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# $Yb(OTf)_3$-Mediated Access to Furans from β-Ketothioamides via Eschenmoser Sulfide Contraction Reaction

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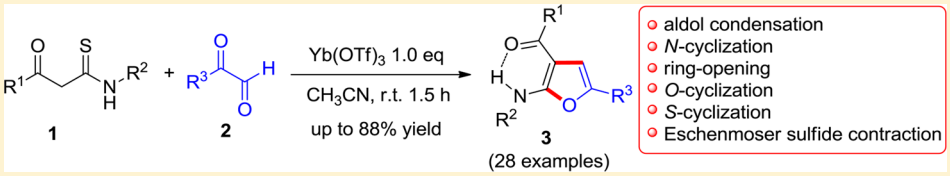
Supporting Information




**ABSTRACT:** A mild and straightforward synthetic protocol for construction of a furan skeleton promoted by $Yb(OTf)_3$ from β-ketothioamides and arylglyoxals has been developed at room temperature. Importantly, this protocol involves a tandem sequence that includes aldol condensation, N-cyclization, ring opening, O-cyclization, S-cyclization, and Eschenmoser sulfide contraction.

## INTRODUCTION

Furans, one of the most important classes of fundamental five-membered heterocyclic compounds, can be found as key structural units in natural products and pharmaceuticals.[1] They are also employed as valuable building blocks in organic synthesis.[2] As a consequence, much attention has been paid to the synthesis of furan derivatives.[3] In addition to traditional methods such as the Paal−Knorr[4] and Feist−Bénary[5] syntheses, numerous heteroannulations catalyzed by transition metals, such as copper,[6] zinc,[7] palladium,[8] gold,[9] cobalt,[10] bismuth,[11] and iron,[12] have been developed with remarkable improvements in terms of the efficiency and wide scope of application.

β-Ketothioamides (KTAs) have emerged as powerful synthons in the construction of heterocycles.[3i,13] Recently, the groups of Singh[14] and Deng[15] reported two methods for the synthesis of pyrroles and thiophenes, respectively, using the KTAs as synthons. Our group developed a one-pot three-component reaction to synthesize novel thiophenes by using KTAs, arylglyoxals, and 5,5-dimethyl-1,3-cyclohexanedione in $CF_3CH_2OH$.[16] These protocols, however, construct only pyrrole or thiophene skeletons, while the reaction of KTAs with arylglyoxals for the synthesis of furans has not been explored.

The Eschenmoser reaction, which couples an α-halocarbonyl compound with a thioamide, provides the unambiguous formation of a special enaminone.[17] Although the episulfide contraction was first studied by Knott (Scheme 1),[18] it has emerged as an important carbon−carbon bond-forming process ever since the Eschenmoser−Woodward collaboration about vitamin $B_{12}$.[19]

As a continuation of our ongoing research interest in the synthesis of heterocycles by utilizing KTAs as synthons,[20] herein we report the first example of a concise $Yb(OTf)_3$-promoted tandem reaction of KTAs with arylglyoxals to construct a furan skeleton via the Eschenmoser sulfide contraction reaction (Scheme 1), which is a new reaction mode of KTAs.[21]

## RESULTS AND DISCUSSION

During the investigation of the reaction of KTA (**1a**) with phenylglyoxal (**2a**) catalyzed by Lewis acid $Yb(OTf)_3$, a new product **3aa** was observed, whereas compound **4**[14] was the predominant product when 0.1 equiv of $InCl_3$ was used. This inspired our interest in further detailed exploration of this new transformation. We first screened the optimal reaction conditions to afford **3aa** efficiently. The results are summarized in Table 1.

Initially, when the mixture of **1a** and **2a** was stirred in $CH_3CN$ without any additives at room temperature for 1 h, only **4**[22] was obtained in 47% yield, but no product **3aa** was observed even after 24 h (Table 1, entry 1). Next, 66% of **4** and a trace of **3aa** were afforded with 0.1 equiv of $InCl_3$ as a catalyst after 3 h (entry 2). When a stoichiometric amount of $InCl_3$ was added, compound **3aa** was exclusively provided in 38% yield within 1.5 h (entry 3). Successively, a stoichiometric amount of $In(OTf)_3$ gave **3aa** in a higher yield of 61% (entry 4). However, when the amount of $In(OTf)_3$ was reduced to 0.1 equiv, only a trace of **3aa** and an 84% yield of **4** were obtained after 3 h (entry 5). Encouraged by this interesting observation, we tested a stoichiometric amount of $Yb(OTf)_3$. To our delight, it gave **3aa** in 83% yield (entry 6). However, neither a smaller (entry 7) nor a larger (entry 8) dose of $Yb(OTf)_3$ could improve the yield of **3aa**. Other Lewis acids (entries 9−14) gave inferior results compared to those seen with $Yb(OTf)_3$. Besides, a Brønsted acid such as HCl afforded **3aa** in 42% yield (entry 15). Confusing, however, was the fact that both catalytic and

