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(Cyclopentadienyl)neodymium borohydrides with auxiliary N_3-heterocyclic ligands

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1. Experimental section, general remarks.

All synthetic manipulations were carried out in prepurified argon atmosphere using anhydrous solvents in a glovebox. Tetrahydrofuran was pre-dried over NaOH and distilled from potassium/benzophenone ketyl. Hexane was distilled from Na/K alloy/benzophenone ketyl. Toluene was distilled from sodium/benzophenone ketyl. [$CpNd(BH_4)_2(THF)_2$] was obtained by published procedure[S1]. 1,4,7-Trimethyl-1,4,7-triazocyclononane was prepared according to the literature procedure[S2], dried over Na_2SO_4 and degassed in high vacuum. 1,3,5-Trimethyl-1,3,5-triazocyclohexane was purchased from Aldrich, dried over sodium and transferred in high vacuum into a Schlenk flask. ε-Caprolactone was distilled from CaH_2.

Elemental analyses were performed with a PerkinElmer 2400 Series II elemental CHNS/O analyzer. The analysis of the lanthanide content was carried out by complexometric titration with standard EDTA solution using Xylenol Orange as an indicator. Infrared spectra were recorded as Nujol mulls between KBr discs using a IFS-66v/s Bruker instrument. The ^{1}H and ^{11}B NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer (400 MHz, Bruker Corporation, Billerica, MA, USA) at 20°C. The chemical shifts are reported in ppm relative to the solvent residual peaks. Size exclusion chromatography (SEC) of polymer samples was performed using an Agilent PL-GPC 220 chromatograph equipped with a PLgel column (Agilent Technologies, Santa Clara, CA, USA), and THF was used as the eluent (1 mL/min). The measurements were recorded with universal calibration based on a polystyrene standard at 40 °C with a correction factor of 0.56.

2. X-ray structure determination

X-ray diffraction data were collected on a Bruker D8 Quest diffractometer equipped with a Photon-III area-detector (shutterless φ- and ω-scan technique), using graphite-monochromatized Mo K_{α}-radiation. The intensity data were integrated by the SAINT program[S3] and corrected for absorption and decay using SADABS.[S4] The structures were solved by direct methods using SHELXT[S5] and refined on F^2 using SHELXL-2018.[S6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Locations of H-atoms at boron atoms were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions (C-H distance = 0.98 Å for methyl, 0.99 Å for methylene, 1.00 Å for cyclopentadienyl hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters taken as $U_{iso}(H)=1.2U_{eq}(C)$. The SHELXTL program suite[S7] was used for molecular graphics. Crystal data, data collection and structure refinement details are summarized in Table S1.

Table S1. The crystallographic parameters and the structure refinement statistics for **1** and **2**

	1	**2**
Formula	$C_{11}H_{28}B_2N_3Nd$	$C_{14}H_{34}B_2N_3Nd$
M	368.22	410.30
T, K	100(2)	120(2)
Crystal system	Orthorhombic	Tetragonal
Space group	$Pna2_1$	$P4_3$
Z	4	4
a, Å	15.2755(2)	9.754(2)
b, Å	7.80440(10)	9.754(2)
c, Å	13.5623(2)	19.962(6)
α, °	90	90
β, °	90	90
γ, °	90	90
V, $Å^3$	1616.84(4)	1898.6(10)
d_{calc}, g cm^{-3}	1.513	1.435
μ, mm^{-1}	3.195	2.728
F(000)	740	836
$2\Theta_{max}$, °	66.31	57.96
Complentess to Θ_{max}	99.9%	99.9%
Reflections collected	65492	16492
Unique reflections	6141	5024
Reflections with $I > 2\sigma(I)$	5523	4454
Number of parameters	215	159
R1	0.0143	0.0554
wR2	0.0269	0.1328
GOF	1.105	1.022
Largest difference in peak / hole (e/$Å^3$)	0.392/-0.515	2.198/-1.160
CCDC number	2221517	2222289

