd*, 16.0, 8.0)		C-6, C-23, C-25, C-26, C-29	H-25
25	6.78 (*tm*, 7.5)	140.64 (CH)	C-23, C-26, C-27, C-28	$H_{a,b}$-24, Me-27
26		129.05 (C)		
27	1.77 (*s*)	12.36 (CH_3)	C-25, C-26, C-28	
28		173.04 (C=O)		
29		174.99 (C=O)		

3.2.20 Compound GF1

Compound **GF1**, a colorless gum, had a molecular formula of $C_{16}H_{26}O_2$ from EIMS (*m/z* 250 $[M]^+$) (**Figure 118**). The IR spectrum (**Figure 120**) suggested the presence of an α, β-unsaturated carbonyl system with absorption bands at 1732 and 1673 cm^{-1}. The UV absorption band (**Figure 119**) at 240 nm supported the presence of an α, β-unsaturated ketone. The ^1H NMR spectrum (**Figure 121**) (**Table 112**) showed signals for an isopropyl group [δ_H 0.89, 0.92 (3H each, *d*, J = 7.0 Hz) and 1.85 (*sept d*, J = 7.0 and 2.5 Hz, 1H)], a trisubstituted olefinic proton at δ_H 6.95 (*dq*, J = 6.3 and 1.5 Hz, 1H), one methoxyl group at δ_H 3.17 (*s*, 3H), three methine protons [δ_H 2.60 (*ddd*, J = 10.2, 6.3 and 5.1 Hz, 1H), 2.25 (*m*, 1H) and 1.47 (*m*, 1H)], three methylene groups [δ_H 2.37 (*m*, 2H), 1.36 (*m*, 2H) and 1.78, 1.29 (each 1H, *m*)], one vinylic methyl group at δ_H 1.79 (*t*, J = 1.5 Hz, 3H) and one methyl group attached to an oxyquaternary carbon at δ_H 1.12 (*s*, 3H). The ^{13}C NMR (**Figure 122**) and DEPT (**Figure 123**) spectra displayed 16 carbon signals for a carbonyl (δ_C 199.55), one trisubstiuted double bond (δ_C 150.98 and 134.69), one methoxyl (δ_C 48.90), three methylenes (δ_C 36.90, 30.26 and 19.19), four methines (δ_C 42.99, 42.63, 35.42 and 27.80), four methyls (δ_C 21.52, 21.35, 16.00 and 15.74) and one oxyquaternary carbon (δ_C 75.01). On the basis of the above evidences, **GF1** had the skeleton of the cadinane type of sesquiterpenes. Comparison of ^{1}H and ^{13}C NMR data (**Table 112**) of **GF1** with those of the 10α-hydroxyamorphane-4-en-3-one (He, 1997) indicated that the hydroxyl group of the 10α-hydroxyamorphane-4-en-3-one was replaced by the methoxyl group. This result demonstrated that the methoxyl group was located at C-10 (δ_C 75.01) which was proved by a HMBC correlation between the methoxy protons and C-10. The ^{1}H-^{1}H COSY, HMQC and HMBC (**Figures 125, 126 and 127**) (**Table 113**) data of **GF1** led to unambiguous assignments of NMR data. The ^{1}H-^{1}H COSY spectrum (**Table 113**) showed connectivities for the methylene protons [H-2, (δ_H 2.37)] with the bridgehead proton, H-1 (δ_H 2.25), which in turn was coupled with the other bridgehead proton, H-6 (δ_H 2.60). H-6 was coupled with the olefinic proton, H-5 (δ_H 6.95), and the methine proton, H-7 (δ_H 1.47). The coupling chain continued from H-7 to H-8 (δ_H 1.36) and then to $H_{a,b}$-9 (δ_H 1.78 and 1.29). The methine proton, H-12 (δ_H 1.85), of the isopropyl side chain, showed COSY correlations with H-7, Me-13 (δ_H 0.92) and Me-14 (δ_H 0.89), indicating the location of the isopropyl group at C-7 (δ_C 42.99). ^{3}J HMBC correlations of Me-13 and Me-14 with C-7 confirmed this assignment. The position of the α, β-unsaturated ketone moiety was the same as that of 10α-hydroxyamorphane-4-en-3-one, according to HMBC correlations between H-5/C-1 (δ_C 42.63), C-3 (δ_C 199.55), C-6 (δ_C 35.42) and C-11 (δ_C 16.00). The downfield signal of H-5 supported the presence of a double bond conjugated with a carbonyl group. The relative stereochemistry was deduced from analyses of splitting pattern together with coupling constant of H-5 and NOEDIFF data between H-1 and H-6. In the ^{1}H NMR spectrum, H-5 was coupled to H-6 with a coupling constant of 6.3 Hz, providing evidence for the *cis*-fusion: in *trans*-fusion, H-5 appeared as a broad *singlet* while the *cis*-fusion, H-5 resonated as a *doublet* with coupling constant of 6.5 Hz (He, 1997). Since H-6 was coupled with H-7 and H-1 with the largest coupling (J = 10.2 Hz) and the smallest coupling (J = 5.1 Hz) constants, respectively, H-6 and 7-isopropyl substituent were located at β-axial and β-equatorial positions, respectively. Irradiation of H_{ax}-6 produced signal enhancement of H_{eq}-1 and 10-OMe (**Figure 124**), supporting the assignment of *cis*-fusion and also indicating the location of 10-OMe at β-axial position, *cis* to both H_{eq}-1 and H_{ax}-6. Thus, **GF1** was identified as 10-methoxyamorphane-4-en-3-one (**20**).



20

Table 112 The ^{1}H and ^{13}C NMR data of 10α-hydroxyamorphane-4-en-3-one and **GF1**

Position	10α-hydroxyamorphane-4-en-3-one		**GF1**	
	δ_H (*mult.*, J_{Hz})^a	δ_C (C-type)	δ_H (*mult.*, J_{Hz})^b	δ_C (C-type)
1	2.15 (*td*, 9.5, 4.5)	45.8 (CH)	2.25 (*m*)	42.63 (CH)
2	2.39 (*d*, 9.5)	37.1 (CH_2)	2.37 (*m*)	36.90 (CH_2)
3		199.2 (C=O)		199.55 (C=O)
4		134.9 (C)		134.69 (C)
5	6.95 (*d*, 6.5)	150.5 (CH)	6.95 (*dq*, 6.3, 1.5)	150.98 (CH)
6	2.67 (*brs*)	35.6 (CH)	2.60 (*ddd*, 10.2, 6.3, 5.1)	35.42 (CH)
7	1.54 (*m*)	43.1 (CH)	1.47 (*m*)	42.99 (CH)
8	1.47-1.61 (*m*)	19.4 (CH_2)	1.36 (*m*)	19.19 (CH_2)
9	1.47-1.61 (*m*)	34.1 (CH_2)	1.78 (*m*), 1.29 (*m*)	30.26 (CH_2)
10		71.3 (C)		75.01 (C)
10-OMe		-	3.17 (*s*)	48.90 (CH_3)
11	1.79 (*d*, 1.0)	16.0 (CH_3)	1.79 (*t*, 1.5, 3H)	16.00 (CH_3)
12	1.89 (*br sept*, 7.0)	27.8 (CH)	1.85 (*sept d*, 7.0, 2.5)	27.80 (CH)
13	0.92 (*d*, 7.0)	21.3 (CH_3)	0.92 (*d*, 7.0, 3H)	21.35 (CH_3)
14	0.92 (*d*, 7.0)	15.7 (CH_3)	0.89 (*d*, 7.0, 3H)	15.74 (CH_3)
15	1.18 (*s*)	28.7 (CH_3)	1.12 (*s*, 3H)	21.52 (CH_3)

$^{a,\ b}$300 MHz ^{1}H NMR spectrum in $CDCl_3$

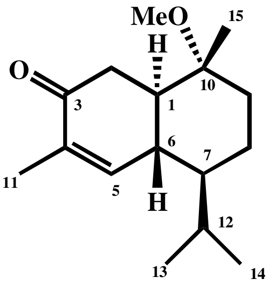
Table 113 The ^{1}H-^{1}H COSY, HMBC and NOE data of compound **GF1**

Proton	^{1}H-^{1}H COSY	HMBC correlations	NOE
H-1	H-2, H_a-9, H-6	C-2	H-6, Me-15, 10-OMe
H-2	H-1	C-1, C-3, C-6	Me-15
H-5	H-6, Me-11	C-1, C-3, C-6, C-11	H-12, Me-11
H-6	H-1, H-5, H-7, Me-11	C-2, C-4, C-5, C-7	H-1, Me-13, 10-OMe
H-7	H-6, H-8, $H_{a,b}$-9, H-12	C-14	Me-13, Me-14
H-8	H-7, H_a-9	C-9, C-10	Me-13, Me-14
H_a-9	H-1, H-7, H-8, H_b-9	C-7, C-10	H_b-9, Me-15, 10-OMe
H_b-9	H-7, H_a-9	C-7, C-8	H_a-9, Me-15
10-OMe	-	C-10	H-1, H-6, H_a-9, Me-15
Me-11	H-5, H-6	C-3, C-4, C-5	H-5
H-12	H-7, Me-13, Me-14	C-8, C-14	H-7, Me-14
Me-13	H-12	C-7, C-12, C-14	H-6, H-7, H-8, H-12
Me-14	H-12	C-7, C-12, C-13	H-6, H-7, H-8, H-12
Me-15	-	C-1, C-9, C-10	H-2, $H_{a,b}$-9, 10-OMe

3.2.21 Compound GF2

Compound **GF2** was obtained as a colorless gum with a molecular formula of $C_{16}H_{26}O_2$ determined by EIMS (*m/z* 250, $[M]^+$) (**Figure 128**). The IR (**Figure 130**) and UV (**Figure 129**) spectra were almost identical to those of **GF1**. The ^{1}H NMR spectrum (**Figure 131**) (**Table 114**) was similar to that of **GF1** except for a signal of an olefinic H-5 (δ_H 6.80) which appeared as a broad *singlet*. This result suggested that **GF2** had a *trans*-fused ring system (He, 1997). The location of the methyl, methoxyl, isopropyl groups and conjugated ketone functionality was identical to that of **GF1**, according to HMBC correlations (**Figure 138**) (**Table 114**). Irradiation of H_{ax}-6 (δ_H 2.14, *m*) enhanced the signal of Me-15 (δ_H 1.12, *s*), not H_{ax}-1 (δ_H 1.98, *m*) (**Figure 135**). These supported the *trans*-fused ring system and also indicated the β-axial and α-equatorial orientations of Me-15 and the methoxyl group, (δ_H 3.20, *s*), respectively. Signal enhancement of H_{ax}-7 (δ_H 1.18, *m*), upon irradiation of H_{ax}-1 (δ_H 1.98, *m*) (**Figure 134**), established the β-equatorial orientation of the isopropyl group.

Therefore, **GF2** (**21**) was a diastereomer of **GF1**, differing in the stereochemistry of C-1 and C-10.



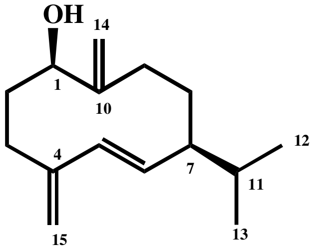
21

Table 114 The NMR data of compound **GF2**

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1	1.98 (*m*)	47.78 (CH)	C-3, C-6, C-10, C-15	H_a-2, H-7, H_b-9, 10-OMe
2	2.71 (*dd*, 15.0, 1.8) 2.07 (*dd*, 15.0,13.5)	38.28 (CH_2)	C-3, C-4, C-6 C-1, C-3, C-6, C-10	H-1, H_b-2 H_a-2, Me-15
3		200.38 (C=O)		
4		135.34 (C)		
5	6.80 (*brs*)	146.15 (CH)	C-1, C-3, C-6, C-7, C-11	H-6
6	2.14 (*m*)	40.48 (CH)	C-1, C-10	H-5, Me-15
7	1.18 (*m*)	45.04 (CH)	C-12, C-13, C-14	H-1, H_a-8, Me-13, Me-14
8	1.69 (*m*) 1.24 (*m*)	21.01 (CH_2)	C-6, C-7, C-10 C-10	H_b-8, Me-13 H_a-8, Me-13, Me-14
9	1.87 (*m*) 1.48 (*m*)	34.86 (CH_2)	C-1, C-7, C-8, C-15 C-8, C-10, C-15	H_b-9, Me-15 H_a-9, 10-OMe
10		74.78 (C)		
10-OMe	3.20 (*s*)	48.20 (CH_3)	C-10	H-1, H_a-2, H_b-9, Me-15
11	1.78 (*dd*, 2.1, 1.5)	15.94 (CH_3)	C-3, C-4, C-5	H-5
12	2.24 (*sept d*, 6.9, 2.1)	26.16 (CH)	C-13, C-14	H-7, Me-13, Me-14
13	0.98 (*d*, 6.9)	21.46 (CH_3)	C-7, C-12, C-14	H_a-8, H-12, Me-14
14	0.83 (*d*, 6.9)	15.18 (CH_3)	C-7, C-12, C-13	H-7, H-12, Me-13
15	1.12 (*s*)	17.86 (CH_3)	C-1, C-9, C-10	H_b-2, H-6, H_a-9, 10-OMe

3.2.22 Compound GF7

Compound **GF7** was obtained as a pale yellow gum. Its IR spectrum (**Figure 140**) displayed the presence of a hydroxyl group (3394 cm^{-1}) while the UV spectrum (**Figure 139**) showed absorption bands at λ_{max} 236 and 280 nm due to a conjugated chromophore. **GF7** was identified as germacra-4(15),5*E*,10(14)-triene-1β-ol (**22**) by direct comparison of its ^{1}H (**Figure 141**), ^{13}C NMR data (**Figure 142**) (**Table 115**) and TLC chromatogram with **DD7** [germacra-4(15),5*E*,10(14)-triene-1-ol] that was obtained from the twigs of *G. merguensis* (Sukavisite, 2003). In addition, the relative stereochemistry was identical based on the value of optical rotation [**GF7**: $[\alpha]_D^{29}$ -200°, c = 0.01, CH_3OH and germacra-4(15),5*E*,10(14)-triene-1β-ol: $[\alpha]_D$ -180.3° (Fattorusso, 1978)].



22

Table 115 The ^{1}H NMR data of **DD7** and **GF7**

Position	**DD7** δ_H (*mult.*, J_{Hz})^a	**GF7** δ_H (*mult.*, J_{Hz})^b
1	3.78 (*dd*, 12.0, 4.0)	3.77 (*dd*, 11.5, 4.0)
2	2.08-2.05 (*m*)	2.06 (*m*)
	1.73-1.58 (*m*)	1.66 (*m*)
3	2.44 (*dt*, 13.0, 5.0)	2.44 (*td*, 13.0, 5.0)
	2.20 (*ddd*, 13.0, 5.0, 2.5)	2.20 (*ddd*, 13.0, 5.0, 2.5)
5	6.00 (*d*, 16.5)	6.00 (*d*, 15.5)
6	5.44 (*dd*, 16.5, 10.5)	5.43 (*dd*, 15.5, 10.0)
7	1.83-1.77 (*m*)	1.80 (*m*)
8	2.03-2.01 (*m*)	2.02 (*m*)
	1.73-1.58 (*m*)	1.66 (*m*)

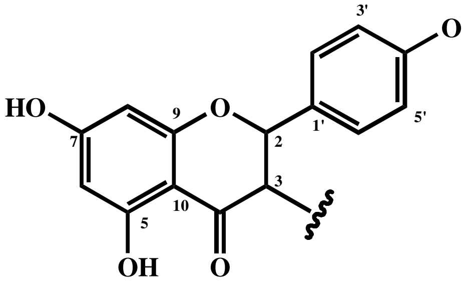
Table 115 (continued)

Position	**DD7** δ_H (*mult.*, J_{Hz})[a]	**GF7** δ_H (*mult.*, J_{Hz})[b]
9	2.65-2.61 (*m*)	2.63 (*m*)
	1.68-1.60 (*m*)	1.64 (*m*)
11	1.53-1.46 (*m*)	1.49 (*septet*, 6.5)
12	0.89 (*d*, 6.5)	0.90 (*d*, 6.5)
13	0.82 (*d*, 6.5)	0.82 (*d*, 6.5)
14	5.28 (*s*)	5.28 (*brs*)
	5.00 (*d*, 2.0)	5.00 (*brs*)
15	4.93 (*d*, 1.0)	4.93 (*brs*)
	4.85 (*s*)	4.85 (*brs*)

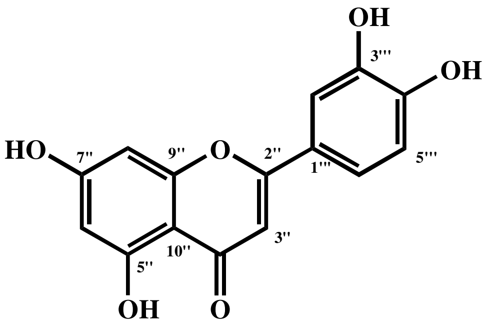
[a, b] 500 MHz ^{1}H NMR spectrum in $CDCl_3$

3.2.23 Compound GF23

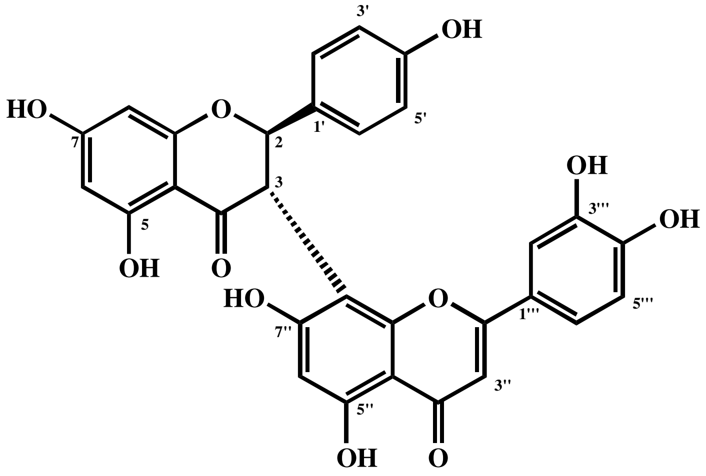
Compound **GF23** was isolated as a yellow solid, decomposed at 248 ^{o}C. In the UV spectrum (**Figure 144**), the absorption bands at λ_{max} 210, 289 and 342 nm were similar to those of morelloflavone (Chen, 1975). Its IR spectrum (**Figure 145**) exhibited absorption bands at 3273 and 1643 cm^{-1} due to hydroxyl and conjugated carbonyl groups. The ^{1}H NMR spectrum (**Figure 146**) (**Table 116**) contained signals of a *para*-disubstituted benzene [δ_H 7.12 and 6.36 (*d*, J = 8.4 Hz, 2H each)], two *meta* aromatic protons [δ_H 5.95 (s, 2H), one chelated hydroxy proton (δ_H 12.25) and two methine protons [δ_H 5.68 and 4.86 (*d*, J = 12.3 Hz, 1H each)]. The chelated hydroxyl group at C-5 gave cross peaks with C-4 (δ_C 196.50), C-5 (δ_C 163.18), C-6 (δ_C 96.54) and C-10 (δ_C 101.81). Two *meta* aromatic protons were then attributed to H-6 and H-8, respectively, based on the HMBC correlations (**Figure 150**) (**Table 116**) of H-6/C-7 (δ_C 164.10), C-8 (δ_C 95.61) and C-10 and those of H-8/C-6 and C-10. Two methine protons (δ_H 5.68 and 4.86) were assigned to H-2 and H-3 of a flavanone moiety, respectively, as both H-2 and H-3 gave cross peaks with C-4. The large coupling constant (J = 12.3 Hz) between H-2 and H-3 established *trans* relationship between H-2 and H-3. HMBC correlations between the aromatic protons [H-2′, 6′ (δ_H 7.12)] of the *para*-disubstituted benzene and C-2 (δ_C 81.24) established the attachment of the *para*-disubstituted benzene at C-2. According to the chemical shift values of C-4′ and C-7, both carbons carried hydroxyl substituents. Therefore, the flavanone moiety had the structure of unit A as shown. Furthermore, its ^{1}H NMR spectrum showed a set of ABC-type aromatic proton signals at δ_H 7.40 (*d*, *J* = 8.0 Hz, 1H), 7.38 (*s*, 1H) and 6.89 (*d*, *J* = 8.0 Hz, 1H), two *singlet* proton signals at δ_H 6.55 and 6.21 and a chelated hydroxy proton at δ_H 13.50 (*s*). The aromatic protons of the ABC-type aromatic ring were assigned to H-2‴, H-5‴ and H-6‴ due to HMBC correlations of H-2‴ (δ_H 7.38)/ C-2″ (δ_C 163.82), C-3‴ (δ_C 145.97) and C-6‴ (δ_C 119.60), H-5‴ (δ_H 6.89)/C-1‴ (δ_C 121.39), C-3‴ (δ_C 145.97) and C-4‴ (δ_C 150.02) and H-6‴ (δ_H 7.40)/C-2‴ (δ_C 113.54) and C-4‴ (δ_C 150.02). In the HMBC spectrum, the chelated hydroxy proton at C-5″ (δ_C 160.83) showed ^3J cross peaks with C-6″ (δ_C 98.95) and C-10″ (δ_C 103.42). One of the *singlet* aromatic protons at δ_H 6.21 was assigned to H-6″ by its HMQC (**Figure 149**) and HMBC correlations with C-5″, C-7″ (δ_C 162.16), C-8″ (δ_C 100.89) and C-10″. The remaining *singlet* aromatic proton (δ_H 6.55) was then attributed to H-3″ due to correlations with C-2″ (δ_C 163.82), C-4″ (δ_C 181.95) and C-10″. A HMBC cross peak between H-2‴ and C-2″ established the linkage of the ABC aromatic ring at C-2″ of the flavone moiety (unit B). These results indicated that the remaining carbon (C-8″, δ_C 100.89) of the unit B linked with C-3 of unit A. HMBC cross peaks of H-3/C-7″ (δ_C 162.16), C-8″ (δ_C 100.89) and C-9″ (δ_C 155.59) supported this conclusion. Thus, **GF23** had the same structure as morelloflavone (**23**). Compound **GF23** exhibited the positive sign of optical rotation ($[\alpha]_D^{29}$ +216^o, c = 0.81, CH_3OH), suggesting that it was (+)-morelloflavone ($[\alpha]_D^{25}$ +188^o, c = 0.1, CH_3OH), previously isolated from *Rheedia acuminata* (Li, 2002).



unit A



unit B



23

Table 116 The NMR data of compound **GF23**

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
2	5.68 (*d*, 12.3)	81.24 (CH)	C-4, C-2′, 6′
3	4.86 (*d*, 12.3)	48.62 (CH)	C-2, C-4, C-1′, C-7″, C-8″, C-9″
4		196.50 (C=O)	
5-OH	12.25 (*s*)	163.18 (C)	C-4, C-5, C-6, C-10
6	5.95 (*s*)	96.54 (CH)	C-7, C-8, C-10
7		164.10 (C)	
8	5.95 (*s*)	95.61 (CH)	C-6, C-7, C-9, C-10
9		166.88 (C)	
10		101.81 (C)	
1′		128.49 (C)	
2′, 6′	7.12 (*d*, 8.4)	128.77 (CH)	C-2, C-4′, C-2′, 6′

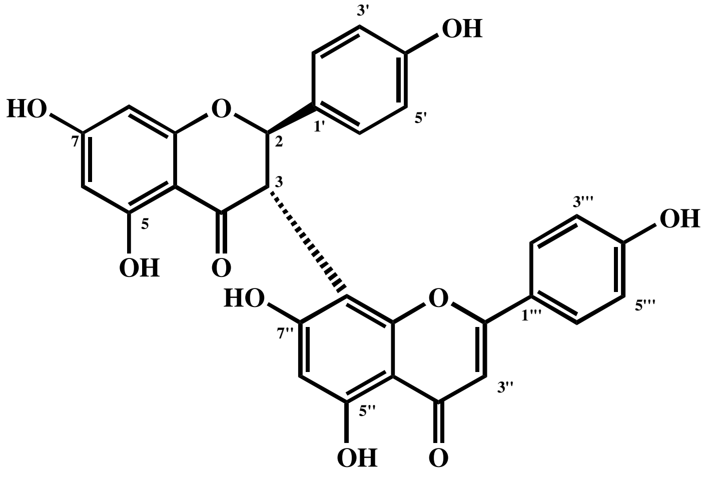
Table 116 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
3′, 5′	6.36 (*d*, 8.4)	114.75 (CH)	C-1′, C-3′, C-4′
4′		157.63 (C)	
2″		163.82 (C)	
3″	6.55 (*s*)	102.53 (CH)	C-2″, C-4″, C-10″, C-1‴
4″		181.95 (C=O)	
5″-OH	13.50 (*s*)	160.83 (C)	C-6″, C-7″, C-10″
6″	6.21 (*s*)	98.95 (CH)	C-5″, C-7″, C-8″, C-10″
7″		162.16 (C)	
8″		100.89 (C)	
9″		155.59 (C)	
10″		103.42 (C)	
1‴		121.39 (C)	
2‴	7.38 (*s*)	113.54 (CH)	C-2″, C-3‴, C-6‴
3‴		145.97 (C)	
4‴		150.02 (C)	
5‴	6.89 (*d*, 8.0)	116.48 (CH)	C-1‴, C-3‴, C-4‴
6‴	7.40 (*d*, 8.0)	119.60 (CH)	C-2‴, C-4‴

3.2.24 Compound GF24

Compound **GF24** was obtained as a yellow solid, decomposed at 258 °C. Its IR (**Figure 152**) and UV (**Figure 151**) spectra were similar to those of **GF23**. Its ^{1}H NMR spectrum (**Figure 153**) (**Table 117**) was also similar to that **GF23** except for the replacement of signals for a 1,3,4-trisubstituted benzene [δ_H 7.40 (*d*, J = 8.0 Hz, 1H), 7.38 (*s*, 1H) and 6.89 (*d*, J = 8.0 Hz, 1H)] with signals for a 1,4-disubstitued benzene [δ_H 8.10 and 7.09 (*d*, J = 9.0 Hz, 2H each)]. This unit was attached at C-2″ of the flavone unit due to HMBC correlations between the aromatic protons (δ_H 8.10, H-2‴ and H-6‴) with C-2″ (δ_C 164.09). The location of other substituents was identical to that of **GF23**, based on HMBC data (**Figure 157**) (**Table 117**). In addition, the ^{1}H

NMR data and optical rotation of **GF24** ($[\alpha]_D^{29}$ +133°, c = 0.80, CH_3OH) were compared with the previously reported data of (+)-volkensiflavone-7-sulfate ($[\alpha]_D^{25}$ +113°, c = 1.32, CH_3OH), indicating that **GF24** was (+)-volkensiflavone (**24**) which was isolated from *Rheedia acuminata* (Li, 2002).



24

Table 117 The NMR data of compound **GF24**

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
2	5.82 (*d*, 12.3)	81.26 (CH)	C-3, C-4, C-2′, 6′
3	5.16 (*d*, 12.3)	48.67 (CH)	C-2, C-4, C-1′, C-7″, C-8″, C-9″
4		196.67 (C=O)	
5-OH	12.48 (*s*)	164.26 (C)	C-5, C-6, C-10
6	6.15 (*s*)	96.67 (CH)	C-7, C-10
7		163.23 (C)	
8	6.09 (*s*)	95.69 (CH)	C-5, C-9, C-10
9		166.83 (C)	
10		102.15 (C)	
1′		127.80 (C)	
2′, 6′	7.25 (*d*, 8.5)	128.76 (CH)	C-2, C-4′, C-2′, 6′, C-3′, 5′
3′, 5′	6.49 (*d*, 8.5)	115.08 (CH)	C-4′, C-2′, 6′, C-3′, 5′
4′		157.80 (C)	
2″		164.09 (C)	

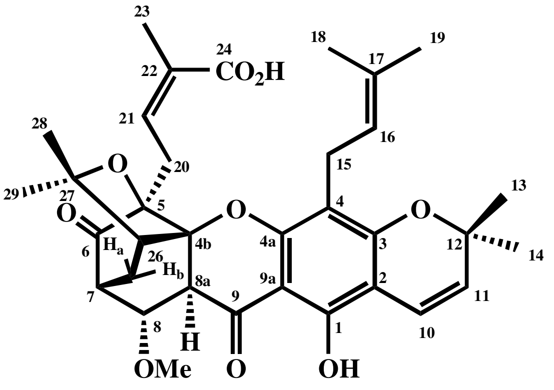
Table 117 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
3″	6.80 (*s*)	103.45 (CH)	C-2″, C-4″, C-10″, C-1‴
4″		182.16 (C=O)	
5″-OH	13.20 (*s*)	160.84 (C)	C-6″, C-7″, C-10″
6″	6.37 (*s*)	99.14 (CH)	C-5″, C-8″, C-10″
7″		162.43 (C)	
8″		101.15 (C)	
9″		155.78 (C)	
10″		104.00 (C)	
1‴		121.23 (C)	
2‴, 6‴	8.10 (*d*, 9.0)	129.12 (CH)	C-2″, C-4‴, C-2‴, 6‴
3‴, 5‴	7.09 (*d*, 9.0)	116.47 (CH)	C-1‴, C-4‴, C-3‴, 5‴
4‴		161.48 (C)	

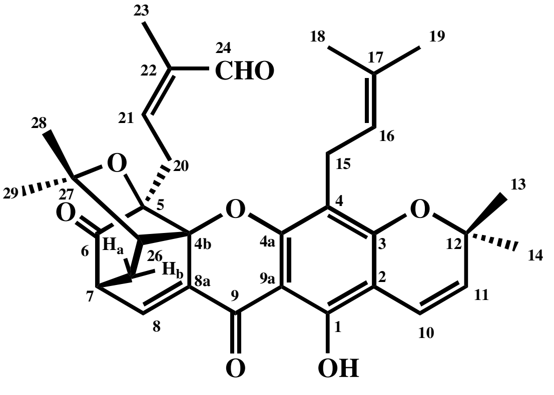
3.3 Characteristic spectroscopic data of caged-polyprenylated xanthones isolated from *G. hanburyi*

All compounds isolated from the fruits of *G. hanburyi* were caged-tetraprenylated xanthones with and without a C8/C8a double bond. Their structures were different from those obtained from *G. scortechinii* in the absence of a bridgehead-7-methoxyl group and a 2,3,3-trimethyldihydrofuran. Their UV spectra showed absorption bands at λ_{max} 227, 276, 290, 315 and 360 nm. The IR spectrum exhibited absorption bands of a hydroxyl group of a carboxylic acid (in the range of 3600-2500 cm^{-1}), an unsaturated carbonyl group (approximately 1740 cm^{-1}) and a chelated *ortho*-hydroxyl carbonyl group (approximately at 1633 cm^{-1}). The ^{1}H NMR spectrum [see moreollic acid (**25**), Asano, 1996] showed characteristic signals for a dimethylchromene unit at δ_H 6.61 (*d*, *J* = 9.9 Hz, 1H, H-10), 5.51 (*d*, *J* = 9.9 Hz, 1H, H-11), 1.46 (*s*, 3H, Me-13) and 1.39 (*s*, 3H, Me-14). This unit was fused to C-2 and C-3 with an ether linkage at C-3 due to the HMBC correlations of the olefinic proton, H-10, with C-1 and C-3. In addition, the caged-polyprenylated xanthones with

C8/C8a double bond [see morellin (**26**)] showed signals for H-7 [δ_H 3.53 (*dd*, J = 7.0 and 4.5 Hz, 1H), H-8 [δ_H 7.56 (*d*, J = 7.0 Hz, 1H) and $H_{a,b}$-25 [δ_H 2.37 (*dd*, J = 14.0 and 4.5 Hz, 1H) and 1.47 (*dd*, J = 14.0 and 9.0 Hz, 1H)] while those without this double bond [see moreollic acid (**25**)] gave signals for those protons at δ_H 2.84 (*t*, J = 4.6 Hz, H-7), 4.35 (*d*, J = 4.6 Hz, H-8), 1.95 and 1.41 (*m*, each 1H, $H_{a,b}$-25) and one additional methine proton at δ_H 3.19 (*s*, H-8a). The relative stereochemistry of the left-handed ring of moreollic acid (**25**) was established by NOEDIFF results (Asano, 1996). Irradiation of the methylene proton (H_b-25) enhanced signal of the oxymethine proton (H-8) but did not affect the signals of the methoxy proton (8-OCH_3) and the methine proton (H-8a). In addition, irradiation of H-8a enhanced signal of H-7 and Me-23 of the C-5 3-carboxybut-2-enyl group. These results indicated that H-8 and H-8a were *trans* and located at β- and α-positions, respectively.



25: moreollic acid

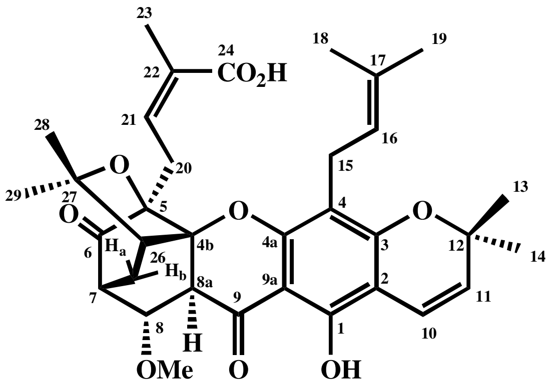


26: morellin

3.3.1 Compound GF28

Compound **GF28** was obtained as a yellow gum. In the UV spectrum (**Figure 158**), the absorption bands at λ_{max} 267, 276, 316 and 362 nm indicated the presence of a caged-polyprenylated xanthone nucleus. The IR spectrum (**Figure 159**) exhibited absorption bands at 3600-2500 (a hydroxyl group of a carboxylic acid), 1742 (an unconjugated carbonyl group), 1682 (an α,β-unsaturated carboxyl group) and 1633 cm^{-1} (a chelated *ortho*-hydroxyl carbonyl group). The carbon signals at δ_C 208.59, 193.81 and 172.76 in the ^{13}C NMR spectrum (**Figure 161**) (**Table 118**) confirmed the presence of three carbonyl groups. The ^{1}H NMR spectrum (**Figure 160**) (**Table 118**) showed characteristic signals of a caged-prenylated moiety, -OC(Me)$_2$-CHCH$_2$-C-, [δ_H 2.49 (*d*, J = 8.4 Hz, 1H, H-26), 1.96 (*dd*, J = 14.5 and 6.3 Hz, 1H, H$_a$-25), 1.41 (*dd*, J = 14.5 and 8.4 Hz, 1H, H$_b$-25), 1.35 (*s*, 3H, Me-28) and 1.15 (*s*, 3H, Me-29)], three methine protons [δ_H 4.34 (*dd*, J = 4.5 and 1.2 Hz, 1H, H-8), 3.19 (*d*, J = 1.2 Hz, 1H, H-8a) and 2.83 (*t*, J = 5.4 Hz, 1H, H-7)], one methoxyl group (δ_H 3.30, *s*, 8-OCH$_3$), one 3-carboxybut-2-enyl group [(δ_H 6.69 (*tm*, J = 6.6 and 1.5 Hz, 1H, H-21), 3.20 (*m*, 2H, H-20) and 1.94 (*d*, J = 1.5 Hz, 3H, Me-23)]. The location of these substituents on the left-handed ring of the caged-polyprenylated xanthone nucleus was established by HMBC data (**Figure 164**) (**Table 118**). A HMBC correlation between the methoxy protons and the oxymethine C-8 established the attachment of the methoxyl group at C-8. In addition, HMBC spectrum showed correlations between the methylene protons, H-20, of the 3-carboxybut-2-enyl group with C-5 (δ_C 86.30) and C-6 (δ_C 208.59) and between the olefinic proton, H-21, with C-5. These data indicated that the carboxyprenyl side chain was located on C-5 of the caged-xanthone. Furthermore, the ^{1}H NMR spectrum also showed a signal of a chelated hydroxy proton (δ_H 11.95, *s*, 1-OH), characteristic signals of a dimethylchromene ring [δ_H 6.61 (*d*, J = 9.9 Hz, 1H, H-10), 5.51 (*d*, J = 9.9 Hz, 1H, H-11), 1.46 (*s*, 3H, Me-13) and 1.39 (*s*, 3H, Me-14)] and a 3-methylbut-2-enyl group [δ_H 5.01 (*tm*, J = 6.3 and 1.2 Hz, 1H, H-16), 3.31 (*m*, 1H, H$_a$-15), 3.13 (*m*, 1H, H$_b$-15), 1.73 (*s*, 3H, Me-18) and 1.62 (*s*, 3H, Me-19)]. The location of all subunits was established by HMBC data (**Table 118**). The chelated hydroxyl group at C-1 (δ_C 156.35) gave ^3J cross peaks with

C-2 (δ_C 103.04) and C-9a (δ_C 101.87). The dimethylchromene ring was fused to C-2 and C-3 (δ_C 160.89) with an ether linkage at C-3 due to the HMBC correlations of the olefinic proton, H-10, with C-1 and C-3. The remaining 3-methylbut-2-enyl unit was attached at C-4 (δ_C 109.08) by the ^3J correlations of the methylene protons, $H_{a,b}$-15, with C-3 and C-4a (δ_C 155.66). **GF28** was then identified as moreollic acid (**25**), which was previously isolated from the latex of *G. hanburyi* (Asano, 1996). In addition, the relative stereochemistry of **GF28** was determined by comparison of its optical rotation ($[\alpha]_D^{29}$ -39°, c = 0.22, $CHCl_3$) with moreollic acid ($[\alpha]_D^{27}$ -31°, c = 0.1, $CHCl_3$, Asano, 1996).



25

Table 118 The NMR data of compound **GF28**

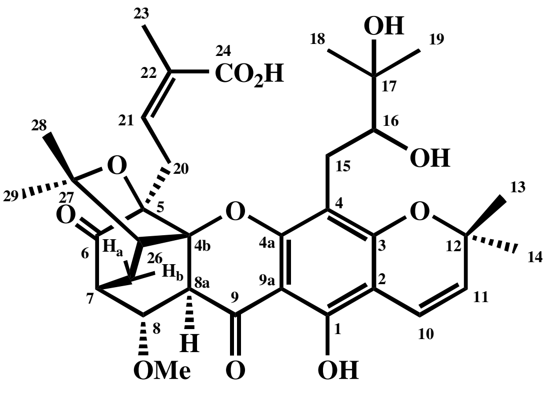
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
1-OH	11.95 (*s*)	156.35 (C)	C-1, C-2, C-9a
2		103.04 (C)	
3		160.89 (C)	
4		109.08 (C)	
4a		155.66 (C)	
4b		88.44 (C)	
5		86.30 (C)	
6		208.59 (C=O)	
7	2.83 (*t*, 5.4)	43.89 (CH)	C-5, C-6, C-8, C-25, C-26
8	4.34 (*dd*, 4.5, 1.2)	73.96 (CH)	C-4b, C-6, C-7, C-8a, C-9, C-25, 8-OCH_3

Table 118 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
8-OCH$_3$	3.30 (*s*)	55.78 (CH$_3$)	C-8
8a	3.19 (*d*, 1.2)	47.89 (CH)	
9		193.81 (C=O)	
9a		101.87 (C)	
10	6.61 (*d*, 9.9)	115.31 (CH)	C-1, C-2, C-3, C-11, C-12
11	5.51 (*d*, 9.9)	126.30 (CH)	C-2, C-3, C-4, C-12, C-13
12		78.14 (C)	
13	1.46 (*s*)	28.55 (CH$_3$)	C-11, C-12, C-14
14	1.39 (*s*)	28.19 (CH$_3$)	C-11, C-12, C-13
15	a: 3.31 (*m*)	21.51 (CH$_2$)	C-3, C-4, C-4a, C-16, C-17
	b: 3.13 (*m*)		C-3, C-4, C-4a, C-16, C-17
16	5.01 (*tm*, 6.3, 1.2)	122.55 (CH)	C-4, C-15, C-18, C-19
17		131.13 (C)	
18	1.73 (*s*)	18.04 (CH$_3$)	C-4, C-16, C-17, C-19
19	1.62 (*s*)	25.61 (CH$_3$)	C-4, C-16, C-17, C-18
20	3.20 (*m*)	28.00 (CH$_2$)	C-5, C-6, C-21, C-22
21	6.69 (*tm*, 6.6, 1.5)	140.15 (CH)	C-5, C-23
22		126.81 (C)	
23	1.94 (*d*, 1.5)	20.50 (CH$_3$)	C-21, C-22, C-24
24		172.76 (C=O)	
25	a: 1.96 (*dd*, 14.5, 6.3)	19.96 (CH$_2$)	C-4b, C-8, C-26, C-27
	b: 1.41 (*dd*, 14.5, 8.4)		C-6, C-7, C-8
26	2.49 (*d*, 8.4)	43.50 (CH)	C-4b, C-5, C-7, C-25, C-28
27		82.14 (C)	
28	1.35 (*s*)	29.73 (CH$_3$)	C-26, C-27, C-29
29	1.15 (*s*)	27.20 (CH$_3$)	C-25, C-26, C-27, C-28

3.3.2 Compound GF27

Compound **GF27**, a yellow gum, was found to have a molecular formula of $C_{34}H_{42}O_{11}$ determined by EIMS spectrum (**Figure 165**) which showed a molecular ion at *m/z* 608 for $[M-H_2O]^+$. The IR spectrum (**Figure 167**) exhibited strong bands due to a hydroxyl group of a carboxylic acid (3600-3200 cm^{-1}), an unconjugated carbonyl group (1739 cm^{-1}), an *α,β*-unsaturated carboxyl group (1697 cm^{-1}) and a chelated *ortho*-hydroxyl carbonyl group (1633 cm^{-1}). The presence of three carbonyl groups was confirmed by the signals at δ_C 207.98, 194.16 and 170.73 in the ^{13}C NMR spectrum (**Figure 169**) (**Table 119**). The UV absorption bands at λ_{max} 204, 276, 316 and 363 nm (**Figure 166**) were similar to those of **GF28**, suggesting that **GF27** had a caged-polyprenylated xanthone moiety without a C8/C8a double bond. The ^{1}H (**Figure 168**) and ^{13}C NMR spectral data (**Figure 169**) (**Table 119**) were similar to those of **GF28** except for the fact that signals of a 3-methylbut-2-enyl group at C-4 were replaced by signals for a 2,3-dihydroxy-3-methylbutyl group [δ_H 3.00 (*dd*, J = 15.0 and 10.5 Hz, 1H, H$_a$-15), 2.86 (*dd*, J = 15.0 and 2.4 Hz, 1H, H$_b$-15), 4.05 (*dd*, J = 10.5 and 2.4 Hz, 1H, H-16), 1.71 (*s*, 3H, Me-18) and 1.70 (*s*, 3H, Me-19); δ_C 25.58 (C-15), 78.20 (C-16), 73.57 (C-17), 28.78 (C-18) and 28.56 (C-19)]. This group was assigned to be at C-4 (δ_C 105.32) by ^3J HMBC correlations of the methylene protons (H$_{a,b}$-15) with C-3 (δ_C 160.50) and C-4a (δ_C 156.97). The attachment of other substituents was identical to **GF28**, based on HMBC data (**Figure 172**) (**Table 119**). The NOEDIFF data (**Table 119**) confirmed the *α*-configuration of H-8a (δ_H 3.29, *d*, J = 1.2 Hz), the *β*-configuration of H-8 (δ_H 4.30, *dd*, J = 4.5 and 1.2 Hz) and the *Z*-configuration of the C21/22 double bond which were identical to those of **GF28**. From these results, **GF27** had the structure **27**, a new naturally occurring caged-tetraprenylated xanthone, having a 2,3-dihydroxy-3-methylbutyl unit at C-4.



27

Table 119 The NMR data of compound **GF27**

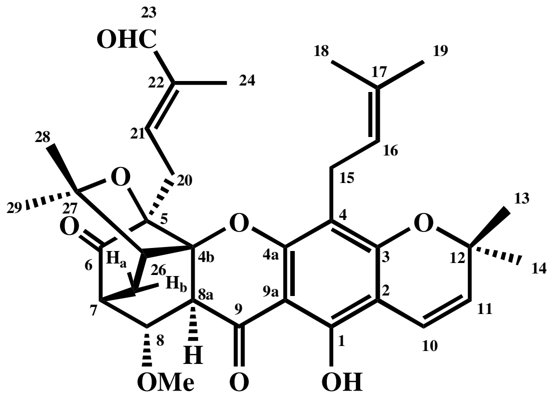
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
1	12.10 (*s*)	157.17 (C)	C-1, C-9a	
2		103.01(C)		
3		160.50 (C)		
4		105.32 (C)		
4a		156.97 (C)		
4b		88.14 (C)		
5		86.12 (C)		
6		207.98 (C=O)		
7	2.83 (*dd*, 6.0, 4.5)	44.48 (CH)	C-5, C-6, C-8, C-8a, C-26	H-8, H-8a, H-25a
8	4.30 (*dd*, 4.5, 1.2)	74.78 (CH)	C-4b, C-6, C-7, C-8a, C-9, C-25	H-7, H-8a, H-25b, 8-OCH_3
8-OCH_3	3.31 (*s*)	55.89 (CH_3)	C-8	H-8, Me-23
8a	3.29 (*d*, 1.2)	47.60 (CH)	C-4b, C-5, C-9, C-26	H-7, H-8, Me-23
9		194.16 (C=O)		
9a		102.07 (C)		
10	6.64 (*d*, 10.0)	115.23 (CH)	C-1, C-2, C-3, C-12	H-11
11	5.53 (*d*, 10.0)	125.99 (CH)	C-2, C-12, C-14	H-10
12		79.01 (C)		
13	1.46 (*s*)	28.71 (CH_3)	C-11, C-12, C-14	
14	1.50 (*s*)	28.54 (CH_3)	C-11, C-12, C-13	
15	a: 3.00 (*dd*, 15.0, 10.5)	25.58 (CH_2)	C-3, C-4, C-4a, C-16	
	b: 2.86 (*dd*, 15.0, 2.4)		C-3, C-4, C-4a, C-16	
16	4.05 (*dd*, 10.5, 2.4)	78.20 (CH)	C-15	Me-18, Me-19
17		73.57 (C)		
18	1.71 (*s*)	28.78 (CH_3)	C-16, C-17, C-19	
19	1.70 (*s*)	28.56 (CH_3)	C-16, C-17, C-18	
20	a: 3.54 (*dd*, 13.8, 10.5) b: 2.99 (*dd*, 13.8, 6.0)	28.16 (CH_2)	C-4b, C-5, C-6, C-21, C-22	
21	5.91 (*ddq*, 10.5, 6.0, 1.5)	132.49 (CH)	C-23, C-24	Me-23
22		131.44 (C)		
23	1.88 (*brs*)	20.46 (CH_3)	C-21, C-22, C-24	H-8a, H-21, 8-OCH_3
24		170.73 (C=O)		

Table 119 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations	NOE
25	a: 1.98 (*dd*, 15.0, 6.0)	20.08 (CH_2)	C-4b, C-7, C-8, C-27	H-7, H-25b, Me-29
	b: 1.35 (*dd*, 15.0, 8.7)		C-6, C-7, C-8, C-27	H-8, H-25a, H-26
26	2.51 (*d*, 8.7)	43.89 (CH)	C-4b, C-7, C-25, C-28	H-25b
27		81.49 (C)		
28	1.29 (*s*)	29.53 (CH_3)	C-26, C-27, C-29	
29	1.14 (*s*)	27.49 (CH_3)	C-26, C-27, C-28	

3.3.3 Compound GF25

Compound **GF25** was obtained as a yellow gum. Its UV (**Figure 173**) and IR (**Figure 174**) spectral data were similar to those of **GF28**. The ^{1}H NMR spectrum (**Figure 175**) (**Table 120**) was almost identical to that of **GF28** with an additional *singlet* of an aldehyde proton at δ_H 9.43. Furthermore, the DEPT spectrum (**Figure 177**) confirmed that a carbon signal at δ_C 195.11 was an aldehyde carbonyl carbon. The HMBC correlations (**Figure 179**) (**Table 120**) between the aldehyde H-23 and C-21 (δ_C 148.79) and C-24 (δ_C 9.26) suggested that the C-5 3-carboxybut-2-enyl substituent in **GF28** was replaced by a 2-butenyl-3-carboxaldehyde unit in **GF25**. The ^3J HMBC data between the methylene protons [$H_{a,b}$-20, δ_H 3.06 (*dd*, J = 16.5 and 7.5 Hz) and 2.94 (*dd*, J = 16.5 and 6.3 Hz)] of the 2-butenyl-3-carboxaldehyde group and C-4b (δ_C 88.30) and C-6 (δ_C 208.10) confirmed the attachment of the 2-butenyl-3-carboxaldehyde substituent at C-5 (δ_C 85.97). Furthermore, the location of other substituents was identical to those of **GF28**, based on HMBC data (**Table 120**). Comparison of its ^{1}H NMR data and optical rotation ($[\alpha]_D^{29}$ -44°, c = 0.11, $CHCl_3$) with those of isomoreollin B (**28**) ($[\alpha]_D^{24}$ -37°, c = 0.1, $CHCl_3$), previously isolated from the latex of *G. hanburyi* (Asano, 1996) indicated that **GF25** had the same structure as **28**.



28

Table 120 The NMR data of compound **GF25**

Position	GF25		HMBC correlations	isomoreollin B
	δ_H (*mult.*, J_{Hz})	δ_C (C-type)		δ_H (*mult.*, J_{Hz})
1-OH	11.90 (*s*)	156.41 (C)	C-1, C-2, C-9a	11.75 (*s*)
2		103.23 (C)		
3		160.92 (C)		
4		109.10 (C)		
4a		155.48 (C)		
4b		88.30 (C)		
5		85.97 (C)		
6		208.10 (C=O)		
7	2.90 (*dd*, 6.3, 4.5)	43.69 (CH)	C-8, C-8a, C-25, C-26	2.91 (*dd*, 6.0, 4.6)
8	4.36 (*dd*, 4.5, 1.2)	74.13 (CH)	C-4b, C-6, C-8a, C-9, C-25, 8-OCH$_3$	4.37 (*dd*, 4.6, 1.1)
8-OCH$_3$	3.34 (*s*)	55.89 (CH$_3$)	C-8	3.33 (*s*)
8a	3.09 (*d*, 1.2)	48.47 (CH)	C-8, C-9, C-26	3.08 (*d*, 1.1)
9		193.25 (C=O)		
9a		101.81 (C)		
10	6.62 (*d*, 10.2)	115.24 (CH)	C-1, C-2, C-3, C-12	6.62 (*d*, 9.9)
11	5.53 (*d*, 10.2)	126.46 (CH)	C-2, C-12, C-13, C-14	5.53 (*d*, 9.9)
12		78.57 (C)		
13	1.47 (*s*)	28.60 (CH$_3$)	C-11, C-12, C-14	1.47 (*s*)
14	1.40 (*s*)	28.19 (CH$_3$)	C-11, C-12, C-13	1.40 (*s*)

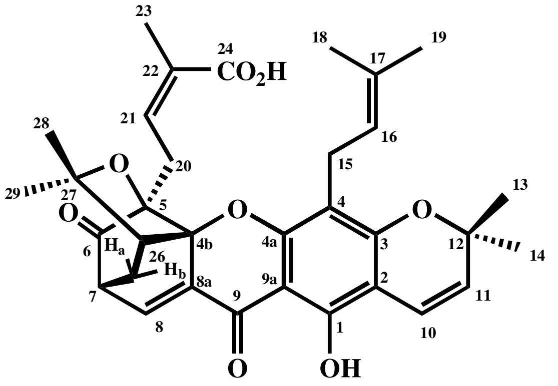
Table 120 (continued)

Position	GF25		HMBC correlations	isomoreollin B
	δ_H (*mult.*, J_{Hz})	δ_C (C-type)		δ_H (*mult.*, J_{Hz})
15	a: 3.31 (*dd*, 14.4, 7.5) b: 3.19 (*dd*, 14.4, 6.0)	21.55 (CH_2)	C-3, C-4, C-4a, C-16, C-17	a: 3.31 (*dd*, 14.1, 7.6) b: 3.19 (*dd*, 14.1, 5.7)
16	4.97 (*tm*, 7.5)	122.36 (CH)	C-18, C-19	4.97 (*m*)
17		131.47 (C)		
18	1.75 (*s*)	18.06 (CH_3)	C-16, C-17, C-18	1.76 (*s*)
19	1.63 (*s*)	25.63 (CH_3)	C-16, C-17, C-19	1.64 (*s*)
20	a: 3.06 (*dd*, 16.5, 7.5) b: 2.94 (*dd*, 16.5, 6.3)	27.56 (CH_2)	C-4b, C-5, C-6, C-21, C-22	a: 3.06 (*dd*, 16.4, 7.5) b: 2.92 (*dd*, 16.4, 6.2)
21	6.97 (*tm*, 7.5)	148.79 (CH)	C-5, C-23, C-24	6.97 (*m*)
22		139.89 (C)		
23	9.43 (*s*)	195.11 (CH)	C-21, C-24	9.54 (*s*)
24	1.75 (*s*)	9.26 (CH_3)	C-21, C-22, C-23	1.76 (*s*)
25	a: 2.00 (*dd*, 14.7, 6.3)	19.96 (CH_2)	C-4b, C-7, C-8, C-26, C-27	a: 2.00 (*dd*, 14.7, 6.0)
	b: 1.44 (*dd*, 14.7, 8.7)		C-6, C-8, C-26	b: 1.41 (*dd*, 14.7, 8.5)
26	2.54 (*d*, 8.7)	43.56 (CH)	C-4b, C-5, C-7, C-25, C-28	2.55 (*d*, 8.5)
27		82.05 (C)		
28	1.37 (*s*)	29.77 (CH_3)	C-26, C-27, C-29	1.37 (*s*)
29	1.17 (*s*)	27.31 (CH_3)	C-27, C-28	1.16 (*s*)

3.3.4 Compound GF29

Compound **GF29** was obtained as a yellow gum. The IR spectrum (**Figure 181**) with absorption bands at 3500-2500 (a hydroxyl group of a carboxylic acid), 1738 (an unconjugated carbonyl group), 1692 (an α,β-unsaturated carboxyl group) and 1633 cm^{-1} (a chelated *ortho*-hydroxyl carbonyl group) and UV absorption bands at λ_{max} 203, 219, 288 and 359 nm (**Figure 180**) suggested that **GF29** was a caged-polyprenylated xanthone. The ^{1}H NMR spectrum (**Figure 182**) (**Table 121**) showed characteristic signals of a caged-prenylated moiety, -OC(Me)$_2$-CHCH$_2$-C-, [δ_H 2.53 (*d*, J = 9.0 Hz, 1H, H-26), 2.32 (*dd*, J = 13.5 and 4.5 Hz, 1H, H$_a$-25), 1.42 (*dd*, J =

13.5 and 9.0 Hz, 1H, H$_b$-25), 1.71 (*s*, 3H, Me-28) and 1.29 (*s*, 3H, Me-29)]. Comparison of its ^{1}H NMR data with those of **GF28** revealed similar results except for the absence of the methoxy protons (δ_H 3.30, 8-OCH$_3$ in **GF28**) and two methine protons (δ_H 4.34, H-8, and 3.19, H-8a in **GF28**). These suggested that **GF29** had a C8/C8a double bond. One additional olefinic proton signal [δ_H 7.55 (*d*, J = 6.9 Hz)] supported above conclusion. The olefinic proton, which was attributed to H-8, showed ^3J cross peaks with C-4b (δ_C 90.84), C-6 (δ_C 203.27), C-7 (δ_C 46.81), C-9 (δ_C 178.95) and C-25 (δ_C 25.16). These corresponded to the ^{13}C NMR (**Figure 183**) (**Table 121**) and DEPT (**Figure 184**) spectra which showed 16 quaternary, 7 methine, 3 methylene and 7 methyl carbons. The attachment of other substituents was also identical to that of **GF28**, according to HMBC data (**Figure 186**) (**Table 121**). Thus, **GF29** was identified as morellic acid (**29**), which was previously isolated from *G. morella* (Karanjgaonkar, 1966). There is no report on optical rotation of morellic acid. However, **GF29** would have the same relative stereochemistry as those isolated from the fruits of this plant since it gave a negative sign of optical rotation ($[\alpha]_D^{29}$ -541°, c = 0.19, CHCl$_3$).



29

Table 121 The NMR data of compound **GF29**

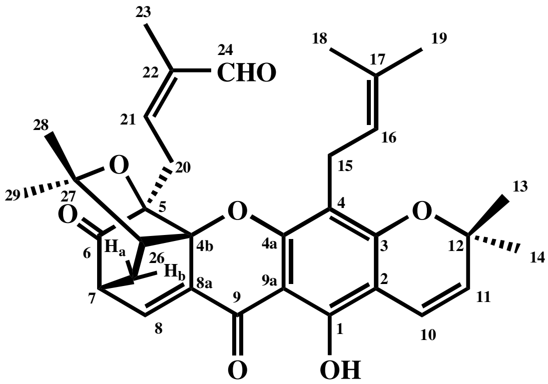
Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
1-OH	12.80 (*s*)	157.59 (C)	C-1, C-2, C-9a
2		103.14 (C)	
3		161.17 (C)	
4		108.04 (C)	

Table 121 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
4a		157.23 (C)	
4b		90.84 (C)	
5		83.77 (C)	
6		203.27 (C=O)	
7	3.50 (*dd*, 6.9, 4.5)	46.81 (CH)	C-5, C-6, C-8a, C-26
8	7.55 (*d*, 6.9)	135.34 (CH)	C-4b, C-6, C-7, C-9, C-25
8a		133.31 (C)	
9		178.95 (C=O)	
9a		100.51 (C)	
10	6.55 (*d*, 9.9)	115.37 (CH)	C-1, C-2, C-3, C-12
11	5.45 (*d*, 9.9)	126.04 (CH)	C-2, C-12, C-13
12		78.59 (C)	
13	1.42 (*s*)	28.47 (CH_3)	C-11, C-14
14	1.38 (*s*)	28.23 (CH_3)	C-11
15	a: 3.31 (*dd*, 14.7, 8.4)	21.60 (CH_2)	C-3, C-4, C-4a, C-16, C-17
	b: 3.14 (*dd*, 14.7, 5.1)		C-3, C-4, C-4a, C-16, C-17
16	5.03 (*tm*, 6.6)	122.10 (CH)	C-18, C-19
17		131.51 (C)	
18	1.74 (*s*)	18.12 (CH_3)	C-16, C-19
19	1.64 (*s*)	25.74 (CH_3)	C-18
20	2.95 (*d*, 7.0)	29.27 (CH_2)	C-4b, C-5, C-6, C-21, C-22, C-24
21	6.06 (*tm*, 7.0)	137.51 (CH)	C-5, C-23, C-24
22		127.88 (C)	
23	1.74 (*s*)	20.75 (CH_3)	C-21, C-24
24		170.32 (C=O)	
25	a: 2.32 (*dd*, 13.5, 4.5)	25.16 (CH_2)	C-4b, C-7, C-8, C-26, C-27
	b: 1.42 (*dd*, 13.5, 9.0)		C-6, C-7, C-8, C-26, C-27
26	2.53 (*d*, 9.0)	48.98 (CH)	C-4b, C-5, C-7, C-25, C-28
27		83.97 (C)	
28	1.71 (*s*)	29.86 (CH_3)	C-26, C-27, C-29
29	1.29 (*s*)	28.84 (CH_3)	C-25, C-26, C-27, C-28

3.3.5 Compound GF26

Compound **GF26** was isolated as a yellow gum. The UV absorption bands at λ_{max} 203, 227, 287 and 357 nm (**Figure 187**) were similar to that of **GF29**. These results suggested that **GF26** had a caged-polyprenylated xanthone unit. The IR spectrum (**Figure 188**) exhibited absorption bands at 3461 (a hydroxyl group), 1738 (an unconjugated carbonyl group), 1689 (an α,β-unsaturated carbonyl group) and 1633 cm^{-1} (a chelated *ortho*-hydroxyl group). The presence of these carbonyl functionalities was confirmed by the carbon signals in the ^{13}C NMR spectrum (**Figure 190**) (**Table 122**) at δ_C 203.05, 194.49 and 178.85. Furthermore, the DEPT spectrum (**Figure 191**) revealed that the carbon signal at δ_C 194.49 was an aldehyde carbonyl carbon. Its ^{1}H NMR spectrum (**Figure 189**) (**Table 122**) was similar to that of **GF29** except for an additional signal of an aldehyde proton at δ_H 9.25. The formyl group was attached at C-22 (δ_C 140.11) due to HMBC data (**Figure 193**) (**Table 128**) between the aldehyde H-24 and C-23 (δ_C 8.60) and those of the olefinic H-21 and C-23 and C-24 (δ_C 194.49). These suggested the replacement at C-5 of the 3-carboxybut-2-enyl group in **GF29** with a 2-butenyl-3-carboxaldehyde unit. The attachment of other substituents was identical to that of **GF29**, according to HMBC data. Thus, the structure of **GF26** was assigned as morellin (**26**), which was previously isolated from the seed of *G. morella* (Rao, 1937). In addition, the relative stereochemistry of **GF26** was determined by comparison of its optical rotation ($[\alpha]_D^{29}$ -600°, c = 0.04, $CHCl_3$) with that of morellin ($[\alpha]_D^{28}$ -594°, c = 4.5, $CHCl_3$, Rao, 1937).



26

Table 122 The NMR data of compound **GF26**

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
1-OH	12.75 (*s*)	157.69 (C)	
2		103.28 (C)	
3		161.35 (C)	
4		108.08 (C)	
4a		157.15 (C)	
4b		90.80 (C)	
5		83.40 (C)	
6		203.05 (C=O)	
7	3.53 (*dd*, 7.0, 4.5)	46.86 (CH)	C-6, C-8a
8	7.56 (*d*, 7.0)	135.62 (CH)	C-4b, C-6, C-9
8a		133.65 (C)	
9		178.85 (C=O)	
9a		100.36 (C)	
10	6.61 (*d*, 9.9)	115.29 (CH)	C-1, C-3, C-12
11	5.53 (*d*, 9.9)	126.41 (CH)	C-2, C-12
12		78.88 (C)	
13	1.49 (*s*)	28.41 (CH_3)	C-11, C-12, C-14
14	1.45 (*s*)	28.41 (CH_3)	C-11, C-12, C-13
15	3.28 (*m*)	21.68 (CH_2)	C-4, C-16, C-17
16	5.10 (*tm*, 7.8)	121.81 (CH)	
17		132.01 (C)	
18	1.75 (*s*)	18.18 (CH_3)	C-16, C-17, C-19
19	1.65 (*s*)	25.78 (CH_3)	C-16, C-17, C-18
20	a: 2.75 (*dd*, 15.5, 7.5)	28.97 (CH_2)	C-4b, C-5,C-21, C-22
	b: 2.64 (*dd*, 15.5, 7.5)		C-4b, C-5,C-21, C-22
21	6.40 (*tm*, 7.5)	146.54 (CH)	C-23, C-24
22		140.11 (C)	
23	1.32 (*s*)	8.60 (CH_3)	C-22, C-24
24	9.25 (*s*)	194.49 (CH)	C-23
25	a: 2.37 (*dd*, 14.0, 4.5)	25.27 (CH_2)	C-4b, C-8, C-27
	b: 1.47 (*dd*, 14.0, 9.0)		C-6, C-8
26	2.57 (*d*, 9.0)	48.99 (CH)	C-4b, C-5, C-7, C-28
27		84.00 (C)	

Table 122 (continued)

Position	δ_H (*mult.*, J_{Hz})	δ_C (C-type)	HMBC correlations
28	1.74 (*s*)	29.97 (CH_3)	C-26, C-27, C-29
29	1.30 (*s*)	28.95 (CH_3)	C-26, C-27, C-28

