JOC The Journal of Organic Chemistry

Article

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Modular Assembly of Furotropones and Benzofurotropones, and Study of Their Physicochemical Properties

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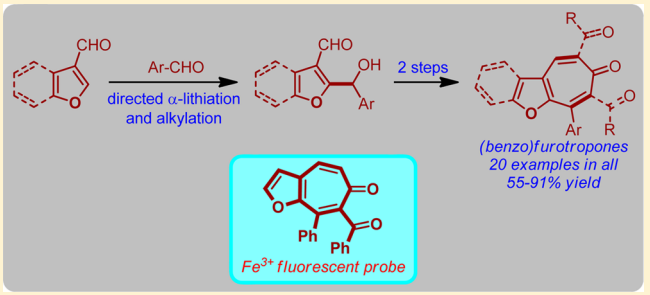
Supporting Information

ABSTRACT: A rapid and straightforward synthesis of a novel series of furo[2,3-*d*]tropones (or cyclohepta[*b*]furan-6-ones) has been developed starting from readily and commercially available materials. Directed α-lithiation of furan-3-carboxaldehydes and subsequent reaction with a variety of aldehydes efficiently provide, in one step, access to 3-formyl-2-furylcarbinols, which are otherwise only accessible with difficulty. The 3-formyl-2-furylcarbinols are further elaborated in two steps to the synthesis of furo[2,3-*d*]tropones in good yields via sequential bismuth(III)chloride-catalyzed furfurylation and an unusual base promoted cyclization strategy. Thus, diverse polysubstituted furotropones and benzofurotropones can be rapidly assembled. This methodology thereby offers a potential approach for the synthesis of several bioactive natural products containing cyclohepta[*b*]furan core and also for the buildup of complex molecular architectures through higher order cycloaddition reactions of tropones. Further, the new chromophores have been found to possess promising fluorescence properties. Selective fluorogenic sensing behavior of furotropones toward Fe^{3+} ions has also been elucidated.



INTRODUCTION

Among nonbenzenoid aromatics, tropones have been studied in great detail from synthetic and theoretical standpoint.[1] Occurrence of several troponoid natural products possessing interesting biological activities spurred several studies directed toward understanding structure activity relationships as well as their physicochemical properties.[2] Tropones traditionally have been employed in several higher order cycloaddition reactions[3] and quite often as synthons in natural product synthesis.[4] Among annulated tropone derivatives, aryl-annulated tropones are well-studied, while heteroaryl-annulated tropones are mostly unfamiliar.[5] A detailed literature review exposes lack of synthetically flexible methods for the synthesis of heteroaryl-annulated tropones and also a general understanding about their physical and biological properties is particularly missing.

Toward this, we have initiated research to establish a short, efficient and scalable approach for the synthesis of previously unknown furo[2,3-*d*]tropones from readily available starting materials. Known methods for the synthesis of furo[2,3-*d*]tropones are depicted in Scheme 1.[6] The key step in El-Borai and Shafiee's approach (method-1, Scheme 1) for tropones involved the cyclocondensation of furan or benzofuran-2,3-dicarboxaldehydes **I** and ketones **II** under strong basic conditions.[6a,b] On the other hand, Takeshita's Claisen rearrangement of (*E*/*Z*)-4-(3-chloro-2-propenyloxy)tropones **III** under thermal conditions furnished furo[2,3-*d*]tropones (method-2, Scheme 1).[6c] Evidently, these methods are associated with the drawbacks such as (i) difficult-to-access starting compounds, (ii) harsh reaction conditions, (iii) poor yields, (iv) limited substrate scope (that hinders diversification). Herein we describe general synthesis of a variety of furo- and benzofuro[2,3-*d*]tropones, study of their physicochemical properties, and especially their ability in cation sensing.

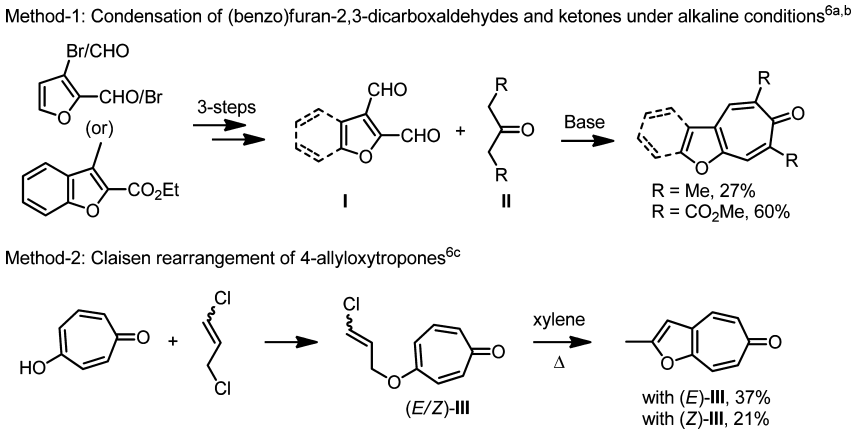
RESULTS AND DISCUSSION

Synthesis and Characterization of Tropones. A general approach toward the synthesis of furotropones is depicted in Scheme 2. To begin with, commercially available 3-furancarboxaldehydes of the type **A** are converted to 3-formyl-2-furylcarbinols **B** in a single step via regioselective directed α-lithiation-alkylation strategy published earlier by our research group.[7] Following this strategy, aldehyde functionality in 3-furancarboxaldehydes **A** can be masked by treatment with lithium *N*-methylpiperazide [LNMP, obtained by the reaction of *N*-methylpiperazine (NMP) and *n*-BuLi]. Chelation controlled lithiation of the resulting adduct at the C-2 position with *n*-BuLi generates 2-lithiofurans in highly selective manner. Reaction of 2-lithiofurans with aldehydes (or ketones) and subsequent hydrolysis generates conveniently 3-formyl-2-furylcarbinols **B**. Bismuth(III) catalyzed reaction of furylcarbinols **B** and 1,3-dicarbonyls **C** generate the tricarbonyls **D** in very good yields via intermolecular Friedel−Crafts-type reaction.[8] Base mediated intramolecular aldol condensation of

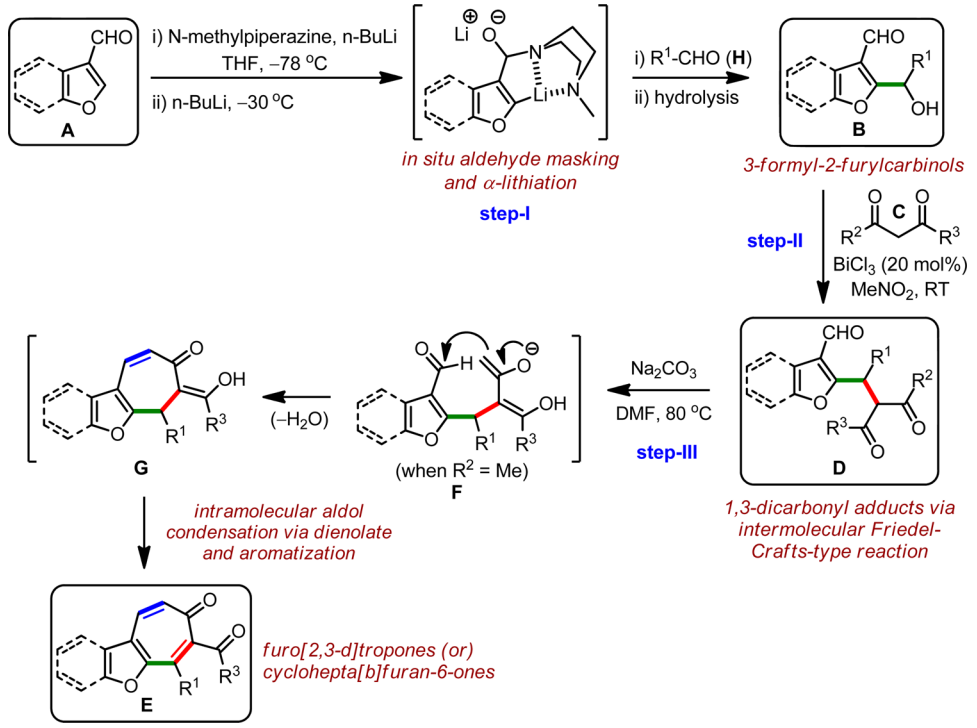
Received: January 31, 2015
Published: April 20, 2015

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

Scheme 1. Known Methods for the Synthesis of Furo[2,3-*d*]tropones



Scheme 2. One-Step Synthesis of 3-Formyl-2-furyl Carbinols (B) and a Two-Step Synthesis of Furotropones and Benzofurotropones (E)



diketoaldehydes **D** delivers furotropones **E** in good to excellent yields via cyclization of the dienolates **F** on to the appropriately positioned aldehyde functionality and subsequent aerobic oxidative aromatization of **G**.[7] This method thus constitutes a general, short, efficient and straightforward approach for the synthesis of cyclohepta[*b*]furan-6-ones (commonly referred to as furotropones). Some advantages of furan-based strategies are the ready availability of starting materials, ease of manipulation and high degree of synthetic flexibility.

Since the general synthetic approach described in Scheme 2 permits diversity across the aldehydes **A** and **H**, and the dicarbonyls **C**, a variety of highly functionalized furotropones and benzofurotropones (**3a**–**3n**) could be rapidly synthesized, Table 1. All the new compounds were fully characterized by comprehensive spectroscopic data. All of these heteroaryl-annulated tropones exhibited good solubility profiles in common organic solvents such as toluene, DCM, THF, DMSO, DMF, ethanol, ACN, etc., at room temperature itself. Most of the tropones were isolated as colorless to pale yellow solids.

Tropones possessing both aliphatic and aromatic *β*-ketone functionality (at C-7) could be accessed efficiently via this methodology (Table 1, entries 1–9), in addition to a diverse range of aryls and heteroaryls at C-8. More interestingly, tropones with *β*,*β*′-diketones are of particular interest from synthesis point of view (Table 1, entries 10–12). This novel class of tropones can be accessed by the reaction of triketones such as **2d** and 3-formyl-2-furylcarbinols under standard conditions. This methodology is found to be particularly efficient in establishing a short and scalable method for the synthesis of new benzofurotropones in good yields (Table 1, entries 13 and 14).

