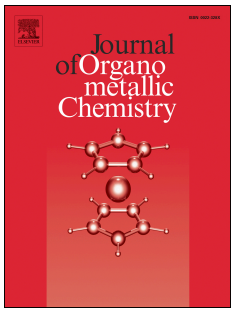

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Propargyl Alcohols as Alkyne Sources: Synthesis of Heterocyclic Compounds under Microwave Irradiation

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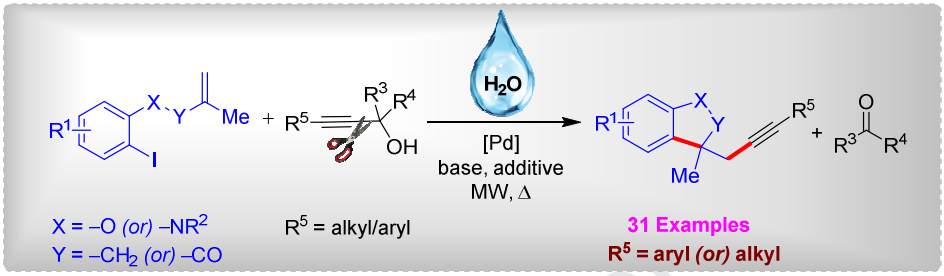


Abstract: Fused heterocyclic compounds with alkyne substituent, have been achieved using a domino microwave-assisted [Pd]-catalysis. Interestingly, *tert*-propargyl alcohols underwent a selective degradative β-carbon cleavage and served as masked alkynyl equivalents, in water as the sole reaction medium. Dihydrobenzofurans, indolines, and oxindoles have been accomplished using this dual C–C bond-forming strategy.

Keywords: [Pd]-Catalysis; *tert*-Propargyl alcohols; Aqueous medium; Microwaves; Heterocycles.

Introduction

By nature, alcohols could be able to form associated complexes with transition metals through their coordinating ability. Further, these complexes may break down into an alkyl-metal species and an elimination product(s) *via* β-elimination.[1] The alkyl-metal species could, in turn, either undergo usual β-hydrogen elimination to give olefin products or subsequent couplings to deliver interesting organic products.[2] Though in the recent past, some interesting examples have appeared in the literature on the cleavage of C–C bond, mediated by transition-metal catalysts,[3] still the concept has been pursued in a limited fashion. Miura et al. disclosed a palladium-catalyzed biaryls synthesis by selective cleaving of Csp^3–Csp^2 bond of dialkylarylmethanols with aryl halides.[4] Later, the research group of Sakae Uemura presented alkynylation of alkenes *via* C–C bond scission of *tert*-propargyl alcohols under oxidative conditions with [Pd]-catalyst.[5]

Of late, Sayuri Hayashi et al. demonstrated the retro-propargylation of *tert*-homopropargyl alcohols providing allenes facilitated by palladium.[6]

Recently, we were succeeded in the synthesis of benzochromenes *via* a domino homocoupling α,α-dialkyl-(2-bromoaryl)methanols, and β-carbon cleavage, under palladium catalysis.[7] Also, demonstrated [Pd]-catalyzed Heck and Sonagashira couplings towards bicyclic systems, under microwave assisting conditions. Further, the concept was extended to Heck and decarboxylative Sonogashira reaction. That affords heterocyclic products possessing short alkyl groups *via* Heck and decarboxylative Sonogashira reaction.[8] Propiolic acids have been utilized as the alkynyl source, for this purpose. In continuation of our research interest on palladium catalysis,[9] in this manuscript, we describe a strategy for the preparation of dihydrobenzofurans, indolines, and oxindoles. The process was smooth under microwave-accelerated conditions and by using utilizing water as the sole green reaction medium in the presence of palladium-catalyst. Notably, *tert*-propargyl alcohols have undergone a selective β-carbon cleavage and served as masked alkynyl equivalents.

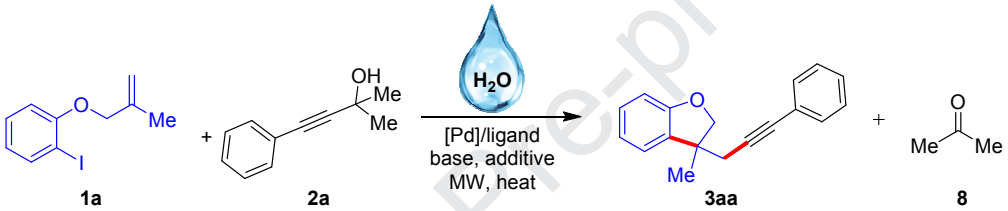
Result and Discussions

It was anticipated that after intramolecular Heck step of allyl *ortho*-iodoaryl ethers, *tert*-propargyl alcohols could act as masked alkynyl sources. That can be accomplished by β-carbon cleavage of *tert*-alcohol function facilitated by palladium catalyst, affording the dihydrobenzofurans linked to an alkynyl moiety.

To begin the optimization study, 2-iodoaryl allyl ether **1a** and propargyl alcohol **2a** were identified as the starting materials. Based on our earlier studies, initially, **1a** and **2a** were irradiated using microwaves with a catalytic amount 1 mol% of $Pd_2(dba)_3$ and K_2CO_3 (4 equiv) in solvent DMF (0.5 mL) at 100 °C (entry 1, Table 1).[10] To our delight, the desired bicyclic ether **3aa** was isolated in 80% yield. As our interest is to use water as the sole solvent, the reactions have been performed with 0.5 mL of water under the same conditions; however, **3aa** was formed in poor yields (entries 2 to 4, Table 1). A significant jump in the yield of **3aa** was noticed by using quaternary ammonium salt TBAI (tetrabutylammonium iodide) as an additive (entry 5, Table 1). Slight improvement in the yield of the product **3aa** (78%) was observed when benzyl

triethylammonium chloride (BTEAC) was used as the additive and in the presence of base K_2CO_3 (entry 6, Table 1). While the reaction with an organic base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), turned out to be very much inferior (entry 7, Table 1). While tetrabutylammonium bromide (TBAB) proved to better, since the product **3aa** was afforded in 80% yield (entry 8, Table 1). However, when the $Pd_2(dba)_3$ loading was increased to 5 mol%, it gave 90% yield of the desired product **3aa** (entry 9, Table 1). Furthermore, the reaction with the additive TBAB and the base K_2CO_3 with the reduced irradiation time 5 and 10 min, delivered **3aa** in 30 and 40% yields, respectively (entries 10 to 11, Table 1).

