

Supporting Information

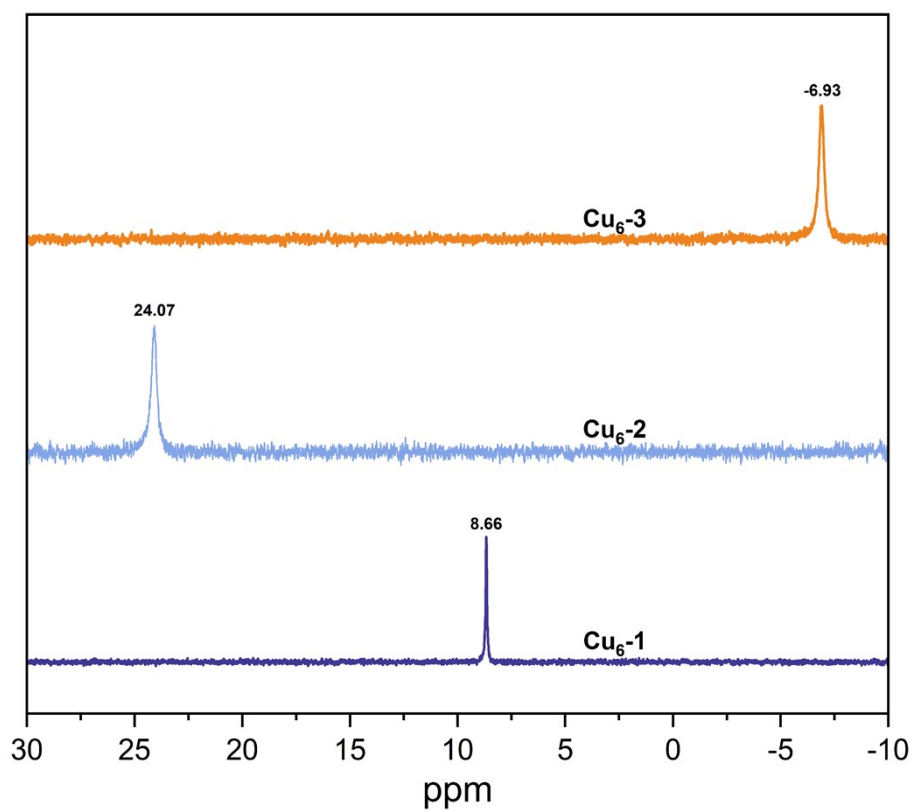


Figure S1. ^{31}P NMR spectrum of $[\text{CuH}]_6$ in C_6D_6 .

