Supporting Information

Copper(II)-Hydroxide Facilitated C−C Bond Formation: Carboxamido Pyridine System versus Methylimino Pyridine System

Yinghua Li[a], Weibin Fan[a,b], Zilong Zhang[a], Xingkun Xie[a], Shiqun Xiang[a,b] and Deguang Huang[a]*

a. State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

b. University of Chinese Academy of Sciences, Beijing 100049, China.

**To whom correspondence should be addressed. E-mail: dhuang@fjirsm.ac.cn*

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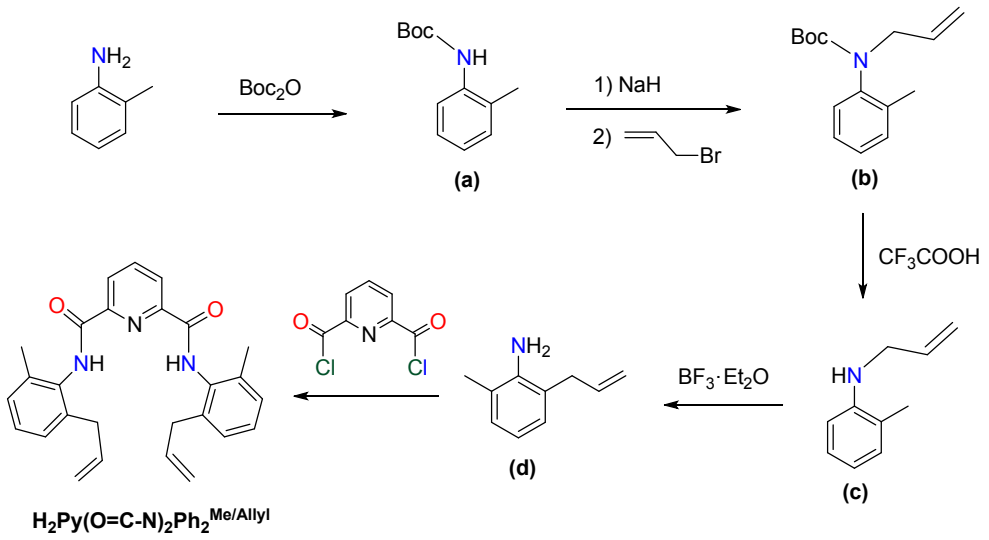
1. Experimental Section

Chemicals. Unless otherwise stated, all inorganic reactions and manipulations are performed under a pure dinitrogen atmosphere using Schlenk techniques or an inert atmosphere box. Volume reduction and drying steps are performed *in vacuo*. All the reagents are purchased from commercial sources and used as received. *N,N'*-dimethylformamide and dichloromethane are freshly distilled over CaH_2. Tetrahydrofuran, diethyl ether, toluene and *n*-hexane are distilled over sodium under N_2. The ligands of $H_2py(N{-}C{=}O)_2ph_2^{Me2}$ and $(py(N{=}C{-}C)_2ph_2^{Me2})$ are synthesized according to the literature procedure.[1-2] Complex $(Et_4N)[Cu(py(N{-}C{=}O)_2ph_2^{Me2})(OH)]$ (**2**) is prepared as described in the literature.[3]

General Physical Measurements. ^1H NMR spectra are recorded on Bruker Avance III (400 MHz) and chemical shifts are expressed in δ ppm values with reference to tetramethylsilane (TMS) as internal standard. UV−vis spectra are recorded with a Lambda365 (190−1100 nm) ultraviolet spectrophotometer. Elemental analyses of C, H and N are performed with a Vario EL III CHNOS elemental analyzer. The X-band fluid and frozen spectra are recorded on a Bruker E500 EPR spectrometer. All the frozen solutions are kept cooled at a temperature of 100 K by an Oxford cooling device throughout the experiments. Cyclic voltammetry is carried out in 10^{-3} M solutions of the complexes under an atmosphere of Ar on a CHI630A potentiostat. A single compartmental cell is used with glassy-carbon, Pt net and Ag/AgCl functioning as the working, counter and reference electrodes, respectively. All potentials are quoted versus the ferrocenium-ferrocene couple.[4] Tetrabutylammonium hexafluorophosphate is used as the supporting electrolyte.



Scheme S1. Synthetic route for *NNN*-pincer ligand $H_2py(N{-}C{=}O)_2ph_2^{Me/Allyl}$.

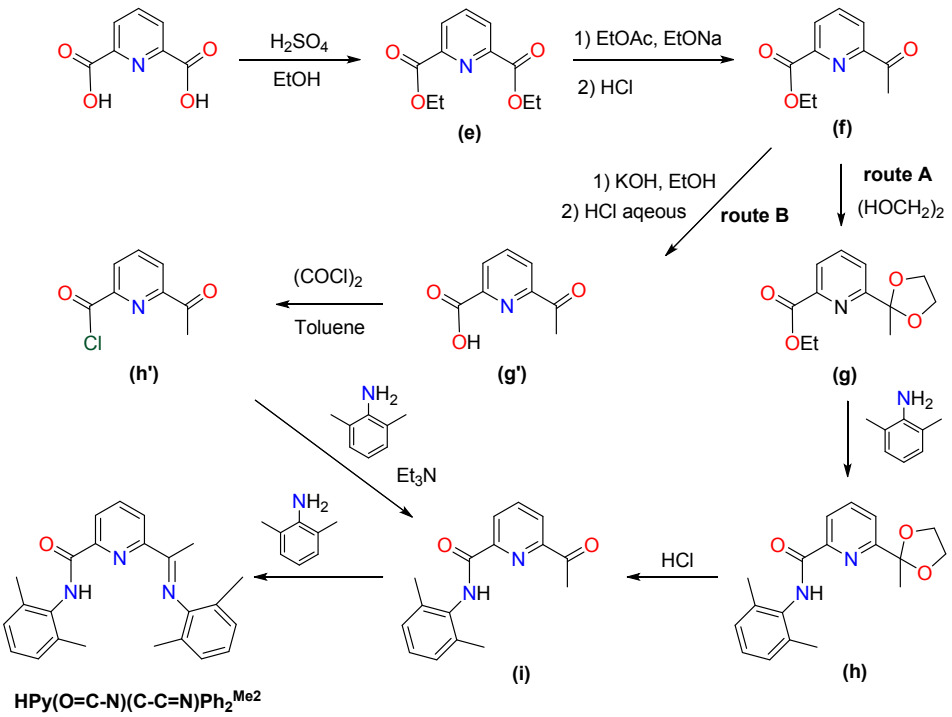
***tert*-Butyl *o*-tolylcarbamate (a).** To a solution of *o*-toluidine (1.22 g, 11.4 mmol) and triethylamine (2.1 mL) in THF (40 mL) is added dropwise a solution of Boc_2O (2.49 g, 11.4 mmol) in THF (20 mL). The solution is stirred for 14 h and solvent is removed in *vacuo*. The solid is stirred in Et_2O (120 mL) for 30 mins and filtered to remove some precipitate. Solvent of filtrate is removed in *vacuo* to afford the product as white solid (2.0 g, 85%). ^1H NMR ($CDCl_3$) δ 1.55 (s, 9H), 2.28 (s, 3H), 7.02 (t, J = 7.2 Hz, 1H), 7.12−7.27 (m, 2H), 7.84 (d, J = 7.8 Hz, 1H).

