SUPPORTING INFORMATION

Metallo-Nucleosides: Synthesis and Biological Evaluation of Hexacarbonyl Dicobalt 5-Alkynyl-2'-Deoxyuridines †

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Table S1. Comparison of ^{1}H NMR shifts for compounds **8a-h** (acetone-d_6).[36]

	N-3	H-6	H-1'	OH-5'	OH-3'	H-3'	H-4'	H-5'	H-2'	Other signals
8a	10.28	8.37	6.39	4.53[a]	4.43	4.32	4.04	3.82[a]	2.30[a]	3.09 (2H, H-1"), 1.71 (2H, H-2"), 1.06 (3H, H-3")
8b	10.27	8.35	6.39	4.53[a]	4.43	4.31	4.03[a]	3.77[a]	2.29[a]	2.51[a] (1H, H-1"), 1.15[a] and 0.80[a] (4H, H-2", H-3")
8c	10.60	8.47	6.38	4.53	4.45	4.34	4.06[a]	3.81[a]	2.30[a]	5.59 ($\underline{H}OC_6H_{10}$), 1.72[a] (9H, *c*-C_6H_{10}), 1.22[a] (1H, *c*-C_6H_{10})
8d	10.32	8.43	6.43	4.52	4.43	4.24	4.04[a]	3.75[a]	2.32[a]	7.53 (2H, *o*-$C_6H_4CH_3$), 7.19 (2H, *m*-C_6H_4 CH_3), 2.32 (3H, CH_3)
8e	10.34	8.43	6.43	4.53[a]	4.46	4.26	4.06[a]	3.78[a]	2.30[a]	7.56 (2H, *o*-C_6H_4), 7.22 (2H, *m*-C_6H_4), 2.61 (2H, H-1"), 1.64[a] (2H, H-2"), 1.34[a] (4H, H-3", H-4"), 0.89 (3H, H-5")
8f	10.33	8.44	6.44	4.52[a]	4.43	4.21[a]	4.05[a]	3.77[a]	2.29[a]	7.60 (2H, *o*-$C_6H_4C(CH_3)_3$), 7.44 (2H, *m*-$C_6H_4C(CH_3)_3$), 1.35 (9H, $C(CH_3)_3$)
8g	10.38	8.29	6.38	4.56[a]	4.44	4.26	4.05	3.85[a]	2.30[a]	0.37 (9H, $Si(CH_3)_3$)
8h	10.25	8.57	6.35	4.53	4.44	4.36	4.02[a]	3.84[a]	2.29[a]	6.71 (1H, C≡C-H)

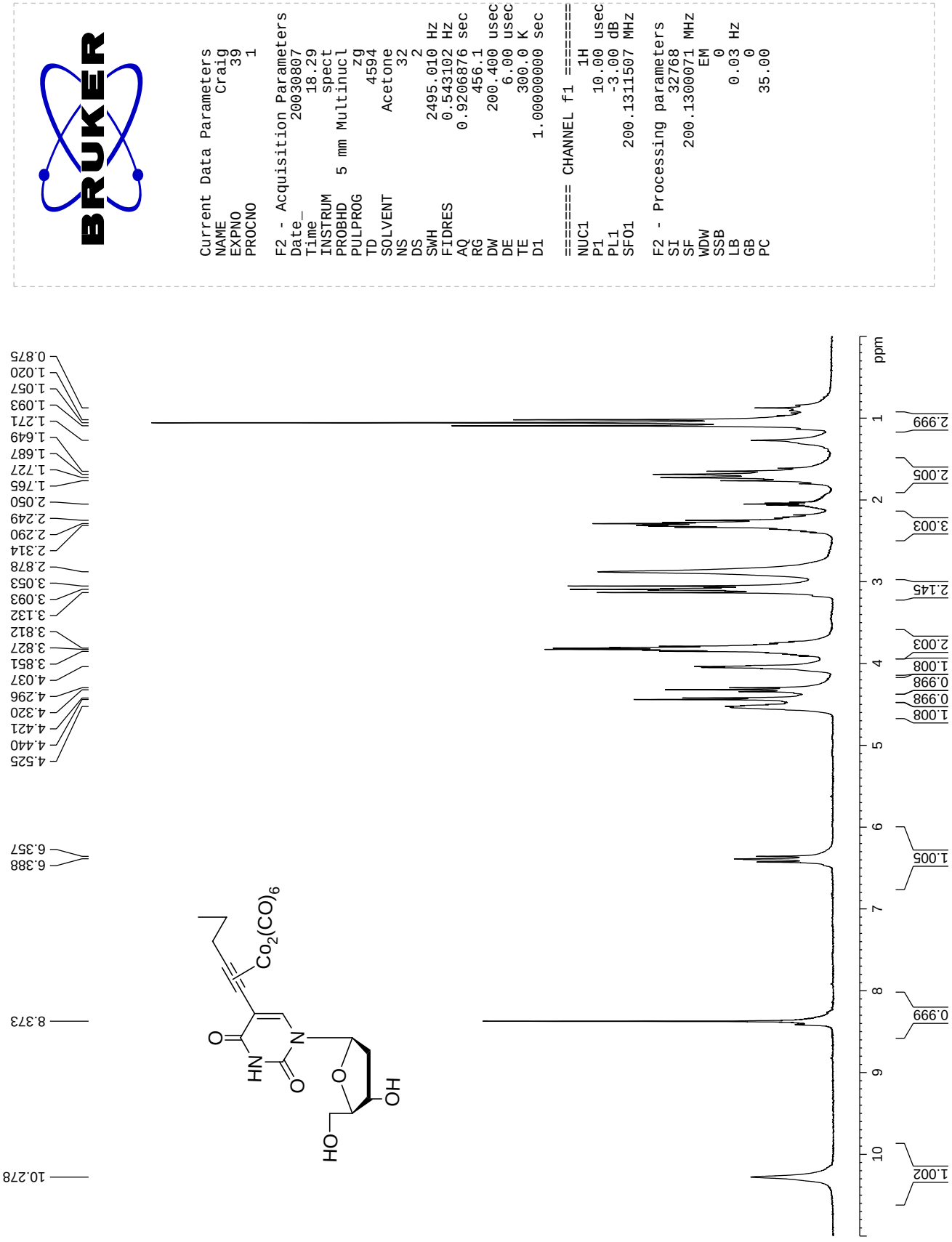
a) center of the multiplet. Ranges given in experimental part.

Table S2. Comparison of ^{13}C NMR shifts for compounds **8a-h** (acetone-d_6).[36]

