

SUPPORTING INFORMATION

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

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Table S1. Comparison of ^1H 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 (<u>H</u> OC ₆ H ₁₀), 1.72 ^a (9H, <i>c</i> -C ₆ H ₁₀), 1.22 ^a (1H, <i>c</i> -C ₆ H 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, <i>o</i> -C ₆ H ₄ CH ₃), 7.19 (2H, <i>m</i> -C ₆ H 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, <i>o</i> -C ₆ H ₄), 7.22 (2H, <i>m</i> -C ₆ H 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, <i>o</i> -C ₆ H ₄ C(CH ₃) ₃), 7.44 (2H, <i>m</i> -C ₆ H ₄ C(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 $\equiv$ C-H)

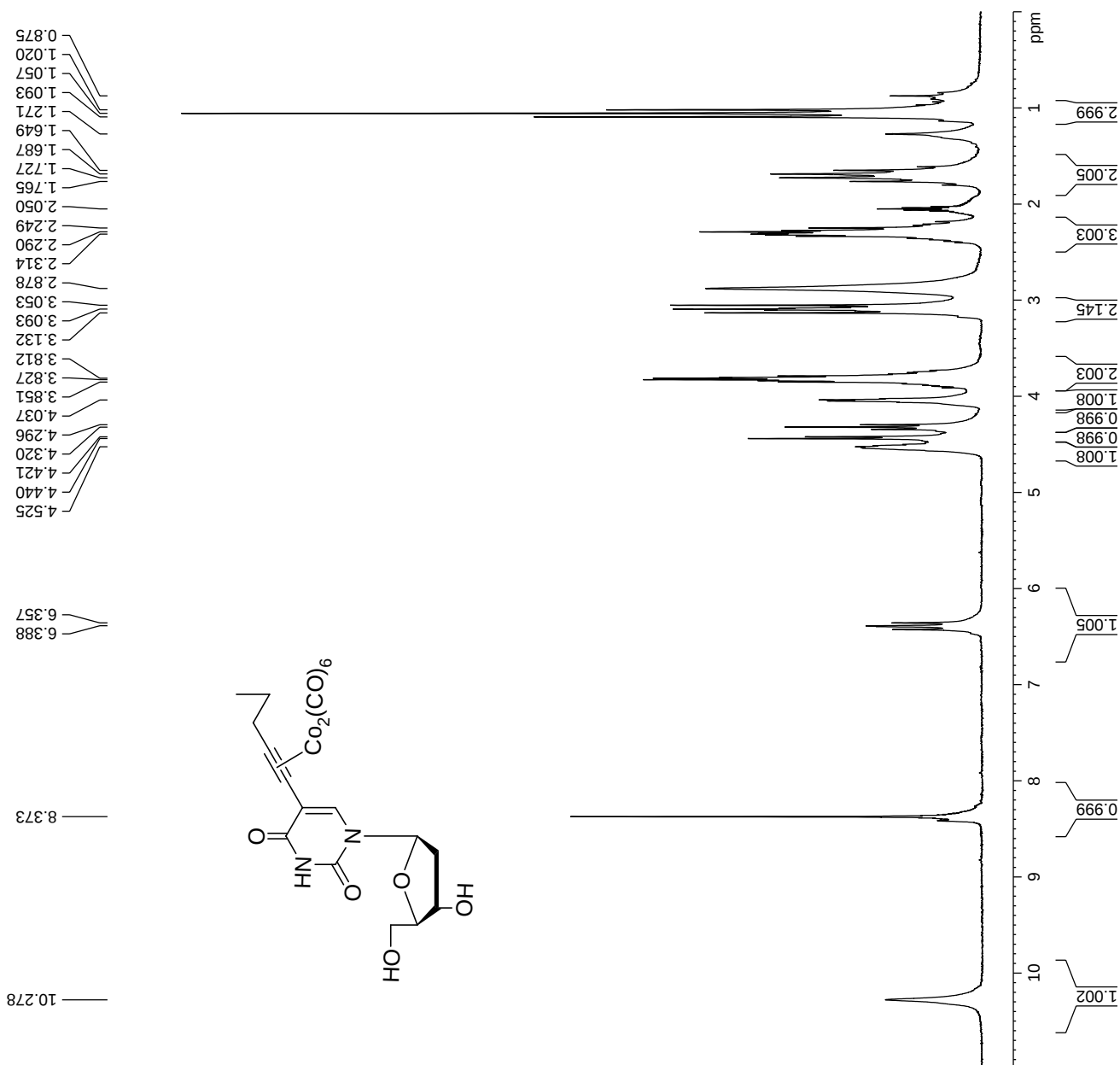
a) center of the multiplet. Ranges given in experimental part.

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	$\text{dUC}\equiv\text{C}$	C-4'	C-1'	$\text{dUC}\equiv\text{C}$	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 (<i>p</i> -C ₆ H ₄ CH ₃), 136.3 (<i>i</i> -C ₆ H ₄ CH ₃), 130.6 (<i>o</i> -C ₆ H ₄ CH ₃), 130.2 (<i>m</i> -C ₆ H ₄ CH 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 (<i>p</i> -C ₆ H ₄), 136.5 (<i>i</i> -C ₆ H ₄), 130.6 (<i>o</i> -C ₆ H ₄), 129.5 (<i>m</i> -C ₆ H 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 (<i>p</i> -C ₆ H ₄), 136.3 (<i>i</i> -C ₆ H ₄), 130.4 (<i>o</i> -C ₆ H ₄), 126.5 (<i>m</i> -C ₆ H ₄), 35.3 $\text{C}(\text{CH}_3)_3$, 31.5 $\text{C}(\text{CH}_3)_3$
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.

