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Domino [Pd]-Catalysis: Heck Followed by Decarboxylative Sonagashira Couplings under Microwave Irradiation in Aqueous Medium

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Abstract: A copper free [Pd]-catalyzed domino intramolecular Heck and intermolecular decarboxylative Sonogashira couplings, for the synthesis of alkyne bearing heterocyclic compounds with a quaternary carbon atom, is described. Notably, this dual bond forming strategy is successful in water solvent, under microwave irradiation. This one-pot operation enabled the formation of a variety of dihydrobenzofurans, indolines and oxindoles, in very good to near quantitative yields. Notably, unlike earlier reports, the present strategy is successful in delivering the products with short alkyl substituents on acetylene carbon, which is first of its kind.

Keywords: Pd-catalysis; Decarboxylation; Aqueous medium; Domino; Microwaves.

Introduction:

In nature, the alkyne moiety is predominant in many products of biological relevance and is also significant in synthetic functional materials.¹ Chemically, the alkyne moiety can be easily converted into different functional groups.² Specifically, for the synthesis of internal alkynes, Sonogashira coupling has been a powerful synthetic method,³ which almost replaced the existing classical synthetic processes.⁴ However, the main constraint of this transformation is the formation of symmetrical 1,3-diyne byproduct (Glaser product) via homocoupling of terminal acetylenes.⁵ Thus noteworthy advancements have been accomplished on this reaction. For example, propiolic acids have been recognized as good alternative source for acetylenes.⁶ probably due to their increased stability and ready availability, compared to that of terminal alkynes. Significantly, versatility of carboxylic acids is not limited to Sonogashira coupling but also well established in various coupling reactions of transition metal catalysis.⁷ Moreover, in organic synthesis, the design and the development of sustainable domino one-pot synthetic strategies is vital and desirable along with investigating new methodologies for the construction of ring systems.

The dihydrobenzofurans,⁸ indolines⁹ and oxindoles¹⁰ with a quaternary carbon atom at their 3-position are some of the core structures that constitute many natural and pharmaceutical products. Hence, many reports have been presented on their synthesis which include classical approaches as well as transition metal catalyzed transformations.¹¹ To the best of our knowledge, there has been no report for the accomplishment of 3,3'-disubtituted dihydrocoumarins, indolines and oxindoles using alkyl propiolic acids as Sonogashira coupling partners. As a part of our interest on palladium catalyzed domino one-pot processes,¹² we have described assisted synthesis 3,3'-disubstituted microwave domino one-pot of dihydrobenzofurans possessing alkyne moiety via intramolecular Heck reaction of orthoiodoarylallyl ethers followed by Sonogashira coupling with terminal acetylenes, catalyzed by palladium.¹³ Inspired by these results, subsequently, it was further applied to the synthesis of alkyne bearing dihydrobenzofurans, indolines and oxindoles with a quaternary carbon centre, in water solvent.¹⁴ Herein, we describe microwave assisted palladium catalyzed one-pot synthesis of dihydrobenzofurans, indolines and oxindoles from alkyl propiolic acid. The reaction proceeds through the intramolecular Heck and intermolecular decarboxylative Sonogashira couplings. Notably, the reaction was feasible in water as the sole solvent, in the presence of quaternary ammonium salts.

Result and Discussions

It was envisioned that propiolic acids **2** could serve as good alkyne source for intermolecular decarboxylative Sonogashira coupling on the bicyclic intermediate **B**, to furnish the target heterocyclic products **5/6/7**. The bicyclic organo palladium intermediate **B** could be resulted from **1/3/4** via intramolecular Heck coupling (Scheme 1).



Scheme 1: Anticipated formation of heterocyclic products.

The optimization study of palladium catalyzed dual coupling process has begun with *ortho*-iodophenyl allyl ether **1a** and phenylpropiolic acid **2a**, particularly, under microwave irradiation conditions. Accordingly, **1a** and **2a** in DMF (0.5 mL) were subjected to microwave irradiation, in the presence of Pd₂(dba)₃ (1 mol%), base K₂CO₃ (3 equiv), at 100 °C for 10 min (Table 1, entry 1). This led to formation of product **5aa** in 95% yield. As we intend to make our method environmentally benign, the reaction was explored in water medium. Hence, the reaction performed between **1a** and **2a** under the same set of conditions (i.e. Table 1, entry 1), by replacing DMF with water (Table 1, entry 2). However, the dihydrobenzofuran **5aa** was isolated in poor yield. Increasing the irradiation time to 20 and 30 min, respectively, could not show much improvement (Table 1, entries 3 & 4). Significantly, when tetrabutylammonium iodide (TBAI) was used as an additive, the reaction was quite successful and afforded **5aa** in 85% yield (Table 1, entry 5). Delightfully, **5aa** was isolated in near quantitative yield with tetrabutylammonium bromide (TBAB) as an additive, the yield of **5aa** was slightly

decreased (Table 1, entry 7). The yield was moderate, in the presence of base 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) (Table 1, entry 8). Reducing the irradiation time to 5 min, afforded **5aa** in 65% yield (Table 1, entry 9). The catalyst $Pd(PPh_3)_4$ furnished **5aa** in 85% yield (Table 1, entry 10). On the other hand, when the reaction was performed under conventional heating conditions, in H₂O and DMF, furnished **5aa** as major product along with minor impurities as inseparable mixture (Table 1, entries 11 & 12). Therefore, it was confirmed that microwave assisting conditions are better than the conventional ones.

A

Table 1. Screening study to the generation of dihydrobenzofuran 5aa from 1a and 2a.^{a,b,c,d}

	U I 1a	HOOC + 2a	[Pd]/liga base, add MW, he	und litive sat	Me 5aa	+	CO₂↑
entry	catalyst	additive	base	solvent	temp	time	yield
	(1 mol%)	(1 equiv)	(3 equiv)		(°C)	(min)	5aa ^b (%)
1	Pd ₂ (dba) ₃	-	K ₂ CO ₃	DMF	100	10	(95%)
2	Pd ₂ (dba) ₃	-	K ₂ CO ₃	H ₂ O	100	10	(15%)
3	$Pd_2(dba)_3$	-	K ₂ CO ₃	H ₂ O	100	20	(20%)
4	Pd ₂ (dba) ₃	- 🤇	K ₂ CO ₃	H ₂ O	100	30	(25%)
5	Pd ₂ (dba) ₃	ТВАІ	K ₂ CO ₃	H ₂ O	100	10	(85%)
6	Pd ₂ (dba) ₃	ТВАВ	K ₂ CO ₃	H ₂ O	100	10	(98%)
7	$Pd_2(dba)_3$	BTEAC	K ₂ CO ₃	H ₂ O	100	10	(92%)
8	$Pd_2(dba)_3$	BTEAC	DBU	H ₂ O	100	10	(40%)
9	$Pd_2(dba)_3$	ТВАВ	K ₂ CO ₃	H ₂ O	100	5	(65%)
10	Pd(PPh ₃) ₄	TBAB	K ₂ CO ₃	H ₂ O	100	10	(85%)
11 ^{<i>c</i>}	$Pd_2(dba)_3$	TBAB	K ₂ CO ₃	H ₂ O	100	60	_d
12 ^{<i>c</i>}	$Pd_2(dba)_3$	-	K ₂ CO ₃	DMF	100	60	_d

^{*a*}Conditions: Reactions were conducted under microwave irradiation (100 °C, 10 minutes, 300 W, closed vessel) using 68.5 mg (0.25 mmol) of 1-iodo-2-((2-methylallyl)oxy)benzene **1a**, 54.7 mg (0.37 mmol) of 3-phenylprop-2-ynoic acid **2a**, base (1 mmol, 3 equiv), Pd-catalyst (1 mol%) and solvent water (0.5 mL) or solvent DMF (0.5 mL). ^{*b*}Isolated yields of **5aa**. ^{*c*}Reactions were performed using conventional heating method. ^{*d*}**5aa** was obtained as major product along with minor inseparable impurities.

Since it was clear that entry 6 of Table 1 were best, for the preparation of dihydrobenzofuran **5aa**, next, it was planned to test the reaction with other ortho-iodophenyl allyl ethers. Thus, ortho-iodophenyl allyl ethers **1b-1h** were subjected to microwave irradiation with phenylpropiolic acid 2a, under standard conditions. Gratifyingly, the reaction was quite suitable and furnished the corresponding dihydrobenzofurans 5ba-5ha, in excellent yields (Table 2). Notably, the alkyl-substituted ortho-iodophenyl allyl ethers 1b-1d were smoothly transformed into dihydrobenzofurans 5ba-5da (Table 2). The protocol was also feasible with phenyl substituted ortho-iodophenyl allyl ether 1e (5ea, Table 2). To our delight, the reaction was tolerable to electron deactivating halo-substituents on the aromatic ring of orthoiodophenyl allyl ethers 1f-1h (5fa-5ha, Table 2). Furthermore, to elaborate the reaction feasibility, we have performed a reaction with 1-bromo-2-((2-methylallyl)oxy)benzene 1i and phenylpropiolic acid 2a, under standard conditions. In this case, the reaction was inferior; probably due to poor reactivity of bromides when compared to iodides (5ia). While bromosubstituted ortho-iodophenyl allyl ether 1h (1 equiv) with phenylpropiolic acid 2a (1.5 or 2.0 equiv) under standard conditions, resulted single product **5ha**, in which bromo group is intact. From these observations, it can be rationalized that bromo moiety is unreactive under these particular conditions. In essence, the bromo-substituted product **5ha**, is interesting, as it can allow the possibility for further elaboration using transition metal catalyzed cross-coupling reactions.



