Supporting Information

A C_2-Symmetric, Basic Fe(III) Carboxylate Complex Derived from a Novel Triptycene-Based Chelating Carboxylate Ligand

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General methods and materials. Reagents were purchased from TCI, Aldrich Chemical Co., and Alfa Aesar and used as received unless otherwise noted. Compound **i** was prepared based on our previously published work.[1] The organic products were purified by column chromatography with Silicycle 60 Å, ultrapure silica gel. ^{1}H and ^{13}C NMR spectra were recorded using a 300 MHz or 500 MHz Varian Mercury spectrometer. IR spectra were measured on a ThermoNicolet Avatar 360 spectrophotometer with *OMNIC* software. Low-resolution electrospray ionization mass spectra were acquired on an Agilent Technologies 1100 series LC-MSD trap. High-resolution mass spectra were recorded on a Brüker Daltonics APEXIV 4.7 Tesla Fourier Transform ion cyclotron resonance mass spectrometer (FT-ICRNS) at the MIT DCIF by MIT staff.

X-ray diffraction studies and refinement details. Complete data sets were collected for **2**, $\mathbf{H_2L2^{Ph4}}$, and $[NaFe_3(\mathbf{L2^{Ph4}})_2(\mu_3\text{-}O)(\mu\text{-}O_2CPh_3)_2(H_2O)_3](OTf)_2$ (**8**). Single crystals suitable for X-ray analysis were coated with Paratone-N oil, suspended in a small fiber loop and then placed in a cooled dry N_2 gas stream on a Brüker APEX CCD X-ray diffractometer. Diffraction intensities were measured using graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) at 100 (2) K with a combination of φ and ω scans traversing their respective scanning angles at 0.5° increments for ω scans and 0.45° increments for φ scans. Data collection, indexing, data reduction, and final unit cell refine-

ment procedures were carried out with APEX2;[2] absorption corrections were applied by using the program SADABS.[3] All structures were solved with direct methods with SHELXS[4] and refined against F^2 on all data by full-matrix least squares with SHELXL,[5] following established refinement strategies.[6]

Single crystals of **2** were grown by slowly cooling an EtOAc solution of the compound at 0 °C. All non-hydrogen atoms were refined anisotropically. The aromatic proton of C2 was placed at an idealized location. The hydrogen atoms of the carboxylic acid and phenol groups were located on a difference Fourier map. The O–H bond distances were constrained to 0.84 Å and the thermal ellipsoids of the protons were set to be 1.5 times that of the oxygen atom to which they are attached.

Single crystals of $\mathbf{H_2L2^{Ph4}}$ were obtained by slow evaporation of a dichloromethane solution. The hydrogen atoms of the carboxylic acids moieties were located on a difference map and refined, constraining their thermal ellipsoid parameters to 1.5 times the of the oxygen atom to which they are attached.

Single crystals of $[NaFe_3(\mathbf{L2^{Ph4}})_2(\mu_3\text{-}O)(\mu\text{-}O_2CPh_3)_2(H_2O)_3](OTf)_2\cdot(C_6H_6)_6\cdot(C_5H_{12})_2$ were grown by the vapor diffusion of pentane into a crude reaction mixture in benzene. The crystals obtained were of poor quality, diffracting only weakly out to 1 Å resolution. The data were integrated to the 1 Å resolution limit, thereby resulting in a low maximum 2θ value of 20°. This 2θ value is significantly less than the 25° value recommended by the International Union of Applied Crystallography, thus resulting in several Level A and B alerts in the CheckCIF algorithm. At this low resolution, precise bond distances and angles are not available, and the reported numbers should be interpreted accordingly. The geometric structure, however, is unambiguous. The low 2θ value resulted in a number

of unobserved reflections, giving rise to a low data-to-parameter ratio. To increase this ratio, similarity restraints on both the magnitude and directionality of the thermal ellipsoids of all atoms were applied.

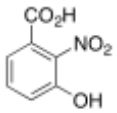
The triiron complex sits on a cryallographic 2-fold axis. The sodium atom was assigned half-occupancy, being positionally disordered about the 2-fold symmetry axis. Two benzene and what was formulated to be a pentane molecule were refined at full occupancy. Two other benzene molecules, located near crystallographic symmetry elements, were refined at half occupancy. The triflate counterion was located in a general position. For the solvent molecules and triflate counterion, restraints on bond distances were applied, as well as restraints on planarity of the benzene ring. Several physically impossible close contacts between solvent molecules are present in the lattice, giving rise to level A CheckCIF alerts. We postulate these close contacts to arise from disorder and imperfect modeling of the solvent.

^{57}Fe Mössbauer spectroscopic data. Mössbauer spectra were recorded on an MSI spectrometer (WEB Research Co.) with a ^{57}Co source in a Rh matrix maintained at room temperature. Solid samples were prepared by suspension in Apiezon M grease and placed in a nylon sample holder. Data were acquired at 77 K, and the isomer shift (δ) values are reported with respect to metallic iron that was used for velocity calibration at room temperature. The spectra were fit to Lorentzian lines using the WMOSS plot and fit program (WEB Research Co.).

Experimental section.

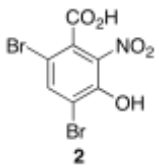
3-Hydroxy-2-nitrobenzoic acid (1). To a solution of 3-chloro-2-nitrobenzoic acid (25.0 g, 124 mmol) in water (125 mL) was added solid KOH (100.0 g, 1.79 mol) in sev-

eral portions. The resulting red mixture was then heated to 120 °C, kept at a gentle reflux for 30 h, and then cooled to 0 °C. The pH of the blood red mixture was adjusted to 3 with concentrated HCl, resulting in a color change to yellow and the precipitation of yellow solid. This crude mixture was extracted with EtOAc (200 mL x 3). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated to dryness to give a yellow solid. Recrystallization of this crude product with EtOAc gave 3-hydroxy-2-nitrobenzoic acid (**1**) (21.8 g, 96%) as a yellow solid. ^{1}H NMR (300 MHz) in DMSO-d_6 δ 7.29 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.38-7.50 (m, 2H), 11.24 (bs, 1H); ^{13}C NMR (75 MHz) in DMSO-d_6 δ 120.56, 121.76, 124.52, 131.21, 139.36, 149.28, 164.58 ppm; IR (KBr) 3301, 3091, 3015, 2840, 2582, 1696, 1614, 1526, 1468, 1454, 1352, 1301, 1262, 1186, 1116, 1054, 901, 858, 816, 783, 753, 700, 650, 627 cm^{-1}; LRMS (ESI-) m/z = 181.8 $[M-H]^-$ (Calc. for $C_7H_4NO_5$: 182.0); Melting point: 180–182 °C.



1

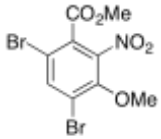
4,6-Dibromo-3-hydroxy-2-nitrobenzoic acid (2). To a solution of 3-hydroxy-2-nitrobenzoic acid (**1**) (16.5 g, 0.09 mol) and NaOAc (22.2 g, 0.27 mol, 3.0 equiv) in EtOH (300 mL) at 0 °C was slowly added a solution of Br_2 (31.8 g, 0.199 mol, 2.2 equiv) in EtOH (100 mL). The resulting mixture was stirred at rt for 3 h. The EtOH was removed by rotary evaporation and EtOAc (600 mL) was added to the remaining residue. The mixture was washed with 10% aqueous HCl (100 mL x 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. Recrystallization with EtOAc gave 4,6-dibromo-3-hydroxy-2-nitrobenzoic acid (**2**) (21.8 g, 71%) as a yellow solid. ^{1}H NMR (300 MHz) in DMSO-d_6 δ 3.00-4.00 (bs, 2H), 8.21 (s, 1H); ^{13}C NMR (75 MHz) in DMSO-d_6 δ 108.18, 116.20, 130.48, 139.14, 146.93,



2

164.46 ppm; IR (KBr) 3473, 3080, 2894, 2522, 1700, 1597, 1527, 1459, 1429, 1340, 1269, 1199, 1160, 1114, 893, 779, 699, 683, 665, 502 cm^{-1}; HRMS (ESI-) m/z = 339.8278 $[M-H]^-$ (Calc. for $C_7H_2Br_2NO_5$: 339.8289); Melting point: 192–194 °C (decompose).

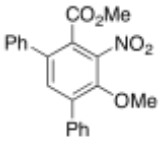
Methyl 4,6-dibromo-3-methoxy-2-nitrobenzoate (3). 4,6-Dibromo-3-hydroxy-2-nitrobenzoic acid (**2**) (3.2 g, 9.4 mmol) was dissolved in Et_2O (100 mL) in a 250-mL Erlenmeyer flask. Another 250-mL Erlenmeyer flask, containing a yellow solution of Diazald in ethanol (50 mL), was capped with a septum and equipped with a long needle. The Diazald solution was sparged with nitrogen gas. A cannula was fitted to join the two flasks. The Diazald solution was treated with portions (~0.3 mL) of 10% NaOH through a syringe, resulting in the formation of CH_2N_2, which was transferred under nitrogen pressure through the cannula into the Et_2O solution containing **2**. The reaction was monitored by TLC analysis until all the carboxylic acid was consumed. The solvents were removed by rotary evaporation. The resulting crude material was dissolved in acetone (80 mL). Me_2SO_4 (1.42 mL, 13.5 mmol, 1.5 equiv) and K_2CO_3 (1.95 g, 13.5 mmol, 1.5 equiv) were added. The resulting mixture was refluxed overnight. The acetone was removed by rotary evaporation. EtOAc (50 mL) was added and it was washed by brine (20 mL). The organic layer was dried over Na_2SO_4 and evaporated to dryness. Flash column chromatography with silica gel (hexanes: EtOAc = 10:1 to 8:1) gave methyl 4,6-dibromo-3-methoxy-2-nitrobenzoate (**3**) (3.2 g, 92%) as a pale yellow oil. ^1H NMR (500 MHz) in $CDCl_3$ δ 3.91 (s, 3H), 4.00 (s, 3H), 7.99 (s, 1H); ^{13}C NMR (125 MHz) in $CDCl_3$ δ 53.98, 63.42, 115.71, 121.81, 129.36, 140.07, 149.52, 163.17 ppm; IR (KBr) 3083, 2952, 1746, 1583, 1457, 1351, 1279, 1245,



3

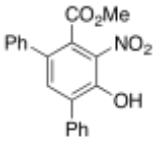
1160, 1120, 1026, 962, 902, 799, 728, 663, 629, 522, 495, 452 cm^{-1}; HRMS (ESI+) m/z = 386.9025 $[M+NH_4]^+$ (Calc. for $C_9H_{11}Br_2N_2O_5$: 386.9013).

Methyl 6'-methoxy-5'-nitro-[1,1':3',1''-terphenyl]-4'-carboxylate (4). A Schlenk flask containing a mixture of methyl 4,6-dibromo-3-methoxy-2-nitrobenzoate (**3**) (3.2 g, 8.67 mmol), phenylboronic acid (4.23 g, 34.7 mmol, 4.0 equiv), K_2CO_3 (4.79 g, 34.7 mmol, 4.0 equiv), and $Pd(PPh_3)_4$ (301 mg, 0.26 mmol, 3 mol%) was evacuated and backfilled with N_2 five times. A mixture of THF (50 mL)/water (50 mL), which was deoxygenated by bubbling N_2 through for over 30 min, was added via a syringe. The resulting solution was refluxed for 42 h under a N_2 atmosphere. It was cooled to room temperature and extracted with EtOAc (150 mL x 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated to dryness. Flash column chromatography (Hexanes: Et_2O = 4:1) gave **4** (2.79 g, 89%) as a white solid. ^1H NMR (500 MHz) in $CDCl_3$ δ 3.54 (s, 3H), 3.66 (s, 3H), 7.33-7.37 (m, 2H), 7.40-7.50 (m, 6H), 7.55 (s, 1H), 7.58-7.64 (m, 2H); ^{13}C NMR (125 MHz) in $CDCl_3$ δ 53.22, 62.51, 125.88, 128.36, 128.47, 128.80, 128.88, 128.99, 129.08, 134.98, 135.73, 137.69, 138.57, 138.62, 145.24, 148.78, 165.41 ppm; IR (KBr) 3060, 3010, 2948, 2851, 1726, 1537, 1440, 1376, 1320, 1250, 1034, 770, 741, 698 cm^{-1}; HRMS (ESI+) m/z = 381.1463 $[M+NH_4]^+$ (Calc. for $C_{21}H_{21}N_2O_5$: 381.1445); Melting point: 138–140 °C.