¹H NMR spectrum for **8a** (acetone-*d*₆)



```

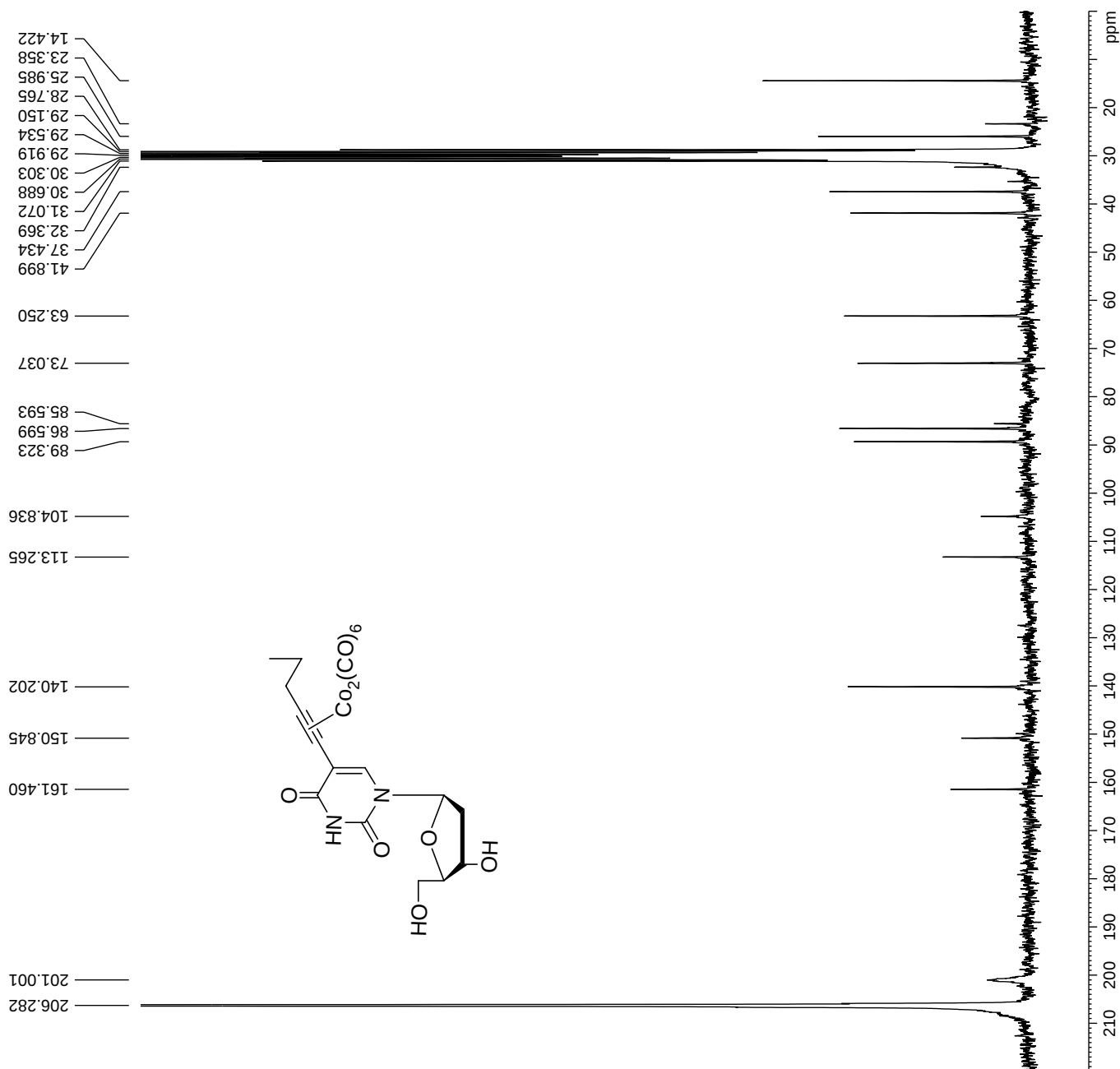
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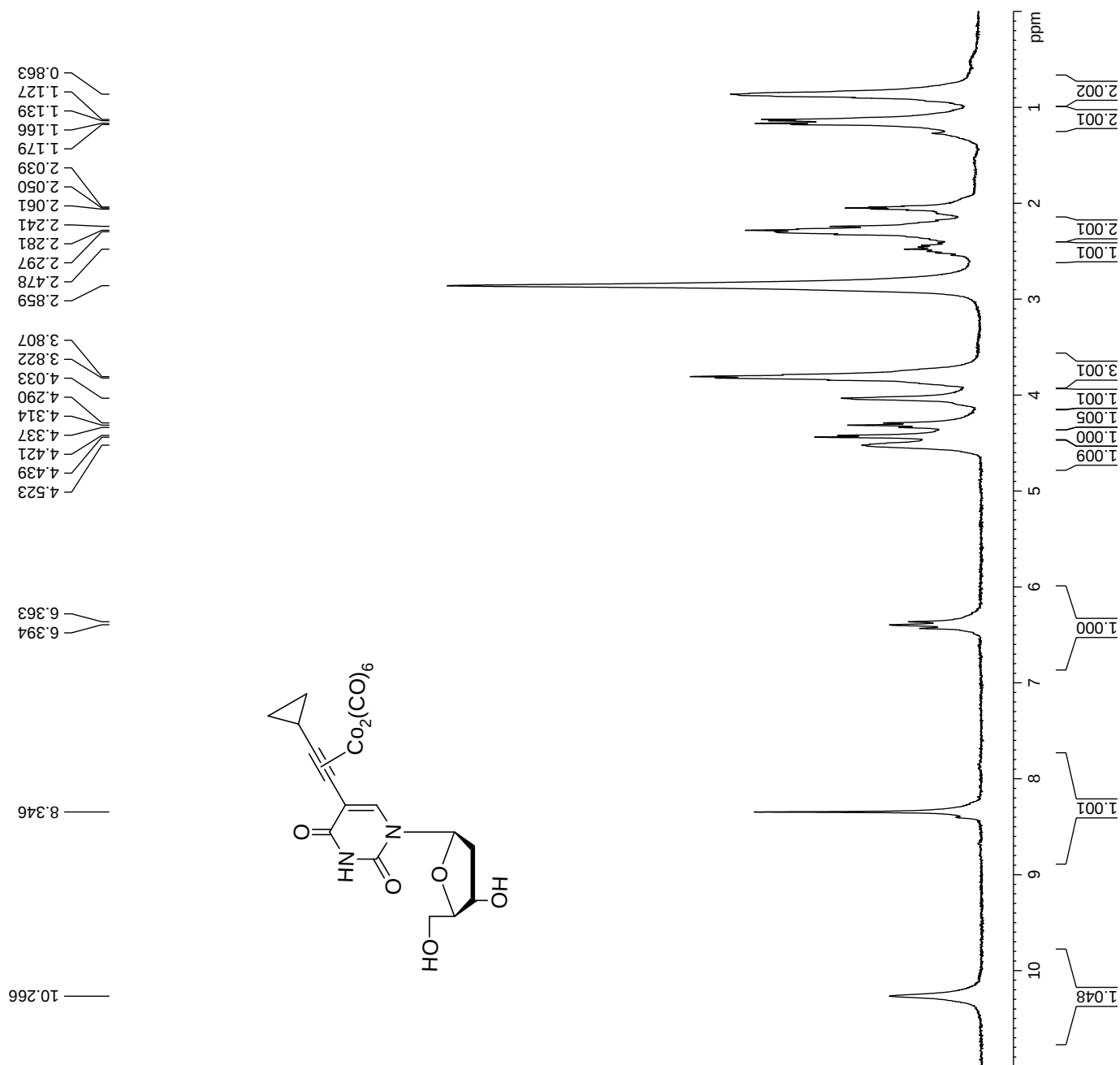
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¹³C NMR spectrum for **8a** (acetone-*d*₆)



¹H NMR spectrum for **8b** (acetone-d₆)



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 PROCNO 1

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 AQ 0.9206876 sec
 RG 456.1
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 D1 1.00000000 sec

