

Pre-nucleation and coalescence of cobalt nanoclusters mediated by multivalent calixarene complexes: Electronic Supplementary Information

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Synthesis and characterization

Reagents. Co₂(CO)₈ and Co₄(CO)₁₂ were purchased from Strem and used as supplied. Sodium hydride (60% in mineral oil), tetrabutylammonium iodide (TBAI), propargyl chloride, oleic acid (OA) and *o*-dichlorobenzene (ODCB) were purchased from Sigma-Aldrich and used without further purification. Tetramethylresorcinarene (TMR) was synthesized using a literature procedure.¹ NMR spectra were acquired using a Varian 300 MHz or a Bruker 400 MHz spectrometer, and replotted using MestReNova v.5.2.3. Infrared spectra were collected from thin films on NaCl plates and acquired using a Perkin-Elmer 2000 FT-IR spectrometer.

Tetramethylresorcinarene octapropargyl ether (1). TMR (500 mg, 0.92 mmol) was dried by azeotropic distillation of toluene (3 × 8 mL), then dissolved in 15 mL of anhydrous DMF under argon and treated with NaH (470 mg of a 60% dispersion in mineral oil, 11.75 mmol) and TBAI (200 mg, 0.54 mmol). The reaction mixture was stirred for 20 min, then treated by the dropwise addition of propargyl chloride (600 μL, 8.30 mmol) at room temperature. The reaction was stirred at room temperature under argon, then quenched with water (20 mL) and extracted with diethyl ether (3 × 15 mL). The organic extracts were washed with saturated aqueous NaCl and dried over MgSO₄, then concentrated into a yellow solid. Silica gel chromatography with a 5:1 mixture of hexanes and EtOAc yielded octapropargyl ether **1** as a white solid (300 mg, 40% yield), which could be recrystallized as colorless needles. Selected spectral data: IR (cm⁻¹): 3278

¹ A. G. S. Hogberg, *J. Am. Chem. Soc.*, **1980**, *102*, 6046.

(s), 2119(m), 1610(m), 1584(m). ^1H NMR (300 MHz, CDCl_3): δ 6.70 (s, 4H, Ar-H), 6.58 (s, 4H, Ar-H), 4.60 (q, $J=7.1$ Hz, 4H, Ar_2CHR), 4.40 (s, 16H, O- CH_2 -), 2.47 (t, $J=2.3$ Hz, 8H, $\text{C}\equiv\text{CH}$), 1.42 (d, $J=6.9$ Hz, 12H, $-\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 154.10, 129.78, 125.73, 101.66, 79.90, 75.15, 57.65, 30.78, 20.26.

Octakis[$\text{Co}_2(\text{CO})_6(\eta^2\text{-alkyne})$]-tetramethylresorcinarene octapropargyl ether complex (**2**). Octapropargyl ether **1** (30 mg, 0.035 mmol) and $\text{Co}_2(\text{CO})_8$ (100 mg, 0.29 mmol) were dissolved in 10 mL of hexanes or toluene, which was deaerated at room temperature. The reaction mixture was stirred for 4 hours, then concentrated and purified by silica gel chromatography with pure hexanes and a 10:1 mixture of hexanes and dichloromethane to yield Co_{16} -calixarene complex **2** as an orange-red solid (60 mg, 60% yield). This could be recrystallized from benzene to yield red needle-like crystals. *Elemental analysis*: calcd. for $\text{C}_{104}\text{H}_{48}\text{O}_{56}\text{Co}_{16}$ 39.83% C, 1.54% H 30.06% Co; found 39.97% C, 1.48% H, 30.07% Co. IR (cm^{-1}): 3101(w), 2097(s), 2054(s), 2020(s), 1610(w), 1583(w), 1540(w). ^1H NMR (400 MHz, C_6D_6): δ 6.62 (s, 4H, Ar-H), 6.57 (s, 4H, Ar-H), 5.7–5.8 (m, 8H, $\text{C}\equiv\text{CH}$), 4.8–5.3 (m, 20H, Ar_2CHR and O- CH_2 -), 1.78 (d, $J=6.9$ Hz, 12H, $-\text{CH}_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 200.05, 154.95, 129.65, 127.89, 109.31, 89.78, 73.55, 73.33, 32.14, 20.90.

Poly[$\text{Co}_4(\eta^2\text{-alkyne})$]-tetramethylresorcinarene octapropargyl ether complex (**3**). Octapropargyl ether **1** (35 mg, 0.041 mmol) and $\text{Co}_4(\text{CO})_{12}$ (200 mg, 0.35 mmol) were dissolved in 10 mL of chloroform, which was deaerated at room temperature. The reaction mixture was heated to 55 °C and stirred for 5 hours under argon, then concentrated and purified by silica gel chromatography with a 10:1 mixture of hexanes and dichloromethane and pure dichloromethane to yield Co_n -calixarene complex **3** as a dark blue solid (85 mg; $n=20$, 60% yield based on molecular formula below). *Elemental analysis*: calcd. for $\text{C}_{106}\text{H}_{48}\text{O}_{58}\text{Co}_{20}$ 37.14% C, 1.41% H, 34.38% Co; found 36.96% C, 1.47% H, 34.51% Co. IR (cm^{-1}): 2094(s), 2031(s), 1995(s), 1869(s; $\mu\text{-CO}$). ^1H NMR and ^{13}C NMR spectra contained multiple broad signals, and were not useful for chemical characterization. It should be noted that polynuclear Co complexes are subject to strong quadrupolar relaxation effects, often preventing the observance of ^{13}C NMR signals at room temperature.²

² P. Chini and B. T. Heaton, in *Top. Curr. Chem.*, Springer-Verlag, Berlin, **1977**, 3.

$\text{Co}_2(\text{CO})_6(\eta^2\text{-HC}\equiv\text{CCH}_2\text{OPh})$ (**4**). Phenyl propargyl ether (PPE, 34 μL , 0.26 mmol) and $\text{Co}_2(\text{CO})_8$ (120 mg, 0.35 mmol) were dissolved in 10 mL of hexanes, which was deaerated at room temperature. The reaction mixture was stirred for 4 hours, then concentrated and purified by silica gel chromatography with pure hexanes and a 10:1 mixture of hexanes and dichloromethane to yield Co_2 -alkyne complex **4** as a red solid (86 mg, 80% yield). IR (cm^{-1}): 3093(w), 3042(w), 2097(s), 2055(s), 2025(s), 1599(m), 1588(m), 1557(w). ^1H NMR (400 MHz, C_6D_6): δ 7.30 (m, 2H, Ar-*H*), 6.95 (m, 3H, Ar-*H*), 6.04 (s, 1H, $\text{C}\equiv\text{CH}$), 5.17 (s, 2H, OCH_2). ^{13}C NMR (100 MHz, C_6D_6): 200.25, 159.11, 130.39, 122.10, 115.49, 109.52, 90.82, 72.50, 68.44.

$\text{Co}_4(\text{CO})_{10}(\eta^2\text{-HC}\equiv\text{CCH}_2\text{OPh})$ (**5**). PPE (15 μL , 0.12 mmol) and $\text{Co}_4(\text{CO})_{12}$ (80 mg, 0.14 mmol) were dissolved in 8 mL of chloroform, which was deaerated at room temperature. The reaction mixture was heated to 55 $^\circ\text{C}$ and stirred for 5 hours under argon, then concentrated and purified by silica gel chromatography with a 10:1 mixture of hexanes and dichloromethane to yield Co_4 -alkyne complex **5** as a dark blue solid (70 mg, 90% yield). *Elemental analysis*: calcd. for $\text{C}_{19}\text{H}_8\text{O}_{11}\text{Co}_4$ 35.22% C, 1.24% H, 36.38% Co; found 35.37% C, 1.20% H, 36.33% Co. IR (cm^{-1}): 2094(s), 2030(s), 1990(s), 1867(s; $\mu\text{-CO}$), 1598(m), 1589(m). ^1H NMR (400 MHz, CDCl_3): δ 8.41 (s, 1H, $\text{C}\equiv\text{CH}$), 7.28 (m, 2H, Ar-*H*), 6.99 (m, 1H, Ar-*H*), 6.86 (m, 2H, Ar-*H*), 4.48 (s, 2H, O- CH_2). ^{13}C NMR signals from the Co_4 -alkyne complex were too broad to be useful for chemical characterization.

