Supporting Information

Copper(II) Facilitated Decarboxylation for the Construction of Pyridyl-pyrazole Skelton

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1. Crystallographic data of ligands and compounds

Table S1. Crystallographic Data [a] for Ligands **1**, **2** and Complex **1, 2**.

Ligand/Complex	**Hppca (CCDC:1865965)**	**3-Me-Hppca (1872941)**	**1 (1865967)**	**2 (1865963)**
formula	$C_9H_7N_3O_2$	$C_{10}H_9N_3O_2$	$C_{40}H_{40}Cu_3N_{10}O_{12}$	$C_{28}H_{22}CuN_8O_4$
M	189.18	203.20	1043.44	598.08
crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
space group	$P2_1/c$	P-1	P-1	C2/c
a, Å	8.8416(2)	5.7124(7)	9.5552(7)	14.1353(7)
b, Å	12.3762(3)	7.3887(5)	9.6001(7)	10.5943(5)
c, Å	15.4438(3)	11.5280(10)	12.4239(9)	17.9376(9)
α, deg	90	92.199(6)	79.964(6)	90
β, deg	92.371(2)	98.583(9)	84.269(6)	106.500(5)
γ, deg	90	99.681(8)	67.980(7)	90
V, Å^3	1688.50(6)	473.26(8)	1039.60(13)	2575.6(2)
Z	8	2	1	4
μ, mm^{-1}	0.919	0.859	2.444	0.901
independent data	3225	1779	3916	2518
refined parameters	261	140	375	187
R_1[b], wR_2[c] (I >2σ(I))	0.0375, 0.1120	0.0488, 0.128	0.0453, 0.123	0. 0377, 0. 0778
R_1, wR_2 (all data)	0.0479, 0.1157	0.0601, 0.1322	0.0542, 0.1285	0. 0536, 0. 0844

[a] T = 100(2) K, Cu Kα radiation (λ = 1.54184 Å). [b] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

Table S2. Crystallographic Data [a] for Complex **3-6** and **8**.

Complex	**3 (1865964)**	**4 (1865966)**	**5 (1876648)**	**6 (1865962)**	**8 (1940796)**
formula	$C_9H_{11}Cl_2CuN_3O_4$	$C_{42}H_{102}CuN_8O_{18}$	$C_{36}H_{58}Cu_2N_8O_{11}$	$C_{28}H_{28}Cu_2N_8O_6$	$C_{38}H_{50}Cu_3N_8O_{15}$
M	359.65	1070.86	905.98	699.66	1049.48
crystal system	Monoclinic	monoclinic	Orthorhombic	Orthorhombic	Monoclinic
space group	$P2_1/n$	C2/c	$P2_12_12_1$	Pbca	$P2_1/n$
a, Å	8.2386(3)	21.6716(4)	22.8690(4)	17.3539(3)	15.3643(2)
b, Å	11.5739(4)	7.91640(15)	10.96066(16)	8.80152(17)	16.8900(2)
c, Å	13.9034(4)	32.9340(5)	8.34393(14)	19.8411(3)	17.5664(2)
α, deg	90	90	90	90	90
β, deg	90.524(3)	93.2825(15)	90	90	104.5437(14)
γ, deg	90	90	90	90	90
V, Å^3	1325.66(8)	5640.92(17)	2091.48(6)	3030.55(10)	4412.46(10)
Z	4	4	2	4	4
μ, mm^{-1}	6.186	1.147	1.811	2.202	2.339
independent data	2520	5324	3927	2851	8355
refined parameters	177	353	391	205	676
R_1[b], wR_2[c] (I >2σ(I))	0.0280, 0.0720	0.0304, 0.0818	0.0635, 0.1764	0.0367, 0.1039	0.0329, 0.0880
R_1, wR_2 (all data)	0.0332, 0.0745	0.0345, 0.0849	0.0670, 0.1806	0.0394, 0.1063	0.0402, 0.0920

[a] T = 100(2) K, Cu Kα radiation (λ = 1.54184 Å). [b] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

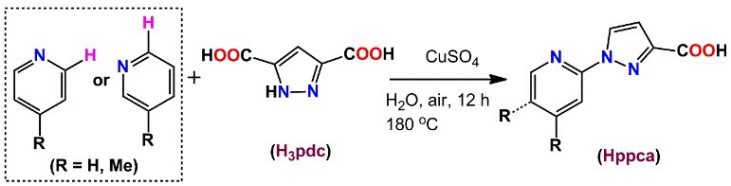
2. Experimental Section

2.1 General Information

The single crystal data of compounds were collected by a Cu-Kα rotating anode source at 100 K, using a Supernova diffractometer with the ω-scan method. ESI-MS were obtained using a Bruker Impact II quardrupole time-of-flight mass spectrometer. ^{1}H NMR spectra were recorded on Bruker Avance III (400 MHz) and chemical shifts are expressed in δ ppm values with reference to tetramethylsilane (TMS) as internal standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet. Coupling constants (J) are expressed in Hz. Pyridines was distilled before used. DMF and THF were dried over CaH_2 and stored in the presence of activated molecular sieve. All other reagents were of analytical grade and employed as received.

2.2 Conditional screening and analysis

Table S3. Optimization of the formation of Hppca



Entry	Cu(II)	Time	Temperature	Atmosphere	Solvents (2/1)	Yield
1	$CuSO_4$	**48 h**	180 °C	air	H_2O/py	55%
2	$CuSO_4$	**24 h**	180 °C	air	H_2O/py	53%
3	$CuSO_4$	**12 h**	180 °C	air	H_2O/py	42%
4	$CuSO_4$	**6 h**	180 °C	air	H_2O/py	23%
5	**$CuCl_2$**	12 h	180 °C	air	H_2O/py	34%
6	**$Cu(OAc)_2$**	12 h	180 °C	air	H_2O/py	18%
7	**$ZnSO_4$**	12 h	180 °C	air	H_2O/py	None
8	**None**	12 h	180 °C	air	H_2O/py	None
9	**$CuSO_4$ (0.1 equi)**	12 h	180 °C	air	H_2O/py	13%
10	$CuSO_4$	12 h	**190 °C**	air	H_2O/py	41%
11	$CuSO_4$	12 h	**170 °C**	air	H_2O/py	27%
12	$CuSO_4$	12 h	**160 °C**	air	H_2O/py	19%
13	$CuSO_4$	12 h	**150 °C**	air	H_2O/Py	trace
14	$CuSO_4$	12 h	180 °C	**N_2**	H_2O/py	18%
15	$CuSO_4$	12 h	180 °C	**O_2**	H_2O/py	44%
16	$CuSO_4$	12 h	180 °C	air	**H_2O/2-me-py**	none
17	$CuSO_4$	12 h	180 °C	air	**H_2O/3-me-py**	18%
18	$CuSO_4$	12 h	180 °C	air	**H_2O/4-me-py**	25%

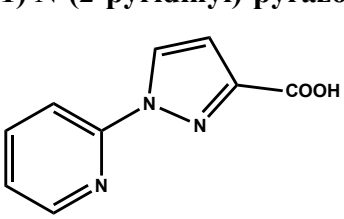
Reaction conditions: Cu(II) salts (1.0 mmol), H_3pdc (1.0 mmol), air, py/H_2O (5/10 mL).

