



[Supporting Information]

Known compounds entry 1-8 (C1.1 – C8.1) were prepared in the previous paper and used as it is [S1].

[S1] Otani, N., Furuya, T., Katsuomi, N., Haraguchi, T., Akitsu, T., Synthesis of amino acid derivative Schiff base copper (II) complexes by microwave and wet mechanochemical methods., Journal of the Indian Chemical Society, 2021, 98, 100004, DOI:10.1016/j.jics.2021.100004.

New compounds entry (C1.2 – C12.2) were prepared and characterized as follows (Table S1).

Table S1. Compounds.

C1.1	C2.1	C3.1	C4.1
C5.1	C6.1	C7.1	C8.1
C1.2	C2.2	C3.2	C4.2
C5.2	C6.2	C7.2	C8.2
C5.2	C6.2	C7.2	C8.2

C9.2	C10.2	C11.2	C12.2
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General Procedures

$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, *L*-Alanine, *L*-Leucine, *L*-Serine and *L*-Threonine used in this study were purchased from WakoFujifilm (Japan), and salicylaldehyde, 3-chlorosalicylaldehyde, 4-chlorosalicylaldehyde and 5-chlorosalicylaldehyde were purchased from TCI (Japan).

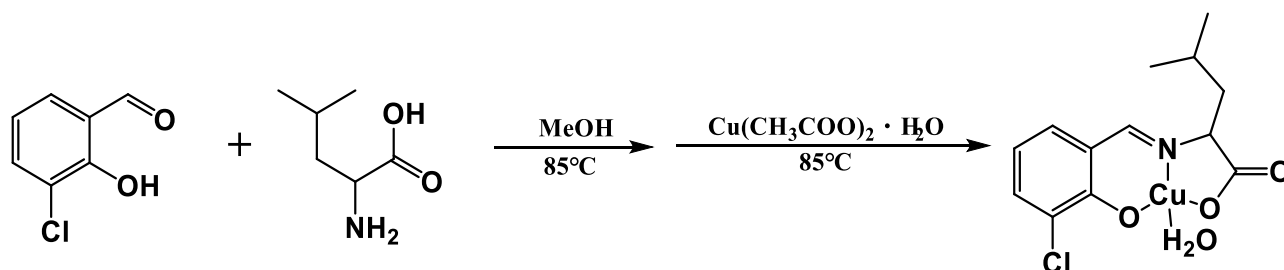
The synthesis of the compounds was carried out at 358 K using an Initiator+ microwave apparatus (Biotage, Tokyo, Japan).

Physical Measurements

Elemental analyses were carried out with a Perkin-Elmer 2400II CHNS/O analyzer Perkin-Elmer, (Waltham, MA, USA) at Tokyo University of Science. Infrared (IR) spectra were recorded on a JASCO FT-IR 4200 spectrophotometer (JASCO, Tokyo, Japan) in the range of 4000–400 cm^{-1} at 298 K. Absorption electronic (UV-Vis) spectra were measured on a JASCO V-570 spectrophotometer in the range of 800–250 nm at 298 K.

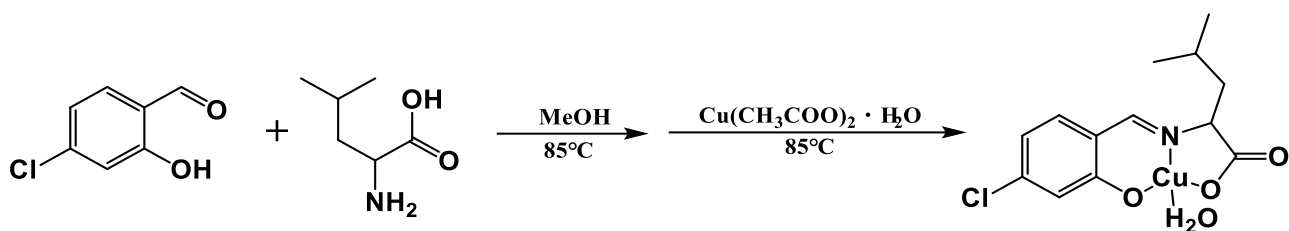
Preparation of C1.2

To a methanol solution (20 mL) of Leucine (0.02623 g, 0.2 mmol) was added 3-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.0399 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.06985 g, 54.73%). The resulting crude compound was filtered and the precipitate was washed with diethylether and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{ClCuNO}_4$: C, 44.71; H, 4.62; N, 4.01%; Found: C, 45.69; H, 3.5; N, 3.84 %.



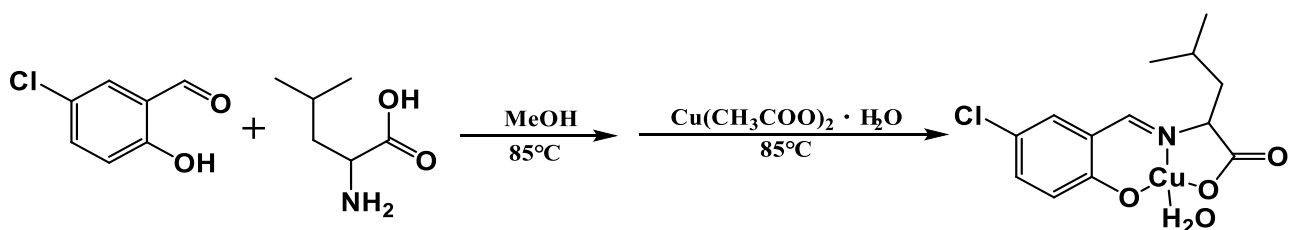
Preparation of C2.2

To a methanol solution (20 mL) of Leucine (0.02623 g, 0.2 mmol) was added 4-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.0399 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.06985 g, 32.85%). The resulting crude compound was filtered and the precipitate was washed with diethylether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{ClCuNO}_4$: C, 44.71; H, 4.62; N, 4.01%; Found: C, 43.39; H, 2.51; N, 1.20 %.



