Supporting Information

Fe-Catalyzed Cycloaddition of Indoles and o-Phthalaldehyde for the Synthesis of Benzo[b]carbazoles with TMSCl- or Acid-responsive Properties

Jin-Feng Zou, Hu Wang, Li Li,* Zheng Xu, Ke-Fang Yang and Li-Wen Xu*

Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education (MOE), Hangzhou Normal University, Hangzhou 311121, and Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education (MOE) and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi’an 710062, P. R. China.
Fax: (+86)-571-28867756; E-mail: liwenxu@hznu.edu.cn, licpxulw@yahoo.com

Table of Contents

1. General information..........................................................................................................1
2. Preparation of indolyl benzo[b]carbazoles..............................................................1
3. The analytical and spectral characterization data of reaction products................3
4. FL analysis of indolyl benzo[b]carbazoles (Figure S1-S5)...............................7
5. $^1$H/$^{13}$C NMR analysis..............................................................................................12
1. **General information**

All reagents and solvents were used directly without purification. Flash column chromatography was performed over silica (200-300 mesh). $^1$H-NMR and $^{13}$C-NMR spectra were recorded at 400 and 100 MHz, respectively on Advance (Brucker) 400 MHz Nuclear Magnetic Resonance Spectrometer. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: DMSO-D6 ($^1$H-NMR: $\delta$ 2.50, singlet; $^{13}$C-NMR: $\delta$ 39.56, singlet). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed on VERTEX70 IR (Bruker). The data were collected over 32 scans with a resolution of 4 cm$^{-1}$ at room temperature. HRMS (Analyzer: TOF) was reported in units of mass of charge ratio (m/z).

2. **Preparation of indolyl benzo[b]carbazoles**

In a typical experiment, to a mixture of phthalaldehyde (5 mmol) and Indoles (15
equiv), FeCl₂ (10 mol%) was added to methanol (10 ml), and the resulting solution was stirred at room temperature for 12 h (monitored by TLC). The crude mixture was directly purified by column chromatography (silica gel, petroleum ethyl acetate mixtures) to obtain pure products.

3. The analytical and spectral characterization data of reaction products

1) 3a: 6-(1H-indol-3-yl)-5H-benzo[b]carbazole

A pale green solid, 88% total yield (S₄/₄ = 83:17). ¹H-NMR (400 MHz, DMSO-D6) δ (ppm) 11.60 (s, 1H), 10.52 (s, 1H), 8.71 (s,1H), 8.28 (d, J = 7.2, 1H), 8.13-8.05 (m, 1H), 7.94-7.61 (m, 3H), 7.45-7.32 (m, 4H), 7.22-7.17 (m, 2H), 7.04-6.90 (m, 2H); ¹³C-NMR (100 MHz, DMSO-D6) δ (ppm) 142.66, 139.15, 136.63, 131.33, 128.65, 128.04, 127.59, 127.05, 125.81, 125.06, 124.75, 124.37, 122.51, 122.05, 121.38, 120.88, 119.44, 119.11, 118.50, 117.44, 111.91, 111.37, 111.07, 109.47; IR (νmax/cm⁻¹): 3932.3, 3406.4, 3238.2, 2068.1, 1617.1, 1400.4, 1129.9, 743.1, 623.2, 488.0, 419.9; HRMS (MALDI-TOF) Calcd for C₂₄H₁₆N₂[M+H]+: 333.1313; found: 333.1323.

