

## Supporting information

# Modification of cobalt bis(dicarbollide) ion with nitrile groups on carbon atoms: a unique low-temperature skeletal rearrangement due to specific electron-donor character of the CN substitution.

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## EXPERIMENTAL METHODS

### 1. Experimental

**General:** Caesium salt of cobalt bis(dicarbollide) was purchased from Katchem, Ltd. Prague, toluenesulfonyl cyanide from Merck and the compound was stored in refrigerator at -33 °C and shortly dried in vacuum before the use. Ethylene glycol dimethyl ether (DME) was distilled from sodium diphenyl ketyl freshly before use. HPLC grade methanol, acetonitrile and acetone, Merck, were used through the study. Other chemicals and solvents were from Aldrich, Merck, Lachner a.s. and Penta Ltd., Czech Republic, respectively, and were used without purification.

## 2. Instrumental Techniques

### Single Crystal X-Ray Diffraction

Data of compounds **3a**<sup>-</sup> and **3c**<sup>-</sup> were collected on the Rigaku Synergy S XtaLAB diffractometer equipped with micro-focus with Cu radiation (Cu/K $\alpha$   $\lambda$  = 1.54184 Å) and a Hybrid Pixel Array Detector (HyPix-6000HE). An Oxford Cryosystems (Cryostream 800) cooling device was used for data collection and the crystals were kept at 100.00(10) K during data collection. CrysAlisPro software<sup>1</sup> was used for data collection, cell refinement, data reduction and absorption correction. Data were corrected for absorption effects using empirical absorption correction (spherical harmonics), implemented in SCALE3 ABSPACK scaling algorithm and numerical absorption correction based on the Gaussian integration over a multifaceted crystal model.<sup>2</sup> The structures of compounds **3a**<sup>-</sup> and **3c**<sup>-</sup> were solved with the ShelXT<sup>3</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>4</sup> refinement package using Least Squares minimization implemented in Olex2.<sup>5</sup> Anisotropic displacement parameters were refined for all non-H atoms. The hydrogen atoms were calculated to idealized positions or found in the residual electron density map. For crystallographic data and structure refinement see the Tables S1 to S2. Molecular graphics for the structures of **3a**<sup>-</sup> and **3c**<sup>-</sup> was generated using DIAMOND software (Version 4.6.8).<sup>6</sup> Crystallographic parameters for each compound are given in Tables S1 and S2 and more details about the structures are displayed in Figures SF1 to SF18.

The crystallographic data were deposited at the Cambridge Crystallographic Data Centre, 12 with CCDC Nos. 2370282 and 2370281 for compounds Me<sub>4</sub>N**3a** and Me<sub>4</sub>N**3c**, respectively. Supplementary crystallographic data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

### NMR Spectroscopy

Compounds **2**, **3a** and **3c** were dissolved in Acetonitrile-*d*<sub>3</sub> prior to the NMR measurements, after drying sufficiently on a Schlenk line. <sup>1</sup>H, <sup>11</sup>B{<sup>1</sup>H}, <sup>11</sup>B, <sup>1</sup>H{<sup>11</sup>B} and <sup>13</sup>C NMR Spectra of the compounds were recorded on a JEOL600 NMR spectrometer. <sup>11</sup>B NMR (193 MHz) chemical shifts are given in ppm to high-frequency (low field) to F<sub>3</sub>B.OEt<sub>2</sub> as the external reference. Residual solvent <sup>1</sup>H resonances were used as internal secondary standards. <sup>1</sup>H NMR (600 MHz) and <sup>13</sup>C NMR (151 MHz): chemical shifts  $\delta$  in ppm relative to Me<sub>4</sub>Si (0 ppm) as the external standard, coupling constants  $J(H, H)$  in Hz. The chemical shifts corresponding to B–H resonances were obtained from <sup>1</sup>H{<sup>11</sup>Bselective}MR spectra. In <sup>1</sup>H{<sup>11</sup>B} spectra the  $\delta_{B-H}$  values and peak assignments were analyzed from <sup>1</sup>H{<sup>11</sup>Bselective} experiments.

### HRMS

High-Resolution Mass spectrometry (HRMS) spectra were recorded by an Orbitrap Exploris<sup>TM</sup> 120 spectrometer equipped with heated electrospray ionization (HESI) in negative mode using nitrogen (5.0 Messer) as a collision gas. For HESI-MS, solutions of concentration approximately 100 ng·mL<sup>-1</sup> in acetonitrile were introduced by infusion into the ion source from a syringe. Molecular ions [M]<sup>-</sup> were detected for all univalent anions as base peaks in the spectra. By comparison, the experimental isotopic distribution in the boron plot of the peaks in the measured spectra corresponded fully to the calculated spectral pattern. The data are presented for the most abundant mass in the boron distribution plot (100%) and the signal corresponding to the *m/z* value. Conditions used for the HESI interface: vaporizer temperature 50 °C; N<sub>2</sub> (isolated from air in Genius XE35, Peak Scientific) as a nebulizing sheath gas and auxiliary gas, flow 3.22 L·min<sup>-1</sup> and 6.12 L·min<sup>-1</sup>, respectively; ion spray voltage 3500 V; capillary temperature 280 °C and mass range from 100 to 1200.

## HPLC

A Merck-Hitachi LaChrom Series 7000 HPLC system equipped with a Diode Array D 7450 detector and a L7250 autoinjector and software was used for monitoring composition of the reaction mixture and the purity control of the isolated reaction intermediates and the final products. Analytical separations were carried out using a previously reported Ion-Pair RP method with recent updates.<sup>7, 8</sup> Polymeric Separon RPS column, 5  $\mu\text{m}$  (300 x 3 mm I. D.), Tessek Prague in RP mode and hexylamine acetate 4.5 mmol in 65 % aqueous  $\text{CH}_3\text{CN}$  (pH 5.9) as mobile phase were utilized for the analyses. The solutes were detected using DAD detection at fixed wavelengths of 235, 280, 285 and 312 nm. All separations were performed in isocratic mode, retention data are given as capacity factors ( $k$ ), the  $k$  for the parent ion under the used chromatographic conditions was 1.40.

## Synthesis

The compounds  $\text{Cs}[1\text{-CN-(1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})\text{-3,3'}\text{-Co(III)}]$  (**Cs2**),  $\text{Me}_4\text{N}[1,1'\text{-(CN)}_2\text{-(1,2-C}_2\text{B}_9\text{H}_{10})_2\text{-3,3'}\text{-Co(III)}]$  (**Me<sub>4</sub>N3a**) and  $[\text{Me}_4\text{N}][1,8\text{-(CN)}_2\text{-(1,8-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})\text{-2,3'}\text{-Co(III)}]$  (**Me<sub>4</sub>N3c**) were prepared by low-temperature reaction of the lithiated **Cs1** with TsCN. For the influence of the ratio of reagents and reaction conditions on the relative ratio of the products see Tab. S1. It can be seen that the reaction produces an equilibrium mixture of the starting ion, monosubstituted, disubstituted and some trisubstituted species. The disubstituted products **3<sup>-</sup>** prevail in the reaction mixture even at lower ration of BuLi/TsCN. The starting ion **1<sup>-</sup>** is almost spent for the ratio 1: 3, however at the expense of formation of larger ratio of the trisubstituted products. Tetra methyl ethylene diamine (TMEDA) was used with the aim to increase formation of the monosubstituted nitrile **2<sup>-</sup>**, however the effect was insignificant.

**Table S1.** The influence of the ratios of the reaction components and reaction conditions on the relative percentage of the starting ion **1<sup>-</sup>**, mono-CN derivative **2<sup>-</sup>**, disubstituted **3<sup>-</sup>** and trisubstituted species **4<sup>-</sup>** calculated in [%] from the relative abundance of the molecular peaks in MS.

No.	Ratio of 1 <sup>-</sup> to BuLi/TsCN	Additive	Molecular ion [M <sup>-</sup> ]			
			[%] calculated from the relative abundance			
			<b>1<sup>-</sup></b>	<b>2<sup>-</sup></b>	<b>3<sup>-</sup></b>	<b>4<sup>-</sup></b>
1	1:1.50 <sup>a</sup>	TMEDA	28	26	44	2
2	1: 1.75 <sup>b</sup>	NA	29	13	37	21
3	1: 1.75 <sup>a</sup>	NA	14	29	52	4
4	1: 3.0 <sup>a</sup>	NA	3	10	74	13

<sup>a</sup>The reaction mixture was stirred at -82 °C for 30 min and then heated to -33 °C, stirred at this temperature for 5h, then left to warm up to rt and stirred for additional 16h. <sup>b</sup>The reaction mixture was stirred at -82 °C for 45 min and then left to warm up to rt. spontaneously and stirred for additional 16h.

### **Cs[1-CN-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-3,3'-Co(III)] (Cs2):**

In an experiment corresponding to entry No. 1 in Table S1, the caesium salt of cobalt bis(dicarbollide) (**Cs1**, 1.0 g, 2.19 mmol) was dried in vacuum 3h at 130 °C and then 8 h at 195 °C in a Schlenk-type flask and then cooled down to room temperature. The salt was dissolved under argon atmosphere in 40 ml of freshly distilled 1,2-dimethoxyethane (DME) added through a rubber septum and the solution was cooled down to -82 °C under stirring in a cooling bath containing a mixture of CO<sub>2</sub>(s) and acetone; then TMEDA (0.4 ml) was injected and n-BuLi (2.5 M in hexane, 1.40 ml, 3.5 mmol) was added dropwise from syringe over 10 min. and the stirring in the cooling bath was continued over 30 min. The bath was then removed and the reaction mixture was left to warm up to the room temperature over 30 min. The dark red reaction mixture was cooled down again to -82 °C and then toluene sulfonyl cyanide (0.60 g 3.32 mmol., dried in vacuum for 30 min and then dissolved in DME 10 ml) was added dropwise from a

syringe. The content of the flask was stirred for 60 min. at -82 °C, then the cooling bath was replaced with another one containing CO<sub>2</sub>(s) and the stirring was continued for 3 h, the bath was then removed and the reaction mixture was left to warm up spontaneously to room temperature over 16 h. The reaction was quenched with the careful addition of H<sub>2</sub>O from a syringe (40 mL), and the organic solvent was then distilled off using a rotary evaporator. The dark coloration persisted even after quenching. The bath temperature was kept below 30 °C during the evaporation. Immediately after the evaporation, the mixture of the products was extracted into diethyl ether (4 x 25 ml), CH<sub>3</sub>CN (2 mL) was added to the combined ether fractions and the ether was removed in vacuum without heating of the flask. The dark coloured aqueous phase was discarded. Excess of aqueous solution of CsCl was quickly added and the solvent was partly evaporated. The solidified material was left to settle down for 10 min, and then the solid was rapidly filtered and dried in vacuum. The separation of compounds **2**<sup>-</sup> from other products was performed in two portions using flash chromatography on Büchi 80 g C18 reverse phase column starting with 45% aqueous acetone and increasing gradually the content of the organic component up to 60%; flow rate 10 mL/min. The composition of the effluent was periodically analysed using HPLC and MS. The fractions containing the ion **2**<sup>-</sup> were combined and acetone was immediately evaporated, Then the product was precipitated with an excess of aqueous CsCl, washed with water (3x 10 mL), rapidly filtered and dried in vacuum. The compounds were stored in vials closed under Ar atmosphere in a refrigerator at -33 °C. Under these conditions the compound remains unchanged over several months period. This is also sufficiently stable at room temperature (days) as solid or in solvent used for NMR measurement. The compound was crystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane. Cs**2**: yellow solid, 190 mg, yield 18%; <sup>1</sup>H NMR (600 MHz, Acetonitrile-D<sub>3</sub>) δ 4.20 (C<sub>cage</sub>-H), 3.88 (C<sub>cage</sub>-H), 3.75 (C<sub>cage</sub>-H). <sup>1</sup>H{<sup>11</sup>B}- (from selective 2D-NMR): δ 3.59 (1H, br, overlap, B(8)-H), 3.51 (1H, br, overlap, B(8')-H), 3.07 (1H, overlap, B(10)-H), 2.95 (1H, br s, B(10')-H), 2.67 (1H, br s, B(9')-H), 1.98 (1H, overlap, B(12)-H), 1.91 (1H, s, overlap, B(12')-H), 1.72 (1H, overlap, B(6')-H), 1.66 (3H, br s, B(5,11,5')-H). <sup>11</sup>B (193 MHz, Acetonitrile-D<sub>3</sub>) δ 7.10 (1B, d, *J* = 104.2 Hz, B8), 6.57 (1B, d, *J* = 100.36 Hz, B8'), 2.80 (1B, d, *J* = 146.7 Hz, B10), -0.17 (1B, d, *J* = 150.5 Hz, B10'), -4.63 (2B, d, *J* = 137.0 Hz, B4,7), -5.39 (2B, d, *J* = 139.0 Hz, B4',7'), -5.75 (1B, d, *J* = 142.8 Hz, B9), -6.19 (1B, overlap, B12), -6.49 (1B, d, *J* = 173.7 Hz, B9'), -7.38 (1B, d, *J* = 146.7 Hz, B12'), -17.20 (3B, d, *J* = 139.0 Hz, B5,11,5'), -18.51 (1B, d, *J* = 171.8 Hz, B11'), -21.12 (1B, d, *J* = 171.8 Hz, B6). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Acetonitrile-D<sub>3</sub>) δ 117.87 (1C, CN), 56.44 (1C, C<sub>cage</sub>-H), 54.73 (1C, C<sub>cage</sub>-H), 53.19 (1C, C<sub>cage</sub>-H), 42.82 (1C, C<sub>cage</sub>); HPLC *k*' = 2.23; HRMS (ESI) *m/z* = 352.2681 (*M*<sup>-</sup>, 11%), 352.2791 (100%); Calcd. for **2**<sup>-</sup> 352.2696 (10%) and 349.2797 (100%).

