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APPLICATION OF SULFAMIC ACID AS AN ECO-FRIENDLY CATALYST IN AN EXPEDIENT SYNTHESIS OF BENZIMIDAZOLES

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Abstract – Sulfamic acid, an eco-friendly and zwitterionic solid, proved to be a very efficient catalyst for the reaction of *ortho*-phenylenediamine with aryl aldehydes in ethanol at room temperature to furnish both 1-arylmethyl-2-aryl- and 2-arylbenzimidazoles in very good to excellent overall yields.

INTRODUCTION

Benzimidazoles are important heterocycles because of their use as anthelmintics in veterinary medicine and human therapeutics.[1] Among the extant synthetic routes to benzimidazoles,[2] an important route comprises the oxidative cyclisation of *ortho*-phenylenediamine (*o*-PD) Schiff bases, often generated *in situ* from *o*-PDs and aldehydes, using a variety of oxidants.[3-6] Most of these methods, however, use stoichiometric or larger amounts of oxidants, often producing toxic wastes, involve tedious work-ups and purifications and furnish benzimidazoles in wide ranging or very poor yields.

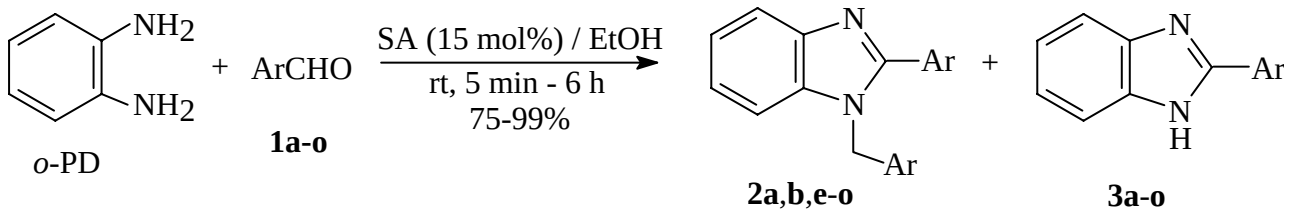
In view of the aforesaid drawbacks of the extant routes and of the rapidly increasing importance of green chemistry,[7] a few green syntheses of benzimidazoles from *o*-PDs and particularly aryl aldehydes have been reported only recently employing $Sc(OTf)_3$,[8, 9] $Yb(OTf)_3$,[10] and montmorillonite K10 clay/μw.[11] But even these methods involve constraints like very long reaction periods (e.g. up to 44 h), employ potentially explosive conditions, etc. Clearly, there is a need to develop newer syntheses of benzimidazoles employing more eco-friendly conditions and catalysts.

In response to this need, we have used the nonvolatile, nonhygroscopic, odourless, uncorrodible and

zwitterionic solid, sulfamic acid (SA) as the catalyst. Because of its insolubility in common organic solvents but solubility in water, high acidity in solution and eco-friendliness,[12] SA is fast coming up as a mild, low-cost and highly efficient green catalyst in organic transformations.[13] We have demonstrated that 15 mol% of SA can efficiently bring about the condensation of *o*-PD with aryl aldehydes under benign conditions to furnish usually a mixture of 1-arylmethyl-2-aryl- and 2-arylbenzimidazoles in (75-99)% overall yields. Our findings, since useful, are presented in this paper.

RESULTS AND DISCUSSION

When *o*-PD was treated separately with 1.5-3.0 equiv.[14] of several benzaldehydes (**1a**-**j**), two naphthaldehydes (**1k**,**l**) and three heteroaryl aldehydes (**1m**-**o**) in ethanol at room temperature, two products (TLC) were formed in all but two cases, viz. those from 2-nitro and 4-nitrobenzaldehydes (**1c**,**d**). These products were identified as the 1-arylmethyl-2-arylbenzimidazoles (**2a**,**b**,**e**-**o**) and 2-arylbenzimidazoles (**3a**-**o**), isolated in (13-67)% and (18-76)% yields, respectively. Only in the case of 4-hydroxybenzaldehyde (**1i**), the two products (TLC) formed could not be separated by any means, and from **1c** and **1d**, the respective 2-arylbenzimidazoles (**3c**,**d**) were the sole products formed in nearly the same yields (75%, 76%) (Scheme 1, Table 1). The appearance of signals for the benzylic methylene group in the NMR spectra of **2** and those for NH in the ^{1}H NMR spectra of **3**, coupled with their observed molecular weights, were crucial in distinguishing the two types of products (*vide* Experimental).



