Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Binuclear Cobalt(II) complexes: Synthesis, structure, characterizations and catalytic applications in acceptorless dehydrogenation (AD) of primary alcohols into aldehydes

Adelew Estifanos filkale[1]*, Manoj Kumar Gangwar[2], Indresh Kumar Pandey[3], Ray Butcher[4]

[1]Department of Chemistry, College of Computational & Natural Sciences, Hawassa University, P.O. Box 05, Hawassa, Ethiopia.

[2]Department of Chemistry, Faculty of Science, University of Allahabad (AoU), Prayagraj–211002, Uttar Pradesh, India.

[3]Department of Chemistry, Deen Dayal Upadhyay Gorakhpur University, Gorakhpur–273009, Uttar Pradesh, India.

[4]Department of Inorganic & Structural Chemistry, Howard University Washington DC 20059, USA

*Correspondence: Authors: *E-mail: adelewshenkora@gmail.com

Experimental Section:

Except where otherwise noted, all substances were commercially available and used in their natural state. Hexane, methanol, and ethyl acetate were obtained from commercial sources and used as reagent-grade solvents. Standard procedures were used to clean and degas the solvents. $CDCl_3$ was used as the solvent for ^1H NMR and ^{13}C $\{^1H\}$ NMR measurements on Bruker 400 MHz and 500 MHz spectrometers. Coupling constants (*J*) are expressed in Hz, and chemical shifts (δ) are expressed in ppm relative to TMS. Chemical shifts and solvent signals ($CDCl_3$, δC 77.0 ppm, δH 7.26 ppm) that were used as references were converted to the TMS scale. Commercial aluminium sheets pre-coated with silica gel were used to monitor all of the reactions using analytical thin layer chromatography (TLC). Silica gel (200-400 mesh, Merck) was used for column chromatography. The abbreviations used for ^1H NMR spectra to indicate the signal multiplicity are singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), doublet of triplet (dt), triplet of triplet (tt), multiplet (m), etc. The crystal data collection and refinement parameters are outlined in Tables 1 and 2. X-ray diffraction data were obtained using a Bruker P4 diffractometer outfitted with a SMART CCD detector. The structures were resolved by full-matrix least-squares procedures on FP 2 P with SHELXTL after being initially solved by direct methods and conventional difference map techniques (Version 6.10). P30P. On a Rigaku Hg 724+ diffractometer, X-ray diffraction data for binuclear cobalt(II) complexes (**1–3**) were gathered. By visiting www.ccdc.cam.ac.uk/data request/cif, you can obtain these data from the Cambridge Crystallographic Data Center for free.

The FT-IR data for binuclear cobalt(II) complexes were captured using a Perkin-Elmer FT-IR 2000 spectrometer using KBr discs with a wavelength range of 4000−400 cm^{-1}. The electronic spectra were captured using a Perkin Elmer Lambda 950 UV/VIS Spectrometer in

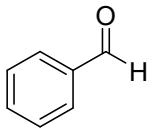
Dichloromethane (CH_2Cl_2) solvent. Micromass Q-Tof and Bruker Maxis Impact Spectrometers were used for the mass spectrometry measurements. An electrochemistry system made by PAR called the model 273A was used to measure cyclic voltammetry. Three electrodes a working platinum disc (2 mm), auxiliary electrodes, and a saturated Calomel Electrode (SCE) were used. Thermo Finnigan FLASH EA 1112 SERIES (CHNS) Elemental Analyzer was used to perform the elemental analysis. A Quantum Design MPMS XL-5 SQUID magnetometer was used to perform variable temperature susceptibility measurements on ground polycrystalline samples of binuclear cobalt(II) complexes **1** and **2** in the temperature range 5-300 K with an applied magnetic field of 0.1 Ton. Using tables of Pascal's constants, the susceptibility data were adjusted for the sample holders previously measured under the same circumstances and for the contributions of the sample's diamagnetic field.

1. Experimental Procedures and Characterizations

1.1 General procedure (A) for binuclear Co(II) catalysed acceptorless dehydrogenation (AD) of primary alcohols into aldehydes: To an oven-dried reaction tube equipped with magnetic stir bar added Binuclear Co(II) catalyst-2 (6.4 mg, 0.005 mmol, 1 mol%), KOH (1.4 mg, 0.025 mmol, 5 mol%) and primary alcohol (54.0 mg, 0.5 mmol, 1 eq) followed by addition of 2 mL of toluene under nitrogen atmosphere. The closed reaction tube containing the reaction mixture was placed in a preheated oil bath and stirred at 80°C for 24 hours. After completion of the reaction time, the reaction mixture was cooled down to room temperature. The crude mixture was purified by flash column chromatography using silica gel as stationary phase and hexane/ethyl acetate (95:5 v/v) as an eluent to afford the pure ketone product **5a** as colorless oil in 90 % (47.7 mg) yield.

1.2 Characterization of all catalysis compounds:

Benzaldehyde (5a):

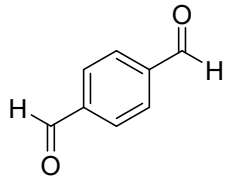


Compound **5a** was prepared according to the general procedure **A** from its corresponding alcohol (54.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5a** as colorless oil in 90 % (47.7 mg) yield. The NMR data of **5a** is in accordance with the literature. [1-2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.97 (dd, J = 161.2, 7.7 Hz, 2H), 7.60 – 7.39 (m, 3H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 192.21, 135.98, 134.13, 129.36, 128.62.

Terephthalaldehyde (5b):

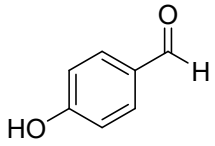


Compound **5b** was prepared according to the general procedure **A** from its corresponding di-alcohol (69.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5b** as white crystalline powder in 92 % (65.3 mg) yield. The NMR data of **5b** is in accordance with the literature.[3]

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.05 (s, 2H), 7.96 (s, 4H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 191.57, 139.96, 130.07.

4-hydroxybenzaldehyde (5c):

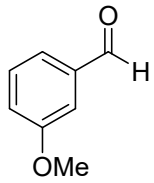


Compound **5c** was prepared according to the general procedure **A** from its corresponding alcohol (62.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5c** as yellow powder in 94 % (57.3 mg) yield. The NMR data of **5c** is in accordance with the literature.[1-2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.81 (d, J = 7.2 Hz, 2H), 6.98 (d, J = 7.2 Hz, 2H), 1.89 (s, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 191.42, 161.94, 132.56, 129.62, 116.03.

3-methoxybenzaldehyde (5d):

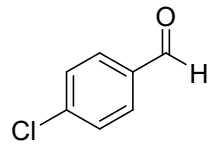


Compound **5d** was prepared according to the general procedure **A** from its corresponding alcohol (69.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5d** as colorless oil in 98 % (66.6 mg) yield. The NMR data of **5d** is in accordance with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.45 – 7.32 (m, 3H), 7.13 (d, J = 7.7 Hz, 1H), 3.80 (s, 3H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 191.84, 159.73, 137.41, 129.65, 122.97, 120.95, 111.89, 54.95.

4-chlorobenzaldehyde (5e):

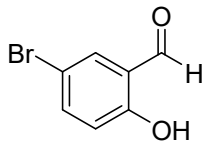


Compound **5e** was prepared according to the general procedure **A** from its corresponding alcohol (71.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5e** as light yellow crystalline powder in 78 % (54.6 mg) yield. The NMR data of **5e** is in accordance with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.80 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 190.75, 140.72, 134.70, 130.82, 129.34.

5-bromo-2-hydroxybenzaldehyde (5f):



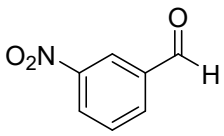
Compound **5f** was prepared according to the general procedure **A** from its corresponding alcohol (101 mg, 0.5 mmol, 1 eq) and the reaction mixture

was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5f** as pale yellow solid in 72 % (72.0 mg) yield. The NMR data of **5f** is in accordance with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.91 (s, 1H), 9.82 (s, 1H), 7.60 (d, J = 42.4 Hz, 2H), 6.88 (s, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 195.28, 160.33, 139.47, 135.45, 121.57, 119.63, 111.18.

3-nitrobenzaldehyde (5g):

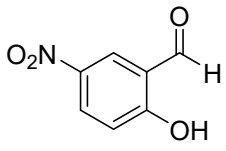


Compound **5h** was prepared according to the general procedure **A** from its corresponding alcohol (76.5 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (3% EtOAc/Hexane) to afford **5h** as brownish crystalline powder in 69 % (52.0 mg) yield. The NMR data of **5h** is in accordance with the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.57 (s, 1H), 8.38 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 7.7 Hz, 1H), 7.74 (t, J = 7.9 Hz, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 189.76, 148.36, 137.07, 134.68, 130.23, 128.22, 123.80.

2-hydroxy-5-nitrobenzaldehyde (5h):

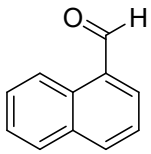


Compound **5g** was prepared according to the general procedure **A** from its corresponding alcohol (84.5 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (3% EtOAc/Hexane) to afford **5g** as reddish yellow powder in 74 % (61.7 mg) yield. The NMR data of **5g** is in accordance with the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.59 (s, 1H), 10.00 (s, 1H), 8.56 (s, 1H), 8.38 (d, J = 9.0 Hz, 1H), 7.11 (d, J = 9.0 Hz, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 13C NMR (151 MHz, CDCl3) δ 195.52, 166.04, 140.53, 131.58, 129.70, 119.33, 118.91.

1-naphthaldehyde (5i):

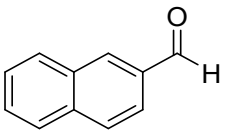


Compound **5i** was prepared according to the general procedure **A** from its corresponding alcohol (79.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5i** as white solid in 88 % (68.6 mg) yield. The NMR data of **5i** is in accordance with the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.22 (s, 1H), 9.17 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.73 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 193.21, 136.31, 134.84, 133.22, 130.81, 130.00, 128.69, 128.10, 126.51, 124.41.

2-naphthaldehyde (5j):

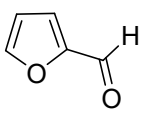


Compound **5j** was prepared according to the general procedure **A** from its corresponding alcohol (79.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5j** as pink crystalline solid in 89 % (69.4 mg) yield. The NMR data of **5j** is in accordance with the literature.[1]

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.02 (s, 1H), 8.11 (s, 1H), 7.83 (dd, J = 14.7, 7.8 Hz, 2H), 7.75 (s, 2H), 7.52 (s, 1H), 7.46 (s, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 191.72, 135.91, 134.07, 133.62, 132.14, 129.09, 128.67, 128.59, 127.63, 126.65, 122.20.

Furan-2-carbaldehyde (5k):

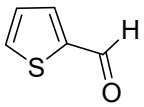


Compound **5k** was prepared according to the general procedure **A** from its corresponding alcohol (49.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5k** as colorless liquid in 63 % (30.2 mg) yield. The NMR data of **5k** is in accordance with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.71 (s, 1H), 7.27 (s, 1H), 6.62 (s, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 177.88, 152.87, 148.07, 121.10, 112.54.

Thiophene-2-carbaldehyde (5l):



Compound **5l** was prepared according to the general procedure **A** from its corresponding alcohol (57.0 mg, 0.5 mmol, 1 eq) and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) to afford **5l** as colorless liquid in 61 % (34.2 mg) yield. The NMR data of **5l** is in accordance with the literature.[2]

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.82 – 7.73 (m, 2H), 7.21 (s, 1H), 2.20 (s, 1H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 182.98, 143.99, 136.29, 135.10, 128.28.

Analytical data for all the compounds:

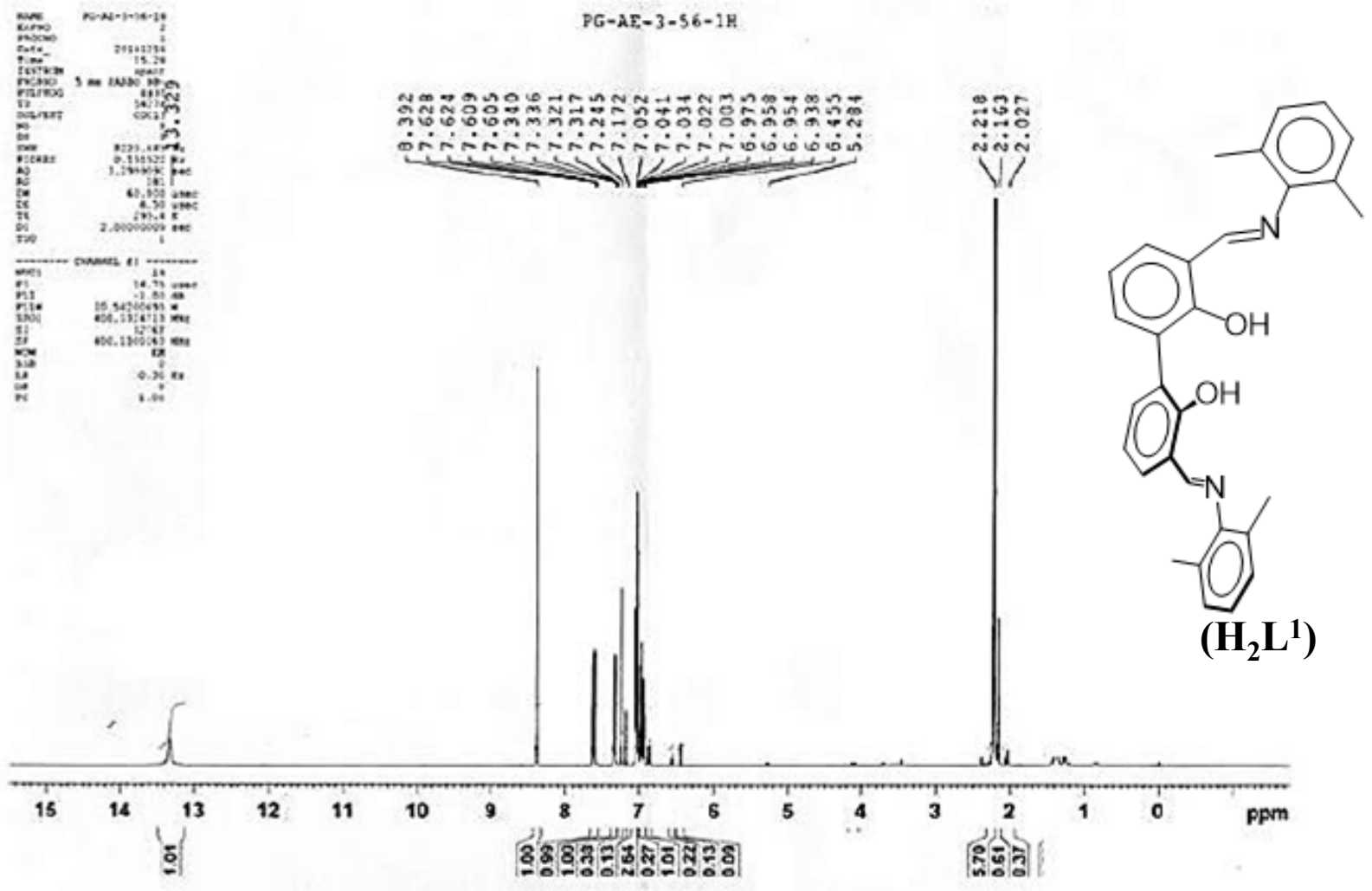


Figure S1. ^{1}H NMR spectrum of the $\mathbf{H_2L^1}$ in $CDCl_3$.

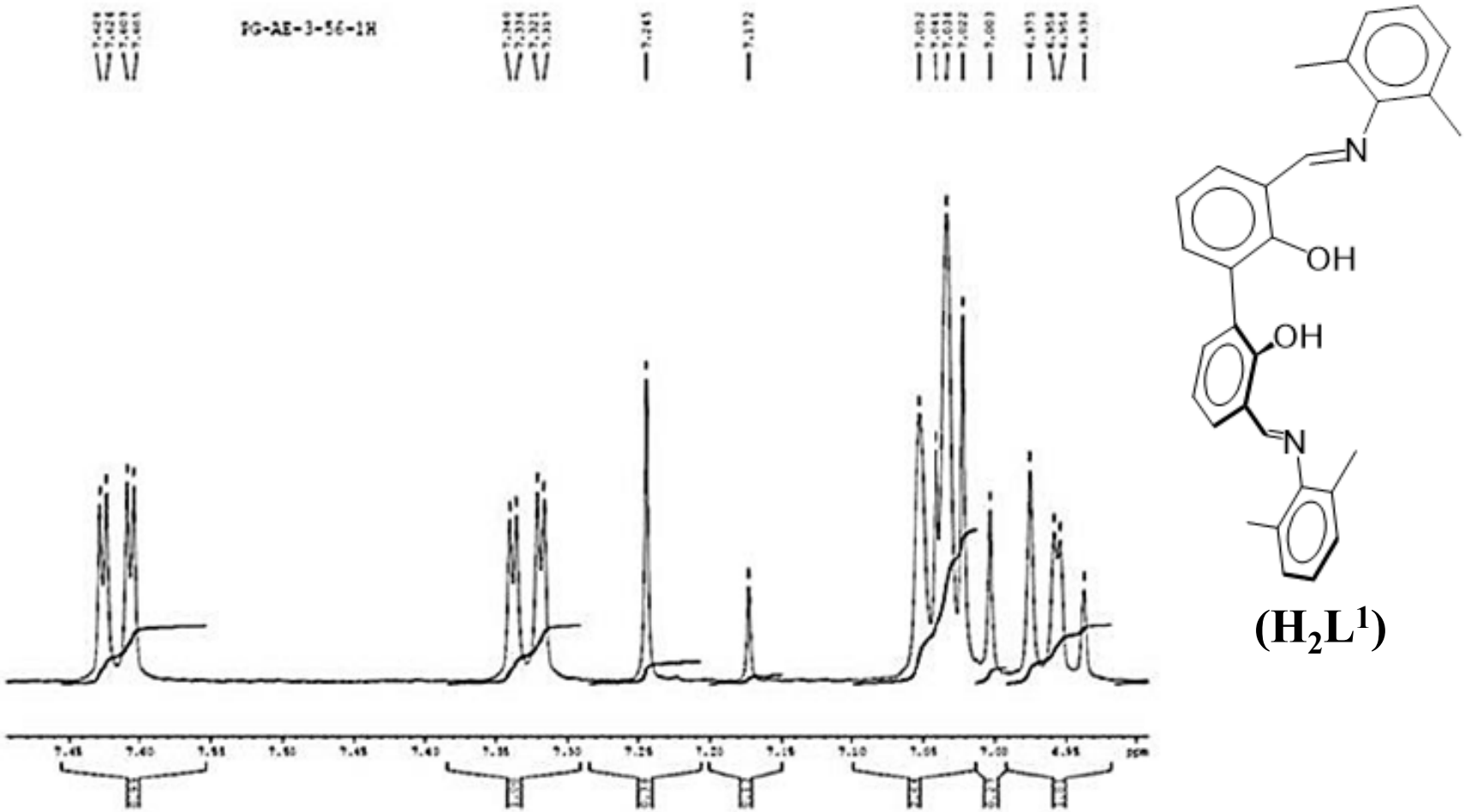
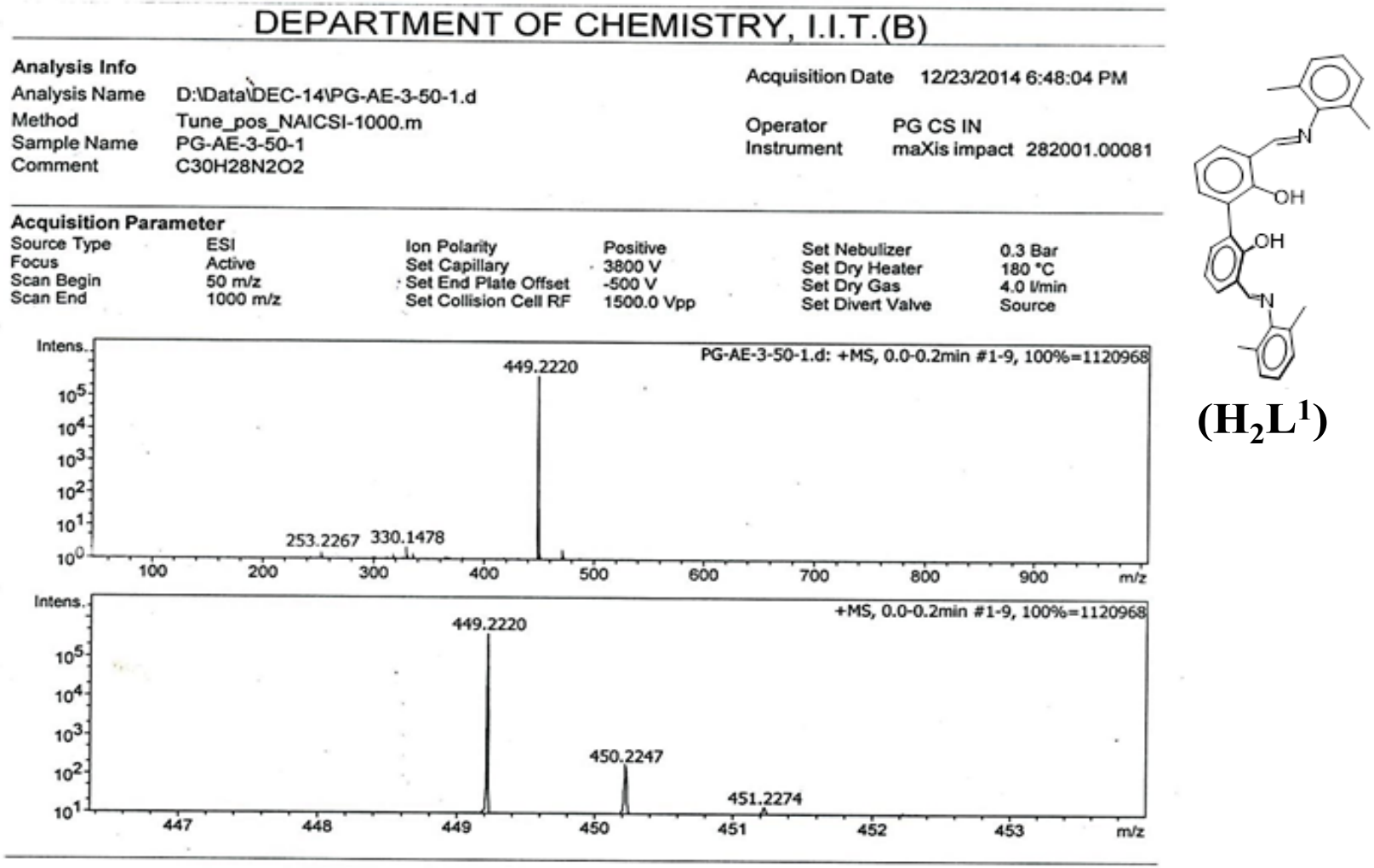
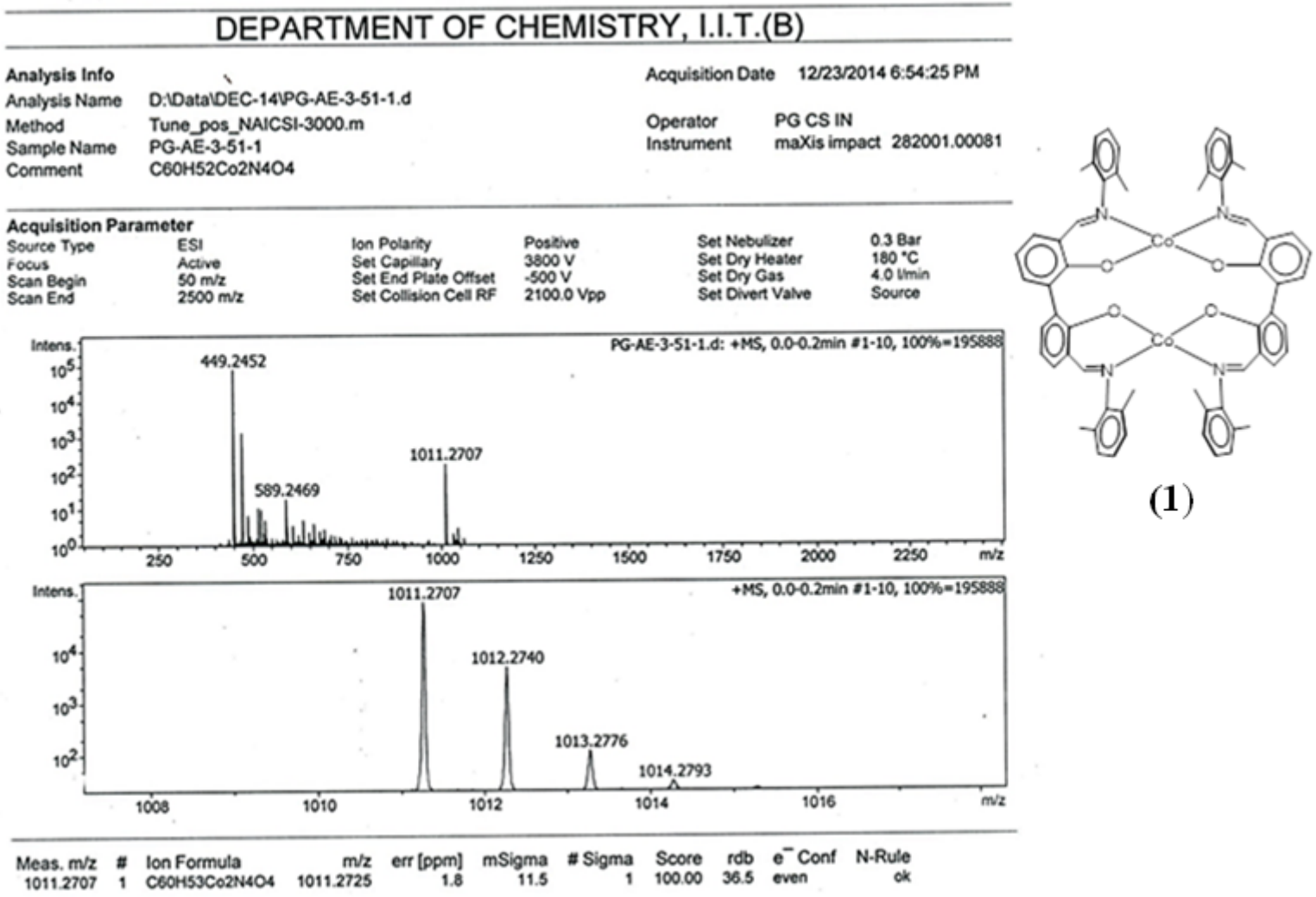


