Supporting Information for

Copper-Catalyzed Homocoupling of Ketoxime Carboxylates for

Synthesis of Symmetrical Pyrroles

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CONTENTS

1. General Information--------------------------------------------------------------- S2
2. General Procedures for Preparation of Ketoxime Carboxylates---------------------S2
3. Typical Procedure for Copper-Catalyzed Homocoupling of Ketoxime Carboxylates for Synthesis of Symmetrical Pyrroles ---------------------------------------------S2
4. Characterization Data of the Products---------------------------------------------S3-S6
5. Copies of $^1$H and $^{13}$C NMR Spectras ----------------------------------------S7-S40
1. General Information

Column chromatography was carried out on silica gel. 1H NMR spectra were recorded on 400 MHz in CDCl₃, and 13C NMR spectra were recorded on 100 MHz in CDCl₃. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. Ketoxime acetates were synthesized by the following procedure.

2. General Procedures for the Preparation of Ketoxime Carboxylates

The mixture of ketoxime (3.0 mmol), anhydride (6.0 mmol, 2.0 eq), was stirred at room temperature to 100 °C for 3h. The reaction mixture was cooled to room temperature, diluted with EtOAc (25 mL) and washed with H₂O (20 mL) and brine (10 mL). The organic layers were dried over anhydrous Na₂SO₄ and evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the ketoxime carboxylates 1 with hexane/ethyl acetate as the eluent.

3. Typical Procedure for Copper-Catalyzed Homocoupling of Ketoxime Carboxylates for Synthesis of Symmetrical Pyrroles

![Chemical Structures]

In a 25 mL round bottom flask, the ketoxime acetate 1 (0.3 mmol), CuBr (5 mol%, 2.2 mg) and NaHSO₃ (0.36 mmol, 37.5 mg) was stirred in DMSO (3.0 mL) at 140 °C under Ar for 2h. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature. The reaction was quenched with H₂O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding pyrrole 2 with hexane/ethyl acetate as the eluent.
4. Characterization Data of the Products

2a: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.89$ (s, 1 H), $\delta = 7.38$-7.29 (m, 8 H), $\delta = 7.17$-7.14 (t, $J = 7.2$ Hz, 2 H), $\delta = 2.14$ (s, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 133.5$, 128.7, 126.6, 126.1, 117.3, 10.4. HRMS Calcd (ESI) m/z for C$_{18}$H$_{16}$N: [M-H]$^-$ 246.1277, found: 246.1275.

2b: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.85$ (s, 1 H), $\delta = 7.26$ (s, 4 H), $\delta = 7.13$ (d, $J = 5.6$ Hz, 4 H), $\delta = 2.28$ (s, 6 H), $\delta = 2.13$ (s, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 135.7$, 130.8, 129.4, 126.5, 116.8, 21.1, 10.4. HRMS Calcd (ESI) m/z for C$_{20}$H$_{20}$N: [M-H]$^-$ 274.1590, found: 274.1597.

2c: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 10.61$ (s, 1 H), $\delta = 7.45$-7.40 (m, 8 H), $\delta = 2.10$ (s, 6 H), $\delta = 1.29$ (s, 18 H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta = 147.7$, 131.1, 128.1, 126.6, 125.1, 115.6, 34.2, 31.2, 10.6. HRMS Calcd (ESI) m/z for C$_{26}$H$_{32}$N: [M-H]$^-$ 358.2529, found: 358.2535.

2d: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.83$ (s, 1 H), $\delta = 7.13$-7.04 (m, 6 H), $\delta = 2.19$ (s, 12 H), $\delta = 2.11$ (s, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 136.8$, 134.4, 131.3, 129.9, 128.3, 127.8, 124.1, 116.6, 19.9, 19.4, 10.4. HRMS Calcd (ESI) m/z for C$_{22}$H$_{24}$N: [M-H]$^-$ 302.1903, found: 302.1908.

