Divergent palladium- and platinum-catalyzed intramolecular hydroamination/hydroarylation of *O*-propargyl-2-aminophenols

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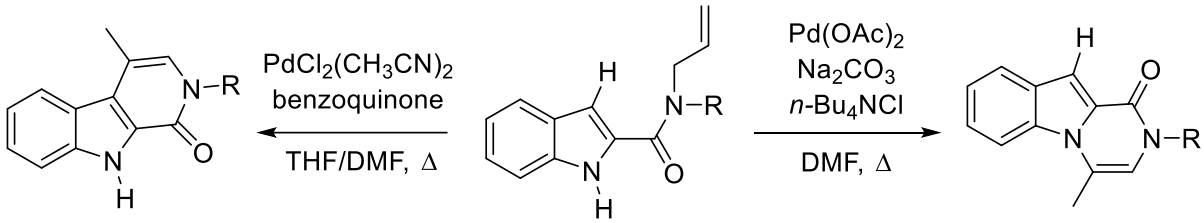
Abstract: A fruitful divergent cyclization of terminal alkynes arising from 2-aminophenols depending on the transition metal employed is reported. Under palladium- and platinum- catalysis, the total regioselective carbon-nitrogen or carbon-carbon bonds formation afforded 1,4-benzoxazines or benzopyrans, through different reaction pathways. The subsequent functionalization of the benzopyran scaffold paved the way for a new synthesis of the tricyclic pyrano[3,2-*h*]quinolines.

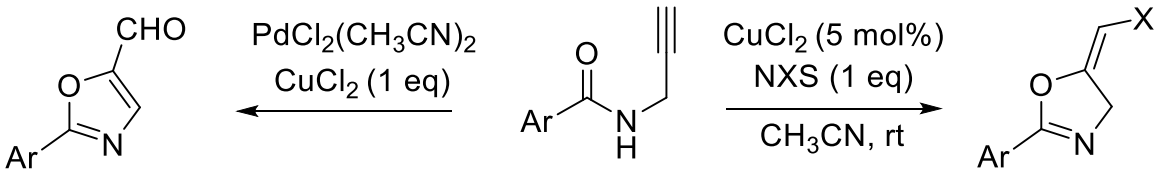
Introduction

The intramolecular transition metal-catalyzed reactions, of unsaturated moieties (alkenes, alkynes and allenes) tethered to a nucleophile, such as aminations, hydroaminations, alkoxylations and hydroalkoxylations reactions, are a fruitful strategy for the construction of heterocyclic systems.[1] The different cyclization products are depended on the transition-metal catalysts used,[2] while the different regioselective pathways are depended on the exo- or endo-cyclization processes arising from the length and rigidity of the linking alkyl chain. Moreover, the presence on the skeleton of different functional groups can result in a C-N or C-O bonds formation. The construction of heteropolycyclic systems can be obtained also through the formation of intramolecular carbon-carbon bonds starting from aromatic substrates bearing suitable unsaturated systems.[3]
Recently, several papers, on the transition-metal catalyzed reactions, describe the divergent reactivity of different substrates, easily modulated by the transition-metal utilized.[4] The interest of this strategy was due to the rapid access to different heterocyclic scaffolds starting from the same building block.
In this context we reported a Pd-catalyzed divergent reactivity of indoles and pyrroles bearing alkene pendant, resulting in different polycyclic systems in a complete regioselective pathways through the C-C or C-N bonds formation, depending on the reaction conditions (Scheme 1).[5]



Scheme 1. Divergent reactivity of indole and pyrrole derivatives

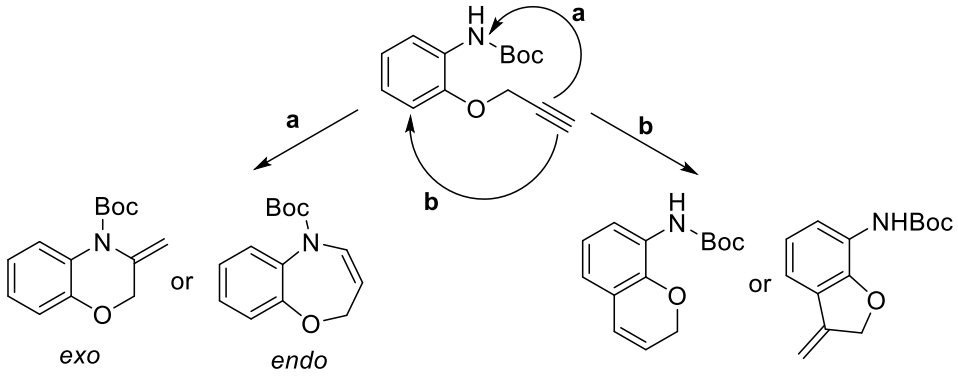
Moreover, working on alkynyl amides we obtained substituted oxazoles through the Pd(II)-catalyzed alkoxylation process[6] and substituted oxazolidines were formed under copper-catalysis, through an alkoxyhalogenation domino process (Scheme 2).[7]



Scheme 2. Divergent reactivity of N-propargyl amides

Continuing our efforts to explore the intramolecular coupling of unactivated unsaturated systems, we envisaged the reactivity of the *O*-propargyl-2-aminophenols exploring different transition-metal catalysts with the aim to

identify reaction conditions able to give divergent reactivity, such as hydroamination (Scheme 3, path a) and hydroarylation processes (Scheme 3, path b).



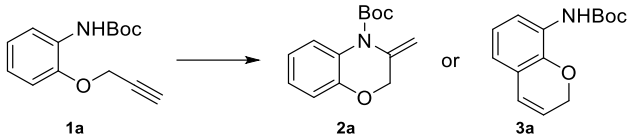
Scheme 3. Divergent reactivity of *N*-Boc-*O*-propargyl-2-aminophenol

Results and Discussion

To test the intramolecular coupling under different transition-metal catalysts, the 2-(propargyloxy)aniline **1a** was chosen as a benchmark. A catalysts screening revealed that the reaction under $AuCl_3$ catalyst in acetonitrile at r.t. or at reflux, gave unreacted starting material (Table 1, entries 1, 2). Also, the addition of Ag(OTf) as a co-catalyst in DMF at reflux resulted unsuccessful (Table 1, entry 3). Using $AgNO_3$ as catalyst, no conversion of **1a** was observed even if the reaction was placed under MW irradiation (Table 1, entries 4, 5), while the employment of copper iodide as catalyst gave a dimeric product, according to the Ullmann type reaction (Table 1, entry 6).[8] The reported literature hydroamination conditions under nickel catalysis were unfruitful (Table 1, entry 7),[9] whilst the use of cationic iridium, gave an unseparable mixture of products containing the 3-methylene-2*H*-benzo[*b*][1,4]oxazine, also testing the reaction on the free amino group (2-(propargyloxy)aniline) (Table 1, entry 8).[10] The utilization of $Pd(PPh_3)_4$ catalyst under thermal heating, gave no coupling product (Table 1, entry 9), but the addition of 10 mol% of triphenylphosphine allowed the cyclization, affording 3-methylene benzoxazine **2a** in a good yield through a hydroamination process (Table 1, entry 10).[11] Although the precise role of PPh_3 is not clear, the added phosphine could probably act as a Bronsted base helping to promote the initial hydropalladation step.[12] The application of $PtCl_2(CH_3CN)_2$ as catalyst in toluene, provided the formation of the dihydrobenzopyran **3a** arised from a hydroarylation process (Table 1, entry 11).[3]

After identifying the transition metal catalysts to obtain divergent cyclization, we extended the Pd-catalyzed reaction conditions to the 2-(propargyloxy)anilines **1b-g** (Table 2). In this case, the 6-*exo*-dig cyclization was entirely selective and compounds **2** bearing the *exo*-methylene pendant were the sole products obtained after the work-up of the reaction. The possible alternative seven-membered ring was never observed. The purification of the products was performed on aluminium oxide column chromatography, in order to avoid the possible isomerization of the exocyclic double bond to the internal double bond. The reaction was proven to be effective on substrates bearing both electron-donor and electron-withdrawing functional groups, as highlighted by the good yields reported in Table 2.

