Supporting Information

Base Induced C−CN Bond Cleavage at Room Temperature: A Convenient Method for the Activation of Acetonitrile

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1. Experimental Section

Preparation of Compounds. Unless otherwise stated, all reactions and manipulations were performed under a pure dinitrogen atmosphere using Schlenk techniques or an inert atmosphere box. Volume reduction and drying steps were performed *in vacuo*. MeCN and DMF were freshly distilled from CaH_2 and dried over 3-Å molecular sieves for 24 h. THF and Et_2O were distilled from metal sodium over 5 h. All solvents were degassed before use. Other commercial-grade chemicals were used without further purification. Compounds were identified by combinations of elemental analysis, spectroscopic measurements and X-ray structure determination. Solvent resonances are omitted from NMR data. Complexes were numerically designated according to Chart 1.

Chart 1. Abbreviations and Designation of Complexes

$[Cu(PyN_2Ph_2^{Me2})L]^{1-}$	L = OH^- **1**, CN^- **2**, CH_2CN^- **10**, $CH{=}C{=}NH^-$ **11**
$[Cu(PyN_2Ph_2^{Et2})L]^{1-}$	L = OH^- **3**, CN^- **4**
$[Cu(PyN_2Ph_2^{iPr2})L]^{1-}$	L = OH^- **5**, CN^- **6,**
$\{[Cu(PyN_2Ph_2)]_2(OH)\}^{1-}$	**7**
$\{[Cu(PyN_2(NaPh)_2)]_2(OH)\}^{1-}$	**8**
$\{[Cu(PyN_2Ph_2(dienO_3))]_2(OH)\}^{1-}$	**9**
$[Ni(PyN_2Ph_2^{Me2})L]^{1-}$	L = OH^- **12**, CN^- **13**
$\{[PhC(O)C(CN)Ph]_2H]\}^{1-}$	**14**

$PyN_2Ph_2^{Me2}$ = *N,N′*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate(2-); $PyN_2Ph_2^{Et2}$ = *N,N′*-bis(2,6-diethylphenyl)-2,6-pyridinedicarboxamidate(2-); $PyN_2Ph_2^{iPr2}$ = *N,N′*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidate (2-); PyN_2Ph_2 = bisphenyl-2,6-pyridinedicarboxamidate(2-); $PyN_2(NaPh)_2$ = bisnaphthyl-2,6-pyridinedicarboxamidate(2-); $PyN_2Ph_2(dienO_3)$ = bis(pheny-3,3'-(2,5,8-trioxa-1,9-nonyl-diethyleneglycolether))-2,6-pyridinedicarbox-amidate(2-).

$(Et_4N)[Cu(PyN_2Ph_2^{Me2})(OH)]$ (1). The reported method[1] was used for the synthesis of complex **1**.

$(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CN)]\cdot CH_2Cl_2$ (2). *Method 1*: To a mixture of $(Et_4N)[Cu(pyN_2^{Me2})(OH)]$ (29 mg, 0.05 mmol) and NaOH (40 mg, 1.0 mmol) in a 100 mL Schlenk flask was added MeCN (20 mL) under N_2. The mixture was opened to air through the knob of outlet, stirred for 24 h and filtered to remove some white precipitate. Solvent was removed by rotary evaporator to leave a dark purple-red oily solid, which was dissolved in THF (2 mL) and stayed for hours to deposit some dark-red crystalline solid. The solid was recrystallized from CH_2Cl_2/Et_2O to deposit product as some shiny dark purple-red crystals (30.4 mg, 90%). IR (KBr): ν_{CN} 2208 cm^{-1}. Anal. Calcd. for $C_{33}H_{43}Cl_2CuN_5O_2$: C, 58.62; H, 6.41; N, 10.36. Found: C, 57.15; H, 6.69; N, 10.44.
Method 2: Under N_2, to a solution of $(Et_4N)[Cu(PyN_2Ph_2^{Me2})(OH)]$ (15 mg, 0.025 mmol) and NaOH (30 mg, 0.75 mmol) in MeCN (10 mL) was added *tert*-butyl hydroperoxide in decane (^tBuOOH) (0.05 mL, 5.0 M) through a syringe. The mixture was stirred for 30 min and filtered. Solvent of filtrate was removed in *vacuo* to leave some dark purple-red solid, which was recrystallized from CH_2Cl_2/Et_2O to deposit product as some purple-red crystals (15 mg, 89%).

$(Et_4N)[Cu(PyN_2Ph_2^{Et2})(OH)]$ (3). $H_2PyN_2Ph_2^{Et2}$ (86 mg, 0.20 mmol) and $Cu(OTf)_2$ (72 mg, 0.20 mmol) was stirred in DMF/THF (2 mL/2 mL) for 15 min. The mixture was treated with Et_4NOH (25% in Methanol, 177 mg, 0.30 mmol) and stirred for 30 min. A second equal portion of Et_4NOH was added, and the mixture was stirred for 3 h and filtered. Et_2O (25 mL) was added to the filtrate and the mixture was stayed over night to deposit some black blue oil, which was taken in THF (4 mL) and treated with Et_2O to leave some blue solid. The solid was recrystallized from DMF/THF/Et_2O to afford the product as some brown blue crystals (89 mg, 70%). IR (KBr): $\nu_{(OH)}$ 3612 cm^{-1}. Anal. Calcd. for $C_{35}H_{50}CuN_4O_3$: C, 65.85; H, 7.89; N, 8.78. Found: C, 64.98; H, 7.66; N, 9.00.

$(Et_4N)[Cu(PyN_2Ph_2^{Et2})(CN)]$ (4). A mixture of $(Et_4N)[Cu(PyN_2Ph_2^{Et2})(OH)]$ (32 mg, 0.05 mmol) and NaOH (40 mg, 1.0 mmol) was added MeCN (20 mL) under N_2. The mixture was opened to air through the knob of outlet, stirred for 24 h and filtered to remove some sticky solid. The solvent of filtrate was removed to leave a dark purple-red solid, which was recrystallized from DMF/Et_2O to deposit product as some dark purple-red crystals (19 mg, 59%). IR (KBr): ν_{CN} 2213 cm^{-1}. Anal. Calcd. for $C_{36}H_{49}CuN_5O_2$: C, 66.79; H, 7.63; N, 10.82. Found: C, 65.33; H, 7.50; N, 10.59.

$(Me_4N)[Cu(PyN_2Ph_2^{iPr2})(OH)]$ (5). $H_2PyN_2Ph_2^{iPr2}$ (73 mg, 0.15 mmol) and $Cu(OTf)_2$ (54 mg, 0.15 mmol) was stirred in DMF/THF (1.5 mL/0.7 mL) for 15 min. The resulting light green solution was treated with Me_4NOH (25% in Methanol, 82 mg, 0.225 mmol) and stirred for 30 min. A second equal portion of Me_4NOH was added, and the mixture was stirred for 3 h and filtered. Addition of Et_2O (5 mL) to the filtrate resulted in the deposition of some off-white precipitate which was filtered off. Et_2O (20 mL) was added to the filtrate and the mixture was stayed to deposit product as some blue-brown crystals (52 mg, 54%). IR (KBr): $\nu_{(OH)}$ 3618 cm^{-1}. Anal. Calcd. for $C_{35}H_{50}CuN_4O_3$: C, 65.85; H, 7.89; N, 8.78. Found: C, 66.70; H, 7.98; N, 8.66.

$(Me_4N)[Cu(PyN_2Ph_2^{iPr2})(CN)(THF)]$ (6) To a mixture of $(Me_4N)[Cu(PyN_2Ph_2^{iPr2})(OH)]$ (32 mg, 0.05 mmol) and NaOH (40 mg, 1.0 mmol) in a 100 mL Schlenk flask was added MeCN (20 mL) under N_2. The mixture was opened to air through the knob of outlet, stirred for 48 h and filtered by Celite to remove some sticky solid. The solvent of filtrate was removed by rotary evaporator to leave a dark purple-red solid, which was recrystallized from DMF/THF (1:1, 2 mL) by diffusion of Et_2O to

deposit product **6** as some dark purple-red crystals (19 mg, 53%). IR (KBr): ν_{CN} 2217 cm^{-1}. Anal. Calcd. for $C_{40}H_{57}CuN_5O_3$: C, 66.78; H, 7.99; N, 9.73. Found: C, 65.82; H, 7.77; N, 9.80.

$(Et_4N)\{[Cu(PyN_2Ph_2)]_2(OH)\}\cdot 2DMF$ (7). $H_2PyN_2Ph_2$ (64 mg，0.20 mmol) and $Cu(OTf)_2$ (72 mg, 0.20 mmol) were mixed and stirred in DMF (3 mL) for 15 min to give a light green solution, which was treated slowly with Et_4NOH (25% in methanol, 353 mg, 0.60 mmol) in 30 mins. The mixture was stirred for 6 h and filtered. Et_2O (20 mL) was added to the filtrate and the resultant black green oil was treated with Et_2O and THF to form a solid, which was recrystallized from DMF/Et_2O to afford product as some blue-brown crystals (78 mg, 74%). IR (KBr): ν_{OH} 3608 cm^{-1}. Anal. Calcd. for $C_{52}H_{61}Cu_2N_9O_7$: C, 59.41; H, 5.85; N, 11.99. Found: C, 58.06; H, 5.76; N, 11.89.

$(Et_4N)\{[Cu(PyN_2(NaPh)_2)]_2(OH)\}\cdot DMF$ (8). $H_2PyN_2(NaPh)_2$ (83.5 mg，0.20 mmol) and $Cu(OTf)_2$ (72 mg, 0.20 mmol) were stirred in DMF (1.5 mL) for 15 min to give a light green solution, which was treated slowly with Et_4NOH (25% in methanol, 353 mg, 0.60 mmol) in 30 mins. The mixture was stirred for 6 h, filtered and Et_2O (20 mL) was added to the filtrate to deposit some dark green oil. The oil was treated with Et_2O and THF to form a solid, which was dissolved in DMF/MeCN (1:4, 3 mL) and diffused with Et_2O to afford some black green crystals (88 mg, 75%). IR (KBr): ν_{OH} 3605 cm^{-1}. Anal. Calcd. for $C_{65}H_{62}Cu_2N_8O_6$: C, 66.25; H, 5.30; N, 9.51. Found: C, 65.91; H, 5.26; N, 9.40.

$(Et_4N)\{[Cu(PyN_2Ph_2(dienO_3))]_2(OH)\}$ (9). $H_2PyN_2Ph_2(dienO_3)$ (67 mg, 0.15 mmol) and $Cu(OTf)_2$ (54 mg, 0.15 mmol) were stirred in DMF/THF (2 mL/1 mL) for 15 min to give a light green solution, which was treated with Et_4NOH (25% in methanol, 265 mg, 0.45 mmol) for 20 mins. The mixture was stirred for 3 h and filtered to remove some sticky precipitate. Et_2O (20 mL) was added to the filtrate to deposit some oil, which was stirred in THF to form a solid. The solid was recrystallized from DMF/Et_2O to afford some blue-brown crystals (60 mg, 69%). IR (KBr): ν_{OH} 3620 cm^{-1}. Anal. Calcd. for $C_{58}H_{67}Cu_2N_7O_{11}$: C, 59.78; H, 5.80; N, 8.41. Found: C, 58.12; H, 5.82; N, 8.37.

