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One-pot synthesis of highly substituted imidazoles using molecular iodine: A versatile catalyst

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Abstract

Molecular iodine has been used an efficient catalyst for an improved and rapid one-pot synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetra substituted imidazoles in excellent yields. The significant features of the iodine-catalyzed condensation are operational simplicity, inexpensive reagents, high yield of products and the use of non-toxic reagents.

Keywords: 2,4,5-Trisubstituted imidazoles; 1,2,4,5-Tetra substituted imidazoles; Molecular iodine

As an important member of the five-membered ring heterocycles, imidazole moiety is present in a wide range of naturally occurring molecule [1]. Compounds with imidazole moiety have many pharmaceutical activities [2]. The biological importance of the imidazole ring system has made it a common structure in numerous synthetic compounds, such as fungicides [3], herbicides [3], plant growth regulators [4] and therapeutic agents [5]. Recently, the advances in green chemistry and organometallic chemistry have extended the boundary of imidazoles to the synthesis and application of a large class of imidazoles as ionic liquid and imidazoles [6] related N-heterocyclic carbenes [7]. Due to their wide range of biological, industrial and synthetic applications, these have recently received a great deal of attention. There are several methods reported in literature for the synthesis of imidazoles, such as hetero-cop rearrangement [8], four component condensation of aryl glyoxals, primary amines, carboxylic acids and isocyanides on wang resin [9], reaction of *N*-(2-oxo)amides with ammonium trifluroracetate [10], 1,2-amino alcohols in the presence of PCl_5 [11], diketones, aldehydes, amine and ammonium acetate in presence of phosphoric acid [12], in acetic acid [13], organocatalyst in acetic acid [14] as well as H_2SO_4 [15], DMSO [16]. Many of the synthetic protocols for imidazoles reported above, suffer from one or more disadvantages, such as harsh reaction conditions, poor yields, prolonged reaction time period, use of hazardous and often expensive acid catalysts. Moreover, DMF and DMSO leads to complex isolation and recovery procedure. There are several efficient methods developed for the synthesis of imidazoles, which comprise the use of MW/silica gel [17], MW/silica gel/H-Y [18], MW/Al_2O_3 [19], MW/acetic acid [20], in DMF [21]. However, the use of high temperature, expensive instruments likes microwave and corrosive reagents limiting these methods. Thus, simple efficient and flexible protocol for the synthesis of imidazoles are still in need as there is a scope for further improvement towards milder reaction conditions, development of simple and inexpensive reagents, convenient procedures and higher product yields.

In recent years, the use of molecular iodine as a catalyst has received considerable interest in different areas of organic transformations [22] to afford the product in good to excellent yields. Owing to several advantages, such as inexpensive non-toxic, eco-friendly nature, iodine has been used as a readily available catalyst in the investigation of different organic reactions [23]. Development of efficient, selective and eco-friendly methods for application in complex organic preparations is the ultimate goal of several research groups, including ours [24], so in continuation of our work here we wish to report the eco-friendly

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Table 1
Optimization of reaction conditions for synthesis of imidazoles[a]

Entry	Iodine (mol%)	Time (h)	Yield (%)[b]
1	0	4	0
2	5	2.5	99
3	10	2	97
4	20	1.5	97
5	30	1.5	99
6	50	1	99

[a] One equiv benzil **1**:1 equiv benzaldehyde **3a**:2.5 equiv NH_4OAc **2** at room temperature.
[b] Isolated and unoptimized yields.

synthesis of highly substituted imidazoles by iodine catalyzed cyclo condensation of aromatic aldehyde, ammonium acetate, aniline and benzil.

Different solvents were tried to standardize the reaction condition. Reaction goes well with I_2/toluene, I_2/acetonitrile, I_2/dichloromethane and I_2/ethanol, but we used only ethanol, which is relatively benign organic solvent. Moreover with ethanol, only aqueous work up is required where as in other solvents, we need hazardous solvents for extraction of products. Minimum amount of solvent was used only to facilitate the homogeneous stirring. Further investigation was carried out for catalytic evaluation of iodine for the best reaction conditions (Table 1). The increase in the quantity of iodine up to 50 mol% not only increases the yield but also lessens the reaction time but results clearly indicate that even 5 mol% of iodine is sufficient to catalyze the cyclocondensation. However, in the absence of iodine, the reaction did not yield any product even after 4 h.