Figure S2. Expanded ^{1}H NMR spectrum of the $\mathbf{H_2L^1}$ in $CDCl_3$.



(H_2L^1)

Figure S3. HRMS spectrum of the $\mathbf{H_2L^1}$ in $CHCl_3$.



(1)

Figure S4. HRMS spectrum of the **[Co(II)H_2L^1]** complex-**1** in $CHCl_3$.

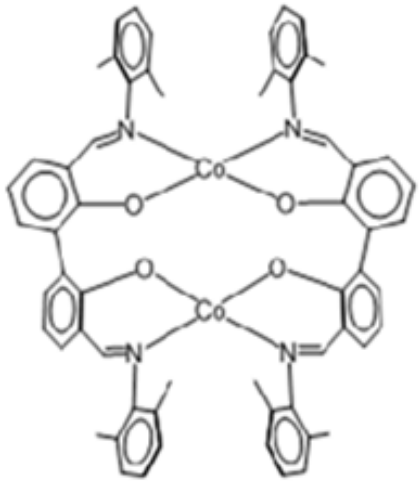
Eager 300 Report

Page: 1 Sample: PG-AE-3-51-2 (PG-AE-3-51-2)

Method Name : PG-SRM-15122014
Method File : D:\CHNS-2014\PG-SRM-15122014.mth
Chromatogram : PG-AE-3-51-2
Operator ID : Sonali
Analysed : 12/15/2014 16:16
Sample ID : PG-AE-3-51-2 (# 19)
Analysis Type : UnkNown (Area)

Calib. method : using 'K Factors'

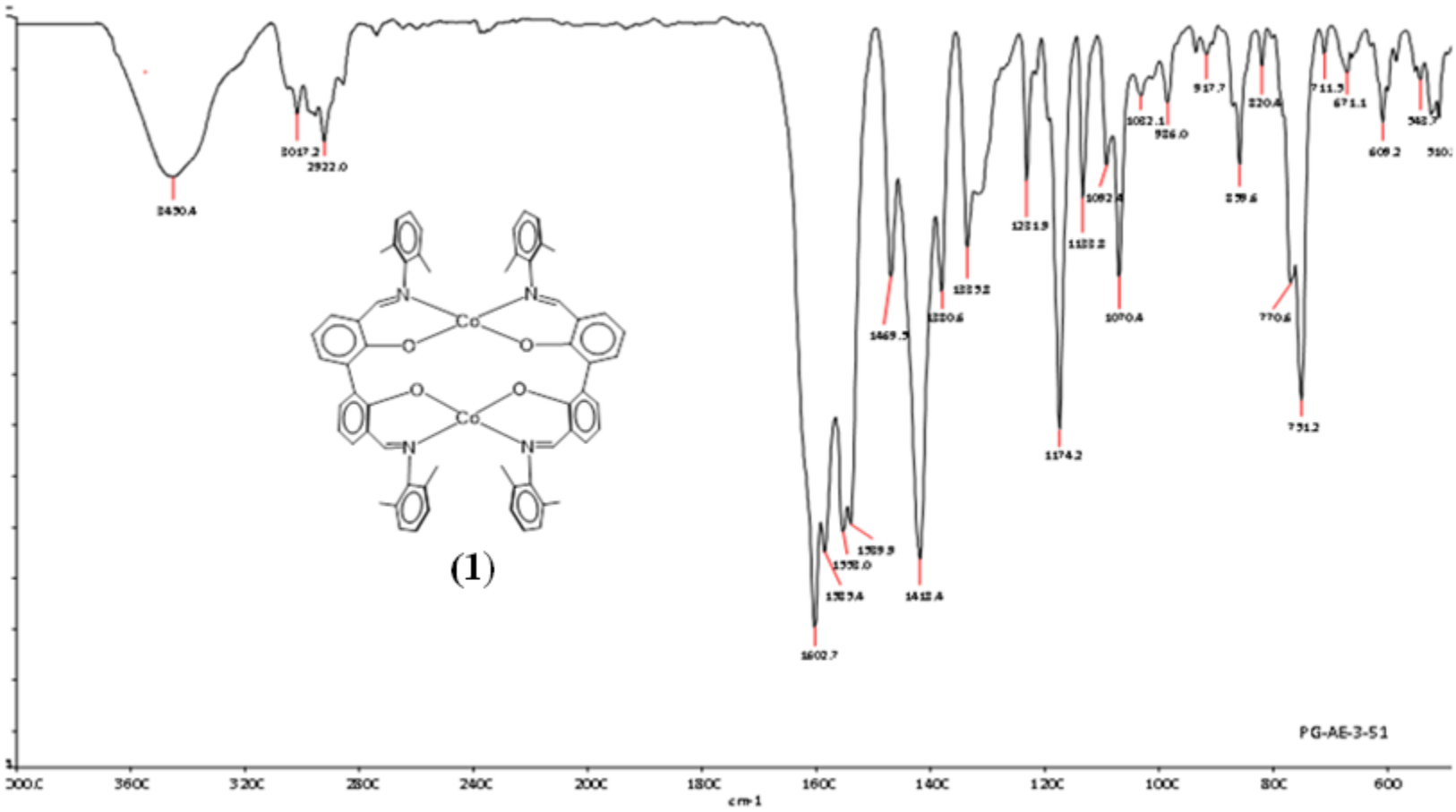
!!! Warning missing one or more peaks.



(1)

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	5.2540	43	74913	FU	29.875300	.149112E+07
2	0.0000	57	265722	FU		0.0000
Carbon	71.7856	66	2238051	FU	1.000000	.275501E+07
Hydrogen	5.2458	181	456530	RS	4.902309	.707107E+07
Totals	82.2854		3035216			

Figure S5. CHN analysis of the **[Co(II)H_2L^1]** complex-**1**.



(1)

Figure S6. FT-IR spectrum of the **[Co(II)H_2L^1]** complex-**1**.

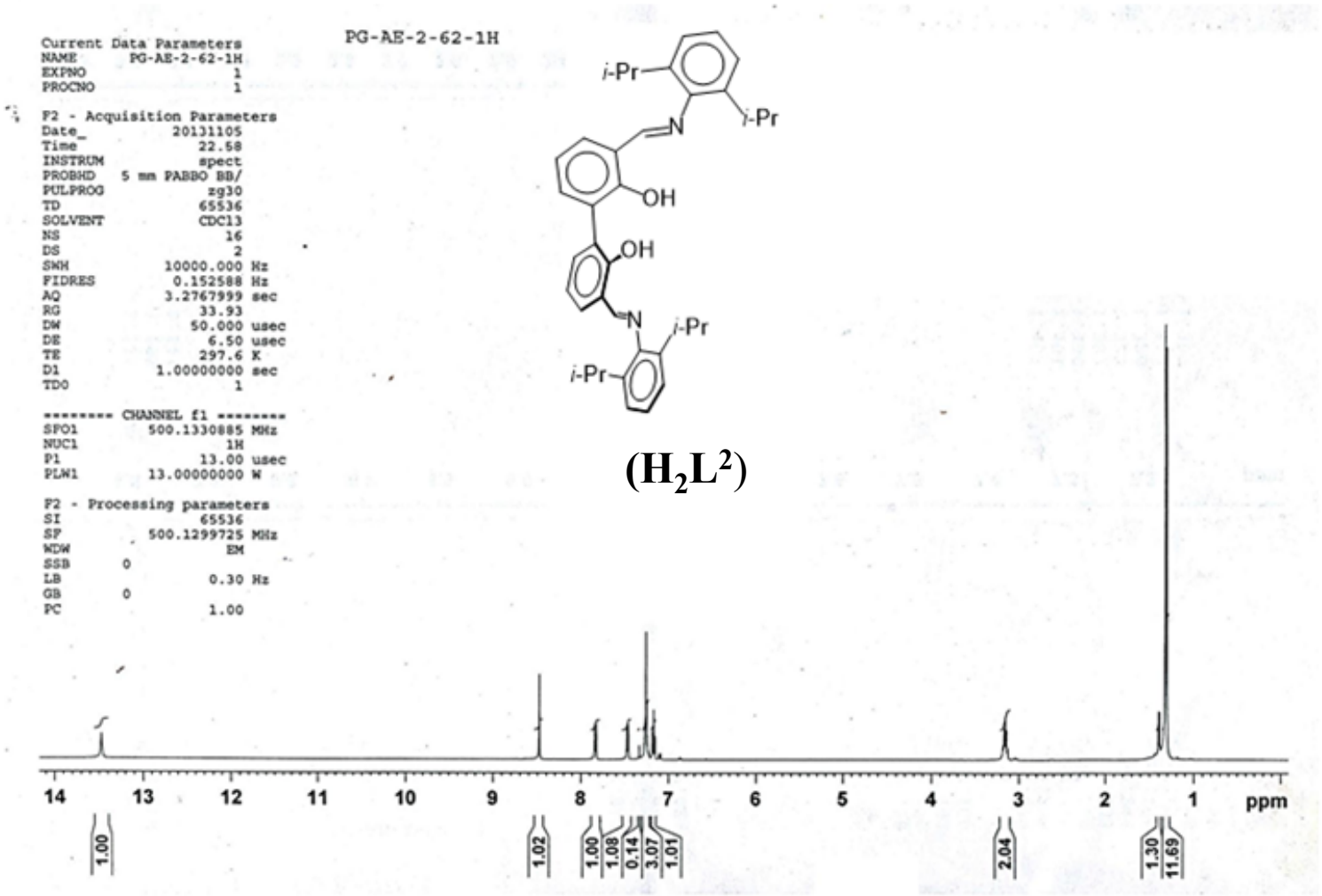


Figure S7. ^{1}H NMR spectrum of the ligand $\mathbf{H_2L^2}$ in $CDCl_3$.

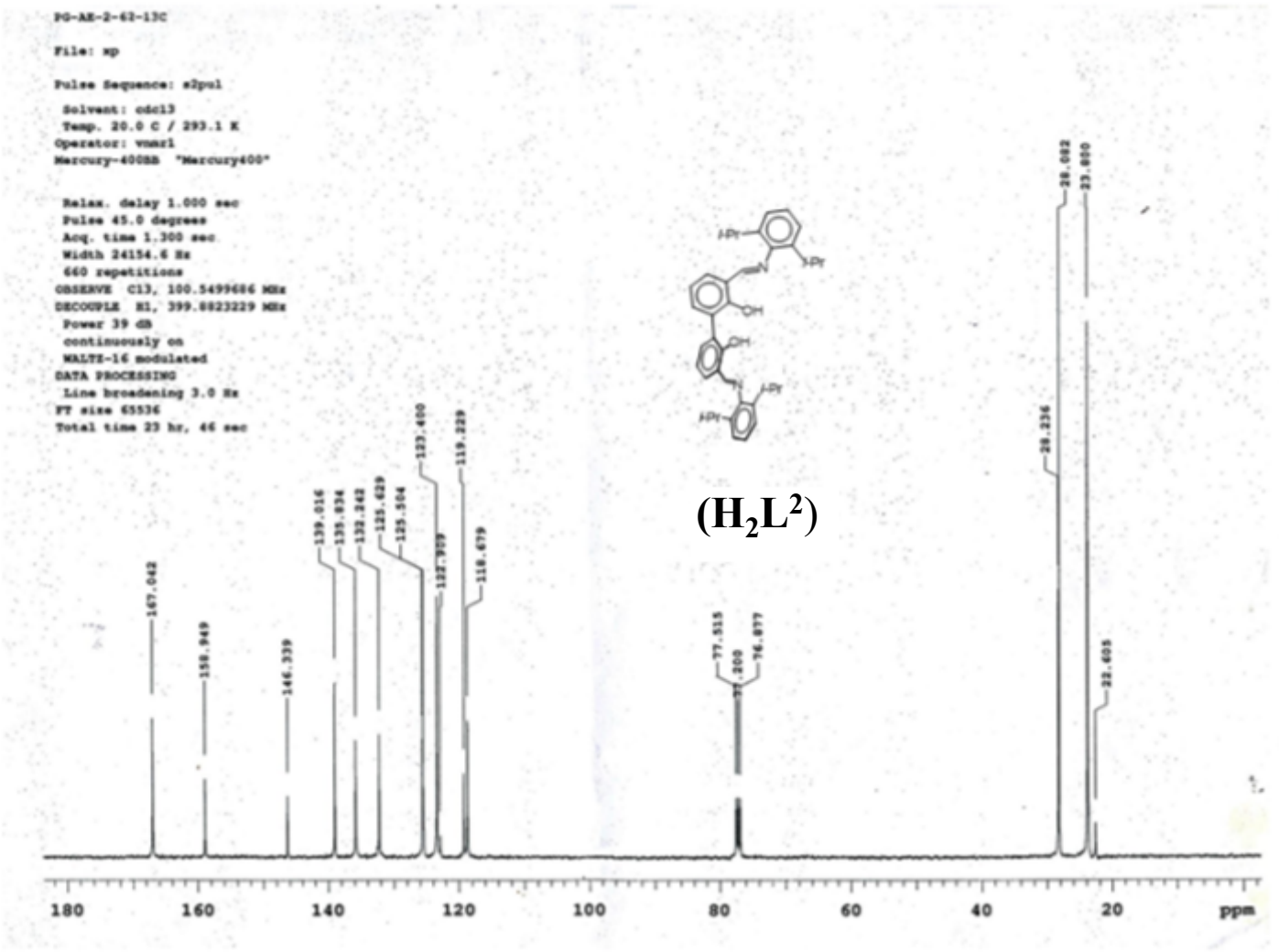
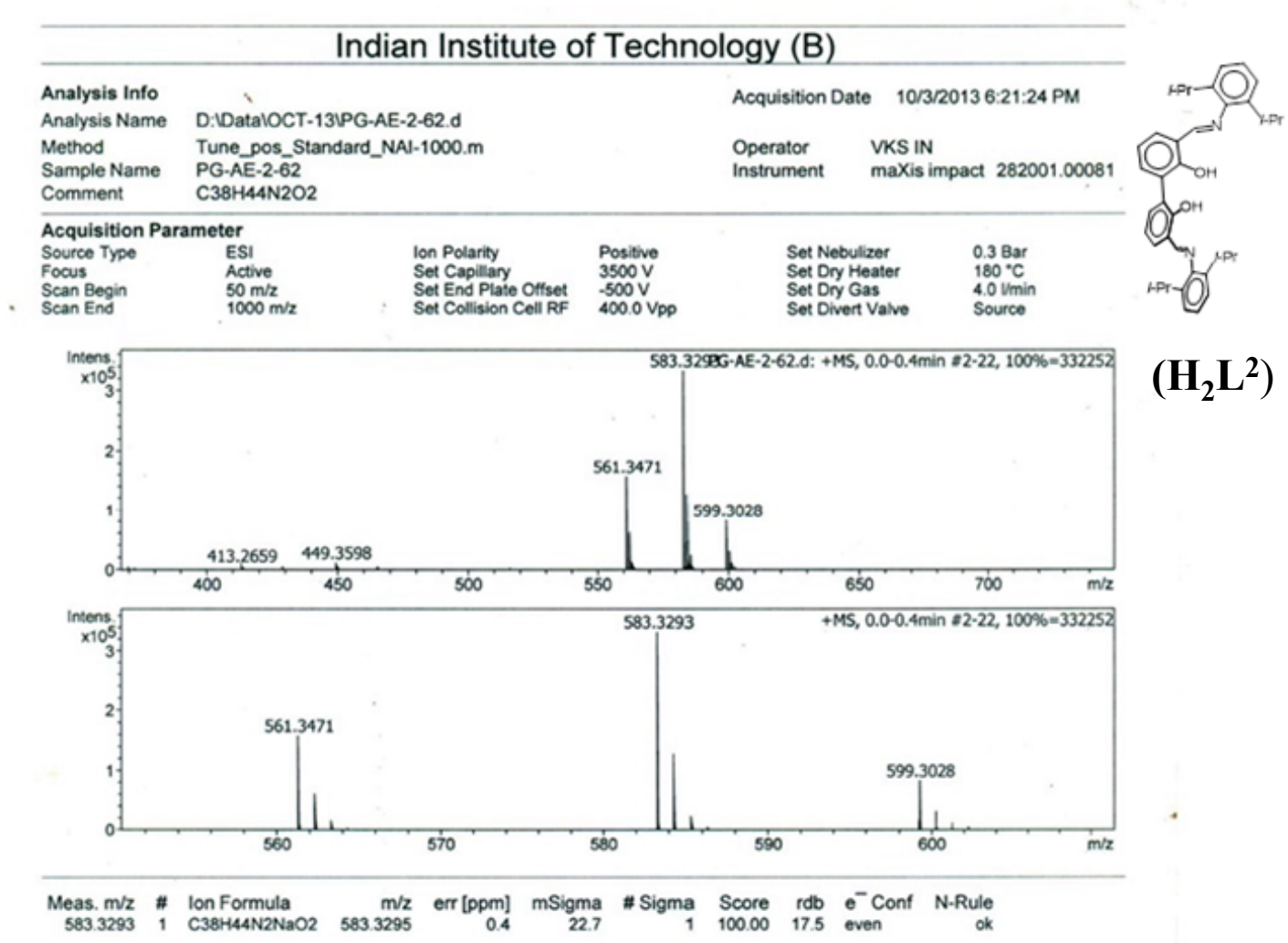
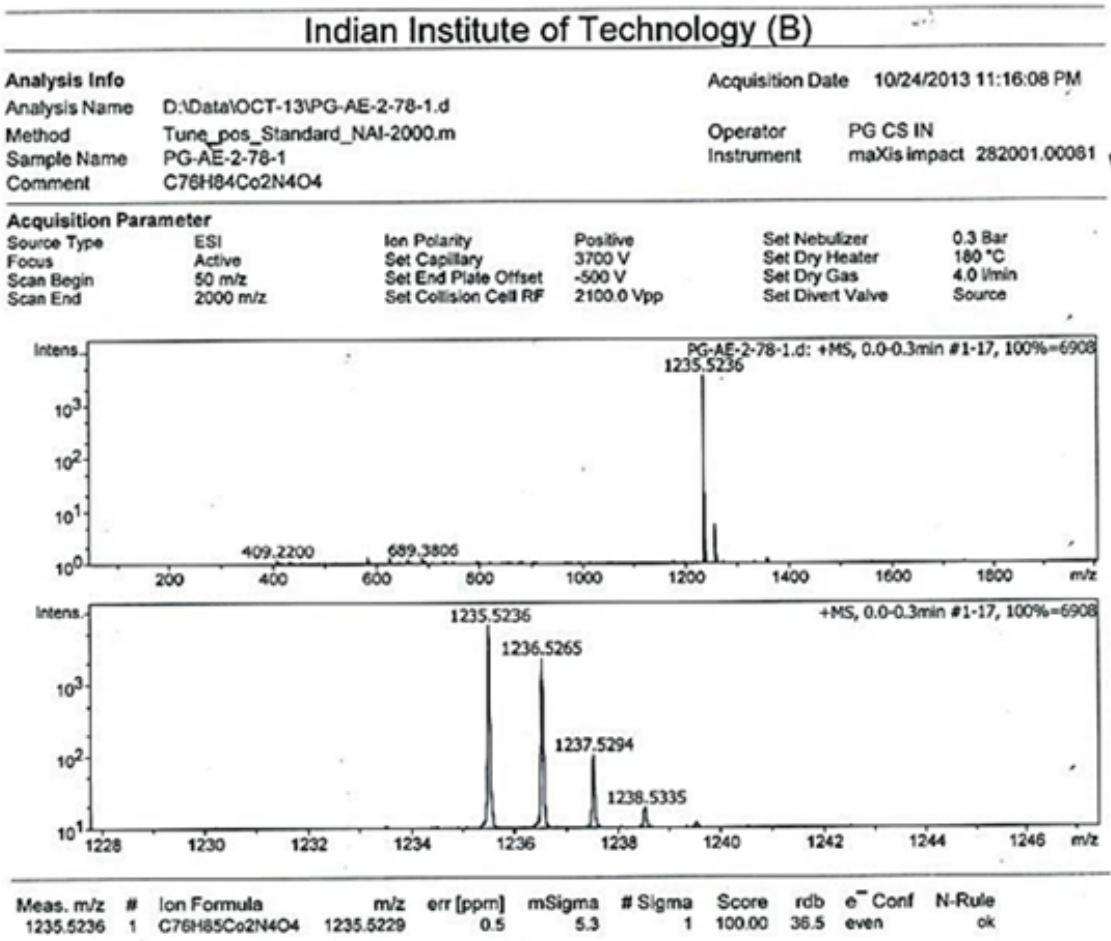