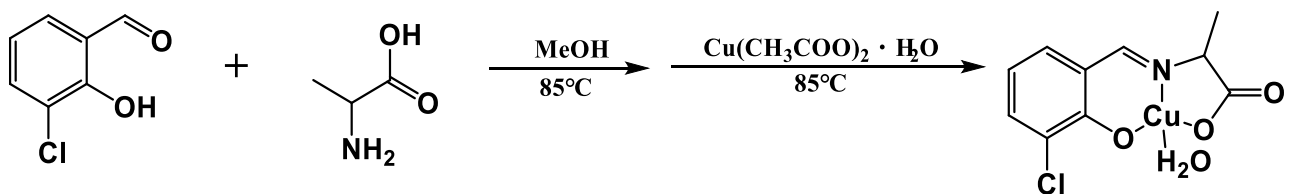
Preparation of C3.2

To a methanol solution (20 mL) of Leucine (0.02623 g, 0.2 mmol) was added 5-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.0399 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.03918 g, 56.09%). The resulting crude compound was filtered and the precipitate was washed with diethylether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{ClCuNO}_4$: C, 44.71; H, 4.62; N, 4.01%; Found: C,45.1; H, 3.71; N, 3.82 %.



Preparation of C4.2

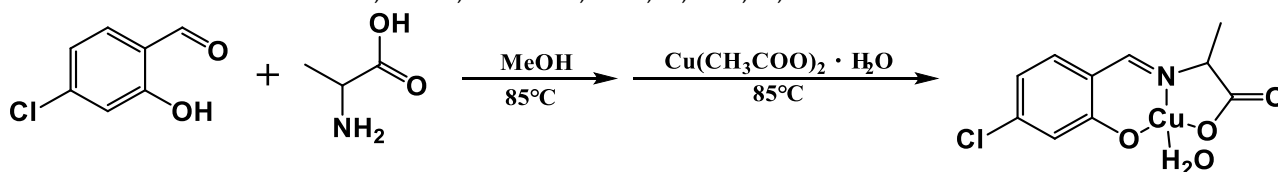
To a methanol solution (20 mL) of Alanine (0.01782 g, 0.2 mmol) was added 3-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.03990 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.40000 g, 65.11%). The resulting crude compound was filtered and the precipitate was washed with diethylether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{ClCuNO}_4$: C,39.10; H, 3.28; N, 4.56%; Found: C,40.78; H, 2.45; N, 4.43 %.



Preparation of C5.2

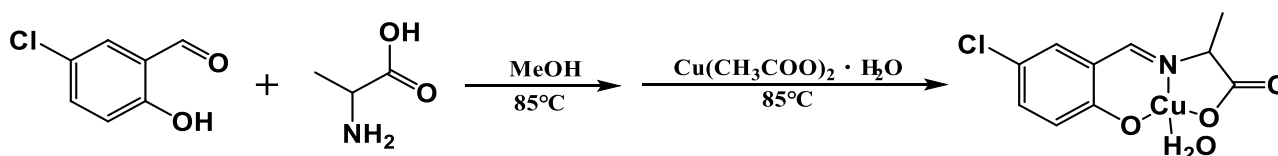
To a methanol solution (20 mL) of Alanine (0.01782 g, 0.2 mmol) was added 4-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.03990 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.04146 g, 67.48%). The resulting crude compound was filtered and the

precipitate was washed with diethylether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{10}H_{10}ClCuNO_4$: C, 39.10; H, 3.28; N, 4.56%; Found: C, 41.39; H, 2.32; N, 4.54 %.



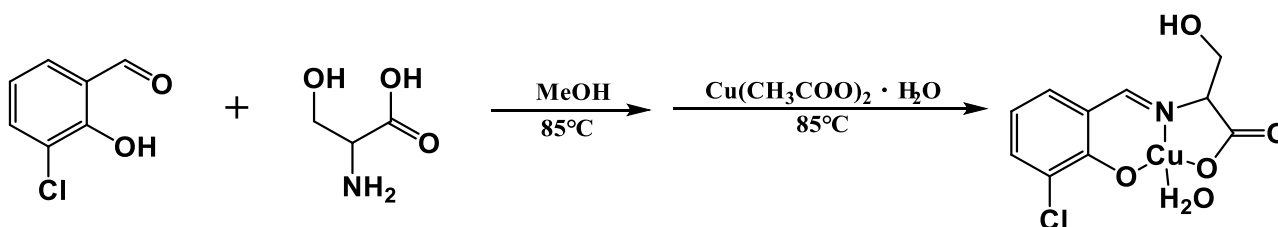
Preparation of C6.2

To a methanol solution (20 mL) of Alanine (0.01782 g, 0.2 mmol) was added 4-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.03990 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.01060 g, 17.25%). The resulting crude compound was filtered and the precipitate was washed with diethylether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{10}H_{10}ClCuNO_4$: C, 39.10; H, 3.28; N, 4.56%; Found: C, 36.6; H, 3.13; N, 4.08 %.



