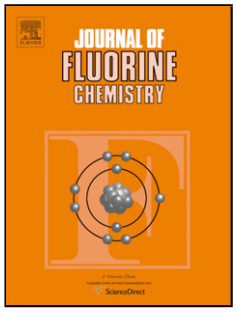

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Transformation of fluorinated 2-alkynylanilines by various catalytic systems

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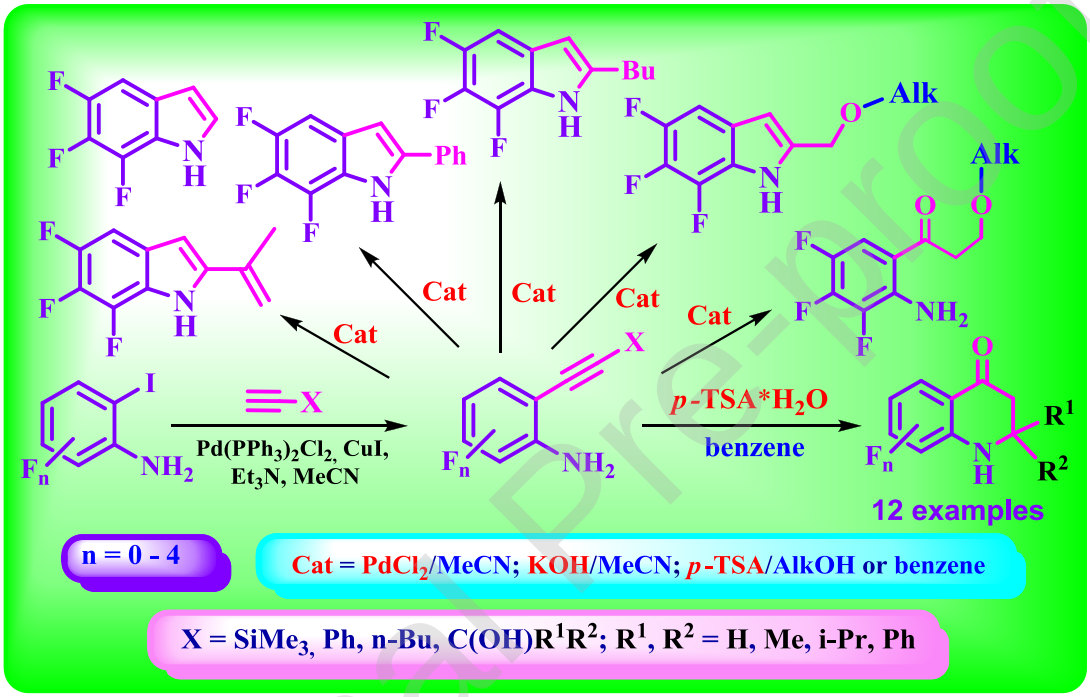
Graphical abstract



Highlights

- Catalytic modification of 2-alkynylanilines into 5-and 6-member azaheterocycles
- Selective *p*-TSA•H_2O - induced *one pot* hydration – cyclisation process in benzene
- Efficient synthesis of fluorinated 2-R-indoles by action of $PdCl_2$ in MeCN

A B S T R A C T

Simple and efficient approaches to the synthesis of fluorinated benzoazaheterocycles with good yields are reported. Firstly a series of polyfluorinated 2-alkynylanilines – the versatile building

blocks – was synthesized by the Sonogashira reaction of *o*-iodoaniline with terminal alkynes. Then the transformations of the obtained 2,3,4-trifluo-6-alkynilanilines in the presence of KOH or $PdCl_2$ in MeCN, and in the presence of monohydrate of *p*-toluenesulfonic acid (*p*-TSA•H_2O) in MeOH, EtOH or benzene were investigated. It was found that Ph- and *n*-Bu-containing alkynylanilines by action of $PdCl_2$ in MeCN underwent an intramolecular cyclization reaction to produce the corresponding indoles in high yields. The reaction of KOH with alkynes containing the tertiary alcohol function at the triple bond produced the unsubstituted on the pyrrole ring indole. It was found that flu
orinated 2-alkynilanilines can be transformated into indoles, 2-arylketones and 2,3-dihydroquinolines by action of *p*-TSA•H_2O in boiling alcohols, depending on the substituent at the triple bond. The use of benzene as a solvent in the reaction of *p*-TSA•H_2O with polyfluorinated alkynes, bearing an alcohol group resulted in representative series of 2,3-dihydroquinolinones containing a substituents R^1 and R^2 in the 2nd position of their structure (R = H, H; Me, Me; H, *i*-Pr; H, Ph).

Keywords Cross-coupling, fluorinated alkynes, triple bond hydration, fluorinated heterocycles, 2,3-dihydroquinolinones

1. Introduction

Fluorine-containing compounds are interesting to organic chemists because they have found a wide range of applications in pharmaceuticals, medicine, agrochemicals, and materials science. The efforts of researchers are directed at finding new synthetic strategies for fluorine incorporation into organic molecules [1] and at demonstrating the unique ability of fluorine to modulate their structural, physical, and biological properties [2].

Functionalisation of alkynes is a fundamental and important class of reaction in organic synthesis. Alkynes have been extensively used as important building blocks and versatile precursors in synthesis of many important products [3–6] such as alkenes [7], alcohols [8–10], amines [10], α-amino ketones [11], 1,2-diketones [12], amides [13], nitriles [14], cyclic acetals [15], ynamides [16], enynes [17], ketones [18–20], arene derivatives and heterocycles [4,21]. Among these important applications, hydration and heterocyclisation of 2-akynylanilines are practical and atom-economical methods for the synthesis of ketones and azaheterocycles, which are basic reactions in alkyne chemistry. The use of fluorinated compounds in these reactions opens up broad prospects for obtaining practically valuable potentially biologically active substances [22–29].

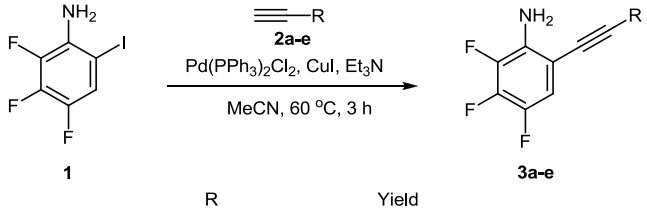
In this regard, the synthesis of new polyfluorinated arylacetylenes and the search for effective reaction systems for their transformation into potentially biologically active compounds is a worthwhile research task. The aim of our work is to study the behavior of fluorinated 2-alkynylanilines under the action of a transition metal salt ($PdCl_2$) as well as under alkaline conditions (KOH) and acid catalysis (*p*-TSA•H_2O) to develop effective approaches to the synthesis of azaheterocycles.

2. Results and discussion

2.1. The synthesis of the starting compounds

At the first stage 2,3,4-trifluoro-6-iodoaniline (**1**) [22] was cross-coupled with acetylenes **2a-e** in MeCN in the presence of $Pd(PPh_3)_2Cl_2$ (5 mol %), CuI (10 mol %) and Et_3N as the catalysts to obtain 2-alkynylanilines **3a–e** in 78–99% yields (Scheme 1) by analogy with the previously described procedure [30].

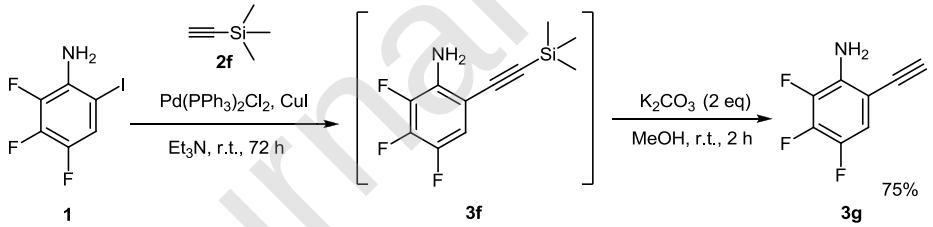
Scheme 1. Synthesis of polyfluorinated arylacetylenes **3a–e**.



	R	Yield
a	Ph	86%
b	*n*-Bu	82%
c	CH_2OH	78%
d	$CH(OH)CH(CH_3)_2$	99%
e	$C(CH_3)_2OH$	82%

In addition, 6-ethynyl-2,3,4-trifluoroaniline (**3g**) was synthesized as described in the literature [22,31] with some modifications. The cross-coupling reaction of iodaniline **1** with trimethylsilylacetylene **2f** was carried out in a similar catalytic system in triethylamine as a solvent at room temperature for 72 h and led to the formation of the previously known [22] silyl derivative **3f** (Scheme 2). The crude product was next introduced into the reaction with K_2CO_3 in methanol solution at r.t. to obtain the desired ethynylaniline **3g** (Scheme 2).

Scheme 2. Synthesis of polyfluorinated arylacetylene **3g**.



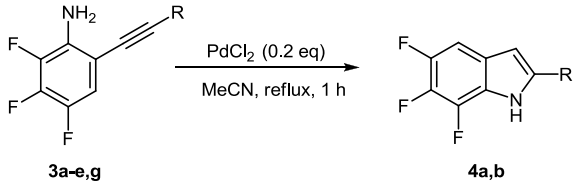
Prepared 2-alkynylanilines **3a–g**, as base compounds, were then subjected to various transformations under different reaction conditions, in accordance with the aim of this study.

2.2. Analysis of the reactivity of 2-alkynylanilines in the presence of $PdCl_2$

Interaction of compounds **3** with transition metal salt ($PdCl_2$) was implemented by refluxing in an acetonitrile solution according to a previously reported method [27]. It was found that 2-alkynylanilins **3a** and **3b** are transformed into the corresponding indoles **4a** and **4b** within 1 h (Scheme 3). 5,6,7-Trifluoro-2-phenyl-1*H*-indole (**4a**) and 5,6,7-trifluoro-2-butyl-1*H*-indole (**4b**) were isolated by thin-layer chromatography (TLC) in 96% and 99% yields, respectively. In contrast, the use of the $PdCl_2$/MeCN catalytic system with compounds **3c–e,g** was not effective.

In these cases, the formation of multicomponent mixtures of products was observed, the separation of which by the TLC method was not successful (Scheme 3). It should be noted that conversion degrees of starting 2-alkynylanilines **3** in all cases were 100%. The results of our experiments are in good agreement with the literature data on the effect of transition metal salts on the cyclization process: the formation of a complex mixture was observed by action of $PtCl_4$ on *o*-alkynylanilines containing primary alcohol function [32].

Scheme 3. Reactivity of polyfluorinated arylacetylenes **3** by action of $PdCl_2$ in MeCN.



3a-e,g **4a,b**

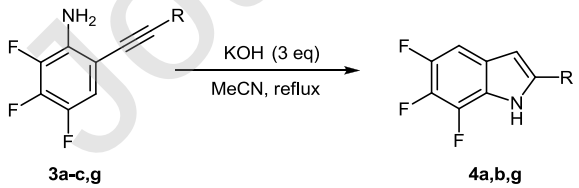
	R	Yield
a	Ph	96%
b	*n*-Bu	99%
c	CH_2OH	multicomponent mixture of products
d	$CH(OH)CH(CH_3)_2$	
e	$C(CH_3)_2OH$	
g	H	

Thus, it was found that arylacetylenes **3** with phenyl (**a**) and butyl (**b**) fragments at the triple bond become selectively transformed to the corresponding indoles by action of $PdCl_2$ in boiling acetonitrile, whereas other studied substrates gave a range of products with unidentified structure.

2.3. Evaluation of the reactivity of 2-alkynylanilines in the presence of KOH

At the next stage the reactions behavior of **3** in an alkaline medium was investigated. It was shown that reflux of arylacetylene **3a** in acetonitrile solution with 3 equivalents of KOH leads to obtaining of indole **4a** in 73% yield (Scheme 4). The required reaction time was 14 h. The reactions were terminated after disappearance of ^{19}F NMR signals belonging to **3** in the reaction mixture.

Scheme 4. Reactivity of polyfluorinated arylacetylenes **3** by action of KOH in MeCN.



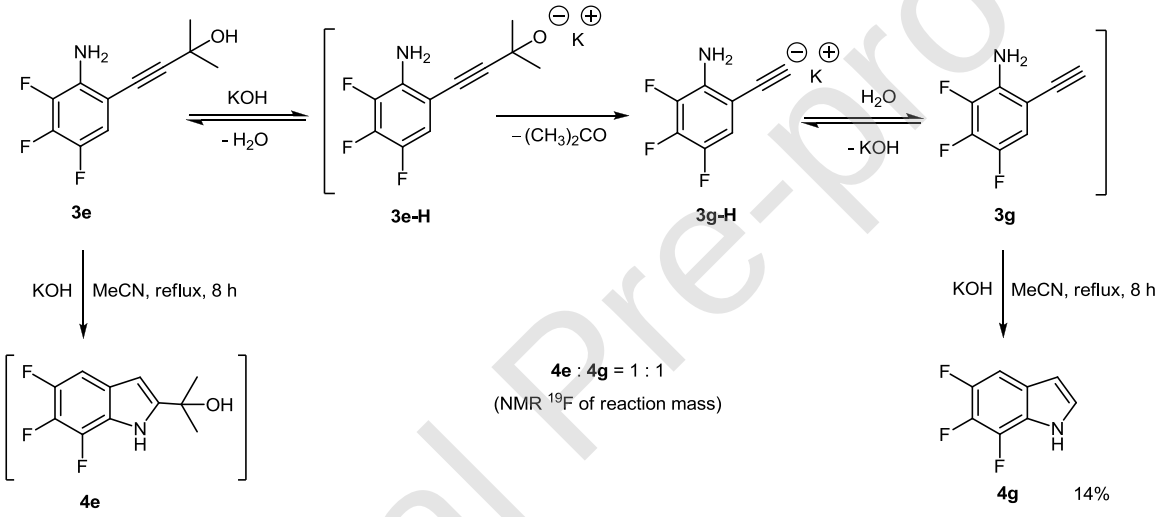
3a-c,g **4a,b,g**

	R	t	Yield
a	Ph	14 h	73%
b	*n*-Bu	9 h	86%
c	CH_2OH	14 h	thickening
g	H	4 h	trice

Arylacetylene **3b** underwent a similar transformation within 9 h. Indole **4b** was isolated by TLC in 86% yield (Scheme 4). The transformation of ethynylaniline **3g** into indole **4g** (unsubstituted on the pyrrole ring) proceeded under the action of KOH with substantial thickening of the reaction mass, resulting in a low yield of the reaction product. It is possible that the additional cause of this low yield of **4g** is the high volatility of this compound. In the case of reaction of compound **3c** with KOH, no individual products could be isolated from the reaction mixture (Scheme 4).

Arylacetylene **3e** in the presence of KOH in MeCN medium gave (besides indole **4e**, supposedly) indole **4g** unsubstituted on the pyrrole ring (Scheme 5). The precursor of **4g** is most likely arylacetylene **3g**, derived from the starting aniline **3e** via the retro-Favorsky reaction. The formation of 2-ethynylanilines has been observed previously in the reaction of polyfluorinated analogs of arylacetylene **3e** in boiling benzene [30] and MeCN [26] in the presence of KOH earlier.

Scheme 5. Reactivity of arylacetylene **3e** in MeCN in the presence of KOH.