4

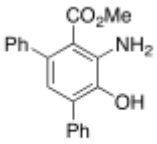
Methyl 6'-hydroxy-5'-nitro-[1,1':3',1''-terphenyl]-4'-carboxylate (5). A mixture of intermediate **4** (2.79 g, 7.68 mmol) and LiCl (1.96 g, 46.1 mmol, 6 equiv) in DMF (30 mL) was heated at 90 °C for 20 h. Another portion of LiCl (1.3 g, 30.7 mmol, 4 equiv) was added and the reaction was heated at 90 °C for another 20 h. The resulting dark red solution was cooled to room temperature. EtOAc



5

(200 mL) was added and the mixture was acidified with 5% aq HCl, followed by washing with water (100 mL x 5) and brine (100 mL). The organic layer was dried over Na_2SO_4, filtered and stripped. Flash column chromatography (Hexanes: EtOAc = 8:1-4:1) gave phenol **5** (2.30 g, 86 %) as a sticky orange oil. ^{1}H NMR (500 MHz) in $CDCl_3$ δ 3.73 (s, 3H), 7.36-7.50 (m, 8H), 7.56-7.60 (m, 2H), 7.65 (s, 1H), 11.05 (s, 1H); ^{13}C NMR (125 MHz) in $CDCl_3$ δ 53.15, 128.49, 128.67, 128.70, 128.81, 129.02, 129.53, 131.89, 133.03, 134.11, 135.20, 137.85, 139.49, 152.01, 166.39 ppm; IR (KBr) 3205, 3057, 3029, 2949, 1957, 1891, 1813, 1740, 1606, 1574, 1535, 1496, 1462, 1449, 1433, 1403, 1335, 1247, 1129, 1060, 1025, 1006, 911, 806, 789, 757, 736, 699, 592 cm^{-1}; HRMS (ESI+) m/z = 367.1277 $[M+NH_4]^+$ (Calc. for $C_{20}H_{19}N_2O_5$: 367.1288).

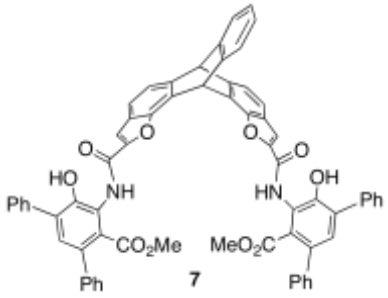
Methyl 5'-amino-6'-hydroxy-[1,1':3',1''-terphenyl]-4'-carboxylate (6). A mixture of phenol **5** (1.50 g, 4.3 mmol) and 10% Pd/C (75 mg, 5 w%) in EtOAc/MeOH (25 mL/25 mL), fitted with a hydrogen balloon, was stirred at room temperature for 24 h. Hydrogen was blown off by nitrogen. The resulting solution was filtrated through a short pad of Celite and the filtrate was concentrated to dryness. Flash column chromatography (Hexanes: EtOAc: MeOH= 8:1:0, 2:1:0, 1:1:0.2) gave aniline **6** (1.32 g, 96 %) as a yellow foam. ^{1}H NMR (500 MHz) in $CDCl_3$ δ 3.47 (s, 3H), 5.20-5.60 (bs, 3H), 6.65 (s, 1H), 7.31-7.42 (m, 6H), 7.48-7.51 (m, 4H), 7.55 (s, 1H), 7.58-7.64 (m, 2H); ^{13}C NMR (125 MHz) in $CDCl_3$ δ 51.44, 113.63, 120.12, 126.58, 128.03, 128.12, 128.46, 128.94, 129.09, 129.57, 135.70, 136.68, 138.01, 139.42, 142.79, 169.86 ppm; IR (KBr) 3529, 3501, 3464, 3393, 3062, 3024, 2992, 2942, 2830, 1960, 1895, 1815, 1696, 1591, 1469, 1431, 1259, 1210, 1158, 1097, 1030, 987, 801,



6

782, 766, 703 cm^{-1}; HRMS (ESI+) m/z = 320.1269 $[M+H]^+$ (Calc. for $C_{20}H_{21}N_2O_3$: 320.1281); Melting point: 143–145 °C.

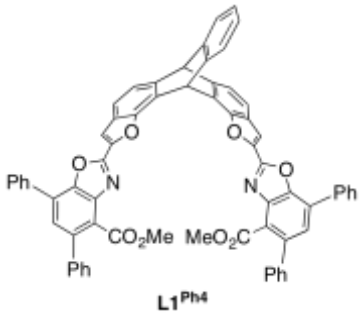
Diamide 7. Compound **i** in this step was prepared from its diacid precursor as previously described.[1] To a suspension of the diacid (84.4 mg, 0.2 mmol) in anhydrous DCM (40 mL) under N_2 atmosphere was added pyridine (646 μL, 8 mmol, 40 equiv.). The suspension became a clear yellow solution immediately. $SOCl_2$ (584 μL, 8 mmol, 40 equiv) and LiCl (84 mg, 4 mmol, 20 equiv) were added and the resulting solution was stirred at room temperature for 24 h. Most of volatiles were removed by rotatory evaporation, and the residue was further dried under high vacuum overnight. To the resulting yellow solid was added anhydrous DCM (20 mL), followed by addition of aniline **6** (128 mg, 0.4 mmol, 2.0 equiv) and pyridine (330 μL, 4 mmol, 20 equiv) in DCM (20 mL). The light brown solution was stirred at room temperature for 40 h. After concentrating the solution in vacuo, the crude material was purified by flash silica gel column chromatography (Hexanes: EtOAc = 8:1 to 2:1), giving diamide **7** (77 mg, 38%) as a yellow solid. ^{1}H NMR (300 MHz) in $CDCl_3$ δ 3.57 (s, 3H), 5.82 (s, 1H), 7.00 (s, 1H), 7.08-7.12 (m, 2H), 7.20-7.33 (m, 10H), 7.38-7.54 (m, 13H), 7.63 (s, 2H), 7.67-7.77 (m, 5H), 9.29 (s, 2H), 11.03 (s, 2H); ^{13}C NMR (75 MHz) in $CDCl_3$ δ 41.69, 52.39, 54.69, 113.81, 119.93, 120.74, 123.34, 124.36, 125.68, 125.73, 125.90, 127.36, 128.00, 128.11, 128.37, 128.52, 128.84, 129.82, 130.87, 135.43, 135.88, 137.63, 141.20, 143.63, 146.28, 147.04, 147.40, 147.86, 150.74, 158.77, 169.61 ppm; IR (KBr) 3371, 3318, 3056, 3026, 2948, 2924, 2851, 2731, 1699, 1650, 1587, 1531, 1497, 1464, 1434, 1288, 1268, 1193, 1145, 1031, 870, 804, 756,



7

732, 699, 680 cm^{-1}; HRMS (ESI+) m/z = 1025.3068 $[M+H]^+$ (Calc. for $C_{66}H_{45}N_2O_{10}$: 1025.3069); Melting point: 190–192 °C.

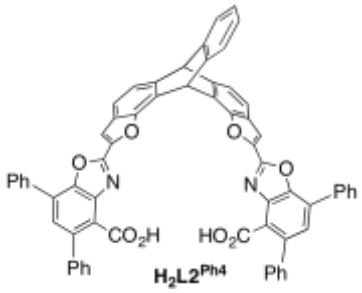
Diester L1^{Ph4}. A mixture of diamide **7** (67 mg, 0.065 mmol) and *p*-TsOH·H_2O (27.3 mg, 0.14 mmol, 2.2 equiv) in HOAc (20 mL) was refluxed under an N_2 atmosphere for 2 h. HOAc was removed under reduced pressure. The residue was dissolved in DCM (4 mL). Solid $NaHCO_3$ (~200 mg) was added to neutralize the solution. The DCM solution was directly loaded onto a silica gel column. Flash column chromatography (Hexanes: EtOAc = 4:1 to 1:1) gave **L1^{Ph4}** (55.3 mg, 85%) as a yellow solid. ^{1}H NMR (500 MHz) in $CDCl_3$ δ 3.86 (s, 3H), 5.76 (s, 1H), 7.01-7.11 (m, 2H), 7.14 (s, 1H), 7.36-7.44 (m, 4H), 7.45-7.52 (m, 13H), 7.58-7.63 (m, 6H), 7.69 (s, 2H), 7.80 (d, *J* = 7.0 Hz, 1H), 7.94-7.98 (m, 4H); ^{13}C NMR (75 MHz) in $CDCl_3$ δ 41.87, 52.85, 54.95, 112.74, 119.23, 120.62, 122.92, 123.99, 125.01, 125.55, 125.59, 126.11, 126.82, 127.20, 127.84, 128.60, 128.64, 128.84, 128.92, 129.10, 129.31, 134.67, 139.18, 140.53, 141.56, 143.63, 144.03, 146.47, 147.33, 147.42, 151.51, 157.13, 167.06 ppm; IR (KBr) 3058, 3026, 2948, 2850, 2246, 1949, 1881, 1732, 1643, 1614, 1507, 1457, 1431, 1264, 1171, 1145, 1122, 1070, 1032, 908, 890, 835, 757, 734, 723, 699 cm^{-1}; HRMS (ESI+) m/z = 989.2857 $[M+H]^+$ (Calc. for $C_{66}H_{41}N_2O_8$: 989.2857); Melting point: 239–241 °C.



L1^{Ph4}

Diacid ligand H$_2$L2^{Ph4}. To a solution of **L1^{Ph4}** (175 mg, 0.18 mmol) in anhydrous DCM (100 mL) under N_2 atmosphere at 0 °C was added BBr_3 (336 μL, 3.54 mmol, 20 equiv). The resulting brown solution was allowed to warm to rt and was then stirred for 72 h. Aqueous $NaHCO_3$ (10 mL) was added and the resulting biphasic mixture was

stirred for 15 min. The separated organic layer was acidified by 10% aqueous HCl to pH = 2.5~3.0, dried over Na_2SO_4, and filtrated. Pentane was added to this DCM solution and **H_2L2^{Ph4}** (166 mg, 98%) was collected as a yellow solid. ^{1}H NMR (300 MHz) in CD_2Cl_2 δ 5.85 (s, 1H), 7.06-7.09 (m, 2H), 7.21 (s, 1H), 7.40-7.62 (m, 23H), 7.65 (s, 2H), 7.75-7.78 (m, 1H), 7.95-7.98 (m, 4H); ^{13}C NMR (125 MHz) in CD_2Cl_2 δ 41.74, 54.71, 112.03, 119.47, 120.91, 121.32, 124.44, 125.09, 125.91, 126.07, 126.20, 128.18, 128.20, 128.41, 128.93, 129.01, 129.21, 129.44, 129.61, 129.66, 134.70, 140.71, 141.04, 142.58, 143.70, 144.54, 146.91, 147.72, 148.10, 151.66, 157.66, 171.76 ppm; IR (KBr) 3438, 3058, 3027, 2959, 1738, 1640, 1613, 1508, 1355, 1176, 1704, 955, 891, 836, 758, 698 cm^{-1}; HRMS (ESI+) m/z = 961.2559 $[M+H]^+$ (Calc. for $C_{64}H_{37}N_2O_8$: 961.2544); Melting point: 286–288 °C.



$[NaFe_3(L2^{Ph4})_2(\mu_3\text{-}O)(\mu\text{-}O_2CCPh_3)_2(H_2O)_3](OTf)_2$ (8). To a solution of **H_2L2^{Ph4}** (100 mg, 0.104 mmol), Ph_3CCO_2Na (26.0 mg, 0.114 mmol, 1.1 equiv.), and Et_3N (43 μL, 0.312 mmol, 3 equiv.) in DCM/MeOH (4 mL/1 mL) was added slowly a solution of $Fe(OTf)_3$ (87.2 mg, 0.156 mmol, 1.5 equiv.) in MeOH (3 mL). The resulting red solution was stirred for 30 min and the solvent was evaporated to dryness. The crude solid was dissolved in benzene (10 mL) and filtered to remove some insoluble material. The diffusion of pentane vapor into this solution afforded red needle-like crystals after two days. These crystals were harvested after washing them with pentane, giving complex **8** (138 mg, 72%) as a red solid. UV-vis: 259 (ε = 98 700 M^{-1} cm^{-1}), 305 (ε = 85 100 M^{-1} cm^{-1}), 355 (ε = 102 600 M^{-1} cm^{-1}), 377 (ε = 75 600 M^{-1} cm^{-1}) nm. IR (KBr): 3587, 3507, 3058, 3031, 1639, 1598, 1505, 1472, 1404, 1274, 1239, 1223, 1171, 1078, 1030, 909, 895,

730, 698, 638 cm^{-1}. Elemental analysis for complex $[NaFe_3(\mathbf{L2^{Ph4}})_2(\mu_3\text{-}O)(\mu\text{-}O_2CCPh_3)_2(H_2O)_3](OTf)_2\cdot C_6H_6$: Found: C, 67.29; H, 3.74; N, 2.03. Calc. for $C_{176}H_{110}F_6Fe_3N_4NaO_{30}S_2$: C 67.55; H, 3.54; N, 1.79%.