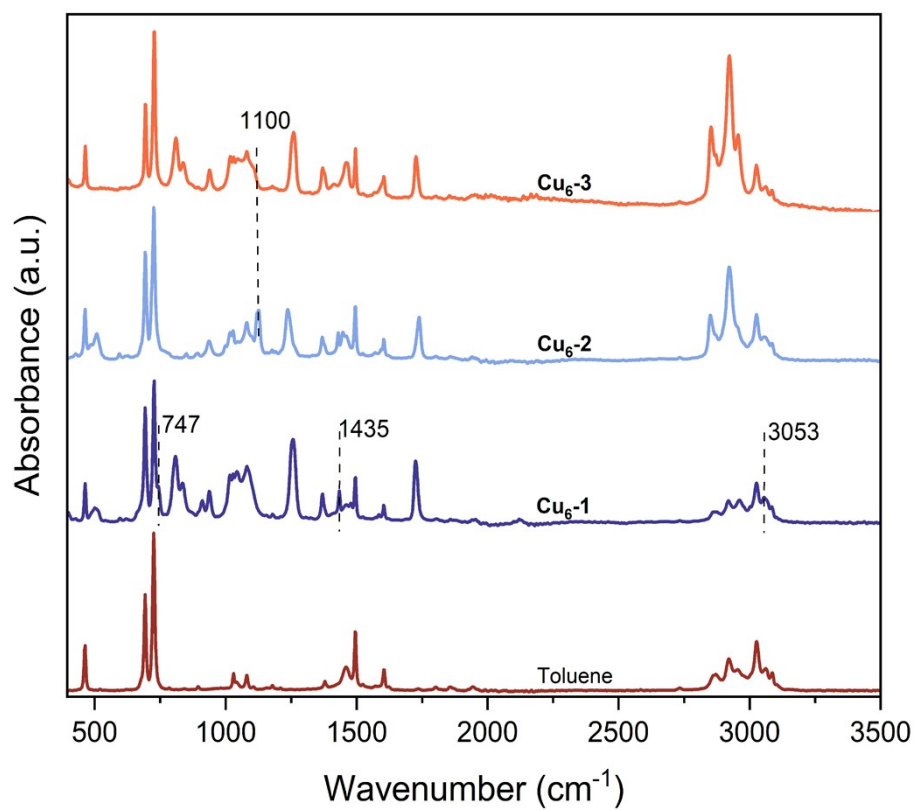
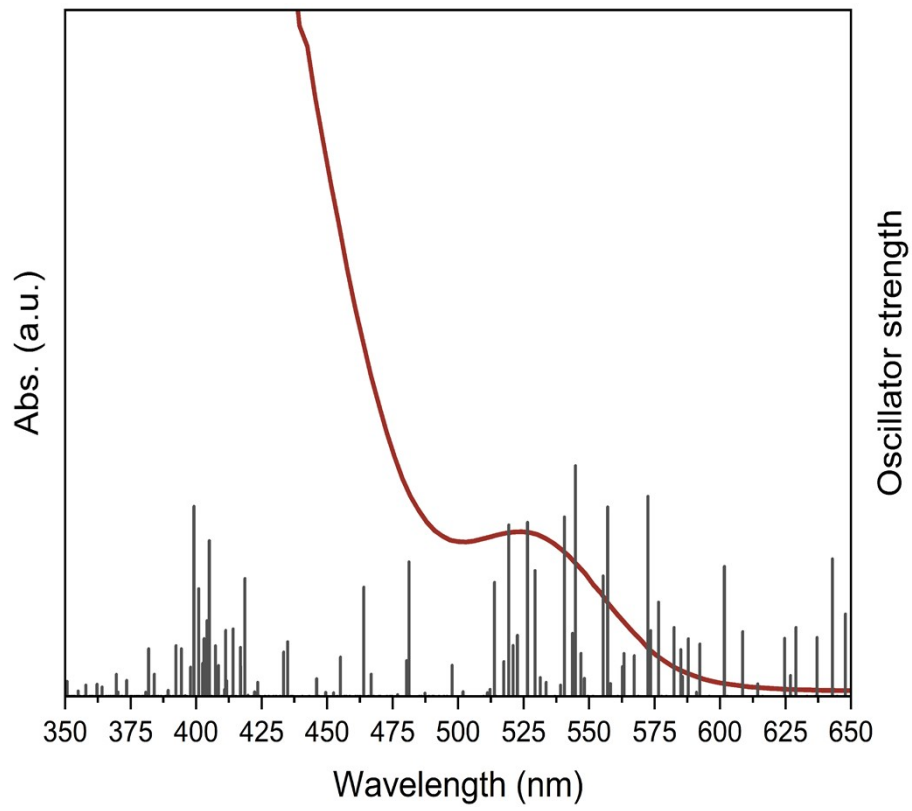
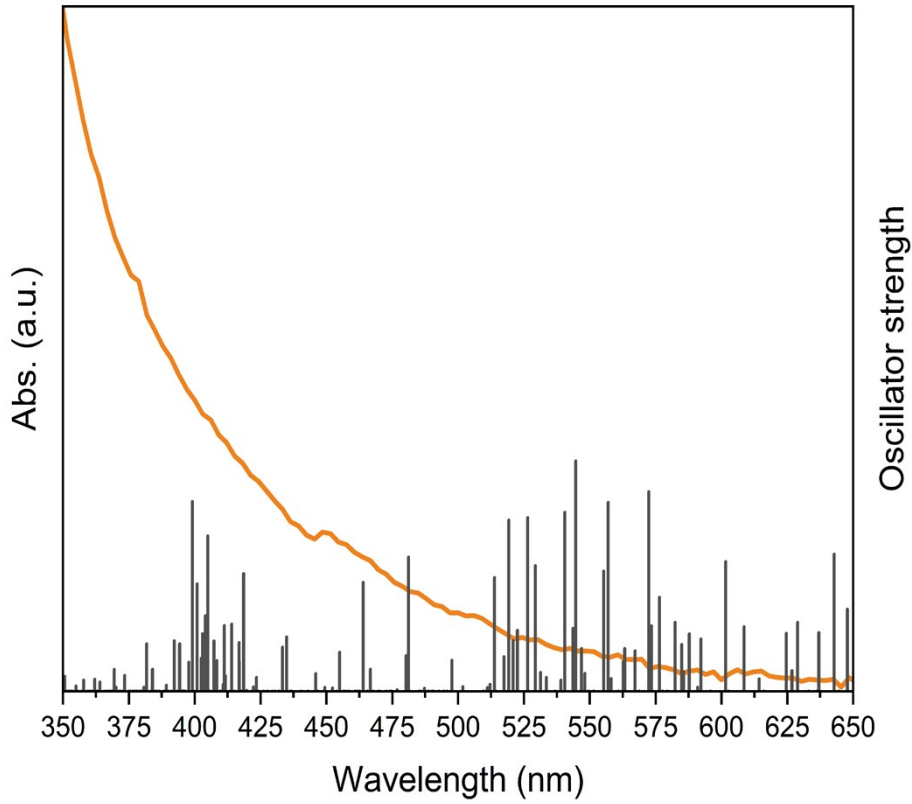


