Supporting Information for

$Bi(OTf)_3$–, TfOH–, and TMSOTf–Mediated, One-Pot Epoxide Rearrangement, Addition and Intramolecular Silyl-Modified Sakurai (ISMS) Cascade Toward Dihydropyrans: Comparison of Catalysts and Role of $Bi(OTf)_3$.

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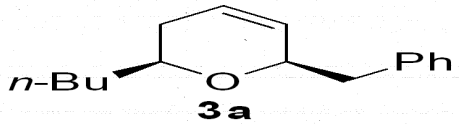
rfl-206C;pure; DHP butyl vinyl side chain and styrene oxide; CDCl3;07/01/2010

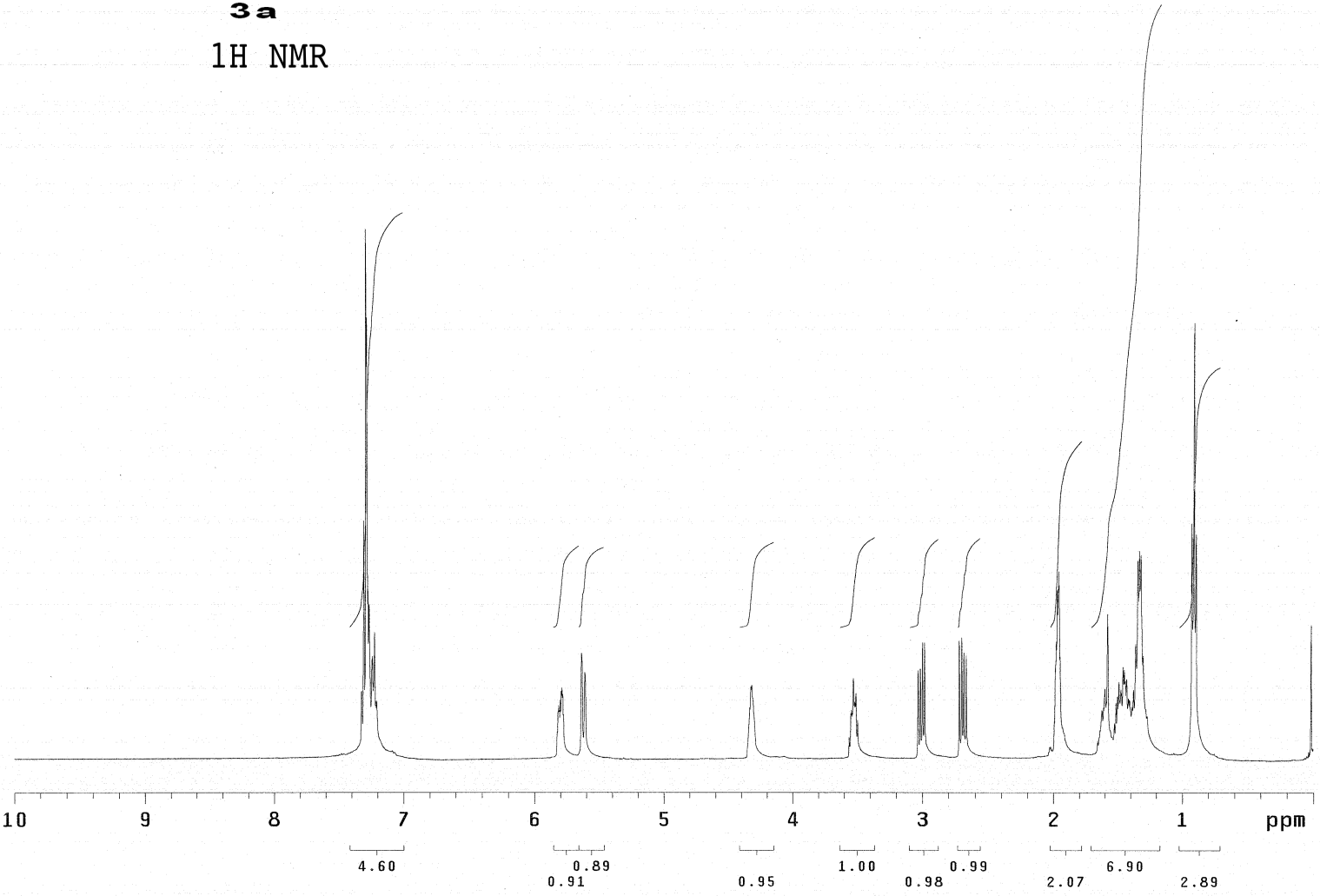
Automation directory:

Pulse Sequence: s2pul



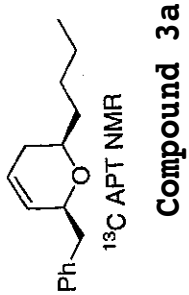
3a

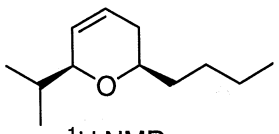
1H NMR



Compound 3a

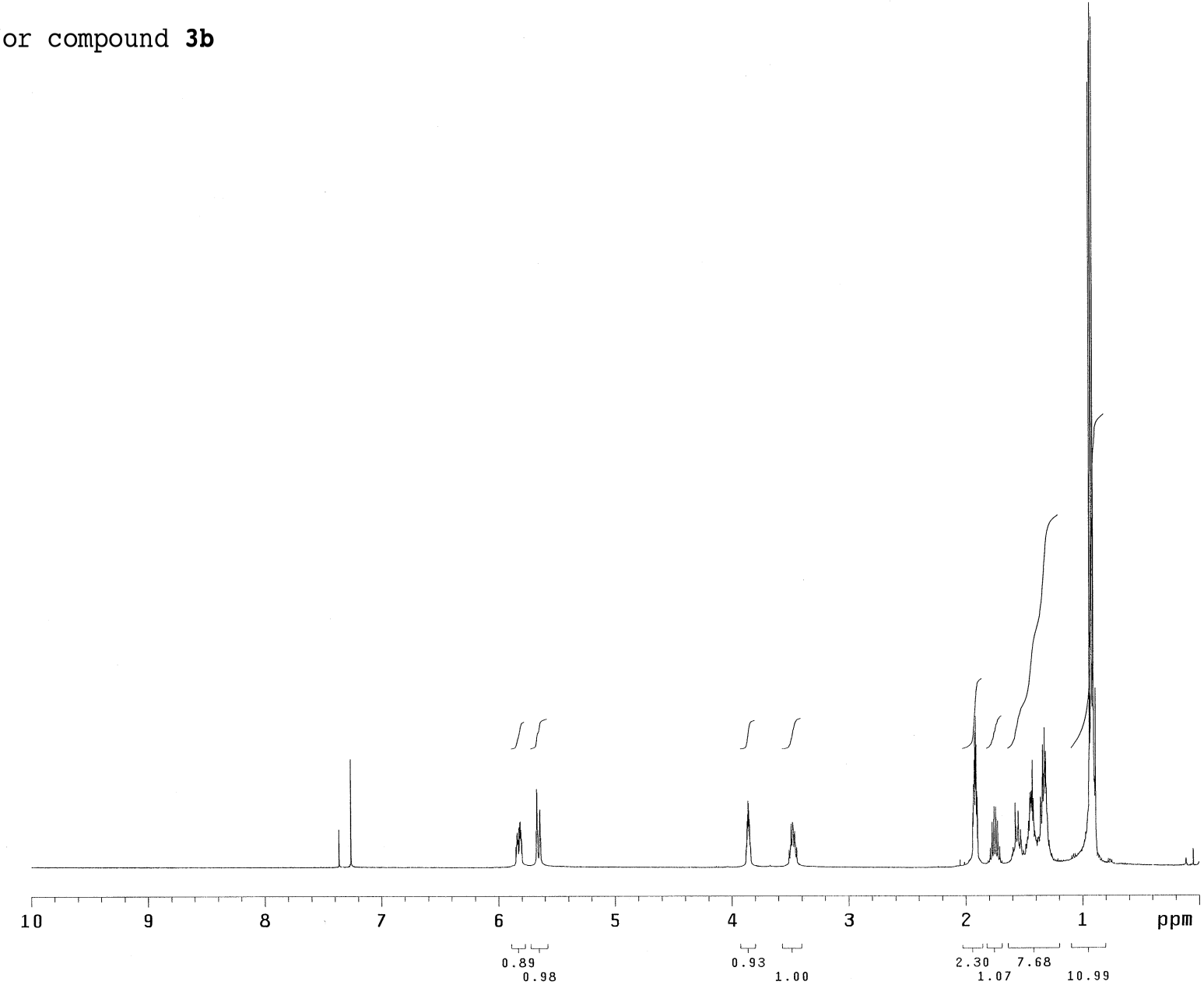
^{13}C APT NMR

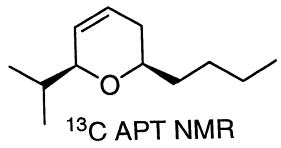




^{1}H NMR

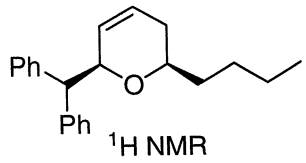
1H NMR for compound **3b**





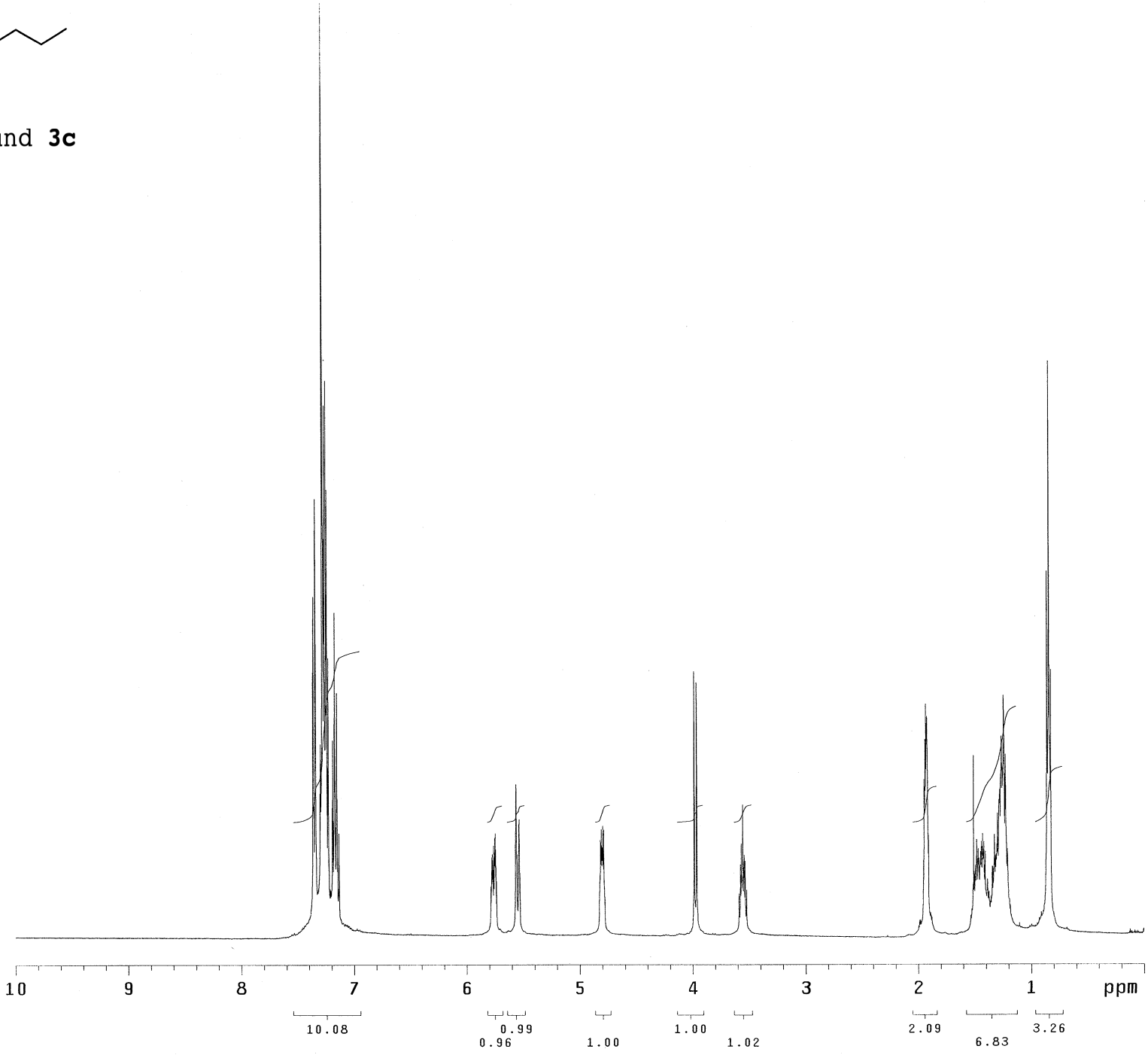
^{13}C APT NMR

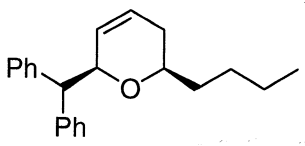
Compound 3b



^{1}H NMR

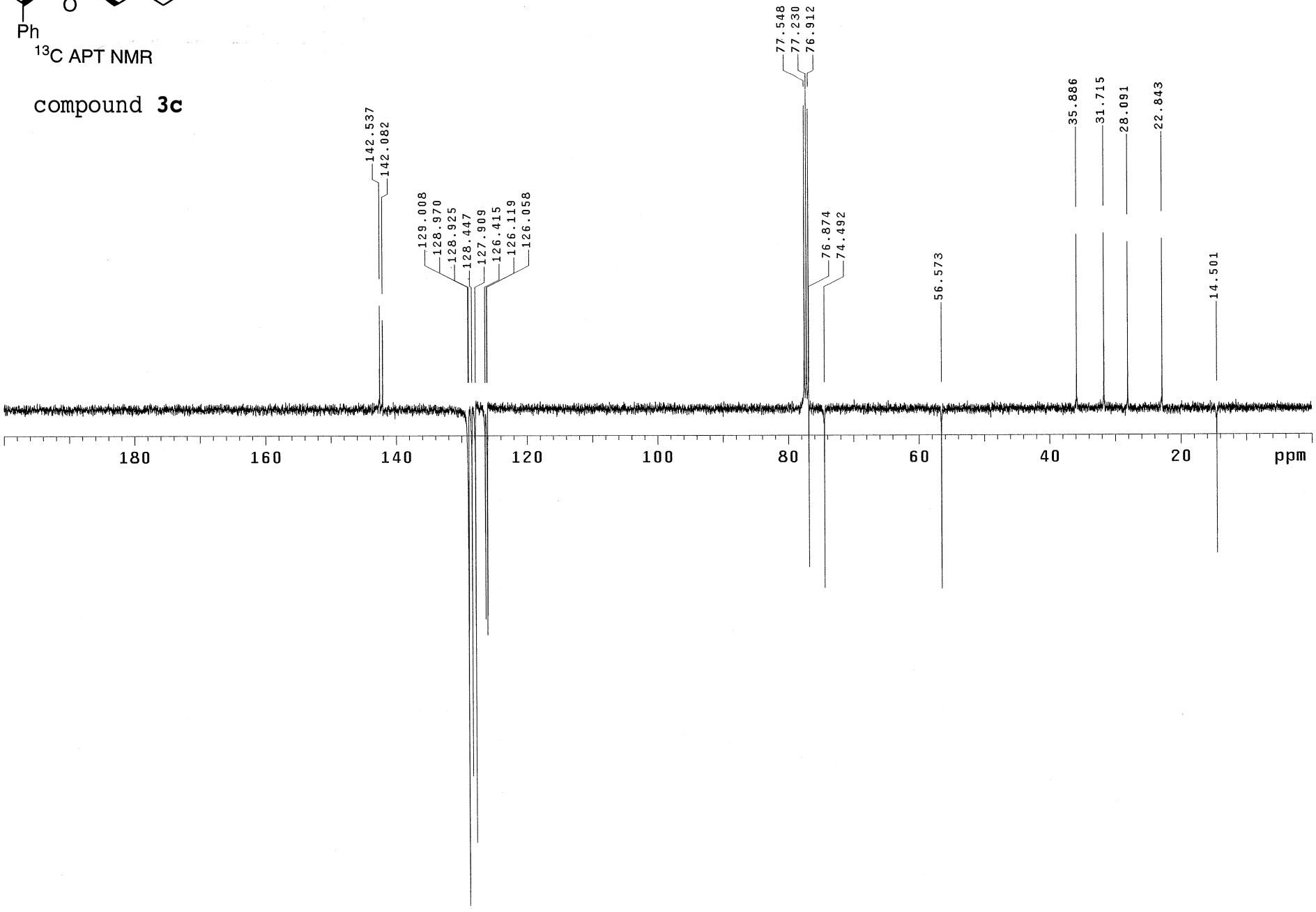
Compound **3c**

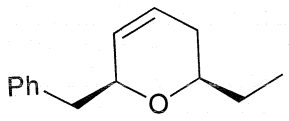




^{13}C APT NMR

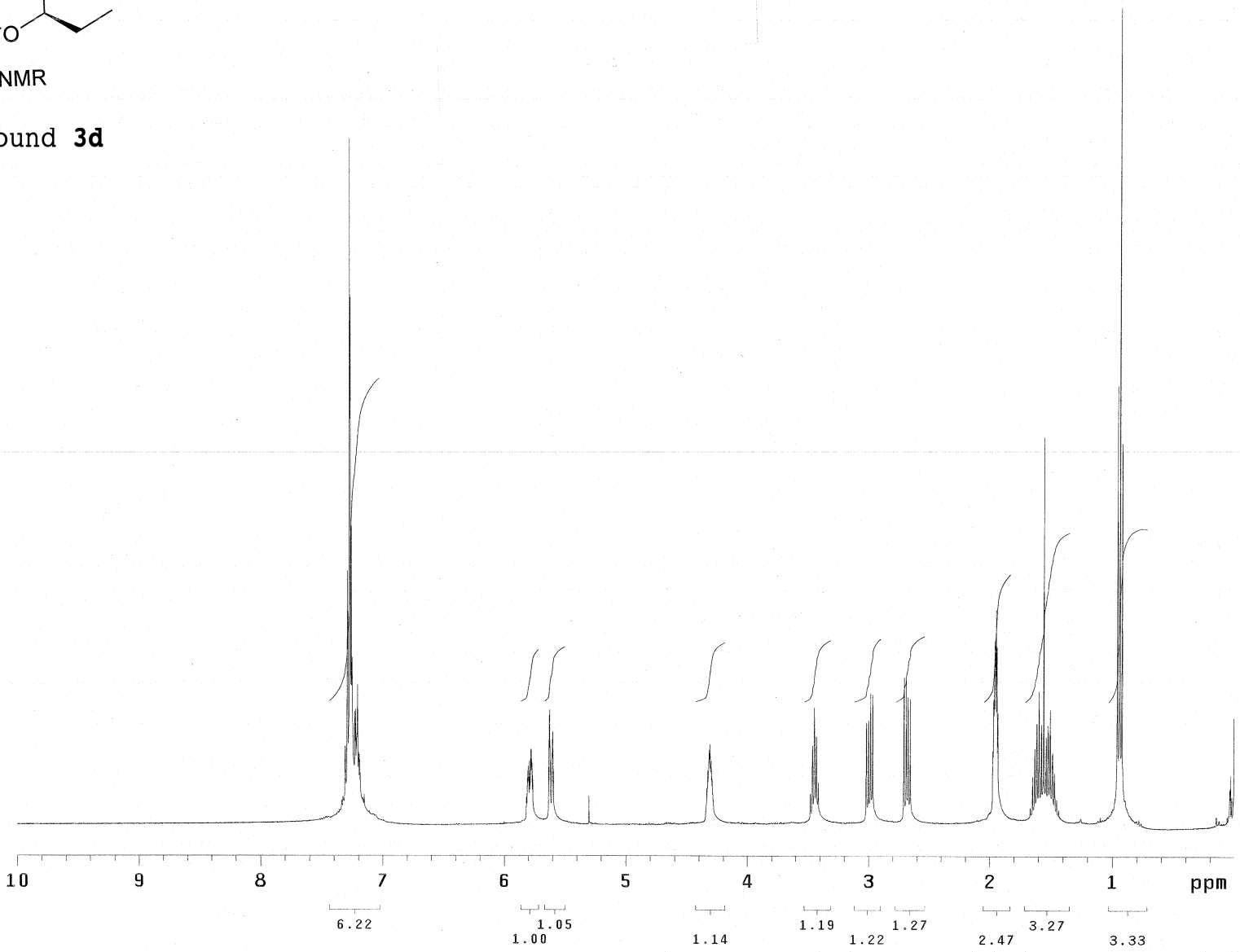
compound **3c**

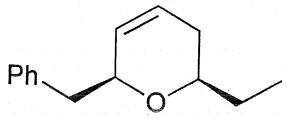




^{1}H NMR

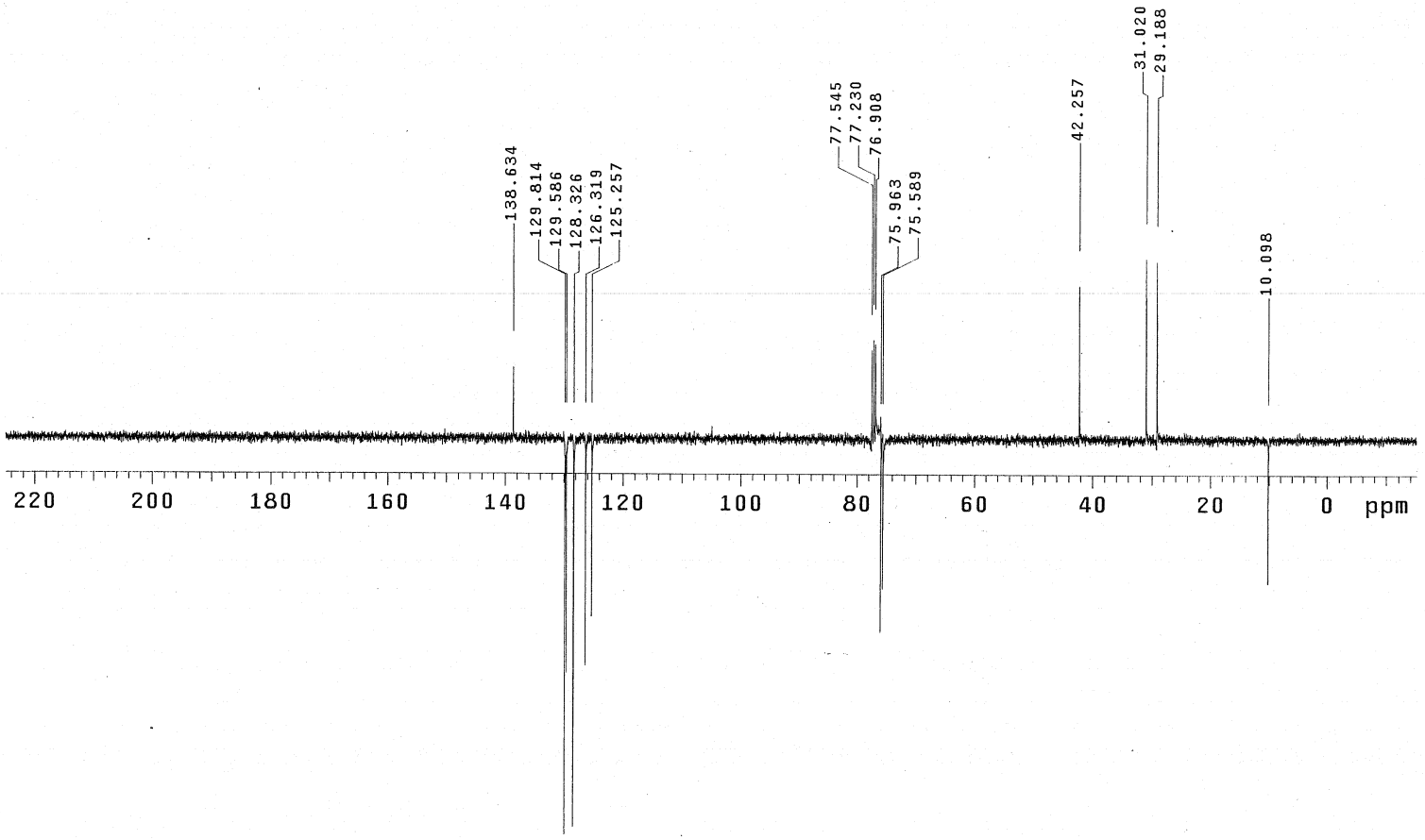
Compound **3d**

