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Supporting Information

for

A Novel quinoline-based NNN-pincer Cu(II) complex as a superior catalyst for oxidative esterification of allylic C(sp³)-H bonds

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General Procedure for gram-scale reaction:

Benzoic acid (A) and 4-hydroxybenzoic acid (B) have been used for exploring the gram-scale reaction.

A Schlenk flask equipped with a stir bar was charged with carboxylic acid derivative (1 g, 8.2 mmol (**A**)/ 7.2 mmol (**B**)) and catalyst (0.08 mmol, 85 mg (**A**)/ 0.07 mmol, 75 mg (**B**)). The Schlenk flask was then evacuated and back-filled with nitrogen. The process was repeated three times. Under nitrogen atmosphere, the Schlenk was charged with cyclohexene (8.2 mL, 82 mmol (**A**)/ 7.2 ml, 72 mmol (**B**)), TBHP (2.36 mL, 24.6 mmol (**A**)/ 2.07 ml, 21.6 mmol (**B**)), and DMF (10 mL) by syringe. The Schlenk flask was then placed in an oil bath preheated at 40 °C. After 1 h, the reaction mixture was cooled to room temperature and extracted with EtOAc and water. Organic phase was dried under reduced pressure. The crude product was purified by column chromatography on silica gel (5% EtOAc/pet ether) to afford the corresponding products **4a** and **4f** in 72% (1.2 g, 5.9 mmol) and 73% (1.14 g, 5.25 mmol) yields respectively.

Known		Unknown
Compound name	Reference	
4a-4e, 4i	1	
4n	2	
4h, 4p, 4q	3	
4k, 4r, 4f	4	4g, 4l, 4m, 40, 4s, 4l, 6b, 6d
4j	5	
<u>6a</u>	6	
6с	7	

Compound characterization Table





Fig. S1. ¹H NMR spectra of compound 4a



Fig. S2. ¹³C NMR spectra of compound 4a



Fig. S3. ¹H NMR spectra of compound 4b



Fig. S4. ¹³CNMR spectra of compound 4b



Fig. S5. ¹H NMR spectra of compound 4c



Fig. S6. ¹³C NMR spectra of compound 4c



Fig. S7. ¹H NMR spectra of compound 4d



Fig. S8. ¹³C NMR spectra of compound 4d



Fig. S9. ¹H NMR spectra of compound 4e



Fig. S10. ¹³C NMR spectra of compound 4e



Fig. S11. ¹H NMR spectra of compound 4f



Fig. S12. ¹³C NMR spectra of compound 4f



Fig. S13. ORTEP representation of the molecular structure of **4f** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) for **4f**: O3-CB 1.481(4), C9-O3 1.334(4), CB-CD 1.488(5), CD-CF 1.339(8), CF-CE 1.44(1), CE-CG 1.464(7), CG-CC 1.396(9), CC-CB 1.498(7); C9-O3-CB 118.8(3), O3-CB-CD 108.4(3), O3-CB-CC 106.1(3), O3-C9-C4 111.6(2), CB-CD-CF 120.4(5), CB-CC-CG 115.0(4), CG-CE-CF 111.0(5).

Empirical formula	$C_{13}H_{14}O_3$
Formula weight	218.24
Crystal size (mm)	0.32 X 0.22 X 0.12
Crystal system	monoclinic
Space group	P21/c
<i>a</i> [Å]	a=10.8811(2)
<i>b</i> [Å]	b=10.233(2)
<i>c</i> [Å]	c=11.017(2)
α [°]	90
β[°]	108.43(3)
γ [°]	90
volume [Å ³]	1163.7(4)
Z	4
F(000)	464
$\mu MoK_{\alpha} [mm^{-1}]$	0.088
Temperature [K]	293(2)
R _{int}	0.4013
Range of h, k, l	-13/13, -13/13, -14/14
$\theta_{\min/\max}$ (°)	1.973/27.290
GOF on F^2	1.048
Final R indices [I > $2\sigma(I)$]	R1 = 0.0565 wR2 = 0.1555
R indices [all data]	R1 = 0.0776 wR2 = 0.1735

