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Selective cyclization of alkynols and alkynylamines catalyzed by potassium *tert*-butoxide

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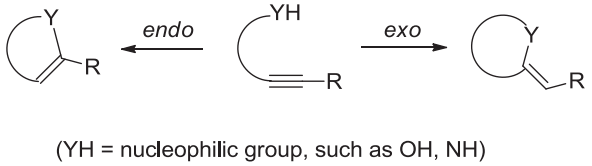
ABSTRACT

Potassium *tert*-butoxide (*t*-BuOK) was found to be an effective catalyst for the cyclization of aromatic alkynols and alkynylamines. In the presence of 10 mol % *t*-BuOK, a range of alkynols were converted to the corresponding *exo*-cyclic enol ethers as pure *Z*-stereoisomers with 100% selectivity and moderate to excellent yields. Moreover, the cyclization of alkynylamines was also achieved to afford indoles and isoindolin-1-ones in good yields.

1. Introduction

Heteroatom-containing compounds are useful building blocks for synthesizing a diverse range of natural products with biological activity.[1] The intramolecular addition of heteroatom–hydrogen bonds across the carbon–carbon triple bond provides a straightforward approach to heterocyclics with 100% atom efficiency, fulfilling the requirements of green chemistry.[2] For example, alkynols and alkynylamines, which are important synthons for numerous structurally fascinating heterocyclic compounds,[3] can undergo cycloisomerization to yield *exo*- or *endo*-heterocycles containing O or N (Scheme 1).[4] *endo*-Cyclization of alkynols has been achieved using Mo, W,[5] Ru,[6] Rh,[7] Ag, Pd and Au complexes or salts[8] as catalysts. Recently, *endo*-iodocyclization of alcohols has also been developed in the presence of I_2/$NaHCO_3$.[9] *endo*-Cyclization of alkynylamines generating indoles, dihydroisoquinolines and dihydroquinolines has also been achieved with diverse catalysts: Cr, Mo, W,[10] Rh,[11] Pd,[12] Ru[13] Cu,[14] $Hg(OTf)_2$,[15] Pt,[16] Et_2Zn,[17] Ir.[18]



Scheme 1. Alkyne nucleophile *endo*- or *exo*-cycloisomerization.

Cyclization of alkynols giving *exo*-cyclic enol ethers was first achieved by the use of HgO and $BF_3 \cdot Et_2O$ as the catalysts.[19] Several more catalysts were later found to work well in this reaction: organolanthanide complexes of the form $Ln[N(SiMe_3)_2]_3$, where Ln refers to La, Sm, Y, Lu, Nd;[20] heavier alkaline earth bis(trimethylsilyl)amides;[21] Bu_4NF;[22] and transition metal catalysts, such as $Pd(OAc)_2$,[23] Ag_2CO_3,[24] AuCl,[25] $Cu(OTf)_2$[26] and the Cu(NHC)(Me) complex.[27] Tandem *exo*-cyclization/isomerization reactions of alkynols, which firstly generate *exo*-intermediates and then undergo the isomerization to give the *endo* products, produce *endo*-cyclic enol ethers or furans in the presence of $RuCl_2(PPh_3)$(*p*-cymene)[28] or palladium catalysts, such as $PdCl_2$,[29] $Pd(OAc)_2$[30] and K_2PdI_4.[31] *exo*-Cyclization of aromatic alkynols promoted by stoichiometric NaH has been described,[32] although the same reaction with catalytic amount base as the catalyst has not been reported yet.

As the applications of cyclization of alkynols, recently we applied *exo*-cyclic enol ethers to the reaction with imines, and dihydroisobenzofuran derivatives were obtained in THF and isoquinolin-1(2*H*)-one products were obtained in DMSO.[33] Moreover, the tandem reaction involving Diels–Alder reaction and an

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intermolecular nucleophilic addition reaction for *exo*-cyclic enol ether with benzyne was achieved to afford phenanthro[10.1-*bc*]furan.[34]

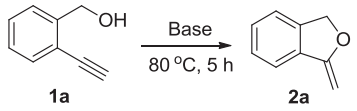
Cyclization of alkynylamines to form *exo*-cyclic products has been developed as the efficient method to construct *N*-heterocyclics,[17,35] and the effective catalysts include phase transfer catalysts,[36] I_2,[37] or Pd.[35d,38] Recently, stoichiometric KH, *t*-BuOK[39] or *t*-BuONa[40] catalyzed cyclization of alkynylamines has been developed to afford indoles or isoindolin-1-ones. To date, however, the same cyclization reaction with catalytic amount base as catalyst has not been reported.

Thus the transition-metal-free cyclization reactions of both alkynylamines and alkynols using commercially available, less expensive catalysts are still highly desirable. Here we report potassium *tert*-butoxide (*t*-BuOK) as the effective catalyst for the *exo*-cycloisomerization of alkynols and alkynylamines. For the alkynols, catalytic reactions exhibit 100% regioselectivity, giving *exo*-cyclic enol ethers in good to excellent yields. The alkynylamines could also do the transformation to give indoles and isoindolin-1-ones in good yields.

2. Results and discussion

First we explored the catalytic activity of *t*-BuOK (10 mol %) in alkynol cyclization using (2-ethynylphenyl)methanol **1a** as the model substrate; we tested the reaction in various solvents at 80 °C (Table 1). Reaction products were analyzed after 5 h by ^{1}H NMR, using $PhSiMe_3$ as the internal standard. The cyclization of **1a** did not proceed in toluene or 1,2-dichloroethane (DCE), and the same reaction in 1,4-dioxane or acetone gave low yields (Table 1, entries 1–4). When the reaction was carried out in THF, **1a** cyclized with 61% yield (entry 5). Yields of cyclic enol ether **2a** were 70–79% when the solvents were acetonitrile, dimethylformamide (DMF), methanol or *N*-methyl-2-pyrrolidone (NMP) (entries 6–9). Surprisingly, when the solvent was dimethyl sulfoxide (DMSO), the reaction produced the cyclized product **2a** exclusively in 94% yield and 100% *exo*-selectivity (entry 10). We suggest that this significant solvent effect is because polar aprotic DMSO stabilizes the anionic reaction intermediate.

Table 1
Cyclization of (2-ethynylphenyl)methanol **1a** under various conditions[a]



1a **2a**

Entry	Solvent	Catalyst	Yield[b] (%)
1	Toluene	*t*-BuOK	0
2	DCE	*t*-BuOK	<5
3	1,4-Dioxane	*t*-BuOK	30
4	Acetone	*t*-BuOK	44
5	THF	*t*-BuOK	61
6	Acetonitrile	*t*-BuOK	70
7	DMF	*t*-BuOK	73
8	Methanol	*t*-BuOK	74
9	NMP	*t*-BuOK	79
10	DMSO	*t*-BuOK	94
11	DMSO	K_2CO_3	64
12	DMSO	KOH	45
13	DMSO	Et_3N	0
14[c]	DMSO	*t*-BuOK	60
15[d]	DMSO	*t*-BuOK	45

[a] Reaction conditions: catalyst (0.1 mmol), **1a** (1.0 mmol), solvent (2 mL), 80 °C, 5 h, unless otherwise noted.
[b] Determined by ^{1}H NMR integration using $PhSiMe_3$ as the internal standard.
[c] *t*-BuOK (0.05 mmol).
[d] At 70 °C.

Changing the cyclization catalyst from *t*-BuOK to weaker bases, such as K_2CO_3 or KOH decreased yields to 64% and 45%, respectively (entries 11 and 12). Similarly, decreasing the loading of *t*-BuOK to 5 mol % or lowering the reaction temperature to 70 °C substantially reduced yields (entries 14 and 15). Note that the organic base triethylamine was ineffective as a catalyst (entry 13).

Next we analyzed the cyclization of various alkynols in DMSO at 80 °C (oil bath temperature), using 10 mol % *t*-BuOK as the catalyst (Table 2). After 5 h, the cyclic enol ether products were obtained with 100% *exo*-selectivity, and their structures were fully consistent with published data for ^{1}H and ^{13}C{^{1}H} NMR and mass spectrometry. ^{1}H NMR analysis of the products, together with single-crystal X-ray diffraction analysis of product **2j** (Fig. 1), indicated that all cyclic enol ether products were pure *Z*-stereoisomers except **2z**. NOESY experiments with **2w** showed that H^1 was close to H^2 and H^3, confirming the *Z*-configuration of the cyclic enol ether products.

