

SUPPORTING INFORMATION

Quantitative Synthesis and Full Characterization of the First Isolated and Stable Pincer Palladium(IV) Complexes. Quantitative and Regioselective Synthesis of the C–X (X = Cl, Br) Reductive Elimination Products

José Vicente, Aurelia Arcas, Francisco Juliá-Hernández and Delia Bautista

Experimental Section

General Procedures. The reactions were carried out without precautions to exclude light, atmospheric oxygen or moisture. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Bruker AC 200, or Avance 300 or 400 spectrometers at room temperature. Chemical shifts were referred to TMS (^1H , ^{13}C). When needed, NMR assignments were performed with the help of APT, HMQC and HMBC techniques. Chart 1 shows the atom numbering used for NMR assignments.

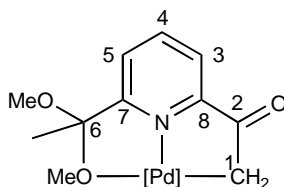


Chart 1

Synthesis of [Pd(O,N,C-L)Br] (1b). To a solution of [Pd(O,N,C-L)Cl] (225.2 mg; 0.643 mmol) in acetone (27 mL), NaBr (265.4 mg; 2.58 mmol) was added. The reaction mixture was stirred for 45 min, concentrated to dryness and extracted with CH_2Cl_2 (20 mL). The solution was concentrated (1 mL) and Et_2O (3 mL) and *n*-pentane (15 mL) were added. The resulting suspension was filtered and the solid washed with *n*-pentane and air-dried to give **1b** as a yellow solid. Yield: 248.3 mg, 98%. Mp: 198–199 °C. IR (cm^{-1}): $\nu(\text{C}=\text{O})$ 1686. ^1H NMR (300 MHz, CDCl_3 , 20 °C): δ 8.17 (t, 1 H, H4, $^3J_{\text{HH}} = 8$ Hz), 7.82 (dd, 1 H, H3, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1.2$ Hz), 7.64 (dd, 1 H, H5, $^3J_{\text{HH}} = 8$ Hz, $^4J_{\text{HH}} = 1.2$ Hz), 3.50 (s, 2 H, CH_2), 3.43 (s, 6 H, OMe), 1.77 (s, 3 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.45 MHz, CDCl_3 , 20 °C): δ 204.0 (CO), 158.3 (C7), 152.2 (C8), 139.3 (C4), 126.5 (C5), 123.6 (C3), 107.0 (C6), 51.6 (MeO), 29.6 (C1), 25.0 (Me). Anal. Calcd

S2

for $C_{11}H_{14}NO_3BrPd$: C, 33.49 ; H, 3.58 ; N, 3.55. Found: C, 33.42; H, 3.38; N, 3.82. Single crystals were obtained by slow diffusion of *n*-pentane into a $CHCl_3$ solution of **1b**.

Synthesis of *mer*-[Pd(*O,N,C-L*)Cl₃] (2a). To a cooled (0 °C) solution of [Pd(*O,N,C-L*)Cl] (**1a**) (48.7 mg, 0.14 mmol) in CH_2Cl_2 (1 mL) was added a saturated solution of Cl_2 in CCl_4 (1 mL). The resulting suspension was stirred for 5 min and Et_2O (6 mL) was added. The suspension was filtered, the solid was washed with Et_2O and air-dried to give **2a** as a yellow solid. Yield: 54.6 mg, 93 %. Mp: 107–108 °C. IR (cm^{-1}): $\nu(C=O)$ 1723, $\nu(Pd-Cl)$ 355. 1H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.33 (t, 1 H, H4, $^3J_{HH} = 7.6$ Hz), 8.14 (dd, 1 H, H3, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.2$ Hz), 7.92 (dd, 1 H, H5, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.2$ Hz), 6.04 (br, 2 H, CH_2), 3.89 (br, 3 H, OMe), 3.28 (br, 3 H, OMe), 1.95 (s, 3 H, Me). 1H NMR (400 MHz, $CDCl_3$, -50 °C): δ 8.50 (t, 1 H, H4, $^3J_{HH} = 7.6$ Hz), 8.24 (dd, 1 H, H3, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.2$ Hz), 8.05 (dd, 1 H, H5, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.2$ Hz), 6.20 (d, 1 H, CH_2 , $^1J_{HH} = 12.4$ Hz), 5.97 (d, 1 H, CH_2 , $^1J_{HH} = 12.4$ Hz), 3.94 (s, 3 H, OMe), 3.28 (s, 3 H, OMe), 1.99 (s, 3 H, Me). Anal. Calcd for $C_{11}H_{14}NO_3Cl_3Pd$: C, 31.38 ; H, 3.35; N, 3.33. Found: C, 31.07; H, 3.11; N, 3.19. Single crystals were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **2a** at 4 °C.

Synthesis of *mer*-[Pd(*O,N,C-L*)Br₃] (2b). To a cooled (0 °C) solution of **1b** (45.0 mg, 0.11 mmol) in CH_2Cl_2 (1 mL) was added Br_2 (20 μ L, 0.39 mmol). The mixture was stirred for 2 min and Et_2O (6 mL) was added. The suspension was filtered, the solid was washed with Et_2O and dried under N_2 to give **2b** as a dark red crystals. Yield: 59.9 mg, 95 %. Mp: 110–111 °C. IR (cm^{-1}): $\nu(C=O)$ 1718. 1H NMR (200 MHz, $CDCl_3$, 20 °C): δ 8.30 (t, 1 H, H4, $^3J_{HH} = 7.6$ Hz), 8.13 (dd, 1 H, H3, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz), 7.87 (dd, 1 H, H5, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz), 6.06 (br, 2 H, CH_2), 3.83 (br, 3 H, OMe), 3.32 (br, 3 H, OMe), 1.96 (s, 3 H, Me). 1H NMR (400 MHz, $CDCl_3$, -55 °C): δ 8.46 (t, 1 H, H4, $^3J_{HH} = 7.6$ Hz), 8.24 (dd, 1 H, H3, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz), 8.01 (dd, 1 H, H5, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.4$ Hz), 6.20 (d, 1 H, CH_2 , $^1J_{HH} = 13$ Hz), 5.96 (d, 1 H, CH_2 , $^1J_{HH} = 13$ Hz), 3.88 (s, 3 H, OMe), 3.31 (s, 3 H, OMe), 2.00 (s, 3 H, Me). Anal. Calcd for $C_{11}H_{14}NO_3Cl_3Pd$: C, 23.83 ; H, 2.55; N, 2.53. Found: C, 23.65 ; H, 2.33 ; N, 2.35. Single crystals were obtained at 4 °C by slow diffusion of Et_2O into a CH_2Cl_2 solution of **2b**.