Preparation of C7.2

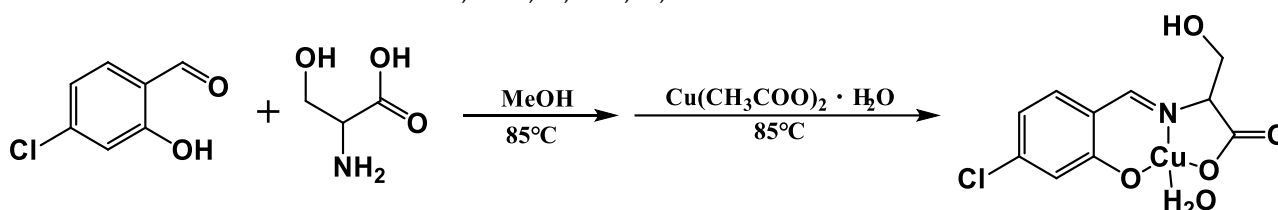
To a methanol solution (20 mL) of Serine (0.02102 g, 0.2 mmol) was added 3-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.0399 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.03737 g, 58.04%). The resulting crude compound was filtered and the precipitate was washed with diethylether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{10}H_{10}ClCuNO_5$: C, 37.16; H, 3.12; N, 4.33%; Found: C, 33.17; H, 3.27; N, 7.17 %.



Preparation of C8.2

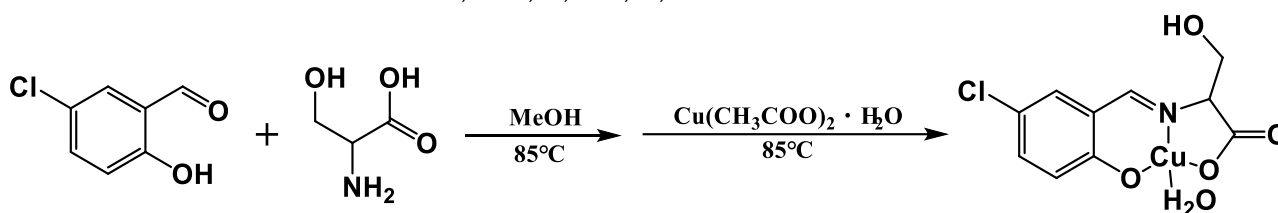
To a methanol solution (20 mL) of Serine (0.02102 g, 0.2 mmol) was added 4-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.0399 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.04404 g, 68.40%). The resulting crude compound was filtered and the precipitate

was washed with diethyl ether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{10}H_{10}ClCuNO_5$: C, 37.16; H, 3.12; N, 4.33%; Found: C, 35.31; H, 2.88; N, 4.95 %.



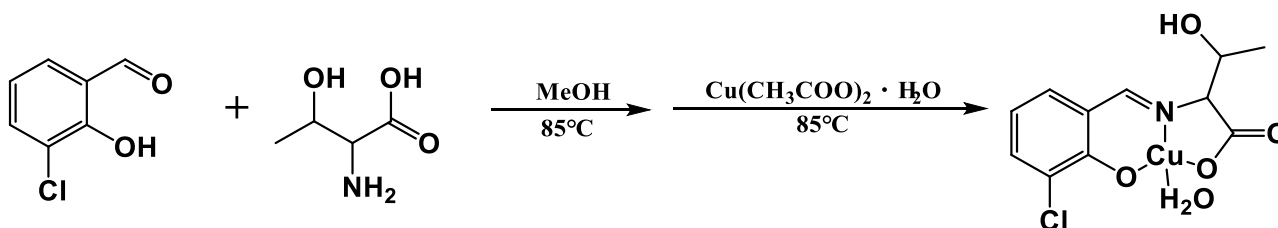
Preparation of C9.2

To a methanol solution (20 mL) of Serine (0.02102 g, 0.2 mmol) was added 5-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.0399 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.04678 g, 72.65%). The resulting crude compound was filtered and the precipitate was washed with diethyl ether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{10}H_{10}ClCuNO_5$: C, 37.16; H, 3.12; N, 4.33%; Found: C, 34.34; H, 2.42; N, 3.17 %.



Preparation of C10.2

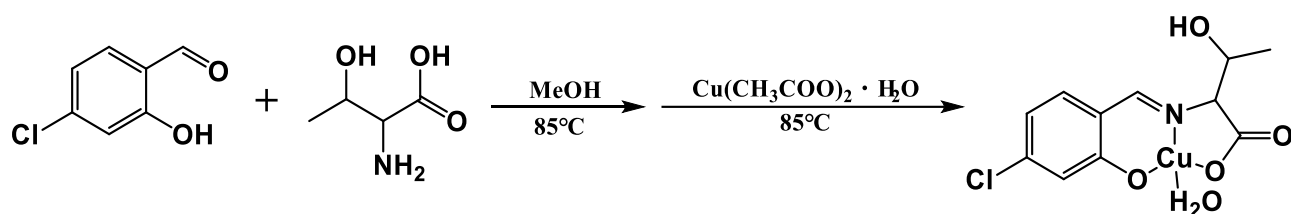
To a methanol solution (20 mL) of Threonine (0.02380 g, 0.2 mmol) was added 4-chlorosalicylaldehyde (0.03131 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.03990 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.03446 g, 51.09%). The resulting crude compound was filtered and the precipitate was washed with diethyl ether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{11}H_{12}ClCuNO_5$: C, 39.18; H, 3.59; N, 4.15%; Found: C, 34.34; H, 3.28; N, 6.37 %.