Cyclization of both the terminal alkynol **1a** and the internal alkynol bearing a phenyl group on the alkynyl group gave product **2b** in similarly high yield around 94%. Alkynols **2c**,**e**,**f**,**h** and **i**, bearing electron-donating functional groups like NH_2, NHBoc, OMe or Me at *ortho*-, *meta*- or *para*-positions on the aromatic rings gave the corresponding *exo*-cyclic enol ethers in excellent isolated yields of 88–97%. Similar results were observed with alkynols **2d**,**g** and **2j**–**l** bearing electron-withdrawing groups like Cl, F or CF_3 at *ortho*-, *meta*- or *para*-positions on the aromatic rings. These results suggest that neither the nature nor position of electron-donating or electron-withdrawing functional groups on the aromatic ring significantly affect substrate cyclization.

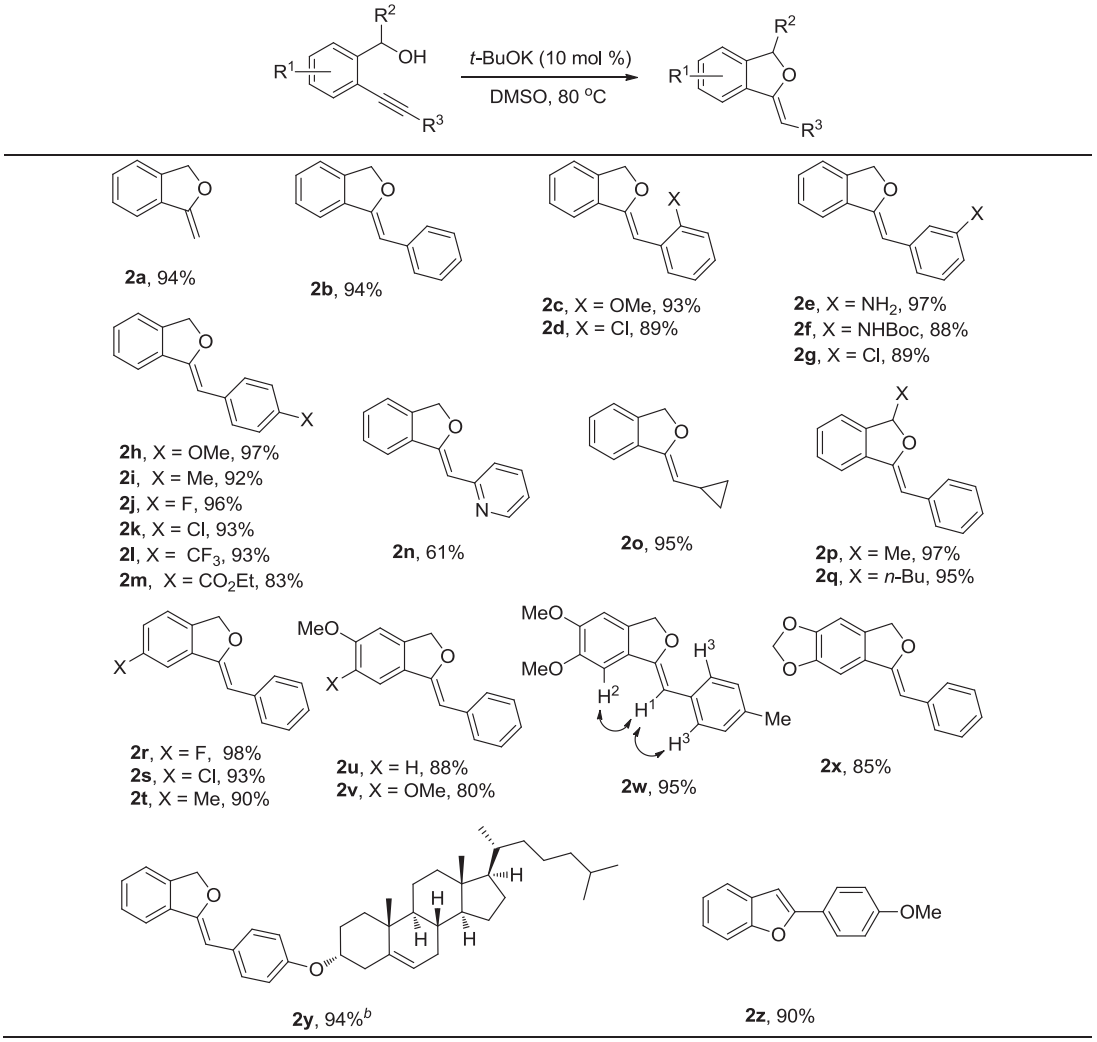
An alkynol with an ester group gave **2m** in slightly lower yield of 83%, demonstrating the tolerance of the ester group under these strongly basic catalytic reaction conditions. The presence of a pyridyl heterocyclic ring on the end of the alkynyl group inhibited cyclization, giving product **2n** in 61% yield. In contrast, the presence of cyclopropyl at the end of the alkynyl group produced the corresponding cyclic enol ether **2o** in 95% yield. The presence of an aliphatic hexyl substituent on the end of the alkynyl group led to complex cyclization results under these reaction conditions.

In the cyclization process, we also investigated the substituent effect of the methylene carbon in the benzyl alcohol. Alkynols with methyl or *n*-butyl substitutions gave products **2p** and **2q** in excellent yields of 97% and 95%, respectively. However, attaching a *tert*-butyl group to the methylene of the benzyl alcohol created so much steric hindrance that cyclization could not proceed. Modifying the aromatic ring of the benzyl alcohol with electron-withdrawing groups, such as F or Cl or with electron-donating groups, such as Me or OMe led to the corresponding products **2r**–**u** in yields of 88–98%. Multisubstituted alkynols were tolerated in the reaction, giving rise to the cyclization products **2v**–**x** in yields of 80–95%. Although these results demonstrate the flexibility of the catalytic system, the highly alkaline conditions may prevent the use of more complicated substrates with base-sensitive functional groups. In addition, cyclization of aliphatic alkynols does not proceed efficiently under these conditions.

To demonstrate the potential usefulness of the alkynol cyclization for generating derivatives of natural products, we focused on an alkynol modified with cholesterol. Cholesterol is an essential structural component of mammalian cell membranes and it serves as a precursor for the biosynthesis of steroid, bile acids and vitamin D.[41] Incubating an alkynol modified with cholesterol **1y** with 10 mol % of *t*-BuOK in THF at 80 °C gave the desired cyclization product **2y** in 94% yield. This reaction did not proceed in DMSO, because the substrate showed poor solubility in that solvent.

To test whether ethynylphenol would react in our cyclization procedure, we incubated 2-((4-methoxyphenyl)ethynyl)phenol with 10 mol % of *t*-BuOK in DMSO at 80 °C. The desired product, 2-(4-methoxyphenyl)benzofuran **2z**, was obtained in 90% yield. This

Table 2
Cyclization of various alkynols using *t*-BuOK as catalyst[a]



