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Synthesis, Structure, and Application of Self-Assembled Copper(II) Aqua Complex by H-Bonding for Acceleration of the Nitroaldol Reaction on Water

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Abstract: Copper(II) aqua complex **1** has been prepared in a one-pot synthesis. The single crystal X-ray analysis showed that the complex is self-assembled through aqua ligands by H-bond interactions and the copper(II) atoms are pentacoordinated with square pyramidal geometry. Complex **1** has been studied for the acceleration of the nitroalodol reaction on water. It is a clean technological process and the catalyst can be recycled without loss of activity.

Keywords: C–C coupling · heterogeneous catalysis · hydrogen bonds · nitroaldol reaction · self-assembly

Introduction

The addition of nitroalkanes to carbonyl compounds, known as the Henry (or nitroaldol) reaction, is a fundamental synthetic tool for the formation of carbon–carbon bonds.[1] The diversity of the transformation of the adducts, such as reduction to amines,[2] Nef reaction to carbonyl compounds,[3] dehydration to nitroalkenes,[4] or nucleophilic displacement, affords numerous applications for this process. In this contribution, we describe the synthesis, structure, and application of a self-assembled copper(II) aqua complex **1** for the acceleration of the nitroaldol reaction on water. The copper(II) atoms are pentacoordinated with square pyramidal geometry. Both the axial aqua ligand, having tetrahedral geometry, and the equatorial aqua ligand, bearing trigonal geometry, exhibit intermolecular H-bond interactions with the carboxylate and aqua ligand oxygen of another molecule to afford the self-assembled structure. Complex **1** floats on water and catalyzes the nitroaldol reaction to obtain high reaction yields. The reaction is a heterogeneous process, no additive is involved and catalyst **1** can be filtered and recycled without a loss of activity.[5]

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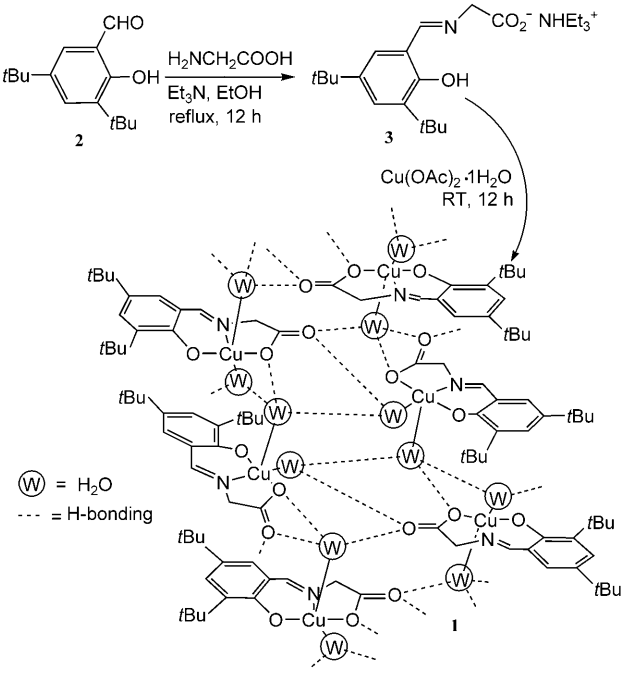
Results and Discussion

The reaction of aldehyde **2** with glycine in the presence of Et_3N in EtOH provided Schiff base **3** that was treated with $Cu(OAc)_2 \cdot 1H_2O$ in situ to give the copper(II) aqua complex **1** as a green powder (Scheme 1). During purification with silica gel column chromatography using 1:9 MeOH/CH_2Cl_2



Scheme 1. Preparation of complex **1**.

as an eluent, complex **1** underwent crystallization to afford single crystals whose X-ray analysis showed that complex **1** is self-assembled through aqua ligands (Figures 1–3).[6] The

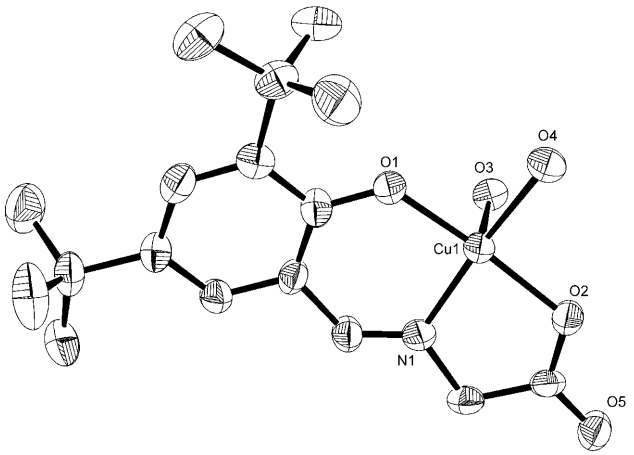


Figure 1. ORTEP diagram of **1** with 50% probability. H-atoms are omitted for clarity.

