Reaction of Polyhaloalkyl-Substituted Chromones, Pyrones, and Furanones with Salicylaldehydes as a Direct Route to Fused 2*H*-Chromenes

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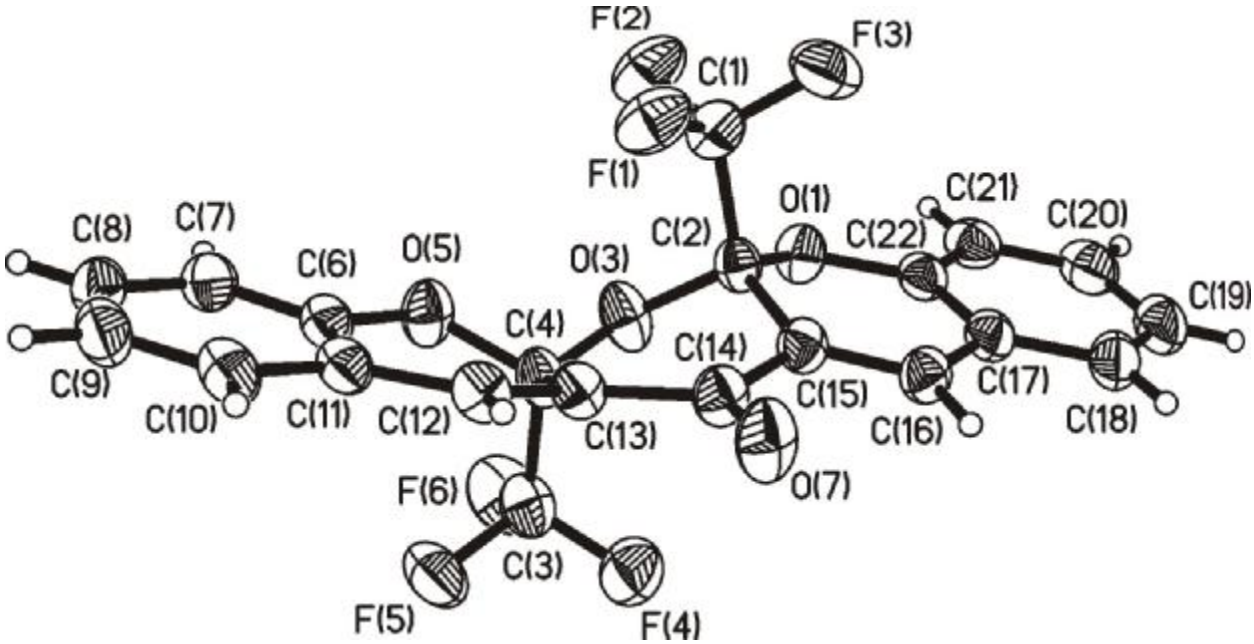
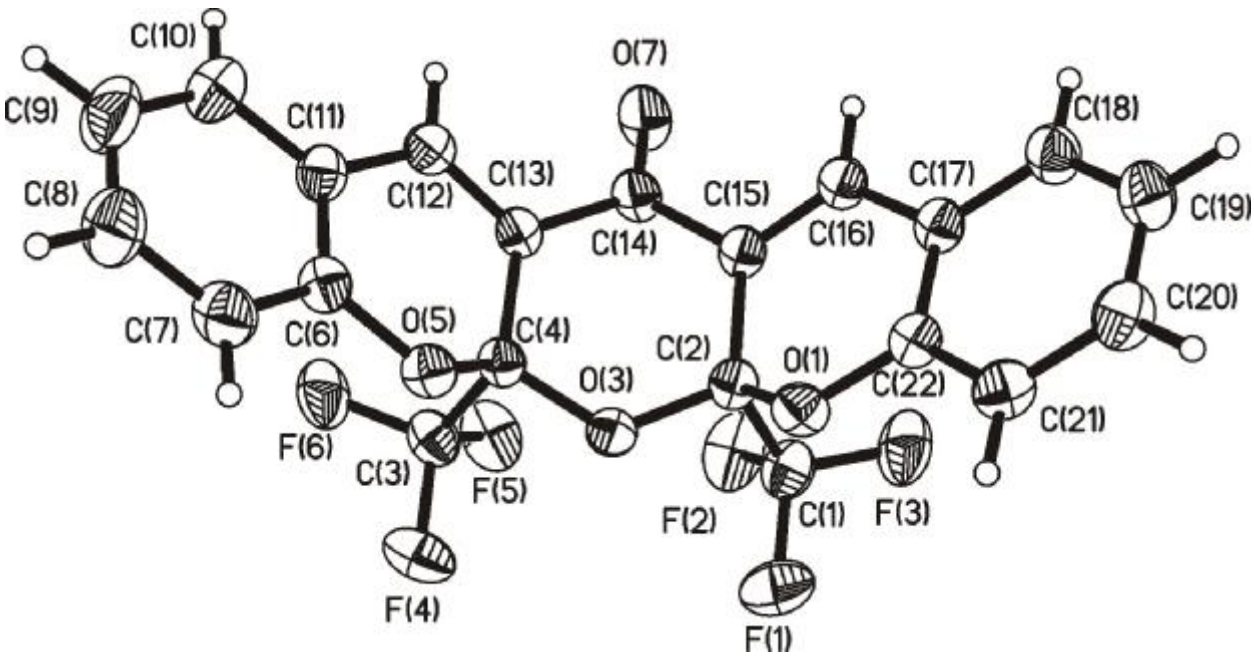
Trans-**6a**



Cis-**6a**



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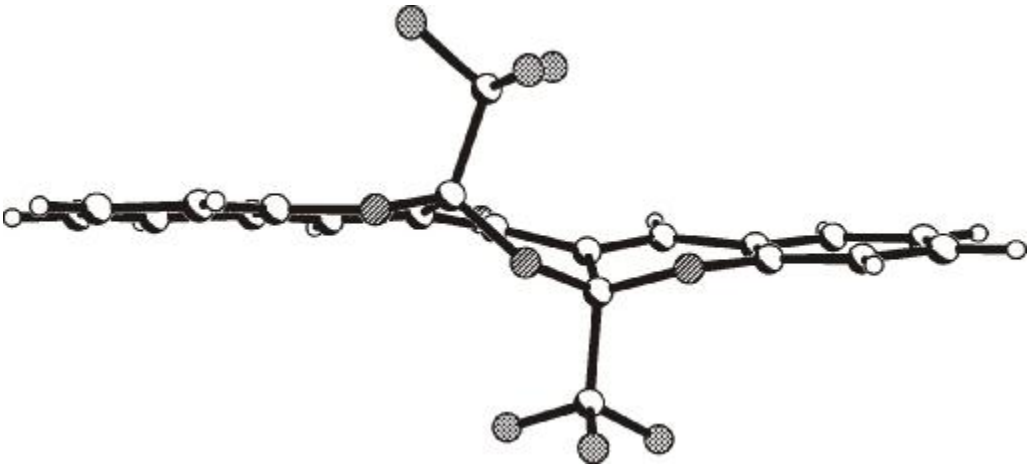

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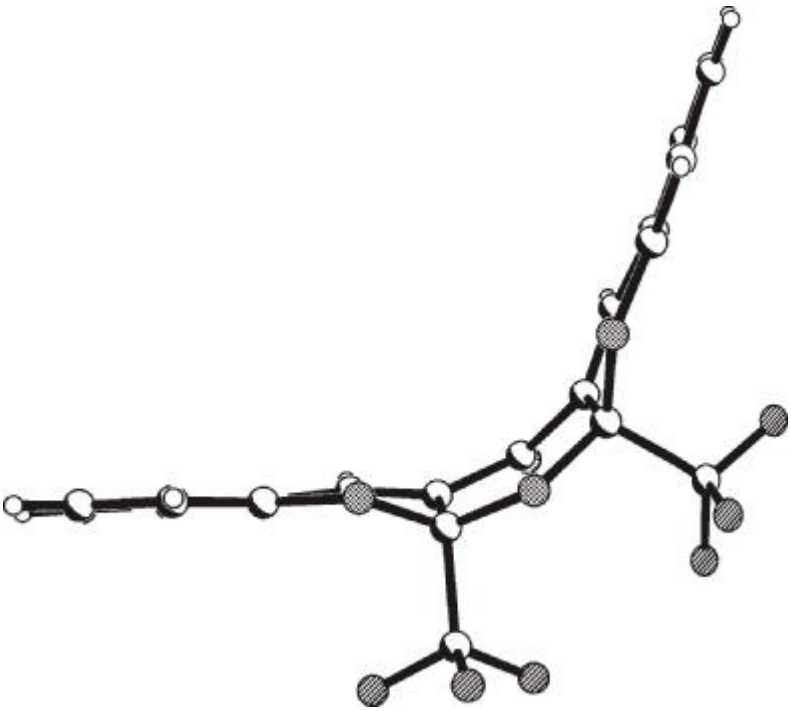


The X-ray studies were performed on a Enraf-Nonius CAD-4 diffractometer (for *trans*- and *cis*-**6a**) with ω/2θ scanning and graphite monochromatic Mo-Kα radiation. The crystal structures were solved by direct methods followed by Fourier synthesis with SHELXS-97 and refined by full-matrix least-squares methods for all non-hydrogen atoms with SHELXL-97 software packages [Sheldrick, G. M. SHELXS-97, SHELXL-97, Programs for Crystal Structure Determination and Refinement, University of Göttingen: Göttingen, Germany, 1997]. The coordinates of H atoms were found experimentally and refined in an isotropic approximation.

Crystallographic Data for *trans*-6a ($C_{21}H_{10}F_6O_4$; M = 440.29, CCDC no. 288999): triclinic, space group $P1$ with a = 7.912(2), b = 9.492(1), c = 12.597(2) Å; a = 102.24(1), b = 99.95(2), g = 96.12(2)°, V = 900.5(3) Å^3; Z = 2, D_{calc} = 1.62 g cm^{-3}; R = 0.036 [$wR(F^2)$ = 0.093] for 2706 reflections with $F_0 > 4s(F_0)$. The number of the parameters in the refinement was 291.

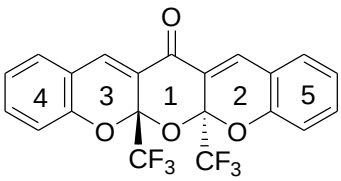
Crystallographic Data for *cis*-6a ($C_{21}H_{10}F_6O_4$; M = 440.29, CCDC no. 289000): monoclinic, space group $P2_1/c$ with a = 11.053(2), b = 12.222(2), c = 13.902(2) Å; b = 97.37(2), V = 1862.5(5) Å^3; Z = 4, D_{calc} = 1.57 g cm^{-3}; R = 0.034 [$wR(F^2)$ = 0.093] for 2545 reflections with $F_0 > 4s(F_0)$.

Table S1. Bond lengths [Å] and angles [°] in compounds *cis*-**6a** and *trans*-**6a**.

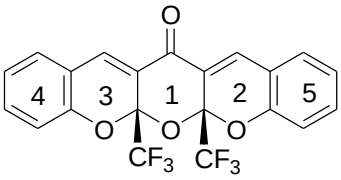
Bond lengths [Å]	*cis*-**6a**	*trans*-**6a**
F(1)-C(1)	1.327(2)	1.326(2)
F(2)-C(1)	1.326(2)	1.327(2)
F(3)-C(1)	1.332(2)	1.331(2)
F(4)-C(3)	1.328(2)	1.333(2)
F(5)-C(3)	1.319(2)	1.311(2)
F(6)-C(3)	1.335(2)	1.335(2)
O(1)-C(22)	1.388(2)	1.386(2)
O(1)-C(2)	1.410(2)	1.402(2)
O(3)-C(4)	1.405(2)	1.409(2)
O(3)-C(2)	1.409(2)	1.414(2)
O(5)-C(6)	1.389(2)	1.384(2)
O(5)-C(4)	1.415(2)	1.402(2)
O(7)-C(14)	1.208(2)	1.220(2)
C(1)-C(2)	1.538(2)	1.527(2)
C(2)-C(15)	1.499(2)	1.504(2)
C(3)-C(4)	1.547(2)	1.534(2)
C(4)-C(13)	1.499(2)	1.507(2)
C(6)-C(7)	1.376(2)	1.371(2)
C(6)-C(11)	1.387(2)	1.396(2)
C(7)-C(8)	1.378(3)	1.383(3)
C(8)-C(9)	1.375(3)	1.369(3)
C(9)-C(10)	1.374(3)	1.373(3)
C(10)-C(11)	1.396(3)	1.397(2)
C(11)-C(12)	1.443(2)	1.438(2)
C(12)-C(13)	1.335(2)	1.337(2)
C(13)-C(14)	1.475(2)	1.473(2)
C(14)-C(15)	1.473(2)	1.473(2)
C(15)-C(16)	1.343(2)	1.332(2)
C(16)-C(17)	1.437(2)	1.441(2)
C(17)-C(22)	1.394(2)	1.383(2)
C(17)-C(18)	1.398(2)	1.400(2)
C(18)-C(19)	1.375(2)	1.375(3)
C(19)-C(20)	1.378(3)	1.381(3)
C(20)-C(21)	1.378(3)	1.378(3)
C(21)-C(22)	1.376(2)	1.378(2)
Angles [°]		
C(22)-O(1)-C(2)	119.3(1)	120.6(1)
C(4)-O(3)-C(2)	124.6(1)	121.4(1)
C(6)-O(5)-C(4)	118.0(1)	119.8(1)
F(2)-C(1)-F(1)	107.6(2)	107.5(1)
F(2)-C(1)-F(3)	107.2(1)	108.0(1)
F(1)-C(1)-F(3)	107.4(1)	107.6(1)
F(2)-C(1)-C(2)	110.8(1)	111.7(1)
F(1)-C(1)-C(2)	112.2(1)	112.1(1)
F(3)-C(1)-C(2)	111.4(1)	109.7(1)
O(3)-C(2)-O(1)	104.9(1)	101.6(1)

O(3)-C(2)-C(15)	116.5(1)	112.3(1)
O(1)-C(2)-C(15)	113.4(1)	115.4(1)
O(3)-C(2)-C(1)	103.5(1)	109.3(1)
O(1)-C(2)-C(1)	106.5(1)	105.1(1)
C(15)-C(2)-C(1)	111.0(1)	112.3(1)
F(5)-C(3)-F(4)	107.5(1)	107.6(1)
F(5)-C(3)-F(6)	107.2(1)	107.9(1)
F(4)-C(3)-F(6)	106.9(1)	106.8(1)
F(5)-C(3)-C(4)	111.6(1)	112.8(1)
F(4)-C(3)-C(4)	111.9(1)	110.6(1)
F(6)-C(3)-C(4)	111.4(1)	110.9(1)
O(3)-C(4)-O(5)	104.9(1)	104.6(1)
O(3)-C(4)-C(13)	116.6(1)	115.7(1)
O(5)-C(4)-C(13)	113.3(1)	113.6(1)
O(3)-C(4)-C(3)	103.7(1)	103.6(1)
O(5)-C(4)-C(3)	106.8(1)	107.6(1)
C(13)-C(4)-C(3)	110.7(1)	110.9(1)
C(7)-C(6)-C(11)	121.8(2)	121.7(2)
C(7)-C(6)-O(5)	117.0(1)	117.5(1)
C(11)-C(6)-O(5)	121.1(1)	120.7(1)
C(6)-C(7)-C(8)	118.9(2)	118.7(2)
C(9)-C(8)-C(7)	120.7(2)	121.0(2)
C(10)-C(9)-C(8)	120.0(2)	120.1(2)
C(9)-C(10)-C(11)	120.7(2)	120.6(2)
C(6)-C(11)-C(10)	117.9(2)	117.8(1)
C(6)-C(11)-C(12)	117.4(1)	117.5(1)
C(10)-C(11)-C(12)	124.4(2)	124.5(1)
C(13)-C(12)-C(11)	121.6(1)	121.9(1)
C(12)-C(13)-C(14)	120.8(1)	123.1(1)
C(12)-C(13)-C(4)	118.1(1)	118.3(1)
C(14)-C(13)-C(4)	120.2(1)	118.5(1)
O(7)-C(14)-C(15)	124.3(1)	123.0(1)
O(7)-C(14)-C(13)	123.2(1)	121.7(1)
C(15)-C(14)-C(13)	111.4(1)	115.2(1)
C(16)-C(15)-C(14)	120.4(1)	123.5(1)
C(16)-C(15)-C(2)	119.1(1)	120.0(1)
C(14)-C(15)-C(2)	119.8(1)	116.5(1)
C(15)-C(16)-C(17)	121.4(1)	121.5(1)
C(22)-C(17)-C(18)	118.4(1)	118.2(2)
C(22)-C(17)-C(16)	117.6(1)	118.2(1)
C(18)-C(17)-C(16)	123.6(1)	123.5(2)
C(19)-C(18)-C(17)	120.3(2)	120.1(2)
C(18)-C(19)-C(20)	119.7(2)	120.1(2)
C(19)-C(20)-C(21)	121.5(2)	121.0(2)
C(22)-C(21)-C(20)	118.6(2)	118.3(2)
C(21)-C(22)-O(1)	117.3(1)	116.2(1)
C(21)-C(22)-C(17)	121.5(1)	122.2(1)
O(1)-C(22)-C(17)	121.1(1)	121.6(1)

Table S2. Selected torsional angles (°)



***trans*-6a**



***cis*-6a**

Cycles	*cis*-**6a**	*trans*-**6a**
1–2	141.4	152.3
1–3	142.0	150.2
1–4	144.9	153.7
1–5	142.5	154.6
2–3	104.9	165.8
2–4	109.3	170.9
2–5	176.4	177.8
3–4	173.3	174.3
3–5	106.8	165.5
4–5	111.5	171.1

Table S3. The deviations of the atoms of the central pyrone ring from the least-squares plane (Å)

Atoms	*cis*-**6a**	*trans*-**6a**
O(3)	-0.08	0.11
C(2)	-0.005	-0.29
C(4)	0.02	0.15
C(13)	0.13	-0.22
C(14)	-0.21	0.04
C(15)	0.15	0.21
O(7)	-0.55	0.09

Experimental Section

^{1}H, ^{19}F and ^{13}C NMR spectra were recorded at 400, 376 and 100 MHz, respectively; chemical shifts are given in δ ppm downfield from tetramethylsilane and hexafluorobenzene as internal standards. IR spectra were measured in KBr or Nujol. Elemental analyses were performed on a microanalyzer. Melting points are uncorrected. The starting polyhaloalkyl-containing chromones, pyrones and furanones were prepared according to the described procedure.[27–29]

9-Chloro-5a-(difluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2b): mp 143–144 ^{o}C; IR (KBr) 1671, 1617, 1602, 1566, 1466, 1423 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (t, 1H, *J* = 54.7 Hz), 7.06–7.12 (m, 3H), 7.37–7.45 (m, 2H), 7.51 (dd, 1H, *J* = 8.8, 2.7 Hz), 7.92 (s, 1H), 7.95 (d, 1H, *J* = 2.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.19 (dd, 1F, *J* = 291.5, 54.9 Hz), 29.38 (dd, 1F, *J* = 291.5, 54.6 Hz). Anal. Calcd for $C_{17}H_9ClF_2O_3$: C, 61.01; H, 2.71. Found: C, 60.93; H, 2.88.

5a-(Difluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2c): mp 126–127 ^{o}C; IR (KBr) 1666, 1610, 1569, 1461 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (t, 1H, *J* = 54.7 Hz), 7.06–7.17 (m, 4H), 7.37–7.43 (m, 2H), 7.58 (ddd, 1H, *J* = 8.4, 7.3, 1.7 Hz), 7.90 (s, 1H), 8.00 (dd, 1H, *J* = 7.8, 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.11 (dd, 1F, *J* = 290.4, 54.8 Hz), 29.07 (dd, 1F, *J* = 290.4, 54.7 Hz). Anal. Calcd for $C_{17}H_{10}F_2O_3$: C, 68.00; H, 3.36. Found: C, 68.07; H, 3.34.

5a-(Difluoromethyl)-9-methyl-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2d): mp 132–133 ^{o}C; IR (KBr) 1673, 1611, 1569, 1488, 1459, 1422 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 5.77 (t, 1H *J* = 54.7 Hz), 7.00–7.10 (m, 3H), 7.36–7.43 (m, 3H), 7.79 (br.d, 1H, *J* = 1.7 Hz), 7.90 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.16 (dd, 1F, *J* = 290.1, 54.8 Hz), 29.08 (dd, 1F, *J* = 290.1, 54.7 Hz). Anal. Calcd for $C_{18}H_{12}F_2O_3$: C, 68.79; H, 3.85. Found: C, 68.60; H, 3.86.