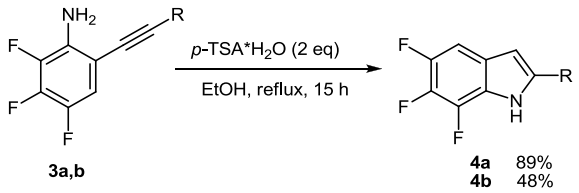


Thus, it was found that polyfluorinated arylacetylenes **3a**,**b**,**e**,**g** are converted in the presence of KOH into indoles. Isolation of reaction products of primary carbinol **3c** was not successful. In the case of the tertiary carbinol **3e**, the reaction system based on KOH may be used to obtain indole **4g** unsubstituted on the pyrrole ring.

2.4. Investigation of the reactivity of 2-alkynylanilines under the action of p-TSA•H_2O in the aliphatic alcohols and benzene medium

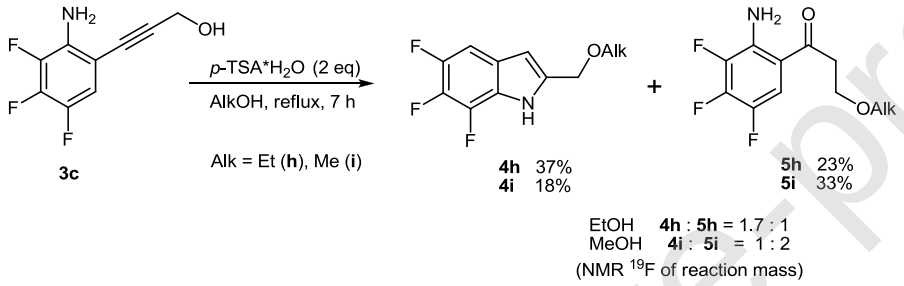
Then we turned to the analysis of the acidic catalytic system, namely, the use of *p*-toluene sulfonic acid monohydrate in boiling ethanol. It was found that alkynes **3a** and **3b** by action of two equivalents of *p*-TSA•H_2O in EtOH for 15 h form the same heterocyclization products **4a** and **4b** as in the case of $PdCl_2$ and KOH in MeCN (Scheme 6).

Scheme 6. Reactivity of polyfluorinated arylacetylenes **3a**,**b** in EtOH in the presence of *p*-TSA•H_2O.



In the case of compound **3c**, the reaction initiated by *p*-TSA•H_2O in EtOH led to the formation of indole **4h** (R = CH_2OEt) isolated in 37% yield. Nevertheless, this was not the only product of 2-alkynylaniline transformation. There was also the formation of ketone **5h** as a result of the triple bond hydration reaction in compound **3c**. In addition, all reaction products with the help of the solvent (EtOH) were transformed into ethers (Scheme 7). In the ^{19}F NMR spectrum of the reaction mixture, the molar ratio of the products **4h** and **5h** was 1.7 : 1.

Scheme 7. Reactivity of **3c** by action of *p*-TSA•H_2O in EtOH and MeOH.

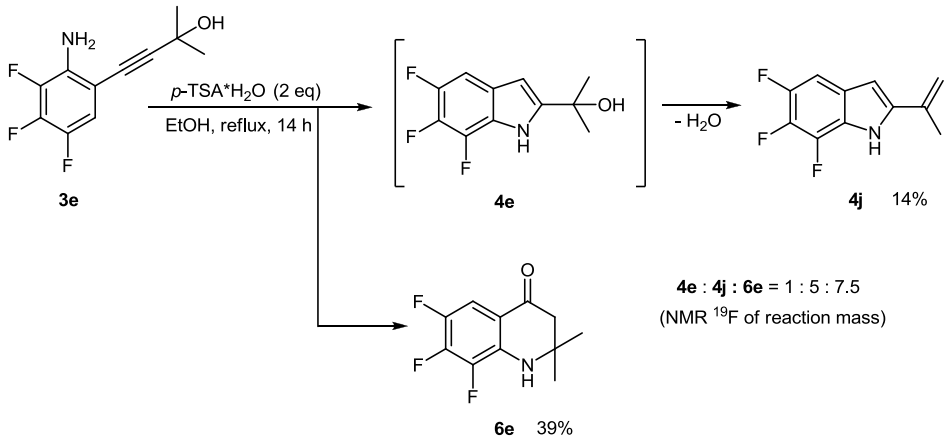


When methanol was used as a solvent (instead of ethanol) in the reaction of **3c** with *p*-TSA•H_2O the qualitative composition of the reaction products remained the same, but the ratio of indole to ketone changed to the opposite : from 1.7 : 1 to 1 : 2. As a result, corresponding indole **4i** (R = CH_2OMe) and ketone **5i** were isolated in 18% and 33% yields, respectively (Scheme 7).

Thus, it was found that the change in the polarity of the solvent affects the ratio of the rates of competing reactions (cyclization and hydration of triple bond). This conclusion is consistent with the literature data [28].

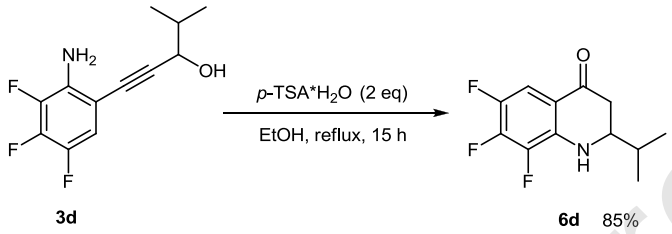
The interaction of **3e** with *p*-TSA•H_2O in boiling ethanol led to the formation of indole **4j** and the cyclic product 2,2-dimethyl-2,3-dihydroquinoline-4(1*H*)-one **6e**, which is a consequence of the triple bond hydration reaction (Scheme 8). A precursor of indole **4j**, apparently, was indole **4e**, which was observed in the ^{19}F NMR spectra of the reaction mass, but failed to be isolated by chromatography. The molar ratio of **4e** : **4j** : **6e** in the reaction mass was 1 : 5 : 7.5. Reaction products **4j** and **6e** were isolated in 14% end 39% yields, respectively (Scheme 8).

Scheme 8. Reactivity of **3e** by action of *p*-TSA•H_2O in EtOH.



Alkyne **3d** showed an even greater propensity (in comparison with **3e**) for hydration of the triple bond by action of *p*-TSA•H_2O in boiling ethanol: after 25 h it was completely transformed into 2,3-dihydroquinolinones **6d** and was isolated in a 85% yield (Scheme 9).

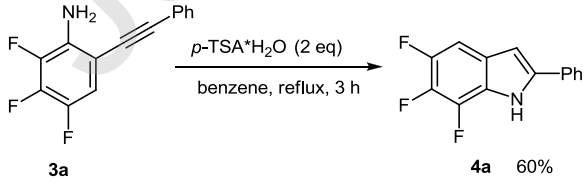
Scheme 9. Reactivity of **3d** under the action of *p*-TSA•H_2O in EtOH.



Thus, alkynes **3** in the presence of *p*-TSA•H_2O in boiling alcohols can be converted into indoles **4**, 2-arylketones **5**, and 2,3-dihydroquinolinones **6**, depending on the substituent R at the triple bond. For substrates with Ph and *n*-Bu groups (R), indoles were obtained as stand-alone products, whereas for alkynes containing an alcohol function in the substituent (R = $C(CH_3)_2OH$, CH_2OH and $CH(OH)CH(CH_3)_2$), triple bond hydration products were also observed.

Further analysis of the reactivity of alkynes **3** in the presence of *p*-TSA•H_2O was carried out in a solution of benzene, which is a less polar media than aliphatic alcohols. It was found that arylacetylene **3a** by action of *p*-TSA•H_2O in boiling benzene underwent an intramolecular cyclization reaction with the formation of indole **4a** (Scheme 10).

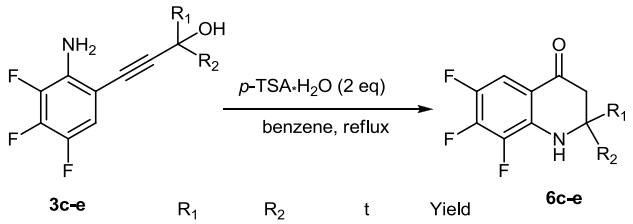
Scheme 10. Reactivity of **3a** by action of *p*-TSA•H_2O in benzene.



In the case of arylacetylenes **3d** and **3e**, the reaction proceeded along the path of formation of 2,3-dihydroquinolinones **6d** and **6e**, isolated by TLC in 81 and 75% yields, respectively (Scheme 11). According to the ^{19}F NMR spectra of the reaction mixtures,

byproducts containing an indole framework were present only in trace amounts. Therefore, the replacement of the alcohol with benzene as a solvent led to that the formation of cyclic ketones became the predominant direction of the hydration reaction. This statement is especially clearly confirmed by the transformation of arylacetylene **3c** by *p*-TSA•H_2O into 2,3-dihydroquinolinone **6c** in benzene (Scheme 11). It is noteworthy that in ethyl and methyl alcohols, **3c** reacted with *p*-TSA•H_2O thereby producing a mixture of indoles **4** and acyclic ketones **5** (Scheme 7). The yield of the product **6c** (R_1, R_2 = H) is less than that for **6d** (R_1 = H; R_2 = *i*-Pr) and **6e** (R_1, R_2 = Me). However, product **6c** was not obtained at all when we varied the reaction conditions and used other solvents such as dioxane, dichloroethane, methylene chloride or lowered the reaction temperature.

Scheme 11. Reactivity of **3c–e** by action of *p*-TSA•H_2O in benzene.



3c-e **6c-e**

	R_1	R_2	t	Yield
c	H	H	1 h	40%
d	H	i-Pr	2 h	81%
e	Me	Me	2.5 h	75%

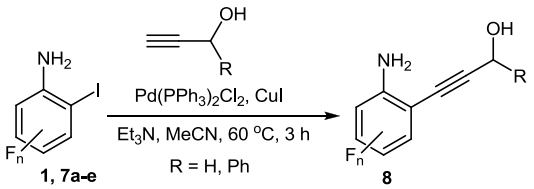
Thus, the use of benzene as a solvent instead of aliphatic alcohol in the reaction of alkynes containing an alcohol group with *p*-TSA•H_2O is more appropriate to produce 2,3-dihydroquinolinones **6**.

To study the scope of this method of 2,3-dihydroquinolinones synthesis, we expanded the range of fluorinated alkynes introduced into these reaction, and also investigated the reactivity of their non-fluorinated analog. We also replaced one of the substituents at the triple bond of alkyne on the aromatic fragment (R = Ph).

2.5. The synthesis of the 2,3-dihydroquinolines from 2-alkynylanilines containing an alcohol group in the substituent at the triple bond by action of p-TSA•H_2O in benzene

The starting materials for this study (a representative series of 2-alkynylanilines **8a**–**i** with different fluorine contents) were prepared *via* the Sonogashira cross-coupling of *o*-iodoanilines **1** and **7a**–e [30] with terminal acetylenes containing an alcohol function (Table 1). Target compounds were obtained in good to excellent yields. Further, the triple bond in arylacetylenes **8** was subjected to a hydration reaction by action of *p*-TSA•H_2O in benzene (Table 2).

Table 1. Synthesis of 2-alkynylanilines **8**.



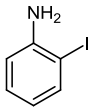
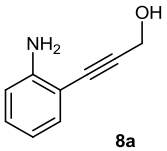
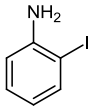
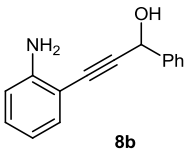
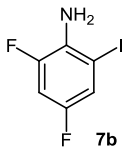
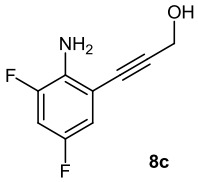
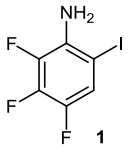
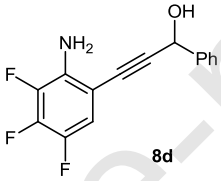
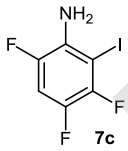
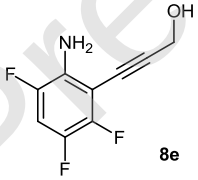
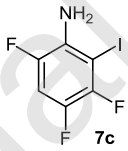
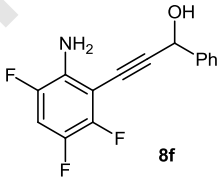
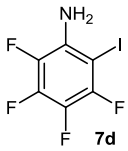
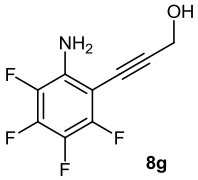
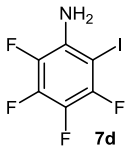
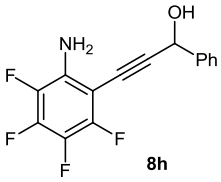
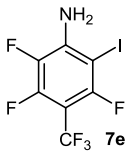
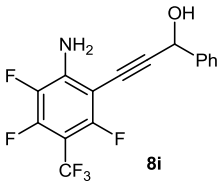
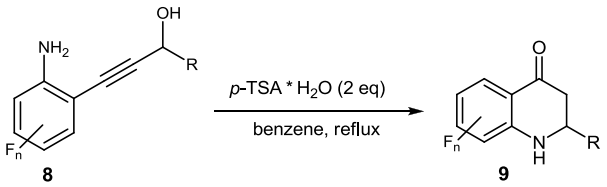
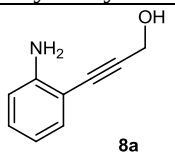
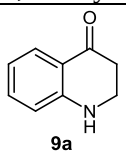
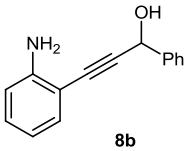
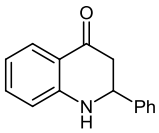
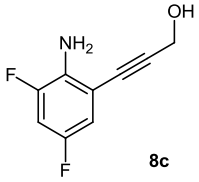
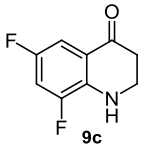
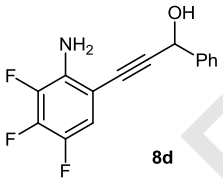
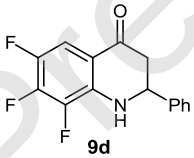
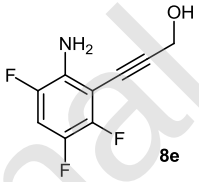
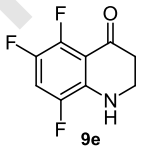
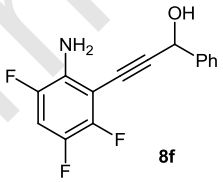
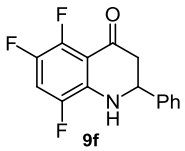
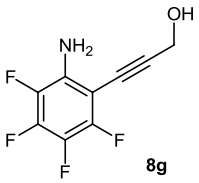
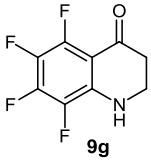
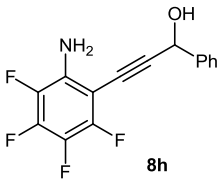
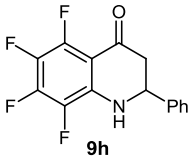
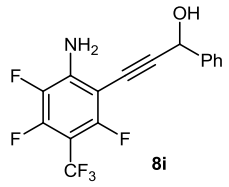
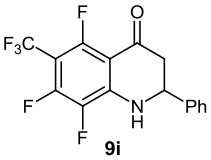
Entry	Iodoaniline **7**	Arylacetylene **8**	Yield (%)
1	 **7a**	 **8a**	75
2	 **7a**	 **8b**	96
3	 **7b**	 **8c**	68
4	 **1**	 **8d**	93
5	 **7c**	 **8e**	94
6	 **7c**	 **8f**	60
7	 **7d**	 **8g**	85
8	 **7d**	 **8h**	84
9	 **7e**	 **8i**	98

Table 2. Synthesis of 2,3-dihydroquinolinones **9**.