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**Scheme 1**

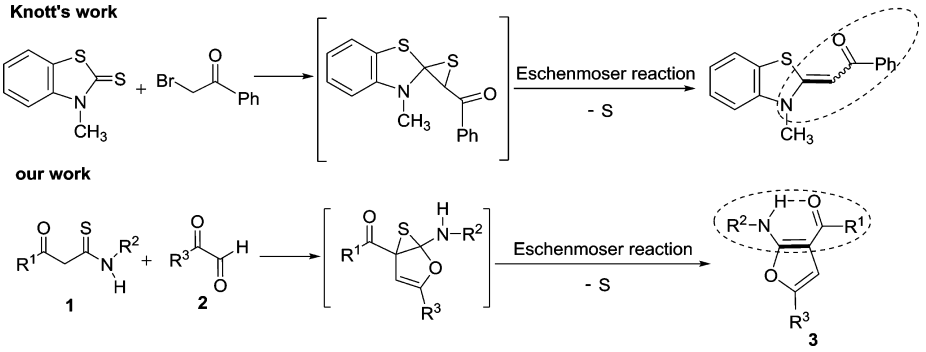


**Table 1. Screening of Optimal Reaction Conditions for 3aa**[a]


| entry | additive (equiv) | solvent (mL) | $T$ (°C) | time (h) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | – | $CH_3CN$ | rt | 1.0 | **4**, 47 |
| 2 | $InCl_3$ (0.1) | $CH_3CN$ | rt | 3.0 | **3aa**, trace; **4**, 66 |
| 3 | $InCl_3$ (1.0) | $CH_3CN$ | rt | 1.5 | 38 |
| 4 | $In(OTf)_3$ (1.0) | $CH_3CN$ | rt | 1.5 | 61 |
| 5 | $In(OTf)_3$ (0.1) | $CH_3CN$ | rt | 3.0 | **3aa**, trace; **4**, 84 |
| 6 | $Yb(OTf)_3$ (1.0) | $CH_3CN$ | rt | 1.5 | 83 |
| 7 | $Yb(OTf)_3$ (0.5) | $CH_3CN$ | rt | 2.0 | 76 |
| 8 | $Yb(OTf)_3$ (1.2) | $CH_3CN$ | rt | 1.5 | 77 |
| 9 | $Sc(OTf)_3$ (1.0) | $CH_3CN$ | rt | 24 | trace |
| 10 | $Cu(OTf)_2$ (1.0) | $CH_3CN$ | rt | 1.5 | 12 |
| 11 | AgOTf (1.0) | $CH_3CN$ | rt | 1.5 | 43 |
| 12 | $CuCl_2{\cdot}2H_2O$ (1.0) | $CH_3CN$ | rt | 1.5 | 38 |
| 13 | $FeCl_3{\cdot}6H_2O$ (1.0) | $CH_3CN$ | rt | 1.5 | 45 |
| 14 | $BF_3{\cdot}Et_2O$ (1.0) | $CH_3CN$ | rt | 24 | trace |
| 15 | HCl (1.0) | $CH_3CN$ | rt | 1.5 | 42 |
| 16 | HOTf (0.1) | $CH_3CN$ | rt | 3.0 | 0 |
| 17 | HOTf (1.0) | $CH_3CN$ | rt | 3.0 | 0 |
| 18 | $Yb(OTf)_3$ (1.0) | dioxane | rt | 1.5 | 56 |
| 19 | $Yb(OTf)_3$ (1.0) | $CH_3NO_2$ | rt | 1.5 | 61 |
| 20 | $Yb(OTf)_3$ (1.0) | DMSO | rt | 1.5 | 37 |
| 21 | $Yb(OTf)_3$ (1.0) | EtOH | rt | 24 | null |
| 22 | $Yb(OTf)_3$ (1.0) | $CH_3CN$ | 40 | 1.0 | 80 |
| 23 | $Yb(OTf)_3$ (1.0) | $CH_3CN$ | 60 | 1.0 | 79 |
| 24 | $Yb(OTf)_3$ (1.0) | $CH_3CN$ | rt | 1.5 | 60[c] |
| 25 | **$Yb(OTf)_3$ (1.0)** | **$CH_3CN$** | **rt** | **1.5** | **88**[d] |

[a]Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2a** (0.2 mmol), and solvent (2 mL). [b]Isolated yields of **3aa** unless otherwise noted. [c]**1a**:**2a** ratio of 1.2:1. [d]**1a**:**2a** ratio of 1:1.2.

stoichiometric HOTf failed to produce **3aa** (entries 16 and 17, respectively). Other aprotic solvents such as 1,4-dioxane, $CH_3NO_2$, and DMSO resulted in yields of **3aa** lower than that with $CH_3CN$ (entries 18–20, respectively). Interestingly, in protic solvent EtOH, neither **3aa** nor **4** was observed (entry 21). The effect of temperature was evaluated, as well, and the results showed a higher temperature could accelerate the reaction but was of no help in improving the yield of **3aa** (entries 22 and 23). Finally, the ratio of **1a** and **2a** was tested, and the results indicated the excess of **2a** can cause a slight improvement in the yield of **3aa** (entries 24 and 25). Consequently, the optimal reaction conditions were established by employing **1a** and **2a** in a ratio of 1:1.2 with a stoichiometric amount of $Yb(OTf)_3$ in $CH_3CN$ at room temperature for 1.5 h.

It is worth mentioning that a conversion from **4** to **3aa** was monitored by TLC, indicating that **4** might be an intermediate in the reaction.

With the optimal conditions in hand, we next turned our attention to explore the scope of this reaction by testing various KTAs **1** and arylglyoxals **2**, and the results are summarized in Table 2.

As one can see from Table 2, when $R^1$ of KTAs **1** was an aromatic group or a heterocyclic ring and $R^2$ was phenyl, the reactions proceeded efficiently to provide the desired products



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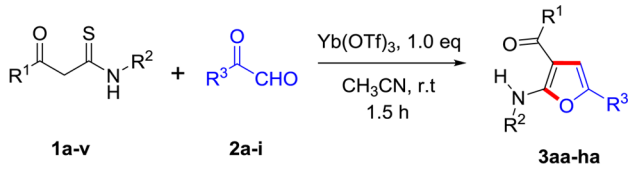
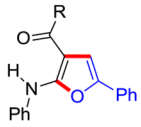
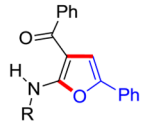
**Table 2. Scopes of KTAs and Arylglyoxals for the Synthesis of Furans**[a,b]



**3aa** R = $C_6H_5$, 86%
**3ba** R = 4-$FC_6H_4$, 55%
**3ca** R = 4-$ClC_6H_4$, 61%
**3da** R = 4-$BrC_6H_4$, 67%
**3ea** R = 3-$ClC_6H_4$, 61%
**3fa** R = 2-$FC_6H_4$, 52%
**3ga** R = 2-$ClC_6H_4$, 43%
**3ha** R = 2-$BrC_6H_4$, 42%
**3ia** R = 4-$MeC_6H_4$, 58%
**3ja** R = 4-$OMeC_6H_4$, 62%
**3ka** R = 2-thienyl, 42%
**3la** R = 2-furyl, 34%



**3ma** R = 4-$FC_6H_4$, 51%
**3na** R = 4-$ClC_6H_4$, 76%
**3oa** R = 4-$BrC_6H_4$, 68%
**3pa** R = 3-$ClC_6H_4$, 47%
**3qa** R = 4-$MeC_6H_4$, 65%
**3ra** R = 4-$OMeC_6H_4$, 62%
**3sa** R = $CH_2C_6H_5$, 46%
**3ta** R = $CH_2CO_2Et$, 53%
**3ua** R = cyclohexyl, trace
**3va** R = H, 0%

**3ab** R = 4-$FC_6H_4$, 51%
**3ac** R = 4-$ClC_6H_4$, 63%
**3ad** R = 4-$BrC_6H_4$, 57%
**3ae** R = 4-$OMeC_6H_4$, 53%
**3af** R = 3-$ClC_6H_4$, 44%
**3ag** R = 3-$OMeC_6H_4$, 43%
**3ah** R = 2-thienyl, 41%

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), $Yb(OTf)_3$ (0.5 mmol), and $CH_3CN$ (5.0 mL). [b]Isolated yields.