In order to understand the C-N bond formation, we optimized the reaction by changing ingredients to find out the most efficient condition (Table **S**3). It was found that the reaction of H_3pdc with one equivalent of $CuSO_4$ as metal salt, air as oxidant and pyridine/H_2O (1:2, v/v) as

solvents at 180 °C afforded the most economical result, yielding the product of Hppca in 53% in 24 h (entry 2). The reaction time was monitored at the points of 6 h, 12 h, 24 h and 48 h. The results showed that a period of 24 h would be enough for a completeness of reaction according to the obtained yields of product (entry 1-4). Other copper sources such as $CuCl_2$ (entry 5) and $Cu(OAc)_2$ (entry 6) afforded the product in lower yields, probably due to high affinity of Cl^- and OAc^- anions to the Cu^{2+} center, and thereby incapability of leaving groups during reaction. The replacement of $CuSO_4$ with $ZnSO_4$ as metal salt or absence of cupric salt led to the failure of production, which implied the indispensability of copper ion in this reaction (entry 7-8). The metal to ligand ratio was explored by using 10% mole amount of $CuSO_4$ to the H_3pdc, resulting in the decreasing of yield from 42% to 13% in 12 h (based on H_3pdc) (entry 9). It is noted that the yield of 13% could be converted to 130% when it was calculated based on $CuSO_4$. This result is consistent with the statement presented above that the Cu(II) salt played a critical role as an electron transfer mediator in the process of C-N bond formation. High temperature of 160-190 °C was found necessary for decarboxylation and thereby generation of Hppca. The temperature of 180 °C was finally determined in term of production efficiency and energy conservation (entry 3, 10-12). Lower temperature would lead to the decline of yield down to trace at 150 °C (entry 13). The role of air was investigated by running the reaction under N_2, from which only a yield of 18% was obtained (entry 14). The air would work as an oxidant in the reaction, and the Cu(II) salt was thought to be responsible for the yield of 18% by means of reduction to Cu(I) (see proposed mechanism below). This result was confirmed by running the reaction under O_2 atmosphere, from which the Hppca was isolated in 44% yield, in consistent with the production rate in air (entry 15). In addition, the steric effect was investigated by using 2-, 3- or 4-methyl-pyridine instead of pyridine. The yields decreased to 0%, 18%, 25% in 12h respectively (entry 16-18), which implied that the substitution on the pyridine ring might have negative influence on production in this reaction.

2.3 Experimental procedure for organic compounds

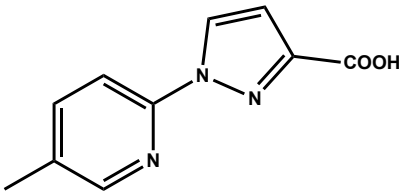
1) N-(2-pyridinyl)-pyrazole-3-carboxylate acid (Hppca, ligand 1)



A mixture of copper sulfate pentahydrate (250.0 mg, 1 mmol) and 3,5-pyrazole-dicarboxylic acid monohydrate (174.0 mg, 1 mmol) was dissolved in H_2O/pyridine (10 mL/5 mL). After stirred for 15 minutes, the blue solution was transferred into a 25 mL Teflon-lined stainless steel vessel and heated to react at 180 ℃ for 12 h. Cooling down to r.t., the solution was rotary-evaporated to give some blue solid. The solid was taken up in deionized water (10 mL), to which saturated aqueous Na_2S solution (3 mL) was added to deposit the cupric ions as some black powder. The mixture was filtered and the pH of filtrate was adjusted to 3 by by 1 M HCl. The resultant solution was extracted with CH_2Cl_2 (3 × 20 mL) and the organic layers were combined and dried with Na_2SO_4 over night. The solvent was removed and the solid was dried in *vacuo* to afford product as some white powder (79.3 mg, 42%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.11 (s, 1H), 8.69 (d, J = 2.6 Hz, 1H), 8.52 (ddd, J =

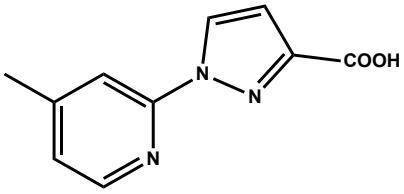
4.9, 1.8, 0.8 Hz, 1H), 8.06 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.98 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.49 – 7.39 (m, 1H), 6.96 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.44, 150.80, 148.17, 144.94, 139.05, 128.91, 122.82, 113.26, 110.63. HRMS m/z (ESI) [M + H^+]: 190.0615.

2) N-(2-(4-methyl)-pyridinyl)-pyrazole-3-carboxylate acid (3-Me-Hppca, ligand 2)



The above method was used for the synthesis of ligand **2** with starting material of 3-methyl-pyridine. The product was obtained as some white powder (35.7 mg, 18%). ^{1}H NMR (400 MHz, CD_3CN): δ 8.58 (d, *J* = 2.6 Hz), 8.30 (s), 7.90 (d, *J* = 8.4 Hz), 7.78 (dd, *J* = 8.4, 1.7 Hz), 6.94 (d, *J* = 2.6 Hz), 2.37 (s). ^{13}C NMR (100 MHz, CD_3CN): δ 162.97, 149.24, 145.97, 140.77, 139.61, 133.93, 129.46, 118.26, 113.04, 110.72, 17.87. HRMS m/z (ESI) [M + Na^+]: 226.0585.