Table 2: Synthesis of dihydrobenzofurans 5aa-5ia from allyl ethers 1a-1i and phenylpropiolic acid 2a.^{a,b,c,d}

^{*a*}Reaction conditions: 1-iodo-2-((2-methylallyl)oxy)benzenes **1a-1i** (0.25 mmol), phenylpropiolic acid **2a** (0.37 mmol), Pd₂(dba)₃ (1 mol%), TBAB (1 equiv), K₂CO₃ (3 equiv), solvent water (0.5 mL), 100 °C, 10 minutes (300 W, closed vessel). ^{*b*}Yields in the parenthesis are chromatographically isolated pure products. ^{*c*}In the products **5aa-5ia** first alphabet refers to the *ortho*-iodophenyl allyl ethers, and the second alphabet indicates the phenylpropyolic acid. ^{*d*}Reaction with 1.5 equiv of phenylpropiolic acid **2a**. ^{*f*}Reaction with 1-bromo-2-((2-methylallyl)oxy)benzenes **1i** instead of **1a**.

Notably, further, the strategy was successfully applied to different 3-alkylpropiolic acids **2b-2d**, under established conditions, and the dihydrobenzofurans **5ab-5fd** were obtained in very good yields (Table 3). It is worth noting that none of the previous reports disclosed the preparation of dihydrobenzofurans with short alkyl-substituents connected to an alkyne carbon atom. This is due to the fact that short terminal alkylacetylenes are volatile enough and very difficult to store and handle. Remarkably, the present strategy was found to be superior over earlier reports and facilitated the synthesis of dihydrobenzofurans **5ab-fd** with short alkyl-substituents on the acetylenic carbon (Table 3). Thus, from these results, it became evident that simple 3-alkylpropiolic acids are the best alternative alkynyl source over the corresponding terminal acetylenes.



Table 3: Synthesis of dihydrobenzofurans 5ab-5fd from allyl ethers 1a-1h and 3-alkylpropiolic acids 2b-2d.^{*a,b,c*}

^{*a*}Reaction conditions: 1-iodo-2-((2-methylallyl)oxy)benzenes **1a-1h** (0.25 mmol), 3-alkylpropiolic acids **2b-2d** (0.37 mmol), Pd₂(dba)₃ (1 mol%), TBAB (1 equiv), K₂CO₃ (3 equiv), solvent water (0.5 mL), 100 °C, 10 minutes (300 W, closed vessel). ^{*b*}Yields in the parenthesis are chromatographically isolated pure products. ^{*c*}In the products **5ab-5fd** first alphabet refers to the *ortho*-iodophenyl allyl ethers, and the second alphabet indicates the 3-alkylpropiolic acids.

With the synthesis of dihydrobenzofurans **5aa-5ha** and **5ab-5fd** (Tables 2 & 3), to further ascertain the utility of this one-pot green process, it was intended to apply the strategy for the synthesis of nitrogen heterocyclic products. Therefore, different *ortho*-iodophenyl alkyl/benzyl/aryl allyl amines **3a-3d** were treated with propiolic acids **2a-2d**, under standard microwave irradiation conditions. Gratifyingly, as expected, the dual C–C bond forming reaction via a dual coupling sequence was quite smooth and gave the corresponding indolines **6aa-6da**, in very good to excellent yields (Table 4).



Table 4: Making of indolines 6aa-6da from allyl amines 3a-3d and propiolic aicds 2a-2d.^{a,b,c}

^{*a*}Reaction conditions: 2-iodo-*N*-alkyl/benzyl/aryl-*N*-(2-methylallyl)anilines **3a-3d** (0.25 mmol), propiolic acids **2a-2d** (0.37 mmol) Pd₂(dba)₃ (1 mol%), TBAB (1 equiv), K₂CO₃ (3 equiv), solvent water (0.5 mL), 100 °C, 10 minutes (300 W, closed vessel). ^{*b*}Yields in the parenthesis are chromatographically isolated pure products. ^{*c*}The first alphabet of products **6aa-6da** refers to the 2-iodo-*N*alkyl/benzyl/aryl-*N*-(2-methylallyl)aniline, while, second letter indicates the propiolic acid.

Furthermore, to emphasize the significance of the present method, *ortho*-iodophenyl enamides **4a-4c** were also reacted with propiolic acids **2a-2d**, under standard reaction conditions. This resulted in the desired oxindoles **7aa-7cd** in very good to excellent yields (Table 5), thus, reveals the usefulness of the present strategy for intramolecular Heck and intermolecular decarboxylative Sonogashira couplings in water as the sole solvent, under microwave assisted palladium catalysis. Moreover, to the extent of our knowledge, we believe

this is the first report by making use of propiolic acids as alkynyl source, under decarboxylative Sonogashira coupling, for the synthesis of dihydrobenzofurans, indolines and oxindoles. It is noteworthy that all accomplished products with short alkyl substituents on acetyelenic carbon, is first of its kind.



Table 5: Synthesis of oxindoles 7aa-7cd from alkylmethacrylamides 4a-4c and propiolic acids 2a-2d.^{a,b,c}

^{*a*}Reaction conditions: *N*-(2-iodophenyl)-*N*-alkyl/benzylmethacrylamides **4a-4c** (0.25 mmol), propiolic aicds **2a-2d** (0.37 mmol) Pd₂(dba)₃ (1 mol%), TBAB (1 equiv), K₂CO₃ (3 equiv), solvent water (0.5 mL), 100 °C, 10 minutes (300 W, closed vessel). ^{*b*}Yields in the parenthesis are chromatographically isolated pure products. ^{*c*}In the products **7aa-7cd** first alphabet refers to the *N*-(2iodophenyl)-*N*-methylmethacrylamides, and the second alphabet indicates the propiolic acids.

In addition, to understand reactivity of propioloic acids, control experiment was carried out in the presence of phenyl propiolic acid **2a** and butynoic acid **2b**, under standard conditions (Scheme 2). It is worth noting that phenyl propiolic acid **2a** is highly reactive than butynoic acid **2b** and

exclusively afforded the product **5aa**. This may be attributed to electron withdrawing nature of phenyl sp^2 carbons and would accelerate the decarboxylation step.



Scheme 2: Control experiments.

The plausible reaction mechanism for the synthesis of **5/6/7** is presented in Scheme 3. The organo palladium(II) intermediate **A** can be formed through the oxidative insertion of Pd(0) across the C(sp²)-I bond of **1/3/4**. Subsequently, bicyclic alkyl-Pd(II) species **B** would be formed via intramolecular Heck cyclization of **A**. Chelation of propiolic acid with palladium(II) of bicyclic intermediate **B**, gives **C** through the removal of KI and KHCO₃. Decarboxylation of **C**, furnishes a new Pd(II) species **D**. Finally, reductive elimination of **D**, yields the desired heterocyclic products **5/6/7** along with the regeneration of Pd(0) catalyst.



Scheme 3: Plausible reaction mechanism for the synthesis of heterocycles 5/6/7.

Conclusions

In conclusion, a [Pd]-catalyzed domino one-pot technique was described, for the construction of alkyne bearing heterocyclic compounds with a quaternary carbon atom. The entire process involved intramolecular Heck reaction and intermolecular decarboxylative copper free Sonogashira coupling. Notably, this domino strategy has been successful in the solvent water as reaction medium, under microwave assisting conditions. Significantly, as far as we know, this is the initial report on the synthesis of heterocyclic products bearing short alkyl substituents on the acetylenic carbon atom. This has become possible due to easy handling of short alkyl-substituted propiolic acids as the Sonogashira coupling partners, as the direct use, handling and storage of short alkyl substituted acetylenes is difficult.

Experimental

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ¹H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl₃; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\rm H}$ = 0.00 ppm) or CHCl₃ ($\delta_{\rm H}$ = 7.25 ppm). ¹³C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl₃; chemical shifts (δ ppm) are reported relative to CDCl₃ [$\delta_{\rm C}$ = 77.00 ppm (central line of triplet)]. In the ¹³C NMR, the nature of carbons (C, CH, CH₂ and CH₃) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH₂) and q = quartet (for CH₃). In the ¹H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of doublets, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ¹H, ¹³C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. The microwave irradiation

experiments were carried out in a dedicated CEM-Discover monomode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W and utilization of the standard absorbance level of 100 W. The reactions were carried out in 10 mL glass vials fitted with Teflon septum. The reactions were irradiated at the required temperature for the stipulated time and then cooled to ambient temperature with air jet cooling. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. Pd₂(dba)₃, and K₂CO₃ were purchased from Sigma-Aldrich and used as received. *ortho*-lodophenols, *ortho*-iodoanilines, TBAB (tetrabutylammonium bromide), 3-chloro-2-methylprop-1-ene and propiolic acids were purchased from Sigma-Aldrich/TCI/local sources and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material). It is worth noting that these sort of experimental procedures have already been published elsewhere.^{12g,13,14}

GP (General Procedure for the Synthesis of 3,3'-Disubstituted Heterocyclic Compounds 5/6/7): An oven dried 10 mL microwave tube fitted with teflon septum was equipped with a magnetic stir bar. The vial was charged with *ortho*-iodoaryl allyl ethers **1** (or) *ortho*-iodophenyl allyl amines **3** (or) *ortho*-iodophenyl enamides **4** (68-88 mg, 0.25 mmol), propiolic acids **2** (31-54 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), K₂CO₃ (103.9 mg, 0.75 mmol) TBAB (80.5 mg, 0.37 mmol), followed by solvent water (0.5mL), at room temperature. The resultant reaction mixture was then subjected to microwave irradiation at 100 °C for 10 min (300 W, closed vessel). Progress of the reaction was monitored by TLC till the reaction is completed. The mixture was cooled to room temperature, quenched with aqueous NaHCO₃ solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), furnished the 3,3'-disubstituted heterocyclic compounds **5/6/7** (80–98%) as oil.