Table 1. Optimizations for **3aa**.[a-c]



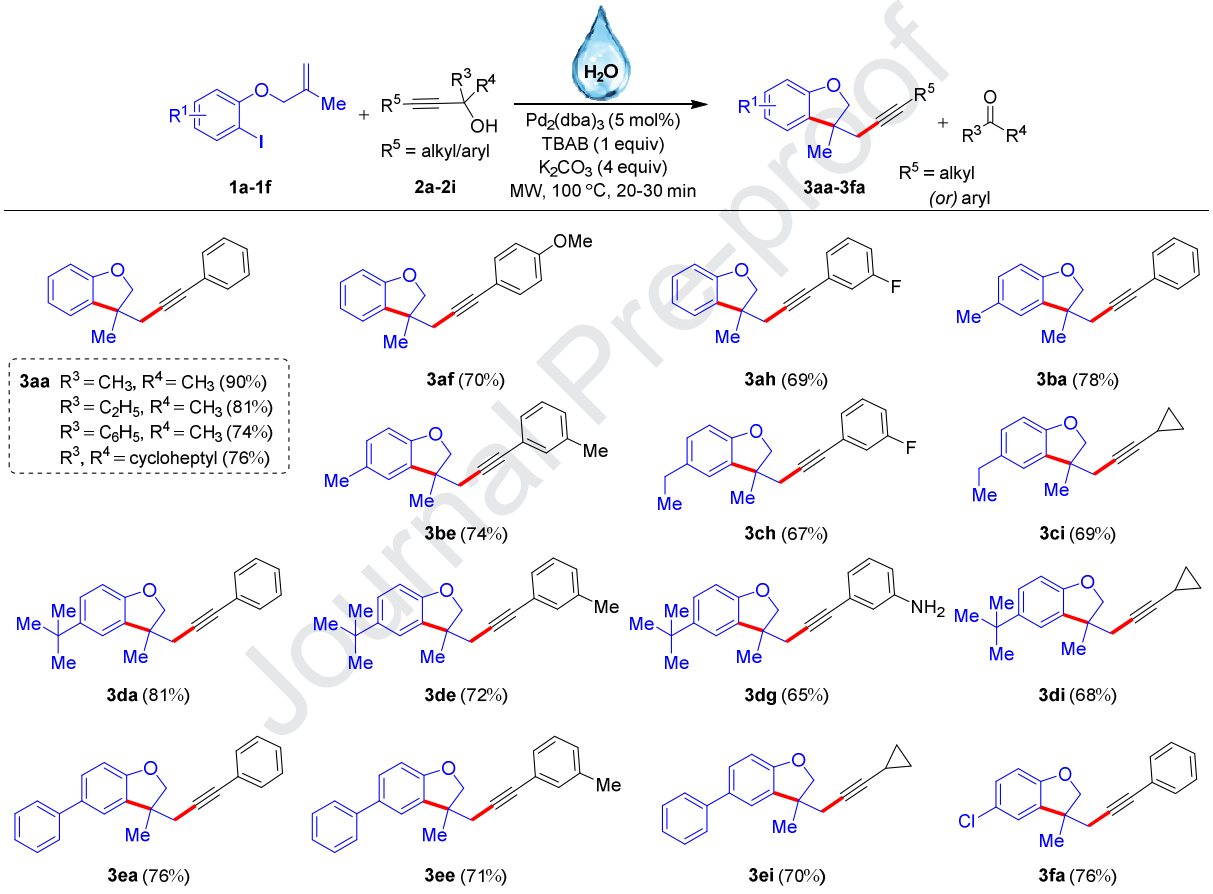
entry	additive (1 equiv)	base (4 equiv)	solvent	time (min)	yield **3aa**[b] (%)
1	-	K_2CO_3	DMF	20	(80%)
2	-	K_2CO_3	H_2O	20	(15%)
3	-	K_2CO_3	H_2O	25	(20%)
4	-	K_2CO_3	H_2O	30	(25%)
5	TBAI	K_2CO_3	H_2O	20	(75%)
6	BTEAC	K_2CO_3	H_2O	20	(78%)
7	BTEAC	DBU	H_2O	20	(40%)
8	TBAB	K_2CO_3	H_2O	20	(80%)
9[c]	**TBAB**	**K_2CO_3**	**H_2O**	**20**	**(90%)**
10[c]	TBAB	K_2CO_3	H_2O	5	(30%)
11[c]	TBAB	K_2CO_3	H_2O	10	(40%)

[a]Conditions: all reactions were performed under microwave irradiation (300 W, closed vessel, 100 °C, 5 to 30 minutes) using **1a** (0.25 mmol), **2a** (0.50 mmol), additive (1 equiv), base (4 equiv), 1 mol% of $Pd_2(dba)_3$ and DMF (or) water (0.5 mL) as solvents. [b]Isolated yield of the product **3aa**. [c]$Pd_2(dba)_3$ (5 mol%).

From the above best-optimized conditions (entry 9, Table 1) to give dihydrobenzofuran **3aa** and hence, decided to explore these conditions with other substrates. Consequently, various allyl *ortho*-iodophenyl ethers **1a-1f**, and *tert*-propargyl alcohols **2a-2i** were reacted using established standard conditions. Significantly, the protocol seemed to be quite smooth and afforded dihydrobenzofruans **3aa-3fa** bearing alkyne moiety, in fair to good yields (Table 2).

Alkyl, as well as phenyl substituted allyl *ortho*-iodophenyl ethers, underwent smoothly to deliver the desired products **3**. Notably, the strategy was also compatible with aliphatic, aryl and cyclic *tert*-propargyl alcohols. Moreover, the strategy was also successful with a free amine functional group connected to the aromatic moiety of propargyl alcohol **2g** (**3dg**, Table 2).

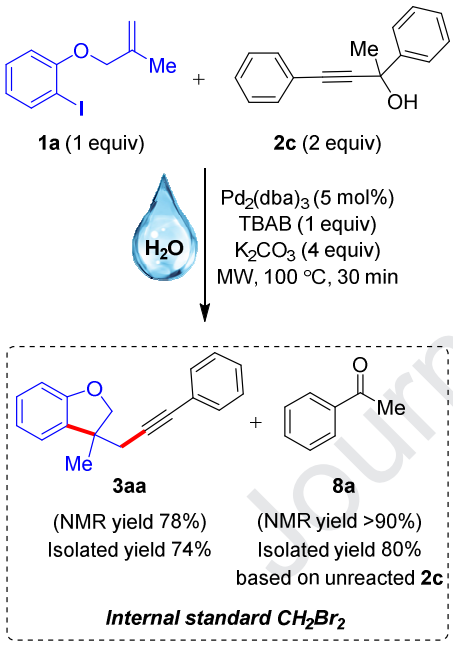
Table 2: Substrate scope of the products **3aa-3fa**.[a-c]



[a]Reaction conditions: **1a-1f** (0.25 mmol), **2a-2i** (0.50 mmol), $Pd_2(dba)_3$ (5 mol%), TBAB (1 equiv), K_2CO_3 (4 equiv), H_2O (0.5 mL), 20-30 minutes, 100 °C (closed vessel, 300 W). [b]Isolated yields. [c]The first alphabet of bicyclic ethers **3aa-3fa** indicating 2-iodophenyl allyl ethers, while, second letter is representing propargyl alcohols **2a-2i**.