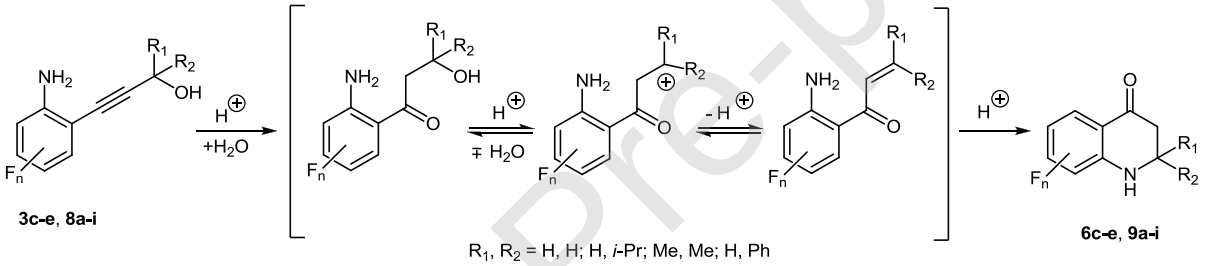
Entry	Arylacetylene **8**	2,3-Dihydroquinolinone **9**	Yield (%)
1	 **8a**	 **9a**	10
2	 **8b**	 **9b**	67
3	 **8c**	 **9c**	9
4	 **8d**	 **9d**	90
5	 **8e**	 **9e**	14
6	 **8f**	 **9f**	85
7	 **8g**	 **9g**	15
8	 **8h**	 **9h**	89

9	 **8i**	 **9i**	54

From the data of Table 2 it follows that the reaction products in all cases were exclusively 2,3-dihydroquinolinones. That means, the proposed approach can be considered as universal and applied to both fluorinated and non-fluorinated substrates. However, the yields of products, unsubstituted at the 2 position are extremely low due to the considerable thickening of the reaction mass (Table 2, entries 1,3,5,7).

The proposed mechanism of the 2,3-dihydroquinolinones **6** and **9** formation (Scheme 12) includes a sequence of hydration, dehydration, and intramolecular cyclization reactions that is consistent with the literature data [25]. It is obvious that R_1 and R_2 = Ph and Alk facilitate the reaction, due to the stabilization of the carbocation in compared with $R_1 = R_2 = H$.

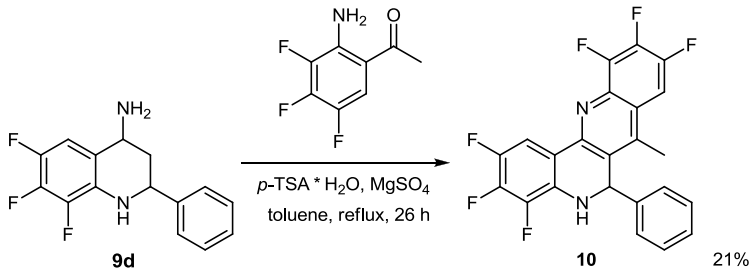
Scheme 12. The proposed mechanism of 2,3-dihydroquinolinones formation in presence of *p*-TSA•H_2O.



Thus, this method is poorly applicable to primary alcohols and for the effective synthesis of 2,3-unsubstituted 2,3-dihydroquinolinones, it seems that preliminary structural modification of substrates is necessary, for example, protection of the amino group [33].

Thus, we propose a simple and convenient *one pot* way to obtain 2-phenyl-substituted 2,3-dihydroquinolinones based on the corresponding alkynes transformation in presence of *p*-TSA•H_2O in benzene. These compounds can not only be of independent value as potentially biologically active substances, but also be precursors of more complex heterocyclic ensembles, for example, derivatives of quinoline. Thus, we obtained a new polyfluorinated heterocycle **10**, which is a structural analogue of compounds that showed promising single-digit micromolar antiproliferative potency toward human cancer cells [23].

Scheme 13. Synthesis of polyfluorinated azaheterocycle **10** from 2,3-dihydroquinolinone **9d** and 1-(2-amino-3,4,5-trifluorophenyl)ethanone in presence of *p*-TSA•H_2O.



3. Conclusion

In summary, we described a simple and efficient protocols for the synthesis of polyfluorinated 2,3-dihydroquinolinones and indoles: biologically important aza-heterocyclic scaffolds. In the course of this study, we synthesized previously unknown fluorinated 2-alkynylanilines and investigated their reactivity in different reaction systems. It was demonstrated that in MeCN by action of $PdCl_2$, the Ph- and *n*-Bu-containing 2-alkynylanilines undergo the intramolecular cyclization reaction producing the corresponding indoles in high yields. The reaction of substrate, containing the tertiary alcohol function in the substituent at the triple bond, with KOH in MeCN was employed for the synthesis of a fluorinated indole unsubstituted on the pyrrole ring. It was revealed that fluorinated 2-alkynylanilines are transformed by *p*-TSA•H_2O into indoles, 2,3-dihydroquinolinones and 2-arylketones, depending on the solvent and nature of substituent R at the triple bond. When benzene serves as a solvent in the reaction of alcohol group-containing alkynes with *p*-TSA•H_2O, selective production of 2,3-dihydroquinolinones is observed. So we have discovered a simple, convenient and universals *one pot* method for synthesis of 2,3-dihydroquinolinones containing an alkyl or phenyl group in 2 position in good yields. The reaction system based on *p*-TSA•H_2O has a number of obvious advantages. Accordingly, in terms of cost, it is much more economical than a palladium catalyst and more environmentally friendly than potassium hydroxide. From the standpoint of synthetic possibilities, this strategy enables to obtain not only indoles, but also cyclic and acyclic carbonyl compounds.

4. Experimental section

4.1 General

All solvents were purified using standard procedures. Toluene was kept over CaH_2 before use. The starting 2,3,4-trifluoro-6-iodoaniline (**1**) was synthesized according to previously described methods [22]. Other chemicals were obtained from commercial sources and were used without further purification. Preparative TLC was performed on Merck precoated silica gel 60 PF254 containing gypsum. Visualization of the developed chromatograms was performed by UV light. To obtain analytically pure samples, the solid synthesized compounds were crystallized from hexane.

NMR spectra were recorded on a Bruker Avance-300 (300.13 MHz for ^1H and 282.37 MHz for ^{19}F) and DRX-500 (500.13 MHz for ^1H, 125.76 MHz for ^{13}C) spectrometers. $CDCl_3$ and acetone-d_6 were used as solvents, with residual $CHCl_3$ (δ_H = 7.26) or $CDCl_3$ (δ_C = 77.0) and acetone (δ_H = 2.15) or acetone-d_6 (δ_C = 28.6 and 205.0) being employed as internal standards. C_6F_6 (δ_F = –163.0 ppm) was used as external reference for recording the ^{19}F NMR spectra. ^{13}C NMR spectra were recorded with C–H spin decoupling. Masses of molecular ions were

determined by HRMS on a DFS Thermo scientific instrument (EI, 70 eV). Melting points were recorded on a Mettler-Toledo FP81 Thermosystem apparatus. The IR spectra were recorded on a Bruker Vector 22 spectrometer (KBr or thin film). The Raman spectra were recorded on Ramanscope Senterra (25 mV, 785 nm).

The structures of all new polyfluorinated compounds **2**–**10** prepared here were corroborated by their ^{19}F, ^{1}H and ^{13}C NMR, high-resolution mass spectrometry, and IR-spectroscopy data (see Supplementary data). Signals in the NMR spectra of **3**–**10** were assigned on the basis of spin coupling constants that are typical for polyfluorinated arenes [22–309].

4.2. Synthetic procedures

*4.2.1. 2-alkynylanilines **3a–e**, **8a–j**; general procedure*

To a solution of iodoaniline **1**, **7a-e** (1 mmol) and acetylenes **2** (1.5 mmol) in dry MeCN (10 mL) in a Schlenk flask under argon were added $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), CuI (17 mg, 0.09 mmol) and Et_3N (3 mL). The reaction mixture was stirred at 60 °C for 3 h. Then, the mixture was allowed to cool down to r.t., and CH_2Cl_2 (10 mL) was added. The mixture was poured into H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O (20 mL) and dried ($MgSO_4$). After evaporation of the solvent *in vacuo*, the crude product was purified by preparative TLC to obtain **3**.

*4.2.1.1. 2,3,4-Trifluoro-6-(phenylethynyl)aniline (**3a**)*

Yellowish solid; yield: 215 mg (86%); R_f = 0.70 (EtOAc/hexane, 1:10, twice); ^{19}F, ^{1}H NMR spectra are similar to those published earlier [29].

*4.2.1.2. 2,3,4-Trifluoro-6-(hex-1-ynyl)aniline (**3b**)*

Yellowish oil; yield: 186 mg (82%); R_f = 0.80 (EtOAc/hexane, 1:10, twice); IR (thin): 3487, 3388, 2960, 2935, 2873, 2227, 1647, 1589, 1522, 1481, 1381, 1302, 1182, 1145, 1022, 955, 858, 712, 555 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 6.91 (ddd, J (H^3,F^4) = 10.8 Hz, J (H^3,F^5) = 8.0 Hz, J (H^3,F^6) = 2.2 Hz, 1 H, H^3), 4.94 (s, 2 H, H^1), 2.46 (t, J (H^9,H^{10}) = 7.0 Hz, 2 H, H^9), 1.62–1.39 (m, 4 H, H^{10} + H^{11}), 0.91 (t, J (H^{12},H^{11}) = 7.0 Hz, 3 H, H^{12}). ^{13}C NMR (125.8 MHz, Acetone-d_6): δ = 142.9 (ddd, ^{1}J (C^4,F^4) ≈ 240 Hz, ^{2}J (C^4,F^5) = 10.9 Hz, C^4), 141.1 (ddd, ^{1}J (C^5,F^5) = 247.7 Hz, ^{2}J (C^5,F^6) = 16.5 Hz, ^{2}J (C^5,F^4) = 13.3 Hz, C^5), 140.4 (ddd, ^{1}J (C^6,F^6) ≈ 240 Hz, ^{2}J (C^6,F^5) = 12.1 Hz, C^6), 136.5 (d, ^{2}J (C^1,F^6) = 10.5 Hz, C^1), 114.6 (dd, ^{2}J (C^3,F^4) = 19.0 Hz, ^{3}J (C^3,F^5) = 3.2 Hz, C^3), 104.9 (m, C^2), 98.1 (m, C^7), 75.2 (m, C^8), 31.6 (s, C^9), 22.7 (s, C^{10}), 19.6 (s, C^{11}), 13.8 (s, C^{12}). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –152.0 (dd, J (F^4,F^5) = 21.4 Hz, J (F^4,H^3) = 10.8 Hz, 1 F, F^4), –155.6 (dt, J (F^6,F^5) = 19.5 Hz, J (F^6,H^3) = 2.2 Hz, 1 F, F^6), –160.7 (m, J (F^5,F^4) = 21.4 Hz, J (F^5,F^6) = 19.5 Hz, J (F^5,H^3) = 8.0 Hz, 1 F, F^5). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{12}F_3N$: 227.0916; found: 227.09017.

*4.2.1.3. 3-(2-Amino-3,4,5-trifluorophenyl)prop-2-yn-1-ol (**3c**)*

White solid; yield: 156 mg (78%); R_f = 0.45 (EtOAc/hexane, 1:5, 4 times); mp 97.9–99.2 °C. IR (KBr): 3396, 3315, 3207, 2227, 1645, 1618, 1524, 1485, 1360, 1308, 1182, 1149, 1014, 978, 870, 850, 715, 588, 472, 445 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 6.99 (ddd, J (H^3,F^4) = 10.6 Hz, J (H^3,F^5) = 8.0 Hz, J (H^3,F^6) = 2.3 Hz, 1 H, H^3), 5.18 (s, 2 H, H^1), 4.44 (s, 2 H, H^9),

3.00 (s, 1 H, OH). ^{13}C NMR (125.8 MHz, Acetone-d_6): δ = 142.5 (ddd, ^1J (C^4,F^4) = 235 Hz, ^2J (C^4,F^5) = 10.7 Hz, C^4), 141.5 (ddd, ^1J (C^5,F^5) = 248.3 Hz, ^2J (C^5,F^6) = 16.6 Hz, ^2J (C^5,F^4) = 13.5 Hz, C^5), 140.1 (ddd, ^1J (C^6,F^6) = 241.2 Hz, ^2J (C^6,F^5) = 12.3 Hz, C^6), 137.1 (d, ^2J (C^1,F^6) = 10.7 Hz, C^1), 114.6 (dd, ^2J (C^3,F^4) = 19.0 Hz, ^3J (C^3,F^5) = 3.2 Hz, C^3), 103.4 (m, C^2), 96.6 (m, C^7), 78.7 (m, C^8), 51.0 (s, C^9). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –152.1 (dd, J (F^4,F^5) = 21.4 Hz, J (F^4,H^3) = 10.6 Hz, 1 F, F^4), –155.5 (dm, J (F^6,F^5) = 19 Hz, J (F^6,H^3) = 2 Hz, 1 F, F^6), –159.8 (td, J (F^5,F^4) ≈ J (F^5,F^6) = 21 Hz, J (F^5,H^3) = 8.0 Hz, 1 F, F^5). HRMS (EI): *m/z* $[M]^+$ calcd for $C_9H_6F_3NO$: 201.0396; found: 201.0395.

*4.2.1.4. 1-(2-Amino-3,4,5-trifluorophenyl)-4-methylpent-1-yn-3-ol (**3d**)*

Yellowish solid; yield: 240 mg (99%); R_f = 0.67 (EtOAc/hexane, 1:5); mp 46.8 °C (dec.). IR (KBr): 3458, 3333, 2964, 2929, 2875, 2227, 1597, 1522, 1481, 1379, 1300, 1178, 1146, 1022, 991, 958, 854, 717, 638, 542 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 (ddd, J (H^3,F^4) = 10.3 Hz, J (H^3,F^5) = 7.8 Hz, J (H^3,F^6) = 2.2 Hz, 1 H, H^3), 4.39 (d, J (H^9,H^{11}) = 5.8 Hz, 1 H, H^9), 4.23 (s, 2 H, H^1), 3.21 (s, 1 H, H^{10}), 1.93 (m, J (H^{11},H^9) = 6 Hz, 1 H, H^{11}), 1.01 (t, J (H^{12},H^{11}) = 7.2 Hz, 6 H, H^{12}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 142.7 (ddd, ^1J (C^4,F^4) = 237.3 Hz, ^2J (C^4,F^5) = 10.8 Hz, C^4), 140.8 (ddd, ^1J (C^5,F^5) = 251.8 Hz, ^2J (C^5,F^6) = 16.5 Hz, ^2J (C^5,F^4) = 13.3 Hz, C^5), 139.9 (ddd, ^1J (C^6,F^6) = 242.3 Hz, ^2J (C^6,F^5) = 12.4 Hz, C^6), 134.4 (dm, ^2J (C^1,F^6) = 10.8 Hz, C^1), 113.9 (dd, ^2J (C^3,F^4) = 19.2 Hz, ^3J (C^3,F^5) = 3.4 Hz, C^3), 102.7 (m, C^2), 95.6 (m, C^7), 79.2 (m, C^8), 68.1 (s, C^9), 34.4 (s, C^{10}), 18.1 (s, C^{11}), 17.4 (s, $C^{11'}$). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –150.9 (dd, J (F^4,F^5) = 21.6 Hz, J (F^4,H^3) = 10.3 Hz, 1 F, F^4), –156.2 (dd, J (F^6,F^5) = 19.7 Hz, J (F^6,H^3) = 2.2 Hz, 1 F, F^6), –159.3 (m, J (F^5,F^4) = 21.6 Hz, J (F^5,F^6) = 19.7 Hz, J (F^5,H^3) = 7.8 Hz, 1 F, F^5). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{12}F_3NO$: 243.0866; found: 243.0868.

