Table 5. Crystal data and structure refinement for **1**.

Identification code	ingg
Empirical formula	$C_{16}H_{16}F_3NO_3$
Formula weight	327.30
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 10.709(2) Å alpha = 90° b = 20.857(4) Å beta = 93.70(3)° c = 14.065(3) Å gamma = 90°
Volume, Z	3135.0(11) Å^3, 8
Density (calculated)	1.387 g/cm^3
Absorption coefficient	0.119 mm^{-1}
F(000)	1360
Crystal size	0.45 x 0.45 x 0.45 mm
θ range for data collection	2.14 to 22.50°
Limiting indices	$-11 \le h \le 11$, $0 \le k \le 22$, $0 \le l \le 15$
Reflections collected	4290
Independent reflections	4097 (R_{int} = 0.0301)
Completeness to θ = 22.50°	99.8 %
Max. and min. transmission	0.9485 and 0.9485
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4097 / 0 / 424
Goodness-of-fit on F^2	1.025
Final R indices [I>2σ(I)]	R1 = 0.0765, wR2 = 0.1601
R indices (all data)	R1 = 0.1476, wR2 = 0.2006
Largest diff. peak and hole	0.533 and -0.446 eÅ^{-3}

Table 2S. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	5388(4)	1789(2)	3471(3)	54(1)
O(2)	6312(5)	837(2)	4479(3)	83(2)
O(3)	5793(5)	-3(2)	3558(4)	91(2)
O(1')	1693(4)	3407(2)	4655(3)	55(1)
O(3')	2286(5)	5060(2)	4745(4)	112(2)
O(2')	3227(4)	4225(2)	5432(3)	68(1)
N(1)	4578(4)	1348(2)	1912(3)	43(1)
N(1')	1070(4)	3681(2)	2967(3)	47(1)
F(1)	8423(5)	-72(3)	4546(4)	145(2)
F(2)	7410(5)	23(2)	5721(3)	136(2)
F(3)	7088(5)	-749(2)	4795(4)	145(2)
F(1')	3158(8)	5215(4)	6846(5)	258(5)
F(2')	3775(8)	5804(2)	5852(5)	224(5)
F(3')	4785(6)	5066(3)	6332(5)	159(3)
C(1)	5512(6)	2421(3)	2088(4)	53(2)
C(2)	6136(7)	2982(3)	2271(4)	82(2)
C(3)	5761(9)	3533(4)	1749(6)	103(3)
C(4)	4810(9)	3525(3)	1069(5)	90(3)
C(5)	3127(8)	2858(4)	180(5)	82(2)
C(6)	2595(7)	2268(4)	58(5)	88(2)
C(7)	3010(6)	1724(3)	598(5)	72(2)
C(8)	3975(5)	1821(3)	1247(4)	46(1)
C(9)	4538(5)	2419(3)	1385(4)	48(2)
C(10)	4131(7)	2952(3)	853(5)	66(2)
C(11)	5695(5)	1770(3)	2542(4)	47(1)
C(12)	6968(5)	1485(3)	2430(5)	72(2)
C(13)	5095(5)	799(3)	1373(4)	60(2)
C(14)	3648(6)	1094(3)	2560(4)	69(2)
C(15)	6354(6)	269(3)	4225(4)	58(2)
C(16)	7282(7)	-136(3)	4830(5)	69(2)
C(1')	613(5)	3227(3)	2216(4)	48(1)
C(2')	96(6)	3359(3)	1325(4)	65(2)
C(3')	-380(6)	2831(4)	805(5)	77(2)
C(4')	-368(6)	2211(4)	1145(5)	69(2)
C(5')	216(5)	1491(3)	2579(5)	60(2)
C(6')	726(5)	1465(3)	3491(5)	60(2)
C(7')	1270(5)	1999(3)	3965(4)	55(2)
C(8')	1250(5)	2574(2)	3499(4)	41(1)
C(9')	659(5)	2611(3)	2581(4)	44(1)
C(10')	154(5)	2081(3)	2076(4)	50(2)
C(11')	1870(5)	3201(3)	3761(4)	44(1)
C(12')	3218(5)	3209(3)	3510(4)	57(2)
C(14')	1803(6)	4223(3)	2591(4)	68(2)
C(13')	-34(6)	3951(3)	3432(5)	68(2)
C(15')	2992(6)	4804(3)	5329(5)	58(2)
C(16')	3681(8)	5226(4)	6050(6)	79(2)

Table 3S. Bond lengths [Å] and angles [°] for 1.