3) N-(2-(5-methyl)-pyridinyl)-pyrazole-3-carboxylate acid (4-Me-Hppca, ligand 3)



The above method was used for the synthesis of ligand **3** with starting material of 4-methyl-pyridine. The product was obtained as some white powder (50.7 mg, 25%). ^{1}H NMR (400 MHz, CDCl3): δ. 8.63 (d, J = 2.6 Hz, 1H), 8.31 (d, J = 5.0 Hz, 1H), 7.99 (s, 1H), 7.11 (d, J = 4.9 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR(100 MHz, CDCl3): δ. 165.90, 150.88, 150.86, 147.78, 144.78, 128.95, 123.95, 113.79, 110.59, 21.19. HR-MS m/z (ESI) [M + Na^+]: 226.0588.

2.3 Experimental procedure for inorganic compounds

$[Cu^{II}_3(pdc)_2(py)_6(H_2O)_2]\cdot 2H_2O$ (1)

A mixture of $CuSO_4\cdot 5H_2O$ (125.0 mg, 0.5 mmol) and 3,5-pyrazole-dicarboxylic acid monohydrate (87.0 mg, 0.5 mmol) was dissolved in H_2O/pyridine (5 mL/2.5 mL). After stirred for 15 minutes, the solution was filtered and the filtrate was layered with THF to deposit some purple block crystals, which were collected and washed with THF (117.0 mg, 65%). Anal. Calcd. (%) for $C_{40}H_{40}Cu_3N_{10}O_{12}$: C, 46.04; H, 3.86; N, 13.42. Found (%): C, 45.68; H, 4.10; N, 13.20.

$[Cu^{II}(py)_2(ppca)_2]$ (2)

A mixture of $CuSO_4\cdot 5H_2O$ (250.0 mg, 1 mmol) and 3,5-pyrazole-dicarboxylic acid monohydrate (174.0 mg, 1 mmol) was dissolved in H_2O/pyridine (10 mL/5 mL). The solution was transferred into a 25 mL Teflon-lined stainless steel vessel and heated to react at 180 ℃ for 12 h. After cooling down to r.t., the resultant solution was evaporated in a fume hood for 4 days to deposit some crystalline solid. The solid was collected and washed with H_2O (3 × 5 mL) to give product as some blue plate

crystal (134.5 mg, 45%). Anal. Calcd. (%) for $C_{28}H_{22}CuN_8O_4$: C, 56.23; H, 3.71; N, 18.74. Found (%): C, 56.06; H, 3.92; N, 18.56.

$[Cu^{II}(Hppca)Cl_2(H_2O)]\cdot H_2O$ (3)

A portion of complex **2** (60.0 mg, 0.1 mmol) was dissolved in 37% HCl aqueous solution (1 mL). The resultant solution was filtered and evaporated in a fume hood to deposit some green needle crystals, washed with THF (29.0 mg, 81%). Anal. Calcd. (%) for $C_9H_{11}Cl_2CuN_3O_4$: C, 30.06; H, 3.08; N, 11.68. Found (%): C, 30.36; H, 2.88; N, 11.84.

$(Et_4N)_4[Cu^{II}(Pdc)_2](H_2O)_{10}$ (4)

A mixture of $CuSO_4\cdot 5H_2O$ (100.0 mg, 0.4 mmol) and 3,5-pyrazole-dicarboxylic acid monohydrate (121.8 mg, 0.7 mmol) was dissolved in ammonium hydroxide (25%, 2 mL). The resultant solution was evaporated in a fume hood to leave an oily residue. The residue was washed with H_2O (2 × 3 mL) and THF (2 × 5 mL), and dissolved in mixture of DMF (20 mL) and Et_4NOH aqueous solution (10%, 3 mL). The solution was diffused with Et_2O to yield the product as some purple needle crystals (123.7 mg, 33%). Anal. Calcd. (%) for $C_{28}H_{22}CuN_8O_4$: C, 56.23; H, 3.71; N, 18.74. Found (%): C, 56.85; H, 3.41; N, 19.12.

$(Et_4N)_2[Cu^{II}_2(pdc)_2(py)_2]\cdot 3H_2O$ (5)

A mixture of $CuSO_4\cdot 5H_2O$ (175.0 mg, 0.7 mmol) and 3,5-pyrazole-dicarboxylic acid monohydrate (121.8 mg, 0.7 mmol) was dissolved in ammonium hydroxide (25%, 2 mL). The resultant solution was evaporated in a fume hood to leave an oily residue. The residue was washed with H_2O (2 × 3 mL) and THF (2 × 5 mL), and dissolved in mixture of DMF (20 mL) and Et_4NOH aqueous solution (10%, 1 mL). Et_2O (50 mL) was added to resultant solution to deposit some blue solid, which was recrystallized from DMF/pyridine (25 mL/5 mL) with the diffusion of Et_2O to afford the product as some blue block crystals (152.0 mg, 24%). Anal. Calcd. (%) for $C_{36}H_{58}Cu_2N_8O_{11}$: C, 47.73; H, 6.45; N, 12.37. Found (%): C, 48.33; H, 6.35; N, 12.45.

$[Cu^{II}_2(pz\text{-}COO)_2(py)_4]\cdot 2H_2O$ (6)

A mixture of $CuSO_4\cdot 5H_2O$ (250.0 mg, 1 mmol) and pyrazole-3-carboxylic acid (112.0 mg, 1 mmol) was dissolved in H_2O/pyridine (10 mL/5 mL). The solution was transferred into a 25 mL Teflon-lined stainless-steel vessel and heated to react at 180 °C for 12 h. After cooling down to r.t., the resultant solution was evaporated in a fume hood for 2 weeks to leave an oily residue. The residue was washed with H_2O (3 × 5 mL) and THF (2 × 3 mL) to give product as some blue crystalline solid (262.1 mg, 75%). Anal. Calcd. (%) for $C_{28}H_{28}Cu_2N_8O_6$: C, 48.07; H, 4.03; N, 16.02. Found (%): C, 47.36; H, 4.09; N, 16.18.

$[Cu_3(pdc)_2(2\text{-}me\text{-}py)_3(H_2O)_4]\cdot 2\text{-}me\text{-}py\cdot THF\cdot 2H_2O$ (8)

A crystal sample of $[Cu^{II}_3(Pdc)_2(py)_6(H_2O)_2]\cdot 2H_2O$ (**1**) (20.9 mg, 0.02 mmol) was dissolved in 2-me-py (2 mL). The resulant blue solution was layered over THF to deposit product as blue crystals at the bottom of vial, yield 3.6 mg, 17% based on copper. The structure of sample was confirmed by X-ray crystallography. Anal. Calcd. (%) for $C_{38}H_{50}Cu_3N_8O_{15}$: C, 43.49; H, 4.80; N, 10.68. Found (%): C, 43.92; H, 4.75; N, 10.76.