 Table S1: Crystallographic details of compound 4f



Fig. S14. ¹H NMR spectra of compound 4g



Fig. S15. ¹³C NMR spectra of compound 4g



Fig. S16. HRMS of compound 4g



Fig. S17. ¹H NMR spectra of compound 4h



Fig. S18. ¹³C NMR spectra of compound 4h



Fig. S19. ¹H NMR spectra of compound 4i



Fig. S20. ¹³C NMR spectra of compound 4i



Fig. S21. ¹H NMR spectra of compound 4j



Fig. S22. ¹³C NMR spectra of compound 4j



Fig. S23. ¹H NMR spectra of compound 4k



Fig. S24. ¹H NMR spectra of compound 4k



Fig. S25. ¹H NMR spectra of compound 4l



Fig. S26. ¹³C NMR spectra of compound 4l



Fig. S27. HRMS of compound 4l



Fig. S28. ¹H NMR spectra of compound 4m



Fig. S29. ¹³C NMR spectra of compound 4m



Fig. S30. HRMS of compound 4m



Fig. S31. ¹H NMR spectra of compound 4n



Fig. S32. ¹³C NMR spectra of compound 4n



Fig. S33. ¹H NMR spectra of compound 40



Fig. S34. ¹³C NMR spectra of compound 40



Fig. S35. HRMS of compound 40



Fig. S36. ¹H NMR spectra of compound 4p



Fig. S37. ¹³C NMR spectra of compound 4p



Fig. S38. ¹H NMR spectra of compound 4q



Fig. S39. ¹³C NMR spectra of compound 4q



Fig. S40. ¹H NMR spectra of compound 4r



Fig. S41. ¹³C NMR spectra of compound 4r



Fig. S42. ¹H NMR spectra of compound 4s



Fig. S43. ¹³C NMR spectra of compound 4s



Fig. S44. HRMS of compound 4s



Fig. S45. ¹H NMR spectra of compound 4t



Fig. S46. ¹³C NMR spectra of compound 4t



Fig. S47. HRMS of compound 4t.



Fig. S48. ¹H NMR spectra of compound 6b



Fig. S49. ¹³C NMR spectra of compound 6b



Fig. S50. ¹H NMR spectra of compound 6c



Fig. S51. ¹³C NMR spectra of compound 6c



Fig. S52. ¹H NMR spectra of compound 6d



Fig. S53. ¹³C NMR spectra of compound 6d



Fig. S54. HRMS spectra of compound 6d



Fig. S55. HRMS of copper complex 1

Empirical formula	C ₂₅ H ₁₃ ClN ₅ O ₂
Formula weight	517.42
Crystal size (mm)	0.2 X 0.2 X 0.1
Crystal system	triclinic
Space group	P -1
<i>a</i> [Å]	a=8.1305(7)
<i>b</i> [Å]	b=9.2545(8)
<i>c</i> [Å]	c=14.7289(13)
α [°]	96.831(3)
β[°]	98.583(3)
γ [°]	104.865(3)
volume [Å ³]	1044.74(16)
Z	2
F(000)	526.0
$\mu \ MoK_{\alpha} \ [mm^{-1}]$	1.21
Temperature [K]	273(2)
R _{int}	0.0589
Range of h, k, l	-10/10, -12/12, -19/14
θ _{min/max} (°)	2.308/28.358
GOF on F^2	1.133
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0785 wR2 = 0.2316
R indices [all data]	R1 = 0.0828 wR2 = 0.2338

 Table S2: Crystallographic details of complex 1



Fig. S56. ¹H NMR spectra of the TEMPO-based alkoxyamine compound 1- (cyclohex-2-en-1-yloxy)-2,2,6,6-tetramethylpiperidine.

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