

Article

Construction of 1,2,3-Triazole-Embedded Polyheterocyclic Compounds via CuAAC and C–H Activation Strategies

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Abstract: Over the past two decades, the copper(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition (CuAAC), commonly known as click chemistry, and C–H bond activation have gained significant attention and have emerged as key synthetic methodologies. In our efforts to synthesize fused nitrogen-containing heterocycles, we developed a palladium-catalyzed protocol for the synthesis of functionalized 7,10-dihydropyrrolo[3,2,1-ij][1,2,3]triazolo[4,5-c]quinolines and 5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-a]indoles from suitable bromo-substituted *N*-propargyl-indoles. The reaction conditions demonstrate broad functional group compatibility including halogen, alkoxy, cyano, ketone, and ester, affording the target compounds in good to high yields.

Keywords: palladium catalysis; 1,2,3-triazoles; triazoloquinolines; triazoloazepinoindoles; CuAAC; C–H bond activation



Received: 21 May 2025

Revised: 10 June 2025

Accepted: 12 June 2025

Published: 13 June 2025

Citation: Iazzetti, A.; Allevi, D.; Fabrizi, G.; Gazzilli, Y.; Goggiamani, A.; Marrone, F.; Stipa, F.; Ullah, K.; Zoppoli, R. Construction of 1,2,3-Triazole-Embedded Polyheterocyclic Compounds via CuAAC and C–H Activation Strategies. *Molecules* **2025**, *30*, 2588. <https://doi.org/10.3390/molecules30122588>

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1. Introduction

The strategic incorporation of multiple pharmacophores, particularly heterocycles, into single molecular frameworks is a powerful approach in designing novel therapeutic agents. This strategy often yields hybrid molecules with enhanced biological properties. Among these, triazole-fused polycyclic heterocycles have attracted significant interest due to their broad spectrum of pharmacological activities, including anticancer, antibacterial, anti-HIV, antifungal, and anti-inflammatory effects [1–7]. The triazole unit is particularly valuable for its metabolic stability, hydrogen-bonding capabilities, and function as a non-classical amide isostere [8]. The widespread relevance of triazole-fused polycyclic heterocycles in medicinal chemistry and interdisciplinary research has spurred efforts to develop efficient and sustainable synthetic methodologies [9–11].

Transition metal-catalyzed strategies have emerged as indispensable tools for constructing complex architectures, offering advantages such as broad functional group tolerance, operational simplicity, and high efficiency. In particular, the copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC), a hallmark of click chemistry, has become the method of choice for triazole formation due to its regioselectivity, modularity, high efficiency, and

facile nature [12–15]. Triazole derivatives have found diverse applications in organic chemistry, medicinal chemistry, and functional materials, with numerous reports highlighting their versatility [16–21]. The C–H bond activation is an attractive alternative to “classical” cross-coupling reactions because it is a process capable of forming carbon–carbon, carbon–nitrogen, or carbon–oxygen bonds via the direct functionalization of a carbon–hydrogen bond with transition metal catalysis, avoiding the preparation and use of organometallic reagents [22,23].

According to our background in the construction of heterocycles [24–27], here we report an efficient process providing ready access to hybrid molecules incorporating key pharmacophores (Figure 1), including pyrroloquinoline [28–30] and azepino[1,2-*a*]indole [31–33] cores linked to triazole moieties by combining CuAAC and palladium-catalyzed C–H bond activation. Furthermore, the pyrroloquinoline moiety has also demonstrated potential in material chemistry as red-emitting dopants (DCQTB) for organic light-emitting diodes [34].

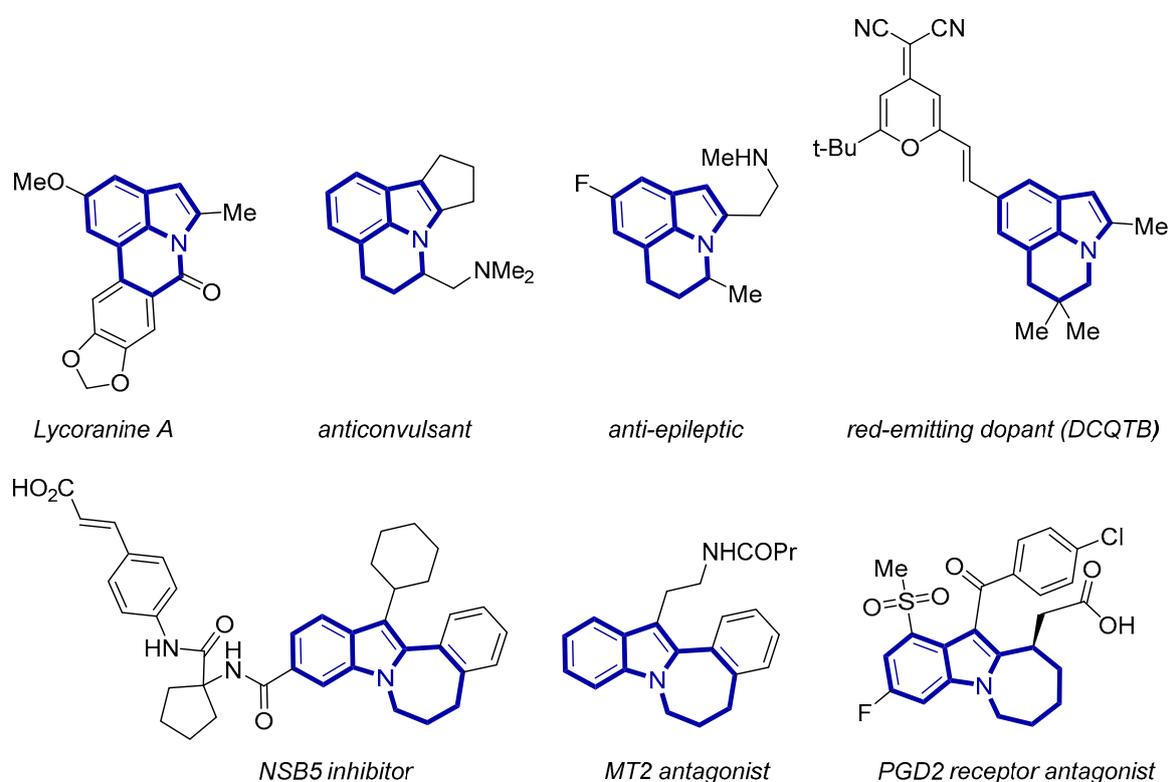
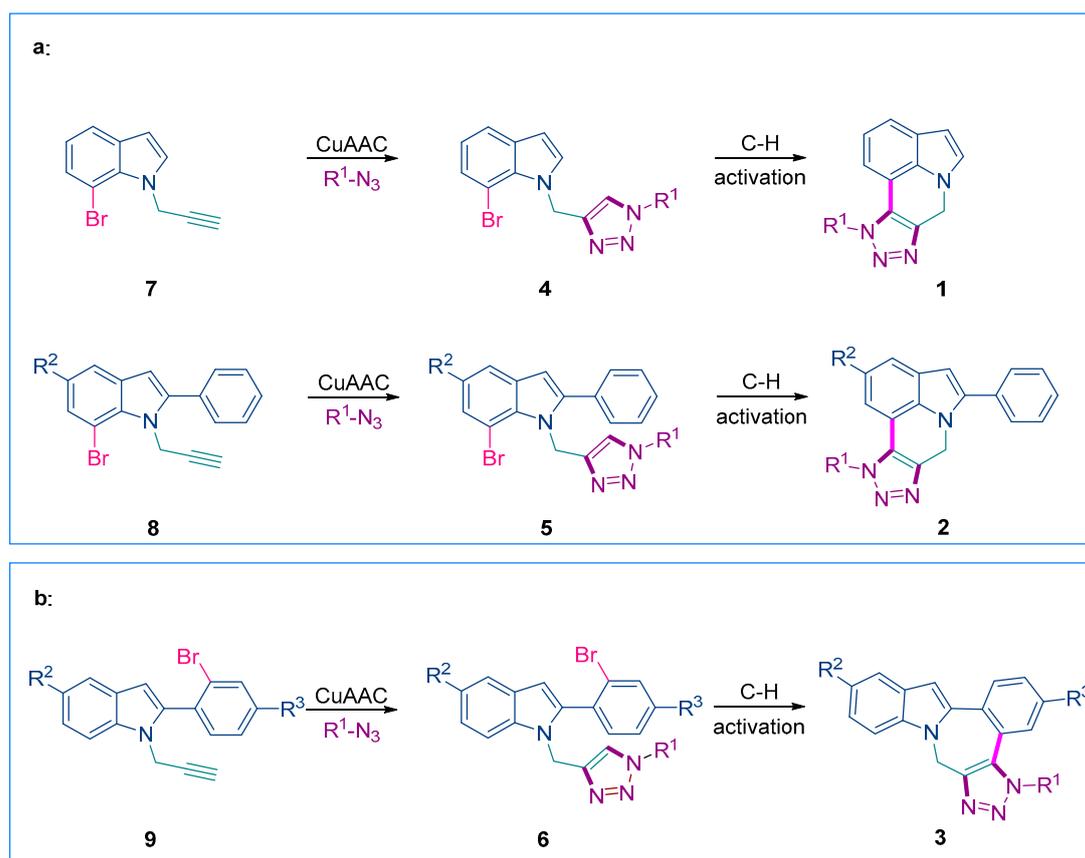


Figure 1. Natural products, biologically active compounds, and red-emitting dopants containing 5,6-dihydro-4*H*-pyrrolo [3,2,1-*ij*]quinoline and azepino[1,2-*a*]indole scaffold.

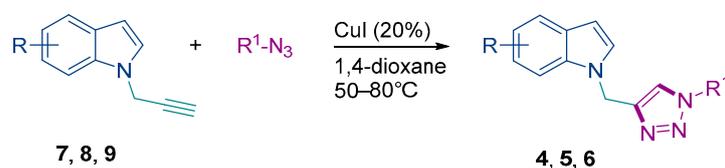
Notably, by designing opportunely the starting materials, we successfully synthesized 10-substituted-1, 5,10-disubstituted-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinolines **2** (Scheme 1a) and 5-substituted-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indoles **3** (Scheme 1b).



Scheme 1. This work. (a): construction of 7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline nucleus; (b): construction of 5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole nucleus.

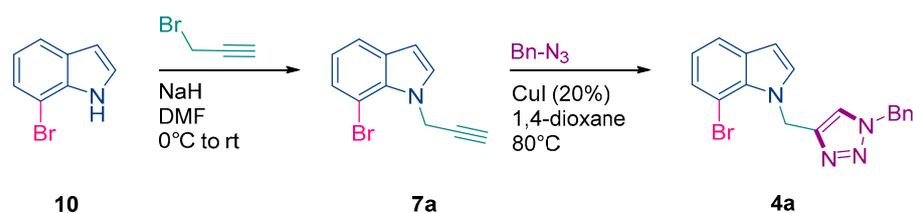
2. Results and Discussion

We selected 1-((1-substituted-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-indoles **4**, **5**, and **6** as the starting materials for the palladium-catalyzed annulation. The synthesis of the triazole core in precursors of types **4**, **5**, and **6** was carried out via a copper-catalyzed azide–alkyne cycloaddition (CuAAC) on functionalized halo *N*-propargyl indoles, specifically designed for this purpose, under reaction conditions previously optimized by our group for structurally related substrates (Scheme 2) [26]. The desired products were obtained in good yields (see Supplementary Materials).



Scheme 2. CuAAC with functionalized halo *N*-propargyl indoles **7**, **8**, and **9**.

To evaluate our working hypothesis, we initiated our investigation with the cyclization of 1-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-7-bromo-1*H*-indole **4a** into 10-benzyl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1a** as a model system to optimize reaction conditions. It is worth noting that **4a** was readily synthesized in two steps from commercially available 7-bromo-1*H*-indole **10** via *N*-propargylation, followed by a CuAAC reaction with benzyl azide (Scheme 3).



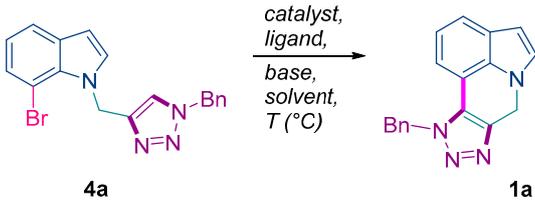
Scheme 3. Preparation of 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a**.

Different reaction parameters were screened, including transition metal catalysts, ligands, solvents, and temperatures (Table 1). For our initial attempt, we employed conditions previously developed in our copper-catalyzed synthesis of heterocycles [35], expecting that copper catalysis could enable a domino or one-pot transformation of **7a** to **1a** [CuAAC/C–H activation]. However, despite testing various Cu catalysts, solvents, and bases (Table 1, entries 1–5), no reaction occurred (Table 1, entries 1–5). Consequently, we switched to palladium catalysis for the intramolecular C–H activation. Using Pd(OAc)₂ as the palladium source, DavePhos as the ligand, and CsOAc as the base in dry DMF at 120 °C, the desired annulation product **1a** was obtained in 14% yield, while the major product was the hydrodebromination derivative 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-1H-indole, isolated in 42% yield (Table 1, entry 6) [36–38]. Interestingly, replacing the ligand with PPh₃ significantly improved the reaction outcome, affording 10-benzyl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1a** in 68% yield. Encouraged by this result, we systematically optimized the reaction parameters (Table 1, entries 8–13). Notably, the combination of Pd(OAc)₂, PPh₃, and CsOAc in dry DMSO provided the best outcome, affording **1a** in excellent 80% yield (Table 1, entry 8). Lowering the temperature (Table 1, entries 9–10) or replacing DMSO with MeCN or 1,4-dioxane led to decreased yields. Furthermore, reducing the palladium catalyst load resulted in less efficient cyclization (Table 1, entry 13).