2-Bromo-5a-(difluoromethyl)-9-nitro-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2e): mp 201–202 ^{o}C; IR (KBr) 1677, 1618, 1589, 1557, 1534, 1472, 1442, 1337 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 5.81 (t, 1H, *J* = 54.7 Hz), 7.00–7.03 (m, 1H), 7.27 (d, 1H, *J* = 9.1 Hz), 7.53–7.57 (m, 2H), 7.90 (s, 1H), 8.44 (dd, 1H, *J* = 9.1, 2.8 Hz), 8.89 (d, 1H, *J* = 2.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.29 (dd, 1F, *J* = 294.2, 54.9 Hz), 29.84 (dd, 1F, *J* = 294.2, 54.5 Hz). Anal. Calcd for $C_{17}H_8BrF_2NO_5$: C, 48.14; H, 1.90; N, 3.30. Found: C, 48.11; H, 1.97; N, 3.46.

2-Bromo-9-chloro-5a-(difluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2f): mp 159–160 °C; IR (KBr) 1677, 1620, 1601, 1560, 1465, 1430 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (t, 1H, *J* = 54.7 Hz), 6.97–7.00 (m, 1H), 7.08 (d, 1H, *J* = 8.8 Hz), 7.48–7.54 (m, 3H), 7.83 (s, 1H), 7.95 (d, 1H, *J* = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.54 (dd, 1F, *J* = 292.7, 54.8 Hz), 29.70 (dd, 1F, *J* = 292.7, 54.7 Hz). Anal. Calcd for $C_{17}H_8BrClF_2O_3$: C, 49.37; H, 1.95. Found: C, 49.38; H, 1.74.

9-Chloro-5a-(difluoromethyl)-2-methoxy-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2g): mp 174–175 °C; IR (KBr) 1672, 1623, 1573, 1489, 1468, 1420 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 5.75 (t, 1H, *J* = 54.7 Hz), 6.87 (d, 1H, *J* = 2.8 Hz), 6.98 (dd, 1H, *J* = 8.9, 2.8 Hz), 7.02 (d, 1H, *J* = 8.9 Hz), 7.07 (d, 1H, *J* = 8.8 Hz), 7.51 (dd, 1H, *J* = 8.8, 2.7 Hz), 7.88 (s, 1H), 7.95 (d, 1H, *J* = 2.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.29 (dd, 1F, *J* = 291.4, 54.9 Hz), 29.38 (dd, 1F, *J* = 291.4, 54.5 Hz). Anal. Calcd for $C_{18}H_{11}ClF_2O_4$: C, 59.28; H, 3.04. Found: C, 59.21; H, 3.00.

5a-(Difluoromethyl)-2-methoxy-9-methyl-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2h): mp 164–165 °C; IR (KBr) 1672, 1619, 1574, 1489, 1453, 1422 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 3.81 (s, 3H), 5.75 (t, 1H, *J* = 54.7 Hz), 6.86 (d, 1H, *J* = 2.9 Hz), 6.96 (dd, 1H, *J* = 8.9, 2.9 Hz), 7.01 (d, 1H, *J* = 8.4 Hz), 7.02 (d, 1H, *J* = 8.9 Hz), 7.38 (br.dd, 1H, *J* = 8.4, 2.0 Hz), 7.78 (br.d, 1H, *J* = 2.0 Hz), 7.85 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.27 (dd, 1F, *J* = 290.1, 54.8 Hz), 29.10 (dd, 1F, *J* = 290.1, 54.6 Hz). Anal. Calcd for $C_{19}H_{14}F_2O_4$: C, 66.28; H, 4.10. Found: C, 66.30; H, 3.96.

9-Nitro-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2i): mp 185–186 °C; IR (KBr) 1683, 1622, 1606, 1592, 1569, 1527, 1472, 1440, 1351 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.15–7.20 (m, 2H), 7.32 (d, 1H, *J* = 9.1 Hz), 7.45–7.54 (m, 2H), 8.05 (s, 1H), 8.46 (dd, 1H, *J* = 9.1, 2.8 Hz), 8.91 (d, 1H, *J* = 2.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 75.82 (s). Anal. Calcd for $C_{17}H_8F_3NO_5$: C, 56.21; H, 2.22; N, 3.86. Found: C, 56.27; H, 2.44; N, 3.88.

9-Methyl-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2k): mp 120–121 ^{o}C; IR (KBr) 1678, 1624, 1608, 1570, 1487, 1459, 1423 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.05–7.16 (m, 3H), 7.39–7.47 (m, 3H), 7.80 (br.d, 1H, *J* = 1.8 Hz), 7.95 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 76.08 (s). Anal. Calcd for $C_{18}H_{11}F_3O_3$: C, 65.07; H, 3.34. Found: C, 64.95; H, 3.39.

2-Bromo-9-nitro-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2l): mp 213–214 ^{o}C; IR (KBr) 1677, 1625, 1589, 1560, 1534, 1472, 1443, 1351 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06–7.10 (m, 1H), 7.33 (d, 1H, *J* = 9.1 Hz), 7.58–7.63 (m, 2H), 7.97 (s, 1H), 8.48 (dd, 1H, *J* = 9.1, 2.8 Hz), 8.90 (d, 1H, *J* = 2.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 75.99 (s). Anal. Calcd for $C_{17}H_7BrF_3NO_5$: C, 46.18; H, 1.60; N, 3.17. Found: C, 46.20; H, 1.42; N, 3.04.

2-Bromo-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2m): mp 196–197 ^{o}C; IR (KBr) 1673, 1615, 1558, 1462 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03–7.07 (m, 1H), 7.15–7.22 (m, 2H), 7.52–7.57 (m, 2H), 7.63 (ddd, 1H, *J* = 8.5, 7.0, 1.6 Hz), 7.88 (s, 1H), 8.02 (dd, 1H, *J* = 7.8, 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 76.12 (s). Anal. Calcd for $C_{17}H_8BrF_3O_3$: C, 51.41; H, 2.03. Found: C, 51.42; H, 2.12.

2-Bromo-9-methyl-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2n): mp 198–199 ^{o}C; IR (KBr) 1675, 1625, 1561, 1488, 1475, 1428 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.03–7.07 (m, 2H), 7.41–7.53 (m, 3H), 7.80 (br.s, 1H), 7.86 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 76.27 (s). Anal. Calcd for $C_{18}H_{10}BrF_3O_3$: C, 52.58; H, 2.45. Found: C, 52.53; H, 2.26.

2-Methoxy-9-nitro-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2o): mp 181–182 ^{o}C; IR (KBr) 1674, 1623, 1575, 1527, 1490, 1471, 1440, 1347 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.93 (d, 1H, *J* = 2.8 Hz), 7.06 (dd, 1H, *J* = 9.0, 2.8 Hz), 7.11 (d, 1H, *J* = 9.0

Hz), 7.32 (d, 1H, *J* = 9.1 Hz), 8.01 (s, 1H), 8.46 (dd, 1H, *J* = 9.1, 2.8 Hz), 8.90 (d, 1H, *J* = 2.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 75.88 (s). Anal. Calcd for $C_{18}H_{10}F_3NO_6$: C, 54.97; H, 2.56; N, 3.56. Found: C, 54.98; H, 2.60; N, 3.55.

2-Methoxy-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2p): mp 170–171 ^{o}C; IR (KBr) 1670, 1617, 1570, 1490, 1462 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.90 (d, 1H, *J* = 2.9 Hz), 7.00 (dd, 1H, *J* = 8.9, 2.9 Hz), 7.08 (d, 1H, *J* = 8.9 Hz), 7.15–7.20 (m, 2H), 7.60 (ddd, 1H, *J* = 8.4, 7.3, 1.7 Hz), 7.92 (s, 1H), 8.01 (dd, 1H, *J* = 7.8, 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 76.06 (s). Anal. Calcd for $C_{18}H_{11}F_3O_4$: C, 62.08; H, 3.18. Found: C, 61.93; H, 3.11.

2-Methoxy-9-methyl-5a-(trifluoromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2q): mp 194–195 ^{o}C; IR (KBr) 1671, 1619, 1573, 1488, 1463, 1418 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.82 (s, 3H), 6.89 (d, 1H, *J* = 2.9 Hz), 6.99 (dd, 1H, *J* = 8.9, 2.8 Hz), 7.04–7.09 (m, 2H), 7.40 (br.dd, 1H, *J* = 8.5, 2.0 Hz), 7.80 (br.s, 1H), 7.91 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 76.20 (s). Anal. Calcd for $C_{19}H_{13}F_3O_4$: C, 62.99; H, 3.62. Found: C, 63.06; H, 3.63.

5a-(1,1,2,2-Tetrafluoroethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2s): mp 119–120 ^{o}C; IR (KBr) 1679, 1630, 1609, 1572, 1487, 1465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (tt, 1H, *J* = 52.4, 6.0 Hz), 7.06–7.21 (m, 4H), 7.40–7.46 (m, 2H), 7.60 (ddd, 1H, *J* = 8.5, 7.2, 1.7 Hz), 7.96 (s, 1H), 8.02 (dd, 1H, *J* = 7.8, 1.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 25.21 (dddd, 1F, *J* = 304.4, 52.6, 8.7, 5.0 Hz), 26.13 (dddd, 1F, *J* = 304.4, 52.6, 8.7, 5.0 Hz), 31.24 (dm, 1F, *J* = 280.4 Hz), 33.62 (ddt, 1F, *J* = 280.4, 8.7, 5.2 Hz). Anal. Calcd for $C_{18}H_{10}F_4O_3$: C, 61.72; H, 2.88. Found: C, 61.59; H, 2.63.

9-Chloro-5a-(perfluoroethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2t): mp 150–151 ^{o}C; IR (KBr) 1676, 1624, 1608, 1569, 1470, 1424 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–7.17 (m, 3H), 7.41–7.49 (m, 2H), 7.54 (dd, 1H, *J* = 8.8, 2.7 Hz), 7.98 (d, 1H, *J* = 2.7 Hz), 8.02 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 35.65 (d, 1F, *J* = 288.4 Hz), 37.50 (d, 1F, *J* = 288.4 Hz), 82.52 (s, 3F). Anal. Calcd for $C_{18}H_8ClF_5O_3$: C, 53.69; H, 2.00. Found: C, 53.45; H, 1.96.

2-Bromo-9-chloro-5a-(perfluoroethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2u): mp 166–167 °C; IR (KBr) 1678, 1624, 1606, 1560, 1469, 1430 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99–7.03 (m, 1H), 7.09 (d, 1H, *J* = 8.8 Hz), 7.53–7.58 (m, 3H), 7.93 (s, 1H), 7.97 (d, 1H, *J* = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 35.88 (d, 1F, *J* = 288.9 Hz), 37.71 (d, 1F, *J* = 288.9 Hz), 82.53 (s, 3F). Anal. Calcd for $C_{18}H_7BrClF_5O_3$: C, 44.89; H, 1.47. Found: C, 44.70; H, 1.26.

9-Chloro-5a-(trichloromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2v): mp 144–145 °C; IR (KBr) 1676, 1620, 1605, 1569, 1468, 1422 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09–7.19 (m, 3H), 7.42–7.54 (m, 3H), 7.96 (d, 1H, *J* = 2.7 Hz), 8.07 (s, 1H). Anal. Calcd for $C_{17}H_8Cl_4O_3$: C, 50.79; H, 2.01. Found: C, 50.65; H, 2.00.

5a-(Trichloromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2w): mp 165–166 °C; IR (KBr) 1675, 1623, 1607, 1569, 1463 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.00–7.19 (m, 4H), 7.41–7.48 (m, 2H), 7.58 (ddd, 1H, *J* = 8.5, 7.3, 1.7 Hz), 8.00 (dd, 1H, *J* = 8.0, 1.7 Hz), 8.04 (s, 1H). Anal. Calcd for $C_{17}H_9Cl_3O_3$: C, 55.54; H, 2.47. Found: C, 55.31; H, 2.37.

9-Chloro-2-methoxy-5a-(trichloromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2x): mp 205–206 °C; IR (KBr) 1677, 1625, 1606, 1577, 1489, 1467, 1419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.91 (d, 1H, *J* = 2.9 Hz), 7.04 (dd, 1H, *J* = 8.9, 2.9 Hz), 7.09–7.12 (m, 2H), 7.51 (dd, 1H, *J* = 8.8, 2.6 Hz), 7.95 (d, 1H, *J* = 2.6 Hz), 8.02 (s, 1H). Anal. Calcd for $C_{18}H_{10}Cl_4O_4$: C, 50.04; H, 2.33. Found: C, 49.91; H, 2.22.

2-Methoxy-5a-(trichloromethyl)-5a*H*,11*H*-chromeno[2,3-*b*]chromen-11-one (2y): mp 164–165 °C; IR (KBr) 1676, 1624, 1578, 1490, 1462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.90 (d, 1H, *J* = 2.9 Hz), 7.02 (dd, 1H, *J* = 8.9, 2.9 Hz), 7.10 (d, 1H, *J* = 8.9 Hz), 7.12–7.17 (m, 2H), 7.58 (ddd, 1H, *J* = 8.5, 7.3, 1.7 Hz), 7.99 (dd, 1H, *J* = 7.8, 1.7 Hz), 8.00 (s, 1H). Found: C, 54.27; H, 2.68. Anal. Calcd for $C_{18}H_{11}Cl_3O_4$: C, 54.37; H, 2.79.

2,2-Dimethyl-10a-(trifluoromethyl)-2,3-dihydro-4*H*,10a*H*-pyrano[2,3-*b*]chromen-4-one (3a): mp 137–138 °C; IR (KBr) 1698, 1619, 1606, 1569, 1482, 1458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ

1.45 (s, 3H), 1.51 (s, 3H), 2.53 (d, 1H, *J* = 17.6 Hz), 2.75 (d, 1H, *J* = 17.6 Hz), 7.02–7.07 (m, 2H), 7.34 (dd, 1H, *J* = 7.8, 1.7 Hz), 7.38 (ddd, 1H, *J* = 8.3, 7.4, 1.7 Hz), 7.76 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 74.50 (s). Anal. Calcd for $C_{15}H_{13}F_3O_3$: C, 60.41; H, 4.39. Found: C, 60.59; H, 4.28.

7-Bromo-2,2-dimethyl-10a-(trifluoromethyl)-2,3-dihydro-4*H*,10a*H*-pyrano[2,3-*b*]chromen-4-one (3b): mp 118–119 °C; IR (KBr) 1700, 1618, 1558, 1470 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 3H), 1.51 (s, 3H), 2.55 (d, 1H, *J* = 17.7 Hz), 2.75 (d, 1H, *J* = 17.7 Hz), 6.94 (m, 1H), 7.44–7.48 (m, 2H), 7.66 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 74.64 (s). Anal. Calcd for $C_{15}H_{12}BrF_3O_3$: C, 47.77; H, 3.21. Found: C, 47.94; H, 3.19.

10a-(Difluoromethyl)-2,2-dimethyl-2,3-dihydro-4*H*,10a*H*-pyrano[2,3-*b*]chromen-4-one (3d): mp 85–86 °C; IR (KBr) 1694, 1619, 1603, 1568, 1480, 1456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 3H), 1.48 (s, 3H), 2.49 (d, 1H, *J* = 17.5 Hz), 2.72 (br.d, 1H, *J* = 17.5 Hz), 5.61 (t, 1H, *J* = 55.4 Hz), 6.98–7.03 (m, 2H), 7.30–7.37 (m, 2H), 7.71 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 25.12 (ddd, 1F, *J* = 282.4, 55.3, 1.3 Hz), 27.81 (dd, 1F, *J* = 282.4, 55.6 Hz). Anal. Calcd for $C_{15}H_{14}F_2O_3$: C, 64.28; H, 5.03. Found: C, 64.02; H, 4.88.

9,9-Dimethyl-7a-(trifluoromethyl)-9,10-dihydro-7a*H*,11*H*-benzo[*f*]pyrano[2,3-*b*]chromen-11-one (3e): mp 183–184 °C; IR (KBr) 1689, 1609, 1559, 1458 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 3H), 1.54 (s, 3H), 2.58 (d, 1H, *J* = 17.4 Hz), 2.79 (d, 1H, *J* = 17.4 Hz), 7.25 (d, 1H, *J* = 8.9 Hz), 7.47 (ddd, 1H, *J* = 8.1, 7.0, 1.0 Hz), 7.63 (ddd, 1H, *J* = 8.3, 7.0, 1.3 Hz), 7.82 (d, 1H, *J* = 8.1 Hz), 7.91 (d, 1H, *J* = 8.9 Hz), 8.12 (d, 1H, *J* = 8.3 Hz), 8.51 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 74.06 (s). Anal. Calcd for $C_{19}H_{15}F_3O_3$: C, 65.52; H, 4.34. Found: C, 65.23; H, 4.30.

9a-(Difluoromethyl)-2,2-dimethyl-9a*H*-furo[2,3-*b*]chromen-3(2*H*)-one (3f): mp 76–77 °C; IR (KBr) 1713, 1629, 1606, 1565, 1477, 1456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 3H), 1.50 (s, 3H), 5.71 (t, 1H, *J* = 55.0 Hz), 7.04–7.09 (m, 2H), 7.37–7.42 (m, 2H), 7.56 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 24.86 (dd, 1F, *J* = 287.6, 54.9 Hz), 28.93 (dd, 1F, *J* = 287.6, 55.1 Hz). Anal. Calcd for $C_{14}H_{12}F_2O_3$: C, 63.16; H, 4.54. Found: C, 63.28; H, 4.39.

9a-(Trichloromethyl)-9a*H*-furo[2,3-*b*]chromen-3(2*H*)-one-2-spirocyclohexane (3h): mp 140–141 °C; IR (KBr) 1726, 1637, 1605, 1566, 1452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.3–2.1 (m, 10H), 7.06 (td, 1H, *J* = 7.5, 1.0 Hz), 7.15 (d, 1H, *J* = 8.2 Hz), 7.38–7.45 (m, 2H), 7.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 24.7, 31.0, 36.3, 87.8, 103.3, 104.2, 116.1, 119.3, 121.3, 122.8, 130.4, 133.8, 134.4, 154.7, 199.5. Anal. Calcd for $C_{17}H_{15}Cl_3O_3$: C, 54.64; H, 4.05. Found: C, 54.65; H, 3.76.

***trans*-5a,6a-Bis(difluoromethyl)-5a*H*,6a*H*,13*H*-chromeno[3',2':5,6]pyrano[2,3-*b*]chromen-13-one (*trans*-6b):** yield 73%; mp 212–213 °C; IR (Nujol) 1679, 1628, 1605, 1569 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (t, 2H, *J* = 55.0 Hz), 7.05–7.09 (m, 4H), 7.34–7.42 (m, 4H), 7.83 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.13 (dd, 2F, *J* = 286.1, 55.0 Hz), 28.66 (dd, 2F, *J* = 286.1, 55.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.7 (t, *J* = 28.0 Hz), 113.1 (t, *J* = 254.0 Hz), 115.9, 118.1, 119.4 (d, *J* = 0.7 Hz), 123.1, 130.5, 133.9, 136.1, 152.5 (d, *J* = 1.0 Hz), 180.0. Anal. Calcd for $C_{21}H_{12}F_4O_4$: C, 62.38; H, 2.99; F, 18.80. Found: C, 62.41; H, 2.93; F, 18.77.

***cis*-5a,6a-Bis(difluoromethyl)-5a*H*,6a*H*,13*H*-chromeno[3',2':5,6]pyrano[2,3-*b*]chromen-13-one (*cis*-6b):** yield 53%; mp 166–167 °C; IR (Nujol) 1679, 1618, 1605, 1567 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.81 (t, 2H, *J* = 54.4 Hz), 7.05–7.10 (m, 4H), 7.33–7.40 (m, 4H), 7.67 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 26.98 (ddm, 2F, *J* = 285.0, 54.2 Hz), 28.20 (ddm, 2F, *J* = 285.0, 54.2 Hz). Anal. Calcd for $C_{21}H_{12}F_4O_4$: C, 62.38; H, 2.99; F, 18.80. Found: C, 62.60; H, 2.91; F, 18.87.