**[Me<sub>4</sub>N][1,1'-(CN)<sub>2</sub>-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>-3,3'-Co(III)] (Me<sub>4</sub>N3a) and [Me<sub>4</sub>N][1,8-(CN)<sub>2</sub>-(1,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-2,3'-Co(III)] (Me<sub>4</sub>N3c)**

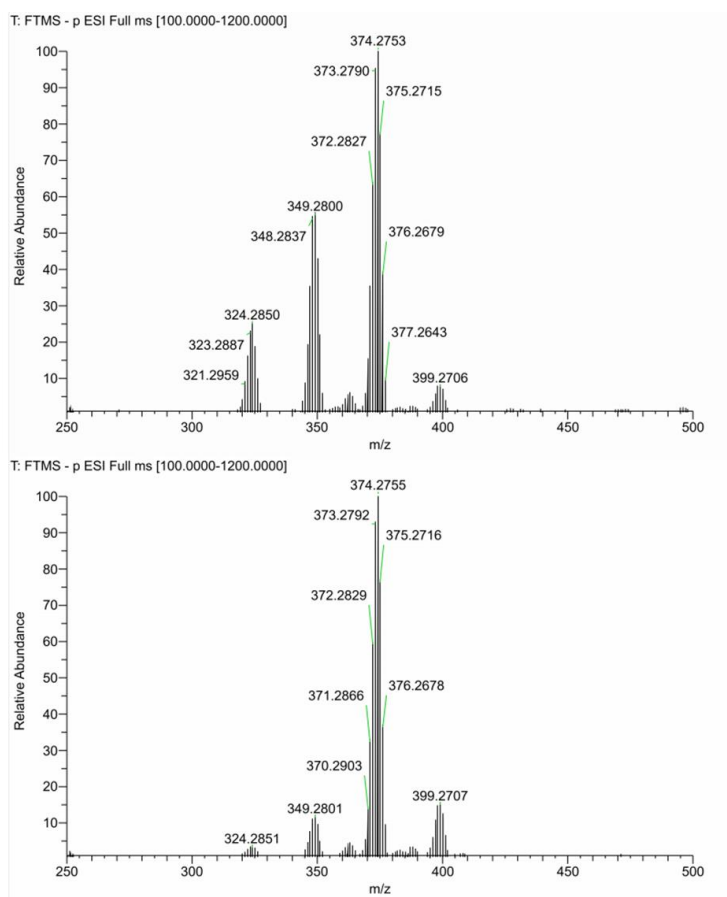
The synthesis of these compounds was performed in analogy with that described for Me<sub>4</sub>N**2**, however using different ratios of the reagents and no TMEDA additive. Two different rates for warming up the reaction mixture were used. Higher ratios of Cs**1** to BuLi and TsCN were used starting from 1: 1.75 to 1: 3.0 for increasing conversion of the starting compound and the isomeric disubstituted compounds. The reaction conditions and relative abundance of compounds **1**<sup>-</sup>, **2**<sup>-</sup>, **3**<sup>-</sup> and trisubstituted species **4**<sup>-</sup> observed by HRMS after reactions is summarized in Table S1. Figure S1 compares HRMS of the reaction mixtures obtained from experiments No. 3 and 4 presented in this Table.

In all cases, the caesium salt of cobalt bis(dicarbollide) (Cs**1**, 1.0 g, 2.19 mmol) was dried and then dissolved in 40 ml of freshly distilled 1,2-dimethoxyethane (DME) at -82 °C with *n*-BuLi (2.5 M in hexane, 1.65ml, 4.125 mmol in experiments No. 2 and 3, or 2.9 ml, 7.25 mmol in exp. No. 4), the reaction mixture was warmed up and cooled -82 °C. Depending on the particular experiment, different quantities of toluene sulfonyl cyanide (95%, 0.75g, 3.83 mmol in exp. 2 and 3, or 0.75g, 3.83 mmol in exp. 2 and 3, or 1.25g, 6.57 mmol in exp. 4, Table S1) were added. The TsCN was dried in vacuum for 30 min and then dissolved in DME 10 ml prior the addition. The content of the flask was stirred for 30 min. at -82 °C, and then either the cooling bath was removed (experiment 2) or replaced with another

one containing only CO<sub>2</sub>(s) and stirred in this bath for 5h and only then the reaction mixture was left to warm up spontaneously to room temperature over 16h. The reaction was quenched and the products were extracted into Et<sub>2</sub>O following the procedure described for the compound **2**<sup>-</sup>, CH<sub>3</sub>CN (10 mL) was added to the combined ether fractions and the ether was removed in vacuum without heating of the flask. An excess of aqueous solution of Me<sub>4</sub>NCl was quickly added to precipitate the crude mixture of products. The precipitate was left to settle down for 10 min, and then the solid was rapidly filtered and dried in vacuum. The separation of compounds **3a**<sup>-</sup> and **3c**<sup>-</sup> was performed using flash chromatography on Büchi 120 g C18 reverse phase column starting with 40% CH<sub>3</sub>CN and increasing the CH<sub>3</sub>CN up to 60%; flow rate 20 mL/min. The separation was performed in two runs. The composition of the effluent was periodically analysed using HPLC and MS. The fractions containing the respective products **3a**<sup>-</sup> and **3c**<sup>-</sup> were combined and CH<sub>3</sub>CN was immediately evaporated, however the evaporation was stopped when a small volume of CH<sub>3</sub>CN persisted in the solution before the compounds started to solidify. Then the products were rapidly precipitated with an excess of aqueous Me<sub>4</sub>NCl, washed with water (3x 10 mL), filtered and immediately dried in vacuum. The isolated isomeric products were crystallized from CH<sub>2</sub>Cl<sub>2</sub> layered carefully with hexane. The compounds were stored in vials closed under Ar atmosphere in a refrigerator at -33 °C. Under these conditions the compounds remain unchanged over several months period. These are also sufficiently stable at room temperature (days) as solid or in solvent used for NMR measurement or crystallization.

**[Me<sub>4</sub>N][1,1'-(CN)<sub>2</sub>-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>-3,3'-Co(III)]** (Me<sub>4</sub>N**3a**): red solid, yield 380 mg, 38% (when isolated from exp. No 4, Table S1). <sup>1</sup>H NMR (600 MHz, Acetonitrile-D<sub>3</sub>) δ 4.18 (2H, s, C<sub>cage</sub>-H), 3.06 (12H, s, Me<sub>4</sub>N<sup>+</sup>). <sup>1</sup>H{<sup>11</sup>B}-(from selective 2D-NMR): δ 3.92 (2H, B(8,8')-H), 3.15 (2H, B(10,10')-H), 2.93 (2H, B(12,12')-H), 2.50 (2H, B(4,4')-H), 2.24 (2H, B(7,7')-H), 2.24 (2H, B(6,6')-H), 2.06 (2H, B(9,9')-H), 2.02 (2H, B(5,5')-H), 1.76 (2H, B(11,11')-H). <sup>11</sup>B (193 MHz, Acetonitrile-D<sub>3</sub>) δ 9.45 (2B, d, *J* = 150.5 Hz, B8,8'), 2.17 (2B, s, *J* = 146.7 Hz, B10,10'), -4.11 (4B, d, *J* = 123.5 Hz, B4,4',7,7'), -4.78 (2B, d, *J* = 137.0 Hz, B9,9'), -5.95 (2B, d, *J* = 156.3 Hz, B12,12'), -14.30 (2B, d, *J* = 160.2 Hz, B5,5'), -17.07 (2B, d, *J* = 162.1 Hz, B11,11'), -20.17 (2B, d, *J* = 179.5 Hz, B6,6'). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Acetonitrile-D<sub>3</sub>) δ 118.78 (1C, CN), 118.66 (1C, CN), 58.00 (2C, C<sub>cage</sub>-H), 56.09 (4C, Me<sub>4</sub>N<sup>+</sup>), 47.34 (2C, C<sub>cage</sub>); HPLC *k* = 2.67; HRMS (ESI) *m/z* = 377.2635 (*M*<sup>-</sup>, 11%), 374.2742 (100%); Calcd. for **3a**<sup>-</sup> 377.2642 (10%) and 374.2751 (100%).

**[Me<sub>4</sub>N][1,8-(CN)<sub>2</sub>-(1,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-2,3'-Co(III)]** (Me<sub>4</sub>N**3c**) yellow-orange solid, yield 195 mg, 20% (when isolated from exp. No. 3, table S1); <sup>1</sup>H NMR (600 MHz, Acetonitrile-D<sub>3</sub>) δ 3.63 (1C, s, C<sub>cage</sub>-H), 3.56 (1C, s, C<sub>cage</sub>-H), 3.05 (4C, s, Me<sub>4</sub>N<sup>+</sup>). <sup>1</sup>H{<sup>11</sup>B}-(from selective 2D-NMR): δ 3.39 (1H, B-H), 3.17 (1H, B-H), 3.16 (1H, B-H), 3.02 (2H, B-H), 2.99 (1H, B-H), 2.98 (1H, B-H), 2.85 (2H, B-H), 2.75 (1H, B-H), 2.72 (1H, B-H), 1.96 (2H, B-H), 1.90 (2H, B-H), 1.85 (1H, B-H), 1.74 (1H, B-H), 1.68 (2H, B-H). <sup>11</sup>B (193 MHz, Acetonitrile-D<sub>3</sub>) δ 4.39 (2B, d, *J* = 142.8 Hz), 2.40 (1B, d, *J* = 158.3 Hz), -0.24 (2B, d, *J* = 140.9 Hz), -2.54 (1B, d, *J* = 162.1 Hz), -4.81 (2B, d, *J* = 158.3 Hz), -5.59 (2B, d, *J* = 140.9 Hz), -6.30 (1B, d, *J* = 135.1 Hz), -6.94 (1B, d, *J* = 111.9 Hz), -15.36 (1B, d, *J* = 150.5 Hz), -16.96 (2B, d, *J* = Hz), -17.02 (1B, d, *J* = 194.9 Hz), -18.40 (1B, d, *J* = 181.4 Hz), -22.21 (1B, d, *J* = 169.8 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, Acetone-D<sub>6</sub>) δ 130.02 (1C, s, -CN), 129.56 (1C, CN), 56.72 (2C, C<sub>cage</sub>-H), 55.19 (Me<sub>4</sub>N<sup>+</sup>), 41.42 (2C, C<sub>cage</sub>); HPLC *k* = 4.62; HRMS (ESI) *m/z* = 377.2644 (*M*<sup>-</sup>, 11%), 374.2737 (100%); Calcd. for **3c**<sup>-</sup> 377.2642 (10%) and 374.2751 (100%).



**Figure S1.** An example of the relative abundance of the products observed in the reaction mixtures that correspond to experiments Nos. 3 and 4 in Table S1.

## 1. Crystallography

### Crystal data and structure refinement for $[\text{Me}_4\text{N}][1,1'-(\text{CN})_2-(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2-3,3'-\text{Co}(\text{III})]$ ( $\text{Me}_4\text{N3a}$ )

#### Experimental

Single crystals of  $\text{Me}_4\text{N3a}$  were obtained from  $\text{CH}_2\text{Cl}_2$ -hexane. A suitable crystal was selected and measured on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2<sup>9</sup>, the structure was solved with the SHELXT<sup>3</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>4</sup> refinement package using Least Squares minimization.

#### Crystal structure determination of $\text{Me}_4\text{N3a}$

**Crystal Data** for  $\text{C}_{10}\text{H}_{32}\text{B}_{18}\text{CoN}_3$  ( $M = 447.89$  g/mol): orthorhombic, space group Aea2 (no. 41),  $a = 20.7855(3)$  Å,  $b = 19.9491(3)$  Å,  $c = 11.25789(16)$  Å,  $V = 4668.09(11)$  Å<sup>3</sup>,  $Z = 8$ ,  $T = 100.00(10)$  K,  $\mu(\text{Cu K}\alpha) = 5.756$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.275$  g/cm<sup>3</sup>, 41813 reflections measured ( $8.508^\circ \leq 2\theta \leq 161.248^\circ$ ), 4759 unique ( $R_{\text{int}} = 0.0696$ ,  $R_{\text{sigma}} = 0.0364$ ) which were used in all calculations. The final  $R_1$  was 0.0473 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1344 (all data).

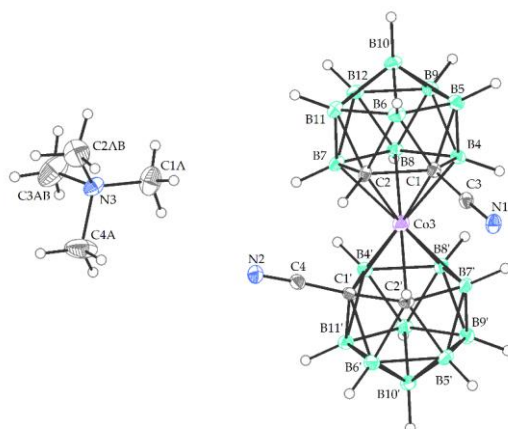
**Table S2.** Crystal data and structure refinement for Me<sub>4</sub>N<sub>3</sub>a.

