Furans are an important class of compounds and exhibit a diverse range of activities and properties. As such, improved synthetic access to furans is an important research goal. In the present report, a solvent- and catalyst-free reaction between 5,5-dimethyl-1,3-cyclohexanedione (dimedone), an aryl aldehyde and an isocyanide under microwave irradiation is presented. This method is significantly improved from previously described protocols in terms of applicability of wide ranging aryl aldehydes, better yields, shorter reaction times, facile work up and essentially no need of column chromatography. The photophysical properties of this series of compounds were studied for their possible applicability in the field of metal ion sensors. In solution, two compounds, 2-(cyclohexylamino)-3-(1H-indol-3-yl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (1i) and 2-(tert-butylamino)-3-(1H-indol-3-yl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (1j), underwent an observable color change from yellow to colorless in the presence of aluminum(III) ions. Further studies to investigate the UV absorption and luminescence behavior of these compounds revealed their utility as “naked-eye sensors” for aluminum detection.

Introduction

Among oxygenated heterocycles, fused and substituted furan analogues form a class compounds worthy of considerable attention. They are the basic scaffolds of a myriad of natural products and possess a wide spectrum of medicinal activities.[1–3] Some of the annulated and polymeric furans show outstanding photosensitivity[4] and are important in the field of conducting polymers,[5] materials science,[5] photovoltaics,[6] and photo-chemotherapeutics[7] (Figure 1). Considering their wide-spread utility, synthetic advancement toward annulated furans and related structures, and assessment of their absorption- and fluorescence-based metal-sensing abilities are important research goals. This selective sensing/signaling of ecologically and biologically important metal ions is a fascinating and emerging area of research because of its simplicity, improved selectivity, real-time detection, portability and non-destructive nature.[8–10]

Consistent with this theme, we undertook the synthesis of 2-(alkylamino)-3-aryl-6,7-dihydrobenzofuran-4(5H)-ones or substituted 4-keto-4,5,6,7-tetrahydrobenzofuran. Although many synthetic routes to these compounds can be found in the literature.[11–21] multicomponent cycloaddition of enones to isocyanides is an important method to synthesize a variety of furans.[16–22] However, the literature reveals that only a few aryl aldehydes[11] (e.g., 4-nitrobenzaldehyde and glyoxals) have been investigated for this reaction, with dimedones as the CH acid, to generate 6,7-dihydrobenzofuran-4(5H)-ones. Given the limited prior reports, further investigation into improving this procedure is warranted.

In this regards, herein we present an improved version of the above-mentioned reaction to afford 6,7-dihydrobenzofuran-4(5H)-ones in a solvent-free, catalyst-free, microwave-assisted environment, constituting a benign and sustainable “green” method.[23–24] More importantly, this reaction, unlike the previ...
ous reports, can be applied to a wide range of benzaldehydes and hence has a greater scope. Moreover, two of the synthesized compounds displayed distinct behavior in the UV absorption and luminescence spectra when evaluated in the presence of aluminum, indicating their potential use as chemical sensors.

Results and Discussion

Synthesis and substrate scope

With our focus on environmentally benign chemistry, initially we ground dimedone 2a, 4-nitrobenzaldehyde 3a and tert-butyisonitrile 4a together without any solvent for 30 min at room temperature (Scheme 1). Interestingly, product 1a was deposited as a red solid in 83% yield. This is the first report of such a facile synthesis of 1a by mechanochemical route. It is worth noting that the product was obtained in lower yields by Shaabani et al. using conventional heating/prolonged reaction times.\[19\] When the aryl aldehyde was changed from 3a to unsubstituted benzaldehyde 3b, the yield of the corresponding product 1b was just 15%, with most of the dimer-done starting material remaining unreacted (Table 1, entry 1).

Under microwave irradiation (120 °C, 850 W, 10 min), the same reaction gave product 1b in 89% yield (Table 1, entry 2). The precise reason(s) for this kind of microwave-assisted yield enhancement is a matter of continuous dispute, and many thermal and nonthermal effects have been suggested by different research groups.\[25–29\] Here, the observed yield improvement was in line with the results of previous reports of improved yields under microwave condition for reactions with polar transition state.\[26,29,30\]