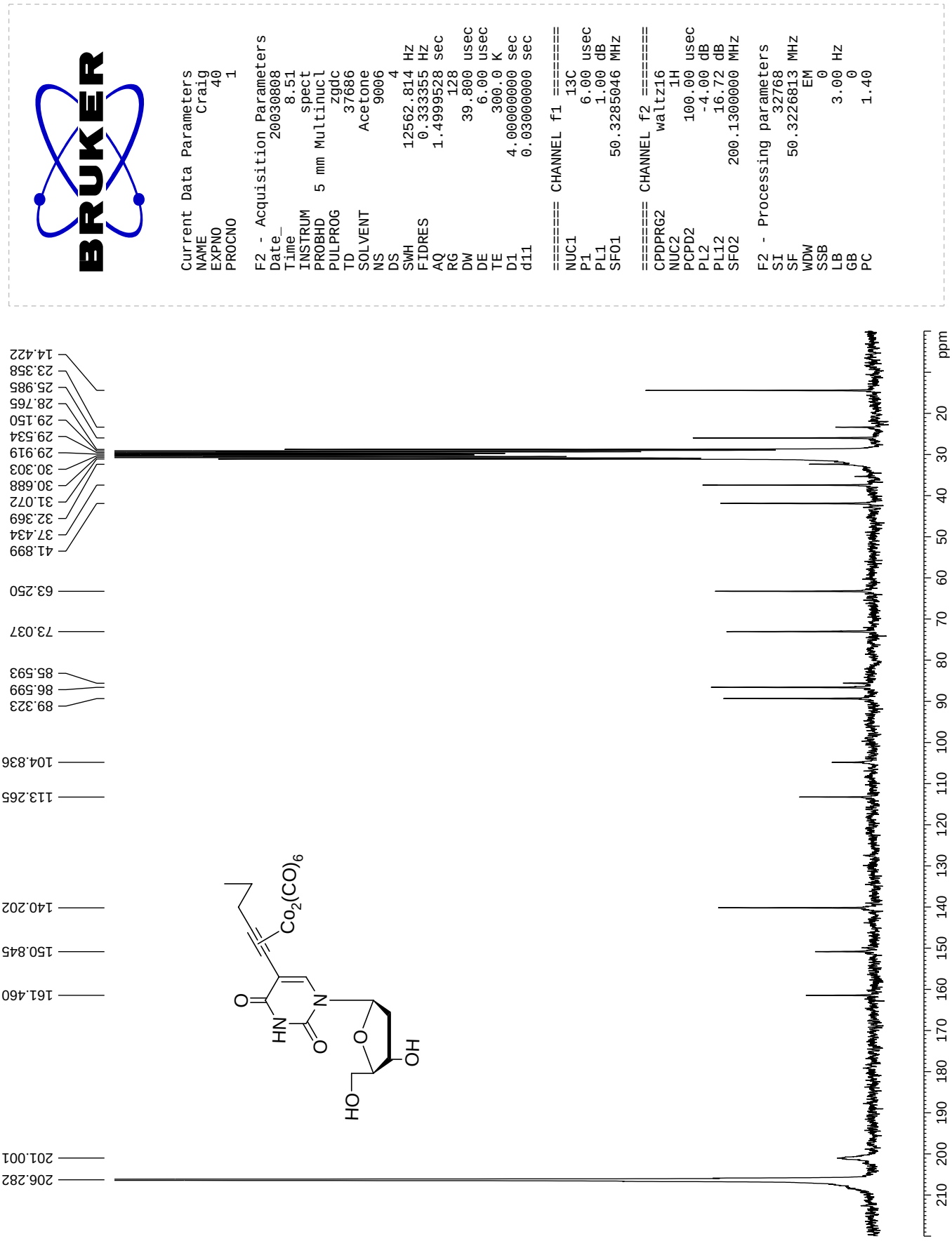
	CO	C-4	C-2	C-6	C-5	dUC≡C	C-4′	C-1′	dUC≡C	C-3′	C-5′	C-2′	Other signals
8a	201.0	161.5	150.8	140.2	113.3	104.8	89.3	86.6	85.6	73.0	63.3	41.9	37.4 (C-1"), 26.0 (C-2"), 14.4 (C-3")
8b	200.8	161.3	150.8	139.6	113.2	109.2	89.2	86.4	85.0	73.0	63.2	41.8	16.3 (C-1"), 13.1 and 12.9 (C-2", C-3")
8c	200.8	162.9	150.3	142.2	113.1	112.6	89.4	86.7	84.4	73.0	63.1	42.0	73.2 (C-1"), 40.6 and 40.4 (C-2"), 26.5 (C-4"), 23.9 and 22.8 (C-3")
8d	200.5	160.8	150.8	139.8	113.6	96.7	89.2[a]	86.4[a]	86.2	73.1	63.3	41.9	138.8 (*p*-$C_6H_4CH_3$), 136.3 (*i*-$C_6H_4CH_3$), 130.6 (*o*-$C_6H_4CH_3$), 130.2 (*m*-$C_6H_4CH_3$), 21.4 (CH_3)
8e	200.6	160.8	150.8	143.8	113.6	96.7	89.2	86.4	86.2	73.1	63.2	41.8	139.8 (*p*-C_6H_4), 136.5 (*i*-C_6H_4), 130.6 (*o*-C_6H_4), 129.5 (*m*-C_6H_4), 36.4 (C-1"), 32.3 (C-3"), 31.8 (C-2"), 23.2 (C-4"), 14.3 (C-5")
8f	200.5	160.9	151.0	139.8	113.6	96.5	89.2	86.4	86.2	73.1	63.3	41.9	151.8 (*p*-C_6H_4), 136.3 (*i*-C_6H_4), 130.4 (*o*-C_6H_4), 126.5 (*m*-C_6H_4), 35.3 $\underline{C}(CH_3)_3$, 31.5 $C(\underline{C}H_3)_3$
8g	201.1	160.8	150.6	140.7	113.7	98.1	89.2	86.5	85.7	73.0	63.1	41.7	1.0 $Si(CH_3)_3$
8h	200.9	161.5	150.8	141.0	111.9	76.6	89.2	86.6	83.1	72.5	62.9	41.9	–

a) reversed assignment to that one reported in ref. 32.

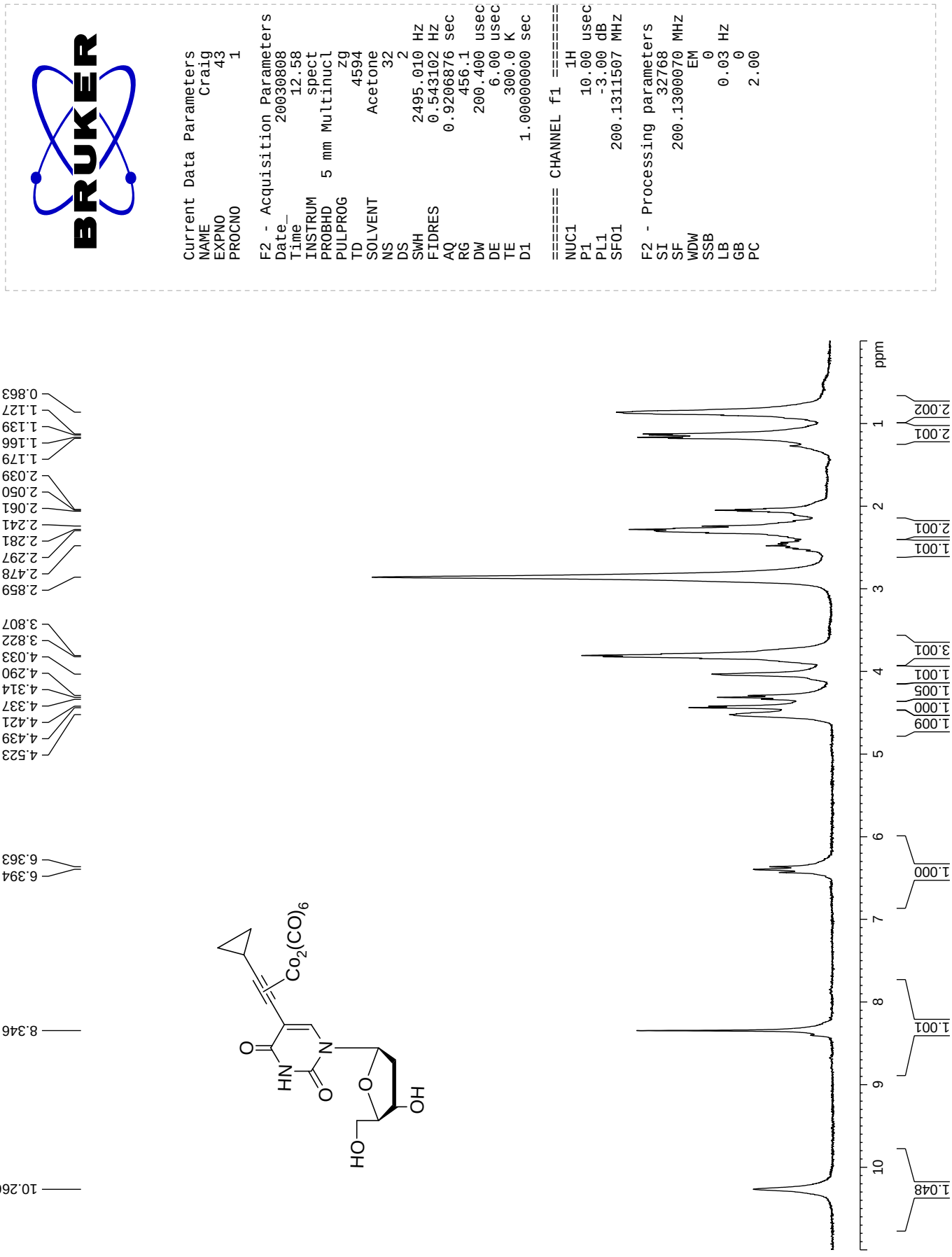
^{1}H NMR spectrum for **8a** (acetone-d_6)