<b>Crystal data</b>	
Identification code	GR-DB-732-3-F2-gg
Empirical formula	C <sub>10</sub> H <sub>32</sub> B <sub>18</sub> CoN <sub>3</sub>
Formula weight	447.89
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Aea2
a/Å	20.7855(3)
b/Å	19.9491(3)
c/Å	11.25789(16)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
Volume/Å <sup>3</sup>	4668.09(11)
Z	8
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.275
$\mu$ /mm <sup>-1</sup>	5.756
F(000)	1840.0
Crystal size/mm <sup>3</sup>	0.29 × 0.12 × 0.068

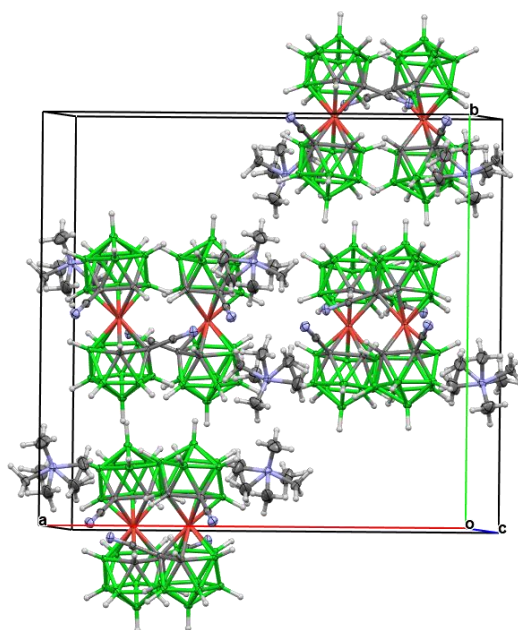
  

<b>Data collection and refinement</b>	
Radiation	Cu K $\alpha$ ( $\lambda$ = 1.54184)
2 $\Theta$ range for data collection/°	8.508 to 161.248
Index ranges	-26 ≤ h ≤ 26, -24 ≤ k ≤ 25, -14 ≤ l ≤ 13
Reflections collected	41813
Independent reflections	4759 [R <sub>int</sub> = 0.0696, R <sub>sigma</sub> = 0.0364]
Data/restraints/parameters	4759/1/309
Goodness-of-fit on F <sup>2</sup>	1.072
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0473, wR <sub>2</sub> = 0.1312
Final R indexes [all data]	R <sub>1</sub> = 0.0493, wR <sub>2</sub> = 0.1344
Largest diff. peak/hole / e Å <sup>-3</sup>	0.79/-0.52





**Figure S2.** The crystal structure of  $[\text{Me}_4\text{N}][1,1'-(\text{CN})_2-(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2-3,3'-\text{Co}(\text{III})]$  ( $\text{Me}_4\text{N3a}$ ) Selected interatomic distances [ $\text{\AA}$ ] and; angles [ $^\circ$ ]: N1 C3 1.151(5), N2 C4 1.153(6), C1 C3 1.443(5), C2 C1 1.636(5), C4 C1' 1.442(5), Co3 C1 2.071(3), Co3 C2 2.079(4), Co3 C1' 2.056(4), Co3 B8 2.123(4), Co3 B8' 2.122(4); N1 C3 C1 178.2(4), N2 C4 C1' 177.8(4), C1 C2 B7 111.2(3), C1 C2 B6 62.3(2), C3 C1 B4 122.8(3), C3 C1 B5 115.4(3), C1 Co3 C2 46.44(15), C2 C1 Co3 67.04(17), C1 Co3 C2' 102.78(15), C1 Co3 B8 83.98(16).



**Figure S3.** The crystal packing in the structure of  $[\text{Me}_4\text{N}][\text{rac}-1,1'-(\text{CN})_2-(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2-3,3'-\text{Co}(\text{III})]$  ( $\text{Me}_4\text{N3a}$ ). The unit cell contains of the racemic crystal contains sets of pairs of enantiomers. (ORTEP view, 40% probability level)

### Crystal data and structure refinement for $[\text{Me}_4\text{N}][1,8-(\text{CN})_2-1,8-\text{C}_2\text{B}_9\text{H}_9](1',2'-\text{C}_2\text{B}_9\text{H}_{11})-2,3'-\text{Co}(\text{III})]$ ( $\text{Me}_4\text{N3c}$ )

#### Experimental

Single crystals of  $\text{Me}_4\text{N3c}$  were obtained from  $\text{CH}_2\text{Cl}_2$ -hexane. A suitable crystal was selected and measured on an XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystal was

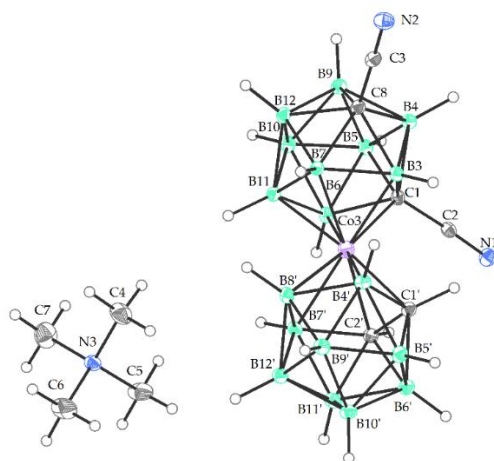
kept at 100.00(10) K during data collection. Using Olex2<sup>9</sup>, the structure was solved with the SHELXT<sup>3</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>4</sup> refinement package using Least Squares minimization.

### Crystal structure determination of Me<sub>4</sub>N3c

**Crystal Data** for C<sub>10</sub>H<sub>32</sub>B<sub>18</sub>CoN<sub>3</sub> ( $M=447.89$  g/mol): orthorhombic, space group Pbcn (no. 60),  $a = 21.3386(3)$  Å,  $b = 10.7908(2)$  Å,  $c = 20.2460(3)$  Å,  $V = 4661.86(13)$  Å<sup>3</sup>,  $Z = 8$ ,  $T = 100.00(10)$  K,  $\mu(\text{Cu K}\alpha) = 5.764$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.276$  g/cm<sup>3</sup>, 34211 reflections measured ( $8.288^\circ \leq 2\Theta \leq 158.002^\circ$ ), 4798 unique ( $R_{\text{int}} = 0.0302$ ,  $R_{\text{sigma}} = 0.0193$ ) which were used in all calculations. The final  $R_1$  was 0.0438 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1283 (all data).

**Table S3.** Crystal data and structure refinement for Me<sub>4</sub>N3c.

<b>Crystal data</b>	
Identification code	GR732-10m-gg
Empirical formula	C <sub>10</sub> H <sub>32</sub> B <sub>18</sub> CoN <sub>3</sub>
Formula weight	447.89
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbcn
$a/\text{\AA}$	21.3386(3)
$b/\text{\AA}$	10.7908(2)
$c/\text{\AA}$	20.2460(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	4661.86(13)
$Z$	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.276
$\mu/\text{mm}^{-1}$	5.764
$F(000)$	1840.0
Crystal size/mm <sup>3</sup>	$0.1 \times 0.07 \times 0.06$
<b>Data collection and refinement</b>	
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )
$2\Theta$ range for data collection/ $^\circ$	8.288 to 158.002
Index ranges	$-26 \leq h \leq 18$ , $-13 \leq k \leq 13$ , $-23 \leq l \leq 25$
Reflections collected	34211
Independent reflections	4798 [ $R_{\text{int}} = 0.0302$ , $R_{\text{sigma}} = 0.0193$ ]
Data/restraints/parameters	4798/0/293
Goodness-of-fit on $F^2$	1.067
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0438$ , $wR_2 = 0.1264$
Final R indexes [all data]	$R_1 = 0.0463$ , $wR_2 = 0.1283$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.19/-0.57



**Figure S4.** The crystal structure of  $[\text{Me}_4\text{N}][1,8\text{-(CN)}_2\text{-}1,8\text{-C}_2\text{B}_9\text{H}_9](1',2'\text{-C}_2\text{B}_9\text{H}_{11})\text{-}2,3'\text{-Co(III)}$  ( $\text{Me}_4\text{N}3\text{c}$ )

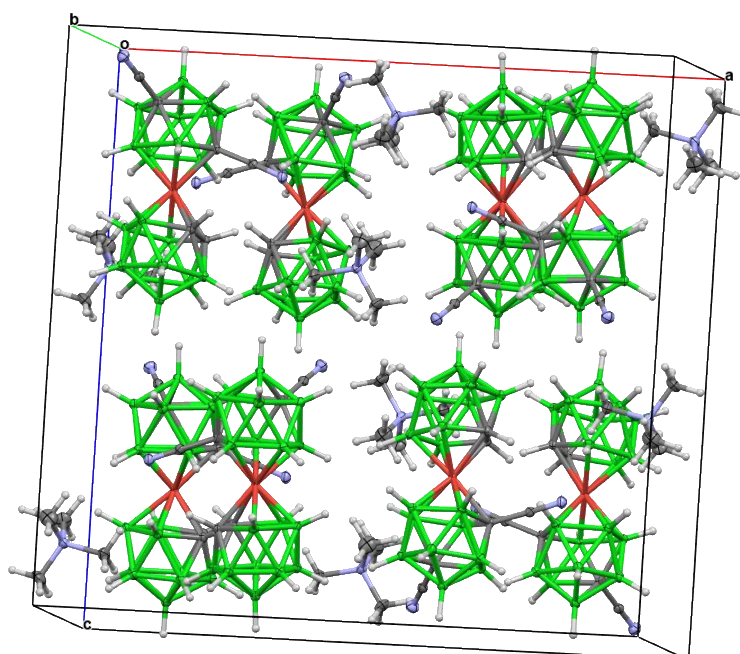
**Table S4.** Selected bond distances in the structure of  $3\text{c}^-$

Bond distances (Å)	Bond distances (Å)
N2 C3 1.145(3)	B11 B10 1.807(3)
N1 C2 1.150(3)	B6 B5 1.817(3)
C2 C1 1.446(3)	B3 B7 1.830(3)
C8 C3 1.450(3)	B3 B4 1.840(3)
C1' C2' 1.626(3)	C2' B7' 1.693(3)
C1 B4 1.709(3)	C1' B4' 1.703(3)
C1 B3 1.711(3)	C1' B5' 1.704(3)
C1 B6 1.729(3)	C2' B11' 1.707(3)
C1 B5 1.739(3)	C1' B6' 1.732(3)
C8 B4 1.696(3)	C2' B6' 1.729(3)
C8 B3 1.709(3)	B5' B6' 1.767(4)
C8 B12 1.723(3)	B4' B9' 1.773(3)
C8 B9 1.729(3)	B11 B12 1.779(3)
B5 B9 1.756(3)	B4' B5' 1.797(4)
C8 B7 1.759(3)	B7' B8' 1.817(3)
B4 B5 1.768(3)	B4' B8' 1.819(3)
B10 B9 1.772(4)	Co3 B3 2.030(2)
B10 B5 1.776(3)	Co3 C1' 2.047(2)
B4 B9 1.780(3)	Co3 C2' 2.054(2)
B10 B12 1.781(3)	Co3 B7 2.069(2)
B6 B10 1.783(3)	Co3 C1 2.087(2)
B12 B9 1.794(3)	Co3 B6 2.088(2)
B11 B7 1.800(3)	Co3 B4' 2.102(2)
B7 B12 1.801(3)	Co3 B11 2.110(2)
B11 B6 1.805(3)	Co3 B7' 2.115(2)

