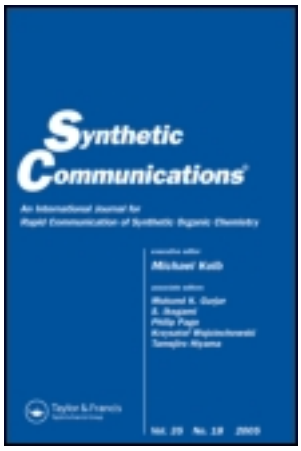

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Solid-State Synthesis of 4-[(Indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolone by Catalysis of Molecular Iodine

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Solid-State Synthesis of 4-[(Indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolones by Catalysis of Molecular Iodine

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Abstract: 4-[(Indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolones could be smoothly and effectively obtained in good yields through the iodine-catalyzed reactions under solid-state conditions at room tempertaure. The three-component approach in a one-pot procedure was reported for the first time. A possible mechanism was suggested to elucidate the remarkable reaction selectivities.

Keywords: Catalysis, iodine, one pot, solid state, three component

Recently, solid-state (solvent-free) reactions have increasingly attracted much attention in the field of organic synthesis because of their inherent environmental advantages.[1] Apart from the absence of organic solvents, solid-state reactions are very different from traditional solution-phase reactions in yields, reaction rates, and conditions,[2] In some cases, mechanisms and selectivities can be dramatically distinguisheded,[3] because the limitation of movements in solid-state molecules lead to different forms of interactions in microenvironments. Moreover, the design of multicomponent reactions (MCR) is an important research field in combinatorial chemistry,[4] and therefore great efforts are being made to find and develop new multicomponent reactions.[5] Because they are usually a one-pot reactions, MCRs

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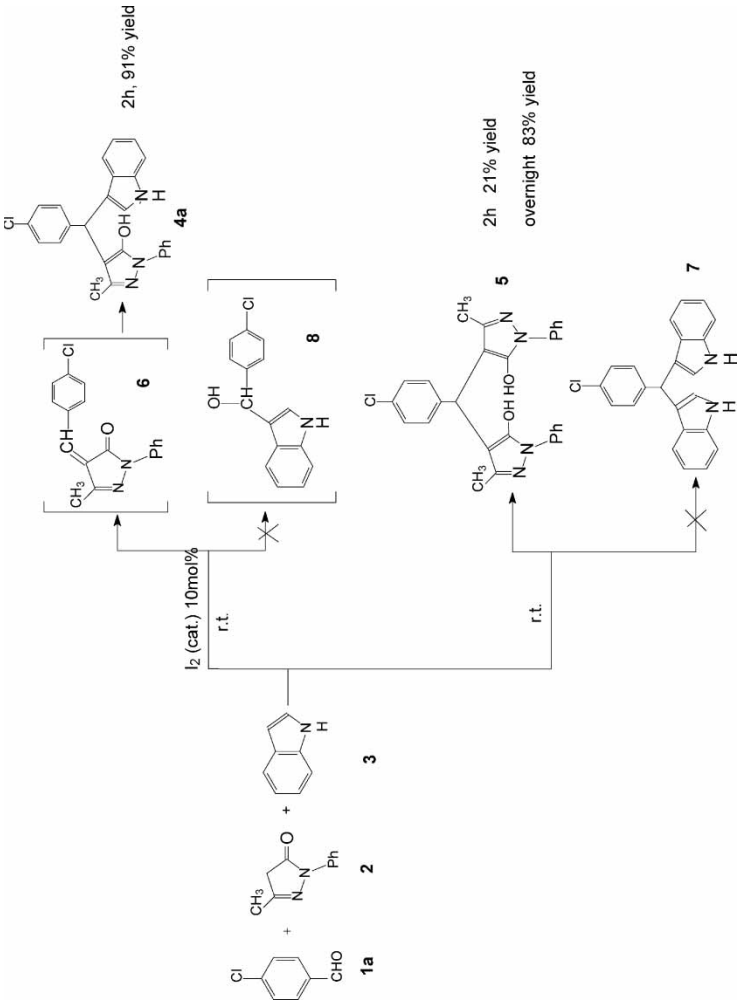
generally afford good yields and ready operations and are fundamentally different from two-component reactions in several aspects.[6]

