Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Pyridine-Based Dicarbene Ligand: Synthesis and Structure of Bis-2-pyridylidene Palladium Complex

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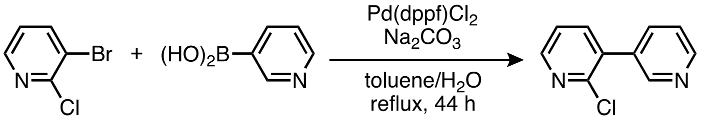
1. Experimental Section

General

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Toluene, tetrahydrofuran (THF), and diethyl ether (Et_2O) were purified by passing through a solvent purification system (Glass Contour). All reactions were performed using standard vacuum-line and Schlenk techniques under nitrogen gas or in the argon-filled glovebox (Miwa MFG). Work-up and purification procedures were carried out with reagent-grade solvents under air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm and 365 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). High-resolution mass spectra (HRMS) was obtained from a Bruker micrOTOF-QII (electrospray ionization, ESI MS). Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer and JEOL JNM-ECS-400 (^{1}H 400 MHz, ^{13}C 100 MHz, ^{11}B 128 MHz, ^{19}F 376 MHz, ^{31}P 162 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CDCl_3$ (δ 7.26 ppm), CD_3CN (δ 1.94 ppm), and CD_3OD (δ 3.31 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm), CD_3CN (δ 118.3 ppm), and CD_3OD (δ 49.0 ppm). Chemical shifts for ^{11}B, ^{19}F, and ^{31}P NMR are expressed in ppm relative to external standards ($BF_3 \cdot OEt_2$, $CFCl_3$, and H_3PO_4 as 0.0 ppm, respectively). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, vt = virtual triplet, m = multiplet, br = broad), coupling constant (Hz), and integration.

Synthesis of 2-chloro-3,3'-bipyridine (1)



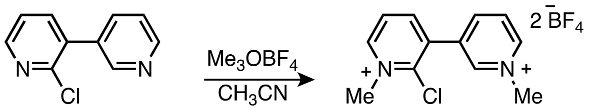
1

65%

To a 300 mL two-necked flask equipped with three-way stopcock and a magnetic stirring bar were added 2-chloro-3-bromopyridine (2.13 g, 11.1 mmol), 3-pyridineboronic acid (2.32 g, 18.9 mmol), sodium carbonate (8.32 g, 78.9 mmol), $PdCl_2(dppf){\cdot}CH_2Cl_2$ (1.28 g, 1.57 mmol), 120 mL of toluene and 30 mL of water under nitrogen atmosphere. The mixture was stirred at reflux for 44 h. The resulting suspension was cooled to room temperature and quenched with 50 mL of water, extracted with EtOAc (50 mL × 3), dried over Na_2SO_4, and evaporated *in vacuo* to afford the crude product. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 1:2, $R_f = 0.4$) to afford 2-chloro-3,3'-bipyridine (**1**) (1.37 g, 65%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (dd, $J = 8, 5$ Hz, 1H), 7.40 (ddd, $J = 8, 5, 1$ Hz, 1H), 7.69 (dd, $J = 8, 2$ Hz, 1H), 7.82 (ddd, $J = 8, 2, 2$ Hz, 1H), 8.45 (dd, $J = 5, 2$ Hz, 1H), 8.67 (dd, $J = 5, 2$ Hz, 1H), 8.68 (dd, $J = 2, 1$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ122.2 (CH), 122.3 (CH), 132.4 (4°), 132.7 (4°), 135.9 (CH), 139.0 (CH), 148.4 (CH), 148.6 (CH), 148.8 (CH), 148.9 (4°)

Synthesis of 2-chloro-1,1'-dimethyl-[3,3'-bipyridine]-1,1'-diium bis(tetrafluoroborate) (2)



1

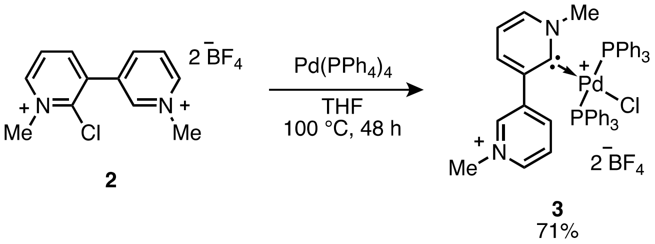
2

57%

To a 100mL two-necked flask equipped with three-way stopcock and a magnetic stirring bar was added **1** (600 mg, 3.15 mmol) and $(CH_3)_3OBF_4$ (2.80 g, 18.9 mmol) and acetonitrile (10 mL) under nitrogen atmosphere. The resulting solution was stirred at 60 °C for 14 h. After the reaction mixture was concentrated *in vacuo*, acetone and Et_2O were added to yield white precipitate. The solid was washed with THF and recrystallized with acetonitrile/Et_2O to afford compound **2** (701 mg, 57%).