In order to make comparisons with the above method, a number of other conditions, such as the use of elevated temperatures through conventional heating or microwave irradiation in the presence of solvents, including water, were investigated (Table 1, entries 3–10) and the use of acid catalyst, like acetic acid, perchloric acid, iron(III) chloride and zinc chloride of CH acidic partner, the reaction was attempted with cyclohexanediones (Table 1, entries 11–13). Unfortunately, in the case of 4-methoxy benzaldehyde, the product did not crystallize and remained too impure to be counted (Table 2, entry 8), while reaction of 2,3-dimethoxy aldehyde provided the anticipated product in moderate yield (Table 2, entry 14). This result was expected as the initial enone formed with an electron-rich aryl aldehyde would be less electrophilic and hence less prone to isocyanide attack (Scheme 2). Moreover, the method also tolerated less reactive imidazole-3-carbaldehyde (Table 2, entries 9 and 10). It is noteworthy that 1a and 1g were synthesized here with improved yields over those previously reported in the literature.\[19\]

Furthermore, to explore the scope of the protocol in terms of CH acidic partner, the reaction was attempted with cyclohexanediones 5a,b and mesityl oxide (5c). The reaction worked well with cyclohexanediones, and the anticipated furans 1b, 6a and 6b were obtained in good yield (Table 3, entries 1–3). Unfortunately, no reaction occurred in the presence of mesityl oxide (5c), and only starting material was recovered (Table 3, entries 4 and 5).

Photophysical study

Many chemical sensors, each with merits and limitations, based on Schiff bases,\[31–37\] rhodamine,\[38–43\] naphthalimide\[44\] and coumarin\[45,46\] etc., have been previously reported. For a scaf-

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**Table 1. Optimization conditions for the synthesis of product 1b.**

| Entry | Solvent | Catalyst[a] | Conditions | T [°C] | t [min] | Yield [%][b] |
|-------|---------|-------------|------------|--------|--------|--------------|
| 1     | –       | –           | grinding   | rt     | 60     | 15           |
| 2     | –       | –           | mw\[^{[10]}\]  | 120    | 10     | 89           |
| 3     | H\(_2\)O | –           | heating    | 75     | 60     | 34           |
| 4     | MeOH    | –           | reflux     | –      | 600    | 35           |
| 5     | IPA     | –           | reflux     | –      | 600    | 56           |
| 6     | PEG     | –           | reflux     | –      | 600    | 47           |
| 7     | PEG + H\(_2\)O | –     | reflux     | –      | 600    | 35           |
| 8     | PEG     | –           | mw\[^{[10]}\]  | 120    | 10     | 67           |
| 9     | PEG + H\(_2\)O | –     | mw\[^{[10]}\]  | 120    | 10     | 79           |
| 10    | H\(_2\)O | –           | mw\[^{[10]}\]  | 120    | 10     | 78           |
| 11    | MeOH    | CH\(_2\)COOH | reflux     | –      | 600    | 40           |
| 12    | MeOH    | HClO\(_4\)  | reflux     | –      | 600    | 42           |
| 13    | MeOH    | FeCl\(_3\)  | reflux     | –      | 600    | 42           |
| 14    | MeOH    | ZnCl\(_2\)  | reflux     | –      | 600    | 50           |

[a] General conditions: dimedone (1 mmol), benzaldehyde (1 mmol), tert-butyisonitrile (1.2 mmol). [b] Catalyst loading: 10 mol%. [c] Anton Paar Monowave 300 microwave reactor; irradiation power: 850 W; ramp time: 1 min at 70 °C. [d] Isolated yield.

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**Scheme 1.** Mechanochemical reaction using 4-nitrobenzaldehyde (3a) as a substrate. Reagents and conditions: a) no solvent, grinding, 30 min, rt, 83%.

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**Figure 1.**
fold to hold promise as a metal-sensing agent, it is desirable that it originate from an easy synthetic route, and it was in this context that we decided to evaluate 6,7-dihydrobenzofuran-4-(5H)-ones for their metal-sensing abilities.

Extensive UV and fluorescence studies were carried out, and the absorption and emission maxima, and molar extinction coefficients in methanol are presented in Table 4 (also see Figures SS1 and SS2 in the Supporting Information). The absorption and emission spectra of all compounds were also recorded in the presence of different metals: Ag⁺, Al³⁺, Ca²⁺, Cd²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Co²⁺, In³⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺ and Zn²⁺. Of the 13 compounds investigated, two compounds (1i and 1j) exhibited a striking color change, from yellow to colorless (turn-off colorimetric sensing), in the UV absorption and fluorescence spectra when in the presence of aluminum metal. Hence, these two candidates were undertaken forward for full investigation (Figure 2A,B).

The fluorescent spectra of compounds 1i and 1j display a significant hyperchromic shift at higher intensity band in the presence of Ag⁺, In³⁺ and Al³⁺ in increasing order: Ag⁺ < In³⁺ < Al³⁺ (Figure 2). In the case of Al³⁺, approximately a tenfold enhancement in intensity was observed. Interestingly, the compounds are structurally similar in the sense that both possess an indole moiety, and it is very likely that extended conjugation due to the indole ring is involved in important interactions at the molecular level.

