Supporting Information

1. Detailed derivation process of the model

The dissociation constant of D- and L-PHG:

$$K_\mathrm{a} = \frac{[\mathrm{D}^-]_\mathrm{w}[\mathrm{H}^+]}{[\mathrm{DH}]_\mathrm{w}} = \frac{[\mathrm{L}^-]_\mathrm{w}[\mathrm{H}^+]}{[\mathrm{LH}]_\mathrm{w}} \tag{1}$$

The complexation equilibrium constants of $CuPF_6$-(s)-BINAP (BINAP-Cu) with PHG enantiomers at the interface can be written as follows:

$$K_\mathrm{D} = \frac{[\mathrm{CuBD}]_\mathrm{org}[\mathrm{PF}_6^-]_\mathrm{w}}{[\mathrm{CuB}]_\mathrm{org}[\mathrm{D}^-]_\mathrm{w}} \tag{2}$$

$$K_\mathrm{L} = \frac{[\mathrm{CuBL}]_\mathrm{org}[\mathrm{PF}_6^-]_\mathrm{w}}{[\mathrm{CuB}]_\mathrm{org}[\mathrm{L}^-]_\mathrm{w}} \tag{3}$$

Due to $V_{aq} = V_\mathrm{org}$, mass balance for D- and L-PHG:

$$C_\mathrm{D}^\mathrm{tot} = [\mathrm{DH}]_\mathrm{w} + [\mathrm{D}^-]_\mathrm{w} + [\mathrm{CuBD}]_\mathrm{org} \tag{4}$$

$$C_\mathrm{L}^\mathrm{tot} = [\mathrm{LH}]_\mathrm{w} + [\mathrm{L}^-]_\mathrm{w} + [\mathrm{CuBL}]_\mathrm{org} \tag{5}$$

where, $C_\mathrm{D}^\mathrm{tot}$ and $C_\mathrm{L}^\mathrm{tot}$ are the initial concentrations of D- and L-PHG in the aqueous phase, respectively; $[\mathrm{DH}]_\mathrm{w}$ and $[\mathrm{LH}]_\mathrm{w}$ are the concentration of molecular D- and L-PHG in the aqueous phase, respectively; $[\mathrm{D}^-]_\mathrm{w}$ and $[\mathrm{L}^-]_\mathrm{w}$ are the anion D- and L-PHG in the aqueous phase, respectively; $[\mathrm{CuBD}]_\mathrm{org}$ and $[\mathrm{CuBL}]_\mathrm{org}$ are the concentrations of the complexes of BINAP-Cu with D- and L-PHG in the organic phase, respectively; $[\mathrm{CuB}]_\mathrm{org}$ are the concentrations of BINAP-Cu in the organic phase at equilibrium.

With eqs 1 - 3 substituted in eqs 4 and 5:

$$C_\mathrm{D}^\mathrm{tot} = [\mathrm{DH}]_\mathrm{w} + [\mathrm{D}^-]_\mathrm{w} + [\mathrm{CuBD}]_\mathrm{org} = \frac{[\mathrm{D}^-]_\mathrm{w}[\mathrm{H}^+]}{K_\mathrm{a}} + [\mathrm{D}^-]_\mathrm{w} + \frac{[\mathrm{CuB}]_\mathrm{org}[\mathrm{D}^-]_\mathrm{w} K_\mathrm{D}}{[\mathrm{PF}_6^-]_\mathrm{w}} \tag{6}$$

$$C_{\mathrm{L}}^{\mathrm{tot}} = [\mathrm{LH}]_{\mathrm{w}} + [\mathrm{L}^-]_{\mathrm{w}} + [\mathrm{CuBL}]_{\mathrm{org}} = \frac{[\mathrm{L}^-]_{\mathrm{w}}[\mathrm{H}^+]}{K_{\mathrm{a}}} + [\mathrm{L}^-]_{\mathrm{w}} + \frac{[\mathrm{CuB}]_{\mathrm{org}}[\mathrm{L}^-]_{\mathrm{w}} K_{\mathrm{L}}}{[\mathrm{PF}_6^-]_{\mathrm{w}}} \tag{7}$$

where $C_{\mathrm{CuB}}^{\mathrm{tot}}$ is the initial concentration of BINAP-Cu in the organic phase; $[PF_6^-]_w$ is the concentration of PF_6^- in aqueous phase.