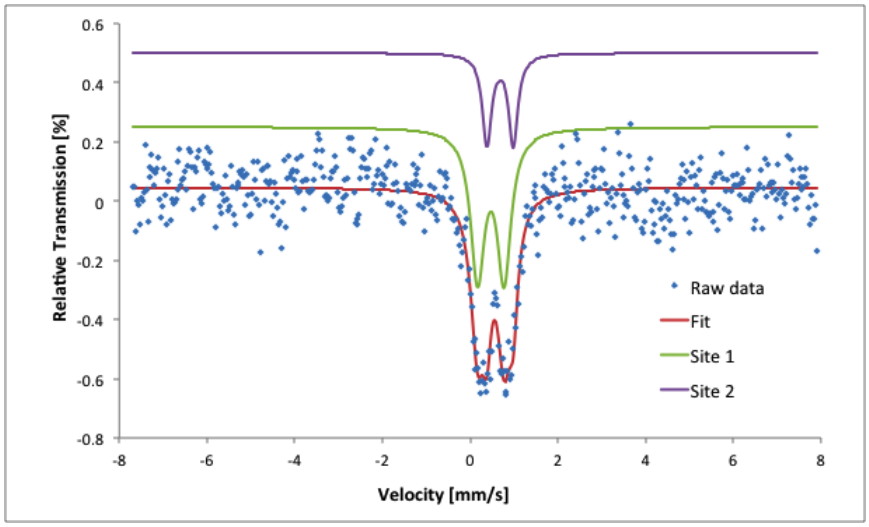


Figure S1. Zero-field ^{57}Fe Mössbauer spectrum of complex **8** recorded at 77 K. Site 1 (71%): δ = 0.472±0.02 mm/s, ΔEq = 0.604±0.02 mm/s; Site 2 (29%): δ = 0.684±0.02 mm/s, ΔEq = 0.600±0.02 mm/s.

X-ray crystal structures.

Figure S2. Thermal ellipsoid plot (50% probability) of the X-ray structure of **2**. Carbon, gray; oxygen, red; nitrogen, blue; bromine, purple; hydrogen, wheat.

Table S1. Crystal data and structure refinement for compound **2**.

Identification code	compound **2**
Empirical formula	$C_7H_3Br_2NO_5$
Formula weight	340.92
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.7083(4) Å b = 15.0200(9) Å β= 110.8300(10)°. c = 8.5232(5) Å
Volume	922.31(9) $Å^3$
Z	4
Density (calculated)	2.455 g/cm^3
Absorption coefficient	8.789 mm^{-1}
F(000)	648
Crystal size	0.33 x 0.23 x 0.23 mm^3
Theta range for data collection	2.71 to 30.15°
Index ranges	-10<=h<=10, -20<=k<=20, -11<=l<=11
Reflections collected	19654
Independent reflections	2692 [R(int) = 0.0318]
Completeness to theta = 26.47°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.2371 and 0.1595
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2692 / 2 / 142
Goodness-of-fit on F^2	1.105
Final R indices [I>2σ (I)]	R_1 = 0.0198, wR_2 = 0.0491
R indices (all data)	R_1 = 0.0226, wR_2 = 0.0500
Largest diff. peak and hole	0.625 and -0.743 e.$Å^{-3}$

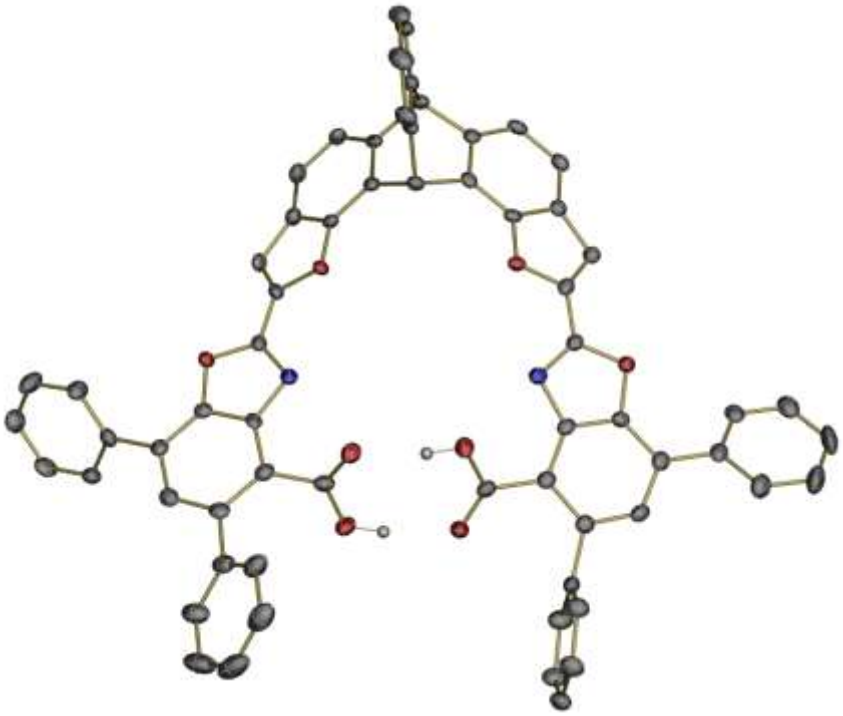


Figure S3. Thermal ellipsoid plot (50% probability) of X-ray structure of ligand $\mathbf{H_2L2^{Ph4}}$. Carbon, gray; oxygen, red; nitrogen, blue; hydrogen, wheat.

Table S2. Crystal data and structure refinement for Ligand $\mathbf{H_2L2^{Ph4}}$.

Identification code	Ligand $\mathbf{H_2L2^{Ph4}}$	
Empirical formula	$C_{66}H_{40}Cl_4N_2O_8$	
Formula weight	1130.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.9567(16) Å	α = 85.563(2)^o
	b = 13.8268(19) Å	β = 80.664(2)^o
	c = 16.050(2) Å	γ = 84.676(2)^o
Volume	2601.8(6) Å^3	
Z	2	
Density (calculated)	1.443 g/cm^3	
Absorption coefficient	0.292 mm^{-1}	
F(000)	1164	
Crystal size	0.10 x 0.07 x 0.05 mm^3	
Theta range for data collection	1.48 to 25.13^o	
Index ranges	-14<=h<=14, -16<=k<=16, -19<=l<=19	
Reflections collected	41574	
Independent reflections	9300 [R(int) = 0.0540]	
Completeness to theta = 25.13^o	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9856 and 0.9714	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9300 / 0 / 727	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ (I)]	R_1 = 0.0568, wR_2 = 0.1435	
R indices (all data)	R_1 = 0.0895, wR_2 = 0.1661	
Largest diff. peak and hole	1.251 and -0.780 e. Å^{-3}	

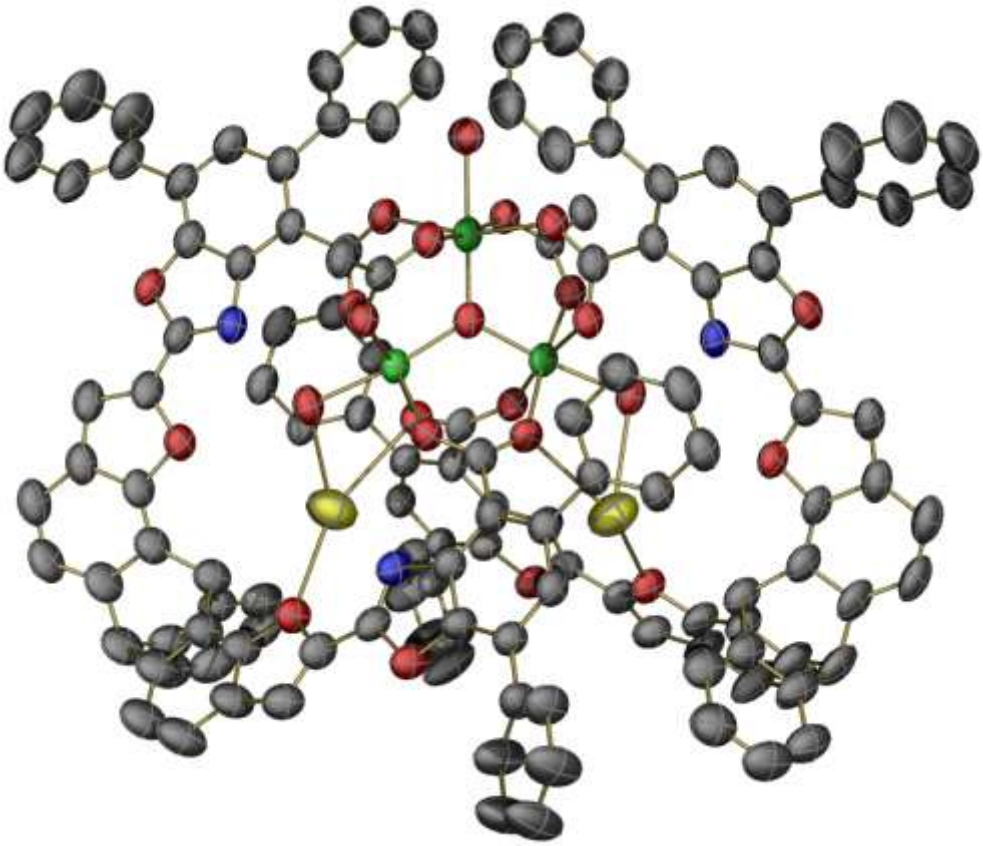


Figure S4. Thermal ellipsoid plot (50% probability) of X-ray structure of $[NaFe_3(\mathbf{L2}^{Ph4})_2(\mu_3\text{-}O)(\mu\text{-}O_2CPh_3)_2(H_2O)_3](OTf)_2$ (**8**). The phenyl groups on 2,2,2-triphenylacetate are omitted for clarity. Each sodium ion has 50% occupancy. Iron, green; carbon, gray; oxygen, red; nitrogen, blue; sodium, yellow.

Table S3. X-ray crystallographic data collection and refinement parameters for $[NaFe_3(\mathbf{L2^{Ph4}})_2(\mu_3\text{-}O)(\mu\text{-}O_2CCPh_3)_2(H_2O)_3](OTf)_2$ (**8**).