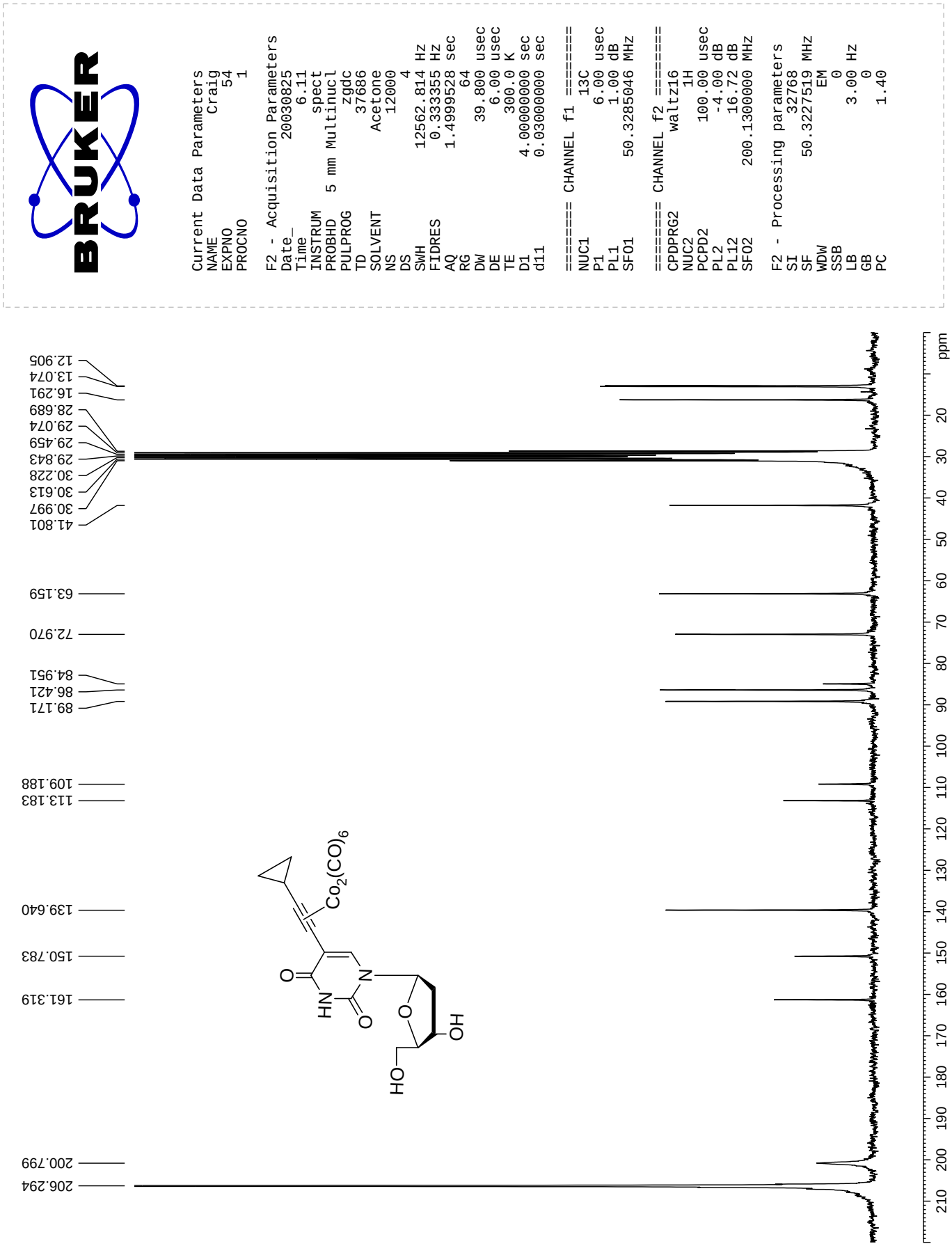
^{13}C NMR spectrum for **8a** (acetone-d_6)



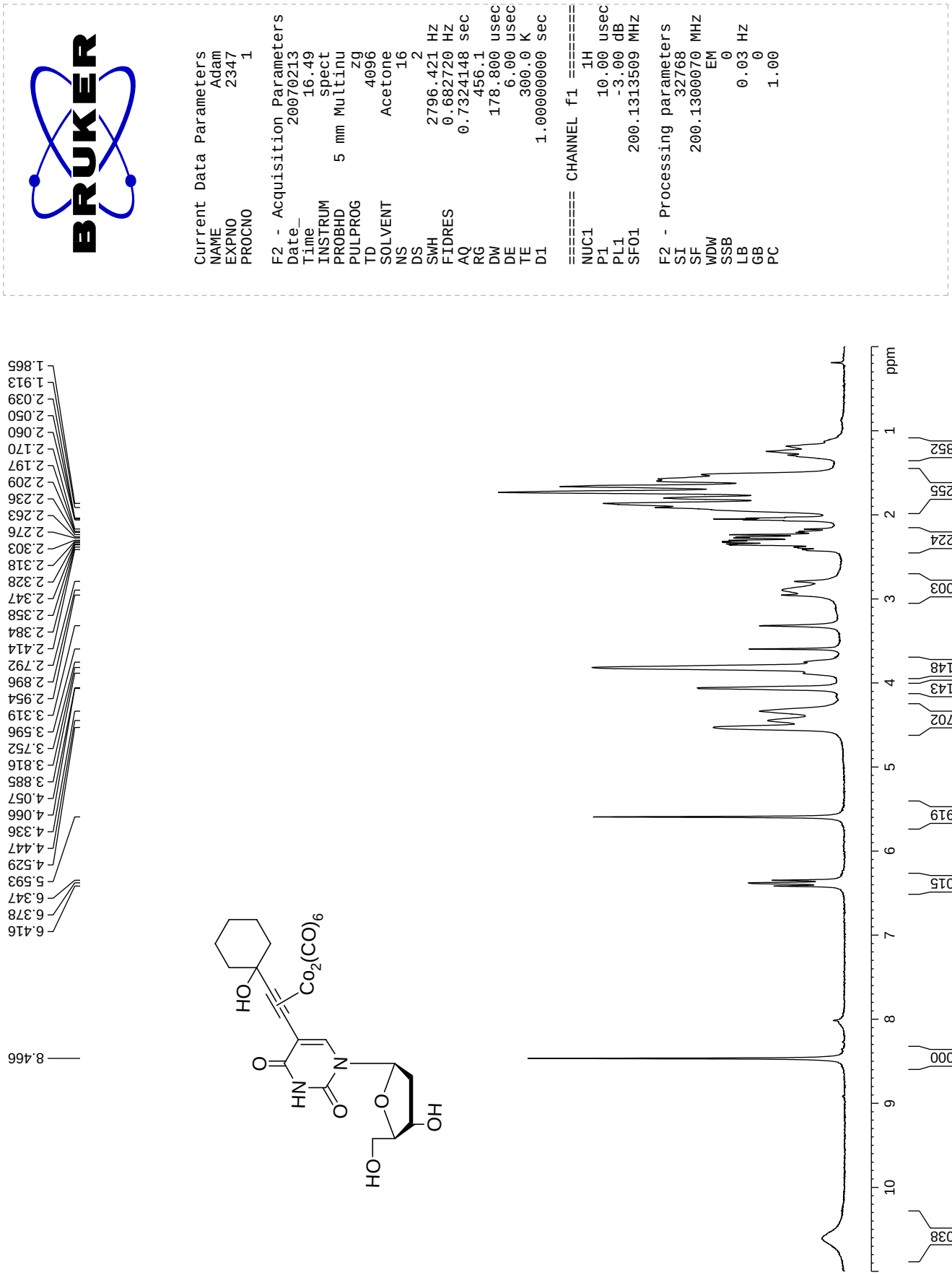
^{1}H NMR spectrum for **8b** (acetone-d_6)