Preparation of C11.2

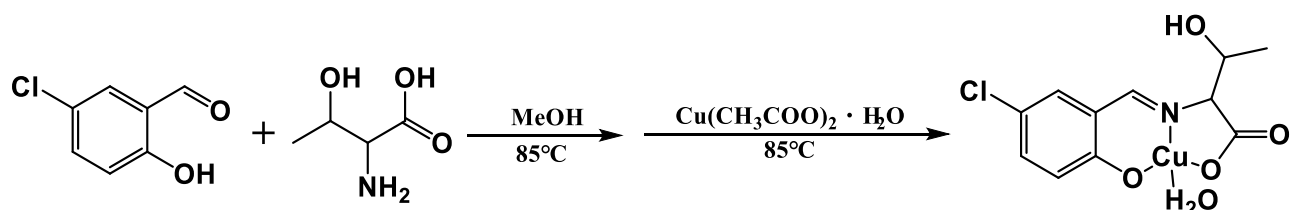
To a methanol solution (20 mL) of Threonine (0.02382 g, 0.2 mmol) was added 4-chlorosalicylaldehyde (0.03135 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.03990 g, 0.2

mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.02844 g, 42.17%). The resulting crude compound was filtered and the precipitate was washed with diethylether, acetone and ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{11}H_{12}ClCuNO_5$: C, 39.18; H, 3.59; N, 4.15%; Found: C, 44.48; H, 1.62; N, 6.71 %.



Preparation of C12.2

To a methanol solution (20 mL) of Threonine (0.02382 g, 0.2 mmol) was added 4-chlorosalicylaldehyde (0.03135 g, 0.2 mmol) and stirred at 358 K for 10 min to obtain a pale yellow color. Then a methanol solution (20 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.03990 g, 0.2 mmol) was added and the mixture was stirred for 10 min at 358 K gave rise to an green compound (yield 0.13912 g, 20.63%). The resulting crude compound was filtered and the precipitate was washed with diethylether, Acetone and Ethanol, dried in a desiccator for several days. This product was filtered Anal. Calcd for $C_{11}H_{12}ClCuNO_5$: C, 39.18; H, 3.59; N, 4.15%; Found: C, 44.62; H, 1.53; N, 14.03 %.



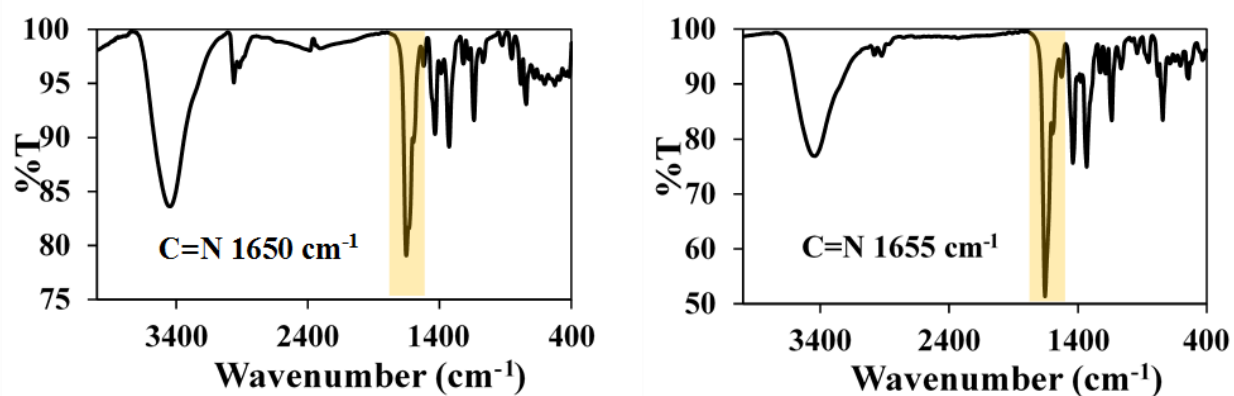


Figure S1. IR spectra of C1.2 (left) and C4.2 (right).

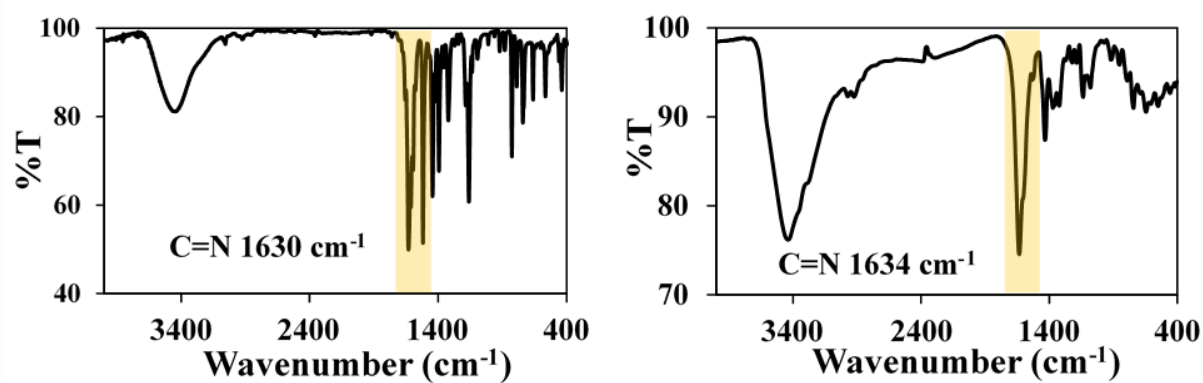


Figure S2. IR spectra of C7.2 (left) and C10.2 (right).