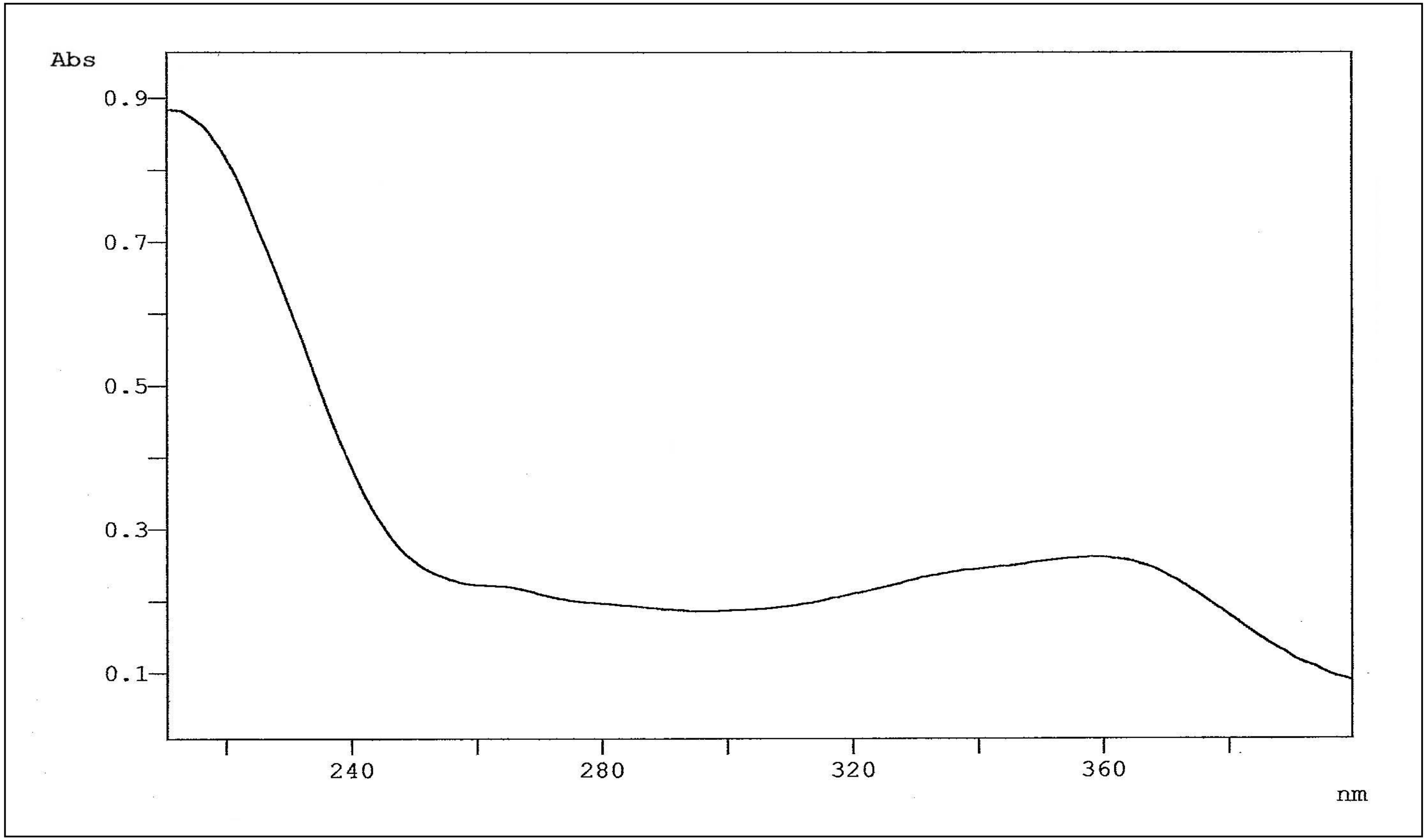


Figure 3 UV (CH_3OH) spectrum of **GF3**

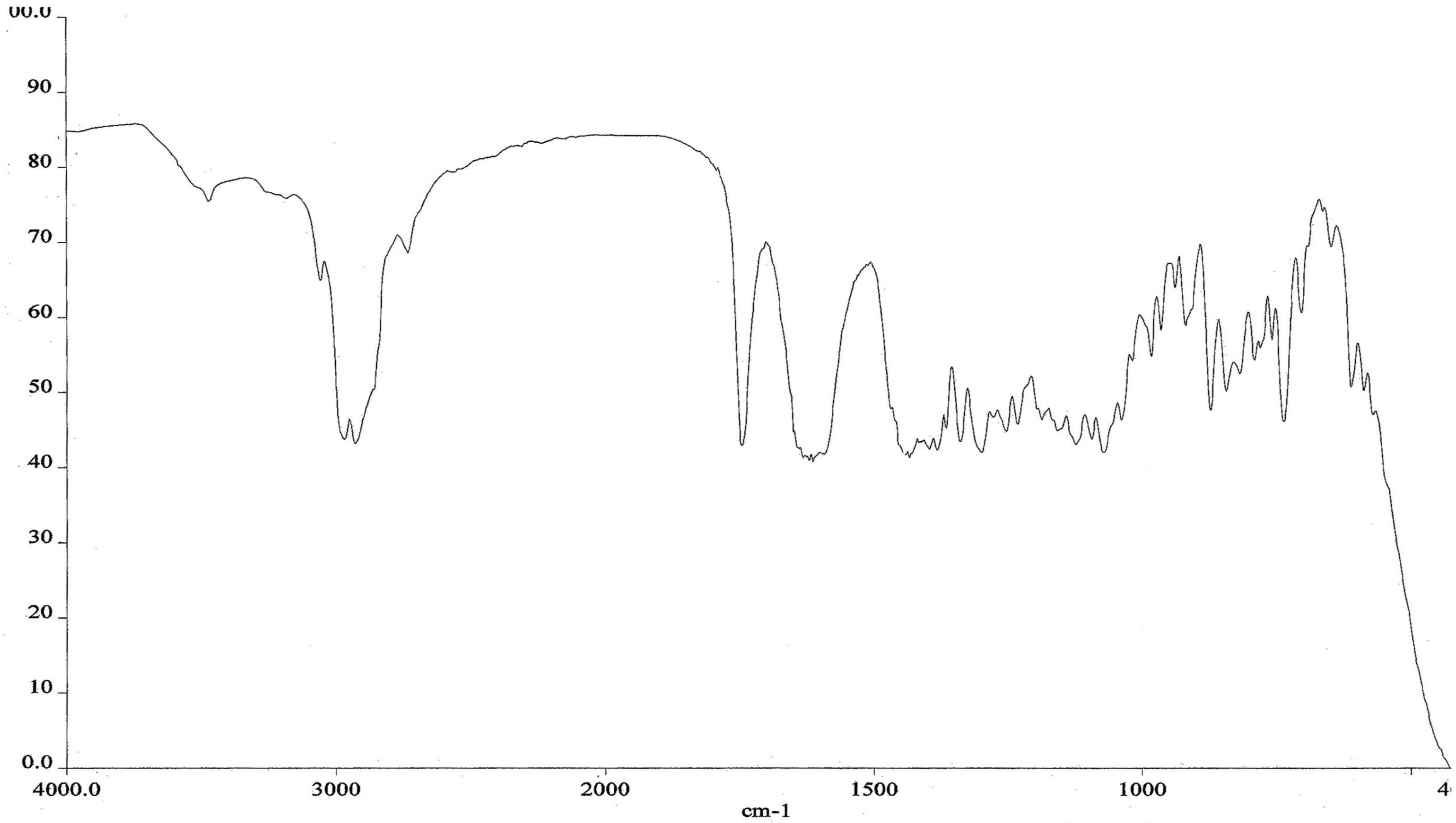


Figure 4 FT-IR (neat) spectrum of **GF3**

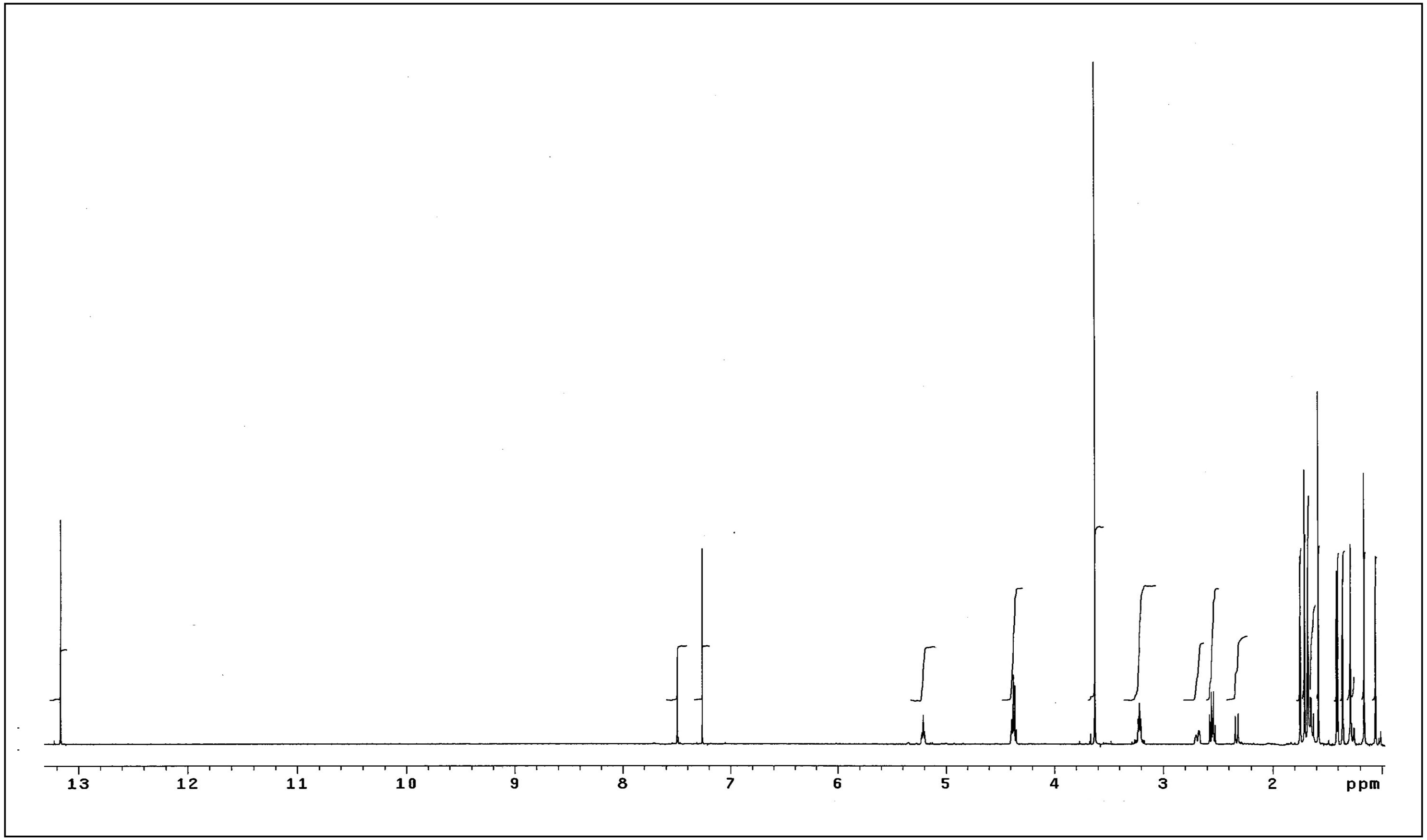


Figure 5 ^{1}H NMR (500 MHz) ($CDCl_3$) spectrum of **GF3**

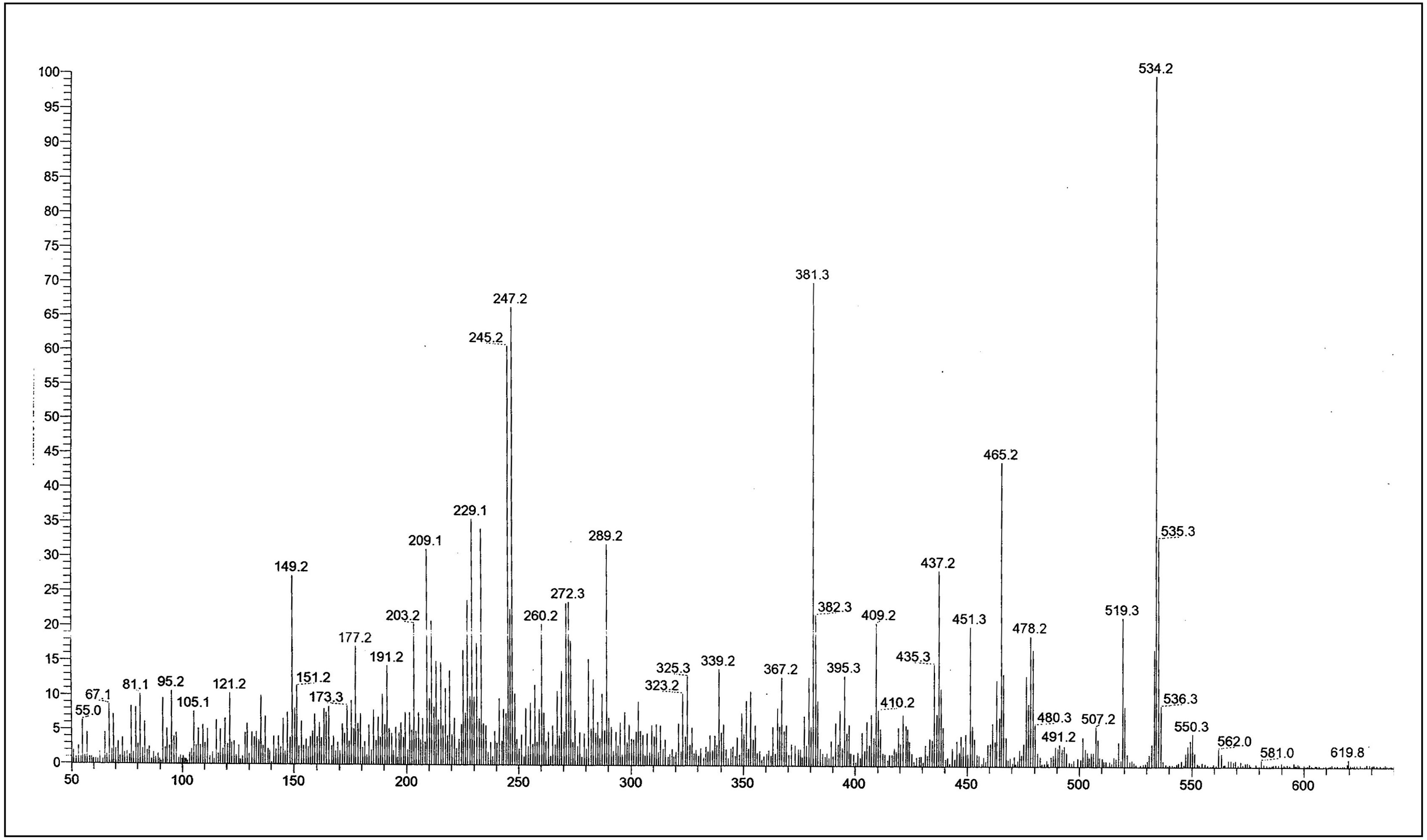


Figure 6 Mass spectrum of **GF4**

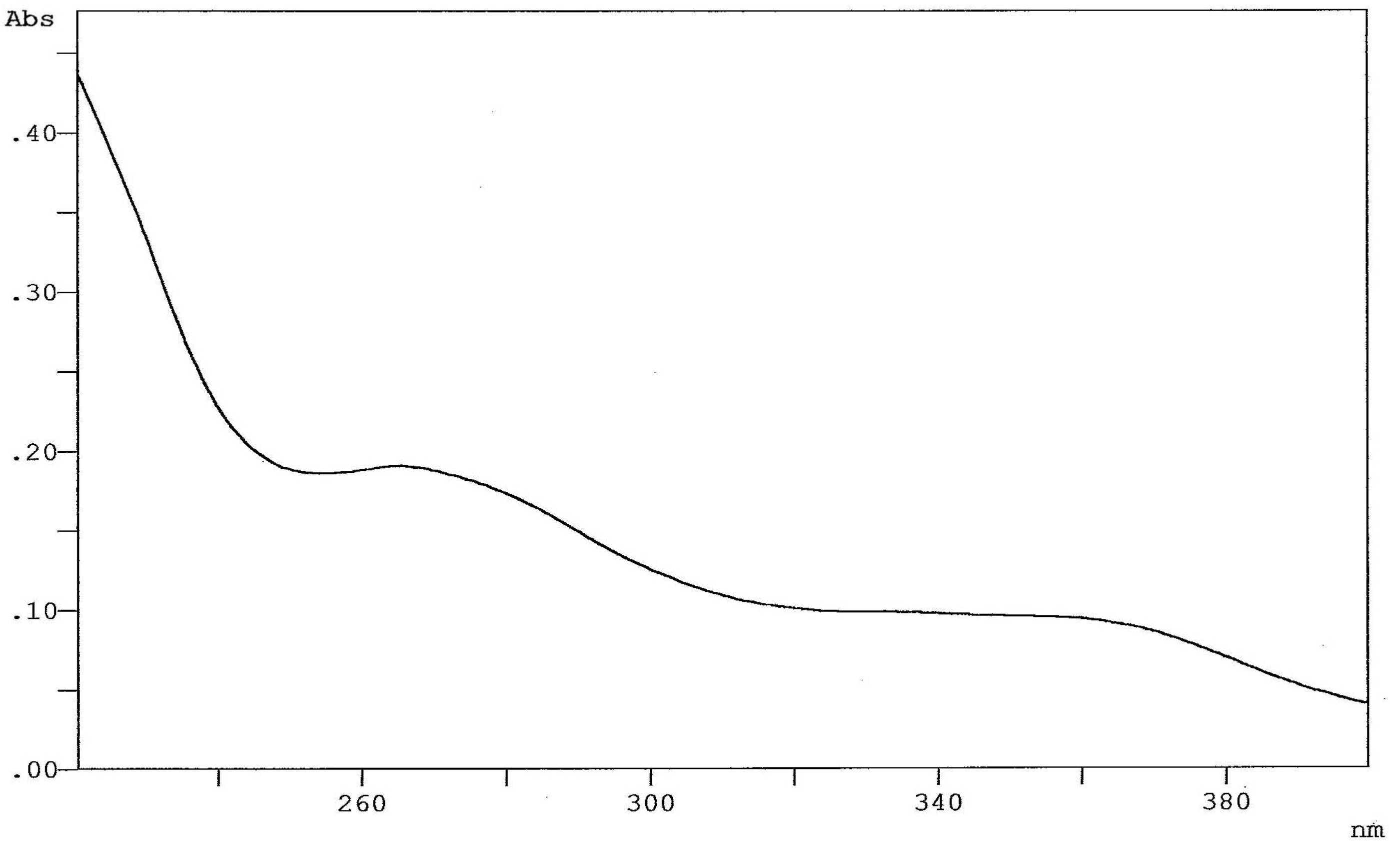


Figure 7 UV (CH_3OH) spectrum of **GF4**

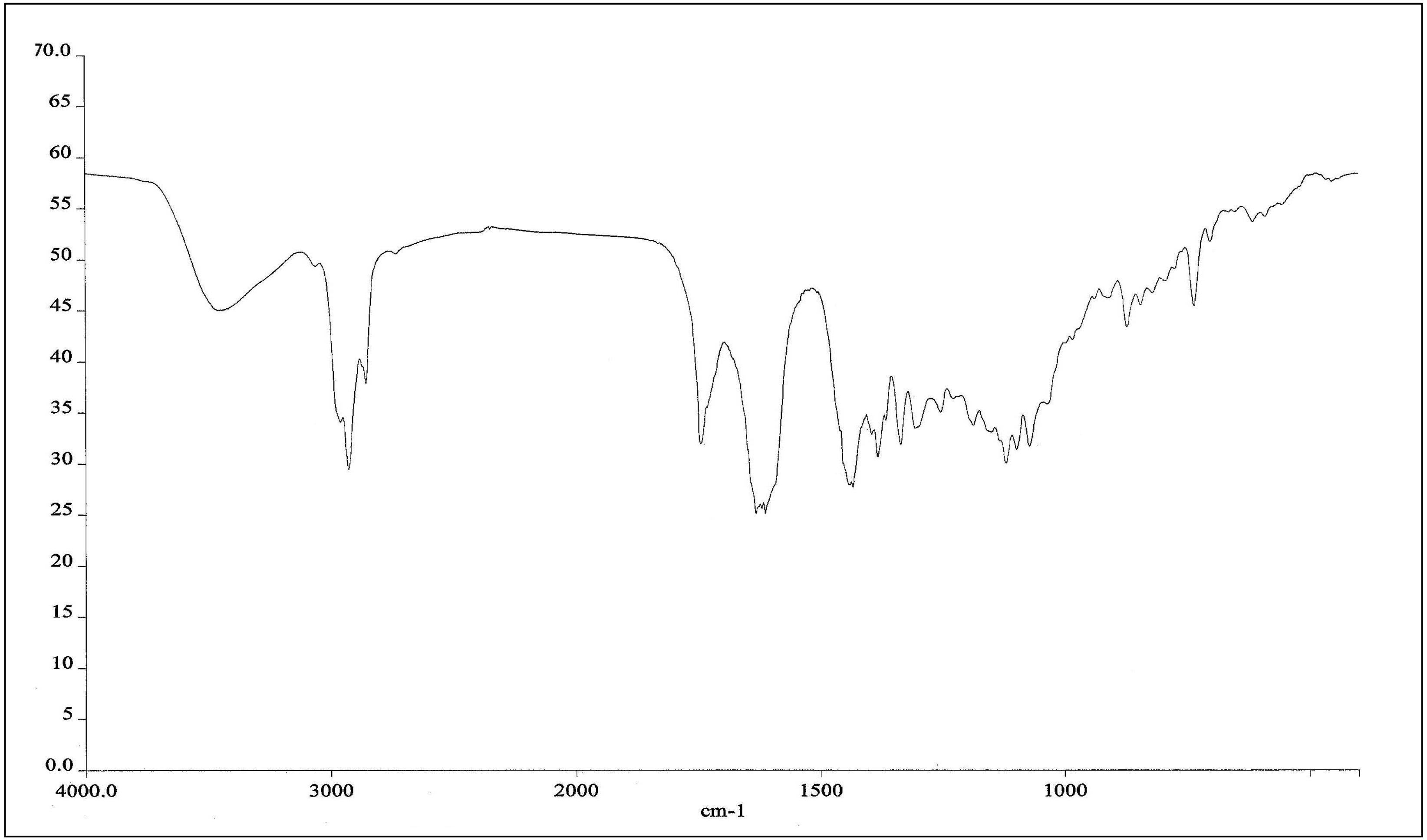


Figure 8 FT-IR (neat) spectrum of **GF4**

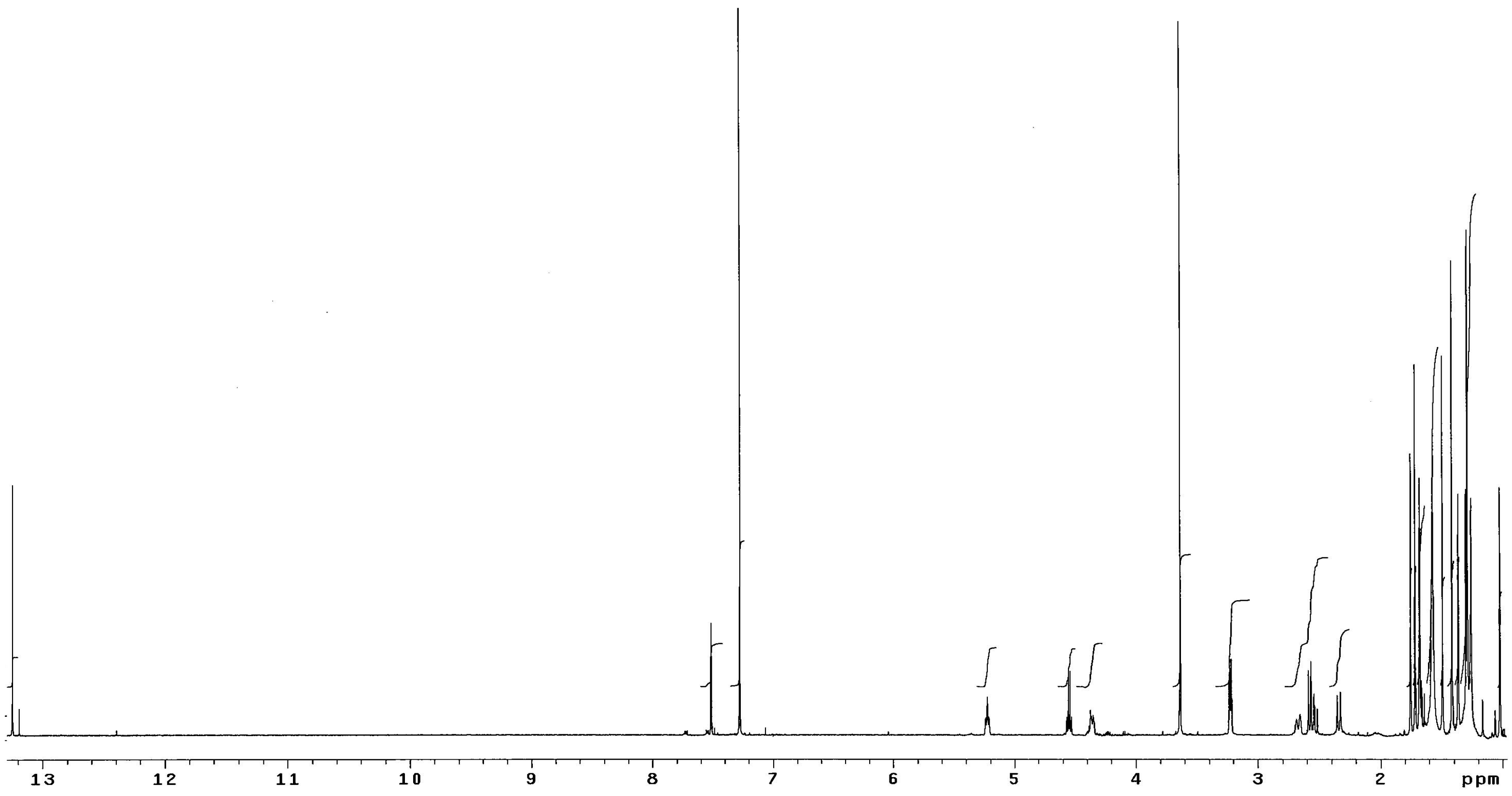


Figure 9 ^{1}H NMR (500 MHz) ($CDCl_3$) spectrum of **GF4**

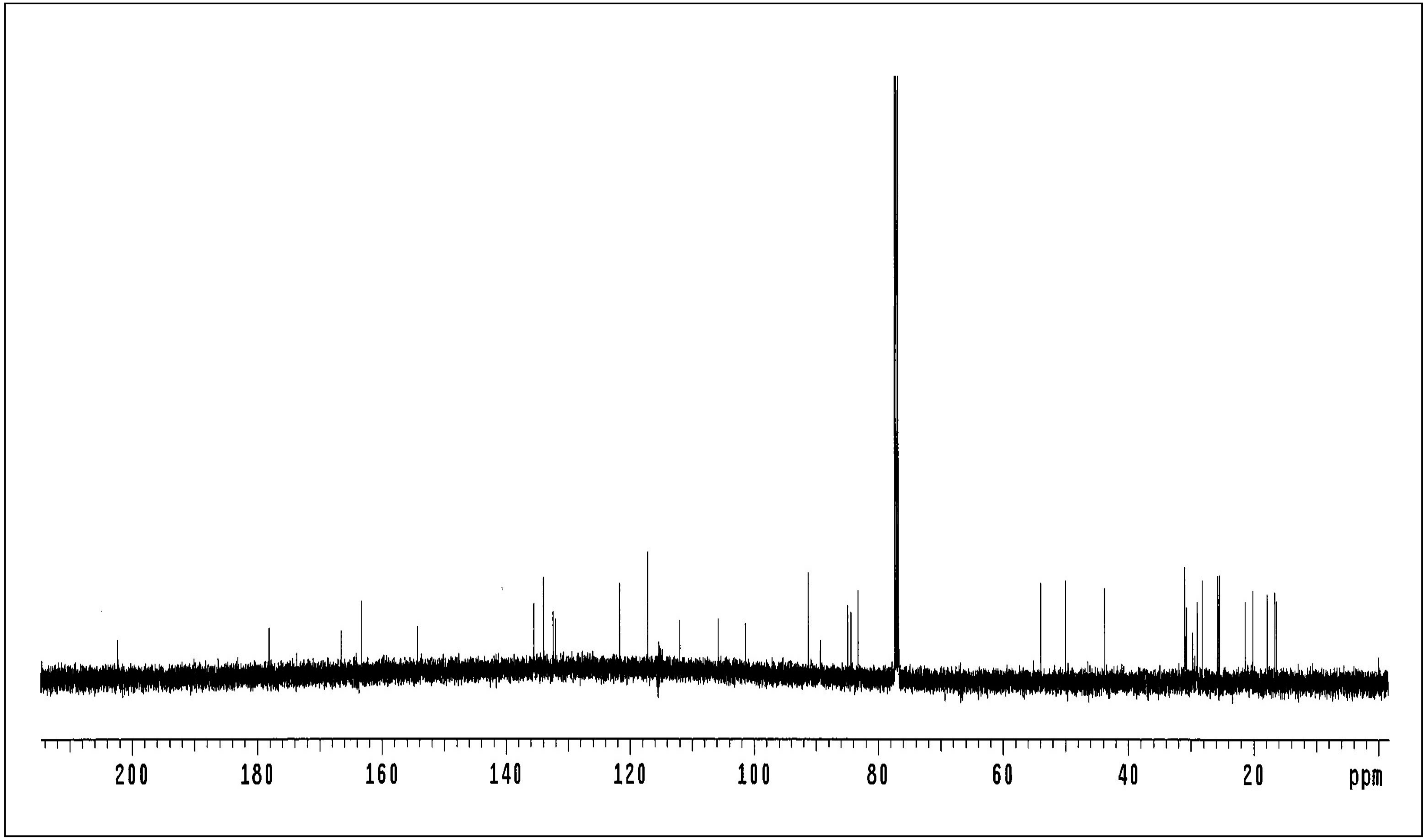


Figure 10 ^{13}C NMR (125 MHz) ($CDCl_3$) spectrum of **GF4**

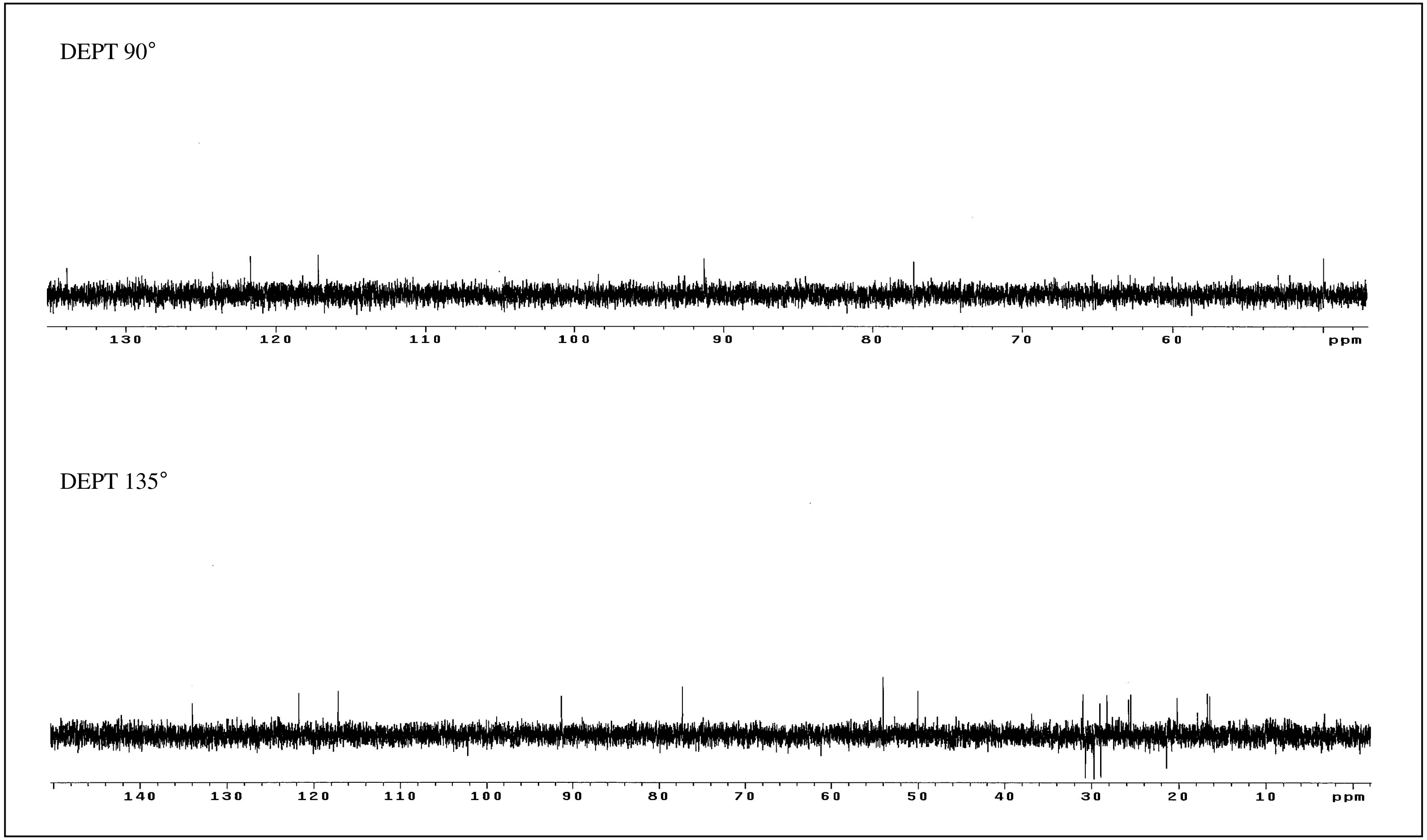


Figure 11 DEPT spectrum of **GF4**

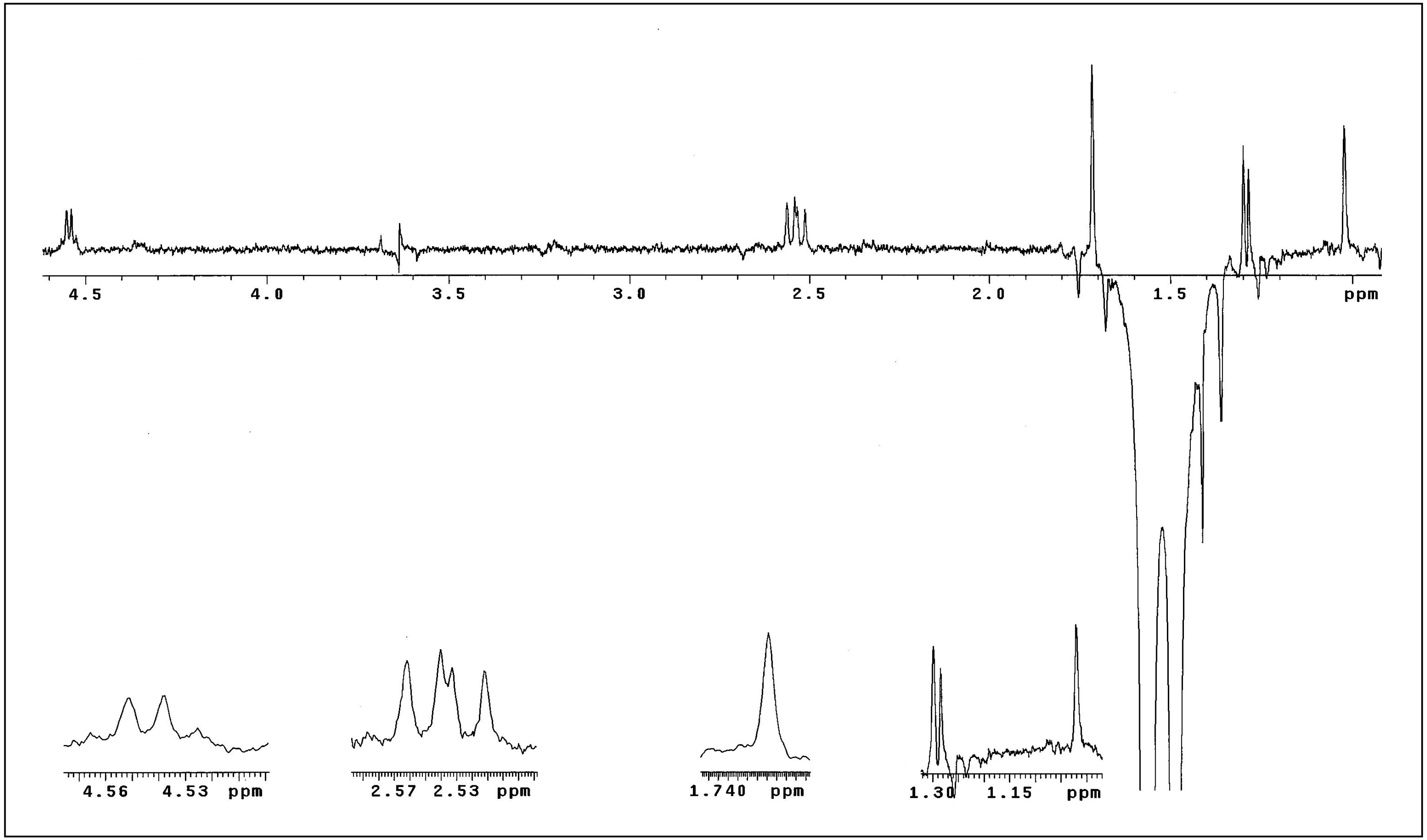


Figure 12 NOEDIFF spectrum of **GF4** after irradiation at δ_H 1.49

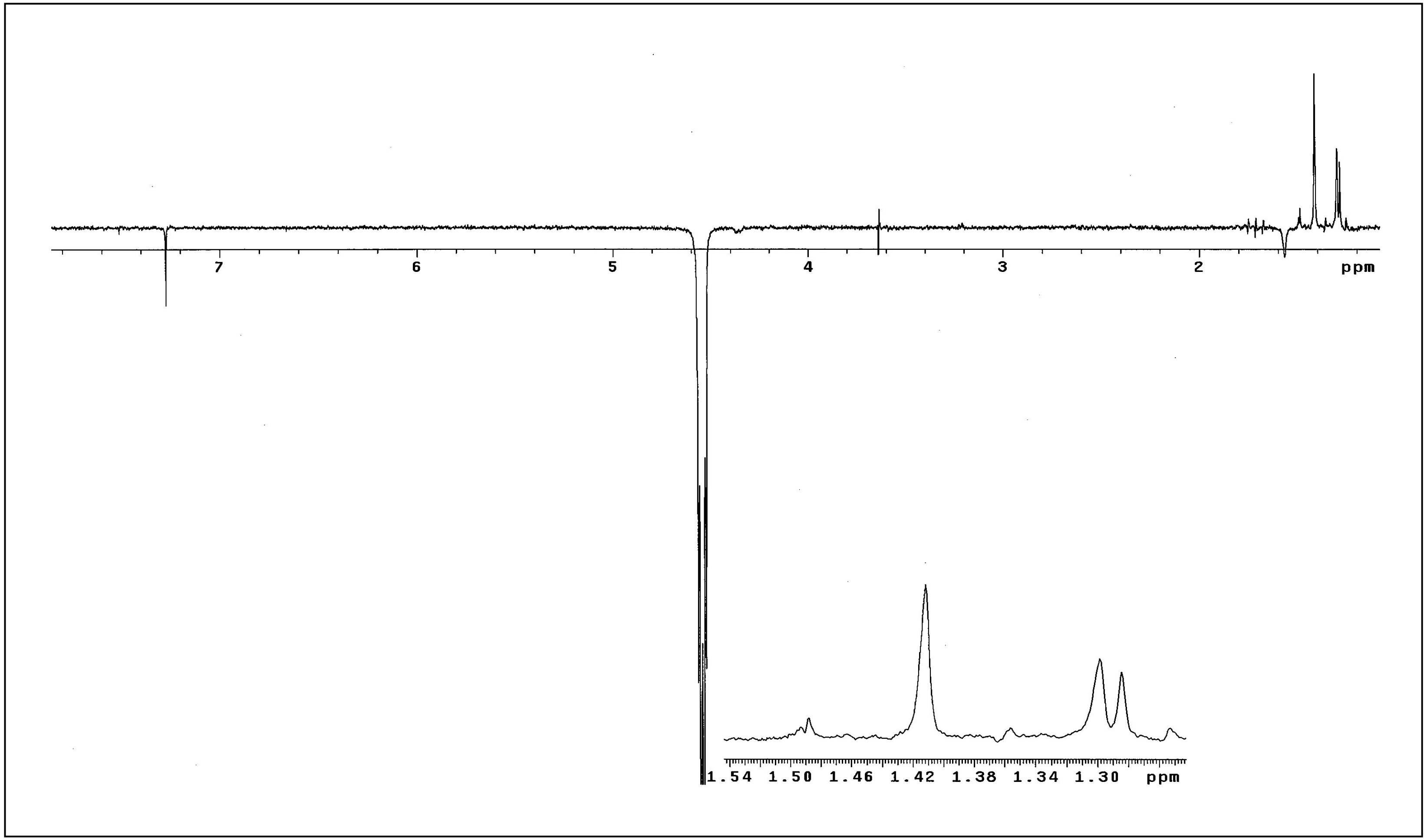


Figure 13 NOEDIFF spectrum of **GF4** after irradiation at δ_H 4.55

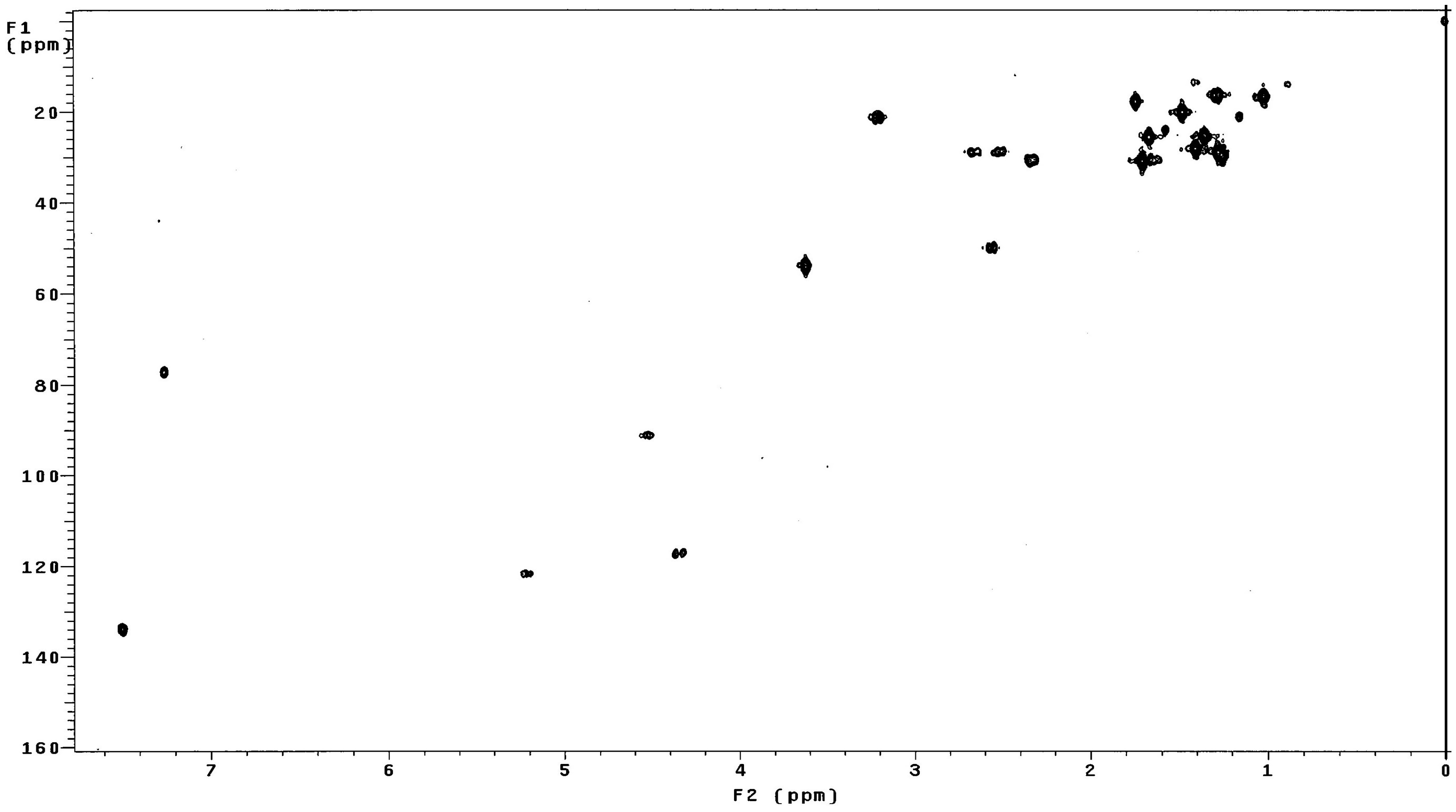


Figure 14 2D HMQC spectrum of **GF4**

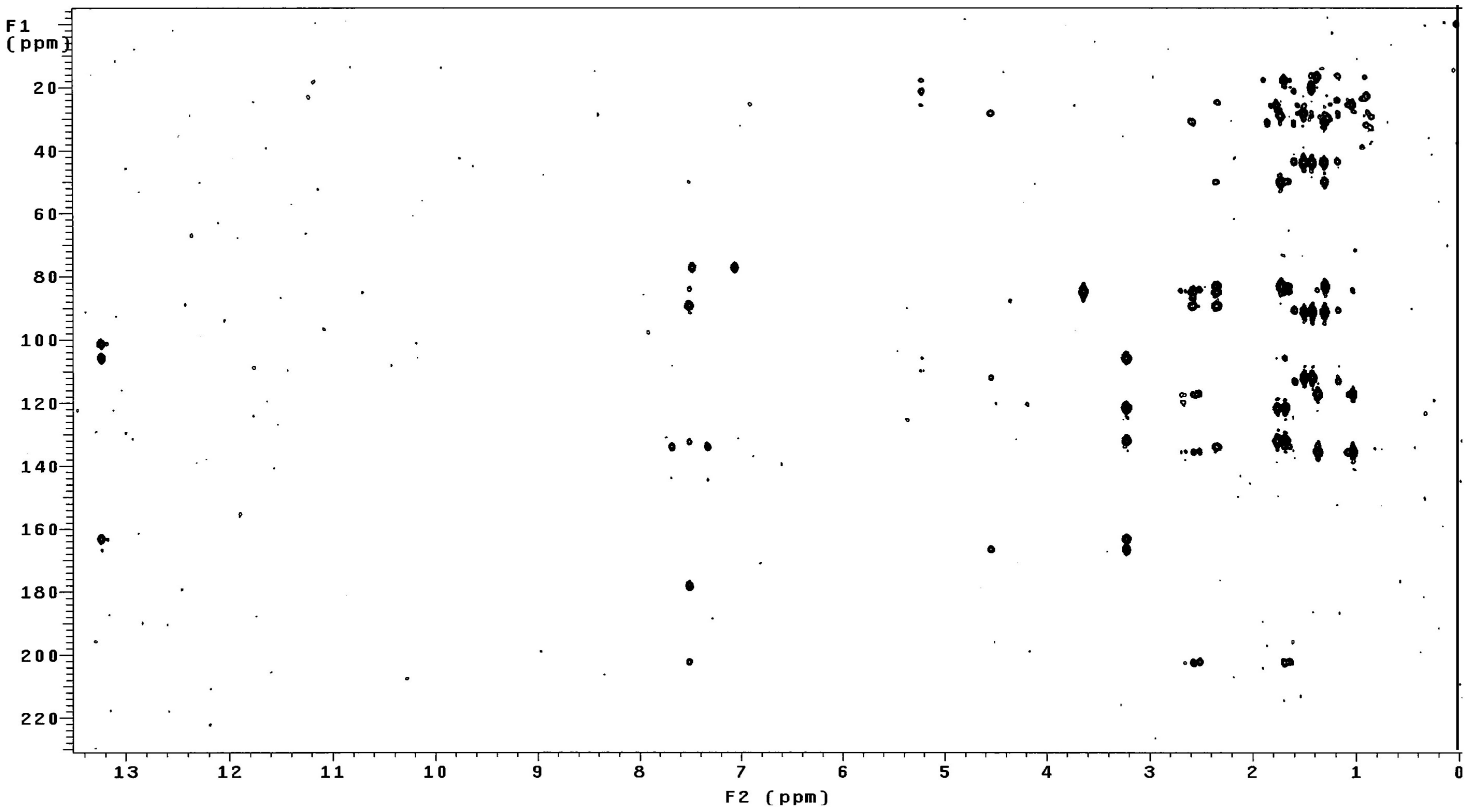


Figure 15 2D HMBC spectrum of **GF4**

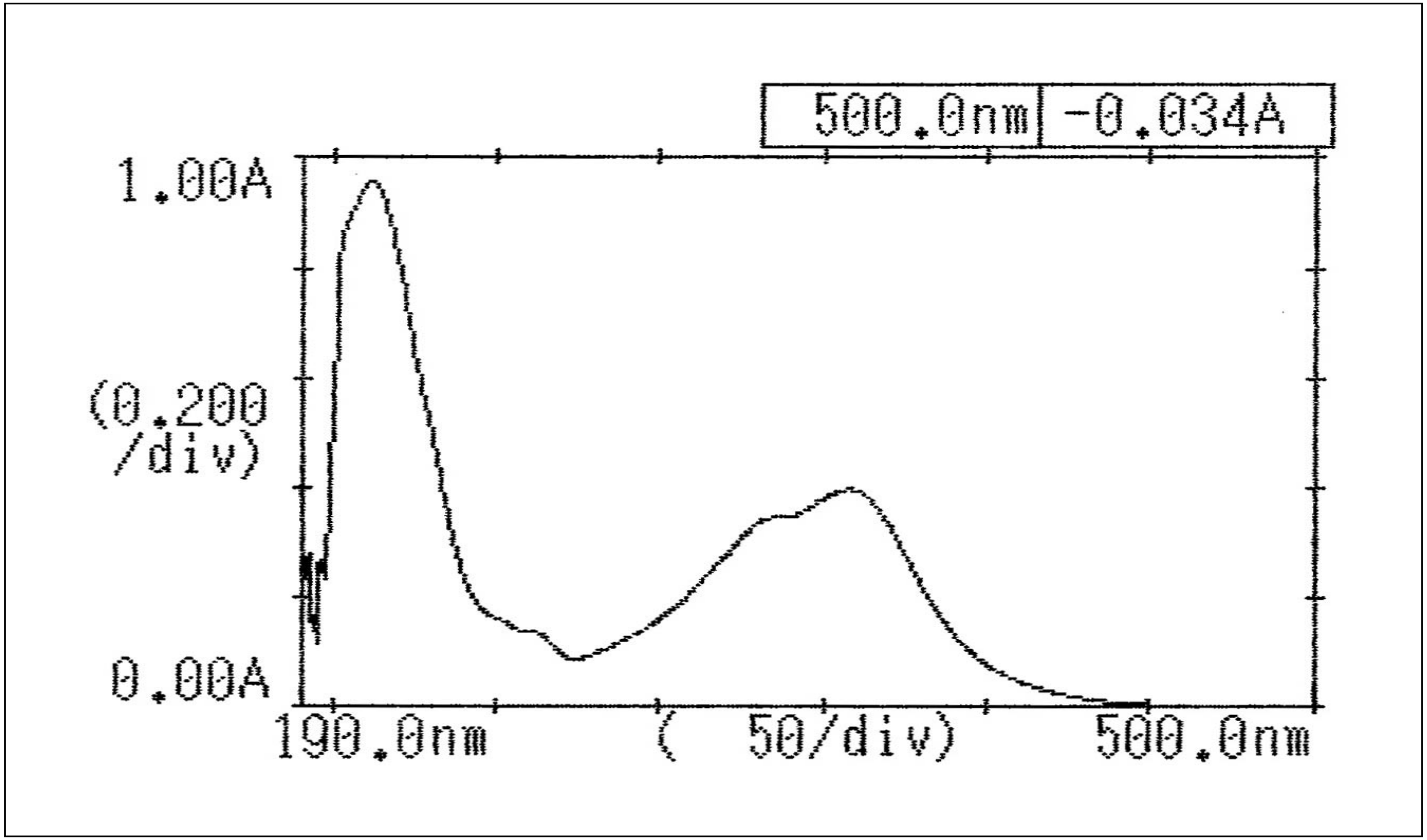


Figure 16 UV (CH_3OH) spectrum of **GF5**

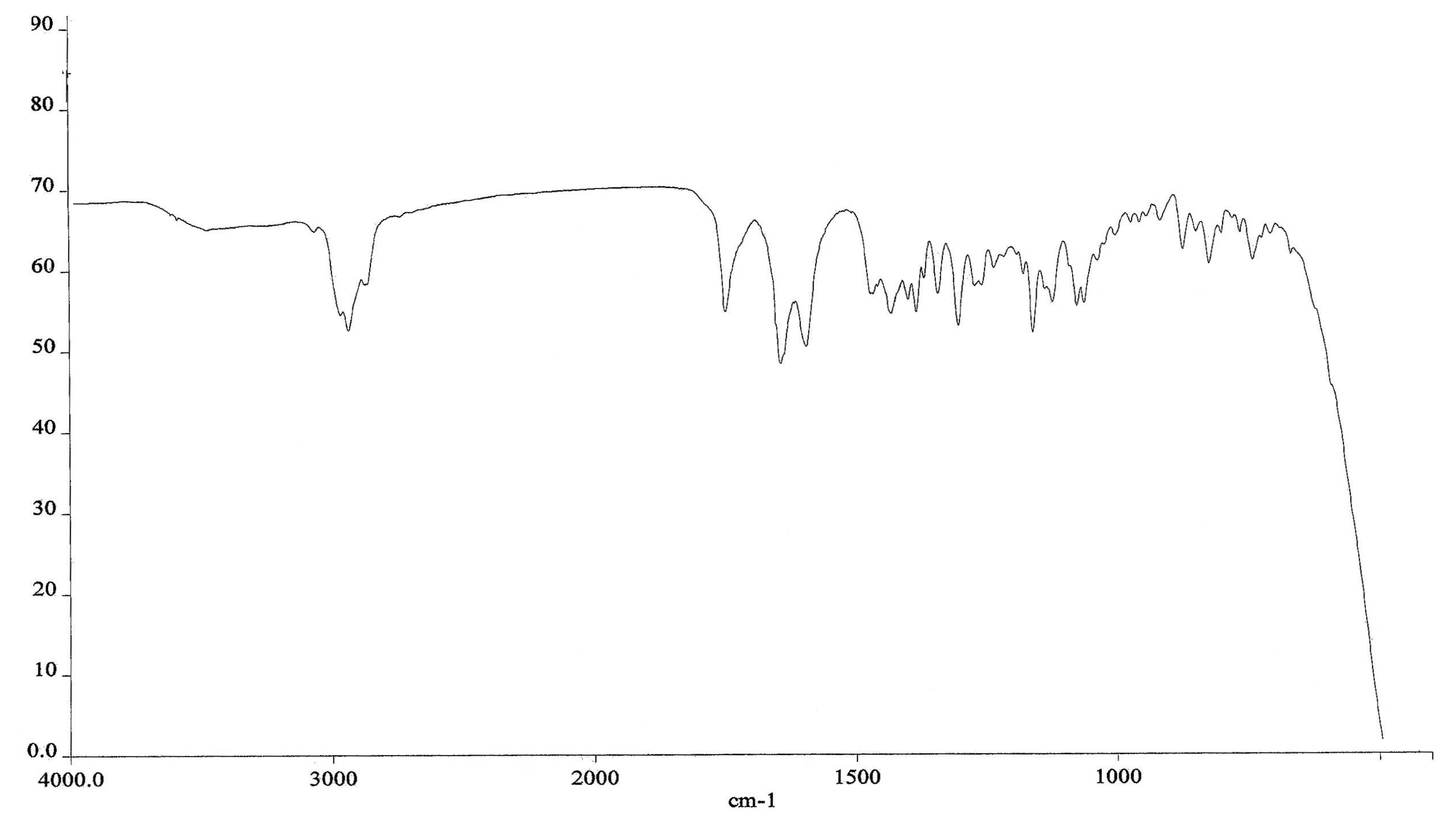


Figure 17 FT-IR (neat) spectrum of **GF5**

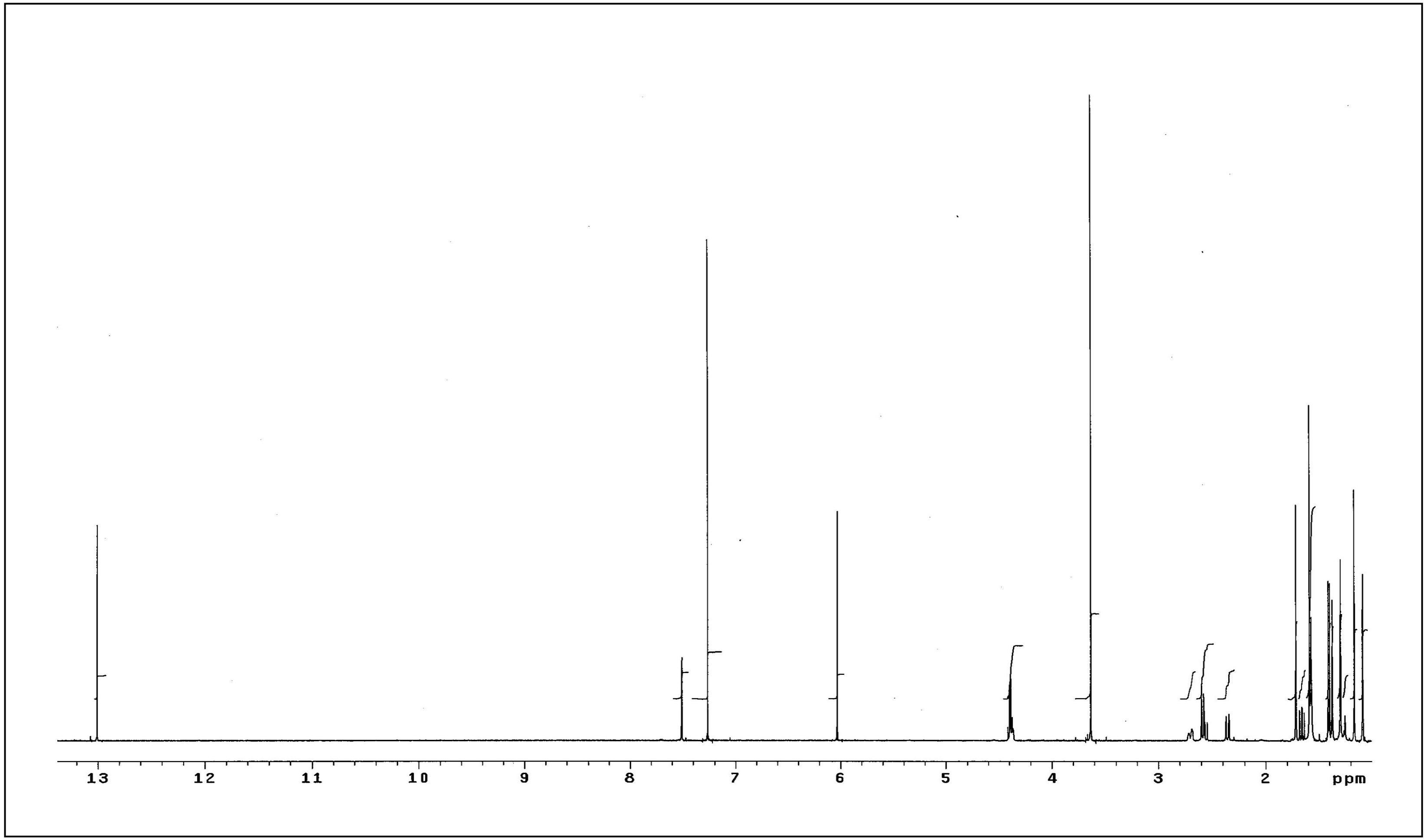


Figure 18 ^{1}H NMR (500 MHz) ($CDCl_3$) spectrum of **GF5**

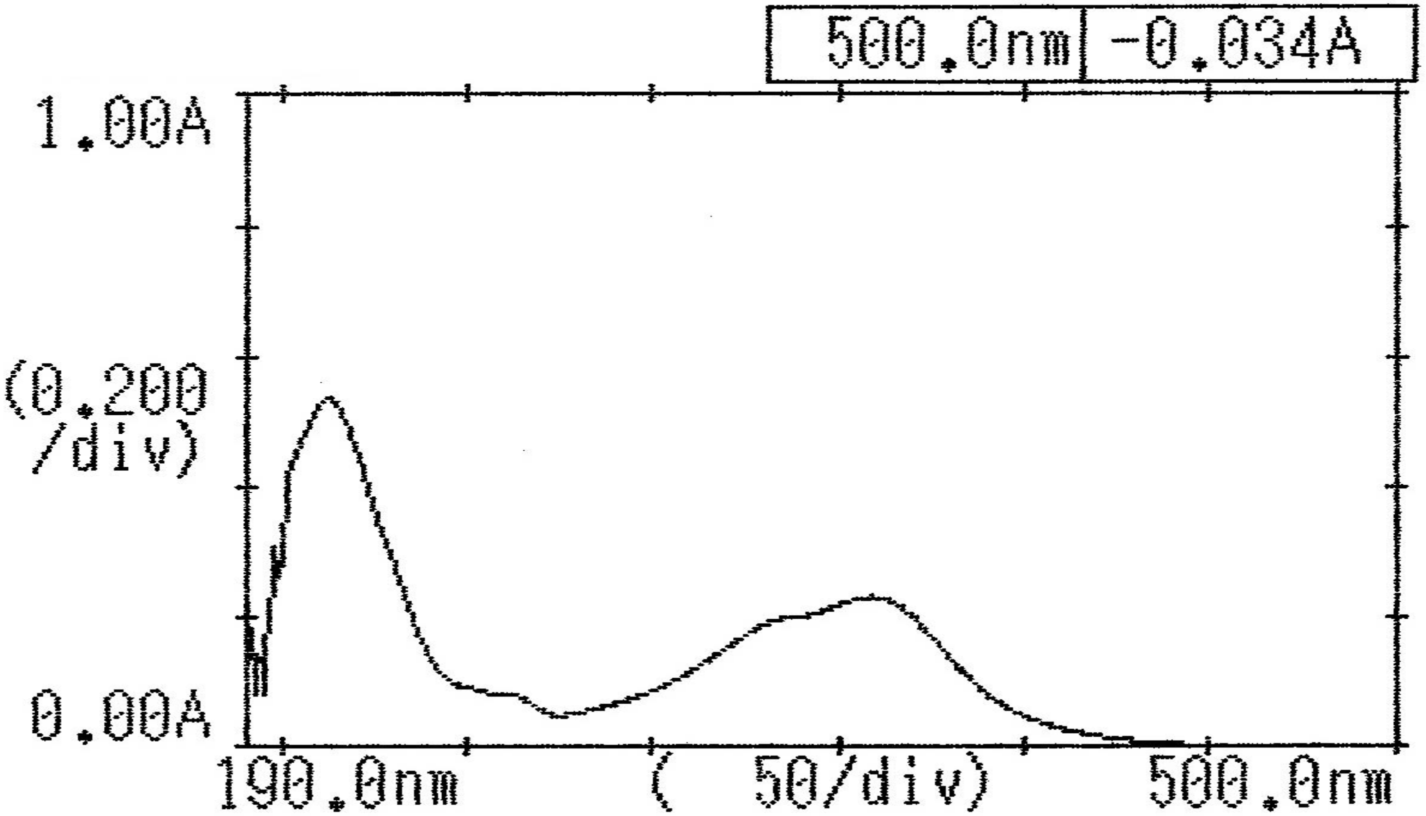


Figure 19 UV (CH_3OH) spectrum of **GF6**

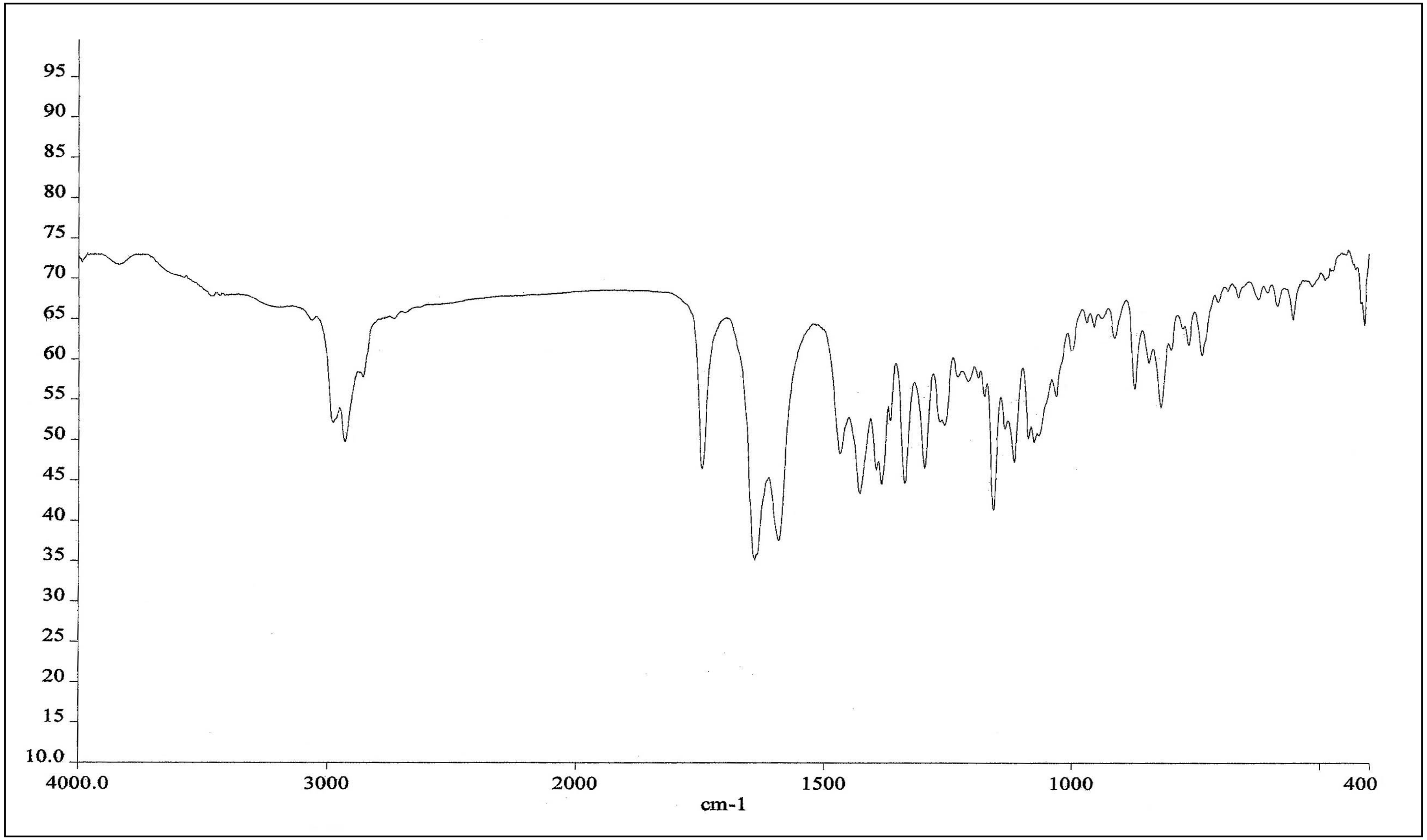


Figure 20 FT-IR (neat) spectrum of **GF6**

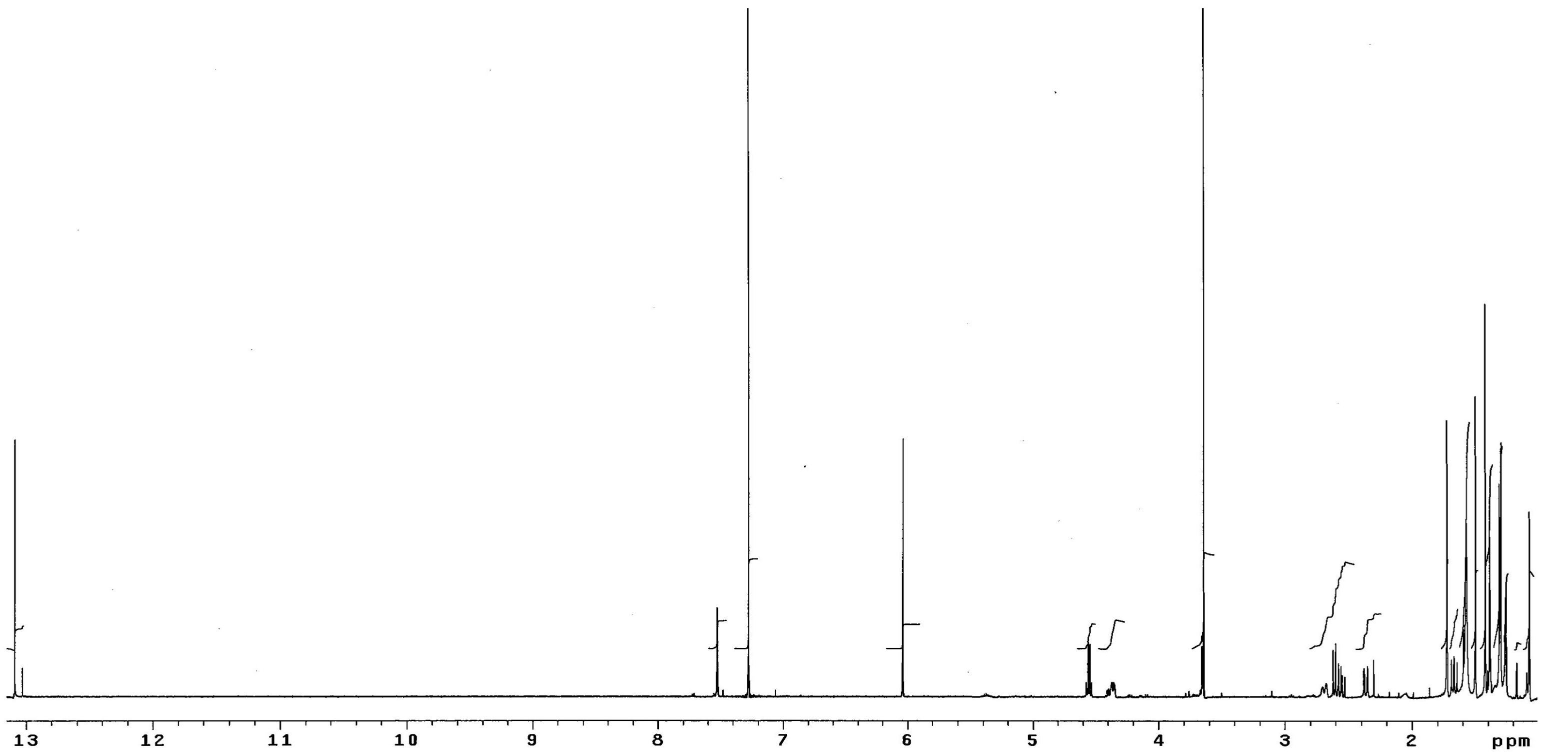


Figure 21 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF6**

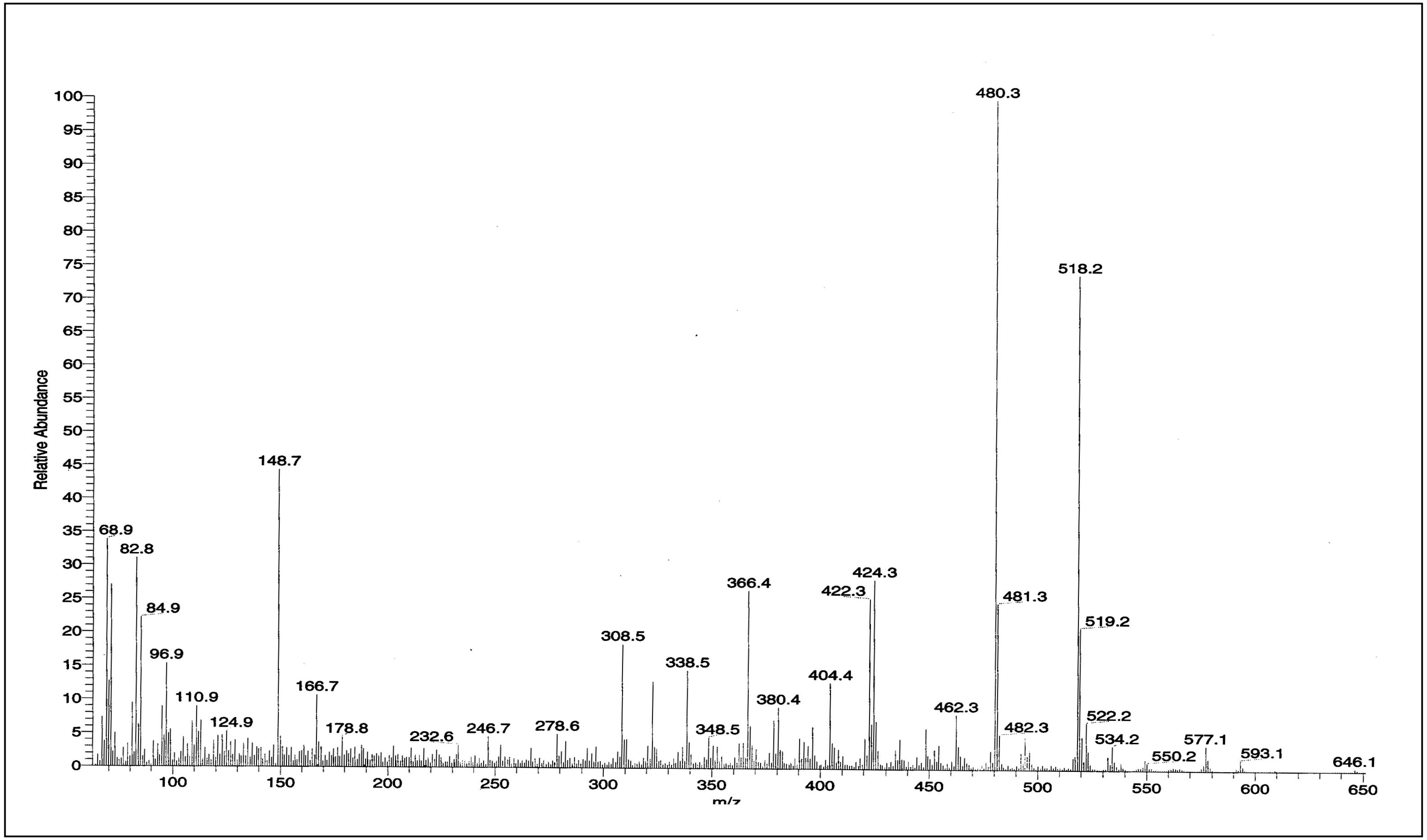


Figure 22 Mass spectrum of **GF8**

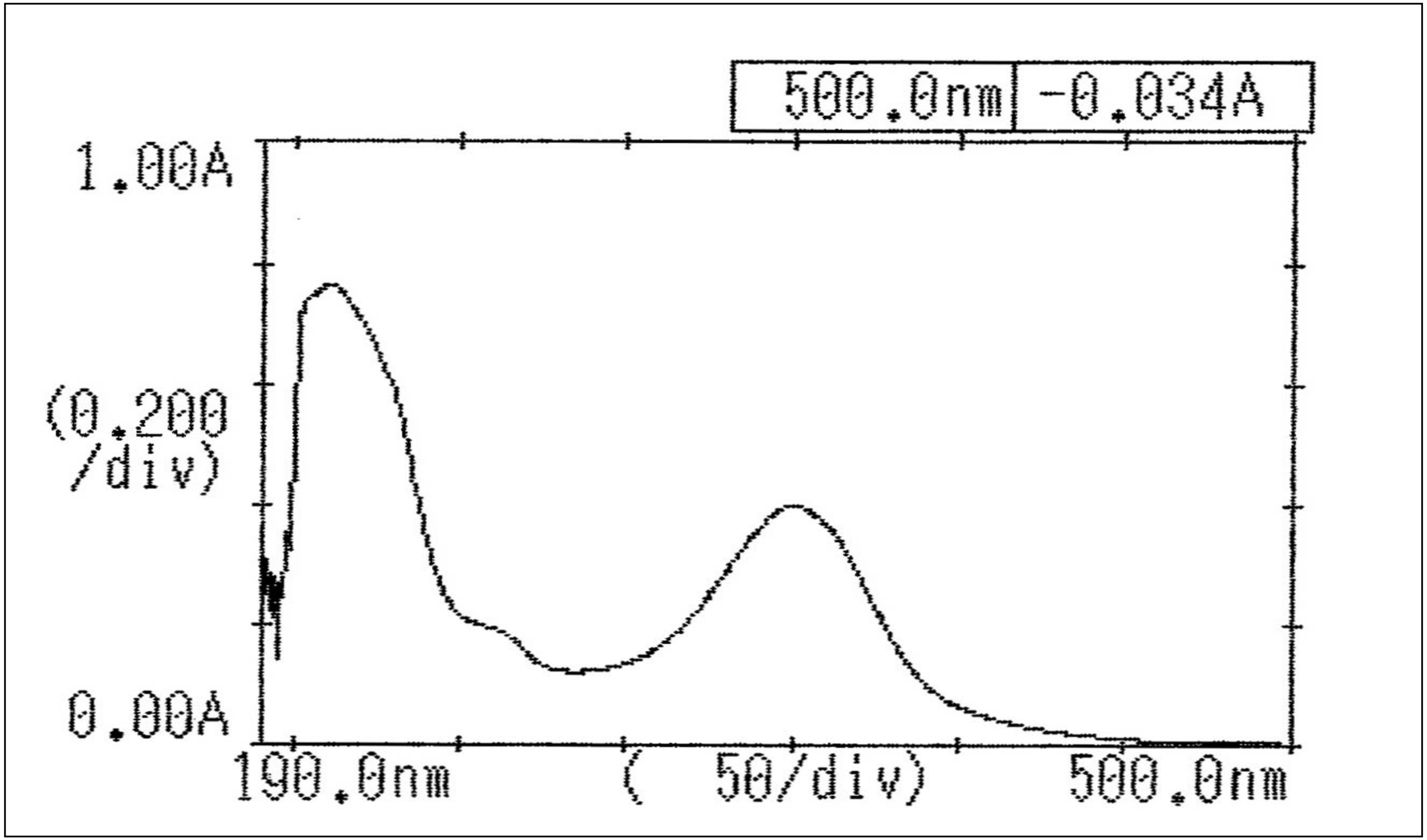


Figure 23 UV (CH_3OH) spectrum of **GF8**

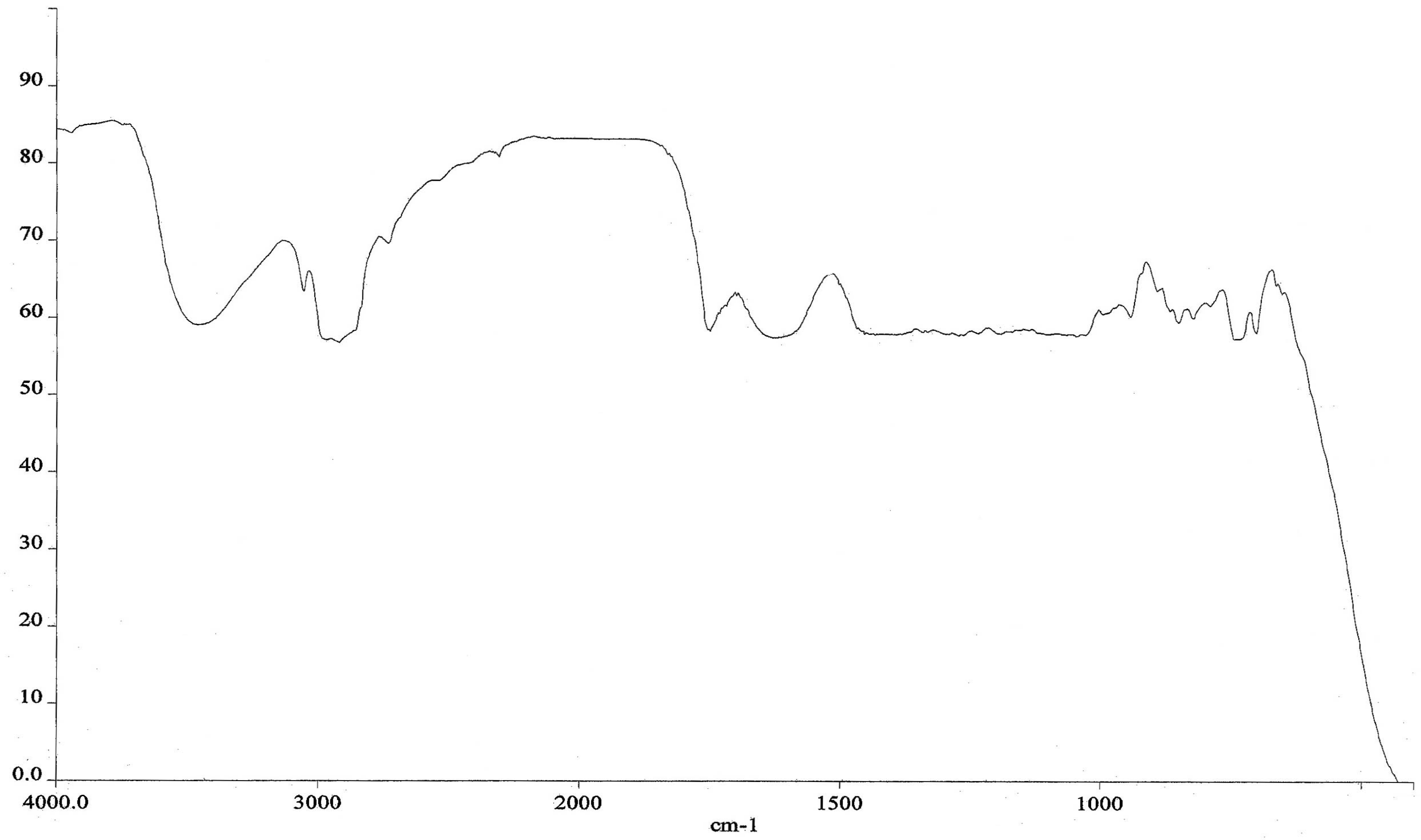


Figure 24 FT-IR (neat) spectrum of **GF8**

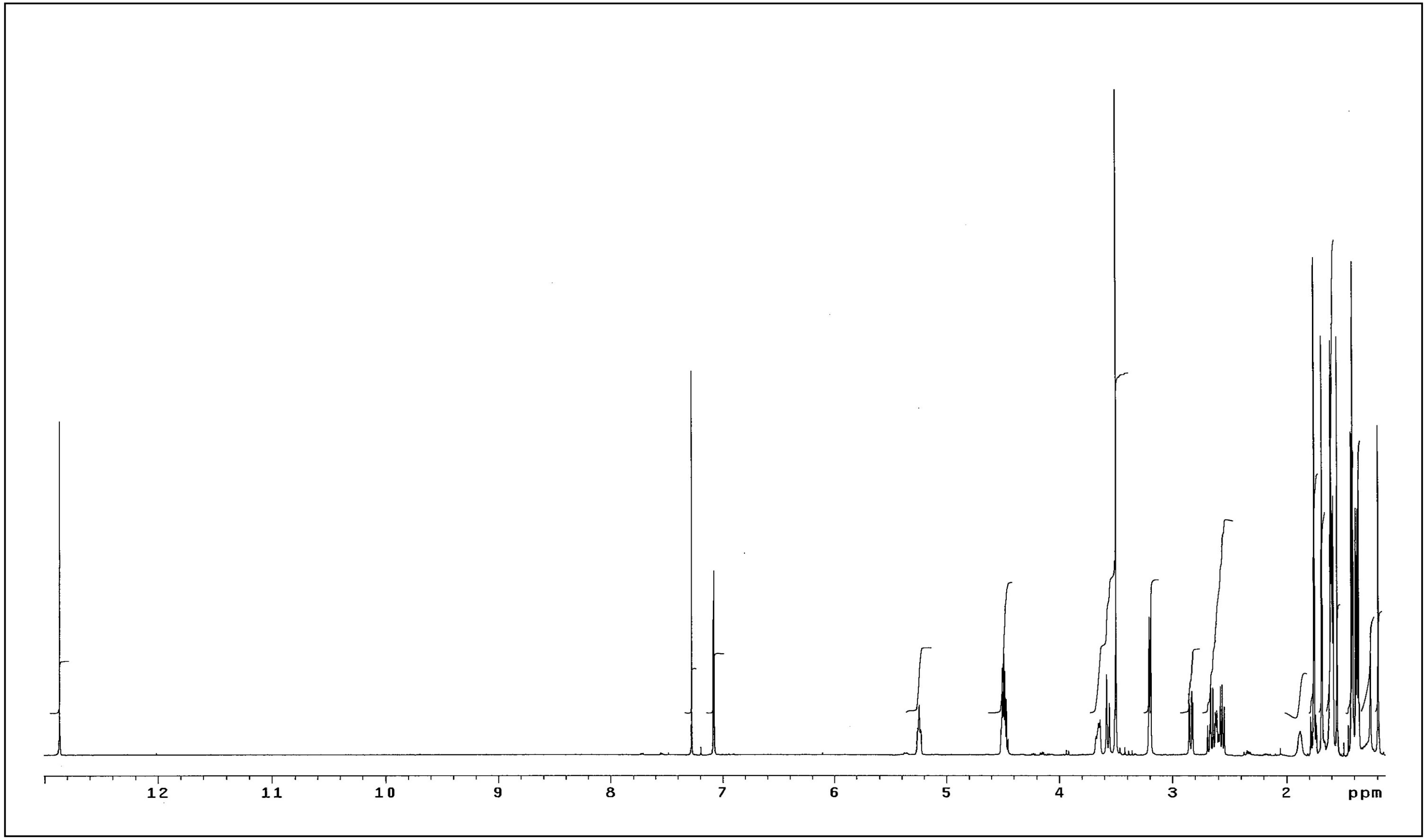


Figure 25 ^{1}H NMR (500 MHz) ($CDCl_3$) spectrum of **GF8**

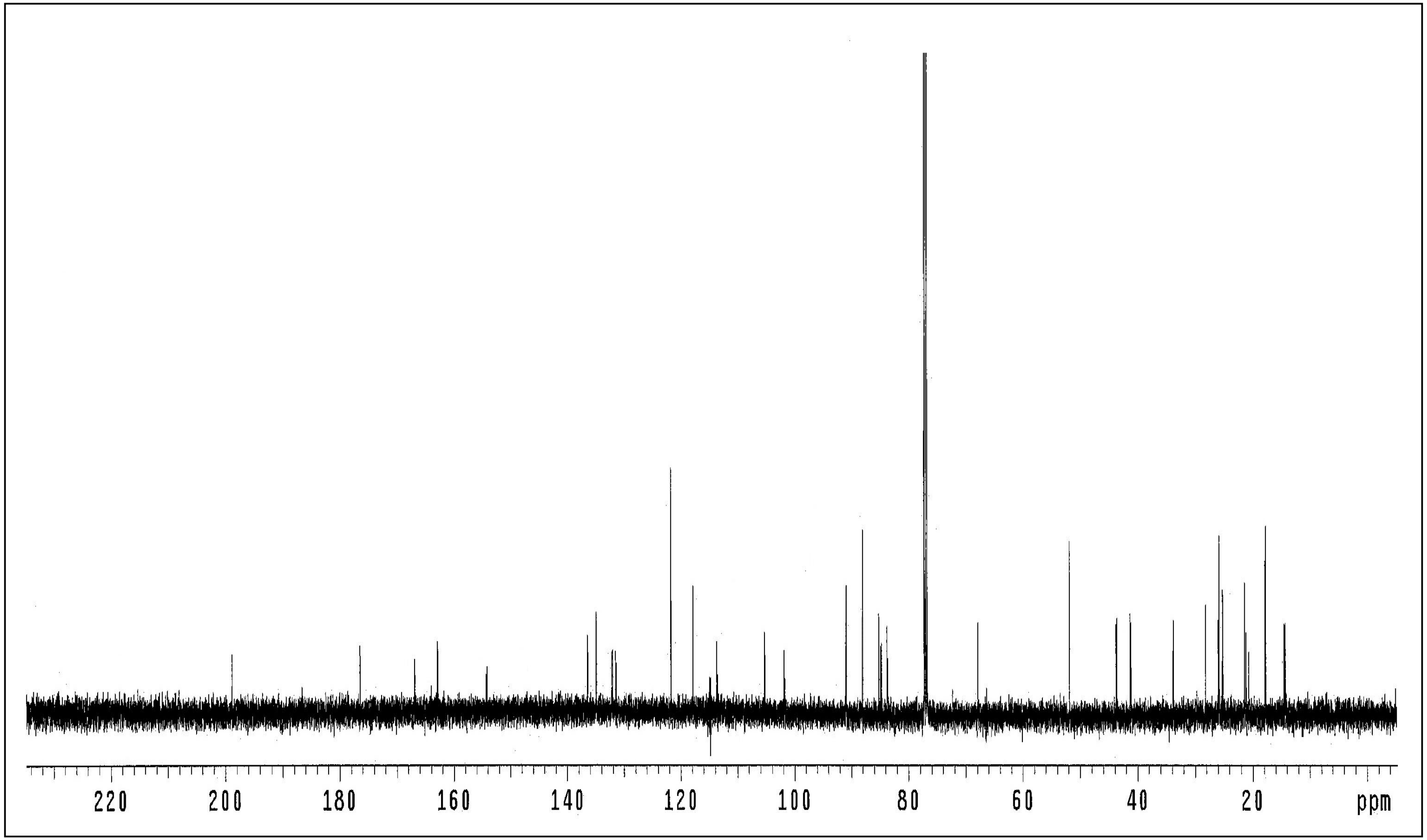


Figure 26 ^{13}C NMR (125 MHz) (CDCl$_3$) spectrum of **GF8**