O(1)-C(11)	1.369(6)	O(2)-C(15)	1.239(7)
O(3)-C(15)	1.221(7)	O(1')-C(11')	1.353(6)
O(3')-C(15')	1.204(7)	O(2')-C(15')	1.240(7)
N(1)-C(8)	1.480(6)	N(1)-C(14)	1.489(6)
N(1)-C(13)	1.498(6)	N(1)-C(11)	1.689(6)
N(1')-C(1')	1.479(7)	N(1')-C(14')	1.493(7)
N(1')-C(13')	1.497(7)	N(1')-C(11')	1.691(6)
F(1)-C(16)	1.317(8)	F(2)-C(16)	1.295(7)
F(3)-C(16)	1.295(7)	F(1')-C(16')	1.284(9)
F(2')-C(16')	1.244(8)	F(3')-C(16')	1.267(8)
C(1)-C(2)	1.365(8)	C(1)-C(9)	1.390(8)
C(1)-C(11)	1.507(8)	C(2)-C(3)	1.408(10)
C(3)-C(4)	1.352(10)	C(4)-C(10)	1.422(10)
C(5)-C(6)	1.362(10)	C(5)-C(10)	1.400(9)
C(6)-C(7)	1.421(9)	C(7)-C(8)	1.349(8)
C(8)-C(9)	1.393(7)	C(9)-C(10)	1.395(8)
C(11)-C(12)	1.505(7)	C(15)-C(16)	1.522(9)
C(1')-C(2')	1.365(7)	C(1')-C(9')	1.383(7)
C(2')-C(3')	1.400(8)	C(3')-C(4')	1.379(9)
C(4')-C(10')	1.417(8)	C(5')-C(6')	1.363(8)
C(5')-C(10')	1.420(8)	C(6')-C(7')	1.404(8)
C(7')-C(8')	1.367(7)	C(8')-C(9')	1.403(7)
C(8')-C(11')	1.500(7)	C(9')-C(10')	1.403(7)
C(11')-C(12')	1.509(7)	C(15')-C(16')	1.501(9)

C(8)-N(1)-C(14)	110.0(4)	C(8)-N(1)-C(13)	110.5(4)
C(14)-N(1)-C(13)	108.8(4)	C(8)-N(1)-C(11)	104.4(4)
C(14)-N(1)-C(11)	110.1(4)	C(13)-N(1)-C(11)	113.0(4)
C(1')-N(1')-C(14')	112.9(4)	C(1')-N(1')-C(13')	108.6(4)
C(14')-N(1')-C(13')	108.5(4)	C(1')-N(1')-C(11')	102.9(4)
C(14')-N(1')-C(11')	115.3(4)	C(13')-N(1')-C(11')	108.4(4)
C(2)-C(1)-C(9)	118.1(6)	C(2)-C(1)-C(11)	130.2(6)
C(9)-C(1)-C(11)	111.7(5)	C(1)-C(2)-C(3)	118.9(7)
C(4)-C(3)-C(2)	122.3(7)	C(3)-C(4)-C(10)	120.9(7)
C(6)-C(5)-C(10)	120.5(7)	C(5)-C(6)-C(7)	122.8(7)
C(8)-C(7)-C(6)	116.1(6)	C(7)-C(8)-C(9)	122.4(6)
C(7)-C(8)-N(1)	127.7(5)	C(9)-C(8)-N(1)	110.0(5)
C(1)-C(9)-C(8)	113.6(5)	C(1)-C(9)-C(10)	125.0(6)
C(8)-C(9)-C(10)	121.4(6)	C(9)-C(10)-C(5)	116.8(6)
C(9)-C(10)-C(4)	114.7(7)	C(5)-C(10)-C(4)	128.4(7)
O(1)-C(11)-C(12)	112.7(5)	O(1)-C(11)-C(1)	110.2(5)
C(12)-C(11)-C(1)	113.9(5)	O(1)-C(11)-N(1)	108.1(4)
C(12)-C(11)-N(1)	110.8(4)	C(1)-C(11)-N(1)	100.3(4)
O(3)-C(15)-O(2)	129.8(6)	O(3)-C(15)-C(16)	116.3(6)
O(2)-C(15)-C(16)	113.8(6)	F(3)-C(16)-F(2)	107.3(7)
F(3)-C(16)-F(1)	103.8(6)	F(2)-C(16)-F(1)	103.0(6)
F(3)-C(16)-C(15)	115.4(6)	F(2)-C(16)-C(15)	115.0(6)
F(1)-C(16)-C(15)	111.0(6)	C(2')-C(1')-C(9')	122.1(6)
C(2')-C(1')-N(1')	128.5(5)	C(9')-C(1')-N(1')	109.1(5)
C(1')-C(2')-C(3')	115.7(6)	C(4')-C(3')-C(2')	124.1(6)
C(3')-C(4')-C(10')	119.6(6)	C(6')-C(5')-C(10')	120.4(6)
C(5')-C(6')-C(7')	123.0(6)	C(8')-C(7')-C(6')	118.4(5)
C(7')-C(8')-C(9')	118.8(5)	C(7')-C(8')-C(11')	130.8(5)
C(9')-C(8')-C(11')	110.1(4)	C(1')-C(9')-C(10')	122.7(5)
C(1')-C(9')-C(8')	113.3(5)	C(10')-C(9')-C(8')	124.0(5)

C(9')-C(10')-C(5')	115.3(5)	C(9')-C(10')-C(4')	115.7(6)
C(5')-C(10')-C(4')	129.0(6)	O(1')-C(11')-C(8')	114.7(5)
O(1')-C(11')-C(12')	114.0(5)	C(8')-C(11')-C(12')	111.5(4)
O(1')-C(11')-N(1')	109.3(4)	C(8')-C(11')-N(1')	99.0(4)
C(12')-C(11')-N(1')	106.9(4)	O(3')-C(15')-O(2')	128.7(6)
O(3')-C(15')-C(16')	117.4(6)	O(2')-C(15')-C(16')	113.9(6)
F(2')-C(16')-F(3')	103.7(8)	F(2')-C(16')-F(1')	105.0(8)
F(3')-C(16')-F(1')	100.0(8)	F(2')-C(16')-C(15')	117.4(7)
F(3')-C(16')-C(15')	117.7(7)	F(1')-C(16')-C(15')	110.8(7)

Symmetry transformations used to generate equivalent atoms:

Table 4s. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 1 .