By virtue of the inherent restrictions the mechanism involves, there exist certain structural limitations for 1,3-dicarbonyls. For

DOI: 10.1021/acs.joc.5b00226
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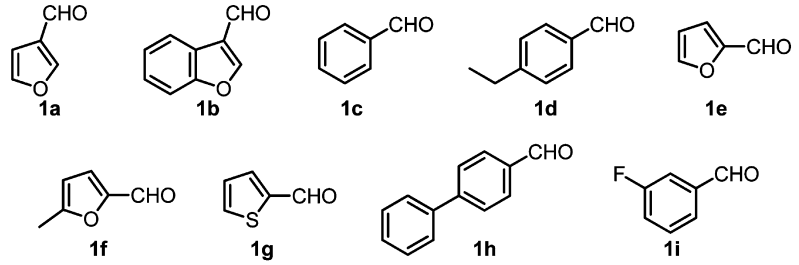
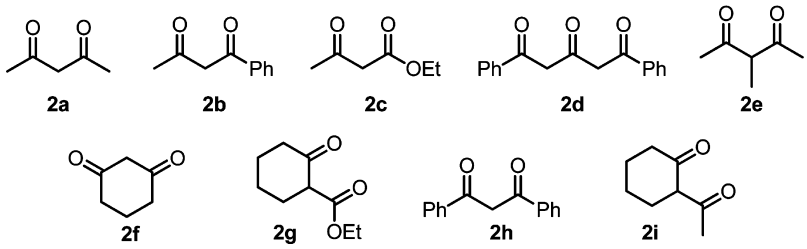
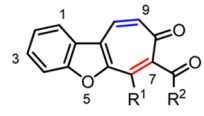
Table 1. Scope of Various Aldehydes and 1,3-Dicarbonyls for the Synthesis of a Variety of Furotropones and Benzofurotropones





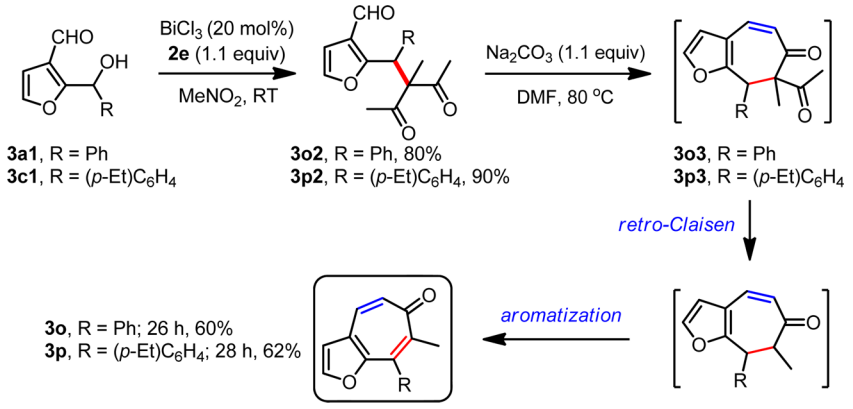
entry	aldehydes	dicarbonyl		tropone	time (h)	%yields of steps-I, II, & III
						
1	**1a**	**1c**	**2a**	**3a**, R^1 = Ph, R^2 = Me	4	70, 85, 69
2	**1a**	**1c**	**2b**	**3b**, $R^1 = R^2$ = Ph	8	70, 94, 75
3	**1a**	**1d**	**2a**	**3c**, R^1 = (*p*-Et)C_6H_4, R^2 = Me	7	68, 95, 74
4	**1a**	**1d**	**2b**	**3d**, R^1 = (*p*-Et) C_6H_4, R^2 = Ph	9	68, 94, 62
5	**1a**	**1e**	**2b**	**3e**, R^1 = 2-furyl, R^2 = Ph	4	60, 71, 91
6	**1a**	**1f**	**2b**	**3f**, R^1 = 5-methyl-2-furyl, R^2 = Ph	8	65, 74, 74
7	**1a**	**1g**	**2a**	**3g**, R^1 = 2-thienyl, R^2 = Me	6	65, 75, 70
8	**1a**	**1g**	**2b**	**3h**, R^1 = 2-thienyl, R^2 = Ph	10	65, 94, 95
9	**1a**	**1h**	**2c**	**3i**, R^1 = 1,1'-biphenyl-4-yl, R^2 = OEt	50	65, 80, 75
						
10	**1a**	**1c**	**2d**	**3j**, $R^1 = R^2$ = Ph	8	70, 73, 76
11	**1a**	**1e**	**2d**	**3k**, R^1 = 2-furyl, R^2 = Ph	7	60, 75, 70
12	**1a**	**1h**	**2d**	**3l**, R^1 = 1,1'-biphenyl-4-yl, R^2 = Ph	7	65, 70, 84
						
13	**1b**	**1c**	**2a**	**3m**, R^1 = Ph, R^2 = Me	1	67, 60, 61
14	**1b**	**1c**	**2b**	**3n**, R^1 = Ph, R^2 = Ph	1	67, 65, 65

example, cyclic diketones (such as 1,3-cyclohexanedione **2f** or the *β*-ketoester **2g**) cannot form tropones obviously because of the inaccessibility of dienolate intermediates toward the aldehydic carbonyl, even otherwise also would lead to highly energetic bridged structures. Likewise, the diketones of the type 1,3-diphenyl-1,3-propanedione **2h** (not possessing *α*-acidic protons and thus dienolate formation is hindered) or **2i** cannot generate tropones. Indeed we prepared respective tricarbonyls with the general structure **D** with aforementioned dicarbonyls, attempted base mediated intramolecular aldol reaction was unsuccessful and yielded no meaningful product. In addition, step-III failed to deliver tropones in cases where R^1 is aliphatic.

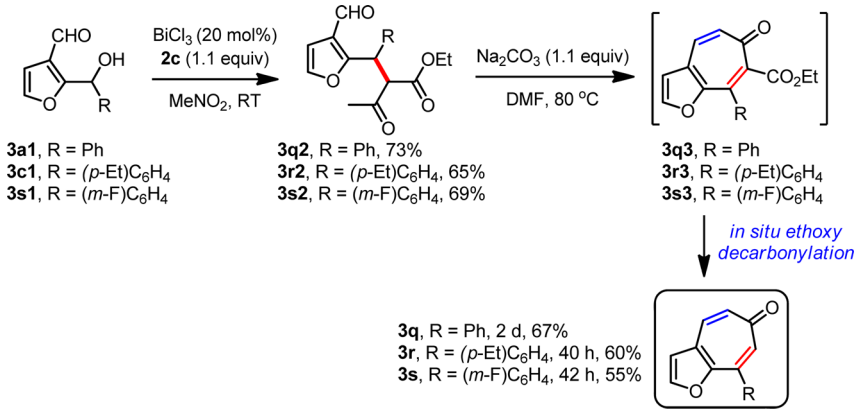
Interestingly, reaction of 3-formyl-2-furylcarbinols **3a1** and **3c1**, and 3-methylpentane-2,4-dione **2e** under bismuth(III)

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

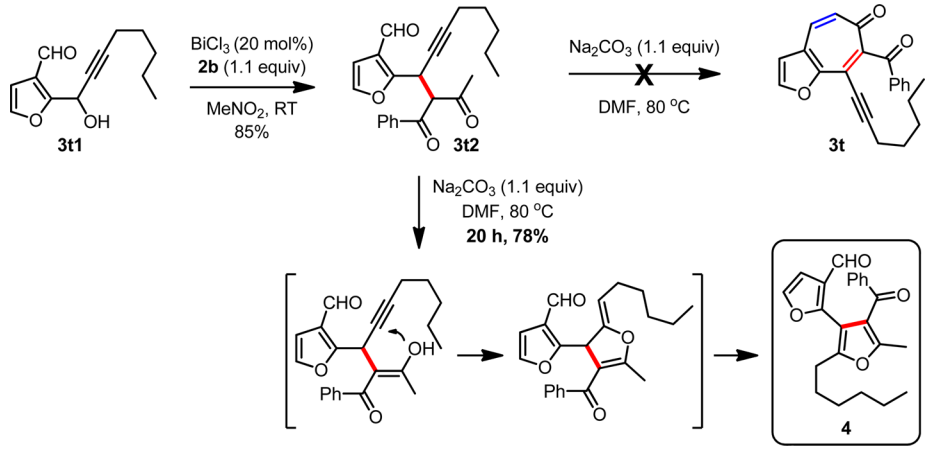
Scheme 3. Synthesis of C-7 and C-8 Disubstituted Furotropones via Retro-Claisen Condensation



Scheme 4. Synthesis of Mono (C-8) Substituted Furotropones via in Situ Ethoxy Decarbonylation



Scheme 5. Synthesis of 2,3′-Bifuran Derivatives



catalysis generated expectedly the diketoaldehyde **3o2** and **3p2**. Reaction of **3o2** and **3p2** under base mediated reaction furnished, surprisingly, 7,8-disubstituted furotropones **3o** and **3p**, respectively, in good yields, presumably via a retro-Claisen-aromatization sequence as shown in Scheme 3. After the initial aldol condensation, in order to attain aromaticity, the 7,7,8-trisubstituted cyclohepta[*b*]furan-6-ones **3o3** and **3p3** undergo base-mediated retro-Claisen cleavage followed by aromatization to form furotropones **3o** and **3p**, respectively.

Further, reaction of the tricarbonyls **3q2**, **3r2** and **3s2**, which were obtained by the reaction of 3-formyl-2-furylcarbinols **3a1**, **3c1** and **3s1**, and ethyl acetoacetate **2c**, respectively, in the presence of a catalytic amount of bismuth(III)chloride, under standard reaction conditions not only furnished the *β*-ketoesters **3q3**, **3r3** and **3s3**, but subsequently underwent in situ ethoxy decarbonylation, generating mono (C-8) substituted furotropones **3q**, **3r** and **3s**, respectively, in good yields, Scheme 4. However, the reaction can be interrupted prematurely to isolate the *β*-ketoesters, but the case of furotropone **3i** may be an exception where formation of ethoxy decarbonylation product was not observed even after prolonged reaction times.

