Electronic Supplementary Information

Octahedral Cobalt(III) Complex Based on Cheap 1,2-Phenylenediamine as a Bifunctional Metal-Templated Hydrogen Bond Donor Catalyst for Fixation of CO_2 with Epoxides at Ambient Conditions

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General information

All solvents purchased from commercial suppliers were used without further purification (CH_2Cl_2, $CDCl_3$, EtOH, DMSO, MeOH, *rac*-propylene carbonate). Purchased 1,2-phenylenediamine, 3,5-di-*tert*-butyl-salicylaldehyde and epoxides **3a-g** from commercial suppliers were used without further purification. $Na_3[Co(CO_3)_3]x3H_2O$ was prepared by a literature procedure.[S1] *N*-(oxiran-2-ylmethyl)-*N*-phenylaniline **3h** was synthesized according to a literature procedure.[S2] If not stated otherwise, flash column chromatography was performed with silica gel 60 M from Macherey-Nagel.

Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz (^{1}H) and 101 MHz ($^{13}C\{^1H\}$). Chemical shifts are reported in ppm relative to the residual solvent peak ($CDCl_3$: $\delta = 7.26$ ppm for ^{1}H NMR, $\delta = 77.1$ for ^{13}C NMR). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constant, integration, and nucleus. Infrared (IR) spectra were collected on a Shimadzu IR Prestige-21 FT-IR spectrometer using the single reflection ATR sampling accessory Miracle from the Pike Technologies. High-resolution mass spectra were recorded on an AB Sciex TripleTOF 5600+ instrument using ESI ionization method (DuoSpray source). X-ray crystallography diffraction data were collected on a Bruker APEX CCD diffractometer [$\lambda(MoK\alpha) = 0.71073$ Å, ω-scans, $2\theta<58^o$] at 120 K. Elemental analyses were carried out in the Laboratory of Microanalysis of the A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

Procedure for the preparation of the complexes 2

Synthesis of the complex ***2a***

1,2-Phenylenediamine (397 mg, 3.68 mmol, 1 equiv.) and NH_4Cl (197 mg, 3.68 mmol, 1 equiv.) were dissolved in dry MeOH (15 mL) by stirring during 5 min, and the solvent was removed on a rotary evaporator. The resulting salt was dissolved in EtOH (25 mL) and 3,5-di-*tert*-butyl-salicylaldehyde (863 mg, 3.68 mmol) was added to the residue, and after 5 min stirring, the reaction solution became a deep yellow. Then, $Na_3[Co(CO_3)_3]x3H_2O$ (724 g, 2.2 mmol, 0.6 equiv) was added to this solution. The resulting dark-brown reaction mixture was heated at reflux for 3 h after which time the mixture was allowed to cool to room temperature. After removal of the solvent on a rotary evaporator, the resulting precipitate was dissolved in DCM (10 mL), and the aqueous solution of sodium chloride (5 g in 10 mL) was added. After 1 h stirring, the organic layer was separated, and the aqueous layer was washed with DCM (2x15 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated on a rotary evaporator, and the resulting residue was purified by silica column chromatography (CH_2Cl_2/acetone 5:1 → acetone

→ DCM/EtOH 1:1) to separate from impurities, and then the pure complex **2a** was isolated as a brown powder (850 mg, 1.15 mmol, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 2H, *CH=N*), 8.33 (d, J = 11.2 Hz, 2H, *NH*^{a}), 7.99 (d, J = 8.3 Hz, 2H, *ArH*), 7.45–7.31 (m, 4H, *ArH*), 7.25–7.12 (m, 6H, *ArH*), 3.53 (d, J = 11.2 Hz, 2H, *NH*^{b}), 1.28 (s, 18H, *t*Bu), 0.82 (s, 18H, *t*Bu) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.6, 158.3, 147.4, 143.3, 137.4, 137.0, 131.3, 128.4, 128.3, 128.2, 127.4, 117.7, 115.4, 35.1, 33.9, 31.2, 28.8 ppm.

Elem. anal. calcd. for $C_{42}H_{54}CoN_4O_2Cl$ x $0.15CH_2Cl_2$ x $0.6C_3H_6O$ x H_2O (%): C, 65.42; H, 7.48; N, 6.94; Co, 7.30, found: C, 65.34; H, 7.90; N, 7.02; Co, 6.90.

IR (film): $\tilde{\nu}$ (cm^{-1}) = 3290, 3278, 3267, 2951, 2904, 2867, 1607, 1587, 1546, 1522, 1494, 1459, 1422, 1385, 1359, 1325, 1249, 1227, 1199, 1164, 1132, 1026, 949, 919, 890, 872, 837, 780, 751.

HRMS (ESI, *m*/*z*) calcd. for $C_{42}H_{54}CoN_4O_2$ $[M]^+$: 705.3579, found: 705.3575.

Synthesis of the complex ***2b***

A solution of the complex **2a** (200 mg, 0.266 mmol, 1 equiv) in CH_2Cl_2 (10 mL) was added to a solution of KBr (642 mg, 5.4 mmol, 20 equiv) in water (10 mL). The mixture was stirred for 2 h, then the organic layer was separated, and, again, a solution of KBr (642 mg, 5.4 mmol, 20 equiv) in water (10 mL) was added to the organic layer. After 2 h stirring, the organic layer was separated, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to leave the complex **2b** as a brown powder (207 mg, 0.263 mmol, 99% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 2H, *CH=N*), 8.00 (d, J = 8.3 Hz, 2H, *ArH*), 7.85 (d, J = 11.4 Hz, 2H, *NH*^{a}), 7.46–7.33 (m, 4H, *ArH*), 7.25–7.12 (m, 6H, *ArH*), 3.56 (d, J = 11.4 Hz, 2H, *NH*^{b}), 1.28 (s, 18H, *t*Bu), 0.82 (s, 18H, *t*Bu) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.6, 158.4, 147.4, 143.3, 137.5, 136.5, 131.4, 128.6, 128.3, 128.2, 127.7, 117.8, 115.4, 35.1, 33.9, 31.2, 28.8 ppm.

Elem. anal. calcd. for $C_{42}H_{54}CoN_4O_2Br$ x $0.8CH_2Cl_2$ x $0.5H_2O$ (%): C, 59.59; H, 6.61; N, 6.49; Co, 6.83, found: C, 59.37; H, 6.24; N, 6.36; Co, 6.81.

IR (film): $\tilde{\nu}$ (cm^{-1}) = 3278, 2951, 2904, 2867, 1607, 1587, 1521, 1493, 1459, 1423, 1385, 1359, 1325, 1248, 1227, 1199, 1163, 1132.

HRMS (ESI, *m*/*z*) calcd. for $C_{42}H_{54}CoN_4O_2$ $[M]^+$: 705.3579, found: 705.3571.

Synthesis of the complex ***2c***

A solution of the complex **2a** (500 mg, 0.665 mmol, 1 equiv) in CH_2Cl_2 (25 mL) was added to a solution of KI (2.2 g, 13.3 mmol, 20 equiv) in water (25 mL). The mixture was stirred for 2 h, then the organic layer was separated, and, again, a solution of KI (2.2 g, 13.3 mmol, 20 equiv) in water (25 mL) was added to the organic layer. After 2 h stirring, the organic layer was separated, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to leave the complex **2c** as a brown powder (538 mg, 0.646 mmol, 97% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.65 (s, 2H, *CH=N*), 8.02 (d, *J* = 8.3 Hz, 2H, *ArH*), 7.48–7.35 (m, 4H, *ArH*), 7.28–7.15 (m, 8H, *ArH*, NH^a), 3.61 (d, *J* = 11.4 Hz, 2H, NH^b), 1.28 (s, 18H, *t*Bu), 0.83 (s, 18H, *t*Bu) ppm.

^{13}C NMR (101 MHz, CDCl$_3$): δ = 163.5, 158.6, 147.6, 143.3, 137.7, 135.7, 131.5, 128.8, 128.4, 128.3, 128.1, 117.8, 115.5, 35.1, 33.9, 31.2, 28.9 ppm.

Elem. anal. calcd. for $C_{42}H_{54}CoN_4O_2I$ x $0.15CH_2Cl_2$ x $0.5C_3H_6O$ x $0.9H_2O$ (%): C, 58.86; H, 6.69; N, 6.29; Co, 6.62, found: C, 58.75; H, 6.48; N, 6.61; Co, 6.80.

IR (film): $\tilde{\nu}$ (cm^{-1}) = 3292, 3246, 2955, 2904, 2868, 1606, 1588, 1522, 1493, 1458, 1424, 1385, 1356, 1323, 1248, 1228, 1201, 1165, 1132, 1038, 975, 939, 919, 888, 870, 837, 779, 753.

HRMS (ESI, *m/z*) calcd. for $C_{42}H_{54}CoN_4O_2$ $[M]^+$: 705.3579, found: 705.3571.

General procedure for the coupling of epoxides 3 with CO_2

A mixture of epoxide **3** (0.35 mmol, 1 equiv.) and catalyst **2** (2.0 mol %) were stirred at indicated temperature (20-40 °C) under CO_2 (1 bar, balloon or 10-20 bars, 10 mL vol. autoclave) for the indicated time (5h, 24 h or 48 h). The conversion was determined by ^{1}H NMR analysis of crude reaction mixture. For substrate screening, the yield was determined by ^{1}H NMR spectroscopy using hexamethyldisiloxane (HMDSO) as an internal standard. For additive screening, the indicated compounds (EtOH, H_2O, DMSO or *rac*-propylene carbonate) (0.5-5 equiv.) was added to the mixture of epoxide **3** and catalyst **2**. The pure cyclic carbonates **4** were isolated by silica gel column chromatography (PE/EtOAc 2:1).

Characterization of the prepared compounds

*Styrene carbonate (**4a**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47–7.40 (m, 3H), 7.38–7.32 (m, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.33 (t, *J* = 8.2 Hz, 1H). Yield: 43.0 mg, 75% (*Method C*).
The spectroscopic data were in agreement with the literature.[S3]

*4-(4-Chlorophenyl)-1,3-dioxolan-2-one (**4b**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.66 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 8.2 Hz, 1H) ppm. Yield: 54.9 mg, 79% (*Method B*).
The spectroscopic data were in agreement with the literature.[S3]

*1,2-Butene carbonate (**4c**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.66 (p, *J* = 7.0 Hz, 1H), 4.52 (t, *J* = 8.1 Hz, 1H), 4.08 (t, *J* = 8.4 Hz, 1H), 1.90–1.68 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H) ppm. Yield: 25.6 mg, 63% (*Method B*).
All spectroscopic data were in agreement with the literature.[S3]

*1,2-Hexene carbonate (**4d**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.69 (qd, J = 7.4, 5.3 Hz, 1H), 4.52 (t, J = 8.1 Hz, 1H), 4.06 (t, J = 7.8 Hz, 1H), 1.86–1.74 (m, 1H), 1.73–1.62 (m, 1H), 1.50–1.28 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H) ppm. Yield: 47.9 mg, 95% (*Method B*).
All spectroscopic data were in agreement with the literature.[S3]

*4-(Chloromethyl)-1,3-dioxolan-2-one (**4e**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.96 (dtd, J = 8.2, 5.6, 3.9 Hz, 1H), 4.59 (t, J = 8.5 Hz, 1H), 4.42 (dd, J = 8.9, 5.7 Hz, 1H), 3.82–3.64 (m, 2H) ppm. Yield: 33.0 mg, 69% (*Method B*).
All spectroscopic data were in agreement with the literature.[S3]

*4-(phenoxymethyl)-1,3-dioxolan-2-one (**4f**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.30 (t, J = 7.7 Hz, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.1 Hz, 2H), 5.02 (dq, J = 8.8, 4.2 Hz, 1H), 4.60 (t, J = 8.4 Hz, 1H), 4.52 (dd, J = 8.6, 5.8 Hz, 1H), 4.23 (dd, J = 10.7, 3.7 Hz, 1H), 4.12 (dd, J = 10.7, 3.7 Hz, 1H) ppm. Yield: 33.6 mg, 49% (*Method C*).
All spectroscopic data were in agreement with the literature.[S3]

*4-((benzyloxy)methyl)-1,3-dioxolan-2-one (**4g**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39–7.27 (m, 5H), 4.86–4.73 (m, 1H), 4.59 (q, J = 12.0 Hz, 2H), 4.47 (t, J = 8.3 Hz, 1H), 4.37 (dd, J = 8.4, 6.0 Hz, 1H), 3.71 (dd, J = 11.1, 3.8 Hz, 1H), 3.61 (dd, J = 11.1, 3.8 Hz, 1H) ppm. Yield: 53.9 mg, 74% (*Method C*).
All spectroscopic data were in agreement with the literature.[S4]

*4-((diphenylamino)methyl)-1,3-dioxolan-2-one (**4h**)*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.31 (t, J = 8.0 Hz, 4H), 7.04 (t, J = 7.3 Hz, 2H), 6.99 (d, J = 8.0 Hz, 4H), 4.97 (p, J = 6.1 Hz, 1H), 4.46 (t, J = 8.3 Hz, 1H), 4.18 (dd, J = 8.8, 6.7 Hz, 1H), 4.12 (dd, J = 15.4, 5.8 Hz, 1H), 4.03 (dd, J = 15.4, 5.8 Hz, 1H) ppm. Yield: 64.0 mg, 68% (*Method B*).
All spectroscopic data were in agreement with the literature.[S5]

X-ray diffraction study of the Co(III) complex 2c

Single crystal X-ray study of the complex **2c** was carried out in Center for molecule composition studies of INEOS RAS. Dark-brown single crystals of the Co(III) complex **2c** was obtained by slow evaporation from mixture $CHCl_3$/hexane. The structure was solved by direct method and refined in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of methyl and aromatic fragments were calculated according to those idealized geometries and refined with constraints applied to C-H and N-H bond lengths and equivalent displacement parameters ($U_{eq}(H) = 1.2U_{eq}(X)$, X - central atom of XH_2 group; $U_{eq}(H) = 1.5U_{eq}(Y)$, Y - central atom of YH_3 group. All structures were solved with the ShelXT program[S6] and refined with the ShelXL program.[S7] Molecular graphics were drawn using OLEX2 program.[S8] Experimental details and crystal parameters are listed in Table S1.