Table 1. Treatment of 2-(propargyloxy)aniline **1a** under transition metal-catalyzed conditions.

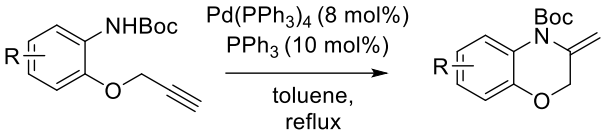


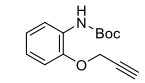
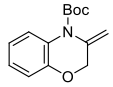
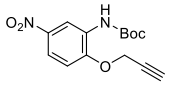
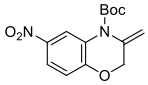
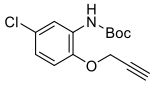
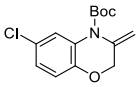
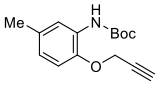
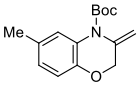
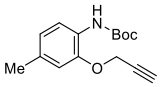
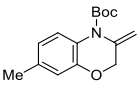
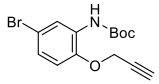
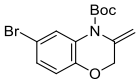
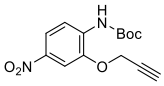
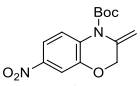
1a **2a** **3a**

Entry	Catalyst (mol%) / Base	Solvent	Temp./ time	Products
1	$AuCl_3$ 8%	CH_3CN	rt 16h	nr[a]
2	$AuCl_3$ 8%	CH_3CN	reflux 6h	nr[a]
3	$AuCl_3$ 8% Ag(OTf) 4%	DMF	120°C 4h	nr[a]
4	$AgNO_3$ 5%	toluene	80°C 10h	nr[a]
5	$AgNO_3$ 10%	toluene	100°C MW 15 min	nr[a]
6	CuI 10% $CaCO_3$ 1.2 eq.	DMF	120°C 4.5h	Dimer
7	$Ni(acac)_2$ 10% PPh_3 40% tBuONa 1.2 eq.	toluene	110°C 6h	nr[a]
8	$[Ir(COD)_2]BArF_4$ 5% / BINAP 10%	dioxane	100°C 16h	mixture
9	$Pd(PPh_3)_4$ 10%	toluene	100 °C 24h	nr[a]
10	$Pd(PPh_3)_4$ 15% PPh_3 10%	toluene	100°C 4h	**2a**
11	$PtCl_2(CH_3CN)_2$ 5%	toluene	90°C 6h	**3a**

[a] nr = no reaction.

Table 2. Pd-catalyzed hydroamination of propargylethers **1a-g**.



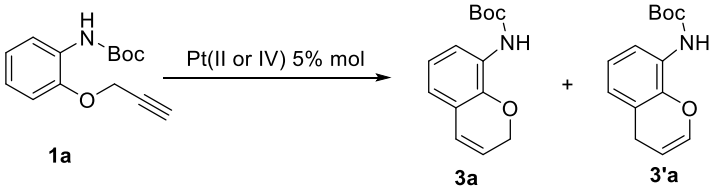
Entry	Substrate	Product	Yield (%)
1	 **1a**	 **2a**	95
2	 **1b**	 **2b**	82
3	 **1c**	 **2c**	87
4	 **1d**	 **2d**	88
5	 **1e**	 **2e**	0
6	 **1f**	 **2f**	30
7	 **1g**	 **2g**	97

The use of $PtCl_2(CH_3CN)_2$ as catalyst provided the bicyclic dihydrobenzopyran **3a** (Table 1) through a hydroarylation process even if some platinum-catalyzed hydroamination processes of alkynes are reported in the literature.[13] To justify the divergent reactivity, we may suppose that the two metal catalyzed reactions follow different mechanisms. In the literature is reported a complexation of the platinum at the unsaturated moiety (Scheme 4),[3c] while palladium may act through C-H activation (outer-sphere mechanism) or through an alternative N-atom activation, first involving the initial addition of the nucleophile to the metal, followed by multiple bond insertion (inner-sphere mechanism).[1b] This mechanism could be attributed for amines with acidic hydrogens,[1i,k,m] due to the large effect of the protecting group on the nitrogen atom.[14]

In order to improve the yield of the Pt-catalyzed dihydrobenzopyran product **3a**, the reaction conditions were optimized (Table 3). The best result was obtained by using $PtCl_2$ in the absence of ligand, using toluene as solvent at reflux (Table 3, entry 3). In some cases, a second product **3'a**, arising from the double bond isomerization was also formed. Although, in the best reaction conditions the use of wet toluene as solvent overcame this problem (Table 3, entry 4).[3b]

The reaction was regioselective, favoring only the bicyclic product 3a, derived from the 6-endo-dig cyclization. The competitive pentatomic ring product, emerging from the 5-exo-dig cyclization, was not observed (Scheme 4).

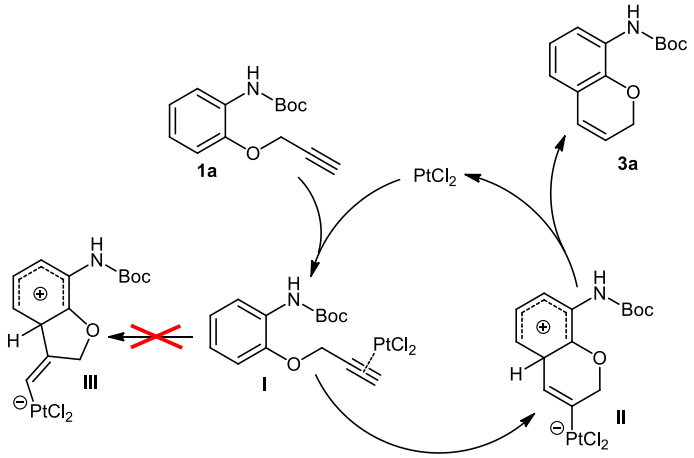
Table 3. Optimization of the Pt-catalyzed hydroarylation process.



1a **3a** **3'a**

Entry	Catalyst (5 mol%)	Solvent	Ligand (10 mol%)	Temp./ Time	Yield (%)[a]
1	$PtCl_2(CH_3CN)_2$	Toluene	--	90°C (6h)	40 (+10)
2	$PtCl_2(CH_3CN)_2$	Dioxane	PPh_3	90°C (3h)	30
3	$PtCl_2$	Toluene	--	90°C (3h)	55 (+10)
4	$PtCl_2$	Toluene-H_2O 10:1	--	90°C (5h)	60
5	$PtCl_2$	CH_3CN	Xantphos	70°C (5h)	30
6	$PtCl_2$	Dioxane	--	90°C (2h)	33 (+23)
7	$PtCl_2$	Dioxane	JohnPhos	70°C (2h)	23 (+10)
8	$PtCl_2$	dioxane	JohnPhos + $AgBF_4$	70°C (24h)	5
9	$PtCl_2$	CH_3CN	--	70°C (3h)	40
10	$PtCl_2$	CH_3OH	--	50°C (3h)	20
11	$PtCl_4$	toluene	--	80°C (8h)	--
12	$PtCl_4$	DCE	--	rt (2h)	35 (+5)

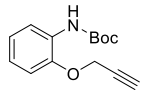
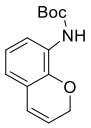
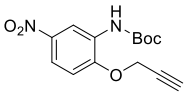
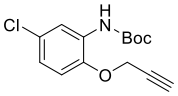
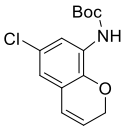
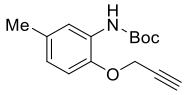
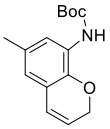
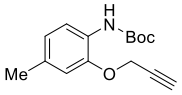
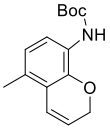
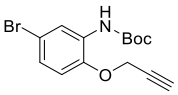
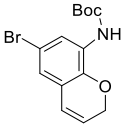
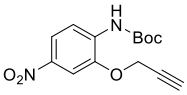
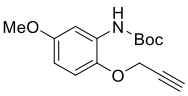
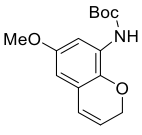
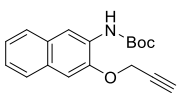
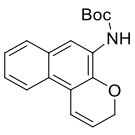
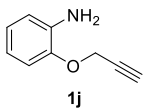
[a] In parentheses the yields of the isomer **3'**.

