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Synthesis of new polyaryl-substituted imidazoles bridged on enamine or urea moieties and evaluation of their optical and electrochemical properties

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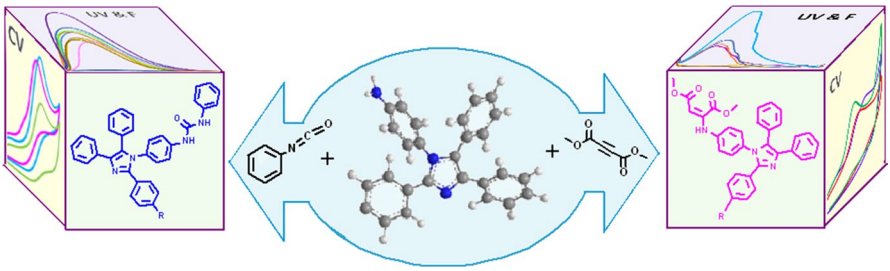
Abstract

The reaction of the free amine group in polyaryl-substituted imidazole structures with phenyl isocyanate or dimethyl acetylenedicarboxylate gave two new series of polyaryl-substituted imidazoles: biaryl ureas or vinyl esters, respectively. Besides their spectroscopic analysis, we explored the optical and electrochemical properties of these highly conjugated scaffolds. Comparing these properties in two categories of products yielded interesting results.

Graphic abstract



Keywords Biarylureas · Cyclic voltammetry · Fluorescence emission · Polyaryl-substituted imidazoles · Vinyl esters

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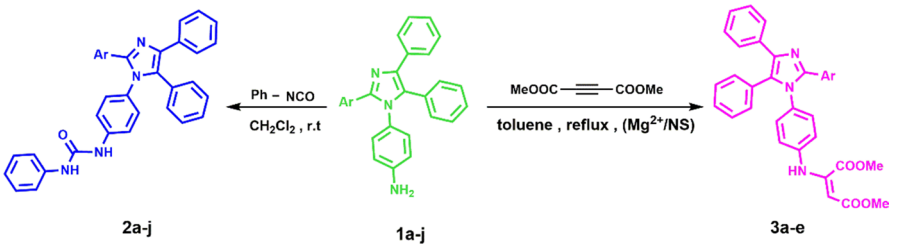
Introduction

Emitting organic compounds possessing extended π-conjugated systems have been of great interest in recent years owing to their variety of applications in OLEDs [1–3], solid-state lasers [4], sensors [5–7], fluorescence imaging [8–10], nonlinear optical materials [11–13] and photophysical devices [14]. Many efforts have been devoted to establishing structure–property relationships in order to develop new materials with desired properties in a smart way and provide valuable insights into conforming fundamental properties of these systems [15, 16]. Depending on the π-electron distribution, the π-conjugated systems may adopt a different impact on their π–π electronic couplings and thus charge transport rate. An extended conjugation system is generally favored for a greater chance of π–π stacking and narrower bandgap. Through structure optimization of the substructures within the expansion of π-conjugation, the optical absorptions, intramolecular charge transfer (ICT) behaviors, and charge carrier property of photosensitizers could be modified and adjusted which would provide an alternative to promote the overall device performance [17]. In this regard, we made a choice of two well-known groups of intermediates for the design of such π-electron systems including enaminoesters and aryl ureas [18–33]. The mentioned simply accessible functionalities have been achieved by various methodologies as mentioned in the literature [34–45]. Following our recent efforts in the synthesis of various polyaryl imidazole derivatives and evaluation of their optical properties [46–49], herein we report the synthesis of novel diversities of this category. With this goal, we attached the enaminoester and also biaryl urea moieties to our systems, by reactions of free amine possessing 1,2,4,5-tetraarylimidazoles with dimethyl acetylenedicarboxylate and phenylisocyanate, respectively. We then represent the emission and electrochemical properties of the obtained products.

Results and discussion

We first prepared 4-(2-aryl-4,5-diphenylimidazol-1-yl)aniline derivatives **1a**–**j** by acid catalyzed four-component reactions of 1,4-phenylenediamine, benzil, ammonium acetate and aryl aldehyde [46–49]. The reaction of the mentioned amines with phenyl isocyanate in dry dichloromethan gave *N*,*N*′-biarylurea products **2a**–**j** (Scheme 1, Table 1).

On the other hand, we decided to use aromatic amines in the reaction with dimethyl acetylenedicarboxylate to obtain enaminoesters [34–38]. Initially, we examined this reaction with commercial aniline derivatives at ambient temperature in the presence of $MgSO_4$ incorporated nanosilica (Mg^{2+}/NS) catalyst [46] and earned products **4a**–**e** in good yields (Table 2). This catalyst which had shown good activity in the multi-component synthesis of substituted pyrroles [46] decreased the reaction time of acetylenediester with anilines relative to catalyst-free conditions (Table 2). We then treated the amines **1a**–**e** with



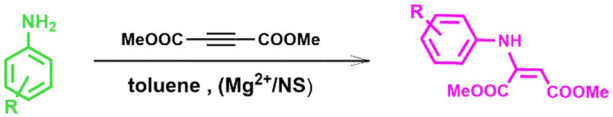
2a-j 1a-j 3a-e

Scheme 1 Synthesis of biaryl ureas (**2a**–**j**) and enaminoesters (**3a**–**e**)

Table 1 The synthesized biarylureas **2a**–**j** and vinyl esters **3a**–**e**

Entry	Ar	Amine	Product	Time (h)	Yield (%)
1	C_6H_5	**1a**	**2a**	16	65
2	4-MeC_6H_4	**1b**	**2b**	12	80
3	4-ClC_6H_4	**1c**	**2c**	2	92
4	3,4-$(MeO)_2C_6H_3$	**1d**	**2d**	5	89
5	2-thienyl	**1e**	**2e**	14	65
6	4-FC_6H_4	**1f**	**2f**	10	77
7	4-MeOC_6H_3	**1 g**	**2 g**	7	82
8	4-isopropylC_6H_4	**1 h**	**2 h**	3	90
9	2-$NO_2C_6H_4$	**1i**	**2i**	28	60
10	3-thienyl	**1j**	**2j**	12	70
11	C_6H_5	**1a**	**3a**	2	77
12	4-MeC_6H_4	**1b**	**3b**	2	82
13	4-ClC_6H_4	**1c**	**3c**	2.1	69
14	3,4-$(MeO)_2C_6H_3$	**1d**	**3d**	1.5	88
15	2-thienyl	**1e**	**3e**	2	53

Table 2 Nano-catalyst capability for synthesis of enaminoesters (**4a**–**e**)



4a-e

Entry	R	Product	Time (h)	Yield (%)
1	2-Br	**4a**	1.5	85
2	2,6-dichloro	**4b**	1.5	73
3	2,6-dimethyl	**4c**	0.5	87
4	4-Cl	**4d**	1	82
5	H	**4e**	1	84

acetylenedicarboxylate under the same conditions and gained no product at room temperature. However, heating of the reaction mixture at 80 °C resulted in the desired vinyl esters **3a**–**e** (Scheme 1 and Table 1). It is worth noting that the stereochemistry of the products **3a**–**e** and also **4a**–**e** was estimated as *E* as described in the literature [50–52].

In order to investigate the optical properties, UV–Vis and fluorescence spectra of the obtained compounds (**2a**–**j**, **3a**–**e** and **4a**–**c**) were recorded in ethanol at a concentration of 10^{-6} M. The absorption and emission spectra and their optical parameters are presented in Fig. 1 and Table 3, respectively. We also studied the corresponding spectra for amine precursors (**1a**–**e**) in order to the comparison of their optical properties with the obtained products (Fig. 2, Table 3).

All compounds display an intense absorption band with a maximum at wavelength (λ_{max}) between 260 and 306 nm, which their molar extinction coefficient confirms the strong π–π* transitions. The increase in conjugation of π-system of aryl ureas (**2a**–**e**) and enamines (**3a**–**e**) compared to amine precursors (**1a**–**e**) resulted in the bathochromic shift of the absorption bands and also an increase in molar

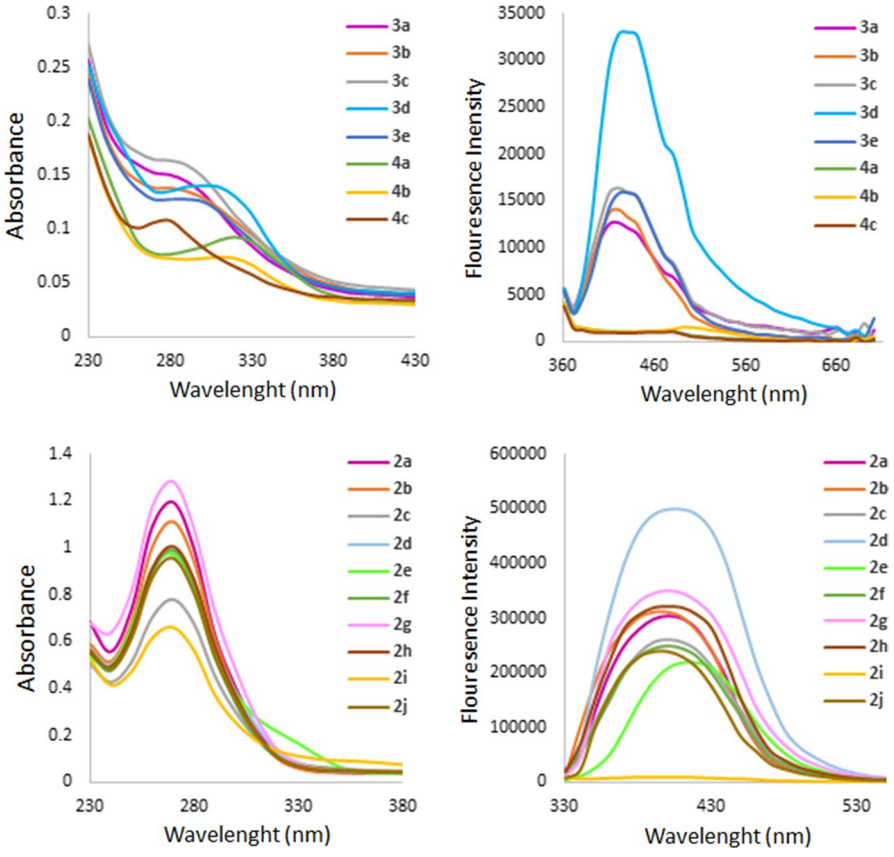


Fig. 1 The absorption and emission spectra of compounds (**2a**–**j**, **3a**–**e** and **4a**–**c**) in ethanol (10^{-6} M)

Table 3 Absorption and emission spectral data of the π-extended pyrrole derivatives in ethanol

Compound	$\lambda^{a}_{max,abs}$ (nm)	$\lambda^{b}_{max,em}$ (nm)	$\varepsilon \times 10^4$ (L mol^{-1} cm^{-1})	Stokes shift[c] (nm)	Φ^{d}
1a	258	406	1.29	148	0.10
1b	260	404	1.30	144	0.14
1c	264	418	1.32	154	0.13
1d	254	410	1.27	156	0.15
1e	252	428	1.26	176	0.12
2a	272	410	1.36	138	0.29
2b	268	396	1.34	128	0.30
2c	274	408	1.37	134	0.35
2d	270	404	1.35	134	0.58
2e	270	416	1.35	146	0.27
2f	272	410	1.36	138	0.30
2 g	270	398	1.35	128	0.32
2 h	272	402	1.36	130	0.35
2i	274	400	1.37	126	0.01
2j	274	394	1.37	120	0.25
3a	294	418	1.47	124	0.05
3b	286	422	1.42	164	0.05
3c	288	420	1.44	132	0.05
3d	306	438	1.53	132	0.12
3e	282	428	1.42	146	0.06
4a	320	454	1.60	134	0.00
4b	312	488	1.56	176	0.01
4c	280	478	1.40	198	0.00

[a]Absorption, [b]emission, [c]stokes shift = $\lambda_{em} - \lambda_{abs}$, [d]quantum yield

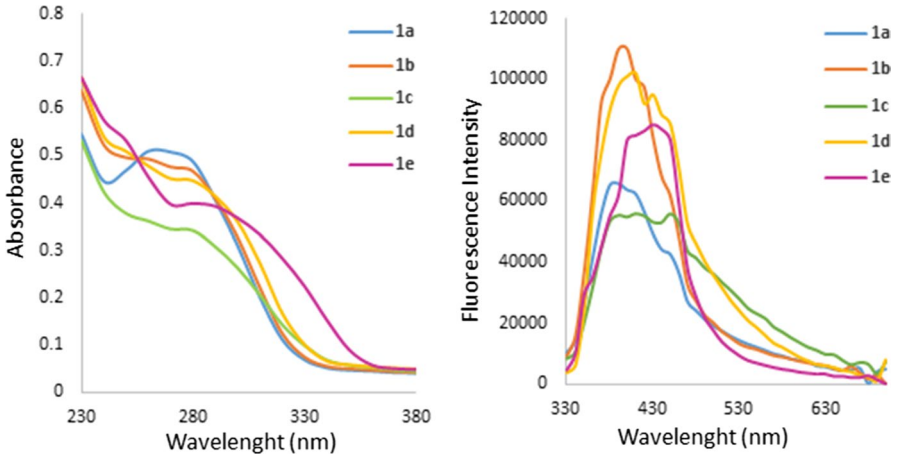


Fig. 2 The absorption and emission spectra of compounds (**1a**–**e**) in ethanol (10^{-6} M)

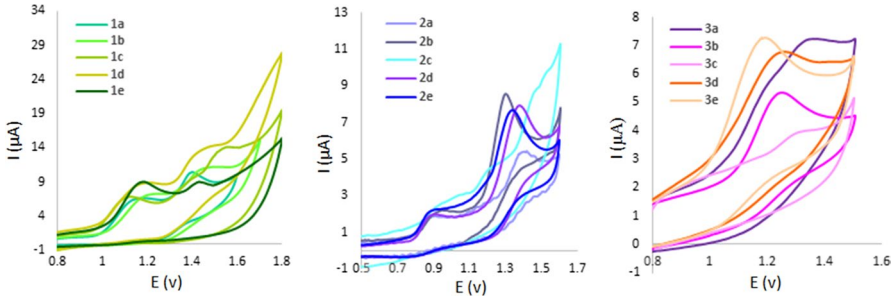


Fig. 3 Cyclic voltammograms of **1a–e**, **2a–e** and **3a–e** in CH_2Cl_2 containing 0.1 M TBAP Experimental conditions: analyte concentration 1 mM, scan rate: 50 mV/S

Table 4 The oxidation potentials of **1a–e**, **2a–e** and **3a–e**

Amine	Eox (v)	Urea	Eox (v)	Enamine	Eox (v)
1a	1.17, 1.42	**2a**	0.88, 1.41	**3a**	1.33
1b	1.22, 1.47	**2b**	0.94, 1.32	**3b**	1.25
1c	1.12, 1.56	**2c**	1.24, 1.49	**3c**	1.31
1d	1.19, 1.48	**2d**	0.90, 1.38	**3d**	1.25
1e	1.18, 1.43	**2e**	0.89, 1.35	**3e**	1.21

extinction coefficient, as expected (Table 3). These shifts were more noticeable in vinyl esters than aryl urea derivatives which could be attributed to higher planarization of the molecules with vinyl ester moieties.

Fluorescence properties of the synthesized molecules were studied, which showed the intense emission of blue light in visible area at about 400 nm. The quantum yields were calculated using anthracene as standard ($\Phi = 0.27$) and are represented in Table 3. The aryl urea derivatives (**2a–e**) had the highest quantum yields compared with both amines **1a–e** and also vinyl esters **3a–e.** Furthermore, the products bearing dimethoxyphenyl group (**1d**, **2d** and **3d**) showed the higher quantum yields. Moderate values of Stokes shifts (120–176 nm) were observed, indicating low overlap between their absorption and emission spectra.

The electrochemical properties of compounds **1a–e**, **2a–e** and **3a–e** were analyzed by cyclic voltammetry (CV) in the presence of tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte, and the results are listed in Table 3. Representative CVs of the chosen compounds are presented in Fig. 3.

Electrochemical data show that all three classes of compounds including **1a–e**, **2a–e** and **3a–e** have an oxidation peak around 0.88–1.25 v. This peak can be attributed to the oxidation of nitrogen in the imidazole ring whose electron pair does not participate in the aromatic system [53, 54]. The positive charge resulting from this oxidation can be sustained by electron resonance of the high conjugated aromatic system.

As can be seen in Table 4, there is also another oxidation peak in voltammograms of amines **1a–e** and urea derivatives **2a–e**. By considering the lack of a similar peak

in the derivatives **3a**–**e** (possessing electron deficient vinyldiester group), it can be probably related to the oxidation of free amine (in **1a**–**e**) or attached urea group (in **2a**–**e**). Furthermore, the cyclic voltammograms of compounds **4a**–**e** did not exhibited anodic or cathodic peaks, indicating that these compounds are electro-inactive.

Conclusion

In summary, new polyaryl-substituted imidazole compounds with attached vinyl ester and aryl urea groups were synthesized and their optical and electrochemical properties were investigated. Optical studies of the products implied noticeable increased quantum yields in the urea derivatives. Electrochemical experiments demonstrated an oxidation peak around 0.88–1.25 v for all three classes of compounds, **1a**–**e**, **2a**–**e** and **3a**–**e**, and the other oxidation peak for **1a**–**e** and **2a**–**e**. It should be noted that except for compounds **4a**, **4d** and **4e** [55–57], all of other products are novel.

Experimental section

Materials and analytical methods

Melting points were measured on an Electrothermal MEL-TEMP apparatus (model 1202D) and are uncorrected. FT-IR spectra were recorded (in KBr) with a Tensor 27-Bruker spectrometer and Shimadzu FT-IR 8101 M and were reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Spectrospin Avance 400 spectrometer operating at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane as internal standard. Elemental analyses were measured by Vario EL III apparatus (Elementar Co.). UV–Vis absorption and Fluorescence emission spectra were recorded on CYTATION 5 Imaging Reader System (BIOTEK). The fluorescence quantum yields (Φ) were determined in ethanol (10^{-6} M) via the comparative method using anthracene as standard ($\Phi = 0.27$). The value of Φ was calculated using the equation: $\Phi_x = (A_s \times F_x \times n_x^2 \times \Phi_s)/(A_x \times F_s \times n_s^2)$, where F is the integrated area under the emission spectrum, A is the absorbance at the excitation wavelength (300 nm), and n is the refractive index of solvent (which is ethanol for both standard and samples, $n_x = n_s = 1.36$). The subscripts S and X correspond to the reference and the sample, respectively. Electrochemical experiments were accomplished using an AUTOLAB PGSTAT 30 electrochemical analysis system and GPES 4.9 software packet (Eco Chemie., The Netherlands). CV measurements were recorded at room temperature with a conventional three electrode configuration consisting of a glassy carbon working electrode, a platinum counter electrode, and a saturated calomel electrode (SCE) as reference electrode. Preparative thin-layer chromatography (PLC) was performed on prepared glass-backed plates using silica gel (Merck Kieselgel 60 $PF_{254+366}$). All starting materials were purchased from commercial sources and used without further purification.

General procedure for the synthesis of urea derivatives 2a–j

A mixture of substituted amine **1** (1 mmol) and phenyl isocyanate (1.5 mmol) in dichloromethane (5 mL) was stirred under argon at ambient temperature. After completion of the reaction which was monitored by TLC (Table 1), the obtained solid was filtered and washed with ethyl acetate.

1-phenyl-3-[4-(2,4,5-triphenyl-1*H*-imidazol-1-yl)phenyl]urea (2a)

White solid; yield 65% (0.33 g); mp > 300 °C; FTIR (KBr): 3358, 3059, 1655, 1602, 1442, 1554, 844, 694 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 6.9 (m, 1H, Ar–H), 7.15 (d, J = 8.6 Hz, 2H, Ar–H), 7.18–7.43 (m, 17H, Ar–H), 7.48 (d, J = 7.2 Hz, 2H, Ar–H), 8.72 (s, 1H, NH), 8.85 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 118.1, 118.4, 118.5, 122.2, 126.5, 126.6, 128.3, 128.4, 128.5, 128.6, 128.9, 129.3, 130.2, 130.5, 130.6, 131.2, 131.6, 134.5, 136.8, 139.5, 139.7, 140.0, 146.3, 152.5; Anal. calcd. for $C_{34}H_{26}N_4O$: C 80.61, H 5.17, N 11.06; found: C 80.45, H 5.09, N 10.09.

1-{4-[4,5-diphenyl-2-(*p*-tolyl)-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2b)

White solid; yield 80% (0.41 g); mp > 300 °C; FTIR (KBr): 3313, 3055, 2922, 2861, 1649, 1602, 1444, 1556, 696 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 3.34 (s, 3H, CH_3), 6.97 (t, J = 7.3 Hz, 1H, Ar–H), 7.10–7.42 (m, 21H, Ar–H), 7.47 (d, J = 7.3 Hz, 2H, Ar–H), 8.69 (s, 1H, NH), 8.81 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 20.7, 117.91, 118.00, 118.23, 118.33, 122.06, 126.36, 128.16, 128.19, 128.37, 128.48, 128.79, 128.83, 129.21, 130.15, 131.16, 131.30, 137.81, 139.84, 146.24, 152.28; Anal. calcd. for $C_{35}H_{28}N_4O$: C 80.74, H 5.42, N 10.76; found: C 80.65, H 5.34, N 10.52.

1-{4-[2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2c)

White solid; yield 92% (0.49 g); mp > 300 °C; FTIR (KBr): 3314, 3057, 1649, 1603,1445, 1555, 1098, 837, 696 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 6.95–6.99 (m, 1H, Ar–H), 7.18 (d, J = 8.3 Hz, 2H, Ar–H), 7.22–7.42 (m, 15H, Ar–H), 7.48 (d, J = 7.5 Hz, 2H, Ar–H), 8.70 (s, 1H, NH), 8.83 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 117.9, 118.0, 118.2, 118.3, 122.0, 126.3, 126.5, 128.1, 128.3, 128.5, 128.8, 129.1, 129.3, 129.8, 130.3, 131.1, 131.8, 133.0, 134.3, 136.8, 139.2, 139.9, 145.0, 152.2; Anal. calcd. for $C_{34}H_{25}ClN_4O$: C 75.48, H 4.66, N 10.36; found: C 75.36, H 4.54, N 10.24.

1-{4-[2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazol-1-yl] phenyl}-3-phenylurea (2d)

White solid; yield 89% (0.50 g); mp > 300 °C; FTIR (KBr): 3291, 3053, 2934,2839, 1715, 1259, 1073, 696 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 3.56 (s, 3H,

–OCH_3), 3.72 (s, 3H, –OCH_3), 5.76 (s, 1H, Ar–H), 6.88 (d, J = 8.3 Hz, 1H, Ar–H), 6.95–7.43 (m, 19H, Ar–H), 7.48 (d, J = 7.3 Hz, Ar–H), 8.70 (s, 1H, NH), 8.82 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.1, 111.2, 111.8, 118.1, 118.3, 120.9, 122.0, 122.9, 126.4, 128.1, 128.3, 128.4, 128.8, 129.3, 130.4, 130.6, 131.1, 134.5, 136.4, 139.4, 139.8, 146.1, 147.9, 148.8, 152.3; Anal. calcd. for $C_{36}H_{30}N_4O_3$: C 76.31, H 5.34, N 9.89; found: C 76.25, H 5.22, N 9.70.

1-{4-[4,5-diphenyl-2-(thiophen-2-yl)-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2e)

White solid; yield 65% (0.33 g); mp > 300 °C; FTIR (KBr): 3373, 3065, 1656, 1608,1443, 1555, 845, 693 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.58 (d, J = 3.1 Hz, 1H, Ar–H), 6.93–6.99 (m, 2H, Ar–H), 7.17 (t, J = 7.1 Hz, 1H, Ar–H), 7.23–7.50 (m, 18H, Ar–H), 8.73 (s, 1H, NH), 8.90 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 118.1, 118.2, 118.3, 122.1, 125.3, 126.3, 126.5, 127.0, 127.5, 128.19, 128.5, 128.8, 129.3, 129.6, 130.1, 131.0, 134.1, 136.6, 139.3, 140.5, 141.6, 152.3; Anal. calcd. for $C_{32}H_{24}N_4OS$: C 74.98, H 4.72, N 10.93, S, 6.25; found: C 74.73, H 4.58, N 10.81, S, 6.13.

1-{4-[2-(4-fluorophenyl)-4,5-diphenyl-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2f)

White solid; yield 77% (0.40 g); mp > 300 °C; FTIR (KBr): 3315, 3057, 1648, 1601,1444, 1559, 1096, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.97 (t, J = 7.3 Hz, 1H, Ar–H), 7.15–7.49 (m, 24H, Ar–H), 8.70 (s, 1H, NH), 8.83 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 115.1, 115.3, 118.0, 118.3, 122.0, 126.3, 126.4, 127.0, 128.1, 128.4, 128.5, 128.8, 129.1, 129.9, 130.4, 131.1, 131.5, 134.4, 136.6, 139.4, 139.9, 145.2, 152.3, 160.7, 163.1; Anal. calcd. for $C_{34}H_{25}FN_4O$: C 77.84, H 4.80, F 3.62, N 10.68; found: C 77.74, H 4.69, F 3.57, N 10.45.

1-{4-[2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2g)

White solid; yield 82% (0.44 g); mp > 300 °C; FTIR (KBr): 3313, 3054, 2931,2832, 1644, 1603, 1443, 1555, 1250, 1060, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.73 (s, 3H, –OCH_3), 6.87 (d, J = 7.0 Hz, 2H, Ar–H), 6.97 (t, J = 7.3 Hz, 1H, Ar–H), 7.14–7.43 (m, 18H, Ar–H), 7.48 (d, J = 7.4 Hz, 2H, Ar–H), 8.69 (s, 1H, NH), 8.81 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.1, 113.6, 117.9, 118.2, 118.3, 122.0, 122.9, 126.3, 128.1, 128.2, 128.4, 128.8, 129.2, 129.5, 130.2, 130.6, 131.1, 134.5, 136.4, 139.3, 139.7, 139.8, 146.1, 152.2, 159.1; Anal. calcd. for $C_{35}H_{28}N_4O_2$: C 78.34, H 5.26, N 10.44; found: C 78.19, H 5.16, N 10.37.

1-{4-[2-(4-isopropylphenyl)-4,5-diphenyl-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2h)

White solid; yield 90% (0.49 g); mp > 300 °C; FTIR (KBr): 3317, 3054, 2959,2869, 1647, 1604, 1446, 1557, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.16 (d,

$J = 6.8$ Hz, 6H, CH_3), 2.79–2.89 (m, 1H, CH_3), 6.96 (t, $J = 7.3$ Hz, 1H, Ar–H), 7.14–7.44 (m, 21H, Ar–H), 7.47 (d, $J = 7.2$ Hz, 2H, Ar–H), 8.75 (s, 1H, NH), 8.90 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 23.7, 33.1, 117.9, 118.0, 118.27, 118.3, 122.1, 126.2, 126.4, 128.0, 128.1, 128.3, 128.5, 128.8, 129.3, 130.2, 130.5, 131.1, 131.4, 134.5, 136.6, 139.4, 139.9, 146.2, 148.5, 152.3; Anal. calcd. for $C_{37}H_{32}N_4O$: C 80.99, H 5.88, N 10.21; found: C 80.76, H 5.71, N 10.17.

1-{4-[2-(3-nitrophenyl)-4,5-diphenyl-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2i)

White solid; Yield 60% (0.33 g); mp > 300 °C; FTIR (KBr): 3305, 3079, 1663, 1608, 1443, 1350, 696 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.97 (t, $J = 7.3$ Hz, 1H, Ar–H), 7.19 (m, 16H, Ar–H), 7.50 (d, $J = 7.8$ Hz, 2H, Ar–H), 7.60 (t, $J = 8.0$ Hz, 1H, Ar–H), 7.80 (d, $J = 7.9$ Hz, 1H, Ar–H), 8.15 (td, $J = 8.2$ Hz, $J = 1.3$ Hz, 1H, Ar–H), 8.25 (s, 1H, Ar–H), 8.71 (s, 1H, NH), 8.87 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 118.2, 118.3, 118.4, 122.1, 122.4, 122.8, 126.4, 126.7, 128.3, 128.6, 128.8, 129.1, 129.5, 130.1, 131.1, 131.8, 132.5, 134.1, 137.3, 139.4, 140.4, 143.8, 147.6, 152.3; Anal. calcd. for $C_{34}H_{25}N_5O_3$: C 74.03, H 4.57, N 12.70; found: C 73.88, H 4.28, N 12.54.

1-{4-[4,5-diphenyl-2-(thiophen-3-yl)-1*H*-imidazol-1-yl]phenyl}-3-phenylurea (2j)

White solid; yield 70% (0.35 g); mp > 300 °C; FTIR (KBr): 3366, 3059, 1656, 1603,1443, 1556, 844, 695 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.97 (t, $J = 7.2$ Hz, 1H, Ar–H), 7.07 (s, 1H, Ar–H), 7.14–7.52 (m, 16H, Ar–H), 8.72 (s, 1H, NH), 8.87 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 118.2, 118.3, 122.0, 123.5, 126.1, 126.3, 127.3, 128.1, 128.3, 128.4, 128.8, 129.3, 129.8, 130.4, 131.0, 131.5, 134.4, 136.3, 139.4, 140.3, 142.8, 152.37; Anal. calcd. for $C_{32}H_{24}N_4OS$: C 74.98, H 4.72; N 10.93, S 6.25; found: C 74.81, H 4.55; N 10.82, S 6.18.

General procedure for the synthesis of vinyl esters 3a–e and 4a–e

A mixture of substituted amine **1** (0.5 mmol) and dimethylacetylene dicarboxylate (0.5 mmol) and the catalyst (Mg^{2+}/N.S, 0.01 g) was stirred at 80 °C in toluene (3 mL). After completion of the reaction which was monitored by TLC (Table 1), the mixture was cooled down to room temperature. The catalyst was removed with centrifuging and the solution was concentrated under vacuum. The obtained crude solid was then purified: products **3a-e** were purified by preparative TLC (n hexane/ethyl acetate 15:3) and Products **4a-e** were simply recrystallized in ethyl acetate.

Dimethyl 2-{[4-(2,4,5-triphenyl-1*H*-imidazol-1-yl)phenyl]amino}maleate (3a)

Pale yellow solid; Yield 77% (0.40 g); mp 120–122 °C; FTIR (KBr): 3452, 3068, 2876, 1743, 1611, 1521, 1444, 1286, 1034, 777, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.55 (s, 3H, CH_3-ester), 3.73 (s, 3H, CH_3-ester), 5.45 (s, 1H, vinylic H), 6.73 (d, $J = 8.6$ Hz, 2H, Ar–H), 6.93 (d, $J = 8.6$ Hz, 2H, Ar–H), 7.12–7.45 (m, 14H,

Ar–H), 7.58 (d, $J=7.5$ Hz, 2H, Ar–H), 9.59 (s, 1H, N–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 163.4, 146.1, 145.8, 139.2, 137.1, 133.2, 131.8, 130.1, 129.7, 129.5, 129.3, 128.0, 127.9, 127.3, 127.3, 127.1, 127.1, 126.9, 126.3, 125.6, 119.8, 111.0, 94.4, 51.6, 50.3; Anal. calcd. for $C_{33}H_{27}N_3O_4$: C 74.84, H 5.14, N 7.93; found: C 74.62, H 5.04, N 7.76.

Dimethyl 2-{[4-(4,5-diphenyl-2-(p-tolyl)-1*H*-imidazol-1-yl)phenyl]amino}maleate (3b)

Pale yellow solid; Yield 82% (0.44 g); mp 164–166 °C; FTIR (KBr): 3431, 3068, 2876, 1743, 1611, 1521, 1440, 1145, 1034, 828, 781, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.31 (s, 3H, CH_3 Methyl), 3.56 (s, 3H, CH_3-ester), 3.74 (s, 3H, CH_3-ester), 5.45 (s, 1H, vinylic H), 6.73 (d, $J=6.8$ Hz, 2H, Ar–H), 6.93 (d, $J=6.6$ Hz, 2H, Ar–H), 7.06 (d, $J=8.0$ Hz, 2H, Ar–H), 7.11–7.26 (m, 11H, Ar–H), 7.31 (d, $J=8.1$ Hz, 2H, Ar–H), 7.58 (d, $J=7.78$ Hz, 2H, Ar–H), 9.60 (s, 1H, N–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.7, 163.4, 146.1, 139.2, 130.1, 129.5, 128.0, 127.9, 127.8, 127.3, 127.1, 126.9, 126.3, 125.6, 119.8, 94.4, 51.6, 50.3; Anal. calcd. for $C_{34}H_{29}N_3O_4$: C 75.12, H 5.38, N 7.73; found: C 74.08, H 5.12, N 7.57.

Dimethyl 2-{[4-(2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazol-1 yl)phenyl]amino} maleate (3c)

Pale yellow solid; Yield 69% (0.38 g); mp 188–190 °C; FTIR (KBr): 3351, 3068, 2871, 1747, 1611, 1521, 1444, 1286, 1145, 1034, 828,786, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.58 (s, 3H, CH_3-ester), 3.74 (s, 3H, CH_3-ester), 5.48 (s, 1H, vinylic H), 6.76 (d, $J=7.7$ Hz, 2H, Ar–H), 6.93 (d, $J=6.7$ Hz, 2H, Ar–H), 7.11–7.28 (m, 11H, Ar–H), 7.37 (d, $J=8.6$ Hz, 2H, Ar–H), 7.57 (d, $J=8.3$ Hz, 2H, Ar–H), 9.60 (s, 1H, N–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 163.3, 145.1, 144.8, 139.2, 137.1, 133.2, 131.8, 130.1, 129.7, 129.5, 129.3, 128.0, 127.9, 127.3, 127.3, 127.1, 127.1, 126.9, 126.3, 125.6, 119.8, 111.0, 94.4, 51.6, 50.3; Anal. calcd. for $C_{33}H_{26}ClN_3O_4$: C 70.27, H 4.65, N 7.45; found: C 70.15, H 4.51, N 7.33.

Dimethyl 2-{[4-(2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1*H*-imidazol-1-yl)phenyl] amino}maleate (3d)

White solid; Yield 88% (0.51 g); mp 172–174 °C; FTIR (KBr): 3452, 3089, 2961, 1735, 1679, 1611, 1521, 1440, 1281, 1226, 1145, 1034, 786, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.58 (s, 3H, CH_3-ester), 3.75 (s, 3H, CH_3-ester), 3.77 (s, 3H, CH_3 Methoxy), 3.88 (s, 3H, CH_3 Methoxy), 5.50 (s, 1H, vinylic H), 6.75 (dd, $J=3.6$ Hz, $J=0.80$ Hz, 1H, Ar–H), 6.84 (d, $J=11.4$ Hz, 2H, Ar–H), 6.88 (t, $J=4.3$ Hz, 1H, Ar–H), 7.09–7.26 (m, 11H, Ar–H), 7.58 (d, $J=7.8$ Hz, 2H, Ar–H), 9.65 (s, 1H, N–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.8, 163.5, 146.1, 139.2, 130.1, 129.5, 128.0, 127.9, 127.8, 127.3, 127.1, 126.9, 126.3, 125.6, 119.8, 94.4, 54.8, 54.6, 51.6, 50.3; Anal. calcd. for $C_{35}H_{31}N_3O_6$: C 71.29, H 5.30, N 7.13; found: C 71.20, H 5.19, N 7.05.

Dimethyl 2-{[4-(4,5-diphenyl-2-(thiophen-2-yl)-1*H*-imidazol-1-yl)phenyl]amino} maleate (3e)

White solid; Yield 53% (0.12 g); mp 110–112 °C; FTIR (KBr): 3453, 3068, 2961, 1747, 1611, 1521, 1286, 1230, 1145, 1034, 781, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 3.59 (s, 3H, CH_3-ester), 3.75 (s, 3H, CH_3-ester), 5.50 (s, 1H, vinylic H), 6.75 (dd, $J=3.7$ Hz, $J=0.9$ Hz, 1H, Ar–H), 6.84 (d, $J=8.6$ Hz, 2H, Ar–H), 6.88 (d, $J=4.2$ Hz, 1H, Ar–H), 7.09–7.26 (m, 12H, Ar–H), 7.58 (d, $J=7.5$ Hz, 2H, Ar–H), 9.65 (s, 1H, N–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 163.3, 145.1, 144.8, 139.2, 137.1, 133.2, 131.8, 130.1, 129.7, 129.5, 129.3, 128.0, 127.9, 127.3, 127.3, 127.1, 127.1, 126.9, 126.3, 125.6, 119.8, 111.5, 94.4, 51.7, 50.4; Anal. calcd. for $C_{31}H_{25}N_3O_4S$: C 69.52, H 4.70, N 7.85, S 5.99; found: C 69.38, H 4.70, N 7.63, S 5.80.

Dimethyl 2-[(2,6-dichlorophenyl)amino]maleate (4b)

Pale yellow solid; Yield 73% (0.22 g); mp 108–110 °C; FTIR (KBr): 3450, 3068, 2961, 1743, 1670, 1623, 1286, 1140, 1034, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 3.70 (s, 3H, CH_3-ester), 3.78 (s, 3H, CH_3-ester), 5.67 (s, 1H, vinylic H), 7.05 (t, $J=8.0$ Hz, 1 H, Ar–H), 7.30 (d, $J=8.0$ Hz, 2 H, Ar–H) 9.59 (s, 1H, N–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 162.1, 146.3, 134.6, 130.3, 127.2, 125.4, 92.0, 51.8, 50.3; Anal. calcd. for $C_{12}H_{11}Cl_2NO_4$: C 47.39, H 3.65, N 4.61; found: C 47.22, H 3.49, N 4.46.

Dimethyl 2-[(2,6-dimethylphenyl)amino]maleate (4c)

Pale yellow solid; Yield 87% (0.23 g); mp 100–102 °C; FTIR (KBr): 3367, 3301, 2961, 1747, 1675, 1611, 1440, 1220, 1149, 1038, 969, 820, 786 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.24 (s, 6H, CH_3 Methyl), 3.56 (s, 3H, CH_3-ester), 3.74 (s, 3H, CH_3-ester), 5.31 (s, 1H, vinylic H), 7.01–7.05 (m, 3 H, Ar–H), 9.27 (s, 1H, N–H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 162.9, 150.4, 136.5, 134.7, 127.0, 125.8, 87.2, 51.4, 51.4, 49.9, 49.9; Anal. calcd. for $C_{14}H_{17}NO_4$: C 63.87, H 6.51, N 5.32; found: C 63.75, H 6.42, N 5.18.

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