3-Methyl-5-phenyl-3-(3-phenylprop-2-ynyl)-2,3-dihydro-1-benzofuran (5ea): GP was carried out with 3-iodo-1,1'-biphenyl-4-yl 2-methylprop-2-enyl ether **1e** (87.5 mg, 0.25 mmol), 3-

phenylprop-2-ynoic acid **2a** (54.7 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the dihydrobenzofuran **5ea** (72.9 mg, 90%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 99:1), R_f (**1e**)=0.8, R_f (**5ea**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2960, 1605, 1482, 1375, 1224, 1067, 979, 813, 757, 693 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.57–7.49 (m, 2H, Ar–H), 7.47 (d, 1H, *J* = 2.0 Hz, Ar–H), 7.44–7.34 (m, 5H, Ar–H), 7.33–7.24 (m, 4H, Ar–H), 6.88 (d, 1H, *J* = 8.3 Hz, Ar–H), 4.60 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 4.30 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 2.73 (s, 2H, CH₂), 1.59 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =159.2 (s, Ar–C), 141.3 (s, Ar–C), 134.6 (s, Ar–C), 127.6 (d, Ar–CH), 126.8 (d, 2 × Ar–CH), 128.7 (d, 2 × Ar–CH), 123.4 (s, Ar–C), 122.0 (d, Ar–CH), 109.9 (d, Ar–CH), 86.7 (s, *C*=C), 82.8 (t, OCH₂), 82.7 (s, C=C), 45.4 (s, C), 31.6 (t, CH₂), 24.2 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₂₄H₂₀KO]⁺=[M+K]⁺: 363.1146; found 363.1116.

3-But-2-ynyl-3-methyl-2,3-dihydro-1-benzofuran (5ab): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5ab** (38.5 mg, 83%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R_f*(**1a**)=0.9, *R_f*(**5ab**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2964, 2928, 2881, 1608, 1478, 1377, 1314, 1227, 1175, 1123, 981, 872, 815, 766, 700 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): *δ*=7.19–7.12 (m, 1H, Ar–H), 7.12 (dd, *J* = 7.8 and 1.4 Hz, 1H, Ar-H), 6.87 (ddd, *J* = 7.3, 7.3 and 1.0 Hz, 1H, Ar–H), 6.78 (d, *J* = 7.8 Hz, 1H, Ar–H), 4.47 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 4.17 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 2.40 (q, *J* = 2.5 Hz, 2H, CH₂), 1.79 (t, *J* = 2.5 Hz, 3H, CH₃), 1.44 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=159.4 (s, Ar–C), 134.3 (s, Ar–C), 128.4 (d, Ar–CH), 122.8 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d,

Ar–CH), 82.3 (t, OCH₂), 77.5 (s, C=C), 75.7 (s, C=C), 45.1 (s, C), 30.8 (t, CH₂), 24.3 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{13}H_{18}NO]^+=[M+NH_4]^+$: 204.1383; found 204.1386.

3-But-2-ynyl-3,5-dimethyl-2,3-dihydro-1-benzofuran (5bb): GP was carried out with 2-iodo-4methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL) , under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5bb** (40 mg, 82%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R_f*(**1b**)=0.9, *R_f*(**5bb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2964, 1608, 1478, 1376, 1230, 1175, 981, 874, 815, 766, 700 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): *δ*=6.94 (s, 1H, Ar–H), 6.93 (d, J = 8.8 Hz, 1H, Ar-H), 6.68 (dd, *J* = 6.8 and 1.9 Hz, 1H, Ar–H), 4.46 (d, *J* = 8.8 Hz, 1H, OC*H*_{*A*}H_B), 4.14 (d, *J* = 8.80 Hz, 1H, OCH_{*A*}H_{*B*}), 2.39 (q, *J* = 2.5 Hz, 2H, CH₂), 2.29 (s, 3H, CH₃), 1.79 (t, *J* = 2.5 Hz, 3H, CH₃), 1.42 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=157.3 (s, Ar–C), 134.3 (s, Ar–C), 129.7 (s, Ar–C), 128.7 (d, Ar–CH), 123.3 (d, Ar–CH), 109.2 (d, Ar–CH), 82.3 (t, OCH₂), 77.5 (s, *C*≡C), 75.8 (s, C≡C), 45.1 (s, C), 30.8 (t, CH₂), 24.2 (q, CH₃), 20.9 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₄H₁₇O]⁺=[M+H]⁺: 201.1274; found 201.1271.

3-But-2-ynyl-5-ethyl-3-methyl-2,3-dihydro-1-benzofuran (5cb): GP was carried out with 4ethyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1c** (75.5 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5cb** (42.9 mg, 81%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R_f*(**1c**)=0.9, *R_f*(**5cb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2964, 2883, 1608, 1478, 1377, 1230, 1176, 981, 815, 766, 700 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=6.97 (s, 1H, Ar–H), 6.95 (dd, *J* = 8.3 and 1.5 Hz, 1H, Ar–H), 6.70 (d, *J* = 8.3 Hz, 1H, Ar–H), 4.45 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 4.15 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 2.59 (q, *J* = 7.6 Hz, 2H, CH₂), 2.39 (q, *J* = 2.5 Hz, 2H, CH₂), 1.80 (t, *J* = 2.7 Hz, 3H, CH₃), 1.43 (s, 3H, CH₃), 1.21 (t, 3H, J = 7.6 Hz) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =157.5 (s, Ar–C), 136.4 (s, Ar–C), 134.3 (s, Ar–C), 127.6 (d, Ar–CH), 122.2 (d, Ar–CH), 109.2 (d, Ar–CH), 82.4 (t, OCH₂), 77.4 (s, *C*=C), 75.8 (s, C=*C*), 45.1 (s, C), 30.8 (t, CH₂), 28.4 (t, CH₂), 24.1 (q, CH₃), 16.0 (q, CH₃), 3.4 (q, CH₃). HR-MS (ESI+) m/z calculated for [C₁₅H₂₂NO]⁺=[M+NH₄]⁺: 232.1696; found 232.1695.

5-tert-Butyl-3-but-2-ynyl-3-methyl-2,3-dihydro-1-benzofuran (5db): GP was carried out with 4-tert-butyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene 1d (82 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran 5db (49.8 mg, 83%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), $R_{f}(1d) = 0.9, R_{f}(5db) = 0.8, UV detection]$. IR (MIR-ATR, 4000–600 cm⁻¹): $v_{max} = 2962, 2922, 2876,$ 1611, 1485, 1375, 1219, 1062, 981, 886, 817, 768, 707, 626 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.19 (d, J = 2.0 Hz, 1H, Ar–H), 7.15 (dd, J = 8.3 and 2.0 Hz, 1H, Ar–H), 6.70 (d, J = 8.3 Hz, 1H, Ar-H), 4.42 (d, J = 8.8 Hz, 1H, OCH_AH_B), 4.15 (d, J = 8.8 Hz, 1H, OCH_AH_B), 2.39 (q, J = 2.4 Hz, 2H, CH₂), 1.80 (t, J = 2.4 Hz, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.30 (s, 9H, 3 × CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=157.2 (s, Ar–C), 143.4 (s, Ar–C), 133.8 (s, Ar–C), 125.1 (d, Ar–CH), 119.8 (d, Ar–CH), 108.8 (d, Ar-CH), 82.6 (t, OCH₂), 77.4 (s, C=C), 75.9 (s, C=C), 45.2 (s, C), 34.4 (s, C), 31.7 (q, 3 × CH₃), 30.9 (t, CH₂), 23.9 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{22}NaO]^{+}=[M+Na]^{+}: 265.1563; found 265.1548.$

3-But-2-ynyl-5-fluoro-3-methyl-2,3-dihydro-1-benzofuran (5fb): GP was carried out with 4fluoro-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1f** (73 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5fb** (40.8 mg, 80%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), $R_f(\mathbf{1f})=0.9$, $R_f(\mathbf{5fb})=0.8$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2965, 2919, 1615, 1477, 1377, 1311, 1240, 1172, 1106, 981, 918, 867, 808, 786, 713 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =6.85 (dd, *J* = 8.1 and 2.7 Hz, 1H, Ar–H), 6.80 (ddd, *J* = 8.8, 8.8 and 2.7 Hz, 1H, Ar–H), 6.67 (dd, *J* = 8.6 and 4.2 Hz, 1H, Ar–H), 4.45 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 4.17 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 2.38 (q, *J* = 2.4 Hz, 2H, CH₂), 1.78 (t, *J* = 2.4 Hz, 3H, CH₃), 1.41 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =157.4 (d, *J* = 237.7 Hz, Ar–C), 155.2 (s, Ar–C), 135.7 (d, *J* = 8.1 Hz, Ar–C), 114.4 (d, *J* = 24.1 Hz, Ar–CH), 110.1 (d, *J* = 24.2 Hz, Ar–CH), 109.8 (d, *J* = 8.1 Hz, Ar–CH), 82.8 (t, OCH₂), 77.9 (s, *C*=C), 75.2 (s, C=*C*), 45.4 (d, *J* = 1.5 Hz, C), 30.6 (t, CH₂), 24.1 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₃H₁₂F]⁺=[M]+[-H₂O]⁺: 187.0918; found 187.0911.