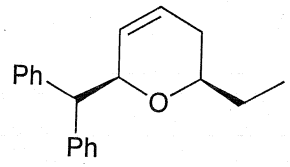




^{13}C APT NMR

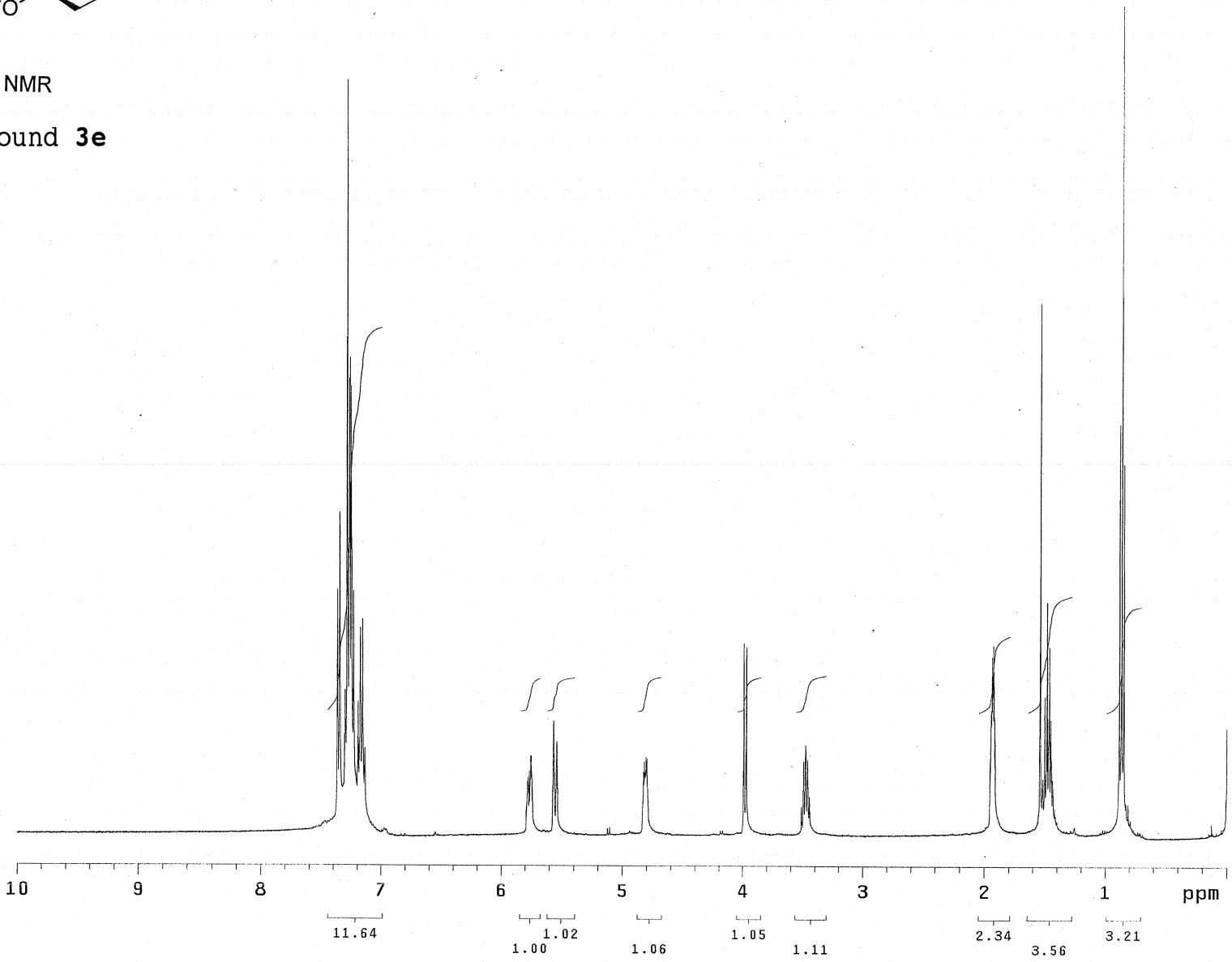
Compound **3d**





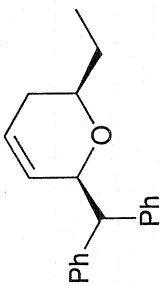
^{1}H NMR

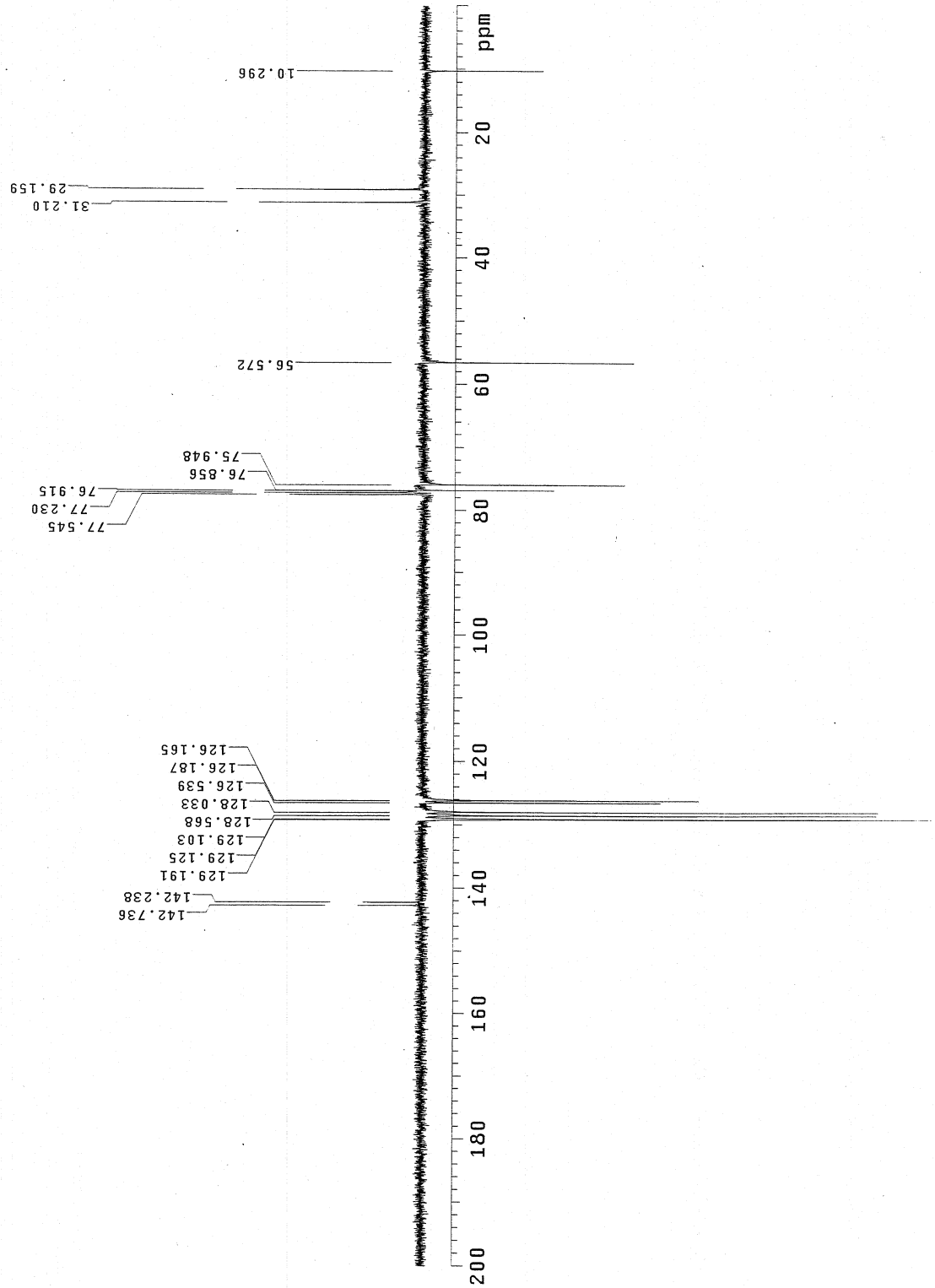
compound **3e**

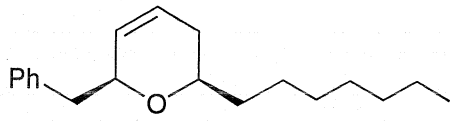


Compound **3e**

^{13}C APT NMR

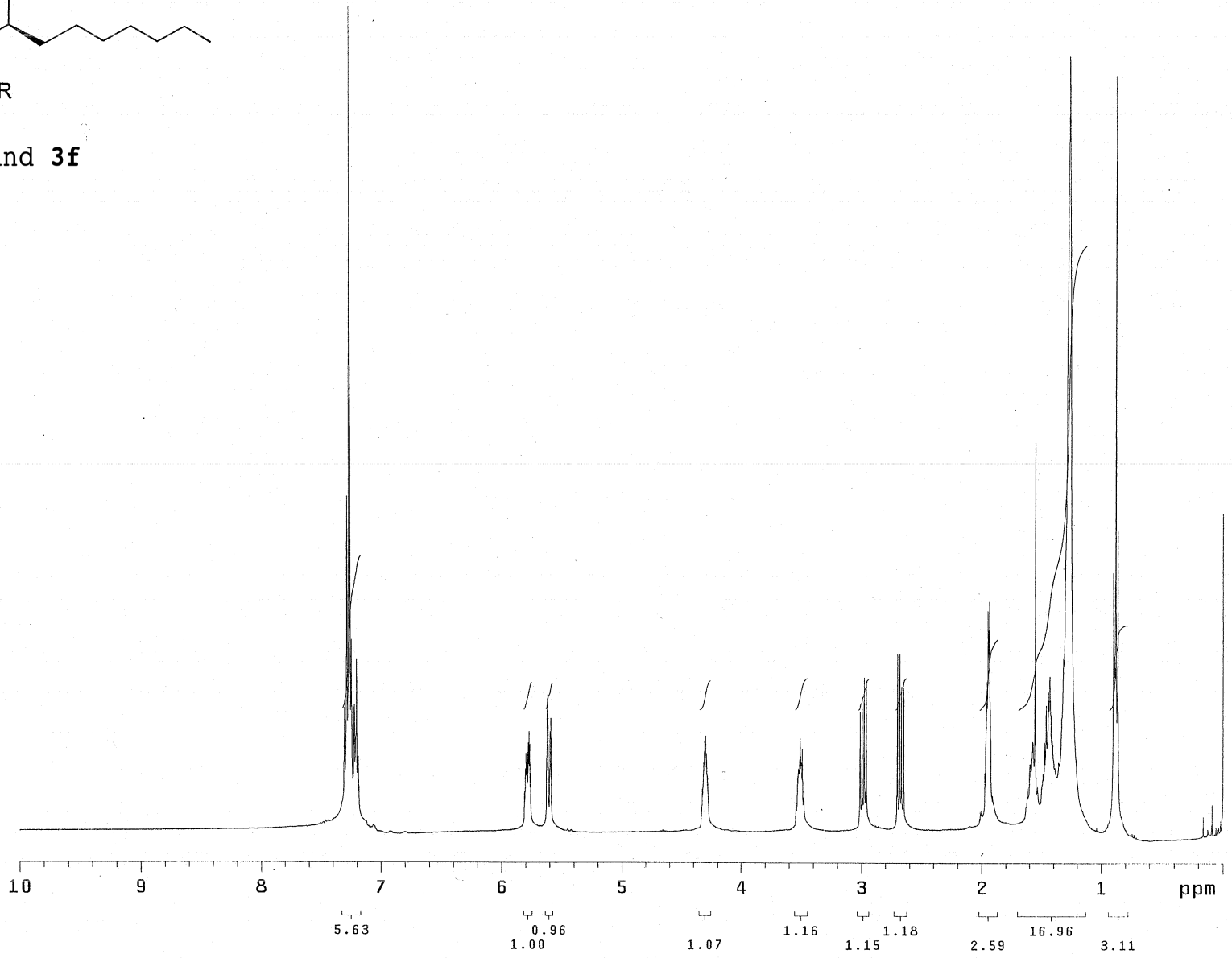


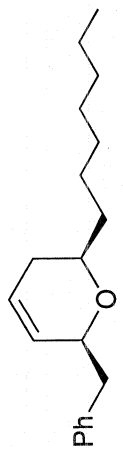




^{1}H NMR

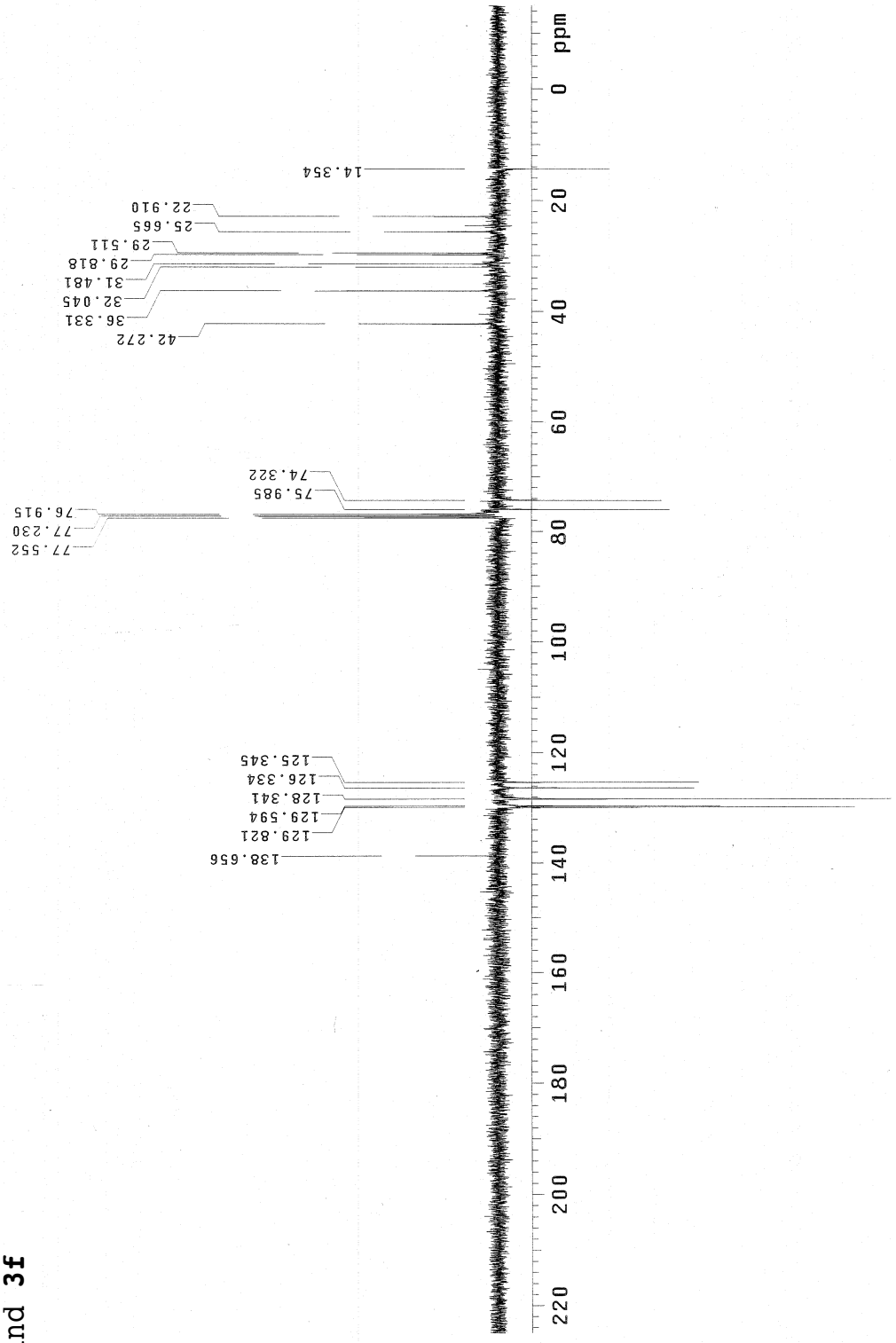
Compound **3f**

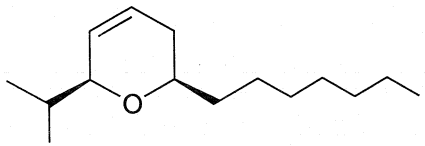




^{13}C APT NMR

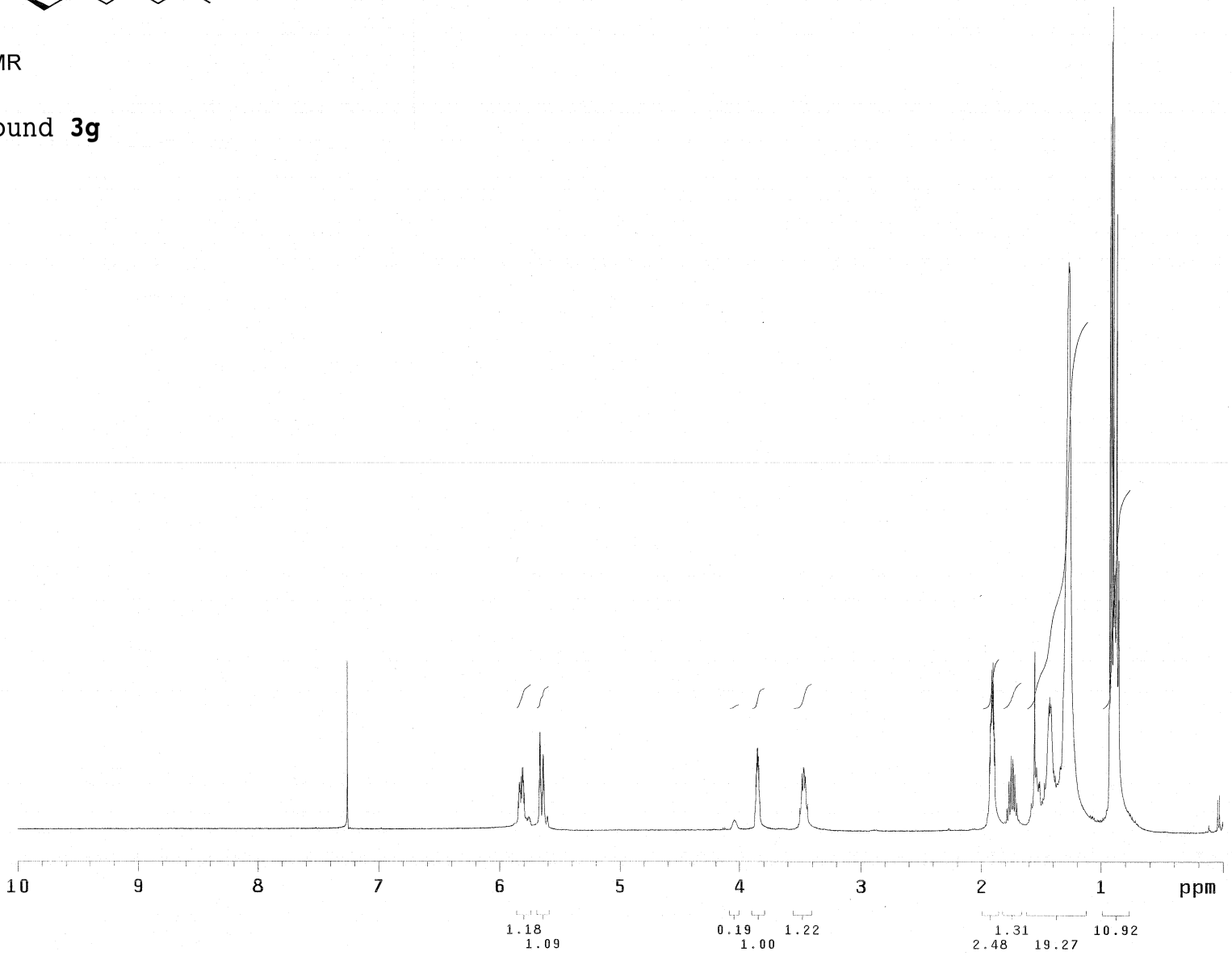
Compound **3f**

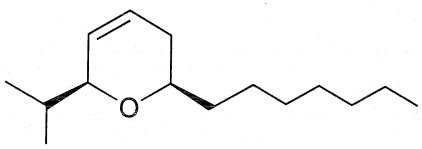




^{1}H NMR

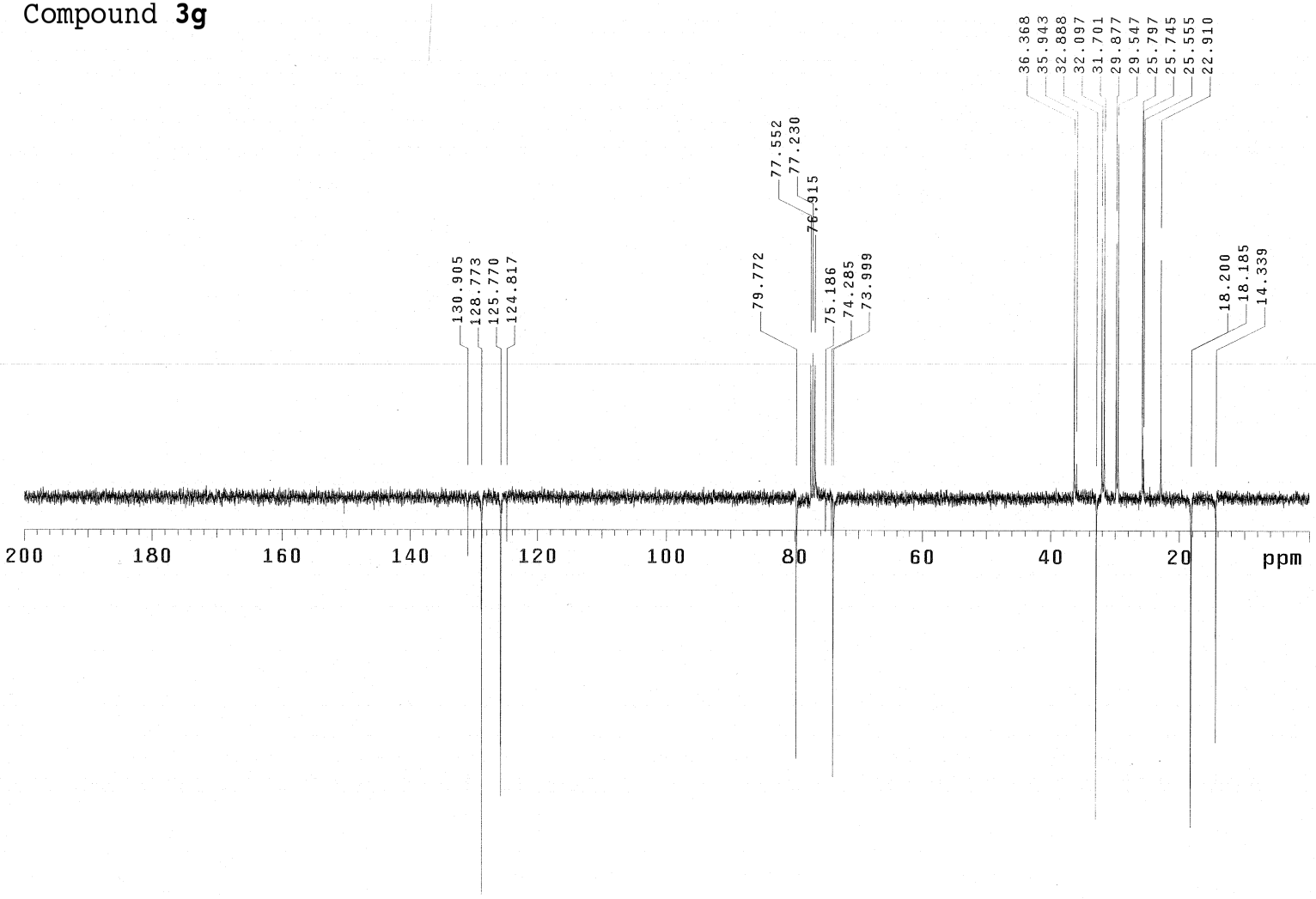
Compound **3g**

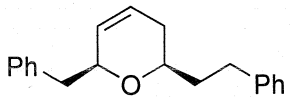