Synthesis of $C_5H_3N\{C(O)Me\}$ -2- $\{C(O)CH_2Cl\}$ -6 (3a). Method a. A mixture of **2a** (181.4 mg, 0.43 mmol) and unanhydridized MeCN (30 mL) was stirred until a solution was obtained (1 h) and then was concentrated to dryness. The resulting residue was vigorously stirred in *n*-pentane

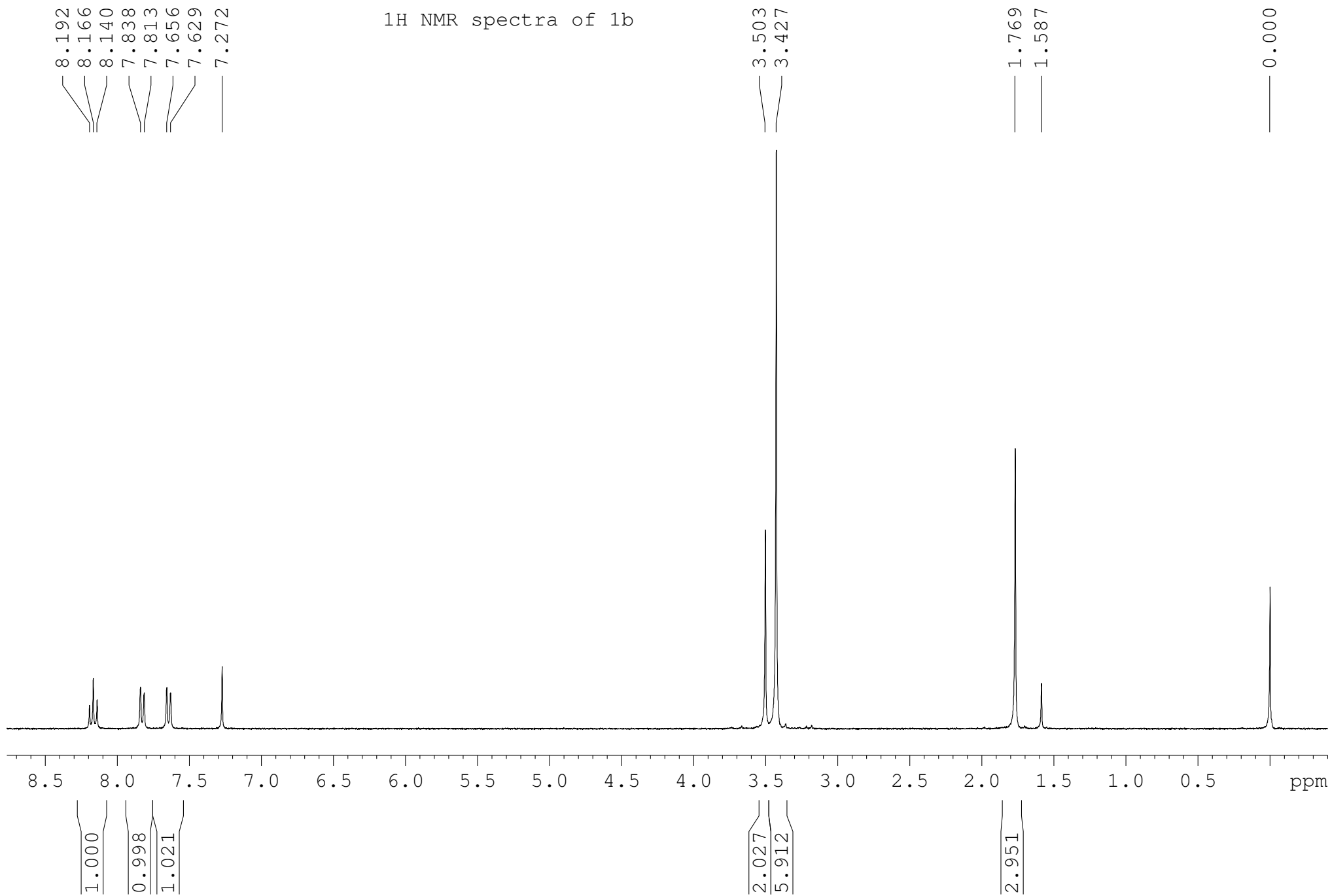
S3

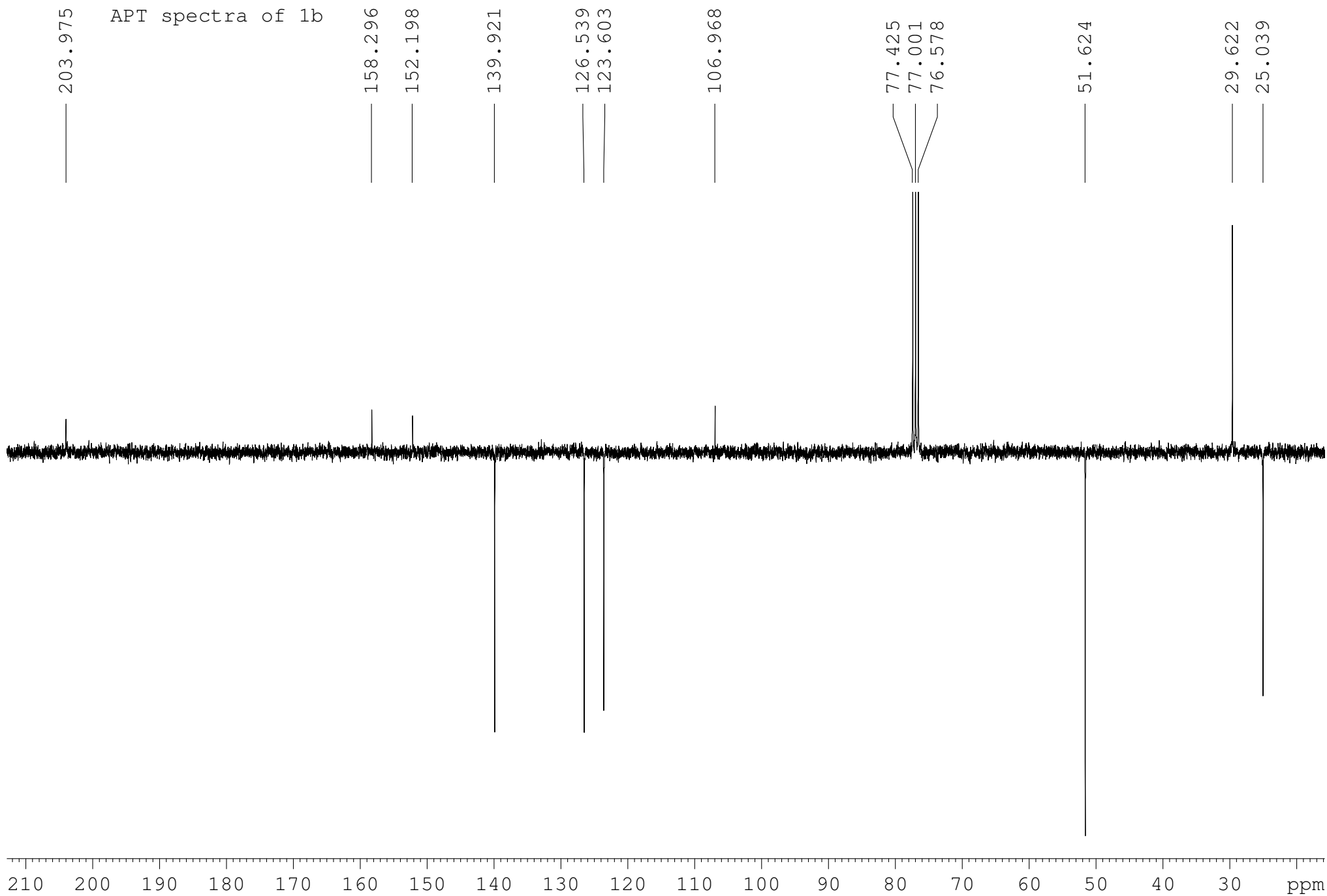
(30 mL) for 30 min to give a suspension, which was filtered, the solid washed with *n*-pentane and air-dried to give [PdCl₂(NCMe)₂] as a yellow solid. The filtrate was concentrated to dryness to give **3a** as a colorless solid. Yield: 80.2 mg, 94%. Mp: 115-116 °C. IR (cm⁻¹): ν(C=O) 1721, 1694; ν(C=N) 1579. ¹H NMR (400 MHz, CDCl₃, 20 °C): δ 8.28 (m, 2H), 8.05 (m, 1H), 5.16 (s, 2H, CH₂), 2.77 (s, 3H, Me). ¹³C{¹H} NMR (100.81 MHz, CDCl₃, 20 °C): δ 198.7 (s, C(O)Me), 191.5 (s, C(O)CH₂Cl), 152.7 (s, CC(O)Me), 150.7 (s, CC(O)Cl), 138.5 (s, CH, *p*-C), 125.7 (s, CH, *m*-C), 125.6 (s, CH, *m*-C), 46.9 (s, CH₂), 25.6 (s, Me). HRMS calc for C₉H₈O₂ClN (M + H⁺) *m/z* 197.024, found *m/z* 197.025. Anal. Calcd for C₉H₈O₂ClN: C, 54.70 ; H, 4.08; N, 7.09. Found: C, 55.05 ; H, 4.19 ; N, 6.96.