***trans*-5a,6a-Bis(1,1,2,2-tetrafluoroethyl)-5a*H*,6a*H*,13*H*-chromeno[3',2':5,6]pyrano[2,3-*b*]-chromen-13-one (*trans*-6c):** yield 68%; mp 186–187 °C; IR (Nujol) 1674, 1624, 1607, 1569 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.28 (tdd, 2H, *J* = 52.7, 9.8, 2.5 Hz), 7.04–7.12 (m, 4H), 7.38–7.44 (m, 4H), 7.91 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 23.28 (dddd, 2F, *J* = 305.0, 52.6, 10.5, 8.0 Hz), 27.77 (ddd, 2F, *J* = 305.0, 52.4, 11.3 Hz), 28.40 (dm, 2F, *J* = 274.8 Hz), 33.10 (ddd, 2F, *J* =

274.8, 10.6, 2.5 Hz). Anal. Calcd for $C_{23}H_{12}F_8O_4$: C, 54.77; H, 2.40; F, 30.14. Found: C, 54.93; H, 2.56; F, 30.01.

***trans*-2,10-Dibromo-5a,6a-bis(trifluoromethyl)-5a*H*,6a*H*,13*H*-chromeno[3',2':5,6]pyrano[2,3-*b*]chromen-13-one (*trans*-6d):** yield 58%; mp >240 °C (subl.); IR (Nujol) 1678, 1621, 1599, 1559 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.03–7.05 (m, 2H), 7.52–7.56 (m, 4H), 7.83 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 75.78 (s). Anal. Calcd for $C_{21}H_8Br_2F_6O_4$: C, 42.17; H, 1.35; F, 19.06. Found: C, 42.21; H, 1.29; F, 19.14.

***cis*-2,10-Dibromo-5a,6a-bis(trifluoromethyl)-5a*H*,6a*H*,13*H*-chromeno[3',2':5,6]pyrano[2,3-*b*]chromen-13-one (*cis*-6d):** yield 30%; mp 230–232 °C (subl.); IR (Nujol) 1679, 1615, 1602, 1555 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.02–7.04 (m, 2H), 7.49–7.52 (m, 4H), 7.56 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 76.48 (s). Anal. Calcd for $C_{21}H_8Br_2F_6O_4$: C, 42.17; H, 1.35; F, 19.06. Found: C, 42.28; H, 1.14; F, 18.97.

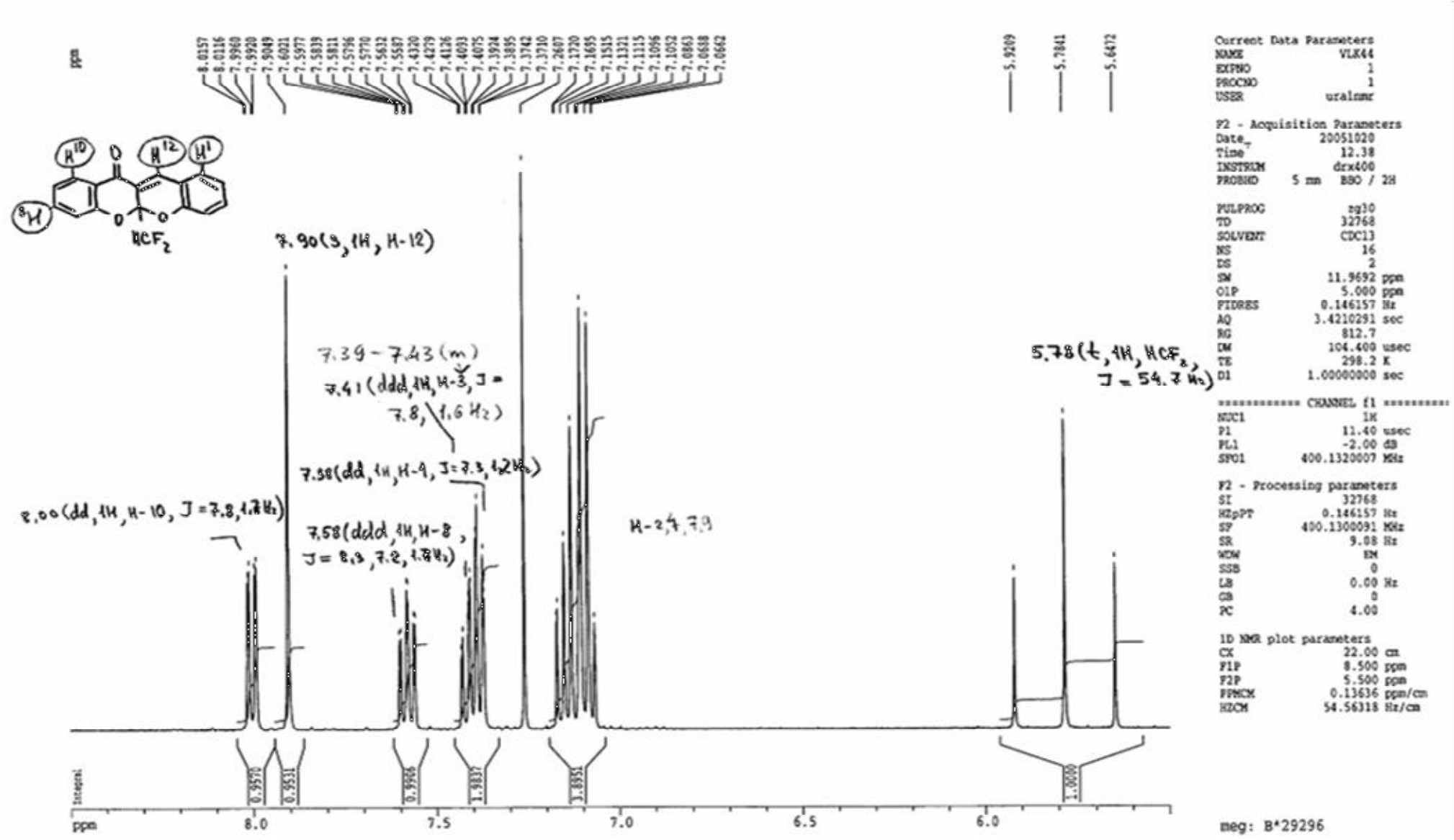
***trans*-2,10-Dibromo-5a,6a-bis(difluoromethyl)-5a*H*,6a*H*,13*H*-chromeno[3',2':5,6]pyrano[2,3-*b*]chromen-13-one (*trans*-6e):** yield 82%; mp >240 °C (subl.); IR (Nujol) 1677, 1618, 1605, 1555 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (t, 2H, J = 54.9 Hz), 6.94–6.96 (m, 2H), 7.48–7.50 (m, 4H), 7.74 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.22 (dd, 2F, J = 287.6, 54.9 Hz), 29.02 (dd, 2F, J = 287.6, 54.9 Hz). Anal. Calcd for $C_{21}H_{10}Br_2F_4O_4$: C, 44.87; H, 1.79; F, 13.52. Found: C, 44.96; H, 1.63; F, 13.58.

***trans*-5a-(Difluoromethyl)-6a-(trifluoromethyl)-5a*H*,6a*H*,13*H*-chromeno[3',2':5,6]pyrano[2,3-*b*]chromen-13-one (*trans*-6f):** yield 70%; mp 198–199 °C; IR (Nujol) 1690, 1634, 1606, 1570 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.81 (t, 1H, J = 55.0 Hz), 7.06–7.12 (m, 4H), 7.35–7.45 (m, 4H), 7.86 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 27.16 (dd, 1F, J = 286.7, 55.0 Hz), 28.95 (dd, 1F, J = 286.7, 55.0 Hz), 75.62 (s, 3F). Found: C, 59.61; H, 2.66; F, 22.36. Anal. Calcd for $C_{21}H_{11}F_5O_4$: C, 59.73; H, 2.63; F, 22.49.

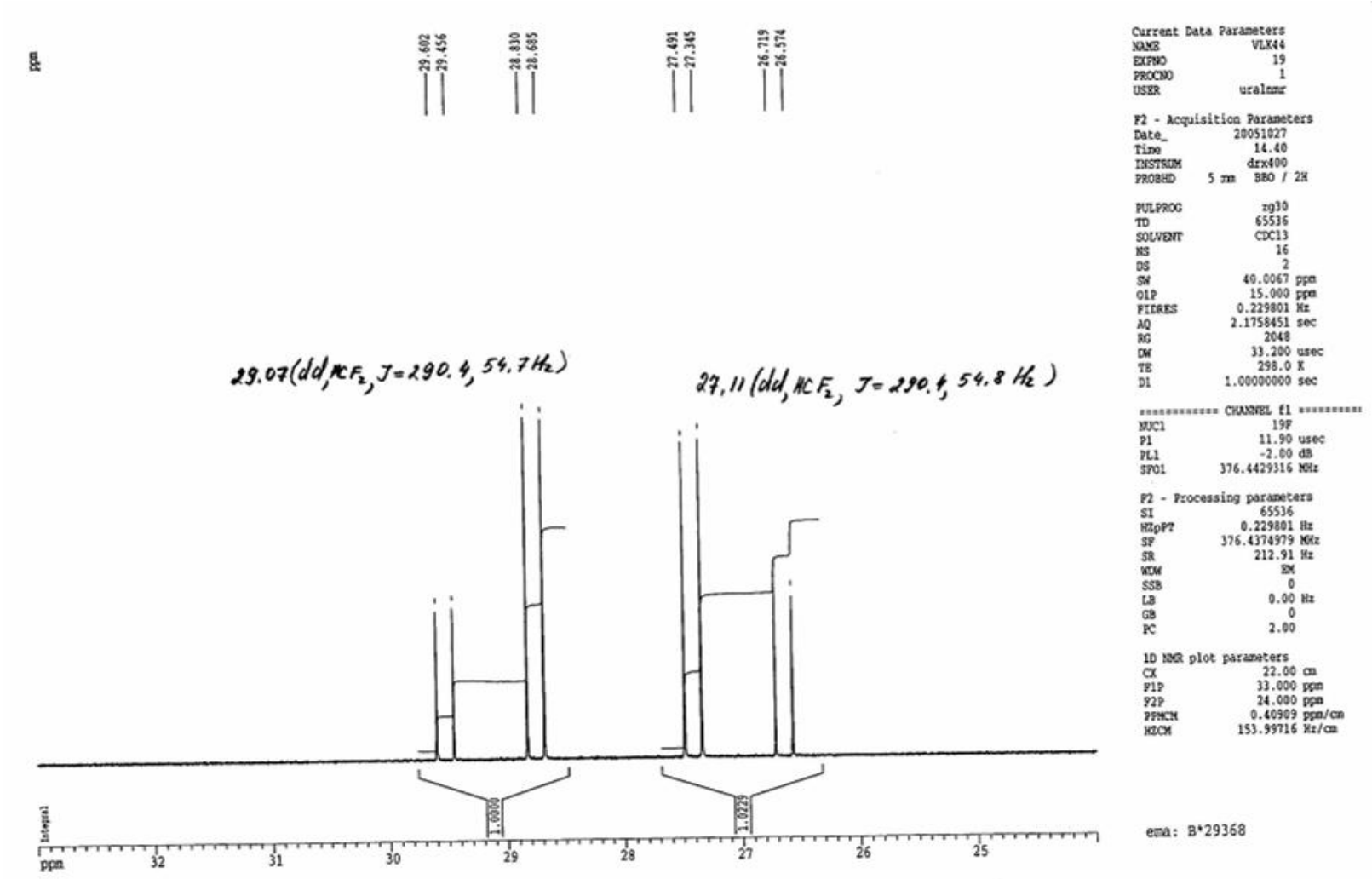
2,10a-Bis(difluoromethyl)-2-hydroxy-2,3-dihydro-4*H*,10a*H*-pyrano[2,3-*b*]chromen-4-one (8). A solution of salicylaldehyde (1.0 mmol) and piperidine (2.0 mmol) in anhydrous benzene (10 mL) in the presence of a catalytic amount of *p*-toluene sulfonic acid (5 mol %) was refluxed for 2 h. The reaction mixture was concentrated and, after addition of *p*-TsOH (1.0 mmol) and 2,6-bis(difluoromethyl)-4*H*-pyran-4-one (2.0 mmol), was heated under reflux for 4 h. Then the resulting mixture was poured into 5% solution HCl (15 mL) and stirred for 15 min. After removal of the solvent, the crystalline material was isolated by filtration, dried, and recrystallized twice from CCl_4 to give the title compound **8** as light-yellow powder. Yield 40%; mp 146–148 ^{o}C; IR (Nujol) 3276, 1691, 1622, 1607, 1568 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (dd, 1H, *J* = 18.0 Hz), 2.83 (dd, 1H, *J* = 18.0 Hz), 3.58 (t, 1H, *J* = 1.6 Hz), 5.69 (t, 1H, *J* = 55.2 Hz), 5.76 (t, 1H, *J* = 55.0 Hz), 6.98–7.05 (m, 2H), 7.32–7.36 (m, 2H), 7.73 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3/C_6F_6$) δ 25.06 (br.dd, 1F, *J* = 286.2, 55.2 Hz), 27.41 (dd, 1F, *J* = 286.2, 55.2 Hz), 25.45 (br.dd, 1F, *J* = 288.0, *J* = 55.0 Hz), 28.06 (dd, 1F, *J* = 288.0, *J* = 55.0 Hz). Anal. Calcd for $C_{14}H_{10}F_4O_4$: C, 52.84; H, 3.17; F, 23.88. Found: C, 52.94; H, 3.23; F, 23.84.

Conversion of 8 to the monoadduct 7b. A solution of **8** (95 mg, 0.3 mmol) in dry benzene (15 mL) in the presence of molecular sieves (3Å, 1 g) and *p*-TsOH (10 mg, 0.06 mmol) was refluxed for 3 h. The reaction mixture was evaporated under reduced pressure, and the resulting precipitate was purified by chromatography (silica gel, CH_2Cl_2). After removal of the solvent, the crystalline material was collected by filtration to give product **7b** as light-yellow crystals, yield 58 mg (64%), mp 131–132 ^{o}C.

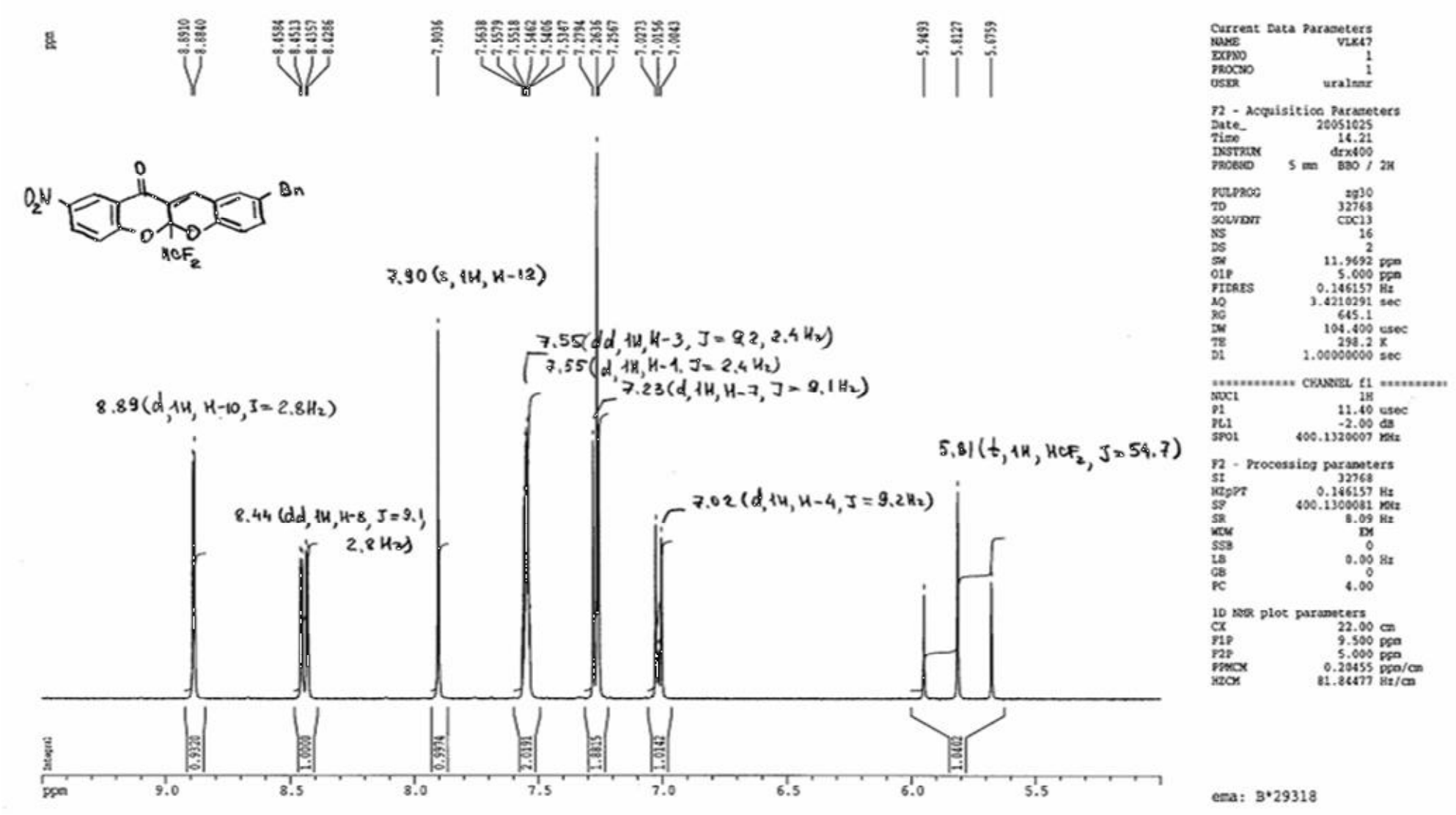
Copy of ^{1}H NMR spectrum of **2c**



Copy of ^{19}F NMR spectrum of **2c**



Copy of ^{1}H NMR spectrum of **2e**

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Current Data Parameters
NAME                  VLK47
EXPNO                     1
PROCNO                    1
USER                uralnmr

F2 - Acquisition Parameters
Date_              20051025
Time                  14.21
INSTRUM              drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SW                  11.9692 ppm
O1P                  5.000 ppm
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                      645.1
DW                  104.400 usec
TE                    298.2 K
D1                  1.00000000 sec

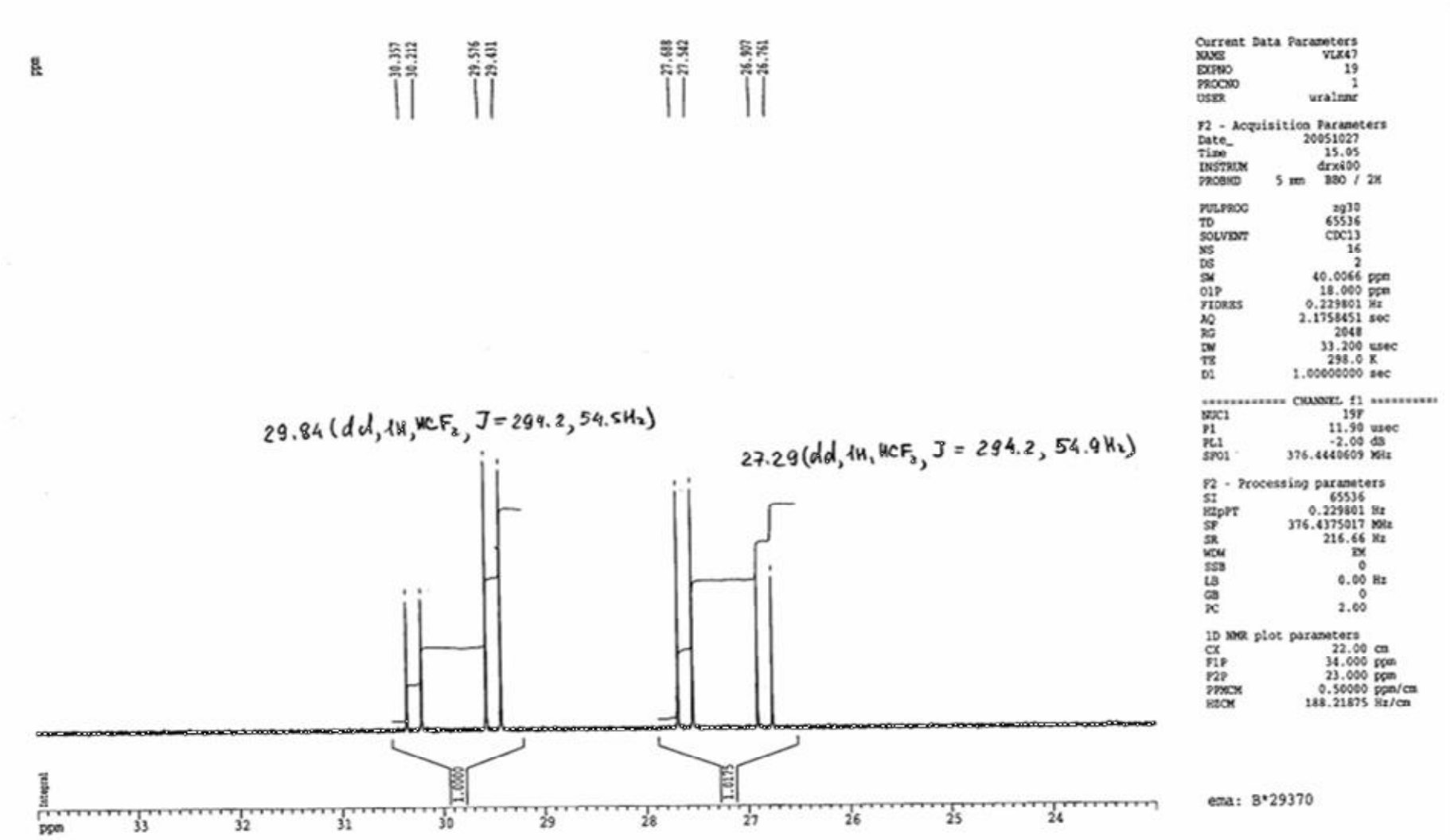
============ CHANNEL f1 ==========
NUC1                      1H
P1                   11.40 usec
PL1                  -2.00 dB
SFO1             400.1320007 MHz

F2 - Processing parameters
SI                        32768
MKpPT               0.146157 Hz
SF               400.1300081 MHz
SR                    8.09 Hz
WDW                      EM
SSB                       0
LB                    0.00 Hz
GB                        0
PC                    4.00

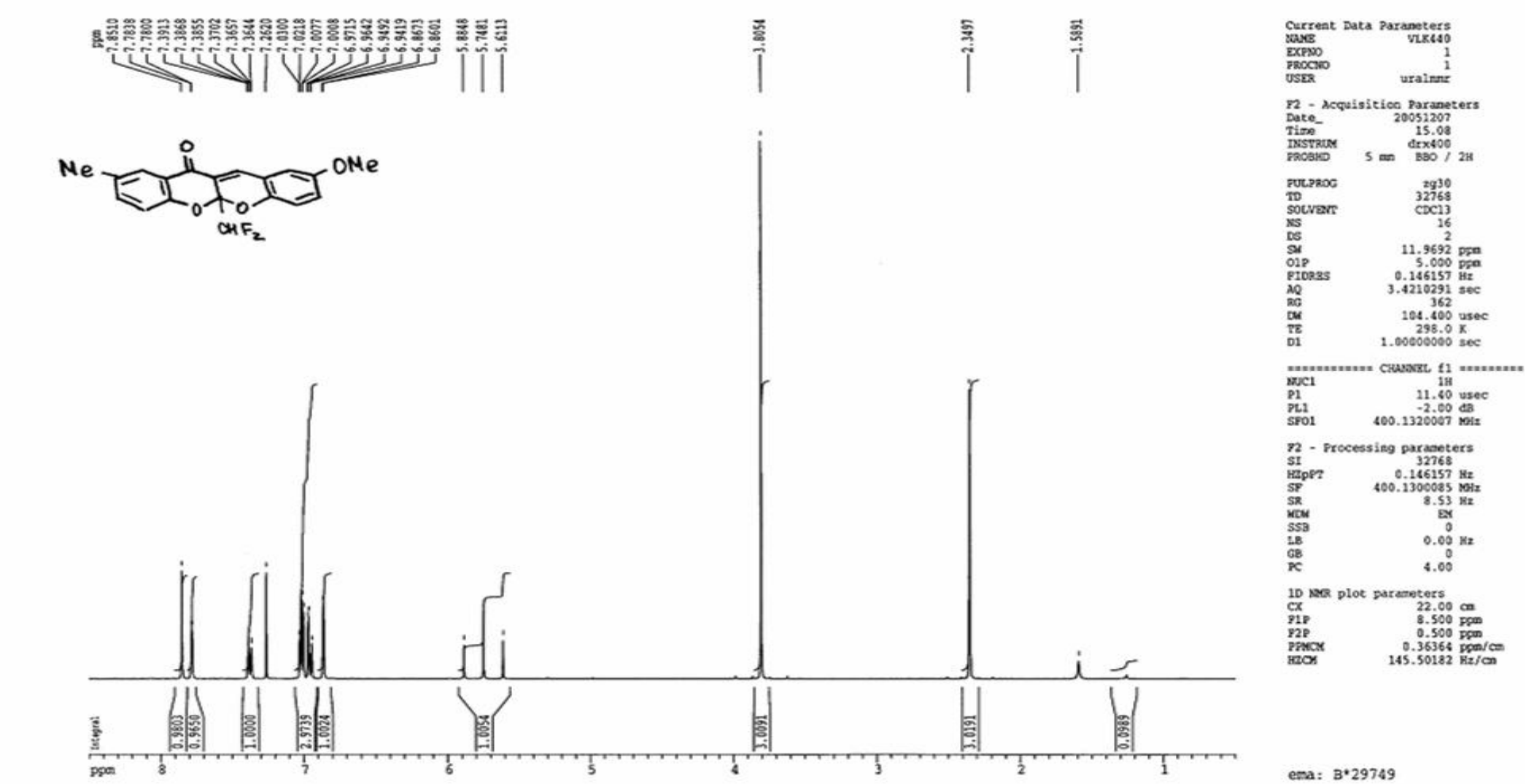
1D NMR plot parameters
CX                   22.00 cm
F1P                  9.500 ppm
F2P                  5.000 ppm
PPMCM               0.20455 ppm/cm
HZCM                81.84477 Hz/cm

ema: B*29318
```

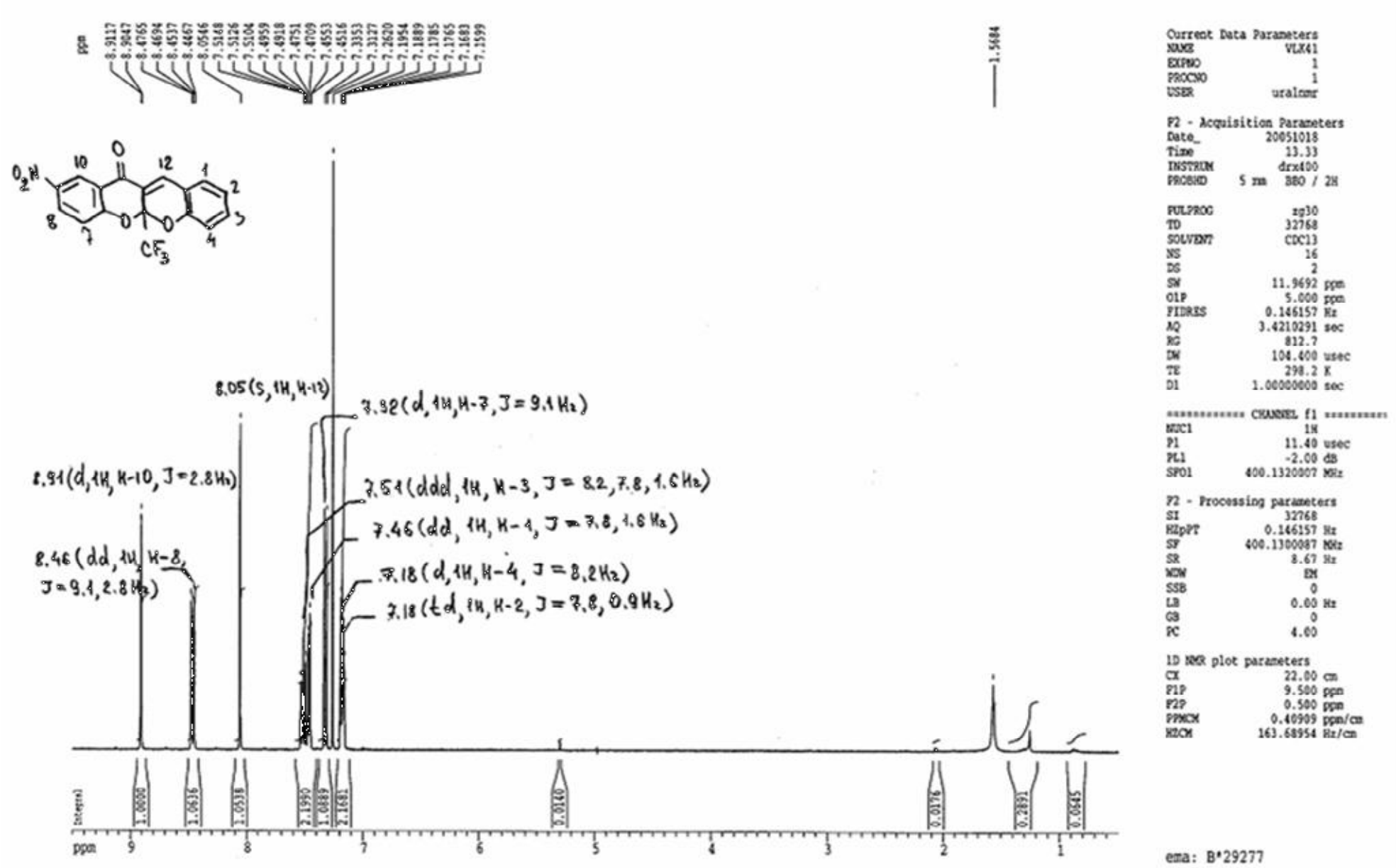
Copy of ^{19}F NMR spectrum of **2e**



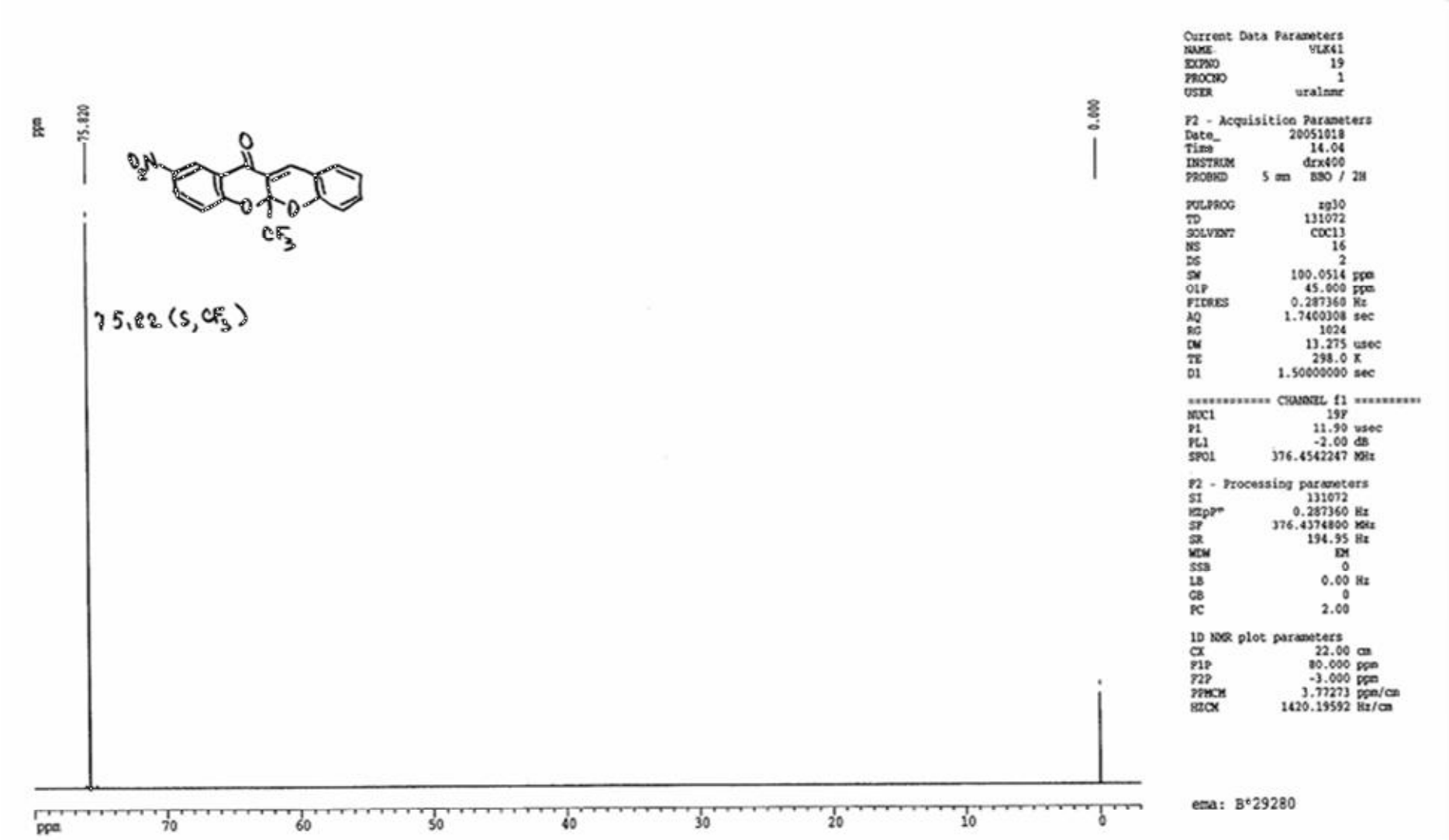
Copy of ^{1}H NMR spectrum of **2h**



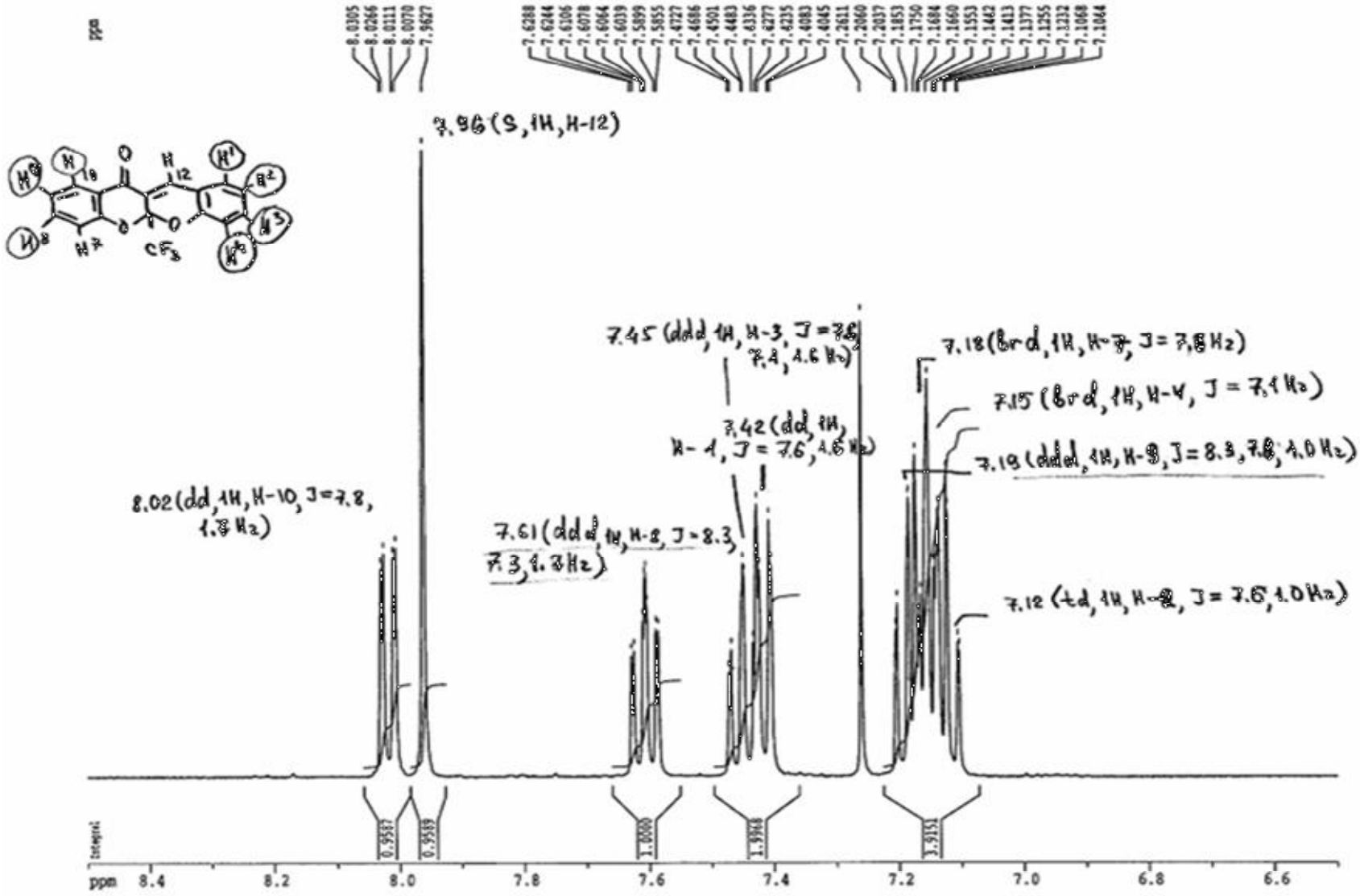
Copy of ^{1}H NMR spectrum of **2i**



Copy of ^{19}F NMR spectrum of **2i**



Copy of ^{1}H NMR spectrum of **2j**

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Current Data Parameters
NAME                  VLK43
EXPNO                     1
PROCNO                    1
USER                uralenr

F2 - Acquisition Parameters
Date_              20051020
Time                  12.06
INSTRUM              drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SW                 11.9692 ppm
O1P                 5.000 ppm
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                     574.7
DW                 104.400 usec
TE                     298.2 K
D1                1.00000000 sec

============ CHANNEL f1 ==========
NUC1                      1H
P1                     11.40 usec
PL1                    -2.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                        32768
HZpPT              0.146157 Hz
SF                 400.1300085 MHz
SR                     8.54 Hz
WDW                       EM
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     4.00

1D NMR plot parameters
CX                    22.00 cm
F1P                  8.500 ppm
F2P                  6.500 ppm
PPMCM              0.09091 ppm/cm
HZCM              36.37545 Hz/cm

meg: B*29295
```
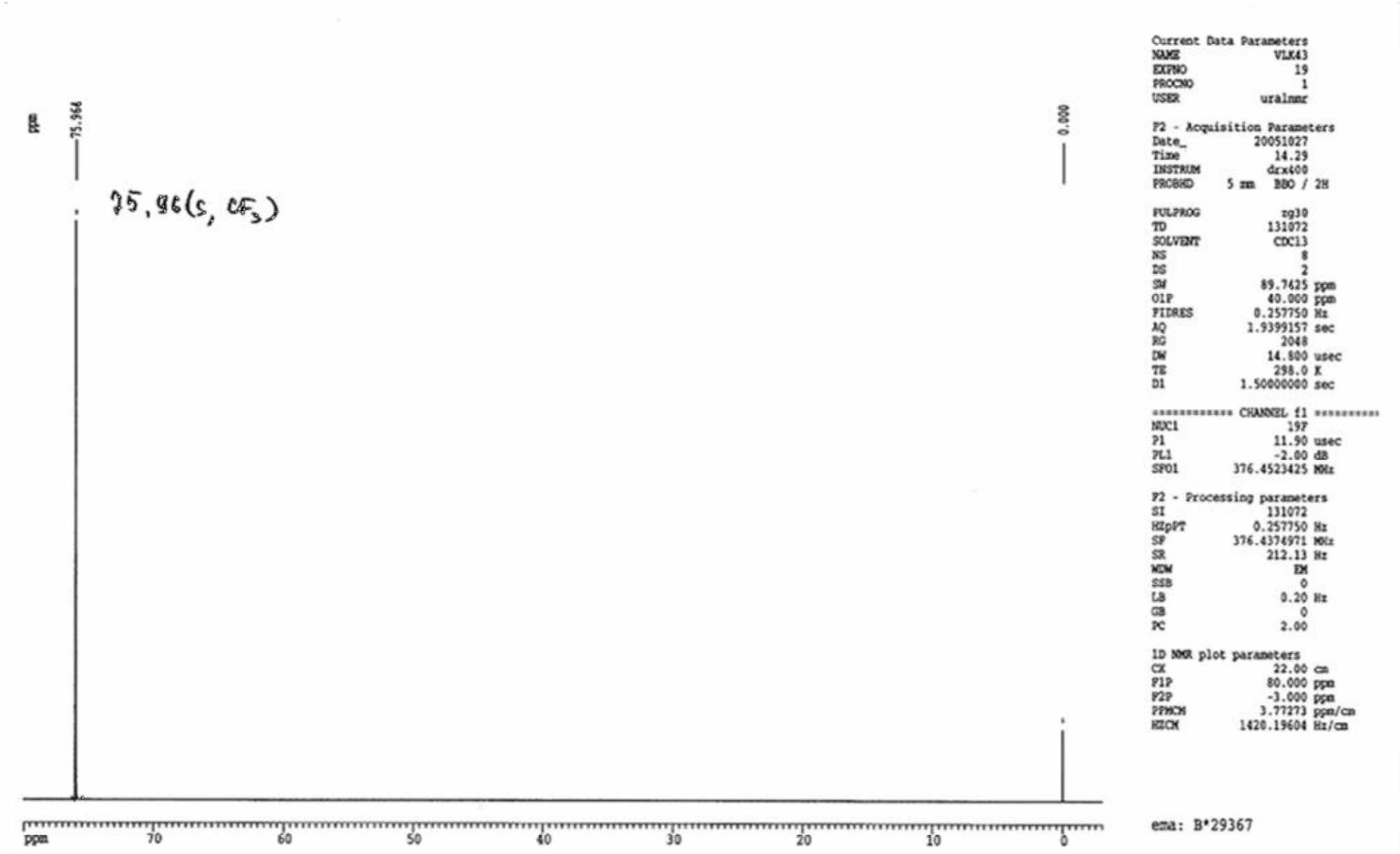
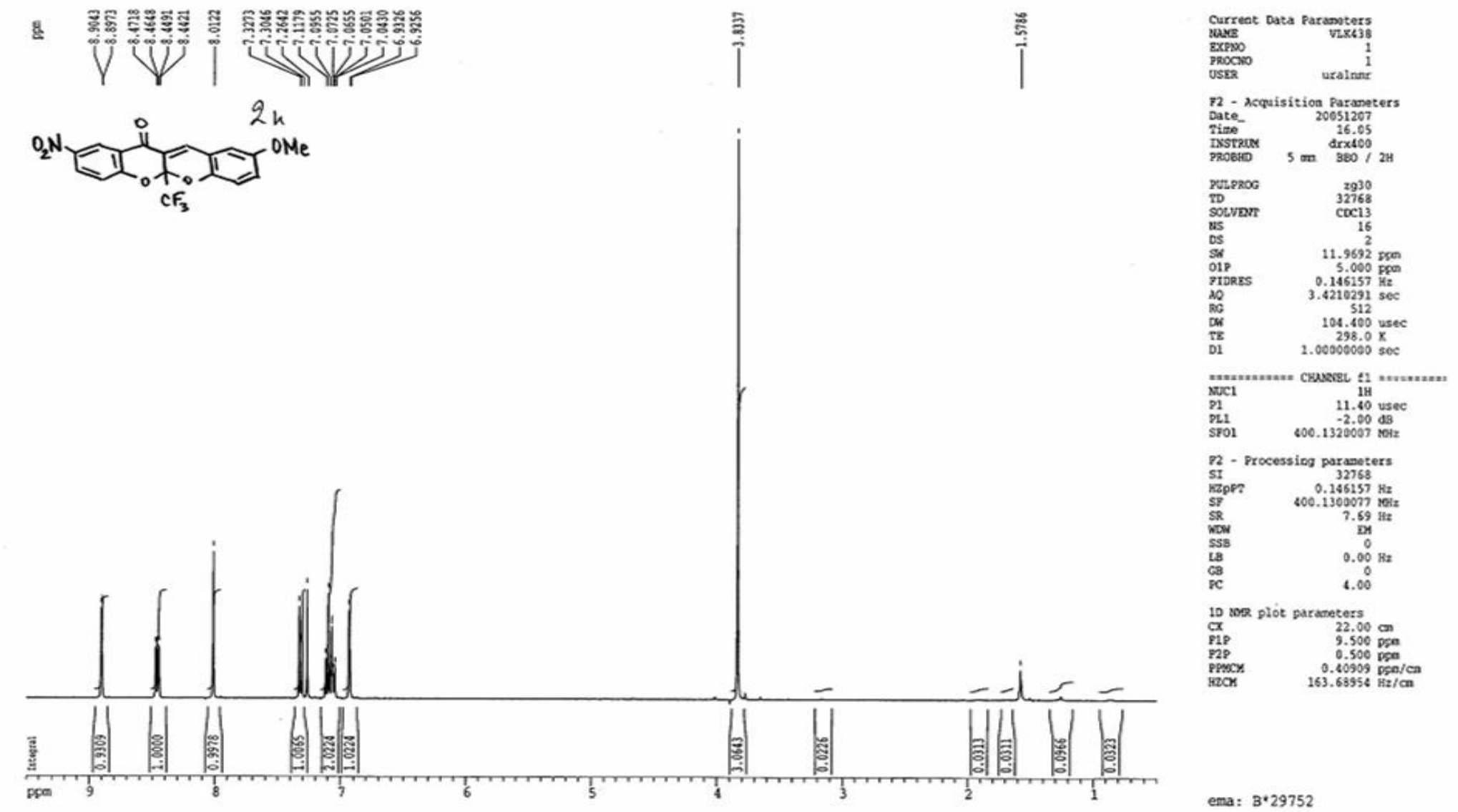