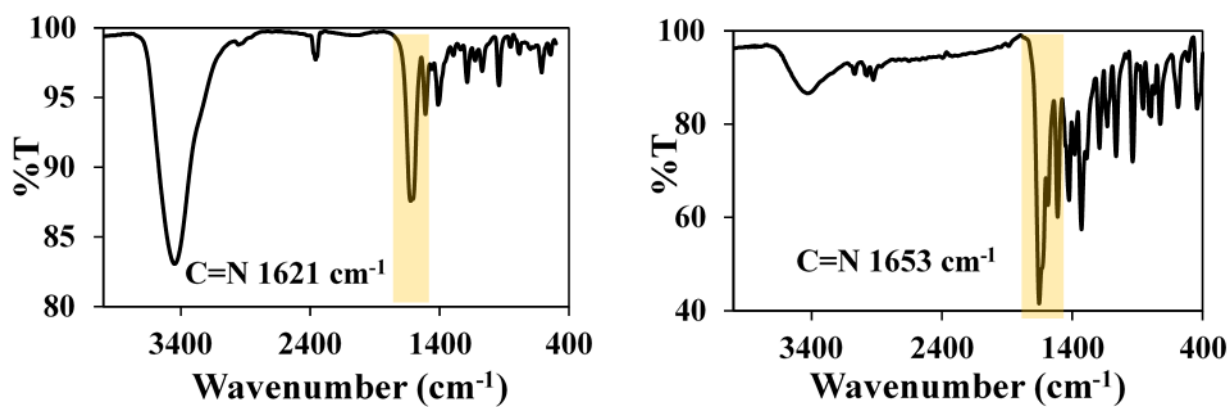


Figure S3. IR spectra of C2.2 (left) and C5.2 (right).

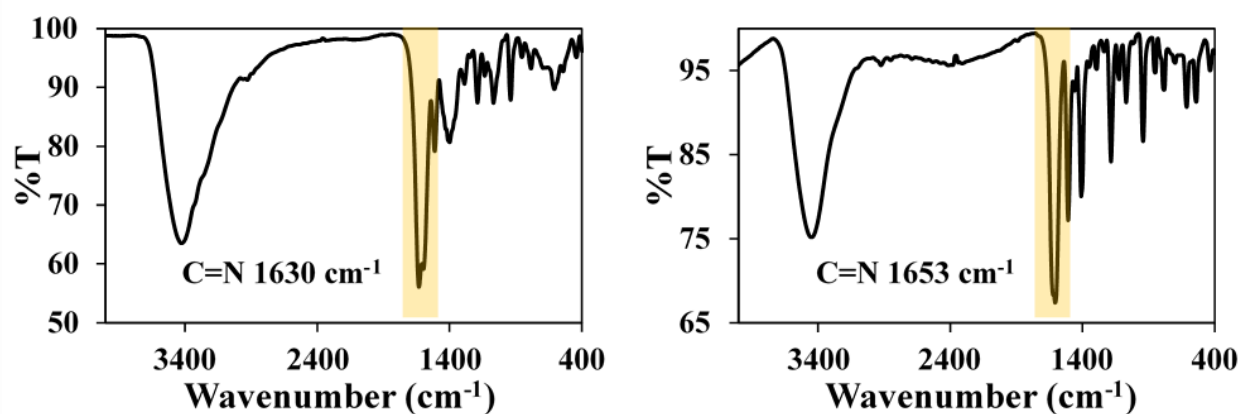


Figure S4. IR spectra of C8.2 (left) and C11.2 (right).

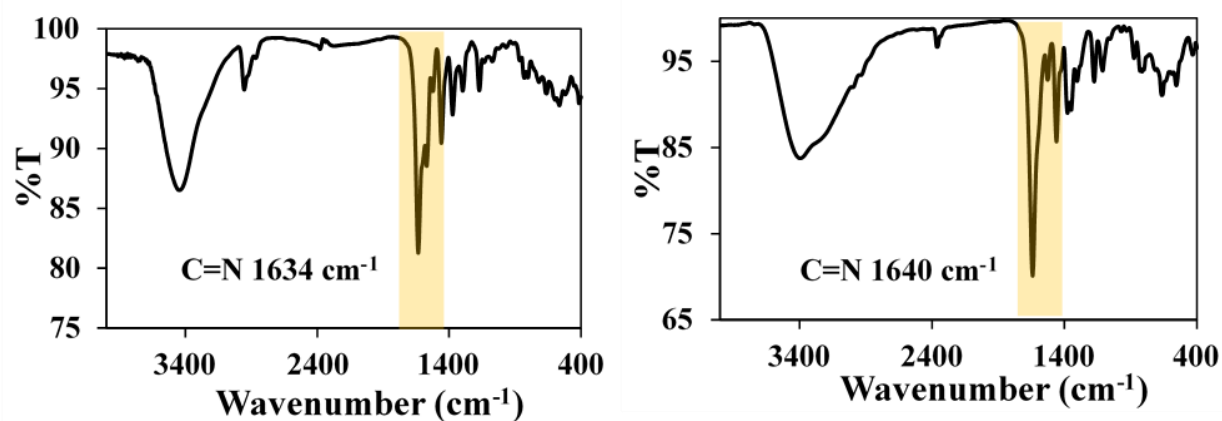


Figure S5. IR spectra of C3.2 (left) and C6.2 (right).