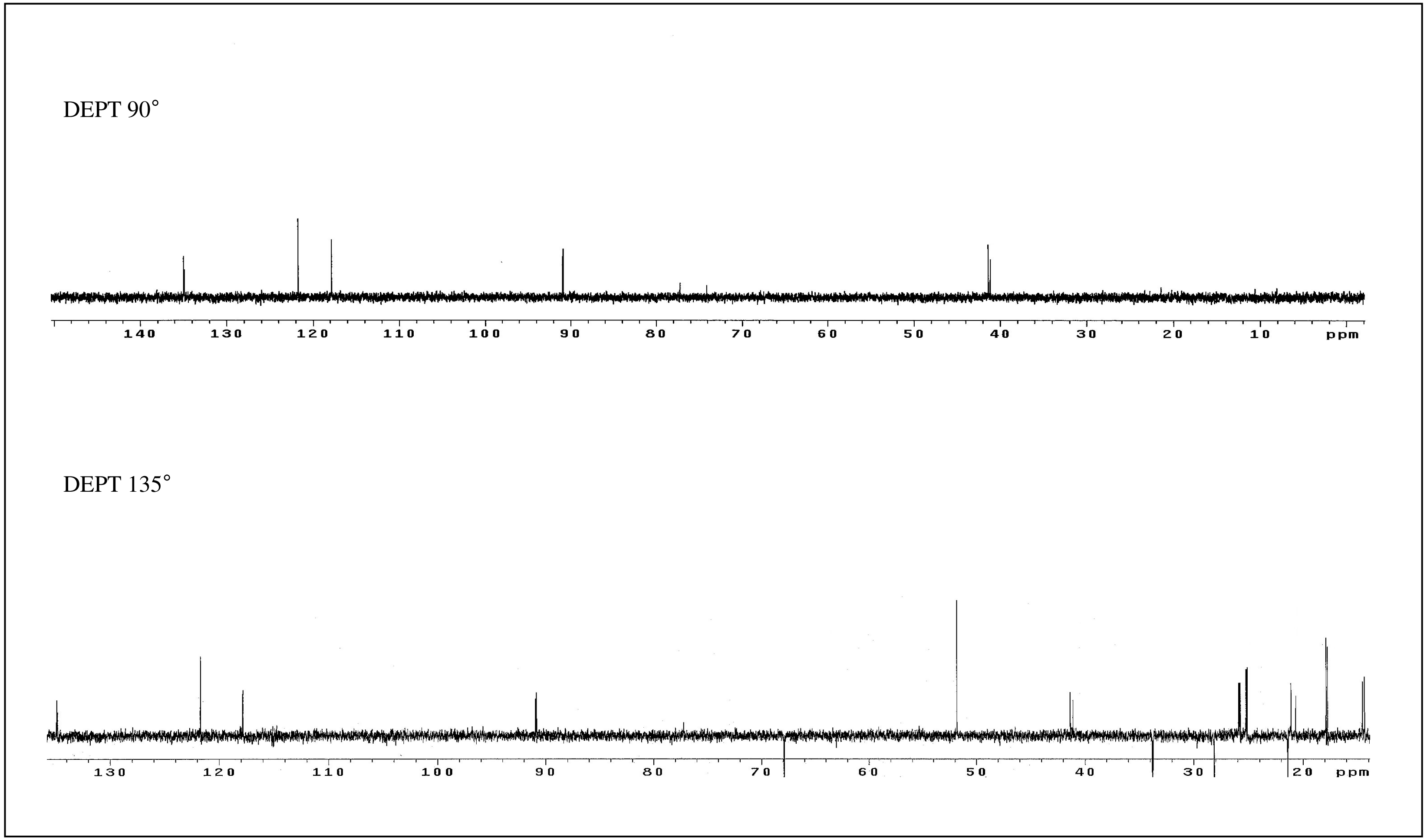


Figure 27 DEPT spectrum of **GF8**

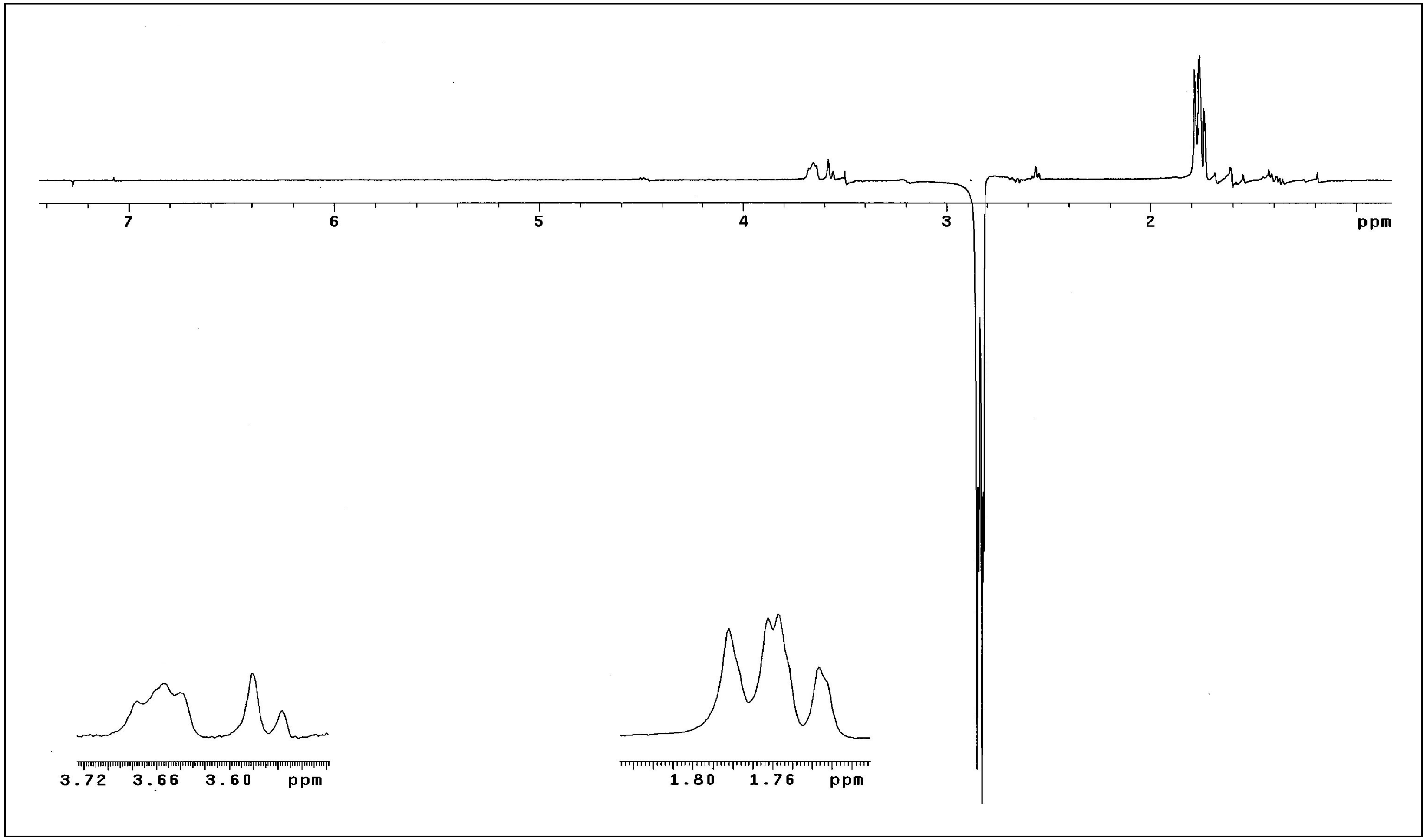


Figure 28 NOEDIFF spectrum of **GF8** after irradiation at δ_H 2.84

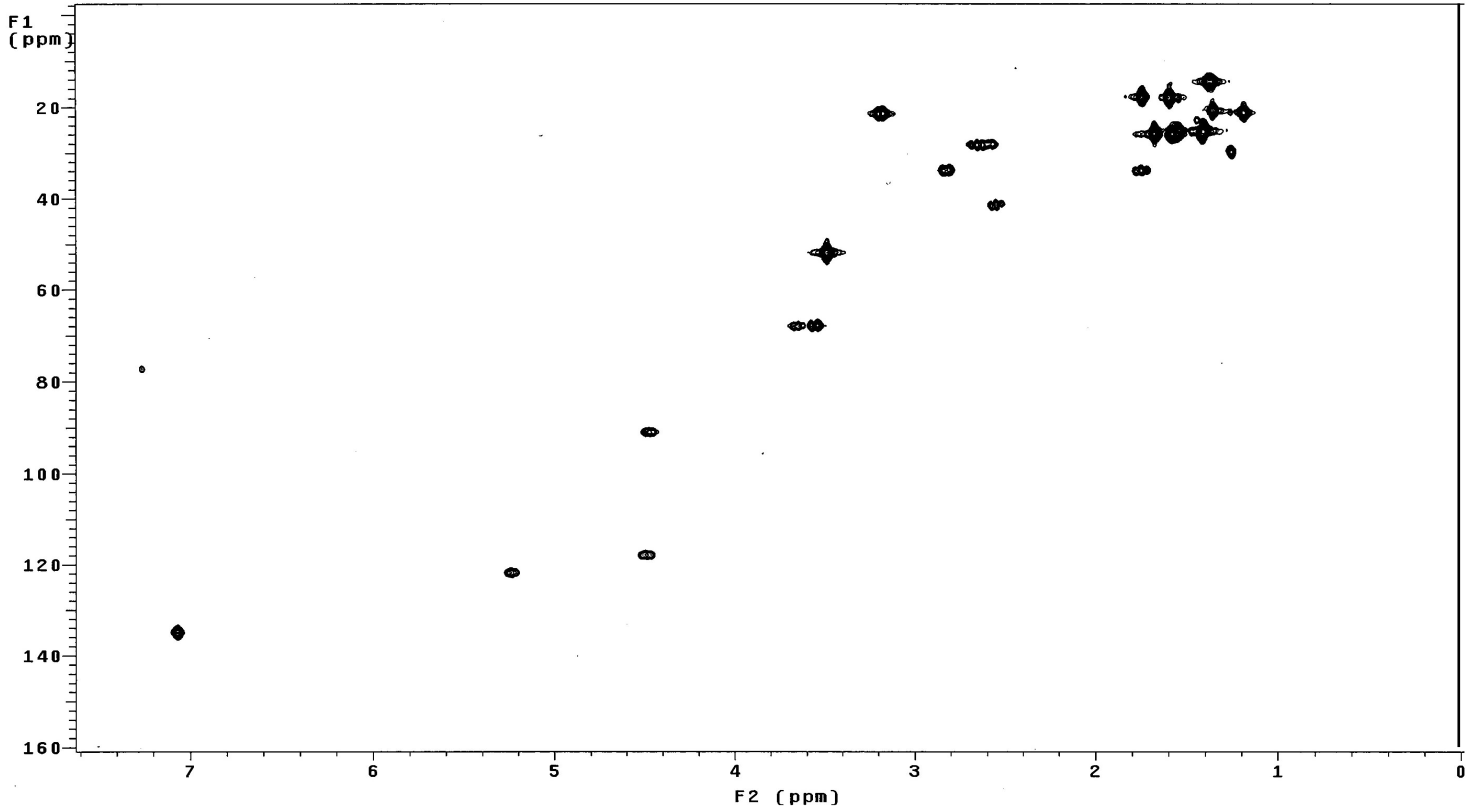


Figure 29 2D HMQC spectrum of **GF8**

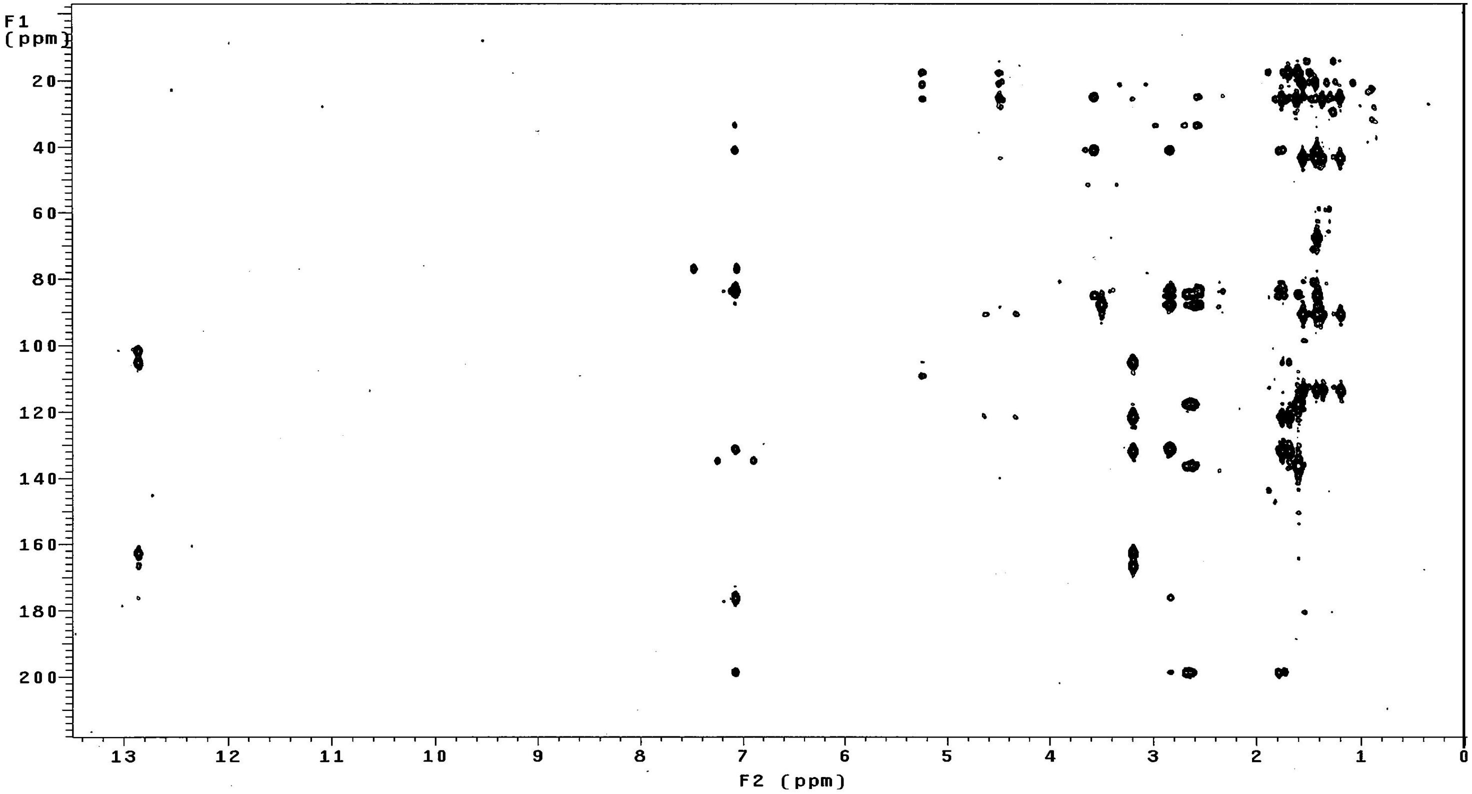


Figure 30 2D HMBC spectrum of **GF8**

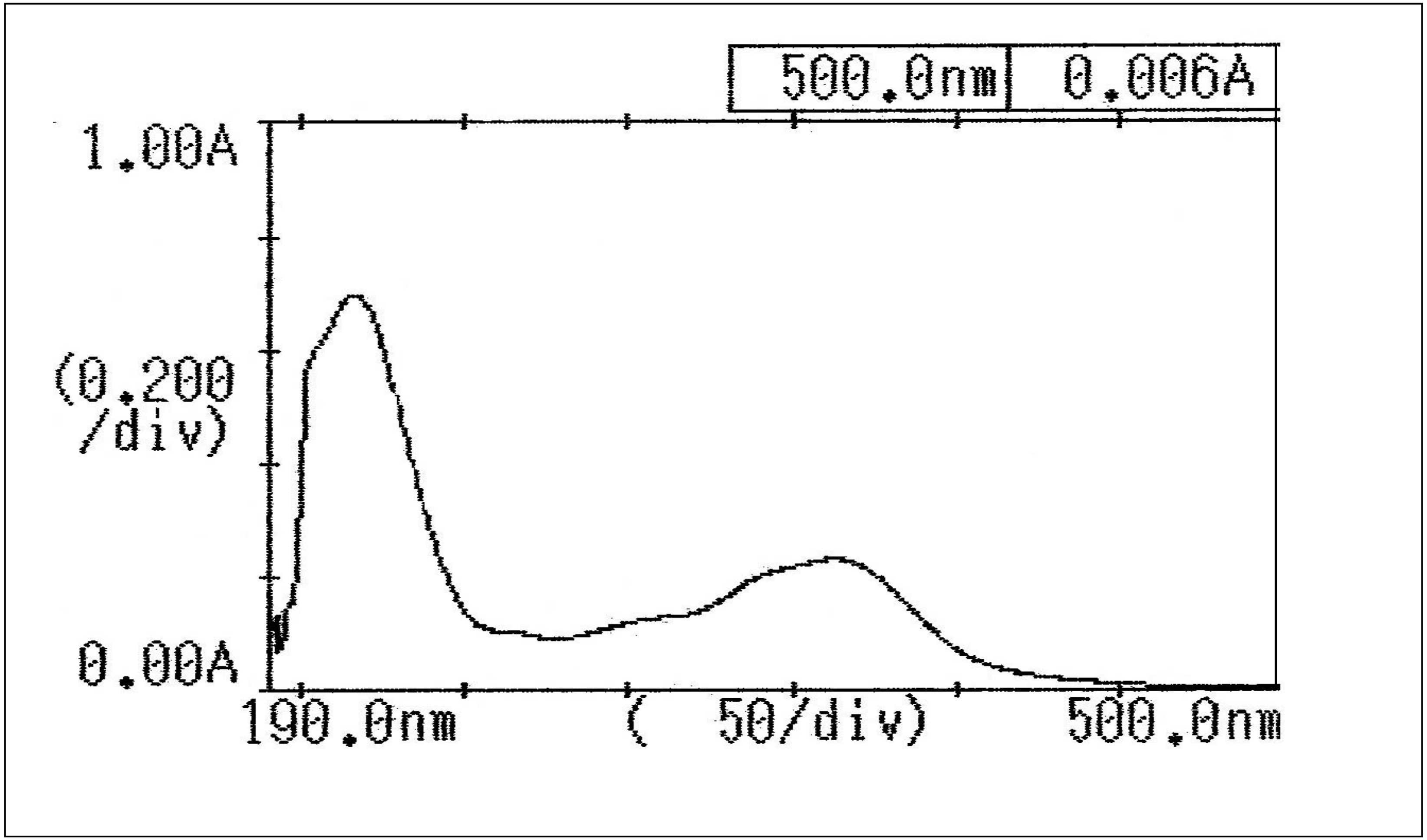


Figure 31 UV (CH_3OH) spectrum of **GF16**

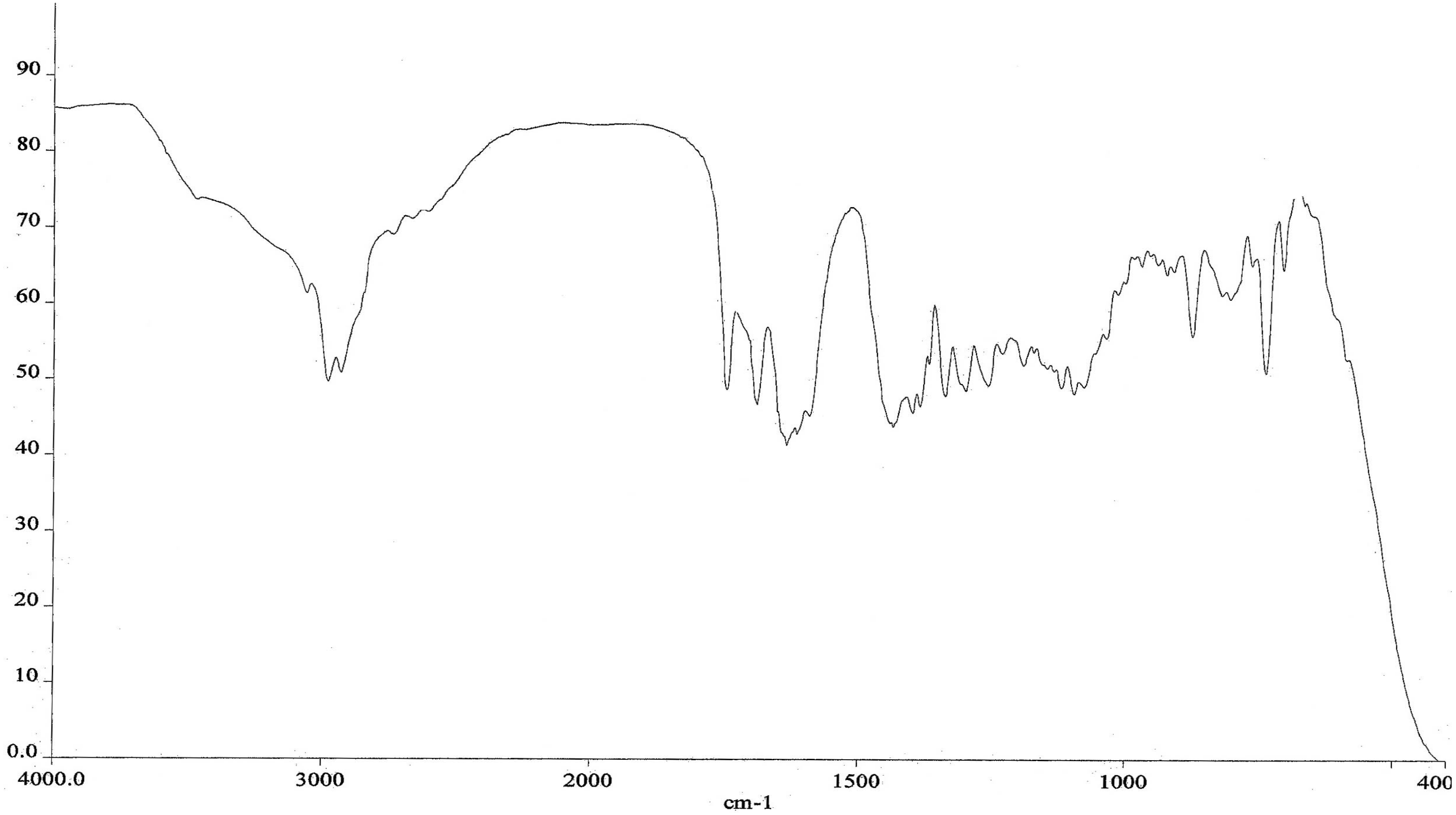


Figure 32 FT-IR (neat) spectrum of **GF16**

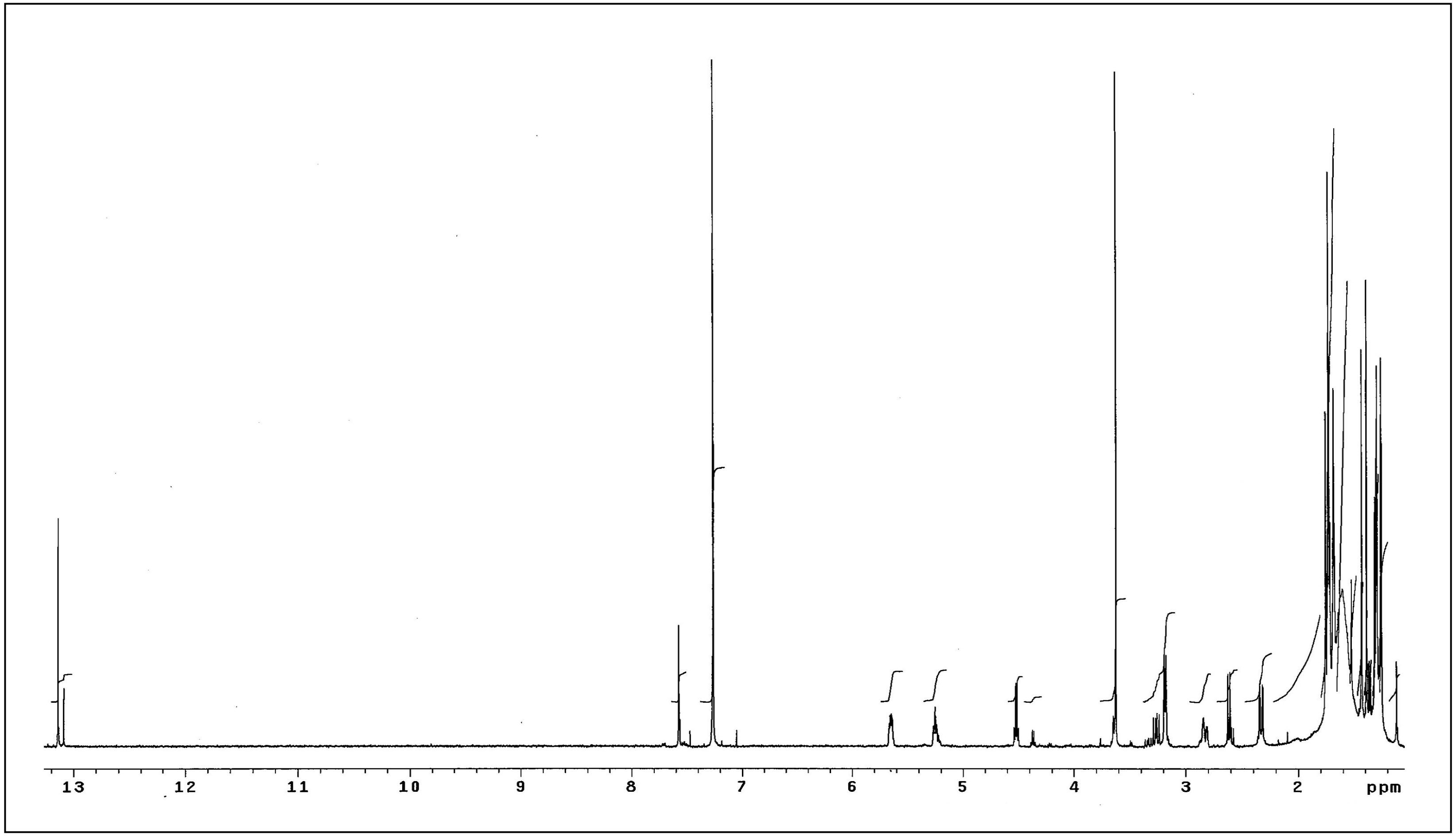


Figure 33 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF16**

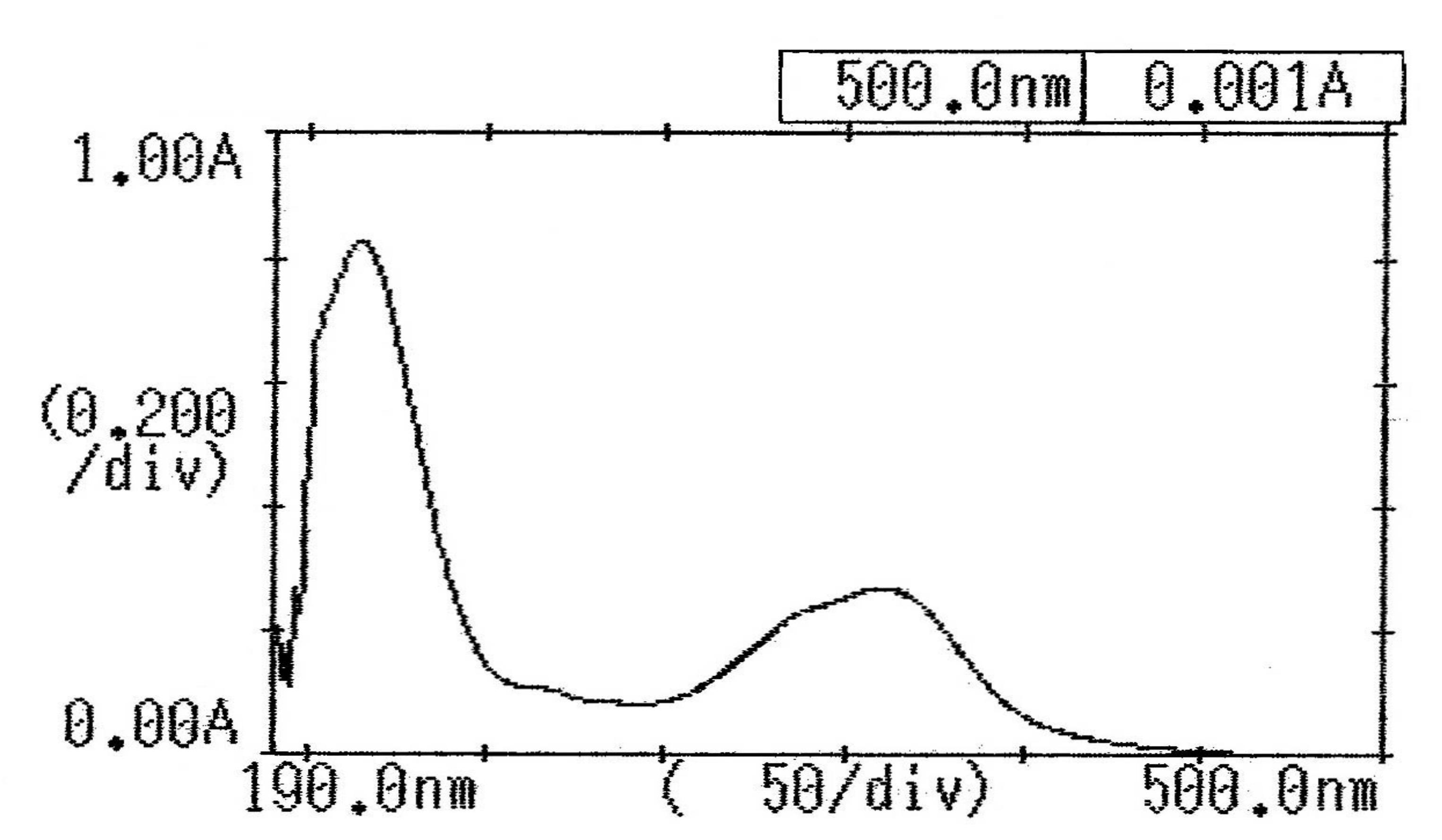


Figure 34 UV (CH_3OH) spectrum of **GF13**

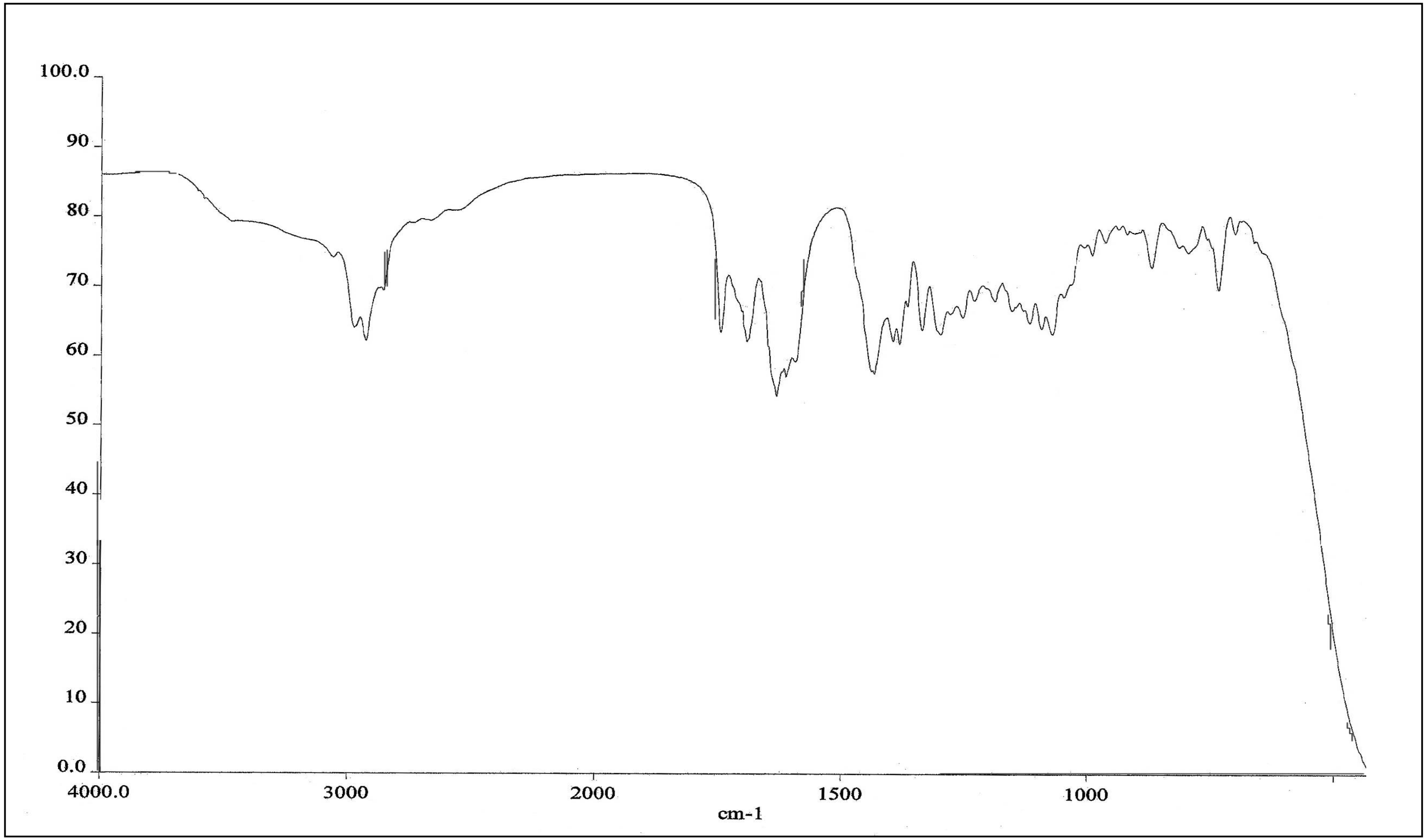


Figure 35 FT-IR (neat) spectrum of **GF13**

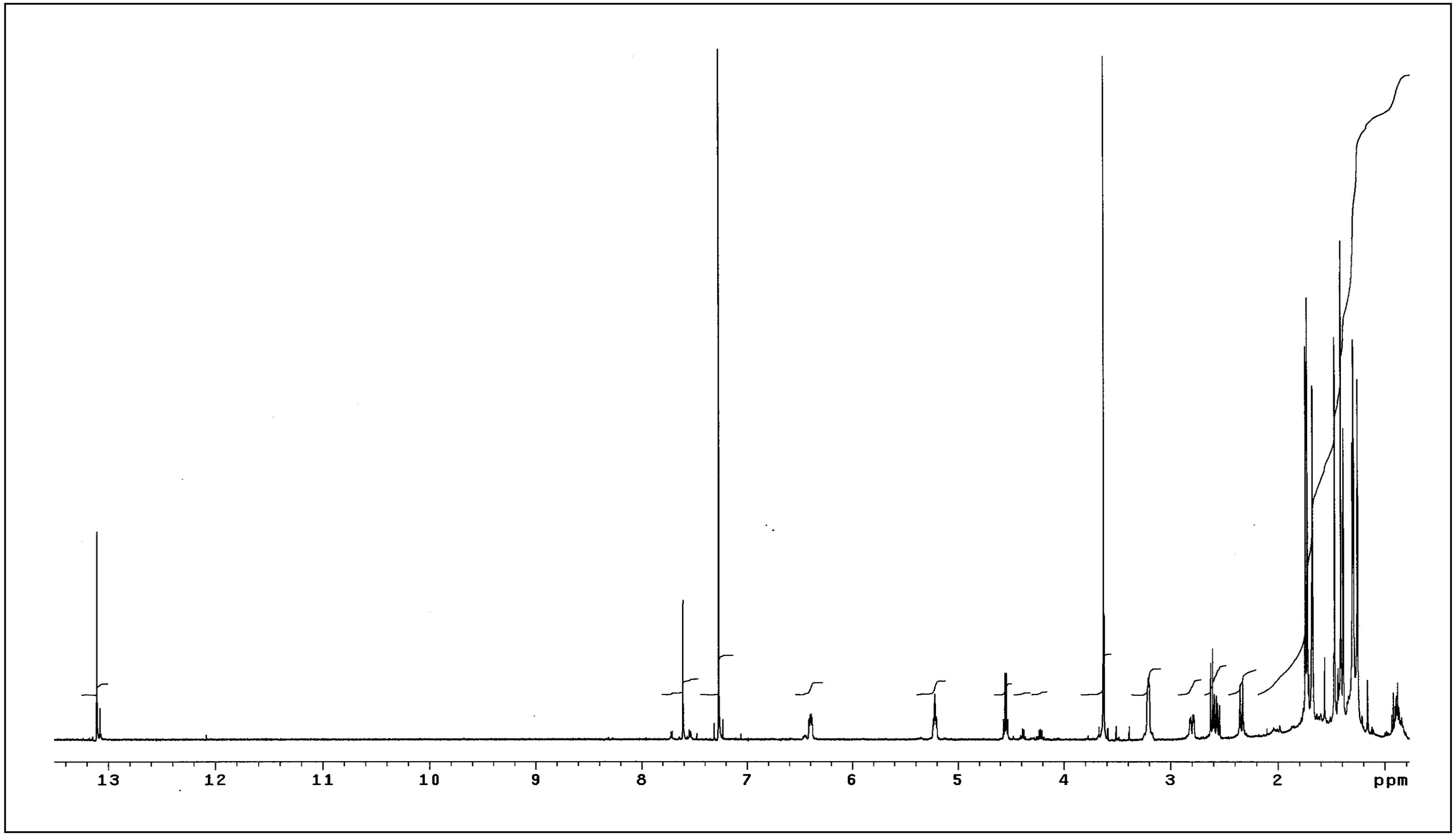


Figure 36 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF13**

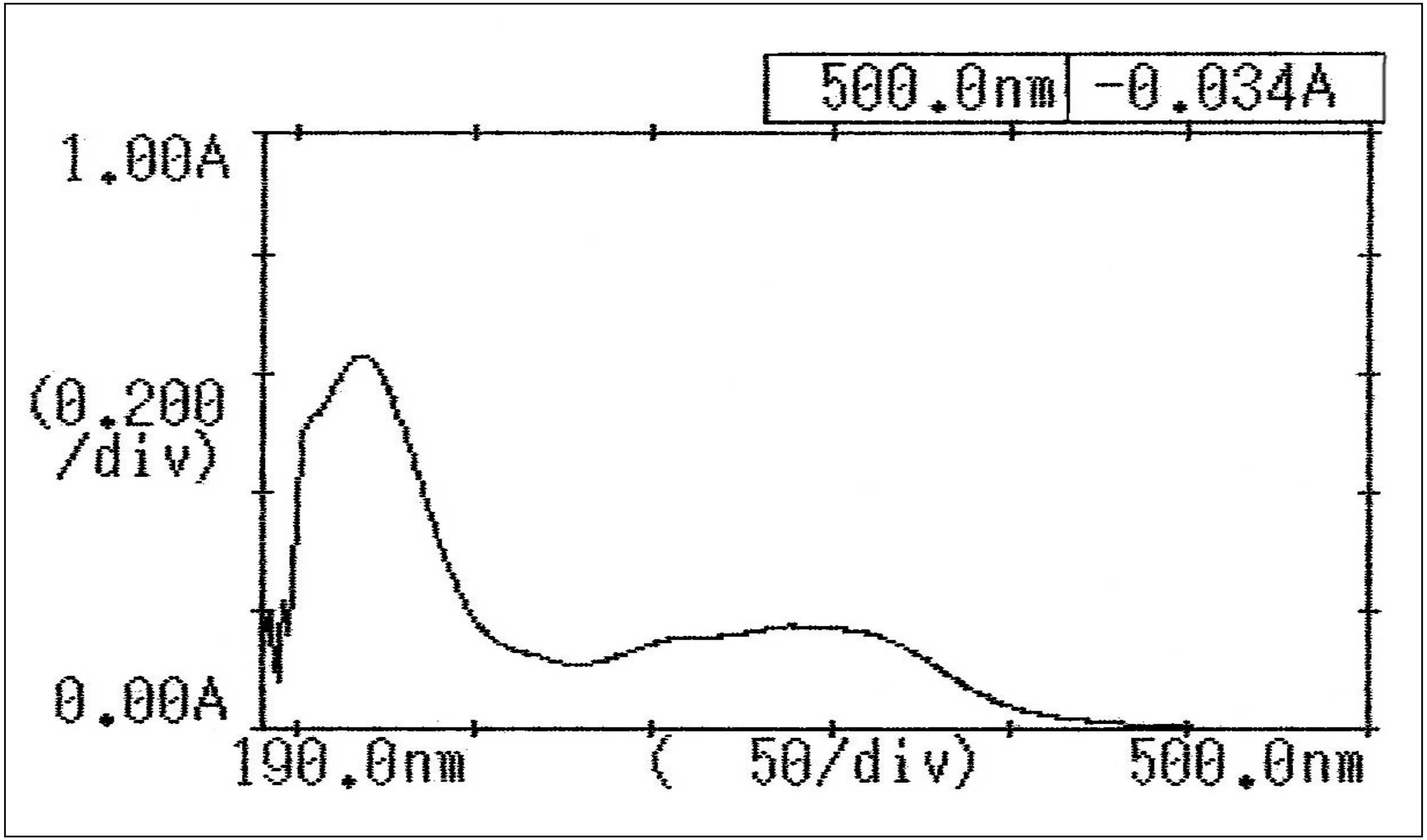


Figure 37 UV (CH_3OH) spectrum of **GF10**

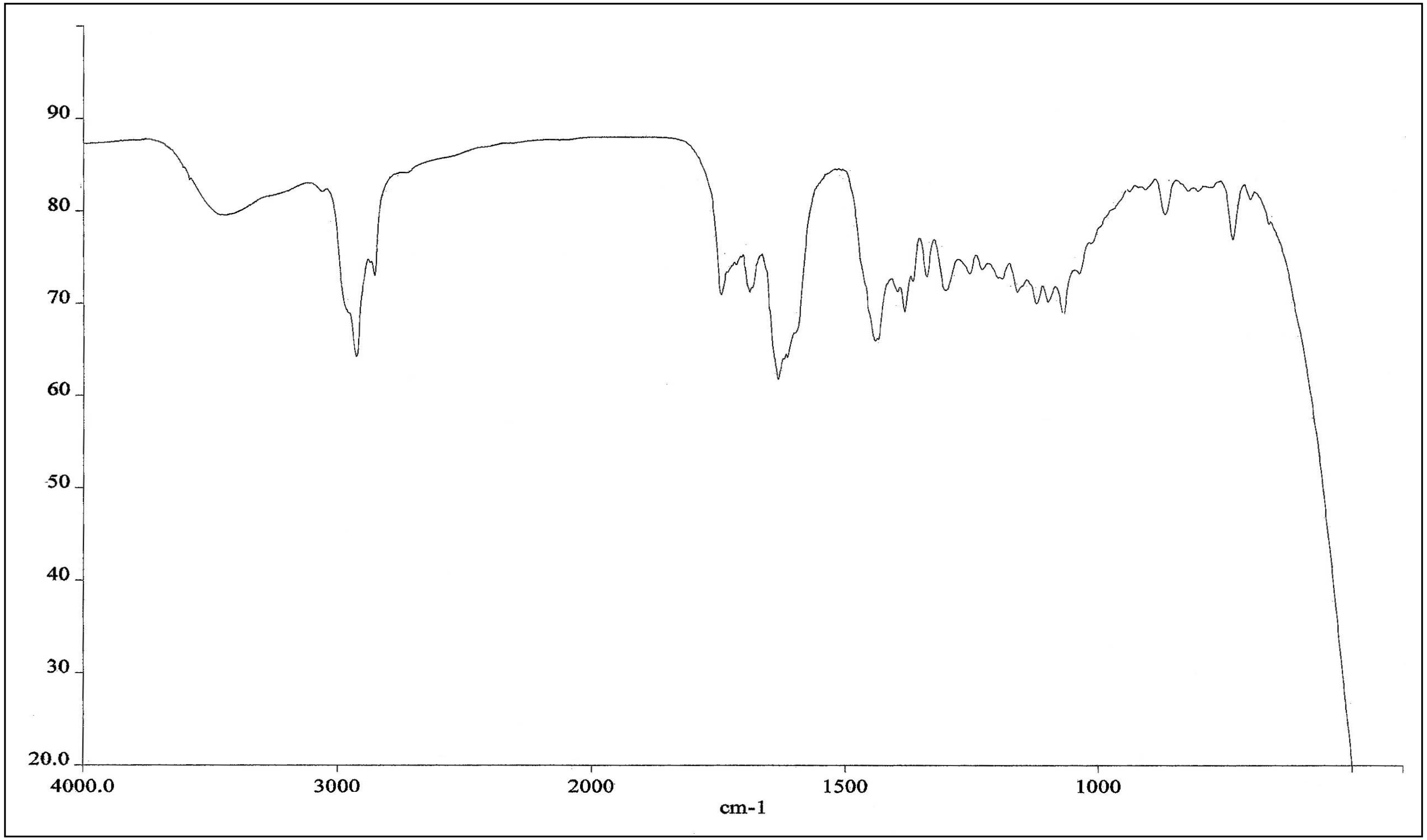


Figure 38 FT-IR (neat) spectrum of **GF10**

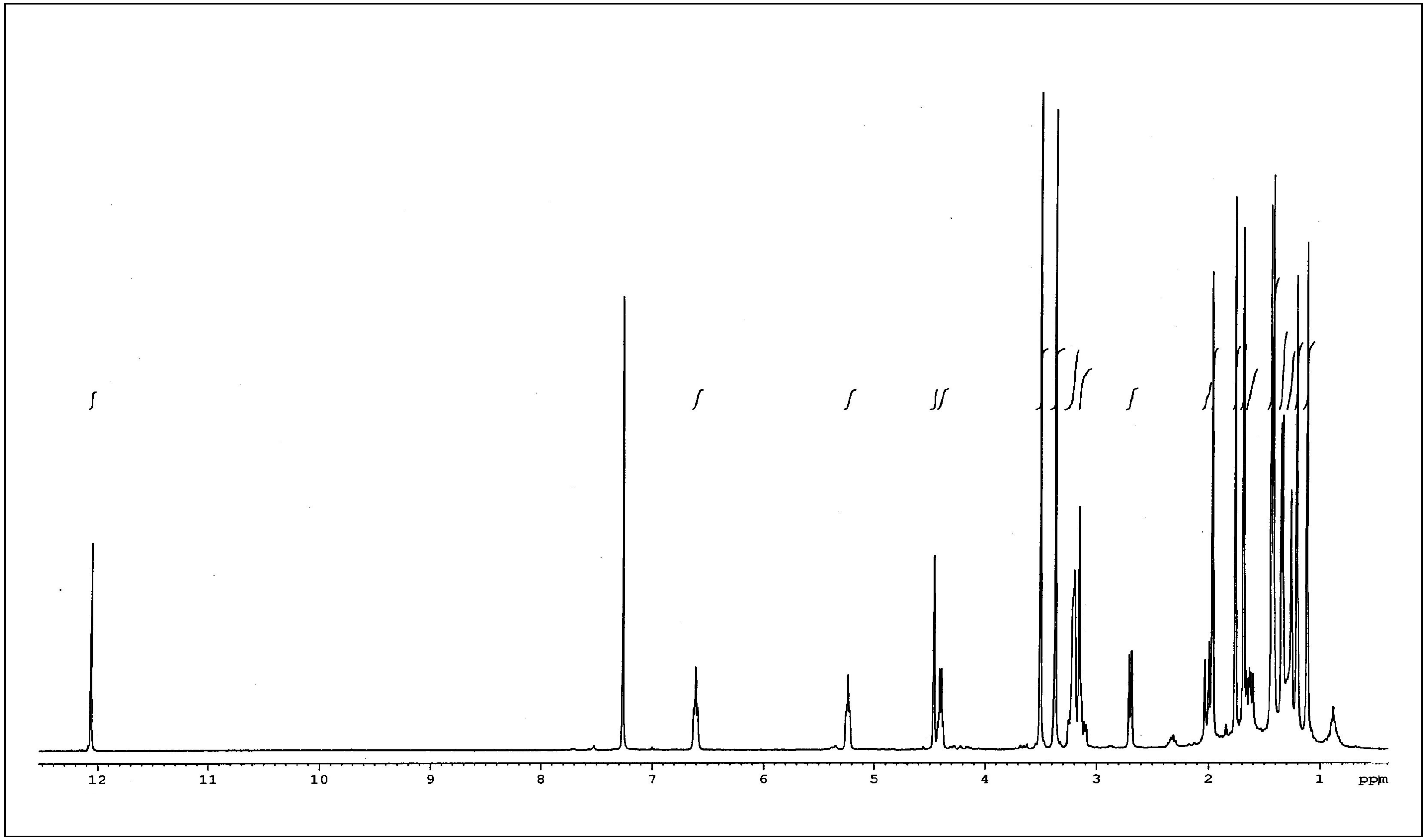


Figure 39 ^{1}H NMR (400 MHz) (CDCl$_3$) spectrum of **GF10**

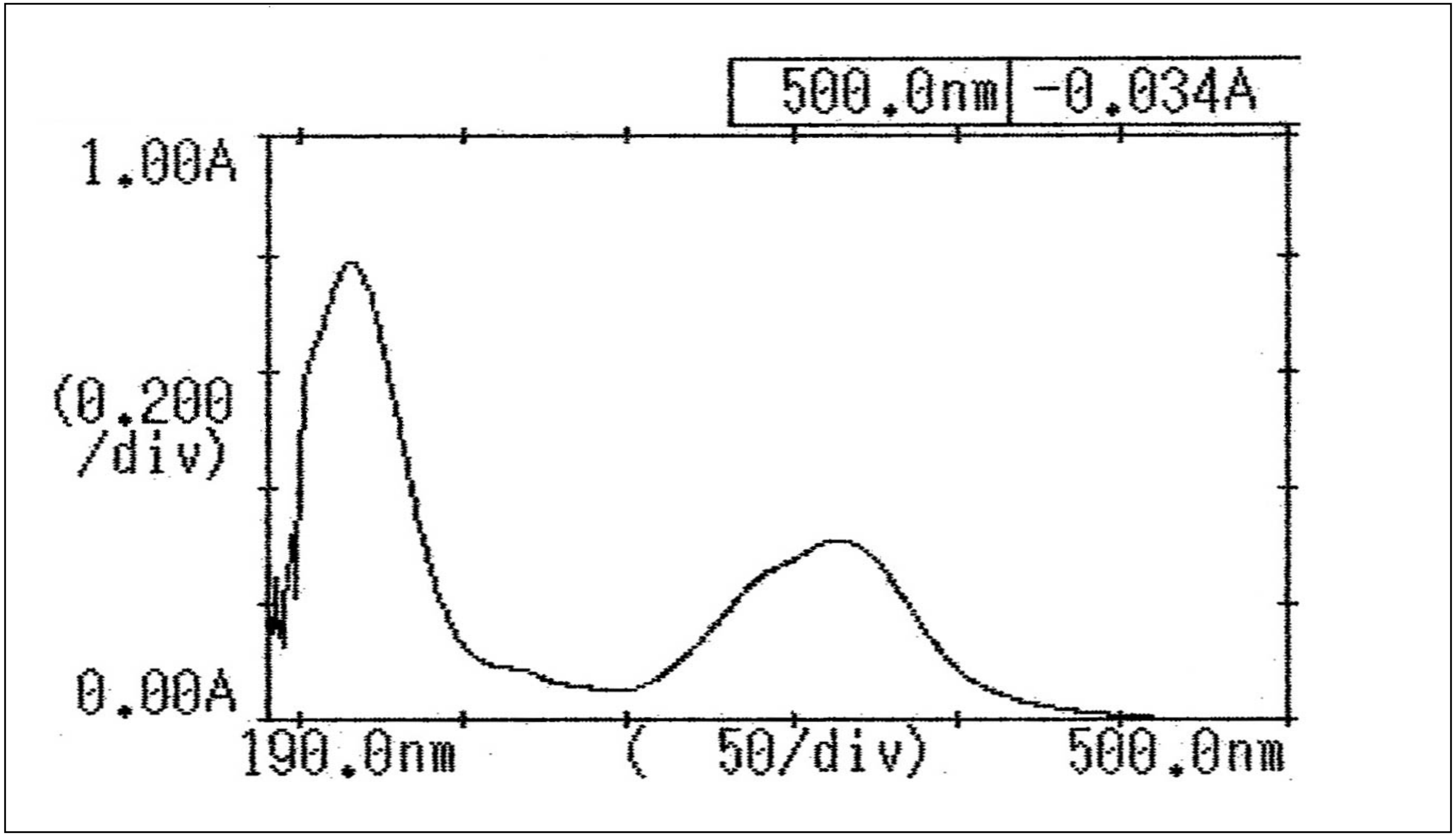


Figure 40 UV (CH_3OH) spectrum of **GF14**

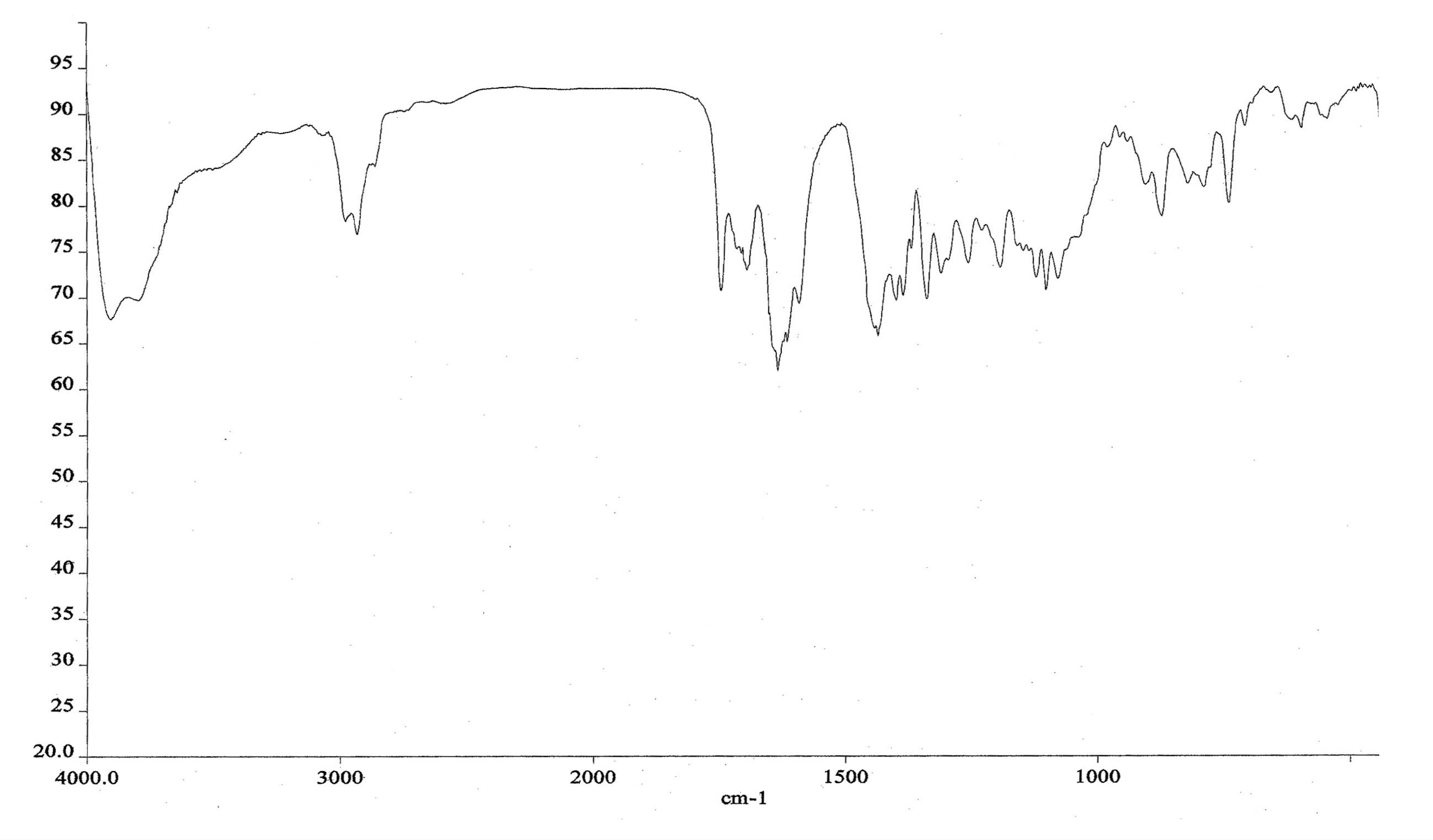


Figure 41 FT-IR (neat) spectrum of **GF14**

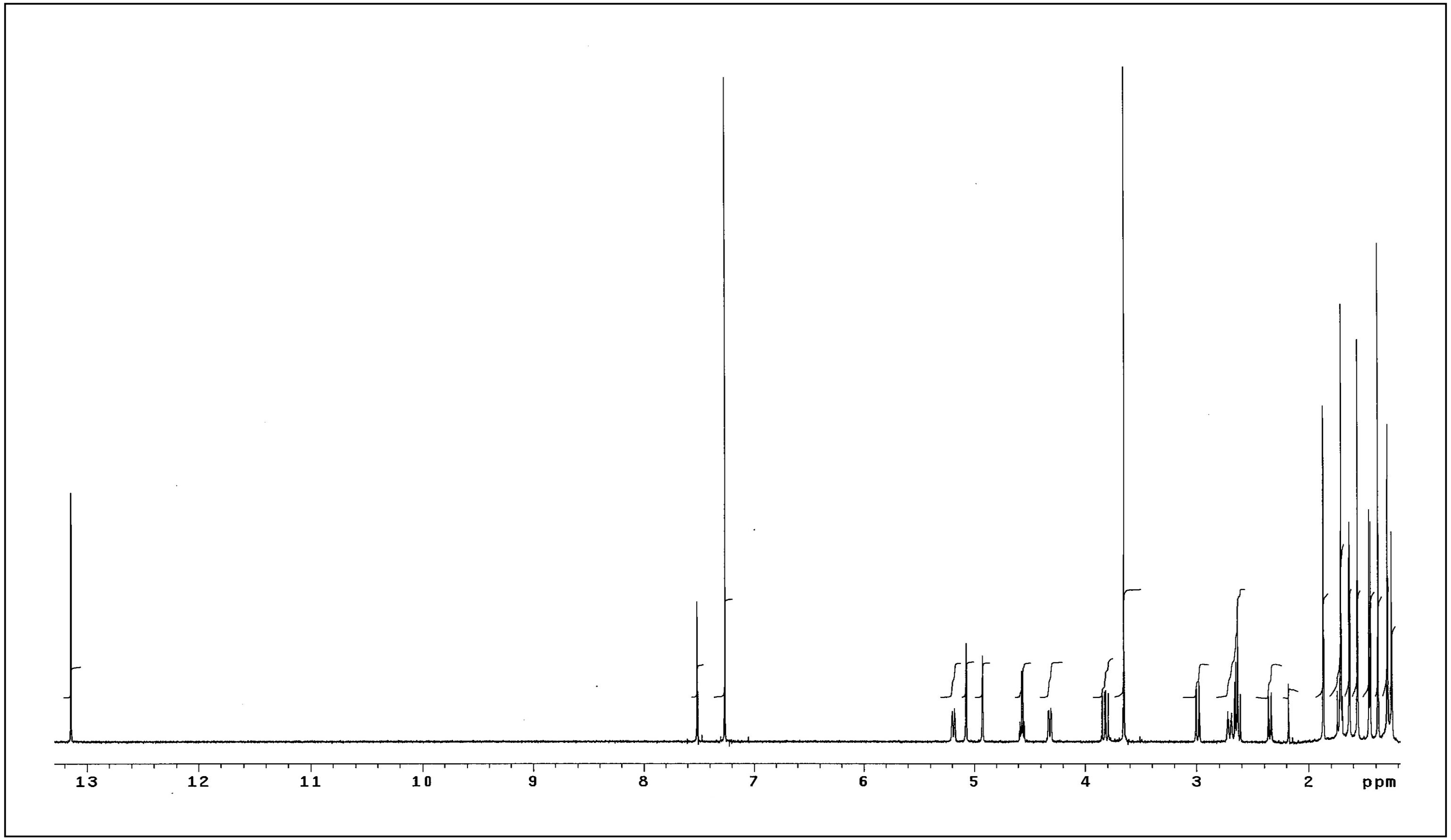


Figure 42 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF14**

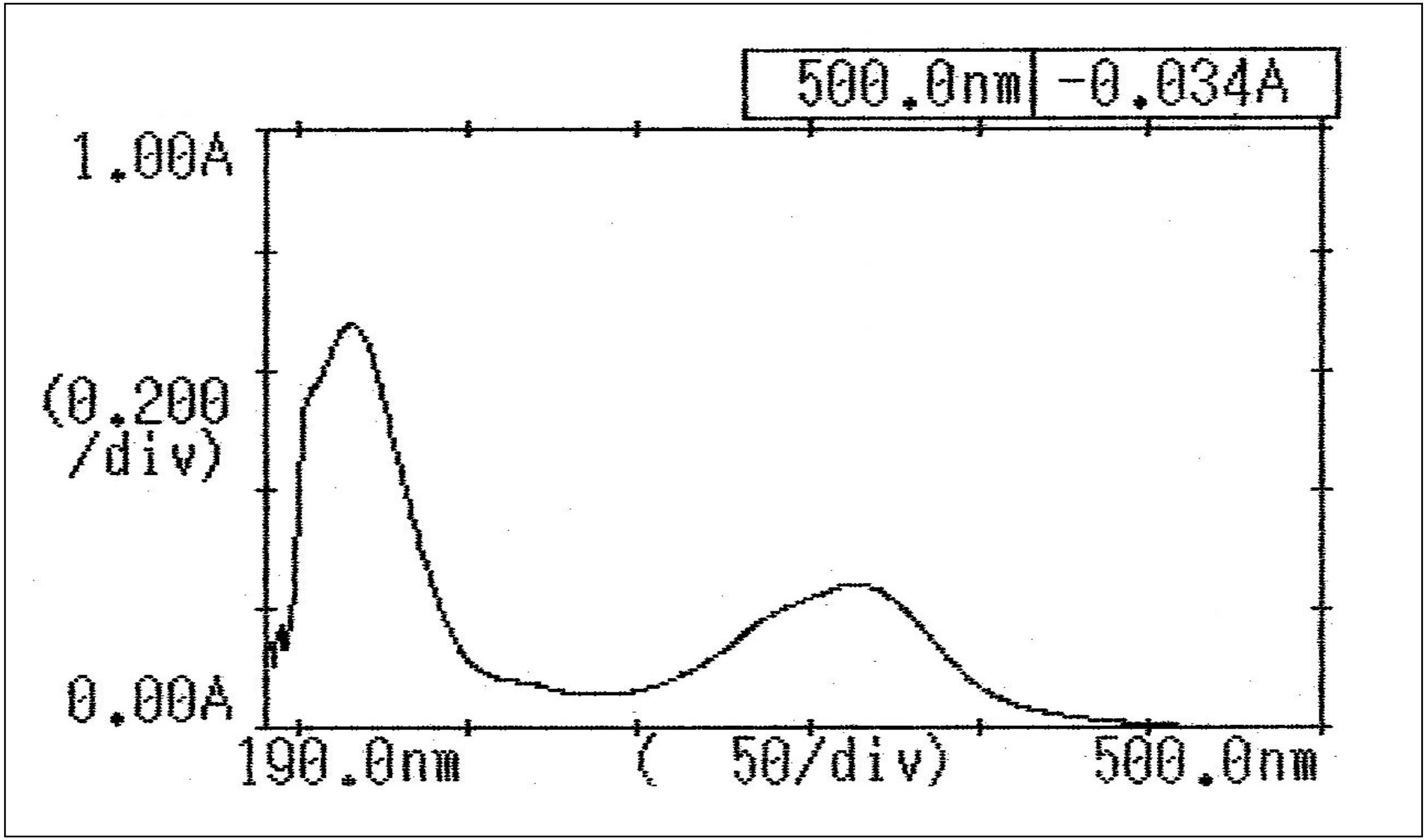


Figure 43 UV (CH_3OH) spectrum of **GF12**

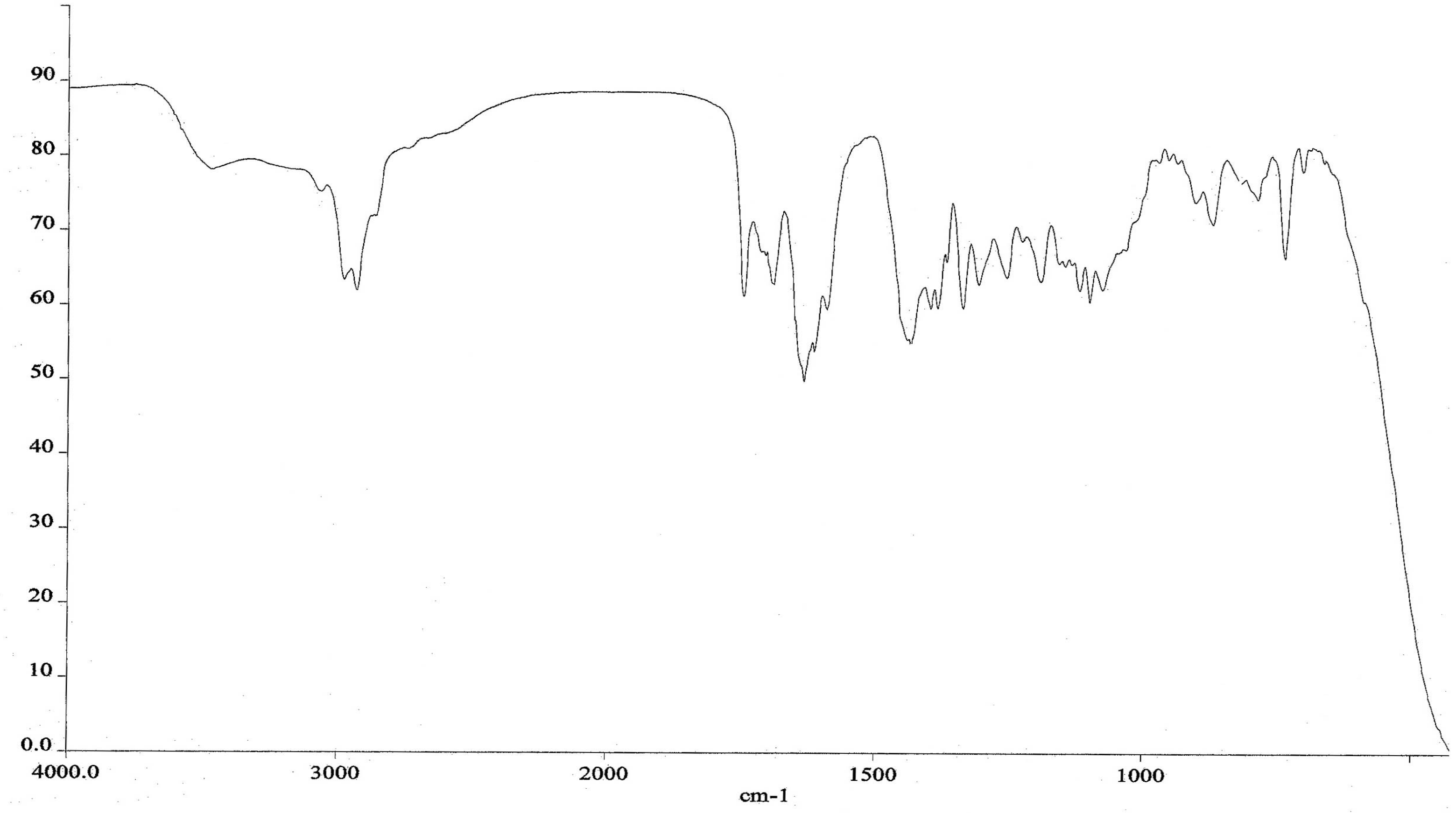


Figure 44 FT-IR (neat) spectrum of **GF12**

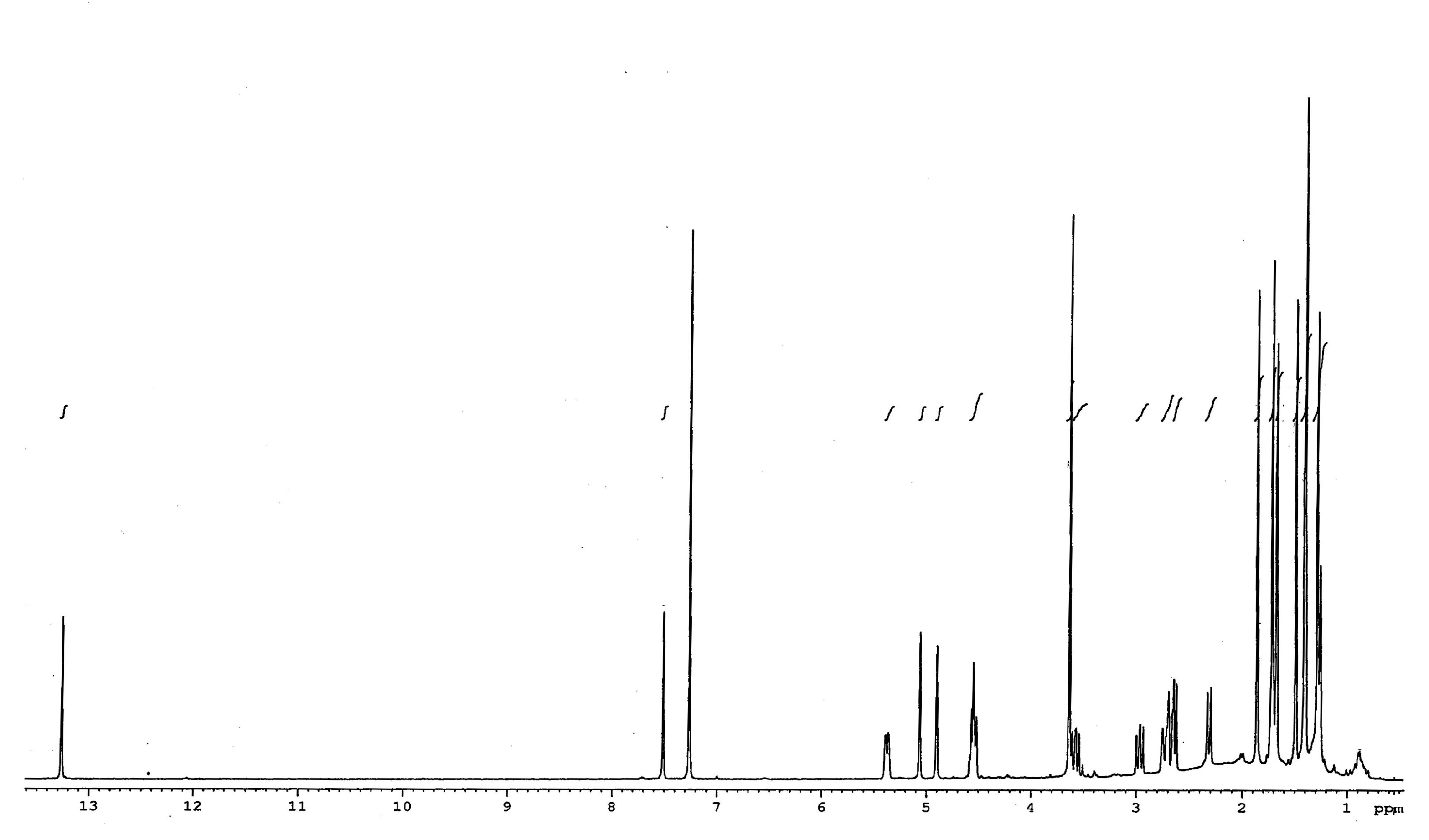


Figure 45 ^{1}H NMR (400 MHz) (CDCl$_3$) spectrum of **GF12**

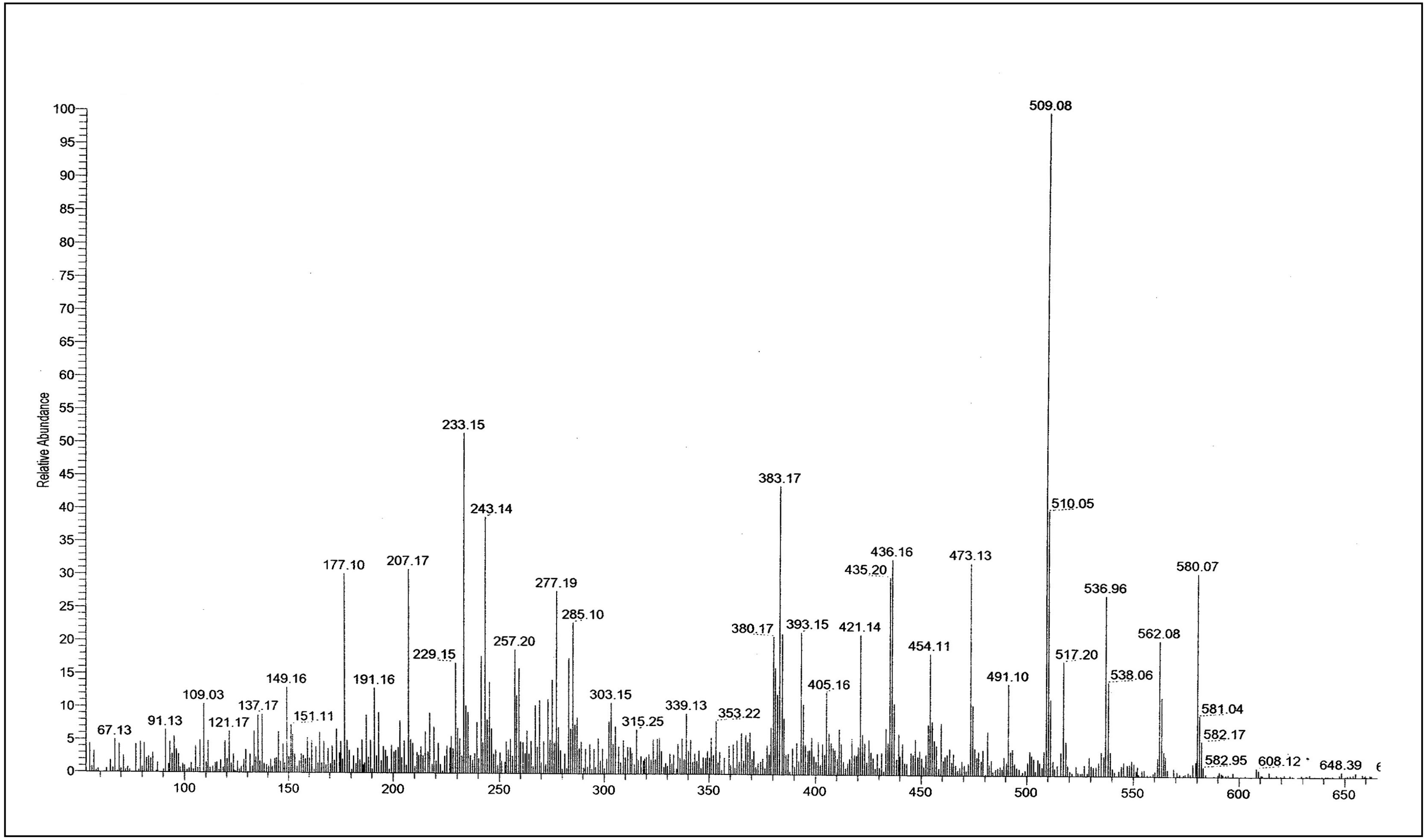


Figure 46 Mass spectrum of **GF15**

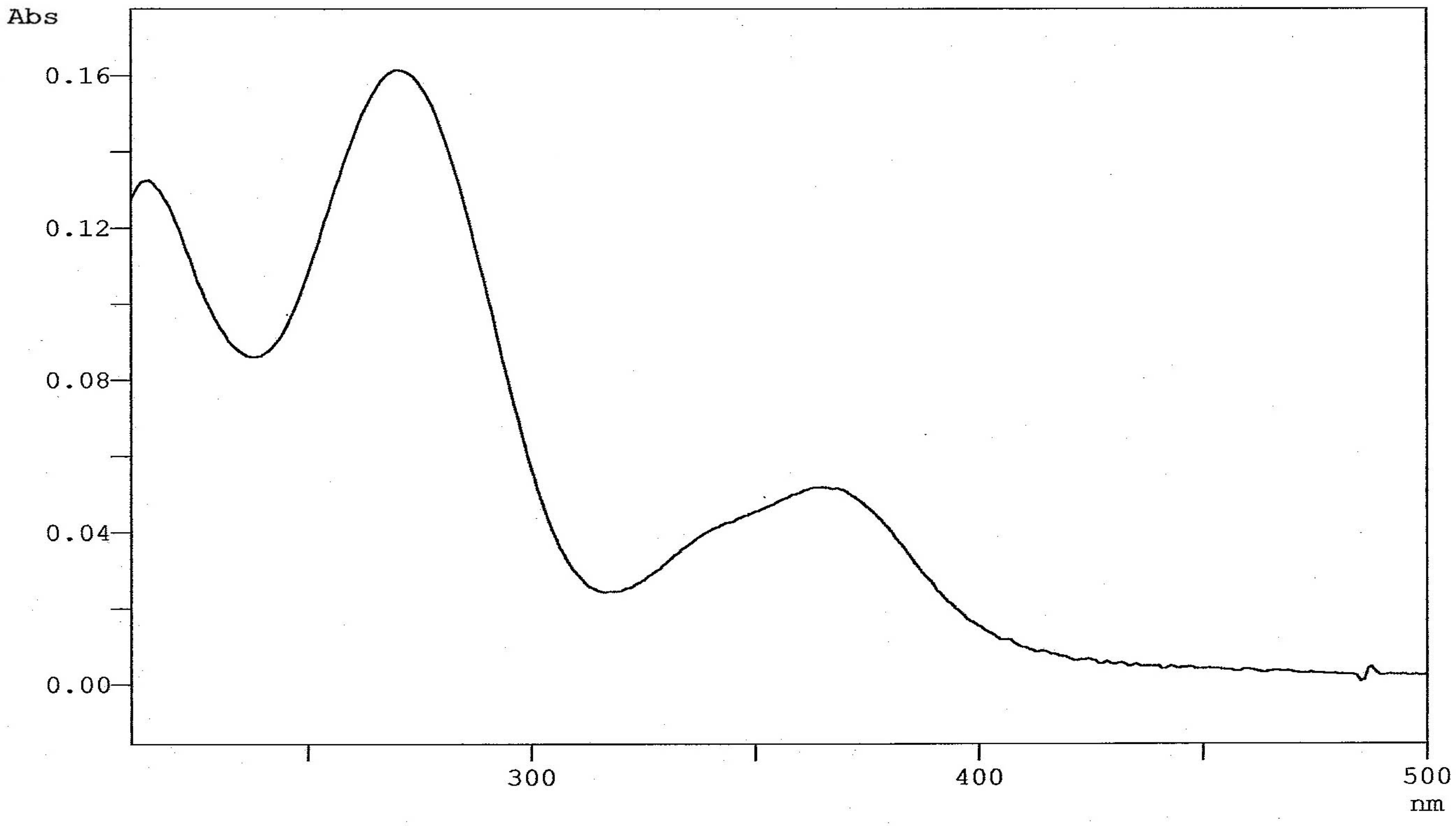


Figure 47 UV (CH_3OH) spectrum of **GF15**

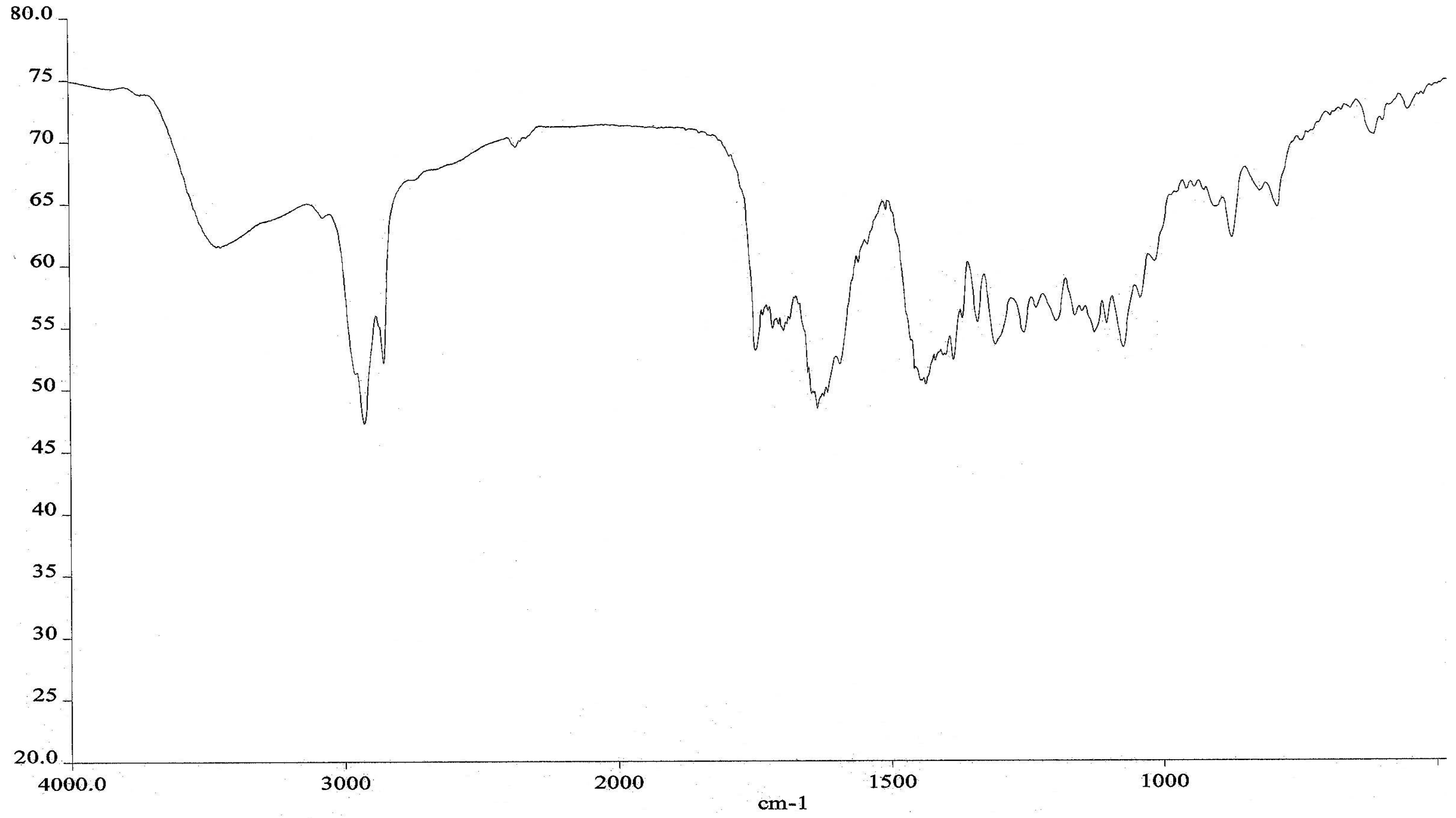


Figure 48 FT-IR (neat) spectrum of **GF15**

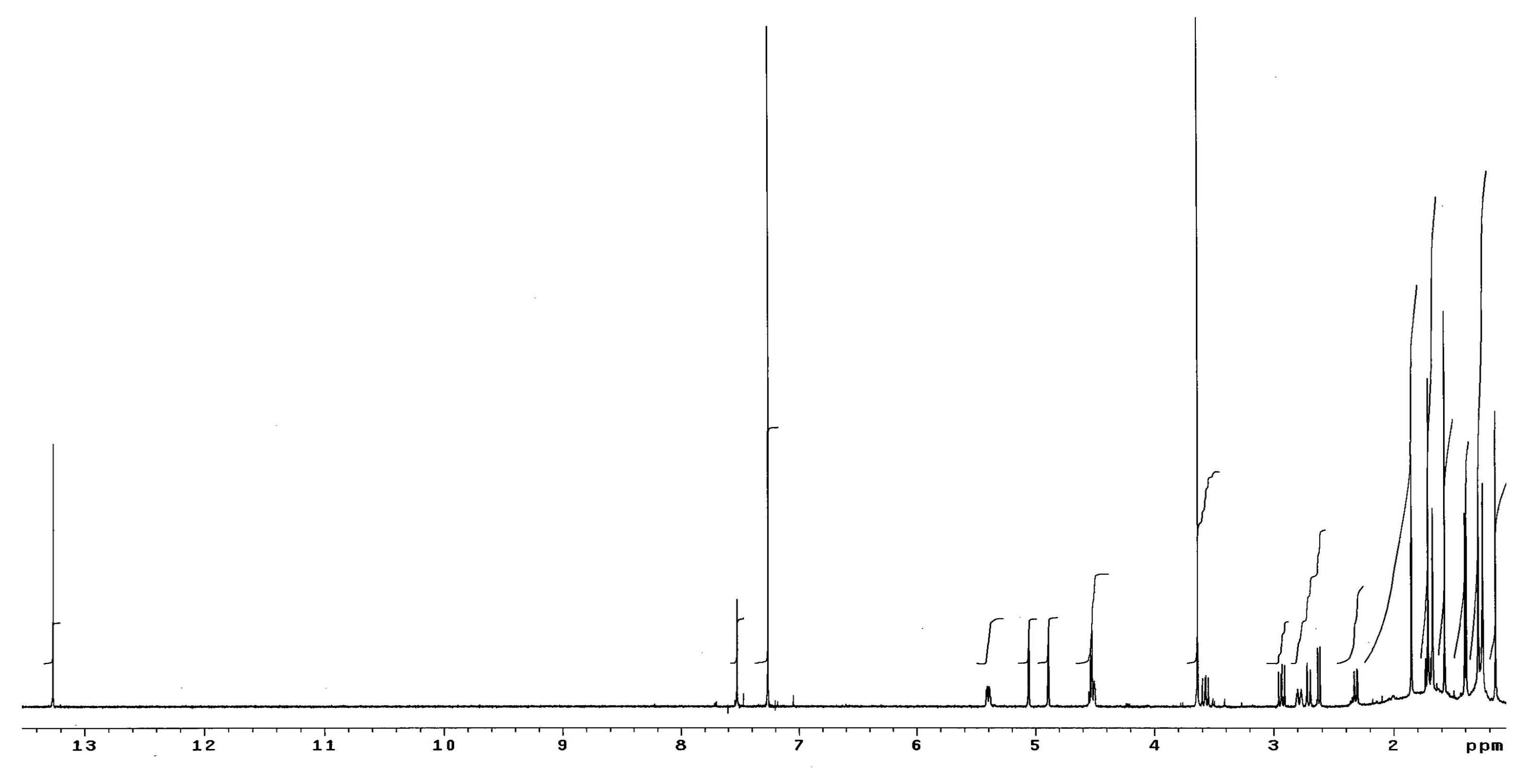


Figure 49 ^{1}H NMR (500 MHz) ($CDCl_3$) spectrum of **GF15**

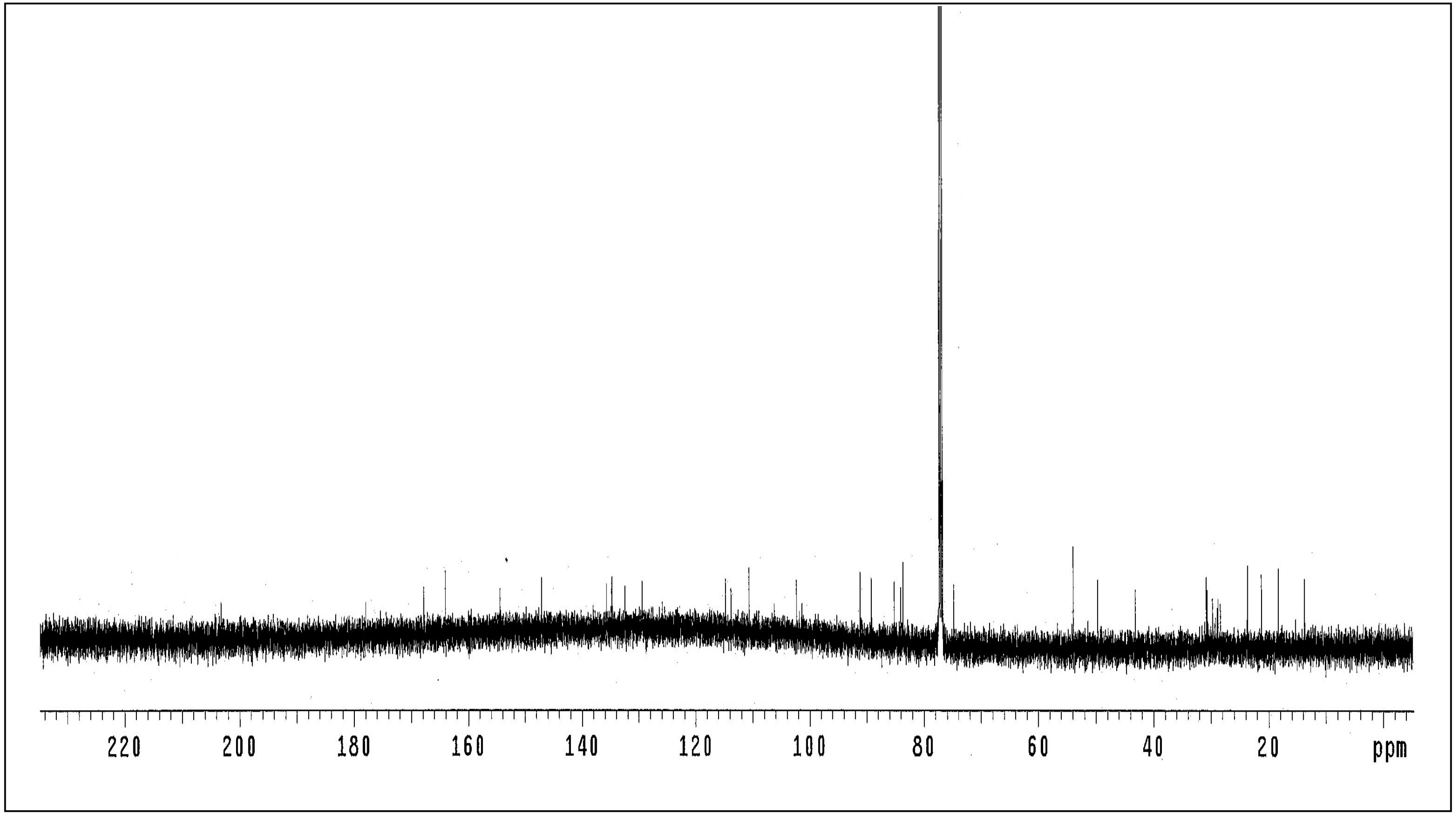


Figure 50 ^{13}C NMR (125 MHz) (CDCl$_3$) spectrum of **GF15**