CCDC 2032213 contains the supplementary crystallographic data for the complex **2c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

Table S1. *Crystallographic data for the complex* ***2c***

Data block	complex **2c**
Brutto formula	$C_{43}H_{54.25}Cl_3CoIN_4O_2$
Formula weight	951.33
Diffractometer	Bruker SMART APEX CCD area detector
Scan mode	ω and ϕ scans
Anode [Wavelength, Å]	MoKα [0.71073] sealed tube
Crystal Dimensions, mm	0.14 × 0.22 × 0.3
Crystal colour	brown
Crystal system	monoclinic
a, Å	26.187(13)
b, Å	21.066(11)
c, Å	19.749(10)
α, °	90
β, °	126.263(10)
γ, °	90
Volume, Å³	8785(8)

Density, gcm^{-3}	1.439
Temperature, K	120
T_{min}/T_{max}	0.708/0.827
μ, mm^{-1}	1.316
Space group	C12/c1
Z	8
F(000)	3898
Reflections collected	54647
Independent reflections	11673
Reflections ($I>2\sigma(I)$)	9048
Parameters	499
R_{int}	0.0493
$2\theta_{min}$ - $2\theta_{max}$, °	3.858 - 58.000
wR_2 (all reflections)	0.1284
$R_1(I>\sigma(I))$	0.0437
GOF	1.034
ρ_{min}/ρ_{max}, eÅ^{-3}	-0.917/1.110

Determination of the order with respect to the catalyst 2c concentration

In the case of our reaction, we expect that the rate-determining transition state is formed by one molecule of epoxide (***epox***), one molecule of CO_2 and *n* molecules of the catalyst (***cat***), see Figure S1.

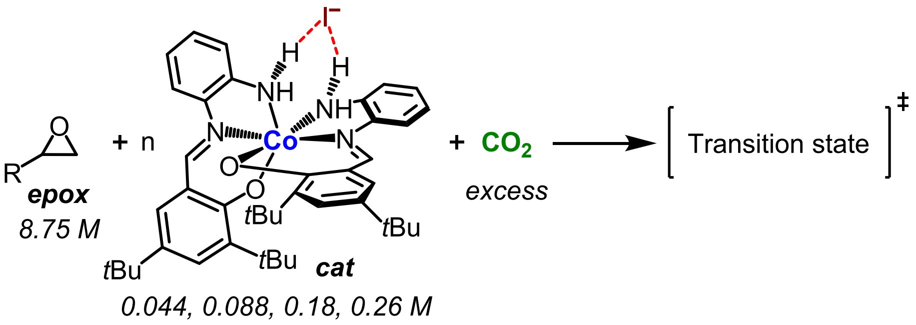


Figure S1. *The reaction used for construction of the kinetic model. Concentrations used in the kinetic experiments are provided below the structures*

This reaction corresponds to the following differential equation:

$$-\frac{d[epox]_t}{dt} = k * [epox]_t * [cat]^n * [CO_2]$$

In the equation above, index “t” in $[epox]_t$ designates that epoxide concentration is time-dependent. Note, that concentration of ***cat*** is constant because it is catalyst, and concentration of CO_2 is constant because it is in great excess.

Since $[CO_2] = constant$, we can define $k^{'} = k * [CO_2]$. Note, that the equation would be the same whether CO_2 participates in the rate-determining step, or not.

The differential equation above can be integrated from $t = 0$ to $t = t$:

$$-\frac{d[epox]_t}{[epox]_t} = k' * [cat]^n * dt$$

$$\int_0^t -\frac{d[epox]_t}{[epox]_t} = \int_o^t k' * [cat]^n * dt$$

$$\ln\left(\frac{[epox]_0}{[epox]_t}\right) = k' * t * [cat]^n$$

With the final equation at hand, we can find k’ values for several experiments differing in catalyst loading, assuming various n. The n, providing the closest k’ for all experiments is actual order in catalyst in this reaction.

We ran four kinetic experiments using identical procedures except for the catalyst quantities (Table S2). Reaction conditions: SO **3a** (0.35 mmol, 40 µL, 1 equiv), catalyst **2c** (0.5, 1, 2, or 3 mol%), CO_2 (1 bar, ballon), RT, 5 h.

Table S2. *Determination of the order in catalyst*

Initial $[epox]_0$ (mol/L)	$[cat]$ (mol/L)	Reaction time (s)	Final $[epox]_t$ (mol/L)	$ln\left(\frac{[epox]_0}{[epox]_t}\right)$	Rate constant (k) if order in catalyst equals to			
					0	1	2	3
8.75	0.0438	18000	8.4088	0.0398	2.21E-06	5.05E-05	1.15E-03	2.64E-02
8.75	0.0875	18000	7.8138	0.1132	6.29E-06	7.19E-05	8.21E-04	9.38E-03
8.75	0.175	18000	7.4288	0.1637	9.09E-06	5.20E-05	2.97E-04	1.70E-03
8.75	0.2625	18000	6.7200	0.2640	1.47E-05	5.59E-05	2.13E-04	8.11E-04

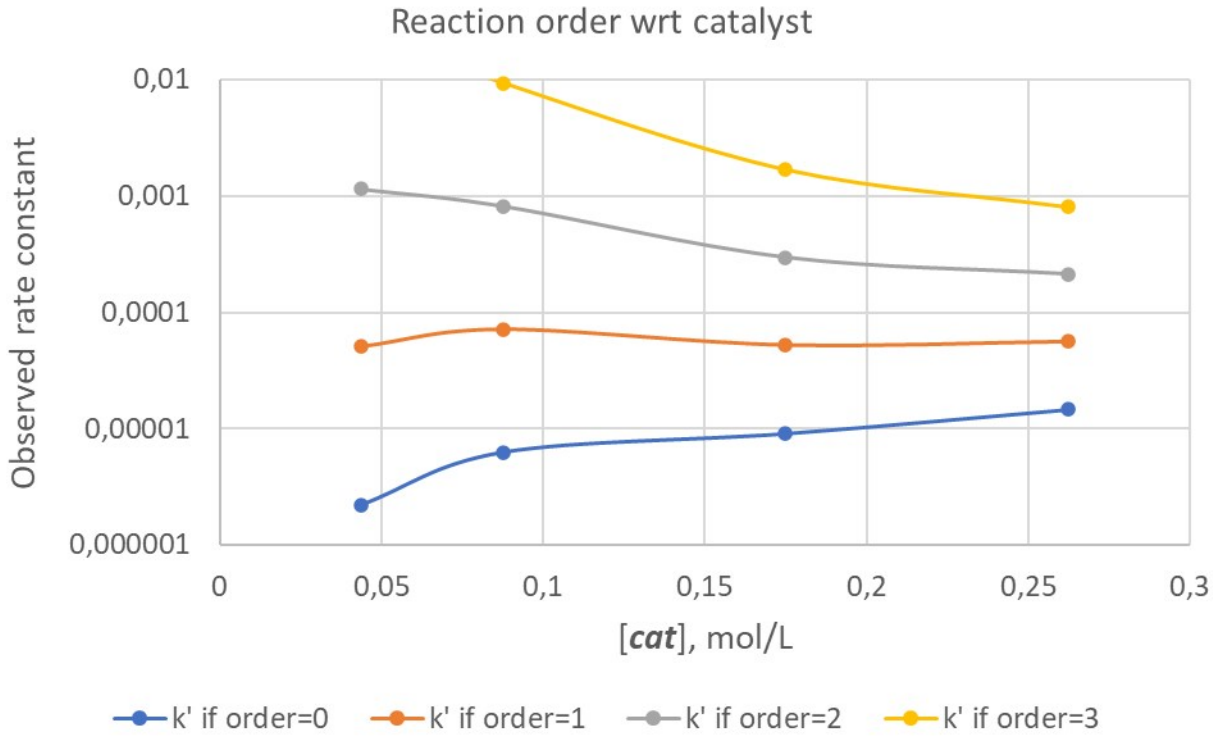


Figure S2. *Rate constants (k') computed under different assumptions about reaction order in catalyst*

From Table S2 it is evident, that 1-st order in catalyst leads to the closest rate constant values, indicating that only one catalyst molecule participates in the rate-determining transition state. To further prove this conclusion, we have plotted natural logarithm of $ln\left(\frac{[epox]_0}{[epox]_t}\right)$ vs. ln([*cat*]), Figure S3. The tangent of the observed trend corresponds to the order in catalyst, proving our previous conclusion.

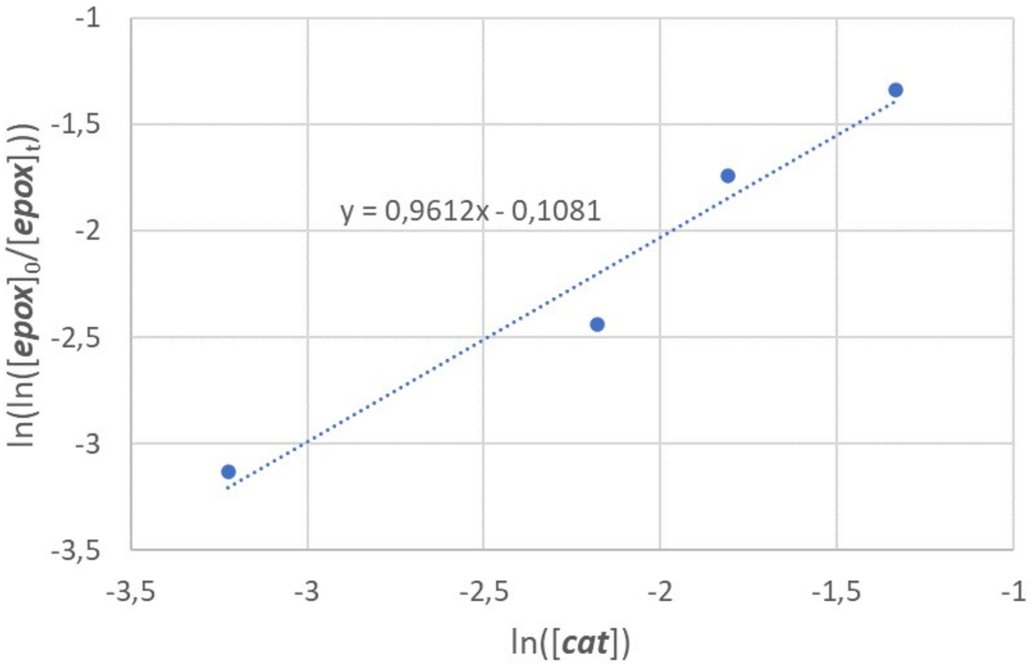


Figure S3. $ln(ln\left(\frac{[epox\ 3a]_0}{[epox\ 3a]_t}\right))$ *vs. ln([**cat 2c**])*

DFT calculations

All intermediates and transition states along the reaction path have located at PBE0[S9]-D3BJ[S10]/def2-SVP[S11]/PCM[S12] level of theory using Gaussian16 program package.[S13] PBE0 functional was selected as widely reliable and physically grounded.[S14,S15] In cases of tricky transition states we have performed constrained pre-optimization.[S16] The solvent effects of styrene oxide were implicitly accounted for with the polarizable continuum model[S12] using parameters ε=16.0, n^2=1.865956. Free energies were calculated using Head-Gordon[S17] and Grimme[S18] quasi-harmonic corrections implemented in GoodVibes 3.0.[S19]

References

[S1] H. F. Bauer, W. C. Drinkard, *J. Am. Chem. Soc.* **1960**, *82*, 5031.

