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Otherwise inert reaction of sulfonamides/carboxamides with formamides *via* proton transfer-enhanced reactivity†

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NBS-mediated addition–elimination reaction of sulfonamides/carboxamides and formamides afforded *N*-sulfonylamidines and *N*-formylarylamides, respectively, depending on the different mechanism of elimination. Hydrogen bond-induced proton transfer leads to enhanced reactivities and was proposed as the key driving force for the reaction to take place. The protocol demonstrates the possibility of constructing chemical bonds based on a proton transfer strategy induced by noncovalent hydrogen bond interaction.

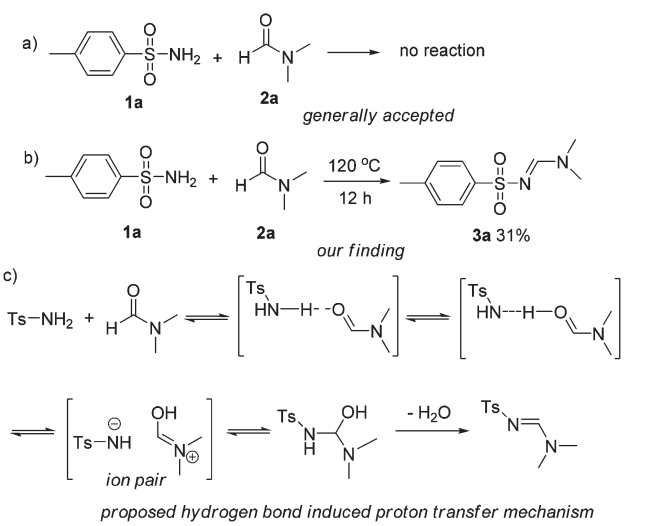
Introduction

As well known noncovalent interactions, hydrogen bonding[1] has found vast applications in areas such as molecular recognition, crystal engineering, and biological systems.[2] Recently, organic catalysis *via* noncovalent weak interactions has attracted increasing interest from synthetic chemists.[3] For instance, Schreiner and Wittkopp reported a H-bonded complex of an *N*-acyloxazolidinone with an *N*,*N*′-disubstituted electron-poor thiourea and used it in Diels–Alder reactions.[4] Jacobsen and co-workers developed hydrogen bond activation of benzhydryl bromide by anion binding to the benzhydryl cations formed.[5] Zhang *et al.* reported C–N bond cleavage of allylic amines *via* hydrogen bond activation with alcohol solvents in Pd-catalyzed allylic alkylation.[6] Thus, the exploration of hydrogen bond activation in organic synthesis is an extremely appealing yet challenging goal.

Results and discussion

In our research on halogen (*e.g.* halogenation, halonium, hypervalent halogen and halogen bond) mediated organic reactions,[7] we would like to communicate here an otherwise inert reaction of sulfonamides/carboxamides with formamides leading to amidines and *N*-formylamides. Proton transfer induced by hydrogen bond interaction led to enhanced reactivity and was proposed as the key driving force for the reaction to take place in this work (Scheme 1).

The initial investigation started from 4-methylbenzenesulfonamide (**1a**) and *N*,*N*-dimethylformamide[8] (**2a**). Generally, the reaction between them is quite difficult, due to their inherent low reactivities (Scheme 1a). However, in our study, we found that the reaction between **1a** and **2a** (both as reactant and solvent, 2.0 mL) *did* take place at 120 °C, affording *N*-sulfonyl amidine **3a** as a single product in reproducible yield (Scheme 1b). The reason for such an unusual reaction to occur may be explained as hydrogen bond activation (Scheme 1c), which leads to simultaneously increased nucleophilicity for $TsNH_2$ and electrophilicity for DMF.[9–11] Consequently, direct



Scheme 1 Initial investigation.

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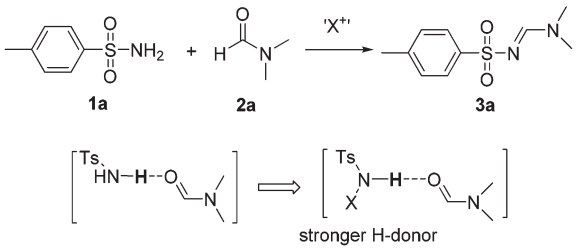
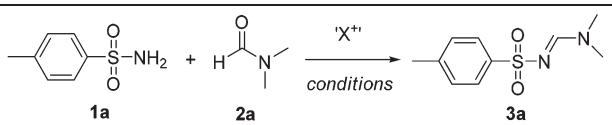


Scheme 2 Proton transfer promoted by halogen activated hydrogen bond interaction.

addition was achieved, along with the subsequent elimination of water, to give **3a**, although in modest yield.

Encouraged by the preliminary results and with the aim of increasing the product yield and lowering the temperature, we subsequently sought a halogen activator to do this reaction (Scheme 2). The role of the halogen activator is to make $TsNH_2$ a stronger H-donor by the formation of TsNHBr,[12,13] and further reinforce the hydrogen bond interaction with DMF.[4] To our delight, with readily available NBS as the halogen source, the reaction of **1a** in anhydrous DMF (**2a**) proceeded at 80 °C, giving **3a** in 63% yield (Table 1, entry 1). It was found that the addition of trace amounts of water can further increase the yield to 89% (entries 2–4), which is consistent with the mechanism proposed afterward. In addition to NBS, NIS and DIB exhibited similar reactivity, while NCS gave lower efficiency (entries 5–7). The screening of other solvents like toluene, THF, $MeNO_2$ and MeCN gave unsatisfactory results (entries 8–11). Thus, in the following work, anhydrous DMF was used as the solvent with the addition of 0.2 equiv. of water, and commercially available and inexpensive NBS was selected as the halogen source.

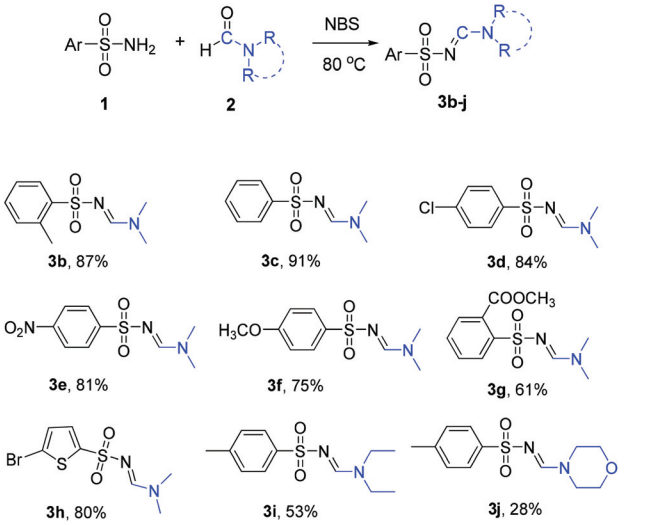
Table 1 Optimization of the reaction conditions[a]



Entry	X^+	Solvent	H_2O (equiv.)	Yield[b] (%)
1	NBS	DMF	—	63
2	NBS	DMF	1.0	77
3	NBS	DMF	0.5	88
4	NBS	DMF	0.2	89
5	NIS	DMF	0.2	89
6	NCS	DMF	0.2	41
7	DIB	DMF	0.2	88
8	NBS	Toluene	0.2	76
9	NBS	THF	0.2	<5
10	NBS	$MeNO_2$	0.2	33
11	NBS	MeCN	0.2	52

[a] *Reaction conditions*: **1a** (1.0 mmol), NBS (1.1 equiv.), H_2O (*x* equiv.) in anhydrous DMF (2.0 mL) at 80 °C for 7.5 h (entries 1–7). **1a** (1.0 mmol), **2a** (2.0 equiv.), NBS (1.1 equiv.), H_2O (0.2 equiv.) in anhydrous solvent (2.0 mL) at 80 °C for 7.5 h (entries 8–11). [b] Isolated yield.

Table 2 NBS-mediated reactions of arylsulfonamides and formamides[a,b]



[a] *Reaction conditions*: **1** (1.0 mmol), **2** (2.0 mL), NBS (1.1 equiv.) and H_2O (0.2 equiv.) at 80 °C for 5–6 h. [b] Yield of isolated product.

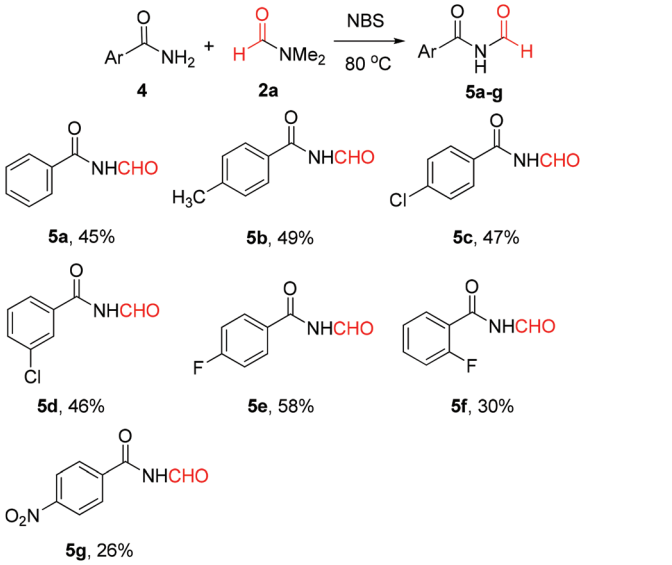
Thus, a variety of substituted sulfonamides including arylsulfonamides and heteroarylsulfonamides were subjected to the reaction conditions (Table 2). All the reactions with DMF proceeded efficiently, giving *N*-sulfonylamidines **3b–h** in 61–91% yield. Additionally, reactions with other formamides like *N*,*N*-diethylformamide and morpholine-4-carbaldehyde also proceeded smoothly, and the corresponding products **3i** and **3j** were attained, albeit in low to moderate yields.[14] Amidine derivatives have been widely used in medicinal chemistry, as well as being key intermediates in organic synthesis.[15] The protocol provides a straightforward and efficient entry to *N*-sulfonyl amidines of type **3**.

In order to further explore the halogen-mediated reaction developed here and its utility in organic synthesis, arylcarboxamides were investigated in the following work. As a result, reactions activated by NBS proceeded smoothly at 80 °C, and a variety of *N*-formylated products **5a–g** were produced in 26–58% yield (Table 3).[16] Such a transformation demonstrates an alternative mild *N*-formylation method.[17]

Computational calculation was conducted with the aim of understanding the role of halogen in the reaction and the possible mechanism. Fig. 1 shows the structures of intermediates and transition states **6–8** involved in the transformation. One can clearly observe the formation of an N–H···O hydrogen bond (H···O distance 1.78 Å; N···C distance 3.51 Å) in **6** and subsequent proton transfer from arylsulfonamide to DMF (H···O distance 0.99 Å; N···C distance 2.52 Å) to give transition state **7**, which causes significant charge density redistribution on the nitrogen atom of the sulfonylamide and the carbonyl carbon atom of DMF (see the ESI† for details). Intermediate **8** corresponds to the structure of the resulting C–N adduct.[18]

On the basis of all the results described above, the possible mechanism for the reaction of sulfonamide/carboxamide and

Table 3 NBS-mediated reactions of arylcarboxamides and DMF[a,b]



[a] *Reaction conditions*: **4** (1.0 mmol), **2a** (2.0 mL), NBS (1.1 equiv.) and H_2O (0.2 equiv.) at 80 °C for 5–6 h. [b] Isolated yield.

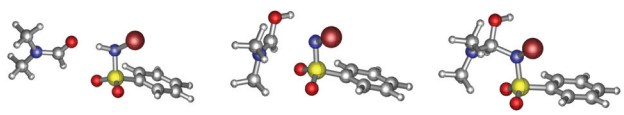
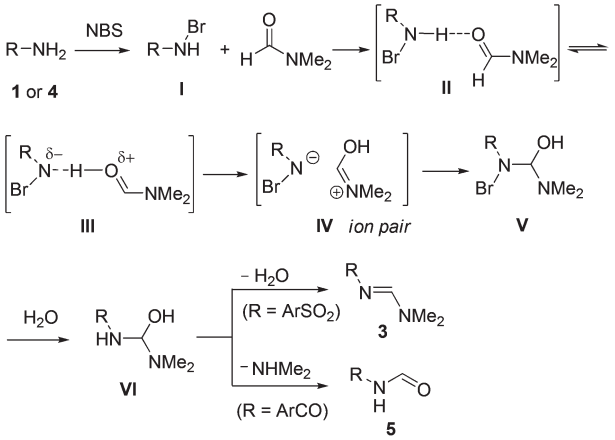


Fig. 1 Selected structures of intermediates and transition states **6–8** (left to right).



Scheme 3 Proposed halogen activated hydrogen bond induced proton transfer mechanism.

DMF is depicted in Scheme 3. The reaction of sulfonylamide/carboxamide with NBS yields *N*-bromosulfonamide or *N*-bromocarboxamide (**I**).[12] The hydrogen bond interaction between intermediate **I** and DMF gives rise to asymmetric hydrogen bond adducts **II** and **III**.[10] Furthermore, ion pair **IV** is proposed to be generated with enhanced nucleophilicity for $TsNH_2$ and electrophilicity for DMF.[11] Obviously, dual activation of the two types of substrates was achieved *via* proton transfer induced by the hydrogen bond interaction. As a result, direct C–N bond formation furnishes the adduct **V**. Hydrolysis of **V** generates acetal **VI**. Finally, amidines **3** are produced upon elimination of water for sulfonamide substrates **1**. For carboxamide substrates **4**, *N*-formylation products **5** are attained *via* elimination of dimethylamine. The protocol demonstrates the possibility of constructing chemical bonds by a proton transfer strategy induced by noncovalent hydrogen bond interaction. It was noteworthy that both *N*-sulfonylamidine and *N*-formylarylamide products were prepared in modest to high yields, which is inferior to the results reported by Wan and co-workers.[19] This is most probably due to the existence of the equilibrium in the proton transfer process (**II** → **III** → **IV** → **V**). Computational calculation indicates a high energy barrier in this step (see the ESI†). The subsequent hydrolysis and elimination of water or dimethylamine (**V** → **VI** → **3**/**5**) lead to the final compounds.

Conclusion

In conclusion, we have reported, for the first time, NBS-mediated addition–elimination of sulfonamides/carboxamides and formamides. The reaction afforded *N*-sulfonylamidines and *N*-formylarylamides, respectively, depending on the type of elimination. The simple and straightforward approach not only provides a synthetic method toward *N*-sulfonylamidines and *N*-formylamides, but also illustrates the possibility and potential of non-covalent hydrogen bond-induced proton transfer as a complementary strategy for chemical bond formation. Further work on hydrogen bond activation and its application in organic synthesis is underway in our laboratory.

Experimental

General methods

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Varian 500 MHz and 125 MHz, respectively, using TMS as internal standard. Elemental analyses were measured on an E-2400 analyzer (Perkin-Elmer). Mass spectra were recorded on an Agilient 1100 LCMsD mass spectrometer.

General procedure for the preparation of 3 and 5 (3a as an example). To a solution of 4-methylbenzenesulfonamide **1a** (171 mg, 1.0 mmol) in DMF (2 mL) was added NBS (196 mg, 1.1 mmol) and water (3.6 μL). The mixture was stirred at 80 °C. After the starting material **1a** was consumed as indicated by TLC, the reaction mixture was cooled to room temperature and poured into water and then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was washed with water (3 × 10 mL), dried over anhydrous $MgSO_4$, filtered and

concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, petroleum ether : ether = 1 : 2) to give **3a** (198 mg, 88%) as a white solid.