Of particular interest, reaction of the diketoaldehyde **3t2**, possessing a pendent alkyne functionality, under standard base

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

mediated conditions failed to generate the expected furotropone **3t**; however, to our surprise, it yielded a 2,3′-bifuran derivative **4** in 78% yield in a mechanism described in Scheme 5. Subtle variations across the alkynes and/or diketones can potentially generate an array of functionalized 2,3′-bifuran derivatives.[9] This method thus can be a general approach for the synthesis of otherwise difficult to access, functionalized and highly substituted bifuran derivatives.

Several natural products possessing cyclohepta[*b*]furan core are known in the literature, some of the representative examples are depicted in Figure 1. This methodology can be very much

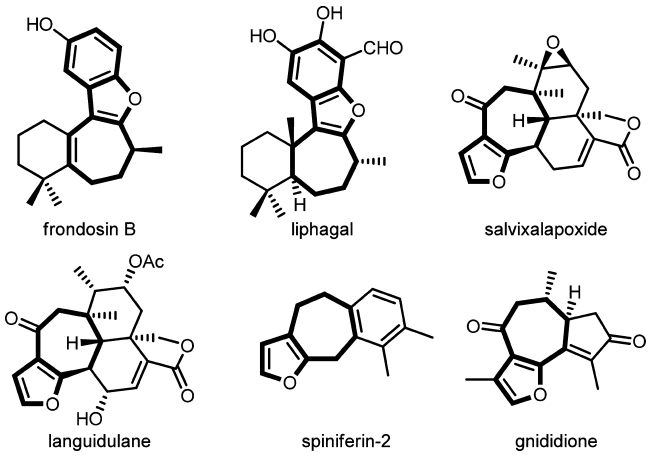


Figure 1. Some natural products possessing cyclohepta[*b*]furan core.

convenient for developing short synthesis of several of these bioactive compounds. For example, frondosin B, liphagal and other natural products are synthetic challenges with their wide structural diversity and stereochemical features coupled with their interesting biological activity profiles.[10]

Crystal Structure of the Furotropone 3j. Molecular structure of the tropone **3j** was confirmed by single crystal X-ray diffraction analysis and the molecular packing arrangement in the solid state were further analyzed (see Supporting Information for details), Figure 2.

Photophysical Properties. In order to better understand the photophysical properties of the newly synthesized furotropones in detail, initially UV−vis absorption spectra of the furotropone **3q** under various solvent systems were recorded and the results are summarized in Figure 3a. A

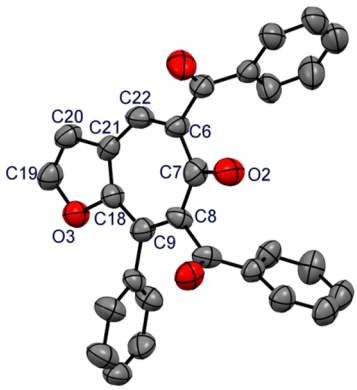


Figure 2. ORTEP diagram of **3j** (CCDC 1046548) with 50% ellipsoidal probability.

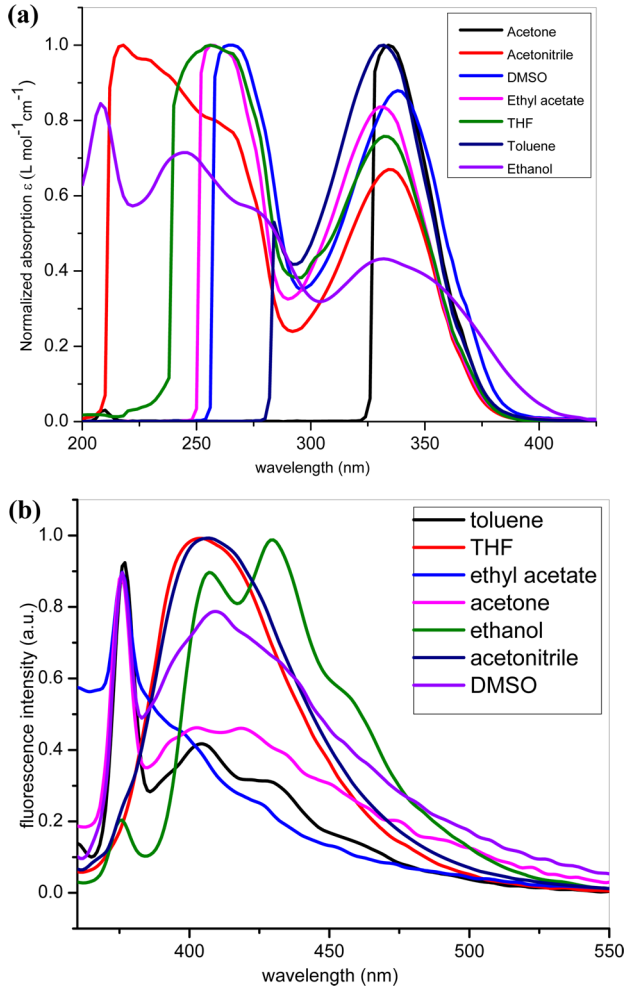


Figure 3. (a) UV−vis absorption spectra of **3q** (10 μM) in different solvents, and (b) fluorescence emission spectra of **3q** (10 μM) in different solvents.

striking impact of solvents on the UV absorption pattern was witnessed. Among the solvents screened, a nonpolar solvent such as toluene at 10 μM concentration exhibited an absorption maximum at 332 nm (due to $n-\pi^*$ transition) while in a polar solvent DMSO at the same concentration, **3q** displayed an absorption maximum at 338 nm, essentially indicating a bathochromic shift (red shift) of about 6 nm. On the other hand, a hypsochromic shift (blue shift) of about 18 nm was observed in case of $\pi-\pi^*$ transitions for furotropone **3q** from toluene to DMSO. Further, UV−vis absorption spectra of few other di- and triketofurotropones (**3b**, **3c**, **3e**, **3g**, **3h**, **3j**, **3k**) were also recorded (see Supporting Information for details).

Subsequently, the fluorescence emission spectra of furotropne **3q** were also recorded in different solvents at 10 μM concentration and the results are summarized in Figure 3b and Table 2. Fluorescence emission patterns were found to be strongly solvent dependent. Solvent effect was more pronounced in $n-\pi^*$ transition when excited the molecule at 340 nm. Interestingly, maximum Stokes shift (97 nm) was observed in DMSO and also in ethanol (94 nm) while minimum Stokes shift was realized in acetone (41 nm). Fluorescence life expectancy (τ_f) was found to be maximum in THF (5.89 ns) and it was found to be least in ethanol (1.34 ns). These results perhaps indicate inherently rigid electronic nature and thus least solvent polarity dependency of

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Table 2. Photophysical Data of 3q in Different Solvents

solvent[a]	λ_{abs} (nm)[b]	ε	log ε	λ_{emi} (nm)	$\Delta\lambda_{stokes}$ (nm)[c]	τ_f (ns)[d]	Φ_f
THF	256, 330	10.84	1.0350	402	72	5.89	0.0048
ACN	260, 334	8.722	0.940	410	76	3.13	0.0145
toluene	284, 332	4.17	0.620	406	74	2.38	0.0011
DMSO	266, 338	5.09	0.7067	435	97	3.31	0.0017
acetone	210, 334	8.34	0.921	375	41	1.41	0.0036
EtOAc	256, 332	7.9	0.8976	376	44	1.47	0.0083
ethanol	244, 337	9.485	0.977	431	94	1.34	0.0081

[a]THF: tetrahydrofuran; ACN: acetonitrile; DMSO: dimethyl sulfoxide; EtOAc: ethyl acetate. [b]$\pi-\pi^*$ and $n-\pi^*$ absorption maxima. [c]Stokes shift = $\lambda_{max}^{emi} - \lambda_{max}^{abs}$. [d]Fluorescent lifetime.

furotropones. These results further point to their strong nonpolar character and also possible absence of push−pull electronic effects in the excited state. From Table 2, it can also be noted that the molar absorptivity (ε) for **3q** in toluene solution is found to be minimum (4.17) and in THF solvent, it is maximum (10.84). Fluorescence emission spectra of few other furotropones (**3b**, **3c**, **3e**, **3g**, **3h**, **3j**, **3k**) were recorded and their fluorescence lifetimes were also measured in ethanol, which indicated that the lifetimes lie within 1.08 to 1.44 ns (see Supporting Information for details).

Interesting electronic and spectroscopic properties, along with the presence of the 1,3- di- and 1,3,5-triketo groups in unique molecular environment inspired us to explore the application of furotropones as fluorescent chemosensors for cations with the potential to coordinate to these functionalities. Furotropone **3b** was chosen as a model substrate and exposed to the aqueous solutions of different metal salts[11] in ethanol. Almost no change in the fluorescence intensity was observed when solutions of other metal ions such as Hg^{2+}, Pb^{2+}, Cr^{2+}, Cd^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+} were tested. Furotropone **3b** was found to exhibit an interesting and highly selective fluorescent molecular sensing property for Fe^{3+}, Figure 4.[12] We surmised that the 1,3-dicarbonyl moiety in **3b** could

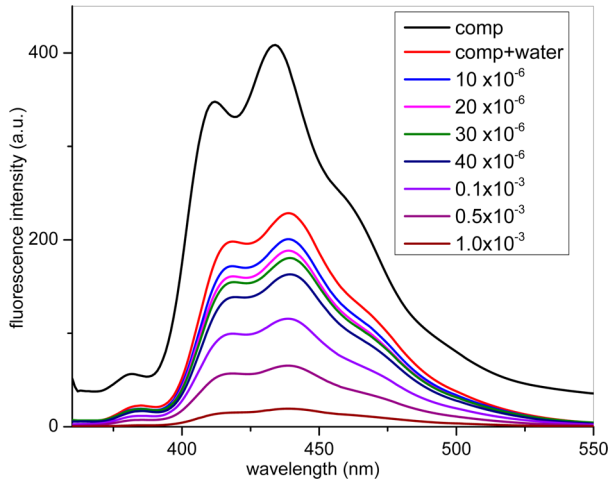

Figure 4. Selective sensing of Fe^{3+} by **3b** in ethanol solvent with different concentrations of Fe^{3+}.

serve as a suitable bidentate ligand for Fe^{3+} while the fused ring system could enhance the structural rigidity and change the π-electron distribution. In other words, the hard cation such as Fe^{3+} interacts with the hard oxygen atoms of the carbonyls present in the furoptopone **3b**. The possibility of cation-π interactions are less favored since the hard cations will not prefer interaction with the soft π-surfaces. Decreasing the metal ion concentration (up to 10 μM), significant influence on the fluorescence intensity was observed. From this study we have realized that furotropone **3b** (and potentially other analogues) could function as a probe for the detection of Fe^{3+} up to 10 μM concentration.