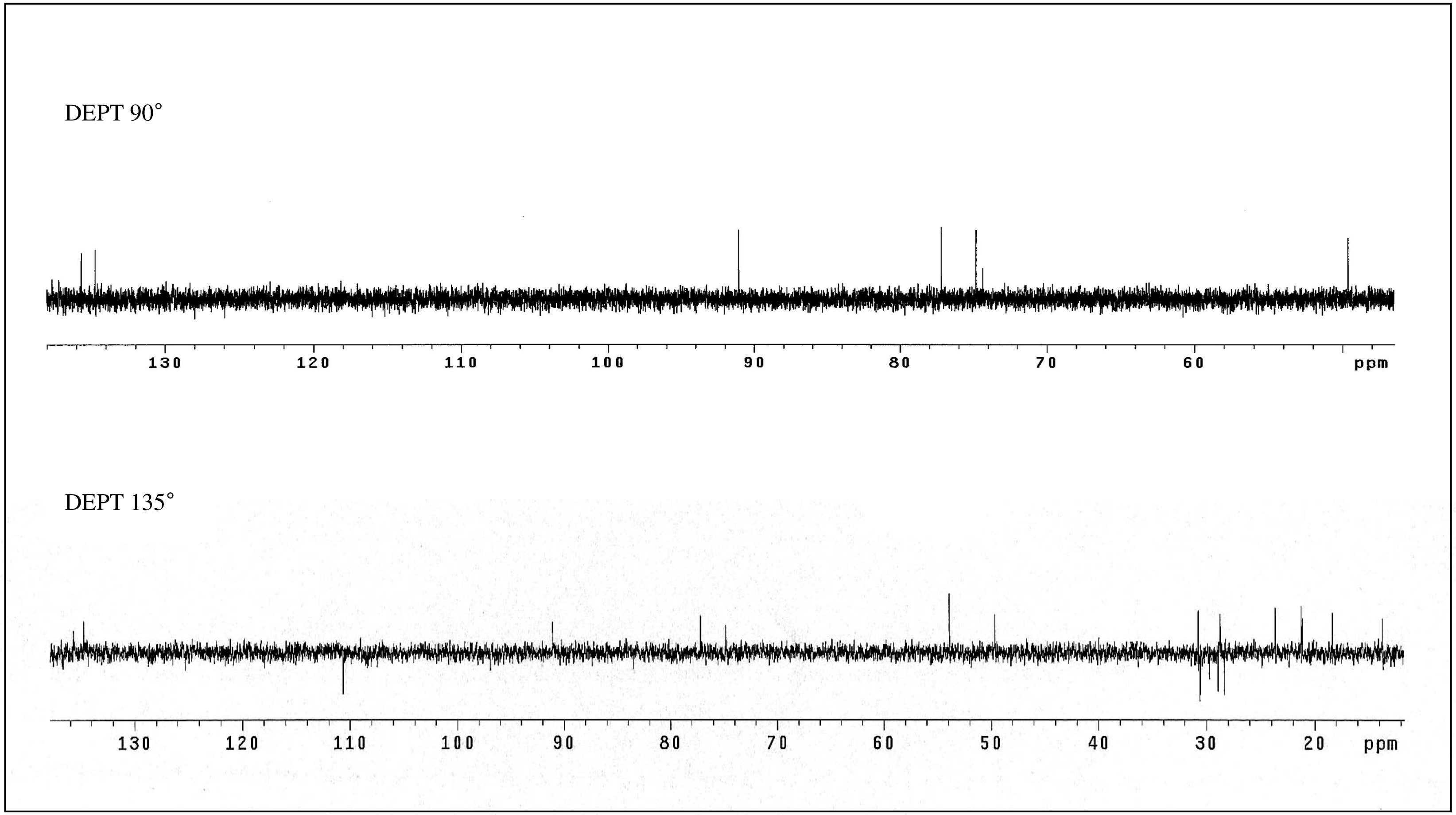


Figure 51 DEPT spectrum of **GF15**

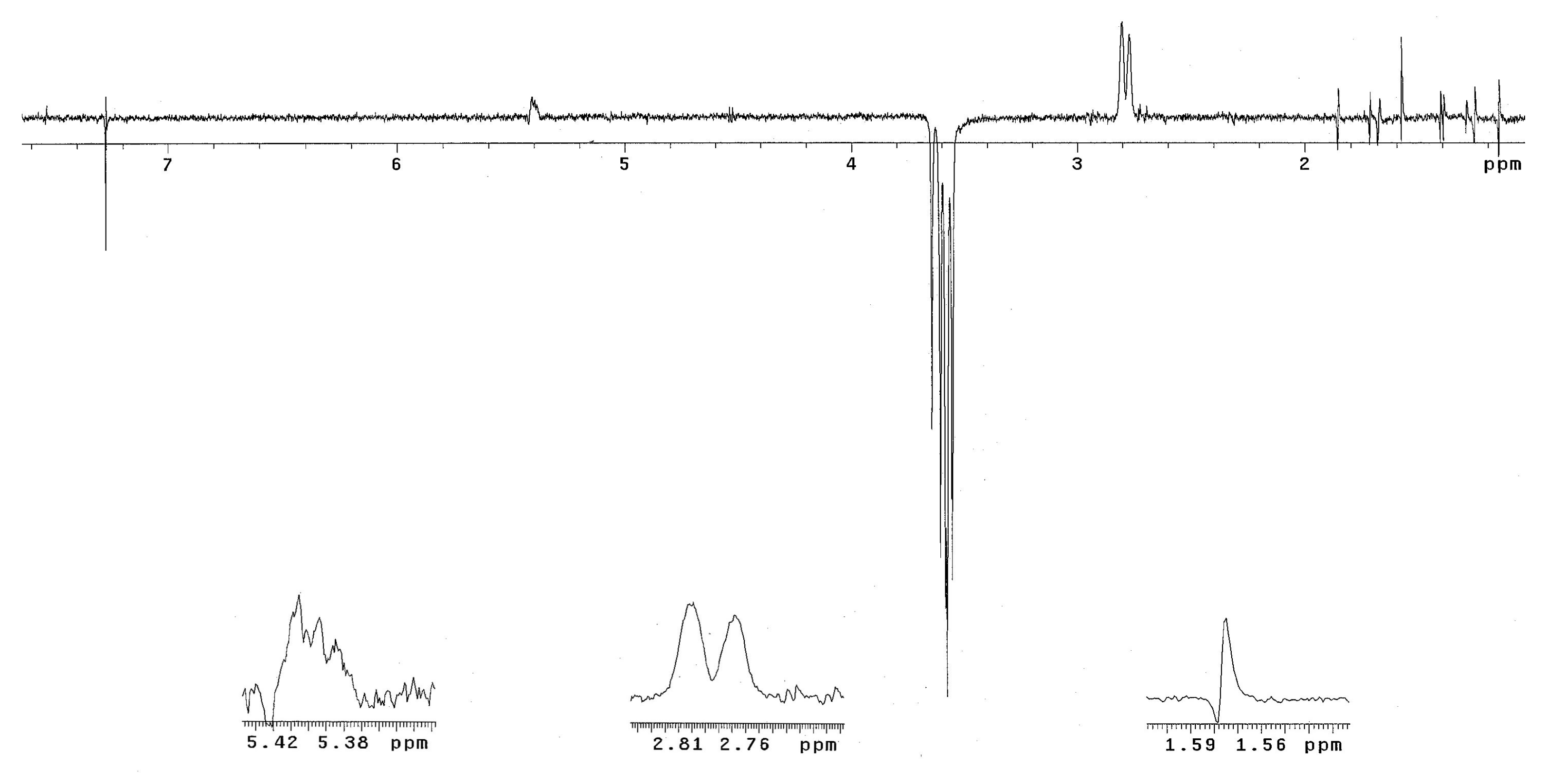


Figure 52 NOEDIFF spectrum of **GF15** after irradiation at δ_H 3.57

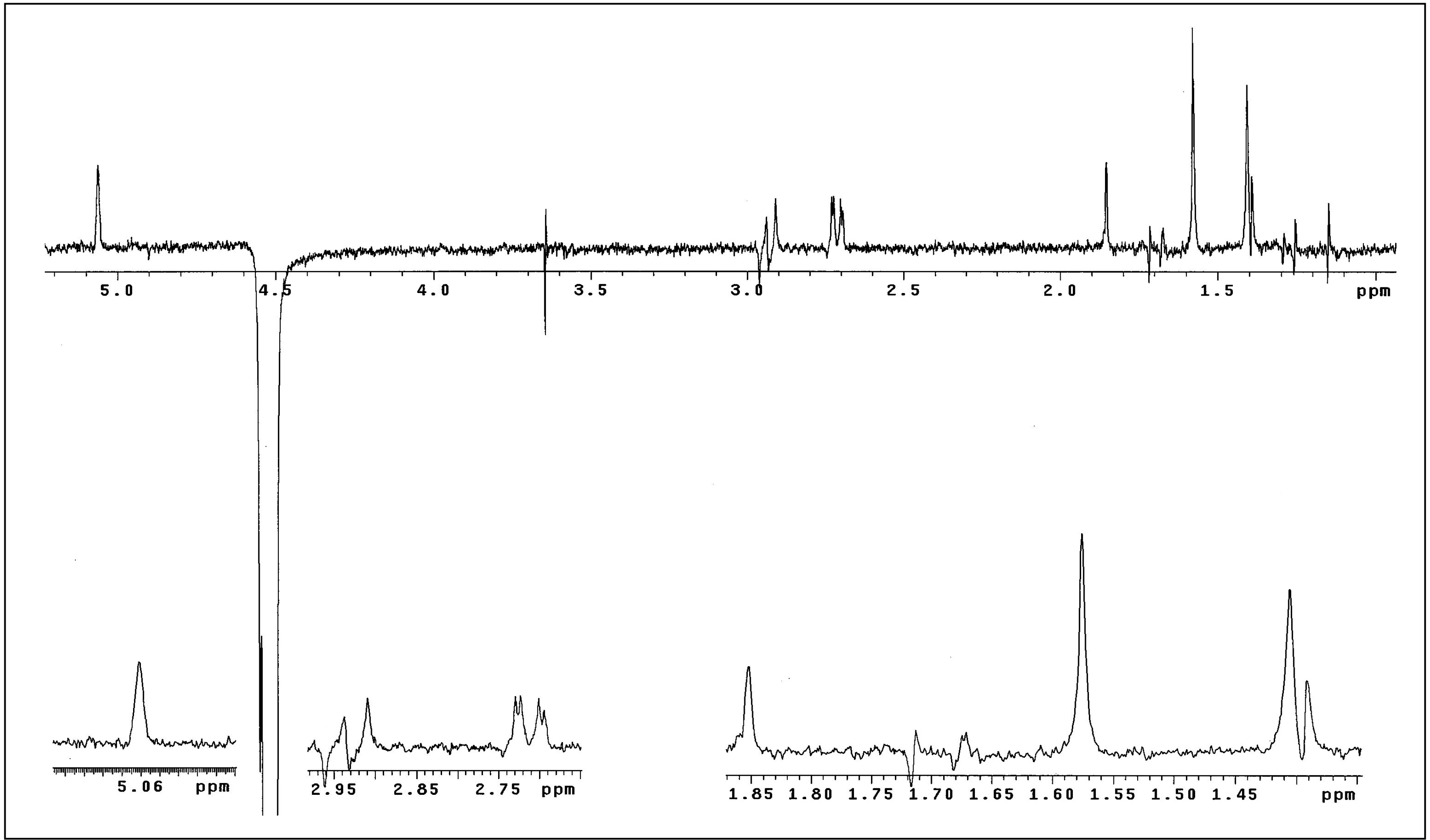


Figure 53 NOEDIFF spectrum of **GF15** after irradiation at δ_H 4.53

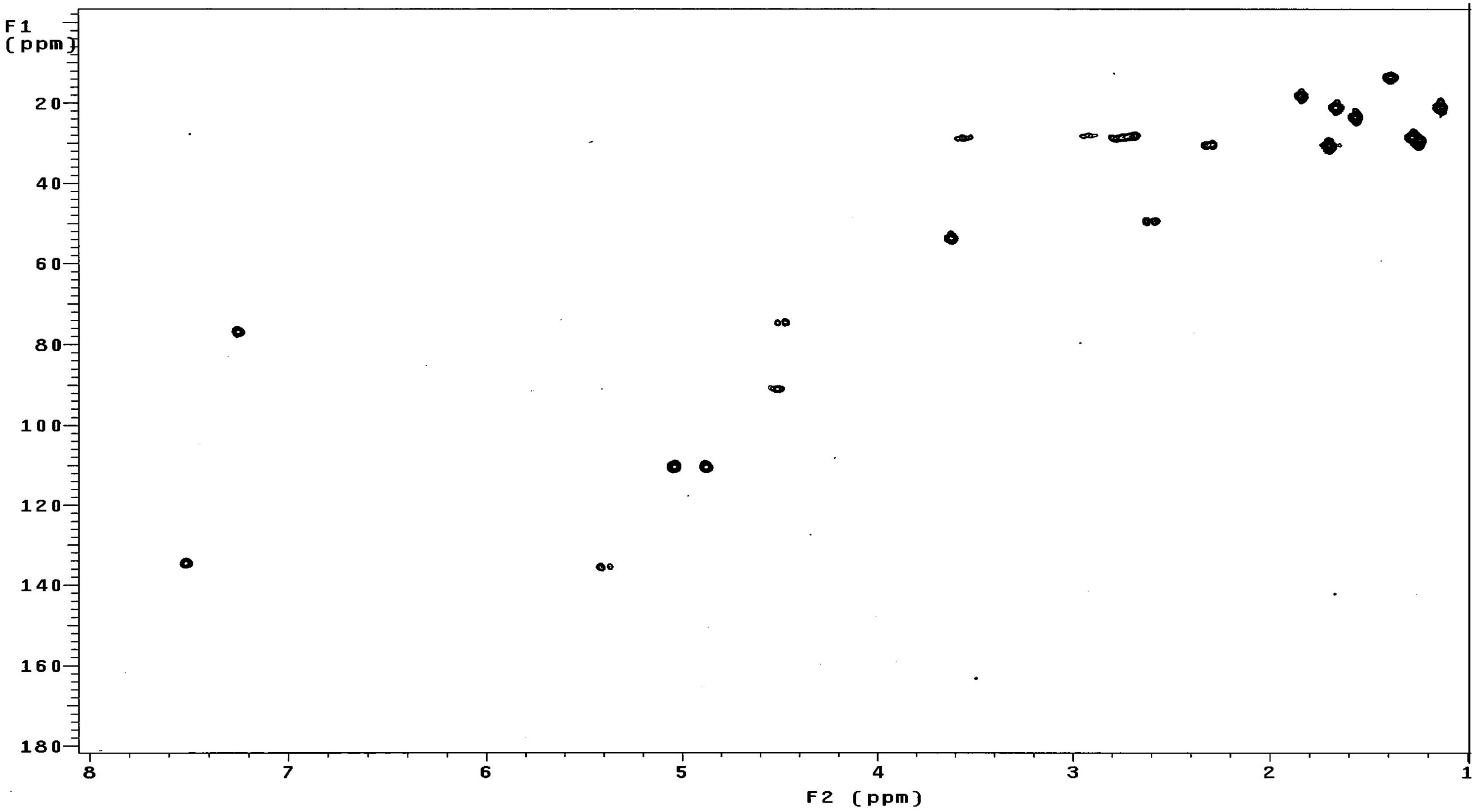


Figure 54 2D HMQC spectrum of **GF15**

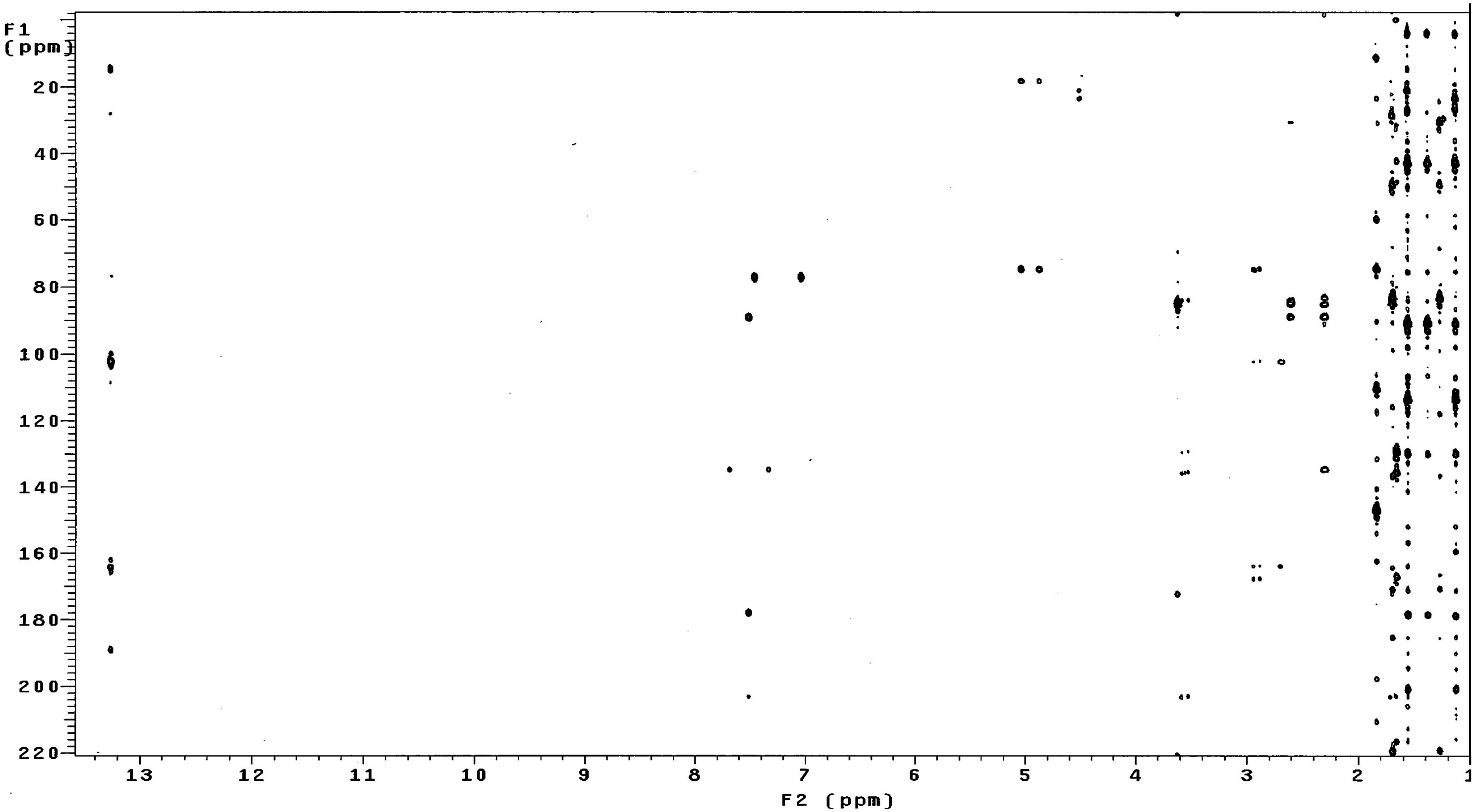


Figure 55 2D HMBC spectrum of **GF15**

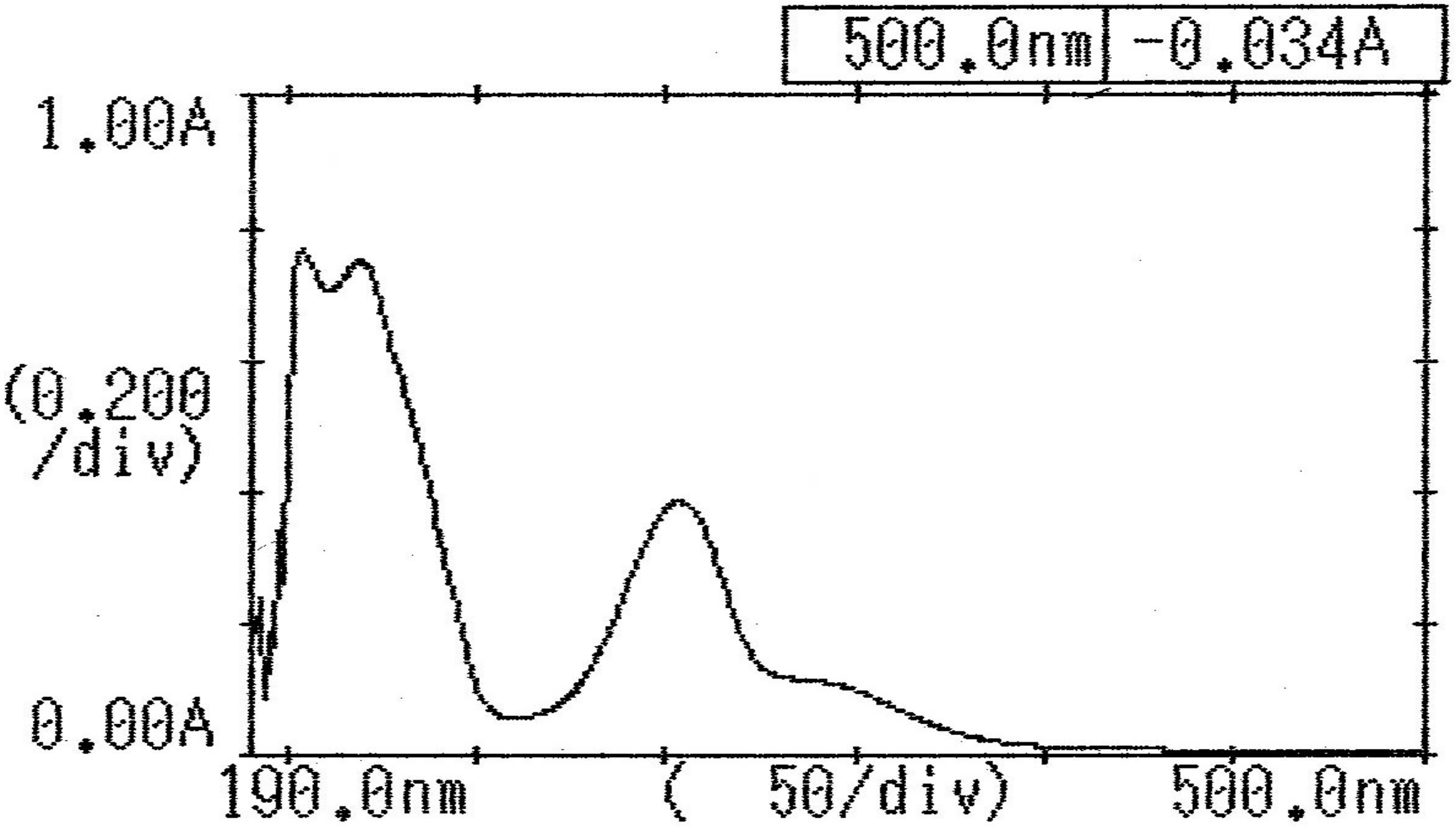


Figure 56 UV (CH_3OH) spectrum of **GF11**

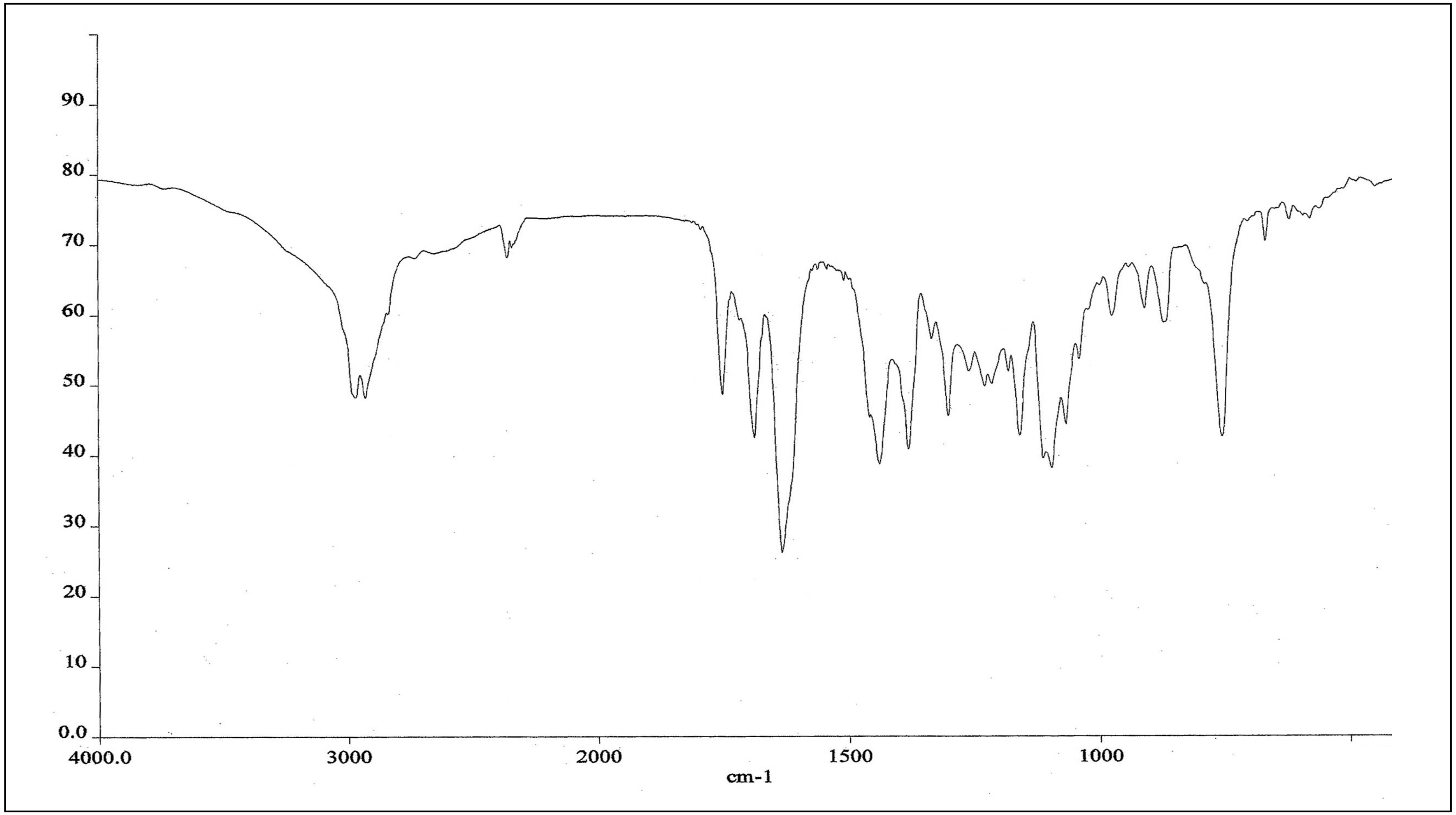


Figure 57 FT-IR (neat) spectrum of **GF11**

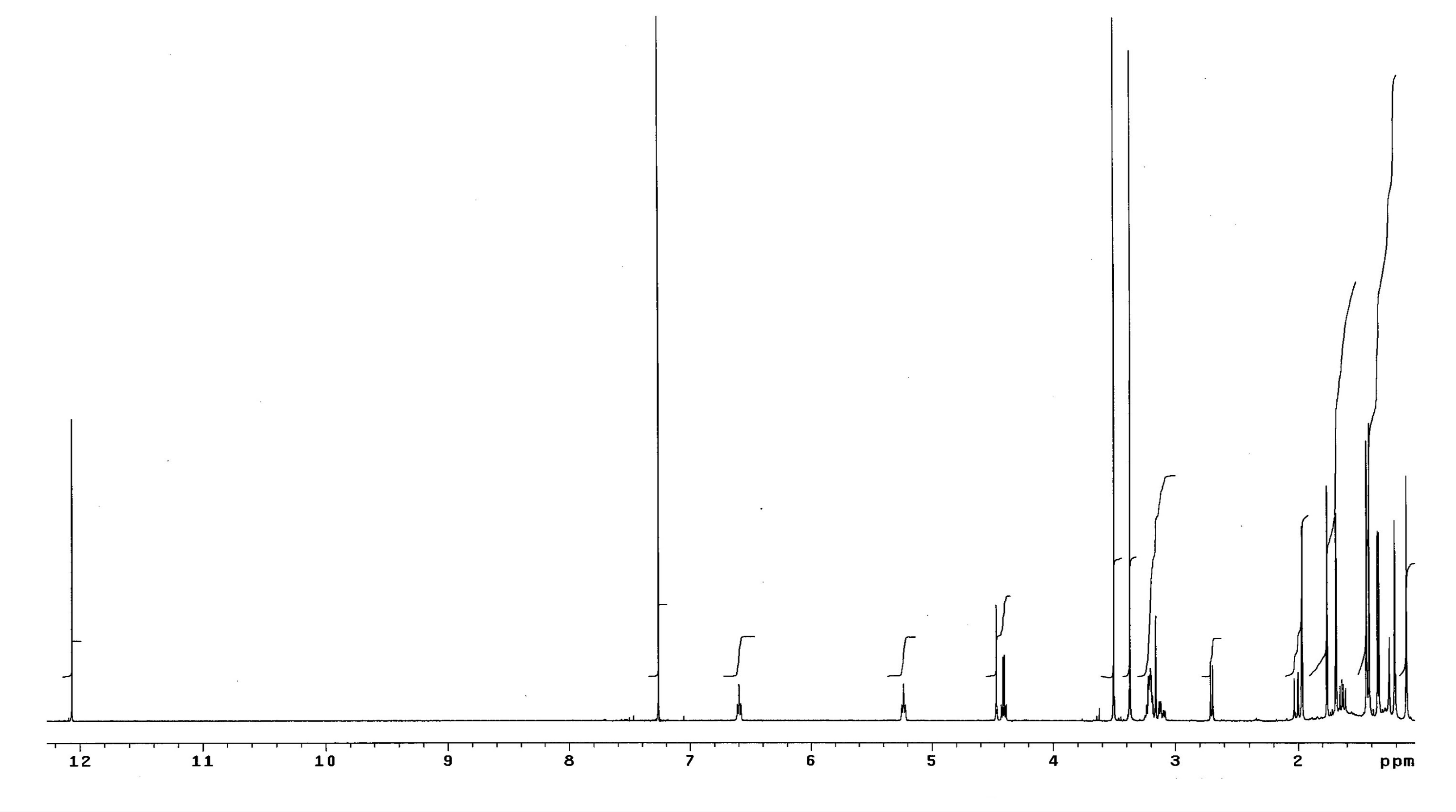


Figure 58 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF11**

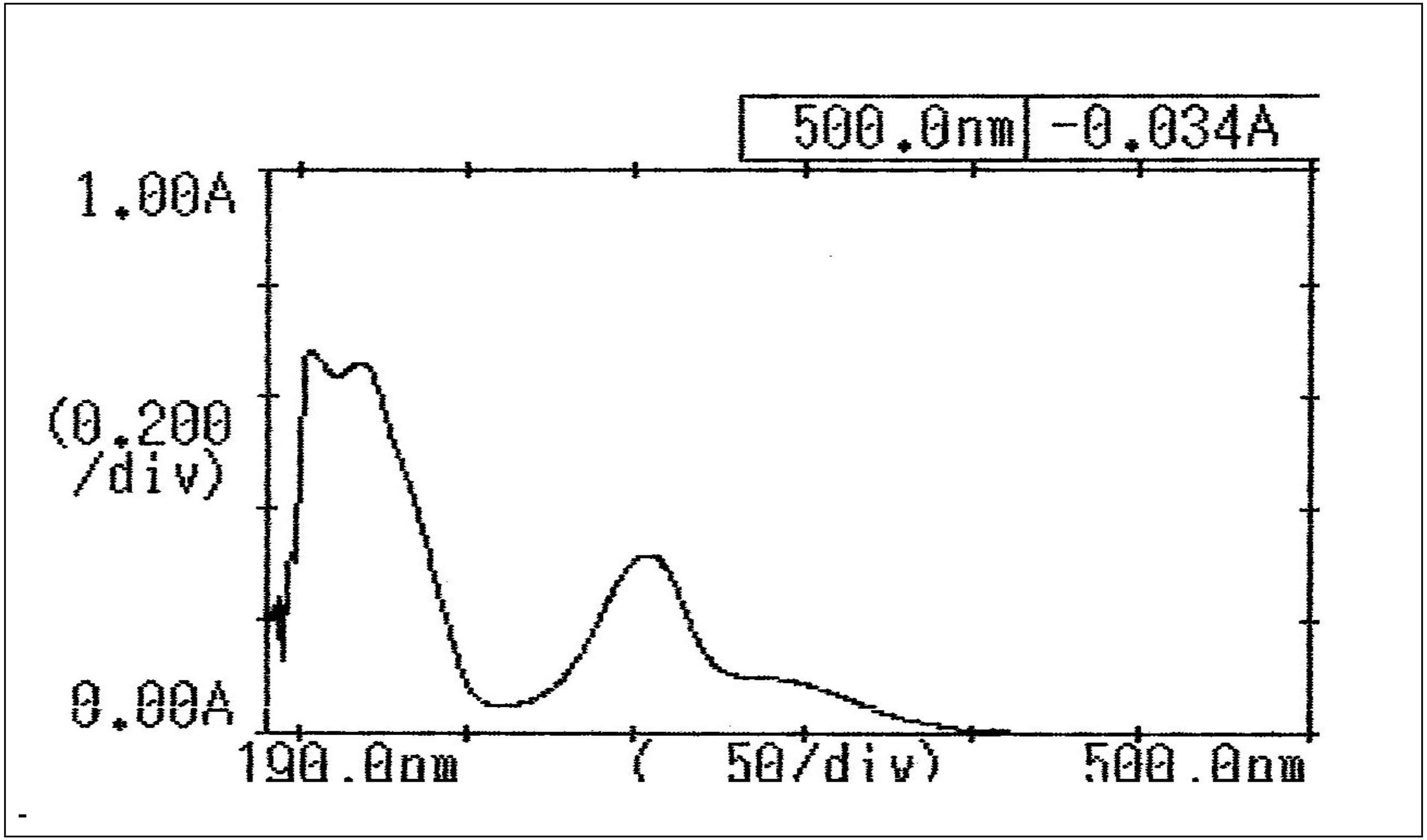


Figure 59 UV (CH_3OH) spectrum of **GF17**

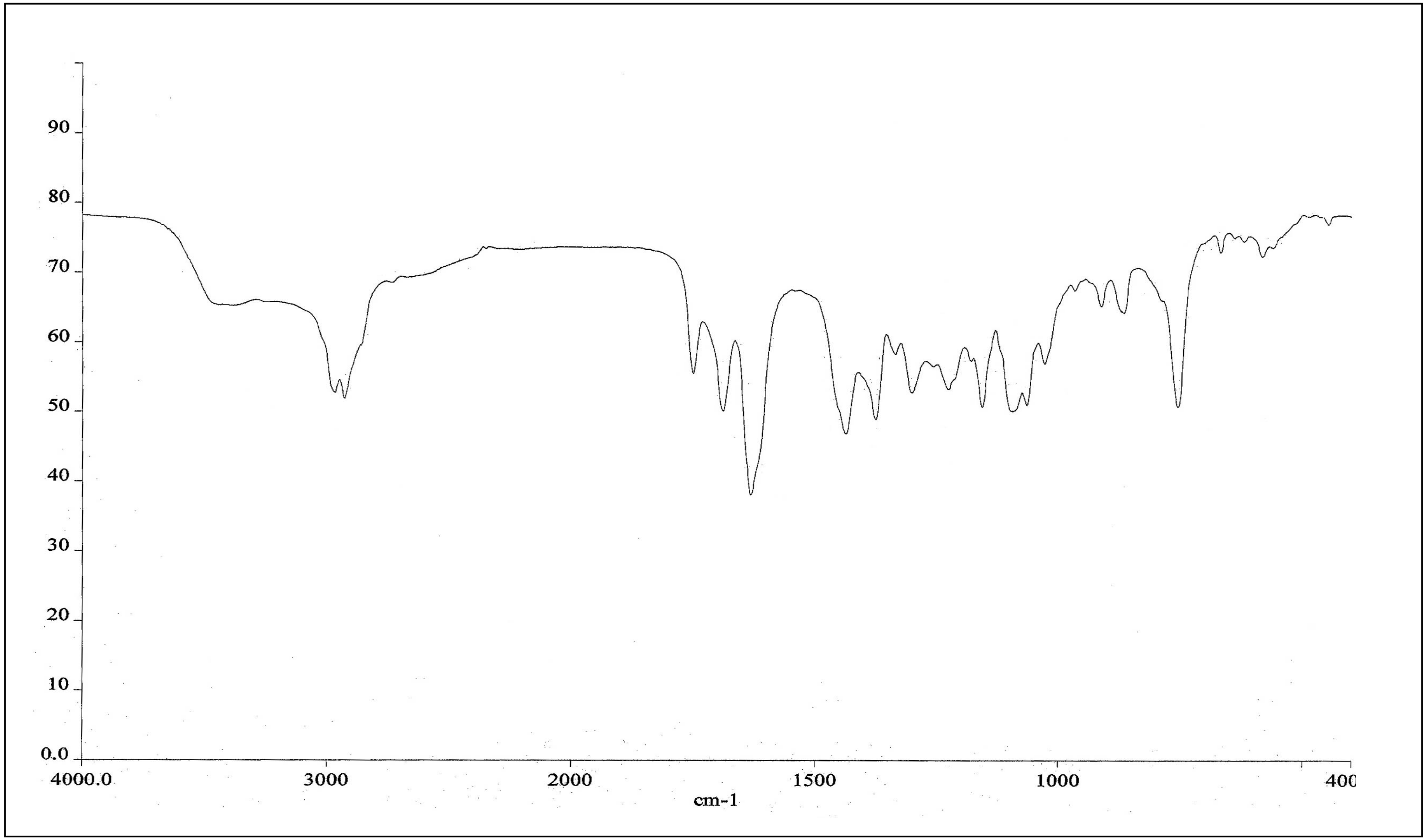


Figure 60 FT-IR (neat) spectrum of **GF17**

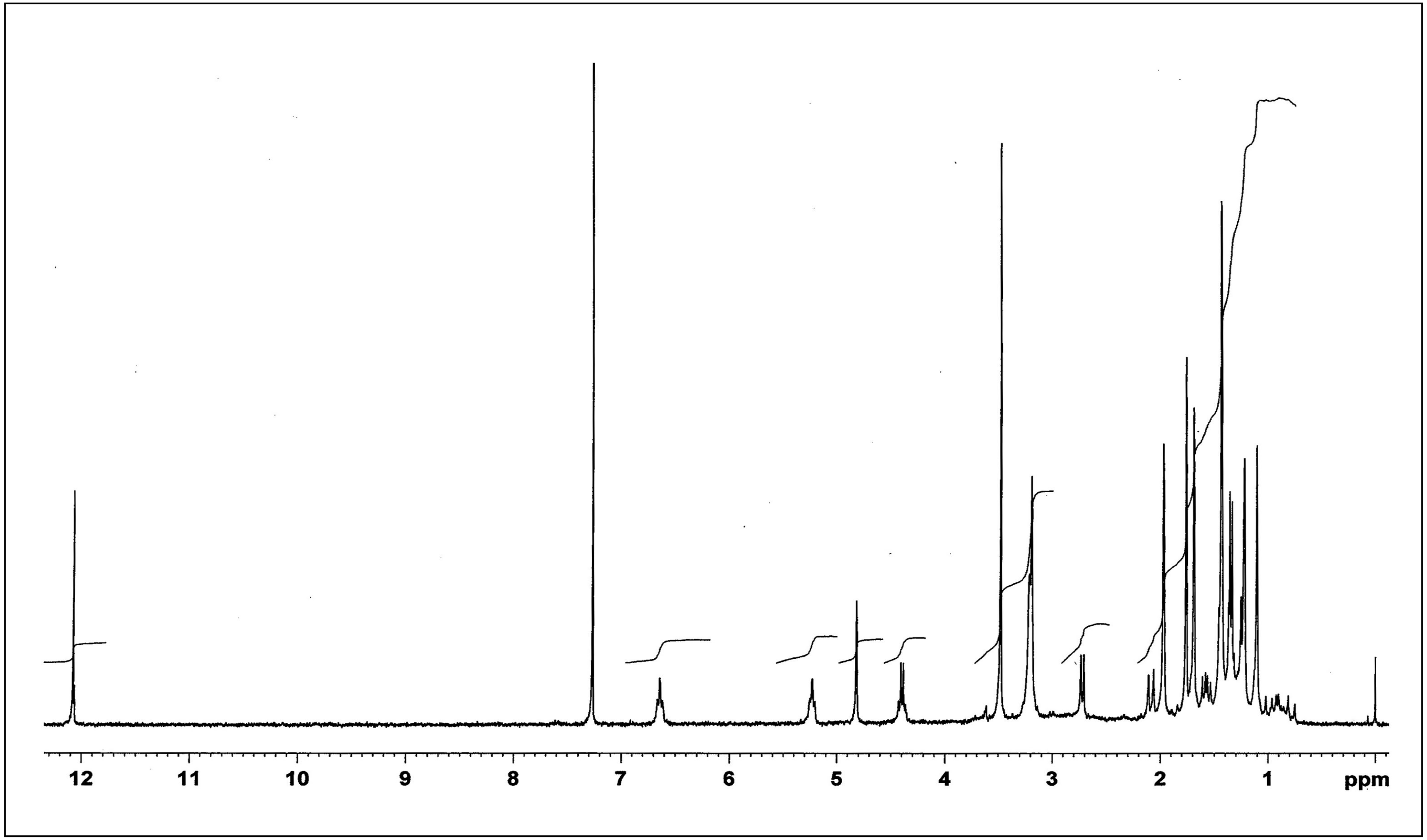


Figure 61 ^{1}H NMR (300 MHz) (CDCl$_3$) spectrum of **GF17**

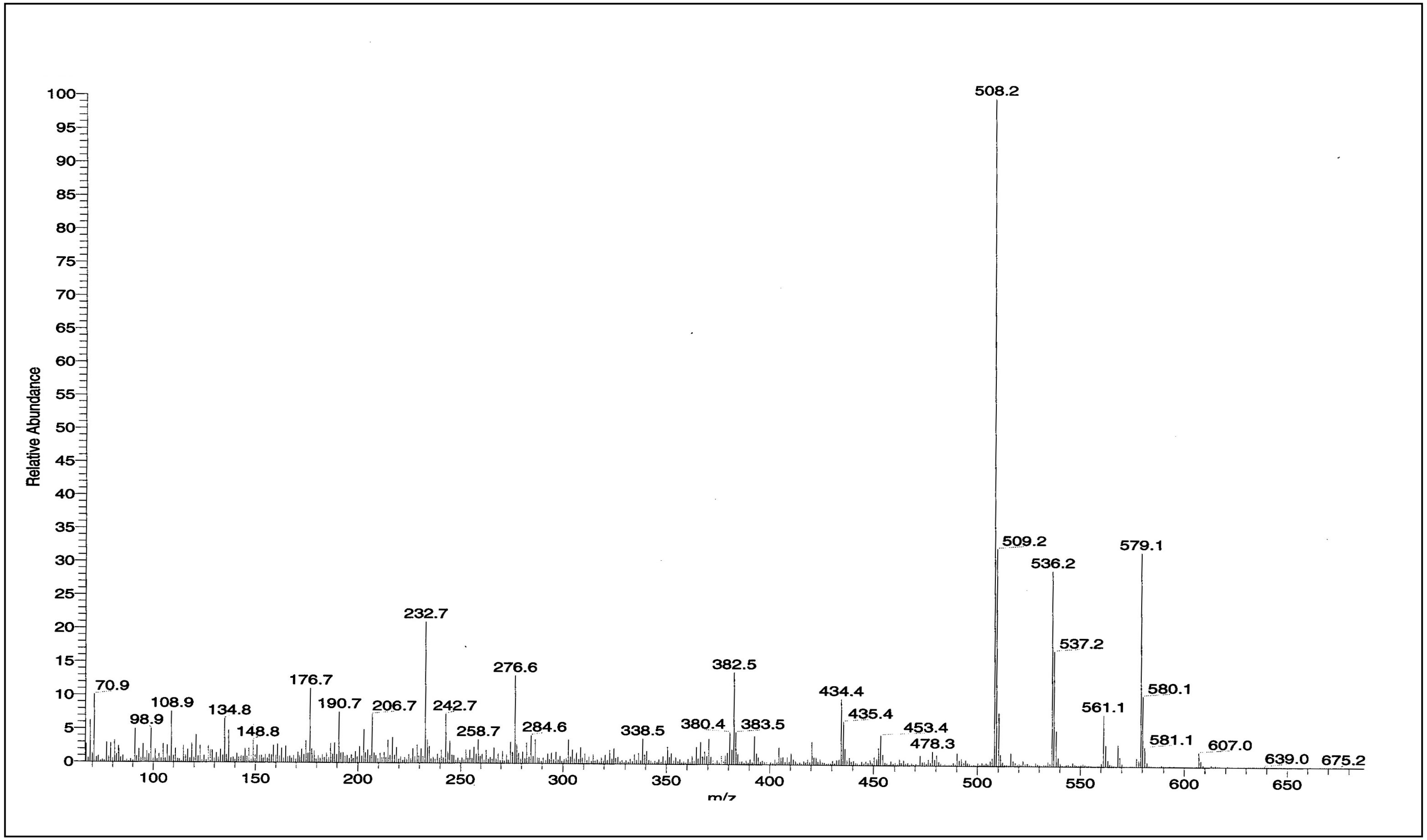


Figure 62 Mass spectrum of **GF18**

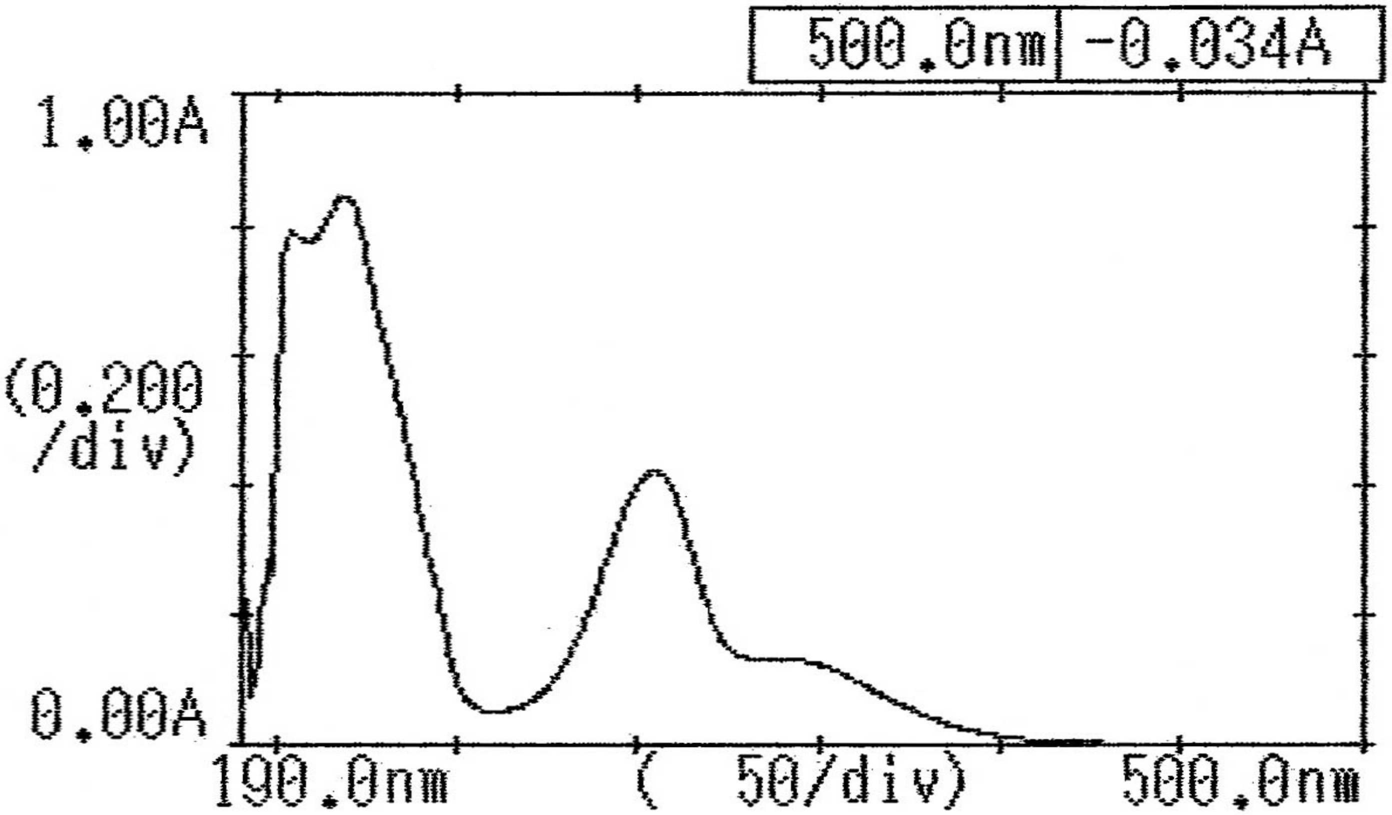


Figure 63 UV (CH_3OH) spectrum of **GF18**

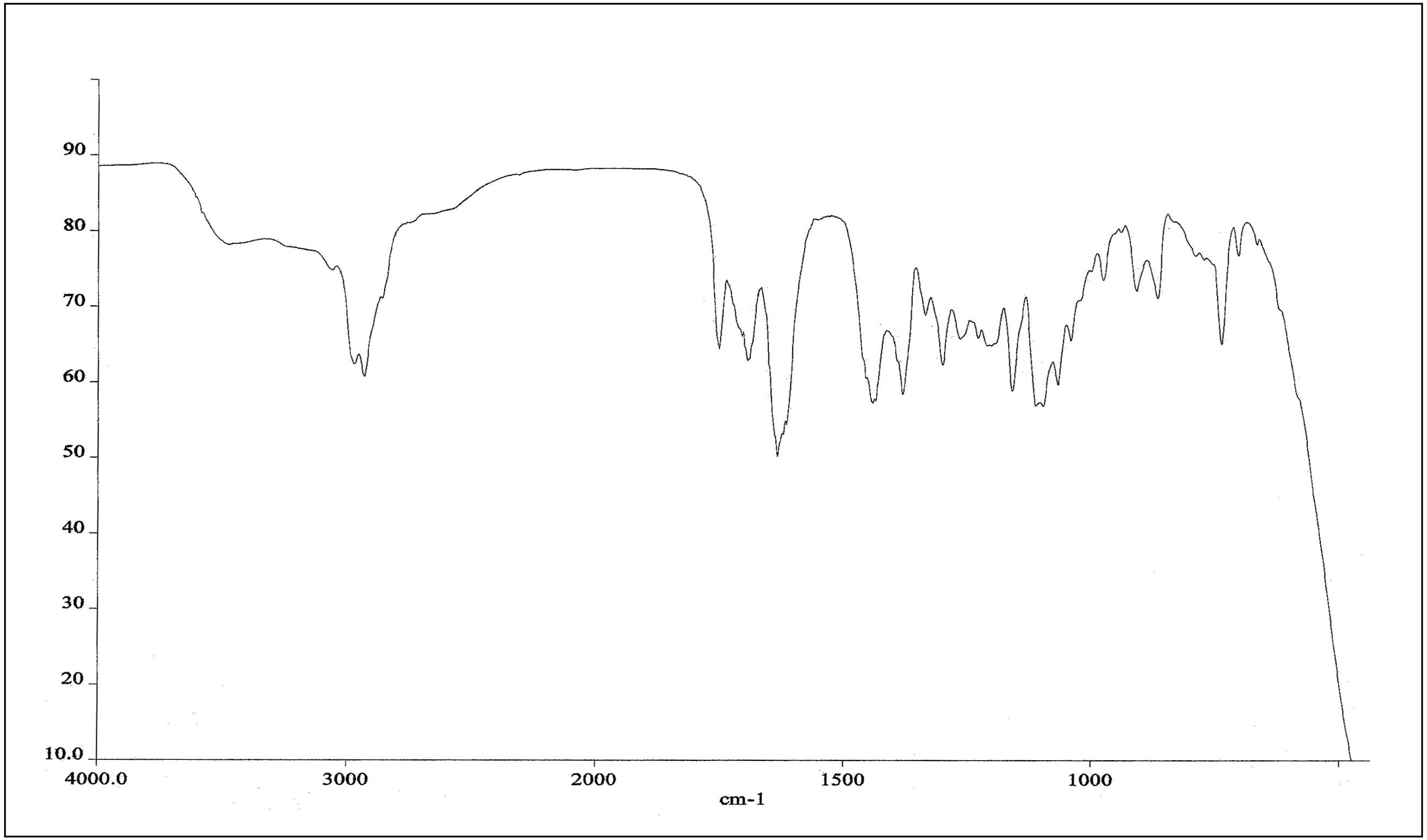


Figure 64 FT-IR (neat) spectrum of **GF18**

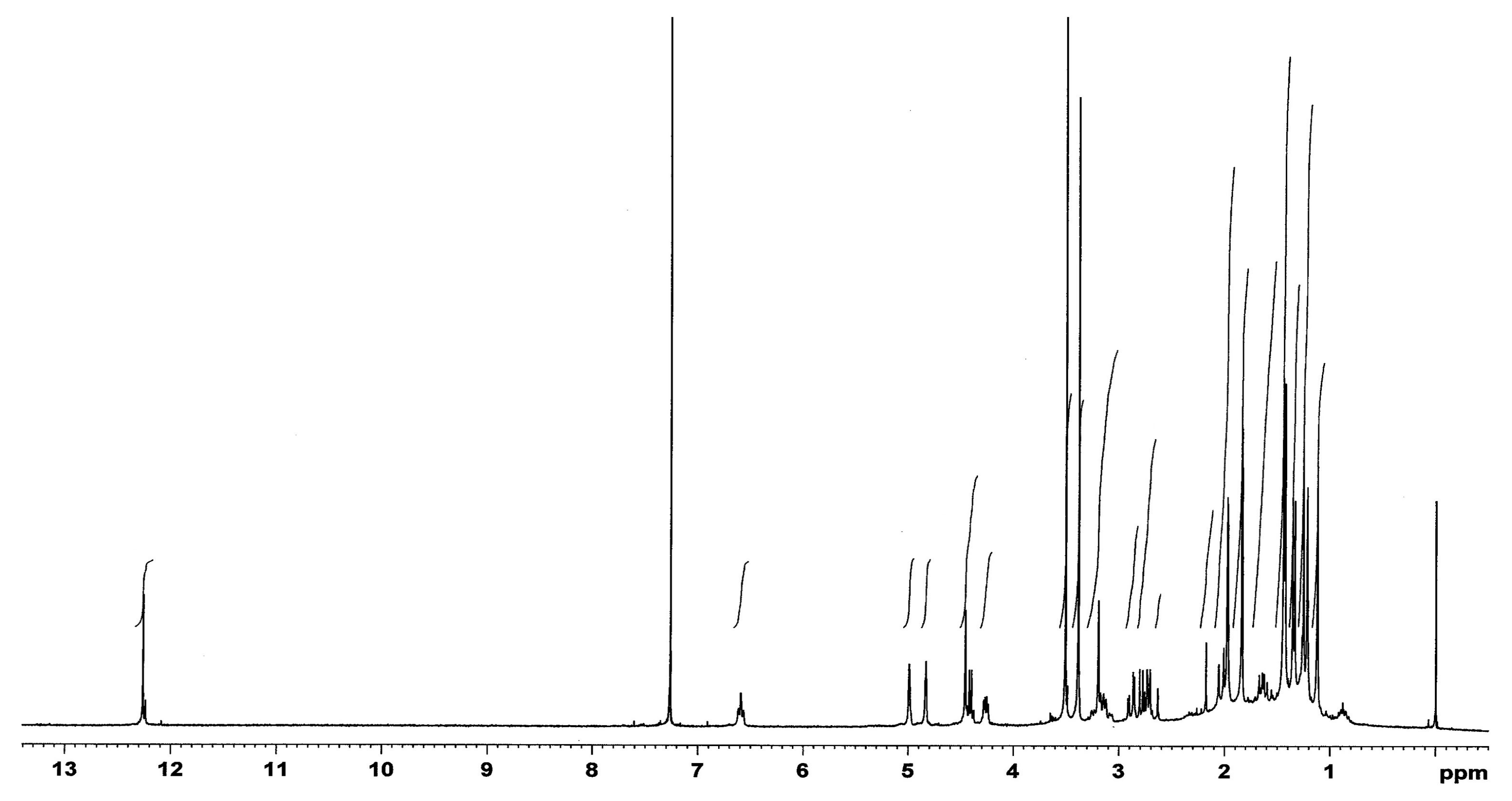


Figure 65 ^{1}H NMR (300 MHz) (CDCl$_3$) spectrum of **GF18**

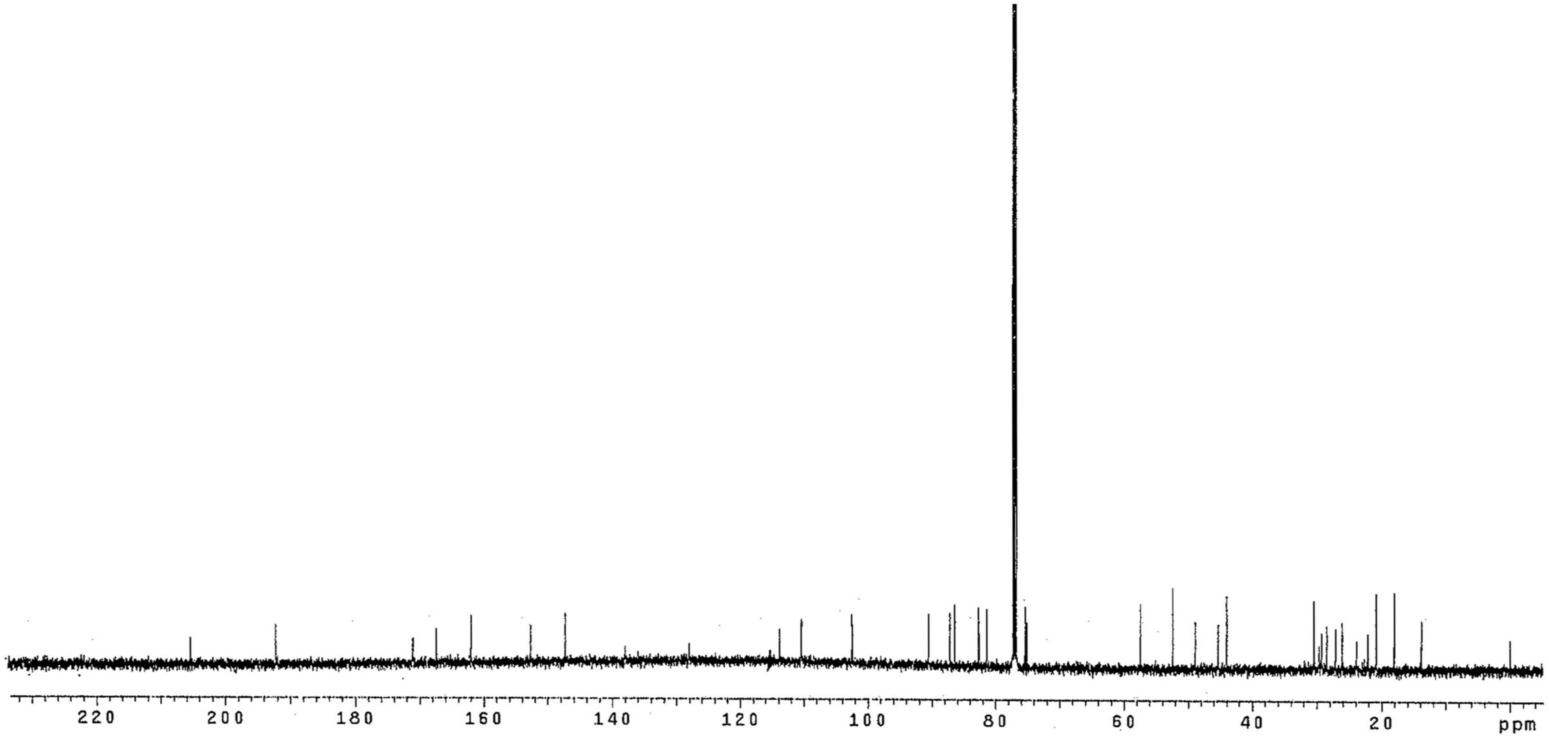


Figure 66 ^{13}C NMR (125 MHz) (CDCl$_3$) spectrum of **GF18**

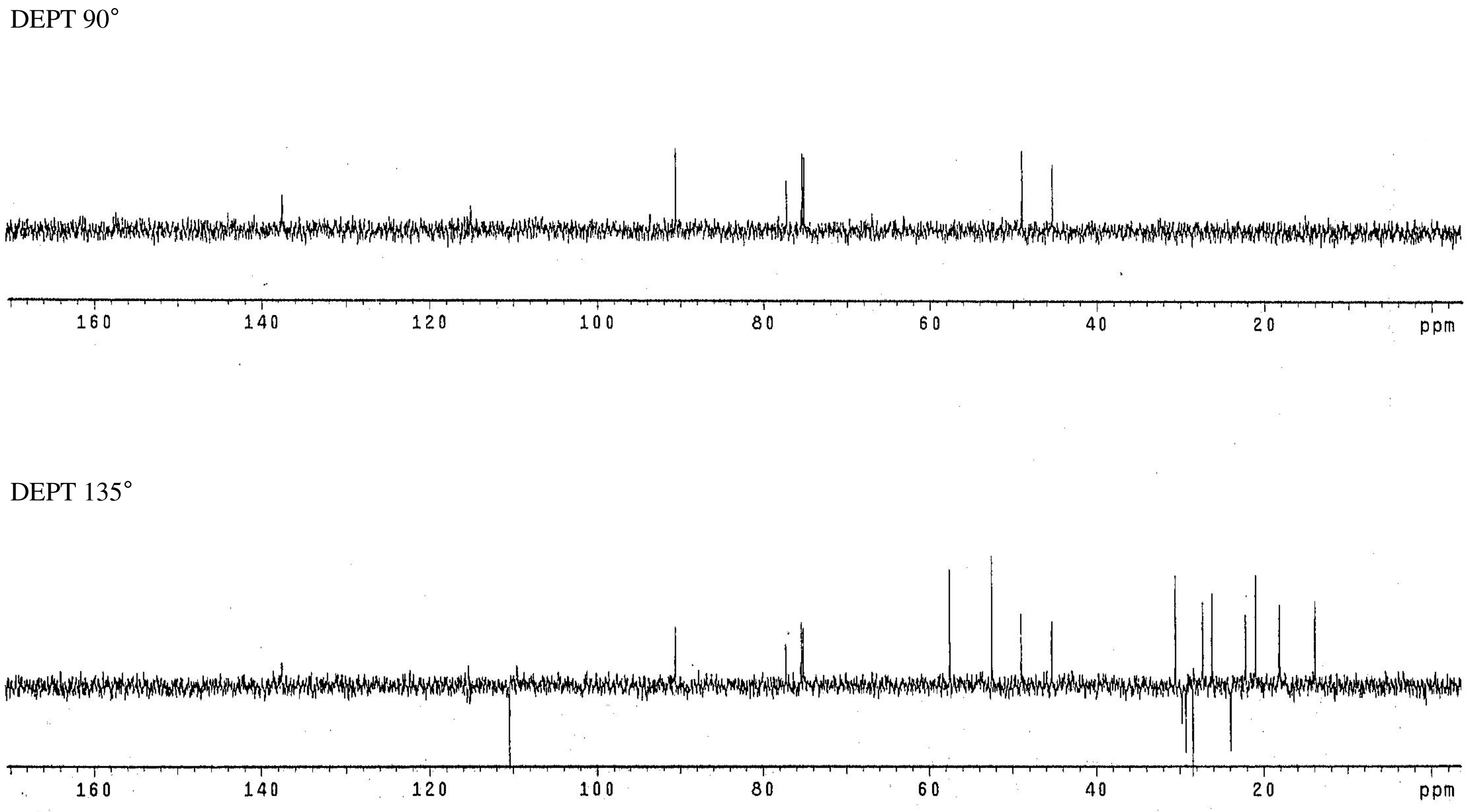


Figure 67 DEPT spectrum of **GF18**

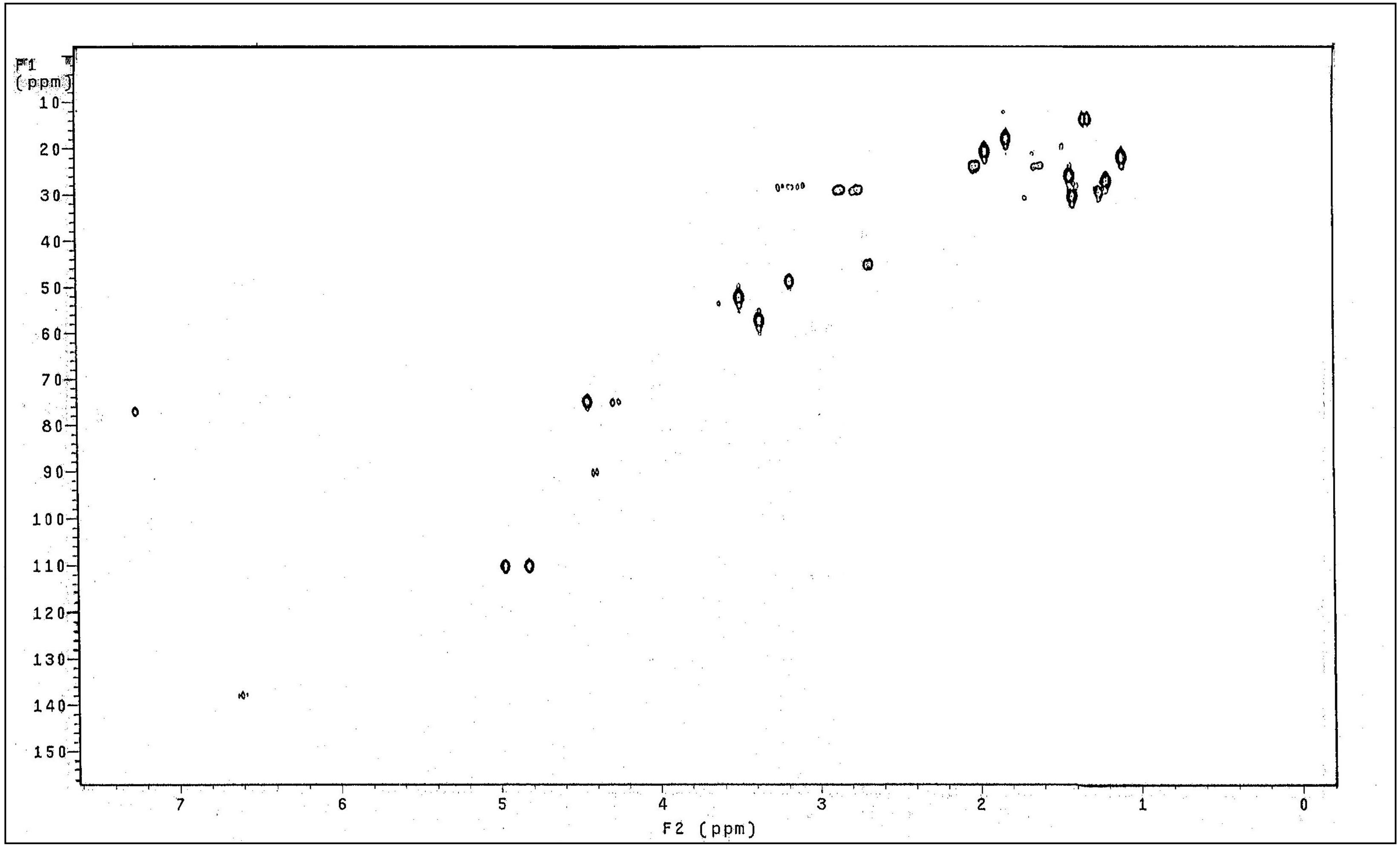


Figure 68 2D HMQC spectrum of **GF18**

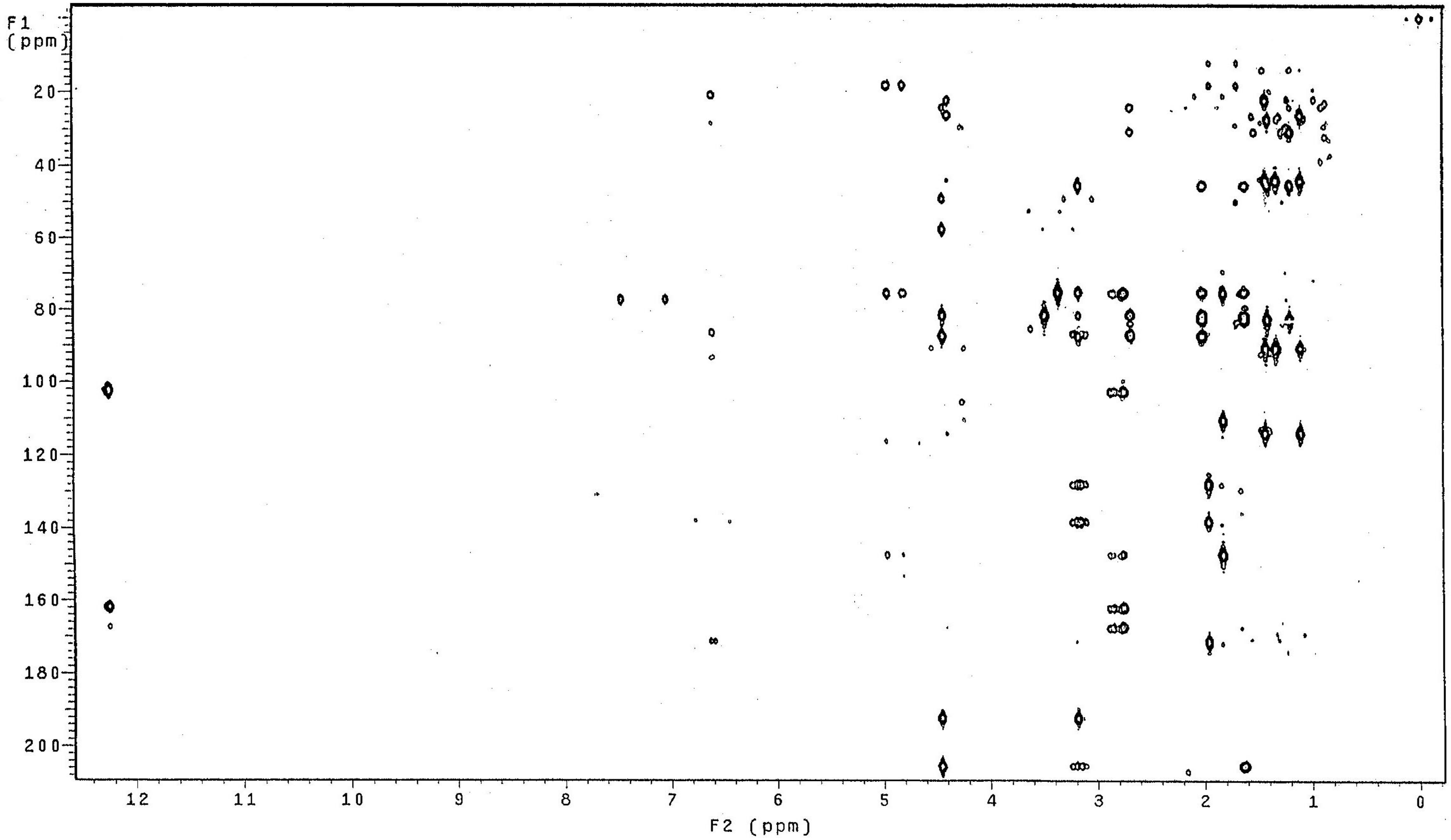


Figure 69 2D HMBC spectrum of **GF18**

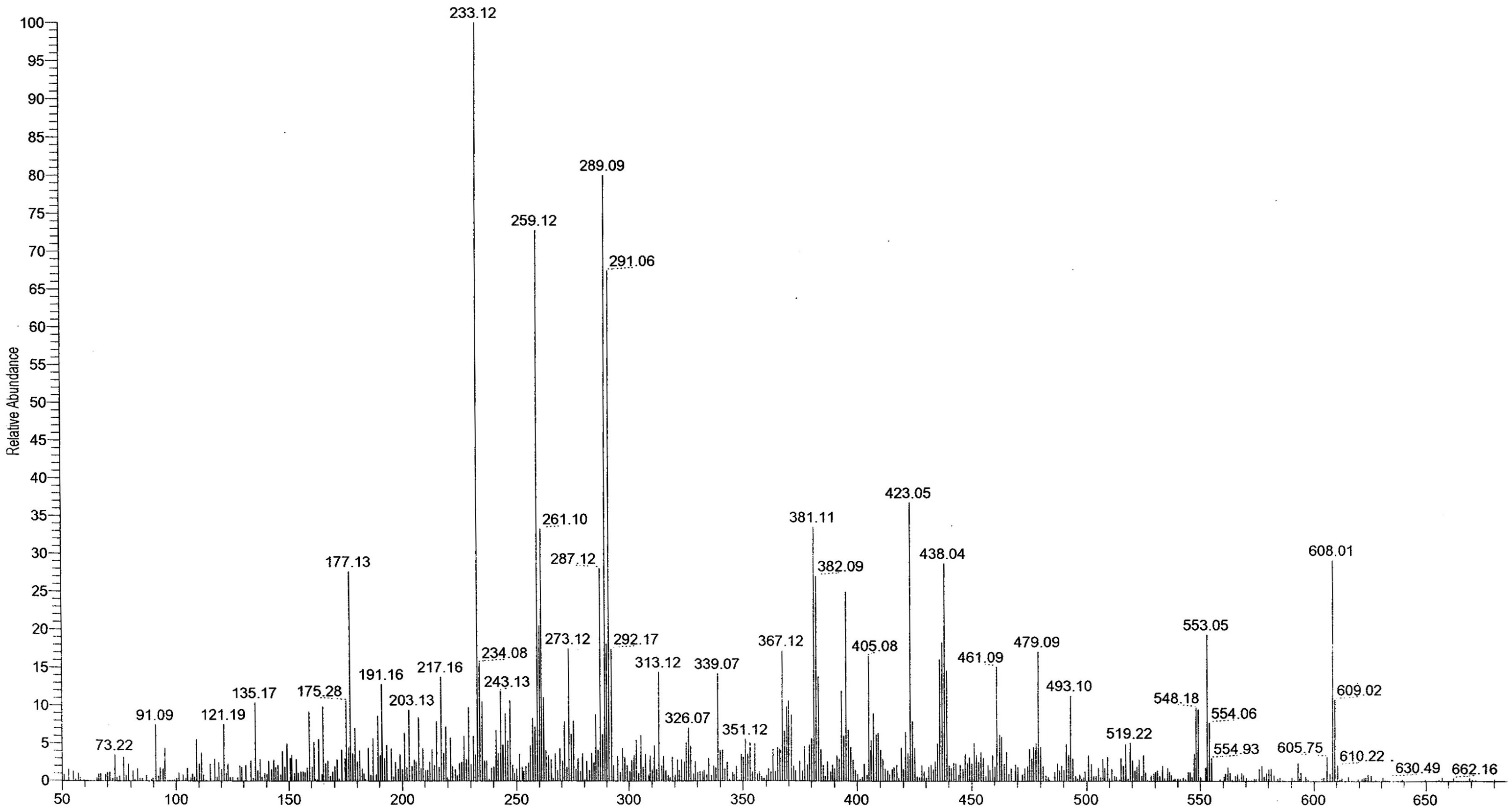


Figure 70 Mass spectrum of **GF9**

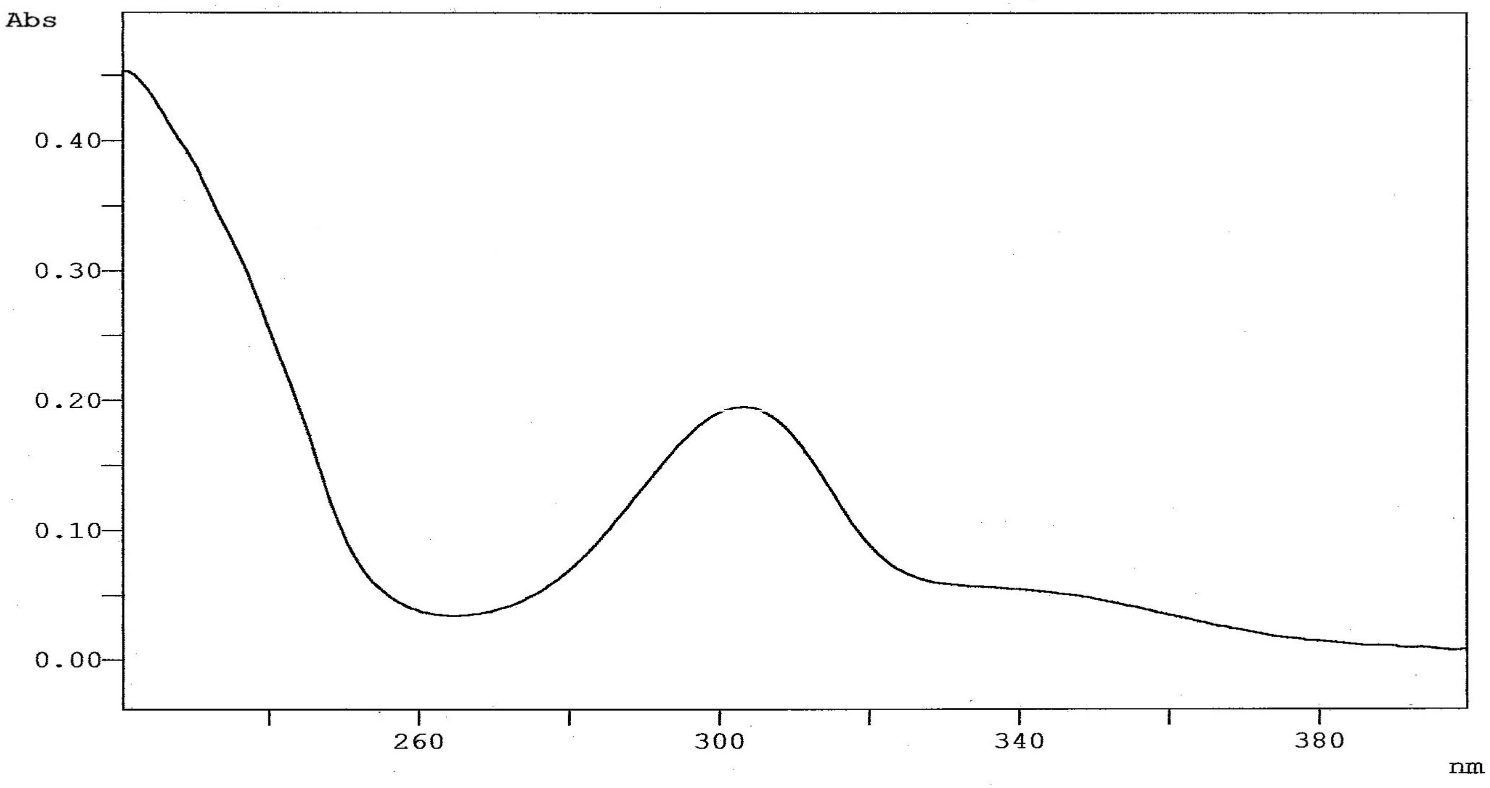


Figure 71 UV (CH_3OH) spectrum of **GF9**

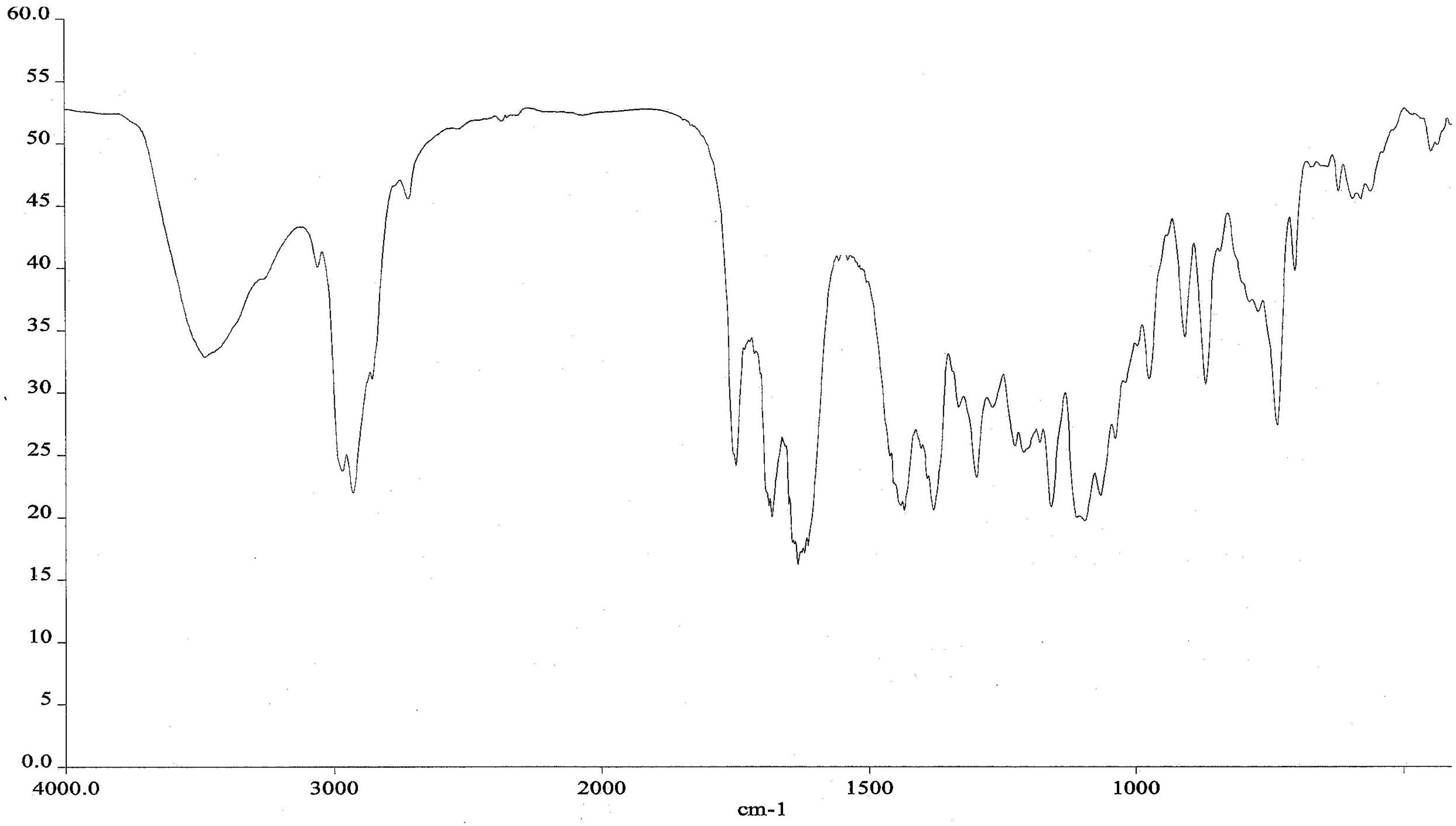


Figure 72 FT-IR (neat) spectrum of **GF9**

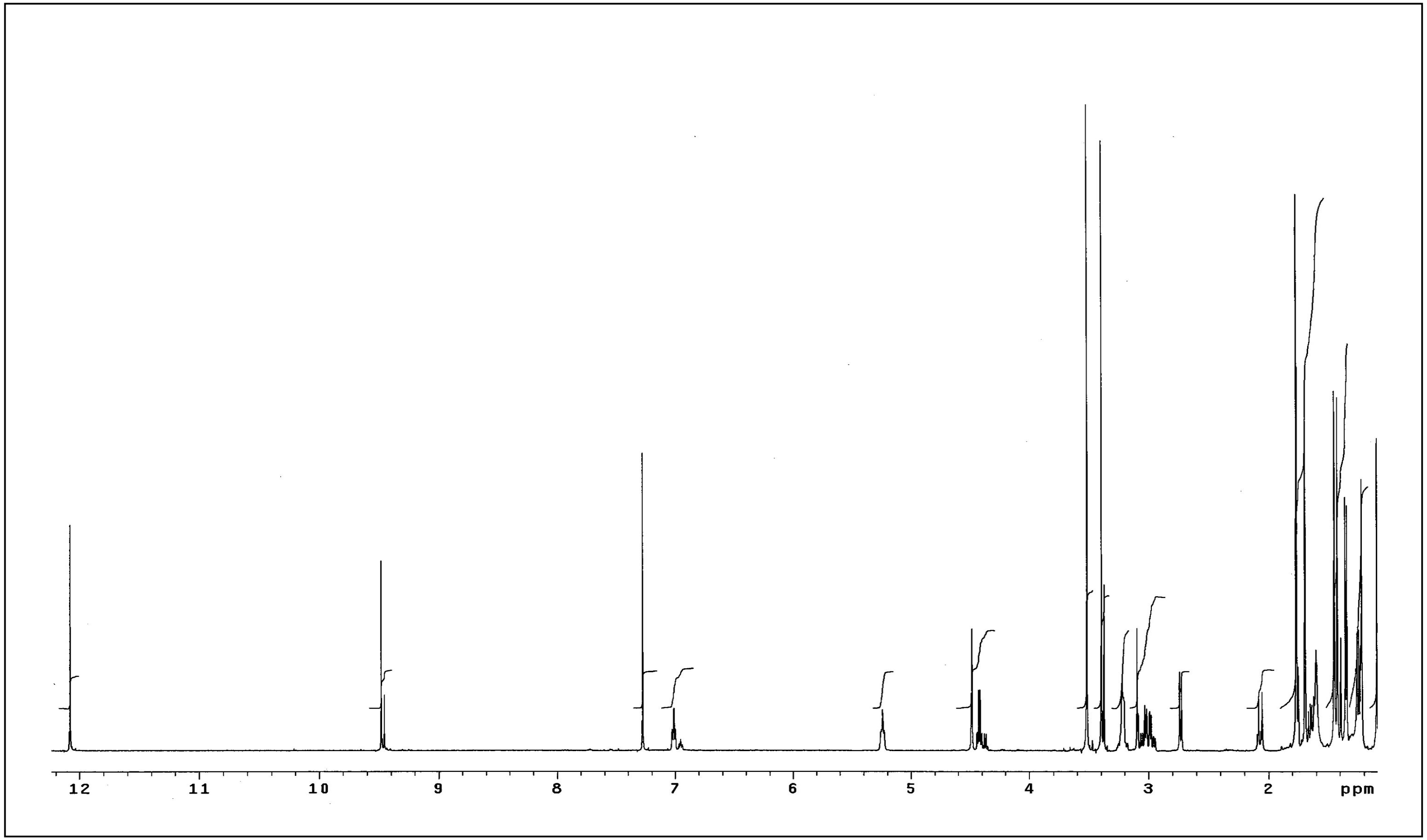


Figure 73 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF9**

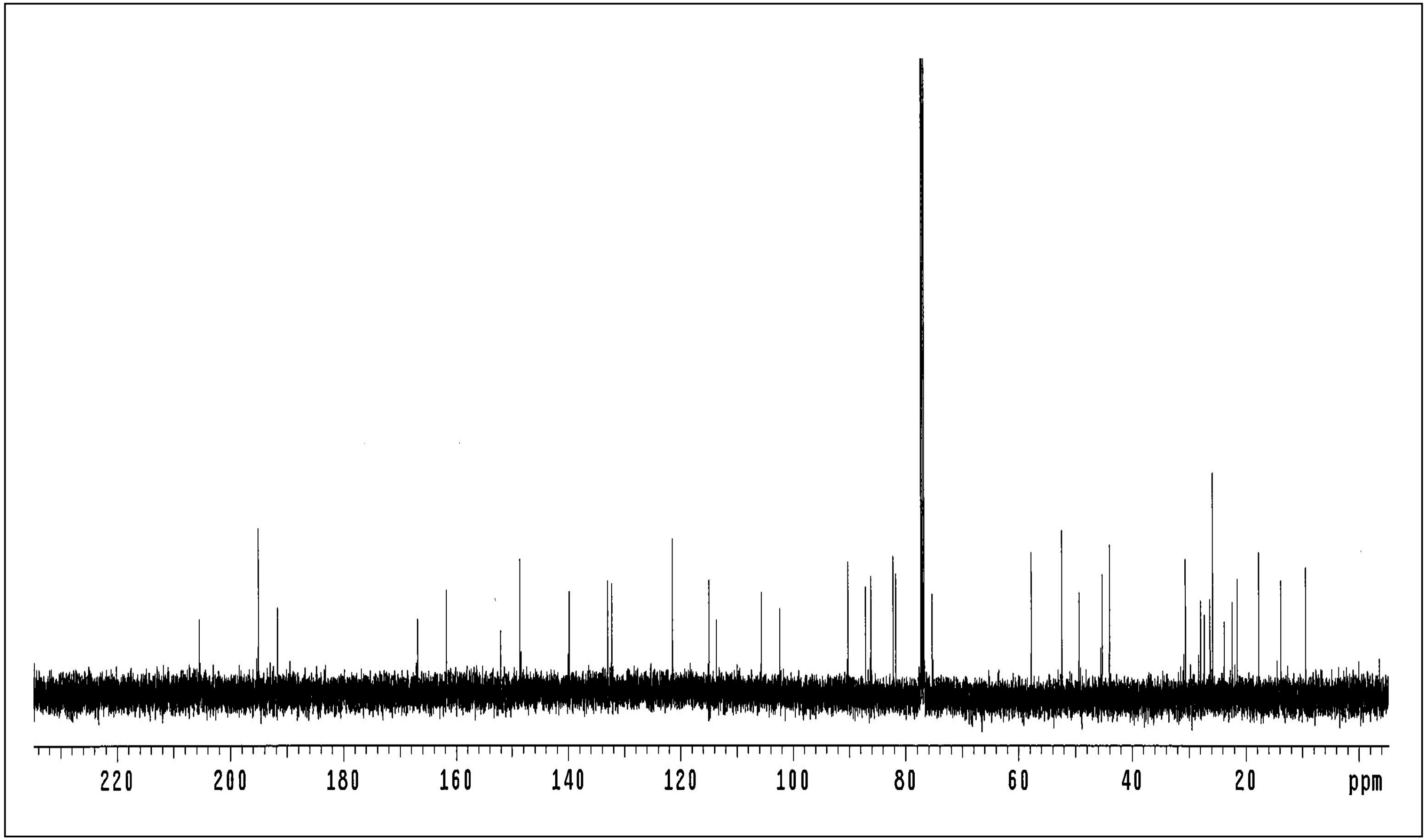


Figure 74 ^{13}C NMR (125 MHz) (CDCl$_3$) spectrum of **GF9**