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¹³C NMR spectrum for **8b** (acetone-*d*₆)



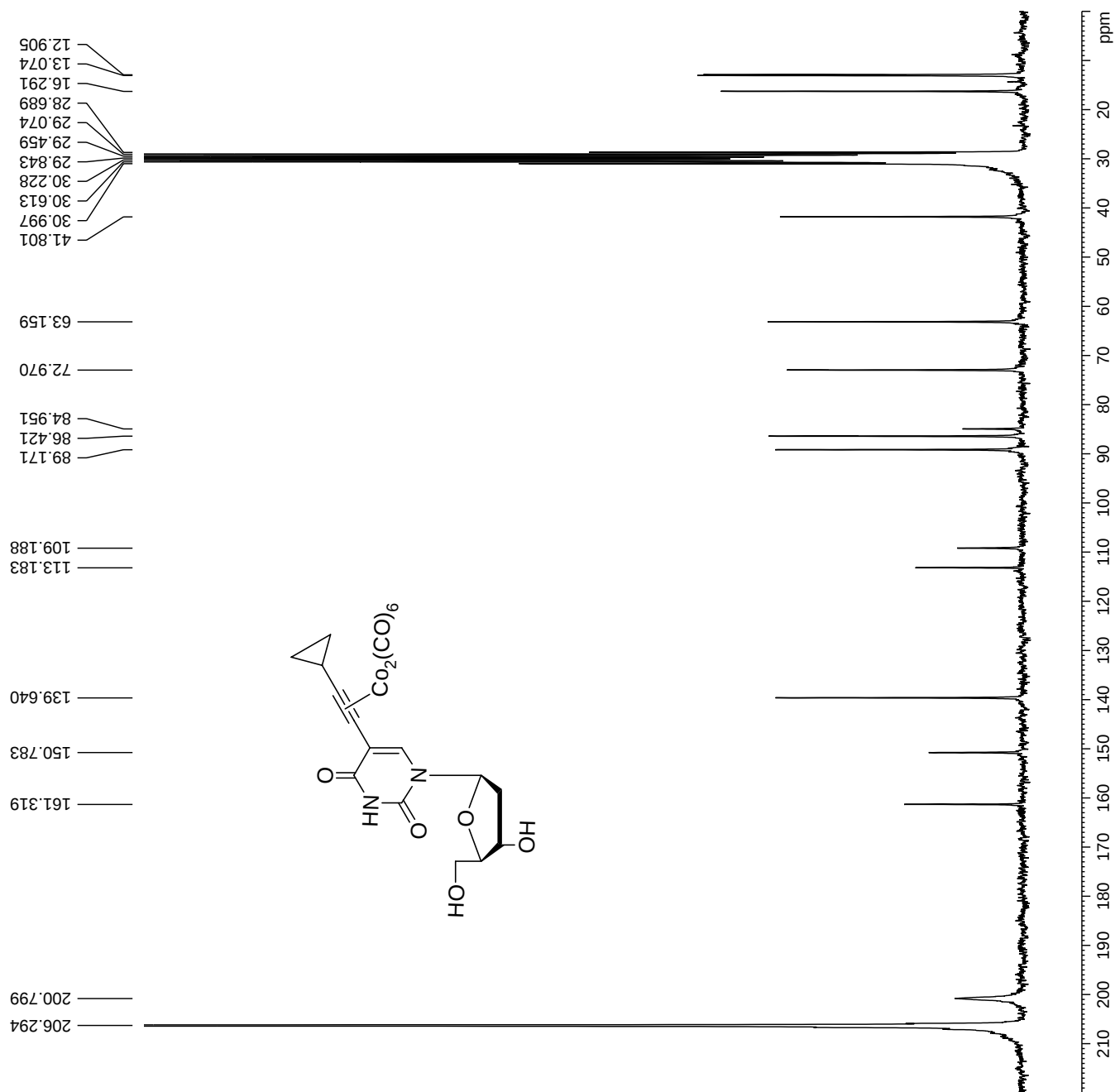
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FIDRES 0.333355 Hz
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TE 6.00 usec
D1 300.0 K
d11 4.00000000 sec
d11 0.03000000 sec

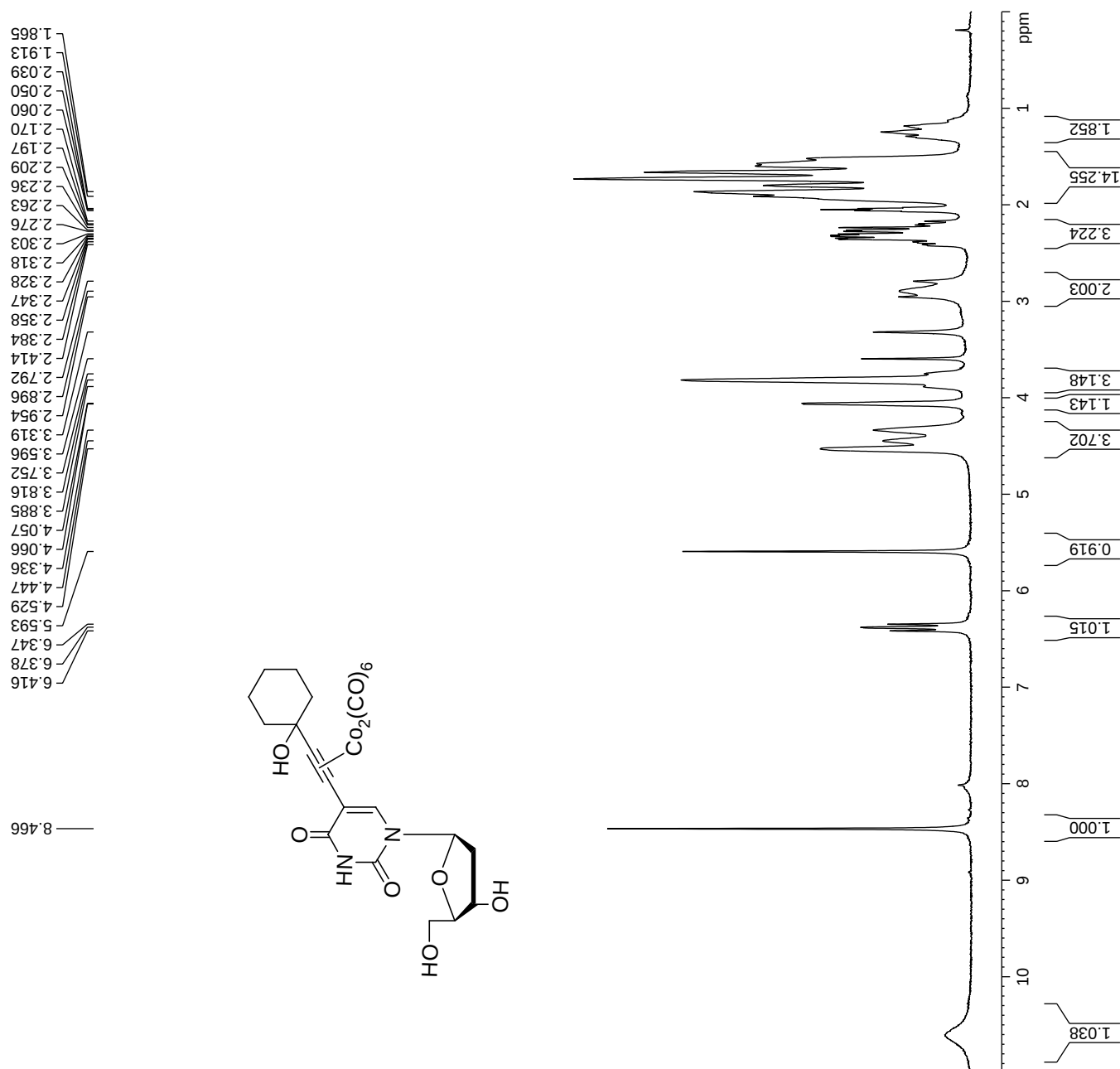
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¹H NMR spectrum for **8c** (acetone-*d*₆)



¹³C NMR spectrum for **8c** (acetone-*d*₆)



