

# Unusually air-stable copper(I) complexes showing high selectivity for carbon monoxide

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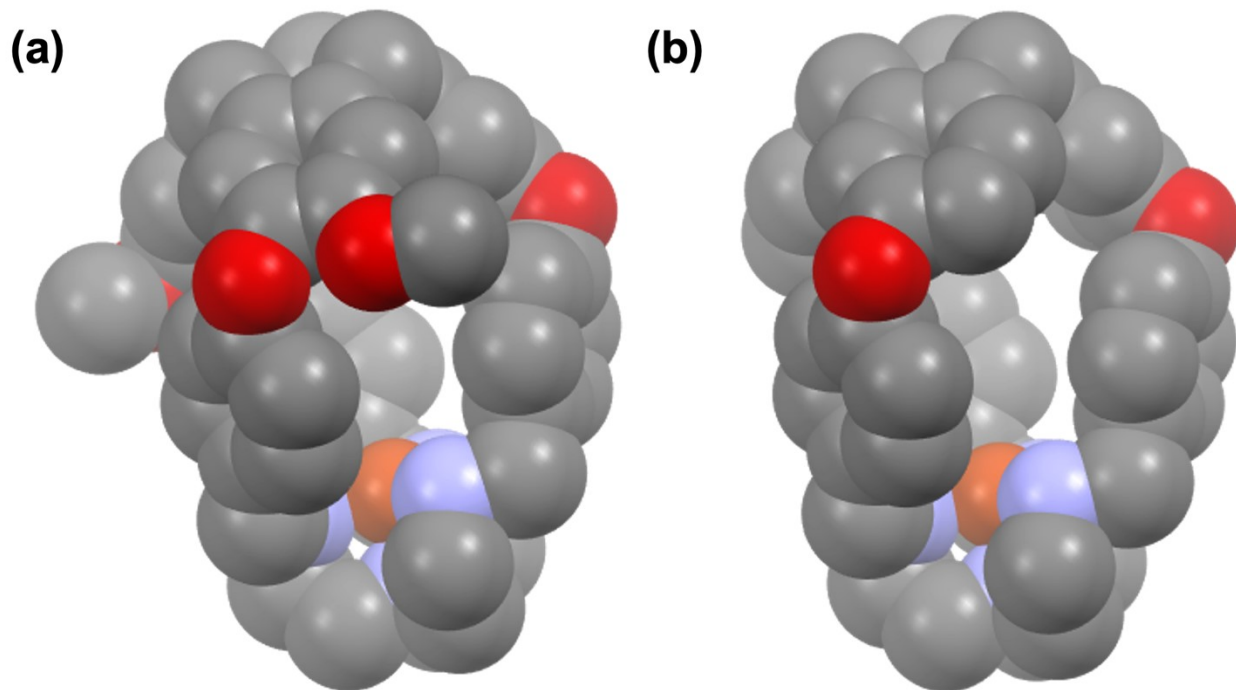
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## General Information

Air-sensitive substances were either handled inside of an inert atmosphere glovebox or with the use of proper Schlenk technique.<sup>1</sup> The use of anhydrous solvents or air-free reaction conditions in a synthetic procedure is explicitly mentioned. The absence of such notes indicates that no such precautions to exclude air or water were taken. Air-stability experiments were undertaken on the benchtop in ambient conditions; that is, 25 °C and 30-50% relative humidity. The air was used 'as-is' and not dried prior to use. Unless otherwise specified, all solvents and chemicals were purchased from Thermo Scientific Chemicals, Fisher, Sigma Aldrich, or TCI, and were used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories. For the post-purification (i.e., after preparative TLC) handling of **L1** and **L2**, all CHCl<sub>3</sub> and CDCl<sub>3</sub> was passed through a plug of basic alumina to ensure neutrality. <sup>1</sup>H NMR, <sup>13</sup>C {<sup>1</sup>H decoupled} NMR, <sup>19</sup>F {<sup>1</sup>H decoupled} NMR and <sup>31</sup>P {<sup>1</sup>H decoupled} NMR spectra were recorded using Bruker AVIII400, AVIII500 or NEO600 NMR spectrometers at ambient temperature unless specified otherwise. <sup>13</sup>C NMR spectra taken under CO were recorded using a Bruker AVIII500 spectrometer equipped with a Bruker 5mm helium-cooled cryogenic DCH probe optimized for <sup>13</sup>C sensitivity. <sup>1</sup>H and <sup>13</sup>C chemical shifts are referenced to the residual non-deuterated solvent.<sup>2</sup> <sup>19</sup>F and <sup>31</sup>P chemical shifts are calibrated with the absolute frequency  $\Xi(^{19}\text{F})$  or  $\Xi(^{31}\text{P})$ , respectively, based on <sup>1</sup>H NMR frequency.<sup>3</sup> Accurate mass measurements were done on a Waters LCT Premier™ XE time-of-flight mass spectrometer. Waters software calibrates and reports by use of neutral atomic masses. The mass of electron is not included. Analytical thin-layer chromatography was performed on Silicycle glass-backed silica gel plates (60 Å porosity, 250 µm thickness). Flash chromatography was performed using Silicycle SiliaFlash® F60 silica gel (40-63 µm particle size, 230-400 mesh). Preparative thin-layer chromatography was performed on Sorbtech neutral alumina TLC plates (20x20 cm with a thickness of 1000 µm). FTIR spectra were obtained in DMSO on a Vertex 70V FT-IR spectrometer scanning between 400 and 4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution using a CaF<sub>2</sub> demountable cell with path length of 0.1 mm. **L1** was synthesized using a previously reported procedure.<sup>4</sup>

## Comparison of Portal Size in L1 and L2

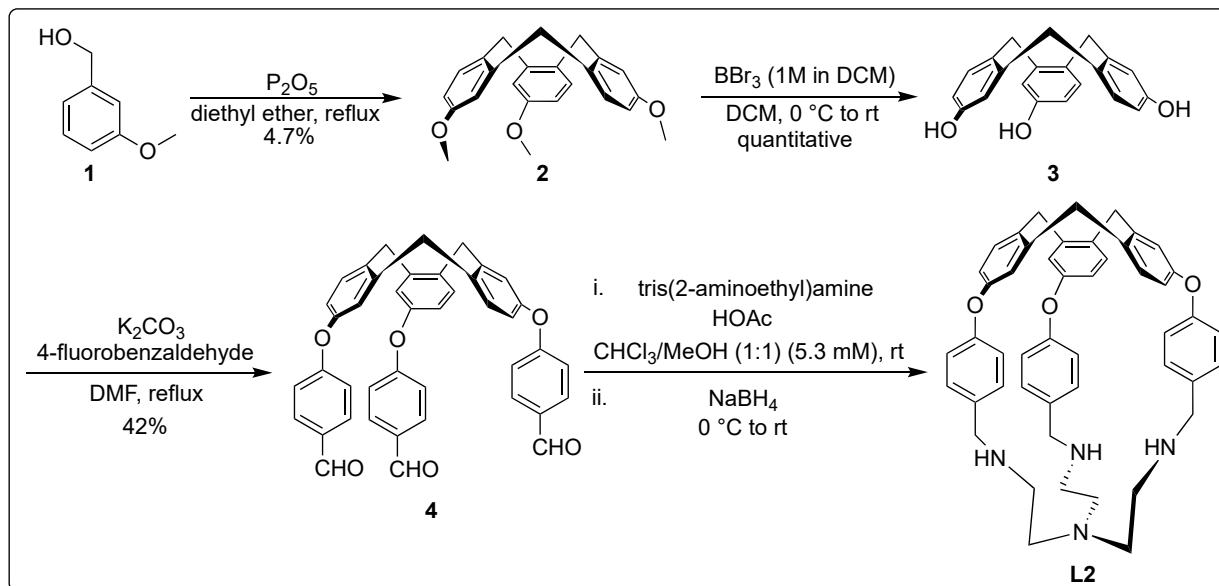
Space-filling illustrations have been generated for **Cu(I)@L1** (Fig. S1a) and **Cu(I)@L2** (Fig. S1b) to help visualize and compare the portal size in the two compounds. The space-filling illustrations have been generated using the X-ray crystal structure for **[CuL1(MeCN)](OTf)<sub>2</sub>** where the guest and counterions for **Cu(I)@L1** and the guest, counterions and the methoxy groups for **Cu(I)@L2** have been removed.



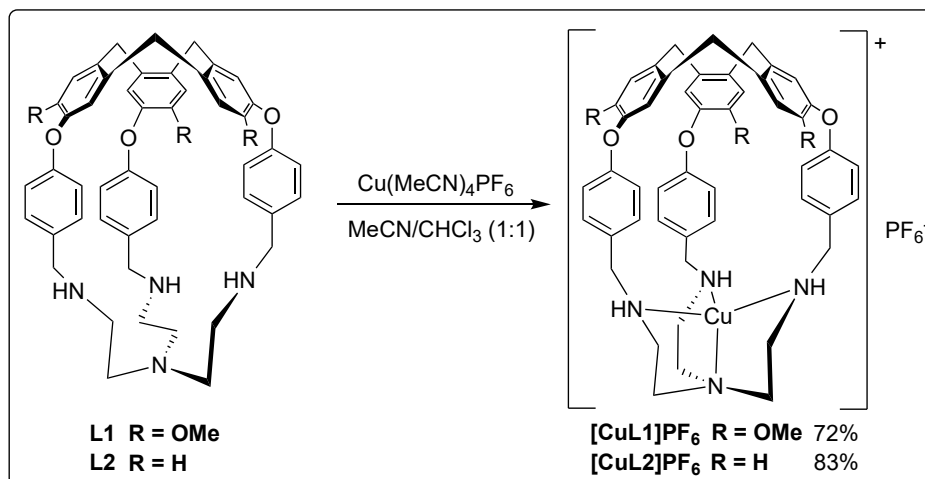
**Fig. S1** Space-filling illustrations of (a) **Cu(I)@L1** and (b) **Cu(I)@L2**.

## Synthesis

**L2** was synthesized as described in **Scheme S1** where compounds **2** and **3** were prepared using previously reported methods.<sup>5</sup> **Scheme S2** describes the synthesis of **[CuL1]PF<sub>6</sub>** and **[CuL2]PF<sub>6</sub>**. Previously unreported compounds were synthesized and characterized according to the procedures detailed in this section.

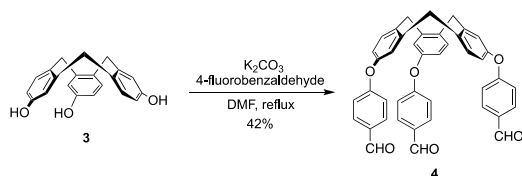


**Scheme S1** Synthesis of **L2**.



**Scheme S2** Synthesis of **[CuL1]PF<sub>6</sub>** and **[CuL2]PF<sub>6</sub>**.

4:

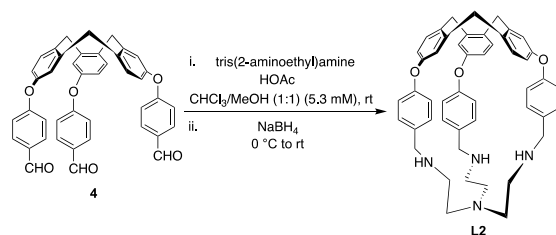


**3** (917 mg, 2.88 mmol, 1.0 equiv.) and potassium carbonate (1.99 g, 14.4 mmol, 5.0 equiv.) were added to an oven-dried two-neck round bottom flask equipped with a stir bar and a condenser. The reaction vessel was subsequently sealed and purged with argon before the addition of 4-fluorobenzaldehyde (1.85 mL, 17.3 mmol, 6.0 equiv.) using a syringe. Lastly, anhydrous DMF (24.0 mL, 0.12 M) was added, and the reaction mixture was refluxed overnight. The reaction mixture was then allowed to cool to room temperature and transferred to a 500 mL separatory funnel and diluted with 75 mL of ethyl acetate. The organic phase was washed with 100 mL of 1.0 M HCl to remove the excess potassium carbonate, followed by 5 x 100 mL of deionized water to remove DMF. The organic phase was then washed with 100 mL of saturated brine and dried over anhydrous sodium sulphate before concentration *in vacuo*. The resulting residue was purified by flash chromatography over silica gel (gradient: 100% DCM to 5:95 acetone/DCM) to yield the desired compound as an orange solid (758.9 mg, 42%).

**$^1H$  NMR** (600 MHz,  $CDCl_3$ )  $\delta$  9.92 (s, 3H), 7.85 – 7.81 (m, 6H), 7.34 (d,  $J$  = 8.4 Hz, 3H), 7.13 (d,  $J$  = 2.6 Hz, 3H), 7.06 – 7.02 (m, 6H), 6.85 (dd,  $J$  = 8.4, 2.6 Hz, 3H), 4.89 (d,  $J$  = 13.6 Hz, 3H), 3.76 (d,  $J$  = 13.6 Hz, 3H).

**$^{13}C$  NMR** (151 MHz,  $CDCl_3$ )  $\delta$  190.86, 163.12, 154.08, 141.61, 135.66, 132.08, 131.94, 131.49, 121.72, 119.17, 117.72, 36.78.

**HRMS** (ESI<sup>+</sup>)  $m/z$  calcd for  $C_{42}H_{30}O_6Na$ : 653.1940 [M+Na]<sup>+</sup>, found: 653.1963.

**L2:**

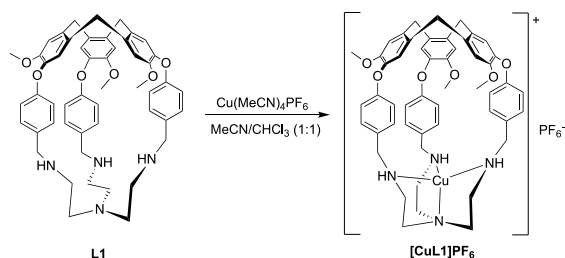
**4** (150 mg, 0.238 mmol, 1.0 equiv.) was added to an oven-dried 250 mL two-neck round bottom flask equipped with a stir bar and a 250 mL pressure-equalizing addition funnel. The reaction vessel was then sealed and purged with argon before 50:50 anhydrous methanol/anhydrous chloroform was added as the reaction solvent (95.2 mL, 0.0025 M). A 0.0055 mM solution of tris(2-aminoethyl)amine (tren) was prepared under argon by dissolving tren (39.2  $\mu$ L, 0.262 mmol, 1.1 equiv.) in 50:50 anhydrous methanol/anhydrous chloroform (48 mL) and was transferred to the addition funnel. Subsequently, the tren solution was added to the reaction flask dropwise over 30 minutes at room temperature and the reaction mixture was allowed to stir overnight. The reaction mixture was cooled down to 0 °C and sodium borohydride was added (270 mg, 7.13 mmol, 30.0 equiv.) while stirring. After 15 minutes, the ice bath was removed, and the reaction mixture was stirred at room temperature for an additional 3 hours. At that point, the reaction mixture was transferred to a 500 mL separatory funnel and 150 mL of 1.0 M sodium hydroxide was added. The contents were shaken, and the chloroform layer was separated. The aqueous layer was extracted further with 2 x 75 mL of chloroform. Lastly, the combined organic layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated *in vacuo*. The resulting residue was then loaded onto two neutral alumina preparatory TLC plates (20x20 cm with a thickness of 1000  $\mu$ m) and the plates were developed using 5:95 methanol/chloroform as the eluent. The desired compound ( $R_f$  = 0.5) was scraped from both plates and the combined scrapings were sonicated with 50 mL of methanol for 15 minutes. The slurry was then filtered, and the filtrate concentrated to near-dryness. In order to remove residual alumina and to ensure that the desired compound is being isolated in its neutral state, the residue was diluted with 50 mL of chloroform (see General Considerations for treatment of chloroform) and transferred to a 250 mL separatory funnel. The chloroform solution was washed with 50 mL of 1.0 M sodium hydroxide, dried over sodium sulphate, and concentrated *in vacuo* to afford the product as an off-white solid (36.4 mg, 21%).

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (d,  $J$  = 8.4 Hz, 3H), 7.17 (d,  $J$  = 2.5 Hz, 3H), 6.89 (d,  $J$  = 8.2 Hz, 6H), 6.76 (dd,  $J$  = 8.3, 2.5 Hz, 3H), 6.30 – 6.24 (m, 6H), 4.90 (d,  $J$  = 13.4 Hz, 3H), 3.80 (d,  $J$  = 13.3 Hz, 3H), 3.55 (d,  $J$  = 12.4 Hz, 3H), 3.44 (d,  $J$  = 12.3 Hz, 3H), 2.78 – 2.57 (m, 8H), 2.40 (dt,  $J$  = 12.3, 3.6 Hz, 3H), 2.05 – 1.78 (m, 8H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  159.72, 153.91, 141.47, 136.67, 133.20, 131.51, 129.26, 124.41, 121.20, 115.00, 55.39, 53.91, 48.48, 36.06.

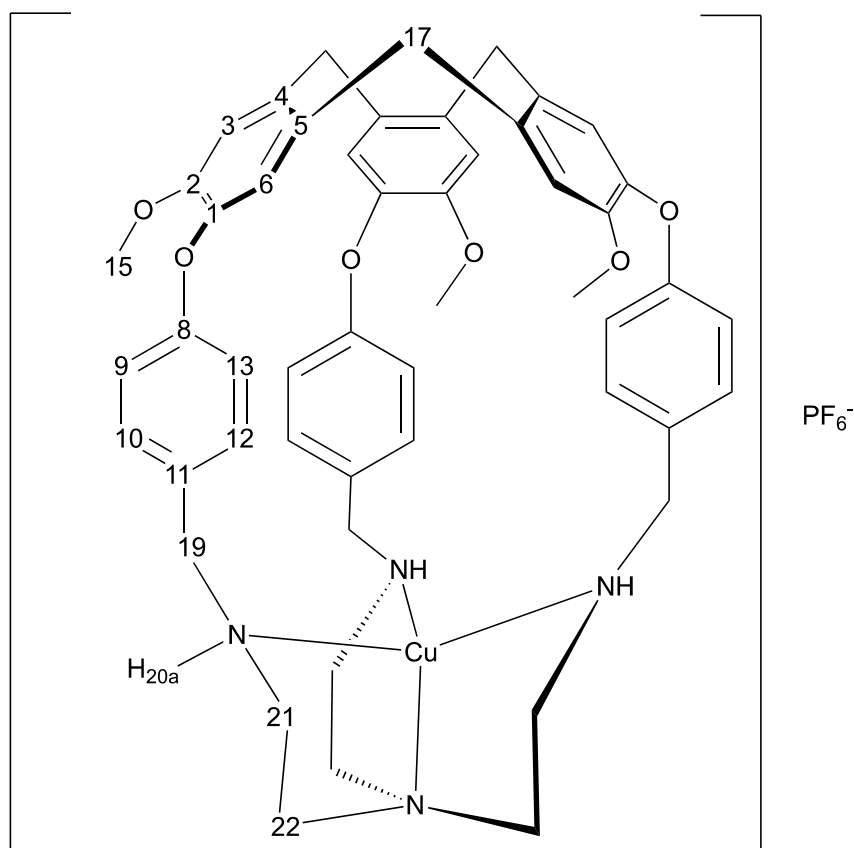
**HRMS** (ESI<sup>+</sup>)  $m/z$  calcd for C<sub>48</sub>H<sub>49</sub>N<sub>4</sub>O<sub>3</sub>: 729.3799 [M+H]<sup>+</sup>, found: 729.3805.