$[Cu^{II}(py)_4(SO_4)]\cdot H_2O$ (10)

The complex 7 was obtained in the same reaction for synthesis of complex 2 (see above). After the the complex 2 was isolated, the remained mother solution was continually evaporated to leave a blue-black oily mixture, from which some blue crystals was collected manually and washed with THF/Et_2O (v/v, 1:1) (25 mg, 5.1% based on $CuSO_4 \cdot 5H_2O$ (1 mmol)). The structure of sample was confirmed by X-ray crystallography. Anal. Calcd. (%) for $C_{20}H_{22}CuN_4O_5S$: C, 48.62; H, 4.49; N, 11.34. Found (%): C, 48.99; H, 4.38; N, 11.46.

2.4 Crystal structure of 3-Me-Hppca and compound 10

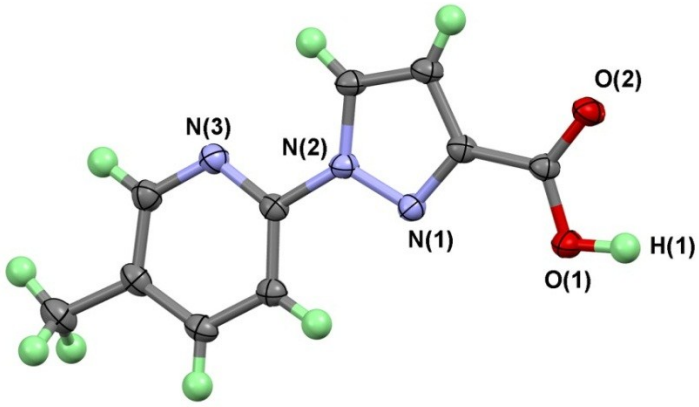


Figure S1. Crystal structure of N-(2-(4-methyl)-pyridinyl)-pyrazole-3-carboxylate acid (3-Me-Hppca, L3) showing the thermal ellipsoids of 50% probability surfaces.

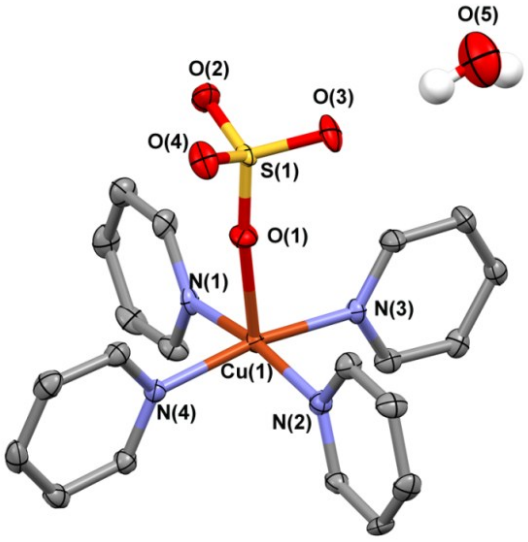


Figure S2. Crystal structure of $[Cu^{II}(py)_4(SO_4)] \cdot H_2O$ (**10**) derived from a fast-collection data, showing the thermal ellipsoids of 50% probability surfaces. Unit cell: 15.1800(6) 10.9335(2) 14.3519(6) 90 117.612(5) 90; formula: $C_{20}H_{22}CuN_4O_5S$; Mr = 494.02; crystal system: monoclinic; space group: Cc; independent data: 2000; completeness: 0.82 (θ = 70°) Selected bond lengths (Å): Cu(1)-N(1) 2.051(4), Cu(1)-N(2) 2.031(4), Cu(1)-N(3) 2.014(4), Cu(1)-N(4) 2.022(4), Cu(1)-O(1)

2.097(3). R_1, wR_2 (I >2σ(I)): 0.392, 0.1027; R_1, wR_2 (all data): 0.397, 0.1036.

3. NMR and Mass spectra

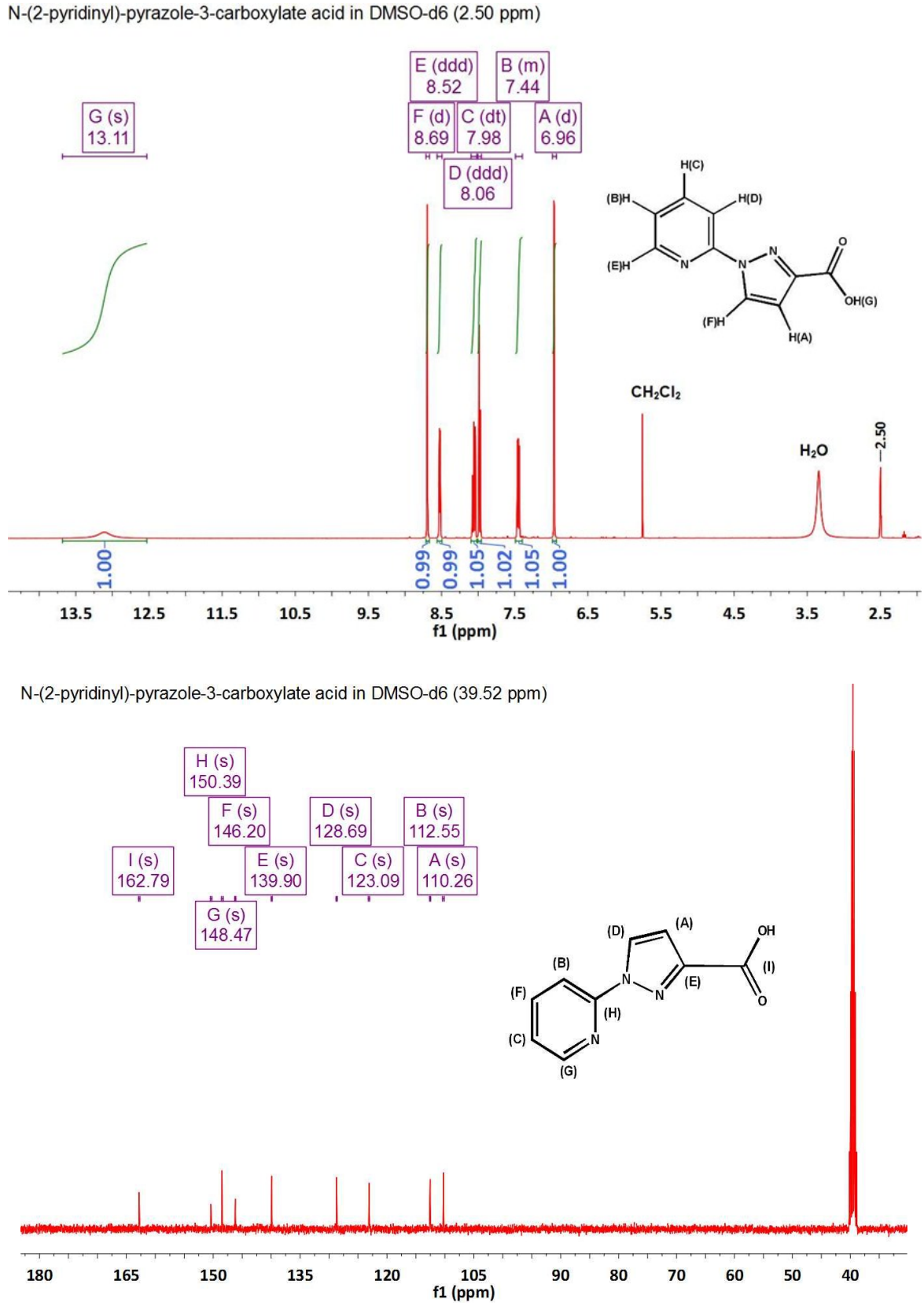


Figure S3. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of N-(2-pyridinyl)-pyrazole-3-carboxylate

acid (L**1**) in DMSO-d_6.

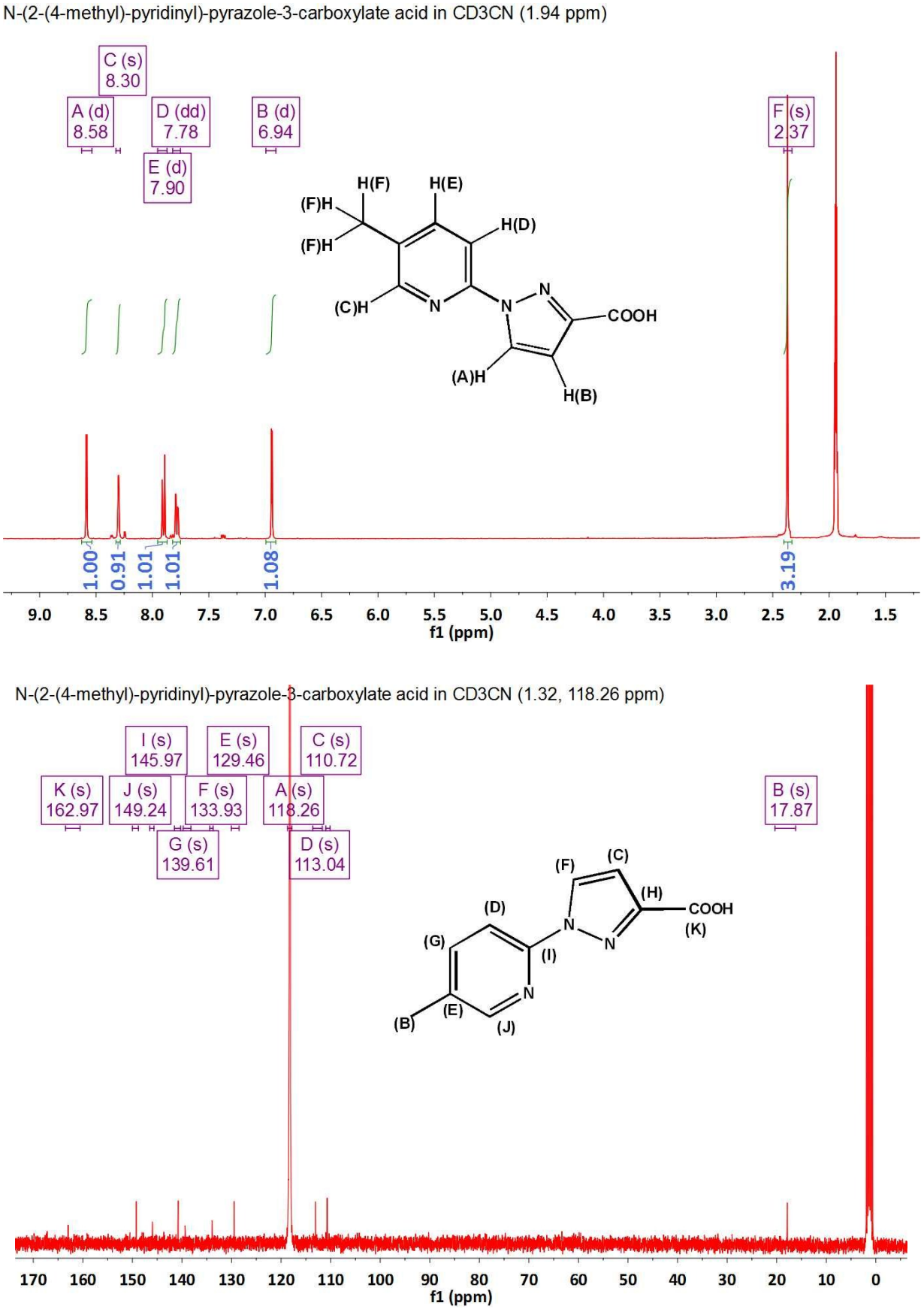


Figure S4. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of N-(2-(4-methyl)-pyridinyl)–pyrazole-3-

carboxylate acid (L**2**) in CD_3CN.

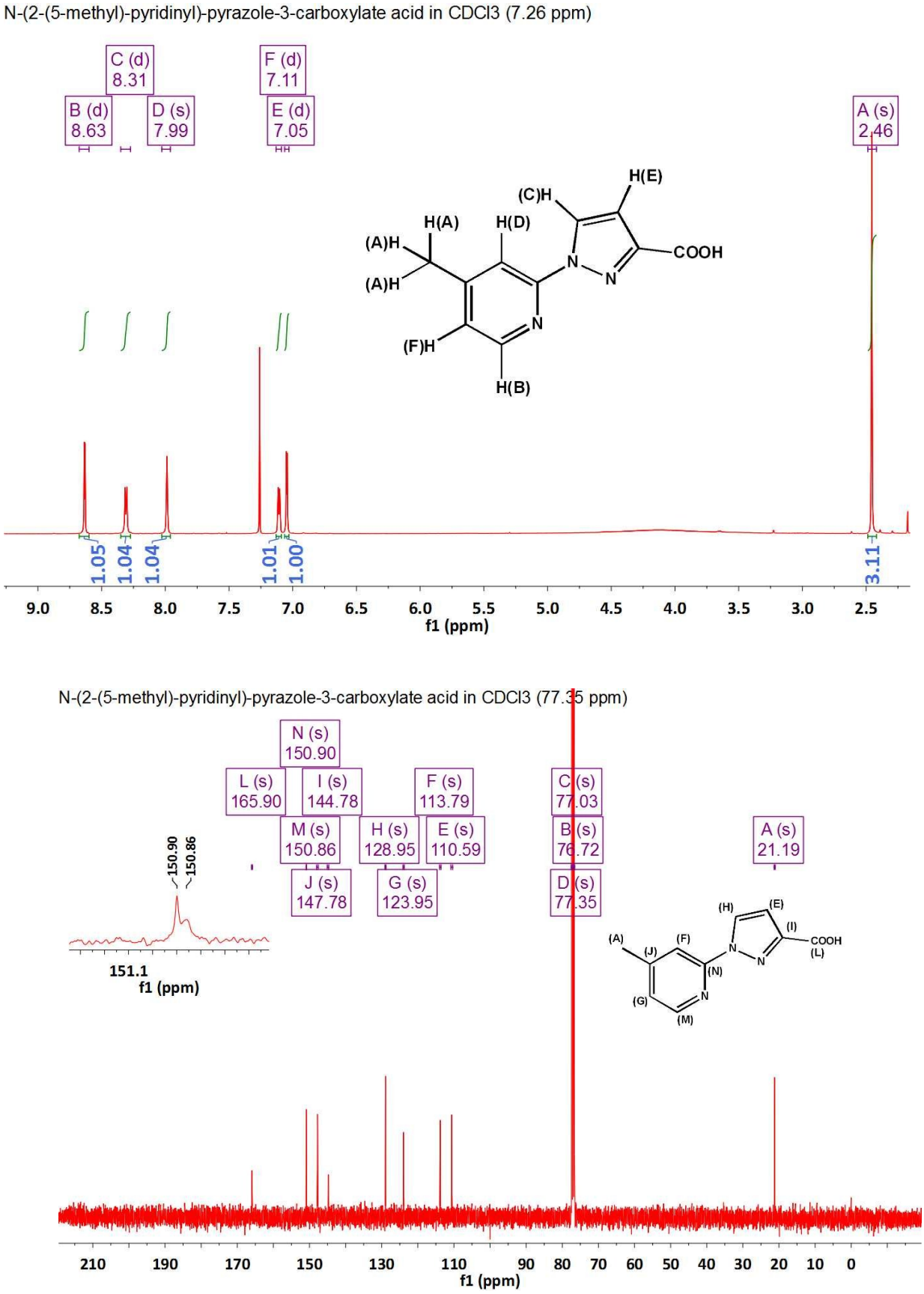


Figure S5. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of N-(2-(5-methyl)-pyridinyl)-pyrazole-3-

carboxylate acid (L**3**) in $CDCl_3$.

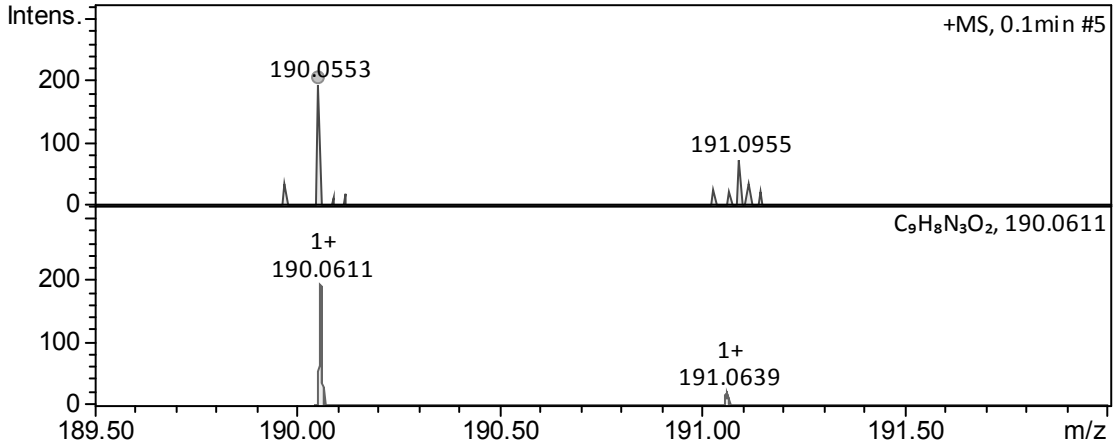


Figure S6. High-resolution spectrum of N-(2-pyridinyl)-pyrazole-3-carboxylate acid (L**1**, $C_9H_7N_3O_2$) in MeOH. HRMS m/z (ESI) $[M + H^+]^+$: 190.0553 (Found, top) and 190.0611 (calculated, bottom).

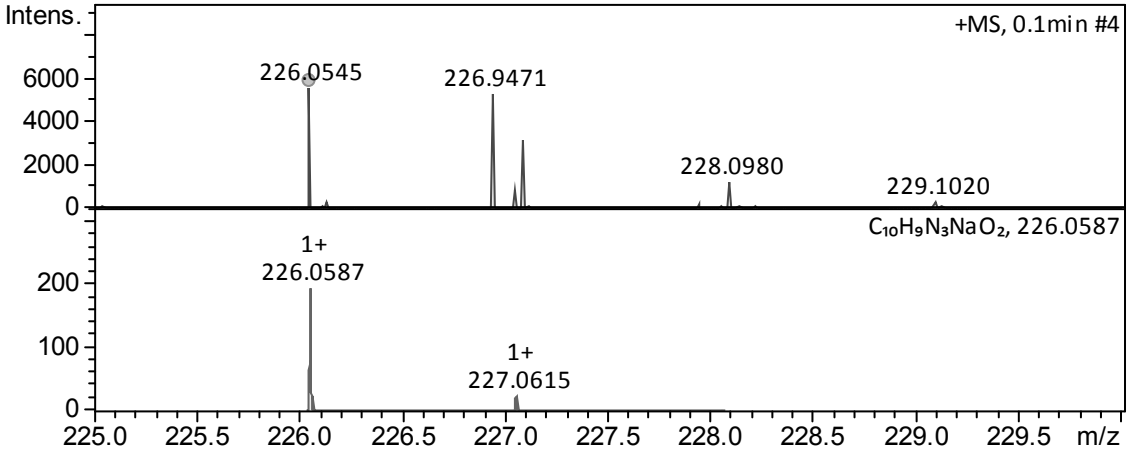


Figure S7. High-resolution spectrum of N-(2-(4-methyl)-pyridinyl)-pyrazole-3-carboxylate acid (L**2**, $C_{10}H_9N_3O_2$) in MeOH. HRMS m/z (ESI) $[M + Na^+]^+$: 226.0545 (Found, top) and 226.0587 (calculated, bottom).