```

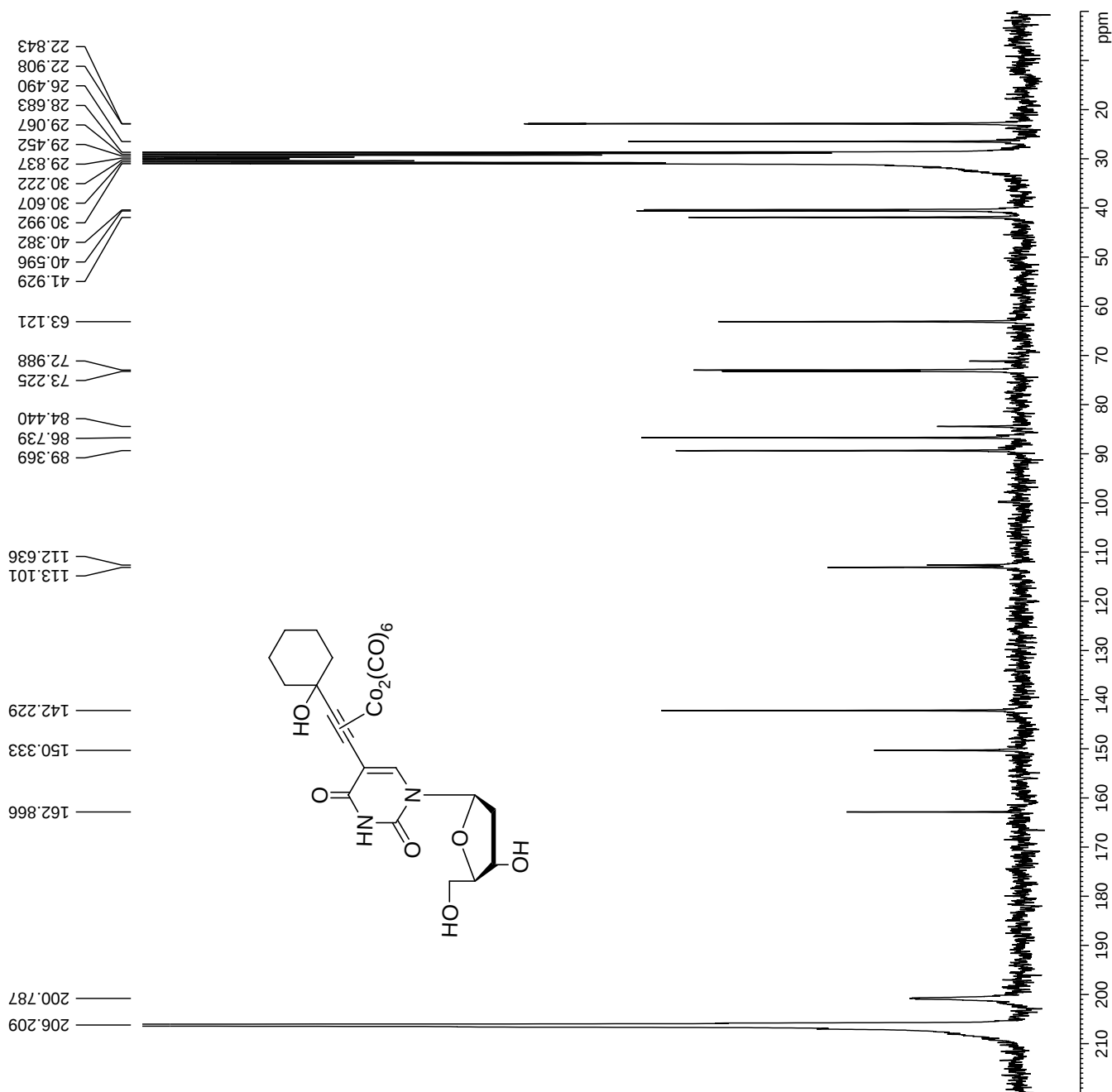
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¹H NMR spectrum for **8e** (acetone-*d*₆)

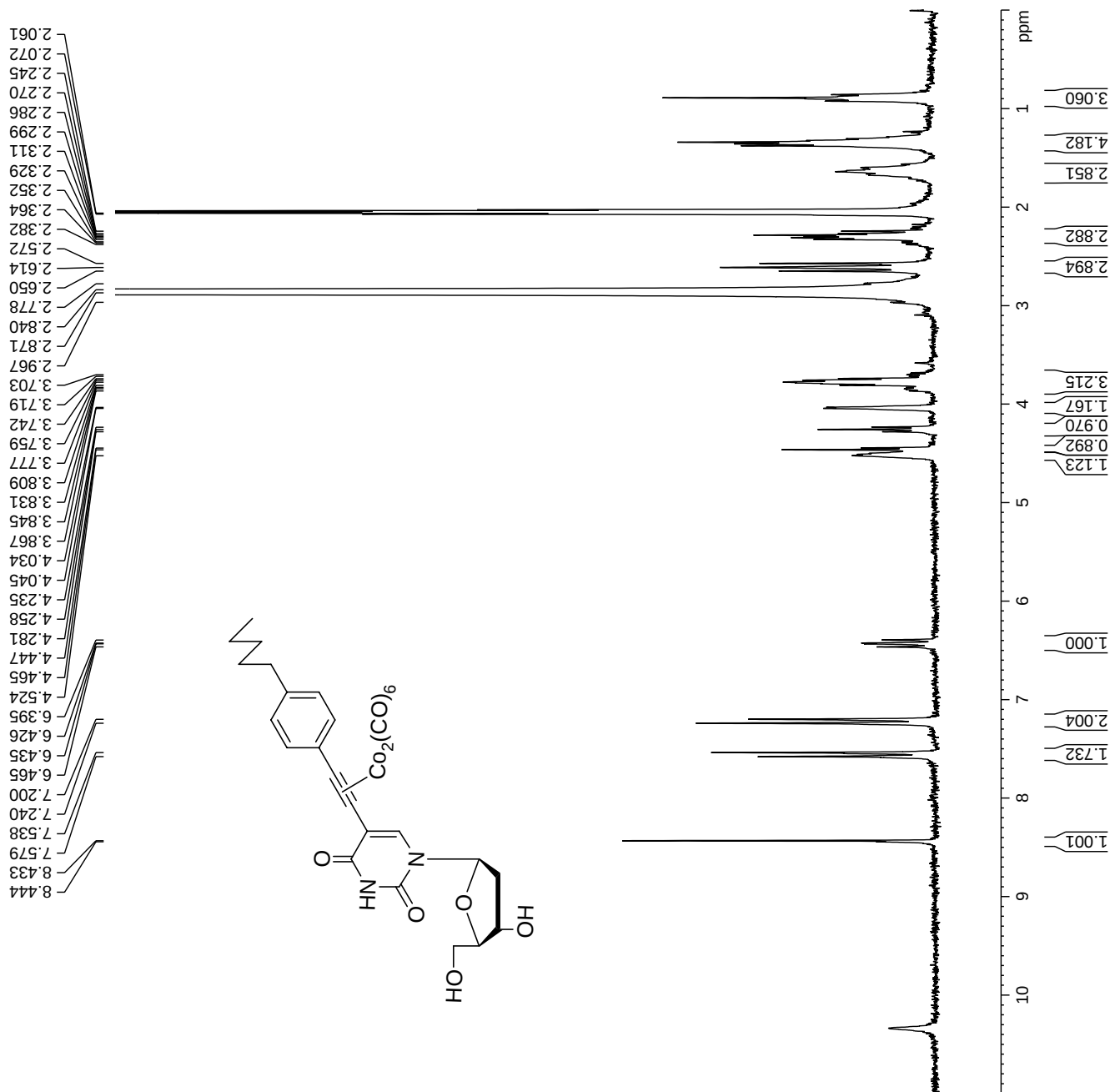


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 AQ 0.7324148 sec
 RG 574.7
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 D1 1.00000000 sec