X-ray crystallography parameters for data collection of Co_{16} -calixarene **2**

A dark violet plate of $\text{C}_{104}\text{H}_{48}\text{Co}_{16}\text{O}_{56}\cdot\text{C}_6\text{H}_6$ having approximate dimensions of $0.44 \times 0.40 \times 0.23$ mm was mounted on a glass fiber. Preliminary examination and data collection were performed using MoK_α radiation ($\lambda = 0.71073\text{\AA}$) on a Nonius KappaCCD equipped with a graphite crystal, incident beam monochromator. Cell constants for data collection were obtained from least-squares refinement, using setting angles in the range of 2 to 23 degrees (35596 reflections). The triclinic cell parameters and calculated volume are: $a = 14.7094(5)$, $b = 18.5694(7)$, $c = 24.4316(9)$ \AA ; $\alpha = 96.7847(14)$, $\beta = 103.493(2)$, $\gamma = 90.824(3)^\circ$; vol. = $6437.6(4)$ \AA^3 . The calculated density is 1.66 g/cm^3 , based on $Z = 2$ and $\text{FW} = 3214.55$. The refined mosaicity from DENZO/SCALEPACK³ was 1.04° indicating mediocre crystal quality. The

³ Z. Otwinowski and W. Minor, *Methods Enzymol.*, **1997**, 276, 307.

space group was determined by the program XPREP.⁴ There were no systematic absences; the space group was determined to be $P\bar{1}$ (No. 2). The data were collected at a temperature of 150.0(2) K. Data were collected to a maximum 2θ of 46.5°. A total of 35596 reflections were collected, of which 17744 were unique, $R_{\text{int}} = 0.043$. $R(F_o) = 0.062$, $R_w(F_o^2) = 0.168$ for observed data.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were recorded on a Q500 Thermogravimetric Analyzer, using a heating rate of 10 °C/min under a nitrogen flow. Data was replotted using Origin v.8.0. Octavalent (Co₂-alkyne)-calixarene complex **2** (Figure 3a) produces a single peak in the first derivative ($\Delta\text{wt}\%/\Delta T$) curve near 160 °C with a gradual decline at higher temperatures, suggesting continuous decarbonylation up to 350 °C. Co₂-PPE **4** (Figure 3c) produces a much sharper $\Delta\text{wt}\%/\Delta T$ peak than Co₁₆-calixarene **2** near 160 °C and also a second peak near 300 °C, which is likely to be related to the decomposition of phenyl propargyl ether. The $\Delta\text{wt}\%/\Delta T$ curves of Co₄-alkyne complexes **3** and **5** (Figures 3b and 3d) reveal a shoulder 20–40 °C below the peak associated with massive decarbonylation. The low-temperature weight loss is approximately 5%, and corresponds to desorption of one CO group per tetracobalt cluster. Co₄-PPE **5** also shows significant mass loss around 300 °C, similar to that noted for Co₂-PPE **4**.

⁴ Bruker, *XPREP in SHELXTL version 6.12*, Bruker AXS Inc., Madison, Wisconsin, USA, 2002.

Co nanocluster formation

(i) *Thermolysis of Co_n-alkyne complexes.* Co_n-alkyne complexes **2–5** were dissolved in 4 mL deaerated *o*-dichlorobenzene (ODCB) at equal Co-atom concentrations ([Co] = 28 mmol) and treated with oleic acid (30 μL, 0.095 mmol). The mixtures were purged with argon and placed in a preheated mantle, and rapidly brought to reflux temperatures. The black reaction mixtures were maintained at reflux for 25 min, cooled to room temperature, then treated with EtOH (8 mL) to precipitate the Co nanoclusters (NCs). These were redispersed in hexanes for TEM sampling.

TEM images were acquired on a Philips CM-10 operating at 80 kV. Particle size analysis was performed by SigmaScan Pro5 on 800 dpi images scanned in by an Epson scanner. A minimum of 100 particles was used in each case. Particle size distributions are presented in Figure S1.

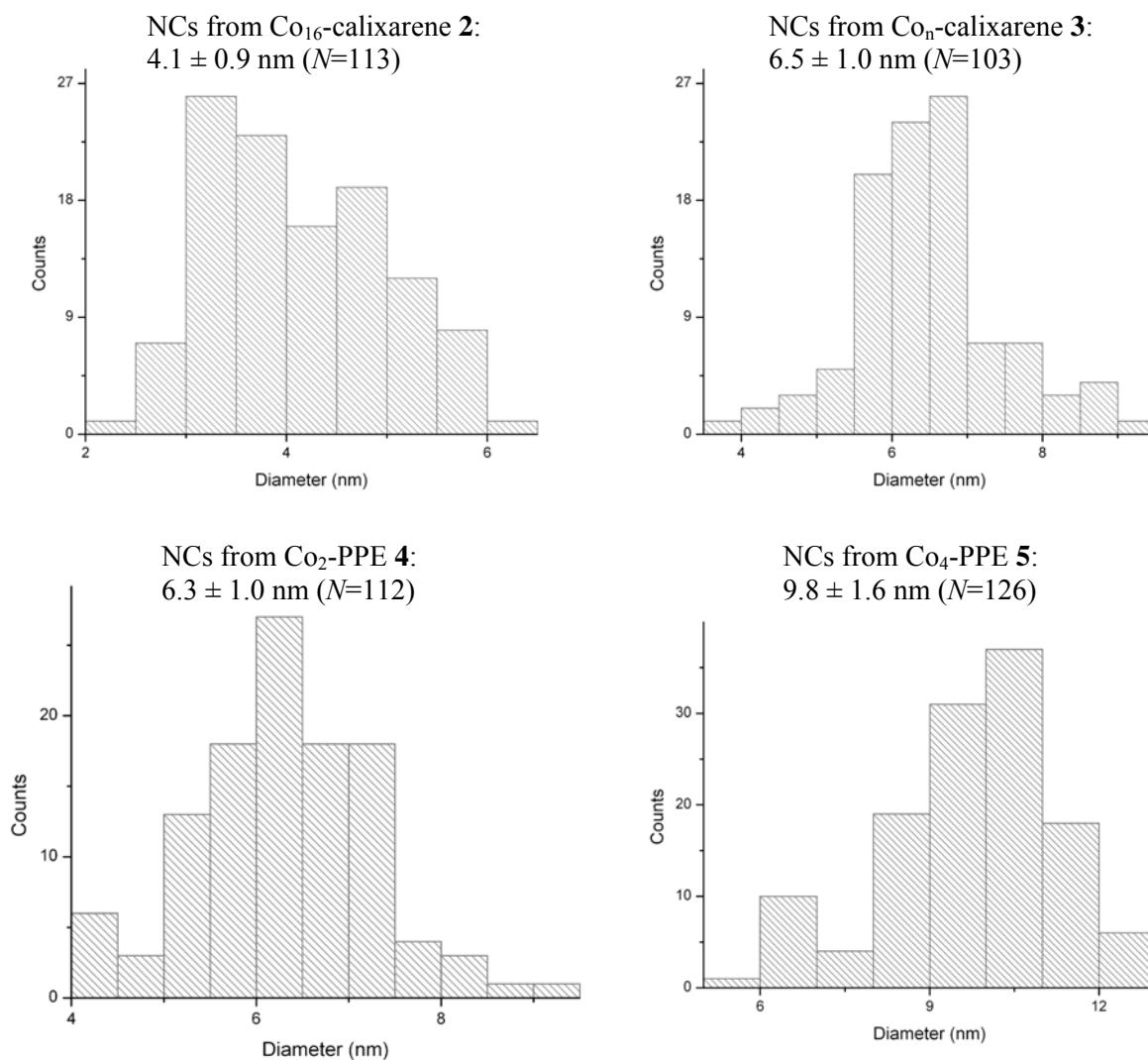


Figure S1. Particle size analyses of Co NCs, obtained by the thermolysis of complexes **2–5**.

(ii) *Rapid injection experiments for testing growth rate.* Co₁₆-calixarene **2** and Co₂-PPE **4** were dissolved in 1 mL deaerated ODCB at equal Co-atom concentrations ([Co] = 28 mmol) respectively. The solutions were injected quickly into a flask with 3 mL ODCB and oleic acid (30 μ L, 0.095 mmol) which was purged with argon and preheated to reflux. In both experiments, small aliquots of the reaction mixture were extracted at 2, 3, 5, 8, and 15 min, and the heating mantle was removed after 25 min. Co NCs were precipitated with EtOH treatment and redispersed in hexanes for TEM sampling.