[S2] B. Barvainiene, A. Stanisauskaite, V. Getautis, *Chem. Heterocycl. Comp.* **2007**, *43*, 718.

[S3] J. A. Castro-Osma, C. Alonso-Moreno, A. Lara -Sánchez, J. Martínez, M. North, A. Otero, *Catal. Sci. Technol.* **2014**, *4*, 1674.

[S4] Y.-D. Li, D.-X. Cui, J.-C. Zhu, P. Huang, Z. Tian, Y.-Y. Jia, P.-A. Wang, *Green Chem.* **2019**, *21*, 5231.

[S5] J. Schörgenhumer, M. Tiffner, M. Waser, *Monatsh. Chem.* **2019**, *150*, 789.

[S6] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3.

[S7] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.

[S8] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

[S9] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.

[S10] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[S11] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[S12] B. Mennucci, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012***, 2,* 386.

[S13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo,

R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 16 Rev. A.03*; Wallingford, CT, 2016.

[S14] M. G. Medvedev, I. S. Bushmarinov, J. Sun, J. P. Perdew, K. A. Lyssenko, *Science* **2017**, *355*, 49.

[S15] A. A. Marjewski, M. G. Medvedev, I. S. Gerasimov, M. V. Panova, J. P. Perdew, K. A. Lyssenko, A. O. Dmitrienko, *Mendeleev Commun.* **2018**, *28*, 225.

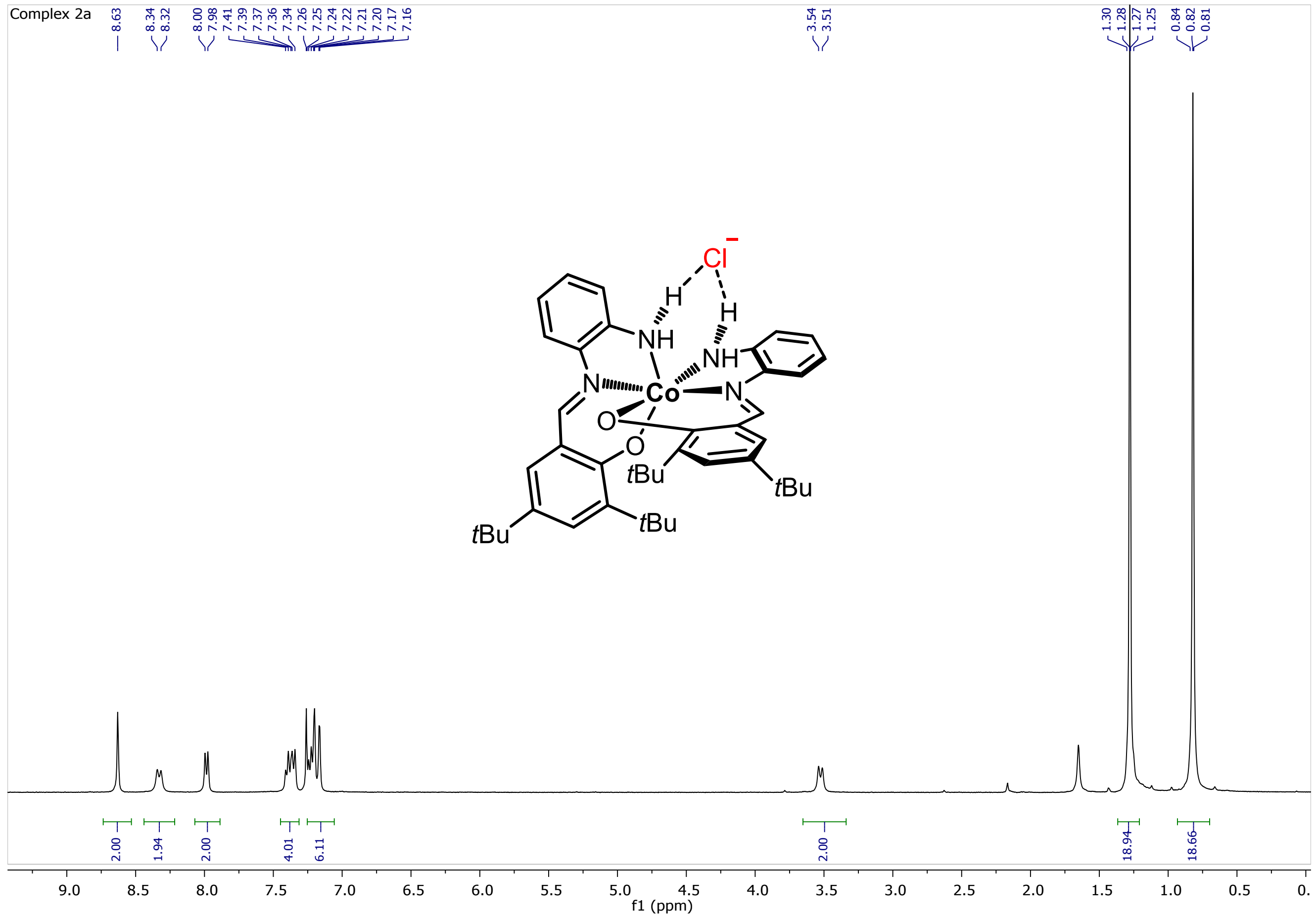
[S16] M. G. Medvedev, M. V. Panova, G. G. Chilov, I. S. Bushmarinov, F. N. Novikov, O. V. Stroganov, A. A. Zeifman, I. V. Svitanko, *Mendeleev Commun.* **2017**, *27*, 224.

[S17] N. Mardirossian, M. Head-Gordon, *Molecular Physics* **2017**, *115*, 2315.

[S18] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955.

[S19] G. Luchini, J. V. Alegre-Requena, I. Funes-Ardoiz, R. S. Paton, *F1000Research* **2020**, *9*, 291.

NMR spectra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8.34
8.32
8.00
7.98
7.41
7.39
7.37
7.36
7.34
7.26
7.25
7.24
7.22
7.21
7.20
7.17
7.16
3.54
3.51
1.30
1.28
1.27
1.25
0.84
0.82
0.81
Cl
H
H
NH
NH
N
Co
N
O
O
tBu
tBu
tBu
tBu
2.00
1.94
2.00
4.01
6.11
2.00
18.94
18.66
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

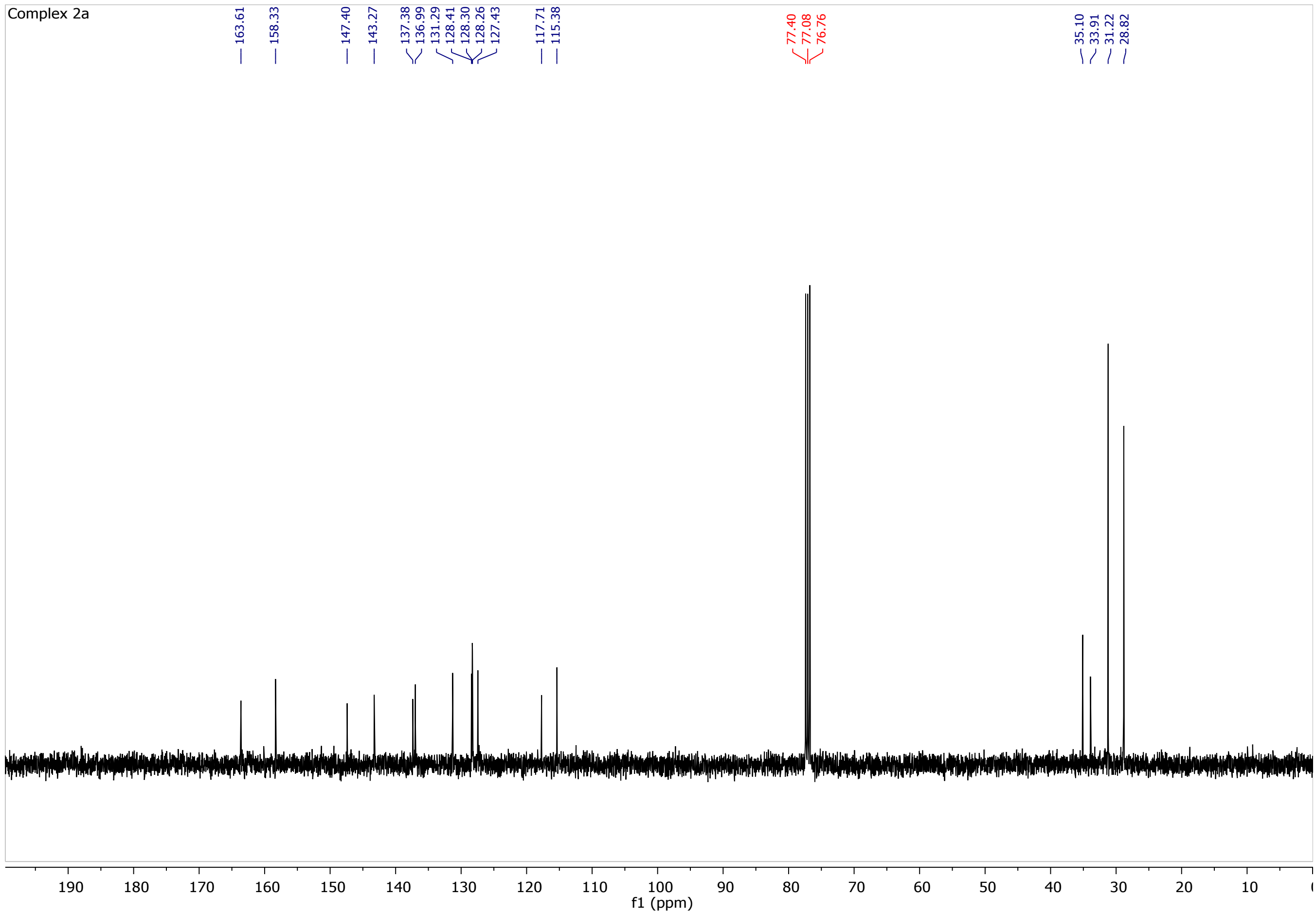
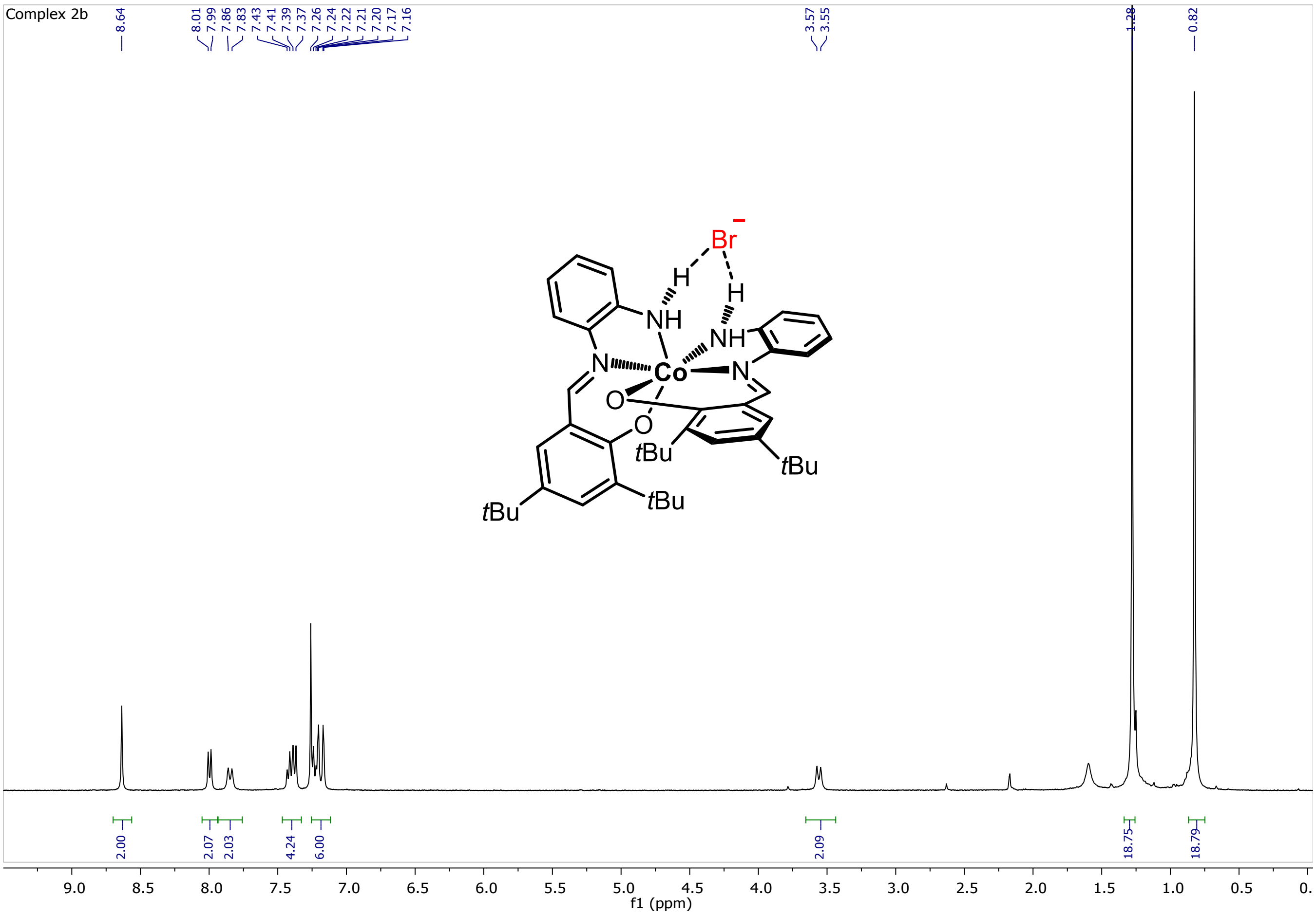

Complex 2a
163.61
158.33
147.40
143.27
137.38
136.99
131.29
128.41
128.30
128.26
127.43
117.71
115.38
77.40
77.08
76.76
35.10
33.91
31.22
28.82
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Figure S4. *^{1}H and ^{13}C NMR spectra of the complex* ***2a***



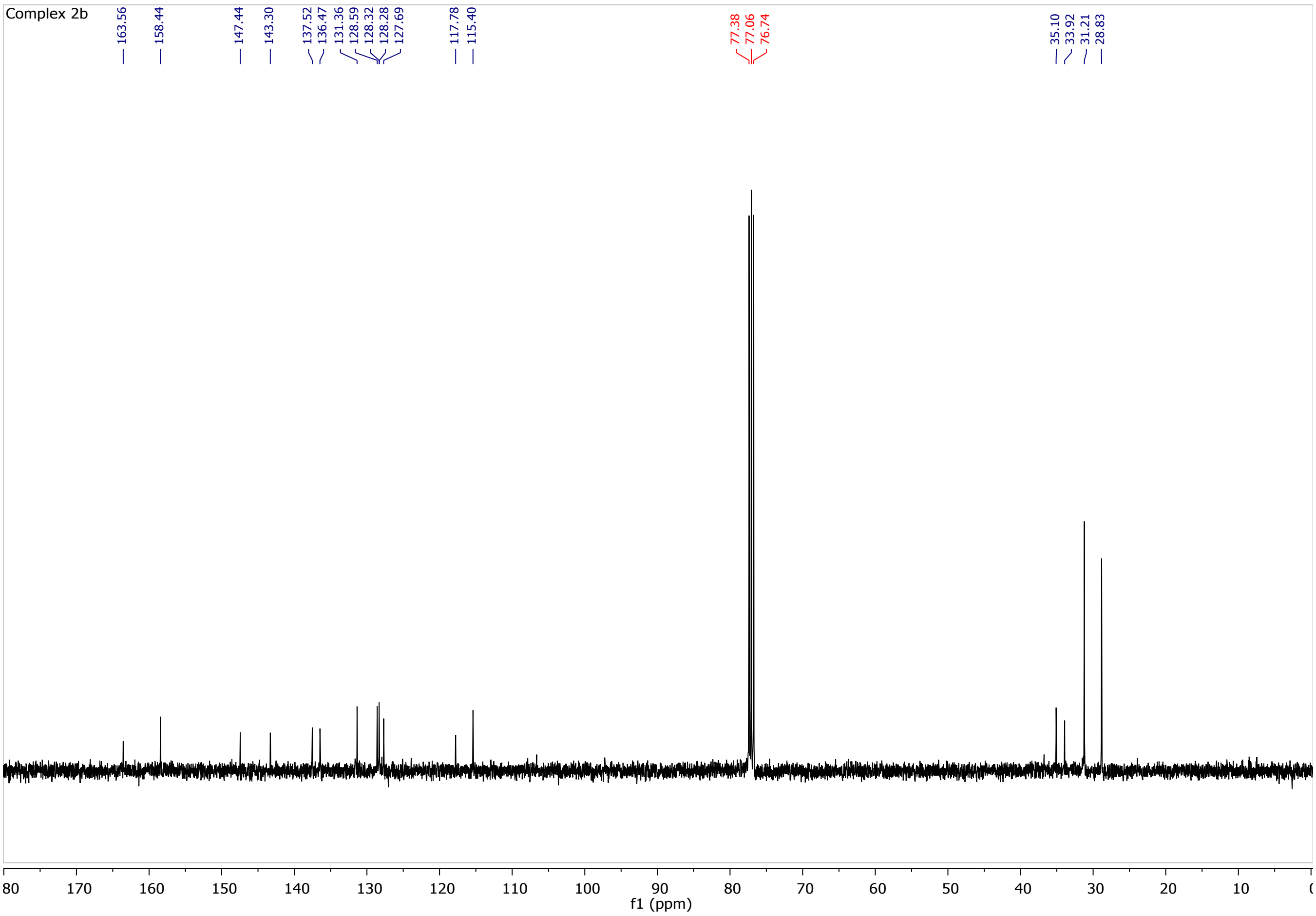
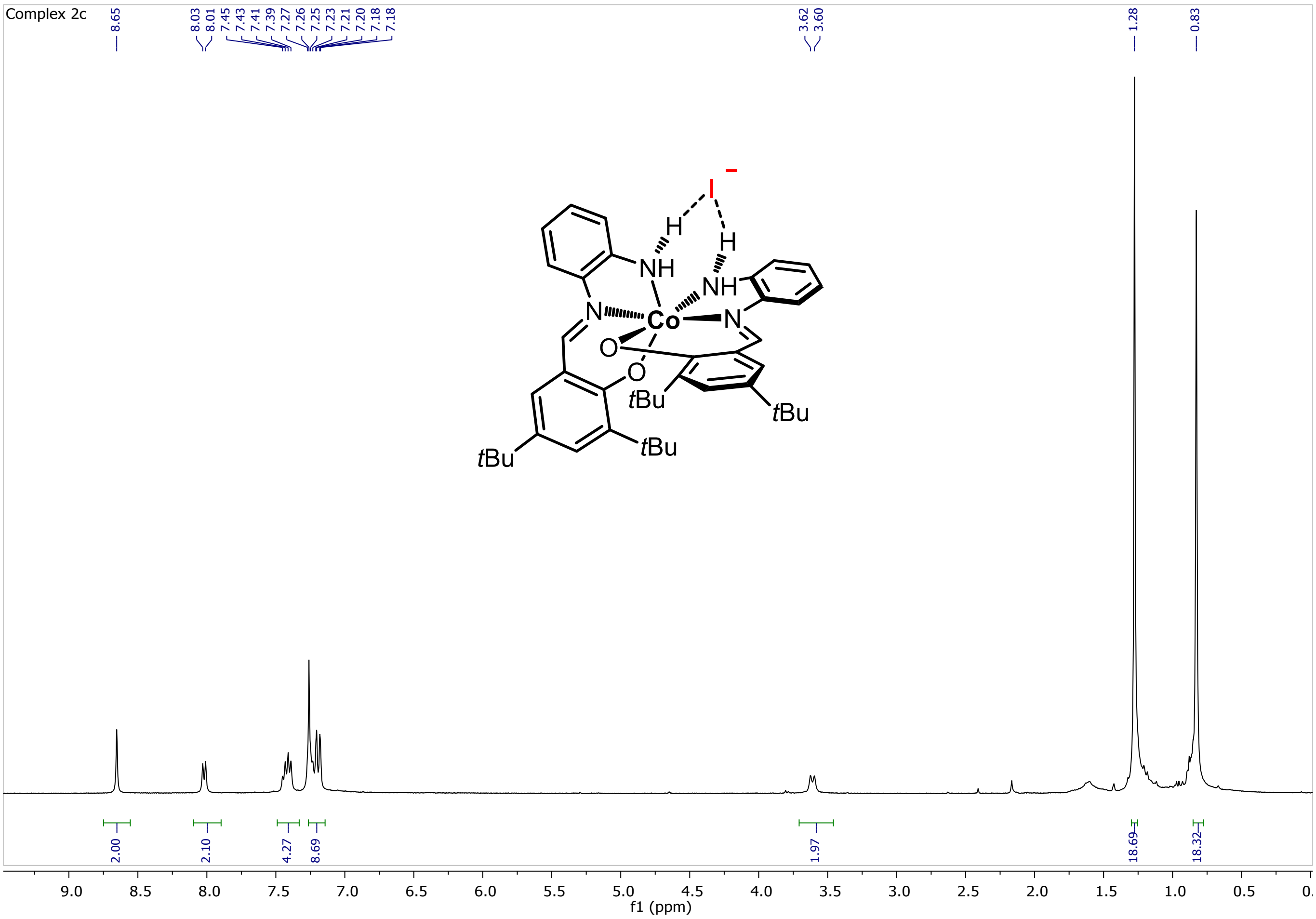


Figure S5. *^{1}H and ^{13}C NMR spectra of the complex **2b***


Complex 2c
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8.03
8.01
7.45
7.43
7.41
7.39
7.27
7.26
7.25
7.23
7.21
7.20
7.18
7.18
3.62
3.60
1.28
0.83
I⁻
H
H
NH
NH
N
Co
N
O
O
tBu
tBu
tBu
tBu
2.00
2.10
4.27
8.69
1.97
18.69
18.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