^{13}C APT NMR

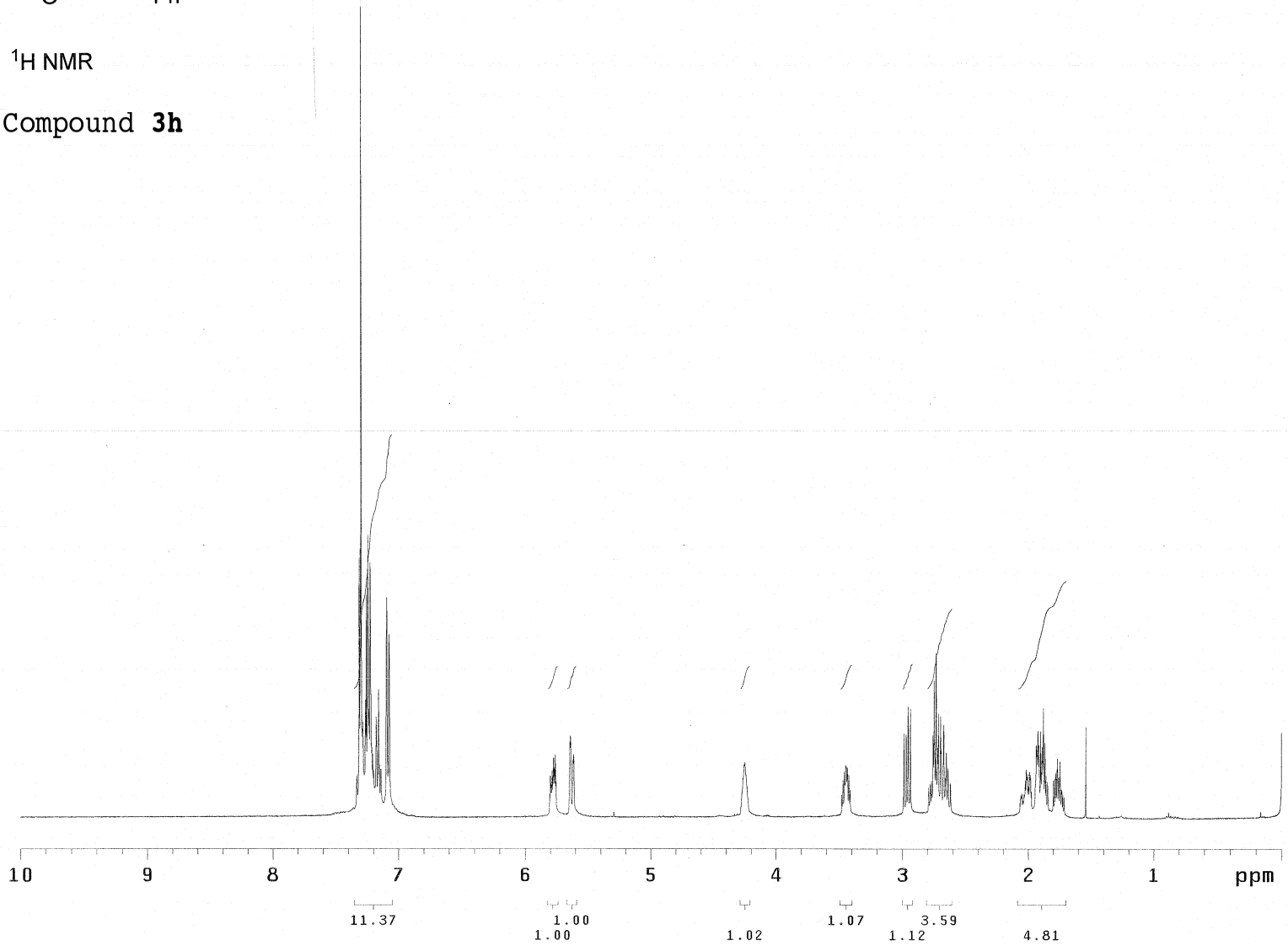
Compound **3g**

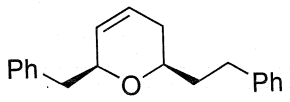




^{1}H NMR

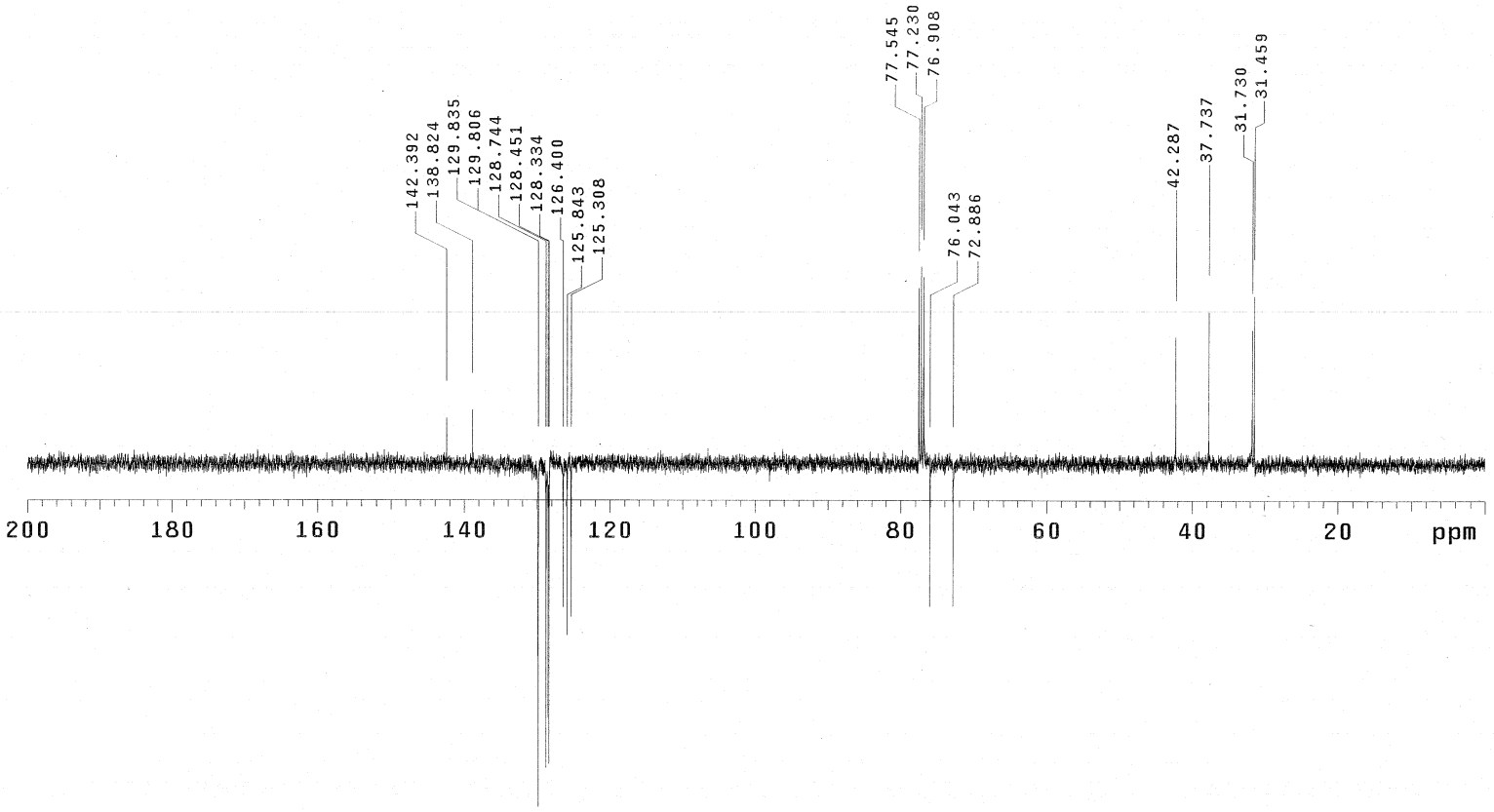
Compound **3h**

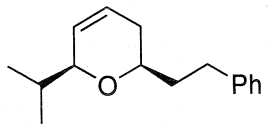




^{13}C APT NMR

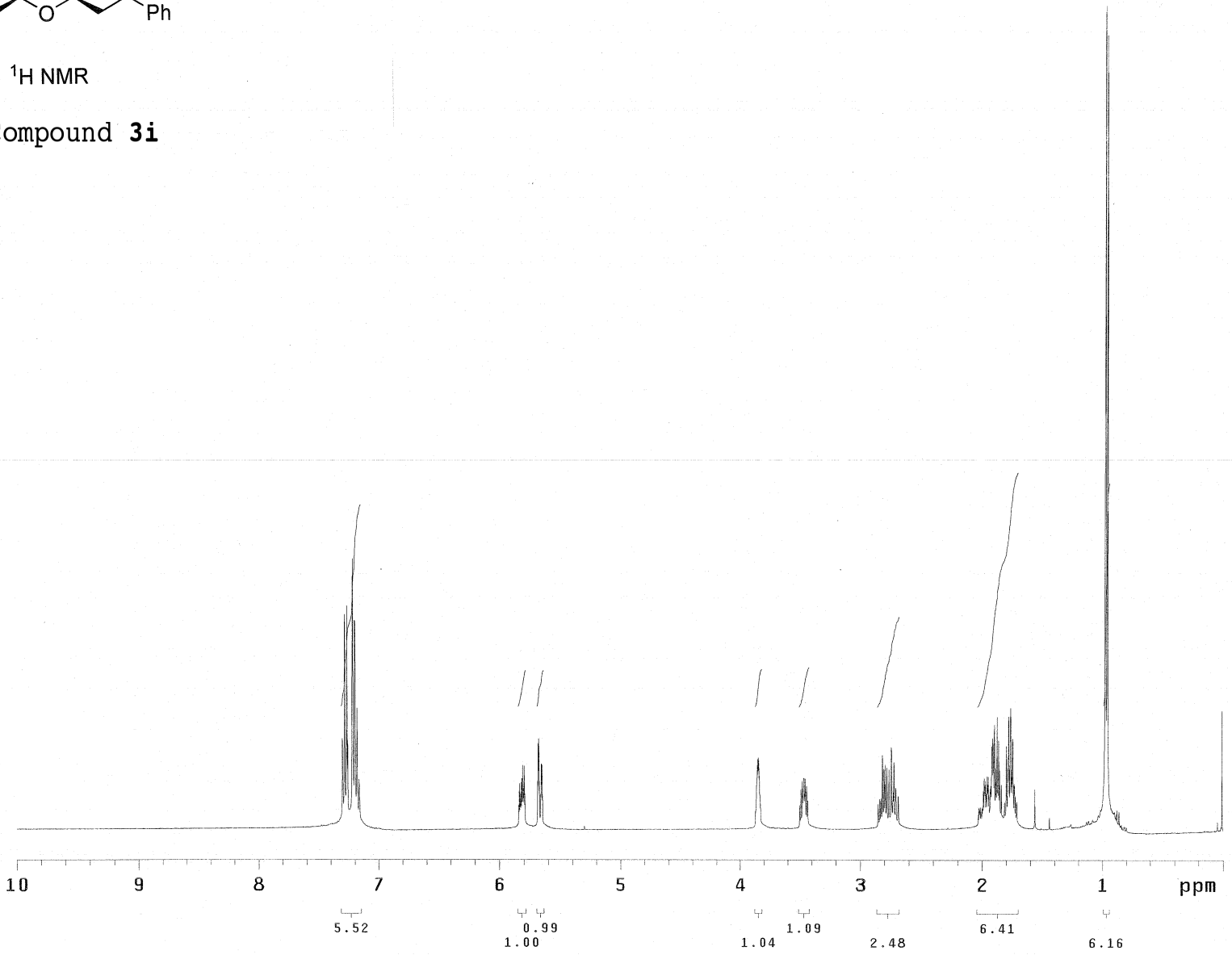
Compound **3h**

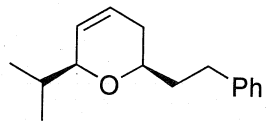




^{1}H NMR

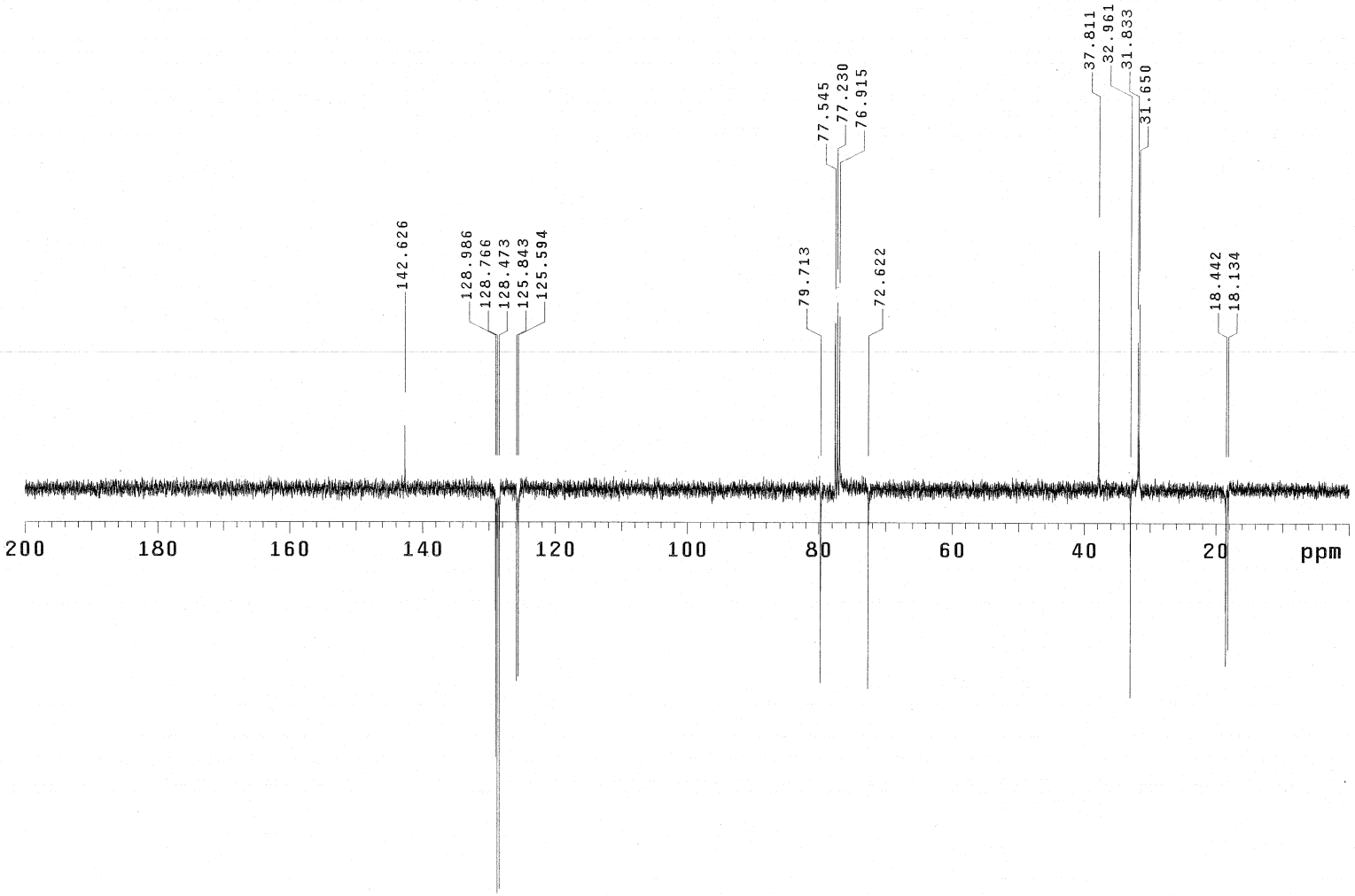
Compound **3i**

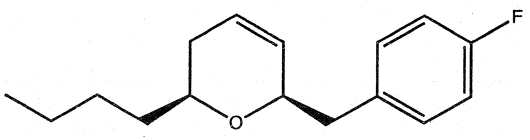




^{13}C APT NMR

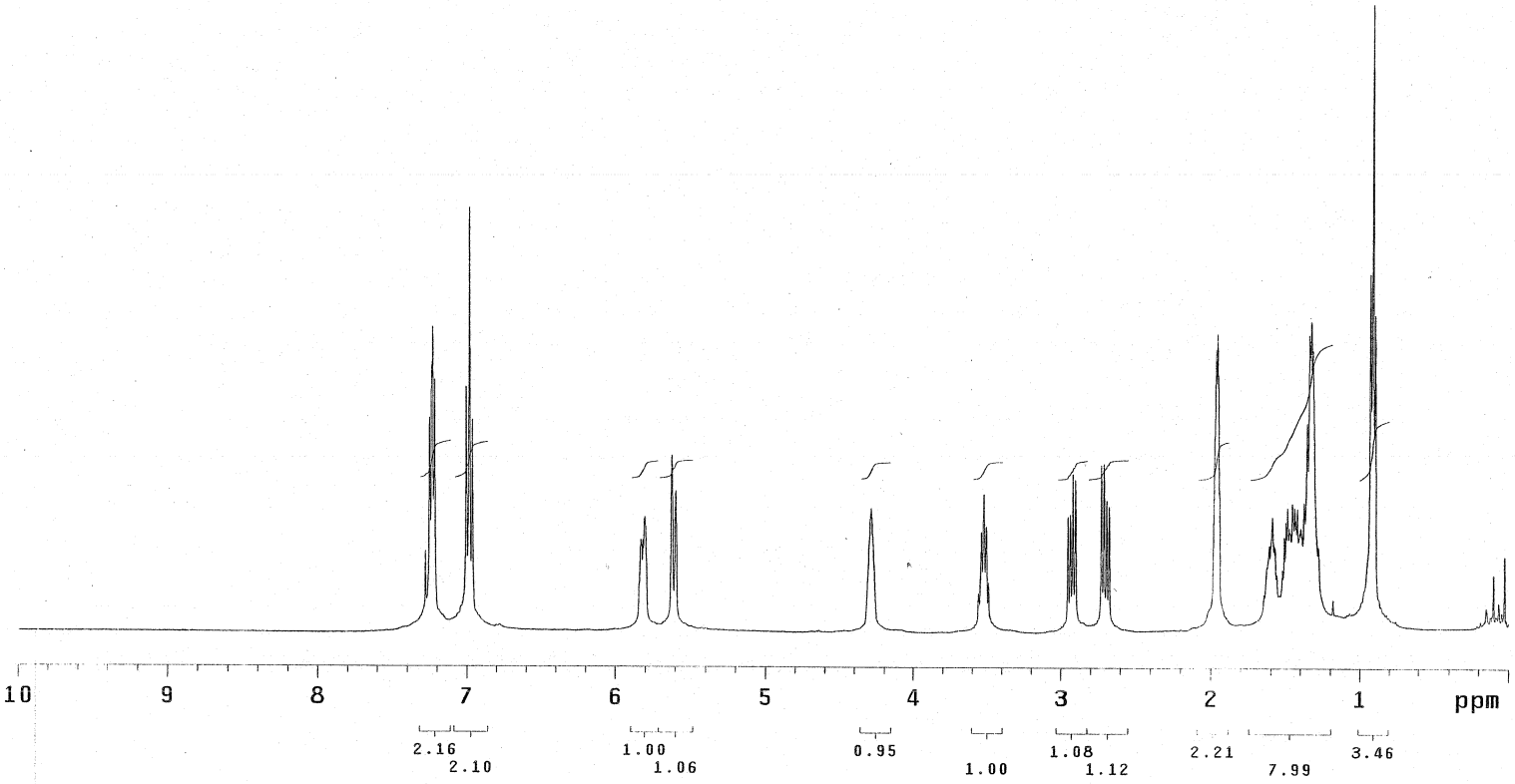
Compound **3i**

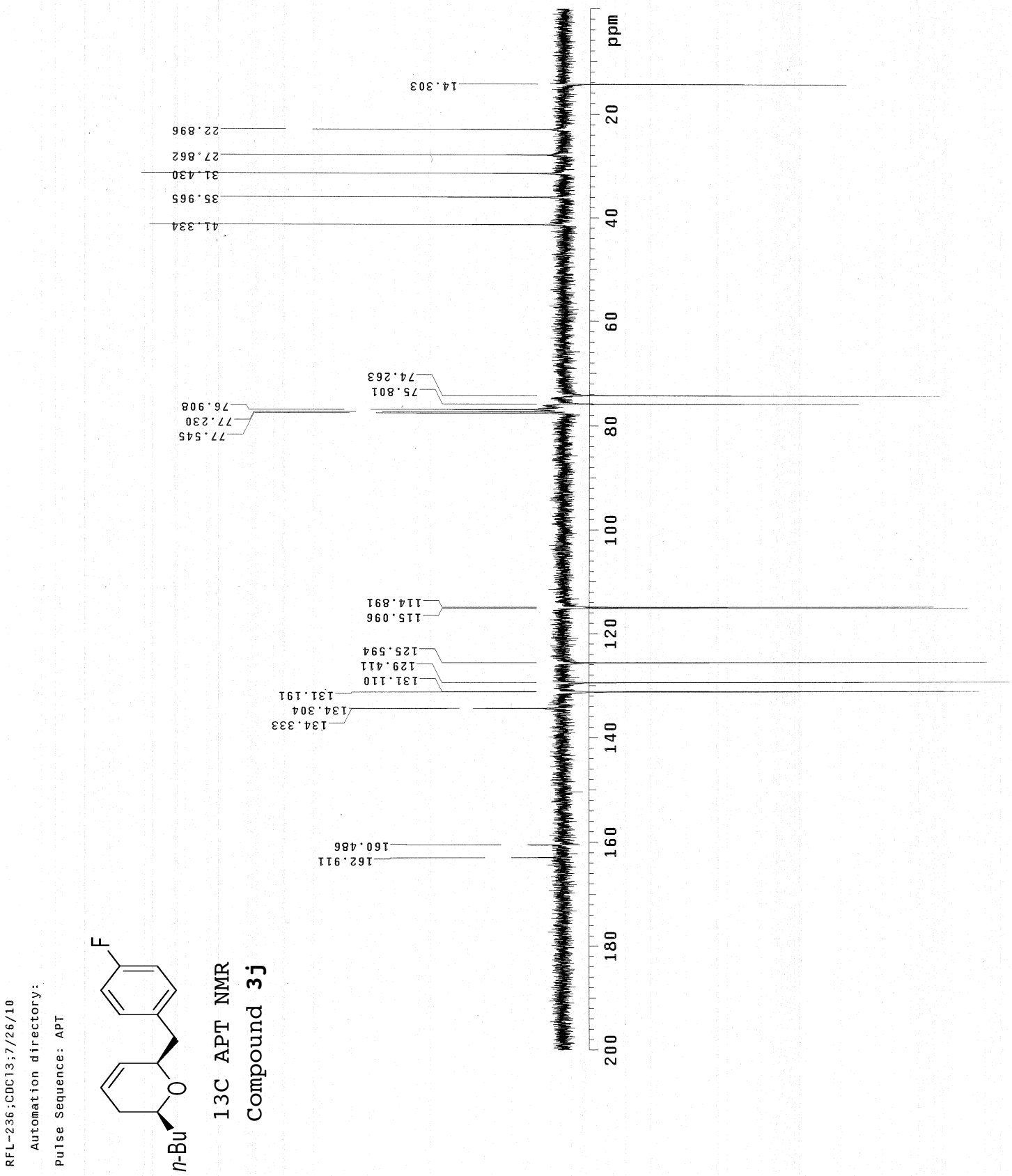




^{1}H NMR

Compound **3j**




RFL-236;CDCl3;7/26/10
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13C APT NMR
Compound 3j