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F2 - Processing parameters
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¹³C NMR spectrum for **8e** (acetone-*d*₆)



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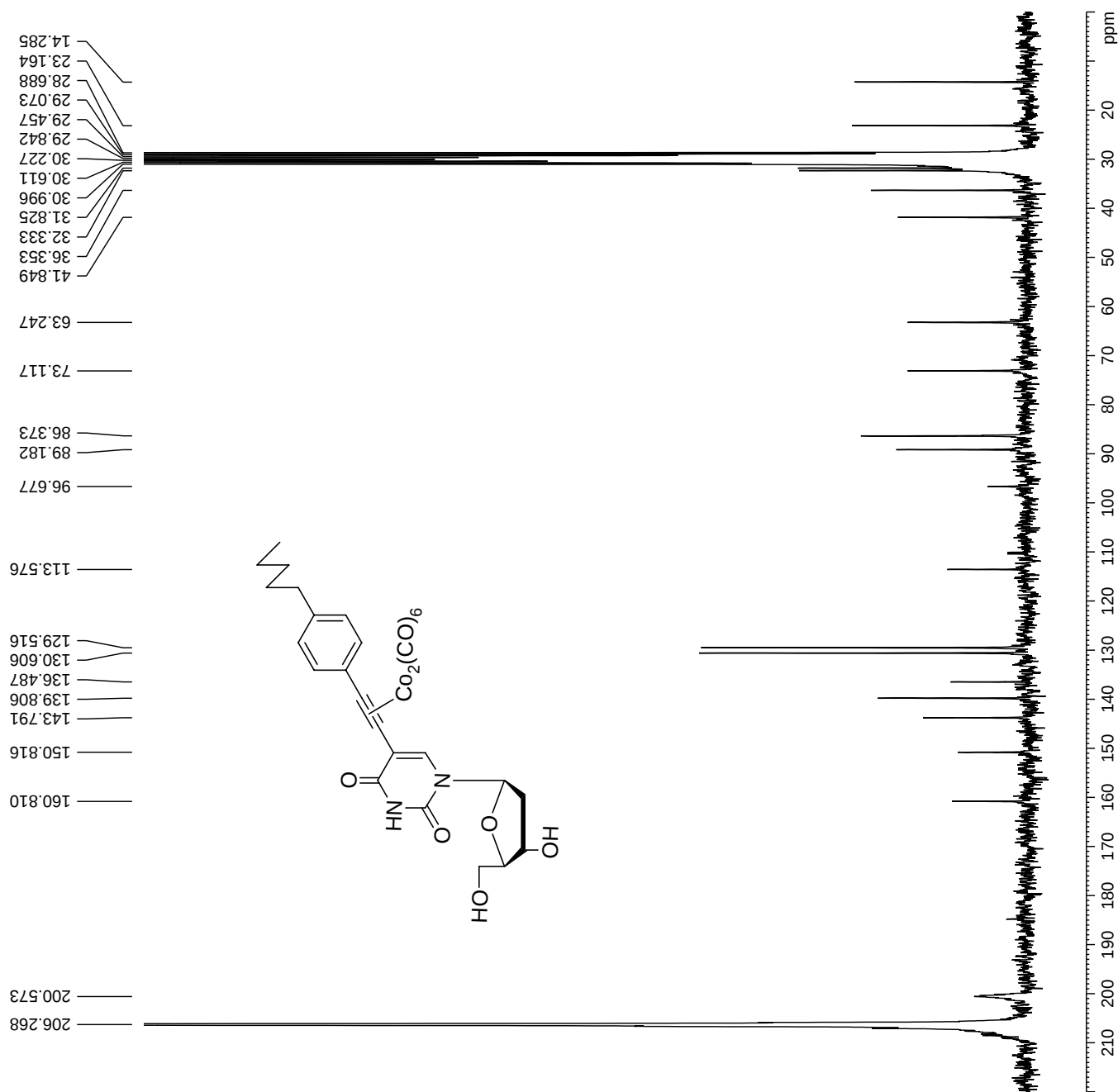
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 SOLVENT Acetone
 NS 9893
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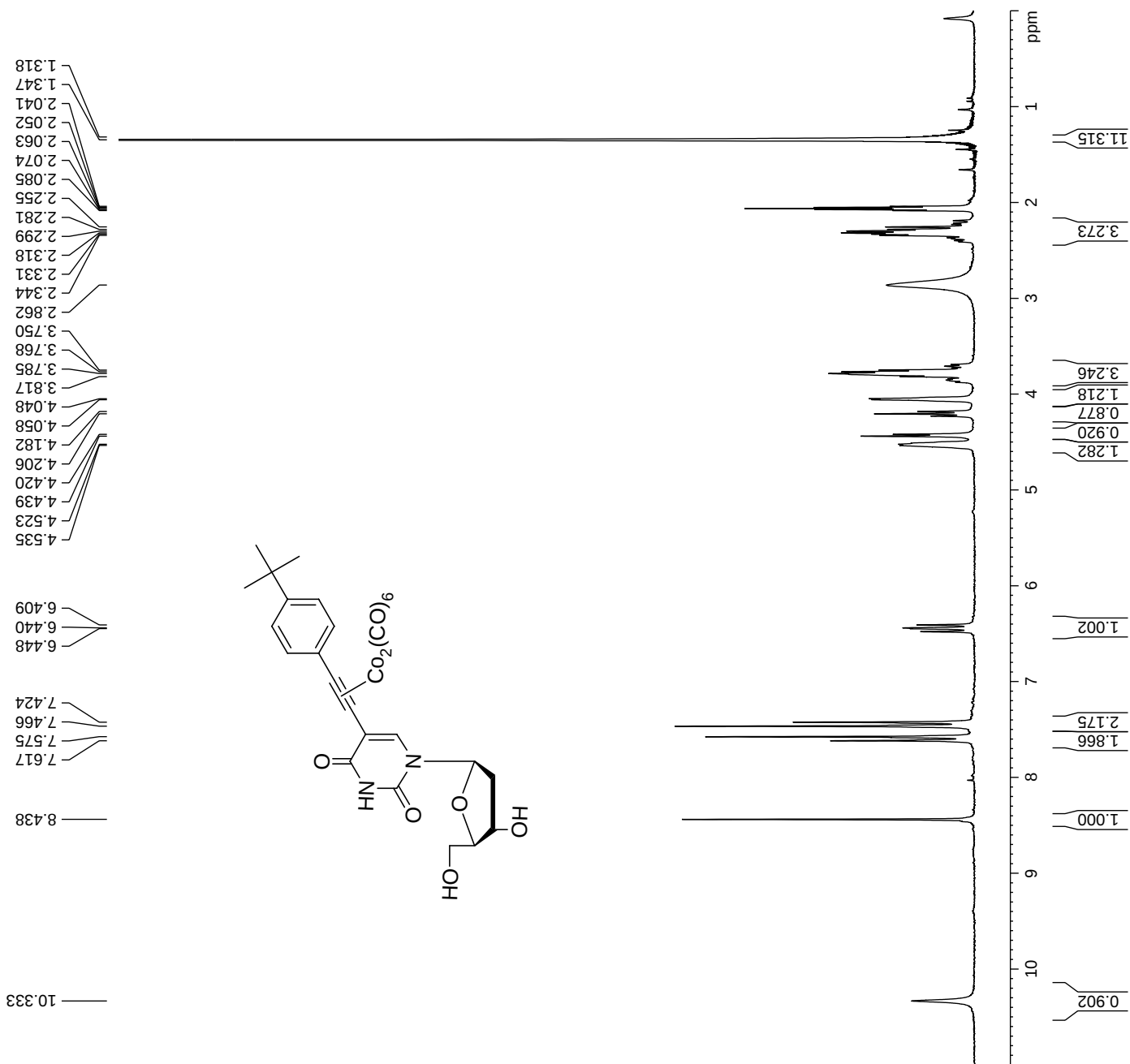
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 PL12 16.72 dB
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 LB 3.00 Hz
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¹H NMR spectrum for **8f** (acetone-d₆)