Scheme 1

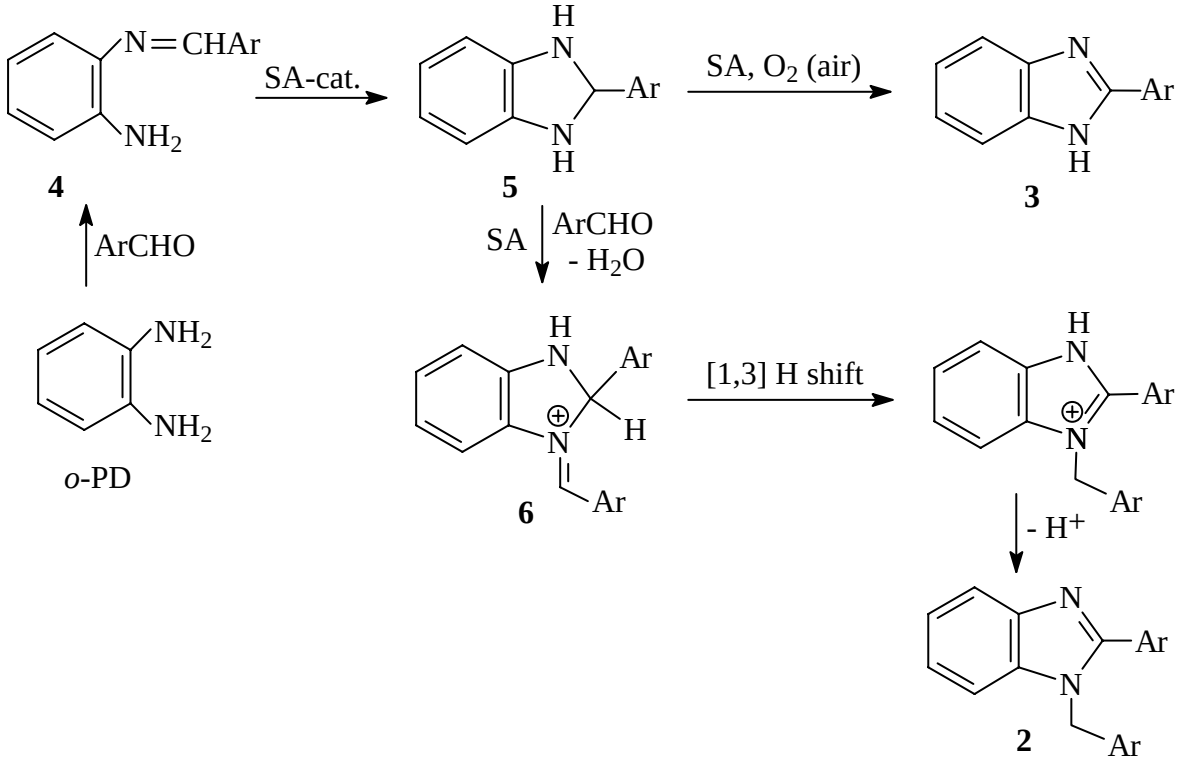
An inspection of the results presented in Table 1 reflects that the presence of an electron-withdrawing group in the aldehydes **1c**-**e** expedited the reactions (30/15/5 min) and generated the 2-arylbenzimidazoles (**3c**-**e**) at the expense of the related 1,2-disubstituted benzimidazoles (**2c**-**e**), the two extreme cases being **1c** and **1d**. Likewise, the presence of an electron-donating group in the aryl aldehydes (**1f**-**j**) decelerated the reactions (1.5-4.25 h) and led to the formation of the 1,2-disubstituted benzimidazoles (**2f**-**j**) in higher yields than their 2-substituted counterparts (**3f**-**j**). Nevertheless, no such systematic observation emerged from the two naphthaldehydes (**1k**,**l**) and the three heteroaryl aldehydes (**1m**-**o**).