Table 1. Optimization studies for the synthesis of 10-benzyl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1a** from 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a**^a.

Entry	Catalyst	Ligand	Base	Solvent	T (°C)	Time (h)	Yield (%) ^b
1 ^c	CuI	1,10-Phen	Li ₂ CO ₃	DMF	120	48	-
2 ^c	CuI	1,10-Phen	K ₂ CO ₃	DMSO	120	48	-
3 ^c	CuI	DMEDA	Cs ₂ CO ₃	DMF	120	48	-
4 ^c	CuOAc	1,10-Phen	K ₂ CO ₃	DMF	120	48	-
5 ^c	CuBr	1,10-Phen	K ₂ CO ₃	DMF	120	48	-
6	Pd(OAc) ₂	DavePhos	Cs(OAc)	DMF	120	2	14 ^d
7	Pd(OAc) ₂	PPh ₃	Cs(OAc)	DMF	120	1	68
8	Pd(OAc) ₂	PPh ₃	Cs(OAc)	DMSO	120	1	80
9	Pd(OAc) ₂	PPh ₃	Cs(OAc)	DMSO	100	2	69
10	Pd(OAc) ₂	PPh ₃	Cs(OAc)	DMSO	80	4	58

Table 1. Cont.

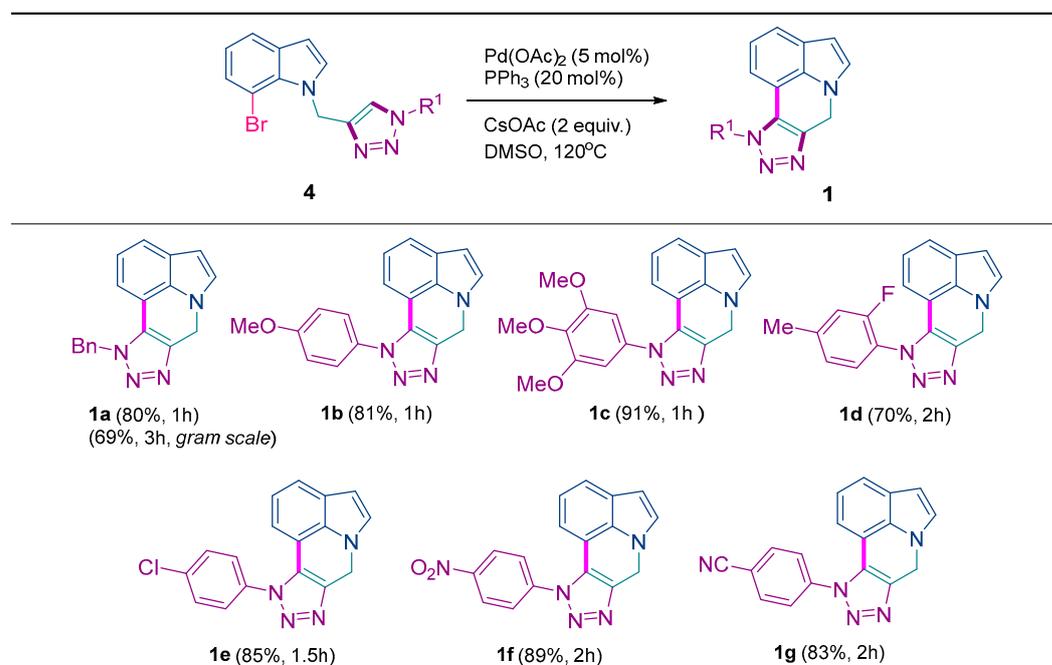


Entry	Catalyst	Ligand	Base	Solvent	T (°C)	Time (h)	Yield (%) ^b
11	Pd(OAc) ₂	PPh ₃	Cs(OAc)	1,4-dioxane	100	24	-
12	Pd(OAc) ₂	PPh ₃	Cs(OAc)	MeCN	100	2	25
13 ^e	Pd(OAc) ₂	PPh ₃	Cs(OAc)	DMSO	120	1	60

^a Unless otherwise stated, reactions were carried out on a 0.30 mmol scale under an argon atmosphere using 0.05 equiv. of catalyst, 0.20 equiv. of ligand, 2.0 equiv. of base in 2.0 mL of solvent. ^b Yields are given for isolated products. ^c 0.10 equiv. of ligand. ^d 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-1H-indole was isolated in 42%. ^e The reaction was carried out using 0.02 equiv. of catalyst, 0.08 equiv. of ligand, and 2 equiv. of base.

Once the optimal reaction conditions were established, we investigated the scope and generality of this method. Initially, we modified only the *N*-substitution on the triazole ring in **4**, introducing aryl groups with electron-donating and electron-withdrawing substituents (**4b–g**). The required starting materials were prepared according to Scheme 3, employing various aryl azides instead of benzyl azide. The resulting 10-aryl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline derivatives **1b–g** were obtained in good to excellent yields (Table 2, 70–91% yields). Subsequently, the newly designed reaction procedure was tested on the gram scale to determine its synthetic scalability, producing **1a** in 69% yield.

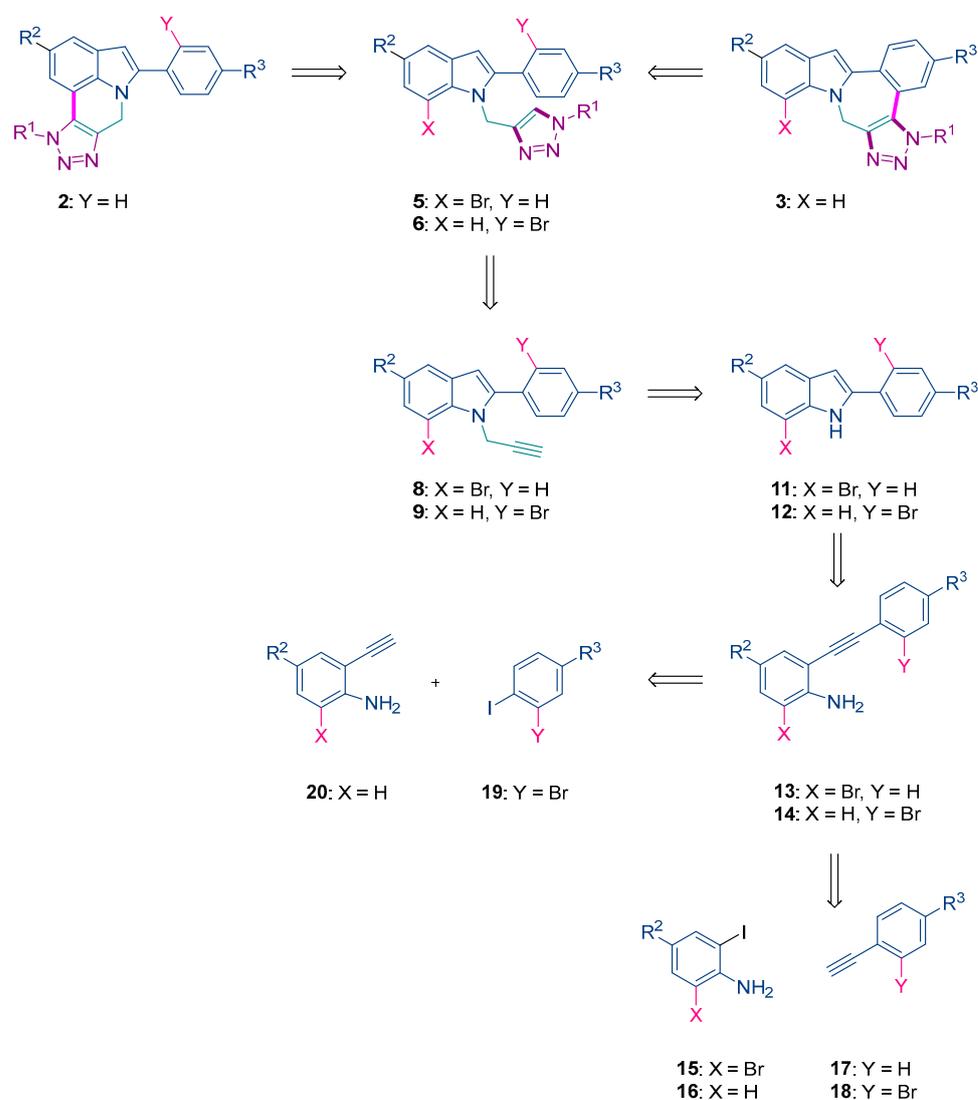
Table 2. Synthesis of 10-substituted-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1** from **4** through a palladium-catalyzed C–H activation^{a,b}.



^a Unless otherwise stated, reactions were carried out on a 0.30 mmol scale under an argon atmosphere using 0.05 equiv. of Pd(OAc)₂, 0.20 equiv. of PPh₃, 2.0 equiv. of CsOAc in 2.0 mL of anhydrous DMSO at 120 °C. ^b Yields are given for isolated products.

We further investigated a domino strategy involving the simultaneous addition of all reagents and catalysts at the beginning of the reaction. However, this approach proved inefficient, resulting in a complex reaction mixture. Consequently, a sequential protocol was adopted: the CuAAC reaction was first performed in DMSO, and, without intermediate workup, the catalyst required for C–H activation was subsequently introduced. This protocol afforded the final compound **1a** in 45% yield, along with the recovery of the starting triazole derivative **4a** in 25% yield after 24 h. Finally, a one-pot strategy incorporating an intermediate workup following the CuAAC reaction was implemented, which enabled the isolation of the desired product **1a** in a good yield of 65%.

With these encouraging results in hand, we envisioned increasing molecular complexity by introducing different substituents on 7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline nucleus. Our approach to assembling the required substrates **5** involves a one-pot, chemoselective Sonogashira cross-coupling of substituted 2-bromo-6-iodoanilines **15** with aryl acetylenes **17**, followed by an endo-dig cyclization of the resulting 2-alkynylanilines **13**. The ensuing indole derivatives **11** are then subjected to *N*-propargylation to afford **8**, which subsequently undergo a Cu-catalyzed azide–alkyne cycloaddition (CuAAC) to yield the desired starting materials (**5a–k**) (Scheme 4).

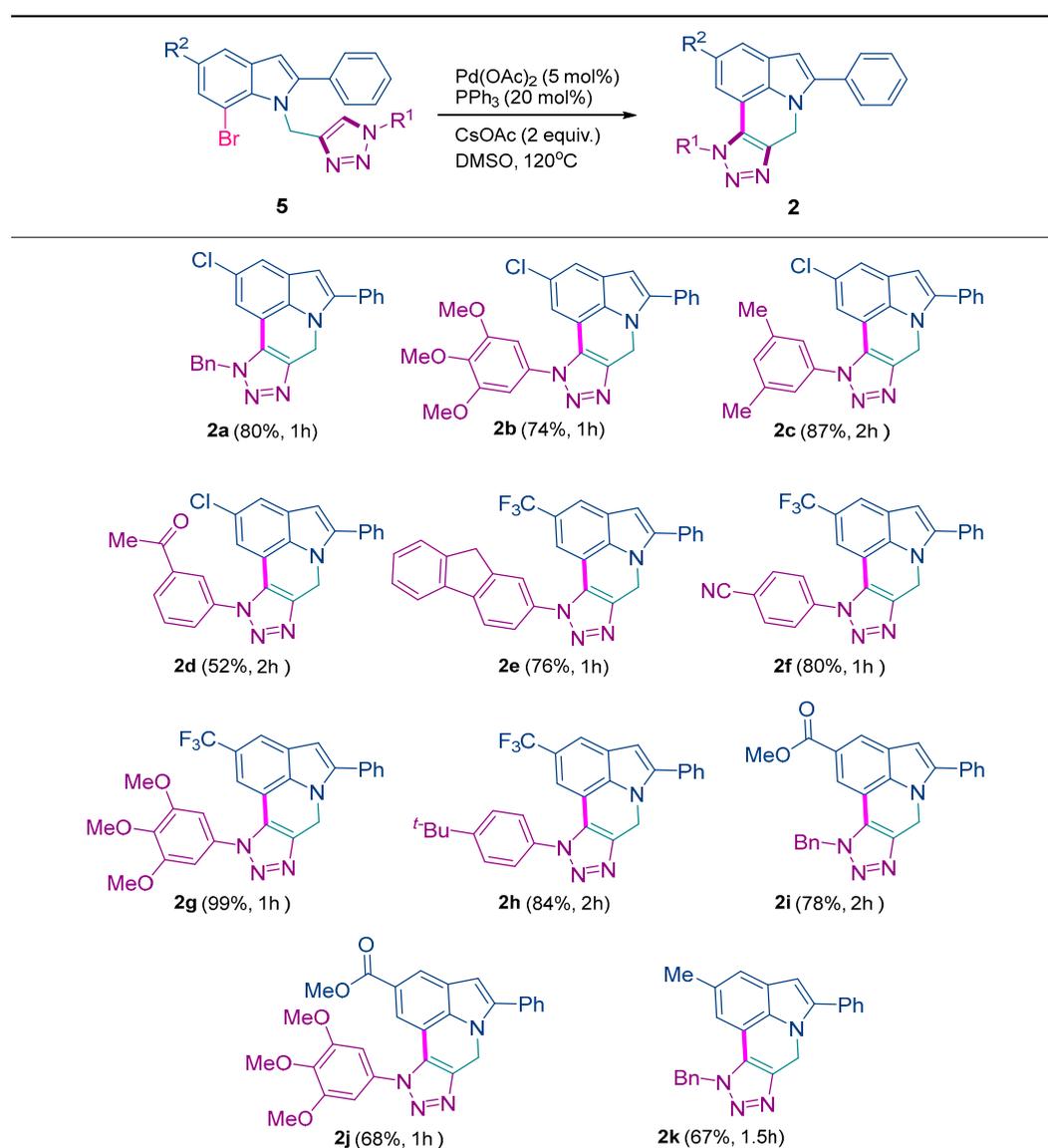


Scheme 4. Retrosynthetic approach for assembly of 7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinolines **2** and 5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indoles **3** derivatives.

