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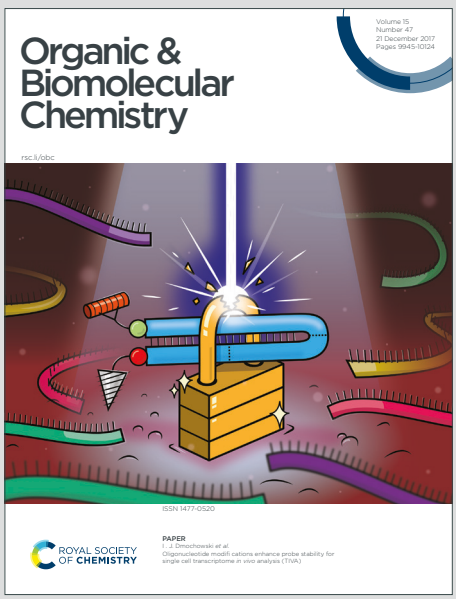

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ARTICLE

Rhodium(III)-catalysed cascade [3+2] annulation of *N*-aryloxyacetamides with 3-(hetero)arylpropiolic acids: synthesis of benzofuran-2(3*H*)-ones

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Herein, a cascade [3+2] annulation of *N*-aryloxyacetamides with 3-(hetero)arylpropiolic acids affording benzofuran-2(3*H*)-ones via rhodium(III)-catalyzed redox-neutral C–H functionalization/isomerization/lactonization using an internal oxidative directing group O–NHAc was achieved. This catalytic system provides a regio- and stereoselective approach to synthesize (*Z*)-3-(amino(aryl)methylene)benzofuran-2(3*H*)-ones with exclusive *Z* configuration selectivity, acceptable yields and good functional group tolerance. Preliminary investigations on ultraviolet-visible and fluorescence behaviors reveals that the annulation products may be applied as a promising fluorescent probe for sensing metal cations, especially for Cerium (Ce^{3+}).

Introduction

Benzofuran-2(3*H*)-one nucleus is a prominent structural motif that is commonly found in various natural products and biologically active compounds, such as hopeahiainol A, radulifolin B, and BHFF (Fig 1).[1] As a result, the development of synthetic methods for benzofuran-2(3*H*)-one skeleton has drawn considerable attention from synthetic chemists in recent years and several methods have been developed to build this valuable architecture, such as transition-metal-catalyzed C–H activation strategy.[2] Researches of novel synthetic methodologies of pharmaceutically relevant molecules including benzofuran-2(3*H*)-ones are also drawing our interest all the time.[3]

In recent years, as an oxidizing directing group, *N*-aryloxyacetamides (O–NHAc)[4] which was designed by Lu and Liu for the synthesis of substituted benzofurans and *ortho*-hydroxyaryl enamides via redox-neutral reaction conditions in 2013,[5] have been used as the privileged substrates to develop new transformations with different coupling partners, such as alkynes,[6] olefins,[7] diazos[8] and others,[9] or based on an intramolecular pattern.[10] Among them, benzofuran-2(3*H*)-ones

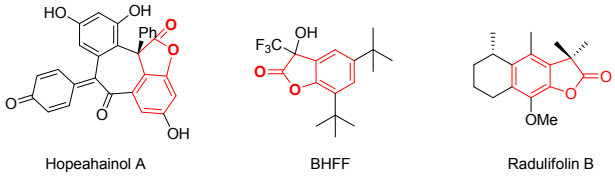
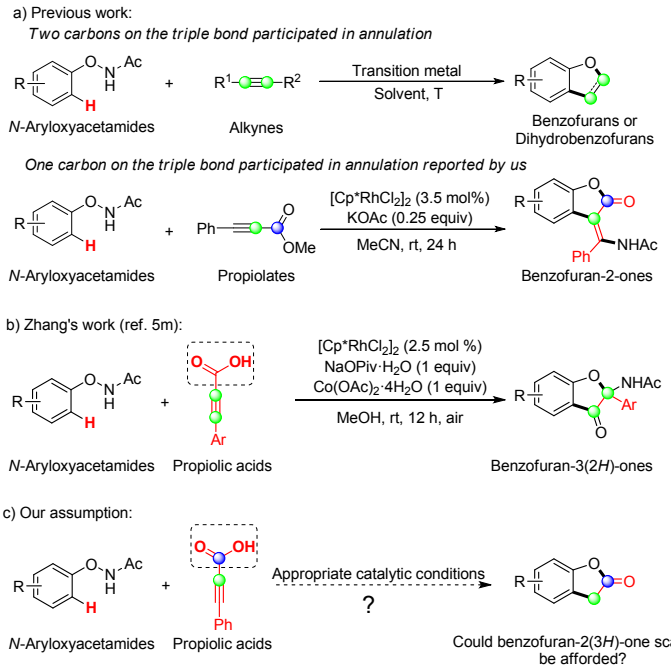


Fig. 1 Selected molecules containing benzofuran-2(3*H*)-one scaffolds.



Scheme 1. Rhodium(III)-catalyzed C–H Functionalization/[3+2] annulation of *N*-aryloxyacetamides.

were first successfully obtained through the transition-metal-catalyzed C–H funtionalization of *N*-aryloxyacetamides with propiolates by us.[6l] It is interesting that only one carbon of the C≡C bond was participate in the annulation in our work which

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† Electronic Supplementary Information (ESI) available: Experimental details, characterization data, copies of ^1H and ^{13}C NMR spectra. CCDC 1918362 (**3aa**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

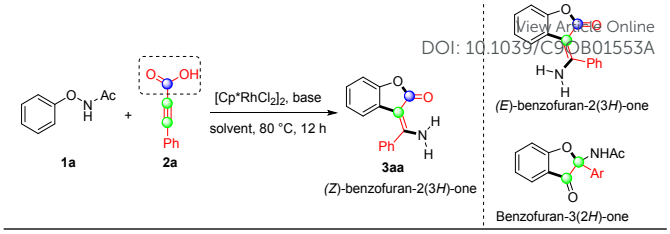
was different from other annulations directed by O–NHAc group (Scheme 1a).[6]

In contrast with other alkynes, propiolic acids were offen empolyed with difficulty in the annulations directed by *N*-aryloxyacetamide group. To our best knowledge, only one work was accomplished by Zhang and co-workers in 2019, in which numerous benzofuran-3(2*H*)-ones were successfully built (Scheme 1b).[6m] Inspired by Zhang's work and our previous related work,[6l] we hope synthesize benzofuran-2(3*H*)-ones via annulations of propiolic acids with *N*-aryloxyacetamides, in which only one carbon of C≡C bond and carboxyl carbon need to participate in appropriate reation conditions (Scheme 1c). Herein, we reported the rhodium(III)-catalyzed redox-neutral cascade [3+2] annulation of *N*-aryloxyacetamides with propiolic acids affording benzofuran-2(3*H*)-ones applied as a promising fluorescent probe for sensing metal cations, especially for Cerium (Ce^{3+}).

Results and discussion

With our hypothesis in mind, we commenced our studies by employing *N*-phenoxyacetamide **1a** and readily available 3-phenylpropiolic acid **2a** as the model substrates for the optimization of the reaction conditions (Table 1). Unfortunately, the annulation could not proceed using our previous reaction conditions at room temperature or 80 °C because of the significance difference of the chemical properties of propiolic acids and propiolates (entry 1).[6l] Delightedly, the reaction of **1a** and **2a** indeed did proceed leading to (*Z*)-3-(amino(phenyl)methylene)benzofuran-2(3*H*)-one **3aa** in the presence of dimeric $[Cp^*RhCl_2]_2$ as catalyst precursor, and Cs_2CO_3 as base in methanol at 80 °C for 12 h, albeit in a low yield (9%, entry 2). Encouraged by the above result, a variety of solvents were thus screened. Interestingly, the desired product **3aa** could be obtained in alcoholic solvents and TFE was found to be the optimal with an acceptable isolated yield (entries 4 and 5), whereas the reactions were sluggish when CH_2Cl_2 was employed as the solvent (entry 3, for detailed optimization studies, see Table S1 in the Supporting Information). A decrease or increase in temperature resulted in lower yields (entries 6 and 7). Other inorganic bases were found less effective (entries 8–14). It is worth mentioning that organic base, such as Et_3N, DBU or TMG, was also an alternative for the above reaction to provide a similar yield (entries 15–17). Control experiments showed that Cp*Rh(III) was crucial for this reaction as its omission led to no formation of **3aa**. Other Cp*M catalysts (M = Ir, Ru, or Co) did not show any catalytic activity under the standard reaction conditions (entry 18). The employment of $[Cp^*Rh(OAc)_2]_2$ or $[Cp^*Rh(MeCN)_3](SbF_6)_2$ afforded **3aa** in lower yields (entry 19). Air atmosphere was found to be not beneficial to the reaction (entry 20). Gratifyingly, the loading of the catalysis precursor could be decreased to 1.0 mol % without loss of its efficiency