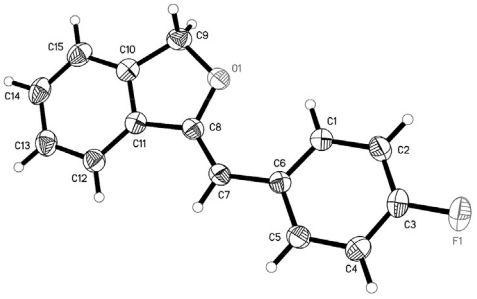


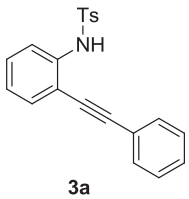
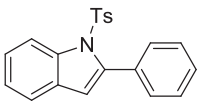
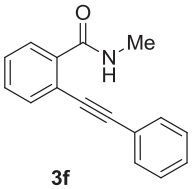
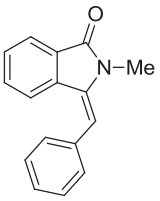
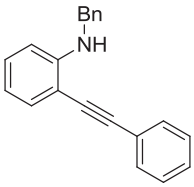
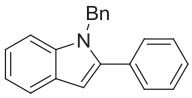
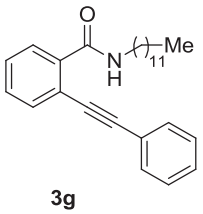
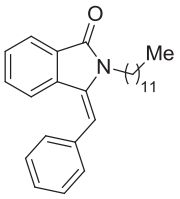
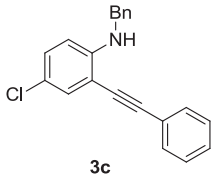
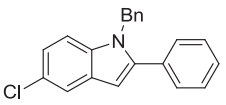
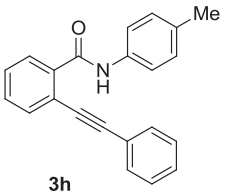
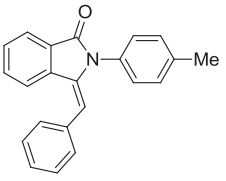
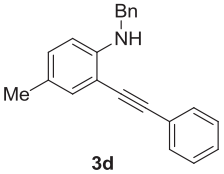
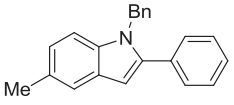
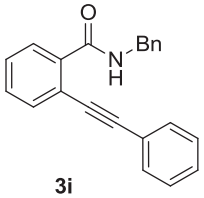
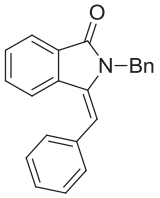
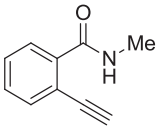
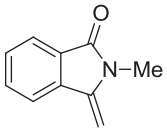
Fig. 1. The ORTEP diagram of product **2j**.

result indicates that the phenolate is sufficiently nucleophilic to attack the alkyne moiety under current catalytic conditions.

To explore whether our alkynols cyclization procedure would also promote the reaction of alkynylamines, which would possesses greater synthetic potential, we incubated a wide range of alkynylamines in DMSO at 80 °C in the presence of 10 mol % of *t*-BuOK catalyst (Table 3). First we tested 2-(phenylethynyl)aniline **3a** and **3b**, which bear the nucleophilic moieties NTs and NBn, and we obtained the indoles **4a** and **4b** as the cyclization products in 92% and 93% yields, respectively (entries 1 and 2). Similar good results were obtained when the aniline aromatic ring was substituted with an electron-withdrawing chlorine or an electron-donating methyl group, giving the indoles **4c** and **4d** in 91% and 98% yields, respectively (entries 3 and 4). The results indicate that such substituents exert negligible electronic effects on the reaction. Interestingly, cyclization of the benzamide derivatives **3e**–**i** led to isoindolin-1-ones **4e**–**i** in good yields with 100% *exo*-selectivity. However, products **4f**–**i** were *E*-stereoisomers, opposite to the configuration obtained in alkynol cyclization, which were fully consistent with published data for ^{1}H and $^{13}C\{^{1}H\}$ NMR and mass spectrometry.[42] We ascribe the different selectivity of *N*-atom attack to the alkyne moiety to the steric effect derived from the substituted groups linked with *N*-atom. The cyclization reaction tolerated alkyl substituents on the benzamide including Me and dodecyl groups, leading to isoindolin-1-ones **4e**–**g** in yields of 67–94% (entries 5–7). Aryl or benzyl substituents on the benzamide led to slightly lower yields of 67% for product **4h** and 56% for **4i**, respectively (entries 8 and 9).

Before speculating on the mechanism of our *t*-BuOK-catalyzed cyclization, we wanted to eliminate the possibility that trace transition metals in our *t*-BuOK were catalyzing the reaction. ICP-AES analysis of *t*-BuOK, which we purchased from TCI, showed that levels of Pd, Ni, Au, Pt, Ru and Rh were below the detection limit of 2 ppm, and that the level of Cu was below the detection

Table 3
Cyclization of alkynylamines using *t*-BuOK as catalyst[a]

Entry	Substrate	Product	Yield (%)	Entry	Substrate	Product	Yield (%)
1	 **3a**	 **4a**	93	6	 **3f**	 **4f**	79
2	 **3b**	 **4b**	93	7	 **3g**	 **4g**	67
3	 **3c**	 **4c**	91	8	 **3h**	 **4h**	67
4	 **3d**	 **4d**	98	9	 **3i**	 **4i**	56
5	 **3e**	 **4e**	94				

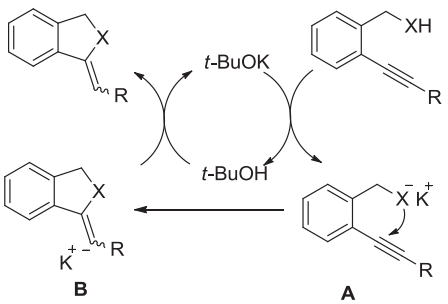
[a] Reaction conditions: alkynamide (0.5 mmol), *t*-BuOK (0.05 mmol), 80 °C, 5 h, 1.5 mL DMSO, unless otherwise noted. Isolated yields are reported.

limit of 5 ppm. This suggests that our results reflect cyclization catalyzed by *t*-BuOK instead of by transition metals.

Based on the transition metal-catalyzed cyclization of alkynols,[25,26] we propose a mechanism for *t*-BuOK-catalyzed cyclization of alkynols and alkynylamines (Scheme 2). The *t*-BuOK deprotonates the X–H bond of the alkynol or alkynylamine, leading to anion intermediate **A**, the alkynyl moiety of which undergoes nucleophilic attack to form alkene anion **B**. Protolysis then generates the cyclic product and regenerates *t*-BuOK, completing the catalytic cycle.

3. Conclusion

In summary, we describe for the first time that commercially available *t*-BuOK effectively catalyzes the *exo*-cyclization of alkynols and alkynylamines to generate *exo*-cyclic enol ethers, indoles



Scheme 2. Proposed reaction mechanism for *t*-BuOK-catalyzed cyclization of alkynols or alkynylamines.

and isoindolin-1-ones in high yields. This approach offers a flexible, robust and efficient alternative to transition metal-catalyzed cyclization.

4. Experimental section

4.1. General

All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium–benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, DMSO, DMF). The organic alkynols[9a,22,26,43] and alkynylamines[11,13b,22] were prepared according to the reported literature methods. Potassium *tert*-butoxide (1 M in THF) used in the catalytic reactions was purchased from TCI. Other commercially available chemicals were used as received. Chemical shifts (δ, ppm) in the ^{1}H NMR spectra were recorded using TMS as internal standard or referenced to the deuterated solvents. Chemical shifts in ^{13}C {^{1}H} NMR spectra were referenced to the deuterated solvents.

4.2. General procedure for the preparation of alkynols

To a mixture of the 2-iodobenzyl alcohol (1.16 g, 5.0 mmol) in DMF (30 mL) were added $PdCl_2(PPh_3)_2$ (0.70 g, 0.10 mmol), and CuI (0.19 g, 0.10 mmol) under nitrogen. After the reaction mixture was stirred for 5 min at room temperature, *N*,*N*-diisopropylamine (2.02 g, 4.0 equiv) was added by a syringe. The reaction mixture was then heated at 70 °C. A solution of the alkynes (1.2 equiv) in DMF (5 mL) was added dropwise over 10 min, and the mixture was allowed to stir at 70 °C for 2 h. After cooling, the reaction mixture was washed with saturated aq NH_4Cl and water, and then extracted with EtOAc (3×25 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under vacuum to give the crude product, which was purified by column chromatography on silica gel using 9:1 to 4:1 hexane/EtOAc as eluent.