## [CuL1]PF<sub>6</sub>:



To a septum-capped 20 mL reaction vial equipped with a stir bar was added **L1** (42.8 mg, 0.0523 mmol, 1.0 equiv.) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (19.5 mg, 0.0523 mmol, 1.0 equiv.). The vial was then sealed and placed under inert atmosphere by evacuation and back-filling with argon three times. Subsequently, 50:50 anhydrous acetonitrile/anhydrous chloroform was added (5.2 mL, 0.01M) and the reaction mixture was stirred at room temperature for 4 hours. At that point, 20 mL of anhydrous ether was added to the reaction mixture, resulting in the formation of a light green precipitate which was collected via filtration. In our experience, once the reaction was complete, oxidation of copper (I) was no longer a concern and thus filtration could be performed under air. The precipitate was washed with an additional 40 mL of ether and dried under reduced pressure to afford the product as a light green solid (38.8 mg, 72%).

Hydrogens and carbons have been assigned via COSY, HSQC and HMBC 2D NMR spectra according to the numbering system depicted below. Hydrogens on the same carbon are differentiated with the help of letters (e.g. 12a, 12b, etc.).



**<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>CN) δ 7.33 (3H, s, H3a), 7.09 (3H, s, H6a), 6.93 (6H, d, J = 8.6 Hz, H12a and H10a), 6.27 (6H, d, J = 8.6 Hz, H13a and H9a), 4.84 (3H, d, J = 13.5 Hz, H17a), 3.74 (3H, d, J = 13.5 Hz, H17b), 3.61 (3H, d, J = 10.8 Hz, H19a), 3.24 (9H, s, H15a, H15b, and H15c), 3.04 (3H, d, J = 10.6 Hz, H19b), 2.77 – 2.72 (6H, m, H21a and H21b), 2.65 (3H, d, J = 12.9 Hz, H22a), 2.61 – 2.55 (3H, m, H22b).

**<sup>13</sup>C NMR** (151 MHz, CD<sub>3</sub>CN) δ 160.78 (s, C8), 151.39 (s, C2), 142.48 (s, C1), 139.90 (s, C4), 133.68 (s, C5), 132.15 (s, C11), 131.18 (s, C10 and C12), 126.98 (s, C3), 115.14 (s, C6), 115.04 (s, C9 and C13), 56.67 (s, C19), 56.16 (s, C15), 52.14 (s, C22), 51.55 (s, C21), 35.26 (s, C17).

**<sup>31</sup>P NMR** (243 MHz, CD<sub>3</sub>CN) δ -144.65 (hept, J = 707.2 Hz).

**<sup>19</sup>F NMR** (565 MHz, CD<sub>3</sub>CN) δ -72.96 (d, J = 706.2 Hz).

**HRMS** (ESI<sup>+</sup>) m/z calcd for C<sub>51</sub>H<sub>54</sub>CuN<sub>4</sub>O<sub>6</sub>: 881.3339 [cation]<sup>+</sup>, found: 881.3350.

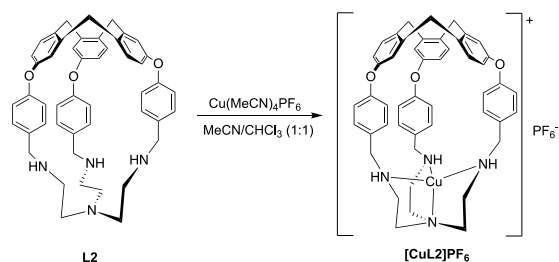
**Table S1** COSY and HMBC data for [CuL1]PF<sub>6</sub>.

No	δ <sub>H</sub>	δ <sub>C</sub>	HMBC	COSY
3a	7.33	-	151.39 (2), 139.90 (4), 35.26 (17)	-
6a	7.09	-	142.48 (1), 151.39 (2), 133.68 (5), 35.26 (17)	-
10a	6.93	-	160.78 (8)	6.27 (9a)
12a	6.93	-	160.78 (8), 56.67 (19)	6.27 (13a)
9a	6.27	-	160.78 (8), 131.18 (10, 12), 115.04 (9, 13)	6.93 (10a)
13a	6.27	-	160.78 (8), 131.18 (10, 12)	6.93 (12a)
17a	4.84	-	139.90 (4), 133.68 (5)	3.74 (17b)
17b	3.74	-	139.90 (4), 133.68 (5)	4.84 (17a)
19a	3.61	-	-	3.04 (19b), 2.74 (21a, 21b)
15a	3.24	-	-	-
15b	3.24	-	151.39 (2)	-
15c	3.24	-	-	-
19b	3.04	-	-	3.61 (19a)
21a	2.74	-	-	3.61 (19a)
21b	2.74	-	-	-
22a	2.65	-	-	-
22b	2.58	-	-	-
8	-	160.78	6.27 (9a, 13a), 6.93 (10a, 12a)	-



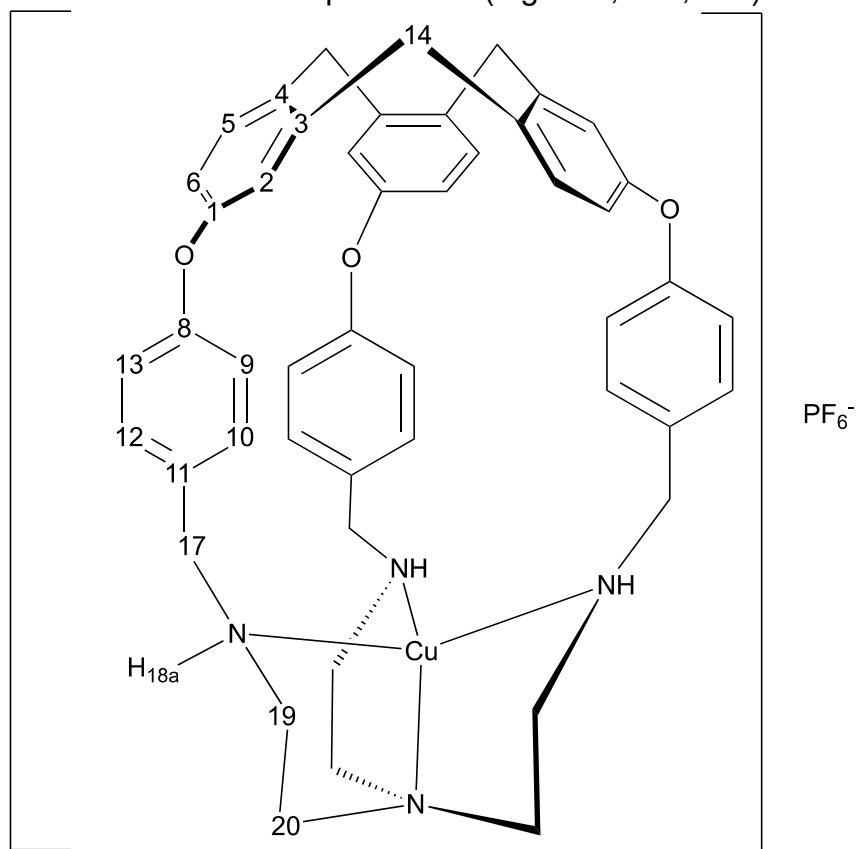
2	-	151.39	7.33 (3a), 7.09 (6a), 15b	-
1	-	142.48	7.09 (6a)	-
4	-	139.90	7.33 (3a), 4.84 (17a), 3.74 (17b)	-
5	-	133.68	7.09 (6a), 4.84 (17a), 3.74 (17b)	-
11	-	132.15	-	-
10	-	131.18	6.27 (9a, 13a)	-
12	-	131.18	6.27 (9a, 13a)	-
3	-	126.98	-	-
6	-	115.14	-	-
9	-	115.04	-	-
13	-	115.04	6.27 (9a)	-
19	-	56.67	6.93 (12a)	-
15	-	56.16	-	-
22	-	52.14	-	-
21	-	51.55	-	-
17	-	35.26	7.33 (3a), 7.09 (6a)	-

## [CuL2]PF<sub>6</sub>:



To a septum-capped 20 mL reaction vial equipped with a stir bar was added **L2** (27.2 mg, 0.0373 mmol, 1.0 equiv.) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (13.9 mg, 0.0373 mmol, 1.0 equiv.) The vial was then sealed and placed under inert atmosphere by evacuation and backfilling with Ar three times. Subsequently, 50:50 anhydrous acetonitrile/anhydrous chloroform was added (3.8 mL, 0.01 M) and the reaction mixture was stirred at rt for 4 h. At that point, 15 mL of anhydrous ether was added to the reaction mixture, resulting in the formation of a light green precipitate which was collected via filtration. In our experience, once the reaction was complete, oxidation of copper(I) was no longer a concern and thus filtration could be done under air. The precipitate was washed with an additional 30 mL of ether and dried under reduced pressure to afford the product as a light green solid (29.1 mg, 83%).

Hydrogens and carbons have been assigned via COSY, HSQC and HMBC 2D NMR spectra according to the numbering system depicted below. Hydrogens on the same carbon are differentiated with the help of letters (e.g. 12a, 12b, etc.).



**<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>CN) δ 7.54 (3H, d, J = 8.4 Hz, H2a), 7.30 (3H, d, J = 2.3 Hz, H5a), 6.90 (6H, d, J = 8.4 Hz, H10a and H12a), 6.71 (3H, dd, J = 8.4, 2.4 Hz, H6a), 6.28 (6H, d, J = 8.5 Hz, H9a and H13a), 4.97 (3H, d, J = 13.4 Hz, H14a), 3.87 (3H, d, J = 13.4 Hz, H14b), 3.60 (3H, d, J = 11.6 Hz, H17a), 3.13 (3H, t, J = 8.8 Hz, H17b), 2.76 – 2.67 (6H, m, H19a and H19b), 2.67 – 2.55 (6H, m, H20a and H20b).

**<sup>13</sup>C NMR** (151 MHz, CD<sub>3</sub>CN) δ 160.93 (s, C8), 154.66 (s, C1), 142.86 (s, C3), 138.50 (s, C4), 132.75 (s, C2), 132.46 (s, C11), 131.16 (s, C10 and C12), 125.65 (s, C5), 121.29 (s, C6), 115.79 (s, C9 and C13), 56.37 (s, C17), 52.81 (s, C20), 51.32 (s, C19), 35.82 (s, C14).

**<sup>31</sup>P NMR** (243 MHz, CD<sub>3</sub>CN) δ -144.62 (hept, J = 706.5 Hz).

**<sup>19</sup>F NMR** (565 MHz, CD<sub>3</sub>CN) δ -72.87 (d, J = 706.6 Hz).

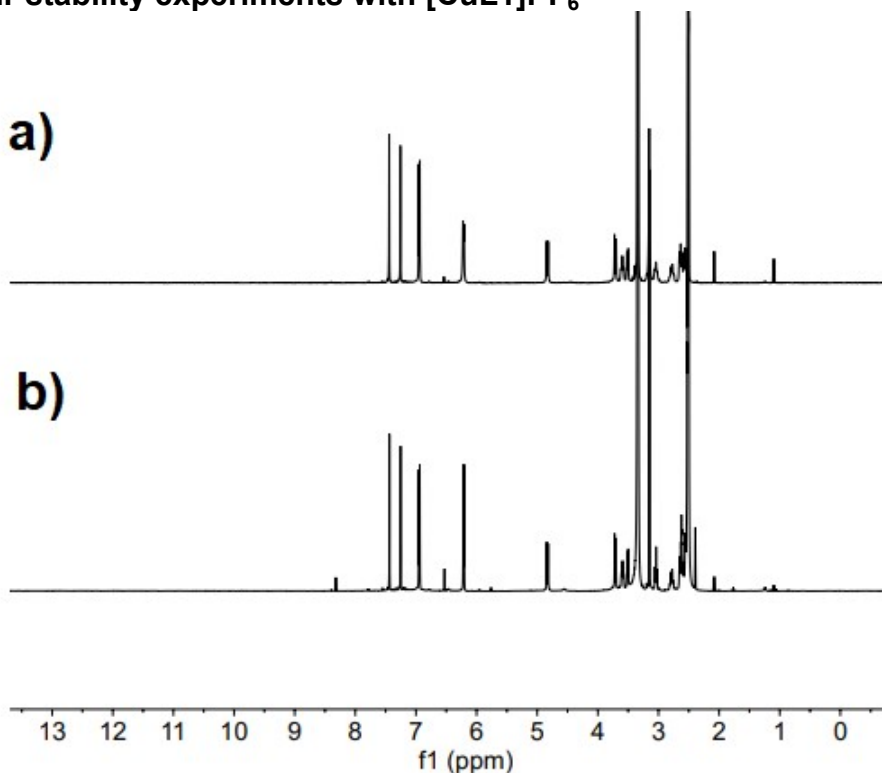
**HRMS** (ESI<sup>+</sup>): m/z calcd for C<sub>48</sub>H<sub>48</sub>CuN<sub>4</sub>O<sub>3</sub>: 791.3022 [cation]<sup>+</sup>, found 791.3010.

**Table S2** COSY and HMBC data for [CuL2]PF<sub>6</sub>.

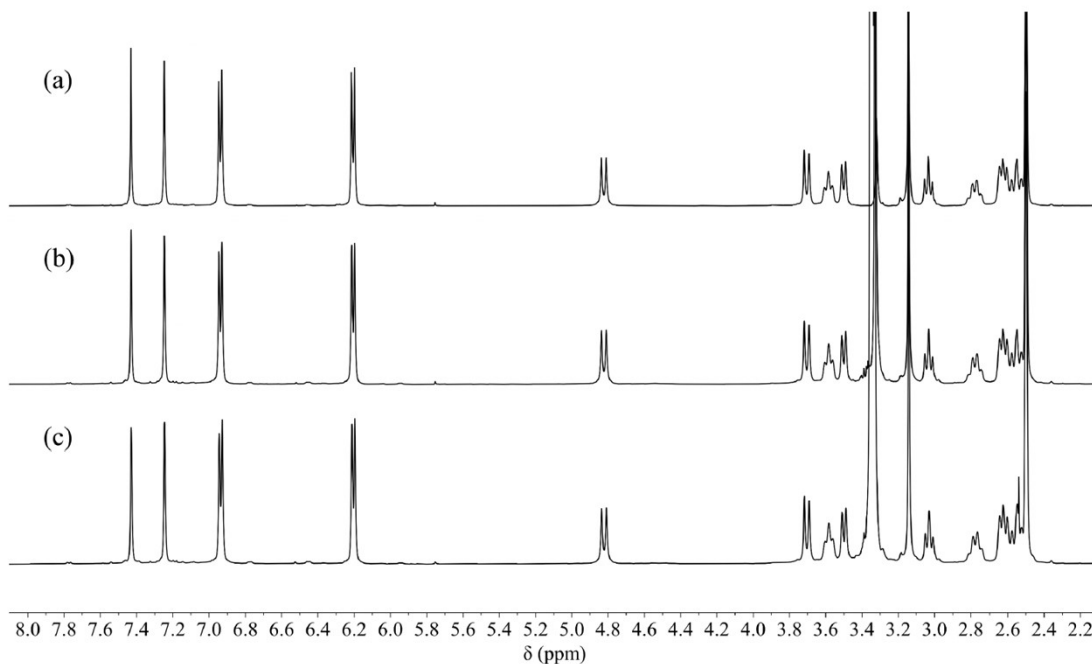
No	δ <sub>H</sub>	δ <sub>C</sub>	HMBC	COSY
2a	7.54	-	-	-
5a	7.30	-	34.8 (14), 120.3 (6), 137.5 (4), 153.7 (1)	-
10a	6.90	-	-	6.28 (9a)
12a	6.90	-	-	6.28 (13a)
6a	6.71	-	124.7 (5), 137.5 (4), 153.7 (1)	-
9a	6.28	-	-	6.90 (10a)
13a	6.28	-	-	6.90 (12a)
14b	4.97	-	124.7 (5), 131.8 (2), 137.5 (4), 141.9 (3), 153.7 (1)	3.87 (14a)
14a	3.87	-	124.7 (5), 131.8 (2), 137.5 (4), 141.9 (3)	4.97 (14b)
17b	3.60	-	50.3 (19)	3.12 (17a)
17a	3.12	-	-	3.60 (17b)
19a	2.71	-	-	-
19b	2.71	-	-	-
20a	2.61	-	-	-
20b	2.61	-	-	-
4	-	137.5	3.87 (14a), 4.97 (14b), 6.71 (6a), 7.30 (5a)	-
3	-	141.9	3.87 (14a), 4.97 (14b)	-
2	-	131.8	3.87 (14a), 4.97 (14b)	-
1	-	153.7	4.97 (14b), 6.71 (6a), 7.30 (5a)	-

6	-	120.3	7.30 (5a)	-
5	-	124.7	3.87 (14a), 4.97 (14b), 6.71 (6a)	-
14	-	34.8	7.30 (5a)	-
9	-	114.8	-	-
10	-	130.2	-	-
12	-	130.2	-	-
13	-	114.8	-	-
17	-	55.4	-	-
19	-	50.3	3.60 (17b)	-
20	-	51.8	-	-

**Air stability experiments with [CuL1]PF<sub>6</sub>**

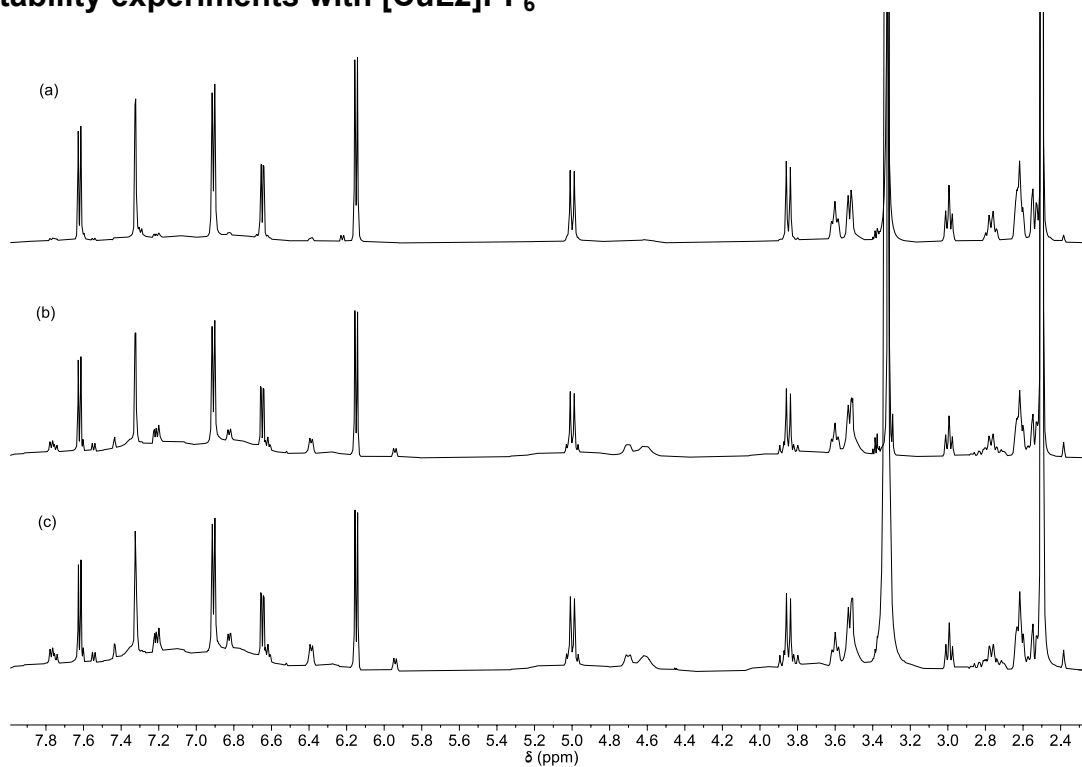


**Fig. S2** <sup>1</sup>H NMR spectra (500 MHz, DMSO-d<sub>6</sub>) of (a) a sample of [CuL1]PF<sub>6</sub> stored as a solid under air (b) an NMR sample made from the same solid sample 7 months later



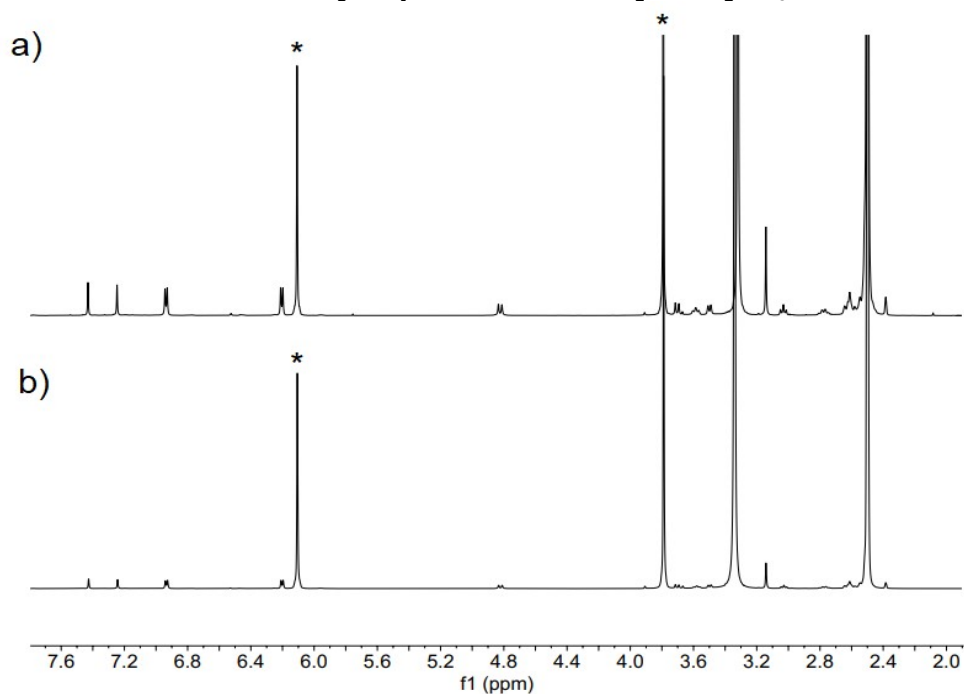
**Fig. S3** <sup>1</sup>H NMR spectra (500 MHz, DMSO-d<sub>6</sub>) of [CuL1]PF<sub>6</sub> before (a) and after (b) air exposure for two weeks, followed by air bubbling (c) for 1 hour.

### Air stability experiments with $[\text{CuL2}]\text{PF}_6$

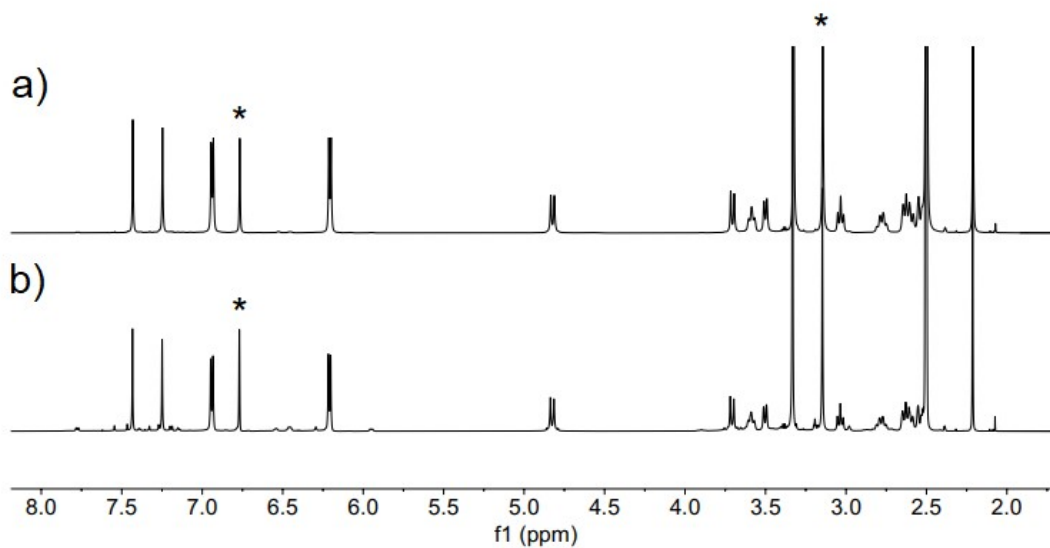


**Fig. S4**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{DMSO-d}_6$ ) of  $[\text{CuL2}]\text{PF}_6$  before (a) and after (b) air exposure for two weeks, followed by air bubbling (c) for 1 hour.

Standardized air stability experiments with  $[\text{CuL1}]\text{PF}_6$

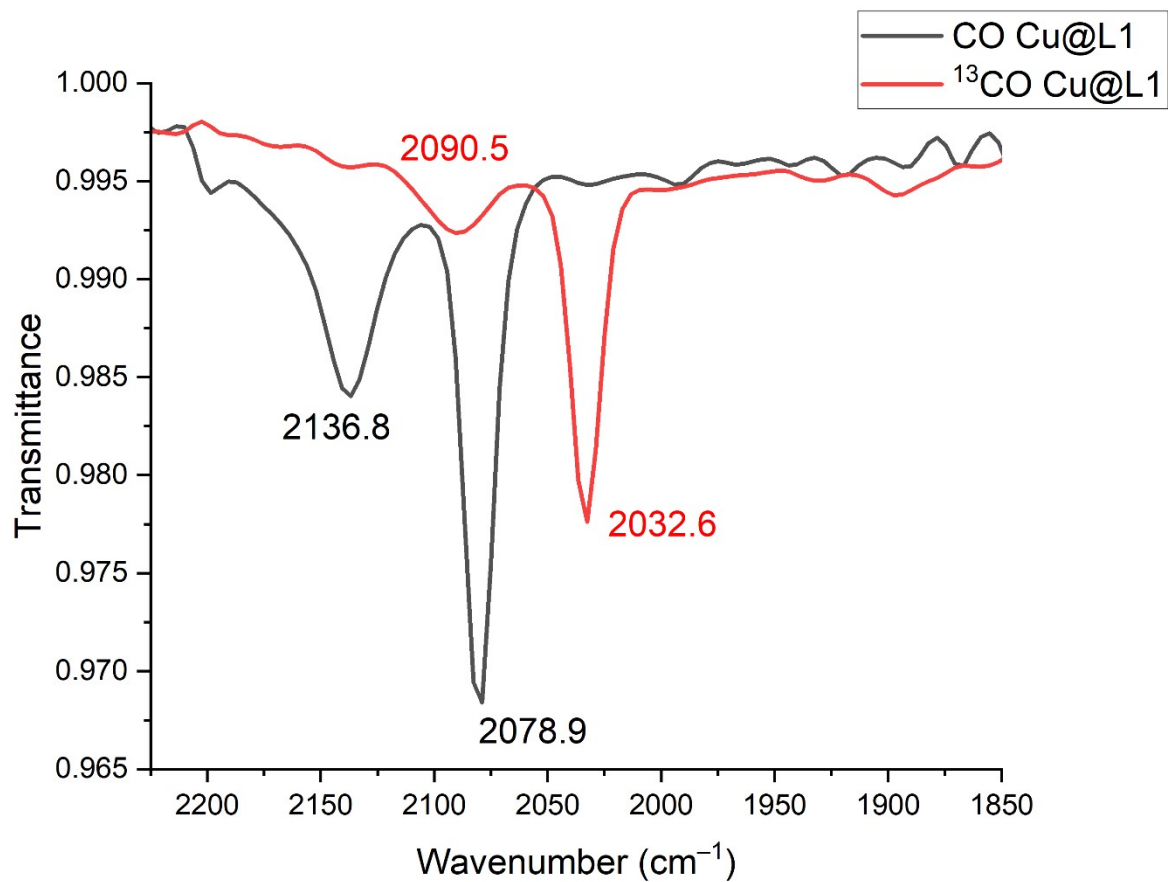


**Fig. S5**  $^1\text{H}$  NMR spectra (600 MHz, DMSO- $d_6$ ) of  $[\text{CuL1}]\text{PF}_6$  before (a) and after (b) bubbling with oxygen for 1 hour. Peaks marked with an asterisk (\*) belong to sulfolene as internal standard.



**Fig. S6**  $^1\text{H}$  NMR spectra (600 MHz, DMSO- $d_6$ ) of  $[\text{CuL1}]\text{PF}_6$  before (a) and after (b) air exposure for two weeks. Peaks marked with an asterisk (\*) belong to mesitylene as internal standard.

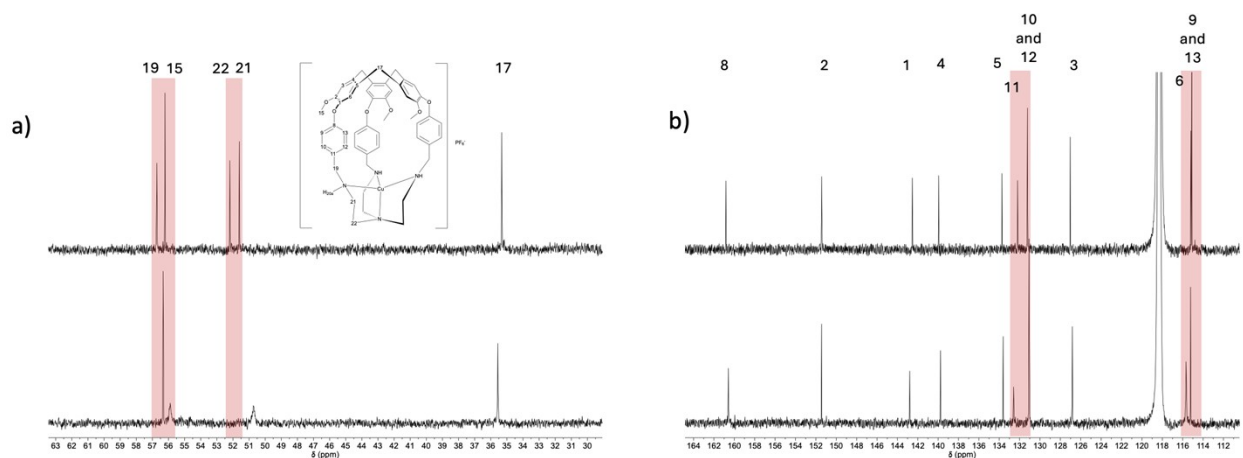
# IR



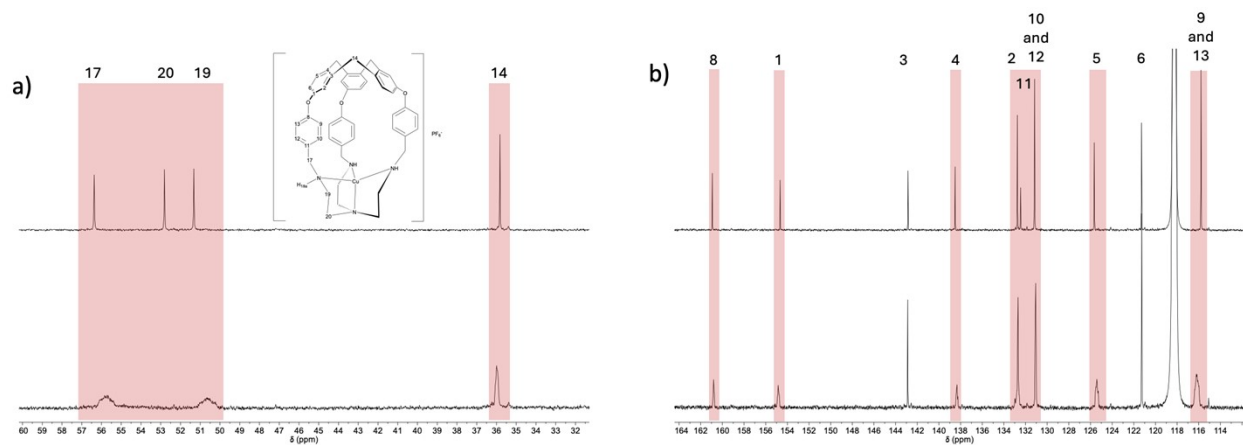
**Fig. S7** IR spectra of **[CuL1]PF<sub>6</sub>** (a) under 14 psi non-isotopically labelled CO (grey) and (b) under 14 psi of <sup>13</sup>C-labelled CO (red).



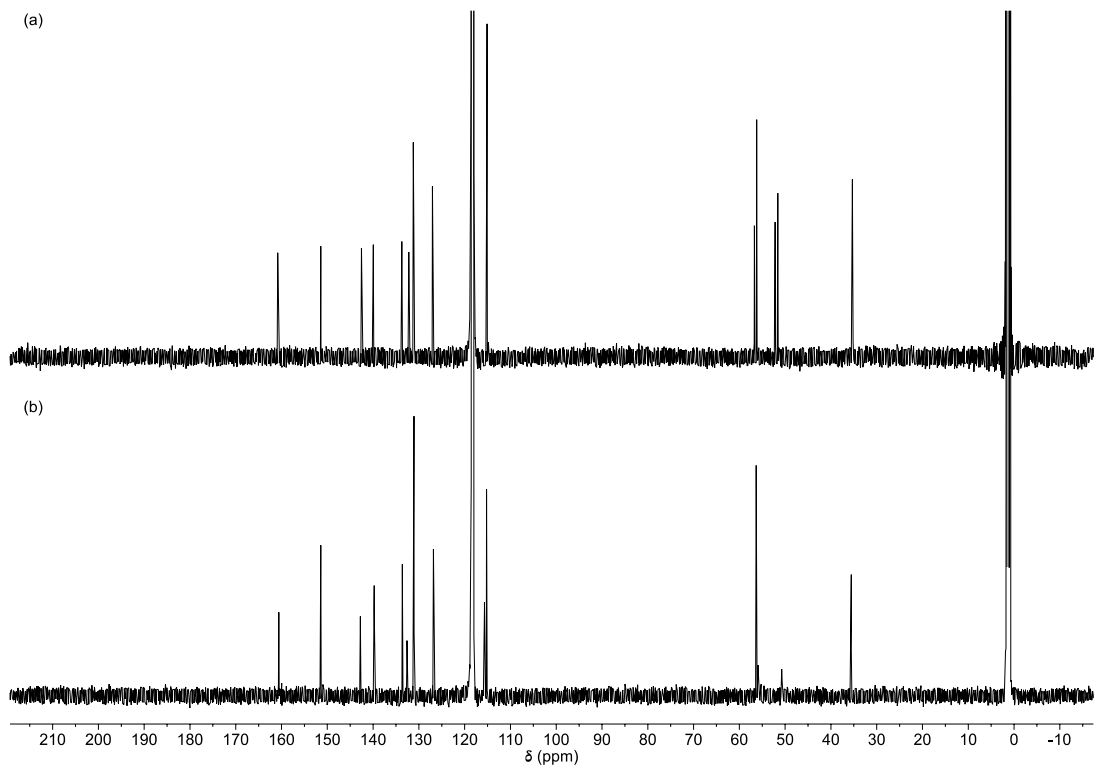
## $^{13}\text{C}$ NMR spectra of $[\text{CuL1}]\text{PF}_6$ and $[\text{CuL2}]\text{PF}_6$ under carbon monoxide



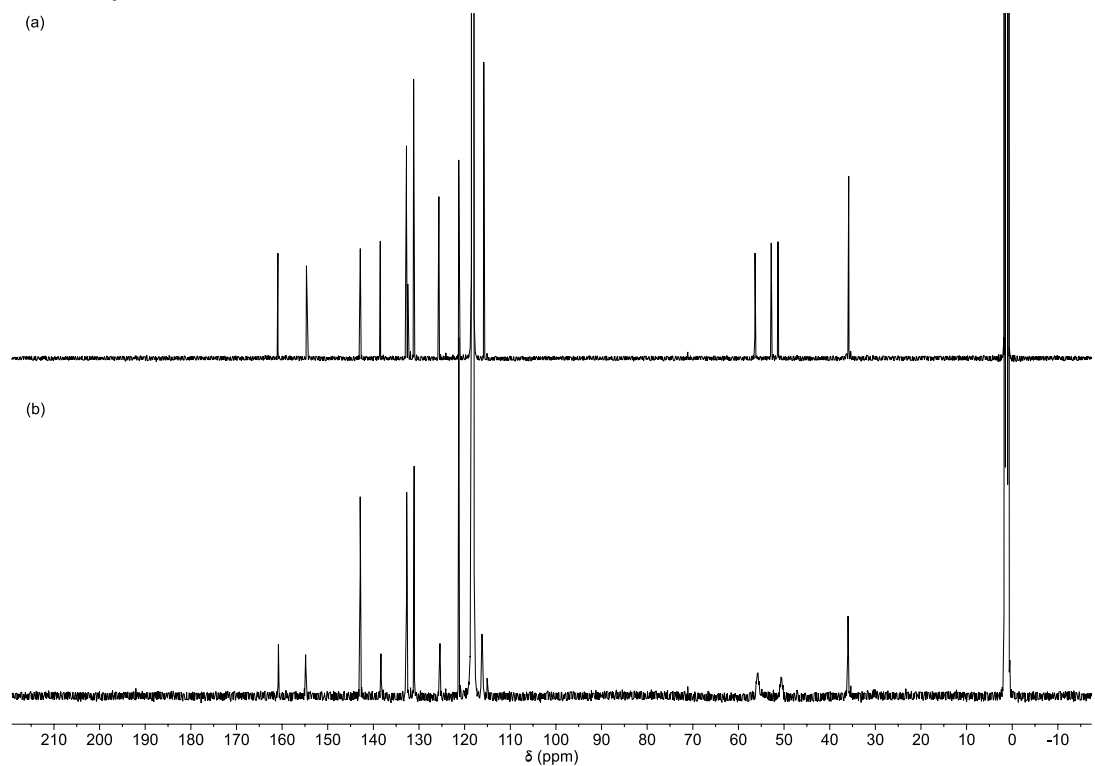
**Fig. S8**  $^{13}\text{C}$  NMR spectra (500 MHz,  $\text{CD}_3\text{CN}$ ) of  $[\text{CuL1}]\text{PF}_6$  zoomed in; (a) from 30 to 65 ppm and (b) from 110 to 165 ppm. Top: under air, bottom: under CO. Peaks that experience movement or broadening have been highlighted.