In order to examine the effect of temperature, concentration of iodine was kept constant at 5 mol% and the reaction was monitored at different temperature as compiled in Table 2. At elevated temperature using 5 mol% of iodine gave better results in terms of yield and reaction time.

Among various conventional procedures for the synthesis of 2,4,5-triarylimidazole **4a–4h**, molecular iodine was found to be more effective catalyst as nearly stoichiometric amount of ammonium acetate was used where as conventionally higher fold of ammonium acetate was required. Thus, this method is advanced with respect to the existing procedures. After optimizing the best condition for the 2,4,5-triarylimidazoles **4a–4h**

Table 2
Effect of tempearture on iodine catalyzed imidazole[a] synthesis

Entry	Aldehyde	Product	Temperature (°C)	Time (min)	Yield (%)[b]
1	**3a**	**4a**	Room temperature	90	99
2	**3a**	**4a**	45	45	99
3	**3a**	**4a**	60	30	98
4	**3a**	**4a**	75	15	99
5	**3a**	**6a**	Room temperature	120	99
6	**3a**	**6a**	45	50	98
7	**3a**	**6a**	60	30	99
8	**3a**	**6a**	75	15	99

[a] Product **4a** from 1 equiv benzil **1**:1 equiv benzaldehyde **3a**:2.5 equiv NH_4OAc **2** and **6a** from 1 equiv benzil **1**:1 equiv benzaldehyde **3a**:1 equiv NH_4OAc **2**:1 equiv aniline **5** with 5 mol% iodine.
[b] Isolated and unoptimized yields.

Table 3
Iodine catalyzed synthesis of 2,4,5-triarylimidazoles[a] **4a–4h**

Entry	Aldehyde	Ar	Time (min)	Product	Yield (%)[b]
1	**3a**	C_6H_5	15	**4a**	99
2	**3b**	*p*-MeO C_6H_4	25	**4b**	99
3	**3c**	*o*-OH C_6H_4	20	**4c**	97
4	**3d**	*p*-Cl C_6H_4	25	**4d**	98
5	**3e**	*m*-$NO_2C_6H_4$	15	**4e**	99
6	**3f**	*p*-OH C_6H_4	15	**4f**	99
7	**3g**	2-Thiophenyl	20	**4g**	97
8	**3h**	Piperonal	20	**4h**	99

[a] Product **4** from 1 equiv benzil **1**:1 equiv aldehyde **3**:2.5 equiv NH_4OAc **2** with 5 mol% at 75 °C.
[b] Isolated and unoptimized yields.

Table 4
Iodine catalyzed synthesis of 1,2,4,5-tetraarylimidazoles[a] **6a–6h**

Entry	Aldehyde	Ar	Time (min)	Product	Yield (%)[b]
1	**3a**	C_6H_5	15	**6a**	99
2	**3b**	*p*-MeO C_6H_4	25	**6b**	99
3	**3c**	*o*-OH C_6H_4	25	**6c**	98
4	**3d**	*p*-Cl C_6H_4	20	**6d**	99
5	**3e**	*m*-$NO_2C_6H_4$	15	**6e**	99
6	**3f**	*p*-OH C_6H_4	20	**6f**	97
7	**3g**	2-Thiophenyl	20	**6g**	99
8	**3h**	Piperonal	15	**6h**	98

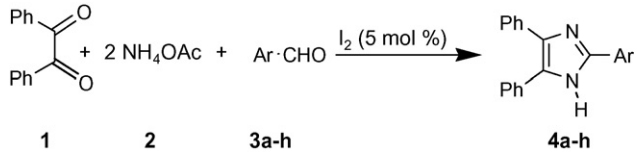
[a] Product **6a** from 1 equiv benzil **1**:1 equiv aldehyde **3a**:1 equiv NH_4OAc **2**:1 equiv aniline **5** with 5mol% iodine at 75 °C.
[b] Isolated and unoptimized yields.