^{1}H NMR (CD_3CN, 400 MHz) δ 4.41 (s, 6H), 8.13 (dd, J = 8, 6 Hz, 1H), 8.21 (dd, J = 8, 6 Hz, 1H), 8.53 (dd, J = 8, 2 Hz, 1H), 8.61 (d, J = 8 Hz, 1H), 8.81 (s, 1H), 8.82 (d, J = 8 Hz, 1H), 8.92 (dd, J = 6, 2 Hz, 1H); ^{13} C NMR (CD_3CN, 100 MHz); δ 49.8 (CH_3), 127.1 (CH), 129.3 (CH), 135.1 (4°), 135.8 (4°), 146.5 (CH), 146.9 (CH), 147.3 (CH), 148.8 (CH), 149.9 (CH); ^{11}B (CD_3CN, 128 MHz) δ –2.14; ^{19}F NMR (CD_3CN, 376 MHz) δ –151.5; mp: 215–218 °C; Anal. calcd. for $C_{12}H_{13}N_2$: C 36.55, H 3.32, N 7.10. found: C 36.49, H 3.32, N 6.70.

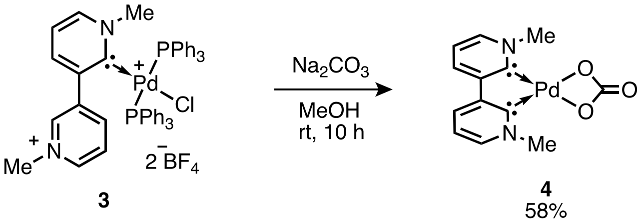
Synthesis of monodentate 2-pyridylidene palladium complex (3)



To a 50-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar were added **2** (62.0 mg, 160 μmol), tetrakis(triphenylphosphine)palladium (200 mg, 176 μmol), and THF (20 mL) in a glovebox. The mixture was stirred at 100 °C for 48 h. The resulting suspension was filtered by Celite® pad and acetonitrile was added to dissolve the white residue. The resulting acetonitrile solution was concentrated and recrystallized with acetonitrile/Et_2O to afford 2-pyridylidene complex **3** (117 mg, 71%) as a white crystal.

^{1}H NMR (CD_3CN, 600 MHz) δ 3.93 (s, 3H), 4.05 (s, 3H), 7.38 (dd, J = 8, 6 Hz, 1H), 7.44 (brs, 24H), 7.59 (brs, 6H), 7.73 (d, J = 8 Hz, 1H), 7.78 (d, J = 6 Hz, 1H), 7.92 (dd, J = 8, 6 Hz, 1H), 8.01 (s, 1H), 8.73 (d, J = 6 Hz, 1H), 9.04 (d, J = 8 Hz, 1H); ^{13}C NMR (CD_3CN, 150 MHz) δ 49.5 (CH_3), 55.3 (CH_3), 124.9 (CH), 128.5 (CH), 128.8 (vt, $^1J_{PC}$ = 24 Hz, 4°), 130.2 (vt, $^2J_{PC}$ = 5 Hz, CH), 132.9 (CH), 134.9 (br, 4°), 140.3 (4°), 141.7 (CH), 144.4 (CH), 145.4 (CH), 146.9 (CH), 147.2 (CH), 190.0 (4°); ^{31}P NMR (CD_3CN, 162 MHz) δ 20.1; ^{11}B (CD_3CN, 128 MHz) δ –2.14; ^{19}F NMR (CD_3CN, 376 MHz) δ –151.5; mp: 213–215 °C; Anal. calcd. for $C_{48}H_{43}N_2$: C 56.23, H 4.23, N 2.73. found: C 56.14, H 4.27, N 3.04.

