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[Cu]-Catalyzed Domino Sonogashira Coupling Followed by Intramolecular 5-*exo-dig* Cyclization: Synthesis of 1,3-Dihydro-2-benzofurans

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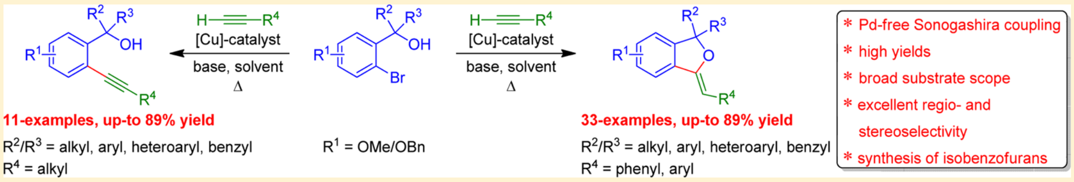
Supporting Information



ABSTRACT: An efficient [Cu]-catalyzed domino Sonogashira coupling of *o*-bromobenzyl tertiary alcohols with terminal aryl acetylenes followed by an intramolecular *anti*-5-*exo-dig* cyclization is presented. The terminal aryl acetylenes were identified as ideal coupling partners that permit in situ intramolecular oxacyclization by the hydroxyl group as a pre-existing nucleophile of the alcohol. Notably, the intramolecular nucleophilic attack of the hydroxyl group took place on the alkyne moiety in a highly regio- and stereoselective manner. Interestingly, this method was amenable to a wide variety of *o*-bromobenzyl tertiary alcohols and furnished the corresponding cyclic ethers. On the other hand, when terminal alkyl acetylenes were used as the coupling partners, the reaction was impeded after the Sonogashira coupling.

INTRODUCTION

Domino one-pot reactions are indispensible and permit the synthesis of complex molecules, since they eliminate the isolation and purification of the intermediate product(s).[1] In this context, transition-metal catalysis plays an important role for the development of new synthetic methods in the domain of organic synthesis via the efficient creation of C−C and C−heteroatom bonds with increasing molecular complexity.[2] In this regard, the Sonogashira reaction[3,4] is one of the useful couplings for the formation of $C(sp^2)-C(sp)$ bonds efficiently with good functional group tolerance. In general, this coupling reaction requires the support of copper salts as cocatalysts along with a [Pd] catalyst in the presence of amine bases. Generally, the use of terminal acetylenes for ring closure requires a two-step process, such as initial Sonogashira coupling and cyclization. The latter one would be promoted by either transition-metal[5,6] or electrophilic activation[7] of the resulting alkynes with an internal nucleophile. Recent developments on this reaction revealed that either palladium[8] or copper[9,10] can act as an effective single catalyst. Of late, one-pot domino Sonogashira coupling followed by intramolecular trapping of the alkyne moiety via nucleophilic attack by a suitably positioned internal nucleophile of the substrate has become an efficient route for the synthesis of heterocyclic compounds.[11−16] On the other hand, a sequence consisting of intermolecular nucleophilic Michael addition followed by intramolecular Heck coupling for the synthesis of isobenzofuran derivatives has also been reported (Scheme 1).[17]

In continuation of our ongoing research interests in the development of new synthetic methodology using transition-metal catalysis,[18] we recently disclosed a novel method[19] involving an unprecedented palladium-catalyzed domino process for the synthesis of benzochromenes and indenols from simple α,α-disubstituted 2-haloarylmethanols. Herein we report a one-pot domino copper-catalyzed intermolecular alkynylation followed by intramolecular oxacyclization for the synthesis of isobenzofuran derivatives (Scheme 1). Significantly, the present method furnishes the cyclic ethers with excellent regio- and stereoselectivity. The *anti*-5-*exo-dig* oxacyclization products with *Z* stereoselectvity were obtained almost exclusively, although both 5-*exo-dig* and 6-*endo-dig* cyclization modes are feasible according to Baldwin's rule.[20,21]

RESULTS AND DISCUSSION

The α,α-disubstituted (2-bromophenyl)methanols **1** required for this study were obtained using established procedures.[20] At this stage, in order to find out the best optimized reaction conditions, the transition-metal-catalyzed $C(sp^2)-C(sp)$ bond formation followed by ring-closure reaction of α,α-dimethyl-(2-bromophenyl)methanol (**1aa**) was screened under different conditions. Thus, treatment of **1aa** with phenylacetylene (**2a**) in the presence of the catalyst CuI (10 mol %)/**L1** (20 mol %) and the base Cs_2CO_3 (2 equiv) in hot DMF at 110 °C for 24 h, as expected, gave the product **3aa** in 62% yield (Table 1, entry

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Scheme 1. Present Study versus Representative Previous Approaches for the Synthesis of Isobenzofurans

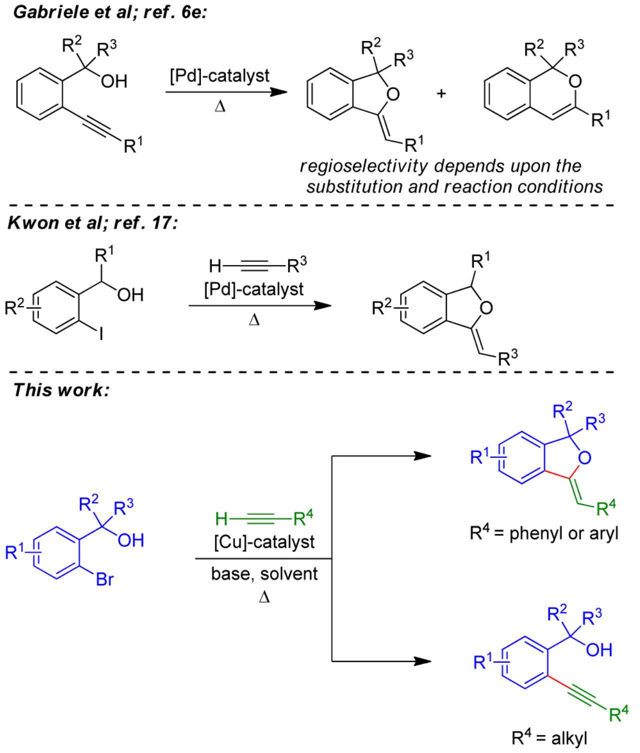
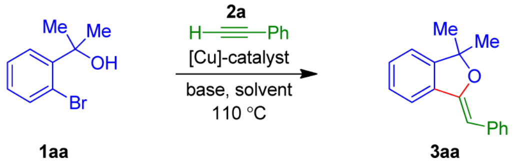
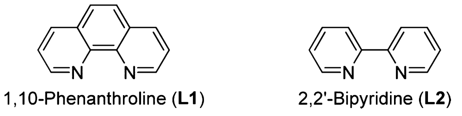


Table 1. Optimization of the Reaction Conditions for the Synthesis of Cyclic Ether **3aa**[a]



entry	[Cu] (10 mol %)	ligand (20 mol %)	solvent	base (2 equiv)	yield of **3aa** (%)[b]
1	CuI	**L1**	DMF	Cs_2CO_3	62
2	none	**L1**	toluene	Cs_2CO_3	–[c]
3	CuI	**L1**	toluene	none	–[c]
4	CuI	**L1**	DMA	Cs_2CO_3	72
5	CuI	**L2**	toluene	Cs_2CO_3	67
6	$Pd(OAc)_2$	PPh_3	toluene	Cs_2CO_3	80[d]
7	**CuI**	**L1**	**toluene**	**Cs_2CO_3**	**88**
8	CuI	**L2**	toluene	K_2CO_3	–[c]
9	CuI	**L1**	toluene	NEt_3	–[c,e]
10	CuI	**L1**	toluene	Na_2CO_3	–[c,e]
11	CuI	**L1**	toluene	K_2CO_3	20[c,e]
12	CuI	**L1**	toluene	$NaHCO_3$	–[c,e]
13	CuI	**L1**	CH_3CN	Cs_2CO_3	80
14	CuI	**L1**	toluene	K_3PO_4	55
15	CuBr	**L1**	toluene	Cs_2CO_3	36

[a] All of the reactions were carried out on a 0.5 mol scale of **1aa**. [b] Isolated yields of chromatographically pure products. [c] Starting material was recovered. [d] A 1:1 mixture of benzochromene and isobenzofuran was obtained. [e] The dimerized acetylene (Glasser product) was formed in 10–20% yield.