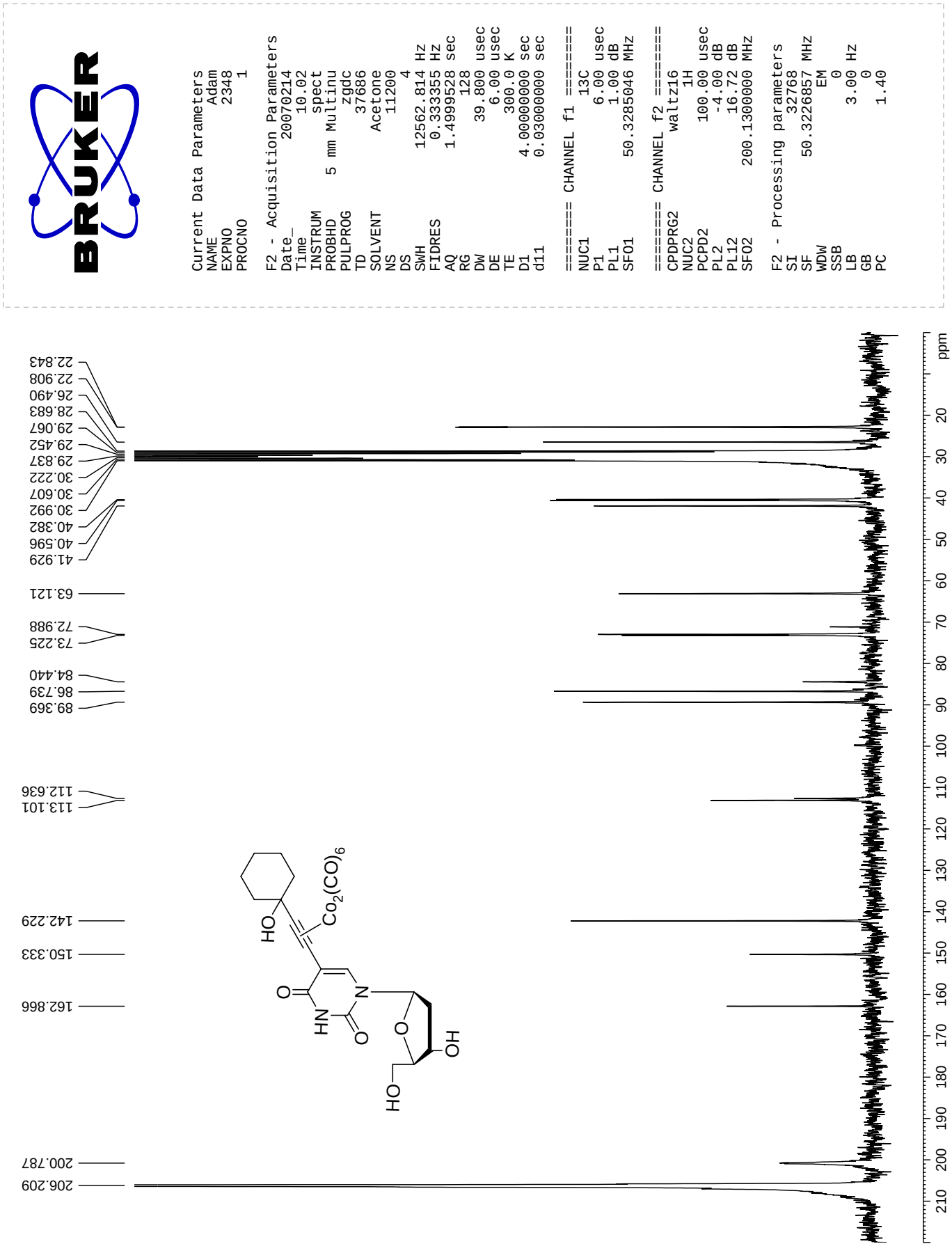
^{13}C NMR spectrum for **8b** (acetone-d_6)



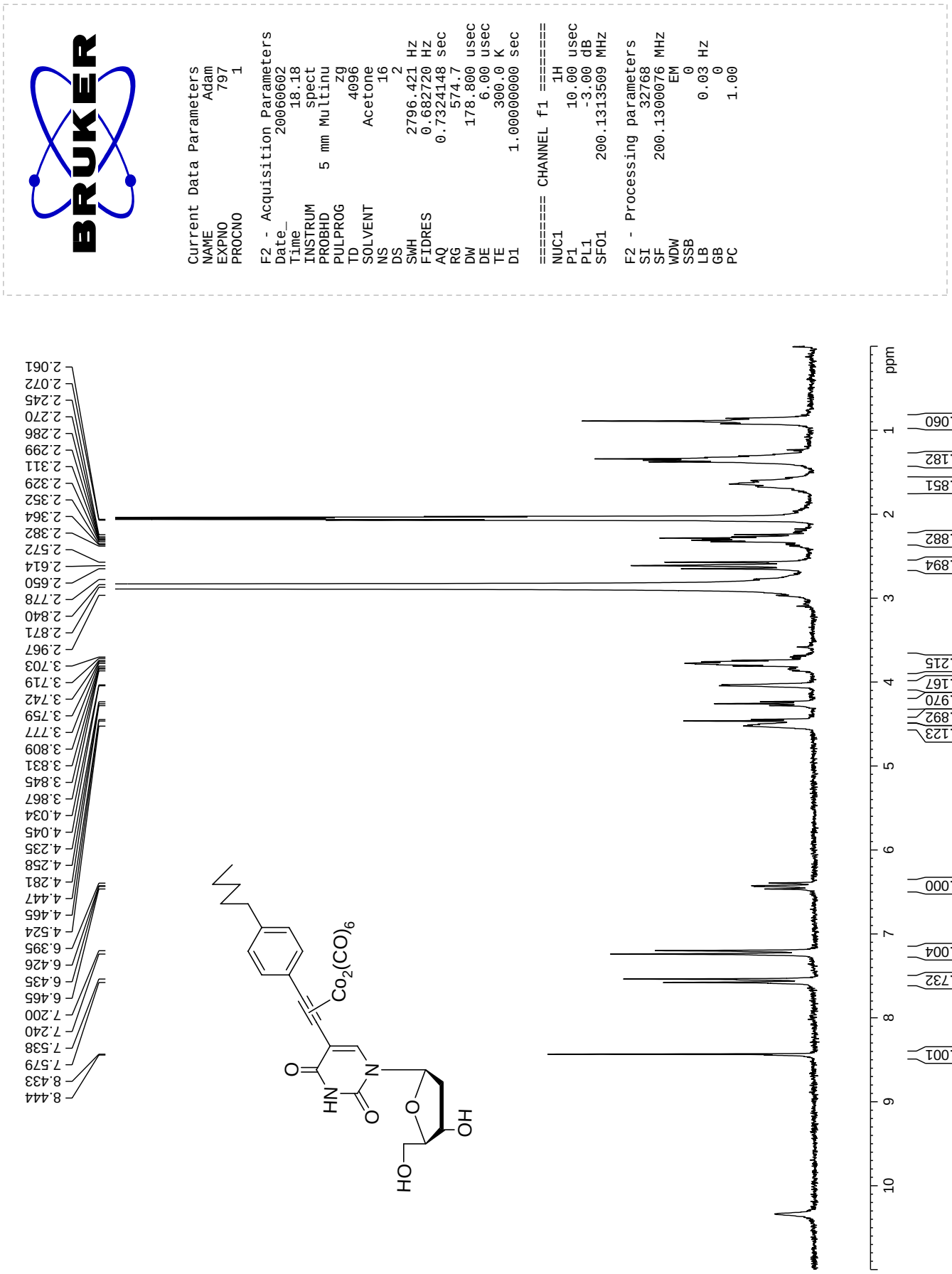
^{1}H NMR spectrum for **8c** (acetone-d_6)