Since selectivity is important for potential applicability as a sensor, an interference study was conducted to measure the influence of other metal ions on the Al³⁺ binding by ligands 1i and 1j. Gratifyingly, with the exception of Cd²⁺ and Ni²⁺, the presence of no other metal produced any significant change in the fluorescent spectra of the compounds (Figure 3A,B).

In order to study the complexation behavior and detection limit of these possible sensors, titration experiments were performed (see Figures SS7–SS10 in the Supporting Information). In methanol, we observed a gradual increase in the fluorescence emission intensity of the band at around 415 nm with increasing concentrations of Al³⁺ from 0 to 50 ppm. Furthermore, the detection limit for the Al³⁺ metal ion was determined by using universal method (LOD = 3σ/slope) to be 4.59 × 10⁻⁷ M and 5.03 × 10⁻⁷ M for compounds 1i and 1j, respectively. Comparable results were also obtained from absorbance measurements (Table 5). These detection limits are better than some of
the previously reported sensors (Table SS1 in the Supporting Information).

Job’s plot experiments were performed for both compounds 1i and 1j at around 415 nm in order to understand the characteristics and stoichiometry of binding (Figure 4). Intensity maxima were observed when the molar fraction of aluminum reached a value of 0.5, indicating a 1:1 stoichiometric complex between the ligand (1i or 1j) and ion (i.e., Al\textsuperscript{3+}). This fact was further supported by the results of high-resolution mass spectrometry (HRMS) (Figures SS13 and SS14 in the Supporting Information). Based on the absorbance and fluorescence titration data, Benesi–Hilderbrand plots\cite{47} were drawn for both compounds with aluminum ion (Figure 5A, B). All of the data and related association constants are included in Table 5.

Finally, the influence of H\textsuperscript{+} ion concentration on sensitivity of both sensors was examined in aqueous methanolic solution at different pH levels. Both compounds retained their sensing abilities in mildly acidic to mildly basic media (Figure 6).

### Table 3. Exploration of reaction between α,β-enones and isocyanides.\cite{[a]}

| Entry | Enone | NC | Product | Yield [%] |[b] |
|-------|-------|----|---------|-----------|----|
| 1     | 5a-c  | 4a | 1b      | 85        |    |
| 2     | 5b    | 4a | 6a      | 83        |    |
| 3     | 4b    | 6b | 79      |           |    |
| 4     | 5c    | 4a | 6c      | 0         |    |
| 5     | 4b    | 6d | 0       |           |    |

[a] General conditions: α,β-enone (1 mmol), isonitrile (1.2 mmol), microwave irradiation (Anton Paar Monowave 300 microwave reactor; irradiation power: 850 W; ramp time: 1 min at 70 °C), reaction temperature: 120 °C, reaction time: 10 min. [b] Isolated yield.

### Table 4. Photophysical properties\cite{[a]} of synthesized compounds 1.

| Product | \(\lambda_{\text{max}}\) [nm] | \(e\) \([10^4, \text{cm}^{-1}, \text{M}^{-1}]\) |
|---------|--------------------------|------------------|
| 1a      | 388.44                   | 227, 263, 350    | 5.82, 1.34, 0.7 |
| 1b      | 398.21                   | 226, 268         | 5.59, 1.05      |
| 1c      | 387.17                   | 227, 271         | 5.77, 1.01      |
| 1d      | 430.66                   | 225, 277         | 5.62, 1.69      |
| 1e      | 388.71                   | 226, 270         | 5.79, 0.94      |
| 1f      | 429.31                   | 226, 278         | 5.53, 1.27      |
| 1g      | 428.14                   | 226, 268, 413    | 5.72, 1.27, 0.61|
| 1i      | 528.06                   | 224, 247, 404    | 5.67, 1.59, 0.29|
| 1j      | 501.47                   | 112, 251, 402    | 5.61, 1.58, 0.25|
| 1k      | 426.61                   | 226, 278         | 5.48, 0.59      |
| 1l      | 386.26                   | 226, 274         | 5.39, 0.92      |
| 1m      | 426.22                   | 225, 276         | 5.27, 1.48      |
| 1n      | 427.09                   | 227, 289         | 5.58, 1.39      |

[a] Wavelength maxima (\(\lambda_{\text{max}}\)) of absorption (abs) and emission (ems), and the molar extinction coefficient (\(e\)) for the given \(\lambda_{\text{max}}\) (abs) values.

