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# Efficient Synthesis of Indole Derivatives Containing the Tetrazole Moiety Utilizing an Ugi-Azide Post-Transformation Strategy

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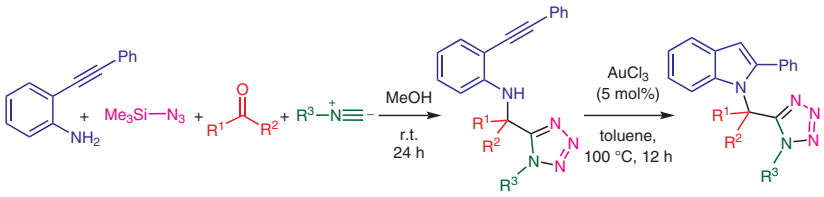
*Dedicated to Prof. Bernhard Breit on the occasion of his birthday*

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**Abstract** An efficient strategy has been developed for the synthesis of indole derivatives containing the tetrazole moiety using a $AuCl_3$-catalyzed cyclization reaction. The precursors of the cycloadduct were easily prepared by an Ugi-azide 4-CR in methanol at room temperature. The merit of this protocol lies in its operational simplicity, readily available starting materials, high yields of product, and good functional group tolerance.

**Key words** Ugi-azide post-transformation strategy, metal catalyzed alkyne cyclization, heterocyclization, indole, tetrazole

Indoles have attracted a great deal of interest due to their presence in natural products and pharmaceutical compounds with extensive biological properties such as anticancer, antibacterial, antifungal, and antimicrobial activity.[1] The presence of the indole scaffold in many natural sources such as serotonin, tryptophan, and plant growth hormones underlines the importance of these compounds.[1] Moreover, synthetic indole derivatives possess the potential to be integrated in technical applications, such as ion sensors, organic-light emitting diodes (OLEDs) or organic field-effect transistors (OFETs).[2]

There are several different strategies for the synthesis of indoles.[3–6] Among these synthetic approaches, the heterocyclization of 2-alkynylanilines to 2-substituted indoles remains the most commonly employed strategy.[7] Different transition metals have exploited in order to carry out this cyclization including Cu,[8,9] Pd,[10–12] Ag, [13] Au,[14–16] and In[17] catalysts.

On the other hand, tetrazole derivatives have attracted considerable attention due to their distinct structural features and their notable biological activities.[18] Tetrazoles are bioisosteres of carboxylic acids and are often used as a replacement for carboxylic acid groups. The tetrazole skeleton is a constituent of a range of drugs including losartan and valsartan that demonstrate antihypertensive activities (Figure 1).[19] It has been reported that the attachment of an indole moiety to the tetrazole nucleus enhances its antimicrobial activity. These hybrid compounds also have peroxisome proliferator-activated receptor (PPAR) activity and can be used for lowering triglycerides and blood sugar (Figure 1).[20]

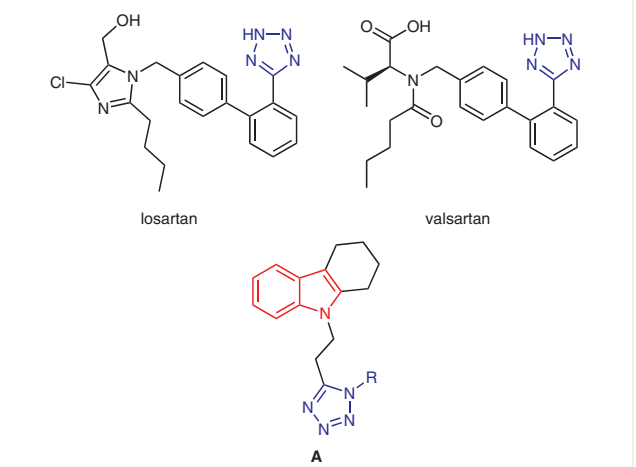
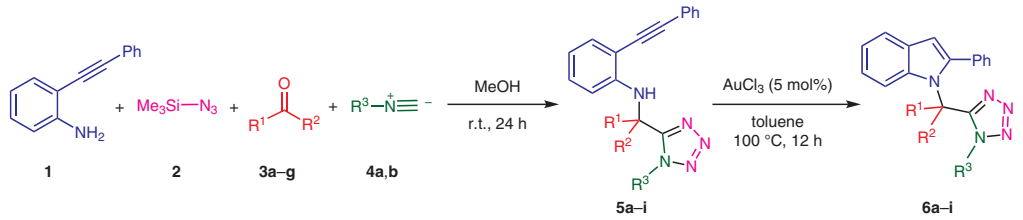



