Chemistry–A European Journal

Supporting Information

Rationalizing the Extent of the "Sergeants-and-Soldiers" Effect in Supramolecular Helical Catalysts: Effect of Copper Coordination

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Supplementary Charts, Figures and Tables (Figures S1-S11)

Figure S1 CD and UV-Vis analyses of the S&S-type experiments with and without [Cu]. Conditions: [BTA P] = 5.80 mM, $[Cu(OAc)_2 \cdot H_2O] = 1.45$, 2.90 or 5.80 mM, $0.006 \le [BTA (R) \cdot Cha] \le 6.35 \text{ mM}$) in toluene at 293 K.



Figure S2 Repeatability of the experiments. Top: g values as a function of fs^0 for S&S-type experiments with and without [Cu] (**BTA P**/[Cu]= 4). Bottom: enantiomeric excesses in NPnol as a function of fs^0 for three series of S&S-type experiments performed with **BTA P**/[Cu]= 4.

a) Solution A: fs⁰= 9%, mixture with [Cu] Solution F: fs⁰= 9%, mixture without [Cu] Solution G: fs⁰= 39%, mixture with [Cu] Solution H: fs⁰= 39%, mixture without [Cu]



Solution A: BTA P/ [Cu]= 4 Solution B: BTA P/ [Cu]= 2 Solution C: BTA P/ [Cu]= 1 Solution F: mixture without [Cu]

b)



Figure S3 Pictures of solutions with and without [Cu]. a) Pictures of solutions A, F, G and H, standing at 293 K, 15 minutes (left) and 1 day (right) after being prepared. **BTA P**/[Cu]= 4 for all copper-containing solutions. b) Pictures of solutions A, B, C and F, standing at 293 K, 15 minutes (left) and 1 day (right) after being prepared. fs^0 = 9% in all cases. All solutions were prepared in C₇D₈. See the corresponding movies as additional files: "movie 1 15 min" (solution A, F, G, H), "movie 1 1 day" (solution A, F, G, H), "movie 2 15 min" (solution A, B, C, F) and "movie 2 1 day" (solution A, B, C, F). Small particles, detected in solution C only, are attributed to non-coordinated [Cu(OAc)₂•H₂O]. The gel formed after 1 day for sample A is very fragile, hence the different aspect in figures S3a and S3b.



Figure S4 CD and UV-Vis analyses of the S&S-type experiments with and without [Cu], $fs^0 = 9\%$, up to 800 nm. No CD or absorption bands are detected in the visible region.



Figure S5 CD and UV-Vis analyses of the S&S-type experiments with and without [Cu], $fs^{0}=$ 9%, 15 minutes and 1 day after dissolution. Evolution of the g values at 295 nm, $g=5.3\times10^{-4}$ (15 minutes) $\rightarrow g=5.3\times10^{-4}$ (1 day) and $g=2.5\times10^{-4}$ (15 minutes) $\rightarrow g=2.3\times10^{-4}$ (1 day) for the copper-free and copper-containing solutions, respectively.



Figure S6 SANS analyses of the individual components and their mixtures. a) SANS analyses: scattered intensity (cm⁻¹) normalized by the (total BTA) concentration for **BTA** (*S*)-**Cha** alone (19.9 g.L⁻¹, dimers),^[1] of **BTA P** alone (6.0 g.L⁻¹, stacks),^[1] and for their S&S-type mixture (stacks + dimers) containing **BTA P** (4.0 g.L⁻¹, 5.8 mM) and **BTA** (*S*)-**Cha** (4.4 g.L⁻¹, 3.8 mM, fs⁰= 39%). b) SANS analyses: scattered intensity (cm⁻¹) normalized by the (total BTA) concentration for **BTA** (*S*)-**Cha** alone (19.9 g.L⁻¹, dimers),^[1] of **BTA P** alone (6.0 g.L⁻¹, stacks),^[1] and for their S&S-type mixture (stacks + dimers),^[1] of **BTA P** alone (6.0 g.L⁻¹, stacks),^[1] and for their S&S-type mixture (stacks + dimers) containing **BTA P** (4.0 g.L⁻¹, 5.8 mM) and **BTA (***S*)-**Cha** (4.4 g.L⁻¹, 3.8 mM, fs⁰= 39%) and [Cu(OAc)₂•H₂O] (0.29 g.L⁻¹, 1.45 mM, BTA P/[Cu]= 4).