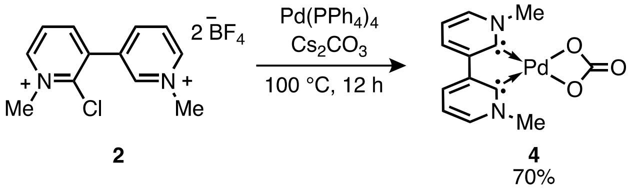
Synthesis of bidentate 2-pyridylidene palladium complex (4) from 3



To a 20-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar were added **3 (**30.0 mg, 290 µmol**)** and Na_2CO_3 (24.0 mg, 1.45 mmol) in a glovebox. Dry methanol (3.0 mL) was added and the mixture was stirred at room temperature for 10 h. The reaction mixture was filtered and the solution was concentrated under reduced pressure. The crude product was purified by recrystallization with MeOH/Et_2O at room temperature to afford bidentate 2-pyridylidene complex (6.9 mg, 58%) as a yellow crystal of **4**·1/2$NaBF_4$. A $NaBF_4$-free crystal of **4** (**4**·2H_2O) was also obtained from the reaction with Cs_2CO_3 instead of Na_2CO_3.

^{1}H NMR (CD_3OD, 400 MHz) δ 4.30 (s, 6H), 7.50 (dd, J = 8, 6 Hz, 2H), 8.18 (d, J = 8 Hz, 2H), 8.32 (d, J = 6 Hz, 2H); ^{13}C NMR (CD_3OD, 150 MHz) δ 50.4 (CH_3), 123.6 (CH), 131.8 (CH), 144.6 (CH), 152.3 (4°), 171.2 (4°), 183.9 (4°).; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_2O_3PdNa$ $[M·Na]^+$: 372.9780, found: 372.9724; mp: 230.0–240.0 °C (dec.)

Synthesis of bidentate 2-pyridylidene palladium complex (4) from 2



To a 20-mL glass vessel equipped with J. Young® O-ring tap containing a magnetic stirring bar were added **2** (15.5 mg, 40.0 μmol), Pd(PPh_3)$_4$ (50.0 mg, 44.0 μmol), Cs_2CO_3 (65.2 mg, 20.0 μmol), and dry THF (5.0 mL). The mixture was stirred at 100 °C for 12 h. The resulting solution was concentrated under reduced pressure. The yield of **4** was estimated to be 70% measured by ^{1}H NMR spectroscopy (solvent: CD_3OD, internal standard: THF).

2. X-ray Crystallography

Details of the crystal data and a summary of the intensity data collection parameters for **3**·2MeCN and **4** are listed in Table S1. In each case, a suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. Graphite-monochromated Mo Kα radiation was used. The structures were solved by direct methods with (SIR-97)[S 1] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[S 2] The intensities were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S1. Crystallographic data and refinement details for **3**·2MeCN, **4**·1/2NaBF$_4$ and **4**·2H$_2$O.

	3·2MeCN	**4**·1/2NaBF$_4$	**4**·2H$_2$O
formula	$C_{52}H_{49}B_2ClF_8N_4P_2Pd$	$C_{26}H_{24}BF_4N_4NaO_6Pd_2$	$C_{13}H_{12}N_2O_5Pd$
fw	107.36	811.09	382.65
T (K)	103(2)	103(2)	103(2)
λ (Å)	0.71075	0.71075	0.71070
cryst syst	Monoclinic	Triclinic	Monoclinic
space group	$P2_1/c$	P-1	$P2_1/a$
a, (Å)	11.8013(7)	6.894(4)	6.8562(12)
b, (Å)	9.4307(6)	10.276(6)	20.450(4)
c, (Å)	44.208(3)	18.762(11)	9.9565(18)
α,□(deg□	90	89.999(13)	90
β, (deg□	92.807(3)	86.530(16)	102.657(2)
γ,□(deg□	90	86.072(14)	90
V, (Å^3)	4914.3(5)	1323.6(139	1362.1(4)
Z	4	2	4
D_{calc}, (g / cm^3)	1.497	2.035	1.866
μ (mm^{-1})	0.569	1.456	1.386
F(000)	2256	800	760
cryst size (mm)	0.20 × 0.20 × 0.20	0.20 × 0.02 × 0.01	0.20 × 0.10 × 0.05
2θ range, (deg□	3.06–25.00	3.10–25.00	3.20–25.00
reflns collected	50454	18004	8946
indep reflns/R_{int}	8608/0.0497	4651/0.0571	2374/0.0279
params	663	401	192
GOF on F^2	1.067	1.095	1.067
R_1, wR_2 [I>2σ(I)]	0.0382, 0.0902	0.0476, 0.1140	0.0289, 0.0713
R_1, wR_2 (all data)	0.0411, 0.0923	0.0561, 0.1205	0.0327, 0.0738