Method b. To a cooled (0 °C) solution of **2a** (36.6 mg, 0.09 mmol) in CH₂Cl₂ (6 mL) was added ^tBubpy, 23.3 mg, 0.09 mmol) and NaClO₄ (21.3 mg, 0.17 mmol). After 10 min the solution was filtered through Celite and concentrated (1 mL). Addition of Et₂O (8 mL) gave a suspension that was filtered off. The resulting solid was identified as [PdCl₂(^tbpy)]. The filtrate was concentrated to dryness to give **3a** as a colorless solid. Yield: 15.8 mg, 92 %.

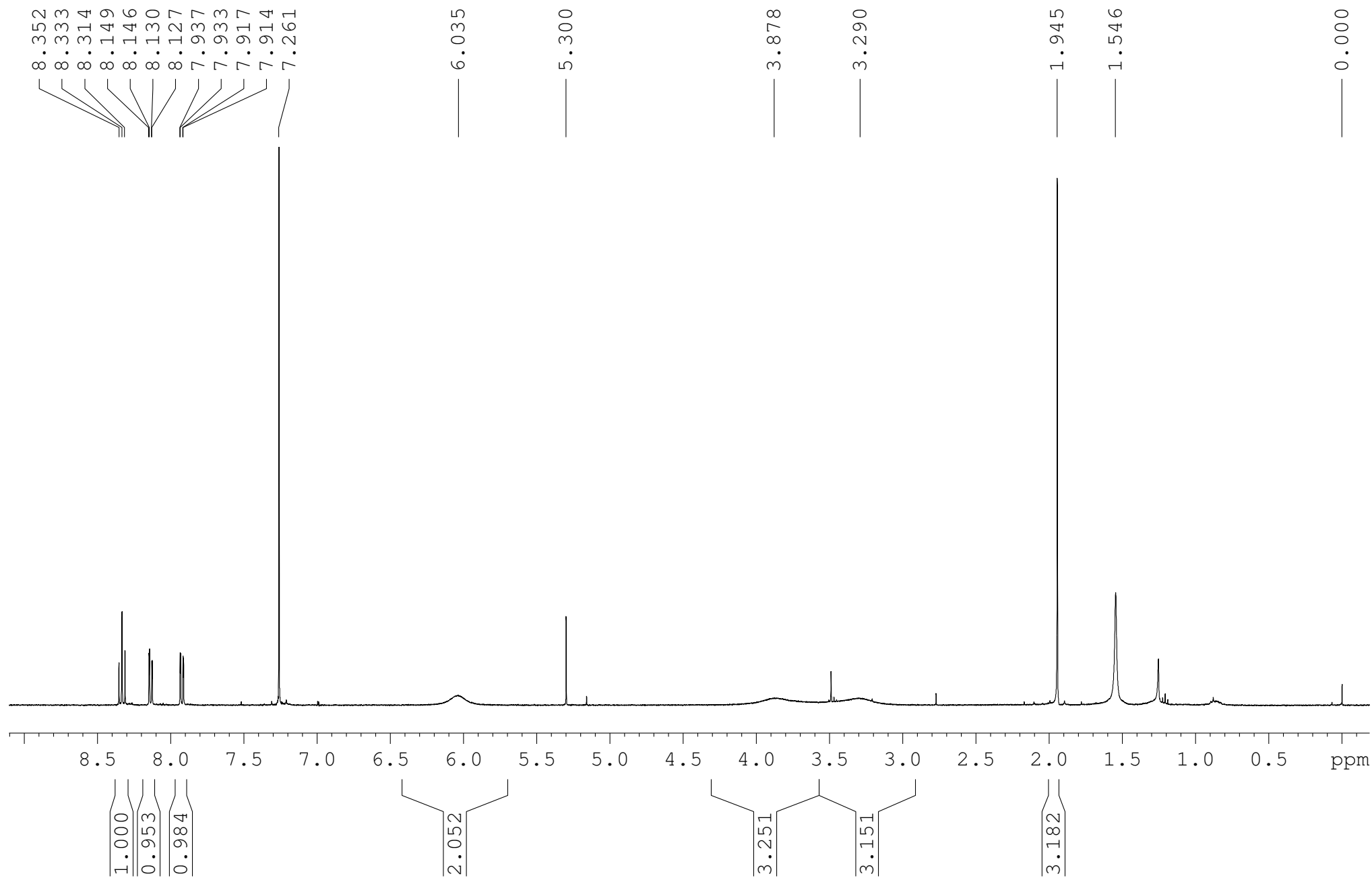
Synthesis of C₅H₃N{C(O)Me}-2-{C(O)CH₂Br}-6 (3b). A mixture of **2b** (216.0 mg, 0.46 mmol) and unanhydridized MeCN (40 mL) was stirred (3 h) and then was concentrated to dryness. The resulting residue was vigorously stirred in *n*-pentane (40 mL) for 30 min to give a suspension, which was filtered to give [PdBr₂(NCMe)₂]. The filtrate was concentrated to dryness to give **3b** as a colorless solid. Yield: 101.9 mg, 93%. Mp: 93-94 °C. IR (cm⁻¹): ν(C=O) 1721, 1694; ν(C=N) 1578. ¹H NMR (200 MHz, CDCl₃, 20 °C): δ 8.31-8.24 (m, 2H), 8.05 (m, 1H), 4.88 (s, 2H, CH₂), 2.79 (s, 3H, Me). ¹³C{¹H} NMR (50.30 MHz, CDCl₃, 20 °C): δ 198.8 (s, C(O)Me), 191.8 (s, C(O)CH₂Br), 152.7 (s, CC(O)Me), 150.3 (s, CC(O)Br), 138.4 (s, CH, *p*-C), 125.8 (s, CH, *m*-C), 125.5 (s, CH, *m*-C), 31.4 (s, CH₂), 25.6 (s, Me). HRMS calc for C₉H₈O₂BrN (M + H⁺) *m/z* 241.9811, found *m/z* 241.9812. Anal. Calcd for C₉H₈O₂BrN: C, 44.66 ; H, 3.33; N, 5.79. Found: C, 44.62; H, 3.29 ; N, 5.89.