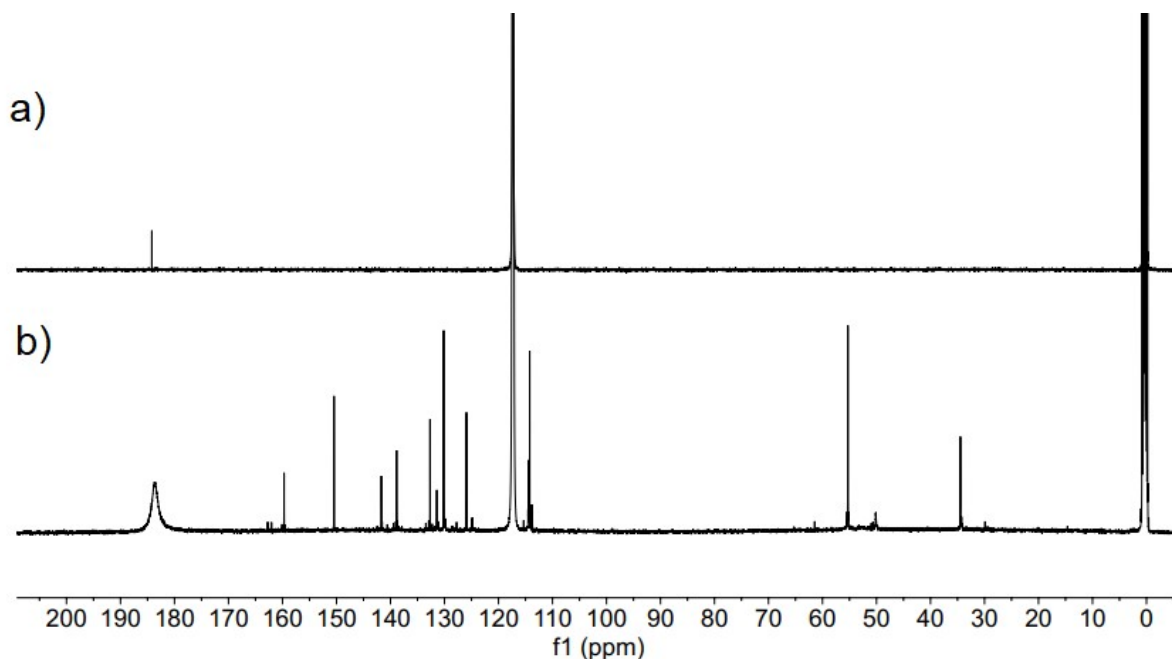
**Fig. S9**  $^{13}\text{C}$  NMR spectra (500 MHz,  $\text{CD}_3\text{CN}$ ) of  $[\text{CuL2}]\text{PF}_6$  zoomed in; (a) from 30 to 65 ppm and (b) from 110 to 165 ppm. Top: under air, bottom: under CO. Peaks that experience movement or broadening have been highlighted.



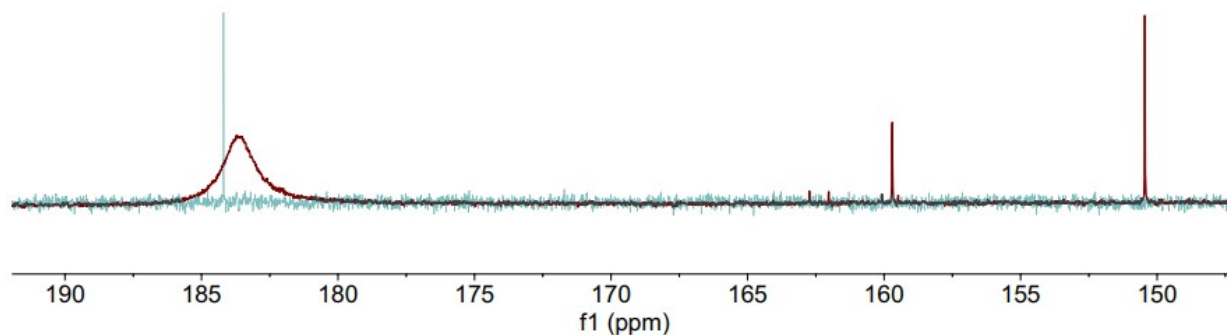
**Fig. S10**  $^{13}\text{C}$  NMR spectra (500 MHz,  $\text{CD}_3\text{CN}$ ) of  $[\text{CuL1}]\text{PF}_6$ ; full spectra. (a) Under air, (b) under 20 psi of  $\text{CO}$ .



**Fig. S11**  $^{13}\text{C}$  NMR spectra (500 MHz,  $\text{CD}_3\text{CN}$ ) of  $[\text{CuL2}]\text{PF}_6$ ; full spectra. (a) Under air, (b) under 20 psi of  $\text{CO}$ .

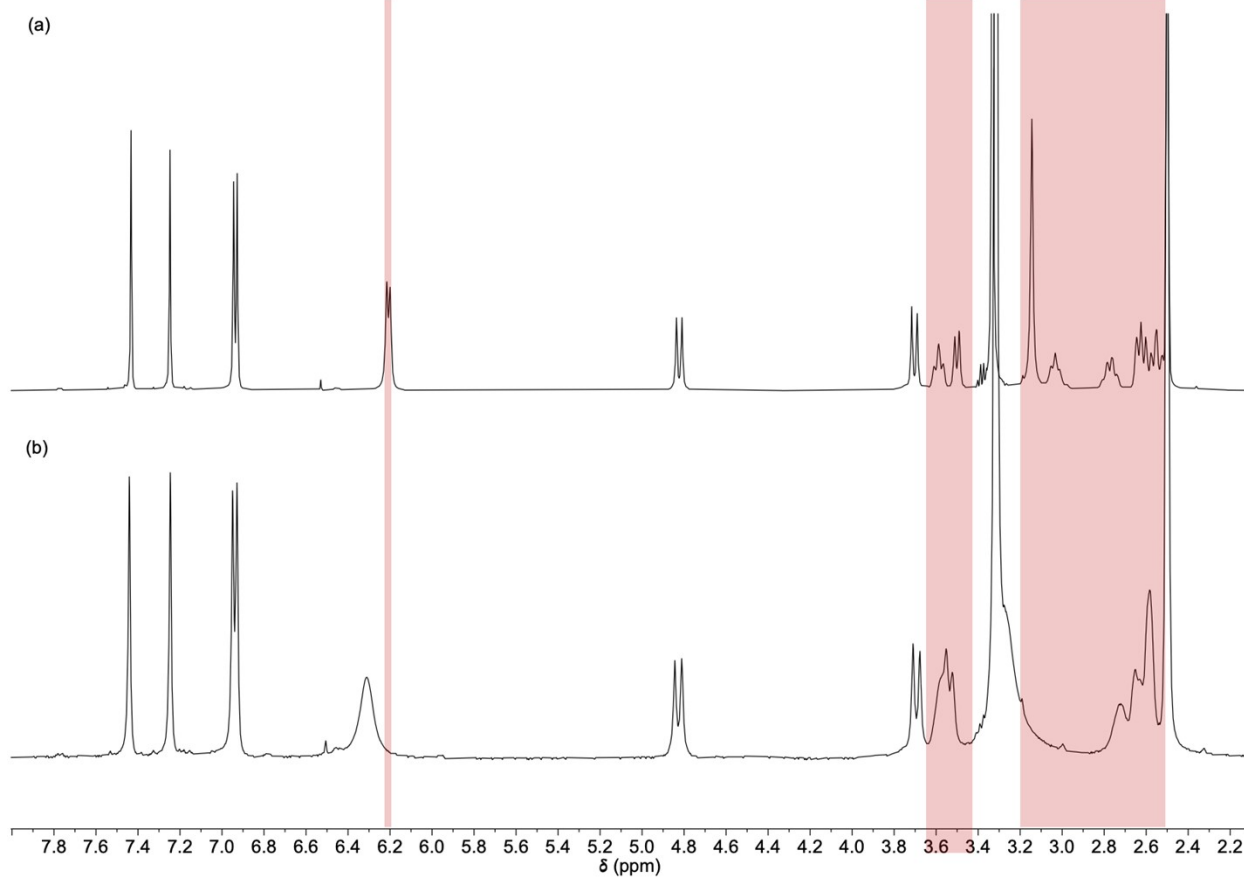


**Fig. S12**  $^{13}\text{C}$  NMR spectra (500 MHz,  $\text{CD}_3\text{CN}$ ) under 20 psi of  $^{13}\text{C}$ -labeled CO; full spectra. (a)  $^{13}\text{CO}$  alone, (b)  $[\text{CuL1}]\text{PF}_6$  under 20 psi of  $^{13}\text{C}$ -labeled CO.



**Fig. S13**  $^{13}\text{C}$  NMR spectra (500 MHz,  $\text{CD}_3\text{CN}$ ) under 20 psi of  $^{13}\text{C}$ -labeled CO; zoomed in and superimposed to demonstrate shift and broadening of  $^{13}\text{CO}$  peak. Blue:  $^{13}\text{CO}$  alone, maroon:  $[\text{CuL1}]\text{PF}_6$  under 20 psi of  $^{13}\text{C}$ -labeled CO.

# $^1\text{H}$ NMR spectrum of $[\text{CuL1}]\text{PF}_6$ under carbon monoxide in $\text{DMSO-d}_6$

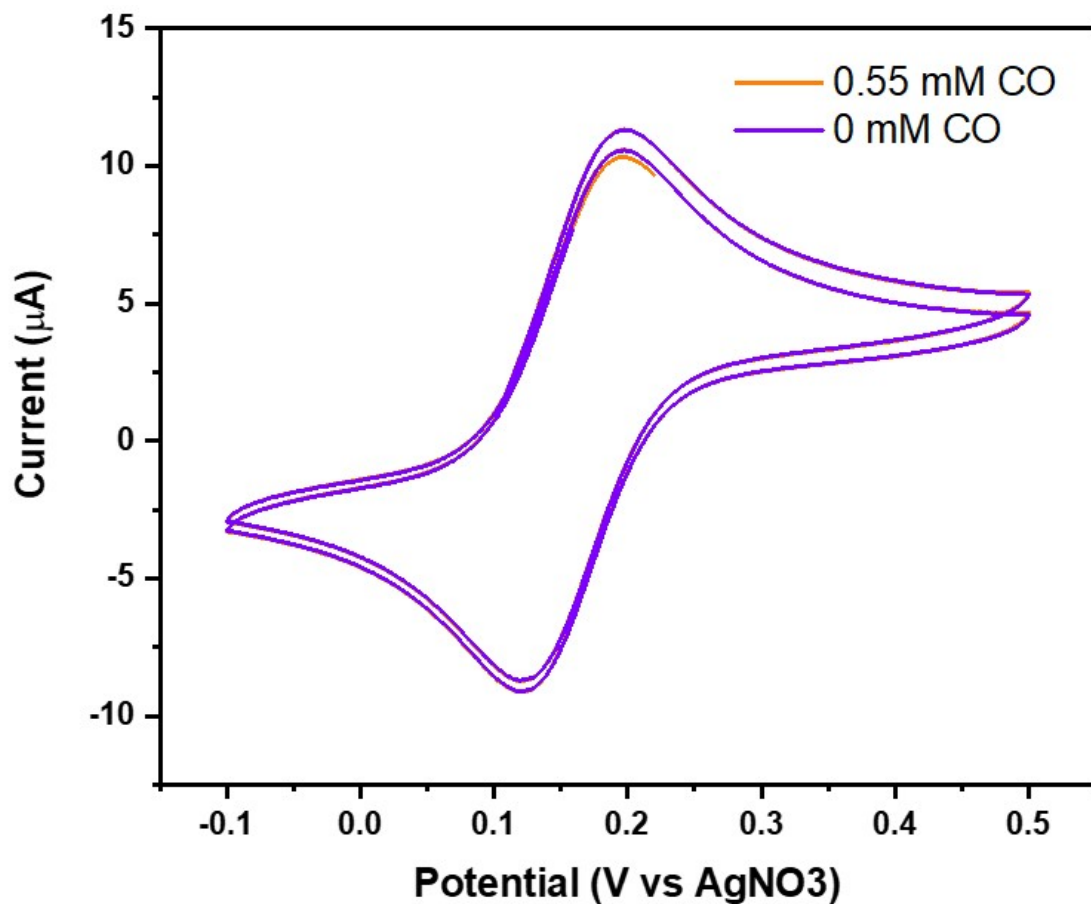


**Fig. S14**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{DMSO-d}_6$ ) of  $[\text{CuL1}]\text{PF}_6$  (a) under air and (b) under 14 psi of CO. Peaks that experience movement or broadening have been highlighted.

## Cyclic Voltammetry

All cyclic voltammetry (CV) experiments were performed using a Metrohm Autolab PGSTAT302N bipotentiostat at 20 °C. A glassy carbon working electrode, platinum mesh counter electrode, and Ag/AgNO<sub>3</sub> non-aqueous reference electrode were used for all voltammograms. Measurements were conducted in a homemade cell containing 5 mL of the sample solution. All measurements were conducted in anhydrous dimethylsulfoxide (DMSO) with an analyte concentration of 1 mM in presence of 250 mM of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte. Anhydrous DMSO used for electrochemical measurements was purchased from Thermo Scientific Chemicals and was maintained under an inert atmosphere. TBAPF<sub>6</sub> was used after 3x recrystallization. All scans were conducted at a rate of 100 mV/s unless indicated otherwise.

**Cyclic Voltammetry experiments in Presence of Carbon Monoxide:** Prior to the first CV, the solution was degassed with pure N<sub>2</sub> for 30 minutes via a pre-bubbler filled with anhydrous DMSO. An initial CV was taken under the pure N<sub>2</sub> atmosphere. Then, the gas mixture was tuned to 1% CO in N<sub>2</sub> using an Alicat Scientific MC-100 mass flow controller. The solution was purged with this new gas composition for 20 min to ensure adequate equilibration. During this time, the Ag/AgNO<sub>3</sub> reference electrode was removed from the cell and replaced in a stock solution of 250 mM TBAPF<sub>6</sub> and 10 mM AgNO<sub>3</sub> to avoid significant drift. After the 20-min purge, another CV was taken. While CVs were performed, the purge needle was withdrawn into the headspace to avoid convection from bubbling while also preventing air from entering the cell. This same procedure was followed for compositions of 5%, 10%, 15%, 25%, 50%, and 100% CO.<sup>6</sup> Similar experiments were performed using a Ferrocene/Ferrocenium redox couple to a) calibrate the reference electrode and b) demonstrate no change in voltammetry with CO concentration (**Figure S14**). The concentration of carbon monoxide in the solution was calculated using the reported solubility value of 1.1 mM at 20 °C for carbon monoxide in DMSO.<sup>7</sup> We corroborated this solubility value using <sup>13</sup>C NMR experiments.



**Fig. S15** Cyclic Voltammetry of Fc/Fc<sup>+</sup> redox couple in DMSO with 0 mM CO (purple) and 0.55 mM CO (orange). Ag/AgNO<sub>3</sub> reference electrode, glassy carbon working electrode, Pt mesh counter electrode, 250 mM TBAPF<sub>6</sub> supporting electrolyte, 50 mV/s scan rate.

## Cavity Analysis

Cavity surfaces for host molecules were calculated from the crystal structures using MoloVol v1.1.1.<sup>8</sup> A two probe algorithm was used where the large probe radius was set to 3.0 Å and the small probe radius was set to 1.2 Å for **[CuL1(MeCN)](OTf)<sub>2</sub>** and **[CuL1(N<sub>3</sub>)](OTf)<sub>2</sub>** and 0.6 Å for **[CuL1]PF<sub>6</sub>**. A grid resolution of 0.1 Å was used in all cases. The generated cavity surfaces were visualized and overlaid with the crystal structures in PyMol. For ligand-included structures, the ligand was removed prior to the cavity surface mapping. In all cases, counterions and co-crystallised solvent molecules were removed before the cavity surface mapping.