Figure S2. The ATR-IR spectra of the toluene and $[\text{CuH}]_6$.

(a)



(b)



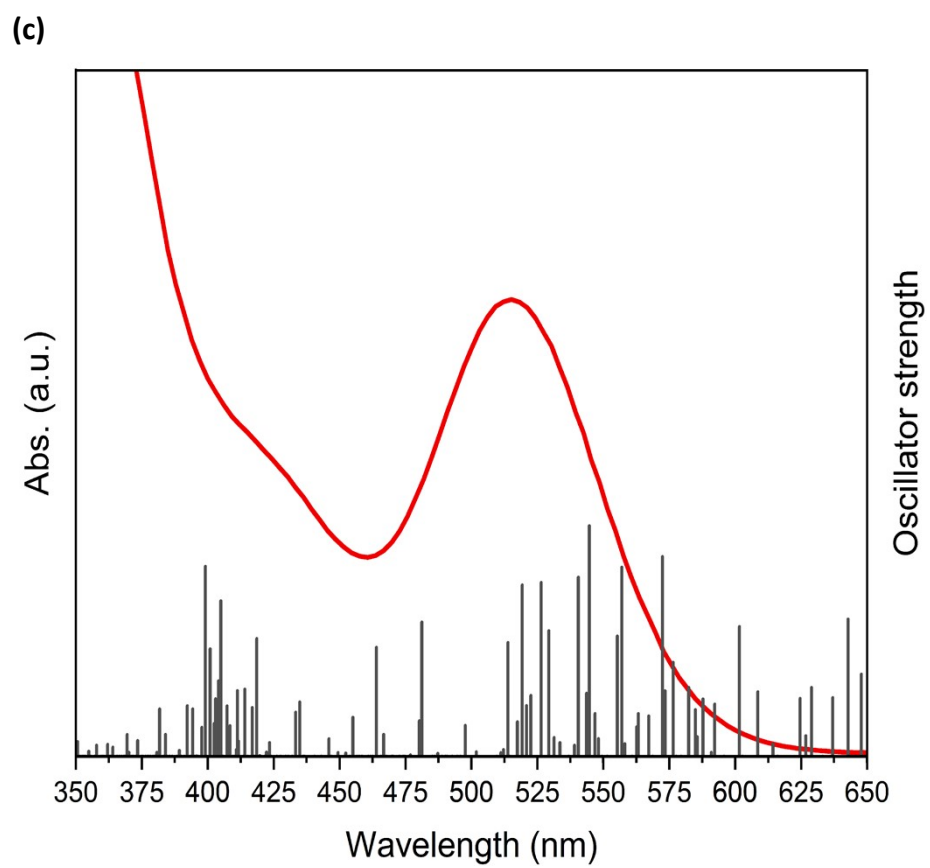


Figure S3. Calculated UV-vis absorption spectra of (a) **Cu₆-1**, (b) **Cu₆-2** and (c) **Cu₆-3**.