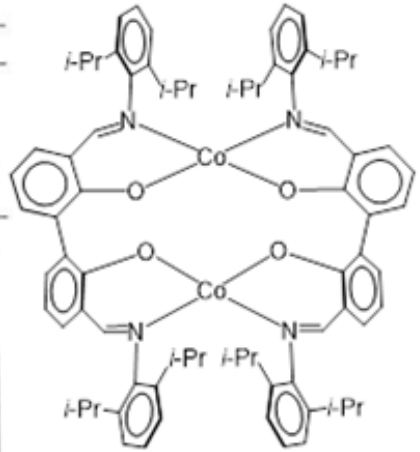
Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of the ligand $\mathbf{H_2L^2}$ in $CDCl_3$.



(H_2L^2)

Figure S9. HRMS spectrum of the ligand $\mathbf{H_2L^2}$ in $CHCl_3$..





(2)

Figure S10. HRMS spectrum of the **[Co(II)H_2L^2]** complex-**2** in $CHCl_3$.

.

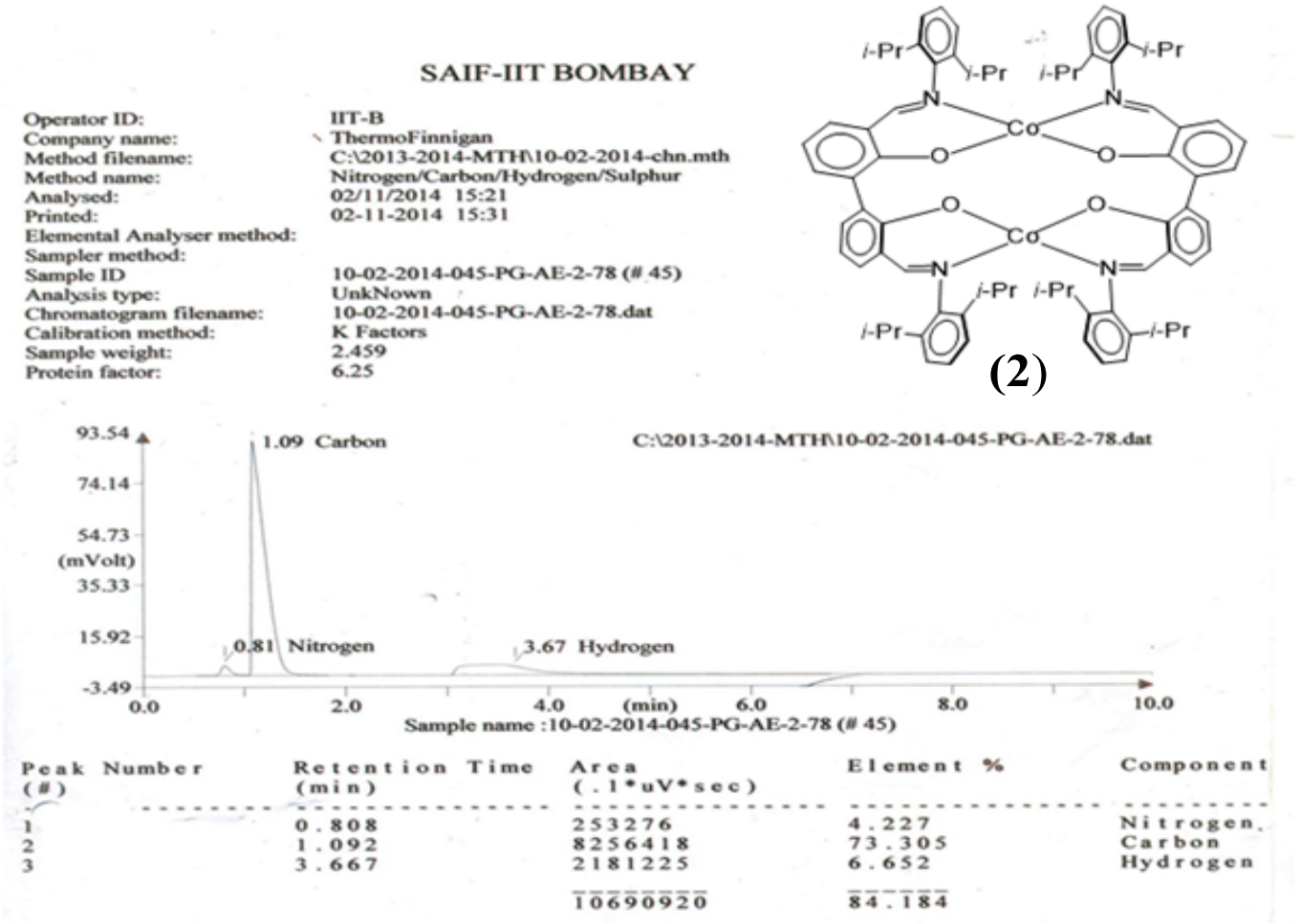
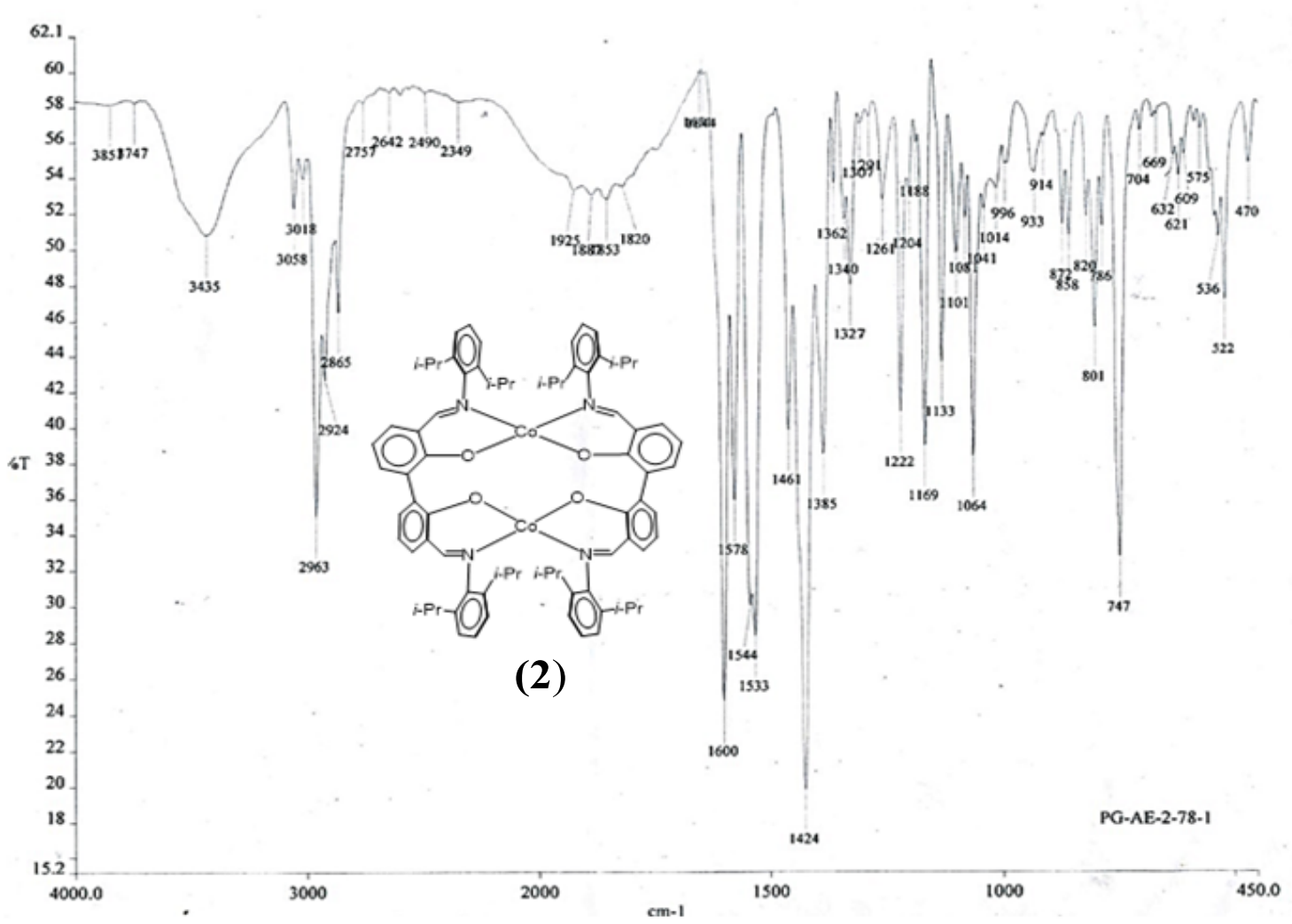


Figure S11. CHN analysis of the **[Co(II)H_2L^2]** complex-**2**.



(2)

Figure S12. FT-IR spectrum of the **[Co(II)H_2L^2]** complex-**2**.

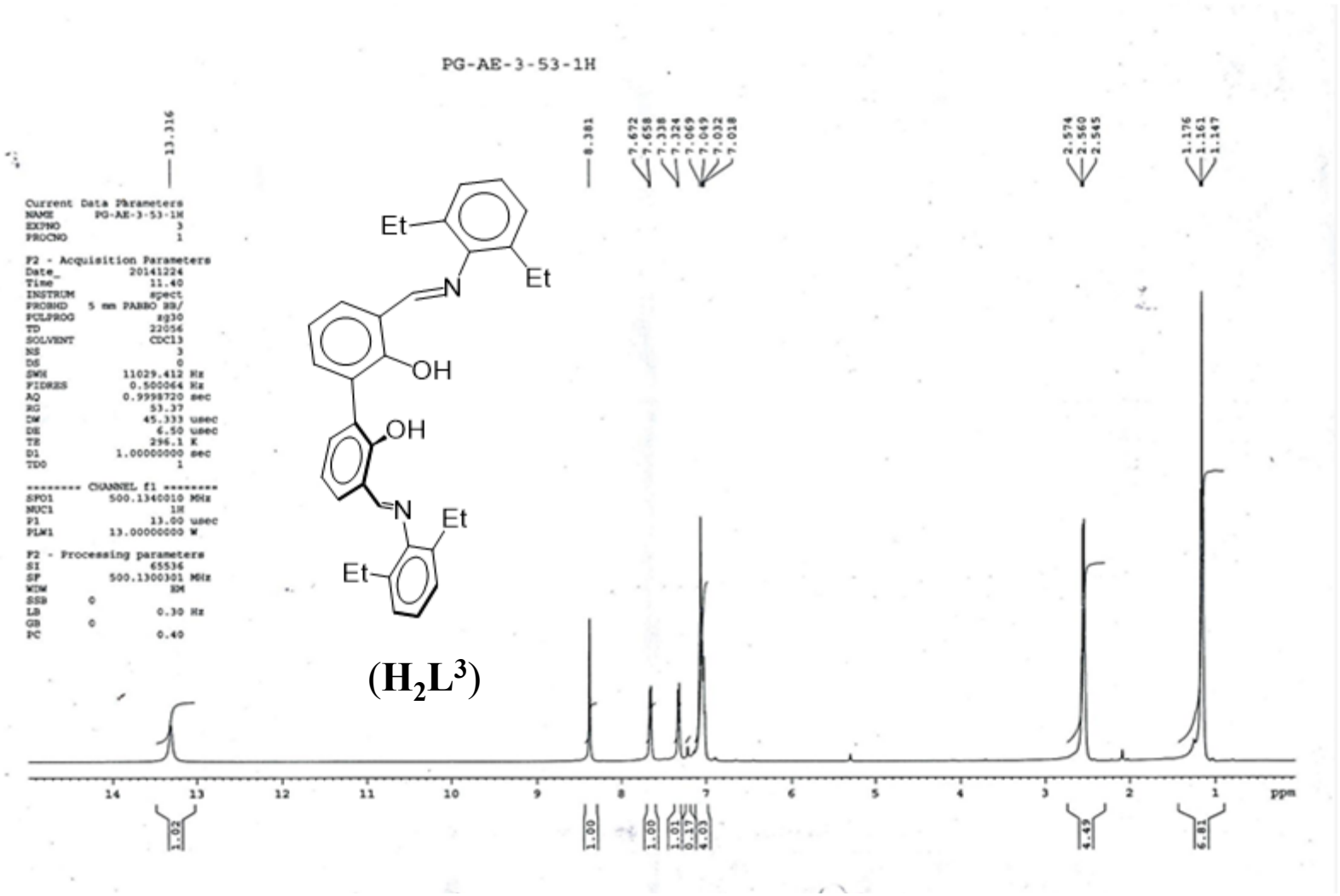


Figure S13. ^{1}H NMR spectrum of the ligand $\mathbf{H_2L^3}$ in $CDCl_3$.

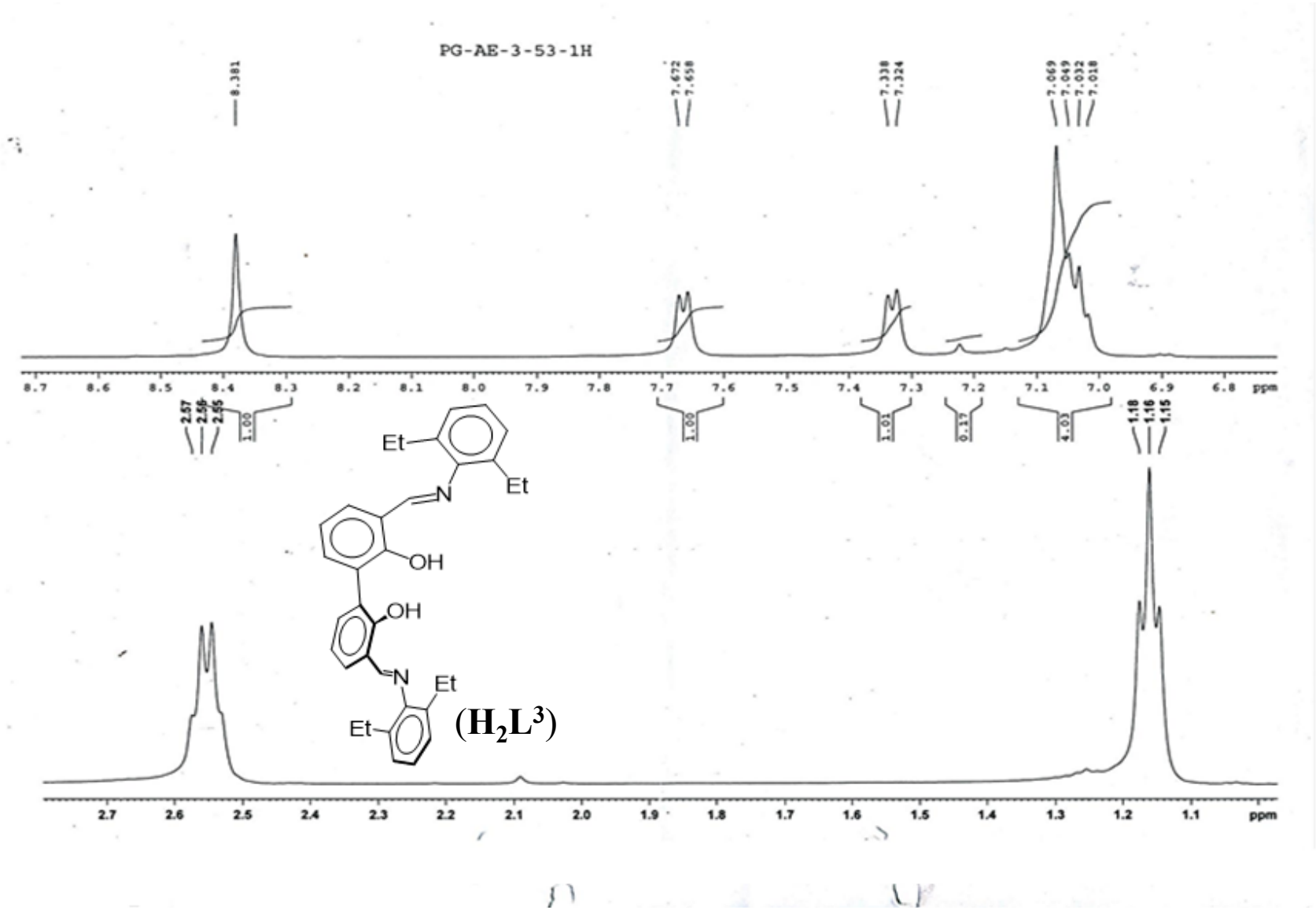
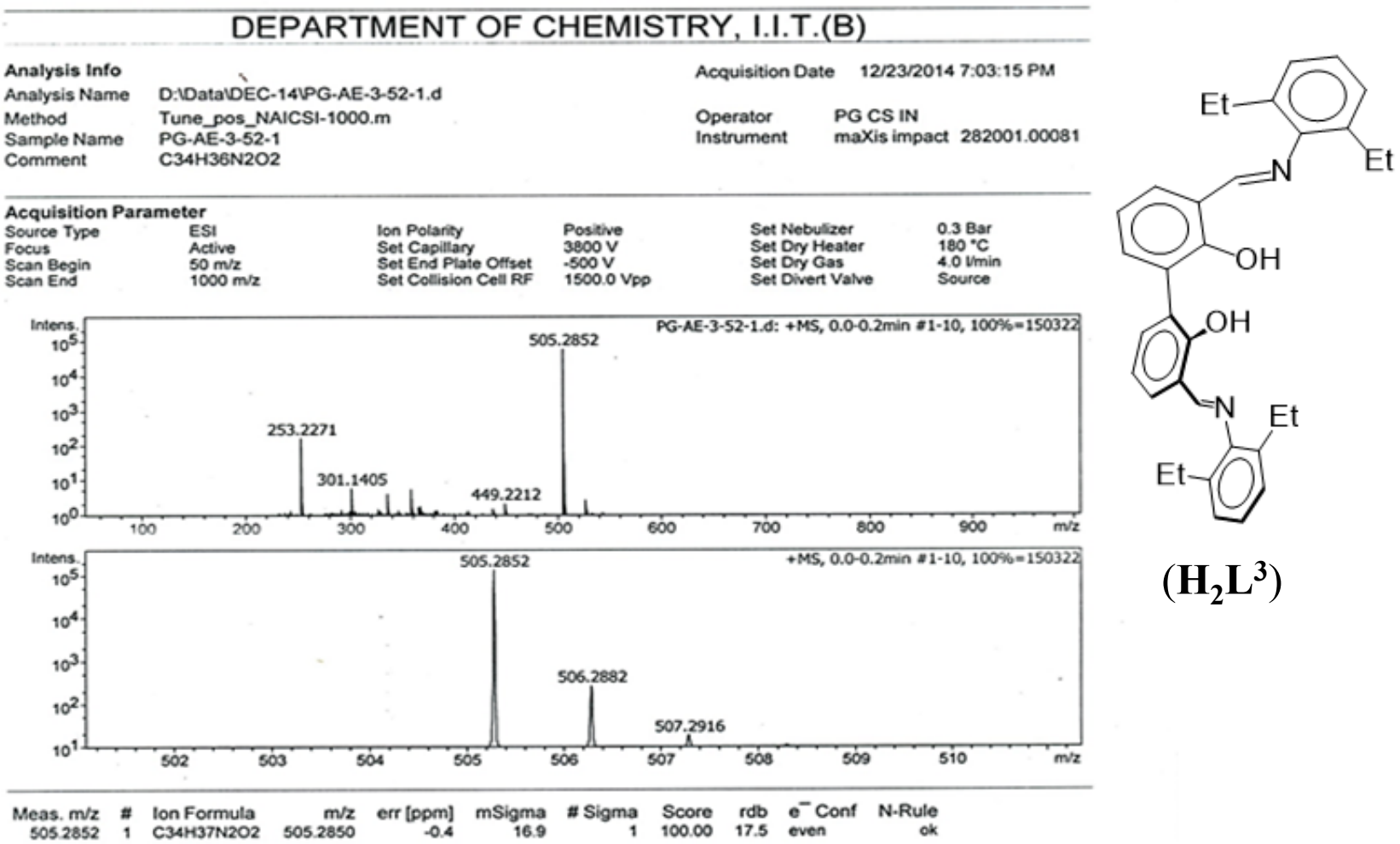


Figure S14. Expanded ^{1}H NMR spectrum of the ligand $\mathbf{H_2L^3}$ in $CDCl_3$.