### Table 5. Comparison of various parameters obtained from absorbance (abs) and fluorescence (fluor) studies.

| Parameter\cite{[a]} | Compd 1i | Compd 1j |
|--------------------|----------|----------|
| LOD (abs) \([10^{-7}\text{M}]\) | 9.21 | 9.83 |
| LOD (fluor) \([\text{M}]\) | 4.59 | 5.03 |
| \(K_a\) \(\text{(abs)} \) \([10^4]\) | 0.78 | 1.03 |
| \(K_a\) \(\text{(fluor)} \) \([10^4]\) | 0.97 | 2.0x10^4 |
| \(r^2\) \(\text{(abs)}\) | 0.99 | 0.99 |
| \(r^2\) \(\text{(fluor)}\) | 0.98 | 0.98 |

[a] Limit of detection (LOD) = 3s/slope; acid dissociation constant \(K_a\); coefficient of determination \(r^2\).

Figure 2. Fluorescence emission changes (at 5.0 \(\times\) \(10^{-5}\) M) upon addition of different metal ions for compounds A) 1i (\(\lambda_{\text{ex}}\) = 417 nm) and B) 1j (\(\lambda_{\text{ex}}\) = 412 nm) in methanol at pH 7.0.
Conclusion

A solvent-less, diversity enabling, high yielding, energy efficient one-step protocol has been devised for 2-(alkylamino)-3-aryl-6,7-dihydrobenzofuran-4(5H)-ones. This method is superior to the previous reports in terms of scope in aryl aldehydes and “greenness”. Extensive UV and fluorescence-based studies of these compounds to evaluate their metal-sensing ability identified two new chemosensors for aluminum detection. Both of these indole-based furanones exhibited potential and warrant further investigatory and developmental work in this direction.

Experimental Section

General details: All solvents were distilled prior to use, and all chemicals were purchased from Sigma–Aldrich and used without further purification. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck 60 F_254). ^1H and ^13C NMR spectra were recorded on a Bruker Avance 500 and 125 MHz spectrometer, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual undeuterated solvent peak. ^13C NMR spectra were obtained with ^1H decoupling. Spectra were processed using Bruker Topspin 3.0.b.8. High-resolution mass spectrometry (HRMS) was performed using a Bruker Daltronics.
micro-ToF-QII spectrometer using electrospray ionization (ESI), with less than 5 ppm error for all HRMS analyses. UV absorbance spectra were recorded on a Shimadzu UV-2450 spectrophotometer, and fluorescence experiments were performed on a Horiba fluoromax-4 spectrophotometer with 1.0 nm excitation and emission slit widths. For statistical analysis and graphical representation of data, Origin 6.0 software was used.

$^1$H and $^{13}$C NMR spectra and complete characterization data for all compounds described, together with supporting figures and data, are given in the Supporting Information.

Microwave irradiation protocol: All microwave experiments were carried out in a dedicated Anton Paar Monowave 300 reactor, operating at a frequency of 2.45 GHz with continuous irradiation power of 0–300 W. The reactions were performed in a G10 Borosilicate glass vial sealed with a Teflon septum and placed in the microwave cavity. Initially, microwaves of the required power were used, and the temperature was ramped from room temperature to the desired temperature. Once this temperature was attained, the process vial was held at this temperature for the required time. The temperature was measured by an IR sensor. The reactions were continuously stirred. After the experiment, a cooling jet was used to cool the reaction vessel to ambient temperature.

General procedure for the microwave-assisted three-component reaction: Dimedone (1.0 mmol), aryl aldehyde (1.0 mmol) and iso-nitrile (1.2 mmol) were mixed well in a G10 process vial capped with a Teflon septum. After pre-stirring for 1–2 min, the mixture was subjected to microwave irradiation (850 W) with an initial ramp time of 1 min at 70 °C. The temperature was then raised to 120 °C and held at 10 min. The reaction was cooled to room temperature, water/EtOH (4:1; 5 mL) was added to the vial, and the mixture was cooled to 0–5 °C for about 3–4 h. The product crystallized in the reaction vessel and was then isolated by filtration. This material was used directly without further purification for spectral elucidation by $^1$H and $^{13}$C NMR and HRMS.

General details of UV and Fluorescence study: For UV and fluorescence studies, stock solutions of the compounds and metal ions (Ag(I), Al(III), Ca(II), Cd(II), Cr(III), Cu(II), Fe(III), Ni(II), Mg(II), Mn(II), Na(II), Ni(II), Pb(II) and Zn(II)) were prepared (1.0 × 10$^{-3}$ M) in MeOH. For spectral recordings, the stock solutions were further diluted to 5.0 × 10$^{-4}$ M with MeOH.

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Keywords: heterocycles · isocyanides · microwave chemistry · multicomponent reactions · sensors

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