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	69(3)	54(3)	38(2)	-1(2)	1(2)	12(2)
O(2)	121(4)	60(3)	65(3)	-4(3)	-18(3)	21(3)
O(3)	115(4)	66(3)	85(3)	-8(3)	-43(3)	-2(3)
O(1')	67(3)	59(3)	38(2)	-3(2)	8(2)	-1(2)
O(3')	121(4)	67(3)	136(5)	-7(3)	-71(4)	21(3)
O(2')	79(3)	53(3)	69(3)	-9(2)	-13(2)	0(2)
N(1)	44(3)	43(3)	43(3)	1(2)	6(2)	-2(2)
N(1')	56(3)	41(3)	45(3)	3(2)	3(2)	-1(2)
F(1)	83(4)	178(6)	174(5)	20(4)	5(4)	34(4)
F(2)	201(5)	141(4)	61(3)	-17(3)	-38(3)	80(4)
F(3)	173(5)	62(3)	189(5)	9(3)	-88(4)	13(3)
F(1')	272(9)	330(11)	184(7)	-195(8)	113(7)	-187(8)
F(2')	341(10)	59(3)	243(8)	21(4)	-198(7)	-56(4)
F(3')	131(5)	137(5)	195(6)	-27(4)	-97(5)	-5(4)
C(1)	71(4)	43(4)	45(4)	1(3)	11(3)	-12(3)
C(2)	122(6)	78(5)	46(4)	2(4)	-2(4)	-51(5)
C(3)	174(9)	66(6)	73(6)	-16(5)	28(6)	-57(6)
C(4)	163(8)	50(5)	59(5)	5(4)	32(5)	-3(5)
C(5)	98(6)	74(5)	74(5)	19(4)	6(5)	35(5)
C(6)	74(5)	109(7)	78(5)	10(5)	-23(4)	15(5)
C(7)	65(4)	74(5)	75(5)	7(4)	-19(4)	-2(4)
C(8)	46(3)	49(4)	42(3)	0(3)	-3(3)	5(3)
C(9)	59(4)	49(4)	38(3)	-5(3)	7(3)	4(3)
C(10)	93(5)	55(4)	50(4)	2(4)	20(4)	14(4)
C(11)	38(3)	58(4)	46(4)	-10(3)	4(3)	-1(3)
C(12)	47(4)	99(5)	71(4)	-31(4)	2(3)	3(4)
C(13)	55(4)	50(4)	73(4)	-12(3)	3(3)	5(3)
C(14)	54(4)	85(5)	68(4)	18(4)	9(3)	-13(4)
C(15)	73(5)	48(4)	52(4)	0(3)	-10(3)	2(4)
C(16)	82(5)	59(5)	62(5)	-20(4)	-14(4)	16(4)
C(1')	51(4)	50(4)	44(3)	1(3)	1(3)	-3(3)
C(2')	74(5)	64(4)	54(4)	13(3)	-12(3)	-7(4)
C(3')	85(5)	91(6)	54(4)	3(4)	-15(4)	-15(4)
C(4')	65(4)	81(5)	60(4)	-16(4)	-8(4)	-15(4)
C(5')	51(4)	45(4)	84(5)	-10(4)	4(4)	-6(3)
C(6')	56(4)	43(4)	80(5)	11(3)	9(4)	-3(3)
C(7')	57(4)	52(4)	55(4)	12(3)	2(3)	5(3)
C(8')	40(3)	44(3)	38(3)	7(3)	5(2)	4(3)
C(9')	41(3)	44(4)	46(4)	-1(3)	7(3)	-3(3)
C(10')	42(3)	54(4)	53(4)	-7(3)	4(3)	-8(3)
C(11')	53(4)	44(3)	35(3)	3(3)	0(3)	3(3)
C(12')	57(4)	61(4)	51(4)	-3(3)	-2(3)	-6(3)
C(14')	83(5)	53(4)	66(4)	12(3)	-2(4)	-11(4)
C(13')	71(4)	57(4)	76(5)	0(4)	8(4)	15(4)
C(15')	55(4)	52(4)	67(4)	-6(4)	-4(3)	10(3)
C(16')	89(6)	67(5)	79(5)	-25(4)	-13(5)	1(4)

Table 5S . Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 1 .

