Supporting Information

Metal-Free Catalyzed Oxidative Trimerization of Indoles by Using NaNO₂ to Construct Quaternary Carbon Centers: The Synthesis of 2-(1*H*-indol-3-yl)-2,3'-biindolin-3-ones

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CONTENTS

1. General Methods and Materials	S2
2. General Procedure and Spectroscopic Data of the Products 7	S2
3. Copies of ¹ H, ¹³ C Spectra	S5
4. Reference.....	S11

1. General Methods

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^1H and ^{13}C NMR spectra. CDCl_3 or $\text{DMSO}-d_6$ was used as the NMR solvent. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis were carried out on a Perkin-Elmer 240B instrument. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

Materials

Commercially available starting materials and solvents were used as supplied, without further purification.

2. General Procedure for the Preparation of 7.

To a solution of indole (0.5 mmol) and NaNO_2 (0.5 mmol) in pyridine (0.6 mL) was added $\text{CH}_3\text{SO}_3\text{H}$ (1.0 mmol) under atmosphere and the mixture was stirred at rt for overnight. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:2) to yield the corresponding product.

Spectroscopic Data of the Products 7.

7a-7h, 7m, 7n, 7q and 7r were known compounds and have been reported by this group.¹

5,5'-Dinitro-2-(5-nitro-1*H*-indol-3-yl)-2,3'-biindolin-3-one (7i)

Yellow solid, mp: 214-216 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max} : 3388, 1621, 1332 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 12.00 (s, 1H, NH), 11.99 (s, 1H, NH), 9.98 (s, 1H, NH), 8.42 (dd, J = 9.1, 2.4 Hz, 1H, Ar-H), 8.37 (d, J = 2.4 Hz, 1H, Ar-H), 8.22 (d, J = 2.2 Hz, 2H, Ar-H), 7.98 (dd, J = 9.0, 2.2 Hz, 2H, Ar-H), 7.62 (d, J = 2.4 Hz, 2H, Ar-H), 7.59 (d, J = 9.0 Hz, 2H, Ar-H), 7.12 (d, J = 9.1 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 198.6, 162.9, 141.0, 140.7, 138.8, 133.7, 128.4, 124.7, 122.8, 117.5, 117.4, 116.7, 115.1, 113.1, 112.3, 68.9. MS (ESI): 499 ($\text{M}+\text{H}^+$, 100), 521 ($\text{M}+\text{Na}^+$, 25). Anal calcd for $\text{C}_{24}\text{H}_{14}\text{N}_6\text{O}_7$: C, 57.84; H, 2.83; N, 16.86. Found C, 57.52;

H, 3.17; N, 16.49.

2-(5-Cyano-1*H*-indol-3-yl)-3-oxo-2,3'-biindoline-5,5'-dicarbonitrile (7j)

Yellow amorphous solid. IR (KBr) $\nu_{\max}$: 3415, 2223, 1626, 1119 cm^{-1} . ^1H NMR (100 MHz, $\text{DMSO-}d_6$): δ 11.80 (s, 2H, NH), 9.44 (s, 1H, NH), 8.03 (d, $J = 1.6$ Hz, 1H, Ar-H), 7.87 (dd, $J = 8.6, 1.6$ Hz, 1H, Ar-H), 7.63 (d, $J = 1.6$ Hz, 2H, Ar-H), 7.57 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.47 (s, 1H, Ar-H), 7.46 (s, 1H, Ar-H), 7.42 (dd, $J = 8.5, 1.6$ Hz, 2H, Ar-H), 7.07 (d, $J = 8.6$ Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 198.5, 161.7, 141.0, 139.3, 131.3, 127.1, 125.8, 125.4, 124.6, 121.0, 119.7, 117.5, 113.9, 113.8, 113.0, 101.4, 99.4, 67.9. MS (ESI): 439 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{27}\text{H}_{14}\text{N}_6\text{O}$: C, 73.96; H, 3.22; N, 19.17. Found C, 73.63; H, 3.49; N, 18.84.

6,6'-Dichloro-2-(6-chloro-1*H*-indol-3-yl)-2,3'-biindolin-3-one (7k)

Yellow solid, mp: 197-199 $^{\circ}\text{C}$ (from EtOAc/PE = 1:2). IR (KBr) $\nu_{\max}$: 3412, 1668, 1611, 1452, 804 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.43 (s, 2H, NH), 8.50 (s, 1H, NH), 7.66 (d, $J = 7.6$ Hz, 1H, Ar-H), 7.57 (d, $J = 7.6$ Hz, 1H, Ar-H), 7.31 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.19 (s, 1H, Ar-H), 7.17 (s, 1H, Ar-H), 7.18 (d, $J = 7.6$ Hz, 2H, Ar-H), 6.94 (t, $J = 8.0$ Hz, 2H, Ar-H), 6.89 (t, $J = 7.6$ Hz, 1H, Ar-H), 5.60 (s, 1H, NH). ^{13}C NMR (100 MHz, CDCl_3): δ 199.5, 161.1, 142.9, 137.8, 126.8, 126.5, 125.6, 124.6, 122.0, 119.4, 118.1, 116.7, 114.1, 111.8, 111.5, 68.2. MS (ESI): 466 ($\text{M}+\text{H}^+$, 100), 468 ($\text{M}+\text{H}^+$, 100), 470 ($\text{M}+\text{H}^+$, 30). Anal calcd for $\text{C}_{24}\text{H}_{14}\text{Cl}_3\text{N}_3\text{O}$: C, 61.76; H, 3.02; N, 9.00. Found C, 62.08; H, 2.84; N, 8.75.