CONCLUSIONS

In summary, we have developed a modular approach to rapidly access functionalized and polysubstituted furotropones and benzofurotropones starting from readily accessible materials. The three-step protocol features directed α-alkylation of 3-furancarboxaldehydes, Bi(III)-mediated furfurylation and an unusual base-mediated intramolecular aldol condensation reaction. Mono substituted (C-8) furotropones could be accessed via in situ alkoxy decarbonylation of furotropone β-ketoesters, disubstituted (C-7 and 8) furotropones could be synthesized in a retro-Claisen-aromatization strategy, and trisubstituted (C-5, 7 and 8) furotropones were conveniently prepared by means of a base-mediated intramolecular aldol reaction of 1,3,5-triketones. Moreover, studies directed at understanding the physicochemical properties of furotropones yielded interesting results. We have identified that these new chromophores, with their unique structural features, have potential to be highly sensitive and selective sensors for the detection of hard cations such as Fe^{3+}, and the detection limit could be as low as 10 μM. We believe that our results could provide guidance for the design and synthesis of new tropone-based polycyclic aromatic heterocycles. Further synthetic modifications of furotropones for chemosensor applications are planned.

EXPERIMENTAL SECTION

General Experimental Methods. *n*-BuLi, 3-methyl benzofuran, all the aldehydes, *N*-methylpiperazine, *N*,*O*-dimethylhydroxylamine hydrochloride and solvents were purchased from commercial sources and were used without further purification. For thin-layer chromatography (TLC), silica aluminum foils with a fluorescent indicator (254 nm) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), concentrated H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Column chromatography was performed using silica gel 100−200 mesh (approximately 15−20 g per 1 g of the crude product). Dry THF was obtained by distillation over sodium and stored over sodium wire. IR spectra were recorded on a FT-IR system as thin films or KBr pellets, as indicated, with ν_{max} values given in reciprocal centimeters. Melting points were recorded on a digital melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm), and coupling constants (J) are reported in hertz (Hz). The following abbreviations are utilized to describe peak patterns when appropriate:

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Proton chemical shifts are given in δ relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$. Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm). High-resolution mass spectra were recorded on a Q-TOF mass spectrometer.

General Procedure for Step-I, Scheme 2 (Synthesis of 3-Formyl-2-furylcarbinols Starting from 3-Furancarboxaldehyes). To a solution of *N*-methylpiperazine (NMP, 0.07 mL, 0.66 mmol) in THF (2 mL) at −78 °C was added *n*-BuLi (2 *M* in cyclohexane, 0.33 mL, 0.66 mmol). After 15 min, 3-furaldehyde (50 mg, 0.045 mL, 0.52 mmol) was added, and then the reaction mixture was stirred for an additional 30 min. A cyclohexane solution of *n*-BuLi (0.66 mL, 1.32 mmol) was added, and the mixture was stirred for an additional 15 min, and then the mixture was warmed to −30 °C in 2 h. The solution was again cooled to −78 °C and an aldehyde (1.02 mmol) was added dropwise over 5 min. The mixture was warmed to room temperature over 30 min. The reaction progress was monitored by TLC. Reaction mixture was quenched with saturated aq. ammonium chloride solution and extracted with ethyl acetate. The organic extracts were combined, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by column chromatography on silica gel (ethyl acetate−hexanes) to afford 3-formyl-2-furylcarbinols in 60−80% yields.

Spectral Data of Newly Synthesized Alcohols. Some of the 3-formyl-2-furylcarbinols prepared during this study are already known in the literature.[7,8] Complete characterization data of newly synthesized compounds is given below.

*2-(Hydroxy(thiophen-2-yl)methyl)furan-3-carbaldehyde (**3g1**).* This compound was isolated as colorless liquid: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 3372, 2872, 1672, 1580, 1516, 1422, 1237, 1127, 1024, 805; ^1H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.42 (d, J = 1.9 Hz, 1H), 7.32 (m, 1H), 6.98 (m, 2H), 6.83 (d, J = 1.9 Hz, 1H), 6.30 (d, J = 7.0 Hz, 1H), 4.69 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 162.1, 143.7, 142.5, 126.9, 126.1, 125.2, 122.5, 110.2, 66.6; HRMS (ESI) m/z calcd for $C_{10}H_9O_3S$ $(M + H)^+$ 209.0272, found 209.0277.

*2-([1,1′-Biphenyl]-4-yl(hydroxy)methyl)furan-3-carbaldehyde (**3i1**).* This compound was isolated as colorless liquid: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 3370, 2870, 1670, 1578, 1514, 1418, 1235, 1022, 703; ^1H NMR (400 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.63−7.58 (m, 4H), 7.51−7.44 (m, 4H), 7.42 (d, J = 2.0 Hz, 1H), 7.37 (tt, J = 8.5 and 1.2 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 6.15 (d, J = 7.3 Hz, 1H), 4.49 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2, 163.2, 142.4, 141.3, 140.5, 139.1, 128.8 (2CH), 127.5 (2CH), 127.3, 127.1 (2CH), 126.6 (2CH), 122.6, 110.2, 70.3; HRMS (ESI) m/z calcd for $C_{18}H_{15}O_3$ $(M + H)^+$ 279.1021, found 279.1026.

*2-(Hydroxy(phenyl)methyl)benzofuran-3-carbaldehyde (**3m1**).* This compound was isolated as colorless liquid: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 3313, 3031, 1661, 1575, 1495, 1479, 1452, 1176, 1011, 748; ^1H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 8.12 (dd, J = 6.8 and 3.3 Hz, 1H), 7.53−7.51 (m, 3H), 7.43−7.36 (m, 5H), 6.29 (d, J = 5.5 Hz, 1H), 4.03 (d, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 166.7, 139.6, 128.9 (2CH), 128.7, 126.4 (2CH), 125.8, 125.0, 124.8, 121.4, 117.5, 111.5, 101.9, 65.4; HRMS (ESI) m/z calcd for $C_{16}H_{13}O_3$ $(M + H)^+$ 253.0865, found 253.0839.

*2-((3-Fluorophenyl)(hydroxy)methyl)furan-3-carbaldehyde (**3s1**).* This compound was isolated as colorless liquid: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 3363, 2927, 1673, 1615, 1592, 1488, 1451, 1250, 1129, 1024, 787; ^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.41 (d, J = 1.8 Hz, 1H), 7.37−7.34 (m, 1H), 7.18 (dd, J = 13.2 and 8.9, 2H), 7.02 (td, J = 8.4 and 2.5 Hz, 1H), 6.82 (d, J = 2.0 Hz, 1H), 6.08 (d, J = 5.3 Hz, 1H), 4.73 (d, J = 6.8 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 162.9 (d, J = 245.06 Hz), 162.6, 142.6, 142.5, 130.1 (d, J = 8.05 Hz), 122.6, 121.7, 115.2 (d, J = 20.9 Hz), 113.2 (d, J = 22.51 Hz), 110.4, 69.8; ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −112.15; HRMS (ESI) m/z calcd for $C_{12}H_8FO_2$ $(M - OH)^+$ 203.0509, found 203.0498.

General Procedure for Step-II, Scheme 2 (Reaction of 3-Formyl-2-furylcarbinols with Various 1,3-Dicarbonyls). To a solution of furfuryl alcohol (0.1 mmol, 1 equiv) in nitromethane (1 mL), were added acetylacetone (0.11 mmol, 1.1 equiv) followed by $BiCl_3$ (0.02 mmol, 0.2 equiv) at room temperature. The reaction was stirred at room temperature until the alcohol was consumed as monitored by TLC, and the reaction mixture was quenched with aqueous saturated sodium bicarbonate solution (1−2 mL). The reaction mixture was diluted with ethyl acetate (1−2 mL), and the layers were separated. The aqueous layer was further extracted with ethyl acetate (1−2 mL). The organic layers were combined, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography (ethyl acetate−hexanes) to afford 1,3-dicarbonyl adducts in 60−95% yields.

Spectral Data of 1,3-Dicarbonyl Adducts. Some of the 1,3-dicarbonyl adducts prepared during study are already known in the literature.[7,8] Complete characterization data of newly synthesized compounds is given below.

*2-(2-Benzoyl-3-oxo-1-phenylbutyl)furan-3-carbaldehyde (**3b2**).* This compound was isolated as colorless liquid starting from 40 mg of **3a1** and obtained 66 mg in 97% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2925, 1722, 1673, 1600, 1546, 1443, 1325, 752; ^1H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.05−8.02 (m, 2H), 7.62 (tt, J = 7.4 and 1.7 Hz, 1H), 7.52−7.47 (m, 4H), 7.38−7.35 (m, 2H), 7.31−7.27 (m, 1H), 7.18 (d, J = 1.9 Hz, 1H), 6.59 (d, J = 2.0 Hz, 1H), 5.78 (d, J = 11.5 Hz, 1H), 5.63 (d, J = 11.6 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 193.1, 184.7, 161.9, 142.4, 137.1, 135.9, 134.1, 129.2 (2CH), 128.9 (2CH), 128.8 (2CH), 128.4 (2CH), 128.1, 122.3, 108.7, 66.3, 43.6, 29.1; HRMS (ESI) m/z calcd for $C_{22}H_{18}O_4Na$ $(M + Na)^+$ 369.1103, found 369.1104.

*2-(2-Acetyl-1-(4-ethylphenyl)-3-oxobutyl)furan-3-carbaldehyde (**3c2**).* This compound was isolated as colorless liquid starting from 50 mg of **3c1** and obtained 67 mg in 95% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2965, 1733, 1702, 1681, 1574, 1514, 1471, 1358, 1124, 746. ^1H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.34 (d, J = 2.0 Hz, 1H), 7.27 (m, 2H), 7.15 (d, J = 8.3 Hz, 2H), 6.68 (d, J = 2.0 Hz, 1H), 5.38 (d, J = 11.8 Hz, 1H), 4.92 (d, J = 12.0 Hz, 1H), 2.60 (q, J = 7.0 Hz, 2H), 2.17 (s, 3H), 2.03 (s, 3H), 1.20 (t, J = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 200.9, 184.7, 161.9, 144.0, 142.5, 134.2, 128.7 (2CH), 128.0 (2CH), 122.0, 109.7, 71.7, 42.8, 30.2, 29.4, 28.3, 15.2; HRMS (ESI) m/z calcd for $C_{19}H_{20}O_4Li$ $(M + Li)^+$ 319.1522, found 319.1565.