**Figure 1** Structure of some bioactive compounds containing tetrazole and indole moieties

Several methods for the synthesis of tetrazoles have been reported in the literature.[21] Synthesis of tetrazoles through the classical Ugi-azide four-component reaction (UA-4CR) has a wide scope with regard to the starting materials.[22]




**Scheme 1** Synthesis of 2-aryl-indoles containing tetrazole moieties through Ugi-azide reaction followed by $AuCl_3$-catalyzed cyclization

The combination of the Ugi-azide four-component reaction with post-transformational reactions has become a useful tool for generating complex and diverse molecular libraries with novel properties.[23] In a continuation of our previous research work on the design of post-transformation reactions, [24] we report herein an efficient approach to 2-aryl-indoles containing a tetrazole moiety through $AuCl_3$-catalyzed cyclization. The precursors of the cycloadduct were easily prepared through Ugi-azide reaction of 2-(phenylacetylenyl)aniline, trimethylsilylazide, isocyanides, and carbonyl compounds (Scheme 1).

The 2-(phenylethynyl)aniline (**1**) was efficiently prepared by the reported procedure.[25] Next, the four-component reaction of 2-(phenylethynyl)aniline (**1**), trimethylsilyl azide (**2**), cyclohexanone (**3a**), and cyclohexyl isocyanide (**4a**) was selected as the model reaction for the screening of suitable reaction conditions. The reaction was carried out in methanol at ambient temperature and product **5a** was formed in 75% yield (Table 1). The structure of the Ugi-azide product was confirmed using spectroscopic analysis.

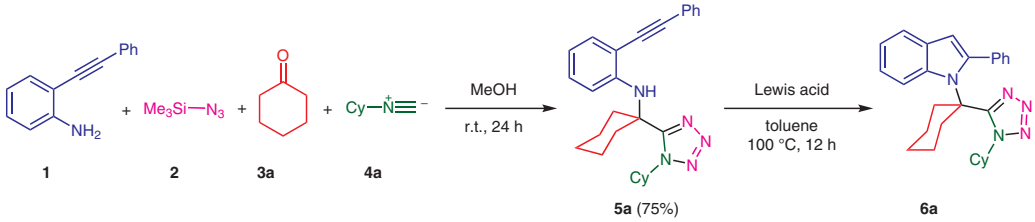
Next, the heterocyclization reaction of **5a** was investigated using different Lewis acid catalysts to access the indole skeleton **6a**. Different attempts were made at the heterocyclization using copper(I) iodide, silver nitrate, zirconium dioxide, and palladium acetate but the reaction did not proceed. However, performing the reaction using $InCl_3$ (10%) or $AuCl_3$ (5%) resulted in the desired product **6a** in 66% and 85% yields, respectively (Table 1, entries 2 and 3). The use of 3% $AuCl_3$ decreased the yield to 78% (Table 1, entry 1). Spectroscopic analysis of **6a** confirmed the formation of the indole moiety. The absence of the acetylenic carbons at δ = 85.0 and 95.0 ppm in the $^{13}C$ NMR spectrum confirmed the cyclization and the C-3 in the indole ring was observed at δ = 108.0 ppm.

With the optimized reaction conditions established, we explored the scope of our methodology using various carbonyl substrates and isocyanides. The reaction conditions were found to be compatible with a range of aromatic aldehydes and ketones (Scheme 2).