***tert*-Butyl allyl(*o*-tolyl)carbamate (b).** A solution of compound **a** (2.0 g, 9.7 mmol) in THF (25 mL) is added dropwise a suspension of NaH (60% in mineral oil, 0.46 g, 11.5 mmol) in THF (25 mL) at 0 °C. The mixture is stirred for 2 h at room temperature before 3-bromopropylene (1.17 g, 9.7 mmol) is added. The resultant mixture is refluxed for 16 h and cooled down to room temperature by itself. The solution is quenched with water (100 mL), and the volume of solvent is reduced to *ca.* 80 mL. The aqueous solution is extracted with hexane/EtOAc (1:1) (3 × 100 mL) and the combined organic layers are dried over anhydrous Na_2SO_4 over night. The solid is filtered off and the solvent is removed under reduced pressure. The crude product is purified on a silica column eluted with hexane/EtOAc to afford the product as pale yellow oil (2.04 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 9H), 2.32 (s, 3H), 4.06 (d, J = 10.3 Hz, 1H), 4.42 (d, J = 10.3 Hz, 1H), 5.20 (d, J = 5.4 Hz, 2H), 6.03 (tdd, J = 17.2, 10.3, 5.2 Hz, 1H), 7.09-7.42 (m, 4H).

***N*-Allyl-2-methylaniline (c).** To a solution of compound **b** (2.04 g, 8.26 mmol) in CH_2Cl_2 (10 mL) is added trifluoroacetic acid (3.5 mL) and the mixture is stirred for 10 h at room temperature. Water (30 mL) is added and the pH value of solution is adjusted to 9 with 2M NaOH. The organic layers are collected and the aqueous layer is extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers are dried over anhydrous Na_2SO_4 over night. Solvent is removed and the residue is purified on a silica column eluted with hexane/EtOAc to afford the product as yellow oil (1.01 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 3.87 (d, J = 5.4 Hz, 2H), 5.23 (d, J = 10.3 Hz, 1H), 5.34 (dt, J = 6.9, 3.4 Hz, 1H), 6.05 (ddd, J = 22.5, 10.5, 5.4 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.72 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 7.3 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H).

2-Allyl-6-methylaniline (d). A mixture of compound **c** (1.01 g, 6.87 mmol), $BF_3{\cdot}Et_2O$ (0.5 mL, 3.43 mmol) and sulfolane (1.8 g, 15.0 mmol) is sealed in a pressure tube under N_2. The mixture is reacted at 190 °C for 3 h and cooled to room temperature slowly. The mixture is diluted with water (20 mL) and the pH value of solution is adjusted to 1 with 10% HCl. The mixture is washed with CH_2Cl_2 (3 × 20 mL). The aqueous layer is collected, alkalized (pH = 12) with 2M NaOH and extracted with CH_2Cl_2 (3 × 30 mL). The organic layers are combined and dried over anhydrous Na_2SO_4 over night. Solvent is removed and the crude product is purified on a silica column eluted with petroleum-ether/EtOAc to afford the product as pale yellow oil (0.4 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 3.37 (d, J = 5.9 Hz, 2H), 3.60 (s, 2H), 5.16 (ddd, J = 6.9, 6.0, 1.5 Hz, 2H), 6.00 (ddt, J = 14.8, 10.9, 6.2 Hz, 1H), 6.72 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H).

Bis(2-allyl-6-methylphenyl)pyridine-2,6-dicarboxamide ($H_2py(N{-}C{=}O)_2ph_2^{Me/Allyl}$). To a solution of **d** (0.40 g, 2.72 mmol) and triethylamine (0.55 g, 5.44 mmol) in THF (40 mL), is added slowly a solution of pyridine-2,6-dicarbonylchloride (0.31 g, 1.50 mmol) in THF (25 mL). The mixture is stirred for 5 h and filtered to remove some white precipitate. Solvent is removed and the crude product is purified on a silica column eluted with dichloromethane/methanol to afford the product as white solid (0.5 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 6H), 3.40 (d, J = 6.1 Hz, 4H), 4.95 (dddd, J = 8.7, 7.0, 3.4, 1.7 Hz, 4H), 5.93 (ddt, J = 16.2, 10.1, 6.1 Hz, 2H), 7.13 (t, J = 4.6 Hz, 2H), 7.23(d, J = 5.0 Hz, 4H), 8.16 (t, J = 7.8 Hz, 1H), 8.53 (d, J = 7.8 Hz, 2H), 9.21 (s, 2H).



Scheme S2. Modified synthetic routes for *NNN*-pincer ligand Hpy(N−C=O)(N=C−C)ph_2^{Me2}.

Two synthetic routes are developed for the preparation of asymmetric carboxamido-methylimino pyridine ligand Hpy(N−C=O)(N=C−C)ph_2^{Me2}.

Route A:

pyridine-2,6-dicarboxylate (e). Dipicolinic acid (3.11 g, 18.6 mmol) and concentrated H_2SO_4 (2 mL) are mixed in absolute ethanol (200 mL) and the solution is refluxed for 10 h. The solvent is removed under reduced pressure and water (50 mL) is added. The pH value of solution is adjusted to 7 with 2M NaOH. The aqueous solution is extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic layers are dried over anhydrous Na_2SO_4 over night. Solvent is removed in *vacuo* to afford the product as a white solid (3.48 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (t, J = 7.1 Hz, 6H), 4.49 (q, J = 7.1 Hz, 4H), 8.00 (t, J = 7.8 Hz, 1H), 8.30 (d, J = 7.8 Hz, 2H).

6-Acetylpyridine-2-carboxylate (f). The modified procedure[5] is used for the preparation of compound **f**. New commercial chemical of EtONa is pumped to dry for 12 h before use. A solution of compound **e** (3.48 g, 15.6 mmol) in freshly distilled EtOAc (40 mL) is added dropwise to a batch of dry EtONa powder (1.27 g, 18.7 mmol) in flask. The yellow mixture is stirred at room temperature for 2 h and refluxed for 8 h under N_2. After that, HCl (37%, 12 mL) is added and the solution is continually refluxed for 5 h. The reaction mixture is cooled and water is added to dissolve the precipitate. The pH value of solution is adjusted to 7 with 1M Na_2CO_3 while stirring, and the aqueous solution is extracted with CH_2Cl_2 (3 × 80 mL). The combined organic layers are dried over anhydrous Na_2SO_4 and solvent is removed under reduced pressure. The residue is purified on a silica column eluted with petroleum ether/EtOAc (4/1) to afford the product as a white solid (0.87 g, 29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (t, J = 7.1 Hz, 3H), 2.83 (s, 3H), 4.51 (q, J = 7.1 Hz, 2H), 8.01 (t, J = 7.8 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.30 (d, J = 7.7 Hz, 1H).