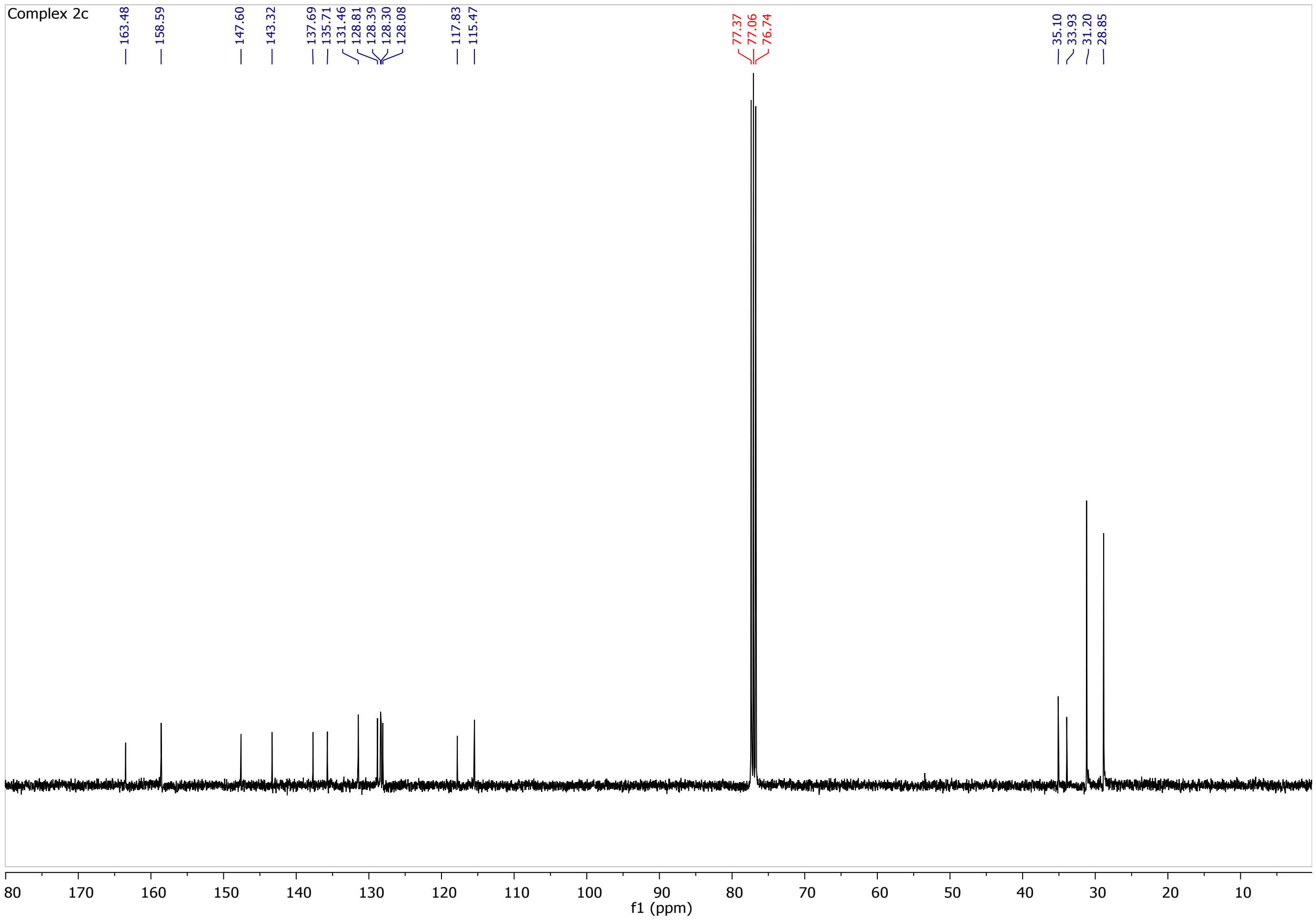


Figure S6. *^{1}H and ^{13}C NMR spectra of the complex* ***2c***

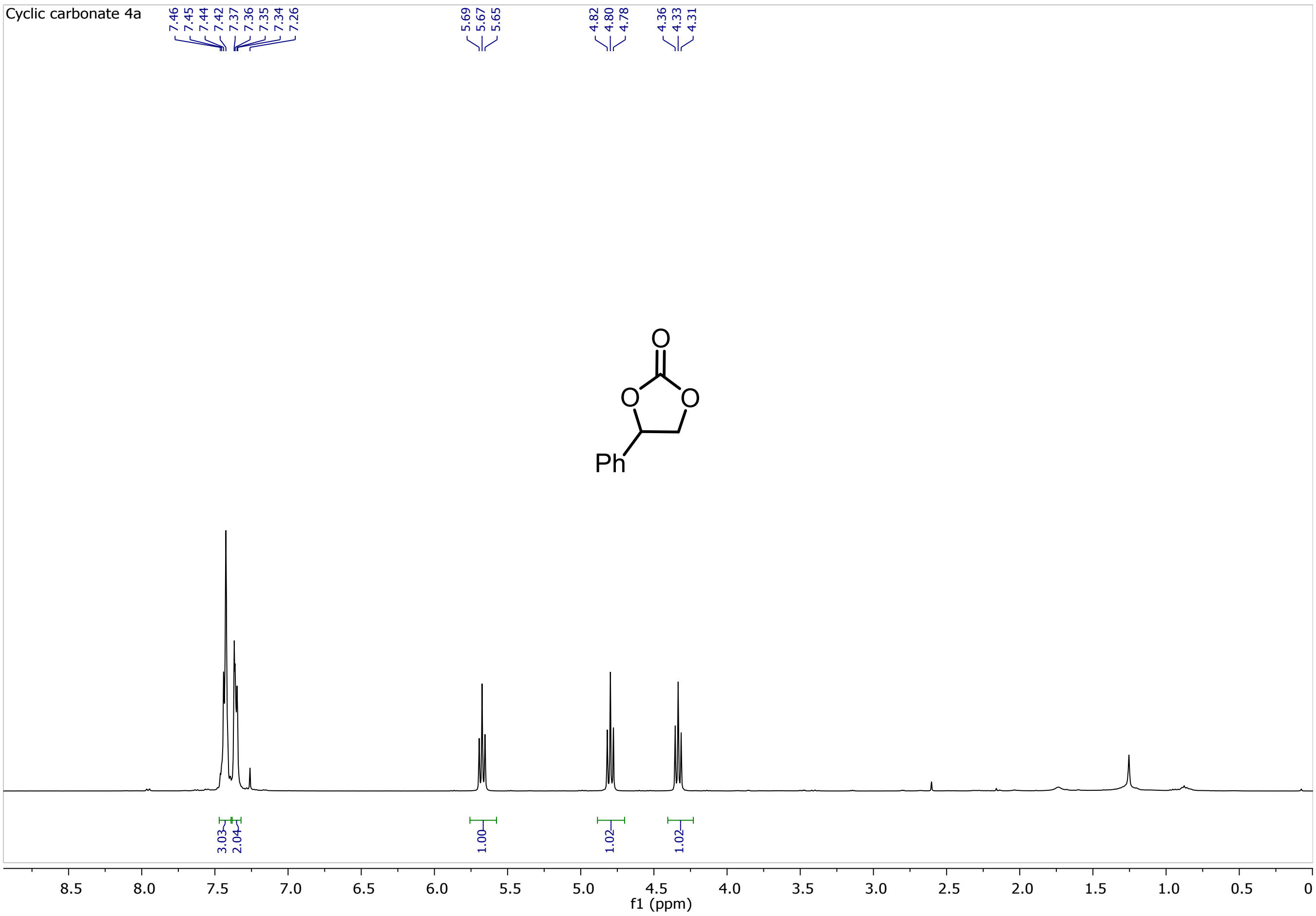


Figure S7. *^{1}H NMR spectrum of the product* ***4a***

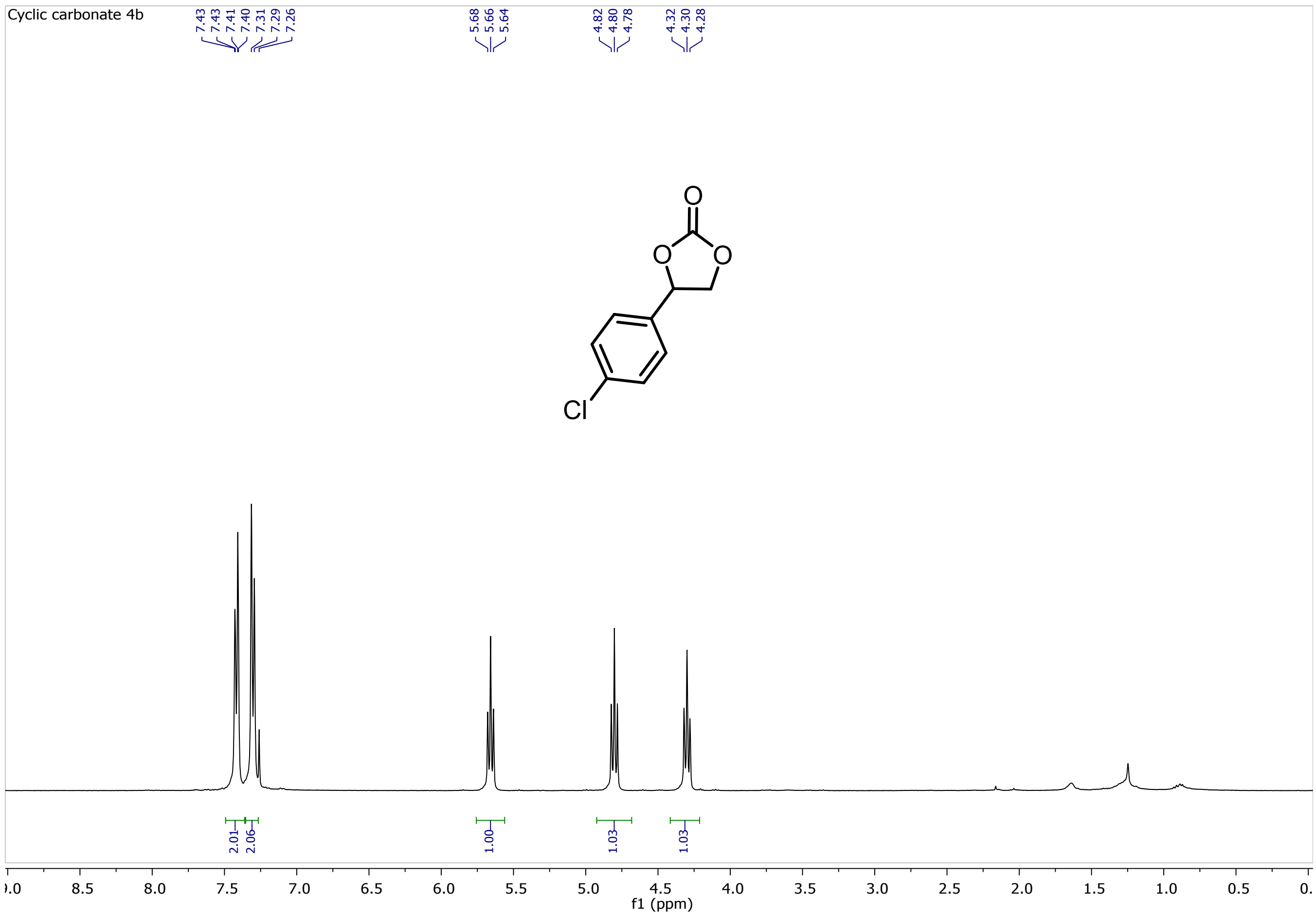


Figure S8. *^{1}H NMR spectrum of the product* ***4b***