Table 1. SA-catalysed synthesis of benzimidazoles from aryl aldehydes and *o*-PD[a]

Entry	Aldehyde (**1**): Ar (No. of equiv.)	Time (h)	Yield (%) of **2**	Yield (%) of **3**	Overall Yield (%)
1	**a**: Ph (1.5)	1.0	**a**: 55	**a**: 35	90
2	**b**: 3-$NO_2C_6H_4$ (1.5)	1.0	**b**: 13	**b**: 69	82
3	**c**: 2-$NO_2C_6H_4$ (1.5)	30 min	**c**: —	**c**: 75	75
4	**d**: 4-$NO_2C_6H_4$ (1.5)	15 min	**d**: —	**d**: 76	76
5	**e**: 4-$CF_3OC_6H_4$ (1.5)	5 min	**e**: 34	**e**: 64	98
6	**f**: 3,4-$(MeO)_2C_6H_3$ (1.75)	1.5	**f**: 67	**f**: 32	99
7	**g**: 3,4-$OCH_2OC_6H_3$ (1.5)	2.5	**g**: 51	**g**: 38	89
8	**h**: 4-$Me_2NC_6H_4$ (2.0)	2.5	**h**: 54	**h**: 21	75
9	**i**: 4-HOC_6H_4 (1.5)	4.0	**i**[b]: major[c]	**i**[b]: minor[c]	78
10	**j**: 4-$MeOC_6H_4$ (2.0)	4.25	**j**: 55	**j**: 25	80
11	**k**: 1-Naphthyl (1.5)	1.0	**k**: 63	**k**: 18	81
12	**l**: 2-Naphthyl (1.5)	45 min	**l**: 40	**l**: 45	85
13	**m**: 2-Pyrrolyl (2.0)	3.0	**m**: 59	**m**: 32	91
14	**n**: 2-Furyl (3.0)	5.0	**n**: 67	**n**: 31	98
15	**o**: 2-Thienyl (2.0)	6.0	**o**: 48	**o**: 49	97

[a]All reactions were carried out in the presence of 15 mol% of SA; [b]Two products formed (TLC) could not be separated by prep. TLC; [c]Ascertained from analytical TLC.

Since both **2** and **3** (except for **1c**,**d**) started forming (TLC) right from the early stages of the reactions, we propose (without any evidence) the following reaction pathway (Scheme 2).



Scheme 2

An aryl aldehyde (**1**) reacts with *o*-PD to form a mono-imine (**4**), which cyclises to 2-arylbenzimidazoline (**5**) under the catalytic influence of SA. Aerial oxidation of **5** leads to the formation of **3**, while SA-catalysed condensation of **5** with a second molecule of the aryl aldehyde results, after SA-catalysed dehydration, in the arylidene imidazolidinium salt (**6**). A subsequent [1,3] hydrogen shift, followed by the loss of a proton, leads to the formation of **2**.

An alternative pathway to **2**, conceivable on the extant state of knowledge on this type of acid-catalysed condensations leading to benzimidazoles,[3, 8] involves a redox reaction between the 2-arylbenzimidazoline (**5**) and the bis-imine (generated in situ and not depicted herein) to form **3** and the corresponding *N*-arylmethyl mono-imine (also not depicted). A subsequent SA-catalysed cyclisation of the latter to 1-arylmethyl-2-arylbenzimidazoline (not shown), followed by its aerial oxidation (possibly, SA-assisted; cf. ref. 3) results in the formation of **2**. But this possibility had to be ruled out because in that case the yields of **3** would have been higher than those of **2**, which is not in keeping with our results.

In order to test the effect of the relative amounts of SA on the outcome of the reactions, each of **1a**, **1j**, **1l** and **1o**, chosen randomly, was subjected to similar conditions but using 5 mol% and 30 mol% of SA separately (not detailed in the Experimental). The results using 5 mol% of SA were similar (in respect of both yields and reaction periods) to those using 15 mol% of SA, but 30 mol% of SA vastly expedited the reactions (15/30/15/30 min vs. 1/4.25/0.75/6 h for **1a**, **1j**, **1l** and **1o**, respectively), furnishing the two types of products in comparable yields. Thus, 30 mol% of SA transpired to be considerably more effective.