$[D^-]_w$ and $[L^-]_w$ can be calculated from eqs 6 and 7 as following:

$$[\mathrm{D}^-]_{\mathrm{w}} = \frac{C_{\mathrm{D}}^{\mathrm{tot}}}{\frac{[\mathrm{H}^+]}{K_{\mathrm{a}}} + 1 + \frac{[\mathrm{CuB}]_{\mathrm{org}} K_{\mathrm{D}}}{[\mathrm{PF}_6^-]_{\mathrm{w}}}} \tag{8}$$

$$[\mathrm{L}^-]_{\mathrm{w}} = \frac{C_{\mathrm{L}}^{\mathrm{tot}}}{\frac{[\mathrm{H}^+]}{K_{\mathrm{a}}} + 1 + \frac{[\mathrm{CuB}]_{\mathrm{org}} K_{\mathrm{L}}}{[\mathrm{PF}_6^-]_{\mathrm{w}}}} \tag{9}$$

Mass balance for C_{CuB}:

$$C_{\mathrm{CuB}}^{\mathrm{tot}} = [\mathrm{CuB}]_{\mathrm{org}} + [\mathrm{CuBD}]_{\mathrm{org}} + [\mathrm{CuBL}]_{\mathrm{org}} \tag{10}$$

With eqs 2 and 3 substituted in eq 8:

$$C_{\mathrm{CuB}}^{\mathrm{tot}} = [\mathrm{CuB}]_{\mathrm{org}} + \frac{[\mathrm{CuB}]_{\mathrm{org}}[\mathrm{D}^-]_{\mathrm{w}} K_{\mathrm{D}}}{[\mathrm{PF}_6^-]_{\mathrm{w}}} + \frac{[\mathrm{CuB}]_{\mathrm{org}}[\mathrm{L}^-]_{\mathrm{w}} K_{\mathrm{L}}}{[\mathrm{PF}_6^-]_{\mathrm{w}}} \tag{11}$$

Defining $A = 1 + \frac{[\mathrm{H}^+]}{K_{\mathrm{a}}}$, and substituting eqs 8 and 9 in eq 11:

$$\begin{aligned} C_{\mathrm{CuB}}^{\mathrm{tot}} &= [\mathrm{CuB}]_{\mathrm{org}} + \frac{K_{\mathrm{D}} C_{\mathrm{D}}^{\mathrm{tot}} [\mathrm{CuB}]_{\mathrm{org}}}{\left(A + \frac{[\mathrm{CuB}]_{\mathrm{org}} K_{\mathrm{D}}}{[\mathrm{PF}_6^-]_{\mathrm{w}}}\right)[\mathrm{PF}_6^-]_{\mathrm{w}}} + \frac{K_{\mathrm{L}} C_{\mathrm{L}}^{\mathrm{tot}} [\mathrm{CuB}]_{\mathrm{org}}}{\left(A + \frac{[\mathrm{CuB}]_{\mathrm{org}} K_{\mathrm{L}}}{[\mathrm{PF}_6^-]_{\mathrm{w}}}\right)[\mathrm{PF}_6^-]_{\mathrm{w}}} \\ &= [\mathrm{CuB}]_{\mathrm{org}} + \frac{K_{\mathrm{D}} \mathrm{C}_{\mathrm{D}}^{\mathrm{tot}} [\mathrm{CuB}]_{\mathrm{org}}}{A[\mathrm{PF}_6^-]_{\mathrm{w}} + [\mathrm{CuB}]_{\mathrm{org}} K_{\mathrm{D}}} + \frac{K_{\mathrm{L}} \mathrm{C}_{\mathrm{L}}^{\mathrm{tot}} [\mathrm{CuB}]_{\mathrm{org}}}{A[\mathrm{PF}_6^-]_{\mathrm{w}} + [\mathrm{CuB}]_{\mathrm{org}} K_{\mathrm{L}}} \end{aligned} \tag{12}$$

With further treatment of eq 10 and changing the form of eq 10 into arrangement in descending powers of [CuB]:

$$\begin{aligned} &(K_{\mathrm{D}}K_{\mathrm{L}} - K_{\mathrm{D}}A - K_{\mathrm{L}}A + A^2)[\mathrm{CuB}]_{\mathrm{org}}^3 + (2K_{\mathrm{D}}AC_{\mathrm{CuB}}^{\mathrm{tot}} + 2K_{\mathrm{L}}AC_{\mathrm{CuB}}^{\mathrm{tot}} - 3A^2C_{\mathrm{CuB}}^{\mathrm{tot}} + K_{\mathrm{D}}K_{\mathrm{L}}C_{\mathrm{D}}^{\mathrm{tot}} - K_{\mathrm{D}}C_{\mathrm{D}}^{\mathrm{tot}}A + \\ &K_{\mathrm{D}}K_{\mathrm{L}}C_{\mathrm{L}}^{\mathrm{tot}} - K_{\mathrm{L}}C_{\mathrm{L}}^{\mathrm{tot}}A - K_{\mathrm{D}}K_{\mathrm{L}}C_{\mathrm{CuB}}^{\mathrm{tot}})[\mathrm{CuB}]_{\mathrm{org}}^2 + (K_{\mathrm{D}}C_{\mathrm{D}}^{\mathrm{tot}}AC_{\mathrm{CuB}}^{\mathrm{tot}} + K_{\mathrm{L}}C_{\mathrm{L}}^{\mathrm{tot}}AC_{\mathrm{CuB}}^{\mathrm{tot}} - C_{\mathrm{CuB}}^2K_{\mathrm{D}}A - C_{\mathrm{CuB}}^{\mathrm{tot}\ 2}K_{\mathrm{L}}A \\ &+3A^2C_{\mathrm{CuB}}^{\mathrm{tot}\ 2})[\mathrm{CuB}]_{\mathrm{org}} - A^2C_{\mathrm{CuB}}^{\mathrm{tot}\ 3} = 0 \end{aligned} \tag{13}$$

$[CuB]_{org}$ can be calculated from the eq 13, and distribution ratios can be written as follows:

$$k_{\mathrm{D}}=\frac{[\mathrm{CuBD}]_{\mathrm{org}}}{[\mathrm{DH}]_{\mathrm{w}}+[\mathrm{D}^{-}]_{\mathrm{w}}}=\frac{\dfrac{[\mathrm{CuB}]_{\mathrm{org}}[\mathrm{D}^{-}]_{\mathrm{w}}K_{\mathrm{D}}}{[\mathrm{PF}_6^{-}]_{\mathrm{w}}}}{\dfrac{[\mathrm{D}]_{\mathrm{w}}[\mathrm{H}^{+}]}{K_{\mathrm{a}}}+[\mathrm{D}^{-}]_{\mathrm{w}}}=\frac{K_{\mathrm{D}}[\mathrm{CuB}]_{\mathrm{org}}}{[\mathrm{PF}_6^{-}]_{\mathrm{w}}\{1+\dfrac{[\mathrm{H}^{+}]}{K_{\mathrm{a}}}\}}=\frac{K_{\mathrm{D}}[\mathrm{CuB}]_{\mathrm{org}}}{A[\mathrm{PF}_6^{-}]_{\mathrm{w}}} \tag{14}$$

$$k_{\mathrm{L}}=\frac{[\mathrm{CuBL}]_{\mathrm{org}}}{[\mathrm{LH}]_{\mathrm{w}}+[\mathrm{L}^{-}]_{\mathrm{w}}}=\frac{\dfrac{[\mathrm{CuB}]_{\mathrm{org}}[\mathrm{L}^{-}]_{\mathrm{w}}K_{\mathrm{L}}}{[\mathrm{PF}_6^{-}]_{\mathrm{w}}}}{\dfrac{[\mathrm{L}^{-}]_{\mathrm{w}}[\mathrm{H}^{+}]}{K_{\mathrm{a}}}+[\mathrm{L}^{-}]_{\mathrm{w}}}=\frac{K_{\mathrm{L}}[\mathrm{CuB}]_{\mathrm{org}}}{[\mathrm{PF}_6^{-}]_{\mathrm{w}}\{1+\dfrac{[\mathrm{H}^{+}]}{K_{\mathrm{a}}}\}}=\frac{K_{\mathrm{L}}[\mathrm{CuB}]_{\mathrm{org}}}{A[\mathrm{PF}_6^{-}]_{\mathrm{w}}} \tag{15}$$

$$[\mathrm{PF}_6^{-}]_{\mathrm{w}}=C_{\mathrm{CuB}}^{\mathrm{tot}}-[\mathrm{CuB}]_{\mathrm{org}} \tag{16}$$