*4.2.1.5. 4-(2-Amino-3,4,5-trifluorophenyl)-2-methylbut-3-yn-2-ol (**3e**)*

Yellowish oil; yield: 187 mg (82%); R_f = 0.86 (EtOAc/hexane, 1:10, twice). IR (thin): 3361, 2983, 2935, 2222, 1649, 1593, 1522, 1483, 1379, 1365, 1279, 1230, 1165, 1124, 1020, 966, 931, 858, 694, 569 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 6.96 (ddd, J (H^3,F^4) = 10.5 Hz, J (H^3,F^5) = 8.0 Hz, J (H^3,F^6) = 2.2 Hz, 1 H, H^3), 5.08 (s, 2 H, H^1), 2.93 (s, 1 H, H^8), 1.54 (t, 6 H, H^9). ^{13}C NMR (125.8 MHz, Acetone-d_6): δ = 142.5 (ddd, ^1J (C^4,F^4) = 235.8 Hz, ^2J (C^4,F^5) = 10.7 Hz, C^4), 141.2 (ddd, ^1J (C^5,F^5) = 248.1 Hz, ^2J (C^5,F^6) = 16.5 Hz, ^2J (C^5,F^4) = 13.3 Hz, C^5), 140.3 (ddd, ^1J (C^6,F^6) = 240.9 Hz, ^2J (C^6,F^5) = 12.2 Hz, C^6), 136.6 (d, ^2J (C^1,F^6) = 10.7 Hz, C^1), 114.5 (dd, ^2J (C^3,F^4) = 19.1 Hz, ^3J (C^3,F^5) = 3.3 Hz, C^3), 103.6 (m, C^2), 102.8 (m, C^7), 75.7 (m, C^8), 65.2 (s, C^9), 31.8 (s, C^{10}). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –152.2 (ddd, J (F^4,F^5) = 21.4 Hz, J (F^4,H^3) = 10.9 Hz, 1 F, F^4), –155.6 (dt, J (F^6,F^5) = 19.1 Hz, J (F^6,H^3) = 2.2 Hz, 1 F, F^6), –160.7 (m, J (F^5,F^4) = 21 Hz, J (F^5,F^6) = 19 Hz, J (F^5,H^3) = 8.0 Hz, 1 F, F^5). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{10}F_3NO$: 229.0709; found: 229.0708.

*4.2.1.6. 3-(2-Aminophenyl)prop-2-yn-1-ol (**8a**)*

Brown solid; yield: 110 mg (75%); R_f = 0.16 (EtOAc/hexane, 1:5, twice); mp 113.1 °C (dec.) (48–49 °C [32]). IR (KBr): 3361, 2920, 2864, 2229, 1616, 1574, 1493, 1454, 1358, 1313, 1246, 1159, 1018, 953, 752, 553, 478 cm^{-1}. ^{1}H NMR (500 MHz, Acetone-d_6): δ = 7.14 (dm, J (H^3,H^4) = 7.7 Hz, J (H^3,H^5) = 1.6 Hz, 1 H, H^3), 7.03 (m, J (H^5,H^6) = 8.2 Hz, J (H^5,H^4) = 7.3 Hz, J (H^5,H^3) = 1.6 Hz, 1 H, H^5), 6.72 (dm, J (H^6,H^5) = 8.2 Hz, 1 H, H^6), 6.53 (m, J (H^4,H^3) = 7.7 Hz,

J (H^4,H^5) = 7.3 Hz, 1 H, H^4), 4.99 (s, 2 H, H^1), 4.47 (s, 1 H, OH), 4.45 (s, 2 H, H^9). ^{13}C NMR (125.8 MHz, Acetone-d_6): δ = 150.1 (s, C^1), 132.4 (s, C^3), 130.2 (s, C^5), 117.1 (s, C^4), 114.6 (s, C^6), 107.4 (s, C^2), 94.4 (s, C^7), 81.8 (s, C^8), 51.1 (s, C^9). HRMS (EI): *m/z* $[M]^+$ calcd for C_9H_9NO: 147.0679; found: 147.0680.

*4.2.1.7. 3-(2-Aminophenyl)-1-phenylprop-2-yn-1-ol (**8b**)*

Brown oil; yield: 214 mg (96%); R_f = 0.39 (EtOAc/hexane, 1:5, twice). IR (thin): 3454, 3373, 3063, 3032, 2873, 2218, 1701, 1614, 1574, 1493, 1454, 1313, 1261, 1190, 1159, 1036, 1014, 962, 918, 818, 752, 700, 638, 584, 553, 478 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 7.64–7.61 (m, 2 H, H_m), 7.40–7.27 (m, 3 H, H_o + H_p), 7.18 (dm, *J* (H^3,H^4) = 7.7 Hz, 1 H, H^3), 7.06 (m, *J* (H^5,H^6) = 8.2 Hz, *J* (H^5,H^4) = 7.3 Hz, 1 H, H^5), 6.74 (dm, *J* (H^6,H^5) = 8.2 Hz, 1 H, H^6), 6.55 (tm, *J* (H^4,H^3) ≈ *J* (H^4,H^5) = 7.5 Hz, 1 H, H^4), 3.73 (s, 1 H, H^9), 5.14 (s, 1 H, OH), 4.98 (s, 1 H, H^1). ^{1}H NMR spectrum is close to that published earlier [32]. ^{13}C NMR (100 MHz, Acetone-d_6): δ = 150.3 (s, C^1), 143.3 (s, C^{10}), 132.5 (s, C^3), 130.4 (s, C^5), 129.1 (s, C^{12}), 128.4 (s, C^{13}), 127.4 (s, C^{11}), 117.1 (s, C^4), 114.7 (s, C^6), 107.2 (s, C^2), 96.3 (s, C^7), 83.0 (s, C^8), 64.9 (s, C^9). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{15}H_{13}NO$: 223.0992; found: 223.0990.

*4.2.1.8. 3-(2-Amino-3,5-difluorophenyl)prop-2-yn-1-ol (**8c**)*

Yellowish solid; yield: 124 mg (68%); R_f = 0.25 (EtOAc/hexane, 1:5, 4 times); mp 91.1 C (dec.). IR (KBr): 3383, 3317, 3219, 3091, 2233, 1641, 1616, 1589, 1493, 1442, 1352, 1311, 1201, 1176, 1120, 1039, 1000, 967, 966, 854, 731, 584, 542, 432 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 6.92 (m, *J* (H^5,F^6) = 11.5 Hz, *J* (H^5,F^4) = 9.0 Hz, *J* (H^5,H^3) = 2.9 Hz, 1 H, H^5), 6.81 (dm, *J* (H^3,F^4) = 9.0 Hz, *J* (H^3,H^5) = 2.9 Hz, 1 H, H^3), 4.87 (s, 2 H, H^1), 4.46 (s, 3 H, 2 H^9 + OH). ^{13}C NMR (125.8 MHz, Acetone-d_6): δ = 153.7 (dd, ^1J (C^4,F^4) = 234.8 Hz, ^3J (C^4,F^6) = 12.4 Hz, C^4), 151.0 (dd, ^1J (C^6,F^6) = 240.6 Hz, ^3J (C^6,F^4) = 12.9 Hz, C^5), 135.6 (dd, ^2J (C^1,F^6) = 13.7 Hz, C^1), 113.6 (dd, ^2J (C^3,F^4) = 23.3 Hz, C^3), 109.6 (dd, ^3J (C^2,F^4) = 11.0 Hz, C^2), 105.1 (dd, ^2J (C^5,F^6) = 27.1 Hz, ^2J (C^5,F^4) = 23.0 Hz, C^5), 96.9 (s, C^7), 79.5 (m, C^8), 51.0 (s, C^9). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –156.3 (tm, *J* (F^4,H^5) ≈ *J* (F^4,H^3) = 9.0 Hz, 1 F, F^4), –129.6 (dm, *J* (F^6,H^5) = 11.5 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_9H_7F_2NO$: 183.0490; found: 183.0494.

*4.2.1.9. 3-(2-Amino-3,4,5-trifluorophenyl)-1-phenylprop-2-yn-1-ol (**8d**)*

Yellowish solid; yield: 258 mg (93%); R_f = 0.27 (EtOAc/hexane, 1:7); mp 72.4–72.8 °C. IR (KBr): 3415, 3334, 3280, 2835, 2231, 1601, 1523, 1475, 1379, 1304, 1286, 1257, 1200, 1145, 1036, 1009, 974, 920, 854, 742, 696, 646, 586, 557 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 – 7.54 (m, 2 H, H_m), 7.43 – 7.32 (m, 3 H, H_o + H_p), 6.90 (m, *J* (H^3,F^4) = 10.2 Hz, *J* (H^3,F^5) = 7.7 Hz, *J* (H^3,F^6) = 2.3 Hz, 1 H, H^3), 5.70 (d, 1 H, H^9), 4.15 (s, 2 H, H^1), 2.60 (d, 1 H, OH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 142.7 (ddd, ^1J (C^4,F^4) = 239.8 Hz, ^2J (C^4,F^5) = 10.8 Hz, C^4), 141.0 (ddd, ^1J (C^5,F^5) = 252.5 Hz, ^2J (C^5,F^6) = 16.6 Hz, ^2J (C^5,F^4) = 13.3 Hz, C^5), 140.1 (s, C^{10}), 139.9 (ddd, ^1J (C^6,F^6) = 242.6 Hz, ^2J (C^6,F^5) = 12.4 Hz, C^6), 134.7 (dm, ^2J (C^1,F^6) = 10.7 Hz, C^1), 128.7 (s, C^{12}), 128.6 (s, C^{13}), 126.4 (s, C^{11}), 114.1 (dd, ^2J (C^3,F^4) = 19.3 Hz, ^3J (C^3,F^5) = 3.5 Hz, C^3), 102.1 (m, C^2), 95.5 (m, C^7), 80.4 (m, C^8), 65.0 (s, C^9). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –147.7 (dd, *J* (F^4,F^5) = 21.6 Hz, *J* (F^4,H^3) = 10.2 Hz, 1 F, F^4), –153.0 (dm, *J* (F^6,F^5) = 19.7 Hz, *J*

(F^6,H^3) = 2.3 Hz, 1 F, F^6), –155.5 (m, *J* (F^5,F^4) = 21.6 Hz, *J* (F^5,F^6) = 19.7 Hz, *J* (F^5,H^3) = 7.7 Hz, 1 F, F^5). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{15}H_{10}F_3NO$: 277.0711; found: 277.0711.

*4.2.1.10. 3-(2-Amino-3,5,6-trifluorophenyl)prop-2-yn-1-ol (**8e**)*

Yellowish solid; yield: 189 mg (94%); R_f = 0.22 (EtOAc/hexane, 1:5, 5 times); mp 111.1–113.6 °C. IR (KBr): 3491, 3373, 3097, 2234, 1616, 1495, 1469, 1396, 1363, 1296, 1190, 1165, 1111, 1063, 1010, 914, 848, 723, 590, 503, 418 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6): δ = 7.13 (m, *J* (H^5,F^4) ≈ *J* (H^5,F^6) = 10.7 Hz, *J* (H^5,F^3) = 7.3 Hz, 1 H, H^5), 5.14 (s, 2 H, H^1), 4.50 (s, 2 H, H^9), 2.94 (s, 1 H, OH). ^{13}C NMR (125.8 MHz, Acetone-d_6): δ = 147.7 (ddd, ^1J (C^3,F^3) = 243.5 Hz, ^2J (C^3,F^4) = 13.7 Hz, C^3), 145.9 (ddd, ^1J (C^6,F^6) = 237.1 Hz, ^3J (C^6,F^4) = 15.9 Hz, C^6), 140.9 (ddd, ^1J (C^4,F^4) = 235.6 Hz, ^2J (C^4,F^3) = 13.9 Hz, ^3J (C^4,F^6) = 12.5 Hz, C^4), 136.2 (dm, ^2J (C^1,F^6) = 15.2 Hz, C^1), 106.1 (m, ^2J (C^5,F^4) = 24.8 Hz, ^2J (C^5,F^6) = 22.6 Hz, C^5), 102.2 (m, C^7), 103.4 (dm, ^2J (C^2,F^3) = 17.7 Hz, C^2), 73.5 (m, C^8), 51.2 (s, C^9). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –136.0 (m, *J* (F^6,F^3) = 13.8 Hz, *J* (F^6,H^5) = 11.0 Hz, *J* (F^6,F^4) = 3.2 Hz, 1 F, F^6), –141.1 (m, *J* (F^3,F^4) ≈ 21.4 Hz, *J* (F^3,F^6) = 13.5 Hz, *J* (F^3,H^5) = 7.3 Hz, 1 F, F^3), –152.1 (ddd, *J* (F^4,F^3) = 21.8 Hz, *J* (F^4,H^5) = 10.6 Hz, *J* (F^4,F^6) = 3.2 Hz, 1 F, F^4). HRMS (EI): *m/z* $[M]^+$ calcd for $C_9H_6F_3NO$: 201.0396; found: 201.0398.

*4.2.1.11. 3-(2-Amino-3,5,6-trifluorophenyl)-1-phenylprop-2-yn-1-ol (**8f**)*

Yellowish solid; yield: 166 mg (60%); R_f = 0.39 (EtOAc/hexane, 1:7, 5 times); mp 63.4 °C (decomp.). IR (KBr): 3450, 3392, 3325, 3205, 2234, 1618, 1497, 1466, 1450, 1387, 1286, 1273, 1157, 1115, 1064, 1003, 920, 847, 739, 694, 646, 592, 553, 488 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.61–7.60 (m, 2 H, H_m), 7.42–7.34 (m, 3 H, H_o + H_p), 6.87 (m, *J* (H^5,F^4) ≈ *J* (H^5,F^6) = 10.2 Hz, *J* (H^5,F^3) = 7.2 Hz, 1 H, H^5), 5.76 (d, 1 H, OH), 4.11 (s, 2 H, H^1), 2.36 (d, 1 H, H^9). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.7 (ddd, ^1J (C^3,F^3) = 247.4 Hz, ^2J (C^3,F^4) = 13.9 Hz, C^3), 144.8 (ddd, ^1J (C^6,F^6) = 238.1 Hz, ^3J (C^6,F^4) = 10.4 Hz, C^6), 140.5 (ddd, ^1J (C^4,F^4) = 239.6 Hz, ^2J (C^4,F^3) = 13.8 Hz, ^3J (C^4,F^6) = 12.2 Hz, C^4), 139.5 (s, C^{10}), 133.1 (dm, ^2J (C^1,F^6) = 15.2 Hz, C^1), 128.4 (s, C^{12}), 128.3 (s, C^{13}), 126.1 (s, C^{11}), 105.3 (m, ^2J (C^5,F^4) ≈ ^2J (C^5,F^6) = 23.9 Hz, C^5), 100.4 (d, C^7), 98.7 (dm, ^2J (C^2,F^3) = 17.5 Hz, C^2), 75.0 (m, C^8), 64.8 (s, C^9). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –137.9 (m, *J* (F^6,F^3) = 13.4 Hz, *J* (F^6,H^5) = 10.5 Hz, *J* (F^6,F^4) = 2.5 Hz, 1 F, F^6), –141.3 (m, *J* (F^3,F^4) ≈ 21.4 Hz, *J* (F^3,F^6) = 13.4 Hz, *J* (F^3,H^5) = 7.1 Hz, 1 F, F^3), –151.3 (ddd, *J* (F^4,F^3) = 22.0 Hz, *J* (F^4,H^5) = 10.1 Hz, *J* (F^4,F^6) = 2.5 Hz, 1 F, F^4). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{15}H_{10}F_3NO$: 277.0709; found: 277.0707.