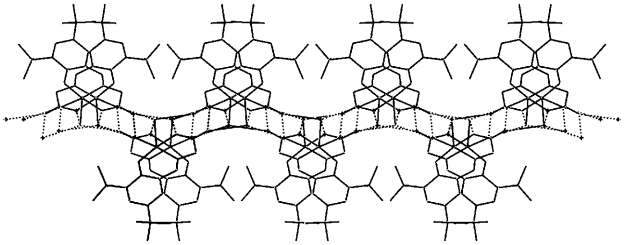


Figure 2. H-bonded network of **1** viewing down "c" flipping 90° around an axis perpendicular to the screen.

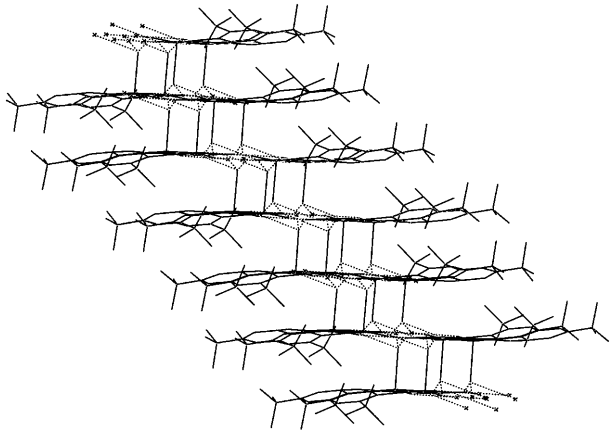


Figure 3. Self-assembly of **1** with a staircase-like structure.

aqua ligands having tetrahedral (axial) and trigonal (equatorial) geometries exhibit intermolecular H-bond interactions with the oxygen of the carboxylate and the aqua ligand of another molecule to provide a staircase-like self-assembled structure. It is well soluble in common organic solvents such as CH_2Cl_2, THF, diethyl ether, $CHCl_3$, and toluene, but insoluble in water owing to its hydrophobic *tert*-butyl groups.

Since complex **1** is self-assembled through aqua ligands,[7,8] we were interested to study its catalysis of organic reactions on water.[9] First, we studied the addition of nitroalkanes to aldehydes. The optimization of the reaction conditions was pursued with 4-nitrobenzaldehyde and nitromethane as model substrates (Table 1). The reaction occurred

Table 1. Reaction of 4-nitrobenzaldehyde with nitroalkanes on water using **1**.

Entry	Catalyst	Conv. [%][a–c]
1	$CuSO_4 \cdot 5H_2O$	7
2	$Cu(OAc)_2 \cdot 1H_2O$	14
3	$CuCl_2 \cdot 2H_2O$	13
4	$Cu(ClO_4)_2 \cdot 6H_2O$	15
5	$Cu(NO_3)_2 \cdot 3H_2O$	16
6	**1**	>99[d]
7	–	no reaction

[a] 4-Nitrobenzaldehyde (1 mmol), catalyst **1** (5 mol%), nitromethane (7.5 mmol), and solvent (3 mL) were stirred for 3 h.[b] Determined from 400-MHz ^{1}H NMR spectrometer. [c] Homogeneous process. [d] Heterogeneous process.

efficiently to afford the desired nitroaldol product in high yield when the substrates were stirred for 3 h with 5 mol% of **1** on water. It was a heterogeneous process and exhibited a greater reactivity compared to that of copper salt ($CuSO_4 \cdot 5H_2O$, $Cu(OAc)_2 \cdot H_2O$, $CuCl_2 \cdot 2H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$)-catalyzed homogeneous systems (Table 2). The reaction on water was accelerated in comparison to those in organic solvents, CH_2Cl_2, $CHCl_3$, CCl_4, $ClCH_2CH_2Cl$, toluene, EtOH, Et_2O, and THF (Table 3).[9c–d] A control experiment without catalyst showed no reaction. Similar results were observed for the reaction of the neat substrates. The reaction of nitromethane was completed in 3 h with 99% conversion, whereas nitroethane

Table 2. Reaction of 4-nitrobenzaldehyde with nitromethane on water: screening of copper source.