(Table 3), the generality and scope of the iodine catalyzed reaction was examined by selecting a four component synthesis of 1,2,4,5-tetraarylimidazoles **6a–6h**. As expected, excellent yields of product were generated under refluxing condition with 5 mol% of iodine (Table 4). The structure of **6g** was also confirmed by single crystal X-ray crystallography [25].

It can be observed from Tables 3 and 4 that the process tolerates both electron withdrawing and electron donating substituents on the aldehydes. The aryl group substituted with different positions of the aromatic ring has not shown much effect on the formation of the final product.

Molecular iodine catalyzes the reaction as a mild Lewis acid. Molecular iodine is capable of bonding with the carbonyl oxygen increasing the reactivities of the parent carbonyl compounds.

As shown in Scheme 1, we give the likely mechanism. Iodine facilitate the formation of a diamine intermediate (I), which under mild acid catalysis of iodine condenses further with the carbonyl carbon of 1,2 diketone followed by dehydration to afford the iso-imidazole (II), which rearranges via [1,5] sigmatropic shift to the required imidazoles.



Scheme 1. Iodine catalyzed synthesis of 2,4,5-triarylimidazoles **4a–4h**.

The overall greenness of this reaction was high as minimum amount of environmentally benign ethanol was used during the course of reaction. Moreover, it is important to note that in all cases, imidazoles were precipitated on dilution of the reaction mixture with water and were isolated by a simple filtration. The dried product thus obtained showed a single spot on TLC and was pure enough for all practical purposes.

In summary, this paper describes a simple and convenient method for the synthesis of Imidazoles. We have successfully developed an easy and efficient method to prepare a variety of tri substituted and tetra substituted imidazoles in the presence of catalytic amount of iodine. The catalytic activity of iodine is remarkable and the use of low cost, commercially available iodine as catalyst for the synthesis of imidazoles in excellent yields is also significant under the aspect of environmentally benign processes. The advantages, such as shorter reaction times, product yields, the easy procedure to carry out the reaction makes the inexpensive and commercially available iodine as a powerful catalyst for the synthesis of imidazoles.

1. Experimental

1.1. General

Melting points were determined using a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were obtained on Perkin-Elmer FTIR-1710 spectrophotometer using Nujol film. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance Spectrospin at 300 and at 75 MHz, respectively, using TMS as internal standard. Analytical TLC's were performed on pre-coated Merck silica gel 60 F_{254} plates; the spots were detected either under UV light or by placing in iodine chamber. Elemental analysis was performed on a Horeaus CHN Rapid analyzer. The temperature of the reaction mixture was measured through a non-contact infrared thermometer (AZ, Mini Gun type, model 8868). X-ray diffraction data was made on a Enraf-Nonius CAD4 Diffractometer (Fig. 1).

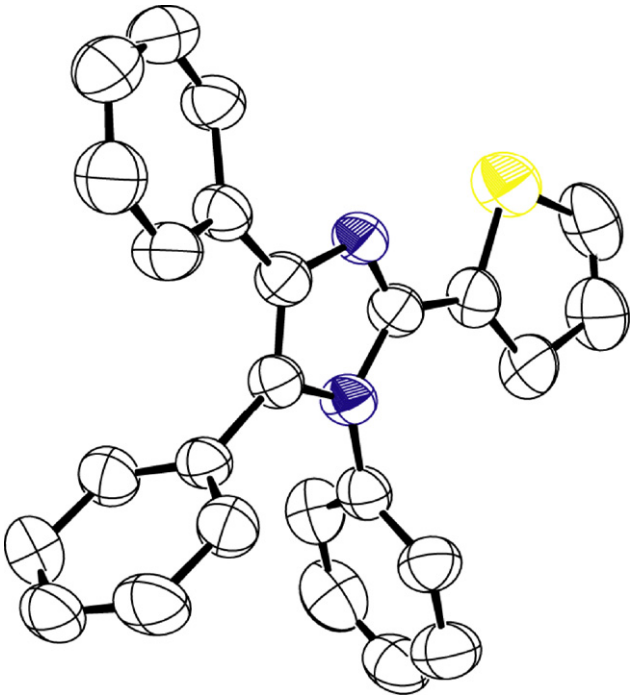


Fig. 1. Compound 1,4,5-triphenyl-2-thiophen-2-yl-1H-imidazole **6g** at 50% ellipsoidal probability.