**3aa**–**la** in 41–88% yields. When $R^1$ was phenyl and $R^2$ of the KTAs **1** was an aromatic group, benzyl or $CH_2CO_2Et$, these substrates showed similar reactivity to provide the desired products **3ma**–**ta** in 51–81% yields. Unfortunately, however, when $R^2$ was an alkyl group such as cyclohexyl, only a trace of **3ua** could be observed. Additionally, when an N-unsubstituted KTA such as 3-oxo-3-phenylpropanethioamide (**1v**) was used, no reaction occurred. Also, various arylglyoxals could be tolerated well, and the reactions proceeded smoothly to afford the corresponding furans **3aa**–**ah** in moderate to good yields. However, when an alkylglyoxal such as methylglyoxal was employed, no desired product was obtained.

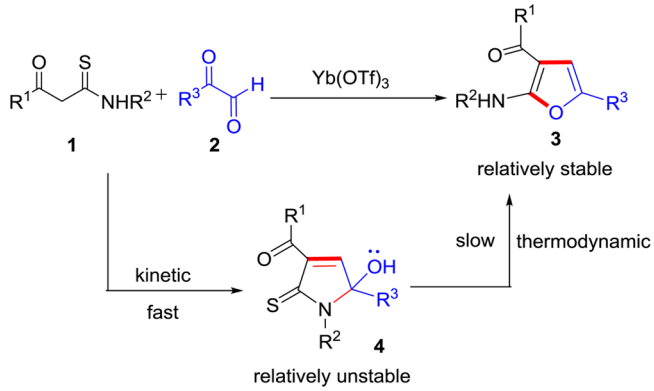
It is noteworthy that neither electron-withdrawing nor electron-donating substituents on benzene rings of KTAs **1** and arylglyoxals **2** showed obvious regulation of reactivity for the formation of **3**.

The structures of all newly synthesized furans were identified by their $^1H$ NMR, $^{13}C$ NMR, and HRMS spectra and unequivocally confirmed by X-ray diffraction analysis of the monocrystal of **3aa** (Figure S1 of the Supporting Information).

To improve our understanding of this reaction, LC–MS was utilized to monitor the reaction of **1a** (0.2 mmol) with **2a** (0.2 mmol) in the presence of $Yb(OTf)_3$ (0.04 mmol) (Figures S2–S4 of the Supporting Information). The analytical results indicated that the aldol condensation between **1a** and **2a** occurred instantly to afford intermediate [**A**] (Scheme 4), and then unsaturated enone [**B**] was afforded with loss of $H_2O$, which subsequently underwent an intramolecular cyclization to form **4**. It can be found that the amount of **4** increased and target **3aa** appeared when the reaction continued for 15 min. When the reaction time further was prolonged, the amount of **4** gradually decreased and that of **3aa** steadily increased. Two hours later, **4** completely converted to **3aa**. These results clearly confirmed that **4** was the key intermediate in the transformation, which was immediately formed belonging to kinetic favored product, but **4** was relatively unstable in the presence of $Yb(OTf)_3$ and finally converted to the thermodynamically favored product **3aa** (Scheme 2).[23]

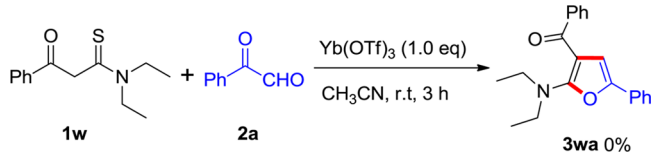
To confirm this conversion, two control experiments were conducted. First, compound **4**, prepared according to Singh's report,[14] was directly stirred at room temperature for 1.5 h in the presence of $Yb(OTf)_3$ (1.0 equiv) and successfully converted to **3aa** in 92% yield. Additionally, we tracked the

**Scheme 2**




reaction system starting from **4** in the presence of $Yb(OTf)_3$ by LC–MS expecting to trap other possible intermediates. To our delight, another episulfide intermediate [**D**][17f] (Scheme 4) was detected (Figures S5–S7 of the Supporting Information). Second, a KTA with tertiary amine (**1w**) was employed in the reaction for 3 h, and no target **3wa** was obtained (Scheme 3).