¹H NMR spectra of 1b

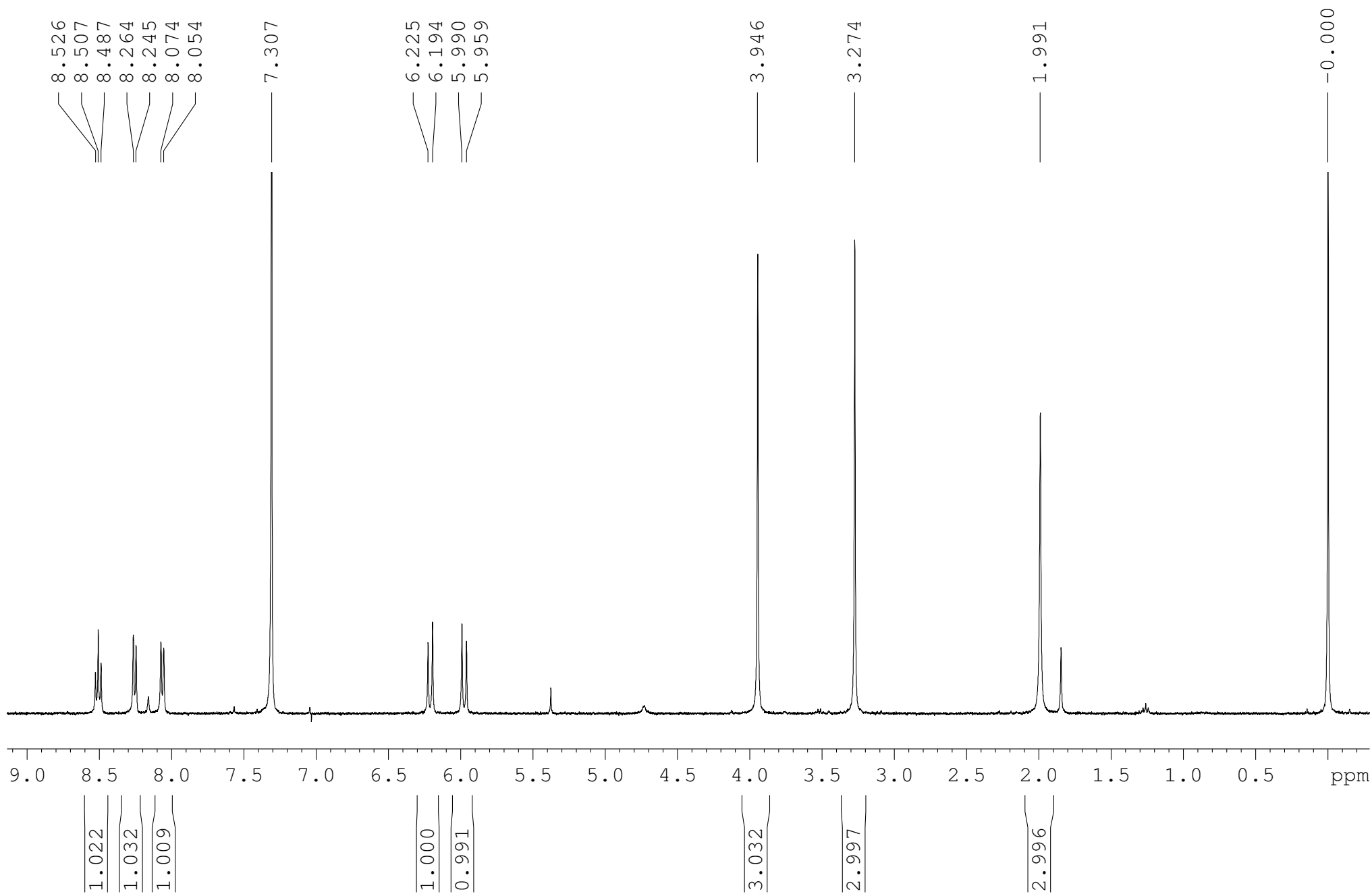




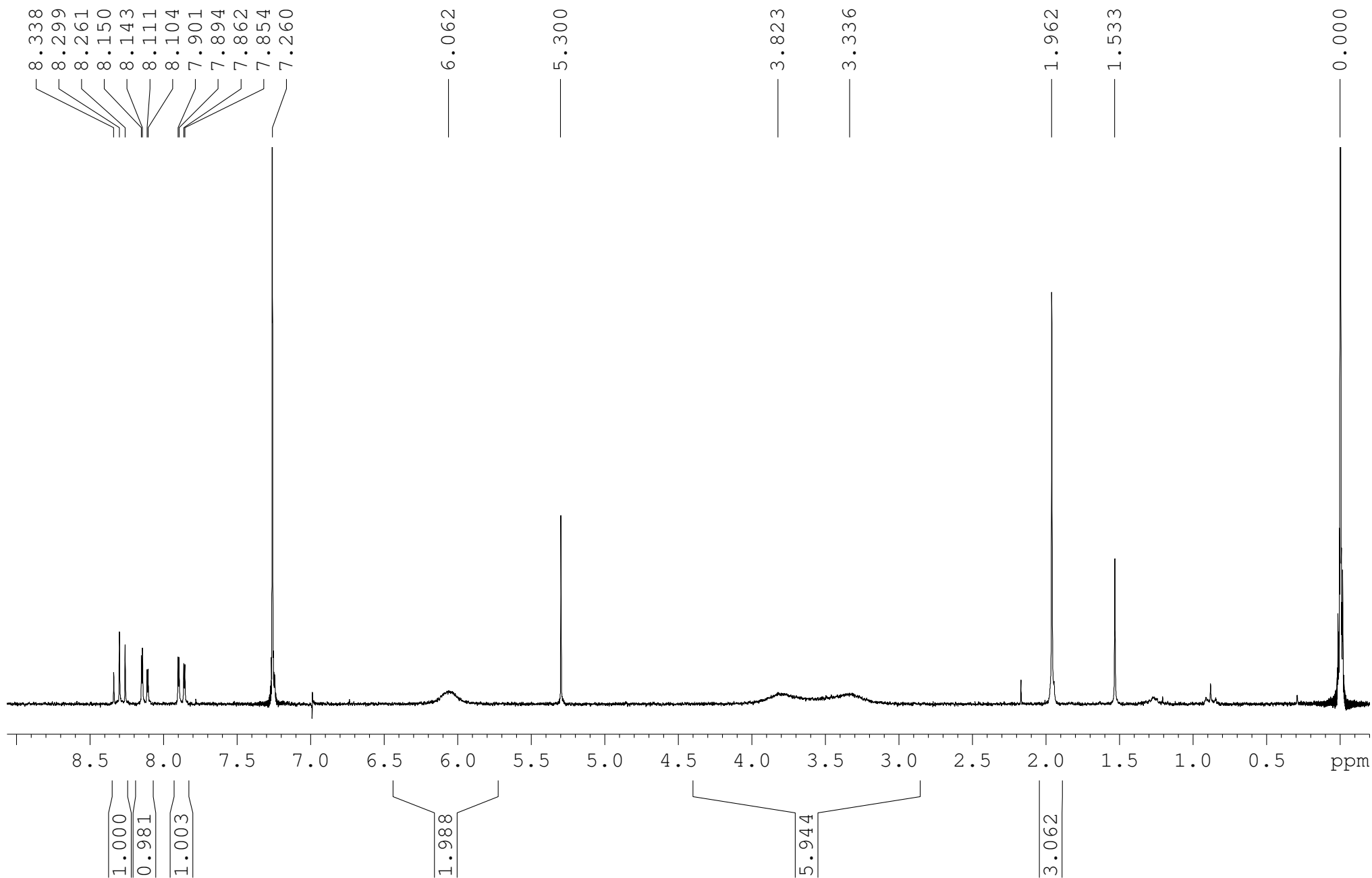
¹H NMR spectra of 2a at 20 °C