Entry	Nitroalkane [mmol]	H_2O [mL]	Time [h]	Conv. [%][a–c]
1	CH_3NO_2 (1)	1	3	15
2	CH_3NO_2 (2.5)	1	3	25
3	CH_3NO_2 (5)	1	3	25
4	CH_3NO_2 (7.5)	1	3	30
5	CH_3NO_2 (1)	3	3	35
6	CH_3NO_2 (2.5)	3	3	44
7	CH_3NO_2 (5)	3	3	77
8	CH_3NO_2 (7.5)	3	3	>99
9	CH_3NO_2 (7.5)	–	3	no reaction
10	$C_2H_5NO_2$ (7.5)	3	30	50 [55:45][d]
11	$nC_3H_7NO_2$ (7.5)	3	30	15 [54:46][d]
12	$iC_3H_7NO_2$ (7.5)	3	30	no reaction

[a] 4-Nitrobenzaldehyde (1 mmol), catalyst **1** (5 mol%), and nitroalkane (1–7.5 mmol) were stirred on water (1–3 mL). [b] Determined from 400-MHz ^{1}H NMR spectrometer. [c] Heterogeneous process. [d] Diastereomeric ratio (syn/anti) determined from 400-MHz ^{1}H NMR spectrometer.

Table 3. Reaction of 4-nitrobenzaldehyde with nitromethane using **1**: effect of solvent.

Entry	Solvent	Conv. [%][a–c]
1	H_2O	>99[d]
2	CH_2Cl_2	12
3	$CHCl_3$	14
4	THF	25
5	Toluene	18
6	EtOH	40
7	CCl_4	14
8	$(CH_2)_2Cl_2$	16
9	Et_2O	20

[a] 4-Nitrobenzaldehyde (1 mmol), complex **1** (5 mol%) and nitromethane (7.5 mmol), and solvent (3 mL) were stirred for 3 h. [b] Determined from 400-MHz ^{1}H NMR spectrometer. [c] Homogeneous process.[d] Heterogeneous process.

and 1-nitropropane required longer reaction times to provide the nitroaldols in 50% and 15% conversions, respectively. No reaction was observed with 2-nitropropane.

Next, the reactions of other aldehydes were investigated with nitromethane (Table 4). Benzaldehyde underwent reaction in 2.5 h with 97% yield. Similar results were observed with aryl aldehydes having 2-nitro-, 3-bromo-, 4-bromo-, 4-chloro-, 4-fluoro-, 4-methyl-, 4-methoxy-, and 3,4-dimethoxy substituents. Aldehydes with electron-withdrawing groups showed greater reactivity compared to those having electron-donating groups. These reaction conditions were also suitable for the reactions of 2-naphthaldehyde and heterocyclic aldehydes, 2-pyridinecarboxaldehyde and 2-thiophenecarboxaldehyde, to afford the nitroaldols in 54–92% yield. In 2,6-pyridinedicarboxaldehyde, both CHO groups underwent reaction with 62% yield. Likewise, aliphatic substrates, propanal, 2-methylpropanal, cyclohexanecarboxaldehyde, and ethyl glyoxalate underwent reaction to provide the nitroaldols in 70–91% yield.

In these reactions, the catalyst **1**, the carbonyl compound, and nitroalkane formed a suspension on water that was stirred. Once the reaction is completed, catalyst **1** floats on the surface of the water and the product dissolves into the water solution. Catalyst **1** can then be filtered quantitatively. The recovered **1** was reused for the fresh reaction of nitromethane with 4-nitrobenzaldehyde for three runs. The reactions occurred to provide the nitroaldol in >99% conversion (Table 5). These studies clearly reveal that catalyst **1** is recyclable without loss of activity.

The enhanced reactivity of the heterogeneous process using **1** on water compared to the homogeneous systems in organic solvents could be attributed to the occurrence of the reaction at the solid–liquid interface of water droplets (Scheme 2).[9b–d] The observed experimental results suggest that complex **1** acts as a bifunctional catalyst in these reactions: first, as Brønsted base,[10] and then as Lewis acid. To confirm this, complex **1** was titrated with HCl in CH_2Cl_2 (Figure 4). The intensity of the bands at 397 nm and 283 nm decreased with respect to an increasing concentration of HCl, and shifted to lower wavelengths at 332 nm and 264 nm, respectively, with clear isobestic points. These observed band shifts suggest that the phenolate oxygen of **1** is selectively protonated (Figure 5). Thus, the phenolate oxygen acts as a stronger base compared to the carboxylate oxygen under these conditions.[10] Hence, complex **1** may undergo reaction with nitroalkane and aldehyde to provide intermediate ***a*** that could lead to intermediate ***b*** by the protonation of the phenolate oxygen (Scheme 3). An intramolecular 1,2-addition of the nitronate to the aldehyde can give intermediate ***c*** that would complete the catalytic cycle by the reaction with fresh nitroalkane and aldehyde.

Conclusions

Synthesis, crystal structure, and application of a self-assembled copper(II) aqua complex **1** by H-bond interaction are described for the acceleration of the nitroaldol reaction on water. It is a heterogeneous process, involves no additive or base, and catalyst **1** can be recycled without a loss of activity.