*2-(2-Benzoyl-1-(4-ethylphenyl)-3-oxobutyl)furan-3-carbaldehyde (**3d2**).* This compound was isolated as colorless liquid starting from 50 mg of **3c1** and obtained 76 mg in 94% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max} $/cm^{-1}$ 2922, 1725, 1680, 1448, 1358, 1267, 1125, 1023, 748; ^1H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.03 (dd, J = 8.5 and 1.3 Hz, 2H), 7.62 (tt, J = 7.4 and 1.3 Hz, 1H), 7.51−7.48 (m, 2H), 7.39 (tt, J = 10.1 and 1.7 Hz, 2H), 7.20−7.147 (m, 3H), 6.58 (d, J = 2.0 Hz, 1H), 5.76 (d, J = 11.5 Hz, 1H), 5.60 (d, J = 11.5 Hz, 1H), 2.63 (q, J = 7.6 Hz, 2H), 2.04 (s, 3H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 193.2, 184.7, 162.3, 144.1, 142.3, 135.9, 134.1, 134.0, 128.9 (2CH), 128.8 (2CH), 128.7 (2CH), 128.3 (2CH), 122.2, 66.4, 43.2, 29.0, 28.4, 18.6, 15.3; HRMS (ESI) m/z calcd for $C_{24}H_{22}O_4Na$ $(M + Na)^+$ 397.1416, found 397.1432.

*2-(2-Benzoyl-1-(furan-2-yl)-3-oxobutyl)furan-3-carbaldehyde (**3e2**).* This compound isolated as colorless liquid starting from 40 mg of **3e1** and obtained 49 mg in 71% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2922, 1725, 1680, 1594, 1417, 1269, 1012, 744; ^1H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.05−8.02 (m, 2H), 7.54−7.47 (m, 4H), 7.40 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 1.8 and 0.7 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 6.14 (dd, J = 3.0 and 1.8 Hz, 1H), 6.11 (d, J = 3.2 Hz, 1H), 5.81 (d, J = 10.3 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 192.9, 184.8, 159.6, 149.7, 142.8, 142.4, 136.1, 134.1, 128.9 (2CH), 128.8 (2CH), 122.9, 110.6, 108.9, 108.0, 63.2, 37.3, 29.0; HRMS (ESI) m/z calcd for $C_{20}H_{16}O_5Na$ $(M + Na)^+$ 359.0895, found 359.0898.

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

*2-(2-Benzoyl-1-(5-methylfuran-2-yl)-3-oxobutyl)furan-3-carbaldehyde (**3f2**).* This compound was isolated as colorless liquid starting from 40 mg of **3f1** and obtained 50 mg in 74% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2922, 1725, 1680, 1448, 1358, 1267, 1125, 1023, 748, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.06−8.04 (m, 2H), 7.54−7.47 (m, 4H), 7.39 (d, J = 1.9 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 5.97 (d, J = 11.3 Hz, 1H), 5.94 (d, J = 3.0 Hz, 1H), 5.79 (d, J = 11.3 Hz, 1H), 2.12 (s, 3H), 2.04 (d, J = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 192.7, 184.8, 159.8, 152.5, 147.7, 142.6, 136.6, 134.1, 128.9 (2CH), 128.8 (2CH), 122.8, 109.1, 108.8, 106.7, 64.3, 37.3, 28.4, 13.5; HRMS (ESI) m/z calcd for $C_{21}H_{18}O_5Na$ (M + Na)$^+$ 373.1052, found 373.1073.

*2-(2-Acetyl-3-oxo-1-(thiophen-2-yl)butyl)furan-3-carbaldehyde (**3g2**).* This compound was isolated as colorless liquid starting from 40 mg of **3g1** and obtained 42 mg in 75% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2997, 2866, 1721, 1698, 1680, 1610, 1512, 1394, 1360, 1250, 1182, 1088, 1045, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.22 (dd, J = 5.2 and 1.0 Hz, 1H), 7.01 (dd, J = 3.5 and 0.6 Hz, 1H), 6.94−6.92 (m, 1H), 6.70 (d, J = 2.0 Hz, 1H), 5.75 (d, J = 5.8 Hz, 1H), 4.91 (d, J = 5.8 Hz, 1H), 2.16 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 200.2, 184.7, 160.2, 142.6, 139.3, 127.1, 126.5, 125.7, 122.1, 109.1, 72.3, 38.1, 30.1, 29.4; HRMS (ESI) m/z calcd for $C_{15}H_{14}O_4SNa$ (M + Na)$^+$ 313.0510, found 313.0520.

*2-(2-Benzoyl-3-oxo-1-(thiophen-2-yl)butyl)furan-3-carbaldehyde (**3h2**).* This compound was isolated as colorless liquid starting from 40 mg of **3g1** and obtained 63 mg in 94% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2956, 2870, 1721, 1698, 1682, 1573, 1519, 1418, 1366, 1124, 759; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.01 (dd, J = 0.9 Hz, 3H), 7.51−7.47 (m, 2H), 7.43 (d, J = 2.0 Hz, 1H), 7.07 (d, J = 1.0 Hz, 1H), 6.95−6.93 (m, 1H), 6.79−6.77 (m, 1H), 6.74 (d, J = 2.0 Hz, 1H), 6.02 (d, J = 11.3 Hz, 1H), 5.79 (d, J = 11.3 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 192.7, 184.7, 160.8, 142.7, 139.6, 136.4, 134.1, 128.9 (2CH), 128.8 (2CH), 126.9, 126.6, 125.3, 122.3, 109.1, 66.6, 38.6, 28.8; HRMS (ESI) m/z calcd for $C_{20}H_{16}O_4SNa$ (M + Na)$^+$ 375.0667, found 375.0663.

*Ethyl 2-([1,1′-biphenyl]-4-yl(3-formylfuran-2-yl)methyl)-3-oxobutanoate (**3i2**).* This compound was isolated as colorless liquid starting from 55 mg of **3i1** and obtained 61 mg in 80% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2957, 2870, 1722, 1697, 1680, 1570, 1514, 1413, 1370, 1124, 766; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.62−7.61 (m, 1H), 7.54−7.53 (m, 3H), 7.44−7.42 (m, 4H), 7.39 (d, J = 2.0 Hz, 1H), 7.36−7.35 (m, 1H), 6.71 (d, J = 2.0 Hz, 1H), 5.38 (d, J = 5.3 Hz, 1H), 4.76 (d, J = 3.3 Hz, 1H), 4.04 (qd, J = 7.1 and 1.8 Hz, 2H), 2.29 (s, 3H), 1.06 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 184.5, 166.7, 161.9, 142.6, 140.7, 140.2, 139.8, 136.4, 128.8 (2CH), 128.7 (2CH), 127.7 (2CH), 127.5 (2CH), 127.3, 109.6, 64.1, 63.1, 61.9, 42.3, 29.0; HRMS (ESI) m/z calcd for $C_{24}H_{22}O_5Na$ (M + Na)$^+$ 413.1365, found 413.1373.

*2-(2-Benzoyl-3,5-dioxo-1,5-diphenylpentyl)furan-3-carbaldehyde (**3j2**).* This compound was isolated as colorless liquid starting from 40 mg of **3a1** and obtained 70 mg in 73% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max} /cm^{-1} 2924, 2852, 1681, 1597, 1493, 1448, 1278, 1026, 744, 695; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.03−8.00 (m, 2H), 7.80−7.78 (m, 1H), 7.63−7.62 (m, 1H), 7.61−7.60 (m, 2H), 7.54−7.53 (m, 1H), 7.52−7.51 (m, 1H), 7.50−7.49 (m, 2H), 7.48−7.47 (m, 2H), 7.34−7.32 (m, 1H), 7.21 (s, 2H), 7.17−7.16 (m, 1H), 7.13−7.11 (m, 1H), 6.38−6.36 (m, 1H), 5.65 (d, J = 11.5 Hz, 1H), 5.55 (d, J = 11.5 Hz, 1H), 5.03 (dd, J = 10.7 and 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 193.6, 193.0, 182.0, 159.0, 142.4, 137.9, 137.3, 135.9, 133.9, 133.5, 132.4, 129.3 (2CH), 128.9 (2CH), 128.8 (2CH), 128.7 (2CH), 128.1 (2CH), 127.1 (2CH), 122.2, 112.6, 62.3, 53.4, 44.4; HRMS (ESI) m/z calcd for $C_{29}H_{22}O_5Na$ (M + Na)$^+$ 473.1365, found 473.1384.

*2-(2-Benzoyl-1-(furan-2-yl)-3,5-dioxo-5-phenylpentyl)furan-3-carbaldehyde (**3k2**).* This compound isolated as colorless liquid starting from 45 mg of **3e1** and obtained 77 mg in 75% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max} /cm^{-1} 2926, 1682, 1597, 1448, 1274, 1250, 1181, 1013, 742; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.07−8.05 (m, 2H), 7.82−7.80 (m, 2H), 7.55−7.53 (m, 2H), 7.51−7.50 (m, 2H), 7.45 (s, 1H), 7.49−7.47 (m, 2H), 7.43−7.43 (m, 1H), 7.37 (dd, J = 1.7 and 0.6 Hz, 1H), 7.24 (d, J = 1.9 Hz, 1H), 6.67 (d, J = 1.9 Hz, 1H), 6.36 (d, J = 3.1 Hz, 1H), 6.30−6.28 (m, 1H), 5.79 (d, J = 11.4 Hz, 1H), 5.60 (d, J = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 190.5, 184.8, 182.1, 159.9, 156.2, 149.7, 143.0, 142.7, 142.6, 134.1, 132.9, 129.0, 128.95, 128.91 (2CH), 128.7 (2CH), 127.1 (2CH), 122.7, 110.8, 108.4, 107.8, 96.2, 60.2, 37.9; HRMS (ESI) m/z calcd for $C_{27}H_{20}O_6Na$ (M + Na)$^+$ 463.1168, found 463.1158.