*4.2.1.12. 3-(2-Amino-3,4,5,6-tetrafluorophenyl)prop-2-yn-1-ol (**8g**)*

Yellowish solid; yield: 186 mg (85%); R_f = 0.34 (EtOAc/hexane, 1:5, 3 times); mp 92.1 °C (decomp.). IR (KBr): 3496, 3363, 3207, 2927, 2239, 1862, 1614, 1518, 1502, 1439, 1304, 1163, 1115, 1032, 997, 968, 827, 692, 578, 521 cm^{-1}. ^1H NMR (500 MHz, Acetone-d_6): 5.48 (s, 2 H, H^1), 4.46 (s, 3 H, 2 H^9 + OH). ^{13}C NMR (125.8 MHz, Acetone-d_6): δ = 148.5 (dm, ^1J (C^3,F^3) = 244.3 Hz, ^2J (C^3,F^4) = 10.9 Hz, C^3), 142.1 (dm, ^1J (C^5,F^5) = 248.3 Hz, ^2J (C^5,F^4) ≈ ^2J (C^5,F^6) = 13.4 Hz, C^5), 136.5 (dm, ^2J (C^1,F^6) = 11.7 Hz, C^1), 136.4 (dm, ^1J (C^6,F^6) = 237.7 Hz, ^2J (C^6,F^5) = 12.4 Hz, C^6), 132.2 (dm, ^1J (C^4,F^4) = 237.6 Hz, ^2J (C^4,F^3) = 16.6 Hz, ^2J (C^4,F^5) = 13.4 Hz, C^4), 102.0 (m, C^7), 94.0 (dm, ^2J (C^2,F^3) = 17.9 Hz, C^2), 72.3 (m, C^8), 51.1 (s, C^9). ^{19}F NMR (282

MHz, Acetone-d_6): δ = –139.2 (dm, J (F^3,F^4) = 22.0 Hz, J (F^3,F^6) = 9.3 Hz, J (F^3,F^5) ≈ 2 Hz, 1 F, F^3), –157.7 (m, J (F^5,F^4) = 21.6 Hz, J (F^5,F^6) ≈ 19.5 Hz, J (F^5,F^3) = 2 Hz, 1 F, F^5), –162.3 (m, J (F^6,F^5) = 19.9 Hz, J (F^6,F^3) = 9.3 Hz, J (F^6,F^4) = 6.9 Hz, 1 F, F^6), –176.0 (m, J (F^4,F^3) ≈ J (F^4,F^5) = 21.6 Hz, J (F^4,F^6) = 6.9 Hz, 1 F, F^4). HRMS (EI): *m/z* $[M]^+$ calcd for $C_9H_5F_4NO$: 219.0302; found: 219.0301.

*4.2.1.13. 3-(2-Amino-3,4,5,6-tetrafluorophenyl)-1-phenylprop-2-yn-1-ol (**8h**)*

Yellowish solid; yield: 248 mg (84%); R_f = 0.19 (EtOAc/hexane, 1:7, twice); mp 81.8–82.4 °C. IR (KBr): 3412, 3298, 3217, 2241, 1660, 1604, 1518, 1498, 1458, 1304, 1269, 1201, 1161, 1125, 1041, 976, 870, 741, 698, 646, 578 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.56 (m, 2 H, H_m), 7.44–7.33 (m, 3 H, H_o + H_p), 5.74 (d, 1 H, OH), 4.25 (s, 2 H, H^1), 2.44 (d, 1 H, H^9). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 147.9 (dm, ^1J (C^3,F^3) = 248.7 Hz, ^2J (C^3,F^4) = 11.0 Hz, C^3), 141.6 (dm, ^1J (C^5,F^5) = 252.9 Hz, ^2J (C^5,F^4) ≈ ^2J (C^5,F^6) = 14.0 Hz, C^5), 139.8 (s, C^{10}), 135.9 (dm, ^1J (C^6,F^6) = 242.8 Hz, ^2J (C^6,F^5) = 14.8 Hz, C^6), 133.7 (dm, ^2J (C^1,F^6) = 12 Hz, C^1), 133.6 (dm, ^1J (C^4,F^4) = 243.1 Hz, ^2J (C^4,F^3) ≈ ^2J (C^4,F^5) = 16.4 Hz, C^4), 128.8 (s, C^{12}), 128.7 (s, C^{13}), 126.5 (s, C^{11}), 100.6 (m, C^7), 93.3 (dm, ^2J (C^2,F^3) = 17.8 Hz, C^2), 74.3 (m, C^8), 65.1 (s, C^9). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –138.6 (dm, J (F^3,F^4) = 22.2 Hz, J (F^3,F^6) = 9.7 Hz, J (F^3,F^5) = 3.4 Hz, 1 F, F^3), –156.1 (m, J (F^5,F^4) ≈ J (F^5,F^6) = 20.9 Hz, J (F^5,F^3) = 3.4 Hz, 1 F, F^5), –163.1 (m, J (F^6,F^5) = 20.5 Hz, J (F^6,F^3) = 9.7 Hz, J (F^6,F^4) = 5.5 Hz, 1 F, F^6), –173.8 (m, J (F^4,F^3) ≈ J (F^4,F^5) = 21.6 Hz, J (F^4,F^6) = 5.5 Hz, 1 F, F^4). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{15}H_9F_4NO$: 295.0615; found: 295.0613.

*4.2.1.14. 3-(2-Amino-3,4,6-trifluoro-5-(trifluoromethyl)phenyl)-1-phenylprop-2-yn-1-ol (**8i**)*

Yellowish oil; yield: 338 mg (98%); R_f = 0.28 (EtOAc/hexane, 1:5, twice). IR (thin): 3495, 3395, 3212, 2233, 1645, 1606, 1495, 1456, 1410, 1344, 1245, 1175, 1130, 1024, 986, 902, 753, 706, 639, 542 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.54 (m, 2 H, H_m), 7.39–7.31 (m, 3 H, H_o + H_p), 5.69 (s, 1 H, H^9), 5.07 (s, 2 H, H^1), 4.76 (br. s, 1 H, OH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 156.2 (dm, ^1J (C^3,F^3) = 256.4 Hz, C^3), 147.9 (dm, ^1J (C^5,F^5) = 258.9 Hz, ^2J (C^5,F^6) = 13.3 Hz, C^5), 141.7 (m, C^1), 139.7 (s, C^{10}), 135.1 (dm, ^1J (C^6,F^6) = 238.4 Hz, ^2J (C^6,F^5) = 15.0 Hz, C^6), 128.5 (s, C^{12}), 128.4 (s, C^{13}), 126.4 (s, C^{11}), 121.7 (q, ^1J (CF_3,F) = 272.1 Hz, CF_3), 100.6 (m, C^7), 96.0 (m, C^4), 93.8 (dm, ^2J (C^2,F^3) = 21.6 Hz, C^2), 73.7 (m, C^7), 64.6 (s, C^9). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –56.4 (t, J (CF_3,F^3) ≈ J (CF_3,F^5) = 21.4 Hz, 3 F, CF_3), –114.7 (qd, J (F^3,CF_3) = 21.6 Hz, J (F^3,F^6) = 11.1 Hz, 1 F, F^3), –137.7 (m, J (F^5,F^6) ≈ J (F^5,CF_3) = 20.7 Hz, 1 F, F^5), –165.0 (dd, J (F^6,F^5) = 20.1 Hz, J (F^6,F^3) = 11.1 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{165}H_9F_6NO$: 345.0583; found: 345.0581.

*4.2.2. 6-Ethynyl-2,3,4-trifluoroaniline (**3g**)*

To a solution of **1** (300 mg, 1 mmol) and ethynyltrimethylsilane **2f** (196 mg, 2 mmol) in dry Et_3N (10 mL) in a Schlenk flask under argon were added $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol) and CuI (17 mg, 0.09 mmol). The reaction mixture was stirred at r.t. for 72 h. Then, the mixture was diluted with CH_2Cl_2 (10 mL), poured into H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O (20 mL) and dried ($MgSO_4$). After evaporation of the solvent *in vacuo*, the crude product (**3f**) was obtained (^{19}F, ^1H NMR spectra are similar to those published earlier [20]). To a solution of **3f** in MeOH (5 mL) K_2CO_3 (300 mg,

2 mmol) was added. The reaction mixture was stirred at r.t. for 2 h, then placed directly onto a chromatography plate (silica gel), and air-dried. 2-Alkynylaniline **3g** was isolated by TLC with EtOAc/hexane (1:7) as an eluent, R_f = 0.65.

Yellowish oil; yield: 128 mg (75%); IR (thin): 3417, 3327, 3304, 3199, 2114, 1653, 1601, 1522, 1481, 1367, 1300, 1167, 1109, 1024, 908, 854, 715, 675, 617, 553, 445 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.93 (ddd, J (H^3,F^4) = 11 Hz, J (H^3,F^5) = 8 Hz, J (H^3,F^6) = 2.3 Hz, 1 H, H^3), 4.20 (s, 2 H, H^1), 3.40 (s, 1 H, H^8). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 142.7 (ddd, ^1J (C^4,F^4) = 239.8 Hz, ^2J (C^4,F^5) = 10.8 Hz, C^4), 141.2 (ddd, ^1J (C^5,F^5) = 252.6 Hz, ^2J (C^5,F^6) = 16.5 Hz, ^2J (C^5,F^4) = 13.4 Hz, C^5), 139.8 (ddd, ^1J (C^6,F^6) = 242.3 Hz, ^2J (C^6,F^5) = 12.5 Hz, C^6), 135.2 (dm, ^2J (C^1,F^6) = 11.1 Hz, C^1), 114.4 (dd, ^2J (C^3,F^4) = 19.4 Hz, ^3J (C^3,F^5) = 3.6 Hz, C^3), 101.7 (m, C^2), 83.8 (m, C^7), 77.6 (m, C^8). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –154.0 (ddd, J (F^4,F^5) = 21.4 Hz, J (F^4,H^3) = 10.7 Hz, 1 F, F^4), –157.8 (dt, J (F^6,F^5) = 19.2 Hz, J (F^6,H^3) = 2 Hz, 1 F, F^6), –162.2 (m, J (F^5,F^4) = 21.4 Hz, J (F^5,F^6) = 19.2 Hz, J (F^5,H^3) = 8.0 Hz, 1 F, F^5). HRMS (EI): *m/z* $[M]^+$ calcd for $C_8H_4F_3N$: 171.0290; found: 171.0289.

*4.2.3. Interaction of 2-alkynylanilines **3** with $PdCl_2$; General Procedure*

To a solution of **3** (1 mmol) in MeCN (10 mL) $PdCl_2$ (35 mg, 0.2 mmol) was added, and the mixture was heated at reflux for 1 h with stirring. The mixture was allowed to cool to r.t., placed directly onto a chromatography plate (silica gel), and air-dried.

*4.2.3.1. 5,6,7-Trifluoro-2-phenyl-1H-indole (**4a**)*

Yellowish solid; yield: 237 mg (96%); R_f = 0.55 (EtOAc/hexane, 1:10); ^{19}F, ^1H NMR spectra are similar to those published earlier [29].

*4.2.3.2. 2-Butyl-5,6,7-trifluoro-1H-indole (**4b**)*

Yellow oil; yield: 224 mg (99%); R_f = 0.75 (EtOAc/hexane, 1:10). IR (thin): 3475, 2960, 2933, 1862, 1601, 1524, 1477, 1414, 1377, 1325, 1198, 1061, 955, 845, 779, 727, 671, 449 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.29 (s, 1 H, H^1), 7.00 (m, J (H^4,F^5) ≈ 9 Hz, J (H^4,F^6) ≈ 6.5 Hz, 1 H, H^4), 6.16 (m, 1 H, H^3), 2.72 (t, J (H^8,H^9) = 7.5 Hz, 2 H, H^8), 1.73–1.63 (m, 2 H, H^9), 1.45–1.35 (m, 2 H, H^{10}), 0.93 (t, J (H^{11},H^{10}) = 7.5 Hz, 3 H, H^{11}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.7 (ddd, ^1J (C^5,F^5) = 238.1 Hz, ^2J (C^5,F^6) = 12.0 Hz, C^5), 142.5 (m, C^2), 137.5 (ddd, ^1J (C^7,F^7) = 246.5 Hz, ^2J (C^7,F^6) = 13.4 Hz, ^3J (C^7,F^5) = 4.6 Hz, C^7), 135.7 (ddd, ^1J (C^6,F^6) = 240.1 Hz, ^2J (C^6,F^5) = 18.4 Hz, ^2J (C^6,F^7) = 12.3 Hz, C^6), 124.4 (ddm, ^2J (C^{7a},F^7) = 9.7 Hz, C^{7a}), 120.3 (dm, ^3J (C^{3a},F) = 9.5 Hz, C^{3a}), 100.9 (dd, ^2J (C^4,F^5) = 19.4 Hz, ^3J (C^4,F^6) = 3.8 Hz, C^4), 100.1 (m, C^3), 31.1 (s, C^8), 27.8 (s, C^9), 22.3 (s, C^{10}), 13.8 (s, C^{11}). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –147.3 (dd, J (F^5,F^6) = 20.4 Hz, J (F^5,H^4) = 10.2 Hz, 1 F, F^5), –158.7 (dm, J (F^7,F^6) = 19.8 Hz, 1 F, F^7), –172.0 (td, J (F^6,F^5) ≈ J (F^6,F^7) = 20.1 Hz, J (F^6,H^4) = 6.5 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{12}F_3N$: 227.0916; found: 227.0917.

*4.2.4. Interaction of 2-alkynylanilines **3** with KOH; General Procedure*

To a solution of **3** (1 mmol) in MeCN (10 mL) KOH (112 mg, 2 mmol) was added, and the mixture was heated at reflux for 4÷14 h (see Tables 4, 5) with stirring. Then, the mixture was allowed to cool down to r.t., and H_2O (10 mL) was added. The mixture was extracted with

CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with H_2O (20 mL) and dried ($MgSO_4$). After evaporation of the solvent *in vacuo*, the crude product was purified by preparative TLC.