Experimental Section

Materials and Methods

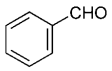
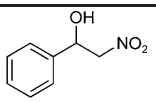
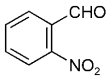
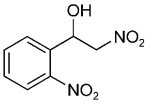
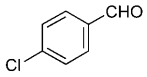
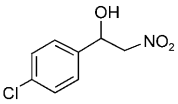
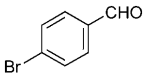
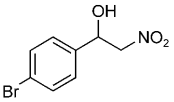
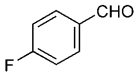
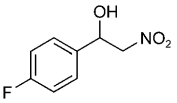
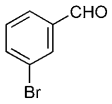
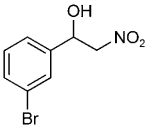
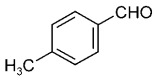
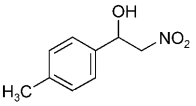
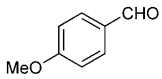
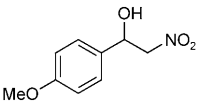
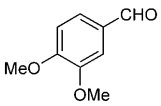
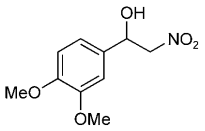
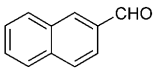
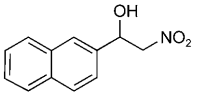
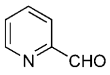
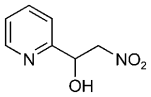
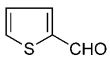
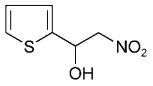
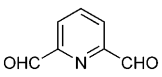
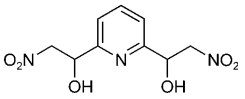
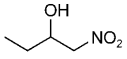
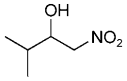
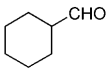
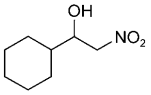
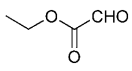
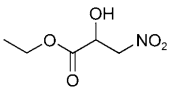
Aldehydes, nitroalkanes, glycine (>99%), 2,4-di-*tert*-butylphenol (98%), and $Cu(OAc)_2{\cdot}1H_2O$ (>99%) were purchased from Aldrich. 3,5-Di-*tert*-butyl salicylaldehyde was prepared from 2,4-di-*tert*-butylphenol.[11] NMR spectra were recorded on a Varian-400 spectrometer. UV/Vis spectra were obtained from a Perkin–Elmer Lambda-25 spectrophotometer. FTIR spectra were obtained from a Nicolet-410 spectrometer. EPR spectrum was recorded on a JES-FA-200 spectrometer. X-ray data were collected on a Bruker SMART APEX equipped with CCD area detector using $Mo_{K\alpha}$ radiation. The structure was solved by using SHELXL-97 Göttingen, Germany. Column chromatography was performed on 230–400 mesh silica gel. Thermogravimetric analysis was recorded on a TGA/SDTA-851 Mettler Toledo analyzer. Elemental analysis was obtained from a Perkin–Elmer-2400 CHNS analyzer. ESI-MS was recorded in MeOH by using a Micromass Quattro II triple quadrupole mass spectrometer.

Preparation of Copper(II) Complex **1**: 3,5-Di-*tert*-butyl salicylaldehyde (234 mg, 1 mmol), glycine (75 mg, 1 mmol), and Et_3N (101 mg, 1 mmol) were refluxed for 12 h in EtOH (5 mL). The reaction mixture was then treated with $Cu(OAc)_2{\cdot}1H_2O$ (199 mg, 1 mmol), and stirred over night at ambient temperature. The solvent was evaporated under reduced pressure, and the residue was purified on silica gel column chromatography using CH_2Cl_2 and MeOH (9:1) as eluent to afford **1** as green colored needles in 85% yield. UV/Vis (CH_2Cl_2): $\lambda_{max}=397$ ($\varepsilon=916\ mol^{-1}\,dm^3\,cm^{-1}$), 283 ($\varepsilon=2669\ mol^{-1}\,dm^3\,cm^{-1}$); FTIR (KBr): $\tilde{\nu}=3421$, 3004, 2961, 2867, 2366, 2346, 1633, 1610, 1528, 1459, 1437, 1419, 1379, 1167, 787, 753, 536 cm^{-1}; EPR (X-band, MeOH): $g_\perp=2.049$, $g_\parallel=2.139$; elemental analysis: calcd (%) for $C_{17}H_{27}O_5NCu$: C 52.50, H 7.00, N 3.60; found: C 52.56, H 7.03, N 3.66.

General Procedure for Nitroaldol Reaction

Aldehyde (1 mmol), nitroalkane (7.5 mmol), and catalyst **1** (5 mol%) were stirred on water (3 mL) at ambient conditions. The progress of the reaction was monitored by using TLC. After completion, catalyst **1** was filtered and the filtrate was extracted with ethyl acetate (2×10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was passed through a short pad of silica gel using ethyl acetate and hexane as eluent to afford analytically pure nitroaldol product.

Table 4. Reaction of aryl and alkyl aldehydes with nitromethane using **1** on water.

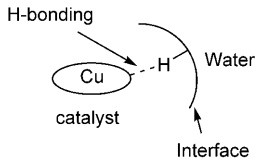
Entry	Substrate	Time [h]	Product	Yield [%][a,b]
1		2.5		97
2		15		81
3		14		76
4		7		98
5		15		82
6		24		72
7		12		89
8		24		75
9		12		82
10		24		54
11		5		92
12		20		70
13		24		62
14		6		88
15		12		85
16		8		91
17		24		70

[a] Substrate (1 mmol), complex **1** (5 mol%), and nitromethane (7.5 mmol) were stirred on water (3 mL). [b] Yield of isolated product.

Table 5. Reaction of 4-nitrobenzaldehyde with nitromethane on water using **1**: recyclability experiments.

Run	Recovery of **1** [%]	Product [conv. %][a,b]
1	99	>99
2	97	>99[c]
3	97	>99[c]

[a] 4-Nitrobenzaldehyde (10 mmol), complex **1** (5 mol%), and nitromethane (75 mmol) stirred on water (30 mL) for 3 h. [b] Determined from 400-MHz ^{1}H NMR spectrometer. [c] Used recovered **1**.



Scheme 2. Reaction at the solid–liquid interface of water droplets.

Recycling experiment: The suspension, which contains 4-nitrobenzaldehyde (10 mmol, 1.51 g), catalyst **1** (5 mol%, 0.194 g), and nitromethane (75 mmol, 4.56 g) was stirred for 3 h on water (30 mL). Catalyst **1** was then filtered and the filtrate was extracted with EtOAc (2×50 mL). The recovered **1** was reused for the new reaction for three runs. The reactions occurred without loss of activity to afford the desired nitroaldol product in >99% conversion.

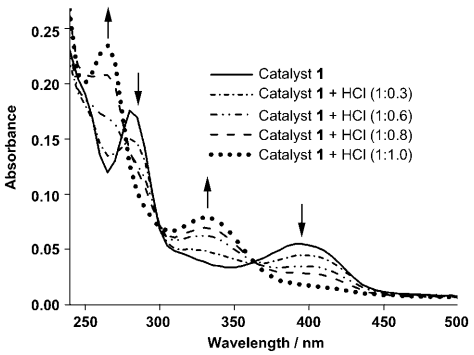


Figure 4. UV/Vis spectra of **1** (6.6×10^{-2} mM) with an increasing concentration of HCl (0.0–6.6×10^{-2} mM) in CH_2Cl_2.

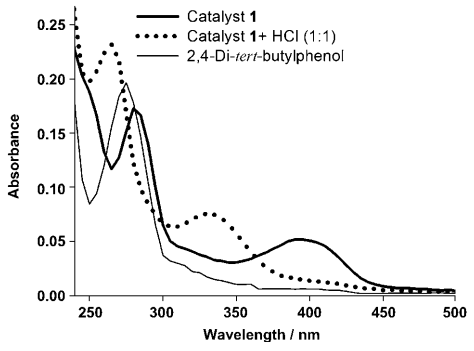
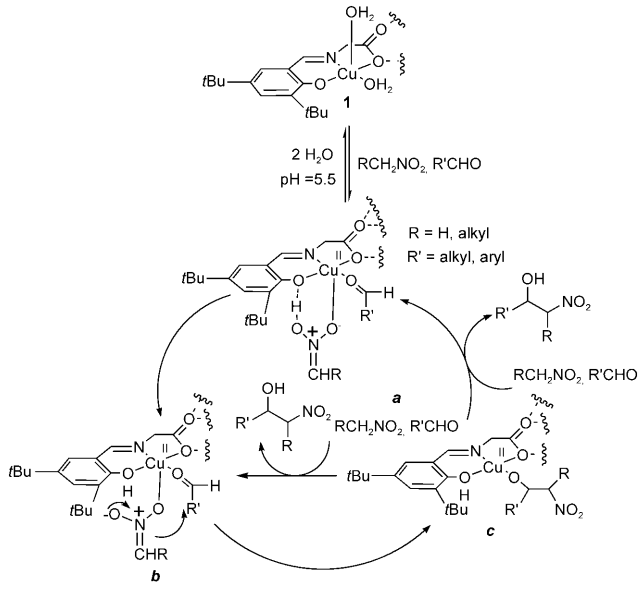


Figure 5. UV/Vis spectra of **1**, **1**+HCl, and 2,4-di-*tert*-butylphenol in CH_2Cl_2 (in all cases the concentration of sample is 6.6×10^{-2} mM).