In addition, to prove that the reaction pathway is proceeding through degradative cleavage of propargyl alcohols and generating ketones as a by-product, it was planned to study the NMR of crude reaction products. Thus, after completion of the reaction, with the help of a short plug of silica filtered the resultant crude mixture, (i.e., products **3aa** and **8a** formed from

the reaction of **1a** and **2c**); bulk solvent was removed under reduced pressure using a rotary evaporator; followed by high vacuum pump. Then submitted the crude reaction mixture to ^{1}H-NMR analysis in $CDCl_3$ using CH_2Br_2 as the internal standard. From NMR study revealed the formation of acetophenone by-product **8a** in 85% of NMR yield (isolated yield 80%), in which the methyl group protons are significant and appeared at δ 2.59 of its ^{1}H-NMR spectrum. Also, the desired product **3aa** was obtained in 78% of NMR yield (isolated yield is 74%, Scheme 1) [See supporting information for crude spectrum]. Thus, it is confirmed that ketones are generated as by-products from propargyl alcohols, and this could be feasible *via* degradative β-cleavage of a C–C bond.[11]

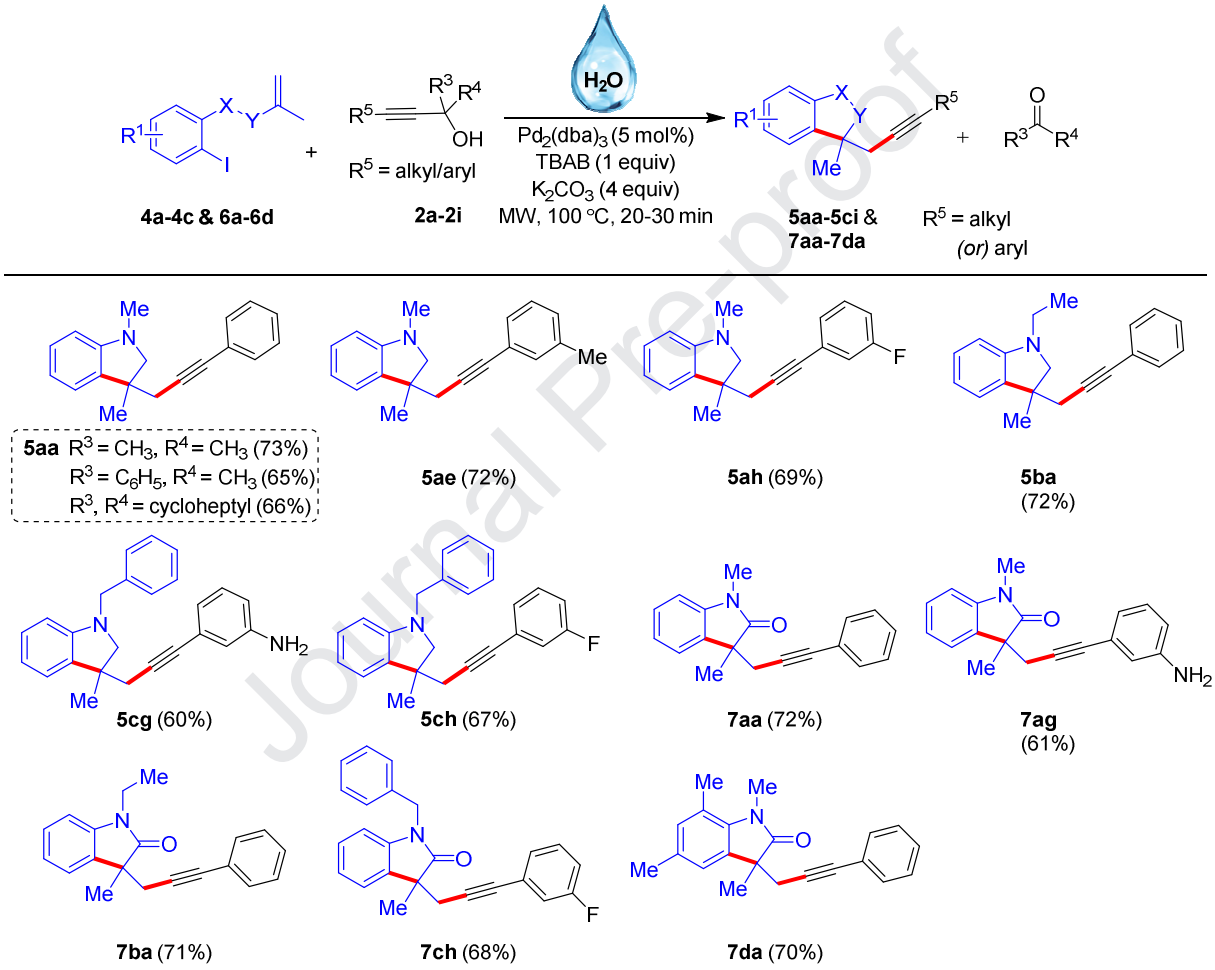


Scheme 1: NMR analysis for crude products of **3aa** and **8a**.

Furthermore, it was intended to demonstrate the scope and diversity of the methodology. Therefore, *ortho*-iodoarylmethallylamines **4a-4c** and *tert*-propargyl alcohols **2a-2i** were reacted, under standard microwave-accelerated conditions. As predicted, indolines **5aa-5ci** were obtained in fair to good yields with broad functional group tolerance (Table 3). In addition, to reveal the importance and applicability of this strategy, *ortho*-iodophenyl enamides **6a-6d** were also irradiated under microwaves with *tert*-propargyl alcohols **2a-2i**, using established reaction parameters. As anticipated, the target oxindoles **7aa-7da** have also been obtained and thus,

reflects the synthetic utility of this methodology (Table 3). It is worth mentioning that the reaction of *N*-Ts protected allyl *ortho*-iodophenyl amine was treated with propargyl alcohol using the standard reaction conditions; however, the reaction was not amenable to deliver the desired indoline product, instead ended up in forming the simple deprotected *ortho*-iodophenyl amine without any cyclization.