3. Synthesis of complexes 1 and 2

*[CpNd(BH$_4$)$_2$(Me$_3$tach)] (**1**).* A solution of Me$_3$tach (0.155 g, 1.2 mmol, 20% excess) in THF (3 mL) was dropwise added to a stirred solution of [CpNd(BH$_4$)$_2$(THF)$_2$] (0.383 g, 1 mmol) in THF (15 mL). The mixture was stirred for 2 hours and centrifuged (4000 rpm, 5 min). The precipitate was washed with THF (5 mL) and centrifuged again. The combined solution was carefully layered with hexane and left undisturbed. Light-blue crystals ormed after several days. The mother liquor was decanted and the crystals were dried under dynamic vacuum for 2 hours. Yielded 0.229 g of **1** (0.622 mmol, 62%). Calcd for $C_{11}H_{28}B_2N_3Nd$: C, 35.85%; H, 7.67%; N, 11.41%; Nd, 39.18%. Found: C, 35.78%; H, 8.27%; N, 11.39%; Nd, 38.70%. ^{1}H NMR (THF-d_8, 298 K, ppm): δ = 2.03, 3.18, 5.12, 6.39, 63.60 (B*H*$_4$). ^{11}B NMR (THF-d_8, 298 K, ppm): δ = 136.95 (*B*H$_4$).

[CpNd(BH$_4$)$_2$(Me$_3$tacn)] (**2**). A solution of Me$_3$tacn (0.205 g, 1.2 mmol, 20% excess) in THF (5 mL) was dropwise added to a stirred solution of [CpNd(BH$_4$)$_2$(THF)$_2$] (0.383 g, 1 mmol) in THF (15 mL). The mixture was stirred for 2 hours and centrifuged (4000 rpm, 5 min). The precipitate was washed with THF (20 mL) and centrifuged again. The combined solution was carefully layered with hexane and left undisturbed. Light-blue crystals formed after several days. The mother liquor was decanted and the crystals were dried under dynamic vacuum for 2 hours. Yielded 0.295 g of **2** (0.719 mmol, 72%). Calcd for $C_{14}H_{34}B_2N_3Nd$: C, 40.95%; H, 8.35%; N, 10.24%; Nd, 35.16%. Found: C, 39.21%; H, 8.22%; N, 10.02%; Nd, 34.71%. The analysis of the complex **2** for the C, H, N content provided lower carbon values, likely resulting from the incomplete combustion and/or carbide formation, repeated experiments with independently obtained **2** resulted in the same values. Analysis of cyclopentadienylborohydride complexes for carbon content sometimes gives low carbon values, which was previously attributed to carbide formation.[S8] Meanwhile, satisfactory results on the content of Nd, N and H allow us to state with confidence the purity of the sample. ^{1}H NMR (THF-d_8, 298 K, ppm): δ = -9.20 (2H, N-C$_2$$H_4$-N), -8.40 (6H, N-C$H_3$), -2.70 (N-C$H_3$ of [Nd(BH$_4$)$_3$(Me$_3$tacn)]), -0.50 (5H, Cp), 2.30 (N-CH_3 of free Me$_3$tacn), 2.46 (N-C$_2$$H_4$-N of free Me$_3$tacn), 4.82 (3H, N-C$H_3$), 5.31 (N-C$_2$$H_4$-N of [Nd(BH$_4$)$_3$(Me$_3$tacn)]), 5.81 (2H, N-C$_2$$H_4$-N), 9.55 (2H, N-C$_2$$H_4$-N), 12.49 (N-C$_2$$H_4$-N of [Nd(BH$_4$)$_3$(Me$_3$tacn)]), 14.19 (2H, N-C$_2$$H_4$-N), 17.43 (2H, N-C$_2$$H_4$-N), 20.17 (2H, N-C$_2$$H_4$-N), 47.96 (8H, B$H_4$), 86.85 (B$H_4$ of [Nd(BH$_4$)$_3$(Me$_3$tacn)]), 97.87 (BH_4 of [CpNd(BH$_4$)$_2$(THF)$_2$])[S1]. ^{11}B NMR (THF-d_8, 298 K, ppm): δ = 96.19 (BH$_4$), 153.35 (BH$_4$ of [CpNd(BH$_4$)$_2$] or [Nd(BH$_4$)$_3$(Me$_3$tacn)]).