**Scheme 3. Control Experiment**




On the basis of the experimental results described above, a possible reaction mechanism is proposed (Scheme 4). First, an aldol condensation of KTAs **1** with arylglyoxals **2** gives rise to [**A**], followed by [**B**], which undergoes an intramolecular N-cyclization to generate **4**. It is worth noting **4** is in equilibrium with [**B**]. Successively, O-cyclization of [**B**] takes place to afford the zwitterion [**C**] through $Yb(OTf)_3$ activating the thiocarbonyl group, and sequentially, episulfide [**D**] is formed via the Michael addition of S anion in [**C**]. The desired product **3** is obtained eventually with the contraction of the elemental sulfur (via the modified Eschenmoser sulfide contraction reaction[24]), which was confirmed by scanning electron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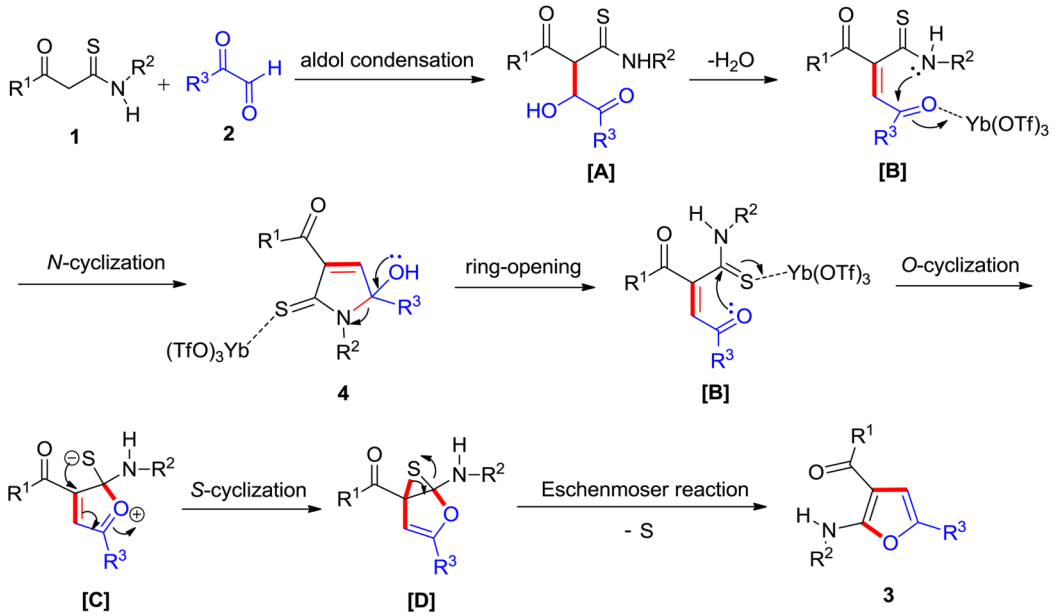
**Scheme 4. Proposed Mechanism for the Formation of 3**




microscope–energy dispersive X-ray spectrometer analysis (Figure S8 of the Supporting Information).

## CONCLUSION

In summary, we have developed a $Yb(OTf)_3$-promoted tandem one-pot synthesis of highly substituted furan derivatives from KTAs and arylglyoxals at room temperature. Control experiments supported the proposed mechanism, in which an aldol condensation/N-cyclization/ring opening/O-cyclization/S-cyclization/Eschenmoser sulfide contraction reaction sequence was involved. Further investigations to expand the scope of KTAs as versatile building blocks by the combined use of the domino reaction are in progress and will be reported elsewhere in due course.

## EXPERIMENTAL SECTION

**General Experimental Methods.** All reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. Melting points were recorded on a microscopic melting apparatus and are uncorrected. $^1H$ NMR and $^{13}C$ NMR spectra were recorded at 500 MHz and 125 MHz in $CDCl_3$, respectively. Chemical shifts are reported in $\delta$ relative to TMS. IR spectra were recorded on a FT-IR spectrometer, and only major peaks are reported in inverse centimeters. HRMS spectra were recorded on a spectrometer with an ESI source. LC–MS spectra were rercorded on a spectrometer with an ESI source. X-ray single-crystal diffraction was performed on a CCD area detector. The analysis of elemental sulfur was performed on a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS).

**General Procedure for the Synthesis of Compounds 3 (3aa for example).** To a 25 mL flask were added **1a** (0.1275 g, 0.5 mmol), **2a** (0.0804 g, 0.6 mmol), $Yb(OTf)_3$ (0.31g, 0.5 mmol), and $CH_3CN$ (5 mL). Then the flask was stirred at room temperature for 1.5 h. After the reaction was finished, the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine (15 mL), dried over $Mg_2SO_4$, filtered, and concentrated under vacuum, and the resulting residue was purified by silica gel column chromatography (30:1 to 15:1 PE:EA) to afford the desired product **3aa** as a yellow solid.

**Procedure for the Separation of Elemental Sulfur.** A 3 mmol (with respect to **1a**) scale reaction was conducted under standard conditions. The resultant system was filtered, and the precipitate was isolated and washed with $Et_2O$ and EtOH. This washing dissolved yellow product **3aa**, leaving a red precipitate (87 mg), which was a mixture containing elemental sulfur. After further purification by silica gel column chromatography (PE), light yellow crystalline sulfur was obtained and used for SEM–EDS analysis.

*Phenyl[5-phenyl-2-(phenylamino)furan-3-yl]methanone (**3aa**).* Isolated yield of 149 mg (88%), yellow solid: mp 142–143 °C; $R_f$ = 0.68 (8:1 PE:EA); IR (KBr) $\upsilon$ 3051, 1632, 1600, 1576, 1563, 1493, 1474, 1391, 1259, 1075, 751, 690 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.92 (s, 1H), 7.14 (t, $J$ = 7.4 Hz, 1H), 7.25 (t, $J$ = 7.4 Hz, 1H), 7.39 (t, $J$ = 7.8 Hz, 2H), 7. 43 (t, $J$ = 8.0 Hz, 2H), 7.50–7.56 (m, 5H), 7.61 (d, $J$ = 7.6 Hz, 2H), 7.84 (d, $J$ = 6.7 Hz, 2H), 10.75 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 101.1, 105.0, 118.7, 122.8, 123.6, 127.1, 128.0, 128.4, 128.8, 129.5, 129.7, 131.2, 137.6, 139.8, 144.4, 160.0, 188.5; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{18}NO_2$ 340.1338, found 340.1330.

*(4-Fluorophenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3ba**).* Isolated yield of 104 mg (58%), yellow solid: mp 132–134 °C; $R_f$ = 0.66 (8:1 PE:EA); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.88 (s, 1H), 7.15 (t, $J$ = 7.4 Hz, 1H), 7.19 (t, $^3J_{H-F}$ = 8.6 Hz, 2H), 7.27 (d, $J$ = 12.2 Hz, 1H), 7.39–7.45 (m, 4H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.61 (d, $J$ = 7.6 Hz, 2H), 7.85–7.88 (m, 2H), 10.71 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 100.9, 104.6, 115.5 (d, $^2J_{C-F}$ = 21.6 Hz), 118.7, 122.8, 123.7, 127.2, 128.8, 129.5, 130.4 (d, $^3J_{C-F}$ = 8.0 Hz), 136.0, 137.5, 192.1, 144.6, 160.1, 164.5 (d, $^1J_{C-F}$ = 251.8 Hz); HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}FNO_2$ 358.1243, found 358.1252.