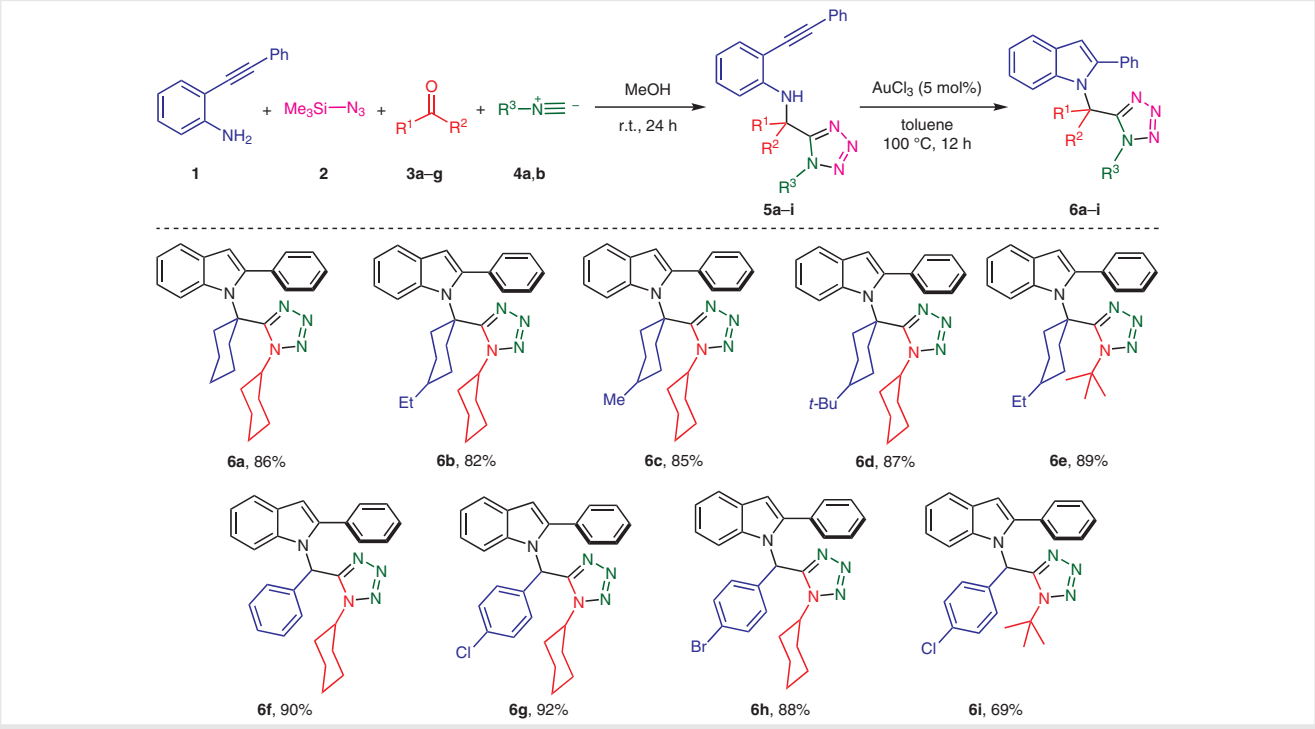
In addition to the spectroscopic analyses, X-ray crystallographic analysis of **6d** confirmed the formation of the desired product (Figure 2).[26] The orientation of the tetrazole ring with the indole ring is interesting, the torsion angle is 54° and the 2-aryl group in position 2 is not coplanar with the indole motif.

To confirm the importance of this strategy, palladium acetate-catalyzed cyclization of *O*-(phenylethynyl)-*N*-ethoxycarbonylanilide for the synthesis of 2-phenylindole was at-

**Table 1** Optimization of the Reaction Conditions for the Synthesis of **6a**




| Entry | Lewis acid | Yield (%) |
|---|---|---|
| 1 | $AuCl_3$(3%) | 78 |
| 2 | $AuCl_3$(5%) | 85 |
| 4 | $InCl_3$ (10%) | 66 |
| 5 | $ZrO_2$ | – |
| 6 | $AgNO_3$ | – |
| 7 | CuI | – |
| 8 | $Pd(OAc)_2$ | – |




**Scheme 2** Scope of the optimized protocol for the synthesis of 2-aryl-indoles containing a tetrazole moiety

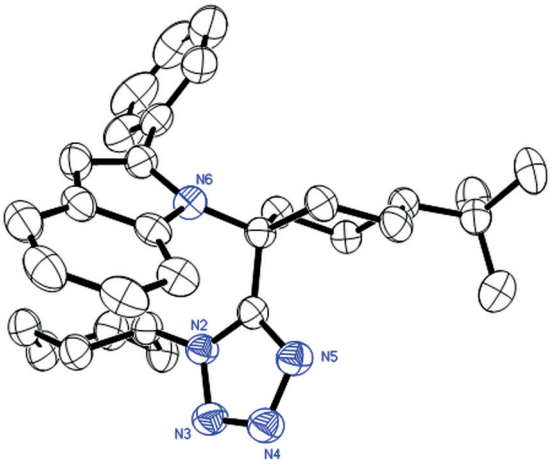
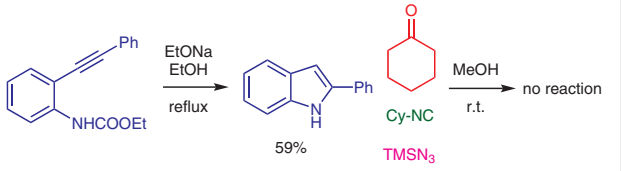