By solving eq 11, $[\mathrm{CuB}]_{\mathrm{org}}$ can be obtained and $[\mathrm{PF}_6^{-}]_{\mathrm{w}}$ is calculated by eq 16. With the calculated $[\mathrm{CuB}]_{\mathrm{org}}$ and $[\mathrm{PF}_6^{-}]_{\mathrm{w}}$ substituted in eq 14 and 15, distribution ratios k_{D} and k_{L} are calculated as a function of the experimental conditions (such as $C_{\mathrm{D}}^{\mathrm{tot}}$, $C_{\mathrm{L}}^{\mathrm{tot}}$, $C_{\mathrm{CuB}}^{\mathrm{tot}}$, pH) and physicochemical constant (such as K_{a}, K_{D}, K_{L}).

Operational enantioselectivity is given by

$$\alpha_{op}=\frac{k_{\mathrm{L}}}{k_{\mathrm{D}}} \tag{17}$$

Intrinsic enantioselectivity is given by

$$\alpha_{int}=\frac{K_{\mathrm{L}}}{K_{\mathrm{D}}} \tag{18}$$

Since $k_{\mathrm{D}}=\dfrac{C_{\mathrm{D,\,org}}^{\mathrm{tot}}}{C_{\mathrm{D,\,aq}}^{\mathrm{tot}}}$, $C_{\mathrm{D,\,org}}^{\mathrm{tot}}+C_{\mathrm{D,\,aq}}^{\mathrm{tot}}=C_{\mathrm{D}}^{\mathrm{tot}}$, $C_{\mathrm{D,\,org}}^{\mathrm{tot}}$ can be expressed as:

$$C_{\mathrm{D,\,org}}^{\mathrm{tot}}=\frac{C_{\mathrm{D}}^{\mathrm{tot}}}{1+1/k_{\mathrm{D}}} \tag{19}$$

Similarly, $C_{\mathrm{L,\,org}}^{\mathrm{tot}}$ can be expressed as:

$$C_{\mathrm{L,\,org}}^{\mathrm{tot}}=\frac{C_{\mathrm{L}}^{\mathrm{tot}}}{1+1/k_{\mathrm{L}}} \tag{20}$$

Therefore, enantiomeric excess in the organic phase is calculated by the following equation:

$$ee_{\text{org}} = \frac{C_{\text{L, org}}^{\text{tot}} - C_{\text{D, org}}^{\text{tot}}}{C_{\text{L, org}}^{\text{tot}} + C_{\text{D, org}}^{\text{tot}}} = \frac{\dfrac{C_{\text{L}}^{\text{tot}}}{1+1/k_{\text{L}}} - \dfrac{C_{\text{D}}^{\text{tot}}}{1+1/k_{\text{D}}}}{\dfrac{C_{\text{L}}^{\text{tot}}}{1+1/k_{\text{L}}} + \dfrac{C_{\text{D}}^{\text{tot}}}{1+1/k_{\text{D}}}} \tag{21}$$

The fraction of L-PHG extracted into the organic phase (f_{L}) is given by

$$f_{\text{L}} = \frac{C_{\text{L, org}}^{\text{tot}}}{C_{\text{L}}^{\text{tot}}} = \frac{\dfrac{C_{\text{L}}^{\text{tot}}}{1+1/k_{\text{L}}}}{C_{\text{L}}^{\text{tot}}} = \frac{k_{\text{L}}}{k_{\text{L}}+1} \tag{22}$$

The extraction performance factor (pf) is defined as

$$pf_{\text{L}} = f_{\text{L}} ee_{\text{org}} \tag{23}$$

Detailed derivation process for Regression of the Complexation Equilibrium Constants