2-Nitro-1-(4-nitrophenyl)ethanol:[12a] Colorless solid; m. p.: 84–85 °C; IR (KBr) $\tilde{\nu}$ = 3534, 1557, 1521, 1348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 5.60 (m, 1H), 4.58 (m, 2H), 3.28 ppm (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.26, 145.24, 127.15, 124.37, 80.83, 70.14 ppm; elemental analysis: calcd (%) for $C_8H_8N_2O_5$: C 45.29, H 3.80, N 13.20; found: C 45.35, H 3.81, N 13.22.



Scheme 3. Proposed catalytic cycle.

2-Nitro-1-(4-nitrophenyl)propanol:[12b] Colorless solid; m. p.: 92–94 °C; syn/anti ratio 55:45; IR (KBr): $\tilde{\nu}$ = 3448, 1556, 1522, 1344 cm^{-1}; syn isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.19 (m, 2H), 7.58–7.54 (m, 2H), 5.16 (d, J = 8.4 Hz, 1H), 4.79–4.67 (m, 1H), 3.24 (s, 1H), 1.35 ppm (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2, 145.5, 128.1, 124.2, 87.9, 75.2, 16.3 ppm; anti isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.19 (m, 2H), 7.58–7.54 (m, 2H), 5.53 (d, J = 3.2 Hz, 1H), 4.76–4.67 (m, 1H), 3.24 (s, 1H), 1.46 ppm (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 145.7, 127.2, 124.0, 86.9, 73.0, 12.0 ppm; elemental analysis: calcd (%) for $C_9H_{10}N_2O_5$: C 47.79, H 4.46, N 12.39; found: C 47.87, H 4.45, N 12.42.

2-Nitro-1-(4-nitrophenyl)butanol:[12b] Colorless solid; m. p. 97–98 °C; syn/anti ratio 54:46; IR (KBr): $\tilde{\nu}$ = 3460, 1557, 1520, 1345 cm^{-1}; syn isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 5.17–5.13 (m, 1H), 4.61–4.56 (m, 1H), 2.96 (d, J = 0.8 Hz, 1H), 1.50–1.41 (m, 2H), 0.90 ppm (t, J = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.40, 145.88, 128.04, 124.30, 94.79, 74.49, 24.01, 10.51 ppm; anti isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 5.17–5.13 (m, 1H), 4.61–4.56 (m, 1H), 2.96 (d, J = 0.8 Hz, 1H), 1.94–1.84 (m, 2H), 0.90 ppm (t, J = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.40, 145.83, 127.46, 128.08, 94.33, 73.43, 21.41, 10.24 ppm; elemental analysis: calcd (%) for $C_{10}H_{12}N_2O_5$: C 50.00, H 5.04, N 11.66; found: C 50.03, H 5.05, N 11.70.

2-Nitro-1-phenylethanol:[12c] Yellow oil; IR (neat): $\tilde{\nu}$ = 3430, 1555, 1347 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (m, 5H), 5.46 (m, 1H), 4.63–4.48 (m, 2H), 3.03 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.33, 129.12, 129.05, 126.10, 81.35, 71.09 ppm; elemental analysis: calcd (%) for $C_8H_9NO_3$: C 57.48, H 5.43, N 8.38; found: C 57.50, H 5.44, N 8.45.

2-Nitro-1-(2-nitrophenyl)ethanol:[12d] Yellow oil; IR (neat): $\tilde{\nu}$ = 3585, 1558, 1529, 1348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.0 Hz, 1H), 7.95 (d , J = 8.0 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 6.06 (dd, J = 7.2, 2.4 Hz, 1H), 4.89 (dd, J = 13.6, 2.4 Hz, 1H), 4.55 (dd, J = 10.0, 5.2 Hz, 1H), 3.39 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.26, 134.61, 134.34, 129.84, 128.89, 125.16, 80.31, 66.92 ppm; elemental analysis: calcd (%) for $C_8H_8N_2O_5$: C 45.29, H 3.80, N 13.20; found: C 45.36, H 3.78, N 13.25.

2-Nitro-1-(4-chlorophenyl)ethanol:[12a] Yellow oil; IR (neat): $\tilde{\nu}=3430$, 1560, 1378 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.38–7.32$ (m, 4H), 5.44–5.41 (m, 1H), 4.59–4.46 (m, 2H), 3.28 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=136.79$, 134.79, 129.27, 127.49, 81.15, 70.38 ppm; elemental analysis: calcd (%) for $C_8H_8NO_3Cl$: C 47.66, H 4.00, N 6.95; found: C 47.73, H 4.02, N 7.01.

2-Nitro-1-(4-bromophenyl)ethanol:[12e] Yellow oil; IR (neat): $\tilde{\nu}=3445$, 1558, 1349 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.54–7.52$ (m, 2H), 7.30–7.25 (m, 2H), 5.45–5.42 (m, 1H), 4.59–4.46 (m, 2H), 3.00 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=137.57$, 132.71, 128.15, 123.49, 81.44, 70.85 ppm; elemental analysis: calcd (%) for $C_8H_8NO_3Br$: C 39.05, H 3.28, N 5.69; found: C 39.12, H 3.26, N 5.73.