4. Representative polymerization procedure (entry 1)

In the glovebox ε-caprolactone (2 g, 17.5 mmol) was placed into a flame-dried vial and dissolved in THF (13.5 mL). A solution of complex **1** (4 mL of 17.5 mM inTHF) was added to the ε-caprolactone solution with stirring to initiate polymerization. After the mixture solidified, or after 2 hours, CH$_2$Cl$_2$ (20 mL) and acetic acid (0.1 mL) were added, the organic phase was poured into MeOH (300 mL). The product was separated by filtration or centrifugation, washed with MeOH (100 mL) and dried at 50°C in the oven for 24 h

5. NMR spectra of complexes 1 and 2

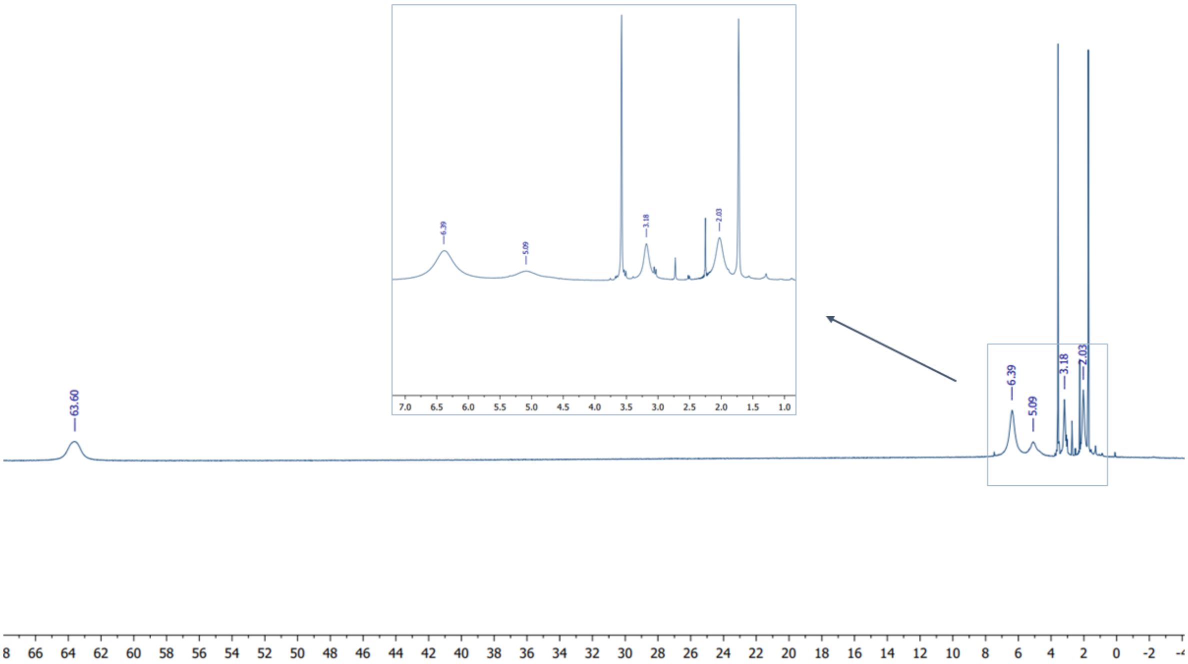

Figure S1. ^{1}H NMR spectrum of complex **1**.

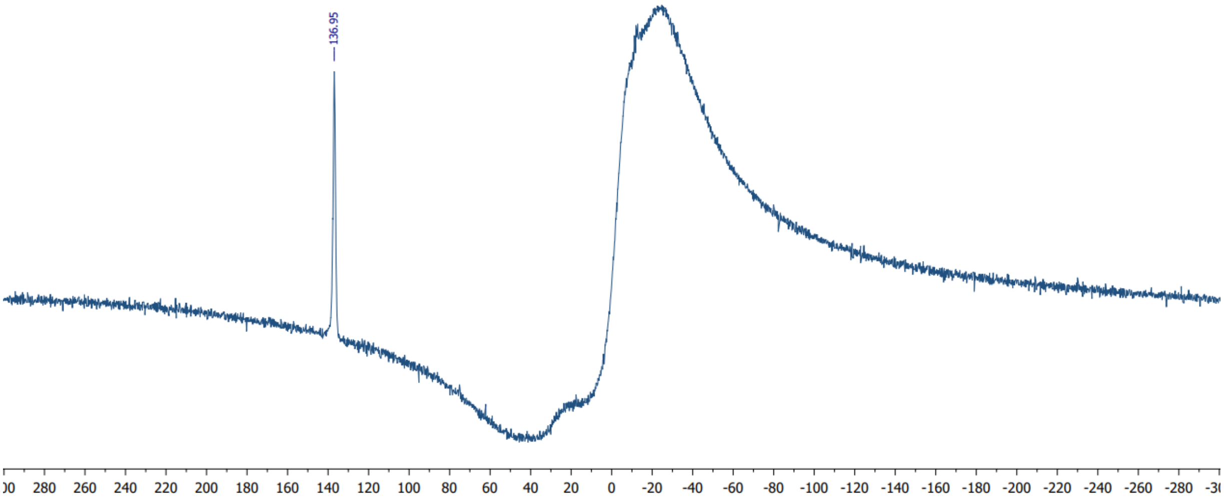

Figure S2. ^{11}B NMR spectrum of complex **1**.

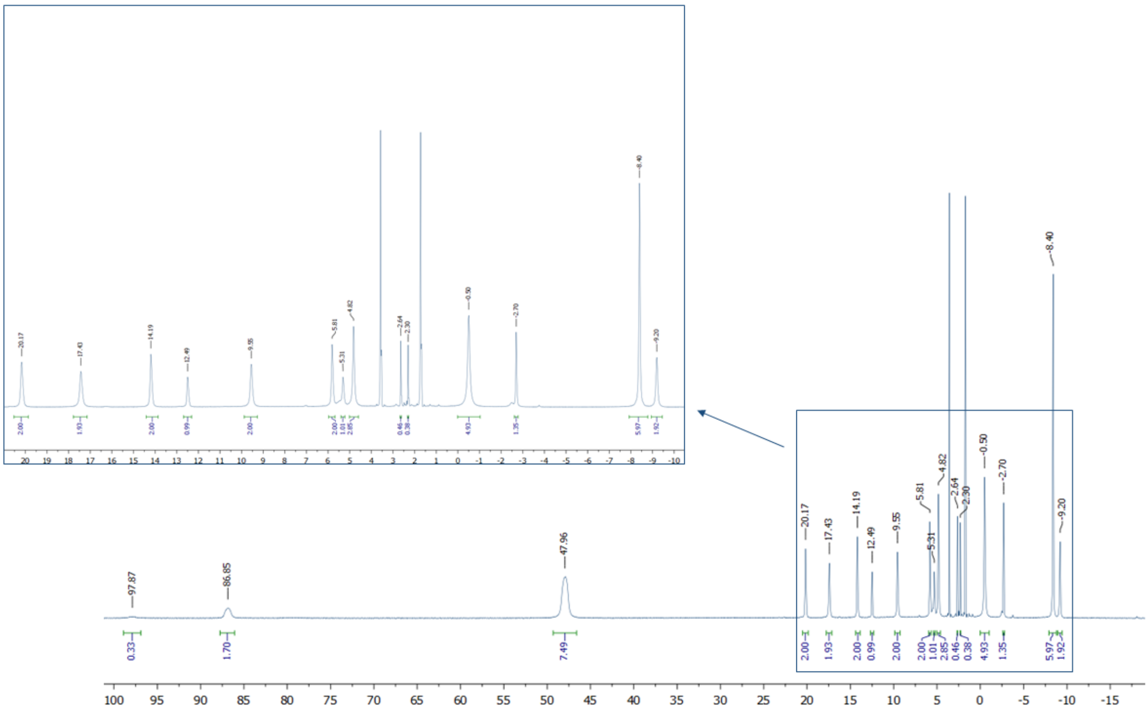

Figure S3. ^{1}H NMR spectrum of complex **2**.

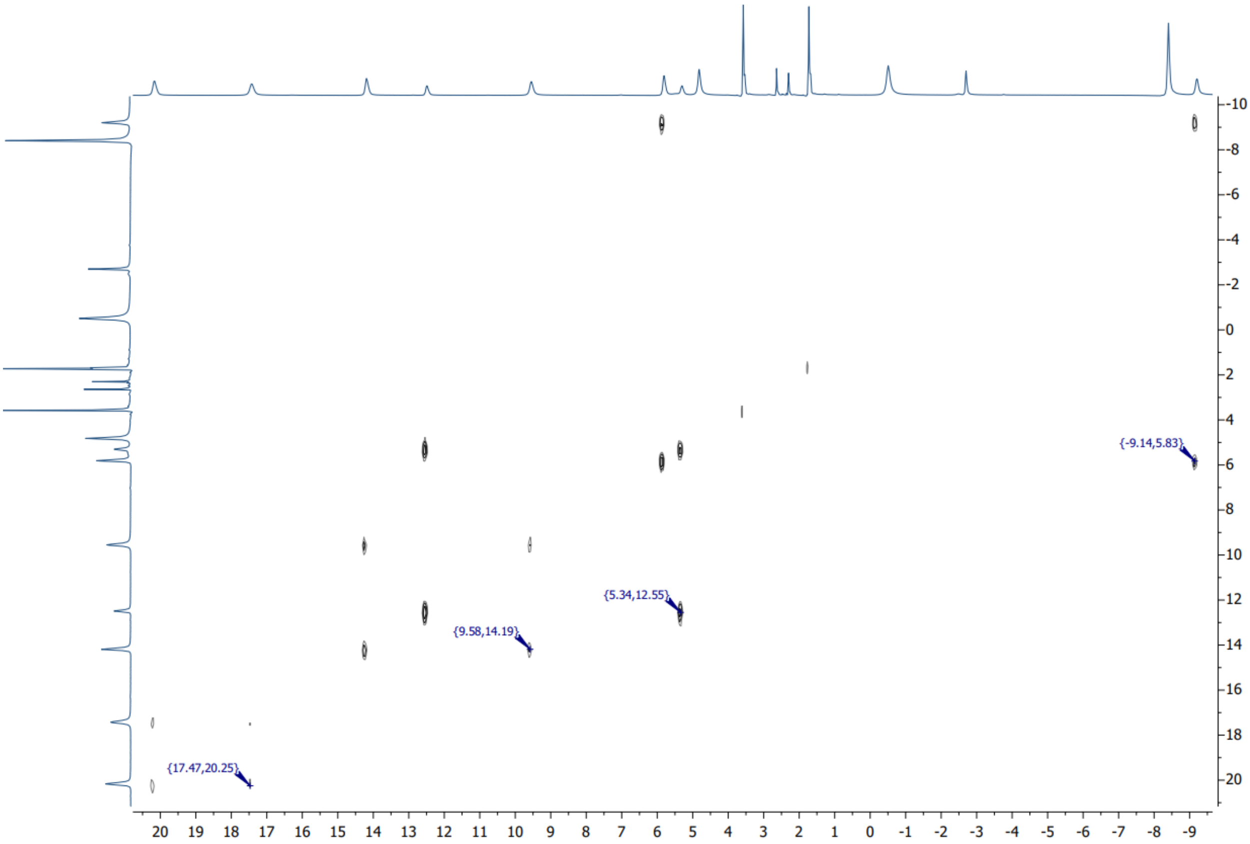

Figure S4. ^{1}H-^{1}H COSY NMR spectrum of complex **2**.

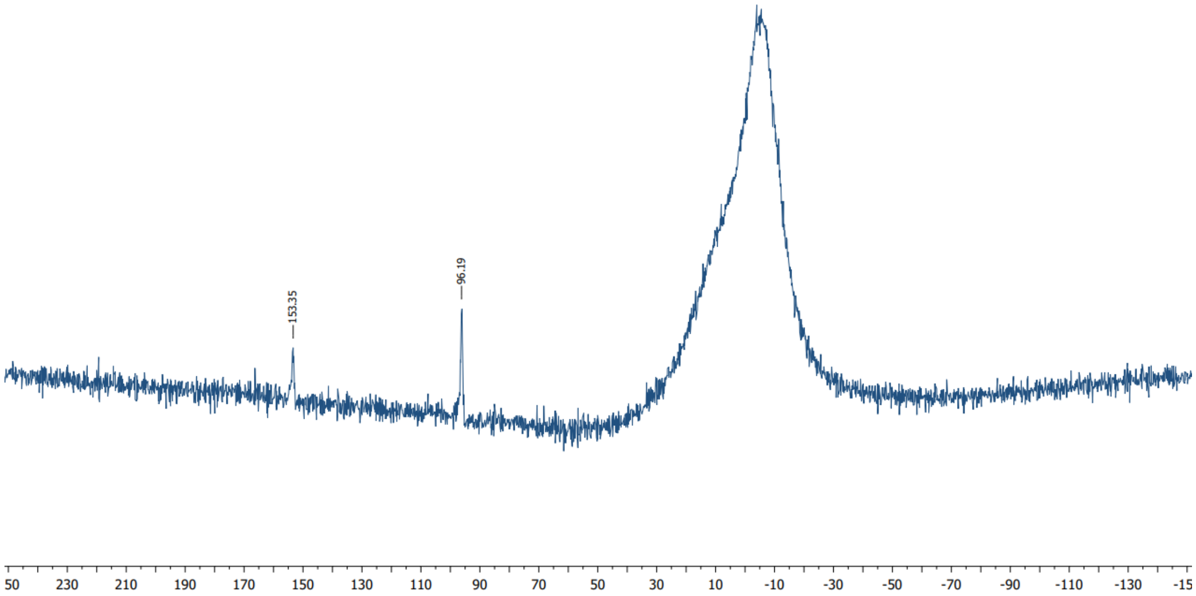

Figure S5. ^{11}B NMR spectrum of complex **2**.