*2-(1-([1,1′-Biphenyl]-4-yl)-2-benzoyl-3,5-dioxo-5-phenylpentyl)-furan-3-carbaldehyde (**3l2**).* This compound was isolated as colorless liquid starting from 40 mg of **3i1** and obtained 52 mg in 70% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max} /cm^{-1} 2925, 2853, 1734, 1681, 1597, 1487, 1448, 1123, 1077, 821, 738; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.07−8.05 (m, 2H), 7.82−7.80 (m, 2H), 7.51−7.47 (m, 7H), 7.45−7.43 (m, 6H), 7.37−7.36 (m, 1H), 7.24 (d, J = 1.9 Hz, 1H), 6.67 (d, J = 2.0 Hz, 1H), 6.35 (d, J = 3.6 Hz, 1H), 6.31 (s, 1H), 6.30−6.29 (m, 1H), 6.20 (d, J = 3.6 Hz, 1H), 5.60 (d, J = 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 190.5, 184.9, 182.1, 159.8, 149.7, 142.7, 142.3, 135.7, 135.7, 134.0, 134.6, 134.0, 133.5, 132.9, 129.0 (2CH), 128.9 (2CH), 128.8 (3CH), 128.7 (3CH), 128.1, 127.1 (2CH), 122.7, 110.8, 108.6, 108.4, 96.2, 60.2, 37.9; HRMS (ESI) m/z calcd for $C_{35}H_{26}O_5Na$ (M + Na)$^+$ 549.1678, found 549.1661.

*2-(2-Acetyl-3-oxo-1-phenylbutyl)benzofuran-3-carbaldehyde (**3m2**).* This compound was isolated as colorless liquid starting from 30 mg of **3m1** and obtained 23 mg in 60% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2947, 2868, 1720, 1697, 1681, 1487, 1451, 1124, 760; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.11−8.09 (m, 1H), 7.52−7.49 (m, 1H), 7.46−7.44 (m, 2H), 7.40 (d, J = 4.8 Hz, 1H), 7.37−7.33 (m, 3H), 5.55 (d, J = 11.8 Hz, 1H), 5.10 (q, J = 11.8 Hz, 2H), 2.23 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 200.3, 184.7, 166.0, 153.8, 136.6, 129.4 (2CH), 128.6, 128.2 (2CH), 125.6, 124.9, 124.6, 121.9, 117.1, 111.0, 71.2, 43.2, 30.3, 29.7; HRMS (ESI) m/z calcd for $C_{21}H_{18}O_4Na$ (M + Na)$^+$ 357.1103, found 357.1103.

*2-(2-Benzoyl-3-oxo-1-phenylbutyl)benzofuran-3-carbaldehyde (**3n2**).* This compound was isolated as colorless liquid starting from 45 mg of **3m1** and obtained 45 mg in 65% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2962, 2929, 1738, 1704, 1681, 1575, 1487, 1125, 765, 747; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.06−8.04 (m, 2H), 7.97−7.95 (m, 2H), 7.49−7.45 (m, 2H), 7.42−7.40 (m, 3H), 7.38−7.35 (m, 3H), 7.22−7.18 (m, 2H), 5.97 (d, J = 11.5 Hz, 1H), 5.80 (d, J = 11.3 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 193.1, 184.8, 166.7, 153.9, 137.0, 134.1, 129.0 (2CH), 128.9 (2CH), 128.8 (2CH), 128.5, 128.3 (2CH), 127.0, 125.5, 124.9, 124.6, 122.07, 117.2, 110.0, 65.3, 43.7, 29.3; HRMS (ESI) m/z calcd for $C_{26}H_{20}O_4Na$ (M + Na)$^+$ 419.1259, found 419.1250.

*2-(2-Acetyl-2-methyl-3-oxo-1-phenylbutyl)furan-3-carbaldehyde (**3o2**).* This compound was isolated as colorless liquid starting from 30 mg of **3a1** and obtained 35 mg in 80% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 2925, 1738, 1716, 1682, 1580, 1494, 1454, 1369, 1246, 1145, 1045, 758; ^{1}H NMR (400 MHz, CDCl3) δ 10.0 (s, 1H), 7.40 (d, J = 1.9 Hz, 1H), 7.29−7.27 (m, 5H), 6.7 (d, J = 1.9 Hz, 1H), 5.98 (s, 1H), 2.05 (s, 3H), 2.06 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 205.2, 204.0, 185.0, 162.2, 142.2, 136.8, 129.8 (2CH), 128.6 (2CH), 127.8, 122.9, 108.8, 71.4, 45.5, 27.2, 26.5, 16.5; HRMS (ESI) m/z calcd for $C_{18}H_{19}O_4$ (M + H)$^+$ 299.1283, found 299.1249.

*2-(2-Acetyl-1-(4-ethylphenyl)-2-methyl-3-oxobutyl)furan-3-carbaldehyde (**3p2**).* This compound was isolated as colorless liquid starting from 47 mg of **3c1** and obtained 59 mg in 90% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 3363, 1673, 1583, 1503, 1418, 1274, 1145, 1128, 1012; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.39 (d, J = 1.9 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.72 (d, J = 1.9 Hz, 1H), 5.90 (s, 1H), 2.60 (q, J = 7.6 Hz, 2H), 2.04 (s, 3H), 2.01 (s, 3H), 1.73 (s, 3H), 1.20

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

(t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 204.2, 185.1, 162.5, 143.8, 142.5, 133.9, 129.7 (2CH), 128.1 (2CH), 122.9, 108.7, 71.5, 45.2, 28.3, 27.2, 26.6, 16.5, 15.2; HRMS (ESI) m/z calcd for $C_{20}H_{22}O_4Na$ $(M + Na)^+$ 349.1416, found 349.1417.

*Ethyl 2-((4-ethylphenyl)(3-formylfuran-2-yl)methyl)-3-oxobutanoate (**3r2**) major.* This compound was isolated as colorless liquid starting from 20 mg of **3c1** and obtained 19 mg in 65% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max} /cm^{-1} 2966, 1743, 1720, 1681, 1514, 1245, 1124, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.30−7.28 (m, 2H), 7.16−7.14 (m, 2H), 6.69 (d, J = 2.0 Hz, 1H), 5.32 (d, J = 4.0 Hz, 1H), 4.70 (d, J = 3.7 Hz, 1H), 4.10−4.07 (m, 2H), 2.60 (q, J = 7.5 Hz, 2H), 2.26 (s, 3H), 1.20 (td, J = 7.6 and 2.6 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 184.7, 166.6, 162.5, 143.9, 142.5, 134.6, 128.6 (2CH), 128.3 (2CH), 122.1, 108.8, 82.6, 61.9, 42.2, 29.4, 28.4, 15.4, 13.7; HRMS (ESI) m/z calcd for $C_{20}H_{22}O_5Na$ $(M + Na)^+$ 365.1365, found 365.1356.

*Ethyl 2-((3-fluorophenyl)(3-formylfuran-2-yl)methyl)-3-oxobutanoate (**3s2**).* This compound was isolated as colorless liquid starting from 30 mg of **3s1** and obtained 31 mg in 69% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max} /cm^{-1} 2958, 2927, 1733, 1681, 1521, 1418, 1359, 1131, 1046, 888; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.35 (d, J = 2.0 Hz, 1H), 7.19−7.16 (m, 2H), 6.99−6.94 (m, 2H), 6.70 (d, J = 2.0 Hz, 1H), 5.37 (d, J = 6.3 Hz, 1H), 5.34 (d, J = 6.3 Hz, 1H), 4.00−4.10 (m, 2H), 2.28 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 184.6, 166.4, 162.8 (d, J = 245.86 Hz), 161.4, 142.7, 139.8 (d, J = 7.00 Hz), 130.6 (d, J = 8.15 Hz), 124.1, 122.5, 115.3 (d, J = 22.23 Hz), 115.0 (d, J = 20.7 Hz), 109.2, 62.9, 62.1, 42.2, 30.9, 13.9; ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −111.8; HRMS (ESI) m/z calcd for $C_{18}H_{17}O_5FNa$ $(M + Na)^+$ 355.0958, found 355.0967.

*2-(1-Phenyloct-2-yn-1-yl)furan-3-carbaldehyde (**3t2**).* This compound was isolated as a colorless liquid starting from 30 mg of **3t1** and obtained 42 mg in 85% yield: R_f = 0.4 (EtOAc/Hexane = 3/7); IR (thin film, neat) ν_{max}/cm^{-1} 3363, 2123, 1705, 1673, 1583, 1503, 1418, 1274, 1145, 1128, 1012, 896, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.94 (dd, J = 8.5 and 1.3 Hz, 2H), 7.60 (m, 3H), 7.23 (dd, J = 2.0 and 0.5 Hz, 1H), 6.62 (d, J = 2.0 Hz, 1H), 5.40 (d, J = 10.4 Hz, 1H), 5.23 (td, J = 10.4 and 2.3 Hz, 1H), 2.35 (s, 3H) 2.19 (td, J = 7.2 and 1.8 Hz, 2H), 1.35−1.29 (m, 4H), 1.11−1.06 (s, 2H), 0.77 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 192.3, 184.4, 158.6, 142.7, 135.6, 134.2, 129.1 (2CH), 128.9 (2CH), 122.8, 108.3, 86.6, 74.4, 66.3, 30.9, 29.9, 28.3, 28.0, 22.1, 18.6, 13.9; HRMS (ESI) m/z calcd for $C_{23}H_{25}O_4$ $(M + H)^+$ 365.1753, found 365.1755.

General Procedure for Step-III, Scheme 2 (Base Mediated Intramolecular Aldol Condensation of the 1,3-Dicarbonyl Adducts for the Synthesis of Furotropones). To a solution of the 1,3-dicarbonyl adduct (0.06 mmol, 1 equiv) in 1 mL DMF, sodium carbonate (5 mg, 1 equiv) was added under nitrogen atmosphere. The flask was placed in an oil bath (80 °C) and stirring was continued for 3 h. The reaction mixture was washed with water and extracted with ethyl acetate. The organic extracts were combined, dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by column chromatography on silica gel (ethyl acetate−hexanes) to afford furotropone.

Spectral Data of Furotropones. Some of the furotropones prepared during study are already known in the literature.[7,8] Complete characterization data of newly synthesized compounds is given below.