2-Nitro-1-(4-fluorophenyl)ethanol:[12f] Yellow oil; IR (neat): $\tilde{\nu}=3425$, 1557, 1511, 1342 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.39–7.37$ (m, 2H), 7.10–7.05 (m, 2H), 5.46–5.42 (dd, $J=3.2$, 5.2 Hz, 1H), 4.59–4.45 (m, 2H), 2.90 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=128.02$, 127.94, 116.36, 116.15, 81.33, 70.54 ppm; elemental analysis: calcd (%) for $C_8H_8NO_3F$: C 51.90, H 4.36, N 7.56; found: C 51.95, H 4.37, N 7.62.

2-Nitro-1-(3-bromophenyl)ethanol:[12g] Colorless oil; IR (neat): $\tilde{\nu}=3437$, 1557, 1343 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.58$ (s, 1H), 7.50–7.47 (m, 1H), 7.33–7.25 (m, 2H), 5.45–5.42 (m, 1H), 4.60–4.48 (m, 2H), 3.1 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=140.53$, 132.14, 130.74, 129.25, 124.73, 123.17, 81.14, 70.35 ppm; elemental analysis: calcd (%) for $C_8H_8NO_3Br$: C 39.05, H 3.28, N 5.69; found: C 39.02, H 3.29, N 5.75.

2-Nitro-1-(4-methylphenyl)ethanol:[12b] Colorless oil; IR (neat): $\tilde{\nu}=3422$, 1557, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.29–7.19$ (m, 4H), 5.44–5.41 (dd, $J=9.6$, 2.4 Hz, 1H), 4.63–4.46 (m, 2H), 2.90 (s, 1H), 2.36 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=139.06$, 135.36, 129.84, 126.05, 81.44, 71.06, 21.33 ppm; elemental analysis: calcd (%) for $C_9H_{11}NO_3$: C 59.66, H 6.12, N 7.73; found: C 59.70, H 6.10, N 7.80.

2-Nitro-1-(4-methoxyphenyl)ethanol:[12a] Yellow oil; IR (neat): $\tilde{\nu}=3445$, 1559, 1377 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.31$ (d, $J=8.8$ Hz, 2H), 6.91 (d, $J=8.8$ Hz, 2H), 5.40 (d, $J=9.2$ Hz, 1H), 4.61–4.44 (m, 2H), 3.79 (s, 3H), 2.73 ppm (d, $J=3.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.17$, 130.45, 127.48, 114.55, 81.45, 70.84, 55.55 ppm; elemental analysis: calcd (%) for $C_9H_{11}NO_4$: C 54.82, H 5.62, N 7.10; found: C 54.90, H 5.63, N 7.16.

2-Nitro-1-(3,4-dimethoxyphenyl)ethanol:[1k] Yellow oil; IR (neat): $\tilde{\nu}=$ 3570, 1565, 1348 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.92–6.82$ (m, 3H), 5.39–5.37 (m, 1H), 4.62–4.46 (m, 2H), 3.87 (s, 6H), 3.22 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=149.42$, 130.93, 118.45, 111.36, 108.94, 81.49, 70.97, 56.04 ppm; elemental analysis: calcd (%) for $C_{10}H_{13}NO_5$: C 52.86, H 5.77, N 6.16; found: C 52.90, H 5.76, N 6.25.

2-Nitro-1-naphthylethanol:[12h] Yellow oil; IR (neat): $\tilde{\nu}=3422$, 1555, 1512, 1342 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.88–7.84$ (m, 4H), 7.54–7.51 (m, 2H), 7.47–7.44 (m, 1H), 5.62–5.59 (m, 1H), 4.71–4.56 (m, 2H), 3.11 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=135.66$, 133.64, 133.42, 129.25, 128.30, 128.03, 126.96, 126.92, 125.56, 123.44, 81.44, 71.38 ppm; elemental analysis: calcd (%) for $C_{12}H_{11}NO_3$: C 66.35, H 5.10, N 6.45; found: C 66.43, H 5.12, N 6.46.

2-Nitro-1-(2-pyridyl)ethanol.[12a] Yellow oil; IR (neat): $\tilde{\nu}=3349$, 2917, 1557,1432,1381 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.58–8.57$ (d, $J=$ 4.8 Hz, 1H), 7.79–7.75 (m, 1H), 7.45 (d, $J=6.0$ Hz, 1H), 7.32–7.26 (m, 1H), 5.48–4.80 (m, 1H), 4.80–4.62 (m, 2H), 4.42 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=157.17$, 148.93, 137.75, 123.70, 121.18, 80.79, 70.64 ppm; elemental analysis: calcd (%) for $C_7H_8N_2O_3$: C 50.00, H 4.80, N 16.66; found: C 50.09, H 4.81, N 16.70.