**Figure 2** ORTEP structure of **6d**

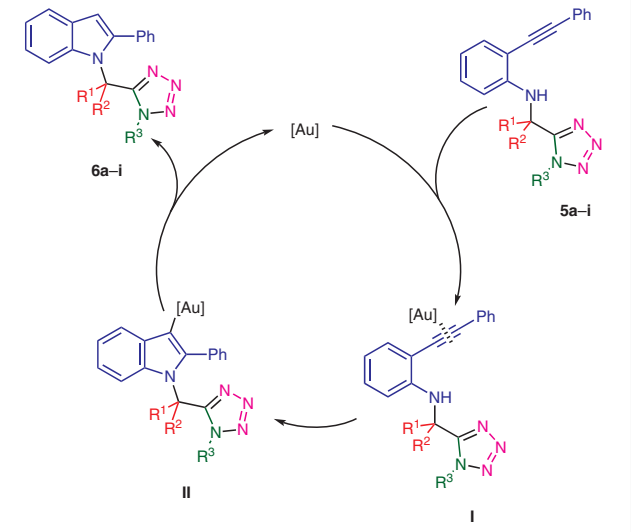
tempted. However, the subsequent Ugi-azide reaction of the 2-phenylindole with cyclohexanone, cyclohexylisocyanide, and trimethylsilyl azide did not take place and the starting materials remained (Scheme 3). This result confirms the importance of the reaction sequence disclosed herein.




**Scheme 3**

A mechanistic rationale for the cyclization reaction is outlined in Scheme 4. The Lewis acidic Au(III) coordinates to the alkynyl moiety of **5a–i**, and the resulting electron-deficient triple bond in **I** undergoes intramolecular nucleophilic attack by the poorly basic nitrogen atom of the free amine moiety leading to the intermediate **II** via a 5-*endo-dig* cyclization in preference to a 4-*exo-dig* mode of cyclization, the latter being disfavored according to Baldwin's rules. Finally, protiodemetallation during the workup affords cyclized **6a–i** (Scheme 4).

In conclusion, we have developed an efficient method for the synthesis of functionalized 2-phenyl indoles containing the tetrazole skeleton. The reaction proceeds through $AuCl_3$ catalyzed cyclization of Ugi-azide products containing an alkyne moiety. Good to high yields and simplicity of the reaction are features of the procedure.




**Scheme 4** Proposed mechanistic pathway for the gold-catalyzed heterocyclization

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## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610502.

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(26) HRMS data were collected using an Apex-QC-FT- ICR instrument with ESI.

**General Procedure for the Synthesis of Compounds 5a–i**

2-(Phenylethynyl)aniline in MeOH (5 ml) and cyclohexanone (1 mmol) were stirred at room temperature for 2 h, then the requisite isocyanide (1 mmol) and trimethylsilyl azide were added. The mixture was stirred for 24 h until the reaction was completed. Then, the desired product was either filtered off as a white solid filtered for **5a–e** (ketone derivatives) or purified using column chromatography on silica gel (*n*-hexane/EtOAc, 9:1) for **5f–i** (aldehyde derivatives). The yields were in the range of 75–92%.

**General Procedure for the Synthesis of Compounds 6a–i**

The products **5a–i** (1mmol) and $AuCl_3$ (5 mol%, 15 mg) were added to a reaction flask containing toluene (10 mL). After 12 h the toluene was evaporated under reduced pressure. The crude products were purified by silica gel chromatography (*n*-hexane/EtOAc, 7:1) to obtain the indole derivatives.