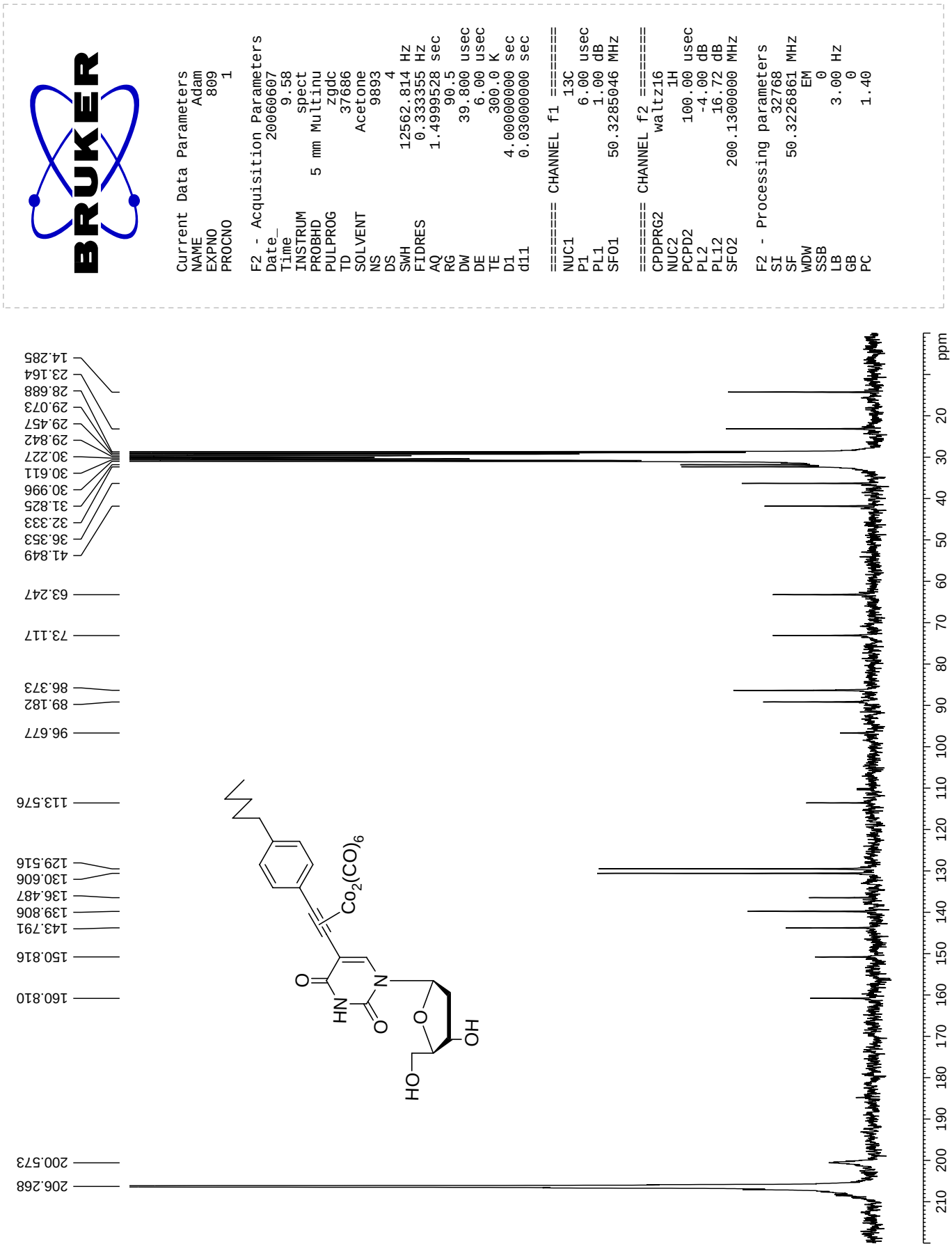
^{13}C NMR spectrum for **8c** (acetone-d_6)



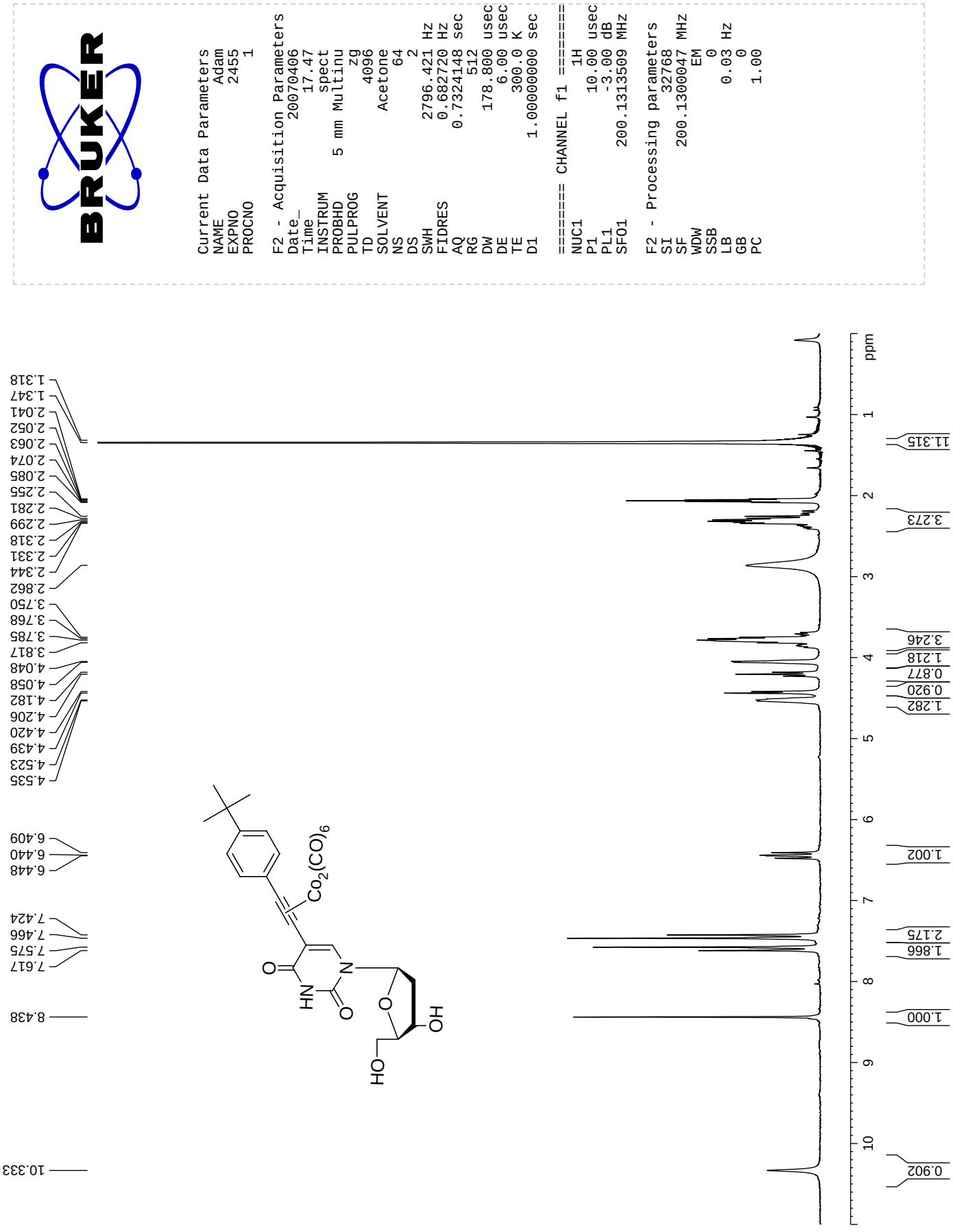
^{1}H NMR spectrum for **8e** (acetone-d_6)