Methane derivatives with aromatic and/or heterocyclic substituents are utilized in various fields such as dyes, synthetic intermediates,[7] potential medicines,[8] host molecules in inclusion complexes,[9] and so on. 4-[(Indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolones are a species in which two different heterocycles with remarkably important bioactivities and pharmaceutical activities are arranged at the same carbon atom. Although the two-component synthesis of them from the reactions of indole and 4-arylidene-3-methyl-1-phenyl-5-pyrazolones under solid-state conditions was reported,[10] the lengthy procedure for the preparation of starting materials and the moderate yields (41–67%) inhibited direct and effective access to this kind of compound. Therefore, for synthetic efficiency, it is necessary to further develop a straightforward and effective one-step approach to them by the three-component reactions of aldehydes, indole, and 1-phenyl-3-methyl-5-pyrazolones. To our best of knowledge, there has been no such report in literature.

In recent years, molecular iodine has been widely applied as an inexpensive and ready available catalyst in various transformations.[11] Because of its moderate Lewis acidity, reactions catalyzed by iodine effectively take place in neutral media under very mild conditions. Moreover, its water-tolerance makes it an excellent candidate, superior to those water-sensitive metal Lewis acids for reactions in which water would be generated in the process. Herein, we described our case in which 4-[(indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolones were smoothly offered in good yields by iodine-catalyzed one-pot reactions of aldehydes, indole, and 1-phenyl-3-methyl-5- pyrazolones under solvent-free conditions.

We selected the reaction of 4-chlorobenzaldehyde and indole with 1-phenyl-3-methyl-5-pyrazolone in the presence of iodine as the model (Scheme 1). The three substrates (in a molar ratio of 1:1:1) and 10 mol% iodine were mixed and ground well at room temperature in a mortar; the resulting mixture was kept for 2 h. As expected, the target product of 4-[(indol-3-yl)-4-chlorophenylmethyl]-1-phenyl-3-methyl-5-pyrazolone **4c** could be provided in 91% yield, prolonged time would not improve the yield even if the amount of iodine was raised from 10 mol% to 50 mol%. It seemed that 10 mol% iodine was sufficient to drive the solid-state, three-component reaction. Interestingly, a kind of white solid could also be obtained in 21% yield within 2 h in the absence of iodine, and its amount could be improved to 83% for overnight. However, its melting point and spectral data were remarkably different from that of **4c**. Compared with the authentic sample prepared through the literature method,[12] it was confirmed that the white solid offered without the catalyst of iodine shoud be 4-chlorophenyl-bis(1-phenyl-3-methyl-5-pyrazolon-4-yl)methane **5**.

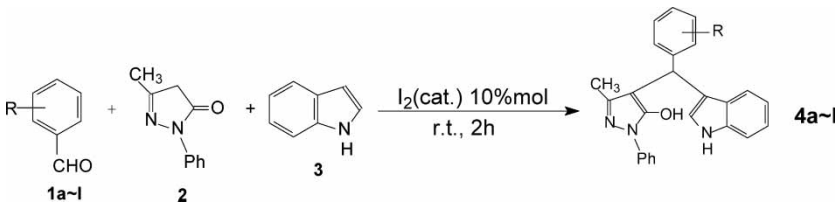
Obviously, there was large distinction in reaction routes between our one-pot, three-component reactions and the reported two-component ones. Based



Scheme 1.