1.2. Synthesis

1.2.1. General procedure for the synthesis of 2,4,5-triarylimidazole *4a–4h*

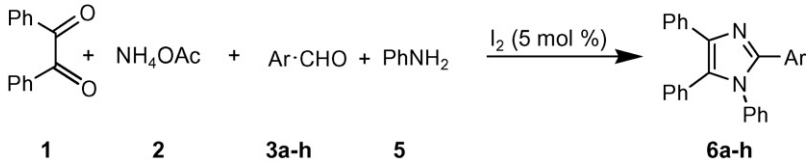
A mixture of benzil **1** (10 mmol), ammonium acetate **2** (20 mmol), aromatic aldehyde **3** (20 mmol) and iodine (5 mol%) in 2 ml of ethanol was stirred at 75 °C for the appropriate time mentioned in Table 3. The completion of reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with water (having small amount of $Na_2S_2O_3$). The solid imidazole products that separated out, were filtered, washed with water and dried. The crude products, thus obtained were pure and subjected to further purification by column chromatography of silica gel (60–120 mesh size) using 25% ethylacetate in petroleum ether as eluent to yield 2,4,5-triarylimidazole **4a–4h**. The structures of all the products were unambiguously established on the basis of their spectral analysis (IR, ^{1}H, ^{13}C NMR and mass spectral data).

1.2.2. General procedure for the synthesis of 1,2,4,5-tetraarylimidazole *6a–6h*

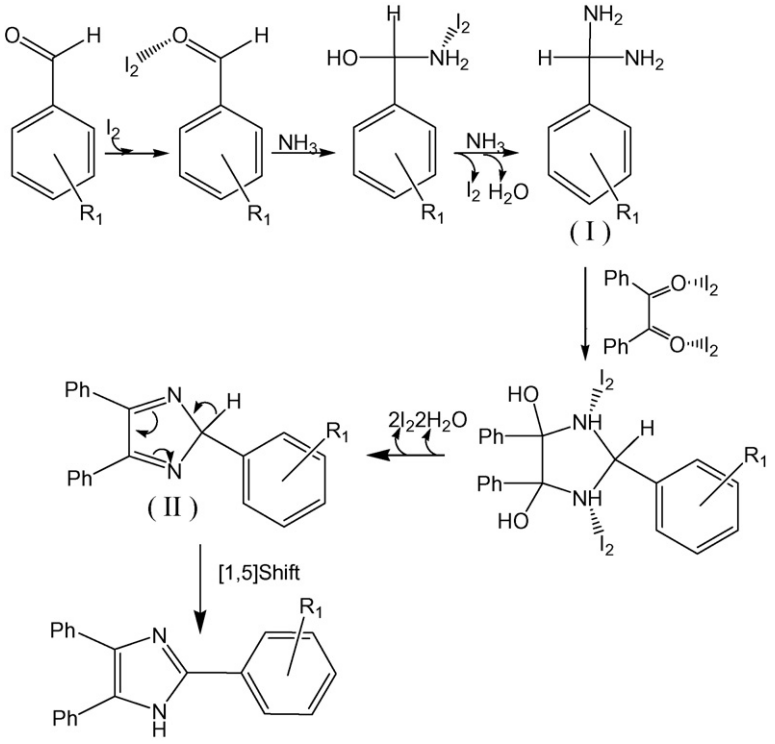
Again a mixture of benzil **1** (10 mmol), ammonium acetate **2** (10 mmol), aromatic aldehyde **3** (10 mmol), aniline **4** (10 mmol) and iodine (5 mol%) in 2 ml of ethanol was stirred at 75 °C for the appropriate time mentioned in Table 4. The completion of reaction was monitored by TLC. After completion of reaction, same work-up procedure was followed as followed in the synthesis of 2,4,5-triarylimidazole **4a–4h)** (Schemes 2 and 3).