S1) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.,* 1999, **32,** 115–119.

S2) G. M. Sheldrick, University of Göttingen: Göttingen, Germany, 1997.

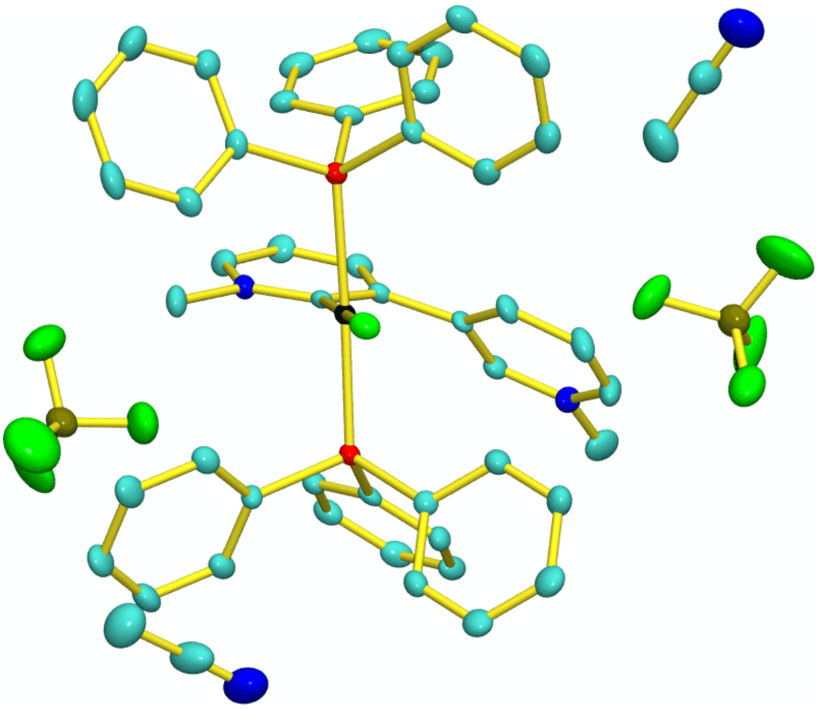


Figure S1. Drawing of **3**·2MeCN with 50% thermal ellipsoid. All hydrogen atoms and minor part of disordered BF_4 are omitted for clarity.

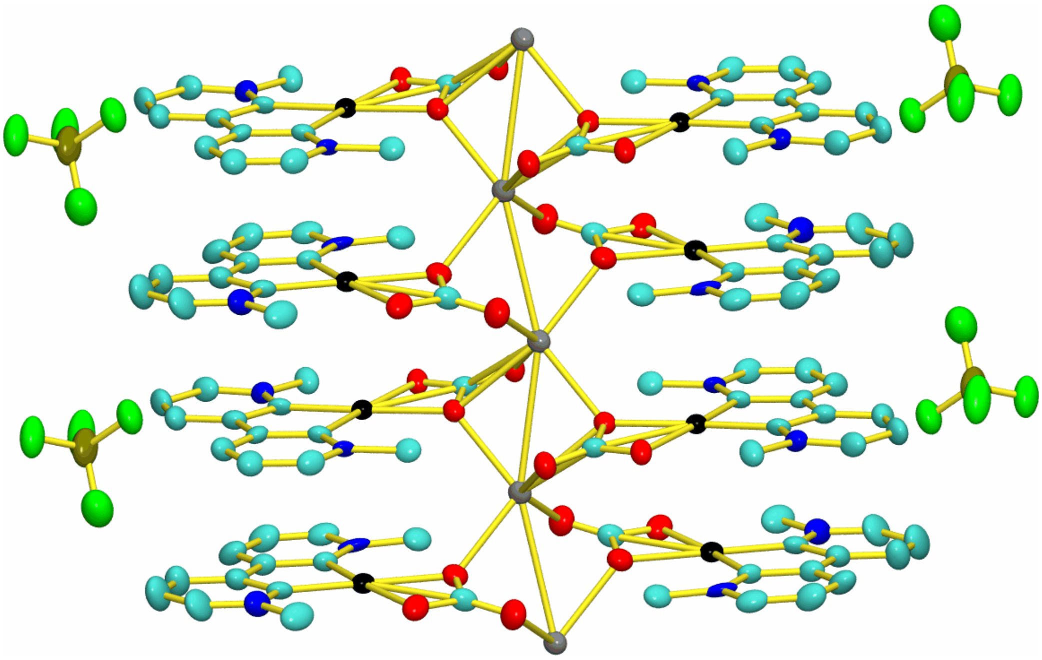


Figure S2. Drawing of **4**·1/2$NaBF_4$ with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

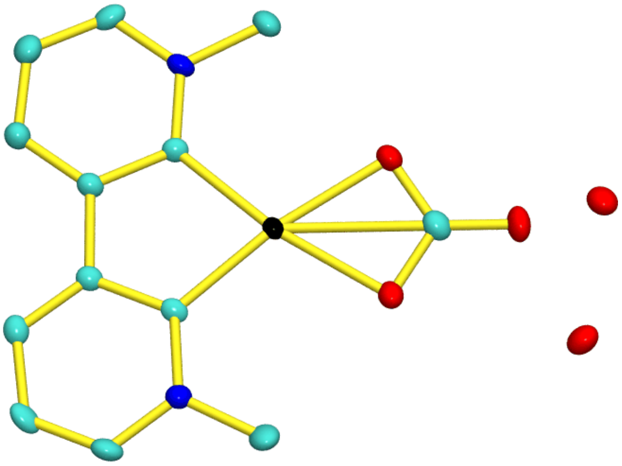
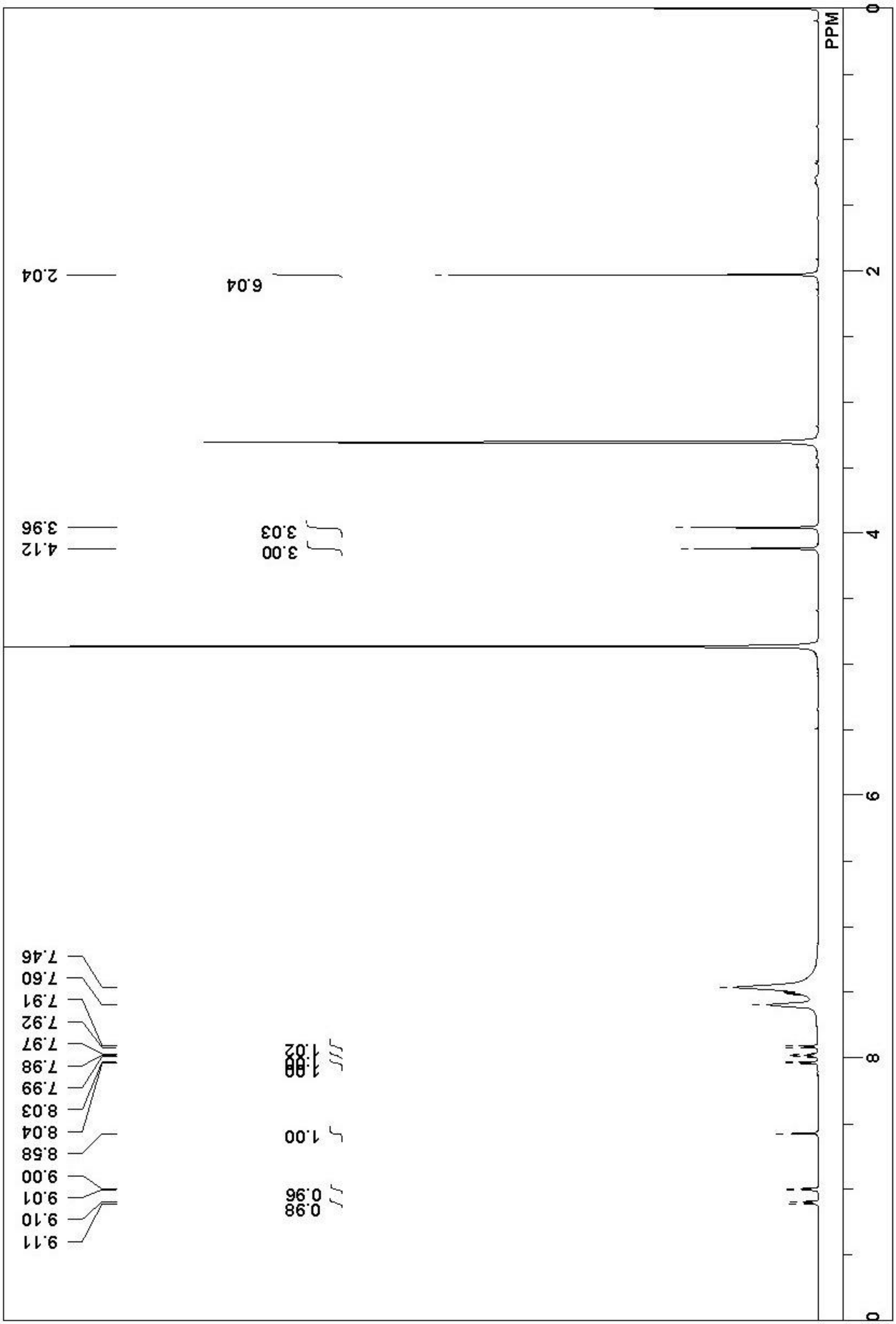