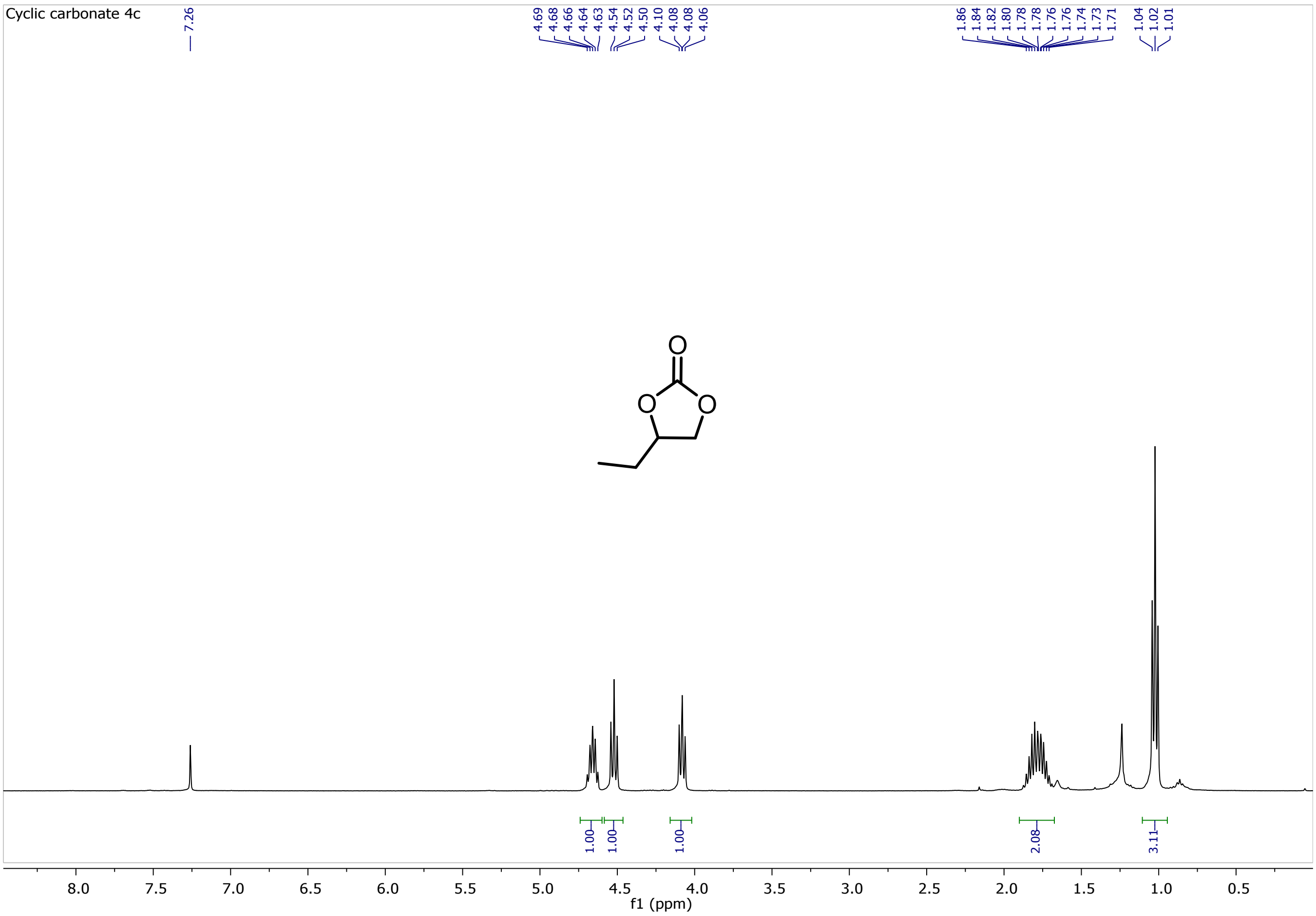


Figure S9. *^{1}H NMR spectrum of the product* ***4c***

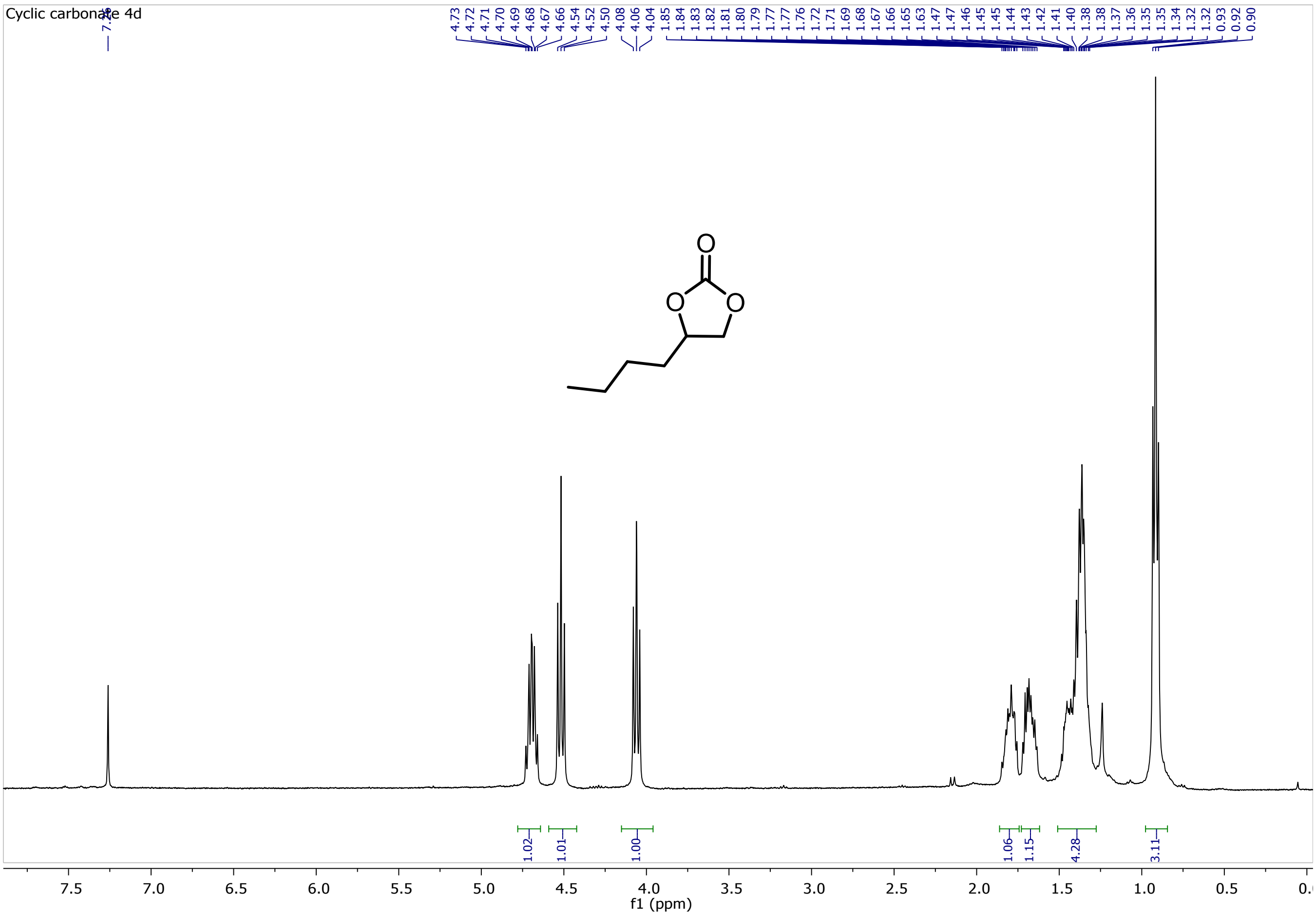


Figure S10. *^{1}H NMR spectrum of the product **4d***

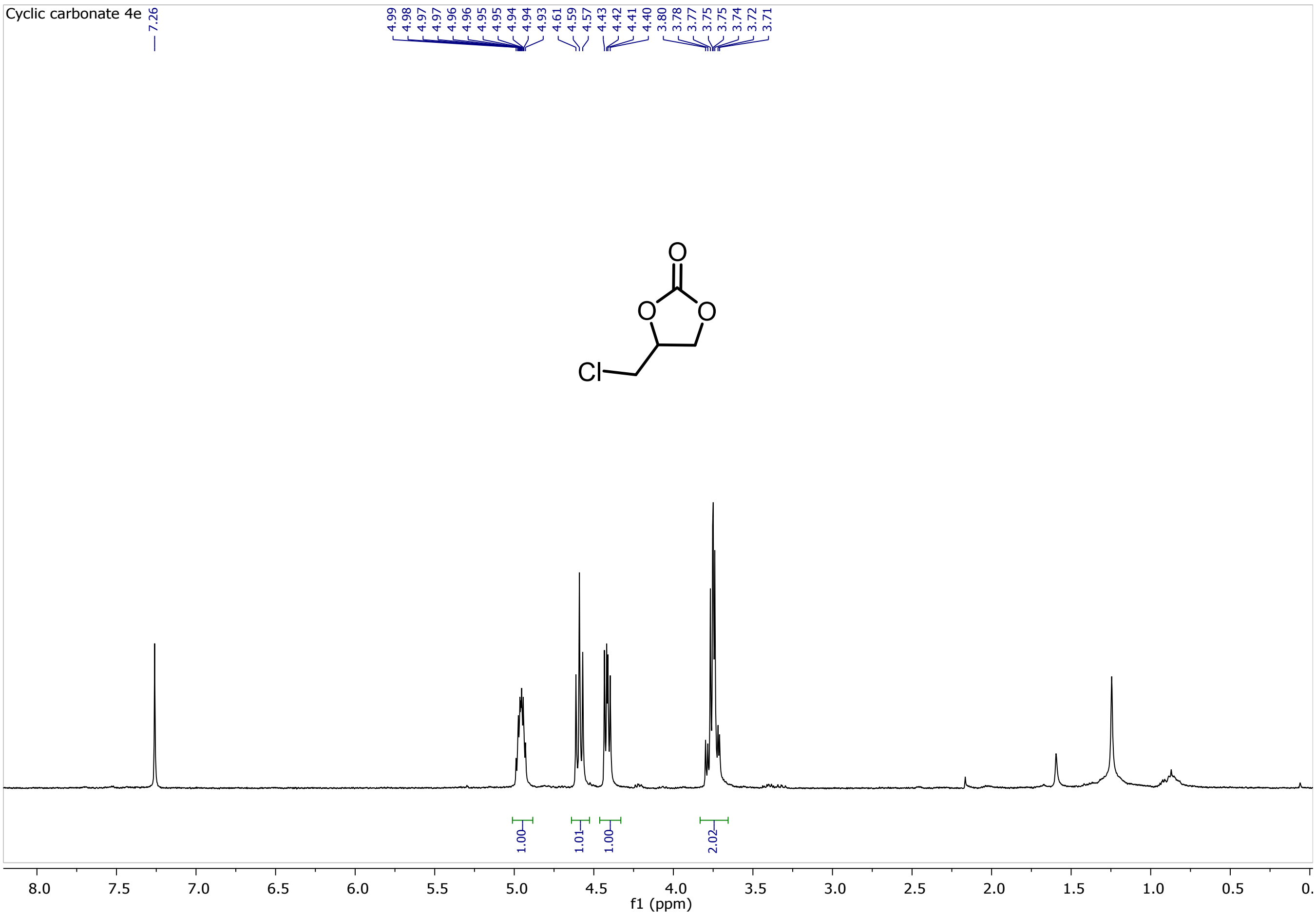


Figure S11. *^{1}H NMR spectrum of the product **4e***