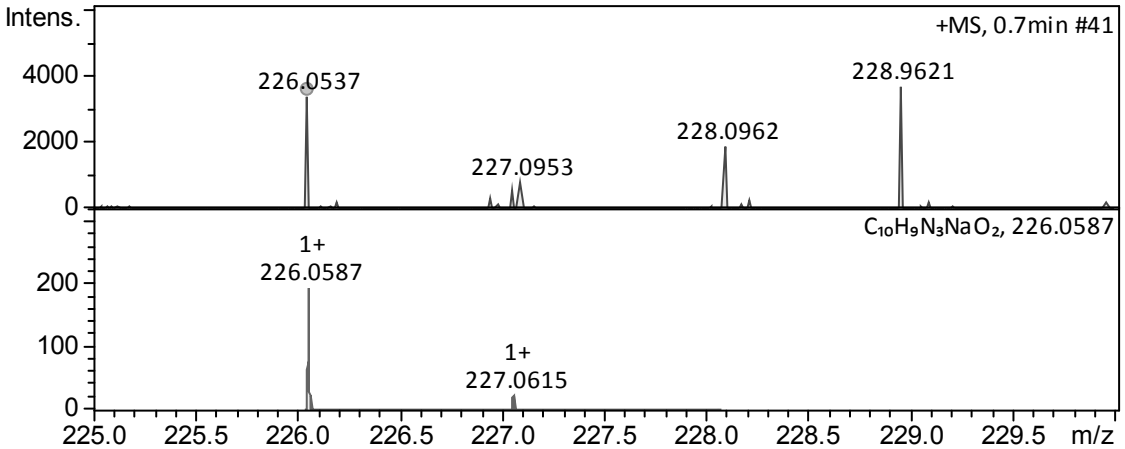


Figure S8. High-resolution spectrum of N-(2-pyridinyl)-pyrazole-3-carboxylate acid (L**3**, $C_{10}H_9N_3O_2$) in MeOH. HRMS m/z (ESI) $[M + Na^+]^+$: 513.9950 (Found, top) and 514.0133 (calculated, bottom).

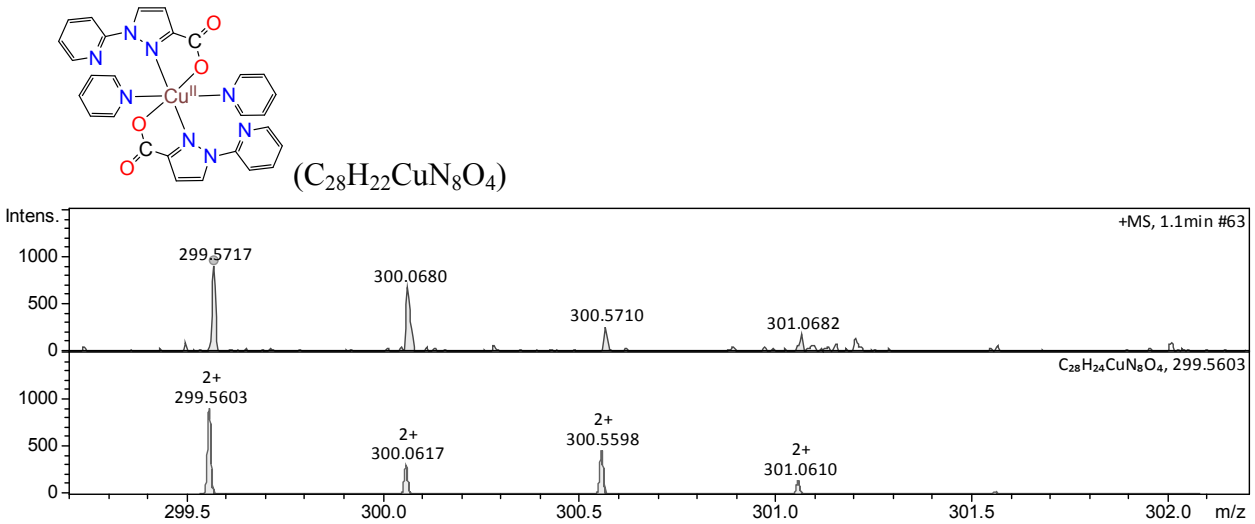


Figure S9. High-resolution mass spectrum of $[Cu^{II}(py)_2(ppca)_2]$ (**2**) in H_2O/py. HRMS m/z (ESI) $[M + 2H^+]^{2+}$: 299.5717 (Found, top) and 299.5603 (calculated, bottom).

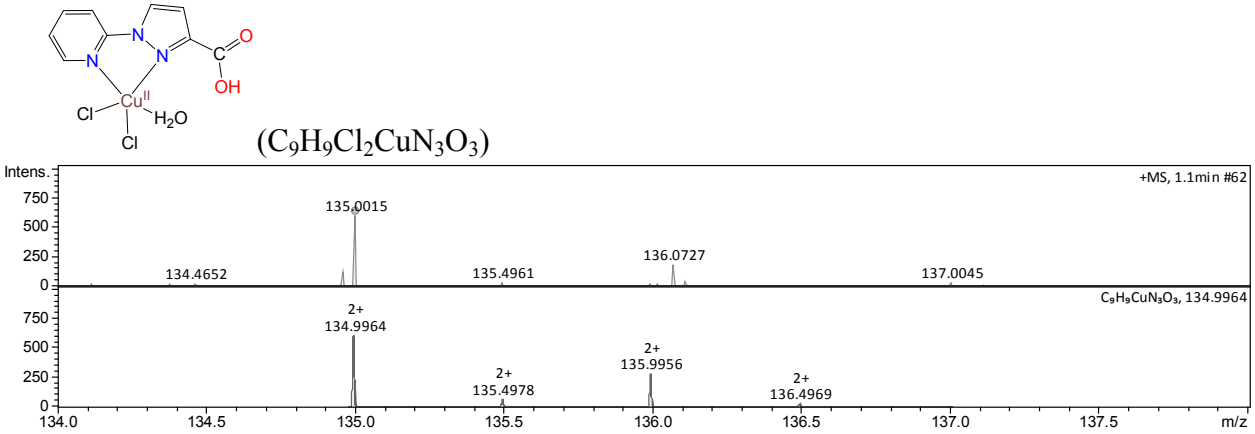


Figure S10. High-resolution mass spectrum of $[Cu^{II}(Hppca)(H_2O)Cl_2]$ (**3**) in H_2O. HRMS m/z (ESI) $[M - 2Cl^-]^{2+}$: 135.0015 (Found, top) and 134.9964 (calculated, bottom).

