Supplementary Information

Concise and collective total syntheses of 2,4-disubstituted furan-derived natural products from hydroxyoxetanyl ketones

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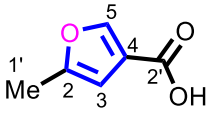
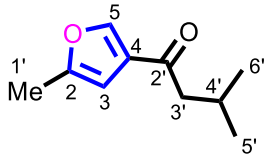
Table S1: Comparison of ^{1}H and ^{13}C NMR data of natural and synthetic methylfuroic acid (1).



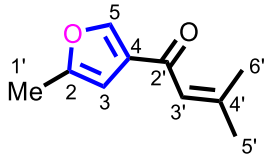
	Methylfuroic acid (**1**) (Natural) in $CDCl_3$ Zhang *et al.*		Methylfuroic acid (**1**) (Synthetic) in $CDCl_3$ Murphree *et al.*		Methylfuroic acid (**1**) (Synthetic) in $CDCl_3$ This work	
	δH (mult, *J* in Hz) (500 MHz)	δC (mult, *J* in Hz) (125 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (100 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (101 MHz)
2	-	154.06	-	154.01	-	154.21
3	6.33 (s, 1H)	105.55	6.33 (s, 1H)	105.54	6.35 (s, 1H)	105.67
4	-	119.72	-	119.76	-	119.40
5	7.93 (s, 1H)	147.56	7.94 (s, 1H)	147.58	7.96 (s, 1H)	147.75
1’	2.29 (s, 3H)	13.35	2.31 (s, 3H)	13.33	2.32 (s, 3H)	13.54
2’	-	168.41	-	168.39	-	168.88

Table S2: Comparison of ^{1}H and ^{13}C NMR data of natural and synthetic rabdoketone A (2).



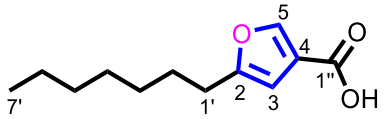
	Rabdoketone A (**2**) (Natural) in $CDCl_3$ Ma *et al.*		Rabdoketone A (**2**) (Synthetic) in $CDCl_3$ Murphree *et al.*		Rabdoketone A (**2**) (Synthetic) in $CDCl_3$ This work	
	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (100 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (100 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (101 MHz)
2	-	148.6	-	154.2	-	154.3
3	6.29 (s, 1H)	115.6	6.33 (s, 1H)	104.5	6.34 (s, 1H)	104.5
4	-	129.8	-	129.3	-	129.3
5	7.31 (s, 1H)	143.7	7.94 (s, 1H)	145.8	7.84 (s, 1H)	145.9
1’	2.31 (s, 3H)	11.6	2.29 (s, 3H)	13.5	2.30 (s, 3H)	13.5
2’	-	191.3	-	195.5	-	195.5
3’	2.63 (d, 2H)	24.7	2.54 (d, 2H)	25.6	2.55 (d, 7.0, 2H)	25.6
4’	2.20 (m, 1H)	47.7	2.15-2.28 (m, 1H)	49.3	2.27-2.20 (m, 1H)	49.4
5’; 6’	0.90 (d, 6H)	22.5	0.95 (d, 6H)	22.8	0.96 (d, 6.6, 6H)	22.9

Table S3: Comparison of ^{1}H and ^{13}C NMR data of natural and synthetic rabdoketone B (3).



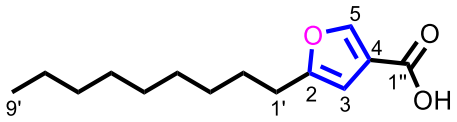
	Rabdoketone B (**3**) (Natural) in $CDCl_3$ Ma *et al.*		Rabdoketone B (**3**) (Synthetic) in $CDCl_3$ This work	
	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (100 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (101 MHz)
2	-	149.3	-	154.1
3	6.30 (s, 1H)	115.7	6.38 (s, 1H)	104.9
4	-	129.9	-	130.6
5	7.31 (s, 1H)	143.1	7.84 (s, 1H)	145.1
1’	2.36 (s, 3H)	11.9	2.30 (s, 3H)	13.6
2’	-	181.5	-	185.7
3’	6.72 (s, 1H)	120.6	6.40-6.39 (m, 1H)	121.8
4’	-	156.4	-	156.1
5’	1.93 (s, 3H)	20.8	1.95 (s, 1H)	21.2
6’	2.20 (s, 3H)	28.0	2.22 (s, 1H)	28.0

Table S4: Comparison of ^{1}H and ^{13}C NMR data of natural and synthetic paleofuran A (4).



Paleofuran A (**4**) (Natural) in DMSO-d_6 Klapper *et al.*			Paleofuran A (**4**) (Synthetic) in $CDCl_3$ Klapper *et al.*		Paleofuran A (**4**) (Synthetic) in $CDCl_3$ This work	
	δH (mult, *J* in Hz) (600 MHz)	δC (mult, *J* in Hz) (150 MHz)	δH (mult, *J* in Hz) (300 MHz)	δC (mult, *J* in Hz) (75 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (101 MHz)
2	-	158.7	-	158.7	-	158.7
3	6.35 (s, 1H)	104.9	6.35 (s, 1H)	104.9	6.35 (s, 1H)	104.9
4	-	119.2	-	119.2	-	119.2
5	7.96 (s, 1H)	147.7	7.96 (s, 1H)	147.7	7.97 (s, 1H)	147.7
1’	2.62 (t, 7.5, 2H)	27.9	2.62 (t, 6.2, 2H)	27.9	2.62 (t, 7.5, 2H)	27.9
2’	1.64 (p, 7.2, 2H)	27.8	1.59–1.69 (m, 2H)	27.8	1.61–1.68 (m, 2H)	27.8
3’	1.33 (m, 2H)	29.1	1.27–1.33 (m, 8H)	29.1	1.26–1.38(m, 8H)	29.1
4’	1.33 (m, 2H)	29.1		29.1		29.1
5’	1.29 (m, 2H)	31.9		31.9		31.9
6’	1.30 (m, 2H)	22.8		22.8		22.8
7’	0.89 (t, 6.6, 3H)	14.2	0.89 (t, 5.2, 3H)	14.2	0.88 (t, 6.63, 3 H)	14.2
1’’	-	169.0	-	169.0	-	169.4

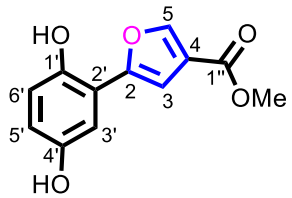
Table S5: Comparison of ^{1}H and ^{13}C NMR data of natural and synthetic paleofuran B (5).



	Paleofuran B (**5**) (Natural) in DMSO-d_6 Klapper *et al.*		Paleofuran B (**5**) (Synthetic) in $CDCl_3$ This work	
	δH (mult, *J* in Hz) (600 MHz)	δC (mult, *J* in Hz) (150 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (101 MHz)
2	-	158.7	-	158.7
3	6.35 (s, 1H)	104.9	6.35 (s, 1H)	104.9
4	-	119.2	-	119.1
5	7.96 (s, 1H)	147.5	7.96 (s, 1H)	147.6
1’	2.62 (t, 7.5, 2H)	28.0	2.62 (t, *J* = 7.63 Hz, 2H)	27.9
2’	1.64 (p, 7.2, 2H)	27.8	1.64 (p, *J* = 7.38 Hz, 2H)	27.8
3’	1.33 (m, 2H)	29.4	1.25 (m, 12H)	29.4
4’	1.27 (m, 2H)	29.2/29.5/29.6		29.2/29.4/29.6
5’	1.27 (m, 2H)	29.2/29.5/29.6		29.2/29.4/29.6
6’	1.27 (m, 2H)	29.2/29.5/29.6		29.2/29.4/29.6
7’	1.27 (m, 2H)	32.0		32.0
8’	1.29 (m, 2H)	22.8		22.8

9’	0.88 (t, 6.8, 3H)	14.2	0.88 (t, *J* = 6.7 Hz, 3H)	14.3
1’’	-	167.8	-	168.2

Table S6: Comparison of ^{1}H and ^{13}C NMR data of natural and synthetic tournefolin C (6).

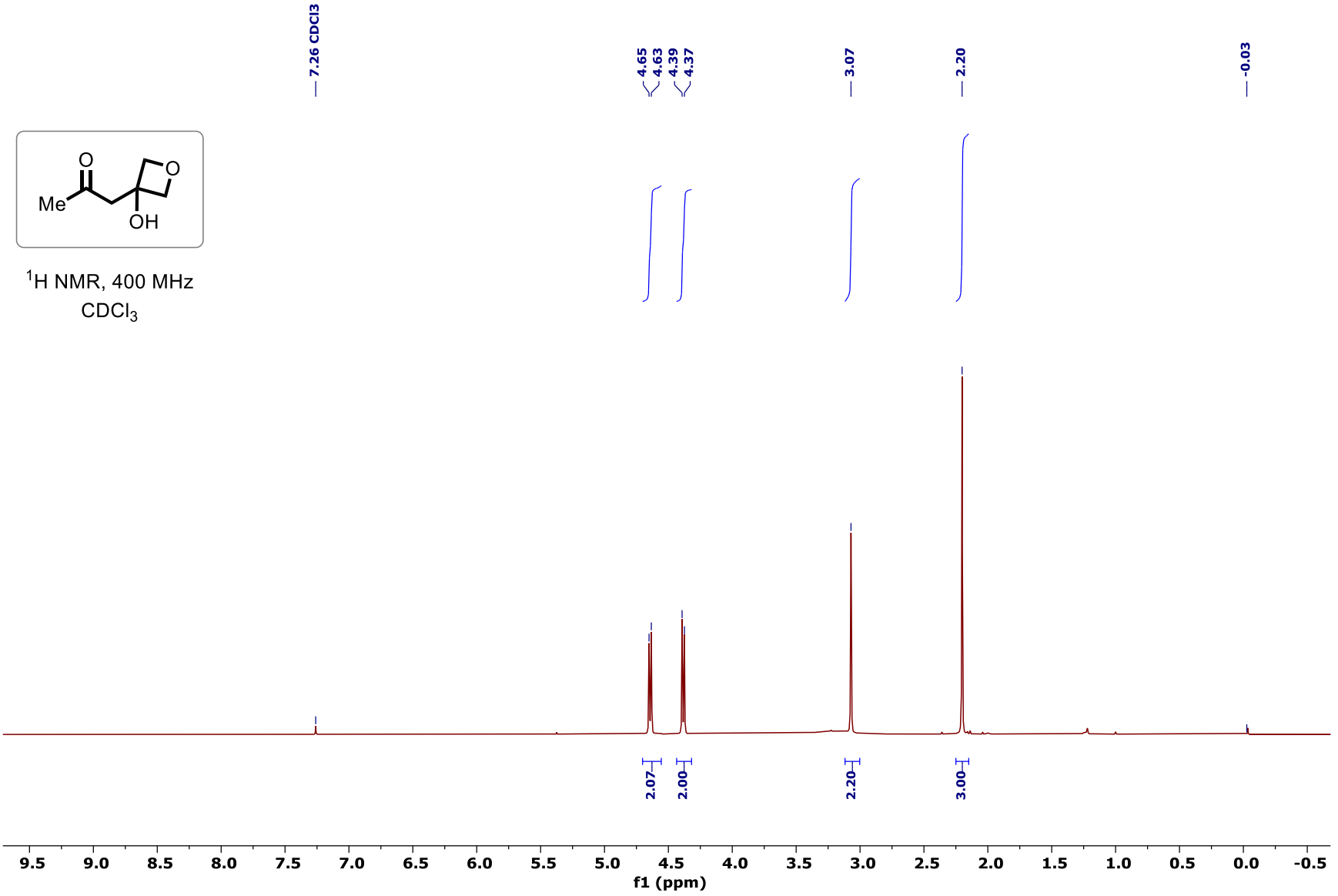


	Tournefolin C (**6**) (Natural) in DMSO-d_6 Lin *et al.*		Tournefolin C (**6**) (Synthetic) in DMSO-d_6 This work	
	δH (mult, *J* in Hz) (300 MHz)	δC (mult, *J* in Hz) (75 MHz)	δH (mult, *J* in Hz) (400 MHz)	δC (mult, *J* in Hz) (101 MHz)
2	-	151.7	-	151.7
3	7.08 (s, 1H)	107.9	7.14 (d, 0.75, 1H)	108.0
4	-	120.1	-	120.2
5	8.35 (s, 1H)	146.4	8.39 (s, 1H)	146.6
1’	-	146.4	-	146.5
2’	-	116.2	-	116.2
3’	7.06 (d, 2.0, 1H)	110.8	7.07 (d, 2.8, 1H)	110.8
4’	-	149.8	-	149.9

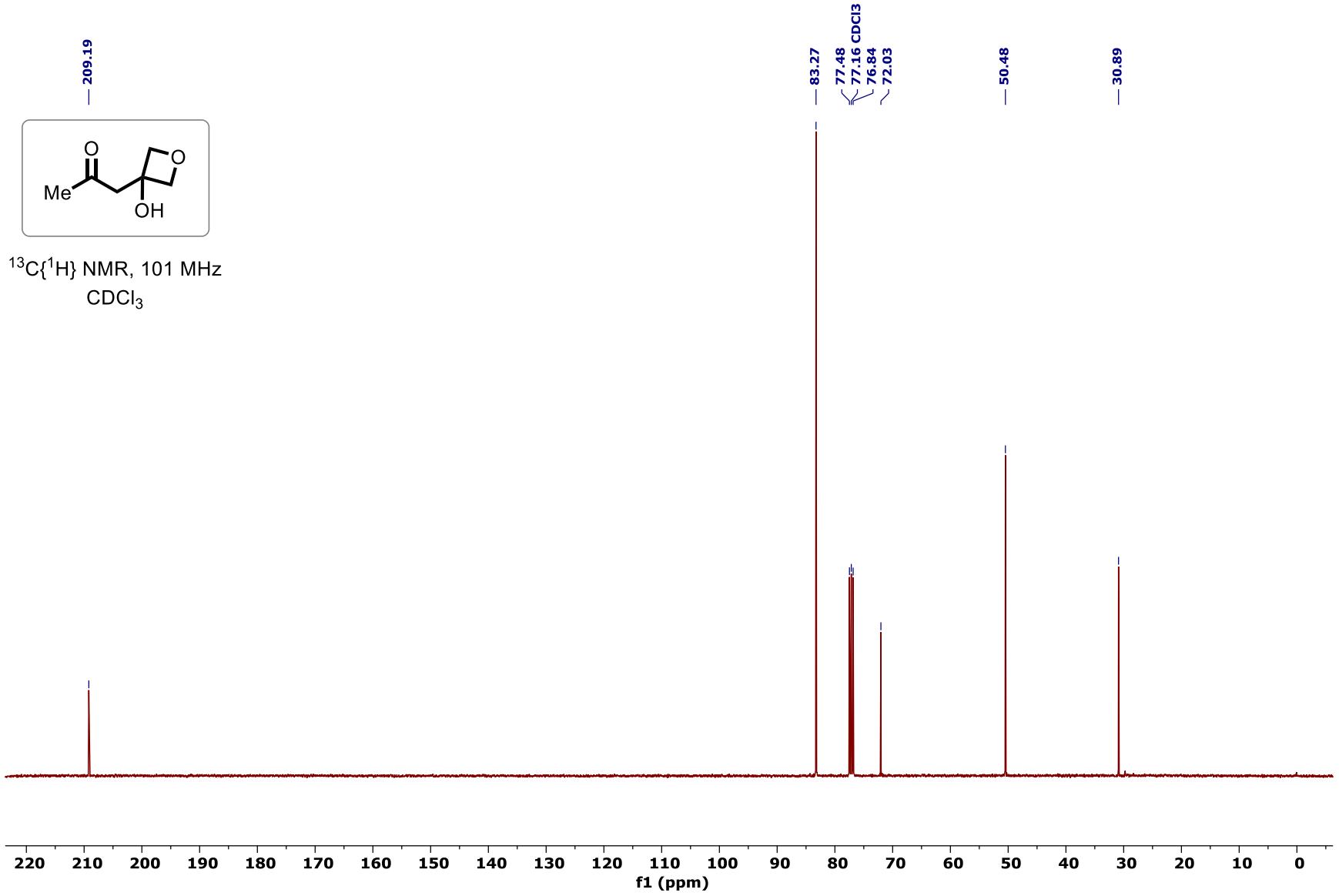
5’	6.59 (dd, 8.7, 2.0, 1H)	116.9	6.60 (dd, 8.7, 2.8, 1H)	117.0
6’	6.77 (d, 8.7, 1H)	116.0	6.79 (d, 8.7, 1H)	116.1
1’’	-	162.9	-	163.0
OMe	3.78 (s, 1H)	51.4	3.79 (s, 1H)	51.5
OH	8.86 (s, 1H)	-	8.93 (s, 1H)	-
OH	9.53 (s, 1H)	-	9.62 (s, 1H)	-

^{1}H and ^{13}C NMR spectra

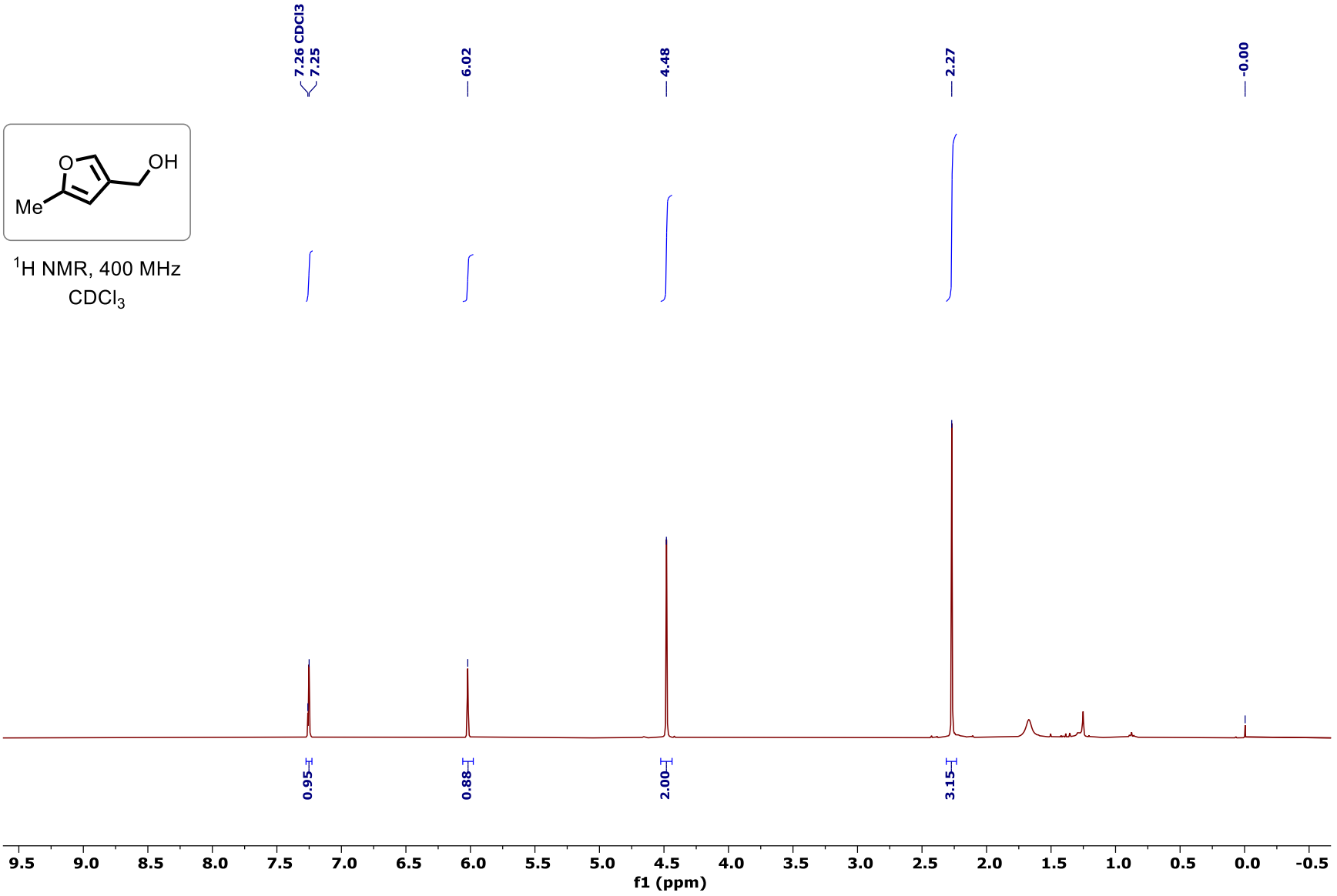
^{1}H NMR spectrum of 1-(3-hydroxyoxetan-3-yl)propan-2-one (11):