Copy of ^{19}F NMR spectrum of **2j**



Copy of ^{1}H NMR spectrum of **2o**

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Current Data Parameters
NAME                  VLK438
EXPNO                      1
PROCNO                     1
USER                 uralnmr

F2 - Acquisition Parameters
Date_               20051207
Time                   16.05
INSTRUM               drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SW                 11.9692 ppm
O1P                 5.000 ppm
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                       512
DW                 104.400 usec
TE                   298.0 K
D1                1.00000000 sec

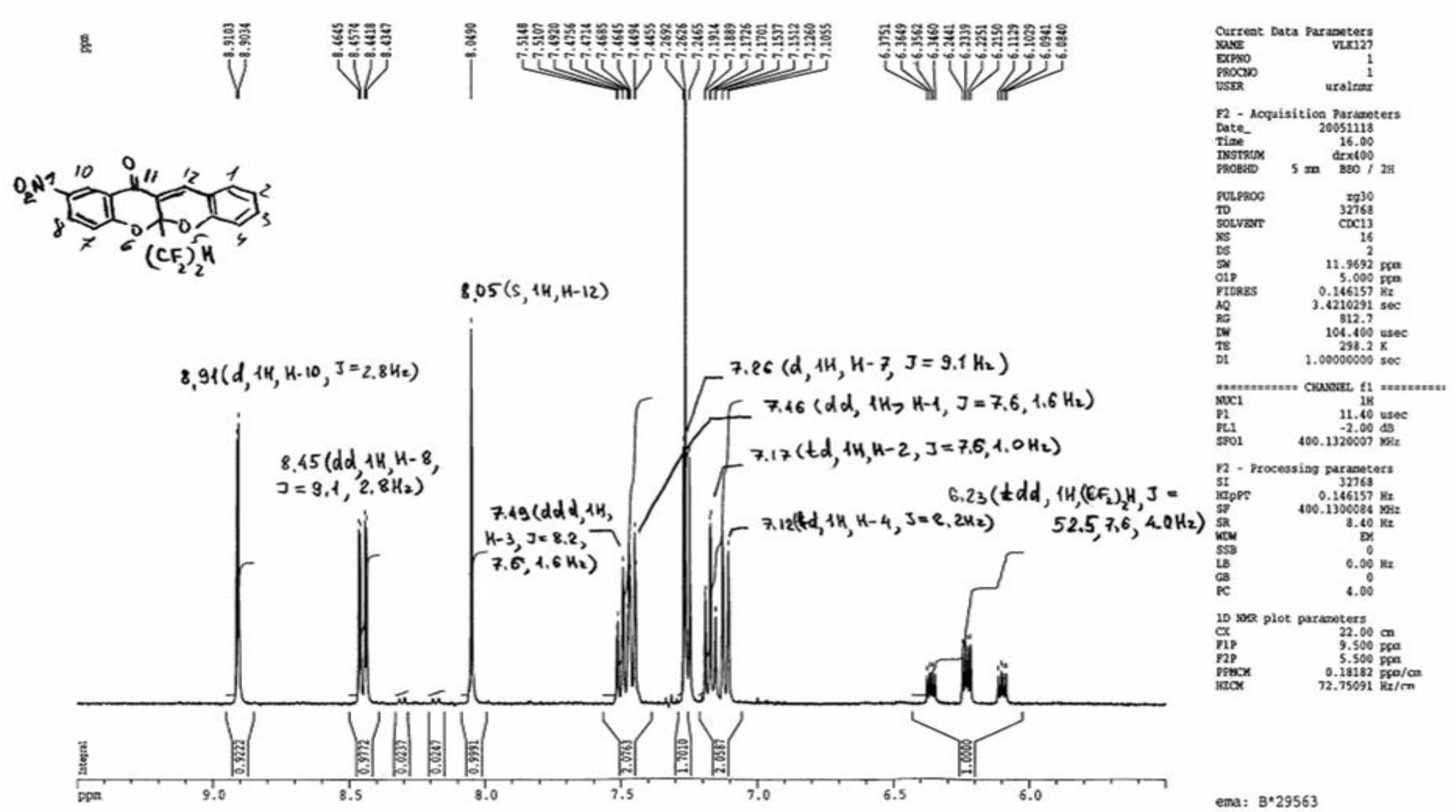
============ CHANNEL f1 ==========
NUC1                     1H
P1                   11.40 usec
PL1                  -2.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                    32768
WDW                      EM
SSB                       0
LB                   0.00 Hz
GB                        0
PC                     4.00

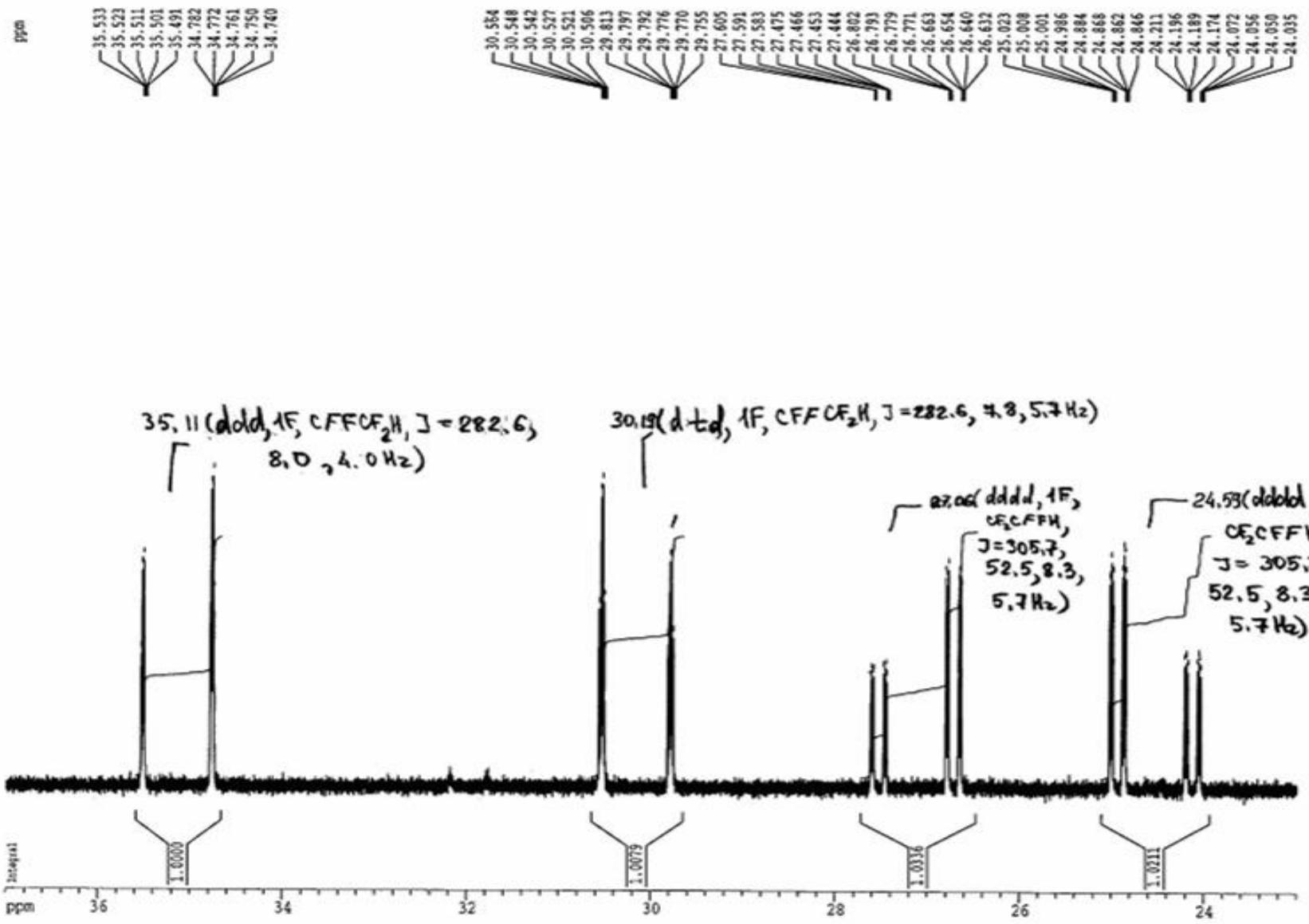
1D NMR plot parameters
CX                   22.00 cm
F1P                  9.500 ppm
F2P                  0.500 ppm
PPMCM              0.40909 ppm/cm
HZCM             163.68954 Hz/cm

ema: B*29752
```

Copy of ^{1}H NMR spectrum of **2r**



Copy of ^{19}F NMR spectrum of **2r**

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Current Data Parameters
NAME                 VLX127
EXPNO                    19
PROCNO                    1
USER                uralnmr

F2 - Acquisition Parameters
Date_              20051124
Time                  12.45
INSTRUM              drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                   131072
SOLVENT                CDCl3
NS                       16
DS                        2
SW                  59.8295 ppm
O1P                 20.000 ppm
FIDRES              0.171833 Hz
AQ                  2.9098485 sec
RG                       2048
DW                  22.200 usec
TE                  298.0 K
D1                  1.00000000 sec

============ CHANNEL f1 ===========
NUC1                     19F
P1                  11.90 usec
PL1                 -2.00 dB
SFO1             376.4448137 MHz

F2 - Processing parameters
SI                   131072
HZpPT               0.171833 Hz
SF               376.4374863 MHz
SR                  201.26 Hz
WDW                      EM
SSB                       0
LB                  0.00 Hz
GB                        0
PC                  2.00

1D NMR plot parameters
CX                  22.00 cm
F1P                 37.000 ppm
F2P                 23.000 ppm
PPMCM               0.63636 ppm/cm
HZCM                239.55113 Hz/cm

ema: B*29620
```
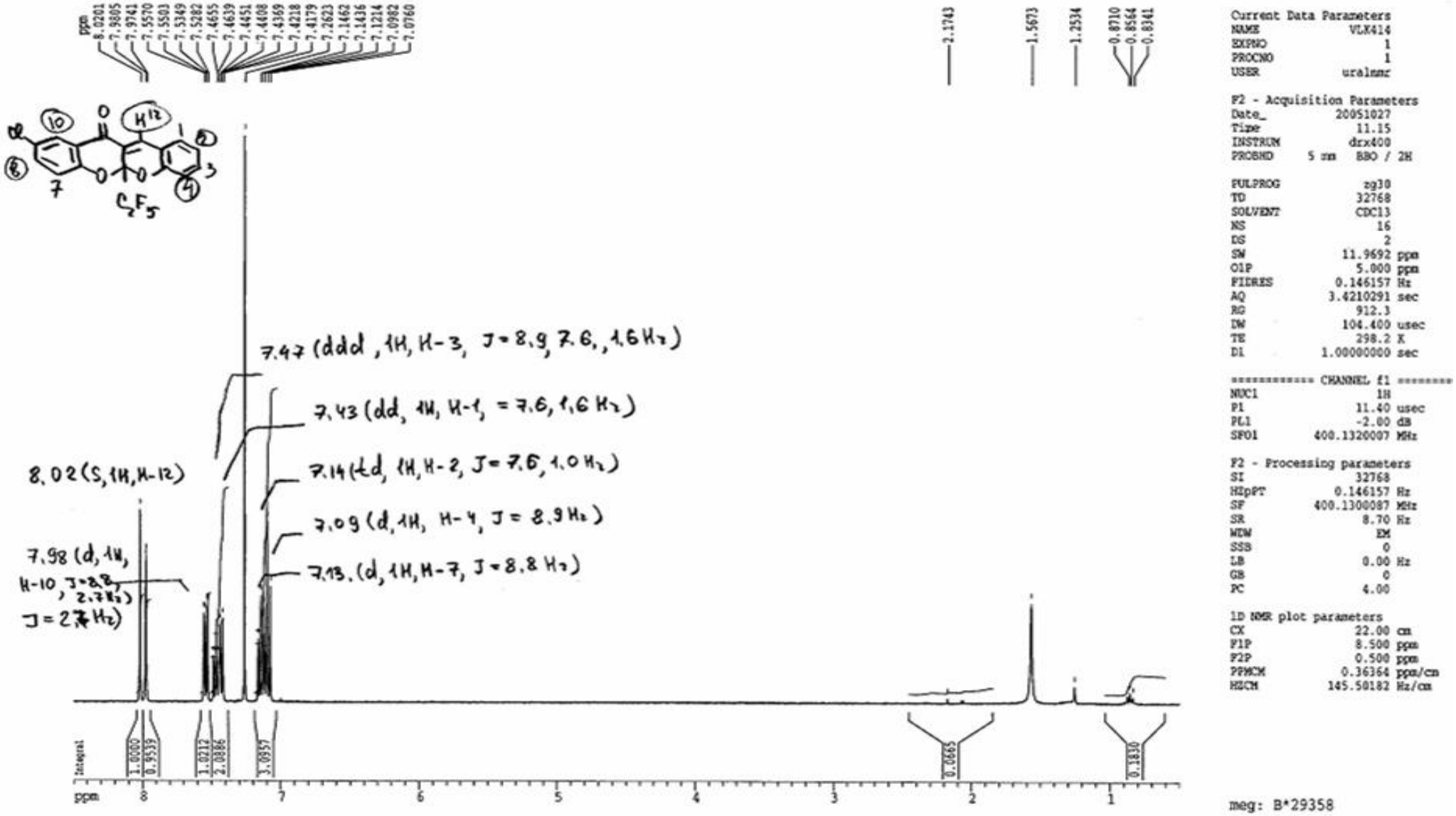
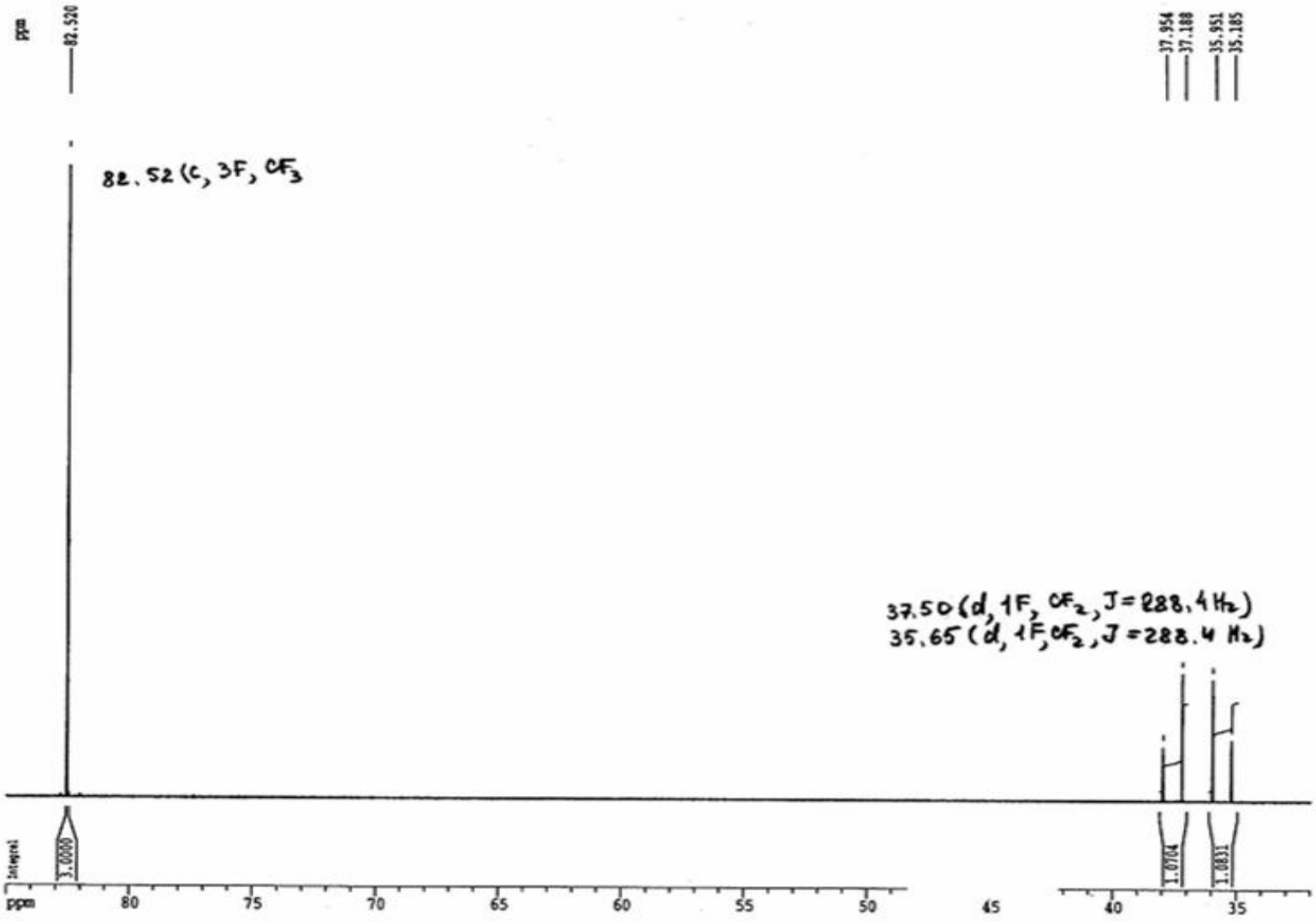