n-Bu
F
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27.862
31.430
35.965
41.334
74.263
75.801
76.908
77.230
77.545
114.891
115.096
125.594
129.411
131.110
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134.333
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162.911
ppm
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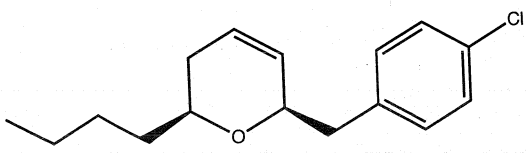
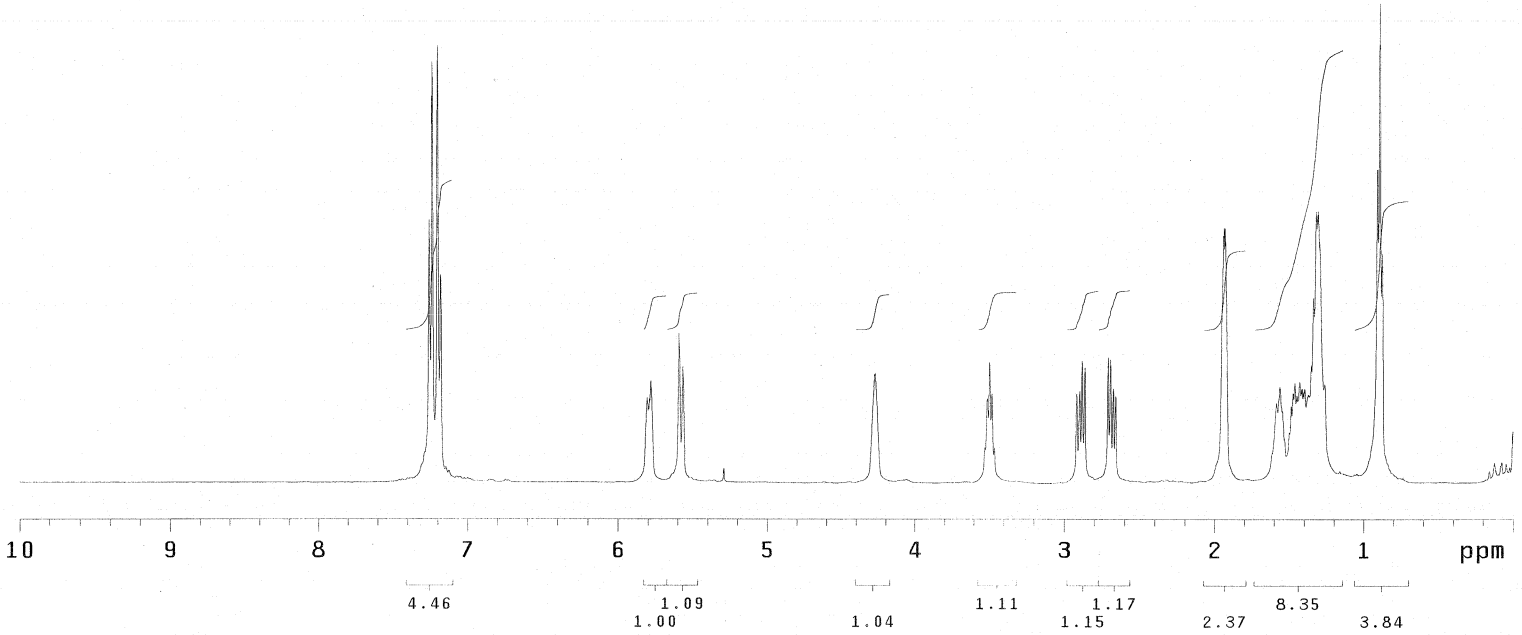


^{1}H NMR

Compound **3k**



RFL-237; chlorophenyl oxirane with butyl vinyl silane; CDCl3;10/6/10

Automation directory:

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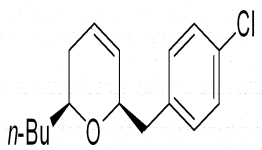
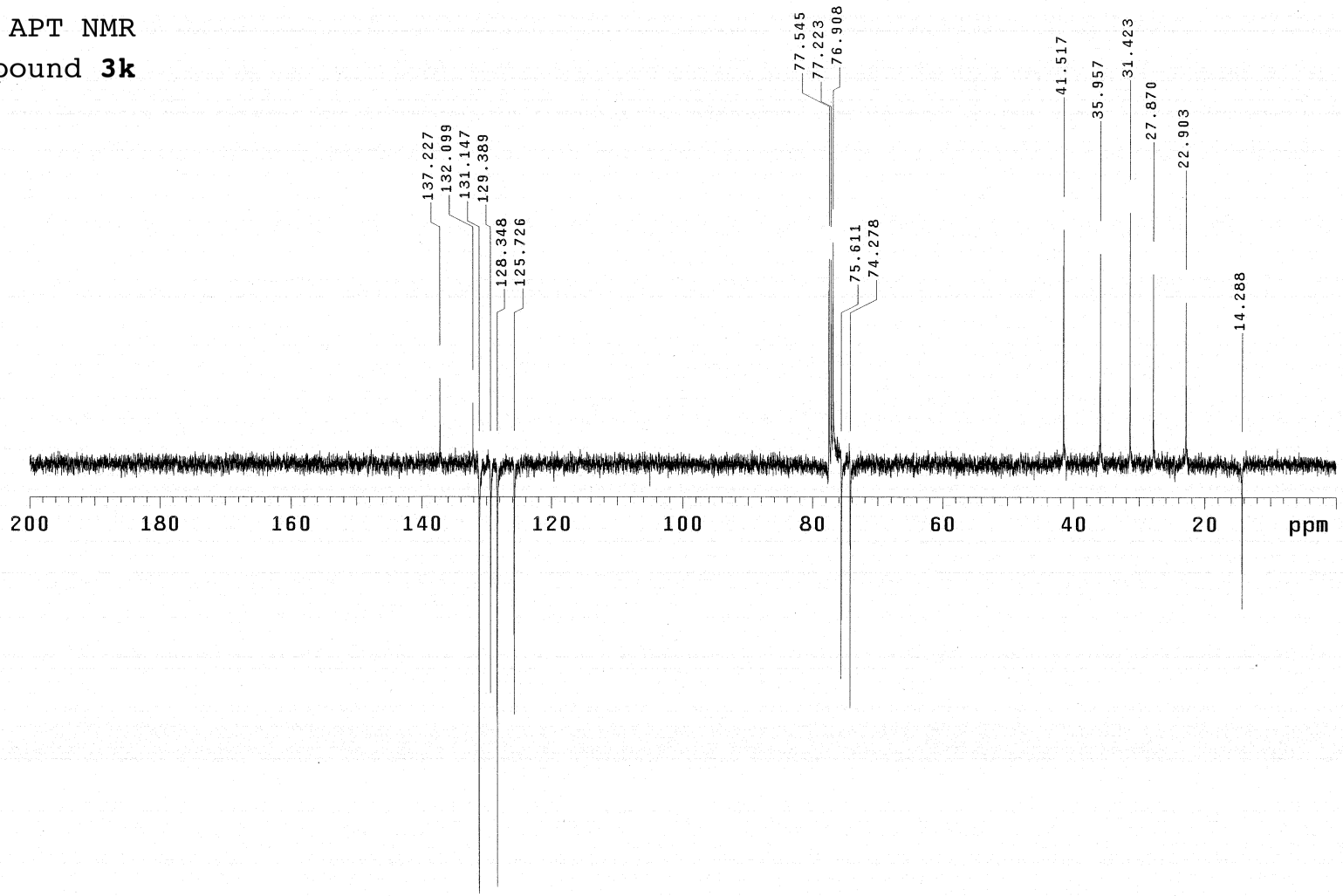
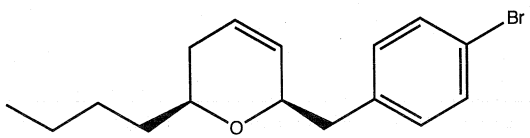