TEM images were acquired on a Philips CM-10 operating at 100 kV. Particle size analysis was performed by SigmaScan Pro5 on 800 dpi images, with a minimum of 100 particles used in each case. TEM images and particle size distributions are presented in Figures S2 and S3; data is summarized in Table S1

Reaction time	2 min	3 min	5 min	8 min	15 min	25 min
Size of Co NCs from 2 (nm)	3.74 \pm 0.63	3.77 \pm 0.52	4.18 \pm 0.66	3.82 \pm 0.63	3.84 \pm 0.75	4.44 \pm 0.78
Size of Co NCs from 4 (nm)	4.28 \pm 0.46	4.48 \pm 0.53	4.76 \pm 0.53	4.89 \pm 0.60	5.54 \pm 0.74	6.14 \pm 1.28

Table S1. Particle size distributions of Co nanoclusters after rapid injection of **2** and **4**.

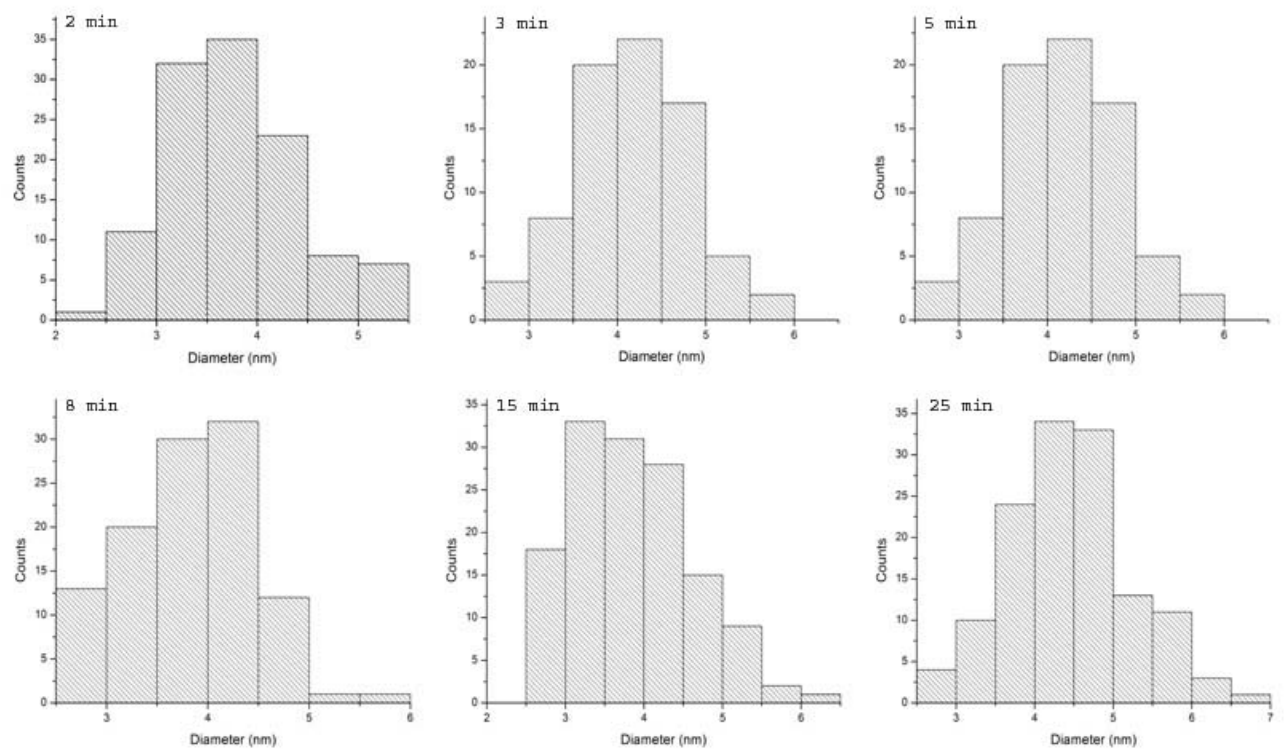
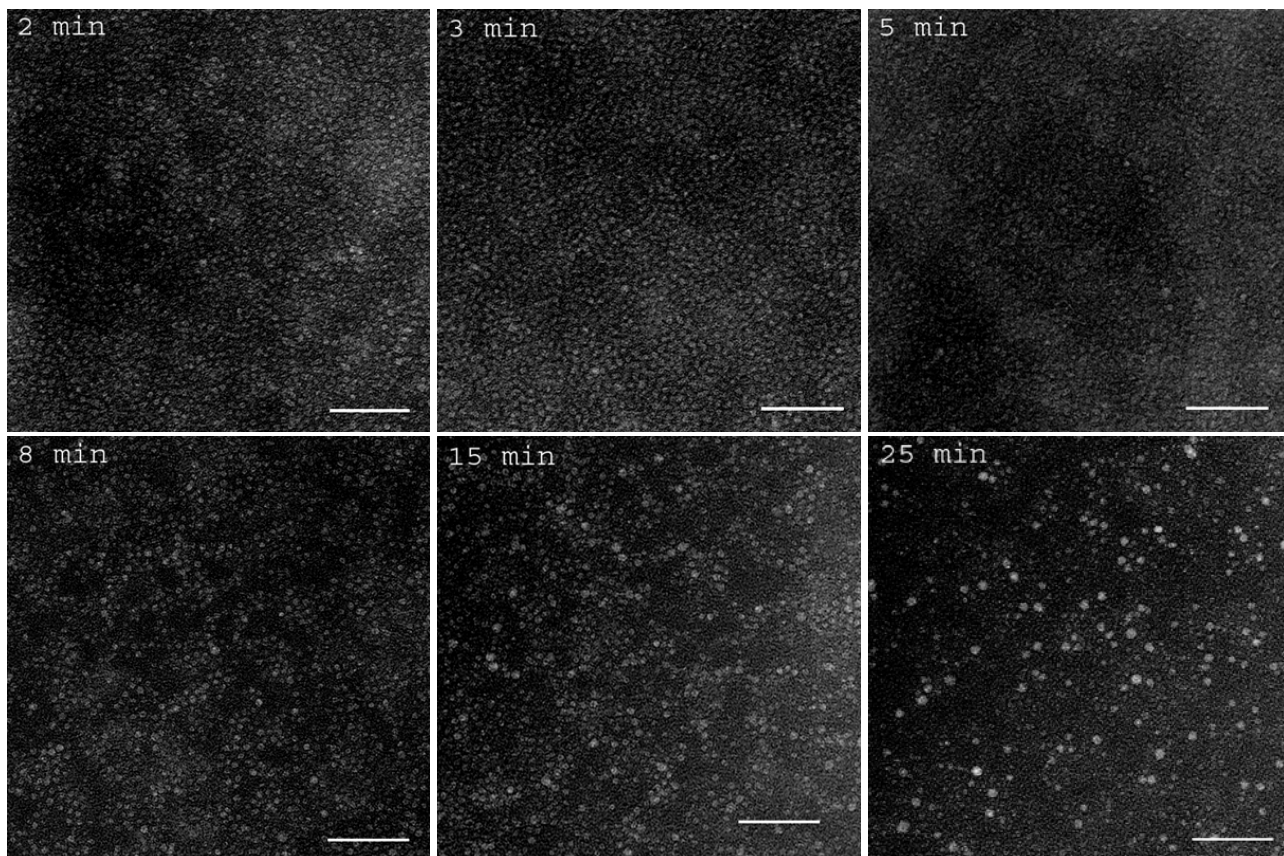


Figure S2. TEM images and size distributions of Co NCs by rapid injection of Co₁₆-calixarene **2**. Scale bar = 50 nm.