6-(2-methyl-1,3-dioxolan-2-yl)picolinate (g).[6] A mixture of compound **f** (0.87 g, 4.5 mmol), ethylene glycol (0.34 g, 5.4 mmol) and *p*-toluenesulfonic acid (PTSA) (78 mg, 0.45 mmol) is refluxed in anhydrous toluene (50 mL) with a Dean-Stark apparatus for 12 h. The solution is cooled, diluted with EtOAc (50 mL), and washed with saturated $NaHCO_3$ aqueous solution (2 × 30 mL) and water (2 × 50 mL). The organic layer is dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product is purified on a silica column eluted with dichloromethane/ethanol (40 / 1) to afford the product as pale yellow oil (0.90, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, J = 7.1 Hz, 3H), 1.75 (s, 3H), 3.89 (t, J = 6.9 Hz, 2H), 4.07 (t, J = 7.1 Hz, 2H), 4.40 (dd, J = 14.2, 7.1 Hz, 2H), 7.70 (d, J = 7.3 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.99 (d, J = 7.3 Hz, 1H).

N-(2,6-dimethylphenyl)-6-(2-methyl-1,3-dioxolan-2-yl)picolinamide (h). To a solution of 2,6-dimethylaniline (0.55 g, 4.56 mmol) in dioxane (40 mL) is added $Al(Me)_3$ in *n*-heptane (4.56 mL, 4.56 mmol), and the mixture is stirred for 4 h. A solution of compound **g** (0.90 g, 3.8 mmol) in dioxane (20 mL) is slowly added, and the solution is refluxed at 140 ^{o}C for 17 h. After the reaction is completed, the solution is cooled down and water (0.5 mL) is slowly added to quench the reaction. The mixture is stirred for 30 mins, and dried over anhydrous Na_2SO_4. Solvent is removed and the crude product is purified on a silica column eluted with petroleum ether/EtOAc to afford the product as white solid (0.90 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 3H), 2.29 (s, 6H), 3.94 (t, J = 6.7 Hz, 2H), 4.12 (t, J = 6.7 Hz, 2H), 7.11 (s, 3H), 7.75 (d, J = 7.7 Hz, 1H), 7.90 (t, J = 7.7 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 9.58 (s, 1H).

6-acetyl-N-(2,6-dimethylphenyl)picolinamide (i). To a solution of compound **h** (0.90 g, 2.88 mmol) in THF (50 ml) is added 2M HCl (2.2 mL) and water (52 mg, 2.88 mmol). The mixture is stirred at 90 ^{o}C for 8 h. Solvent is removed and the residue is dissolved in a mixture of water (20 mL) and EtOAc (20 mL). The pH value of solution is adjusted to 7 with 2M NaOH. Organic layer is collected and the aqueous layer is extracted with CH_2Cl_2 (3 × 50 mL). The organic layers are combined and dried over anhydrous Na_2SO_4. Solvent is removed under reduced pressure and the residue is purified on a silica column eluted with petroleum ether/EtOAc to give the product as white solid (0.74 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 6H), 2.79 (s, 3H), 7.16 (s, 3H), 8.08 (t, J = 7.4 Hz, 1H), 8.26 (d, J = 7.3 Hz, 1H), 8.50 (d, J = 7.3 Hz, 1H), 9.39 (s, 1H).

6-acetyl-N-(2,6-dimethylphenyl)picolinamide (Hpy(N−C=O)(N=C−C)ph$_2^{Me2}$). To a solution of compound **i** (0.74 g, 2.76 mmol) in anhydrous toluene (40 mL) is added *p*-toluenesulfonic acid (PTSA) (42 mg, 0.24 mmol) and 2,6-dimethylaniline (0.35 g, 2.9 mmol). The mixture is refluxed in flask equipped with a Dean-Stark apparatus for 10 h under N_2, cooled to room temperature and diluted with EtOAc (40 mL). The solution is washed with 5% Na_2CO_3 solution (2 × 30 mL) and water (30 mL), dried over anhydrous Na_2SO_4. Solvent is removed to afford the product as pale yellow solid (0.94 g, 92%). The crystallization of ligand in CH_2Cl_2/Et_2O could lead to the decomposition of compound. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (s, 6H), 2.24 (s, 3H), 2.34 (s, 6H), 6.95-7.16 (m, 6H), 8.05 (t, J = 7.8 Hz, 1H), 8.42 (d, J = 7.6 Hz, 1H), 8.61 (d, J = 7.9 Hz, 1H), 9.50 (s, 1H).

Route B:

6-acetyl-2-pyridinecarboxylic acid (g'). A solution of KOH (1.0 g, 18.0 mmol) in ethanol (12 mL) is added to a solution of compound **f** (0.87 g, 4.5 mmol) in ethanol (22 mL). The mixture is

stirred at room temperature for 2 h. Solvent is removed and the white residue is dissolved in CH_2Cl_2/H_2O (50/50 mL). The pH value of solution is adjusted to *ca*. 2.0 with 10% of HCl while stirring, and the aqueous layer is extracted with CH_2Cl_2 (2 × 80 mL). The organic layers are combined and dried over $MgSO_4$. Solvent is removed in *vacuo* to give the product as an off-white powder (0.68 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.75 (s, 3H), 8.10 (t, J = 7.8 Hz, 1H), 8.29 (d, J = 7.3 Hz, 1H), 8.40 (d, J = 7.3 Hz, 1H), 9.93 (s, 1H).

6-acetyl-N-(2,6-dimethylphenyl)picolinamide (i). The reported procedure is used for the preparation of compound **i** from **g'** (g'→h'→i).[7]

[Cu(py(N−C=O)$_2$ph$_2^{Me2}$)(DMF)] (1). *Method 1*. H_2py(N−C=O)$_2$ph$_2^{Me2}$ (75 mg, 0.20 mmol) and $Cu(OTf)_2$ (72 mg, 0.20 mmol) are stirred in DMF/THF (1mL/3 mL) for 15 mins. The light green solution is slowly treated with Et_4NOH (25% in methanol, 236 mg, 0.40 mmol) and stirred for 2 hours to give a dark-green solution. The solution is filtered through Celite and the filtrate is added hexane (15 mL) to deposit the compound as dark-green oil. The oil is redissolved in THF (2 mL) and Et_2O (30 mL) is added to form a suspension, which stays for 1 week to deposit product as dark-green block crystals (43 mg, 42 %). The structure of this compound is confirmed by X-ray crystallography. Absorption spectrum (DMF): λ_{max} (ε_M) 596 (br, 544), 384 (sh, 3709), 306 (sh, 11835) nm. $E_p^{c}{}_{(Cu2+/Cu+)}$ = -1.10 V *vs*. Fc^+/Fc (DMF, 0.1 M NBu_4PF_6, 298 K). Anal. Calcd. for $C_{26}H_{28}CuN_4O_3$: C, 61.46; H, 5.55; N, 11.03. Found: C, 61.82; H, 5.51; N, 10.95.