Identification code	**8**·$(C_6H_6)_6$·$(C_5H_{12})_2$
Empirical formula	$C_{216}H_{158}F_6Fe_3N_4NaO_{30}S_2$
Formula weight	3658.12
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 26.025(2) Å
	b = 37.392(3) Å β = 93.5390(10)°
	c = 17.9887(14) Å
Volume	17472(2) Å^3
Z	4
Calculated density	1.391 g/cm^3
Absorption coefficient	0.357 mm^{-1}
F(000)	7588
Crystal size	0.21 x 0.18 x 0.16 mm
Theta range for data collection	1.44 to 20.88°
Limiting indices	-26<=h<=26, -37<=k<=37, -17<=l<=18
Reflections collected / unique	78354 / 9198 [R(int) = 0.0960]
Completeness to theta = 24.71°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7446 and 0.6504
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9198 / 1411 / 1240
Goodness-of-fit on F^2	1.044
Final R indices [I>2σ (I)]	R_1 = 0.0976, wR_2 = 0.2645
R indices (all data)	R_1 = 0.1526, wR_2 = 0.3192
Largest diff. peak and hole	1.539 and -0.653 e. Å^{-3}

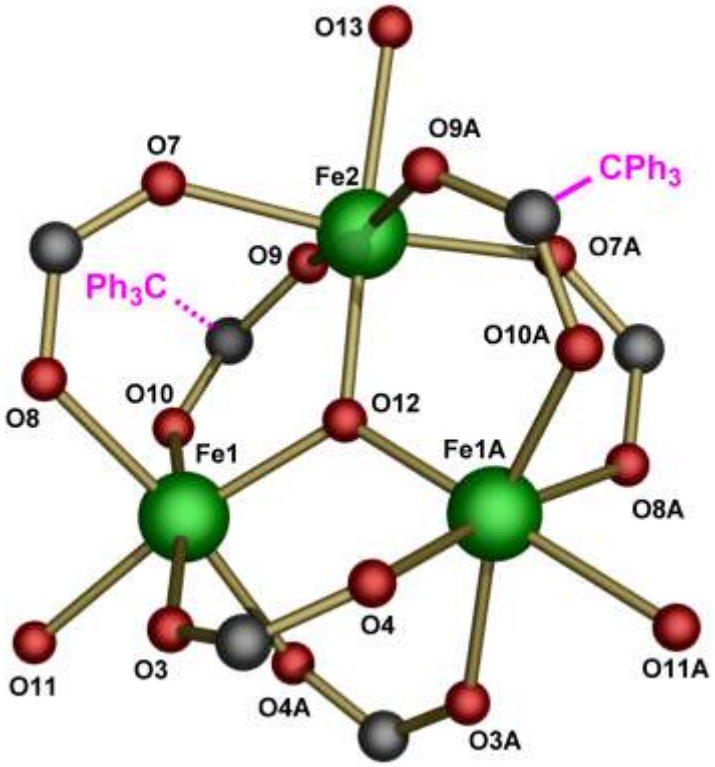


Figure S5. Core structure of complex **8** with labels. Selected bond lengths [Å], distances [Å], and angels [°]: Fe1–O12, 1.898(4); Fe1A–O12, 1.898(4); Fe2–O12, 1.882(9); Fe1–O11, 2.083(6); Fe1A–O11A, 2.083(6); Fe2–O13, 2.146(10); Fe1–O3, 2.016(6); Fe1A–O3A, 2.016(6); Fe1–O4A, 2.023(6); Fe1A–O4, 2.023(6); Fe1–O8, 2.009(6); Fe1A–O8A, 2.009(6); Fe1–O10, 2.013(6); Fe1A–O10A, 2.013(6); Fe2–O7, 2.006(6); Fe2–O7A, 2.006(6); Fe2–O9, 2.019(6); Fe2–O9A, 2.019(6); Fe1···Fe2, 3.274; Fe1A···Fe2, 3.274; Fe1···Fe1A, 3.285; Fe1–O12–Fe2, 120.0(2); Fe1A–O12–Fe2, 120.0(2); Fe1–O12–Fe1A, 119.9(4).

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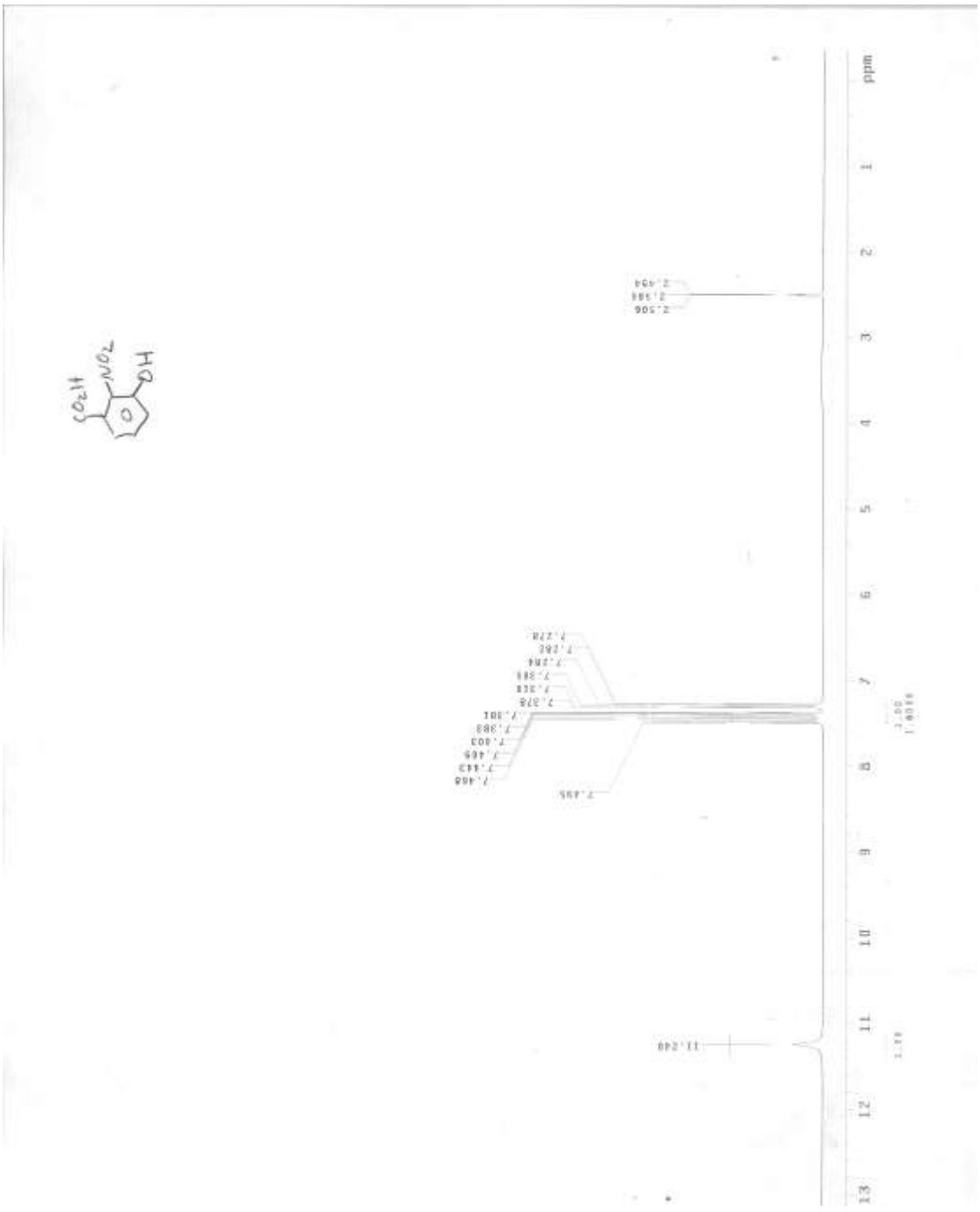
(5) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