$(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CH_2CN)]$ (10). A solution of $(Et_4N)[Cu(pyN_2^{Me2})(OH)]$ (15 mg, 0.025 mmol) was stirred in dry MeCN (8 mL) under N_2 for 2 days to give a dark brown solution with some white precipitate suspended on the surface of solution. The solid was filtered off and the filtrate was added with Et_2O/hexane (20/20 mL) to deposit some brown black oil, which was recrystallized from CH_3CN/Et_2O to deposit some brown-red plate crystals (13.6 mg, 90%). IR (KBr): ν_{CN} 2173 cm^{-1}. Anal. Calcd. for $C_{33}H_{43}CuN_5O_2$: C, 65.48; H, 7.16; N, 11.57. Found: C, 64.30; H, 7.08; N, 11.21.

$(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CH{=}C{=}NH)]$ (11). A solution of $(Et_4N)[Cu(pyN_2^{Me2})(OH)]$ (17.5 mg, 0.03 mmol) was stirred in dry MeCN (2.5 mL) under N_2 for 5 days and filtered to remove some white precipitate. The filtrate was diffused with Et_2O to deposit product as some brown-red rhombic prism crystals, mixed with a minor amount of plate crystals. The rhombic prism crystals were collected manually (10 mg, 55%). The plate crystal was found as complex **10** (4 mg, 26%). Anal. Calcd. for $C_{33}H_{43}CuN_5O_2$: C, 65.48; H, 7.16; N, 11.57. Found: C, 63.95; H, 7.05; N, 11.36.

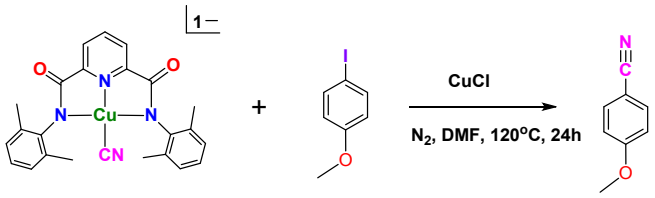
$(Et_4N)[Ni(PyN_2Ph_2^{Me2})(OH)]$ (12) The reported method[2] was used for the preparation of **12**.

$(Et_4N)[Ni(PyN_2Ph_2^{Me2})(CN)]$ (13) Same method for the synthesis of complex **2** was used for the preparation of complex **13** in yield of 75%. The stirring of **12** in other nitriles of propionitrile, butyronitrile, isobutyronitrile, pentanenitrile, isovaleronitrile, 1-piperidinepropionitrile,

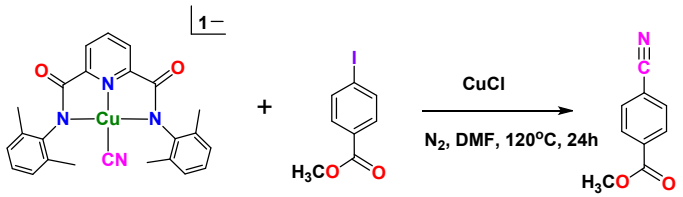
cyclohexanecarbonitrile, phenylacetonitrile, 3-phenylpropionitrile and 4-phenylbutyronitrile also led to the generation of complex **13**. IR (KBr): ν_{CN} 2127 cm^{-1}. Anal. Calcd. for $C_{32}H_{41}N_5NiO_2$: C, 65.54; H, 7.05; N, 11.94. Found: C, 64.38; H, 6.99; N, 11.74.

(Et_4N)\{[PhC(OH)C(CN)Ph][PhC(O)C(CN)Ph]\} (14) A mixture of $(Et_4N)[Ni(PyN_2Ph_2^{Me2})(OH)]$ (15 mg, 0.026 mmol) and NaOH (20 mg, 0.5 mmol) in a 50 mL Schlenk flask was added phenylacetonitrile (3 mL) under N_2. The mixture was opened to air through the knob of outlet and stirred for 72 h. Some sticky solid was filtered off to leave a light yellow filtrate, which was added Et_2O (40 mL) to deposit some light yellow solid. The solid was recrystallized from DMF/Et_2O to yield the product as some colourless block crystals (5 mg, 34% based on [Ni-OH] compound). Anal. Calcd. for $C_{38}H_{41}N_3O_2$: C, 79.83; H, 7.23; N, 7.35. Found: C, 78.37; H, 7.16; N, 7.22.

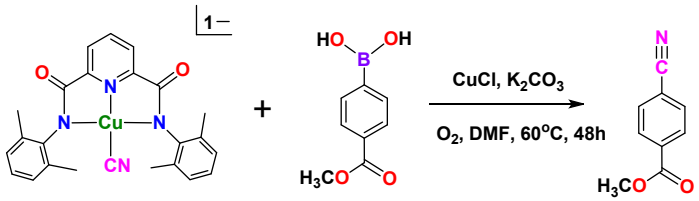
Organometallic Catalytic Reactions:



Under N_2, a mixture of $(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CN)]$ (100 mg, 0.17 mmol), 4-Iodoanisole (52 mg, 0.22 mmol) and CuCl (17 mg, 0.17 mmol) in anhydrous DMF (1 mL) was stirred in a Teflon sealed tube at 120º for 24 hours. After the reaction was completed, solvent was removed in *vacuo* and the residue was purified on a silica column eluted with petroleum ether/ethyl acetate (10/1 v/v) to yield the product as a white solid (18 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, 2H), 6.95 (d, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.98, 134.14, 119.36, 114.89, 104.13, 55.68.

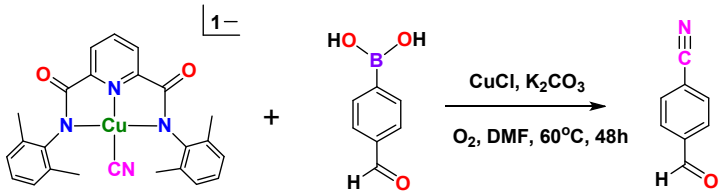


Under N_2, a mixture of $(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CN)]$ (89 mg, 0.15 mmol), methyl-4-iodobenzoate (51 mg, 0.195 mmol) and CuCl (15 mg, 0.15 mmol) in anhydrous DMF (1 mL) was stirred in a Teflon sealed tube at 120º for 24 hours. After the reaction was completed, solvent was removed in *vacuo* and the residue was purified on a silica column eluted with petroleum ether/ethyl acetate (10/1 v/v) to yield some white solid (18.6 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.08 (m, 2H), 7.79-7.68 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.53, 134.02, 132.32, 130.19, 118.06, 116.49, 52.83.

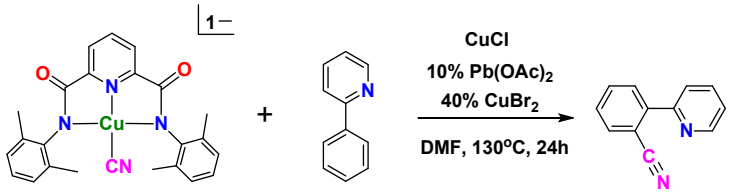


Under dioxygen, a mixture of $(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CN)]$ (89 mg, 0.15 mmol), 4-Methoxycarbonylphenylboronic acid (40.5 mg, 0.225 mmol), CuCl (15 mg, 0.15 mmol) and K_2CO_3 (62 mg, 0.45 mmol) in anhydrous DMF (1 mL) was stirred in a Teflon sealed tube at 60º for 48 hours. After the reaction was completed, solvent was removed in *vacuo* and the residue was purified on a silica column eluted with petroleum ether/ethyl acetate (10/1 v/v) to yield the product as a white

solid (13 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.08 (m, 2H), 7.79-7.68 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.53, 134.02, 132.32, 130.19, 118.06, 116.49, 52.83.



Under dioxygen, a mixture of 4-methoxycarbonylphenylboronic acid (34 mg, 0.225 mmol), $(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CN)]$ (89 mg, 0.15 mmol), CuCl (15 mg, 0.15 mmol) and K_2CO_3 (62 mg, 0.45 mmol) in anhydrous DMF (1 mL) was stirred in a Teflon sealed tube at 60º for 48 hours. After the reaction was completed, solvent was removed in *vacuo* and the residue was purified on a silica column eluted with petroleum ether/ethyl acetate (10/1 v/v) to yield the product as a white solid (8.0 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s. 1H), 8.02-7.97 (m, 2H), 7.88-7.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.63, 138.75, 132.92, 129.91, 117.72, 117.63.



In air, a mixture of $(Et_4N)[Cu(PyN_2Ph_2^{Me2})(CN)]$ (77 mg, 0.13 mmol), 2-phenylpyridine (26 mg, 0.17 mmol), CuCl (13 mg, 0.13 mmol), $Pd(OAc)_2$ (3 mg, 0.013 mmol) and $CuBr_2$ (11.6 mg, 0.052 mmol) in anhydrous DMF (1 mL) was stirred in a Teflon sealed tube at 130º for 24 h. After the reaction was completed, solvent was removed in *vacuo* and the residue was purified on a silica column eluted with hexane/Et_2O (1/2 v/v) to yield some colorless oil (20 mg, 85%). ^{1}H NMR ($CDCl_3$): δ 8.76 (d, 1H), 7.86-7.80 (m, 2H), 7.78 (d, 2H), 7.68 (t, 1H), 7.49 (t, 1H) 7.34 (d, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.31, 150.02, 143.54, 136.93, 134.21, 132.93, 130.05, 128.84, 123.43, 123.32, 118.79, 111.11.

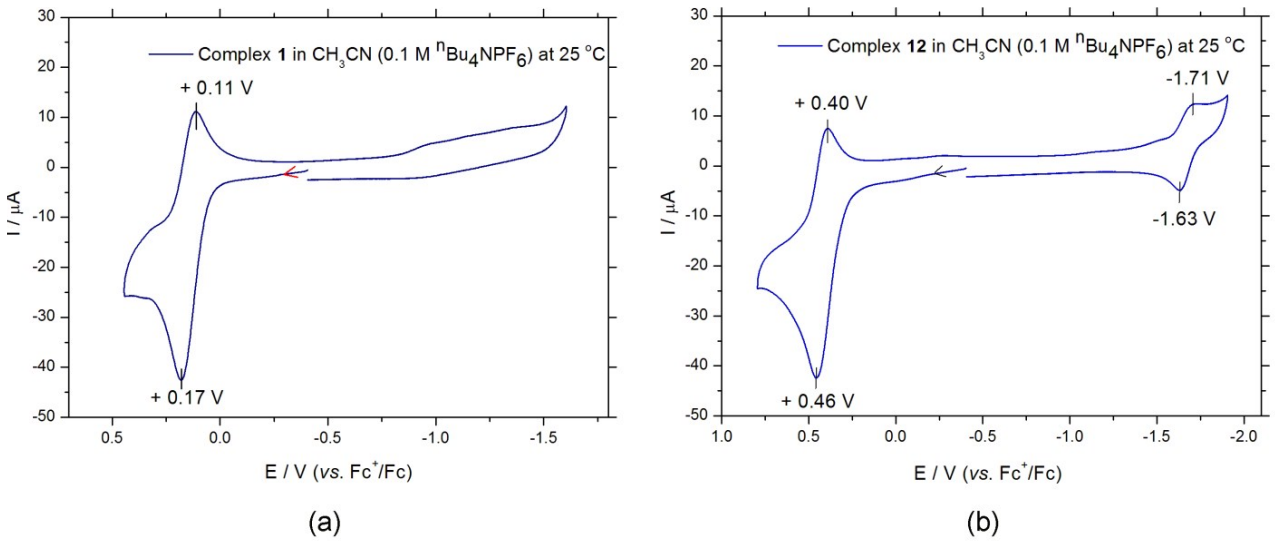


Figure S1. Cyclic voltammogram of complex **1** (a) and **12** (b) in CH_3CN (0.1 M $^{n}Bu_4NPF_6$, 298 K) at a scan rate of 100 mV s^{-1}. Working electrode: glass-carbon; Second electrode: Pt wire; Reference electrode: Ag/AgCl. The measurement was completed in 10 mins respectively.