(H_2L^3)

Figure S15. HRMS spectrum of the ligand $\mathbf{H_2L^3}$ in $CHCl_3$.

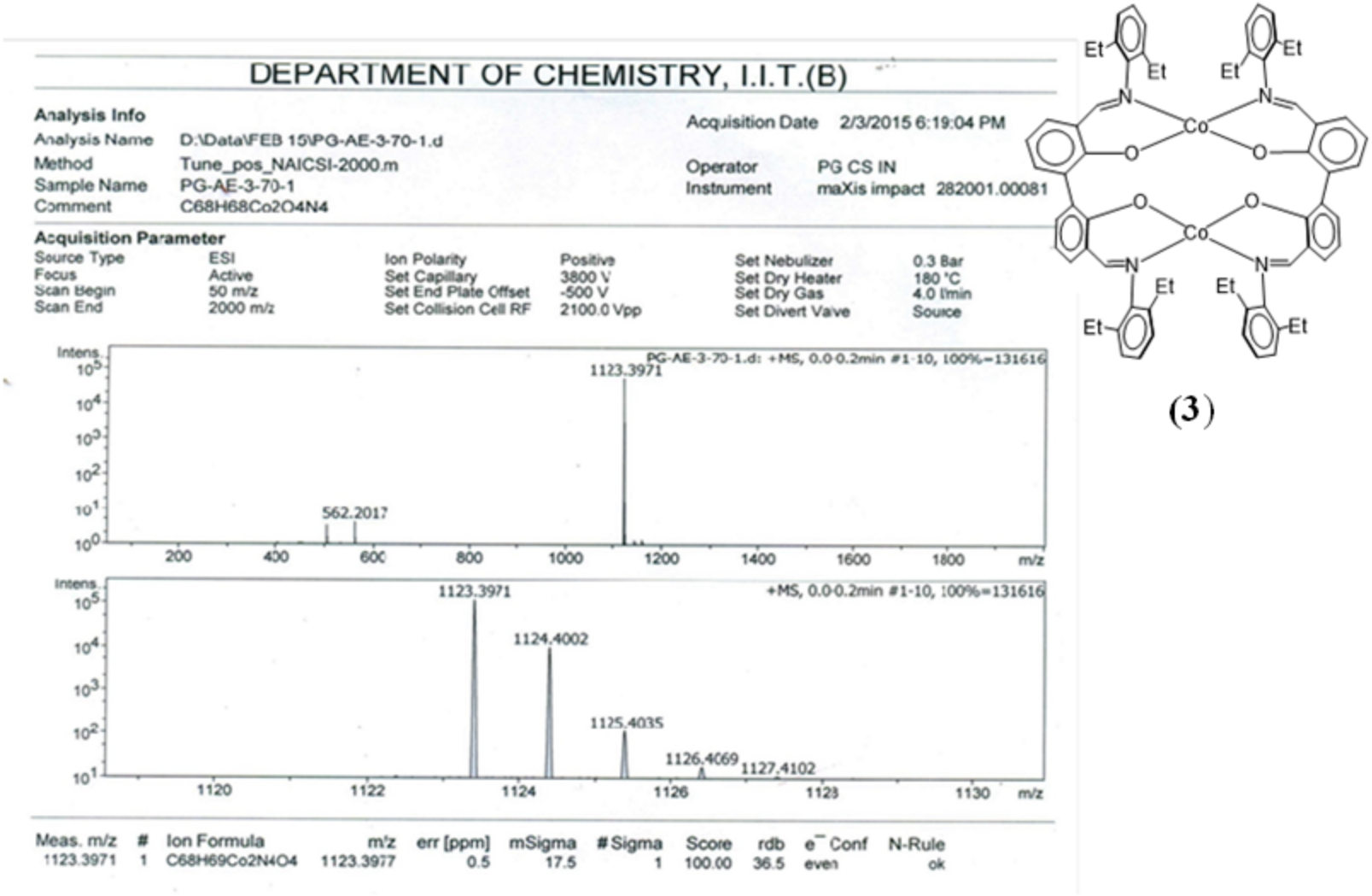


Figure S16. HRMS spectrum of the **[Co(II)H_2L^3]** complex-**3** in $CHCl_3$.

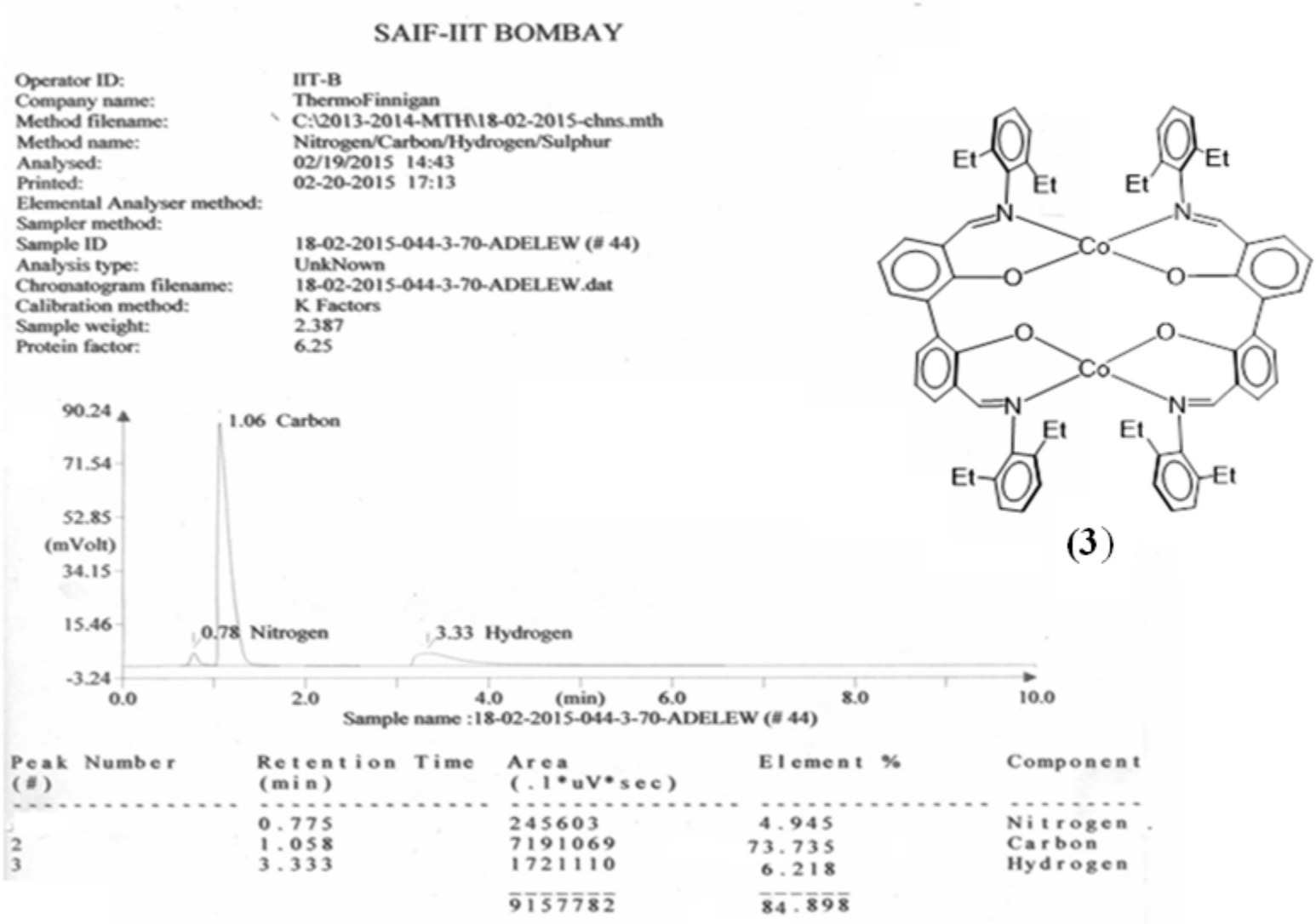


Figure S17. CHN analysis of the **[Co(II)H_2L^3]** complex-**3**.

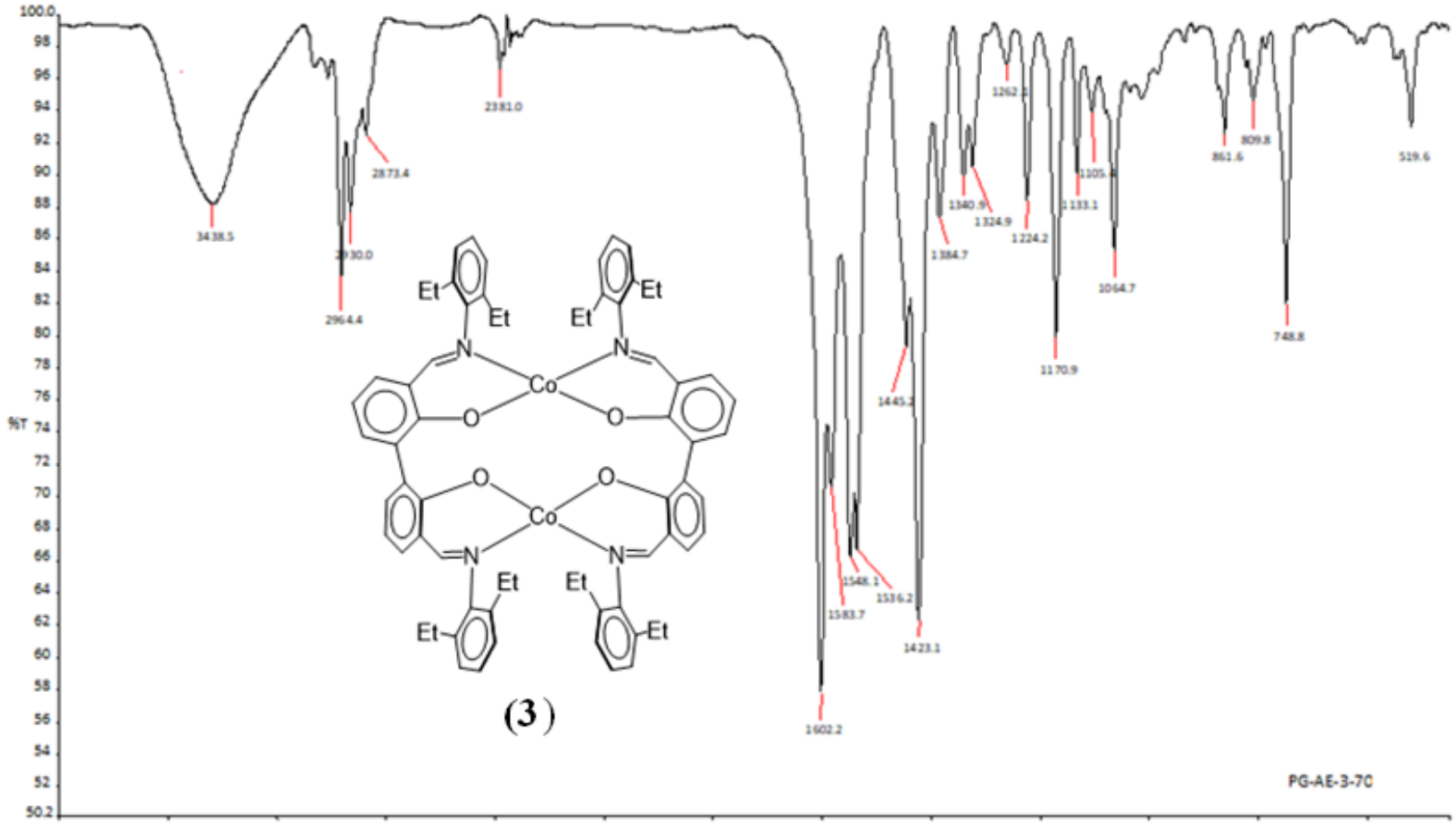


Figure S18. FT-IR spectrum of the **[Co(II)H_2L^3]** complex-**3**.

Table 1 S19. Important FT-IR bands of the ligand $\mathbf{H_2L^1}$ and binuclear Co(II) complexes (**1−3)**

Compounds	***v*(O–H)/H_2O (cm^{-1})**	***v*(C=N) (cm^{-1})**	***v*(C–O) (cm^{-1})**	***v*(C=C) (cm^{-1})**
Ligand (H_2L^1)	3440	1618	1203	1427
Co(II) complex-1	3446	1599	1143	1421
Co(II) complex-2	3450	1585	1174	1418
Co(II) complex-3	3435	1600	1169	1424

Table 2 S20. UV–Visible spectra of ligands (**H_2L^1, H_2L^2 and H_2L^3**) and binuclear cobalt(II) complexes **(1-3)**

Compounds	λ_{max}, nm	absorbance	ε, $M^{-1}cm^{-1}$	transitions
Ligand (H_2L^1)	257 350	0.27 0.12	27000 12000	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
Ligand (H_2L^2)	264 341	0.26 0.11	26000 11000	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
Ligand (H_2L^3)	263 350	0.27 0.11	27000 11000	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
Co(II) complex-1	236 277 410	0.71 0.33 0.21	10,600 4,900 3,100	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $d \rightarrow \pi^*$
Co(II) complex-2	233 277 400	0.78 0.36 0.21	11600 5400 3100	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $d \rightarrow \pi^*$
Co(II) complex-3	233 275 400	0.84 0.39 0.22	12500 5800 3200	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $d \rightarrow \pi^*$

Table 3 S21. X-ray crystallographic data for the binuclear cobalt(II) complexes (**1-3**)

Compounds	**Co(II) complex-1 (**$CH_3CN.H_2O$)	**Co(II) complex-2 (**CH_2Cl_2)	**Co(II) complex-3 (**CH_3CN)
Moiety formula	$C_{60}\ H_{52}\ Co_2\ N_4\ O_4.C_2\ H_3N.H_2$	$C_{68}\ H_{68}\ Co_2\ N_4O_4.CH_2Cl_2$	$C_{76}\ H_{84}\ Co_2\ N_4\ O_4.C_2H_3\ N$
Sum formula	$C_{62}H_{57}Co_2N_5O_5$	$C_{69}H_{70}Cl_2Co_2N_4O_4$	$C_{78}\ H_{87}\ Co_2\ N_5\ O_4$
Crystal system	Orthorhombic	Triclinic	Triclinic
Formula weight	1070.041	1208.121	1276.458
Crystal color	Green	Green	Green
Space group	$P2_12_12_1$	P -1	P-1
a/Å	12.078(2)	12.2854(15)	14.022(9)
b/Å	13.095(2)	13.8933(19)	16.557(10)
c/Å	33.434(5)	18.666(3)	16.724(11)
α/◦	90	85.816(4)	105.310(8)
β/◦	90	80.738(5)	108.728(5)
γ/◦	90	78.222(4)	100.126(5)

Z	4	2	2
temperature (K)	100(2)	100(2)	100(2)
Radiation (λ, Å)	0.71075	0.71075	0.71075
ρ(calcd.) gcm^{-3}	1.344	1.305	1.247
F000	2236.205	1266.712	1354.189
Mu (mm^{-1})	0.683	0.678	0.541
θ max, deg.	25.000	25.000	25.000
No. of data	9179	10814	12313
h, k, l max	14, 15, 39	14, 16, 22	14, 15, 39
No. of parameters	679	730	803
Data completeness	0.98	0.995	0.991
R1	0.0414	0.0474	0.1053

wR2	0.1041	0.1205	0.2390
GOF	0.9260	1.0408	1.0376
CCDC	**1049317**	**1044421**	**978972**
Flack Parameter	**0.249(15)**	**n/a**	**n/a**

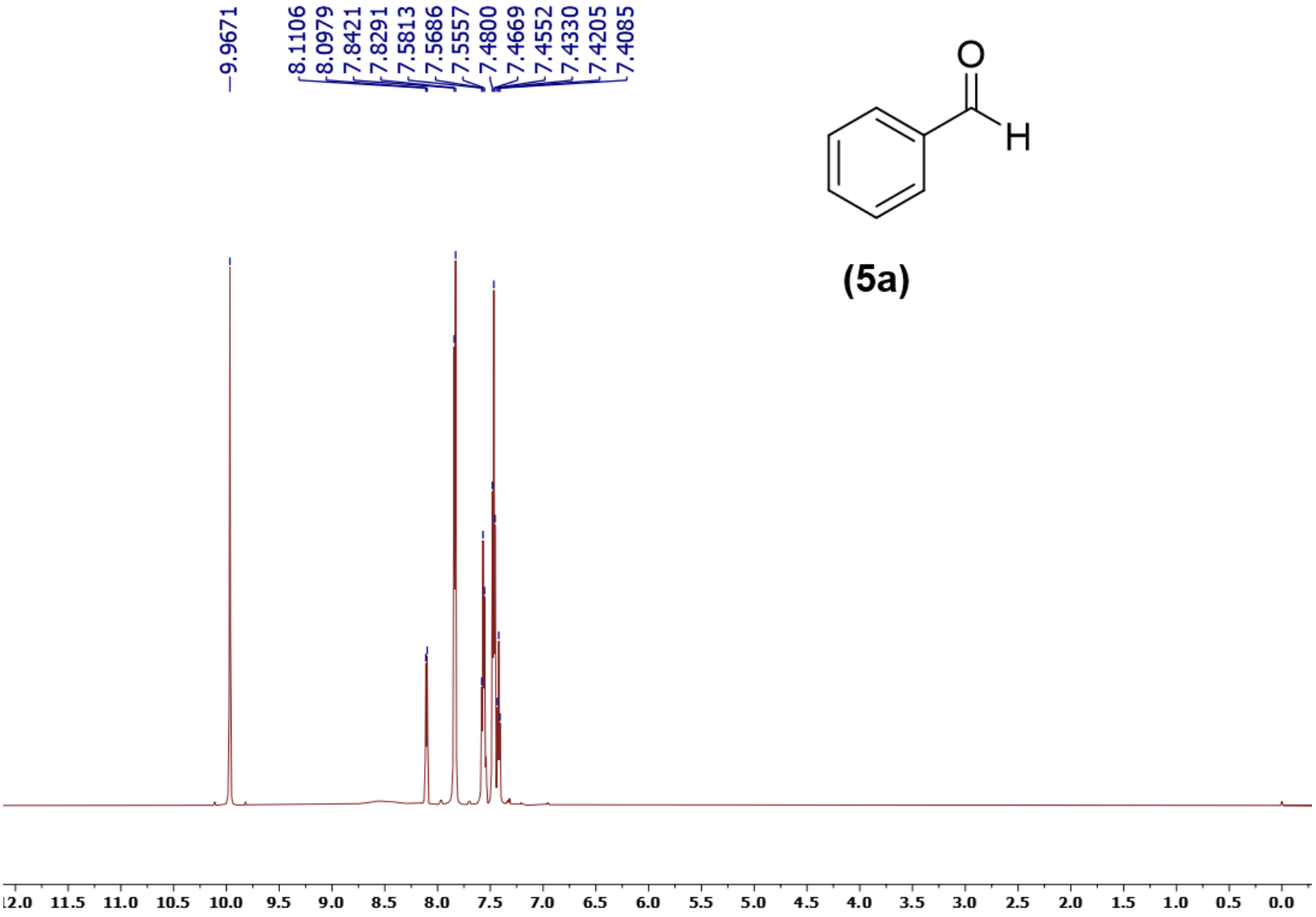


Figure S22. ^{1}H NMR spectrum of **5a** in $CDCl_3$.

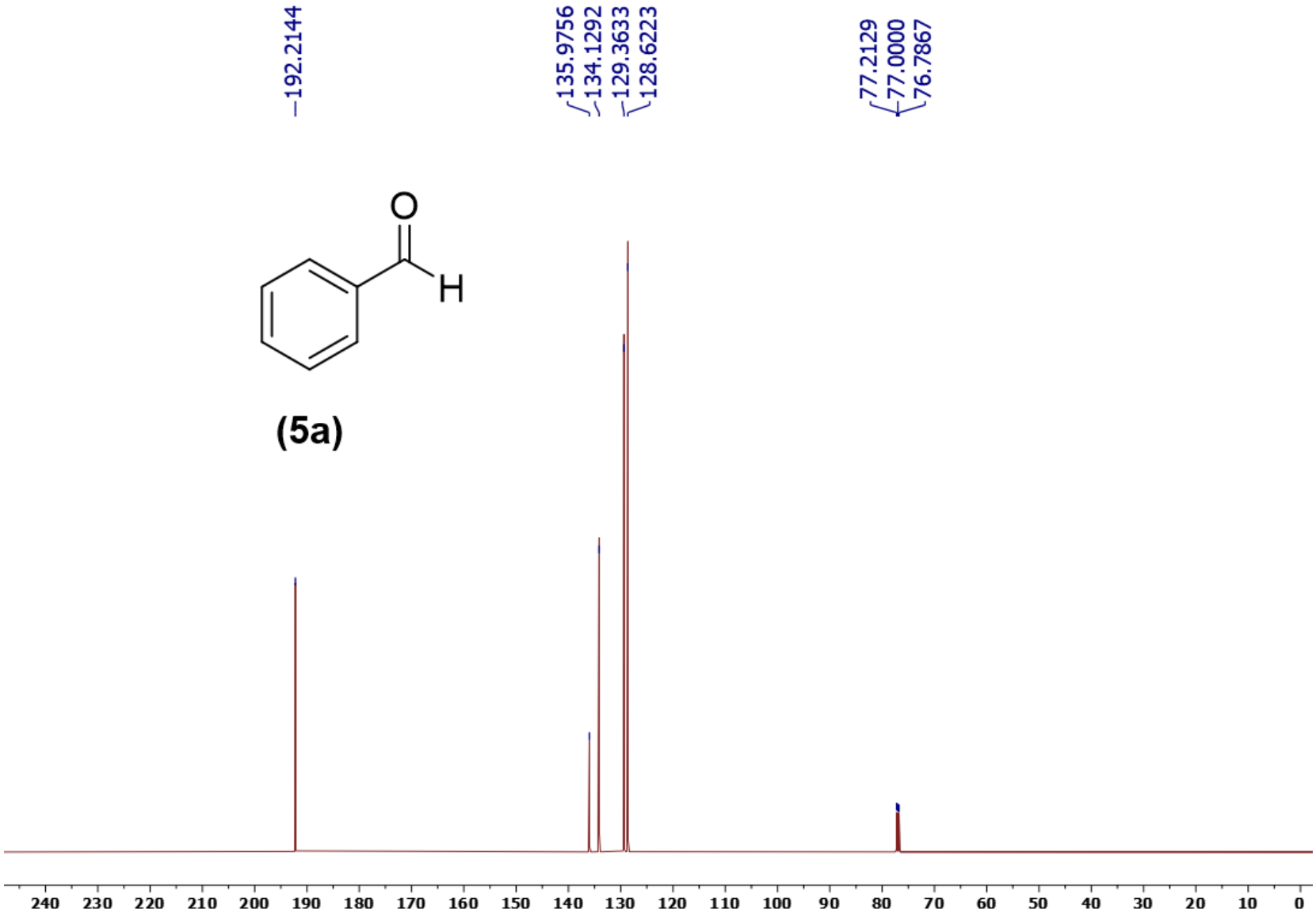


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$.

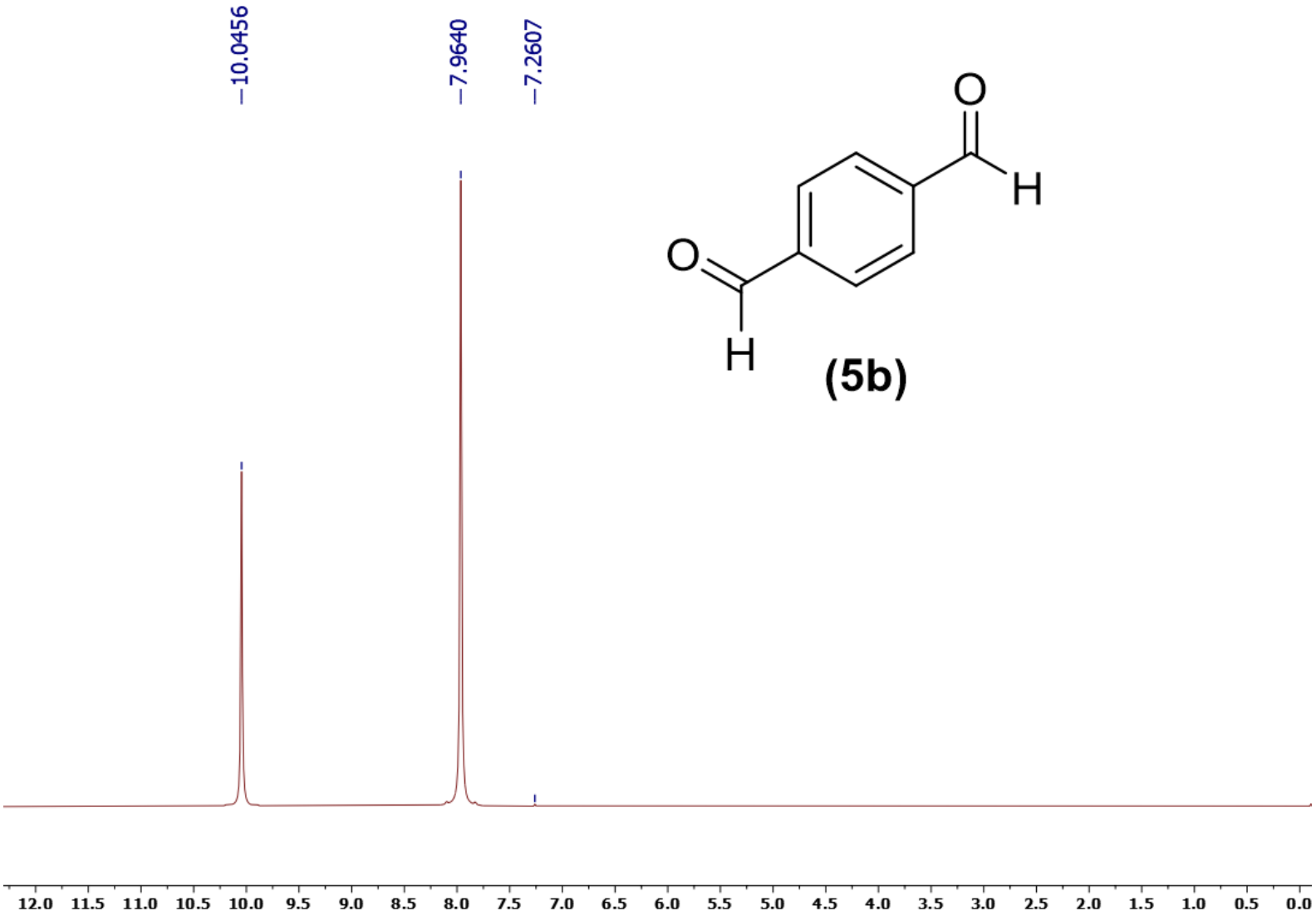


Figure S24. ^{1}H NMR spectrum of **5b** in $CDCl_3$.

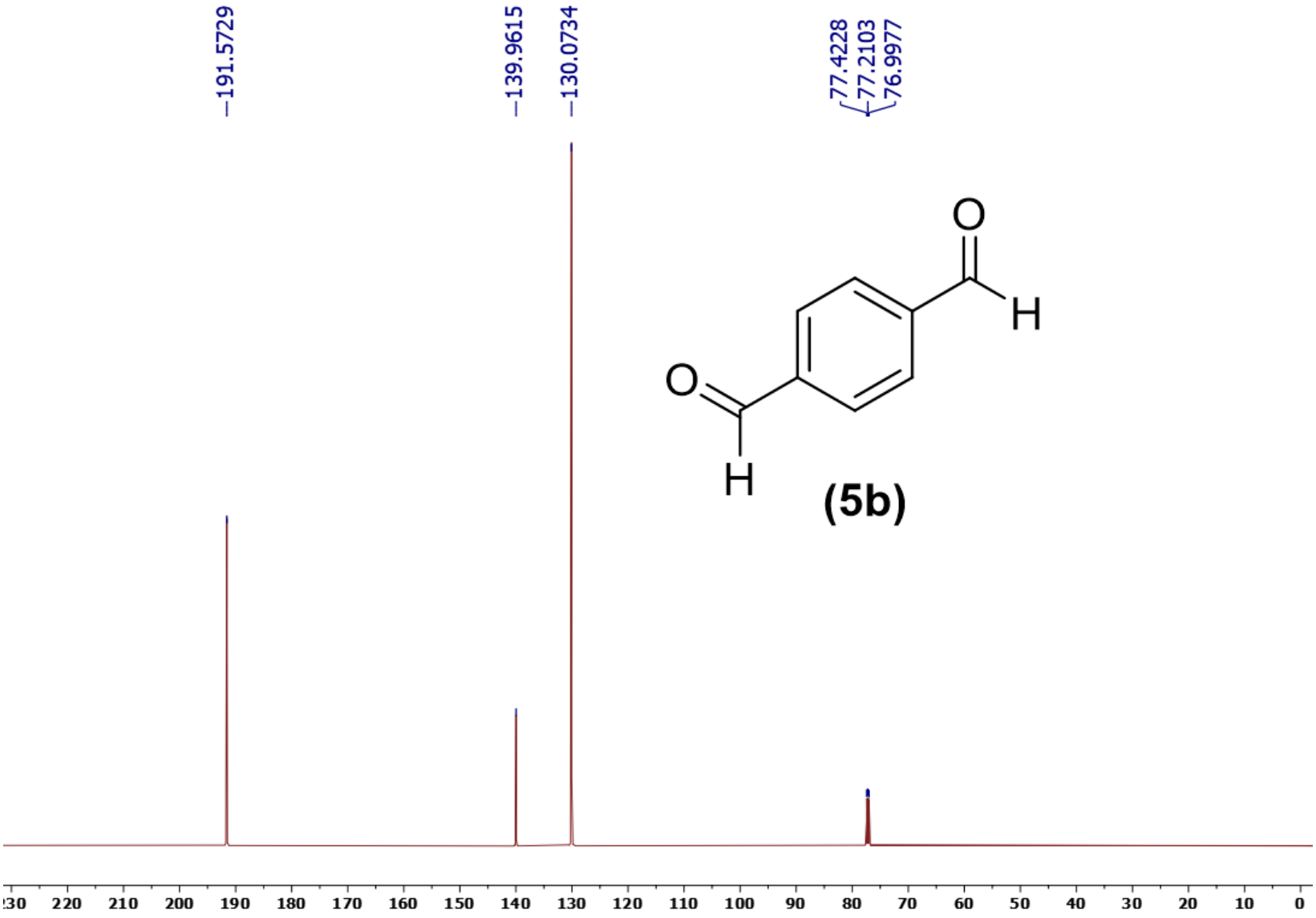


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in $CDCl_3$.

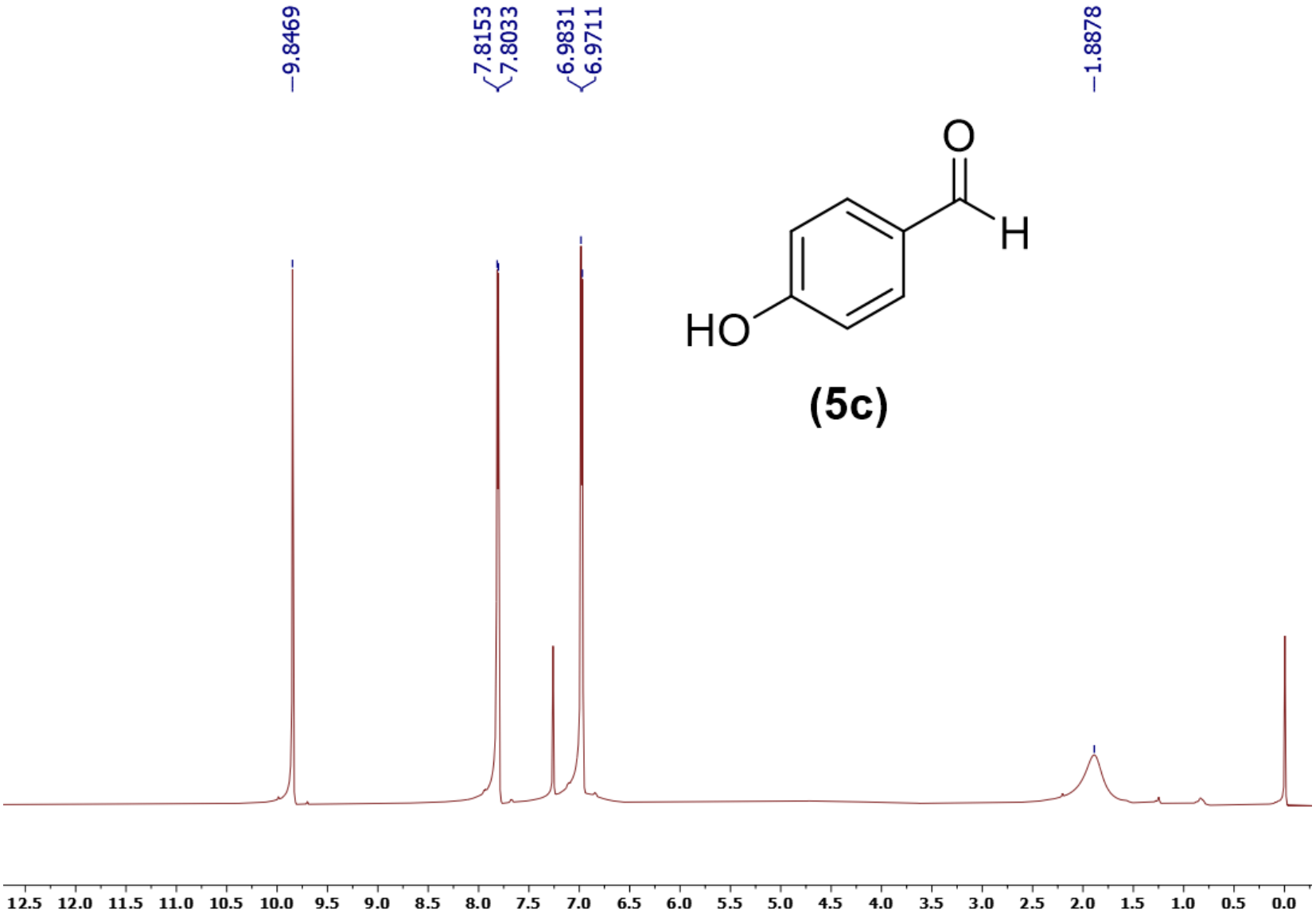


Figure S26. ^{1}H NMR spectrum of **5c** in $CDCl_3$.

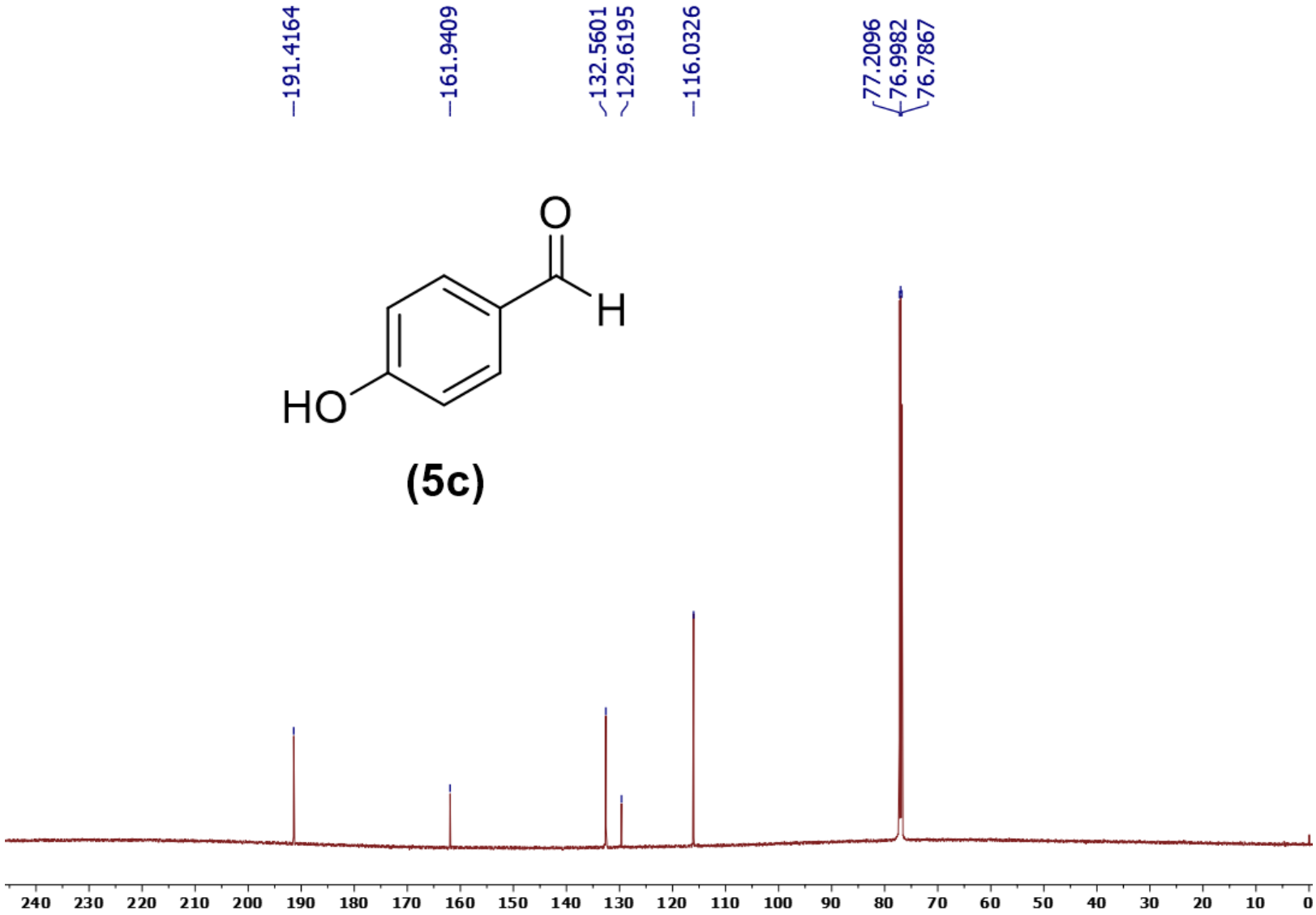


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **5c** in $CDCl_3$.

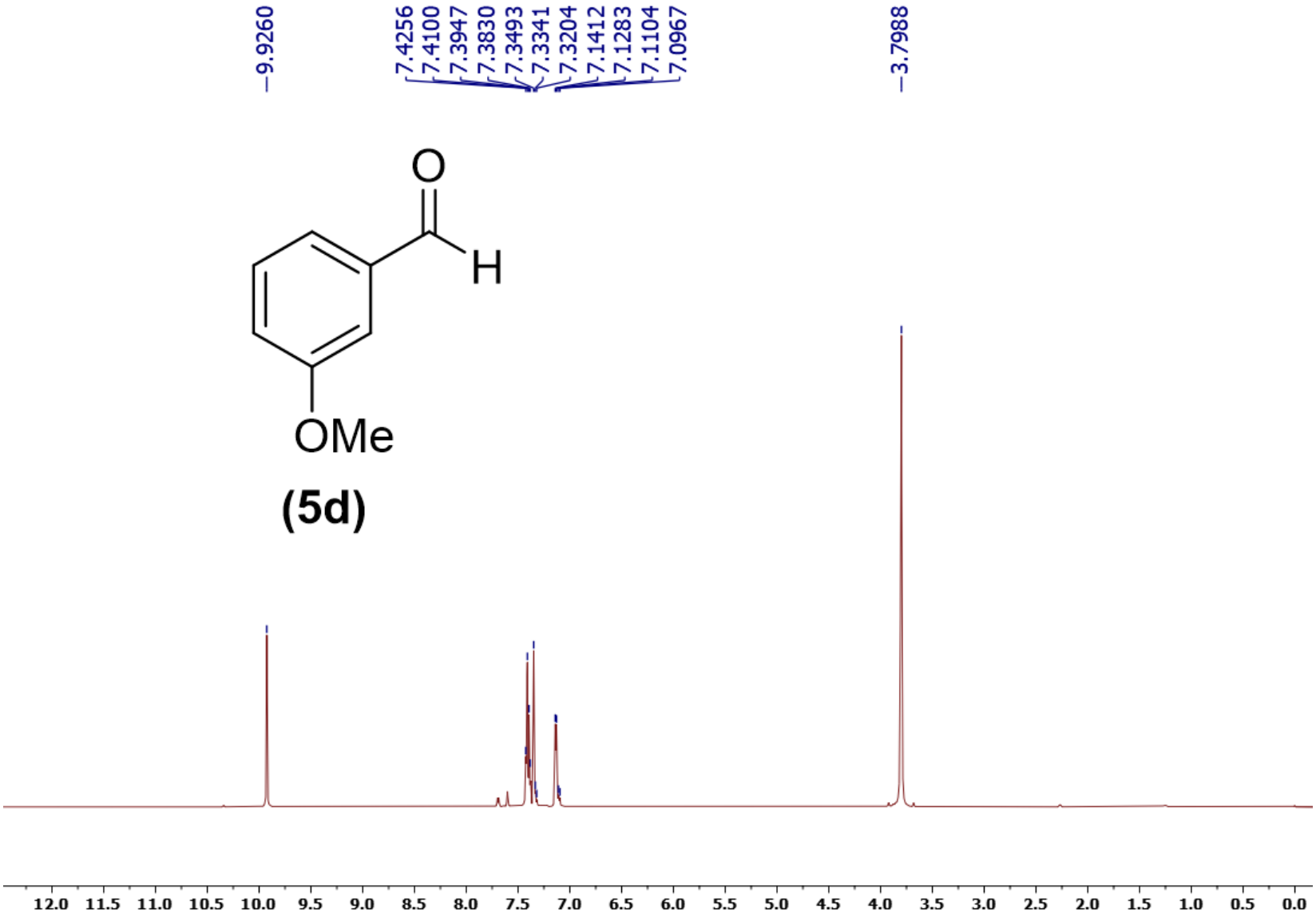


Figure S28. ^{1}H NMR spectrum of **5d** in $CDCl_3$.

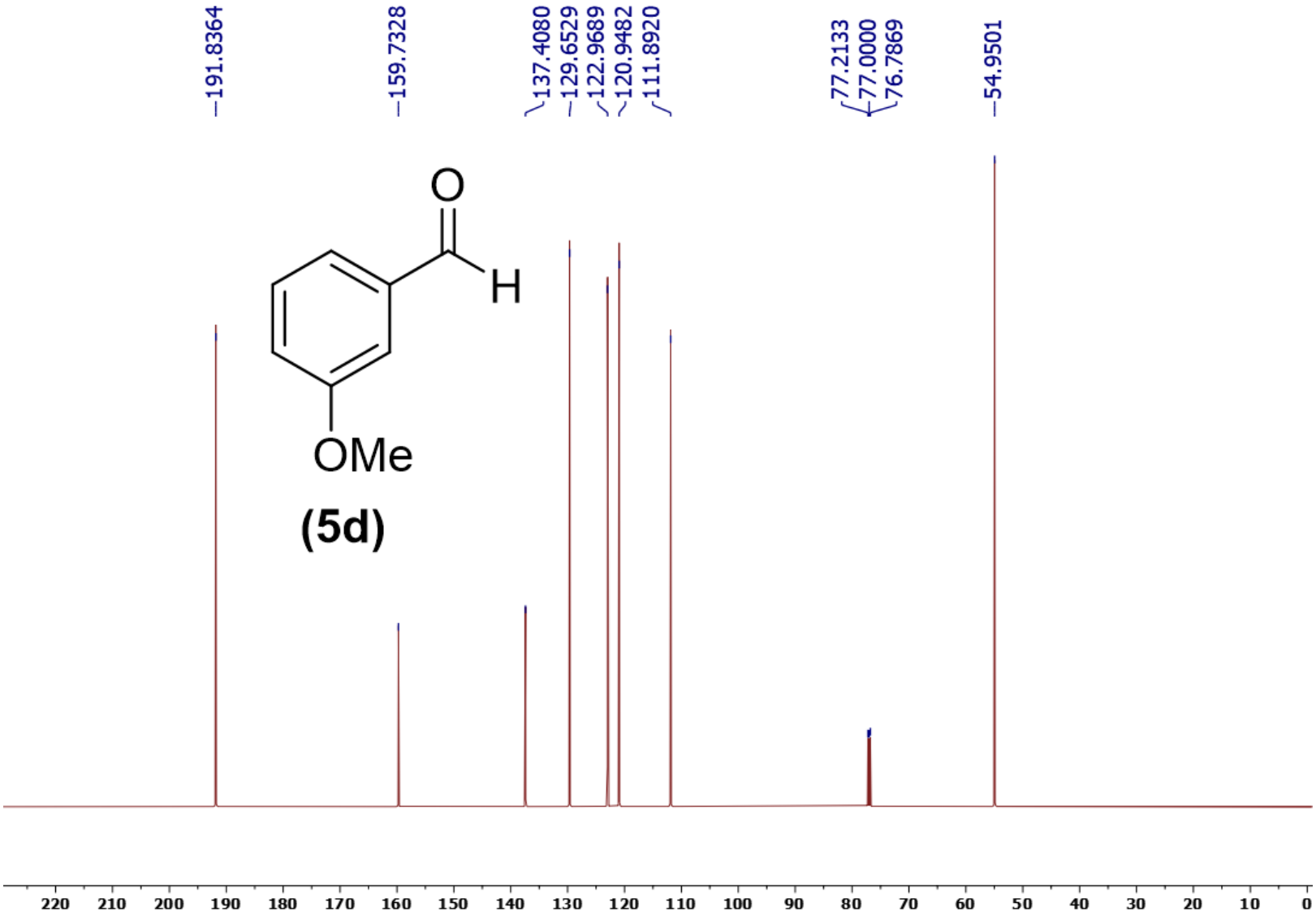


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **5d** in $CDCl_3$.

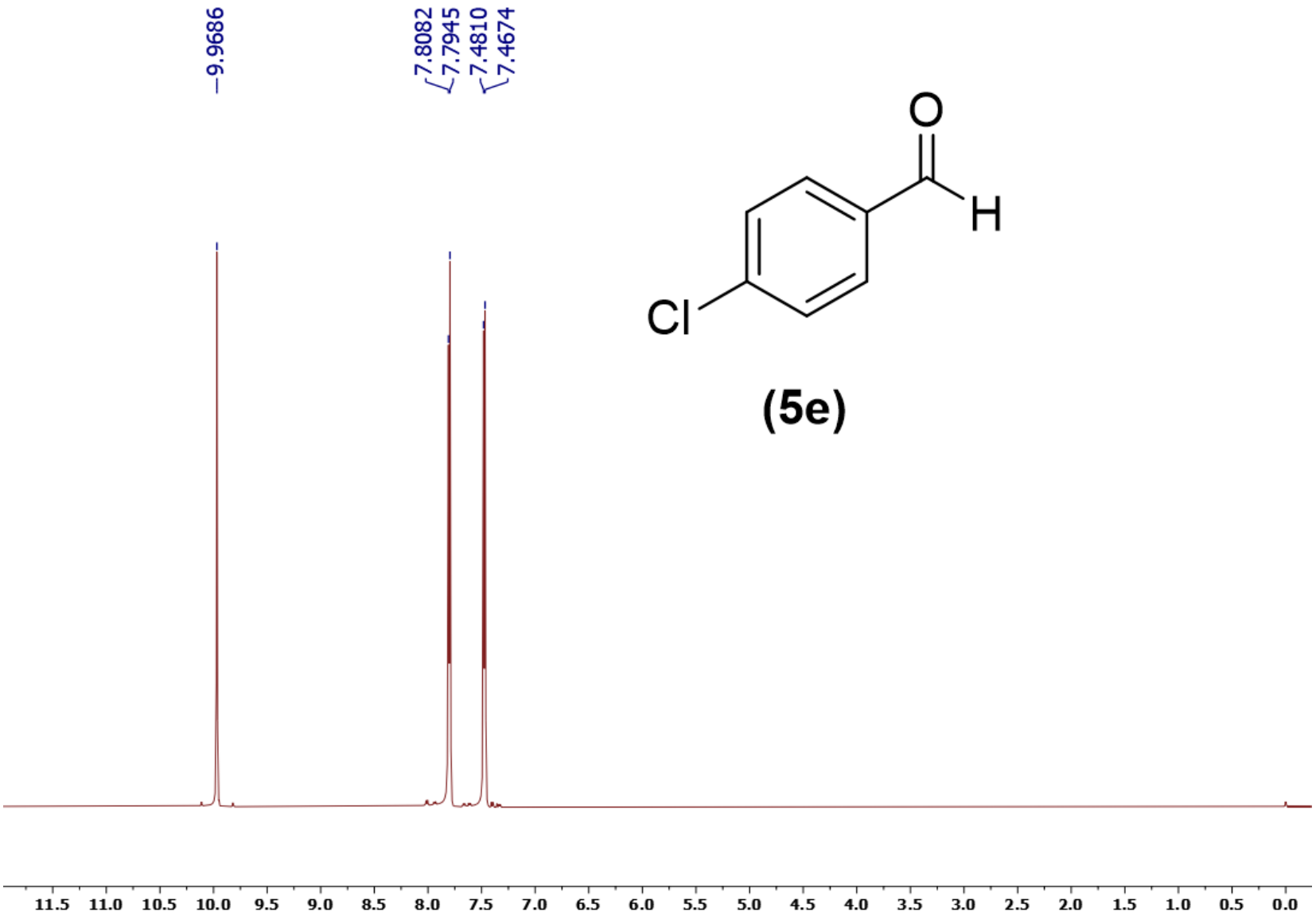


Figure S30. ^{1}H NMR spectrum of **5e** in $CDCl_3$.

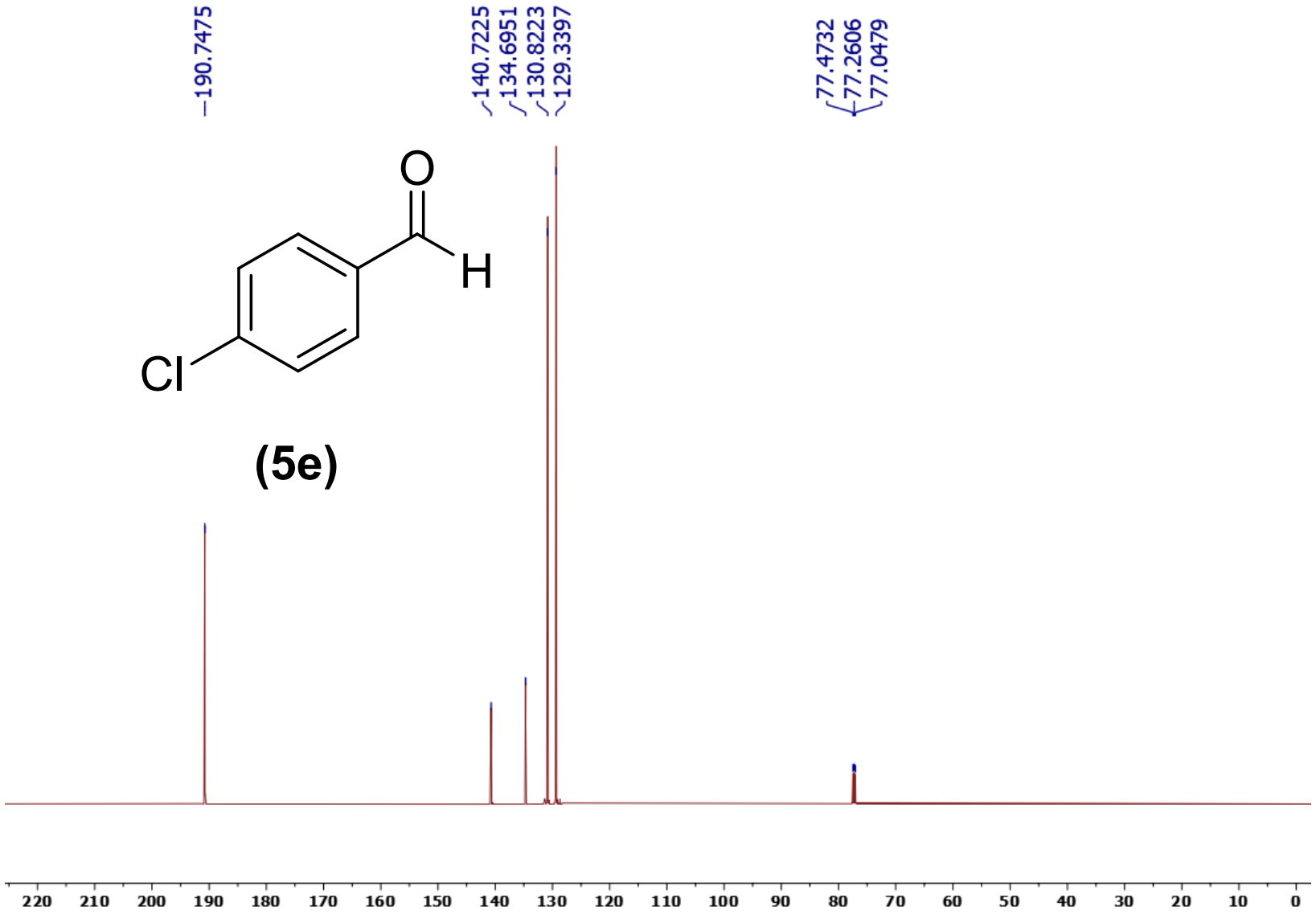


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **5e** in $CDCl_3$.

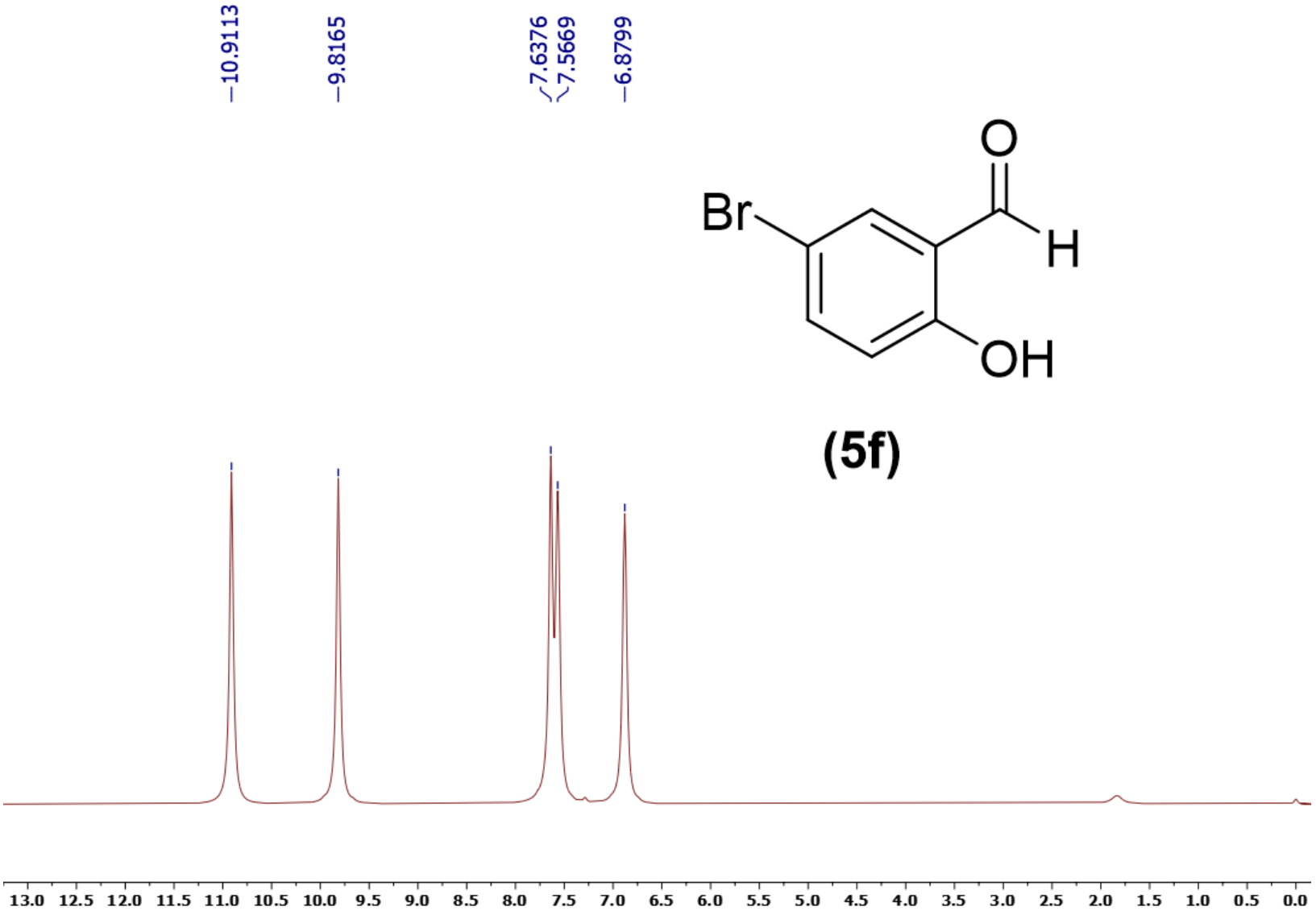


Figure S32. ^{1}H NMR spectrum of **5f** in $CDCl_3$.

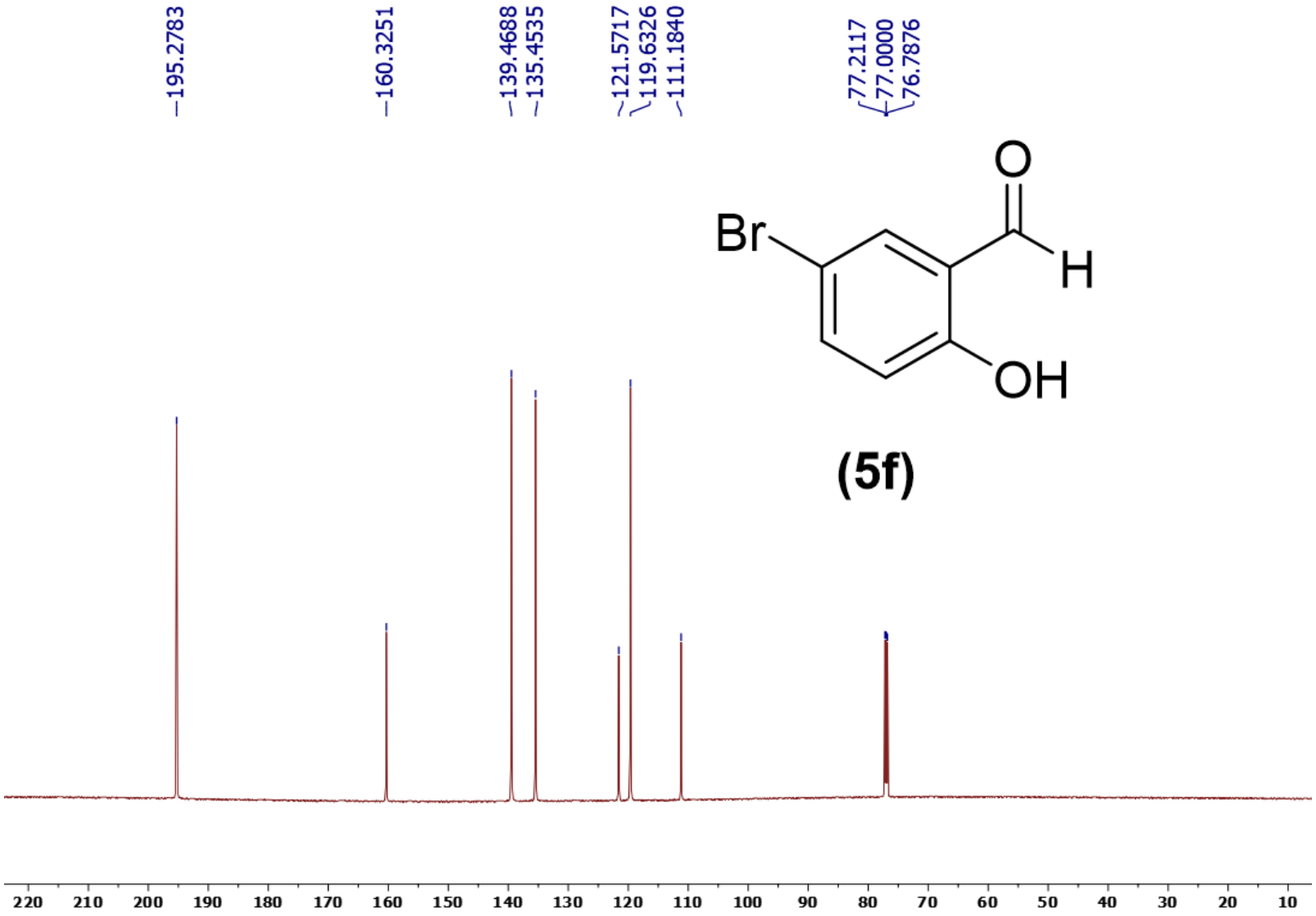


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **5f** in $CDCl_3$.

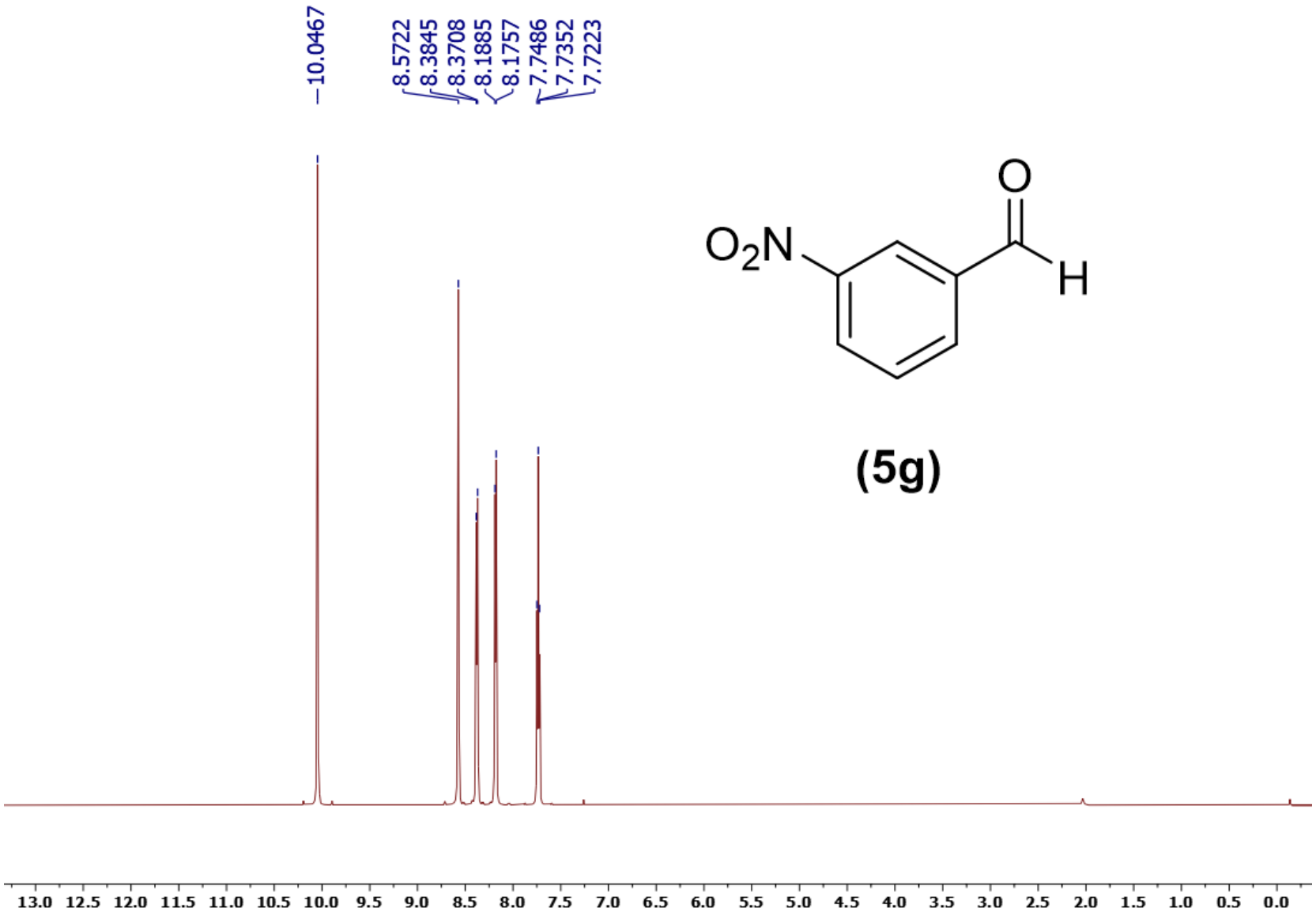


Figure S34. ^{1}H NMR spectrum of **5g** in $CDCl_3$.