Though not generalised, the reaction of *o*-PD with an alkanal, viz. *n*-propanal (**1p**; 1.5 equiv.; 15 mol% of SA) appeared to be considerably less effective, furnishing 2-ethyl-1-*n*-propyl-1*H*-benzimidazole (**2p**) (33%) and 2-ethylbenzimidazole[4] (**3p**; 16%).

To conclude, we have presented herein a successful application of environmentally benign sulfamic acid as an efficient catalyst for an expedient synthesis of 1,2-disubstituted and 2-substituted benzimidazoles starting from *o*-PD and (hetero)aryl aldehydes. Additionally, the present method offers an opportunity to prepare only 1,2-disubstituted benzimidazoles if *N*-substituted *o*-PD is used instead of *o*-PD itself.

EXPERIMENTAL

Melting points were recorded on a Toshniwal apparatus and are uncorrected. The IR spectra were recorded on a Nicolet Impact 410 FT-IR spectrophotometer, the ^{1}H (500/400/300 MHz) and ^{13}C (125/100 MHz) NMR spectra, including DEPT 135/HMQC, on Bruker DRX 500/Varian UNITY-400/Bruker DPX-300 NMR spectrometers, respectively. The individual ^{1}H and ^{13}C NMR assignments made for **2e** and **3e** were ascertained additionally from their HOMO-COSY and HMBC spectra. The LRMS (EI/ESI) spectra were recorded on JEOL JMS-AX505HA/Q-TOF-Micromass mass spectrometers. The molecular formulae of all new compounds were determined by HRMS (EI) on a JEOL JMS-700 Mstation mass spectrometer and/or

elemental analyses. The analytical and preparative TLCs were carried out on silica gel G (Merck, India) plates. PE refers to petroleum ether, bp 60-80 °C. Sulfamic acid was procured from Merck, India.

General experimental procedure. To a solution of *o*-PD (0.5 mmol; 54 mg) in EtOH at rt were successively added with stirring a solution of the aryl aldehyde (0.75-1.5 mmol) in EtOH (total volume of solution ~10 mL) and SA (15 mol%; 7-8 mg). The stirring was continued until *o*-PD was fully consumed (TLC). The reaction mixture was then diluted with water (20 mL), ethanol boiled off, the reaction mixture cooled to rt and extracted with EtOAc (3 × 20 mL). The pooled extracts were dried (Na_2SO_4), filtered and solvent distilled off from the filtrate. Except for **3c** and **3d**, which were purified by crystallisation, the resulting residue was subjected to preparative TLC to furnish **2** and **3**, which, if solid, were then recrystallised from PE-EtOAc, unless stated otherwise.

The known compounds were identified from their ^{1}H NMR spectroscopic data (not reproduced here) and by comparing their mps (*vide infra*) with those reported in the literature (references cited). **2a**: mp 132-133 °C (lit.,[11] 132 °C); **2b**: mp 168-170 °C (decomp) (lit.,[15] 170 °C); **2g**: mp 171-172 °C (lit.,[16] 175 °C); **2h**: mp 168-170 °C (lit.,[17] 168-169 °C); **2j**: mp 126-128 °C (lit.,[11] 131 °C); **2k**: mp 158-160 °C (PE-CH_2Cl_2) (lit.,[6] 160 °C); **2n**: mp 174-176 °C (decomp) (lit.,[17] 98.4-99.3 °C); **2o**: mp 146-148 °C (lit.,[17] 152.0-153.2 °C); **3a**: mp 288-290 °C (decomp) (lit.,[18] 293-295 °C); **3b**: mp 203-205 °C (lit.,[15] 206 °C); **3c**: mp 260 °C (H_2O-EtOH) (lit.,[4] 210 °C); **3d**: mp 308-310 °C (lit.,[4] 316 °C); **3g**: mp 246 °C (lit.,[4] 252 °C); **3h**: mp 233-236 °C (decomp) (lit.,[19] 275-277 °C); **3j**: mp 224 °C (lit.,[4] 226 °C); **3k**: mp 261-263 °C (lit.,[21] 266 °C); **3m**: mp 260-261 °C (decomp) (lit.,[20] 257-258 °C); **3n**: mp 283-285 °C (lit.,[4] 288 °C); **3o**: mp 326 °C (lit.,[7] >330 °C); **3p**: mp 165-167 °C (lit.,[4] 176 °C). Although the mps of **2n**, **3c** and **3h** differed from their reported mps, their structures were fully compatible with their ^{1}H NMR spectral data (not detailed here, since known).