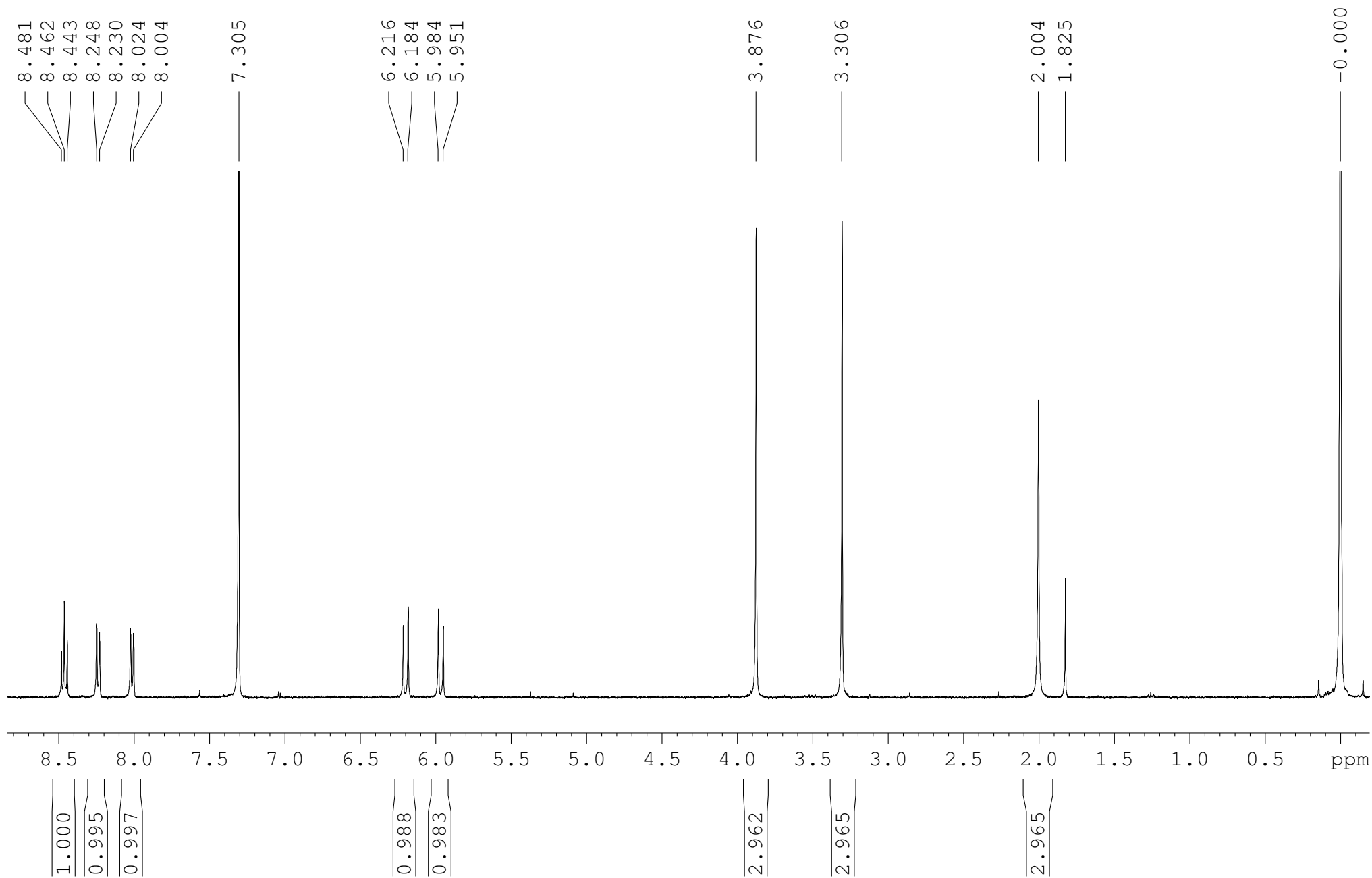
¹H NMR spectra of 2a at -55 °C



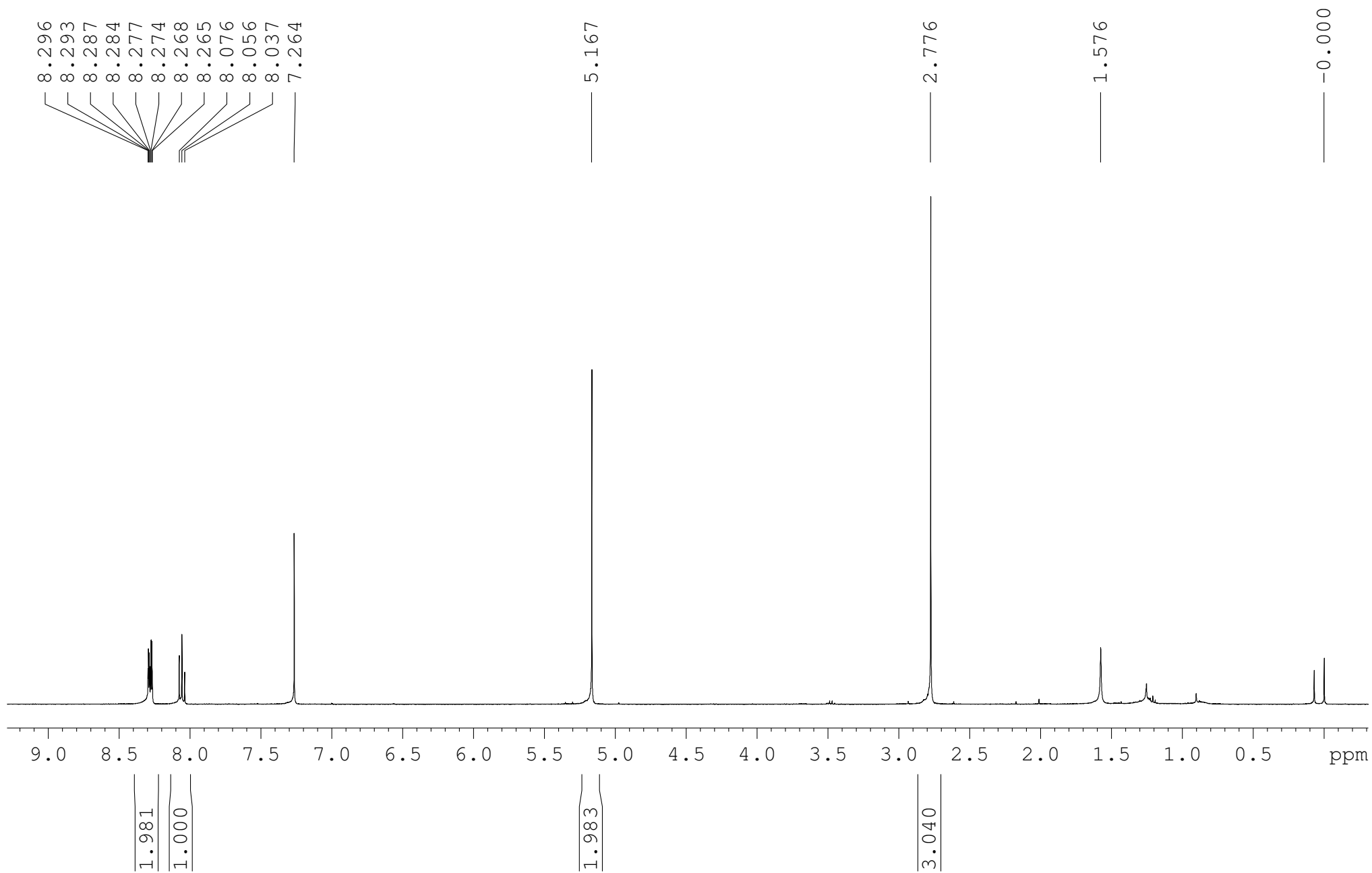
¹H NMR spectra of 2b at 20 °C