(6) Müller, P. *Crystallography Reviews* **2009**, *15*, 57-83.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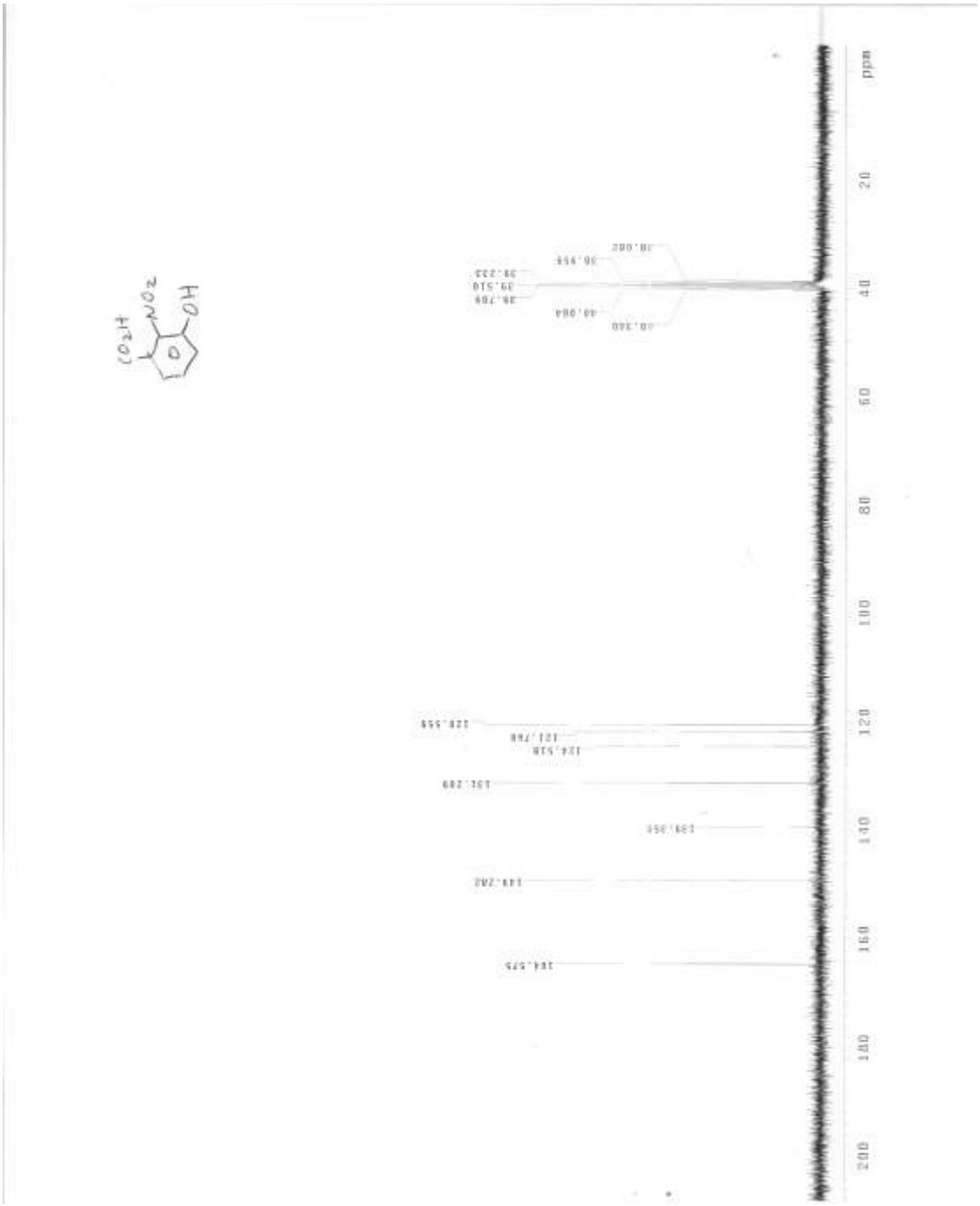
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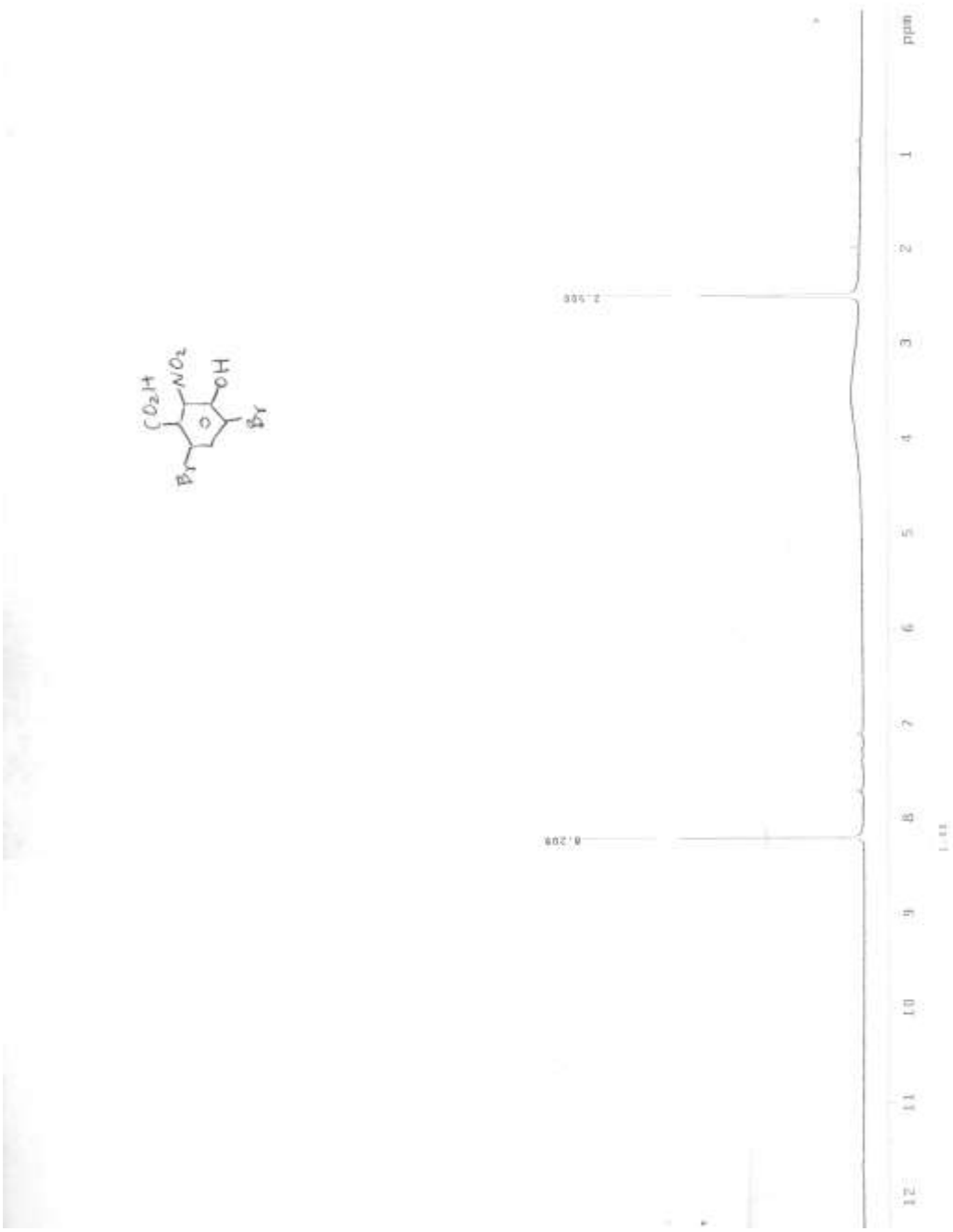
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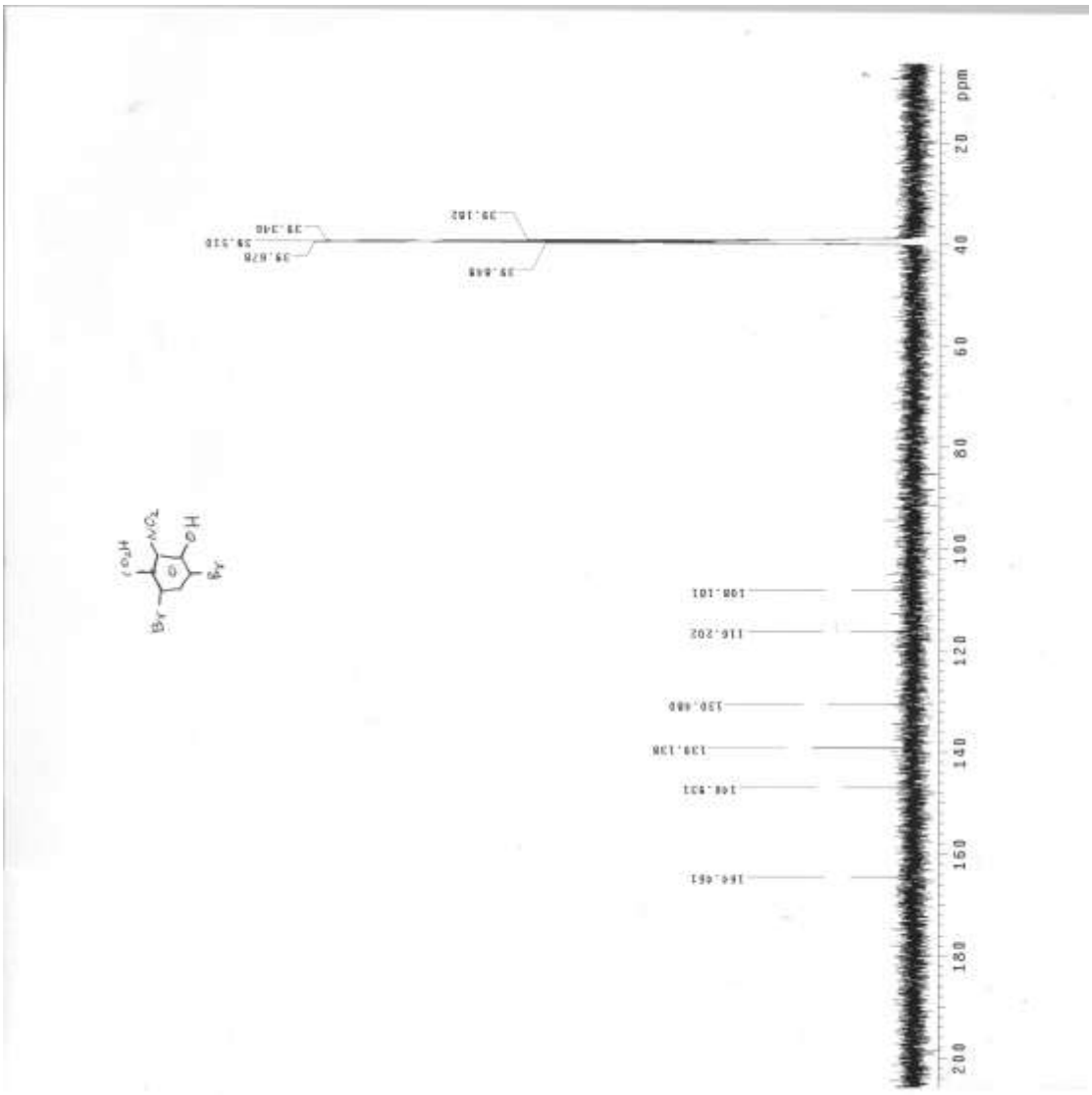
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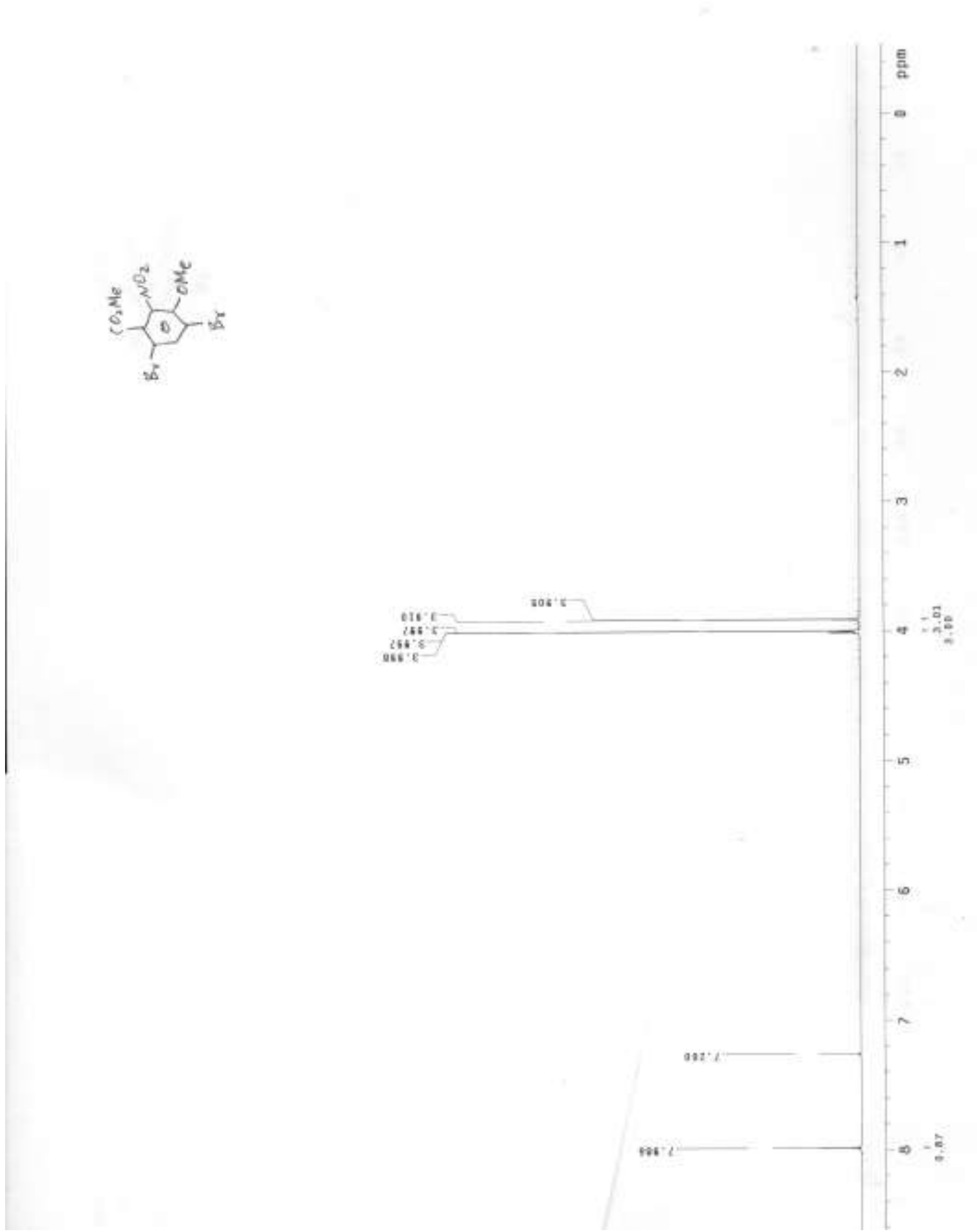