*(4-Chlorophenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3ca**).* Isolated yield of 136 mg (73%), yellow solid: mp 157–158 °C; $R_f$ = 0.62 (8:1 PE:EA); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.86 (s, 1H), 7.15 (t, $J$ = 7.4 Hz, 1H), 7.27 (t, $J$ = 6.4 Hz, 1H), 7.39–7.45 (m, 4H), 7. 49 (d, $J$ = 8.4 Hz, 2H), 7.54 (d, $J$ = 8.0 Hz, 2H), 7.60 (d, $J$ = 7.6 Hz, 2H), 7.78 (d, $J$ = 8.4 Hz, 2H), 10.72 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 101.0, 104.5, 118.8, 122.8, 123.8, 127.2, 128.7, 128.8, 1289.4 129.5, 137.4, 138.1, 144.7, 160.2, 187.0; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NClO_2$ 374.0948, found 374.0952.

*(4-Bromophenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3da**).* Isolated yield of 150 mg (72%), yellow solid: mp 176–177 °C; $R_f$ = 0.60 (8:1 PE:EA); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.86 (s, 1H), 7.16 (t, $J$ = 7.3 Hz, 1H), 7.27 (t, $J$ = 6.8 Hz, 1H), 7.39–7.45 (m, 4H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.60 (d, $J$ = 7.6 Hz, 2H), 7.65 (d, $J$ = 8.4 Hz, 2H), 7.71 (d, $J$ = 8.3 Hz, 2H), 10.73 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 100.9, 104.5, 118.8, 122.8, 123.8, 125.8, 127.3,



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128.8, 129.5, 129.5, 129.6, 131.7, 137.4, 138.5, 144.7, 160.1, 187.0; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NBrO_2$ 418.0443, found 418.0450.

*(3-Chlorophenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3ea**).* Isolated yield of 123 mg (66%), yellow solid: mp 149−150 °C; $R_f$ = 0.65 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.85 (s, 1H), 7.14 (t, $J$ = 7.4 Hz, 1H), 7.25 (t, $J$ = 6.4 Hz, 1H), 7.37−7.44 (m, 4H), 7. 47 (d, $J$ = 8.4 Hz, 2H), 7.53 (d, $J$ = 8.0 Hz, 2H), 7.59 (d, $J$ = 7.6 Hz, 2H), 7.77 (d, $J$ = 8.4 Hz, 2H), 10.70 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.0, 104.5, 118.8, 122.8, 123.8, 127.2, 128.7, 128.8, 129.4, 129.5, 137.4, 138.1, 144.7, 160.1, 186.9; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NClO_2$ 374.0948, found 374.0956.

*(2-Fluorophenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3fa**).* Isolated yield of 100 mg (56%), yellow solid: mp 144−146 °C; $R_f$ = 0.69 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.68 (d, $J$ = 2.8 Hz, 1H), 7.16 (t, $J$ = 7.4 Hz, 1H), 7.20 (t, $^3J_{H-F}$ = 9.2 Hz, 1H), 7.23−7.29 (m, 2H), 7.38 (t, $J$ = 7.7 Hz, 2H), 7.44 (t, $J$ = 7.8 Hz, 2H), 7.48−7.52 (m, 1H), 7.56 (d, $J$ = 8.2 Hz, 2H), 7.58 (d, $J$ = 7.8 Hz, 2H), 7.61 (t, $J$ = 7.3 Hz, 1H), 10.63 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 102.7, 104.7, 116.4 (d, $^2J_{C-F}$ = 21.6 Hz), 118.9, 122.9, 123.8, 124.3, 127.2, 128.2 (d, $^3J_{C-F}$ = 10.6 Hz), 128.8, 129.5, 129.9, 132.2, 137.4, 144.8, 159.3 (d, $^1J_{C-F}$ = 251.6 Hz), 159.7, 184.9; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NFO_2$ 358.1243, found 358.1249.

*(2-Chlorophenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3ga**).* Isolated yield of 97 mg (52%), yellow solid: mp 159−161 °C; $R_f$ = 0.63 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.49 (s, 1H), 7.16 (t, $J$ = 7.4 Hz, 1H), 7.23 (t, $J$ = 7.4 Hz, 1H), 7.35−7.40 (m, 3H), 7.41−7.45 (m, 3H), 7.48 (t, $J$ = 9.2 Hz, 2H), 7.55 (t, $J$ = 6.7 Hz, 4H), 10.46 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 102.4, 104.7, 118.8, 122.8, 123.9, 126.7, 127.2, 128.8, 129.5, 130.3, 130.7, 130.9, 137.3, 139.1, 144.8, 159.5, 187.4; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{16}NClO_2$ 374.0948, found 374.0955.

*(2-Chlorophenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3ha**).* Isolated yield of 102 mg (49%), yellow solid: mp 187−188 °C; $R_f$ = 0.59 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.47 (s, 1H), 7.16 (t, $J$ = 7.3 Hz, 1H), 7.23 (t, $J$ = 7.6 Hz, 1H), 7.31−7.38 (m, 3H), 7.40−7.45 (m, 4H), 7.55 (t, $J$ = 8.1 Hz, 4H), 7.68 (d, $J$ = 8.1 Hz, 1H), 10.43 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 102.1, 104.8, 118.8, 119.3, 122.8, 123.9, 127.2, 127.2, 128.8, 129.5, 130.8, 133.4, 137.3, 141.4, 144.8, 159.5, 188.2; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{16}NBrO_2$ 418.0443, found 418.0448.

*[5-Phenyl-2-(phenylamino)furan-3-yl](p-tolyl)methanone (**3ia**).* Isolated yield of 111 mg (63%), yellow solid: mp 107−108 °C; $R_f$ = 0.64 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.45 (s, 3H), 6.94 (s, 1H), 7.14 (t, $J$ = 7.4 Hz, 1H), 7.25 (t, $J$ = 7.4 Hz, 2H), 7.32 (d, $J$ = 7.8 Hz, 2H), 7.38−7.44 (m, 4H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.61 (d, $J$ = 7.6 Hz, 2H), 7.76 (d, $J$ = 8.0 Hz, 2H), 10.75 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 21.5, 101.1, 105.1, 118.6, 122.7, 123.4, 127.0, 128.1, 128.7, 129.1, 129.4, 129.7, 137.0, 137.6, 141.7, 144.3, 159.8, 188.3; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{20}NO_2$ 354.1494, found 354.1495.