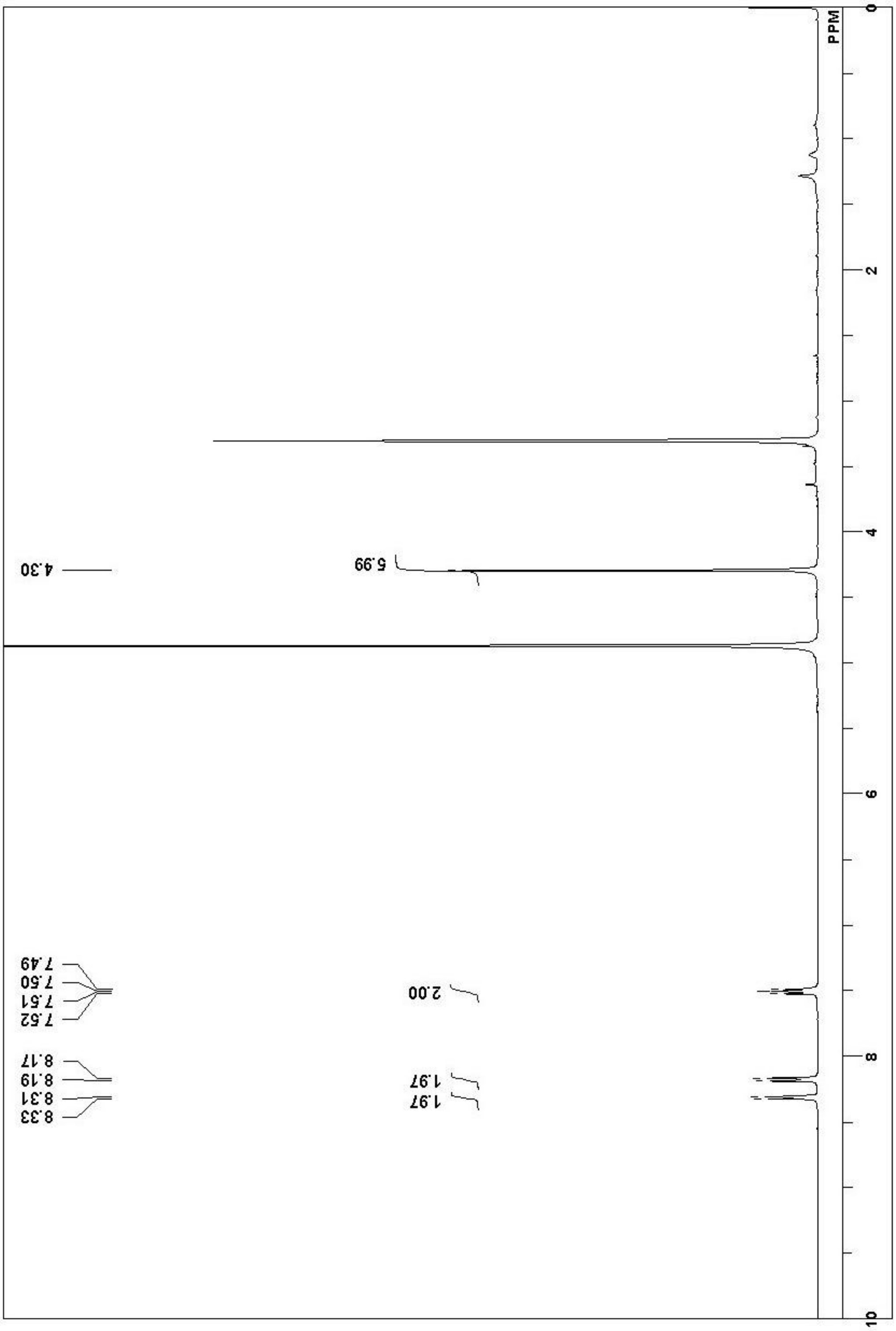
Figure S2. Drawing of **4**·$2H_2O$ with 50% thermal ellipsoid. All hydrogen atoms are omitted for clarity.