2) 3b: 2-methyl-6-(5-methyl-1H-indol-3-yl)-5H-benzo[b]carbazole

A yellow solid, 79% total yield (S₃/₄ = 98:2). ¹H-NMR (400 MHz, DMSO-D6) δ (ppm)
11.45 (s, 1H), 10.35 (s, 1H), 8.65 (s, 1H), 8.11-8.08 (m, 2H), 7.78 (d, J = 8, 1H), 7.64 (d, J = 2.4, 1H), 7.50 (d, J = 8.4, 1H), 7.40-7.24 (m, 4H), 7.02 (d, J = 9.2, 1H), 6.83 (s, 1H), 2.50 (s, 3H), 2.25 (s, 3H); 13C-NMR (100 MHz, DMSO-D6) δ (ppm) 140.79, 139.44, 134.94, 131.31, 128.58, 128.21, 127.87, 127.48, 127.06, 125.71, 125.02, 124.59, 124.21, 122.96, 122.59, 121.87, 120.73, 118.86, 117.19, 111.56, 111.33, 110.79, 108.94, 21.18, 21.08; IR (v\text{max}/cm\textsuperscript{-1}): 3930.2, 3413.3, 3237.9, 2067.9, 1617.4, 1399.2, 1131.3, 798.7, 619.8, 418.9, 417.1; HRMS (MALDI-TOF) Calcd for C\textsubscript{26}H\textsubscript{20}N\textsubscript{2} [M+H\textsuperscript{+}]: 361.1626; found: 361.1702.

3) 3c: 4-methyl-6-(7-methyl-1H-indol-3-yl)-5H-benzo[b]carbazole

![Chemical structure](image)

A white solid, 64% total yield \(\text{S}_{3c} = 73:27\). \textsuperscript{1}H-NMR (400 MHz, DMSO-D6) δ (ppm) 1.45 (s, 1H), 9.93 (s, 1H), 8.63 (s, 1H), 8.07-7.89 (m, 2H), 7.72-7.50 (m, 2H), 7.31-7.04 (m, 4H), 6.93-6.81 (m, 3H), 2.58 (s, 3H), 2.42 (s, 3H); 13C-NMR (100 MHz, DMSO-D6) δ (ppm) 140.79, 139.95, 131.32, 128.58, 128.20, 127.87, 127.48, 127.06, 125.71, 125.03, 124.60, 124.20, 122.96, 122.59, 121.86, 120.73, 118.86, 117.18, 111.56, 111.33, 110.79, 108.95, 21.18, 21.08; IR (v\text{max}/cm\textsuperscript{-1}): 3418.5, 2067.4, 1615.2, 1400.1, 1131.3, 775.5, 746.2, 616.1, 418.8; HRMS (MALDI-TOF) Calcd for C\textsubscript{26}H\textsubscript{20}N\textsubscript{2} [M+Na\textsuperscript{+}]: 361.1626; found: 361.1702.

4) 3d: 2-methoxy-6-(5-methoxy-1H-indol-3-yl)-5H-benzo[b]carbazole
A yellow solid, 85% total yield ($S_{3/4} = >99:1$). $^1$H-NMR (400 MHz, DMSO-D6) $\delta$ (ppm) 11.42 (s, 1H), 10.26 (s, 1H), 8.71 (s, 1H), 8.11-8.09 (m, 1H), 7.88-7.78 (m, 2H), 7.65 (d, $J = 2.4$, 1H), 7.49 (d, $J = 8.8$, 1H), 7.38-7.33 (m, 3H), 7.09-7.06 (m, 1H), 6.86-6.84 (m, 1H), 6.46 (d, $J = 2$, 1H), 3.89 (s, 3H), 3.52 (s, 3H); $^{13}$C-NMR (100 MHz, DMSO-D6) $\delta$ (ppm) 153.53, 153.01, 139.67, 137.34, 131.72, 131.06, 128.67, 127.80, 127.75, 126.39, 125.05, 124.86, 124.24, 122.88, 121.90, 117.49, 115.87, 112.58, 111.76, 111.62, 111.34, 109.28, 104.20, 101.07, 55.71, 55.19; IR ($\nu_{\text{max}}$/cm$^{-1}$): 3411.3, 2943.9, 2829.6, 2067.1, 1621.7, 1485.6, 1396.4, 1158.9, 783.9, 746.2, 615.5; HRMS (MALDI-TOF) Calcd for C$_{26}$H$_{20}$N$_2$O$_2$ [M]$^+$: 392.1525; found: 392.1537.

