

One-pot Multi-component Synthesis of Mono- and Bis-indolyimidazole Derivatives Using Zn^{2+} @KSF and Their Antibacterial Activity

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The preparation of mono- and bis-indolyimidazole derivatives using Zn^{2+} supported on montmorillonite KSF (Zn^{2+} @KSF) as an efficient heterogeneous catalyst is described. The structures of these compounds were characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy. The antibacterial activity of the selected products was examined. Some products exhibit promising activities.

Key words: Zn^{2+} @KSF, Clay Catalyst, Bis-indole, Indolyimidazole, Multicomponent Reaction (MCR)

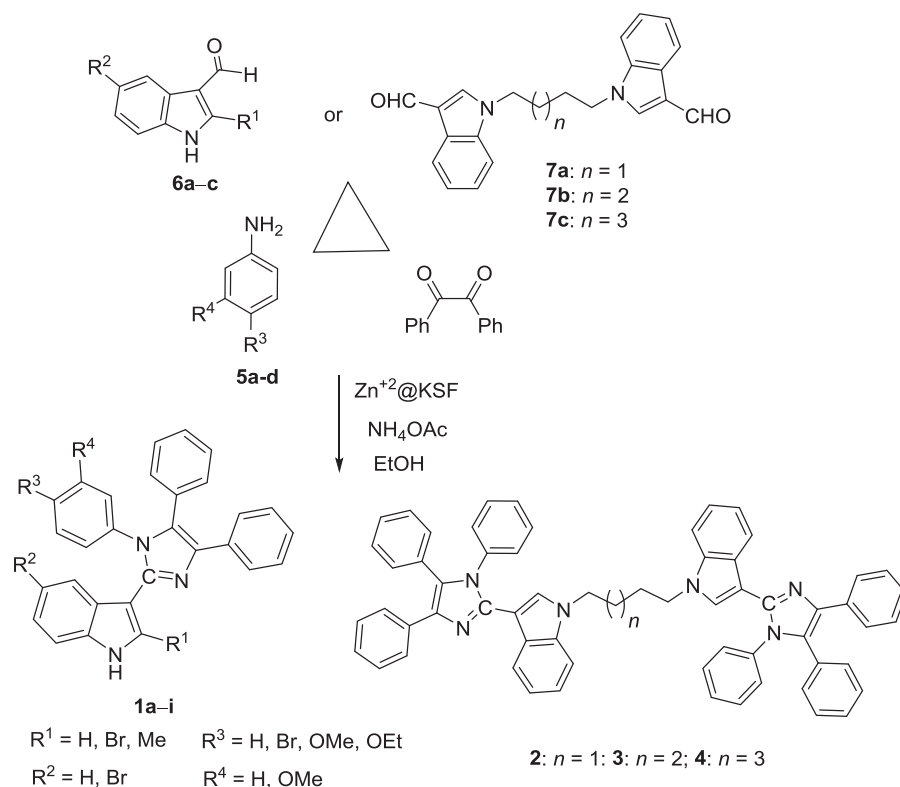
Introduction

Click chemistry was first presented by Sharpless and depicts a set of powerful, highly reliable, and selective reactions for the rapid synthesis of valuable new compounds and MCRs *via* heteroatom links, and also refers to a group of reactions that are simple to achieve, high-yielding, regiospecific, wide in scope, versatile, with safe by-products that can be removed by nonchromatographic methods [1]. One such reaction is the synthesis of various mono- and bis-indolyimidazole derivatives using Zn^{2+} supported on montmorillonite KSF (Zn^{2+} @KSF). Indoles and imidazoles are two families of compounds which have been widely investigated due to their significant biological activities. Indole and its derivatives have been termed as ‘privileged pharmacologic structures’ since they bind to many biological receptors with high affinity [2–4]. In addition, imidazole derivatives are fluorescent, show numerous pharmacological properties and participate in several vital biochemical processes [5–7]. Several substituted imidazoles have been used as inhibitors of P38 α MAP kinase, as herbicides, fungicides and therapeutic agents [8–10].

The most common synthetic routes to the *N*-substituted imidazole ring system involves the cyclocondensation of a diketone, an aldehyde and ammonia in the presence of an acid catalyst, known as the Debus-Radziszewski imidazole synthesis [11]. It is an example of a multicomponent reaction (MCR). In this reaction, typically homogeneous acids are used as catalysts, which pose problems of separation and reuse of the acids or treatment of acidic waste material. Solid acids are being used as substitutes for liquid acids for a number of superior chemical processes [12]. Several inorganic oxides, mixed oxides, including alumina, silica, titania, zirconia, and zeolites and clays have been used as both supports and solid acid catalysts [13]. Clay minerals have a different and interesting set of properties. They are very effective catalysts for a wide variety of organic reactions, often displaying highly sought product-, regio- or shape-selectivity [14–18].

Results and Discussion

Following our prior efforts in the design and click synthesis of bis-heterocyclic compounds [19–26], we report an efficient method for the synthesis of mono-

Scheme 1. MCRs for the synthesis of **1–4**.

and bis-indolylimidazoles *via* an MCR by using Zn^{2+} supported on montmorillonite KSF as a mild and heterogeneous catalyst (Scheme 1). In this effort, the reaction of both one equivalent of indole-3-carbaldehyde derivatives **6a–c** or half-equivalent of bis-aldehydes **7a–c** together with one equivalent of aniline derivatives **5a–d**, benzil and NH_4OAc in the presence of $Zn^{2+}@KSF$ afforded the desired compounds **1–4** in good yields. Bis-aldehydes **7a–c** were prepared according to the literature [27]. The reports claiming that a combination of two or more different heterocyclic moieties in a single molecule would enhance significantly the biological activity, prompted us to pursue our efforts.

Initially, we attempted to find a click synthetic route for the preparation of mono- and bis-indolylimidazoles **1–4**. For this reason, the reaction of indole-3-carbaldehyde **6a** and aniline **5a** was selected under the aspects of catalyst, temperature, solvent and reaction time. The conditions were optimized, and the results are shown in Table 1.

As shown in Table 1, entry 1, in the absence of catalyst this MCR was very slow, and only 15% of the desired product was isolated. When this reaction was carried out over various acid catalysts the yield and rate of the reaction were increased. Using Zn^{2+} supported on montmorillonite-KSF as catalyst led to higher yields and shorter reaction time (entry 7). Several solvents such as MeOH, $CHCl_3$ and DMF were examined, but longer reaction times and low yields were observed with $CHCl_3$ and DMF (entries 9, 10).

In other efforts, the effect of the amount of catalyst on the yield and the rate of the reaction was examined. It was found that 0.03 g of $Zn^{2+}@KSF$ per 1 mmole of substrates was sufficient. An increase in the amount of $Zn^{2+}@KSF$ to 0.05 mg showed no substantial improvement in the yield, while the yield of the reaction was reduced by decreasing the amount of $Zn^{2+}@KSF$ to 0.01 g.

The mono- and bis-indolylimidazoles **1–4** were synthesized by using $Zn^{2+}@KSF$ in EtOH at 70 °C. All products were fully characterized by IR, 1H NMR, ^{13}C

Table 1. Variation of reaction conditions for the synthesis of **4a**.

Entry	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	–	EtOH	70	240	15
2	<i>p</i> -TsOH	EtOH	70	100	43
3	KSF	EtOH	70	80	50
4	<i>p</i> -TsOH@KSF	EtOH	70	45	68
5	H ⁺ @KSF	EtOH	70	40	72
6	Fe ³⁺ @KSF	EtOH	70	45	70
7	Zn ²⁺ @KSF	EtOH	70	40	77
8	Zn ²⁺ @KSF	MeOH	65	40	72
9	Zn ²⁺ @KSF	CHCl ₃	50	60	25
10	Zn ²⁺ @KSF	DMF	100	45	48

Table 2. Mono- and bis-indolylimidazoles **1–4**, reaction times and yields.

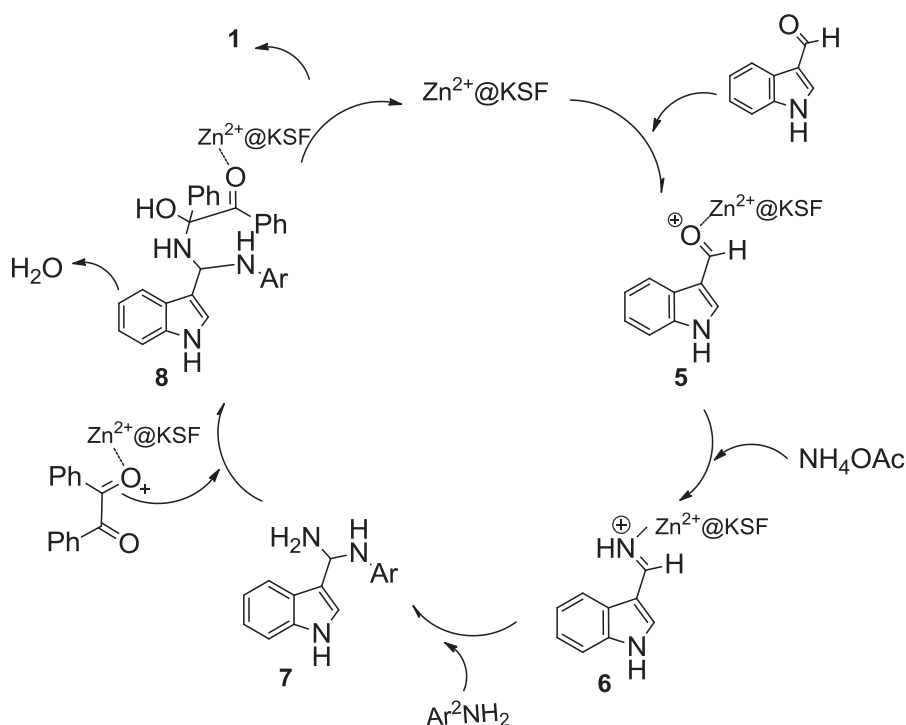
Entry	R ¹	R ²	R ³	R ⁴	Time (min)	Product	Yield (%)
1	H	H	H	H	40	1a	77
2	H	H	OMe	H	35	1b	78
3	H	H	OEt	H	35	1c	80
4	H	H	OMe	OMe	35	1d	78
5	H	Br	H	H	80	1e	57
6	Br	Br	OMe	H	50	1f	65
7	H	Br	OEt	H	50	1g	67
8	Me	H	H	H	20	1h	80
9	Me	H	OEt	H	16	1i	88
10	–	–	–	–	45	2	87
11	–	–	–	–	50	3	95
12	–	–	–	–	60	4	91

NMR spectroscopic and elemental analyses. The results are summarized in Table 2.

The proposed mechanism for the formation of **1–4** in the presence of Zn²⁺@KSF initially involves formation of diamine **6** via nucleophilic addition of aniline to the *in situ*-prepared imine **5**. Diamine **6**, in the presence of catalyst, undergoes double condensation reactions with benzil to produce the target imidazoles **1–3** (Scheme 2).

The *in vitro* antibacterial activities of compounds **1a–i** and **2–4** were evaluated against Gram-positive

and Gram-negative bacteria using the cultures of four different standard microorganisms: *Pseudomonas aeruginosa* (PS) and *Salmonella enteritis* (SE) as Gram-negative models and *Bacillus subtilis* (BS) and *Bacillus subtilis* (BS) and *Micrococcus luteus* (ML) as a Gram-positive model. The priorities for antibacterial activity against *Micrococcus luteus* are: **1a** > **1b** > **1i** > **1e** > **1g** > **1h** = **1c** > **2** > **1f**. All of them indicate a good activity. However, mono-indolylimidazoles



Scheme 2. Proposed mechanism for the formation of indoles **1** catalyzed by Zn²⁺@KSF.

Entry	Compound	Conc. in DMSO (μg per 0.1 mL)	Antimicrobial activity (zone of inhibition in mm)			
			<i>Pseudomonas aeruginosa</i>	<i>Salmonella enteritis</i>	<i>Bacillus subtilis</i>	<i>Micrococcus luteus</i>
1	1a	100	–	–	10	25
2	1b	100	–	13	11	21
3	1c	100	–	–	–	14
4	1d	100	–	–	12	–
5	1e	100	–	–	13	17
6	1f	100	–	–	9	11
7	1g	100	–	–	11	15
8	1h	100	–	–	11	14
9	1i	100	–	–	16	18
10	2	100	–	11	10	13
11	3	100	–	–	–	–
12	4	100	–	–	9	–
13	Erythromycin	100	10	8	12	10
14	Tetracycline	100	18	7	14	16
15	DMSO	100	–	–	–	–

Table 3. Antimicrobial activity of compounds **1a–i** and **2–4**.

in comparison to bis-indolyimidazoles indicate higher activity. The results are shown in Table 3.

Compounds **1–4** were inactive against *Pseudomonas aeruginosa*. The range of activities against *Bacillus subtilis* are good to moderate: **1i** > **1e** > **1d** > **1b** = **1g** = **1h** > **1c** > **2** = **1d** > **1f**. Compounds **2** and **1b** showed superior activities against *Salmonella enteritis*.

Experimental Section

Zn^{2+} @KSF was prepared according to the literature procedure [28]. The ^1H NMR spectra were obtained on a Bruker Avance 400-MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker 100 MHz instrument using the solvent as an internal standard. IR spectra were measured with a Shimadzu IR-470 spectrophotometer. Mass spectra were recorded with a Termo-LCQ Deca mass spectrometer operating at an ionization potential of 70 eV or lower. Melting points are uncorrected and were determined using a Mettler Fp5 apparatus.

General procedure for the synthesis of mono- and bis-indolyimidazoles

Benzil (1 mmol, 0.21 g), aldehyde (1 mmol), aniline (1 mmol, 0.09 g), ammonium acetate (1 mmol, 0.07 g), and Zn^{2+} @KSF were dissolved in EtOH. The mixture was stirred at 70 °C for 40 min. The progress of the reaction was monitored by TLC (EtOAc : petroleum ether 6 : 3). After completion of the reaction, the mixture was cooled to 0 °C, and the resulting precipitate was filtered off, washed with cold EtOH and recrystallized from EtOH to yield the desired mono-indolyimidazoles. Bis-indolyimidazoles **2–4** were prepared by a similar procedure using di-aldehydes

(0.5 mmol) instead of indole-3-carbaldehyde derivatives (1 mmol).

3-(1,4,5-Triphenyl-1H-imidazol-2-yl)-1H-indole (**1a**)

Yield 77%. Colorless solid, m.p. 234–236 °C. – IR (KBr): ν = 3400, 3050, 1580, 1560, 1490, 1480, 760, 740, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 6.32 (d, J = 2.4 Hz, 1H), 7.36–7.15 (m, 16H), 7.73 (dd, J = 1.2, 8 Hz, 2H), 8.49–8.47 (m, 2H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 106.7, 110.9, 120.7, 122.0, 122.7, 123.9, 126.4, 126.4, 127.2, 127.8, 128.1, 128.3, 128.5, 128.8, 129.2, 129.5, 130.8, 131.1, 134.6, 135.5, 137.3, 137.4, 143.6 ppm. – HRMS ((+)-ESI): m/z = 411.1741 (calcd. 411.1735 for $\text{C}_{29}\text{H}_{21}\text{N}_3$).

3-(1-(4-Methoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)-1H-indole (**1b**)

Yield 78%. Colorless solid, m.p. 240–242 °C. – IR (KBr): ν = 3400, 3050, 2850, 2950, 2980, 1600, 1580, 1570, 1510, 1490, 1440, 1385, 1250, 1025, 840, 778, 740, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 3.80 (s, 1H), 6.32 (d, J = 2.4 Hz, 1H), 6.81 (d, J = 9.2 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 7.31–7.19 (m, 11H), Hd, 7.73 (dd, J = 1.2, 7.6 Hz, 2H), 8.45 (brs, 1H), 8.57 (t, J = 4.2 Hz, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 55.4, 106.8, 110.8, 114.3, 120.6, 122.2, 122.7, 123.8, 126.3, 126.5, 127.2, 127.8, 128.1, 128.3, 129.7, 129.8, 130.0, 130.9, 131.2, 134.7, 135.5, 137.3, 143.8, 159.3 ppm. – HRMS ((+)-ESI): m/z = 441.1844 (calcd. 441.1841 for $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}$).

3-(1-(4-Ethoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)-1H-indole (**1c**)

Yield 81%. Colorless solid, m.p. 206–208 °C. – IR (KBr): ν = 3400, 3100, 3050, 2870, 2930, 2980, 1600, 1570, 1510, 1465, 1440, 1390, 1250, 1040, 840, 778, 740,

690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 1.44 (t, J = 6.8 Hz, 3H), 4.04–3.96 (m, 2H), 6.31 (d, J = 8 Hz, 1H), 6.82–6.78 (m, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.29–7.17 (m, 11H), 7.73 (d, J = 7.6 Hz, 2H), 8.41 (brs, 1H), 8.58 (s, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 14.7, 63.6, 110.8, 114.8, 120.7, 122.2, 122.7, 123.7, 126.3, 126.5, 127.2, 127.7, 128.1, 128.3, 129.7, 131.0, 131.2, 135.9, 137.3, 143.8, 158.8 ppm. – HRMS ((+)-ESI): m/z = 455.2005 (calcd. 455.1998 for $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}$).

3-(1-(3,4-Dimethoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)-1H-indole (1d)

Yield 78%. Colorless solid, m.p. 243–245 °C. – IR (KBr): ν = 3380, 3050, 2980, 2930, 1590, 1560, 1500, 1490, 1435, 1390, 1250, 1220, 1020, 780, 760, 740, 693 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 3.63 (s, 3H), 3.86 (s, 3H), 6.35 (d, J = 2.8 Hz, 1H), 6.61 (s, 1H), 6.73 (s, 2H), 7.18–7.31 (m, 11H), 7.73 (dd, J = 3.4, 9.2 Hz, 2H), 8.55 (d, J = 8 Hz, 1H), 8.66 (brs, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 55.9, 56.0, 106.7, 110.7, 110.9, 112.0, 120.6, 121.1, 122.1, 122.6, 123.9, 126.4, 126.5, 127.2, 127.8, 128.1, 128.3, 129.7, 130.0, 131.0, 131.1, 134.7, 135.5, 137.3, 143.8, 148.8, 149.0 ppm. – HRMS ((+)-ESI): m/z = 471.1953 (calcd. 471.1947 for $\text{C}_{31}\text{H}_{25}\text{N}_3\text{O}_2$).

5-Bromo-3-(1,4,5-triphenyl-1H-imidazol-2-yl)-1H-indole (1e)

Yield 57%. Colorless solid, m.p. 246–248 °C. – IR (KBr): ν = 3450, 3050, 1590, 1570, 1559, 1540, 1490, 790, 760, 695 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 6.29 (s, 1H), 7.46–7.12 (m, 15H), 7.68 (d, J = 7.2 Hz, 2H), 8.51 (s, 1H), 8.88 (brs, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 112.5, 114.0, 124.2, 125.1, 125.6, 126.6, 127.3, 127.9, 128.2, 128.3, 128.7, 128.7, 129.2, 129.7, 130.4, 131.1, 134.0, 134.1, 136.9, 137.5, 142.9 ppm. – HRMS ((+)-ESI): m/z = 489.0846 (calcd. 489.0841 for $\text{C}_{29}\text{H}_{20}\text{BrN}_3$).

2,5-Dibromo-3-(1-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)-1H-indole (1f)

Yield 66%. Colorless solid, m.p. 238–240 °C. – IR (KBr): ν = 3400, 3050, 2980, 2950, 2880, 1650, 1600, 1510, 1470, 1440, 1390, 1240, 1040, 840, 790, 770, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 3.79 (s, 3H), 6.29 (s, 1H), 6.80 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 1H), 7.30–7.19 (m, 9H), 7.67 (dd, J = 1.6, 7.6 Hz, 2H), 8.51 (s, 1H), 9.05 (brs, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 55.4, 112.5, 113.9, 114.4, 124.2, 125.2, 125.4, 126.6, 127.3, 127.9, 128.0, 128.1, 128.3, 129.6, 129.7, 130.0, 130.6, 131.1, 134.2, 137.3, 143.3, 159.4 ppm. – HRMS ((+)-ESI): m/z = 597.0054 (calcd. 597.0051 for $\text{C}_{30}\text{H}_{21}\text{Br}_2\text{N}_3\text{O}$).

5-Bromo-3-(1-(4-ethoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)-1H-indole (1g)

Yield 66%. Colorless solid, m.p. 162–164 °C. – IR (KBr): ν = 3150, 3050, 2980, 2900, 2850, 1600, 1570, 1510, 1470, 1440, 1390, 1250, 1040, 790, 780, 760, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 1.42 (t, J = 7 Hz, 3H), 3.98 (q, J = 7.12 Hz, 2H), 6.29 (d, J = 1.6 Hz, 1H), 6.78 (d, J = 9.2 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 1H), 7.29–7.19 (m, 9H), 7.67 (dd, J = 1.2 Hz, 7.6 Hz, 2H), 8.52 (s, 1H), 9.07 (brs, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 14.7, 63.7, 112.5, 113.9, 114.8, 124.3, 125.2, 125.43, 126.5, 127.3, 127.8, 128.0, 128.1, 128.3, 129.4, 129.6, 130.0, 130.6, 131.1, 134.2, 134.4, 137.3, 143.3, 158.8 ppm. – HRMS ((+)-ESI): m/z = 533.1120 (calcd. 533.1103 for $\text{C}_{31}\text{H}_{24}\text{BrN}_3\text{O}$).

2-Methyl-3-(1,4,5-triphenyl-1H-imidazol-2-yl)-1H-indole (1h)

Yield 80%. Colorless solid, m.p. 266–268 °C. – IR (KBr): ν = 3150, 3050, 2980, 2900, 2850, 1590, 1570, 1490, 1450, 1390, 740, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 2.00 (s, 3H), 7.32–6.91 (m, 16 H), 7.46 (d, J = 8 Hz, 1H), 7.65 (dd, J = 1.2, 7.8 Hz, 2H), 8.74 (brs, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 12.6, 110.3, 119.1, 119.9, 121.3, 126.5, 127.4, 127.6, 127.9, 128.1, 128.4, 128.5, 129.0, 129.1, 130.8, 131.1, 135.2, 136.1, 136.7, 143.2 ppm. – HRMS ((+)-ESI): m/z = 425.1898 (calcd. 425.1892 for $\text{C}_{30}\text{H}_{23}\text{N}_3$).

3-(1-(4-Ethoxyphenyl)-4,5-diphenyl-1H-imidazol-2-yl)-2-methyl-1H-indole (1i)

Yield 84%. Colorless solid, m.p. 278–280 °C. – IR (KBr): ν = 3400, 3050, 2980, 2930, 2850, 1570, 1510, 1455, 1440, 1390, 1240, 1040, 820, 780, 730, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 1.35 (t, J = 6.8 Hz, 3H), 2.05 (s, 3H), 3.89 (q, J = 7 Hz, 14 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 7.30–6.93 (m, 15H), 7.46 (d, J = 7.2 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 8.75 (brs, 1H) ppm. – HRMS ((+)-ESI): m/z = 469.2157 (calcd. 469.2154 for $\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}$).

1,4-Bis(3-(1,4,5-triphenyl-1H-imidazol-2-yl)-1H-indol-1-yl)butane (2)

Yield 87%. Colorless solid, m.p. 307–309 °C. – IR (KBr): ν = 3050, 2950, 2850, 1610, 1590, 1560, 1490, 1470, 1440, 760, 740, 690 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 1.43 (s, 2H), 3.81 (s, 2H), 6.10 (s, 1H), 7.39–7.10 (m, 16H), 7.74 (dd, J = 1.2, 7.8 Hz, 2H), 8.63–8.62 (m, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 27.1, 45.7, 106.0, 108.9, 120.6, 122.5, 122.8, 126.3, 126.7, 127.1, 127.3, 127.8, 128.1, 128.3, 128.5, 128.9, 129.1, 129.4, 130.9, 131.1,

134.9, 135.6, 137.4, 137.7, 143.4 ppm. – HRMS ((+)-ESI): m/z = 876.3947 (calcd. 876.3940 for $C_{62}H_{48}N_6$).

1,5-Bis(3-(1,4,5-triphenyl-1H-imidazol-2-yl)-1H-indol-1-yl)pentane (3)

Yield 93%. Colorless solid, m.p. 273–275 °C. – IR (KBr): ν = 3050, 2900, 2850, 1600, 1580, 1560, 1490, 1440, 760, 735, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 1.03–0.99 (m, 1H), 1.63–1.56 (m, 2H), 3.85 (t, J = 6.6 Hz, 2H), 6.25 (brs, 1H), 7.32–7.14 (m, 16H), 7.74 (dd, J = 1.6 Hz, 8 Hz, 2H), 8.52 (brs, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 23.9, 29.3, 46.0, 109.0, 120.6, 122.4, 122.6, 126.4, 127.1, 127.8, 128.1, 128.3, 128.5, 128.9, 129.1, 129.4, 130.8, 131.2, 135.7, 137.4, 143.5 ppm. – HRMS ((+)-ESI): m/z = 890.4103 (calcd. 890.4097 for $C_{63}H_{50}N_6$).

1,6-Bis(3-(1,4,5-triphenyl-1H-imidazol-2-yl)-1H-indol-1-yl)hexane (4)

Yield 91%. Colorless solid, m.p. 299–301 °C. – IR (KBr): ν = 3050, 2900, 2850, 1600, 1580, 1560, 1490, 1470, 1450, 760, 740, 690 cm^{-1} . – ^1H NMR (400 MHz, CDCl_3): δ = 1.04 (s, 2H), 1.58 (s, 2H), 3.86–3.88 (m, 2H), 6.25 (brs, 1H) 7.38–7.17 (m, 16H), 7.73 (d, J = 6.8 Hz, 2H), 8.52 (brs, 1H) ppm. – ^{13}C NMR (100 MHz, CDCl_3): δ = 26.3, 29.6, 46.1, 120.0, 120.5, 122.3, 122.6, 127.1, 127.2, 127.8, 127.9, 128.0, 128.3, 128.4, 128.9, 129.1, 129.3, 130.4, 131.1, 135.7, 136.4, 143.4 ppm. – HRMS ((+)-ESI): m/z = 904.4258 (calcd. 904.4253 for $C_{64}H_{52}N_6$).

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