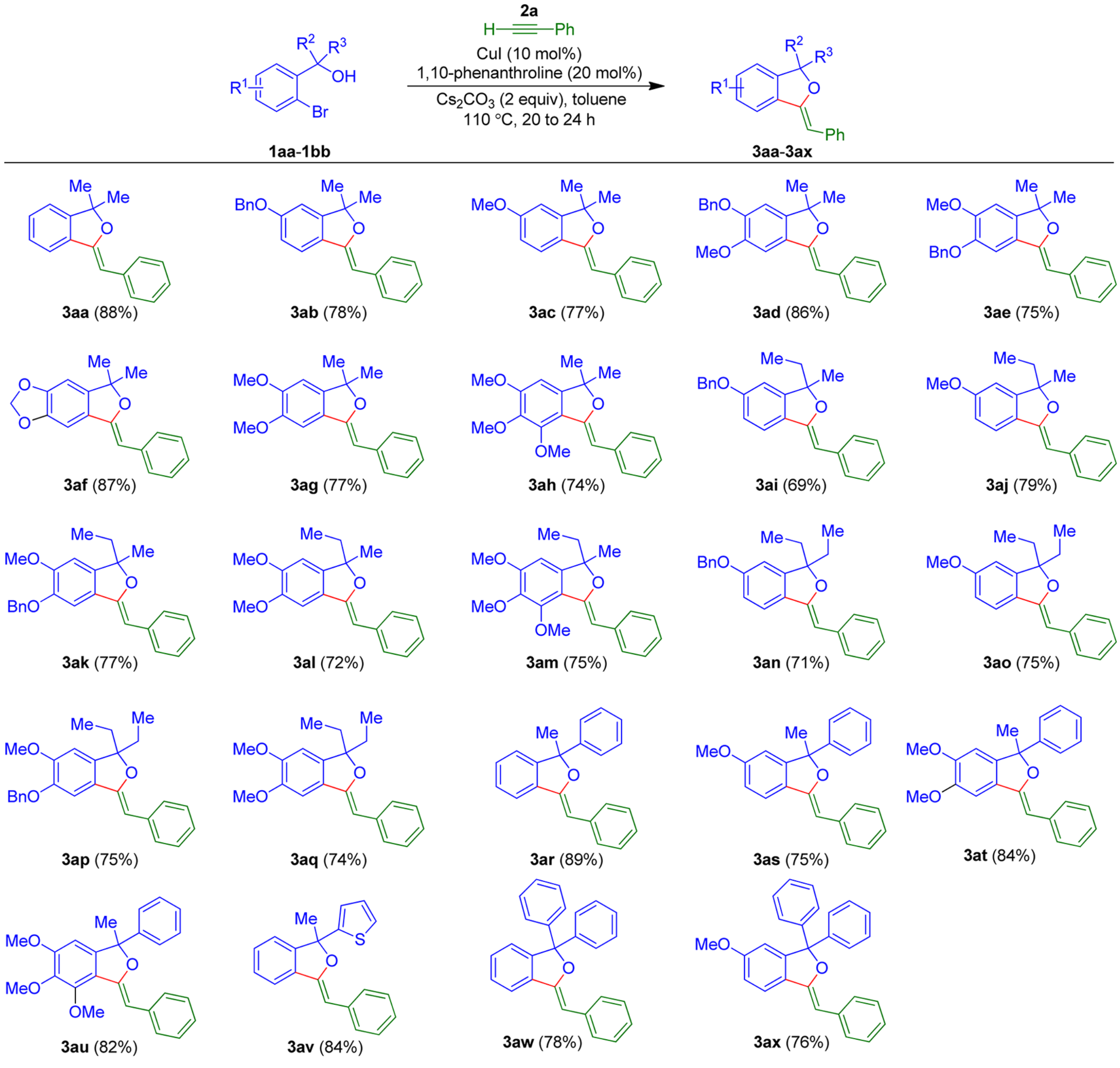


1). On the other hand, the reaction either in the presence of the catalyst CuI (10 mol %)/**L1** (20 mol %) without the base or in the presence of the base Cs_2CO_3 (2 equiv) without the catalyst in hot toluene at 110 °C for 24 h led to the recovery of the starting maerial **1aa**, thus signifying the importance of both the catalyst and the base in promoting the reaction (Table 1, entries 2 and 3). Results similar to those shown in entry 1 of Table 1 were noticed with DMA as the solvent (Table 1, entry 4) or with ligand **L2** instead of **L1** in toluene (Table 1, entry 5). However, when a Pd catalyst was used, as expected, the usual benzochromene[20] was formed along with the product **3aa** (Table 1, entry 6). Gratifyingly, the reaction with the catalyst CuI (10 mol %)/**L1** (20 mol %) and the base Cs_2CO_3 (2 equiv) in hot toluene at 110 °C for 24 h furnished the product **3aa** in a very good yield of 88% (Table 1 entry 7). In contrast, there was no progress with the mild base K_2CO_3 (Table 1, entry 8), and a similar trend was observed with other mild bases as well (Table 1, entries 9–12). CH_3CN proved to be a good solvent, furnishing cyclic ether **3aa** in 80% yield (Table 1, entry 13). On the other hand, the use of K_3PO_4 as the base showed a moderate effect (Table 1, entry 14). CuBr was found to be very much inferior to CuI (Table 1, entry 15). Signficantly, all of the optimization trials in Table 1 that gave the cyclic ether **3aa** furnished it as a single diastereomeric product with excellent regioselectivity (i.e., *anti*-5-*exo*-*dig* cyclization) and stereoselectivity (i.e., *Z* selectivity).

Among all of the reaction conditions screened, those in entry 7 of Table 1 were found to be the best with regard to the yield of cyclic ether **3aa**. Therefore, to examine the scope and generality of the method, these above optimized conditions were applied to the other 2-bromobenzyl tertiary alcohols **1aa**–**bb** with **2a** as the Sonogashira coupling partner. Delightfully, the reaction showed broad substrate scope and furnished the corresponding cyclic ethers **3aa**–**ax** in good to very good yields, as summarized in Table 2. Interestingly, the method was successfully applied to systems containing simple to dense electron-rich 2-bromoaryl moieties as well as a wide variety of substituents on the benzylic carbon of alcohols **1aa**–**bb** (i.e., dimethyl, ethyl and methyl, diethyl, methyl and phenyl, methyl and thiophenyl, and diphenyl tertiary alcohol moieties). In addition to spectroscopic evidence, the structures of **3** were confirmed by single-crystal X-ray diffraction analysis of **3af** (see the Supporting Information for the X-ray data of **3af**). It is worth mentioning that while our work was in progress, we came across a similar concept reported by Lee and coworkers,[22] which was mainly focused on the Sonogashira coupling between alkynes and aryl iodides. However, their method was applied for only two examples, particularly on more reactive 2-iodobenzyl alcohols.

After the successful synthesis of cyclic ethers **3aa**–**ax**, we became interested in checking the generality and limitations of the method by exploring the reactions of 2-bromobenzyl tertiary alcohols **1ab**–**bb** with other terminal aryl acetylenes **2b**–**d** as the coupling partners. Thus, the [Cu]-catalyzed reactions of 2-bromobenzyl tertiary alcohols **1ab**–**bb** with terminal aryl acetylenes **2b**–**d** were attempted. Gratifyingly, the results were quite consistent with those observed in the above case of 2-bromobenzyl tertiary alcohols **1aa**–**bb** with simple phenylacetylene **2a** (Table 2), as the corresponding products **4aa**–**ai** with dense functionality on the aromatic rings were obtained in very good yields, as depicted in Table 3.

Table 2. Scope of the Sonogashira Coupling Followed by Oxacyclization to Give 3[a]



[a]Reaction conditions: **1aa**−**bb** (0.50 mmol), Cs_2CO_3 (2 equiv), CuI (10 mol %), and 1,10-phenanthroline (20 mol %) in 0.5 mL of toluene at 110 °C for 20−24 h. The yields shown in parentheses are isolated yields of chromatographically pure products.

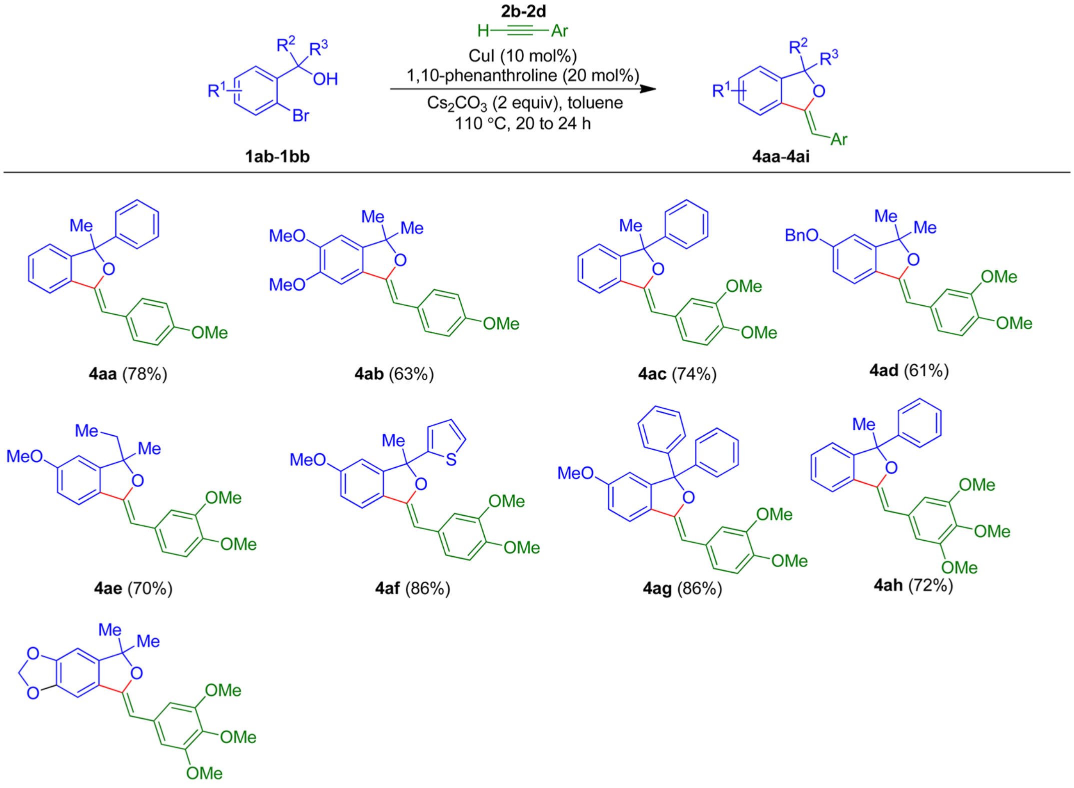
We also performed the reaction with a terminal aryl acetylene containing an electron-withdrawing group (methyl 4-ethynylbenzoate) as a coupling partner. However, the reaction was not very clean, producing very little of the requisite product along with a considerable amount of the Glaser coupling product and the recovery of starting material. This may be due to less nucleophilic nature of the corresponding Cu acetylide, which may be less efficient in the subsequent coupling with the aryl bromide to give the product. Moreover, when we conducted the reaction with electron-deficient ethyl propiolate, it failed to yield any clean product. It is worth mentioning that the Glaser coupling product was generally observed as the minor byproduct (10−20% yield).

Furthermore, to study the scope and limitations of this method, [Cu] catalysis was also explored in the reactions of 2-bromobenzyl tertiary alcohols **1aa**−**at** with terminal alkyl acetylenes 1-octyne, 1-nonyne, and 1-decyne (**2e**−**g**). However, under the standard reaction conditions, the reaction was impeded after the Sonogashira coupling (Table 4). This can be justified on the basis of the difficulty of forming an olefinic carbanion via internal nucleophilic attack by the hydroxyl group on the alkyne moiety because there is no stabilizing group connected to that carbon atom. In contrast, in the case of terminal aryl acetylenes, the corresponding carbanion would be easily formed because it can be stabilized via the extended conjugation with the aromatic ring of the aryl acetylene.

■ CONCLUSION

We have developed an efficient domino [Cu]-catalyzed Sonogashira coupling followed by intramolecular 5-*exo-dig* oxacyclization for the synthesis of isobenzofuran derivatives. Significantly, the present method furnishes the cyclic ethers in a highly regio- and stereoselective manner. The reaction was quite successful with different 2-bromobenzyl tertiary alcohols and terminal aryl acetylenes.

Table 3. Scope of the Transformation with Different Terminal Aryl Acetylenes 2b−d[a]



4aa (78%)
4ab (63%)
4ac (74%)
4ad (61%)
4ae (70%)
4af (86%)
4ag (86%)
4ah (72%)
4ai (83%)

[a] Reaction conditions: **1ab−bb** (0.50 mmol), Cs_2CO_3 (2 equiv), CuI (10 mol %), and 1,10-phenanthroline (20 mol %) in 0.5 mL of toluene at 110 °C for 20−24 h. The yields shown in parentheses are isolated yields of chromatographically pure products.

■ EXPERIMENTAL SECTION

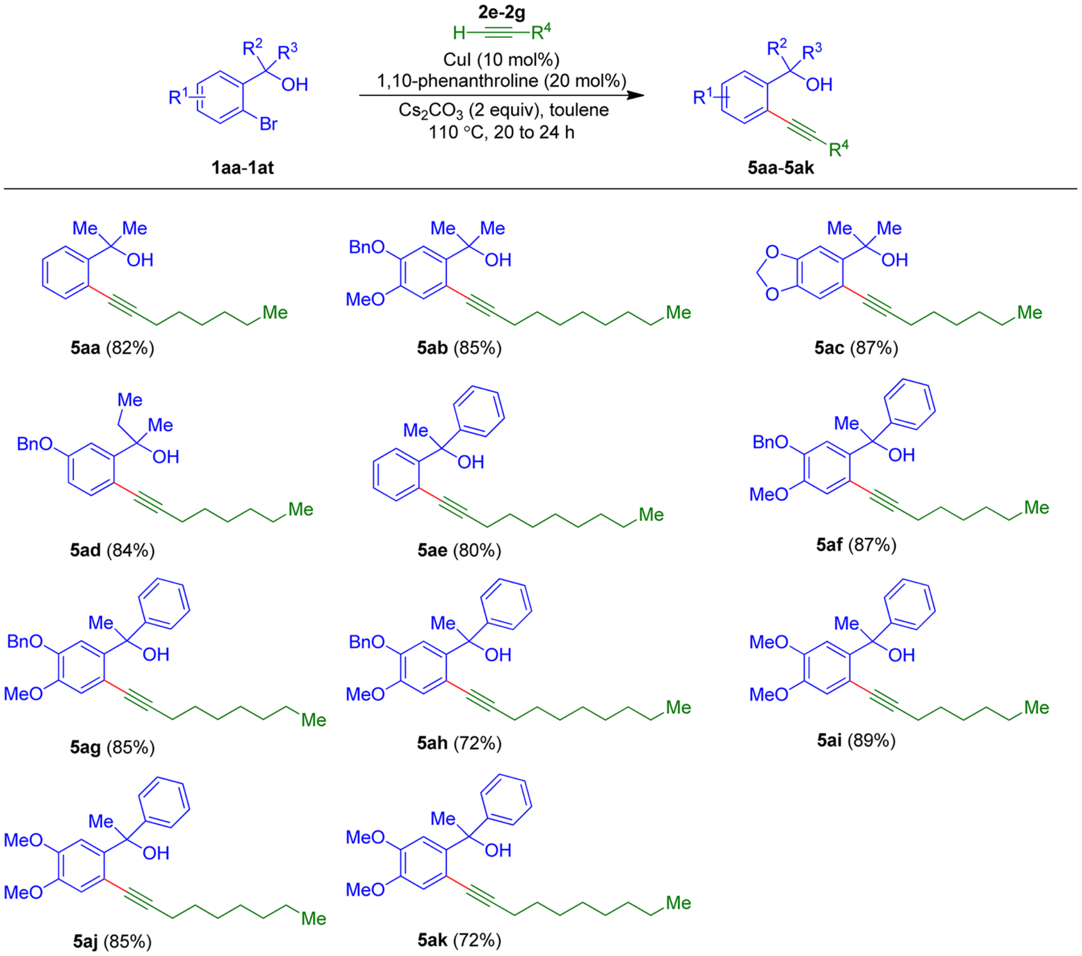
General Considerations. IR spectra were recorded on an FTIR spectrophotometer. ^1H NMR spectra were recorded on a 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on a 100 MHz spectrometer at room temperature in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of the triplet)]. In the ^{13}C NMR data, the natures of the carbons (C, CH, CH_2, and CH_3) were determined by recording DEPT-135 spectra and are given in parentheses (C_q is used for C). In the ^1H NMR data, the following abbreviations are used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet, and br s = broad singlet. The assignments of signals were confirmed by $^1H,^{13}C$-decoupled and DEPT spectra. High-resolution mass spectrometry (HRMS) was performed using a Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Benzaldehydes, phenyl acetylene, alkyl acetylenes, aryl halides, methyl iodide, Mg metal, Na_2SO_4, and NH_4Cl were commercially available (locally made) and used without further purification. CuI, 1,10-phenanthraline, and Cs_2CO_3 purchased from a commercial source. All of the solvents (diethyl ether, THF, DCM, DMF, and DMSO) were commercially available, and all were used dry. Diethyl ether, toluene, and THF were dried over sodium metal, and DCM and DMF were dried over calcium hydride; dry DMSO was purchased from a commercial source.