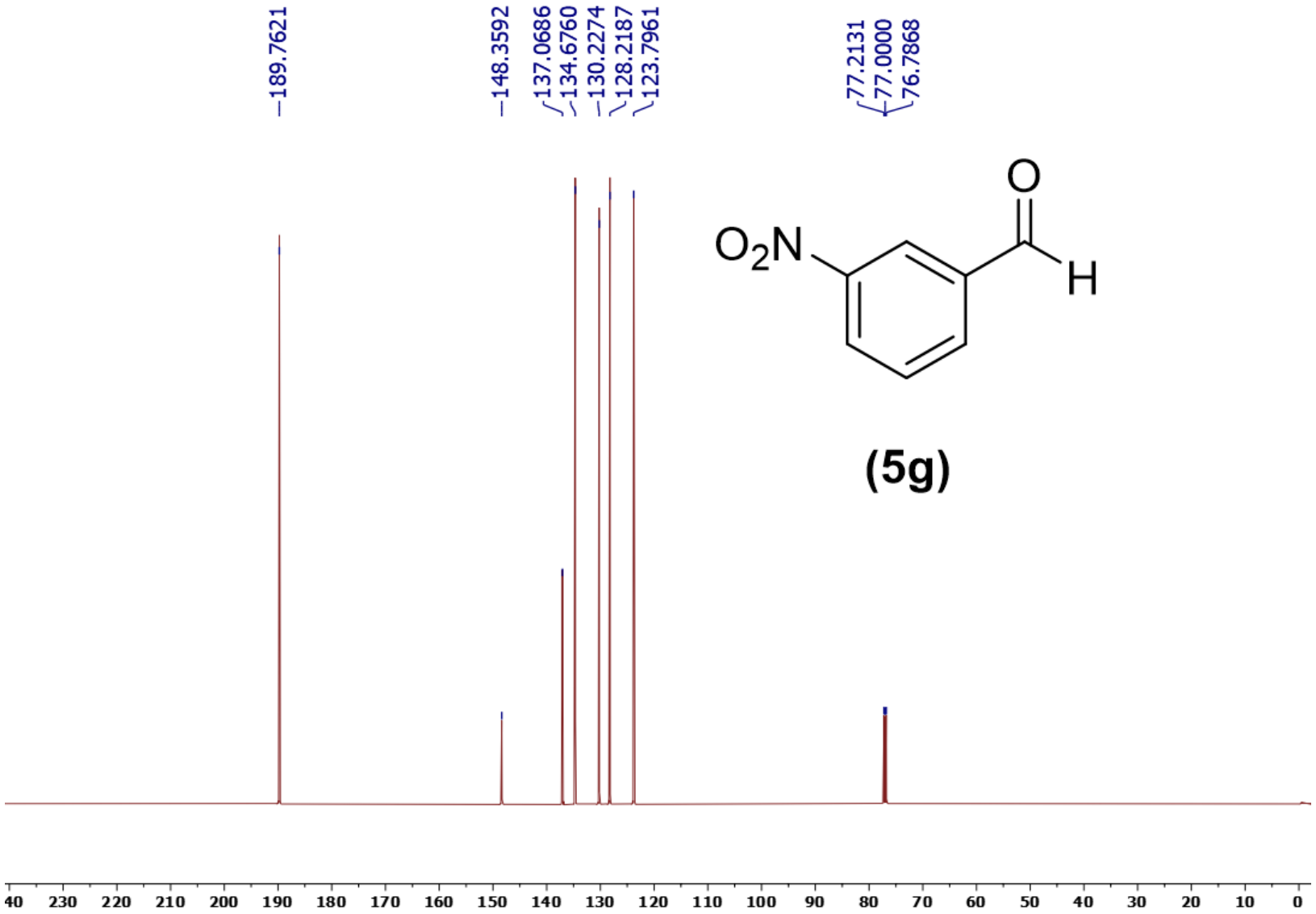


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **5g** in $CDCl_3$.

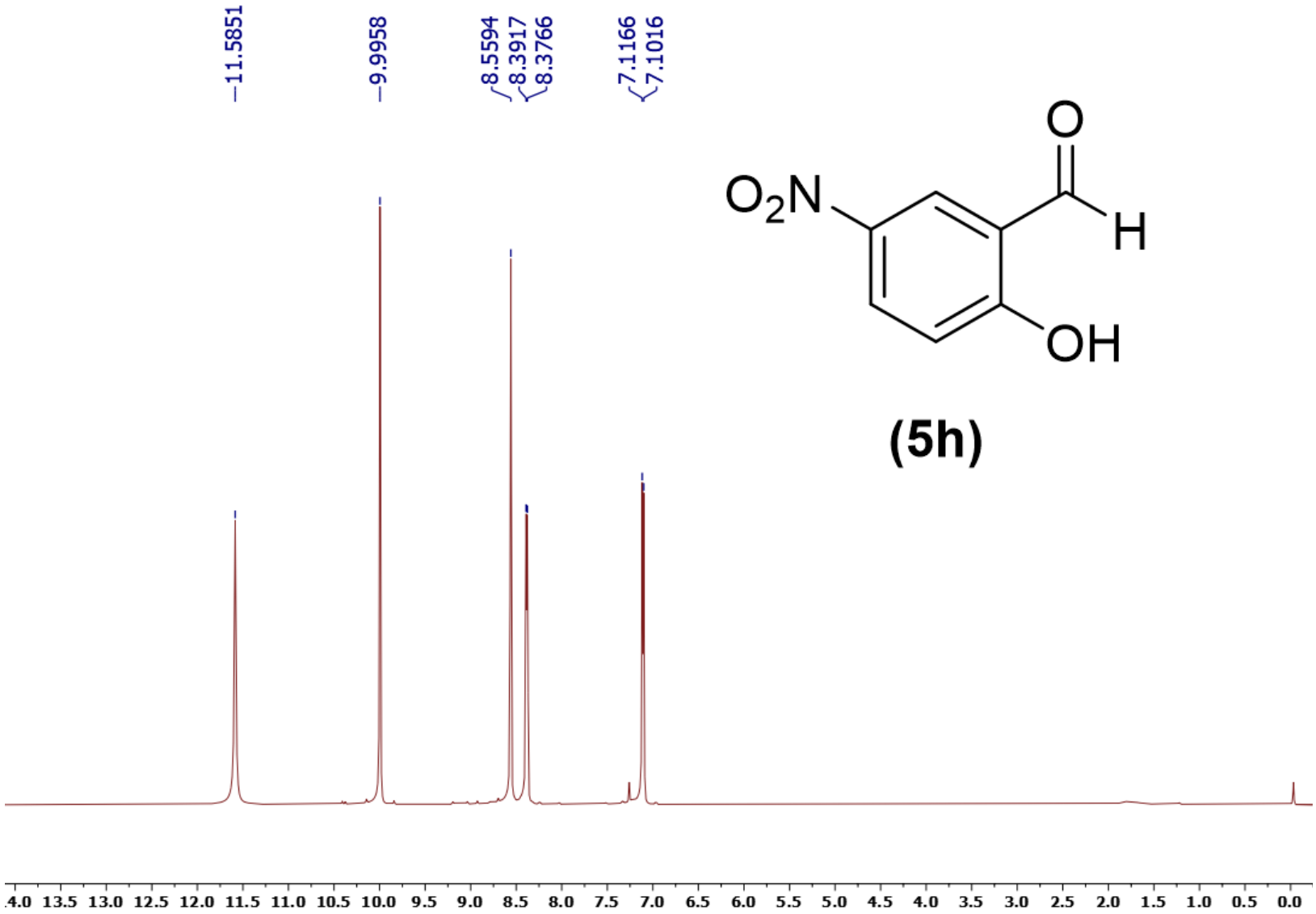


Figure S36. ^{1}H NMR spectrum of **5h** in $CDCl_3$.

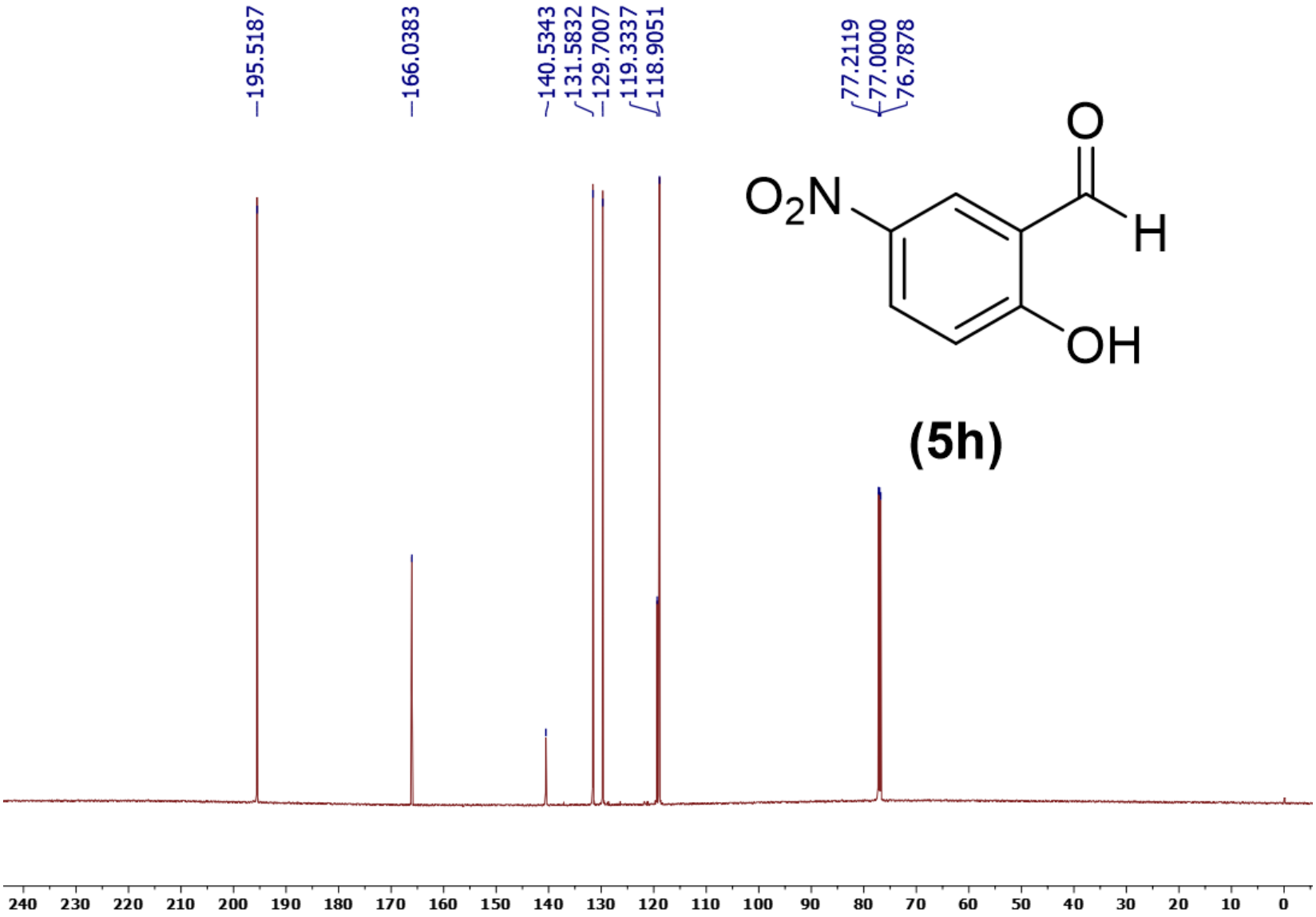


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **5h** in $CDCl_3$.

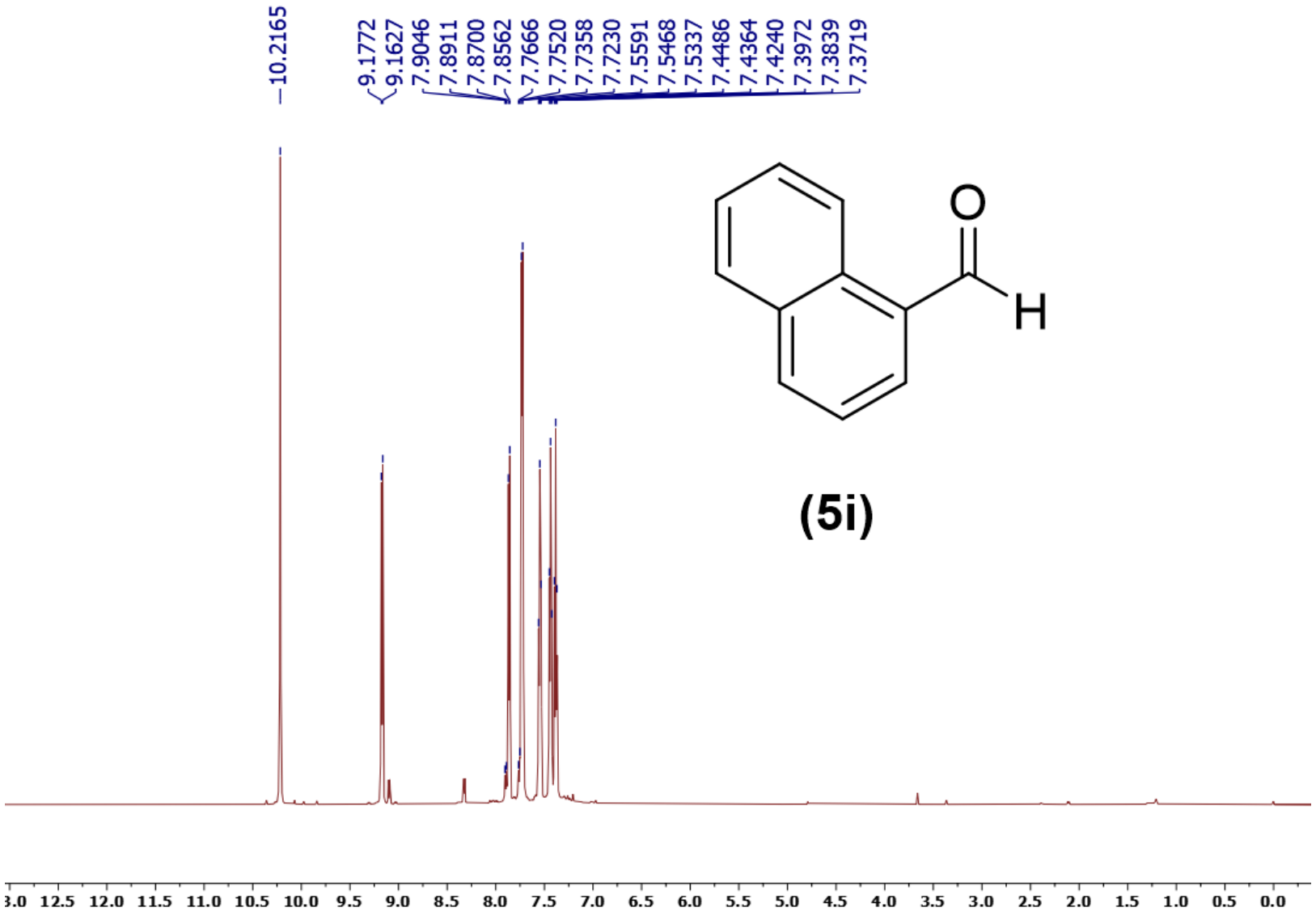


Figure S38. ^{1}H NMR spectrum of **5i** in $CDCl_3$.

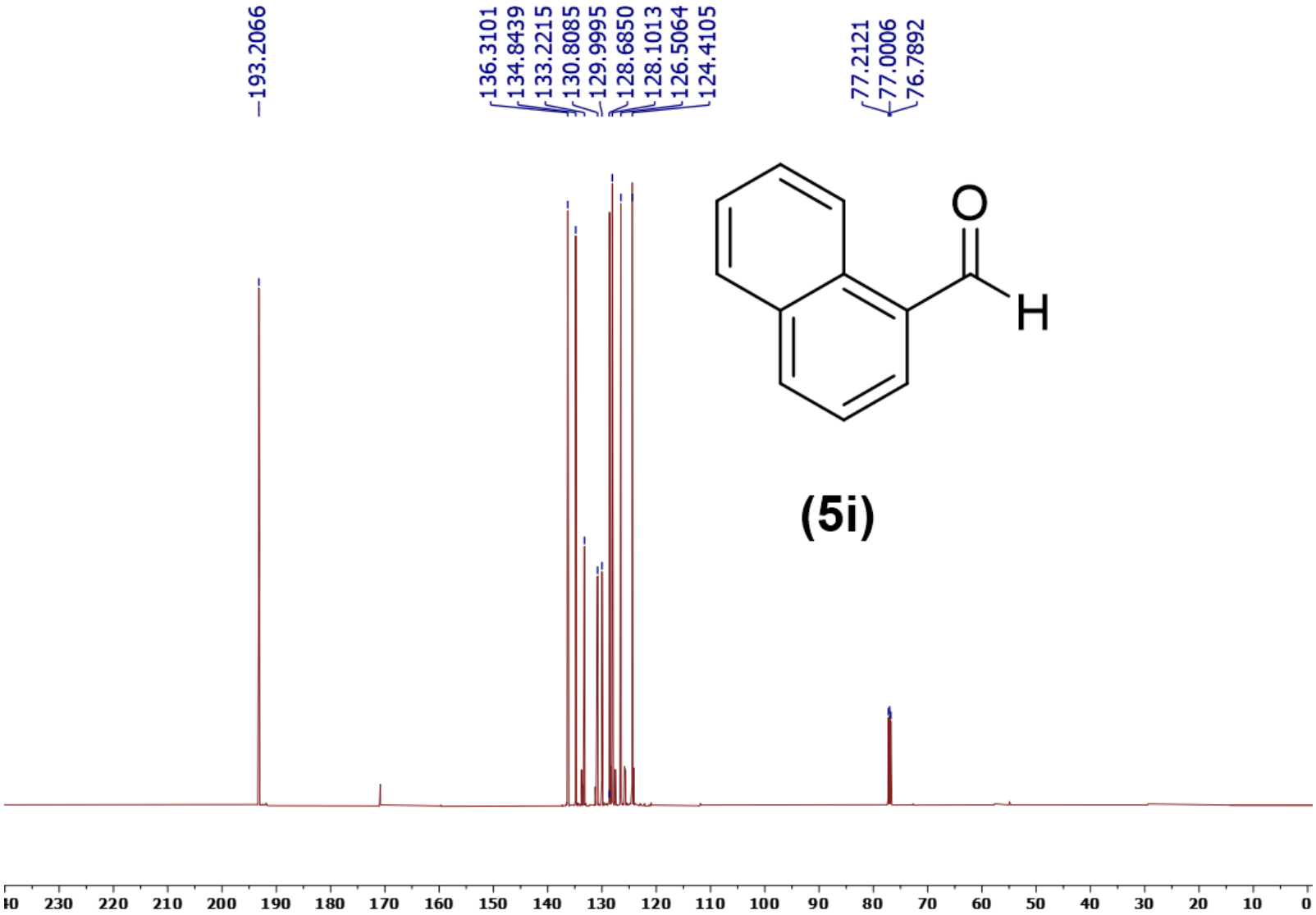


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **5i** in $CDCl_3$.

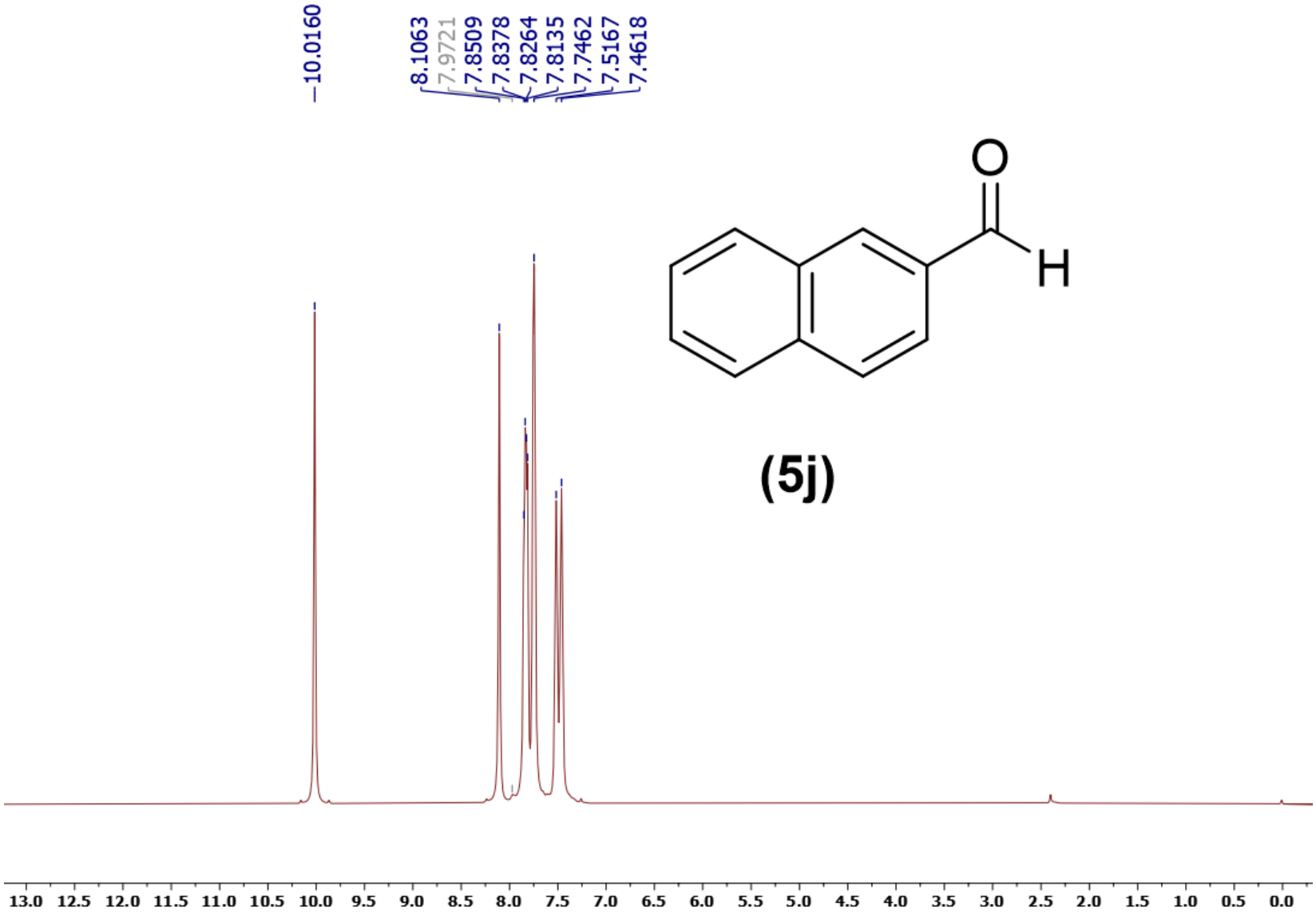


Figure S40. ^{1}H NMR spectrum of **5j** in $CDCl_3$.