Method 2. To a dark blue solution of **2** (29 mg, 0.05 mmol) in DMF (1 mL) is added a solution of $Fe(OTf)_2$ (18 mg, 0.05 mmol) in DMF (1 mL). The reaction mixture is stirred for 1 h and filtered to remove some brown-black precipitate. The solid is filtered off, and the filtrate is added Et_2O (15 mL) and filtered to give a green solution. The green solution is diluted with hexane (15 mL), and the mixture stays for five days to deposit product as block dark-green crystals (9 mg, 35 %).

(Et$_4$N)[Cu(py(N−C=O)$_2$ph$_2^{Me2}$)(OH)] (2). The reported method[3] is used for the preparation of compound **2**.

(Et$_4$N)$_2$[Cu(py(N−C=O)$_2$ph$_2^{Me2}$)]$_2$·MeCN (3·MeCN). To a dark blue solution of **2** (29 mg, 0.05 mmol) in MeCN (2 mL) is added a solution of ethylenediamine (0.50 mL) in MeCN (2 mL). The solution turn to purple red immediately and stir for 3 days. The mixture is diluted with MeCN (3 mL) and stir for a second 3 days. Some suspended white crystalline solid is filtered off and the filtrate is diffused with Et_2O over weeks to deposit some dark red crystals of **3** mixed with some dark green crystals [Cu(py(N−C=O)$_2$ph$_2^{Me2}$)(EDA)] **3a** (12.4 mg, 50%) (Fig. S1). The target dark red crystals are collected manually (6 mg, 10%). The structure of this compound is checked with X-ray crystallography. Anal. Calcd. for $C_{64}H_{85}Cu_2N_9O_4$: C, 65.61; H, 7.31; N, 10.76. Found: C, 65.49; H, 7.35; N, 10.83.

[Cu(py(N−C=O)$_2$ph$_2^{Me/Allyl}$)(DMF)] (4). The synthetic method of compound **1** is used for the preparation of compound **4** with the starting material of ligand H_2py(N−C=O)$_2$ph$_2^{Me/Allyl}$ (85 mg, 0.20 mmol) and $Cu(OTf)_2$ (72 mg, 0.20 mmol). Yield 45 mg, 40%. Anal. Calcd. for $C_{30}H_{32}CuN_4O_3$: C, 64.33; H, 5.76; N, 10.00. Found: C, 64.05; H, 5.68; N, 9.93.

(Me_4N)[Cu(py(N−C=O)$_2$ph$_2^{Me/Allyl}$)(OH)] (5). *Method 1.* A solution of H_2py(N−C=O)$_2$ph$_2^{Me/Allyl}$ (64 mg, 0.15 mmol) and Cu(OTf)$_2$ (55 mg, 0.15 mmol) in DMF/THF (1.5 mL/1.5 mL) is added slowly Me_4NOH (25% in MeOH, 73 mg, 0.20 mmol). The mixture is stirred for 30 mins to give a dark blue solution. A second portion of Me_4NOH (25% in MeOH, 91 mg, 0.25 mmol) is added and the solution is stirred for 10 hours. The mixture is filtered through Celite. The filtrate is added with Et_2O (16 mL) and the mixture stay over 1 day to deposit some purple-blue crystalline solid. The solid is collected, washed with Et_2O (3 mL) and DMF/THF (3 mL, 1:4), and dissolved in DMF/THF (2 mL, 1:1). Diffusion of Et_2O into this DMF/THF solution over days affords the target product as block dark-blue crystals (33 mg, 38%), mixed with a little amount of golden yellow particles (compound **6**). The structure of dark-blue crystal is checked with X-ray crystallography. Anal. Calcd. for $C_{31}H_{38}CuN_4O_3$: C, 64.39; H, 6.62; N, 9.69. Found: C, 64.25; H, 6.56; N, 9.65.

Method 2. To a dark green solution of **4** (28 mg, 0.05 mmol) in DMF/THF (1/1 mL) is added a solution of Me_4NOH (25% in MeOH, 18 mg, 0.05 mmol). The reaction mixture is stirred for 15 mins and filtered to form a dark blue solution. The solution is treated Et_2O (15 mL) to give some blue precipitate, which is collected, dissolved in DMF/THF (0.5/1 mL) and diffused with Et_2O to afford product as block blue crystals (16 mg, 55 %).

(Me_4N)$_2$[Cu(py(N−C=O)$_2$ph$_2^{Me/Allyl}$)]$_2$·DMF (6·DMF). A solution of **5** (23 mg, 0.04 mmol) in DMF (1.5 mL) is layered over toluene (5 mL) for 2 weeks. The resulted DMF/toluene solution is diffused with Et_2O to deposit product as golden yellow microcrystal (7 mg, 30%). The structure of compound is checked with X-ray crystallography. Anal. Calcd. for $C_{65}H_{81}Cu_2N_9O_5$: C, 65.30; H, 6.83; N, 10.54. Found: C, 65.61; H, 6.90; N, 10.42.

[Cu(⊂$_{20}$-py(N−C=O)$_2$ph$_2$dien^{Me3})(DMF)] (7). The synthetic method of compound **1** is used for the preparation of compound **7** with the starting material of ligand ⊂$_{20}$-H_2py(N−C=O)$_2$ph$_2$dien^{Me3} (97 mg, 0.20 mmol) and Cu(OTf)$_2$ (72 mg, 0.20 mmol). Yield 43 mg, 35%. Anal. Calcd. for $C_{31}H_{37}CuN_7O_3$: C, 60.13; H, 6.02; N, 15.83. Found: C, 59.55; H, 6.10; N, 15.53.

(Me_4N)[Cu(⊂$_{20}$-py(N−C=O)$_2$ph$_2$dien^{Me3})(OH)] (8). *Method 1.* A solution of ligand ⊂$_{20}$-H_2py(N−C=O)$_2$ph$_2$dien^{Me3} (73 mg, 0.15 mmol) and Cu(OTf)$_2$ (55 mg, 0.15 mmol) in DMF/THF (1 mL/2 mL) is added Me_4NOH (25% in MeOH, 73 mg, 0.20 mmol). The mixture is stirred for 30 mins to give a dark blue solution. A second portion of Me_4NOH (25% in MeOH, 91 mg, 0.25 mmol) is added and the solution is stirred for 5 hours. The mixture is filtered through Celite and the filtrate is added Et_2O (16 mL) to deposit some sticky blue solid. The solid is collected, washed with Et_2O (3 mL) and THF (3 mL), and dissolved in DMF/THF (2 mL, 1:2). Diffusion of Et_2O into this DMF/THF solution affords product as brown blue crystals (53 mg, 55%). A fast X-ray diffraction data of brown blue crystal confirms the structure of **8** as a mononuclear terminal hydroxo group coordinated copper(II) compound (Fig. S1). Anal. Calcd. for $C_{32}H_{45}CuN_7O_3$: C, 60.12; H, 7.09; N, 15.34. Found: C, 60.35; H, 7.05; N, 15.46.