3-But-2-ynyl-5-chloro-3-methyl-2,3-dihydro-1-benzofuran (5gb): GP was carried out with 4chloro-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1g** (77 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5gb** (44.5 mg, 81%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R_f*(**1g**)=0.9, *R_f*(**5gb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} =2960, 2923, 2879, 1607, 1473, 1376, 1227, 1173, 1122, 980, 872, 814, 765, 700 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.08 (d, *J* = 2.4 Hz, 1H, Ar–H), 7.06 (dd, *J* = 8.8 and 2.4 Hz, 1H, Ar–H), 6.69 (d, *J* = 8.8 Hz, 1H, Ar–H), 4.47 (d, *J* = 8.8 Hz, 1H, OCH_{*A*}H_B), 4.18 (d, *J* = 8.8 Hz, 1H, OCH_{*A*}H_{*B*}), 2.38 (q, *J* = 2.4 Hz, 2H, CH₂), 1.78 (t, *J* = 2.4 Hz, 3H, CH₃), 1.41 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =158.1 (s, Ar–C), 136.2 (s, Ar–C), 128.2 (d, Ar–CH), 125.1 (s, Ar–C), 123.2 (d, Ar–CH), 110.7 (d, Ar–CH), 82.8 (t, OCH₂), 78.0 (s, *C*=C), 75.2 (s, C=*C*), 45.4 (s, C), 30.7 (t, CH₂), 24.2 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₃H₁₃ClO]⁺=[M]⁺: 220.0649; found 220.0661.

5-Bromo-3-but-2-ynyl-3-methyl-2,3-dihydro-1-benzofuran (5hb): GP was carried out with 4bromo-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1h** (88 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5hb** (52.8 mg, 80%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f (**1h**)=0.9, R_f (**5hb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =3038, 2923, 1611, 1484, 1452, 1336, 1187, 1098, 982, 763, 696 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.22 (s, 1H, Ar–H), 7.20 (dd, J = 7.8 and 2.0 Hz, 1H, Ar–H), 6.65 (dd, J = 7.8 and 1.0 Hz, 1H, Ar–H), 4.46 (d, J = 8.8 Hz, 1H, OCH_AH_B), 4.17 (d, J = 8.8 Hz, 1H, OCH_AH_B), 2.37 (q, J = 2.2 Hz, 2H, CH₂), 1.78 (t, J = 2.4 Hz, 3H, CH₃), 1.41 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =158.6 (s, Ar–C), 136.7 (s, Ar–C), 131.1 (d, Ar–CH), 126.1 (d, Ar–CH), 112.2 (s, Ar–C), 111.3 (d, Ar–CH), 82.7 (t, OCH₂), 78.0 (s, C=C), 75.2 (s, C=*C*), 45.4 (s, C), 30.7 (t, CH₂), 24.2 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₃H₁₄⁷⁹BrO]⁺=[M+H]⁺: 265.0223; found 265.0227; [C₁₃H₁₄⁸¹BrO]⁺=[M+H]⁺: 267.0203; found 265.0204.

3-Methyl-3-pent-2-ynyl-2,3-dihydro-1-benzofuran (5ac): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene 1a (68.2 mg, 0.25 mmol), pent-2-ynoic acid 2c (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5ac** (41.1 mg, 84%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), $R_f(1a)=0.9$, $R_f(5ac)=0.8$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2963, 2881, 1480, 1379, 1318, 1240, 1175, 1105, 984, 920, 867, 810, 715 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.15 (dd, J = 7.3 and 1.0 Hz, 1H, Ar– H), 7.12 (dd, J = 7.3 and 1.5 Hz, 1H, Ar–H), 6.87 (ddd, J = 7.3, 7.3 and 1.0 Hz, 1H, Ar–H), 6.79 (d, J = 7.3 Hz, 1H, Ar–H), 4.47 (d, J = 8.8 Hz, 1H, OCH_AH_B), 4.16 (d, J = 8.8 Hz, 1H, OCH_AH_B), 2.41 (t, J = 2.5 Hz, 2H, CH₂), 2.23–2.08 (m, 2H, CH₂), 1.45 (s, 3H, CH₃), 1.12 (t, *J* = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=159.4 (s, Ar–C), 134.3 (s, Ar–C), 128.4 (d, Ar–CH), 122.9 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 83.8 (s, C=C), 82.3 (t, OCH₂), 75.9 (s, C=C), 45.1 (s, C), 30.9 (t, CH₂), 24.2 (q, CH₃), 14.2 (q, CH₃), 12.4 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{14}H_{18}N]^{+}=[M+NH_{4}]+[-H_{2}O]^{+}: 200.1434; found 200.1425.$

3,5-Dimethyl-3-pent-2-ynyl-2,3-dihydro-1-benzofuran (5bc): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene 1b (72 mg, 0.25 mmol), pent-2-ynoic acid 2c (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran 5bc (46.6 mg, 88%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(1b)=0.9, R_f(5bc)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2962, 2922, 2876, 1612, 1485, 1375, 1217, 1136, 1062, 981, 886, 817, 770, 711, 620 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =6.95 (s, 1H, Ar–H), 6.92 (dd, J = 8.3 and 2.0 Hz, 1H, Ar-H), 6.67 (d, J = 8.3 Hz, 1H, Ar-H), 4.44 (d, J = 8.8 Hz, 1H, OCH_AH_B),4.14 (d, J = 8.8 Hz, 1H, OCH_AH_B), 2.39 (t, J = 2.4 Hz, 2H, CH₂), 2.28 (s, 3H, CH₃), 2.21–2.12 (m, 2H, CH₂), 1.42 (s, 3H, CH₃), 1.11 (t, J = 7.6 Hz, 3H, CH₂) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =157.3 (s, Ar-C), 134.3 (s, Ar-C), 129.6 (s, Ar-C), 128.7 (d, Ar-CH), 123.5 (d, Ar-CH), 109.2 (d, Ar-CH), 83.7 (s, C≡C), 82.4 (t, OCH₂), 76.0 (s, C≡C), 45.1 (s, C), 30.8 (t, CH₂), 24.1 (q, CH₃), 20.9 (q, CH₃), 14.2 (q, CH₃), 12.4 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{15}H_{22}NO]^{+}=[M+NH_{4}]^{+}$: 232.1696; found 232.1688.

3-Methyl-3-pent-2-ynyl-5-phenyl-2,3-dihydro-1-benzofuran (5ec): GP was carried out with 3iodo-1,1'-biphenyl-4-yl 2-methylprop-2-enyl ether **1e** (87.5 mg, 0.25 mmol), pent-2-ynoic acid **2c** (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran **5ec** (56.5 mg, 82%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R_f*(**1e**)=0.8, *R_f*(**5ec**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2962, 2922, 1719, 1605, 1484, 1375, 1226, 1068, 980, 888, 813, 757, 693 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): *δ*=7.57–7.50 (m, 2H, Ar–H), 7.44–7.36 (m, 2H, Ar–H), 7.38 (s, 1H, Ar-H), 7.37 (dd, *J* = 7.9 and 2.0 Hz, 1H, Ar-H), 7.28 (m, 1H, Ar–H), 6.84 (dd, *J* = 8.8 and 0.7 Hz, 1H, Ar–H), 4.52 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 4.22 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 2.46 (t, *J* = 2.4 Hz, 2H, CH₂), 2.23–2.12 (m, 2H, CH₂), 1.49 (s, 3H, CH₃), 1.11 (t, *J* = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=159.2 (s, Ar–C), 141.4 (s, Ar–C), 135.0 (s, Ar–C), 134.1 (s, Ar–C), 128.7 (d, 2 × Ar–CH), 127.5 (d, Ar–CH), 126.8 (d, Ar–CH), 126.5 (d, Ar–CH), 121.9 (d, Ar–CH), 109.8 (d, Ar–CH), 83.9 (s, *C*=C), 82.8 (t, OCH₂), 75.9 (s, C=*C*), 45.2 (s, C), 30.8 (t, CH₂), 24.3 (q, CH₃), 14.3 (q, CH₃), 12.4 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{24}NO]^+=[M+NH_4]^+$: 294.1852; found 294.1840.