Figure S7 FT-IR analyses of S&S-type assemblies with and without [Cu] in C₇D₈. Zoom on the N—H (left) and C=O (right) regions. Bands are attributed according to previous work.^[1–9] # weakly hydrogen-bonded N—H and C=O belonging to stacks also have contribution in these regions. a) FT-IR analyses of **BTA** (*S*)-Cha alone (0.58 mM, dimers), of **BTA** P•[Cu] (**BTA** $P= 5.8 \text{ mM} + [Cu(OAc)_2 \cdot H_2O]$ 1.45 mM, stacks) and of the corresponding S&S-type mixtures (dimers+stacks) containing **BTA** P (5.8 mM) and **BTA** (*S*)-Cha (0.58 mM, fs⁰= 9%) with or without [Cu(OAc)_2 \cdot H_2O] (1.45 mM, **BTA** P/[Cu]= 4). b) FT-IR analyses of **BTA** (*S*)-Cha alone (3.8 mM, dimers), of **BTA** P•[Cu] (**BTA** $P= 5.8 \text{ mM} + [Cu(OAc)_2 \cdot H_2O]$ (1.45 mM, stacks) and of the corresponding **BTA** P (5.8 mM) and **BTA** (*S*)-Cha (3.8 mM, dimers), of **BTA** P•[Cu] (**BTA** $P= 5.8 \text{ mM} + [Cu(OAc)_2 \cdot H_2O]$ 1.45 mM, stacks) and of the corresponding S&S-type mixtures (dimers+stacks) containing **BTA** P•[Cu] (**BTA** $P= 5.8 \text{ mM} + [Cu(OAc)_2 \cdot H_2O]$ 1.45 mM, stacks) and of the corresponding S&S-type mixtures (dimers+stacks) containing **BTA** P (5.8 mM) and **BTA** (*S*)-Cha (3.8 mM, fs⁰= 39%) with or without [Cu(OAc)_2 \cdot H_2O] (1.45 mM, BTA P/[Cu]= 4).



Figure S8 Simulation of FT-IR analyses. Simulation of the experimental spectra according to the procedure described in the methods of the experimental section. a) FT-IR spectra **BTA** (*S*)-Cha alone (0.58 or 3.8 mM, dimers), of **BTA** P (5.8 mM, stacks) and of the corresponding S&S-type mixtures (dimers+stacks) containing **BTA** P (5.8 mM) and **BTA** (*S*)-Cha (0.58 mM, $fs^0 = 9\%$; or 3.8 mM, $fs^0 = 39\%$) without [Cu(OAc)₂•H₂O]. b) FT-IR spectra of **BTA** (*S*)-Cha alone (0.58 or 3.8 mM, dimers), of **BTA** P•[Cu] (**BTA** P= 5.8 mM + [Cu(OAc)₂•H₂O] 1.45 mM, stacks) and of the corresponding S&S-type mixtures (dimers+stacks) containing **BTA** P (5.8 mM) and **BTA** (*S*)-Cha (0.58 mM, $fs^0 = 9\%$; or 3.8 mM, fs⁰ = 39\%) with [Cu(OAc)₂•H₂O] 1.45 mM, stacks) and of the corresponding S&S-type mixtures (dimers+stacks) containing **BTA** P (5.8 mM) and **BTA** (*S*)-Cha (0.58 mM, $fs^0 = 9\%$; or 3.8 mM, $fs^0 = 39\%$) with [Cu(OAc)₂•H₂O] (1.45 mM, **BTA** P/[Cu]= 4). The quality of the fit allows to determine the fraction of **BTA** (*S*)-Cha in the co-assemblies, fs^s (%) from FT-IR= [**BTA** (*S*)-Cha in stacks]/([**BTA** (*S*)-Cha in stacks]+ [**BTA** P]), as indicated above each spectrum.



Figure S9 Normalized CD and UV-Vis analyses. a) CD and UV-Vis spectra of Figure 1a (S&S-type experiments without [Cu]) with intensity normalized to 1 at λ = 295 nm. b) CD and UV-Vis spectra of Figure 1a (S&S-type experiments with [Cu]) with intensity normalized to 1 at λ = 295 nm.