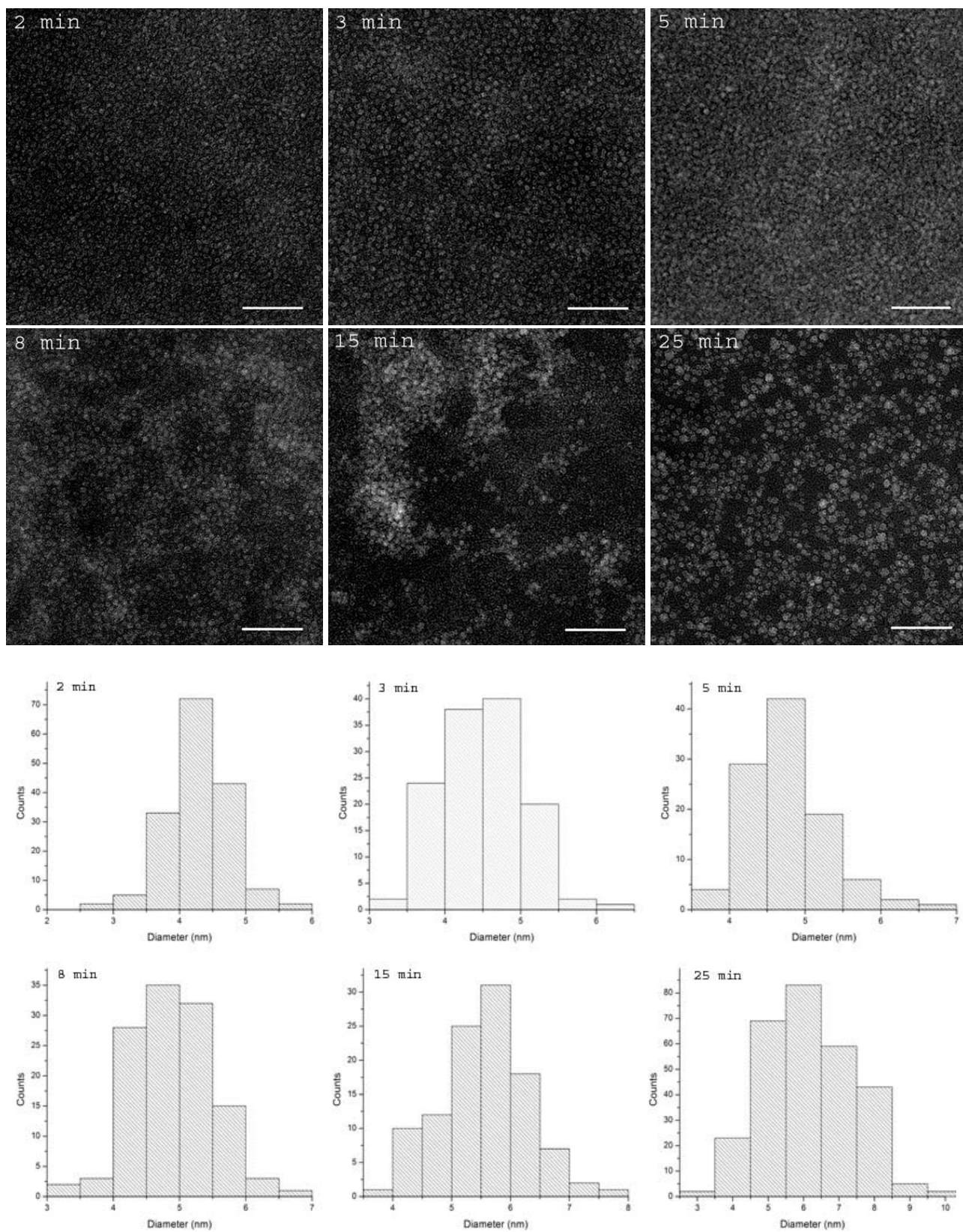
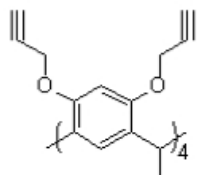
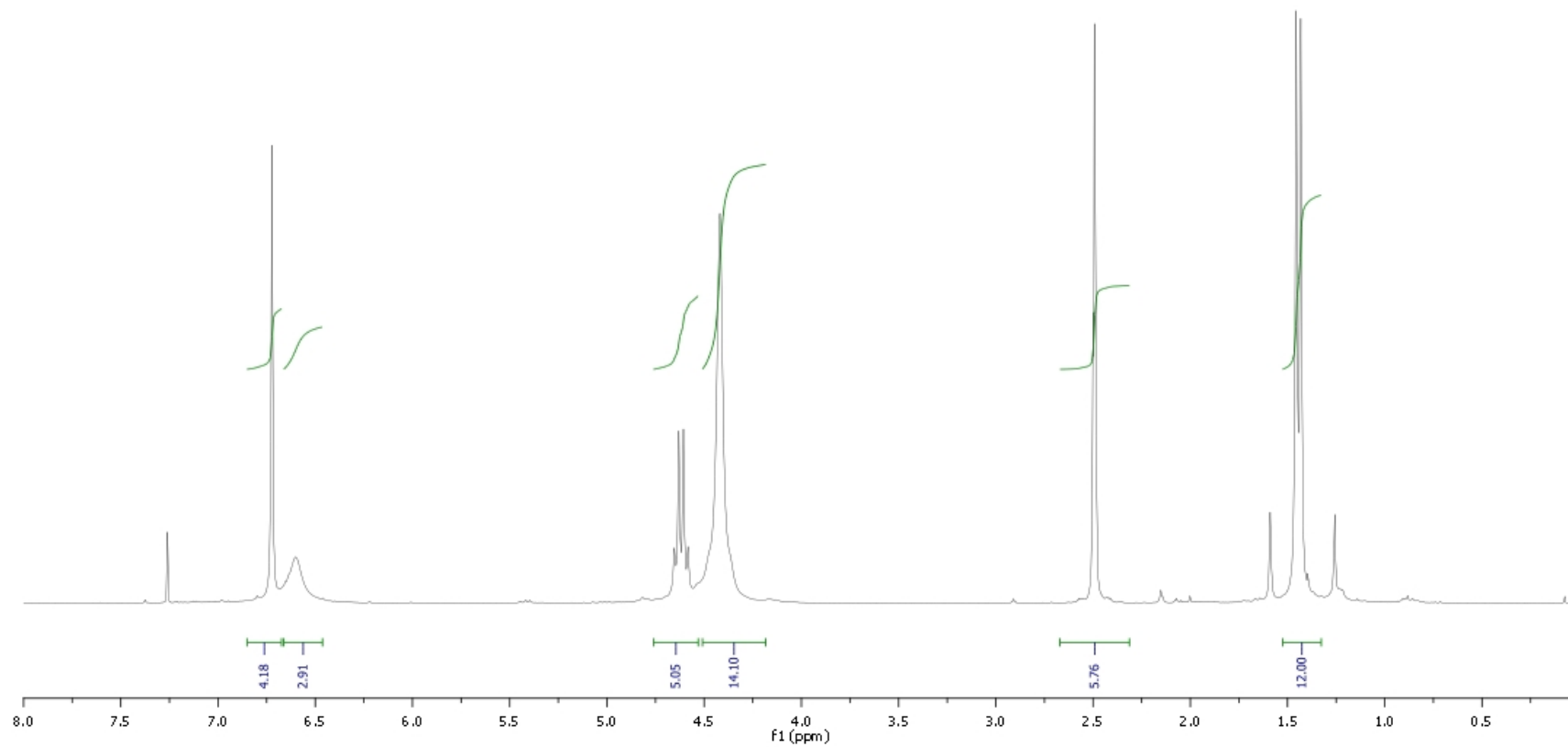


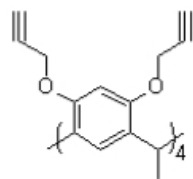
Figure S3. TEM images and size distributions of Co NCs by rapid injection of Co₂-PPE **4**. Bar = 50 nm.