*4.2.1. Ethyl 4-((2-(hydroxymethyl)phenyl)ethynyl)benzoate (**1m**).* The compound was prepared from 2-iodobenzyl alcohol (1.17 g, 5 mmol) and ethyl 4-ethynylbenzoate[44] (1.04 g, 6 mmol) following typical procedure. The product **1m** was obtained as a white solid in 67% yield (1.40 g) as white solid after column chromatography (eluent=petroleum ether/ethyl acetate 10:1 v/v). Mp: 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.04 (d, *J*=7.96 Hz, 2H), 7.50–7.59 (m, 4H), 7.40 (t, *J*=7.56 Hz, 1H), 7.29–7.33 (m, 1H), 4.93 (d, *J*=6.32 Hz, 2H), 4.39 (q, *J*=7.08 Hz, 2H), 2.07 (t, *J*=6.32 Hz, 1H), 1.41 (t, *J*=7.08 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 166.2, 143.0, 132.4, 131.5, 130.1, 129.6, 129.3, 127.6, 127.5, 127.2, 120.7, 93.4, 89.7, 63.8, 61.3, 14.4; HRMS (ESI, TOF) calcd for $C_{18}H_{17}O_3^+$ $[M+H]^+$: 281.1172, found: 281.1175.

*4.2.2. (2-(Cyclopropylethynyl)phenyl)methanol (**1o**).* The compound was prepared from 2-iodobenzyl alcohol (1.17 g, 5 mmol) and ethynylcyclopropane (0.40 g, 6 mmol) following typical procedure. The product **1o** was obtained in 85% yield (0.86 g) as a pale yellow oil after column chromatography (eluent=petroleum ether/ethyl acetate 10:1 v/v). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.36–7.39 (m, 2H), 7.27–7.29 (m, 1H), 7.19–7.22 (m, 1H), 4.77 (d, *J*=6.52 Hz, 2H), 2.14 (t, *J*=6.56 Hz, 1H), 1.45–1.52 (m, 1H), 0.80–0.93 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 142.7, 132.4, 128.0, 127.5, 127.3, 122.1, 98.7, 73.4, 64.2, 9.0, 0.5; HRMS (ESI, TOF) calcd for $C_{12}H_{13}O^+$ $[M+H]^+$: 173.0961, found: 173.0960.

4.2.3. 4-(3R)-5-Cholesten-3β-oxybenzylethynyl. To a mixture of cholesterol (1.93 g, 5.0 mmol) in THF (50 mL) were added PPh_3 (1.96 g, 7.5 mmol), and diisopropyl azodicarboxylate (2.02 g, 10 mmol). Then, ((4-iodophenyl)ethynyl)trimethylsilane (1.45 g, 5.5 mmol) was added. The reaction mixture was stirred at room temperature for 2 days. The reaction mixture was concentrated under vacuum to give the crude product, which was purified by column chromatography on silica gel using 50:1 hexane/EtOAc as eluent. Then the obtained product was dissolved in THF (30 mL) at 0 °C and stirred for 30 min. The reaction mixture was concentrated under vacuum to give the crude product, which was purified by column chromatography on silica gel using 50:1 hexane/EtOAc as eluent to afford 4-(3*R*)-5-cholesten-3β-oxybenzylethynyl as a white solid in 70% yield (1.70 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.39 (d, *J*=8.72 Hz, 2H), 6.83 (d, *J*=8.72 Hz, 2H), 5.24 (t, *J*=2.60 Hz, 1H), 4.54 (t, *J*=2.40 Hz, 1H), 2.98 (s, 1H), 2.50–2.54 (m, 1H), 2.31–2.35 (m, 1H), 0.86–2.04 (m, 38H), 0.69 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 158.3, 138.4, 133.6, 122.5, 116.5, 114.0, 84.0, 75.7, 73.1, 56.9, 56.3, 50.0, 42.4, 39.9, 39.6, 37.1, 36.3, 36.0, 33.2, 32.0, 29.8, 28.4, 28.1, 25.9, 24.4, 24.0, 23.0, 22.7, 20.9, 18.8, 14.3, 12.0; HRMS (ESI, TOF) calcd for $C_{35}H_{51}O^+$ $[M+H]^+$: 487.3934, found: 487.3944.

*4.2.4. (2-(4-(3R)-5-Cholesten-3β-oxybenzylethynyl)phenyl)-methanol (**1y**).* The compound was prepared from 2-iodobenzyl alcohol (468.1 mg, 2 mmol) and 4-(3*R*)-5-cholesten-3β-oxybenzylethynyl (973.5 mg, 2.4 mmol) following the typical procedure. The product **1y** was obtained in 75% yield (888 mg) as white solid after column chromatography (eluent=petroleum ether/ethyl acetate 10:1 v/v). Mp: 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.50–7.52 (m, 1H), 7.41–7.46 (m, 3H), 7.25–7.34 (m, 2H), 6.88 (d, *J*=8.76 Hz, 2H), 5.25 (t, *J*=2.64 Hz, 1H), 4.89 (d, *J*=5.88 Hz, 2H), 4,56 (s, 1H), 2.53 (d, *J*=15.00 Hz, 1H), 2.35 (d, *J*=15.08 Hz, 1H), 2.21 (t, *J*=6.28 Hz, 1H), 0.86–2.03 (m, 38H), 0.69 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 158.2, 142.4, 138.4, 133.0, 132.1, 128.5, 127.6, 127.4, 122.6, 121.9, 116.7, 114.8, 94.6, 85.4, 73.2, 64.3, 56.9, 56.3, 50.0, 22.4, 39.9, 39.6, 37.1, 36.3, 36.0, 33.2, 32.0, 28.4, 28.2, 25.9, 24.4, 24.0, 23.0, 22.7, 20.9, 19.2, 18.8, 12.0; HRMS (ESI, TOF) calcd for $C_{42}H_{57}O_2^+$ $[M+H]^+$: 593.4353, found: 593.4360.

4.3. Typical procedure for the cyclization of alkynols

To a solution of alkynol (**1**, 1.0 mmol) in DMSO (2 mL) was added *t*-BuOK (0.1 mmol, 100 μL, 1 M in THF). The resulting solution was stirred at 80 °C for 5 h. The reaction mixture was then cooled to room temperature and extracted from brine water (10 mL) with diethyl ether (3×5 mL). The combined organic extracts were dried with anhydrous Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the desired product. **2d**–**g**, **2j**–**m**, **2o**, **2p**, **2r**–**w**, **2y** and **2z** are new compounds and the other products are known compounds. Note that the yield of **2a** in the optimization of the reaction conditions was determined by ^{1}H NMR integration using $PhSiMe_3$ as the internal standard.

*4.3.1. 1-Methylene-1,3-dihydroisobenzofuran (**2a**).*[22] The compound was prepared from **1a** (132.2 mg, 1.0 mmol) following typical procedure. The reaction mixture was cooled to room temperature and extracted by *n*-hexane (3×5 mL). The combined organic extracts were evaporated in vacuo to obtain the **2a** (124 mg, 94%) as a pale yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.64 (d, *J*=6.68 Hz, 1H), 7.36–7.43 (m, 3H), 5.30 (s, 2H), 4.59 (d, *J*=1.84 Hz, 1H), 4.35 (d, *J*=1.72 Hz, 1H); ^{13}C NMR (100.6 MHz, DMSO-d_6, 25 °C): δ 161.4, 140.2, 132.9, 129.2, 128.0, 121.7, 120.6, 77.8, 73.3; HRMS (ESI, TOF) calcd for $C_9H_9O^+$ $[M+H]^+$: 133.0647, found: 133.0650.

*4.3.2. (Z)-1-Benzylidene-1,3-dihydroisobenzofuran (**2b**).*[45,46] The compound was prepared from **1b** (208.3 mg, 1.0 mmol) following

typical procedure. 196 mg (94% yield) of product **2b** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 100–102 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.00 (d, *J*=7.44 Hz, 2H), 7.34 (t, *J*=7.84 Hz, 2H), 7.09–7.21 (m, 2H), 6.94–7.02 (m, 2H), 6.69 (d, *J*=6.92 Hz, 1H), 6.02 (s, 1H), 4.85 (s, 2H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 156.6, 139.6, 137.1, 135.3, 128.7, 128.6, 128.5, 125.7, 121.2, 120.2, 97.1, 74.8; HRMS (ESI, TOF) calcd for $C_{15}H_{13}O^+$ $[M+H]^+$: 209.0960, found: 209.0967.