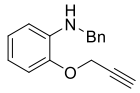


Scheme 4. Regioselective hydroarylation of **1a**

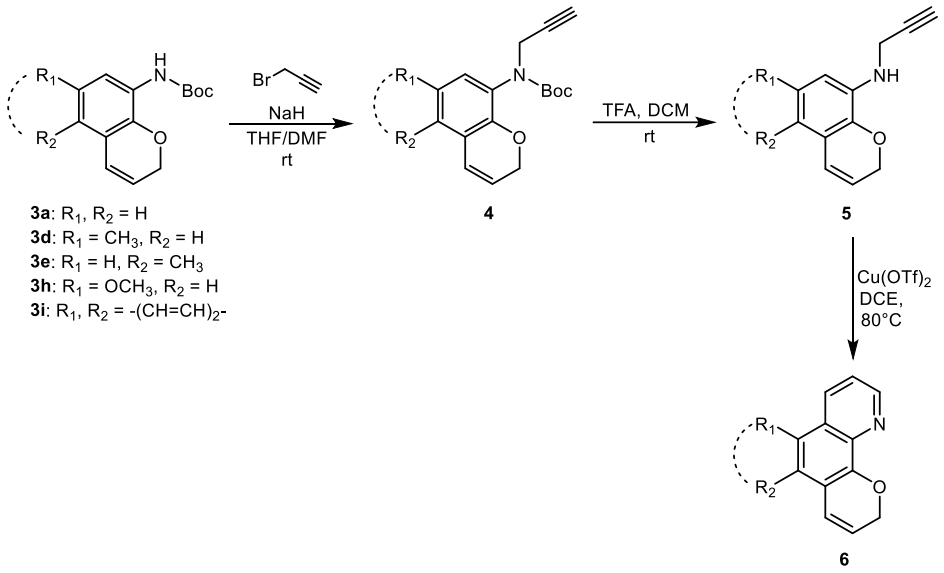
With the optimized reaction conditions in hand, the reaction was extended to the substituted 2-(propargyloxy)anilines **1b-i** in order to study the influence of the substituents on the cyclization reaction (Table 4). The reaction gave good results on the electron-poor *N*-Boc amino group, while no reaction occurred on the free amino group (Table 4, entry 10), as well as on *N*-alkyl aniline (Table 4, entry 11). The presence of substituents on the phenol ring showed great influence on the cyclization reaction. Electron-donor substituents such as the methoxy moiety enhanced the reactivity. Chloro and bromo substituents decreased the yields of the reaction, while the presence of a stronger electron-withdrawing group, such as nitro, hampered completely the hydroarylation process (Table 4).

Table 4. Pt-catalyzed hydroarylation of propargylethers **1a-k**

Entry	Substrate	Time	Product	Yield (%)
1	 **1a**	5h	 **3a**	60
2	 **1b**	18h		0
3	 **1c**	12h	 **3c**	35
4	 **1d**	4h	 **3d**	70
5	 **1e**	3h	 **3e**	65
6	 **1f**	2h	 **3f**	20
7	 **1g**	24h		0
8	 **1h**	7h	 **3h**	75
9	 **1i**	24h	 **3i**	44
10	 **1j**	24h		0

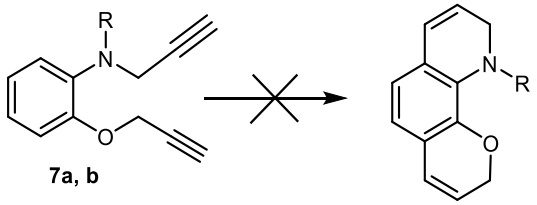
11	 **1k**	24h	0

In the case of the electron-rich benzopyrans (**3a, d, e, h, i**), which were obtained in good yields, the presence of an unreacted amino group prompted us to investigate a further functionalization with the insertion of a new alkynyl group on the nitrogen atom, paving the way for a second hydroarylation step. The propargylation reaction of compounds **3**, followed by deprotection of the amino group afforded compounds **5**. The subsequent hydroarylation was achieved under copper catalysis, due to the unproductive platinum catalysis, providing the pyranoquinoline skeleton **6** (Scheme 5). The complete synthetic path resulted in a new and efficient synthesis of the pyrano[3,2-*h*]quinoline skeleton.



Scheme 5. Copper-catalyzed hydroarylation coupling

The possible one-pot reaction on *N,O*-dipropargyl-2-aminophenol **7a,b** to obtain the pyranoquinolines directly failed in all the reaction conditions tested and with different metal catalysts (Scheme 6).



a) R = Boc
b) R = H

Scheme 6. Domino process of **7a,b**

The great interest of the cyclization processes is based on the fact that the pyrano[3,2-*h*]quinoline scaffold presents: a) antiproliferative[15] and antioxidant activities useful in the treatment of the Alzheimer's disease[16] and b) promising metal-chelating properties.

Conclusions

In summary we have developed a fruitful regioselective cyclization of terminal alkynes depending on the transition-metal catalyst employed. It must be emphasized, that the *O*-propargyl-2-aminophenols **1** showed different reactivity, switching from the hydroamination under the $Pd(PPh_3)_4$ catalysis to the hydroarylation processes using $PtCl_2$ as catalyst. The hydroamination afforded bicyclic 3-methylene-1,4-benzoxazines **2** through the C-N bond formation, while the *N*-Boc-8-amino-(2*H*)-benzopyrans **3** were the result of the C-C bond formation in the hydroarylation

process. The subsequent functionalization of compounds **3** paved the way for a new and efficient synthesis of the tricyclic pyrano[3,2-*h*]quinolines **6**.

Experimental Section

General information. Melting points were determined by the capillary method with a Büchi B-540 apparatus and are uncorrected. IR spectra were measured with a Jasco FT/IR 5300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with: AVANCE 400 Bruker spectrometer at 400 and 100 MHz, Varian Gemini 200 MHz spectrometer at 200 MHz and 50 MHz and Varian Oxford 300 MHz spectrometer at 300 and 75 MHz, respectively. Chemical shifts are given as δ values in ppm relative to residual solvent peaks ($CHCl_3$) as the internal reference. ^{13}C NMR spectra are ^{1}H-decoupled and the determination of the multiplicities was achieved by the APT pulse sequence. Mass spectra were determined with a LCQ Advantage Thermo Finningan. Elemental analyses were executed on Perkin-Elmer CHN Analyzer Series II 2400. Thin-layer chromatographic separations were performed on Merck silica-gel 60-F_{254} precoated. Preparative separations were performed by flash chromatography by using Merck silica gel 0.035-0.070 mm. Compounds **1a,**[17] **1b-d, h**[18] were prepared as previously reported.