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	x	y	z	U(eq)
H(2A)	6834	2994	2734	80
H(3A)	6184	3932	1887	80
H(4A)	4582	3912	732	80
H(5A)	2809	3212	-198	80
H(6A)	1924	2216	-422	80
H(7A)	2603	1315	532	80
H(12A)	7588	1733	2791	80
H(12B)	6973	1053	2668	80
H(12C)	7153	1482	1772	80
H(13A)	4424	575	1032	80
H(13B)	5653	970	930	80
H(13C)	5543	509	1801	80
H(14A)	3012	857	2199	80
H(14B)	4062	819	3028	80
H(14C)	3271	1447	2872	80
H(2'A)	59	3788	1078	80
H(3'A)	-738	2905	171	80
H(4'A)	-714	1869	755	80
H(5'A)	-101	1107	2275	80
H(6'A)	719	1065	3827	80
H(7'A)	1639	1966	4604	80
H(12D)	3709	2944	3949	80
H(12E)	3265	3044	2875	80
H(12F)	3537	3639	3538	80
H(14D)	1293	4474	2146	80
H(14E)	2120	4491	3107	80
H(14F)	2490	4043	2275	80
H(13D)	-508	4221	2989	80
H(13E)	-552	3606	3626	80
H(13F)	250	4198	3980	80
H(8A)	5750(60)	1460(30)	3740(50)	80(20)
H(8'A)	2270(90)	3800(50)	4830(70)	190(40)

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Table ~~7S~~. H^1 NMR Shifts[a] of **1** at ambient Temperature.

Solvent	NMeA	NMeB	COMe	H2	H3	H4	H5	H6	H7
CD_2Cl_2	2.5586		2.2975	7.1962	7.4494	7.8188	7.6429	7.4763	7.3238
HOAc	2.6010		2.3338	7.2888	7.4716	7.8484	7.6788	7.4990	7.3926
$PhNO_2$	2.6764		2.4234	7.3910	7.5482	7.9193	7.7278	7.5772	7.5627
CD_3CN	2.4984		2.2691	7.1968	7.4726	7.8640	7.6861	7.5097	7.3952
Me_2CO	2.5972		2.2788	7.2103	7.4919	7.8933	7.7158	7.5242	7.4276
DMSO	*ca.* 2.75	*ca.* 2.35	2.294	7.239	7.540	7.952	7.776	7.574	7.489
CD_3OD	2.7649 br	2.2754 br	2.3189	7.1920	7.4657	7.8532	7.6777	7.4975	7.4105
TFE	2.7577 br	2.3226 br	2.3677	7.1869	7.4587	7.8459	7.6760	7.4990	7.2926

a) Relative to δ C_6H_{12} = 1.42 ppm:

Table 8S. ^{13}C NMR Shifts[a] of 8-Dimethylamino-1-acetonaphthone, **1**.

Ci	Me_2CO	$PhNO_2$	DMSO	$CDCl_3$	HOAc	CD_3CN	CD_3OD	TFE
	ε = 20.7	ε = 34.8	ε = 46.7	ε =4.8	ε =6.2	ε =37.5	ε =32.7	ε = 26.1
C1	141.2517	141.109	140.9184	140.550	139.524	141.125	140.171	139.26
C2	123.3057	123.253	123.4774	123.113	123.253	123.301	122.970	122.86
C3	126.0797	125.970	126.4564	125.847	126.229	126.180	125.881	126.09
C4	128.7884	128.817	129.0977	128.697	129.043	128.849	128.978	129.51
C5	125.0191	124.967	125.3027	124.725	125.258	125.016	125.080	125.57
C6	127.0534	126.941	127.4869	126.606	127.199	127.215	127.045	127.51
C7	118.7923	118.562	119.5057	118.175	118.789	119.031	118.966	119.54
C8	150.5683	150.328	150.4290	150.131	149.810	150.619	150.053	149.65
C9	128.3738	128.299	128.2062	128.306	128.784	128.380	128.639	129.27
C10	135.3921	135.189	135.0124	135.004	135.124	135.319	135.407	135.49
NMeA	47.0928		≈46.3307	44.486	≈45(br)	47.8	42.0	45.27
NMeB	42.6818		"	"		43.5	43.3	
C-O	200.0102	200.436	200.5388	201.540	202.409	200.856	203.834	205.97
COMe	31.0635	31.125	31.9299	31.568	30.866	31.093	30.834	30.74
R								
R								

a) Relative to $\delta(C_6H_{12})$ = 26.92 ppm . At ambient temperature.