2. X-ray Structure Determinations

Diffraction-quality crystals were obtained from the following solvents: CH_2Cl_2/Et_2O **2**; DMF/THF/Et_2O **3**, **5**, **6**; DMF/Et_2O **4**, **7**, **9**, **14**; DMF/MeCN/Et_2O **8**; MeCN/Et_2O **10**, **11**. Diffraction data were collected on an Oxford Diffraction Supernova dual diffractometer equipped with an Oxford Cryostream 700 low-temperature apparatus. Single crystals were coated with Paratone-N oil and mounted on a Nylon loop for diffraction (Cu *Kα*, *λ* = 1.54184 Å) at 100 K and 150 K. The data reduction and cell refinement were processed using CrysAlisPro software.[3] Structures were solved by direct methods using the SHELXTL program package.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically except for O–H···O in **14**, where it was located from difference Fourier Maps and refined isotropically. Refinement details and explanations were included in individual CIF files.

Table S1. Crystallographic Data[a] for Compounds **2-6** (CCDC: 1589998−1590002).

compounds	(Et_4N)[**2**]·CH_2Cl_2	(Et_4N)[**3**]	(Et_4N)[**4**]	(Me_4N)[**5**]	(Me_4N)[**6**]
formula	$C_{33}H_{43}Cl_2CuN_5O_2$	$C_{35}H_{50}CuN_4O_3$	$C_{36}H_{49}CuN_5O_2$	$C_{35}H_{50}CuN_4O_3$	$C_{40}H_{57}CuN_5O_3$
M	676.16	638.33	647.34	638.33	719.45
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	*Imm2*	*Pbca*	*Pna2(1)*	*P2(1)/n*	*P2(1)*
a, Å	9.1357(4)	16.1634(4)	15.7451(18)	13.63106(16)	10.7968(3)
b, Å	16.0102(6)	15.8968(3)	10.6651(10)	17.20745(19)	16.0879(3)
c, Å	11.0362(5)	26.1094(6)	20.5900(16)	14.4003(2)	12.1844(3)
α, deg	90	90	90	90	90
β, deg	90	90	90	101.1073(13)	112.318(3)
γ, deg	90	90	90	90	90
V, Å^3	1614.20(12)	6708.7(2)	3457.5(6)	3314.41(7)	1957.87(8)
Z	2	8	4	4	2
μ, mm^{-1}	2.778	1.223	1.181	1.237	1.111
independent data	1380	6611	4720	6261	6414
refined parameters	131	744	397	388	534
R_1[b],wR_2[c] (I >2σ(I))	0.0444, 0.1131	0.0774, 0.1746	0.0847, 0.2226	0.0322, 0.0867	0.0366, 0.1008
R_1, wR_2 (all data)	0.0452, 0.1144	0.0820, 0.1767	0.1038, 0.2378	0.0361, 0.0894	0.0375, 0.1017

[a]T = 100(2) K for complexes **2-5**, 150(2) K for complex **6**, Cu Kα radiation (λ = 1.54184 Å). [b]$R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c]$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{½}$.

Table S2. Crystallographic Data[a] for Compounds **7-9** (CCDC: 1590004−1590006).

compounds	(Et_4N)[**7**]·2DMF	(Et_4N)[**8**]·DMF	(Et_4N)[**9**]
formula	$C_{52}H_{61}Cu_2N_9O_7$	$C_{65}H_{62}Cu_2N_8O_6$	$C_{58}H_{67}Cu_2N_7O_{11}$
M	1051.18	1178.31	1165.27
crystal system	triclinic	monoclinic	monoclinic
space group	*P-1*	*I2*	*P2/c*
a, Å	13.2403(4)	14.5931(5)	22.1278(3)
b, Å	14.0874(5)	12.2058(5)	12.06401(15)
c, Å	15.1112(5)	16.6043(5)	21.5418(3)
α, deg	87.056(3)	90	90
β, deg	66.165(3)	95.409(3)	107.8352(14)
γ, deg	73.731(3)	90	90
V, Å^3	2468.80(14)	2944.41(17)	5474.21(12)
Z	2	2	4
μ, mm^{-1}	1.567	1.361	1.516
independent data	9305	4158	5180
refined parameters	668	596	390
R_1[b], wR_2[c] (I >2σ(I))	0.0436, 0.1225	0.0527, 0.1495	0.0301, 0.0820
R_1, wR_2 (all data)	0.0489, 0.1261	0.0534, 0.1517	0.0326, 0.0836

[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 S3. Crystallographic Data[a] for Compounds **10** (CCDC: 1590007), **11** (CCDC: 1590008) and **14** (CCDC: 1590010).

compounds	(Et_4N)[**10**]	(Et_4N)[**11**]	(Et_4N)[**14**]
formula	$C_{33}H_{43}CuN_5O_2$	$C_{33}H_{43}CuN_5O_2$	$C_{38}H_{41}N_3O_2$
M	605.26	605.26	571.74
crystal system	triclinic	monoclinic	orthorhombic
space group	*P-1*	*P2(1)/c*	*Pbca*
a, Å	9.9439(5)	9.71595(18)	15.6043(3)
b, Å	13.5474(7)	11.2474(2)	12.4174(3)
c, Å	13.6659(7)	29.0701(5)	16.1889(3)
α, deg	116.907(5)	90	90
β, deg	93.266(4)	98.9634(18)	90
γ, deg	101.939(4)	90	90
V, Å^3	1582.06(14)	3137.96(10)	3136.83(11)
Z	2	4	4
μ, mm^{-1}	1.256	1.267	0.583
independent data	5945	5912	2962
refined parameters	370	370	214
R_1[b], wR_2[c] (I >2σ(I))	0.0301, 0.0793	0.0532, 0.1508	0.0411, 0.1098
R_1, wR_2 (all data)	0.0338, 0.0815	0.0615, 0.1570	0.0473, 0.1146

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

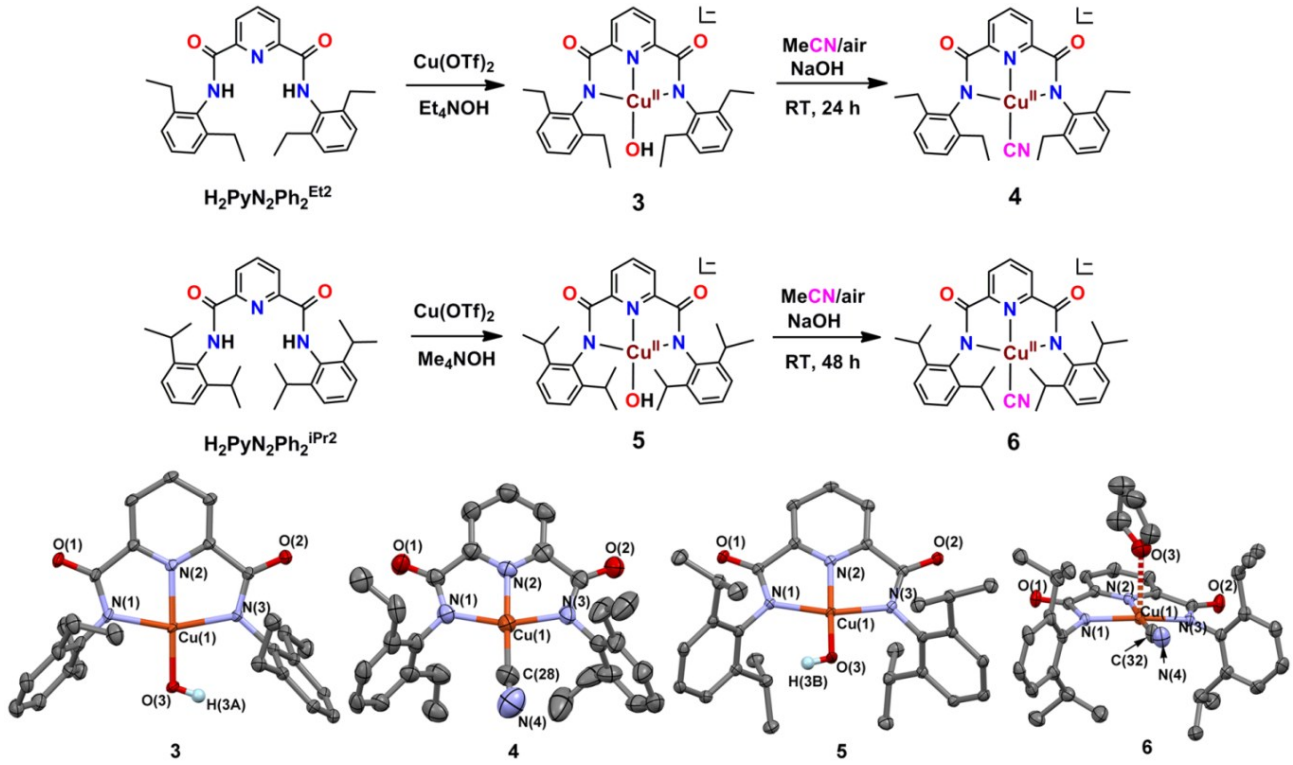


Figure S2. Structures of NNN-pincer mononuclear [Cu^{II}-L] (L = OH, CN) complexes of $[Cu(PyN_2Ph_2^{Et2})(OH)]^{1-}$ (**3**) (CCDC 1589999), $[Cu(PyN_2Ph_2^{Et2})(CN)]^{1-}$ (**4**) (CCDC 1590000), $[Cu(PyN_2Ph_2^{iPr2})(OH)]^{1-}$ (**5**) (CCDC 1590001) and $[Cu(PyN_2Ph_2^{iPr2})(CN)]^{1-}$ (**6**) (CCDC 1590002). Bond lengths (Å) and bond angle (°): Cu(1)-O(3) 1.836(11) for **3**; Cu(1)-C(28) 1.975(10), C(28)-N(4) 1.138(15), Cu(1)-C(28)-N(4) 170.6(11) for (**4**); Cu(1)-O(3) 1.881(1) for (**5**) ; Cu(1)-C(32) 2.004(6), C(32)-N(4) 1.105(7), Cu(1)···O(3) 2.642(3), Cu(1)-C(32)-N(4) 170.2(14) for (**6**).