Further details on the preparation of the starting materials, based on slightly modified known procedures, are provided in Supplementary Materials [39].

As shown in Table 3, good to excellent results were usually obtained with a variety of 7-bromo-1-((1-substituted-1*H*-1,2,3-triazol-4-yl)methyl)-2-phenyl-1*H*-indoles **5** containing different functionalities such as ether, ester, benzyl, and halogens both in indole and triazole cores (Table 3, **2a–k**, 52–99%).

Table 3. Synthesis of functionalized 2,5,10-trisubstituted-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2** from **5** through a palladium-catalyzed C–H activation ^{a,b}.



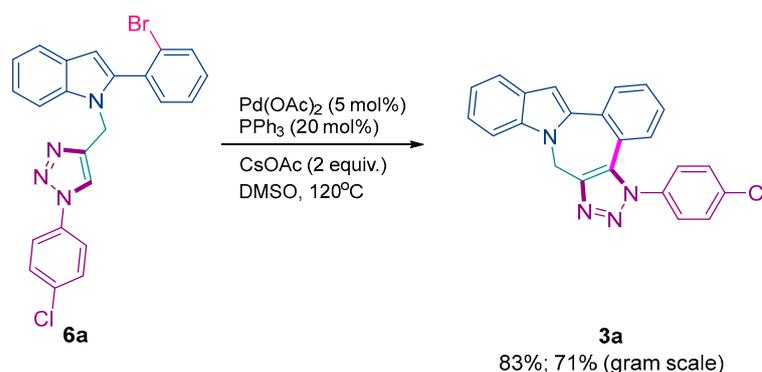
^a Unless otherwise stated, reactions were carried out on a 0.30 mmol scale under an argon atmosphere using 0.05 equiv. of Pd(OAc)₂, 0.20 equiv. of PPh₃, and 2.0 equiv. of CsOAc in 2.0 mL of anhydrous DMSO at 120 °C.

^b Yields are given for isolated products.

The potential of the reported strategy for the synthesis of polyfused *N*-heterocycles containing triazole was further demonstrated by the ready construction of the 5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole skeleton, albeit through a slight modification in the starting 1-((1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-indole. In particular, we envisaged that 2-((2-bromoaryl)ethynyl)-4-substituted aniline **14** might represent suitable building blocks for the synthesis of this core through a process that involves the

assembly of the indole ring followed by *N*-propargylation/CuAAC/palladium-catalyzed intramolecular C–H bond activation. (Scheme 3)

We selected 2-(2-bromophenyl)-1-((1-(4-chlorophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-indole **6a** as the model substrate for obtaining the corresponding 5-(4-chlorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3a**. Fortunately, under the optimized reaction condition [Pd(OAc)₂ (2 mol %), PPh₃ (4 mol %), and CsOAc (2.0 equiv.) in DMSO at 120 °C], we successfully isolated **3a** in 83% yield after one hour (Scheme 5) and on the gram scale in 71% yield.



Scheme 5. Synthesis of 5-(4-chlorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3a** from 2-(2-bromophenyl)-1-((1-(4-chlorophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-indole **6a** on a 0.30 mmol scale and a gram scale.

To demonstrate the versatility of intramolecular C–H annulation, we prepared several 2-(2-bromoaryl)-1-((1-substituted-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-indole **6**. All the tested starting materials (**6b–n**) were converted into the corresponding functionalized 5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole derivative **3** in good to excellent yield (Table 4, **3b–q**, 55–96%), regardless of the electronic effect of the substituents.

It is worth noting that the developed protocol tolerates a–Cl substituent in the indole (Table 3, **2a–d**; Table 4, **3o**, **3p**) and/or triazole framework (Scheme 5, **3a**; Table 2, **1e**; Table 4, **3f**, **3g**, **3k**, **3o**) of hybrid heterocycles **1**, **2**, and **3**, which may serve as a useful handle for introducing other functional groups through cross-coupling reactions. For example, we performed post-synthetic modification of **1e** and **3a** via palladium-catalyzed Suzuki–Miyaura coupling and Buchwald–Hartwig C–N bond-forming reactions. As shown in Scheme 6, compounds **1e** and **3a** were successfully treated with different aryl and heteroaryl boronic acids under reaction conditions previously reported by us [Pd₂dba₃, Sphos, K₃PO₄, 1,4-dioxane, 100 °C] (Scheme 6, *path a*; **21a**, **23a–c**, 71–98%) [40].

Table 4. Synthesis of polysubstituted 5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3** from **6** through a palladium-catalyzed C–H activation ^{a,b}.

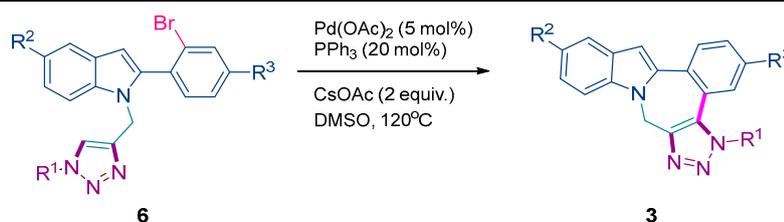
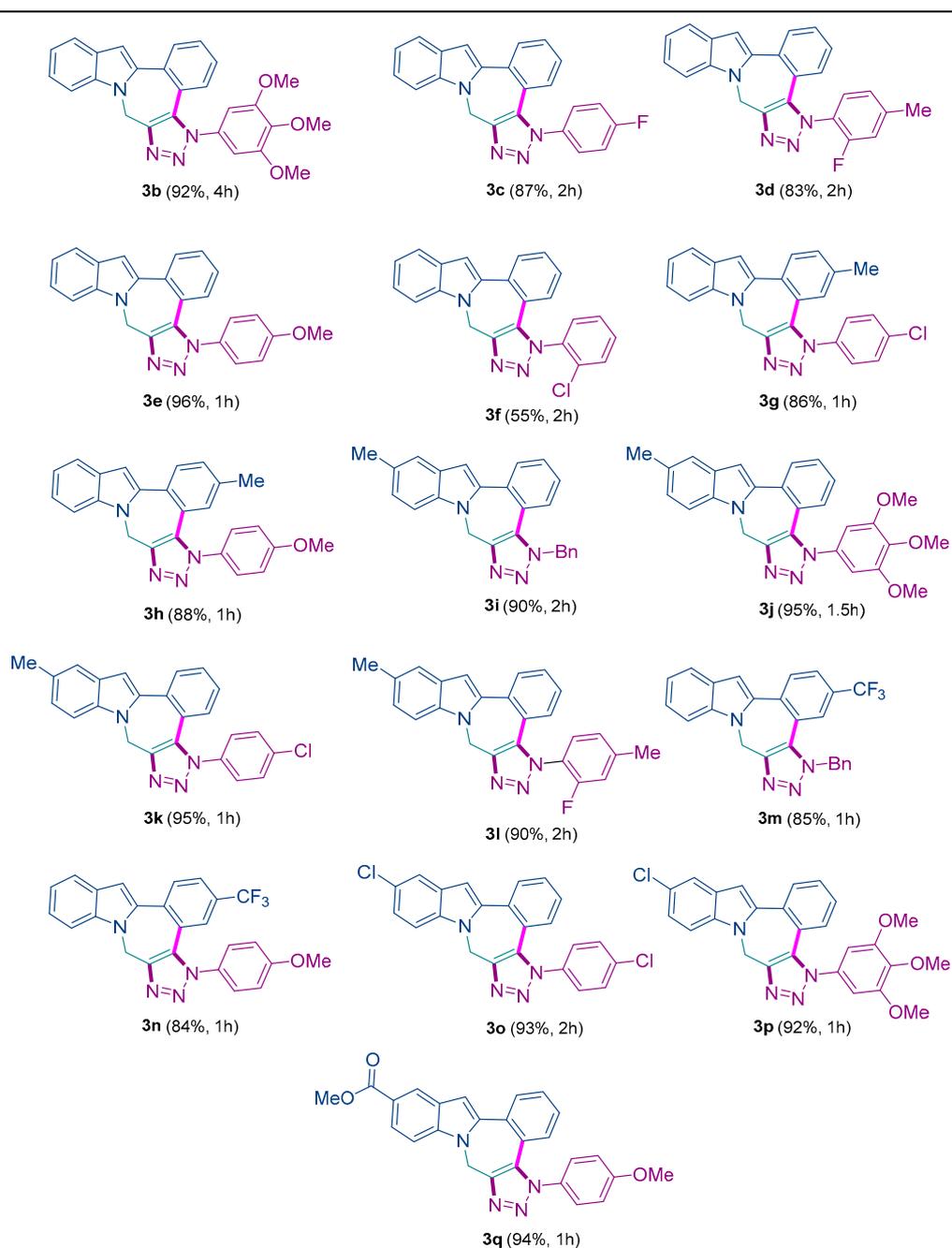


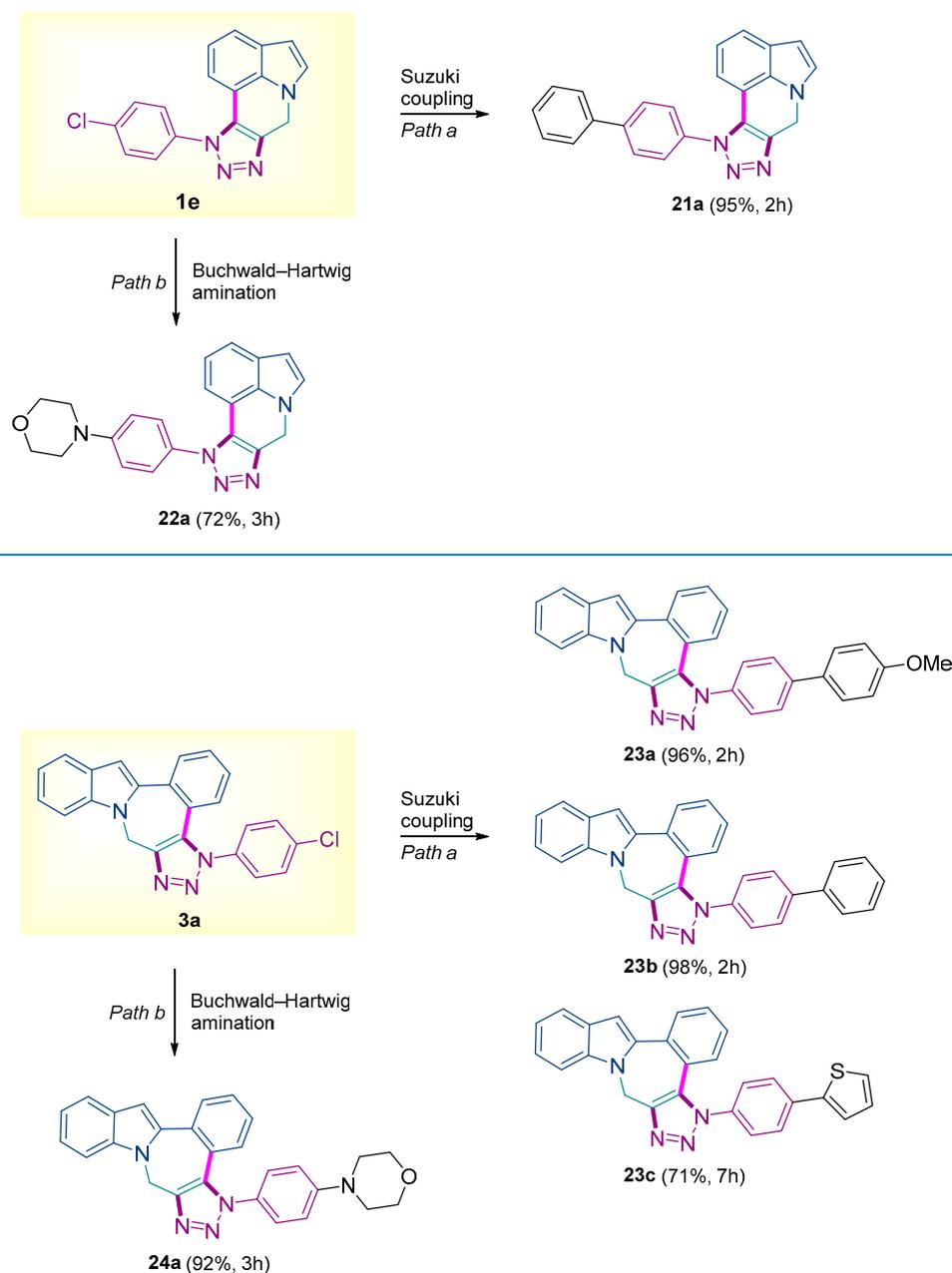
Table 4. Cont.