*4.2.4.1. 5,6,7-Trifluoro-1H-indole (**4g**)*

Yellow oil; yield: 24 mg (14%); R_f = 0.65 (EtOAc/hexane, 1:10). IR (thin): 3483, 3305, 2962, 2927, 2854, 1714, 1651, 1601, 1516, 1473, 1373, 1336, 1321, 1261, 1194, 1055, 1018, 951, 881, 845, 800, 758, 719, 671, 571, 540, 457 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, 1 H, H^1), 7.10 (m, J (H^4,F^5) = 9.7 Hz, J (H^4,F^6) = 6.5 Hz, 1 H, H^4), 6.57 (s, 1 H, H^2), 6.45 (m, 1 H, H^3). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 147.0 (dd, ^1J (C^5,F^5) = 241.6 Hz, ^2J (C^5,F^6) = 12.9 Hz, C^5), 138.6 (ddd, ^1J (C^7,F^7) ≈ 240 Hz, ^2J (C^7,F^6) = 14.1 Hz, ^3J (C^7,F^5) = 4.3 Hz, C^7), 136.8 (ddd, ^1J (C^6,F^6) = 243.3 Hz, ^2J (C^6,F^5) = 18.5 Hz, ^2J (C^6,F^7) = 13.5 Hz, C^6), 129.6 (dd, C^2), 124.8 (m, ^2J (C^{7a},F^7) = 9.4 Hz, C^{7a}), 119.7 (dm, ^3J (C^{3a},F) = 6.9 Hz, C^{3a}), 104.8 (m, C^3), 102.5 (dd, ^2J (C^4,F^5) = 19.1 Hz, ^3J (C^4,F^6) = 3.7 Hz, C^4). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –144.8 (dd, J (F^5,F^6) = 20.5 Hz, J (F^5,H^4) = 9.7 Hz, 1 F, F^5), –157.7 (dm, J (F^7,F^6) = 19.8 Hz, 1 F, F^7), –168.5 (td, J (F^6,F^5) ≈ J (F^6,F^7) = 20.1 Hz, J (F^6,H^4) = 6.5 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_8H_4F_3N$: 171.0290; found: 171.0291.

4.2.5. Interaction of 2-alkynylanilines with p-TSA•H_2O; General Procedure

To a solution of **3**, **8a-e** (1 mmol) in EtOH, MeOH or benzene (15 mL) *p*-TSA monohydrate (380 mg, 2 mmol) was added, and the mixture was heated at reflux for 1÷15 h (see Tables 6 – 11) with stirring. The mixture was allowed to cool to r.t., placed directly onto a chromatography plate (silica gel), and air-dried. Reaction products were isolated by TLC with EtOAc/hexane as an eluent.

*4.2.5.1. 2-(Ethoxymethyl)-5,6,7-trifluoro-1H-indole (**4h**)*

Yellow solid; yield: 85 mg (37%); R_f = 0.25 (CH_2Cl_2/hexane, 1:1); mp 121.3–123.6 °C. IR (KBr): 3439, 2927, 2856, 1632, 1525, 1477, 1429, 1385, 1200, 1105, 953, 876, 843, 791, 671, 567, 472 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H, H^1), 7.06 (m, J (H^4,F^5) ≈ J (H^4,F^6) ≈ 8 Hz, 1 H, H^4), 6.35 (m, 1 H, H^3), 4.61 (s, 2 H, H^8), 3.56 (q, J (H^9,H^{10}) = 6.9 Hz, 2 H, H^9), 1.24 (t, J (H^{10},H^9) = 6.9 Hz,3 H, H^{10}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.7 (ddd, ^1J (C^5,F^5) = 239.0 Hz, ^2J (C^5,F^6) = 13.4 Hz, C^5), 137.7 (m, C^2), 137.6 (ddd, ^1J (C^7,F^7) = 247.7 Hz, ^2J (C^7,F^6) = 13.5 Hz, ^3J (C^7,F^5) = 4.6 Hz, C^7), 136.1 (ddd, ^1J (C^6,F^6) = 241.9 Hz, ^2J (C^6,F^5) = 18.5 Hz, ^2J (C^6,F^7) = 12.3 Hz, C^6), 123.4 (ddm, ^2J (C^{7a},F^7) = 9.8 Hz, C^{7a}), 120.9 (dm, ^3J (C^{3a},F) = 10.2 Hz, C^{3a}), 101.7 (m, C^3), 101.4 (dd, ^2J (C^4,F^5) = 19.4 Hz, ^3J (C^4,F^6) = 3.9 Hz, C^4), 65.9 (s, C^8), 69.2 (s, C^9), 14.9 (s, C^{10}). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –146.5 (dd, J (F^5,F^6) = 20.3 Hz, J (F^5,H^4) = 10.1 Hz, 1 F, F^5), –158.1 (dm, J (F^7,F^6) = 19.6 Hz, 1 F, F^7), –172.3 (td, J (F^6,F^5) ≈ J (F^6,F^7) = 20.0 Hz, J (F^6,H^4) = 6.5 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{10}F_3NO$: 229.0709; found: 229.0707.

*4.2.5.2. 5,6,7-Trifluoro-2-(methoxymethyl)-1H-indole (**4i**)*

Yellowish solid; yield: 39 mg (18%); R_f = 0.25 (CH_2Cl_2/hexane, 1:1); mp 122.5–123.4 °C. IR (KBr): 3240, 2956, 2929, 2837, 1601, 1568, 1525, 1475, 1381, 1350, 1317, 1200, 1163, 1080,

1061, 1001, 978, 949, 897, 845, 795, 727, 669, 627, 575, 546, 496 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (s, 1 H, H^1), 7.07 (m, *J* (H^4,F^5) = 10.1 Hz, *J* (H^4,F^6) = 6.7 Hz, *J* (H^4,H^3) = 2 Hz,1 H, H^4), 6.36 (m, *J* (H^3,H^4) = 2 Hz,1 H, H^3), 4.57 (s, 2 H, H^8), 3.39 (s, 3 H, H^9). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.6 (ddd, ^{1}J (C^5,F^5) = 239.1 Hz, ^{2}J (C^5,F^6) = 12 Hz, C^5), 138.4 (ddd, ^{1}J (C^7,F^7) = 247.6 Hz, ^{2}J (C^7,F^6) = 13.5 Hz, ^{3}J (C^7,F^5) = 4.5 Hz, C^7), 137.2 (m, C^2), 136.3 (ddd, ^{1}J (C^6,F^6) = 242.1 Hz, ^{2}J (C^6,F^5) = 18.6 Hz, ^{2}J (C^6,F^7) = 12.3 Hz, C^6), 123.4 (ddm, ^{2}J (C^{7a},F^7) = 10 Hz, C^{7a}), 121.0 (dm, ^{3}J (C^{3a},F) = 10 Hz, C^{3a}), 102.1 (m, C^3), 101.5 (dd, ^{2}J (C^4,F^5) = 19.4 Hz, ^{3}J (C^4,F^6) = 3.9 Hz, C^4), 67.1 (s, C^8), 57.9 (s, C^9). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –143.6 (dd, *J* (F^5,F^6) = 20.3 Hz, *J* (F^5,H^4) = 10.1 Hz, 1 F, F^5), –155.3 (dm, *J* (F^7,F^6) = 19.7 Hz, 1 F, F^7), –164.3 (td, *J* (F^6,F^5) ≈ *J* (F^6,F^7) = 19.9 Hz, *J* (F^6,H^4) = 6.5 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{10}H_8F_3NO$: 215.0553; found: 215.0550.

*4.2.5.3. 5,6,7-Trifluoro-2-(prop-1-en-2-yl)-1H-indole (**4j**)*

White solid; yield: 29 mg (14%); R_f = 0.65 (EtOAc/hexane, 1:5, twice); mp 66.9 °C (dec.). IR (KBr): 3479, 3070, 2926, 2854, 1792, 1713, 1630, 1599, 1520, 1477, 1379, 1315, 1269, 1230, 1186, 1142, 1101, 1059, 958, 891, 864, 798, 719, 675, 553, 501, 436 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (s, 1 H, H^1), 7.07 (m, *J* (H^4,F^5) = 9.9 Hz, *J* (H^4,F^6) = 6.5 Hz, 1 H, H^4), 6.47 (m, 1 H, H^3), 5.34 (s, 1 H, $H^{9'}$), 5.13 (m, 1 H, H^9), 2.15 (m, 3 H, H^{10}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 146.9 (dd, ^{1}J (C^5,F^5) = 239.1 Hz, ^{2}J (C^5,F^6) = 11.8 Hz, C^5), 140.7 (m, C^2), 137.4 (ddd, ^{1}J (C^7,F^7) = 247.3 Hz, ^{2}J (C^7,F^6) = 14.0 Hz, ^{3}J (C^7,F^5) = 4.6 Hz, C^7), 136.8 (ddd, ^{1}J (C^6,F^6) = 243.6 Hz, ^{2}J (C^6,F^5) = 18.8 Hz, ^{2}J (C^6,F^7) = 12.6 Hz, C^6), 134.3 (s, C^8), 124.2 (ddm, ^{2}J (C^{7a},F^7) = 10.5 Hz, C^{7a}), 121.2 (dm, ^{3}J (C^{3a},F) = 10 Hz, C^{3a}), 110.9 (s, C^9), 101.8 (dd, ^{2}J (C^4,F^5) = 19.6 Hz, ^{3}J (C^4,F^6) = 3.9 Hz, C^4), 101.5 (m, C^3), 20.3 (s, C^{10}). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –146.3 (dd, *J* (F^5,F^6) = 20.2 Hz, *J* (F^5,H^4) = 10.0 Hz, 1 F, F^5), –158.3 (dm, *J* (F^7,F^6) = 19.5 Hz, 1 F, F^7), –169.2 (td, *J* (F^6,F^5) ≈ *J* (F^6,F^7) = 19.9 Hz, *J* (F^6,H^4) = 6.6 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_8F_3N$: 211.0603; found: 211.0609.

*4.2.5.4. 1-(2-Amino-3,4,5-trifluorophenyl)-3-ethoxypropan-1-one (**5h**)*

Yellowish solid; yield: 57 mg (23%); R_f = 0.30 (CH_2Cl_2/hexane, 1:1); mp 51.5–64.6 °C. IR (KBr): 3458, 3340, 2982, 2943, 2893, 1657, 1597, 1560, 1525, 1456, 1389, 1325, 1300, 1275, 1223, 1155, 1101, 1066, 1026, 978, 877, 852, 696, 600, 496, 444 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (ddd, *J* (H^3,F^4) = 10.7 Hz, *J* (H^3,F^5) = 8.0 Hz, *J* (H^3,F^6) = 2.2 Hz, 1 H, H^3), 6.28 (s, 2 H, H^1), 3.76 (t, *J* (H^9,H^8) = 6.4 Hz, 2 H, H^9), 3.48 (q, *J* (H^{10},H^{11}) = 7.0 Hz, 2 H, H^{10}), 3.07 (t, *J* (H^8,H^9) = 6.4 Hz, 2 H, H^8), 1.14 (t, *J* (H^{11},H^{10}) = 7.0 Hz, 3 H, H^{11}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 198.8 (m, C^7), 143.4 (dm, ^{1}J (C^4,F^4) = 240.5 Hz, C^4), 141.1 (dm, ^{1}J (C^5,F^5) = 245.4 Hz, C^5), 139.8 (ddd, ^{1}J (C^6,F^6) = 243.8 Hz, ^{2}J (C^6,F^5) = 11.5 Hz, C^6), 137.8 (dm, ^{2}J (C^1,F^6) = 10.4 Hz, C^1), 112.7 (m, C^2), 112.4 (dm, ^{2}J (C^3,F^4) = 17.7 Hz, ^{3}J (C^3,F^5) = 3.7 Hz, C^3), 66.5 (s, C^9), 65.5 (s, C^{10}), 39.4 (s, C^8), 15.0 (s, C^{11}). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –149.4 (ddd, *J* (F^4,F^5) = 22.0 Hz, *J* (F^4,H^3) = 11.2 Hz, 1 F, F^4), –149.8 (m, *J* (F^5,F^4) = 22.0 Hz, *J* (F^5,F^6) = 18.5 Hz, *J* (F^5,H^3) = 8.0 Hz, 1 F, F^5), –155.6 (dt, *J* (F^6,F^5) = 18.5 Hz, *J* (F^6,H^3) = 2.2 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{12}F_3NO_2$: 247.0815; found: 247.0819.

*4.2.5.5. 1-(2-Amino-3,4,5-trifluorophenyl)-3-methoxypropan-1-one (**5i**)*

Yellowish solid; yield: 77 mg (33%); R_f = 0.34 (CH_2Cl_2/hexane, 1:1); mp 61.0–61.3 °C. IR (KBr): 3442, 3327, 2983, 2929, 2818, 1662, 1599, 1574, 1525, 1464, 1423, 1394, 1333, 1300, 1275, 1203, 1153, 1119, 1072, 1028, 964, 862, 810, 696, 575, 501, 447 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.38 (ddd, *J* (H^3,F^4) = 10.7 Hz, *J* (H^3,F^5) = 8.0 Hz, *J* (H^3,F^6) = 2.2 Hz, 1 H, H^3), 6.33 (s, 2 H, H^1), 3.78 (t, *J* (H^9,H^8) = 6.2 Hz, 2 H, H^9), 3.38 (s, Hz, 3 H, H^{10}), 3.11 (t, *J* (H^8,H^9) = 6.2 Hz, 2 H, H^8). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 198.6 (m, C^7), 143.3 (dm, ^1J (C^4,F^4) = 240.4 Hz, C^4), 139.9 (dm, ^1J (C^5,F^5) = 243.5 Hz, C^5), 139.5 (ddd, ^1J (C^6,F^6) = 243.7 Hz, ^2J (C^6,F^5) = 11.5 Hz, C^6), 137.9 (dm, ^2J (C^1,F^6) = 10.3 Hz, C^1), 112.5 (m, C^2), 112.3 (dm, ^2J (C^3,F^4) = 17.7 Hz, ^3J (C^3,F^5) = 3.6 Hz, C^3), 67.5 (s, C^9), 58.8 (s, C^{10}), 39.1 (s, C^8). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –149.4 (ddd, *J* (F^4,F^5) = 22.0 Hz, *J* (F^4,H^3) = 11.2 Hz, 1 F, F^4), –149.7 (m, *J* (F^5,F^4) = 22.0 Hz, *J* (F^5,F^6) = 18.5 Hz, *J* (F^5,H^3) = 8.0 Hz, 1 F, F^5), –155.5 (dm, *J* (F^6,F^5) = 18.5 Hz, 1 F, F^6). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{10}H_{10}F_3NO_2$: 233.0658; found: 233.0661.

*4.2.5.6. 6,7,8-Trifluoro-2,3-dihydroquinolin-4(1H)-one (**6c**)*

Yellowish solid; yield: 80 mg (40%); *Rf* = 0.50 (EtOAc/hexane, 1:3, twice); mp 174.9–176.3 °C. IR (KBr): 3325, 3070, 2991, 2875, 1668, 1651, 1597, 1539, 1504, 1398, 1342, 1281, 1197, 1163, 1109, 1059, 1041, 997, 883, 845, 658, 627, 579, 523, 472, 417 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45 (m, *J* (H^5,F^6) = 10.2 Hz, *J* (H^5,F^7) = 8.1 Hz, 1 H, H^5), 4.57 (s, 1 H, H^1), 3.63 (t, *J* (H^2,H^3) = 7 Hz, 2 H, H^2), 2.72 (t, *J* (H^3,H^2) = 7 Hz, 2 H, H^3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.4 (m, C^4), 144.1 (ddd, ^1J (C^7,F^7) = 258.3 Hz, ^2J (C^7,F^6) = 17.7 Hz, ^2J (C^7,F^8) = 12.7 Hz, C^7), 143.7 (ddd, ^1J (C^6,F^6) = 243.0 Hz, ^2J (C^6,F^7) = 11.2 Hz, C^6), 139.6 (ddd, ^1J (C^8,F^8) = 245.9 Hz, ^2J (C^8,F^7) = 12.4 Hz, C^8), 138.8 (dm, ^2J (C^{8a},F^8) = 10 Hz, C^{8a}), 114.2 (m, C^{4a}), 109.1 (ddm, ^2J (C^5,F^6) = 18.1 Hz, ^3J (C^5,F^7) = 3.8 Hz, C^5), 42.2 (s, C^2), 37.7 (s, C^3). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –149.7 (ddd, *J* (F^6,F^7) = 21.7 Hz, *J* (F^6,H^5) = 10.2 Hz, 1 F, F^6), –151.8 (m, *J* (F^7,F^6) = 21.7 Hz, *J* (F^7,F^8) = 18.5 Hz, *J* (F^7,H^5) = 8.1 Hz, 1 F, F^7), –157.4 (dm, *J* (F^8,F^7) = 18.5 Hz, 1 F, F^8). HRMS (EI): *m/z* $[M-H]^+$ calcd for $C_9H_5F_3NO$: 200.0318; found: 200.0319.