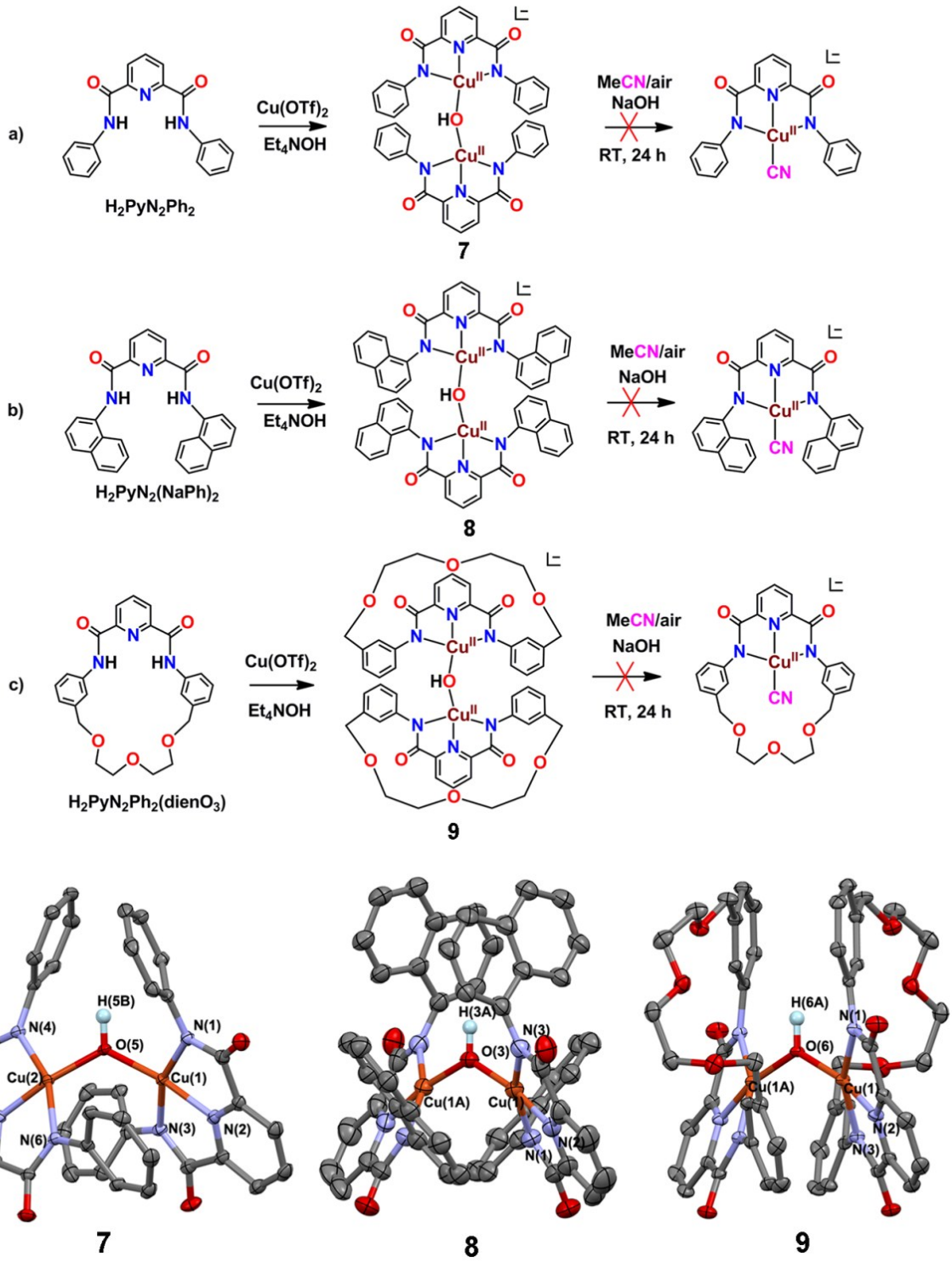


Figure S3. Structures of NNN-pincer dinuclear [Cu^{II}-OH-Cu^{II}] complexes of $\{[Cu(PyN_2Ph_2)]_2(OH)\}^{1-}$ (**7**) (CCDC 1590004), $\{[Cu(PyN_2(NaPh)_2)]_2(OH)\}^{1-}$ (**8**) (CCDC 1590005) and $\{[Cu(PyN_2Ph_2(dienO_3))]_2(OH)\}^{1-}$ (**9**) (CCDC 1590006). Bond lengths (Å) and bond angle (°): Cu(1)-O(5) 1.892(1), Cu(2)-O(5) 1.899(1), Cu(1)-O(5)-Cu(2) 125.6(1) for (**7**); Cu(1)-O(3) 1.887(1), Cu(1)-O(3)-Cu(1A) 126.6(2) for (**8**); Cu(1)-O(6) 1.895(1), Cu(1)-O(3)-Cu(1A) 127.3(1) for (**9**).

3. EPR Spectroscopy Simulation and Calculations

3.1 EPR Spectroscopy Simulation. The X-band fluid and frozen spectra were recorded on a Bruker E500 EPR spectrometer. All the frozen solutions were kept cooled at a temperature of 100 K by an Oxford cooling device throughout the experiments. All the EPR simulations of Cu(II) spectra were performed using EasySpin Matlab Toolbox.[5]

3.2 EPR theoretical calculations. The near axial EPR spectra of **1** and **10** are consistent with the approximate square-planar molecular structures determined by X-ray crystallography. The largest principal *g*-value (g_{zz}) lies perpendicular to the distorted N_3O and N_3C planes with $g_\parallel$ and $A_\parallel$ lying along this axis, and the direction of *xy* orbital defined as pointing along the orientation of N(2)-Cu(1)-O(2) for **1** and N(2)-Cu(1)-C(24) for **10** ($g_\perp$ and $A_\perp$). Thus, crystal field theory predicts a $3d_{xy}$-based SOMO for the formal Cu^{II} (d^9) complexes, which is consistent with the observed $g_\parallel > g_\perp > g_e$ pattern in the EPR spectra of the complexes. In this case, the principal components of the *g* and *A*-matrices are given by the following equations (1)-(6) according to the perturbation theory.[6]

$$\Delta g_{xx} = 2\lambda/\delta_{yz} = g_{xx} - g_e \quad (1)$$

$$\Delta g_{yy} = 2\lambda/\delta_{xz} = g_{yy} - g_e \quad (2)$$

$$\Delta g_{zz} = 8\lambda/\delta_{x^2-y^2} = g_{zz} - g_e \quad (3)$$

$$A_{xx} = A_s + P_d[2\alpha^2/7 + \Delta g_{xx} - 3\Delta g_{yy}/14] \quad (4)$$

$$A_{yy} = A_s + P_d[2\alpha^2/7 + \Delta g_{yy} - 3\Delta g_{xx}/14] \quad (5)$$

$$A_{zz} = A_s + P_d[-4\alpha^2/7 + \Delta g_{zz} + 3(\Delta g_{xx} + \Delta g_{yy})/14] \quad (6)$$

where g_e is the *g*-value of the free electron 2.00232, λ is the spin-orbit coupling constant for Cu(II), δ_{ij} is the weighted average energy difference between the ground and excited states, α is the LCAO coefficient of the Cu ($3d_{xy}$) orbital in the SOMO, A_s is the isotropic Fermi contact term and P_d is the electron-nuclear dipolar coupling parameter for Cu(II), which was calculated as 447.4×10^{-4} cm^{-1} using Rieger's methodology.[7] A combination of equations (1) - (6) gives:

$$A_{zz} = \langle A \rangle + P_d[-4\alpha^2/7 + 2\Delta g_{zz}/3 - 5(\Delta g_{xx} + \Delta g_{yy})/42] \quad (7) \quad \text{where } \langle A \rangle = (A_{xx} + A_{yy} + A_{zz})/3$$

Solution of (7) with the simulated *g* and *A*-values from the EPR spectra gave $\alpha^2 = 62.1\%$ with for **1** and 47.7% for **10** with $A_{zz} \equiv A_\parallel$ and $g_{zz} = g_\parallel$. Positive *A*-values gave invalid negative values for α^2. Thus, the contribution of $3d_{xy}$ metal orbital to the SOMO is 62.1% for **1** and 47.7% for **10** as determined by the EPR spectroscopy.

4. Quantum Chemical Calculations

Density functional theory (DFT) calculations of the transformation of complex **11** to **2** were performed using the BP86[8] functional implemented in the Gaussian 09 software package[9]. The basis set of 6-31G(d) was applied for calculation. Stationary points and associated transition states were verified by frequency calculations.

Table S4. Calculated energies for stationary points on complexes **11** and **2,** transition states (**b**) and (**d**), and intermediate (**c**) with BP86/6-31G(d) method.

11 + O_2 (a.u.)	**(b)-TS + O (a.u.)**	***ΔE* (a.u.)**	***ΔE* (Kcal/mol)**
-3126.8789	-3126.8588	+0.02	+12.6
11 + O_2 (a.u.)	**(c) + O (a.u.)**	***ΔE* (a.u.)**	***ΔE* (Kcal/mol)**
-3126.8789	-3126.8890	-0.01	-6.3
11 + O_2 (a.u.)	**(d)-TS + O (a.u.)**	***ΔE* (a.u.)**	***ΔE* (Kcal/mol)**
-3126.8789	-2126.8389	+0.04	+25.1
11 + O_2 (a.u.)	**2 + CH_2O + O (a.u.)**	***ΔE* (a.u.)**	***ΔE* (Kcal/mol)**
-3126.8789	-3126.8991	-0.02	-12.6

[a] $\Delta E = E_a - E_{11}$

Table S5. Calculated bond lengths (Å) and bond angles (deg) of complexes **11** and **2**, transition states (**c**) and (**e**), and intermediate (**d**) with BP86/6-31G(d) method.

11		**2**			
Cu(1)-C(24)	1.917	Cu(1)-C(25)	1.886		
C(24)-C(25)	1.311	C(25)-N(4)	1.182		
C(25)-N(4)	1.260	Cu(1)-C(25)-N(4)	178.1		
Cu(1)-C(24)-C(25)	124.7				
C(24)-C(25)-N(4)	173.6				
(c)		**(d)**		**(e)**	
Cu(1)-N(4)	1.865	Cu(1)-N(4)	1.859	Cu(1)-C(25)	1.919
N(4)-C(25)	1.206	N(4)-C(25)	1.243	C(25)-N(4)	1.225
C(25)-C(24)	1.465	C(25)-C(24)	1.460	C(25)-O(3)	1.383
C(24)-O(3)	1.256	C(24)-O(3)	1.500	C(24)-O(3)	1.374
C(25)····O(3)	2.427	C(25)-O(3)	1.419	Cu(1)-C(25)-N(4)	101.2
H(25)····C(25)	1.547	Cu(1)-N(4)-C(25)	132.9	Cu(1)-C(25)-O(3)	123.9
H(25)····C(24)	1.502	N(4)-C(25)-C(24)	154.6	C(25)-O(3)-C(24)	118.9
Cu(1)-N(4)-C(25)	147.3	C(25)-C(24)-O(3)	57.2		
N(4)-C(25)-C(24)	170.3	C(24)-O(3)-(25)	60		
C(25)-C(24)-O(3)	126.0	C(24)-C(25)-O(3)	62.8		

Geometry optimized coordinates for complex 11 with BP86/6-31G(d) method.

Cu	-0.07408200	0.08012300	-0.10890800
O	3.36524900	2.35178600	0.24056900
O	-3.69611200	2.06259300	0.02719700
N	1.90321400	0.48747300	0.19513100
N	-0.15304900	1.99456800	0.00160900
N	-2.08244000	0.33192200	0.13696700
C	2.23363800	1.81706400	0.17430400
C	0.99686000	2.68373400	0.13012500
C	0.97923000	4.07928700	0.25690500
H	1.93253000	4.60835200	0.34720600

Geometry optimized coordinates for transition state (c) with BP86/6-31G(d) method.