Physical data of compounds isolated

***N*,*N*-Dimethyl-*N*′-tosylformimidamide (3a).** White solid, m.p. 134–136 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 2.40 (s, 3H), 3.01 (s, 3H), 3.13 (s, 3H), 7.25–7.27 (d, J = 9.5 Hz, 2H), 7.77–7.78 (d, J = 8.5 Hz, 2H), 8.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 21.4, 35.5, 41.4, 126.4, 129.3, 139.4, 142.4, 159.0; MS calcd m/z 226.08, found 227.08 $[(M + 1)]^+$. Anal. Calcd for $C_{10}H_{14}N_2O_2S$: C, 53.08; H, 6.24; N, 12.38; Found: C, 53.29; H, 6.26; N, 12.43%.

***N*,*N*-Dimethyl-*N*′-(*o*-tolylsulfonyl)formimidamide (3b).** Yellowish oil. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 7.85–7.83 (d, J = 8.5 Hz, 2H), 7.32–7.30 (d, J = 8.0 Hz, 2H), 3.70 (s, 2H), 3.29–3.27 (t, J = 5.5 Hz, 2H), 2.43 (s, 3H), 1.70–1.68 (t, J = 3 Hz, 4H), 1.55–1.53 (d, J = 5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ = 191.6, 165.6, 145.8, 130.7, 129.63, 129.59, 46.9, 42.0, 26.1, 25.4, 24.3, 21.8; MS calcd m/z 231.1, found 232.1 $[(M + 1)]^+$. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06; Found: C, 72.79; H, 7.40; N, 6.05%.

***N*,*N*-Dimethyl-*N*′-(phenylsulfonyl)formimidamide (3c).** White solid, m.p. 128–129 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 3.03 (s, 3H), 3.14 (s, 3H), 7.45–7.52 (m, 3H), 7.89–7.91 (m, 2H), 8.15 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 35.4, 41.4, 126.2, 128.6, 131.7, 142.2, 159.1; MS calcd m/z 212.27, found 213.27 $[(M + 1)]^+$. Anal. Calcd for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20; Found: C, 51.03; H, 5.75; N, 13.11.

***N*′-(4-Chlorophenylsulfonyl)-*N*,*N*-dimethylformimidamide (3d).** White solid, m.p. 117–119 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 3.03 (s, 3H), 3.15 (s, 3H), 7.43–7.45 (d, J = 8.5 Hz, 2H), 7.82–7.84 (d, J = 8.5 Hz, 2H), 8.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 35.8, 41.8, 128.2, 128.3, 129.0, 129.2, 138.4, 141.1, 159.4; MS calcd m/z 246.02, found 247.02 $[(M + 1)]^+$. Anal. Calcd for $C_9H_{11}ClN_2O_2S$: C, 43.81; H, 4.49; N, 11.35; Found: C, 43.89; H, 4.47; N, 11.28%.

***N*,*N*-Dimethyl-*N*′-(4-nitrophenylsulfonyl)formimidamide (3e).** White solid, m.p. 197–201 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 3.06 (s, 3H), 3.19 (s, 3H), 8.07–8.09 (d, J = 9.0 Hz, 2H), 8.16 (s, 1H), 8.31–8.32 (d, J = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 35.7, 41.7, 124.0, 127.9, 148.1, 149.5, 159.4; MS calcd m/z 257.05, found 258.05 $[(M + 1)]^+$. Anal. Calcd for $C_9H_{11}N_3O_4S$: C, 42.02; H, 4.31; N, 16.33; Found: C, 42.25; H, 4.35; N, 16.39%.

***N*′-(4-Methoxyphenylsulfonyl)-*N*,*N*-dimethylformimidamide (3f).** White solid, m.p. 133–135 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 3.01 (s, 3H), 3.12 (s, 3H), 3.85 (s, 3H), 6.93–6.95 (t, J = 7.0 Hz, 2H), 7.82–7.84 (d, J = 9.0 Hz, 2H), 8.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 35.5, 41.4, 55.5, 113.8, 128.5, 134.2, 158.8, 162.2; MS calcd m/z 242.07, found 243.07 $[(M + 1)]^+$. Anal. Calcd for $C_{10}H_{14}N_2O_3S$: C, 49.57; H, 5.82; N, 11.56; Found: C, 49.68; H, 5.89; N, 11.69%.