*4.3.3. (Z)-1-(2-Methoxybenzylidene)-1,3-dihydroisobenzo-furan (**2c**).*[32a] The compound was prepared from **1c** (119.1 mg, 0.5 mmol) following typical procedure. 111 mg (93% yield) of product **2c** was obtained as a pale yellow solid after column chromatography (eluent=petroleum ether/ethyl acetate 30:1 v/v). Mp: 136–138 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 8.22 (d, *J*=7.68 Hz, 1H), 7.66–7.68 (m, 1H), 7.46–7.48 (m, 1H), 7.40–7.42 (m, 2H), 7.10–7.14 (m, 1H), 6.91–6.96 (m, 2H), 6.44 (s, 1H), 5.54 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 157.0, 156.5, 140.3, 135.8, 129.6, 129.4, 129.0, 127.1, 126.0, 122.4, 121.1, 120.6, 111.0, 89.8, 75.5, 55.8; HRMS (EI, TOF) calcd for $C_{16}H_{14}O_2$ $[M]^+$: 238.0994, found: 238.0998.

*4.3.4. (Z)-1-(2-Chlorobenzylidene)-1,3-dihydroisobenzofuran (**2d**).* The compound was prepared from **1d** (121.4 mg, 0.5 mmol) following typical procedure. 108 mg (89% yield) of product **2d** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 40:1 v/v). Mp: 102–104 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 8.35 (d, *J*=7.96 Hz, 1H), 7.77–7.79 (m, 1H), 7.46–7.52 (m, 3H), 7.41 (d, *J*=8.04 Hz, 1H), 7.29–7.33 (m, 1H), 7.11–7.15 (m, 1H), 6.41 (s, 1H), 5.59 (s, 2H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 159.0, 140.8, 135.1, 134.9, 131.8, 130.4, 130.0, 129.1, 127.6, 127.1, 122.5, 121.1, 91.4, 76.0; HRMS (EI, TOF) calcd for $C_{15}H_{11}ClO$ $[M]^+$: 242.0498, found: 242.0495.

*4.3.5. (Z)-3-(Isobenzofuran-1(3H)-ylidenemethyl)aniline (**2e**).* The compound was prepared from **1e** (223.3 mg, 1.0 mmol) following typical procedure. 217 mg (97% yield) of product **2e** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 5:1 v/v). Mp: 113–115 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.66–7.68 (m, 1H), 7.45–7.46 (m, 1H), 7.38–7.40 (m, 2H), 7.12 (s, 1H), 6.98–7.03 (m, 2H), 6.47–6.49 (m, 1H), 5.95 (s, 1H), 5.52 (s, 2H), 4.54 (br, NH_2); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 156.6, 149.0, 140.3, 138.0, 135.7, 129.5, 128.9, 122.4, 120.6, 118.1, 114.6, 112.8, 97.5, 75.5; HRMS (ESI, TOF) calcd for $C_{15}H_{14}NO^+$ $[M+H]^+$: 224.1070, found: 224.1076.

*4.3.6. (Z)-tert-Butyl(3-(isobenzofuran-1(3H)-ylidenemethyl)-phenyl) carbamate (**2f**).* The compound was prepared from **1f** (323.4 mg, 1.0 mmol) following typical procedure. 285 mg (88% yield) of product **2f** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 15:1 v/v). Mp: 164–166 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 8.34 (br, 1H), 7.85 (s, 1H), 7.73–7.75 (m, 1H), 7.40–7.48 (m, 4H), 7.36 (d, *J*=7.44 Hz, 1H), 7.21 (t, *J*=7.88 Hz, 1H), 6.05 (s, 1H) 5.55 (s, 2H), 1.50 (s, 9H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 157.3, 153.8, 140.5, 138.0, 135.5, 129.8, 129.2, 129.0, 122.9, 122.4, 120.8, 118.5, 116.3, 96.9, 79.7, 75.7, 28.6; HRMS (ESI, TOF) calcd for $C_{20}H_{22}NO_3^+$ $[M+H]^+$: 324.1594, found: 324.1596.

*4.3.7. (Z)-1-(3-Chlorobenzylidene)-1,3-dihydroisobenzofuran (**2g**).* The compound was prepared from **1g** (242.7 mg, 1.0 mmol) following typical procedure. 216 mg (89% yield) of product **2g** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 70–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.81 (s, 1H), 7.55–7.57 (m, 1H), 7.53 (d, *J*=8.04 Hz, 1H), 7.35–7.38 (m, 3H), 7.21–7.25 (m, 1H), 7.10 (d, *J*=8.04 Hz, 1H), 5.87 (s, 1H), 5.52 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 157.5, 139.6, 138.4, 134.6, 134.3, 129.6, 129.3, 128.3, 127.5, 125.9, 125.2, 121.4, 120.3, 95.1, 75.3; HRMS (EI, TOF) calcd for $C_{15}H_{11}ClO$ $[M]^+$: 242.0498, found: 242.0497.

*4.3.8. (Z)-1-(4-Methoxybenzylidene)-1,3-dihydroisobenzo-furan (**2h**).*[26] The compound was prepared from **1h** (238.3 mg, 1.0 mmol) following typical procedure. 231 mg (97% yield) of product **2h** was obtained as a brown oil after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 118–129 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.96 (d, *J*=8.76 Hz, 2H), 7.25 (d, *J*=7.44 Hz, 1H), 6.96–7.02 (m, 4H), 6.71 (d, *J*=7.40 Hz, 1H), 6.03 (s, 1H), 4.90 (s, 2H), 3.35 (s, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 158.3, 155.0, 139.3, 135.6, 129.9, 129.7, 128.2, 121.3, 119.9, 114.3, 96.9, 74.6, 54.8; HRMS (ESI, TOF) calcd for $C_{16}H_{15}O_2^+$ $[M+H]^+$: 239.1066, found: 239.1070.

*4.3.9. (Z)-1-(4-Methylbenzylidene)-1,3-dihydroisobenzofuran (**2i**).*[26] The compound was prepared from **1i** (222.3 mg, 1.0 mmol) following typical procedure. 204 mg (92% yield) of product **2i** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 95–97 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.96 (d, *J*=8.12 Hz, 2H), 7.16–7.24 (m, 3H), 6.96–7.02 (m, 2H), 6.69 (d, *J*=7.40 Hz, 1H), 6.05 (s, 1H), 4.88 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 156.6, 140.3, 135.6, 135.3, 134.7, 129.7, 129.6, 128.9, 128.6, 122.4, 120.6, 96.7, 75.6, 21.2; HRMS (ESI, TOF) calcd for $C_{16}H_{15}O^+$ $[M+H]^+$: 223.1117, found: 223.1127.

*4.3.10. (Z)-1-(4-Fluorobenzylidene)-1,3-dihydroisobenzofuran (**2j**).* The compound was prepared from **1j** (226.2 mg, 1.0 mmol) following typical procedure. 217 mg (96% yield) of product **2j** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 114–115 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.76 (dd, J_1=8.84 Hz, J_2=5.64 Hz, 2H), 7.68–7.70 (m, 1H), 7.47–7.49 (m, 1H), 7.40–7.43 (m, 2H), 7.08 (t, *J*=8.96 Hz, 2H), 6.10 (s, 1H), 5.55 (s, 2H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 161.3 (d, J_{C-F}=227.96 Hz), 156.9, 140.4, 135.3, 134.0 (d, J_{C-F}=3.36 Hz), 130.1 (d, J_{C-F}=7.58 Hz), 129.8, 129.0, 122.4, 120.7, 115.7 (d, J_{C-F}=21.35 Hz), 95.5, 75.7; HRMS (ESI, TOF) calcd for $C_{15}H_{12}OF^+$ $[M+H]^+$: 227.0866, found: 227.0871.

*4.3.11. (Z)-1-(4-Chlorobenzylidene)-1,3-dihydroisobenzofuran (**2k**).* The compound was prepared from **1k** (242.7 mg, 1.0 mmol) following typical procedure. 226 mg (93% yield) of product **2k** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.67 (d, *J*=8.60 Hz, 2H), 7.55–7.58 (m, 1H), 7.34–7.39 (m, 3H), 7.28 (d, *J*=8.56 Hz, 2H), 5.90 (s, 1H), 5.52 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 156.9, 139.4, 135.0, 134.7, 130.6, 129.1, 129.0, 128.5, 128.3, 121.4, 120.1, 95.2, 75.1; HRMS (EI, TOF) calcd for $C_{15}H_{11}ClO$ $[M]^+$: 2423.0498, found: 242.0497.

