Supplementary Information (SI) for Organic Chemistry Frontiers. This journal is © the Partner Organisations 2024

Synthesis of four regioisomeric Ni(II) azacorroles via oxidative ring-expansion of prefunctionalised norcorroles Sha Li, Shaowei Zhang, Kohei Ohtake, Hiroshi Shinokubo* and Xiaofang Li*

Electronic Supporting Information

Synthesis of four regioisomeric Ni(II) azacorroles via oxidative ring-expansion of prefunctionalised norcorroles

Sha Li,^a Shaowei Zhang,^a Kohei Ohtake,^b Hiroshi Shinokubo^{*,b} and Xiaofang Li^{*,a}

^a Key Laboratory of Theoretical Organic Chemistry and Functional Molecules, Ministry of Education, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 411201, China

^b Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Research Institute for Quantum and Chemical Innovation, Institutes of Innovation for Future Society, and Integrated Research Consortium on Chemical Science (IRCCS), Nagoya University, Furo-cho, Chikusa-ku, 464-8603 Nagoya, Japan

E-mail: lixiaofang@hnust.edu.cn, hshino@chembio.nagoya-u.ac.jp

Table of contents

31G(d)+SDD level.

Figs. S1-S4 NMR spectra of 2. Figs. S5-S8 NMR spectra of 3. Figs. S9-S11 NMR spectra of NC-1. Figs. S12-S15 NMR spectra of NC-2. Figs. S16-S17 NMR spectra of 4. Figs. S18-S19 NMR spectra of 5. Figs. S20-S21 NMR spectra of 6. Figs. S22-S23 NMR spectra of 7. Figs. S24-S25 NMR spectra of 8. Figs. S26-S27 NMR spectra of 9. Figs. S28-S29 NMR spectra of a mixture of 10 and 11. Fig. S30 HR-MS spectrum of 2. Fig. S31 HR-MS spectrum of 3. Fig. S32 HR-MS spectrum of NC-1. Fig. S33 HR-MS spectrum of NC-2. Fig. S34 HR-MS spectrum of 4. Fig. S35 HR-MS spectrum of 5. Fig. S36 HR-MS spectrum of 6. Fig. S37 HR-MS spectrum of 7. Fig. S38 HR-MS spectrum of 8. Fig. S39 HR-MS spectrum of 9. Fig. S40 HR-MS spectrum of a mixture of 10 and 11. Fig. S41 UV-vis absorption spectrum of 2. Fig. S42 UV-vis absorption spectrum of 3. Fig. S43 UV-vis absorption spectrum of NC-1. Fig. S44 UV-vis absorption spectrum of NC-2. Fig. S45 UV-vis absorption spectrum of 4. Fig. S46 UV-vis absorption spectrum of 5. Fig. S47 UV-vis absorption spectrum of 6. Fig. S48 UV-vis absorption spectrum of 7. Fig. S49 UV-vis absorption spectrum of 8. Fig. S50 UV-vis absorption spectrum of 9. Fig. S51 Cyclic and differential pulse voltammograms for 2. Fig. S52 Cyclic and differential pulse voltammograms for 3. Fig. S53 Cyclic and differential pulse voltammograms for NC-1. Fig. S54 Cyclic and differential pulse voltammograms for NC-2. Fig. S55 Cyclic and differential pulse voltammograms for 4. Fig. S56 Cyclic and differential pulse voltammograms for 5. Fig. S57 Cyclic and differential pulse voltammograms for 6. Fig. S58 Cyclic and differential pulse voltammograms for 7. Fig. S59 Cyclic and differential pulse voltammograms for 8. Fig. S60 Cyclic and differential pulse voltammograms for 9. Fig. S61 (A) HOMO-1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole 2 calculated at the B3LYP/6-31G(d)+SDD level. Fig. S62 (A) HOMO-1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole 3 calculated at the B3LYP/6-31G(d)+SDD level. Fig. S63 (A) HOMO–1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole 4 calculated at the B3LYP/6-31G(d)+SDD level. Fig. S64 (A) HOMO-1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole 5 calculated at the B3LYP/6-



Figure S1. ¹H NMR spectrum of 2 (500 MHz, 298 K, CDCl₃).



Figure S2. ¹³C NMR spectrum of 2 (125 MHz, 298 K, CDCl₃).



Figure S3. ¹H–¹H NOESY spectrum of 2 (500 MHz, 298 K, CDCl₃).



Figure S4. Magnified ¹H–¹H NOESY spectrum of 2 (500 MHz, 298 K, CDCl₃).



Figure S5. ¹H NMR spectrum of **3** (500 MHz, 298 K, CDCl₃).



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 Figure S6. ¹³C NMR spectrum of **3** (125 MHz, 298 K, CDCl₃).



Figure S7. ¹H–¹H NOESY spectrum of **3** (500 MHz, 298 K, CDCl₃).



Figure S8. Magnified ¹H–¹H NOESY spectrum of 3 (500 MHz, 298 K, CDCl₃).



Figure S9. ¹H NMR spectrum of NC-1 (500 MHz, 298 K, CDCl₃).



Figure S11. ¹H–¹H NOESY spectrum of **NC-1** (500 MHz, 298 K, CDCl₃).



Figure S12. ¹H NMR spectrum of NC-2 (500 MHz, 298 K, CDCl₃).



Figure S13. ^{13}C NMR spectrum of NC-2 (125 MHz, 298 K, CDCl₃).





Figure S14. ¹H–¹H NOESY spectrum of **NC-2** (500 MHz, 298 K, CDCl₃).



Figure S15. Magnified ¹H, ¹H NOESY spectrum of NC-2 (500 MHz, 298 K, CDCl₃).