Copy of ^{1}H NMR spectrum of **2t**



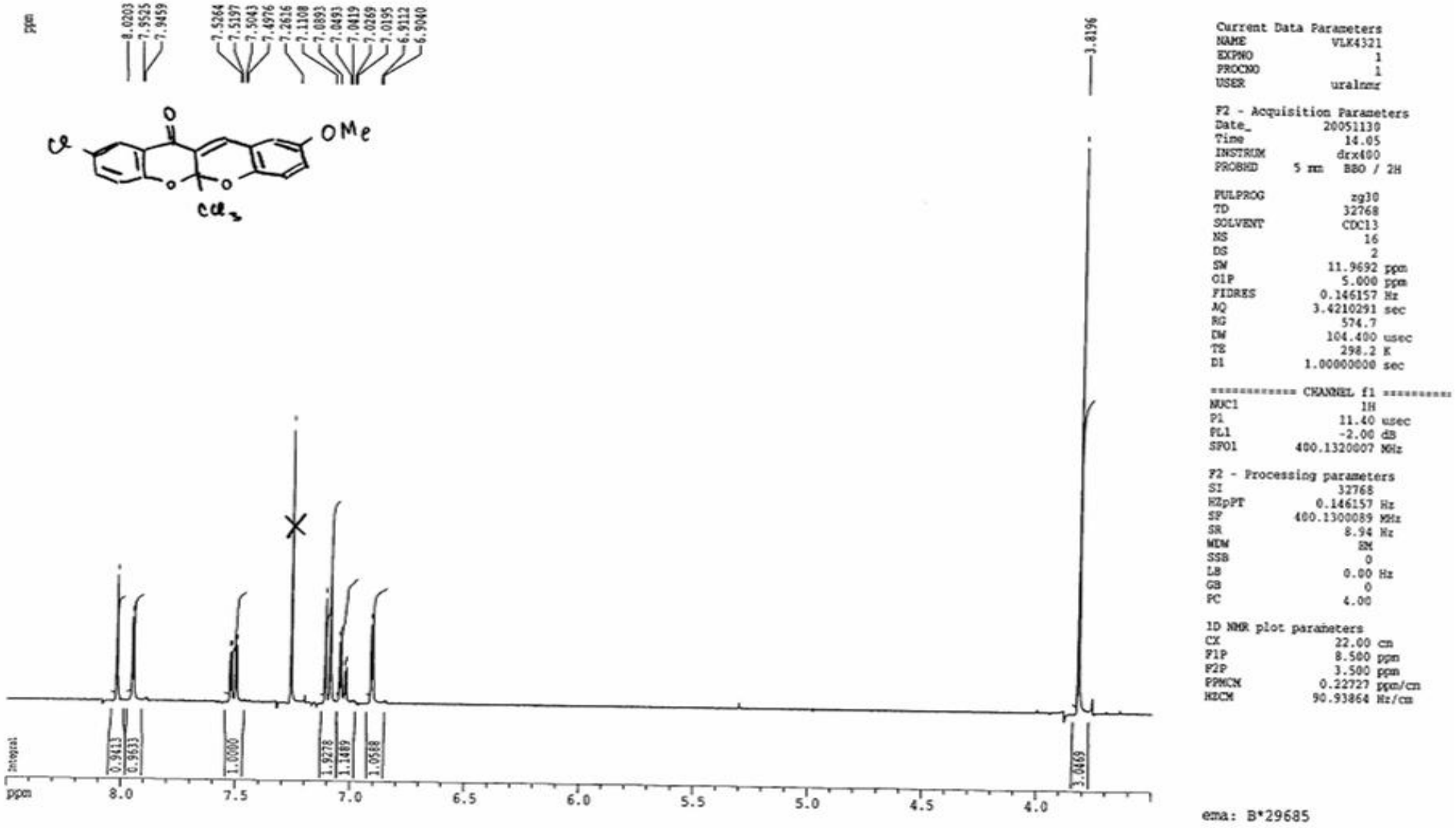

```
Current Data Parameters
NAME                  VLK414
EXPNO                      1
PROCNO                     1
USER                 uralnmr

F2 - Acquisition Parameters
Date_              20051027
Time                  11.15
INSTRUM               drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SW                 11.9692 ppm
O1P                 5.000 ppm
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                    912.3
DW                  104.400 usec
TE                    298.2 K
D1                 1.00000000 sec

============ CHANNEL f1 ========
NUC1                      1H
P1                  11.40 usec
PL1                 -2.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                    32768
HZPPT              0.146157 Hz
SF             400.1300087 MHz
SR                  8.70 Hz
WDW                       EM
SSB                       0
LB                  0.00 Hz
GB                        0
PC                     4.00

1D NMR plot parameters
CX                    22.00 cm
F1P                  8.500 ppm
F2P                  0.500 ppm
PPMCM              0.36364 ppm/cm
HZCM             145.50182 Hz/cm

meg: B*29358
```

Copy of ^{19}F NMR spectrum of **2t**




```
Current Data Parameters
NAME                  VLX414
EXPNO                     19
PROCNO                     1
USER                 uralnmr

F2 - Acquisition Parameters
Date_               20051027
Time                   15.48
INSTRUM                drx400
PROBHD     5 mm   BBO / 2H

PULPROG                 zg30
TD                    131072
SOLVENT               CDCl3
NS                        16
DS                         2
SW                 100.0514 ppm
O1P                 45.000 ppm
FIDRES              0.287360 Hz
AQ                  1.7400308 sec
RG                       2048
DW                   13.275 usec
TE                    298.0 K
D1                 1.50000000 sec

============ CHANNEL f1 ==========
NUC1                     19F
P1                    11.90 usec
PL1                   -2.00 dB
SFO1              376.4542247 MHz

F2 - Processing parameters
SI                    131072
HZPPT               0.287360 Hz
SF                376.4374978 MHz
SR                   212.77 Hz
WDW                      EM
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     2.00

1D NMR plot parameters
CX                    22.00 cm
F1P                  85.000 ppm
F2P                  32.000 ppm
PPMCM                2.40909 ppm/cm
HZCM               906.87213 Hz/cm

ema: B*29373
```

Copy of ^{1}H NMR spectrum of **2x**

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Current Data Parameters
NAME                  VLK4321
EXPNO                       1
PROCNO                      1
USER                  uralnmr

F2 - Acquisition Parameters
Date_              20051130
Time                  14.05
INSTRUM             drx400
PROBHD     5 mm   BBO / 2H

PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       2
SW                 11.9692 ppm
O1P                 5.000 ppm
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                   574.7
DW                 104.400 usec
TE                   298.2 K
D1              1.00000000 sec

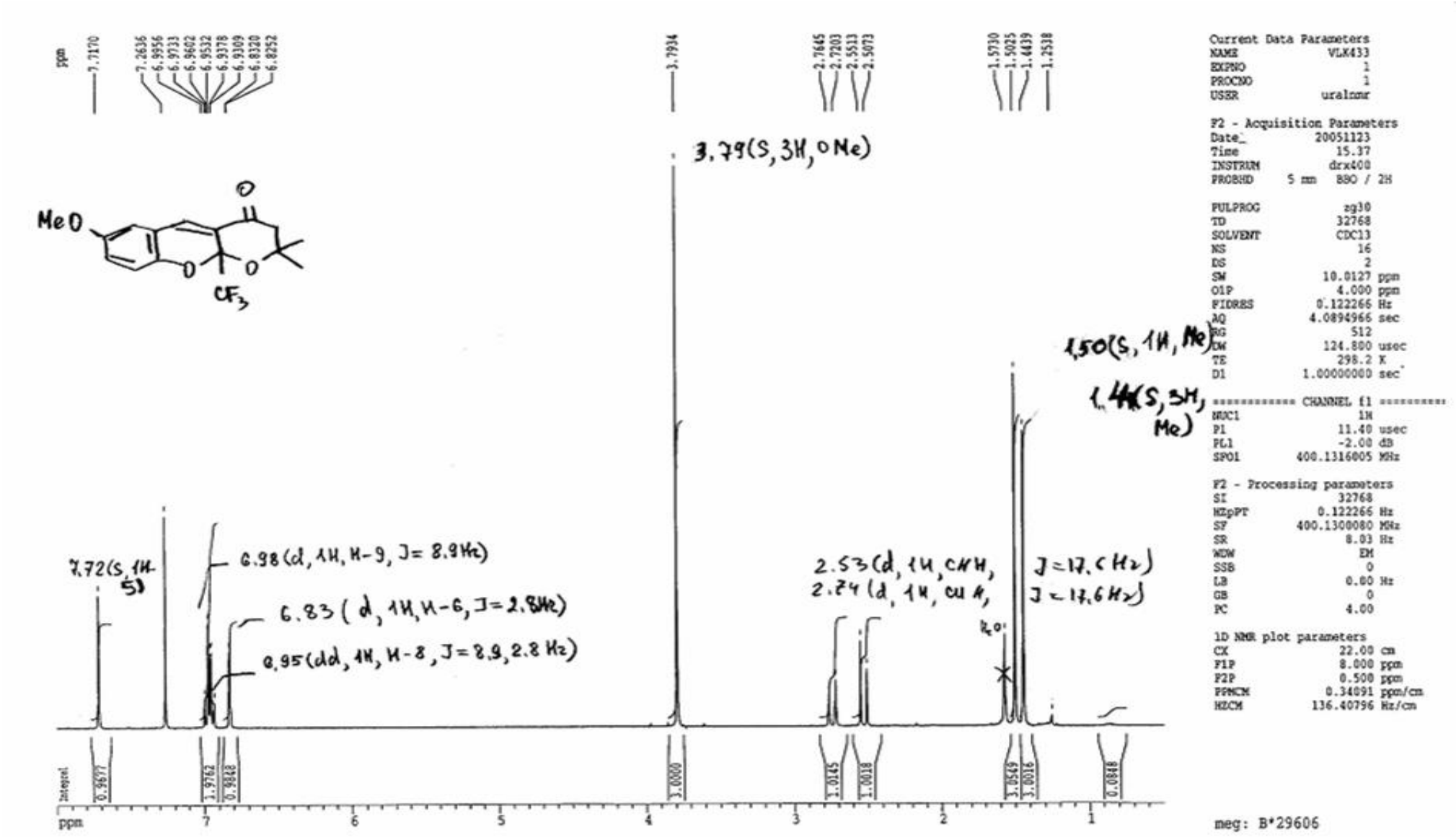
============ CHANNEL f1 ==========
NUC1                    1H
P1                  11.40 usec
PL1                -2.00 dB
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                   32768
HZpPT              0.146157 Hz
SF            400.1300089 MHz
SR                  8.94 Hz
WDW                    EM
SSB                     0
LB                  0.00 Hz
GB                      0
PC                   4.00

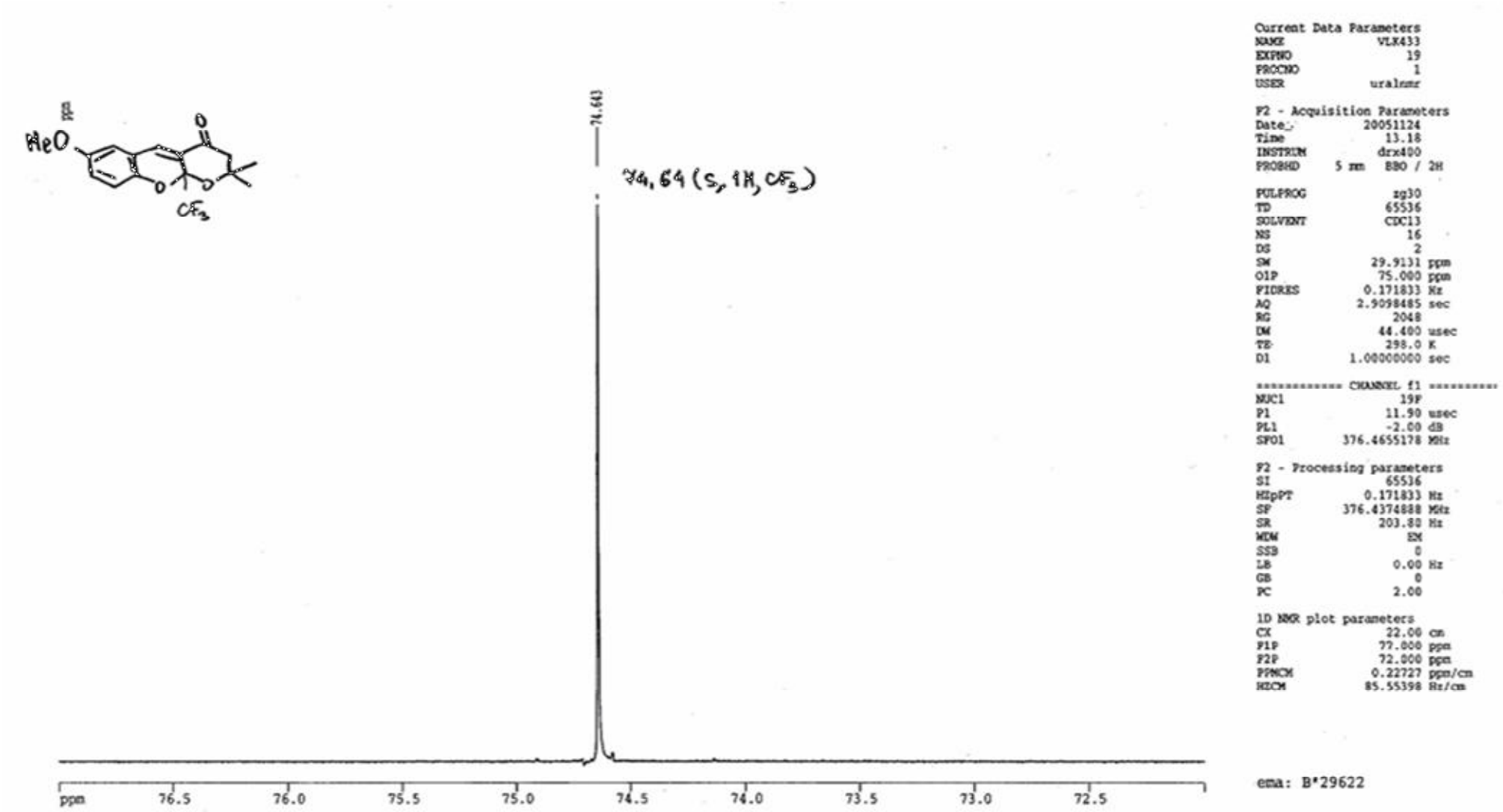
1D NMR plot parameters
CX                  22.00 cm
F1P                 8.500 ppm
F2P                 3.500 ppm
PPMCM              0.22727 ppm/cm
HZCM              90.93864 Hz/cm