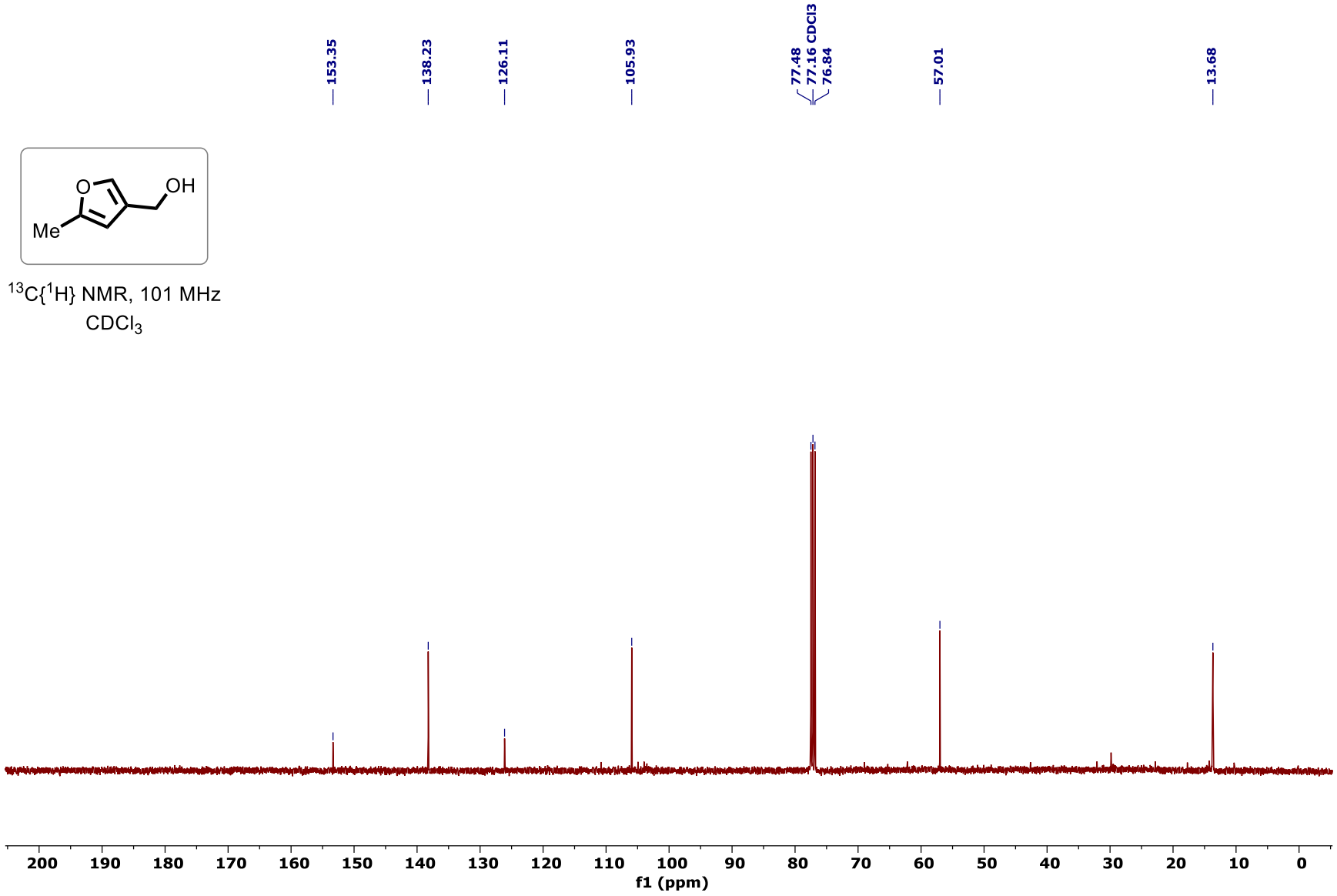
^{13}C NMR spectrum of 1-(3-hydroxyoxetan-3-yl)propan-2-one (11):



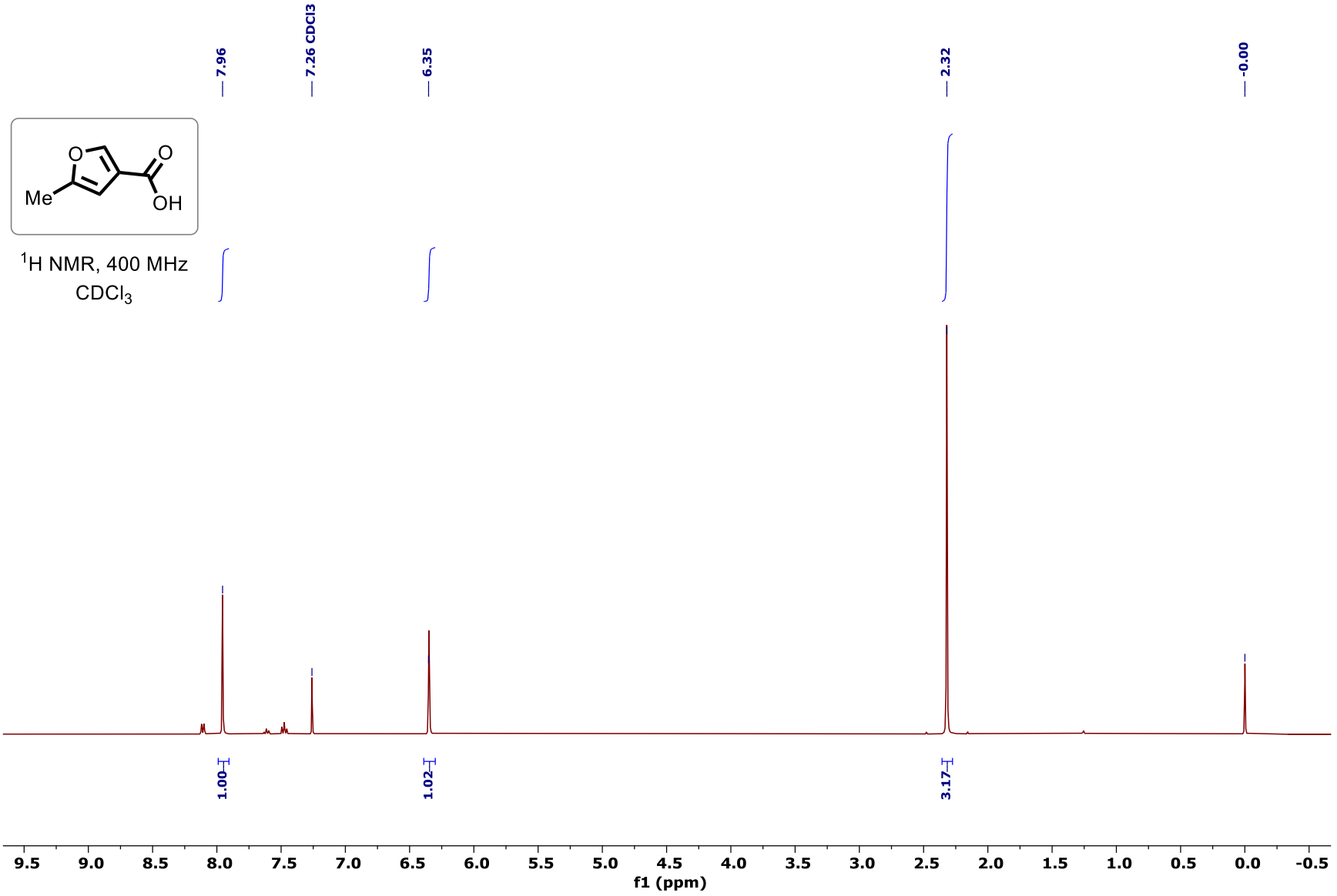
^{1}H NMR spectrum of (5-methylfuran-3-yl)methanol (12):



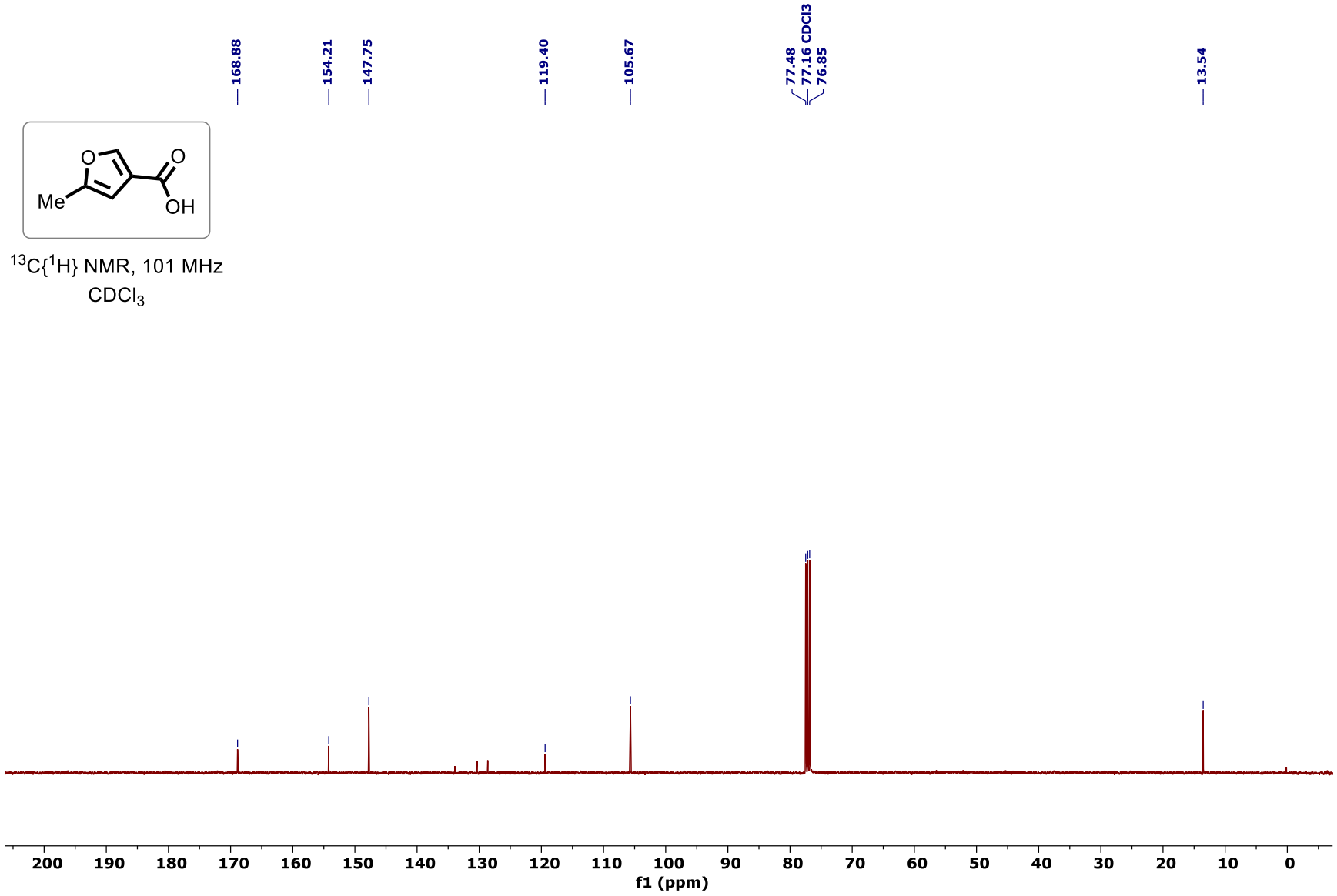
^{13}C NMR spectrum of (5-methylfuran-3-yl)methanol (12):



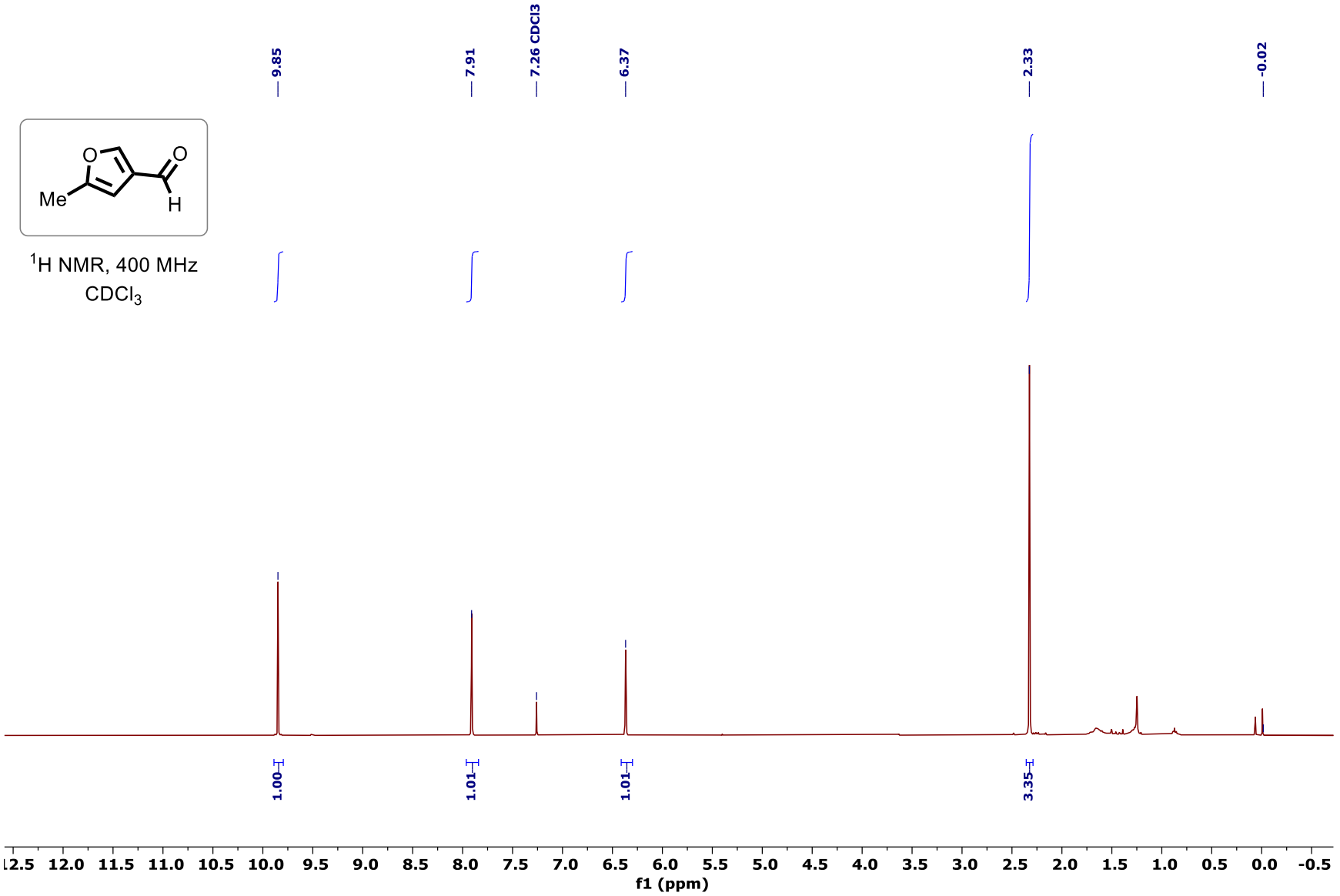
^{1}H NMR spectrum of methylfuroic acid (1):



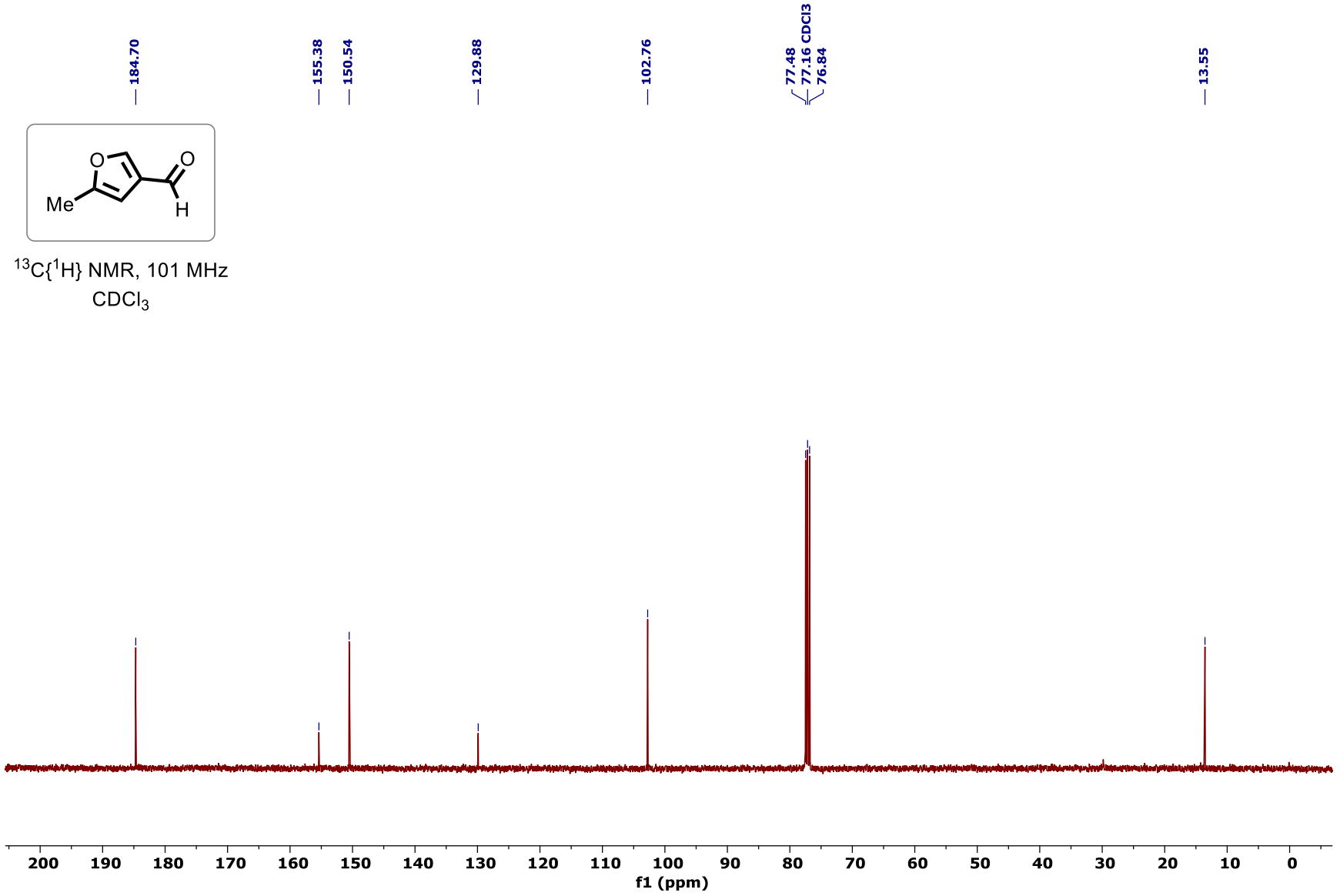
^{13}C NMR spectrum of methylfuroic acid (1):