Cu	0.02348700	0.32249000	-0.09316500
O	3.60159200	2.34229700	0.09172500
O	-3.46277100	2.50656500	0.11619000
N	2.01091200	0.58678300	0.13128800
N	0.06491900	2.23464000	-0.04479500
N	-1.95318300	0.68145800	0.14621800
C	2.43471300	1.88880300	0.08164700
C	1.25972300	2.84095000	0.07644500
C	1.33330800	4.23224300	0.22898300
H	2.31928700	4.69975600	0.30634500

C	-0.26743500	4.73156200	0.27700100
H	-0.31286200	5.82329300	0.37283700
C	-1.45665000	3.98338300	0.19878600
H	-2.45165900	4.43632900	0.24045000
C	-1.35847500	2.59102500	0.07678300
C	-2.52132300	1.62721700	0.05954800
C	-3.04433400	-0.70643600	0.11892500
C	-3.85310300	-0.96408300	-1.02467300
C	-4.74960200	-2.04767700	-0.99252000
H	-5.37233600	-2.24182000	-1.87609700
C	-4.85026600	-2.88194300	0.12995800
H	-5.55088700	-3.72608700	0.13108200
C	-4.03649000	-2.63497600	1.24470600
H	-4.09974400	-3.28433000	2.12802500
C	-3.13253400	-1.55808200	1.25538800
C	-2.26512600	-1.28294300	2.46098100
H	-1.20662800	-1.17673900	2.16085100
H	-2.34411400	-2.09330800	3.20749700
H	-2.54149100	-0.32964800	2.95024500
C	-3.73619000	-0.09935400	-2.25600000
H	-4.32448700	-0.51734900	-3.09231600
H	-2.68118800	-0.01744700	-2.57751600
H	-4.09247700	0.92491400	-2.04102500
C	2.95278500	-0.46318400	0.25087200
C	3.90608900	-0.60330200	-0.79823900
C	4.89539100	-1.59926700	-0.68780100
H	5.63024400	-1.70031600	-1.49779700
C	4.95021200	-2.46007100	0.41792800
H	5.72699200	-3.23233500	0.48093600
C	3.99620900	-2.32819600	1.43742100
H	4.02200800	-2.99876500	2.30659900
C	2.99895300	-1.34065200	1.37026400
C	1.97503500	-1.19635700	2.46869000
H	0.95775800	-1.21665900	2.03508400
H	2.07058500	-0.22667600	2.99296000
H	2.06259800	-2.00769000	3.21320000
C	3.84253200	0.27544900	-2.02366600
H	4.57682300	-0.05142900	-2.78131300
H	4.04425200	1.32811700	-1.75483800
H	2.83653900	0.23100100	-2.47968400
C	-0.07934300	-1.73000700	-0.73948100
H	-0.94546200	-2.33975100	-0.44692300
C	0.81716600	-2.24045600	-1.54909000
N	1.64864000	-2.62503300	-2.41343200
H	2.48435400	-3.06317300	-1.98787000

C	0.13057500	4.95945100	0.29352600
H	0.15688800	6.04955800	0.41107200
C	-1.10595300	4.29029000	0.23700000
H	-2.06791000	4.80436100	0.32101000
C	-1.09908200	2.89718800	0.08374600
C	-2.31751600	2.00142000	0.09718800
C	-2.96553100	-0.30897000	0.12533100
C	-3.84360100	-0.46730700	-0.98494800
C	-4.78685200	-1.51076500	-0.95864600
H	-5.46355000	-1.62912400	-1.81534300
C	-4.86590400	-2.40072800	0.12175000
H	-5.60282700	-3.21298600	0.11670500
C	-3.98332000	-2.25203400	1.20085500
H	-4.02650300	-2.94770200	2.04864900
C	-3.03233900	-1.21700100	1.21870800
C	-2.09271000	-1.04594400	2.38811700
H	-2.29648100	-0.10846300	2.94008600
H	-1.04771100	-0.97289600	2.03412500
H	-2.16642900	-1.89206500	3.09266200
C	-3.75762100	0.45202000	-2.17938200
H	-4.38241900	0.08015500	-3.01076700
H	-2.71507500	0.53640400	-2.53931600
H	-4.08735200	1.47152800	-1.90726600
C	2.98539700	-0.44385400	0.10828800
C	3.84328000	-0.63995800	-1.01068600
C	4.75768500	-1.70861600	-0.98325900
H	5.41724000	-1.85864500	-1.84826100
C	4.82717700	-2.58444900	0.10824400
H	5.53811600	-3.41937600	0.10312800
C	3.96430600	-2.39690900	1.19663500
H	3.99816500	-3.08498200	2.05099900
C	3.04114400	-1.33819600	1.21237200
C	2.11976100	-1.13320300	2.39096800
H	1.06825900	-1.06621200	2.05559700
H	2.33546200	-0.18483400	2.91894500
H	2.20187400	-1.96318000	3.11422000
C	3.76930000	0.26872300	-2.21416000
H	4.37110400	-0.13181100	-3.04919600
H	4.13588300	1.28001000	-1.95859900
H	2.72553000	0.38148300	-2.56216700
C	-0.61591800	-3.99291300	-0.67943800
C	-0.32959500	-2.55668100	-0.64592900
N	-0.06610500	-1.39280300	-0.81991900
H	-0.71696200	-3.30411300	0.65143600
O	0.22738300	-4.91104600	-0.83383300
H	-1.72370500	-4.15350300	-0.73460600

Geometry optimized coordinates for intermediate (d) with BP86/6-31G(d) method.

Cu	-0.01988500	0.25306600	0.22399000
O	3.52779600	2.34103400	-0.00427400
O	-3.53796300	2.37488600	-0.12764300
N	1.97390100	0.55990200	0.09650500
N	-0.00990200	2.16584800	0.14098000
N	-1.98862800	0.58029900	-0.13281200
C	2.36914500	1.86880400	0.05653900
C	1.17456600	2.79778500	0.04281100
C	1.22542100	4.18866600	-0.11913100
H	2.20443100	4.67256700	-0.18502400
C	0.01073800	4.89387800	-0.20831200
H	0.01851000	5.98411400	-0.32937200
C	-1.21280800	4.20012500	-0.17592500
H	-2.18306400	4.69411200	-0.28339100
C	-1.18281700	2.80735800	-0.02010000
C	-2.38323800	1.88941000	-0.07843200
C	-2.97867600	-0.42942700	-0.19843800
C	-2.98211300	-1.28886600	-1.33202800
C	-3.91937600	-2.33374500	-1.40172800
H	-3.91629200	-2.99045600	-2.28164700
C	-4.84805000	-2.54162800	-0.37155200
H	-5.57539700	-3.36054400	-0.43760300
C	-4.82980300	-1.70010300	0.74980600
H	-5.54271200	-1.86353700	1.56944100
C	-3.90283400	-0.64775400	0.86231100
C	-3.87591300	0.22239200	2.09536300
H	-2.85184100	0.28230400	2.50899100
H	-4.54602200	-0.17668300	2.87803900
H	-4.18559900	1.25390700	1.84542100
C	-1.99099400	-1.05869500	-2.44789400
H	-2.02815400	-1.87378900	-3.19148900
H	-0.96437600	-1.00180100	-2.04349800
H	-2.17951100	-0.09932500	-2.96653100
C	2.99792400	-0.42581200	0.07764500
C	3.63144300	-0.76706100	-1.14755300
C	4.60191200	-1.78493200	-1.15688500
H	5.08552000	-2.04766700	-2.10738000
C	4.95371200	-2.46007800	0.02035600
H	5.70994000	-3.25480300	-0.00190300
C	4.33195700	-2.10835600	1.22717000
H	4.60828100	-2.62309000	2.15733200
C	3.35615200	-1.09613700	1.27832500
C	2.70553300	-0.71061300	2.58701000
H	3.12268100	-1.30065800	3.42339400

Geometry optimized coordinates for transition state (e) with BP86/6-31G(d) method.

Cu	0.02399500	0.19275100	0.41159400
O	3.53761100	2.16401600	-0.15214000
O	-3.49820400	2.19530800	-0.10066600
N	1.92914100	0.43059600	-0.08178600
N	0.02185600	2.09619000	0.23981800
N	-1.92447500	0.44477900	0.10378500
C	2.36678900	1.73502100	-0.05215400
C	1.20137600	2.70113200	0.01966200
C	1.24372900	4.07979600	-0.23182900
H	2.21369100	4.56121300	-0.38851700
C	0.02220100	4.77720700	-0.30613000
H	0.02293500	5.85695100	-0.49963600
C	-1.20118500	4.08902200	-0.18858500
H	-2.17257400	4.57618200	-0.31567600
C	-1.15978500	2.71166900	0.06977000
C	-2.33561600	1.75648700	0.04265300
C	-2.95656200	-0.53233500	-0.03251700
C	-3.40744700	-0.87536900	-1.33920400
C	-4.36113900	-1.89503500	-1.49372500
H	-4.69820200	-2.15920100	-2.50512200
C	-4.88360700	-2.56868700	-0.37959600
H	-5.62266000	-3.36863000	-0.51230400
C	-4.45763400	-2.20476200	0.90297100
H	-4.87394200	-2.71453300	1.78245500
C	-3.50373700	-1.18616900	1.10208200
C	-3.12064300	-0.78976000	2.51193200
H	-2.77654200	-1.66212000	3.09605900
H	-3.99040300	-0.35368100	3.04121600
H	-2.30468600	-0.05366600	2.51656500
C	-2.87593500	-0.12735000	-2.54063900
H	-3.25378500	-0.56553300	-3.48176200
H	-1.76960100	-0.13057800	-2.57126000
H	-3.18561500	0.93343400	-2.49995100
C	2.93013300	-0.57275700	-0.23618900
C	3.04591100	-1.23349400	-1.48788800
C	3.99173900	-2.26460500	-1.63518100
H	4.07710900	-2.77288300	-2.60514600
C	4.82243500	-2.63854500	-0.57001900
H	5.55479000	-3.44575700	-0.69605600
C	4.71097500	-1.96984300	0.65756200
H	5.36047200	-2.25276000	1.49665100
C	3.77574600	-0.93606400	0.84654100
C	3.66274400	-0.22339400	2.17326600
H	4.35579800	-0.65974500	2.91497800

H	1.61431300	-0.88295800	2.53736600	H	2.63297300	-0.29476300	2.56973400
H	2.86005600	0.36158400	2.81009300	H	3.90597300	0.84857300	2.05478500
C	3.26820100	-0.02887900	-2.41482300	C	2.17514500	-0.81179300	-2.64919200
H	3.77142800	-0.47219200	-3.29277600	H	2.37115700	-1.43616100	-3.53964800
H	3.56408600	1.03411800	-2.34031300	H	2.35015500	0.24553300	-2.92147800
H	2.17653300	-0.04752500	-2.59021400	H	1.10197300	-0.89450000	-2.39353600
C	-0.11145200	-2.58710200	0.48903400	C	0.14341500	-1.52578800	1.25746800
H	0.70703500	-4.63875000	0.84031600	N	0.21845400	-1.20598100	2.43737500
N	-0.12401400	-1.44384000	0.97547000	C	-0.34027800	-2.79843900	-0.68760400
C	-0.17272700	-4.04519600	0.54525100	O	0.21658600	-2.72104300	0.56629400
H	-1.13899600	-4.56461000	0.64292600	H	-0.77516800	-1.88951000	-1.10773800
O	-0.00597100	-3.28878100	-0.73955800	H	0.08490300	-3.59985700	-1.29381100