5-Fluoro-3-methyl-3-pent-2-ynyl-2,3-dihydro-1-benzofuran (5fc): GP was carried out with 4fluoro-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene 1f (73 mg, 0.25 mmol), pent-2-ynoic acid 2c (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran 5fc (43.7 mg, 81%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(1f)=0.9, R_f(5fc)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =3035, 2923, 1654, 1611, 1485, 1451, 1336, 1186, 1097, 982, 881, 817, 763, 696 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =6.86 (dd, J = 8.1 and 2.7 Hz, 1H, Ar–H), 6.80 (ddd, J = 8.8, 8.8 and 2.9 Hz, 1H, Ar–H), 6.67 (dd, J = 8.8 and 3.9 Hz, 1H, Ar–H), 4.45 (d, J = 8.8 Hz, 1H, OCH_AH_B), 4.18 (d, J = 8.8 Hz, 1H, OCH_AH_B), 2.39 (t, J = 2.4 Hz, 2H, CH₂), 2.22–2.11 (m, 2H, CH₂), 1.42 (s, 3H, CH₃), 1.10 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=157.4 (d, J = 236.9 Hz, Ar–C), 155.3 (s, Ar–C), 135.7 (d, J = 8.1 Hz, Ar–C), 114.4 (d, J = 24.2 Hz, Ar–CH), 110.1 (d, J = 24.9 Hz, Ar–CH), 109.8 (d, J = 8.1 Hz, Ar–CH), 84.1 (s, C=C), 82.8 (t, OCH_2), 75.5 (s, C=C), 45.5 (d, J = 2.0 Hz, C), 30.7 (t, CH₂), 24.0 (q, CH₃), 14.2 (q, CH₃), 12.3 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{14}H_{13}F]^{+}=[M]+[-H_2O]^{+}$: 200.0966; found 200.1007.

5-tert-Butyl-3-hex-2-ynyl-3-methyl-2,3-dihydro-1-benzofuran (5dd): GP was carried out with 4-tert-butyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **4d** (75.5 mg, 0.25 mmol), hex-2-ynoic acid **2d** (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5dd** (56.9 mg, 85%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f (**4d**)=0.9, R_f (**5dd**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2962, 2884, 1480,

1241, 1176, 985, 869, 807 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.18 (d, *J* = 2.0 Hz, 1H, Ar–H), 7.15 (dd, *J* = 8.3 and 2.0 Hz, 1H, Ar–H), 6.70 (d, *J* = 8.3 Hz, 1H, Ar–H), 4.43 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 4.15 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 2.42 (t, *J* = 2.2 Hz, 2H, CH₂), 2.18–2.10 (m, 2H, CH₂), 1.50 (sext, *J* = 7.3 Hz, 2H, CH₂), 1.45 (s, 3H, CH₃), 1.29 (s, 9H, 3 × CH₃), 0.95 (t, *J* = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =157.2 (s, Ar–C), 143.3 (s, Ar–C), 133.8 (s, Ar–C), 125.1 (d, Ar–CH), 119.8 (d, Ar–CH), 108.8 (d, Ar–CH), 82.6 (t, OCH₂), 82.1 (s, *C*≡C), 76.9 (s, *C*≡*C*), 45.2 (s, C), 34.4 (s, C), 31.7 (q, 3 × CH₃), 30.9 (t, CH₂), 24.0 (q, CH₃), 22.4 (t, CH₂), 20.7 (t, CH₂), 13.5 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₉H₃₀NO]⁺=[M+NH₄]⁺: 288.2322; found 288.2340.

3-Hex-2-ynyl-3-methyl-5-phenyl-2,3-dihydro-1-benzofuran (5ed): GP was carried out with 3iodo-1,1'-biphenyl-4-yl 2-methylprop-2-enyl ether 1e (87.5 mg, 0.25 mmol), hex-2-ynoic acid 2d (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran 5ed (63.3 mg, 88%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(1e)=0.8, R_f(5ed)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2962, 2923, 1606, 1485, 1375, 1226, 1068, 980, 890, 813, 758, 693 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.59–7.49 (m, 2H, Ar–H), 7.45–7.35 (m, 2H, Ar–H), 7.38 (s, 1H, Ar–H), 7.37 (dd, J = 7.6 and 2.0 Hz, 1H, Ar–H), 7.33–7.25 (m, 1H, Ar–H), 6.84 (dd, J = 7.6 and 1.2 Hz, 1H, Ar–H), 4.53 (d, J = 8.8 Hz, 1H, OCH_AH_B), 4.23 (d, J = 8.8 Hz, 1H, OCH_AH_B , 2.47 (t, J = 2.0 Hz, 2H, CH₂), 2.17–2.10 (m, 2H, CH₂), 1.48 (sext, J = 7.3 Hz, 2H, CH₂), 1.49 (s, 3H, CH₃), 0.93 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=159.2 (s, Ar–C), 141.4 (s, Ar–C), 135.0 (s, Ar–C), 134.1 (s, Ar–C), 128.6 (d, 2 × Ar–CH), 127.5 (d, Ar–CH), 126.8 (d, 2 × Ar–CH), 126.5 (d, Ar–CH), 121.8 (d, Ar–CH), 109.8 (d, Ar–CH), 82.7 (t, OCH₂), 82.4 (s, *C*=C), 77.0 (s, C=C), 45.2 (s, C), 30.9 (t, CH₂), 24.3 (q, CH₃), 22.4 (t, CH₂), 20.7 (t, CH₂), 13.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{23}O]^+=[M+H]^+$: 291.1743; found 291.1734.

5-Fluoro-3-hex-2-ynyl-3-methyl-2,3-dihydro-1-benzofuran (5fd): GP was carried out with 4-fluoro-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1f** (73 mg, 0.25 mmol), hex-2-ynoic acid **2d** (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg,

0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **5fd** (47.5 mg, 82%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f (**1f**)=0.9, R_f (**5fd**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =3037, 2923, 1654, 1610, 1484, 1452, 1336, 1250, 1186, 1097, 981, 881, 817, 762, 695 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=6.85 (dd, *J* = 8.1 and 2.7 Hz, 1H, Ar–H), 6.79 (ddd, *J* = 8.8, 8.8 and 2.4 Hz, 1H, Ar–H), 6.67 (dd, *J* = 8.6 and 4.2 Hz, 1H, Ar–H), 4.46 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 4.18 (d, *J* = 8.8 Hz, 1H, OCH_AH_B), 2.41 (q, *J* = 2.5 and 1.0 Hz, 2H, CH₂), 2.15–2.08 (m, 2H, CH₂), 1.48 (sext, *J* = 7.3 Hz, 2H, CH₂), 1.42 (s, 3H, CH₃), 0.94 (t, *J* = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =157.5 (d, *J* = 236.9 Hz, Ar–C), 155.3 (s, Ar–C), 135.6 (d, *J* = 8.1 Hz, Ar–C), 114.4 (d, *J* = 24.2 Hz, Ar–CH), 110.1 (d, *J* = 24.2 Hz, Ar–CH), 109.8 (d, *J* = 8.1 Hz, Ar–CH), 82.8 (t, OCH₂), 82.6 (s, *C*=C), 76.3 (s, C=C), 45.5 (s, C), 30.7 (t, CH₂), 24.1 (q, CH₃), 22.3 (t, CH₂), 20.6 (t, CH₂), 13.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₅H₂₁FNO]⁺=[M+NH₄]⁺: 250.1602; found 250.1609.

3-But-2-ynyl-1,3-dimethylindoline (6ab): GP was carried out with 2-iodo-*N*-methyl-*N*-(2-methylallyl)aniline **3a** (71.7 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 95:5) furnished the indoline **6ab** (44.5 mg, 89%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R_f*(**3a**)=0.8, *R_f*(**6ab**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2965, 2918, 2862, 2806, 1605, 1488, 1454, 1376, 1310, 1247, 1215, 1155, 1110, 1018, 966, 742 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): *δ*=7.10 (ddd, *J* = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 7.05 (dd, *J* = 7.3 and 1.0 Hz, 1H, Ar–H), 6.69 (ddd, *J* = 7.3, 7.3 and 1.0 Hz, 1H, Ar–H), 6.47 (d, *J* = 7.8 Hz, 1H, Ar–H), 3.33 (d, *J* = 8.8 Hz, 1H, NCH_{*A*}H_B), 2.97 (d, *J* = 8.8 Hz, 1H, NCH_{*A*}H_B), 2.74 (s, 3H, CH₃), 2.37 (dq, *J* = 16.4 and 2.8 Hz, 1H), 2.36 (dq, *J* = 16.4 and 2.8 Hz, 1H), 1.81 (t, *J* = 2.8 Hz, 3H), 1.40 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=152.2 (s, Ar–C), 137.0 (s, Ar–C), 127.9 (d, Ar–CH), 122.2 (d, Ar–CH), 117.6 (d, Ar–CH), 107.3 (d, Ar–CH), 77.1 (s, *C*=C), 76.0 (s,

C=C), 67.8 (t, CH₂), 43.5 (s, C), 35.8 (q, CH₃), 30.1 (t, CH₂), 23.9 (q, CH₃), 3.5 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{14}H_{18}N]^+ = [M+H]^+$: 200.1434; found 200.1436.