*4.3.12. (Z)-1-(4-(Trifluoromethyl)benzylidene)-1,3-dihydroiso-benzofuran (**2l**).* The compound was prepared from **1l** (276.3 mg, 1.0 mmol) following typical procedure. 257 mg (93% yield) of product **2l** was obtained as a pale yellow solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 138–140 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.77 (d, *J*=8.20 Hz, 2H), 7.54 (d, *J*=8.28 Hz, 2H), 7.18–7.20 (m, 1H), 6.95–7.02 (m, 2H), 6.68 (d, *J*=6.48 Hz, 1H), 5.83 (s, 1H), 4.78 (s,

2H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 158.6, 140.7, 139.9, 134.6, 129.3, 128.2, 127.9, 126.9 (q, J_{C-F}=32.19 Hz), 125.5 (q, J_{C-F}=271.36 Hz), 125.2 (q, J_{C-F}=3.86 Hz), 121.3, 120.4, 95.5, 75.1; HRMS (ESI, TOF) calcd for $C_{16}H_{12}OF_3^+$ $[M+H]^+$: 277.0835, found: 277.0849.

*4.3.13. (Z)-Ethyl 4-(isobenzofuran-1(3H)-ylidenemethyl)-benzoate (**2m**).* The compound was prepared from **1m** (280.3 mg, 1.0 mmol) following typical procedure. 233 mg (83% yield) of product **2m** was obtained as a pale yellow solid after column chromatography (eluent=petroleum ether/ethyl acetate 20:1 v/v). Mp: 133–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.00 (d, J=8.44 Hz, 2H), 7.78 (d, J=8.48 Hz, 2H), 7.59–7.79 (m, 1H), 7.35–7.42 (m, 3H), 5.99 (s, 1H), 5.56 (s, 2H), 4.37 (q, J=7.12 Hz, 2H), 1.40 (t, J=7.12 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 166.9, 158.5, 141.3, 139.8, 134.6, 129.8, 129.5, 128.4, 127.4, 126.7, 121.4, 120.4, 95.7, 75.4, 60.8, 14.5; HRMS (ESI, TOF) calcd for $C_{18}H_{17}O_3^+$ $[M+H]^+$: 281.1172, found: 281.1172.

*4.3.14. (Z)-2-(Isobenzofuran-1(3H)-ylidenemethyl)pyridine (**2n**).*[26,47] The compound was prepared from **1n** (209.2 mg, 1.0 mmol) following typical procedure. 128 mg (61% yield) of product **2n** was obtained as a yellow oil after column chromatography (eluent=petroleum ether/ethyl acetate 2:1 v/v). ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 8.47–8.48 (m, 1H), 8.13 (d, J=8.16 Hz, 1H), 7.78–7.80 (m, 1H), 7.66–7.71 (m, 1H), 7.45–7.54 (m, 3H), 7.03–7.60 (m, 1H), 6.24 (s, 1H), 5.61 (s, 2H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 159.8, 156.8, 150.0, 141.0, 136.4, 135.0, 130.5, 129.2, 123.1, 122.5, 121.3, 120.5, 98.4, 76.2; HRMS (ESI, TOF) calcd for $C_{14}H_{12}NO^+$ $[M+H]^+$: 210.0913, found: 210.0914.

*4.3.15. (Z)-1-(Cyclopropylmethylene)-1,3-dihydroisobenzo-furan (**2o**).* The compound was prepared from **1o** (172.2 mg, 1.0 mmol) following typical procedure. The reaction mixture was cooled room temperature and extracted by *n*-hexane (3×5 mL). The combined organic extracts were evaporated in vacuo to obtain the **2o** (164 mg, 95%) as a pale yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.43–7.46 (m, 1H), 7.37–7.39 (m, 1H), 7.29–7.32 (m, 2H), 5.33 (s, 2H), 4.60 (d, J=9.44 Hz, 1H), 1.64–1.73 (m, 1H), 0.73–0.77 (m, 2H), 0.36–0.40 (m, 2H); ^{13}C NMR (100.6 MHz, DMSO-d_6, 25 °C): δ 154.5, 138.8, 133.3, 128.0, 127.8, 121.6, 119.1, 99.2, 73.1, 8.1, 7.0; HRMS (ESI, TOF) calcd for $C_{12}H_{13}O^+$ $[M+H]^+$: 173.0960, found: 173.0961.

*4.3.16. (Z)-1-Benzylidene-3-methyl-1,3-dihydroisobenzofuran (**2p**).* The compound was prepared from **1p** (222.3 mg, 1.0 mmol) following typical procedure. 229 mg (97% yield) of product **2p** was obtained as a brown oil after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.75 (d, J=7.32 Hz, 2H), 7.69–7.71 (m, 1H), 7.40–7.46 (m, 3H), 7.28–7.32 (m, 2H), 7.11 (t, J=7.40 Hz, 1H), 6.05 (s, 1H), 5.81 (q, J=6.52 Hz, 1H), 1.62 (d, J=6.52 Hz, 3H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 156.2, 144.9, 137.7, 135.3, 129.8, 129.1, 129.0, 128.6, 125.8, 122.2, 120.8, 96.5, 83.2, 22.0; HRMS (ESI, TOF) calcd for $C_{16}H_{15}O^+$ $[M+H]^+$: 223.1117, found: 223.1120.

*4.3.17. (Z)-1-Benzylidene-3-butyl-1,3-dihydroisobenzofuran (**2q**).*[25] The compound was prepared from **1q** (264.4 mg, 1.0 mmol) following typical procedure. 251 mg (95% yield) of product **2q** was obtained as a yellow oil after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.76 (d, J=7.32 Hz, 2H), 7.68–7.72 (m, 1H), 7.40–7.46 (m, 3H), 7.31 (t, J=7.92 Hz, 2H), 7.11 (t, J=7.40 Hz, 1H), 6.05 (s, 1H), 5.73 (dd, J_1=3.80 Hz, J_2=7.68 Hz, 1H), 2.08–2.14 (m, 1H), 1.73–1.82 (m, 1H), 1.48–1.59 (m, 2H), 1.38–1.47 (m, 2H), 0.92 (t, J=7.12 Hz, 3H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 156.4, 143.6, 137.8, 135.6, 129.7, 129.1, 129.0, 128.6, 125.8, 122.3, 120.7, 96.4, 86.9, 36.3, 27.9, 23.2, 14.3; HRMS (ESI, TOF) calcd for $C_{19}H_{21}O^+$ $[M+H]^+$: 265.1587, found: 265.1592.

*4.3.18. (Z)-1-Benzylidene-6-fluoro-1,3-dihydroisobenzofuran (**2r**).* The compound was prepared from **1r** (226.3 mg, 1.0 mmol) following typical procedure. 222 mg (98% yield) of product **2r** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 30:1 v/v). Mp: 77–79 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.73 (d, J=7.40 Hz, 2H), 7.48–7.52 (m, 2H), 7.30–7.34 (m, 2H), 7.12–7.21 (m, 2H), 6.14 (s, 1H), 5.54 (s, 2H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 164.0 (d, J_{C-F}=242.86 Hz), 156.4 (d, J_{C-F}=4.39 Hz), 137.9 (d, J_{C-F}=9.68 Hz), 137.2, 136.2 (d, J_{C-F}=1.99 Hz), 129.1, 128.7, 126.3, 124.2 (d, J_{C-F}=9.36 Hz), 117.0 (d, J_{C-F}=24.07 Hz), 107.3 (d, J_{C-F}=24.66 Hz), 97.9, 75.5; HRMS (ESI, TOF) calcd for $C_{15}H_{12}OF^+$ $[M+H]^+$: 227.0866, found: 227.0868.