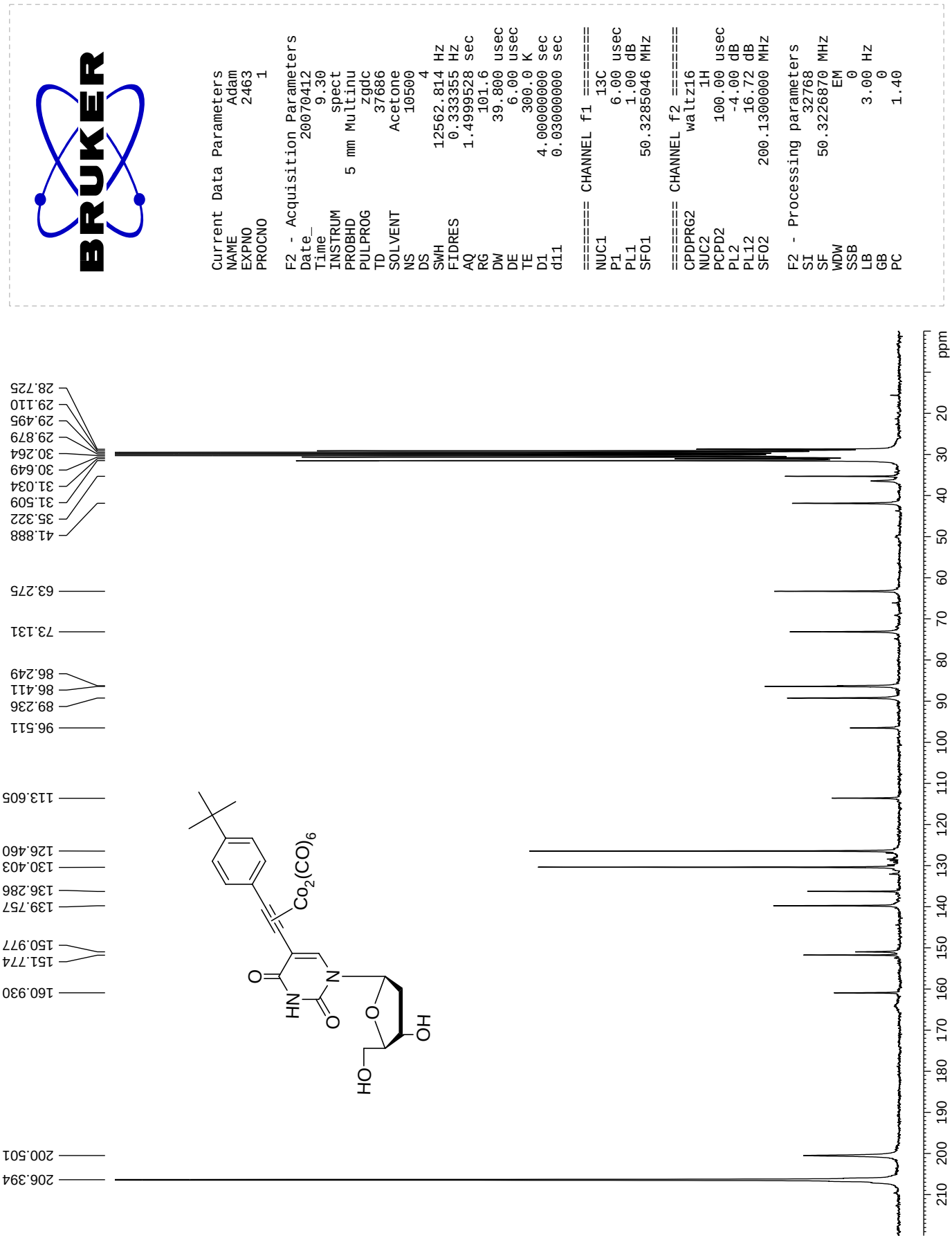
^{13}C NMR spectrum for **8e** (acetone-d_6)



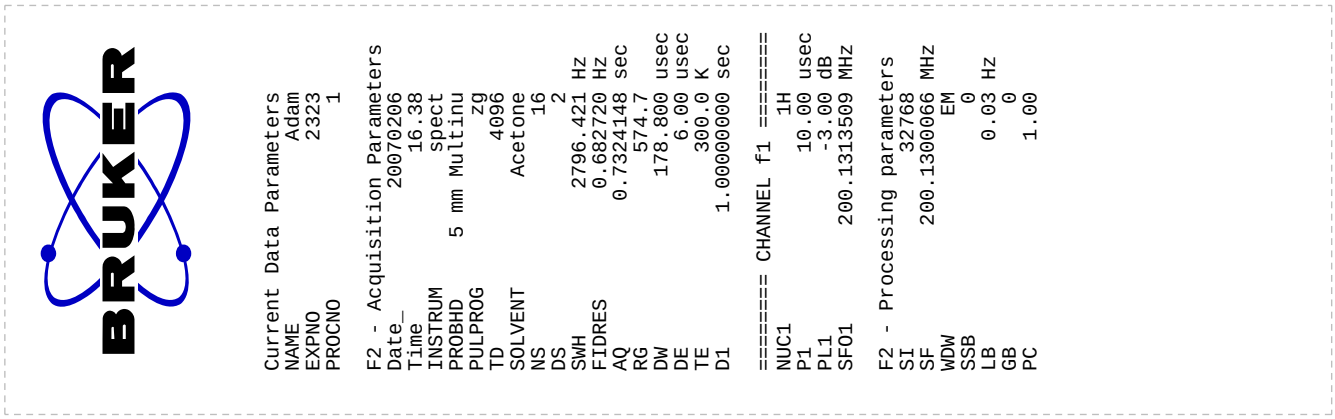
^{1}H NMR spectrum for **8f** (acetone-d_6)

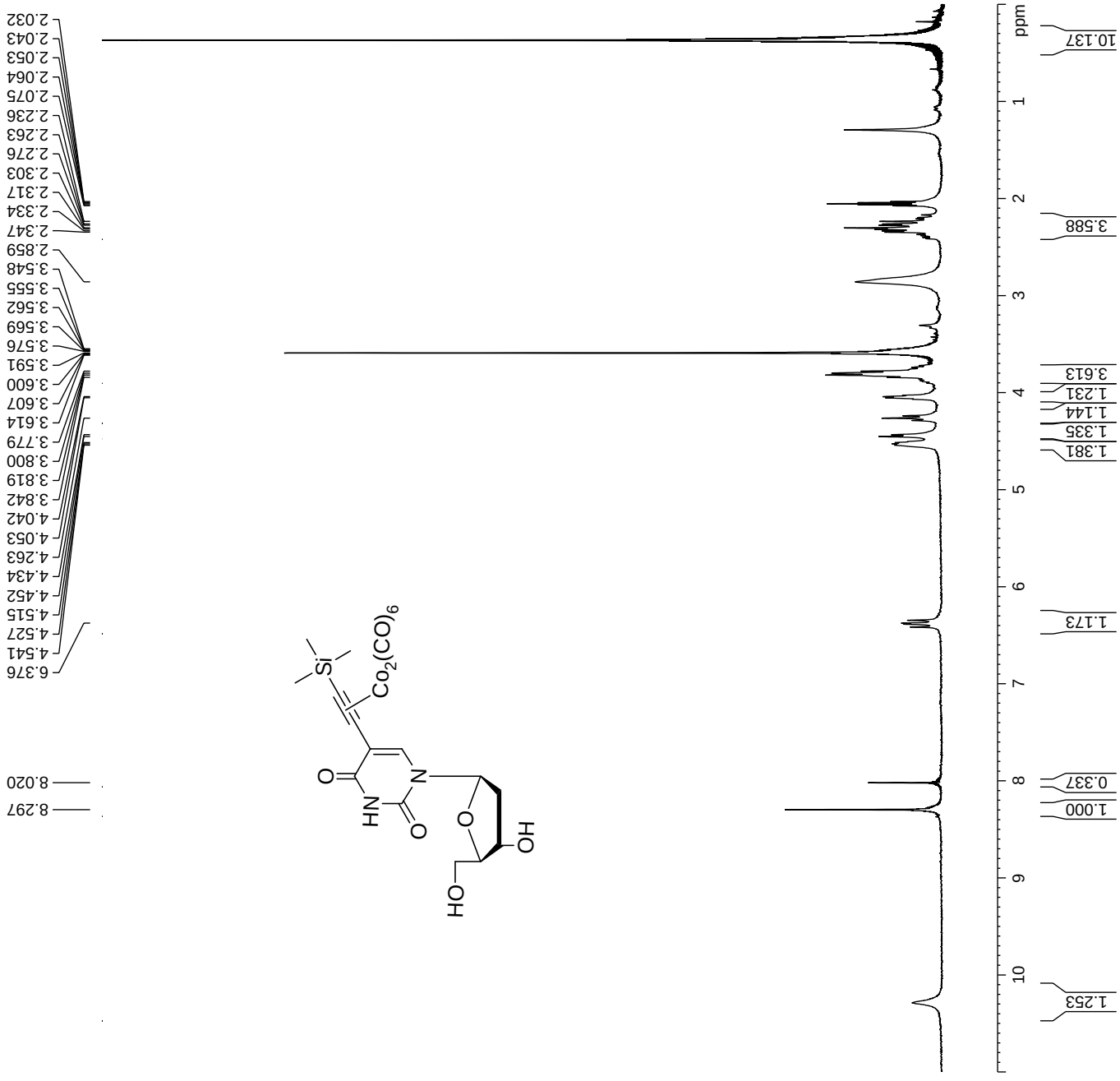


^{13}C NMR spectrum for **8f** (acetone-d_6)