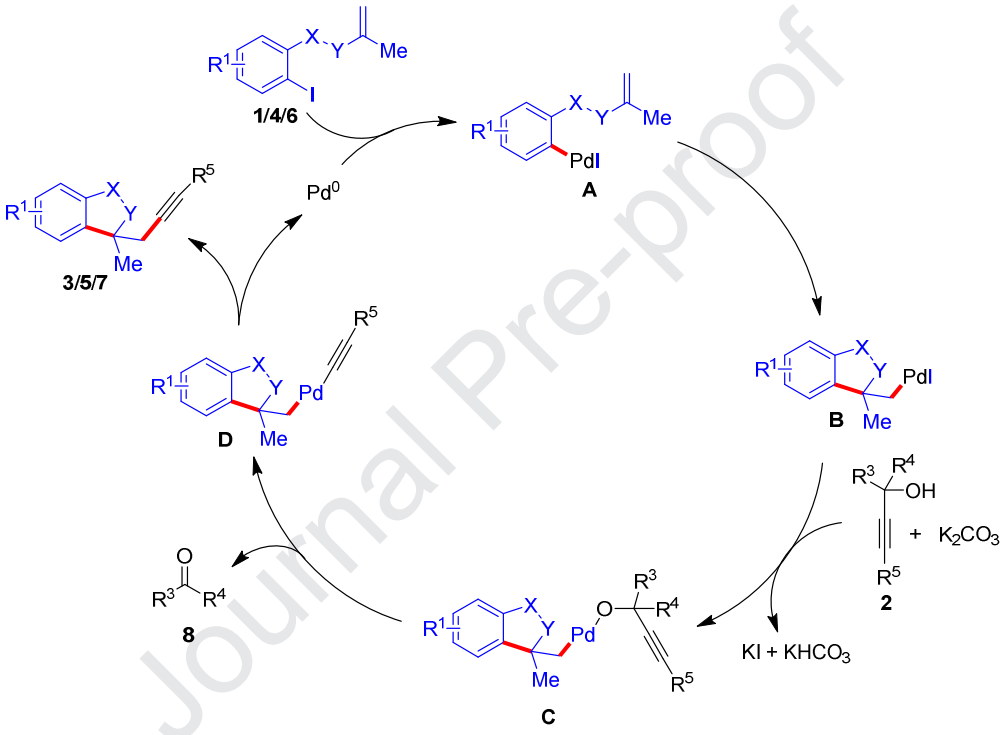
Table 3: Synthesis of indolines & oxindoles **(5aa-5ci** & **7aa-7da)**.[a-c]



[a]Reaction conditions: **4a-4c** (0.25 mmol)/**6a-6c** (0.25 mmol), **2a-2i** (0.50 mmol), $Pd_2(dba)_3$ (5 mol%), TBAB (1 equiv), K_2CO_3 (4 equiv), H_2O (0.5 mL), 20-30 minutes, 100 °C (closed vessel, 300 W). [b]Isolated yields. [c]The first alphabet of products **5aa-5ci** & **7aa-7da** indicating 2-iodo-*N*-alkyl/aryl-*N*-(2-methylallyl)anilines/*N*-(2-iodophenyl)-*N*-alkylmethacrylamide while, second letter is for propargyl alcohols **2a-2i**.

A plausible mechanism for the formation of **3/5/7** is outlined in Scheme 2. Initially, active Pd(0) catalyst inserts onto across the C(sp^2)-I bond of starting material **1/4/6** *via* oxidative insertion and leads to organopalladium(II) intermediate **A**. Consequently, intramolecular Heck

cyclization of the intermediate **A** affords the bicyclic alkyl-Pd(II) species **B**. Combination of propargyl alcohol **2** with the bicyclic Pd(II) intermediate **B** affords **C** through the removal of KI and $KHCO_3$. Subsequently, degradative C–C bond β-cleavage of ethereal species **C** furnishes a new Pd(II) intermediate **D** *via* the expulsion of ketone by-product **8**. Finally, the reductive elimination of the palladium catalyst from **D** through concomitant C–C bond formation produces the desired heterocyclic product **3/5/7** along with the regeneration of the Pd(0) catalyst.



Scheme 2: Plausible reaction mechanism for the formation of heterocycles **3**/**5**/**7**.

Conclusions

In conclusion, we have established a domino palladium-catalyzed procedure for constructing a quaternary carbon-containing fused heterocyclic compounds with alkynyl functionality. Significantly, *tert*-propargyl alcohols were employed as masked alkyne sources and proceeds *via* the cleavage of the β-carbon atom of the alcoholic group. Also, the reaction was successful by means of water as the sole green reaction medium under microwave-accelerated conditions.

Experimental

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (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 $CDCl_3$ (δ_H = 7.25 ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ_C = 77.00 ppm (central line of the triplet)]. In the $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) 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 CH_2) and q = quartet (for CH_3). In the ^{1}H-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 ^{1}H, $^{13}C\{^{1}H\}$ 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. Solvent(s) were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. $Pd_2(dba)_3$, and K_2CO_3 were purchased from Sigma-Aldrich and used as received. *ortho*-Iodophenols, *ortho*-iodoanilines, TBAB (tetrabutylammonium bromide), 3-chloro-2-methylprop-1-ene, and terminal acetylenes 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.[7-9]

GP (General Procedure for the Synthesis of 3,3'-Disubstituted Heterocyclic Compounds 3/5/7): 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 **4** (or) *ortho*-iodophenyl enamides **6** (68-88 mg, 0.25 mmol), propargylic alcohols **2** (60-106.5 mg, 0.5 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), K_2CO_3 (138.6 mg, 1 mmol) TBAB (80.5 mg, 0.25 mmol), followed by solvent water (0.5mL), at room temperature. The resultant reaction mixture was then subjected to microwave irradiation at 100 °C for 20-30 min (300 W, closed vessel). The progress of the reaction was monitored by TLC until the reaction is completed. The mixture was cooled to room temperature, quenched with aqueous $NaHCO_3$ solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with a saturated NaCl solution, dried (Na_2SO_4), 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 **3/5/7** (60–90%) as oil/semi-solid.