General procedure for the preparation of *O*-propargyl ethers 1e-g, i. Under N_2 atmosphere, to a stirred solution of the suitable *tert*-butyl(2-hydroxyphenyl)carbamate (2.4 mmol) in THF/DMF (9 mL / 3 mL) at room temperature, K_2CO_3 was added (2.9 mmol, 0.396 g). The mixture was cooled to 0 °C and a solution of propargyl bromide (80% in toluene, 2.9 mmol, 0.342 g) was added dropwise. The resulting mixture was stirred at rt overnight. The solvent was removed under reduced pressure, the mixture was extracted with AcOEt (3 x 20 mL) and then washed with brine. The organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by crystallization or chromatographed on a flash silica gel column.

***tert*-Butyl (4-methyl-2-(prop-2-yn-1-yloxy)phenyl)carbamate (1e):** Yield 81% (510 mg). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 7.2 Hz, 1H), 6.96 (br s, 1H, exchange with D_2O), 6.78 (m, 2H), 4.71 (d, *J* = 2.0 Hz, 2H) 2.54 (t, *J* = 2.0 Hz, 1H), 2.30 (s, 3H), 1.53 (s, 9H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.7 (s), 145.6 (s), 132.0 (s), 126.0 (s), 122.4 (d), 118.5 (d), 112.7 (d), 80.1 (s), 78.3 (s), 75.8 (d), 56.5 (t), 28.3 (q), 21.1 (q) ppm. IR: ν = 3220, 2930, 2120, 1720, 1550 cm^{-1}. MS (ESI): *m/z* = 284.1 [M+Na]$^{+}$. Anal. calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found C, 69.16; H, 7.55; N, 5.22.

***tert*-Butyl (5-bromo-2-(prop-2-yn-1-yloxy)phenyl)carbamate (1f):** yield 76% (590 mg). White solid, mp = 82-83 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.07 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.04 (br s, 1H, exchange with D_2O), 6.83 (d, *J* = 8.6 Hz, 1H), 4.73 (d, *J* = 2.4 Hz, 2H), 2.55 (t, *J* = 2.4 Hz, 1H), 1.53 (s, 9H), ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.3 (s), 144.4 (s), 129.9. (s), 124.6 (d), 121.1 (d), 114.8 (s), 113.1 (s), 80.9 (s), 77.7 (d), 76.4 (s), 56.6 (t), 28.3 (q) ppm. IR: ν = 3180, 2920, 2140, 1730, 1530 cm^{-1}. MS (ESI): *m/z* = 327.2 [M+H]$^{+}$. Anal. Calcd for $C_{14}H_{16}BrNO_3$: C, 51.55; H, 4.94; N, 4.29. Found: C, 51.74; H, 4.99; N, 4.19.

***tert*-Butyl-(4-nitro-2-(prop-2-yn-1-yloxy)phenyl)carbamate (1g):** Yield 80% (560 mg) . Yellow solid, mp = 110.3-112.1 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 9.1 Hz, 1H), 7.95 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.32 (br s, 1H, exchange with D_2O), 4.87 (d, *J* = 2.2 Hz, 2H), 2.62 (t, *J* = 2.2 Hz, 1H), 1.54 (s, 9H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 151.9 (s), 144.5 (s), 141.9 (s), 135.1 (s), 118.6 (d), 116.8 (d), 107.0 (d), 83.8 (s), 81.8 (s), 77.4 (d), 56.9 (t), 28.2 (q) ppm. IR: ν = 3427, 3274, 1729, 1506, 1475, 1339, 1230, 1149 cm^{-1}. MS (ESI): (*m/z*) = 293.3 [M+H]$^{+}$. Anal. calcd for $C_{14}H_{16}N_2O_5$: C, 57.53; H, 5.52; N, 9.58. Found: C, 57.74; H, 5.58; N, 9.52.

***tert*-Butyl (3-(prop-2-yn-1-yloxy)naphthalene-2-yl)carbamate (1i):** yield 96% (680 mg). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 7.72 (m, 1H), 7.67 (m, 1H), 7.35 (m, 3H, 2H after D_2O), 7.23 (s, 1H), 4.89 (d, *J* = 2.4 Hz, 2H), 2.59 (t, *J* = 2.4 Hz, 1H), 1.57 (s, 9H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.6 (s), 145.4 (s), 129.7 (s), 129.3 (s), 128.3 (s), 127.3 (d), 126.3 (d), 124.7 (d), 124.6 (d), 114.7 (d), 106.7 (d), 80.6 (s), 76.8 (s), 76.3 (d), 56.3 (t), 28.4 (q) ppm. IR: ν = 3430, 3240, 2124, 1710, 1536 cm^{-1}. MS (ESI): *m/z* = 320.5 [M+Na]$^{+}$. Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found; C, 72.80; H, 6.40; N, 4.61.

General procedure for the Pd-catalyzed hydroamination reactions on alkyne derivatives. Synthesis of compounds 2a-g. $Pd(PPh_3)_4$ (8% mol) and PPh_3 (10% mol) were added to a solution of the suitable propargyl derivative **1a-g** (0.4 mmol) in toluene (5 mL) under nitrogen atmosphere. The reaction mixture was stirred at reflux at 90 °C for 4h. The reaction mixture was filtered under reduced pressure through a Celite® pad washing with AcOEt. The solvent was removed under reduced pressure and the crude purify by silica gel chromatography. (hexane/AcOEt 10:1).

***tert*-Butyl 3-methylene-2*H*-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate (2a):** Yield 95% (94 mg). Colourless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.01-6.76 (m, 4H), 5.34 (s, 1H), 5.13 (s, 1H), 4.56 (s, 2H), 1.53 (s, 9H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 152.0 (s), 147.2 (s), 133.7 (s), 131.6 (s), 124.7 (d), 123.6 (d), 120.9 (d), 117.1 (d), 107.9 (t), 82.5 (s), 69.8 (t), 28.4 (q) ppm. IR: ν = 3433, 3058, 2979, 2932, 2870, 1717, 1602 cm^{-1}. MS (ESI): (*m/z*) = 248.3 [M+H]$^{+}$, 270.1 [M+Na]$^{+}$. Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 68.19; H, 6.99; N, 5.59.

***tert*-Butyl 3-methylene-6-nitro-2*H*-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate (2b):** Yield: 82% (96 mg). Orange solid, mp 134-136 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 2.7 Hz, 1H), 7.89 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 5.43 (s, 1H), 5.35 (s, 1H), 4.66 (s, 2H), 1.57 (s, 9H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 156.1 (s), 151.6 (s), 143.0 (s), 134.0 (s), 129.6 (s), 120.3 (d), 119.6 (d), 117.3 (d), 111.5 (t), 81.8 (s), 69.7 (t), 28.5 (q), ppm. IR: v = 3436, 3128, 2923, 2851, 1721, 1588 cm^{-1}. MS (ESI): *m/z* = 315.0 $[M+Na]^+$. Anal calcd for $C_{14}H_{16}N_2O_5$: C, 57.53; H, 5.52; N, 9.58. Found: 57.60; H, 5.70; N, 9.48.

***tert*-Butyl 6-chloro-3-methylene-2*H*-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate (2c):** Yield: 87% (98 mg). Colourless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.79 (d, *J* = 8.7 Hz 1H), 5.35 (d, *J* = 0.5 Hz, 1H), 5.19 (d, *J* = 0.5 Hz, 1H), 4.54 (d, *J* = 0.5 Hz, 2H), 1.54 (s, 9H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 151.5 (s), 145.5 (s), 135.7 (s), 127.7 (s), 125.7 (s), 124.5 (d), 123.2 (d), 118.0 (d), 109.0 (t), 83.0 (s), 69.5 (t), 28.3 (q) ppm. IR: v = 3422, 3086, 2979, 2930, 1858, 1719 cm^{-1}. MS (ESI): *m/z* = 281.0 $[M]^+$. Anal. calcd for $C_{14}H_{16}ClNO_3$: C, 59.68; H, 5.72; N, 4.97. Found: C, 59.79; H, 5.79; N, 4.90.