## X-Ray Crystallography

### [CuL1]PF<sub>6</sub>

Single crystals suitable for X-ray diffraction were obtained for [CuL1]PF<sub>6</sub> by vapour diffusion of ether into acetonitrile. A suitable single crystal was then mounted in inert oil and transferred to the gas stream of the diffractometer. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at a temperature of 100 K. Preliminary indexing was performed from a series of thirty-six  $0.5^\circ$  rotation frames with exposures of 10 s. A total of 3015 frames were collected with a crystal to detector distance of 37.8 mm, rotation widths of  $0.5^\circ$  and exposures of 20 s. Rotation frames were integrated using CrysAlisPro (Rigaku Oxford Diffraction, version 1.171.40.53, 2019). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS v2014/5<sup>9</sup> (minimum and maximum transmission 0.7024, 0.7456). The structure was solved with ShelXS-1997<sup>10</sup> and refined (using all reflections) with SHELXL-2018.<sup>11</sup>

**Table S3** Crystallographic data and structure refinement for [CuL1]PF<sub>6</sub>.

<b>Identification code</b>	<b>CCDC-2359098</b>
Empirical formula	C <sub>54</sub> H <sub>60.7</sub> CuF <sub>6</sub> N <sub>4.4</sub> O <sub>6.55</sub> P
Formula weight	1084.68
Temperature (K)	100
Crystal system	triclinic
Space group	P-1
<i>a</i> (Å)	11.8395(6)
<i>b</i> (Å)	14.4553(7)
<i>c</i> (Å)	15.7362(8)
$\alpha$ (°)	70.349(2)
$\beta$ (°)	82.732(2)
$\gamma$ (°)	88.868(2)
Volume (Å <sup>3</sup> )	2515.2(2)
Z	2
$d_{\text{calc}}$ (g/cm <sup>3</sup> )	1.432
$\mu$ (mm <sup>-1</sup> )	0.545
F(000)	1132.0
Crystal size, mm	0.2 × 0.15 × 0.08
2 $\theta$ range for data collection (°)	2.77 - 55.102
Index ranges	-15 ≤ <i>h</i> ≤ 15, -12 ≤ <i>k</i> ≤ 18, -20 ≤ <i>l</i> ≤ 20
Reflections collected	84884
Independent reflections	11588 [R <sub>int</sub> = 0.0304]
Data/restraints/parameters	11588/898/979
Goodness-of-fit on F <sup>2</sup>	1.030
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0508, wR <sub>2</sub> = 0.1329
Final R indexes [all data]	R <sub>1</sub> = 0.0665, wR <sub>2</sub> = 0.1429



Largest diff. peak/hole (eÅ <sup>-3</sup> )	1.08/-0.92
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### [CuL1(MeCN)](OTf)<sub>2</sub>

**L1** was crystallised in presence of Cu(OTf)<sub>2</sub> to afford single crystals of [CuL1(MeCN)](OTf)<sub>2</sub> suitable for X-ray diffraction analysis according to the procedure that follows: **L1** (1.0 equiv.) and Cu(OTf)<sub>2</sub> (1.0 equiv.) were stirred for 45 min in 2:1 acetonitrile/chloroform (10 mM). Subsequently the solution was concentrated, dissolved in minimal acetonitrile, filtered through a cotton plug to remove particulates and subjected to vapor diffusion by ether. A suitable single crystal was then mounted in inert oil and transferred to the gas stream of the diffractometer. X-ray intensity data were collected on a Bruker D8QUEST CMOS area detector employing graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at a temperature of 100K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. A total of 538 frames were collected with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 30 seconds. Rotation frames were integrated using SAINT (Bruker-AXS, version 8.38A, 2014). The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS v2016/2<sup>9</sup> (minimum and maximum transmission 0.6672, 0.7456). The structure was solved with ShelXT<sup>11</sup> and refined (using all reflections) with SHELXL-2018.<sup>11</sup>

**Table S4** Crystallographic data and structure refinement for [CuL1(MeCN)](OTf)<sub>2</sub>.

<b>Identification code</b>	<b>CCDC-2359099</b>
Empirical formula	C <sub>62</sub> H <sub>69.5</sub> CuF <sub>6</sub> N <sub>7.5</sub> O <sub>12.5</sub> S <sub>2</sub>
Formula weight	1361.41
Temperature (K)	100
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	15.4717(5)
<i>b</i> (Å)	18.0548(7)
<i>c</i> (Å)	22.9196(7)
Volume (Å <sup>3</sup> )	6402.3(4)
<i>Z</i>	4
$d_{\text{calc}}$	1.412 g/cm <sup>3</sup>
$\mu$	0.491 mm <sup>-1</sup>
<i>F</i> (000)	2836.0
Crystal size, mm	0.24 × 0.19 × 0.11
2 $\theta$ range for data collection (°)	4.966 - 55.044
Index ranges	-20 ≤ <i>h</i> ≤ 19, -23 ≤ <i>k</i> ≤ 23, -29 ≤ <i>l</i> ≤ 29
Reflections collected	76202
Independent reflections	14690 [R <sub>int</sub> = 0.0510]
Data/restraints/parameters	14690/820/996
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.052
Final R indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0432, wR <sub>2</sub> = 0.1041
Final R indexes [all data]	R <sub>1</sub> = 0.0555, wR <sub>2</sub> = 0.1119

Largest diff. peak/hole (eÅ <sup>-3</sup> )	0.70/-0.62
Flack parameter	0.007(3)

### [CuL1(N<sub>3</sub>)](OTf)<sub>2</sub>

**L1** was crystallised in presence of Cu(OTf)<sub>2</sub> and tetrabutylammonium azide to afford single crystals of [CuL1(N<sub>3</sub>)](OTf)<sub>2</sub> suitable for X-ray diffraction analysis according to the procedure that follows: **L1** (1.0 equiv.) and Cu(OTf)<sub>2</sub> (1.0 equiv.) were stirred for 45 min in 2:1 acetonitrile/chloroform (10 mM). Subsequently, the solution was concentrated, and solid tetrabutylammonium azide (1.0 eq.) was added before dissolving in minimal isobutyronitrile. The solution was then filtered through a cotton plug to remove particulates and subjected to vapor diffusion by ether. A suitable single crystal was then mounted in inert oil and transferred to the gas stream of the diffractometer. X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S HPC area detector (Dectris PILATUS3 R 200K), employing confocal multilayer optic-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at a temperature of 100 K. Preliminary indexing was performed from a series of thirty 0.5° rotation frames with exposures of 2.5 s. A total of 1116 frames (10 runs) were collected employing  $\omega$  scans with a crystal to detector distance of 34.000 mm, rotation widths of 0.5° and exposures of 15 s. Rotation frames were integrated using CrysAlisPro (Rigaku Oxford Diffraction, version 1.171.40.53, 2019). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK (Oxford Diffraction, version 1.0.7, 2005) (minimum and maximum transmission 0.82343, 1.00000). The structure was solved with ShelXT<sup>11</sup> and refined (using all reflections) with SHELXL-2018.<sup>11</sup>

**Table S5.** Crystallographic data and structure refinement for [CuL1(N<sub>3</sub>)](OTf)<sub>2</sub>.

<b>Identification code</b>	<b>CCDC-2359100</b>
Empirical formula	C <sub>56</sub> H <sub>61</sub> CuF <sub>3</sub> N <sub>8</sub> O <sub>9</sub> S
Formula weight	1142.72
Temperature/K	100
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
<i>a</i> (Å)	18.0509(4)
<i>b</i> (Å)	16.2265(2)
<i>c</i> (Å)	20.4026(5)
$\beta$ (°)	115.111(3)
Volume (Å <sup>3</sup> )	5411.2(2)
<i>Z</i>	4
$d_{\text{calc}}$	1.403 g/cm <sup>3</sup>
$\mu$	0.517 mm <sup>-1</sup>
<i>F</i> (000)	2388.0
Crystal size, mm	0.3 × 0.13 × 0.1
2 $\theta$ range for data collection (°)	4.694 - 54.964
Index ranges	-23 ≤ <i>h</i> ≤ 23, -19 ≤ <i>k</i> ≤ 21, -26 ≤ <i>l</i> ≤ 26
Reflections collected	101561

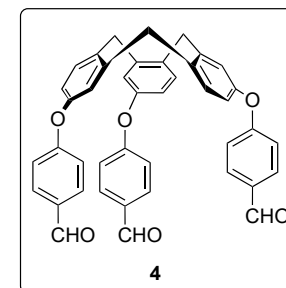
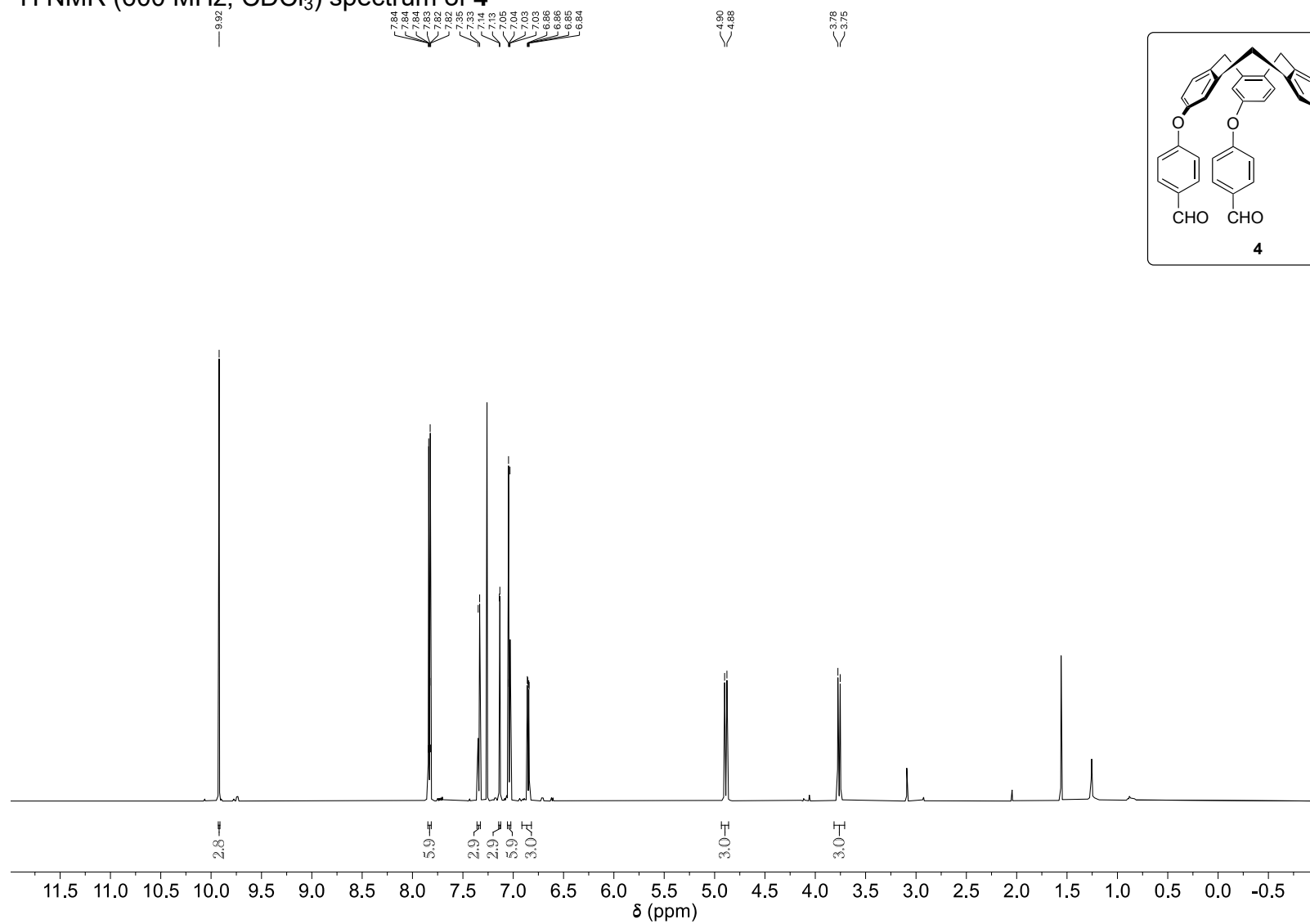
Independent reflections	12400 [ $R_{\text{int}} = 0.0459$ ]
Data/restraints/parameters	12400/66/735
Goodness-of-fit on $F^2$	1.047
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0403$ , $wR_2 = 0.0969$
Final R indexes [all data]	$R_1 = 0.0474$ , $wR_2 = 0.0998$
Largest diff. peak/hole ( $\text{e}\text{\AA}^{-3}$ )	0.90/-0.70

## References

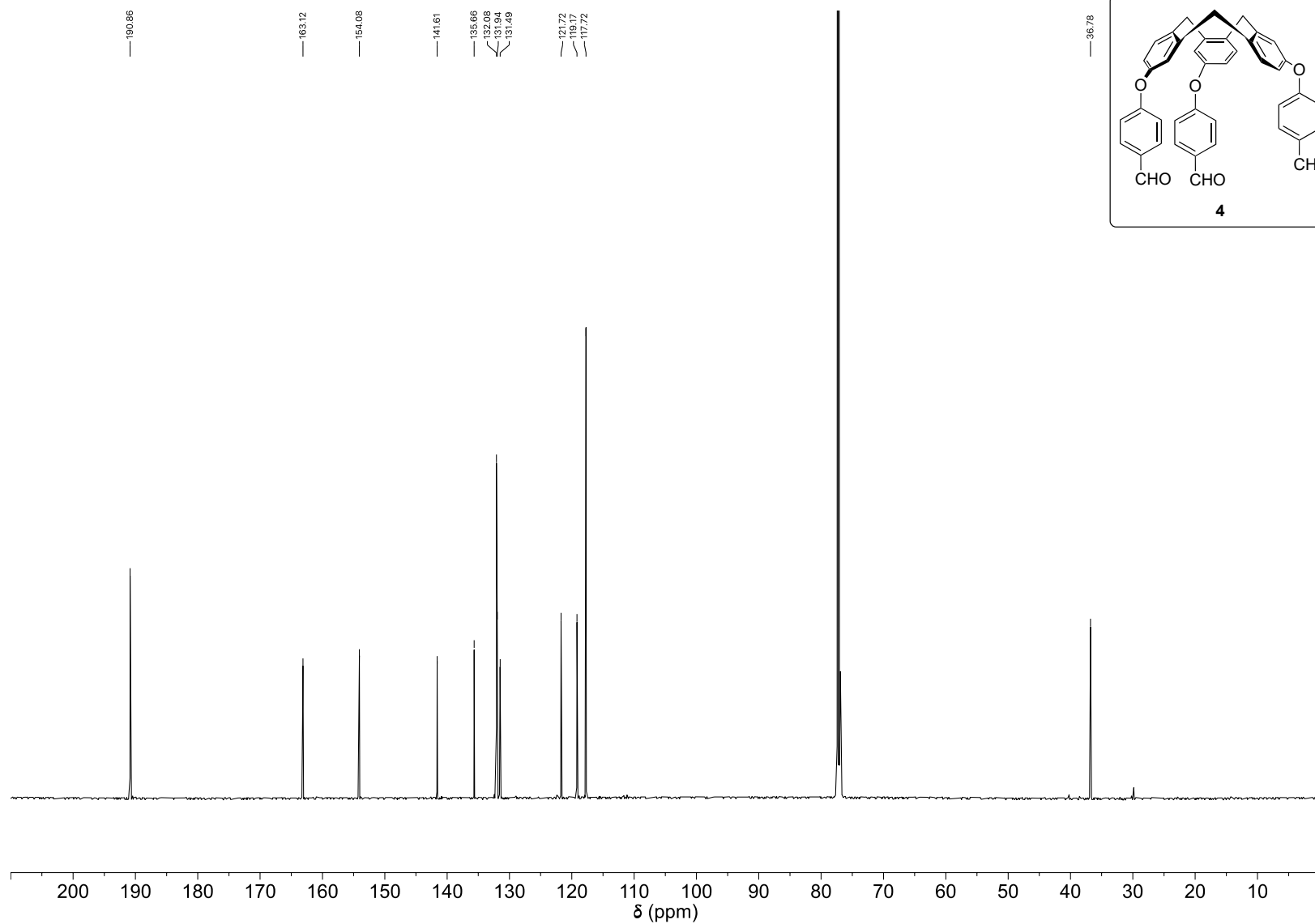
- 1 A. M. Borys, *Organometallics*, 2023, **42**, 182–196.
- 2 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512–7515.
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- 5 O. Della-Negra, Y. Cirillo, T. Brotin, J.-P. Dutasta, P.-L. Saaidi, B. Chatelet and A. Martinez, *Chem. Commun.*, 2022, **58**, 3330–3333.
- 6 W. D. Johnsen, M. Deegbey, D. C. Grills, D. E. Polyansky, K. I. Goldberg, E. Jakubikova and T. E. Mallouk, *Inorg. Chem.*, 2023, **62**, 9146–9157.
- 7 C. Ercolani, F. Monacelli, G. Pennesi, G. Rossi, E. Antonini, P. Ascenzi and M. Brunori, *J. Chem. Soc., Dalton Trans.*, 1981, 1120–1123.
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- 10 G. M. Sheldrick, *Acta Cryst A*, 2008, **64**, 112–122.
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# NMR Spectra

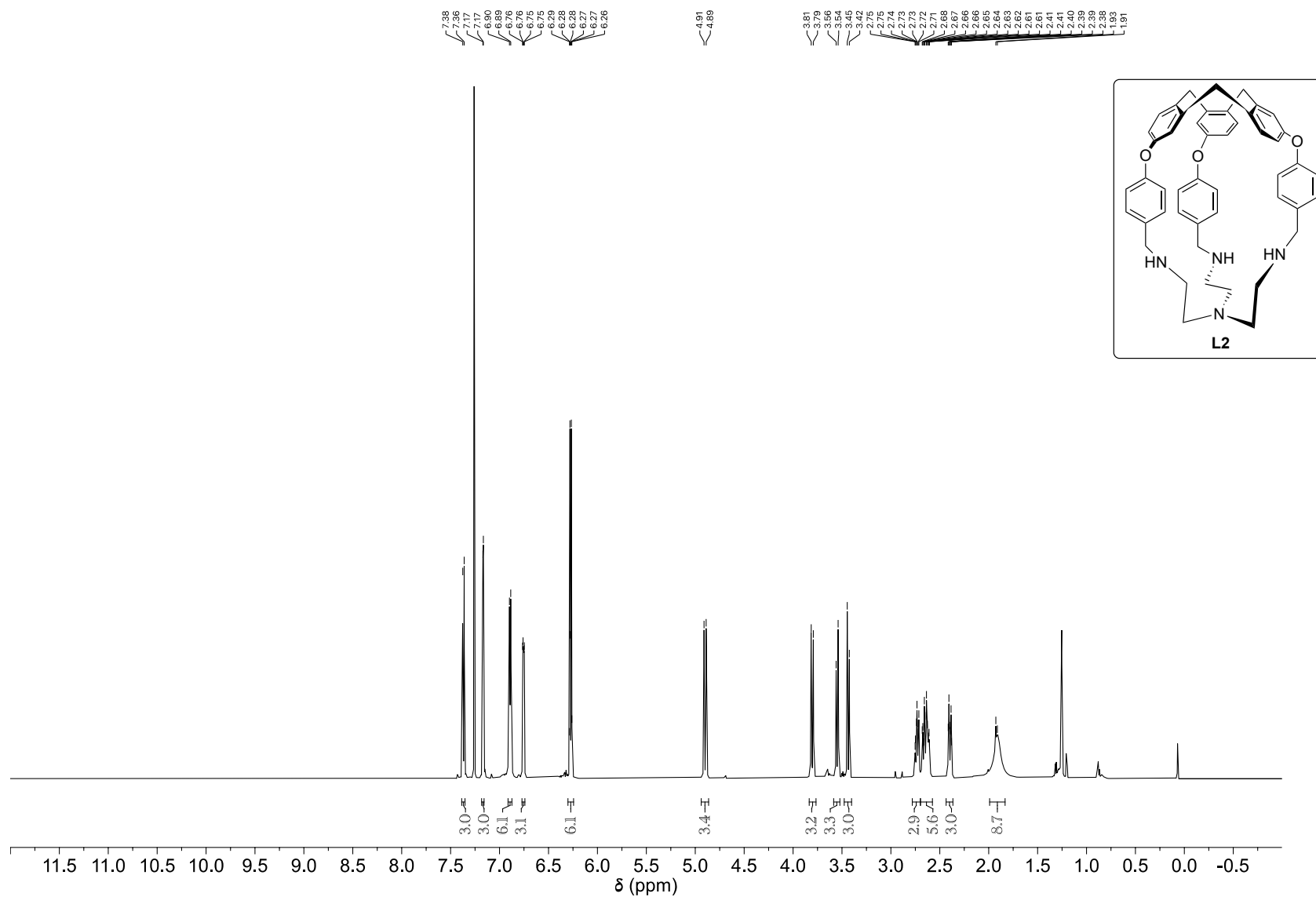
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of **4**