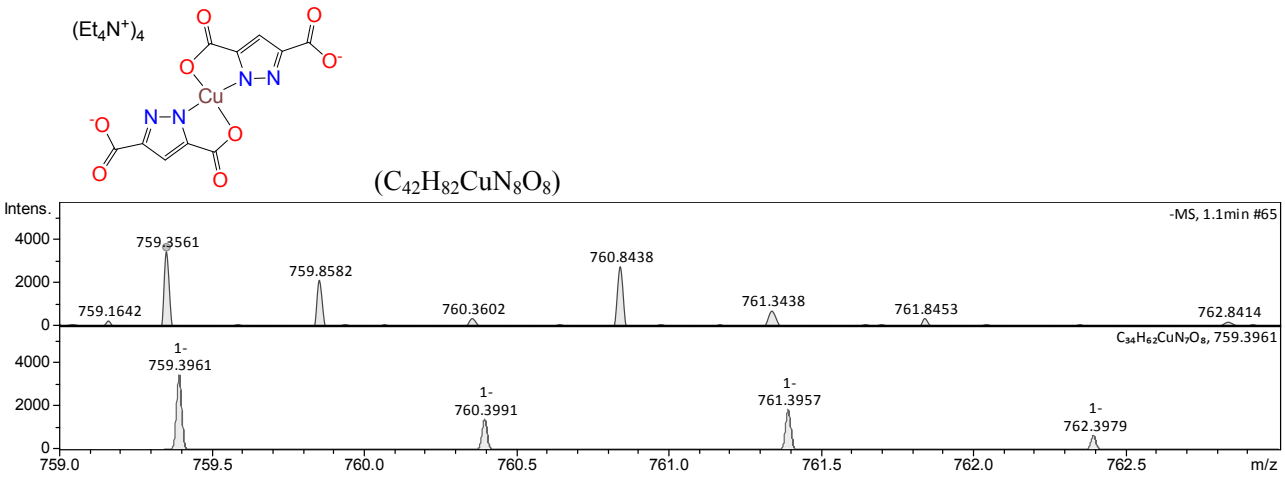
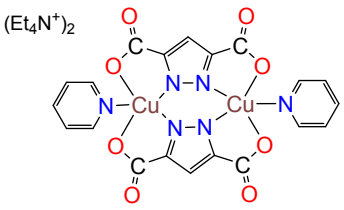


Figure S11. High-resolution mass spectrum of $[Cu(pdc)_2](Et_4N)_4$ (**4**) in H_2O/DMF. HRMS m/z (ESI) $[M - Et_4N^+]^-$: 759.3561 (Found, top) and 759.3961 (calculated, bottom).



($C_{36}H_{52}Cu_2N_8O_8$)

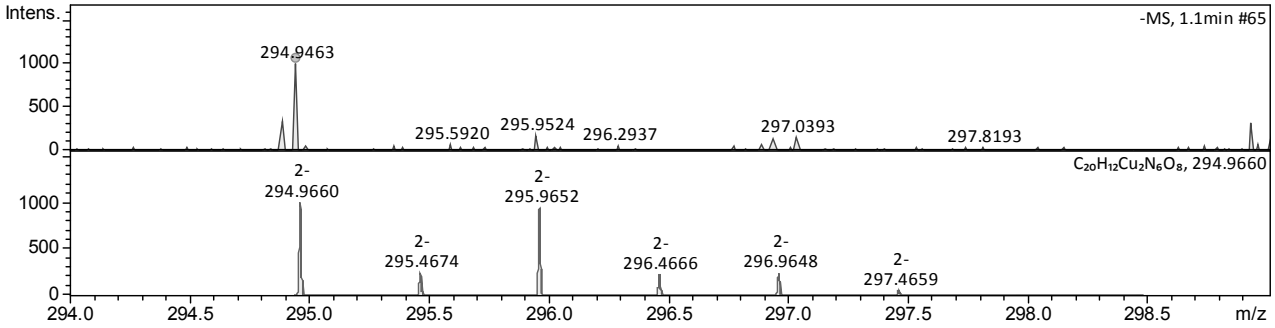
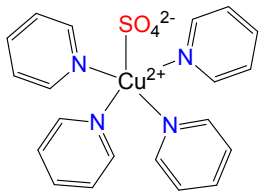


Figure S12. High-resolution mass spectrum of $[Cu_2(pdc)_2(py)_2](Et_4N)_2$ (**5**) in H_2O/py/DMF. HRMS m/z (ESI) $[M - 2Et_4N^+]^{2-}$: 294.9463 (Found, top) and 294.9660 (calculated, bottom).



($C_{20}H_{20}CuN_4O_4S$)

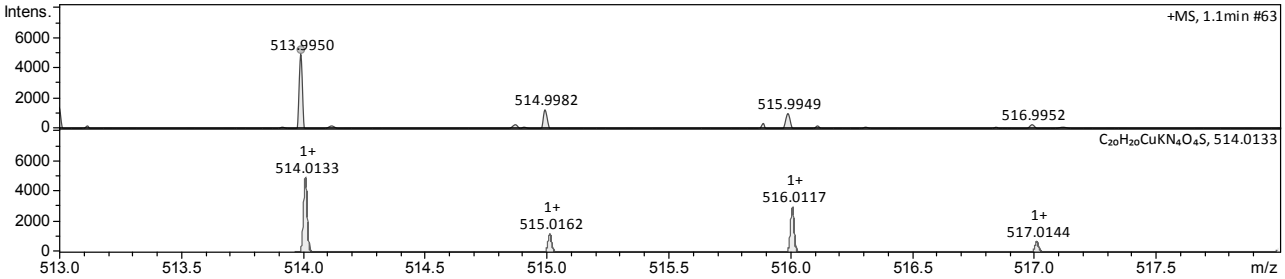


Figure S13. High-resolution mass spectrum of $[Cu^{II}(py)_4(SO_4)]$ (**10**) in H_2O/py. HRMS m/z (ESI) $[M + K^+]^+$: 513.9950 (Found, top) and 514.0133 (calculated, bottom).