2e: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.84$ (s, 1 H), $\delta = 7.12$ (d, $J = 5.6$ Hz, 2 H), $\delta = 7.07$ (s, 2 H), $\delta = 7.02$ (d, $J = 7.2$ Hz, 2 H), $\delta = 2.72$ (s, 8 H), $\delta = 2.12$ (s, 6 H), $\delta = 1.73$ (s, 8 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 137.3$, 135.0, 130.9, 129.4, 128.3, 127.1, 124.0, 116.6, 29.5, 29.1, 23.1, 10.4. HRMS Calcd (ESI) m/z for C$_{26}$H$_{28}$N: [M-H]$^-$ 354.2216, found: 354.2204.
2f: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.47 (s, 1 H), $\delta$ = 7.08-7.04 (m, 4 H), $\delta$ = 6.96 (d, $J$ = 7.6 Hz, 2 H), $\delta$ = 2.25 (s, 6 H), $\delta$ = 2.19 (s, 6 H), $\delta$ = 1.91 (s, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 134.8, 133.7, 133.2, 131.2, 130.2, 127.9, 127.4, 116.1, 20.8, 19.8, 10.2. HRMS Calcd (ESI) m/z for C$_{22}$H$_{24}$N: [M-H]$^-$ 302.1903, found: 302.1892.

2g: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.46 (s, 1 H), $\delta$ = 7.12 (d, $J$ = 7.6 Hz, 2 H), $\delta$ = 7.01 (s, 2 H), $\delta$ = 6.97-6.94 (t, $J$ = 4.0 Hz, 2 H), $\delta$ = 2.27 (s, 6 H), $\delta$ = 2.20 (s, 6 H), $\delta$ = 1.90 (s, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 136.9, 136.8, 131.1, 130.5, 127.2, 126.3, 124.1, 116.1, 21.1, 20.3, 10.2. HRMS Calcd (ESI) m/z for C$_{22}$H$_{24}$N: [M-H]$^-$ 302.1903, found: 302.1906.

2h: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ = 10.56 (s, 1 H), $\delta$ = 7.43 (d, $J$ = 8.0 Hz, 4 H), $\delta$ = 6.97 (d, $J$ = 8.0 Hz, 4 H), $\delta$ = 3.76 (s, 6 H), $\delta$ = 2.08 (s, 6 H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ = 157.3, 128.0, 127.5, 126.5, 114.8, 113.9, 55.1, 10.6. HRMS Calcd (ESI) m/z for C$_{20}$H$_{20}$NO$_2$: [M-H]$^-$ 306.1489, found: 306.1485.

2i: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 9.65 (s, 1 H), $\delta$ = 6.97 (d, $J$ = 2.4 Hz, 2 H), $\delta$ = 6.78 (d, $J$ = 9.2 Hz, 2 H), $\delta$ = 6.65-6.62 (m, 2 H), $\delta$ = 3.72 (s, 6 H), $\delta$ = 3.69 (s, 6 H), $\delta$ = 2.14 (s, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 153.5, 150.3, 124.2, 123.0, 117.4, 115.4, 112.2, 111.2, 56.2, 55.6, 11.1. HRMS Calcd (ESI) m/z for C$_{22}$H$_{25}$NNaO$_4$: [M+Na]$^+$ 390.1676, found: 390.1685.

2j: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ = 10.78 (s, 1 H), $\delta$ = 7.50 (d, $J$ = 4.8 Hz, 4 H), $\delta$ = 7.24-7.20 (m, 4 H), $\delta$ = 2.07 (s, 6 H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ = 160.5 (d, $J_F$ = 241.3 Hz), 130.1, 128.6 (d, $J_F$ = 8.4 Hz), 127.3, 115.9, 115.2 (d, $J_F$ = 20.5 Hz), 10.5. HRMS Calcd (ESI)
m/z for C_{18}H_{14}F_{2}N: [M-H] - 282.1089, found: 282.1090.

2k: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 10.88$ (s, 1 H), $\delta = 7.52$ (d, $J = 8.0$ Hz, 4 H), $\delta = 7.43$ (d, $J = 8.0$ Hz, 4 H), $\delta = 2.08$ (s, 6 H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta = 132.2$, 130.1, 128.4, 128.3, 127.6, 116.9, 10.6. HRMS Calcd (ESI) m/z for C_{18}H_{14}Cl_{2}N: [M-H] - 314.0498, found: 314.0489.