2-Nitro-1-(2-thiophenyl)ethanol:[12i] Yellow oil; IR (neat): $\tilde{\nu}=3416$, 1618, 1557, 1415, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.33–7.31$(m, 1H), 7.06–7.04 (m, 1H), 7.01–6.99 (m, 1H), 5.72–5.70 (m, 1H), 4.73–4.57 (m, 2H), 3.00 ppm (d, $J=4.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 141.59, 127.37, 126.25, 125.19, 81.01, 67.24 ppm; elemental analysis: calcd (%) for $C_6H_7NO_3S$: C 41.61, H 4.07, N 8.09; found: C 41.68, H 4.05, N 8.17.

2,6-Pyridine-di-2-nitro-1-ethanol: Yellow oil; IR (neat): $\tilde{\nu}=3394$, 1554, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.87–7.83$ (t, $J=8.0$ Hz, 1H), 7.52 (d, $J=8.0$ Hz, 2H), 5.44 (m, 2H), 4.84–4.80 (m, 2H), 4.71–4.65 (m, 2H), 3.73 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=156.34$, 139.15, 121.05, 80.24, 70.69 ppm; elemental analysis: calcd (%) for $C_9H_{11}N_3O_6$: C 42.03, H 4.31, N 16.34; found: C 42.08, H 4.30, N 16.45.

1-Nitro-2-butanol:[12j] Colorless oil; IR (KBr): $\tilde{\nu}=3449$, 1556, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=4.46–4.38$ (m, 2H), 4.25 (m, 1H), 2.54 (d, $J=4.8$ Hz, 1H), 1.59 (m, 2H), 1.04 ppm (t, $J=6.8$, 8.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=80.53$, 70.10, 27.04, 9.74 ppm; elemental analysis: calcd (%) for $C_4H_9NO_3$: C 40.33, H 7.62, N 11.76; found: C 40.41, H 7.63, N 11.84.

3-Methyl-1-nitro-2-butanol:[12d] Colorless oil; IR (neat): $\tilde{\nu}=3420$, 1558, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.49–4.38 (m, 2H), 4.11 (m, 1H), 2.48 (s, 1H), 1.83–1.78 (m, 1H), 1.01–0.98 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=79.46$, 73.53, 31.94, 18.66, 17.66 ppm; elemental analysis: calcd (%) for $C_5H_{11}NO_3$: C 45.10, H 8.33, N 10.52; found: C 45.18, H 8.36, N 10.50.

2-Nitro-1-cyclohexylethanol:[12j] Yellow oil; IR (neat): $\tilde{\nu}=3432$, 1550, 1384 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=4.51–4.40$ (m, 2H), 4.10–4.09 (m, 1H), 2.51–2.49 (d, $J=5.2$ Hz, 1H), 1.85–1.03 ppm (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=79.52$, 73.05, 41.63, 29.03, 28.17, 26.29, 26.10, 25.96 ppm; elemental analysis: calcd (%) for $C_8H_{15}NO_3$: C 55.47, H 8.73, N 8.09; found: C 55.52, H 8.79, N 8.17.

2-Hydroxy-3-nitropropanoic acid ethyl ester:[12k] Colorless oil; IR (neat): $\tilde{\nu}=3417$, 1555, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=4.75–4.74$ (m, 2H), 4.60 (m, 1H), 4.37–4.28 (m, 2H), 3.35 (s, 1H), 1.31 ppm (t, $J=$ 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=170.90$, 77.01, 67.66, 62.88, 13.93 ppm; elemental analysis: calcd (%) for $C_5H_9NO_5$: C 36.81, H 5.56, N 8.59; found: C 36.86, H 5.55, N 8.65.

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[6] During purification on silica gel column chromatography using CH_2Cl_2/MeOH (9:1), complex **1** underwent crystallization whose X-ray data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo-K_α radiation in the scan range 1.20°–28.31°. $C_{17}H_{23}CuNO_5$, Mr = 384.90, monoclinic, space group *P*21/*c*, *a* = 17.175(10), *b* = 10.451(6), *c* = 10.449(6) Å; α = 90°, β = 98.769(4)° ã = 90°, *V* = 1853.76(19) Å^3, *Z* = 4, Dcal*c* = 1.379 Mg/m3, *T* = 296(2) K, crystal size 0.48 × 0.24 × 0.10 mm3; 23855 reflections, 4340 unique reflections; (I > 2σ(I)); *R*1 = 0.0810, *wR*2 = 0.3409, (all data), GOF (on F2) = 2.501. The structure is solved by direct method using SHELXL-97 Göttingen, Germany. CCDC 705157 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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