Figure S10 ¹H NMR analyses of S&S-type mixtures with and without [Cu]. a) ¹H NMR analyses of BTA P alone (5.8 mM), and of the S&S-type mixtures containing BTA P (5.8 mM) and BTA (*S*)-Cha (0.58 mM, fs⁰= 9%; or 3.8 mM, fs⁰= 39%) with [Cu(OAc)₂•H₂O] (1.45 mM, BTA P/[Cu]= 4) in THF-d₈ at 293 K. Residual THF signals at δ = 1.71 ppm and δ = 3.61 ppm. H₂O and HDO at δ = 2.47 ppm and δ = 2.51 ppm. b) ¹H NMR analyses of the S&S-type mixtures containing BTA P (5.8 mM) and BTA (*S*)-Cha (0.58 mM, fs⁰= 9%; or 3.8 mM, fs⁰= 39%) with and without [Cu(OAc)₂•H₂O] (1.45 mM, BTA P/[Cu]=4) in C₇D₈ at 293 K. #= HOAc or ⁻OAc. Residual toluene signals at δ = 2.09 ppm, δ = 6.98 ppm, δ = 7.01 ppm and δ = 7.09 ppm. Signals corresponding to BTA P and BTA P•[Cu].



Figure S11 ³¹P{¹H} NMR analyses of S&S-type mixtures with and without [Cu]. Assignment of the peaks according to related phosphine complexes reported in the literature.^[10] a) ³¹P{¹H} NMR analyses of **BTA P** alone (5.8 mM), and of the S&S-type mixtures containing **BTA P** (5.8 mM) and **BTA (***S***)-Cha** (0.58 mM, fs⁰= 9%; or 3.8 mM, fs⁰= 39%) with [Cu(OAc)₂•H₂O] (1.45 mM, **BTA P**/[Cu]= 4) in THF-d₈ at 293 K. b) ³¹P{¹H} NMR analyses of the S&S-type mixtures containing **BTA P** (5.8 mM) and **BTA (***S***)-Cha** (0.58 mM) and **BTA (***S***)-Cha** (0.58 mM, fs⁰= 9%; or 3.8 mM, fs⁰= 39%) with and without [Cu(OAc)₂•H₂O] (1.45 mM, **BTA P**/[Cu]= 4) in C₇D₈ at 293 K. Zoom on the phosphine oxide-free region is shown in Figure 4.

Comment on the coordination chemistry of related copper complexes and interpretation

of the NMR spectra (Figures S10-S11): In this work, phosphine copper complexes are prepared in THF by using [Cu(OAc)₂•H₂O] as a convenient copper precursor and these precatalysts are subsequently solubilized in toluene (for characterization of the precatalyst) and transformed *in situ* into copper hydride active species (for catalysis). Structural characterization of these types of monophosphine copper complexes is poorly established in the case of conventional phosphine ligands (for well-defined copper complexes of diphosphine ligands see reference ^[11]). For the precatalysts, π -base type ligands, such as PPh₃, are known to reduce copper(II) salts into copper(I) compounds^[12,13] whose structure can be greatly altered by the experimental conditions; mixed valence Cu(II)-Cu(I) complexes with various compositions might form^[14,15] and the generated PPh₃=O is also a potent ligand of copper centers.^[16]

In the present system, the absence of a band in the visible region of the UV-Vis spectra, even for copper-rich mixtures, seems to discard the presence of $[Cu_2(OAc)_4]$ dimeric species (Figure S4).^[15,17] S&S-type mixtures containing either **BTA P** only or **BTA P**•[Cu] generated from $[Cu(OAc)_2 \cdot H_2O]$ were analyzed since the chiroptical properties of the latter correlated well with the outcome of the catalytic experiments (Figure 2c) and catalytically-active copper hydride species are elusive by essence.

¹H NMR analyses in THF-d₈ show well-resolved signals for all hydrogens belonging to **BTA P** and **BTA** (*S*)-Cha monomers, because BTAs are molecularly dissolved in this solvent (Figure S10a). The slight chemical shift of the ³¹P NMR signal relatively to free **BTA P** ($\Delta\delta \approx +0.3$ ppm) and more unequivocally the broadening of this signal ($\delta = -6.1$ ppm) demonstrate the coordination of **BTA P** to quadrupolar copper in THF-d₈ (Figure S11a). Similar small chemical shifts have been reported between free phosphine and phosphine bound to Cu(I) centers.^[10] The formation of phosphine oxide ($\delta = 23.4$ ppm), and potentially phosphine oxide copper complexes, is the consequence of the generation of copper(I) complexes but a mixture of copper(II) and copper(I), denoted as [Cu] in this manuscript, is more likely to be present in solution. The presence of a single ³¹P NMR signal for phosphine species in THF-d₈ (Figure S11a), despite the stoichiometry of four **BTA P** for one [Cu(OAc)₂•H₂O] engaged in the mixture, suggests a fast exchange rate of [Cu] between **BTA P** and **BTA P**•[Cu] species, relatively to their ³¹P NMR frequencies.