2l: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 10.88$ (s, 1 H), $\delta = 7.56$ (d, $J = 8.0$ Hz, 4 H), $\delta = 7.45$ (d, $J = 8.0$ Hz, 4 H), $\delta = 2.08$ (s, 6 H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta = 132.5$, 131.3, 128.6, 127.6, 118.5, 117.0, 10.5. HRMS Calcd (ESI) m/z for C_{18}H_{14}Br_{2}N: [M-H] - 401.9488, found: 401.9482.

2m: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.90$ (s, 1 H), $\delta = 7.37$ (d, $J = 7.2$ Hz, 4 H), $\delta = 7.32$-7.29 (t, $J = 7.2$ Hz, 4 H), $\delta = 7.17$-7.14 (t, $J = 6.4$ Hz, 2 H), $\delta = 2.61$-2.56 (m, 4 H), $\delta = 1.16$-1.13 (t, $J = 7.2$ Hz, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 133.7$, 128.7, 128.4, 126.6, 126.2, 123.5, 17.8, 16.2. HRMS Calcd (ESI) m/z for C_{20}H_{20}N: [M-H] - 274.1590, found: 274.1591.

2n: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.03$ (s, 1 H), $\delta = 7.50$ (d, $J = 7.6$ Hz, 4 H), $\delta = 7.46$-7.42 (t, $J = 7.2$ Hz, 4 H), $\delta = 7.30$-7.27 (t, $J = 7.6$ Hz, 2 H), $\delta = 2.66$-2.62 (t, $J = 8.0$ Hz, 4 H), $\delta = 1.69$-1.62 (m, 4 H), $\delta = 1.04$-1.00 (t, $J = 7.6$ Hz, 6 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 133.9$, 128.7, 128.5, 126.5, 126.1, 122.3, 27.2, 24.9, 14.6. HRMS Calcd (ESI) m/z for C_{22}H_{24}N: [M-H] - 302.1903, found: 302.1904.

2o: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.25$ (s, 1 H), $\delta = 7.10$-7.08 (m, 6 H), $\delta = 6.95$ (s, 6 H), $\delta = 2.85$-2.82 (t, $J = 7.6$ Hz, 4 H), $\delta = 2.58$ (d, $J = 6.0$ Hz, 4 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta =$
134.9, 130.9, 129.0, 128.3, 126.5, 125.0, 119.1, 118.3, 29.7, 19.9. HRMS Calcd (ESI) m/z for C_{20}H_{16}N: [M-H] - 270.1277, found: 270.1285.

2p: ^1^H NMR (CDCl₃, 400 MHz): δ = 8.38 (s, 1 H), δ = 7.18 (d, J = 4.0 Hz, 10 H), δ = 7.08-7.06 (m, 6 H), δ = 7.01-6.99 (m, 4 H); ^1^C NMR (CDCl₃, 100 MHz): δ = 135.3, 132.7, 130.9, 128.9, 128.5, 127.9, 127.2, 126.6, 125.9, 123.1. HRMS Calcd (ESI) m/z for C_{28}H_{20}N: [M-H] - 370.1590, found: 370.1606.

2q: ^1^H NMR (CDCl₃, 400 MHz): δ = 8.78 (s, 1 H), δ = 7.59 (d, J = 7.6 Hz, 4 H), δ = 7.45-7.41 (t, J = 7.2 Hz, 4 H), δ = 7.29-7.26 (t, J = 7.6Hz, 2 H), δ = 6.64 (d, J = 2 Hz, 2 H); ^1^C NMR (CDCl₃, 100 MHz): δ = 133.1, 132.4, 128.8, 126.2, 123.7, 107.8. HRMS Calcd (ESI) m/z for C_{16}H_{14}N: [M+H]^+ 220.1120, found: 220.1109.
5. Copies of $^1$H and $^{13}$C NMR Spectra