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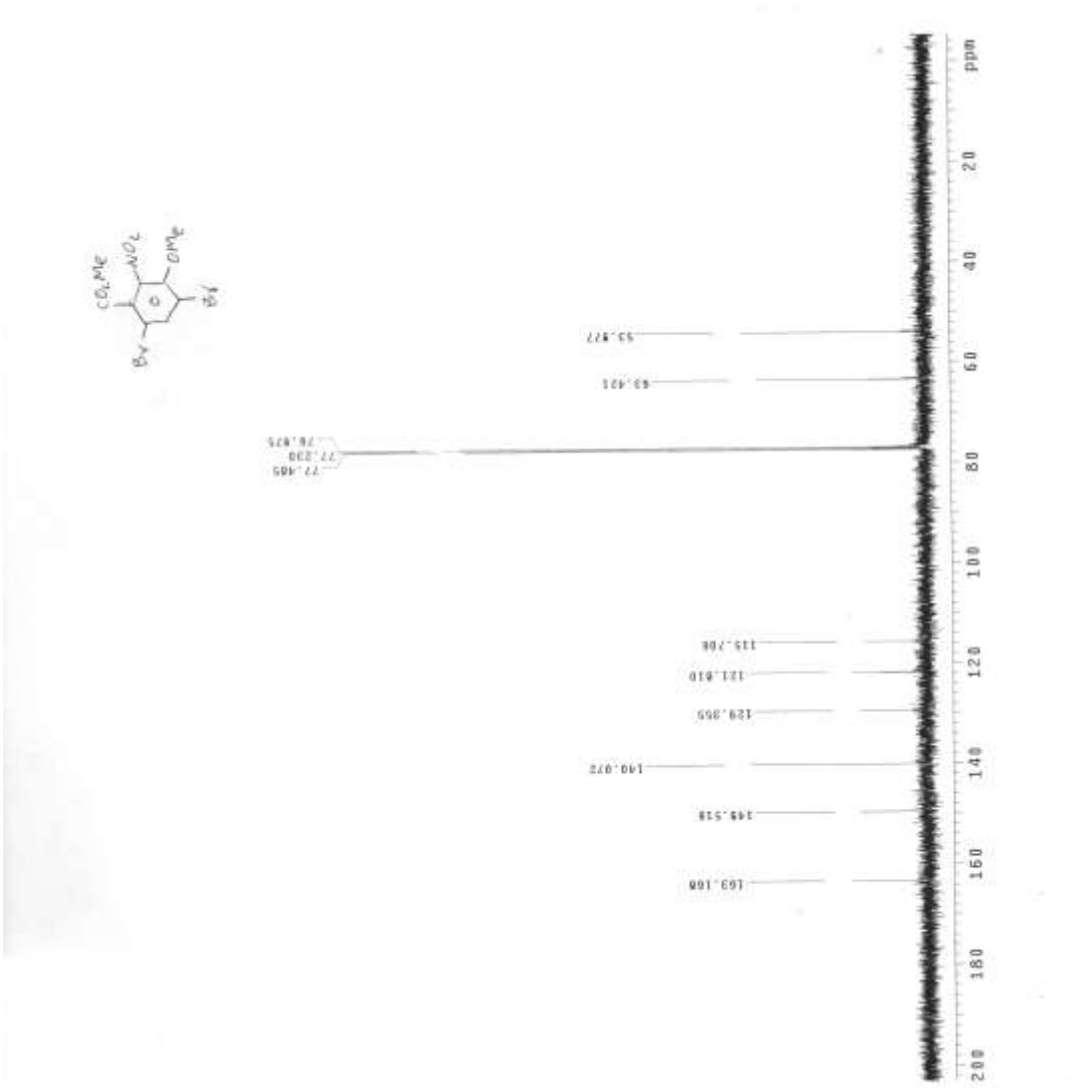
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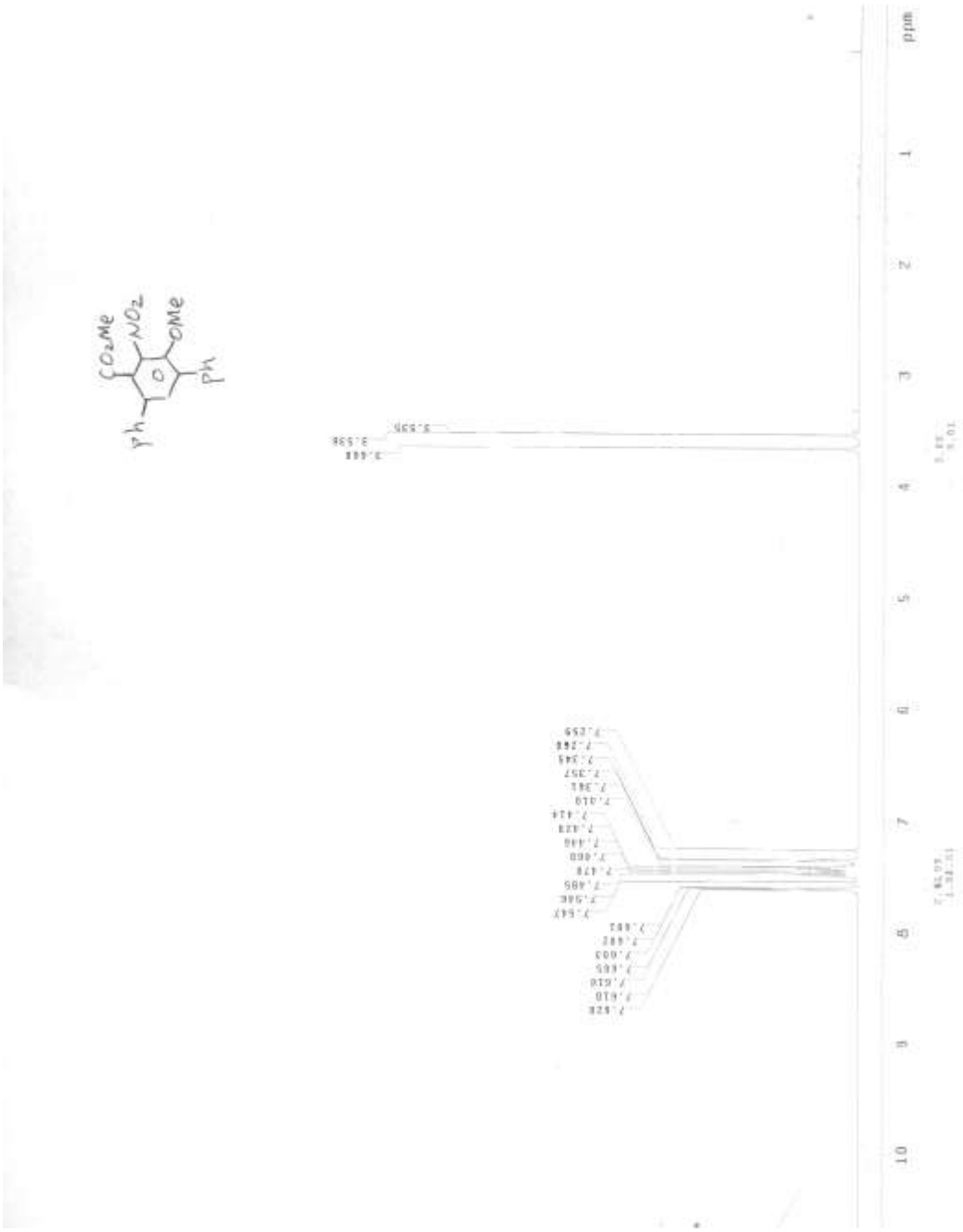
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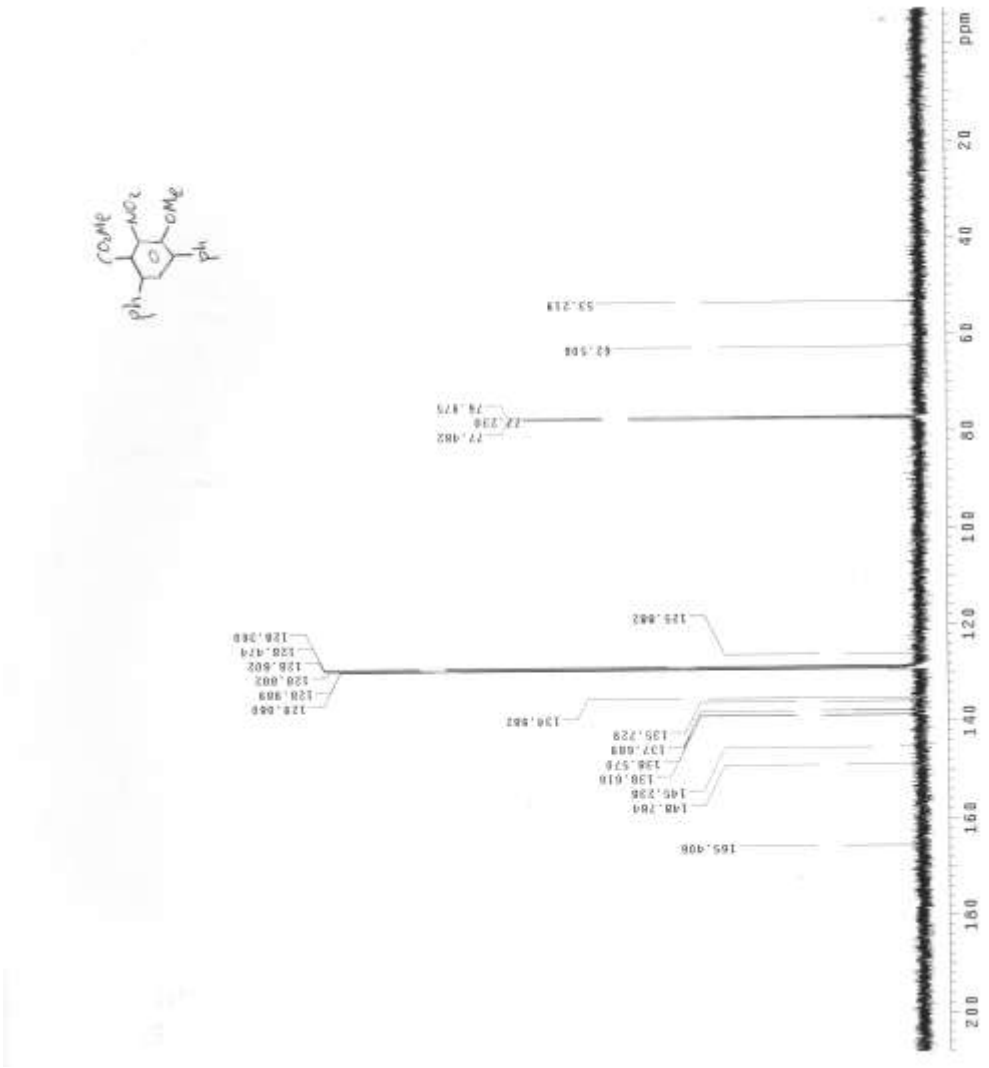
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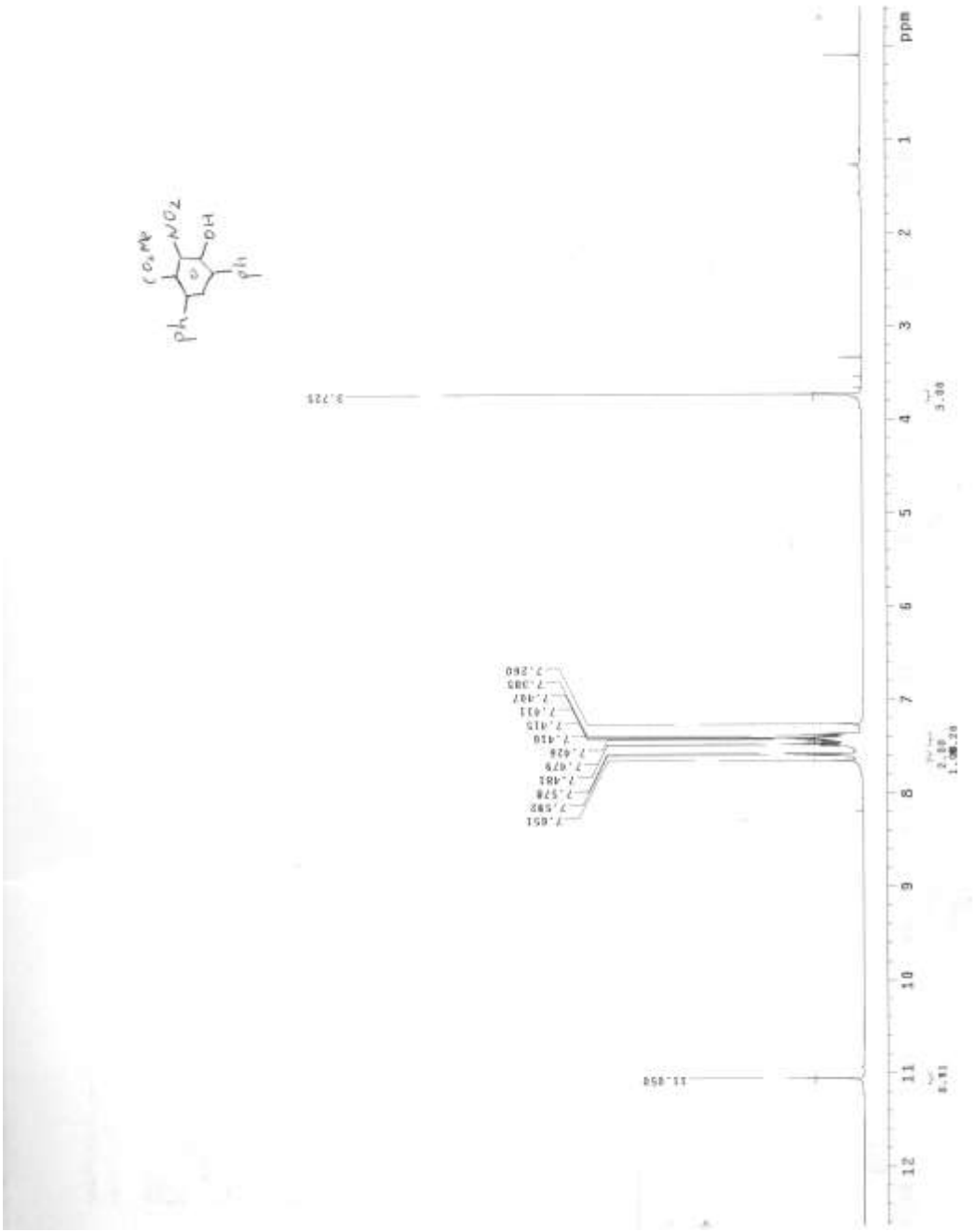