*(4-Methoxyphenyl)[5-phenyl-2-(phenylamino)furan-3-yl]-methanone (**3ja**).* Isolated yield of 125 mg (68%), yellow solid: mp 138−140 °C; $R_f$ = 0.63 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.90 (s, 3H), 6.95 (s, 1H), 7.01 (d, $J$ = 8.6 Hz, 2H), 7.13 (t, $J$ = 7.3 Hz, 1H), 7.25 (t, $J$ = 7.3 Hz, 1H), 7.38−7.44 (m, 4H), 7.54 (d, $J$ = 8.0 Hz, 2H), 7.61 (d, $J$ = 7.8 Hz, 2H), 7.86 (d, $J$ = 8.6 Hz, 2H), 10.74 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 55.4, 101.0, 105.1, 113.7, 118.6, 122.8, 123.4, 127.0, 128.8, 129.5, 129.8, 130.1, 132.4, 137.8, 144.3, 159.9, 162.2, 187.5; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{20}NO_3$ 370.1443, found 370.1452.

*[5-Phenyl-2-(phenylamino)furan-3-yl](thiophen-2-yl)methanone (**3ka**).* Isolated yield of 81 mg (47%). yellow solid: mp 187−188 °C; $R_f$ = 0.45 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.14 (t, $J$ = 7.3 Hz, 1H), 7.20−7.22 (m, 2H), 7.28 (t, $J$ = 7.4 Hz, 1H), 7.43 (t, $J$ = 7.8 Hz, 4H), 7.54 (d, $J$ = 8.2 Hz, 2H), 7.65 (t, $J$ = 7.4 Hz, 3H), 7.86 (d, $J$ = 3.6 Hz, 1H), 10.83 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 100.4, 103.8, 118.7, 122.9, 123.6, 127.3, 127.9, 128.8, 129.5, 130.4, 131.4, 137.5, 144.5, 145.0, 160.3, 178.7; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{21}H_{16}NO_2S$ 346.0902, found 346.0912.

*Furan-2-yl[5-phenyl-2-(phenylamino)furan-3-yl]methanone (**3la**).* Isolated yield of 67 mg (41%), yellow solid: mp 195−196 °C; $R_f$ = 0.43 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.61−6.62 (m, 1H), 7.14 (t, $J$ = 7.4 Hz, 1H), 7.28 (d, $J$ = 7.4 Hz, 1H), 7.31 (d, $J$ = 3.4 Hz, 1H), 7.41−7.44 (m, 4H), 7.48 (s, 1H), 7.54 (d, $J$ = 8.0 Hz, 2H), 7.68 (d, $J$ = 7.2 Hz, 3H), 10.90 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 100.0, 104.4, 112.2, 116.0, 118.7, 122.8, 123.6, 127.1, 128.8, 129.5, 129.8, 137.5, 145.0, 145.2, 154.0, 160.6, 174.1; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{21}H_{16}NO_3$ 330.1130, found 330.1142.

*{2-[(4-Fluorophenyl)amino]-5-phenylfuran-3-yl}(phenyl)-methanone (**3ma**).* Isolated yield of 100 mg (56%), yellow solid: mp 139−141 °C; $R_f$ = 0.63 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.90 (s, 1H), 7.12 (t, $^3J_{H-F}$ = 8.6 Hz, 2H), 7.24 (t, $J$ = 7.4 Hz, 1H), 7.38 (t, $J$ = 7.7 Hz, 2H), 7.47−7.54 (m, 5H), 7.57 (d, $J$ = 8.0 Hz, 2H),7.82 (d, $J$ = 7.0 Hz, 2H), 10.68 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.0, 105.0, 116.2 (d, $^2J_{C-F}$ = 22.7 Hz), 120.4 (d, $^3J_{C-F}$ = 6.6 Hz), 122.8, 127.2, 128.0, 128.4, 128.8, 129.6, 131.2, 133.8, 139.7, 144.4, 158.1, 159.9, 188.5; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NFO_2$ 358.1243, found 358.1239.

*{2-[(4-Chlorophenyl)amino]-5-phenylfuran-3-yl}(phenyl)-methanone (**3na**).* Isolated yield of 151 mg (81%), yellow solid: mp 188−190 °C; $R_f$ = 0.57 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.92 (s, 1H), 7.27 (d, $J$ = 7.4 Hz, 1H), 7.38−7.42 (m, 4H), 7.47−7.59 (m, 7H), 7.83 (d, $J$ = 7.2 Hz, 2H), 10.74 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.3, 105.0, 119.8, 122.8, 127.2, 128.0, 128.5, 128.8, 129.5, 131.4, 136.2, 139.6, 144.7, 159.5, 188.7; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NClO_2$ 374.0948, found 374.0942.

*{2-[(4-Bromophenyl)amino]-5-phenylfuran-3-yl}(phenyl)-methanone (**3oa**).* Isolated yield of 152 mg (73%), yellow solid: mp 204−205 °C; $R_f$ = 0.55 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.93 (s, 1H), 7.27 (d, $J$ = 6.5 Hz, 1H), 7.39−7.44 (m, 4H), 7.51−7.57 (m, 5H), 7.59 (d, $J$ = 7.7 Hz, 2H), 7.83 (d, $J$ = 7.2 Hz, 2H), 10.74 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.4, 105.0, 116.0, 120.2, 122.8, 127.3, 128.0, 128.4, 128.8, 129.5, 131.4, 132.5, 136.7, 139.6, 144.8, 159.5, 188.8; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NBrO_2$ 418.0443, found 418.0452.

*{2-[(3-Chlorophenyl)amino]-5-phenylfuran-3-yl}(phenyl)-methanone (**3pa**).* Isolated yield of 102 mg (55%), yellow solid: mp 160−162 °C; $R_f$ = 0.56 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.93 (s, 1H), 7.11 (d, $J$ = 7.6 Hz, 1H), 7.28 (d, $J$ = 7.4 Hz, 1H), 7.34 (t, $J$ = 8.0 Hz, 1H), 7.38−7.43 (m, 3H), 7.51−7.58 (m, 3H), 7.61−7.63 (m, 3H), 7.84 (d, $J$ = 7.0 Hz, 2H), 10.75 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 41.0, 101.5, 104.9, 116.6, 118.5, 122.8, 123.3, 127.3, 128.1, 128.5, 128.8, 129.4, 130.5, 131.4, 135.1, 138.7, 139.5, 144.8, 159.2, 188.8; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NClO_2$ 374.0948, found 374.0952.