^a Unless otherwise stated, reactions were carried out on a 0.30 mmol scale under an argon atmosphere using 0.05 equiv. of Pd(OAc)₂, 0.20 equiv of PPh₃, and 2.0 equiv. of CsOAc in 2.0 mL of anhydrous DMSO at 120 °C.

^b Yields are given for isolated products.

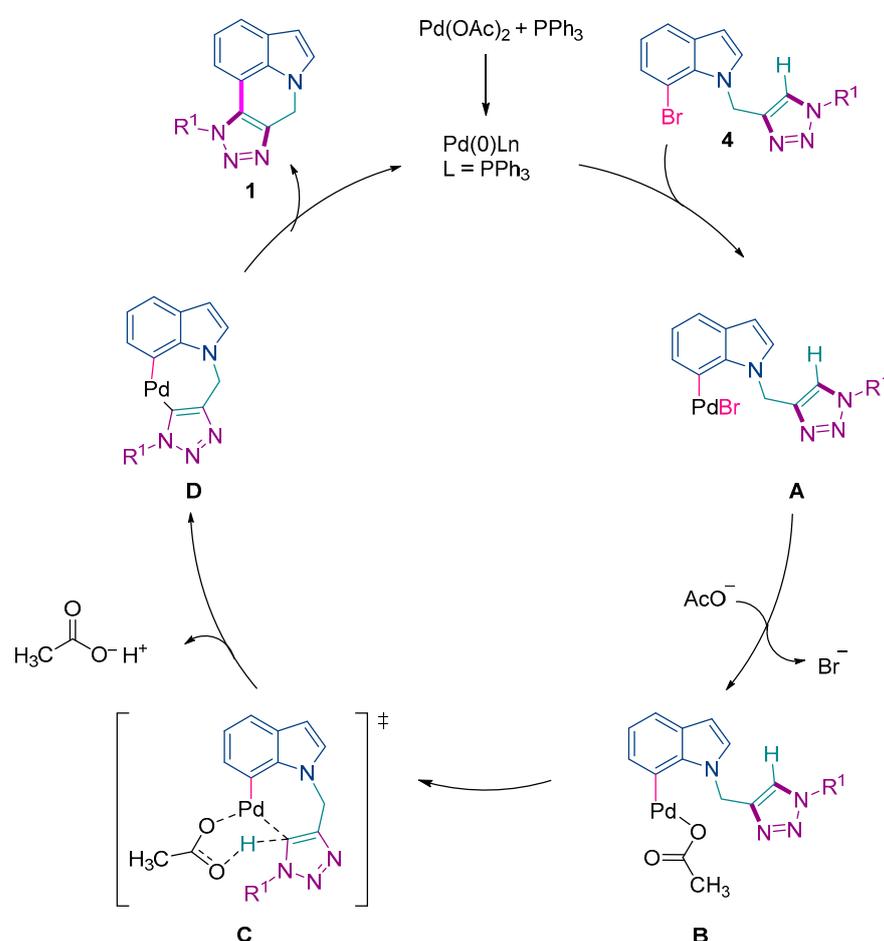
Furthermore, the Buchwald–Hartwig amination reactions were carried out in the presence of Pd₂(dba)₃, Xphos, and ^tBuOK in toluene, leading to the desired *N*-derivatives **22a** and **24a** in a yield of 72% and 92%, respectively (Scheme 6, *path b*).



Scheme 6. Post-synthetic modification of **1e** and **3a**. Path (a): reactions were carried out on a 0.25 mmol scale using 1.0 equiv. of **1e** or **3a**, 1.5 equiv. of boronic acid derivatives, 0.02 equiv. of $\text{Pd}_2(\text{dba})_3$, 0.04 equiv. of Sphos, and 3.0 equiv. of K_3PO_4 in 2.0 mL of dry 1,4-dioxane under argon at 100 °C. Path (b): reaction was carried out on a 0.25 mmol scale using 1.0 equiv. of **1e** or **3a**, 1.5 equiv. of morpholine, 0.02 equiv. of $\text{Pd}_2(\text{dba})_3$, 0.04 equiv. of Xphos, and 2.0 equiv. of $t\text{BuOK}$ in 2.0 mL of dry toluene under argon at 100 °C.

Based on the literature reports highlighting the role of the acetate ion in promoting the cyclization process [41], the mechanism of palladium-catalyzed C–H functionalization/C–C bond formation can be rationalized, as depicted in Scheme 7, for the formation of the final product **1** (ligands omitted for clarity). Following the in situ reduction of Pd(II) to Pd(0), oxidative addition of substrate **4** to Pd(0) generates the aryl palladium complex **A**. In the presence of the acetate ion, a rapid ligand exchange occurs, affording the palladium(II)-acetate complex **B**. This intermediate undergoes cyclopalladation via transition state **C**, forming the seven-member palladacycle **D**. The transition state likely involves a concerted metalation–deprotonation (CMD) process, where the Pd–C bond formation and C–H bond

cleavage occur simultaneously, facilitated by the acetate ligand acting as base. Finally, reductive elimination regenerates the active Pd(0) species and delivers the triazole-fused heterocycle **1**.



Scheme 7. Proposed reaction mechanism.

However, the involvement of an electrophilic mechanism reported for direct Pd-catalyzed arylation of 1,2,3-triazoles cannot be definitively ruled out [42].

3. Materials and Methods

3.1. General Information

All of the commercially available reagents, catalysts, bases, and solvents were used as purchased, without further purification. Starting materials and reaction products were purified by flash chromatography using SiO₂ as the stationary phase, eluting with *n*-hexane/ethyl acetate (EtOAc) mixtures. ¹H NMR (400.13 MHz), ¹³C NMR (100.6 MHz), and ¹⁹F spectra (376.5 MHz) were recorded with a Bruker Avance 400 spectrometer equipped with a Nanobay console and Cryoprobe Prodigy probe (Bruker, Billerica, MA, USA). Splitting patterns are designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or bs (broad singlet). IR spectra were recorded with a Jasco FT/IR-430 spectrometer (JASCO Corporation, Tokyo, Japan). HRMS were recorded with an Orbitrap Exactive Mass spectrometer with ESI source (Thermo Fisher, Waltham, MA, USA). Melting points were determined with a Büchi B-545 apparatus and are uncorrected.

3.2. General Experimental Procedures

3.2.1. Synthetic Procedures for Starting Materials

General Procedure for the Preparation of 1-((1-Substituted)-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4**

Typical procedure for the preparation of 1-((1-benzyl)-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a**

STEP 1: Synthesis of 7-bromo-1-(prop-2-yn-1-yl)-1H-indole **7a**

A flame-dried 100 mL three-necked round-bottom flask, equipped with a magnetic stirring bar, was charged under argon with NaH (60% dispersion in mineral oil, 240.0 mg, 6.00 mmol, 1.2 equiv.). The solid was washed three times with *n*-hexane and then suspended in anhydrous DMF (15.0 mL). The suspension was cooled to 0 °C, and a solution of 7-bromo-1H-indole **10** (980.0 mg, 5.00 mmol, 1.0 equiv.) in DMF (15.0 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 5 min. After cooling again to 0 °C, propargyl bromide (solution 80 wt % in toluene) (808 µL, 7.50 mmol, 1.5 equiv.) was added dropwise. The mixture was subsequently warmed to room temperature and stirred for 30 min. Upon completion, the reaction was quenched with water, diluted with diethyl ether, and washed with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on SiO₂ (25–40 µm), followed by eluting with a 90/10 (*v/v*) *n*-hexane-AcOEt mixture (*R_f* = 0.25) to obtain 7-bromo-1-(prop-2-yn-1-yl)-1H-indole **7a** (1.111 g, 95% yield).

7-bromo-1-(prop-2-yn-1-yl)-1H-indole **7a**: 95% yield; white solid; mp: 65–67 °C; IR (neat): 3267, 1303, 917, 779, 710 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.46 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.15 (s, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.45 (d, *J* = 3.3 Hz, 1H), 5.29 (d, *J* = 2.5 Hz, 2H), 2.35 (d, *J* = 2.5 Hz, 1H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 132.4 (C), 132.2 (C), 130.1 (CH), 127.2 (CH), 121.2 (CH), 120.6 (CH), 103.6 (C), 102.8 (CH), 78.8 (C), 74.2 (CH), 38.1 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₁₁H₉BrN: 233.9913; found: 233.9926.

STEP 2: synthesis of 1-((1-benzyl)-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a**

In a 50 mL Radley's Discovery Technology Carousel reactor equipped with a magnetic stirrer (Radley, London, UK), 7-bromo-1-(prop-2-yn-1-yl)-1H-indole **7a** (1.0 g, 4.27 mmol, 1.0 equiv.) was dissolved in 4 mL of 1,4-dioxane. Then, CuI (162.3 mg, 0.85 mmol, 0.20 equiv.) and benzyl azide (624.7 mg, 4.70 mmol, 1.1 equiv.) were sequentially added, the vial was sealed, and the reaction mixture was stirred at 80 °C overnight. Upon completion, the mixture was concentrated under reduced pressure, and the crude product was purified by flash chromatography on SiO₂ (25–40 µm), eluting with an 80/20 (*v/v*) *n*-hexane-AcOEt mixture (*R_f* = 0.25) to afford 1-((1-benzyl)-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a** (1.489 g, 95% yield).

1-((1-benzyl)-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a**: 95% yield; off-white solid; mp: 85–87 °C; IR (neat): 3067, 1554, 1313, 912, 709 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.46–7.36 (m, 1H), 7.25–7.15 (m, 4H), 7.15–7.09 (m, 2H), 7.04 (dd, *J*₁ = 6.7, *J*₂ = 2.9 Hz, 2H), 6.80 (t, *J* = 7.7 Hz, 1H), 6.39 (d, *J* = 3.3 Hz, 1H), 5.75 (s, 2H), 5.26 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 146.1 (C), 134.6 (C), 132.1 (C), 132.1 (C), 131.1 (CH), 129.1 (CH), 128.7 (CH), 127.8 (CH), 127.2 (CH), 122.1 (CH), 120.9 (CH), 120.7 (CH), 103.5 (C), 102.9 (CH), 54.1 (CH₂), 43.6 (CH₂); HRMS: *m/z* [M + H]⁺ calcd for C₁₈H₁₆BrN₄: 367.0553; found: 367.0561.

One-Pot Protocol for the Preparation of 1-((1-Substituted)-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4** Starting from **10**

Starting materials **4a–e** were prepared through a one-pot, two-steps protocol omitting the isolation of **7a–e**.

Starting materials **5a–5k** and **6a–6q** were prepared according to slightly modified literature procedures described in the Supplementary Materials [43] through the retrosynthesis depicted in Scheme 3.

3.2.2. Synthetic Procedures for Final Products

Typical Procedure for the Preparation of Functionalized 10-Substituted 7,10-dihydropyrrolo[3,2,1-ij][1,2,3]triazolo[4,5-c]quinoline **1** and **2**: Synthesis of 10-benzyl-7,10-dihydropyrrolo[3,2,1-ij][1,2,3]triazolo[4,5-c]quinoline **1a**

In a 50 mL Carousel Tube Reactor (Radley, London, UK), equipped with a magnetic stirrer, Pd(OAc)₂ (3.4 mg, 0.015 mmol, 0.05 equiv.) and PPh₃ (7.9 mg, 0.03 mmol, 0.10 equiv.) were dissolved in anhydrous DMSO (2 mL) under an argon atmosphere at room temperature. To this solution, 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a** (110.2 mg, 0.30 mmol, 1.0 equiv.) and Cs(OAc) (114.6 mg, 0.60 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at 120 °C and monitored by TLC (*n*-hexane/EtOAc, 80/20) for the conversion of **4a** into 10-benzyl-7,10-dihydropyrrolo[3,2,1-ij][1,2,3]triazolo[4,5-c]quinoline **1a**. Upon completion, the mixture was diluted with diethyl ether, washed with saturated NaCl solution, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on SiO₂ (25–40 μm), eluting with an 80/20 (*v/v*) *n*-hexane–AcOEt mixture (*R_f* = 0.20) to afford **1a** (68.6 mg, 80% yield).

Gram-Scale Synthesis of 10-Benzyl-7,10-dihydropyrrolo[3,2,1-ij][1,2,3]triazolo[4,5-c]quinoline **1a**

In a 50 mL Carousel Tube Reactor (Radley, London, UK), equipped with a magnetic stirrer, Pd(OAc)₂ (10.2 mg, 0.045 mmol, 0.05 equiv.) and PPh₃ (23.7 mg, 0.09 mmol, 0.10 equiv.) were dissolved in anhydrous DMSO (6.0 mL) under an argon atmosphere at room temperature. To this solution, 1-((1-benzyl-1H-1,2,3-triazol-4-yl)methyl)-7-bromo-1H-indole **4a** (1.10 g, 3.00 mmol, 1.0 equiv.) and CsOAc (343.8 mg, 1.8 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at 120 °C and monitored by TLC (*n*-hexane/EtOAc, 80/20) for the conversion of **4a** into 10-benzyl-7,10-dihydropyrrolo[3,2,1-ij][1,2,3]triazolo[4,5-c]quinoline **1a**. Upon completion, the mixture was diluted with diethyl ether, washed with saturated NaCl solution, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on SiO₂ (25–40 μm), eluting with an 80/20 (*v/v*) *n*-hexane–AcOEt mixture (*R_f* = 0.20) to afford **1a** (592.7 mg, 69% yield).

10-benzyl-7,10-dihydropyrrolo[3,2,1-ij][1,2,3]triazolo[4,5-c]quinoline **1a**: white solid; mp: 246–248 °C; IR (neat): 3156, 1309, 1230, 684, 599 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.37 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.0 Hz, 1H), 7.29–7.09 (m, 5H), 7.03 (d, *J* = 3.1 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.43 (d, *J* = 3.2 Hz, 1H), 5.73 (s, 2H), 5.57 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 139.9 (C), 134.6 (C), 133.4 (C), 129.1 (CH), 128.3 (CH), 126.84 (CH), 126.82 (C), 126.6 (CH), 125.9 (C), 122.4 (CH), 120.1 (CH), 114.5 (CH), 109.1 (C), 103.6 (CH), 53.3 (CH₂), 44.6 (CH₂); HRMS: *m/z* [M + H]⁺ calcd for C₁₈H₁₅N₄: 287.1291; found: 287.1287.

Typical Procedure for the Preparation of Functionalized

5-Substituted-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-a]indole **3**:

5-(4-chlorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-a]indole **3a**

In a 50 mL Carousel Tube Reactor (Radley, London, UK), equipped with a magnetic stirrer, Pd(OAc)₂ (3.4 mg, 0.015 mmol, 0.05 equiv.) and PPh₃ (7.9 mg, 0.03 mmol, 0.10 equiv.) were dissolved in anhydrous DMSO (2 mL) under argon. Then, 2-(2-bromophenyl)-1-((1-(4-chlorophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-1*H*-indole **6a** (139.1 mg, 0.3 mmol, 1 equiv.) and CsOAc (114.6 mg, 0.6 mmol, 2.0 equiv.) were added, and the reaction mixture was stirred at 120 °C and monitored by TLC. Upon completion, the mixture was diluted with diethyl ether, washed with saturated NaCl solution, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on SiO₂ (25–40 μm), eluting with an 70/30 (*v/v*) *n*-hexane-AcOEt mixture (*R_f* = 0.19) to afford **3a** (95.3 mg, 83% yield).

5-(4-chlorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-a]indole **3a**: 83% yield; yellow solid; IR (neat): 1600, 1459, 1053, 786, 765 cm⁻¹; mp: 232–234 °C; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.50–7.44 (m, 3H), 7.39–7.37 (m, 2H), 7.31 (td, *J*₁ = 8.3 Hz, *J*₂ = 1.2 Hz, 1H), 7.25 (td, *J*₁ = 8.6 Hz, *J*₂ = 1.2 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.86 (s, 1H), 5.44 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 145.0 (C), 138.4 (C), 137.0 (C), 135.7 (C), 135.2 (C), 133.8 (C), 132.5 (C), 131.9 (CH), 129.9 (CH), 129.8 (CH), 128.6 (CH), 127.9 (C), 127.8 (CH), 126.3 (CH), 122.7 (CH), 122.6 (C), 121.0 (CH), 120.2 (CH), 109.3 (CH), 104.0 (CH), 39.4 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₂₃H₁₆ClN₄: 383.1058; found: 383.1066.

3.2.3. Synthetic Procedures for Post-Synthetic Derivatives Compounds **21a**, **23a–c**, **22a**, and **24a**

Typical Procedure for the Suzuki Cross-Coupling: Synthesis of

10-([1,1'-Biphenyl]-4-yl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinolone **21a**

A Carousel Tube Reactor (Radley, London, UK), equipped with a magnetic stirrer, was charged with Pd₂(dba)₃ (4.6 mg, 0.005 mmol, 0.02 equiv.), Sphos (4.1 mg, 0.010 mmol, 0.04 equiv.), and dry dioxane (2.0 mL). After solubilization of this precatalyst system at room temperature under an argon atmosphere, compound **1e** (76.7 mg, 0.25 mmol, 1.0 equiv.), phenyl boronic acid (45.7 mg, 0.375 mmol, 1.5 equiv.), and K₃PO₄ (0.159 g, 0.750 mmol, 3.0 equiv.) were added. The resulting mixture was heated at 100 °C and stirred for 2 h. Afterwards, the mixture was cooled, added with ethyl acetate, and washed with brine. The organic phase was separated, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on SiO₂ (25–40 μm), (90:10 *n*-hexane/EtOAc) to obtain **21a** (82.6 mg, 95% yield).

10-([1,1'-biphenyl]-4-yl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **21a**: 95% yield; red solid; mp: 220–222 °C; IR (neat): 3152, 1333, 1248, 1068, 708 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.77 (d, *J* = 8.30 Hz, 2H), 7.65–7.60 (m, 5H), 7.46–7.41 (m, 3H), 7.14 (d, *J* = 3.00 Hz, 1H), 6.80–6.70 (m, 2H), 6.5 (d, *J* = 3.00 Hz, 1H), 5.73 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 143.4 (C), 139.6 (C), 136.0 (C), 133.7 (C), 129.9 (C), 129.1 (CH), 128.4 (C), 128.3 (CH), 128.2 (CH), 127.3 (C), 126.9 (CH), 126.3 (CH), 126.0 (C), 122.7 (CH), 120.0 (CH), 114.4 (CH), 109.2 (C), 103.8 (CH), 44.6 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₂₃H₁₇N₄: 349.1448; found: 349.1432.

Typical Procedure for the Buchwald–Hartwig N-Arylation: Synthesis of

4-(4-(Benzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-a]indol-5(8H)-yl)phenyl)morpholine **24a**

In a 50 mL Carousel Tube Reactor (Radley, London, UK) containing a magnetic stirring bar, Pd₂(dba)₃ (4.6 mg, 0.0053 mmol, 0.02 equiv.) and Xphos ligand (4.8 mg, 0.01 mmol, 0.04 equiv.) were dissolved at room temperature with 2.0 mL of toluene under argon. Then, 5-(4-chlorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-a]indole

3a (95.7 mg, 0.25 mmol, 1.0 equiv.), morpholine (33 μ L, 0.375 mmol, 1.5 equiv.), and *t*BuOK (56.1 mg, 0.50 mmol, 2.0 equiv.) were added. The reaction mixture was stirred for 3 h at 100 °C. Afterwards, the reaction mixture was cooled to room temperature, diluted with EtOAc, and washed with a saturated NaCl solution. The organic layer was separated, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO₂ 25–40 μ m, *n*-hexane/EtOAc 70/30) to afford 4-(4-(benzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indol-5(8*H*)-yl)phenyl)morpholine **24a** (92% yield, 43.2 mg).

4-(4-(benzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indol-5(8*H*)-yl)phenyl)morpholine **24a**: 92% yield; brown solid; mp: 238–240 °C; IR (neat): 3115, 2980, 1365, 911, 709 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.23–7.09 (m, 4H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.75 (s, 1H), 5.35 (s, 2H), 3.79 (t, *J* = 4.8 Hz, 4H), 3.14 (t, *J* = 4.8 Hz, 4H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 151.7 (C), 144.5 (C), 138.7 (C), 136.9 (C), 133.6 (C), 132.3 (C), 131.6 (CH), 129.3 (CH), 128.5 (CH), 127.8 (C), 127.6 (CH), 126.0 (CH), 123.19 (C), 123.18 (C), 122.5 (CH), 120.9 (CH), 120.1 (CH), 115.5 (CH), 109.3 (CH), 103.8 (CH), 66.7 (CH₂), 48.6 (CH₂), 39.5 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₂₇H₂₄N₅O: 434.1974; found: 434.1988.

3.3. Characterization Data of Synthesized Compounds

Characterization data for the starting materials **4b–e**, **5a–k**, and **6a–q**, with their precursors reported in the Supplementary Materials.

3.3.1. Characterization Data of Final Compounds **1b–g** and **2a–k**

10-(4-methoxyphenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1b**: 81% yield; brown solid; mp: 238–240 °C; IR (neat): 3115, 2980, 1365, 911, 709 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 3.1 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.76 (t, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 3.1 Hz, 1H), 5.69 (s, 2H), 3.85 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 161.0 (C), 139.1 (C), 133.6 (C), 129.9 (C), 129.8 (C), 127.4 (CH), 126.8 (CH), 125.9 (C), 122.5 (CH), 119.9 (CH), 114.8 (CH), 114.2 (CH), 109.3 (C), 103.7 (CH), 55.7 (CH₃), 44.6 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₁₈H₁₅N₄O: 303.1240; found: 303.1233.

10-(3,4,5-trimethoxyphenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1c**: 91% yield; yellow solid; mp: 240–242 °C; IR (neat): 3109, 2991, 1344, 924, 715 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 2.9 Hz, 1H), 6.84–6.72 (m, 4H), 6.46 (d, *J* = 2.9 Hz, 1H), 5.63 (s, 2H), 3.88 (s, 3H), 3.80 (s, 6H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 153.8 (C), 139.4 (C), 139.2 (C), 133.6 (C), 132.3 (C), 129.8 (C), 126.9 (CH), 126.0 (C), 122.7 (CH), 120.0 (CH), 114.4 (CH), 109.1 (C), 103.7 (CH), 103.6 (CH), 61.2 (CH₃), 56.5 (CH₃), 44.5 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₂₀H₁₉N₄O₃: 363.1452; found: 363.1466.

10-(2-fluoro-4-methylphenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1d**: 70% yield; brown solid; mp: 270–272 °C; IR (neat): 2877, 1537, 1194, 820, 722 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.46–7.36 (m, 2H), 7.21–7.10 (m, 3H), 6.77 (t, *J* = 7.7 Hz, 1H), 6.52–6.45 (m, 2H), 5.73 (s, 2H), 2.46 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 156.6 (d, *J*_{C-F} = 253.0 Hz, C), 143.8 (d, *J*_{C-F} = 7.7 Hz, C), 138.9 (C), 133.6 (C), 131.0 (C), 128.3 (CH), 126.8 (CH), 125.9 (C), 125.79 (d, *J*_{C-F} = 3.8 Hz, CH), 122.7 (CH), 122.4 (d, *J*_{C-F} = 12.4 Hz, C), 120.1 (CH), 117.6 (d, *J*_{C-F} = 18.6 Hz, CH), 113.7 (CH), 109.0 (C), 103.7 (CH), 44.6 (CH₂), 21.6 (CH₃); ¹⁹F NMR (376.5 MHz) (CDCl₃): δ -121.29 (m). HRMS: *m/z* [M + H]⁺ calcd for C₁₈H₁₄FN₄: 305.1197; found: 305.1181.

10-(4-chlorophenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1e**: 85% yield; yellow solid; mp: 230–232 °C; IR (neat): 3059, 1508, 1198, 1087, 717 cm⁻¹; ¹H NMR

(400.13 MHz) (CDCl₃): δ 7.59–7.47 (m, 4H), 7.41 (d, J = 8.1 Hz, 1H), 7.11 (d, J = 3.2 Hz, 1H), 6.77 (t, J = 7.7 Hz, 1H), 6.61 (d, J = 7.3 Hz, 1H), 6.49 (d, J = 3.2 Hz, 1H), 5.68 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 139.4 (C), 136.5 (C), 135.5 (C), 133.6 (C), 130.0 (C), 129.8 (CH), 127.3 (CH), 126.9 (CH), 126.1 (C), 122.9 (CH), 120.0 (CH), 114.2 (CH), 108.9 (C), 103.8 (CH), 44.5 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₁₇H₁₂ClN₄: 307.0745; found: 307.0730.

10-(4-nitrophenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **1f**: 89% yield; yellow solid; mp: 246–248 °C; IR (neat): 3102, 1486, 1092, 815 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 8.51 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 3.0 Hz, 1H), 6.87 (t, J = 7.7 Hz, 1H), 6.75 (d, J = 7.1 Hz, 1H), 6.59 (d, J = 2.6 Hz, 1H), 5.80 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 148.8 (C), 142.1 (C), 140.3 (C), 133.9 (C), 130.2 (C), 127.3 (CH), 127.0 (CH), 126.6 (C), 125.4 (CH), 123.6 (CH), 120.3 (CH), 114.6 (CH), 108.7 (C), 104.3 (CH), 44.8 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₁₇H₁₂N₅O₂: 318.0985; found: 318.0973.

4-(pyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinolin-10(7*H*)-yl)benzotrile **1g**: 83% yield; yellow solid; mp: 232–234 °C; IR (neat): 3048, 1517, 1185, 1076, 678 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.96 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 3.2 Hz, 1H), 6.90 (t, J = 7.7 Hz, 1H), 6.75 (d, J = 7.3 Hz, 1H), 6.61 (d, J = 3.2 Hz, 1H), 5.79 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 140.5 (C), 140.0 (C), 133.8 (CH), 133.7 (C), 129.9 (C), 127.1 (CH), 126.7 (CH), 126.3 (C), 123.4 (CH), 120.0 (CH), 117.6 (C), 114.4 (C), 114.3 (CH), 108.6 (C), 104.0 (CH), 44.6 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₁₈H₁₂N₅: 298.1087; found: 298.1099.

10-benzyl-2-chloro-5-phenyl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2a**: 80% yield; white solid; mp: 240–242 °C; IR (neat): 3014, 1489, 1347, 1015, 985 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.63–7.21 (m, 10H), 7.16 (s, 1H), 6.91 (s, 1H), 6.43 (s, 1H), 5.77 (s, 2H), 5.54 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 142.0 (C), 140.8 (C), 134.2 (C), 132.9 (C), 131.4 (C), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.0 (C), 127.1 (C), 126.8 (CH), 126.0 (C), 121.0 (CH), 114.7 (CH), 110.3 (C), 102.9 (CH), 53.5 (CH₂), 44.2 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₂₄H₁₈ClN₄: 397.1214; found: 397.1225.