Method 2. To a dark green solution of **7** (31 mg, 0.05 mmol) in DMF/THF (1/1 mL) is added a solution of Me_4NOH (25% in MeOH, 18 mg, 0.05 mmol). The reaction mixture is stirred for 15 mins and filtered to form a dark blue solution. The solution is treated Et_2O (15 mL) to give some blue precipitate, which is collected, dissolved in DMF/THF (0.5/1 mL) and diffused with Et_2O to afford product as block blue crystals (20 mg, 63 %).

[Cu_3(⊂$_{20}$-py(N−C=O)$_2$$ph_2$$dien^{Me3}$)$_2$](OTf)·MeCN (9·MeCN). A mixture of compound **8** (32 mg, 0.05 mmol) and $Cu(OTf)_2$ (18 mg, 0.05 mmol) is stirred in DMF (2 mL) for 15 mins. The solution is filtered and the filtrate is diffused with Et_2O to deposit green particles, mixing with some oily residue. The mixture is washed with THF (3 mL), dissolved in THF/MeCN (2/2 mL) and diffused with Et_2O to deposit product as needle green crystals (15 mg, 45%). The structure of this compound is checked with X-ray crystallography (Fig. 3). Anal. Calcd. for $C_{59}H_{67}Cu_3F_3N_{13}O_7S$: C, 52.49; H, 5.00; N, 13.49. Found: C, 51.99; H, 5.08; N, 13.55.

{[Cu(py(N−C=O)(N=C−C)ph_2^{Me2})(DMF)](OTf)}$_n$ (10). A mixture of $Cu(OTf)_2$ (36 mg, 0.10 mmol) and Hpy(N−C=O)(N=C−C)ph_2^{Me2} (37 mg, 0.10 mmol) is dissolved in DMF/THF (0.5/1 mL). Et_4NOH (25% in MeOH, 59 mg, 0.10 mmol) is added and the mixture is stirred for 6 h to give a dark green solution. The solution is filtered and the filtrate is added with Et_2O (15 mL) to deposit a dark green oil. The oil is dissolved in THF (1 mL), treated with Et_2O (10 mL) to form a cloudy mixture, from which the product deposits as green column crystals (29 mg, 44%) after 4 days. Single crystals suitable for X-ray diffraction are obtained from diffusion of Et_2O into a concentrated THF solution. Absorption spectrum (DMF): λ_{max} (ε_M) 652 (br, 352), 394 (sh, 2247) nm. $E_p^{c}{}_{(Cu2+/Cu+)}$ = -0.72 V *vs*. Fc^+/Fc (DMF, 0.1 M NBu_4PF_6, 298 K). Anal. Calcd. for $C_{28}H_{31}CuF_3N_4O_5S$: C, 51.25; H, 4.76; N, 8.54. Found: C, 51.57; H, 4.70; N, 8.49.

{[Cu(py(N−C=O)(N=C−C)ph_2^{Me2})(Cl)}$_n$ (10a). A solution of compound **10** (33 mg, 0.05 mmol) in DMF/THF (0.5/1 mL) is treated with Et_4NCl (8.3 mg, 0.05 mmol). The mixture is filtered and filtrate is diffused with Et_2O to afford the product as dark green block crystals (15 mg, 64%). The structure of this compound is checked with X-ray crystallography (Fig. S1). Anal. Calcd. for $C_{24}H_{24}ClCuN_3O$: C, 61.40; H, 5.15; N, 8.95. Found: C, 61.77; H, 5.13; N, 8.89.

(Me_4N)[Cu^I(py(N−C=O)(N=C−C)ph_2^{Me2})$_2$]·1.5Et_2O·0.5H_2O (12). To a dark green solution of **10** (20 mg, 0.03 mmol) in DMF (1 mL) is slowly added Me_4NOH (25% in MeOH, 11 mg, 0.03 mmol). The mixture is stirred for 1 h and filtered to give a light-brown solution. The filtrate is treated with Et_2O (20 mL) to deposit some brown-red solid, which is washed with THF (2 mL) and dissolved in DMF (1.5 mL). The resultant solution is diffused with Et_2O to deposit the product as block brown-red crystals (6 mg, 40%). The structure of compound is checked with X-ray crystallography. Anal. Calcd. for $C_{58}H_{74}CuN_7O_4$: C, 69.89; H, 7.48; N, 9.84. Found: C, 69.68; H, 7.58; N, 9.99.

{[Ni(py(N−C=O)(N=C−C)ph_2^{Me2})(DMF)](OTf)}$_n$ (13). The synthetic method of compound **10** is used for the preparation of compound **13** with the ligand of Hpy(N−C=O)(**N=C−C**)ph_2^{Me2} (37 mg, 0.10 mmol) and $Ni(OTf)_2$ (36 mg, 0.1 mmol). Yield 26 mg, 40%. Anal. Calcd. for $C_{28}H_{31}NiF_3N_4O_5S$: C, 51.63; H, 4.80; N, 8.60. Found: C, 51.10; H, 4.69; N, 8.42.

(Et_4N)[Ni(py(N−C=O)(N=C−C)ph_2^{Me2})(OH)] (14). *Method 1*. A mixture of Hpy(N−C=O)(N=C−C)ph_2^{Me2} (37 mg, 0.10 mmol) and $Ni(OTf)_2$ (36 mg, 0.10 mmol) is stirred in DMF/THF (1 mL/2 mL) for 2 h. The light yellow suspension is treated with Et_4NOH (25% in methanol, 59 mg, 0.10 mmol) and stirred for 1 h to give a dark red solution. A second portion of Et_4NOH (59 mg, 0.10 mmol) is added, and the mixture is stirred for 1 h and filtered through Celite to remove some sticky precipitate. Et_2O (13 mL) is added to the filtrate and filtered to leave a deep-red solution, which is diffused with Et_2O to afford the product as block dark brown

crystal (24 mg, 42%). The structure of compound has been checked with X-ray crystallography. Anal. Calcd. for $C_{32}H_{44}N_4NiO_2$: C, 66.79; H, 7.71; N, 9.74. Found: C, 66.57; H, 7.79; N, 9.90.

Method 2. To a solution of **13** (32.5 mg, 0.05 mmol) in DMF (1.5 mL) is slowly added Et_4NOH (25% in MeOH, 44 mg, 0.075 mmol). The mixture is stirred for 1 h and filtered. The filtrate is treated with Et_2O/hexane (15/10 mL) to deposit all the brown species, which is collected and dissolved in DMF/THF (0.5/1.0 mL). The resultant solution is diffused with Et_2O to deposit the product as block dark brown crystals (17 mg, 59% based on complex **13**).

