### **Supporting Information**

#### for

# A new approach for the synthesis of bisindoles through AgOTf as catalyst

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# <sup>1</sup>H NMR for all synthesized compounds, <sup>13</sup>C APT NMR spectra for compounds 6ac and 6ad and crystallographic data for compounds 6ad and 6al

**General experimental methods**. Purification of reaction products was carried out by flash chromatography using silical-gel (0.063-0.200 mm). Analytical thin layer chromatography was performed on 0.25 mm silical gel 60-F plates. <sup>1</sup>H-NMR spectra were recorded at 400 MHz; <sup>13</sup>APT-NMR spectra were recorded at 100 MHz; CDCl<sub>3</sub> as the solvent. Chemical shifts were reported in the  $\delta$  scale relative to central line of CDCl<sub>3</sub> (77 ppm) for <sup>13</sup>APT-NMR.

**Materials**. All commercially available solvents and reagents were used as received. The <sup>1</sup>H and <sup>13</sup>C NMR spectra for compounds **6aa** [1], **6ab** [2], **6ac** [3], **6ad** [4], **6ae** [5], **6af** [6], **6ag** [7], **6ah** [8], **6ai** [9], **6aj** [4], **6ak** [3], **6ba** [10], **6ca** [11], **6da** [12], **6ea** [12], are consistent with values previously reported in the literature.

<sup>1</sup>H NMR spectrum for the crude of the reaction giving 6aa (400 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectrum for the crude of the reaction giving 6ab (400 MHz, CDCl<sub>3</sub>)





<sup>13</sup>C NMR spectrum for compound 6ac (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectrum for compound 6ad (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum for compound 6ad (100 MHz, CDCI<sub>3</sub>)



ppm (t1)



<sup>1</sup>H NMR spectrum for compound 6af (400 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR spectrum for compound 6ag (400 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectrum for compound 6ah (400 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR spectrum for the crude of the reaction giving 6ai (400 MHz,  $CDCI_3$ )

<sup>1</sup>H NMR spectrum compound 6aj (400 MHz, CDCI<sub>3</sub>)







<sup>1</sup>H NMR spectrum for compound 6ba (400 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR spectrum for the crude of the reaction giving 6ca (400 MHz, CDCl<sub>3</sub>)

<sup>1</sup>H NMR spectrum for compound 6da (400 MHz, CDCl<sub>3</sub>)



## <sup>1</sup>H NMR spectrum for compound 6ea (400 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectrum for compound 6al (400 MHz, CDCl<sub>3</sub>)



#### X-RAY CRYSTALLOGRAPHY

The crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of an Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo K $\alpha$  radiation ( $\lambda$ = 0.71073 Å). Scan type:  $\omega$ . Absorption correction based on multiple scans was applied using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm [13]. The structures were solved by direct methods and refined on F<sup>2</sup> using the program SHELXL-97 [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model, with the exception of NH atoms. Refinements were carried out by fullmatrix least-squares on F<sup>2</sup> for all data.



Crystal data of **6ad**:  $[C_{21}H_{22}N_2]$ , orthorhombic,  $Pna2_1$ , a = 11.099(2) Å, b = 19.895(4) Å, c = 7.6414(15) Å, Z = 4,  $M_r = 302.41$  g mol<sup>-1</sup>, V = 1687.3(6) Å<sup>3</sup>,  $D_{calcd} = 1.190$  g cm<sup>-3</sup>,  $\lambda$ (Mo K $\alpha$ ) = 0.71073 Å, T = 100 K,  $\mu = 0.070$  mm<sup>-1</sup>, 9103 reflections collected, 3055 unique ( $R_{int} = 0.0565$ ),  $R1(F_0) = 0.0502$  [ $I > 2\sigma(I)$ ], wR2 ( $F_0^2$ ) = 0.0852 (all data), GOF = 1.012. CCDC 1007024.



Crystal data of **6al**:  $[C_{18}H_{16}N_2]$ , orthorhombic,  $P2_12_12_1$ , a = 6.5030(13) Å, b = 9.927(2) Å, c = 21.129(4) Å, Z = 4,  $M_r = 260.33$  g mol<sup>-1</sup>, V = 1363.9(3) Å<sup>3</sup>,  $D_{calcd} = 1.268$  g cm<sup>-3</sup>,  $\lambda$ (Mo K $\alpha$ ) = 0.71073 Å, T = 173 K,  $\mu = 0.075$  mm<sup>-1</sup>, 7915 reflections collected, 2518 unique ( $R_{int} = 0.0438$ ),  $R1(F_0) = 0.0374$  [ $I > 2\sigma(I)$ ], wR2 ( $F_0^2$ ) = 0.0692 (all data), GOF = 1.031. CCDC 1007025.

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