1.3. Spectral and analytical data

Compound **4a**, mp: 272–273 °C; IR (cm^{-1}, Nujol): 3432 (NH), 1660 (C=C), 1550 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6): δ = 7.52–7.91 (m, 15H), 12.62 (br, s, NH) ppm; ^{13}C NMR



Scheme 2. Iodine catalyzed synthesis of 1,2,4,5-tetraarylimidazoles **6a–6h**.



Scheme 3. Probable mechanism.

($CDCl_3$/DMSO-d_6): δ = 122.5, 127.0, 128.7, 129.2, 136.4 ppm; Anal. Calcd. for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.22; H, 5.37; N, 9.41.

Compound **4b**, mp: 222–224 °C; IR (cm^{-1}, Nujol): 3431 (NH), 1607 (C=C), 1519 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6): δ = 3.67 (s, 3H), 6.91–6.94 (d, J = 8.8 Hz, 2H), 7.20–7.35 (m, 10H), 7.81–7.84 (d, J = 8.8 Hz, 2H), 12.48 (br, s, NH) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6): δ = 55.7, 113.4, 122.6, 126.3, 126.6, 128.0, 128.3, 133.4, 145.7, 159.6 ppm; Anal. Calcd. for $C_{22}H_{18}N_2O$: C, 80.98; H, 5.52; N, 8.58. Found: C, 80.89; H, 5.49; N, 8.50.

Compound **4c**, mp: 203–205 °C; IR (cm^{-1}, Nujol): 3428 (NH), 3215 (OH), 1602 (C=C), 1532 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6): δ = 6.86–6.93 (d, J = 7.5 Hz, 2H), 6.97–7.01 (d, J = 7.8 Hz, 2H), 7.2–7.52 (m, 10H), 12.49 (br, s, NH) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 112.8, 116.5, 119.0, 124.7, 126.9, 127.9, 128.3, 129.1, 145.4, 156.6 ppm; Anal. Calcd. for $C_{21}H_{16}N_2O$: C, 80.97; H, 5.12; N, 8.97. Found: C, 80.84; H, 5.14; N, 8.92.

Compound **4d**, mp: 262–263 °C; IR (cm^{-1}, Nujol): 3432 (NH), 1604 (C=C), 1489 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6): δ = 7.05–7.37 (m, 10H), 7.51–7.53 (d, J = 8 Hz, 2H), 7.80–7.92 (d, J = 8.6 Hz, 2H), 12.47 (br, s, NH) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 12.2, 125.4, 126.5, 126.8, 128.3, 128.8, 129.2, 129.9, 132.8, 144.3 ppm; Anal. Calcd. for $C_{21}H_{15}N_2Cl$: C, 76.25; H, 4.53; N, 8.47. Found: C, 76.16; H, 4.51; N, 8.39.

Compound **4e**, mp: 265-267 °C; IR (cm^{-1}, Nujol): 3458 (NH), 1664 (C=C), 1593 (C=N), 1523 (NO_2), 1349 (NO_2); ^{1}H NMR ($CDCl_3$/DMSO-d_6): δ = 7.20–7.62 (m, 10H), 7.81–7.98 (m, 4H), 12.54 (br, s, NH) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 122.7, 124.2, 127.8, 128.7, 129.6, 132.8, 133.2, 146.3, 158.1 ppm; Anal. Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.90; H, 4.39; N, 12.31. Found: C, 73.62; H, 4.51; N, 12.37.

Compound **4f**, mp: 260–261 °C; IR (cm^{-1}, Nujol): 3572 (OH), 3437 (NH), 3291 (OH), 1644 (C=C), 1547 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 6.99–7.04 (d, J = 8 Hz, 2H), 7.51–7.86 (m, 10H), 7.87–7.90 (d, J = 8.5 Hz, 2H), 12.61 (s, br, NH) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 113.5, 119.7, 125.7, 125.8, 126.1, 126.9, 145.2, 159.7 ppm; Anal. Calcd. for $C_{21}H_{16}N_2O$: C, 80.77; H, 5.12; N, 8.97. Found: C, 80.87; N, 5.07; N, 8.99.