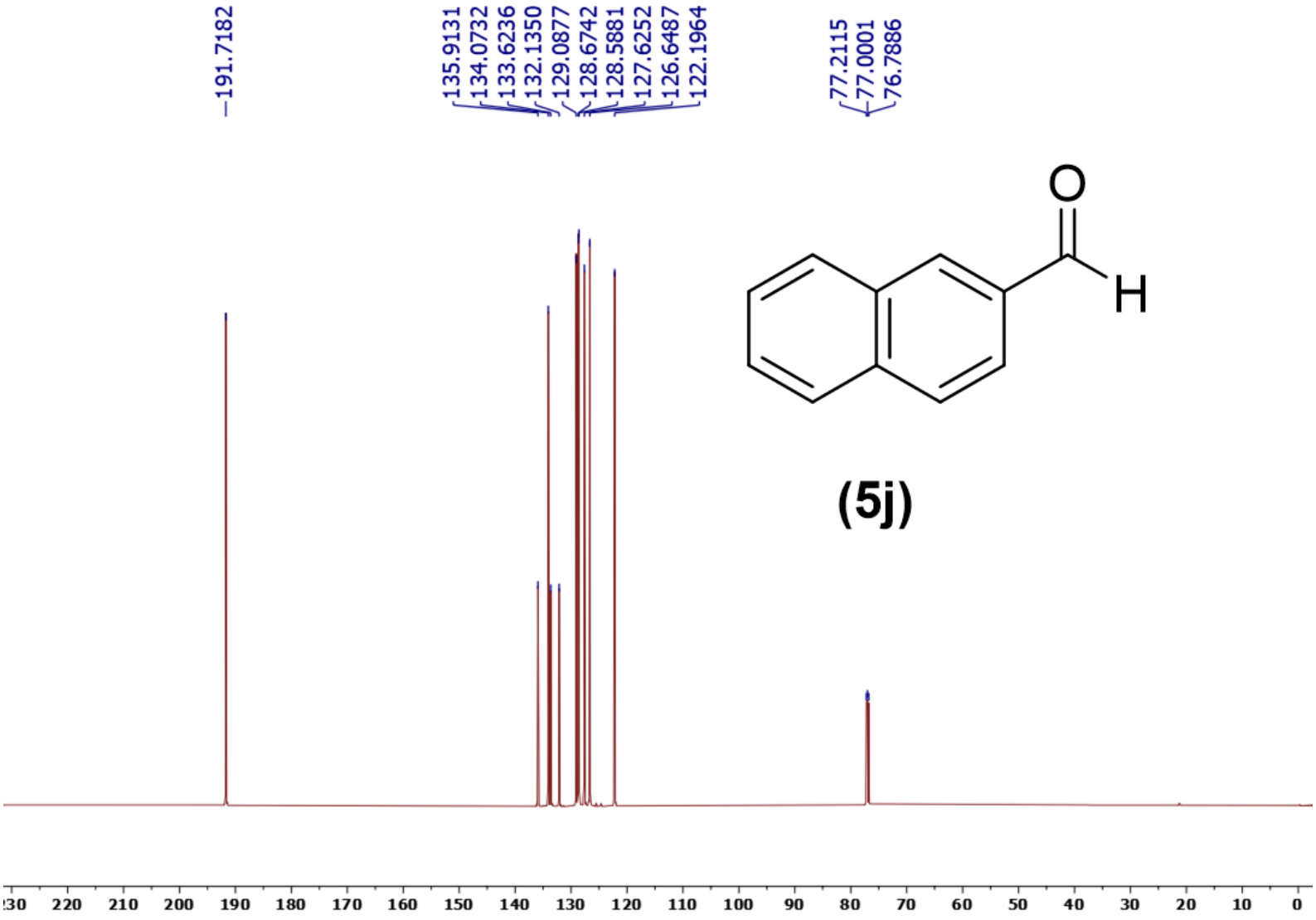


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **5j** in $CDCl_3$.

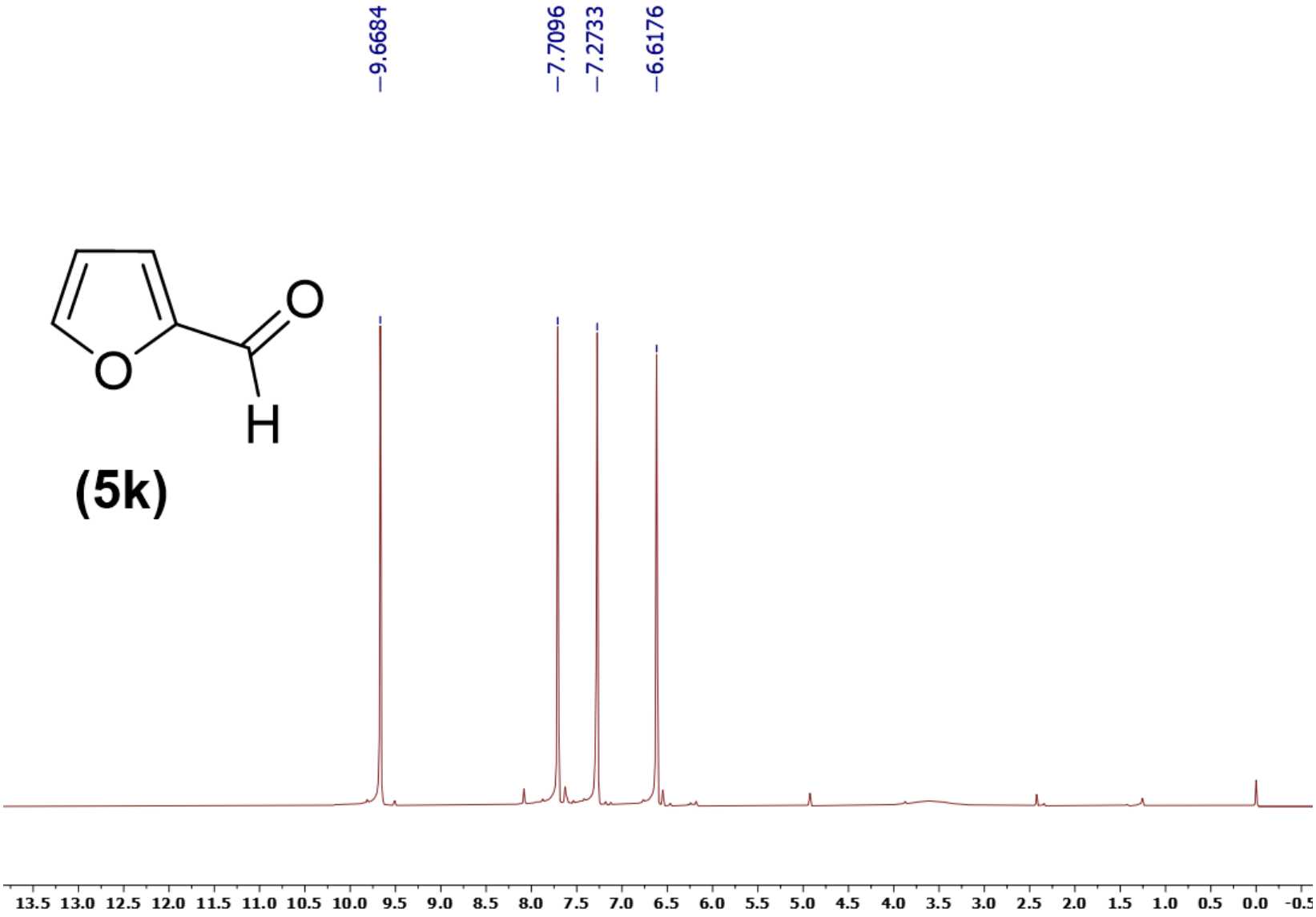


Figure S42. ^{1}H NMR spectrum of **5k** in $CDCl_3$.

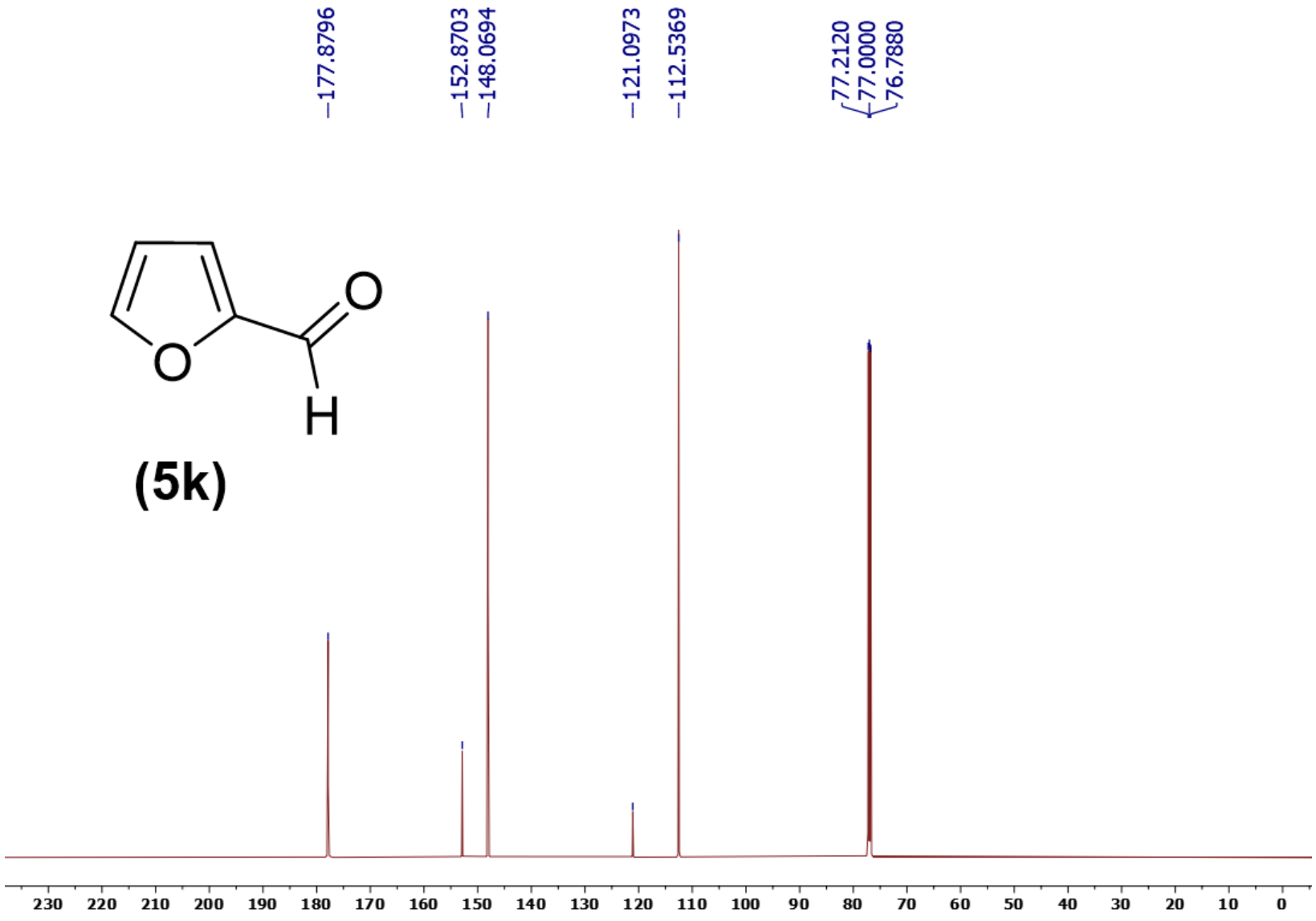


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **5k** in $CDCl_3$.

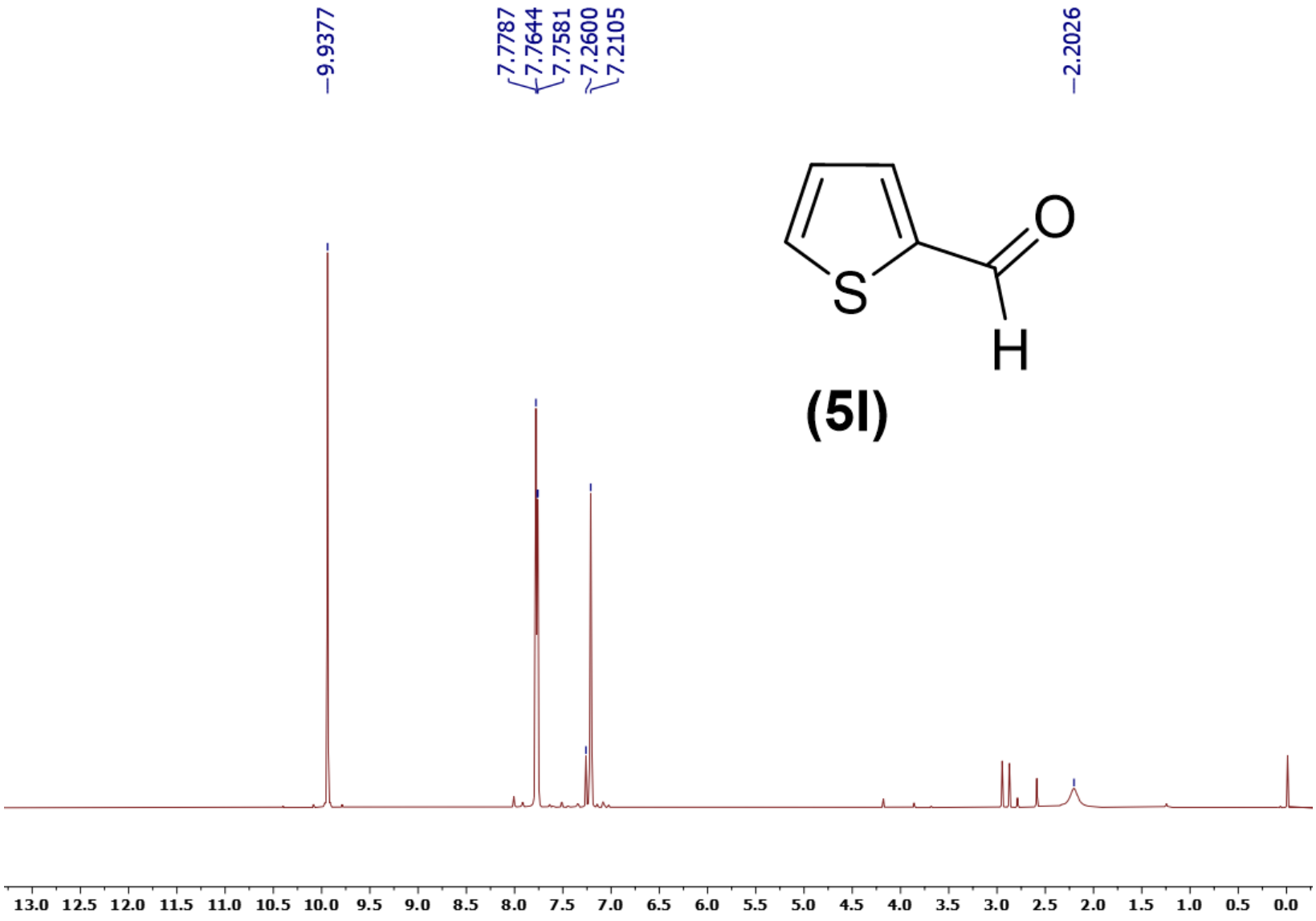


Figure S44. ^{1}H NMR spectrum of **5l** in $CDCl_3$.

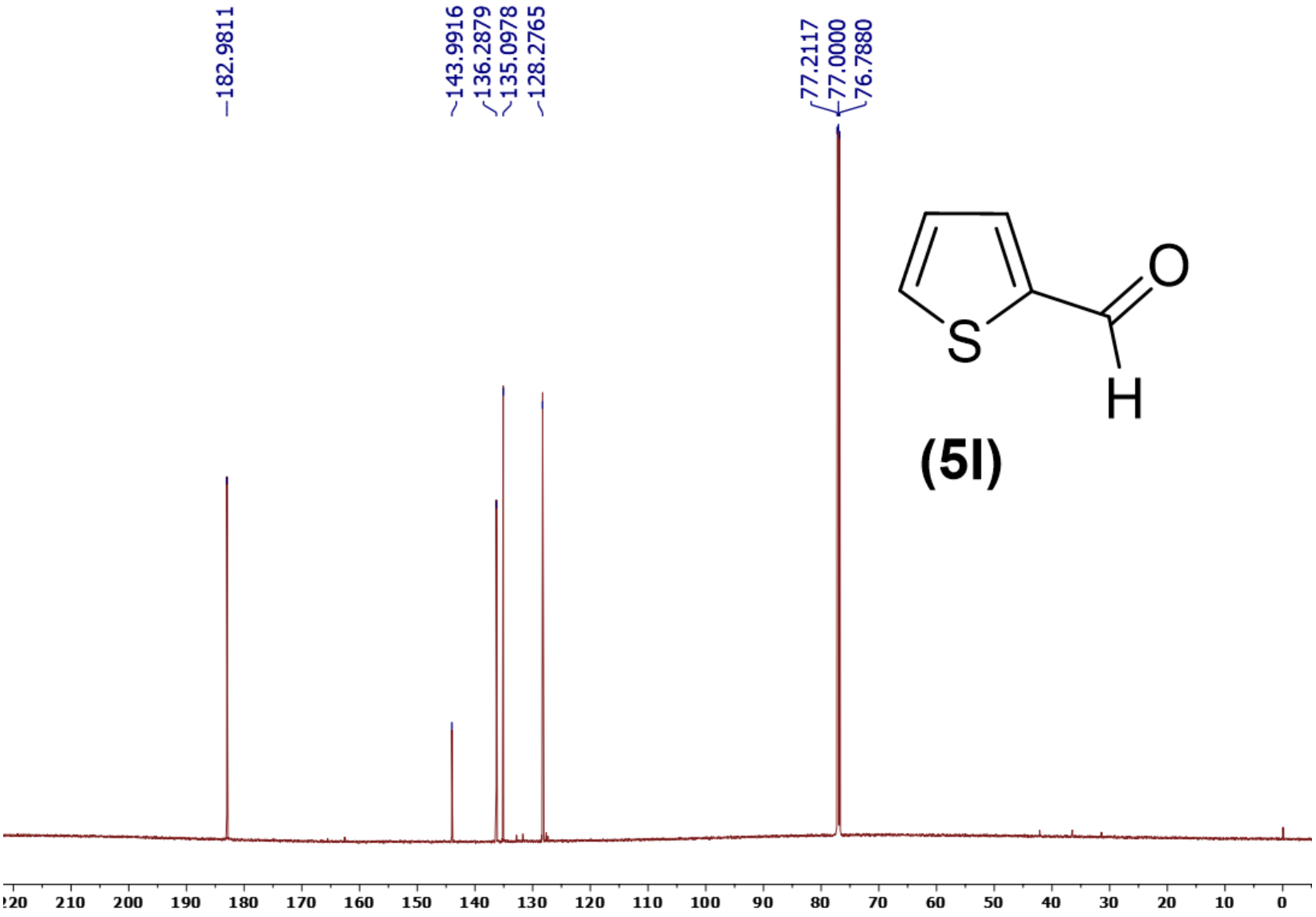


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **5l** in $CDCl_3$.

References:

1. (a) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. Electron-Rich, Bulky Ruthenium PNP-Type Complexes Acceptorless Catalytic Alcohol Dehydrogenation. *Organometallics* **2004**, *23*, 4026−4033. (b) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. Facile Conversion of Alcohols into Esters and Dihydrogen Catalyzed by New Ruthenium Complexes. *J. Am. Chem. Soc.* **2005**, *127*, 10840−10841. (c) Dutta, I.; Sarbajna, A.; Pandey, P.; Rahaman, S. M. W.; Singh, K.; Bera, J. K. Acceptorless Dehydrogenation of Alcohols on a Diruthenium(II,II) Platform. *Organometallics* **2016**, *35*, 1505−1513. (d) Wang, Z.; Pan, B.; Liu, Q. B.; Yue, E. L.; Solan, G. A.; Ma, Y. P.; Sun, W.-H. Efficient Acceptorless Dehydrogenation of Secondary Alcohols to Ketones Mediated by a PNN-Ru(II) Catalyst. *Catal. Sci. Technol.* **2017**, *7*, 1654−1661. (e) Wang, Q.; Chai, H.; Yu, Z. Dimeric Ruthenium(II)- NNN Complex Catalysts Bearing a Pyrazolyl-Pyridylamino-Pyridine Ligand for Transfer Hydrogenation of Ketones and Acceptorless Dehydrogenation of Alcohols. *Organometallics* **2017**, *36*, 3638−3644. (f) Hao, Z.; Liu, K.; Feng, Q.; Dong, Q.; Ma, D.; Han, Z.; Lu, G.-L.; Lin, J. Ruthenium(II) Complexes Bearing Schiff Base Ligands for Efficient Acceptorless Dehydrogenation of Secondary Alcohols. *Chin. J. Chem.* **2021**, *39*, 121−128. (g) Komiya, N.; Nakae, T.; Sato, H.; Naota, T. Water-Soluble Diruthenium Complexes Bearing Acetate and Carbonate Bridges: Highly Efficient Catalysts for Aerobic Oxidation of Alcohols in Water. *Chem. Commun.* **2007**, 4829−4831.
2. Han, L.; Xing, P.; Jiang, B. Selective Aerobic Oxidation of Alcohols to Aldehydes, Carboxylic Acids, and Imines Catalyzed by a Ag-NHC Complex. Org. Lett. 2014, 16, 3428−3431.