ema: B*29685
```

Copy of ^{1}H NMR spectrum of **3c**



Copy of ^{19}F NMR spectrum of **3c**

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Current Data Parameters
NAME                  VLX433
EXPNO                     19
PROCNO                     1
USER                 uralnmr

F2 - Acquisition Parameters
Date_              20051124
Time                  13.18
INSTRUM              drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SW                  29.9131 ppm
O1P                 75.000 ppm
FIDRES              0.171833 Hz
AQ                  2.9098485 sec
RG                       2048
DW                   44.400 usec
TE                   298.0 K
D1                1.00000000 sec

============ CHANNEL f1 ==========
NUC1                     19F
P1                   11.90 usec
PL1                  -2.00 dB
SFO1             376.4655178 MHz

F2 - Processing parameters
SI                       65536
HZpPT               0.171833 Hz
SF               376.4374888 MHz
SR                   203.80 Hz
WDW                      EM
SSB                       0
LB                    0.00 Hz
GB                        0
PC                     2.00

1D NMR plot parameters
CX                    22.00 cm
F1P                  77.000 ppm
F2P                  72.000 ppm
PPMCM               0.22727 ppm/cm
HZCM                85.55398 Hz/cm

ema: B*29622
```
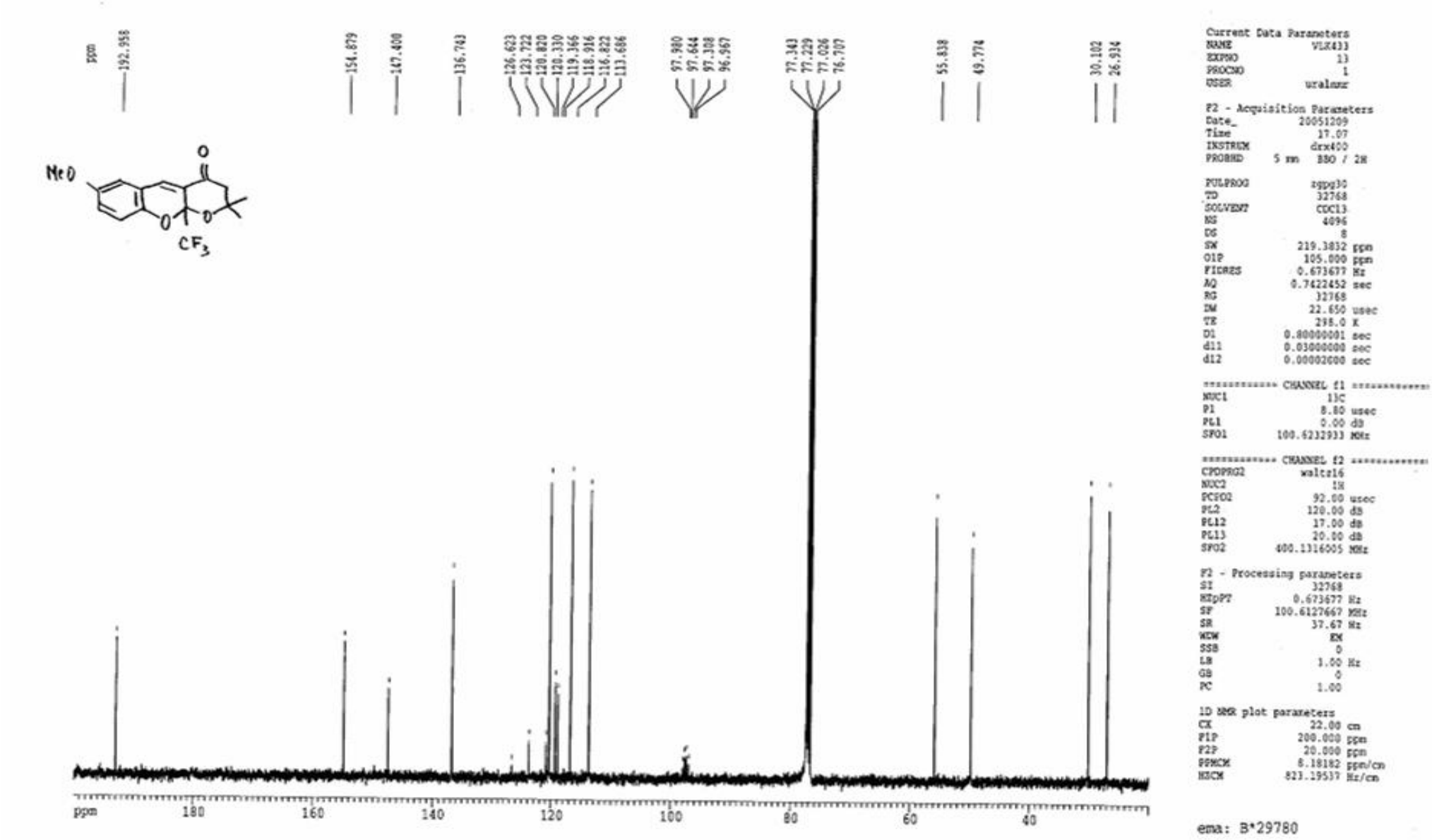
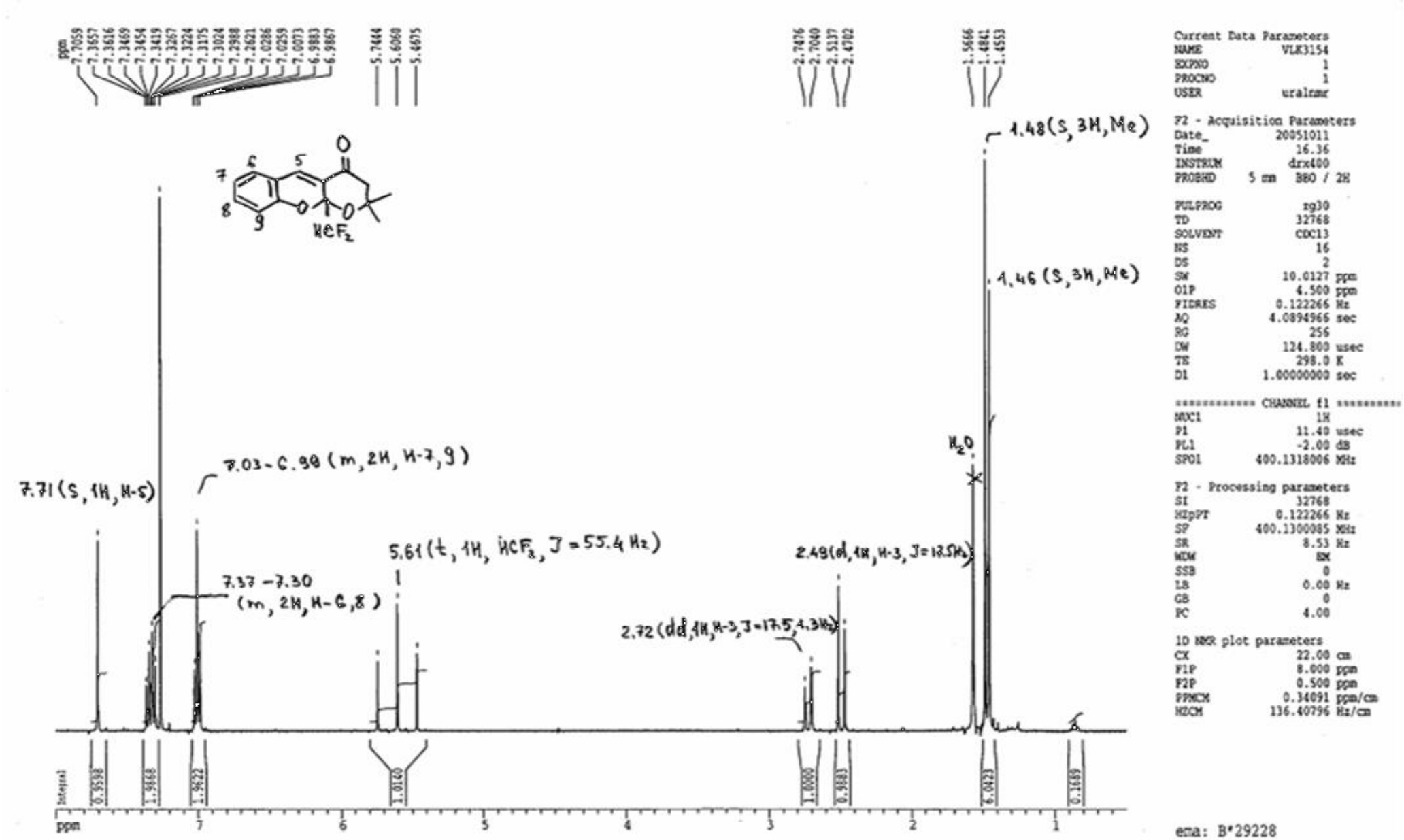
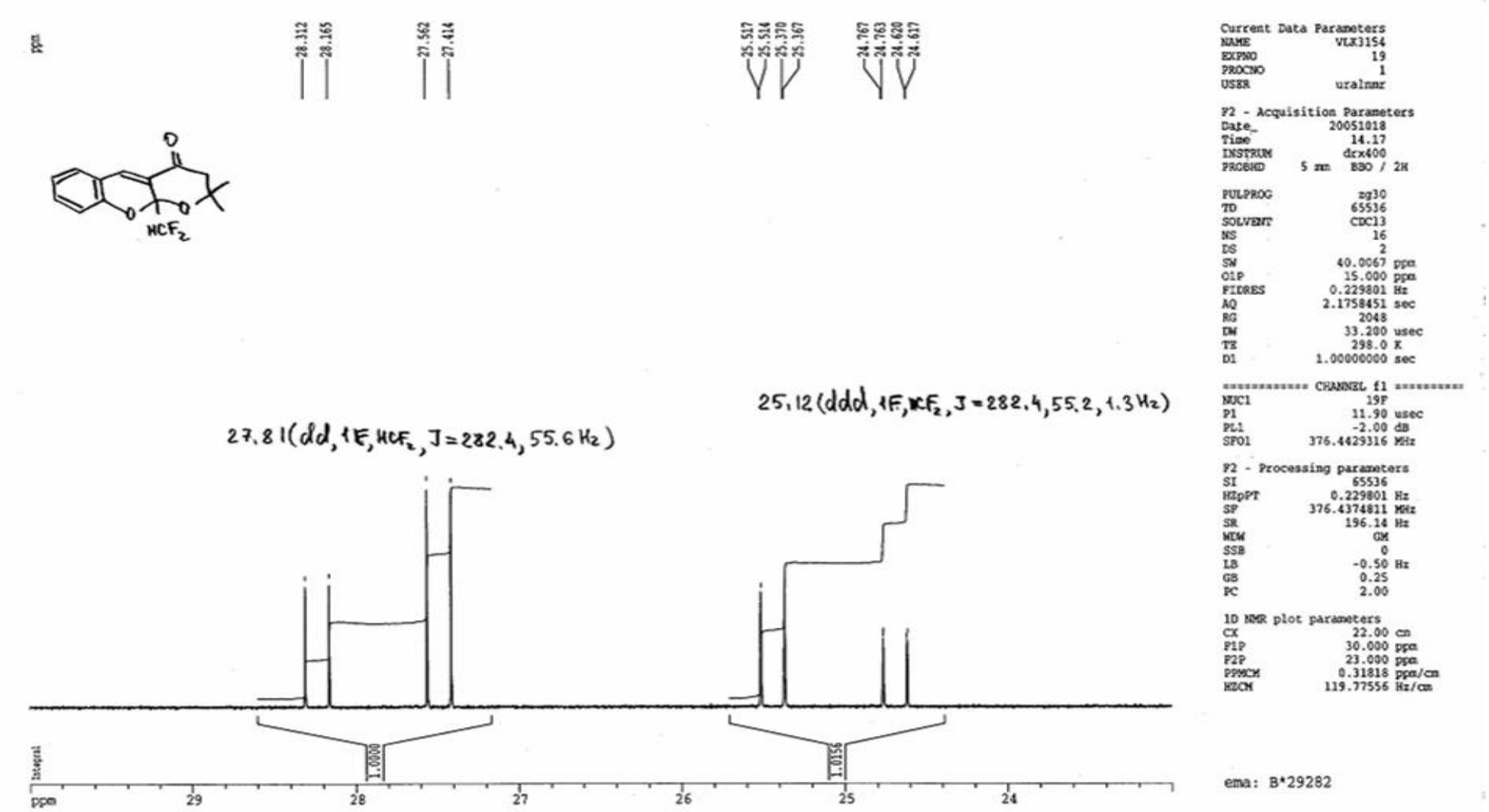

Copy of ^{13}C NMR spectrum of **3c**



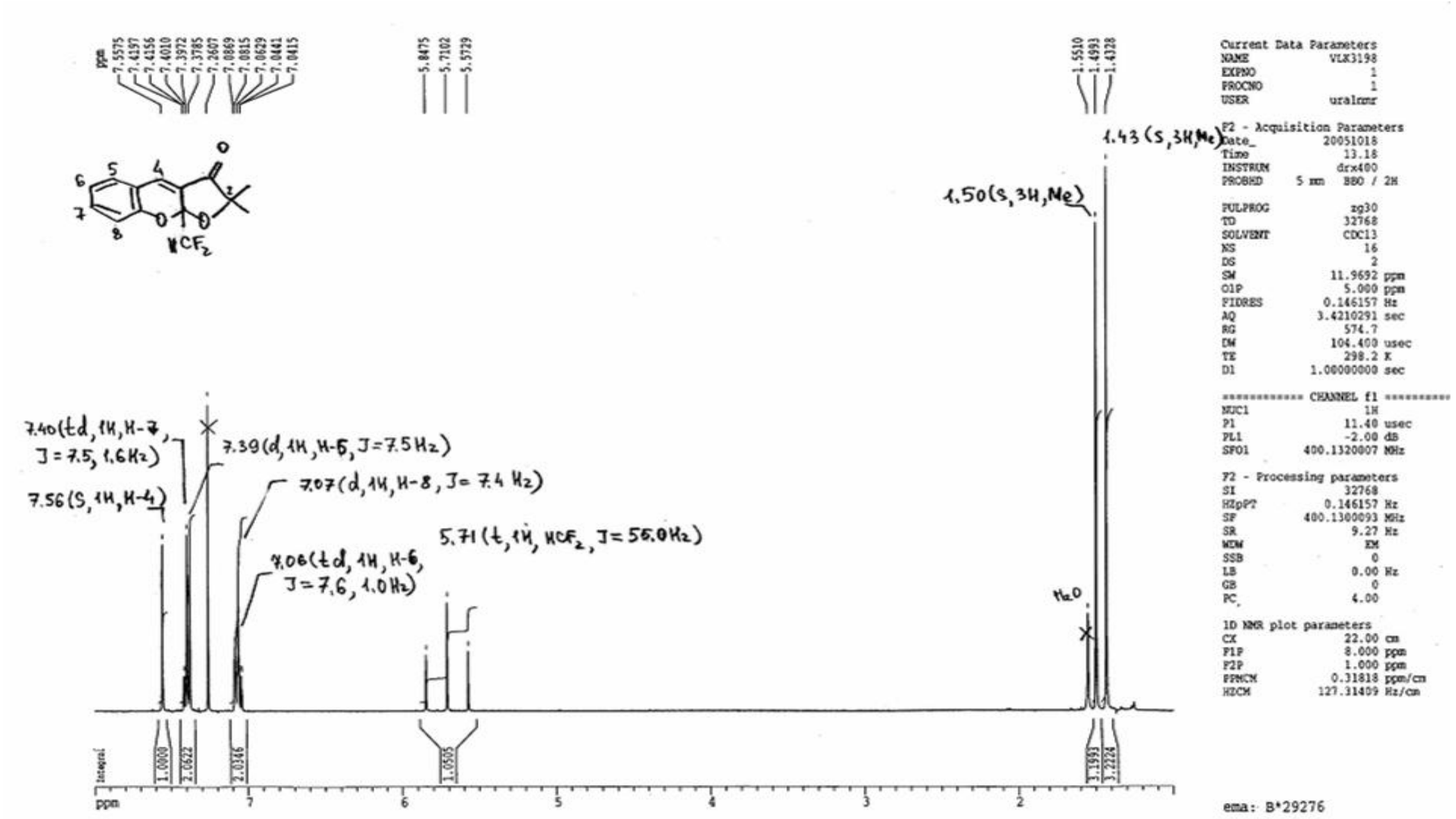
Copy of ^{1}H NMR spectrum of **3d**



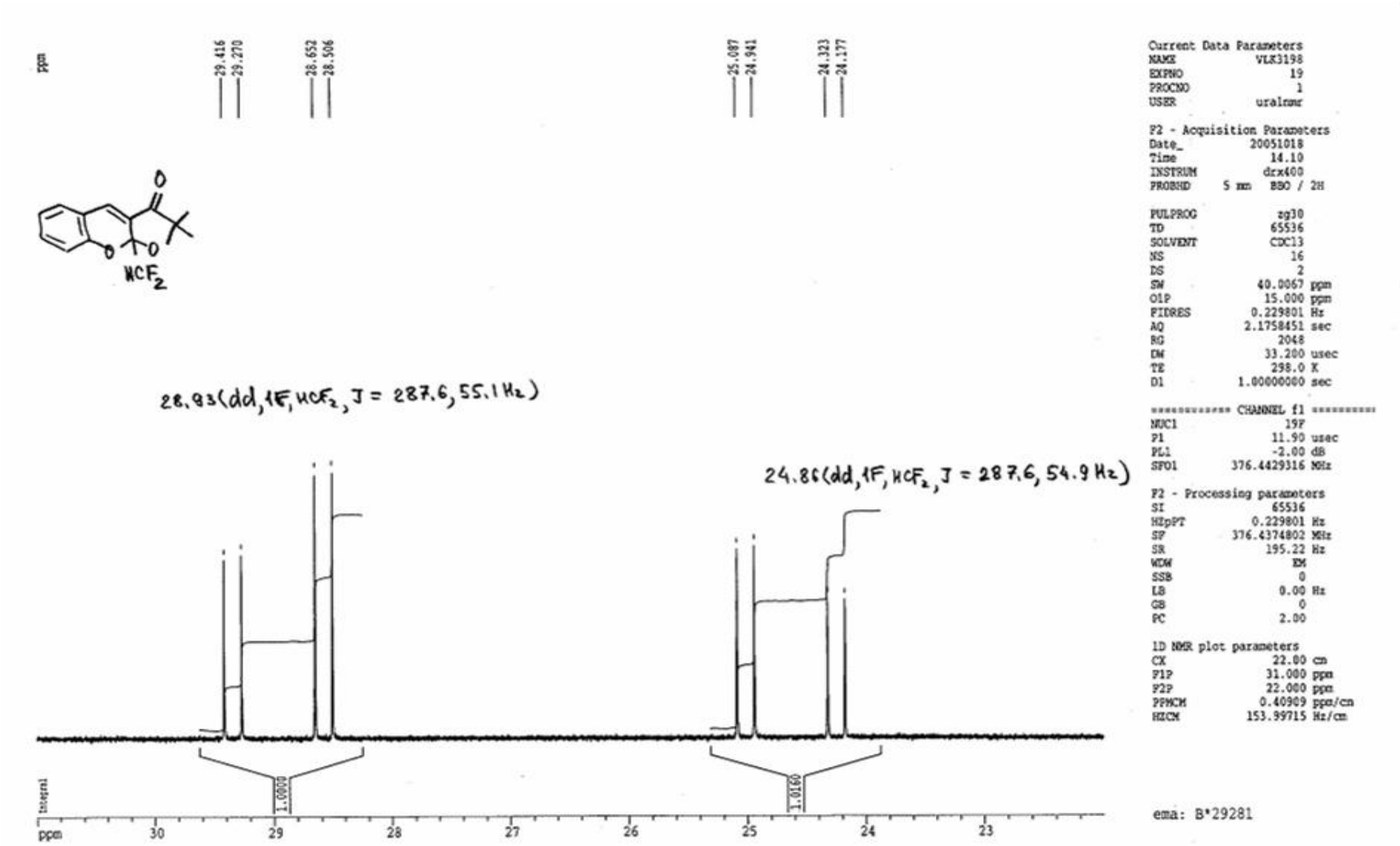
Copy of ^{19}F NMR spectrum of **3d**



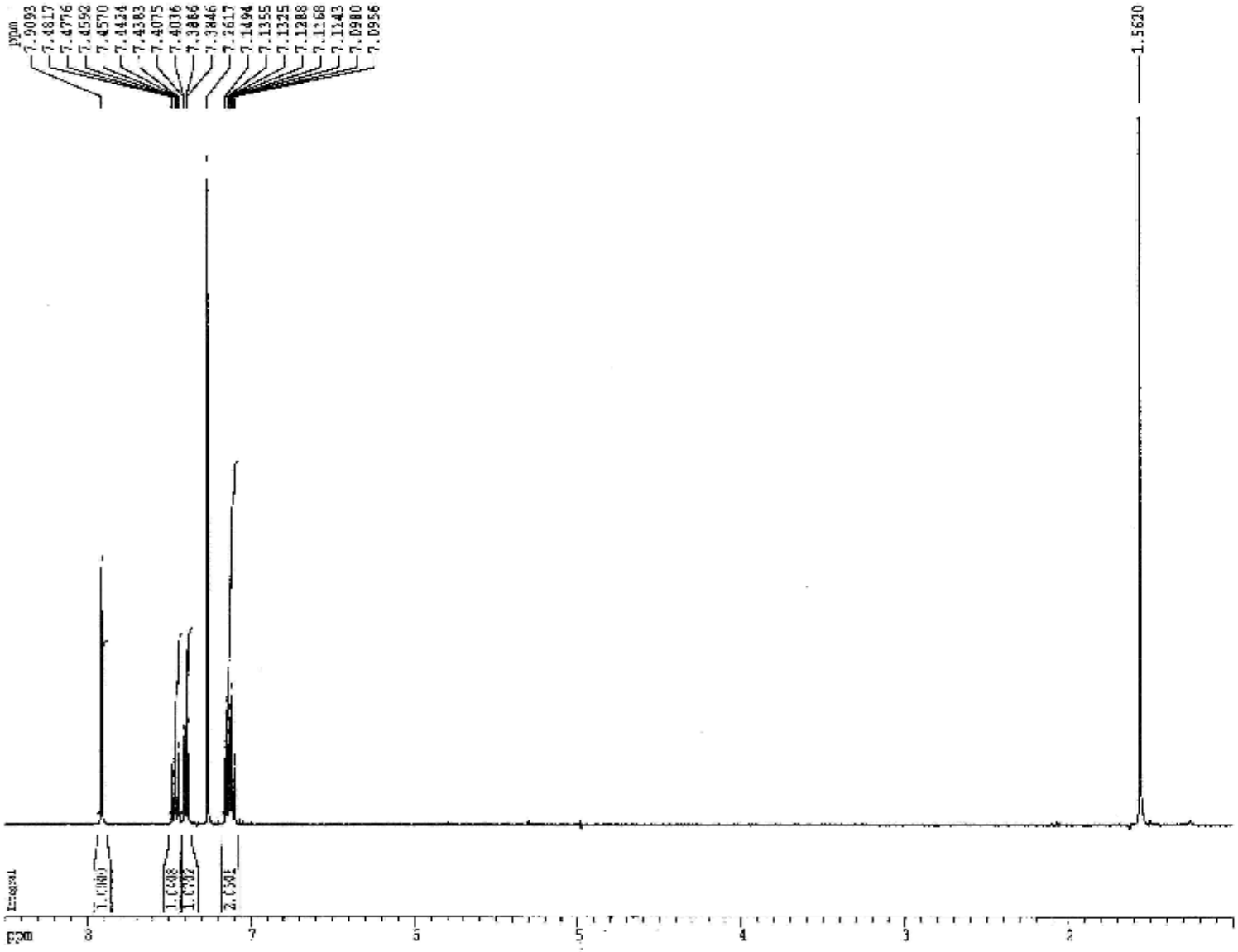
Copy of ^{1}H NMR spectrum of **3f**



Copy of ^{19}F NMR spectrum of **3f**



Copy of ^{1}H NMR spectrum of *trans*-**6a**

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Current Data Parameters
NAME                  CHD547a
EXPNO                       1
PROCNO                      1
USER                  uralomr