Compound **4g**, mp: 255–257 °C; IR (cm^{-1}, Nujol): 3438 (NH), 1665 (C=C), 1597 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 6.71–6.72 (d, J = 7.6 Hz, 1H), 6.93–6.97 (m, 1H), 7.39–7.61 (m, 10H), 12.29 (br s NH) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 122.1, 125.4, 126.2, 126.5, 127.8, 128.1, 129.5, 136.7, 141.4 ppm; Anal. Calcd. for $C_{19}H_{14}N_2S$: C, 75.50; H, 4.63; N, 9.27; S, 10.60. Found: C, 75.44; H, 4.62; N, 9.38; S, 10.62.

Compound **4h**, mp: 248–250 °C; IR (cm^{-1}, Nujol): 3442 (NH), 1659 (C=C), 1598 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 6.02 (s, 2H), 6.89 (m, 1H), 7.39–7.74 (m, 12H), 12.41 (br s NH) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6, TMS): δ = 92.9, 113.4, 117.1, 121.6, 122.7, 126.3, 127.3, 129.4, 136.8, 147.7, 149.7 ppm; Anal. Calcd. for $C_{22}H_{16}N_2O_2$: C, 77.65; H, 4.71; N, 8.24. Found: C, 77.64; H, 4.69; N, 8.31.

Compound **6a**, mp: 221 °C; IR (cm^{-1}, Nujol): 1596 (C=C), 1571 (C=N); ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ = 7.26–7.49 (m, 20H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ = 122.9, 124.2,

124.8, 125.7, 127.1, 128.4, 128.6, 129.1, 129.8, 129.6, 136.4 ppm; Anal. Calcd. for $C_{27}H_{20}N_2$ (372): C, 87.07; H, 5.41; N, 7.52. Found: C, 87.12; H, 5.36; N, 7.48.

Compound **6b**, mp: 184–185 °C; IR (cm^{-1}, Nujol): 1617 (C=C), 1578 (C=N); ^1H NMR ($CDCl_3$/DMSO-d_6) $\delta = 3.75$ (s, 3H), 6.81–6.83 (d, $J = 8.5$ Hz, 2H), 7.21–7.37 (m, 15H), 7.49–7.51 (d, $J = 7.2$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) $\delta = 54.7$, 114.2, 125.2, 126.1, 126.7, 128.0, 128.2, 128.3, 128.6, 129.1, 130.8, 131.3, 131.9, 136.7, 137.1, 138.1, 146.5, 160.4 ppm; Anal. Calcd. for $C_{28}H_{22}N_2O$ (402): C, 83.56; H, 5.51; N, 6.96. Found: C, 83.51; H, 5.42; N, 6.87.

Compound **6c**, mp: 255–257 °C; IR (cm^{-1}, Nujol): 1603 (C=C), 1578 (C=N); ^1H NMR ($CDCl_3$/DMSO-d_6) $\delta = 6.60$–6.69 (d, $J = 7.5$ Hz, 2H), 6.93–6.96 (d, $J = 8$, Hz, 2H), 7.19–7.46 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) $\delta = 115.9$, 122.1, 124.7, 125.2, 126.1, 127.9, 128.4, 129.2, 130.8, 131.9, 135.1, 136.5, 137.4, 139.7, 145.3, 155.7 ppm; Anal. Calcd. for $C_{27}H_{20}N_2O$ (388): C, 83.48; H, 5.19; N, 7.29. Found: C, 83.54; H, 5.17; N, 7.21.

Compound **6d**, mp: 149–151 °C; IR (cm^{-1}, Nujol): 1600 (C=C), 1578 (C=N); ^1H NMR ($CDCl_3$/DMSO-d_6) $\delta = 7.33$–7.61 (m, 15H), 7.66–7.68 (d, $J = 8.2$ Hz, 2H), 7.94–7.97 (d, $J = 8.4$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) $\delta = 124.1$, 124.6, 126.1, 127.7, 128.5, 129.1, 130.2, 130.4, 132.9, 134.3, 139.8, 143.4, 144.6 ppm; Anal. Calcd. for $C_{27}H_{19}N_2Cl$ (406.5): C, 79.70; H, 4.71; N, 6.88. Found: C, 79.76; H, 4.62; N, 6.83.