The interfacial reaction equations for D- and L-PHG are

$$\text{[(S)-BINAP(CH}_3\text{CN)}_2\text{Cu]PF}_6 + \text{D-PHG}^- \xleftrightarrow{K_D} \text{[(S)-BINAP(CH}_3\text{CN)}_2\text{Cu][D-PHG}^-] + \text{PF}_6^-$$

$$\text{[(S)-BINAP(CH}_3\text{CN)}_2\text{Cu]PF}_6 + \text{L-PHG}^- \xleftrightarrow{K_D} \text{[(S)-BINAP(CH}_3\text{CN)}_2\text{Cu][L-PHG}^-] + \text{PF}_6^-$$

The complexation equilibrium constants are written as defined above (eqs 2 and 3):

$$K_{\text{D}} = \frac{[\text{CuBD}]_{\text{org}}[\text{PF}_6^-]_{\text{w}}}{[\text{CuB}]_{\text{org}}[\text{D}^-]_{\text{w}}}$$

$$K_{\text{L}} = \frac{[\text{CuBL}]_{\text{org}}[\text{PF}_6^-]_{\text{w}}}{[\text{CuB}]_{\text{org}}[\text{L}^-]_{\text{w}}}$$

$[\text{CuBD}]_{\text{org}}$, $[\text{PF}_6^-]_{\text{w}}$, $[\text{CuB}]_{\text{org}}$ and $[\text{D}^-]_{\text{w}}$ can be expressed in terms of k_{D} and k_{L} by the following equations:

$$[\text{CuBD}]_{\text{org}} = C_{\text{D, org}}^{\text{tot}} = \frac{C_{\text{D}}^{\text{tot}}}{1+1/k_{\text{D}}} \tag{24}$$

$$[\mathrm{CuB}]_{\mathrm{org}} = C_{\mathrm{CuB}}^{\mathrm{tot}} - [\mathrm{CuBD}]_{\mathrm{org}} - [\mathrm{CuBL}]_{\mathrm{org}}$$

$$= C_{\mathrm{CuB}}^{\mathrm{tot}} - C_{\mathrm{D,\,org}}^{\mathrm{tot}} - C_{\mathrm{L,\,org}}^{\mathrm{tot}}$$

$$= C_{\mathrm{CuB}}^{\mathrm{tot}} - \frac{C_{\mathrm{D}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{D}}}} - \frac{C_{\mathrm{L}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{L}}}} \tag{25}$$

$$[\mathrm{PF_6^-}]_{\mathrm{w}} = C_{\mathrm{D,\,org}}^{\mathrm{tot}} + C_{\mathrm{L,\,org}}^{\mathrm{tot}}$$

$$= \frac{C_{\mathrm{L}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{L}}}} + \frac{C_{\mathrm{D}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{D}}}} \tag{26}$$

$$[\mathrm{D^-}]_{\mathrm{w}} = \frac{[\mathrm{D^-}]_{\mathrm{w}}}{[\mathrm{D^-}]_{\mathrm{w}} + [\mathrm{DH}]_{\mathrm{w}}} C_{\mathrm{D,\,aq}}^{\mathrm{tot}}$$

$$= \frac{[\mathrm{D^-}]_{\mathrm{w}}}{[\mathrm{D^-}]_{\mathrm{w}} + \frac{[\mathrm{D^-}]_{\mathrm{w}}[\mathrm{H^+}]}{K_{\mathrm{a}}}} C_{\mathrm{D,\,aq}}^{\mathrm{tot}}$$

$$= \frac{1}{1+\frac{[\mathrm{H^+}]}{K_{\mathrm{a}}}} C_{\mathrm{D,\,aq}}^{\mathrm{tot}}$$

$$= \frac{C_{\mathrm{D}}^{\mathrm{tot}}}{A(1+k_{\mathrm{D}})} \tag{27}$$

With eqs 24-27 substituted in eq 2:

$$K_{\mathrm{D}} = \frac{\frac{C_{\mathrm{D}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{D}}}} \left(\frac{C_{\mathrm{L}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{L}}}} + \frac{C_{\mathrm{D}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{D}}}} \right)}{\left(C_{\mathrm{CuB}}^{\mathrm{tot}} - \frac{C_{\mathrm{D}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{D}}}} - \frac{C_{\mathrm{L}}^{\mathrm{tot}}}{1+ {}^{1}\!/_{k_{\mathrm{L}}}} \right) \left(\frac{C_{\mathrm{D}}^{\mathrm{tot}}}{A(1+k_{\mathrm{D}})} \right)} \tag{28}$$