F2 - Acquisition Parameters
Date_              20050610
Time                   12.35
INSTRUM                drx400
PROBHD     5 mm   BBO / 2H

PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SW                 11.9692 ppm
O1P                 5.000 ppm
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                     912.3
DW                 104.400 usec
TE                     298.0 K
D1                1.00000000 sec

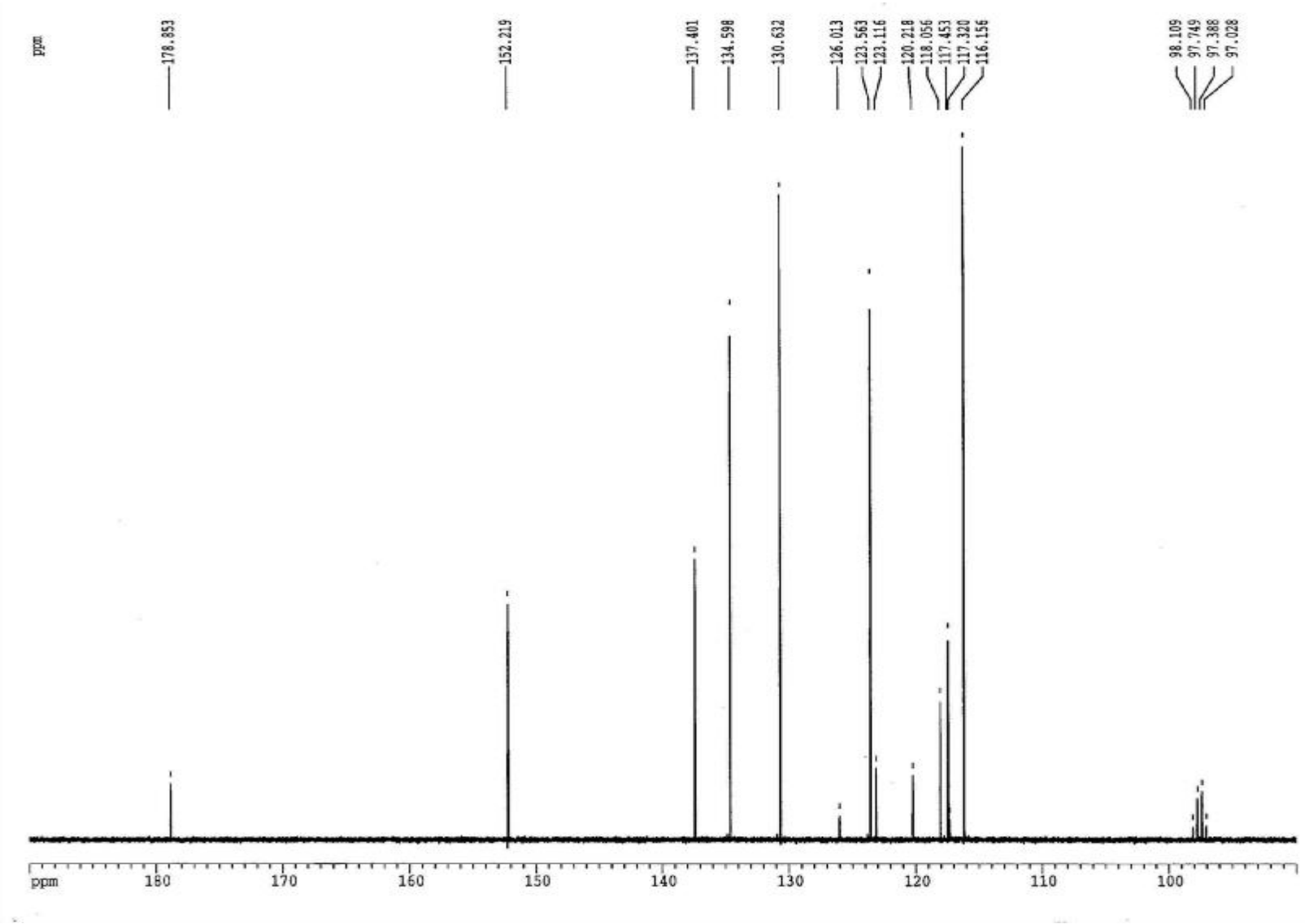
========== CHANNEL f1 ==========
NUC1                      1H
P1                     11.40 usec
PL1                    -2.00 dB
SFO1             400.1320007 MHz

F2 - Processing parameters
SI                        32768
SFO1             400.1300089 MHz
BF                     8.86 Hz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                     4.00

1D NMR plot parameters
CX                     22.00 cm
F1P                    8.500 ppm
F2P                    1.000 ppm
PPMCM                 0.34091 ppm/cm
HZCM                136.40796 Hz/cm

ema: B*28330
```

Copy of ^{13}C NMR spectrum of *trans*-**6a**

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Current Data Parameters
NAME                  CHD528
EXPNO                     13
PROCNO                     1
USER                 uralnmr

F2 - Acquisition Parameters
Date_               20050525
Time                   18.38
INSTRUM                drx400
PROBHD     5 mm   BBO / 2H

PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                     18432
DS                         8
SW                 219.3832 ppm
O1P                105.000 ppm
FIDRES             0.336839 Hz
AQ                 1.4844404 sec
RG                     32768
DW                  22.650 usec
TE                   298.0 K
D1                 1.50000000 sec
d11                0.03000000 sec
d12                0.00002000 sec

============ CHANNEL f1 ============
NUC1                     13C
P1                    8.80 usec
PL1                   0.00 dB
SFO1           100.6232933 MHz

============ CHANNEL f2 ============
CPDPRG2              waltz16
NUC2                     1H
PCPD2                92.00 usec
PL2                  120.00 dB
PL12                  17.00 dB
PL13                  20.00 dB
SFO2           400.1324008 MHz

F2 - Processing parameters
SI                     65536
EZpPT              0.336839 Hz
SF             100.6127668 MHz
SR                  37.83 Hz
WDW                    GM
SSB                     0
LB                  -0.50 Hz
GB                    0.25
PC                    1.40

1D NMR plot parameters
CX                   22.00 cm
F1P                190.000 ppm
F2P                 90.000 ppm
PPMCM              4.54545 ppm/cm
HZCM             457.33078 Hz/cm


ema: B*28159
```
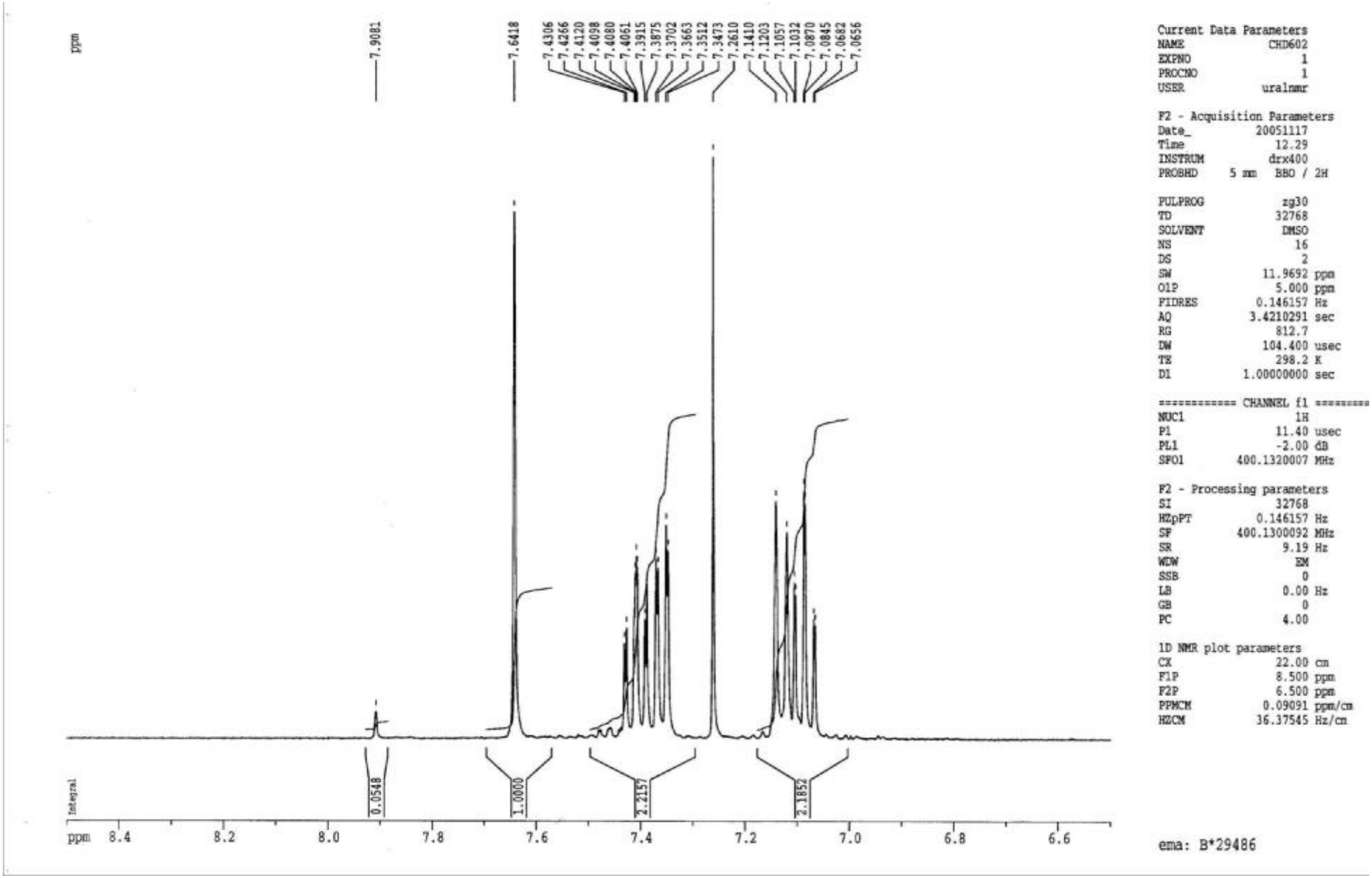
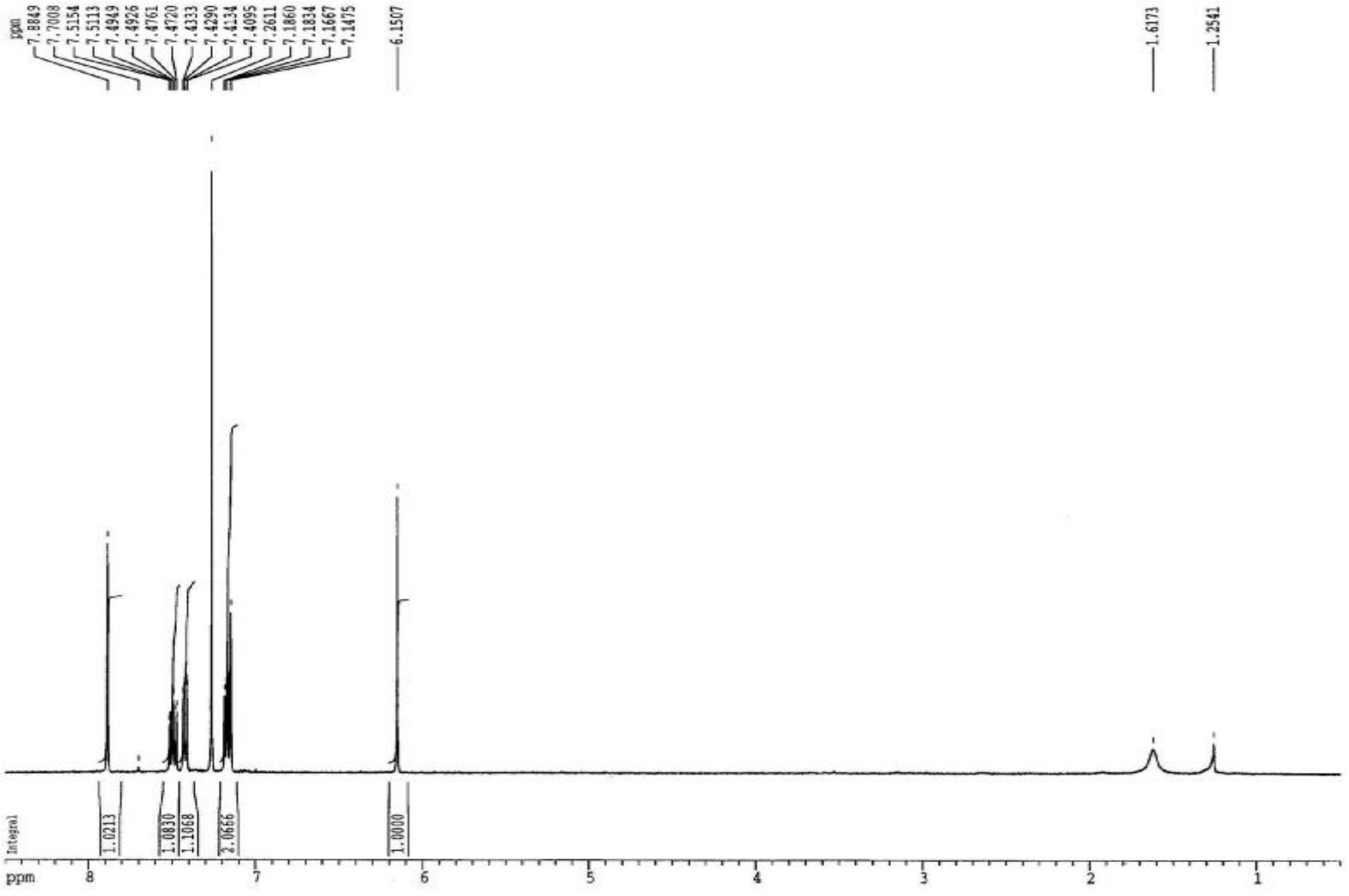

Copy of ^{1}H NMR spectrum of *cis*-**6a**



Copy of ^{1}H NMR spectrum of **7a**

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Current Data Parameters
NAME                  CHD614
EXPNO                      1
PROCNO                     1
USER                uralnmr

F2 - Acquisition Parameters
Date_              20051209
Time                  13.27
INSTRUM             drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SW                  11.9692 ppm
O1P                  5.000 ppm
FIDRES              0.146157 Hz
AQ                  3.4210291 sec
RG                     812.7
DW                   104.400 usec
TE                     298.2 K
D1                1.00000000 sec

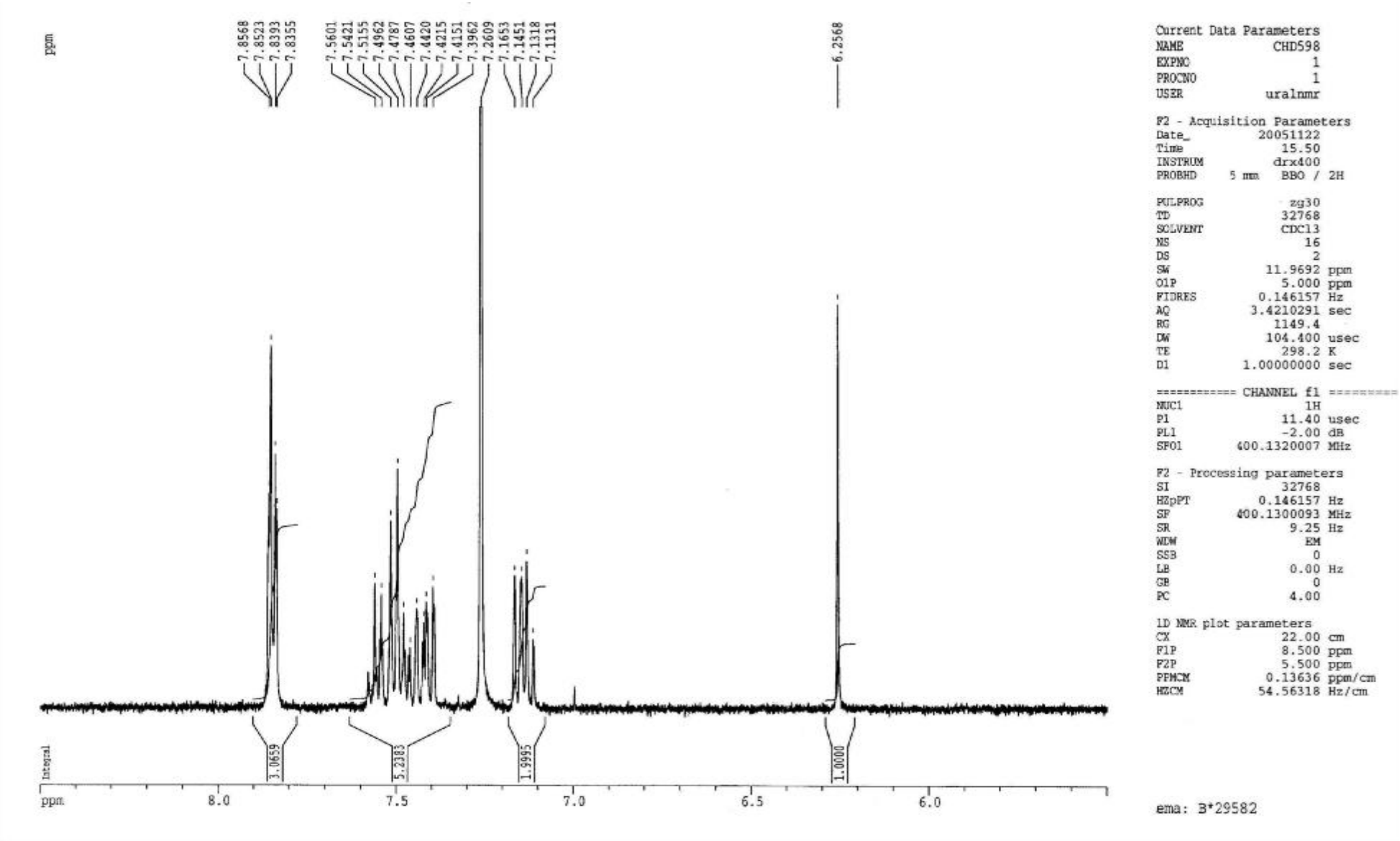
============ CHANNEL f1 =======
NUC1                      1H
P1                     11.40 usec
PL1                    -2.00 dB
SFO1             400.1320007 MHz

F2 - Processing parameters
SI                    32768
HZpPT               0.146157 Hz
SF               400.1300091 MHz
SR                     9.11 Hz
WDW                      EM
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     4.00

1D NMR plot parameters
CX                    22.00 cm
F1P                   8.500 ppm
F2P                   0.500 ppm
PPMCM                0.36354 ppm/cm
HZCM               145.50182 Hz/cm
```

meg: B*29772

Copy of ^{1}H NMR spectrum of **7c**

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Current Data Parameters
NAME                  CHD598
EXPNO                      1
PROCNO                     1
USER                uralnmr

F2 - Acquisition Parameters
Date_              20051122
Time                  15.50
INSTRUM              drx400
PROBHD     5 mm   BBO / 2H

PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SW                 11.9692 ppm
O1P                 5.000 ppm
FIDRES             0.146157 Hz
AQ                 3.4210291 sec
RG                    1149.4
DW                   104.400 usec
TE                    298.2 K
D1              1.00000000 sec

============ CHANNEL f1 =========
NUC1                      1H
P1                     11.40 usec
PL1                    -2.00 dB
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                    32768
HZpPT              0.146157 Hz
SF             400.1300093 MHz
SR                    9.25 Hz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.00 cm
F1P                  8.500 ppm
F2P                  5.500 ppm
PPMCM              0.13636 ppm/cm
HZCM              54.56318 Hz/cm

ema: B*29582
```