Geometry optimized coordinates for complex 2 with BP86/6-31G(d) method

Cu	-0.01074400	0.14758600	0.00000000	H	-1.21713300	1.90875900	4.09851700
O	-2.11934800	-0.21709500	3.53177300	O	-2.11934800	-0.21709500	-3.53177300
N	-0.32231300	-0.12149000	1.99132900	N	-0.32231300	-0.12149000	-1.99132900
N	-1.91851400	-0.07684800	0.00000000	C	-1.63535000	-0.16703600	-2.37791800
C	-1.63535000	-0.16703600	2.37791800	C	-2.55138600	-0.21816200	-1.17828500
C	-2.55138600	-0.21816200	1.17828500	C	-3.93615600	-0.43032000	-1.21920500
C	-3.93615600	-0.43032000	1.21920500	H	-4.42205500	-0.52550300	-2.19465500
H	-4.42205500	-0.52550300	2.19465500	C	0.67055400	-0.04536600	-3.00198100
C	-4.63161900	-0.52357000	0.00000000	C	0.76342000	1.06964300	-3.88087500
H	-5.71613500	-0.68720400	0.00000000	C	1.79071500	1.08960800	-4.84161300
C	0.67055400	-0.04536600	3.00198100	H	1.85999100	1.95068200	-5.51957500
C	0.76342000	1.06964300	3.88087500	C	2.72531200	0.04958300	-4.93539400
C	1.79071500	1.08960800	4.84161300	H	3.52373400	0.08957600	-5.68655800
H	1.85999100	1.95068200	5.51957500	C	2.64312500	-1.03150100	-4.04676200
C	2.72531200	0.04958300	4.93539400	H	3.37860300	-1.84506400	-4.09818200
H	3.52373400	0.08957600	5.68655800	C	1.62880000	-1.09233000	-3.07683100
C	2.64312500	-1.03150100	4.04676200	C	1.53855300	-2.25449400	-2.11759800
H	3.37860300	-1.84506400	4.09818200	H	2.42174300	-2.91225300	-2.19776100
C	1.62880000	-1.09233000	3.07683100	H	1.46850900	-1.88417000	-1.07849400
C	1.53855300	-2.25449400	2.11759800	H	0.63106900	-2.86322700	-2.29349100
H	2.42174300	-2.91225300	2.19776100	C	-0.20650100	2.22192000	-3.77784300
H	1.46850900	-1.88417000	1.07849400	H	-0.29059700	2.57313500	-2.73263800
H	0.63106900	-2.86322700	2.29349100	H	0.12160100	3.07135400	-4.40297500
C	-0.20650100	2.22192000	3.77784300	H	-1.21713300	1.90875900	-4.09851700
H	-0.29059700	2.57313500	2.73263800	C	1.68984600	0.96249800	0.00000000
H	0.12160100	3.07135400	4.40297500	N	2.77227700	1.43726200	0.00000000

5. GC-MS Examination of the Formation of Aldehyde

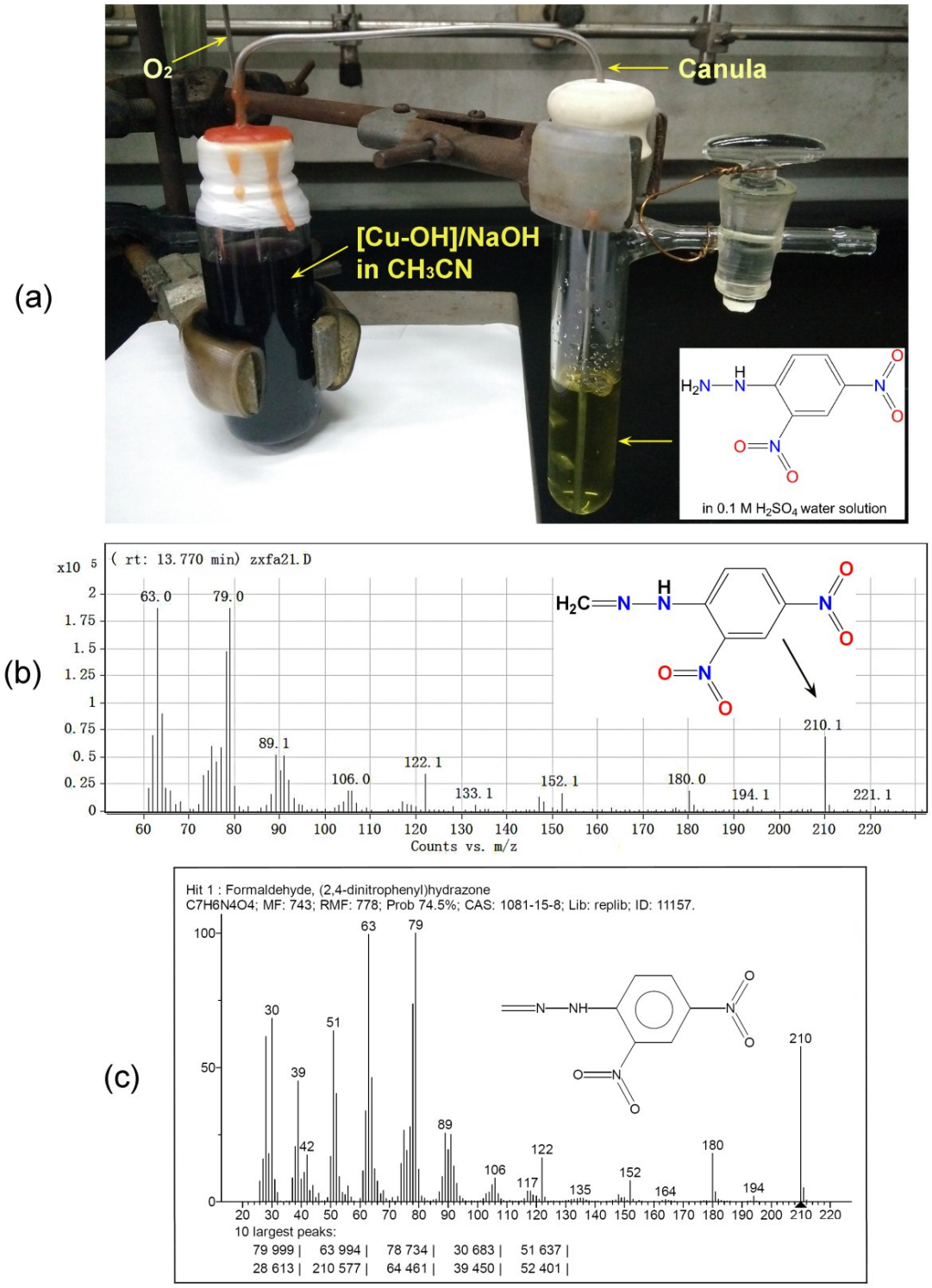


Figure S4. (a) Bubbling of the reaction atmosphere of [Cu^{II}-OH]/NaOH/CH_3CN by O_2 into a 2,4-dinitrophenylhydrazine ($(NO_2)_2(C_6H_3)NHNH_2$) aqueous solution (0.1 M H_2SO_4); (b) GC-MS signal of the product of $(NO_2)_2(C_6H_3)NHN{=}CH_2$ showing the generation of formaldehyde; (c) The MS signal of $(NO_2)_2(C_6H_3)NHN{=}CH_2$ in the database of Agilent Technologies 7890B-GC/5977B-MSD spectrometer.

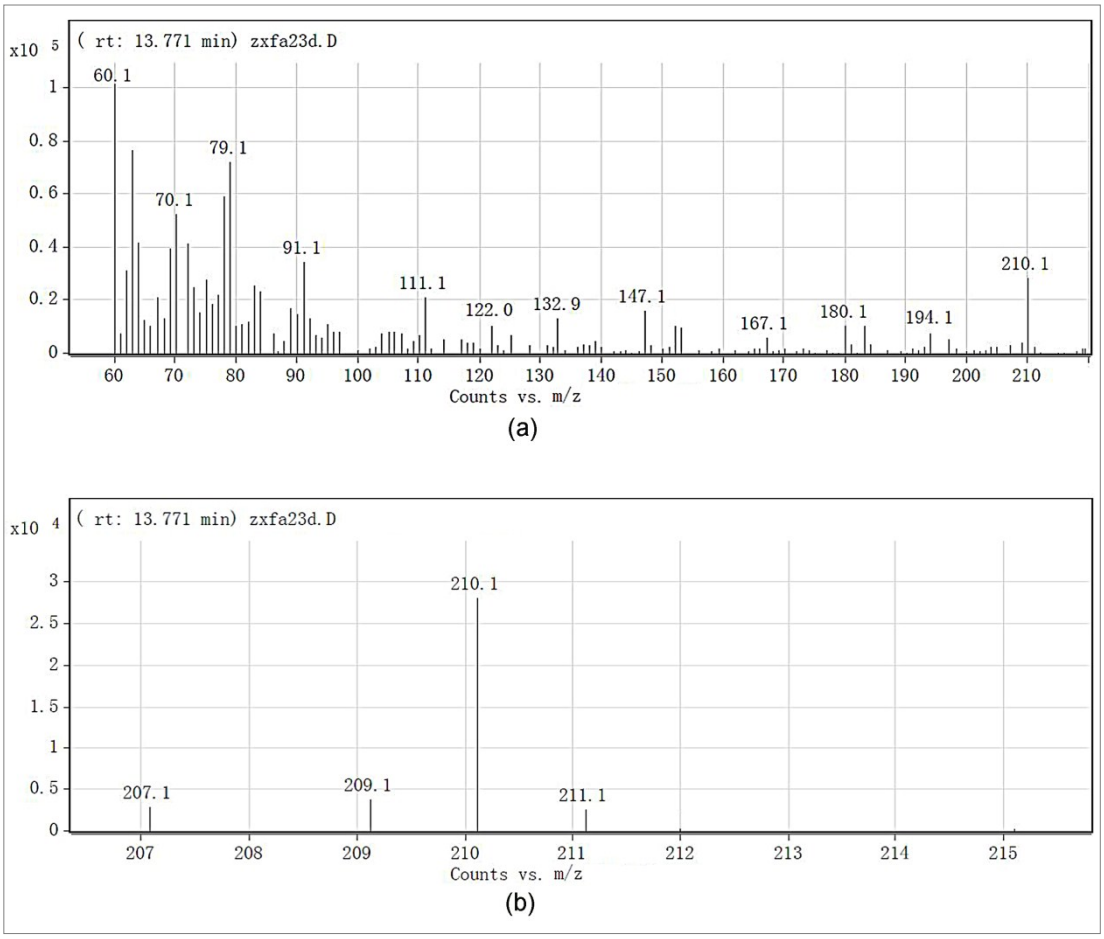


Figure S5. (a) GC-MS signal of the product of $(NO_2)_2(C_6H_3)NHN{=}CH_2$ obtained from the bubbling of the reaction atmosphere of $[Cu^{II}\text{-}CH_2CN]$/NaOH/CD_3CN by O_2 into a 2,4-dinitrophenylhydrazine ($(NO_2)_2(C_6H_3)NHNH_2$) aqueous solution (0.1 M H_2SO_4), showing the generation of CH_2O rather than CD_2O (data was recorded on a Agilent Technologies 7890B GC/5977B MSD spectrometer); (b) The magnification of signal (a) in the region of 206-216 m/z.