1-(4′-Trifluoromethoxyphenyl)methyl-2-(4′′-trifluoromethoxyphenyl)benzimidazole (**2e**): oil; IR (Nujol): 1613, 1593, 1513, 1414, 1260, 1212, 1171, 1109, 1023, 990, 923, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$; 400 MHz): δ 5.47 (2H, s, NCH_2Ar), 7.11 (2H, d, *J*=9 Hz, H-2′, 6′), 7.20 (2H, d, *J*=9 Hz, H-3′, 5′), 7.23 (1H, d (further ill-split), *J*=8 Hz, H-7), 7.30 (1H, dt, J_1=8 Hz, J_2=1 Hz, H-6), 7.32 (2H, d, *J*=9 Hz, H-3′′, 5′′), 7.37 (1H, dt, J_1=8 Hz, J_2=1 Hz, H-5), 7.72 (2H, d, *J*=9 Hz, H-2′′, 6′′), 7.90 (1H, d, *J*=8 Hz, H-4); ^{13}C NMR: δ 47.7 (NCH_2Ar), 110.3 (CH-7), 120.0 (CH-4), 120.3 (2×OCF_3), 121.1 (CH-3′′, 5′′), 121.6 (CH-3′, 5′), 123.4 (CH-5), 123.8 (CH-6), 127.3 (CH-2′, 6′), 127.9 (C-1′′), 130.8 (C-2′′, 6′′), 134.4 (C-1′), 135.6 (C-7a), 142.2 (C-3a), 148.8 (C-4′), 150.6 (C-4′′), 152.3 (C-2); EI-MS: *m*/*z* (%) 452 (M^+, 57), 367 (5), 175 (100); HRMS (EI): calcd for $C_{22}H_{14}N_2O_2F_6$, 452.0960; found 452.0959; Anal. Calcd for $C_{22}H_{14}N_2O_2F_6$: C, 58.41; H, 3.09; N, 6.19. Found: C, 58.49; H, 3.10; N, 6.17.

1-(3′,4′-Dimethoxyphenyl)methyl-2-(3″,4″-dimethoxyphenyl)benzimidazole (**2f**): mp 174-175 °C; IR (Nujol): 1613, 1593, 1513, 1493, 1328, 1255, 1142, 1023, 877, 817, 744 cm^{-1}; ^1H NMR (DMSO-d_6; 500 MHz): δ 3.43, 3.47, 3.51 and 3.62 (3H, s each, 4×OCH_3), 5.29 (2H, s), 6.25 (1H, d, *J*=8 Hz), 6.54 (1H, d, *J*=1 Hz), 6.63 (1H, d, *J*=8 Hz), 6.91 (1H, d, *J*=8.5 Hz), 6.98-7.05 (2H, m), 7.09 (1H, d, *J*=7 Hz), 7.094 (1H, slightly split s), 7.26-7.31 and 7.46-7.51 (1H, m each); ^{13}C NMR: δ 48.1 (CH_2), 56.23, 56.28, 56.3, 56.4 (all OCH_3), 111.1, 111.7, 112.6, 112.8, 113.3, 118.9, 119.8, 122.5, 122.9, 123.2 (all Ar-CH), 123.3, 130.2, 136.8, 143.4, 148.9, 149.5, 149.7, 150.9, 154.1 (all Ar-C); EI-MS: *m*/*z* (%) 404 (M^+, 43), 151 (100); HRMS (EI): calcd for $C_{24}H_{24}N_2O_4$, 404.1737; found 404.1732; Anal. Calcd for $C_{24}C_{24}N_2O_4$: C, 71.29; H, 5.94; N, 6.93. Found: C, 71.21; H, 5.97; N, 6.91.