All of the small-scale dry reactions were carried out using standard syringe−septum techniques. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as the eluents. Reactions were generally run under an argon or nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 40−60 °C was used. Acme's silica gel (60−120 mesh) was used for column chromatography (approximately 20 g per gram of crude material).

1-(2-Bromo-3,4,5-trimethoxyphenyl)propan-1-ol (7a). To a cold (−10 °C) magnetically stirred solution of 2-bromo-3,4,5-trimethoxybenzaldehyde (**6h**) (1.0 g, 3.63 mmol) in dry ether (50 mL) in an oven-dried 100 mL round-bottom flask was added ethylmagnesium bromide [18.18 mmol, prepared from magnesium (436 mg, 18.18 mmol), ethyl bromide (1.30 mL, 18.18 mmol), and a catalytic amount of iodine in 30 mL of dry ether]. The reaction mixture was stirred at −10 °C for 3 h. It was then poured into saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The ethyl acetate extract was dried with anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using petroleum ether/ethyl acetate (85:15 to 80:20) as the eluent furnished secondary alcohol **7a** (1.05 g, 95%) as a pale-yellow liquid. [TLC control (petroleum ether/ethyl acetate 80:20, R_f(**6h**) = 0.85, R_f(**7a**) = 0.40, UV detection)]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.89 (s, 1H), 4.95 (dd, 1H, J = 8.3 and 4.4 Hz), 3.84 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 2.38 (br s, 1H), 1.85−1.68 (m, 1H), 1.67−1.50 (m, 1H), 0.96 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.8 (C_q), 150.2 (C_q), 141.9 (C_q), 139.5 (C_q), 108.0 (C_q), 105.8 (CH), 74.0 (CH), 60.9 (CH_3), 60.8 (CH_3), 56.0 (CH_3), 30.6 (CH_2), 10.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3401, 2926, 2852, 1590, 1490, 1454, 1311, 1195, 1098, 1004, 909 cm^{-1}. HRMS (ESI^+) m/z: calcd for $[C_{12}H_{16}BrO_3]^+$ = $[M + H - H_2O]^+$ 287.0277, found 287.0272.

1-(2-Bromo-3,4,5-trimethoxyphenyl)propan-1-one (8a). To a solution of secondary alcohol **7a** (1.0 g, 2.84 mmol) in dry CH_2Cl_2 (10 mL) in an oven-dried 50 mL round-bottom flask was added a homogeneous mixture of PCC (1.83 g, 8.55 mmol) and silica gel (1.83 g). The resulting reaction mixture was stirred at room temperature for 2 h and then filtered through a short silica gel column and eluted with excess CH_2Cl_2. Evaporation of the solvent furnished ketone **8a** (975 g, 98%) as a pale-brown viscous liquid. [TLC control (petroleum ether/

Table 4. Reaction with Terminal Alkyl Acetylenes 2e−g[a]



5aa (82%)
5ab (85%)
5ac (87%)
5ad (84%)
5ae (80%)
5af (87%)
5ag (85%)
5ah (72%)
5ai (89%)
5aj (85%)
5ak (72%)

[a]Reaction conditions: **1aa−at** (0.50 mmol), Cs_2CO_3 (2 equiv), CuI (10 mol %), and 1,10-phenanthroline (20 mol %) in 0.5 mL of toluene at 110 °C for 20−24 h. The yields shown in parentheses are isolated yields of chromatographically pure products.

ethyl acetate 80:20, R_f(**7a**) = 0.40, R_f(**8a**) = 0.55, UV detection)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.67 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.84 (s, 3H), 2.92 (q, 2H, J = 7.3 Hz), 1.18 (t, 2H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.8 (C_q), 152.9 (C_q), 151.0 (C_q), 144.6 (C_q), 137.7 (C_q), 107.1 (CH), 105.6 (C_q), 61.1 (CH_3), 61.0 (CH_3), 56.2 (CH_3), 36.1 (CH_2), 8.2 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2921, 2851, 1704, 1563, 1482, 1461, 1383, 1199, 1165, 1107, 1009, 929 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{12}H_{15}BrNaO_4]^+$ = $[M + Na]^+$ 325.0046, found 325.0039.

2-(2-Bromo-3,4,5-trimethoxyphenyl)butan-2-ol (1am). To a cold (−10 °C) magnetically stirred solution of bromoketone **8a** (500 mg, 1.65 mmol) in dry ether (50 mL) in an oven-dried 100 mL round-bottom flask was added methylmagnesium iodide [13.20 mmol, prepared from magnesium (316 mg, 13.20 mmol), methyl iodide (1.60 mL, 18.18 mmol), and a catalytic amount of iodine in 50 mL of dry ether]. The reaction mixture was stirred at −10 °C for 3 h. It was then poured into saturated aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The ethyl acetate extract was dried with anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using petroleum ether/ethyl acetate (85:15 to 80:20) as the eluent furnished tertiary alcohol **1am** (420 g, 80%) as a pale-yellow liquid. [TLC control (petroleum ether/ethyl acetate 80:20, R_f(**8a**) = 0.55, R_f(**1am**) = 0.35, UV detection)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.15 (s, 1H), 3.87 (s, 3H), 3.86 (s, 6H), 2.45−2.25 (m, 2H), 2.05−1.85 (m, 1H), 1.70 (s, 3H), 0.77 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.0 (C_q), 151.1 (C_q), 141.6 (C_q), 141.2 (C_q), 107.5 (CH), 107.0 (C_q), 76.4 (C_q), 60.9 (CH_3), 60.8 (CH_3), 56.0 (CH_3), 33.3 (CH_2), 27.6 (CH_3), 8.3 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3482, 2924, 2852, 1564, 1481, 1375, 1316, 1196, 1153, 1105, 1009, 925, 836, 752 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{13}H_{19}BrNaO_4]^+$ = $[M + Na]^+$ 341.0359, found 341.0351.

General Procedure (GP) for the Formation of Isobenzofurans (3 and 4) and Acyclic Alcohols (5). In an oven-dried Schlenk tube under a nitrogen atmosphere were added tertiary alcohol **1** (0.50 mmol), aryl or aliphatic terminal alkyne **2** (0.75 mmol), CuI (10 mol %), 1,10-phenthroline (20 mol %), Cs_2CO_3 (1.0 mmol), and toluene (0.5 mL). The resulting reaction mixture was stirred at 110 °C for 20−24 h. The progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aq. NH_4Cl solution and extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the cyclic ether **3** or **4** or acyclic alcohol **5**.

*(3Z)-3-Benzylidene-1,1-dimethyl-1,3-dihydro-2-benzofuran (**3aa**).* This compound was prepared according to the GP and isolated as a yellow semisolid in 88% yield (105 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1aa**) = 0.60, R_f(**3aa**) = 0.80, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (dd, 2H, J = 8.3 and 1.5 Hz), 7.53−7.43 (m, 1H), 7.35−7.23 (m, 4H), 7.18−7.13 (m, 1H), 7.10 (dd, 1H, J = 7.3 and 7.3 Hz), 5.86 (s, 1H), 1.60 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.3 (C_q), 147.4 (2 × C_q), 136.7 (2 × C_q), 134.0 (C_q), 128.7 (CH), 128.2 (2 × CH), 128.0 (CH), 127.7 (2 × CH), 125.0 (CH), 120.4 (CH), 119.9 (CH), 95.7 (CH), 89.1 (C_q), 28.4 (2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2971, 2904, 1650, 1514, 1474, 1305, 1233, 1140, 1036, 820, 766 cm^{-1}.

HRMS (ESI$^+$) *m/z*: calcd for $[C_{17}H_{17}O]^+$ = $[M + H]^+$ 237.1274, found 237.1274.

*(3Z)-3-Benzylidene-6-(benzyloxy)-1,1-dimethyl-1,3-dihydro-2-benzofuran (**3ab**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 78% yield (133 mg). [TLC control (petroleum ether/ethyl acetate 85:15, R_f(**1ab**) = 0.30, R_f(**3ab**) = 0.70, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.73 (d, 2H, J = 7.8 Hz), 7.53−7.28 (m, 8H), 7.11 (t, 1H, J = 7.3 Hz), 6.97 (dd, 1H, J = 8.3 and 2.0 Hz), 6.80 (d, 1H, J = 2.0 Hz), 5.76 (s, 1H), 5.10 (s, 2H), 1.64 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 159.9 (C$_q$), 154.3 (C$_q$), 149.4 (C$_q$), 137.0 (C$_q$), 136.5 (C$_q$), 128.6 (2 × CH), 128.2 (2 × CH), 128.1 (CH), 127.6 (2 × CH), 127.5 (2 × CH), 127.0 (C$_q$), 124.6 (CH), 121.2 (CH), 115.4 (CH), 106.5 (CH), 94.2 (CH), 88.7 (C$_q$), 70.4 (CH$_2$), 28.3 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2922, 1652, 1608, 1593, 1492, 1452, 1298, 1220, 1090, 1026, 736, 695 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{24}H_{23}O_2]^+$ = $[M + H]^+$ 343.1693, found 343.1698.

*(3Z)-3-Benzylidene-6-methoxy-1,1-dimethyl-1,3-dihydro-2-benzofuran (**3ac**).* This compound was prepared according to the GP and isolated as a brown oil in 77% yield (112 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1ac**) = 0.40, R_f(**3ac**) = 0.50, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.74 (d, 2H, J = 7.3 Hz), 7.44 (d, 1H, J = 8.3 Hz), 7.33 (dd, 2H, J = 7.8 and 7.3 Hz), 7.12 (t, 1H, J = 7.3 Hz), 6.90 (dd, 1H, J = 8.3 and 2.4 Hz), 6.72 (d, 1H, J = 2.4 Hz), 5.77 (s, 1H), 3.86 (s, 3H), 1.65 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 160.8 (C$_q$), 154.3 (C$_q$), 149.4 (C$_q$), 137.0 (C$_q$), 128.2 (2 × CH), 127.4 (2 × CH), 126.7 (C$_q$), 124.6 (CH), 121.2 (CH), 114.7 (CH), 105.3 (CH), 94.1 (CH), 88.6 (C$_q$), 55.6 (CH$_3$), 28.3 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2961, 2906, 1658, 1524, 1478, 1304, 1231, 1130, 1034, 827, 768 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{18}H_{18}O_2]^+$ = $[M]^+$ 266.1301, found 266.1309.