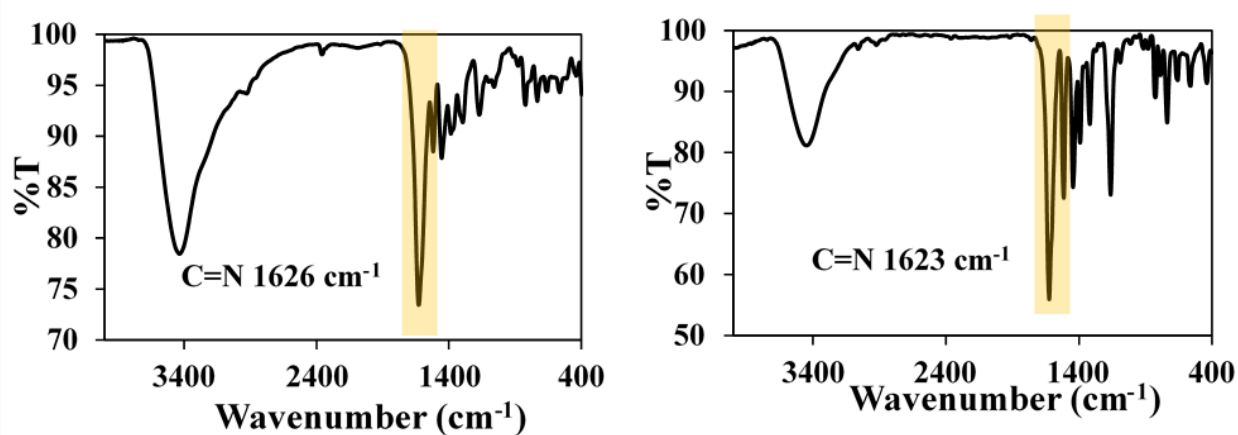


Figure S6. IR spectra of C9.2 (left) and C12.2 (right).

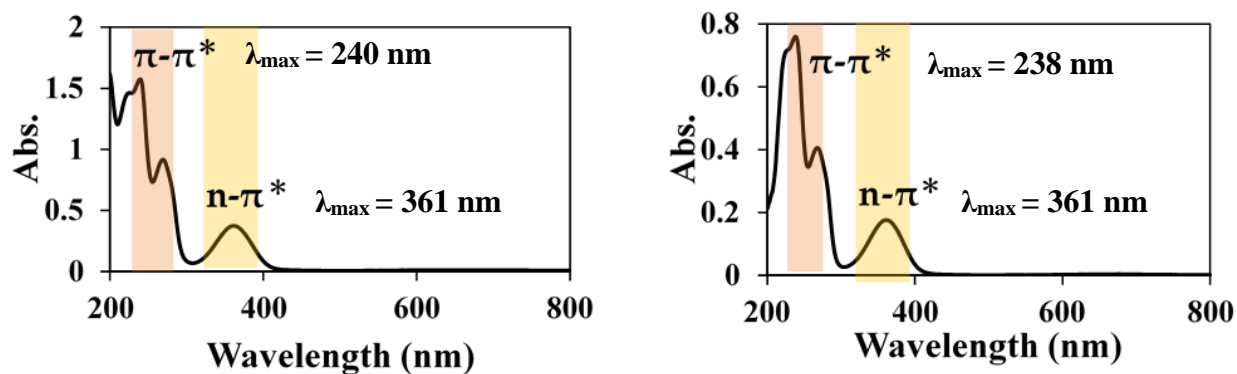


Figure S7. UV-vis spectra of C1.2 (left) and C4.2 (right).

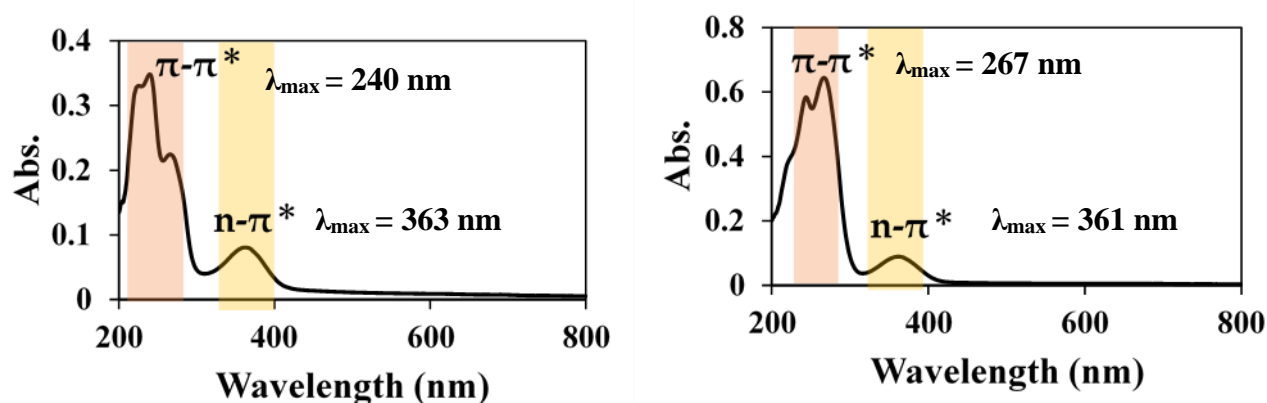


Figure S8. UV-vis spectra of C7.2 (left) and C10.2 (right).

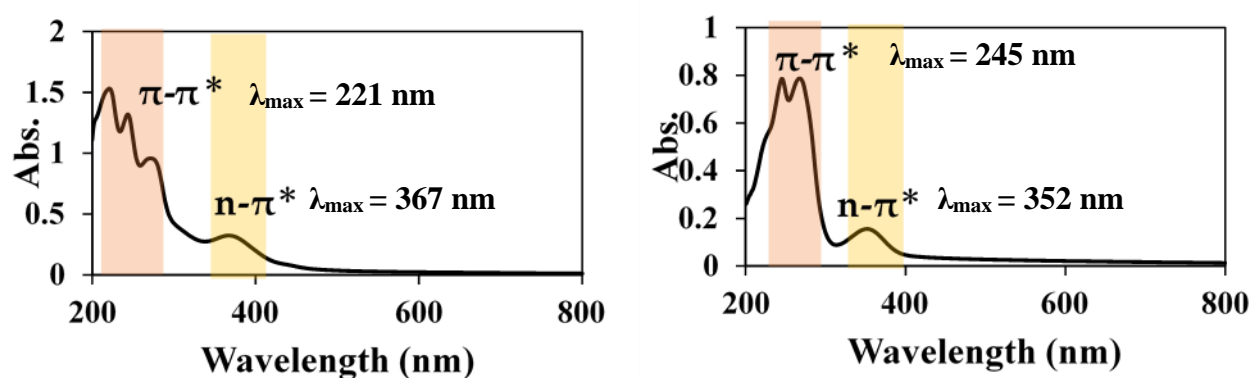


Figure S9. UV-vis spectra of C2.2 (left) and C5.2 (right).

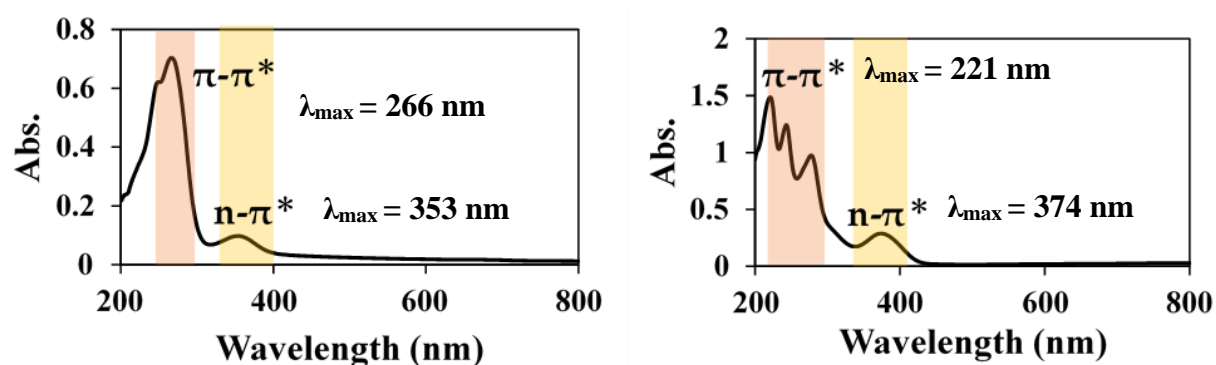


Figure S10. UV-vis spectra of C8.2 (left) and C11.2 (right).

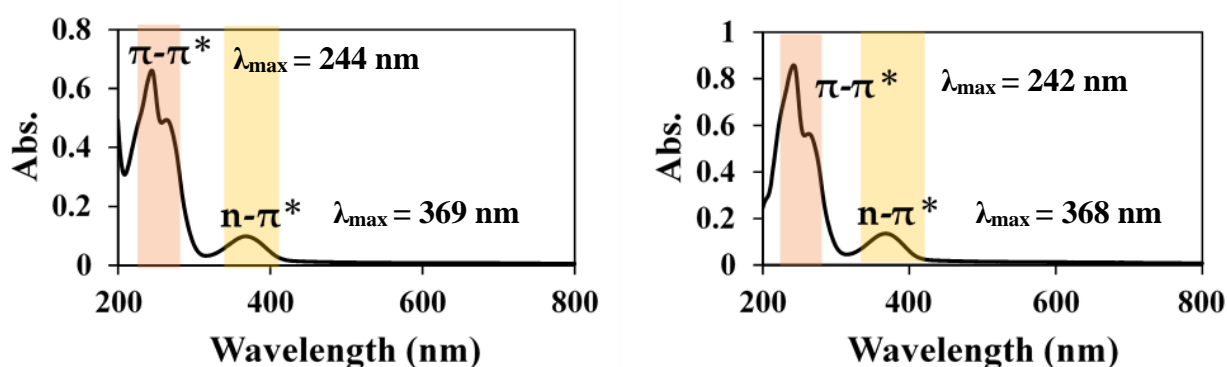


Figure S11. UV-vis spectra of C3.2 (left) and C6.2 (right).

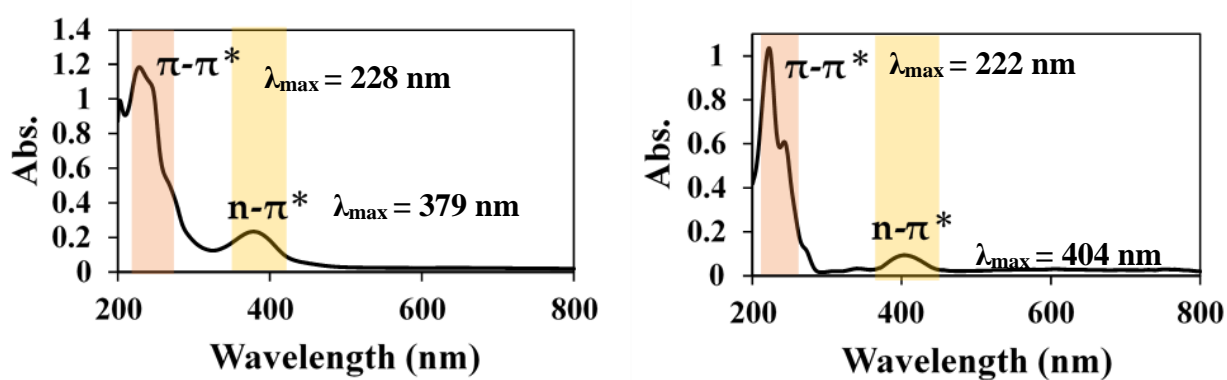


Figure S12. UV-vis spectra of C9.2 (left) and C12.2 (right).

X-ray Crystallography

Crystal structures of some of known compounds (*e.g.* **C1.1** [S1] and **C10.2** [S2]) have been already reported elsewhere.

[S2] Katsuumi, N., Onami, Y., Pradha, S., Haraguchi, T., Akitsu, T., Crystal structure and Hirshfeld surface analysis of (aqua- κ O)(methanol- κ O)[N-(2-oxidobenzylidene)-threoninato- κ 3O,N,O']copper(II), *Acta Crystallographica*, 2020, E76, 98, 1539-1542, <https://doi.org/10.1107/S2056989020011706>.

Because of the lack of suitable single crystals, powder X-ray diffraction patterns were collected at 298 K on Rigaku Smart lab at the University of Tokyo. Structural analysis with Rietveld method was carried out using PDXL2 ver.2.2.1.0 (Rigaku Corporation). Non H-atoms were refined using isotropic displacement parameters, and the R values were too high to report reliable structures (Fig. S13) due to low data quality.

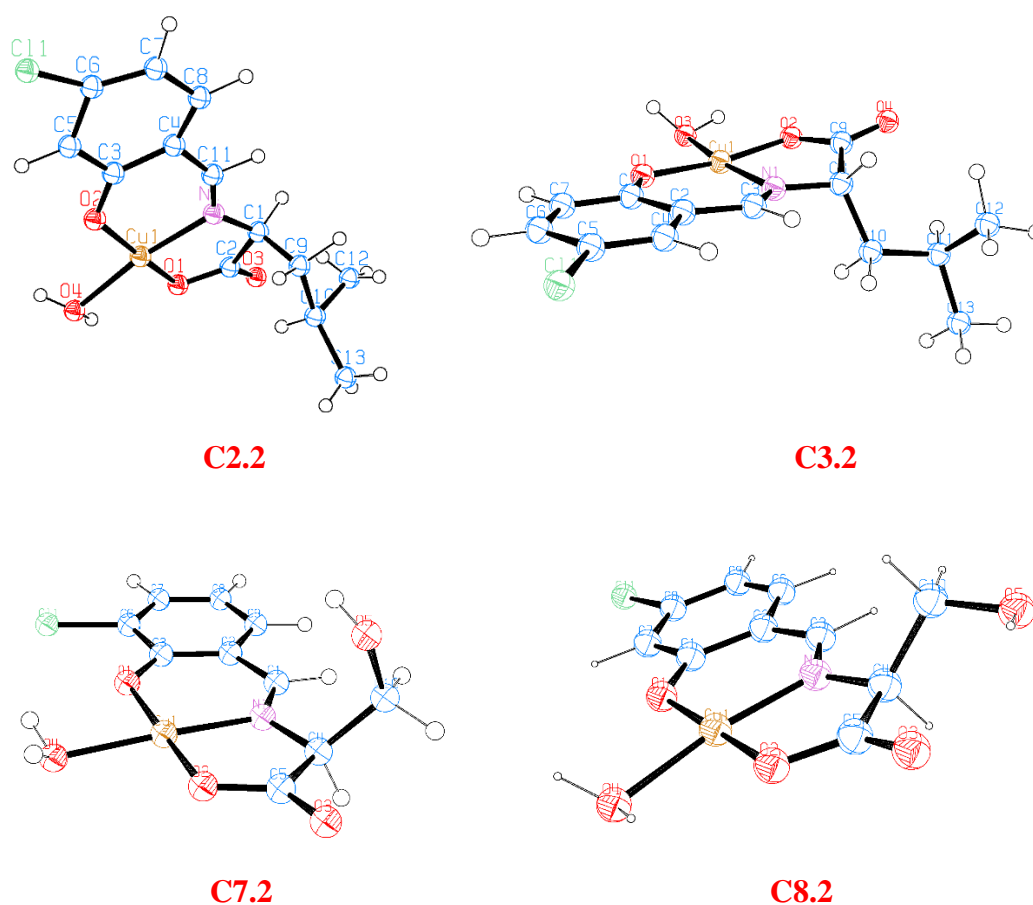


Figure S13. Tentative crystal structures of **C2.2**, **C3.2**, **C7.2**, and **C8.2** from powder diffraction data.