7,7'-Dimethoxy-2-(7-methoxy-1*H*-indol-3-yl)-2,3'-biindolin-3-one (7o)

Yellow solid, mp: 209-210 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max} : 3406, 1660, 1615, 1452, 1116, 1061 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.30 (s, 2H, NH), 7.37 (d, $J = 7.8$ Hz, 1H, Ar-H), 7.16 (s, 1H, Ar-H), 7.15 (s, 1H, Ar-H), 7.05 (d, $J = 8.1$ Hz, 2H, Ar-H), 6.99 (d, $J = 7.8$ Hz, 1H, Ar-H), 6.92 (t, $J = 8.1$ Hz, 2H, Ar-H), 6.86 (t, $J = 7.8$ Hz, 1H, Ar-H), 6.62 (d, $J = 7.8$ Hz, 2H, Ar-H), 5.58 (s, 1H, NH), 3.95 (s, 6H, 2XOCH_3), 3.88 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 201.0, 151.9, 146.7, 146.2, 127.6, 127.1, 123.5, 120.6, 120.2, 119.3, 116.7, 115.8, 115.7, 113.3, 102.0, 68.6, 55.4, 55.3. MS (ESI): 454 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_4$: C, 71.51; H, 5.11; N, 9.27. Found C, 71.43; H, 5.30; N, 8.92.

7,7'-Dinitro-2-(7-nitro-1*H*-indol-3-yl)-2,3'-biindolin-3-one (7p)

Yellow solid, mp: 302-305 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max} : 3411, 1630, 1513, 1478, 1309 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 10.07 (s, 2H, NH), 8.47 (dd, $J = 7.5, 2.2$ Hz, 1H, Ar-H), 8.19 (d, $J = 8.0$ Hz, 2H, Ar-H), 8.08 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.92 (s, 1H, NH), 7.76 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.47 (d, $J = 2.2$ Hz, 2H, Ar-H), 7.15 (t, $J = 8.0$ Hz, 2H, Ar-H), 7.05 (t, $J = 7.5$ Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.6, 152.0, 133.4, 133.0, 131.9, 130.5, 128.7, 128.5, 126.1, 126.0, 122.9, 120.1, 120.0, 118.5, 115.0, 67.7. MS (ESI): 499 ($\text{M}+\text{H}^+$, 100), 521 ($\text{M}+\text{Na}^+$, 20). Anal calcd for $\text{C}_{24}\text{H}_{14}\text{N}_6\text{O}_7$: C, 57.84; H, 2.83; N, 16.86. Found C, 60.03; H, 2.52; N, 16.67.

1,1'-Diethyl-2-(1-ethyl-1*H*-indol-3-yl)-2,3'-biindolin-3-one (7s)

Yellow solid, mp: 238-241 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max} : 3413, 1699, 1609, 1486, 1463, 740 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, $J = 7.4$ Hz, 1H, Ar-H), 7.56 (dt, $J = 8.3, 1.2$ Hz, 1H, Ar-H), 7.35 (t, $J = 7.9$ Hz, 4H, Ar-H), 7.18 (t, $J = 7.9$ Hz, 2H, Ar-H), 7.06 (s, 2H, Ar-H), 6.97 (t, $J = 7.4$ Hz, 2H, Ar-H), 6.86 (d, $J = 8.3$ Hz, 1H, Ar-H), 6.76 (t, $J = 7.4$ Hz, 1H, Ar-H), 4.13 (q, $J = 7.3$ Hz, 4H, 2XCH_2), 3.59 (q, $J = 7.1$ Hz, 2H, CH_2), 1.43 (t, $J = 7.3$ Hz, 6H, 2XCH_3), 0.67 (t, $J = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 200.7, 158.7, 137.5, 136.7, 128.2, 126.6, 125.9, 121.8, 121.5, 119.2, 118.7, 116.4, 111.9, 109.3, 108.0, 72.7, 41.0, 38.2, 15.5, 13.3. MS (ESI): 448 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{30}\text{H}_{29}\text{N}_3\text{O}$: C, 80.51; H, 6.53; N, 9.39. Found C, 80.17; H, 6.74; N, 9.25.

3. Copies of ^1H , ^{13}C NMR Spectra

Compound **7i**

Compound 7j

Compound 7k

Compound **7o**

Compound 7p

Compound 7s

4. Reference

1. Qin, W. B.; Chang, Q.; Bao, Y. H.; Wang, N.; Chen, Z. W.; Liu, L. X. Metal-free catalyzed oxidative trimerization of indoles by using TEMPO in air: a biomimetic approach to 2-(1*H*-indol-3-yl)-2,3'-biindolin-3-ones. *Org. Biomol. Chem.* **2012**, *10*, 8814-8821.