*4.2.5.7. 6,7,8-Trifluoro-2-isopropyl-2,3-dihydroquinolin-4(1H)-one (**6d**)*

Yellowish solid; yield: 197 mg (81%); *Rf* = 0.45 (EtOAc/hexane, 1:10); mp 99.4–99.5 °C. IR (KBr): 3346, 3095, 2964, 2935, 2877, 1668, 1653, 1527, 1508, 1462, 1387, 1259, 1275, 1178, 1082, 1059, 1007, 916, 883, 852, 704, 621, 602, 501, 455 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 (m, *J* (H^5,F^6) = 10.2 Hz, *J* (H^5,F^7) = 8.1 Hz, 1 H, H^5), 4.45 (s, 1 H, H^1), 3.44 (m, 1 H, H^2), 2.67–2.47 (m, 2 H, H^3), 1.90 (m, 1 H, H^9), 1.02 (s, 3 H, H^{10}), 1.00 (s, 3 H, $H^{10'}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.8 (m, C^4), 145.6 (ddd, ^1J (C^7,F^7) = 258.1 Hz, ^2J (C^7,F^6) = 17.7 Hz, ^2J (C^7,F^8) = 12.8 Hz, C^7), 145.0 (ddd, ^1J (C^6,F^6) = 242.9 Hz, ^2J (C^6,F^7) = 11.2 Hz, C^6), 141.1 (ddd, ^1J (C^8,F^8) = 245.6 Hz, ^2J (C^8,F^7) = 12.4 Hz, C^8), 140.0 (dm, ^2J (C^{8a},F^8) = 10 Hz, C^{8a}), 115.3 (m, C^{4a}), 110.2 (ddm, ^2J (C^5,F^6) = 18.0 Hz, ^3J (C^5,F^7) = 3.8 Hz, C^5), 60.4 (s, C^2), 41.7 (s, C^3), 33.0 (s, C^9), 19.6 (s, C^{10}), 19.2 (s, $C^{10'}$). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –149.9 (ddd, *J* (F^6,F^7) = 21.7 Hz, *J* (F^6,H^5) = 10.2 Hz, 1 F, F^6), –152.0 (m, *J* (F^7,F^6) = 21.7 Hz, *J* (F^7,F^8) = 18.5 Hz, *J* (F^7,H^5) = 8.1 Hz, 1 F, F^7), –157.5 (dm, *J* (F^8,F^7) = 18.5 Hz, 1 F, F^8). HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{12}F_3NO$: 243.0866; found: 243.0867.

*4.2.5.8. 6,7,8-Trifluoro-2,2-dimethyl-2,3-dihydroquinolin-4(1H)-one (**6e**)*

Yellowish solid; yield: 172 mg (75%); *Rf* = 0.53 (EtOAc/hexane, 1:7, twice); mp 118.8–120.2 °C. IR (KBr): 3334, 3005, 3078, 2976, 2889, 1670, 1649, 1533, 1500, 1471, 1311, 1282, 1207, 1165, 1115, 1078, 1026, 922, 883, 862, 771, 658, 619, 590, 528, 442 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (m, *J* (H^5,F^6) = 10.0 Hz, *J* (H^5,F^7) = 8.0 Hz, 1 H, H^5), 4.32 (s, 1 H, H^1), 2.59 (s, 2 H, H^3), 1.33 (s, 6 H, H^9). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.0 (m, C^4), 144.3 (ddd, ^{1}J (C^7,F^7) = 257.8 Hz, ^{2}J (C^7,F^6) = 17.6 Hz, ^{2}J (C^7,F^8) = 12.9 Hz, C^7), 143.1 (ddd, ^{1}J (C^6,F^6) = 242.3 Hz, ^{2}J (C^6,F^7) = 11.1 Hz, C^6), 139.4 (ddd, ^{1}J (C^8,F^8) = 245.3 Hz, ^{2}J (C^8,F^7) = 12.5 Hz, C^8), 136.8 (dm, ^{2}J (C^{8a},F^8) = 10 Hz, C^{8a}), 112.7 (m, C^{4a}), 108.6 (ddm, ^{2}J (C^5,F^6) = 18.0 Hz, ^{3}J (C^5,F^7) = 3.7 Hz, C^5), 54.1 (s, C^2), 50.2 (s, C^3), 27.4 (s, C^9). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –150.6 (ddm, *J* (F^6,F^7) = 21.7 Hz, *J* (F^6,H^5) = 10.0 Hz, 1 F, F^6), –151.9 (m, *J* (F^7,F^6) = 21.7 Hz, *J* (F^7,F^8) = 18.5 Hz, *J* (F^7,H^5) = 8.0 Hz, 1 F, F^7), –157.7 (dm, *J* (F^8,F^7) = 18.5 Hz, 1 F, F^8). HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{10}F_3NO$: 229.0709; found: 229.0712.

*4.2.5.9. 2,3-Dihydroquinolin-4(1H)-one (**9a**)*

Yellow oil; yield: 15 mg (10%); *Rf* = 0.60 (EtOAc/hexane, 1:2, 5 times). IR (thin): 3392, 2958, 2925, 2854, 1660, 1612, 1512, 1439, 1359, 1240, 1153, 1122, 1095, 1055, 895, 762, 559, 445 cm^{-1}. ^{1}H NMR (400 MHz, Acetone-d_6): δ = 7.68 (dm, *J* (H^5,H^6) = 7.9 Hz, 1 H, H^5), 7.25 (tm, *J* (H^7,H^8) = 8.4 Hz, *J* (H^7,H^6) = 7.0 Hz, 1 H, H^7), 6.78 (dm, *J* (H^8,H^7) = 8.4 Hz, 1 H, H^8), 6.62 (tm, *J* (H^6,H^5) = 7.9 Hz, *J* (H^6,H^7) = 7.0 Hz, 1 H, H^6), 5.97 (s, 1 H, H^1), 3.52 (m, 2 H, H^2), 2.55 (t, *J* (H^3,H^2) = 7.6 Hz, 2 H, H^3). ^{1}H NMR spectrum is close to that published earlier [32]. ^{13}C NMR (125 MHz, Acetone-d_6): δ = 193.3 (s, C^4), 153.8 (s, C^{8a}), 135.4 (s, C^7), 127.7 (s, C^5), 119.6 (s, C^{4a}), 117.4 (s, C^6), 116.8 (s, C^8), 42.4 (s, C^2), 38.6 (s, C^3). HRMS (EI): *m*/*z* $[M\text{-}H]^+$ calcd for C_9H_9NO: 147.0679; found: 147.0679.

*4.2.5.10. 2-Phenyl-2,3-dihydroquinolin-4(1H)-one (**9b**)*

Yellowish solid; yield: 149 mg (67%); *Rf* = 0.33 (EtOAc/hexane, 1:5, 4 times); mp 148.9 °C (decomp.) (149–150 °C [34]). IR (KBr): 3332, 1657, 1604, 1508, 1495, 1481, 1333, 1304, 1261, 1215, 1153, 1115, 1026, 997, 916, 766, 700, 650, 565, 492, 442 cm^{-1}. ^{1}H NMR (500 MHz, Acetone-d_6): δ = 7.71 (dm, *J* (H^5,H^6) = 8.0 Hz, 1 H, H^5), 7.55 – 7.51 (m, 2 H, H_m), 7.39 – 7.20 (m, 4 H, 2 H_o + H^7 + H_p), 6.96 (dm, *J* (H^8,H^7) = 8.3 Hz, 1 H, H^8), 6.70 (tm, *J* (H^6,H^5) = 8.0 Hz, *J* (H^6,H^7) = 7.0 Hz, 1 H, H^6), 6.21 (s, 1 H, H^1), 4.79 (dd, *J* (H^2,H^3) = 12.9 Hz, *J* (H^2,$H^{3'}$) = 4.0 Hz, 1 H, H^2), 2.82 (dd, *J* (H^3,$H^{3'}$) = 16.1 Hz, *J* (H^3,H^2) = 12.9 Hz, 1 H, H^3), 2.67 (dm, *J* ($H^{3'}$,H^2) = 16.1 Hz, *J* ($H^{3'}$,H^2) = 4.0 Hz, 1 H, $H^{3'}$). ^{1}H NMR spectrum is close to that published earlier [33]. ^{13}C NMR (125 MHz, Acetone-d_6): δ = 192.9 (s, C^4), 153.3 (s, C^{8a}), 142.1 (s, C^9), 135.7 (s, C^7), 129.4 (s, C^{11}), 128.7 (s, C^{12}), 127.6 (s, C^{10}), 127.5 (s, C^5), 119.4 (s, C^{4a}), 118.0 (s, C^6), 117.1 (s, C^8), 58.4 (s, C^2), 46.8 (s, C^3). HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{13}NO$: 223.0992; found: 223.0993.

*4.2.5.11. 6,8-Difluoro-2,3-dihydroquinolin-4(1H)-one (**9c**)*

Yellowish solid; yield: 16 mg (9%); *Rf* = 0.22 (EtOAc/hexane, 1:5, 3 times). IR (KBr): 3349, 2927, 2856, 1676, 1660, 1539, 1510, 1423, 1346, 1279, 1184, 1157, 1101, 1059, 1018, 893, 848, 667, 592, 550 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 7.23 – 7.13 (m, 2 H, H^5 + H^7), 5.93 (s, 1 H, H^1), 3.62 (m, 2 H, H^2), 2.65 (t, *J* (H^3,H^2) = 6.5 Hz, 2 H, H^3). ^{13}C NMR (125 MHz, Acetone-d_6): δ = 191.9 (t, C^4), 153.8 (dd, ^{1}J (C^6,F^6) = 236.9 Hz, ^{3}J (C^6,F^8) = 10.5 Hz, C^6), 151.9 (dd, ^{1}J

(C^8,F^8) = 245.3 Hz, ^3J (C^8,F^6) = 11.1 Hz, C^8), 139.7 (dd, ^2J (C^{8a},F^8) = 13.5 Hz, C^{8a}), 120.7 (dd, C^{4a}), 109.5 (dd, ^2J (C^7,F^6) = 28.7 Hz, ^2J (C^7,F^8) = 22.0 Hz, C^7), 107.6 (dd, ^2J (C^5,F^6) = 22.0 Hz, C^5), 42.4 (s, C^2), 38.4 (s, C^3). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –125.8 (t, J (F^6,H^5) ≈ J (F^6,H^7) = 11 Hz, 1 F, F^6), –130.4 (d, J (F^8,F^6) = 11 Hz, 1 F, F^8). HRMS (EI): m/z $[M]^+$ calcd for $C_9H_7F_2NO$: 183.0490; found: 183.0485.

*4.2.5.12. 6,7,8-Trifluoro-2-phenyl-2,3-dihydroquinolin-4(1H)-one (**9d**)*

Yellowish solid; yield: 249 mg (90%); *Rf* = 0.39 (EtOAc/hexane, 1:7, twice); mp 155.6 °C (decomp.). IR (KBr): 3315, 3062, 3035, 2974, 2872, 1668, 1647, 1601, 1527, 1502, 1456, 1383, 1365, 1277, 1209, 1157, 1063, 1020, 997, 920, 870, 854, 760, 706, 663, 621, 598, 530, 509, 478, 436 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 – 7.36 (m, 6 H, H^5 + 2 H_m + 2 H_o + H_p), 4.76 – 4.73 (m, 2 H, H^2 + H^1), 2.91 – 2.77 (m, 2 H, H^3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.3 (m, C^4), 144.3 (ddd, ^1J (C^7,F^7) = 258.8 Hz, ^2J (C^7,F^6) = 17.7 Hz, ^2J (C^7,F^8) = 12.8 Hz, C^7), 143.8 (ddd, ^1J (C^6,F^6) = 243.6 Hz, ^2J (C^6,F^7) = 12.5 Hz, C^6), 139.7 (s, C^9), 139.6 (ddd, ^1J (C^8,F^8) = 246.3 Hz, ^2J (C^8,F^7) = 12.5 Hz, C^8), 138.4 (dm, ^2J (C^{8a},F^8) = 10.4 Hz, C^{8a}), 129.0 (s, C^{11}), 128.8 (s, C^{12}), 126.4 (s, C^{10}), 113.8 (m, C^{4a}), 109.0 (dm, ^2J (C^5,F^6) = 18.2 Hz, C^5), 58.4 (s, C^2), 46.0 (s, C^3). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –148.8 (dd, J (F^6,F^7) = 21.7 Hz, J (F^6,H^5) = 10.1 Hz, 1 F, F^6), –151.2 (m, J (F^7,F^6) = 21 Hz, J (F^7,F^8) = 19 Hz, J (F^7,H^5) = 8 Hz, 1 F, F^7), –156.6 (dm, J (F^8,F^7) = 19 Hz, 1 F, F^8). HRMS (EI): m/z $[M-H]^+$ calcd for $C_{15}H_{10}F_3NO$: 277.0709; found: 277.0705.

*4.2.5.13. 5,6,8-Ttrifluoro-2,3-dihydroquinolin-4(1H)-one (**9e**)*

Yellowish solid; yield: 28 mg (14%); *Rf* = 0.40 (EtOAc/hexane, 1:7, 3 times); mp 131.2 °C (decomp.). IR (KBr): 3338, 3080, 2983, 1666, 1527, 1454, 1394, 1346, 1306, 1261, 1188, 1138, 1076, 1051, 999, 864, 839, 714, 575, 496 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 7.36 (td, J (H^7,H^8) ≈ J (H^7,H^6) = 10.6 Hz, J (H^7,F^5) = 6.9 Hz, 1 H, H^7), 6.14 (s, 1 H, H^1), 3.63 (m, 2 H, H^2), 2.64 (t, 2 H, J (H^3,H^2) = 6.9 Hz, H^3). ^{13}C NMR (125 MHz, Acetone-d_6): δ = 190.3 (t, C^4), 146.5 (ddd, ^1J (C^5,F^5) = 257.8 Hz, ^2J (C^5,F^6) = 12.8 Hz, C^5), 146.3 (ddd, ^1J (C^8,F^8) = 240.7 Hz, ^3J (C^8,F^6) = 9.5 Hz, C^8), 140.5 (ddd, ^1J (C^6,F^6) = 236.7 Hz, ^2J (C^6,F^5) = 14.0 Hz, C^6), 139.5 (dt, ^2J (C^{8a},F^8) = 14.1 Hz, C^{8a}), 110.1 (td, ^2J (C^7,F^6) ≈ ^2J (C^7,F^8) = 23.6 Hz, C^7), 108.0 (dm, C^{4a}), 41.8 (s, C^2), 39.3 (s, C^3). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –136.4 (m, J (F^8,F^5) = 17 Hz, J (F^8,H^7) = 10.9 Hz, J (F^8,F^6) = 2.7 Hz, 1 F, F^8), –145.8 (m, J (F^5,F^6) = 20 Hz, J (F^5,F^8) = 17.1 Hz, J (F^5,H^7) = 6.9 Hz, 1 F, F^5), –153.6 (ddd, J (F^6,F^5) = 19.7 Hz, J (F^6,H^7) = 10.4 Hz, J (F^6,F^8) = 3 Hz, 1 F, F^6). HRMS (EI): m/z $[M-H]^+$ calcd for $C_9H_5F_3NO$: 200.0318; found: 200.0317.