*Phenyl[5-phenyl-2-(p-tolylamino)furan-3-yl]methanone (**3qa**).* Isolated yield of 124 mg (70%), yellow solid: mp 161−162 °C; $R_f$ = 0.57 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 2.37 (s, 3H), 6.91 (s, 1H), 7.23−7.26 (m, 4H), 7.39 (t, $J$ = 7.8 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 7.50−7.56 (m, 3H), 7.60 (d, $J$ = 7.6 Hz, 2H), 7.83 (t, $J$ = 4.1 Hz, 2H), 10.69 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 20.8, 100.9, 105.0, 118.8, 122.7, 127.0, 128.0, 128.4, 128.8, 129.8, 130.0, 131.1, 133.3, 135.0, 139.9, 144.3, 160.2, 188.2; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{20}NO_2$ 354.1494, found 354.1492.

*{2-[(4-Methoxyphenyl)amino]-5-phenylfuran-3-yl}(phenyl)-methanone (**3ra**).* Isolated yield of 131 mg (71%), yellow solid: mp 148−150 °C; $R_f$ = 0.64 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H), 6.91 (s, 1H), 6.98 (d, $J$ = 8.9 Hz, 2H), 7.24 (d, $J$ = 7.4 Hz, 1H), 7.38 (t, $J$ = 7.7 Hz, 2H), 7.47−7.55 (m, 5H), 7.58 (d, $J$ = 7.6 Hz, 2H), 7.83 (d, $J$ = 6.6 Hz, 2H), 10.66 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 55.5, 100.6, 105.0, 114.7, 120.5, 122.7, 127.0, 128.0, 128.4, 128.8, 129.7, 130.7, 131.1, 139.9, 144.0, 156.1, 160.4, 188.1; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{20}NO_3$ 370.1443, found 370.1449.

*[2-(Benzylamino)-5-phenylfuran-3-yl](phenyl)methanone (**3sa**).* Isolated yield of 90 mg (51%), yellow solid: mp 142−144 °C; $R_f$ = 0.41 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.78 (d, $J$ = 6.3 Hz, 2H), 6.84 (s, 1H), 7.20 (t, $J$ = 7.4 Hz, 1H), 7.30−7.40 (m, 5H), 7.44 (d, $J$ = 7.4 Hz, 2H), 7.46−7.52 (m, 5H), 7.78 (t, $J$ = 4.0 Hz, 2H), 8.78


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(t, $J$ = 6.0 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 46.1, 99.5, 105.5, 122.5, 125.9, 126.6, 127.5, 127.8, 127.9, 128.3, 128.7, 128.8, 130.0, 130.8, 137.5, 140.1, 143.5, 164.2, 187.7; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{20}NO_2$ 354.1494, found 354.1498.

*Ethyl (3-Benzoyl-5-phenylfuran-2-yl)glycinate (**3ta**).* Isolated yield of 101 mg (58%), yellow solid: mp 137−138 °C; $R_f$ = 0.38 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.32 (t, $J$ = 7.2 Hz, 3H), 4.29 (q, $J$ = 7.1 Hz, 2H), 4.34 (d, $J$ = 6.0 Hz, 2H), 6.83 (s, 1H), 7.20 (t, $J$ = 7.3 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 2H), 7.46−7.51 (m, 5H), 7.80 (d, $J$ = 7.0 Hz, 2H), 8.60 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 14.2, 43.8, 61.8, 99.9, 105.6, 122.6, 126.8, 128.0, 128.3, 128.7, 129.9, 130.9, 140.0, 143.8, 163.4, 168.8, 188.2; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{21}H_{20}NO_4$ 350.1392, found 350.1385.

*[5-(4-Fluorophenyl)-2-(phenylamino)furan-3-yl](phenyl)-methanone (**3ab**).* Isolated yield of 100 mg (56%), yellow solid: mp 176−178 °C; $R_f$ = 0.68 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.91 (s, 1H), 7.16 (t, $J$ = 7.3 Hz, 1H), 7.36 (d, $J$ = 8.2 Hz, 2H), 7.44 (t, $^3J_{H-F}$ = 7.6 Hz, 2H), 7.52−7.57 (m, 7H), 7.82 (d, $J$ = 7.2 Hz, 2H), 10.73 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.2, 105.6, 118.8, 123.9, 123.8, 128.0, 128.2, 128.5, 129.0, 129.6, 131.3, 132.6, 137.5, 139.7, 143.4, 160.0, 188.6; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NFO_2$ 358.1243, found 358.1249.

*[5-(4-Chlorophenyl)-2-(phenylamino)furan-3-yl](phenyl)-methanone (**3ac**).* Isolated yield of 127 mg (68%), yellow solid: mp 163−164 °C; $R_f$ = 0.61 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.84 (s, 1H), 7.08 (t, $J$ = 8.6 Hz, 2H), 7.13 (t, $J$ = 7.3 Hz, 1H), 7.42 (t, $J$ = 7.8 Hz, 2H), 7.52−7.57 (m, 7H), 7.81 (d, $J$ = 6.9 Hz, 2H), 10.72 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.0, 104.7, 115.8, 116.0, 118.7, 123.7, 124.5, 124.5, 126.0, 128.0, 128.5, 129.5, 131.3, 137.5, 139.7, 143.6, 160.0, 160.9, 162.9, 183.1, 188.5; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NClO_2$ 374.0948, found 374.0956.

*[5-(4-Bromophenyl)-2-(phenylamino)furan-3-yl](phenyl)-methanone (**3ad**).* Isolated yield of 129 mg (62%), yellow solid: mp 160−161 °C; $R_f$ = 0.65 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.95 (s, 1H), 7.18 (t, $J$ = 7.3 Hz, 1H), 7.44−7.49 (m, 4H), 7.52−7.60 (m, 7H), 7.84 (d, $J$ = 7.2 Hz, 2H), 10.75 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.1, 105.7, 118.7, 120.6, 123.7, 124.1, 128.0, 128.5, 129.5, 131.3, 131.9, 137.4, 139.6, 143.3, 160.0, 188.5; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NBrO_2$ 418.0443, found 418.0454.