*4.3.19. (Z)-1-Benzylidene-6-chloro-1,3-dihydroisobenzofuran (**2s**).* The compound was prepared from **1s** (226.3 mg, 1.0 mmol) following typical procedure. 226 mg (93% yield) of product **2s** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.71 (d, J=7.96 Hz, 2H), 7.52 (s, 1H), 7.29–7.35 (m, 3H), 7.24 (d, J=8.28 Hz, 1H), 7.14–7.18 (m, 1H), 5.91 (s, 1H), 5.47 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 155.1, 137.6, 137.0, 136.0, 134.4, 129.0, 128.5, 128.0, 125.8, 122.5, 120.2, 97.6, 74.7; HRMS (EI, TOF) calcd for $C_{15}H_{11}ClO$ $[M]^+$: 242.0498, found: 242.0499.

*4.3.20. (Z)-1-Benzylidene-6-methyl-1,3-dihydroisobenzofuran (**2t**).* The compound was prepared from **1t** (222.3 mg, 1.0 mmol) following typical procedure. 200 mg (90% yield) of product **2t** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 50:1 v/v). Mp: 106–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.73 (d, J=7.28 Hz, 2H), 7.39 (s, 1H), 7.31–7.35 (m, 2H), 7.22 (d, J=7.84 Hz, 1H), 7.12–7.17 (m, 2H), 5.92 (s, 1H), 5.48 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 156.5, 138.0, 136.7, 136.6, 135.2, 130.0, 128.5, 127.8, 125.3, 121.0, 120.4, 96.0, 74.9, 21.6; HRMS (EI, TOF) calcd for $C_{16}H_{14}O$ $[M]^+$: 222.1045, found: 222.1044.

*4.3.21. (Z)-1-Benzylidene-5-methoxy-1,3-dihydroisobenzo-furan (**2u**).* The compound was prepared from **1u** (238.3 mg, 1.0 mmol) following typical procedure. 210 mg (88% yield) of product **2u** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 25:1 v/v). Mp: 118–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.70 (d, J=7.24 Hz, 2H), 7.47 (d, J=8.52 Hz, 1H), 7.30–7.33 (m, 2H), 7.09–7.13 (m, 1H), 6.92 (dd, J_1=8.52 Hz, J_2=2.24 Hz, 1H), 6.83 (d, J=1.52 Hz, 1H), 5.81 (s, 1H), 5.47 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 160.9, 156.4, 141.3, 136.8, 128.4, 127.6, 127.5, 125.0, 121.2, 115.3, 105.8, 94.7, 74.7, 55.7; HRMS (EI, TOF) calcd for $C_{16}H_{14}O_2$ $[M]^+$: 238.0994, found: 238.0995.

*4.3.22. (Z)-1-Benzylidene-5,6-dimethoxy-1,3-dihydroisobenzo-furan (**2v**).* The compound was prepared from **1v** (268.3 mg, 1.0 mmol) following typical procedure. 215 mg (80% yield) of product **2v** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 5:1 v/v). Mp: 115–117 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.68 (d, J=7.28 Hz, 2H), 7.09–7.29 (m, 3H), 7.05–7.09 (m, 2H), 5.94 (s, 1H), 5.46 (s, 2H), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100.6 MHz, acetone-d_6, 25 °C): δ 158.1, 152.3, 151.2, 138.1, 133.2, 129.0, 128.2, 127.5, 125.4, 105.1,

103.5, 94.9, 75.6, 56.3; HRMS (EI, TOF) calcd for $C_{17}H_{16}O_3$ $[M]^+$: 268.1099, found: 268.1100.

*4.3.23. (Z)-5,6-Dimethoxy-1-(4-methylbenzylidene)-1,3-dihydroisobenzofuran (**2w**).* The compound was prepared from **1w** (282.3 mg, 1.0 mmol) following typical procedure. 268 mg (95% yield) of product **2w** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 5:1 v/v). Mp: 196–198 °C; ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 7.58 (d, J=8.16 Hz, 2H), 7.24 (s, 1H), 7.09 (d, J=8.00 Hz, 2H), 7.04 (s, 1H), 5.90 (s, 1H), 5.44 (s, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 156.3, 150.7, 149.8, 134.6, 133.8, 132.0, 129.2, 127.4, 127.2, 103.6, 102.1, 94.5, 74.8, 56.3, 56.2, 21.3; HRMS (ESI, TOF) calcd for $C_{18}H_{19}O_3^+$ $[M+H]^+$: 283.1328, found: 283.1331.

*4.3.24. (Z)-5-Benzylidene-5,7-dihydro-[1,3]dioxolo[4,5-f]isobenzofuran (**2x**).*[26] The compound was prepared from **1x** (126.1 mg, 1.0 mmol) following typical procedure. 107 mg (85% yield) of product **2x** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 5:1 v/v). Mp: 83–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.69 (d, J=7.28 Hz, 2H), 7.29–7.33 (m, 2H), 7.10–7.13 (m, 1H), 6.96 (s, 1H), 6.74 (s, 1H), 6.04 (s, 2H), 5.73 (s, 1H), 5.41 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 156.6, 149.4, 148.6, 136.6, 133.6, 128.6, 128.5, 127.5, 125.1, 102.0, 101.5, 100.2, 94.8, 74.8; HRMS (EI, TOF) calcd for $C_{16}H_{12}O_3$ $[M]^+$: 252.0786, found: 252.0784.

*4.3.25. (Z)-1-(4-(3R)-5-Cholesten-3β-oxybenzylidene)-1,3-dihydroisobenzofuran (**2y**).* The compound was prepared from **1y** (118.6 mg, 0.2 mmol) following typical procedure but using THF (1 mL) as solvent. 112 mg (94% yield) of product **2y** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 5:1 v/v). Mp: 179–181 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.97 (d, J=8.68 Hz, 2H), 7.24 (d, J=7.52 Hz, 1H), 7.08 (d, J=8.68 Hz, 2H), 6.95–7.04 (m, 2H), 6.71 (d, J=7.36 Hz, 1H), 6.04 (s, 1H), 5.39 (t, J=2.48 Hz, 1H), 4.91 (s, 2H), 4.35 (s, 1H), 2.48 (d, J=14.88 Hz, 1H), 2.34 (d, J=14.88 Hz, 1H), 0.93–2.08 (m, 38H), 0.71 (s, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 156.4, 155.0, 139.3, 138.8, 135.7, 129.8, 128.2, 127.9, 122.6, 121.3, 119.9, 116.8, 97.0, 74.6, 72.8, 57.0, 56.6, 50.2, 42.6, 40.2, 40.0, 37.3, 36.7, 36.3, 33.6, 32.3, 28.7, 28.4, 26.2, 24.6, 24.5, 23.1, 22.8, 21.2, 19.2, 19.1, 12.2; HRMS (ESI, TOF) calcd for $C_{42}H_{57}O_2^+$ $[M+H]^+$: 593.4353, found: 593.4362.

*4.3.26. 2-(4-Methoxyphenyl)benzofuran (**2z**).* The compound was prepared from **1z** (224.2 mg, 1.0 mmol) following typical procedure. 213 mg (95% yield) of product **2z** was obtained as a yellow oil after column chromatography (eluent=petroleum ether/ethyl acetate 25:1 v/v). Mp: 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.78 (d, J=8.80 Hz, 2H), 7.54 (d, J=7.08 Hz, 1H), 7.49 (d, J=7.84 Hz, 1H), 7.18–7.26 (m, 2H), 6.96 (d, J=8.80 Hz, 2H), 6.87 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 160.1, 156.2, 154.8, 129.6, 126.5, 123.8, 123.4, 122.9, 120.7, 114.3, 111.1, 99.8, 55.4; HRMS (EI, TOF) calcd for $C_{15}H_{12}O_2$ $[M]^+$: 224.0837, found: 224.0839.

4.4. Typical procedure for the cyclization of alkynylamines

To a solution of alkynylamines (**3**, 0.5 mmol) in DMSO (1.5 mL) was added *t*-BuOK (0.1 mmol, 100 μL, 1 M in THF). The resulting solution was stirred at 80 °C for 5 h. The reaction mixture was then cooled to room temperature and extracted from brine water (10 mL) with diethyl ether (3×5 mL). The combined organic extracts were dried with anhydrous Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the desired product. **4c** and **4g**–**i** are new compounds and the other products are known compounds.