Methyl 2-(*N*-((dimethylamino)methylene)sulfamoyl)benzoate (3g). White solid, m.p. 128–129 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 3.03 (s, 3H), 3.17 (s, 3H), 3.95 (s, 3H), 7.28–7.57 (m, 3H), 8.10 (s, 1H), 8.12–8.14 (t, J = 6.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 35.5, 41.5, 52.9, 128.5, 129.0, 130.5, 131.6, 131.6, 140.2, 160.7, 168.4; MS calcd m/z 270.30, found 271.30 $[(M + 1)]^+$. Anal. Calcd for $C_{11}H_{14}N_2O_4S$: C, 48.88; H, 5.22; N, 10.36; Found: C, 48.99; H, 5.26; N, 10.27%.

***N*′-(5-Bromothiophen-2-ylsulfonyl)-*N*,*N*-dimethylformimidamide (3h).** White solid, m.p. 102–104 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 3.06 (s, 3H), 3.17 (s, 3H), 7.00–7.01 (d, J = 4.0 Hz, 1H), 7.33–7.34 (d, J = 4.0 Hz, 1H), 8.11 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 35.7, 41.7, 118.4, 130.0, 130.5, 145.0, 159.4; MS calcd m/z 297.19, found 298.19 $[(M + 1)]^+$. Anal. Calcd for $C_7H_9BrN_2O_2S_2$: C, 28.29; H, 3.05; N, 9.43; Found: C, 28.50; H, 3.09; N, 9.59%.

***N*,*N*-Diethyl-*N*′-tosylformimidamide (3i).** Yellow solid, m.p. 69–71 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 1.13–1.16 (t, J = 7.0 Hz, 3H), 1.24–1.27 (q, J = 7.3 Hz, 3H), 3.36–3.39 (m, 2H), 3.45–3.48 (m, 2H), 7.25–7.27 (d, J = 9.5 Hz, 2H), 7.76–7.78 (d, J = 8.5 Hz, 2H), 8.15 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 12.1, 14.5, 21.5, 40.1, 47.0, 126.3, 129.2, 139.7, 142.3, 158.0; MS calcd m/z 254.35, found 255.35 $[(M + 1)]^+$. Anal. Calcd for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.01; Found: C, 56.88; H, 7.19; N, 11.22%.

4-Methyl-*N*-(morpholinomethylene)benzenesulfonamide (3j). White solid, m.p. 166–168 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 2.41 (s, 3H), 3.48–3.50 (t, J = 5.0 Hz, 2H), 3.68 (s, 4H), 3.75–3.77 (t, J = 4.8 Hz, 2H), 7.27–7.28 (d, J = 8.5 Hz, 2H), 7.76–7.78 (d, J = 8.5 Hz, 2H), 8.19 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 21.5, 44.1, 50.2, 65.9, 66.7, 126.5, 129.3, 139.0, 142.7, 157.5; MS calcd m/z 268.33, found 269.33 $[(M + 1)]^+$. Anal. Calcd for $C_{12}H_{16}N_2O_3S$: C, 53.71; H, 6.01; N, 10.44; Found: C, 53.62; H, 6.09; N, 10.66%.

***N*-Formylbenzamide (5a).** White solid, m.p. 107–109 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 7.53–7.56 (t, J = 7.8 Hz, 2H), 7.64–7.67 (t, J = 7.3 Hz, 1H), 8.02–8.03 (d, J = 7.5 Hz, 2H), 9.41–9.43 (d, J = 9.5 Hz, 1H), 10.32–10.34 (d, J = 6.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 128.1, 129.0, 130.9, 133.9, 165.0, 166.7; MS calcd m/z 149.15, found 150.15 $[(M + 1)]^+$. Anal. Calcd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39; Found: C, 64.65; H, 4.75; N, 9.50%.

***N*-Formyl-4-methylbenzamide (5b).** White solid, m.p. 130–132 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ = 2.43 (s, 3H), 7.32–7.33 (d, J = 8.0 Hz, 2H), 7.91–7.93 (d, J = 8.0 Hz, 2H), 9.38–9.40 (d, J = 9.5 Hz, 1H), 10.34 (s, 1H). ^{13}C NMR, ($CDCl_3$, 125 MHz, ppm): 21.6, 128.2, 128.2, 129.7, 144.9, 165.1, 166.6; MS calcd m/z 163.17, found 164.17 $[(M + 1)]^+$. Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58; Found: C, 66.36; H, 5.59; N, 8.69%.