1,3-Dimethyl-3-pent-2-ynylindoline (6ac): GP was carried out with 2-iodo-N-methyl-N-(2methylallyl)aniline 3a (71.7 mg, 0.25 mmol), pent-2-ynoic acid 2c (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 95:5) furnished the indoline **6ac** (45.5 mg, 86%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), $R_f(3a)=0.8$, $R_f(6ac)=0.7$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2956, 2914, 2858, 2806, 1605, 1489, 1454, 1375, 1298, 1245, 1214, 1156, 1110, 1020, 965, 741 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.10 (ddd, J = 7.7, 7.7 and 1.2 Hz, 1H, Ar–H), 7.06 (dd, J = 7.7 and 1.0 Hz, 1H, Ar–H), 6.68 (ddd, J = 7.7, 7.7 and 1.2 Hz, 1H, Ar–H), 6.47 (d, J = 7.7 Hz, 1H, Ar–H), 3.33 (d, J = 8.8 Hz, 1H, NCH_AH_B), 2.97 (d, J = 8.8 Hz, 1H, NCH_AH_B), 2.74 (s, 3H, CH₃), 2.38 (dq, J = 16.1 and 2.0 Hz, 1H), 2.37 (dq, J = 16.1 and 2.0 Hz, 1H), 2.23–2.13 (m, 2H, CH₂), 1.40 (s, 3H, CH₃), 1.13 (t, J = 7.6 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =152.2 (s, Ar-C), 137.0 (s, Ar-C), 127.9 (d, Ar-CH), 122.2 (d, Ar-CH), 117.6 (d, Ar-CH), 107.3 (d, Ar-CH), 83.4 (s, C=C), 76.9 (s, C=C), 67.9 (t, CH₂), 43.5 (s, C), 35.8 (q, CH₃), 30.2 (t, CH₂), 23.9 (q, CH₃), 14.3 (q, CH₃), 12.4 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{15}H_{20}N]^{+}=[M+H]^{+}$: 214.1590; found 214.1589.

3-Hex-2-ynyl-1,3-dimethylindoline (6ad): GP was carried out with 2-iodo-*N*-methyl-*N*-(2-methylallyl)aniline **3a** (71.7 mg, 0.25 mmol), hex-2-ynoic acid **2d** (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 95:5) furnished the indoline **6ad** (47.6 mg, 85%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f (**3a**)=0.8, R_f (**6ad**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} =2956, 2866, 2807, 1605, 1487, 1455, 1376, 1250, 1155, 1109, 1020, 968, 742 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.11 (ddd, *J* = 7.7, 7.7 and 1.2 Hz, 1H, Ar–H), 7.07 (dd, *J* =

7.3 and 1.0 Hz, 1H, Ar–H), 6.69 (ddd, J = 7.7, 7.7 and 1.2 Hz, 1H, Ar–H), 6.48 (d, J = 7.8 Hz, 1H, Ar–H), 3.35 (d, J = 8.8 Hz, 1H, NCH_AH_B), 2.99 (d, J = 8.8 Hz, 1H, NCH_AH_B), 2.75 (s, 3H, CH₃), 2.41 (dq, J = 16.1 and 2.1 Hz, 1H), 2.40 (dq, J = 16.1 and 2.1 Hz, 1H), 2.21–2.12 (m, 2H, CH₂), 1.55 (sext, J = 7.3 Hz, 2H), 1.43 (s, 3H, CH₃), 1.00 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =152.2 (s, Ar–C), 136.9 (s, Ar–C), 127.9 (d, Ar–CH), 122.2 (d, Ar–CH), 117.7 (d, Ar–CH), 107.3 (d, Ar–CH), 81.8 (s, *C*=C), 77.7 (s, C=*C*), 67.8 (t, CH₂), 43.5 (s, C), 35.8 (q, CH₃), 30.2 (t, CH₂), 24.0 (q, CH₃), 22.5 (t, CH₂), 20.8 (t, CH₂), 13.5 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₆H₂₂N]⁺=[M+H]⁺: 228.1747; found 228.1736.

1-Ethyl-3-hex-2-ynyl-3-methylindoline (6bd): GP was carried out with 2-iodo-N-ethyl-2-iodo-N-(2-methylallyl)aniline 3b (75.2 mg, 0.25 mmol), hex-2-ynoic acid 2d (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the indoline 6bd (49.2 mg, 82%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), $R_f(3b)=0.8$, $R_f(6bd)=0.7$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2961, 2872, 2820, 1604, 1483, 1457, 1377, 1325, 1268, 1191, 1020, 740 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.10 (ddd, J = 7.6, 7.6 and 1.5 Hz, 1H, Ar–H), 7.07 (dd, J = 7.3 and 1.5 Hz, 1H, Ar–H), 6.67 (dd, J = 7.3 and 7.3 Hz, 1H, Ar–H), 6.48 (d, J = 7.6 Hz, 1H, Ar–H), 3.38 $(d, J = 8.8 Hz, 1H, NCH_AH_B), 3.26-3.06 (m, 2H), 3.04 (d, J = 8.8 Hz, 1H, NCH_AH_B), 2.43 (dq, J = 16.1)$ and 2.0 Hz, 1H), 2.40 (dq, J = 16.1 and 2.0 Hz, 1H), 2.22–2.13 (m, 2H, CH₂), 1.53 (sext, J = 7.3 Hz, 2H), 1.43 (s, 3H, CH₃), 1.18 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.3 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=151.0 (s, Ar–C), 136.9 (s, Ar–C), 127.8 (d, Ar–CH), 122.3 (d, Ar–CH), 117.2 (d, Ar–CH), 107.1 (d, Ar–CH), 81.8 (s, C=C), 77.7 (s, C=C), 64.1 (t, CH₂), 43.2 (s, C), 42.5 (t, CH₂), 30.4 (t, CH₂), 24.2 (q, CH₃), 22.5 (t, CH₂), 20.8 (t, CH₂), 13.5 (q, CH₃), 11.7 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{24}N]^{+}=[M+H]^{+}$: 242.1903; found 242.1886.

1-Benzyl-3-methyl-3-(3-phenylprop-2-ynyl)indoline (6ca): GP was carried out with *N*-benzyl-*N*-(2-iodophenyl)-N-(2-methylprop-2-enyl)amine **3c** (90.7 mg, 0.25 mmol), 3-phenylprop-2ynoic acid **2a** (54.7 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 93:7) furnished the indoline **6ca** (76.3 mg, 92%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f (**3c**)=0.7, R_f (**6ca**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2965, 2922, 2817, 1602, 1485, 1378, 1316, 1266, 1189, 1072, 1022, 914, 745, 694 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.43–7.24 (m, 10H, Ar–H), 7.20 (d, *J* = 7.3 Hz, 1H, Ar–H), 7.13 (dd, *J* = 7.3 and 7.3 Hz, 1H, Ar–H), 6.54 (d, *J* = 7.8 Hz, 1H, Ar–H), 4.40 (d, *J* = 15.2 Hz, 1H, *N*–CH_AH_B–Ar), 4.24 (d, *J* = 15.2 Hz, 1H, *N*–CH_AH_B–Ar), 3.45 (d, *J* = 8.8 Hz, 1H, NCH_AH_B), 3.13 (d, *J* = 8.8 Hz, 1H, NCH_AH_B), 2.71 (dd, *J* = 17.1 and 1.5 Hz, 2H, CH₂), 1.53 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =151.1 (s, Ar–C), 138.3 (s, Ar–C), 136.3 (s, Ar–C), 131.6 (d, 2 × Ar–CH), 128.5 (d, 2 × Ar–CH), 128.0 (d, Ar–CH), 127.7 (d, 2 × Ar–CH), 127.5 (d, Ar–CH), 127.1 (d, Ar–CH), 123.8 (s, Ar–C), 122.6 (d, Ar–CH), 117.7 (d, Ar–CH), 107.1 (d, Ar–CH), 87.7 (s, *C*=C), 82.2 (s, C=*C*), 65.6 (t, CH₂), 52.8 (t, CH₂), 43.6 (s, C), 31.0 (t, CH₂), 24.2 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₂₅H₂₄AN]⁺=[M+H]⁺: 338.1903; found 338.1910.

1-Benzyl-3-but-2-ynyl-3-methylindoline (**6cb**): **GP** was carried out with *N*-benzyl-*N*-(2-iodophenyl)-*N*-(2-methylprop-2-enyl)amine **3c** (90.7 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the indoline **6cb** (59.8 mg, 88%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R_f*(**3c**)=0.9, *R_f*(**6cb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2956, 2868, 2808, 1605, 1487, 1457, 1375, 1292, 1157, 1110, 1022, 970, 744 cm^{-1.} ¹H NMR (CDCl₃, 400 MHz): *δ*=7.40–7.23 (m, 5H, Ar–H), 7.13–7.02 (m, 2H, Ar–H), 6.69 (ddd, *J* = 7.3, 7.3 and 1.0 Hz, 1H, Ar–H), 6.48 (d, *J* = 7.3 Hz, 1H, Ar–H), 4.33 (d, *J* = 15.2 Hz, 1H, *N*–CH_AH_B–Ar), 4.22 (d, *J* = 15.2 Hz, 1H, *N*–CH_AH_B–Ar), 3.34 (d, *J* = 8.8 Hz, 1H, NCH_AH_B), 2.41 (dq, *J* = 16.4 and 2.4 Hz, 1H), 2.40 (dq, *J* = 16.4 and 2.4 Hz, 1H), 1.78 (t, *J* = 2.4 Hz, 3H, CH₃), 1.40 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=151.3 (s, Ar–C), 138.5 (s, Ar–C), 138.6 (s, Ar–C), 128.5 (d, 2 × Ar–CH), 127.9 (d, Ar–CH),

127.6 (d, 2 × Ar–CH), 127.0 (d, Ar–CH), 122.4 (d, Ar–CH), 117.5 (d, Ar–CH), 107.0 (d, Ar–CH), 77.1 (s, *C*=C), 76.5 (s, C=*C*), 65.5 (t, CH₂), 52.8 (t, CH₂), 43.4 (s, C), 30.4 (t, CH₂), 24.3 (q, CH₃), 3.5 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{22}N]^{+}=[M+H]^{+}$: 276.1747; found 276.1749.