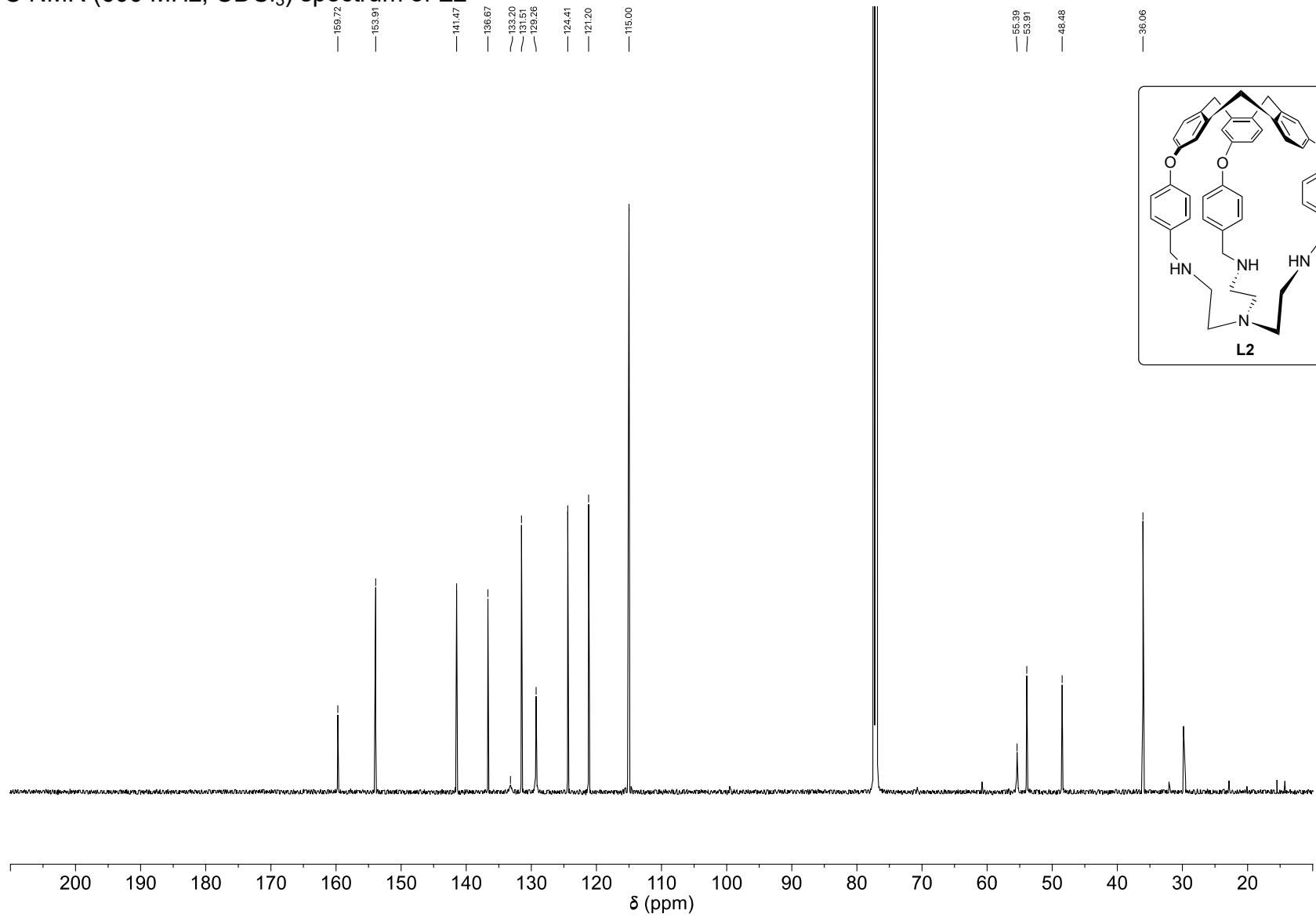
$^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **4**



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **L2**

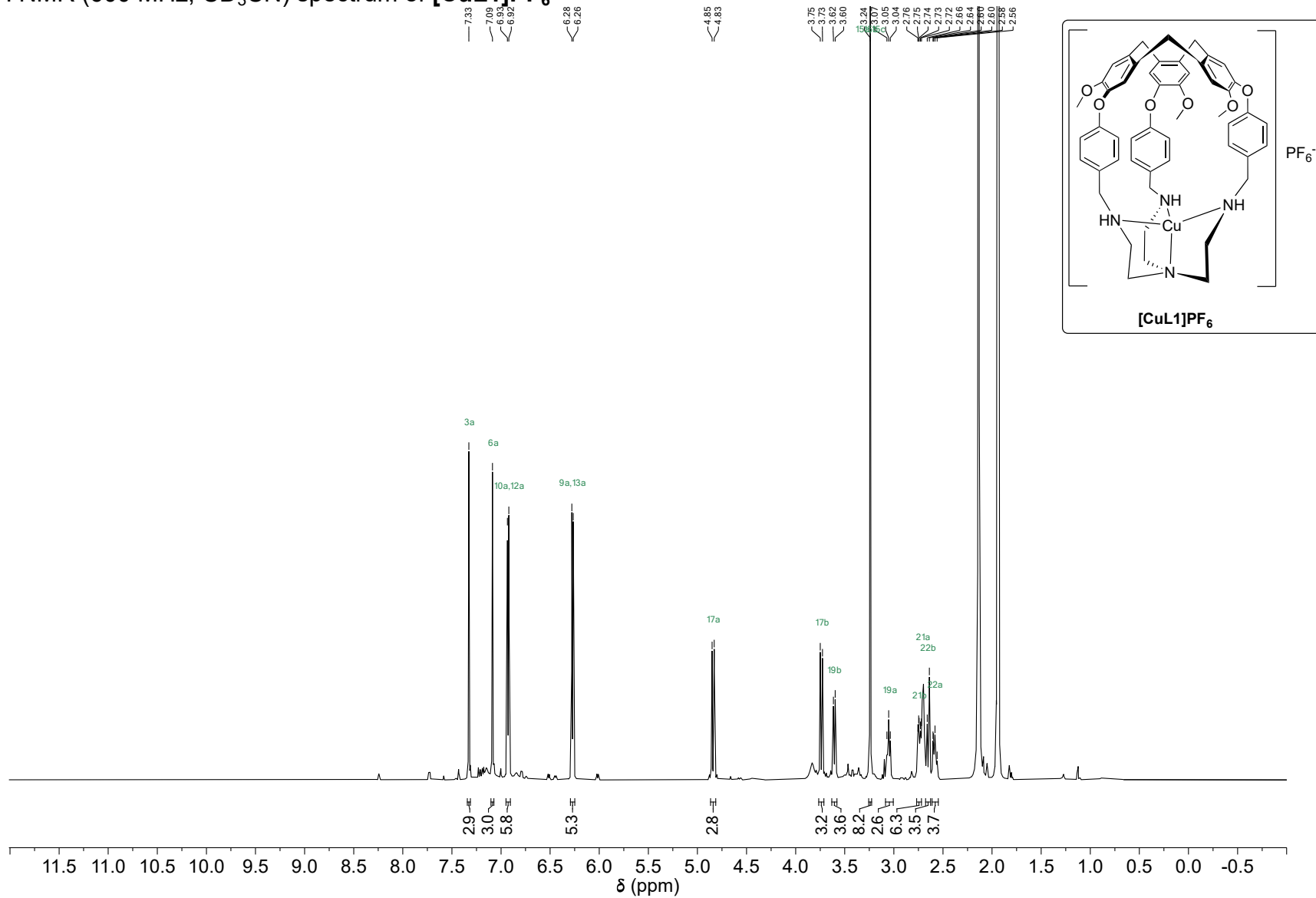


$^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ ) spectrum of **L2**

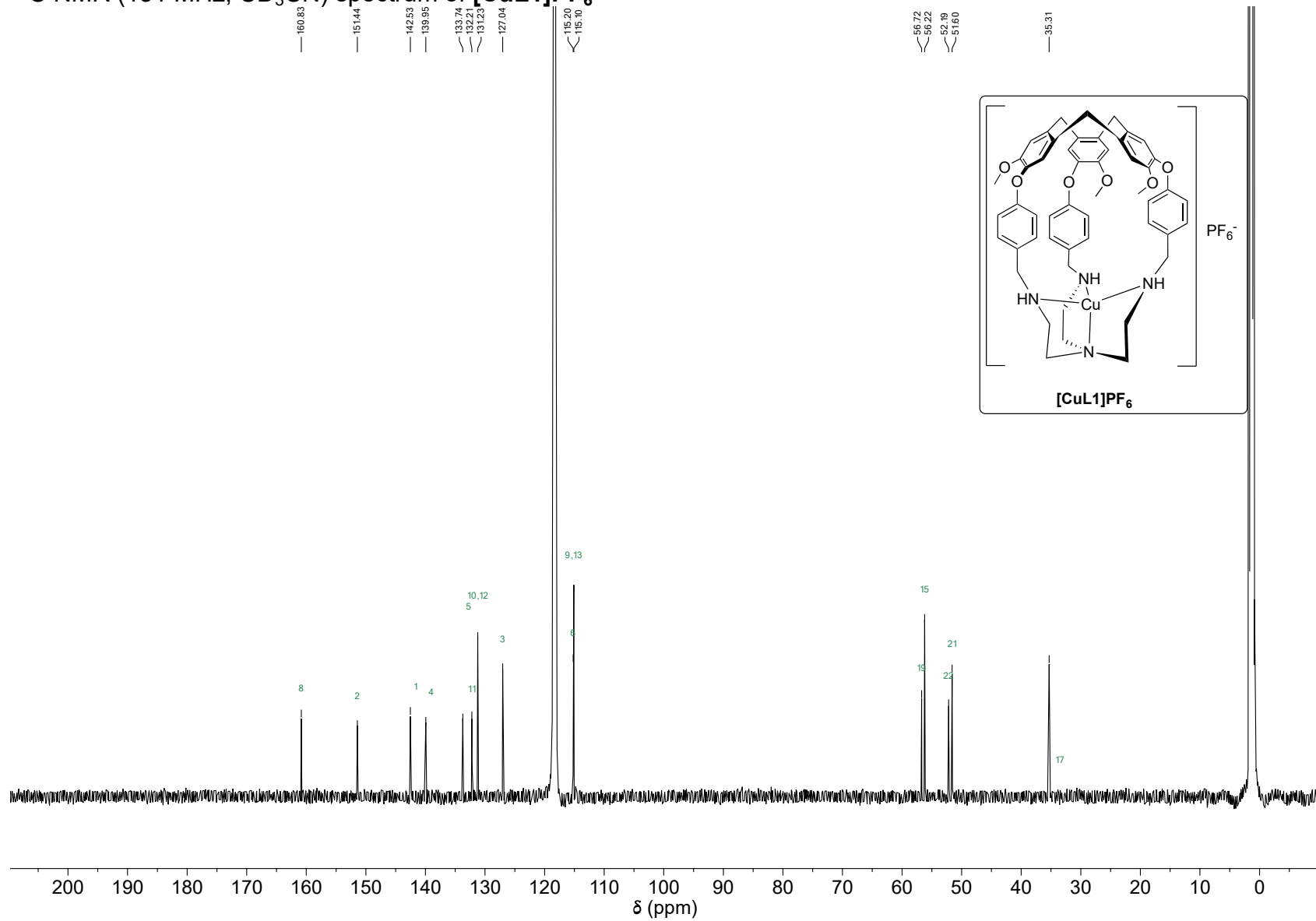




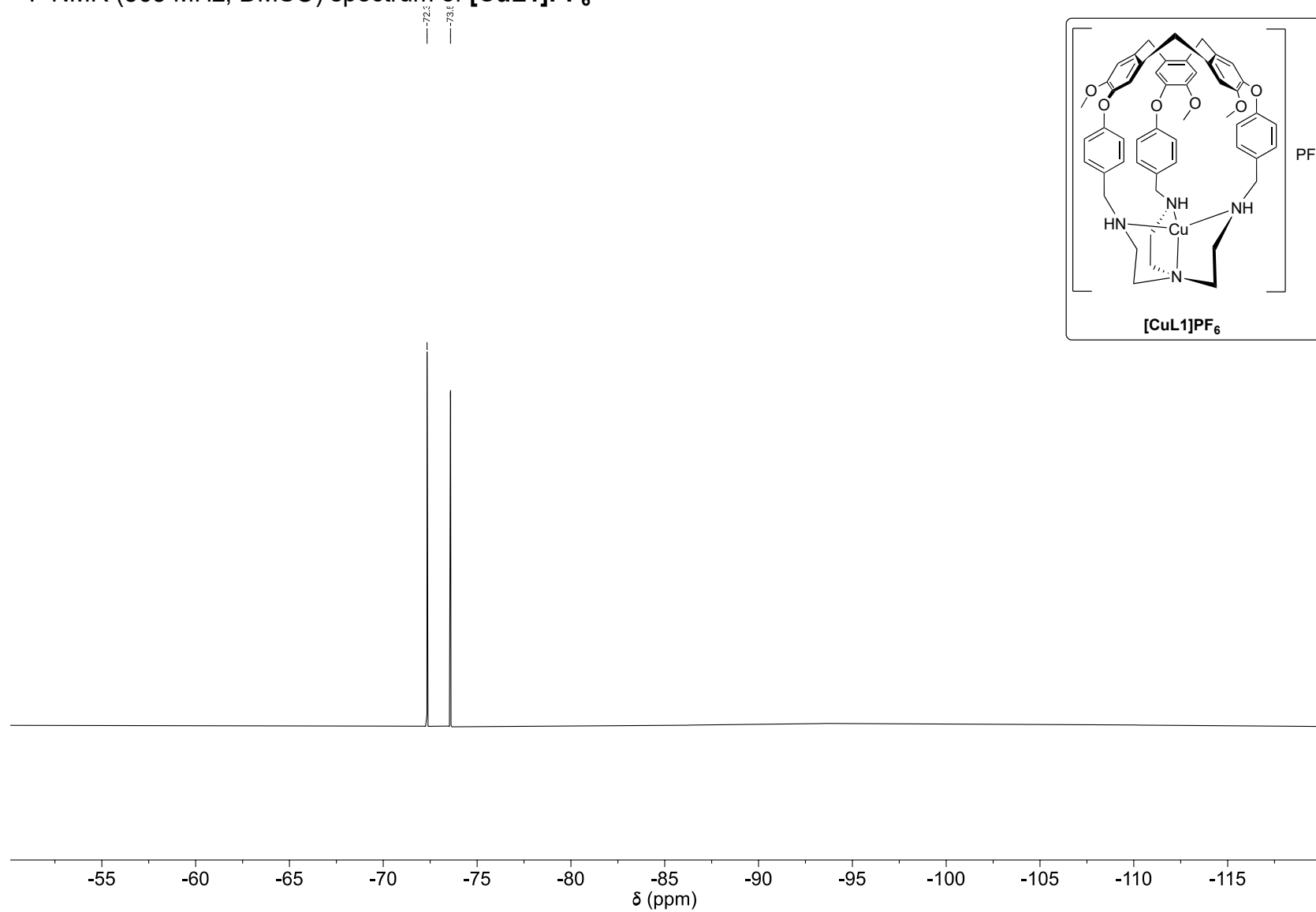
$^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of  $[\text{CuL1}]\text{PF}_6$



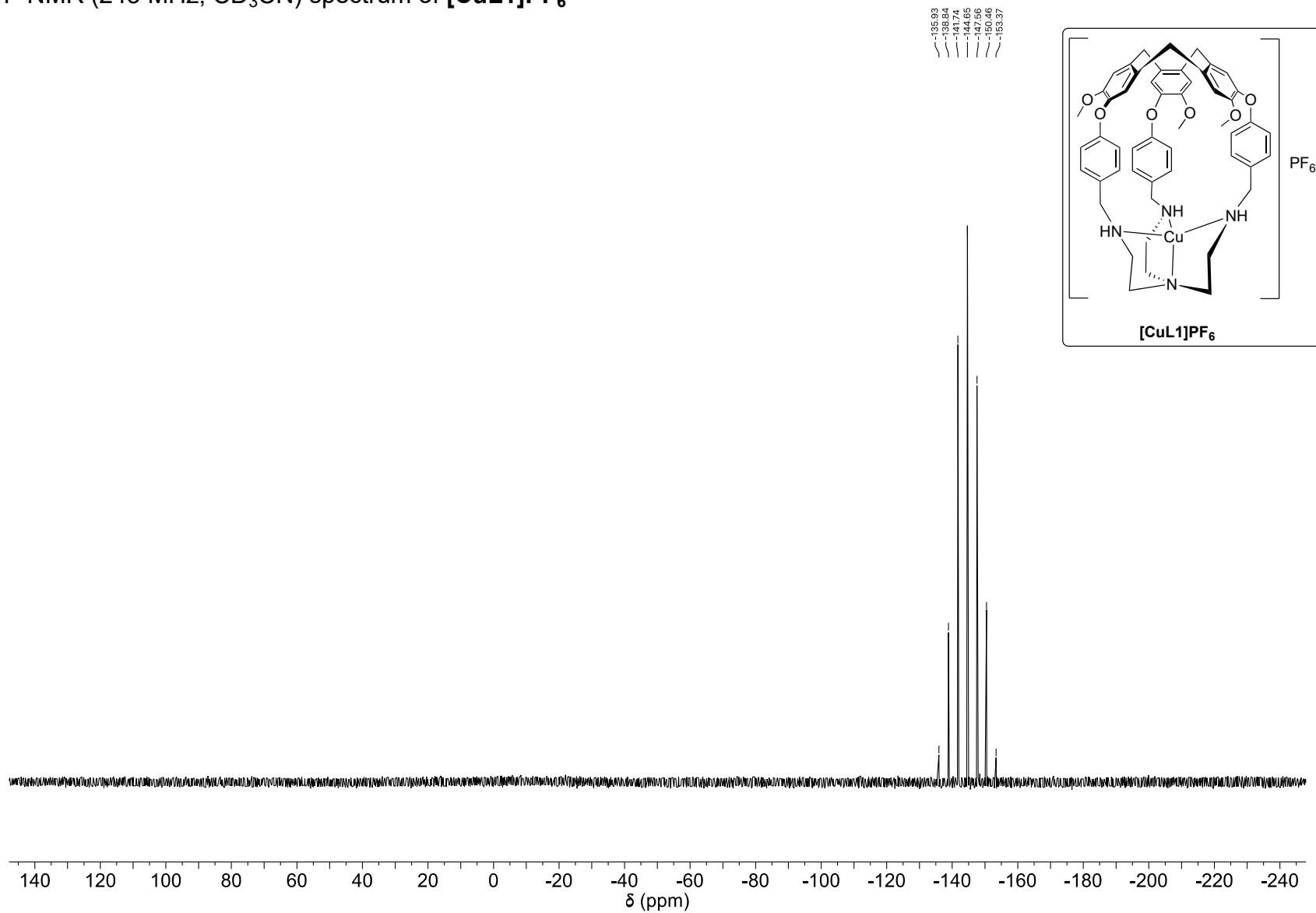
$^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of  $[\text{CuL1}]\text{PF}_6$