4. ^{1}H and ^{13}C NMR Spectra

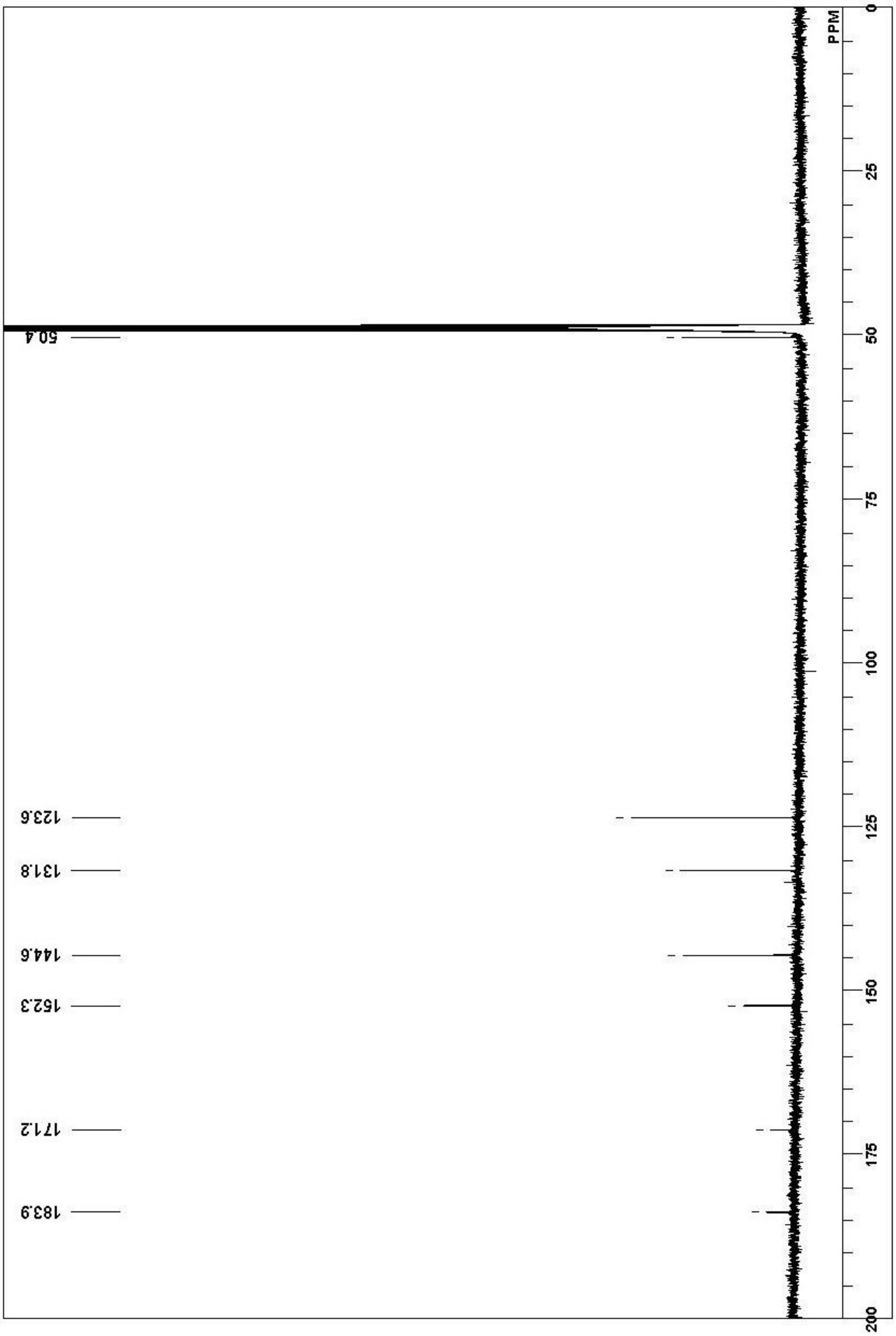
^{1}H NMR spectrum of the single crystal of **3**·2CH_3CN (600 MHz, CD_3OD)