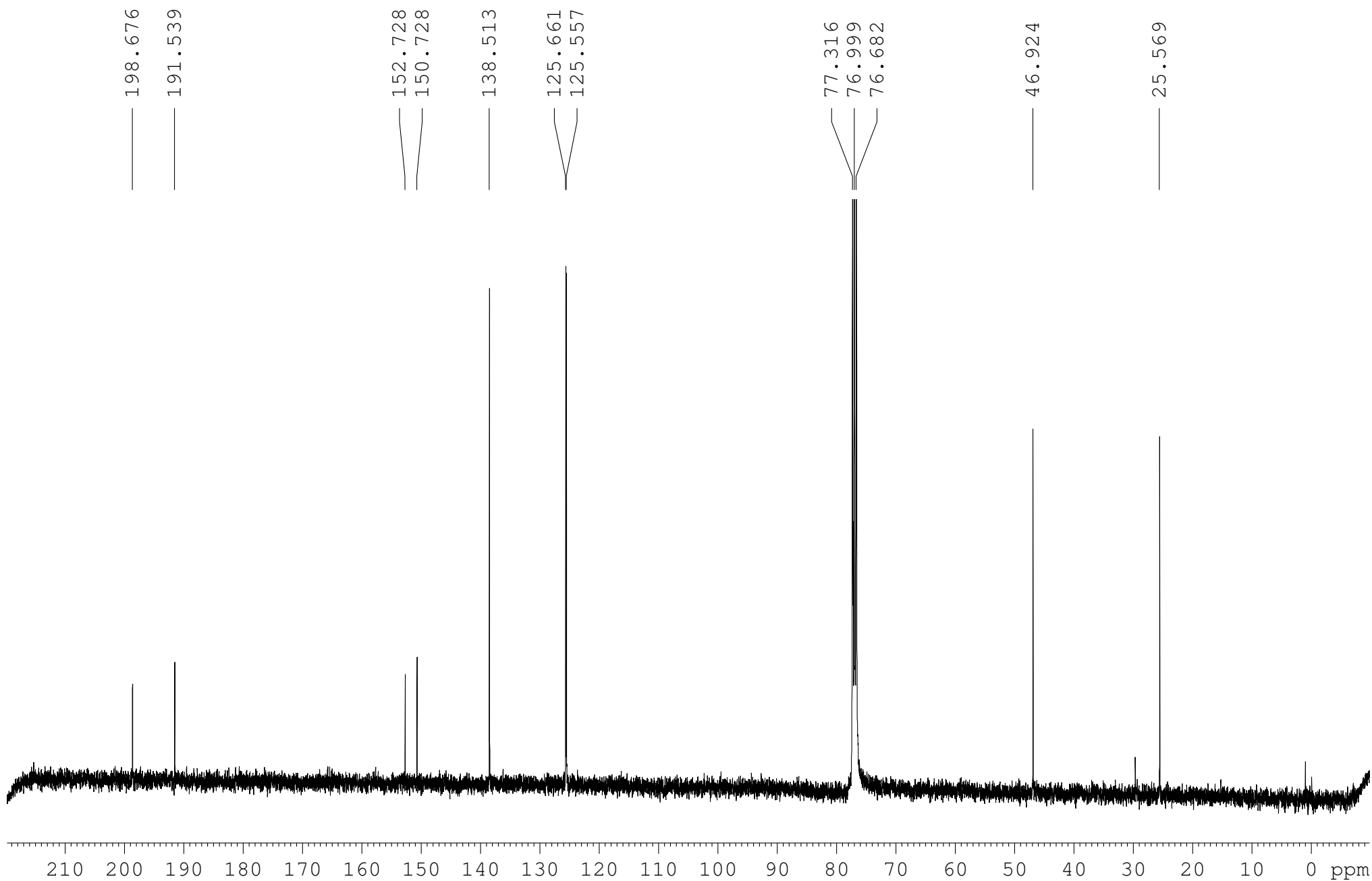
¹H NMR spectra of 2b at -55 °C



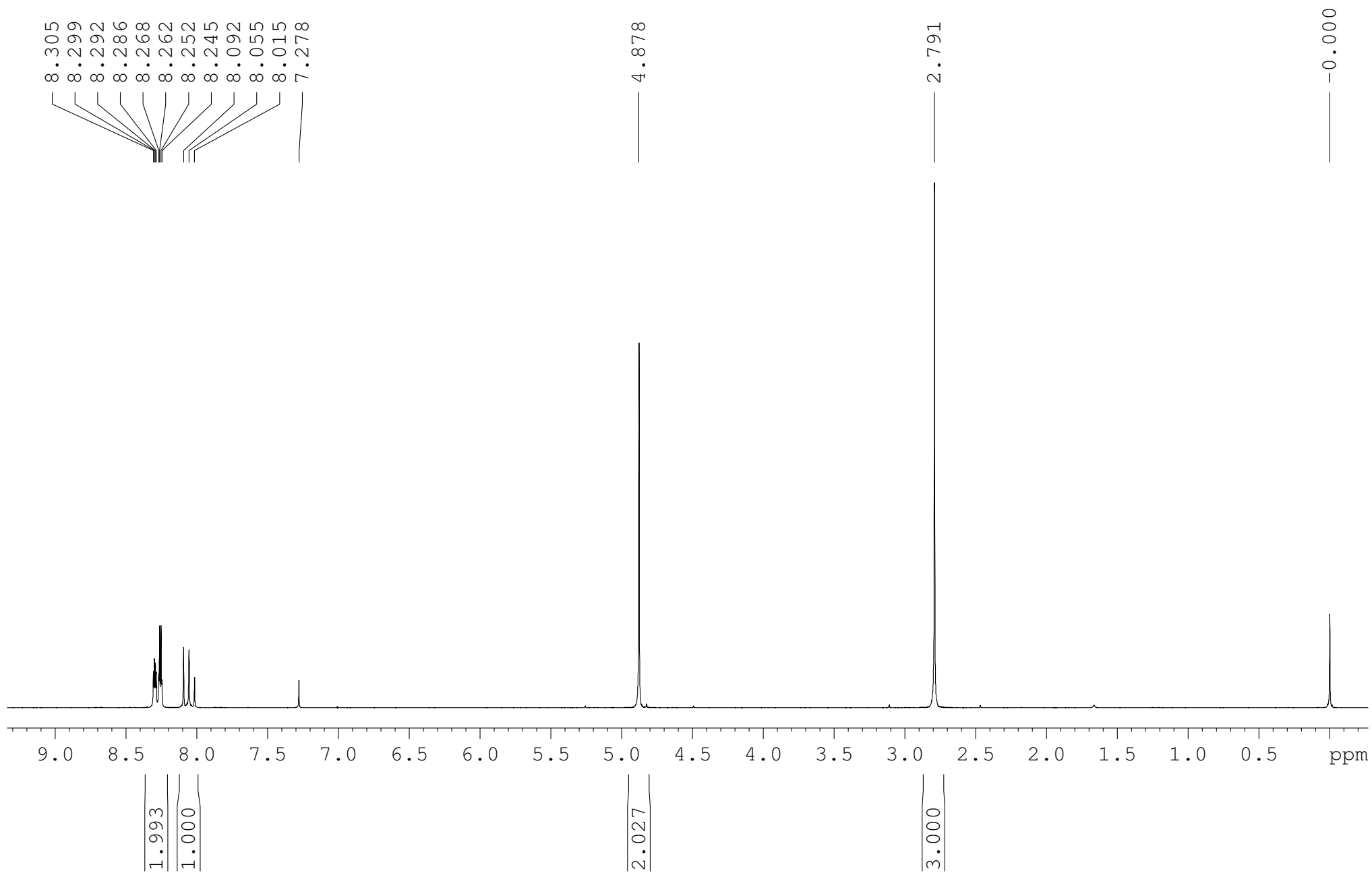
^1H NMR spectra of 3a