1

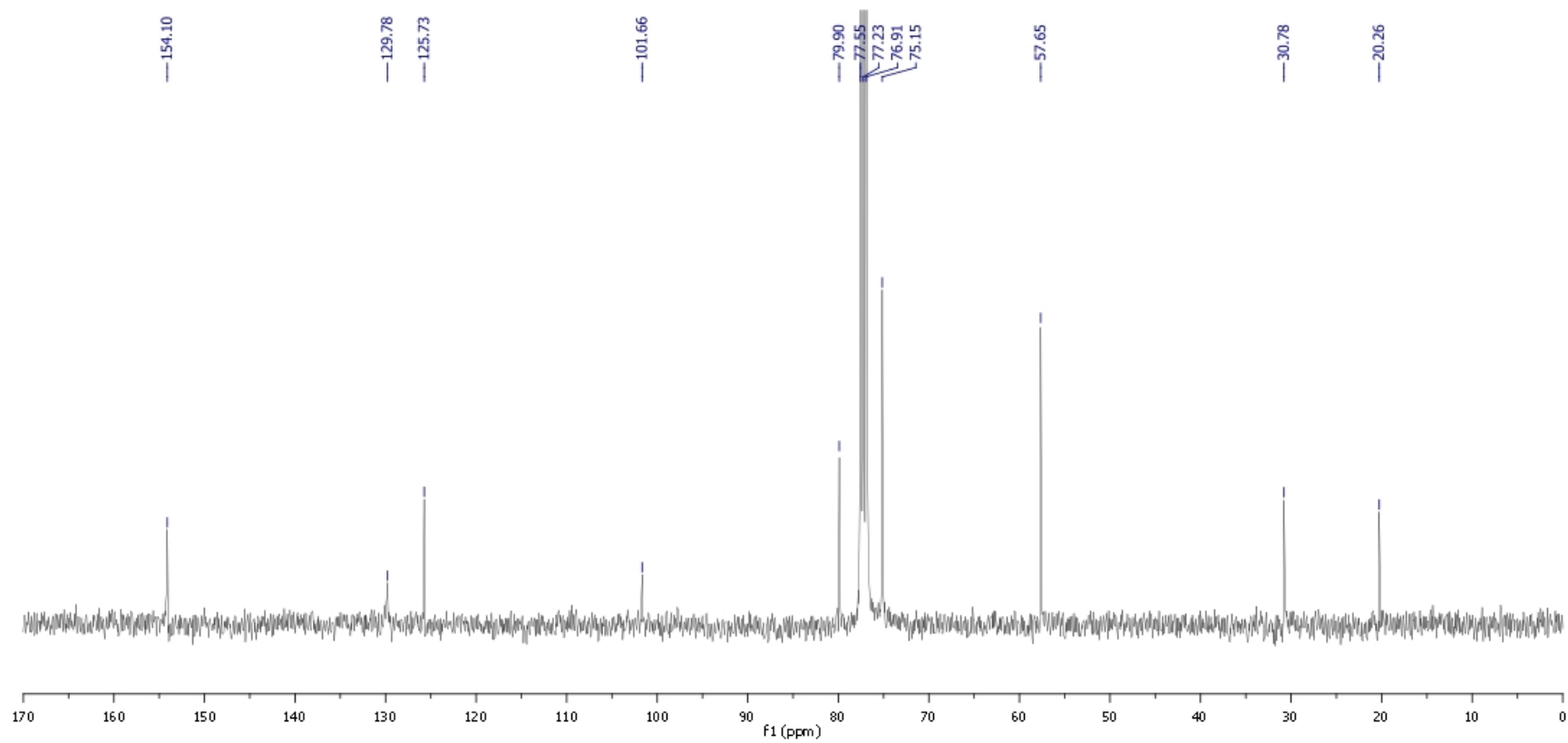
¹H NMR, 300 MHz, CDCl₃

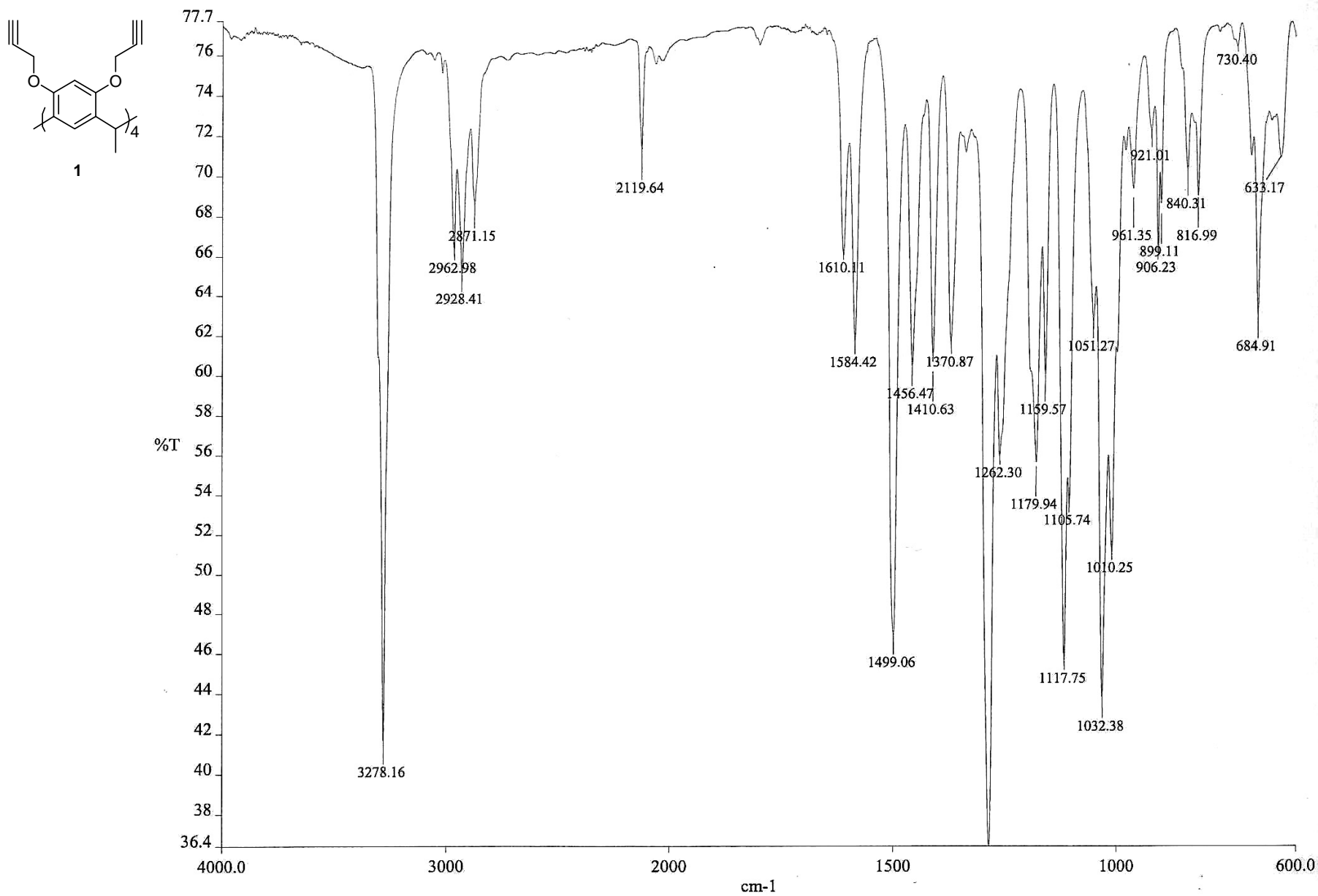


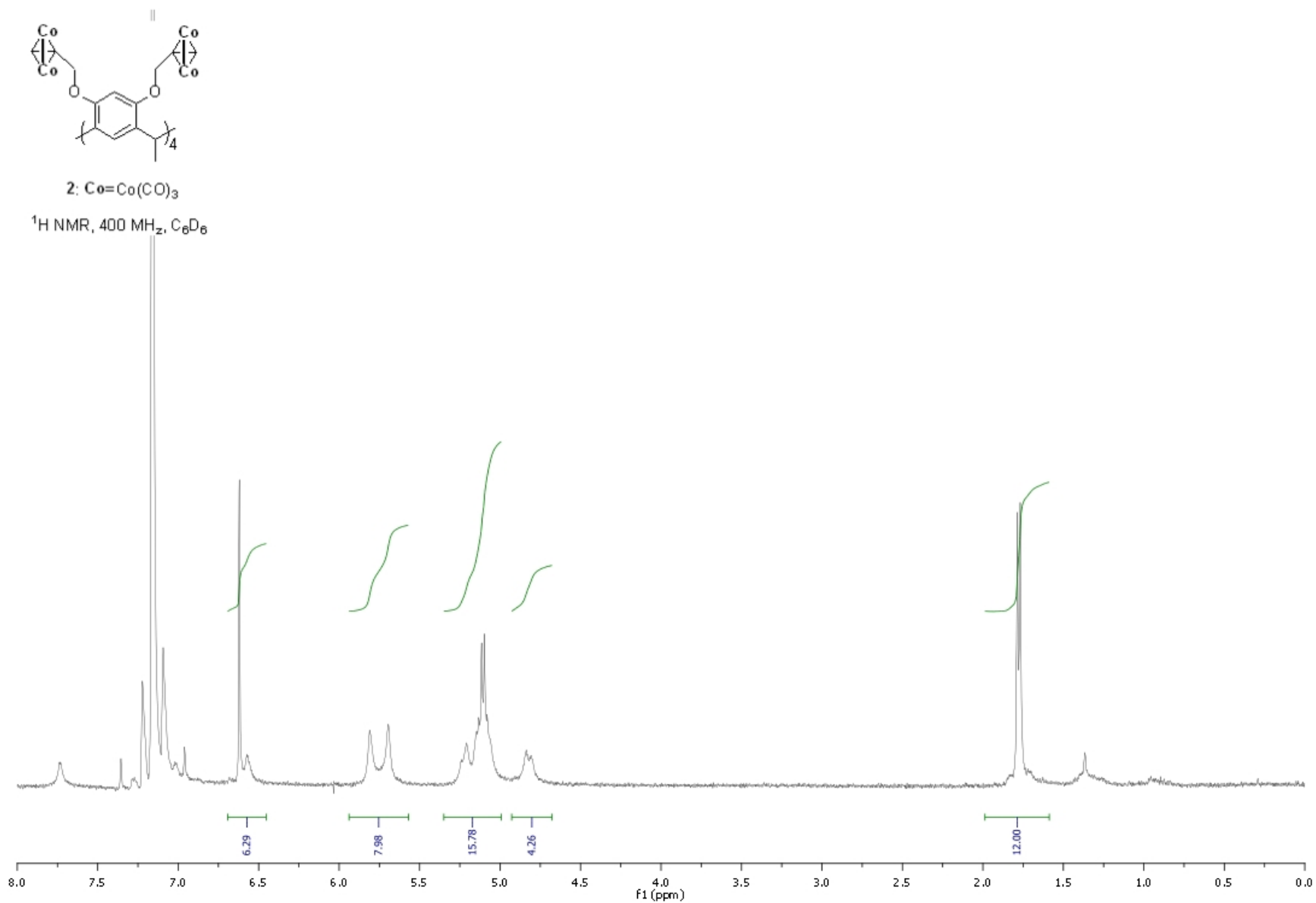


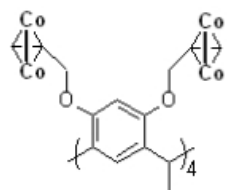