In C₇D₈, the formation of helical co-assemblies leads to severe broadening of the NMR signals. In ¹H NMR, hydrogens for the BTA ring and NH groups are barely detected (Figure S10b) but those corresponding to the side chains and the terminal aryl groups of PPh₂ can be observed. Even though being widened compared to THF-d₈, a single signal is present in ³¹P NMR ($\delta = -5.2$ ppm) that accounts for the free phosphine moiety in helical co-assemblies without [Cu] (Figures 4 and 11b). Copper complexes for the two selected S&S compositions exhibit drastically different ³¹P NMR traces. Crosslinked helices, present in the sample embedding 9% of **BTA** (*S*)-**Cha**, show a broad asymmetric signal ($\delta max \approx -3$ ppm) whilst single helices, present in the sample containing 39% of **BTA** (*S*)-**Cha**, exhibit two broad but distinguishable signals at $\delta = -1.8$ ppm and $\delta = -5.2$ ppm. The latter and former signals are attributed to **BTA P**•[**Cu**] and free **BTA P**, respectively.

The ³¹P NMR traces for copper-containing mixtures are interpreted as follows: In the dissociated state, in THF-d₈, copper centers are rapidly exchanged between **BTA P** monomers leading to a single ³¹P signal. In C₇D₈, for copper crosslinked helices with a small fraction of

"sergeants", **BTA P** sites are sufficiently close to exchange their copper atoms, and consequently close to coalescence (or large broadening) of the ³¹P signals is observed. Finally, exchange rate of copper atoms between **BTA P** and **BTA P**•[Cu] centers is expected to be rather slow in single helices as these groups are separated by a larger fraction of "sergeants" and thus two well separated signals corresponding to each species are observed in the corresponding ³¹P NMR spectra.

Preparation of solutions and analytical data Circular Dichroism analyses (Tables S1–S4)

<u>S&S-type solutions without [Cu]</u>: A given amount of a stock solution of **BTA P** in toluene was divided in order to get **BTA P** (2.4 mg, 3.5 µmol) in each vial. A 17.4 mM stock solution of BTA Cha was prepared in dry toluene as well as a 1.74 mM stock solution by dilution. Then the desired amount of BTA Cha stock solution was added to each vial. Finally, dry toluene was added to each vial in order to get a total volume of 600 µL. Samples were briefly heated up to solvent boiling point (\approx 383 K) and analysed at 293 K.

<u>S&S-type solutions with [Cu]</u>: A given amount of a stock solution prepared by mixing **BTA P** and [Cu(OAc)₂·H₂O] was divided in order to get **BTA P** (2.4 mg, 3.5 µmol) and [Cu(OAc)₂·H₂O] (0.17 mg, 0.9 µmol for **BTA P**/[Cu]= 4; 0.34 mg, 1.7 µmol for **BTA P**/[Cu]= 2; 0.68 mg, 3.5 µmol for **BTA P**/[Cu]= 1) in dry THF (500 µL) in each vial. The mixture was stirred for 20 minutes. The solvent was removed under vacuum and the vials were kept under vacuum (10⁻³ mbar) for 1 hour. A 17.4 mM stock solution of BTA Cha was prepared in dry toluene as well as a 1.74 mM stock solution by dilution. Then the desired amount of BTA Cha stock solution was added to each vial. Finally, dry toluene was added to each vial in order to get a total volume of 600 µL. Samples were briefly heated up to solvent boiling point (\approx 383 K) and analysed at 293 K.