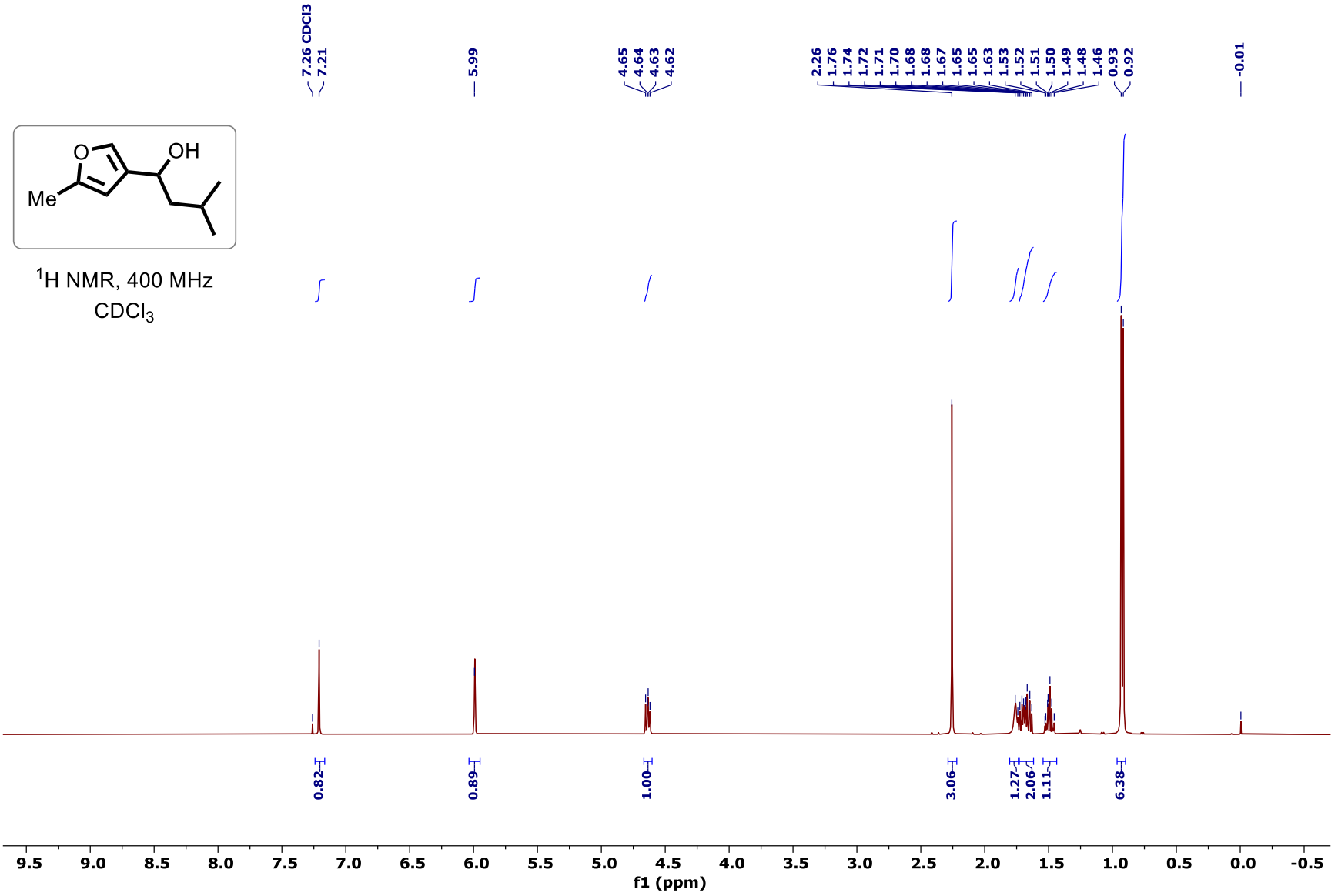
^{1}H NMR spectrum of 5-methylfuran-3-carbaldehyde (14):



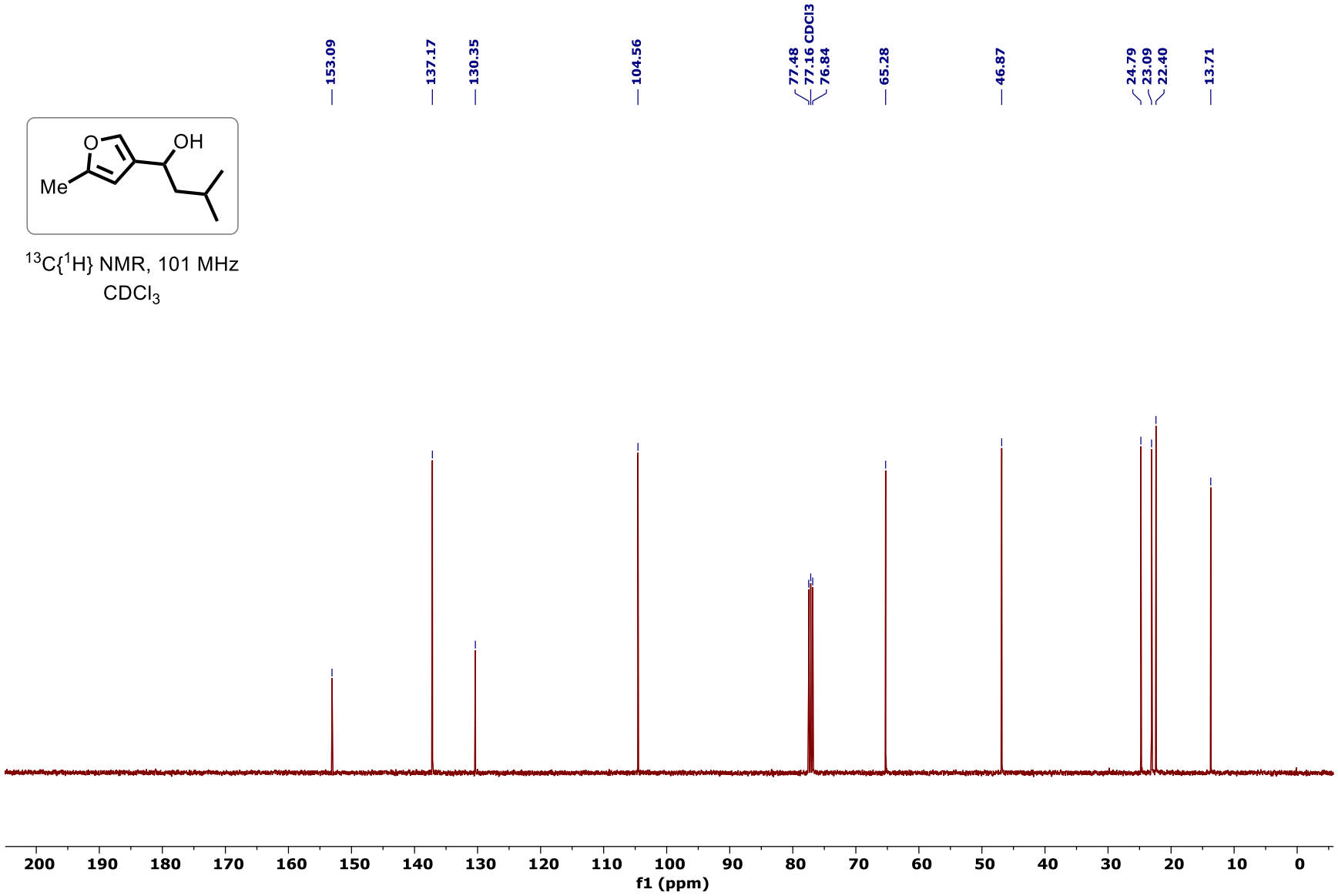
^{13}C NMR spectrum of 5-methylfuran-3-carbaldehyde (14):



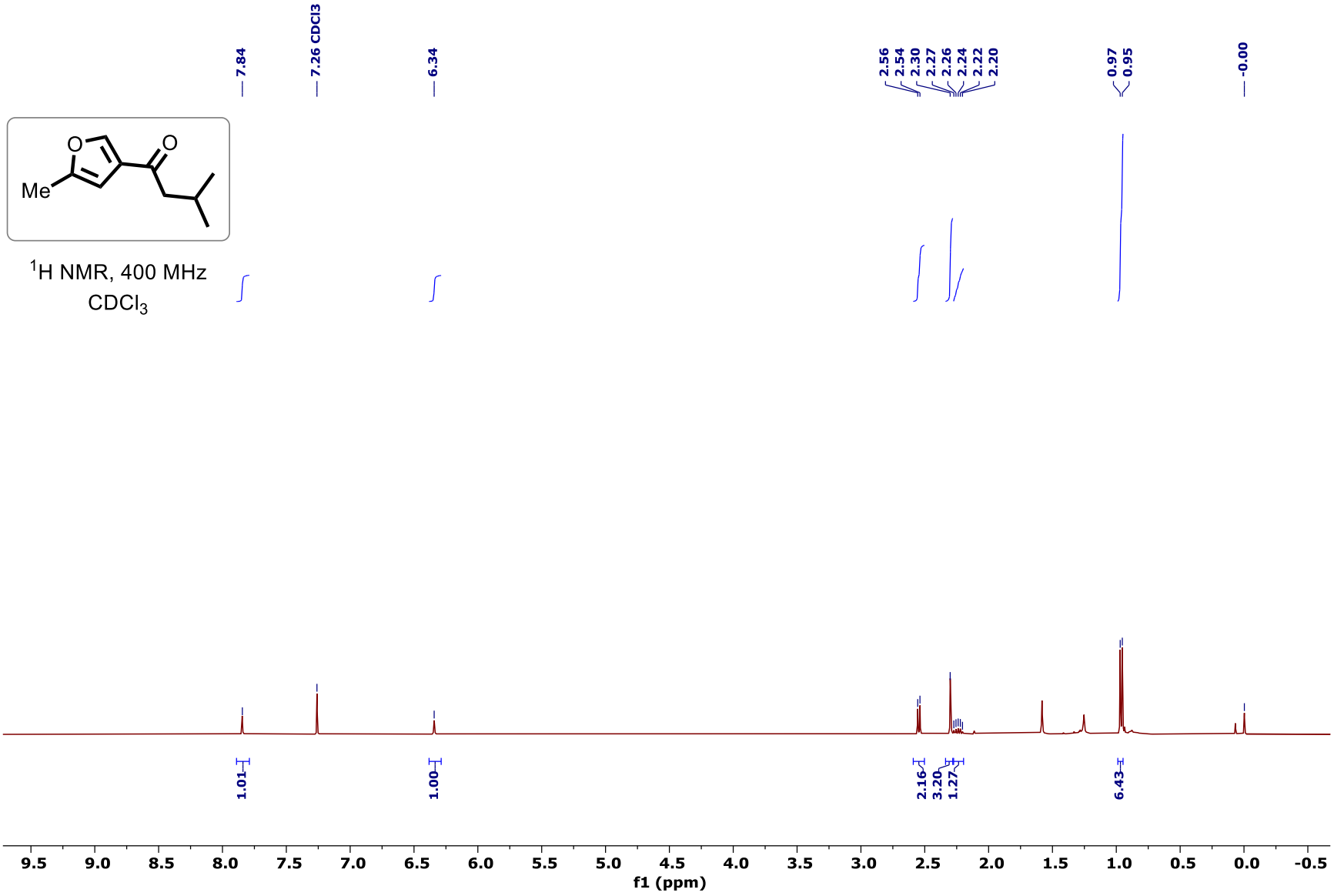
^{1}H NMR spectrum of 3-methyl-1-(5-methylfuran-3-yl)butan-1-ol (16):



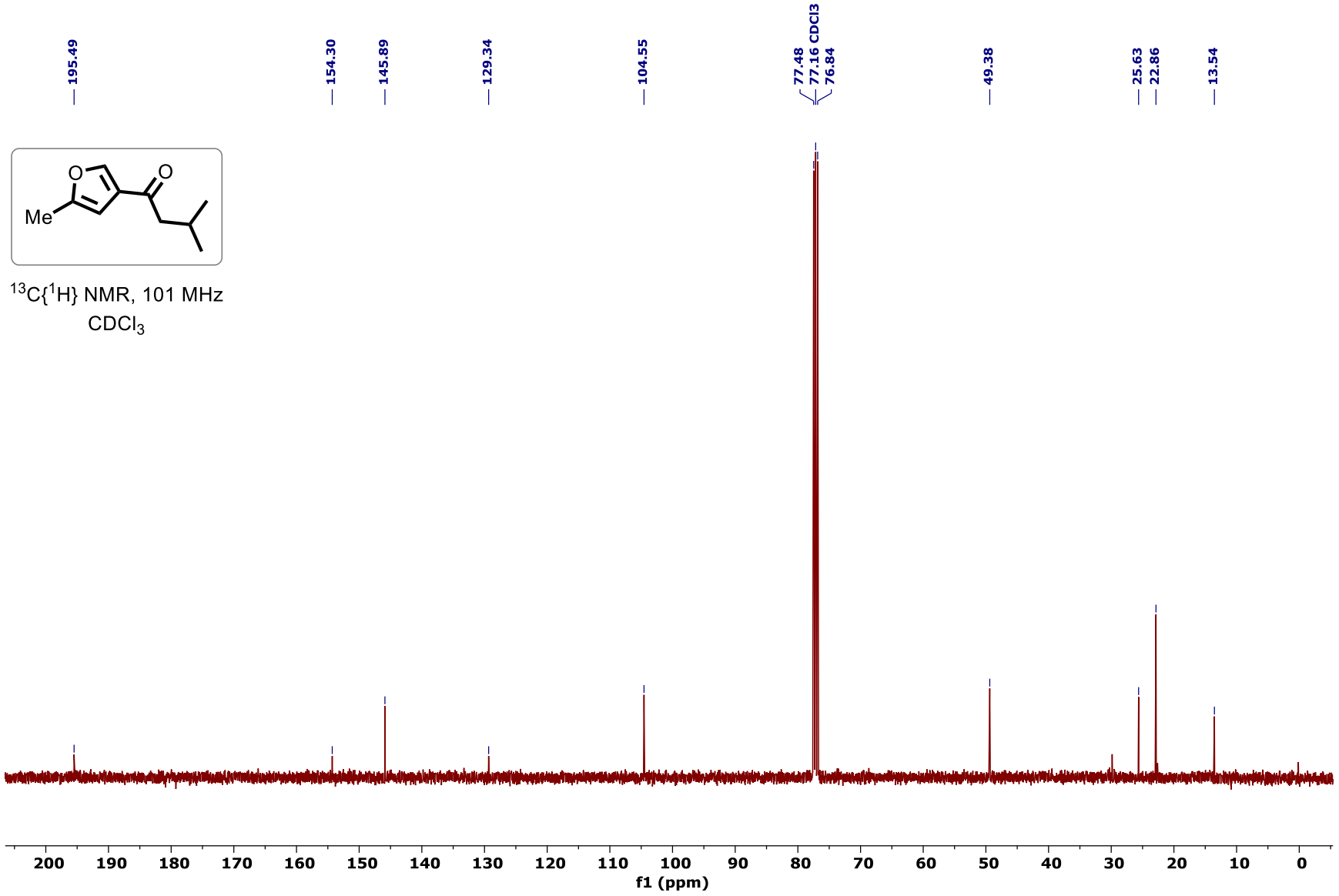
^{13}C NMR spectrum of 3-methyl-1-(5-methylfuran-3-yl)butan-1-ol (16):



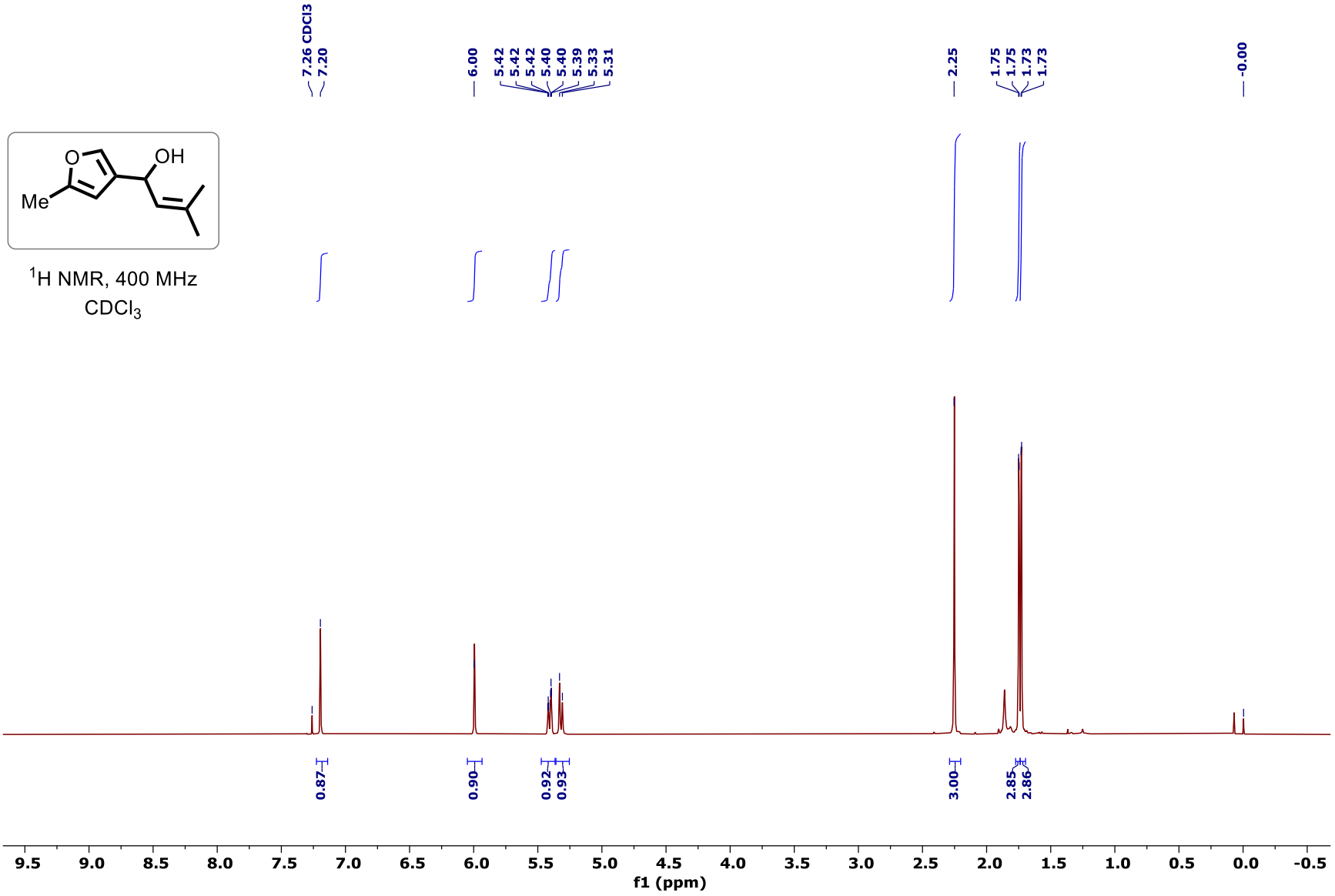
^{1}H NMR spectrum of rabdoketone A (2):