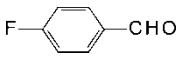
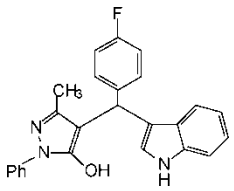
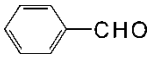
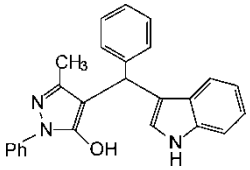
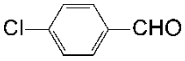
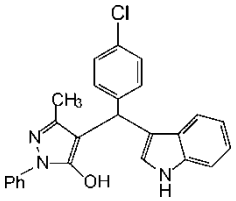
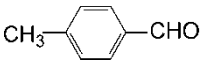
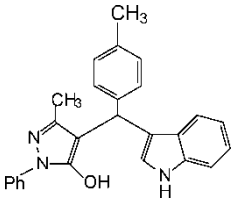
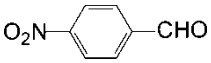
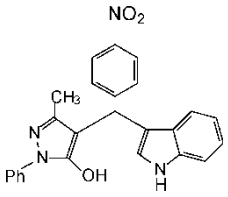
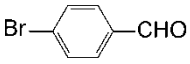
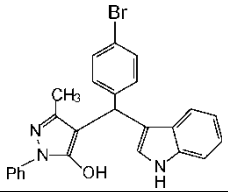
on these facts and other literature,[10,12] a possible mechanism of the iodine-catalyzed one-pot reactions was proposed to explain the remarkable reaction selectivities: in the absence of iodine as a catalyst, the three-component mixture could provide only the product **5** at room temperature, because it was well known[13] that bis(indolyl)methane derivative **7** could not be obtained without the presence of Lewis acids. Moreover, it was reported[14] that bis(pyrazolonyl)methane derivatives would be formed smoothly at room temperature in the absence of Lewis acids. With the catalysis of iodine as an effective Lewis acid, however, the intermediate **6** was offered in preference to the intermediate **8**, because the latter was too unstable to undergo the further transformation. Similarly, the formation of **6** was in accordance with literature[14] that Lewis acids largely promoted the generation of arylmethylenylpyrazolone derivatives at room temperature. The subsequent Michael addition of indole with the intermediate **6** was successfully carried out to afford the target compound **4a** in excellent yields. Because of the catalysis of iodine, the yield of **4a** in our case was dramatically improved to 91%, compared with the yield of 56% in the reported two-component reactions.[10] The evident difference in yields could be attributed to the mild Lewis acidity of iodine, because there were some reports[15] that iodine was an efficient catalyst in Michael addition of indole with α,β-unsaturated carbonyl compounds (i.e., the intermediate **6**, in our case).

According to the results of the model reaction, we extended the one-pot, three-component synthesis of 4-[(indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolones to other aldehydes (Scheme 2), and the results are indicated in Table 1. Generally, the one-pot reactions could be carried out conveniently in the catalysis of iodine to give expected products **4a**–**l** in good yields. Although aldehydes with electron-donating groups such as CH_3- and CH_3O- efficiently provided the target compounds in good yields (Table 1, 4d and 4 g), the hydroxyl group seemed an exception because 4-hydroxybenzaldehyde afforded quite low yield of a mixture with 4-hydroxyphenyl- bis(1-phenyl-3-methyl-5-pyrazolon-4-yl) methane and 4-[(indol-3-yl)-4- hydroxyphenyl-methyl]- 1-phenyl-3-methyl-5-pyrazolone. As for vanillin, only starting materials could be recovered. The iodine-catalyzed three-component reactions seemed to have steric effect also, because both 2,4-dichlorobenzaldehyde and 2,6-dichlorobenzaldehyde were unable to undergo the needed



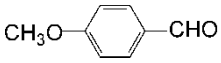
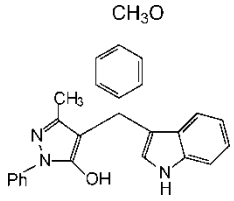
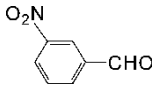
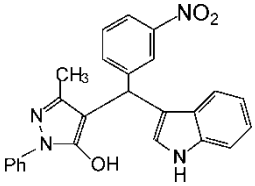
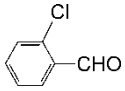
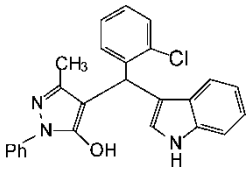
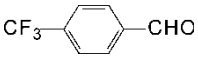
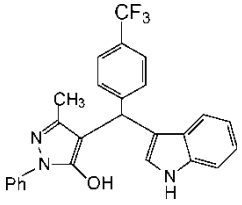
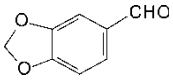
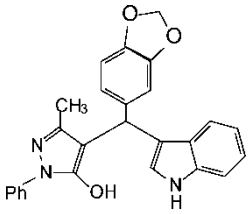
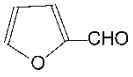
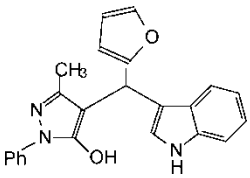
Scheme 2.