1-Benzyl-3-methyl-3-pent-2-ynylindoline (6cc): GP was carried out with N-benzyl-N-(2iodophenyl)-N-(2-methylprop-2-enyl)amine 3c (90.7 mg, 0.25 mmol), pent-2-ynoic acid 2c (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the indoline 6cc (60.3 mg, 85%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), $R_f(3c)=0.9$, $R_f(6cc)=0.8$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2959, 2915, 2821, 1602, 1487, 1452, 1362, 1249, 1155, 1025, 945, 736, 698, cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.39–7.27 (m, 4H, Ar–H), 7.30– 7.23 (m, 1H, Ar–H), 7.11 (d, J = 7.3 Hz, 1H, Ar–H), 7.09 (d, J = 8.8 and 1.0 Hz, 1H, Ar–H), 6.70 (dd, J = 7.8 and 7.8 Hz, 1H, Ar–H), 6.48 (d, J = 7.8 Hz, 1H, Ar–H), 4.34 (d, J = 15.2 Hz, 1H, N–CH_AH_B– Ar), 4.22 (d, J = 15.2 Hz, 1H, N–CH_AH_B–Ar), 3.35 (d, J = 9.3 Hz, 1H, NCH_AH_B), 3.05 (d, J = 9.3 Hz, 1H, NCH_AH_B), 2.43 (dq, J = 16.1 and 2.2 Hz, 1H), 2.42 (dq, J = 16.4 and 2.4 Hz, 1H), 2.21–2.11 (m, 2H, CH₂), 1.42 (s, 3H, CH₃), 1.11 (t, J = 7.6 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =151.3 (s, Ar-C), 138.5 (s, Ar-C), 136.6 (s, Ar-C), 128.5 (d, 2 × Ar-CH), 127.9 (d, Ar-CH), 127.6 (d, 2 × Ar-CH), 127.0 (d, Ar-CH), 122.5 (d, Ar-CH), 117.5 (d, Ar-CH), 107.0 (d, Ar-CH), 83.4 (s, C=C), 76.8 (s, C=C), 65.5 (t, CH₂), 52.8 (t, CH₂), 43.4 (s, C), 30.4 (t, CH₂), 24.2 (q, CH₃), 14.3 (q, CH₃), 12.4 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{24}N]^+=[M+H]^+$: 290.1903; found 290.1882.

1-Benzyl-3-hex-2-ynyl-3-methylindoline (6cd): GP was carried out with *N*-benzyl-*N*-(2-iodophenyl)-*N*-(2-methylprop-2-enyl)amine **3c** (90.7 mg, 0.25 mmol), hex-2-ynoic acid **2d** (42 mg, 0.37 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the indoline **6cd** (66.6 mg, 89%) as a light yellow oily

compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f (**3**c)=0.9, R_f (**6**cd)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2959, 2920, 2825, 1604, 1488, 1454, 1362, 1237, 1155, 1028, 736, 700, 682 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.38–7.23 (m, 5H, Ar–H), 7.10 (dd, J = 7.8 and 1.0 Hz, 1H, Ar–H), 7.07 (ddd, J = 7.5, 7.5 and 1.3 Hz, 1H, Ar–H), 6.70 (ddd, J = 7.5, 7.5 and 1.0 Hz, 1H, Ar–H), 6.48 (d, J = 7.8 Hz, 1H, Ar–H), 4.33 (d, J = 15.2 Hz, 1H, N–CH_AH_B–Ar), 4.21 (d, J = 15.2 Hz, 1H, N–CH_AH_B–Ar), 3.35 (d, J = 8.8 Hz, 1H, NCH_AH_B), 3.04 (d, J = 8.8 Hz, 1H, NCH_AH_B), 2.43 (dq, J = 16.1 and 2.2 Hz, 1H), 2.42 (dq, J = 16.4 and 2.4 Hz, 1H), 2.17–2.08 (m, 2H, CH₂), 1.46 (sext, J = 7.3 Hz, 2H, CH₂), 1.42 (s, 3H, CH₃), 0.95 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =151.2 (s, Ar–C), 138.5 (s, Ar–C), 136.6 (s, Ar–C), 128.5 (d, 2 × Ar–CH), 127.9 (d, Ar–CH), 127.7 (d, 2 × Ar–CH), 127.0 (d, Ar–CH), 122.5 (d, Ar–CH), 117.6 (d, Ar–CH), 107.0 (d, Ar–CH), 81.9 (s, *C*=C), 77.6 (s, *C*=*C*), 65.6 (t, CH₂), 52.9 (t, CH₂), 43.5 (s, C), 30.5 (t, CH₂), 24.3 (q, CH₃), 22.5 (t, CH₂), 20.8 (t, CH₂), 13.5 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₂₂H₂₆N]⁺=[M+H]⁺: 304.2060; found 304.2063.

3-But-2-ynyl-1,3-dimethyl-1,3-dihydro-2*H***-indol-2-one (7ab): GP was carried out with** *N***-(2-iodophenyl)-***N***,2-dimethylacrylamide 4a** (75 mg, 0.25 mmol), but-2-ynoic acid **2b** (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 90:10) furnished the dihydrobenzofuran **7ab** (47.7 mg, 90%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), *R_f*(**4a**)=0.6, *R_f*(**7ab**)=0.5, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{mox}*=2966, 2924, 1710, 1612, 1462, 1371, 1251, 1186, 1103, 754, 699 cm^{-1.} ¹H NMR (CDCl₃, 400 MHz): *δ*=7.41 (dd, *J* = 7.3 and 1.0 Hz, 1H, Ar–H), 7.28 (ddd, *J* = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 7.07 (ddd, *J* = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 6.84 (d, *J* = 7.8 Hz, 1H, Ar–H), 3.20 (s, 3H), 2.63 (dq, *J* = 16.4 and 2.4 Hz, 1H), 2.40 (dq, *J* = 16.4 and 2.4 Hz, 1H), 1.73 (t, *J* = 2.4 Hz, 3H), 1.42 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=179.7 (s, N–CO), 142.9 (s, Ar–C), 133.5 (s, Ar–C), 128.0 (d, Ar–CH), 123.2 (d, Ar–CH), 122.4 (d, Ar–CH), 107.8 (d, Ar–CH), 78.0 (s, *C*=C), 74.3 (s, *C*=*C*), 47.0 (s, *C*), 28.1 (t, CH₂), 26.2 (q, CH₃), 21.6 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for [C₁₄H₁₆NO]⁺=[M+H]⁺: 214.1226; found 214.1227.

1,3-Dimethyl-3-pent-2-ynyl-1,3-dihydro-2H-indol-2-one (7ac): GP was carried out with N-(2iodophenyl)-N,2-dimethylacrylamide 4a (75 mg, 0.25 mmol), pent-2-ynoic acid 2c (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 91:9) furnished the dihydrobenzofuran 7ac (49.2 mg, 88%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(4a)=0.8, R_f(7ac)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2962, 2926, 2871, 1708, 1609, 1455, 1355, 1174, 1001, 742, 698, 636 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.41 (dd, J = 7.3 and 1.0 Hz, 1H, Ar–H), 7.28 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar-H), 7.07 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar-H), 6.84 (d, J = 7.8 Hz, 1H, Ar–H), 3.20 (s, 3H), 2.63 (dt, J = 16.1 and 2.4 Hz, 1H), 2.43 (dt, J = 16.1 and 2.4 Hz, 1H), 2.13-2.03 (m, 2H), 1.44 (s, 3H, CH₃), 1.02 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=179.8 (s, N-CO), 143.1 (s, Ar-C), 133.5 (s, Ar-C), 127.9 (d, Ar-CH), 123.2 (d, Ar-CH), 122.4 (d, Ar-CH), 107.8 (d, Ar-CH), 84.1 (s, C=C), 74.7 (s, C=C), 47.1 (s, C), 28.3 (t, CH₂), 26.2 (q, CH₃), 21.6 (q, CH₃), 14.1 (q, CH₃), 12.3 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for $[C_{15}H_{18}NO]^{+}=[M+H]^{+}: 228.1383;$ found 228.1389.

3-Hex-2-ynyl-1,3-dimethyl-1,3-dihydro-2*H***-indol-2-one (7ad): GP** was carried out with *N*-(2-iodophenyl)-*N*,2-dimethylacrylamide **4a** (75 mg, 0.25 mmol), hex-2-ynoic acid **2d** (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 89:11) furnished the dihydrobenzofuran **7ad** (51.6 mg, 86%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), *R_f*(**4a**)=0.7, *R_f*(**7ad**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2962, 2927, 2871, 1709, 1610, 1456, 1355, 1174, 1080, 1001, 927, 739, 697, 635 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): *δ*=7.39 (dd, *J* = 7.3 and 1.0 Hz, 1H, Ar–H), 7.28 (ddd, *J* = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 7.07 (ddd, *J* = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 6.84 (d, *J* = 7.8 Hz, 1H, Ar–H), 3.21 (s, 3H), 2.65 (dt, *J* = 16.1 and 2.5 Hz, 1H), 2.46 (dt, *J* = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): *δ*=179.7 (s, N–CO), 143.1 (s, Ar–C), 133.5 (s,

Ar–C), 127.9 (d, Ar–CH), 123.1 (d, Ar–CH), 122.4 (d, Ar–CH), 107.8 (d, Ar–CH), 82.5 (s, $C\equiv$ C), 75.4 (s, C \equiv C), 47.2 (s, C), 28.2 (t, CH₂), 26.2 (q, CH₃), 22.2 (t, CH₂), 21.7 (q, CH₃), 20.6 (t, CH₂), 13.3 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{16}H_{20}NO]^+=[M+H]^+$: 242.1539; found 242.1539.