**Table S5.** Selected angles in the structure of **3c**

Angles (°)	Angles (°)
N2 C3 C8 178.7(2)	C2' Co3 C1 101.41(9)
N1 C2 C1 177.0(2)	B7 Co3 C1 86.53(9)
C8 B4 C1 100.22(15)	C1 B4 B5 60.00(13)
C8 B7 B12 57.89(13)	C1 B4 B9 105.31(17)
C8 B4 B3 57.64(12)	C1 B3 Co3 67.19(11)
C8 B7 B3 56.83(12)	C1 B6 Co3 65.51(10)
C8 B7 B11 102.60(16)	C1 B6 B11 107.20(16)
C8 B12 B11 104.95(16)	C1 B6 B10 104.73(16)
C8 B12 B7 59.84(13)	C1 B6 B5 58.68(13)
C8 B12 B10 103.51(16)	C1 B3 B7 107.05(16)
C8 B12 B9 58.86(13)	C1 B3 B4 57.42(13)
C3 C8 B4 116.18(18)	B5 B9 B4 60.01(13)
C3 C8 B12 117.98(18)	B5 B9 B12 108.41(17)
C3 C8 B9 117.52(18)	B4 B5 B6 106.81(16)
B3 C8 B7 63.69(13)	C1 B4 B3 57.49(12)
B3 C8 B12 114.87(17)	B3 Co3 C1 49.08(9)
B3 C8 B9 116.59(16)	C2' Co3 C1 101.41(9)
B4 C8 B3 65.41(14)	B5 B10 B11 110.39(17)
B4 C8 B7 118.65(16)	B5 B10 B12 108.11(17)
B4 C8 B12 115.28(17)	B5 B4 B3 107.56(16)
B4 C8 B9 62.61(13)	B11 B6 B5 108.62(16)
B12 C8 B7 62.27(13)	B5 B6 Co3 118.55(14)
B12 C8 B9 62.61(13)	C1' Co3 C1 101.97(8)
C3 C8 B3 116.44(18)	C1' Co3 C2' 46.72(8)
C3 C8 B7 115.71(17)	C1' Co3 B7 129.54(9)
B9 C8 B7 115.80(17)	C1 Co3 B11 85.35(9)
C8 B4 B5 104.38(16)	C2' Co3 B7 171.68(9)
C8 B4 B9 59.60(13)	B3 Co3 C1' 96.22(9)
C8 B3 C1 99.64(16)	C2' Co3 B6 98.61(9)
C8 B3 B7 59.48(13)	B3 Co3 B11 89.21(10)
C8 B3 B4 56.95(13)	B3 Co3 B6 87.54(9)
C8 B9 B4 57.79(12)	B3 Co3 B7 53.03(10)
C8 B9 B10 103.64(17)	B3 B7 Co3 62.40(10)
C8 B9 B5 103.53(16)	B4 B3 Co3 118.87(14)
C8 B9 B12 58.53(13)	B6 B11 Co3 63.89(10)
C8 B7 Co3 110.64(13)	B6 Co3 B11 50.94(9)
C8 B3 Co3 114.67(14)	B7 Co3 B11 51.00(9)
C1 B5 B6 58.13(12)	B7 Co3 B6 88.46(9)
C1 B5 B4 58.32(13)	B7 B3 Co3 64.57(11)
C1 B5 B10 104.63(16)	B7 B11 Co3 63.31(10)
C1 B5 B9 105.08(17)	B10 B6 Co3 118.09(14)
C2 C1 Co3 113.31(15)	B10 B11 Co3 115.84(14)
C2 C1 B3 122.10(17)	B11 B7 Co3 65.68(11)
C2 C1 B6 118.07(17)	B11 B6 Co3 65.18(10)
C2 C1 B4 114.90(17)	B12 B7 Co3 116.51(14)
C2 C1 B5 112.43(17)	B12 B11 Co3 115.51(14)
B3 C1 Co3 63.73(10)	B12 B10 B6 106.93(17)

B3 C1 B6 111.83(16)	B9 B10 B11 109.19(17)
B3 C1 B5 115.07(17)	B9 B10 B6 108.12(17)
B6 C1 Co3 65.55(10)	B11 B7 B3 106.47(16)
B6 C1 B5 63.19(13)	B4 B9 B12 107.83(17)
B4 C1 Co3 122.53(14)	B7 B11 B6 107.08(15)
B4 C1 B3 65.09(14)	B9 B5 B6 107.33(16)
B4 C1 B6 113.71(16)	B7 B3 B4 108.13(16)
B4 C1 B5 61.68(13)	B9 B12 B7 110.57(16)
B5 C1 Co3 122.54(13)	B10 B9 B4 108.07(17)
C1 Co3 B6 48.94(8)	B12 B7 B3 105.61(16)
C1 Co3 B4' 132.48(9)	B9 B4 B3 107.81(16)
C1 Co3 B8' 174.01(9)	B12 B11 B6 106.08(16)



**Figure S5.** The crystal packing in the structure of  $[\text{Me}_4\text{N}][1,8\text{-(CN)}_2\text{-}1,8\text{-C}_2\text{B}_9\text{H}_9(1',2'\text{-C}_2\text{B}_9\text{H}_{11})\text{-}2,3'\text{-Co(III)}]$  ( $\text{Me}_4\text{N3c}$ ). The unit cell contains 8 anions and four pairs of enantiomers. The CN groups in each pair are located in the same direction (upwards or downwards), however the second pair has the substituted part rotated in a opposite directions, (ORTEP view, 40% probability level).

## 2. DFT Calculations

The BP86/AE1 model chemistry was chosen for searching the reaction pathway that includes the geometry optimizations of the stationary points found. Second derivative analyses confirmed their nature. The final refinement of searching the rearrangement was carried out in terms of computing SMD energies in  $(\text{C}_2\text{H}_5)_2\text{O}$  at the same level. Dimethylether could not be used in the last computations since it is not available in G16 library. Gaussian16<sup>10</sup> was used for all the computations.

**Table S6** Cartesian geometries of the stationary points as computed at the BP86/AE1 level (in Å)

a) {3b}

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27	0.053258	-0.298023	-0.008114
6	-1.423168	0.599800	-1.134794
5	-1.254159	-1.002481	-1.508681
6	-1.435587	0.608186	1.130383
5	-1.204609	-1.999522	0.019356
5	-1.274510	-0.976711	1.521981
5	-2.770181	-1.778322	0.898768
5	-2.881299	-0.094864	1.473966
5	-2.759528	-1.789570	-0.869002
5	-2.694629	0.958426	0.000982
5	-2.860813	-0.109321	-1.466629
5	-3.725991	-0.572328	0.002187
6	-1.039904	1.764964	-1.871282
1	-0.802624	-1.317978	-2.569502
6	-0.999039	1.736578	1.888530
1	-0.713277	-3.091599	0.035310
1	-0.797652	-1.262269	2.583112
1	-3.275016	-2.664523	1.534167
1	-3.473903	0.351104	2.416231
1	-3.264287	-2.677210	-1.502371
1	-3.149584	2.064533	-0.008520
1	-3.451134	0.321166	-2.417139
1	-4.926282	-0.547486	-0.009990
6	1.608052	0.255434	1.254172
5	1.609796	-1.436196	0.937553
6	1.563831	1.141406	-0.094154
5	1.616528	-1.569243	-0.860248
5	1.529262	0.130195	-1.478671
5	3.093987	-0.714079	-1.435415

5	3.018851	1.007352	-0.968896
5	3.149488	-1.681210	0.070385
5	3.042508	1.110001	0.793717
5	3.091693	-0.539658	1.439111
5	4.024268	-0.124653	-0.026856
1	1.160255	0.688714	2.152451
1	1.235798	-2.211899	1.765658
1	1.086722	2.125350	-0.048559
1	1.252435	-2.527265	-1.478916
1	1.052416	0.508997	-2.506235
1	3.635470	-1.050710	-2.454285
1	3.382622	1.950362	-1.612045
1	3.737074	-2.726011	0.159409
1	3.344414	2.084414	1.417112
1	3.512990	-0.709903	2.548451
1	5.222901	-0.046013	-0.012992
7	-0.765179	2.767383	-2.429146
7	-0.607064	2.669414	2.496653

**b) TS=DSD**

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27	-0.120786	-0.367429	-0.051573
6	1.434340	0.175132	1.203410
5	1.253945	-1.496131	1.030839
6	2.147522	1.498602	-1.035025
5	1.135242	-1.825753	-0.728723
5	1.269317	-0.358687	-1.761460
5	2.753088	-1.421322	-1.520065
5	2.892078	0.227864	-1.306681
5	2.742473	-2.038191	0.140481
5	2.757747	0.910123	0.413387
5	2.824026	-0.718855	1.343641

5	3.790804	-0.629441	-0.193379
6	1.069649	0.913624	2.378902
1	0.868078	-2.189876	1.928379
6	1.141235	2.466723	-1.235080
1	0.662759	-2.790647	-1.271410
1	0.896727	-0.078860	-2.864634
1	3.201897	-2.010726	-2.465864
1	3.096651	1.788930	-1.692998
1	3.217609	-3.114449	0.383843
1	3.490351	1.701055	0.948885
1	3.438425	-0.720937	2.371826
1	4.988877	-0.664251	-0.126426
6	-1.572363	0.733244	-1.013661
5	-1.636922	-0.940329	-1.414521
6	-1.562000	0.981026	0.581905
5	-1.719335	-1.792670	0.163418
5	-1.619163	-0.498677	1.441104
5	-3.196161	-1.190543	1.004642
5	-3.055714	0.566482	1.289937
5	-3.225234	-1.454990	-0.767744
5	-3.004080	1.378353	-0.277985
5	-3.076264	0.140447	-1.543186
5	-4.053370	-0.038866	-0.062195
1	-1.093112	1.485881	-1.644239
1	-1.250605	-1.331791	-2.479657
1	-1.050173	1.871151	0.960100
1	-1.399496	-2.935612	0.341825
1	-1.152640	-0.585308	2.539888
1	-3.783609	-1.900536	1.778284
1	-3.427750	1.183989	2.247773
1	-3.846107	-2.343454	-1.289874
1	-3.258669	2.533546	-0.456711



1	-3.461584	0.458946	-2.634127
1	-5.248574	0.092635	-0.070465
7	0.781014	1.593821	3.299826
7	0.398911	3.372852	-1.392995

c)  $3e^-$

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27	-0.321147	0.065106	-0.217688
6	1.150810	-1.372253	0.155221
5	0.824204	-1.067048	-1.540846
6	2.754783	0.726795	0.390767
5	0.948522	0.737620	-1.755040
5	1.235707	1.451226	-0.137518
5	2.603894	1.202803	-1.265651
5	1.291549	0.083081	1.047035
5	2.347901	-0.335708	-2.136609
5	2.743505	-0.953829	0.637937
5	2.445157	-1.659780	-0.957326
5	3.521436	-0.271117	-0.809455
6	0.680296	-2.556117	0.840622
1	0.248350	-1.880692	-2.200058
6	3.595550	1.508238	1.267784
1	0.483886	1.347699	-2.675315
1	1.089658	2.568024	0.272604
1	3.236868	2.146708	-1.642030
1	1.136009	0.153722	2.233475
1	2.730521	-0.493952	-3.263303
1	3.309514	-1.473151	1.549960
1	2.788873	-2.787409	-1.160399
1	4.716350	-0.291343	-0.866524
6	-1.598592	1.085223	1.054533
5	-1.665641	1.634189	-0.581982
6	-1.773241	-0.516557	1.137979

5	-1.999141	0.149948	-1.574382
5	-1.993988	-1.222711	-0.417129
5	-3.549353	-0.539498	-0.965662
5	-3.355739	-0.999546	0.742805
5	-3.340605	1.234633	-1.074960
5	-3.078447	0.467452	1.694333
5	-3.037367	1.841220	0.579313
5	-4.202292	0.515548	0.319046
1	-0.994895	1.576336	1.821673
1	-1.160708	2.673230	-0.895377
1	-1.277257	-1.045122	1.958140
1	-1.750956	0.056029	-2.743843
1	-1.686278	-2.365956	-0.595042
1	-4.277443	-1.161407	-1.692771
1	-3.810807	-1.960879	1.295733
1	-3.917144	1.922489	-1.875226
1	-3.258418	0.555851	2.874452
1	-3.266759	2.940722	0.999839
1	-5.378106	0.667845	0.515636
7	0.314334	-3.506244	1.431008