Table 1. Solid-state synthesis of **4a–l** by catalysis of iodine in a one-pot operation

Entry	ArCHO	Product	Yield (%)[a]
4a			89
4b			87
4c			91
4d			74
4e			93
4f			85

(*continued*)

Table 1. Continued

Entry	ArCHO	Product	Yield (%)[a]
4 g			77
4 h			89
4i			81
4j			88
4 k			72
4l			79

[a]Referred to isolated yields.

transformation. Surprisingly, however, 2-chlorobenzaldehyde was an effective candidate for the one-pot procedure to supply the product **4i** in 81%. Besides, heterocyclic aldehyde such as 2-furaldehyde (**4l**) could also be selected as an active substrate for the iodine-catalyzed solvent-free reaction, whereas α,β-unsaturated aldehydes such as cinnamaldehyde could not be successfully utilized in our case. It was unfortunate to find that aliphatic aldehydes could not efficiently undergo such solid-state three-component reactions.

The spectral data supported that enolic hydroxyl groups instead of carbonyl groups existed at 5-pyrazolonyl moieties in products **4**. The IR spectra showed bands at ca. 3200 and 1600 cm^{-1} for O-H and C=C absorptions respectively, whereas the absorption of carbonyl ($\sim$1650 cm^{-1}) in 3-methyl-1-phenyl-5-pyrazolone was not observed in compound **4**. Moreover, the signals of methine protons in ^{1}H NMR spectra appeared as broad singlet peaks instead of apparently doublet peaks, but the enolic hydroxyl protons could not be detected in DMSO-d_6 solution.

In conclusion, we herein described a novel and convenient approach to 4-[(indol-3-yl)-4-hydroxyphenyl-methyl]-1-phenyl-3-methyl-5-pyrazolones in good yields through a solid-state procedure under iodine catalysis. The straightforward route, environmentally-friendly operation, readily available catalyst, and dramatically improved yields make our reactions one of the most efficient methods to rapidly access this kind of species. The further research on these compounds is in process.

EXPERIMENTAL

Melting points were determined on X4 mp apparatus, and the thermometer was not corrected. ^{1}H NMR spectra were obtained on a Bruker Avance DMX 400-MHz instrument using TMS as internal standard in DMSO-d6. FT-IR spectra were recorded on Nicolet Avatar spectrophotometer. Elemental analysis was carried out on a Carlo-Ebbra instrument. All reactions were carried out without dry media and inert gas protection.

Solid-State Preparation of 4-Chlorophenyl-bis(1-phenyl-3-methyl-5-pyrazolon-4-yl)methane 5

At room temperature, aldehyde (1 mmol) and 1-phenyl-3-methyl-5-pyrazolone (1 mmol, 0.16 g) were mixed and ground well in a mortar with a pestle; the mixture was kept overnight and dissolved in EtOH (10 mL). The concentrated residue was purified by silica-gel column chromatograhy (ethyl acetate/petrolem = 1:3) to provide products pure enough for spectral analysis. The products utilized for elemental analysis were obtained by further recrystallization from EtOH/$CHCl_3$.

White solid; mp 207 ∼ 208°C (lit.[12] 210°C); IR (KBr) 3060, 1604, 1499, 1408, 1297, 1194, 1070, 1021, 834, 745, 698 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.22 (s, 6H), 4.83 (s, 1H), 7.16–7.26 (m, 6H), 7.27–7.41 (m, 4H), 7.69 (d, $J = 8.0$ Hz, 4H); anal. calcd. for $C_{27}H_{23}N_4O_2$: C, 74.48; H, 5.29; N, 12.87. Found: C, 75.62; H, 5.19; N, 12.71%.

General Procedure for the Preparation of 4-[(Indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolones 4 under I_2-Catalyzed Solid-State Conditions

At room temperature, aldehyde (1 mmol), indole (1 mmol, 0.107 g), 1-phenyl-3-methyl-5-pyrazolone (1 mmol, 0.16 g) and iodine (0.1 mmol, 0.0254 g) were mixed and ground well in a mortar with a pestle; the mixture was kept for 2 h and dissolved in ethanol (10 mL). The resulting solution was treated with aq. $Na_2S_2O_3$ (5%, 10 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layer was dried over anhydrous sodium sulphate, concentrated in vacuo, and purified by silica-gel column chromatograhy (ethyl acetate/petrolem = 2:1) to provide products pure enough for spectral analysis. The products utilized for elemental analysis were obtained by further recrystallization from $EtOH/CHCl_3$.

Data

4a: white solid; mp 203 ∼ 205°C (lit[10] 207°C); IR (KBr): 3413, 3227, 3060, 2921, 2868, 1604, 1569, 1503, 1457, 1221, 1094, 745 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.85(s, 3H), 5.50(s, br, 1H), 6.86 ∼ 6.90(m, 2H), 7.05 ∼ 7.12(m, 3H), 7.20(t, 2H, $J = 8.4$ Hz), 7.31 ∼ 7.37(m, 3H), 7.42(t, 2H, $J = 8.0$ Hz), 7.75(d, 2H, $J = 8.0$ Hz), 10.86(s, 1H); anal. calcd. for $C_{25}H_{20}N_3OF$: C, 75.56; H, 5.04; N, 10.58. Found: C, 75.72; H, 5.09; N, 10.51%

4b: white solid; mp 235–236°C (lit.[10] 236°C); IR (KBr): 3415, 3239, 3056, 2921, 2864, 1601, 1544, 1499, 1405, 739, 706 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.83 (s, 3H), 5.52 (s, br, 1H), 6.83 (s, 1H), 6.89 (t, 1H, $J = 7.6$ Hz), 7.05 (t, 1H, $J = 7.6$ Hz), 7.18–7.22 (m, 3H), 7.26–7.31 (m, 4H), 7.36 (d, 1H, $J = 8.0$ Hz), 7.42 (t, 2H, $J = 8.0$ Hz), 7.75 (d, 2H, $J = 8.0$ Hz), 10.84 (s, 1H); anal. calcd. for $C_{25}H_{21}N_3O$: C, 79.15; H, 5.54; N, 11.08. Found: C, 79.33; H, 5.61; N, 10.98%.

4c: white solid; mp 173–175°C (lit.[10] 176°C); IR (KBr): 3415, 3227, 3056, 2917, 1868, 1609, 1568, 1486, 1409, 1090, 1012, 743 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.86 (s, 3H), 5.50 (s, br, 1H), 6.88–6.92 (m, 2H), 7.05 (t, 1H, $J = 7.6$ Hz), 7.20 (t, 2H, $J = 8.0$ Hz), 7.32 ∼ 7.37 (m, 5H), 7.42 (t, 2H, $J = 8.0$ Hz), 7.74 (d, 2H, $J = 8.0$ Hz), 10.88(s, 1H); anal. calcd. for $C_{25}H_{21}N_3OCl$: C, 72.64; H, 4.84; N, 10.17. Found: C, 72.81; H, 4.91; N, 10.10%.

4d: white solid; mp 180–182°C (lit.[10] 178°C); IR (KBr): 3415, 3256, 3051, 2917, 2859, 1609, 1572, 1499, 1450, 1409, 1311, 1094, 743, 698 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.82 (s, 3H), 2.26 (s, 3H), 5.47 (s, br, 1H), 6.82 (s, 1H), 6.88 (t, 1H, $J = 7.6$ Hz), 7.03–7.09 (m, 3H), 7.16–7.20 (m, 4H), 7.35 (d, 1H, $J = 8.0$ Hz), 7.42 (t, 2H, $J = 8.0$ Hz), 7.75 (d, 2H, $J = 8.0$ Hz), 10.82(s, 1H); anal. calcd. for $C_{26}H_{23}N_3O$: C, 79.39; H, 5.85; N, 10.69. Found: C, 79.54; H, 5.94; N, 10.77%.

4e: yellowish solid; mp 184–186°C (lit.[10] 184°C); IR (KBr): 3415, 3223, 3056, 2921, 2864, 1597, 1519, 1413, 1348, 1111, 743 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.92 (s, 3H), 5.65 (s, br, 1H), 6.93 (t, 1H, $J = 7.2$ Hz), 6.97 (s, 1H), 7.07 (t, 1H, $J = 7.6$ Hz), 7.19–7.25 (m, 2H), 7.27–7.45 (m, 3H), 7.56(d, 2H, $J = 8.4$ Hz), 7.74 (d, 2H, $J = 8.0$ Hz), 8.16 (d, 2H, $J = 8.4$ Hz), 10.96 (s, 1H); anal. calcd. for $C_{25}H_{20}N_4O_2$: C, 70.75; H, 4.72; N, 11.32. Found: C, 70.94; H, 4.81; N, 11.45%.

4f: pale red solid; mp 182–184°C (lit.[10] 188°C); IR (KBr): 3415, 3219, 3056, 2970, 2847, 2786, 1605, 1568, 1495, 1409, 1298, 1102, 1008, 747 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.86 (s, 3H), 5.49 (s, br, 1H), 6.88–6.92 (m, 2H), 7.05 (t, 1H, $J = 7.6$ Hz), 7.18–7.26 (m, 4H), 7.36 (d, 1H, $J = 8.0$ Hz), 7.40–7.47(m, 4H), 7.74(d, 2H, $J = 8.0$ Hz), 10.88(s, 1H); anal. calcd. for $C_{25}H_{20}N_3OBr$: C, 65.64; H, 4.38; N, 9.19. Found: C, 65. 82; H, 4.41; N, 9.27%.

4g: white solid; mp 170–171°C (lit.[10] 168°C); IR (KBr): 3415, 3248, 3056, 2921, 1609, 1568, 1503, 1454, 1245, 1172, 1106, 1033, 743, 698 cm^{-1}; ^1H NMR (DMSO-d_6): $\delta = 1.82$ (s, 3H), 3.72 (s, 3H), 5.45 (s, br, 1H), 6.82–6.90 (m, 4H), 7.04 (t, 1H, $J = 7.6$ Hz), 7.16–7.21 (m, 4H), 7.35 (d, 1H, $J = 8.0$ Hz), 7.42 (t, 2H, $J = 7.6$ Hz), 7.75 (d, 2H, $J = 8.0$ Hz), 10.82 (s, 1H); anal. calcd. for $C_{26}H_{23}N_3O_2$: C, 76.28; H, 5.62; N, 10.27. Found: C, 76.44; H, 5.69; N, 10.21%.

4h: yellowish solid; mp 242–244°C (lit.[10] 246°C); IR (KBr): 3421, 3186, 3064, 2924, 2871, 1599, 1529, 1499, 1456, 1415, 1350, 714 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.96 (s, 3H), 5.66 (s, br, 1H), 6.91 (t, 1H, $J = 7.2$ Hz), 6.99 (s, 1H), 7.07 (t, 1H, $J = 8.0$ Hz), 7.19 (t, 1H, $J = 8.0$ Hz), 7.26 (d, 1H, $J = 7.6$ Hz), 7.38 (d, 1H, $J = 8.0$ Hz), 7.43 (t, 2H, $J = 7.6$ Hz), 7.59 (t, 1H, $J = 8.0$ Hz), 7.74 (d, 2H, $J = 7.6$ Hz), 7.80 (d, 1H, $J = 8.0$ Hz), 8.08 (d, 1H, $J = 8.0$ Hz), 8.16 (s, 1H), 10.96 (s, 1H); anal. calcd. for $C_{25}H_{20}N_4O_3$: C, 70.75; H, 4.72; N, 11.32. Found: C, 70.98; H, 4.77; N, 11.23%.

4i: white solid; mp 161–163°C; IR (KBr): 3419, 3272, 3056, 2925, 2864, 1601, 1556, 1499, 1405, 1102, 1041, 739, 690 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.81 (s, 3H), 5.75 (s, br, 1H), 6.81 (s, 1H), 6.89 (t, 1H, $J = 7.2$ Hz), 7.05 (t, 1H, $J = 7.6$ Hz), 7.11 (d, 1H, $J = 7.6$ Hz), 7.18–7.22 (m, 3H), 7.30 (d, 1H,

$J = 7.6$ Hz), 7.36–7.43 (m, 4H), 7.74 (d, 2H, $J = 7.6$ Hz), 10.88 (s, 1H); anal. calcd. for $C_{25}H_{20}N_3OCl$: C, 72.64; H, 4.84; N, 10.17. Found: C, 72.81; H, 4.91; N, 10.26%.

4j: white solid; mp 176–178°C; IR (KBr): 3414, 3254, 3061, 2921, 2868, 1617, 1570, 1498, 1457, 1416, 1325, 1164, 1124, 1068, 1017, 743, 703 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.89 (s, 3H), 5.60 (s, br, 1H), 6.91 (d, 2H, $J = 7.2$ Hz), 7.06 (t, 1H, $J = 7.2$ Hz), 7.18–7.24 (m, 2H), 7.37 (d, 1H, $J = 8.0$ Hz), 7.42 (t, 2H, $J = 8.0$ Hz), 7.51 (d, 2H, $J = 7.6$ Hz), 7.64 (d, 2H, $J = 8.0$ Hz), 7.74 (d, 2H, $J = 8.0$ Hz), 10.92 (s, 1H); anal. calcd. for $C_{26}H_{20}N_3OF_3$: C, 70.75; H, 4.53; N, 9.52. Found: C, 70.93; H, 4.58; N, 9.44%.

4k: white solid; mp 152–154°C; IR (KBr): 3415, 3256, 3060, 2884, 1609, 1568, 1482, 1229, 1041, 931, 747 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.87 (s, 3H), 5.39 (s, br, 1H), 5.94 (s, 2H), 6.76–6.81 (m, 2H), 6.84–6.90 (m, 3H), 7.04 (t, 1H, $J = 7.2$ Hz), 7.17–7.21 (m, 2H), 7.34 (d, 1H, $J = 8.0$ Hz), 7.41 (t, 2H, $J = 8.0$ Hz), 7.73 (d, 2H, $J = 7.6$ Hz), 10.82 (s, 1H); anal. calcd. for $C_{26}H_{21}N_3O_3$: C, 73.76; H, 4.99; N, 9.93. Found: C, 73.92; H, 5.03; N, 10.07%.

4l: pale solid; mp 191–193°C; IR (KBr): 3413, 3243, 3057, 2922, 1602, 1552, 1498, 1405, 1009, 738, 704 cm^{-1}; ^1H NMR (DMSO-d_6): δ 1.88 (s, 3H), 5.56 (s, br, 1H), 6.05 (s, 1H), 6.39 (s, 1H), 6.90–6.94 (m, 2H), 7.06 (t, 1H, $J = 7.6$ Hz), 7.19 (t, 1H, $J = 7.2$ Hz), 7.31 (d, 1H, $J = 8.0$ Hz), 7.36 (d, 1H, $J = 8.0$ Hz), 7.43 (t, 2H, $J = 8.0$ Hz), 7.58 (s, 1H), 7.75 (d, 2H, $J = 8.0$ Hz), 10.89 (s, 1H); anal. calcd. for $C_{23}H_{19}N_3O_2$: C, 74.80; H, 5.15; N, 11.38. Found: C, 74.93; H, 5.17; N, 11.27%.

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