*(3Z)-3-Benzylidene-6-(benzyloxy)-5-methoxy-1,1-dimethyl-1,3-dihydro-2-benzofuran (**3ad**).* This compound was prepared according to the GP and isolated as a pale-green viscous liquid in 86% yield (162 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1ad**) = 0.40, R_f(**3ad**) = 0.60, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.76 (d, 2H, J = 6.8 Hz), 7.48 (d, 2H, J = 7.3 Hz), 7.41 (dd, 2H, J = 7.8 and 6.8 Hz), 7.38−7.30 (m, 3H), 7.13 (t, 1H, J = 7.3 Hz), 7.01 (s, 1H), 6.73 (s, 1H), 5.76 (s, 1H), 5.19 (s, 2H), 3.96 (s, 3H), 1.61 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.6 (C$_q$), 150.4 (C$_q$), 149.8 (C$_q$), 140.3 (C$_q$), 137.0 (C$_q$), 136.6 (C$_q$), 128.5 (2 × CH), 128.2 (2 × CH), 128.0 (CH), 127.5 (2 × CH), 127.4 (2 × CH), 126.6 (C$_q$), 124.6 (CH), 105.8 (CH), 102.6 (CH), 94.1 (CH), 88.8 (C$_q$), 71.4 (CH$_2$), 56.2 (CH$_3$), 28.3 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2968, 2902, 1667, 1513, 1472, 1301, 1232, 1147, 1039, 828, 765 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{25}H_{23}O_2]^+$ = $[M + H - H_2O]^+$ 355.1693, found 355.1687.

*(3Z)-3-Benzylidene-5-(benzyloxy)-6-methoxy-1,1-dimethyl-1,3-dihydro-2-benzofuran (**3ae**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 75% yield (127 mg). [TLC control (petroleum ether/ethyl acetate 80:20, R_f(**1ae**) = 0.20, R_f(**3ae**) = 0.40, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.72 (d, 2H, J = 8.8 Hz), 7.49 (d, 2H, J = 6.8 Hz), 7.40 (dd, 2H, J = 7.8 and 6.8 Hz), 7.37−7.28 (m, 3H), 7.10 (t, 1H, J = 7.3 Hz), 7.02 (s, 1H), 6.69 (s, 1H), 5.65 (s, 1H), 5.19 (s, 2H), 3.93 (s, 3H), 1.63 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.6 (C$_q$), 151.4 (C$_q$), 148.9 (C$_q$), 141.0 (C$_q$), 137.0 (C$_q$), 136.7 (C$_q$), 128.6 (2 × CH), 128.2 (2 × CH), 128.0 (CH), 127.4 (4 × CH), 126.0 (C$_q$), 124.6 (CH), 104.8 (CH), 103.4 (CH), 94.0 (CH), 88.9 (C$_q$), 71.3 (CH$_2$), 56.3 (CH$_3$), 28.4 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2923, 2852, 1651, 1596, 1500, 1449, 1321, 1235, 1169, 1037, 802, 695 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{25}H_{24}O_3Na]^+$ = $[M + Na]^+$ 395.1618, found 395.1616.

*(7Z)-7-Benzylidene-5,5-dimethyl-5,7-dihydrofuro[3,4-f][1,3]-benzodioxole (**3af**).* This compound was prepared according to the GP and isolated as a brown solid in 87% yield (123 mg), mp 110−112 °C. [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1af**) = 0.40, R_f(**3af**) = 0.50, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.70 (d, 2H, J = 6.8 Hz), 7.31 (dd, 1H, J = 7.8 and 7.3 Hz), 7.10 (t, 1H, J = 7.3 Hz), 6.90 (s, 1H), 6.62 (s, 1H), 6.01 (s, 2H), 5.67 (s, 1H), 1.60 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.5 (C$_q$), 149.2 (C$_q$), 148.3 (C$_q$), 142.2 (C$_q$), 136.9 (C$_q$), 128.2 (2 × CH), 127.6 (C$_q$), 127.5 (2 × CH), 124.7 (CH), 101.7 (CH$_2$), 100.9 (CH), 99.9 (CH), 94.2 (CH), 88.7 (C$_q$), 28.4 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2969, 2903, 1660, 1513, 1472, 1302, 1237, 1142, 1032, 821, 768 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{18}H_{16}O_3]^+$ = $[M]^+$ 280.1094, found 280.1096.

*(3Z)-3-Benzylidene-5,6-dimethoxy-1,1-dimethyl-1,3-dihydro-2-benzofuran (**3ag**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 77% yield (114 mg). [TLC control (petroleum ether/ethyl acetate 70:30, R_f(**1ag**) = 0.30, R_f(**3ag**) = 0.68, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.72 (d, 2H, J = 7.8 Hz), 7.31 (dd, 2H, J = 7.8 and 7.3 Hz), 7.10 (t, 1H, J = 7.3 Hz), 6.96 (s, 1H), 6.67 (s, 1H), 5.72 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 1.63 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.7 (C$_q$), 150.7 (C$_q$), 149.7 (C$_q$), 140.5 (C$_q$), 137.0 (C$_q$), 128.2 (2 × CH), 127.4 (2 × CH), 126.0 (C$_q$), 124.6 (CH), 102.9 (CH), 102.1 (CH), 94.0 (CH), 88.9 (C$_q$), 56.2 (CH$_3$), 56.1 (CH$_3$), 28.4 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2925, 1651, 1597, 1501, 1465, 1322, 1235, 1209, 1169, 1038, 802, 695 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{19}H_{21}O_3]^+$ = $[M + H]^+$ 297.1485, found 297.1476.

*(3Z)-3-Benzylidene-4,5,6-trimethoxy-1,1-dimethyl-1,3-dihydro-2-benzofuran (**3ah**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 74% yield (121 mg). [TLC control (petroleum ether/ethyl acetate 80:20, R_f(**1ah**) = 0.25, R_f(**3ah**) = 0.60, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.74 (d, 2H, J = 7.8 Hz), 7.31 (dd, 2H, J = 7.8 and 7.3 Hz), 7.10 (t, 1H, J = 7.3 Hz), 6.47 (s, 1H), 6.23 (s, 1H), 4.03 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 1.61 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.9 (C$_q$), 152.8 (C$_q$), 148.5 (C$_q$), 144.2 (C$_q$), 141.9 (C$_q$), 137.5 (C$_q$), 128.1 (2 × CH), 127.8 (2 × CH), 124.7 (CH), 119.0 (C$_q$), 99.0 (CH), 98.5 (CH), 88.3 (C$_q$), 61.0 (CH$_3$), 60.5 (CH$_3$), 56.2 (CH$_3$), 28.5 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2932, 1642, 1592, 1471, 1343, 1253, 1138, 1085, 1017, 825 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{20}H_{23}O_4]^+$ = $[M + H]^+$ 327.1591, found 327.1591.

*(3Z)-3-Benzylidene-6-(benzyloxy)-1-ethyl-1-methyl-1,3-dihydro-2-benzofuran (**3ai**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 69% yield (123 mg). [TLC control (petroleum ether/ethyl acetate 85:15, R_f(**1ai**) = 0.32, R_f(**3ai**) = 0.70, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.74 (d, 2H, J = 8.3 Hz), 7.53−7.28 (m, 8H), 7.12 (t, 1H, J = 7.3 Hz), 6.98 (dd, 1H, J = 8.3 and 2.4 Hz), 6.76 (d, 1H, J = 2.4 Hz), 5.75 (s, 1H), 5.10 (s, 2H), 2.15−1.97 (m, 1H), 1.95−1.80 (m, 1H), 1.61 (s, 3H), 0.82 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 159.9 (C$_q$), 154.9 (C$_q$), 148.1 (C$_q$), 137.1 (C$_q$), 136.5 (C$_q$), 128.6 (2 × CH), 128.2 (2 × CH), 128.1 (CH), 127.9 (C$_q$), 127.6 (2 × CH), 127.4 (2 × CH), 124.6 (CH), 121.1 (CH), 115.3 (CH), 106.7 (CH), 93.8 (CH), 91.3 (C$_q$), 70.5 (CH$_2$), 34.1 (CH$_2$), 26.6 (CH$_3$), 8.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2970, 1652, 1593, 1492, 1448, 1264, 1208, 1025, 907, 756, 732, 693 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{25}H_{25}O_2]^+$ = $[M + H]^+$ 357.1849, found 357.1846.

*(3Z)-3-Benzylidene-1-ethyl-6-methoxy-1-methyl-1,3-dihydro-2-benzofuran (**3aj**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 79% yield (111 mg). [TLC control (petroleum ether/ethyl acetate 85:15, R_f(**1aj**) = 0.25, R_f(**3aj**) = 0.65, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.73 (d, 2H, J = 7.8 Hz), 7.44 (d, 1H, J = 8.3 Hz), 7.32 (dd, 2H, J = 7.8 and 7.3 Hz), 7.11 (t, 1H, J = 7.8 and 7.3 Hz), 6.89 (dd, 1H, J = 8.3 and 2.4 Hz), 6.66 (d, 1H, J = 2.4 Hz), 5.74 (s, 1H), 3.85 (s, 3H), 2.15−1.95 (m, 1H), 1.94−1.80 (m, 1H), 1.61 (s, 3H), 0.81 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 160.7 (C$_q$), 155.0 (C$_q$), 148.1 (C$_q$), 137.2 (C$_q$), 128.2 (2 × CH), 127.7 (C$_q$), 127.4 (2 × CH), 124.5 (CH), 121.1 (CH), 114.6 (CH), 105.5 (CH), 93.6 (CH), 91.3 (C$_q$), 55.6 (CH$_3$), 34.1 (CH$_2$), 26.6 (CH$_3$), 8.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2922, 1651, 1593, 1493, 1450, 1284, 1220, 1051, 1030, 927, 802, 694 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{19}H_{21}O_2]^+$ = $[M + H]^+$ 281.1536, found 281.1571.

*(3Z)-3-Benzylidene-5-(benzyloxy)-1-ethyl-6-methoxy-1-methyl-1,3-dihydro-2-benzofuran (**3ak**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in

77% yield (148 mg). [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1ak**) = 0.20, R_f(**3ak**) = 0.45, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.71 (d, 2H, J = 7.3 Hz), 7.49 (d, 2H, J = 7.3 Hz), 7.40 (dd, 2H, J = 7.8 and 6.8 Hz), 7.37−7.26 (m, 3H), 7.10 (t, 1H, J = 7.3 Hz), 7.03 (s, 1H), 6.65 (s, 1H), 5.63 (s, 1H), 5.19 (s, 2H), 3.92 (s, 3H), 2.10−1.95 (m, 1H), 1.90−1.80 (m, 1H), 1.60 (s, 3H), 0.80 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 155.3 (C$_q$), 151.4 (C$_q$), 148.9 (C$_q$), 139.6 (C$_q$), 137.1 (C$_q$), 136.8 (C$_q$), 128.6 (2 × CH), 128.2 (2 × CH), 128.0 (CH), 127.4 (2 × CH), 127.3 (2 × CH), 127.0 (C$_q$), 124.5 (CH), 104.7 (CH), 103.6 (CH), 93.5 (CH), 91.5 (C$_q$), 71.3 (CH$_2$), 56.3 (CH$_3$), 34.1 (CH$_2$), 26.7 (CH$_3$), 8.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2922, 2851, 1650, 1596, 1499, 1452, 1426, 1347, 1230, 1202, 1050, 1027, 801, 736, 693 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{26}$H$_{27}$O$_3$]$^+$ = [M + H]$^+$ 387.1955, found 387.1952.