1

¹³C NMR, 400 MHz, CDCl₃



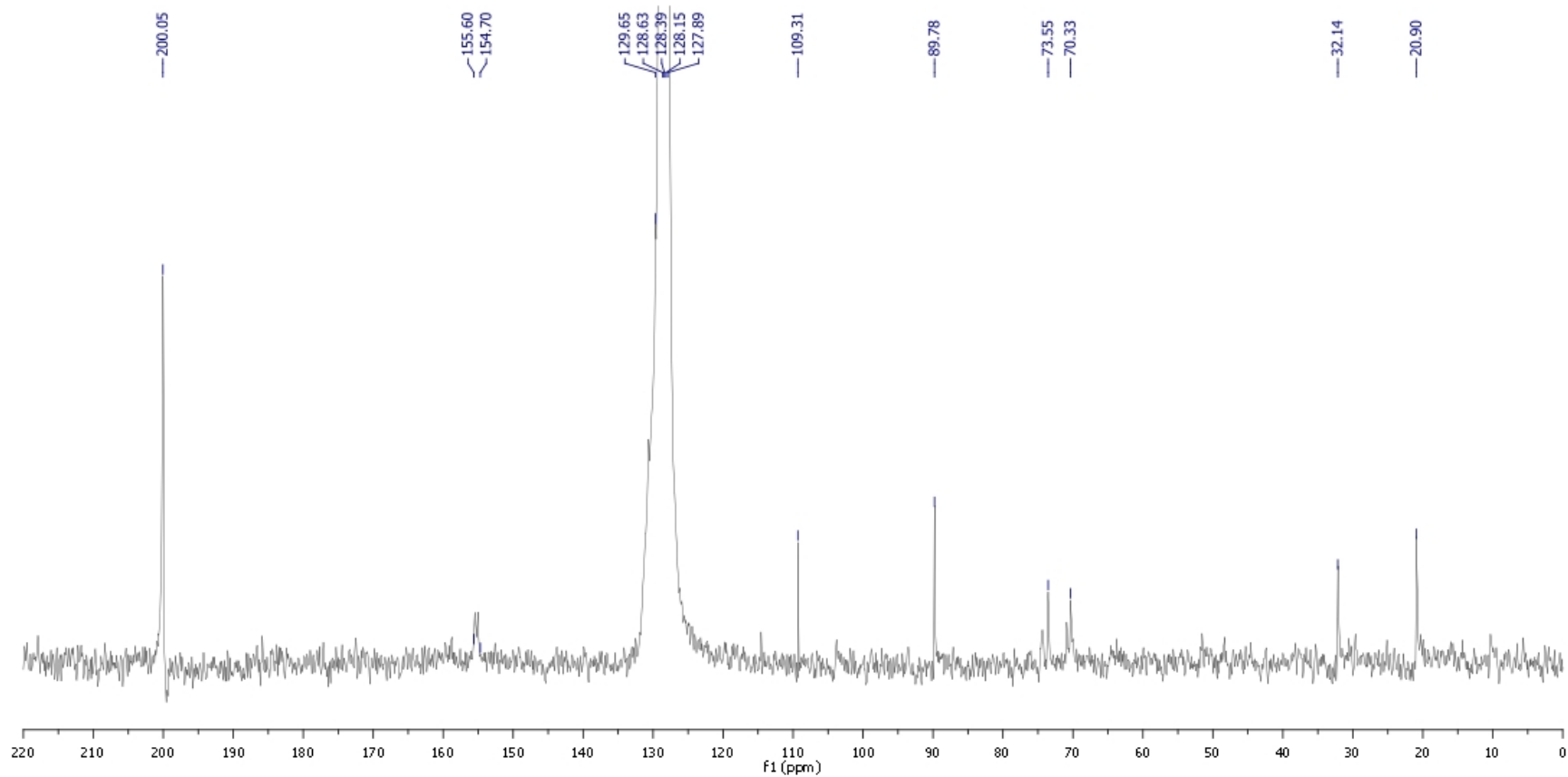


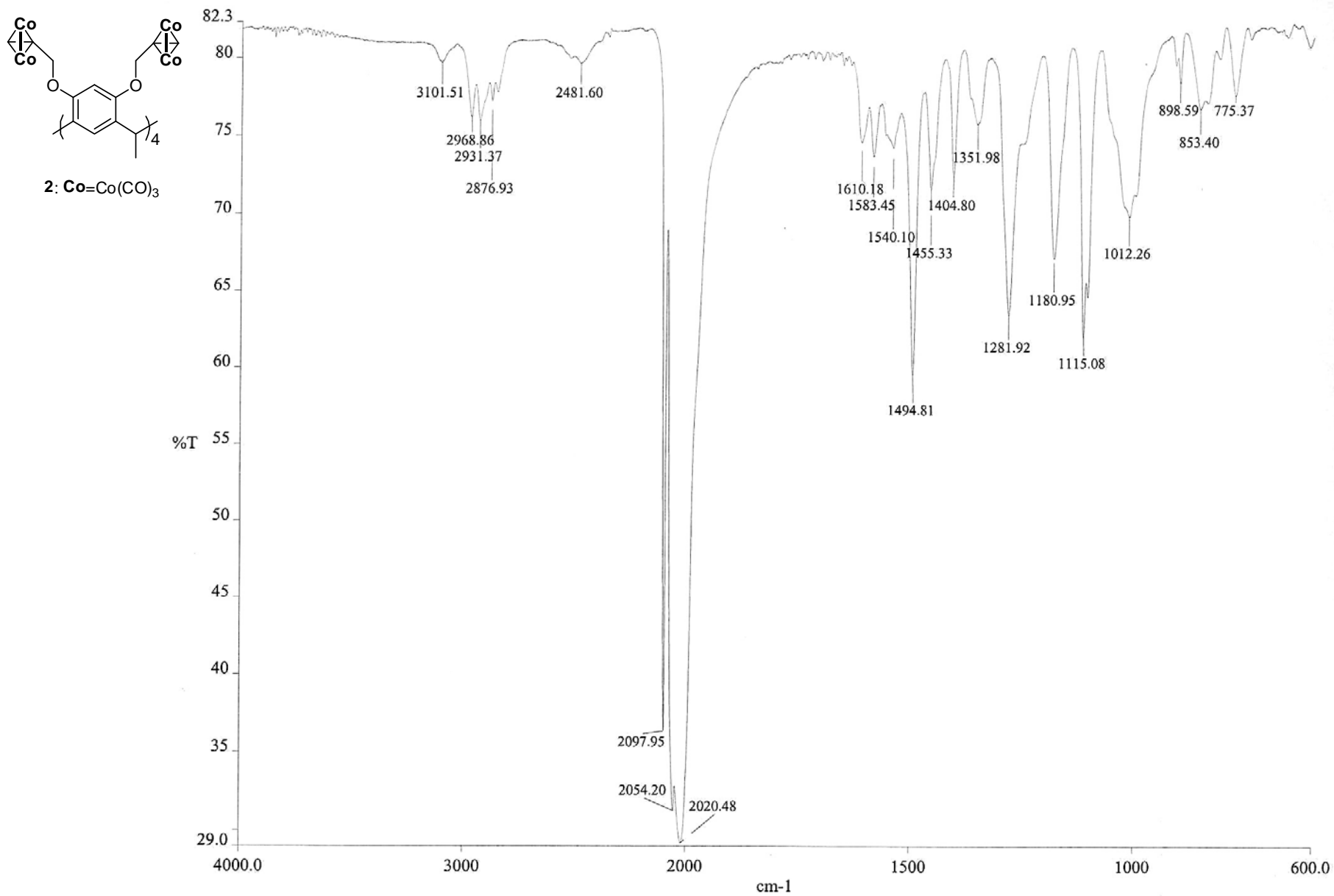


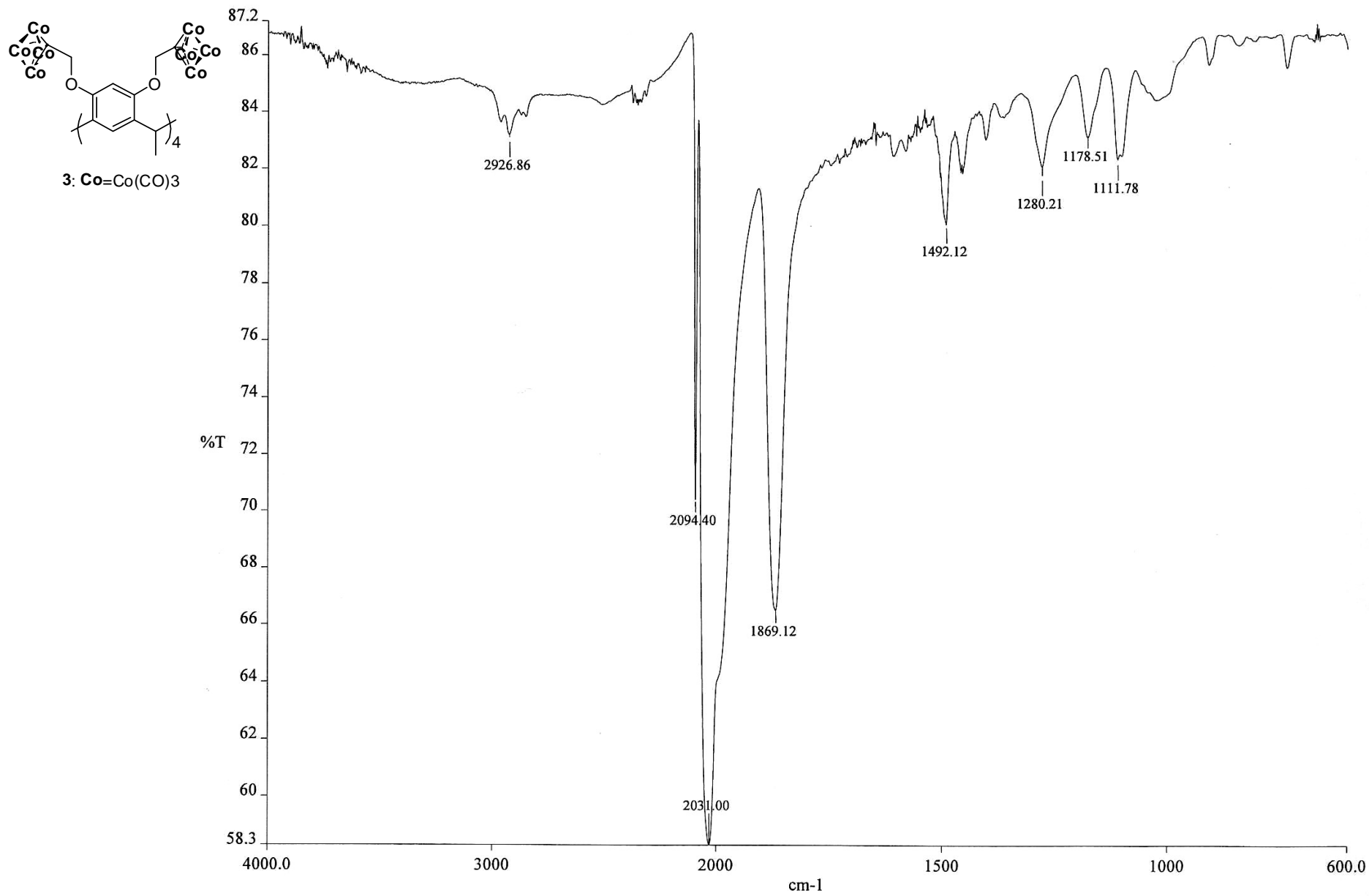


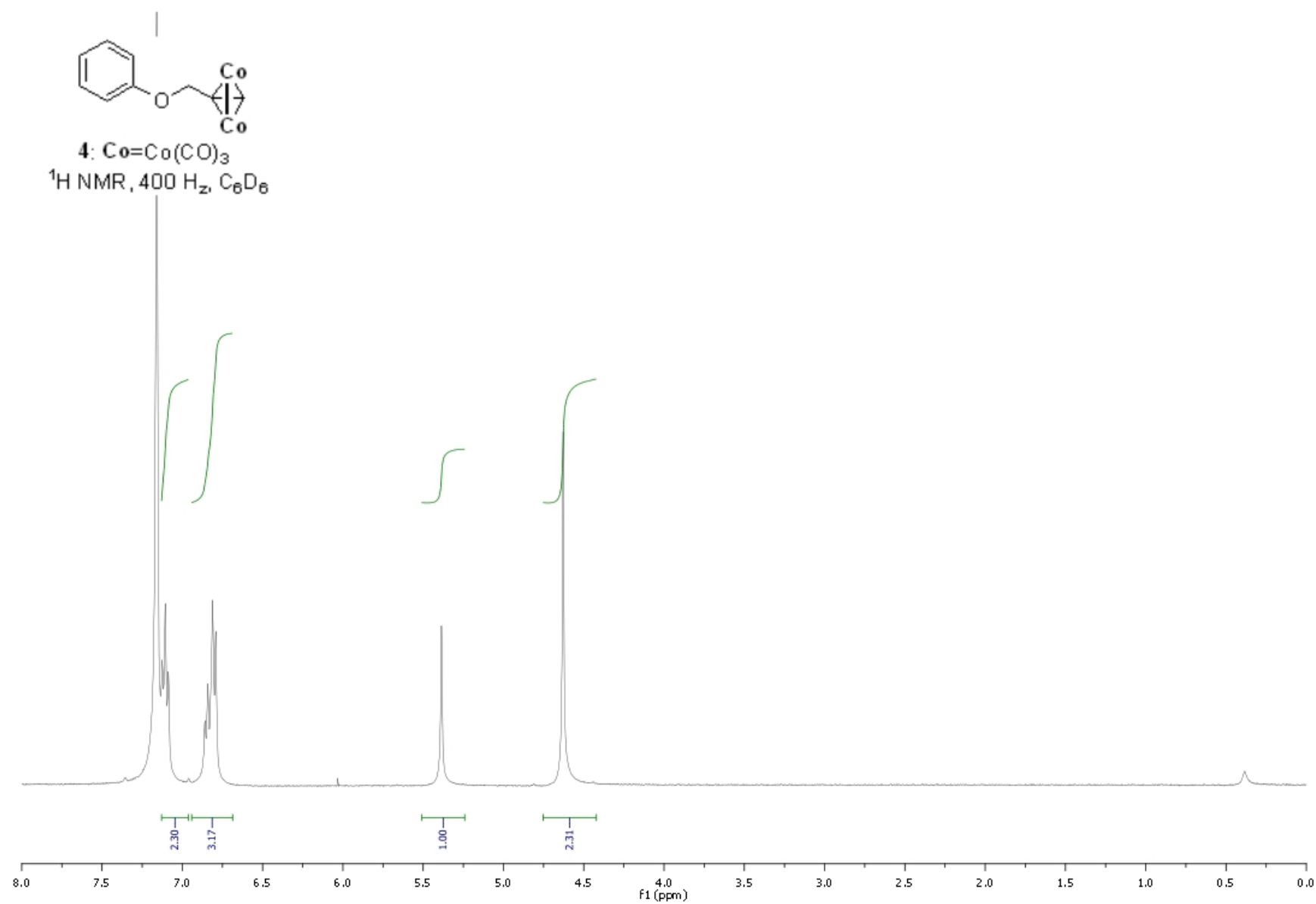