2-chloro-5-phenyl-10-(3,4,5-trimethoxyphenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2b**: 74% yield; brown solid; mp: 250–252 °C; IR (neat): 2924, 1596, 1414, 1228, 1127 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.53–7.48 (m, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.42–7.39 (m, 2H), 6.83 (s, 1H), 6.80 (s, 2H), 6.49 (s, 1H), 5.62 (s, 2H), 3.91 (s, 3H), 3.85 (s, 6H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 153.9 (C), 142.1 (C), 139.6 (C), 133.3 (C), 131.9 (C), 131.4 (C), 129.4 (C), 129.0 (CH), 128.9 (CH), 128.6 (CH), 127.9 (C), 127.3 (C), 125.9 (C), 121.4 (CH), 114.7 (CH), 110.4 (C), 103.3 (CH), 103.1 (CH), 61.2 (CH₃), 56.5 (2CH₃), 44.1 (CH₂); HRMS: m/z [M + H]⁺ calcd for C₂₆H₂₂ClN₄O₃: 473.1375; found: 473.1383.

2-chloro-10-(3,5-dimethylphenyl)-5-phenyl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2c**: 87% yield; white solid; mp: 258–260 °C; IR (neat): 3179, 1380, 1259, 1170, 999 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.53–7.34 (m, 6H), 7.21–7.13 (m, 3H), 6.65 (d, J = 1.8 Hz, 1H), 6.46 (s, 1H), 5.60 (s, 2H), 2.38 (s, 6H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 142.0 (C), 140.0 (C), 139.8 (C), 136.4 (C), 133.2 (C), 132.2 (CH), 131.4 (C), 129.0 (CH), 128.8 (CH), 128.6 (CH), 128.4 (C), 127.2 (C), 125.8 (C), 123.4 (CH), 121.1 (CH), 114.6 (CH), 110.5 (C), 103.0 (CH), 44.1 (CH₂), 21.3 (CH₃); HRMS: m/z [M + H]⁺ calcd for C₂₅H₂₀ClN₄: 411.1371; found: 411.1389.

1-(3-(2-chloro-5-phenylpyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinolin-10(7*H*)-yl)phenyl)ethan-1-one **2d**: 52% yield; yellow solid; mp: 250–252 °C; IR (neat): 3185, 1734, 1495, 1107, 662 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 8.24–8.14 (m, 2H), 7.81–7.70 (m, 2H), 7.52–7.38 (m, 6H), 6.56 (d, J = 1.8 Hz, 1H), 6.48 (s, 1H), 5.62 (s, 2H), 2.61 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 196.2 (C), 142.2 (C), 140.4 (C), 138.6 (C), 137.0 (C), 133.2 (C), 131.3 (C), 130.3 (CH), 130.2 (CH), 129.9 (CH), 129.0 (CH), 128.9 (CH), 128.7 (C), 128.59 (C), 128.56 (CH),

127.4 (C), 125.8 (C), 125.7 (CH), 121.6 (CH), 114.3 (CH), 110.1 (C), 103.1 (CH), 44.1 (CH₂), 26.8 (CH₃); HRMS: m/z [M + H]⁺ calcd for C₂₅H₁₈ClN₄O: 425.1164; found: 425.1152.

10-(9*H*-fluoren-2-yl)-5-phenyl-2-(trifluoromethyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2e**: 76% yield; brown solid; mp: 280–282 °C; IR (neat): 2921, 1487, 1294, 1109, 735 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.94 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.77–7.70 (m, 2H), 7.61–7.50 (m, 4H), 7.48–7.30 (m, 5H), 7.00 (s, 1H), 6.62 (s, 1H), 5.67 (s, 2H), 3.97 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 144.8 (C), 144.1 (C), 143.8 (C), 142.6 (C), 140.2 (C), 140.1 (C), 136.0 (C), 134.7 (C), 131.2 (C), 129.1 (CH), 128.64 (CH), 128.55 (C), 127.9 (CH), 127.2 (CH), 125.7 (C), 125.35 (CH), 125.34 (CH), 124.4 (CH), 124.7 (q, J_{C-F} = 273.0 Hz, C), 122.9 (q, J_{C-F} = 31.3 Hz, C), 122.5 (CH), 120.72 (CH), 120.68 (CH), 119.7 (q, J_{C-F} = 4.4 Hz, CH), 110.8 (q, J_{C-F} = 4.4 Hz, CH), 110.0 (C), 104.2 (CH), 44.2 (CH₂), 37.0 (CH₂); ¹⁹F NMR (376.5 MHz) (CDCl₃): δ -60.92 (s); HRMS: m/z [M + H]⁺ calcd for C₃₁H₂₀F₃N₄: 505.1635; found: 505.1647.

4-(5-phenyl-2-(trifluoromethyl)pyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinolin-10(7*H*)-yl) benzonitrile **2f**: 80% yield; white solid; mp: 224–226 °C; IR (neat): 3176, 2284, 1240, 789, 655 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.84 (s, 1H), 7.67–7.52 (m, 9H), 7.00 (s, 1H), 6.73 (s, 1H), 5.75 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): 142.7 (C), 140.3 (C), 136.9 (C), 135.9 (C), 135.0 (C), 131.1 (C), 130.1 (CH), 129.1 (CH), 129.1 (CH), 128.6 (CH), 127.0 (CH), 125.8 (C), 124.5 (q, J_{C-F} = 273.0 Hz, C), 122.9 (q, J_{C-F} = 31.8 Hz, C), 120.0 (q, J_{C-F} = 4.3 Hz, CH), 110.6 (q, J_{C-F} = 4.3 Hz, CH), 109.6 (C), 104.3 (CH), 44.2 (CH₂); ¹⁹F NMR (376.5 MHz) (CDCl₃): δ -60.93 (s); HRMS: m/z [M + H]⁺ calcd for C₂₅H₁₅F₃N₅: 442.1274; found: 442.1283.

5-phenyl-2-(trifluoromethyl)-10-(3,4,5-trimethoxyphenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2g**: 99% yield; white solid; mp: 212–214 °C; IR (neat): 3125, 1602, 1336, 1126, 816 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.91 (s, 1H), 7.65 (s, 1H), 7.49 (s, 4H), 7.40 (s, 1H), 6.83 (s, 2H), 6.74 (s, 1H), 5.99 (s, 2H), 3.91 (s, 6H), 3.87 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 153.9 (C), 146.7 (C), 145.8 (C), 138.4 (C), 135.2 (C), 132.7 (C), 131.3 (C), 131.1 (C), 129.8 (CH), 129.2 (CH), 128.8 (CH), 124.0 (CH), 124.0 (q, J_{C-F} = 273.0 Hz, C), 124.1 (q, J_{C-F} = 31.8 Hz, C), 124.0 (q, J_{C-F} = 3.6 Hz, CH), 119.9 (CH), 117.7 (q, J_{C-F} = 3.6 Hz, CH), 105.0 (CH), 104.2 (C), 98.5 (CH), 61.0 (CH₃), 56.4 (CH₃), 41.5 (CH₂); ¹⁹F NMR (376.5 MHz) (CDCl₃): δ -60.78 (s); HRMS: m/z [M + H]⁺ calcd for C₂₇H₂₂F₃N₄O₃: 507.1638; found: 507.1645.

10-(4-(*tert*-butyl)phenyl)-5-phenyl-2-(trifluoromethyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2h**: 84% yield; orange solid; mp: 230–232 °C; IR (neat): 3152, 2978, 1325, 1254, 595 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.91 (s, 1H), 7.65 (s, 1H), 7.57–7.52 (m, 2H), 7.51–7.46 (m, 6H), 7.37 (s, 1H), 6.73 (s, 1H), 6.00 (s, 2H), 1.35 (s, 9H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 154.4 (C), 142.5 (C), 139.9 (C), 136.0 (C), 133.8 (C), 131.2 (C), 129.1 (CH), 128.71 (C), 128.62 (CH), 126.8 (CH), 125.67 (C), 125.45 (CH), 124.7 (q, J_{C-F} = 273.2 Hz, C) 122.8 (q, J_{C-F} = 31.5 Hz, C), 120.5 (d, J_{C-F} = 4.0 Hz, C), 119.6 (q, J_{C-F} = 3.7 Hz, CH), 110.6 (q, J_{C-F} = 3.7 Hz, CH), 109.8 (C), 104.1 (CH), 44.2 (CH₂), 35.1 (C), 31.3 (CH₃); ¹⁹F NMR (376.5 MHz) (CDCl₃): δ -60.93 (s); HRMS: m/z [M + H]⁺ calcd for C₂₈H₂₄F₃N₄: 473.1948; found: 473.1961.

methyl 10-benzyl-5-phenyl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline-2-carboxylate **2i**: 78% yield; white solid; mp: 242–244 °C; IR (neat): 3042, 1768, 1225, 1015, 966 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 8.15 (s, 1H), 7.74 (s, 1H), 7.50–7.34 (m, 5H), 7.33–7.16 (m, 5H), 6.56 (s, 1H), 5.83 (s, 2H), 5.56 (s, 2H), 3.85 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 167.4 (C), 161.4 (C), 142.1 (C), 140.4 (C), 136.8 (C), 134.3 (C), 131.3 (C), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 127.1 (CH), 125.7 (C), 124.8 (CH), 122.6 (C), 115.5 (CH), 109.1 (C), 104.6 (CH), 53.6 (CH₂), 52.1 (CH₃), 44.3 (CH₂); HRMS: m/z [M + H]⁺ calcd for C₂₆H₂₁N₄O₂: 421.1659; found: 421.1677.

methyl 5-phenyl-10-(3,4,5-trimethoxyphenyl)-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline-2-carboxylate **2j**: 68% yield; white solid; mp: 242–244 °C; IR (neat): 3108, 2897, 1759, 1047, 987 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 8.34 (s, 1H), 8.12 (s, 1H), 7.48 (s, 4H), 7.42 (s, 1H), 6.83 (s, 2H), 6.74 (s, 1H), 5.99 (s, 2H), 3.96 (s, 3H), 3.90 (s, 6H), 3.87 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 166.7 (C), 153.9 (C), 147.0 (C), 145.2 (C), 138.4 (C), 136.2 (C), 132.7 (C), 131.4 (C), 131.2 (C), 129.8 (CH), 129.1 (CH), 128.8 (CH), 128.6 (CH), 123.8 (C), 122.7 (CH), 119.9 (CH), 105.5 (CH), 103.7 (C), 98.5 (CH), 61.1 (CH₃), 56.5 (CH₃), 52.2 (CH₃), 41.6 (CH₂); HRMS: *m/z* [M + H]⁺ calcd for C₂₈H₂₅N₄O₅: 497.1819; found: 497.1826.

10-benzyl-2-methyl-5-phenyl-7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline **2k**: 67% yield; white solid; mp: 250–252 °C; IR (neat): 3314, 3111, 1487, 1019, 971 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.65–7.42 (m, 5H), 7.42–7.22 (m, 6H), 6.91 (s, 1H), 6.53 (s, 1H), 5.91 (s, 2H), 5.67 (s, 2H), 2.37 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 140.9 (C), 140.5 (C), 134.7 (C), 133.3 (C), 132.0 (C), 129.7 (C), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.5 (CH), 128.41 (CH), 128.36 (CH), 126.8 (CH), 126.6 (C), 121.5 (CH), 116.0 (CH), 109.1 (C), 102.8 (CH), 53.4 (CH₂), 44.1 (CH₂), 21.7 (CH₃); HRMS: *m/z* [M + H]⁺ calcd for C₂₅H₂₁N₄: 377.1761; found: 377.1749.

3.3.2. Characterization Data of Final Compounds **3b–k**

5-(3,4,5-trimethoxyphenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **3b**: 92% yield; yellow solid; mp: 192–194 °C; IR (neat): 1506, 1460, 1230, 1032, 748 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.22–7.15 (m, 2H), 7.05–6.99 (m, 2H), 6.77 (s, 1H), 6.53 (s, 2H), 5.33 (s, 2H), 3.80 (s, 3H), 3.65 (s, 6H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 153.8 (C), 144.6 (C), 138.9 (C), 138.5 (C), 136.9 (C), 133.7 (C), 132.2 (C), 132.1 (C), 131.6 (CH), 129.62 (CH), 128.6 (CH), 127.7 (CH), 127.6 (C), 122.7 (C), 122.6 (CH), 120.8 (CH), 120.2 (CH), 109.3 (CH), 103.9 (CH), 102.82 (CH), 61.10 (CH₃), 56.40 (CH₃), 39.4 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₂₆H₂₃N₄O₃: 439.1765; found: 439.1774.