***tert*-Butyl 6-methyl-3-methylene-2H-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate (2d):** Yield: 88% (92 mg). Colourless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.53 (s, 1H), 6.95-6.67 (m, 2H), 5.34 (s, 1H), 5.15 (s, 1H), 4.54 (d, *J* = 0.6 Hz, 2H), 2.30 (s, 3H), 1.54 (s, 9H), ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 152.0 (s), 145.0 (s), 136.9 (s), 133.8 (s), 126.8 (s), 125.3 (d), 123.8 (d), 116.7 (d), 107.6 (t), 82.4 (s), 69.8 (t), 28.4 (q), 21.1 (q) ppm. IR: v = 3432, 3056, 2977, 2928, 1715 cm^{-1}. MS (ESI): *m/z* = 279.0 $[M+H_2O]^+$. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.88; H, 7.50; N, 5.30.

***tert*-Butyl 6-bromo-3-methylene-2*H*-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate (2f):** Yield: 30% (39 mg). Colourless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 2.3 Hz, 1H), 7.07 (dd, *J* = 8.6, 2.3 Hz, 1H),6.74 (d, *J* = 8.6 Hz, 1H), 5.35 (d, *J* = 0.6 Hz, 1H), 5.19 (d, *J* = 0.6Hz, 1H), 4.54 (d, *J* = 0.7 Hz, 2H), 1.56 (s, 9H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 151.3 (s), 145.8 (s), 135.5 (s), 130.3 (s), 127.9 (s), 127.1 (d), 125.9 (d), 118.2 (d), 108.7 (t), 83.0 (s), 69.3 (t), 28.1 (q) ppm. IR: v = 3320, 2930, 2333, 1719 cm^{-1}. MS (ESI): *m/z* = 349.2 $[M+Na]^+$. Anal. calcd for $C_{14}H_{16}BrNO_3$: C, 51.55; H, 4.94; N, 4.29. Found: C, 51.60; H, 4.95; N, 4.26.

***tert*-Butyl 3-methylene-7-nitro-2*H*-benzo[*b*][1,4]oxazine-4(3*H*)-carboxylate (2g):** Yield: 97% (113 mg). Yellow solid, mp = 95.6-97.9 °C. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 9.0 Hz, 1H), 7.77 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 5.38 (s, 1H), 5.27 (s, 1H), 4.61 (s, 2H), 1.55 (s, 9H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 151.1 (s), 146.1 (s), 143.6 (s), 134.4 (s), 132.6 (s), 122.5 (d), 116.0 (d), 112.7 (d), 110.2 (t), 83.7 (s), 69.1 (t), 28.1 (q) ppm. IR: v = 3432, 3127, 2922, 1926, 1719, 1515 cm^{-1} MS (ESI): *m/z* = 315.0 $[M+Na]^+$. Anal calcd for $C_{14}H_{16}N_2O_5$: C, 57.53; H, 5.52; N, 9.58. Found: 57.70; H, 5.60; N, 9.60.

General procedure for the Pt-catalyzed hydroarylation reactions on alkyne derivatives. Synthesis of compounds 3. To a solution of propargyl derivative **1** (0.5 mmol) in toluene (2.5 ml) was added $PtCl_2$ (5% mol) and was stirred at 80 °C for 3 h. The reaction mixture was concentrated in vacuo, brine was added and the mixture extracted with AcOEt (3 × 10 mL). The combined organic phases were dried with Na_2SO_4, filtered and the solvent removed in vacuo. The product was purified by flash chromatography on silica gel.

***tert*-Butyl 2*H*-chromen-8-ylcarbamate (3a):** Yield: 60% (74 mg). Colorless oil. H-NMR (200 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.9 Hz, 1H), 6.93 (br. s, 1H, exchange with D_2O), 6.84 (t, *J* = 7.9 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.41 (dt, *J* = 9.9, 1.8 Hz, 1H), 5.76 (dt, *J* = 9.9, 3.5 Hz, 1H), 4.83 (dd, *J* = 3.5, 1.9 Hz, 2H), 1.54 (s, 9H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 152.9 (s), 141.8 (s), 127.1 (s), 124.9 (d), 123.3 (d), 121.6 (d), 121.4 (d), 120.3 (d), 118.7 (d), 80.5 (s), 66.0 (t),28.6 (q) ppm. IR: v = 3425, 2970, 1920, 1720 cm^{-1}. ^{1}MS (ESI): *m/z* = 270.0 $[M+Na]^+$. Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.03; H, 6.99; N, 5.69.

***tert*-Butyl (6-chloro-2*H*-chromen-8-yl)carbamate (3c):** Yield: 35% (49 mg) Colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.99 (s, 1H), 6.94 (br s, 1H, exchange with D_2O), 6.63 (d, *J* = 2.5 Hz, 1H), 6.34 (dt, *J* = 9.9, 1.9 Hz, 1H), 5.81 (dt, *J* = 9.9, 3.5 Hz, 1H), 4.84 (dd, *J* = 3.5, 1.9 Hz, 2H), 1.54 (s, 9H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 152.6 (s), 140.1 (s), 128.1 (s), 126.7 (s), 124.1 (d), 122.6 (s), 122.6 (d), 119.7 (d), 118.2 (d), 81.1 (s), 66.1 (t), 28.5 (q) ppm. IR: v = 3432, 2979, 2930, 1728 cm^{-1}. MS (ESI): *m/z* = 304.0 $[M+Na]^+$. Anal. Calcd for $C_{14}H_{16}ClNO_3$: C, 59.68; H, 5.72; N, 4.97. Found: C, 59.85; H, 5.51; N, 5.03.

***tert*-Butyl (6-methyl-2*H*-chromen-8-yl)carbamate (3d):** Yield: 70% (91 mg). Colourless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.72 (m, 1H), 6.88 (m, 1 H), 6.46 (br. s, 1 H, exchange with D_2O), 6.37 (dt, *J* = 9.8, 1.8 Hz, 1 H), 5.75 (dt, *J* = 9.8, 3.5 Hz, 1 H), 4.79 (dd, *J* = 3.5, 1.8 Hz, 2 H) 2.24 (s, 3 H), 1.53 (s, 9 H) ppm. ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 153.2 (s), 139.8 (s), 131.1 (s), 126.9 (s), 125.2 (d), 122.0 (d), 121.8 (s), 121.0 (d), 119.2 (d), 80.7 (s), 66.1 (t),

28.8 (q), 21.4 (q) ppm. IR: v = 3436, 2977, 2920, 1728 cm^{-1}. MS (ESI): *m/z* = 284.0 $[M+Na]^+$. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.12; H, 7.17; N, 5.45.

***tert*-Butyl (5-methyl-2*H*-chromen-8-yl)carbamate (3e):** Yield 65% (85 mg). Colourless oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ = 7.79 (d, *J* = 8.4 Hz, 1H), 6.86 (br. s, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.60 (dt, *J* = 10, 1.7 Hz, 1H), 5.82 (dt, *J* = 10, 3.7 Hz, 1H), 4.76 (dd, *J* = 3.7, 1.7 Hz, 2H), 2.23 (s, 3H), 1.60 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$). δ = 152.8 (s), 141.9 (s), 127.6 (s), 124.8 (s), 122.5 (d), 122.1 (d), 121.1 (d), 120.3 (s), 118.0 (d), 80.2 (s), 65.0 (t), 28.3 (q), 17.8 (q) ppm. IR: v = 3432, 2975, 2918, 1725 cm^{-1}. MS (ESI): *m/z* = 284.2 $[M+Na]^+$. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.11; H, 7.15; N, 5.47.