*(3Z)-3-Benzylidene-1-ethyl-5,6-dimethoxy-1-methyl-1,3-dihydro-2-benzofuran (**3al**).* This compound was prepared according to the GP and isolated as a pale-brown viscous liquid in 72% yield (112 mg). [TLC control (petroleum ether/ethyl acetate 70:30, R_f(**1al**) = 0.31, R_f(**3al**) = 0.70, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.72 (d, 2H, J = 7.8 Hz), 7.31 (dd, 2H, J = 7.8 and 7.3 Hz), 7.09 (t, 1H, J = 7.3 Hz), 6.96 (s, 1H), 6.62 (s, 1H), 5.69 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 2.10−1.95 (m, 1H), 1.92−1.78 (m, 1H), 1.60 (s, 3H), 0.78 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 155.4 (C$_q$), 150.7 (C$_q$), 149.6 (C$_q$), 139.0 (C$_q$), 137.1 (C$_q$), 128.2 (2 × CH), 127.4 (2 × CH), 127.0 (C$_q$), 124.6 (CH), 103.0 (CH), 102.0 (CH), 93.5 (CH), 91.5 (C$_q$), 56.2 (CH$_3$), 56.1 (CH$_3$), 34.2 (CH$_2$), 26.7 (CH$_3$), 8.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2970, 1651, 1596, 1502, 1466, 1349, 1233, 1208, 1031, 926, 803, 695 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{20}$H$_{23}$O$_3$]$^+$ = [M + H]$^+$ 311.1642, found 311.1642.

*(3Z)-3-Benzylidene-1-ethyl-4,5,6-trimethoxy-1-methyl-1,3-dihydro-2-benzofuran (**3am**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 75% yield (127 mg). [TLC control (petroleum ether/ethyl acetate 80:20, R_f(**1am**) = 0.20, R_f(**3am**) = 0.45, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.73 (d, 2H, J = 8.8 Hz), 7.31 (dd, 2H, J = 7.8 and 7.3 Hz), 7.10 (t, 1H, J = 7.3 Hz), 6.42 (s, 1H), 6.20 (s, 1H), 4.02 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 2.10−1.90 (m, 1H), 1.87−1.75 (m, 1H), 1.58 (s, 3H), 0.82 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.9 (C$_q$), 153.5 (C$_q$), 148.5 (C$_q$), 142.9 (C$_q$), 141.9 (C$_q$), 137.7 (C$_q$), 128.1 (2 × CH), 127.8 (2 × CH), 124.6 (CH), 119.9 (C$_q$), 99.2 (CH), 98.1 (CH), 90.9 (C$_q$), 61.0 (CH$_3$), 60.5 (CH$_3$), 56.2 (CH$_3$), 34.2 (CH$_2$), 26.7 (CH$_3$), 8.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2925, 1642, 1591, 1470, 1417, 1350, 1136, 1085, 1016, 821, 694 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{21}$H$_{25}$O$_4$]$^+$ = [M + H]$^+$ 341.1747, found 341.1745.

*(3Z)-3-Benzylidene-6-(benzyloxy)-1,1-diethyl-1,3-dihydro-2-benzofuran (**3an**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 71% yield (131 mg). [TLC control (petroleum ether/ethyl acetate 85:15, R_f(**1an**) = 0.32, R_f(**3an**) = 0.70, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.74 (d, 2H, J = 8.3 Hz), 7.50−7.30 (m, 8H), 7.11 (t, 1H, J = 7.3 Hz), 6.98 (dd, 1H, J = 8.3 and 2.4 Hz), 6.73 (d, 1H, J = 2.4 Hz), 5.72 (s, 1H), 5.10 (s, 2H), 2.14−1.98 (m, 2H), 1.94−1.76 (m, 2H), 0.76 (t, 6H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 159.8 (C$_q$), 155.7 (C$_q$), 146.3 (C$_q$), 137.3 (C$_q$), 136.5 (C$_q$), 129.0 (C$_q$), 128.6 (2 × CH), 128.2 (2 × CH), 128.1 (CH), 127.6 (2 × CH), 127.4 (2 × CH), 124.5 (CH), 120.9 (CH), 115.3 (CH), 107.0 (CH), 94.2 (CH), 93.3 (C$_q$), 70.4 (CH$_2$), 32.6 (2 × CH$_2$), 7.7 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2969, 1652, 1590, 1493, 1448, 1357, 1266, 1201, 1049, 1026, 943, 803, 755, 692 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{26}$H$_{27}$O$_2$]$^+$ = [M + H]$^+$ 371.2006, found 371.2005.

*(3Z)-3-Benzylidene-1,1-diethyl-6-methoxy-1,3-dihydro-2-benzofuran (**3ao**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 75% yield (110 mg). [TLC control (petroleum ether/ethyl acetate 85:15, R_f(**1ao**) = 0.26, R_f(**3ao**) = 0.65, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.72 (d, 2H, J = 7.8 Hz), 7.43 (d, 1H, J = 8.3 Hz), 7.31 (dd, 2H, J = 7.8 and 7.3 Hz), 7.10 (t, 1H, J = 7.3 Hz), 6.89 (dd, 1H, J = 8.3 and 2.0 Hz), 6.63 (d, 1H, J = 2.0 Hz), 5.70 (s, 1H), 3.85 (s, 3H), 2.15−1.98 (m, 2H), 1.94−1.78 (m, 2H), 0.75 (t, 6H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 160.7 (C$_q$), 155.7 (C$_q$), 146.4 (C$_q$), 137.3 (C$_q$), 128.8 (C$_q$), 128.2 (2 × CH), 127.4 (2 × CH), 124.4 (CH), 120.9 (CH), 114.5 (CH), 105.8 (CH), 94.2 (C$_q$), 93.2 (CH), 55.6 (CH$_3$), 32.7 (2 × CH$_2$), 7.7 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2963, 1652, 1598, 1565, 1497, 1460, 1438, 1372, 1248, 1205, 1029, 858, 779, 731 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{20}$H$_{23}$O$_2$]$^+$ = [M + H]$^+$ 295.1693, found 295.1694.

*(3Z)-3-Benzylidene-5-(benzyloxy)-1,1-diethyl-6-methoxy-1,3-dihydro-2-benzofuran (**3ap**).* This compound was prepared according to the GP and isolated as brown viscous liquid in 75% yield (150 mg). [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1ap**) = 0.3, R_f(**3ap**) = 0.45, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.72 (d, 2H, J = 7.3 Hz), 7.50 (d, 2H, J = 7.3 Hz), 7.41 (dd, 2H, J = 7.3 and 7.3 Hz), 7.37−7.27 (m, 3H), 7.10 (t, 1H, J = 7.3 Hz), 7.05 (s, 1H), 6.62 (s, 1H), 5.62 (s, 1H), 5.19 (s, 2H), 3.92 (s, 3H), 2.20−1.95 (m, 2H), 1.93−1.78 (m, 2H), 0.76 (t, 6H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 156.0 (C$_q$), 151.4 (C$_q$), 148.9 (C$_q$), 137.8 (C$_q$), 137.3 (C$_q$), 136.8 (C$_q$), 128.6 (2 × CH), 128.2 (2 × CH), 128.0 (CH), 127.5 (2 × CH), 127.4 (2 × CH), 124.4 (CH), 104.6 (CH), 103.8 (CH), 94.4 (C$_q$), 93.1 (CH), 71.4 (CH$_2$), 56.3 (CH$_3$), 32.7 (2 × CH$_2$), 7.7 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2923, 1653, 1600, 1499, 1452, 1355, 1282, 1228, 1055, 940, 698 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{27}$H$_{29}$O$_3$]$^+$ = [M + H]$^+$ 401.2111, found 401.2107.

*(3Z)-3-Benzylidene-1,1-diethyl-5,6-dimethoxy-1,3-dihydro-2-benzofuran (**3aq**).* This compound was prepared according to the GP and isolated as yellow viscous liquid in 74% yield (120 mg). [TLC control (petroleum ether/ethyl acetate 70:30, R_f(**1aq**) = 0.33, R_f(**3aq**) = 0.70, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.72 (d, 2H, J = 7.8 Hz), 7.31 (dd, 2H, J = 7.8 and 7.3 Hz), 7.09 (t, 1H, J = 7.3 Hz), 6.97 (s, 1H), 6.58 (s, 1H), 5.66 (s, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 2.15−1.96 (m, 2H), 1.90−1.75 (m, 2H), 0.73 (t, 6H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 156.1 (C$_q$), 150.7 (C$_q$), 149.6 (C$_q$), 137.3 (C$_q$), 137.2 (C$_q$), 128.3 (2 × CH), 128.1 (C$_q$), 127.4 (2 × CH), 124.5 (CH), 103.2 (CH), 101.9 (CH), 94.4 (C$_q$), 93.1 (CH), 56.2 (CH$_3$), 56.1 (CH$_3$), 32.7 (2 × CH$_2$), 7.7 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2921, 1651, 1597, 1500, 1463, 1355, 1230, 1206, 1033, 943, 800, 693 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{21}$H$_{25}$O$_3$]$^+$ = [M + H]$^+$ 325.1798, found 325.1789.

*(3Z)-3-Benzylidene-1-methyl-1-phenyl-1,3-dihydro-2-benzofuran (**3ar**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 89% yield (133 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1ar**) = 0.50, R_f(**3ar**) = 0.60, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.82 (dd, 2H, J = 7.8 and 1.0 Hz), 7.57−7.43 (m, 3H), 7.38−7.18 (m, 8H), 7.13 (t, 1H, J = 7.3 Hz), 5.99 (s, 1H), 2.01 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.4 (C$_q$), 146.7 (C$_q$), 144.0 (C$_q$), 136.5 (C$_q$), 133.7 (C$_q$), 128.9 (CH), 128.5 (2 × CH), 128.4 (2 × CH), 128.2 (CH), 128.0 (2 × CH), 127.5 (CH), 125.3 (CH), 124.8 (2 × CH), 121.6 (CH), 120.0 (CH), 96.4 (CH), 91.4 (C$_q$), 27.7 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2971, 2931, 1652, 1513, 1474, 1324, 1233, 1140, 1034, 819, 767 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for [C$_{22}$H$_{19}$O]$^+$ = [M + H]$^+$ 299.1430, found 299.1428.

*(3Z)-3-Benzylidene-6-methoxy-1-methyl-1-phenyl-1,3-dihydro-2-benzofuran (**3as**).* This compound was prepared according to the GP and isolated as a pale-yellow oil in 75% yield (124 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1as**) = 0.40, R_f(**3as**) = 0.50, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.78 (dd, 2H, J = 7.8 and 1.5 Hz), 7.49 (d, 2H, J = 6.8 Hz), 7.46 (d, 1H, J = 8.8 Hz), 7.38−7.28 (m, 4H), 7.26 (d, 1H, J = 7.3 Hz), 7.11 (ddd, 1H, J = 7.8, 7.3, and 1.5 Hz), 6.87 (dd, 1H, J = 8.3 and 2.4 Hz), 6.71 (d, 1H, J = 2.4 Hz), 5.85 (s, 1H), 3.78 (s, 3H), 2.02 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 160.8 (C$_q$), 154.4 (C$_q$), 148.7 (C$_q$), 144.0 (C$_q$), 136.8 (C$_q$), 128.5 (2 × CH), 128.3 (2 × CH), 127.6 (3 × CH), 126.4 (C$_q$), 124.9 (CH), 124.8 (CH), 121.2 (CH), 114.9 (CH), 106.4 (CH), 94.7 (CH), 91.0 (C$_q$), 55.6 (CH$_3$), 27.5 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2973, 2906, 1653, 1512, 1471, 1302, 1237, 1141,

1038, 822, 769 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{23}H_{19}O]^+$ = [M + H − H_2O]$^+$ 311.1430, found 311.1437.