3-[3-(3-Fluorophenyl)prop-2-ynyl]-3-methyl-2,3-dihydro-1-benzofuran (3ah): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.5 mg, 0.25 mmol), 4-(3-fluorophenyl)-2-methylbut-3-yn-2-ol **2h** (87.5mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the product **3ah** (45.8 mg, 69%) as a colourless oily compound, [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**)=0.8, R_f(**3ah**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2933, 2891, 1586, 1471, 1297, 1252, 971, 872, 774, 727, 686 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.30–7.21 (m, 2H), 7.20–7.13 (m, 2H), 7.10–7.04 (m, 1H), 7.03–6.96 (m, 1H), 6.91 (ddd, J = 7.4, 7.4 and 1.0 Hz, 1H), 6.83 (dd, J = 7.4 and 1.0 Hz, 1H), 4.54 (d, J = 8.8 Hz, 1H), 4.24 (d, J = 8.8 Hz, 1H), 2.68 (s, 2H), 1.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=162.3 (d, J = 246.1 Hz), 161.1, 159.4, 133.8, 129.8 (d, J = 8.7 Hz), 128.6, 127.5 (d, J = 3.1 Hz), 122.9, 120.6, 118.4 (d, J = 22.6 Hz), 115.2 (d, J = 21.2 Hz) 109.8, 87.8, 82.2, 81.3, 45.3, 31.5, 24.2 ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{16}FO]^+$=$[M+H]^+$: 267.1180; found 267.1157.

5-Ethyl-3-[3-(3-fluorophenyl)prop-2-ynyl]-3-methyl-2,3-dihydro-1-benzofuran (3ch): GP was carried out with 4-ethyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1c** (75.5 mg, 0.25 mmol), 4-(3-fluorophenyl)-2-methylbut-3-yn-2-ol **2h** (87.5 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the product **3ch** (49.2 mg, 67%) as a pale yellow oily compound, [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1c**)=0.8, R_f(**3ch**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2933, 1592, 1563, 1468, 1256, 1213, 1144, 971, 865, 811, 773 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.25 (td, J = 7.8 and 3.9 Hz, 1H), 7.17 (d, J = 7.7 Hz, 1H), 7.07 (dd, J = 11.8 and 5.4 Hz, 2H), 7.00 (ddd, J = 5.8, 3.7 and 2.2 Hz, 2H), 6.75 (d, J = 8.1 Hz, 1H), 4.53 (d, J = 8.8 Hz, 1H), 4.23 (d, J = 8.8 Hz, 1H), 2.68 (s, 2H), 2.62 (q, J = 7.6 Hz, 2H), 1.54 (s, 3H), 1.23 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=163.6, 161.1, 157.5, 136.6, 133.8, 129.8, 129.7, 127.9, 127.4, 127.4, 125.4, 125.3, 122.2, 118.5, 118.3, 115.3, 115.1, 109.4, 88.0, 82.4, 81.3, 45.3, 31.5, 28.4, 24.0, 16.0 ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{20}FO]^+$=$[M+H]^+$: 295.1493; found 295.1496.

3-(3-Cyclopropylprop-2-ynyl)-5-ethyl-3-methyl-2,3-dihydro-1-benzofuran (3ci): GP was carried out with 4-ethyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1c** (75.5 mg, 0.25 mmol), 4-cyclopropyl-2-phenylbut-3-yn-2-ol **2i** (93 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the product **3ci** (43.5 mg, 69%) as a colorless compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**1c**)=0.8, R_f(**3ci**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2933, 2891, 1586, 1471, 1297, 1252, 970, 871, 774, 727, 686 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=6.97 (s, 1H, Ar–H), 6.95 (dd, J = 7.8 and 1.0 Hz, 1H, Ar–H), 6.69 (dd, J = 7.8 and 1.0 Hz, 1H, Ar–H), 4.42 (d, J = 8.8 Hz, 1H, OCH_AH_B), 4.13 (d, J = 8.8 Hz, 1H, OCH_AH_B), 2.58 (q, J = 7.8 Hz, 2H), 2.37 (s, 2H), 1.42 (s, 3H, CH_3), 1.21 (t, J = 7.6 Hz, 3H), 1.25–1.15 (m, 1H), 0.76–0.67 (m, 2H), 0.66–0.55 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.4, 136.3, 134.2, 127.6, 122.2, 109.2, 85.3, 82.4, 72.0, 45.2, 30.9, 28.4, 24.0, 16.0, 8.0, -0.50 ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{21}O]^+$=$[M+H]^+$: 241.1587; found 241.1588.

5-*tert*-butyl-3-methyl-3-[3-(3-methylphenyl)prop-2-ynyl]-2,3-dihydro-1-benzofuran (3de): GP was carried out with 4-*tert*-butyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1d** (82.5 mg, 0.25 mmol), 2-methyl-4-(3-methylphenyl)but-3-yn-2-ol **2e** (87 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:01) furnished the product **3de** (69.9 mg, 72%) as a colorless oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**1d**)=0.8, R_f(**3de**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2928, 1588, 1471, 1352, 1247, 972, 875, 810, 774, 685 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.27 (d, J = 2.0 Hz, 1H, Ar–H), 7.24–7.14 (m, 4H, Ar–H), 7.10 (dd, J = 8.3 and 1.0 Hz, 1H, Ar–H), 6.74 (d, J = 8.3 Hz, 1H, Ar–H), 4.51 (d, J = 8.8 Hz, 1H, OCH_AH$_B$), 4.22 (d, J = 8.8 Hz, 1H, OCH$_A$$H_B$), 2.67 (s, 2H, CH_2), 2.32 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.30 (s, 9H, 3 × CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=157.2, 143.6, 137.9, 133.6, 132.2, 128.7, 128.6, 128.1, 125.3, 123.3, 119.8, 108.9, 86.5, 82.6, 82.5, 45.4, 34.4, 31.7, 31.5, 23.9, 21.1 ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{27}O]^+$=$[M+H]^+$: 319.2056; found 319.2056.

3-[3-(5-*tert*-Butyl-3-methyl-2,3-dihydro-1-benzofuran-3-yl)prop-1-ynyl]aniline (3dg): GP was carried out with 4-*tert*-butyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1d** (82.5 mg, 0.25 mmol), 4-(3-aminophenyl)-2-methylbut-3-yn-2-ol **2g** (87.5 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the product **3dg** (51.9 mg, 65%) as a semi solid, [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1d**)=0.8, R_f(**3dg**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 3340, 2928, 1592, 1471, 1351, 1287, 1250, 1195, 968, 860, 809, 771, 730, 678 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.79–7.73 (m, 1H), 7.68 (dd, J = 8.4, 2.1 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.26–7.20 (m, 2H), 7.11 (ddd, J = 8.0, 2.3, 0.8 Hz, 1H), 5.01 (d, J = 8.8 Hz, 1H), 4.71 (d, J = 8.8 Hz, 1H), 4.13 (s, 2H), 3.16 (s, 2H), 2.03 (s, 3H), 1.79 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=157.1, 146.2, 143.6, 133.6, 129.2, 125.3, 124.2, 122.0, 119.8, 117.9, 114.9, 108.9, 86.2, 82.6, 45.4, 34.4, 31.7,

31.5, 23.9 ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{26}NO]^+$=$[M+H]^+$: 320.2009; found 320.2026.