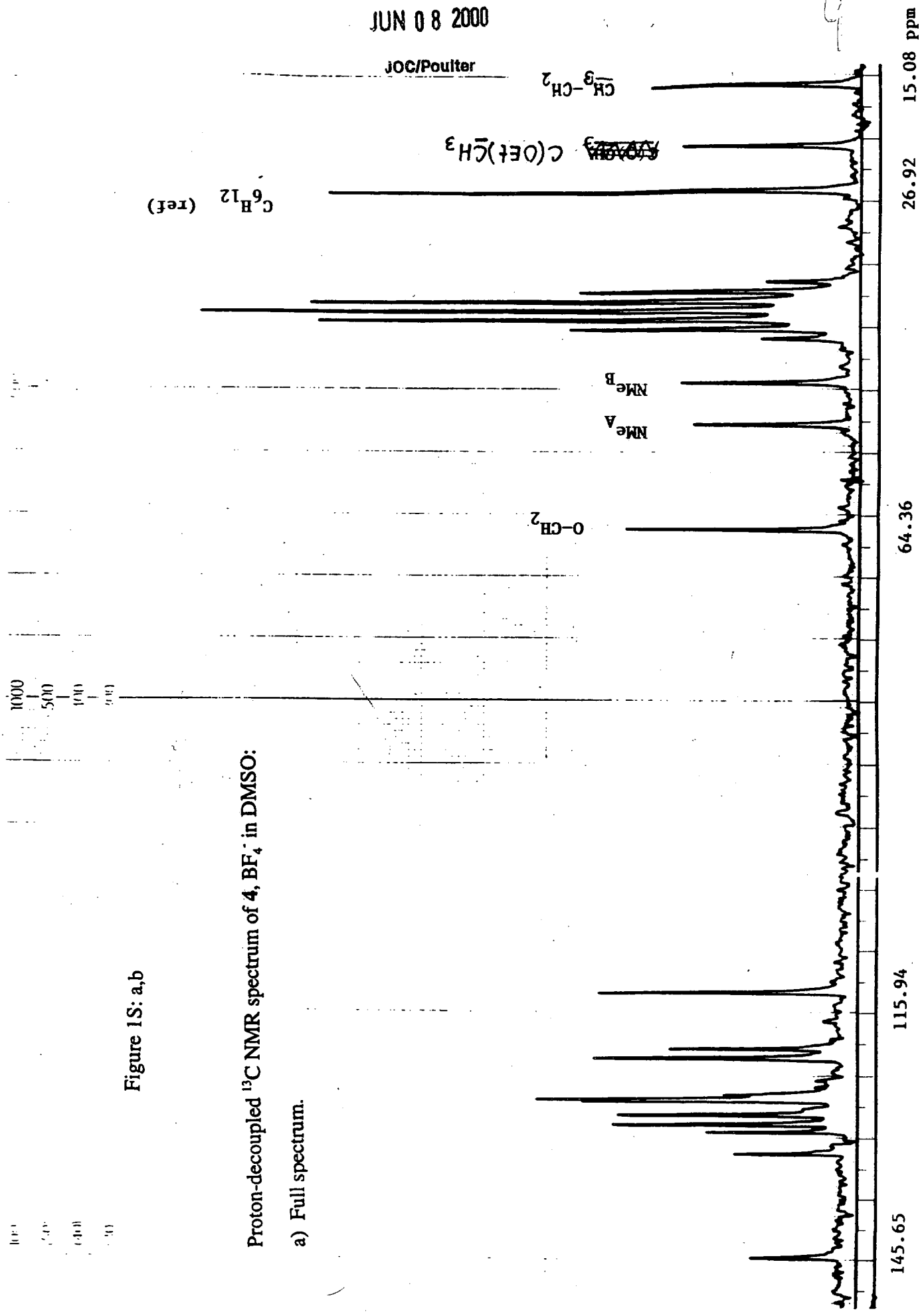


Figure 1S: a,b

Proton-decoupled ^{13}C NMR spectrum of **4**, BF_4^- in DMSO:

a) Full spectrum.