13C APT NMR

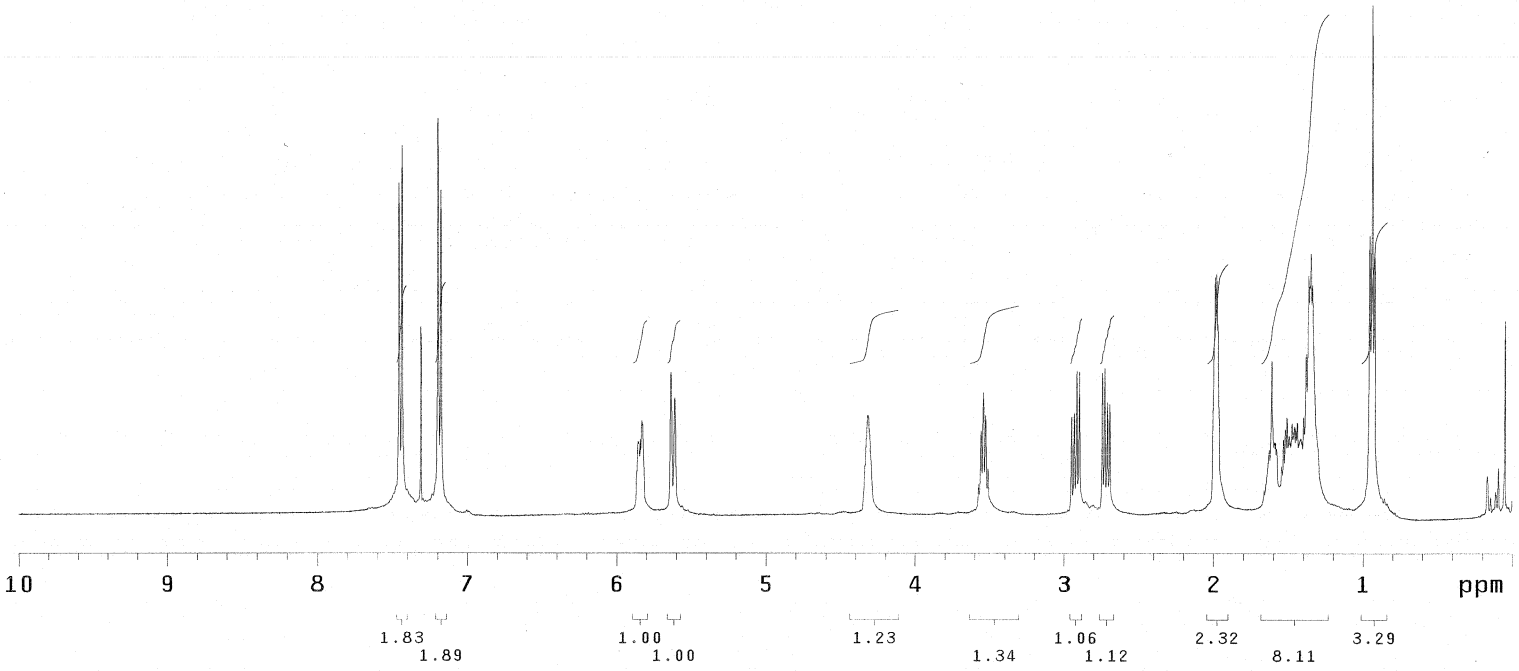
Compound **3k**

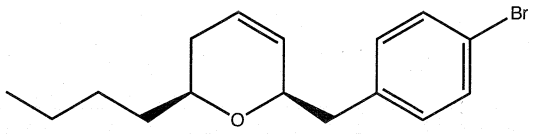




^{1}H NMR

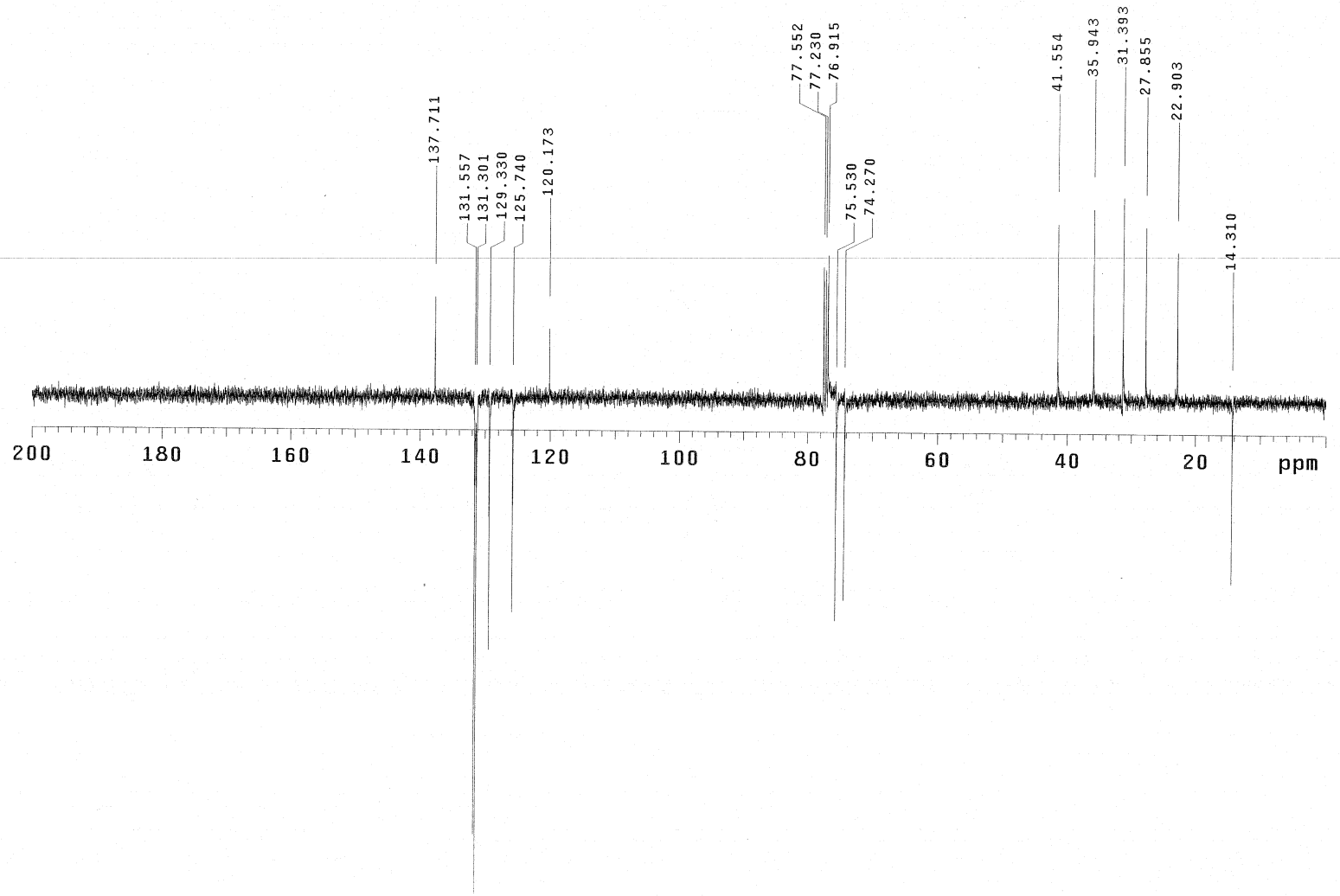
Compound **31**

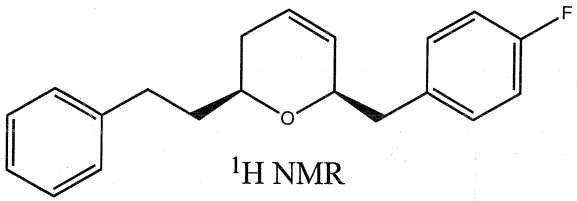




^{13}C APT NMR

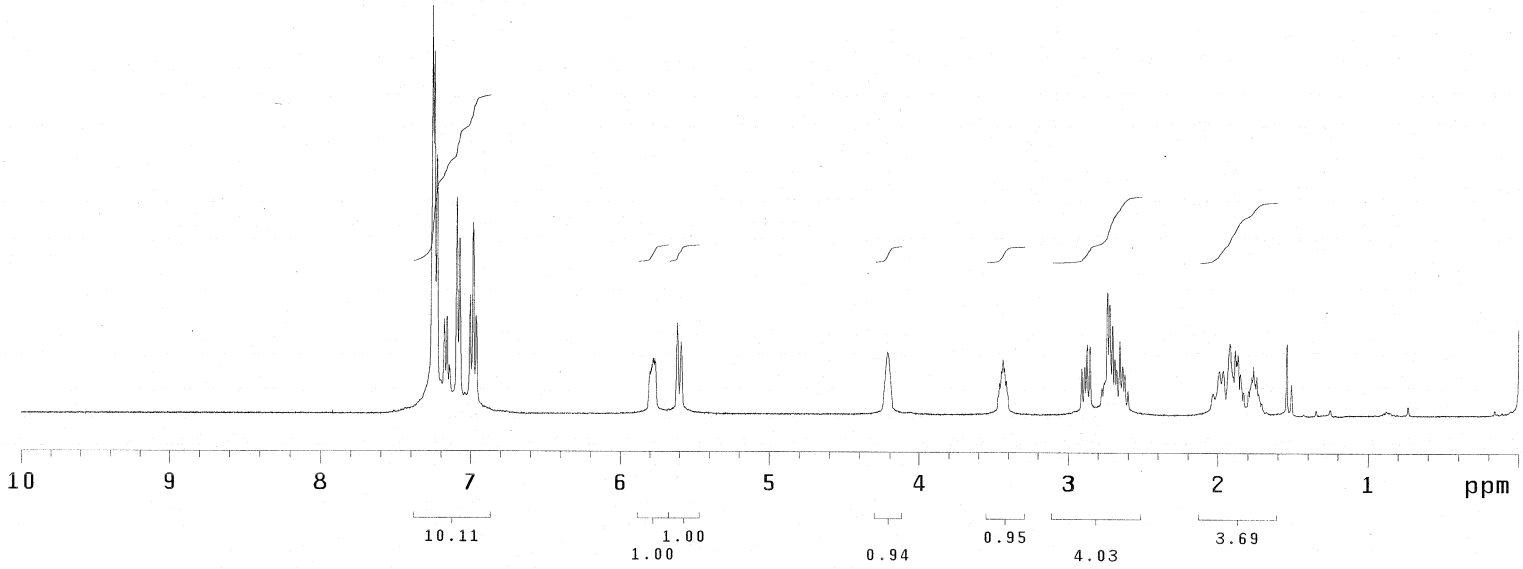
Compound **31**





^{1}H NMR

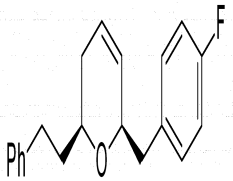
Compound **3m**



RFL-238; fluoropheynl oxirane with CH2CH2Ph side chain DHP; CDCl3;10/6/10

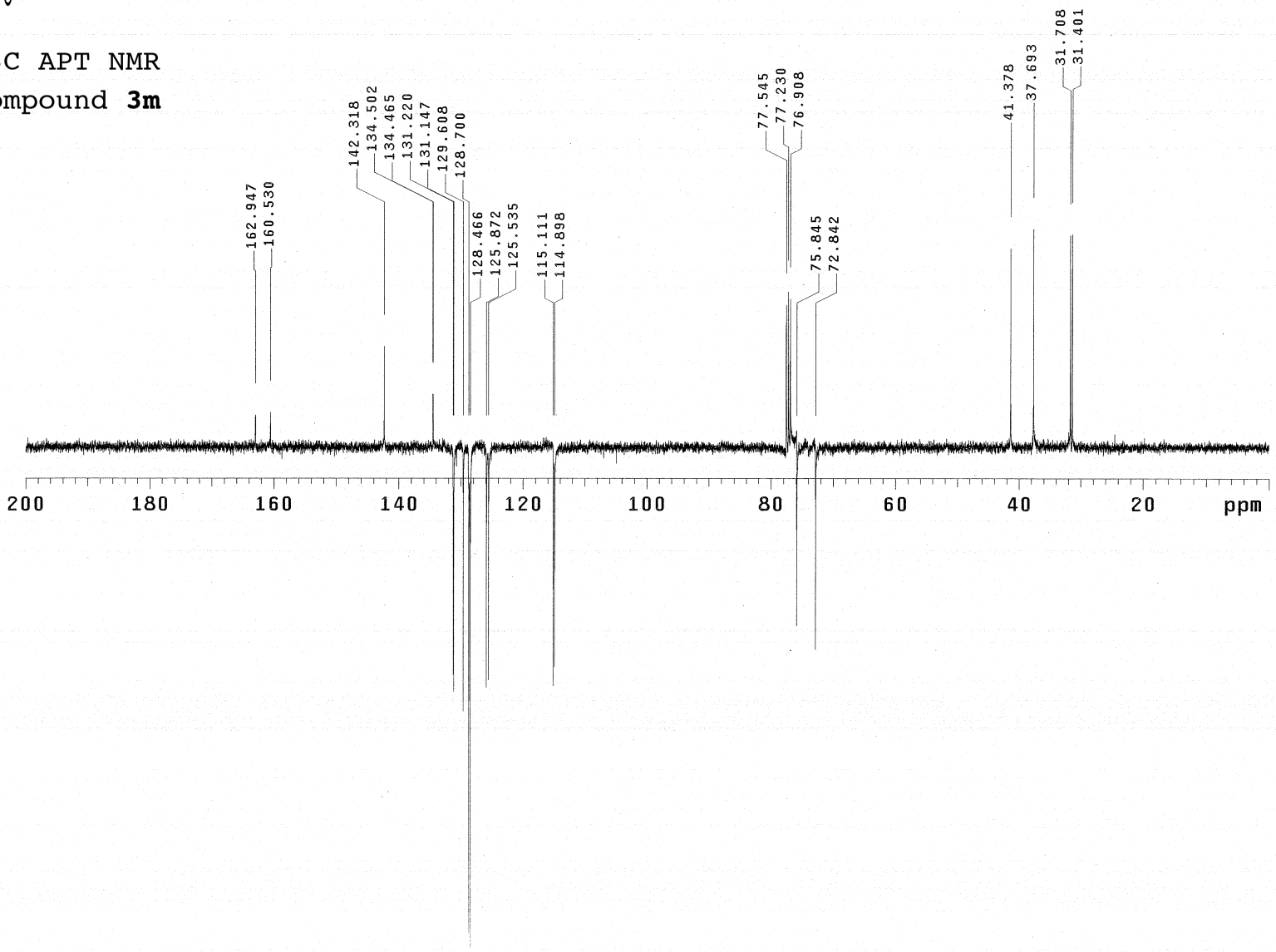
Automation directory:

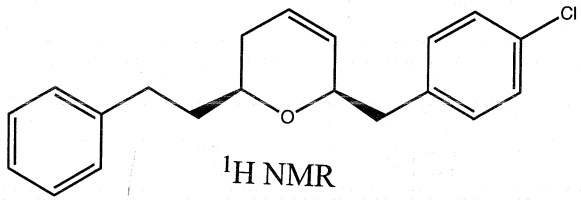
Pulse Sequence: APT



13C APT NMR

Compound **3m**

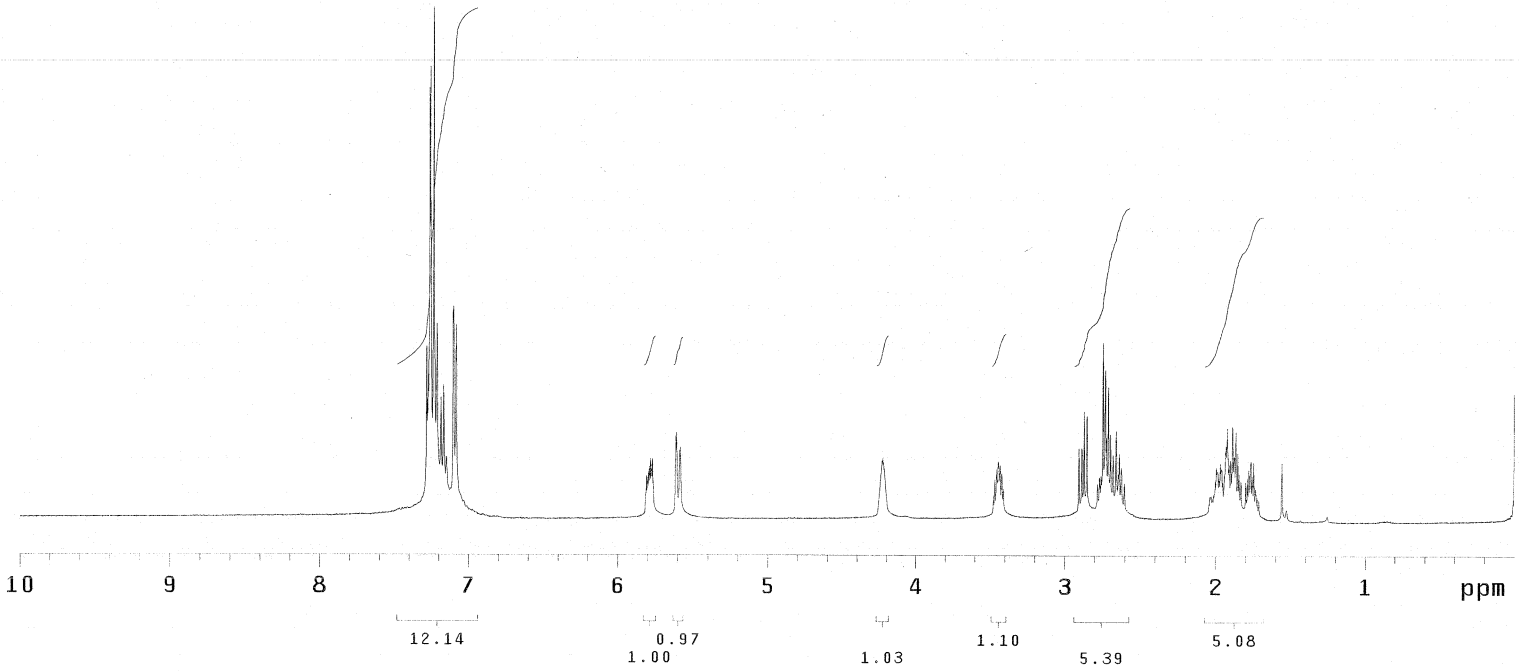


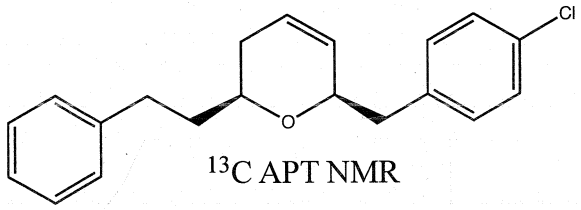


^{1}H NMR

1H NMR

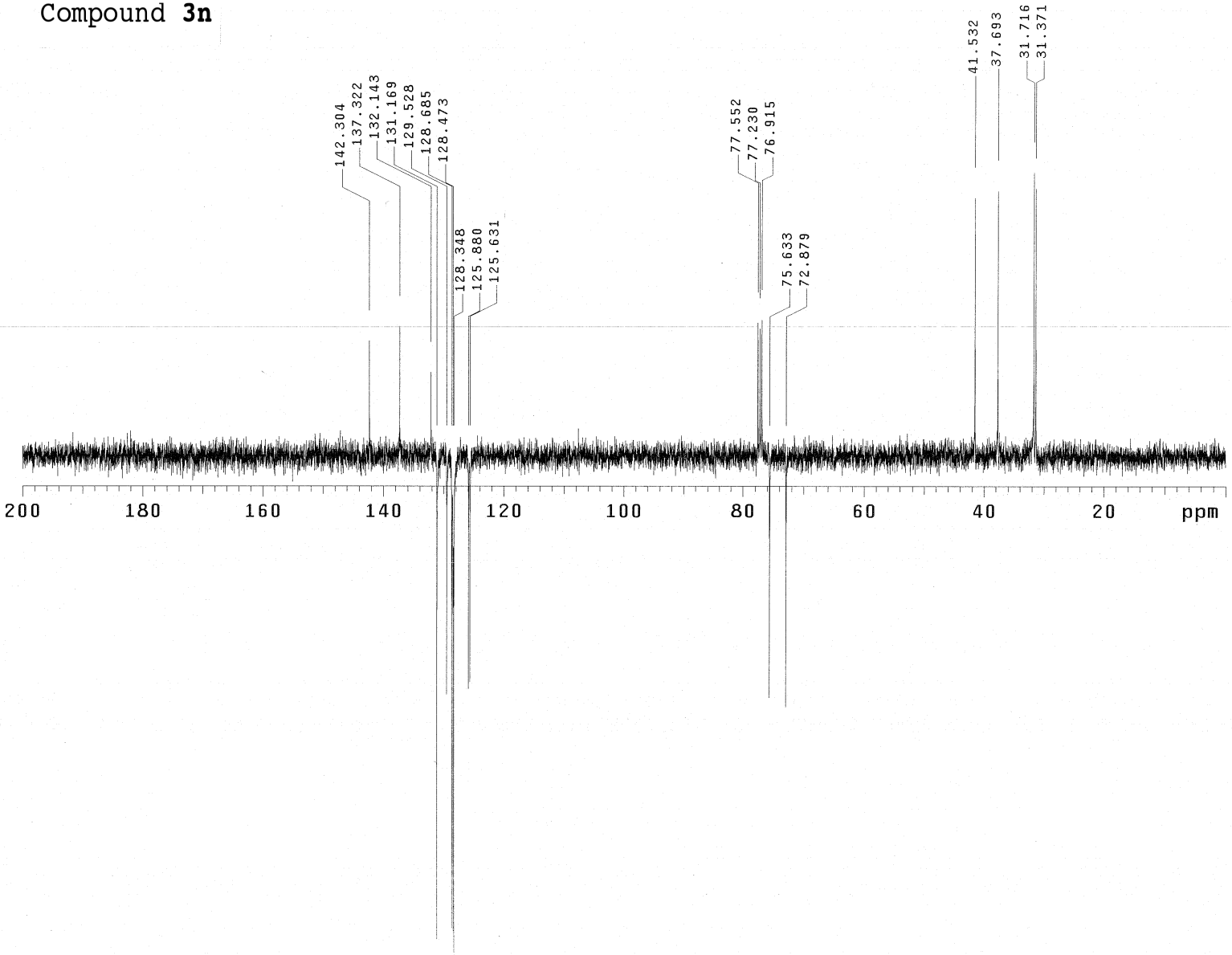
Compound **3n**

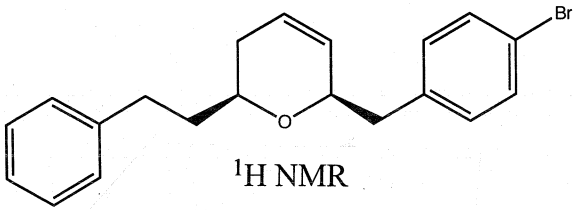




^{13}C APT NMR

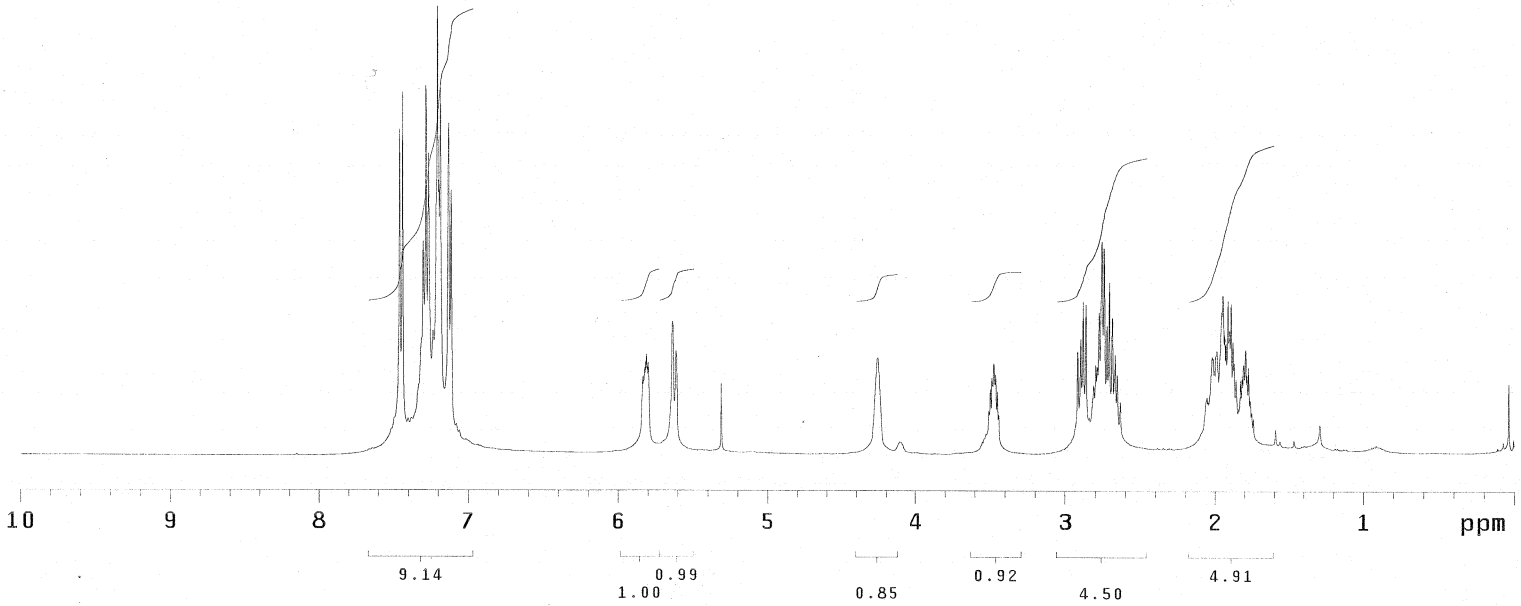
Compound **3n**

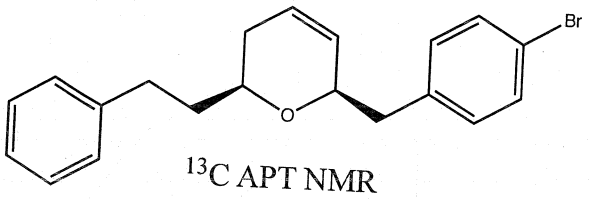




^{1}H NMR

Compound **3o**





^{13}C APT NMR

Compound **3o**

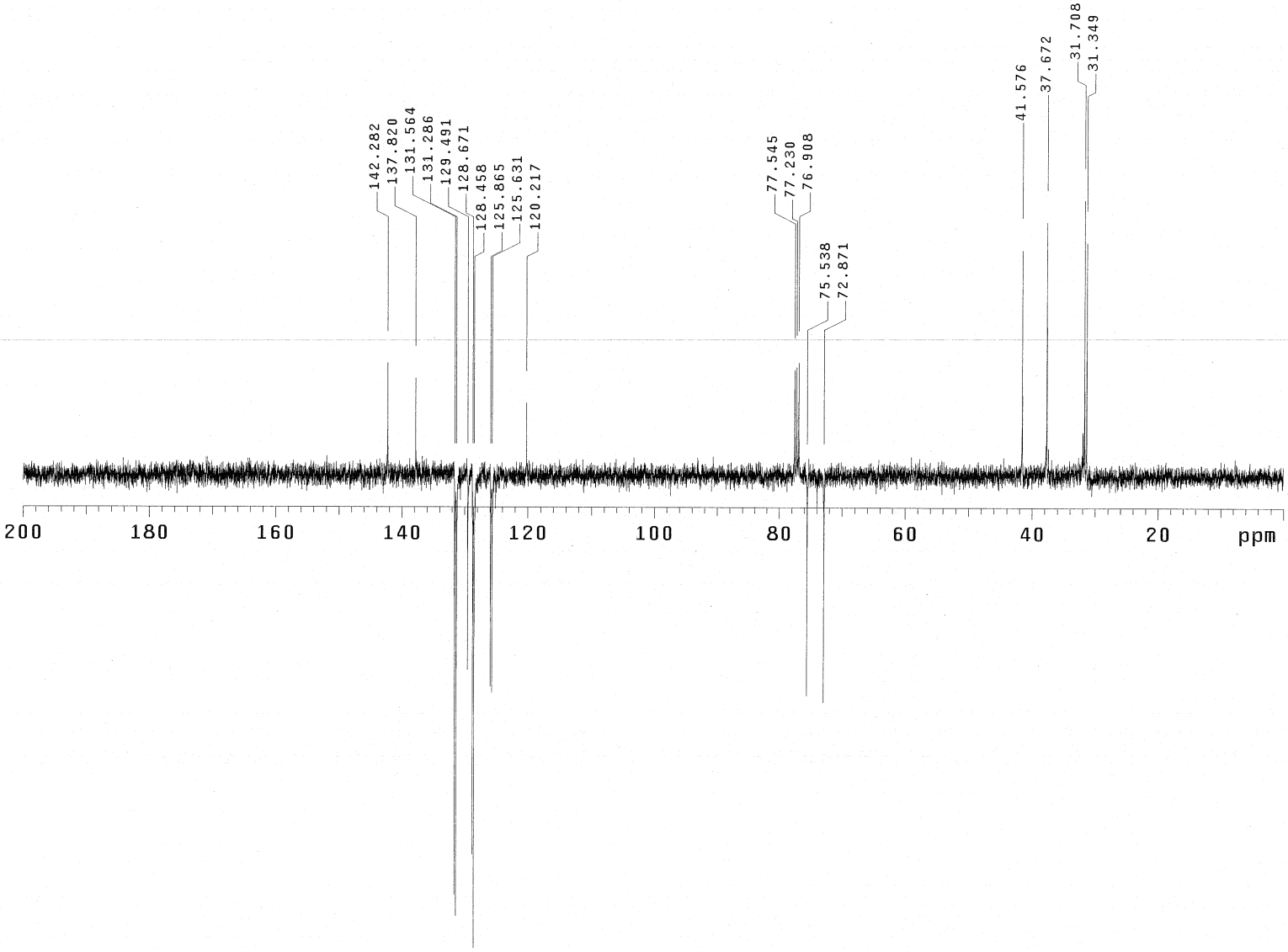
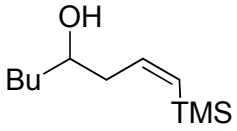
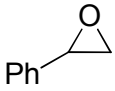
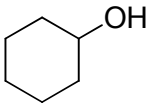
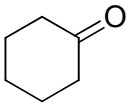
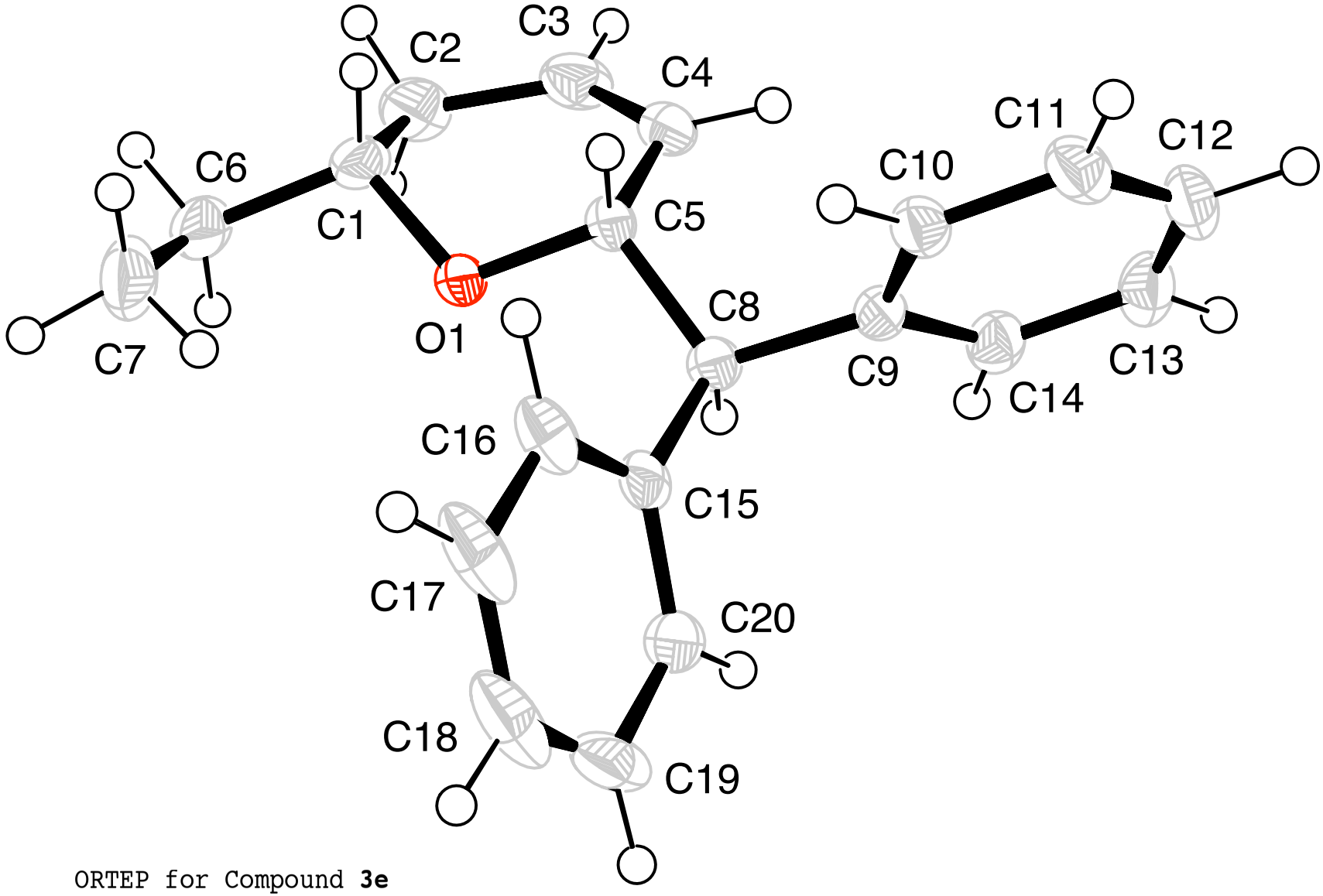