3-Methyl-3-[3-(3-methylphenyl)prop-2-ynyl]-5-phenyl-2,3-dihydro-1-benzofuran (3ee): GP was carried out with 3-iodo-1,1'-biphenyl-4-yl 2-methylprop-2-enyl ether **1e** (87.5 mg, 0.25 mmol), 2-methyl-4-(3-methylphenyl)but-3-yn-2-ol **2e** (87 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:01) furnished the product **3ee** (59.9 mg, 71%) as a yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**1e**)=0.7, R_f(**3ee**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3000, 1586, 1459, 1252, 1026, 877, 813, 752, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.57–7.50 (m, 2H, Ar–H), 7.48 (d, 1H, *J* = 2.0 Hz, Ar–H), 7.44–7.35 (m, 4H, Ar–H), 7.33–7.25 (m, 2H, Ar–H), 7.23–7.14 (m, 2H, Ar–H), 6.87 (d, 1H, *J* = 8.3 Hz, Ar–H), 4.58 (d, *J* = 8.8 Hz, 1H, OC$H_A$$H_B$), 4.29 (d, *J* = 8.8 Hz, 1H, OC$H_A$$H_B$), 2.71 (s, 2H, CH_2), 2.28 (s, 3H, CH_3), 1.54 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=159.2, 141.3, 137.9, 134.7, 134.2, 132.2, 128.8, 128.7, 128.1, 127.6, 126.8, 126.5, 123.2, 122.1, 109.9, 86.2, 82.8, 82.7, 45.4, 31.6, 24.1, 21.2 ppm. HR-MS (ESI+) m/z calculated for $[C_{25}H_{23}O]^+$=$[M+H]^+$: 339.1743; found 339.1746.

3-(3-Cyclopropylprop-2-ynyl)-3-methyl-5-phenyl-2,3-dihydro-1-benzofuran (3ei): GP was carried out with 3-iodo-1,1'-biphenyl-4-yl 2-methylprop-2-enyl ether **1e** (87.5 mg, 0.25 mmol), 4-cyclopropyl-2-phenylbut-3-yn-2-ol **2i** (93 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:01) furnished the product **3ei** (50 mg, 70%) as a pale yellow oily compound, [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1e**)=0.8, R_f(**3ei**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2933, 1703, 1472, 1359, 1211, 1019, 969, 877, 807, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.59–7.54 (m, 2H, Ar–H), 7.44–7.38 (m, 4H, Ar–H), 7.34–7.27 (m, 2H, Ar–H), 6.87 (d, *J* = 7.8 Hz, 1H, Ar–H), 4.52 (d, *J* = 8.8 Hz, 1H, OC$H_A$$H_B$), 4.24 (d, *J* = 8.8 Hz, 1H, OC$H_A$$H_B$), 2.46 (d, *J* = 2.0 Hz, 2H), 1.50 (s, 3H, CH_3), 1.27–1.16 (m, CH, 1H), 0.80–0.70 (m, CH_2, 2H), 0.63–0.58 (m, CH_2, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100

MHz): δ= 159.1, 141.3, 134.9, 134.0, 128.6, 127.4, 126.7, 126.5, 121.8, 109.8, 85.6, 82.7, 71.8, 45.2, 31.0, 24.2, 8.0, -0.52 ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{21}O]^+$=$[M+H]^+$: 289.1587; found 289.1589.

1,3-Dimethyl-3-[3-(3-methylphenyl)prop-2-ynyl]indoline (**5ae**)**: GP** was carried out with 2-iodo-*N*-methyl-*N*-(2-methylallyl)aniline **4a** (71.7 mg, 0.25 mmol), 2-methyl-4-(3-methylphenyl)but-3-yn-2-ol **2e** (87 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the product **5ae** (49.4 mg, 72%) as a colorless oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**4a**)=0.9, R_f(**5ae**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2888, 1586, 1471, 1439, 1254, 1092, 773, 737, 688 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.28–7.18 (m, 3H, Ar–H), 7.17-7.07 (m, 3H, Ar–H), 6.70 (ddd, *J* = 7.3, 7.3 and 1.0 Hz, 1H, Ar–H), 6.50 (d, *J* = 7.3 Hz, 1H, Ar–H), 3.43 (d, *J* = 8.8 Hz, 1H, NC$H_A$$H_B$), 3.04 (d, *J* = 8.8 Hz, 1H, NC$H_A$$H_B$), 2.77 (s, 3H, CH_3), 2.64 (s, 2H, CH_2), 2.33 (s, 3H, CH_3), 1.51 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=152.2, 137.8, 136.6, 132.2, 128.6, 128.5, 128.1, 128.0, 123.6, 122.3, 117.7, 107.4, 87.4, 82.3, 67.9, 43.7, 35.8, 30.8, 23.9, 21.2 ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{22}N]^+$=$[M+H]^+$: 276.1747; found 276.1755.

3-[3-(3-Fluorophenyl)prop-2-ynyl]-1,3-dimethylindoline (**5ah**)**: GP** was carried out with 2-iodo-*N*-methyl-*N*-(2-methylallyl)aniline **4a** (71.7 mg, 0.25 mmol), 4-(3-fluorophenyl)-2-methylbut-3-yn-2-ol **2h** (87.5 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the product **5ah** (48 mg, 69%) as a colorless oily compound, [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4a**)=0.8, R_f(**5ah**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2926, 2891, 1588, 1475, 1254, 744, 687 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.29–7.21 (m, 1H), 7.19–7.13 (m, 1H), 7.13–7.06 (m, 2H), 7.04–6.94 (m, 2H), 6.72 (ddd, *J* = 7.4, 7.4 and 0.8 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 3.40 (d, *J* = 8.8 Hz, 1H), 3.03 (d, *J* = 8.8 Hz, 1H), 2.77 (s, 3H), 2.67–2.61 (m, 2H), 1.49 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=163.6, 161.1, 152.2, 136.4, 129.8, 129.7, 128.1, 127.5, 122.3, 118.5, 118.3, 117.8,

115.1, 114.9, 107.5, 89.0, 81.1, 43.7, 35.8, 30.7, 23.9 ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{19}FN]^+=[M+H]^+$: 280.1496; found 280.1503.