without [Cu] (data of Figures 1a and S2)		without [Cu] (data of Figures S1a and S2)		without [Cu] (data of Figures S1b and S2)		without [Cu] averaged values (data of Figure 1c)		
fs ⁰ (%)	g values (×10 ⁴)	$\begin{array}{c c} \text{lues} \\ 0^4 \end{array} fs^0 (\%) \begin{array}{c} \text{g values} \\ (\times 10^4) \end{array}$		fs ⁰ (%)	G values (×10 ⁴)	fs ⁰ (%)	g values (×10 ⁴)	
0.1	-0.3	2.5	4.1	2.5	3.6	0.1	0.3	
0.5	-1.1	10	5.6	10	5.4	0.5	1.1	
1	-2.0	16	5.8	16	5.6	1	2.0	
9	-5.4	19	6.0	19	5.8	2.5	3.9	
21	-5.7	39	6.7	39	6.3	9*	5.5±0.1	
36	-6.1	50	7.2	50	7.0	16	5.7±0.1	
52	-6.9					19*	5.8±0.1	
						36	6.1	
						39	6.5±0.2	
						52*	7.1±0.1	

Table S1. Composition and g values (λ = 295 nm) of the S&S-type experiments without Cu analysed by CD spectroscopy ([**BTA P**]=5.80 mM, 0.006≤ [BTA Cha]≤6.35 mM). * values for fs⁰=9% and fs⁰=10%, fs⁰=19% and fs⁰=21%, as well as fs⁰= 50% and fs⁰=52% have been averaged. Error bars for g values correspond to one standard deviation (calculated from repeated measurements).

with [Cu] (data of Figures 1a and S2) ^[8]			with [Cu] (data of Figures S1c and S2)			with [Cu] (data of Figures S1d and S2)		
fs ⁰ (%)	g values (×10 ⁴)	<i>e.e.</i> values (%, ±1%)	fs ⁰ (%)	$\begin{array}{c} \begin{array}{c} g \text{ values} \\ (\times 10^4) \end{array} \begin{array}{c} v_{10} \\ (\% \end{array}$		fs ⁰ (%)	g values (×10 ⁴)	
0.1	-0.2	0	2.5	0.8	6	2.5	0.6	
0.5	-0.5	0	10	2.4	18	10	1.9	
1	-0.8	-4	15	2.8	22	16	2.7	
9	-3.9	-18	20	4.1	29	19	3.7	
21	-5.4	-42	40	5.5	50	39	5.3	
36	-6.3	-53	50	6.1	58	50	6.2	
52	-6.9	-58						

with [Cu] (data of Figures S1e and S2)			wit (additi	h [Cu] onal data)	with [Cu] averaged values (data of Figures 1c and S2)			
fs ⁰ (%)	g values (×10 ⁴)	<i>e.e.</i> values (%, ±1%)	fs ⁰ (%)	g values (×10 ⁴)	fs ⁰ (%) $ g $ values (×10 ⁴)		<i>e.e.</i> values (%, ±1%)	
2.5	1.1	6	50	6.8	0.1	0.2	0	
10	2.8	18	58	7.1	0.5	0.5	0	
15	3.2	22			1	0.8	4	
20	4.0	29			2.5	0.8±0.2	6 (±0%)	
39	6.0	50			10*	2.8±0.7	18 (±0%)	
50	6.7	58			15*	2.9±0.2	22 (±0%)	
					21*	4.3±0.7	33 (±6%)	
					36	6.3	53	
					39*	5.6±0.3	50 (±0%)	
					50*	6.5±0.3	58 (±0%)	
					58	7.1	nd	

Table S2. Composition and g values (λ = 295 nm) of the S&S-type experiments with Cu (**BTA P**/[Cu]= 4) analysed by CD spectroscopy ([**BTA P**]= 5.80 mM, [Cu(OAc)₂· H₂O]=1.45 mM, 0.006≤ [BTA Cha]≤ 8.00 mM) as well as *e.e.* values in NPnol obtained in catalysis from the corresponding solutions. * values for fs⁰=9% and fs⁰=10%, fs⁰= 15% and fs⁰= 16%, fs⁰= 19%, fs⁰=20%, fs⁰=21% and fs⁰=22%, fs⁰=39% and fs⁰=40%, fs⁰= 50% and fs⁰=52% have been averaged. Error bars for g values correspond to one standard deviation (calculated from repeated measurements). Standard deviations of *e.e.* for repeated experiments are indicated between parenthesis; there are lower than the uncertainty for *e.e.* measurement (± 1%, HPLC analysis) except for fs⁰= 21% (± 6%). Accordingly, an error bar of 6% for fs⁰=21% and of 1%, for all the other mixtures, respectively, have been reported in Figure 1c.