Table of ^{19}F resonances for substrates and various triflate species.

Substrate	Catalyst	^{19}F Chemical Shifts (in ppm)
–	$Bi(OTf)_3$	none
–	TfOH	-76.3
–	TMSOTf	-77.4
–	Bu_4NOTf	-78.7
	5% $Bi(OTf)_3$	-78.8
	10% $Bi(OTf)_3$	-78.8
	10% TfOH	-78.8
	10% TMSOTf	-78.8
	10% $Bi(OTf)_3$, 10% TfOH	-78.8
	10% $Bi(OTf)_3$, 10% TfOH, 10% TMSOTf	-78.9
	5% $Bi(OTf)_3$	-78.0
	5% TfOH	-78.7
	5% $Bi(OTf)_3$, 5% TfOH	-78.1
	10% $Bi(OTf)_3$	-78.9
	10% $Bi(OTf)_3$, 10% TfOH	-78.9
	10% $Bi(OTf)_3$	-78.8
	10% $Bi(OTf)_3$, 10% TfOH	-78.7



ORTEP for Compound **3e**

Table 1. Crystal data and structure refinement for **3e**.

Identification code	cc	
Empirical formula	C20 H22 O	
Formula weight	278.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 17.2161(3) Å	α= 90°.
	b = 5.95830(10) Å	β= 116.2110(10)°.
	c = 17.2485(3) Å	γ = 90°.
Volume	1587.39(5) $Å^3$	
Z	4	
Density (calculated)	1.165 Mg/m^3	
Absorption coefficient	0.533 mm^{-1}	
F(000)	600	
Crystal size	0.28 x 0.26 x 0.15 mm^3	
Theta range for data collection	5.72 to 66.90°.	
Index ranges	-18<=h<=20, -7<=k<=6, -19<=l<=20	
Reflections collected	8161	
Independent reflections	2425 [R(int) = 0.0308]	
Completeness to theta = 66.90°	99.6 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9233 and 0.8672	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2425 / 2 / 278	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0748	
R indices (all data)	R1 = 0.0284, wR2 = 0.0749	
Absolute structure parameter	0.17(19)	
Largest diff. peak and hole	0.110 and -0.156 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8475(1)	3003(2)	9174(1)	27(1)
C(1)	9164(1)	3297(3)	8929(1)	33(1)
C(2)	9070(1)	5572(3)	8505(1)	43(1)
C(3)	8161(1)	5953(3)	7851(1)	38(1)
C(4)	7512(1)	4697(2)	7812(1)	31(1)
C(5)	7652(1)	2817(2)	8448(1)	26(1)
C(6)	10010(1)	3022(3)	9731(1)	39(1)
C(7)	10147(1)	721(3)	10135(1)	46(1)
C(8)	6971(1)	2796(2)	8794(1)	24(1)
C(9)	6070(1)	2480(2)	8058(1)	24(1)
C(10)	5832(1)	512(2)	7570(1)	28(1)
C(11)	5021(1)	322(3)	6866(1)	35(1)
C(12)	4439(1)	2093(3)	6645(1)	37(1)
C(13)	4661(1)	4030(3)	7132(1)	36(1)
C(14)	5471(1)	4227(2)	7835(1)	30(1)
C(15)	7181(1)	1102(2)	9522(1)	26(1)
C(16)	7609(1)	-907(2)	9567(1)	34(1)
C(17)	7796(1)	-2396(3)	10245(1)	48(1)
C(18)	7549(1)	-1933(4)	10880(1)	54(1)
C(19)	7121(1)	57(4)	10851(1)	54(1)
C(20)	6941(1)	1593(3)	10173(1)	36(1)

Table 3. Bond lengths [Å] and angles [°] for **3e**.

O(1)-C(5)	1.4221(15)
O(1)-C(1)	1.4350(17)
C(1)-C(6)	1.511(2)
C(1)-C(2)	1.514(2)
C(1)-H(1)	1.024(18)
C(2)-C(3)	1.488(2)
C(2)-H(2A)	0.98(2)
C(2)-H(2B)	0.99(2)
C(3)-C(4)	1.322(2)
C(3)-H(3)	0.95(2)
C(4)-C(5)	1.5096(19)
C(4)-H(4)	0.97(2)
C(5)-C(8)	1.5310(18)
C(5)-H(5)	1.051(16)
C(6)-C(7)	1.508(3)
C(6)-H(6A)	0.95(2)
C(6)-H(6B)	1.007(19)
C(7)-H(7A)	1.01(2)
C(7)-H(7B)	0.99(2)
C(7)-H(7C)	0.95(3)
C(8)-C(9)	1.5214(18)
C(8)-C(15)	1.5251(17)
C(8)-H(8)	0.985(17)
C(9)-C(10)	1.395(2)
C(9)-C(14)	1.395(2)
C(10)-C(11)	1.393(2)
C(10)-H(10)	0.992(16)
C(11)-C(12)	1.387(2)
C(11)-H(11)	1.004(19)
C(12)-C(13)	1.379(2)
C(12)-H(12)	0.952(19)
C(13)-C(14)	1.391(2)
C(13)-H(13)	0.974(19)
C(14)-H(14)	0.98(2)

C(15)-C(16)	1.389(2)
C(15)-C(20)	1.389(2)
C(16)-C(17)	1.389(2)
C(16)-H(16)	0.984(19)
C(17)-C(18)	1.365(3)
C(17)-H(17)	1.07(2)
C(18)-C(19)	1.385(3)
C(18)-H(18)	0.97(3)
C(19)-C(20)	1.408(3)
C(19)-H(19)	0.89(3)
C(20)-H(20)	0.963(19)

C(5)-O(1)-C(1)	112.43(9)
O(1)-C(1)-C(6)	107.72(11)
O(1)-C(1)-C(2)	109.01(13)
C(6)-C(1)-C(2)	113.16(13)
O(1)-C(1)-H(1)	109.8(11)
C(6)-C(1)-H(1)	108.0(11)
C(2)-C(1)-H(1)	109.1(10)
C(3)-C(2)-C(1)	110.77(13)
C(3)-C(2)-H(2A)	112.4(12)
C(1)-C(2)-H(2A)	107.3(12)
C(3)-C(2)-H(2B)	112.4(14)
C(1)-C(2)-H(2B)	107.6(12)
H(2A)-C(2)-H(2B)	106.1(18)
C(4)-C(3)-C(2)	122.32(14)
C(4)-C(3)-H(3)	121.4(14)
C(2)-C(3)-H(3)	116.3(13)
C(3)-C(4)-C(5)	121.54(14)
C(3)-C(4)-H(4)	123.2(11)
C(5)-C(4)-H(4)	115.2(11)
O(1)-C(5)-C(4)	111.06(11)
O(1)-C(5)-C(8)	107.06(10)
C(4)-C(5)-C(8)	112.62(11)
O(1)-C(5)-H(5)	108.1(9)
C(4)-C(5)-H(5)	108.5(8)

C(8)-C(5)-H(5)	109.3(9)
C(7)-C(6)-C(1)	114.37(14)
C(7)-C(6)-H(6A)	111.8(11)
C(1)-C(6)-H(6A)	104.4(12)
C(7)-C(6)-H(6B)	110.3(10)
C(1)-C(6)-H(6B)	107.4(10)
H(6A)-C(6)-H(6B)	108.3(15)
C(6)-C(7)-H(7A)	112.2(13)
C(6)-C(7)-H(7B)	112.7(13)
H(7A)-C(7)-H(7B)	107.3(18)
C(6)-C(7)-H(7C)	112.9(15)
H(7A)-C(7)-H(7C)	110(2)
H(7B)-C(7)-H(7C)	101(2)
C(9)-C(8)-C(15)	112.83(10)
C(9)-C(8)-C(5)	110.50(10)
C(15)-C(8)-C(5)	112.49(11)
C(9)-C(8)-H(8)	107.2(10)
C(15)-C(8)-H(8)	107.6(9)
C(5)-C(8)-H(8)	105.9(10)
C(10)-C(9)-C(14)	118.49(13)
C(10)-C(9)-C(8)	121.76(11)
C(14)-C(9)-C(8)	119.69(12)
C(11)-C(10)-C(9)	120.55(13)
C(11)-C(10)-H(10)	119.1(9)
C(9)-C(10)-H(10)	120.4(9)
C(12)-C(11)-C(10)	120.12(14)
C(12)-C(11)-H(11)	119.0(11)
C(10)-C(11)-H(11)	120.9(11)
C(13)-C(12)-C(11)	119.85(14)
C(13)-C(12)-H(12)	119.7(10)
C(11)-C(12)-H(12)	120.4(10)
C(12)-C(13)-C(14)	120.18(14)
C(12)-C(13)-H(13)	122.0(11)
C(14)-C(13)-H(13)	117.8(11)
C(13)-C(14)-C(9)	120.79(13)
C(13)-C(14)-H(14)	118.8(11)

C(9)-C(14)-H(14)	120.4(11)
C(16)-C(15)-C(20)	118.42(13)
C(16)-C(15)-C(8)	122.91(12)
C(20)-C(15)-C(8)	118.67(13)
C(15)-C(16)-C(17)	121.15(16)
C(15)-C(16)-H(16)	120.4(11)
C(17)-C(16)-H(16)	118.4(11)
C(18)-C(17)-C(16)	120.54(19)
C(18)-C(17)-H(17)	120.8(13)
C(16)-C(17)-H(17)	118.6(13)
C(17)-C(18)-C(19)	119.55(16)
C(17)-C(18)-H(18)	118.5(14)
C(19)-C(18)-H(18)	121.9(14)
C(18)-C(19)-C(20)	120.29(18)
C(18)-C(19)-H(19)	122.2(15)
C(20)-C(19)-H(19)	117.5(15)
C(15)-C(20)-C(19)	120.04(17)
C(15)-C(20)-H(20)	119.0(11)
C(19)-C(20)-H(20)	121.0(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **3e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	19(1)	41(1)	20(1)	-4(1)	8(1)	-5(1)
C(1)	24(1)	51(1)	28(1)	-12(1)	14(1)	-9(1)
C(2)	36(1)	61(1)	36(1)	-2(1)	19(1)	-19(1)
C(3)	43(1)	46(1)	28(1)	0(1)	19(1)	-12(1)
C(4)	29(1)	42(1)	22(1)	0(1)	11(1)	-3(1)
C(5)	19(1)	35(1)	21(1)	-3(1)	7(1)	-4(1)
C(6)	23(1)	59(1)	35(1)	-13(1)	13(1)	-8(1)
C(7)	24(1)	59(1)	45(1)	-12(1)	5(1)	4(1)
C(8)	23(1)	26(1)	23(1)	-2(1)	10(1)	-3(1)
C(9)	21(1)	31(1)	23(1)	2(1)	10(1)	-4(1)
C(10)	26(1)	32(1)	25(1)	2(1)	10(1)	-3(1)
C(11)	33(1)	43(1)	25(1)	-1(1)	9(1)	-13(1)
C(12)	23(1)	54(1)	27(1)	11(1)	3(1)	-9(1)
C(13)	24(1)	42(1)	39(1)	14(1)	11(1)	4(1)
C(14)	26(1)	33(1)	32(1)	4(1)	14(1)	-2(1)
C(15)	18(1)	36(1)	21(1)	-1(1)	4(1)	-10(1)
C(16)	31(1)	31(1)	26(1)	0(1)	1(1)	-6(1)
C(17)	41(1)	41(1)	32(1)	6(1)	-10(1)	-15(1)
C(18)	42(1)	62(1)	31(1)	18(1)	-8(1)	-26(1)
C(19)	37(1)	101(2)	20(1)	-2(1)	9(1)	-36(1)
C(20)	23(1)	57(1)	26(1)	-5(1)	10(1)	-12(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3e**.

	x	y	z	U(eq)
H(1)	9131(13)	2070(30)	8499(12)	34(4)
H(2A)	9478(15)	5620(30)	8253(13)	55(6)
H(2B)	9269(16)	6710(40)	8967(15)	54(5)
H(3)	8073(14)	7120(40)	7447(14)	47(5)
H(4)	6925(12)	4860(30)	7369(13)	36(4)
H(5)	7631(10)	1280(30)	8138(10)	23(4)
H(6A)	9995(13)	4150(30)	10112(13)	38(4)
H(6B)	10489(12)	3390(30)	9569(11)	33(4)
H(7A)	10681(16)	650(40)	10711(15)	56(6)
H(7B)	9651(16)	220(40)	10233(15)	55(6)
H(7C)	10165(17)	-430(40)	9760(17)	68(7)
H(8)	6989(11)	4300(30)	9036(10)	28(4)
H(10)	6238(11)	-780(30)	7723(10)	24(4)
H(11)	4855(12)	-1070(30)	6500(12)	38(4)
H(12)	3880(12)	1960(30)	6172(12)	33(4)
H(13)	4259(12)	5280(30)	7011(12)	33(4)
H(14)	5610(12)	5610(30)	8182(12)	39(5)
H(16)	7800(12)	-1290(30)	9122(12)	38(5)
H(17)	8117(15)	-3940(40)	10249(15)	58(6)
H(18)	7700(16)	-2990(40)	11351(16)	63(6)
H(19)	6934(16)	400(40)	11243(17)	59(6)
H(20)	6644(13)	2980(30)	10147(12)	37(4)