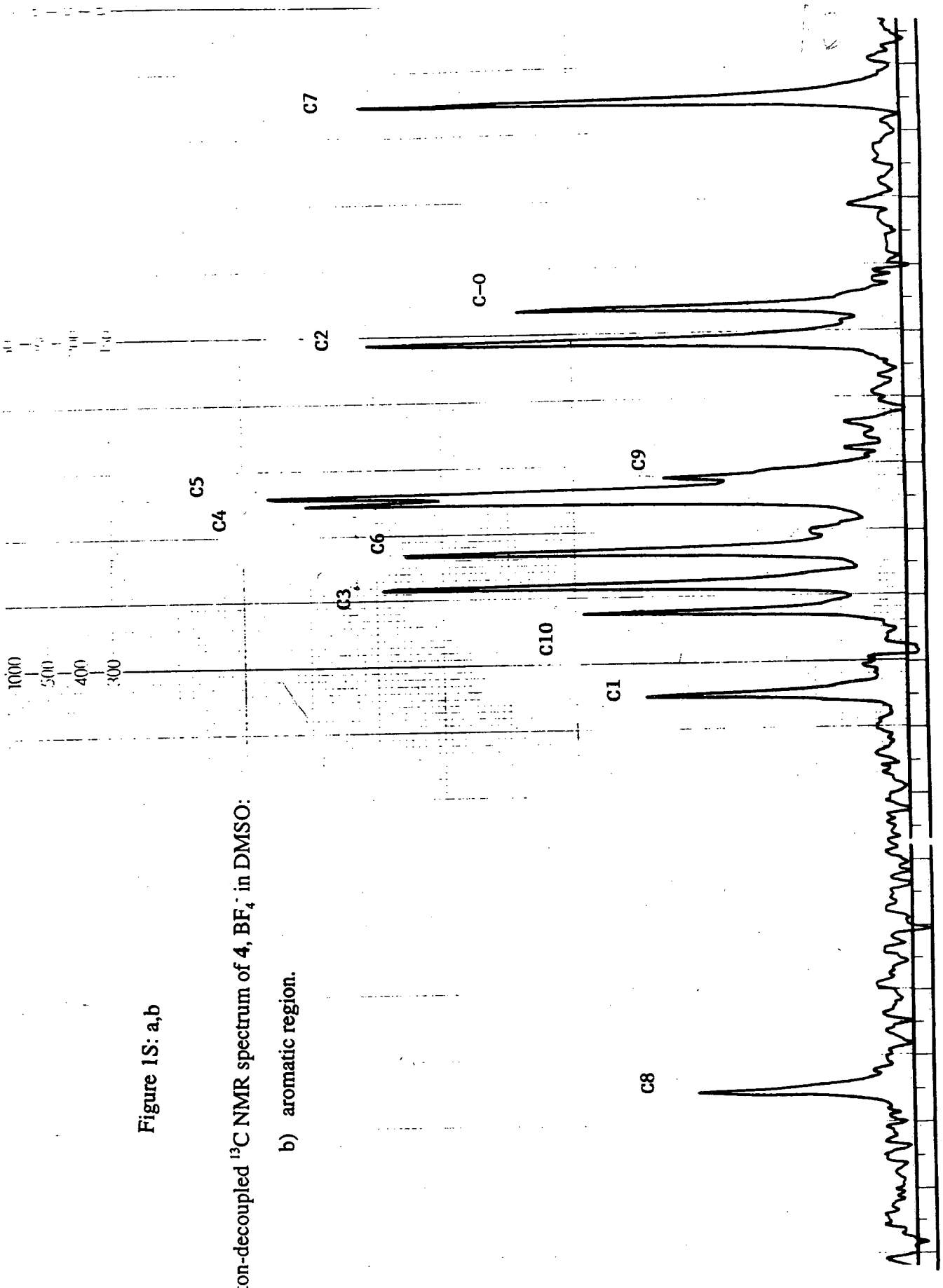


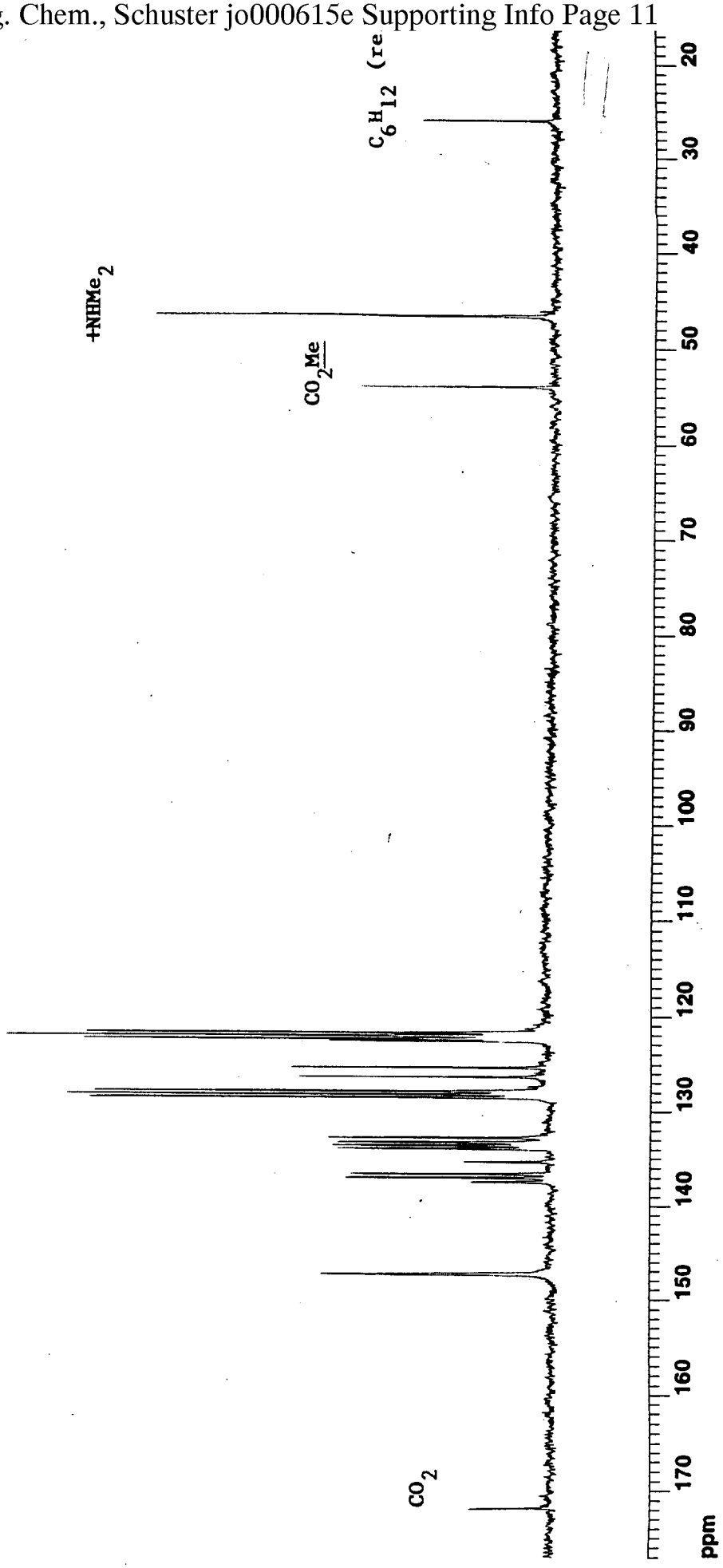
Figure 1S: a,b

Proton-decoupled ^{13}C NMR spectrum of **4**, BF_4^- in DMSO:

b) aromatic region.