^{13}C NMR spectra of 3a



¹H NMR spectra of 3b



APT spectra of 3b

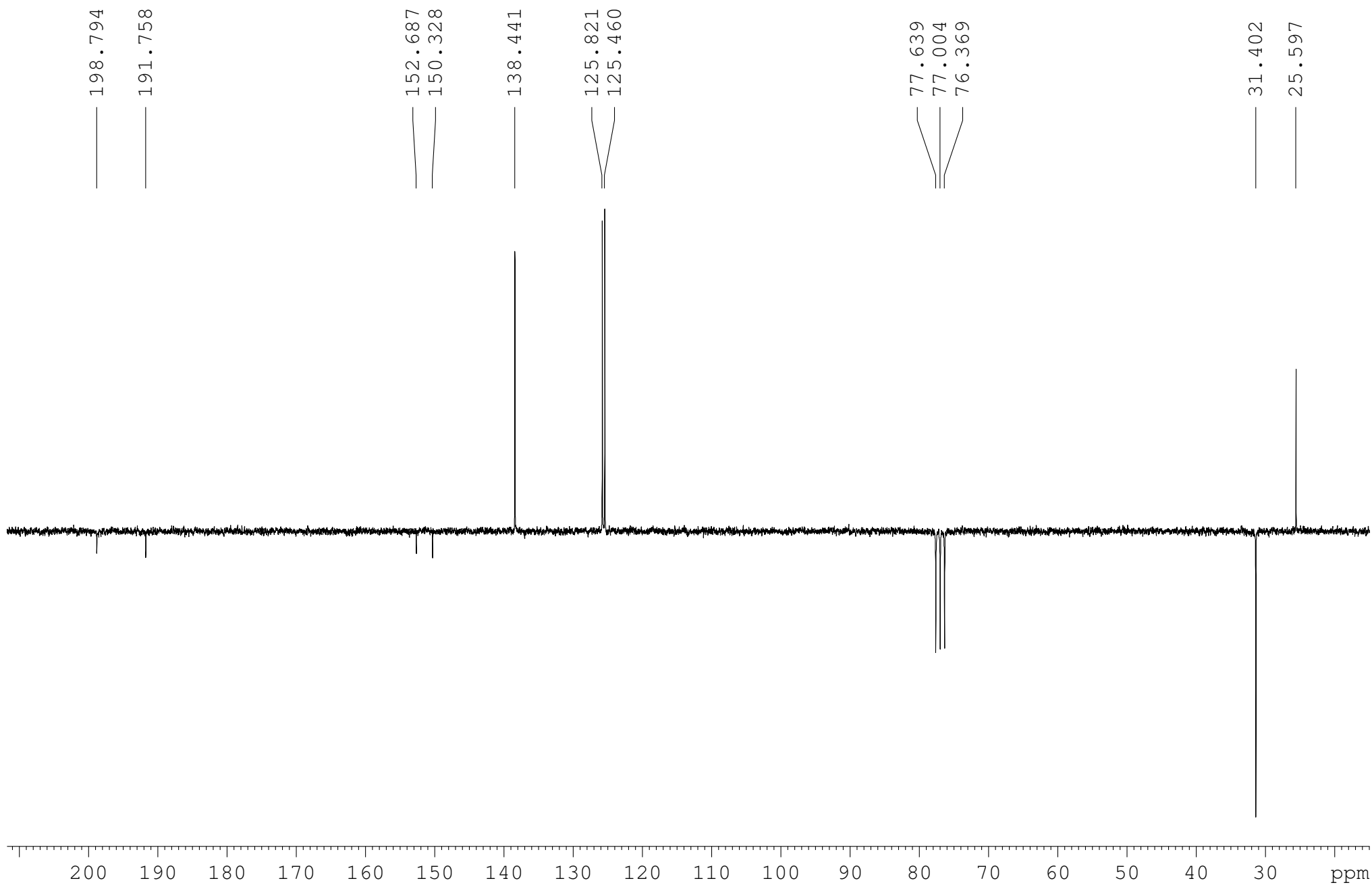
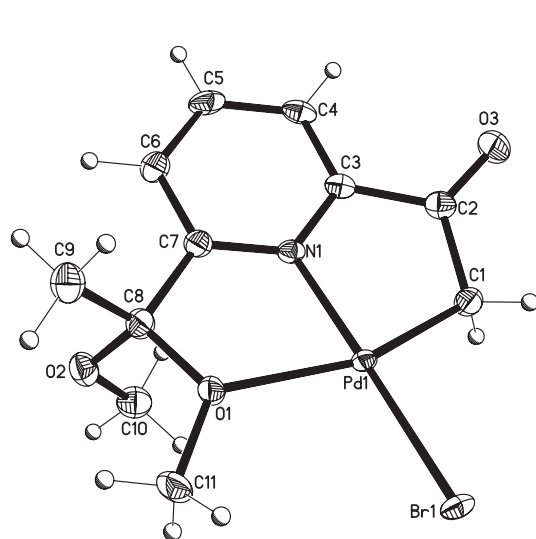