***tert*-Butyl (6-bromo-2*H*-chromen-8-yl)carbamate (3f):** Yield 20% (33 mg). Colourless oil. ^{1}H-NMR (300 MHz, CD_3OD): δ =7.91 (d, *J* = 2.1 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.37 (dt, *J* = 9.9, 2.1 Hz, 1H), 5.86 (dt, *J* = 9.9, 3.6 Hz, 1H), 4.84 (dd, *J* = 3.3, 2.1 Hz, 2H), 1.52 (s, 9H) ppm. ^{13}C-NMR (75 MHz, CD_3OD): δ = 153.1 (s), 141.6 (s), 127.9 (s), 123.6 (s), 123.3 (d), 122.9 (d), 122.6 (d), 121.5 (d), 112.6 (s), 80.3 (s), 65.5 (t), 27.3 (q) ppm. IR: v = 3437, 2984, 2923, 1730 cm-1. MS (ESI): *m/z* = 349.2 $[M+Na]^+$. Anal. Calcd for $C_{14}H_{16}BrNO_3$: C, 51.55; H, 4.94; N, 4.97. Found: C, 51.77; H, 5.03; N, 4.90.

***tert*-Butyl (6-methoxy-2*H*-chromen-8-yl)carbamate (3h):** Yield: 75% (104 mg). Colourless oil. ^{1}H NMR (200 MHz; $CDCl_3$): δ = 7.61 (d, *J* = 2.6 Hz, 1H), 6.94 (s, 1H), 6.37 (m, 1H), 6.23 (d, *J* = 2.6 Hz, 1H), 5.81 (m, 1H), 4.75 (m, 2H), 3.76 (s, 3H), 1.52 (s, 9H) ppm. ^{13}C NMR (50 MHz; $CDCl_3$) δ = 154.1 (s), 152.6 (s), 135.5 (s), 127.4 (s), 124.8 (d), 122.6 (d), 122.2 (s), 105.8 (d), 103.8 (d), 80.4 (s), 65.6 (t), 55.8 (q), 28.4 (q) ppm. IR: v = 3435, 2911, 2934, 2844, 1727 cm^{-1}. MS (ESI): m/z = 300.1 $[M+Na]^+$. Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 65.16; H, 6.81; N, 5.09.

***tert*-Butyl 3*H*-benzo[*f*]chromen-5-ylcarbamate (3i):** Yield 44% (65 mg). Colourless oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ = 8.43 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 2H), 7.22 (br. s, 1H), 7.13 (dt, *J* = 10.0, 1.6 Hz, 1H), 5.93 (dt, *J* = 10.0, 3.9 Hz, 1H), 4.90 (dd, *J* = 3.9, 1.6 Hz, 2H), 1.60 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$). δ = 152.7 (s), 141.9 (s), 129.5 (s), 128.2 (d), 127.1 (s), 125.6 (s), 124.9 (d), 124.3 (d), 121.1 (d), 120.9 (d), 119.9 (d), 115.0 (s), 114.9 (d), 80.6 (s), 65.6 (t), 28.3 (q) ppm. IR: v = 3300, 2950, 1940, 1720 cm^{-1}. ^{1}MS (ESI): *m/z* = 320.4 $[M+Na]^+$. Anal. calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.92; H, 6.32; N, 4.78.

General procedure for the preparation of *tert*-butyl 2*H*-chromen-8-yl(prop-2-ynyl)carbamates. Synthesis of compounds 4. Under N_2 atmosphere, to a stirred solution of the compound **3** (1 mmol) in THF/DMF (5 mL / 1 mL) cooled at 0 °C, NaH (1.5 eq.) was added and then a solution of propargyl bromide (80% in toluene, 1.5 eq.) was added dropwise. The resulting mixture was stirred at rt 3h. The solvent was removed under reduced pressure, the mixture was extracted with AcOEt (3 x 20 mL) and then washed with brine. The organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluent hexane/AcOEt 5:1).

***tert*-Butyl (2*H*-chromen-8-yl)(prop-2-ynyl)carbamate (4a):** Yield: 72% (205 mg). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.10 (s, 1H), 6.91 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 5.79 (dt, *J* = 9.7, 3.4 Hz, 1H), 4.84 (dd, *J* = 3.3, 1.8 Hz, 2H), 4.30 (br s, 2H), 2.19 (t, *J* = 2.2 Hz, 1H), 1.35 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$). δ = 149.4 (s), 129.4 (d), 128.8 (s), 126.4 (s), 125.5 (d), 124.5 (d), 123.2 (s), 122.0 (d), 120.5 (d), 80.4 (s), 72.0 (s), 71.5 (d), 65.5 (t), 38.3 (t), 28.2 (q) ppm. IR: v = 3291, 2978, 2932, 2121, 1697, 1604, 1583 cm^{-1}. MS (ESI): *m/z* = 308.4 $[M+Na]^+$. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.50; H, 6.68; N, 4.99.

***tert*-Butyl (6-methyl-2*H*-chromen-8-yl)(prop-2-ynyl)carbamate (4d):** Yield 70% (210 mg). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.91 (m, 1H), 6.70 (d, *J* = 1.6 Hz, 1H), 6.38 (d, *J* = 9.8 Hz, 1H), 5.76 (dt, *J* = 9.8, 3.4 Hz, 1H), 4.77 (s, 2H), 4.27 (br s, 2H), 2.24 (s, 3H), 2.17 (t, *J* = 2.2 Hz, 1H), 1.38 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.0 (s), 147.3 (s), 130.2 (s), 129.7 (d), 128.8 (s), 126.3 (d), 124.9 (d), 123.2 (s), 122.3 (d), 80.6 (s), 71.6 (2C, s and d), 65.7 (t), 38.8 (t), 28.5 (q), 20.7 (q) ppm. IR: v = 3290, 2977, 2930, 2120, 1700, 1639, 1588 cm^{-1}. MS (ESI): *m/z* = 322.1 $[M+Na]^+$. Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72,41; H, 7.11; N, 4.69.

***tert*-Butyl (5-methyl-2*H*-chromen-8-yl)(prop-2-ynyl)carbamate (4e):** Yield 88% (263 mg). Colorless oil, (decompose). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.97 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 10 Hz, 1H), 5.83 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.73 (d, *J* = 1.7 Hz, 2H), 4.25 (br. s, 2H), 2.27 (s, 3H), 2.15 (s, 1H), 1.37 (s, 9H) ppm. MS (ESI): *m/z* = 322.4 $[M+Na]^+$.

***tert*-Butyl (6-methoxy-2*H*-chromen-8-yl)(prop-2-ynyl)carbamate (4h):** Yield 72% (227 mg). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.67 (d, *J* = 2.8 Hz, 1H), 6.49 (d, *J* = 2.8 Hz, 1H), 6.39 (d, *J* = 9.6 Hz, 1H), 5.82 (dt, *J* = 9.6, 3.5 Hz, 1H), 4.73 (dd, *J* = 3.2, 1.7 Hz, 2H), 4.29 (br s, 2H), 3.74 (s, 3H), 2.18 (s, 1H), 1.39 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.1 (s), 153.2 (s), 143.4 (s), 129.2 (s), 124.6 (d), 123.6 (s), 123.1 (d), 114.3 (d), 111.0

(d), 80.4 (s), 72.0 (s), 71.5 (d), 65.3 (t), 55.7 (q), 40.6 (t), 28.2 (q) ppm. IR: v = 3291; 2976; 2932; 2119; 1699; 1603; 1588 cm^{-1}. MS (ESI): *m/z* = 338.8 $[M+Na]^+$. Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.72; H, 6.65; N, 4.49.