Compound **6e**, mp: 244–246 °C; IR (cm^{-1}, Nujol): 1595 (C=C), 1577 (C=N); ^1H NMR ($CDCl_3$/DMSO-d_6) $\delta = 7.27$–7.71 (m, 16H), 7.84–8.21 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) $\delta = 123.1$, 125.2, 126.0, 128.1, 128.3, 128.4, 128.6, 128.8, 129.9, 130.7, 133.2, 134.6, 137.2, 137.4, 144.3, 153.4 ppm; Anal. Calcd. for $C_{27}H_{19}N_3O_2$ (417): C, 77.68; H, 4.59; N, 10.07. Found: C, 77.78; H, 4.53; N, 10.20.

Compound **6f**, mp: 280–281 °C; IR (cm^{-1}, Nujol): 1604 (C=C), 1578 (C=N); ^1H NMR ($CDCl_3$/DMSO-d_6) $\delta = 6.87$–6.91 (d, $J = 8$ Hz, 2H), 7.15–7.49 (m, 15H), 7.61–7.65 (d, $J = 8.2$Hz) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) $\delta = 115.3$, 119.8, 125.3, 126.0, 126.7, 127.9, 128.2, 128.5, 128.6, 129.3, 131.6, 131.8, 135.3, 137.3, 146.6, 159.3 ppm; Anal. Calcd. for $C_{27}H_{20}N_2O$ (388): C, 83.48; H, 5.19; N, 7.21. Found: C, 83.44; H, 5.11; N, 7.09.

Compound **6g**, mp: 247–251 °C; IR (cm^{-1}, Nujol): 1596 (C=C), 1577 (C=N); ^1H NMR ($CDCl_3$/DMSO-d_6) $\delta = 6.70$–6.89 (m, 2H), 7.19–7.32 (m, 15H), 7.57–7.64 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) $\delta = 125.4$, 126.1, 126.5, 127.1, 127.4, 128.1, 128.4, 129.2, 129.4, 130.0, 131.1, 132.9, 134.0, 134.1, 134.2 136.2, 136.8, 141.4 ppm; Anal. Calcd. for $C_{25}H_{18}N_2S$ (378): C, 79.33; H, 4.79; N, 7.40. Found: C, 79.37; H, 4.70; N, 7.32.

Compound **6h**, mp: 194–196 °C; IR (cm^{-1}, Nujol): 1596 (C=C), 1570 (C=N); ^1H NMR ($CDCl_3$/DMSO-d_6) $\delta = 6.03$ (s, 2H), 6.98–7.48 (m, 18H) ppm; ^{13}C NMR ($CDCl_3$/DMSO-d_6) $\delta = 91.6$, 113.2, 116.8, 120.9, 125.9, 126.2, 126.7, 127.3, 128.1, 128.3, 129.4, 130.1, 131.0, 132.8, 134.2, 136.6, 137.3, 147.3, 148.1 ppm; Anal. Calcd. for $C_{28}H_{20}N2O_2$ (416): C, 80.75; H, 4.84; N, 6.73. Found: C, 80.63; H, 4.81; N, 6.75.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.10.009.

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[25] Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 615706 for compounds **6g**. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: linstead@ccdc.cam.ac.uk or deposit@ccdc.cam.ac.uk; Fax: +44 1223 336033). Structure parameter for **6g**: wavelength: $\lambda = 1.54178$ Å; crystal size: 0.30 mm × 0.20 mm × 0.15 mm; crystal system: triclinic; space group: *P*-1; unit cell: $a = 9.7490(10)$ Å, $b = 10.1460(10)$ Å, $c = 21.1030(10)$ Å, $\alpha = 79.39(2)^\circ$, $\beta = 77.51(2)^\circ$, $\gamma = 76.92(2)^\circ$. Supporting data contain more information (2000).