*Phenyl{2-(phenylamino)-5-[4-(trifluoromethyl)phenyl]furan-3-yl}methanone (**3ae**).* Isolated yield of 65 mg (32%), yellow solid: mp 152−153 °C; $R_f$ = 0.66 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.01−7.05 (m, 1H), 7.17 (t, $J$ = 7.3 Hz, 1H), 7.24 (t, $J$ = 6.9 Hz, 1H), 7.38 (t, $J$ = 7.7 Hz, 1H), 7.43−7.49 (m, 2H), 7.51−7.61 (m, 6H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.68 (d, $J$ = 8.3 Hz, 1H), 7.83 (d, $J$ = 7.2 Hz, 1H), 7.90 (d, $J$ = 7.8 Hz, 1H), 10.73 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.3, 107.5, 118.9, 120.6, 123.9, 125.5, 125.8, 128.2 (q, $^3J_{C-F}$ = 70.6 Hz), 129.3 (q, $^4J_{C-F}$ = 22.2 Hz), 129.8, 131.4, 131.6, 134.8, 136.2 (q, $^2J_{C-F}$ = 279.9 Hz), 142.8, 150.5 (q, $^1J_{C-F}$ = 604.0 Hz), 160.2, 188.7, 191.5; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{17}NF_3O_2$ 408.1211, found 408.1205.

*[5-(3-Chlorophenyl)-2-(phenylamino)furan-3-yl](phenyl)-methanone (**3af**).* Isolated yield of 90 mg (48%), yellow solid: mp 146−147 °C; $R_f$ = 0.66 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.96 (s, 1H), 7.17 (t, $J$ = 7.3 Hz, 1H), 7.21 (d, $J$ = 7.9 Hz, 1H), 7.32 (t, $J$ = 7.9 Hz, 1H), 7.43−7.49 (m, 3H), 7.51−7.58 (m, 6H), 7.82 (d, $J$ = 7.2 Hz, 2H), 10.73 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 101.1, 106.4, 118.8, 120.7, 122.6, 123.8, 126.9, 128.0, 128.5, 129.6, 130.1, 131.3, 134.8, 137.4, 139.6, 142.9, 160.0, 188.6; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{23}H_{17}NO_2Cl$ 374.0948, found 374.0936.

*[5-(4-Methoxyphenyl)-2-(phenylamino)furan-3-yl](phenyl)-methanone (**3ag**).* Isolated yield of 109 mg (59%), yellow solid: mp 151−153 °C; $R_f$ = 0.67 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.87 (s, 3H), 6.80 (s, 1H), 6.97 (d, $J$ = 8.7 Hz, 2H), 7.16 (t, $J$ = 7.4 Hz, 1H), 7.45 (t, $J$ = 7.8 Hz, 2H), 7.52−7.58 (m, 7H), 7.86 (d, $J$ = 7.0 Hz, 2H), 10.79 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 55.3, 101.0, 103.1, 114.3, 118.6, 122.6, 123.4, 124.3, 128.0, 128.4, 129.5, 131.1, 137.7, 139.9, 144.6, 158.9, 159.8, 188.3; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{20}NO_3$ 370.1443, found 370.1446.

*[5-(3-Methoxyphenyl)-2-(phenylamino)furan-3-yl](phenyl)-methanone (**3ah**).* Isolated yield of 94 mg (51%), yellow solid: mp 134−136 °C; $R_f$ = 0.69 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.86 (s, 3H), 6.80−6.82 (m, 1H), 6.92 (s, 1H), 7.15 (t, $J$ = 6.8 Hz, 2H), 7.21 (d, $J$ = 7.8 Hz, 1H), 7.32 (t, $J$ = 8.0 Hz, 1H), 7.43 (t, $J$ = 7.8 Hz, 2H), 7.51−7.56 (m, 5H), 7.84 (d, $J$ = 6.8 Hz, 2H), 10.74 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 55.3, 101.1, 105.4, 108.5, 112.4, 115.4, 118.7, 123.6, 128.0, 128.4, 129.5, 129.9, 131.0, 131.2, 137.6, 139.8, 144.2, 159.9, 188.5; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{20}NO_3$ 370.1443, found 370.1452.

*Phenyl[2-(phenylamino)-5-(thiophen-2-yl)furan-3-yl]methanone (**3ai**).* Isolated yield of 78 mg (45%), yellow solid: mp 115−117 °C; $R_f$ = 0.56 (8:1 PE:EA); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.76 (s, 1H), 7.05 (t, $J$ = 4.3 Hz, 1H), 7.14 (t, $J$ = 7.4 Hz, 1H), 7.21−7.24 (m, 2H), 7.42 (t, $J$ = 7.9 Hz, 2H), 7.50−7.57 (m, 5H), 7.82 (t, $J$ = 4.0 Hz, 2H), 10.76 (s, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 100.9, 104.8, 118.7, 122.0, 123.7, 127.7, 128.0, 128.5, 129.5, 131.3, 132.5, 137.5, 139.7, 140.1, 159.6, 188.4; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{21}H_{16}NO_2S$ 346.0902, found 346.0918.

*1-Phenyl-3-(phenylamino)-3-{[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]thio}prop-2-en-1-one (**5**).* Isolated yield of 90 mg (44%), yellow solid: mp 142−143 °C; $R_f$ = 0.68 (8:1 PE:EA); IR (KBr) $\upsilon$ 3291, 3067, 2936, 1672, 1598, 1497, 1397, 1254, 1028, 743, 682 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 9.91 (s, 1H), 8.24 (d, $J$ = 7.6 Hz, 2H), 7.83 (d, $J$ = 8.0 Hz, 2H), 7.61 (t, $J$ = 8.0 Hz, 1H), 7.52 (t, $J$ = 7.7 Hz, 2H), 7.42 (t, $J$ = 7.8 Hz, 2H), 7.28 (t, $J$ = 7.3 Hz, 1H), 6.21 (s, 1H), 1.55−1.21 (m, 15H), 0.87 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 196.1, 193.1, 137.8, 135.5, 133.7, 130.1, 129.0, 128.5, 126.9, 122.8, 94.0, 60.3, 40.3, 40.0, 33.3, 33.0, 20.7, 20.1, 16.9; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{24}H_{31}N_2O_2S$ 411.2106, found 411.2109.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01924.

X-ray data for **3aa** (CIF)

LC−MS data and $^1$H and $^{13}$C NMR spectra of all new compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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