w (data	vith BTA P/[1 of Figures 1	Cu]= 2 lc and S1f)	with BTA P/[Cu]= 1 (data of Figures 1c and S1g)				
fs ⁰ (%)	g values (×10 ⁴)	<i>e.e.</i> values (%, ±1%)	fs ⁰ (%)	g values (×10 ⁴)	<i>e.e.</i> values (%, ±1%)		
2.8	0.7	6	2.5	1.7	4		
10	2.9	16	10	3.3	29		
15	3.8	31	16	4.1	42		
21	4.6	39	21	4.7	47		
25	4.9	50	40	6.0	61		
39	6.1	56	51	6.4	61		
50	6.5	58					
52	6.6	58					

Table S3. Composition and g values (λ = 295 nm) of the S&S-type experiments with Cu (**BTA P**/[Cu]= 2 and **BTA P**/[Cu]= 1) analysed by CD spectroscopy ([**BTA P**]= 5.80 mM, [Cu(OAc)₂·H₂O]= 2.90 or 5.80 mM, 0.006≤ [BTA Cha]≤ 6.35 mM) as well as *e.e.* values in NPnol obtained in catalysis from the corresponding solutions. For *e.e.* measurement, uncertainty is related to HPLC analyses (± 1%).

without [Cu] with BTA P/[Cu]= 4			witl	h BTA P/[Cu]= 2	with BTA P/[Cu]= 1				
fs ⁰ (%)	g values (×10 ⁴)	fs ⁰ (%)	<i>e.e.</i> values (%)	g values (×10 ⁴)	fs ⁰ (%)	<i>e.e.</i> values (±1%)	g values (×10 ⁴)	fs ⁰ (%)	<i>e.e.</i> values (±1%)	g values (×10 ⁴)
0	0	0	0	0	0	0	0	0	0	0
0.1	0.3	0.1	0±1	0.2	2.8	6	0.7	2.5	4	1.7
0.5	1.1	0.5	0±1	0.5	10	16	2.9	10	29	3.3
1	2.0	1	4±1	0.8	15	31	3.8	16	42	4.1
2.5	3.9	2.5	6±1	0.8 ± 0.2	21	39	4.6	21	47	4.7
9	5.5±0.1	10	18±1	2.8±0.7	25	50	4.9	40	61	6
16	5.7±0.1	15	22±1	2.9±0.2	39	56	6.1	51	61	6.4
19	5.8±0.1	21	33±6	4.3±0.7	50	58	6.5			
36	6.1	36	53±1	6.3	52	58	6.6			
39	6.5±0.2	39	50±1	5.6±0.3						
52	7.1±0.1	50	58±1	6.5±0.3						

Table S4 Compiled averaged *e.e.* and g values as a function of fs⁰ (data plotted in Figure 2b and 2c).

Catalytic experiments

A given amount of a stock solution prepared by mixing **BTA P** and $[Cu(OAc)_2 \cdot H_2O]$ was divided in order to get **BTA P** (2.4 mg, 3.5 µmol) and $[Cu(OAc)_2 \cdot H_2O]$ (0.17 mg, 0.9 µmol for **BTA P**/[Cu]= 4; 0.34 mg, 1.7 µmol for **BTA P**/[Cu]= 2; 0.68 mg, 3.5 µmol for **BTA P**/[Cu]= 1) in dry THF (500 µL) in each vial. The solvent was removed under vacuum and the tubes were kept under vacuum (10⁻³ mbar) for 1 hour. Then 1-(4-nitrophenyl)ethanone (NPnone, 4.8 mg, 0.029 mmol for **BTA P**/[Cu]= 4, 9.6 mg; 0.058 mmol for **BTA P**/[Cu]= 2; 19.2 mg, 0.116 mmol for **BTA P**/[Cu]= 1) was added.

A 17.4 mM stock solution of BTA Cha was prepared in dry toluene as well as a 1.74 mM stock solution by dilution. Then the desired amount of BTA Cha stock solution was added to each vial. Finally, dry toluene was added to each vial in order to get a total volume of 600 µL. The mixtures were stirred for 15 min at 293 K and then briefly heated up to solvent boiling point (\approx 383 K). After cooling to room temperature, PhSiH₃ (8.0 µL, 0.058 mmol for **BTA P**/[Cu]= 4; 16.0 µL, 0.116 mmol for **BTA P**/[Cu]= 2; 32.0 µL, 0.232 mmol for **BTA P**/[Cu]= 1) was added to each test tube and the mixtures were stirred for 17 hours.