Table 1. Optimization of Reaction Conditions.[a]



Entry	Solvent	Base	Yield [%][b]
1	CH_3CN	KOAc	0
2	MeOH	Cs_2CO_3	9
3	CH_2Cl_2	Cs_2CO_3	<2
4	EtOH	Cs_2CO_3	11
5	TFE	Cs_2CO_3	53
6[c]	TFE	Cs_2CO_3	49
7[d]	TFE	Cs_2CO_3	48
8	TFE	Na_2CO_3	30
9	TFE	K_2CO_3	44
10	TFE	CsOAc	<2
11	TFE	$KHCO_3$	32
12	TFE	$CsHCO_3$	46
13	TFE	KOH	46
14	TFE	K_3PO_4	45
15	TFE	Et_3N	52
16	TFE	DBU	51
17	TFE	TMG	51
18[e]	TFE	Cs_2CO_3	0
19[f]	TFE	Cs_2CO_3	48
20[g]	TFE	Cs_2CO_3	39
21[h]	TFE	Cs_2CO_3	53
22[i]	TFE	Cs_2CO_3	47

[a]Reactions conditions **1a** (0.2 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %) and base (0.2 mmol) in solvent (2.0 mL) at the indicated temperature under argon for 12 h. Cp* = pentamethylcyclopentadienyl; TFE = 2,2,2-trifluoroethanol; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; TMG = 1,1,3,3-tetramethylguanidine. [b]Isolated yield. [c]60 °C. [d]100 °C. [e] $[Cp^*IrCl_2]_2$, $[Cp^*RuCl_2]_n$, or $[Cp^*Co(MeCN)_3](SbF_6)_2$ were used as the catalyst. [f]$[Cp^*Rh(OAc)_2]_2$ or $[Cp^*Rh(MeCN)_3](SbF_6)_2$ were used as the catalyst. [g]Under air. [h]$[Cp^*RhCl_2]_2$ (1.0 mol %) was used. [i]$[Cp^*RhCl_2]_2$ (0.5 mol %) was used.

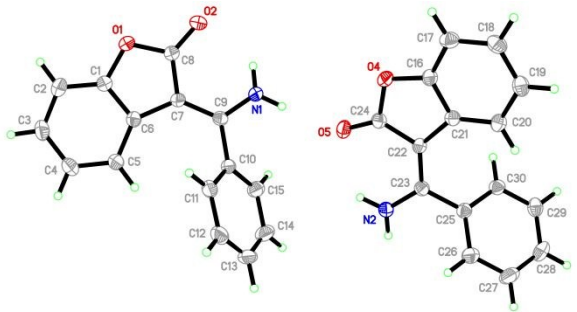


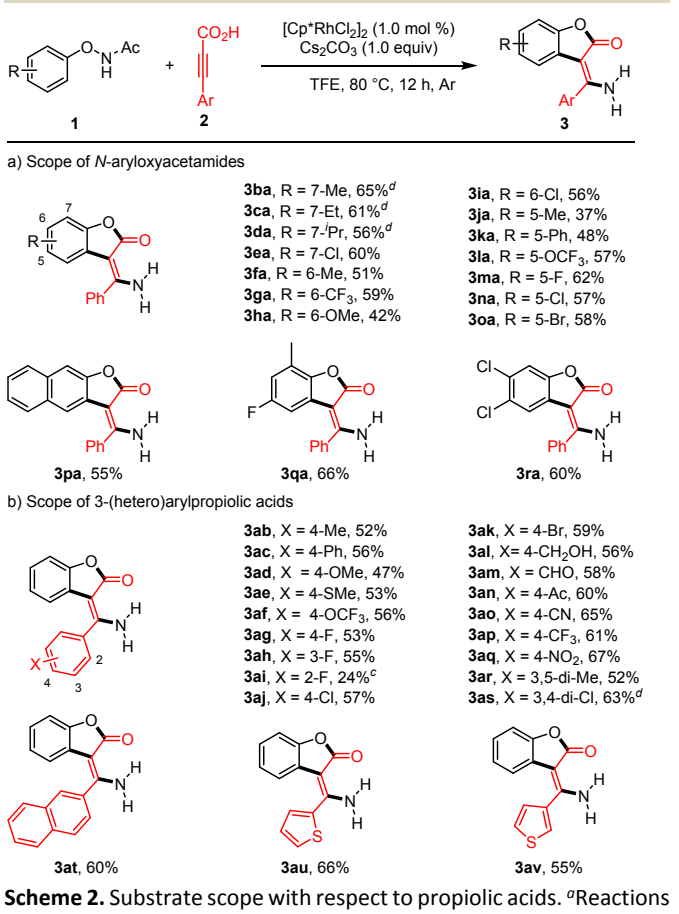
Fig. 2 X-ray crystal structure of **3aa** (hydrogen-bonded dimer).

(entry 21 and 22). It is interesting that no (*E*)-benzofuran-2(3*H*)-one and benzofuran-3(2*H*)-one reported by zhang' group was detected in those catalytic conditions. The molecular structure of **3aa** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Fig. 2), which was well supported by ^1H and ^{13}C NMR spectra and high resonance mass spectrometry data. Selective formation of the *Z* isomer is likely due to the strong

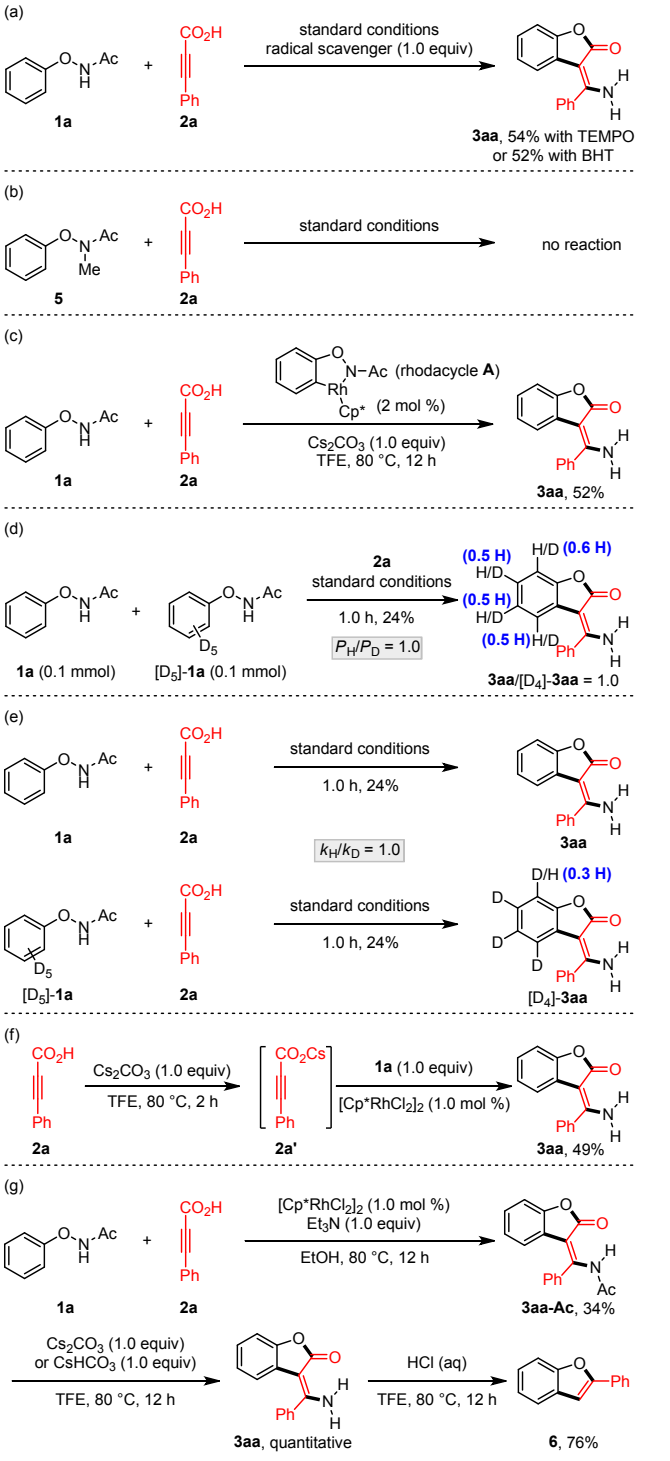
hydrogen-bonding between the amino proton and the oxygen atom of the carbonyl group (2.164 Å and 2.111 Å for the intramolecular O–H distances, and 2.030 Å for the intermolecular O–H distance).[11]