## NMR SPECTRA

### NMR Spectra of Cs[1-CN-(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-3,3'-Co(III)] (Cs2)

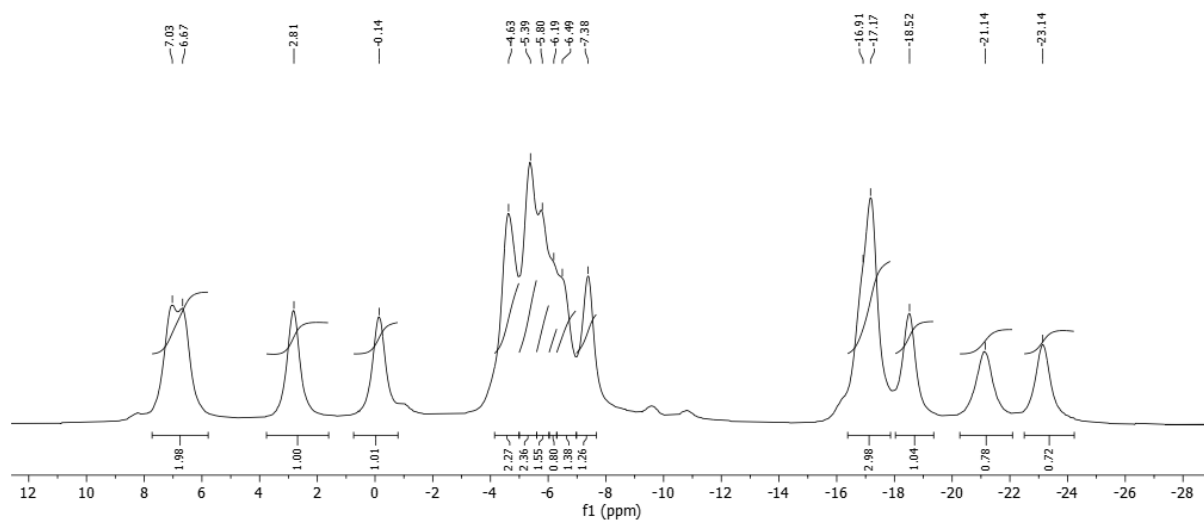


Figure S6.  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of Cs2

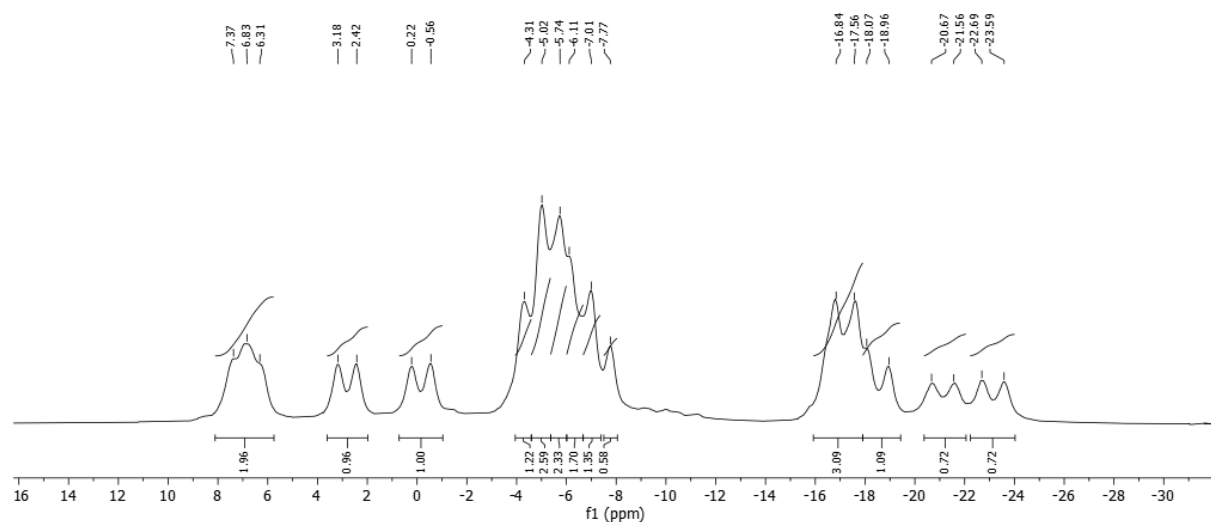
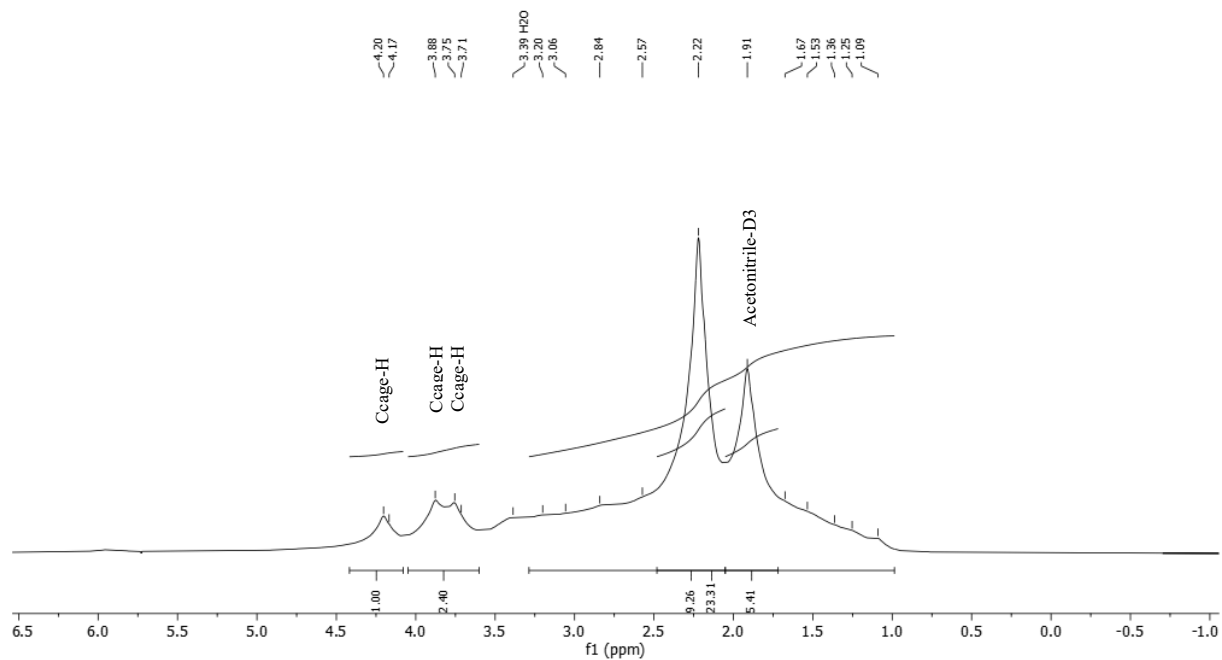
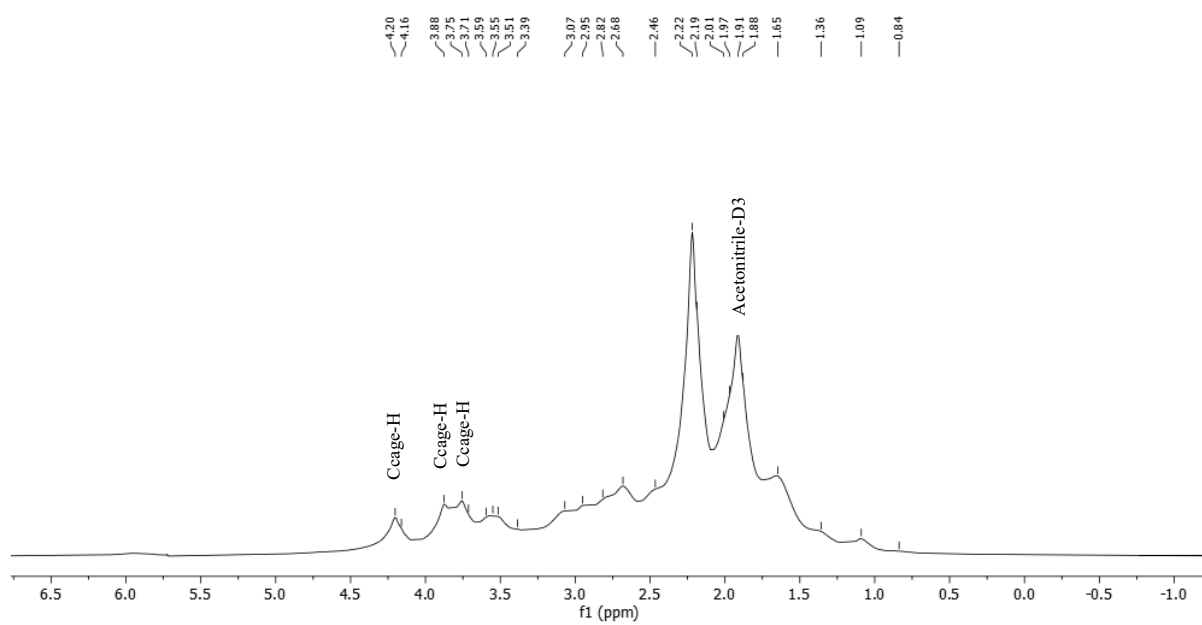


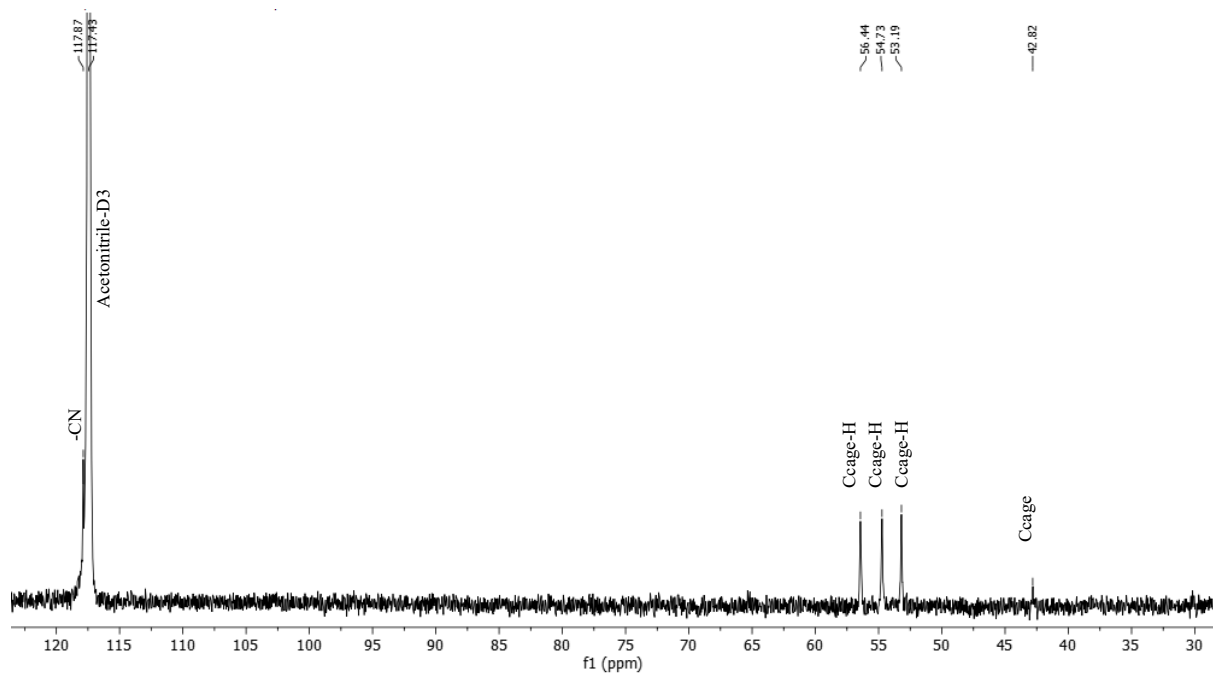
Figure S7.  $^{11}\text{B}$  NMR Spectrum of Cs2