*4.4.1. 2-Phenyl-1-tosyl-1H-indole (**4a**).*[48] The compound was prepared from **3a** (173.7 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 160 mg (92% yield) of product **4a** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 10:1 v/v). Mp: 145–147 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.31 (d, J=8.36 Hz, 1H), 7.48–7.50 (m, 2H), 7.42–7.45 (m, 4H), 7.33–8.37 (m, 1H), 7.24–7.28 (m, 3H), 7.04 (d, J=8.08 Hz, 2H), 6.54 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 144.6, 142.3, 138.4, 134.8, 132.6, 130.7, 130.5, 129.3, 128.8, 127.6, 126.9, 124.9, 124.4, 120.8, 116.8, 113.7, 21.6; HRMS (EI, TOF) calcd for $C_{21}H_{17}NO_2S$ $[M]^+$: 347.0980, found: 347.0985.

*4.4.2. 1-Benzyl-2-phenyl-1H-indole (**4b**).*[49] The compound was prepared from **3b** (141.7 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 132 mg (93% yield) of product **4b** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 100:1 v/v). Mp: 89–91 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.67 (d, J=5.12 Hz, 1H), 7.43 (d, J=5.96 Hz, 2H), 7.36–7.37 (m, 3H), 7.22–7.28 (m, 3H), 7.13–7.17 (m, 3H), 7.02 (d, J=7.08 Hz, 2H), 6.65 (s, 1H), 5.36 (s, 2H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 142.0, 138.3, 138.1, 132.8, 129.4, 128.9, 128.7, 128.4, 128.2, 127.3, 126.1, 122.0, 120.7, 120.3, 110.7, 102.5, 47.9; HRMS (ESI, TOF) calcd for $C_{21}H_{18}N^+$ $[M+H]^+$: 284.1434, found: 284.1435.

*4.4.3. 1-Benzyl-5-chloro-2-phenyl-1H-indole (**4c**).* The compound was prepared from **3c** (158.9 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 145 mg (91% yield) of product **4c** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 100:1 v/v). Mp: 102–104 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.62 (s, 1H), 7.37–7.43 (m, 5H), 7.22–7.30 (m, 3H), 7.05–7.10 (m, 2H), 6.98 (d, J=7.04 Hz, 2H), 6.58 (s, 1H), 5.34 (s, 2H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 143.3, 137.9, 136.4, 132.3, 129.4, 129.3, 129.0, 128.8, 128.5, 127.5, 126.0, 125.9, 122.2, 120.0, 111.7, 102.0, 48.0; HRMS (EI, TOF) calcd for $C_{21}H_{16}ClN^+$ $[M]^+$: 317.0971, found: 317.0970.

*4.4.4. 1-Benzyl-5-methyl-2-phenyl-1H-indole (**4d**).*[50] The compound was prepared from **3d** (148.7 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 146 mg (98% yield) of product **4d** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 100:1 v/v). Mp: 125–127 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.45 (s, 1H), 7.41–7.44 (m, 2H), 7.32–7.39 (m, 3H), 7.20–7.28 (m, 3H), 7.06 (d, J=8.36 Hz, 1H), 7.02 (d, J=7.20 Hz, 2H), 6.97 (d, J=8.32 Hz, 1H), 6.57 (s, 1H), 5.34 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 142.0, 138.5, 136.6, 133.0, 129.5, 129.3, 128.8, 128.7, 128.6, 128.0, 127.2, 126.1, 123.6, 120.4, 110.4, 102.0, 47.09, 21.6; HRMS (EI, TOF) calcd for $C_{22}H_{19}N^+$ $[M]^+$: 297.1517, found: 297.1518.

*4.4.5. 2-Methyl-3-methyleneisoindolin-1-one (**4e**).*[51] The compound was prepared from **3e** (79.6 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 75 mg (94% yield) of product **4e** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 25:1 v/v). Mp: 68–70 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.82 (d, J=7.52 Hz, 1H), 7.68 (d, J=7.64 Hz, 1H), 7.55–7.59 (m, 1H), 7.47–7.51 (m, 1H), 5.18 (d, J=1.60 Hz, 1H), 4.85 (d, J=1.60 Hz, 1H), 3.29 (s, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 167.2, 143.0, 136.2, 133.9, 131.9, 129.5, 123.1, 119.8, 88.6, 25.8; HRMS (EI, TOF) calcd for $C_{10}H_9NO$ $[M+H]^+$: 159.0684, found: 159.0685.

*4.4.6. (E)-3-Benzylidene-2-methylisoindolin-1-one (**4f**).*[42] The compound was prepared from **3f** (117.6 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 93 mg (79% yield) of

product **4f** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 5:1 v/v). Mp: 114–116 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.83 (d, J=7.52 Hz, 1H), 7.36–7.46 (m, 6H), 7.29–7.32 (m, 2H), 6.51 (s, 1H), 3.39 (s, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 166.7, 137.6, 135.3, 135.0, 131.5, 130.7, 129.6, 129.3, 128.8, 127.9, 123.2, 123.1, 110.3, 26.2; HRMS (EI, TOF) calcd for $C_{16}H_{13}NO$ $[M]^+$: 235.0997, found: 235.0998.

*4.4.7. (E)-3-Benzylidene-2-dodecylisoindolin-1-one (**4g**).* The compound was prepared from **3g** (155.7 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 104 mg (67% yield) of product **4g** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 10:1 v/v). Mp: 45–47 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.83 (d, J=7.48 Hz, 1H), 7.38–7.45 (m, 6H), 7.28–7.31 (m, 2H), 6.54 (s, 1H), 3.88 (t, J=7.36 Hz, 2H), 1.71–1.78 (m, 2H), 1.34–1.42 (m, 5H), 1.25 (br, 13H), 0.87 (t, J=6.36 Hz, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 166.7, 136.4, 135.5, 135.2, 131.4, 130.6, 129.7, 129.3, 128.8, 127.9, 123.2, 110.2, 39.7, 32.0, 29.8, 29.7, 29.5, 28.5, 27.2, 22.8, 14.2; HRMS (EI, TOF) calcd for $C_{27}H_{35}NO$ $[M]^+$: 389.2719, found: 3890.2722.

*4.4.8. (E)-3-Benzylidene-2-(p-tolyl)isoindolin-1-one (**4h**).* The compound was prepared from **3h** (155.7 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 104 mg (67% yield) of product **4h** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate 5:1 v/v). Mp: 124–126 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.93 (d, J=7.56 Hz, 1H), 7.46–7.50 (m, 1H), 7.40–7.44 (m, 5H), 7.30–7.37 (m, 6H), 6.35 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 166.5, 138.5, 138.3, 135.3, 135.0, 132.1, 131.9, 130.3, 130.2, 129.6, 129.5, 128.8, 128.7, 127.9, 123.7, 123.2, 112.3, 21.4; HRMS (ESI, TOF) calcd for $C_{22}H_{18}NO^+$ $[M+H]^+$: 312.1383, found: 312.1385.

*4.4.9. (E)-2-Benzyl-3-benzylideneisoindolin-1-one (**4i**).* The compound was prepared from **3i** (155.7 mg, 0.5 mmol) following typical procedure but using DMSO (1.5 mL) as solvent. 87 mg (56% yield) of product **4i** was obtained as a white solid after column chromatography (eluent=petroleum ether/ethyl acetate v/v). Mp: 118–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.95 (d, J=7.52 Hz, 1H), 7.43–7.47 (m, 1H), 7.31–7.40 (m, 11H), 7.25–7.28 (m, 1H), 6.46 (s, 1H), 5.13 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 166.9, 136.9, 136.1, 135.2, 135.1, 131.8, 130.3, 129.6, 129.4, 128.8, 128.7, 127.9, 127.5, 127.1, 123.5, 123.3, 111.7, 43.4; HRMS (EI, TOF) calcd for $C_{22}H_{17}NO$ $[M]^+$: 311.1310, found: 311.1313.

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Supplementary data

The X-ray crystallographic data of **2j**, the copies of ^{1}H spectra for products **2a**–**z** and **4a**–**i**, ^{13}C NMR spectra for new compounds **2d**–**g**, **2j**–**m**, **2o**, **2p**, **2r**–**w**, **2y**, **2z**, **4c** and **4g**–**i**. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.06.078.

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