1-Ethyl-3-methyl-3-(3-phenylprop-2-ynyl)indoline (**5ba**)**: GP** was carried out with 2-iodo-*N*-ethyl-2-iodo-*N*-(2-methylallyl)aniline **4b** (75.2 mg, 0.25 mmol), 2-methyl-4-phenylbut-3-yn-2-ol **2a** (80 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the product **5ba** (45.1 mg, 72%) as a colorless compound, [TLC control (petroleum ether/ethyl acetate 99:01), R_f(**4b**)=0.8, R_f(**5ba**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2936, 1587, 1473, 1440, 1256, 1178, 1013, 742, 688 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.44 (m, 2H, Ar–H), 7.33 (m, 3H, Ar–H), 7.15 (m, 2H, Ar–H), 6.73 (t, J = 7.3 Hz, 1H, Ar–H), 6.53 (d, J = 7.3 Hz, 1H, Ar–H), 3.47 (d, J = 8.8 Hz ,1H, NCH_AH_B), 3.30 (m, 2H), 3.12 (d, J = 8.8 Hz ,1H, NCH_AH_B), 2.69 (s, 2H, CH_2), 1.54 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=151.1, 136.6, 131.6, 128.2, 128.0, 127.6, 123.9, 122.4, 117.4, 107.3, 87.9, 82.1, 64.2, 43.4, 42.5, 31.0, 24.2, 11.8 ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{22}N]^+=[M+H]^+$: 276.1747; found 276.1746.

3-[3-(1-Benzyl-3-methyl-2,3-dihydro-1*H*-indol-3-yl)prop-1-ynyl]aniline (**5cg**)**: GP** was carried out with *N*-benzyl-*N*-(2-iodophenyl)-*N*-(2-methylprop-2-enyl)amine **4c** (90.7 mg, 0.25 mmol), 4-(3-aminophenyl)-2-methylbut-3-yn-2-ol **2g** (87.5 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the product **5cg** (52.8 mg, 60%) as a semi solid, [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**4c**)=0.8, R_f(**5cg**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3341, 2929, 1589, 1471, 1251, 969, 809, 733, 681 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.40–7.22 (m, 5H), 7.16 (d, J = 7.3 Hz, 1H), 7.12–7.02 (m, 2H), 6.78 (dd, J = 7.6 and 1.0 Hz, 1H), 6.75–6.65 (m, 2H), 6.60 (dd, J = 8.1 and 1.1 Hz, 1H), 6.50 (d, J = 7.9 Hz, 1H), 4.36 (d, J = 15.2 Hz, 1H), 4.21 (d, J = 15.2 Hz, 1H), 3.41 (dd, J = 9.0 and 1.2 Hz, 1H), 3.09 (dd, J = 9.0 and 1.2 Hz, 1H), 2.65 (s, 2H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=151.3, 146.0, 138.4, 136.3, 129.1, 128.5, 128.0, 127.7, 127.1, 124.5, 122.6,

122.1, 118.0, 117.7, 114.8, 107.1, 87.1, 82.4, 65.7, 52.9, 43.7, 31.1, 24.3 ppm. HR-MS (ESI+) m/z calculated for $[C_{25}H_{25}N_2]^+$=$[M+H]^+$: 353.2012; found 353.2022.

1-Benzyl-3-[3-(3-fluorophenyl)prop-2-ynyl]-3-methylindoline (**5ch**)**: GP** was carried out with *N*-benzyl-*N*-(2-iodophenyl)-*N*-(2-methylprop-2-enyl)amine **4c** (90.7 mg, 0.25 mmol), 4-(3-fluorophenyl)-2-methylbut-3-yn-2-ol **2h** (87.5 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 93:7) furnished the product **5ch** (59.4 mg, 67%) as a pale yellow compound, [TLC control (petroleum ether/ethyl acetate 99:01), R_f(**4c**)=0.8, R_f(**5ch**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3033, 1656, 1563, 1469, 1423, 1250, 1081, 969, 863, 737 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.39–7.29 (m, 4H, Ar–H), 7.28–7.18 (m, 2H, Ar–H), 7.14 (dd, *J* = 7.3 and 1.5 Hz, 1H, Ar–H), 7.13 (dd, *J* = 7.3 and 1.5 Hz, 1H, Ar–H), 7.09 (dd, *J* = 7.8 and 1.5 Hz, 1H, Ar–H), 7.04 (dt, *J* = 7.8 and 2.5 Hz, 1H, Ar–H), 6.97 (ttt, *J* = 7.8, 7.8 and 2.5 Hz, 1H, Ar–H), 6.72 (ddd, *J* = 7.3, 7.3 and 1.0 Hz, 1H, Ar–H), 6.51 (d, *J* = 7.8 Hz, 1H, Ar–H), 4.37 (d, *J* = 15.2 Hz, 1H, NCH_AH_BAr), 4.20 (d, *J* = 15.2 Hz, 1H, NCH_AH_BAr), 3.39 (d, *J* = 8.8 Hz, 1H, NCH_AH_B), 3.09 (d, *J* = 8.8 Hz, 1H, NCH_AH_B), 2.66 (s, 2H, CH_2), 1.48 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=162.3 (d, *J* = 246.5 Hz), 151.3, 138.3, 136.1, 129.7 (d, *J* = 8.9 Hz), 128.5, 128.1, 127.7, 127.4 (d, *J* = 3.0 Hz), 127.1, 125.7 (d, *J* = 9.5 Hz), 122.6, 118.4 (d, *J* = 22.6 Hz), 117.7, 115.0 (d, *J* = 21.2 Hz), 107.2, 88.9, 81.1 (d, *J* = 2.9 Hz), 65.6, 52.8, 43.6, 40.0, 31.0, 24.2 ppm. HR-MS (ESI+) m/z calculated for $[C_{25}H_{23}FN]^+$=$[M+H]^+$: 356.1809; found 356.1795.