**Figure S8.**  $^1\text{H}$  NMR Spectrum of Cs2

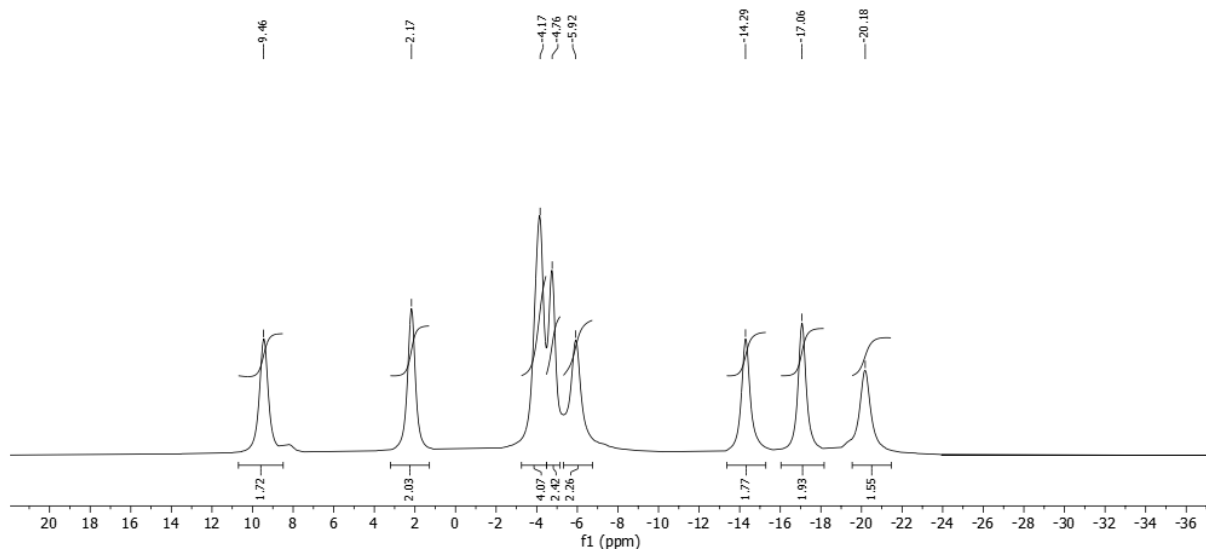


**Figure S9.**  $^1\text{H}\{^{11}\text{B}\}$  NMR Spectrum of Cs2

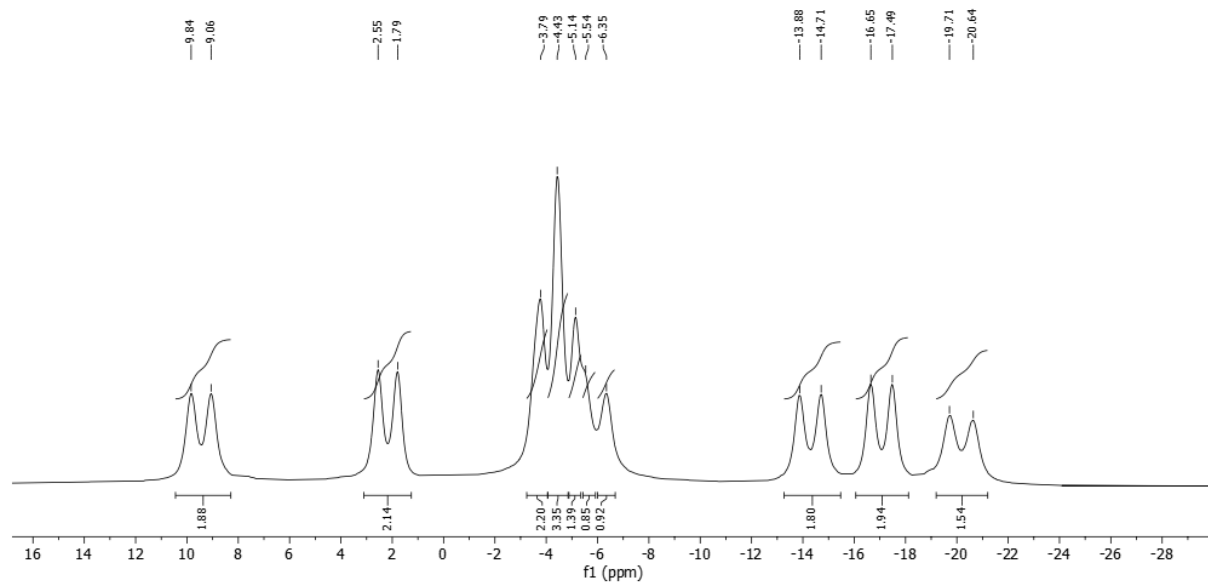


**Figure S10.**  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Cs2

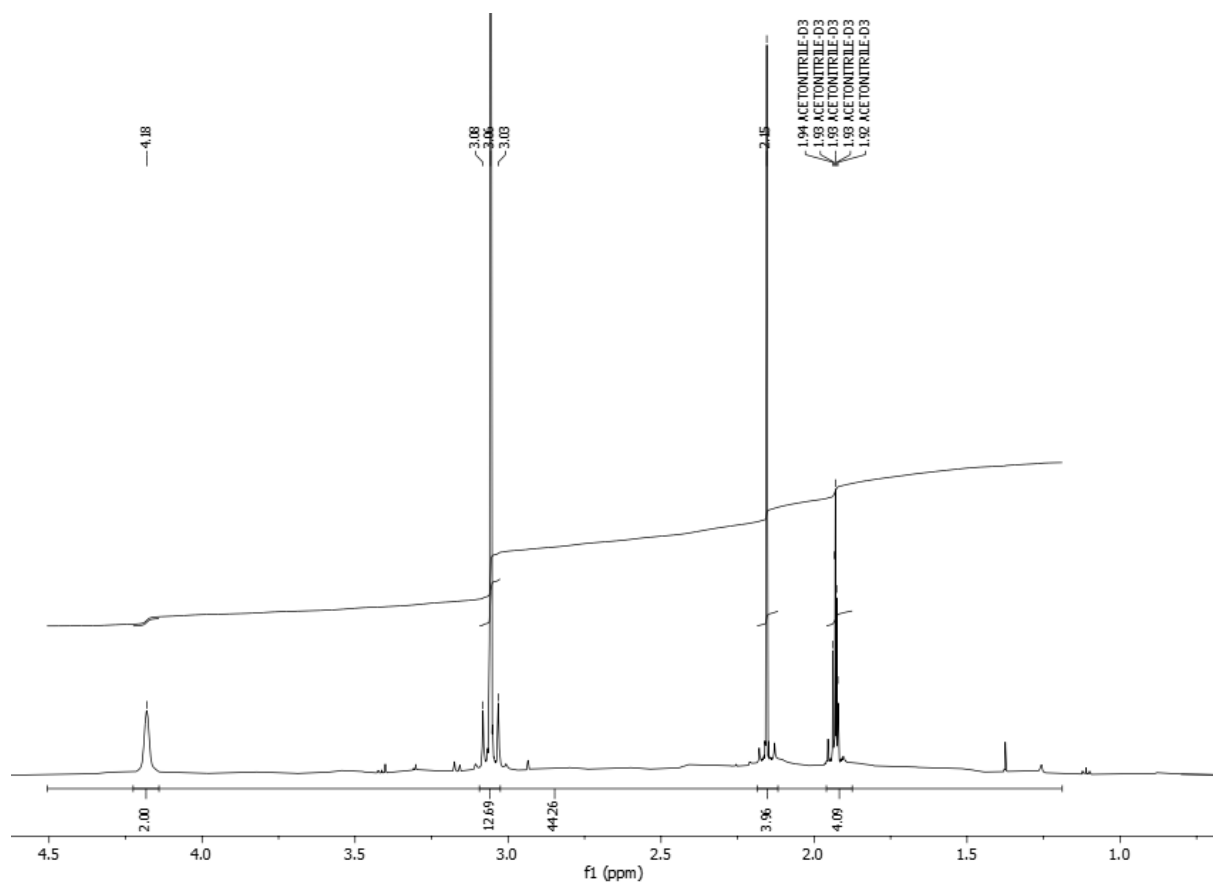
**NMR Spectra of  $[\text{Me}_4\text{N}][1,1'-(\text{CN})_2-(1,2-\text{C}_2\text{B}_9\text{H}_{10})_2-3,3']\text{-Co(III)}$  ( $\text{Me}_4\text{N3a}$ )**



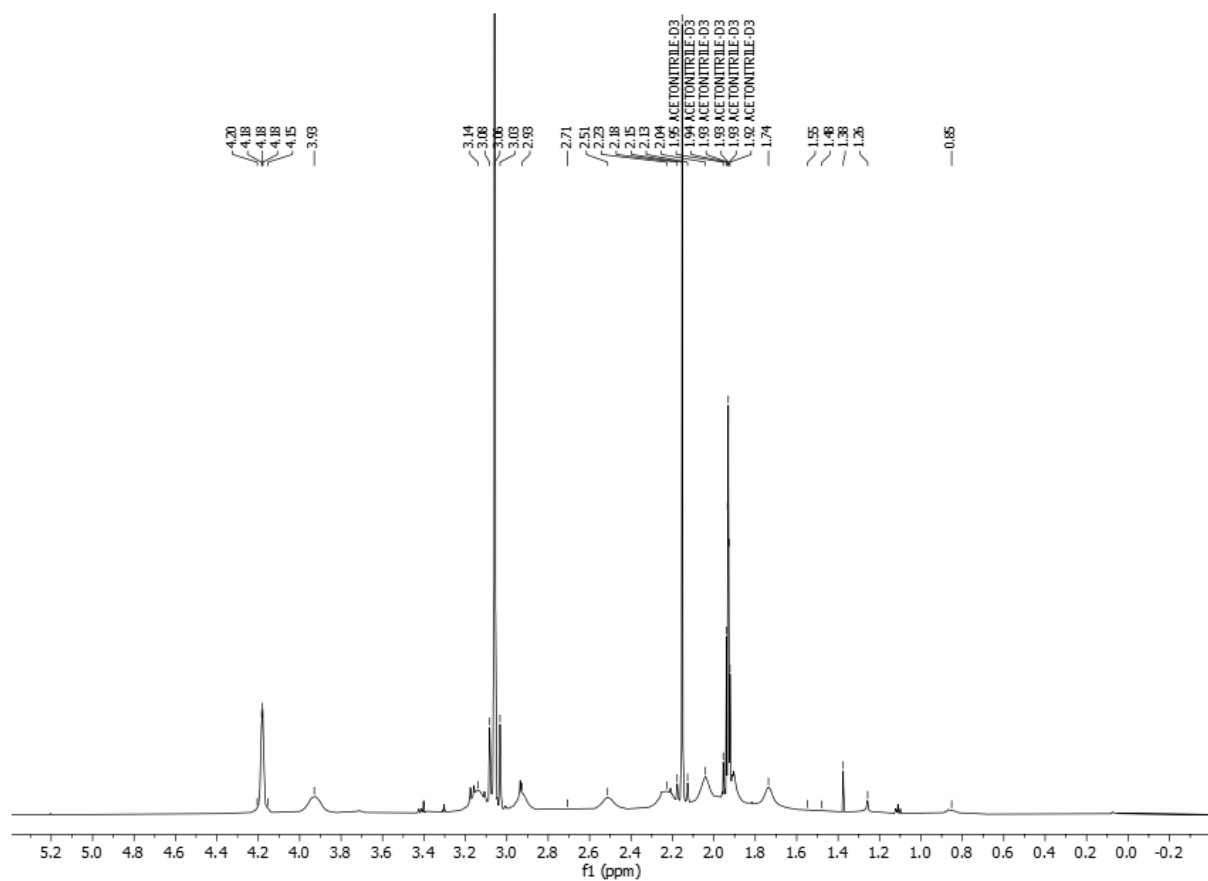
**Figure S11.**  $^{11}\text{B}\{^1\text{H}\}$  NMR Spectrum of  $\text{Me}_4\text{N3a}$



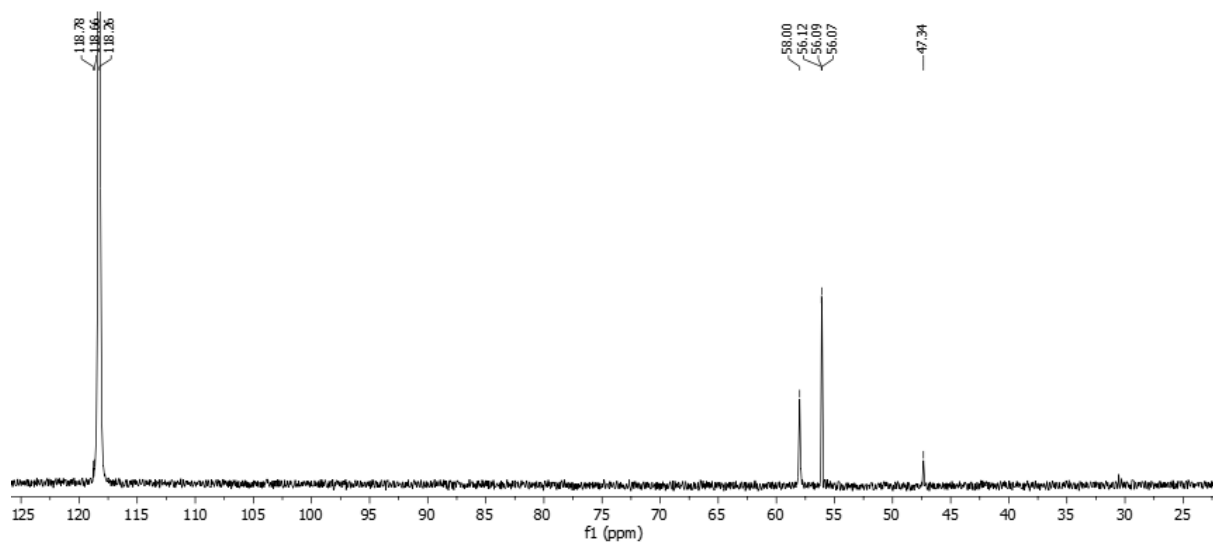
**Figure S12.**  $^{11}\text{B}$  NMR Spectrum of  $\text{Me}_4\text{N3a}$



**Figure S13.**  $^1\text{H}$  NMR Spectrum of  $\text{Me}_4\text{N3a}$



**Figure S14.**  $^1\text{H}\{^{11}\text{B}\}$  NMR Spectrum of  $\text{Me}_4\text{N3a}$



**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $\text{Me}_4\text{N3a}$

### NMR Spectra of [Me<sub>4</sub>N][1,8-(CN)<sub>2</sub>-(1,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-2,3'-Co(III)] (Me<sub>4</sub>N3c)