1-(2′-Naphthyl)methyl-2-(2″-naphthyl)benzimidazole (**2l**): mp 124-125 °C; IR (Nujol): 1600, 1328, 1149, 917, 830, 744 cm^{-1}; ^1H NMR (DMSO-d_6; 500 MHz): δ 5.65 (2H, s), 7.01 (1H, dd, J_1=8.5 Hz, J_2=1.5 Hz), 7.05 and 7.09 (1H, t each, *J*=7 Hz), 7.22-7.29 (1H, m), 7.25 (1H, d, *J*=7 Hz), 7.33-7.42 (3H, m), 7.35 (1H, s), 7.53 (1H, dd, J_1=7.5 Hz, J_2=2 Hz), 7.59 (1H, d, *J*=7.5 Hz), 7.65 (2H, d, *J*=8.5 Hz), 7.71 (2H, d, *J*=8 Hz), 7.77 (1H, d, *J*=7.5 Hz), 7.84 (1H, d, *J*=8.5 Hz), 8.16 (1H, s); ^{13}C NMR: δ 48.8 (CH_2), 112.0, 123.2, 125.2, 125.5, 126.9, 127.0, 127.3, 127.7, 128.2, 128.45, 128.49, 128.5, 129.2, 129.3, 129.4, 129.6 (all Ar-CH), 120.2, 123.7, 133.3, 135.5, 137.0, 143.7, 154.1 (all Ar-C); EI-MS: *m*/*z* (%) 384 (M^+, 66), 141 (100), 115 (12); HRMS (EI): calcd for $C_{28}H_{20}N_2$, 384.1627; found 384.1625; Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.50; H, 5.21; N, 7.29. Found: C, 87.42; H, 5.23; N, 7.27.

1-(2′-Pyrrolyl)methyl-2-(2″-pyrrolyl)benzimidazole (**2m**): mp > 340 °C; IR (Nujol): 3397, 3332, 1606, 1573, 1341, 1288, 1135, 1049, 757, 724 cm^{-1}; ^1H NMR (DMSO-d_6; 500 MHz): δ 5.55 (2H, s), 5.67 (1H, br s), 5.90 (1H, dd, J_1=5.5 Hz, J_2=2.5 Hz), 6.21 (1H, dd, J_1=5 Hz, J_2=2.5 Hz), 6.63-6.71 (2H, m), 6.98 (1H, m), 7.16 (1H, dt, J_1=7.5 Hz, J_2=1.5 Hz), 7.18 (1H, dt, J_1=7.5 Hz, J_2=1.5 Hz), 7.46 (1H, dd, J_1=6.5 Hz, J_2=2 Hz), 7.59 (1H, dd, J_1=6.5 Hz, J_2=2 Hz), 10.92 (1H, s), 11.79 (1H, s); ^{13}C NMR: δ 42.4 (CH_2), 106.7, 108.6, 110.2, 110.8, 111.2, 118.4, 118.8, 122.3, 122.5, 122.6 (all Ar-CH), 121.8, 127.5, 136.7, 143.4, 147.7 (all Ar-C), ESI-MS TOF (+ve): *m*/*z* (%) 285.02 $(M+Na)^+$, 185.01 (4), 184.00 (100); Anal. Calcd for $C_{16}H_{14}N_4$: C, 73.28; H, 5.34; N, 21.37. Found: C, 73.21; H, 5.35; N, 21.40.

1-*n*-Propyl-2-ethylbenzimidazole (**2p**): oil; IR (neat): 1613, 1513, 1467, 1413, 1378, 1295, 1248, 1218, 1067, 1008, 743 cm^{-1}; ^1H NMR ($CDCl_3$; 300 MHz): δ 0.98 (3H, t, *J*=7.5 Hz); 1.48 (3H, t, *J*=7.5 Hz); 1.84 (2H, sextet, *J*=7.5 Hz); 2.90 (2H, q, *J*=7.5 Hz); 4.07 (2H, t, *J*=7.5 Hz); 7.17-7.25 (2H, m); 7.27-7.33 (1H, m); 7.69-7.77 (1H, m); EI-MS: *m*/*z* (%) 188 (M^+, 80), 173 (70), 159 (100), 145 (63); HRMS (EI): calcd for $C_{12}H_{16}N_2$, 188.1313; found 188.1328; Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.59; H, 8.51; N, 14.89. Found: C,

76.52; H, 8.53; N, 14.92.