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PROCNO 1

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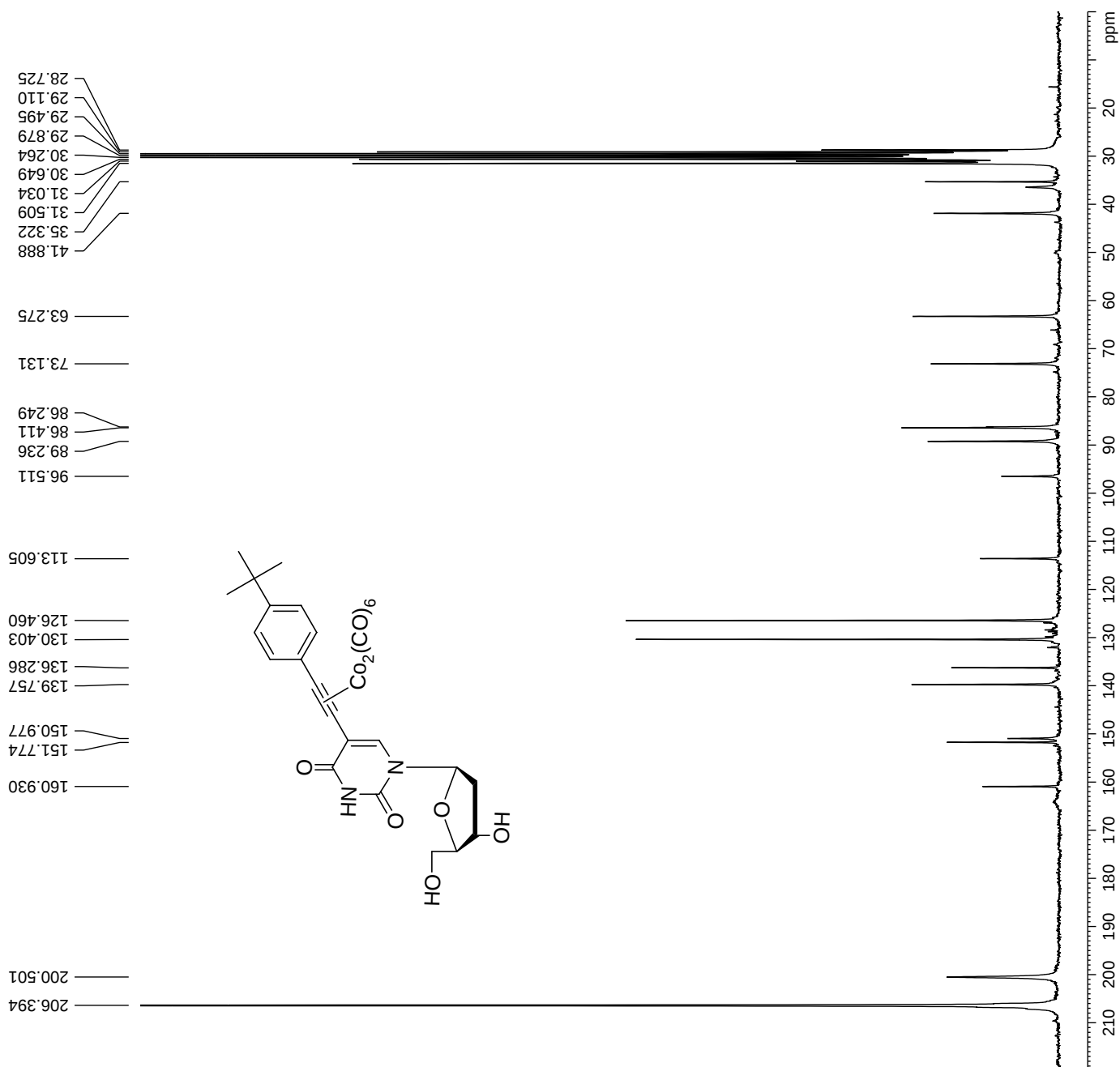
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

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P1 10.00 usec
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F2 - Processing parameters

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¹³C NMR spectrum for **8f** (acetone-*d*₆)



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FIDRES 0.333355 Hz
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RG 101.6
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TE 6.00 usec
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d11 4.00000000 sec
d11 0.03000000 sec

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F2 - Processing parameters
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¹H NMR spectrum for **8g** (acetone-d₆)



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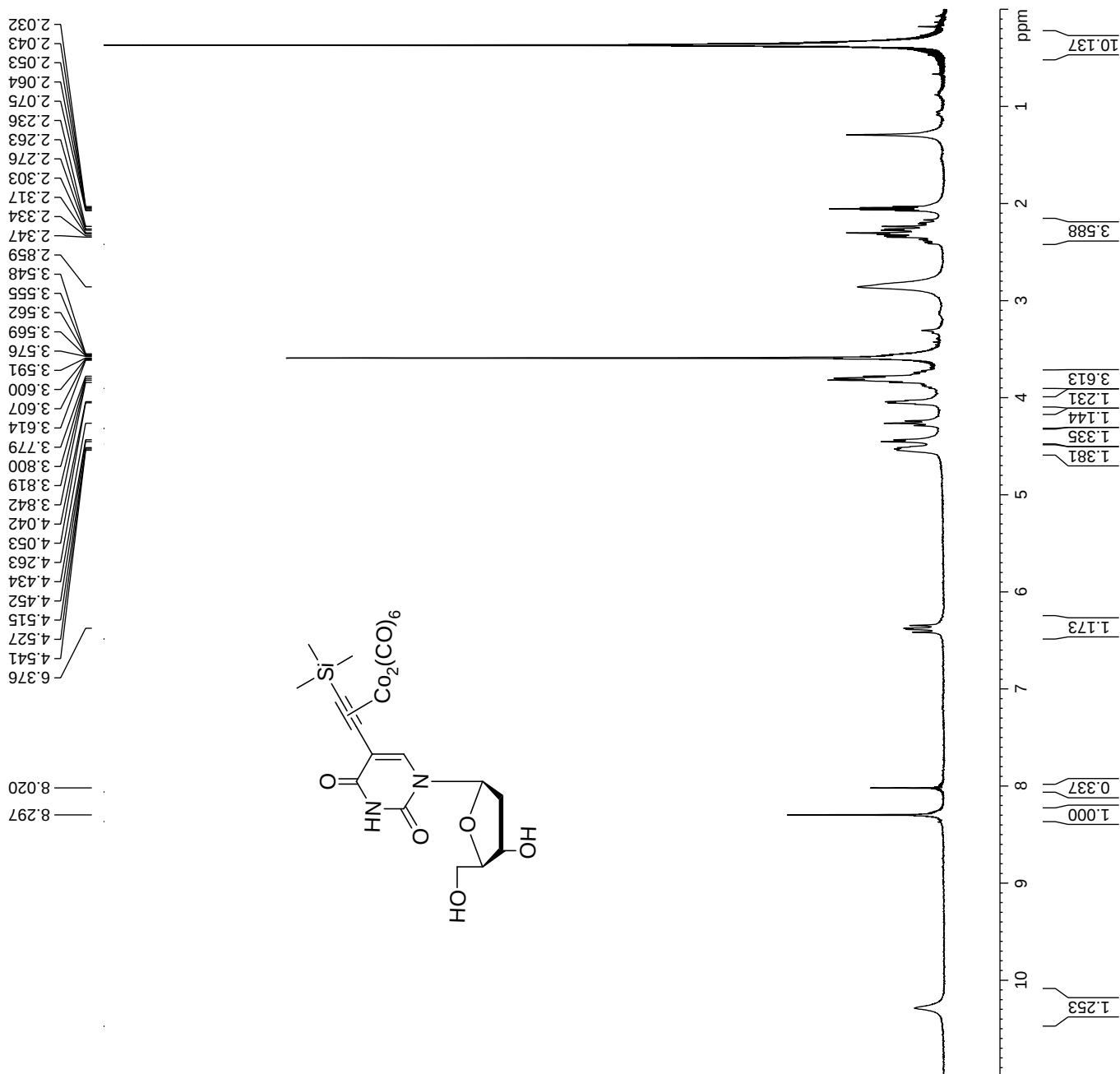
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¹³C NMR spectrum for **8g** (acetone-*d*₆)