4-Chloro-*N*-formylbenzamide (5c). White solid, m.p. 183–187 °C. ^{1}H NMR (DMSO, 500 MHz, ppm): δ = 7.59–7.61 (m, 2H), 8.00–8.03 (m, 2H), 9.24 (s, 1H), 11.77 (s, 1H). ^{13}C NMR (DMSO, 125 MHz, ppm): 129.3, 130.8, 138.9, 164.9, 167.1 (one of the signals was not observed); MS calcd m/z 183.59, found 184.59 $[(M + 1)]^+$. Anal. Calcd for $C_8H_6ClNO_2$: C, 52.34; H, 3.29; N, 7.63; Found: C, 52.55; H, 3.38; N, 7.76%.

3-Chloro-*N*-formylbenzamide (5d). White solid, m.p. 135–139 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 7.48–7.51

(t, J = 8.0 Hz, 1H), 7.62–7.64 (m, 1H), 7.87–7.89 (m, 1H), 8.01–8.02 (t, J = 1.8 Hz, 1H), 9.39–9.41 (d, J = 9.5 Hz, 1H), 10.18–10.19 (d, J = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 125.9, 128.5, 130.3, 132.8, 133.9, 135.5, 164.7, 165.5; MS calcd m/z 183.59, found 184.59 $[(M + 1)]^+$. Anal. Calcd for $C_8H_6ClNO_2$: C, 52.34; H, 3.29; N, 7.63; Found: C, 52.16; H, 3.34; N, 7.76%.

4-Fluoro-*N*-formylbenzamide (5e). White solid, m.p. 155–156 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 7.21–7.25 (t, J = 8.3 Hz, 2H), 8.06–8.08 (m, 2H), 9.39–9.41 (d, J = 9.5 Hz, 1H), 10.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 116.3, 116.4, 127.17, 127.2, 130.8, 130.9, 165.0, 165.2, 165.5, 167.2 (more signals were observed due to tautomerization); MS calcd m/z 167.14, found 168.14 $[(M + 1)]^+$. Anal. Calcd for $C_8H_6FNO_2$: C, 57.49; H, 3.62; N, 8.38; Found: C, 57.60; H, 3.69; N, 8.49%.

2-Fluoro-*N*-formylbenzamide (5f). White solid, m.p. 78–82 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 7.20–7.24 (m, 1H), 7.34–7.37 (m, 1H), 7.62–7.66 (m, 1H), 8.11–8.14 (m, 1H), 9.15 (s, 1H), 9.38–9.40 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): 116.5, 116.7, 118.6, 118.6, 125.4, 125.4, 132.2, 135.9, 136.0, 160.1, 162.1, 162.5, 163.1 (more signals were observed due to tautomerization); MS calcd m/z 167.14, found 168.14 $[(M + 1)]^+$. Anal. Calcd for $C_8H_6FNO_2$: C, 57.49; H, 3.62; N, 8.38; Found: C, 57.31; H, 3.65; N, 8.52%.

***N*-Formyl-4-nitrobenzamide (5g).** Yellow solid, m.p. 162–165 °C. ^{1}H NMR (DMSO, 500 MHz, ppm) δ = 8.21–8.23 (d, J = 8.5 Hz, 2H), 8.34–8.36 (d, J = 8.5 Hz, 2H), 9.26 (s, 1H), 11.98 (s, 1H). ^{13}C NMR (DMSO, 125 MHz, ppm): 124.2, 130.5, 137.7, 150.6, 164.8, 166.9; MS calcd m/z 194.14, found 195.14 $[(M + 1)]^+$. Anal. Calcd for $C_8H_6N_2O_4$: C, 49.49; H, 3.12; N, 14.43; Found: C, 49.60; H, 3.16; N, 14.25%.

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