*7-Benzoyl-8-phenyl-6H-cyclohepta[b]furan-6-one (**3b**).* This compound was isolated as a pale yellow solid (22 mg, 75%): mp = 266−269 °C; R_f = 0.4 (EtOAc/Hexane= 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 2923, 1711, 1673, 1535, 1497, 1454, 1343, 1260, 1096, 734; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.70 (m, 2H), 7.62 (d, J = 11.8 Hz, 1H), 7.60 (d, J = 1.9 Hz, 1H), 7.46 (tt, J = 7.3 and 1.2 Hz, 1H), 7.34−7.30 (m, 3H), 7.30−7.20 (m, 4H), 7.14 (d, J = 11.8 Hz, 1H), 6.90 (d, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 185.6, 153.6, 145.8, 144.1, 138.4, 137.4, 136.7, 133.7, 133.0, 131.5, 129.4, 129.3, 129.3, 128.7 (2CH), 128.7, 128.6, 128.3 (2CH), 127.8, 113.0; HRMS (ESI) m/z calcd for $C_{22}H_{15}O_3$ $(M + H)^+$ 327.1000, found 327.0990.

*7-Acetyl-8-(4-ethylphenyl)-6H-cyclohepta[b]furan-6-one (**3c**).* This compound was isolated as a pale yellow solid (28 mg, 74%): mp = 250−253 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 2963, 2925, 2854, 1711, 1621, 1578, 1538, 1496, 1454, 1340, 1136, 1091, 816; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 1.8 Hz, 1H), 7.55 (d, J = 11.8 Hz, 1H), 7.28 (m, 4H), 7.10 (d, J = 11.8 Hz, 1H), 6.85 (d, J = 1.8 Hz, 1H), 2.73 (q, J = 7.6 Hz, 2H), 2.10 (s, 3H), 1.30 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 185.1, 153.7, 146.3, 145.7, 145.2, 137.5, 136.8, 131.6, 131.0, 129.2 (2CH), 128.3, 127.8 (2CH), 113.0, 31.0, 28.6, 15.1; HRMS (ESI) m/z calcd for $C_{19}H_{17}O_3$ $(M + H)^+$ 293.1178, found 293.1176.

*7-Benzoyl-8-(4-ethylphenyl)-6H-cyclohepta[b]furan-6-one (**3d**).* This compound was isolated as a pale yellow solid (23 mg, 62%): mp = 260−262 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max} /cm^{-1} 2960, 2926, 1671, 1636, 1536, 1494, 813; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 6.4 and 1.3 Hz, 2H), 7.63 (d, J = 2.0 Hz, 1H), 7.61 (d, J = 11.8, 1H), 7.46 (tt, J = 8.6, 2.4, and 1.2 Hz, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.14 (d, J = 11.8 Hz, 2H), 7.08 (brs, 3H), 6.90 (d, J = 2.0 Hz, 1H), 2.60 (q, J = 7.5 Hz, 2H), 1.19 (t, J = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 185.6, 153.7, 145.7, 145.7, 144.7, 144.2, 138.7, 137.4, 136.8, 132.9, 131.5, 130.9, 128.7 (2CH), 128.6, 128.3 (2CH), 127.4, 127.3, 127.3, 113.0, 28.5, 15.0; HRMS (ESI) m/z calcd for $C_{24}H_{19}O_3$ $(M + H)^+$ 355.1334, found 355.1337.

*7-Benzoyl-8-(furan-2-yl)-6H-cyclohepta[b]furan-6-one (**3e**).* This compound was isolated as a pale yellow solid (34 mg, 91%): mp = 252−255 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 3145, 2924, 2853, 1675, 1574, 1544, 1498, 1449, 1336, 1255, 831, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.87 (m, 2H), 7.75 (d, J = 1.9 Hz, 1H), 7.55−7.49 (m, 2H), 7.42−7.38 (m, 2H), 7.32 (dd, J = 1.7 and 0.7, 1H), 7.05 (d, J = 11.7 Hz, 1H), 6.93 (dd, J = 3.4 and 0.6 Hz, 1H), 6.90 (d, J = 1.9 Hz, 1H). 6.42 (q, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 185.5, 151.8, 145.4, 145.2, 144.2, 142.5, 137.2, 136.7, 132.9, 131.1, 128.7, 128.6 (2CH), 128.4 (2CH), 127.4, 116.8, 113.1, 111.8; HRMS (ESI) m/z calcd for $C_{20}H_{13}O_4$ $(M + H)^+$ 317.0814, found 317.0823.

*7-Benzoyl-8-(5-methylfuran-2-yl)-6H-cyclohepta[b]furan-6-one (**3f**).* This compound was isolated as a pale yellow solid (30 mg, 74%): mp = 255−258 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 2923, 2852, 1678, 1623, 1535, 1497, 1448, 1361, 1249, 1096, 833; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.92 (m, 2H), 7.74 (d, J = 1.9 Hz, 1H), 7.53−7.49 (m, 2H), 7.44−7.40 (m, 2H), 7.04−7.00 (m, 2H), 6.88 (d, J = 1.9 Hz, 1H), 6.06−6.04 (m, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 185.8, 155.0, 151.5, 144.9, 143.7, 141.1, 137.3, 137.2, 132.6, 130.8, 128.5 (3CH), 128.3 (2CH), 127.2, 119.0, 113.1, 108.6, 13.1; HRMS (ESI) m/z calcd for $C_{21}H_{15}O_4$ $(M + H)^+$ 331.0970, found 331.0953.

*7-Acetyl-8-(thiophen-2-yl)-6H-cyclohepta[b]furan-6-one (**3g**).* This compound was isolated as a pale yellow solid (13 mg, 70%): mp = 250−253 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 3132, 2922, 1708, 1616, 1573, 1537, 1496, 1452, 1325, 1165, 1089, 830, 794; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 1.9 Hz, 1H), 7.57 (dd, J = 4.9 and 1.4 Hz, 1H), 7.57 (d, J = 11.8 Hz, 1H), 7.14 (m, 2H), 7.08 (d, J = 11.8 Hz, 1H), 6.87 (d, J = 1.9 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 184.6, 147.2, 145.6, 137.4, 137.1, 132.9, 131.6, 131.3, 130.1, 128.5, 128.1, 127.0, 113.1, 30.6; HRMS (ESI) m/z calcd for $C_{15}H_{11}O_3S$ $(M + H)^+$ 271.0429, found 271.0440.

*7-Benzoyl-8-(thiophen-2-yl)-6H-cyclohepta[b]furan-6-one (**3h**).* This compound was isolated as a pale yellow solid (18 mg, 95%): mp = 260−263 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 3112, 2954, 2853, 1673, 1537, 1494, 1452, 1356, 1328, 1258, 1092, 823; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.76 (m, 2H), 7.68 (d, J = 1.9 Hz, 1H), 7.59 (d, J = 11.8 Hz, 1H), 7.48 (tt, J = 7.4 and 1.7 Hz, 1H), 7.35 (m, 3H), 7.11 (d, J = 11.8 Hz, 1H), 7.01 (dd, J = 3.6 and 1.2 Hz, 1H), 6.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 185.1, 153.2, 145.7, 145.2, 137.3, 136.3, 133.2, 133.1, 132.1, 131.5, 131.2, 128.8 (2CH), 128.5, 128.4 (2CH), 128.41, 126.5, 113.2. HRMS (ESI) m/z calcd for $C_{20}H_{13}O_3S$ $(M + H)^+$ 333.0585, found 333.0598.

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

*Ethyl 8-([1,1′-biphenyl]-4-yl)-6-oxo-6H-cyclohepta[b]furan-7-carboxylate (**3i**).* This compound was isolated as a pale yellow solid (21 mg, 75%): mp = 273−276 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 3031, 2925, 2854, 1730, 1620, 1590, 1539, 1496, 1043, 758; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (tt, J = 5.3 and 1.9 Hz, 1H), 7.69 (t, J = 1.9 Hz, 1H), 7.67−7.66 (m, 1H), 7.65−7.64 (m, 2H), 7.55 (d, J = 11.9 Hz, 1H), 7.51−7.48 (m, 4H), 7.43−7.39 (m, 1H), 7.15 (d, J = 11.9 Hz, 1H), 6.87 (d, J = 1.8 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 166.6, 146.0, 141.8, 140.2, 137.4, 133.4, 131.3, 129.6, 129.4 (2CH), 128.9 (2CH), 128.8 (2CH), 127.7, 127.2, 127.17 (2CH), 127.11, 126.7, 113.1, 61.3, 13.6; HRMS (ESI) m/z calcd for $C_{24}H_{19}O_4$ $(M + H)^+$ 371.1283, found 371.1287.

*6-Oxo-8-phenyl-6H-cyclohepta[b]furan-5,7-diyl)bis-(phenylmethanone) (**3j**).* This compound was isolated as a pale yellow solid (15 mg, 76%): mp = 290−293 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 3060, 2924, 2853, 1674, 1597, 1540, 1448, 1286, 1208, 872; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.93 (m, 1H), 7.92 (t, J = 4.0 and 2.0 Hz, 2H), 7.71 (m, 1H), 7.69 (t, J = 4.0 Hz, 2H), 7.54 (tt, J = 8.0 and 4.0 Hz, 1H), 7.46−7.40 (m, 3H), 7.32−7.26 (m, 7H), 6.98 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 194.7, 183.9, 154.0, 146.6, 146.2, 145.3, 138.4, 136.7, 135.8, 133.4, 133.2, 133.2, 131.7, 129.3, 129.2 (2CH), 128.9 (2CH), 128.8 (2CH), 128.5 (2CH), 128.3 (2CH), 128.0 (2CH), 127.7, 113.7; HRMS (ESI) m/z calcd for $C_{29}H_{19}O_4$ $(M + H)^+$ 431.1283, found 431.1267.