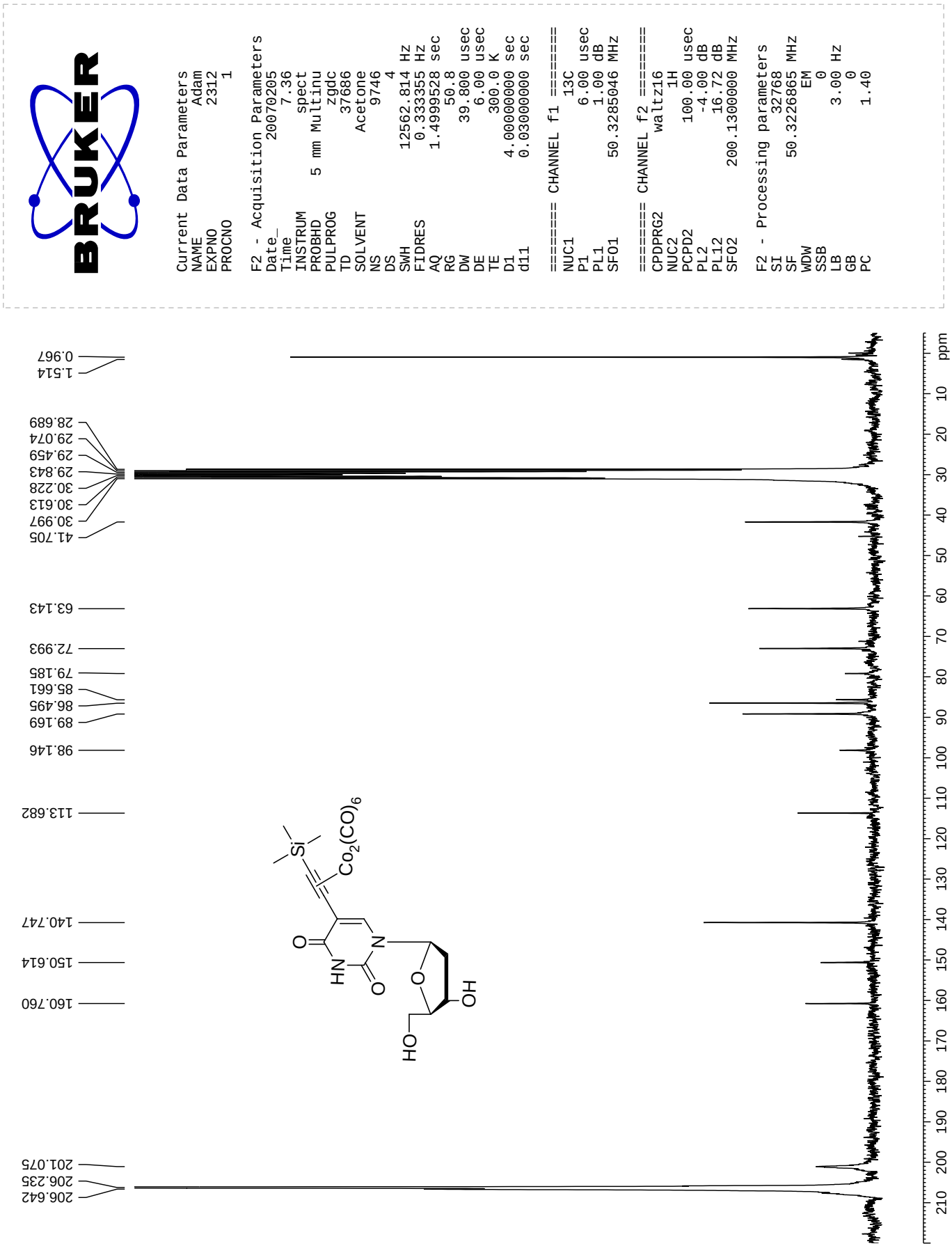


^{1}H NMR spectrum for **8g** (acetone-d_6)