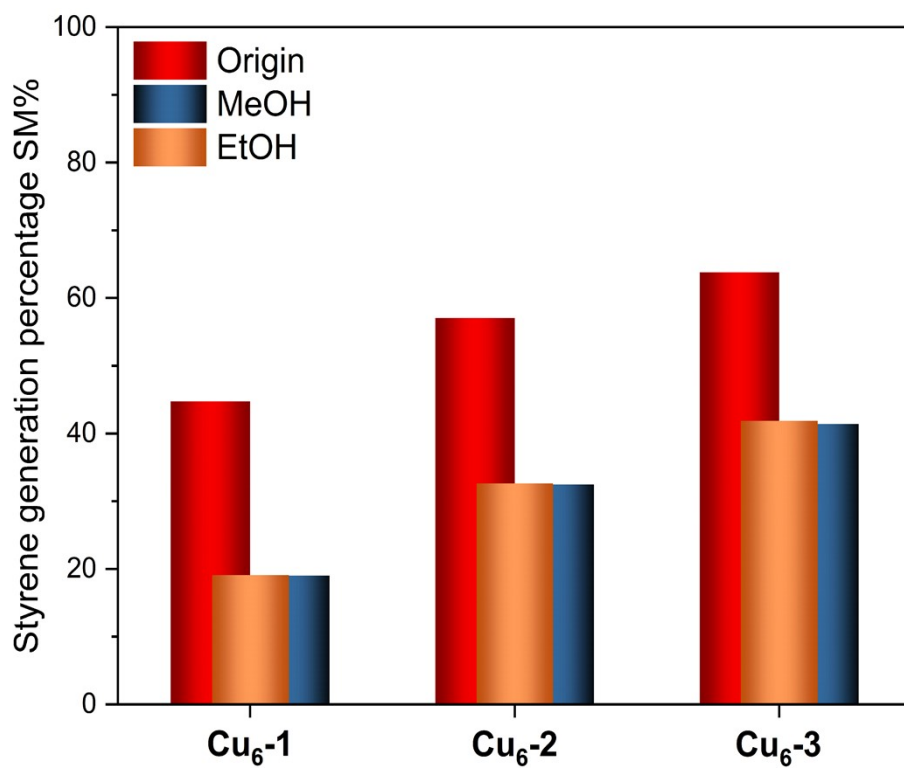


Figure S4. Hydrometallation of phenylacetylene using [CuH]₆.