<u>Typical work-up</u>: Aqueous solution of HCl (10 wt%, 500 μ L) was added and the mixtures were stirred for 30 min (until the solution became transparent). Then, the products were extracted with Et₂O (500 μ L) and AcOEt (500 μ L), the organic phases were collected and passed through a small silica plug. The solvents were evaporated and the crude material was analyzed by ¹H NMR and by chiral GC. Conversion >99% was obtained for all catalytic experiments, as determined by GC and ¹H NMR analyses. The optical purity was determined by chiral GC analysis.

<u>Chiral GC analyses</u>: The optical purity was determined by GC analysis: Chiral Cyclosil-B column, 30 m × 250 μ m x 0.25 μ m, inlet pressure= 12.6 psi. Injection temperature= 250°C; detector temperature= 300°C; column temperature= 145°C. Retention times: 18 min (1-(4-nitrophenyl)ethenone, NPnone), 45 min ((*R*)-enantiomer of NPnol), 47 min ((*S*)-enantiomer of NPnol).^[18]

SANS and FT-IR analyses

<u>S&S-type solutions without [Cu]</u>: A given amount of a stock solution of **BTA P** in C₇D₈ was divided in order to get **BTA P** (4.0 mg, 5.83 µmol) in each vial. A 17.4 mM stock solution of BTA Cha was prepared in C₇D₈ as well as a 1.74 mM stock solution by dilution. Then the desired amount of BTA Cha stock solution was added to each vial. Finally, C₇D₈ was added to each vial in order to get a total volume of 1000 µL. Samples were briefly heated up to solvent boiling point (\approx 383 K) and analyzed at 293 K.

<u>S&S-type solutions with [Cu]</u>: A given amount of a stock solution prepared by mixing **BTA P** and [Cu(OAc)₂·H₂O] was divided in order to get **BTA P** (4.0 mg, 5.83 µmol) and [Cu(OAc)₂·H₂O] (0.28 mg, 1.5 µmol for **BTA P**/[Cu]= 4; 0.56 mg, 3.0 µmol for **BTA P**/[Cu]= 2) in dry THF (500 µL) in each vial. The mixture was stirred for 20 minutes. The solvent was removed under vacuum and the vials were kept under vacuum (10⁻³ mbar) for 1 hour. A 17.4 mM stock solution of BTA Cha was prepared in C₇D₈ as well as a 1.74 mM stock solution by dilution. Then the desired amount of BTA Cha stock solution was added to each vial. Finally, C₇D₈ was added to each vial in order to get a total volume of 1000 µL. Samples were briefly heated up to solvent boiling point (\approx 383 K) and analyzed at 293 K.

NMR analyses

<u>S&S-type solutions without [Cu]</u>: A given amount of a stock solution of **BTA P** in C₇D₈ was divided in order to get **BTA P** (4.0 mg, 5.83 µmol) in each vial. A 17.4 mM stock solution of BTA Cha was prepared in dry toluene as well as a 1.74 mM stock solution by dilution. Then the desired amount of BTA Cha stock solution was added to each vial. Finally, C₇D₈ was added to each vial in order to get a total volume of 1000 µL. Samples were briefly heated up to solvent boiling point (\approx 383 K) and analyzed at 293 K.

<u>S&S-type solutions with [Cu]</u>: A given amount of a stock solution prepared by mixing **BTA P** and [Cu(OAc)₂·H₂O] was divided in order to get **BTA P** (4.0 mg, 5.83 µmol) and [Cu(OAc)₂·H₂O] (0.28 mg, 1.5 µmol for BTA P/[Cu]= 4) in dry THF (500 µL) in each vial. A 17.4 mM stock solution of BTA Cha was prepared in dry THF as well as a 1.74 mM stock solution by dilution. Then the desired amount of BTA Cha stock solution was added to each vial. The mixture was stirred for 20 minutes. The solvent was removed under vacuum and the vials were kept under vacuum (10⁻³ mbar) for 1 hour. The samples were dissolved in 1000 µL of THF-d₈ and analyzed by NMR (Figures S10a and S11a). The solvent was removed under vacuum and the vials were kept under to get a total volume of 1000 µL. Samples were briefly heated up to solvent boiling point (\approx 383 K) and analyzed by NMR at 293 K (Figures 4, S10b and S11b).

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