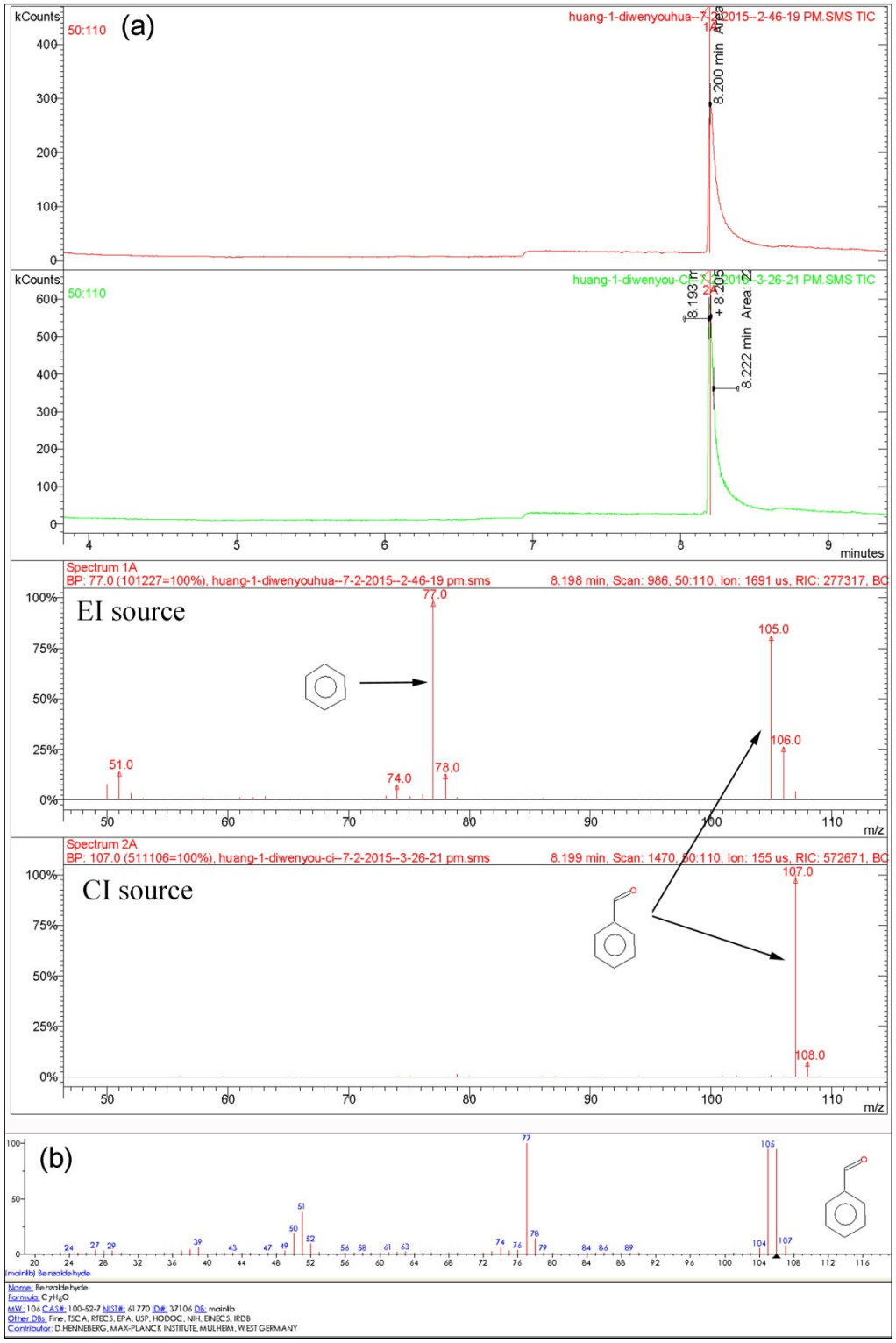
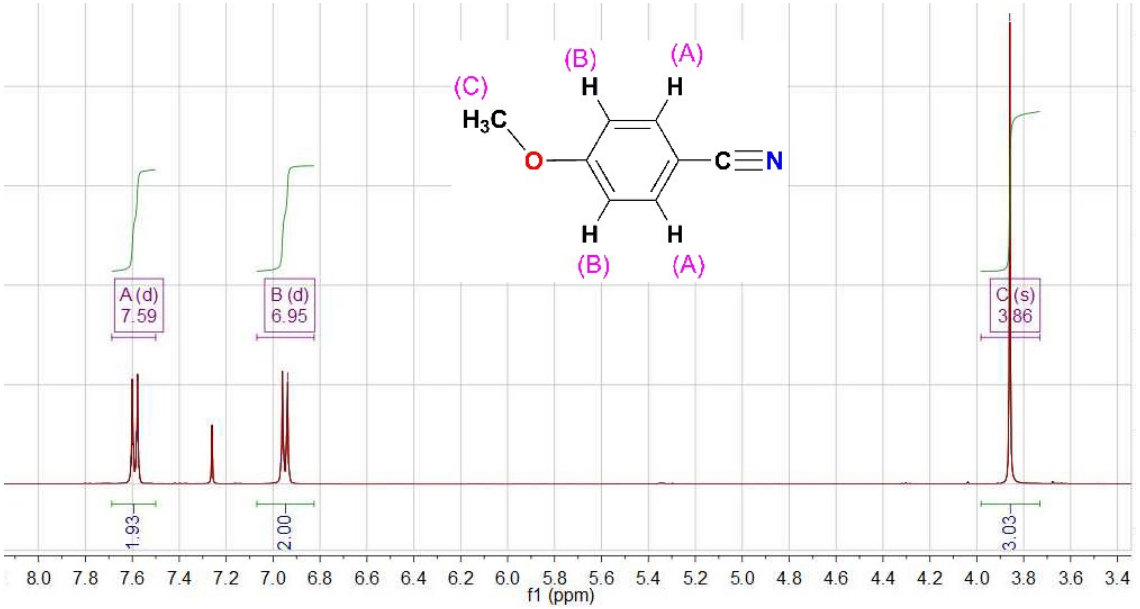
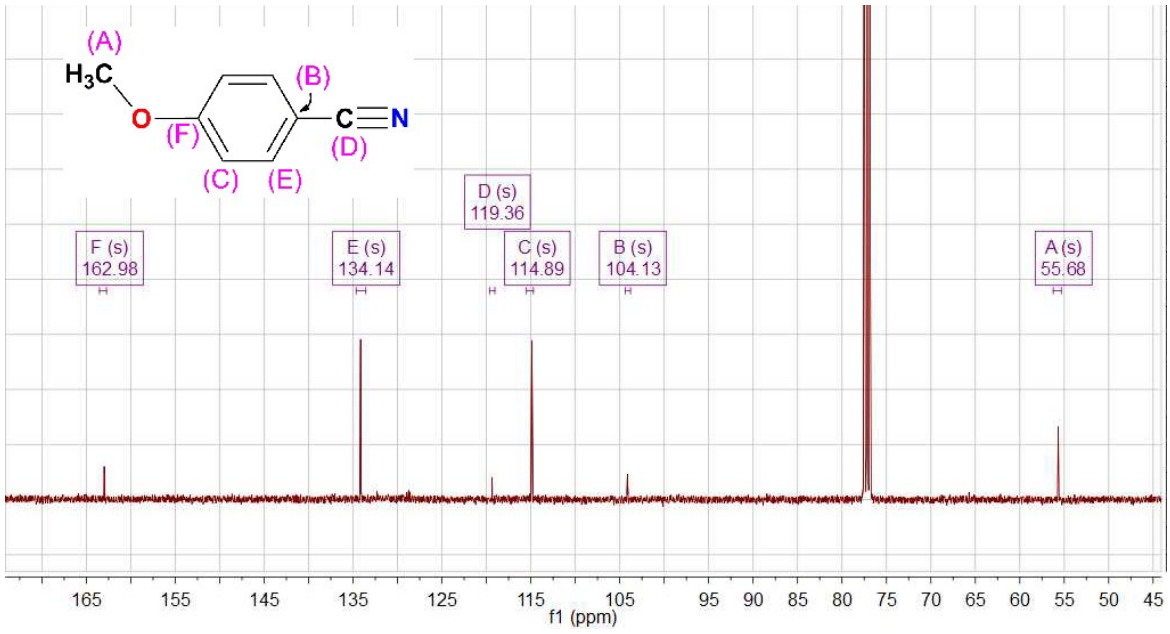
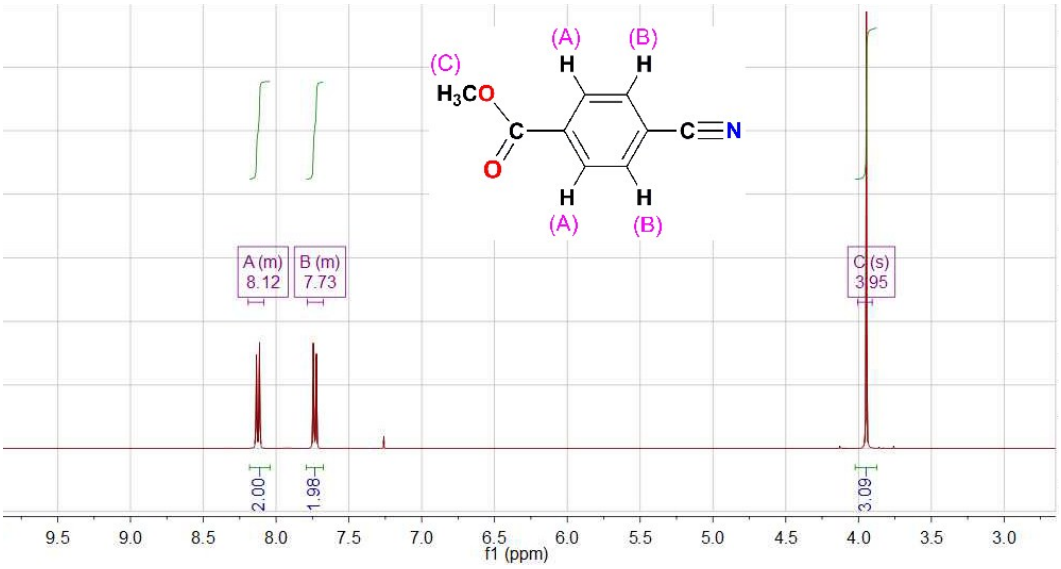


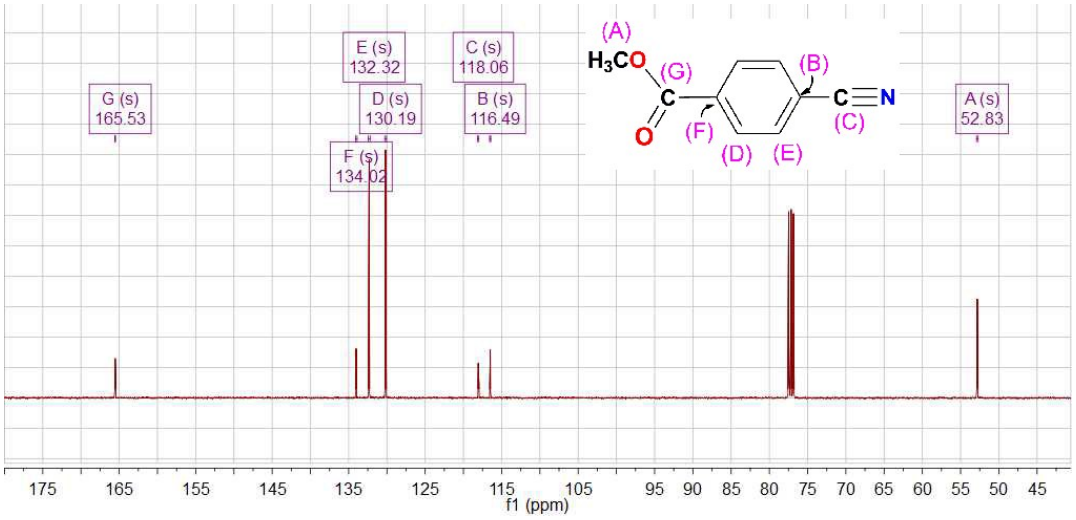
Figure S6. (a) GC-MS spectrum of the reaction solution of [Cu^{II}-OH]/NaOH/phenylacetonitrile under dioxygen atmosphere, showing the generation of benzaldehyde species; (b) The MS signal of benzaldehyde given by the GC-MS database (data was recorded on a Varian 4000 GC-MS spectrometer (EI: 70 eV)).