[Cu(py(N=C−C)$_2$ph$_2^{Me2}$)(DMF)(OTf)](OTf)·CH$_2$Cl$_2$ (16). A mixture of $Cu(OTf)_2$ (36 mg, 0.10 mmol) and py(N=C−C)$_2$ph$_2^{Me2}$ (37 mg, 0.10 mmol) is dissolved in DMF (1 mL) and the mixture is stirred for 6 h to give a green solution. The solution is filtered and Et_2O (10 mL) is added. The mixture stay for 4 days to deposit product as block blue crystals (51 mg, 57%). Single crystal suitable for X-ray diffraction was grown from CH_2Cl_2/*n*-hexane solution. Absorption spectrum (DMF): λ_{max} (ε_M) 637 (br, 130), 357 (sh, 2264) nm. $E_p^{c}$$_{(Cu2+/Cu+)}$ = -0.43 V, $E_p^{a}$$_{(Cu2+/Cu+)}$ = -0.34 V and $E_{½(Cu2+/Cu+)}$ = -0.385 V *vs*. Fc^+/Fc (DMF, 0.1 M NBu_4PF_6, 298 K). Anal. Calcd. for $C_{31}H_{36}Cl_2CuF_6N_4O_7S_2$: C, 41.87; H, 4.08; N, 6.30. Found: C, 41.78; H, 4.12; N, 6.39.

2. X-ray Structure Determinations

Diffraction data are collected on an Oxford Diffraction Supernova dual diffractometer equipped with an Oxford Cryostream 700 low-temperature apparatus. Cu K\a radiation source (λ = 1.54184 Å) is used for the data collection except for **8**, **12** and **16** which are collected with Mo X-ray source (λ = 0.71073 Å). Single crystals are coated with Paratone-N oil and mounted on a Nylon loop for diffraction at 100 K. The data of complex **12** is collected at 150 K. The data reduction and cell refinement are processed using CrysAlisPro software.[8] Structures are solved by direct methods using the SHELXTL program packages.[9] All non-hydrogen atoms are refined anisotropically. Hydrogen atoms are added geometrically except for the hydrogens of water in complex **12**, where they are located from difference Fourier Maps and refined isotropically. All the structures are finally refined using a modern refinement program.[10] Crystal data and refinement details are given in Tables S1-S3. Other refinement details and explanations are included in individual CIF files.

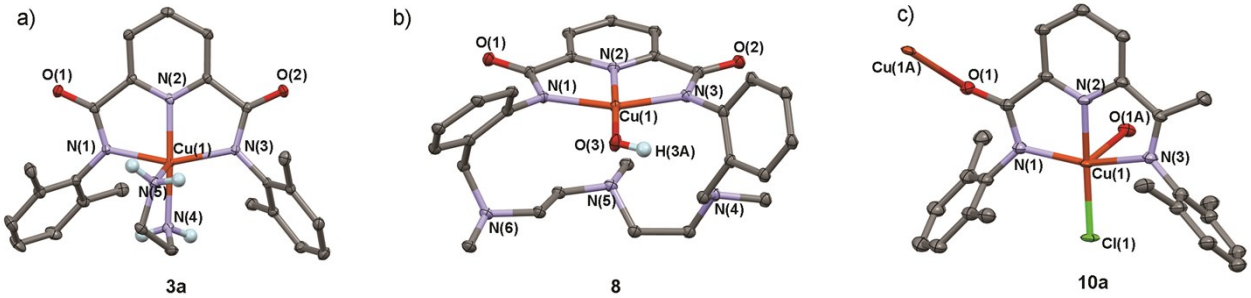


Fig. S1 Crystal structures of [Cu(py(N−C=O)$_2$ph$_2^{Me2}$)(EDA)] (**3a**), [Cu(⊂$_{20}$-py(N−C=O)$_2$ph$_2$dien^{Me3})(OH)]$^-$ (**8**) and {[Cu(py(N−C=O)(N=C−C)ph$_2^{Me2}$)(Cl)}$_n$ (**10a**) with all non-hydrogen atoms shown as 50% probability ellipsoids. The structure of complex **8** is solved by a fast-data collection with the crystallographic data shown in Table S2. The reported structure of **10a** is shown here for comparison.

3. Crystallographic Data of Complexes

Table S1. Crystallographic Data[a] for Complexes **1**, **3**, **3a** and **5**

	1	**3**	**3a**	**5**
formula	$C_{26}H_{28}CuN_4O_3$	$C_{64}H_{85}Cu_2N_9O_4$	$C_{25}H_{29}CuN_5O_2$	$C_{31}H_{38}CuN_4O_3$
M	508.06	1171.49	495.07	578.19
crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$Pna2_1$	$P2_1/n$	$P\text{-}42_1c$	$P2_12_12_1$
a, Å	15.3269(3)	14.36064(14)	23.8766(1)	18.1135(10)
b, Å	13.8051(2)	16.83191(16)	23.8766(1)	12.8871(6)
c, Å	11.6358(2)	25.6876(3)	7.9379(1)	12.7862(5)
α, deg	90	90	90	90
β, deg	90	105.8272(11)	90	90
γ, deg	90	90	90	90
V, Å^3	2461.99(7)	5973.73(10)	2984.7(2)	2984.7(2)
Z	4	4	8	4
μ, mm^{-1}	1.532	1.307	1.628	1.325
independent data	4289	11522	4607	4557
refined parameters	307	713	298	600
R_1[b], wR_2[c] ($I>2\sigma(I)$)	0.0366, 0.0998	0.0452, 0.1247	0.0301, 0.0796	0.1262, 0.3111
R_1, wR_2 (all data)	0.0388, 0.1025	0.0509, 0.1294	0.0319, 0.0812	0.1423, 0.3276

[a]T = 100(2) K, Cu Kα radiation (λ = 1.54178 Å). [b]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(Fo^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

Table S2. Crystallographic Data[a] for Complexes **6** and **8**-**10**.

	6	**8**[b] (fast data)	**9**	**10**
formula	$C_{65}H_{81}Cu_2N_9O_5$	$C_{32}H_{45}CuN_7O_3$	$C_{59}H_{67}Cu_3F_3N_{13}O_7S$	$C_{28}H_{31}CuF_3N_4O_5S$
M	1195.46	639.29	1349.94	656.17
crystal system	orthorhombic	monoclinic	Triclinic	monoclinic
space group	$C222_1$	$P2_1/n$	P-1	$P2_1/c$
a, Å	13.7621(4)	11.0739(15)	14.2445(4)	14.2458(2)
b, Å	21.9194(4)	13.3821(17)	19.3006(5)	8.57344(11)
c, Å	19.9436(4)	21.461(3)	23.1317(6)	24.9685(4)
α, deg	90	90	94.181(2)	90
β, deg	90	98.860(3)	91.182(2)	104.1134(15)
γ, deg	90	90	106.030(2)	90
V, Å^3	6016.1(2)	3142.3(7)	6090.5(3)	2957.48(7)
Z	4	4	4	4
μ, mm^{-1}	1.324	0.740	2.141	2.256
independent data	5070	4450	23092	5675
refined parameters	444	388	2065	379
R_1[c], wR_2[d] ($I>2\sigma(I)$)	0.0538, 0.1460	0.0482, 0.0815	0.0554, 0.1477	0.0424, 0.1163
R_1, wR_2 (all data)	0.0578, 0.1511	0.0894, 0.0905	0.0711, 0.1598	0.0489, 0.1219

[a]T = 100(2) K, Cu Kα radiation (λ = 1.54178 Å). [b]T = 100(2) K, Mo Kα radiation (λ = 0.71073 Å). [c]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d]$wR_2 = \{\Sigma[w(Fo^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

Table S3. Crystallographic Data[a] for Complexes **12**, **14** and **16**.