With further treatment of eq 28, the following equation is obtained:

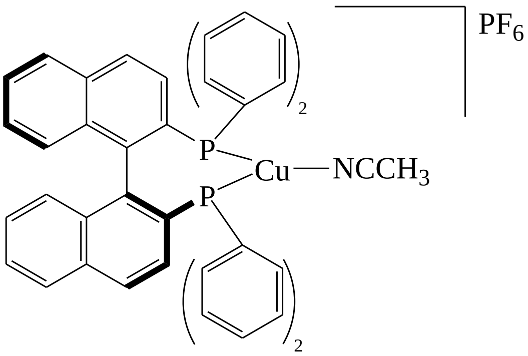
$$Ak_{\mathrm{D}}^2 C_{\mathrm{D}}^{\mathrm{tot}}(k_{\mathrm{L}}+1) + Ak_{\mathrm{D}}k_{\mathrm{L}}C_{\mathrm{L}}^{\mathrm{tot}}(k_{\mathrm{D}}+1) = K_{\mathrm{D}}[C_{\mathrm{CuB}}^{\mathrm{tot}}(k_{\mathrm{D}}+1)(k_{\mathrm{L}}+1) - k_{\mathrm{D}}C_{\mathrm{D}}^{\mathrm{tot}}(k_{\mathrm{L}}+1) - k_{\mathrm{L}}C_{\mathrm{L}}^{\mathrm{tot}}(k_{\mathrm{D}}+1)] \tag{29}$$

Similarly, the following equation can be obtained for K_{L}:

$$Ak_{\mathrm{L}}^2 C_{\mathrm{L}}^{\mathrm{tot}}(k_{\mathrm{D}}+1) + Ak_{\mathrm{D}}k_{\mathrm{L}}C_{\mathrm{D}}^{\mathrm{tot}}(k_{\mathrm{L}}+1) = K_{\mathrm{L}}[C_{\mathrm{CuB}}^{\mathrm{tot}}(k_{\mathrm{D}}+1)(k_{\mathrm{L}}+1) - k_{\mathrm{D}}C_{\mathrm{D}}^{\mathrm{tot}}(k_{\mathrm{L}}+1) - k_{\mathrm{L}}C_{\mathrm{L}}^{\mathrm{tot}}(k_{\mathrm{D}}+1)] \tag{30}$$

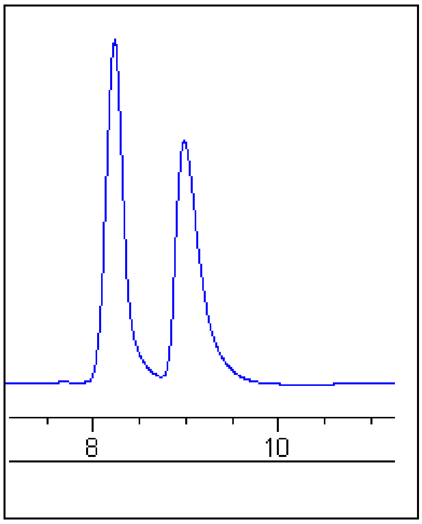
Information about the structure of the selector ([(S)-BINAP(CH_3CN)$_2$Cu][PF_6])

[(S)-BINAP(CH_3CN)$_2$Cu][PF_6] was prepared by literature method.[S1] Chemical structure of [(S)-BINAP(CH_3CN)$_2$Cu][PF_6] is shown in the following figure.



Chromatogram of enantiomeric separation of phenylglycine

A typical chromatogram of enantiomeric separation of phenylglycine



The retention time is 8.222 min for L-PHG and 8.975 min for D-PHG. Each test was run in triplicate under identical conditions, and the standard deviation is in the range of 2%.

Reference

S1. Blue, E. D.; Davis, A.; Conner, D.; Gunnoe, T. B.; Boyle, P. D.; White, P. S. Synthesis, Solid-State Crystal Structure, and Reactivity of a Monomeric Copper(I) Anilido Complex. *J. Am. Chem. Soc.* **2003**, *125*, 9435-9441.