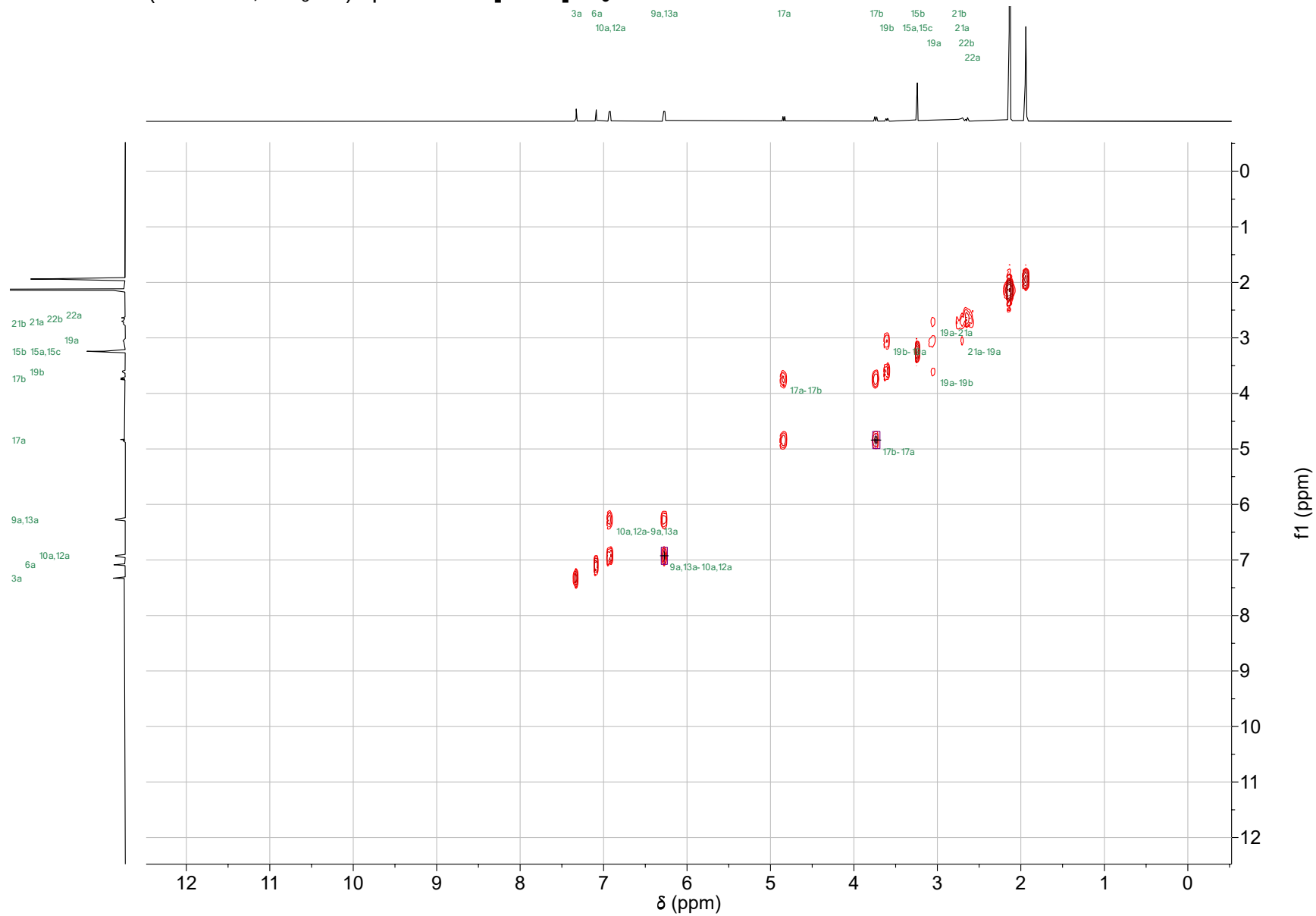
$^{19}\text{F}$  NMR (565 MHz, DMSO) spectrum of  $[\text{CuL1}]\text{PF}_6$



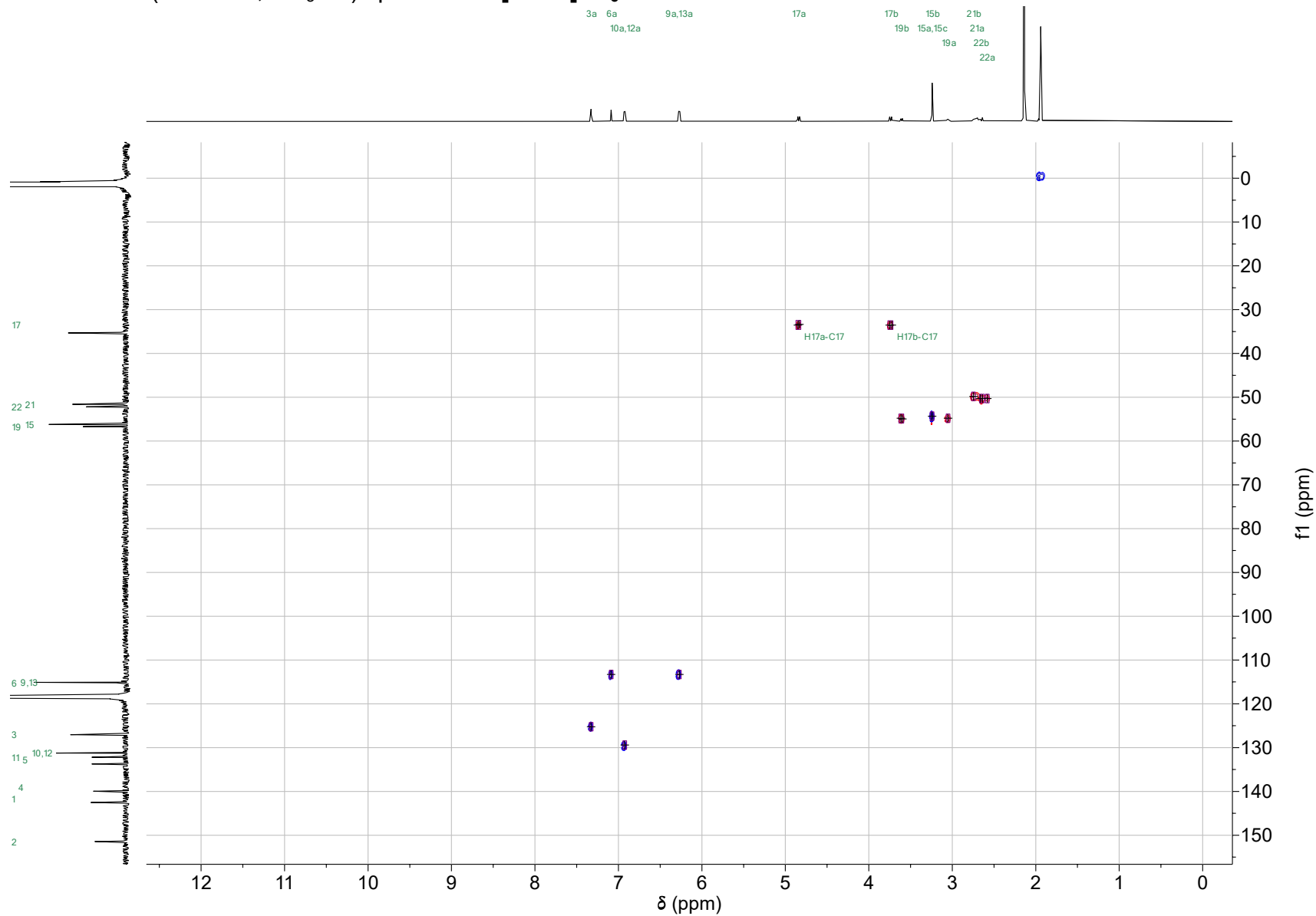
$^{31}\text{P}$  NMR (243 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of  $[\text{CuL1}]\text{PF}_6$



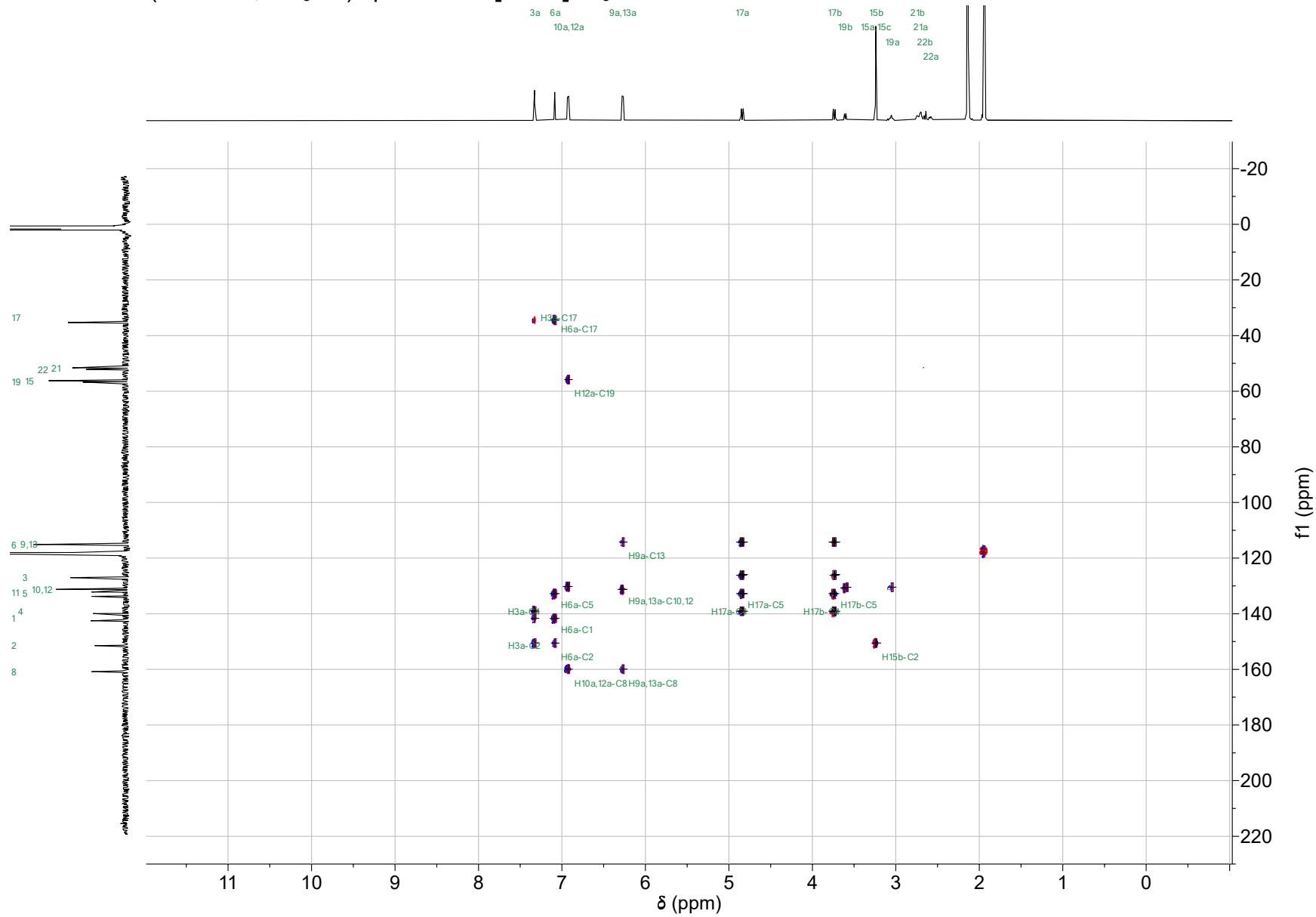
COSY NMR (600 MHz, CD<sub>3</sub>CN) spectrum of [CuL1]PF<sub>6</sub>



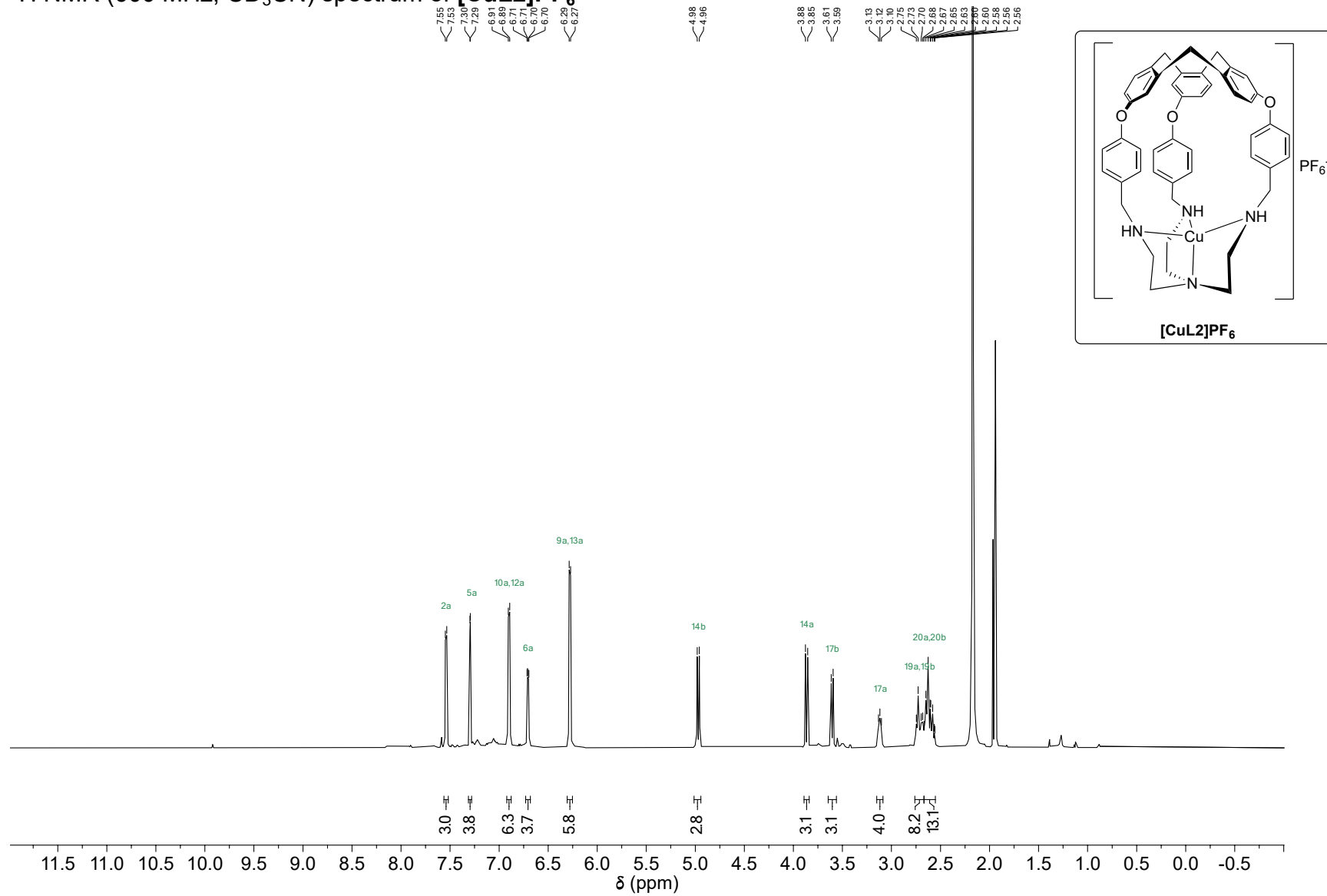
HSQC NMR (600 MHz, CD<sub>3</sub>CN) spectrum of [CuL1]PF<sub>6</sub>