1-Benzyl-3-but-2-ynyl-3-methyl-1,3-dihydro-2H-indol-2-one (7bb): GP was carried out with N-benzyl-N-(2-iodophenyl)-2-methylacrylamide 4b (94 mg, 0.25 mmol), but-2-ynoic acid 2b (32 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 86:14) furnished the dihydrobenzofuran 7bb (63.3 mg, 88%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**4b**)=0.8, R_f(**7bb**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2921, 2853, 1709, 1606, 1501, 1455, 1357, 1290, 1245, 1173, 1103, 1029, 831, 743, 698, 642 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.36 (dd, J = 7.3 and 1.0 Hz, 1H, Ar-H), 7.34-7.20 (m, 5H, Ar-H), 7.15 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar-H), 7.03 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar-H), 6.70 (d, J = 7.8 Hz, 1H, Ar-H), 5.08 (d, J = 15.6 Hz, 1H, N– CH_AH_B –Ar), 4.76 (d, J = 15.6 Hz, 1H, N– CH_AH_B –Ar), 2.69 (dq, J = 16.1 and 2.4 Hz, 1H), 2.57 (dq, J = 16.1 and 2.4 Hz, 1H), 1.66 (t, J = 2.4 Hz, 3H), 1.46 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100)MHz): δ=179.8 (s, N–CO), 142.2 (s, Ar–C), 135.9 (s, Ar–C), 133.4 (s, Ar–C), 128.7 (d, 2 × Ar–CH), 127.8 (d, Ar-CH), 127.4 (d, Ar-CH), 127.2 (d, 2 × Ar-CH), 123.0 (d, Ar-CH), 122.4 (d, Ar-CH), 108.9 (d, Ar–CH), 77.9 (s, C=C), 74.4 (s, C=C), 47.3 (s, C), 43.6 (t, CH₂), 28.2 (t, CH₂), 22.4 (q, CH₃), 3.4 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{20}NO]^{+}=[M+H]^{+}$: 290.1539; found 290.1550.

1-Benzyl-3-methyl-3-pent-2-ynyl-1,3-dihydro-2H-indol-2-one (7bc): GP was carried out with *N*-benzyl-*N*-(2-iodophenyl)-2-methylacrylamide **4b** (94 mg, 0.25 mmol), pent-2-ynoic acid **2c** (37 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 92:8) furnished the dihydrobenzofuran **7bc** (66.7 mg, 89%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f (**4b**)=0.9, R_f (**7bc**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): v_{max} =2968, 2923, 1707, 1608, 1466, 1359, 1174, 1106, 1022, 923, 747, 695 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.38 (dd, *J* = 7.3 and 1.0 Hz, 1H, Ar–H), 7.35–7.20 (m, 5H, Ar–H), 7.15 (ddd, *J* = 7.3, 7.3 and 1.5 Hz, 1H, Ar–H), 7.03 (ddd, *J* = 7.3, 7.3 and 1.5 Hz, 1H, Ar–H), 6.71 (d, *J* = 7.8 Hz, 1H, Ar–H), 5.02 (d, *J* = 15.6 Hz, 1H, N–CH_AH_B–Ar), 4.80 (d, *J* = 15.6 Hz, 1H, N–CH_AH_B–Ar), 2.70 (dt, *J* = 16.6 and 2.4 Hz, 1H), 2.57 (dt, *J* = 16.6 and 2.4 Hz, 1H), 2.07-2.01 (m, 2H), 1.47 (s, 3H, CH₃), 0.95 (t, *J* = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =179.9 (s, N–CO), 142.2 (s, Ar–C), 136.0 (s, Ar–C), 133.5 (s, Ar–C), 128.7 (d, 2 × Ar–CH), 127.8 (d, Ar–CH), 127.5 (d, Ar–CH), 127.2 (d, 2 × Ar–CH), 123.2 (d, Ar–CH), 122.4 (d, Ar–CH), 108.9 (d, Ar–CH), 84.1 (s, *C*=C), 74.7 (s, C=*C*), 47.3 (s, C), 43.6 (t, CH₂), 28.2 (t, CH₂), 22.2 (q, CH₃), 13.9 (q, CH₃), 12.3 (t, CH₂) ppm. HR-MS (ESI+) m/z calculated for [C₂₁H₂₂NO]⁺=[M+H]⁺: 304.1696; found 304.1675.

1-Benzyl-3-hex-2-ynyl-3-methyl-1,3-dihydro-2H-indol-2-one (7bd): GP was carried out with N-benzyl-N-(2-iodophenyl)-2-methylacrylamide 4b (94 mg, 0.25 mmol), hex-2-ynoic acid 2d (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 90:10) furnished the dihydrobenzofuran 7bd (63.2 mg, 80%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**4b**)=0.8, R_f(**7bd**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v_{max}*=2970, 2924, 1710, 1609, 1485, 1446, 1355, 1267, 1176, 999, 872, 786, 747, 694 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.37 (dd, J = 7.3 and 1.0 Hz, 1H, Ar–H), 7.34–7.20 (m, 5H, Ar–H), 7.14 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 7.02 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 6.71 (d, J = 7.8 Hz, 1H, Ar–H), 5.00 (d, J = 15.6 Hz, 1H, N–CH_AH_B– Ar), 4.82 (d, J = 15.6 Hz, 1H, N–CH_AH_B–Ar), 2.72 (dt, J = 16.1 and 2.4 Hz, 1H), 2.58 (dt, J = 16.1and 2.4 Hz, 1H), 2.05-1.97 (m, 2H), 1.47 (s, 3H, CH₃), 1.32 (sext, J = 7.3 Hz, 2H), 0.79 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=179.8 (s, N–CO), 142.2 (s, Ar–C), 136.0 (s, Ar– C), 133.5 (s, Ar–C), 128.7 (d, 2 × Ar–CH), 127.8 (d, Ar–CH), 127.5 (d, Ar–CH), 127.2 (d, 2 × Ar– CH), 123.2 (d, Ar–CH), 122.4 (d, Ar–CH), 108.9 (d, Ar–CH), 82.6 (s, C=C), 75.4 (s, C=C), 47.3 (s, C), 43.7 (t, CH₂), 28.2 (t, CH₂), 22.3 (q, CH₃), 22.1 (t, CH₂), 20.6 (t, CH₂), 13.3 (q, CH₃) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{24}NO]^{+}=[M+H]^{+}$: 318.1852; found 318.1832.

3-Hex-2-ynyl-1,3,5,7-tetramethyl-1,3-dihydro-2H-indol-2-one (7cd): GP was carried out with N-(2-iodo-4,6-dimethylphenyl)-N,2-dimethylacrylamide 4c (82.2 mg, 0.25 mmol), hex-2-ynoic acid 2d (42 mg, 0.37 mmol), Pd₂(dba)₃ (2.28 mg, 1 mol%), TBAB (80.5 mg, 0.25 mmol), K₂CO₃ (103.9 mg, 0.75 mmol) water (0.5 mL), under microwave irradiation (100 °C, 10 min, 300 W, closed vessel). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 90:10) furnished the dihydrobenzofuran 7cd (59.6 mg, 89%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), $R_{f}(4c)=0.8$, $R_{f}(7cd)=0.7$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $v_{max}=2921$, 2856, 1720, 1657, 1610, 1444, 1336, 1265, 1184, 1093, 1029, 984, 805, 759, 695 cm⁻¹, ¹H NMR (CDCl₃, 400 MHz): δ =7.04 (s, 1H, Ar–H), 6.80 (s, 1H, Ar–H), 3.45 (s, 3H), 2.58 (dt, J = 16.1 and 2.4 Hz, 1H), 2.42 (dt, J = 16.1 and 2.4 Hz, 1H), 2.52 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 2.10-2.02 (m, 2H), 1.40 (sext, J = 7.3 Hz, 2H), 1.37 (s, 3H, CH₃), 0.86 (t, J = 7.3 Hz, 3H, CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=180.4 (s, N-CO), 138.3 (s, Ar-C), 134.2 (s, Ar-C), 132.0 (d, Ar-CH), 131.6 (s, Ar-C), 121.8 (d, Ar-CH), 119.0 (s, Ar-C), 82.4 (s, C=C), 75.6 (s, C=C), 46.5 (s, C), 29.5 (q, CH₃), 28.6 (t, CH₂), 22.2 (t, CH₂), 22.1 (q, CH₃), 20.8 (q, CH₃), 20.6 (t, CH₂), 18.8 (q, CH₃), 13.2 (q, CH₃). HR-MS (ESI+) m/z calculated for $[C_{18}H_{24}NO]^{+}=[M+H]^{+}$: 270.1852; found 270.1859.

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