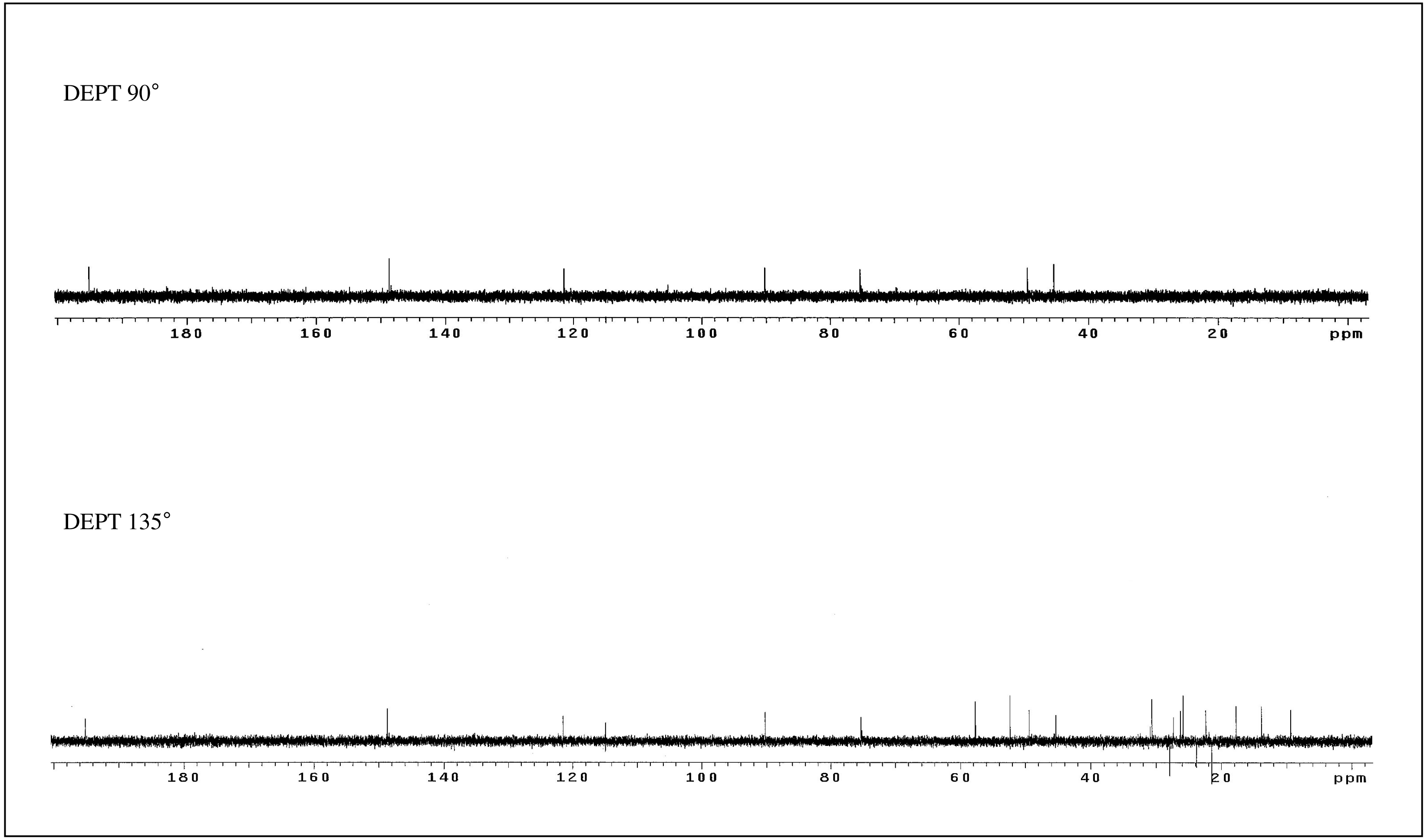


Figure 75 DEPT spectrum of **GF9**

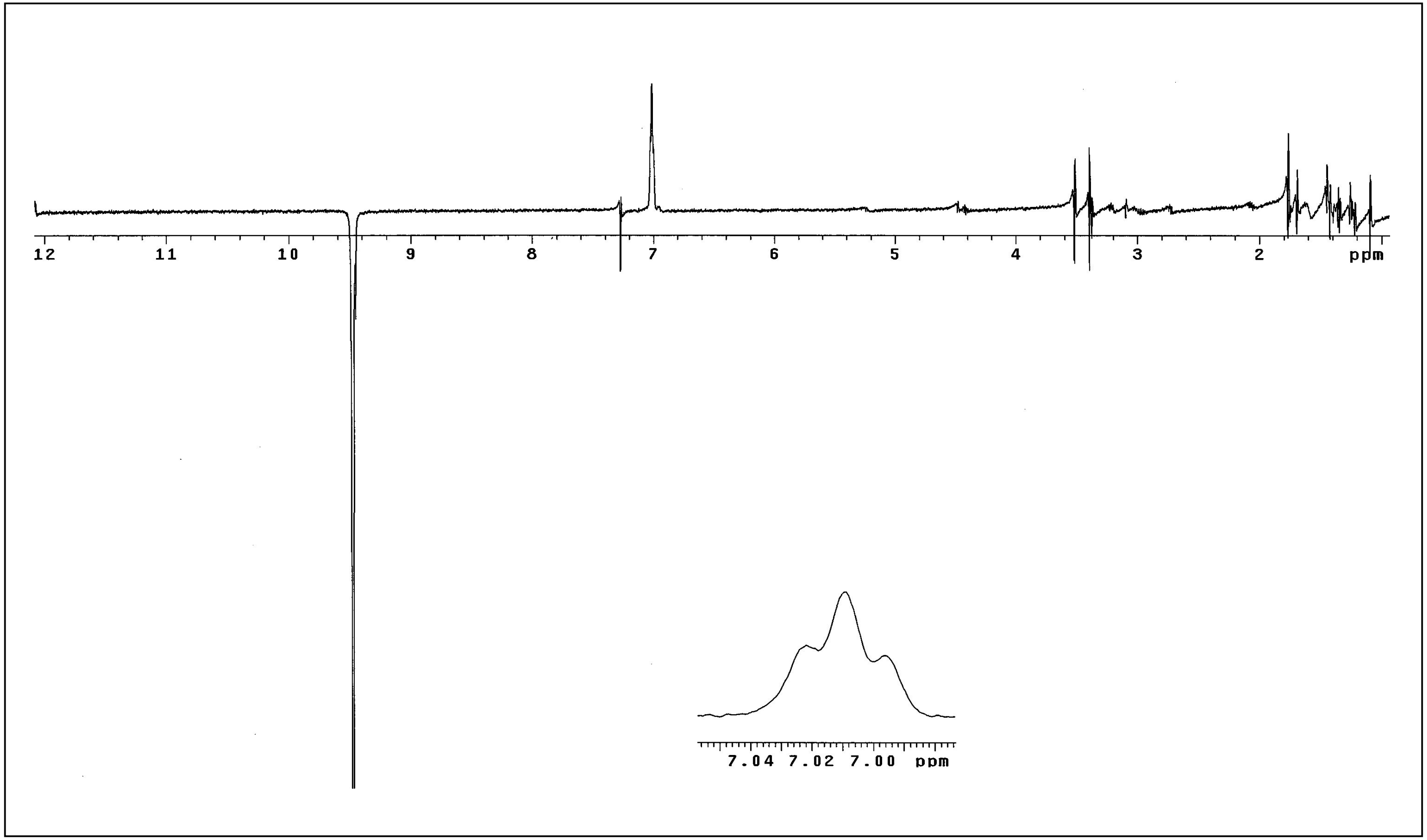


Figure 76 NOEDIFF spectrum of **GF9** after irradiation at δ_H 9.48

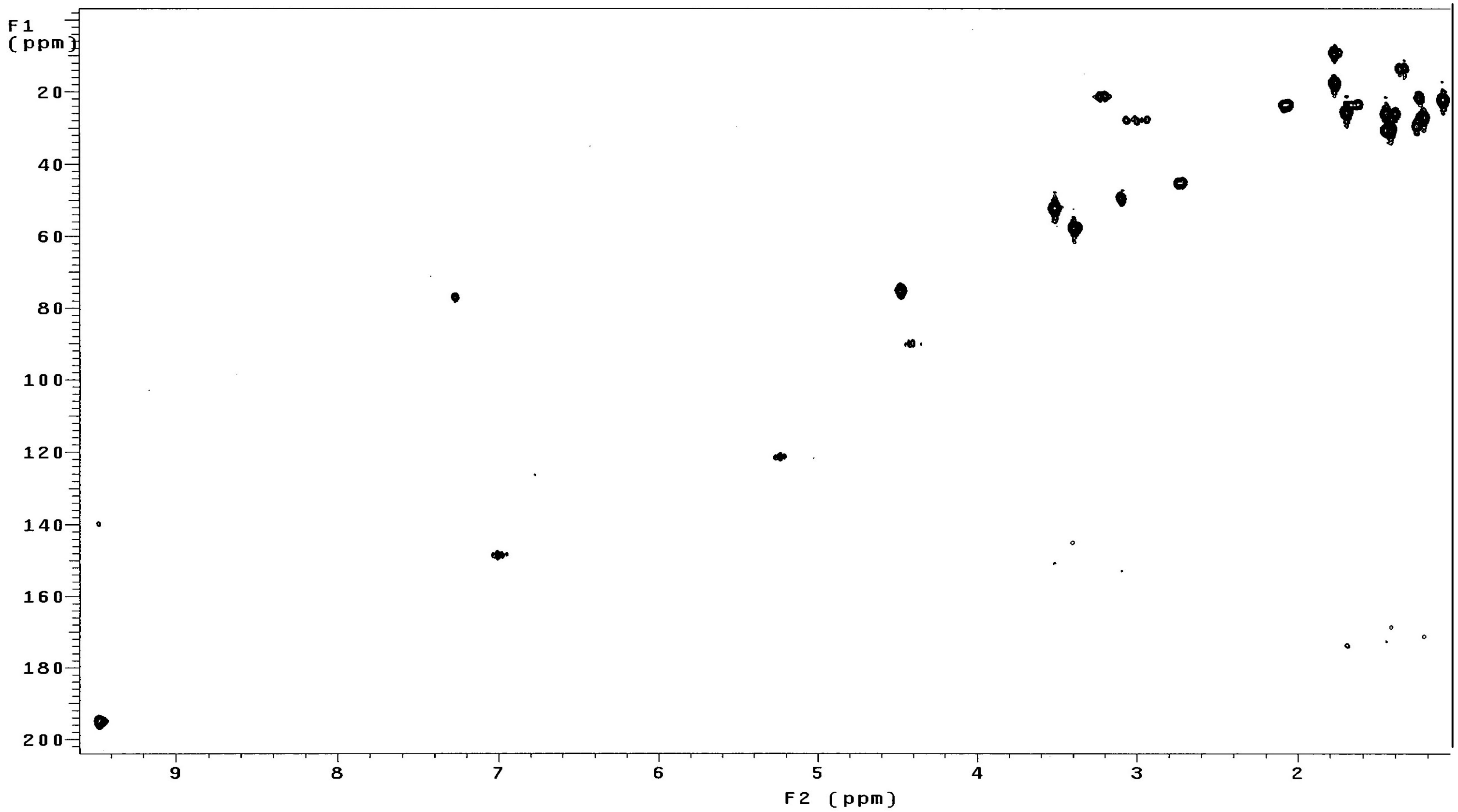


Figure 77 2D HMQC spectrum of **GF9**

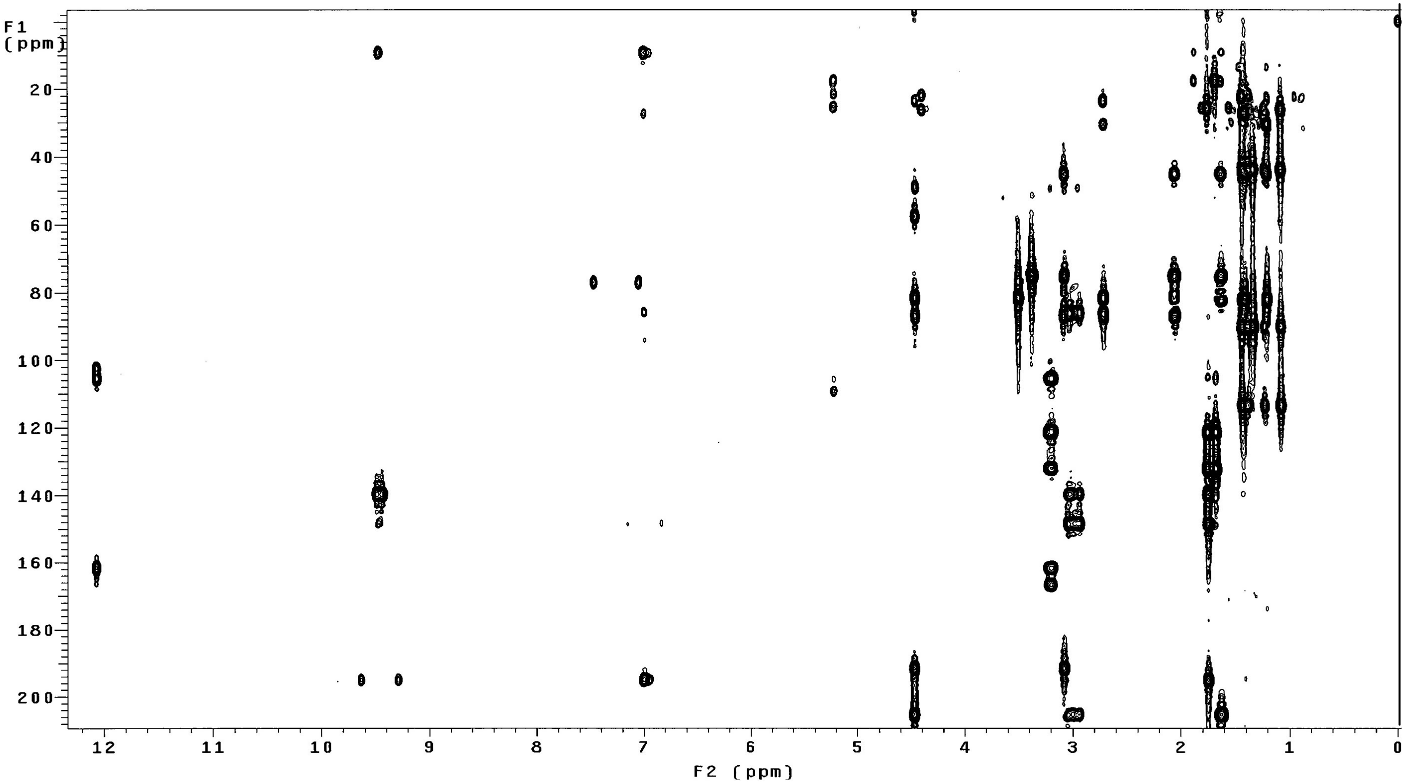


Figure 78 2D HMBC spectrum of **GF9**

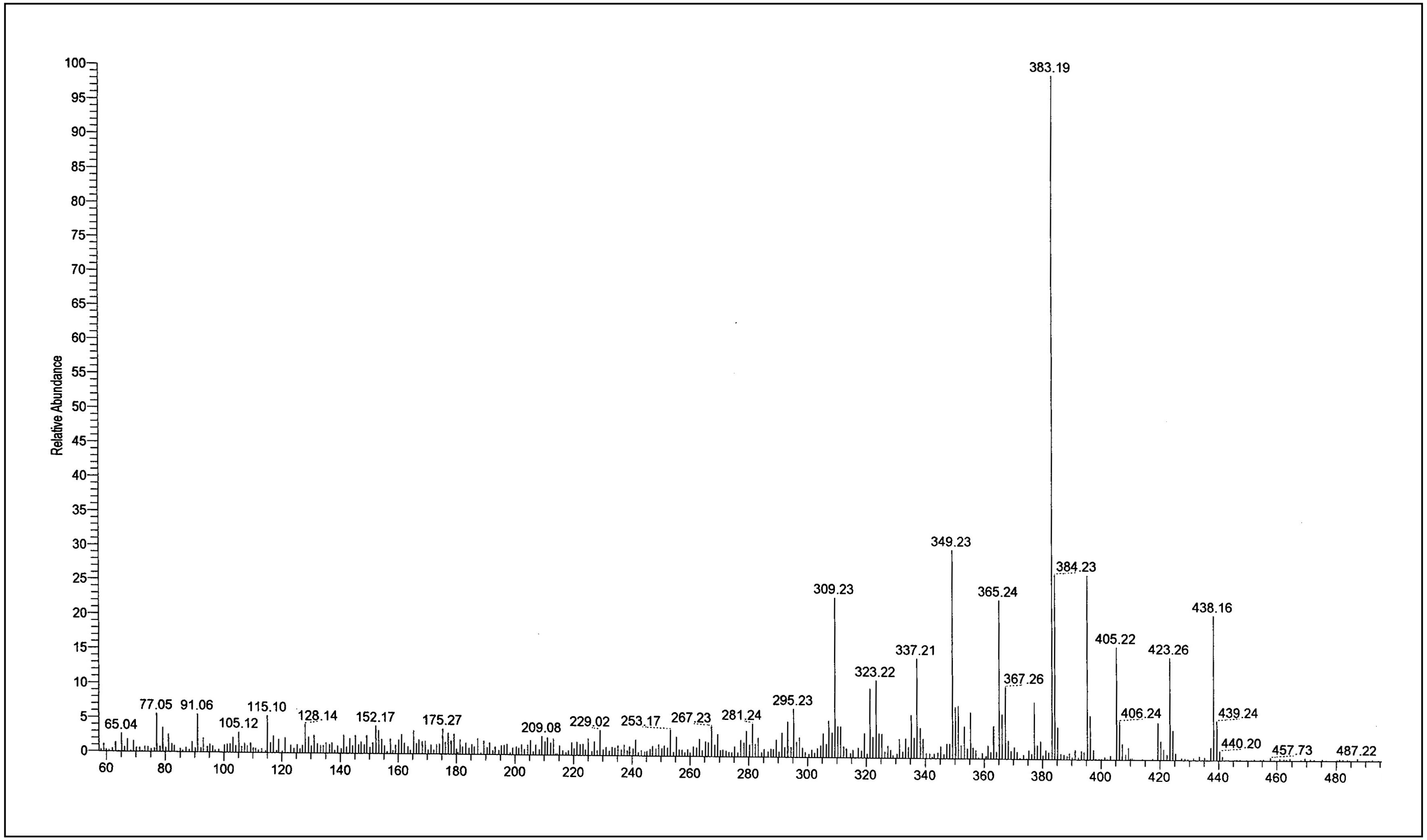


Figure 79 Mass spectrum of **GF19**

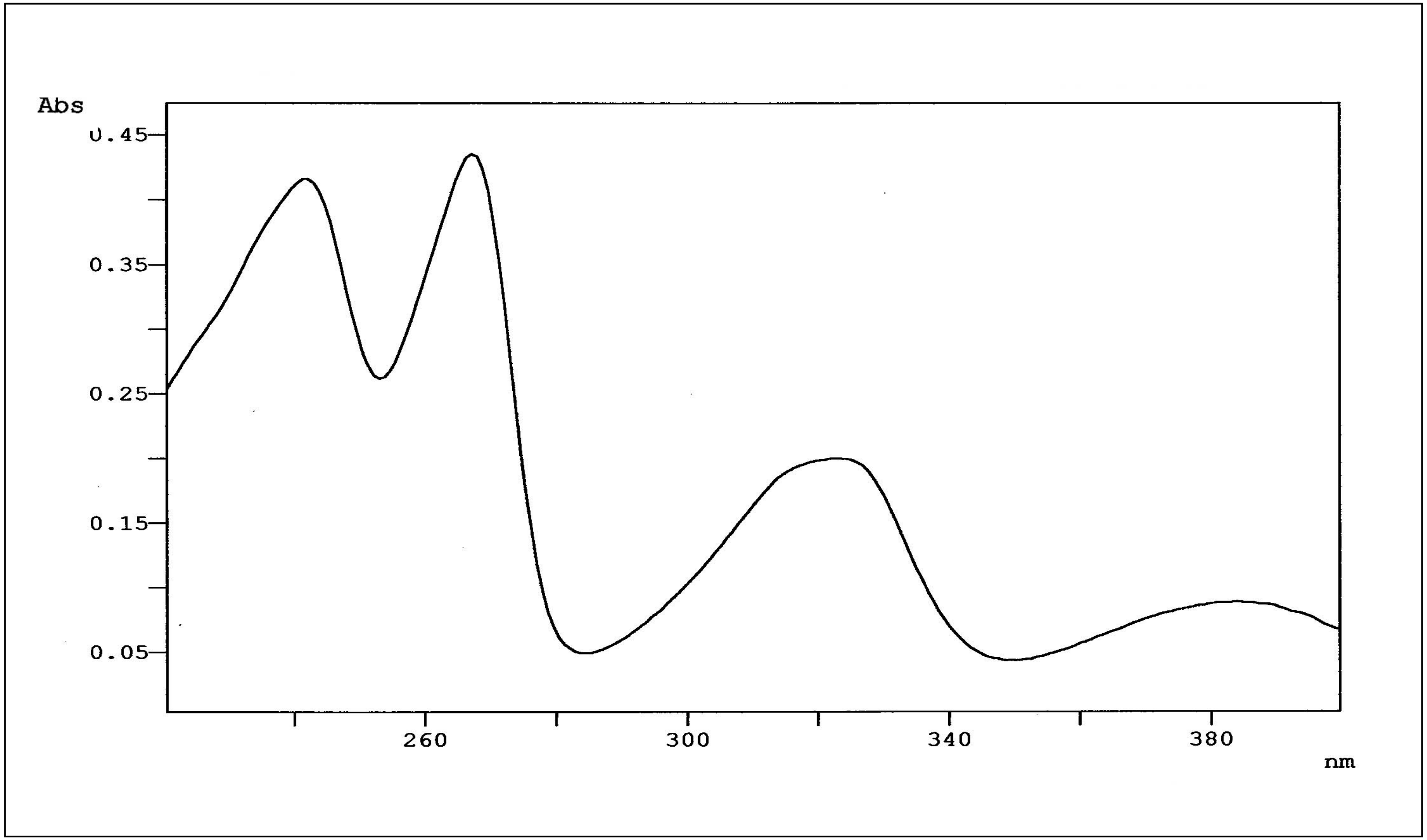


Figure 80 UV (CH_3OH) spectrum of **GF19**

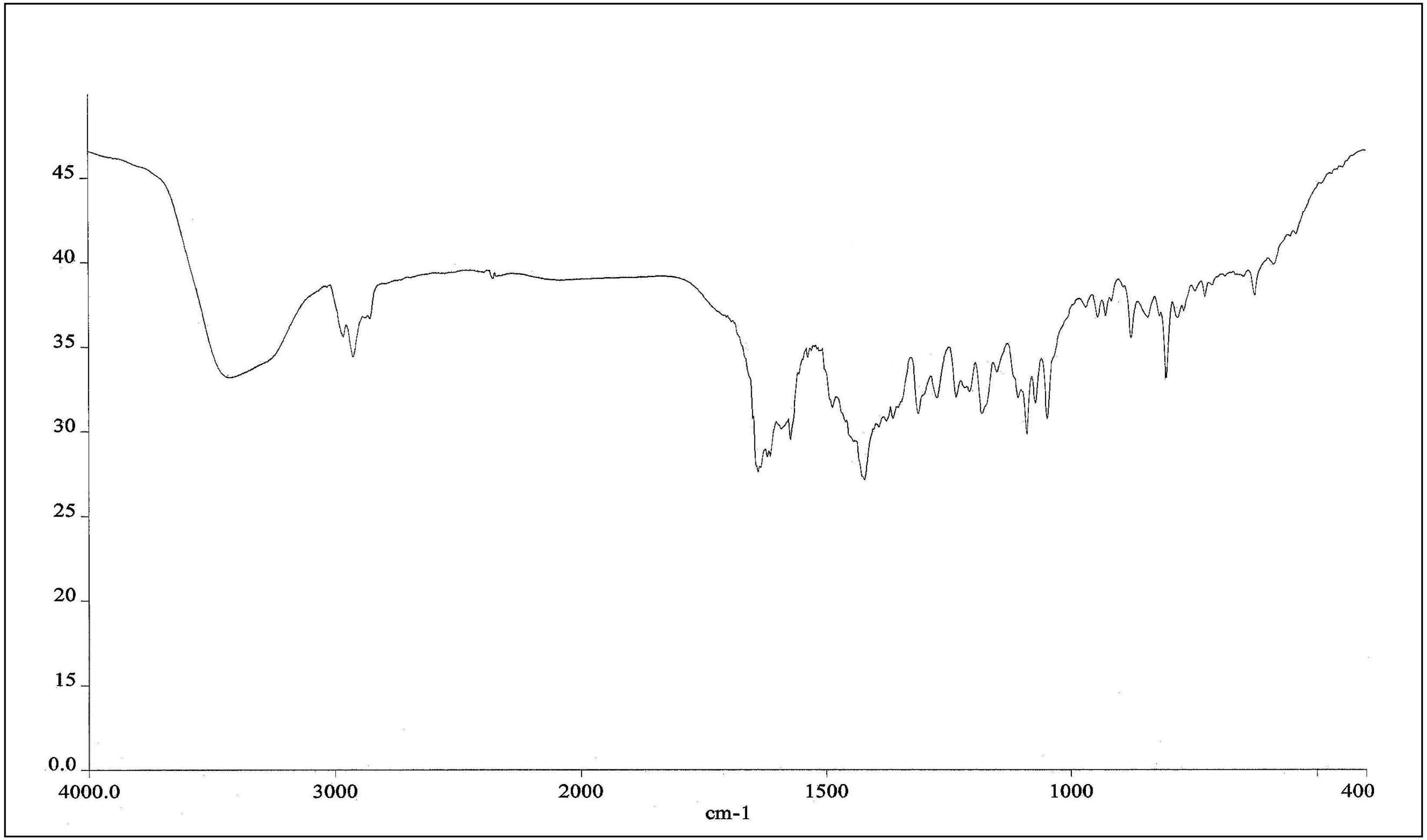


Figure 81 FT-IR (neat) spectrum of **GF19**

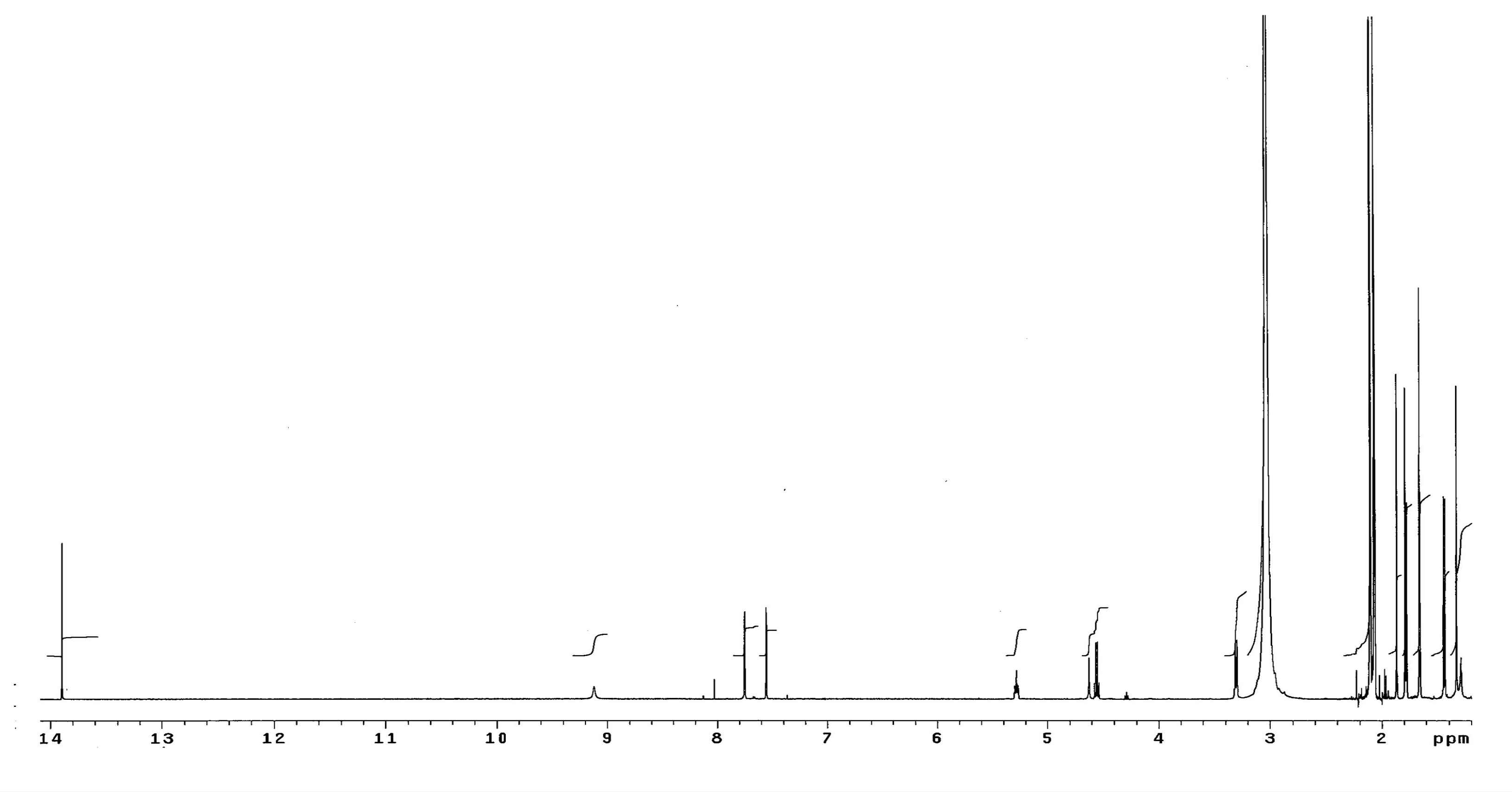


Figure 82 ^{1}H NMR (500 MHz) (Acetone-d_6) spectrum of **GF19**

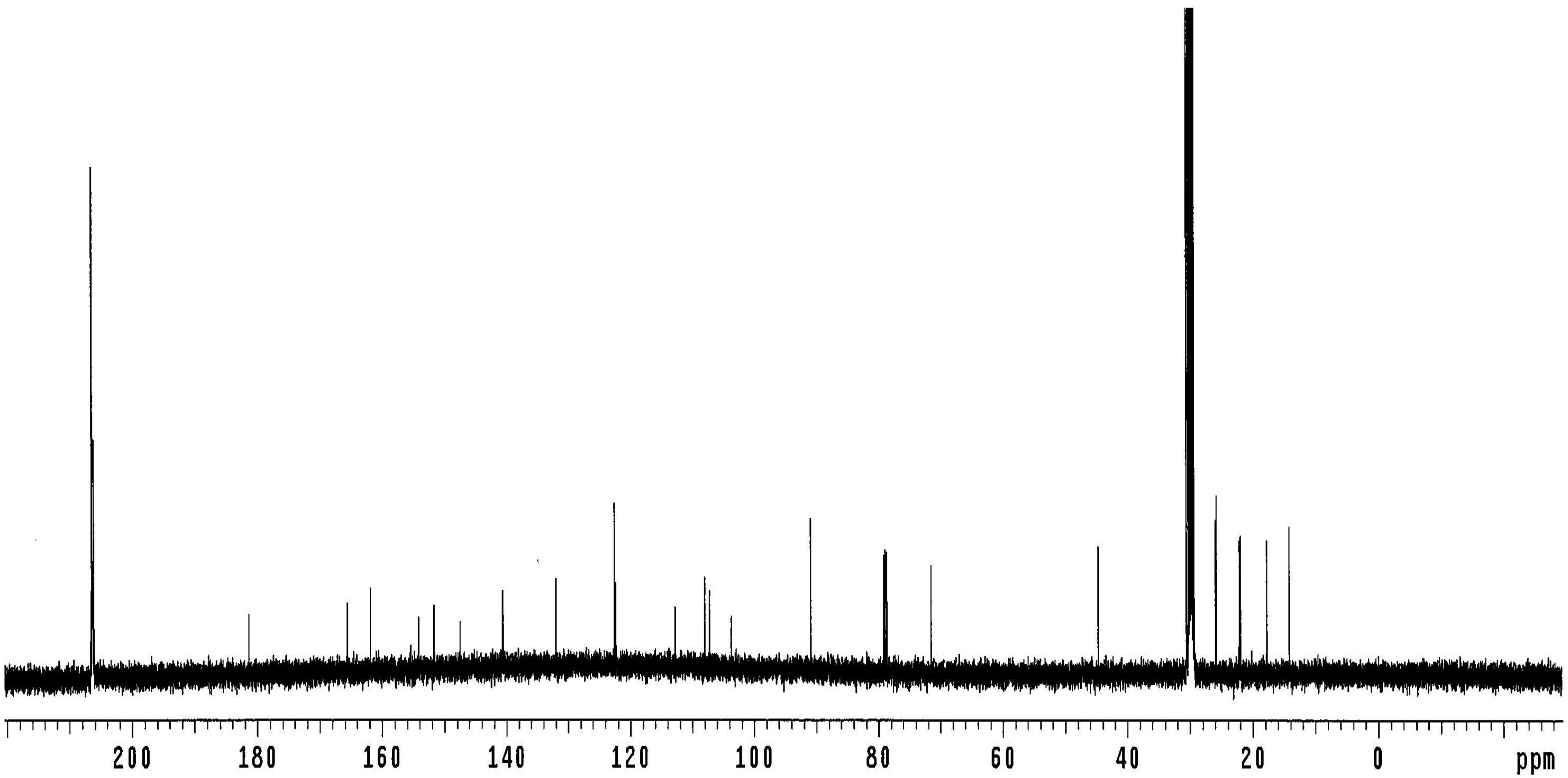


Figure 83 ^{13}C NMR (125 MHz) (Acetone-d_6) spectrum of **GF19**

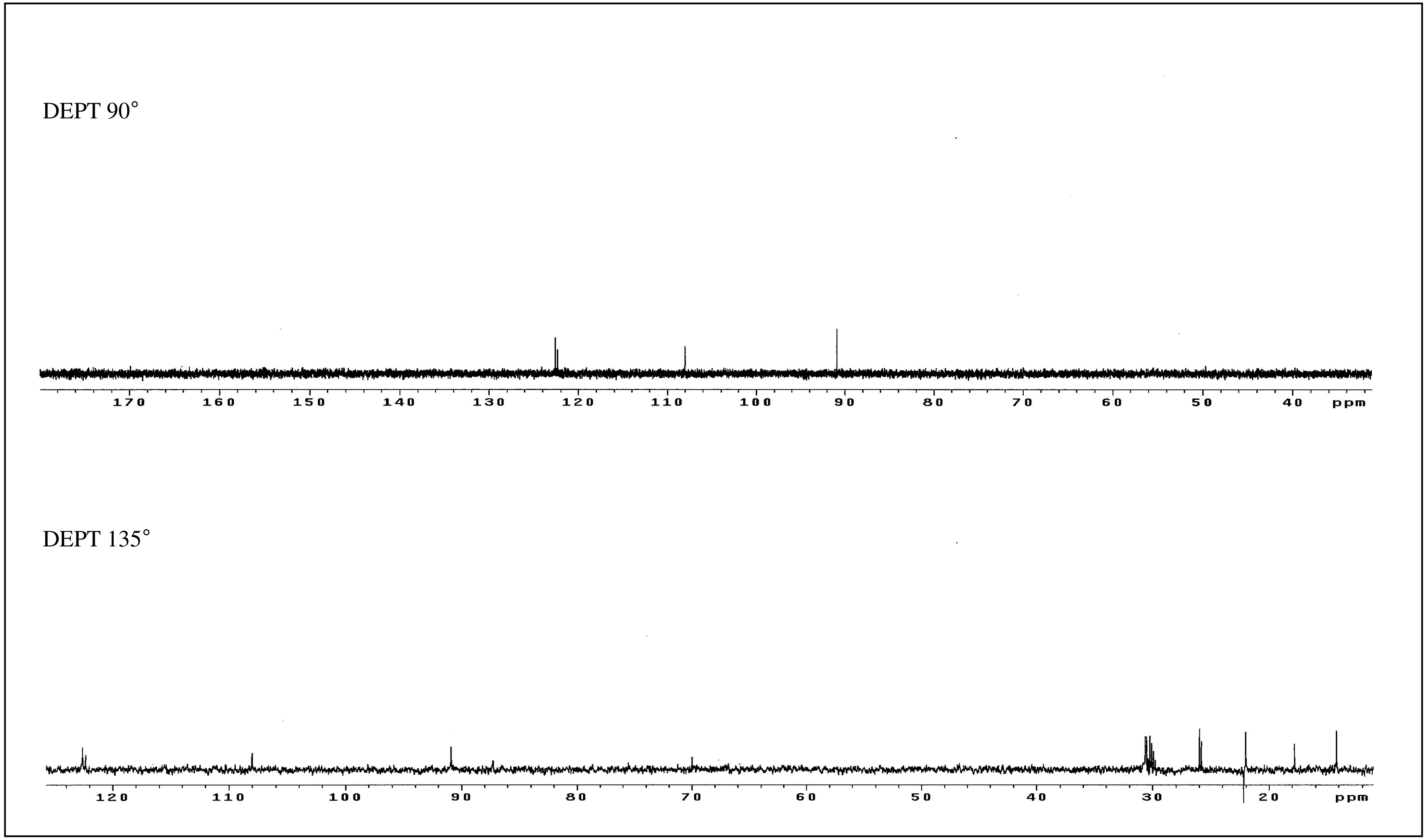


Figure 84 DEPT spectrum of **GF19**

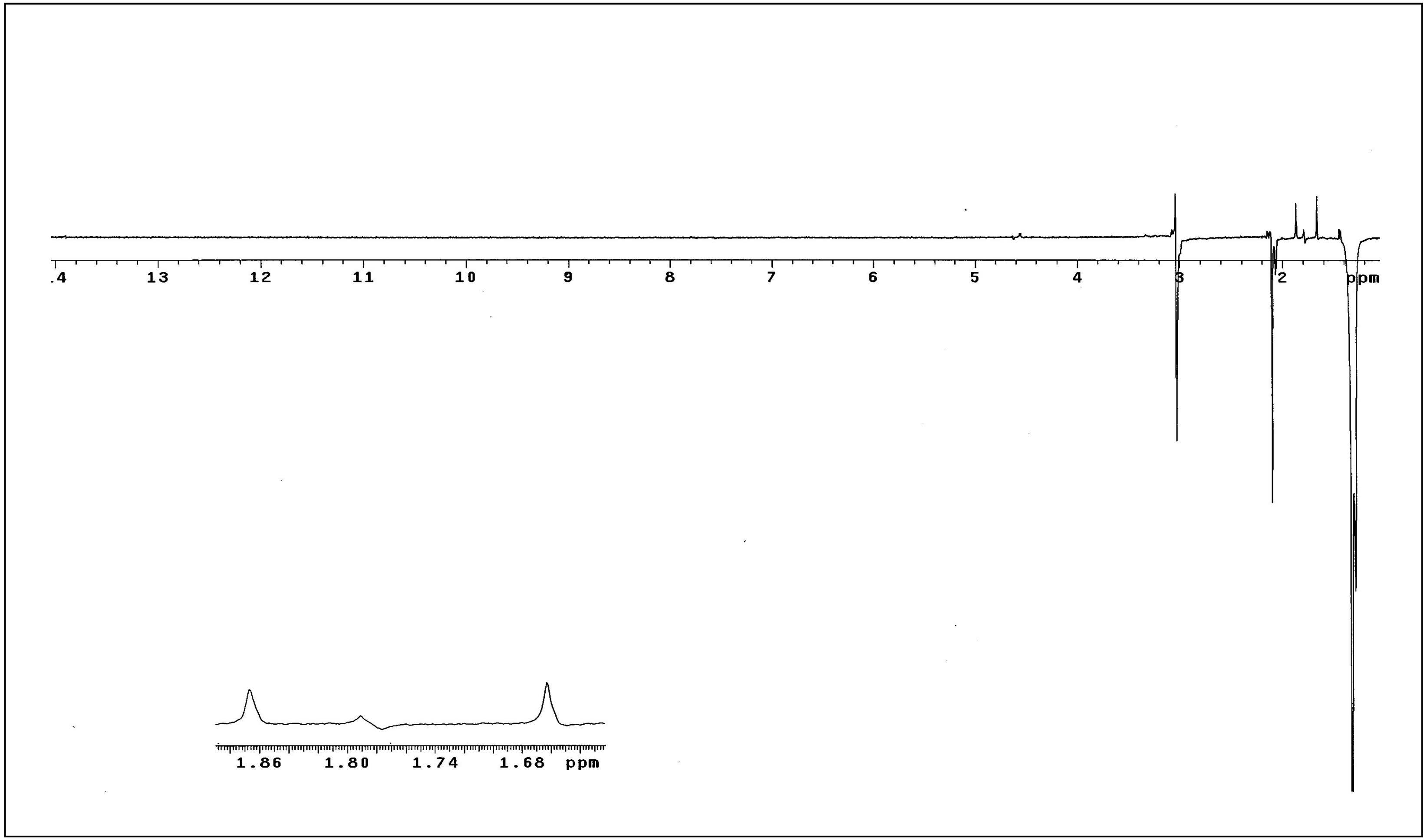


Figure 85 NOEDIFF spectrum of **GF19** after irradiation at δ_H 1.33

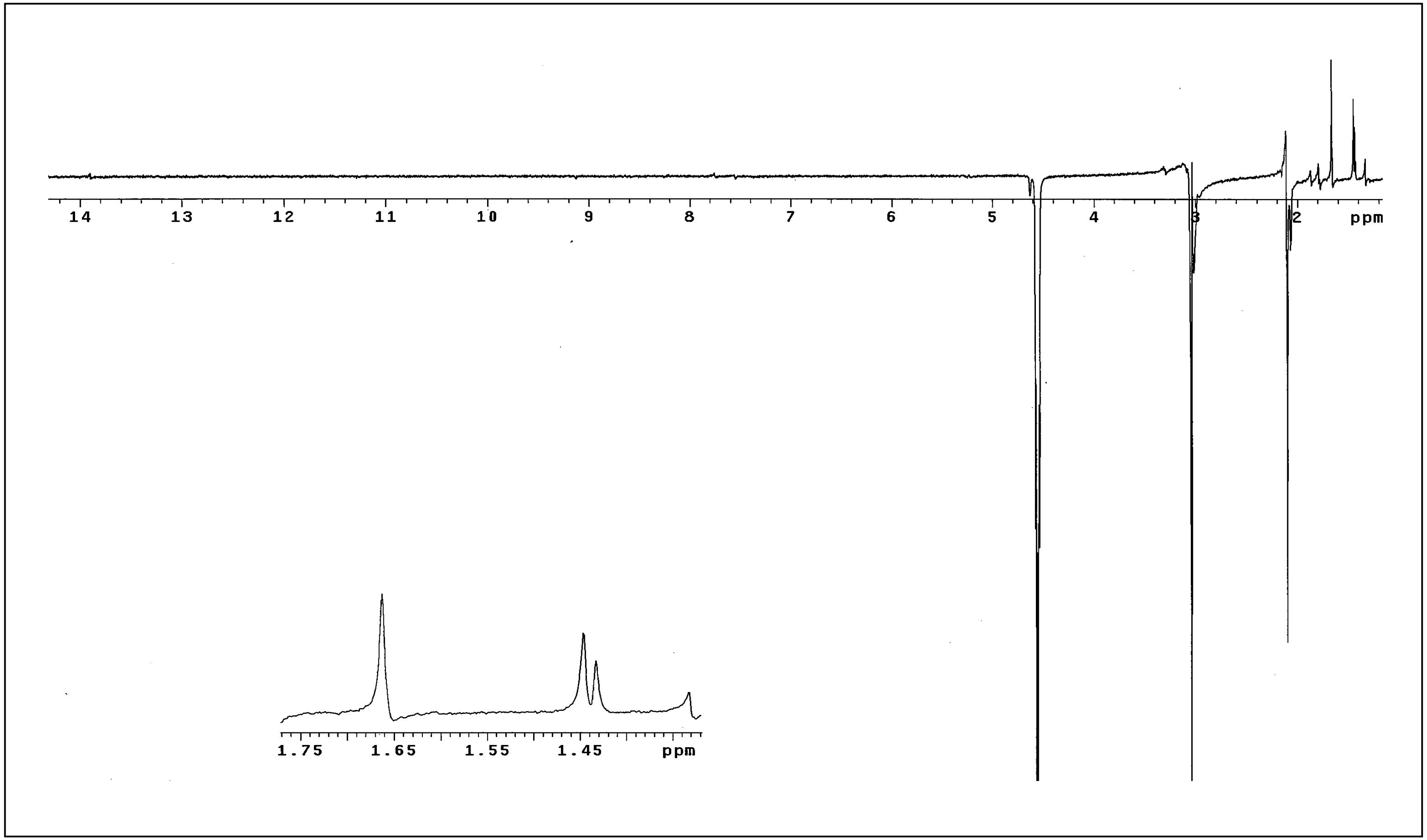


Figure 86 NOEDIFF spectrum of **GF19** after irradiation at δ_H 4.55

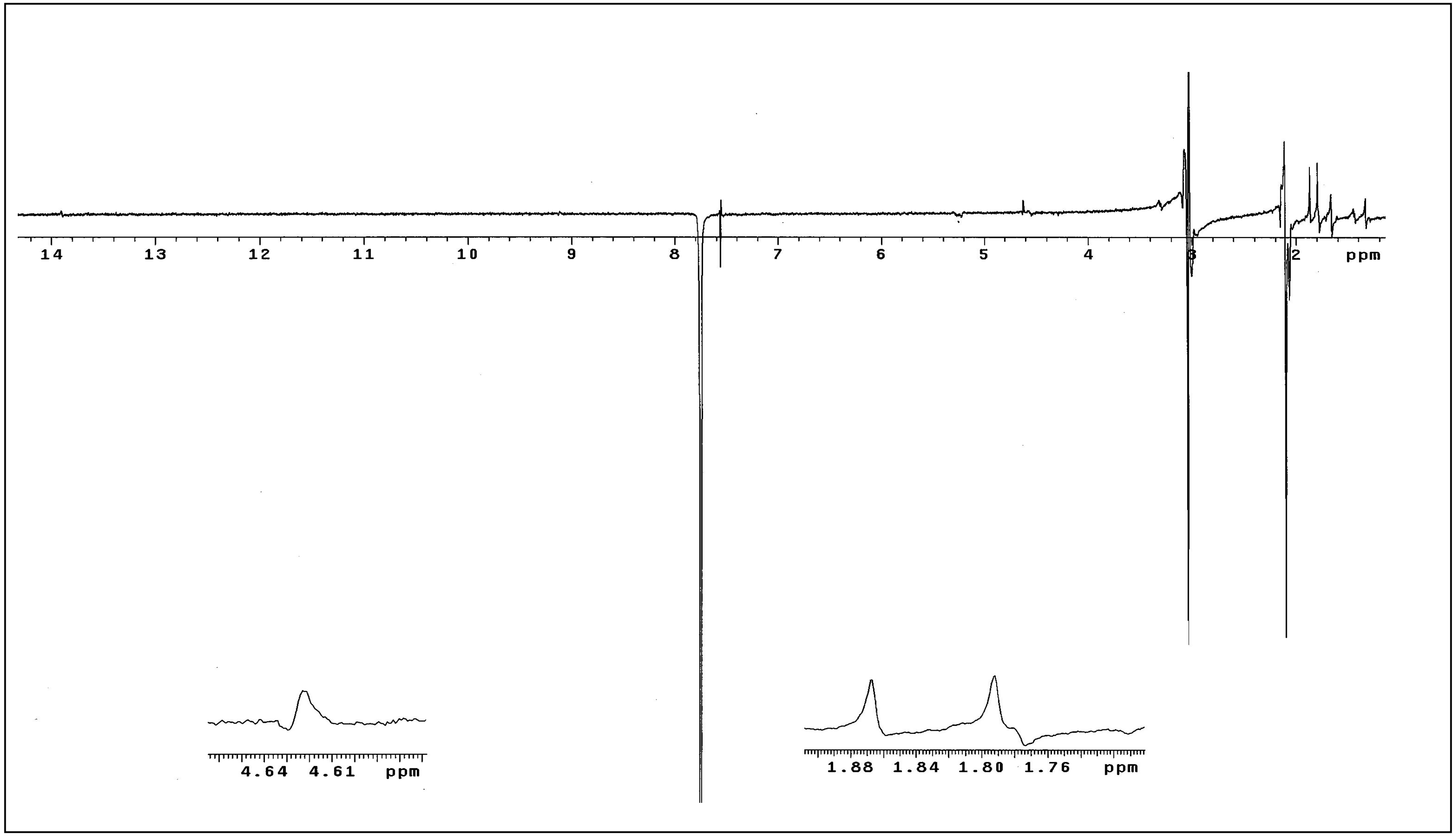


Figure 87 NOEDIFF spectrum of **GF19** after irradiation at δ_H 7.75

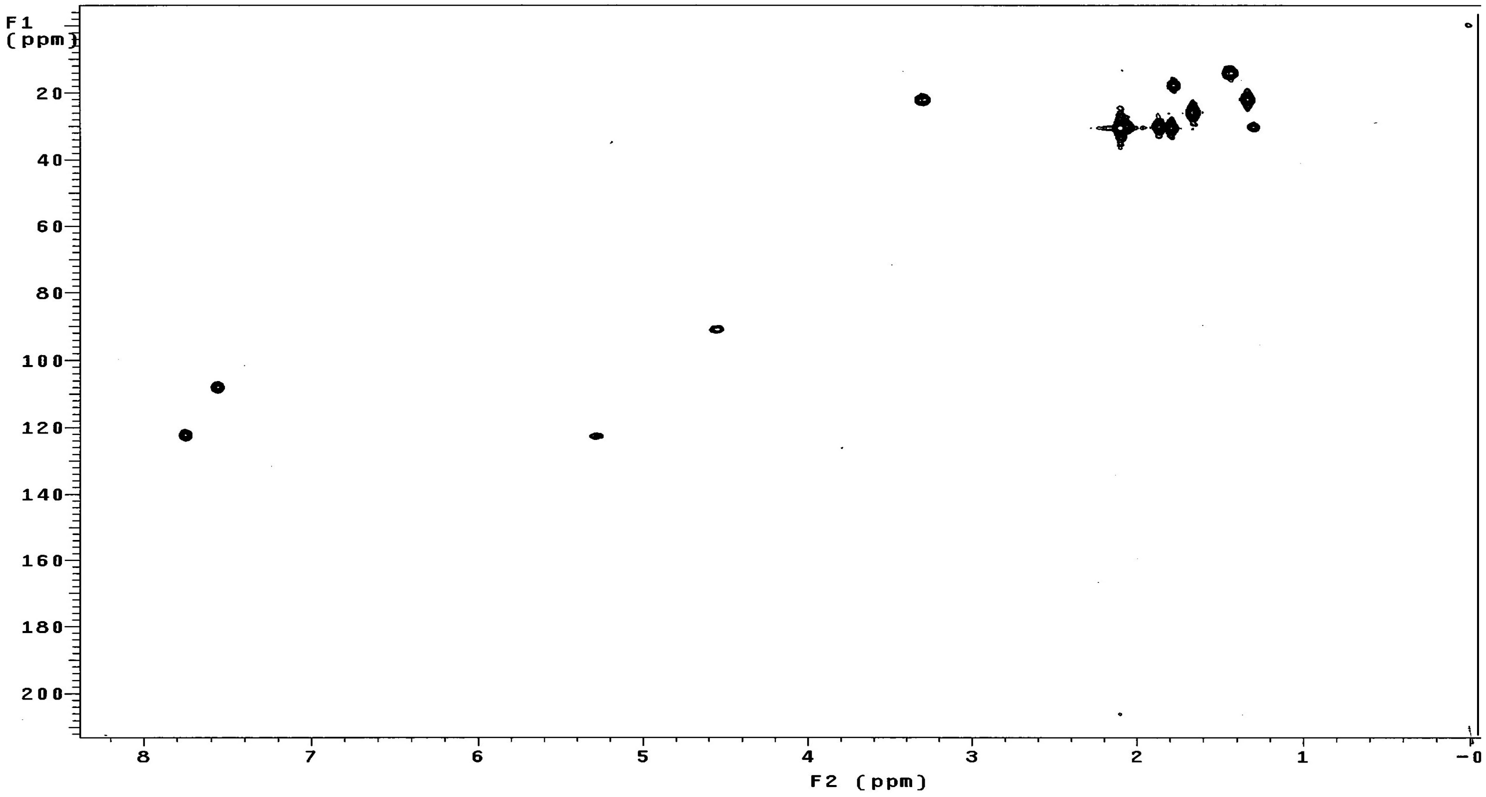


Figure 88 2D HMQC spectrum of **GF19**

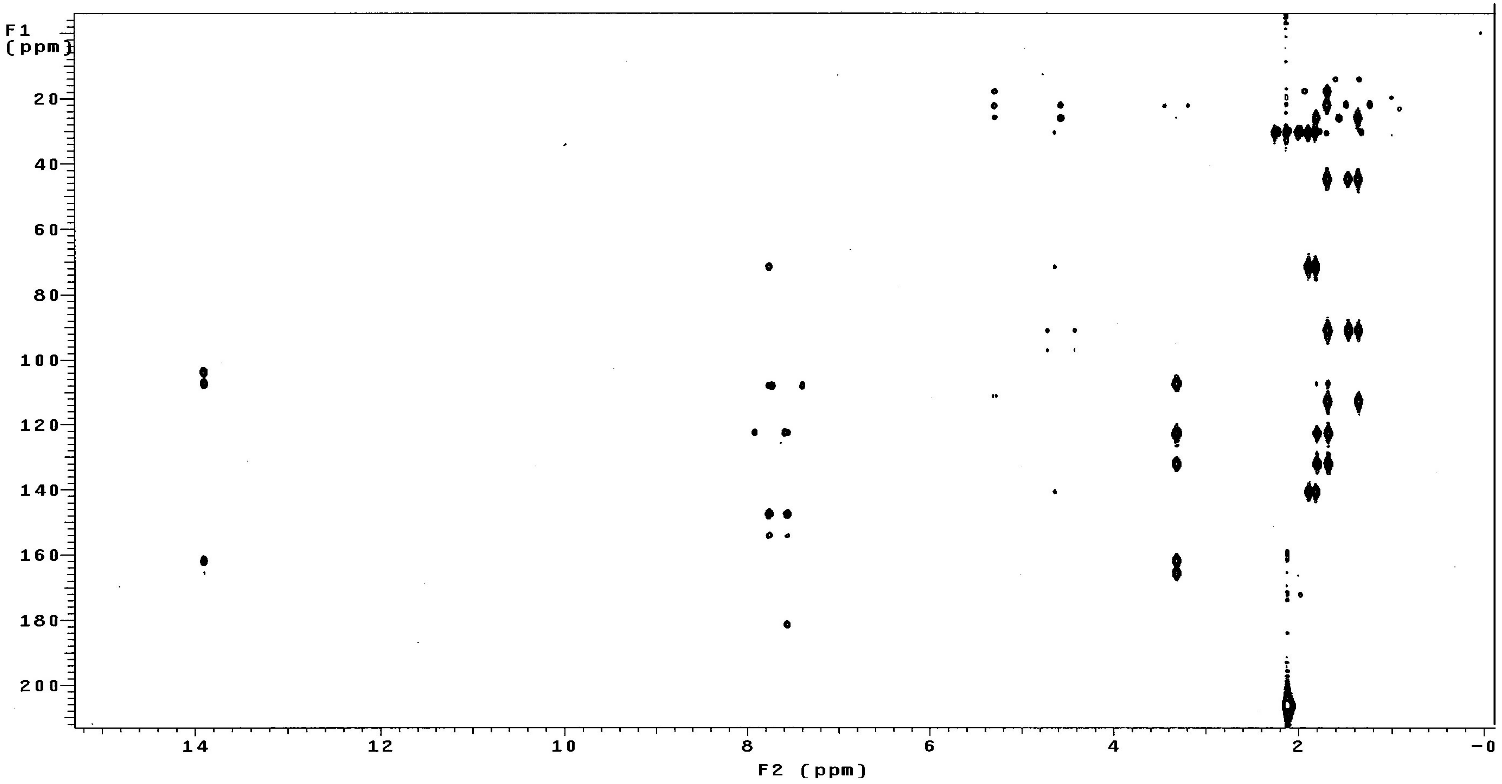


Figure 89 2D HMBC spectrum of **GF19**

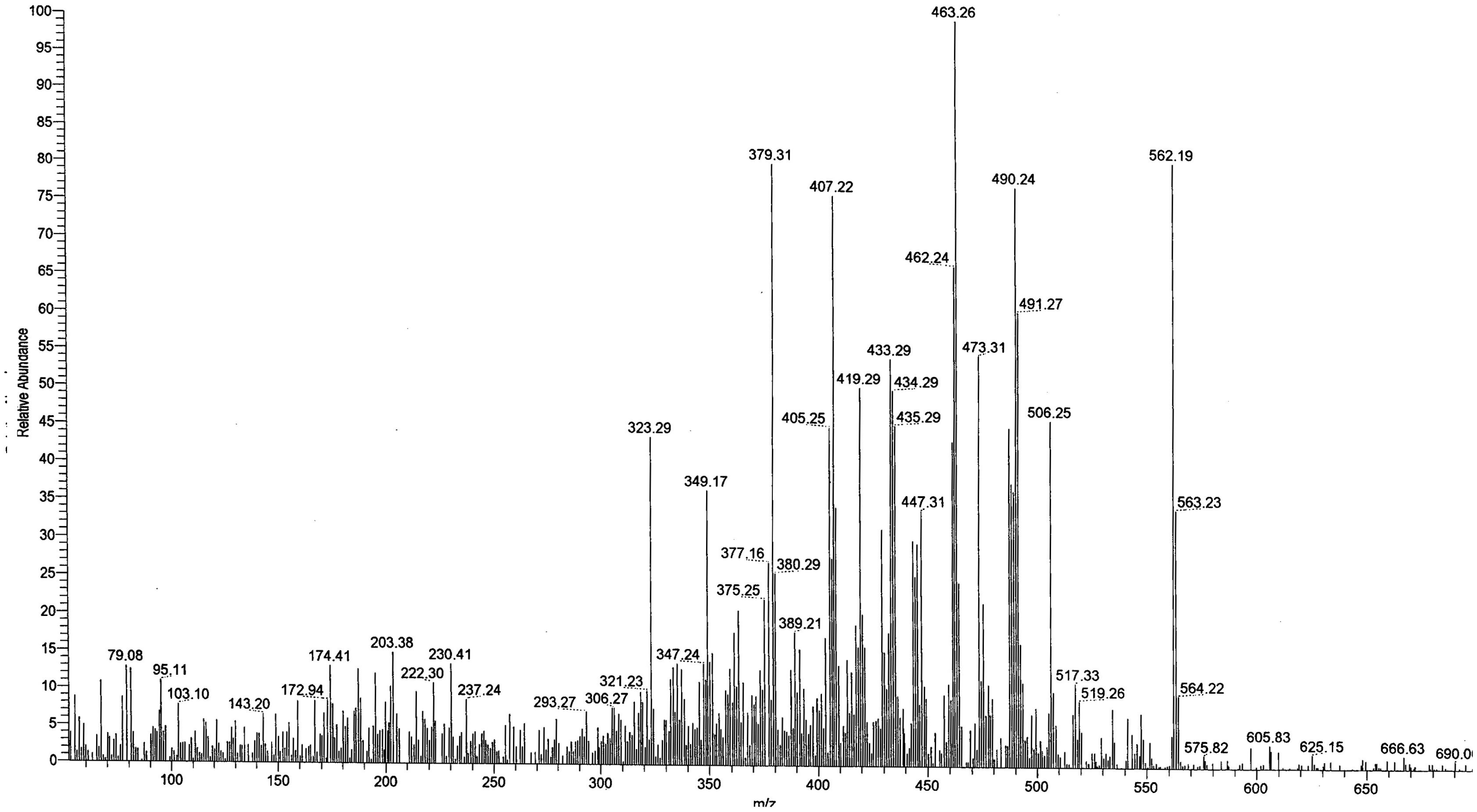


Figure 90 Mass spectrum of **GF21**

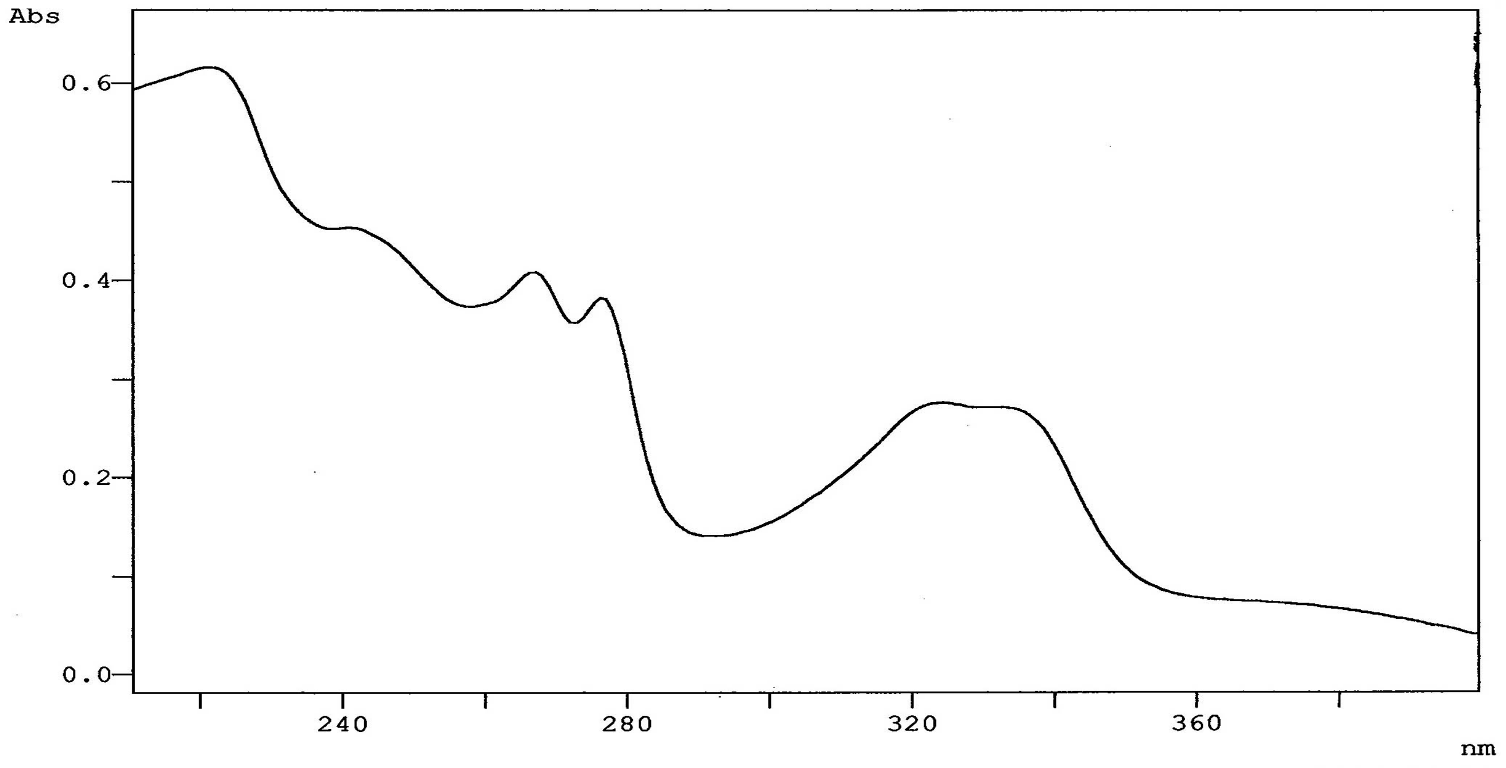


Figure 91 UV (CH_3OH) spectrum of **GF21**

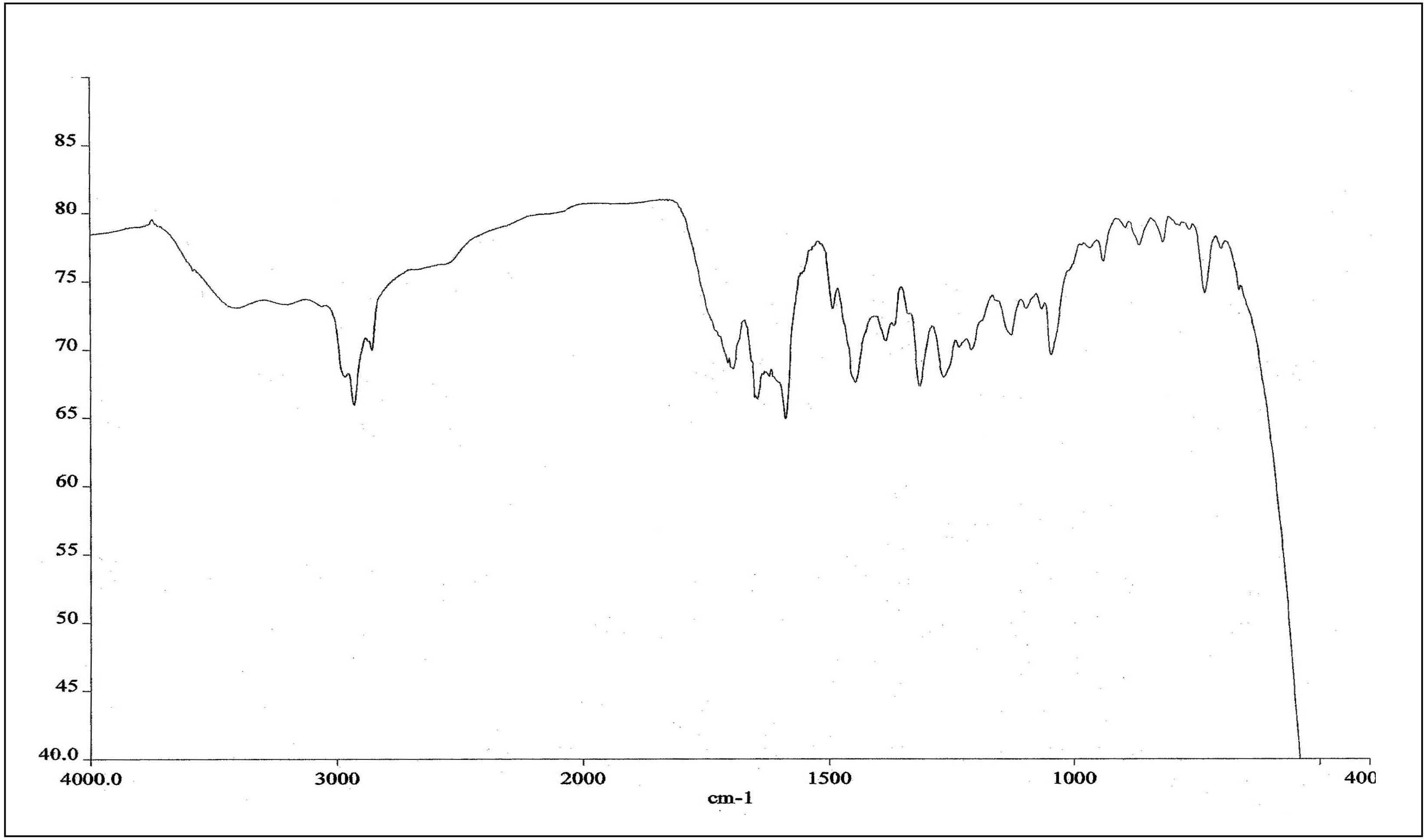


Figure 92 FT-IR (neat) spectrum of **GF21**

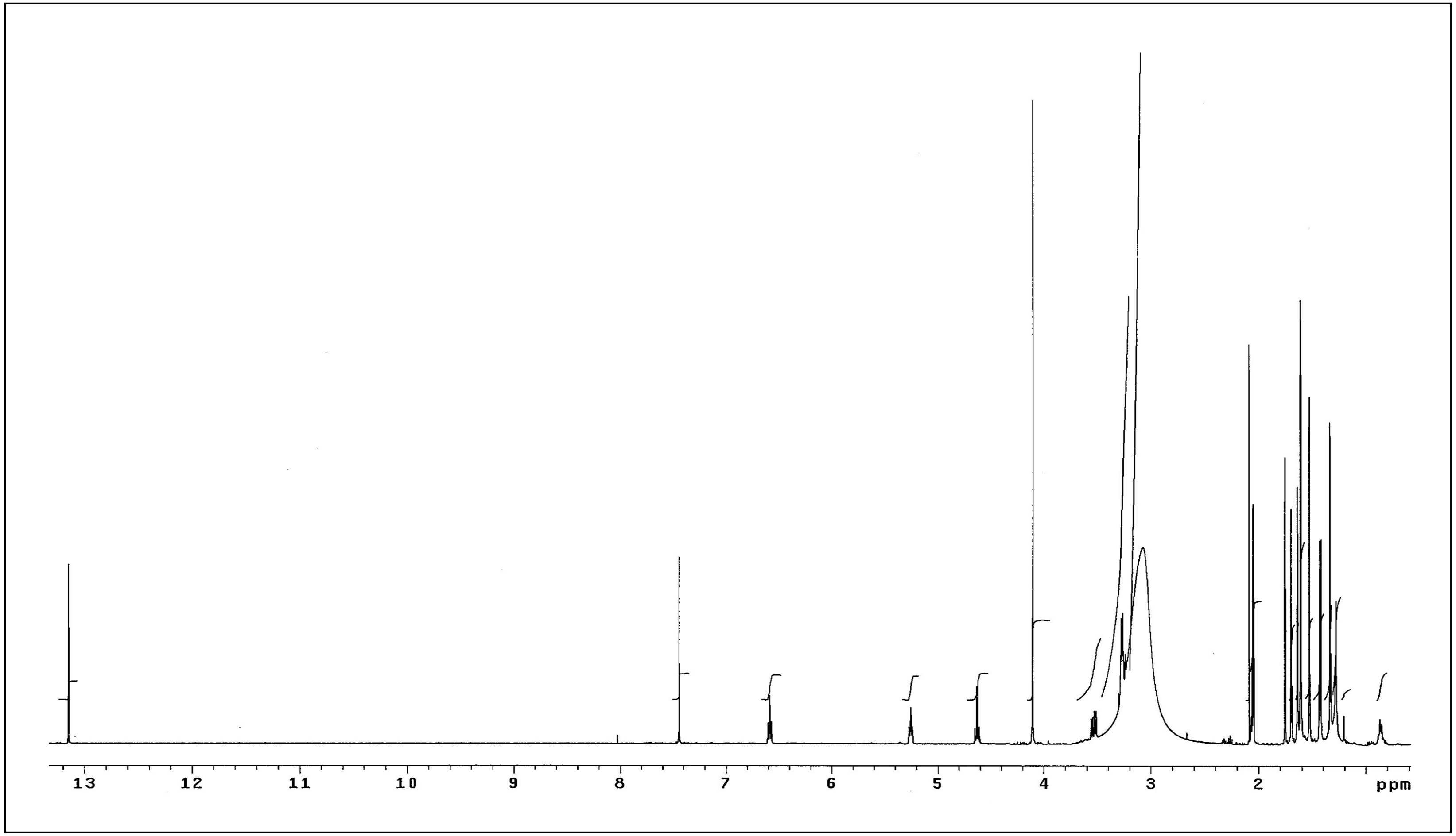


Figure 93 ^{1}H NMR (500 MHz) (Acetone-d_6) spectrum of **GF21**

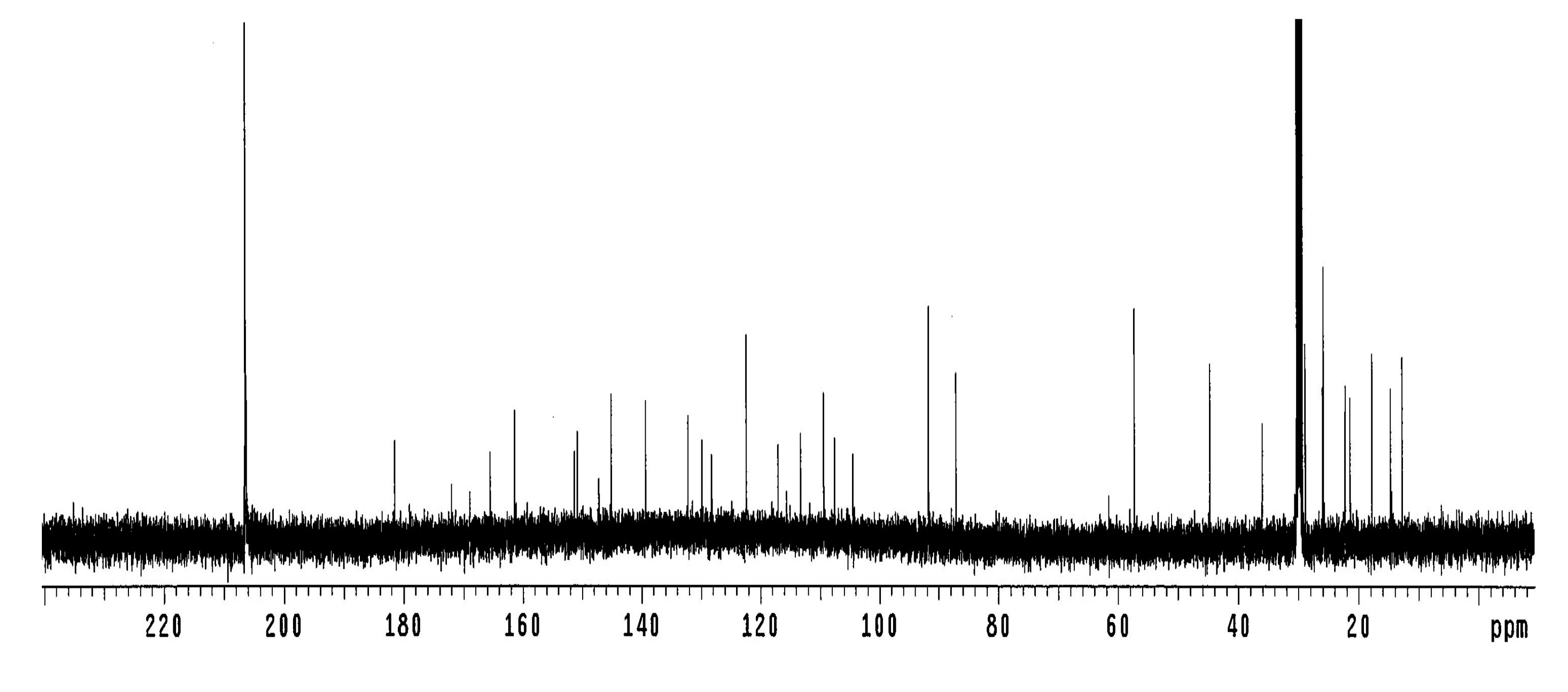


Figure 94 ^{13}C NMR (125 MHz) (Acetone-d_6) spectrum of **GF21**

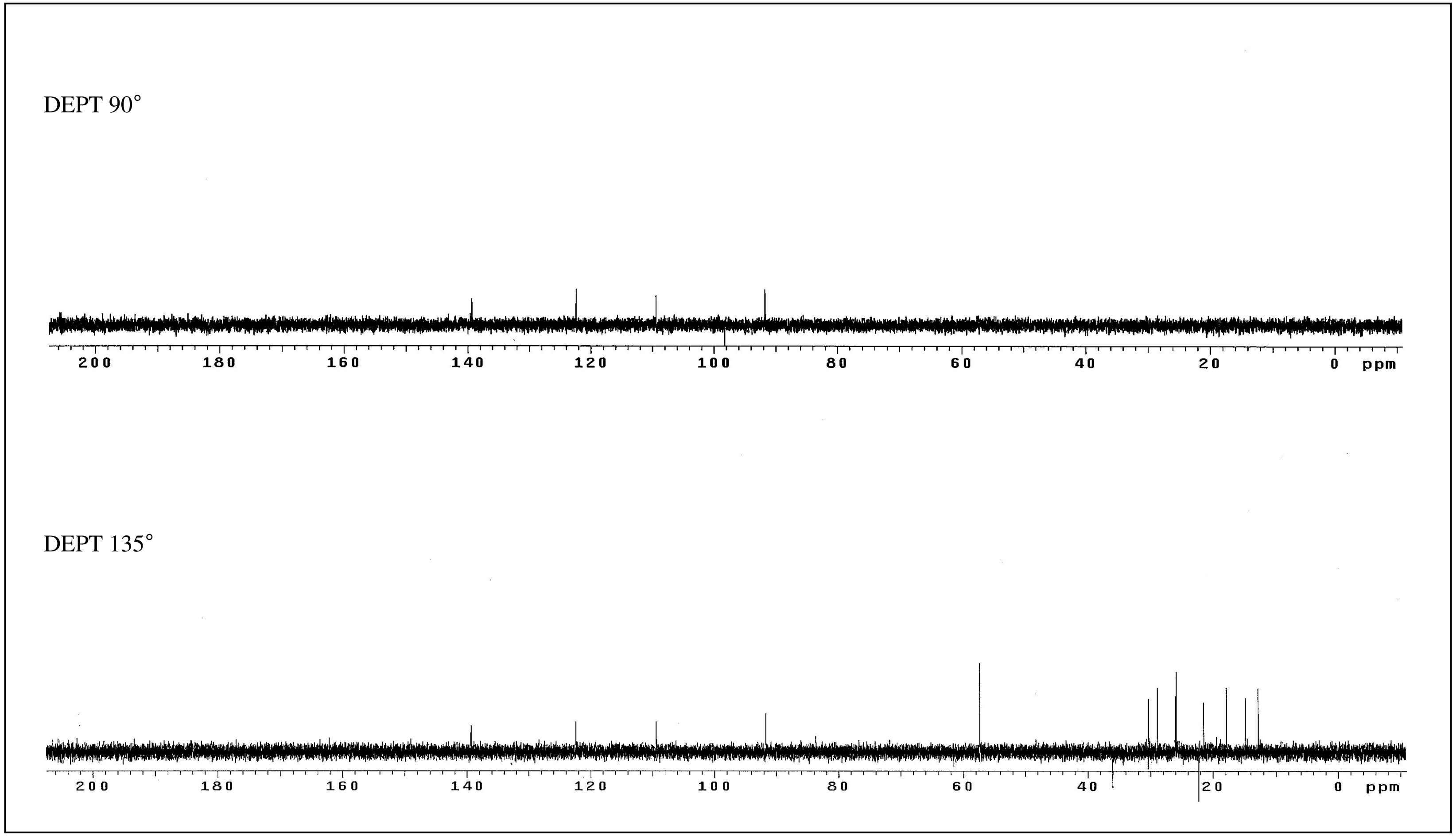


Figure 95 DEPT spectrum of **GF21**

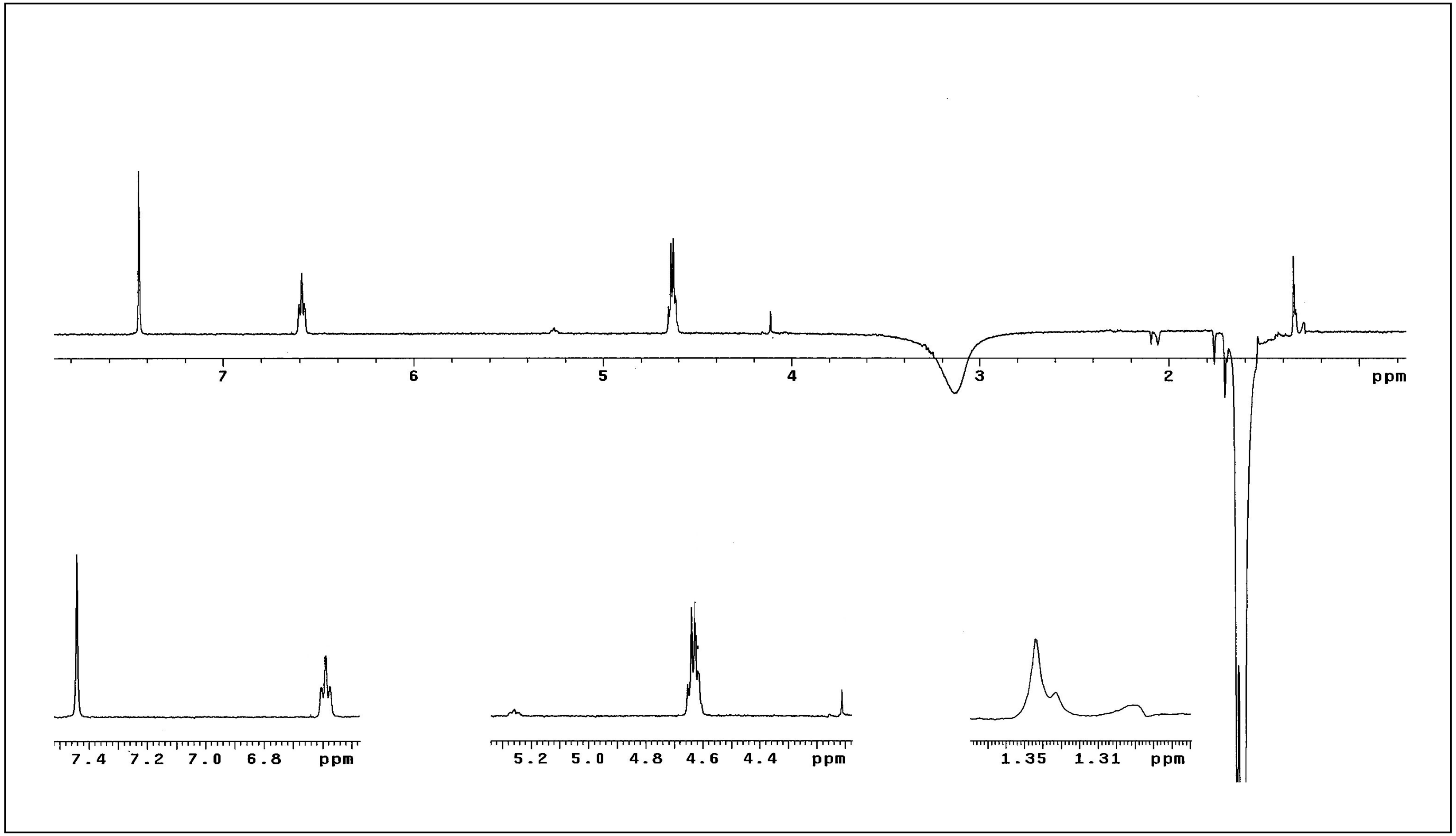


Figure 96 NOEDIFF spectrum of **GF21** after irradiation at δ_H 1.61

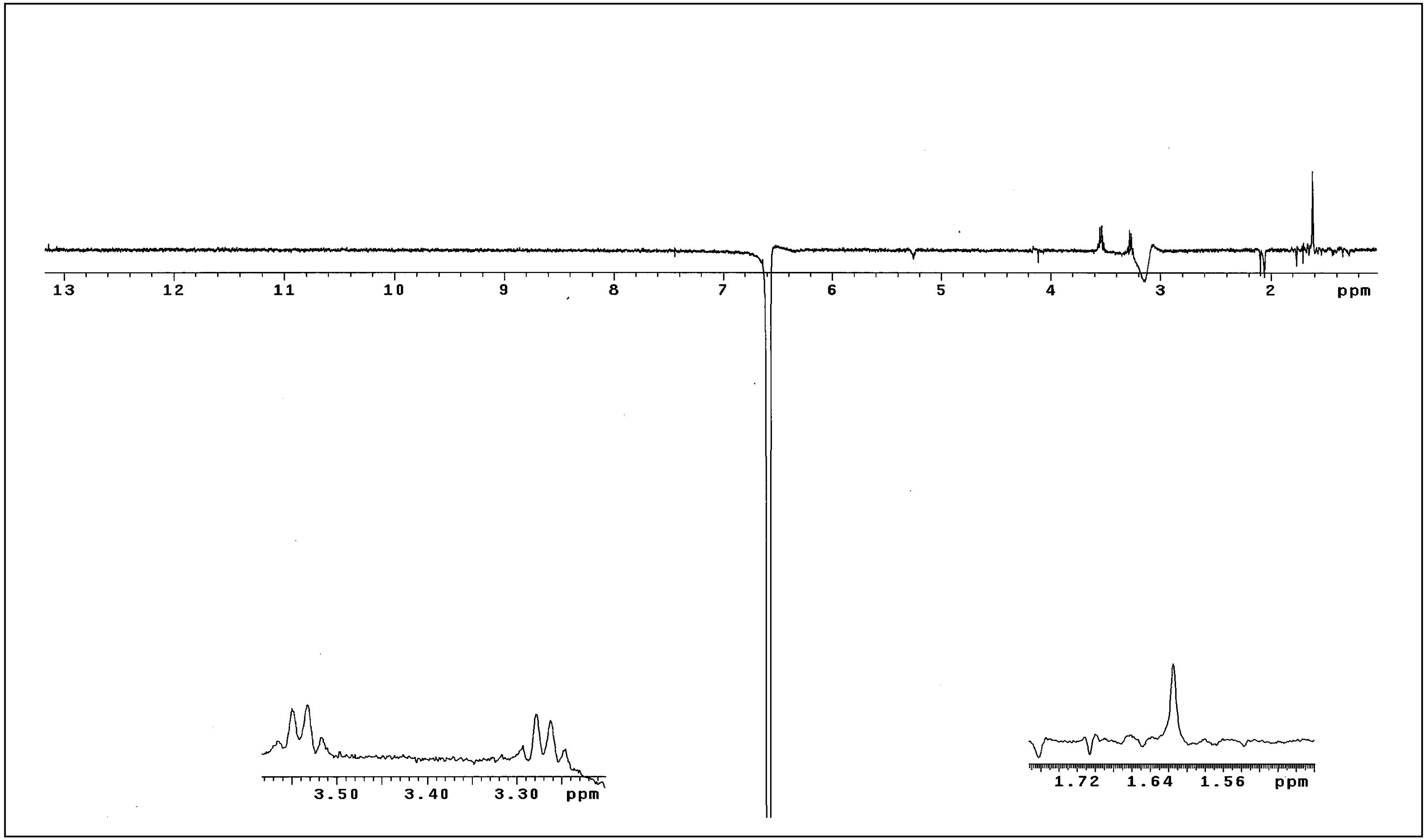


Figure 97 NOEDIFF spectrum of **GF21** after irradiation at δ_H 6.59

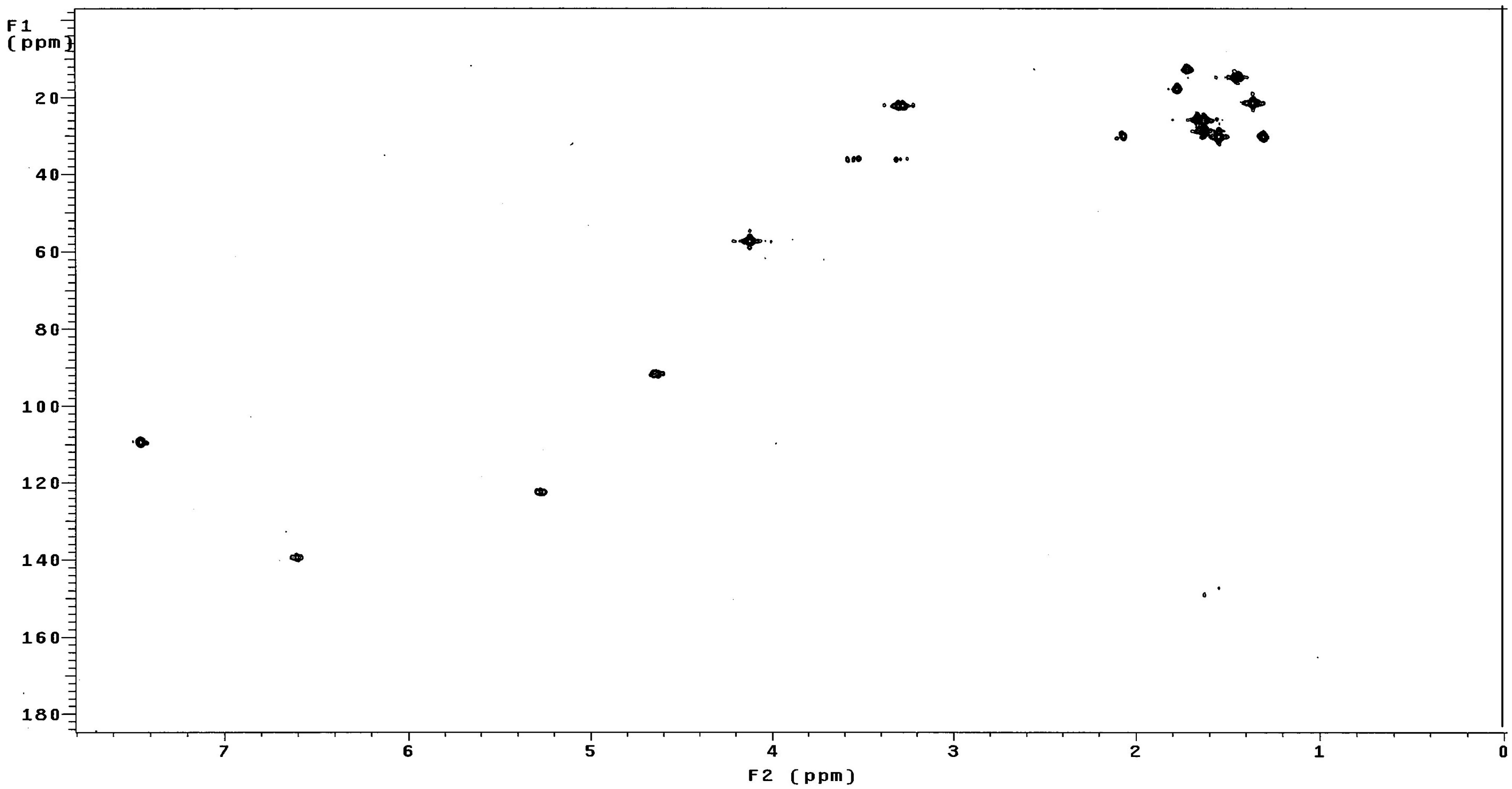


Figure 98 2D HMQC spectrum of **GF21**

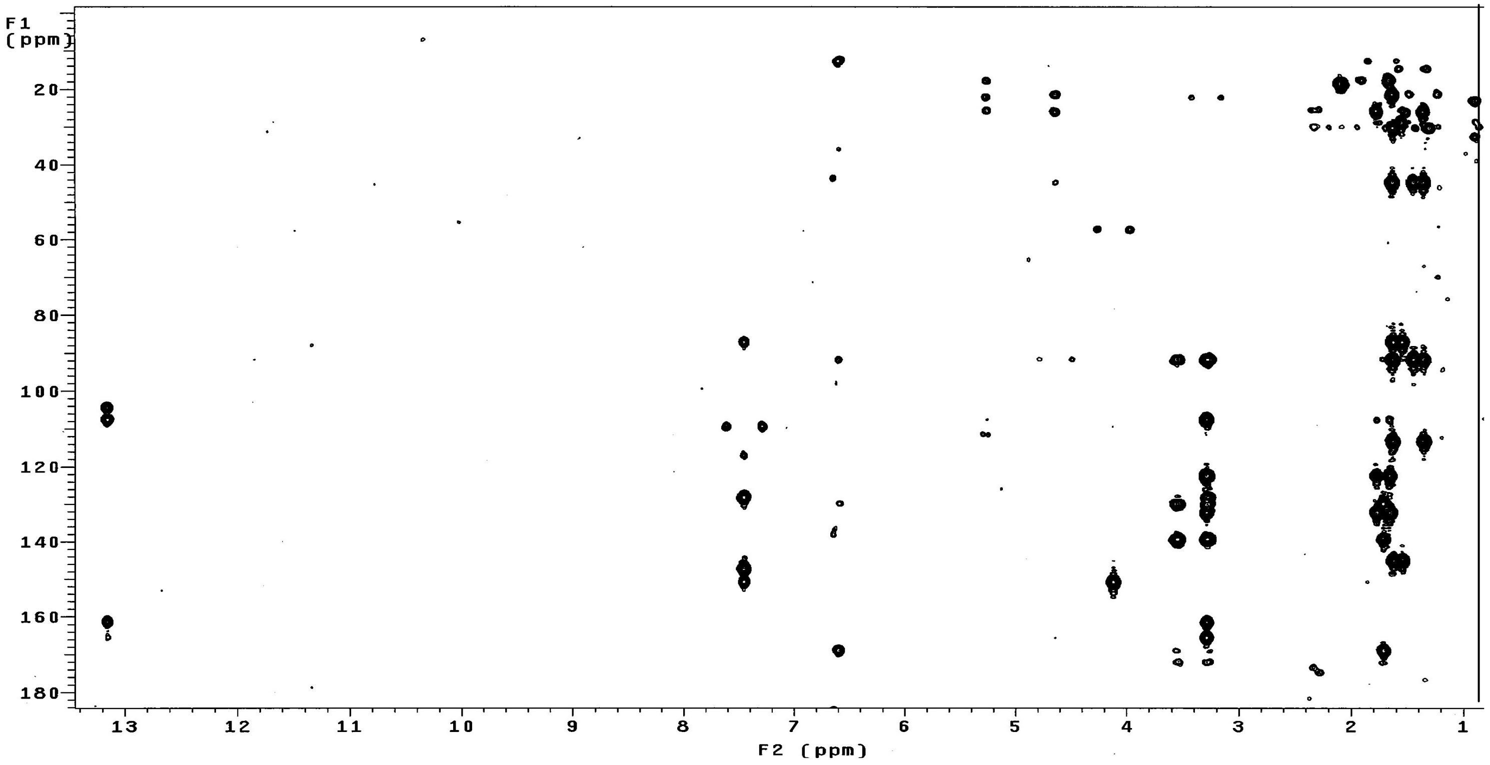


Figure 99 2D HMBC spectrum of **GF21**

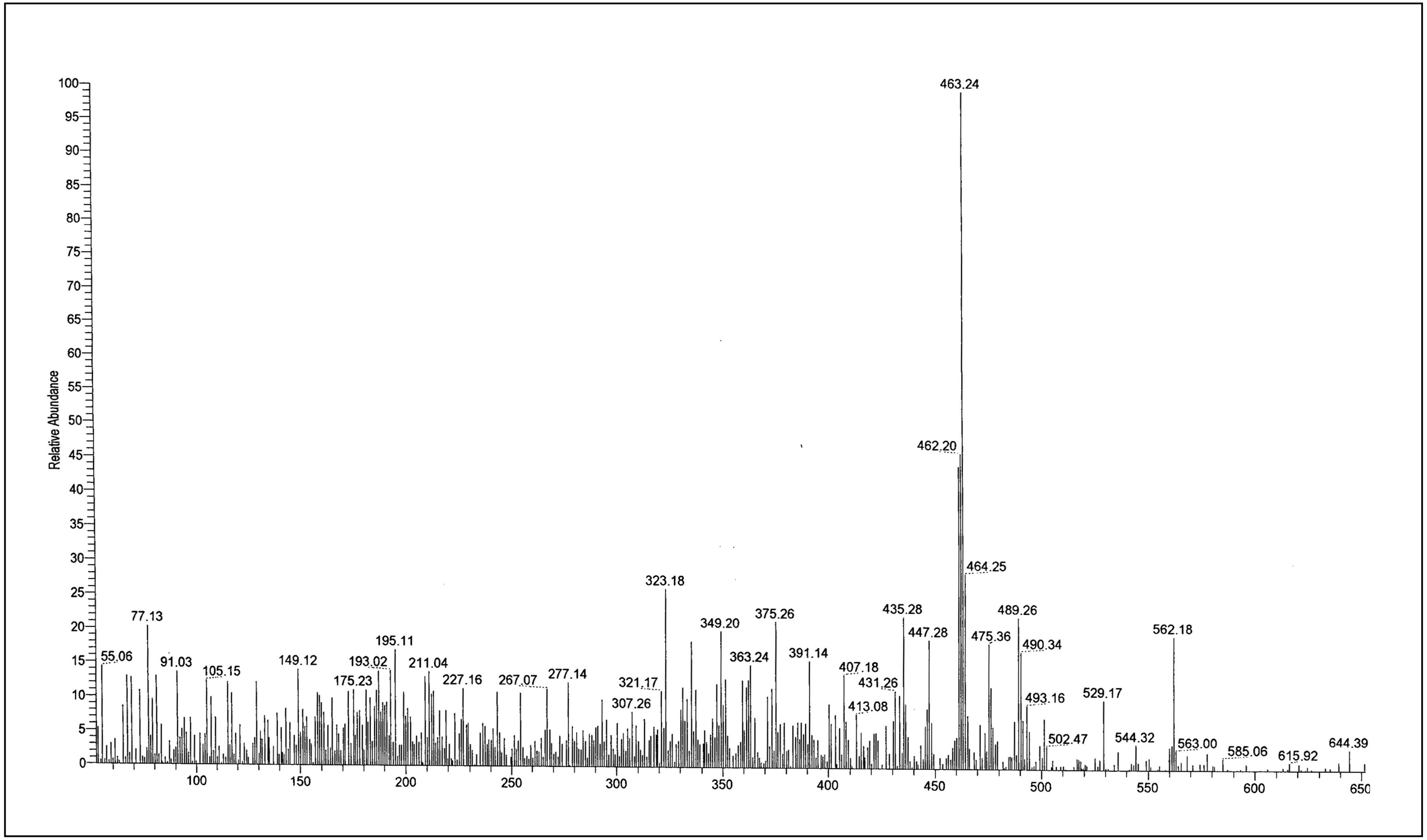


Figure 100 Mass spectrum of **GF20**

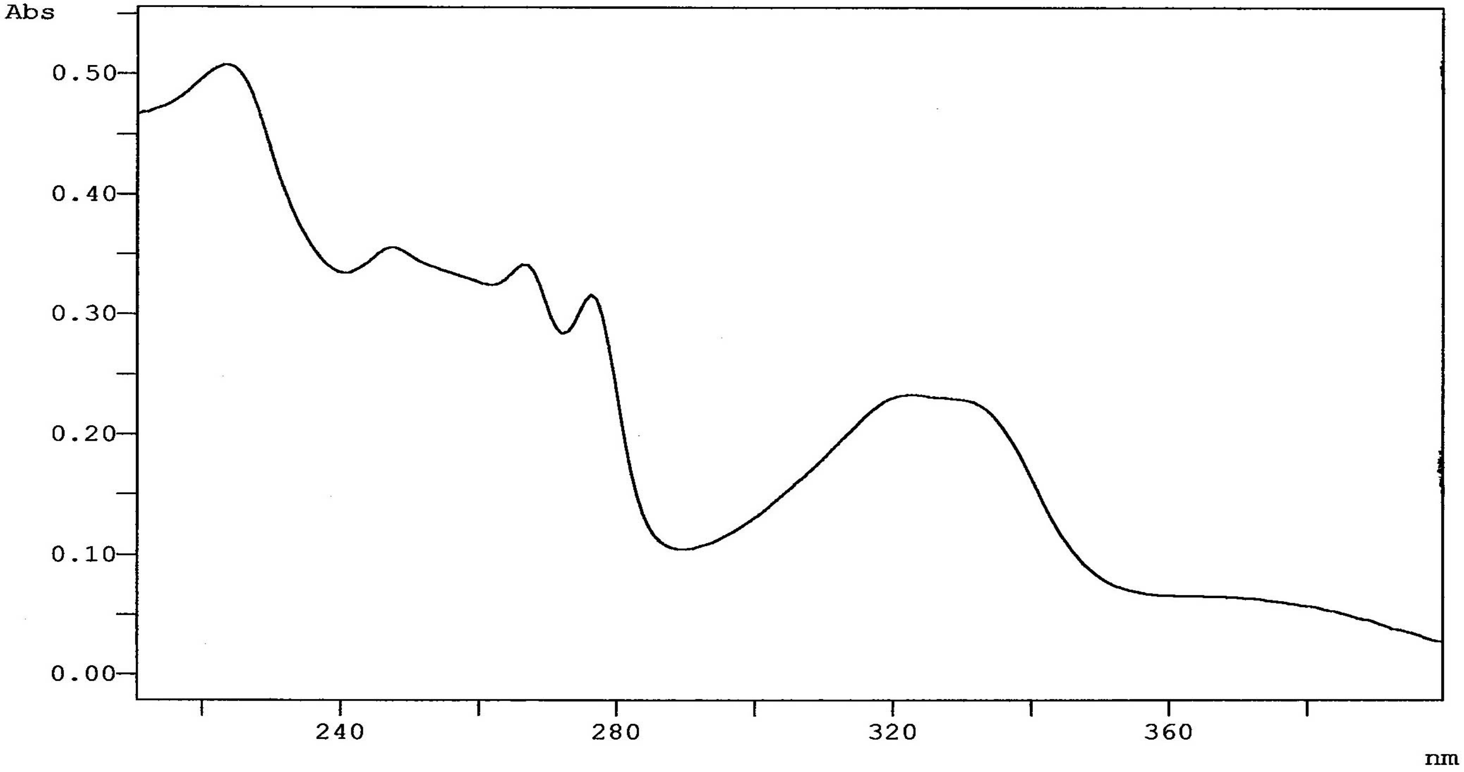


Figure 101 UV (CH_3OH) spectrum of **GF20**

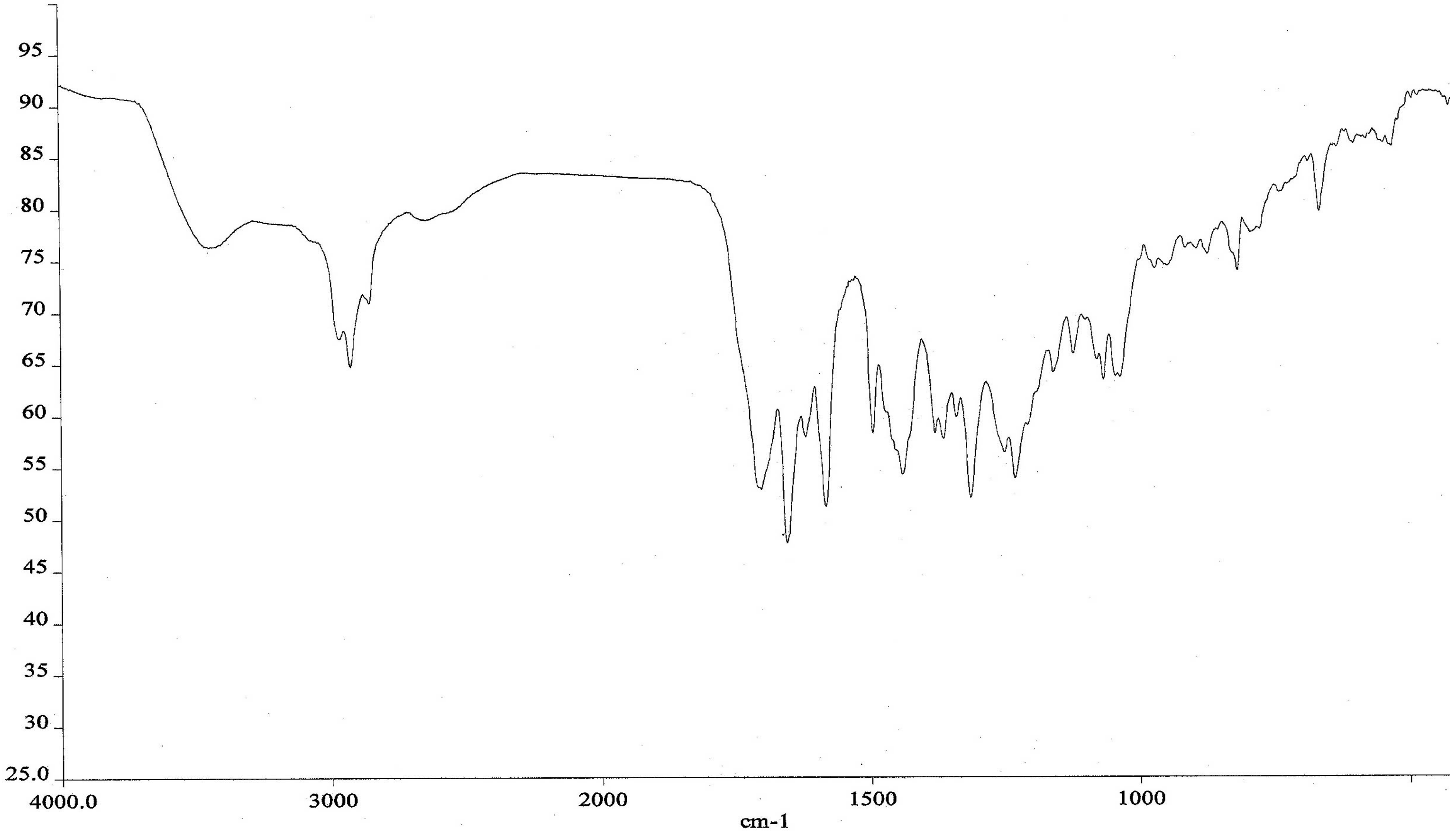


Figure 102 FT-IR (neat) spectrum of **GF20**

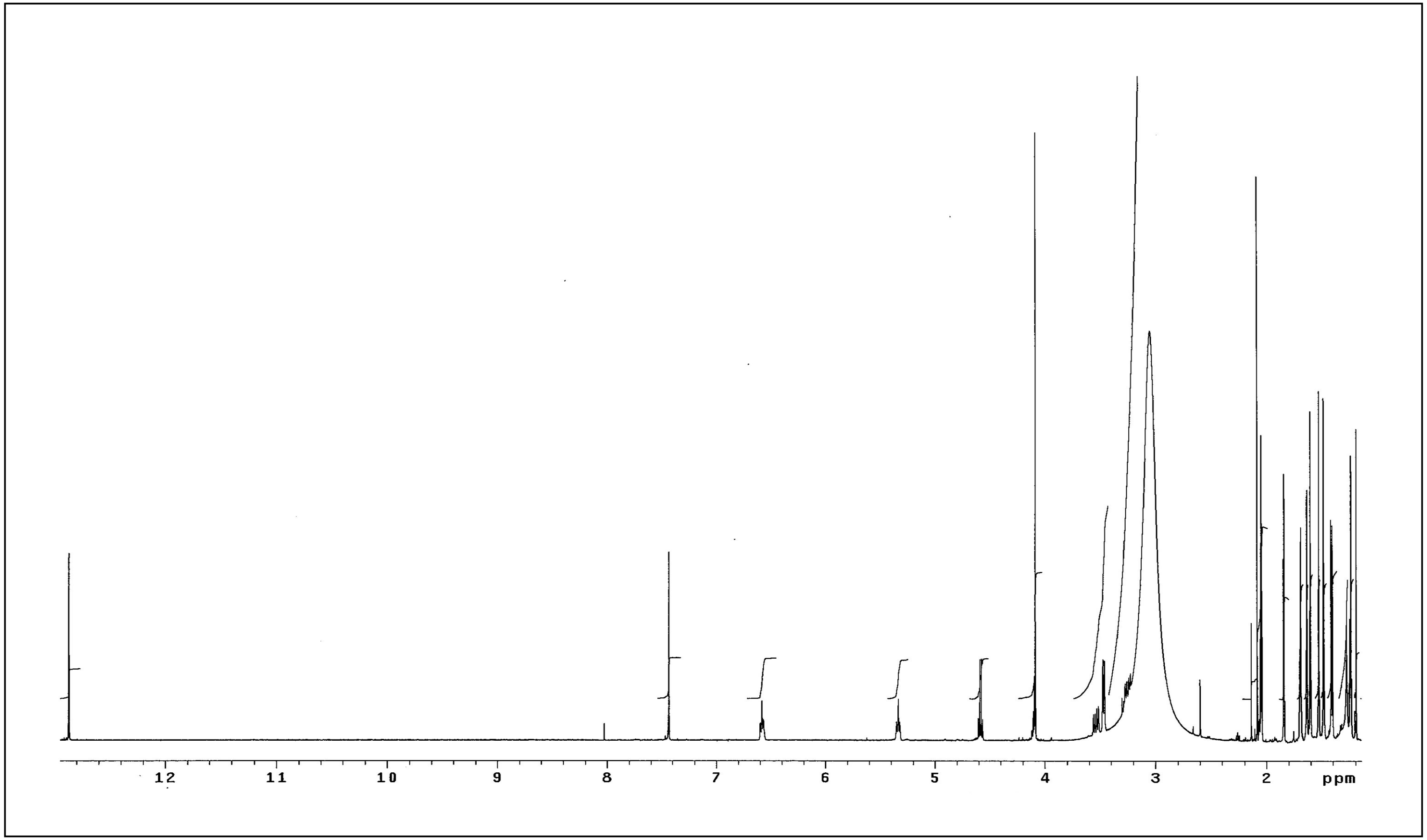


Figure 103 ^{1}H NMR (500 MHz) (Acetone-d_6) spectrum of **GF20**

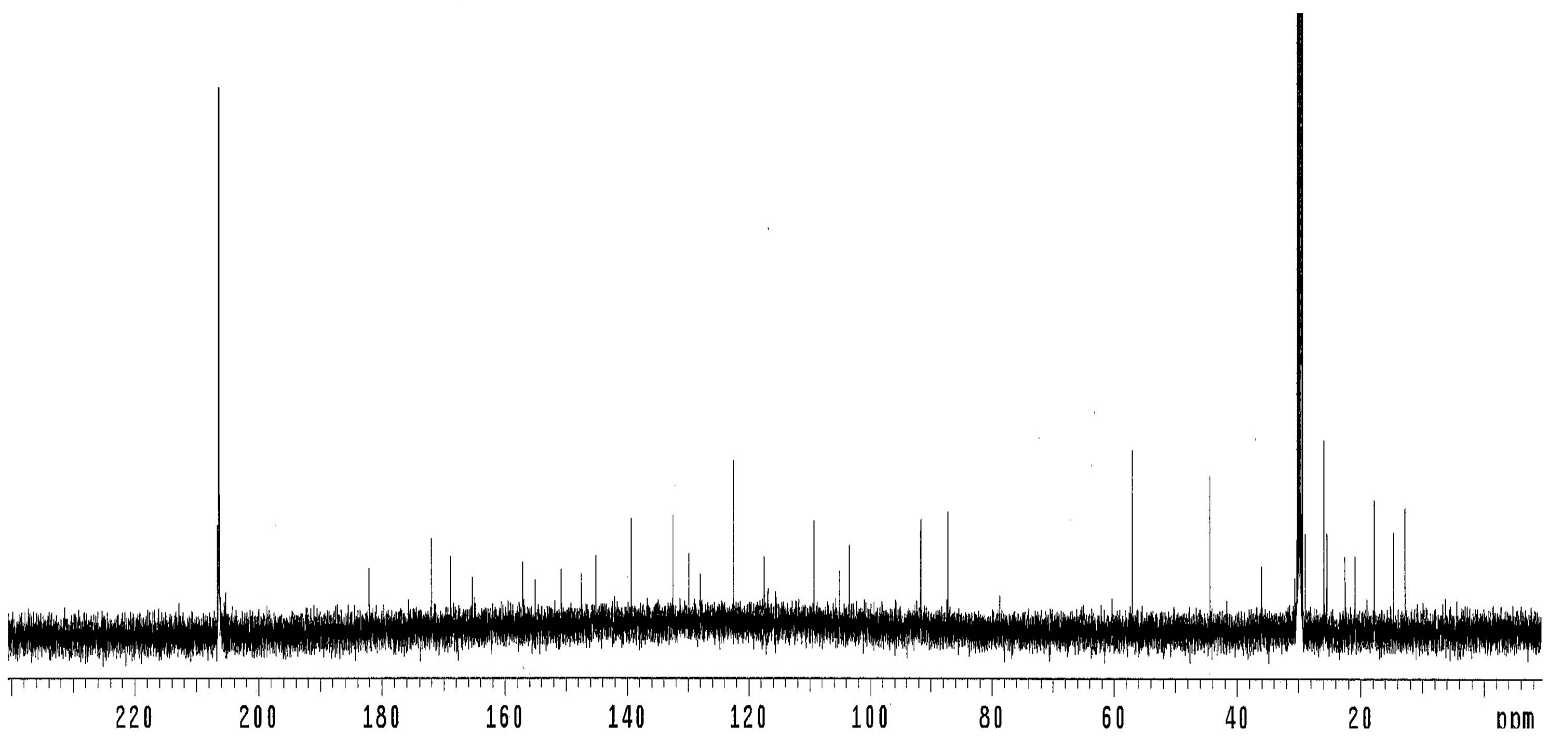


Figure 104 ^{13}C NMR (125 MHz) (Acetone-d_6) spectrum of **GF20**

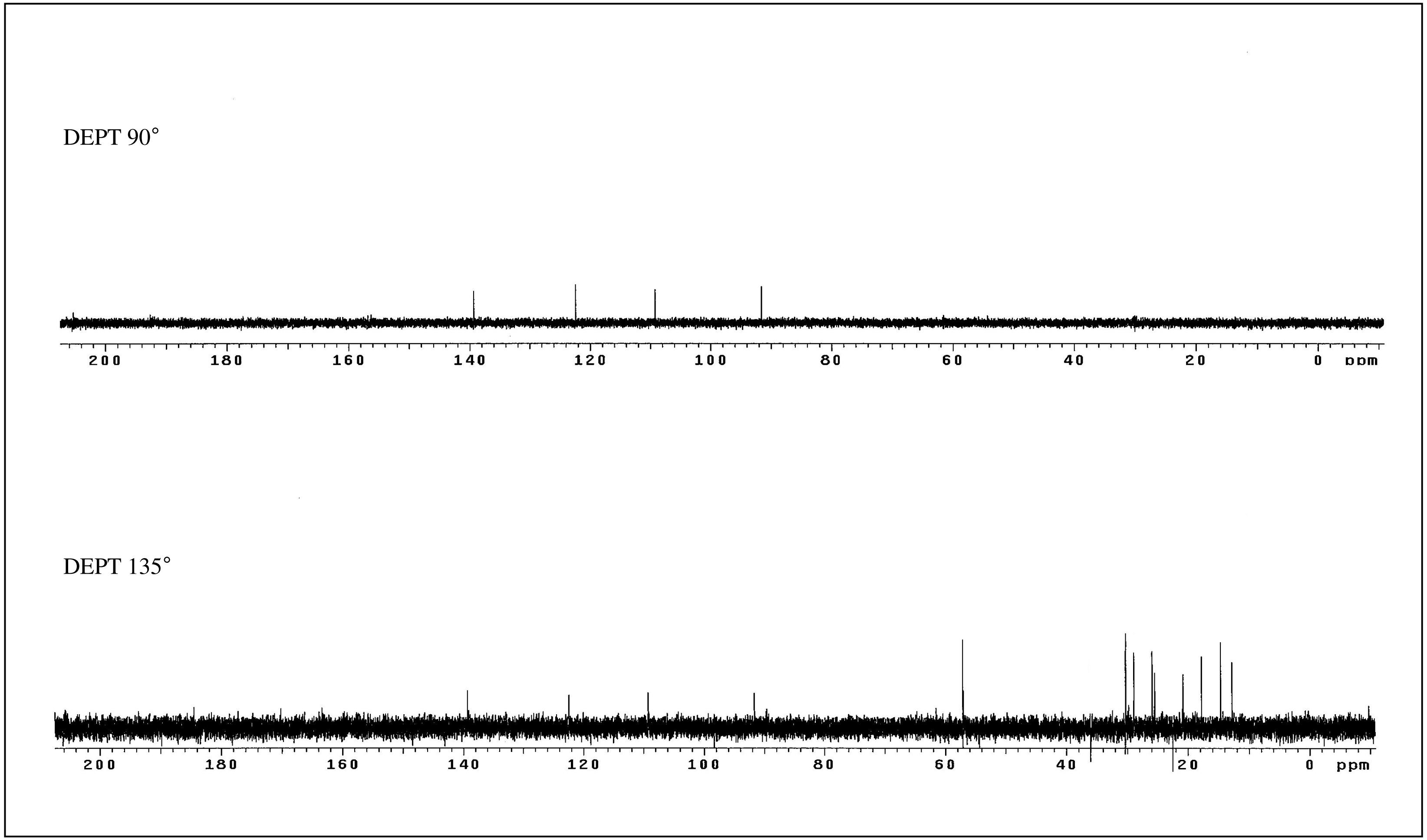


Figure 105 DEPT spectrum of **GF20**

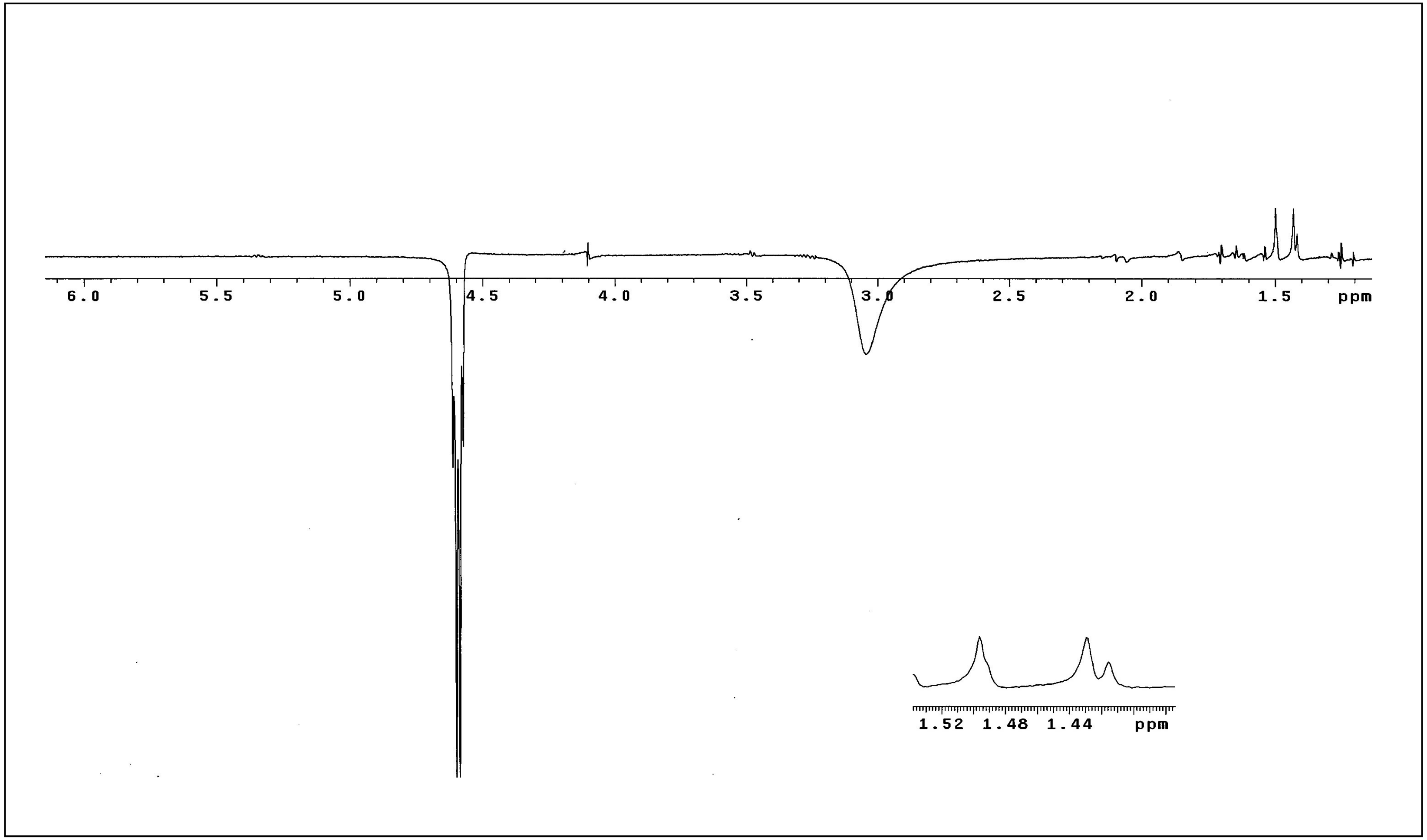


Figure 106 NOEDIFF spectrum of **GF20** after irradiation at δ_H 4.58

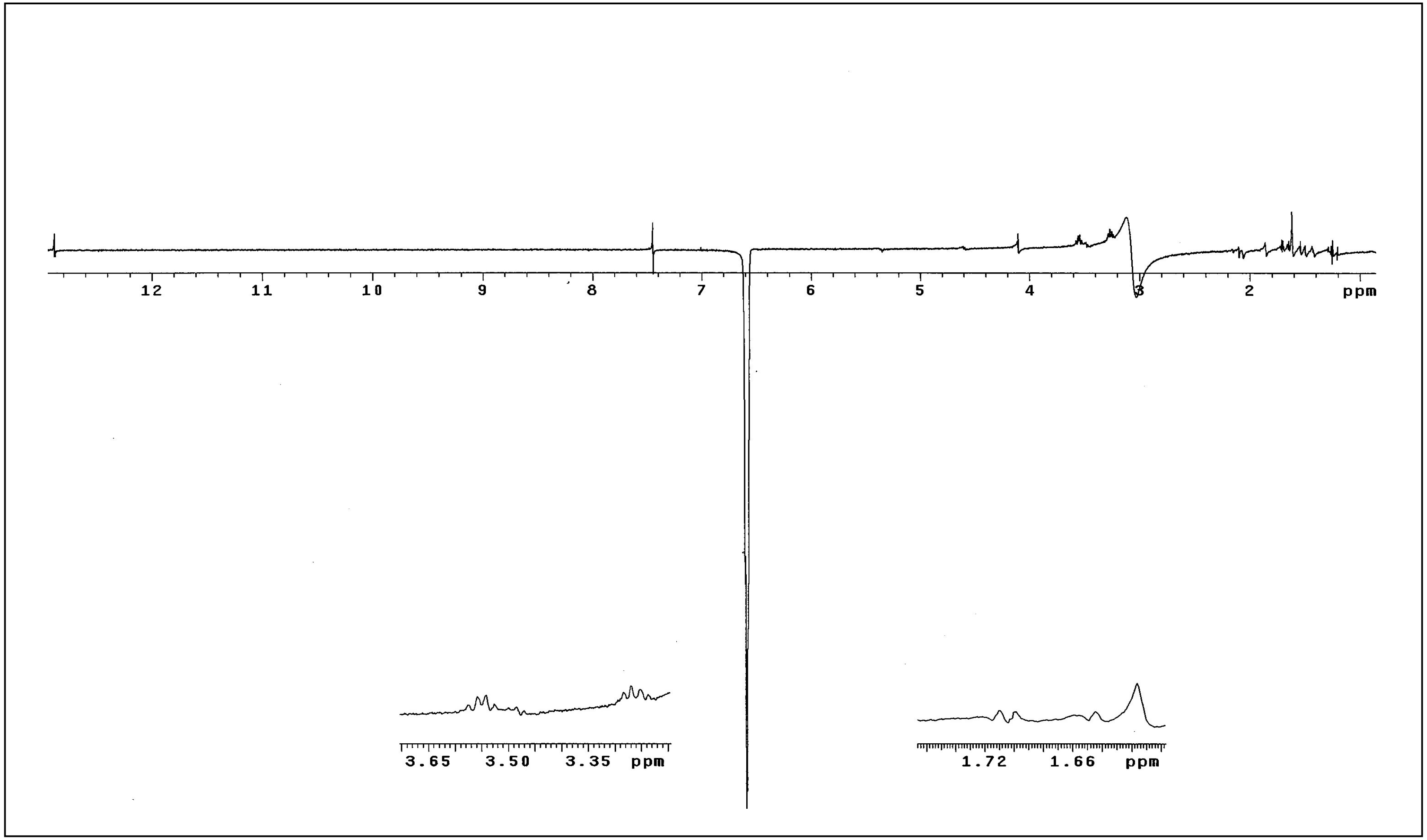


Figure 107 NOEDIFF spectrum of **GF20** after irradiation at δ_H 6.58

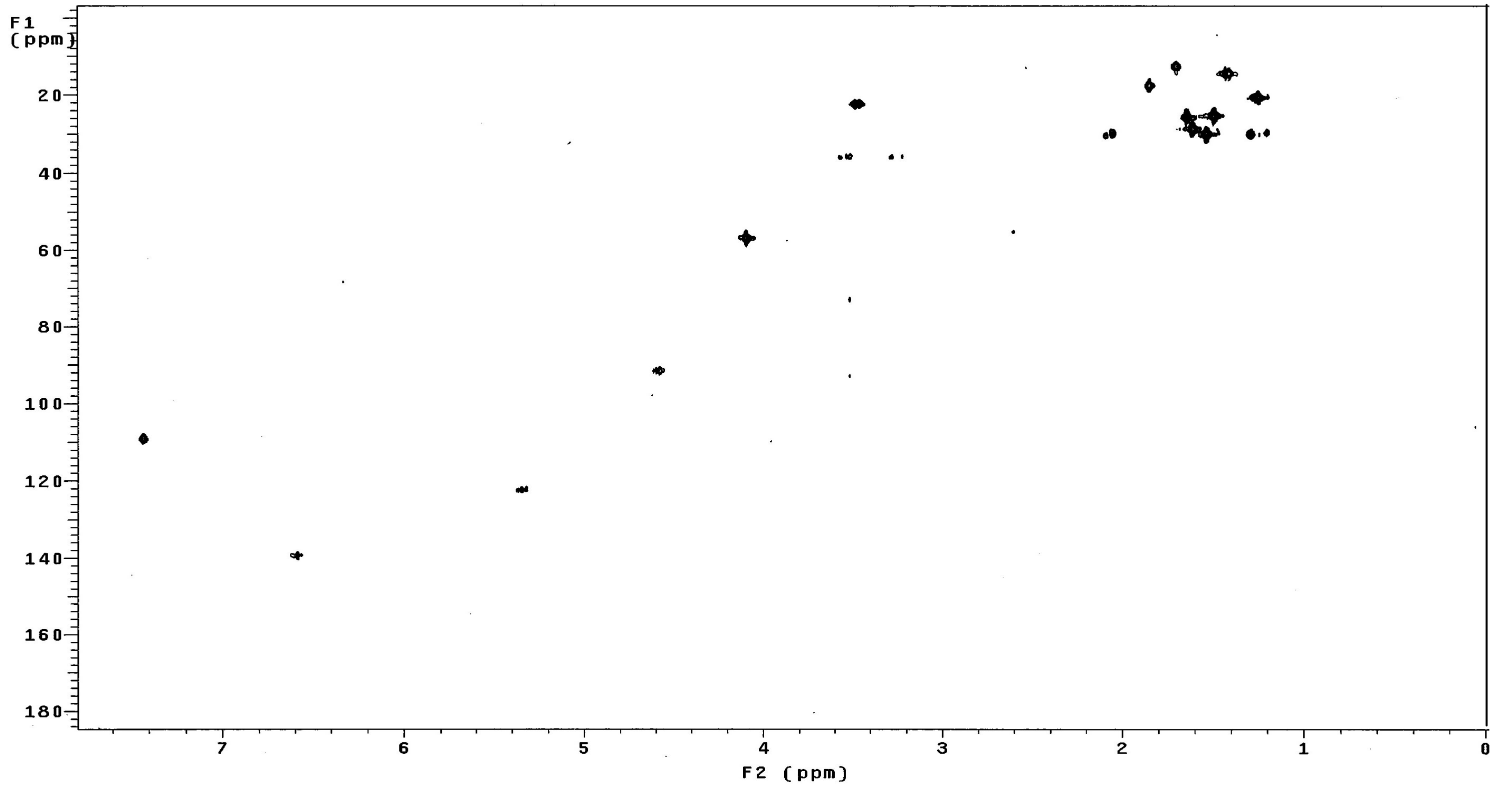


Figure 108 2D HMQC spectrum of **GF20**

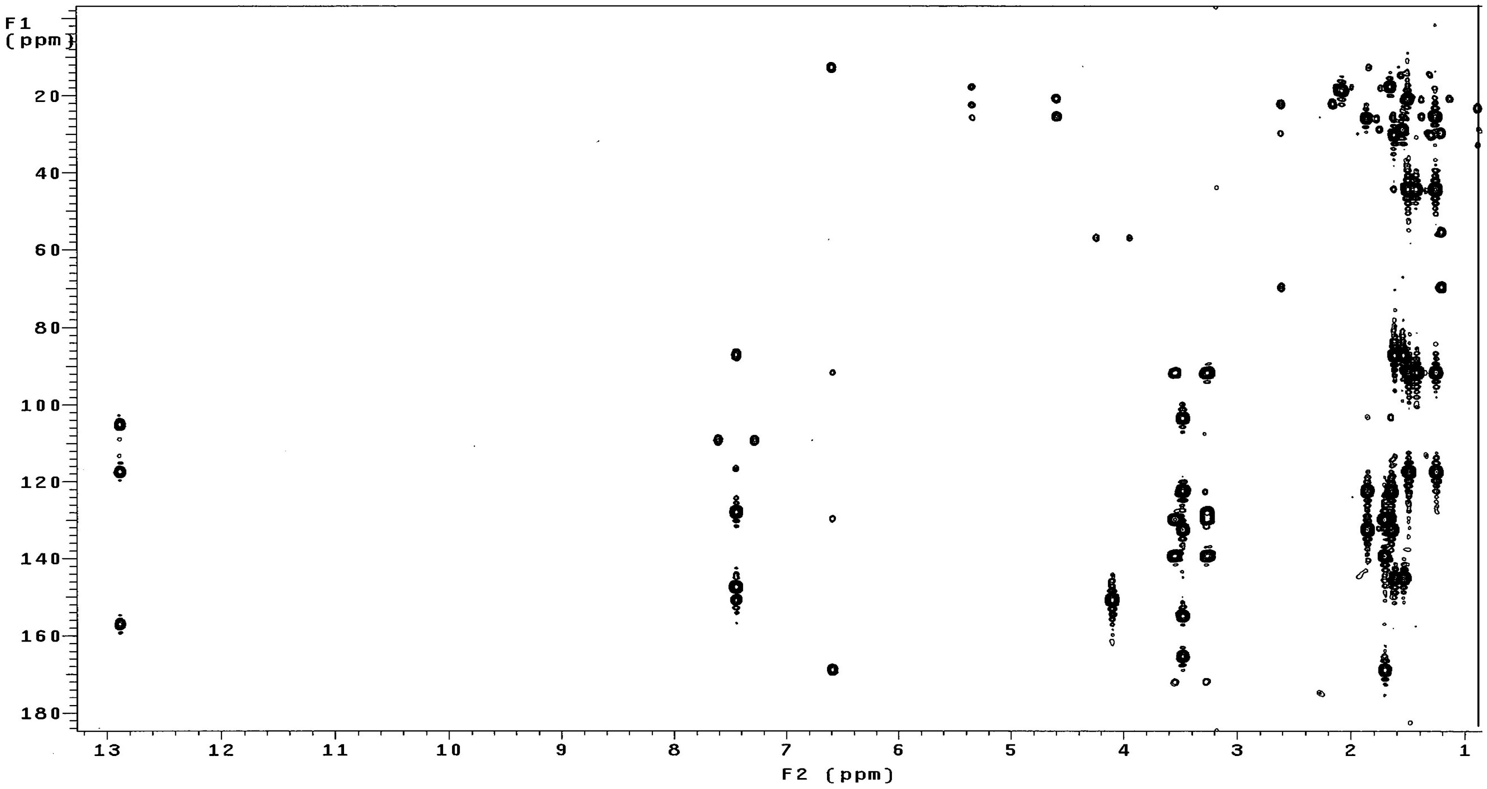


Figure 109 2D HMBC spectrum of **GF20**

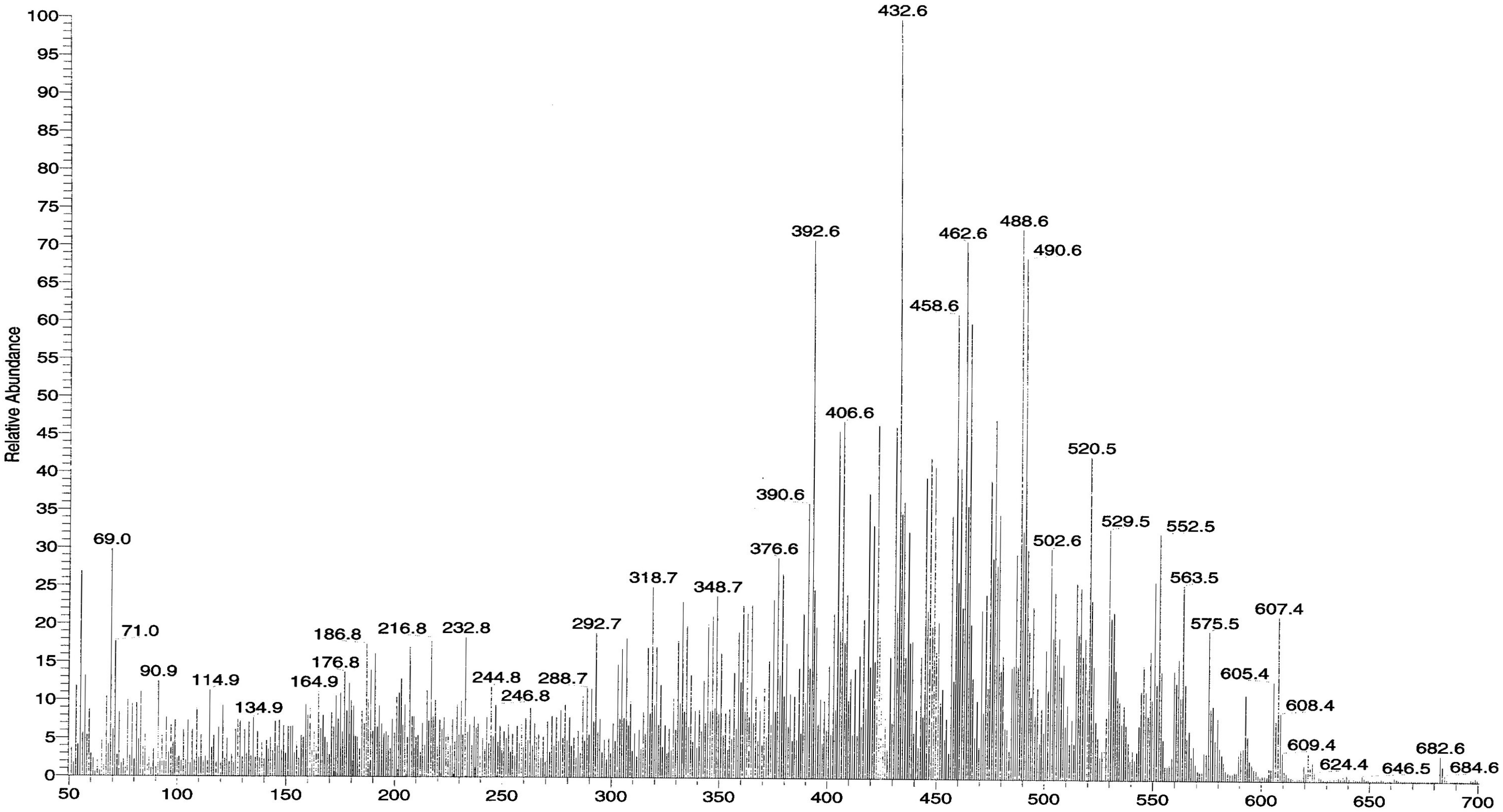


Figure 110 Mass spectrum of **GF22**

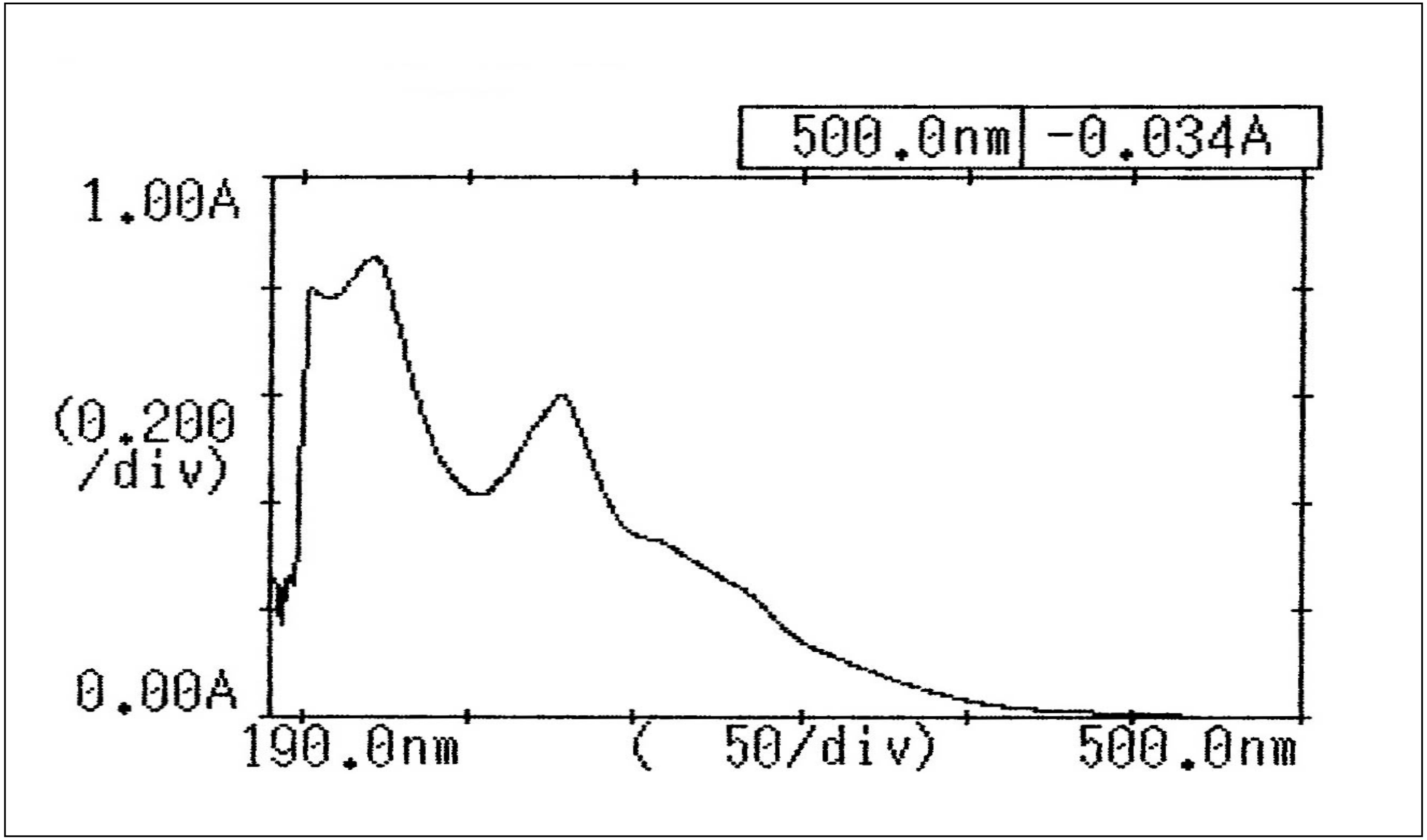


Figure 111 UV (CH_3OH) spectrum of **GF22**

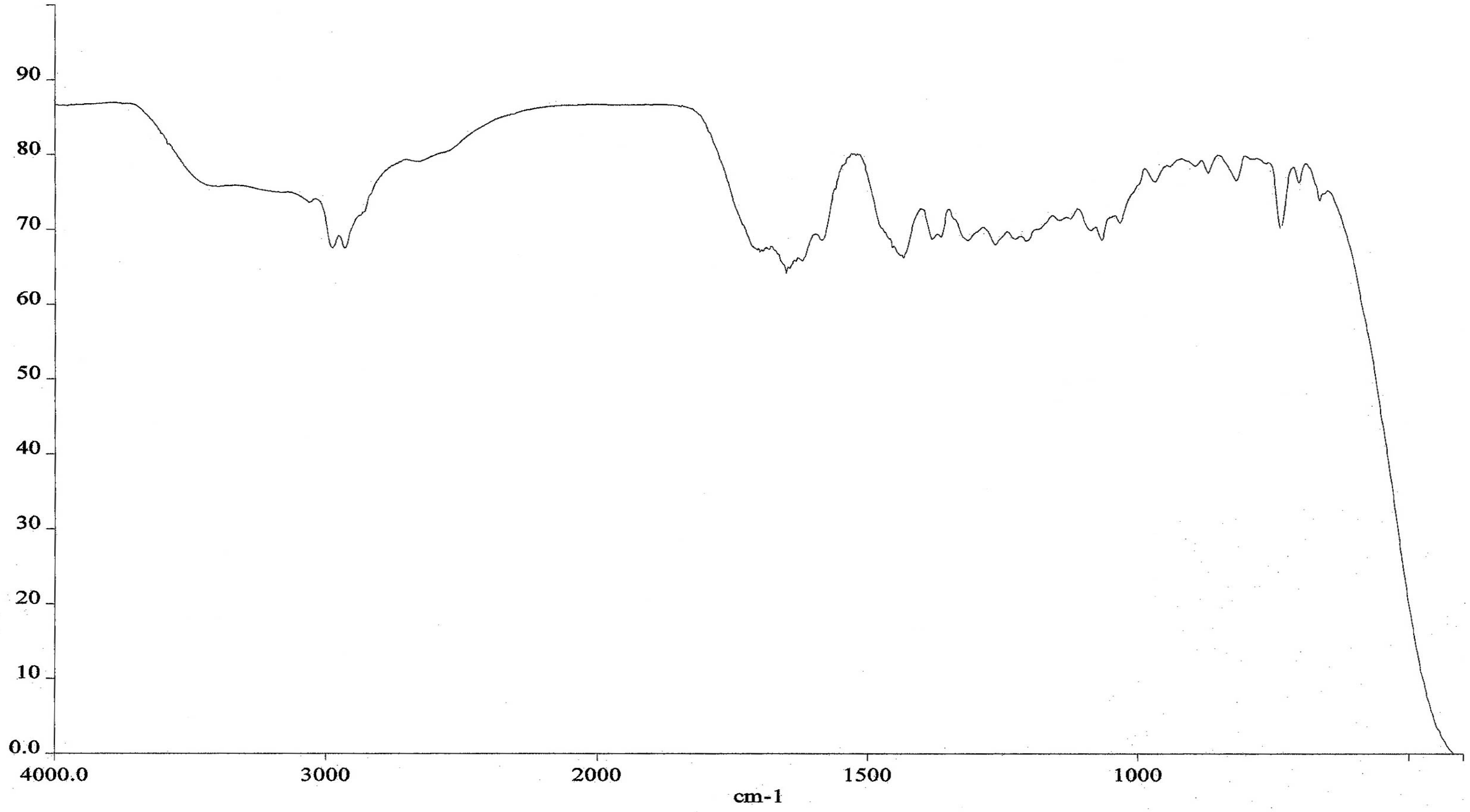


Figure 112 FT-IR (neat) spectrum of **GF22**

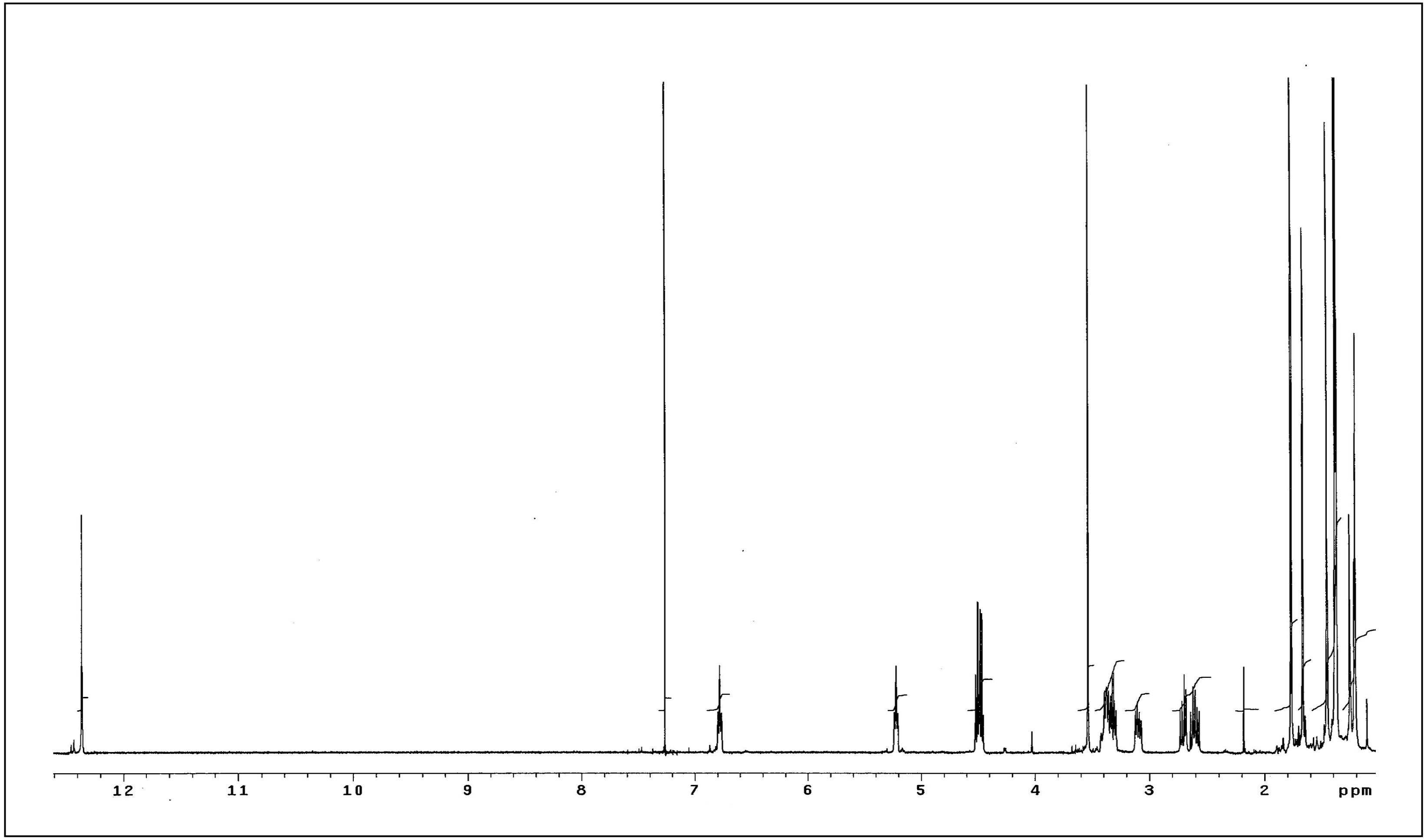


Figure 113 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF22**

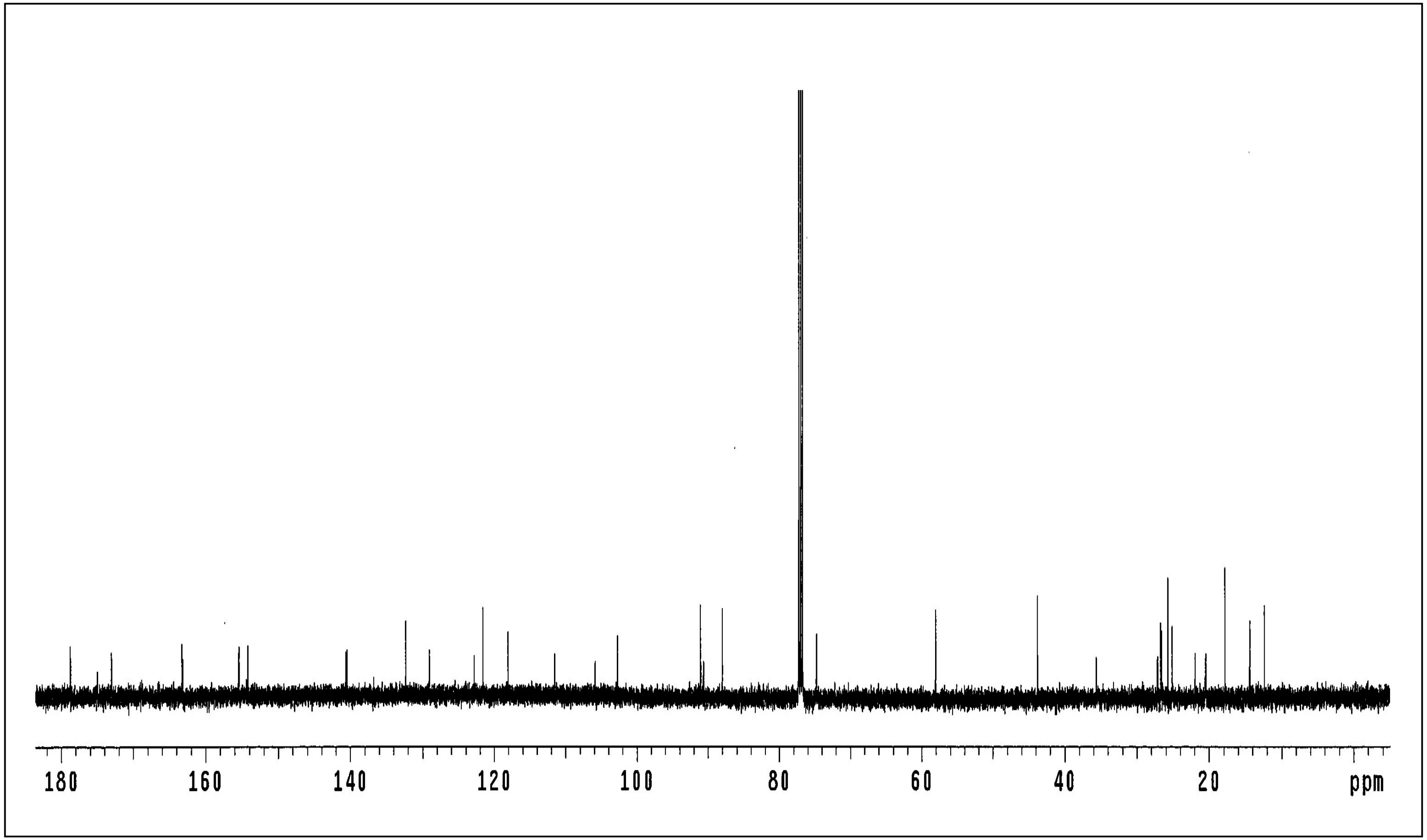


Figure 114 ^{13}C NMR (125 MHz) ($CDCl_3$) spectrum of **GF22**

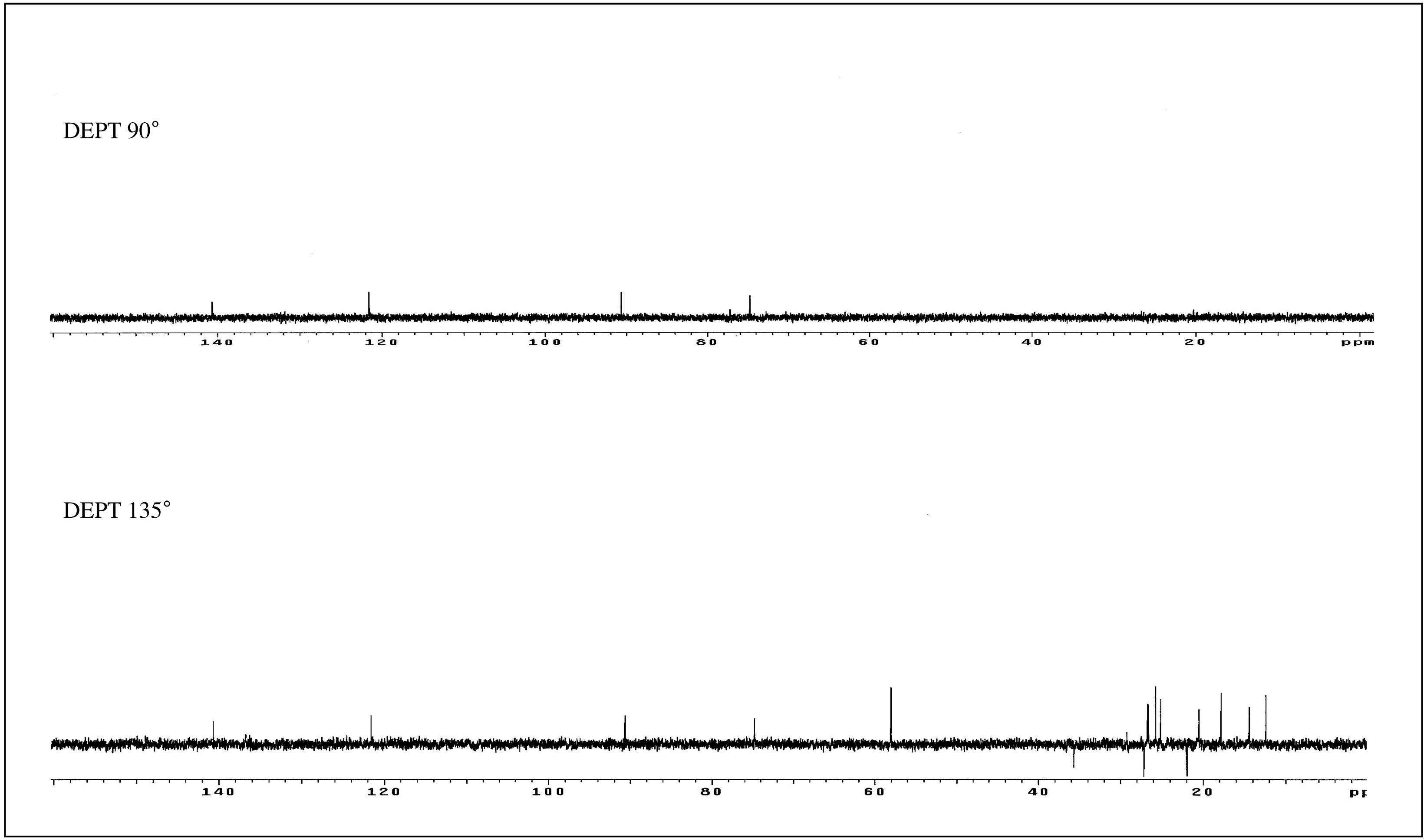


Figure 115 DEPT spectrum of **GF22**

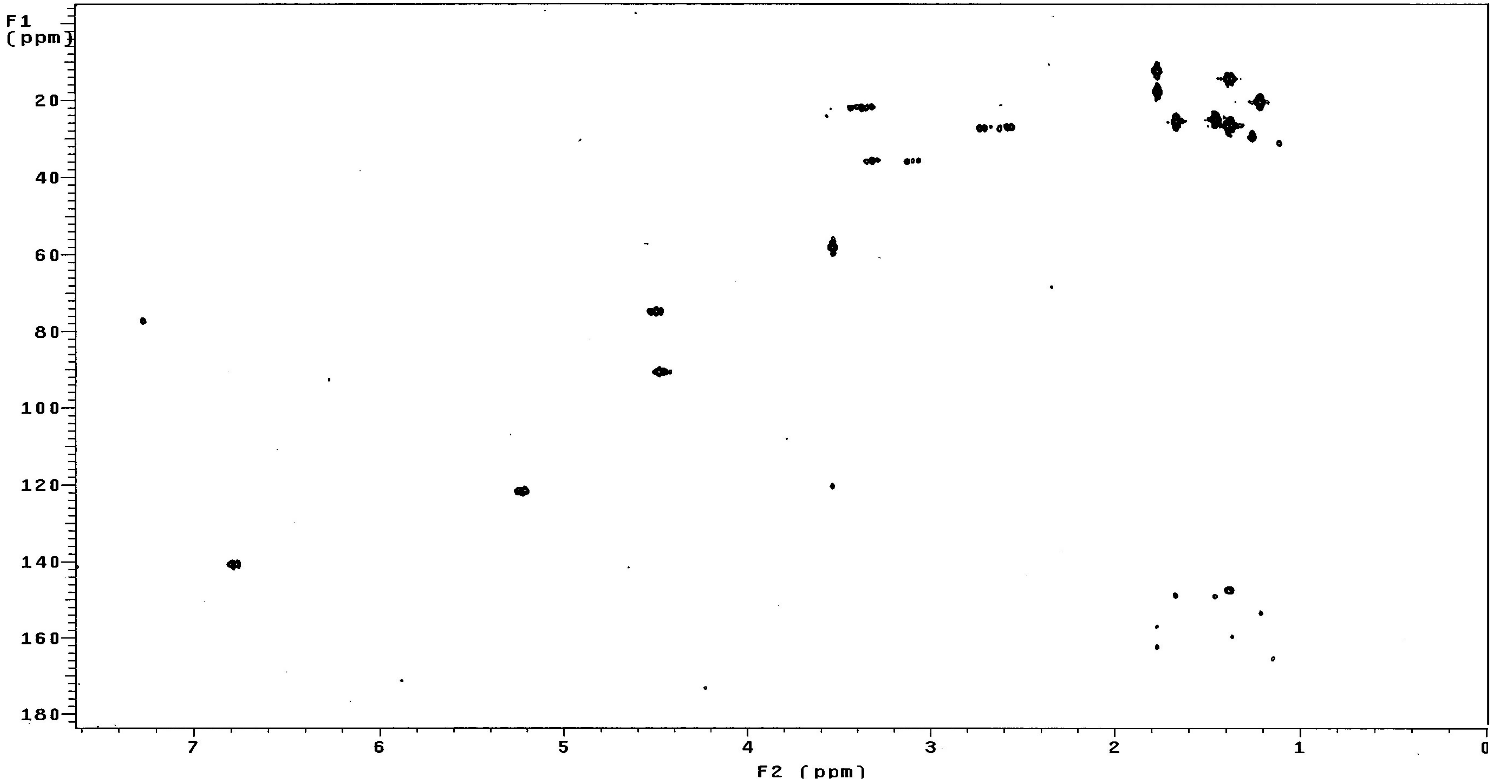


Figure 116 2D HMQC spectrum of **GF22**

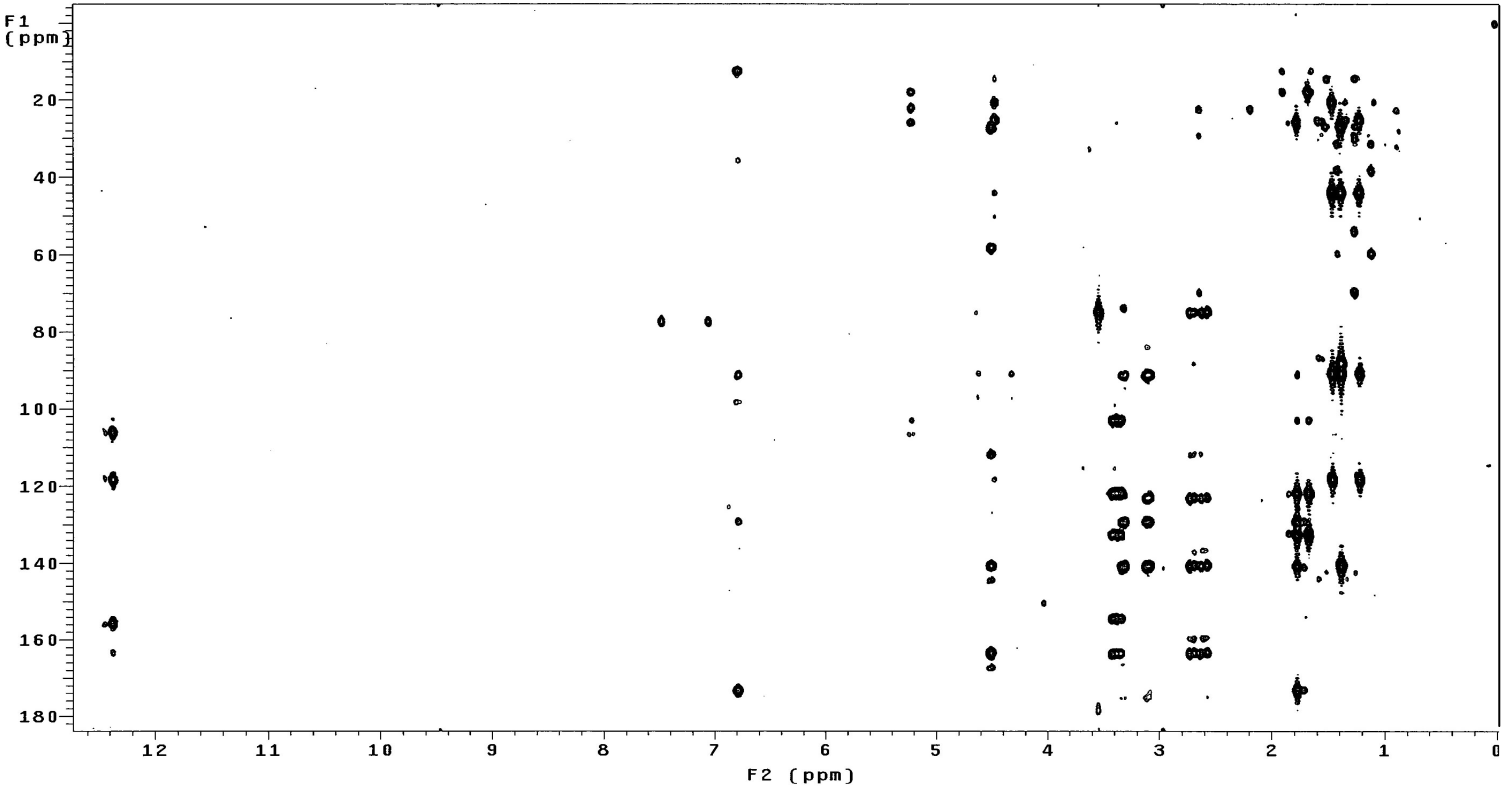


Figure 117 2D HMBC spectrum of **GF22**

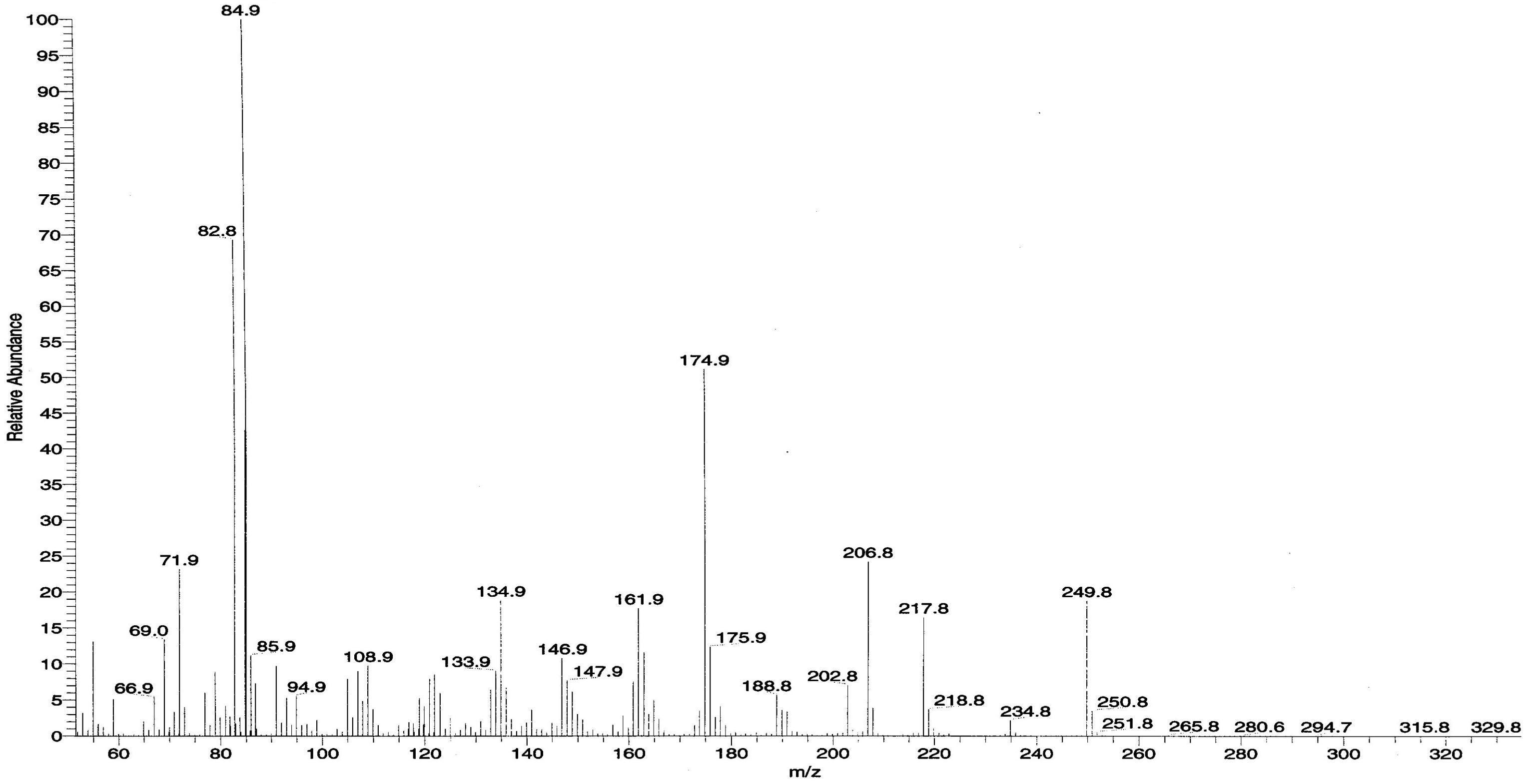


Figure 118 Mass spectrum of **GF1**

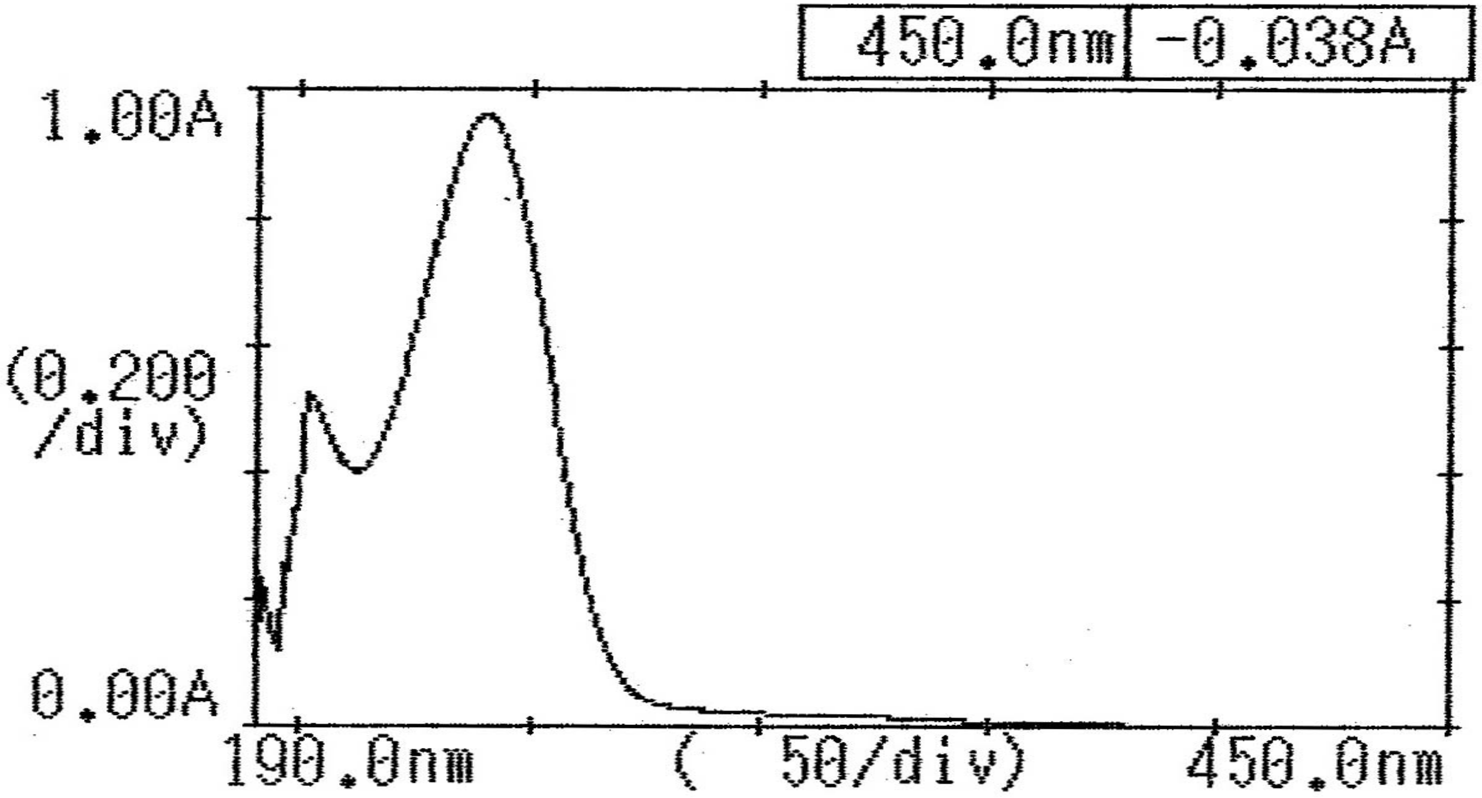


Figure 119 UV (CH_3OH) spectrum of **GF1**

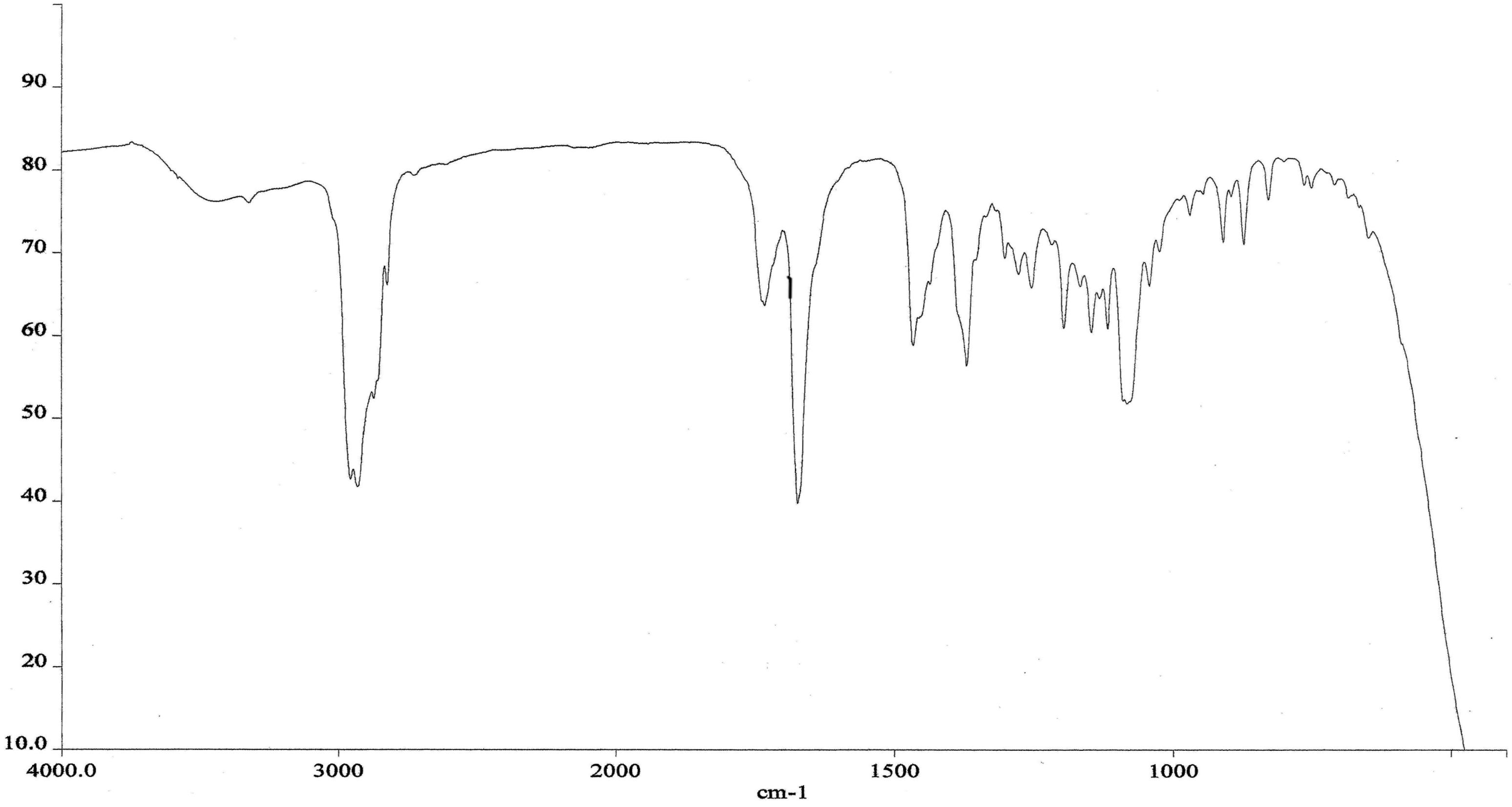


Figure 120 FT-IR (neat) spectrum of **GF1**

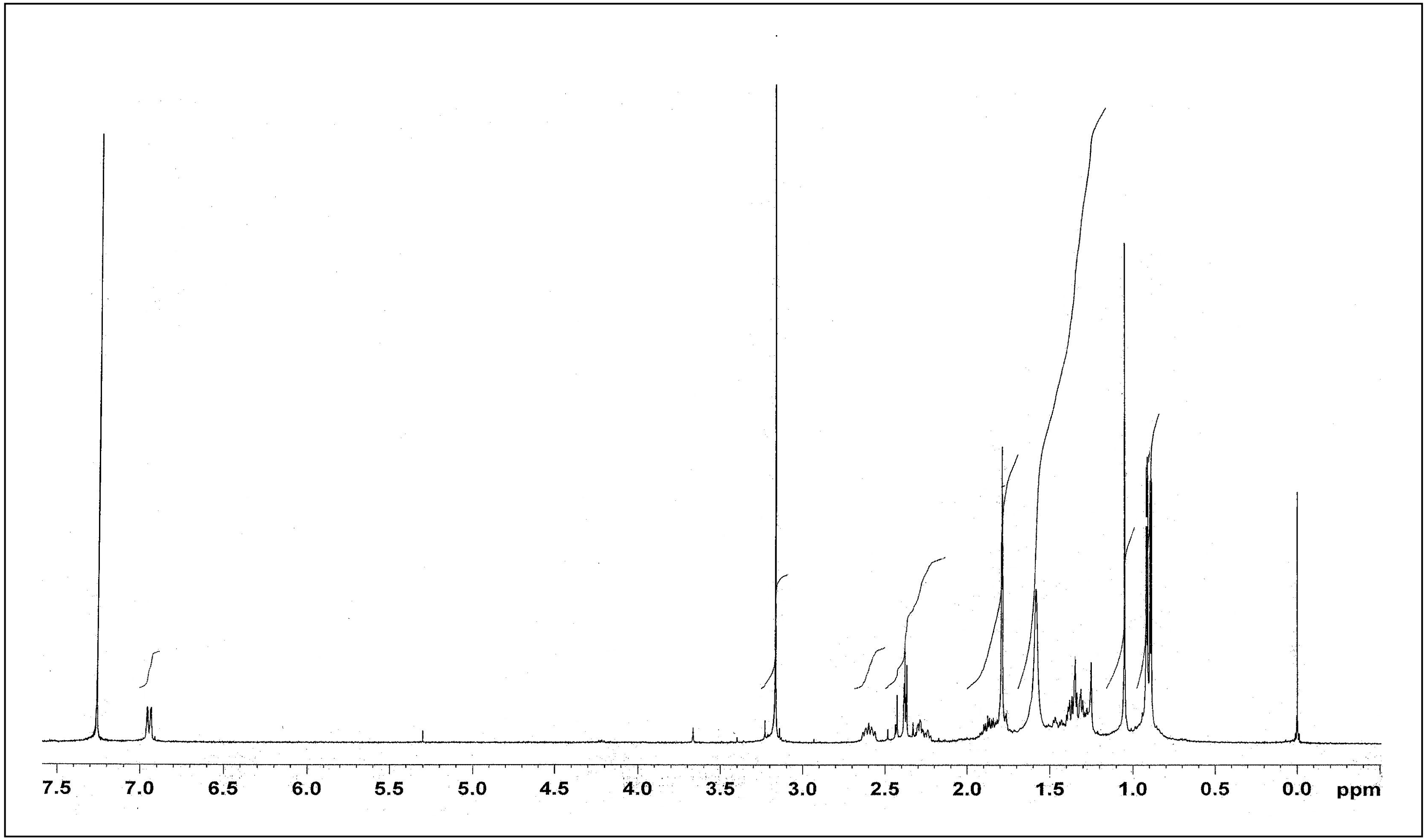


Figure 121 ^{1}H NMR (300 MHz) (CDCl$_3$) spectrum of **GF1**

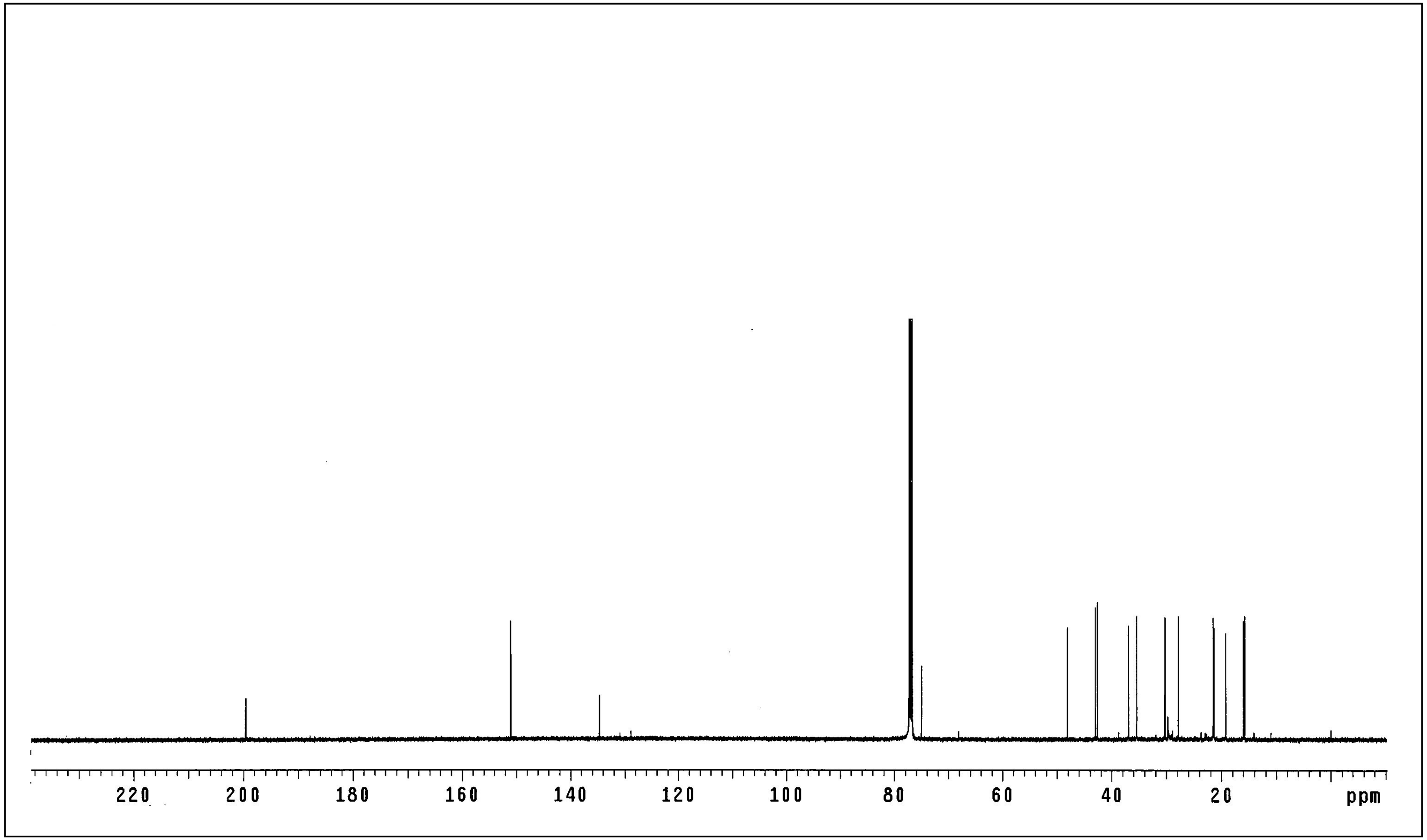
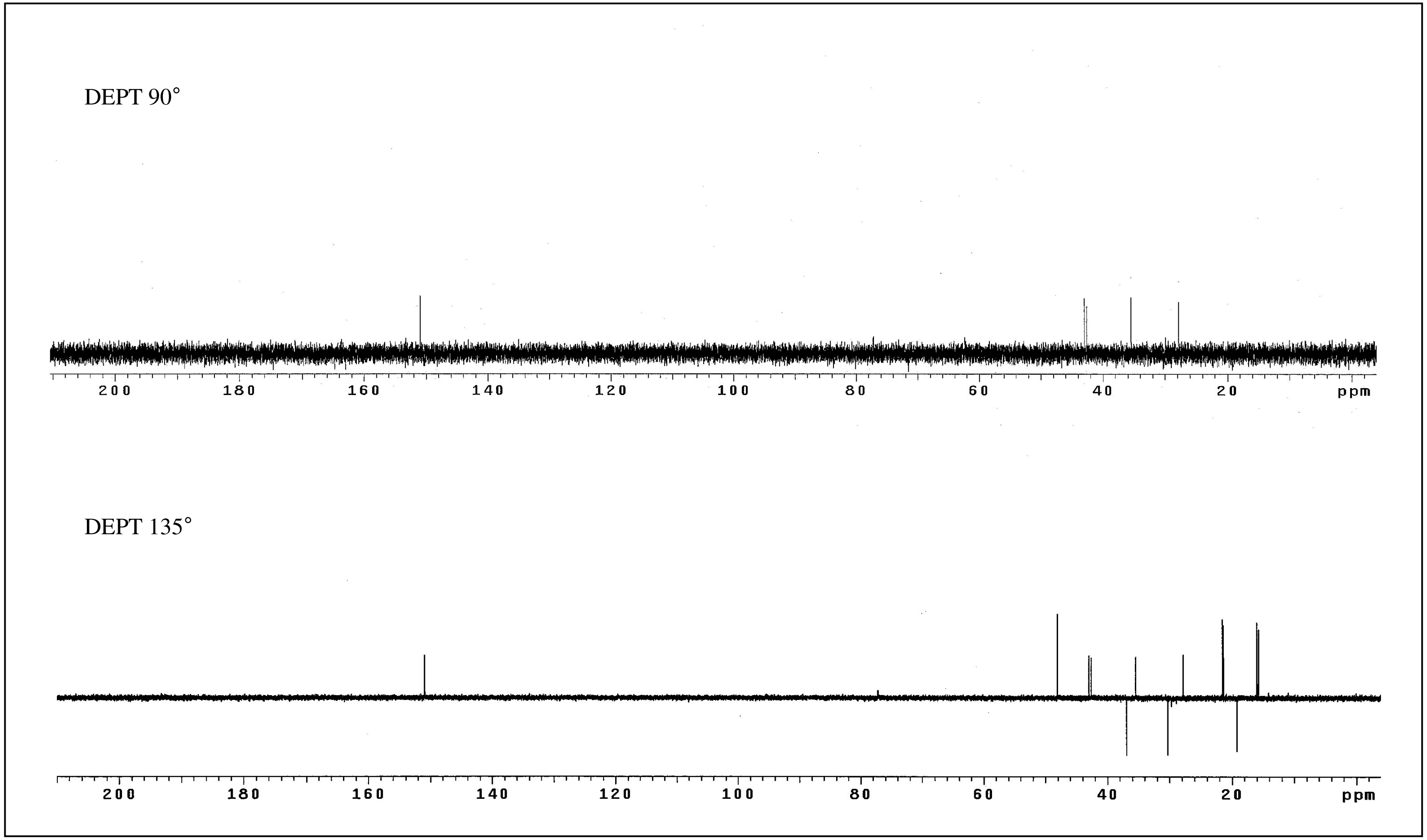


Figure 122 ^{13}C NMR (125 MHz) (CDCl$_3$) spectrum of **GF1**


DEPT 90°

DEPT 135°

Figure 123 DEPT spectrum of **GF1**

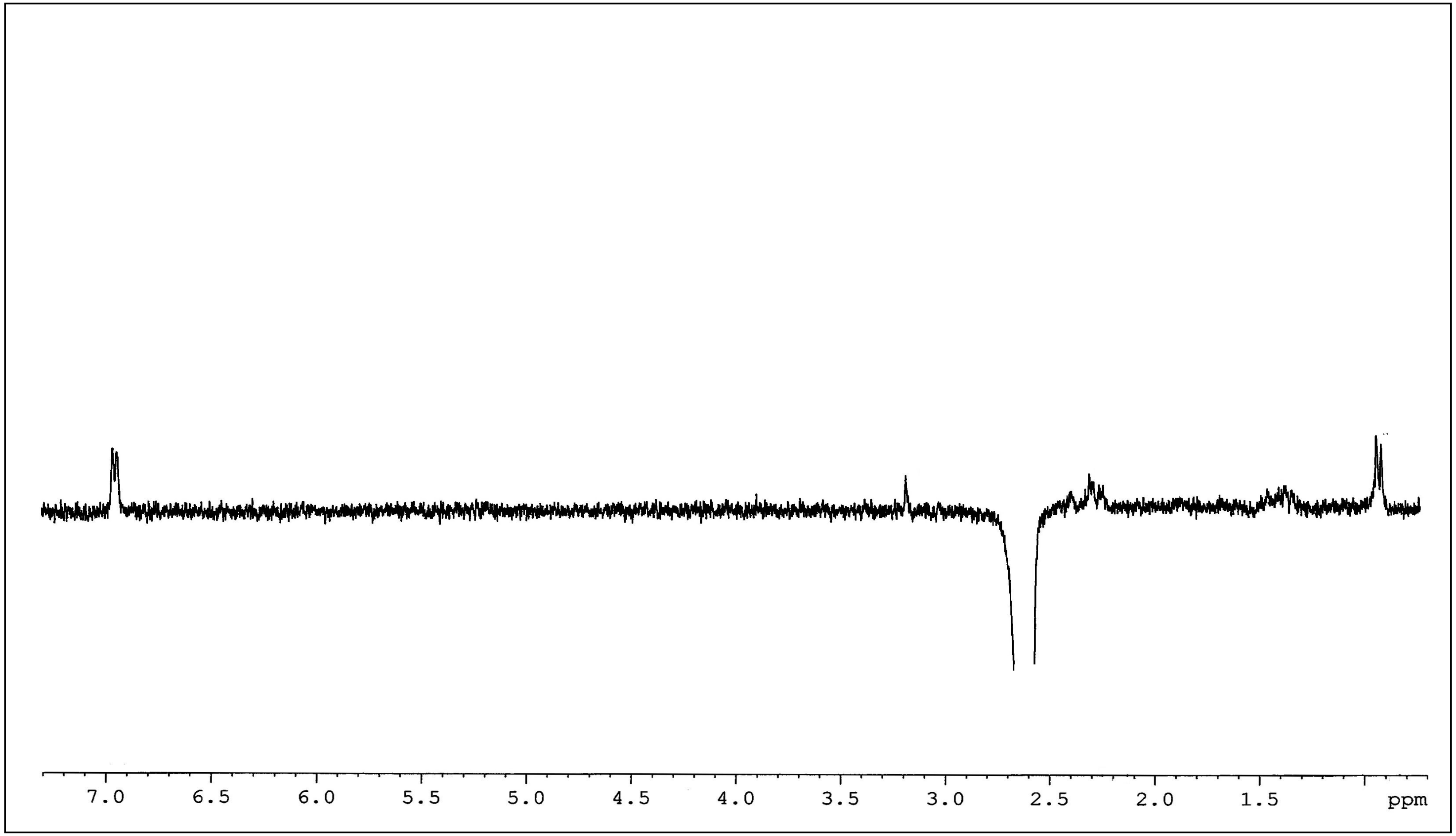


Figure 124 NOEDIFF spectrum of **GF1** after irradiation at δ_H 2.60

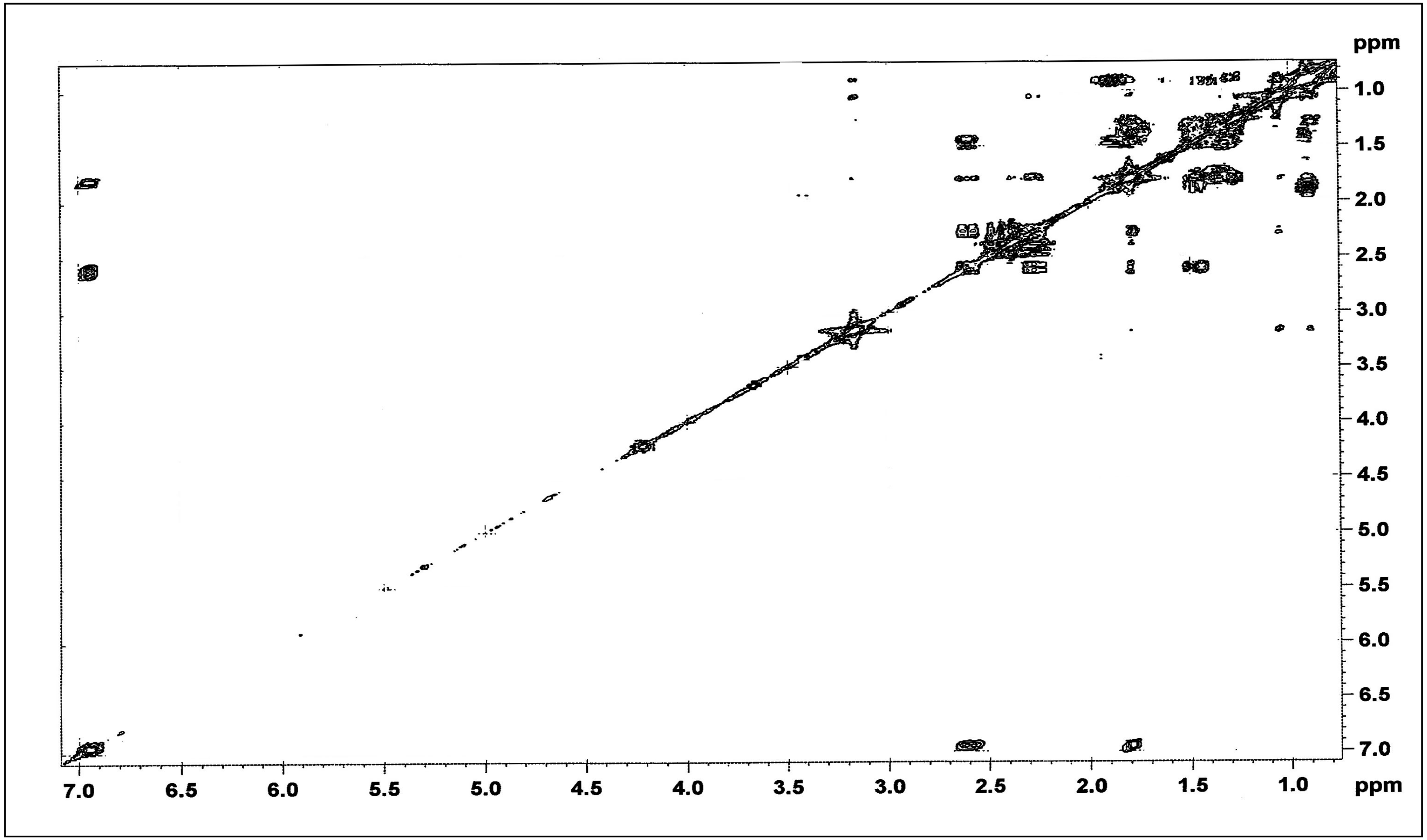


Figure 125 ^{1}H-^{1}H COSY spectrum of **GF1**

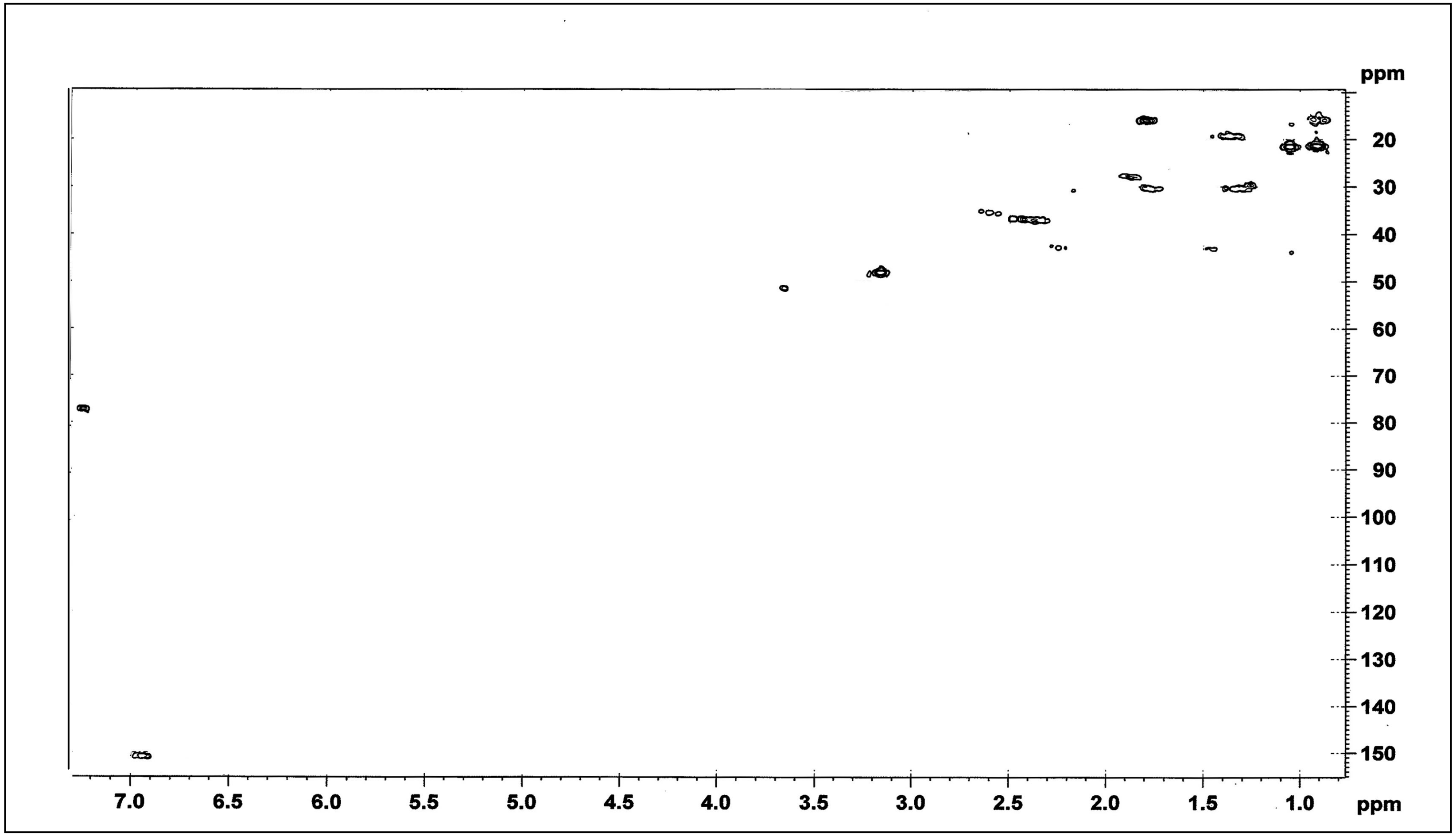


Figure 126 2D HMQC spectrum of **GF1**

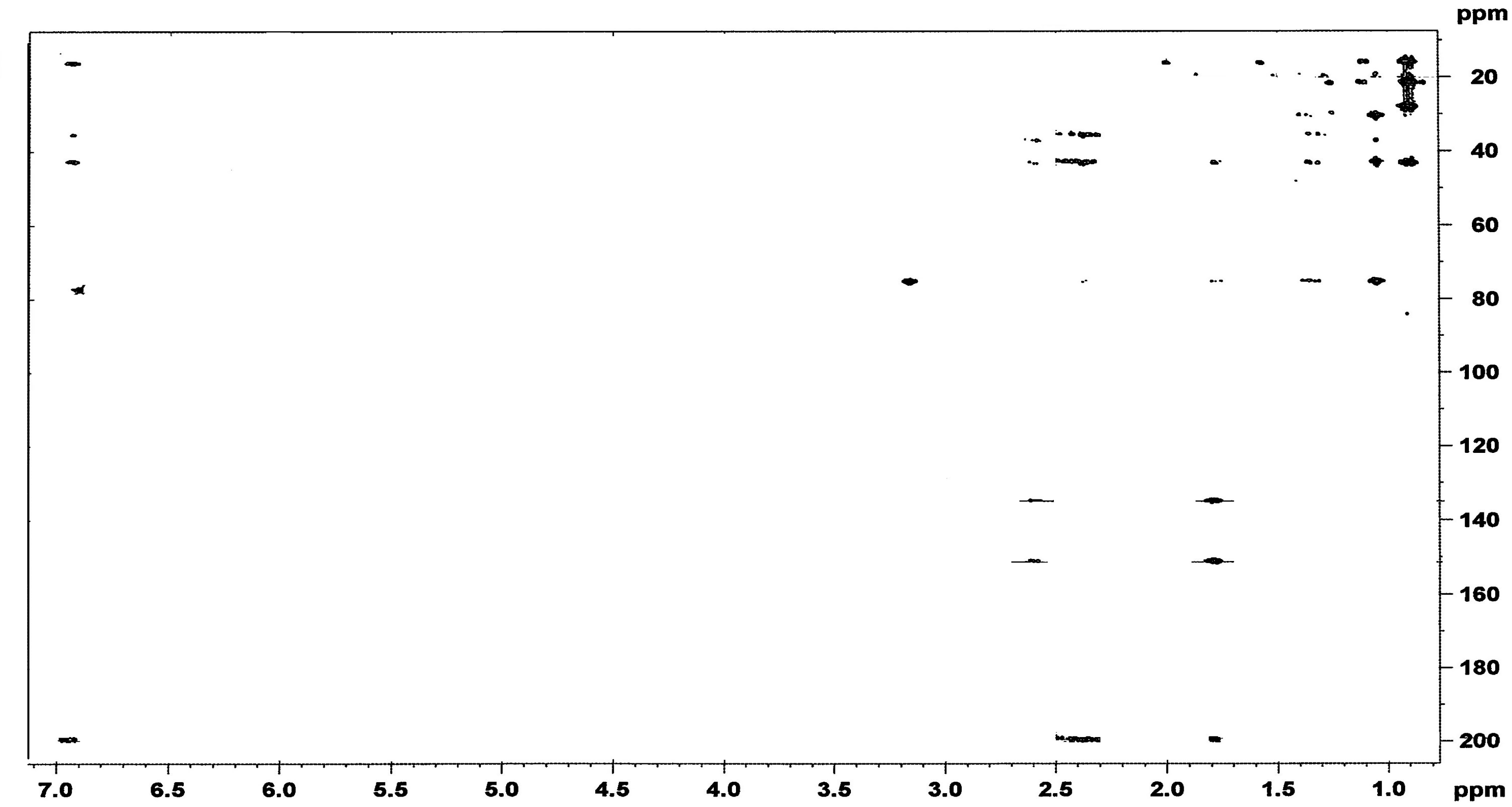


Figure 127 2D HMBC spectrum of **GF1**

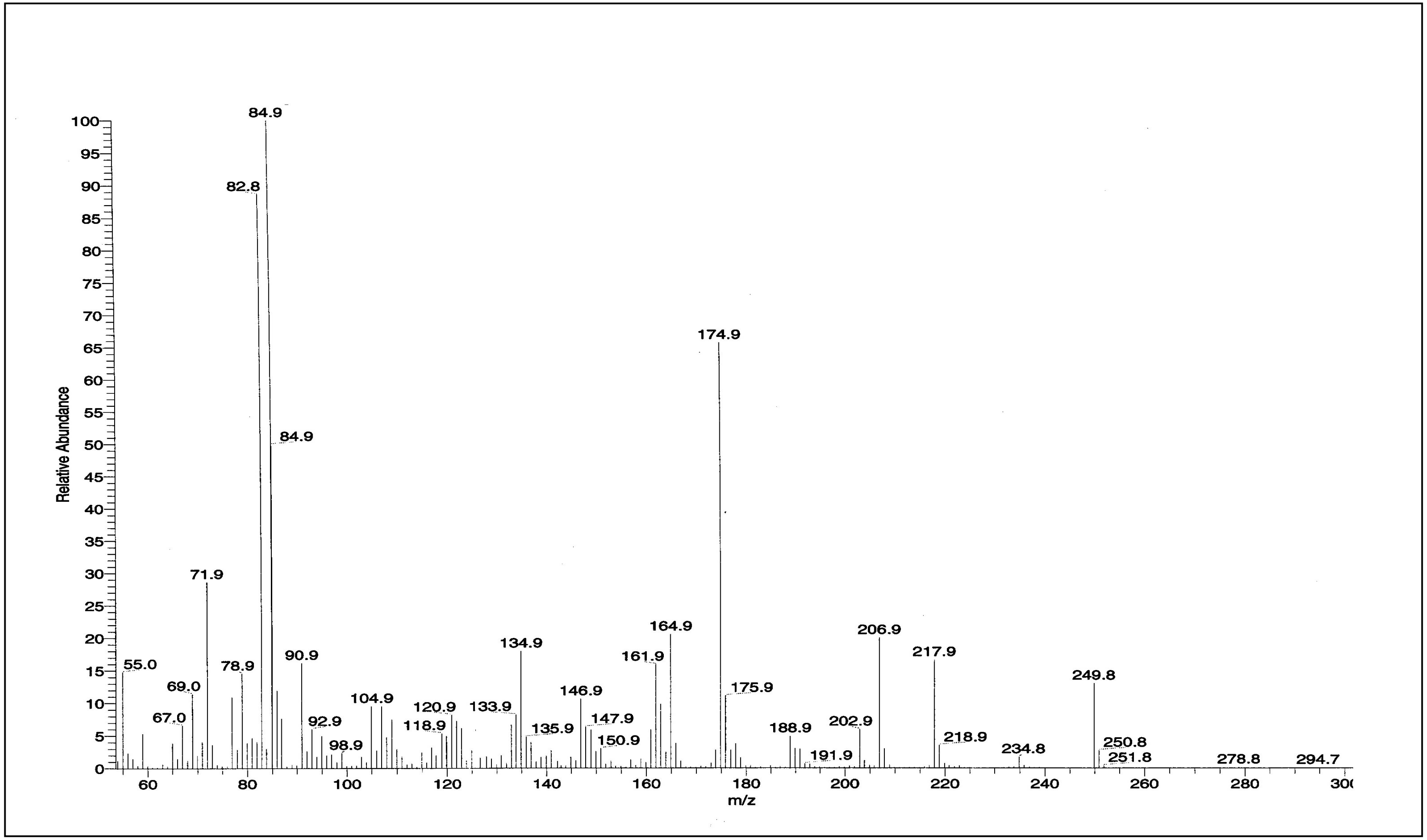


Figure 128 Mass spectrum of **GF2**

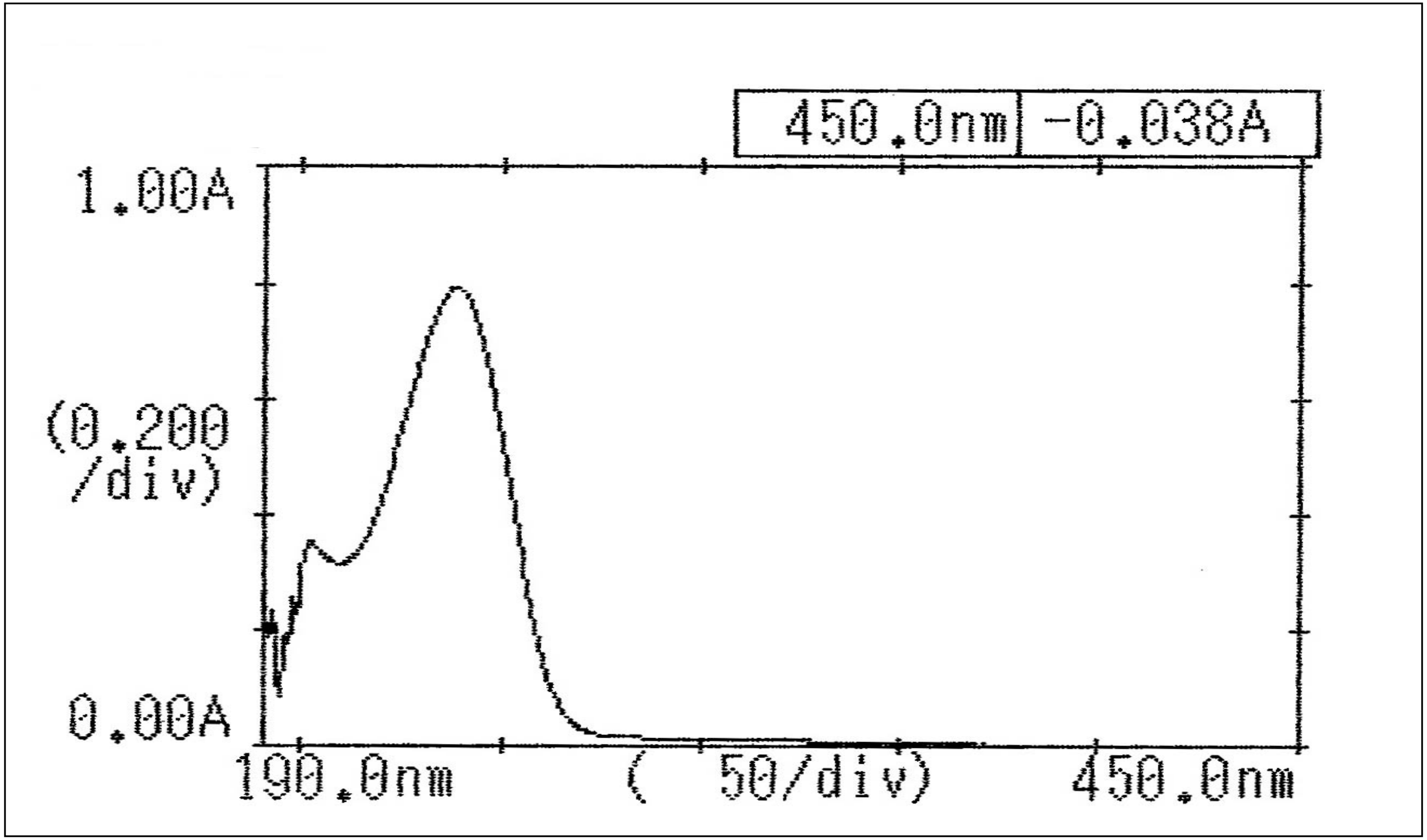


Figure 129 UV (CH_3OH) spectrum of **GF2**

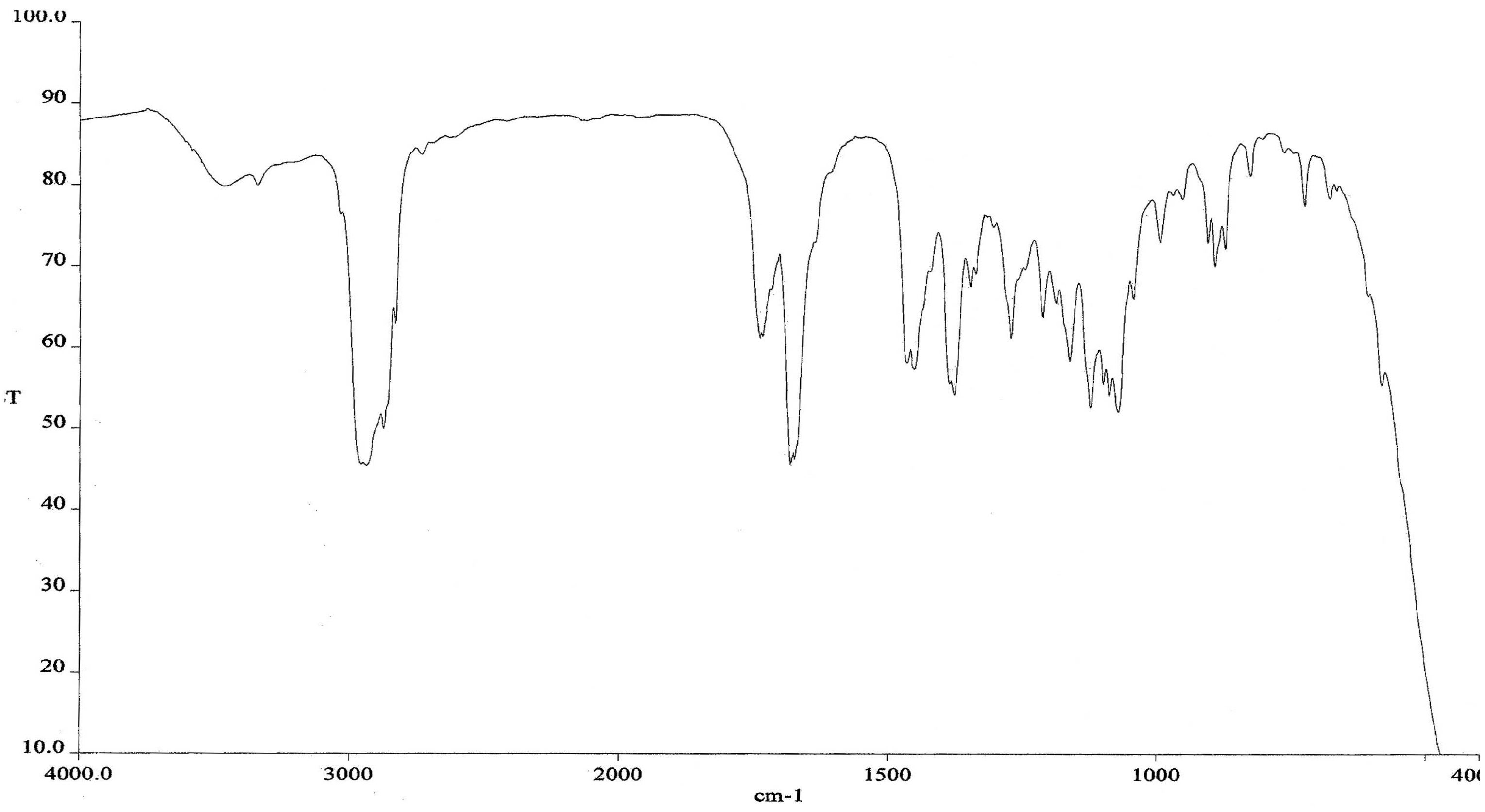


Figure 130 FT-IR (neat) spectrum of **GF2**

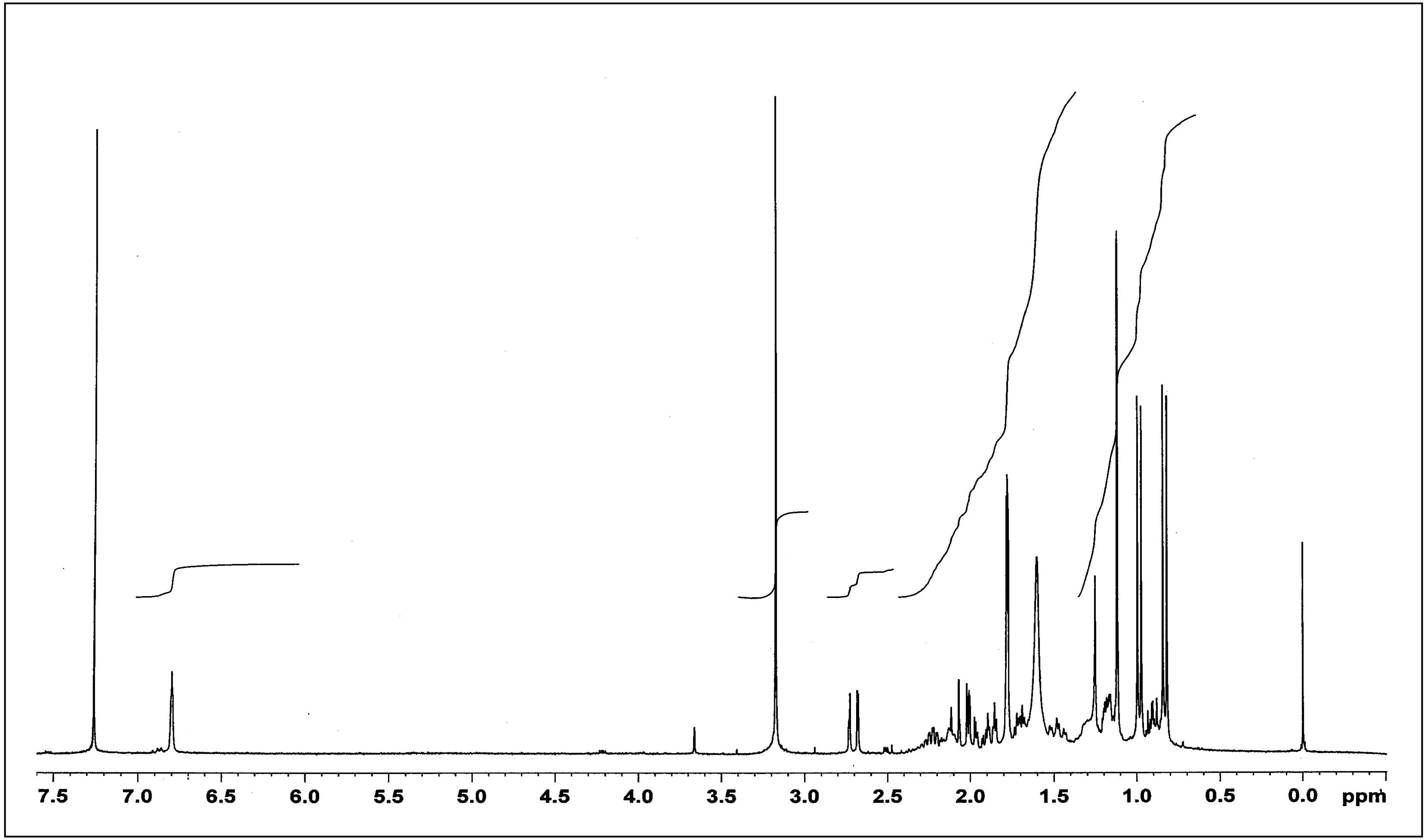


Figure 131 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of **GF2**

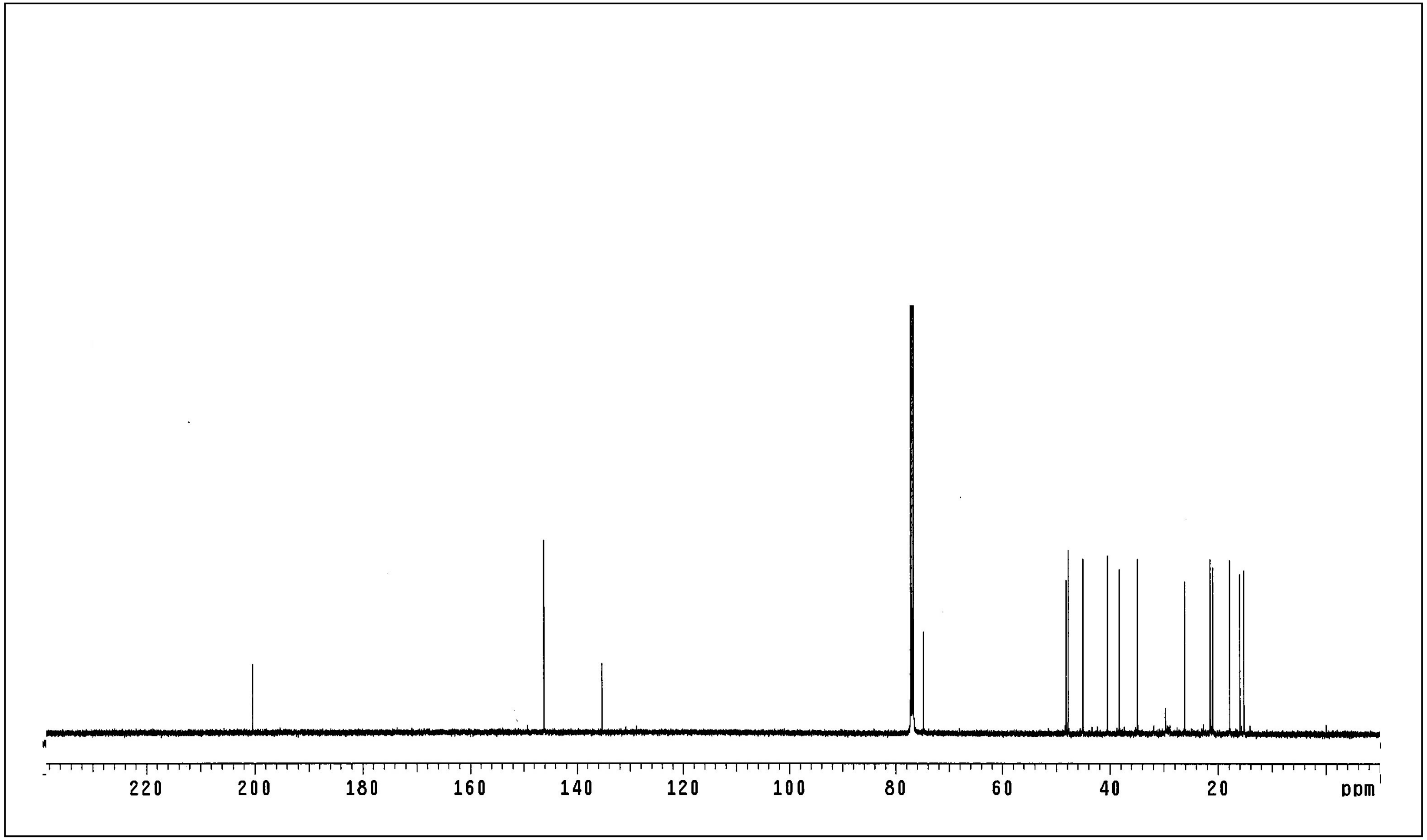


Figure 132 ^{13}C NMR (125 MHz) (CDCl$_3$) spectrum of **GF2**

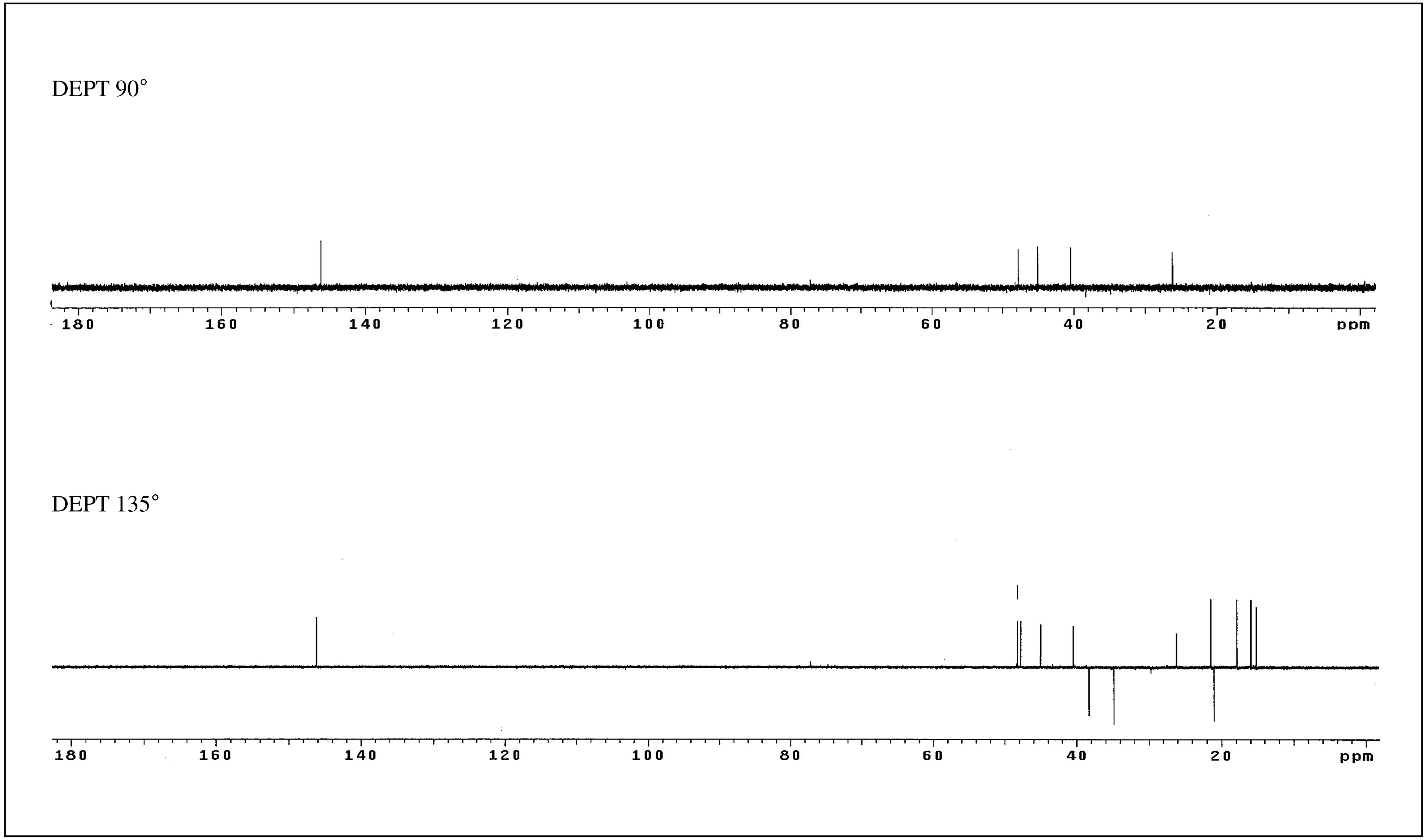


Figure 133 DEPT spectrum of **GF2**

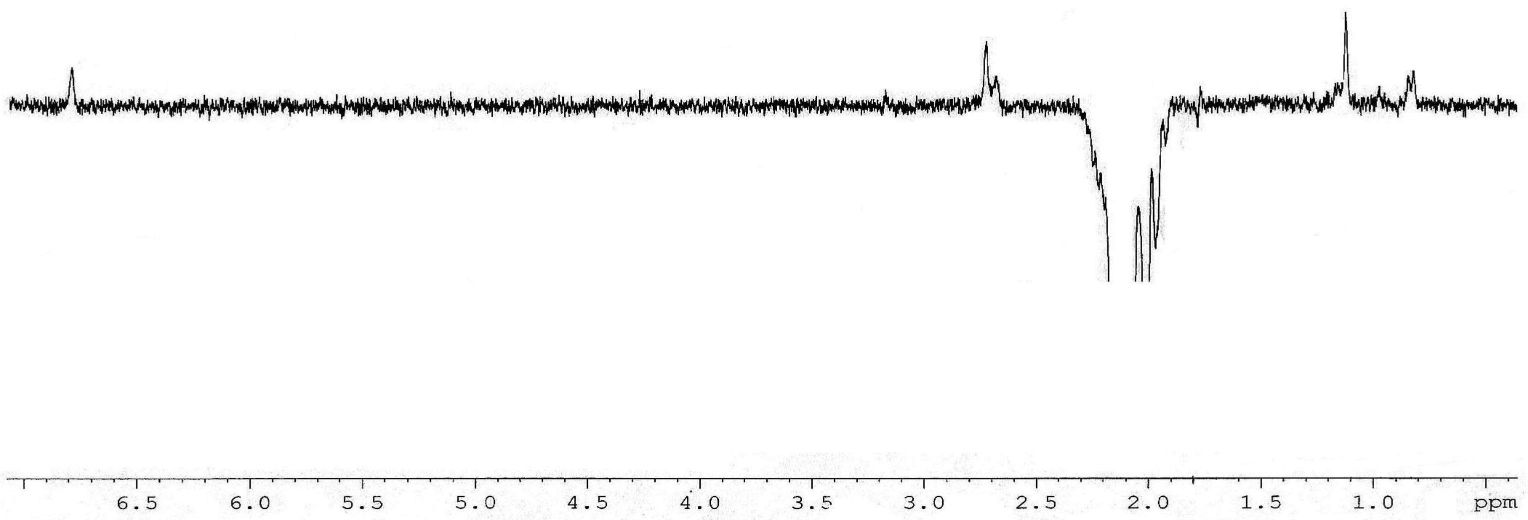


Figure 134 NOEDIFF spectrum of **GF2** after irradiation at δ_H 1.98

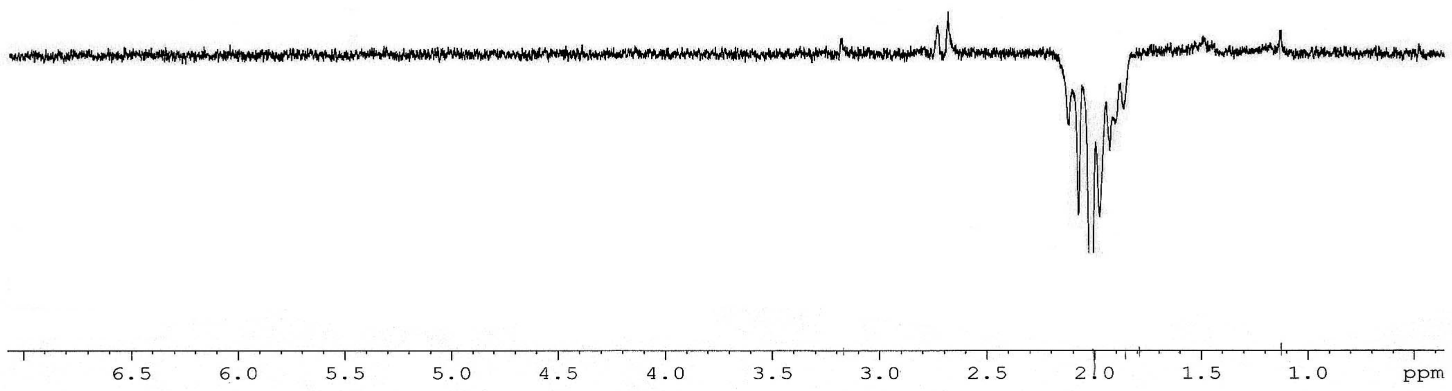


Figure 135 NOEDIFF spectrum of **GF2** after irradiation at δ_H 2.14

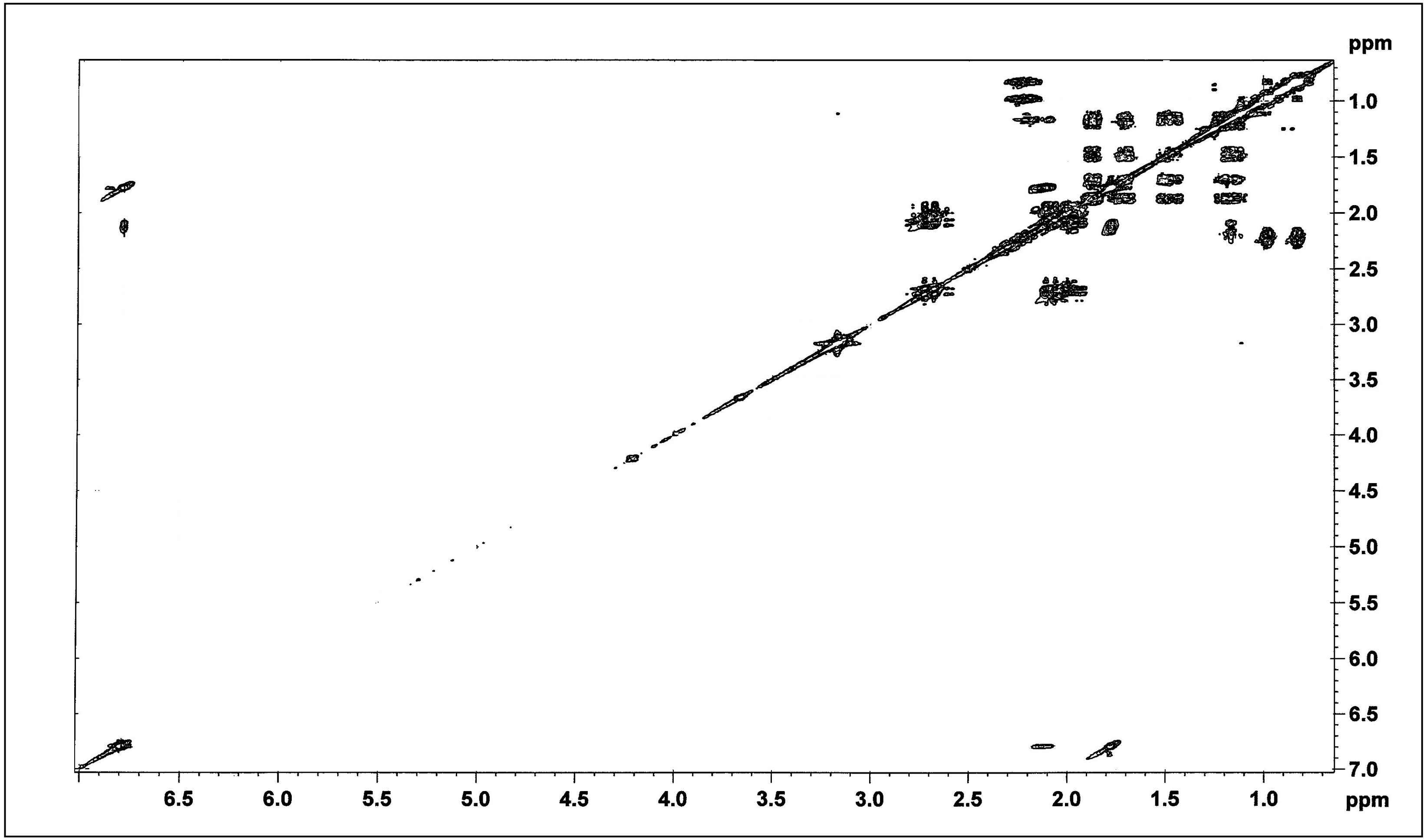


Figure 136 ^{1}H-^{1}H COSY spectrum of **GF2**

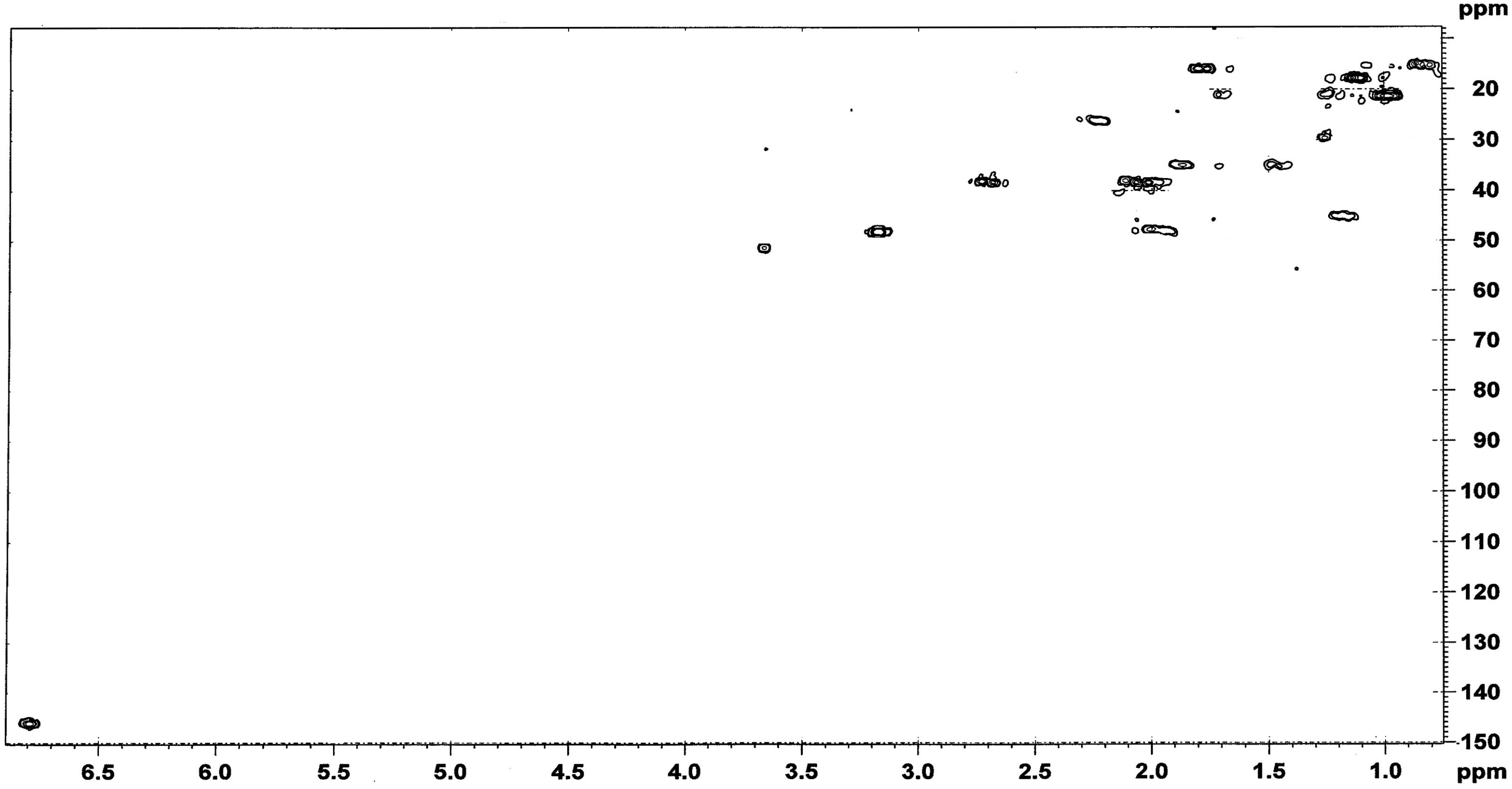


Figure 137 2D HMQC spectrum of **GF2**

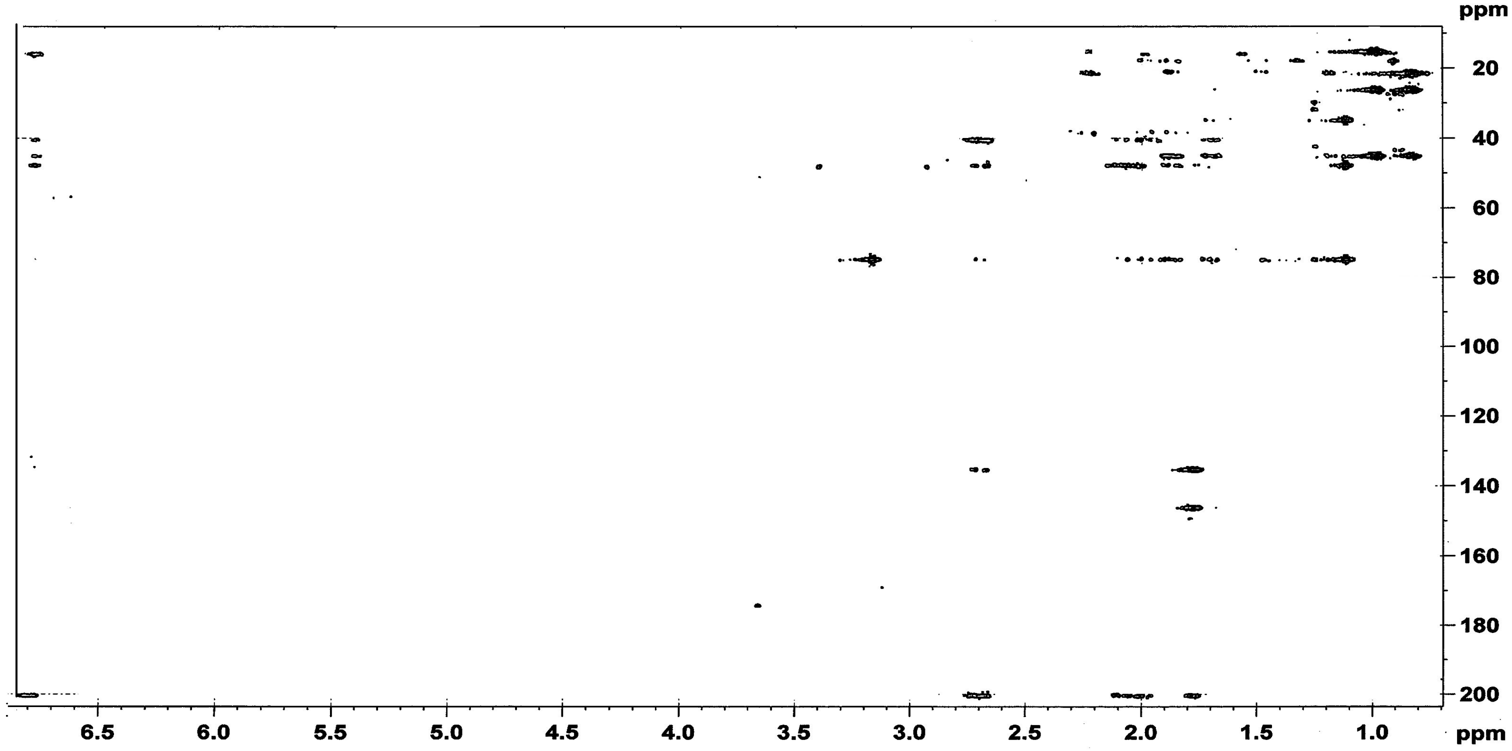


Figure 138 2D HMBC spectrum of **GF2**

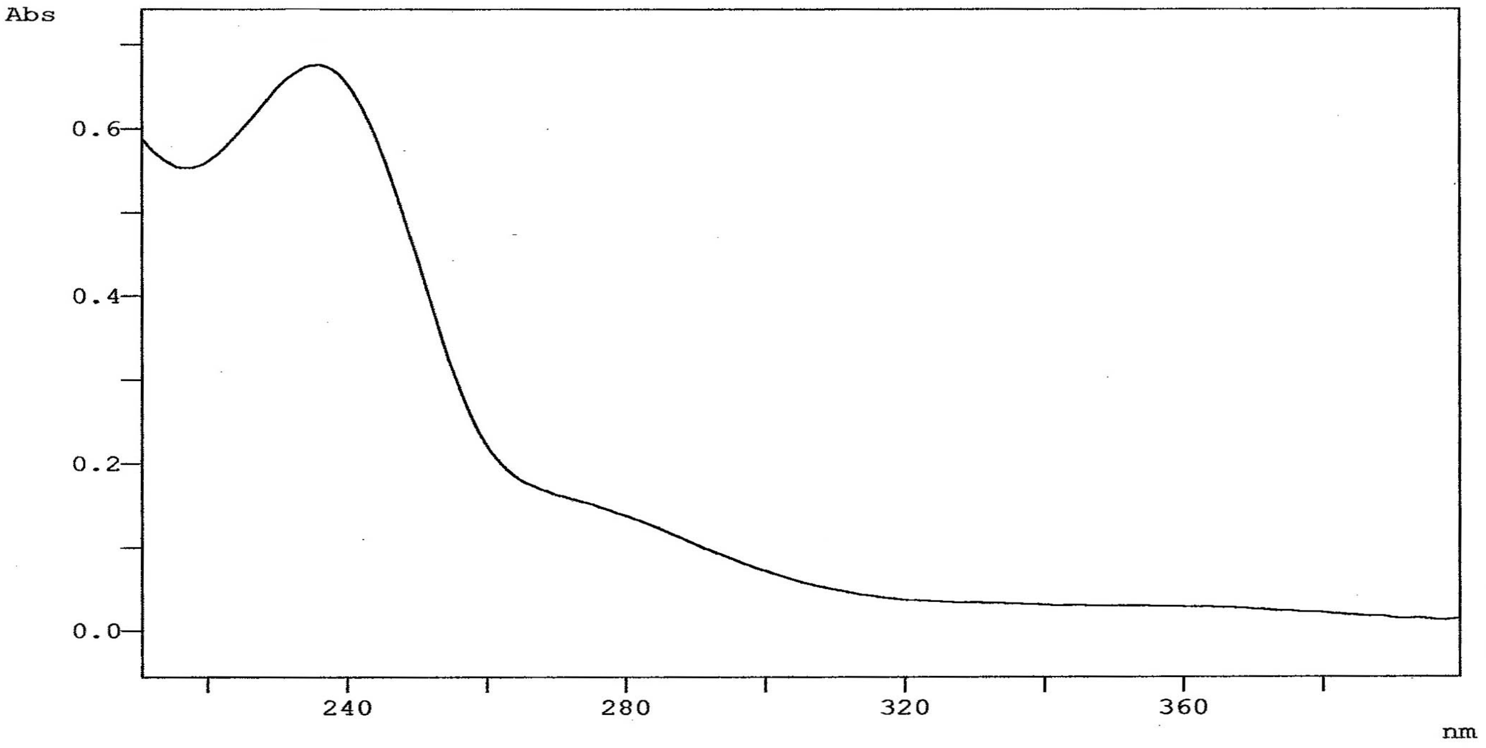


Figure 139 UV (CH_3OH) spectrum of **GF7**

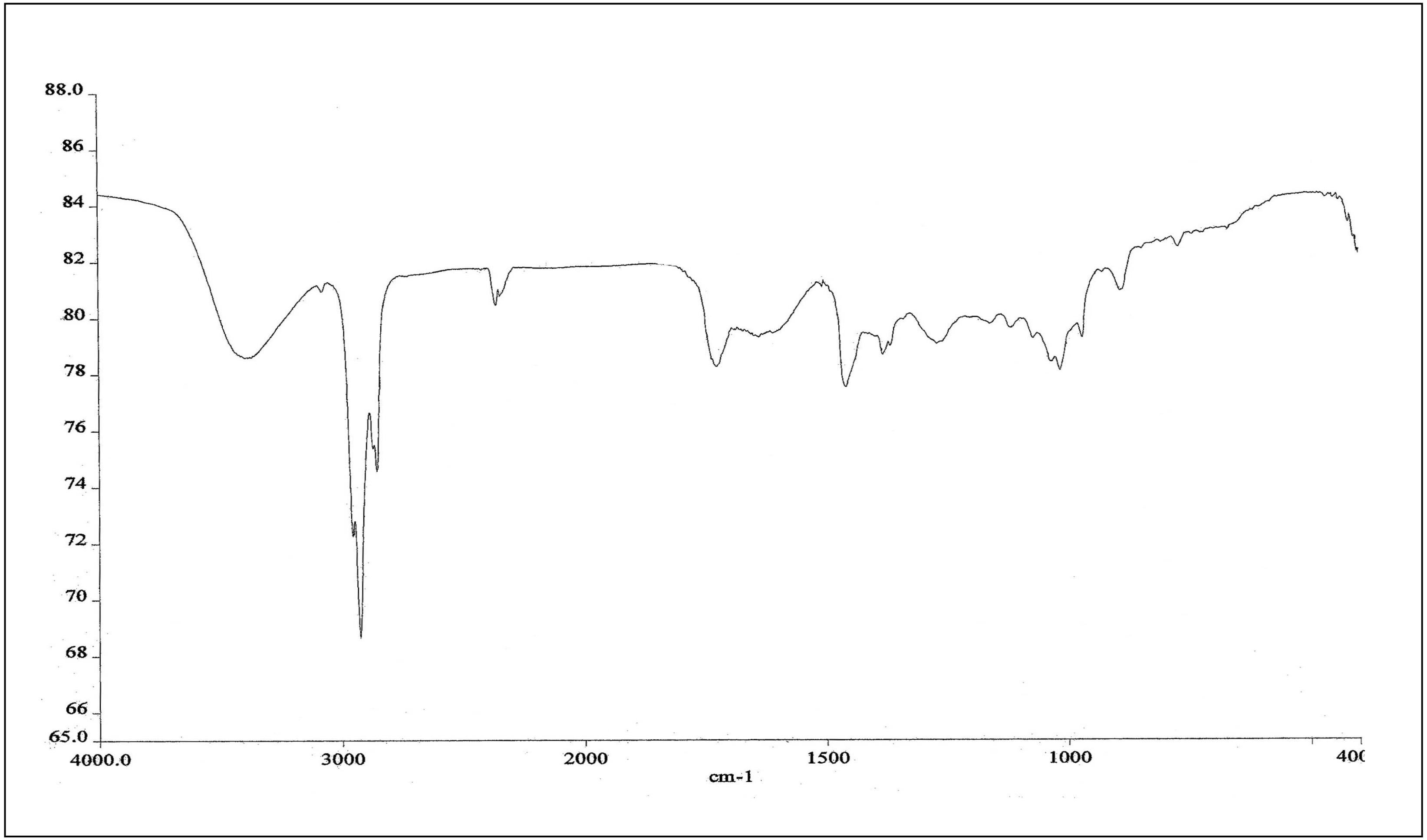


Figure 140 FT-IR (neat) spectrum of **GF7**

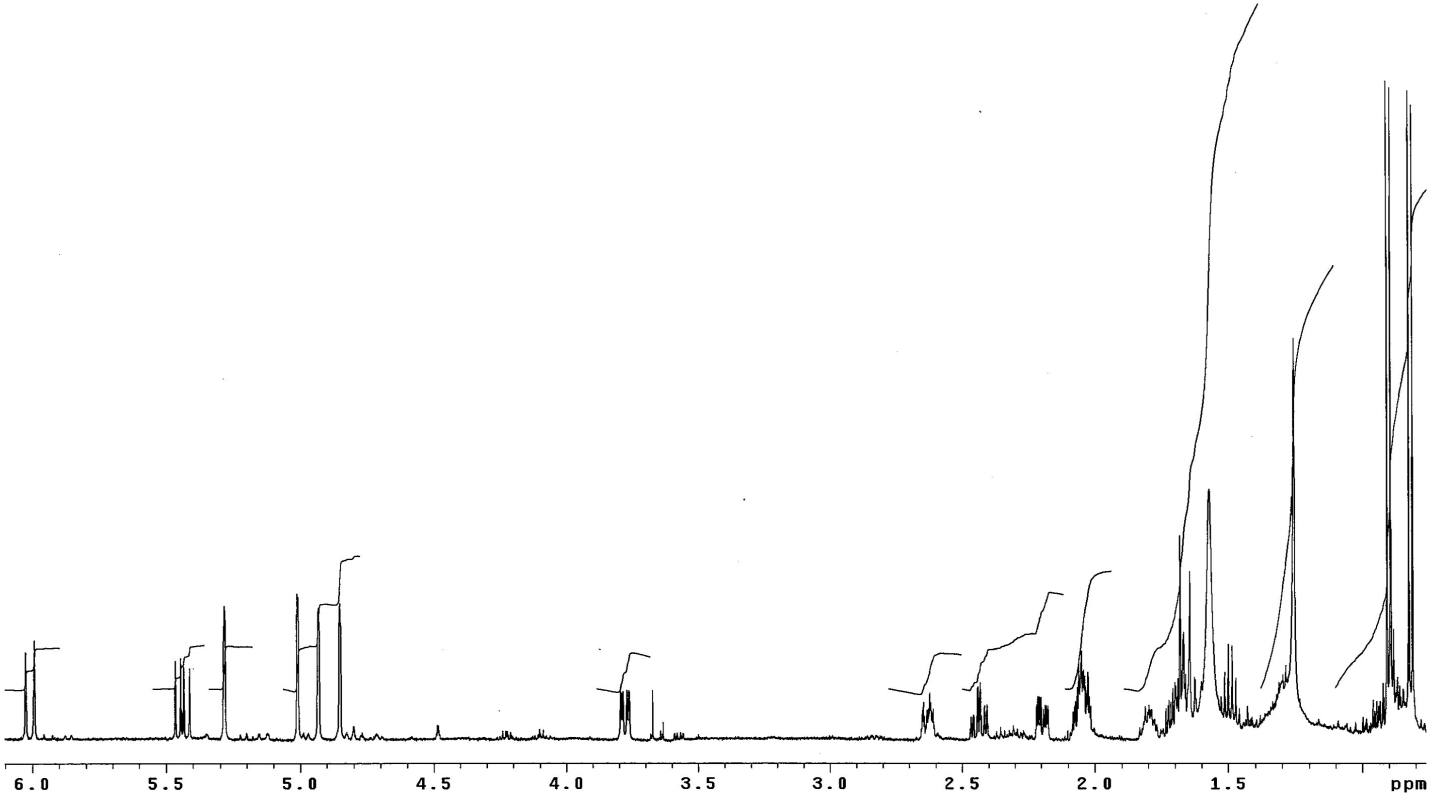


Figure 141 ^{1}H NMR (500 MHz) (CDCl$_3$) spectrum of **GF7**

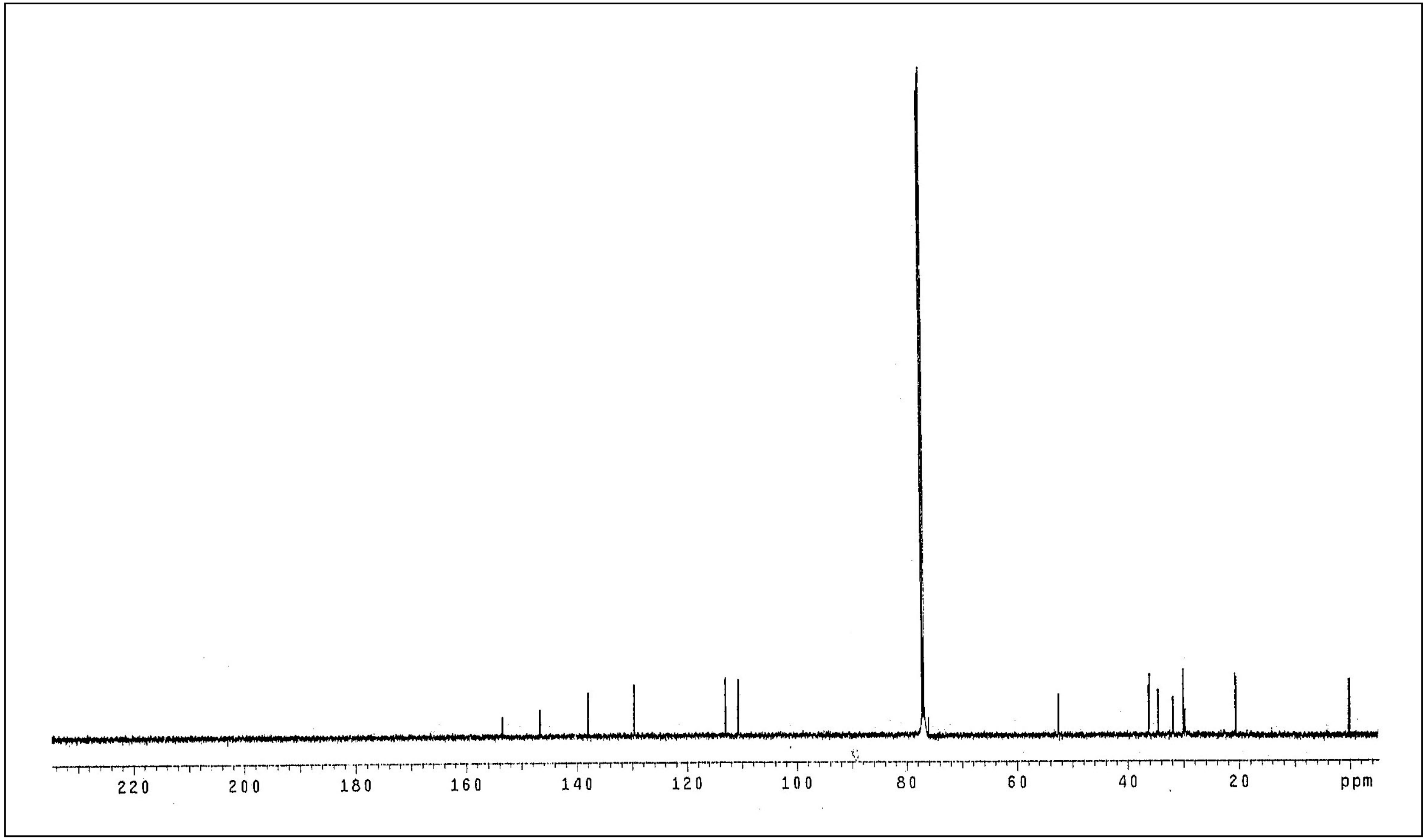


Figure 142 ^{13}C NMR (125 MHz) (CDCl$_3$) spectrum of **GF7**

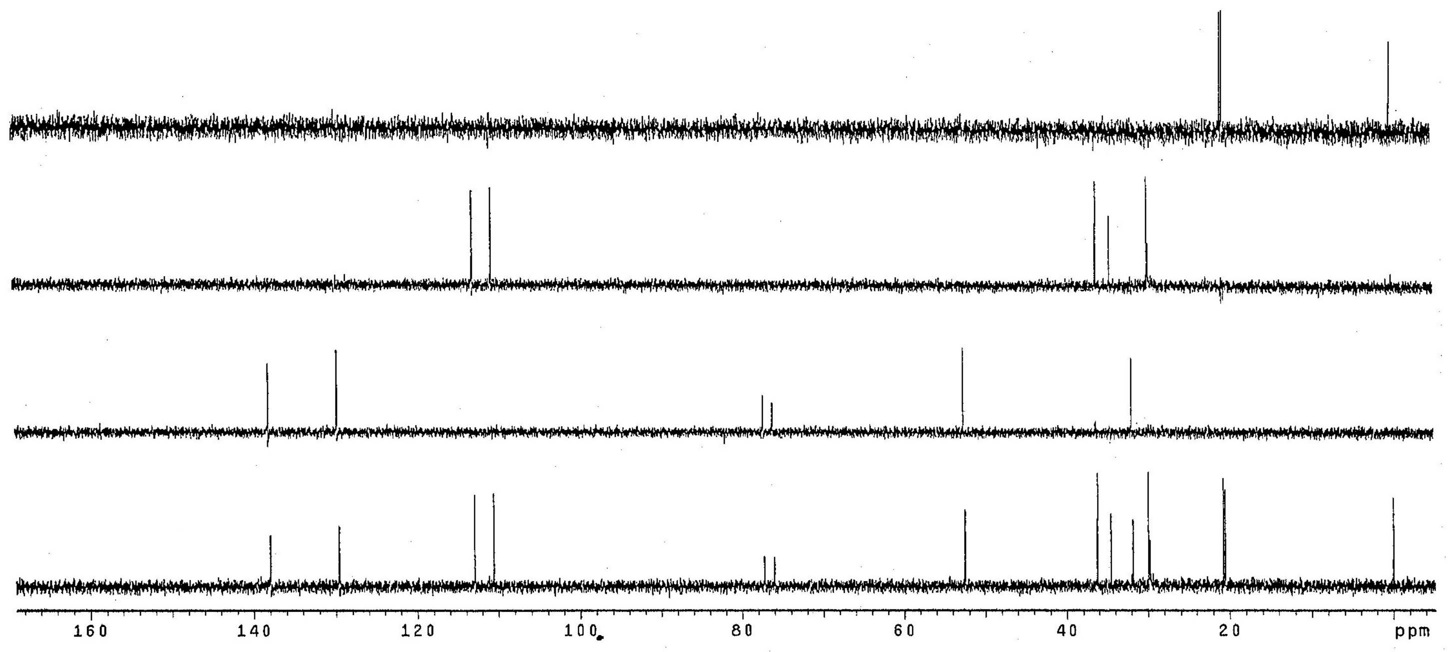


Figure 143 DEPT spectrum of **GF7**

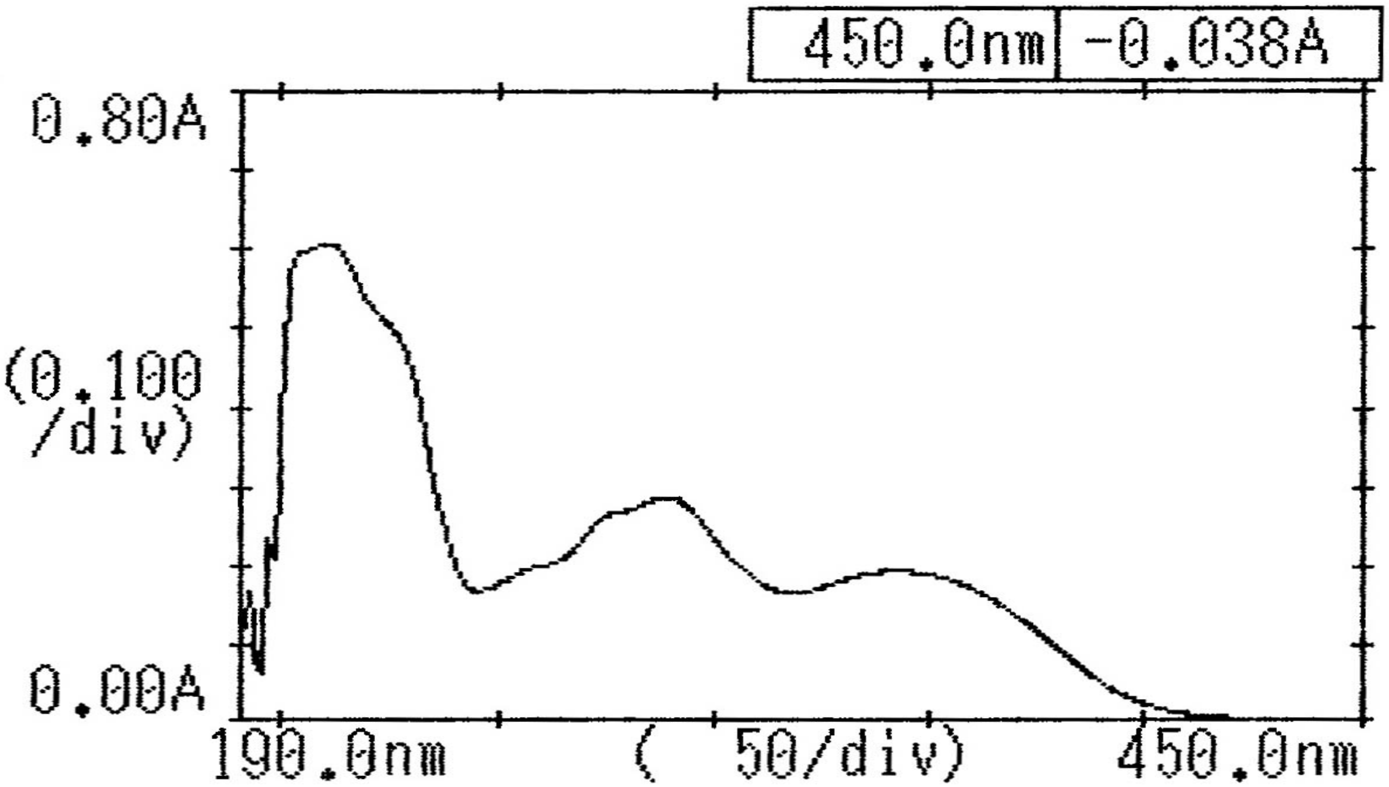


Figure 144 UV (CH_3OH) spectrum of **GF23**

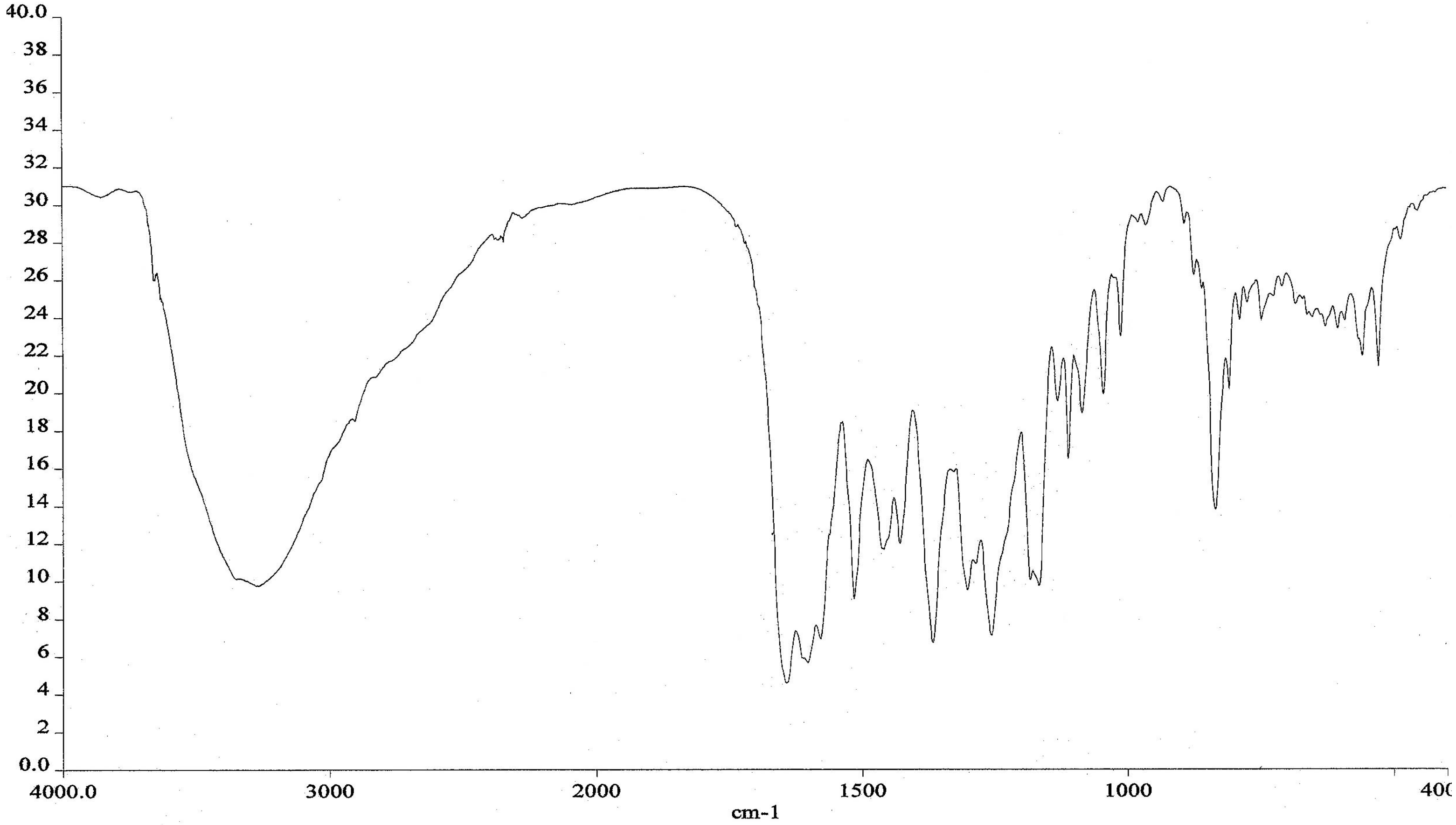


Figure 145 FT-IR (neat) spectrum of **GF23**

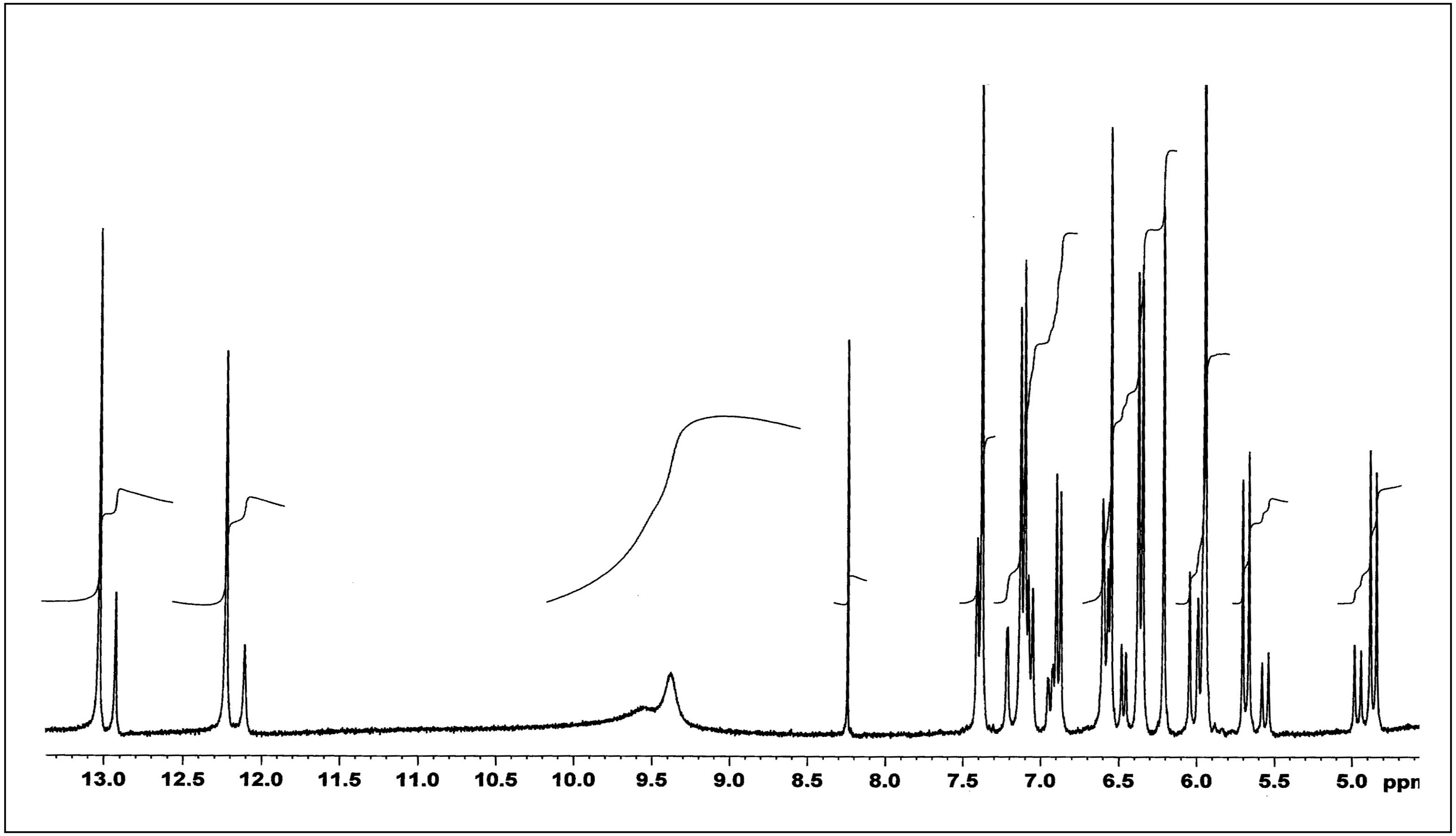


Figure 146 ^{1}H NMR (300 MHz) (DMSO-d_6) spectrum of **GF23**

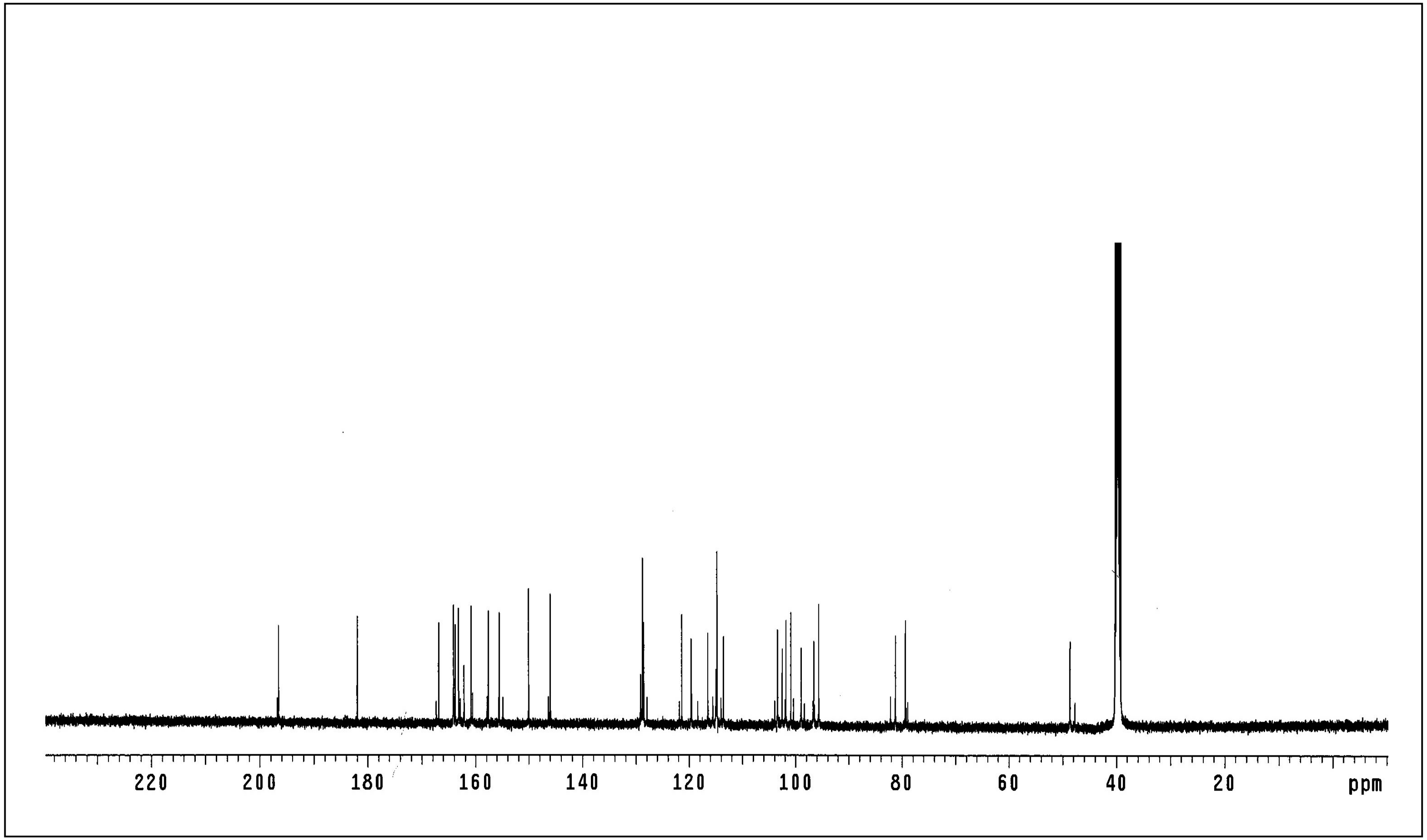


Figure 147 ^{13}C NMR (125 MHz) (DMSO-d_6) spectrum of **GF23**

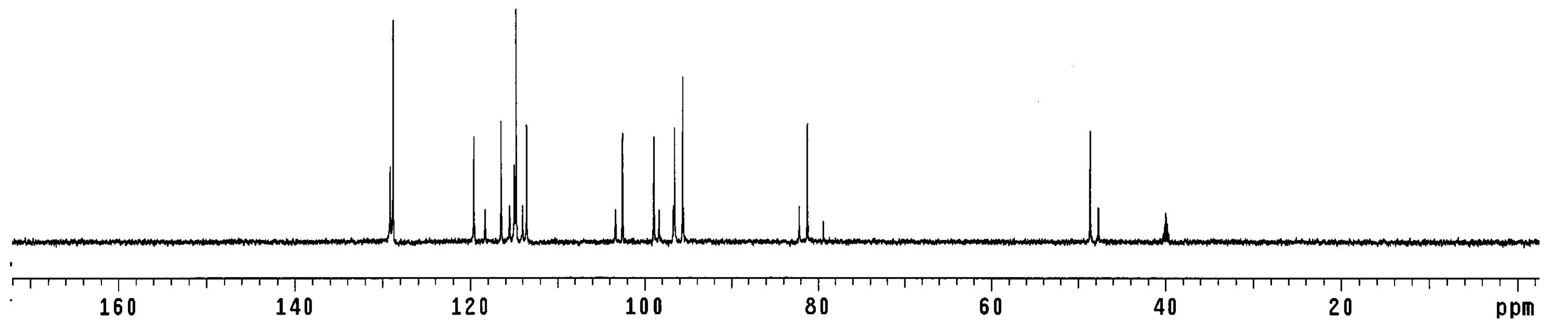


Figure 148 DEPT spectrum of **GF23**

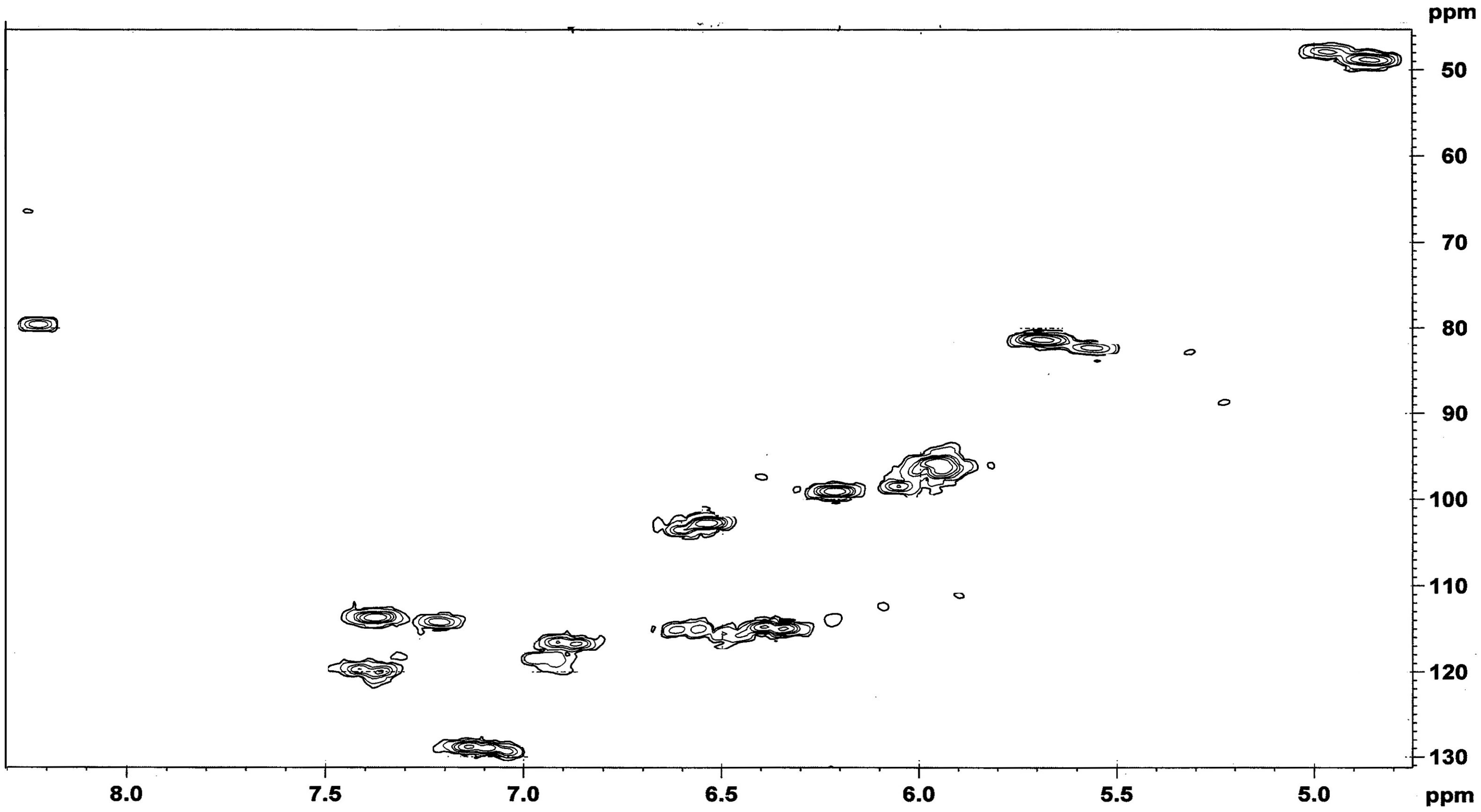


Figure 149 2D HMQC spectrum of **GF23**

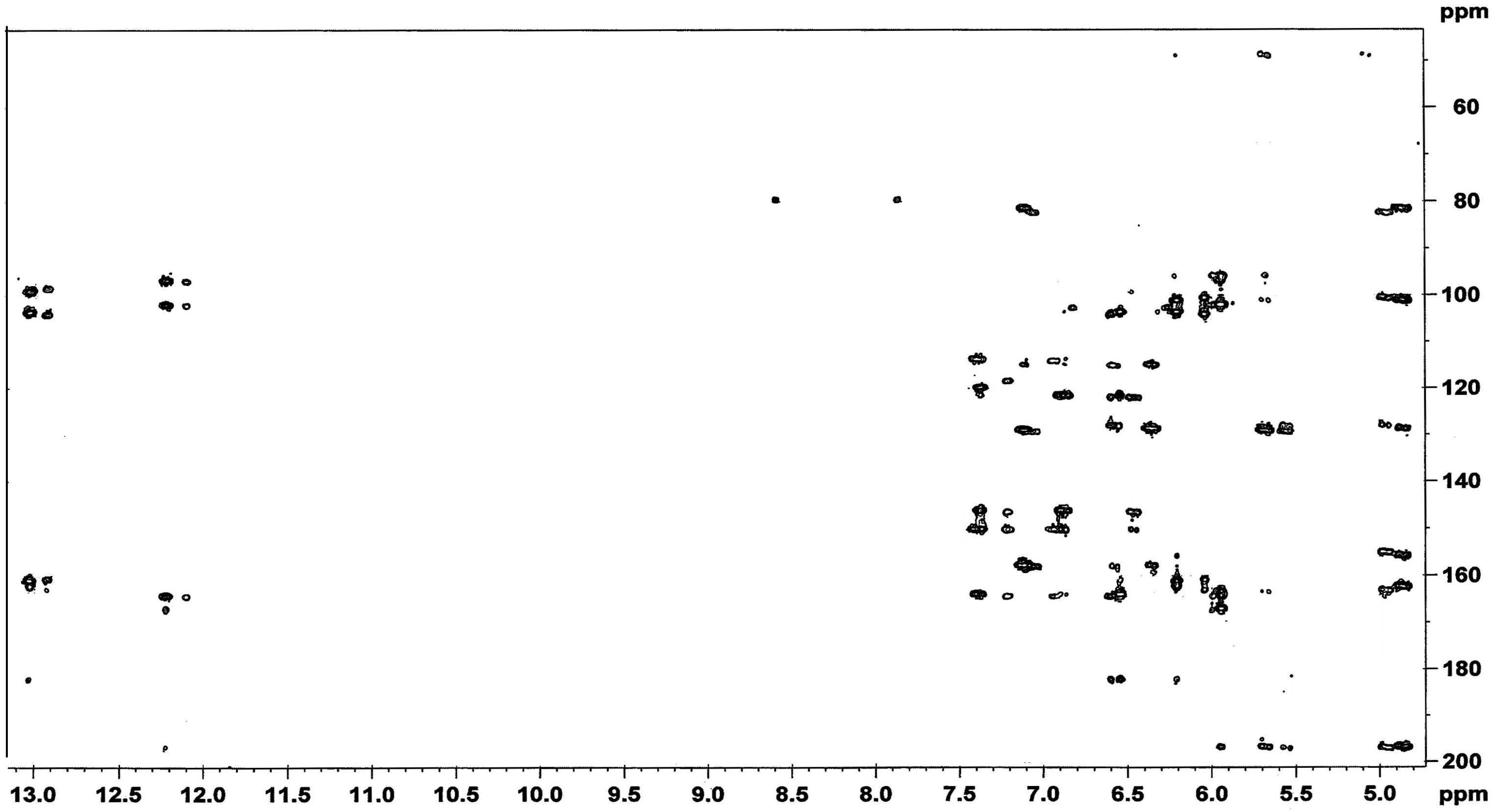


Figure 150 2D HMBC spectrum of **GF23**

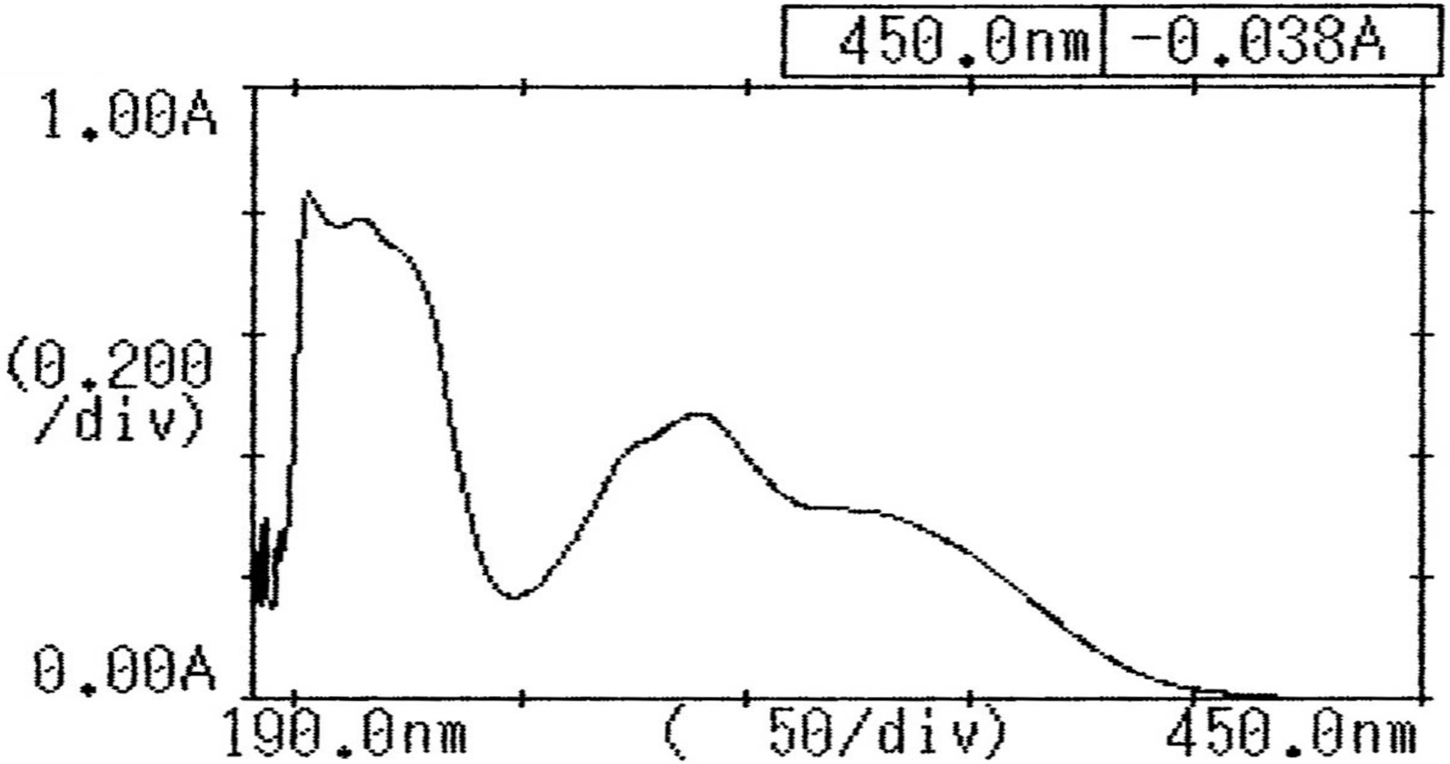


Figure 151 UV (CH_3OH) spectrum of **GF24**

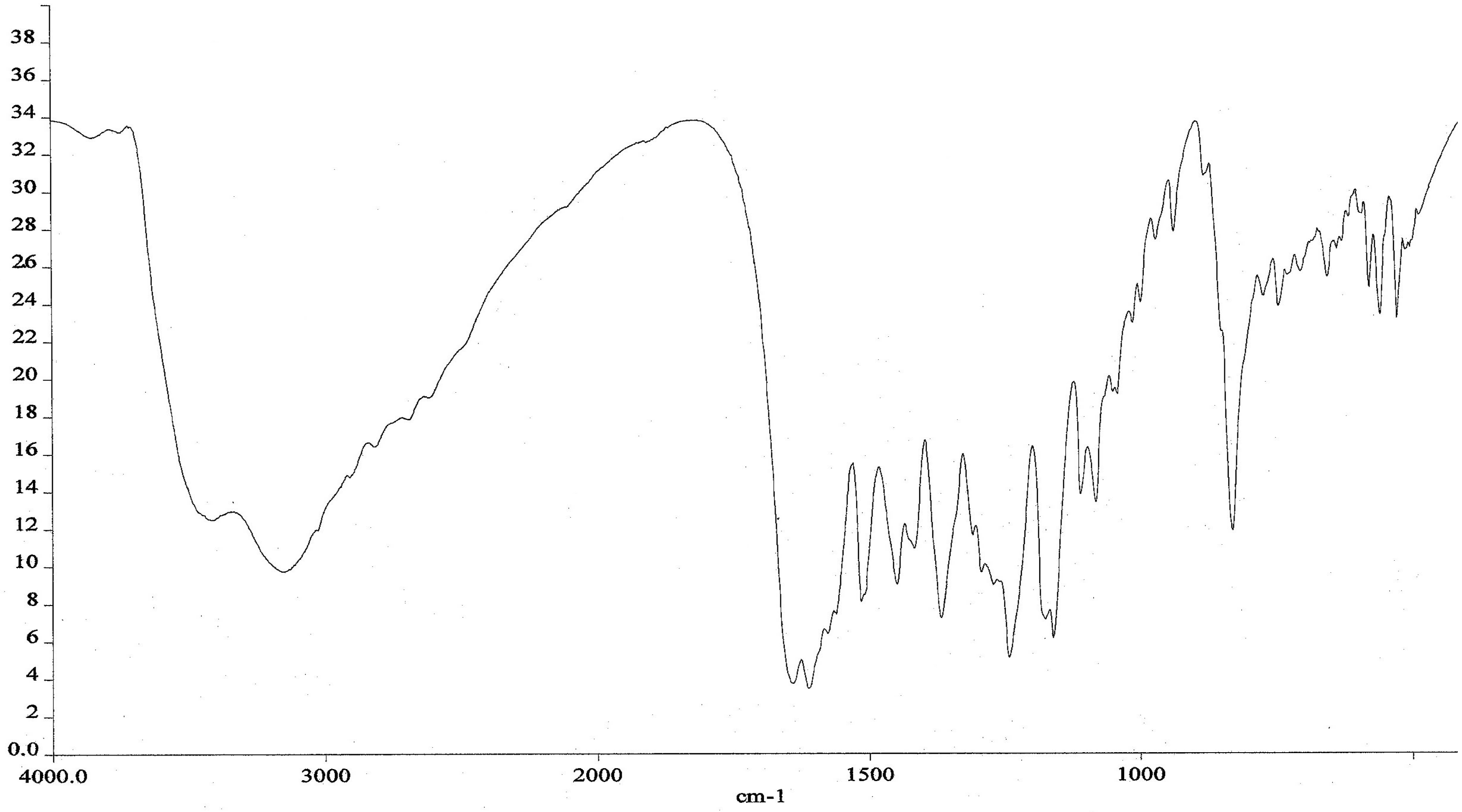


Figure 152 FT-IR (neat) spectrum of **GF24**

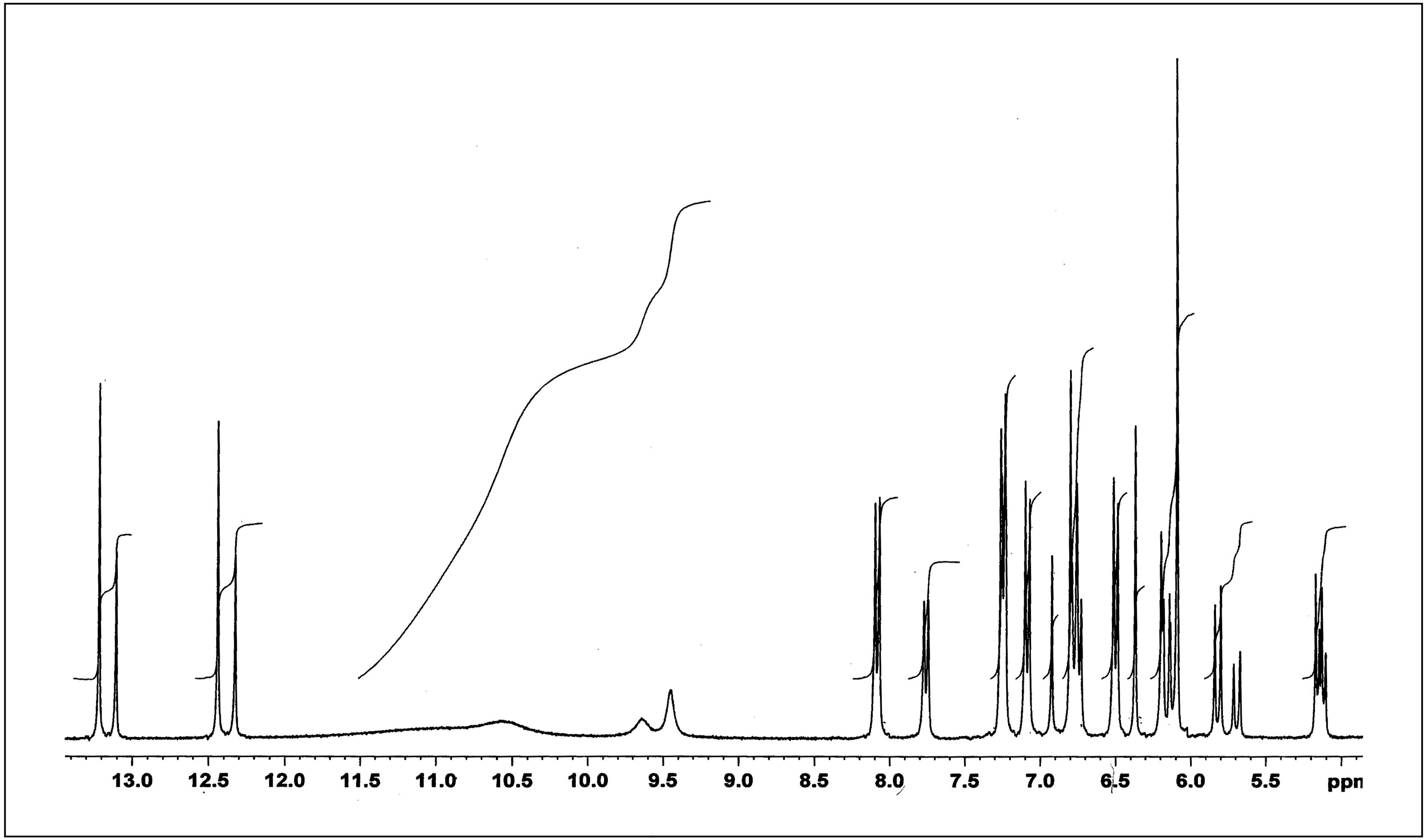


Figure 153 ^{1}H NMR (300 MHz) (DMSO-d_6) spectrum of **GF24**

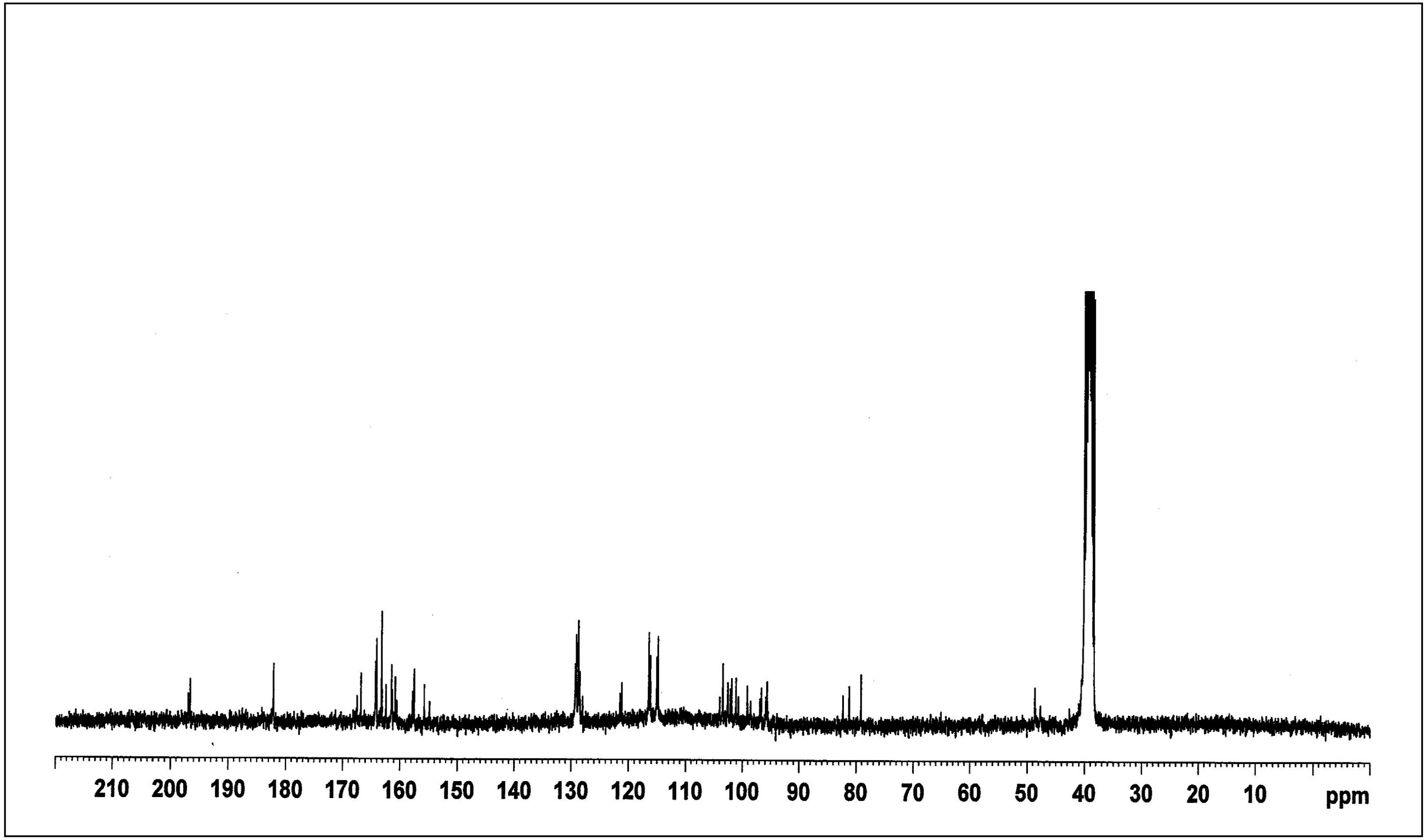


Figure 154 ^{13}C NMR (75 MHz) (DMSO-d_6) spectrum of **GF24**

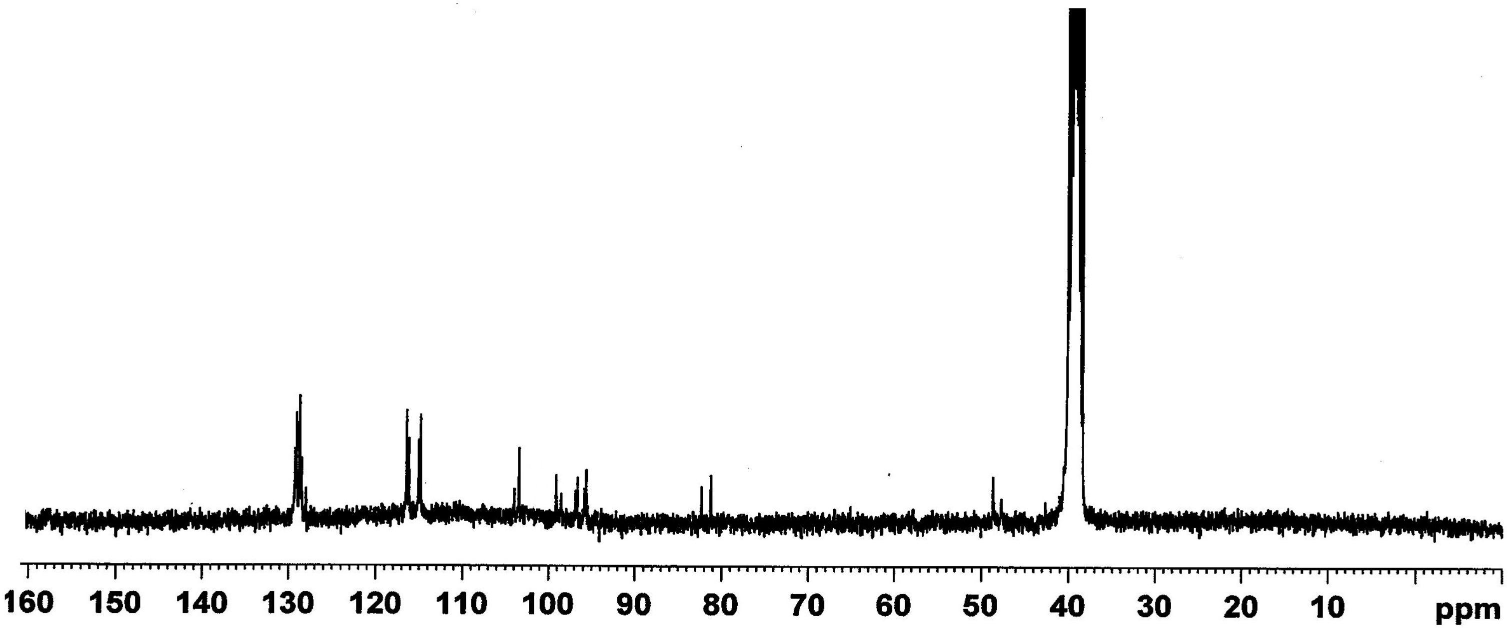


Figure 155 DEPT spectrum of **GF24**

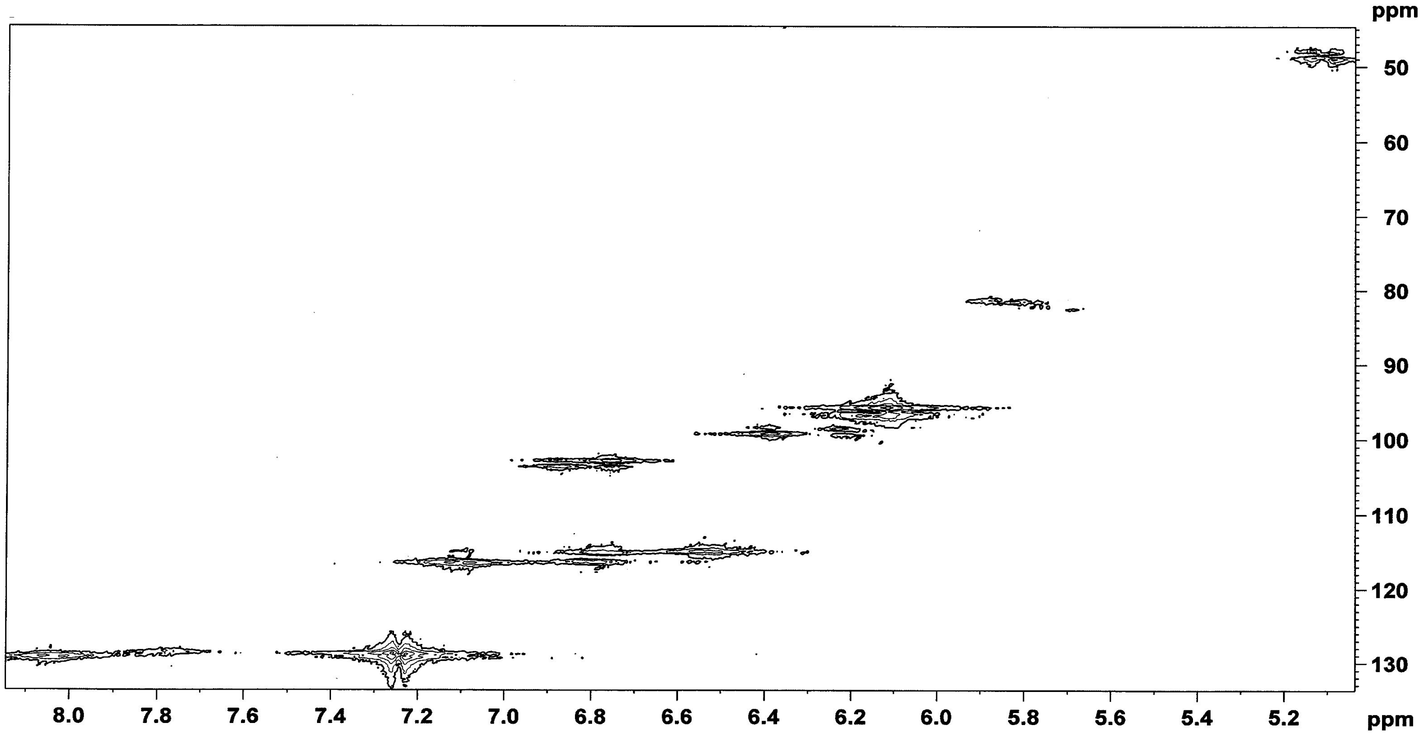


Figure 156 2D HMQC spectrum of **GF24**

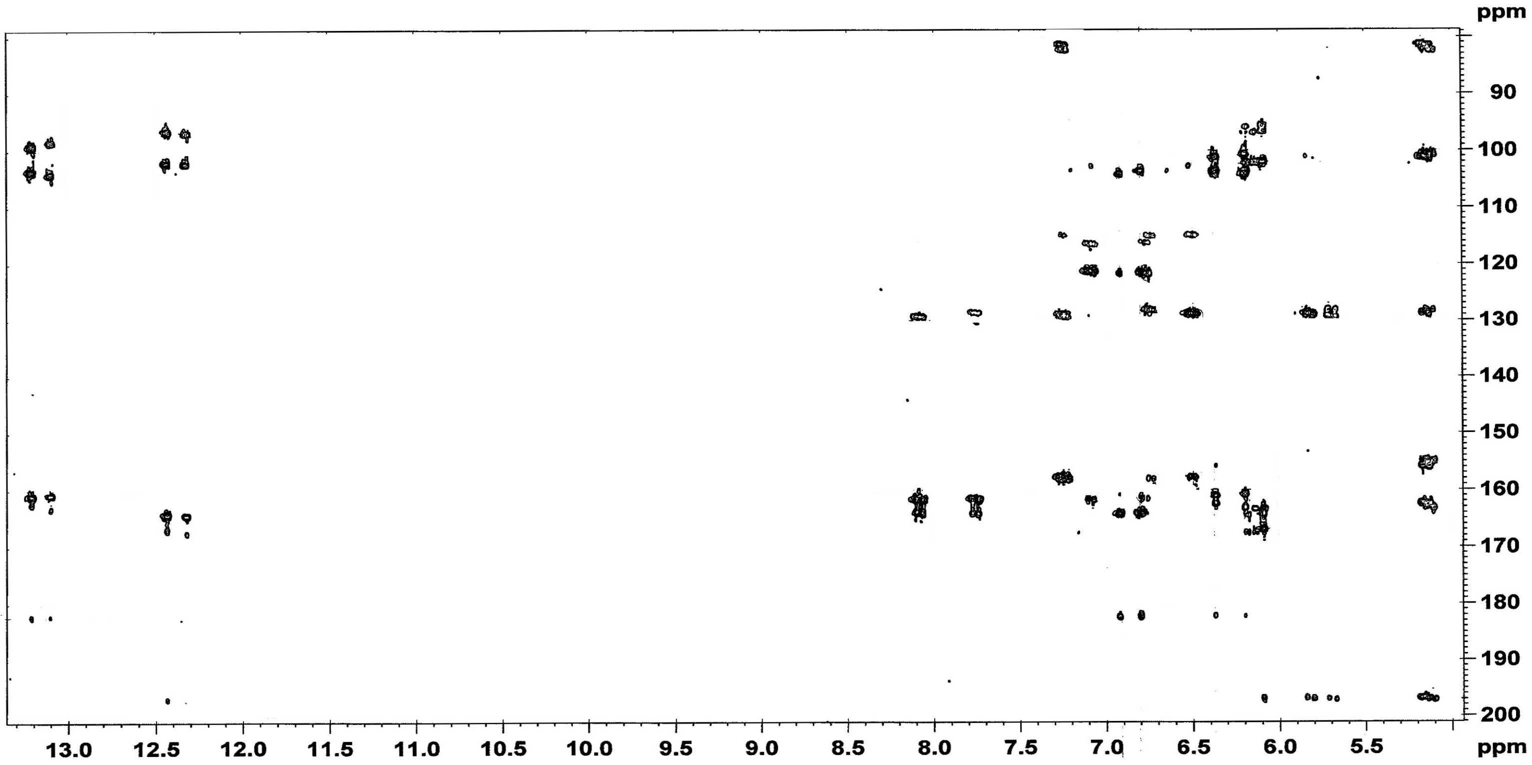


Figure 157 2D HMBC spectrum of **GF24**

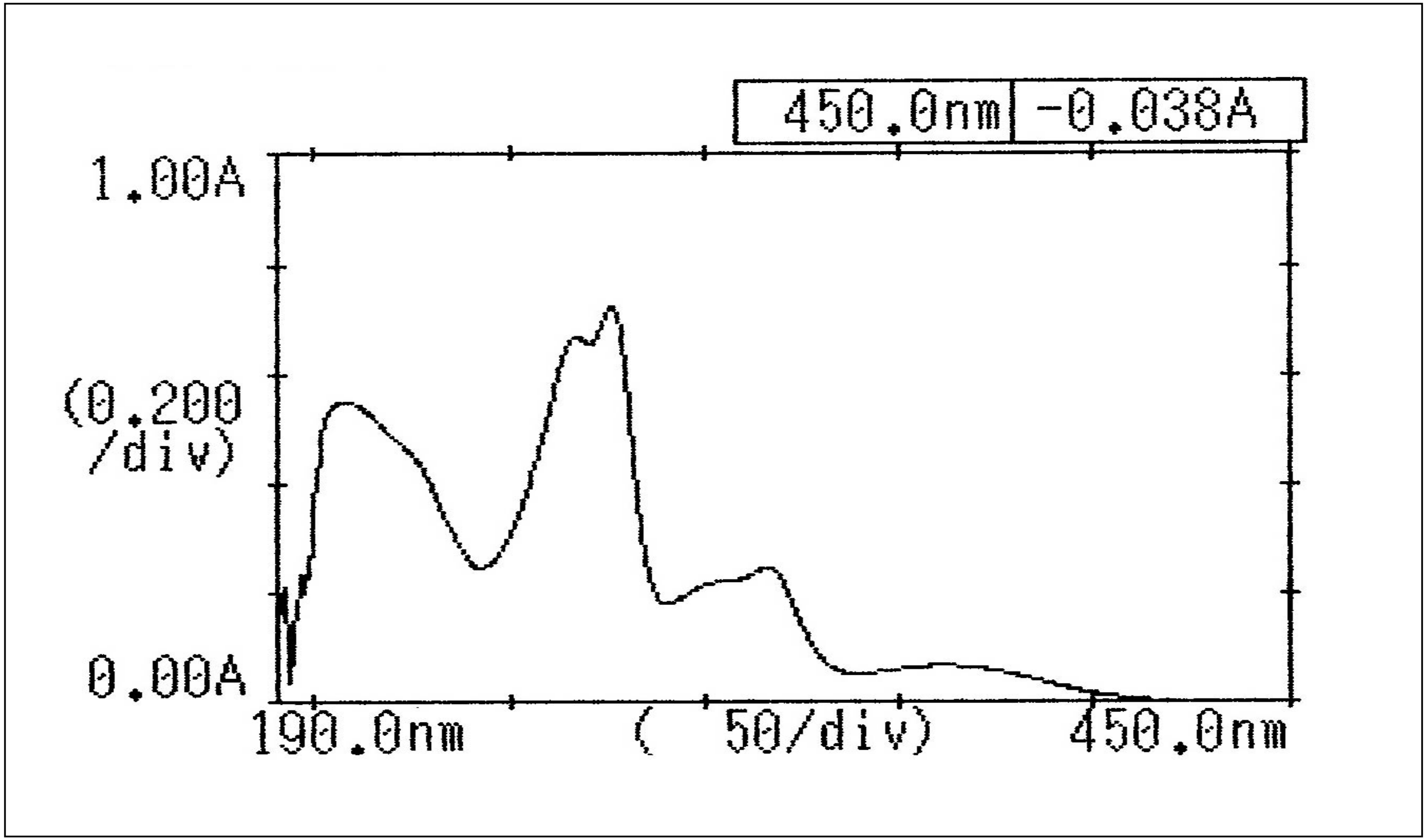


Figure 158 UV (CH_3OH) spectrum of **GF28**

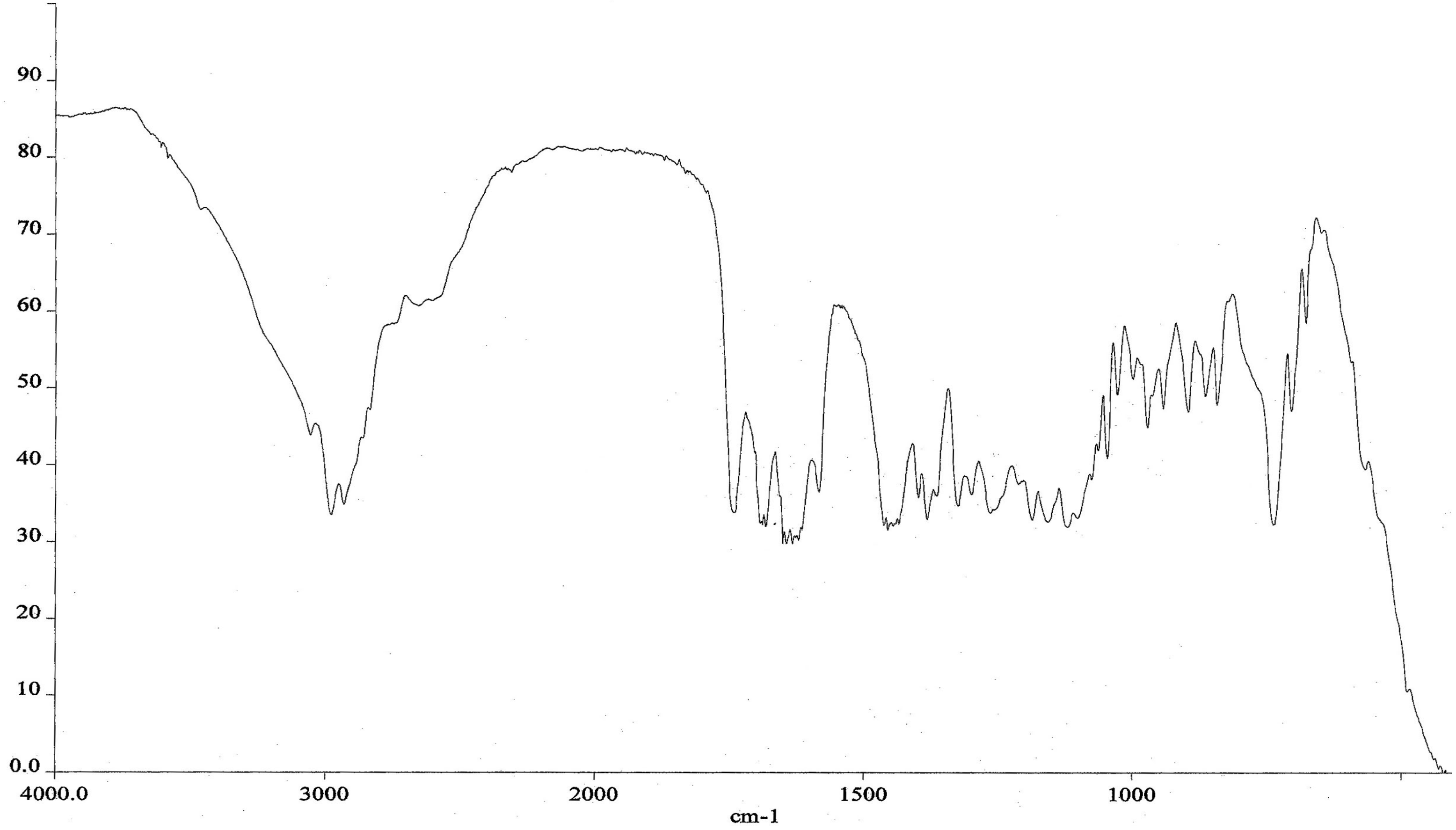


Figure 159 FT-IR (neat) spectrum of **GF28**

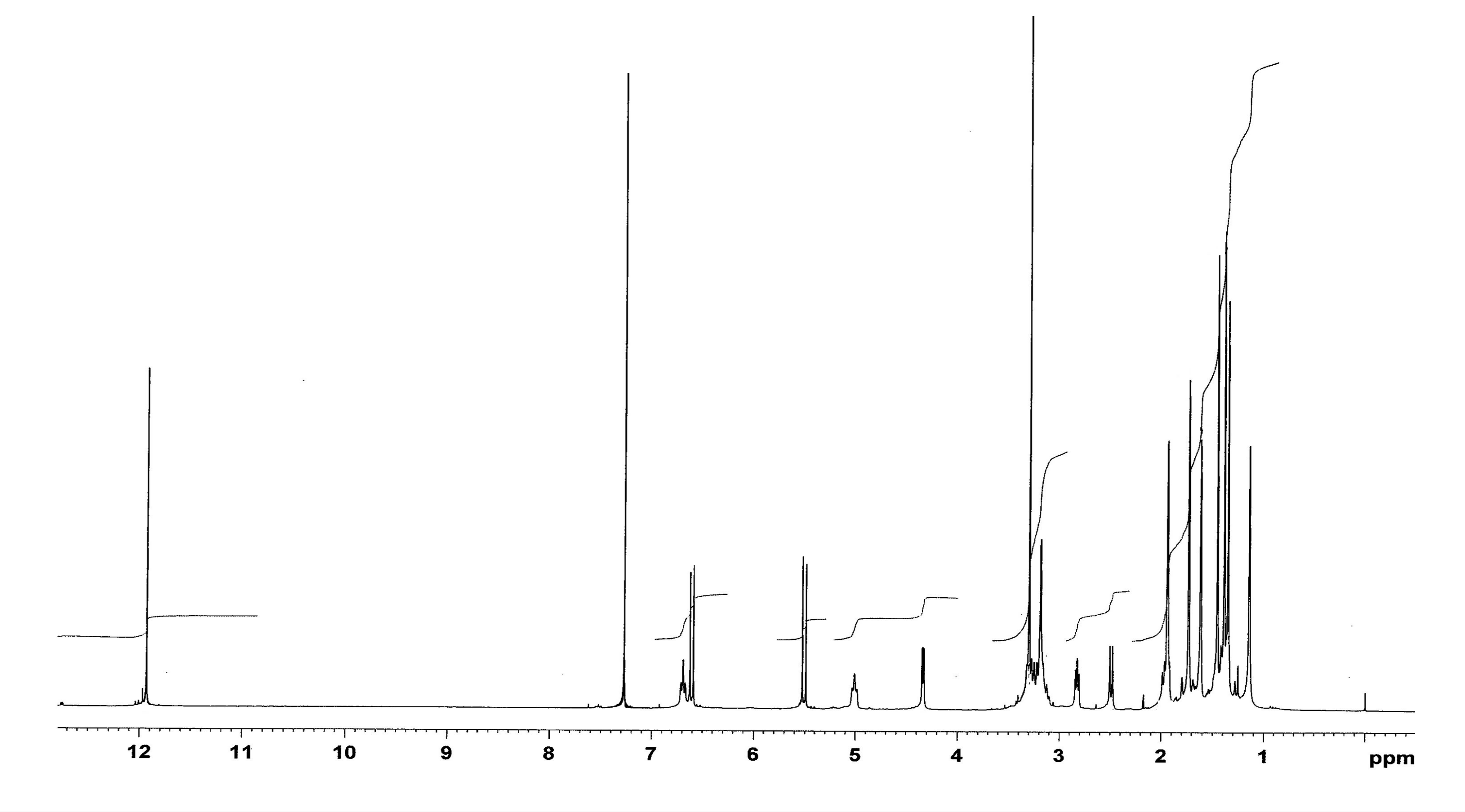


Figure 160 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of **GF28**

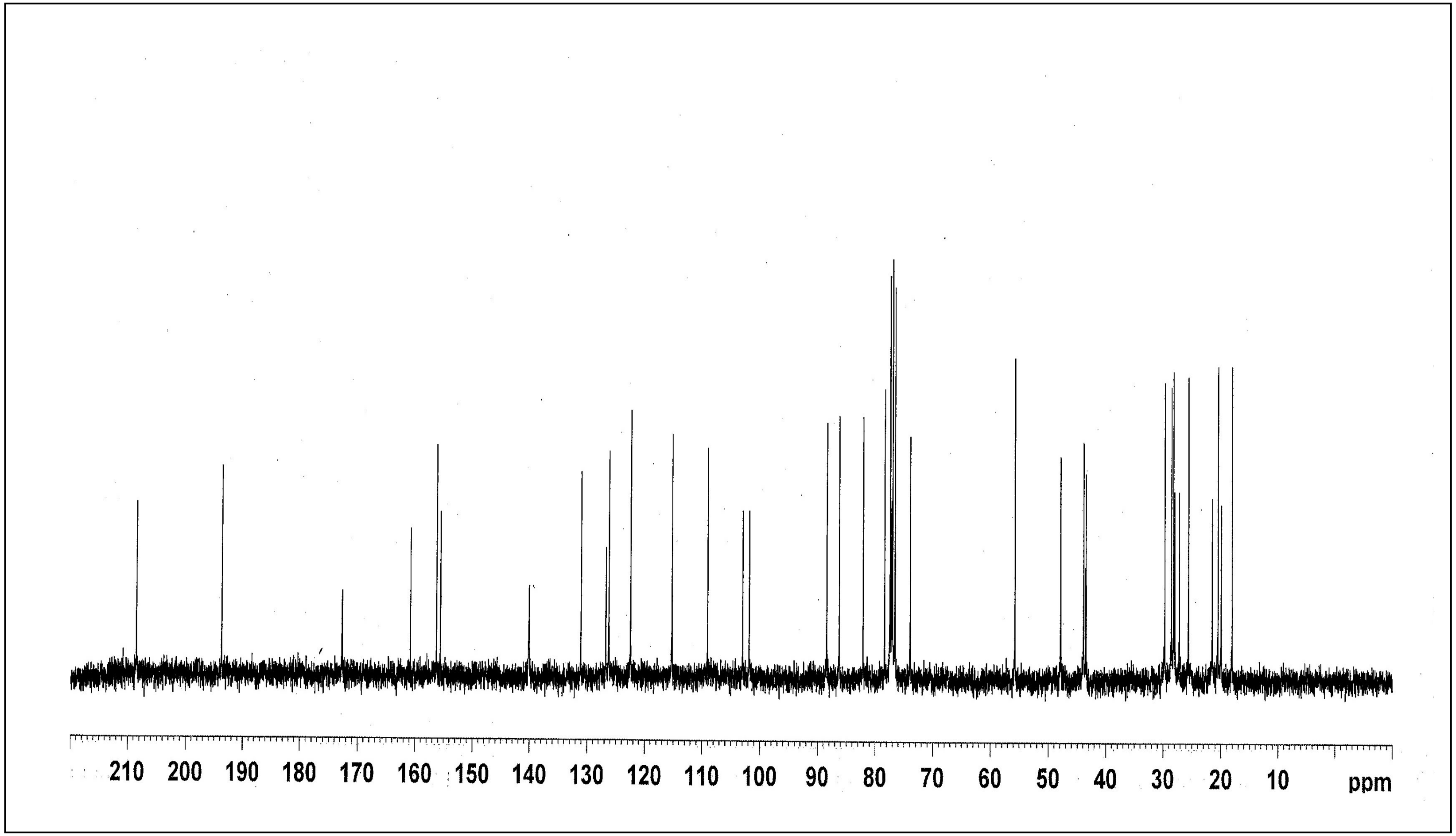


Figure 161 ^{13}C NMR (75 MHz) (CDCl$_3$) spectrum of **GF28**

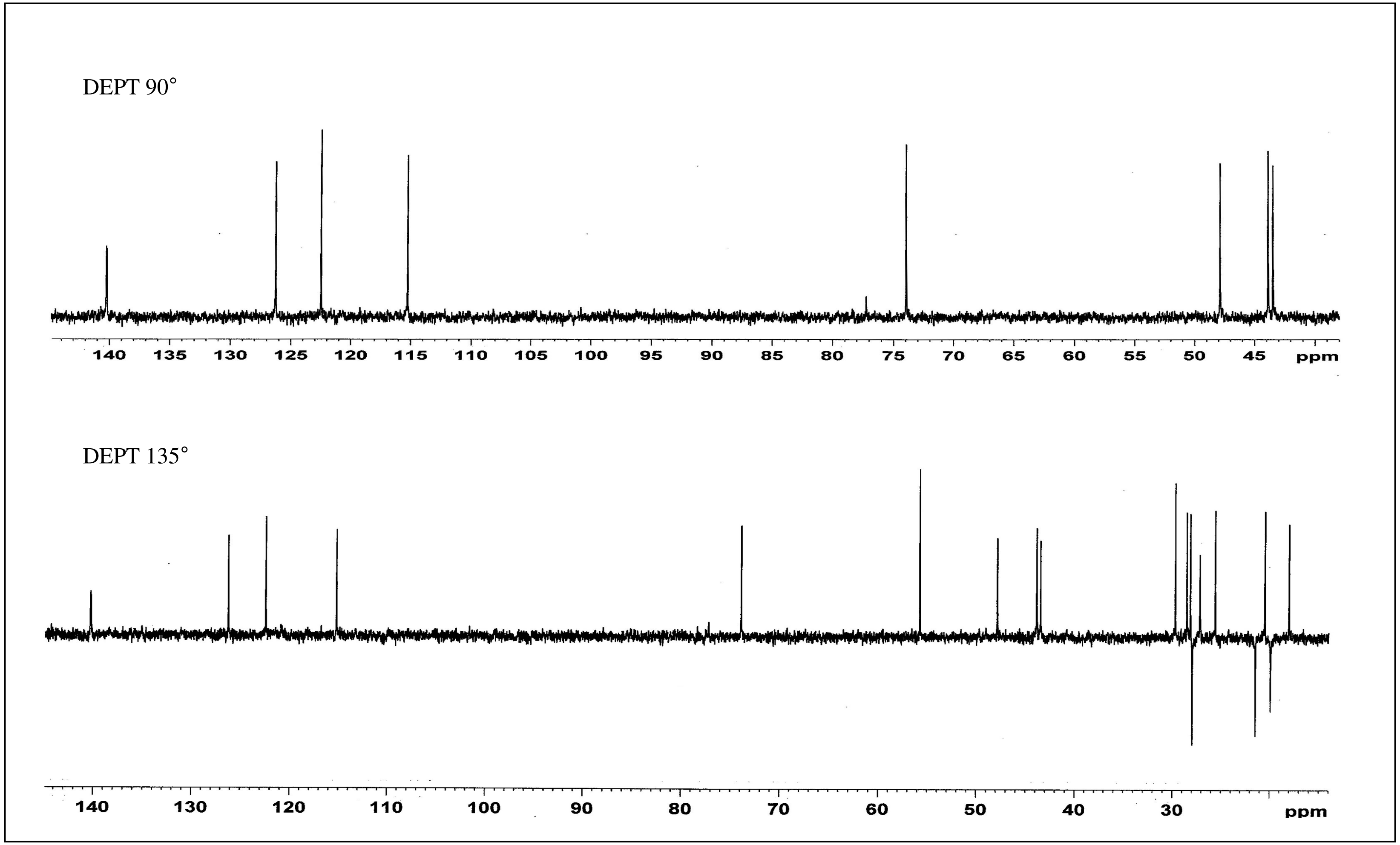


Figure 162 DEPT spectrum of **GF28**

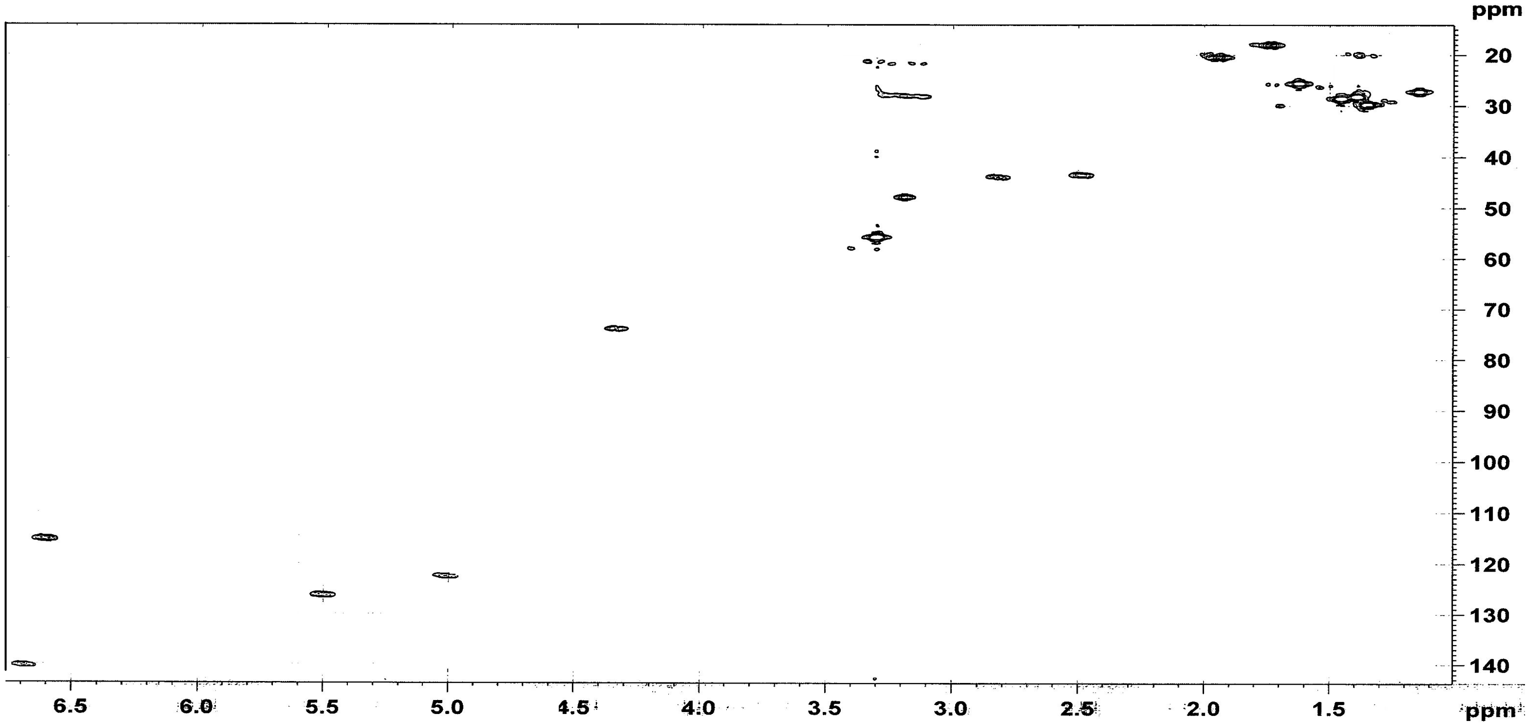


Figure 163 2D HMQC spectrum of **GF28**

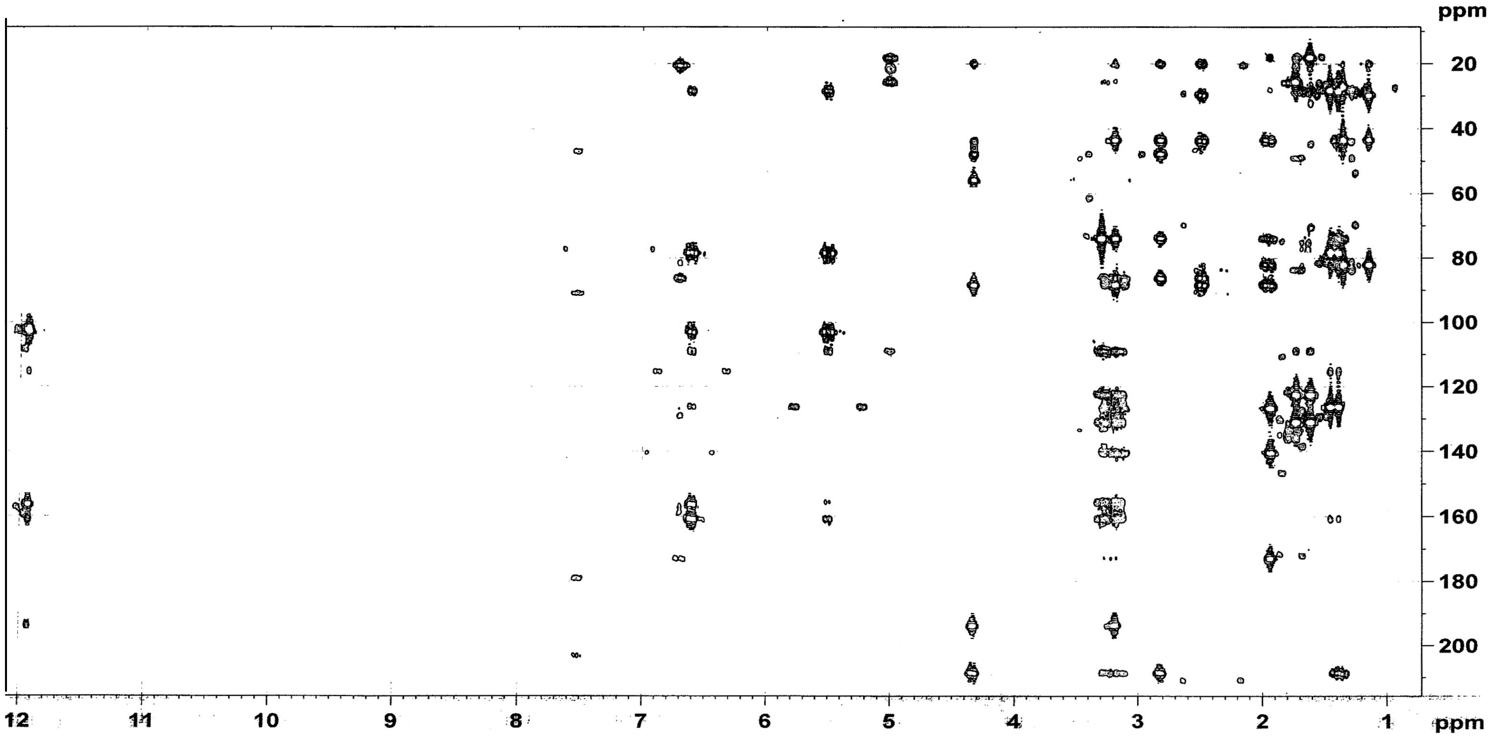


Figure 164 2D HMBC spectrum of **GF28**

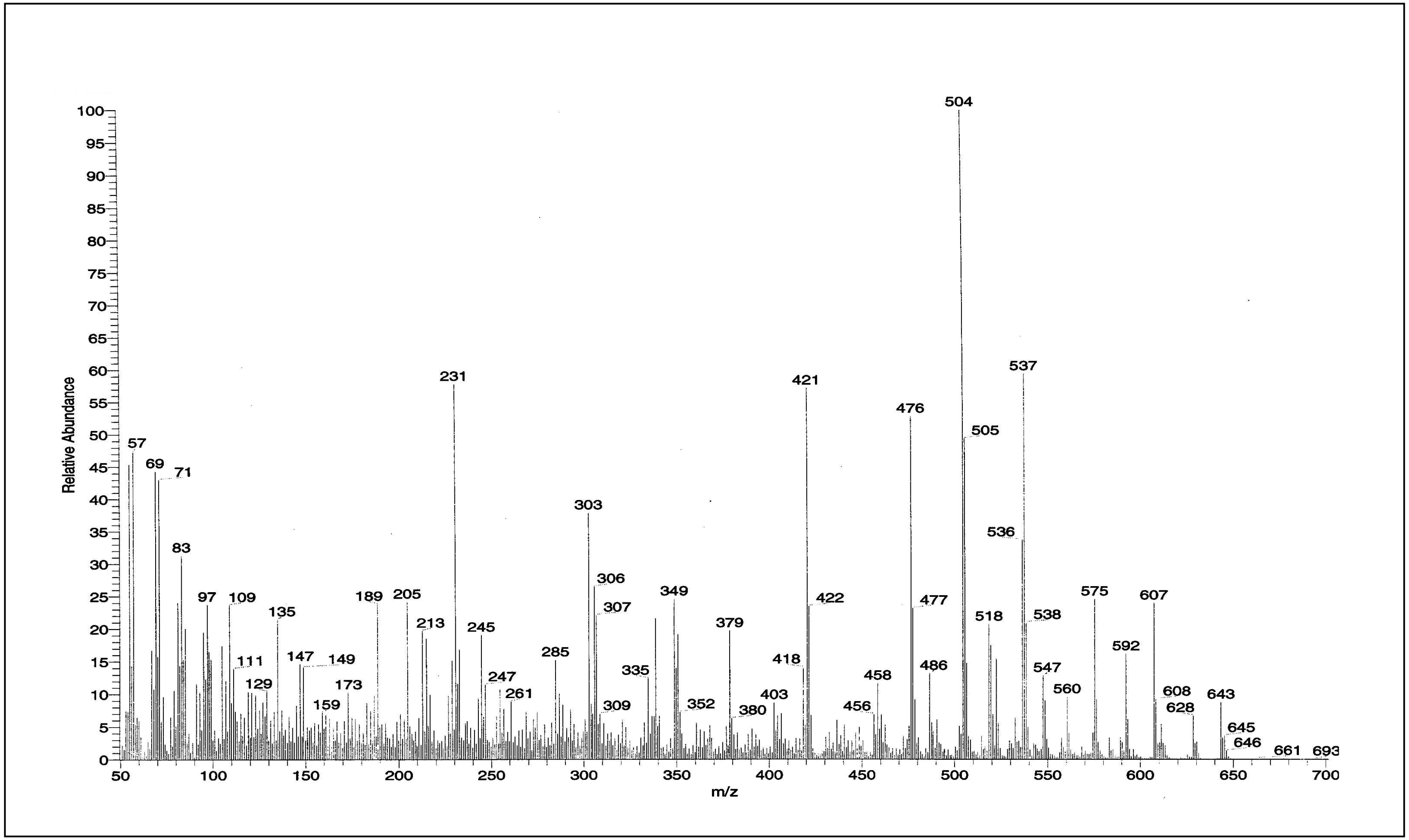


Figure 165 Mass spectrum of **GF27**

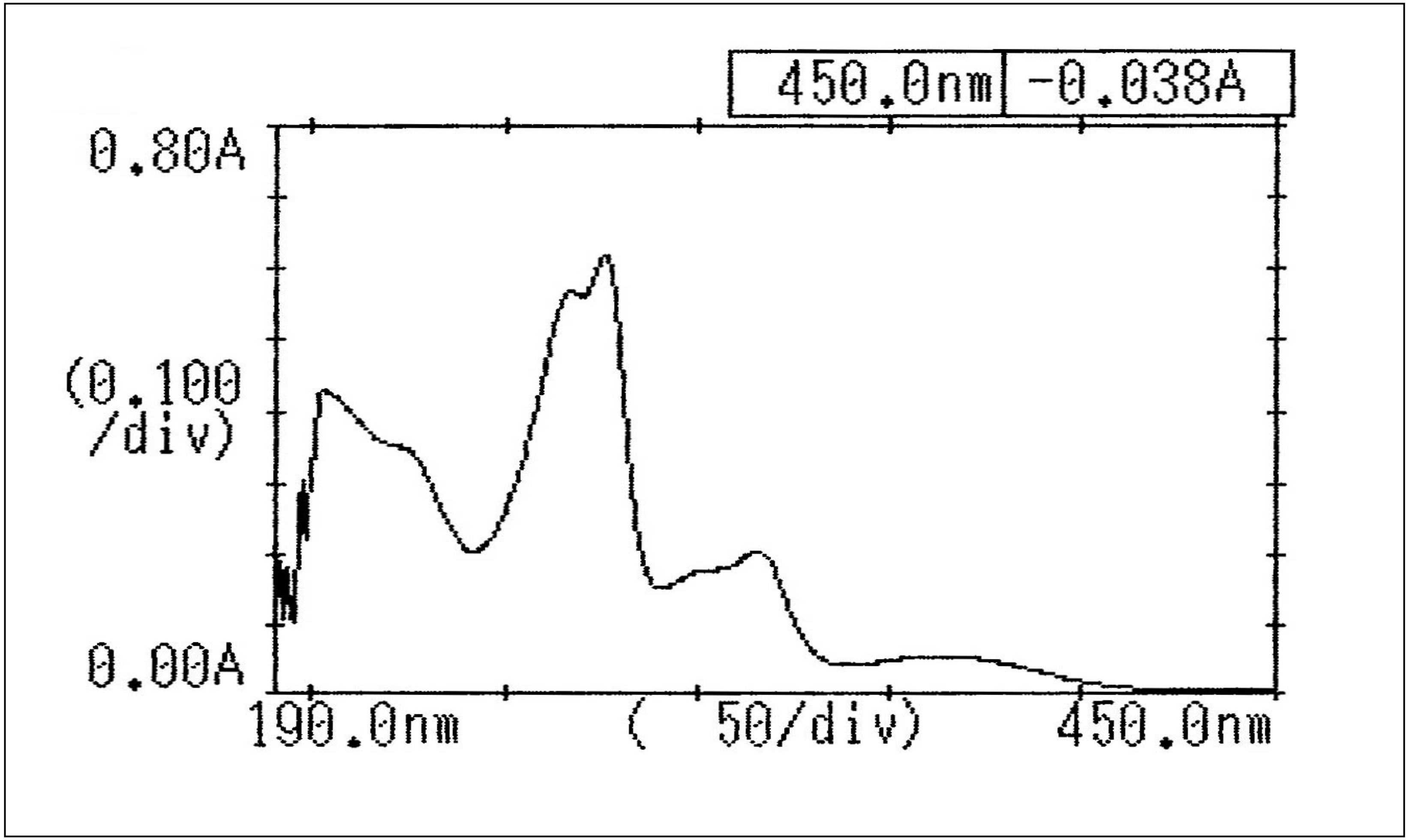


Figure 166 UV (CH_3OH) spectrum of **GF27**

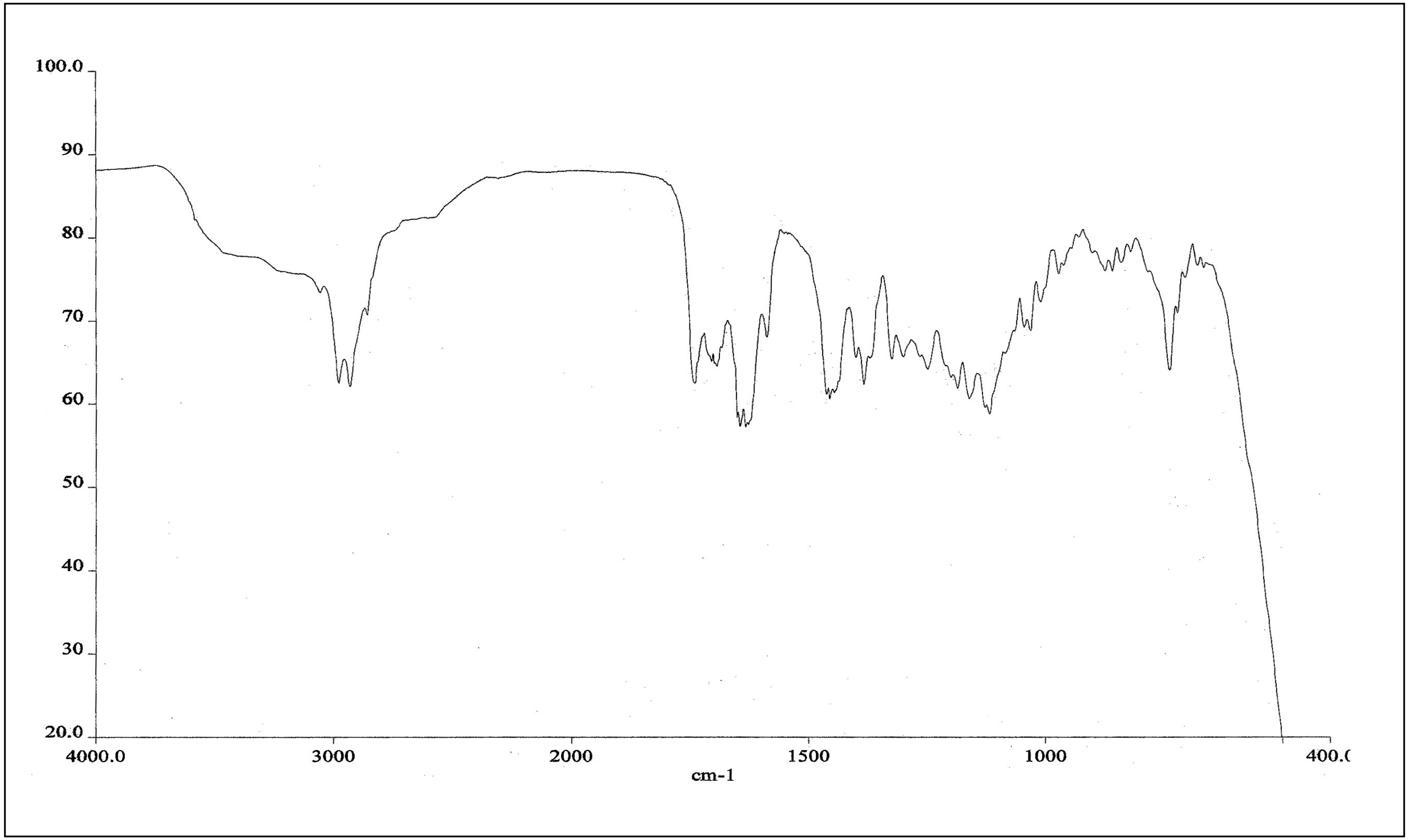


Figure 167 FT-IR (neat) spectrum of **GF27**

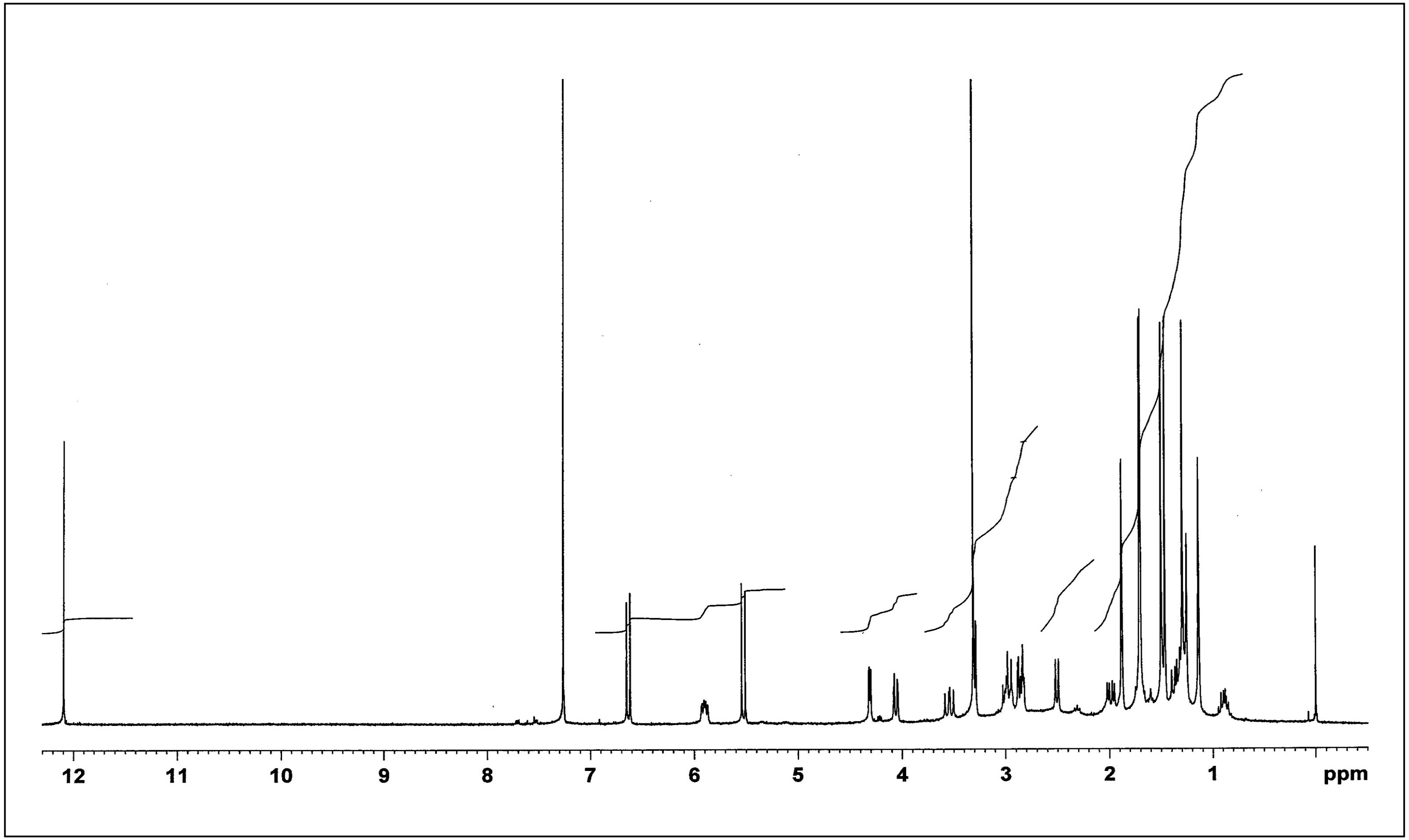


Figure 168 ^{1}H NMR (300 MHz) (CDCl$_3$) spectrum of **GF27**

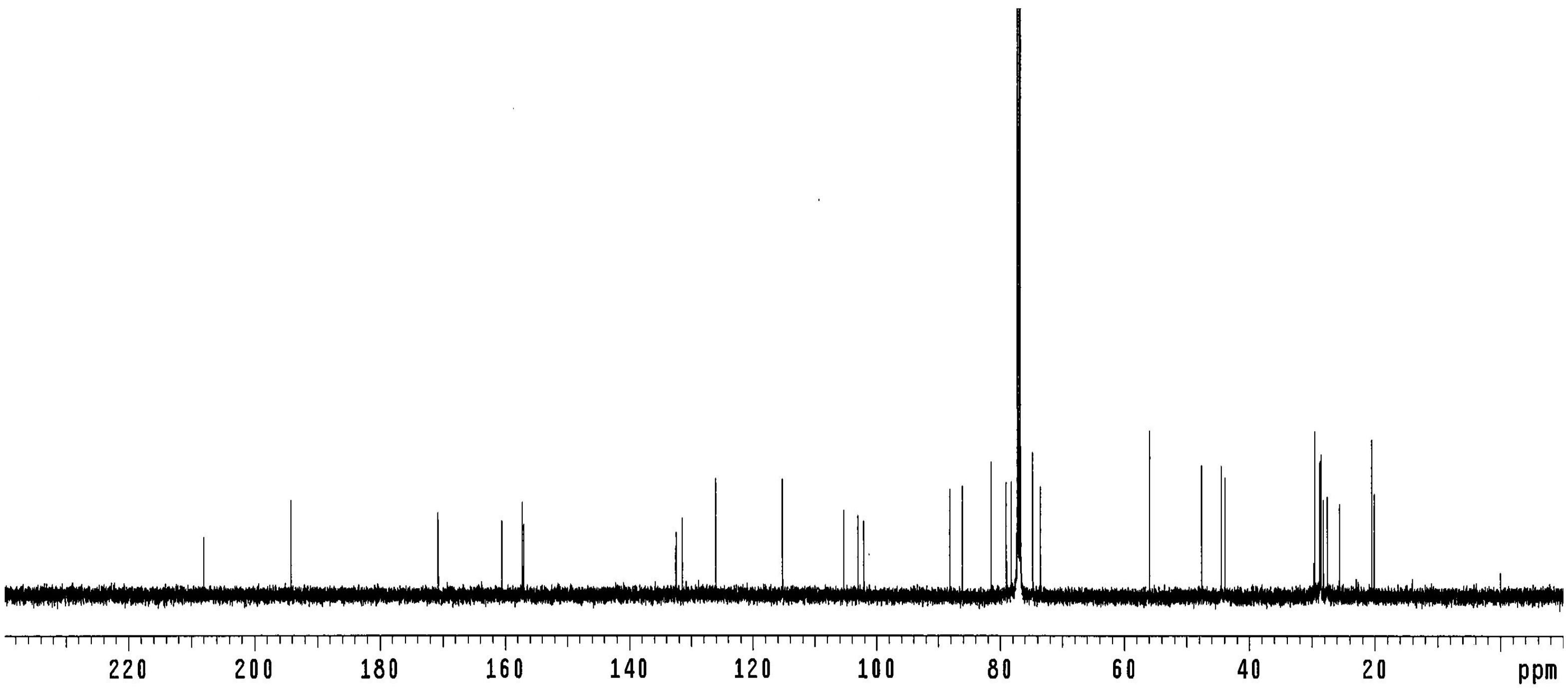


Figure 169 ^{13}C NMR (125 MHz) ($CDCl_3$) spectrum of **GF27**

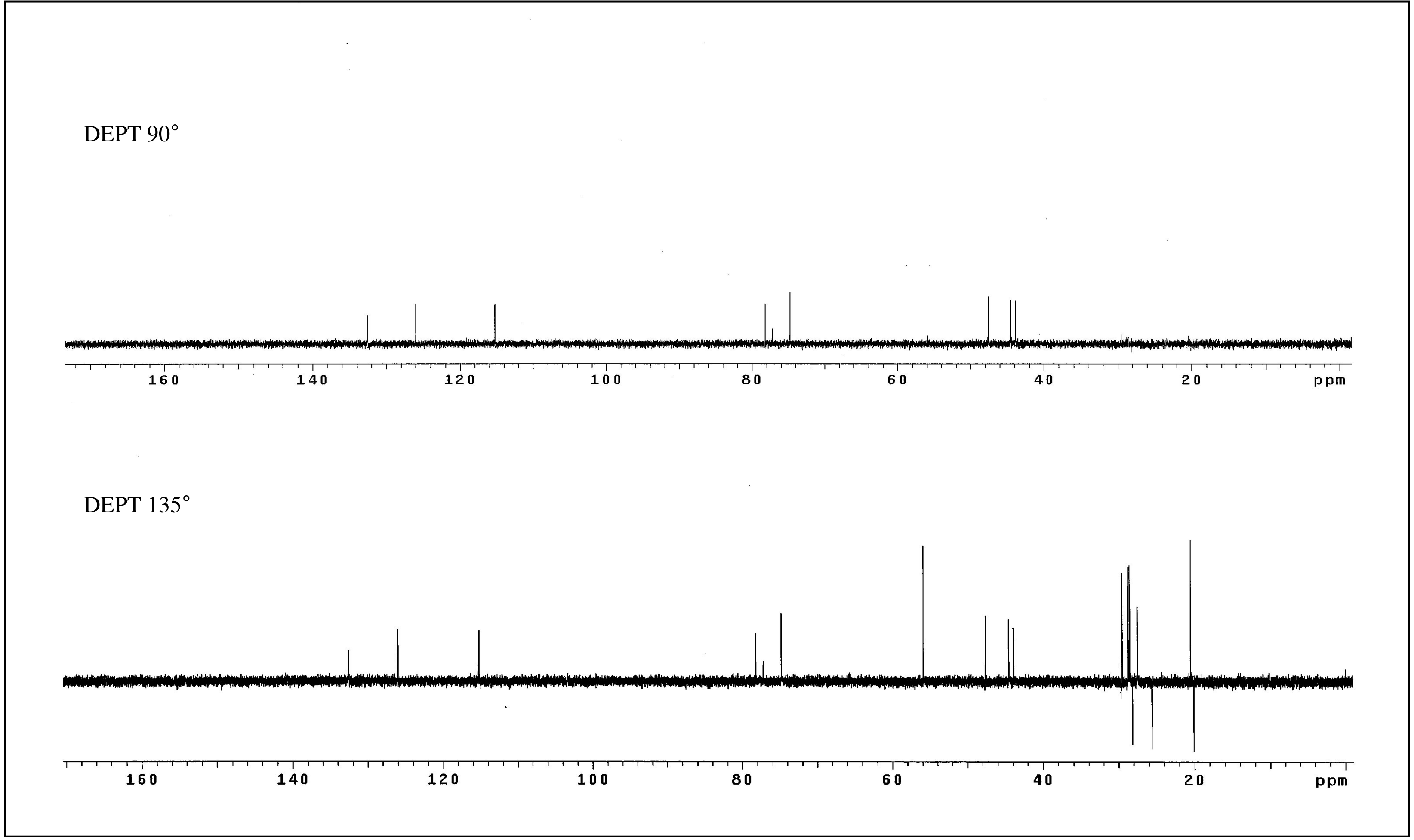


Figure 170 DEPT spectrum of **GF27**

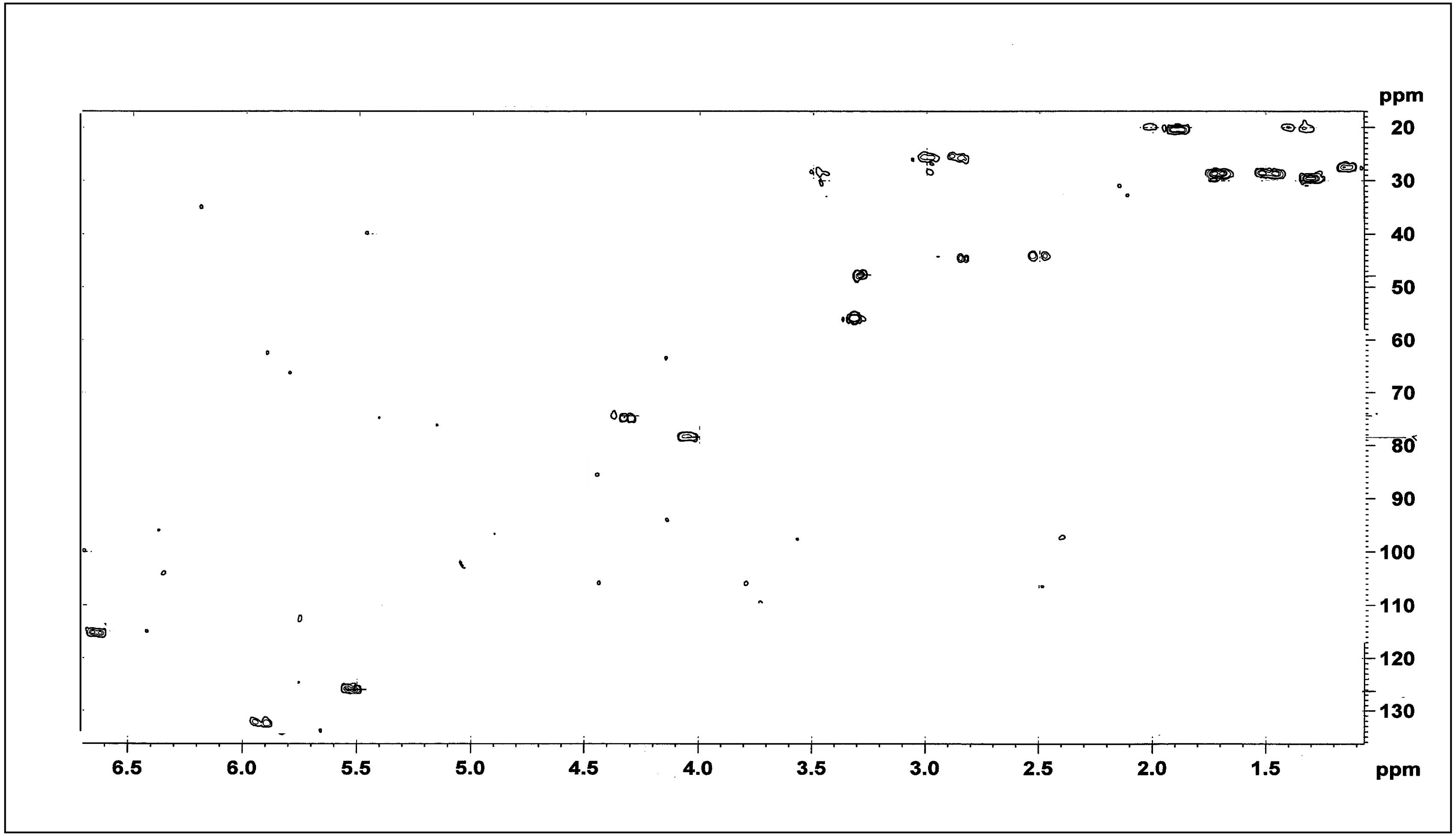


Figure 171 2D HMQC spectrum of **GF27**

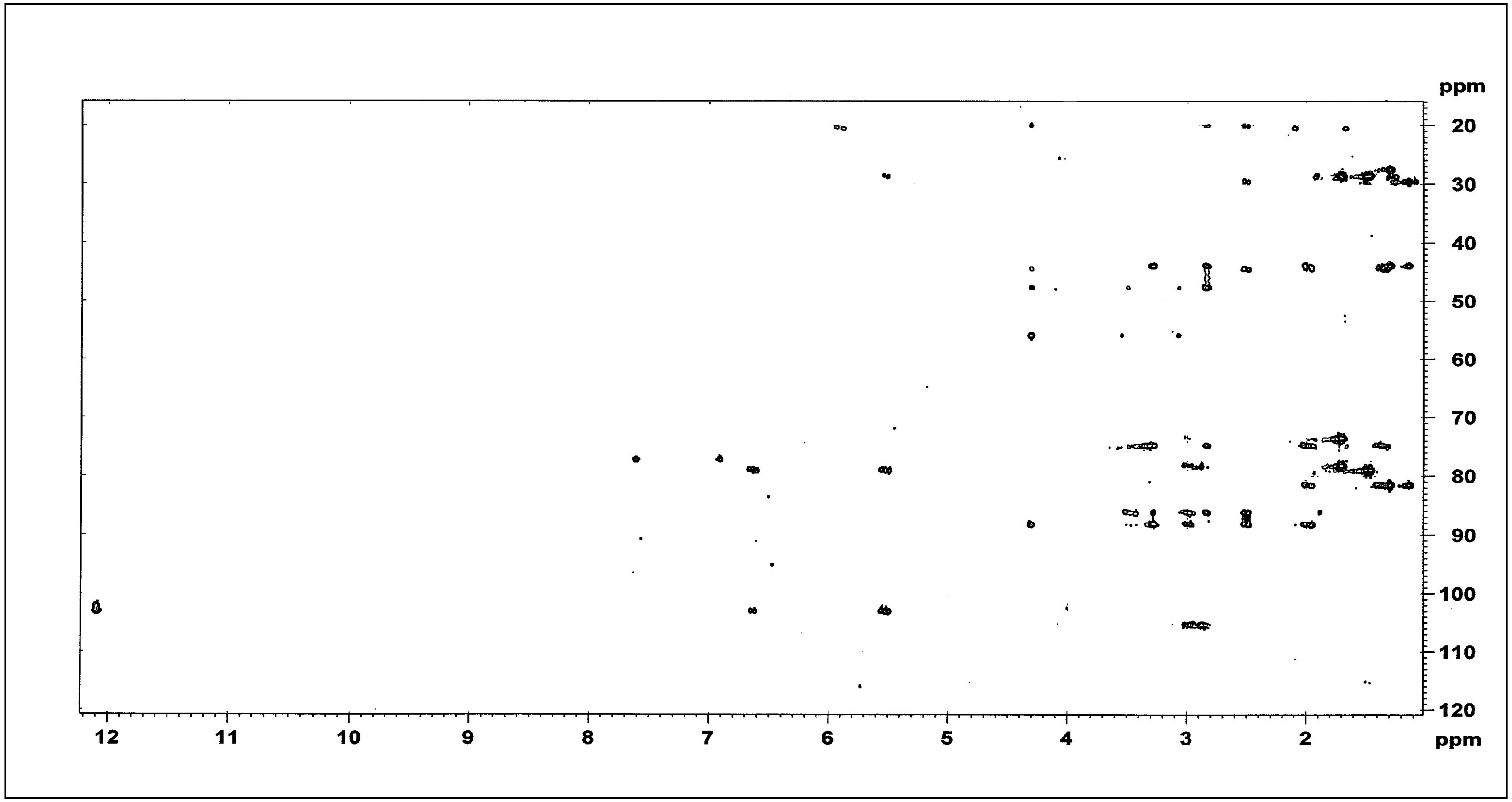


Figure 172 2D HMBC spectrum of **GF27**

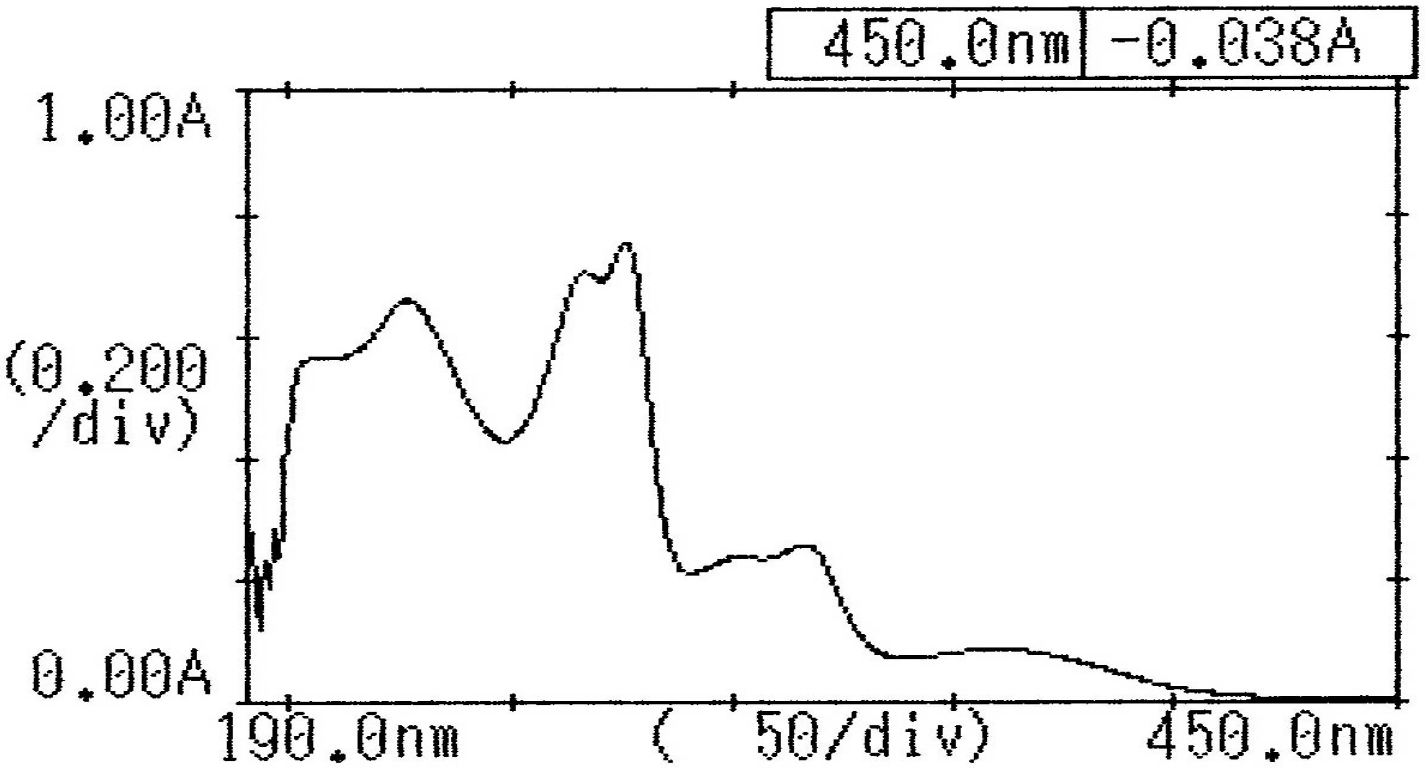


Figure 173 UV (CH_3OH) spectrum of **GF25**

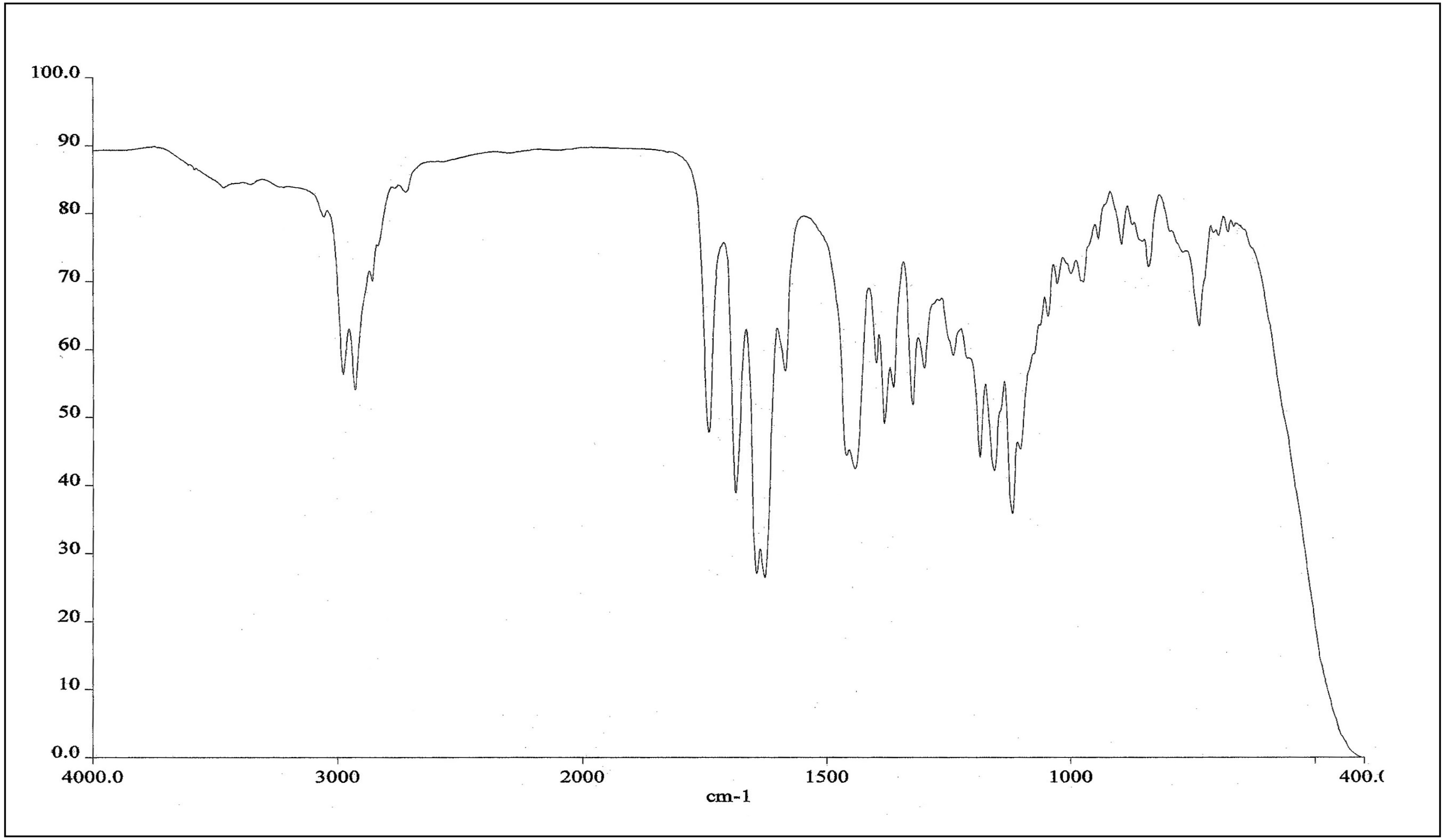


Figure 174 FT-IR (neat) spectrum of **GF25**

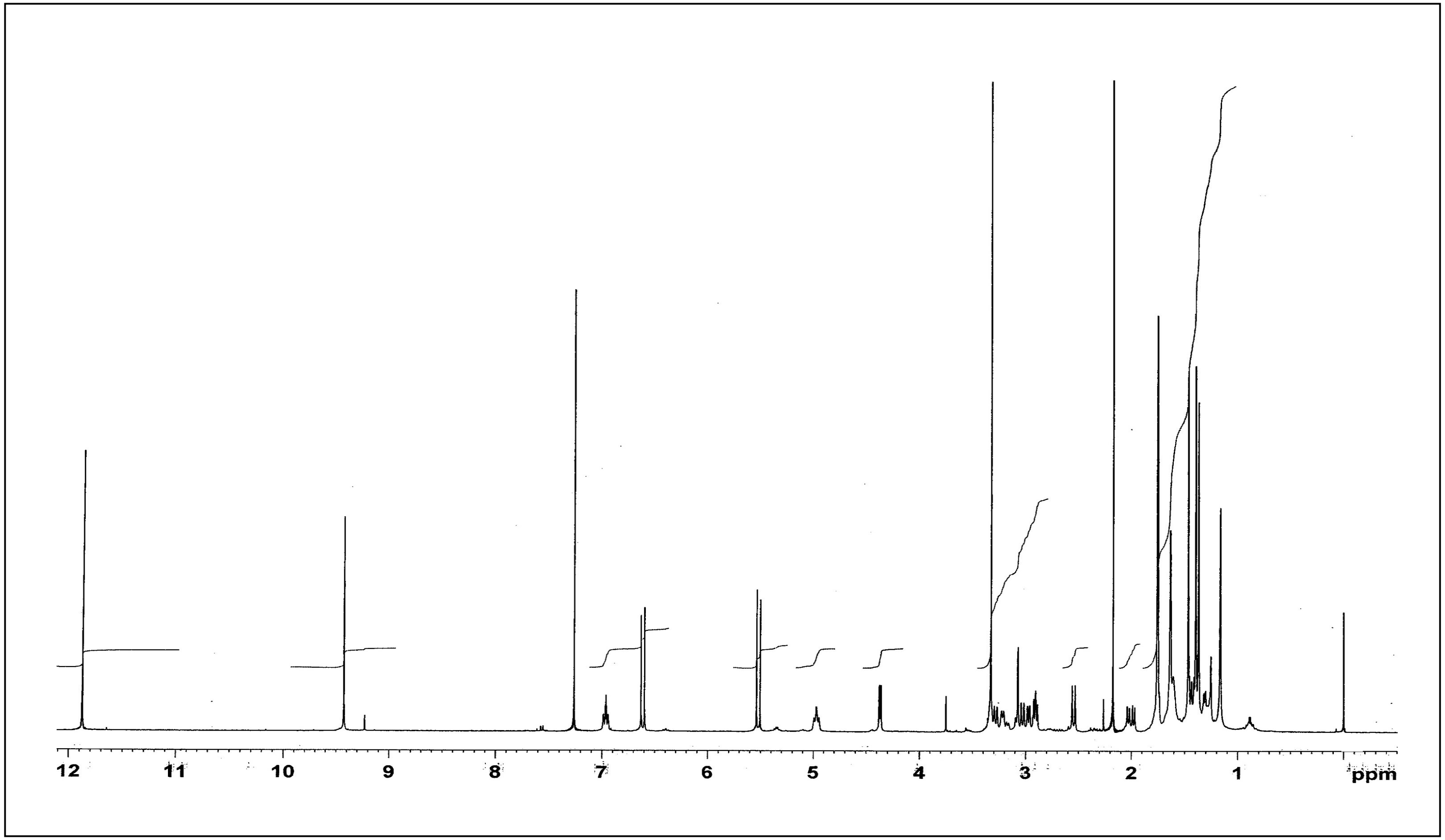


Figure 175 ^{1}H NMR (300 MHz) (CDCl$_3$) spectrum of **GF25**

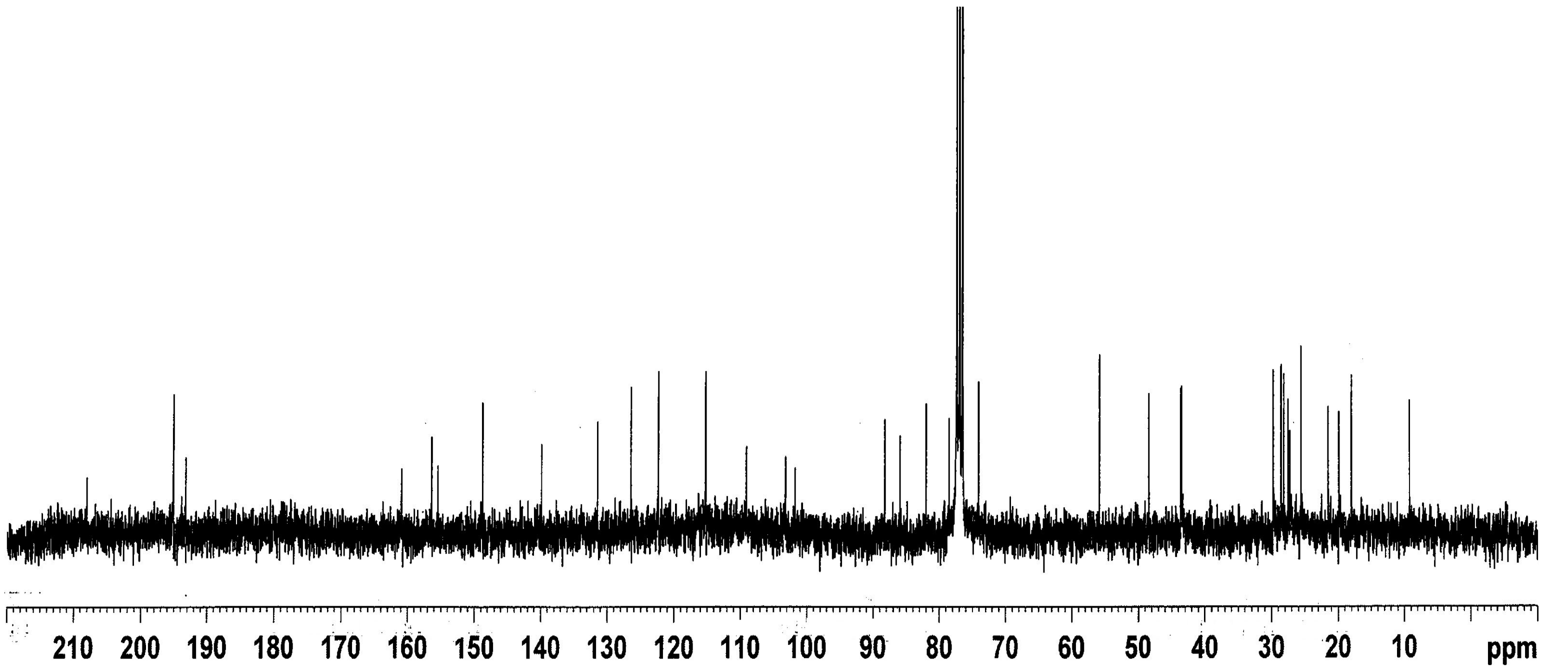


Figure 176 ^{13}C NMR (75 MHz) (CDCl$_3$) spectrum of **GF25**

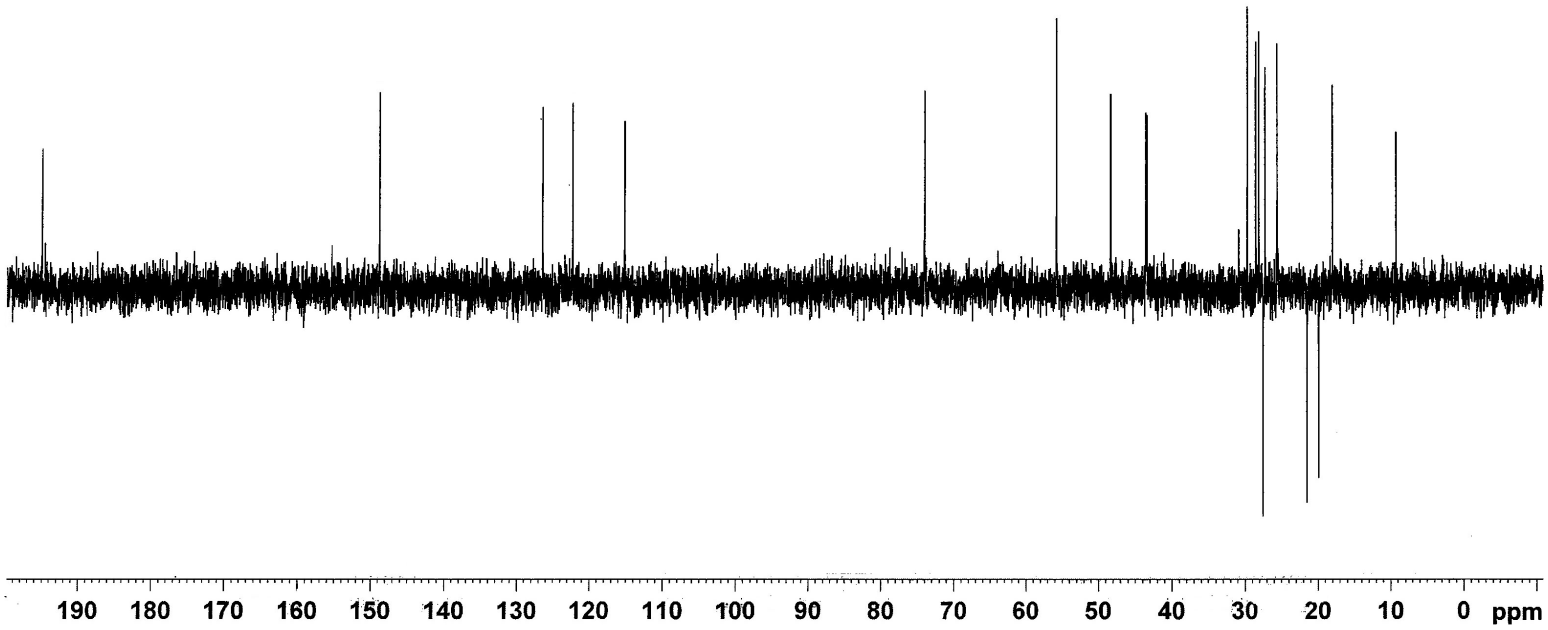


Figure 177 DEPT spectrum of **GF25**

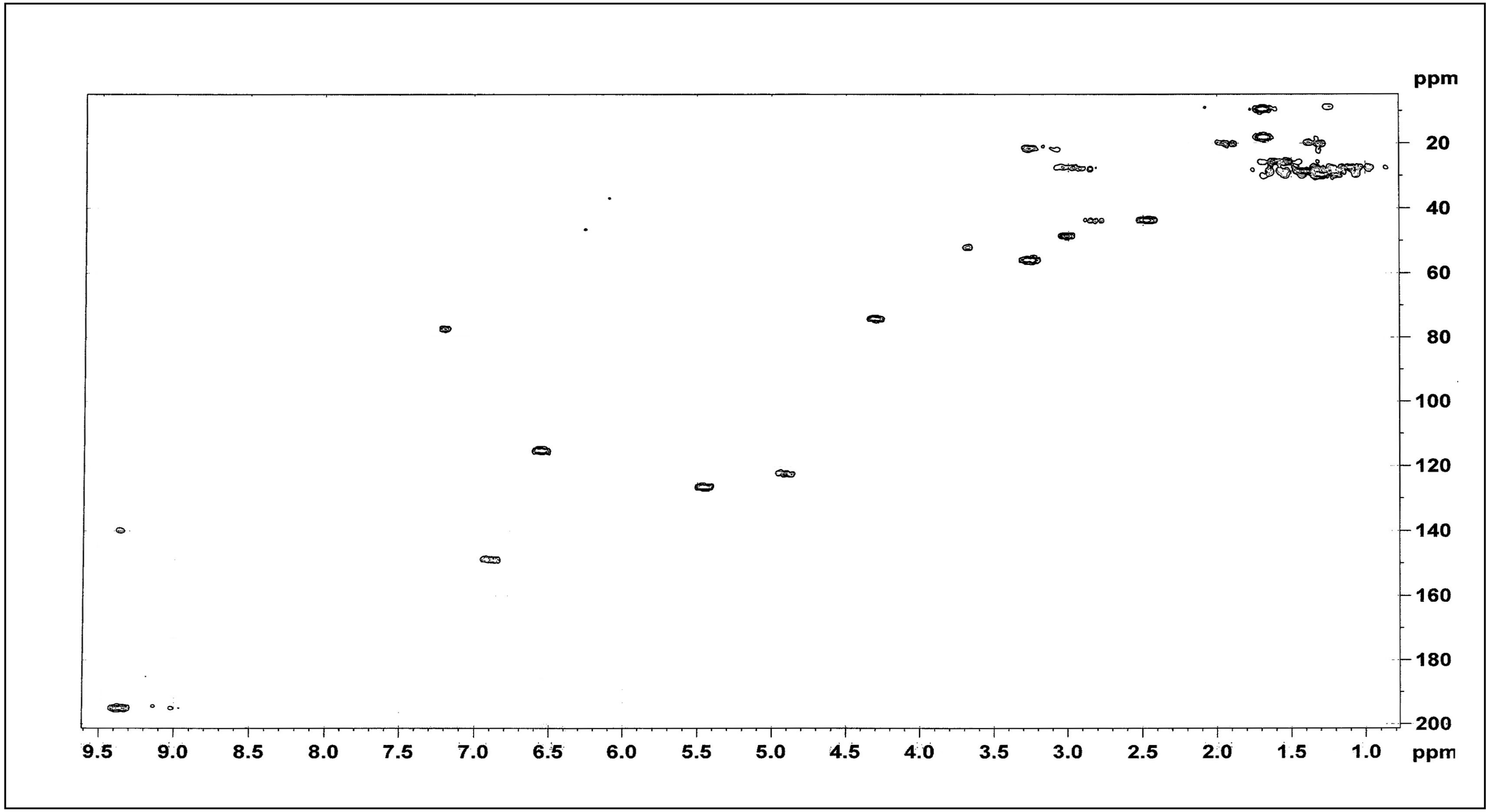


Figure 178 2D HMQC spectrum of **GF25**

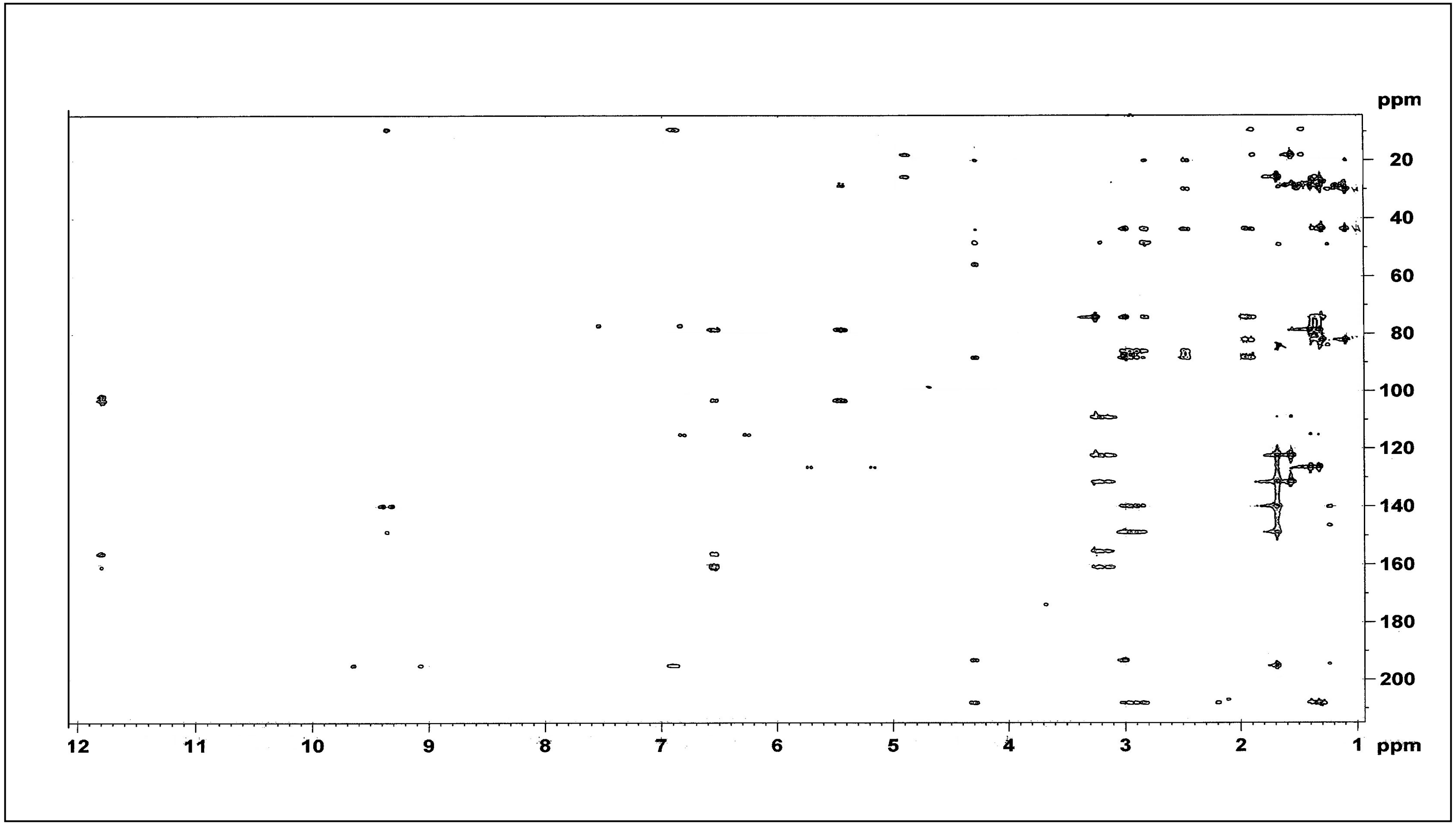


Figure 179 2D HMBC spectrum of **GF25**

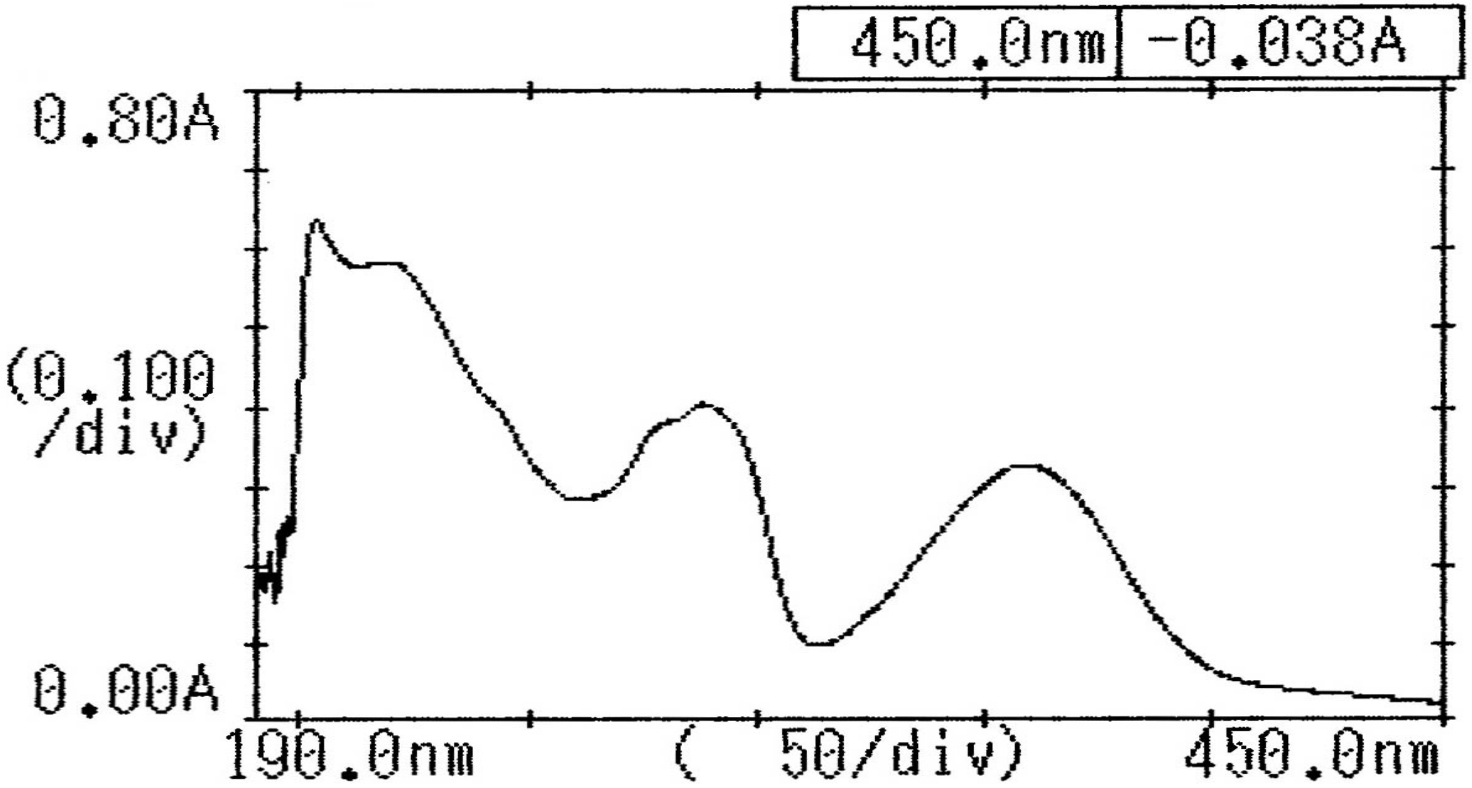


Figure 180 UV (CH_3OH)) spectrum of **GF29**

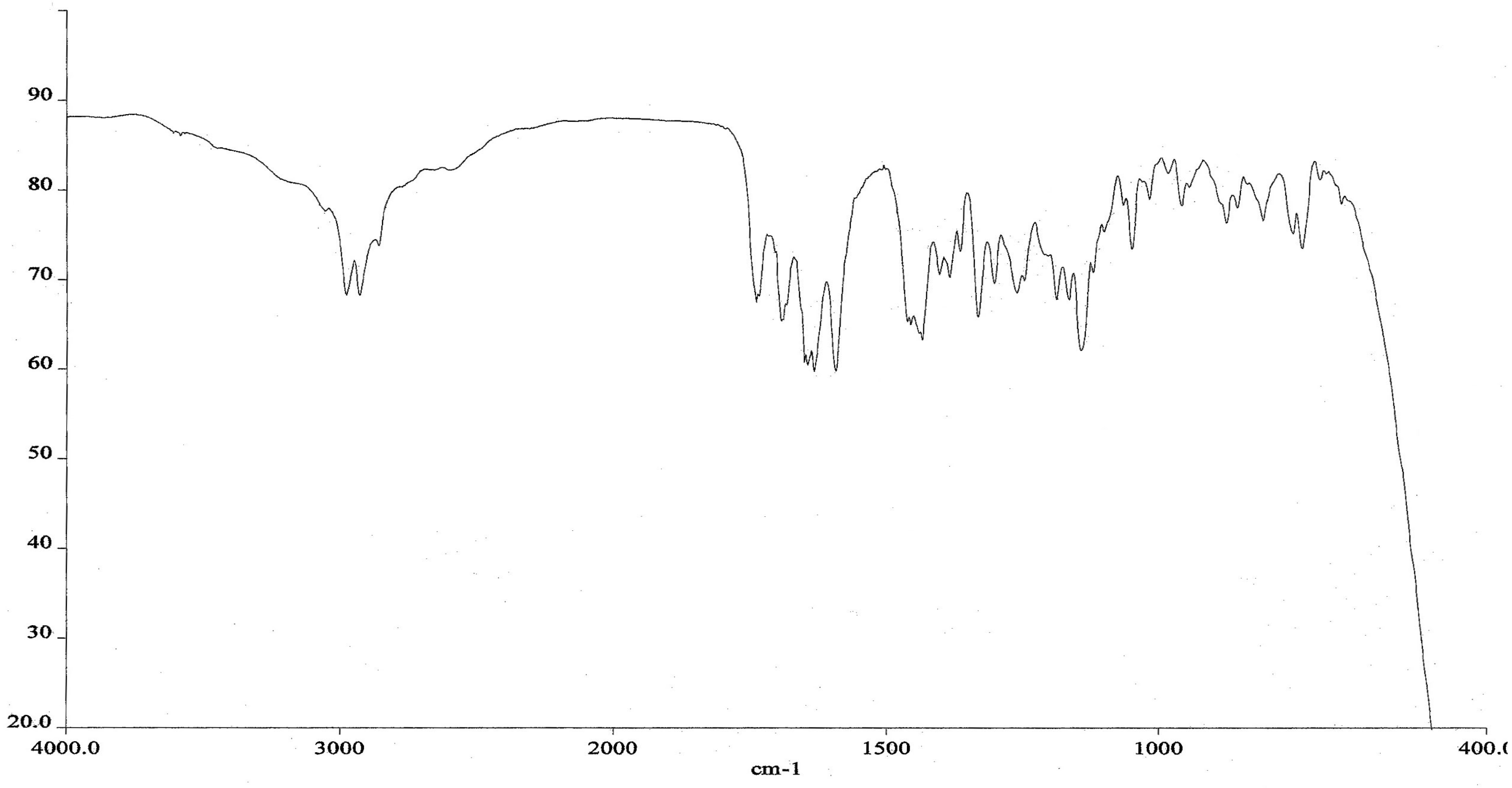


Figure 181 FT-IR (neat) spectrum of **GF29**

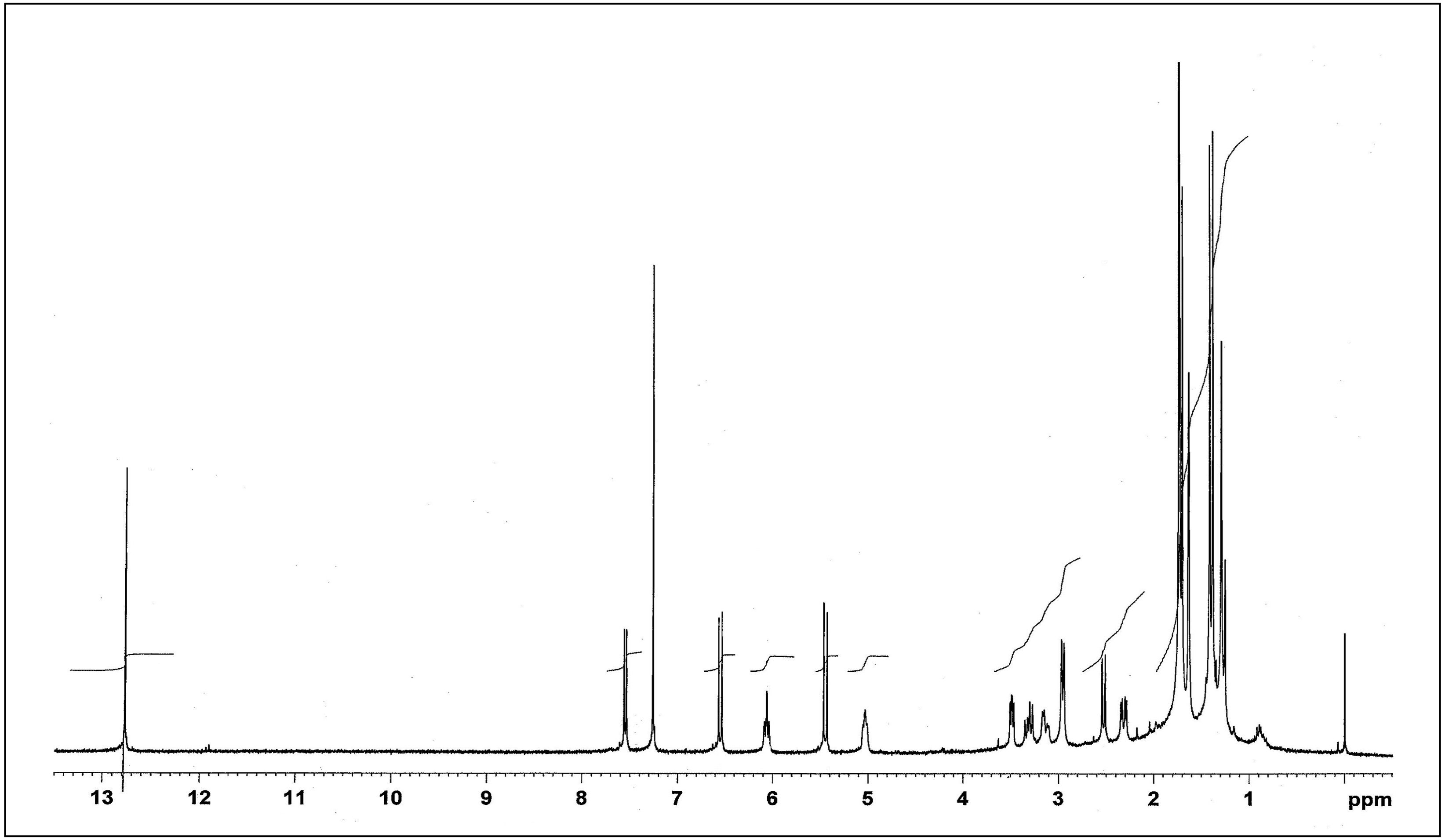


Figure 182 ^{1}H NMR (300 MHz) (CDCl$_3$) spectrum of **GF29**

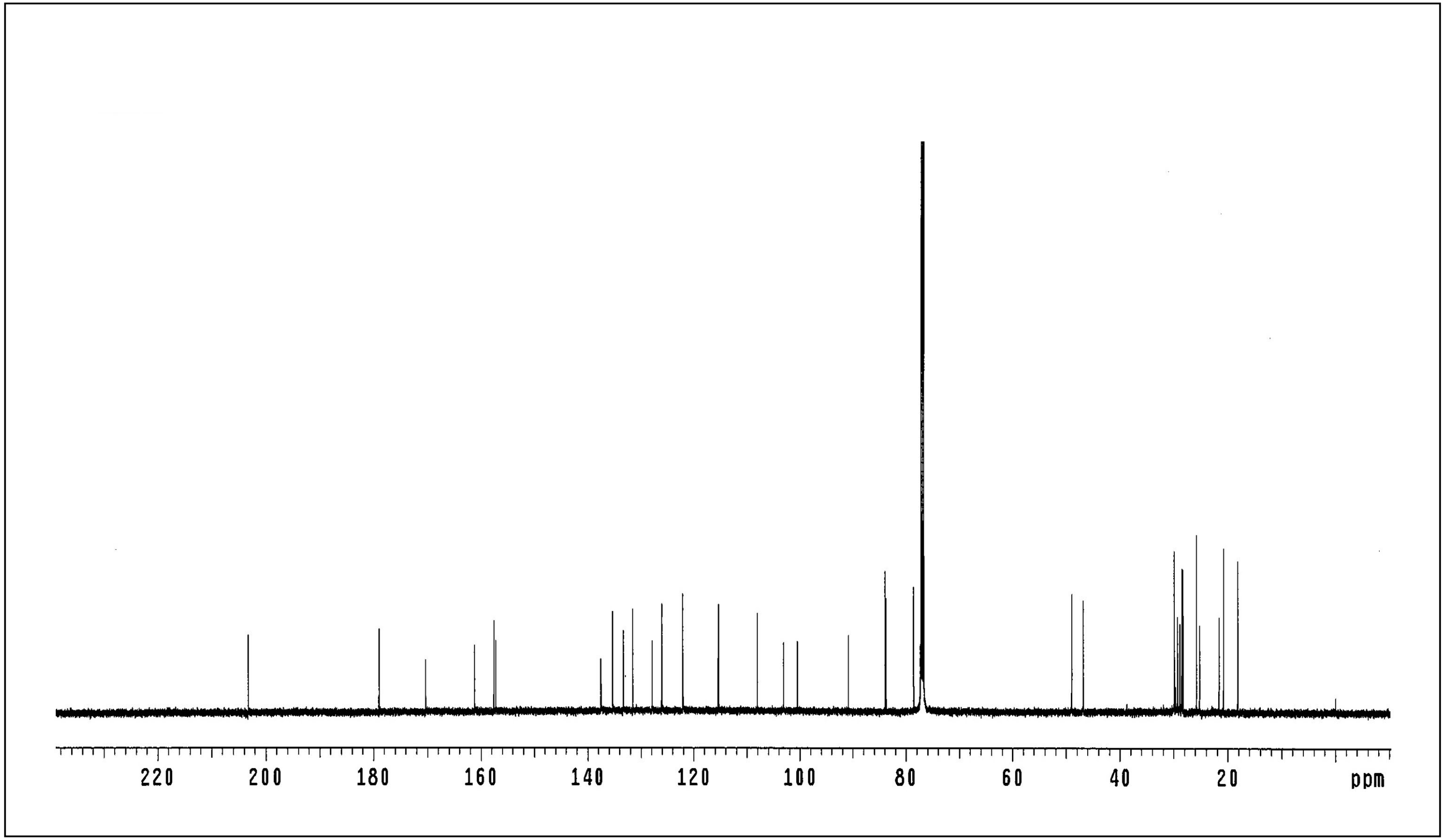


Figure 183 ^{13}C NMR (125 MHz) ($CDCl_3$) spectrum of **GF29**

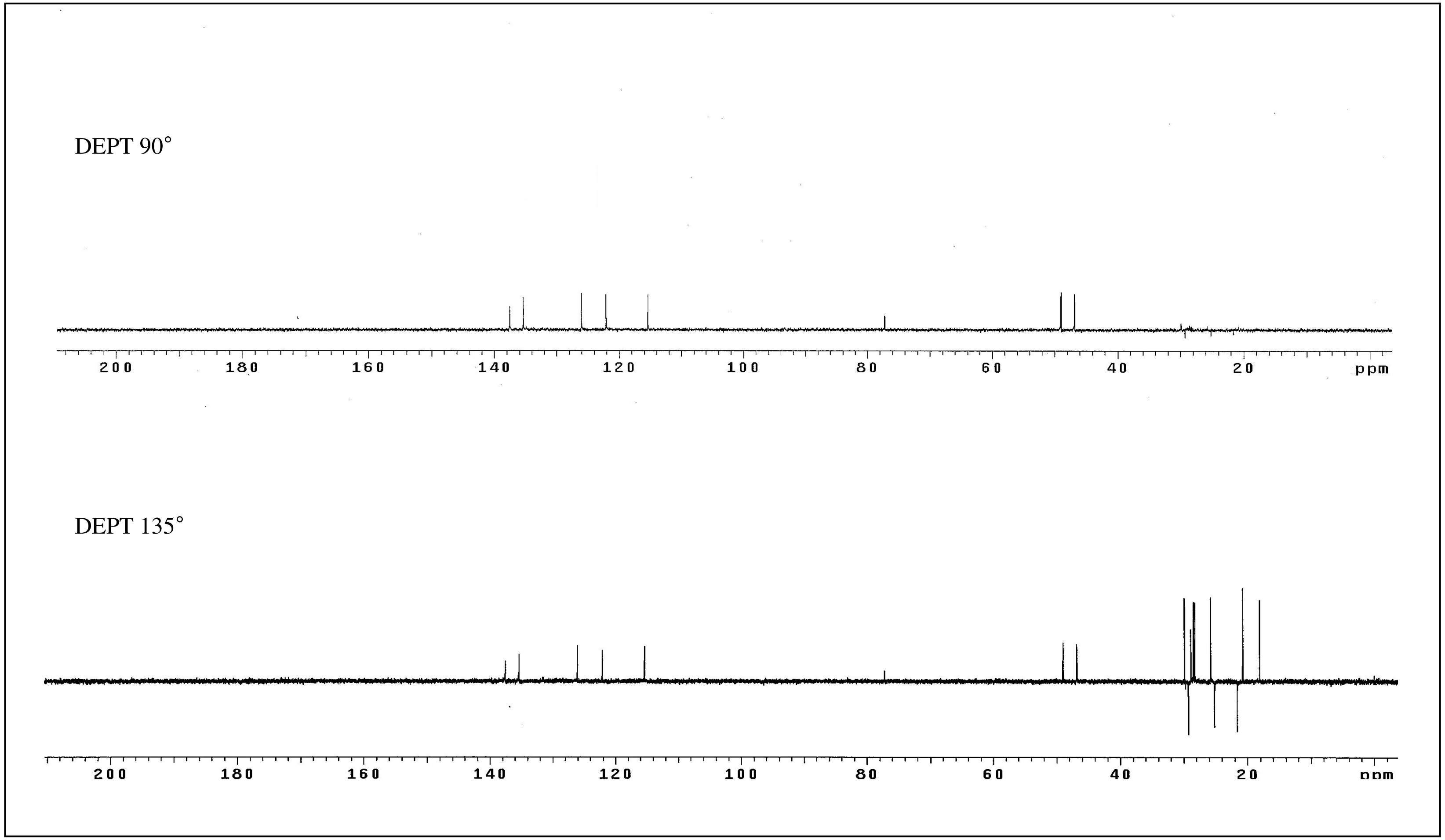


Figure 184 DEPT spectrum of **GF29**

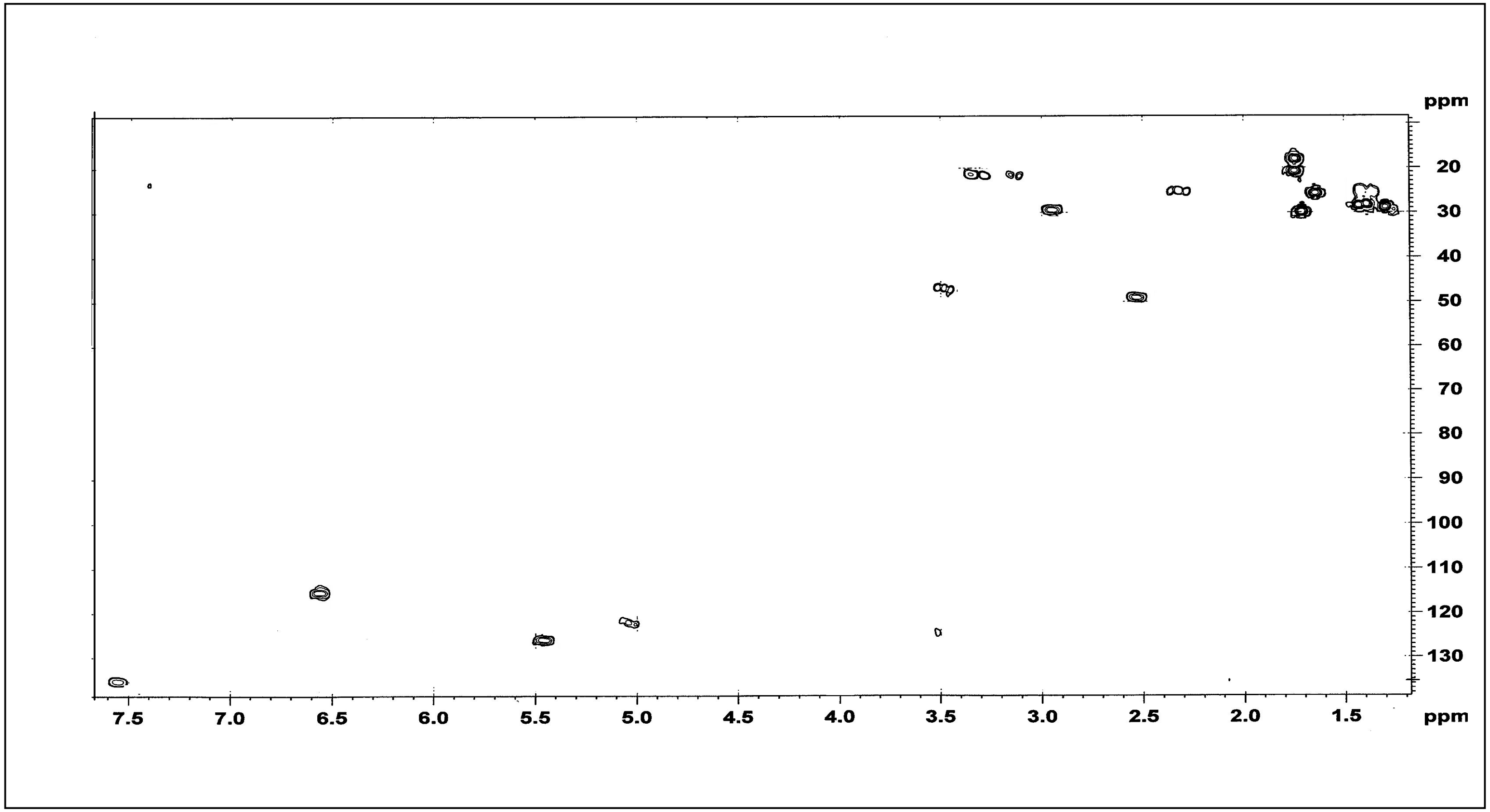


Figure 185 2D HMQC spectrum of **GF29**

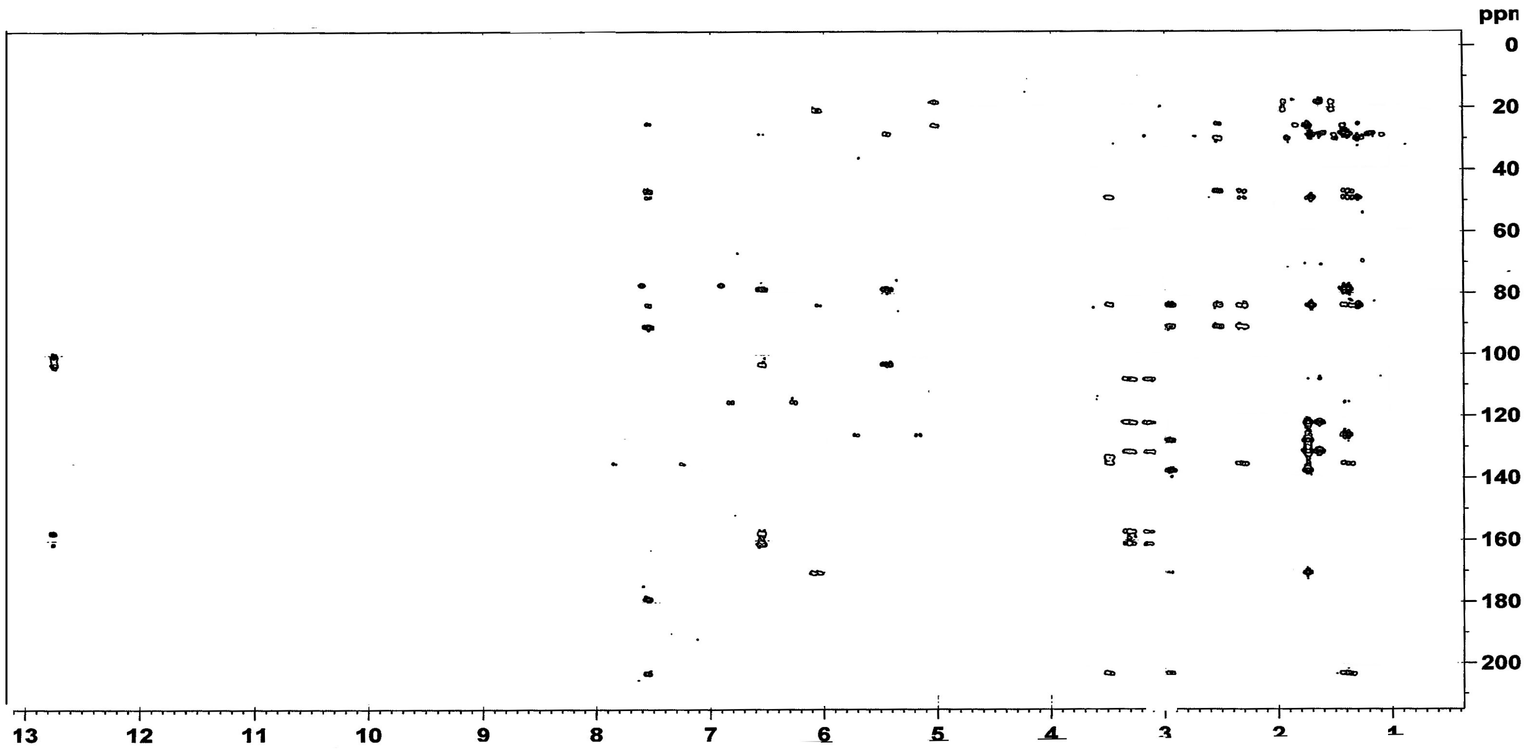


Figure 186 2D HMBC spectrum of **GF29**

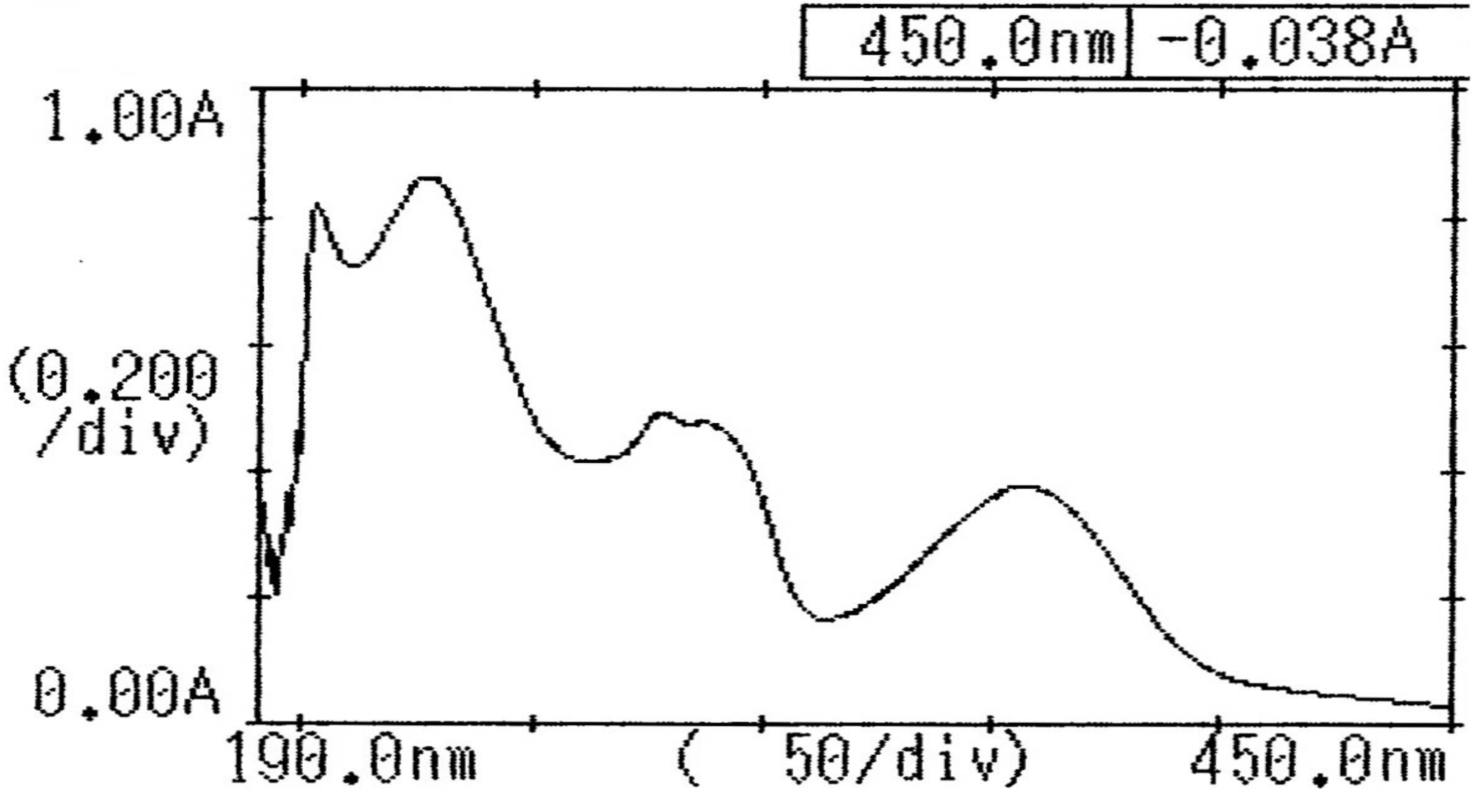


Figure 187 UV (CH_3OH) spectrum of **GF26**

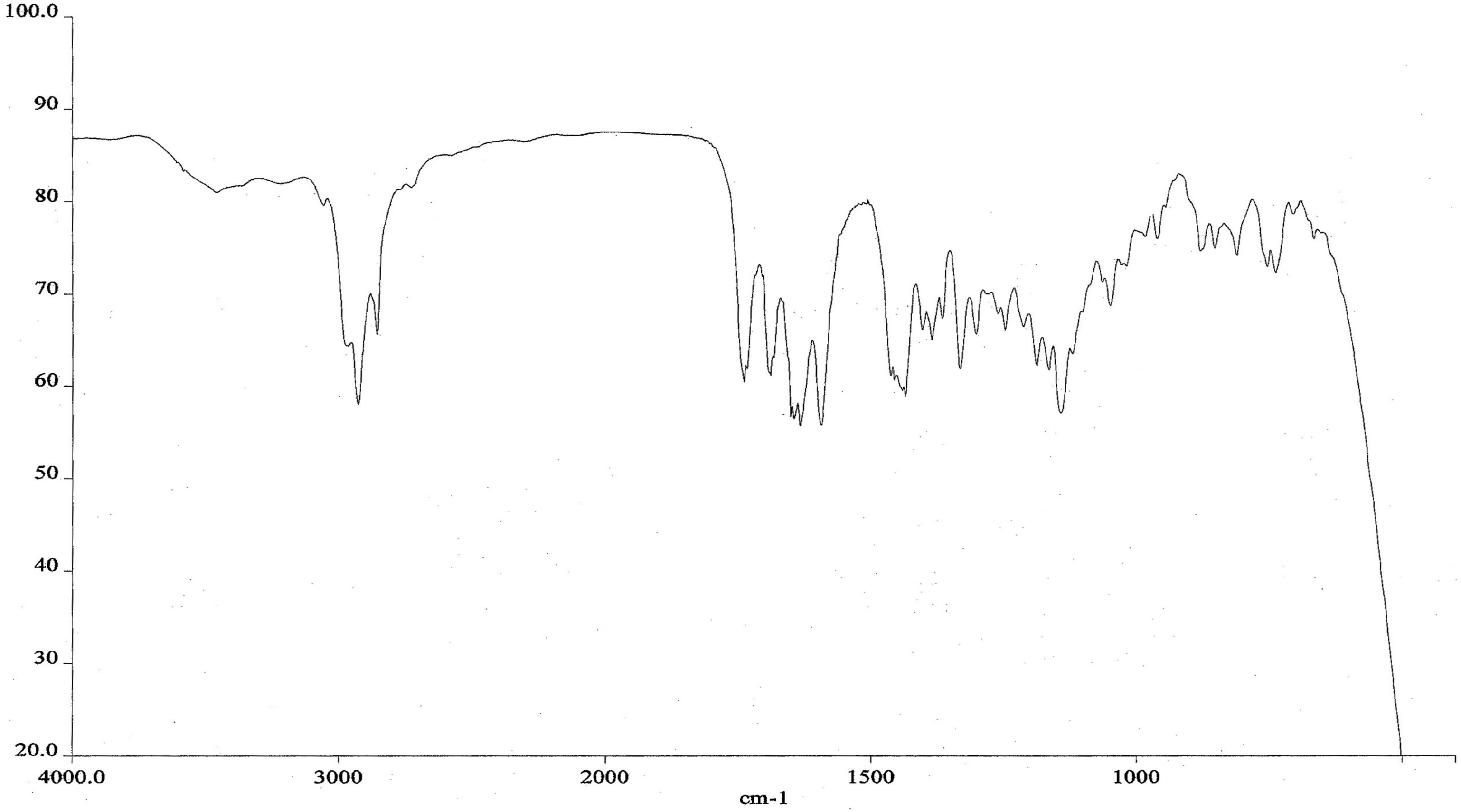


Figure 188 FT-IR (neat) spectrum of **GF26**

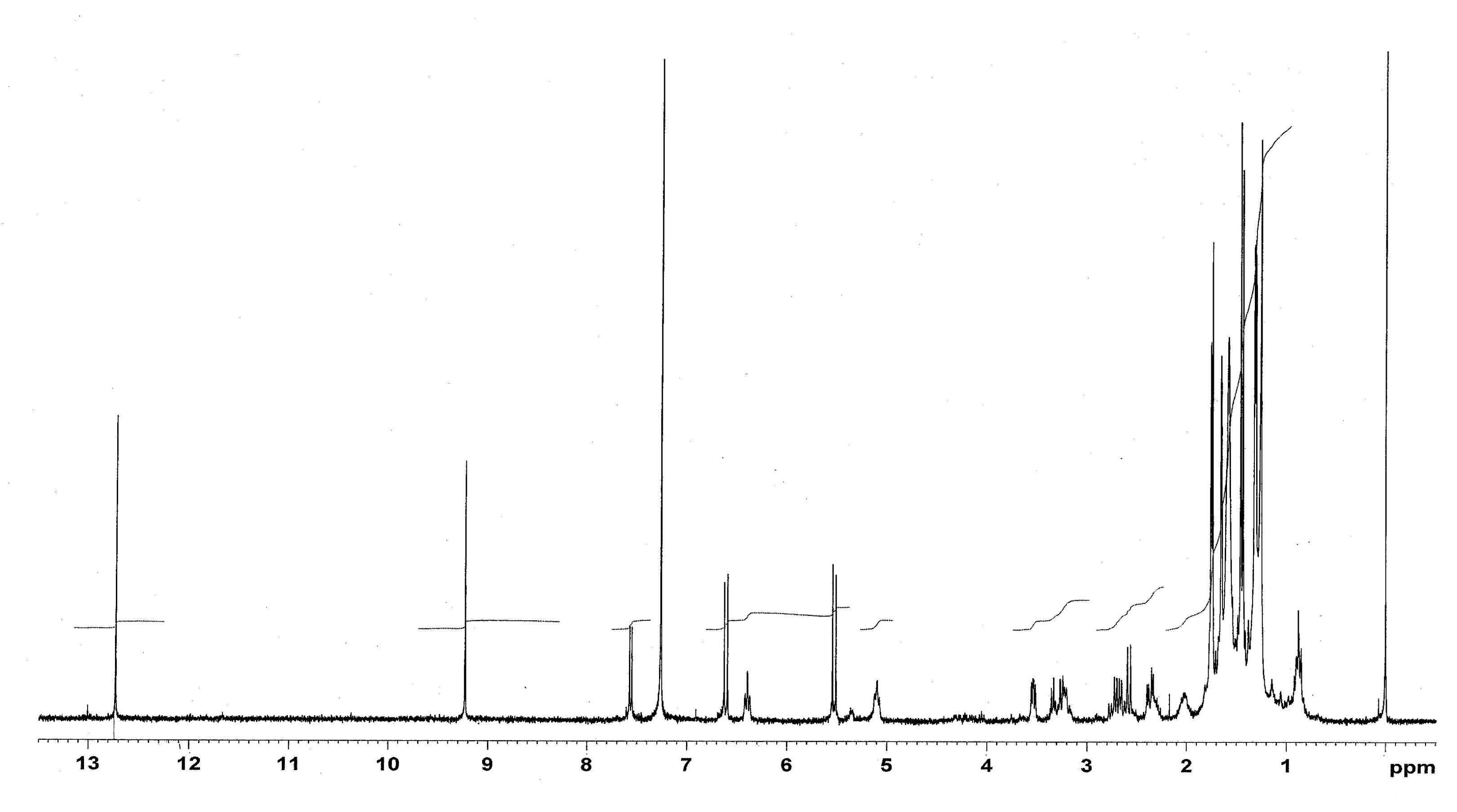


Figure 189 ^{1}H NMR (300 MHz) ($CDCl_3$) spectrum of **GF26**

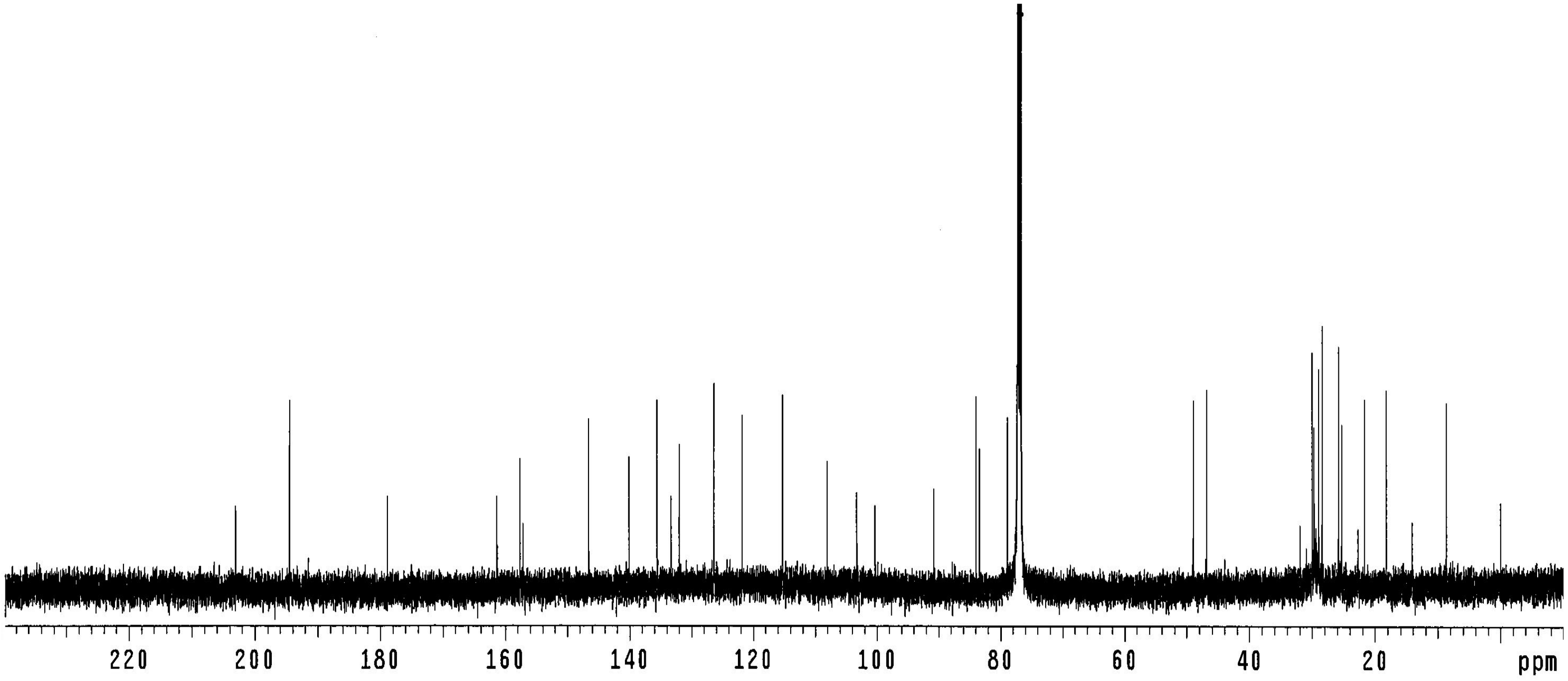


Figure 190 ^{13}C NMR (125 MHz) ($CDCl_3$) spectrum of **GF26**

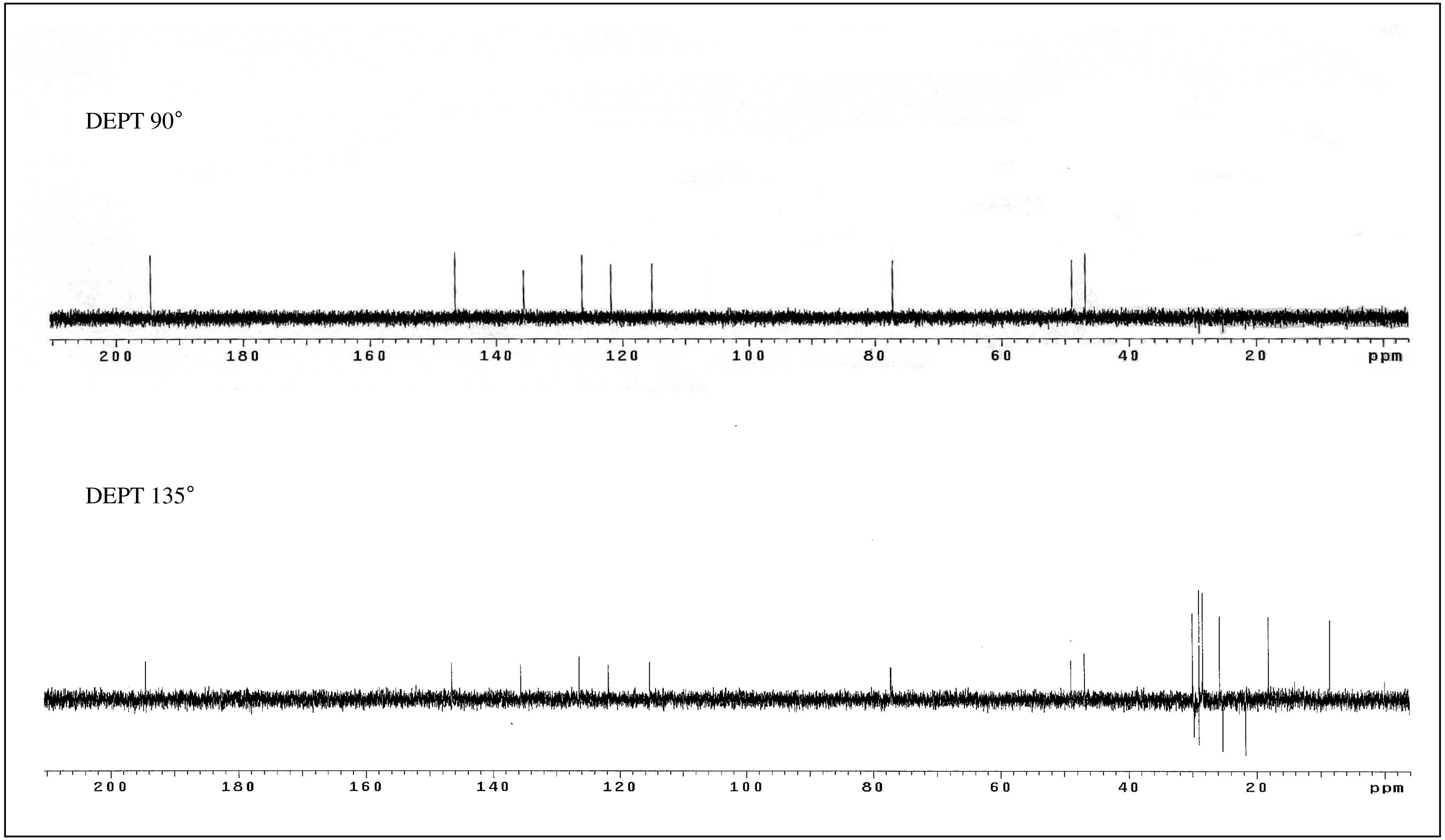


Figure 191 DEPT spectrum of **GF26**

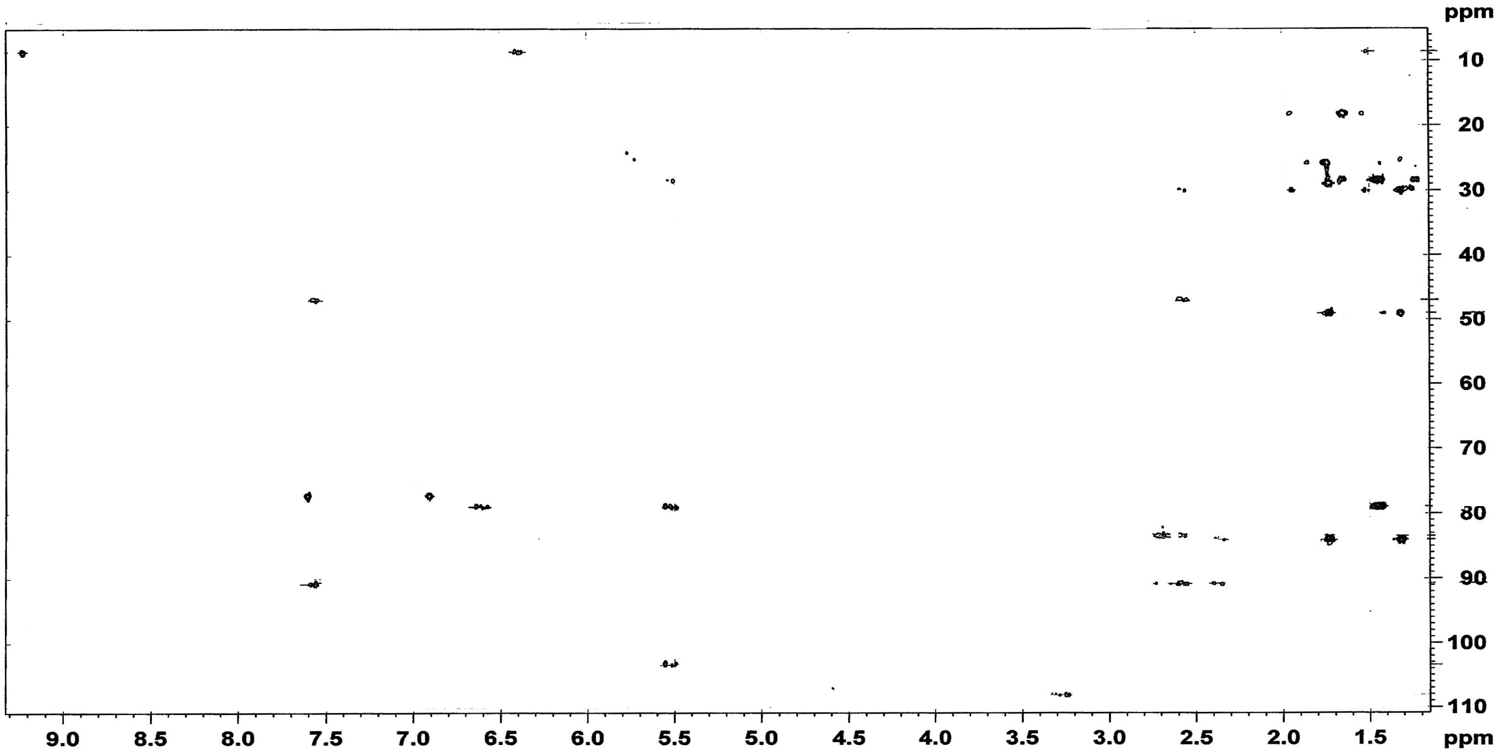


Figure 192 2D HMQC spectrum of **GF26**

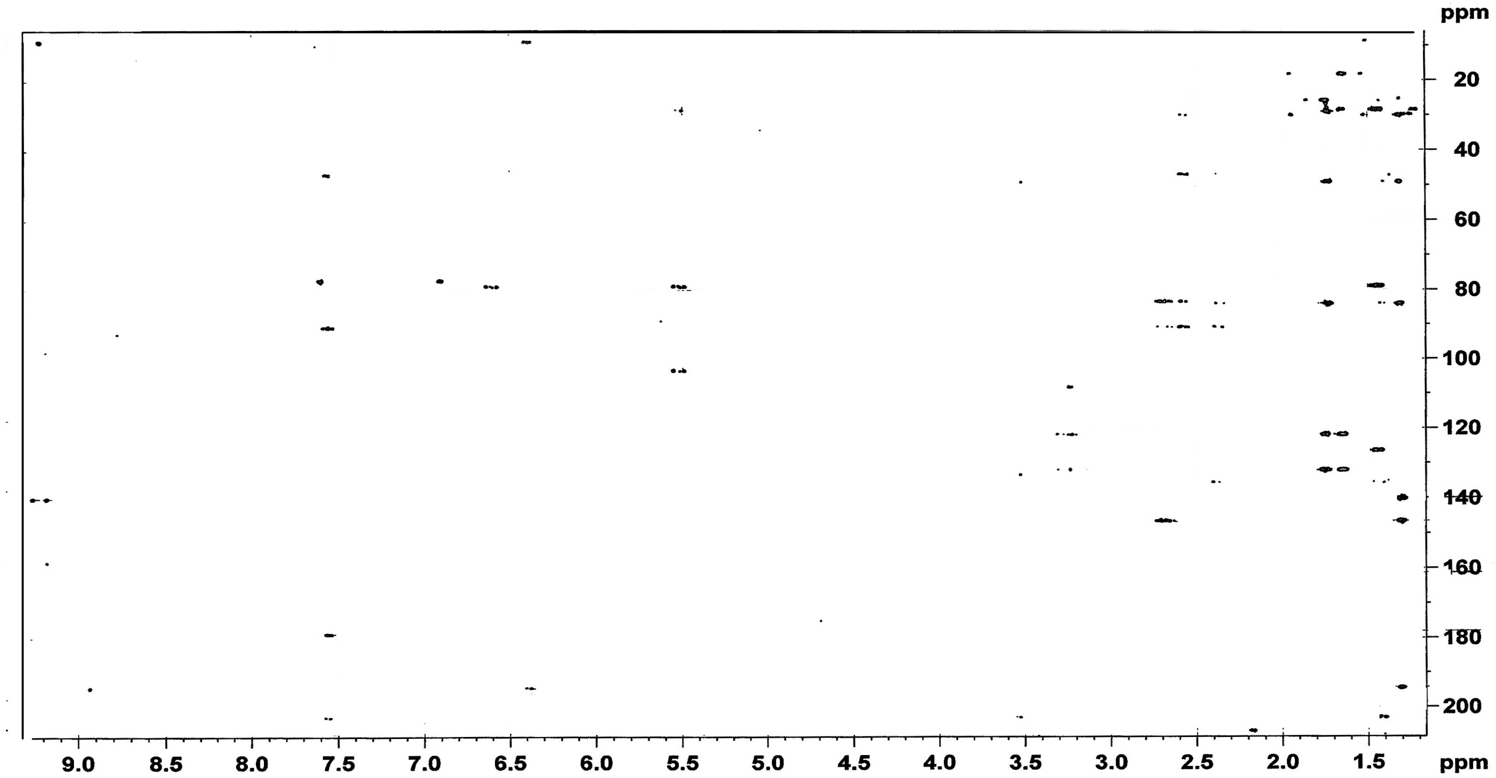


Figure 193 2D HMBC spectrum of **GF26**