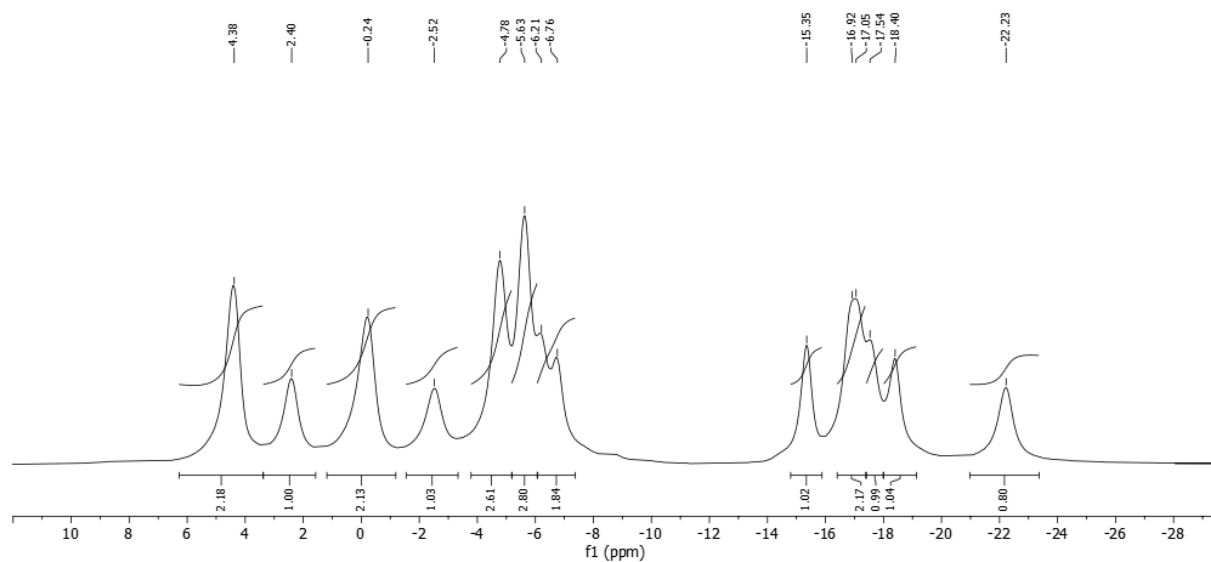


Figure S16. <sup>11</sup>B{<sup>1</sup>H} NMR Spectrum of Me<sub>4</sub>N3c

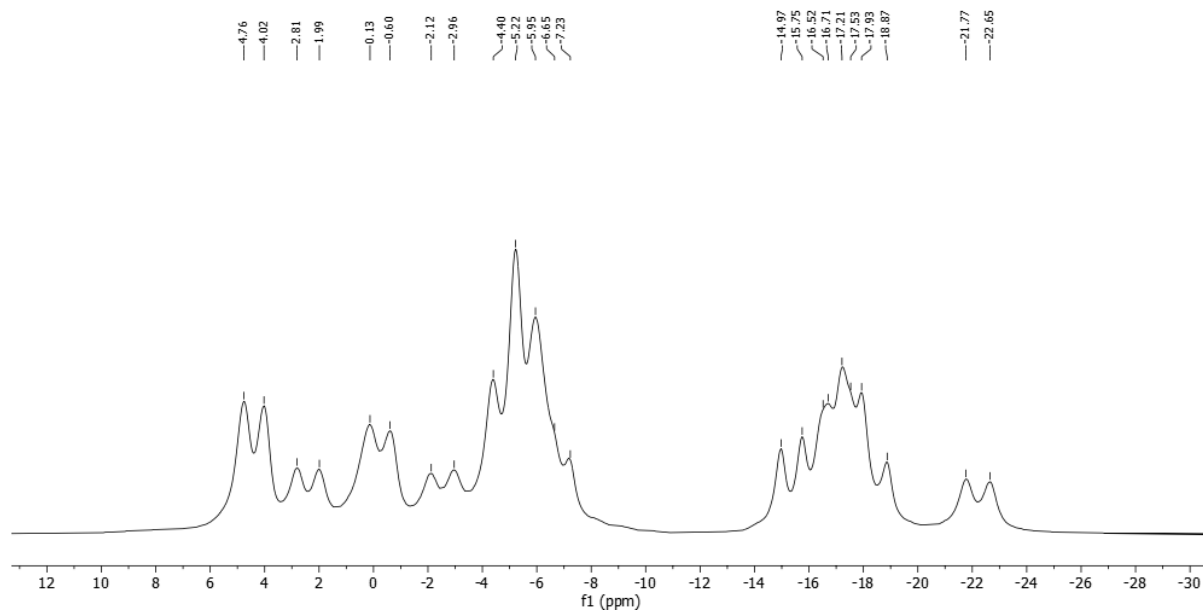
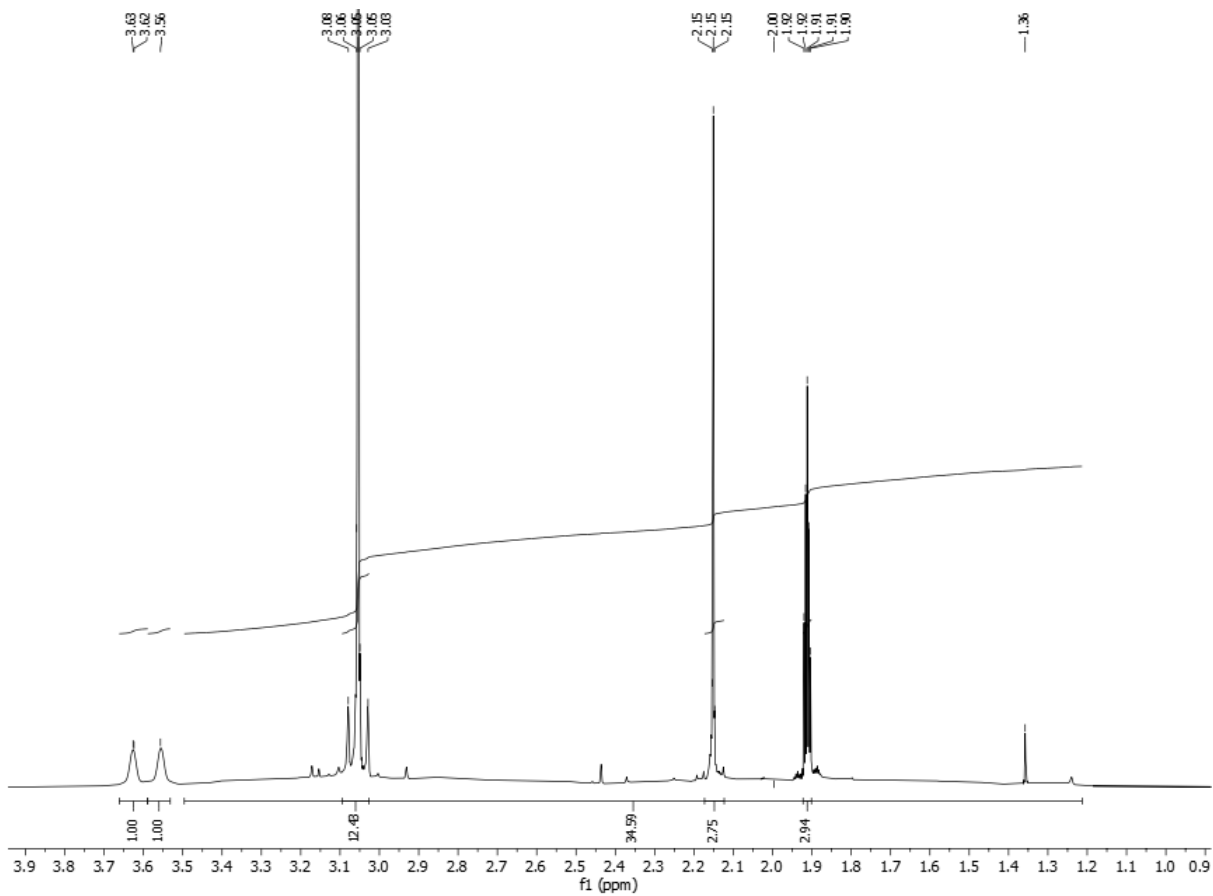
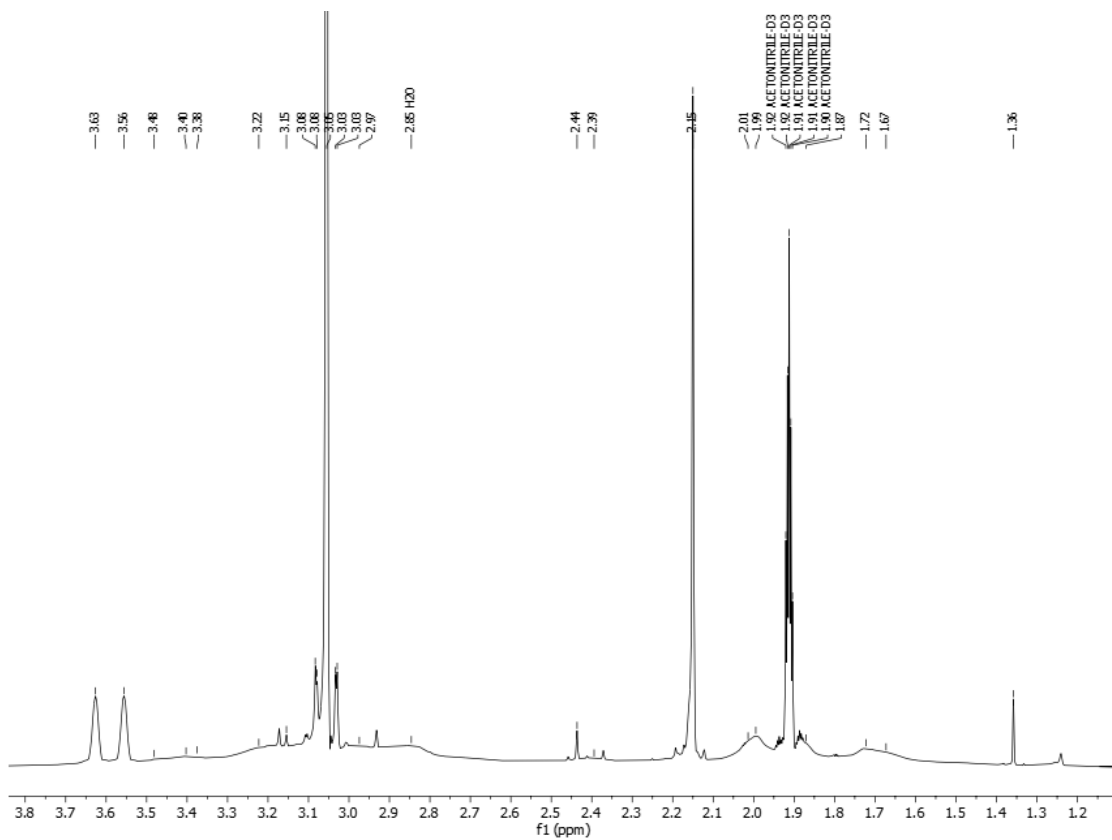


Figure S17. <sup>11</sup>B NMR Spectrum of Me<sub>4</sub>N3c

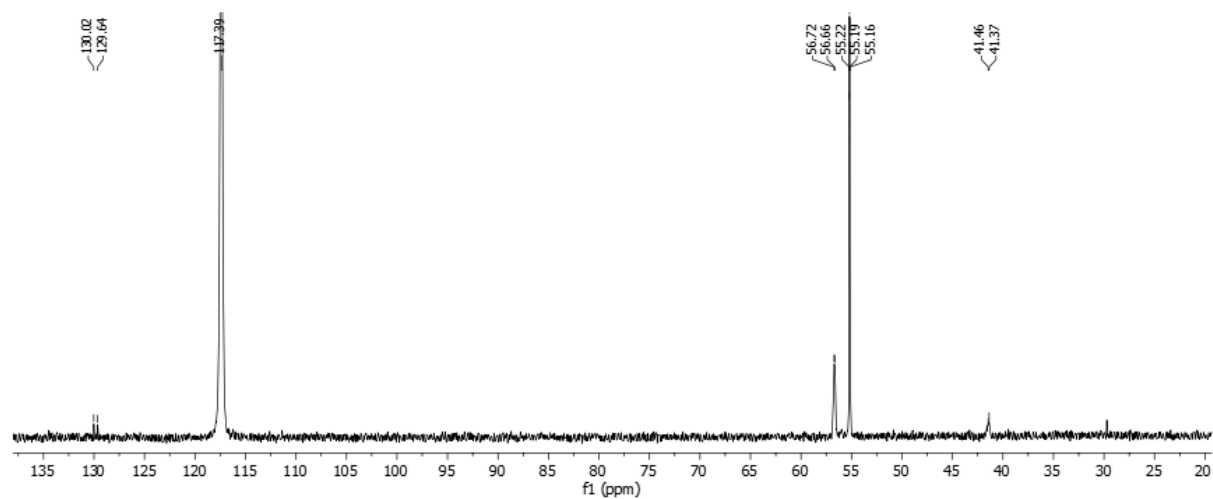




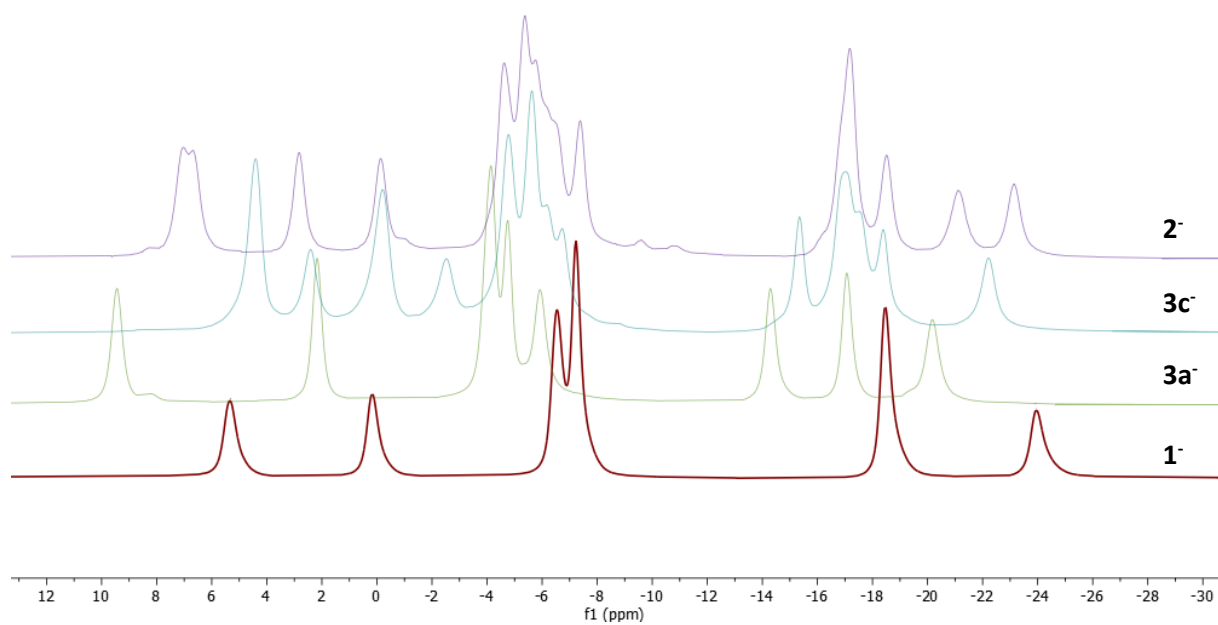
**Figure S18.**  $^1\text{H}$  NMR Spectrum of  $\text{Me}_4\text{N3c}$



**Figure S19.**  $^1\text{H}\{^{11}\text{B}\}$  NMR Spectrum of  $\text{Me}_4\text{N3c}$



**Figure S20.**  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of  $\text{Me}_4\text{N}3\text{c}$



**Figure S21.** Overlay of  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of  $1^-$ ,  $2^-$ ,  $3a^-$ ,  $3c^-$ .