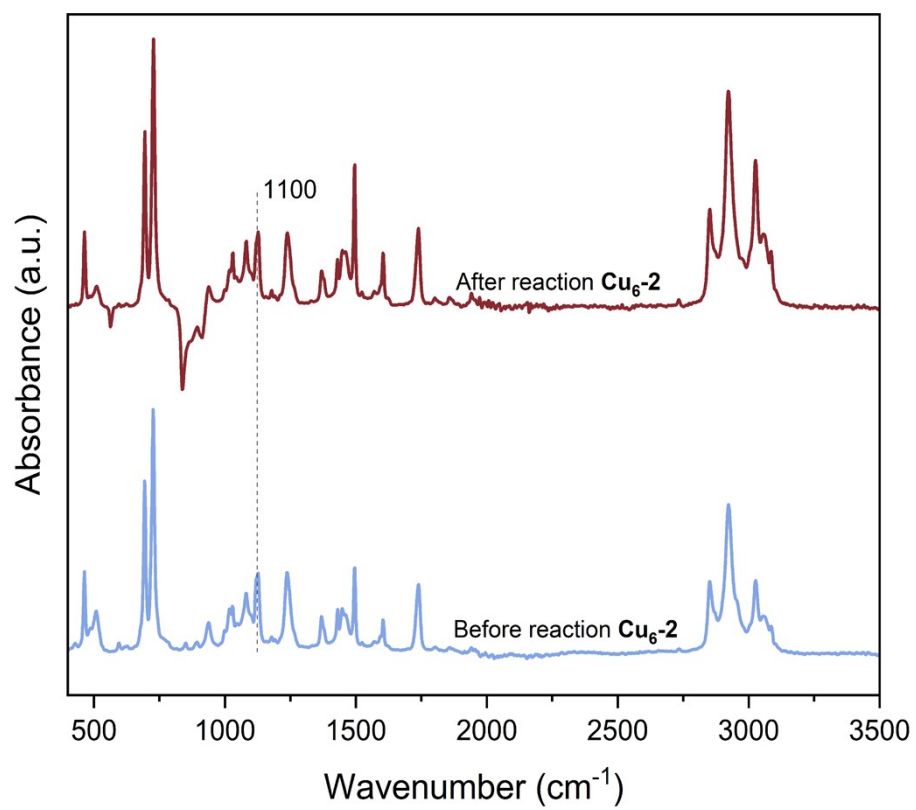
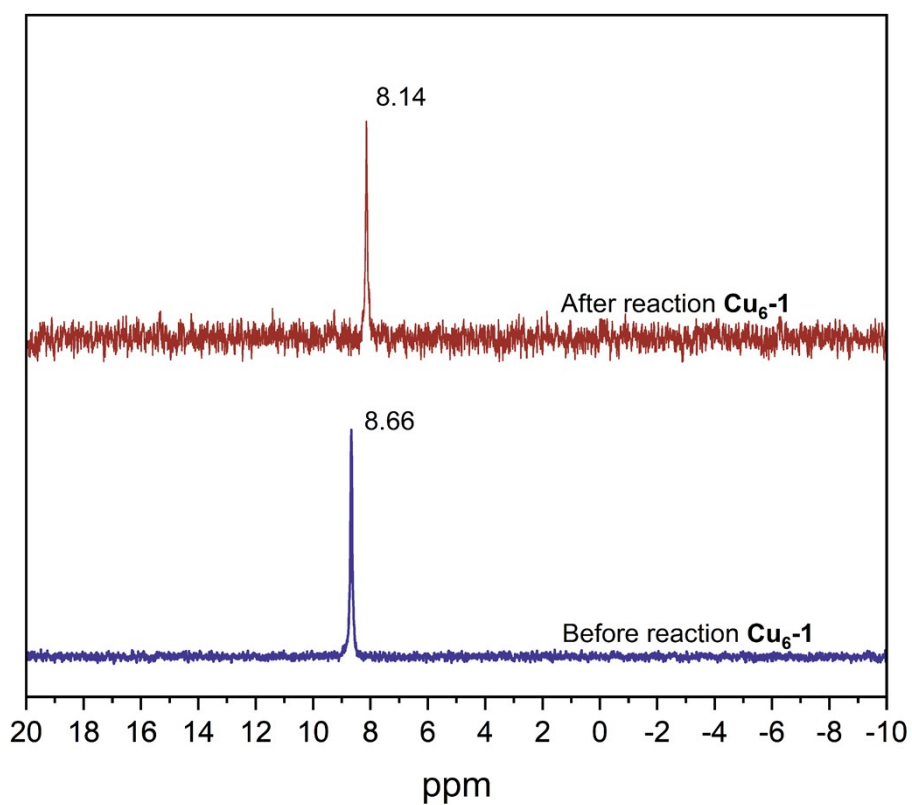
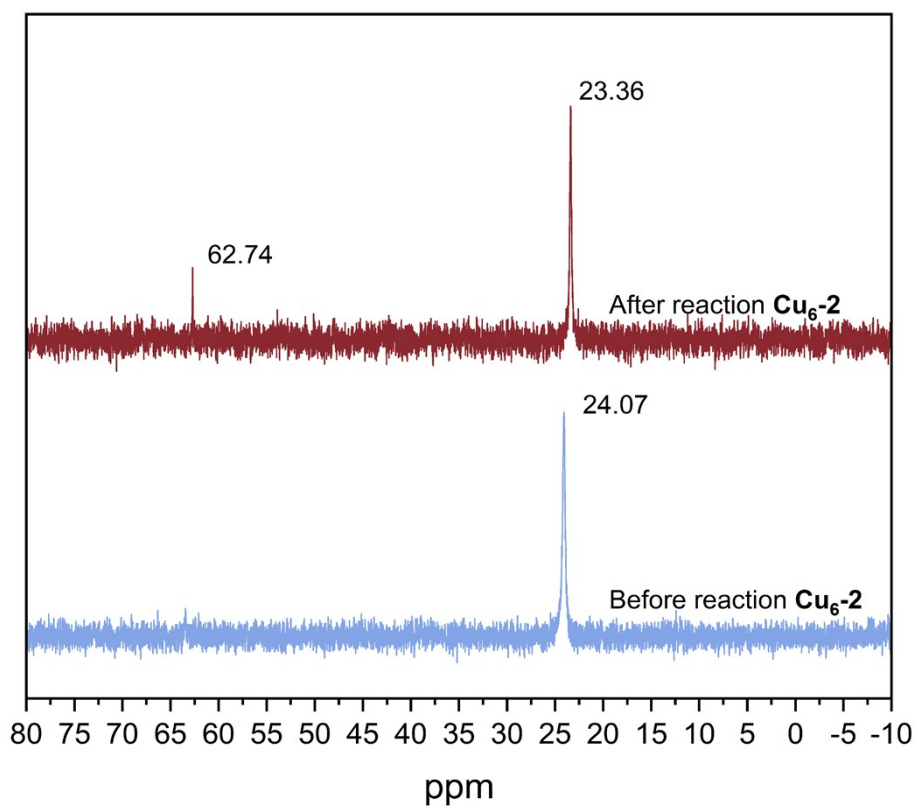