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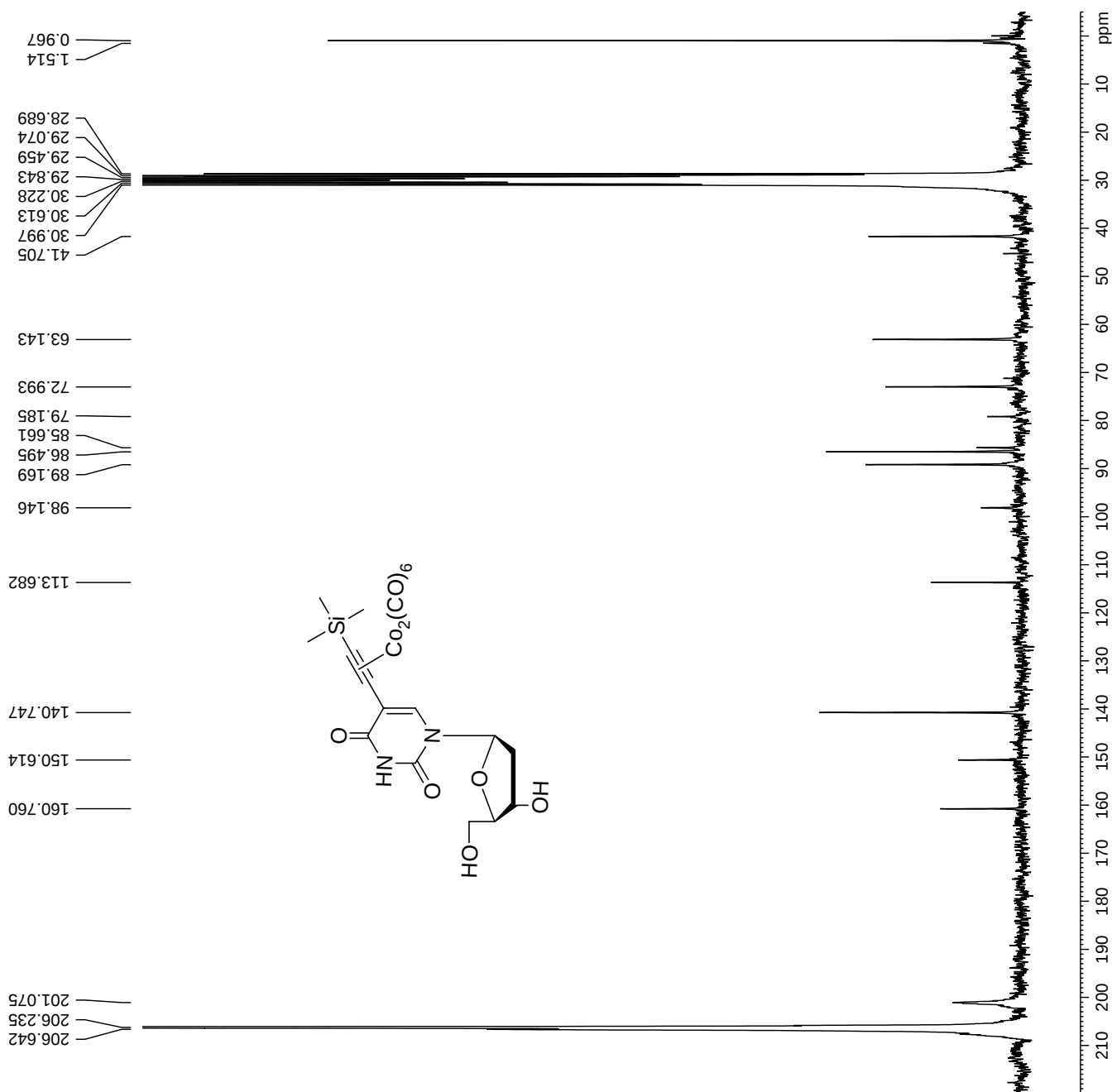
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 d11 0.03000000 sec

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 PL1 1.00 dB
 SF01 50.3285046 MHz

===== CHANNEL f2 =====
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 NUC2 1H
 PCPD2 100.00 usec
 PL2 -4.00 dB
 PL12 16.72 dB
 SF02 200.1300000 MHz

F2 - Processing parameters
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 SF 50.3226865 MHz
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S16