**N-[4-(*tert*-Butyl)-1-(1-cyclohexyl-1*H*-tetrazol-5-yl) cyclohexyl]-2-(phenylethynyl) aniline (5d)**

Colorless solid; yield 440 mg, (80%); $R_f$ = 0.45 (PE/EtOAc 3:1); mp 142–146 °C. IR (KBr): ν = 1586, 2197, 3377 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.84 (s, 9 H, *t*-Bu), 1.16–1.34 (m, 4 H, $H_{Cyclohexyl}$), 1.42–1.68 (m, 5 H, $H_{Cyclohexyl}$), 1.73–1.93 (m, 8 H, $H_{Cyclohexyl}$), 2.87–2.91 (m, 2 H, $H_{Cyclohexyl}$), 4.72 (m, 1 H, CHN), 5.07 (s, 1 H, NH), 6.08 (d, 1 H, *J* = 8.1 Hz, H-Ar), 6.63 (t, 1 H, *J* = 7.5 Hz, H-Ar), 6.86–6.92 (dt, 1 H, *J* = 7.2, 1.5 Hz, H-Ar), 7.3(dd, 1 H, *J* = 8.1, 1.2 Hz, H-Ar), 7.34–7.43(m, 3 H, H-Ar), 7.53–7.56 (m, 2 H, H-Ar) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 23.7, 24.8, 25.6, 27.5, 32.4, 33.5, 39.0, 47.6, 54.4, 59.2, 85.6, 95.7, 108.8, 111.8, 118.0, 123.0, 128.6, 128.7, 129.9, 131.3, 132.1, 145.4, 153.3 ppm.

**1-[4-(*tert*-Butyl)-1-(1-cyclohexyl-1*H*-tetrazol-5-yl) cyclohexyl]-2-phenyl-1*H*-indole (6d)**

Colorless solid; yield 417.6 mg (87%); $R_f$ = 0.38 (PE/EtOAc, 3:1); mp 178–181 °C. IR (KBr): ν = 1453, 1611, 2940 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 9 H, *t*-Bu), 0.88–1.56 (m, 17 H, $H_{Cyclohexyl}$), 2.10–2.30 (m, 2 H, $H_{Cyclohexyl}$), 3.10–3.15 (m, 1 H, $H_{Cyclohexyl}$), 6.47 (s, 1 H, H-3 indole), 6.82 (t, 1 H, *J* = 8.4 Hz, H-Ar), 6.89(dt, 1 H, *J* = 7.2, 1.2 Hz, H-Ar), 7.01 (t, 1 H, *J* = 7.2, H-Ar), 7.46–7.59(m, 6 H, H-Ar) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 14.1, 23.9, 24.7, 25.3, 25.4, 26.9, 27.4, 31.2, 32.3, 32.8, 38.1, 38.6, 46.9, 47.0, 58.1, 62.5, 108.1, 112.4, 120.5, 121.3, 122.6, 124.0, 126.0, 128.3, 128.4, 137.1, 137.5, 140.9, 156.4 ppm. HRMS (ESI): *m/z* calcd for $C_{31}H_{40}N_5$ $[M + H]^+$: 482.3272; found: 482.3288; $C_{31}H_{39}N_5Na$ $[M + Na]^+$: 504.3097; found: 504.3106.

Colorless crystal (polyhedron), dimensions 0.130 × 0.120 × 0.050 $mm^3$, crystal system triclinic, space group P, *Z* = 2, *a* = 10.4530(5) Å, *b* = 12.9781(6) Å, *c* = 13.3411(6) Å, α = 108.2879(14)°, β = 112.3234(14)°, γ = 100.5989(14)°, *V* = 1491.99(12) $Å^3$, ρ = 1.189 g $cm^{-3}$, *T* = 200(2) K, $\theta_{max}$= 22.980°, raduiation Mo Kα, λ = 0.71073 Å, 0.5° ω scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.1 and a completeness of 98.3% to a resoltion of 0.91 Å, 12857 reflections measured, 4082 unique ($R_{(int)}$ = 0.0380), 2672 observed (I > 2σ(I)), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, μ = 0.09 $mm^{-1}$, $T_{min}$ = 0.93, $T_{max}$ = 0.96, structure refined against $F^2$ with a full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software, 393 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.05 for observed reflections, final residual values *R*1(F) = 0.052, *wR*($F^2$) = 0.125 for observed reflections, residual electron density –0.21 to 0.14 e$Å^{-3}$. 27CCDC 1551544 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

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