2-(4′-Trifluoromethoxyphenyl)benzimidazole (**3e**): mp 222 °C; IR (Nujol): 1593, 1500, 1434, 1401, 1301, 1281, 1162, 1109, 970, 857, 744 cm^{-1}; ^1H NMR (DMSO-d_6; 400 MHz): δ 7.22 (2H, dd, J_1=6 Hz, J_2=3 Hz, H-5, 6), 7.55 (2H, d, J=9 Hz, H-3′, 5′), 7.61 (2H, m, H-4, 7), 8.29 (2H, d, J=9 Hz, H-2′, 6′); ^{13}C NMR: δ 115.1 (CH-4, 7), 120.7 (OCF_3), 121.4 (CH-3′, 5′), 122.4 (CH-5, 6), 128.4 (CH-2′, 6′), 129.1 (C-1′), 139.0 (C-3a, 7a), 149.3 (C-4′), 149.8 (C-2); EI-MS: *m*/*z* (%) 278 (M^+, 100), 279 (15), 209 (13), 181 (14); HRMS (EI): calcd for $C_{14}H_9N_2OF_3$, 278.0667; found 278.0657; Anal. Calcd for $C_{14}H_9N_2OF_3$: C, 60.43; H, 3.24; N, 10.07. Found: C, 60.38; H, 3.23; N, 10.10.

2-(3′,4′-Dimethoxyphenyl)benzimidazole (**3f**): mp 227-228 °C; IR (Nujol): 1606, 1507, 1454, 1261, 1142, 1029, 983, 744 cm^{-1}; ^1H NMR (DMSO-d_6; 500 MHz): δ 3.63 and 3.68 (3H, s each, 2×OCH_3), 6.92 (1H, d, J=8.5 Hz), 6.97 (2H, t, J=7 Hz), 7.29 and 7.42 (1H, d each, J=7 Hz), 7.54 (1H, dd, J_1=8.5 Hz, J_2=1.5 Hz), 7.57 (1H, d, J=1.5 Hz), 12.52 (1H, s); ^{13}C NMR (DMSO-d_6; 125 MHz): δ 56.47, 56.49 (both OCH_3), 110.6 (×2), 112.7 (×2), 120.1 (×2), 122.6 (all Ar-CH), 123.6, 149.8, 151.1, 152.3 (all Ar-C); EI-MS: *m*/*z* (%) 254 (M^+, 100), 239 (39), 223 (16), 211 (41), 209 (15), 196 (14), 168 (23), 127 (14); HRMS (EI): calcd for $C_{15}H_{14}N_2O_2$, 254.1055; found 254.1067; Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.87; H, 5.51; N, 11.02. Found: C, 70.81; H, 5.52; N, 11.06.

2-(2′-Naphthyl)benzimidazole (**3l**): mp 210-212 °C (PE-CH_2Cl_2); IR (Nujol): 1586, 1546, 1500, 1407, 1334, 1281, 1228, 1135, 1096, 1009, 983, 917, 864, 824, 751 cm^{-1}; ^1H NMR (DMSO-d_6; 500 MHz): δ 7.01 and 7.04 (1H, t each, J=7 Hz), 7.37 (1H, d, J=8 Hz), 7.38-7.44 (2H, m), 7.50 (1H, d, J=7.5 Hz), 7.79 and 7.84 (1H, split d each, J= 7.5 Hz), 7.88 (1H, d, J=8.5 Hz), 8.11 (1H, dd, J_1=8.5 Hz, J_2=1 Hz), 8.54 (1H, s), 12.86 (1H, s); ^{13}C NMR: δ 124.8, 126.6, 127.7, 127.9, 128.6, 129.3, 129.4 (all Ar-CH), 123.0, 128.4, 133.6, 134.3, 152.1 (all Ar-C); EI-MS: *m*/*z* (%) 244 (M^+, 100), 243 (45), 153 (8), 127 (6), 122 (12); HRMS (EI): calcd for $C_{17}H_{12}N_2$, 244.1001; found 244.1019; Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.60; H, 4.92; N, 11.47. Found: C, 83.69; H, 4.90; N, 11.51.

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