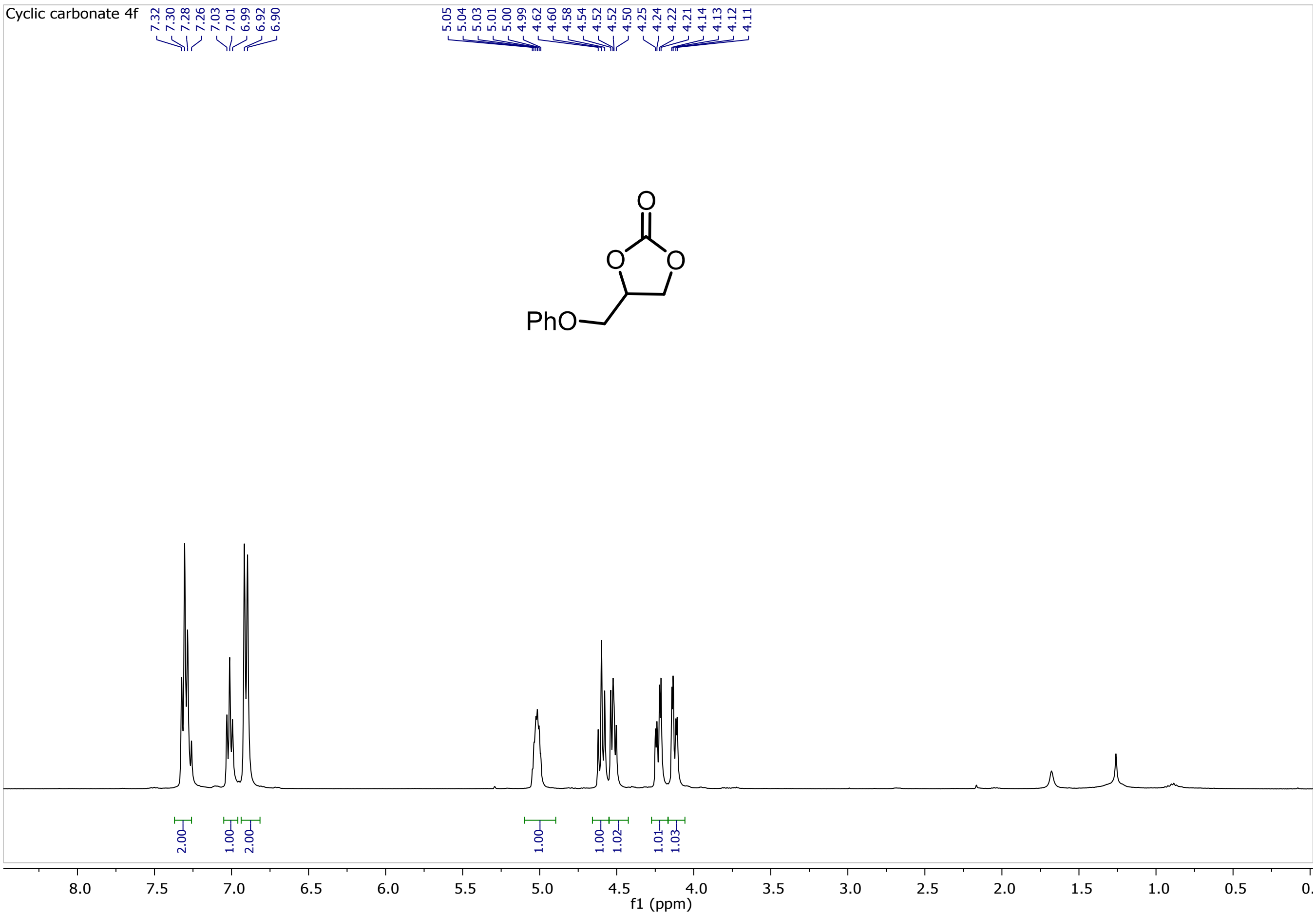


Figure S12. *^{1}H NMR spectrum of the product **4f***

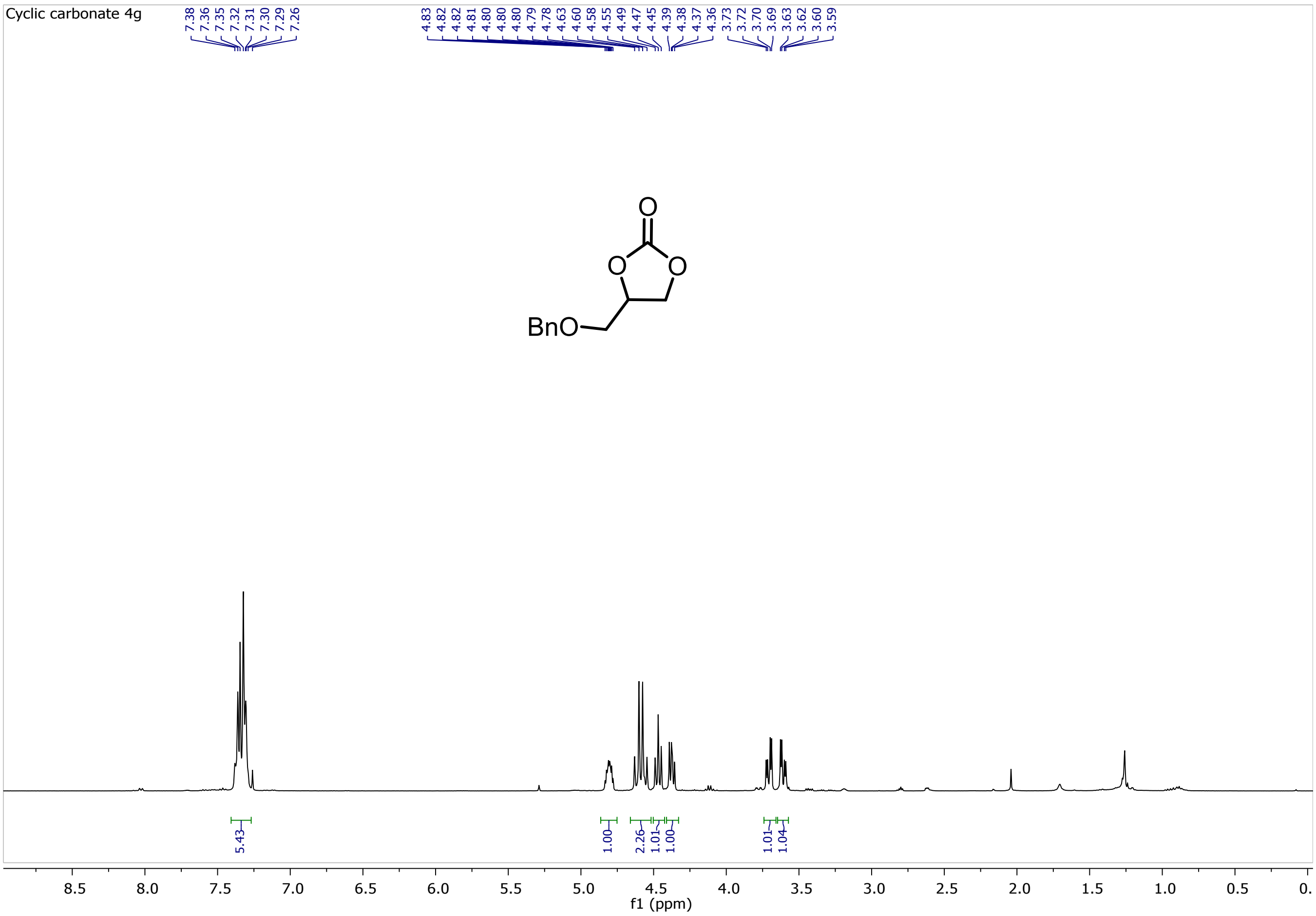


Figure S13. *^{1}H NMR spectrum of the product* ***4g***

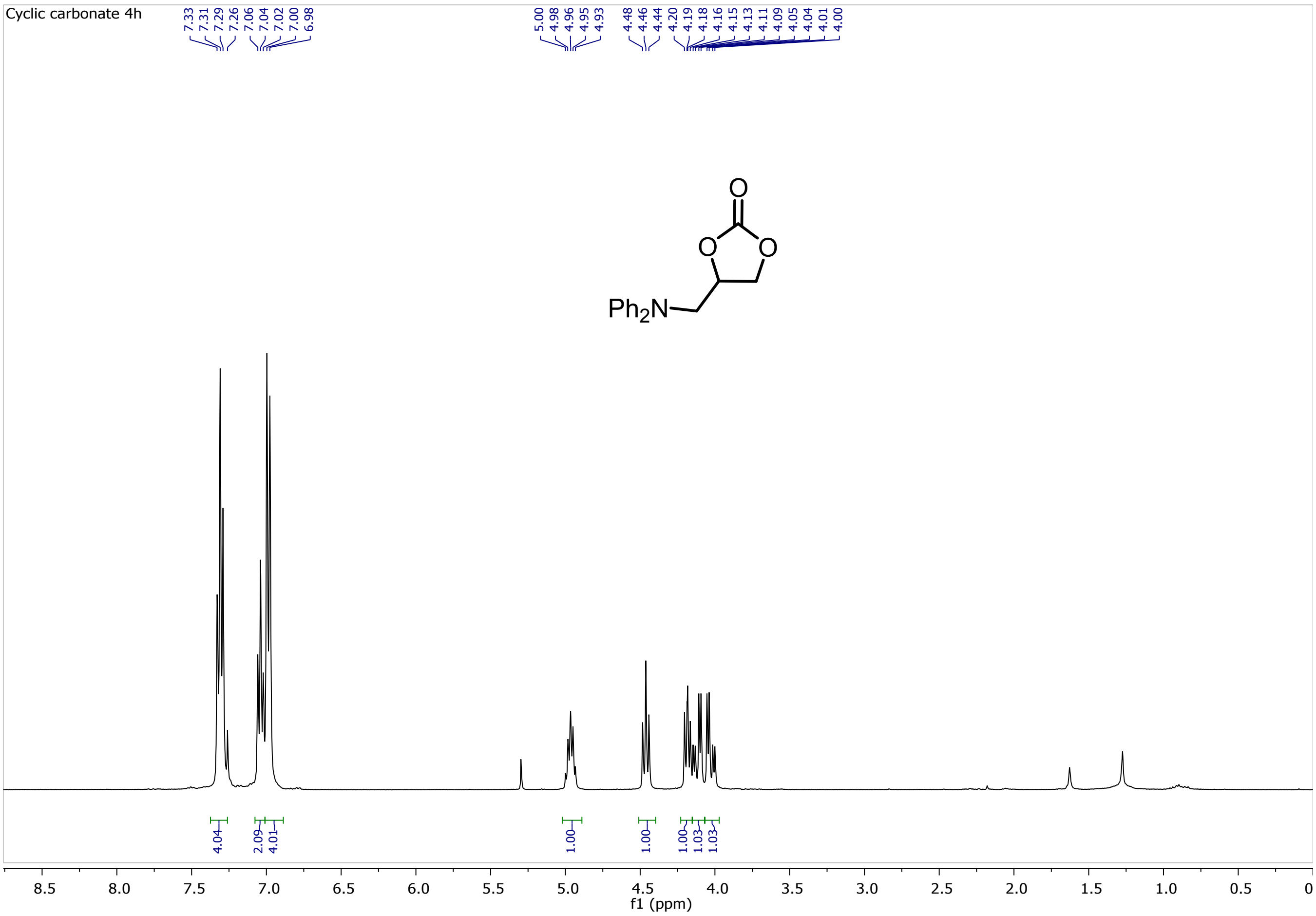
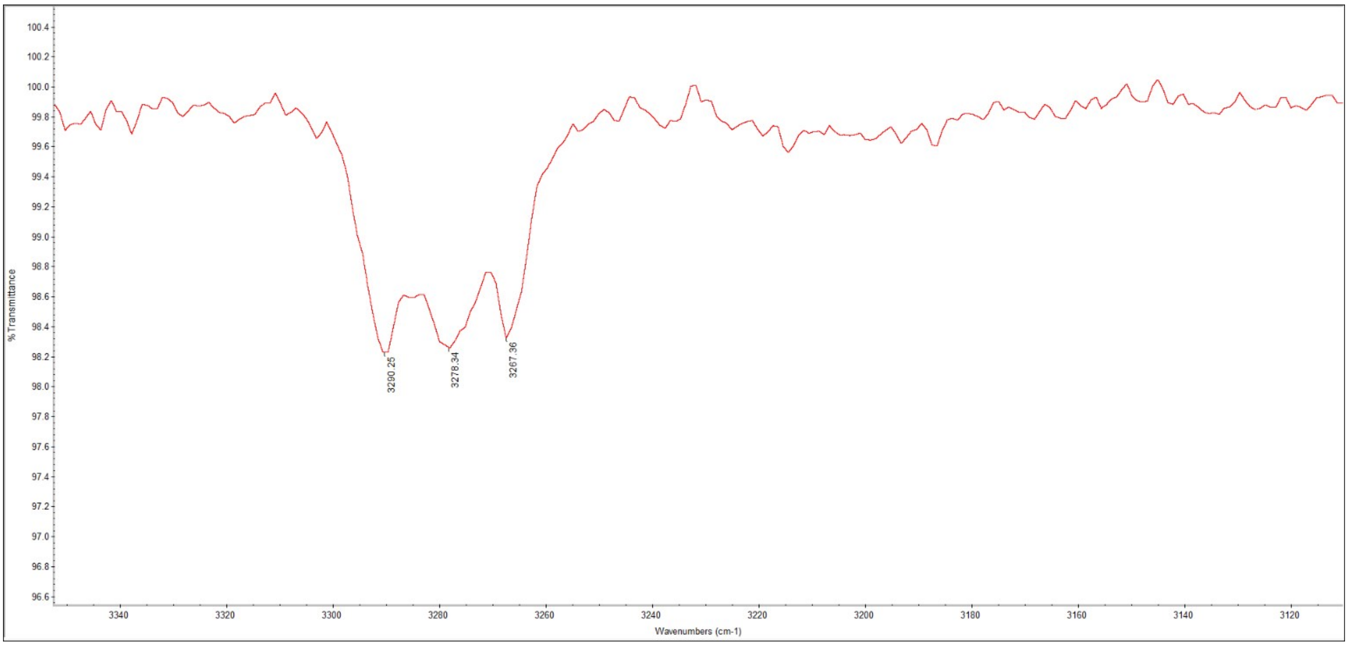