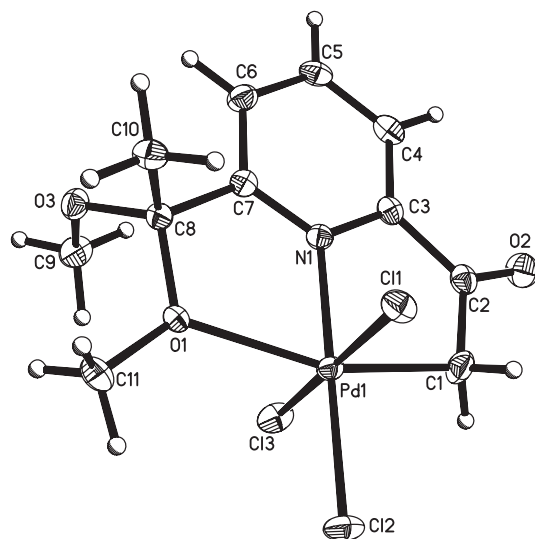
Table 1. Crystal Data for Complexes 1b, 2a and 2b.

	1b	2a	2b
formula	C ₁₁ H ₁₄ BrN ₃ O ₃ Pd	C ₁₁ H ₁₄ C ₁₃ N ₃ O ₃ Pd	C ₁₁ H ₁₄ Br ₃ N ₃ O ₃ Pd
<i>M</i> _r	394.54	420.98	554.36
cryst size (mm)	0.17 x 0.12 x 0.10	0.21 x 0.15 x 0.09	0.24 x 0.22 x 0.16
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)/c	P2(1)/n	P2(1)/n
cell constants			
a, Å	9.6687(7)	8.5235(4)	8.8728(8)
b, Å	9.9942(7)	13.5319(7)	13.3587(12)
c, Å	13.8064(11)	12.8239(7)	13.1184(12)
α, deg	90	90	90
β, deg	107.748(2)	98.407(2)	99.193(2)
γ, deg	90	90	90
volume, (Å ³), Z	1270.63(16), 4	1463.20(13), 4	1534.9(2), 4
λ (Å)	0.71073	0.71073	0.71073
ρ(calc) (Mgm ⁻³)	2.062	1.911	2.399
F(000)	768	832	1048
<i>T</i> (K)	100(2)	100(2)	100(2)
μ, mm ⁻¹	4.600	1.817	9.020
transmissions	0.656 - 0.568	0.854 - 0.767	0.326 - 0.212
θ, range (deg)	2.56 - 28.67	2.20 - 28.15	2.19 - 28.72
limiting indices	-13 ≤ h ≤ 12 -13 ≤ k ≤ 12 -17 ≤ l ≤ 18	-10 h ≤ 11 -17 ≤ k ≤ 117 -16 ≤ l ≤ 16	-11 ≤ h ≤ 11 -17 ≤ k ≤ 17 -17 ≤ l ≤ 17
no. of reflns			
measd	15327	16440	18602
indep	3089	3390	3734
<i>R</i> _{int}	0.021	0.0193	0.019
abs. corr	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
refinement method	full- matrix least squares on F ²	full- matrix least squares on F ²	full- matrix least squares on F ²
no. data/rest/params	3089 / 0 / 157	3390 / 5 / 190	3734 / 0 / 190
<i>S</i> (F ²)	1.059	1.083	1.078
<i>R</i> 1 ^a	0.019	0.019	0.016
w <i>R</i> 2 ^b	0.046	0.049	0.040
largest diff peak (e Å ⁻³)	0.764	0.422	0.434
max. Dr (e Å ⁻³)	-0.593	-0.684	-0.744

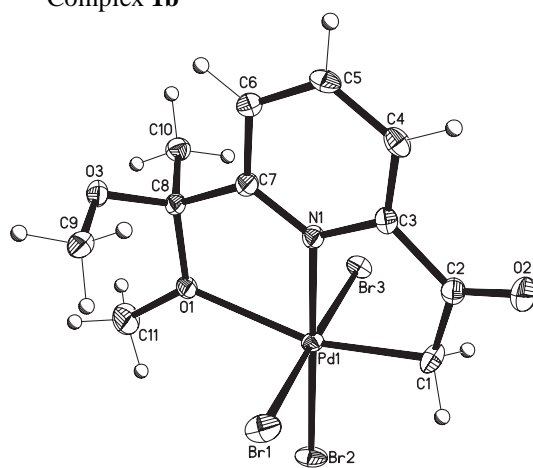
^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for reflections with $I > 2\sigma(I)$. ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$ for all reflections;
 $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.



Complex 1b



Complex 2a



Complex 2b