*(3Z)-3-Benzylidene-5,6-dimethoxy-1-methyl-1-phenyl-1,3-dihydro-2-benzofuran (**3at**).* This compound was prepared according to the GP and isolated as a brown viscous liquid in 84% yield (152 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1aw**) = 0.40, R_f(**3at**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (dd, 2H, J = 8.3 and 1.0 Hz), 7.49 (d, 2H, J = 7.3 Hz), 7.40−7.20 (m, 5H), 7.13 (t, 1H, J = 7.3 Hz), 7.00 (s, 1H), 6.68 (s, 1H), 5.83 (s, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 2.03 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.9 (C_q), 150.9 (C_q), 149.9 (C_q), 144.0 (C_q), 139.9 (C_q), 136.8 (C_q), 128.5 (2 × CH), 128.3 (2 × CH), 127.6 (3 × CH), 127.5 (CH), 125.8 (C_q), 124.9 (2 × CH), 124.8 (CH), 103.8 (CH), 102.0 (CH), 94.6 (CH), 91.2 (C_q), 56.2 (2 × CH_3), 27.4 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2978, 2930, 1654, 1594, 1497, 1301, 1229, 1150, 1025, 905, 727, 692 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{24}H_{23}O_3]^+$ = [M + H]$^+$ 359.1642, found 359.1637.

*(3Z)-3-Benzylidene-4,5,6-trimethoxy-1-methyl-1-phenyl-1,3-dihydro-2-benzofuran (**3au**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 82% yield (159 mg). [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1ax**) = 0.20, R_f(**3au**) = 0.35, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, 2H, J = 8.8 Hz), 7.49 (d, 2H, J = 7.3 Hz), 7.37−7.20 (m, 5H), 7.10 (t, 1H, J = 7.3 Hz), 6.46 (s, 1H), 6.32 (s, 1H), 4.03 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 155.1 (C_q), 153.0 (C_q), 148.5 (C_q), 144.2 (C_q), 143.5 (C_q), 142.1 (C_q), 137.4 (C_q), 128.5 (2 × CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.6 (CH), 124.9 (3 × CH), 118.8 (C_q), 100.1 (CH), 99.1 (CH), 90.7 (C_q), 61.0 (CH_3), 60.5 (CH_3), 56.2 (CH_3), 27.5 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2923, 2852, 1646, 1594, 1471, 1335, 1085, 1016, 695 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{25}H_{25}O_4]^+$ = [M + H]$^+$ 389.1747, found 389.1746.

*(3Z)-3-Benzylidene-1-methyl-1-thien-2-yl-1,3-dihydro-2-benzofuran (**3av**).* This compound was prepared according to the GP and isolated as black viscous liquid in 84% yield (123 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1ay**) = 0.40, R_f(**3av**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79 (d, 2H, J = 7.3 Hz), 7.57 (d, 1H, J = 6.8 Hz), 7.41−7.27 (m, 5H), 7.17 (d, 1H, J = 4.9 Hz), 7.16 (t, 1H, J = 7.3 Hz), 7.03 (dd, 1H, J = 3.9 and 1.5 Hz), 6.95 (s, 1H, J = 4.9 and 3.9 Hz), 5.99 (s, 1H), 2.09 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.6 (C_q), 148.3 (C_q), 145.8 (C_q), 136.3 (C_q), 133.8 (C_q), 129.0 (CH), 128.6 (CH), 128.3 (2 × CH), 128.1 (2 × CH), 126.8 (CH), 125.4 (CH), 125.3 (CH), 123.7 (CH), 121.7 (CH), 120.1 (CH), 97.0 (CH), 89.5 (C_q), 28.8 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2971, 2903, 1652, 1513, 1474, 1324, 1233, 1140, 1034, 819, 767 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{19}H_{15}S]^+$ = [M + H − H_2O]$^+$ 275.0889, found 275.0895.

*(3Z)-3-Benzylidene-1,1-diphenyl-1,3-dihydro-2-benzofuran (**3aw**).* This compound was prepared according to the GP and isolated as a brown semisolid in 78% yield (142 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1ba**) = 0.50, R_f(**3aw**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, 2H, J = 7.3 Hz), 7.61 (dd, 1H, J = 6.4 and 1.5 Hz), 7.48−7.26 (m, 15H), 7.16 (t, 1H, J = 7.3 Hz), 6.02 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.0 (C_q), 144.2 (C_q), 143.4 (C_q), 136.3 (C_q), 134.6 (C_q), 128.7 (CH), 128.5 (CH), 128.4 (2 × CH), 128.2 (3 × CH), 128.1 (2 × CH), 127.8 (2 × CH), 127.1 (4 × CH), 125.4 (CH), 123.9 (CH), 120.2 (CH), 96.8 (CH), 95.7 (C_q) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2971, 2834, 1652, 1513, 1474, 1305, 1233, 1140, 1034, 861, 767, 597 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{27}H_{21}O]^+$ = [M + H]$^+$ 361.1587, found 361.1593.

*(3Z)-3-Benzylidene-6-methoxy-1,1-diphenyl-1,3-dihydro-2-benzofuran (**3ax**).* This compound was prepared according to the GP and isolated as a pale-green viscous liquid in 76% yield (149 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1bb**) = 0.40, R_f(**3ax**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.76 (d, 2H, J = 7.8 Hz), 7.48 (d, 1H, J = 8.3 Hz), 7.39 (dd, 4H, J = 7.8 and 1.5 Hz), 7.35−7.24 (m, 8H), 7.09 (t, 1H, J = 7.3 Hz), 6.89 (dd, 1H, J = 8.3 and 2.0 Hz), 6.85 (d, 1H, J = 2.0 Hz), 5.85 (s, 1H), 3.76 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.6 (C_q), 154.1 (C_q), 146.0 (C_q), 143.3 (2 × C_q), 136.7 (C_q), 128.3 (2 × CH), 128.2 (3 × CH), 128.1 (CH), 127.8 (2 × C_q), 127.3 (C_q), 127.1 (3 × CH), 125.8 (CH), 124.9 (CH), 121.3 (CH), 115.2 (CH), 108.8 (CH), 95.3 (C_q), 95.1 (CH), 55.6 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2972, 2903, 1652, 1516, 1475, 1307, 1236, 1141, 1035, 822, 768 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{28}H_{23}O_2]^+$ = [M + H]$^+$ 391.1693, found 391.1696.

*(3Z)-3-(4-Methoxybenzylidene)-1-methyl-1-phenyl-1,3-dihydro-2-benzofuran (**4aa**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 78% yield (128 mg). [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1ar**) = 0.35, R_f(**4aa**) = 0.45, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (d, 2H, J = 8.8 Hz), 7.55−7.45 (m, 3H), 7.40−7.20 (m, 6H), 6.90 (d, 2H, J = 8.8 Hz), 5.95 (s, 1H), 3.81 (s, 3H), 2.02 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.4 (C_q), 152.8 (C_q), 146.4 (C_q), 144.3 (C_q), 133.9 (C_q), 129.4 (C_q), 129.2 (2 × CH), 128.5 (CH), 128.4 (2 × CH), 128.1 (CH), 127.5 (CH), 124.8 (2 × CH), 121.6 (CH), 119.7 (CH), 113.9 (2 × CH), 96.0 (CH), 91.1 (C_q), 55.2 (CH_3), 27.7 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2955, 1657, 1603, 1508, 1463, 1444, 1296, 1245, 1175, 1022, 837, 757, 697 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{23}H_{21}O_2]^+$ = [M + H]$^+$ 329.1536, found 329.1526.

*(3Z)-5,6-Dimethoxy-3-(4-methoxybenzylidene)-1,1-dimethyl-1,3-dihydro-2-benzofuran (**4ab**).* This compound was prepared according to the GP and isolated as a yellow viscous liquid in 63% yield (103 mg). [TLC control (petroleum ether/ethyl acetate 70:30, R_f(**1ag**) = 0.30, R_f(**4ab**) = 0.50, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66 (d, 2H, J = 8.8 Hz), 6.93 (s, 1H), 6.88 (d, 2H, J = 8.8 Hz), 6.65 (s, 1H), 5.67 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 1.61 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.0 (C_q), 153.2 (C_q), 150.4 (C_q), 149.6 (C_q), 140.1 (C_q), 129.9 (C_q), 128.6 (2 × CH), 126.2 (C_q), 113.8 (2 × CH), 102.9 (CH), 101.9 (CH), 93.5 (CH), 88.6 (C_q), 56.2 (CH_3), 56.1 (CH_3), 55.2 (CH_3), 28.5 (2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2926, 1655, 1605, 1510, 1465, 1325, 1237, 1172, 1035, 804 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{20}H_{23}O_4]^+$ = [M + H]$^+$ 327.1591, found 327.1592.

*(3Z)-3-(3,4-Dimethoxybenzylidene)-1-methyl-1-phenyl-1,3-dihydro-2-benzofuran (**4ac**).* This compound was prepared according to the GP and isolated as a pale-green oil in 74% yield (133 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1ar**) = 0.60, R_f(**4ac**) = 0.40, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (d, 4H, J = 6.8 Hz), 7.42−7.18 (m, 7H), 6.88 (d, 1H, J = 8.3 Hz), 5.96 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.0 (C_q), 148.7 (C_q), 147.0 (C_q), 146.3 (C_q), 144.3 (C_q), 133.9 (C_q), 129.7 (C_q), 128.6 (CH), 128.5 (2 × CH), 128.2 (CH), 127.5 (CH), 124.7 (2 × CH), 121.6 (CH), 120.6 (CH), 119.8 (CH), 111.3 (CH), 111.2 (CH), 96.2 (CH), 91.2 (C_q), 55.9 (CH_3), 55.7 (CH_3), 28.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2978, 2932, 1654, 1512, 1462, 1330, 1239, 1140, 1023, 910, 757, 697 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{24}H_{23}O_3]^+$ = [M + H]$^+$ 359.1642, found 359.1641.

*(3Z)-6-(Benzyloxy)-3-(3,4-dimethoxybenzylidene)-1,1-dimethyl-1,3-dihydro-2-benzofuran (**4ad**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 61% yield (123 mg). [TLC control (petroleum ether/ethyl acetate 75:25, R_f(**1ab**) = 0.40, R_f(**4ad**) = 0.38, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50−7.32 (m, 7H), 7.25 (dd, 1H, J = 8.3 and 1.9 Hz), 6.95 (dd, 1H, J = 8.3 and 2.4 Hz), 6.85 (d, 1H, J = 8.3 Hz), 6.79 (d, 1H, J = 1.9 Hz), 5.72 (s, 1H), 5.09 (s, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 1.63 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.8 (C_q), 153.0 (C_q), 149.0 (C_q), 148.6 (C_q), 146.6 (C_q), 136.6 (C_q), 130.3 (C_q), 128.6 (2 × CH), 128.1 (CH), 127.5 (2 × CH), 127.1 (C_q), 120.9 (CH), 120.0 (CH), 115.3 (CH), 111.3 (CH), 111.0 (CH), 106.6 (CH), 94.0 (CH), 88.4 (C_q), 70.5 (CH_2), 55.9 (CH_3), 55.7 (CH_3), 28.4 (2 × CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2927, 1654, 1611, 1512, 1462, 1267, 1222, 1141, 1024, 914, 813, 737, 697 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{26}H_{27}O_4]^+$ = [M + H]$^+$ 403.1904, found 403.1885.