HMBC NMR (600 MHz, CD<sub>3</sub>CN) spectrum of [CuL1]PF<sub>6</sub>

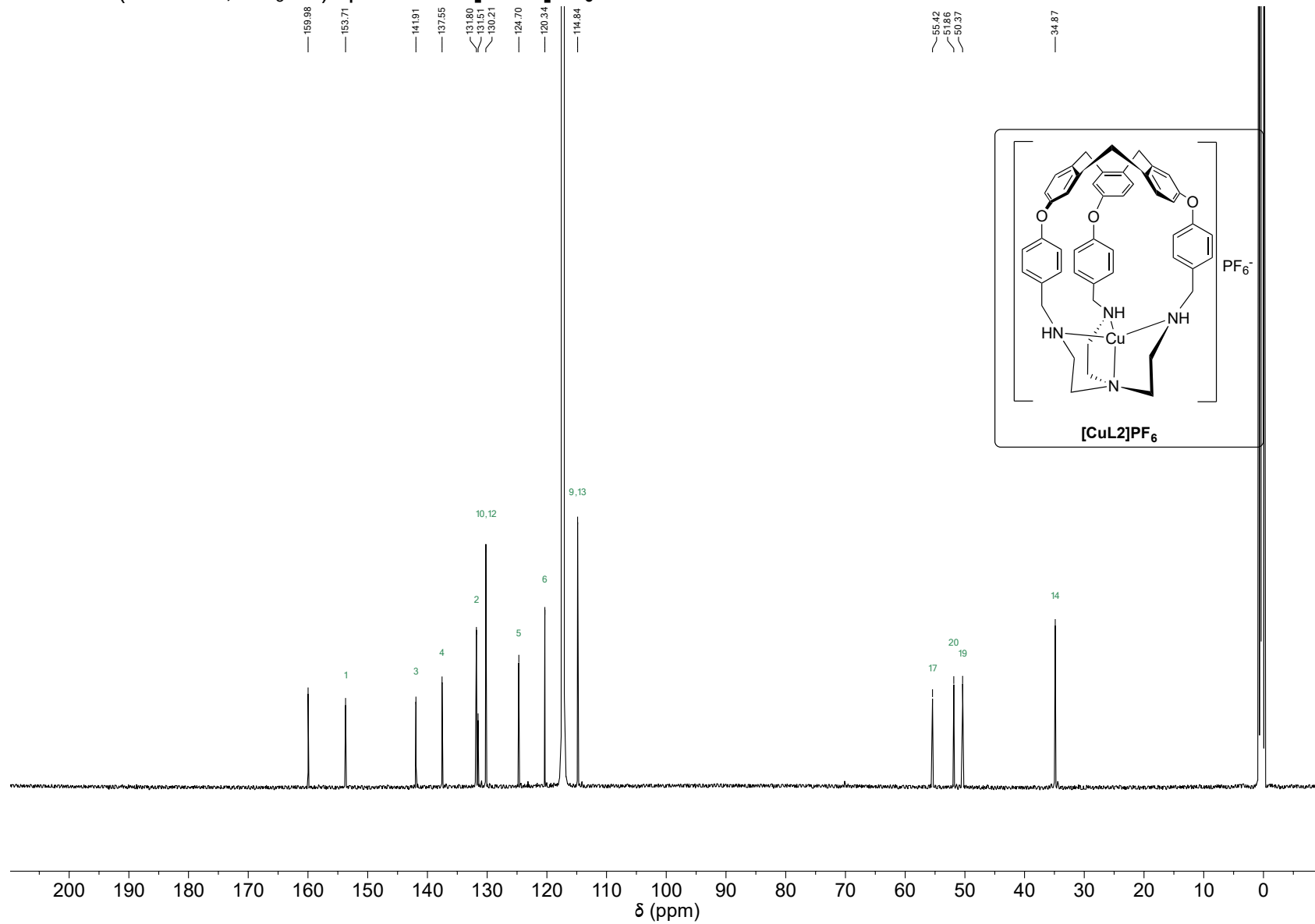


$^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of  $[\text{CuL}_2]\text{PF}_6$

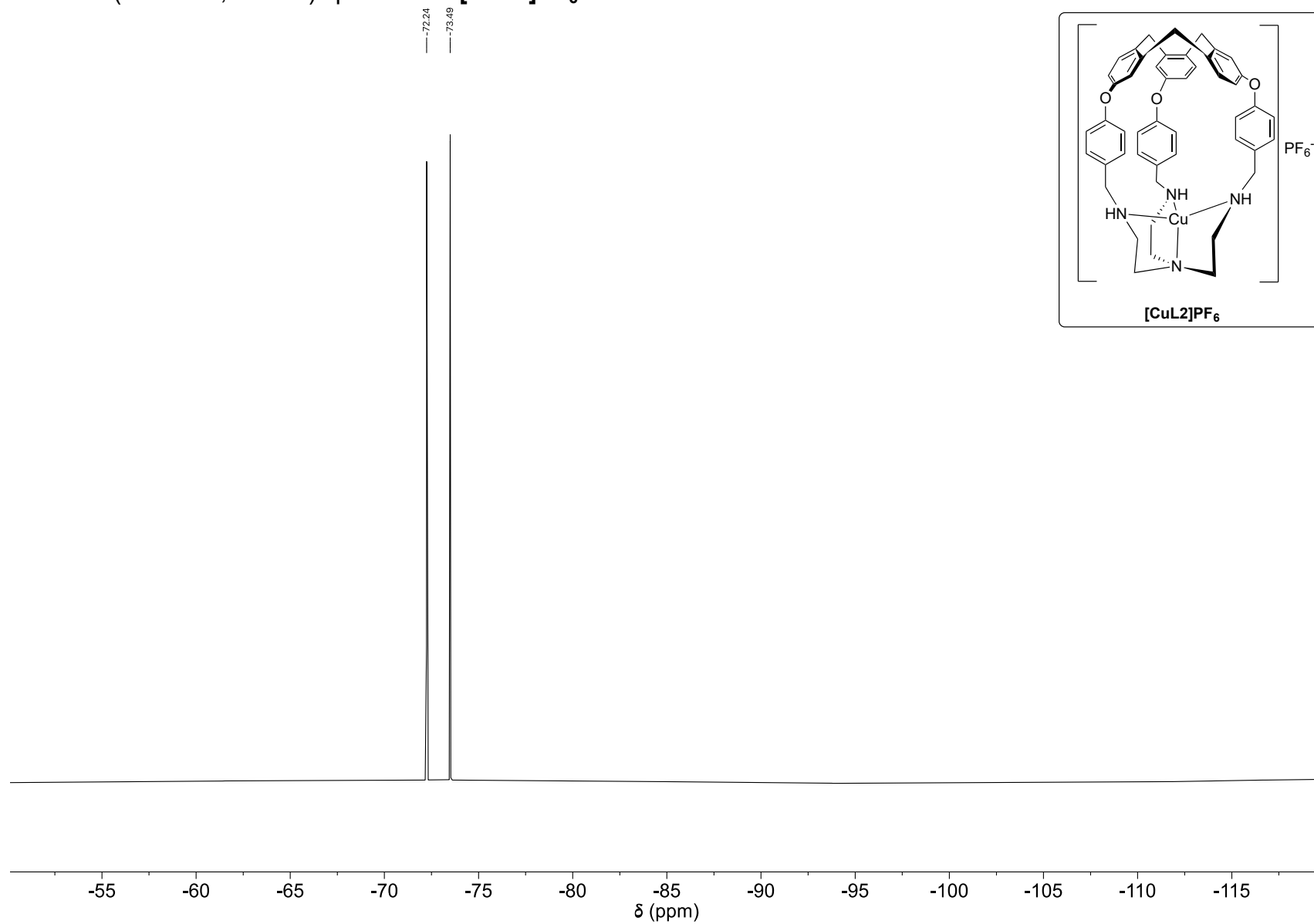




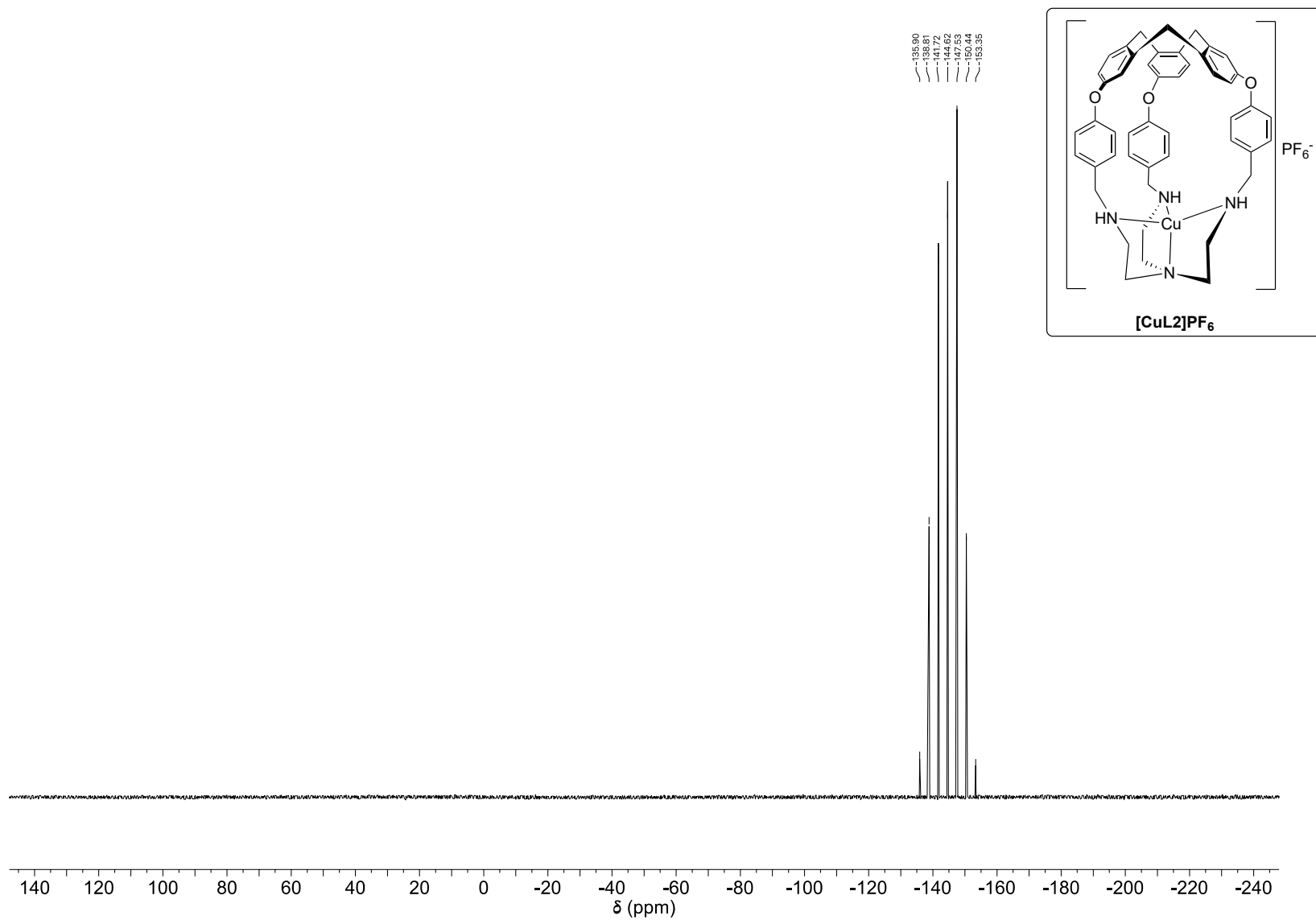
$^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of  $[\text{CuL2}]\text{PF}_6$



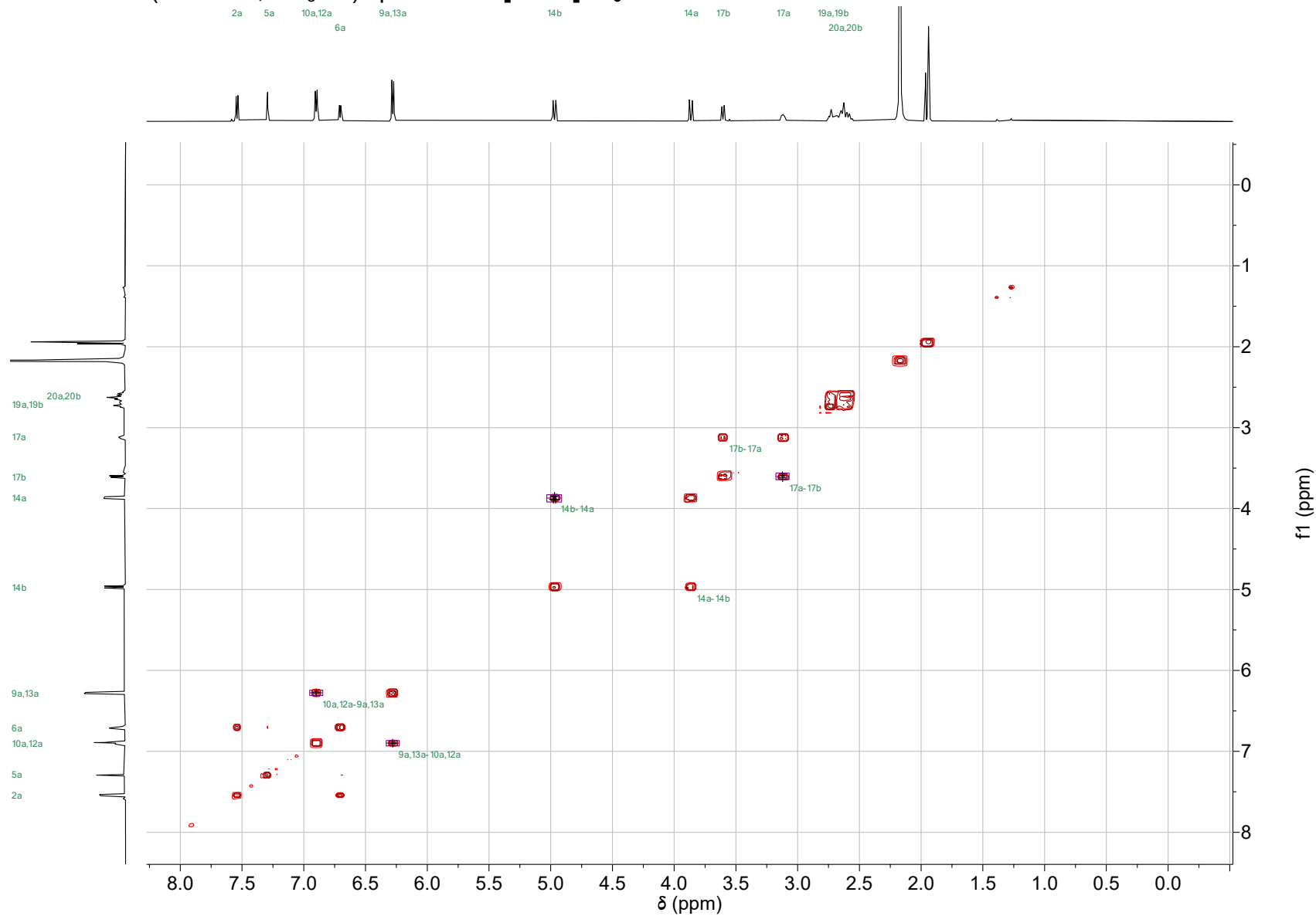
$^{19}\text{F}$  NMR (565 MHz, DMSO) spectrum of  $[\text{CuL2}]\text{PF}_6$



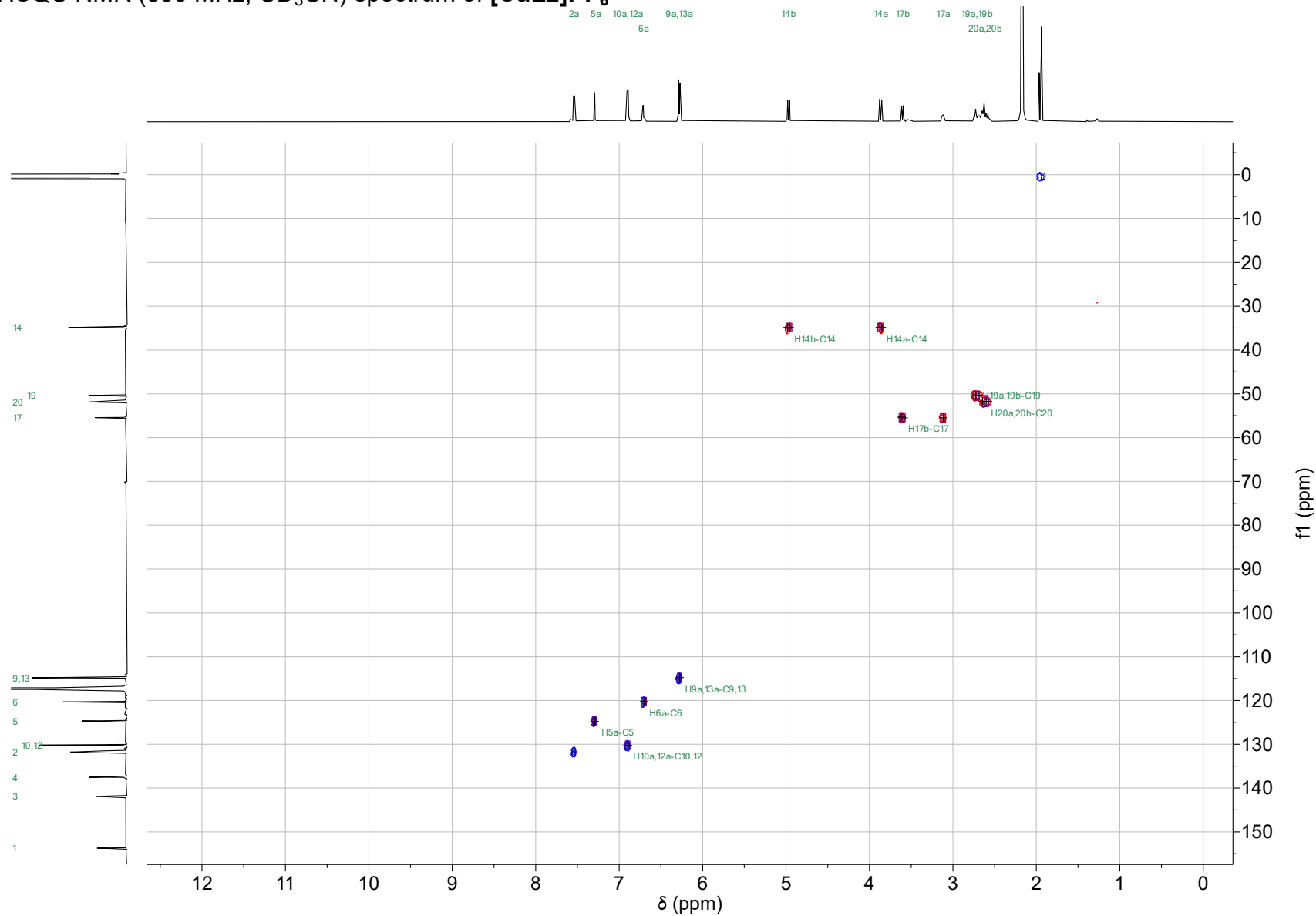
$^{31}\text{P}$  NMR (243 MHz,  $\text{CD}_3\text{CN}$ ) spectrum of  $[\text{CuL}_2]\text{PF}_6$



COSY NMR (600 MHz, CD<sub>3</sub>CN) spectrum of [CuL<sub>2</sub>]PF<sub>6</sub>



HSQC NMR (600 MHz, CD<sub>3</sub>CN) spectrum of [CuL<sub>2</sub>]PF<sub>6</sub>



HMBC NMR (600 MHz, CD<sub>3</sub>CN) spectrum of [CuL<sub>2</sub>]PF<sub>6</sub>