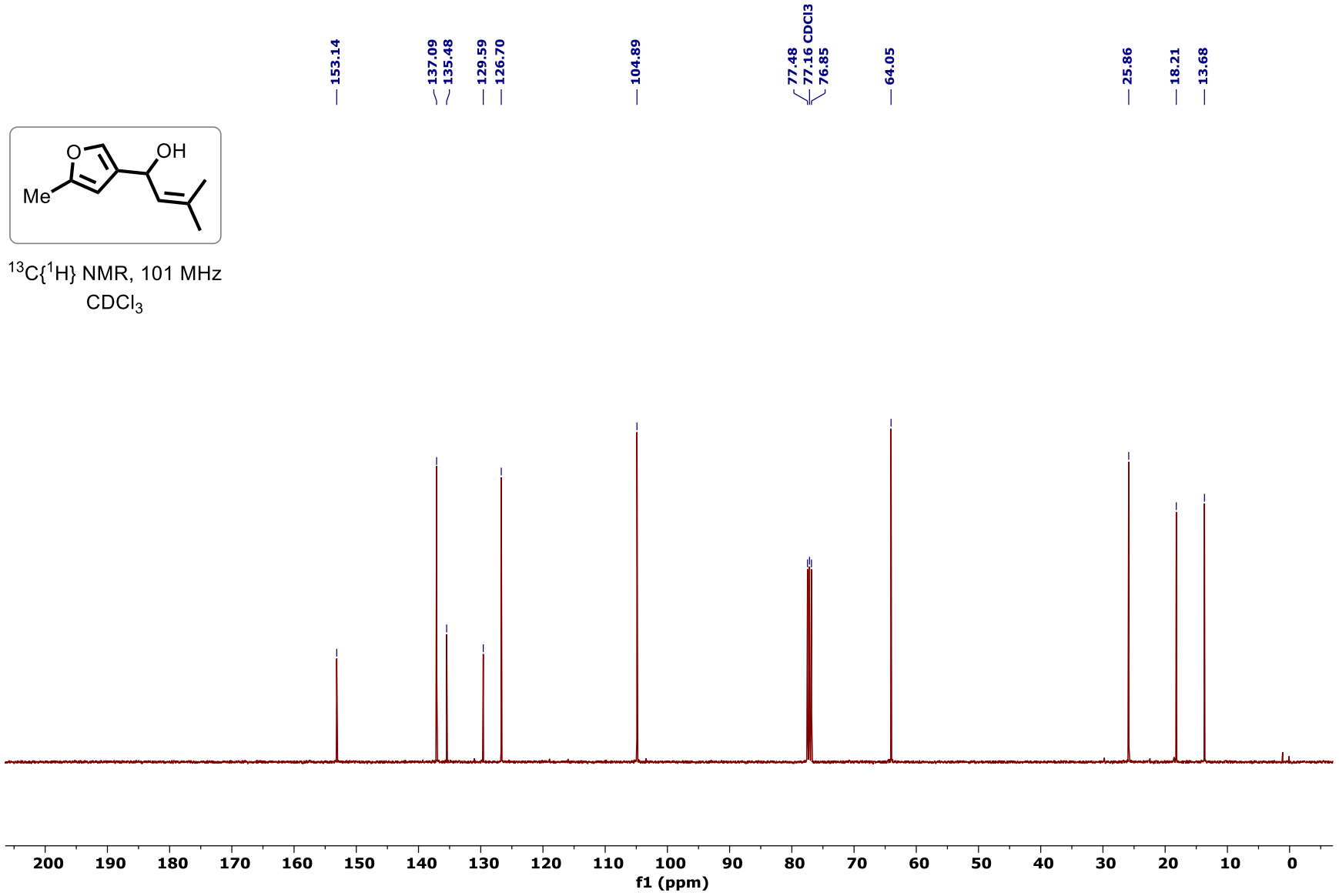
^{13}C NMR spectrum of rabdoketone A (2):



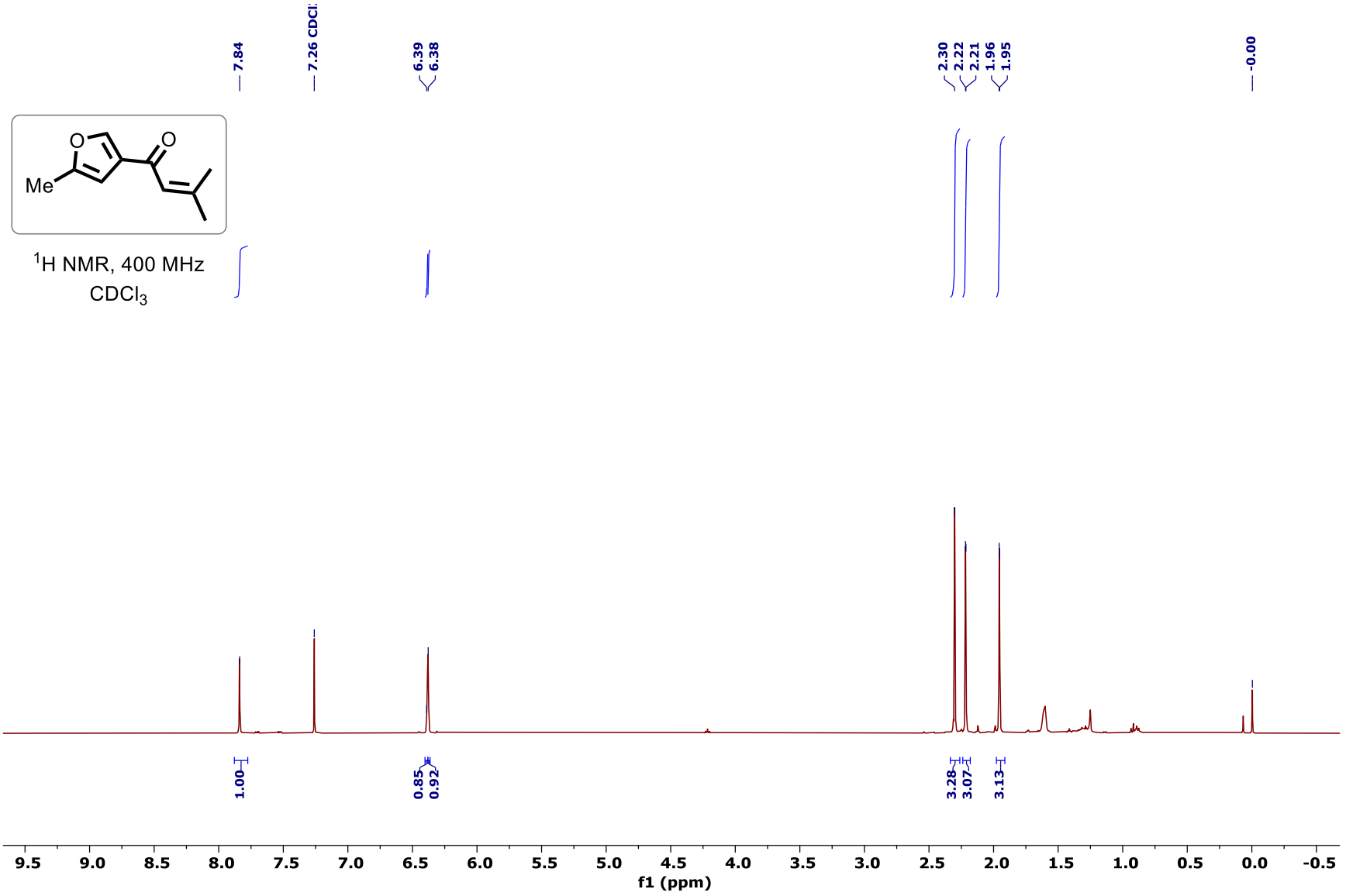
^{1}H NMR spectrum of 3-methyl-1-(5-methylfuran-3-yl)but-2-en-1-ol (18):



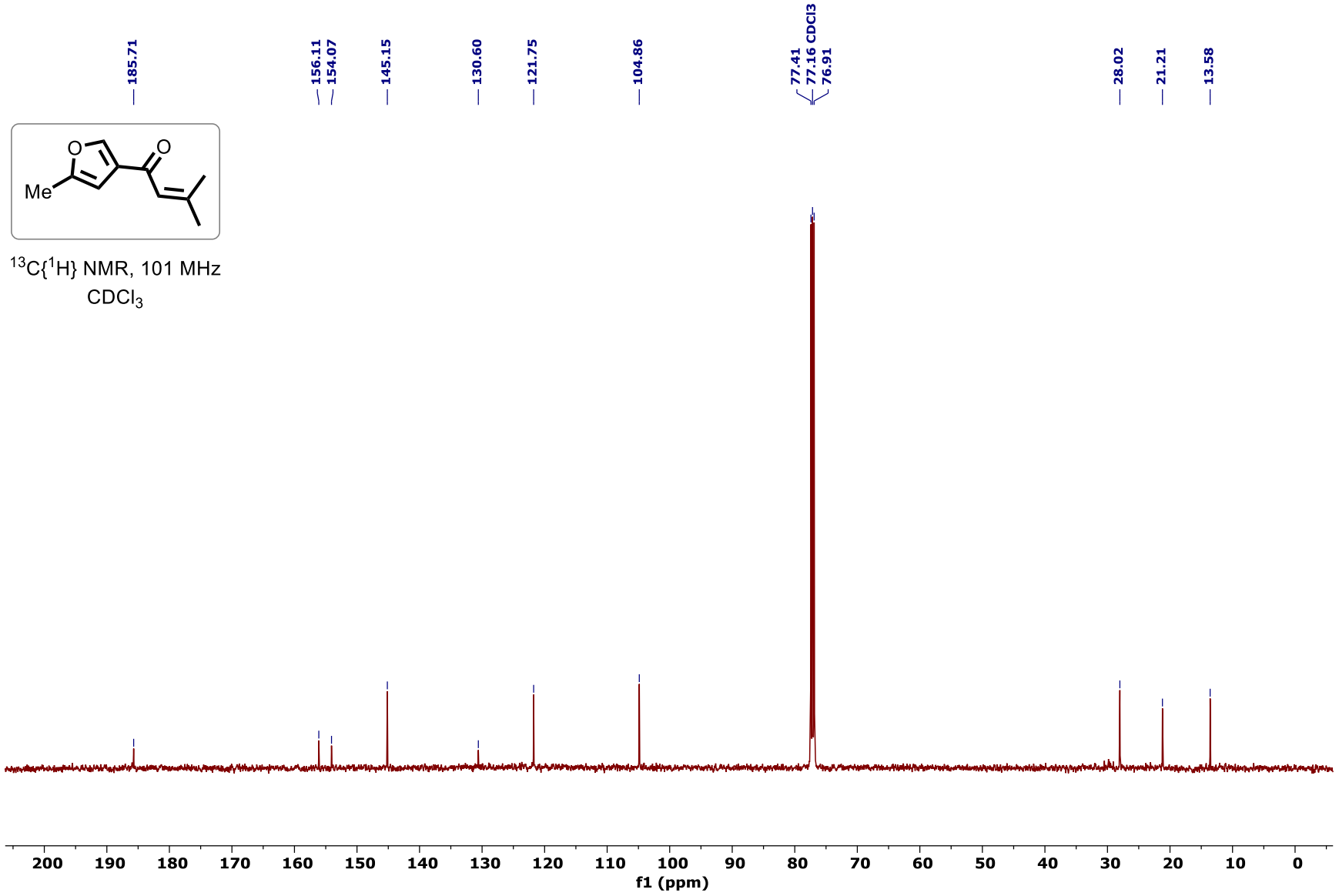
^{13}C NMR spectrum of 3-methyl-1-(5-methylfuran-3-yl)but-2-en-1-ol (18):



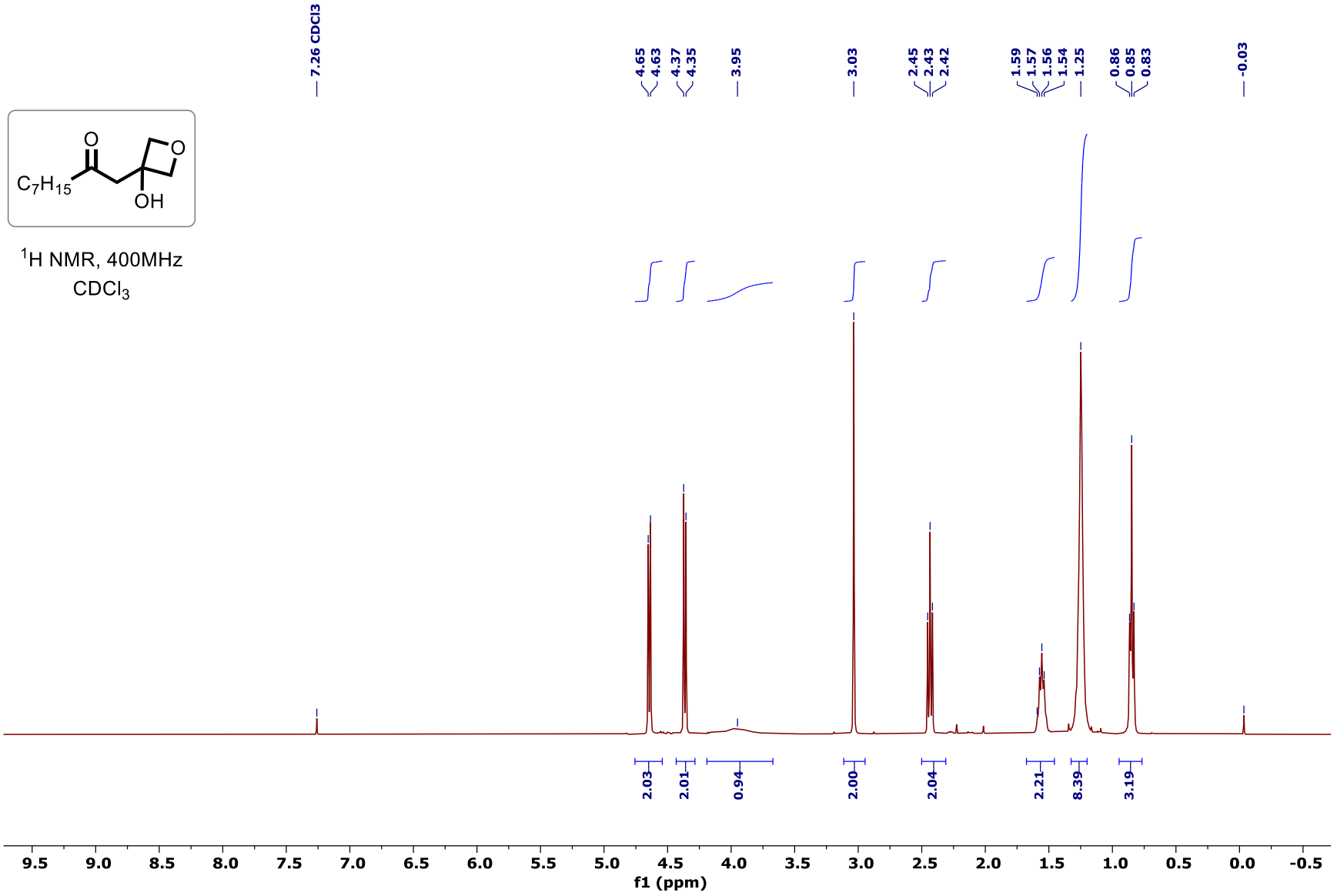
^{1}H NMR spectrum of rabdoketone B (3):



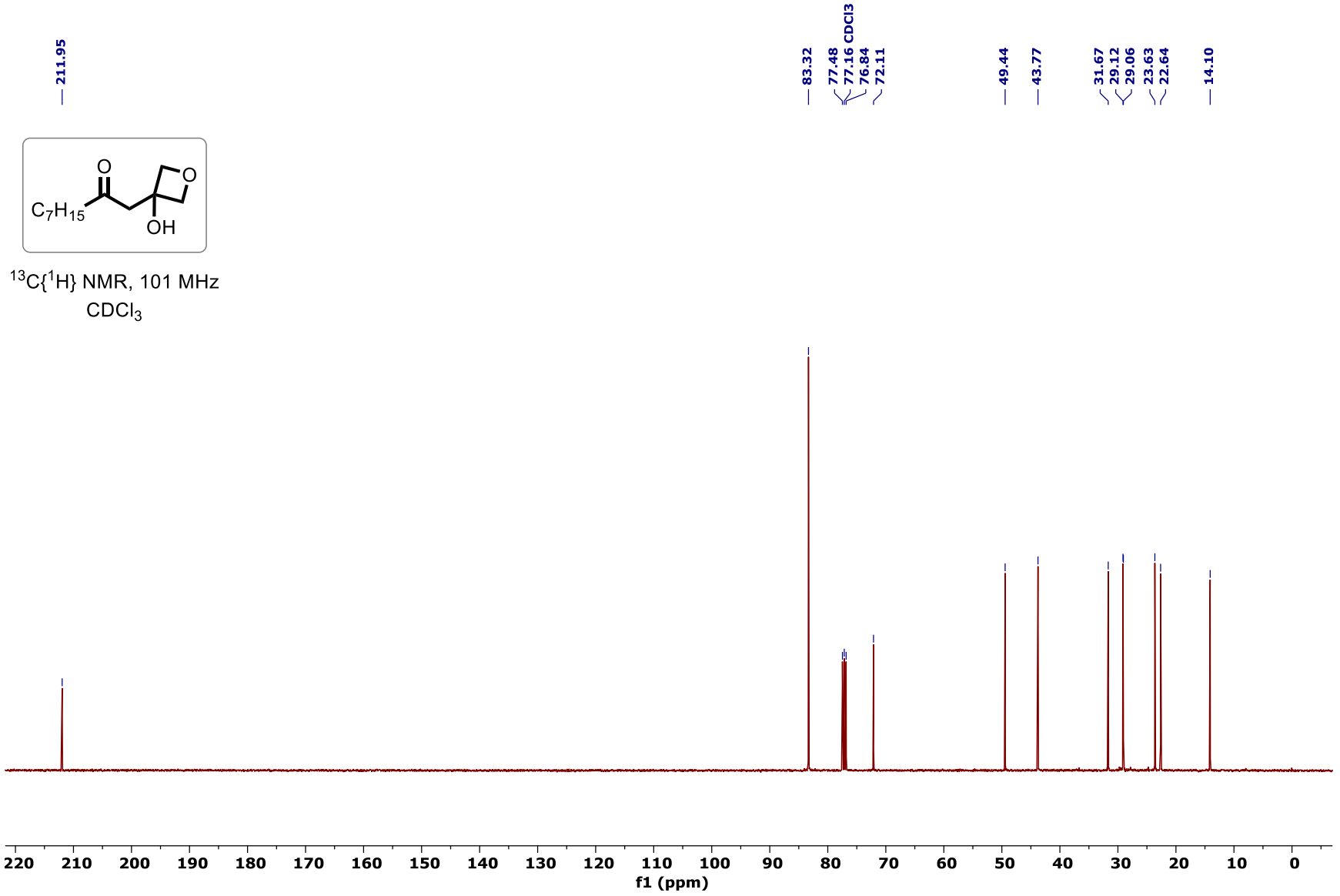
^{13}C NMR spectrum of rabdoketone B (3):