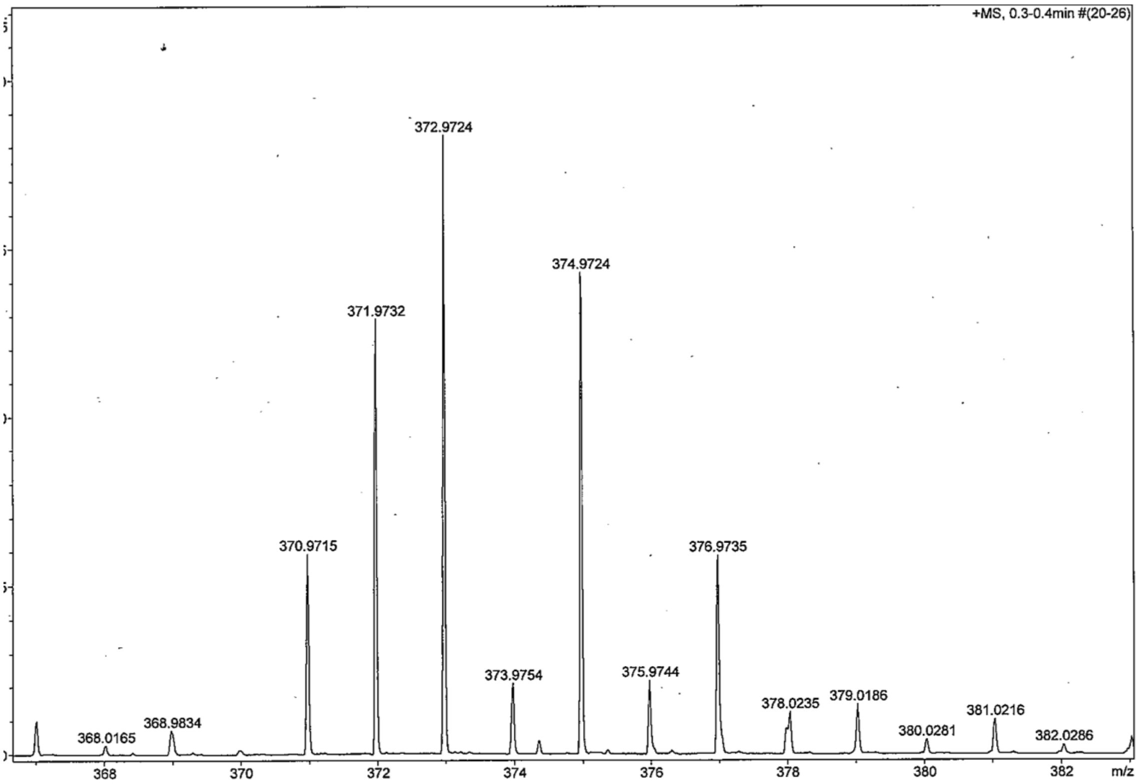
^{1}H NMR spectrum of **4** (400 MHz, CD_3OD)



^{13}C NMR spectrum of **4** (150 MHz, CD_3OD)



Mass spectrum of **4**·Na$^+$ (ESI)



Simulated isotope pattern of **4**·Na$^+$