# HRMS Spectra

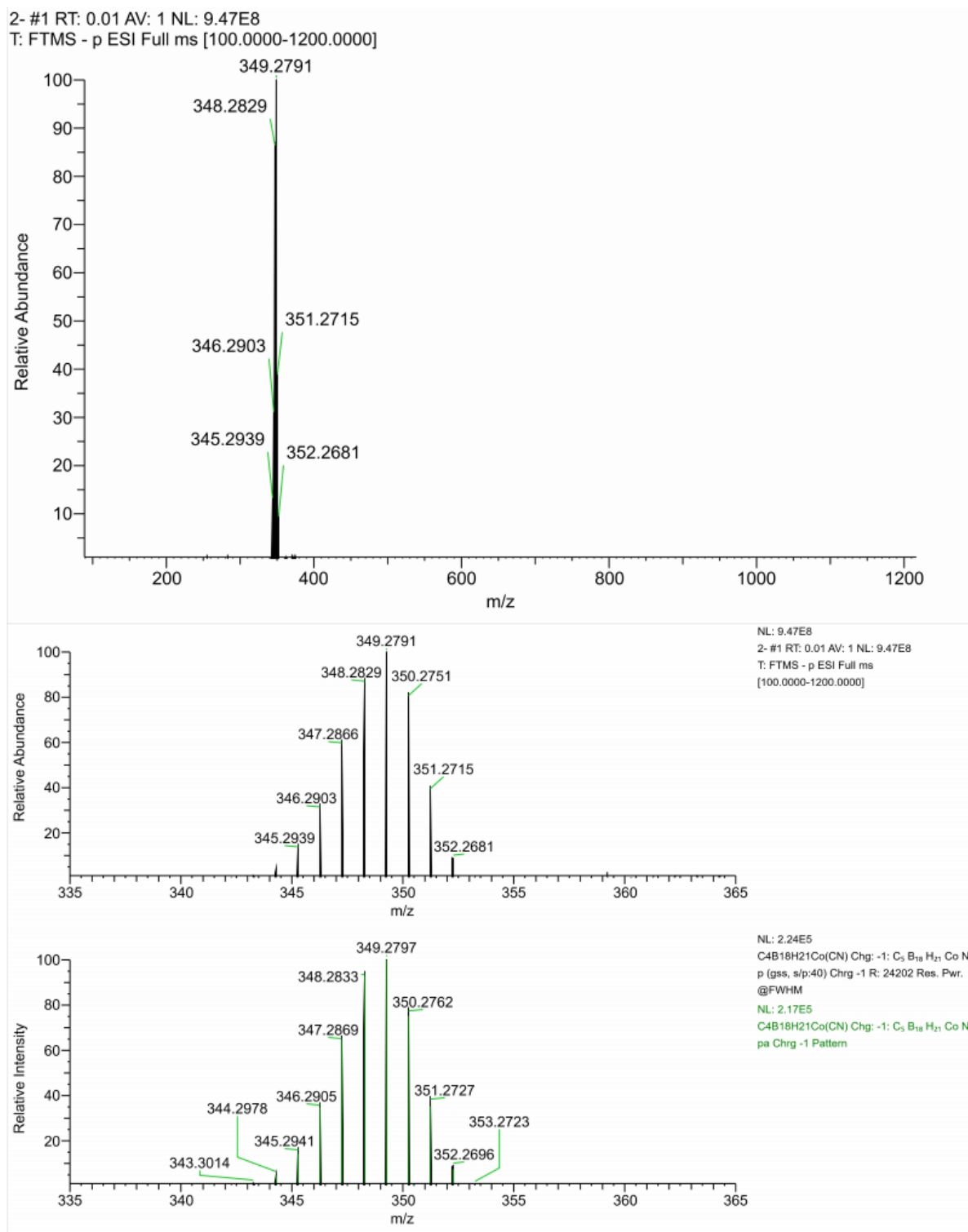


Figure S22. HRMS spectrum of **2**<sup>-</sup> with a calculated isotopic pattern.

2- #1 RT: 0.01 AV: 1 NL: 9.47E8  
 T: FTMS - p ESI Full ms [100.0000-1200.0000]  
 3- #1 RT: 0.01 AV: 1 NL: 4.35E9  
 T: FTMS - p ESI Full ms [100.0000-1200.0000]

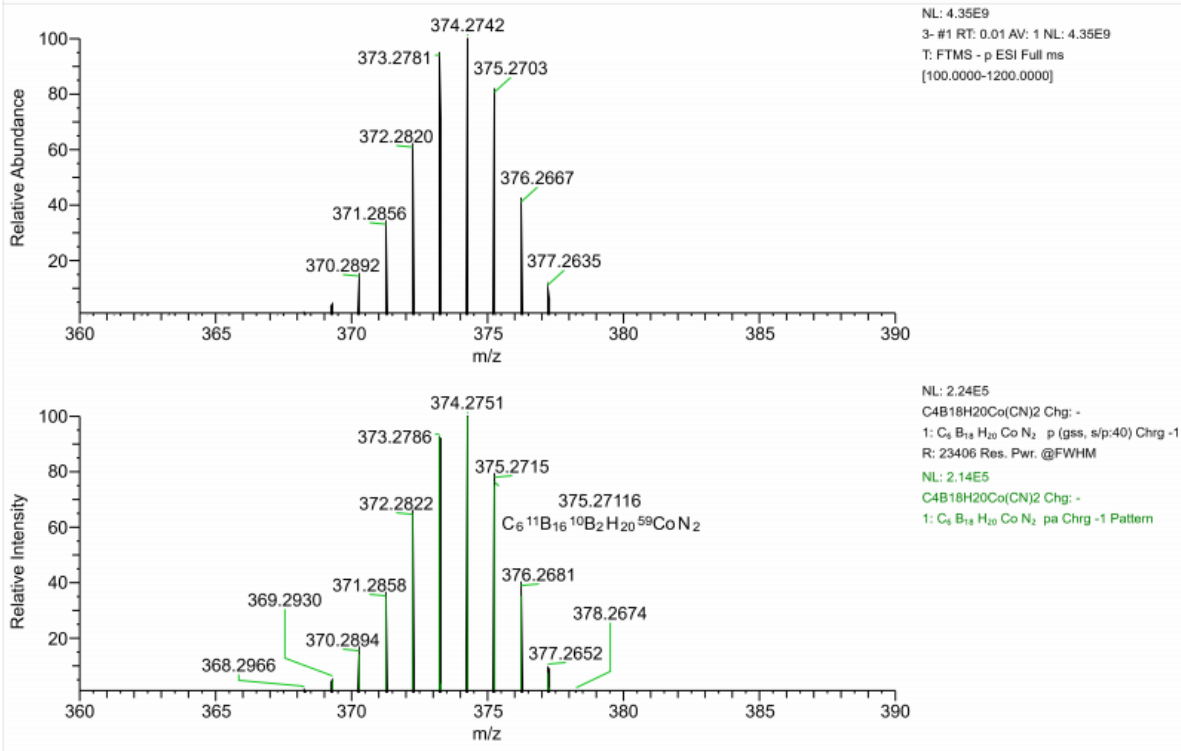
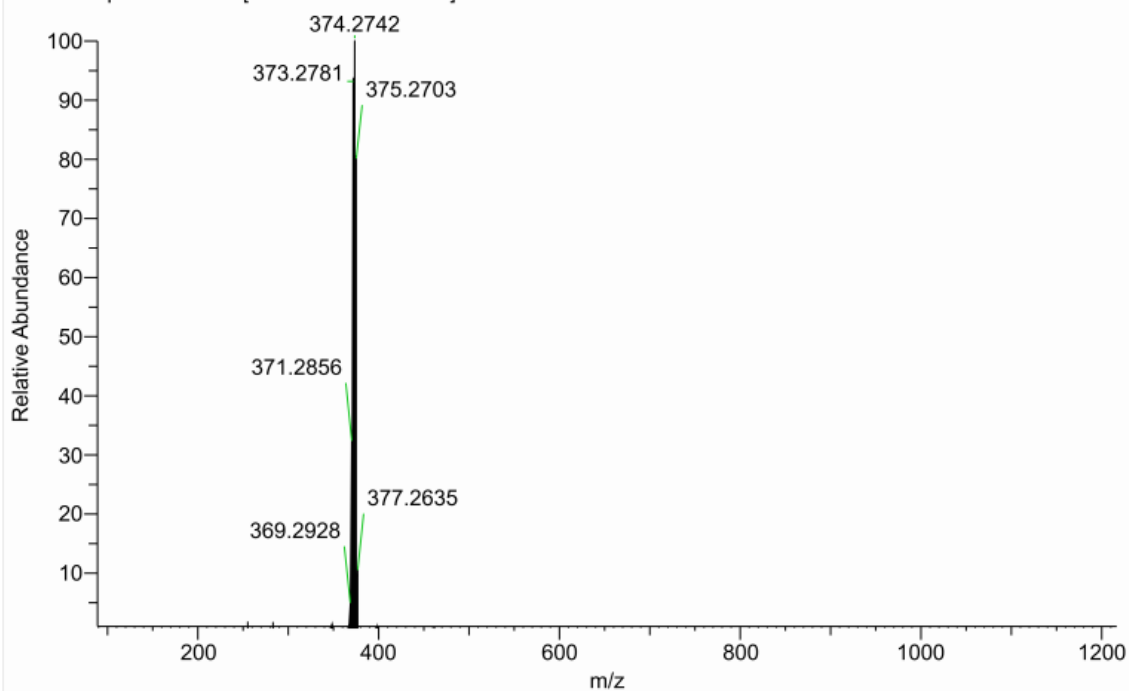
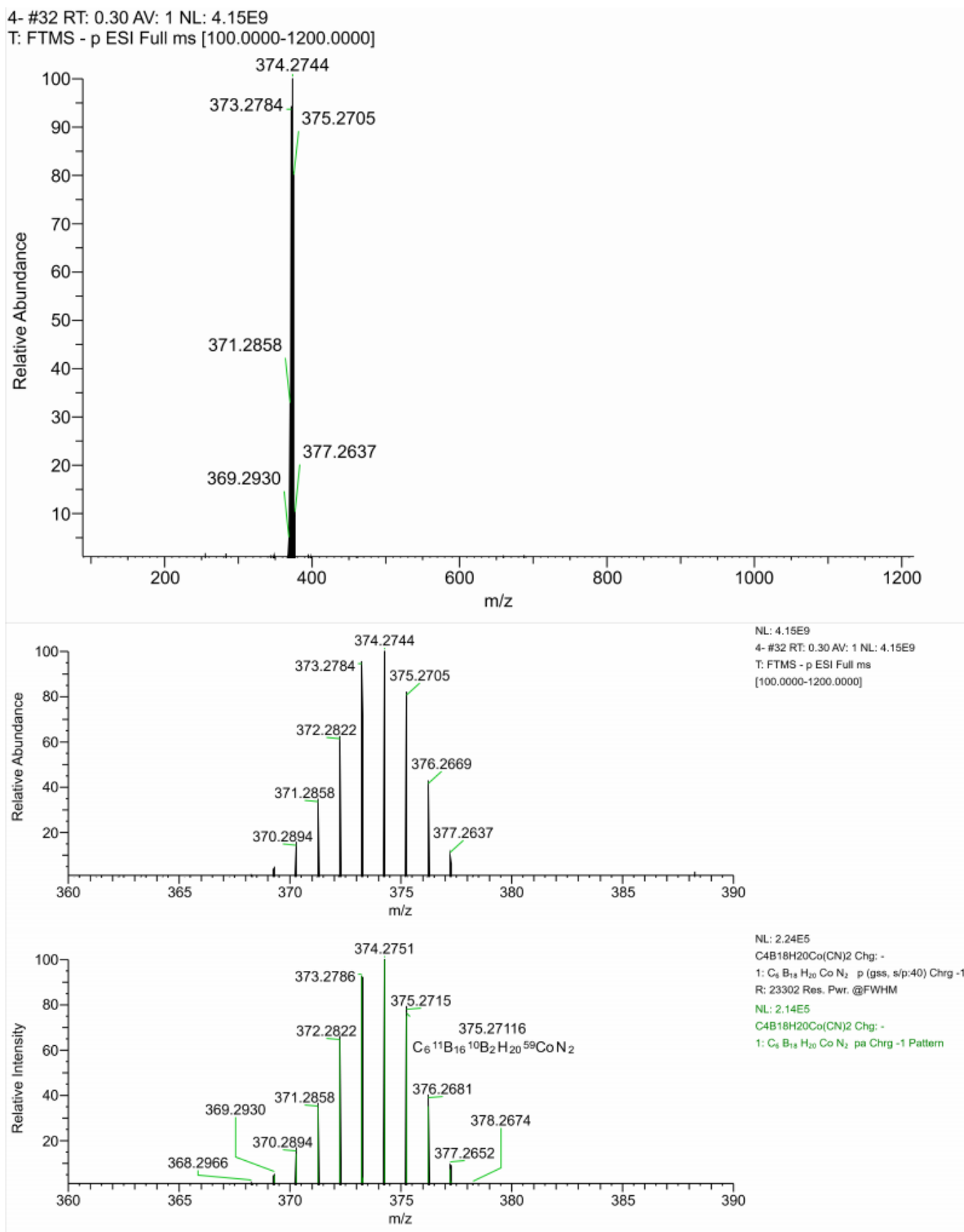


Figure S23. HRMS spectrum of  $3a^-$  with a calculated isotopic pattern.



**Figure S24.** HRMS spectrum of **3c<sup>-</sup>** with a calculated isotopic pattern.

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