***tert*-Butyl (3*H*-benzo[*f*]chromen-5-yl)(prop-2-yn-1-yl)carbamate (4i):** yield: 52% (174 mg). Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.92 (d *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.71 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 9.9 Hz, 1H), 5.94 (dt, *J* = 9.9, 3.8 Hz, 1H), 4.86 (dd, *J* = 3.8, 1.5 Hz, 2H), 4.41 (br s, 2H), 2.23 (s, 1H), 1.42 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.7 (s), 148.6 (s), 130.1 (s), 129.1 (s), 128.8 (s), 128.6 (d), 128.2 (d), 126.8 (d), 124.1 (d), 121.3 (d), 121.2 (d), 120.6 (d), 116.7 (s), 80.7 (s), 79.9 (s), 71.9 (d), 65.2 (t), 38.9 (t), 28.3 (q) ppm. IR: v = 3200; 2910; 2110; 1700; 1590 cm^{-1}. (MS (ESI): *m/z* = 358.4 $[M+Na]^+$. Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.42; H, 6.24; N, 4.22.

General procedure for the preparation of *N*-(prop-2-ynyl)-2*H*-chromen-8-amines. Synthesis of compounds 5. To a solution of compound **4** (1 mmol) in DCM (5 mL) cooled at 0 °C, TFA (30 eq.) was added under stirring. The resulting mixture was stirred at rt 1h, then diluted with a Na_2CO_3 solution (60 eq.) and filtered. The filtered was extracted with DCM (3 x 20 mL) and washed with brine. The organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluent hexane/AcOEt 10:1).

***N*-(prop-2-ynyl)-2*H*-chromen-8-amine (5a):** Yield 70% (130 mg). Light yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.85 (t, *J* = 7.8 Hz, 1H), 6.66 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.49 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.43 (dt, *J* = 9.8, 1.8 Hz, 1H), 5.78 (dt, *J* = 9.8, 3.6 Hz, 1H), 4.85 (dd, *J* = 3.6, 1.8 Hz, 2H), 4.11 (br s, 1H), 3.98 (d, *J* = 2.4 Hz, 2H), 2.25 (t, *J* = 2.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.1 (s), 135.5 (s), 125.0 (d), 121.5 (s), 121.4 (d), 121.3 (d), 116.2 (d), 111.7 (d), 81.2 (s), 71.1 (d), 65.5 (t), 33.4 (t) ppm. IR: v = 3288, 3044, 2840, 2113 cm^{-1}. MS (ESI): *m/z* =186.2 $[M+H]^+$. Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.66; H, 5.82; N, 7.45.

***N*-(prop-2-ynyl)-6-methyl-2*H*-chromen-8-amine (5d):** Yield 70% (139 mg). Light yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.45 (s, 1H), 6.38 (d, *J* = 9.8 Hz, 1H), 6.29 (s, 1H), 5.76 (dt, *J* = 9.8, 3.6 Hz, 1H), 4.78 (dd, *J* = 3.6, 1.8 Hz, 2H), 4.26 (s, 1H), 3.95 (d, *J* = 2.2 Hz, 2H), 2.26 (s, 3H), 2.23 (t, *J* = 2.2 Hz, 1H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 139.0 (s), 135.2 (s), 130.6 (s), 125.0 (d), 121.4 (d), 121.3 (s), 116.5 (d), 112.4 (d), 81.2 (s), 71.1 (d), 65.4 (t), 33.4 (t), 21.1 (q) ppm. IR: v = 3288, 2917, 2848, 2175 cm^{-1}. MS (ESI): *m/z* = 200.1 $[M+H]^+$. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.40; H, 6.44; N, 7.11.

***N*-(prop-2-ynyl)-5-methyl-2*H*-chromen-8-amine (5e):** Yield 93% (185 mg). Brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.66 (d, *J* = 8.1 Hz, 1H), 6.60 (dt, *J* = 10.0, 1.8 Hz, 1H), 6.55 (d, *J* = 8.1 Hz, 1H), 5.82 (dt, *J* = 10.0, 3.6 Hz, 1H), 4.77 (dd, *J* = 3.6, 1.8 Hz, 2H), 4.04 (br. s, 1H), 3.93 (d, *J* = 2.4 Hz, 2H), 2.25 (s, 3H); 2.22 (t, *J* = 2.4 Hz, 1H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 141.6 (s), 133.7 (s), 123.6 (s), 122.5 (d), 122.4 (d), 121.1 (d), 120.4 (s), 111.6 (d), 81.3 (s), 71.1 (t), 64.8 (t), 33.7 (d), 17.8 (q) ppm. IR: v = 3290, 2914, 2851, 2178 cm^{-1}. MS (ESI): m/z = 222.3 $[M+Na]^+$. Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.42; H, 6.45; N, 7.10.

***N*-(prop-2-ynyl)-6-methoxy-2*H*-chromen-8-amine (5h):** Yield 75% (161 mg). Light yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.39 (dt, *J* = 9.8, 1.8 Hz, 1H), 6.26 (d, *J* = 2.7 Hz, 1H), 6.03 (d, *J* = 2.7 Hz, 1H), 5.81 (dt, *J* = 9.8, 3.6 Hz, 1H), 4.76 (dd, *J* = 3.6, 1.8 Hz, 2H) 4.35 (br s, 1H), 3.95 (d, *J* = 2.4 Hz, 2H), 3.78 (s, 3H), 2.24 (t, *J* = 2.4 Hz, 1H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.6 (s), 136.5 (s), 135.4 (s), 125.2 (d), 122.2 (d), 121.8 (s), 99.5 (d), 99.1 (d), 80.9 (s), 71.3 (d), 65.4 (t), 55.6 (q), 33.3 (t) ppm. IR: v = 3283, 3198, 2848, 2113 cm^{-1}.MS (ESI): *m/z* = 238.2 $[M+Na]^+$. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.68, H, 6.30; N, 6.61.

***N*-(prop-2-yn-1-yl)-3*H*-benzo[*f*]chromen-5-amine (5i):** yield 70% (165 mg). Light yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.0 Hz, 1H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.29 (m, 2H), 7.12 (dt, *J* = 10.0, 1.7 Hz, 1H), 6.87 (s, 1H), 5.91 (dt, *J* = 10.0, 3.8 Hz, 1H), 4.88 (dd, *J* = 3.8, 1.7 Hz, 2H), 4.63 (br s, 1H), 4.10 (d, *J* = 2.4 Hz, 2H), 2.25 (t, *J* = 2.4 Hz, 1H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 142.6 (s), 135.9 (s), 130.2 (s), 126.5 (d), 124.1 (d), 123.9 (s), 123.0 (d), 121.3 (d), 121.0 (d), 119.7 (d), 114.8 (s), 105.8 (d), 80.6 (s), 71.3 (d), 65.4 (t), 33.1 (t) ppm. IR: v = 3310, 2910, 2100 cm^{-1}. MS (ESI): *m/z* = 258,3 $[M+Na]^+$. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.52; H, 5.62; N, 5.92.

General procedure for the preparation of pyrano[3,2-*h*]quinolines 6. Compound **5** (1 mmol) was added to a suspension of $Cu(OTf)_2$ (0.2 eq.) in DCE (20 mL), under N_2. The mixture was heated at 80 °C under stirring for 5h, then filtered and extracted with DCM (3 x 20 mL) and washed with brine. The organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluent hexane/AcOEt 7:1 to 1:2).

2*H*-Pyrano[3,2-*h*]quinoline (6a): Yield 60% (110 mg). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.84 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.29 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.50 (dt, *J* = 9.8, 1.8 Hz, 1H), 5.85 (dt, *J* = 9.8, 3.6 Hz, 1H), 5.12 (dd, *J* = 3.6, 1.9 Hz, 2H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 150.0 (d); 149.6 (s); 139.3 (s); 136.2 (d); 129.5 (s); 125.6 (d); 124.8 (d); 122.3 (d); 121.4 (d); 120.6 (s); 120.0 (d); 66.7 (t) ppm. IR: v = 2916, 2849, 2316 cm^{-1}. MS (ESI): *m/z* = 184.2 $[M+H]^+$. Anal. Calcd for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65: Found: C, 78.80; H, 5.02; N, 7.63.