3-[3-(3-Aminophenyl)prop-2-ynyl]-1,3-dimethyl-1,3-dihydro-2*H*-indol-2-one (7ag): GP was carried out with *N*-(2-iodophenyl)-*N*,2-dimethylacrylamide **6a** (75 mg, 0.25 mmol), 4-(3-aminophenyl)-2-methylbut-3-yn-2-ol **2g** (87.5 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 85:15) furnished the product **7ag** (44.2 mg, 61%) as a semi solid, [TLC control (petroleum ether/ethyl acetate 88:12), R_f(**6a**)=0.7, R_f(**7ag**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2929, 1689, 1593, 1470, 1354, 1248, 969, 738, 682 cm^{-1}. ^{1}H

NMR ($CDCl_3$, 400 MHz): δ=7.48 (dd, J = 7.3 and 1.0 Hz, 1H, Ar–H), 7.29 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 7.08 (ddd, J = 7.8, 7.8 and 1.5 Hz, 1H, Ar–H), 7.02 (d, J = 7.8 Hz, 1H, Ar–H), 6.85 (d, J = 7.8 Hz, 1H, Ar–H), 6.64–6.53 (m, 2H, Ar–H), 3.21 (s, 3H), 2.88 (d, J = 16.6 Hz, 1H), 2.63 (d, J = 16.6 Hz, 1H), 1.50 (s, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=179.5, 146.1, 143.0, 133.3, 129.1, 128.1, 124.0, 123.4, 122.5, 121.9, 117.8, 114.9, 107.9, 84.8, 83.0, 47.1, 28.8, 26.3, 21.6 ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{18}KN_2O]^+$=$[M+K]^+$: 329.1051; found 329.1049.

1-Ethyl-3-methyl-3-(3-phenylprop-2-ynyl)-1,3-dihydro-2*H*-indol-2-one (7ba): GP was carried out with *N*-ethyl-*N*-(2-iodophenyl)-2-methylacrylamide **6b** (78.7 mg, 0.25 mmol), 2-methyl-4-phenylbut-3-yn-2-ol **2a** (80 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 85:15) furnished the product **7ba** (52.7 mg, 71%) as a jelly compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**6b**)=0.6, R_f(**7ba**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3024, 1691, 1593, 1469, 1359, 1239, 1091, 1018, 744, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.46 (dd, J = 7.3 and 1.0 Hz, 1H, Ar–H), 7.28 (ddd, J = 7.3, 7.3 and 1.5 Hz, 1H, Ar–H), 7.07 (ddd, J = 7.3, 7.3 and 1.5 Hz, 1H, Ar–H), 7.24 (m, 5H, Ar–H), 6.88 (dd, J = 7.3 and 1.0 Hz, 1H, Ar–H), 3.83 (q, J = 7.3 Hz, 1H, NCH_AH$_B$CH$_3$), 3.71 (q, J = 7.3 Hz, 1H, NCH$_A$$H_BCH_3$), 2.90 (d, J = 16.6 Hz, 1H), 2.71 (d, J = 16.6 Hz, 1H), 1.49 (s, 3H, CH_3), 1.22 (t, J = 7.1 Hz, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=179.0, 142.2, 133.4, 131.5, 128.1, 128.0 127.8, 123.4, 123.3, 108.0, 85.4, 82.6, 47.1, 34.6, 28.8, 21.7, 12.7 ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{20}NO]^+$=$[M+H]^+$: 290.1539; found 290.1540.

1-Benzyl-3-[3-(3-fluorophenyl)prop-2-ynyl]-3-methyl-1,3-dihydro-2*H*-indol-2-one (7ch): GP was carried out with *N*-benzyl-*N*-(2-iodophenyl)-*N*-(2-methylprop-2-enyl)amine **6c** (94.2 mg, 0.25 mmol), 4-(3-fluorophenyl)-2-methylbut-3-yn-2-ol **2h** (87.5 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 88:12) furnished the product **7ch** (62.6 mg, 68%) as a jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**6c**)=0.6,

R_f(**7ch**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3024, 1692, 1594, 1471, 1359, 1241, 1092, 746, 687 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.41 (dd, J = 7.3 and 0.8 Hz, 1H), 7.26 (dd, J = 5.7 and 4.1 Hz, 2H), 7.24–7.04 (m, 6H), 7.00–6.91 (m, 2H), 6.86–6.78 (m, 1H), 6.74 (d, J = 7.8 Hz, 1H), 5.09 (d, J = 15.2 Hz, 1H), 4.77 (d, J = 15.2 Hz, 1H), 2.97 (d, J = 16.6 Hz, 1H), 2.87 (d, J = 16.6 Hz, 1H), 1.55 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=179.5, 163.4, 161.0, 142.3, 135.6, 133.0, 129.7, 129.6, 128.7, 128.6, 128.1, 127.5, 127.5, 127.4, 127.1, 123.1, 122.6, 118.5, 118.3, 115.3, 115.1, 109.1, 86.6, 81.6, 47.4, 43.8, 28.8, 22.5 ppm. HR-MS (ESI+) m/z calculated for $[C_{25}H_{21}FNO]^+$=$[M+H]^+$: 370.1602; found 370.1581.

1,3,5,7-Tetramethyl-3-(3-phenylprop-2-ynyl)-1,3-dihydro-2*H*-indol-2-one (7da): GP was carried out with *N*-(2-iodo-4,6-dimethylphenyl)-*N*,2-dimethylacrylamide **6d** (82.2 mg, 0.25 mmol), 2-methyl-4-phenylbut-3-yn-2-ol **2a** (80 mg, 0.50 mmol), $Pd_2(dba)_3$ (11.4 mg, 5 mol%), TBAB (80.5 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol) water (0.5 mL), under microwave irradiation. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 90:10) furnished the product **7da** (52.9 mg, 70%) as a jelly compound, [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**6d**)=0.7, R_f(**7da**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2940, 1689, 1587, 1445, 1340, 1076, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.34–7.20 (m, 5H), 7.14 (d, J = 0.5 Hz, 1H), 6.89–6.79 (m, 1H), 3.48 (s, 3H), 2.86 (d, J = 16.5 Hz, 1H), 2.65 (d, J = 16.5 Hz, 1H), 2.54 (s, 3H), 2.30 (s, 3H), 1.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=180.2, 138.3, 134.0, 132.2, 131.8, 131.5, 128.2, 127.8, 123.5, 122.0, 119.2, 85.7, 82.7, 46.5, 29.6, 29.2, 22.0, 20.9, 18.8 ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{22}NO]^+$=$[M+H]^+$: 304.1696; found 304.1702.

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- [Pd]-Catalysis.
- *tert*-Propargyl alcohols Served as Alkyne Sources
- Aqueous Mediated Reaction.
- Microwave-assisted Synthesis.
- Heterocyclic Compounds have been synthesized.
- Environmentally Benign Process.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

There are no conflicts to declare.