*8-(Furan-2-yl)-6-oxo-6H-cyclohepta[b]furan-5,7-diyl)bis-(phenylmethanone) (**3k**).* This compound was isolated as a pale yellow solid (23 mg, 70%): mp = 285−288 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 2923, 2853, 1690, 1674, 1542, 1498, 1261, 835; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.86 (m, 4H), 7.83 (d, J = 2.0 Hz, 1H), 7.50 (tt, J = 8.0 and 1.2 Hz, 2H), 7.42−7.37 (m, 4H), 7.35 (dd, J = 2.0 and 0.8 Hz, 1H), 7.07 (dd, J = 3.6 and 0.6 Hz, 2H), 6.99 (d, J = 2.0 Hz, 1H), 6.47 (dd, J = 2.0 and 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 184.0, 180.5, 152.1, 146.3, 145.5, 144.6, 143.1, 136.9, 135.7, 133.3, 133.0, 131.2, 129.2 (2CH), 128.7 (2CH), 128.56, 128.54 (2CH), 128.50, 128.4 (2CH), 127.6, 117.5, 113.8, 112.1; HRMS (ESI) m/z calcd for $C_{27}H_{17}O_5$ $(M + H)^+$ 421.1076, found 421.1072.

*8-([1,1′-Biphenyl]-4-yl)-6-oxo-6H-cyclohepta[b]furan-5,7-diyl)bis-(phenylmethanone) (**3l**).* This compound was isolated as a pale yellow solid (32 mg, 84%): mp = 297−300 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 3059, 2925, 1673, 1597, 1579, 1538, 1494, 1337, 1286, 1006; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 1.0 Hz, 1H), 7.93−7.92 (m, 2H), 7.73 (d, J = 1.0 Hz, 1H), 7.72−7.71 (m, 2H), 7.57−7.55 (m, 1H), 7.54 (s, 2H), 7.52 (t, J = 1.2 Hz, 1H), 7.50 (s, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.44−7.43 (m, 2H), 7.42−7.41 (m, 2H), 7.38 (t, J = 1.2 Hz, 1H), 7.36 (t, J = 2.2 Hz, 1H), 7.35 (t, J = 1.2 Hz, 1H), 7.32 (s, 1H), 7.30 (s, 1H), 6.99 (d, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 194.8, 183.9, 154.0, 146.7, 146.2, 145.4, 141.6, 140.0, 138.2, 136.8, 135.8, 133.4, 133.2, 132.1, 131.7, 129.8, 129.8, 129.2 (2CH), 128.9 (2CH), 128.8 (2CH), 128.6 (2CH), 128.3 (2CH), 127.78, 127.74, 127.1 (2CH), 126.6 (2CH), 113.7; HRMS (ESI) m/z calcd for $C_{35}H_{23}O_4$ $(M + H)^+$ 507.1596, found 507.1608.

*7-Acetyl-6-phenyl-8H-cyclohepta[b]benzofuran-8-one (**3m**).* This compound was isolated as a pale yellow solid (12 mg, 61%): mp = 201−202 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 2919, 2852, 1716, 1668, 1635, 1480, 1385, 1284, 819; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 11.9 Hz, 1H), 7.96−7.94 (m, 1H), 7.53−7.50 (m, 3H), 7.49−7.47 (m, 2H), 7.47−7.39 (m, 2H), 7.28 (d, J = 7.4 Hz, 1H), 6.70 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 185.0, 154.5, 149.2, 137.6, 133.8, 129.4 (2CH), 129.3, 129.1, 128.5, 128.4, 128.4 (2CH), 125.8, 124.5, 123.5, 120.1, 116.1, 112.3, 30.9; HRMS (ESI) m/z calcd for $C_{21}H_{15}O_3$ $(M + H)^+$ 315.1021, found 315.1026.

*7-Benzoyl-6-phenyl-8H-cyclohepta[b]benzofuran-8-one (**3n**).* This compound was isolated as a pale yellow solid (15 mg, 65%): mp = 207−210 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 2922, 2852, 1709, 1668, 1635, 1557, 1480, 1446, 1281, 883, 819; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 11.8 Hz, 1H), 7.99−7.97 (m, 1H), 7.74−7.71 (m, 2H), 7.54−7.51 (m, 1H), 7.50−7.45 (m, 4H), 7.35 (t, J = 1.5 Hz, 1H), 7.33−7.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 185.4, 155.1, 154.5, 147.6, 147.3, 146.3, 139.0, 137.5, 136.5, 133.7, 133.1, 129.1, 128.7 (2CH), 128.6, 128.5, 128.4 (2CH), 127.9, 127.9, 125.9, 124.5, 123.7, 120.1, 112.3; HRMS (ESI) m/z calcd for $C_{26}H_{17}O_3$ $(M + H)^+$ 377.1178, found 377.1179.

*7-Methyl-8-phenyl-6H-cyclohepta[b]furan-6-one (**3o**).* This compound was isolated as a pale yellow solid (14 mg, 60%): mp = 261−263 °C; R_f = 0.4 (EtOAc/Hexane = 1/1); IR (thin film, neat) ν_{max}/cm^{-1} 2928, 1710, 1620, 1575, 1536, 1452, 1356, 1352, 1326, 830, 716; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.47 (m, 5H), 7.26−7.24 (m, 2H), 7.10 (d, J = 11.9 Hz, 1H), 6.79 (d, J = 1.9 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 154.2, 144.3, 142.3, 139.1, 138.3, 134.5, 129.8, 128.5 (2CH), 128.2 (2CH), 127.9, 126.6, 112.0, 19.5; HRMS (ESI) m/z calcd for $C_{16}H_{13}O_2$ $(M + H)^+$ 237.0900, found 237.0909.

*7-Benzoyl-8-(4-ethylphenyl)-6H-cyclohepta[b]furan-6-one (**3p**).* This compound was isolated as a pale yellow solid (14 mg, 62%): mp = 268−271 °C; R_f = 0.4 (EtOAc/Hexane = 2/3); IR (thin film, neat) ν_{max}/cm^{-1} 2900, 1715, 1690, 1620, 1470, 1430, 1356, 1351, 1315, 1270, 830; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 1.9 Hz, 1H), 7.47 (d, J = 11.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 11.8 Hz, 1H), 6.78 (d, J = 1.9 Hz, 1H), 2.78 (q, J = 7.6 Hz, 2H), 2.04 (s, 3H), 1.34 (t, J = 7.6 Hz, 3H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 144.3, 143.8, 142.9, 139.3, 135.5, 134.5, 130.2, 129.8, 128.1 (2CH), 128.0 (2CH), 126.5, 112.0, 28.6, 19.6, 15.3; HRMS (ESI) m/z calcd for $C_{18}H_{17}O_2$ $(M + H)^+$ 265.1229, found 265.1227.

*8-(4-Ethylphenyl)-6H-cyclohepta[b]furan-6-one (**3r**).* This compound was isolated as a pale yellow liquid (12 mg, 60%): R_f = 0.4 (EtOAc/Hexane = 1/1); IR (thin film, neat) ν_{max}/cm^{-1} 2963, 2926, 2854, 1710, 1620, 1590, 1540, 1496, 1460, 1350, 1090, 847; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 2.0 Hz, 1H), 7.52−7.48 (m, 3H), 7.36−7.33 (m, 2H), 7.06−7.02 (m, 2H), 6.85 (d, J = 1.8 Hz, 1H), 2.76 (q, J = 7.7 Hz, 2H), 1.33 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 153.4, 145.5, 144.6, 140.7, 136.3, 136.0, 134.8, 131.4, 129.1 (2CH), 128.4, 127.9 (2CH), 113.0, 28.6, 15.3; HRMS (ESI) m/z calcd for $C_{17}H_{15}O_2$ $(M + H)^+$ 251.1072, found 251.1071.

*8-(3-Fluorophenyl)-6H-cyclohepta[b]furan-6-one (**3s**).* This compound was isolated as a pale yellow liquid (12 mg, 55%): R_f = 0.4 (EtOAc/Hexane = 1/1); IR (thin film, neat) ν_{max}/cm^{-1} 2924, 2853, 1730, 1621, 1545, 1498, 1455, 1343, 1259, 1092, 1041, 867, 789; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 11.5 Hz, 1H), 7.49−7.45 (m, 1H), 7.34−7.29 (m, 2H), 7.21 (dt, J = 8.4 and 1.9, 1H), 7.04 (dd, J = 11.7 and 2.3 Hz, 2H), 6.87 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7, 156.2 (d, J = 226.96 Hz), 144.8, 139.4, 136.5, 136.1, 131.5, 130.9, 130.0 (d, J = 8.16 Hz), 128.6, 126.3, 124.8, 116.4 (d, J = 22.77 Hz), 116.1 (d, J = 20.71 Hz), 113.1; ^{19}F NMR (376.4 MHz, $CDCl_3$) δ −112.6; HRMS (ESI) m/z calcd for $C_{15}H_{10}FO_2$ $(M + H)^+$ 241.0665, found 241.0667.

*4′-Acetyl-2′-hexyl-5′-methyl-[2,3′-bifuran]-3-carbaldehyde (**4**).* This compound was isolated as a colorless liquid (27 mg, 78%): R_f = 0.3 (EtOAc/Hexane = 1/5); IR (thin film, neat) ν_{max}/cm^{-1} 3059, 2925, 1673, 1597, 1579, 1538, 1494, 1337, 1286, 1006, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.66−7.64 (m, 2H), 7.46 (tt, J = 7.4 and 1.2 Hz, 1H), 7.34−7.30 (m, 2H), 7.23 (dd, J = 2.0 and 0.5 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 2.67 (t, J = 7.7 Hz, 2H), 2.42 (s, 3H), 1.71−1.66 (m, 2H), 1.32−1.26 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 184.9, 156.6, 155.8, 155.0, 143.2, 138.2, 132.5, 128.8 (2CH), 128.2 (2CH), 124.1, 121.3, 109.8, 108.0, 31.3, 28.7, 27.9, 26.7, 22.4, 14.0, 13.8; HRMS (ESI) m/z calcd for $C_{23}H_{25}O_4$ $(M + H)^+$ 365.1753, found 365.1766.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^{1}H and ^{13}C NMR of all new compounds, some physicochemical data and figures, tables, and CIF files giving

DOI: 10.1021/acs.joc.5b00226
J. Org. Chem. 2015, 80, 4893−4903

single crystal X-ray diffraction analysis data of compound **3j**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00226.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Department of Science and Technology (DST), New Delhi for financial support through Fast Track Scheme (SR/FT/CS-156/2011) and Indian Institute of Science Education and Research (IISER) Mohali for funding. We thank NMR and X-ray facilities of IISER-Mohali. We thank DCS colleagues for their help in recording and analyzing UV−vis and fluorescence data. R.S. thanks IISER-Mohali for a research fellowship.

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J. Org. Chem. 2015, 80, 4893−4903