Figure 2S: a,b Proton-decoupled ^{13}C NMR Spectrum of **5**, BF_4^- in $PhNO_2$:

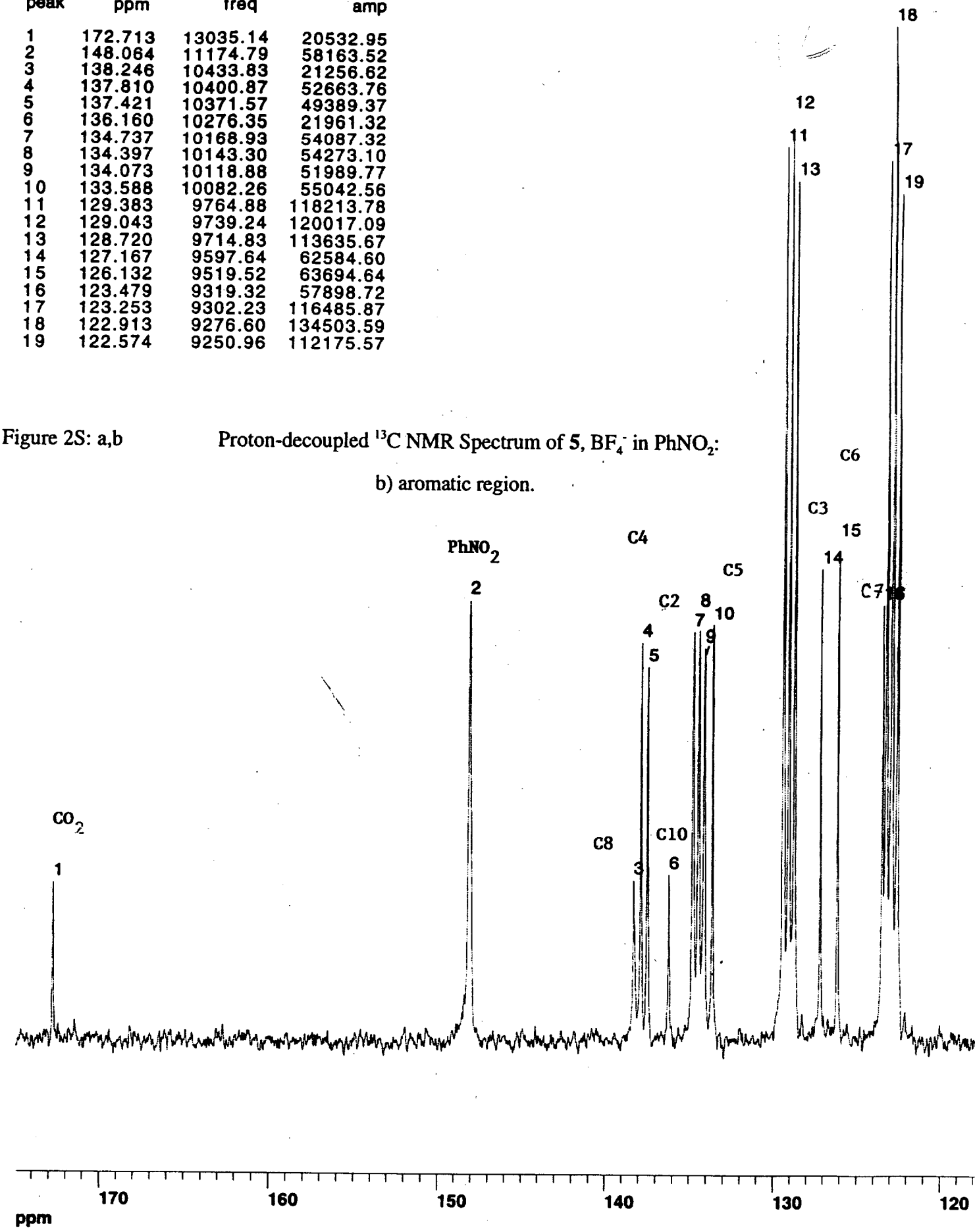
a) Full spectrum.



peak	ppm	freq	amp
1	172.713	13035.14	20532.95
2	148.064	11174.79	58163.52
3	138.246	10433.83	21256.62
4	137.810	10400.87	52663.76
5	137.421	10371.57	49389.37
6	136.160	10276.35	21961.32
7	134.737	10168.93	54087.32
8	134.397	10143.30	54273.10
9	134.073	10118.88	51989.77
10	133.588	10082.26	55042.56
11	129.383	9764.88	118213.78
12	129.043	9739.24	120017.09
13	128.720	9714.83	113635.67
14	127.167	9597.64	62584.60
15	126.132	9519.52	63694.64
16	123.479	9319.32	57898.72
17	123.253	9302.23	116485.87
18	122.913	9276.60	134503.59
19	122.574	9250.96	112175.57

Figure 2S: a,b Proton-decoupled ^{13}C NMR Spectrum of **5**, BF_4^- in $PhNO_2$:

b) aromatic region.