	12	**14** (fast data)	**16**[b] (fast data)
formula	$C_{58}H_{74}CuN_7O_4$	$C_{32}H_{44}N_4NiO_2$	$C_{31}H_{36}Cl_2CuF_6N_4O_7S_2$
M	996.78	575.42	889.20
crystal system	triclinic	monoclinic	monoclinic
space group	P-1	$P2_1$	$P2_1/n$
a, Å	12.7226(11)	8.9760(3)	12.4967(4)
b, Å	15.0739(14)	17.2459(4)	15.7161(6)
c, Å	16.6986(15)	10.4455(3)	19.2679(5)
α, deg	82.653(4)	90	90
β, deg	68.845(3)	109.360(3)	96.609(3)
γ, deg	68.250(3)	90	90
V, Å^3	2773.9(4)	1525.51(7)	3759.1(2)
Z	2	2	4
μ, mm^{-1}	0.444	1.175	0.914
independent data	10899	4266	6599
refined parameters	961	352	748
R_1[c], wR_2[d] ($I > 2\sigma(I)$)	0.0672, 0.1974	0.0350, 0.0991	0.0398, 0.0972
R_1, wR_2 (all data)	0.1237, 0.2307	0.0362, 0.1007	0.0533, 0.1042

[a] T = 100(2) K, Cu Kα radiation (λ = 1.54178 Å). [b]T = 100(2) K, Mo Kα radiation (λ = 0.71073 Å). [c]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d]$wR_2 = \{\Sigma[w(Fo^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

4. EPR Spectra Simulation and Calculations

4.1 EPR Spectroscopy and Simulation. The X-band fluid and frozen spectra are recorded on a Bruker E500 EPR spectrometer. All the frozen solutions are kept cooled at a temperature of 100 K by an Oxford cooling device throughout the experiments. All the EPR simulations of spectra are performed using EasySpin Matlab Toolbox.[11]

4.2 EPR theoretical calculations. The near axial EPR spectra of **1**, **10** and **16** 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 plane 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(3) for **1**, N(2)-Cu(1)-O(2) for **10** and N(2)-Cu(1)-O(1) for **16** ($g_\perp$ 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.[12]

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

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

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

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

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

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

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 is calculated as 447.4 $\times 10^{-4}$ cm^{-1} using Rieger's methodology.[13] A combination of equations (1) - (6) gives:

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

Solution of (7) with the simulated g and A-values from the EPR spectra gives $\alpha^2 = 67.8\%$ for **1**, 67.6% for **10** and 64.3% for **16** with $A_{zz} \equiv A_{\parallel}$ and $g_{zz} = g_{\parallel}$. Positive A-values gives invalid negative values for α^2. Thus, the contribution of $3d_{xy}$ metal orbital to the SOMO is 67.8% for **1**, 67.6% for **10** and 64.3% for **16** as determined by the EPR spectroscopy.

5. Quantum Chemical Calculations

Density functional theory (DFT) geometry optimization of intermediates **11** and **P1** are performed using the M06-L[14] functional implemented in the Gaussian 09 program package.[15] A basis set of 6-311G** is used for the ligand atoms (C, H, N, and O), and the Stuttgart/Dresden basis set and pseudopotential (SDD) is used for Cu. Stationary points are verified by frequency analysis. The optimized structures are found to be stable. Solvent contributions to energies are included with the SMD solvent model in DMF by performing single point calculations at the previously optimized geometry.[16]

Geometry optimized coordinates for complex 11

Cu	-0.054600	-0.128200	-0.119600
O	-3.500600	2.104400	0.108500
N	-2.045900	0.288400	0.05200
N	0.005900	1.822900	0.045500
N	2.041600	0.279900	-0.054300
C	-2.375600	1.592600	0.072500
C	-1.151600	2.474100	0.084500
C	-1.174600	3.864300	0.150100
H	-2.12700	4.380800	0.181600
C	0.036400	4.545300	0.176100
H	0.050700	5.628600	0.227300
C	1.238900	3.840400	0.137700
H	2.189900	4.359300	0.160700
C	1.186800	2.452800	0.069200
C	2.345100	1.532200	0.023100
C	3.718800	2.088900	0.062600
H	4.476600	1.306700	0.058900
H	3.850500	2.712200	0.95200
H	3.877600	2.741800	-0.801900
C	3.014500	-0.748300	-0.072600

Geometry optimized coordinates for transition state P1

Cu	0.010400	0.026400	-0.042500
O	-3.479300	2.10700	-0.049800
O	0.003100	-2.013500	0.302800
H	0.787700	-2.475300	-0.0300
N	-1.951300	0.354400	-0.017300
N	0.035400	1.952500	-0.158200
N	1.954600	0.302100	-0.232800
C	-2.332600	1.652400	-0.05500
C	-1.142500	2.576200	-0.153500
C	-1.185900	3.955900	-0.261100
H	-2.139300	4.471800	-0.256500
C	0.027400	4.638200	-0.378700
H	0.029100	5.719700	-0.465900
C	1.236400	3.951900	-0.391400
H	2.172700	4.488200	-0.491600
C	1.219400	2.559700	-0.273800
C	2.362300	1.613900	-0.255100
C	3.638500	2.082500	-0.289900
H	4.488100	1.40900	-0.274400
H	3.842600	3.143700	-0.346700