Figure S5. The ATR-IR spectrum of **Cu₆-2** before and after hydrometallation of Alkynes.

(a)



(b)



(c)

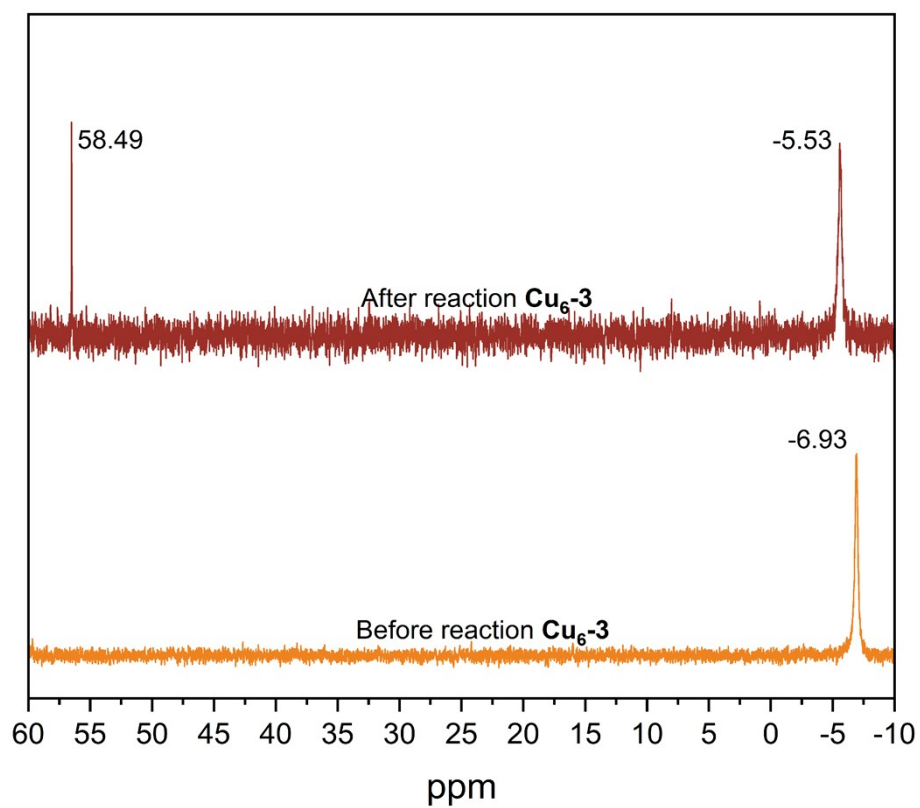


Figure S6. ^{31}P NMR spectrum of (a) $\text{Cu}_6\text{-1}$, (b) $\text{Cu}_6\text{-2}$ and (c) $\text{Cu}_6\text{-3}$ before and after hydrometallation of Alkynes.

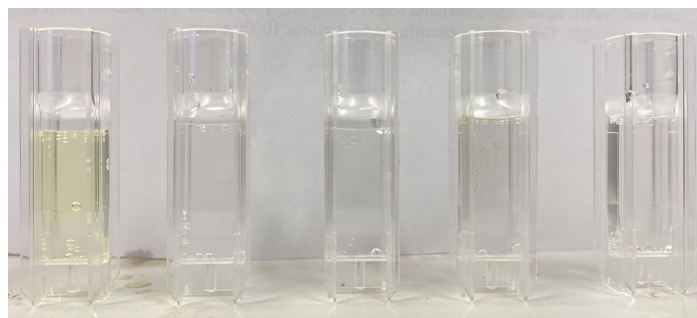


Figure S7. Reusability tests of **Cu₆-3** and changes in solution colour on 4-NP conversion (From right to left indicating the first time to fifth time).