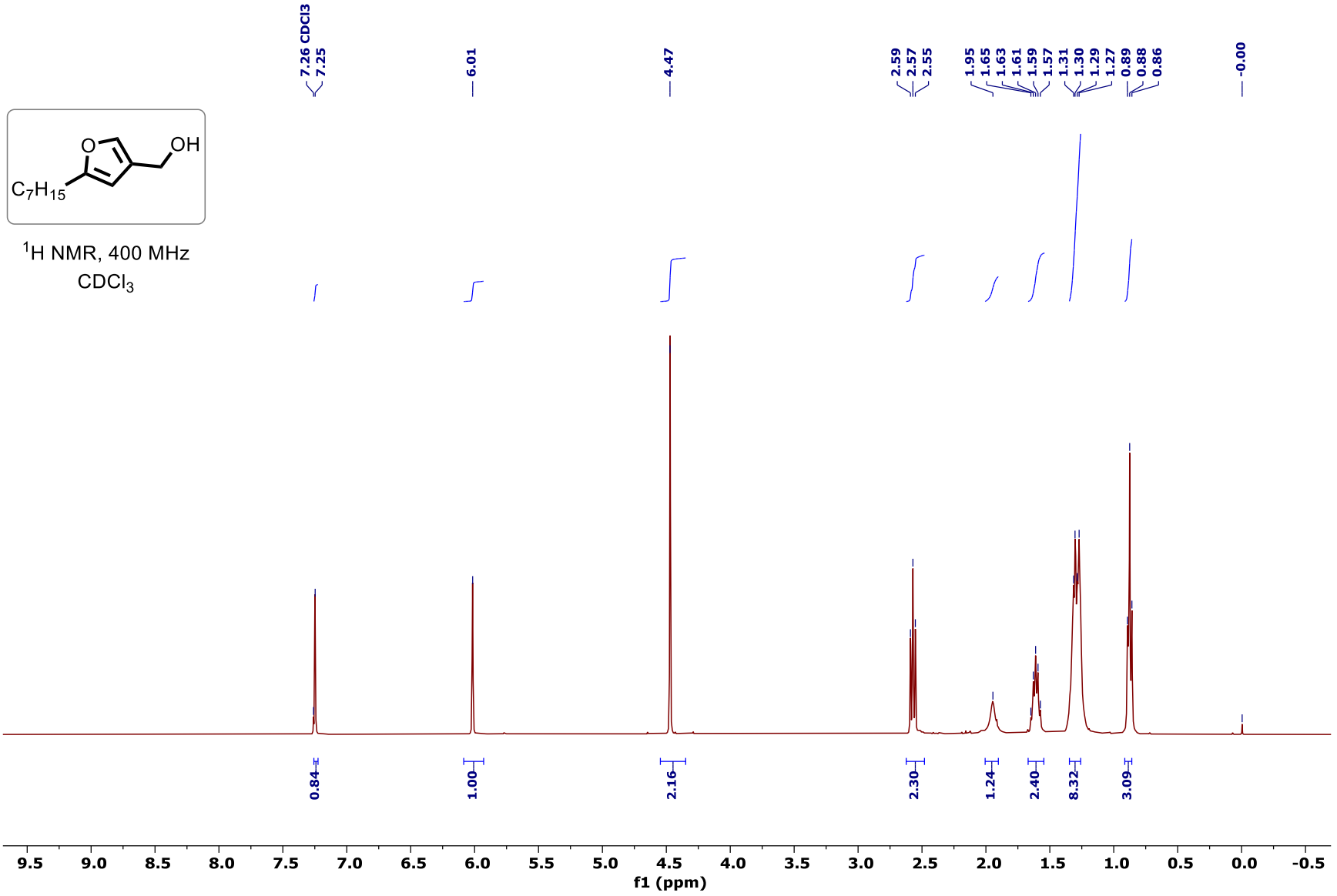
^{1}H NMR spectrum of 1-(3-hydroxyoxetan-3-yl)nonan-2-one (21):



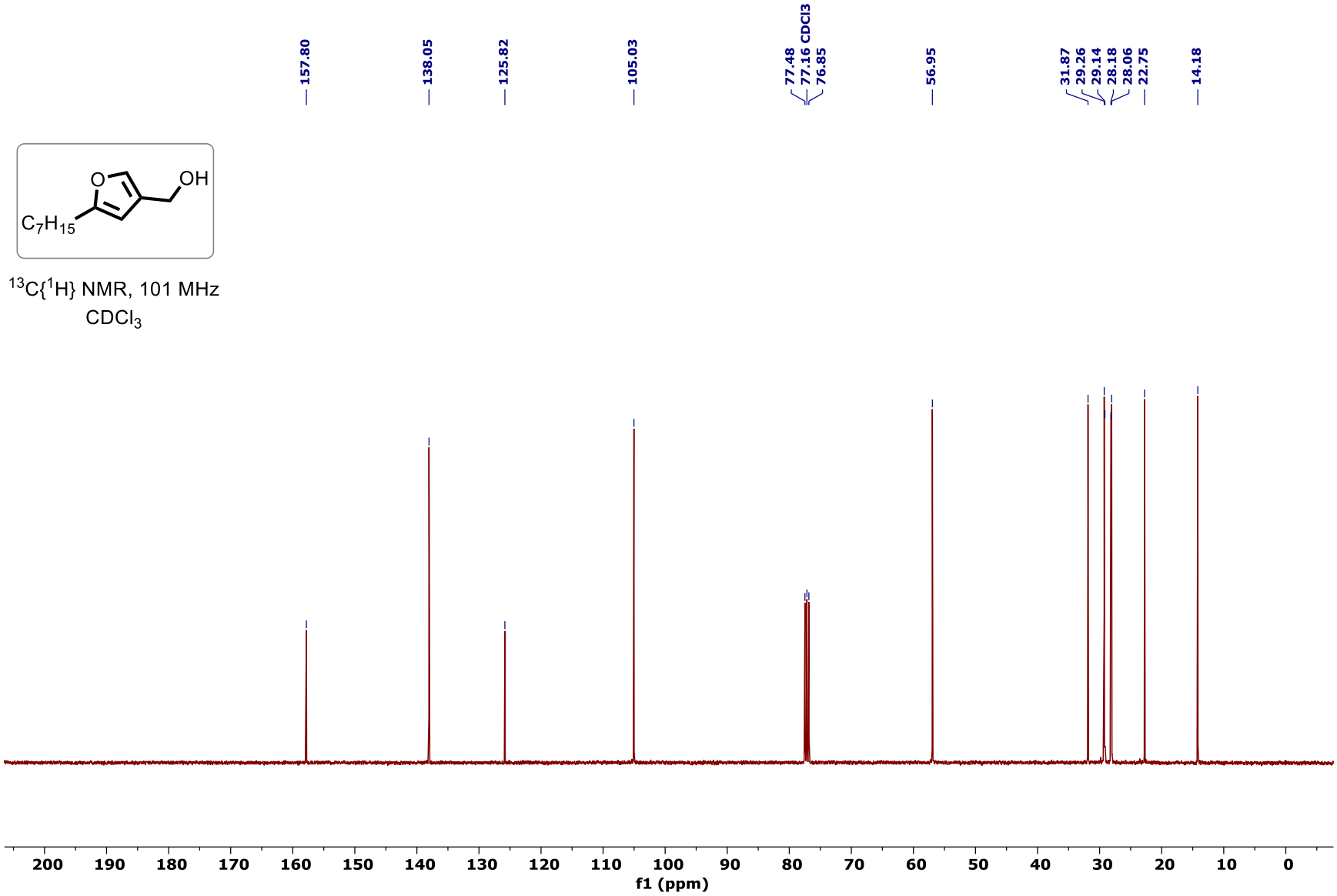
^{13}C NMR spectrum of 1-(3-hydroxyoxetan-3-yl)nonan-2-one (21):



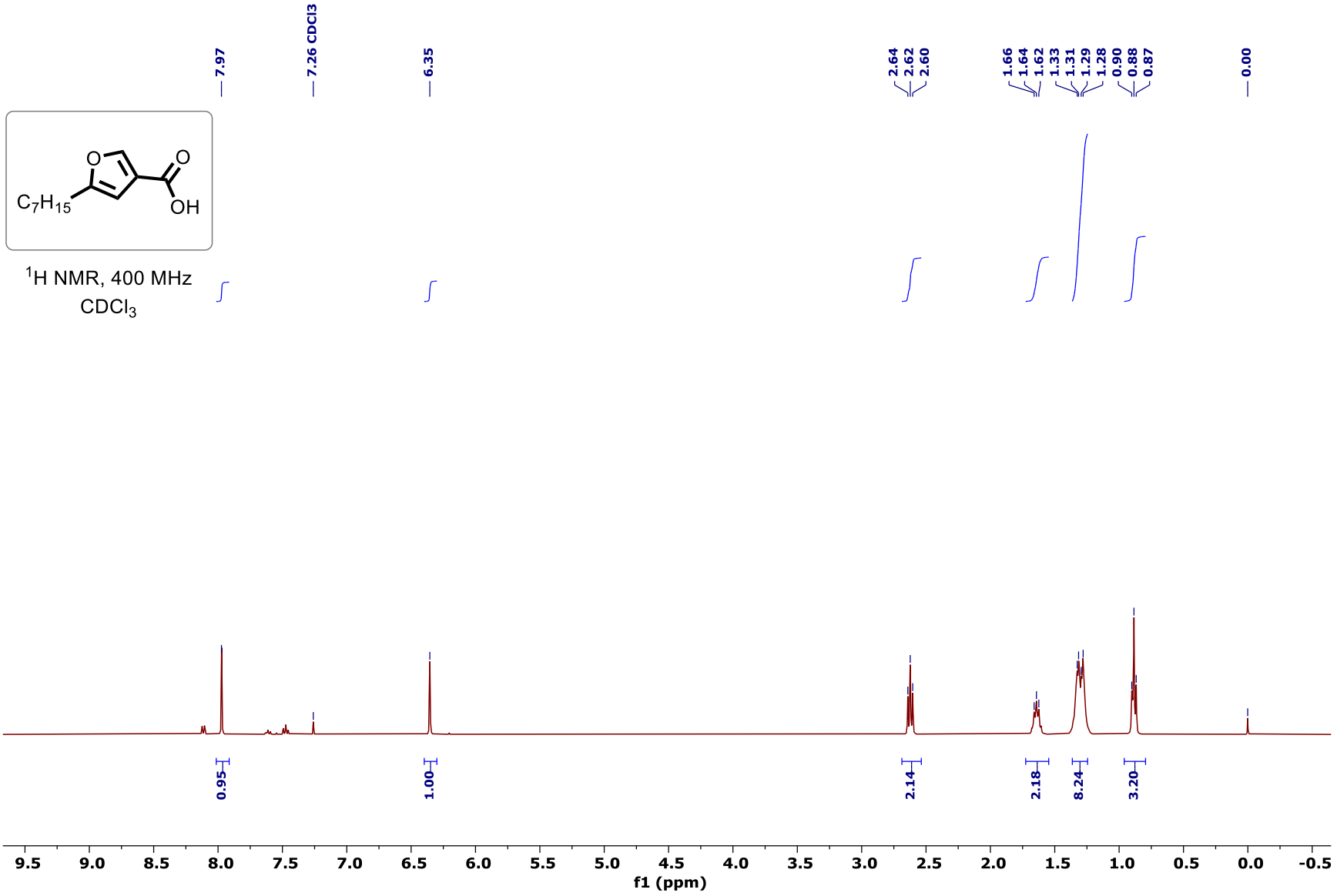
^{1}H NMR spectrum of (5-heptylfuran-3-yl)methanol (23):



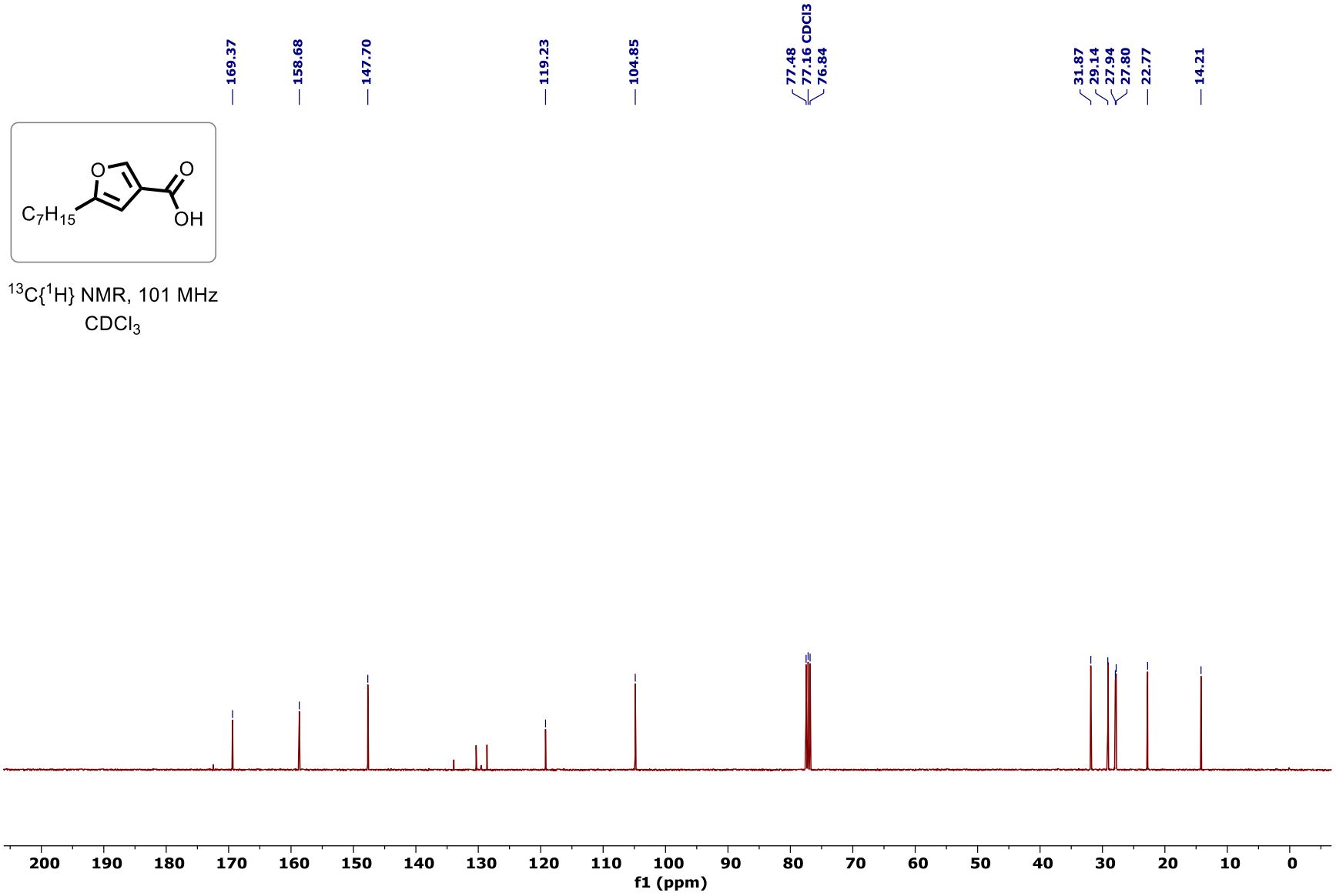
^{13}C NMR spectrum of (5-heptylfuran-3-yl)methanol (23):



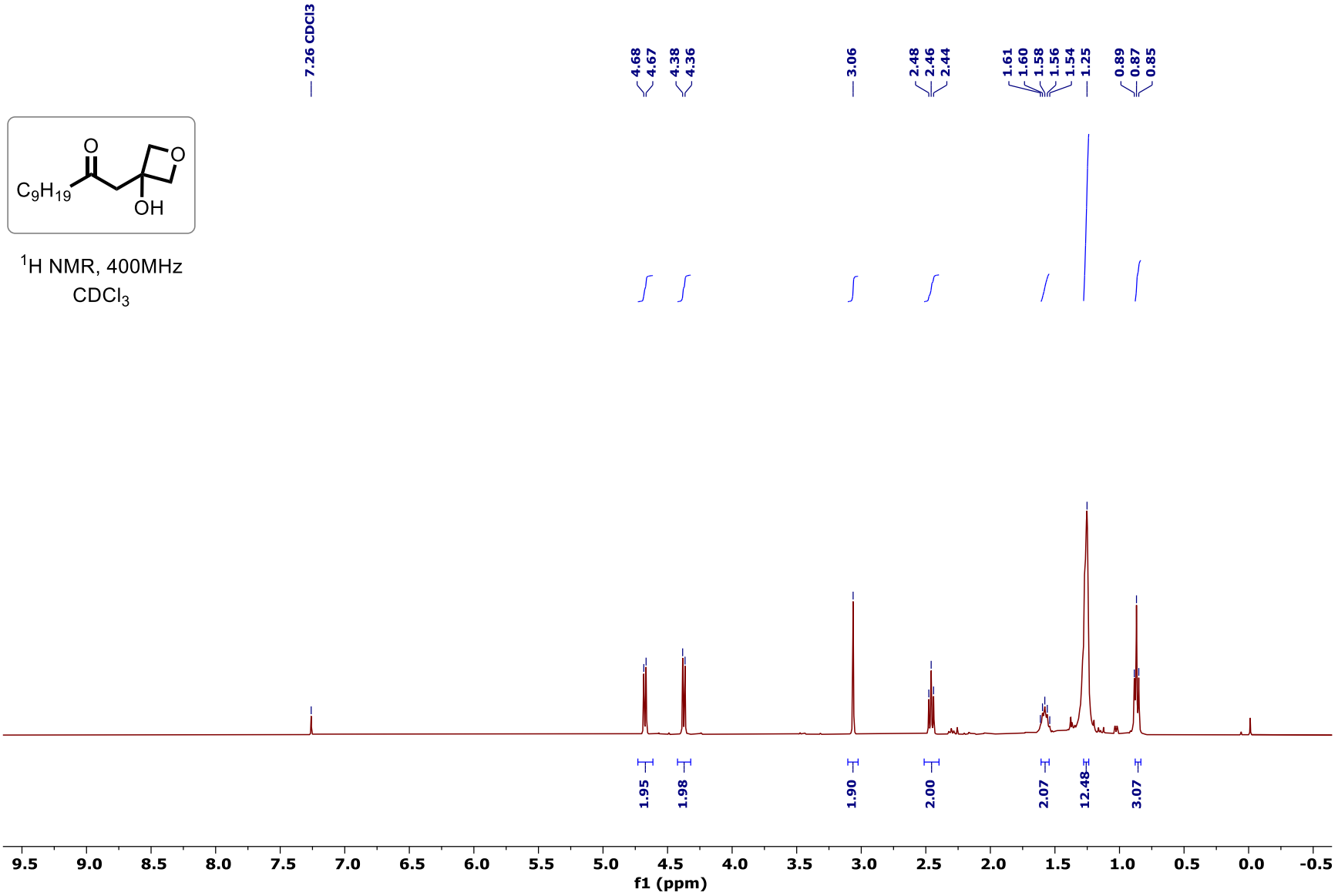
^{1}H NMR spectrum of paleofuran A (4):



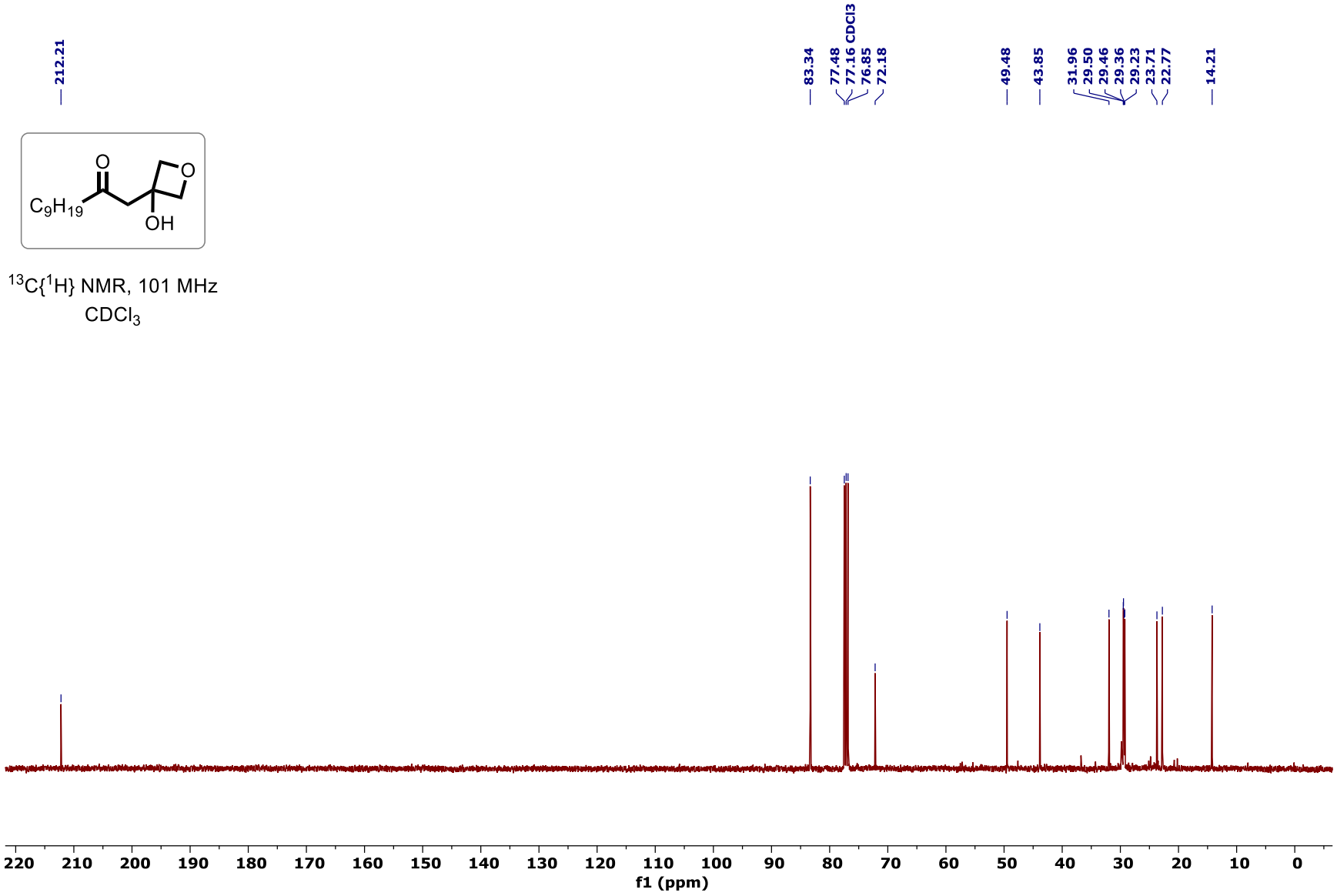
^{13}C NMR spectrum of paleofuran A (4):



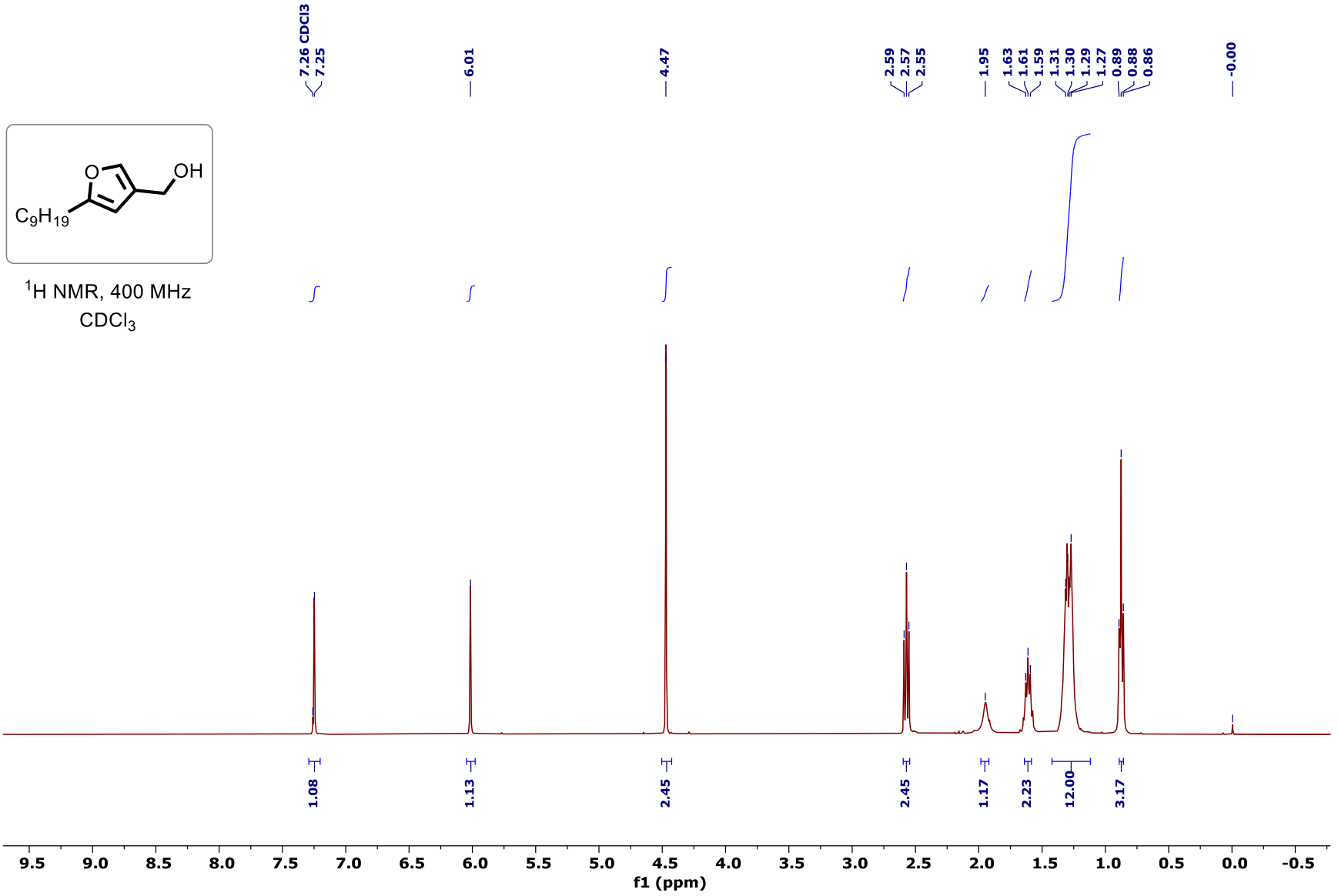
^{1}H NMR spectrum of 1-(3-hydroxyoxetan-3-yl)undecan-2-one (22):



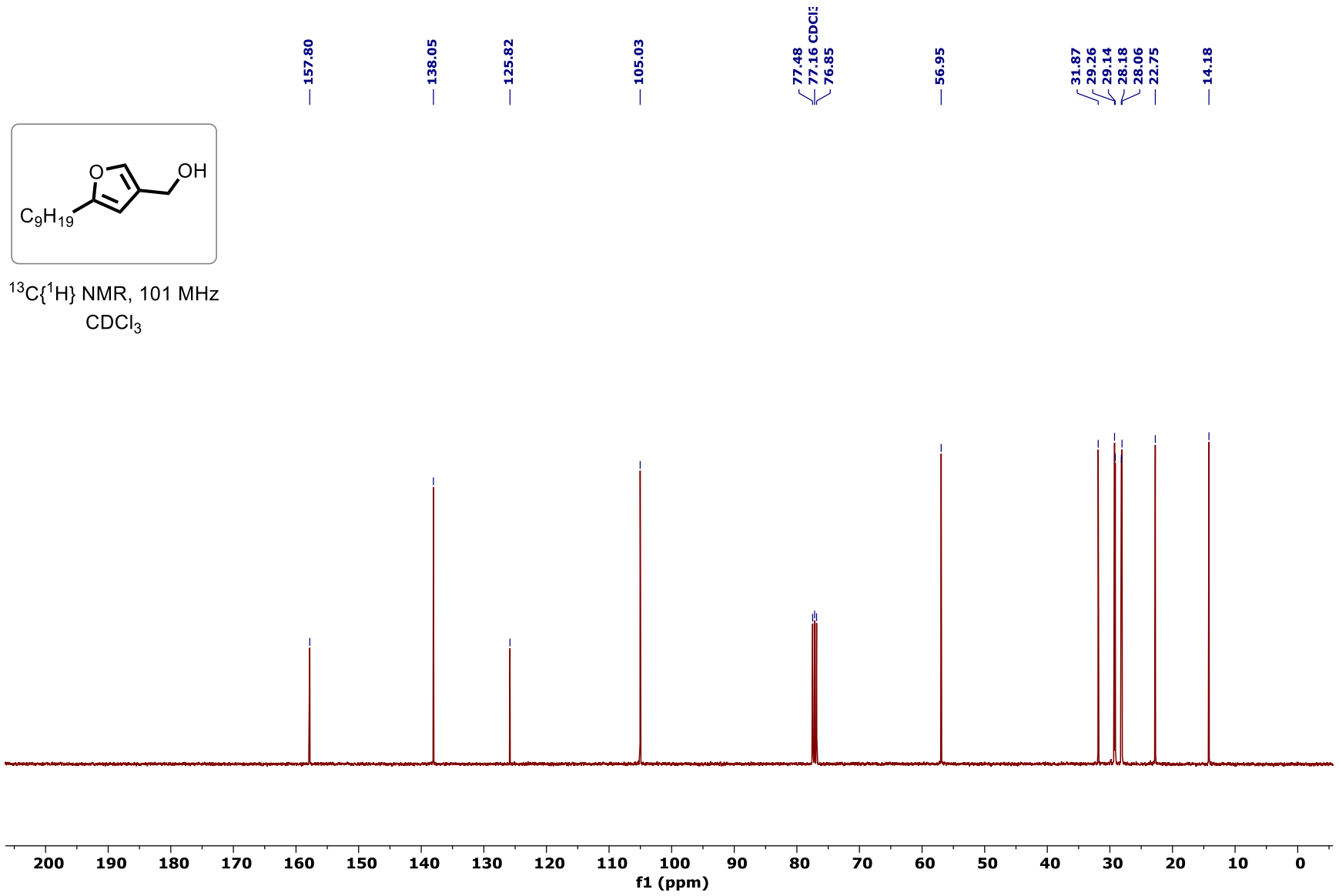
^{13}C NMR spectrum of 1-(3-hydroxyoxetan-3-yl)undecan-2-one (22):



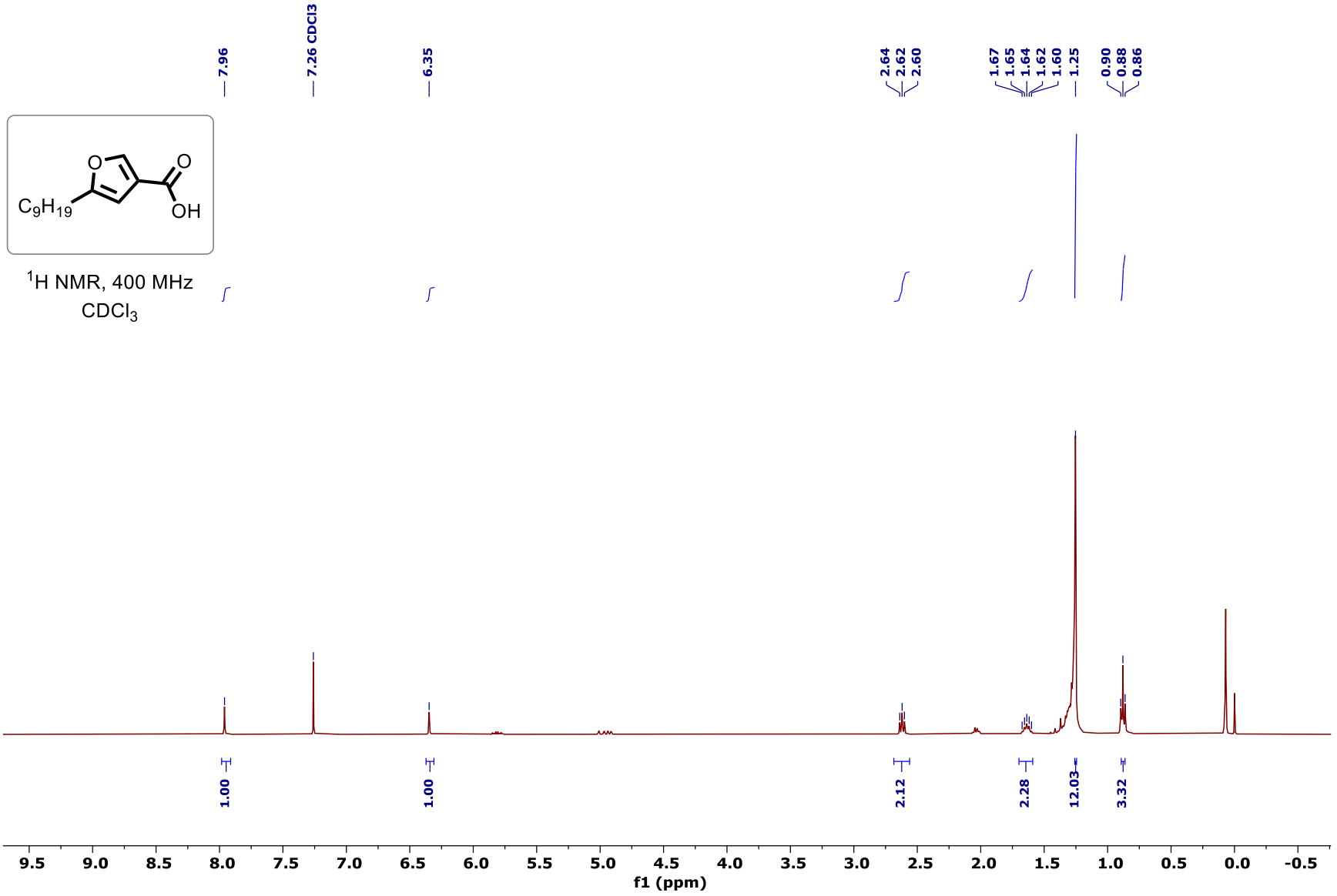
^{1}H NMR spectrum of (5-nonylfuran-3-yl)methanol (24):



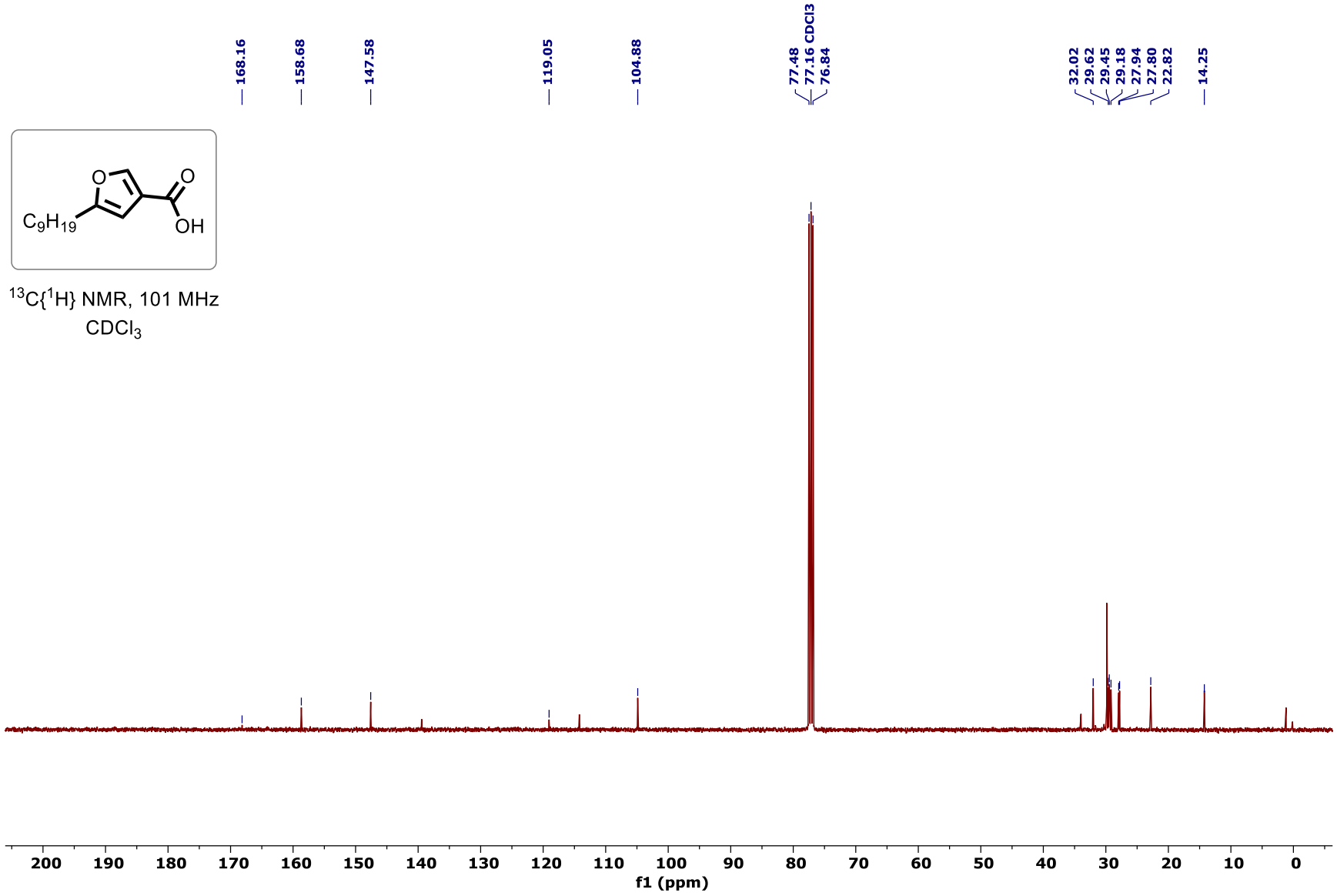
^{13}C NMR spectrum of (5-nonylfuran-3-yl)methanol (24):



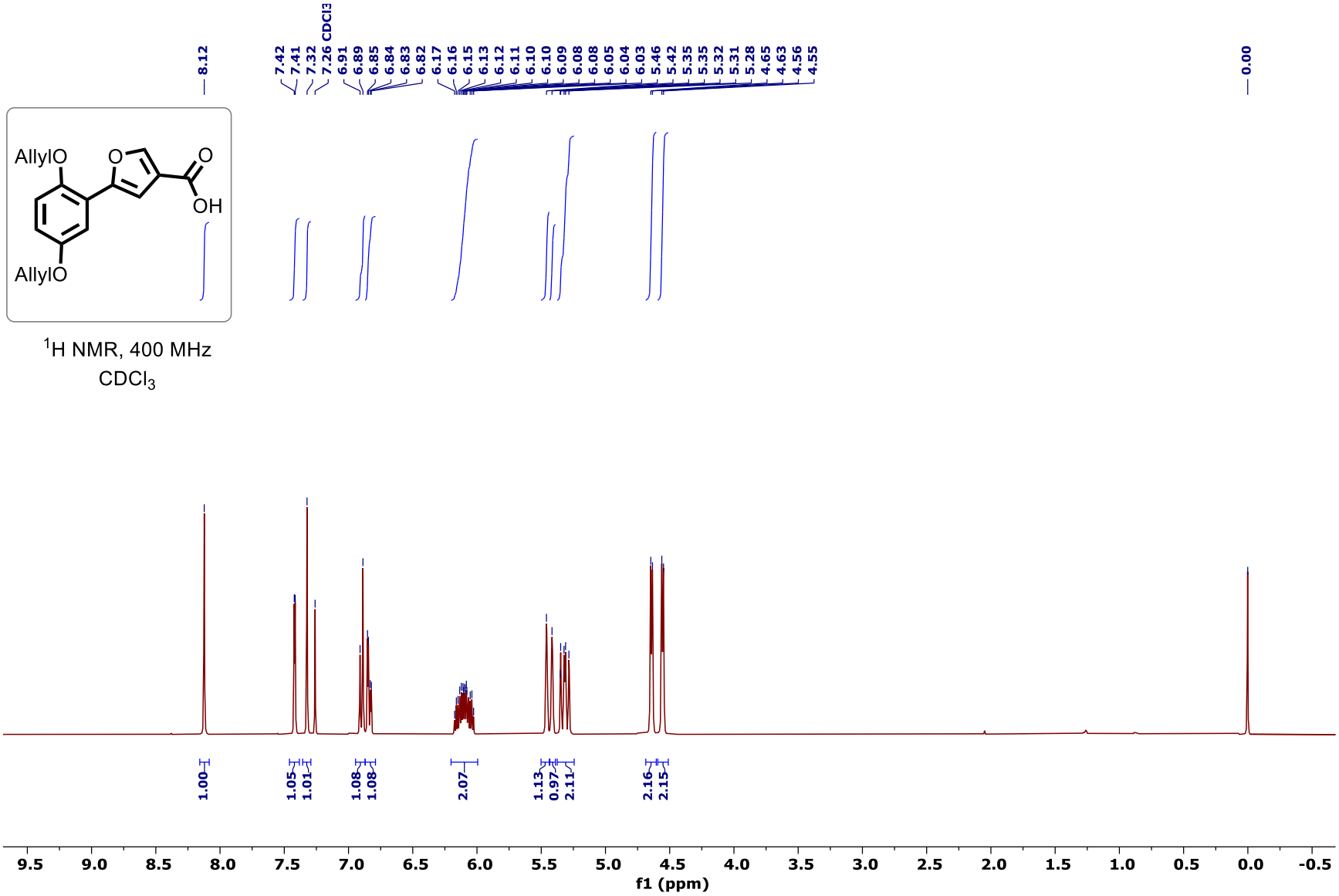
^{1}H NMR spectrum of paleofuran B (5):



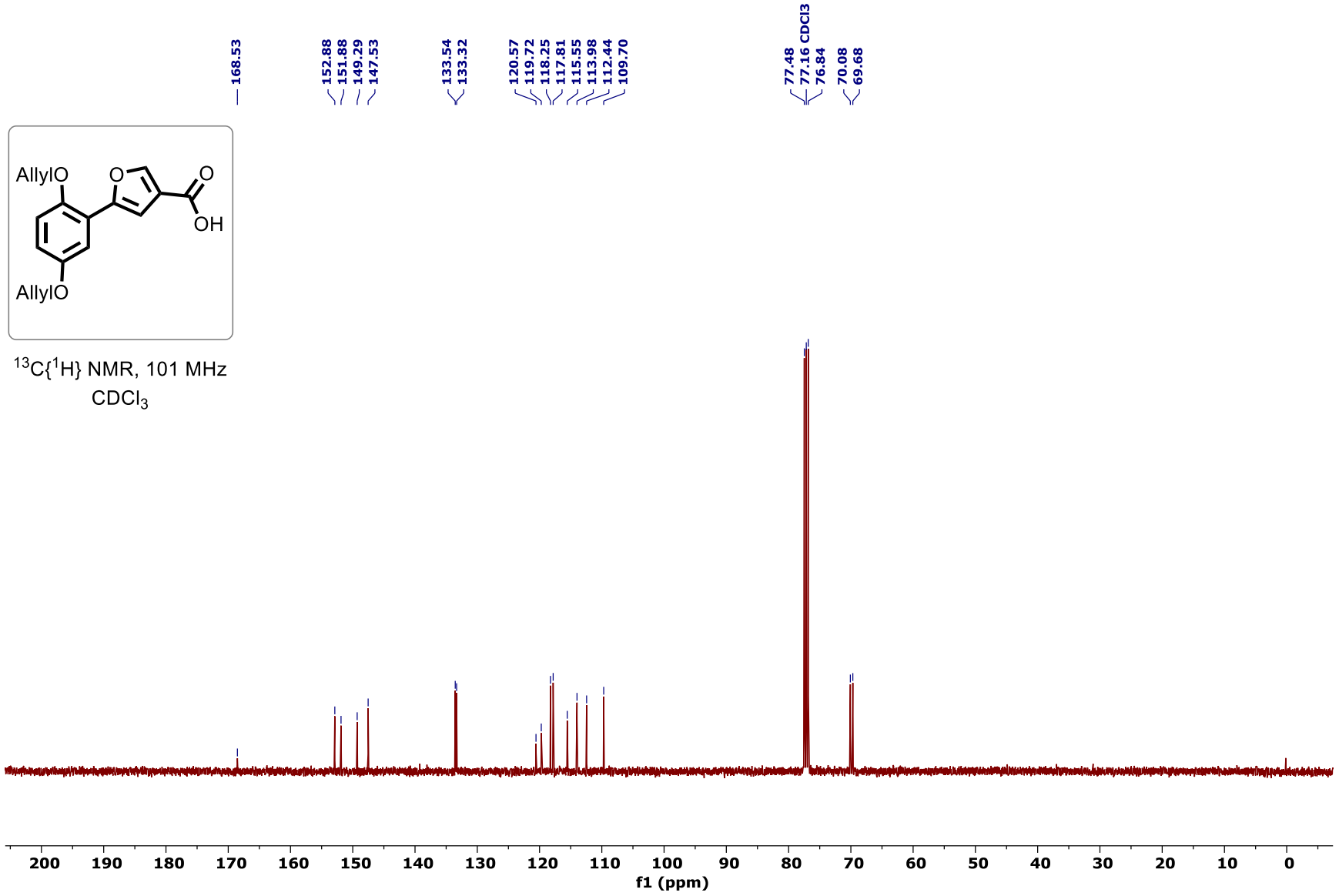
^{13}C NMR spectrum of paleofuran B (5):



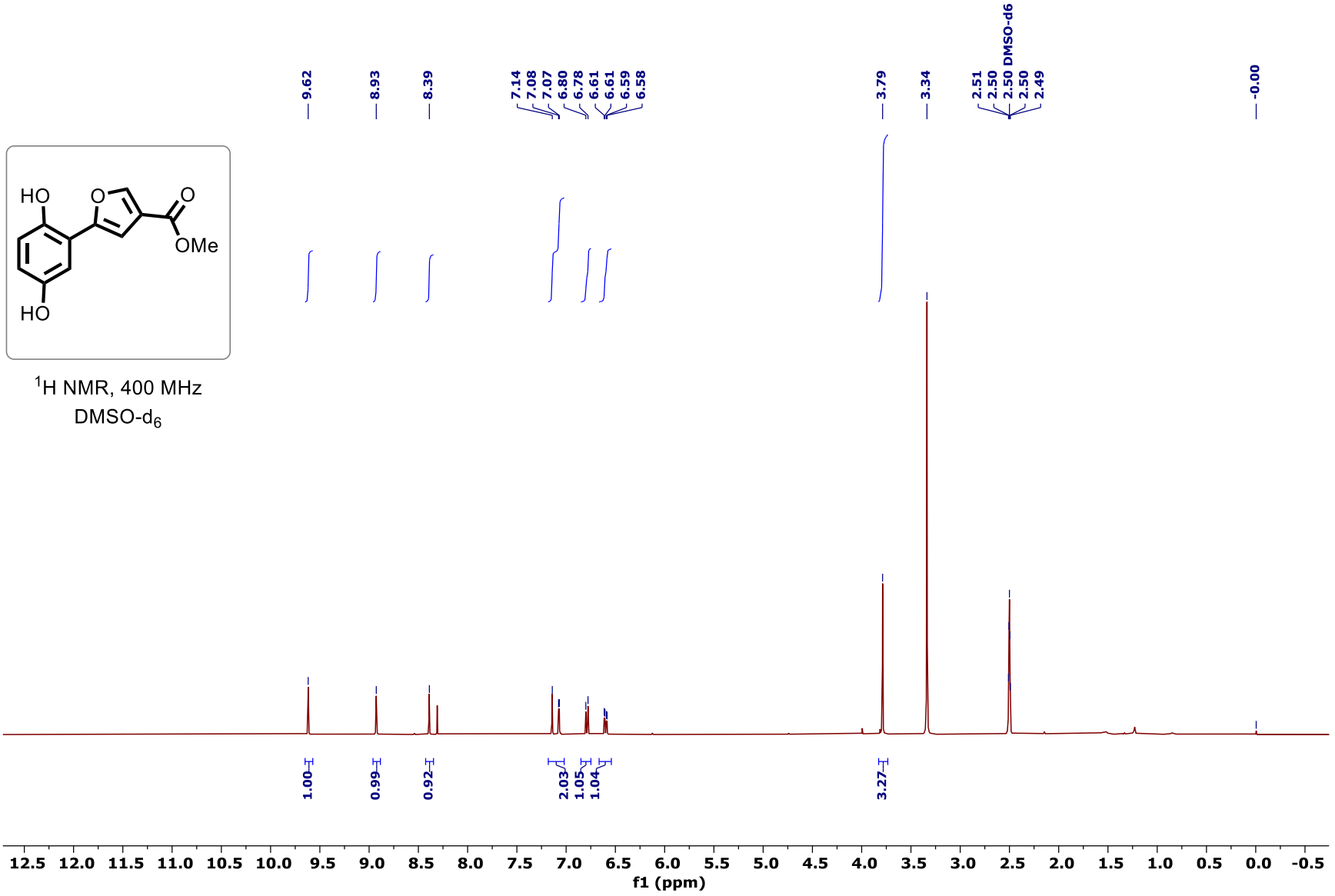
^{1}H NMR spectrum of 5-(2,5-bis(allyloxy)phenyl)furan-3-carboxylic acid (27):



^{13}C NMR spectrum of 5-(2,5-bis(allyloxy)phenyl)furan-3-carboxylic acid (27):

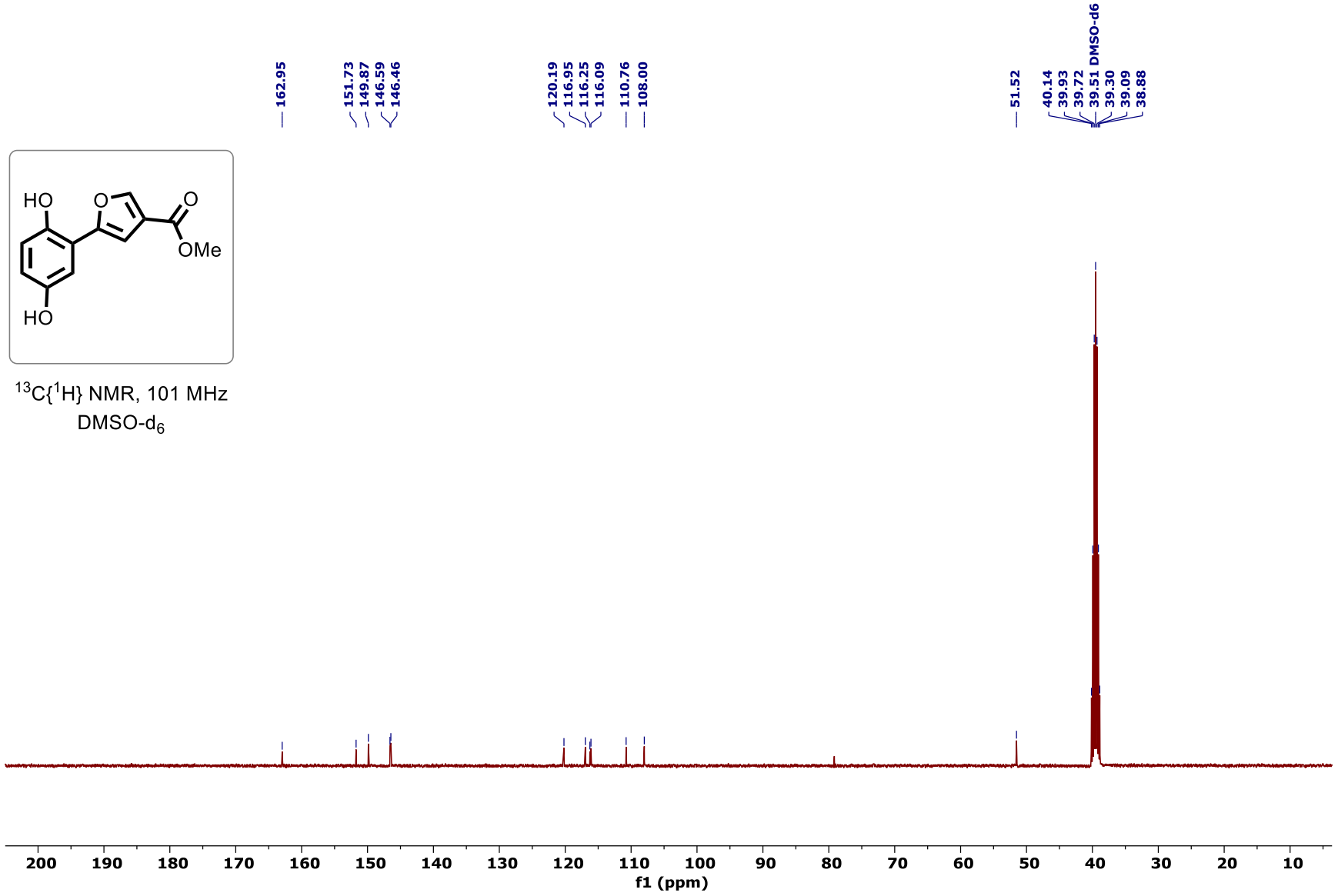


^{1}H NMR spectrum of tournefolin C (6):



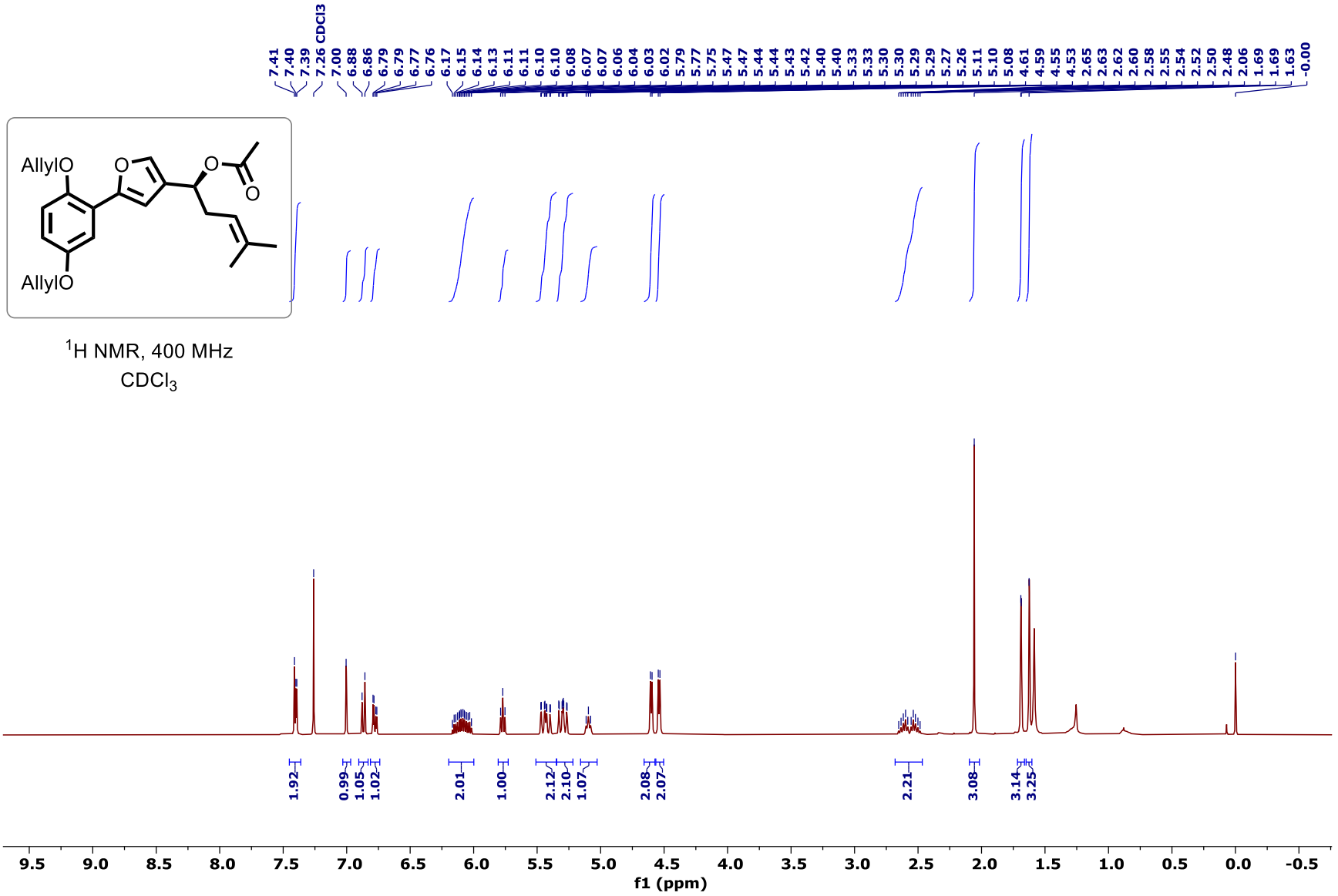
^{1}H NMR, 400 MHz
DMSO-d_6

^{13}C NMR spectrum of tournefolin C (6):

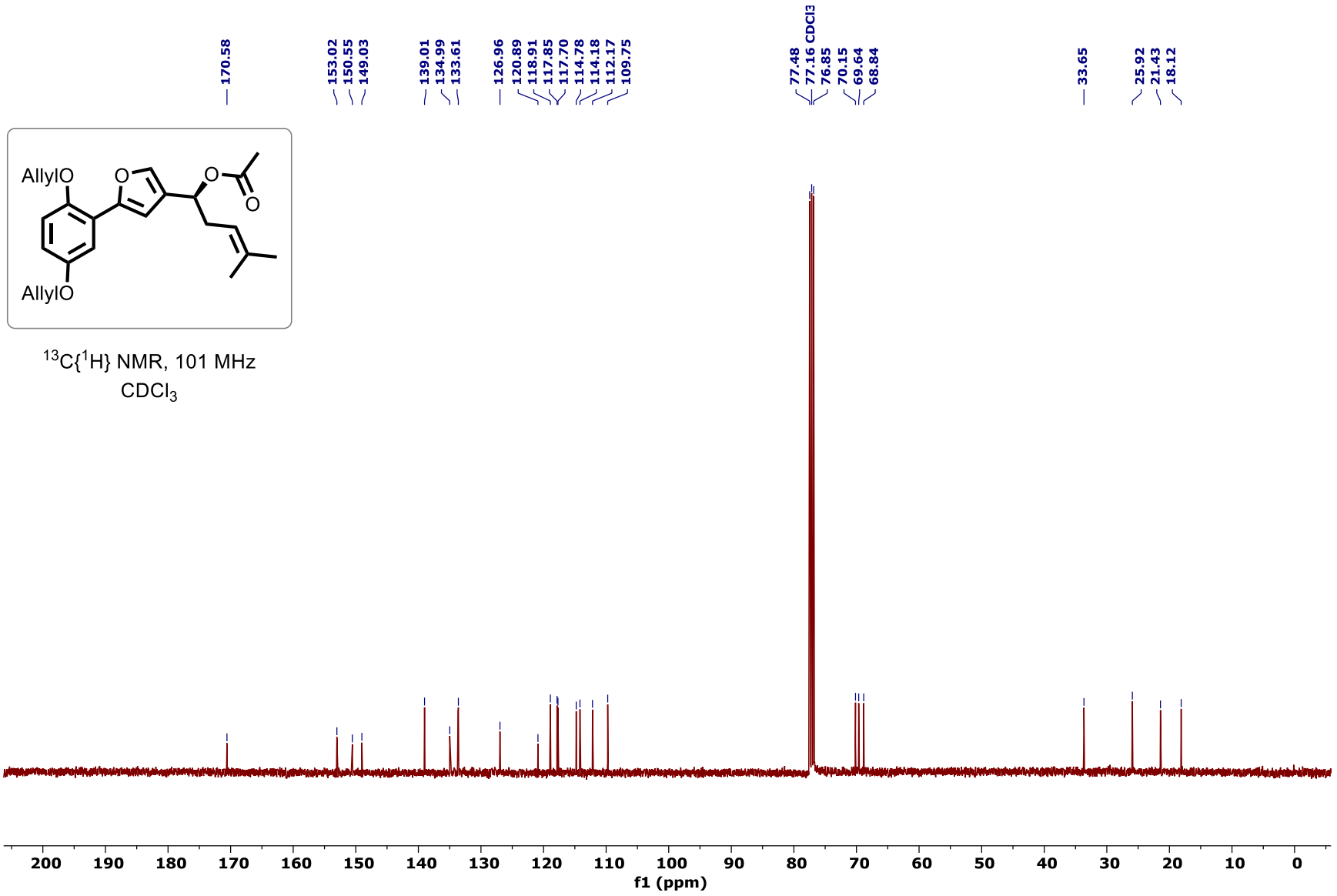


^{13}C{^{1}H} NMR, 101 MHz
DMSO-d_6

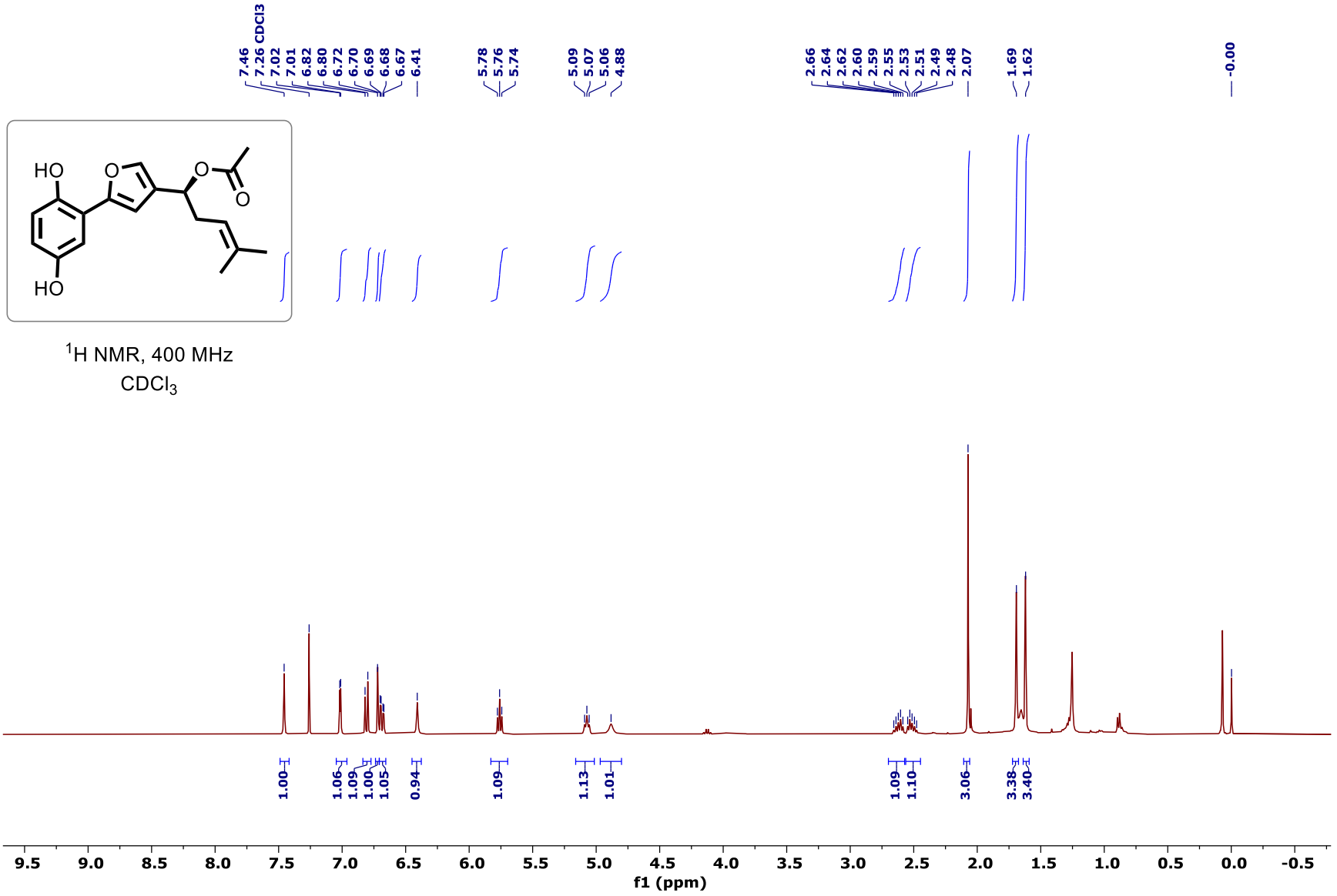
^{1}H NMR spectrum of 1-(5-(2,5-bis(allyloxy)phenyl)furan-3-yl)-4-methylpent-3-en-1-yl acetate [(*S*)-29]:



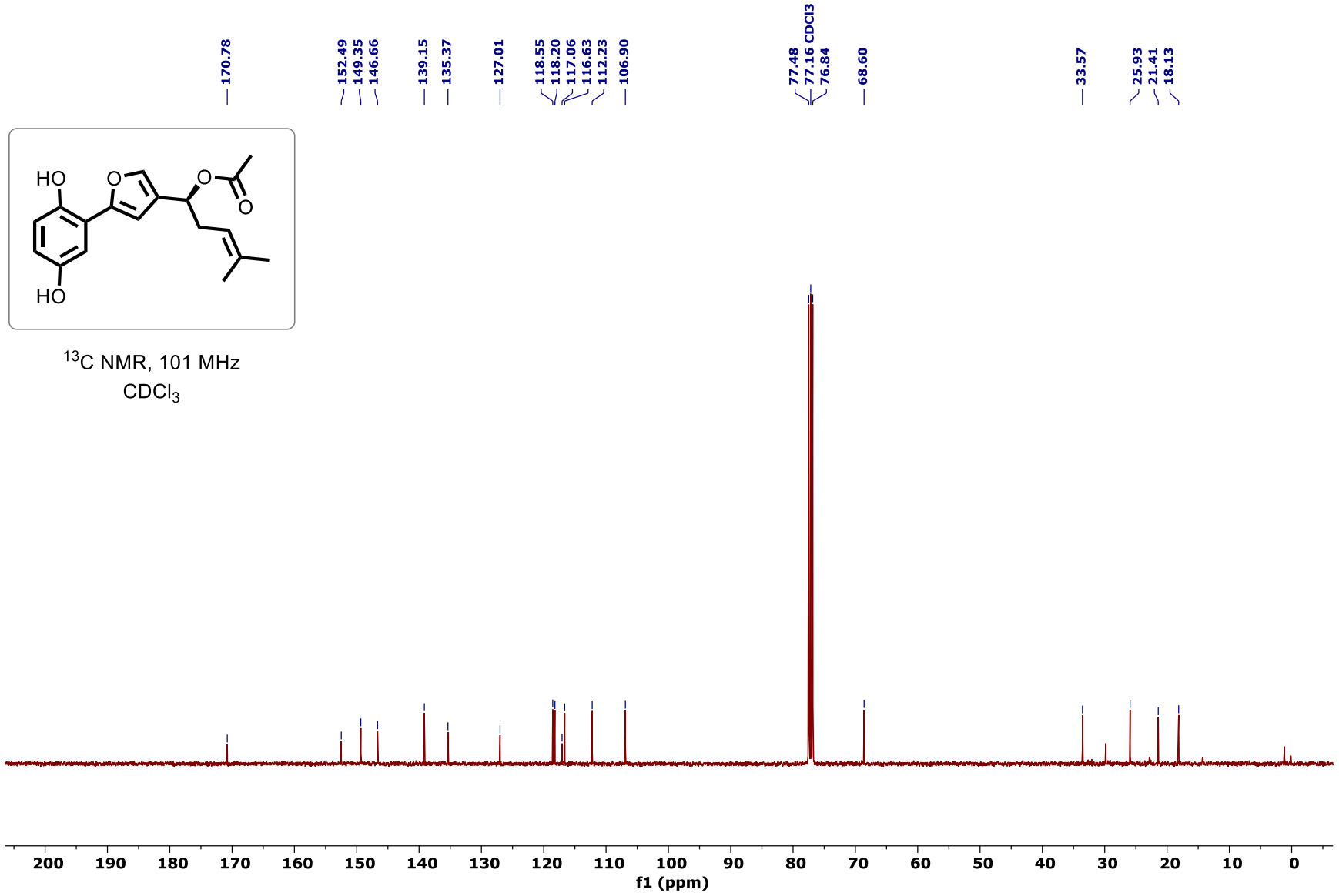
^{13}C NMR spectrum of 1-(5-(2,5-bis(allyloxy)phenyl)furan-3-yl)-4-methylpent-3-en-1-yl acetate [(*S*)-29]:



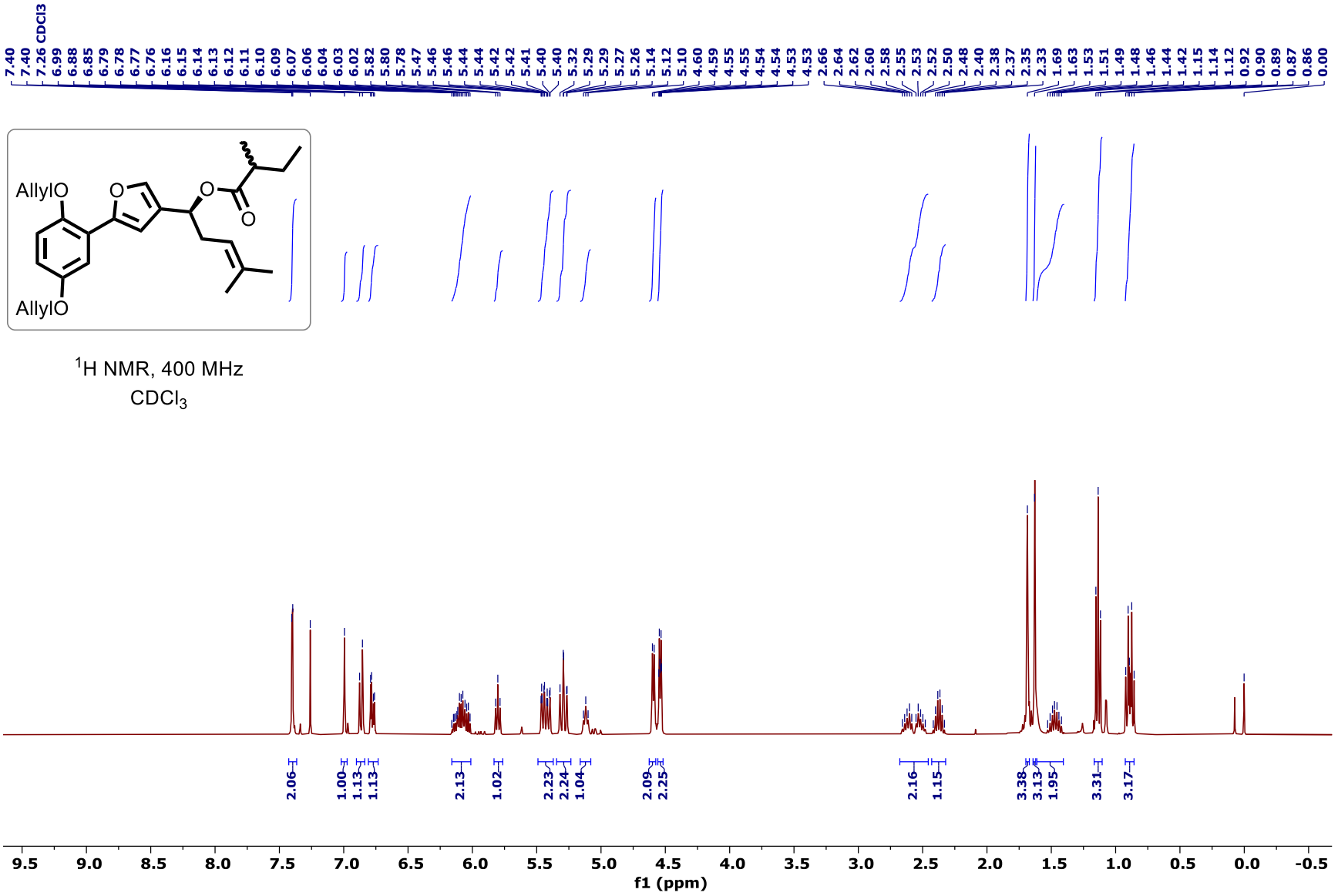
^{1}H NMR spectrum of shikonofuran A [(*S*)-(7)]:



^{13}C NMR spectrum of shikonofuran A [(*S*)-(7)] :

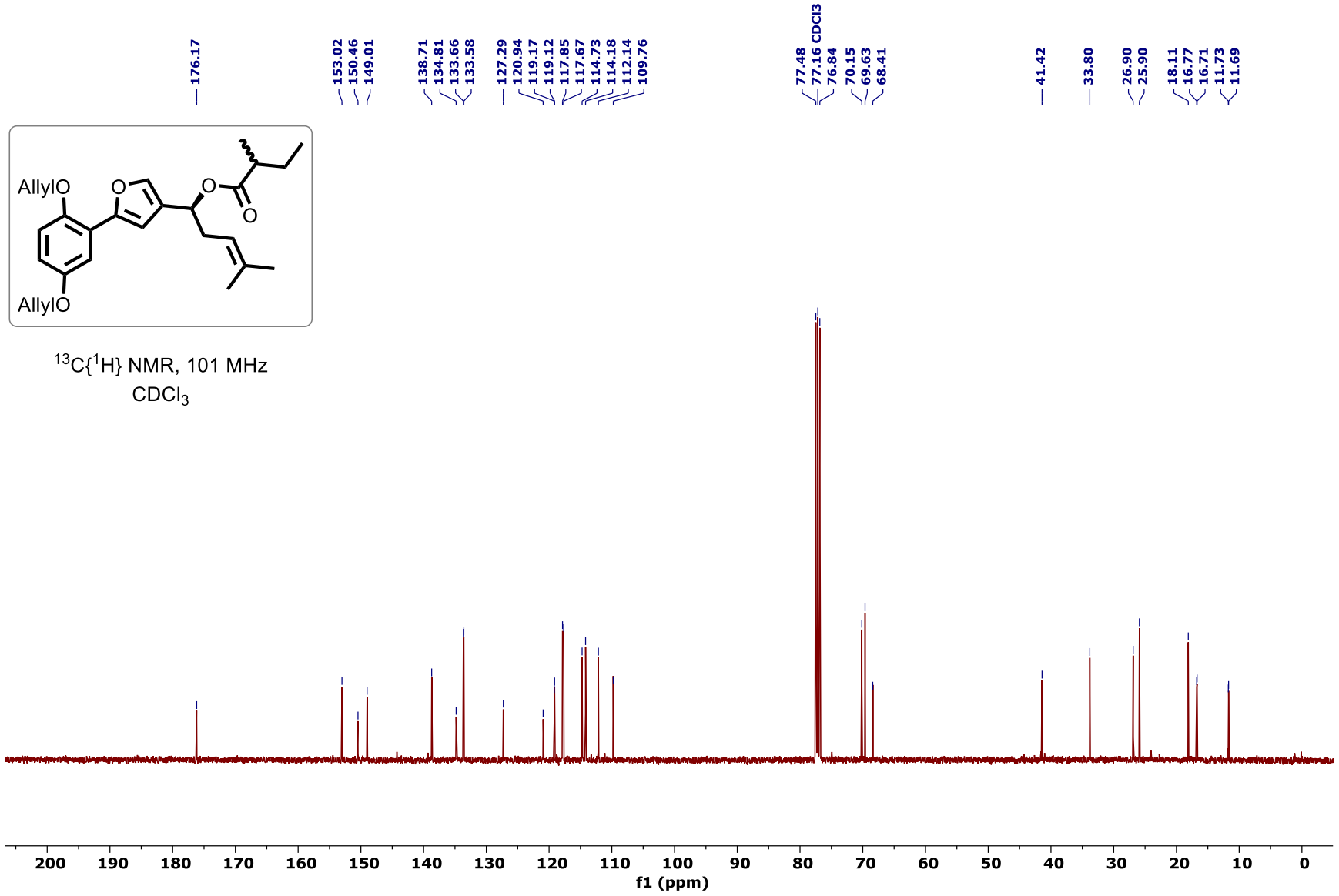


^{1}H NMR spectrum of 1-(5-(2,5-bis(allyloxy)phenyl)furan-3-yl)-4-methylpent-3-en-1-yl 2-methylbutanoate (31):

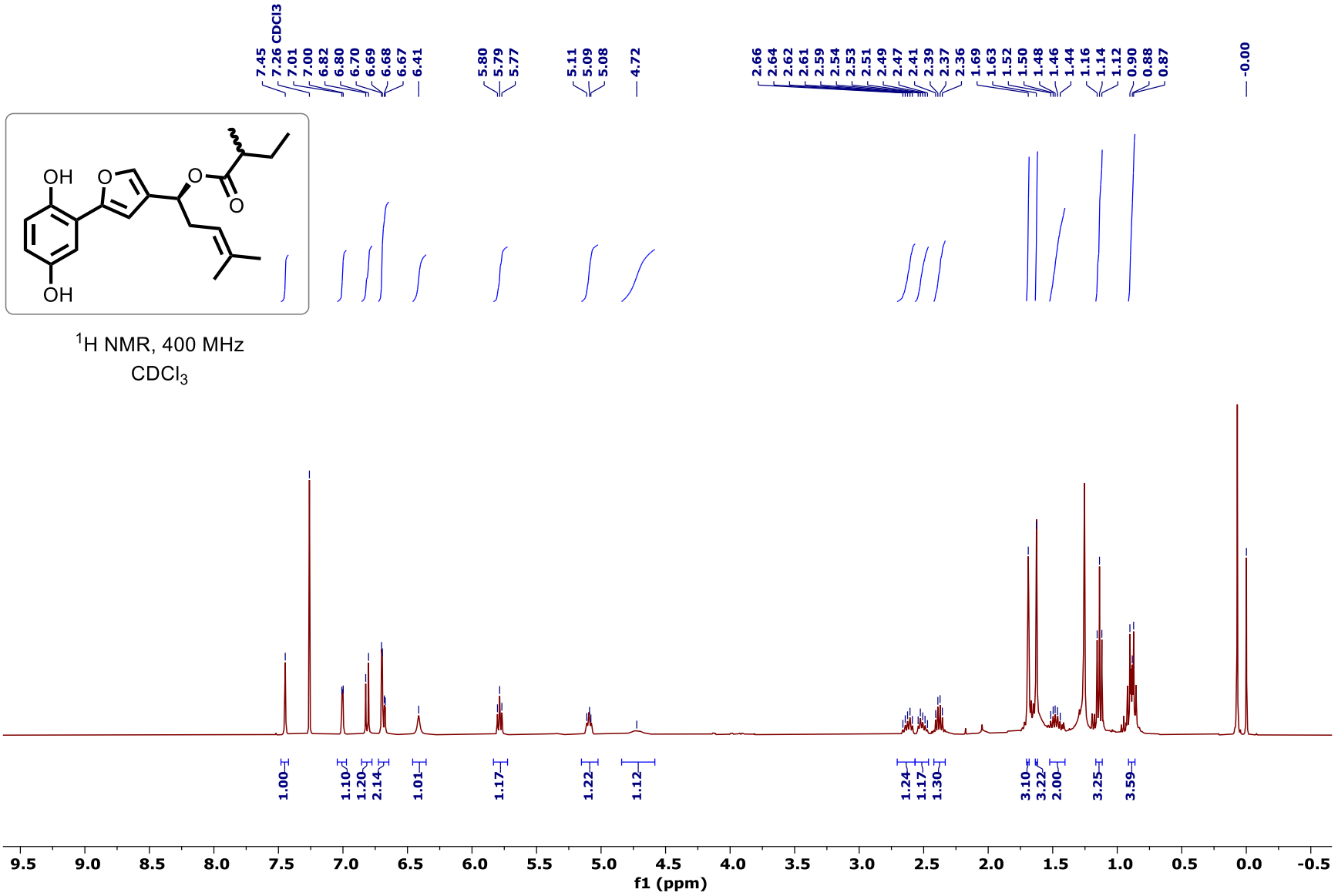


^{1}H NMR, 400 MHz
$CDCl_3$

^{13}C NMR spectrum of 1-(5-(2,5-bis(allyloxy)phenyl)furan-3-yl)-4-methylpent-3-en-1-yl 2-methylbutanoate (31):



^{1}H NMR spectrum of shikonofuran B (8):



^{13}C NMR spectrum of shikonofuran B (8):