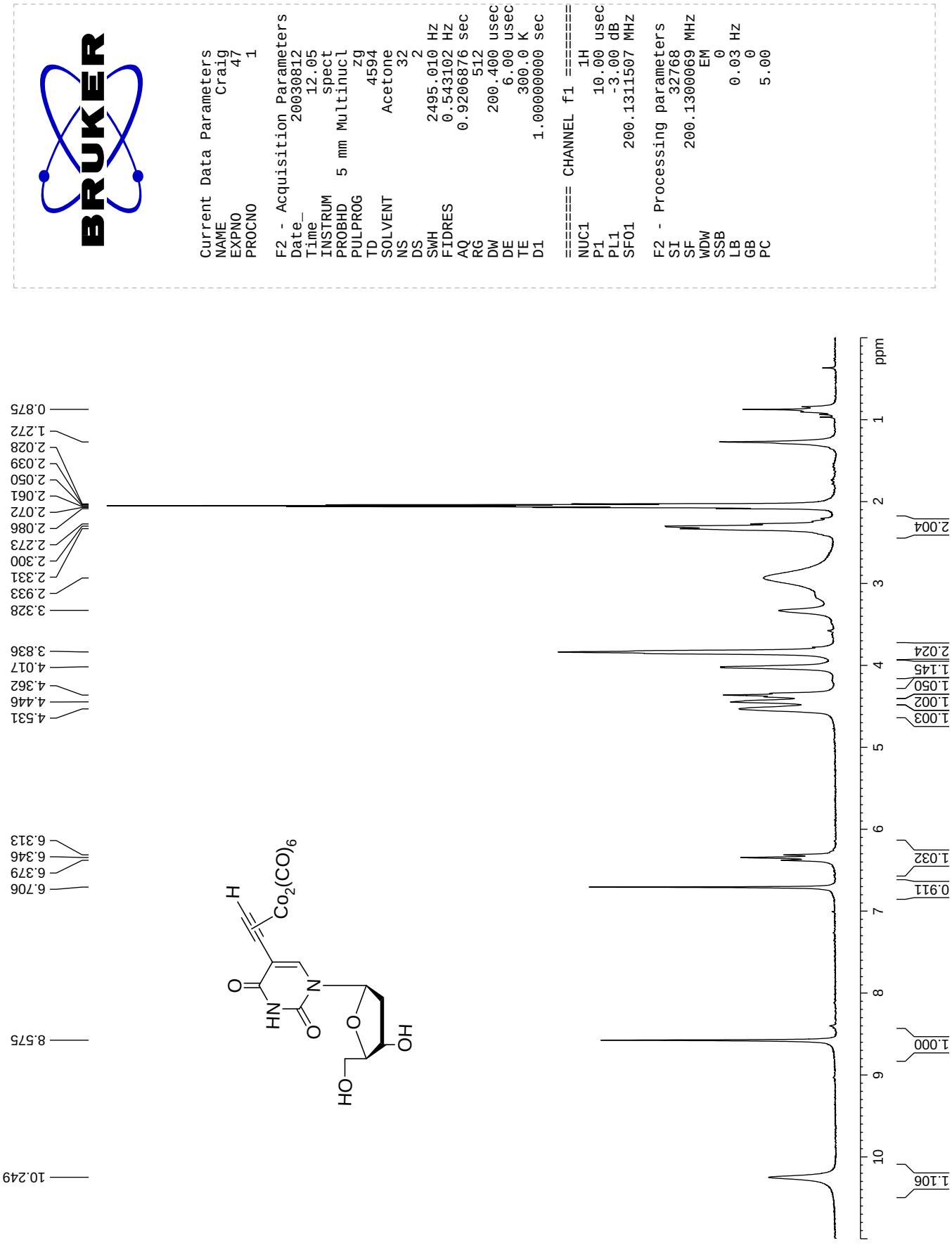




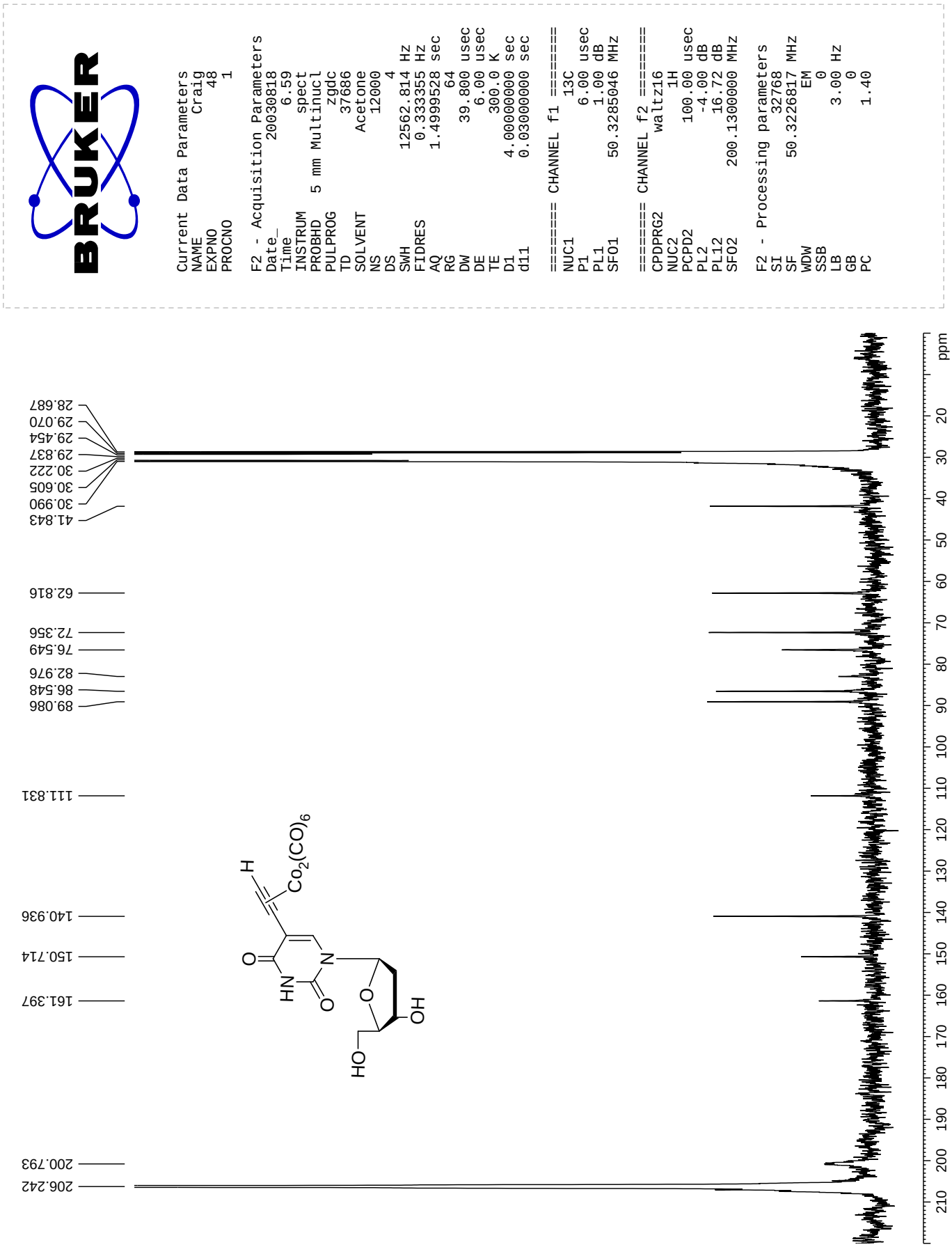
^{13}C NMR spectrum for **8g** (acetone-d_6)



^{1}H NMR spectrum for **8h** (acetone-d_6)



^{13}C NMR spectrum for **8h** (acetone-d_6)

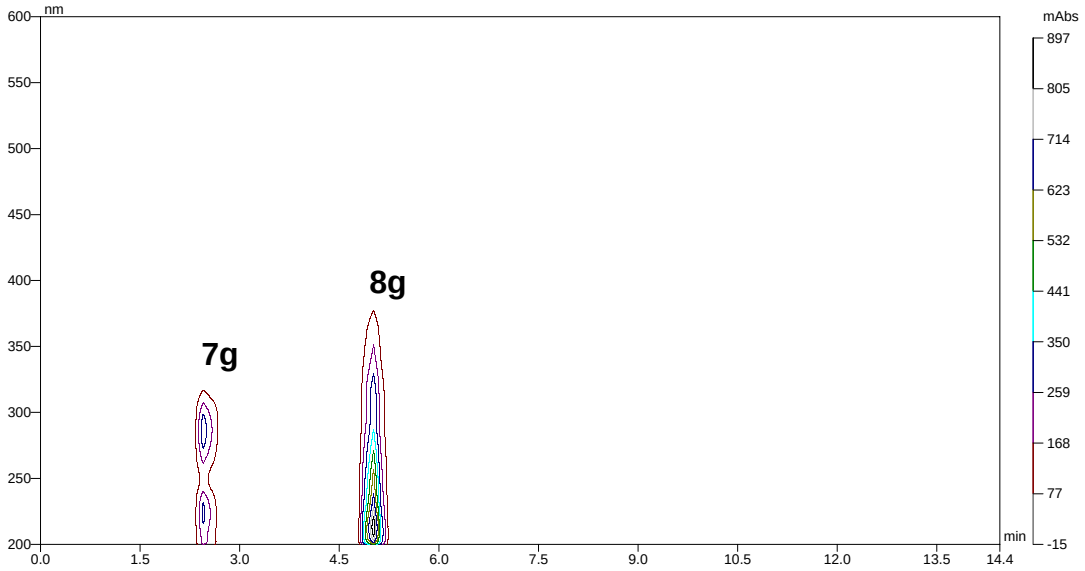


Comparison of R_f for pairs of nucleosides 7g/8g and 7h/8h with the use of HPLC.

Instrument: Kontron System 522 equipped with an autosampler (Kontron 565) and diode array detector (Kontron 540). Stationary phase: Eurospher 100-5 C18, 250 x 4 mm. Mobile phase: MeOH/H_2O 80:20. Mode: isocratic, flow rate: 0.8 mL/min.

Samples: Methanolic solutions of compounds were injected.

Compounds pair: 7g/8g



Compounds pair: 7h/8h

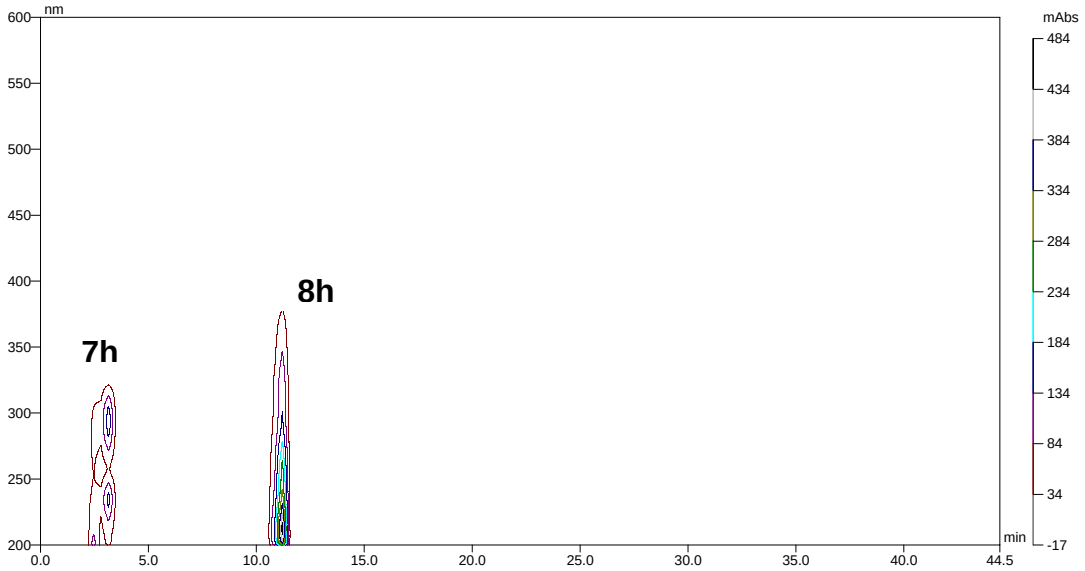


Table S3. Crystal data and structure refinement for **8c**.

Empirical formula	C23 H22 Co2 N2 O12	
Formula weight	636.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.7674(9) Å	α= 90°
	b = 9.3303(9) Å	β= 90°
	c = 31.529(3) Å	γ = 90°
Volume	2579.1(4) $Å^3$	
Z	4	
Density (calculated)	1.639 g/cm^3	
Absorption coefficient	1.354 mm^{-1}	
F(000)	1296	
Crystal size	0.11 x 0.06 x 0.04 mm^3	
Theta range for data collection	1.29 to 28.27°	
Index ranges	-11<=h<=11, -12<=k<=12, -41<=l<=40	
Reflections collected	22063	
Independent reflections	5984 [R(int) = 0.0564]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5984 / 0 / 355	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0760	
R indices (all data)	R1 = 0.0431, wR2 = 0.0786	
Absolute structure parameter	0.010(12)	
Largest diff. peak and hole	0.804 and -0.276 e $Å^{-3}$	

Figure S1. Packing diagrams for **8c**.