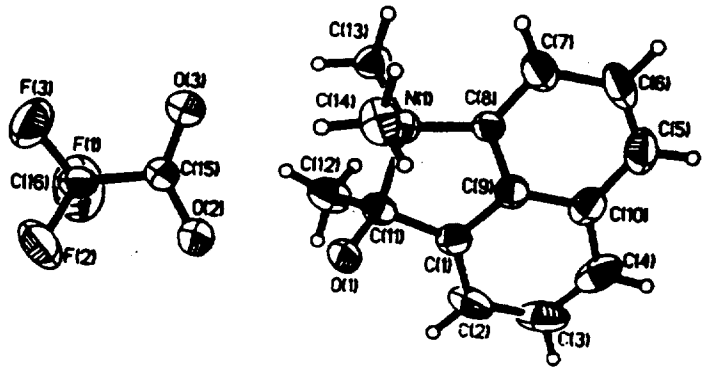


Figure 3S ORTEP Drawing of O-Protonated 3, TFA^-

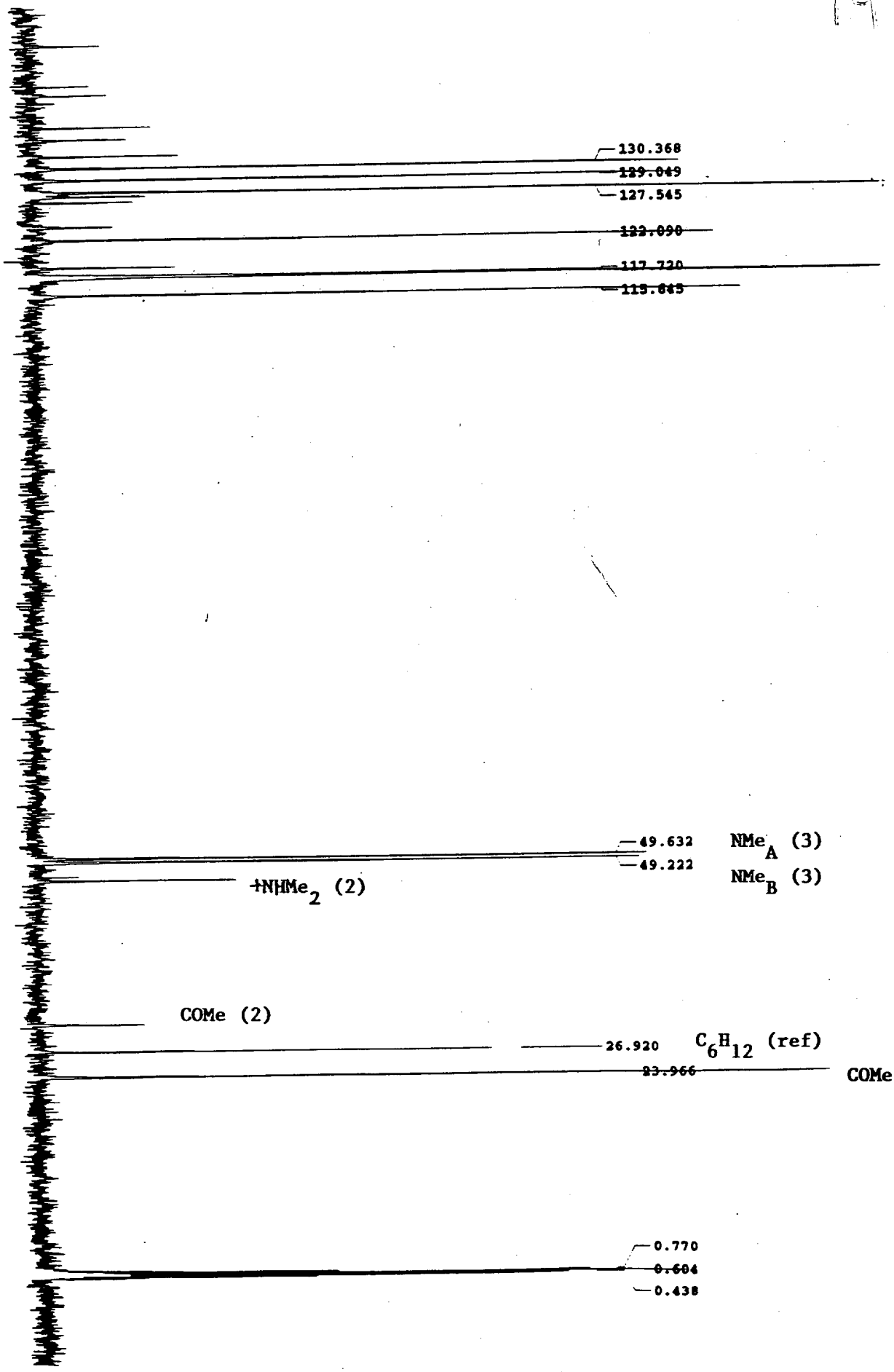


Figure 4S

Proton-decoupled ^{13}C NMR Spectrum of **3**, BF_4^- in CD_3CN