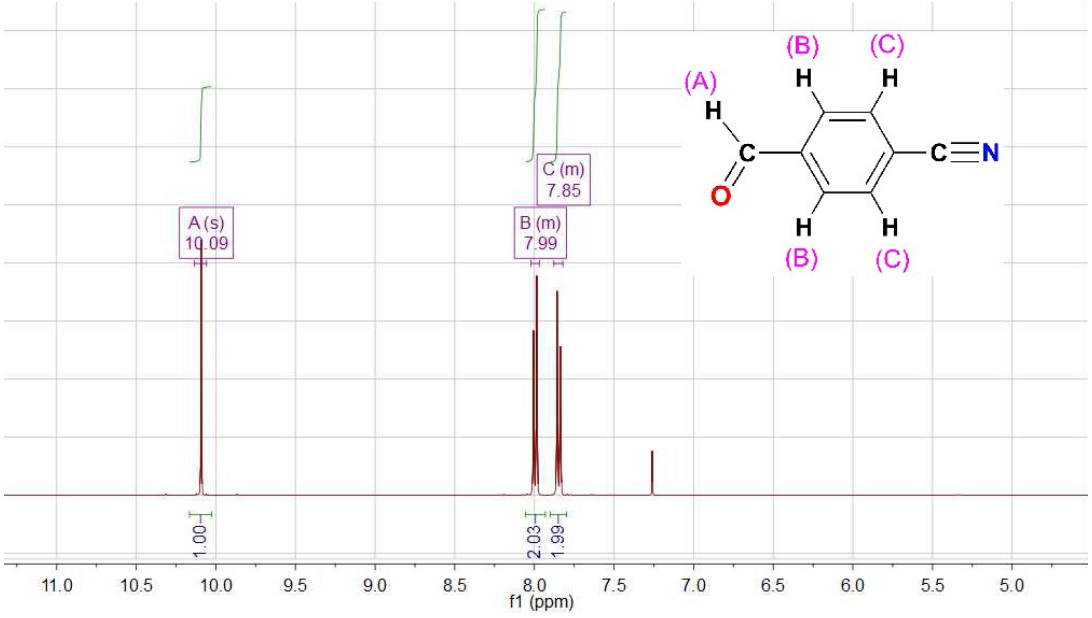
6. NMR spectra

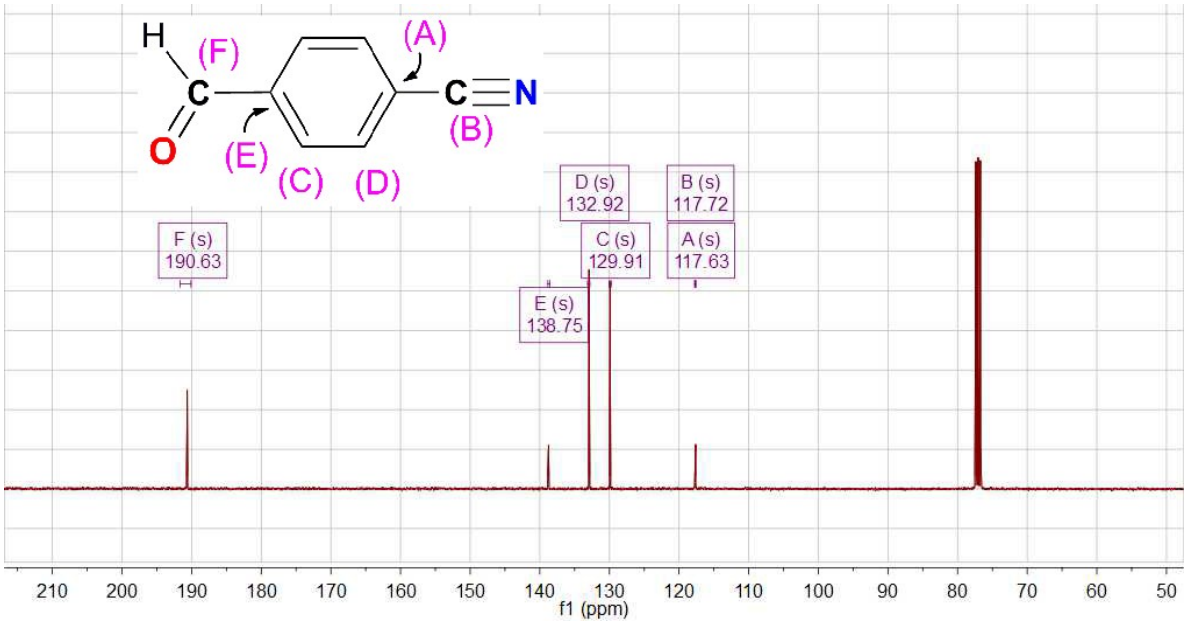


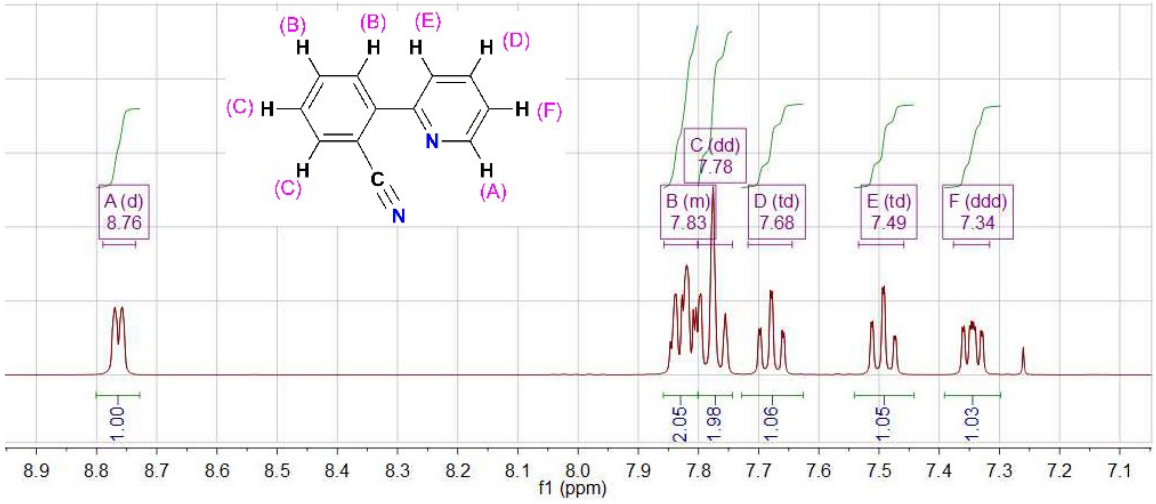


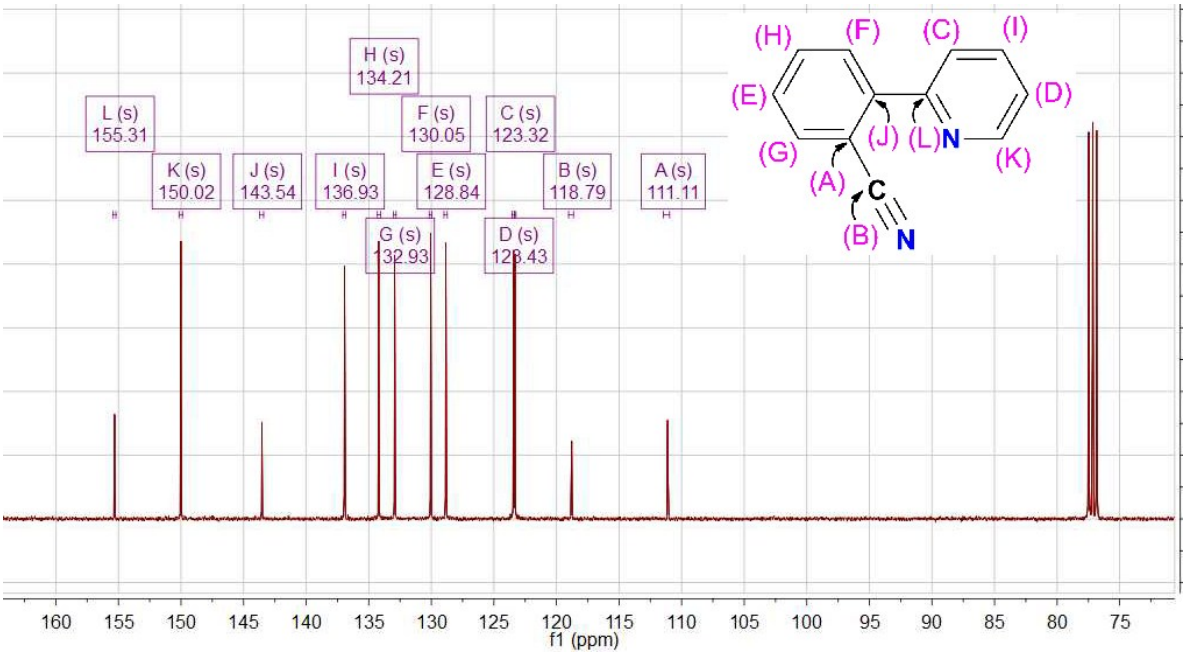

(A)
(B)
(C)
H3CO
C
O
C≡N
H
H
H
H
(A)
(B)
A (m)
8.12
B (m)
7.73
C (s)
3.95
2.00
1.98
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f1 (ppm)


G (s)
165.53
E (s)
132.32
D (s)
130.19
F (s)
134.02
C (s)
118.06
B (s)
116.49
A (s)
52.83
(A)
H3CO
(G)
(B)
C≡N
(C)
O
(F)
(D)
(E)
175
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
f1 (ppm)


(A)
(B)
(C)
H
H
H
C
O
C≡N
H
H
(B)
(C)
A (s)
10.09
C (m)
7.85
B (m)
7.99
1.00
2.03
1.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)


H
(F)
(A)
C
C≡N
O
(B)
(E)
(C)
(D)
F (s)
190.63
D (s)
132.92
B (s)
117.72
C (s)
129.91
A (s)
117.63
E (s)
138.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50
f1 (ppm)


(B)
(B)
(E)
(D)
(C)
(F)
(C)
(A)
A (d)
8.76
C (dd)
7.78
B (m)
7.83
D (td)
7.68
E (td)
7.49
F (ddd)
7.34
1.00
2.05
1.98
1.06
1.05
1.03
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)


(H)
(F)
(C)
(I)
(E)
(D)
(G)
(J)
(L)N
(K)
(A)
C
(B)
N
H (s)
134.21
L (s)
155.31
F (s)
130.05
C (s)
123.32
K (s)
150.02
J (s)
143.54
I (s)
136.93
E (s)
128.84
B (s)
118.79
A (s)
111.11
G (s)
132.93
D (s)
128.43
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75
f1 (ppm)

7. References

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