*4.2.5.14. 5,6,8-Trifluoro-2-phenyl-2,3-dihydroquinolin-4(1H)-one (**9f**)*

Yellowish solid; yield: 235 mg (85%); *Rf* = 0.53 (EtOAc/hexane, 1:7, 3 times); mp 160.5 °C (decomp.). IR (KBr): 3396, 3055, 1678, 1645, 1601, 1516, 1387, 1331, 1298, 1259, 1192, 1142, 1018, 982, 897, 847, 786, 731, 698, 586, 488 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 – 7.33 (m, 5 H, 2 H_m + 2 H_o + H_p), 7.07 (m, J (H^7,H^8) ≈ J (H^7,H^6) = 10.1 Hz, J (H^7,F^5) = 6.7 Hz, 1 H, H^7), 4.75 – 4.72 (m, 2 H, H^2 + H^1), 2.94 – 2.76 (m, 2 H, H^3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.6 (s, C^4), 145.8 (dm, ^1J (C^5,F^5) = 257.5 Hz, ^2J (C^5,F^6) = 13.0 Hz, C^5), 145.2 (dm, ^1J (C^8,F^8) = 241.6 Hz, ^3J (C^8,F^6) = 9.1 Hz, C^8), 140.8 (dm, ^1J (C^6,F^6) = 241.9 Hz, ^2J (C^6,F^5) = 14.1 Hz, C^6), 139.6 (s, C^9), 136.9 (dm, ^2J (C^{8a},F^8) = 14.0 Hz, C^{8a}), 129.0 (s, C^{11}), 128.7 (s, C^{12}), 126.4 (s, C^{10}),

109.9 (tm, ^2J (C^7,F^6) ≈ ^2J (C^7,F^8) = 24.6 Hz, C^7), 109.8 (m, C^{4a}), 57.7 (s, C^2), 47.0 (s, C^3). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –138.1 (m, J (F^8,F^5) = 17.0 Hz, J (F^8,H^7) = 10.3 Hz, J (F^8,F^6) = 2.7 Hz, 1 F, F^8), –145.8 (m, J (F^5,F^6) = 20.2 Hz, J (F^5,F^8) = 17.0 Hz, J (F^5,H^7) = 6.7 Hz, 1 F, F^5), –151.3 (ddd, J (F^6,F^5) = 20.2 Hz, J (F^6,H^7) = 9.6 Hz, J (F^6,F^8) = 2.7 Hz, 1 F, F^6). HRMS (EI): *m*/*z* $[M-H]^+$ calcd for $C_{15}H_{10}F_3NO$: 277.0709; found: 277.0712.

*4.2.5.15. 5,6,7,8-Tetrafluoro-2,3-dihydroquinolin-4(1H)-one (**9g**)*

White solid; yield: 32 mg (15%); *Rf* = 0.57 (EtOAc/hexane, 1:2, 3 times); mp 162.5 °C (decomp.). IR (KBr): 3359, 2927, 2856, 1676, 1660, 1539, 1510, 1423, 1346, 1279, 1184, 1157, 1101, 1059, 1018, 893, 848, 667, 592, 561 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 6.47 (s, 1 H, H^1), 3.66 (m, 2 H, H^2), 2.65 (t, J (H^3,H^2) = 6.7 Hz, 2 H, H^3). ^{13}C NMR (125 MHz, Acetone-d_6): δ = 189.4 (s, C^4), 147.9 (dm, ^1J (C^5,F^5) = 259.6 Hz, ^2J (C^5,F^6) = 10.2 Hz, C^5), 144.6 (dm, ^1J (C^7,F^7) = 252.9 Hz, ^2J (C^7,F^6) ≈ ^2J (C^7,F^8) = 13.5 Hz, C^7), 138.4 (dm, ^1J (C^8,F^8) = 250 Hz, C^8), 135.5 (m, C^{8a}), 132.4 (dm, ^1J (C^6,F^6) = 238.5 Hz, ^2J (C^6,F^5) ≈ ^2J (C^6,F^7) = 16 Hz, C^6), 105.4 (m, C^{4a}), 41.7 (s, C^2), 39.1 (s, C^3). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –143.1 (m, J (F^5,F^6) = 20.6 Hz, J (F^5,F^8) = 12.4 Hz, J (F^5,F^7) = 8.2 Hz, 1 F, F^5), –151.5 (m, J (F^7,F^6) = 20.6 Hz, J (F^7,F^8) = 19.5 Hz, J (F^7,F^5) = 8.2 Hz, 1 F, F^7), –163.0 (m, J (F^8,F^7) = 19.5 Hz, J (F^8,F^5) = 12.4 Hz, J (F^8,F^6) = 7.1 Hz, 1 F, F^8), –177.2 (m, J (F^6,F^7) ≈ J (F^6,F^5) = 20.4 Hz, J (F^6,F^8) = 7.1 Hz, 1 F, F^6). HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_9H_5F_4NO$: 219.0302; found: 219.0304.

*4.2.5.16. 5,6,7,8-Tetrafluoro-2-phenyl-2,3-dihydroquinolin-4(1H)-one (**9h**)*

White solid; yield: 262 mg (89%); *Rf* = 0.44 (EtOAc/hexane, 1:7, twice); mp 188.9–189.3 °C. IR (KBr): 3315, 3035, 2974, 2885, 1674, 1656, 1508, 1458, 1365, 1333, 1311, 1271, 1211, 1173, 1145, 1080, 1036, 989, 924, 862, 764, 702, 642, 559, 478 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 7.50 – 7.46 (m, 2 H, H_m), 7.41 – 7.30 (m, 3 H, 2 H_o + H_p), 6.65 (s, 1 H, H^1), 4.96 (dm, J (H^2,H^3) = 11.0 Hz, J (H^2,$H^{3'}$) = 4.6 Hz,1 H, H^2), 2.97 (dd, J (H^3,$H^{3'}$) = 15.8 Hz, J (H^3,H^2) = 11.0 Hz, 1 H, H^3), 2.85 – 2.78 (m, J ($H^{3'}$,H^3) = 15.8 Hz, J ($H^{3'}$,H^2) = 4.6 Hz, 1 H, $H^{3'}$). ^{13}C NMR (125 MHz, Acetone-d_6): δ = 189.4 (s, C^4), 148.2 (dm, ^1J (C^5,F^5) = 260.0 Hz, ^2J (C^5,F^6) = 10.0 Hz, C^5), 145.5 (dm, ^1J (C^7,F^7) = 253.8 Hz, ^2J (C^7,F^6) ≈ ^2J (C^7,F^8) = 13.8 Hz, C^7), 141.9 (s, C^9), 139.4 (m, C^{8a}), 137.1 (dm, ^1J (C^8,F^8) = 242.4 Hz, ^2J (C^8,F^7) = 12.1 Hz, C^8), 133.4 (dm, ^1J (C^6,F^6) = 240.4 Hz, ^2J (C^6,F^5) ≈ ^2J (C^6,F^7) = 15.3 Hz, C^6), 130.1 (s, C^{11}), 129.5 (s, C^{12}), 128.0 (s, C^{10}), 106.1 (dm, ^2J (C^{4a},F^5) = 8 Hz, C^{4a}), 57.9 (s, C^2), 47.5 (s, C^3). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –143.3 (m, J (F^5,F^6) = 20.4 Hz, J (F^5,F^8) = 12.4 Hz, J (F^5,F^7) = 8.3 Hz, 1 F, F^5), –150.8 (m, J (F^7,F^6) = 20.9 Hz, J (F^7,F^8) ≈ 19.5 Hz, J (F^7,F^5) = 8.3 Hz, 1 F, F^7), –161.3 (m, J (F^8,F^7) ≈ 19.5 Hz, J (F^8,F^5) = 12.4 Hz, J (F^8,F^6) = 6.5 Hz, 1 F, F^8), –176.2 (m, J (F^6,F^7) ≈ J (F^6,F^5) = 20.5 Hz, J (F^6,F^8) = 6.5 Hz, 1 F, F^6). HRMS (EI): *m*/*z* $[M-H]^+$ calcd for $C_{15}H_8F_4NO$: 294.0537; found: 294.0536.

*4.2.5.17. 5,7,8-Trifluoro-2-phenyl-6-(trifluoromethyl)-2,3-dihydroquinolin-4(1H)-one (**9i**)*

Yellowish solid; yield: 186 mg (54%); *Rf* = 0.44 (EtOAc/hexane, 1:5, twice); mp 131.2 °C (decomp.). IR (KBr): 3317, 3035, 2974, 2927, 1678, 1647, 1603, 1523, 1496, 1460, 1346, 1329, 1280, 1240, 1176, 1136, 1068, 958, 910, 870, 616, 764, 700, 640, 611, 542, 492, 457 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 7.49 – 7.46 (m, 2 H, H_m), 7.41 – 7.33 (m, 3 H, 2 H_o + H_p), 5.11 (m, 1 H, H^2), 3.06 – 2.90 (m, 2 H, H^3), 2.82 (s, 1 H, H^1). ^{13}C NMR (125 MHz, $CDCl_3$): δ =

187.8 (s, C^4), 156.1 (dm, ^1J (C^5,F^5) = 273.5 Hz, C^5), 150.4 (dm, ^1J (C^7,F^7) = 262.5 Hz, ^2J (C^7,F^8) = 13.1 Hz, C^7), 143.7 (m, C^{8a}), 138.6 (s, C^9), 135.1 (dm, ^1J (C^8,F^8) = 241.3 Hz, ^2J (C^8,F^7) = 14.9 Hz, C^8), 129.1 (s, C^{11}), 128.9 (s, C^{12}), 126.2 (s, C^{10}), 121.4 (q, ^1J (CF_3,F) = 270.9 Hz, CF_3), 105.0 (dm, ^2J (C^{4a},F^5) = 11.2 Hz, C^{4a}), 96.9 (m, C^6), 56.8 (s, C^2), 45.9 (s, C^3). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –53.6 (t, J (CF_3,F^5) ≈ J (CF_3,F^7) = 22.1 Hz, 3 F, CF_3), –115.8 (qm, J (F^5,CF_3) = 21.6 Hz, J (F^5,F^8) = 13.5 Hz, 1 F, F^5), –133.2 (m, J (F^7,CF_3) = 21.6 Hz, J (F^7,F^8) = 19.0 Hz, 1 F, F^7), –162.6 (m, J (F^8,F^7) = 19.0 Hz, J (F^8,F^5) = 13.5 Hz, 1 F, F^8). HRMS (EI): *m*/*z* $[M\text{-}H]^+$ calcd for $C_{16}H_8F_6NO$: 344.0505; found: 344.0510.

*4.2.6. 2,3,4,9,10,11-Hexafluoro-7-methyl-6-phenyl-5,6-dihydrodibenzo[b,h][1,6]naphthyridine (**10**)*

To a solution of **9d** (138 mg, 0.5 mmol) in toluene (10 mL), 1-(2-amino-3,4,5-trifluorophenyl)ethanone (94 mg, 0.5 mmol), *p*-TSA monohydrate (190 mg, 1.0 mmol) and $MgSO_4$ (360 mg, 3.0 mmol) were added, and the mixture was heated at reflux for 26 h with stirring. The mixture was allowed to cool to r.t., placed directly onto a chromatography plate (silica gel), and air-dried. The target product was isolated by TLC with EtOAc/hexane as an eluent.

Yellowish solid; yield: 45 mg (21%); *Rf* = 0.47 (EtOAc/hexane, 1:10, 4 times); mp 217.7 °C (decomp.). IR (KBr): 3408, 1647, 1574, 1510, 1468, 1396, 1338, 1286, 1265, 1199, 1171, 1107, 1041, 1016, 974 920, 868, 843, 767, 702, 555 cm^{-1}. ^{1}H NMR (300 MHz, Acetone-d_6): δ = 8.11 (m, J (H^{16},F^{17}) = 13 Hz, 1 H, H^{16}), 7.87 (m, J (H^3,F^4) = 12 Hz, J (H^3,F^5) = 8 Hz,1 H, H^3), 7.24 (s, 5 H, H_{ar}), 6.63 (s, 1 H, NH), 6.24 (d, 1 H, H^9), 2.57 – 2.52 (m, 3 H, H^{21}). ^{13}C NMR (125 MHz, Acetone-d_6): δ = 150.4 (dm, ^1J (C^{17},F^{17}) = 248.8 Hz, ^2J (C^{17},F^{18}) = 12.3 Hz, C^{17}), 148.9 (s, C^7), 146.7 (dm, ^1J (C^{19},F^{19}) = 256.5 Hz, ^2J (C^{19},F^{18}) = 9.0 Hz, C^{19}), 144.3 (dm, ^1J (C^4,F^4) = 237 Hz, ^2J (C^4,F^5) = 9.6 Hz, C^4), 143.4 (s, C^{10}), 142.7 (dm, ^1J (C^{18},F^{18}) = 252.2 Hz, ^2J (C^{18},F^{17}) = 16.9 Hz, ^2J (C^{18},F^{19}) = 14.6 Hz, C^{18}), 142.4 (s, C^{20}), 141.3 (dm, ^1J (C^5,F^5) = 252.4 Hz, ^2J (C^5,F^6) = 19.0 Hz, ^2J (C^5,F^4) = 13.4 Hz, C^5), 140.3 (dm, ^1J (C^6,F^6) = 243.2 Hz, ^2J (C^6,F^5) = 13.6 Hz, C^6), 136.5 (dm, ^2J (C^{14},F^{19}) = 8.4 Hz, C^{14}), 133.3 (t, ^2J (C^1,F^6) = 7 Hz, C^1), 129.7 (s, C^{12}), 129.7 (s, C^{12}), 128.8 (s, C^{13}), 128.6 (s, C^8), 127.7 (s, C^{11}), 125.3 (d, ^3J (C^{15},F^{17}) = 9.0 Hz, C^{15}), 117.0 (m, C^2), 108.8 (dm, ^2J (C^3,F^4) = 20.7 Hz, C^3), 106.1 (dd, ^2J (C^{16},F^{17}) = 19.0 Hz, C^{16}), 56.2 (s, C^9), 14.3 (m, C^{21}). ^{19}F NMR (282 MHz, Acetone-d_6): δ = –134.1 (m, J (F^{17},F^{18}) ≈ 20 Hz, J (F^{17},H^{16}) ≈ 12.5 Hz, 1 F, F^{17}), –146.0 (dm, J (F^{19},F^{18}) = 17.1 Hz, 1 F, F^{19}), –150.2 (m, J (F^4,F^5) ≈ 19 Hz, J (F^4,H^3) ≈ 12.5 Hz, 1 F, F^4), –157.5 (m, J (F^{18},F^{17}) = 20.3 Hz, J (F^{18},F^{19}) = 17.1 Hz, J (F^{18},H^{16}) = 8.0 Hz, 1 F, F^{18}), –157.4 – –157.9 [m, J (F^5,F^4) ≈ 19 Hz, 2 F, F^5 + F^6). HRMS (EI): *m*/*z* $[M\text{-}H]^+$ calcd for $C_{23}H_{13}F_6N_2$: 431.0977; found: 431.0965.

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