6. IR spectra of complexes 1 and 2

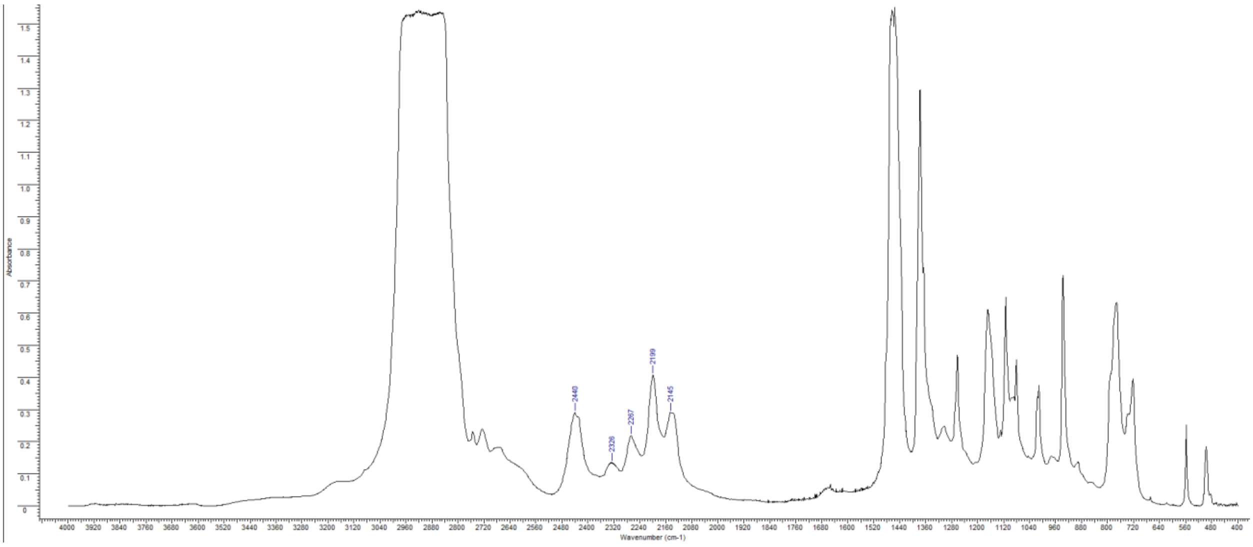

Figure S6. IR spectrum of complex **1**.

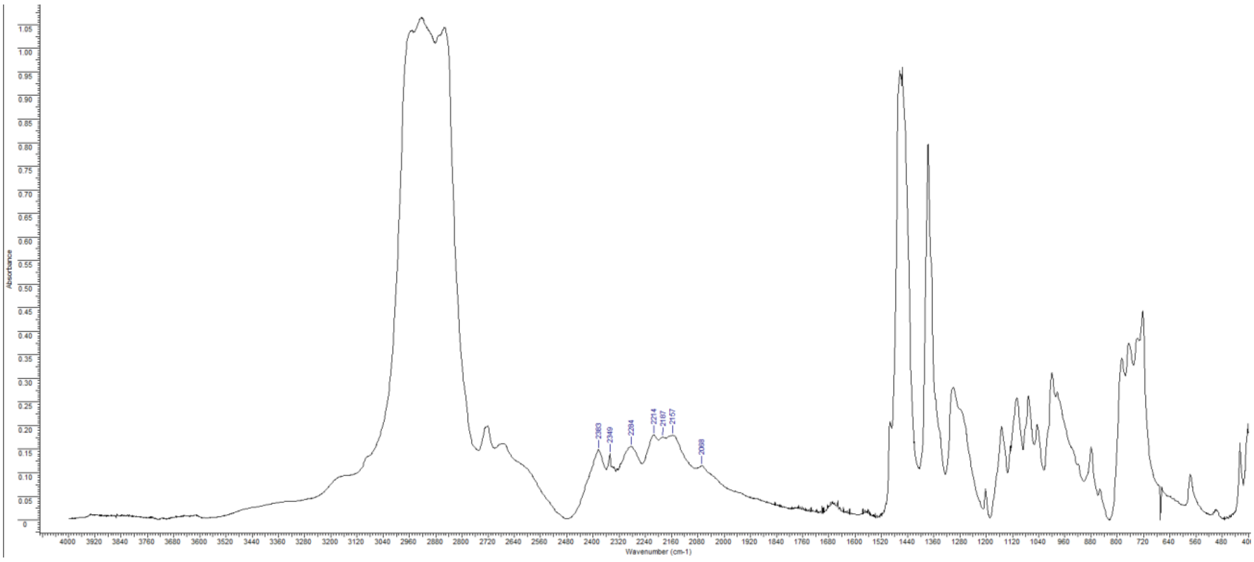

Figure S7. IR spectrum of complex **2**.

References

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