*(3Z)-3-(3,4-Dimethoxybenzylidene)-1-ethyl-6-methoxy-1-methyl-1,3-dihydro-2-benzofuran (**4ae**).* This compound was prepared

according to the GP and isolated as a yellowish-brown viscous liquid in 70% yield (119 mg). [TLC control (petroleum ether/ethyl acetate 75:25, R_f(**1aj**) = 0.40, R_f(**4ae**) = 0.36, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.45 (d, 1H, J = 2.0 Hz), 7.40 (d, 1H, J = 8.3 Hz), 7.20 (dd, 1H, J = 8.3 and 2.0 Hz), 6.87 (dd, 1H, J = 8.3 and 2.4 Hz), 6.84 (d, 1H, J = 8.3 Hz), 6.64 (d, 1H, J = 2.4 Hz), 5.68 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 2.05−1.92 (m, 1H), 1.91−1.78 (m, 1H), 1.59 (s, 3H), 0.84 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 160.5 (C$_q$), 153.6 (C$_q$), 148.6 (C$_q$), 147.9 (C$_q$), 146.4 (C$_q$), 130.4 (C$_q$), 127.6 (C$_q$), 120.8 (CH), 119.9 (CH), 114.6 (CH), 111.3 (CH), 110.8 (CH), 105.5 (CH), 93.4 (CH), 90.9 (C$_q$), 55.9 (CH$_3$), 55.6 (CH$_3$), 55.5 (CH$_3$), 34.1 (CH$_2$), 26.3 (CH$_3$), 8.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2929, 1655, 1601, 1513, 1462, 1269, 1222, 1141, 1027, 925, 815, 769 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{21}H_{25}O_4]^+$ = $[M + H]^+$ 341.1747, found 341.1742.

*(3Z)-3-(3,4-Dimethoxybenzylidene)-6-methoxy-1-methyl-1-thien-2-yl-1,3-dihydro-2-benzofuran (**4af**).* This compound was prepared according to the GP and isolated as a black viscous liquid in 86% yield (170 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1az**) = 0.50, R_f(**4af**) = 0.40, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.50 (d, 1H, J = 1.5 Hz), 7.43 (d, 1H, J = 8.3 Hz), 7.24−7.15 (m, 2H), 6.99 (dd, 1H, J = 3.4 and 1.5 Hz), 6.98−6.88 (m, 2H), 6.84 (d, 1H, J = 8.3 Hz), 6.80 (d, 1H, J = 2.4 Hz), 5.79 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 160.6 (C$_q$), 152.3 (C$_q$), 148.6 (C$_q$), 148.4 (C$_q$), 147.0 (C$_q$), 146.7 (C$_q$), 129.8 (C$_q$), 126.8 (CH), 126.5 (C$_q$), 125.2 (CH), 123.4 (CH), 121.0 (C$_q$), 120.3 (CH), 115.5 (CH), 111.2 (CH), 111.0 (CH), 106.4 (CH), 95.0 (CH), 88.8 (C$_q$), 55.8 (CH$_3$), 55.7 (CH$_3$), 55.6 (CH$_3$), 29.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2932, 2834, 1656, 1512, 1462, 1308, 1226, 1140, 1026, 814, 729, 611 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{23}H_{23}O_4S]^+$ = $[M + H]^+$ 395.1312, found 395.1310.

*(3Z)-3-(3,4-Dimethoxybenzylidene)-6-methoxy-1,1-diphenyl-1,3-dihydro-2-benzofuran (**4ag**).* This compound was prepared according to the GP and isolated as a brown viscous liquid in 86% yield (194 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1bb**) = 0.50, R_f(**4ag**) = 0.40, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.57 (d, 1H, J = 2.0 Hz), 7.45 (d, 1H, J = 8.8 Hz), 7.38 (dd, 4H, J = 8.3 and 2.0 Hz), 7.33−7.25 (m, 6H), 7.21 (dd, 1H, J = 7.8 and 2.9 Hz), 6.89 (dd, 1H, J = 8.3 and 2.4 Hz), 6.85 (d, 1H, J = 2.4 Hz), 6.82 (d, 1H, J = 8.3 Hz), 5.81 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.78 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 160.4 (C$_q$), 152.7 (C$_q$), 148.6 (C$_q$), 146.7 (C$_q$), 145.4 (C$_q$), 143.5 (2 × C$_q$), 129.9 (C$_q$), 128.2 (4 × CH), 127.8 (2 × CH), 127.4 (C$_q$), 127.0 (4 × CH), 121.0 (CH), 120.3 (CH), 115.1 (CH), 111.3 (CH), 111.0 (CH), 108.9 (CH), 95.0 (C$_q$), 94.9 (CH), 55.9 (CH$_3$), 55.7 (CH$_3$), 55.6 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2934, 2834, 1656, 1599, 1512, 1486, 1338, 1231, 1139, 1024, 905, 724, 696 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{29}H_{24}O_3]^+$ = $[M - H_2O]^+$ 420.1720, found 420.1695.

*(3Z)-1-Methyl-1-phenyl-3-(3,4,5-trimethoxybenzylidene)-1,3-dihydro-2-benzofuran (**4ah**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 72% yield (140 mg). [TLC control (petroleum ether/ethyl acetate 90:10, R_f(**1ar**) = 0.80, R_f(**4ah**) = 0.50, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.65−7.45 (m, 3H), 7.40−7.15 (m, 6H), 7.12 (s, 2H), 5.92 (s, 1H), 3.86 (s, 6H), 3.85 (s, 3H), 2.01 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 153.9 (C$_q$), 153.0 (3 × C$_q$), 146.3 (C$_q$), 144.0 (C$_q$), 133.6 (C$_q$), 132.2 (C$_q$), 128.9 (CH), 128.5 (2 × CH), 128.2 (CH), 127.5 (CH), 124.6 (3 × CH), 121.7 (CH), 119.9 (CH), 105.1 (CH), 96.4 (CH), 91.5 (C$_q$), 60.9 (CH$_3$), 55.9 (2 × CH$_3$), 28.1 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2923, 2852, 1576, 1505, 1418, 1337, 1237, 1124, 761, 699 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{25}H_{24}NaO_4]^+$ = $[M + Na]^+$ 411.1567, found 411.1555.

*(7Z)-5,5-Dimethyl-7-(3,4,5-trimethoxybenzylidene)-5,7-dihydrofuro[3,4-f][1,3]benzodioxole (**4ai**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 83% yield (153 mg). [TLC control (petroleum ether/ethyl acetate 80:20, R_f(**1af**) = 0.50, R_f(**4ai**) = 0.40, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.00 (s, 2H), 6.87 (s, 1H), 6.62 (s, 1H), 6.00 (s, 2H), 5.61 (s, 1H), 3.89 (s, 6H), 3.84 (s, 3H), 1.59 (s, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 154.1 (C$_q$), 152.9 (3 × C$_q$), 149.2 (C$_q$), 148.3 (C$_q$), 141.9 (C$_q$), 135.7 (C$_q$), 132.6 (C$_q$), 127.4 (C$_q$), 104.7 (2 × CH), 101.7 (CH$_2$), 100.9 (CH), 99.7 (CH), 94.2 (CH), 88.6 (C$_q$), 60.9 (CH$_3$), 55.9 (2 × CH$_3$), 28.4 (2 × CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 2923, 2852, 1580, 1462, 1377, 1316, 1128, 1108 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{21}H_{22}NaO_6]^+$ = $[M + Na]^+$ 393.1309, found 393.1302.

*2-(2-Oct-1-ynylphenyl)propan-2-ol (**5aa**).* This compound was prepared according to the GP and isolated as a yellow oil in 82% yield (101 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1aa**) = 0.60, R_f(**5aa**) = 0.60, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.50−7.40 (m, 2H), 7.24 (ddd, 1H, J = 7.8, 7.3, and 1.5 Hz), 7.16 (ddd, 1H, J = 7.8, 7.3, and 1.5 Hz), 3.81 (br s, 1H), 2.46 (t, 2H, J = 6.8 Hz), 1.70 (s, 6H), 1.67−1.20 (m, 8H), 0.89 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 149.6 (C$_q$), 134.5 (CH), 127.8 (CH), 126.5 (CH), 124.5 (CH), 120.0 (C$_q$), 97.5 (C$_q$), 80.5 (C$_q$), 73.1 (C$_q$), 31.3 (CH$_2$), 29.7 (2 × CH$_3$), 28.7 (CH$_2$), 28.5 (CH$_2$), 22.5 (CH$_2$), 19.6 (CH$_2$), 14.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3520, 2922, 1605, 1502, 1464, 1341, 1262, 1143, 1025, 907, 864, 764, 697 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{17}H_{23}]^+$ = $[M + H - H_2O]^+$ 227.1794, found 227.1792.

*2-[5-(Benzyloxy)-2-dec-1-ynyl-4-methoxyphenyl]propan-2-ol (**5ab**).* This compound was prepared according to the GP and isolated as a pale-yellow viscous liquid in 85% yield (174 mg). [TLC control (petroleum ether/ethyl acetate 80:20, R_f(**1ad**) = 0.25, R_f(**5ab**) = 0.35, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.42 (d, 2H, J = 7.3 Hz), 7.35 (dd, 2H, J = 7.3 and 6.8 Hz), 7.28 (t, 1H, J = 7.3 Hz), 7.03 (s, 1H), 6.93 (s, 1H), 5.14 (s, 2H), 3.85 (s, 3H), 3.52 (br s, 1H), 2.44 (t, 2H, J = 7.3 Hz), 1.62 (s, 6H), 1.50−1.15 (m, 12H), 0.88 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 147.6 (C$_q$), 147.5 (C$_q$), 143.2 (C$_q$), 136.9 (C$_q$), 128.5 (2 × CH), 127.9 (CH), 127.4 (2 × CH), 117.4 (CH), 112.5 (C$_q$), 111.4 (CH), 95.8 (C$_q$), 80.3 (C$_q$), 72.8 (C$_q$), 71.1 (CH$_2$), 56.0 (CH$_3$), 31.8 (CH$_2$), 29.8 (2 × CH$_3$), 29.2 (CH$_2$), 29.1 (CH$_2$), 29.0 (CH$_2$), 28.6 (CH$_2$), 22.6 (CH$_2$), 19.6 (CH$_2$), 14.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3443, 2923, 2853, 1600, 1501, 1457, 1365, 1256, 1163, 1025, 736, 697 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{27}H_{36}NaO_3]^+$ = $[M + Na]^+$ 431.2557, found 431.2551.

*2-(6-Oct-1-ynyl-1,3-benzodioxol-5-yl)propan-2-ol (**5ac**).* This compound was prepared according to the GP and isolated as a brown oil in 87% yield (126 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1af**) = 0.50, R_f(**5ac**) = 0.55, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 6.96 (s, 1H), 6.86 (s, 1H), 5.93 (s, 2H), 3.77 (br s, 1H), 2.43 (t, 2H, J = 7.3 Hz), 1.66 (s, 6H), 1.64−1.20 (m, 8H), 0.88 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 147.4 (C$_q$), 145.6 (C$_q$), 145.2 (C$_q$), 113.8 (CH), 113.1 (C$_q$), 105.7 (CH), 101.3 (CH$_2$), 96.1 (C$_q$), 80.3 (C$_q$), 72.9 (C$_q$), 31.3 (CH$_2$), 29.9 (2 × CH$_3$), 28.7 (CH$_2$), 28.5 (CH$_2$), 22.5 (CH$_2$), 19.6 (CH$_2$), 14.0 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3521, 2925, 1608, 1501, 1466, 1346, 1264, 1146, 1024, 902, 865, 763, 694 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{18}H_{23}O_2]^+$ = $[M + H - H_2O]^+$ 271.1693, found 271.1690.