5-(4-fluorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **3c**: 87% yield; white solid; mp: 243–245 °C; IR (neat): 1596, 1457, 1237, 1032, 762, 669 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.34 Hz, 1H), 7.38–7.30 (m, 3H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.1 Hz, 1H), 7.10–7.03 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.76 (s, 1H), 5.34 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 162.9 (d, *J*_{C-F} = 254 Hz, C), 144.8 (C), 138.5 (C), 137.0 (C), 133.9 (C), 132.8 (d, *J*_{C-F} = 3.1 Hz, C), 132.5 (C), 131.8 (CH), 129.7 (CH), 128.5 (CH), 127.8 (C), 127.7 (CH), 127.1 (d, *J*_{C-F} = 8.7 Hz, CH), 122.7 (C), 122.7 (CH), 121.0 (CH), 120.2 (CH), 116.8 (d, *J*_{C-F} = 22.6 Hz, CH), 109.3 (CH), 104.0 (CH), 39.5 (CH₂); ¹⁹F NMR (376.5 MHz) (CDCl₃): δ -110.36 (m). HRMS: *m/z* [M + H]⁺ calcd for C₂₈H₂₅N₄O₅: 497.1819; found: 497.1827.

5-(2-fluoro-4-methylphenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **3d**: 83% yield; orange solid; mp: 255–257 °C; IR (neat): 1506, 1456, 1230, 1019, 989 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.34–7.26 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.10 (td, *J*₁ = 7.9 Hz, *J*₂ = 0.8 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.92–6.89 (m, 2H), 6.74 (s, 1H), 5.34 (s, 2H), 2.32 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 155.6 (d, *J*_{C-F} = 254 Hz, C), 143.8 (C), 143.1 (d, *J*_{C-F} = 7.41 Hz, C), 138.6 (C), 137.0 (C), 135.3 (C), 132.2 (C), 131.7 (CH), 129.7 (CH), 127.9 (C), 127.8 (d, *J*_{C-F} = 8.1 Hz, CH), 126.9 (CH), 125.9 (d, *J*_{C-F} = 3.54 Hz, CH), 122.9 (C), 122.5 (CH), 122.2 (d, *J*_{C-F} = 12.56 Hz, C), 120.9 (CH), 120.1 (CH), 117.6 (d, *J*_{C-F} = 18.30 Hz, CH), 109.3 (CH), 104.0 (CH), 39.4 (CH₂), 21.5 (CH₃); ¹⁹F NMR (376.5 MHz) (CDCl₃): δ -121.03 (bs). HRMS: *m/z* [M + H]⁺ calcd for C₂₄H₁₈FN₄: 381.1510; found: 381.1531.

5-(4-methoxyphenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3e**: 96% yield; white solid; mp: 211–213 °C; IR (neat): 1509, 1458, 1250, 1032, 832 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.81 (d, *J*₁ = 8.2 Hz, *J*₂ = 0.6 Hz 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.36 (td, *J*₁ = 7.7 Hz, *J*₂ = 0.7 Hz, 1H), 7.27–7.20 (m, 3H), 7.13 (td, *J*₁ = 7.5 Hz, *J*₂ = 1.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.93–6.87 (m, 3H), 6.76 (s, 1H), 5.36 (s, 2H), 3.78 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): 160.4 (C), 144.6 (C), 138.7 (C), 137.0 (C), 133.8 (C), 132.4 (C), 131.7 (CH), 129.7 (C), 129. (CH), 128.5 (CH), 127.9 (C), 127.7 (CH), 126.6 (CH), 123.1 (C), 122.6 (CH), 120.9 (CH), 120.2 (CH), 114.8 (CH), 109.4 (CH), 103.9 (CH), 55.7 (CH₃), 39.5 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₂₄H₁₉N₄O: 379.1553; found: 379.1565.

5-(2-chlorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3f**: 55% yield; white solid; mp: 210–212 °C; IR (neat): 1508, 1457, 1125, 1037, 764 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.83 (dd, *J*₁ = 7.85 Hz, *J*₂ = 0.54 Hz, 1H), 7.60 (d, *J* = 7.86 Hz, 1H), 7.54 (d, *J* = 8.40 Hz, 1H), 7.50–7.35 (m, 5H), 7.25 (td, *J*₁ = 15.39 Hz, *J*₂ = 7.67 Hz, *J*₃ = 0.92 Hz, 1H), 7.13–7.06 (m, 2H), 6.82 (dd, *J*₁ = 8.05 Hz, *J*₂ = 0.53 Hz, 1H), 6.77 (s, 1H), 5.49–5.34 (m, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 14.72 (C), 138.64 (C), 137.13 (C), 135.56 (C), 134.78 (C), 132.36 (C), 131.81 (CH), 131.71 (CH), 131.61 (C), 131.05 (CH), 129.78 (CH), 129.21 (CH), 128.22 (CH), 127.97 (C), 127.95 (CH), 127.02 (CH), 122.96 (C), 122.65 (CH), 121.04 (CH), 120.20 (CH), 109.43 (CH), 104.13 (CH), 39.54 (CH₂). HRMS: *m/z* [M + H]⁺ calcd for C₂₃H₁₆ClN₄: 383.1058; found: 383.1073.

5-(4-chlorophenyl)-3-methyl-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **3g**: 86% yield; yellow solid; mp: 281–283 °C; IR (neat): 1501, 1460, 1228, 989, 750 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.63 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.37–7.35 (m, 2H), 7.29–7.27 (m, 2H), 7.23–7.19 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.97 (dd, *J*₁ = 7.9 Hz, *J*₂ = 0.9 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 2H), 5.33 (s, 2H), 2.36 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 144.7 (C), 140.0 (C), 138.6 (C), 136.9 (C), 135.6 (C), 135.3 (C), 133.9 (C), 132.4 (C), 132.3 (CH), 129.9 (CH), 128.8 (CH), 128.5 (CH), 127.8 (C), 126.3 (CH), 122.6 (CH), 120.9 (CH), 120.2 (CH), 119.9 (C), 109.3 (CH), 103.8 (CH), 39.4 (CH₂), 21.5 (CH₃). HRMS: *m/z* [M + H]⁺ calcd for C₂₄H₁₈ClN₄: 397.1214; found: 397.1203.

5-(4-methoxyphenyl)-3-methyl-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **3h**: 88% yield; yellow solid; mp: 237–238 °C; IR (neat): 1513, 1555, 1034, 742, 670 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.63 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.26–7.20 (m, 3H), 7.05 (t, *J* = 7.4, 1H), 6.95 (dd, *J*₁ = 7.9 Hz, *J*₂ = 1.1 Hz, 1H), 6.91–6.87 (m, 2H), 6.80 (d, *J* = 8.05 Hz, 1H), 6.76 (s, 1H), 5.33 (s, 2H), 3.78 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 160.4 (C), 144.2 (C), 139.7 (C), 138.9 (C), 136.9 (C), 133.9 (C), 132.3 (C), 132.1 (CH), 129.8 (C), 128.7 (CH), 128.4 (CH), 127.9 (C), 126.5 (CH), 122.5 (CH), 120.9 (CH), 120.4 (C), 120.1 (CH), 114.8 (CH), 109.4 (CH), 103.7 (CH), 55.7 (CH₃), 39.6 (CH₂), 21.5 (CH₃). HRMS: *m/z* [M + H]⁺ calcd for C₂₅H₂₁N₄O: 393.1710; found: 393.1722.

5-benzyl-12-methyl-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*] indole **3i**: 90% yield; white solid; mp: 163–165 °C; IR (neat): 1510, 1452, 1032, 762, 738 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.43–7.37 (m, 2H), 7.33 (s, 1H), 7.3–7.24 (m, 5H), 7.14–7.12 (m, 2H), 7.03 (dd, *J*₁ = 8.5 Hz, *J*₂ = 1.3 Hz, 1H), 6.61 (s, 1H), 5.59 (s, 2H), 5.29 (s, 2H), 2.37 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 144.3 (C), 138.4 (C), 135.5 (C), 134.6 (C), 132.7 (C), 131.9 (CH), 129.8 (CH), 129.3 (C), 129.2 (CH), 128.4 (CH), 128.1 (C), 128.0 (CH), 127.7 (CH), 126.8 (CH), 124.3 (CH), 122.9 (C), 120.5 (CH), 109.1 (CH), 103.3 (CH), 52.5 (CH₂), 39.6 (CH₂), 21.5 (CH₃). HRMS: *m/z* [M + H]⁺ calcd for C₂₅H₂₁N₄: 377.1761; found: 377.1778.

12-methyl-5-(3,4,5-trimethoxyphenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3j**: 95% yield; white solid; mp: 234–236 °C; IR (neat): 1596, 1450, 1224, 1024, 1031 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ (dd, *J*₁ = 7.9 Hz, *J*₂ = 0.78 Hz, 1H), 7.51–7.46 (m, 3H), 7.29–7.25 (m, 1H), 7.16 (dd, *J*₁ = 8.5 Hz, *J*₂ = 1.2 Hz, 1H), 7.10 (dd,

$J_1 = 7.9$ Hz, $J_2 = 0.8$ Hz, 1H), 6.81 (s, 1H), 6.65 (s, 2H), 5.44 (s, 2H), 3.93 (s, 3H), 3.78 (s, 6H), 2.49 (s, 3H); ^{13}C NMR (100.6 MHz) (CDCl_3): δ 153.8 (C), 144.7 (C), 138.9 (C), 138.6 (C), 135.5 (C), 133.8 (C), 132.4 (C), 132.3 (C), 131.6 (CH), 129.6 (C), 129.5 (CH), 128.7 (CH), 128.1 (C), 127.5 (CH), 124.5 (CH), 122.7 (C), 120.4 (CH), 109.1 (CH), 103.4 (CH), 102.9 (CH), 61.2 (CH_3), 56.5 (CH_3), 39.6 (CH_2), 21.5 (CH_3). HRMS: m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{N}_4\text{O}_3$: 453.1921; found: 453.1907.

5-(4-chlorophenyl)-12-methyl-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3k**: 95% yield; white solid; mp: 215–217 °C; IR (neat): 1499, 1456, 1120, 1041, 789 cm^{-1} ; ^1H NMR (400.13 MHz) (CDCl_3): δ (dd, $J_1 = 7.9$ Hz, $J_2 = 0.7$ Hz, 1H), 7.39–7.36 (m, 5H), 7.30–7.28 (m, 2H), 7.17–7.13 (m, 1H), 7.05 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.1$ Hz, 1H), 6.88 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.8$ Hz, 1H), 6.68 (s, 1H), 5.32 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100.6 MHz) (CDCl_3): δ 145.1 (C), 138.4 (C), 135.7 (C), 135.6 (C), 135.3 (C), 133.8 (C), 132.6 (C), 131.8 (CH), 130.0 (CH), 129.8 (CH), 129.5 (C), 128.6 (CH), 128.1 (C), 127.7 (CH), 126.4 (CH), 124.5 (CH), 122.6 (C), 120.5 (CH), 109.0 (CH), 103.5 (CH), 39.6 (CH_2), 21.5 (CH_3). HRMS: m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{18}\text{ClN}_4$: 397.1214; found: 397.1228.

5-(2-fluoro-4-methylphenyl)-12-methyl-5,8-dihydrobenzo[3,4][1,2,3]triazolo [4',5':5,6]azepino[1,2-*a*]indole **3l**: 90% yield; white solid; mp: 231–233 °C; IR (neat): 1499, 1448, 1338, 1053, 767 cm^{-1} ; ^1H NMR (400.13 MHz) (CDCl_3): δ 7.78 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.39–7.27 (m, 4H), 7.12–7.08 (m, 1H), 7.05–6.99 (m, 2H), 6.94–6.89 (m, 2H), 6.66 (s, 1H), 5.33 (s, 2H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100.6 MHz) (CDCl_3): δ 155.7 ($J_{\text{C-F}} = 253.0$ Hz, C), 143.9 (C), 143.14 ($J_{\text{C-F}} = 7.5$ Hz, C), 138.6 (C), 135.5 (C), 135.3 (C), 132.14 (C), 131.7 (CH), 129.6 (CH), 129.4 (C), 128.2 (C), 127.8 ($J_{\text{C-F}} = 10.2$ Hz, CH), 126.9 (CH), 125.9 ($J_{\text{C-F}} = 3.16$ Hz, CH), 124.3 (CH), 122.9 (C), 122.3 ($J_{\text{C-F}} = 12.5$ Hz, C), 120.5 (CH), 117.6 ($J_{\text{C-F}} = 18.8$ Hz, CH), 109.0 (CH), 103.5 (CH_3), 39.5 (CH_2), 21.5 (CH_3); ^{19}F NMR (376.5 MHz) (CDCl_3): δ –121.01 (bs). HRMS: m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{20}\text{FN}_4$: 395.1666; found: 395.1681.

5-benzyl-3-(trifluoromethyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **3m**: 85% yield; gray solid; mp: 227–229 °C; IR (neat): 1455, 1338, 1124, 1031, 738 cm^{-1} ; ^1H NMR (400.13 MHz) (CDCl_3): δ 7.90 (d, $J = 8.2$ Hz, 1H), 7.62 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.2$ Hz, 1H), 7.57 (d, $J = 8.06$ Hz, 1H), 7.54–7.47 (m, 2H), 7.33–7.23 (m, 4H), 7.21 (m, 2H), 7.09–7.05 (m, 1H), 6.67 (s, 1H), 5.58 (s, 2H), 5.33 (s, 2H); ^{13}C NMR (100.6 MHz) (CDCl_3): δ 144.6 (C), 137.4 (C), 137.0 (C), 135.6 (C), 134.8 (C), 133.4 (C), 132.3 (CH), 131.2 (C), 130.0 ($J_{\text{C-F}} = 33.0$ Hz) (C), 129.4 (CH), 128.8 (CH), 127.7 (C), 127.1 (CH), 126.2 ($J_{\text{C-F}} = 3.5$ Hz, CH), 125.1 ($J_{\text{C-F}} = 3.6$ Hz, CH), 123.8 ($J_{\text{C-F}} = 272.0$ Hz, C), 123.4 (CH), 121.3 (CH), 120.5 (CH), 109.5 (CH), 105.2 (CH), 53.1 (CH_2), 39.5 (CH_2); ^{19}F NMR (376.5 MHz) (CDCl_3): δ –62.64 (s). HRMS: m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{18}\text{F}_3\text{N}_4$: 431.1478; found: 431.1485.