Having identified the optimized reaction conditions, we then probed the scope and limitations of the present Cp*Rh(III)-catalysed redox-neutral cascade [3 + 2] annulation. To our satisfaction, the reactions of **2a** with a wide range of substituted *N*-aryloxyacetamides were generally performed smoothly to provide the corresponding (*Z*)-3-aminomethylene benzofuran-2-one derivatives (Scheme 2a). *Ortho*-alkyl and chloro-substituted *N*-aryloxyacetamides could led to the construction of the desired benzofuran-2-one derivatives in moderate yields (**3b**–**3ea**). High site-selectivities were observed when *meta*-substituted *N*-aryloxyacetamides were subjected to the reactions, yielding the expected products at the sterically less hindered sites (**3fa**–**3ia**). A comparison of the results reveals that *para*-substituted *N*-aryloxyacetamides gave lower yields of the desired products than those of the corresponding *ortho* ones (**3ja** and **3na**). The reaction could also be successfully extended to *para*-phenyl (**3ka**), ether (**3la**) and halo (**3ma** and **3oa**) substituted *N*-aryloxyacetamides and *N*-(naphthalen-2-yloxy)acetamide (**3pa**). To our delight, the disubstituted substrates underwent the reaction smoothly to afford products **3qa** and **3ra**, respectively.

To further illustrate the substrate scope, we subsequently investigated a variety of differently substituted 3-(hetero)arylpropiolic acids under the optimal reaction conditions (Scheme 2b). For para-substituted 3-arylpropiolic acids, substituents, including alkyl (**3ab**), aryl (**3ac**), ether (**3ad**, **3ae** and **3af**), and halo (**3ag**, **3aj** and **3ak**), were well tolerated



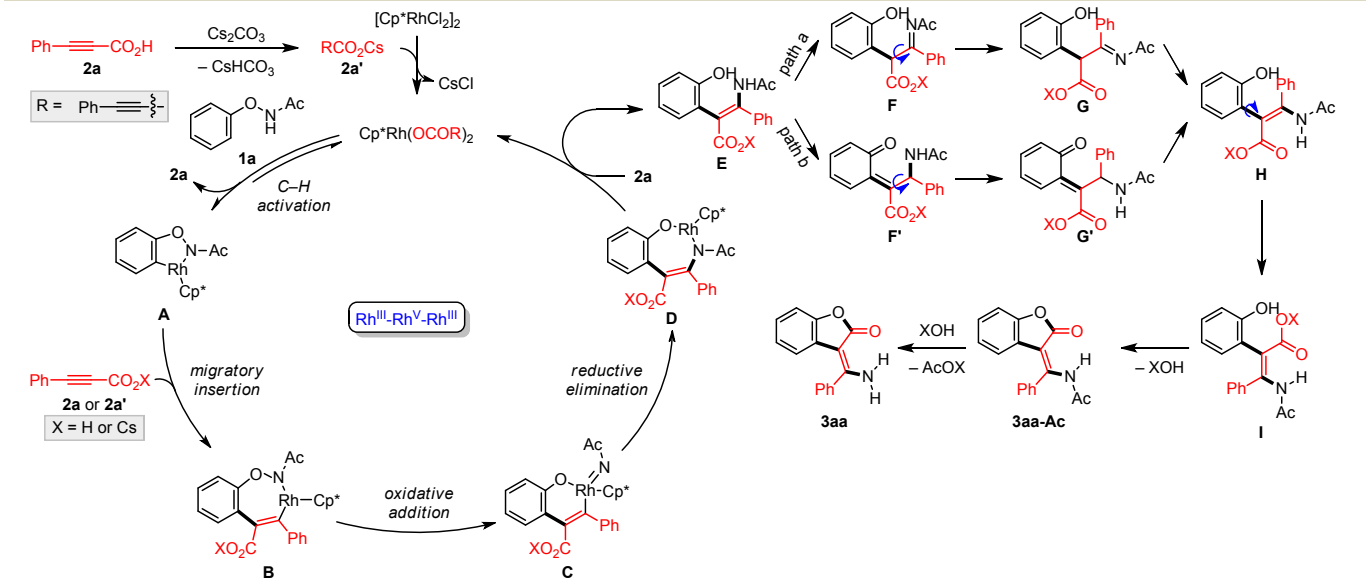
Scheme 2. Substrate scope with respect to propiolic acids. [a]Reactions were carried out with **1** (0.2 mmol), **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (1.0 mol %), and Cs_2CO_3 (0.2 mmol) in TFE (2.0 mL) at 80 °C under argon for 12 h. TFE = 2,2,2-trifluoroethanol. [b]Isolated yield. [c]$[Cp^*RhCl_2]_2$ (2.5 mol %) was used. [d]The reaction time was prolonged to 24 h.



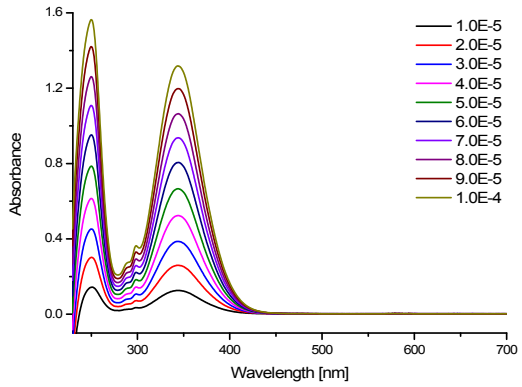
Scheme 3. Mechanistic investigations.

along with 52%–59% isolated yields. 3-Arylpropiolic acid featuring a hydroxymethyl group worked well to give **3al** in 56% yield. Electron-donating groups resulted in relative lower reaction efficiency, as exemplified by **3ad**. In contrast, substrates bearing electron-withdrawing groups, such as formyl, acetyl, cyano, trifluoromethyl, and even nitro, afforded the expected products in relative higher yields (**3am**–**3aq**). The presence of a fluoro at meta position of aryl group did not significantly affect the yield (**3ah**), whereas the reaction efficiency dramatically decreased with an fluoro at ortho position of the aromatic ring (**3ai**). Furthermore, disubstituted 3-(3,5-dimethylphenyl)propiolic acid and 3-(3,4-dichlorophenyl)propiolic acid could deliver the desired products in moderate yields (**3ar** and **3as**). Using 3-(naphthalen-2-yl)propiolic acid, the corresponding product 3at could be isolated in a yield of 60%. Notably, the reaction was not limited to 3-arylpropiolic acids, and 3-heteroarylpropiolic acids, such as 3-(thiophen-2-yl)propiolic acid and 3-(thiophen-3-yl)propiolic acid, tolerated the same conditions to provide the expected products 3au in 66% and 3av in 55%, respectively. Unfortunately, 3-alkyl- and terminal propiolic acids gave unsatisfactory results. To gain mechanistic insights into the cascade annulation, a series of experiments were carried out. With the addition of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) or butylated hydroxytoluene (BHT) as a radical scavenger, the desired product **3aa** could still be isolated in maintained yields, implying that the reaction was most likely not invloved in a radical pathway (Scheme 3a). When *N*-methyl-*N*-phenoxyacetamide **5** was subjected to the standard reaction conditions, no desired product was generated, highlighting that the N–H bond played an essential role in the present reaction (Scheme 3b). The isolated and stable five-membered rhodacycle **A**[9d,10a] could successfully catalyzed the cascade annulation of **1a** and **2a** with a yield of 52%, suggesting that the rhodium complex was most likely involvd in the catalytic cycle (Scheme 3c). Intermolecular competition experiments using equimolar amount of **1a** and [D_5]-**1a** under standard conditions for 1 h led to the mixed products **3aa**/[D_4]-**3aa** with a ratio of 1.0. Simultaneously, deuterium incorporation was observed at the *ortho*-position of **3aa** (Scheme 3d). In the parallel experiments, an identical KIE value (k_H/k_D = 1.0) and more obvious deuterium incorporation were observed. Thus, the above results indicated that C–H bond cleavage was not involved in the rate-determining step, and that the C–H cleavage might be reversible under the reaction conditions. The results of the deuterium incorporation at the *ortho*-position of **3aa** was not in accordance with our previous results[6l], which may due to the enhanced reaction conditions (Scheme 3e). The reaction of **2a** with Cs_2CO_3 in TFE at 80 °C for 2 h delieved cesium 3-phenylpropiolate **2a'**, which was confirmed by NMR (see the ESI for details). Employemt of **2a'** with **1a** catalyzed with $[Cp^*RhCl_2]_2$ gave the desired product in 49% yield. The result suggested that the cesium salt was likely to be involved in the reaction (Scheme 3f). The reaction of **1a** and **2a** employing Et_3N as the base in EtOH (without further optimization) gave the product **3aa-Ac**, which could be transformed to **3aa** in quantitative yield. Product **3aa** could be further converted to 2-phenylbenzofuran **6** or 2*H*-azirine[6l,12] (Scheme 3g).

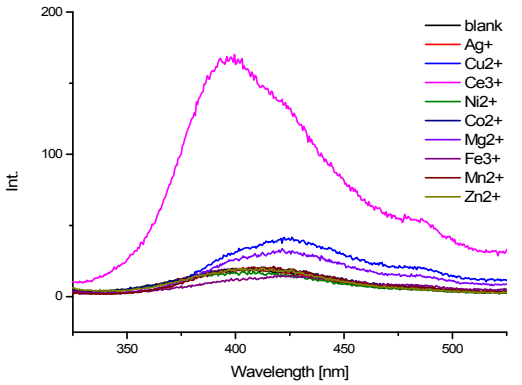
Based on the aforementioned experimental results, together with precedent literature[6l,13], we have proposed a plausible mechanism for the Cp*Rh(III)-catalyzed redox-neutral cascade [3+2] annulation, as depicted in Scheme 4. Initially, the reversible N–H deprotonation and C–H activation of **1a** generated rhodacycle **A**. The regioselective migratory insertion of **2a** into the C–Rh bond gave **B**. The formation of **D** was quite facile through oxidative addition of Rh into the O–N bond via Rh(V) nitrenoid **C** followed by reductive elimination. The protonation was involved to facilitate the generation of **E**. The isomerizaiton of C–C double bond was achieved through enamine-imine (path a) or phenol-semiquinone (path b) tautomerization with promotion of the N–H···O type intramolecular interaction. The consecutive C–C single bond rotation, lactonization and hydrolysis afforded benzofuran-2-



Scheme 4. Proposed catalytic pathway for the synthesis of **3aa**



Scheme 5. Variation of absorbance intensity of **3aa** in MeOH at different concentrations ranging from 1.0×10^{-5} to 1.0×10^{-4} M.



Scheme 6. Variation of the fluorescence intensity of **3aa** in MeOH (1.0×10^{-4} M) upon excitation at 285 nm in the presence of different metal cations.

one derivative **3aa**.

UV-Visible absorption spectroscopy was employed to investigate the spectral behavior of 3aa under UV-visible-light irradiation (220−700 nm). (Scheme 5). The K band was observed with an absorption maximum at 250 nm (lg ε = 4.20) due to a π-π* transition in UV region at around 220 to 270 nm. The R band was detected with an absorption maximum at 344 nm (lg ε = 4.13) due to an n-π* transition in around 310 to 450 nm region. In addition, the absorbance intensity of K and R bands increased in parallel with concentration gradient ranging from 1.0×10^{-5} to 1.0×10^{-4} M and strictly followed the Lambert-Beer's Law.

The sensing behavior of **3aa** with Ag^{+}, Cu^{2+}, Ce^{3+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Fe^{3+}, Mn^{2+} and Zn^{2+} was evaluated through the fluorescence spectroscopy in a range of 300−550 nm (Scheme 6). A significant enhancement in the emission intensity (λemis = 398 nm) was observed which may be attributed to selective. interaction and accessibility for Ce^{3+} cation with compound **3aa**, which exhibited higher emission sensitivity towards Cerium (Ce^{3+}) compared to other tested metal cations. Analogues of **3aa** may be applied as a promising fluorescent probe for sensing metal cations, especially for Ce^{3+}.[14]

Conclusions

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In summary, employment of a oxidizing directing group O−NHAc, a rhodium(III)-catalyzed redox-neutral cascade [3+2] annulation of *N*-aryloxyacetamides and 3-(hetero)arylpropiolic acids affording benzofuran-2(3*H*)-ones was developed. This methodology features exclusive Z-configuration selectivity, moderate yields, broad substrate scope, and good functional group compatibility to provide an access to (*Z*)-3-aminomethylene benzofuran-2-one derivatives. Considering the valuable structure of the products, together with good emission sensitivity towards cerium (Ce^{3+}), this cascade annulation may have potential synthetic utility.

Experimental

General Information

All commercially available chemicals were used as received. $[Cp^*RhCl_2]_2$, (98%, Energy), $[Cp^*IrCl_2]_2$, (98%, Energy), and $[Cp^*RuCl_2]n$ (98%, Adamas-beta) were purchased from commercial suppliers. Other transition metal catalysts, such as $[Cp^*Rh(OAc)_2]_2$[15a], $[Cp^*Rh(MeCN)_3](SbF_6)_2$[15b], $[Cp^*CoI_2(CO)]$[15c], $[Cp^*Co(MeCN)_3](SbF_6)_2$[15d], were prepared according to the reported literatures. All reactions were carried out under an argon atmosphere in oven-dried glassware, unless otherwise noted. Thin layer chromatography (TLC) was performed on precoated glass plates (HSGF254, Huanghai) and visualized by irradiation under a 254 nm UV lamp. Flash column chromatography was carried out using silica gel (200 – 300 mesh, Greagent), eluting with a mixture of petroleum ether (b.p. 60 – 90 °C) and ethyl acetate at increased pressure. 1H NMR and 13C NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer in the indicated deuterated solvents. The residual solvent peak was used as an internal reference (CDCl3: δH = 7.26 ppm, δC = 77.16 ppm; DMSO-d6: δH = 2.50 ppm, δC =39.52 ppm; acetone-d6: δH = 2.05 ppm, δC = 29.84 ppm). Data were reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet, and associated combinations, e.g. dd = doublet of doublets), coupling constant (J) in Hertz (Hz), and integration. High-resolution mass spectra (HRMS) were obtained on a Waters ACQUITYTM UPLC & Q-TOF MS Premier using the electrospray ionization (ESI) technique. Melting points (m.p.) were measured on a WRS-1B digital melting point apparatus (Shanghai Precision & Scientific Instrument Co., Ltd) and were uncorrected. X-ray diffraction data were collected on a Bruker D8 VENTURE diffractometer. UV-Visible absorption spectra were recorded on a SHIMADZU UV-2700 UV-VIS Spectrophotometer. Fluorescence spectra were a PerkinElmer LS 55 Luminescence Spectrometer. Substrates synthesis are described in the ESI.

General procedure

An oven-dried 15-mL test tube equipped with a Teflon-coated magnetic stir bar was sequentially charged with acetamide 1 (0.2 mmol, 1.0 equiv), acid 2 (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$

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(1.2 mg, 2 μmol, 1.0 mol %), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and 2,2,2-trifluoroethanol (2.0 mL) under a positive pressure of argon. After sealing the tube with PTFE-lined screw cap, the mixture was heated at 80 °C (oil bath) for 12 h. Then the reaction mixture was cooled to ambient temperature, transferred to 25-mL round bottom flask, and washed with CH2Cl2 (2 mL × 3). The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph on silica gel using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to provide the desired product **3**.

(*Z*)-3-(Amino(phenyl)methylene)benzofuran-2(3H)-one (3aa). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3aa** (25.2 mg, 53% yield) as a yellow solid. mp 189 – 191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 7.63 – 7.56 (m, 5H), 7.08 (dd, J = 8.0, 0.7 Hz, 1H), 7.02 (td, J = 7.4, 1.2 Hz, 1H), 6.79 (td, J = 7.6, 1.2 Hz, 1H), 6.35 (dd, J = 7.7, 0.7 Hz, 1H), 5.54 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 161.1, 149.9, 135.0, 131.2, 129.5, 127.7, 125.3, 124.4, 122.8, 118.4, 110.2, 90.9. HRMS (ESI) *m/z* calculated for $C_{15}H_{12}NO_2^+$ [M+H$^+$] 238.0863, found 238.0866.

(*Z*)-3-(Amino(phenyl)methylene)-7-methylbenzofuran-2(3*H*)-one (3ba). According to the general procedure, the reaction was carried out using **1b** (33.0 mg, 0.2 mmol), **2a** (29.2 mg, 0.2 mmol) and $[Cp^*RhCl_2]_2$ (3.0 mg, 2.5 mol %). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ba** (32.6 mg, 65% yield) as a yellow solid. mp 191 – 193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 7.62 – 7.52 (m, 5H), 6.85 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.18 (d, J = 7.6 Hz, 1H), 5.58 (brs, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 161.2, 148.3, 134.9, 131.1, 129.4, 127.7, 125.9, 124.7, 122.6, 120.2, 116.0, 91.3, 15.1. HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_2^+$ [M+H$^+$] 252.1019, found 252.1023.

(*Z*)-3-(Amino(phenyl)methylene)-7-ethylbenzofuran-2(3*H*)-one (3ca). According to the general procedure, the reaction was carried out using **1c** (35.8 mg, 0.2 mmol), **2a** (29.2 mg, 0.2 mmol) and $[Cp^*RhCl_2]_2$ (3.0 mg, 2.5 mol %). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ca** (32.5 mg, 61% yield) as a yellow solid. **mp** 156 – 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 7.62 – 7.53 (m, 5H), 6.89 (d, J = 7.6 Hz, 1H), 6.73 (t, J = 7.7 Hz, 1H), 6.19 (dd, J = 7.7, 0.9 Hz, 1H), 5.53 (brs, 1H), 2.74 (q, J = 7.6 Hz, 1H), 1.26 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 161.0, 147.9, 135.0, 131.1, 129.4, 127.7, 126.5, 124.8, 124.4, 122.8, 116.1, 91.4, 22.9, 14.4. HRMS (ESI) *m/z* calculated for $C_{17}H_{16}NO_2^+$ [M+H$^+$] 266.1176, found 266.1176.

(*Z*)-3-(Amino(phenyl)methylene)-7-isopropylbenzofuran-2(3*H*)-one (3da). According to the general procedure, the reaction was carried out using **1d** (38.6 mg, 0.2 mmol), **2a** (29.2 mg, 0.2 mmol) and $[Cp^*RhCl_2]_2$ (3.0 mg, 2.5 mol %). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3da** (31.3 mg, 56% yield) as a yellow solid. **mp** 145 – 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (brs. 1H), 7.63 – 7.53 (m, 5H), 6.94 – 6.92 (m, 1H), 6.75 (t, J = 7.7 Hz, 1H), 6.18 (dd, J = 7.7, 1.1 Hz, 1H), 5.45 (brs, 1H), 3.35 – 3.24 (m, 1H), 1.30 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 161.0, 147.4, 135.0, 131.1, 131.0, 129.4, 127.7, 124.9, 122.8, 121.8, 116.0, 91.4, 28.2, 22.6. HRMS (ESI) *m/z* calculated for $C_{18}H_{18}NO_2^+$ [M+H$^+$] 280.1332, found 280.1341.

(*Z*)-3-(Amino(phenyl)methylene)-7-chlorobenzofuran-2(3*H*)-one (3ea). According to the general procedure, the reaction was carried out using **1e** (37.1 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ea** (32.7 mg, 60% yield) as a yellow solid. mp 195 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (brs, 1H), 7.63 – 7.53 (m, 5H), 7.00 (d, J = 8.1 Hz, 1H), 6.71 (t, J = 7.9 Hz, 1H), 6.21 (d, J = 7.8 Hz, 1H), 5.74 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 162.4, 145.7, 134.4, 131.5, 129.6, 127.6, 127.0, 124.5, 123.5, 116.6, 115.6, 90.5. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}ClNO_2^+$ [M+H$^+$] 272.0473, found 272.0473.

(*Z*)-3-(Amino(phenyl)methylene)-6-methylbenzofuran-2(3*H*)-one (3fa). According to the general procedure, the reaction was carried out using **1f** (33.0 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3fa** (25.6 mg, 51% yield) as a yellow solid. mp 196 – 198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (brs, 1H), 7.62 – 7.52 (m, 5H), 6.91 (s, 1H), 6.62 – 6.59 (m, 1H), 6.24 (d, J = 7.9 Hz, 1H), 5.47 (brs, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.3, 150.1, 135.1, 134.7, 131.1, 129.4, 127.7, 123.5, 122.4, 118.1, 110.8, 91.1, 21.6. HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_2^+$ [M+H$^+$] 252.1019, found 252.1019.

(*Z*)-3-(Amino(phenyl)methylene)-6-(trifluoromethyl)benzofuran-2(3*H*)-one (3ga). According to the general procedure, the reaction was carried out using **1g** (43.8 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3ga** (35.9 mg, 59% yield) as a yellow solid. mp 192 – 194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (brs, 1H), 7.67 – 7.54 (m, 5H), 7.29 (d, J = 0.7 Hz, 1H), 7.05 (dd, J = 8.1, 0.7 Hz, 1H), 6.38 (d, J = 8.1 Hz, 1H), 5.88 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 163.1, 149.2, 134.3, 131.7, 129.7, 129.0, 127.5, 126.1 (q, J = 32.8 Hz), 121.6 (q, J = 271.5 Hz), 120.0 (q, J = 3.9 Hz), 118.1, 107.2 (q, J = 3.9 Hz), 90.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.6. HRMS (ESI) *m/z* calculated for $C_{16}H_{11}F_3NO_2^+$ [M+H$^+$] 306.0736, found 306.0747.

(*Z*)-3-(Amino(phenyl)methylene)-6-methoxybenzofuran-2(3*H*)-one (3ha). According to the general procedure, the reaction was carried out using **1h** (36.2 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3ha** (22.5 mg, 42% yield) as a yellow solid. mp 213 – 214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (brs, 1H), 7.61 – 7.52 (m, 5H), 6.70 (d, J = 2.4 Hz, 1H), 6.38 (dd, J = 8.6, 2.4 Hz, 1H), 6.26 (d, J = 8.6 Hz, 1H), 5.34 (brs, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 159.3, 157.8, 150.9, 135.3, 131.1, 129.5, 127.7, 118.9, 118.0, 108.9, 97.0, 91.0, 55.8. HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_3^+$ [M+H$^+$] 268.0968, found 268.0967.

(*Z*)-3-(Amino(phenyl)methylene)-6-chlorobenzofuran-2(3*H*)-one (3ia). According to the general procedure, the reaction was carried out using **1i** (37.1 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3ia** (30.7 mg, 56% yield) as a yellow solid. **mp** 179 – 181 °C. ^{1}H NMR (400 MHz,

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$CDCl_3$) δ 8.84 (brs, 1H), 7.64 – 7.53 (m, 5H), 7.08 (d, J = 1.9 Hz, 1H), 6.77 (dd, J = 8.3, 1.9 Hz, 1H), 6.23 (d, J = 8.3 Hz, 1H), 5.63 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 161.5, 150.0, 134.7, 131.5, 129.6, 129.6, 127.6, 124.0, 123.0, 118.9, 110.9, 90.2. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}ClNO_2^+$ [M+H$^+$] 272.0473, found 272.0482.

(*Z*)-3-(Amino(phenyl)methylene)-5-methylbenzofuran-2(3*H*)-one (3ja). According to the general procedure, the reaction was carried out using **1j** (33.0 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3ja** (18.5 mg, 37% yield) as a yellow solid. **mp** 173 – 175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (brs, 1H), 7.64 – 7.54 (m, 5H), 6.96 (d, J = 8.1 Hz, 1H), 6.83 (dd, J = 8.1, 1.1 Hz, 1H), 6.14 (d, J = 0.5 Hz, 1H), 5.51 (brs, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 160.9, 148.1, 135.0, 132.0, 131.2, 129.4, 127.7, 125.1, 125.0, 119.0, 109.7, 91.1, 21.5. HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_2^+$ [M+H$^+$] 252.1019, found 252.1019.

(*Z*)-3-(Amino(phenyl)methylene)-5-phenylbenzofuran-2(3*H*)-one (3ka). According to the general procedure, the reaction was carried out using **1k** (45.5 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ka** (30.3 mg, 48% yield) as a yellow solid. **mp** 200 – 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (brs, 1H), 7.64 – 7.56 (m, 5H), 7.36 – 7.23 (m, 6H), 7.14 (d, J = 8.3 Hz, 1H), 6.57 (d, J = 1.8 Hz, 1H), 5.63 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 161.4, 149.5, 141.4, 136.0, 134.9, 131.4, 129.5, 128.8, 127.7, 126.9, 126.8, 125.8, 123.5, 117.2, 110.3, 90.9. HRMS (ESI) *m/z* calculated for $C_{21}H_{16}NO_2^+$ [M+H$^+$] 314.1176, found 314.1184.

(*Z*)-3-(Amino(phenyl)methylene)-5-(trifluoromethoxy)benzofuran-2(3*H*)-one (3la). According to the general procedure, the reaction was carried out using **1l** (47.0 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3la** (36.9 mg, 57% yield) as a yellow solid. **mp** 181 – 182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (brs, 1H), 7.66 – 7.54 (m, 5H), 7.04 (d, J = 8.6 Hz, 1H), 6.88 – 6.85 (m, 1H), 6.16 – 6.15 (m, 1H), 5.74 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 162.3, 147.9, 144.7 (d, J = 2.0 Hz), 134.2, 131.7, 129.7, 127.5, 126.6, 120.5 (q, J = 256.2 Hz), 117.0, 111.7, 110.6, 90.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.4. HRMS (ESI) *m/z* calculated for $C_{16}H_{11}F_3NO_3^+$ [M+H$^+$] 322.0686, found 322.0689.

(*Z*)-3-(Amino(phenyl)methylene)-5-fluorobenzofuran-2(3*H*)-one (3ma). According to the general procedure, the reaction was carried out using **1m** (33.8 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ma** (31.8 mg, 62% yield) as a yellow solid. mp 193 – 195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (brs, 1H), 7.65 – 7.53 (m, 5H), 6.97 (dd, J = 8.7, 4.4 Hz, 1H). 6.69 (td, J = 9.0, 2.7 Hz, 1H), 6.01 (dd, J = 9.4, 2.7 Hz, 1H), 5.73 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 162.0, 159.0 (d, J = 237.6 Hz), 145.7, 134.4, 131.6, 129.6, 127.5, 126.5 (d, J = 10.5 Hz), 110.6 (d, J = 2.8 Hz), 110.4 (d, J = 13.1 Hz), 105.5 (d, J = 27.5 Hz), 91.0 (d, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}FNO_2^+$ [M+H$^+$] 256.0768, found 256.0765.

(*Z*)-3-(Amino(phenyl)methylene)-5-chlorobenzofuran-2(3*H*)-one (3na). According to the general procedure, the reaction was carried out using **1n** (37.1 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3na** (31.2 mg, 57% yield) as a yellow solid. mp 224 – 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (brs, 1H), 7.66 – 7.53 (m, 5H), 7.00 – 6.95 (m, 2H), 6.28 (s, 1H), 5.69 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 162.1, 148.2, 134.4, 131.7, 129.7, 128.1, 127.5, 126.9, 124.0, 118.3, 111.1, 90.3. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}ClNO_2^+$ [M+H$^+$] 272.0473, found 272.0467.

(*Z*)-3-(Amino(phenyl)methylene)-5-bromobenzofuran-2(3*H*)-one (3oa). According to the general procedure, the reaction was carried out using **1o** (46.0 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3oa** (36.8 mg, 58% yield) as a yellow solid. mp 217 – 218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (brs, 1H), 7.67 – 7.53 (m, 5H), 7.13 (dd, J = 8.4, 2.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.42 (d, J = 2.0 Hz, 1H), 5.66 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 162.1, 148.6, 134.4, 131.7, 129.7, 127.5, 127.4, 126.9, 121.2, 115.7, 111.6, 90.1. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}BrNO_2^+$ [M+H$^+$] 315.9968, found 315.9974.

(*Z*)-3-(Amino(phenyl)methylene)naphtho[2,3-*b*]furan-2(3*H*)-one (3pa). According to the general procedure, the reaction was carried out using **1q** (40.2 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3qa** (31.8 mg, 55% yield) as a yellow solid. mp 216 – 218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (brs, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.70 – 7.60 (m, 5H), 7.43 (s, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.23 (m, 1H), 6.71 (s, 1H), 5.57 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 161.4, 149.5, 135.0, 131.4, 130.5, 129.6, 127.7, 127.7, 127.5, 126.2, 124.9, 124.4, 116.0, 105.6, 90.2. HRMS (ESI) *m/z* calculated for $C_{19}H_{14}NO_2^+$ [M+H$^+$] 288.1019, found 288.1030.

(*Z*)-3-(Amino(phenyl)methylene)-5-fluoro-7-methylbenzofuran-2(3*H*)-one (3qa). According to the general procedure, the reaction was carried out using **1q** (36.6 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ra** (35.3 mg, 66% yield) as a yellow solid. mp 213 – 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (brs, 1H), 7.63 – 7.52 (m, 5H), 6.54 (ddd, J = 10.0, 2.6, 0.6 Hz, 1H), 5.86 – 5.83 (m, 1H), 5.66 (brs, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 161.9, 158.8 (d, J = 237.1 Hz), 144.2 (d, J = 1.4 Hz), 134.4, 131.5, 129.6, 127.5, 125.6 (d, J = 11.6 Hz), 121.3 (d, J = 8.9 Hz), 112.0 (d, J = 24.4 Hz), 102.9 (d, J = 27.2 Hz), 91.4 (d, J = 3.1 Hz), 15.2 (d, J = 1.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.8. HRMS (ESI) *m/z* calculated for $C_{16}H_{13}FNO_2^+$ [M+H$^+$] 270.0925, found 270.0930.

(*Z*)-3-(Amino(phenyl)methylene)-5,6-dichlorobenzofuran-2(3*H*)-one (3ra). According to the general procedure, the reaction was carried out using **1r** (44.0 mg, 0.2 mmol) and **2a** (29.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3sa** (31.3 mg, 51% yield) as a yellow solid. **mp** 286 – 288 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.23 (brs, 1H), 8.93 (brs, 1H), 7.72 – 7.62 (m, 3H), 7.57 – 7.54 (m, 2H), 7.41 (s, 1H), 5.91 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.5, 164.5, 147.3, 133.8, 131.2, 129.3, 127.6, 127.1, 124.6, 124.3, 117.5, 111.5, 85.9. HRMS (ESI) *m/z* calculated for $C_{15}H_{10}Cl_2NO_2^+$ [M+H$^+$] 306.0083, found 306.0081.

(*Z*)-3-(Amino(p-tolyl)methylene)benzofuran-2(3*H*)-one (3ab). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2b** (32.0 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ab** (26.2 mg, 52% yield) as a yellow solid. mp 161 – 163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 7.07 (dd, J = 7.9, 0.7 Hz, 1H), 7.02 (td, J = 7.9, 1.2 Hz, 1H), 6.80 (dd, J = 7.5, 1.3 Hz, 1H), 6.45 (dd, J = 7.7, 0.7 Hz, 1H), 5.55 (brs, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 161.5, 149.8, 141.7, 132.1, 130.1, 127.6, 125.5, 124.2, 122.7, 118.5, 110.1, 90.7, 21.7. HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_2^+$ [M+H$^+$] 252.1019, found 252.1026.

(*Z*)-3-([1,1'-Biphenyl]-4-yl(amino)methylene)benzofuran-2(3*H*)-one (3ac). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2c** (44.4 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ac** (35.2 mg, 56% yield) as a yellow solid. mp 197 – 198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (brs, 1H), 7.79 – 7.78 (m, 2H), 7.70 – 7.64 (m, 4H), 7.53 – 7.50 (m, 2H), 7.46 – 7.42 (m, 1H), 7.11 – 7.09 (m, 1H), 7.04 (td, J = 7.7, 1.1 Hz, 1H), 6.82 (td, J = 7.6, 1.0 Hz, 1H), 6.53 – 6.51 (m, 1H), 5.61 (brs,1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 160.9, 149.9, 144.1, 139.8, 133.7, 129.2, 128.4, 128.3, 128.0, 127.3, 125.3, 124.5, 122.8, 118.5, 110.2, 90.9. HRMS (ESI) *m/z* calculated for $C_{21}H_{16}NO_2^+$ [M+H$^+$] 314.1176, found 314.1180.

(*Z*)-3-(Amino(4-methoxyphenyl)methylene)benzofuran-2(3*H*)-one (3ad). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2d** (35.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3ad** (25.2 mg, 47% yield) as a yellow solid. mp 137 – 139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (brs, 1H), 7.54 – 7.50 (m, 2H), 7.08 – 7.00 (m, 4H), 6.82 (td, J = 7.6, 1.3 Hz, 1H), 6.53 (dd, J = 7.7, 0.7 Hz, 1H), 5.57 (brs, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 162.0, 161.3, 149.8, 129.4, 127.1, 125.6, 124.2, 122.7, 118.4, 114.7, 110.1, 90.5, 55.6. HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_3$ [M+H$^+$] 268.0968, found 268.0973.

(*Z*)-3-(Amino(4-(methylthio)phenyl)methylene)benzofuran-2(3*H*)-one (3ae). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2e** (38.4 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3ae** (29.8 mg, 53% yield) as a yellow solid. mp 156 – 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 7.51 – 7.48 (m, 2H), 7.38 – 7.35 (m, 2H), 7.09 – 7.07 (m, 1H), 7.05 – 7.01 (m, 1H), 6.84-6.80 (m, 1H), 6.52 – 6.50 (m, 1H), 5.55 (brs, 1H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 160.8, 149.8, 143.4, 130.9, 128.2, 126.1, 125.3, 124.4, 122.8, 118.5, 110.2, 90.7, 15.1. HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_2S^+$ [M+H$^+$] 284.0740, found 284.0757.

(*Z*)-3-(Amino(4-(trifluoromethoxy)phenyl)methylene)benzofuran-2(3*H*)-one (3af). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2f** (46.0 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3af** (36.7 mg, 57% yield) as a yellow solid. mp 152 – 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 7.66 – 7.62 (m, 2H), 7.42 – 7.40 (m, 2H), 7.09 – 7.02 (m, 2H), 6.84 – 6.80 (m, 1H), 6.34 – 6.32 (m, 1H), 5.64 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 159.3, 151.2, 150.0, 133.3, 129.7, 124.8, 124.8, 122.9, 121.7, 120.5 (q, J = 258.7 Hz), 118.2, 110.4, 91.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.7. HRMS (ESI) *m/z* calculated for $C_{16}H_{11}F_3NO_3^+$ [M+H$^+$] 322.0686, found 322.0691.

(*Z*)-3-(Amino(4-fluorophenyl)methylene)benzofuran-2(3*H*)-one (3ag). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2g** (32.8 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ag** (27.1 mg, 53% yield) as a yellow solid. mp 188 – 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 7.61 – 7.56 (m, 2H), 7.29 – 7.23 (m, 2H), 7.10 – 7.02 (m, 2H), 6.82 (dd, J = 7.5, 1.4 Hz, 1H), 6.38 (dd, J = 7.6, 0.5 Hz, 1H), 5.55 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 164.3 (d, J = 251.9 Hz), 160.0, 149.9, 131.0 (d, J = 3.6 Hz), 130.0 (d, J = 8.5 Hz), 125.1, 124.6, 122.9, 118.3, 116.7 (d, J = 22.0 Hz), 110.3, 91.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.0. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}FNO_2^+$ [M+H$^+$] 256.0768, found 256.0772.

(*Z*)-3-(Amino(3-fluorophenyl)methylene)benzofuran-2(3*H*)-one (3ah). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2h** (32.8 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ah** (28.2 mg, 55% yield) as a yellow solid. **mp** 163 – 164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (brs, 1H), 7.58 – 7.52 (m, 1H), 7.38 – 7.36 (m, 1H), 7.32 – 7.27 (m, 2H), 7.09 – 7.02 (m, 2H), 6.84 – 6.80 (m, 1H), 6.36 (d, J = 7.6 Hz, 1H), 5.64 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.0, 163.0 (d, J = 249.5 Hz), 159.2 (d, J = 1.9 Hz), 150.0, 136.8 (d, J = 7.8 Hz), 131.4 (d, J = 8.1 Hz), 124.8, 124.7, 123.6 (d, J = 3.2 Hz), 122.9, 118.4, 118.2 (d, J = 21.0 Hz), 115.0 (d, J = 23.1 Hz), 110.3, 91.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.2. **HRMS** (ESI) *m/z* calculated for $C_{15}H_{11}FNO_2^+$ [M+H$^+$] 256.0768, found 256.0769.

(*Z*)-3-(Amino(2-fluorophenyl)methylene)benzofuran-2(3*H*)-one (3ai). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol), **2i** (32.8 mg, 0.2 mmol) and $[Cp^*RhCl_2]_2$ (3.0 mg, 2.5 mol %). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ai** (12.1 mg, 24% yield) as a yellow solid. mp 196 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 7.63 – 7.57 (m, 1H), 7.52 – 7.48 (m, 1H), 7.37 – 7.33 (m, 1H), 7.32 – 7.28 (m, 1H), 7.10 – 7.08 (m, 1H), 7.06 – 7.02 (m, 1H), 6.83 – 6.79 (m, 1H), 6.18 (d, J = 7.6 Hz, 1H), 5.49 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 159.1 (d, J = 251.9 Hz), 154.6, 150.1, 133.0 (d, J = 8.0 Hz), 130.0 (d, J = 2.3 Hz), 125.2 (d, J = 3.8 Hz), 124.9, 124.8, 123.1, 122.6 (d, J = 15.3 Hz), 118.1, 117.0 (d, J = 20.8 Hz), 110.3, 92.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}FNO_2^+$ [M+H$^+$] 256.0768, found 256.0771.

(*Z*)-3-(Amino(4-chlorophenyl)methylene)benzofuran-2(3*H*)-one (3aj). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2j** (36.1 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3aj** (31.2 mg, 57% yield) as a yellow solid. mp 178 – 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (brs, 1H), 7.53 – 7.51 (m, 4H), 7.08 – 7.02 (m, 2H), 6.84 – 6.80 (m, 1H), 6.39 – 6.37 (m, 1H), 5.65 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 159.6, 150.0, 137.4, 133.3, 129.8, 129.3, 124.9, 124.7, 122.9, 118.4, 110.3, 91.2. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}ClNO_2^+$

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[M+H$^+$] 272.0473, found 272.0473.

(*Z*)-3-(Amino(4-bromophenyl)methylene)benzofuran-2(3*H*)-one (3ak). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2k** (45.0 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ak** (36.8 mg, 58% yield) as a yellow solid. mp 170 – 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (brs, 1H), 7.72 – 7.68 (m, 2H), 7.47 – 7.44 (m, 2H), 7.09 – 7.02 (m, 2H), 6.84 – 6.80 (m, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 5.59 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 159.6, 149.9, 133.7, 132.8, 129.4, 125.7, 124.9, 124.7, 122.9, 118.4, 110.3, 91.2. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}BrNO_2^+$ [M+H$^+$] 315.9968, found 315.9972.

(*Z*)-3-(Amino(4-(hydroxymethyl)phenyl)methylene)benzofuran-2(3*H*)-one (3al). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2l** (35.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 4:1→1:2) afforded the title compound **3al** (30.0 mg, 56% yield) as a yellow solid. mp 208 – 209 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.95 (brs, 1H), 7.67 (brs, 1H), 7.62 – 7.57 (m, 4H), 7.04 (dd, *J* = 7.9, 0.8 Hz, 1H), 6.99 (td, *J* = 7.4, 1.2 Hz, 1H), 6.76 (td, *J* = 7.5, 1.3 Hz, 1H), 6.32 (dd, *J* = 7.8, 0.8 Hz, 1H), 4.79 (d, *J* = 5.7 Hz, 2H), 4.52 (t, *J* = 5.7 Hz, 1H). ^{13}C NMR (101 MHz, acetone-d_6) δ 171.0, 163.7, 150.3, 146.6, 134.2, 128.5, 127.8, 126.8, 124.4, 123.2, 118.8, 110.3, 89.5, 64.1 (64.0). HRMS (ESI) *m/z* calculated for $C_{16}H_{14}NO_3^+$ [M+H$^+$] 268.0968, found 268.0982.

(*Z*)-4-(Amino(2-oxobenzofuran-3(2*H*)-lidene)methyl)benzaldehyde (3am). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2m** (34.8 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 4:1→1:1) afforded the title compound **3am** (31.0 mg, 58% yield) as a yellow solid. mp 166 – 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.84 (brs, 1H), 8.08 – 8.05 (m, 2H), 7.76 – 7.74 (m, 2H), 7.09 – 7.01 (m, 2H), 6.80 – 6.76 (m, 1H), 6.25 – 6.23 (m, 1H), 5.71 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 170.9, 159.1, 150.0, 140.4, 138.0, 130.6, 128.7, 125.0, 124.6, 123.0, 118.3, 110.4, 91.5. HRMS (ESI) *m/z* calculated for $C_{16}H_{12}NO_3^+$ [M+H$^+$] 266.0812, found 266.0809.

(*Z*)-3-((4-Acetylphenyl)(amino)methylene)benzofuran-2(3*H*)-one (3an). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2n** (37.6 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 4:1→1:1) afforded the title compound **3an** (33.3 mg, 60% yield) as a yellow solid. mp 176 – 178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 8.12 – 8.10 (m, 2H), 7.69 – 7.66 (m, 2H), 7.08 – 7.01 (m, 2H), 6.80 – 6.76 (m, 1H), 6.28 – 6.26 (m, 1H), 5.72 (brs, 1H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 170.9, 159.6, 150.0, 139.1, 139.0, 129.3, 128.2, 124.8, 124.8, 122.9, 118.3, 110.3, 91.3, 26.9. HRMS (ESI) *m/z* calculated for $C_{17}H_{14}NO_3^+$ [M+H$^+$] 280.0968, found 280.0969.

(*Z*)-4-(Amino(2-oxobenzofuran-3(2*H*)-ylidene)methyl)benzonitrile (3ao). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2o** (34.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 4:1→1:1) afforded the title compound **3ao** (34.2 mg, 65% yield) as a yellow solid. mp 200 – 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (brs, 1H), 7.89 – 7.87 (m, 2H), 7.73 – 7.71 (m, 2H), 7.11 – 7.05 (m, 2H), 6.84 – 6.80 (m, 1H), 6.22 (d, *J* = 7.6 Hz, 1H), 5.48 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 157.9, 150.2, 139.2, 133.3, 128.8, 125.3, 124.3, 123.1, 118.2, 117.9, 115.1, 110.6, 91.9. HRMS (ESI) *m/z* calculated for $C_{16}H_{11}N_2O_2^+$ [M+H$^+$] 263.0815, found 263.0819.

(*Z*)-3-(Amino(4-(trifluoromethyl)phenyl)methylene)benzofuran-2(3*H*)-one (3ap). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2p** (42.8 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3ap** (37.2 mg, 61% yield) as a yellow solid. **mp** 162 – 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.03 (m, 2H), 6.84 – 6.79 (m, 1H), 6.27 (d, *J* = 7.6 Hz, 1H), 5.56 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 159.0, 150.0, 138.4, 133.1 (q, *J* = 32.9 Hz), 128.4, 126.5 (q, *J* = 3.7 Hz), 125.0, 124.6, 123.7 (q, *J* = 272.8 Hz), 123.0, 118.3, 110.4, 91.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8. HRMS (ESI) *m/z* calculated for $C_{16}H_{11}F_3NO_2^+$ [M+H$^+$] 306.0736, found 306.0739.

(*Z*)-3-(Amino(4-nitrophenyl)methylene)benzofuran-2(3*H*)-one (3aq). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2q** (38.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 6:1→3:1) afforded the title compound **3aq** (38.0 mg, 67% yield) as a yellow solid. mp 219 – 221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (brs, 1H), 8.46 – 8.43 (m, 2H), 7.81 – 7.78 (m, 2H), 7.12 – 7.06 (m, 2H), 6.83 – 6.79 (m, 1H), 6.24 – 6.22 (m, 1H), 5.42 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 157.4, 150.3, 149.5, 140.9, 129.3, 125.5, 124.9, 124.2, 123.2, 118.2, 110.7, 92.2. HRMS (ESI) *m/z* calculated for $C_{15}H_{11}N_2O_4^+$ [M+H$^+$] 283.0713, found 283.0714.

(*Z*)-3-(Amino(3,5-dimethylphenyl)methylene)benzofuran-2(3*H*)-one (3ar). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2r** (34.8 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 10:1→6:1) afforded the title compound **3ar** (27.4 mg, 52% yield) as a yellow solid. mp 174 – 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 7.22 (s, 1H), 7.17 (s, 2H), 7.08 – 7.06 (m, 1H), 7.04 – 7.00 (m, 1H), 6.81 (td, *J* = 7.6, 1.2 Hz, 1H), 6.43 – 6.41 (m, 1H), 5.60 (brs, 1H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 161.9, 149.8, 139.2, 134.8, 132.7, 125.5, 125.2, 124.1, 122.7, 118.5, 110.1, 90.5, 21.4. HRMS (ESI) *m/z* calculated for $C_{17}H_{16}NO_2^+$ [M+H$^+$] 266.1176, found 266.1175.

(*Z*)-3-(Amino(3,4-dichlorophenyl)methylene)benzofuran-2(3*H*)-one (3as). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol), **2s** (43.0 mg, 0.2 mmol) and $[Cp^*RhCl_2]_2$ (3.0 mg, 2.5 mol %). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3as** (37.4 mg, 61% yield) as a yellow solid. mp 179 – 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (brs, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.44 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.88 – 6.84 (m, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 5.52 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 158.0, 150.0, 135.6, 134.5, 134.0, 131.6, 129.8, 127.3, 125.0, 124.5, 123.1, 118.3, 110.4, 91.4. HRMS (ESI) *m/z* calculated for $C_{15}H_{10}Cl_2NO_2^+$ [M+H$^+$] 306.0083, found 306.0082.

(*Z*)-3-(Amino(naphthalen-2-yl)methylene)benzofuran-2(3*H*)-one (3at). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2t** (39.2 mg, 0.2 mmol). Purification of the crude product by flash column chromatography

on silica gel (PE/EA 8:1→5:1) afforded the title compound **3at** (34.2 mg, 60% yield) as a yellow solid. mp 177 – 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (brs, 1H), 8.09 (d, J = 1.0 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.09 (dd, J = 8.0, 0.6 Hz, 1H), 7.02 (td, J = 7.7, 1.2 Hz, 1H), 6.73 (td, J = 7.6, 1.2 Hz, 1H), 6.36 (dd, J = 7.8, 0.8 Hz, 1H), 5.64 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 161.2, 149.9, 134.4, 133.1, 132.3, 129.4, 128.7, 128.1, 128.0, 127.7, 127.4, 125.3, 124.6, 124.4, 122.8, 118.5, 110.2, 91.0. HRMS (ESI) *m/z* calculated for $C_{19}H_{14}NO_2^+$ [M+H$^+$] 288.1019, found 288.1027.

(*Z*)-3-(Amino(thiophen-2-yl)methylene)benzofuran-2(3*H*)-one (3au). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2u** (30.4 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→5:1) afforded the title compound **3au** (32.0 mg, 66% yield) as a yellow solid. mp 185 – 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (brs, 1H), 7.61 (dd, J = 5.0, 1.2 Hz, 1H), 7.54 (dd, J = 3.6, 1.2 Hz, 1H), 7.23 (dd, J = 5.0, 3.6 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.90 – 6.86 (m, 1H), 6.83 – 6.81 (m, 1H), 5.47 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 153.6, 149.9, 134.9, 130.1, 129.3, 128.2, 125.0, 124.9, 122.9, 118.7, 110.3, 92.1. HRMS (ESI) *m/z* calculated for $C_{13}H_{10}NO_2S^+$ [M+H$^+$] 244.0427, found 244.0435.

(*Z*)-3-(Amino(thiophen-3-yl)methylene)benzofuran-2(3*H*)-one (3av). According to the general procedure, the reaction was carried out using **1a** (30.2 mg, 0.2 mmol) and **2v** (30.4 mg, 0.2 mmol). Purification of the crude product by flash column chromatography on silica gel (PE/EA 8:1→4:1) afforded the title compound **3av** (26.9 mg, 55% yield) as a yellow solid. mp 206 – 207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 7.73 (dd, J = 2.9, 1.2 Hz, 1H), 7.55 (dd, J = 5.0, 3.0 Hz, 1H). 7.33 (dd, J = 5.0, 1.1 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.87 (td, J = 7.5, 1.3 Hz, 1H), 6.65 (d, J = 7.4 Hz, 1H), 5.46 (brs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 155.9, 149.9, 135.7, 127.9, 127.1, 127.0, 125.2, 124.6, 122.9, 118.5, 110.3, 91.4. HRMS (ESI) *m/z* calculated for $C_{13}H_{10}NO_2S^+$ [M+H$^+$] 244.0427, found 244.0425.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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