*2-[5-(Benzyloxy)-2-oct-1-ynylphenyl]butan-2-ol (**5ad**).* This compound was prepared according to the GP and isolated as a colorless viscous liquid in 84% yield (153 mg). [TLC control (petroleum ether/ethyl acetate 85:15, R_f(**1ai**) = 0.30, R_f(**5ad**) = 0.55, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.50−7.28 (m, 6H), 7.09 (d, 1H, J = 2.9 Hz), 6.76 (dd, 1H, J = 8.3 and 2.9 Hz), 5.05 (s, 2H), 3.41 (br s, 1H), 2.43 (t, 2H, J = 7.3 Hz), 2.25−2.10 (m, 1H), 2.05−1.90 (m, 1H), 1.62 (s, 3H), 1.65−1.55 (m, 2H), 1.52−1.38 (m, 2H), 1.37−1.20 (m, 4H), 0.89 (t, 3H, J = 6.8 Hz), 0.79 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 158.1 (C$_q$), 150.4 (C$_q$), 136.7 (C$_q$), 135.8 (CH), 128.6 (2 × CH), 128.0 (CH), 127.5 (2 × CH), 113.3 (CH), 112.5 (C$_q$), 112.0 (CH), 95.3 (C$_q$), 80.3 (C$_q$), 75.7 (C$_q$), 70.0 (CH$_2$), 34.4 (CH$_2$), 31.3 (CH$_2$), 28.7 (CH$_2$), 28.6 (CH$_2$), 26.9 (CH$_3$), 22.6 (CH$_2$), 19.6 (CH$_2$), 14.1 (CH$_3$), 8.6 (CH$_3$) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3490, 2928, 2120, 1601, 1563, 1484, 1455, 1378, 1291, 1228, 1162, 1024, 810, 735, 696 cm^{-1}. HRMS (ESI$^+$) *m/z*: calcd for $[C_{25}H_{31}O]^+$ = $[M + H - H_2O]^+$ 347.2369, found 347.2362.

1-(2-Dec-1-ynylphenyl)-1-phenylethanol (**5ae**). This compound was prepared according to the GP and isolated as a colorless oil in 80% yield (136 mg). [TLC control (petroleum ether/ethyl acetate 9:1, R_f(**1ar**) = 0.50, R_f(**5ae**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50 (d, 1H, J = 7.8 Hz), 7.32 (dd, 1H, J = 7.3 and 1.5 Hz), 7.26 (dd, 1H, J = 7.3 and 1.5 Hz), 7.24−7.22 (m, 1H), 7.21−7.16 (m, 4H), 7.15−7.08 (m, 1H), 4.36 (br s, 1H), 2.08 (t, 2H, J = 7.3 Hz), 1.83 (s, 3H), 1.40−1.05 (m, 12H), 0.82 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.9 (C_q), 148.5 (C_q), 134.2 (CH), 127.7 (2 × CH), 127.5 (CH), 127.1 (CH), 126.5 (CH), 126.0 (CH), 125.5 (2 × CH), 121.5 (C_q), 98.3 (C_q), 79.7 (C_q), 76.9 (C_q), 31.8 (CH_2), 30.2 (CH_3), 29.1 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.1 (CH_2), 22.6 (CH_2), 19.4 (CH_2), 14.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3524, 2925, 1445, 1345, 1221, 1119, 1027, 908, 755, 697 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{24}H_{29}]^+$ = $[M + H - H_2O]^+$ 317.2264, found 317.2266.

1-[5-(Benzyloxy)-4-methoxy-2-oct-1-ynylphenyl]-1-phenylethanol (**5af**). This compound was prepared according to the GP and isolated as a pale-yellow oil in 87% yield (194 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1at**) = 0.50, R_f(**5af**) = 0.55, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, 2H, J = 6.8 Hz), 7.36 (dd, 2H, J = 7.8 and 6.8 Hz), 7.31 (d, 1H, J = 6.8 Hz), 7.26−7.14 (m, 5H), 7.07 (s, 1H), 6.90 (s, 1H), 5.19 (s, 2H), 4.29 (br s, 1H), 3.86 (s, 3H), 2.15 (t, 2H, J = 6.8 Hz), 1.78 (s, 3H), 1.40−1.15 (m, 8H), 0.88 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.8 (C_q), 148.1 (C_q), 146.9 (C_q), 142.0 (C_q), 136.7 (C_q), 128.5 (2 × CH), 127.9 (CH), 127.7 (2 × CH), 127.5 (2 × CH), 126.4 (CH), 125.4 (2 × CH), 117.1 (CH), 114.0 (C_q), 113.4 (CH), 96.6 (C_q), 79.4 (C_q), 76.5 (C_q), 71.2 (CH_2), 56.0 (CH_3), 31.3 (CH_2), 30.1 (CH_3), 28.6 (CH_2), 28.2 (CH_2), 22.4 (CH_2), 19.3 (CH_2), 14.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3517, 2929, 1600, 1505, 1445, 1339, 1262, 1146, 1025, 908, 864, 732, 696 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{30}H_{33}O_2]^+$ = $[M + H - H_2O]^+$ 425.2475, found 425.2474.

1-[5-(Benzyloxy)-4-methoxy-2-non-1-ynylphenyl]-1-phenylethanol (**5ag**). This compound was prepared according to the GP and isolated as a pale-yellow oil in 85% yield (194 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1at**) = 0.50, R_f(**5ag**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.41 (d, 2H, J = 6.8 Hz), 7.35 (dd, 2H, J = 7.3 and 7.3 Hz), 7.30 (t, 1H, J = 7.3 Hz), 7.27−7.13 (m, 5H), 7.07 (s, 1H), 6.90 (s, 1H), 5.19 (s, 2H), 4.29 (br s, 1H), 3.85 (s, 3H), 2.15 (t, 2H, J = 6.8 Hz), 1.78 (s, 3H), 1.40−1.15 (m, 10H), 0.89 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.8 (C_q), 148.1 (C_q), 146.8 (C_q), 142.0 (C_q), 136.7 (C_q), 128.5 (2 × CH), 127.9 (CH), 127.7 (2 × CH), 127.5 (2 × CH), 126.4 (CH), 125.4 (2 × CH), 117.1 (CH), 113.9 (C_q), 113.4 (CH), 96.6 (C_q), 79.4 (C_q), 76.5 (C_q), 71.2 (CH_2), 55.9 (CH_3), 31.6 (CH_2), 30.1 (CH_3), 28.8 (CH_2), 28.7 (CH_2), 28.2 (CH_2), 22.6 (CH_2), 19.3 (CH_2), 14.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3522, 2929, 1601, 1507, 1445, 1340, 1263, 1106, 1024, 906, 727, 697 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{31}H_{37}O_3]^+$ = $[M + H]^+$ 457.2737, found 457.2738.

1-[5-(Benzyloxy)-2-dec-1-ynyl-4-methoxyphenyl]-1-phenylethanol (**5ah**). This compound was prepared according to the GP and isolated as a pale-yellow oil in 72% yield (171 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1at**) = 0.50, R_f(**5ah**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33 (d, 2H, J = 6.8 Hz), 7.27 (dd, 2H, J = 7.8 and 6.8 Hz), 7.21 (t, 1H, J = 7.3 Hz), 7.18−7.04 (m, 5H), 6.99 (s, 1H), 6.82 (s, 1H), 5.10 (s, 2H), 4.18 (br s, 1H), 3.77 (s, 3H), 2.06 (t, 2H, J = 6.8 Hz), 1.70 (s, 3H), 1.35−1.05 (m, 12H), 0.81 (t, 3H, J = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.9 (C_q), 148.1 (C_q), 146.9 (C_q), 142.1 (C_q), 136.8 (C_q), 128.6 (2 × CH), 128.0 (CH), 127.8 (2 × CH), 127.5 (2 × CH), 126.5 (CH), 125.5 (2 × CH), 117.2 (CH), 114.0 (C_q), 113.4 (CH), 96.7 (C_q), 79.5 (C_q), 76.6 (C_q), 71.3 (CH_2), 56.0 (CH_3), 31.9 (CH_2), 30.2 (CH_3), 29.2 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.3 (CH_2), 22.7 (CH_2), 19.4 (CH_2), 14.2 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3522, 2926, 1600, 1506, 1445, 1340, 1262, 1146, 1025, 907, 729, 696 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{32}H_{37}O_2]^+$ = $[M + H - H_2O]^+$ 453.2788, found 453.2782.

1-(4,5-Dimethoxy-2-oct-1-ynylphenyl)-1-phenylethanol (**5ai**). This compound was prepared according to the GP and isolated as a yellow oil in 89% yield (163 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1aw**) = 0.40, R_f(**5ai**) = 0.45, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40−7.16 (m, 5H), 7.12 (s, 1H), 6.90 (s, 1H), 4.20 (br s, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 2.15 (t, 2H, J = 7.3 Hz), 1.92 (s, 3H), 1.40−1.15 (m, 8H), 0.89 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.9 (C_q), 148.0 (C_q), 147.3 (C_q), 142.3 (C_q), 127.7 (2 × CH), 126.5 (CH), 125.5 (2 × CH), 116.6 (CH), 113.5 (C_q), 109.9 (CH), 96.5 (C_q), 79.5 (C_q), 76.6 (C_q), 55.9 (CH_3), 55.8 (CH_3), 31.3 (CH_2), 30.1 (CH_3), 28.6 (CH_2), 28.2 (CH_2), 22.5 (CH_2), 19.4 (CH_2), 14.0 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3519, 2930, 1601, 1507, 1445, 1339, 1263, 1145, 1026, 909, 865, 729, 698 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{24}H_{29}O_2]^+$ = $[M + H - H_2O]^+$ 349.2162, found 349.2163.

1-(4,5-Dimethoxy-2-non-1-ynylphenyl)-1-phenylethanol (**5aj**). This compound was prepared according to the GP and isolated as a pale-yellow oil in 85% yield (162 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1aw**) = 0.50, R_f(**5aj**) = 0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37−7.17 (m, 5H), 7.12 (s, 1H), 6.90 (s, 1H), 4.20 (br s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 2.14 (t, 2H, J = 7.3 Hz), 1.92 (s, 3H), 1.40−1.14 (m, 10H), 0.90 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.9 (C_q), 148.0 (C_q), 147.3 (C_q), 142.3 (C_q), 127.7 (2 × CH), 126.5 (CH), 125.5 (2 × CH), 116.6 (CH), 113.5 (C_q), 109.9 (CH), 96.5 (C_q), 79.5 (C_q), 76.6 (C_q), 55.9 (CH_3), 55.8 (CH_3), 31.6 (CH_2), 30.1 (CH_3), 28.9 (CH_2), 28.8 (CH_2), 28.2 (CH_2), 22.6 (CH_2), 19.4 (CH_2), 14.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3518, 2928, 1601, 1507, 1445, 1340, 1263, 1145, 1026, 908, 865, 763, 698 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{25}H_{31}O_2]^+$ = $[M + H - H_2O]^+$ 363.2319, found 363.2316.

1-(2-Dec-1-ynyl-4,5-dimethoxyphenyl)-1-phenylethanol (**5ak**). This compound was prepared according to the GP and isolated as a pale-yellow oil in 72% yield (142 mg). [TLC control (petroleum ether/ethyl acetate 8:2, R_f(**1aw**) = 0.50, R_f(**5ak**) = 0.55, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.30−7.13 (m, 5H), 7.08 (s, 1H), 6.85 (s, 1H), 4.13 (br s, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 2.10 (t, 2H, J = 7.3 Hz), 1.87 (s, 3H), 1.40−1.10 (m, 12H), 0.85 (t, 3H, J = 7.3 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.9 (C_q), 148.0 (C_q), 147.3 (C_q), 142.3 (C_q), 127.8 (2 × CH), 126.5 (CH), 125.5 (2 × CH), 116.6 (CH), 113.5 (C_q), 109.9 (CH), 96.5 (C_q), 79.5 (C_q), 76.6 (C_q), 56.0 (CH_3), 55.9 (CH_3), 31.8 (CH_2), 30.1 (CH_3), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.2 (CH_2), 22.6 (CH_2), 19.4 (CH_2), 14.1 (CH_3) ppm. IR (MIR-ATR, 4000−600 cm^{-1}): ν_{max} = 3519, 2926, 1601, 1508, 1462, 1342, 1263, 1145, 1026, 908, 865, 763, 699 cm^{-1}. HRMS (ESI$^+$) m/z: calcd for $[C_{26}H_{35}O_3]^+$ = $[M + H]^+$ 395.2581, found 395.2579.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of known compounds **1**, synthetic scheme for compound **1am**, copies of NMR spectra, and a CIF file for **3af**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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