6-Methyl-2*H*-pyrano[3,2-*h*]quinoline (6d): Yield 47% (93 mg). Brownish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.87 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.35 (dd, *J* = 8.2, 3.7 Hz, 1H), 7.00 (s, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 5.10 (s, 2H), 2.54 (s, 3H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.3 (d), 147.8 (s), 139.4 (s), 132.5 (d), 128.3 (s), 126.1 (s), 125.6 (d), 124.6 (d), 122.2 (d), 120.7 (d), 119.8 (s), 66.3 (t), 17.9 (q) ppm. IR: v = 2919, 2850 cm^{-1}. MS (ESI): *m/z* = 198.2 $[M+H]^+$. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.37; H, 5.71; N, 6.98.

5-Methyl-2*H*-pyrano[3,2-*h*]quinoline (6e): Yield 55% (108 mg). yellowish oil. ^{1}H-NMR (300 MHz, CD_3OD): δ = 8.63 (dd, *J* = 4.2, 1.2 Hz, 1H), 8.06 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.36 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.16 (d, *J* = 0.6 Hz, 1H), 6.71 (dt, *J* = 9.9, 1.8 Hz, 1H), 5.99 (dt, *J* = 9.9, 3.6 Hz, 1H), 4.94 (dd, *J* = 3.6, 1.8 Hz, 2H), 2.40 (d, *J* = 0.9 Hz, 3H) ppm. ^{13}C-NMR (75 MHz, CD_3OD): δ = 148.6 (s), 148.0 (d), 137.3 (s), 135.8 (d), 133.4 (s), 129.0 (s), 122.2 (d), 121.4 (d), 121.2 (d), 120.6 (s), 119.4 (d), 64.9 (t), 17.8 (q) ppm. IR: v = 2923, 2847 cm^{-1}. MS (ESI): *m/z* = 198.2 $[M+H]^+$. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.39; H, 5.69; N, 6.71.

6-Methoxy-2*H*-pyrano[3,2-*h*]quinoline (6h): Yield 40% (85 mg). Light yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.87 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.45 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.31 (dd, *J* = 8.5, 4.2 Hz, 1H), 6.51 (s, 1H), 6.48 (dd, J = 9.7, 2.6 Hz, 1H), 5.90 (dt, *J* = 9.7, 3.6 Hz, 1H), 5.03 (dd, *J* = 3.6, 2.6 Hz, 2H), 3.93 (s, 3H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 150.0 (d), 148.8 (s); 143.0 (s), 139.1 (s), 131.1 (d), 124.9 (d), 122.8 (d), 121.3 (s), 120.3 (d), 120.1 (s), 103.2 (d), 66.0 (t), 55.8 (q) ppm. IR: v = 2917, 2849 cm^{-1}. MS (ESI): *m/z* = 214.3 $[M+H]^+$. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.34; H, 5.33; N, 6.50.

2*H*-benzo[f]pyrano[3,2-*h*]quinoline (6i): yield 45% (105 mg). Light yellow oil. ^{1}H-NMR (300 MHz, CD_3OD): δ = 9.17 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.86 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.71 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.68 (m, 3H), 7.29 (dt, *J* = 10.0, 1.8 Hz, 1H), 6.18 (dt, *J* = 10.0, 3.9 Hz, 1H), 5.04 (dd, *J* = 3.9, 1.8 Hz, 2H) ppm. ^{13}C-NMR (75 MHz, CD_3OD): δ = 148.5 (2C, s and d), 139.2 (s), 131.7 (d), 127.9 (s), 125.1 (d), 122.9 (d), 122.5 (d), 122.2 (s), 122.1 (s), 122.0 (d), 121.9 (2C, d), 120.6 (s), 120.5 (d), 65.2 (t), ppm. IR: v = 2928, 2841 cm^{-1}. MS (ESI): m/z = 256.3 $[M+Na]^+$. Anal. Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.00. Found: C, 82.22; H, 4.85; N, 6.12.

Synthesis of *tert*-Butyl (prop-2-yn-1-yl)-2-(prop-2-yn-1-yloxy)-phenyl)carbamate (7a): Under N_2 atmosphere, to a stirred solution of *tert*-butyl (2-hydroxyphenyl)carbamate (1g, 4.78 mmol) in THF/DMF (25 mL / 5 mL) cooled at 0 °C, NaH (2 eq.) was added and then a solution of propargyl bromide (80% in toluene, 1.3 eq.) was added dropwise. The resulting mixture was stirred at rt 3h. The solvent was removed under reduced pressure, the mixture was extracted with AcOEt (3 x 20 mL) and then washed with brine. The organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluent hexane/AcOEt 7:1). Yield: 90% (1.23 g). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.26 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.98 (t, *J* = 8.1 Hz, 1H), 4.70 (d, *J* = 2.4 Hz, 2H) 4.27 (br s, 2H), 2.49 (t, *J* = 2.4 Hz, 1H), 2.16 (s, 1H), 1.35 (s, 9H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 154.9 (s), 153.3 (s), 131.0 (s), 130.3 (d), 128.5 (d), 121.5 (d), 113.2 (d), 80.6 (s), 80.2 (s), 78.6 (s), 75.9 (d), 71.8 (d), 56.2 (t), 38.7 (t), 28.4 (q) ppm. IR: v = 3292; 2978; 2930; 2121; 1699; 1598 cm^{-1}. MS (ESI): *m/z* = 308.3 $[M+Na]^+$. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.80; H, 6.68, N, 4.96.

Synthesis of N-(prop-2-yn-1-yl)-2-(prop-2-yn-1-yloxy)-aniline (7b): To a solution of compound **7a** (1g, 3.5 mmol) in DCM (8 mL), cooled at 0°C, TFA (8 mL, 30 eq.) was added under stirring. The resulting mixture was stirred at rt 1h, then diluted with a Na_2CO_3 solution (60 eq.) and filtered. The filtered was extracted with DCM (3 x 20 mL) and washed with brine. The organic phases were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluent hexane/AcOEt 7:1). Yield: 87% (0.56 g). Colourless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.95 (m, 2H), 6.75 (m, 2H), 4.72 (d, *J* = 2.4 Hz, 2H), 4.47 (br s, 1H), 3.98 (d, *J* = 2.4 Hz, 2H), 2.53 (t, *J* = 2.4 Hz, 1H), 2.22 (t, *J* = 2.4 Hz, 1H) ppm. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 145.3 (s); 137.2 (s); 122.3 (d); 117.6 (d); 111.7 (d); 111.2 (d); 81.0 (s); 78.6 (s); 75.6 (d); 71.2 (d); 56.4 (t); 33.2 (t) ppm. IR: v = 3284, 3261, 2914, 2868, 2130, 2110 cm^{-1}. MS (ESI): *m/z* = 186.2 $[M+H]^+$. Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.79; H, 6.01, N, 7.52.

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Keywords: hydroamination • hydroarylation • Pd-catalysis • Pt-catalysis • catalyst-controlled divergent synthesis

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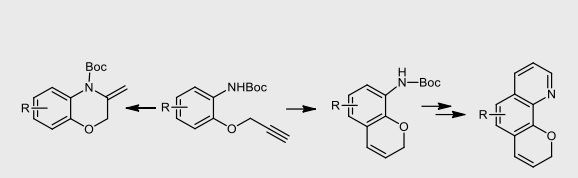

Divergent reactivity of *O*-propargyl-2-aminophenols under palladium-and platinum catalysis is reported, resulting in the intramolecular hydroamination and hydroarylation processes. The C-N and C-C bonds formation afford 1,4-benzoxazines and benzopyrans. The subsequent functionalization of the benzopyran scaffold provides a new synthesis of the tricyclic pyrano[3,2-*h*]quinolines.

Key Topic hydroamination, hydroarylation

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