2: Co=Co(CO)₃

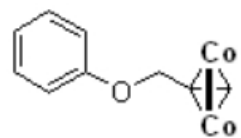
¹³C NMR, 100 MHz, C₆D₆





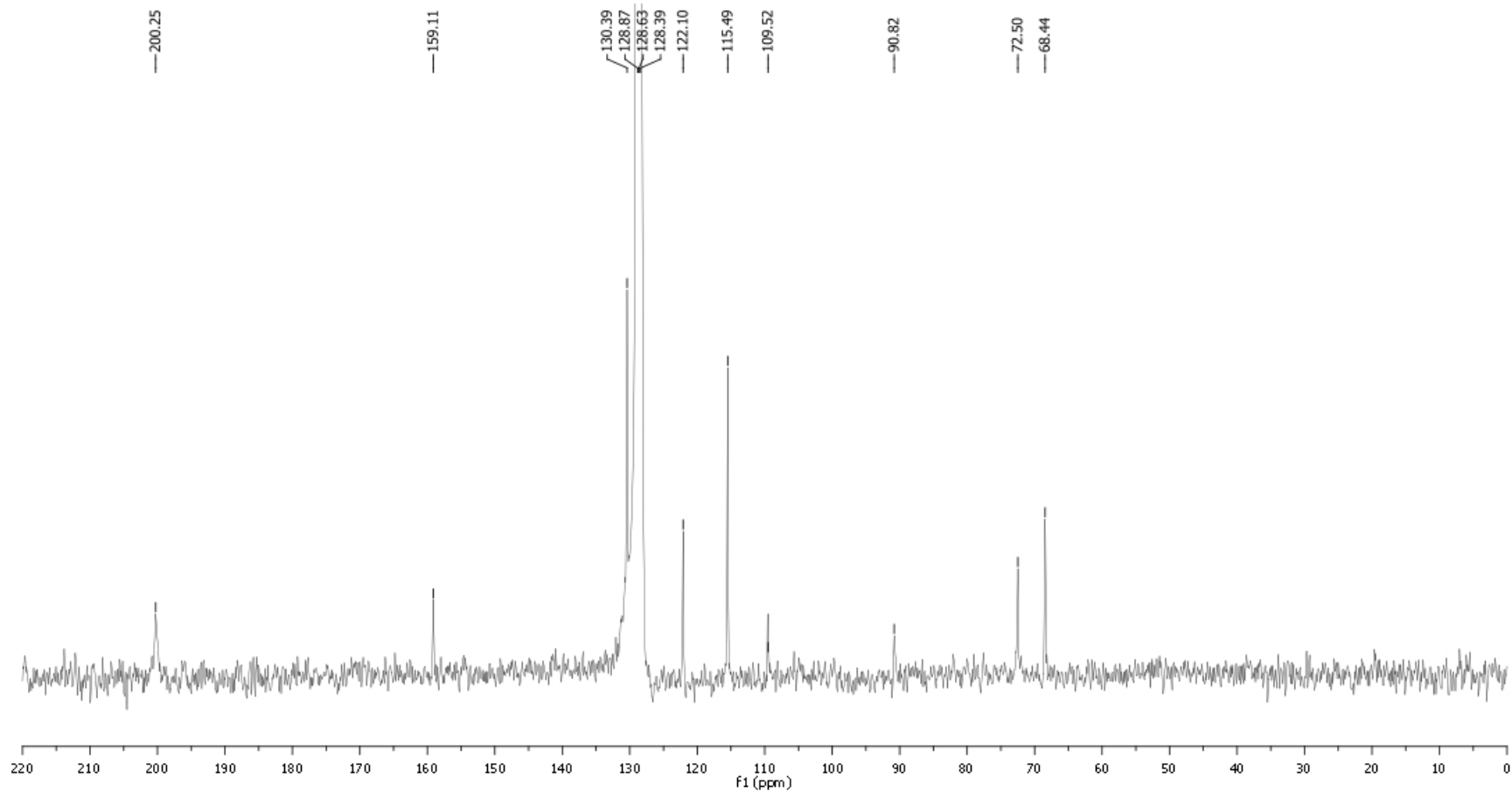


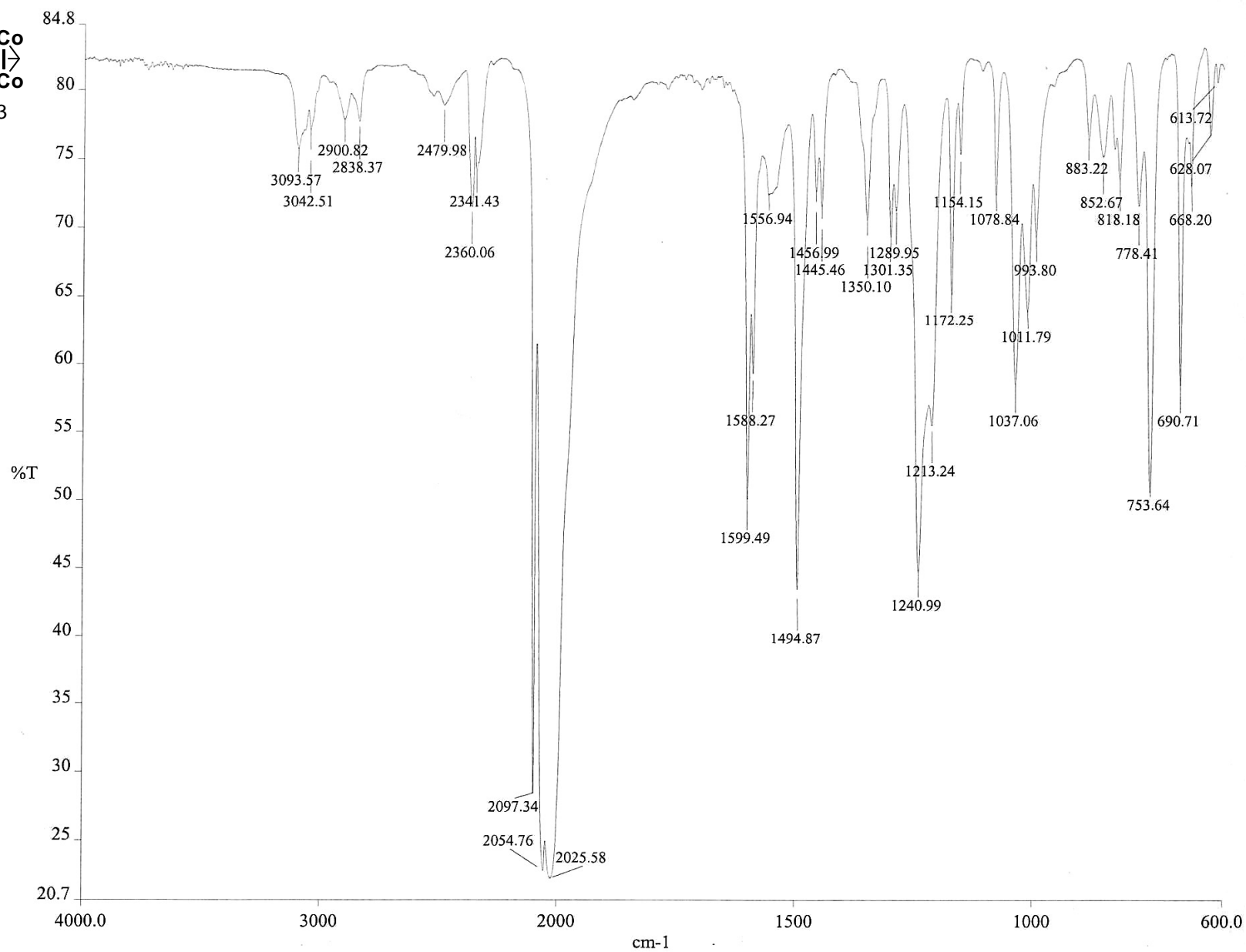
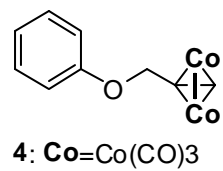


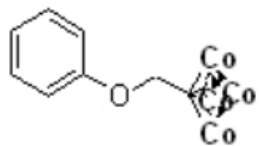


4: Co=Co(CO)₃

¹³C NMR, 100 MHz, C₆D₆







5: $\text{Co}=\text{Co}(\text{CO})_3$

^1H NMR, 400 MHz, CDCl_3