C	3.480500	-1.262100	1.147500	C	2.860700	-0.735400	0.018100
C	4.377500	-2.329200	1.10500	C	3.497400	-0.875500	1.27400
H	4.750300	-2.736600	2.040700	C	4.320400	-1.980800	1.492400
C	4.789500	-2.870800	-0.107500	H	4.804200	-2.089500	2.460200
H	5.488400	-3.701400	-0.120800	C	4.505800	-2.949300	0.51200
C	4.297400	-2.357500	-1.302200	H	5.142700	-3.807100	0.705700
H	4.60900	-2.785200	-2.251200	C	3.8600	-2.820300	-0.71300
C	3.396100	-1.292900	-1.308300	H	3.996900	-3.574600	-1.483800
C	2.838300	-0.732600	-2.577100	C	3.039500	-1.723200	-0.978500
H	3.163300	-1.311900	-3.442800	C	2.357600	-1.574400	-2.304100
H	3.148600	0.306900	-2.732800	H	2.588500	-2.414200	-2.962900
H	1.741700	-0.728700	-2.55900	H	2.661900	-0.651600	-2.809400
C	3.010800	-0.675400	2.440300	H	1.266600	-1.512400	-2.207900
H	3.377600	-1.251600	3.291300	C	3.259700	0.115200	2.368300
H	1.91600	-0.646800	2.49200	H	2.203500	0.399500	2.424700
H	3.352800	0.358100	2.566200	H	3.817500	1.04500	2.207600
C	-3.053600	-0.688800	0.074300	H	3.560600	-0.290200	3.336900
C	-3.245200	-1.430800	1.255400	C	-2.897700	-0.682900	0.042300
C	-4.210400	-2.437700	1.271200	C	-3.662400	-0.911700	1.204100
H	-4.362200	-3.00900	2.18400	C	-4.516500	-2.015400	1.235600
C	-4.97200	-2.714500	0.140300	H	-5.107800	-2.194600	2.130500
H	-5.720600	-3.501100	0.165700	C	-4.610300	-2.886200	0.155900
C	-4.766100	-1.984200	-1.025300	H	-5.275100	-3.743300	0.203600
H	-5.352100	-2.202500	-1.91500	C	-3.848800	-2.655300	-0.984200
C	-3.809700	-0.969100	-1.079200	H	-3.922100	-3.32700	-1.835700
C	-3.565400	-0.19800	-2.336500	C	-2.990500	-1.557800	-1.06100
H	-4.167900	-0.581700	-3.162600	C	-2.196100	-1.288600	-2.302400
H	-2.511300	-0.244200	-2.633200	H	-1.115900	-1.241500	-2.111200
H	-3.803800	0.86300	-2.206100	H	-2.457400	-0.3200	-2.741900
C	-2.408600	-1.136400	2.459600	H	-2.367600	-2.060100	-3.055900
H	-1.341300	-1.256200	2.236400	C	-3.544200	0.005400	2.378100
H	-2.659300	-1.799500	3.290800	H	-4.095100	-0.379200	3.238800
H	-2.535100	-0.103500	2.80200	H	-3.929900	1.00200	2.139800
O	-0.081400	-1.971900	-0.392900	H	-2.498600	0.143100	2.67500
H	0.827700	-2.250100	-0.547400	H	-0.762100	-2.486800	-0.056400

6. HR-MS Examination of Complex 12

The HR-MS spectrum is recorded on an Agilent Technologies 7890B GC/5977B MSD spectrometer with the source type of ESI and negative ion polarity.

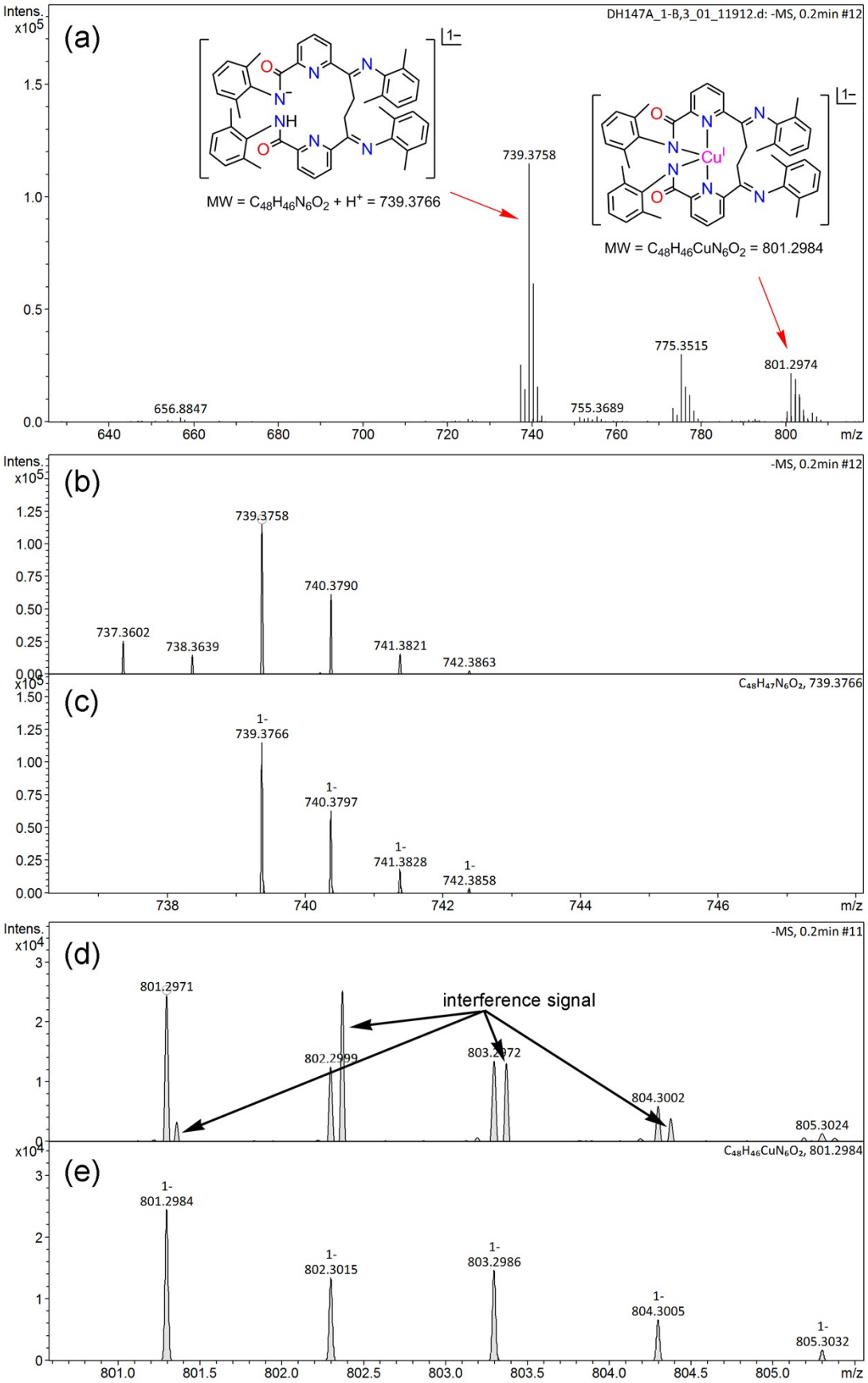


Fig. S2 (a) HR-MS spectrum of complex **12** showing the signals of ligated Cu(I) anion and its ligand; (b) Magnification of the MS signal of ligand; (c) The MS signal of ligand in the database of Agilent Technologies 7890B-GC/5977B-MSD spectrometer; (d) Magnification of the signal of Cu(I) anion; (e) The signal of ligand in the database.

7. References

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