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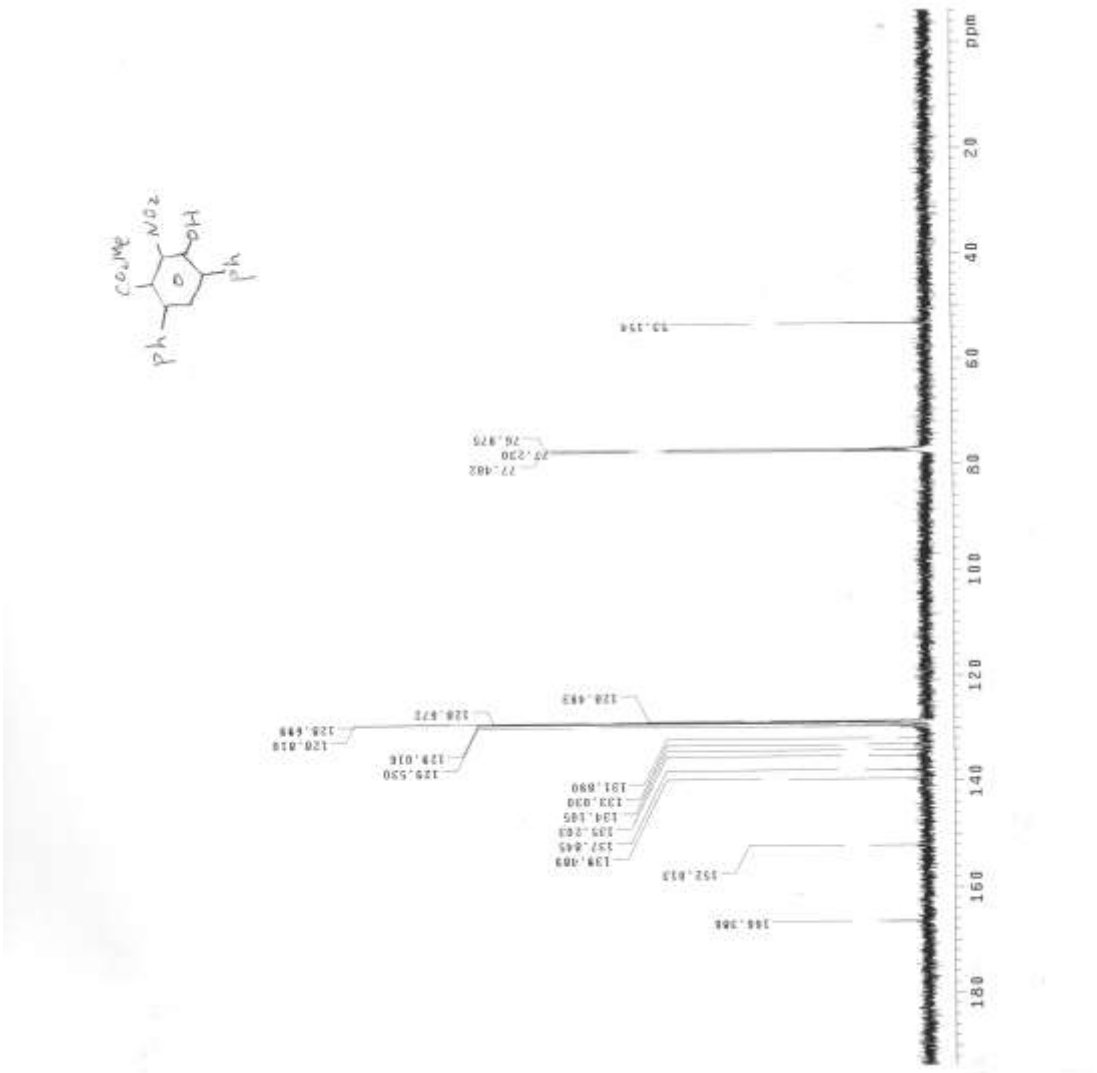
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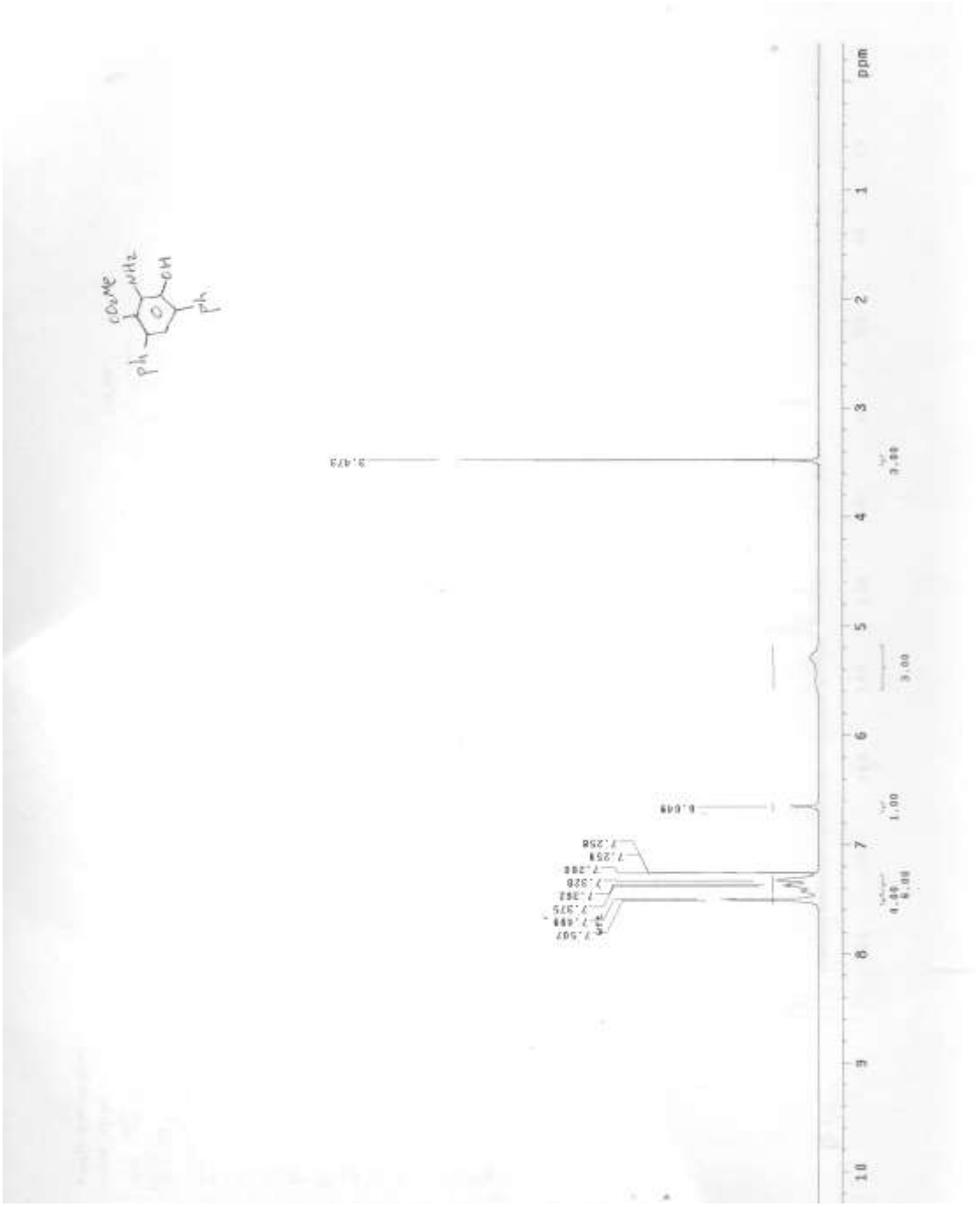
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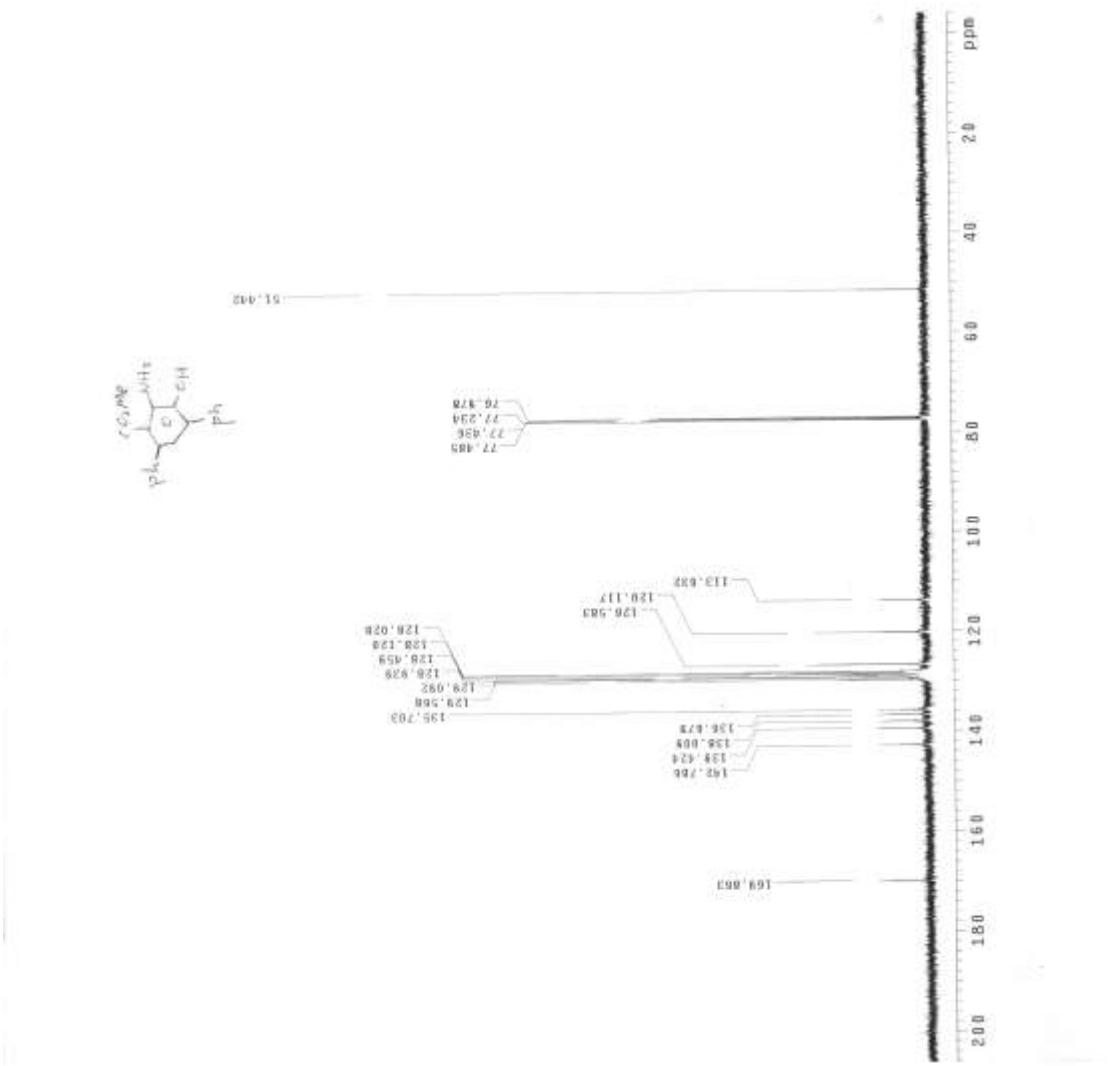
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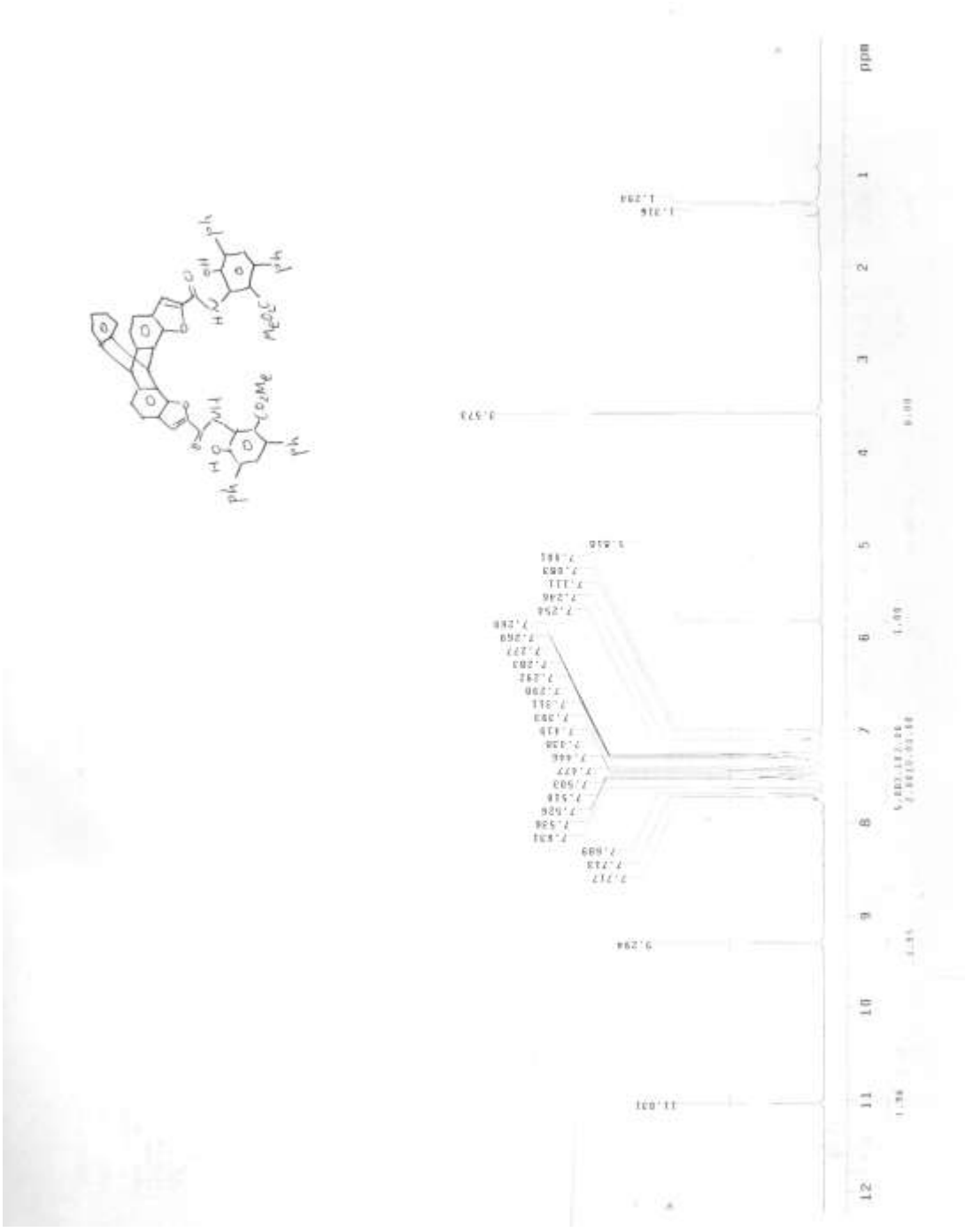