Figure S14. *^{1}H NMR spectrum of the product **4h***

IR spectra



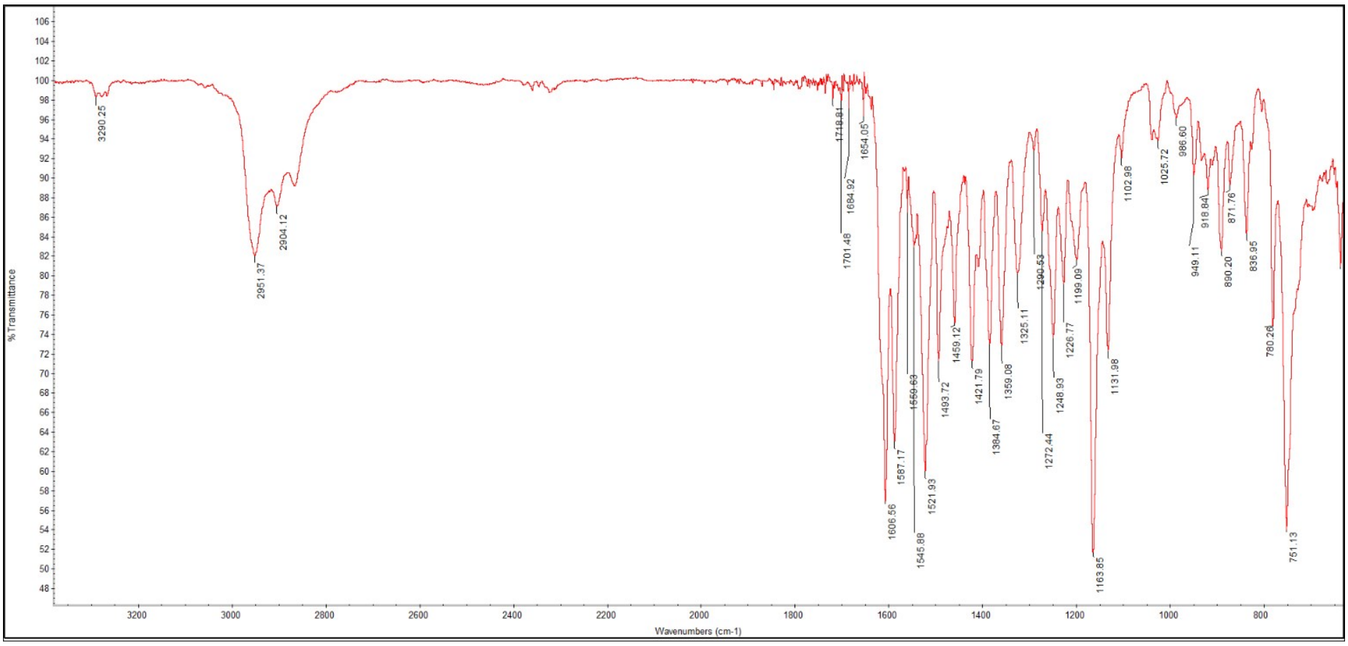


Figure S15. *IR spectra of the complex* ***2a***

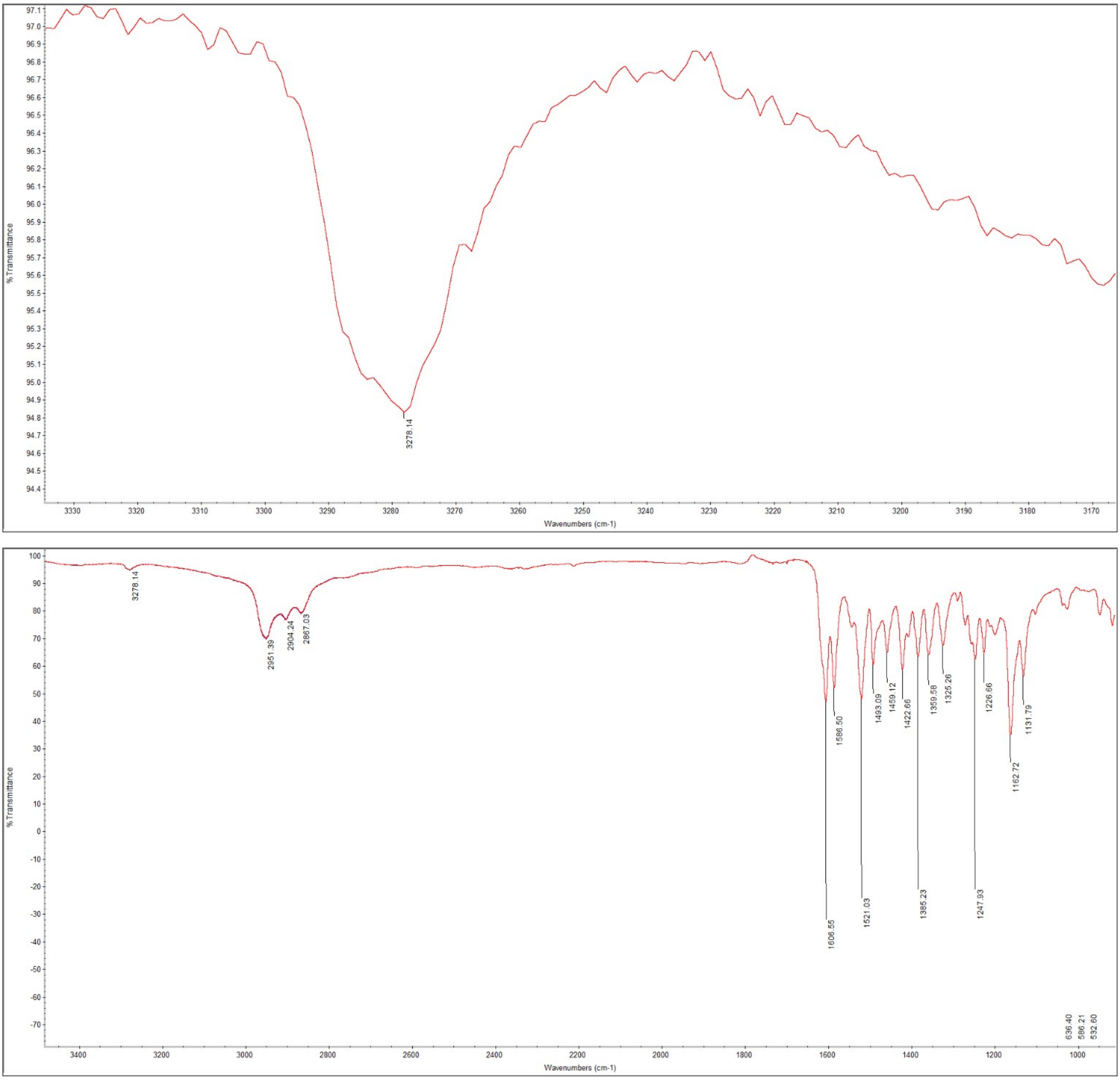


Figure S16. *IR spectra of the complex* ***2b***

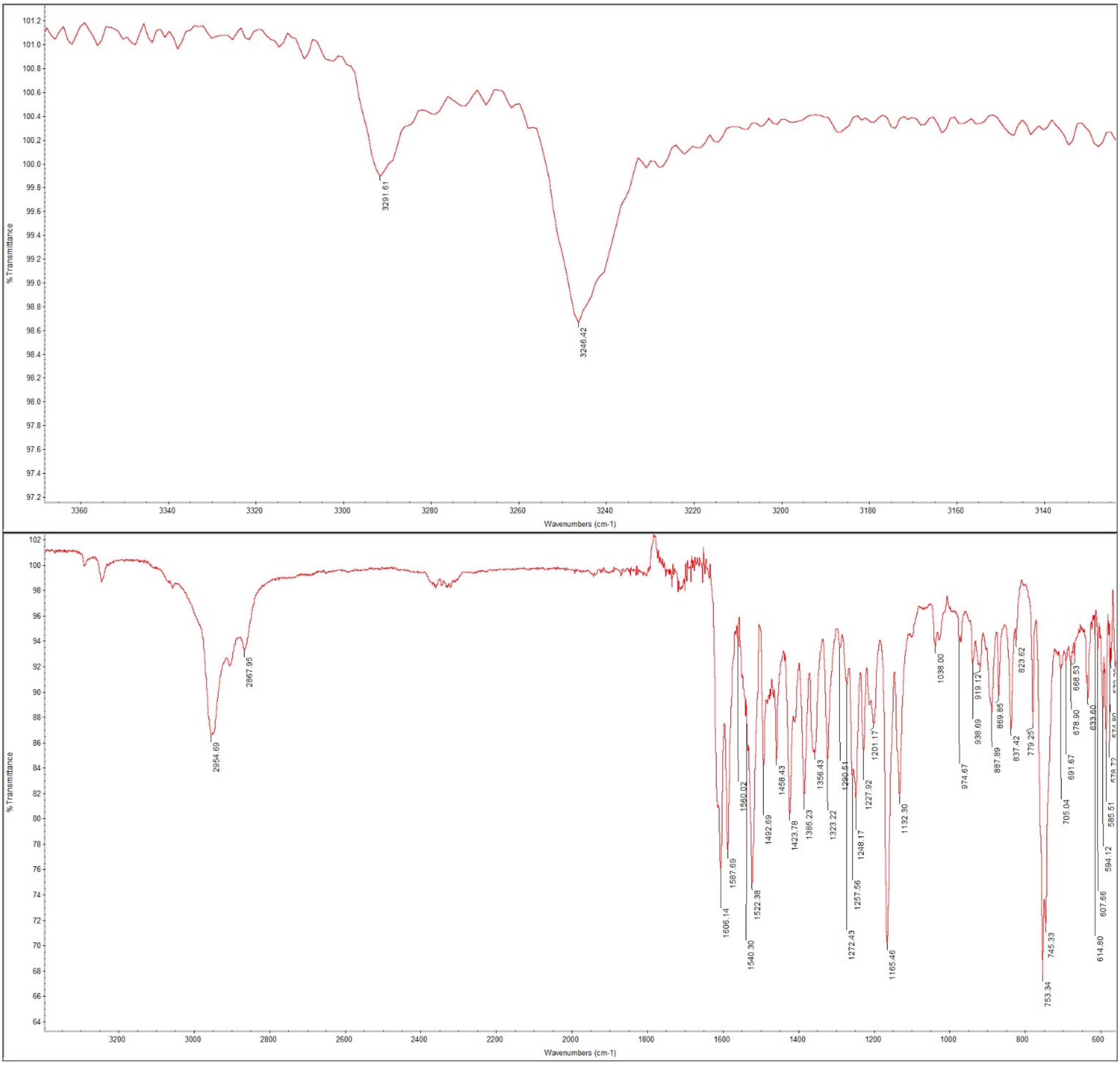


Figure S17. *IR spectra of the complex* ***2c***

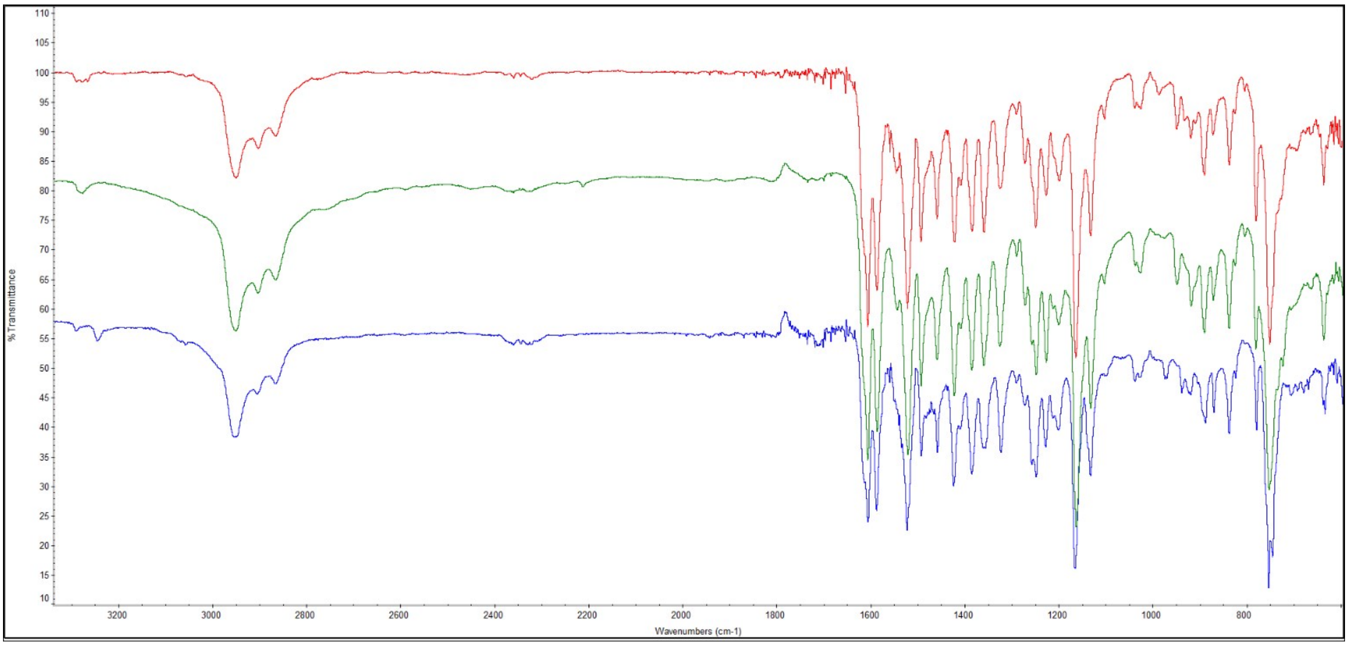


Figure S18. *Combined IR spectra of the Co(III) complexes: red (**2a**), green (**2b**), blue (**2c**)*