Figure S16. ¹H NMR spectrum of 4 (500 MHz, 298 K, CDCl₃).



Figure S17. ¹³C NMR spectrum of 4 (125 MHz, 298 K, CDCl₃).



Figure S19. ¹³C NMR spectrum of **5** (125 MHz, 298 K, CDCl₃).



Figure S21. ¹³C NMR spectrum of 6 (125 MHz, 298 K, CDCl₃).



Figure S22. ¹H NMR spectrum of **7** (500 MHz, 298 K, CDCl₃).



Figure S25. ¹³C NMR spectrum of 8 (125 MHz, 298 K, CDCl₃).



Figure S27. ¹³C NMR spectrum of 9 (125 MHz, 298 K, CDCl₃).



Figure S28. ¹H NMR spectrum of a mixture of 10 and 11 (400 MHz, 298 K, CDCl₃).



Figure S29. ¹³C NMR spectrum of a mixture of **10** and **11** (100 MHz, 298 K, CDCl₃).



Figure S30. HR-APCI-TOF-MS spectrum of **2** (experimental: upper trace; simulated: red bottom trace).



Figure S31. HR-APCI-TOF-MS spectrum of 3 (experimental: upper trace; simulated: red bottom trace).



Figure S32. HR-APCI-TOF-MS spectrum of **NC-1** (experimental: upper trace; simulated: red bottom trace).



Figure S33. HR-APCI-TOF-MS spectrum of **NC-2** (experimental: upper trace; simulated: red bottom trace).



Figure S34. HR-APCI-TOF-MS spectrum of 4 (experimental: upper trace; simulated: red bottom trace).



Figure S35. HR-APCI-TOF-MS spectrum of 5 (experimental: upper trace; simulated: red bottom trace).



Figure S36. HR-APCI-TOF-MS spectrum of 6 (experimental: upper trace; simulated: red bottom trace).



Figure S37. HR-APCI-TOF-MS spectrum of 7 (experimental: upper trace; simulated: red bottom trace).



Figure S38. HR-APCI-TOF-MS spectrum of 8 (experimental: upper trace; simulated: red bottom trace).



Figure S39. HR-APCI-TOF-MS spectrum of 9 (experimental: upper trace; simulated: red bottom trace).



Figure S40. HR-ESI-MS spectrum of a mixture of 10 and 11.



Figure S41. UV-vis absorption spectrum of 2 in CH₂Cl₂.



Figure S42. UV-vis absorption spectrum of 3 in CH₂Cl₂.



Figure S43. UV-vis absorption spectrum of NC-1 in CH₂Cl₂.



Figure S44. UV-vis absorption spectrum of NC-2 in CH₂Cl₂.



Figure S45. UV-vis absorption spectrum of 4 in CH₂Cl₂.



Figure S46. UV-vis absorption spectrum of 5 in CH₂Cl₂.



Figure S47. UV-vis absorption spectrum of 6 in CH₂Cl₂.



Figure S48. UV-vis absorption spectrum of 7 in CH₂Cl₂.



Figure S49. UV-vis absorption spectrum of 8 in CH₂Cl₂.



Figure S50. UV-vis absorption spectrum of 9 in CH₂Cl₂.



Figure S51 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **2** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S52 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **3** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S53 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **NC-1** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S54 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **NC-2** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S55 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **4** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S56 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **5** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S57 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **6** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S58 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **7** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S59 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **8** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.



Figure S60 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **9** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

Compound	State	λ [nm]	energy [eV]	f	Major transition
2	S1	675.12	1.8365	0.0000	HOMO→LUMO (99.5%)
	S ₂	571.08	2.1711	0.0000	HOMO–1→LUMO (99.3%)
	S₃ (Q-band)	553.86	2.2385	0.0614	HOMO–3→LUMO+1 (3.1%) HOMO–1→LUMO+2 (4.7%) HOMO→LUMO+1 (89.0%)
3	S_1	682.68	1.8161	0.0000	HOMO→LUMO (99.5%)
	S ₂	578.88	2.1418	0.0001	HOMO–1→LUMO (99.3%)
	S ₃ (Q-band)	537.23	2.3078	0.0636	HOMO–1→LUMO+1 (2.2%) HOMO–1→LUMO+2 (5.6%) HOMO→LUMO+1 (76.4%) HOMO→LUMO+2 (9.5%)
4	S_1	642.76	1.9289	0.0016	HOMO→LUMO (99.5%)
	S ₂ (Q-band)	562.53	2.2040	0.0949	HOMO-3→LUMO+1 (3.4%) HOMO-1→LUMO (2.1%) HOMO-1→LUMO+2 (3.6%) HOMO→LUMO+1 (87.9%)
5	S ₁	635.25	1.9517	0.0000	HOMO→LUMO (99.7%)
	S ₂ (Q-band)	591.53	2.0960	0.0959	HOMO–3→LUMO+1 (3.2%) HOMO–1→LUMO+ (3.8%) HOMO→LUMO+1 (89.8%)

Table S1. Selected absorption wavelengths, energies, and oscillator strengths (f) of **2**, **3**, **4** and **5** calculated at the TD-B3LYP/6-31G(d)+SDD level.



Figure S61 (A) HOMO–1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole **2** calculated at the B3LYP/6-31G(d)+SDD level.



Figure S62 (A) HOMO–1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole **3** calculated at the B3LYP/6-31G(d)+SDD level.



Figure S63 (A) HOMO–1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole **4** calculated at the B3LYP/6-31G(d)+SDD level.



Figure S64 (A) HOMO–1, (B) HOMO, (C) LUMO and (D) LUMO+1 of azacorrole **5** calculated at the B3LYP/6-31G(d)+SDD level.