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DS	2
SWH	2495.010 Hz
FIDRES	0.543102 Hz
AQ	0.9206876 sec
RG	512
DW	200.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

```
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¹³C NMR spectrum for **8h** (acetone-d₆)



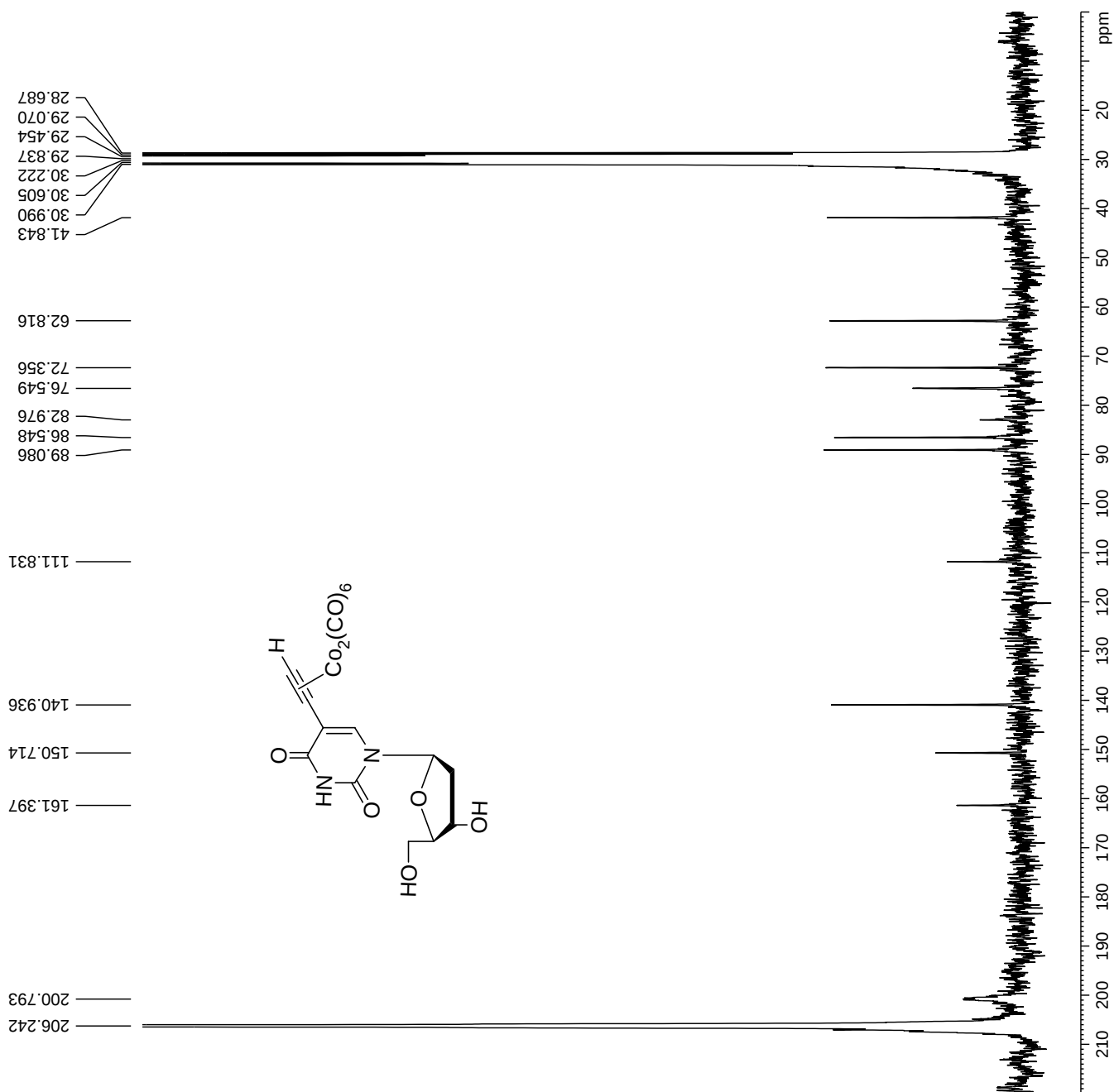
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NS 12000
DS 4
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FIDRES 0.333355 Hz
AQ 1.4999528 sec
RG 64
DW 39.800 usec
DE 6.00 usec
TE 300.0 K
D1 4.00000000 sec
d11 0.03000000 sec

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P1 6.00 usec
PL1 1.00 dB
SF01 50.3285046 MHz

===== CHANNEL f2 =====
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NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 16.72 dB
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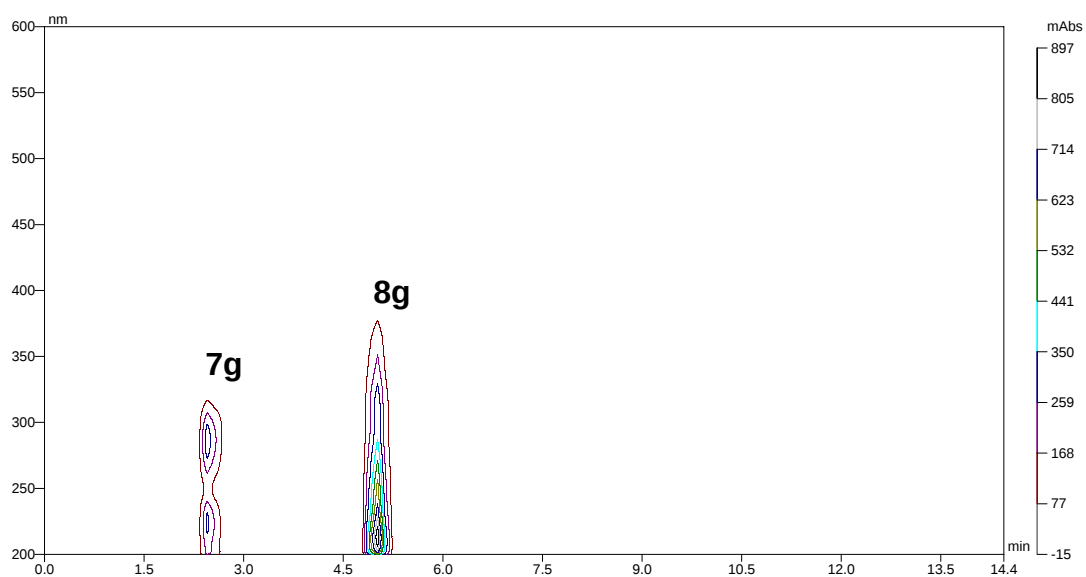


Comparison of R_f for pairs of nucleosides 7g/8g and 7h/8h with the use of HPLC.

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/H₂O 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

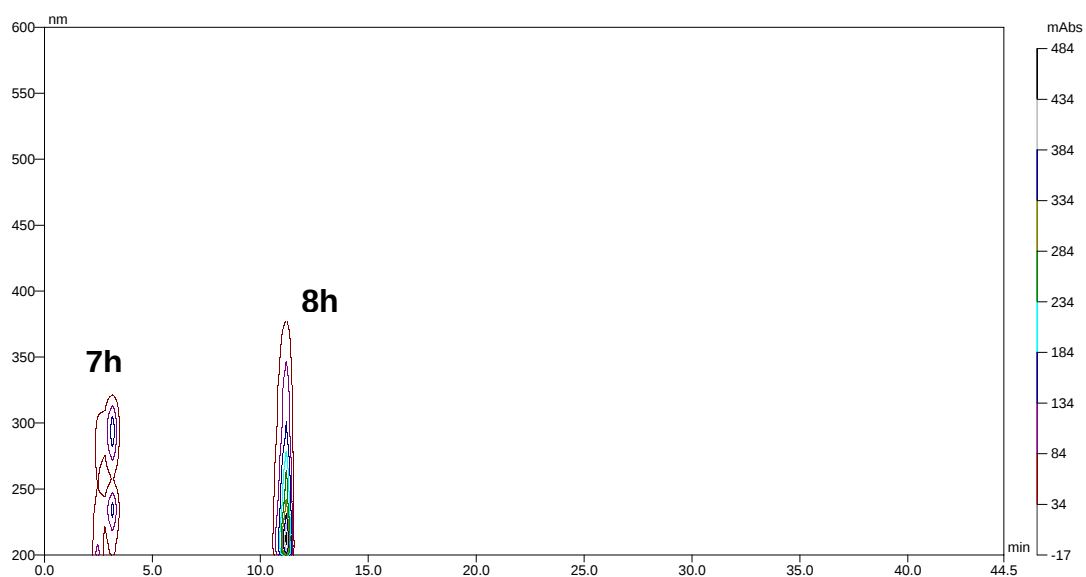


Table S3. Crystal data and structure refinement for **8c**.

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	$\alpha = 90^\circ$
	b = 9.3303(9) Å	$\beta = 90^\circ$
	c = 31.529(3) Å	$\gamma = 90^\circ$
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 > 2σ(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**.