Table S1. Mulliken population analysis of selected HOMO and LUMO energy levels.

Orbital	Energy (eV)	% Cu (3d)	% Cu (sp)	% P
HOMO -6	-11.02	18.28	3.64	21.20
HOMO -5	-10.84	35.06	9.36	14.07
HOMO -4	-10.70	26.99	8.63	16.44
HOMO -3	-10.49	31.51	6.43	14.35
HOMO -2	-10.47	35.75	6.72	13.84
HOMO -1	-10.22	40.11	7.66	11.93
HOMO	-10.21	39.50	11.06	11.70
LUMO	-9.31	50.47	15.28	7.64
LUMO +1	-9.15	49.33	15.31	8.57
LUMO +2	-9.14	46.00	18.30	7.90
LUMO +3	-9.03	52.54	14.49	7.09
LUMO +4	-8.58	62.62	9.55	12.14
LUMO +5	-8.24	80.70	0	8.01

Table S2. The orbital-orbital transitions, energies and oscillator strengths of excited state 130.

Transition	Nature of transitions	Energy (eV)	Oscillator strengths
187 <i>a</i> → 216 <i>a</i>	HOMO-29 → HOMO	2.434	0.058
188 <i>a</i> → 216 <i>a</i>	HOMO-28 → HOMO	2.263	0.023
188 <i>a</i> → 218 <i>a</i>	HOMO-28 → LUMO+1	3.321	0.032
190 <i>a</i> → 218 <i>a</i>	HOMO-26 → LUMO+1	3.152	0.020
190 <i>a</i> → 219 <i>a</i>	HOMO-26 → LUMO+2	3.157	0.018
192 <i>a</i> → 216 <i>a</i>	HOMO-24 → HOMO	2.07	0.027
192 <i>a</i> → 217 <i>a</i>	HOMO-24 → LUMO	2.964	0.012
193 <i>a</i> → 218 <i>a</i>	HOMO-23 → LUMO+1	3.118	0.026
194 <i>a</i> → 218 <i>a</i>	HOMO-22 → LUMO+1	2.948	0.027
195 <i>a</i> → 217 <i>a</i>	HOMO-21 → LUMO	2.718	0.037
196 <i>a</i> → 219 <i>a</i>	HOMO-20 → LUMO+2	2.869	0.034
199 <i>a</i> → 219 <i>a</i>	HOMO-17 → LUMO+2	2.649	0.033
199 <i>a</i> → 220 <i>a</i>	HOMO-17 → LUMO+3	2.764	0.047
201 <i>a</i> → 220 <i>a</i>	HOMO-15 → LUMO+3	2.674	0.011
203 <i>a</i> → 220 <i>a</i>	HOMO-13 → LUMO+3	2.571	0.060
205 <i>a</i> → 221 <i>a</i>	HOMO-11 → LUMO+4	2.908	0.022
206 <i>a</i> → 222 <i>a</i>	HOMO-10 → LUMO+5	3.16	0.012
208 <i>a</i> → 221 <i>a</i>	HOMO-8 → LUMO+4	2.604	0.029
210 <i>a</i> → 222 <i>a</i>	HOMO-6 → LUMO+5	2.784	0.170

Table S3. The conversion rate of 4-NP in 4 min

[CuH] ₆	Cu₆-1	Cu₆-2	Cu₆-3
Conversion rate %	49	62	100

Table S4. Catalysis recycle test of **Cu₆-3**

Number of cycles ^a	Conversion rate % ^b
1	100
2	100
3	100
4	100
5	40

^aReaction condition: 4-NP (1 mL, 0.1 mM), NaBH₄ (2.5 mg, 6.48×10^{-2} mmol), **Cu₆-3** (1.02×10^{-3} mmol). ^bMonitored by UV-vis absorption spectra.

Spectroscopic Data

Cu₆-2, ¹H NMR (500 MHz, C₆D₆) δ 1.20-1.46 (m, 90H), 1.62-1.73 (m, 36H), 1.73-1.81 (m, 36H), 1.91-2.00 (m, 36H), 2.41 (s, 6H)

Cu₆-3, ¹H NMR (500 MHz, C₆D₆) δ 0.90-0.92 (m, 54H), 1.36-1.45 (m, 252H), 2.36 (s, 6H)