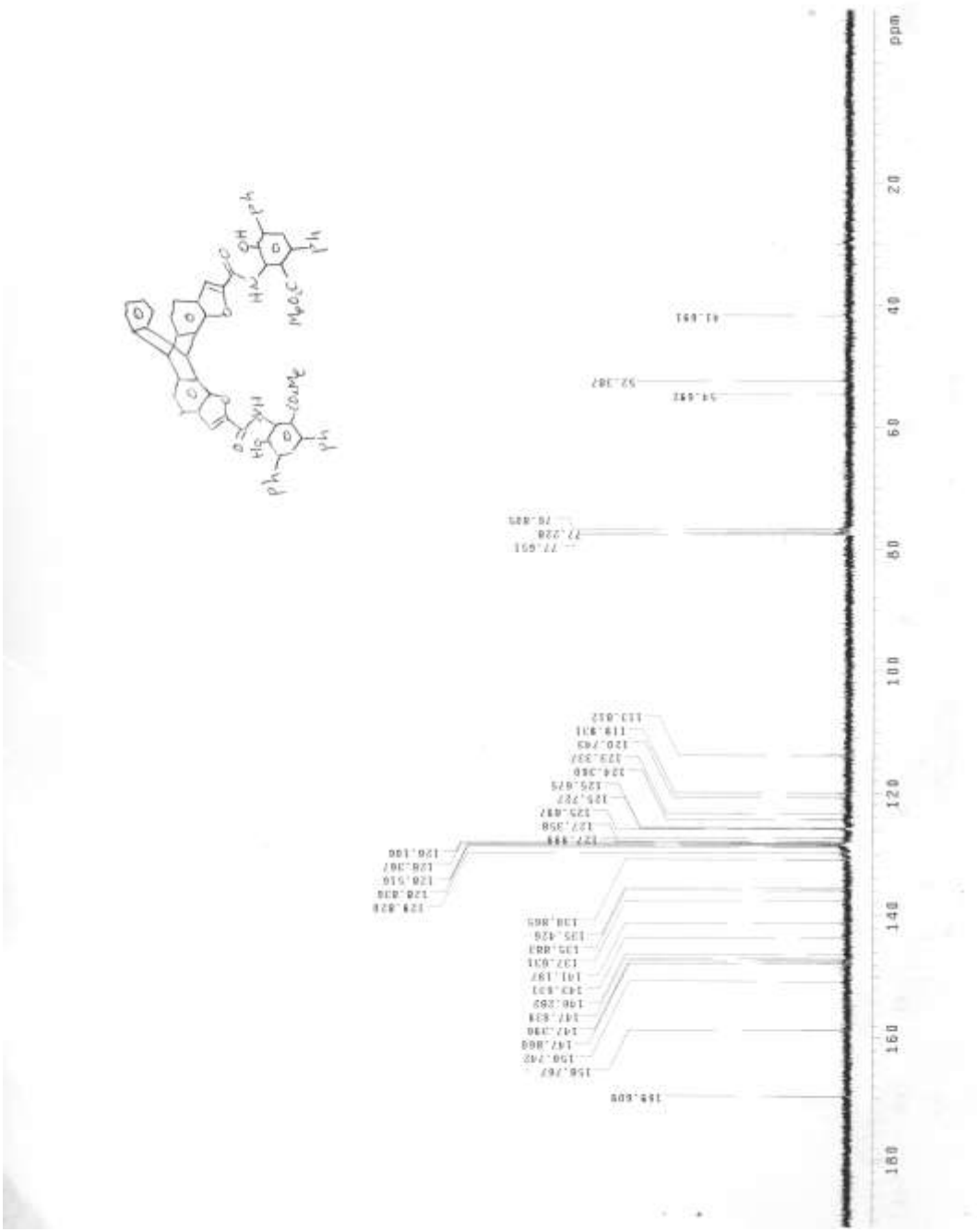

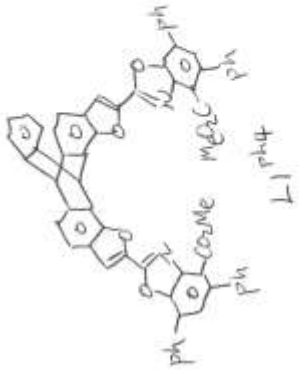
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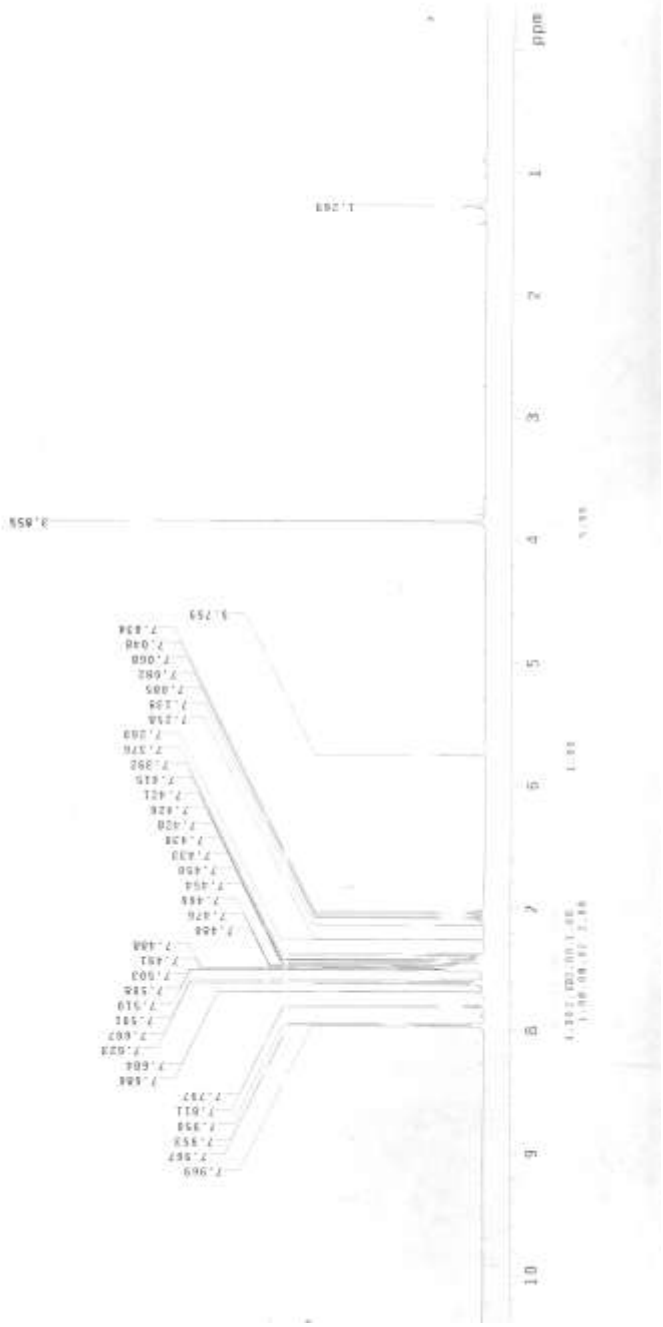

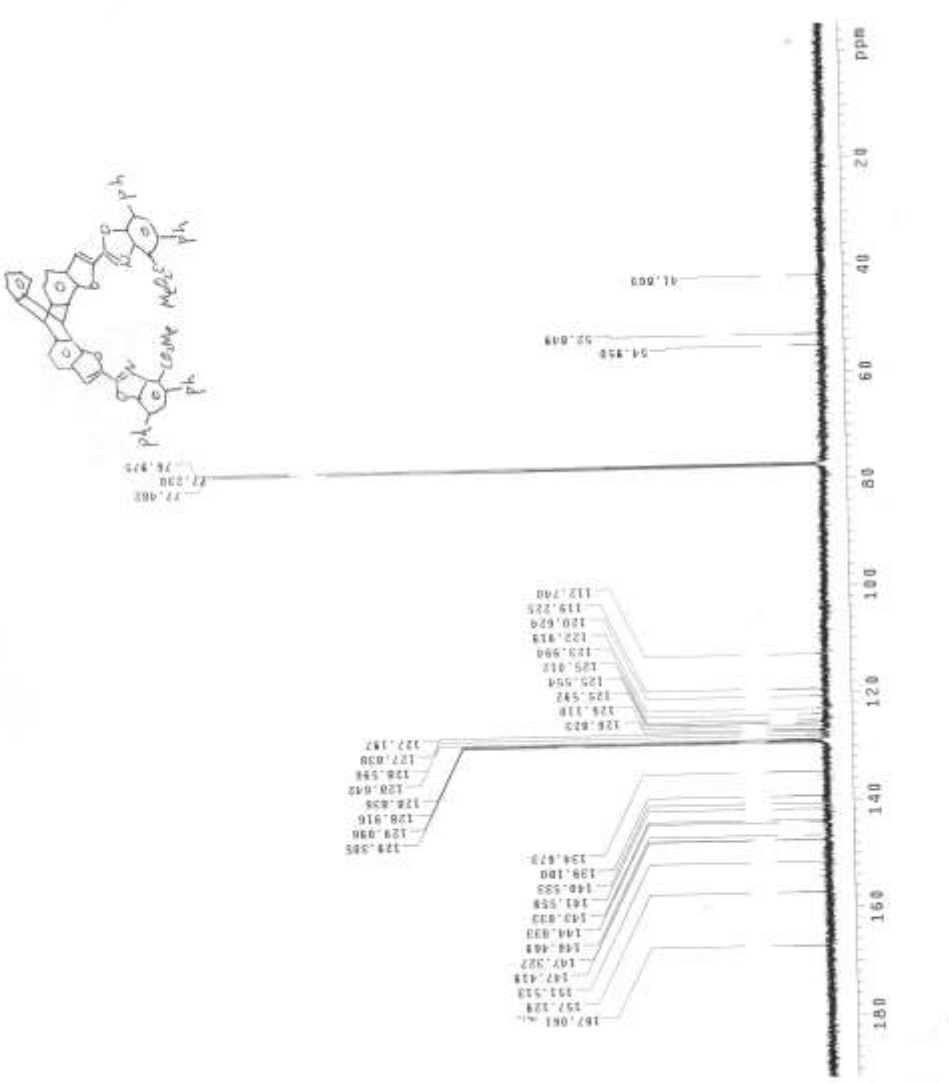
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