5-(4-methoxyphenyl)-3-(trifluoromethyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo [4',5':5,6]azepino[1,2-*a*]indole **3n**: 84% yield; yellow solid; mp: 260–262 °C; IR (neat): 1513, 1336, 1296, 1251, 1123 cm^{-1} ; ^1H NMR (400.13 MHz) (CDCl_3): δ 7.93 (d, $J = 8.3$ Hz, 1H), 7.62–7.57 (m, 2H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.29–7.22 (m, 3H), 7.14–7.07 (m, 2H), 6.95–6.90 (m, 2H), 6.85 (s, 1H), 5.40 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100.6 MHz) (CDCl_3): δ 160.8 (C), 144.8 (C), 137.4 (C), 137.2 (C), 135.5 (C), 132.76 (C), 132.0 (CH), 129.6 (q, $J_{\text{C-F}} = 33.0$ Hz, C), 129.1 (C), 127.8 (C), 126.6 (CH), 125.8 (q, $J_{\text{C-F}} = 3.5$ Hz, CH), 125.5 (q, $J_{\text{C-F}} = 3.8$ Hz, CH), 123.5 (C), 123.4 (CH), 123.2 (q, $J_{\text{C-F}} = 270.3$ Hz), 121.3 (CH), 120.6 (CH), 115.09 (CH), 109.53 (CH), 105.41 (CH), 55.8 (CH_3), 39.6 (CH_2); ^{19}F NMR (376.5 MHz) (CDCl_3): δ –62.24 (s). HRMS: m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{18}\text{F}_3\text{N}_4\text{O}$: 447.1427; found: 447.1411.

12-chloro-5-(4-chlorophenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **3o**: 93% yield; yellow solid; mp: 273–275 °C; IR (neat): 1497, 1333, 992, 760, 539 cm^{-1} ; ^1H NMR (400.13 MHz) (CDCl_3): δ 7.81 (d, $J_1 = 7.9$ Hz, 1H), 7.55 (d, $J = 1.8$ Hz, 1H), 7.43–7.38 (m, 4H), 7.4–7.28 (m, 2H), 7.20–7.16 (m, 2H), 6.91 (dd, $J_1 = 7.9$ Hz, $J_2 = 0.9$ Hz, 1H), 6.71 (s, 1H), 5.33 (s, 2H); ^{13}C NMR (100.6 MHz) (CDCl_3): δ 144.8 (C), 139.7 (C), 135.8

(C), 135.4 (C), 135.1 (C), 133.8 (C), 132.0 (C), 131.9 (CH), 130.0 (CH), 129.9 (CH), 128.7 (C), 128.6 (CH), 128.2 (CH), 126.3 (CH), 125.9 (C), 123.0 (CH), 122.7 (C), 120.3 (CH), 110.4 (CH), 103.5 (CH), 39.8 (CH₃). HRMS: m/z [M + H]⁺ calcd for C₂₃H₁₅Cl₂N₄: 417.0668; found: 417.0653.

12-chloro-5-(3,4,5-trimethoxyphenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **3p**: 92% yield; yellow solid; mp: 232–234 °C; IR (neat): 1605, 1461, 1125, 826, 774 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.81 (dd, $J_1 = 7.9$ Hz, $J_2 = 0.7$ Hz, 1H), 7.54 (d, $J = 1.9$ Hz, 1H), 7.43–7.38 (m, 2H); 7.24–7.14 (m, 2H); 7.02 (dd, $J_1 = 7.9$ Hz, $J_2 = 0.7$ Hz; 1H), 6.72 (s, 1H), 6.56 (s, 2H), 5.33 (s, 2H), 3.83 (s, 3H), 3.68 (s, 6H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 153.9 (C), 144.4 (C), 139.9 (C), 139.0 (C), 135.3 (C), 133.7 (C), 132.1 (C), 131.8 (C), 131.7 (CH), 129.8 (CH), 128.7 (CH), 128.7 (C), 128.0 (CH), 125.8 (C), 122.9 (CH), 122.8 (C), 120.2 (CH), 110.4 (CH), 103.4 (CH), 102.9 (CH), 61.2 (CH₃), 56.5 (CH₃), 39.8 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₂₆H₂₂ClN₄O₃: 473.1375; found: 473.1389.

methyl 5-(4-methoxyphenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole-12-carboxylate **3q**: 94% yield; white solid; mp: 200–202 °C; IR (neat): 1703, 1508, 1243, 1053, 1032 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 8.34 (d, $J = 1.1$ Hz, 1H), 7.90 (dd, $J_1 = 8.8$ Hz, $J_2 = 1.4$ Hz, 1H), 7.79 (d, $J = 7.9$ Hz, 1H), 7.49 (d, $J = 8.8$ Hz, 1H), 7.35 (dt, $J_1 = 8.0$ Hz, $J_2 = 1.1$ Hz, 1H), 7.23 (d, $J = 8.8$ Hz, 2H), 7.15 (dt, $J_1 = 8.0$ Hz, $J_2 = 1.1$ Hz, 1H), 6.93–6.87 (m, 3H), 6.82 (s, 1H), 5.35 (s, 2H), 3.84 (s, 3H), 3.76 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 168.0 (C), 160.5 (C), 144.1 (C), 140.2 (C), 139.2 (C), 133.7 (C), 131.8 (CH), 131.7 (C), 129.6 (CH), 129.5 (C), 128.5 (CH), 128.1 (CH), 127.4 (C), 126.5 (CH), 124.1 (CH), 123.7 (CH), 123.2 (C), 122.1 (C), 114.8 (CH), 109.0 (CH), 105.1 (CH), 55.7 (CH₃), 51.9 (CH₃), 39.9 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₂₆H₂₁N₄O₃: 437.1608; found: 437.1621.

3.3.3. Characterization Data of Post-Synthetic Derivatives Compounds **22a** and **23a–c**

4-(4-(pyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinolin-10(7*H*)-yl)phenyl)morpholine **22a**: 72% yield; yellow solid; mp: 190–192 °C; IR (neat): 2876, 1582, 1236, 1132, 991 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.63–7.53 (m, 1H), 7.51–7.30 (m, 5H), 7.10 (d, $J = 3.2$ Hz, 1H), 7.02–6.94 (m, 2H), 6.75 (t, $J = 7.6$ Hz, 1H), 6.64 (d, $J = 7.3$ Hz, 1H), 6.47 (d, $J = 3.2$ Hz, 1H), 5.68 (s, 2H), 3.83 (t, $J = 4.8$ Hz, 4H), 3.22 (dd, $J = 6.1, 3.6$ Hz, 4H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 152.4 (C), 139.0 (C), 133.6 (C), 132.9 (C), 132.2 (CH), 132.1 (CH), 132.0 (CH), 131.9 (CH), 129.9 (C), 128.6 (CH), 128.5 (CH), 128.4 (C), 126.9 (CH), 126.8 (CH), 125.9 (C), 122.5 (CH), 119.9 (CH), 115.3 (CH), 114.3 (CH), 109.4 (C), 103.6 (CH), 66.7 (CH₂), 48.5 (CH₂), 44.6 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₂₁H₂₀N₅O: 358.1662; found: 358.1654.

5-(4'-methoxy-[1,1'-biphenyl]-4-yl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **23a**: 96% yield; yellow solid; mp: 248–250 °C; IR (neat): 1460, 1340, 1058, 763, 740 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.84 (d, $J = 7.7$ Hz, 1H), 7.61–7.57 (m, 3H), 7.53 (d, $J = 8.6$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.40–7.38 (m, 3H), 7.24 (td, $J_1 = 8.2$ Hz, $J_3 = 0.8$ Hz, 1H), 7.18–7.16 (m, 1H), 7.07 (t, $J = 7.4$ Hz, 1H), 7.00 (dd, $J_1 = 7.9$ Hz, $J_2 = 0.9$ Hz, 1H), 6.93 (d, $J = 7.7$ Hz, 2H), 6.79 (s, 1H), 5.39 (s, 2H), 3.79 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 159.9 (C), 144.9 (C), 142.2 (C), 138.7 (C), 137.0 (C), 135.2 (C), 133.8 (C), 131.4 (C), 132.0 (C), 131.8 (CH), 129.6 (CH), 128.7 (CH), 128.3 (CH), 127.8 (CH), 125.4 (CH), 123.1 (C), 122.7 (CH), 121.0 (CH), 120.2 (CH), 114.6 (CH), 109.4 (CH), 103.9 (CH), 55.5 (CH₃), 39.6 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₃₀H₂₃N₄O: 455.1866; found: 455.1879.

5-([1,1'-biphenyl]-4-yl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole **23b**: 98% yield; white solid; mp: 220–222 °C; IR (neat): 1439, 1160, 1054, 995, 767 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.84 (d, $J = 7.9$ Hz, 1H), 7.63–7.59 (m, 3H), 7.55–7.51 (m, 3H), 7.43–7.37 (m, 5H), 7.33 (m, 1H), 7.23 (td, $J_1 = 7.7$ Hz, $J_2 = 0.8$ Hz, 1H), 7.18–7.14 (m, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 7.00 (dd, $J_1 = 7.9$ Hz, $J_2 = 0.6$ Hz, 1H), 6.80 (s, 1H), 5.38 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 144.8 (C), 142.5 (C), 139.5 (C), 138.6 (C), 136.9 (C), 135.7 (C),

133.7 (C), 132.4 (C), 131.7 (CH), 129.6 (CH), 129.0 (CH), 128.7 (CH), 128.2 (CH), 128.1 (CH), 127.8 (C), 127.7 (CH), 127.2 (CH), 125.3 (CH), 122.9 (C), 122.6 (CH), 120.9 (CH), 120.1 (CH), 109.3 (CH), 103.8 (CH), 39.5 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₂₉H₂₁N₄: 425.1766; found: 425.1753.

5-(4-(thiophen-2-yl)phenyl)-5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino [1,2-*a*]indole **23c**: 71% yield; gray solid; mp: 218–220 °C; IR (neat): 1458, 1319, 1032, 994, 728 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.62–7.59 (m, 3H), 7.52 (d, *J* = 8.3, 1H), 7.46–7.44 (m, 1H), 7.39–7.32 (m, 5H), 7.23 (dt, *J*₁ = 6.9 Hz, *J*₂ = 0.8 Hz, 1H), 7.17–7.12 (m, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.86 Hz, 1H), 6.79 (s, 1H), 5.33 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 144.9 (C), 140.8 (C), 138.6 (C), 137.2 (C), 137.0 (C), 135.4 (C), 133.8 (C), 132.4 (C), 131.8 (CH), 129.6 (CH), 128.7 (CH), 127.9 (C), 127.8 (CH), 127.5 (CH), 127.0 (CH), 126.2 (CH), 126.0 (C), 125.5 (CH), 122.7 (CH), 121.6 (CH), 121.0 (CH), 120.2 (CH), 109.4 (CH), 103.9 (CH), 39.6 (CH₂). HRMS: m/z [M + H]⁺ calcd for C₂₇H₁₉N₄S: 431.1330; found: 431.1346.

4. Conclusions

We have developed an efficient protocol for the synthesis of polysubstituted 7,10-dihydropyrrolo[3,2,1-*ij*][1,2,3]triazolo[4,5-*c*]quinoline and 5,8-dihydrobenzo[3,4][1,2,3]triazolo[4',5':5,6]azepino[1,2-*a*]indole from bromo-substituted *N*-propargyl-indoles. The reaction conditions exhibit broad functional group tolerance, accommodating halogens, alkoxy, cyano, ketone, and ester functionalities, with yields from good to high. Notably, their compatibility with chloro substituent provides a valuable handle for further molecular diversification through transition metal-catalyzed transformations, expanding the synthetic utility of this methodology.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules30122588/s1>. References [39,43,44] are cited in Supplementary Materials.

Author Contributions: Conceptualization, G.F. and A.I.; methodology, A.I. and A.G.; formal analysis, G.F. and A.G.; investigation, D.A., Y.G., F.M., F.S., R.Z. and K.U.; writing—original draft preparation, G.F. and A.G.; writing—review and editing, A.I.; supervision, G.F. and A.I.; project administration, G.F.; funding acquisition, G.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work is part of the activities of the National Center for Gene Therapy and Drugs Based on RNA Technology, funded in the framework of the National Recovery and Resilience Plan (NRRP), Mission 4 “Education and Research”, Component 2 “From Research to Business”, Investment 1.4 “Strengthening research structures for supporting the creation of National Centers, national R&D leaders on some Key Enabling Technologies”, funded by the European Union—Next Generation EU, Project CN00000041, CUP B93D21010860004, Spoke 2.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article or Supplementary Materials.

Acknowledgments: We gratefully acknowledge the Sapienza University of Rome and Catholic University of Sacred Heart, Rome. Some of the experimental data presented in this manuscript are derived from the PhD theses of Allevi and Ullah, carried out, respectively, under the supervision of Iazzetti at Università Cattolica del Sacro Cuore and Fabrizi at Sapienza.

Conflicts of Interest: The authors declare no conflicts of interest.

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