5) 3e: 2-bromo-6-(5-bromo-1H-indol-3-yl)-5H-benzo[b]carbazole

A yellow solid, 65% total yield ($S_{3/4} = >99:1$). $^1$H-NMR (400 MHz, DMSO-D6) $\delta$ (ppm) 10.84 (s, 1H), 10.72 (s, 1H), 8.81 (s, 1H), 8.53 (d, $J = 1.6$, 1H), 8.13-8.10 (m, 1H), 7.80-7.73 (m, 2H), 7.60-7.55 (m, 2H), 7.41-7.30 (m, 4H), 7.10 (d, $J = 1.2$, 1H); $^{13}$C-NMR (100 MHz, DMSO-D6) $\delta$ (ppm) 141.33, 139.31, 135.29, 131.53, 129.47, 129.30, 128.82, 128.01, 127.61, 125.04, 124.70, 124.54, 123.92, 123.58, 123.51, 122.41, 121.70, 118.62, 113.98, 112.86, 111.74, 110.65, 110.39, 108.80; IR ($\nu_{\text{max}}$/cm$^{-1}$): 3414.9, 3237.9, 2067.2, 1617.4, 1398.4, 1279.1, 1131.6, 616.5, 473.9, 419.2; HRMS (MALDI-TOF) Calcd for C$_{24}$H$_{14}$Br$_2$N$_2$ [M]$^+$: 488.9599; found: 488.9591.
6) 3f: 2-chloro-6-(5-chloro-1H-indol-3-yl)-5H-benzo[b]carbazole

A pale green solid, 71% total yield ($S_{3/4} = >99:1$). $^1$H-NMR (400 MHz, DMSO-D6) δ (ppm) 11.84 (s, 1H), 10.71 (s, 1H), 8.80 (s, 1H), 8.39 (s, 1H), 8.12-8.10 (m, 1H), 7.82-7.74 (m, 2H), 7.63 (d, J = 8.4, 1H), 7.45-7.37 (m, 4H), 7.22-7.19 (m, 1H), 7.70 (s, 1H); $^{13}$C-NMR (100 MHz, DMSO-D6) δ (ppm) 141.05, 139.47, 135.07, 131.51, 128.82, 128.61, 128.00, 127.77, 126.85, 125.01, 124.72, 123.91, 123.84, 123.72, 122.77, 122.38, 121.41, 120.57, 118.57, 118.18, 113.51, 112.36, 110.72, 108.94; IR ($ν_{max}$/cm$^\text{-1}$): 3410.1, 2918.3, 2067.5, 1618.0, 1484.3, 1396.8, 1292.4, 1131.5, 797.4, 615.0.
4. FL analysis of indolyl benzo[b]carbazoles

(a) Solvent Effect

(b) FL of 3a-3f

Figure S1. Solvents effect on the fluorescence emission spectrum of 3e (5 × 10^{-6} M) in various solvents.
Figure S2. Changes observed in the fluorescence emission spectrum of 3e ($5 \times 10^{-6}$ M) upon addition of TFA (1 ~ 100 eq.) in CH$_3$CN.
Figure S3. Changes observed in the fluorescence emission spectrum of 3e ($5 \times 10^{-6}$ M) upon addition of TMSCl (1 ~ 100 eq.) in CH$_3$CN.
**Figure S4.** Changes observed in the fluorescence emission spectrum of the mixture of 3e (5 × 10^{-6} M) with TMSCI (40 eq.) upon addition of Et_{3}N (1-100 eq.) in CH_{3}CN.
**Figure S5.** Changes observed in the fluorescence emission spectrum of the mixture of 3e ($5 \times 10^{-6}$ M) upon addition of Et$_3$N and TMSCl (1:1, 1-100 eq.) in CH$_3$CN.
5. $^1$H/$^{13}$C NMR analysis

Product 3a:
Product 3b:
Product 3c:
Product 3d:
Product 3e:

![Chemical Structure Image]

![Chemical Structure Image]
Product 3f: