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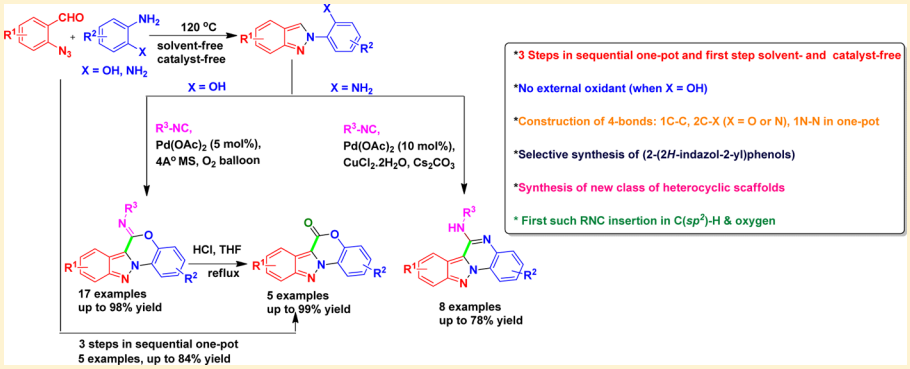
C(sp^2)−H Functionalization of 2*H*-Indazoles at C3-Position via Palladium(II)-Catalyzed Isocyanide Insertion Strategy Leading to Diverse Heterocycles

Shinde Vidyacharan, Arumugavel Murugan, and Duddu S. Sharada*

Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Medak District 502285, Telangana, India

Supporting Information



ABSTRACT: Herein, we have reported an efficient Pd-catalyzed C−H functionalization of 2*H*-indazole at C3-position via an isocyanide insertion strategy for the synthesis of unprecedented benzoxazinoindazoles, indazoloquinaoxalines and benzoxazinoindazolones for the first time. Our new method provides an operationally simple and versatile route for a selective synthesis of 2-(2*H*-indazol-2-yl)phenols. Furthermore, we developed a sequential one-pot strategy for the synthesis of benzoxazinoindazolone under metal-oxidant-free conditions. We also achieved the isocyanide insertion between C(sp^2)−H and oxygen heteroatom for the first time. The key features of the present protocol are construction of 4 bonds in one-pot, synthesis of new skeletally diverse scaffolds, broad substrate scope, high yields and environmentally benign conditions.

INTRODUCTION

Heterocyclic compounds are widely distributed among natural products and biologically active molecules and have vast number of applications in various fields.[1] Among them indazoles occupy a special place owing to their wide range of biological activities,[2] including antitumor,[3] antimicrobial,[4] anti-inflammatory,[5] HIV-protease inhibition,[6] etc. For example, drugs like MK-4827 (anticancer)[7] and pazopanib (tyrosine kinase inhibitor)[8] incorporate this basic scaffold. The benzo-1,4-oxazine,[9] quinoxaline[10] and cyclic amidine ring[11] systems have also been proved to exhibit various potent biological activities (Figure 1).

Though many methods are well documented in the literature for the construction of 2*H*-indazoles,[12] there are very few reports on further exploration of 2*H*-indazoles leading to fused indazoles.[13] Very recently, there have been reports on C3-functionalization of 2*H*-indazoles like direct arylation,[14] Heck,[15] and cross coupling[12b] reactions (Figure 2, eq 1, a−c and e) however there are no reports developed for the construction of fused indazoles systems via C−H activation except annulation[13c] reaction reported by Lautens (Figure 2, eq 1, d). Moreover, most of the C3−functionalization methods used expensive ligand, base, oxidant and additives. As a part of our research program on C−H functionalization,[13b,d] we were interested in developing a new approach for the C3−functionalization of 2*H*-indazoles. Herein, we are delighted to report for the first time, C(sp^2)−H functionalization of 2*H*-indazole leading to fused indazole scaffolds by isocyanide insertion strategy in a mild and convenient manner.

The versatility of C−H activation reactions has been well established by its applications in synthesis of natural products and drugs over the past decades.[16] The key features of its being directing group assisted selective functionalization of specific/proximate C−H bonds. Usage of isocyanides as one carbon unit for a facile and simultaneous Pd-catalyzed stitching of C−C and C-heteroatom bonds has an impact on contemporary synthetic methods development in the production of structural and diverse heterocyclic molecules.[17] Though isocyanide insertion chemistry was developed in the past decades[18] using transition metals, only recently after substantial efforts made by several groups[17] it gained eminence owing to its significance in replacement of hazardous CO gas.[19]

Though inter- and intramolecular isocyanide insertion reactions were reported for the synthesis of diverse heterocycles, in most of the cases starting materials were

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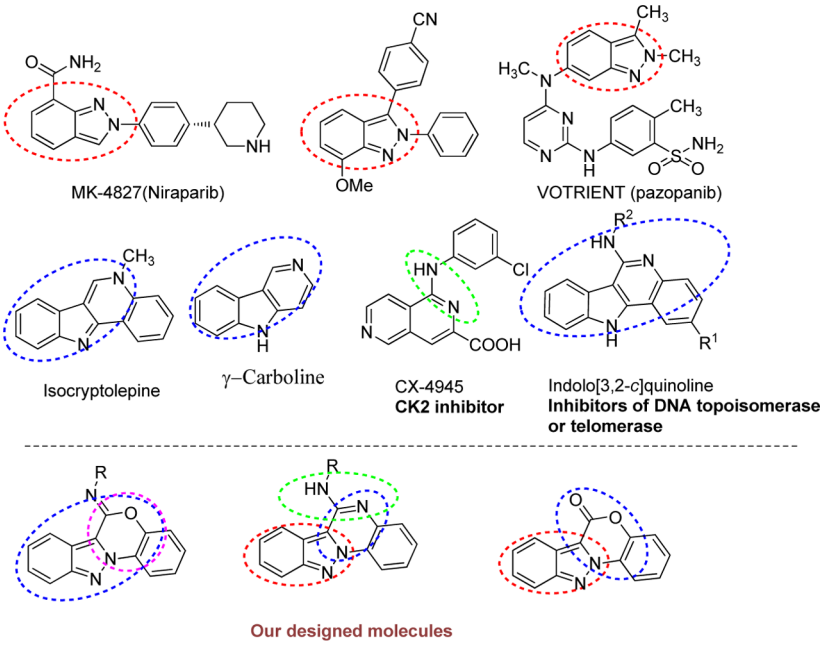

Figure 1. Representative example of bioactive scaffolds and our designed target molecules.

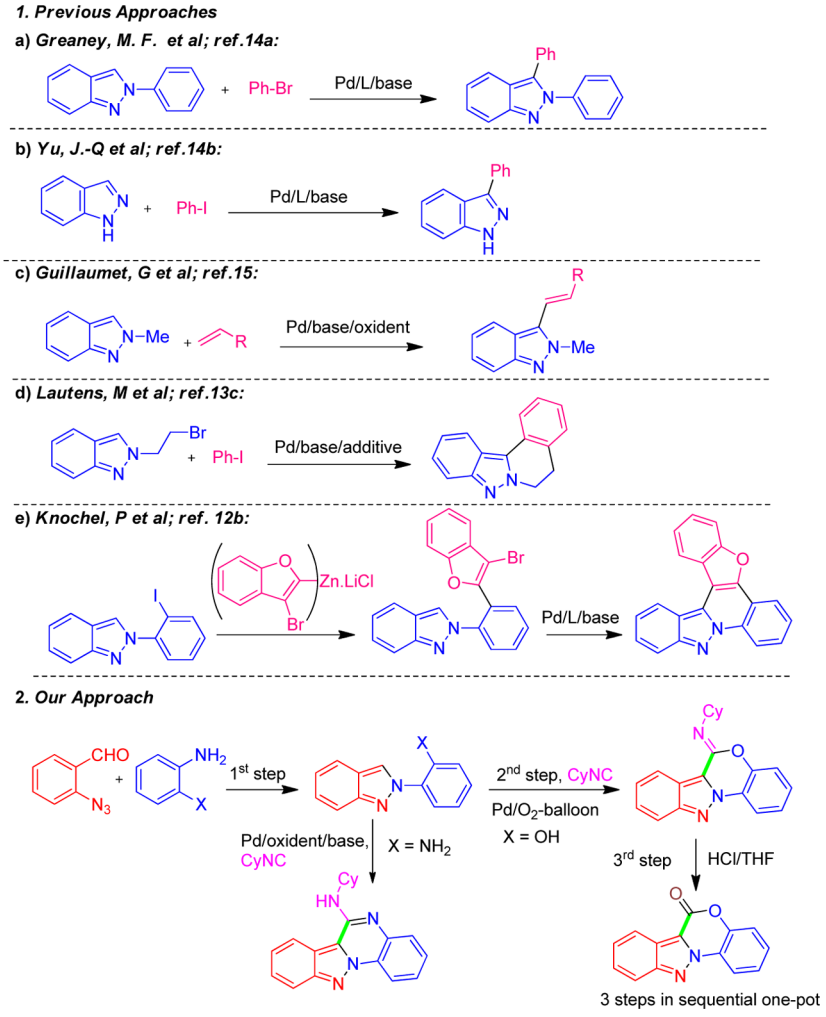

Figure 2. Present study vs representative previous approaches for the C3-functionalization and synthesis of fused-indazoles.

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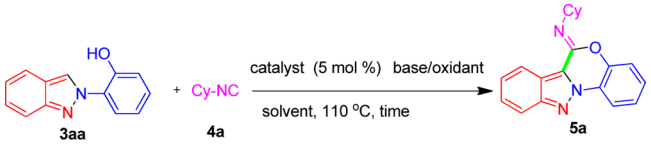
prefunctionalized,[19] and very few reactions[20] are reported employing in situ generated functionalized starting materials.

Nowadays mild and ecofriendly reactions are more interesting and are in demand, in this regard, oxidative palladium catalysis using molecular oxygen as the terminal oxidant have drawn much attention, due to avoidance of expensive and toxic metal oxidants.[17,19] Recently, we have reported one-pot palladium-catalyzed ligand- and metal-oxidant-free aerobic oxidative isocyanide insertion leading to 2-aminosubstituted-4(3*H*)-quinazolinones.[20b] Encouraged by the result, we envisioned the aerobic oxidative C(sp^2)−H functionalization of 2*H*-indazole via isocyanide insertion using palladium catalysis could provide a wide range of fused benzoxazinoindazoles and indazoloquinaoxalines.

RESULTS AND DISCUSSION

We started our probe by a benchmark reaction between 2-(2*H*-indazol-2-yl)phenol **3aa** and cyclohexylisocyanide **4a** in the presence of $Pd(OAc)_2$ as catalyst, toluene as solvent at 110 °C. As expected, isocyanide insertion product **5a** was obtained, albeit in very poor yield (Table 1, entry 1). Inspired by this result, we screened various catalysts, bases, solvents and isocyanide equivalents (see in Table 4 of SI), and found very good yield, i.e., 90% with Ag_2CO_3 as oxidant (Table 1, entry 14). As aimed, we pursued our efforts to increase the yields further, by replacing the metal-oxidant with molecular oxygen under various solvents (Table 1, entries 15−22) and were pleased to obtained good yields of the products. Surprisingly, on addition of 4 Å MS in the reaction, we obtained quantitative yield of the product with decrease in the reaction time (Table 1, entry 22). We are delighted to mention here that this is first such report for the isocyanide insertion between C(sp^2)-H and oxygen heteroatom under metal-oxidant free condition.

Table 1. Optimization Conditions for the Synthesis of Benzoxazinoindazole 5a[a,b]



entry	catalyst	base/ oxidant	solvent (2 mL)	time (h)	product (%)[b]
1	$Pd(OAc)_2$	–	toluene	24	10[c]
2	$Pd(OAc)_2$	K_2CO_3	toluene	24	60
3	$PdCl_2$	K_2CO_3	toluene	24	50
4	$PdCl_2(PPh_3)_2$	K_2CO_3	toluene	24	58
5	$Pd(PPh_3)_4$	K_2CO_3	toluene	24	40
6	–	–	toluene	24	nd[c]
7	$Cu(OAc)_2$	K_2CO_3	toluene	24	nd[c]
8	$Pd(OAc)_2$	Et_3N	toluene	24	20
9	$Pd(OAc)_2$	CS_2CO_3	toluene	24	80
10	$Pd(OAc)_2$	KOAc	toluene	24	65
11	$Pd(OAc)_2$	NaOAc	toluene	24	63
12	$Pd(OAc)_2$	NaO^{t}Bu	toluene	24	70
13	$Pd(OAc)_2$	KO^{t}Bu	toluene	24	62
14	$Pd(OAc)_2$	Ag_2CO_3	toluene	24	90
15	$Pd(OAc)_2$	O_2	toluene	24	92
16	$Pd(OAc)_2$	O_2	THF	24	55
17	$Pd(OAc)_2$	O_2	CH_3CN	24	70
18	$Pd(OAc)_2$	O_2	DMSO	24	80
19	$Pd(OAc)_2$	O_2	DMF	24	75
20	$Pd(OAc)_2$	O_2	1,4-dioxane	24	70
21	$Pd(OAc)_2$	O_2	DME	24	85
22[d]	**$Pd(OAc)_2$**	**O_2**	**toluene**	**21**	**98**

[a]All reactions were carried out on 1 mmol scale of **3** and 1.5 mmol of **4**, and entry 3−14 used 1 equiv of base. [b]Isolated yields of chromatographically pure products. [c]Starting material was recovered. [d]4 Å MS (100 mg) were used.

Having established the optimal reaction conditions, we wanted to investigate the scope of methodology for the various 2*H*-indazoles and isocyanides. Accordingly, we focused our efforts towords synthesis of 2-(2*H*-indazol-2-yl)phenols, unfortunately our attempts to make the same from 2-azidobenzaldehyde and 2-aminophenol by reported methods went in vain. However, we were successful in developing an alternative method for the synthesis of 2-(2*H*-indazol-2-yl)phenols in a selective and efficient manner under solvent-free and catalyst-free conditions (Table 2).

When we evaluated the scope of this methodology for different 2*H*-indazoles, the methelenedioxy substitution (**5d**) gave more yields compared to halo substitution at fifth and sixth position (Table 3, **5b**, **5c**). Similarly, good yields were obtained in the case of Me-, Cl- substitution on amine partner of aryl group (Table 3, **5e**, **5f**) whereas nitro substituent resulted in comparatively less yield (Table 3, **5g**). When we investigated the influence of different isocyanides on the efficiency of insertion reaction, cyclohexyl isocyanide (Cy-NC) provided more yields (Table 3, **5a**−**5g**) compared to *tert*-butyl isocyanide, (^{t}Bu-NC) (Table 3, **5h**−**n**) while other isocyanides failed to give the expected products (Table 3, **5o**−**5q**). Compound **5a** was further confirmed by single crystal X-ray diffraction (See SI, Figure 1).

To our surprise, when we used excess of isocyanide in the case of halo substitution at sixth position of indazole, we observed along with insertion, amidation of halo group (C−C coupling) with isocyanide (**5r**). The literature methods for the amidation of halo group with isocyanides used metal-oxidants, ligand and base,[21] conversely, we have achieved the same using mild catalyst with molecular oxygen as oxidant (Scheme 1).

Furthermore, at the next diversity point, we wanted to expand our method for the synthesis of indazoloquinaoxalines by replacing one of the starting material 2-(2*H*-indazol-2-yl)phenol with 2-(2*H*-indazol-2-yl)aniline, as this entity is present in various alkaloids and drugs.[10,11] Accordingly, we envisioned to perform the reaction between 2-(2*H*-indazol-2-yl)aniline **3ba** and cyclohexylisocyanide **4a** under standard conditions (Table 1, entry 22), and to our gratification it resulted in the expected product in 45% yield. Then, to increase the yield we tuned the reaction with respect to catalyst, base, oxidant and solvents (Table 5 in SI), and found good yield (72%) with $Pd(OAc)_2$ as catalyst, $CuCl_2{\cdot}2H_2O$ as oxidant and Cs_2CO_3 as base (Table 5 entry 17 in SI). After successfully establishing the optimized conditions we employed various 2*H*-indazoles and obtained indazoloquinaoxalines (**6a**−**6h**) in moderate to good yields (Table 4).

On the basis of the literature reports,[17a,19d,e] we have proposed a plausible reaction mechanism for the synthesis of benzoxazinoindazole and indazoloquinaoxaline as shown in Figure 3. At first, indazole XH (**3**) (XH = OH, NH) forms a coordination complex with isocyanide ligated Pd(II) giving complex **I**. Subsequent electrophilic palladation[22] of the indazole ring furnishes Pd(II) intermediate **II** followed by migratory insertion of an isocyanide resulting in cyclic imidoyl

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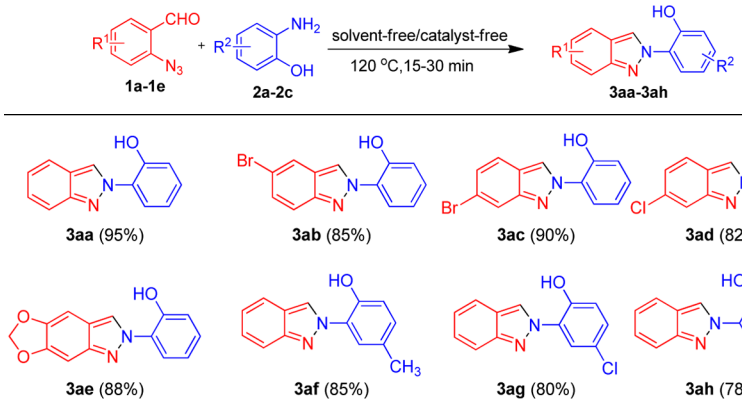
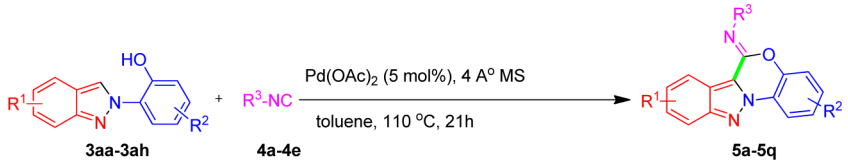
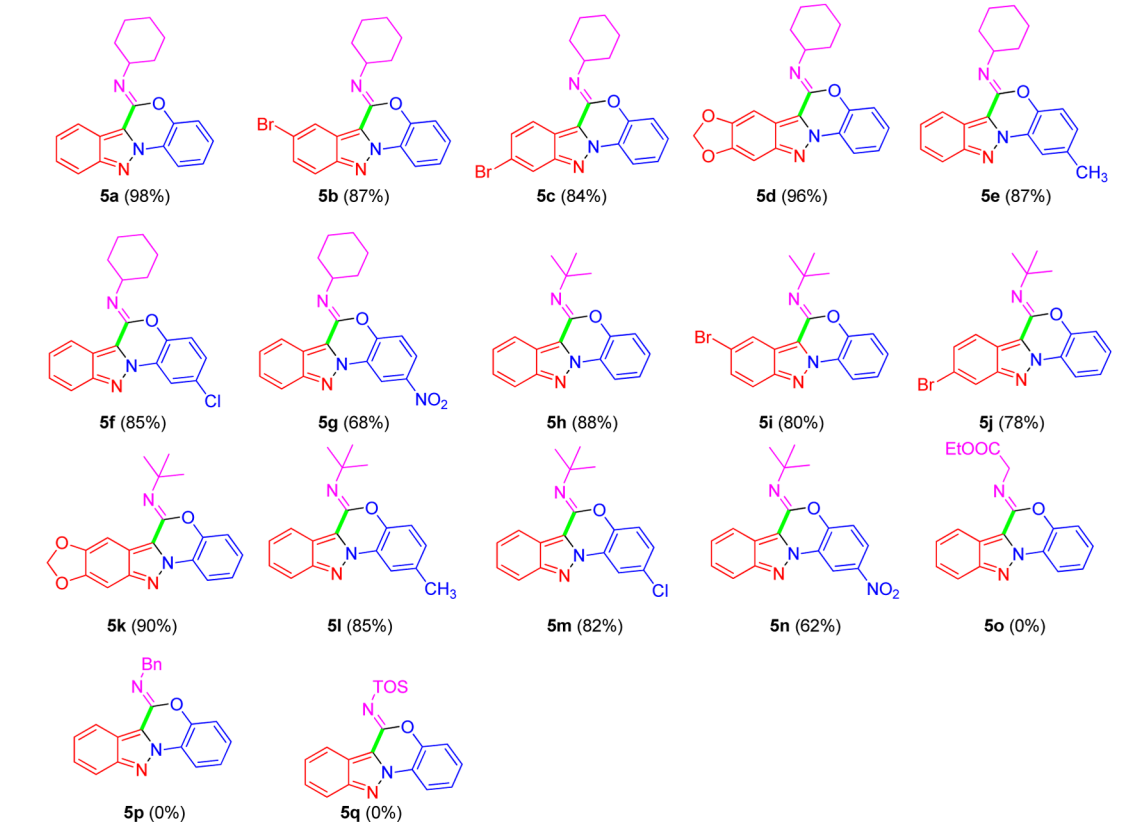
Table 2. Synthesis of 2-(2*H*-Indazol-2-yl)phenols 3aa−3ah[a,b]



[a]Reaction conditions: **1a** (1 mmol), **2a** (1 mmol). [b]Yields in the parentheses are isolated yields of chromatographically pure products.

Table 3. Scope and Generality for the Synthesis of Benzoxazinoindazoles 5a−5q[a,b]





[a]Reaction conditions: **3aa−3ah** (1 mmol), **4a−4e** (1.5 equiv), $Pd(OAc)_2$ (5 mol %), 4 Å MS (100 mg) in 2 mL of toluene, at 110 °C for 21 h. [b]Yields in the parentheses are isolated yields of chromatographically pure products. Compound **5a** was further confirmed by single crystal XRD (see SI, Figure S1).

palladium intermediate **III**. This further undergoes reductive elimination to form **5** (XH = OH) and **IV** (XH = NH) and resultant Pd(0) species is reoxidized to Pd(II) by molecular oxygen. **IV** further undergoes tautomerization to afford the product **6** (Figure 3).

To examine the synthetic utility of the synthesized compounds benzoxazinoindazoles (**5**) we explored the *N*-alkylimine hydrolysis leading to benzoxazinoindazolones, as this entity is present in biopotent molecules.[9] To our delight, we have demonstrated the utility of **5** leading to diverse

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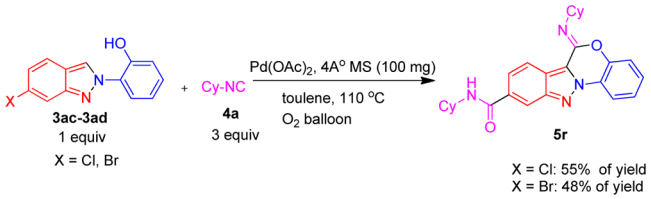
Scheme 1



benzoxazinoindazolones (**7a**–**7e**) in quantitative yields (95–99%, Table 5).

Recent achievements made by our group in the area of developing sustainable chemistry,[23,13a,d] intrigued us to further probe the scope of one-pot method for the synthesis of fused indazole scaffolds starting from 2-azidobenzaldehyde **1a** and 2-aminophenol **2a**. Delightfully, we obtained the expected product **7a** in 84% of yield. The robustness of this one-pot protocol was demonstrated by the synthesis of diverse benzoxazinoindazolones (**7a**–**7e**) in good yields (58–80%) shown in Table 6. This straightforward synthesis of tetracyclic frameworks constitutes an interesting alternative to the conventional stepwise isocyanide insertion reactions.

CONCLUSION

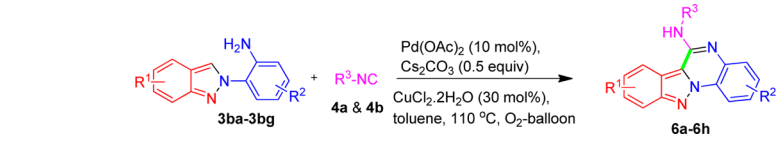
We have successfully demonstrated an efficient Pd-catalyzed direct C–H activation of 2*H*-indazole via an isocyanide insertion strategy for the synthesis of unprecedented benzoxazinoindazoles, indazoloquinaoxalines and benzoxazinoindazolones for the first time. Our new method provides an operationally simple and versatile route for a selective synthesis of 2-(2*H*-indazol-2-yl)phenols. Furthermore, we developed a sequential one-pot strategy for the synthesis of benzoxazinoindazolone under metal-oxidant-free conditions. We also achieved the isocyanide insertion between C(sp^2)-H and oxygen heteroatom under metal-oxidant-free conditions for the first time. The key features of the present protocol are construction of 4 bonds in one-pot, synthesis of new skeletally diverse scaffolds, broad substrate scope, high yields and environmentally benign conditions. This methodology can open up opportunities for development of various diverse heterocycles via C–H functionalization of 2*H*-indazoles and in our laboratory selective C–H functionalization of 2*H*-indazoles is under way.

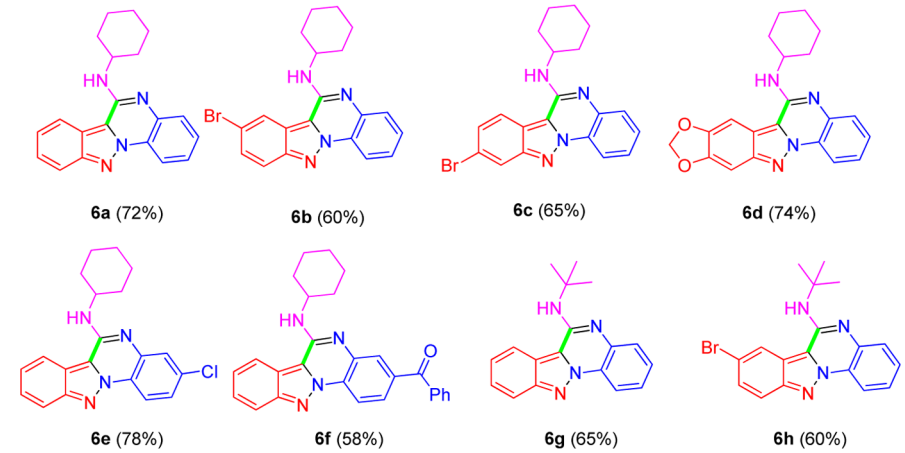
EXPERIMENTAL SECTION

General Considerations. IR spectra were recorded on a FTIR spectrophotometer. ^{1}H NMR spectra were recorded on 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s. = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Q-TOF multimode source. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. *o*-Azidobenzaldehydes prepared by using literature known procedures, 2-aminophenols all were commercial available. Pd-catalysts and all bases were purchased from Sigma-Aldrich. All dry solvents were used, toluene and THF were dried over sodium metal and DMSO, CH_3CN and DMF were dried over calcium hydride and which are commercial available.

All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of petroleum ether and ethyl acetate as eluents. Reactions were generally run under argon, nitrogen and oxygen atmosphere wherever necessary. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material). All 2-azidobenzaldehydes (**1a**–**1c** and **1e**) except **1d** have been synthesized by using literature known procedures.[24]

Table 4. Scope and Generality for the Synthesis of Indazoloquinaoxalines 6a–6h[a,b]





[a]Reaction conditions: **3ba**–**3bg** (1 mmol), **4a** and **4b** (2 mmol), $Pd(OAc)_2$ (10 mol %), $CuCl_2{\cdot}2H_2O$ (30 mol %) and Cs_2CO_3 (0.5 equiv) in 2 mL of toluene, at 110 °C for 12–15 h. [b]Yields in the parentheses are isolated yields of chromatographically pure products.

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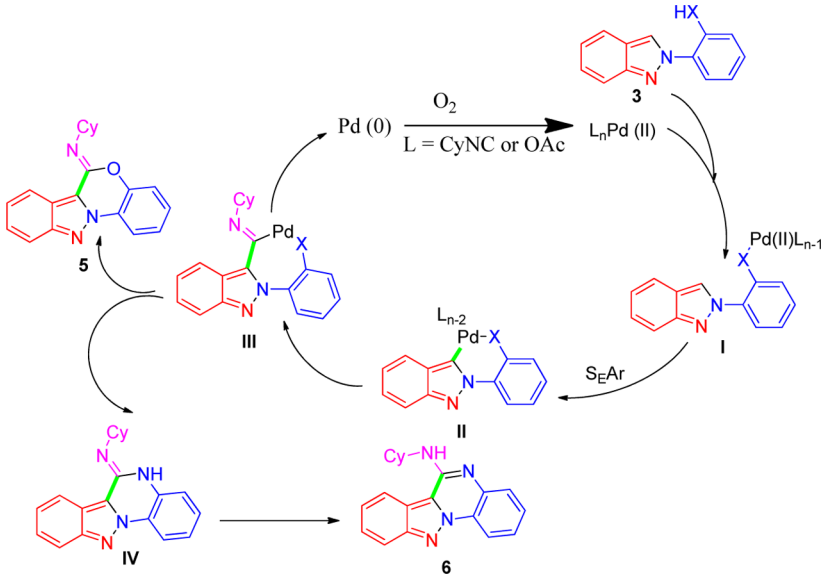
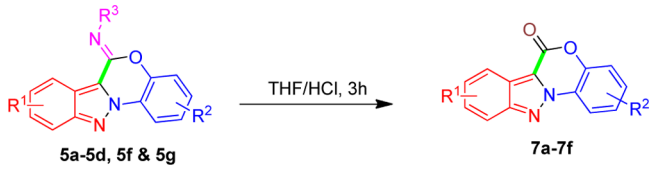
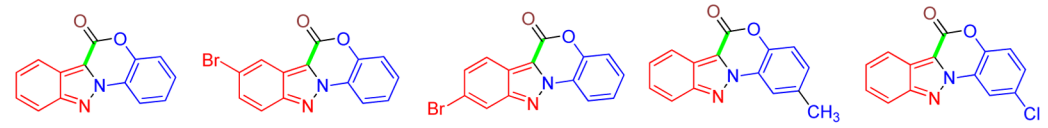


Figure 3. Credible pathway for the synthesis of benzoxazinoindazole/indazoloquinoxaline (**5**/**6**).

Table 5. Synthesis of Benzoxazinoindazolones 7a–7e[a,b]

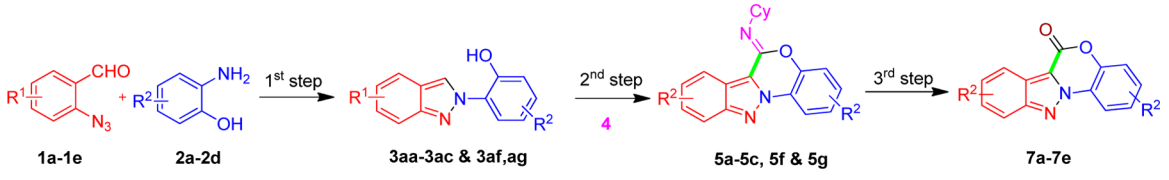


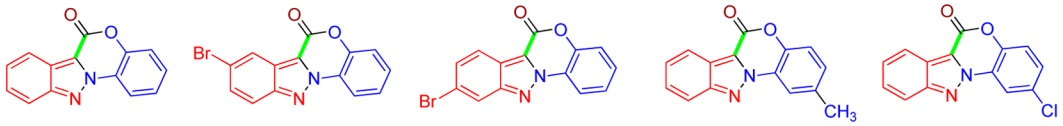


7a (99%) **7b** (95%) **7c** (96%) **7d** (97%) **7e** (97%)

[a]Reaction conditions: **5** (1 mmol) refluxed in THF/HCl (5 mL of THF and 1M, 1 mL HCl) for 3 h. [b]Yields in the parentheses are isolated yields of chromatographically pure products.

Table 6. Sequential One-Pot Strategy for the Synthesis of Benzoxazinoindazolones 7a–7e[a,b]





7a (84%) **7b** (72%) **7c** (75%) **7d** (75%) **7e** (58%)

[a]Reaction conditions: First step, **1a–1e** (1 mmol), **2a–2d** (1 mmol). Second step, Cy-NC (**4**), $Pd(OAc)_2$ (5 mol %), 4 Å MS (100 mg) in 2 mL of toluene, at 110 °C for 21 h. Third step, refluxed in THF/HCl for 3 h. [b]Yields in the parentheses are isolated yields of chromatographically pure products.

1. Synthesis of 2-Azido-4-chlorobenzaldehyde (1d). To a stirring solution of 2-Nitro-4-chlorobenzaldehyde (1.0 equiv) in HMPA was added sodium azide (2.0 equiv). The reaction mixture was stirred at ambient temperature and monitored by TLC. After consumption of the starting material, the mixture was diluted with ice-cold water and extracted with diethyl ether (3 × 25 mL). The ether layer was washed with water (3 × 25 mL), brine (1 × 10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated to give the crude compound, which was further purified by column chromatography to give the final analytically pure product (82% yield).

*2-Azido-4-chlorobenzaldehyde (**1d**).* White solid (3.9 mg, 80%); mp 84–86 °C; IR (MIR-ATR, 4000–600 cm^{-1}) υ_{max} = 3340, 3261, 3034, 2864, 2768, 2408, 2342, 2216, 2120, 1679, 1591, 1568, 1492, 1426, 1396, 1330, 1289, 1265, 1203, 1077, 949, 841, 816; ^1H NMR

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($CDCl_3$, 400 MHz) δ_H = 10.22 (s, 1H), 7.88 (d, 1H, J = 8.3 Hz), 6.89 (dd, 1H, J_a = 8.3 and J_b = 1.5 Hz), 6.81 (d, 1H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) 187.1 (s, −CHO), 147.4 (s, Ar−C), 144.8 (s, Ar−C), 130.9 (d, Ar−CH), 123.9 (s, Ar−C), 115.5 (d, Ar−CH), 109.1 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_7H_4ClN_3O]^+ = [M]^+$ 181.0037, found 181.0030.

2. General Procedure (GP I) for the Synthesis of 2-(2*H*-Indazol-2-yl)phenols (3aa−3ah). 2-Azidobenzaldehyde **1** (1 mmol) and 2-aminophenol **2** (1 mmol) were taken in a 10 mL oven-dried schlenck tube and it was closed with stopcock with argon balloon and placed in external heating oil bath at 120 °C for 15−30 min (oil bath temperature). After completion of the starting material, the mixture was cooled to room temperature and was purified on a silica gel column chromatography (hexane/ethyl acetate 95:5) which furnished the respective solids. All the compounds were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS spectral analyses.

3. General Procedure (GP II) for the Synthesis of 2-(2*H*-Indazol-2-yl)aniline (3ba−3bg). 2-Azidobenzaldehyde **1** (1 mmol) and Boc protected *o*-phenylenediamine **2** (1 mmol) were taken in a 10 mL round-bottom flask and it was closed with stopper and placed in external heating oil bath at 120 °C (oil bath temperature) for 1−1.5h. After completion of the starting materials, the mixture was cooled to room temperature and DCE solvent was added followed by $BF_3{\cdot}Et_2O$ and refluxed at 85 °C. Progress of the reaction was monitored by TLC until the reaction completed. The reaction mixture was quenched by addition of aq. $NaHCO_3$ solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as eluent (hexane/ethyl acetate 85:15 to 80:20) provided the product (**3ba−3bg**). For known compounds (**3ba−3bc**), see refs 13b and 24a.

4. General Procedure (GP III) for the Synthesis of Benzaoxizinoindazoles (5a−5r). In an oven-dried 10 mL schlenck tube, under oxygen atmosphere, 2-(2*H*-indazol-2-yl)phenols **3aa−3ah** (1 mmol), $Pd(OAc)_2$ (5 mol %) and 4 Å MS (100 mg) were added. Subsequently, the vessel was placed under vacuum and backfilled with O_2. Then, toluene solvent (2.5 mL) and isocyanide (**4a−4e**) were added and the resulting mixture was stirred at 110 °C for 21 h under oxygen atmosphere. Progress of the reaction was monitored by TLC until the reaction is completed. The mixture was filtered through Celite, concentrated, then washed with water and extracted in ethyl acetate (3 × 10 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as eluent (hexane/ethyl acetate 95:5 to 90:10) yielded the product benzoxazinoindazoles (**5a−5q**).

5. General Procedure (IV) for the Synthesis of Indazoloquinaoxalines (6a−6h). In an oven-dried 10 mL schlenck tube, under oxygen atmosphere, 2-(2*H*-indazol-2-yl)aniline **3ba−3bg** (1 mmol), isocyanides **4a−4b** (2 mmol), $Pd(OAc)_2$ (10 mol %) and $CuCl_2{\cdot}2H_2O$ (10 mol %) were added and followed by addition of toluene (2 mL). The resulting reaction mixture was stirred at 110 °C for 12−15 h under oxygen atmosphere. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by addition of aq. NH_4Cl solution and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as (hexane/ethyl acetate 90:10 to 85:15) eluent furnished the product indazoloquinaoxalines (**6a−6h**).

6. General Procedure (V) for the Synthesis of Benzoxazinoindazolone (7a−7e). To a 10 mL round-bottom flask containing **5a−5c**, **5e** and **5f** (1 mmol) THF (5 mL) and hydrochloric acid (1 M, 1 mL) were added. The resulting reaction mixture was stirred at 85 °C for 2−3 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by addition of aq. $NaHCO_3$ solution and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as eluent (hexane/ethyl acetate 85:15to 80:20) provided the product **7a−7e**.

7. General Procedure (VI) for Sequential One-Pot Synthesis of Benzoxazinoindazolone (7a−7e). 2-Azidobenzaldehyde **1** (1 mmol) and 2-aminophenol **2** (1 mmol) were taken in a 25 mL oven-dried schlenck tube and it was closed with stopcock with argon balloon and placed in external heating oil bath at 120 °C (oil bath temperature) for 15−30 min. The completion of first step was monitored by TLC. Once intermediate **A** (dinucleophile) was formed $Pd(OAc)_2$ (5 mol %), CyNC (1.5 equiv) and solvent were added in same pot under argon atmosphere. Subsequently, the vessel was placed under vacuum and backfilled with O_2. The resulting reaction mixture was heated at 110 °C. Progress of the reaction was monitored by TLC, which took 21h. On confirming the completion of reaction, to the same pot THF (10 mL) and hydrochloric acid (1 M, 2 mL) were added and the resulting reaction mixture was stirred at 85 °C for 2−3h. Progress of the reaction was monitored by TLC until the reaction was completed. The mixture was filtered through Celite, concentrated, Then reaction mixture was quenched by addition of aq. $NaHCO_3$ solution and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as (hexane/ethyl acetate 85:15 to 80:20) eluent yielded the product **7a−7e**.

8. Spectroscopic Data of All Unknown Compounds. *2-(2H-Indazol-2-yl)phenol (**3aa**).* White solid (202 mg, 95%); mp 80−82 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3134, 3056, 2923, 2853, 1741, 1631, 1595, 1517, 1499, 1459, 1420, 1396, 1373, 1309, 1281, 1253, 1253, 1160, 1128, 1035, 964, 915, 839, 792, 779, 749, 523; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 12.1 (s, 1H), 8.45 (s, 1H), 7.72 (dd, 2H, J_a = 8.8 and J_b = 3.4 Hz), 7.56 (dd, 1H, J_a = 8.3 and J_b = 1 Hz), 7.38−7.35 (m, 1H), 7.28−7.23 (m, 1H), 7.17−7.13 (m, 2H), 6.97−6.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.5 (s, Ar−C), 147.6 (s, Ar−C), 129.1 (d, Ar−CH), 127.7 (d, Ar−CH), 124.9 (s, Ar−C), 123.0 (d, Ar−CH), 121.3 (s, Ar−C), 120.3 (d, Ar−CH), 120.2 (d, Ar−CH), 119.7 (d, Ar−CH), 119.5 (d, Ar−CH), 119.2 (d, Ar−CH), 116.8 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{13}H_{11}N_2O]^+ = [M + H]^+$ 211.0866, found 211.0865.

*2-(5-Bromo-2H-indazol-2-yl)phenol (**3ab**).* Light yellow solid (163 mg, 85%); mp 140−142 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3147, 2921, 2852, 1743, 1599, 1498, 1454, 1422, 1377, 1329, 1284, 1250, 1193, 1161, 1034, 795, 735, 536; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 11.78 (s, 1H), 8.43 (s, 1H), 7.9 (s, 1H), 7.63−7.56 (m, 2H), 7.44 (dd, 1H, J_a = 9.3 and J_b = 1.5 Hz), 7.31−7.26 (m, 1H), 7.18 (d, 1H, J = 7.8 Hz), 6.99 (t, 1H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.4 (s, Ar−C), 146.0 (s, Ar−C), 131.4 (d, Ar−CH), 129.5 (d, Ar−CH), 124.6 (s, Ar−C), 122.6 (s, Ar−C), 122.3 (d, Ar−CH), 119.8 (d, Ar−CH), 119.7 (d, Ar−CH), 119.6 (d, Ar−CH), 119.3 (d, Ar−CH), 118.6 (d, Ar−CH), 116.5 (s, Ar−C); HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}BrN_2O]^+ = [M + H]^+$ 288.9971, found 288.9966.

*2-(6-Bromo-2H-indazol-2-yl)phenol (**3ac**).* Light yellow solid (168 mg, 88%); mp 124−126 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3139, 3076, 2924, 2855, 1745, 1700, 1600, 1496, 1458, 1417, 1390, 1356, 1277, 1249, 1187, 1123, 1036, 924, 880, 798, 735, 741, 588; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 11.7 (s, 1H), 8.41 (s, 1H), 7.91 (s, 1H), 7.59−7.52 (m, 2H), 7.29−7.21 (m, 2H), 7.16 (dd, 1H, J_a = 8.3 and J_b = 1.5 Hz), 6.98−6.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.4 (s, Ar−C), 148.2 (s, Ar−C), 129.5 (d, Ar−CH), 126.9 (d, Ar−CH), 124.6 (s, Ar−C), 121.9 (d, Ar−CH), 121.6 (s, Ar−C), 120.9 (d, Ar−CH), 120.0 (d, Ar−CH), 119.8 (s, Ar−C), 119.3 (d, Ar−CH), 119.2 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}BrN_2O]^+ = [M + H]^+$ 288.9971, found 288.9971.

*2-(6-Chloro-2H-indazol-2-yl)phenol (**3ad**).* Dark golden rod solid (166 mg, 82%); mp 116−118 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3612, 3140, 2727, 2309, 2107, 1934, 1807, 1597, 1553, 1500, 1425, 1360, 1312, 1258, 1148, 1092, 1032, 956, 816, 781, 741, 706, 655, 608, 527; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 11.89 (s, 1H), 8.39 (s, 1H) 7.67 (d, 1H, J = 8.8 Hz), 7.51 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 7.30−7.23 (m, 2H), 7.15 (dd, 1H, J_a = 8.3 and J_b = 1.5 Hz), 6.97−6.93 (m, 1H), 6.82 (dd, 1H, J_a = 8.8 and J_b = 2 Hz); ^{13}C NMR ($CDCl_3$, 100

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MHz) 150.4 (s, Ar−C), 147.8 (s, Ar−C), 139.9 (s, Ar−C), 129.2 (d, Ar−CH), 124.7 (s, Ar−C), 122.0 (d, Ar−CH), 120.7 (d, Ar−CH), 119.7 (d, Ar−CH), 119.5 (d, Ar−CH), 119.2 (s, Ar−C), 119.1 (d, Ar−CH), 117.3 (d, Ar−CH), 104.4 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}ClN_2O]^+$ = $[M + H]^+$ 245.0476, found 245.0478.

2-(2H-[1,3]Dioxolo[4,5-f]indazol-2-yl)phenol (**3ae**). White solid (81 mg, 88%); mp 134−136 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3145, 2911, 1651, 1622, 1602, 1555, 1504, 1486, 1437, 1379, 1356, 1285, 1254, 1219, 1181, 1115, 1046, 1036, 951, 820, 728; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 11.91 (s, 1H), 8.23 (s, 1H), 7.47 (d, 1H, J = 7.8 Hz), 7.23−7.19 (m, 1H), 7.14−7.12 (m, 1H), 6.96−6.90 (m, 3H), 5.99 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.3 (s, Ar−C), 149.9 (s, Ar−C), 146.5 (s, Ar−C), 145.2 (s, Ar−C), 128.3 (d, Ar−CH), 125.0 (s, Ar−C), 119.6 (d, Ar−CH), 119.5 (d, Ar−CH), 119.2 (d, Ar−CH), 118.5 (s, Ar−C), 101.3 (t, $-CH_2-$), 94.8 (d, Ar−CH), 93.4 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{14}H_{11}N_2O_3]^+$ = $[M + H]^+$ 255.0764, found 255.0774.

2-(2H-Indazol-2-yl)-4-methylphenol (**3af**). White solid (194 mg, 85%); mp 76−78 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3135, 3061, 2923, 2854, 1737, 1632, 1603, 1520, 1463, 1392, 1370, 1284, 1251, 1210, 1128, 1049, 917, 795, 754; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 11.85 (br s, 1H), 8.48 (s, 1H), 7.48 (d, 2H, J = 8.8 Hz), 7.39−7.36 (m, 2H), 7.17 (dd, 1H, J_a = 8.1 and J_b = 7.1 Hz), 7.08 (s, 1H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 148.2 (s, 2C, Ar−C), 147.7 (s, Ar−C), 129.8 (d, Ar−CH), 129.1 (s, 2C, Ar−C), 127.6 (d, Ar−CH), 124.4 (s, Ar−C), 122.9 (d, Ar−CH), 121.3 (s, Ar−C), 120.3 (d, Ar−CH), 120.2 (d, Ar−CH), 119.6 (d, Ar−CH), 119.7 (d, Ar−CH), 116.9 (d, Ar−CH), 20.7 (q, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{14}H_{13}N_2O]^+$ = $[M + H]^+$ 225.1022, found 225.1021.

4-Chloro-2-(2H-indazol-2-yl)phenol (**3ag**). White solid (200 mg, 80%); mp 118−120 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3449, 3322, 3148, 3057, 2919, 1621, 1591, 1497, 1458, 1395, 1366, 1330, 1284, 1247, 1155, 1099, 1043, 965, 917, 842, 772, 746, 713, 654, 626, 535; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 12.16 (s, 1H), 8.44 (s, 1H), 7.72 (d, 2H, J = 9.3 Hz), 7.58 (d, 1H, J = 2.4 Hz), 7.40 (dd, 1H, J_a = 8.6 and J_b = 7.1 Hz), 7.26−7.16 (m, 2H), 7.11 (d, 1H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.2 (s, Ar−C), 147.7 (s, Ar−C), 128.9 (d, Ar−CH), 128.1 (d, Ar−CH), 125.2 (s, Ar−C), 124.2 (s, Ar−C), 123.3 (d, Ar−CH), 121.4 (s, Ar−C), 120.6 (d, Ar−CH), 120.4 (d, Ar−CH), 120.2 (d, Ar−CH), 119.1 (d, Ar−CH), 116.8 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}ClN_2O]^+$ = $[M + H]^+$ 245.0476, found 245.0475.

2-(2H-Indazol-2-yl)-4-nitrophenol (**3ah**). Yellow solid (202 mg, 78%); mp 166−168 °C; IR (MIR-ATR, 4000−600 cm_{-1}) υ = 3449, 3138, 3087, 2752, 2348, 1632, 1618, 1521, 1412, 1399, 1374, 1342, 1304, 1285, 1252, 1193, 1148, 1079, 1036, 967, 943, 880, 815, 796, 752, 739, 623; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 12.8 (br s, 1H), 8.55 (s, 1H), 8.01 (d, 1H, J = 2.4 Hz), 7.84 (dd, 1H, J_a = 8.8 and J_b = 2.4 Hz), 7.75−7.70 (m, 3H), 7.45−7.41 (m, 1H), 7.23 (dd, 1H, J_a = 15.9 and J_b = 8.6 Hz); ^{13}C NMR (CDCl3, 100 MHz) 151.1 (s, Ar−C), 147.9 (s, Ar−C), 147.3 (s, Ar−C), 129.1 (s, Ar−C), 128.9 (d, Ar−CH), 124.0 (d, Ar−CH), 121.6 (s, Ar−C), 121.0 (d, Ar−CH), 120.3 (d, Ar−CH), 119.2 (d, Ar−CH), 116.9 (d, Ar−CH), 115.2 (d, Ar−CH), 114.7 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{13}H_{10}N_3O_3]^+$ = $[M + H]^+$ 256.0717, found 256.0716.

2-(6-Chloro-2H-indazol-2-yl)aniline (**3bd**). Golden yellow solid (171 mg, 85%); mp 114−116 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3447, 3343, 3200, 3127, 3060, 2105, 1616, 1552, 1510, 1462, 1392, 1356, 1317, 1285, 1261, 1224, 1194, 1158, 1099, 1048, 1027, 953, 810, 749, 615; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.18 (s, 1H), 7.71 (d, 1H, J = 8.8 Hz), 7.37 (s, 1H), 7.31 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 7.26−7.20 (m, 1H), 6.88−6.81 (m, 3H), 4.90 (br s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) 149.7 (s, Ar−C), 141.3 (s, Ar−C), 138.8 (s, Ar−C), 129.6 (d, Ar−CH), 126.3 (s, Ar−C), 124.7 (d, Ar−CH), 124.1 (d, Ar−CH), 122.2 (d, Ar−CH), 119.8 (s, Ar−C), 118.1 (d, Ar−CH), 117.6 (d, Ar−CH), 116.4 (d, Ar−CH), 105.2 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{13}H_{11}ClN_3]^+$ = $[M + H]^+$ 244.0636, found 244.0639.

2-(2H-[1,3]Dioxolo[4,5-f]indazol-2-yl)aniline (**3be**). Light yellow solid (72 mg, 88%); mp 132−134 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3451, 3347, 3128, 2920, 2779, 1732,1613, 1548, 1503, 1478, 1389, 1346, 1316, 1264, 1221, 1169, 1040, 950, 831, 792, 734, 702; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 7.98 (s,1H), 7.27−7.26 (m, 1H), 7.18 (t, 1H, J = 7.1 Hz), 7.01 (s, 1H), 6.92 (s, 1H), 6.86−6.78 (m, 2H), 5.97 (s, 2H), 4.84 (br s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.5 (s, Ar−C), 147.0 (s, Ar−C), 145.9 (s, Ar−C), 141.2 (s, Ar−C), 128.9 (d, Ar−CH), 126.7 (s, Ar−C), 124.6 (d, Ar−CH), 123.0 (d, Ar−CH), 118.1 (d, Ar−CH), 117.4 (s, Ar−C), 117.4 (d, Ar−CH), 101.0 (t, $-CH_2-$), 95.0 (d, Ar−CH), 94.0 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{14}H_{12}N_3O_2]^+$ = $[M + H]^+$ 254.0924, found 254.0934.

4-Chloro-2-(2H-indazol-2-yl)aniline (**3bf**). Light yellow solid (164 mg, 82%); mp 96−98 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3452, 3335, 3202, 3124, 3060, 1619, 1582, 1499, 1460, 1426, 1385, 1350, 1304, 1263, 1199, 1151, 1099, 1042, 962, 864, 813, 788, 751, 731, 652; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.18 (s, 1H), 7.74 (dd, 2H, J_a = 14.9 and J_b = 8.6 Hz), 7.37−7.34 (m, 2H), 7.17−7.12 (m, 2H), 6.78 (d, 1H, J = 8.8 Hz), 4.98 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.6 (s, Ar−C), 140.1 (s, Ar−C), 129.2 (d, Ar−CH), 127.1 (d, Ar−CH), 126.7 (s, Ar−C), 124.6 (d, Ar−CH), 123.6 (d, Ar−CH), 122.6 (d, Ar−CH), 122.2 (s, Ar−C), 121.9 (s, Ar−C), 120.4 (d, Ar−CH), 118.4 (d, Ar−CH), 117.5 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{13}H_{11}ClN_3]^+$ = $[M + H]^+$ 244.0636, found 244.0625.

(3-Amino-4-(2H-indazol-2-yl)phenyl)(phenyl)methanone (**3bg**). Light yellow solid (249 mg, 78%); mp 166−168 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3457, 3355, 3057, 2124, 1652, 1609, 1516, 1439, 1384, 1321, 1258, 1198, 1136, 1076, 991, 949, 883, 853, 824, 788, 747, 709, 659; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.3 (s, 1H), 7.84−7.82 (m, 2H), 7.76 (t, 2H, J = 8.1 Hz), 7.62−7.58 (m, 1H), 7.51−7.43 (m, 3H), 7.38−7.32 (m, 2H), 7.22 (dd, 1H, J_a = 8.1 and J_b = 1.7 Hz), 7.17−7.13 (m, 1H), 5.25 (br s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) 196.2 (s, −CO−), 149.7 (s, Ar−C), 141.2 (s, Ar−C), 138.1 (s, Ar−C), 137.4 (s, Ar−C), 132.6 (d, Ar−CH), 130.1 (d, 2C, Ar−CH), 128.9 (s, Ar−C), 128.4 (d, 2C, Ar−CH), 127.2 (d, Ar−CH), 124.3 (d, Ar−CH), 123.6 (d, Ar−CH), 122.7 (d, Ar−CH), 121.9 (s, Ar−C), 120.4 (d, Ar−CH), 119.7 (d, Ar−CH), 119.0 (d, Ar−CH), 117.6 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{20}H_{16}N_3O]^+$ = $[M + H]^+$ 314.1288, found 314.1287.

(Z)-N-(6H-Benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)-cyclohexanamine (**5a**). White solid (102 mg, 98%); mp 116−118 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3069, 2926, 2852, 1671, 1606, 1529, 1498, 1488, 1448, 1432, 1371, 1305, 1281, 1229, 1188, 1116, 1096, 1030, 994, 933, 746, 634; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.25 (d, 2H, J = 8.3 Hz), 7.8 (d, 1H, J = 8.8 Hz), 7.42−7.38 (m, 1H), 7.31−7.20 (m, 4H), 4.15−4.09 (m, 1H), 1.90−1.85 (m, 4H), 1.68−1.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.5 (s, Ar−C), 144.7 (s, Ar−C), 139.6 (s, Ar−C), 128.2 (d, Ar−CH), 128.0 (d, Ar−CH), 124.4 (d, Ar−CH), 124.1 (s, Ar−C), 124.0 (d, Ar−CH), 122.2 (d, Ar−CH), 122.1 (s, Ar−C), 120.8 (s, Ar−C), 117.6 (d, Ar−CH), 116.9 (d, Ar−CH), 116.6 (d, Ar−CH), 54.1 (d, −CH−), 33.9 (t, 2C, $-CH_2-$), 26.1 (t, $-CH_2-$), 24.6 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{20}N_3O]^+$ = $[M + H]^+$ 318.1601, found 318.1599.

(Z)-N-(8-Bromo-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)cyclohexanamine (**5b**). White solid (84 mg, 87%); mp 128−130 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3070, 2927, 2853, 1675, 1605, 1517, 1490, 1446, 1416, 1367, 1339, 1301, 1271, 1229, 1178, 1133, 1096, 1030, 989, 941, 909, 882, 803, 748, 701, 668; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.38 (d, 1H, J = 1.5 Hz), 8.21 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 7.66 (d, 1H, J = 9.3 Hz), 7.44 (dd, 1H, J_a = 9.0 and J_b = 1.7 Hz), 7.36−7.31 (m, 1H), 7.27−7.22 (m, 2H), 4.12−4.05 (m, 1H), 1.88−1.84 (m, 4H), 1.61−1.32 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 147.9 (s, Ar−C), 144.8 (s, Ar−C), 139.2 (s, Ar−C), 131.7 (d, Ar−CH), 128.6 (d, Ar−CH), 124.4 (d, Ar−CH), 124.1 (d, Ar−CH), 123.8 (s, Ar−C), 121.8 (s, Ar−C), 121.6 (s, Ar−C), 119.2 (d, Ar−CH), 118.1 (s, Ar−C), 117.0 (d, Ar−CH), 116.7 (d, Ar−CH), 54.4 (d, −CH−), 33.8 (t, 2C, $-CH_2-$), 26.0 (t, $-CH_2-$), 24.8 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{19}BrN_3O]^+$ = $[M + H]^+$ 396.0706, found 396.0705.

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*(Z)-N-(9-Bromo-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)cyclohexanamine (**5c**).* White solid (80 mg, 84%); mp 182−154; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3067, 2926, 2853, 1674, 1604, 1540, 1487, 1440, 1366, 1320, 1280, 1255, 1225, 1188, 1119, 1031, 989, 933, 850, 803, 750, 700, 590; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.10 (d, 1H, J = 8.3 Hz), 7.99 (d, 1H, J = 8.8 Hz), 7.86 (s, 1H), 7.26−7.20 (m, 2H), 7.17−7.12 (m, 2H), 4.04−3.99 (m, 1H), 1.81−1.79 (m, 4H), 1.6 (d, 2H, J = 9.8 Hz), 1.49−1.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.0 (s, Ar−C), 144.8 (s, Ar−C), 139.9 (s, Ar−C), 128.5 (d, Ar−CH), 128.0 (d, Ar−CH), 124.1 (d, Ar−CH), 123.8 (s, Ar−C), 123.6 (d, Ar−CH), 122.6 (s, Ar−C), 122.1 (s, Ar−C), 120.0 (d, Ar−CH), 119.2 (s, Ar−C), 117.0 (d, Ar−CH), 116.6 (d, Ar−CH), 54.2 (d, −CH−), 33.8 (t, 2C, $-CH_2-$), 26.0 (t, 2C, $-CH_2-$), 24.5 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{19}BrN_3O]^+$ = $[M + H]^+$ 396.0706, found 396.0694.

*(Z)-N-(6H-Benzo[5,6][1,4]oxazino[4,3-b][1,3]dioxolo[4,5-f]-indazol-6-ylidene)cyclohexanamine (**5d**).* White solid (95 mg, 96%); mp 194−196 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 2927, 2854, 2780, 1674, 1605, 1508, 1469, 1397, 1360, 1337, 1287, 1215, 1097, 1036, 986, 957, 850, 819, 751; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.13 (s, 1H), 7.49 (s, 1H), 7.27−7.21 (m, 3H), 7.06 (s, 1H), 6.03 (s, 2H), 4.13−4.07 (m, 1H), 1.88 (d, 4H, J = 8.3 Hz), 1.69−1.67 (m, 1H), 1.56−1.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.5 (s, Ar−C), 147.4 (s, Ar−C), 147.2 (s, Ar−C), 144.1 (s, Ar−C), 139.7 (s, Ar−C), 127.2 (d, Ar−CH), 124.2 (s, Ar−C), 123.9 (d, Ar−CH), 121.7 (s, Ar−C), 117.0 (s, Ar−C), 116.5 (d, Ar−CH), 116.1 (d, Ar−CH), 101.4 (t, $-CH_2-$), 97.3 (d, Ar−CH), 94.2 (d, Ar−CH), 53.9 (d, Ar−CH−), 33.9 (t, 2C, $-CH_2-$), 26.0 (t, $-CH_2-$), 25.6 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{21}H_{20}N_3O_3]^+$ = $[M + H]^+$ 362.1499, found 362.1501.

*(Z)-N-(2-Methyl-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)cyclohexanamine (**5e**).* White solid (89 mg, 87%); mp 118−120 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ = 3066, 2927, 2852, 1672, 1617, 1529, 1504, 1490, 1435, 1370, 1330, 1309, 1276, 1249, 1229, 1187, 1118, 1098, 1010, 945, 808, 749, 637; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.23 (d, 1H, J = 8.8 Hz), 7.98 (s, 1H), 7.78 (d, 1H, J = 8.8 Hz), 7.38 (t, 1H, J = 7.6 Hz), 7.24−7.22 (m, 1H), 7.05 (d, 1H, J = 7.8 Hz), 8.99−8.97 (m, 1H), 4.12−4.06 (m, 1H), 2.33 (s, 3H), 1.90−1.87 (m, 4H), 1.69−1.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.4 (s, Ar−C), 142.6 (s, Ar−C), 139.9 (s, Ar−C), 133.9 (s, Ar−C), 128.7 (d, Ar−CH), 127.9 (d, Ar−CH), 124.2 (d, Ar−CH), 123.5 (s, Ar−C), 122.2 (d, Ar−CH), 122.1 (s, Ar−C), 120.7 (s, Ar−C), 117.5 (d, Ar−CH), 116.9 (d, Ar−CH), 116.1(d, Ar−CH), 54.0 (d, −CH−), 33.9 (t, 2C, $-CH_2-$), 26.1 (t, $-CH_2-$), 24.6 (t, 2C, $-CH_2-$), 20.8 (q, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{21}H_{22}N_3O]^+$ = $[M + H]^+$ 332.1757, found 332.1754.

*(Z)-N-(2-Chloro-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)cyclohexanamine (**5f**).* White solid (85 mg, 85%); mp 140−142 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3071, 2926, 2852, 1673, 1605, 1528, 1489, 1448, 1432, 1369, 1307, 1262, 1231, 1186, 1146, 1109, 1073, 996, 941, 871, 845, 809, 749, 632; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.27 (d, 1H, J = 2H), 8.23 (d, 1H, J = 8.8 Hz), 7.8 (d, 1H, J = 8.8 Hz), 7.44−7.40 (m, 1H), 7.29−7.24 (m, 2H), 7.22−7.20 (m, 1H), 4.13−4.10 (m, 1H), 1.88−1.80 (m, 4H), 1.60−1.35 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.8 (s, Ar−C), 143.3 (s, Ar−C), 138.9 (s, Ar−C), 129.3 (s, Ar−C), 128.4 (d, Ar−CH), 128.0 (d, Ar−CH), 124.7 (d, Ar−CH), 122.2 (d, Ar−CH), 122.1 (s, 2C, Ar−C), 120.8 (s, Ar−C), 117.8 (d, Ar−CH), 117.7 (d, Ar−CH), 117.0 (d, Ar−CH), 54.2 (d, −CH−), 33.8 (t, 2C, $-CH_2-$), 26.0 (t, 2C, $-CH_2-$), 24.5 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{19}ClN_3O]^+$ = $[M + H]^+$ 352.1211, found 352.1207.

*(Z)-N-(2-Nitro-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)cyclohexanamine (**5g**).* Yellow solid (67 mg, 68%); mp 140−142 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3054, 2926, 2852, 1676, 1602, 1531, 1502, 1450, 1423, 1374, 1342, 1308, 1263, 1184, 1143, 1119, 1074, 994, 961, 894, 838, 735, 702, 662, 624, 603, 582; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.27 (d, 1H, J = 2H), 8.23 (d, 1H, J = 8.8 Hz), 7.8 (d, 1H, J = 8.8 Hz), 7.44−7.40 (m, 1H), 7.29−7.24 (m, 2H), 7.22−7.20 (m, 1H), 4.13−4.10 (m, 1H), 1.88−1.80 (m, 4H), 1.60−1.35 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150 (s, Ar−C), 146.6 (s, Ar−C), 144.4 (s, Ar−C), 137.8 (s, Ar−C), 129.2 (d, Ar−CH), 128.7 (s, Ar−C), 125.4 (d, Ar−CH), 122.5 (d, Ar−CH), 122.3 (s, Ar−C), 121.1 (s, Ar−C), 119.4 (d, Ar−CH), 117.9 (d, Ar−CH), 117.5 (d, Ar−CH), 112.7 (d, Ar−CH), 54.5 (d, −CH−), 33.8 (t, 2C, $-CH_2-$), 26.0 (t, $-CH_2-$), 24.4 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{19}N_4O_3]^+$ = $[M + H]^+$ 363.1452, found 363.1448.

*(Z)-N-(6H-Benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)-2-methylpropan-2-amine (**5h**).* White solid (85 mg, 88%); mp 128−130 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3068, 2966, 2928, 2905, 1681, 1606, 1528, 1498, 1488, 1430, 1360, 1306, 1281, 1213, 1182, 1114, 1093, 1030, 994, 933, 746, 636; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.29 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 8.25 (d, 1H, 8.3 Hz), 7.82 (d, 1H, J = 8.3 Hz), 7.44−7.40 (m, 1H), 7.34−7.30 (m, 1H), 7.30−7.27 (m, 2H), 7.27−7.24 (m, 1H), 1.54 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.6 (s, Ar−C), 144.7 (s, Ar−C), 138.2 (s, Ar−C), 128.2 (d, Ar−CH), 128.0 (d, Ar−CH), 124.4 (d, Ar−CH), 124.0 (d, Ar−CH), 122.6 (s, Ar−C), 122.3 (d, Ar−CH), 120.8 (s, 2C, Ar−C), 117.6 (d, Ar−CH), 117.0 (d, Ar−CH), 116.7 (d, Ar−CH), 54.8 (s, -C−), 30.4 (q, 3C, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{18}H18N_3O]^+$ = $[M + H]^+$ 292.1444, found 292.1445.

*(Z)-N-(8-Bromo-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)-2-methylpropan-2-amine (**5i**).* White solid (77 mg, 80%); mp 140−142 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3070, 2967, 2927, 1680, 1606, 1516, 1490, 1446, 1414, 1361, 1335, 1300, 1267, 1249, 1216, 1171, 1130, 1094, 1032, 985, 913, 882, 803, 751, 700, 671 640; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.37 (d, 1H, J = 1.5 Hz), 8.24 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 7.67 (d, 1H, J = 9.3 Hz), 7.45 (dd, 1H, J_a = 9 and J_b = 1.7 Hz), 7.35−7.33 (m, 1H), 7.28−7.23 (m, 2H), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 147.9 (s, Ar−C), 144.7 (s, Ar−C), 137.8 (s, Ar−C), 131.7 (d, Ar−CH), 128.6 (d, Ar−CH), 124.4 (d, Ar−CH), 124.1 (d, Ar−CH), 123.8 (s, Ar−C), 122.0 (s, Ar−C), 121.8 (s, Ar−C), 119.2 (d, Ar−CH), 118.0 (s, Ar−C), 117.1 (d, Ar−CH), 116.8 (d, Ar−CH), 54.9 (q, -C−), 30.3 (q, CH_3); HR-MS (ESI+) m/z calculated for $[C_{18}H_{17}BrN_3O]^+$ = $[M + H]^+$ 370.0550, found 370.0550.

*(Z)-N-(9-Bromo-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)-2-methylpropan-2-amine (**5j**).* White solid (70 mg, 78%); mp 116−118 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3069, 2968, 2929, 2123, 1680, 1638, 1605, 1556, 1497, 1457, 1390, 1363, 1311, 1281, 1213, 1183, 1117, 1102, 1031, 988, 950, 914, 810, 751, 700, 598; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.26 (dd, 1H, J_a = 7.8 and J_b = 1.5 Hz), 8.17 (d, 1H, J = 8.8 Hz), 7.47 (s, 1H), 7.37−7.33 (m, 1H), 7.30−7.26 (m, 2H), 7.07 (dd, 1H, J_a = 8.8 and J_b = 1.5 Hz), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.2 (s, Ar−C), 144.6 (s, Ar−C), 141.0 (s, Ar−C), 128.1 (d, Ar−CH), 124.1 (d, Ar−CH), 123.2 (d, Ar−CH), 122.7 (s, 2C, Ar−C), 122.5 (d, Ar−CH), 120.8 (s, Ar−C), 116.9 (d, Ar−CH), 116.7 (d, Ar−CH), 109.5 (d, Ar−CH), 106.1 (s, Ar−C) 54.8 (s, -C−), 30.3 (q, 3C, Ar−CH_3); HR-MS (ESI+) m/z calculated for $[C_{18}H_{17}BrN_3O]^+$ = $[M + H]^+$ 370.0550, found 370.0554.

*(Z)-N-(6H-Benzo[5,6][1,4]oxazino[4,3-b][1,3]dioxolo[4,5-f]-indazol-6-ylidene)-2-methylpropan-2-amine (**5k**).* White solid (83 mg, 90%); mp 136−138 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3738, 2955, 2900, 2781, 2133, 1744, 1664, 1597, 1553, 1503, 1473, 1433, 1352, 1282, 1255, 1205, 1123, 1093, 1032, 953, 912, 853, 815, 736; ^1H NMR ($CDCl_3$, 400 MHz) δ_H = 8.15 (d, 1H, d, J = 6.8 Hz), 7.48 (s, 1H), 7.29−7.22 (m, 3H), 7.07 (s, 1H), 6.08 (s, 2H), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.5 (s, Ar−C), 147.3 (s, Ar−C), 147.2 (s, Ar−C), 144.1 (s, Ar−C), 138.4 (s, Ar−C), 127.2 (d, Ar−CH), 124.2 (s, Ar−C), 124.0 (d, Ar−CH), 122.2 (s, Ar−C), 117.1 (s, Ar−C), 116.6 (d, Ar−CH), 116.2 (d, Ar−CH), 101.4 (t, $-CH_2-$), 97.3 (d, Ar−CH), 94.2 (d, Ar−CH), 54.6 (s, -C−), 30.4 (q, 3C, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{19}H_{18}N_3O_3]^+$ = $[M + H]^+$ 336.1343, found 336.1341.

*(Z)-2-Methyl-N-(2-methyl-6H-benzo[5,6][1,4]oxazino[4,3-b]-indazol-6-ylidene)propan-2-amine (**5l**).* White solid (81 mg, 85%); mp 138−140 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3040, 2989, 2961, 2952, 2870, 1670, 1616, 1525, 1498, 1431, 1367, 1331, 1275, 1249, 1216, 1182, 1116, 1190, 1010, 944, 862, 804, 740, 635; ^1H NMR

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($CDCl_3$, 400 MHz) δ_H = 8.22 (d, 1H, J = 8.3 Hz), 8.08 (s, 1H), 7.79 (d, 1H, J = 8.8 Hz), 7.41−7.35 (m, 1H), 7.26−7.21 (m, 1H), 7.16−7.09 (m, 2H), 2.41 (s, 3H), 1.5 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.5 (s, Ar−C), 142.7 (s, Ar−C), 138.5 (s, Ar−C), 134.1 (s, Ar−C), 128.9 (d, Ar−CH), 128.0 (d, Ar−CH), 124.3 (d, Ar−CH), 123.6 (s, Ar−C), 122.7 (s, Ar−C), 122.3 (d, Ar−CH), 120.8 (s, Ar−C), 117.5 (d, Ar−CH), 117.1 (d, Ar−CH), 116.4 (d, Ar−CH), 54.7 (s, -C−), 30.4 (q, 3C, CH_3), 20.9 (q, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{19}H_{20}N_3O]^+ = [M + H]^+$ 306.1601, found 306.1601.

*(Z)-N-(2-Chloro-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-ylidene)-2-methylpropan-2-amine (**5m**).* Golden yellow solid (76 mg, 82%); mp 110−112 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3054, 2968, 2925, 2853, 1679, 1602, 1526, 1485, 1431, 1361, 1306, 1262, 1214, 1182, 1146, 1106, 1067, 998, 891, 858, 842, 803, 752, 633, 607; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.32 (d, 1H, J = 2.4 Hz), 8.23 (d, 1H, J = 8.3 Hz), 7.82 (d, 1H, J = 8.8 Hz), 7.46−7.43 (m, 1H), 7.32−7.29 (m, 1H), 7.27−7.22 (m, 2H), 1.53 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.8 (s, Ar−C), 143.2 (s, Ar−C), 137.4 (s, Ar−C), 129.4 (s, Ar−C), 128.4 (d, Ar−CH), 128.0 (d, Ar−CH), 127.0 (s, Ar−C), 124.7 (d, Ar−CH), 122.5 (s, Ar−C), 122.2 (d, Ar−CH), 120.9 (s, Ar−C), 117.8 (d, Ar−CH), 117.7 (d, Ar−CH), 117.1 (d, Ar−CH), 55.0 (s, -C−), 30.4 (q, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{18}H_{17}ClN_3O]^+ = [M + H]^+$ 326.1055, found 326.1052.

*(Z)-2-Methyl-N-(2-nitro-6H-benzo[5,6][1,4]oxazino[4,3-b]-indazol-6-ylidene)propan-2-amine (**5n**).* Golden yellow solid (57 mg, 62%); mp 152−154 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3058, 2955, 2920, 2851, 1688, 1619, 1603, 1527, 1502, 1458, 1421, 1373, 1343, 1307, 1285, 1263, 1224, 1177, 1119, 1075, 992, 878, 840, 796, 737, 703, 668, 628, 571; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.42 (d, 1H, J = 9.3 Hz), 8.22−8.14 (m, 3H), 7.81 (d, 1H, J = 8.8 Hz), 7.48−7.44 (m, 1H), 7.33−7.26 (m, 1H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.5 (s, Ar−C), 146.5 (s, Ar−C), 144.4 (s, Ar−C), 136.1 (s, Ar−C), 129.2 (d, Ar−CH), 128.6 (s, Ar−C), 125.4 (d, Ar−CH), 122.9 (s, Ar−C), 122.3 (d, Ar−CH), 121.2 (s, Ar−C), 119.4 (d, Ar−CH), 117.9 (d, Ar−CH), 117.5 (d, Ar−CH), 112.7 (d, Ar−CH), 55.4 (s, -C−), 30.4 (q, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{18}H_{17}N_4O_3]^+ = [M + H]^+$ 337.1295, found 337.1313.

*N-Cyclohexyl-6-(cyclohexylamino)-6H-benzo[5,6][1,4]oxazino-[4,3-b]indazole-9-carboxamide (**5r**).* White solid (69 mg, 55%); mp 128−130 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3736, 2926, 2853, 2120, 1674, 1638, 1605, 1555, 1495, 1447, 1367, 1312, 1272, 1227, 1188, 1114, 1029, 990, 952, 916, 851, 811, 752, 619; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.24 (dd, 1H, J_a = 7.8 and J_b = 1.5 Hz), 8.18 (d, 1H, J = 8.8 Hz), 7.46 (d, 1H, J = 1H), 7.36−7.24 (m, 3H), 7.08 (dd, 1H, J_a = 9 and J_b = 1.7 Hz), 4.15−4.09 (m, 1H), 3.57−3.50 (m, 1H), 2.05 (dd, 2H, J_a = 8.6 and J_b = 4.2 Hz), 1.89−1.66 (m, 6H), 1.59−1.25 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) 150.3 (s, Ar−C), 144.6 (s, Ar−C), 141.1 (s, Ar−C), 139.5 (s, Ar−C), 135.6 (s, Ar−C), 128.1 (d, Ar−CH), 124.1 (s, Ar−C), 124.2 (d, Ar−CH), 123.1 (d, Ar−CH), 122.6 (d, Ar−CH), 122.4 (s, Ar−C), 118.4 (s, Ar−C), 116.8 (d, Ar−CH), 116.6 (d, Ar−CH), 109.5 (d, Ar−CH), 56.8 (d, −CH−), 54.1 (d, −CH−), 35.0 (t, 2C, $-CH_2-$), 33.8 (t, 2C, $-CH_2-$), 26.0 (t, 2C, $-CH_2-$), 25.3 (t, $-CH_2-$), 24.5 (t, 2C, $-CH_2-$), 24.4 (t, $-CH_2-$); HR-MS (ESI+) m/z calculated for ($[C_{27}H_{31}N_4O_2]$ + NH_4) + $[-H_2O]$ = ([M]+NH_4)+[-H_2O] 440.2450, found 440.2443.

*N-Cyclohexylindazolo[2,3-a]quinoxalin-6-amine (**6a**).* Light yellow solid (75 mg, 72%); mp 122−124 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3742, 3447, 3284, 3059, 2926, 2853, 1652, 1583, 1527, 1444, 1369, 1219, 1156, 1107, 890, 748, 635; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.64 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 8.05 (d, 1H, J = 8.8 Hz), 7.92 (d, 1H, J = 8.3 Hz), 7.84−7.82 (m, 1H), 7.58−7.53 (m, 2H), 7.45−7.37 (m, 2H), 5.26 (d, 1H, J = 7.3 Hz), 4.49−4.42 (m, 1H), 2.29 (dd, 2H, Ja = 12.2 and J_b = 2.9 Hz),1.87−1.71 (m, 4H), 1.64−1.41 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.3 (s, Ar−C), 148.8 (s, Ar−C), 138.9 (s, Ar−C), 128.1 (d, Ar−CH), 127.3 (d, Ar−CH), 126.8 (d, Ar−CH), 125.8 (s, Ar−C), 123.9 (d, Ar−CH), 123.1 (d, Ar−CH), 119.2 (s, Ar−C), 118.8 (d, Ar−CH), 117.9 (d, Ar−CH), 116.2 (d, Ar−CH), 115.7 (s, Ar−C), 49.2 (d, −CH−), 33.4 (t, 2C, $-CH_2-$), 25.9 (t, $-CH_2-$), 24.9 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{21}N_4]^+ = [M + H]^+$ 317.1761, found 317.1762.

*8-Bromo-N-cyclohexylindazolo[2,3-a]quinoxalin-6-amine (**6b**).* Light yellow solid (58 mg, 60%); mp 136−138 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3742, 3447, 2925, 2851, 2116, 1631, 1579, 1524, 1441, 1356, 1265, 1244, 1217, 1189, 1153, 1104, 1040, 926, 890, 853, 790, 742, 669, 564; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.57 (d, 1H, J = 8.3 Hz), 8.18 (s, 1H), 7.83 (d, 1H, J = 8.3 Hz), 7.74 (d, 1H, J = 8.8 Hz), 7.56 (t, 1H, J = 7.8 Hz), 7.44−7.40 (m, 2H), 5.12 (d, 1H, J = 7.3 Hz), 4.46−4.39 (m, 1H), 2.28 (dd, 2H, J_a = 12 and J_b = 3.2 Hz), 1.86−1.72 (m, 4H), 1.60−1.42 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.4 (s, Ar−C), 148.9 (s, Ar−C), 139.0 (s, Ar−C), 128.4 (d, Ar−CH), 126.9 (d, Ar−CH), 126.6 (d, Ar−CH), 125.5 (s, Ar−C), 124.2 (d, Ar−CH), 121.2 (s, Ar−C), 120.3 (d, Ar−CH), 120.0 (d, Ar−CH), 119.4 (s, Ar−C), 116.2 (d, Ar−CH), 114.3 (s, Ar−C), 49.4 (d, −CH−), 33.3 (t, 2C, $-CH_2-$), 25.8 (t, $-CH_2-$), 24.9 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{20}BrN_4]^+ = [M + H]^+$ 395.0866, found 395.0863.

***9**-Bromo-N-cyclohexylindazolo[2,3-a]quinoxalin-6-amine (**6c**).* Light yellow solid (63 mg, 65%); mp 158−160 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3742, 3447, 3062, 2922, 2851, 1727, 1620, 1578, 1527, 1454, 1360, 1217, 1156, 1105, 1042, 928, 854, 793, 752, 590; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.59 (dd, 1H, J_a = 8.3 and J_b = 1 Hz), 8.2 (d, 1H, J = 1 Hz), 7.83 (d, 1H, J = 7.3 Hz), 7.77 (d, 1H, J = 8.8 Hz), 7.59−7.55 (m, 1H), 7.46−7.41 (m, 2H), 5.14 (d, 1H, J = 7.3 Hz), 4.47−4.70 (m, 1H), 2.28 (dd, 2H, J_a = 12 and J_b = 3.2 Hz), 1.87−1.62 (m, 4H), 1.54−1.36 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.4 (s, Ar−C), 148.9 (s, Ar−C), 139.0 (s, Ar−C), 128.4 (d, Ar−CH), 126.9 (d, Ar−CH), 126.5 (d, Ar−CH), 125.5 (s, Ar−C), 124.2 (d, Ar−CH), 121.2 (s, Ar−C), 120.3 (d, Ar−CH), 120.0 (d, Ar−CH), 119.4 (s, Ar−C), 116.3 (d, Ar−CH), 114.3 (s, Ar−C), 49.4 (d, −CH−), 33.3 (t, 2C, $-CH_2-$), 25.9 (t, $-CH_2-$), 24.9 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{20}BrN_4]^+ = [M + H]^+$ 395.0866, found 395.0873.

*N-Cyclohexyl-[1,3]dioxolo[4′,5′:5,6]indazolo[2,3-a]quinoxalin-6-amine (**6d**).* Light yellow solid (73 mg, 74%); mp 180−182 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3447, 3055, 2925, 2852, 2782, 1704, 1651, 1585, 1526, 1473, 1399, 1337, 1268, 1200, 1158, 1118, 1041, 955, 891, 825, 754, 693, 526. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.46 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 7.77−7.75 (m, 1H), 7.49−7.45 (m, 1H), 7.39−7.35 (m, 1H), 7.25 (s, 1H), 7.05 (s, 1H), 6.04 (s, 2H), 4.93 (d, 1H, J = 7.3 Hz), 4.43−4.36 (m, 1H), 2.27 (dd, 2H, J_a = 12.2 and J_b = 2.9 Hz), 1.86−1.71 (m, 4H), 1.62−1.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.6 (s, Ar−C), 148.9 (s, Ar−C), 146.5 (s, Ar−C), 146.3 (s, Ar−C), 138.0 (s, Ar−C), 127.2 (d, Ar−CH), 126.6 (d, Ar−CH), 126.1 (s, Ar−C), 123.8 (d, Ar−CH), 119.4 (s, Ar−C), 115.4 (d, Ar−CH), 110.7 (s, Ar−C), 101.6 (t, $-CH_2-$), 94.9 (d, Ar−CH), 94.6 (d, Ar−CH), 49.2 (d, −CH−), 33.4 (d, 2C, $-CH_2-$), 25.9 (d, $-CH_2-$), 24.9 (d, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for ($[C_{21}H_{20}N_4NaO_2]$ + $[-H_2O]$) = ([M + Na] + $[-H_2O]$) 365.1372, found 365.1355.

*3-Chloro-N-cyclohexylindazolo[2,3-a]quinoxalin-6-amine (**6e**).* Light yellow solid (78 mg, 78%); mp 172−174 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3055, 2929, 2349, 2330, 2121, 2100, 1997, 1955, 1717, 1528, 1420, 1264, 967, 895, 731, 702, 643; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.62 (s, 1H), 8.01 (d, 1H, J = 8.8 Hz), 7.88 (d, 1H, J = 8.3 Hz), 7.74 (d, 1H, J = 8.8 Hz), 7.56 (t, 1H, J = 7.8 Hz), 7.48 (dd, 1H, J_a = 8.8 and J_b = 2 Hz), 7.41−7.37 (m, 1H), 5.26 (d, 1H, J = 7.3 Hz), 4.46−4.37 (m, 1H), 2.27 (dd, 2H, J_a = 12.2 and J_b = 2.9 Hz), 1.85 (dt, 2H, J_a = 13.4 and J_b = 3.8 Hz), 1.64−1.53 (m, 3H), 1.49−1.31 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.3 (s, Ar−C), 148.8 (s, Ar−C), 137.4 (s, Ar−C), 129.2 (s, Ar−C), 128.4 (d, Ar−CH), 127.9 (d, Ar−CH), 127.6 (d, Ar−CH), 126.0 (s, Ar−C), 123.5 (d, Ar−CH), 119.2 (s, Ar−C), 118.7 (d, Ar−CH), 118.0 (d, Ar−CH), 116.0 (d, Ar−CH), 115.7 (s, Ar−C), 49.3 (d, −CH−), 33.3 (t, 2C, $-CH_2-$), 25.8 (t, $-CH_2-$), 24.9 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{20}H_{20}ClN_4]^+ = [M + H]^+$ 351.1371, found 351.1366.

*(6-(Cyclohexylamino)indazolo[2,3-a]quinoxalin-3-yl)(phenyl)-methanone (**6f**).* Light yellow solid (54 mg, 58%); mp 166−168 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3857, 3736, 3447, 3050, 2928, 2854, 1655, 1577, 1531, 1444, 1369, 1263, 1109, 895, 733; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.7 (d, 1H, J = 8.8 Hz), 8.23 (d, 1H, J = 2H),

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8.04 (d, 1H, J = 8.3 Hz), 7.91−7.86 (m, 4H), 7.64−7.57 (m, 2H), 7.55−7.51 (m, 2H), 7.42−7.38 (m, 1H), 5.33 (d, 1H, J = 7.8 Hz), 4.43−4.41 (m, 1H), 2.20 (dd, 2H, J_a = 11.7 and J_b = 2.9 Hz), 1.86−1.80 (m, 4H), 1.61−1.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) 196.2 (s, −CO−), 149.8 (s, Ar−C), 149.2 (s, Ar−C), 138.4 (s, Ar−C), 137.8 (s, Ar−C), 136.9 (s, Ar−C), 132.5 (d, Ar−CH), 130.1 (d, 2C, Ar−CH), 129.4 (d, Ar−CH), 128.4 (d, 2C, Ar−CH), 128.2 (s, Ar−C), 127.8 (d, Ar−CH), 124.8 (d, Ar−CH), 123.7 (d, Ar−CH), 119.6 (s, Ar−C), 118.8 (d, Ar−CH), 118.1 (d, Ar−CH), 116.4 (d, Ar−CH), 115.8 (s, Ar−C), 49.4 (d, −CH−), 33.3 (t, 2C, $-CH_2-$), 25.8 (t, $-CH_2-$), 24.9 (t, 2C, $-CH_2-$); HR-MS (ESI+) m/z calculated for $[C_{27}H_{25}N_4O]^+ = [M + H]^+$ 421.2023, found 421.2016.

N-(tert-Butyl)indazolo[2,3-a]quinoxalin-6-amine (**6g**). Light yellow solid (63 mg, 65%); mp 84−86 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3736, 3455, 2959, 2924, 2855, 1717, 1582, 1527, 1465, 1442, 1365, 1313, 1210, 1161, 1097, 967, 743, 643; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.63 (m, 1H), 8.04 (d, 1H, J = 8.8 Hz), 7.89−7.84 (m, 2H), 7.58−7.54 (m, 2H), 7.45−7.39 (m, 2H), 5.24 (s, 1H), 1.73 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 149.3 (s, Ar−C), 148.7 (s, Ar−C), 138.7 (s, Ar−C), 128.0 (d, Ar−CH), 127.3 (d, Ar−CH), 127.1 (d, Ar−CH), 125.6 (s, Ar−C), 123.9 (d, Ar−CH), 123.0 (d, Ar−CH), 119.5 (s, Ar−C), 118.8 (d, Ar−CH), 117.9 (d, Ar−CH), 116.1 (d, Ar−CH), 115.5 (s, Ar−C), 52.8 (s, −C−), 29.3 (q, 3C,-CH3); HR-MS (ESI+) m/z calculated for $[C_{18}H_{19}N_4]^+ = [M + H]^+$ 291.1604, found 291.1607.

8-Bromo-N-(tert-butyl)indazolo[2,3-a]quinoxalin-6-amine (**6h**). Light yellow solid (53 mg, 60%); mp 150−152 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3738, 3454, 3060, 2926, 2924, 2856, 1719, 1527, 1471, 1438, 1386, 1292, 1263, 1210, 1101, 1066, 1040, 948, 804, 752; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.6 (dd, 1H, J_a = 8.3 and J_b = 1 Hz), 7.99 (d, 1H, J = 1 Hz), 7.91 (d, 1H, J = 9.3 Hz), 7.85−7.83 (m, 1H), 7.63−7.53 (m, 2H), 7.46−7.42 (m, 1H), 5.1 (s, 1H), 1.73 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) 148.9 (s, Ar−C), 147.1 (s, Ar−C), 137.1 (s, 2C, Ar−C), 130.8 (d, Ar−CH), 128.3 (d, Ar−CH), 127.2 (d, Ar−CH), 125. Four (s, Ar−C), 124.2 (d, Ar−CH), 121.2 (d, Ar−CH), 119.5 (d, Ar−CH), 118.9 (s, Ar−C), 116.72 (s, Ar−C), 116.2 (d, Ar−CH), 53.04 (s, -C−), 29.31 (q, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}BrN_4]^+ = [M + H]^+$ 369.0709, found 369.0705.

6H-Benzo[5,6][1,4]oxazino[4,3-b]indazol-6-one (**7a**). White solid (37 mg, 99%); mp 190−192 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3067, 2921, 1739, 1605, 1528, 1484, 1422, 1283, 1226, 1184, 1119, 1099, 1032, 999, 895, 744; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.43 (d, 1H, J = 8.3 Hz), 8.27 (d, 1H, J = 8.8 Hz), 7. 99 (d, 1H, J = 8.3 Hz), 7.58−7.52 (m, 3H), 7.50−7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) 167.6 (s, −CO−), 149.3 (s, Ar−C), 138.7 (s, Ar−C), 133.0 (d, Ar−CH), 132.9 (d, Ar−CH), 129.3 (d, Ar−CH), 127.8 (s, Ar−C), 126.7 (d, Ar−CH), 125.6 (d, Ar−CH), 123.0 (d, Ar−CH), 122.4 (s, 2C, Ar−C), 120.6 (d, Ar−CH), 117.2 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{14}H_9N_2O_2]^+ = [M + H]^+$ 237.0659, found 237.0656.

8-Bromo-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-one (**7b**). White solid (37 mg, 95%); mp 208−210 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3096, 2924, 2853, 2152, 1747, 1516, 1483, 1404, 1298, 1275, 1175, 1137, 1098, 991, 894, 807, 756; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.42 (d, 1H, J = 1.5 Hz), 8.38 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 7.84 (d, 1H, J = 9.3 Hz), 7.6 (dd, 1H, J_a = 9.3and J_b = 2.1 Hz) 7.56−7.52 (m, 2H), 7.50−7.44 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 152.5 (s, −CO−), 147.7 (s, Ar−C), 144.0 (s, Ar−C), 132.4 (d, Ar−CH), 129.8 (d, Ar−CH), 125.8 (d, Ar−CH), 123.8 (s, Ar−C), 123.5 (s, Ar−C), 122.9 (d, Ar−CH), 120.9 (s, Ar−C), 120.1 (d, Ar−CH), 118.1 (d, Ar−CH), 117.8 (s, Ar−C), 117.1 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{14}H_8BrN_2O_2]^+ = [M + H]^+$ 314.9764, found 314.9766.

9-Bromo-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-one (**7c**). White solid (38 mg, 96%); mp 196−198 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3059, 2921, 2853, 2152, 1939, 1743, 1603, 1540, 1482, 1412, 1281, 1248, 1183, 1129, 1097, 1033, 993, 899, 808, 750; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.38 (dd, 1H, J_a = 8.3 and J_b = 1 Hz), 8.12−8.09 (m, 2H), 7.56−7.50 (m, 3H), 7.48−7.44 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 152.5 (s, −CO−), 149.8 (s, Ar−C), 144.0 (s, Ar−C), 130.4 (d, Ar−CH), 129.7 (d, Ar−CH), 125.8 (d, Ar−CH), 123.5 (s, Ar−C), 122.7 (s, Ar−C), 121.9 (d, Ar−CH), 121.3 (s, Ar−C), 121.0 (d, Ar−CH), 118.9 (s, Ar−C), 118.0 (d, Ar−CH), 117.1 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{14}H_8BrN_2O_2]^+ = [M + H]^+$ 314.9764, found 314.9762.

2-Methyl-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-one (**7d**). White solid (37 mg, 97%); mp 140−142 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3070, 2923, 1736, 1527, 1503, 1421, 1369, 1335, 1275, 1184, 1120, 1096, 1016, 815, 752; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.25 (d, 1H, J = 8.3 Hz), 8.2 (s, 1H), 7.96 (d, 1H, J = 8.8 Hz), 7.56−7.52 (m, 1H), 7.48−7.44 (m, 1H), 7.39−7.37 (m, 1H), 7.30−7.26 (m, 1H), 2.5 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 153.0 (s, −CO−), 149.2 (s, Ar−C), 142.0 (s, Ar−C), 136.0 (s, Ar−C), 130.2 (d, Ar−CH), 128.5 (d, Ar−CH), 126.6 (d, Ar−CH), 123.2 (s, Ar−C), 122.8 (s, 2C, Ar−C), 120.7 (d, Ar−CH), 118.4 (d, Ar−CH), 117.6 (d, Ar−CH), 116.9 (d, Ar−CH), 21.1 (q, $-CH_3$); HR-MS (ESI+) m/z calculated for $[C_{15}H_{11}N_2O_2]^+ = [M + H]^+$ 251.0815, found 251.0812.

2-Chloro-6H-benzo[5,6][1,4]oxazino[4,3-b]indazol-6-one (**7e**). White solid (37 mg, 97%); mp 178−180 °C; IR (MIR-ATR, 4000−600 cm^{-1}) υ_{max} = 3065, 2924, 2851, 2156, 1751, 1603, 1523, 1479, 1416, 1363, 1302, 1258, 1225, 1178, 1115, 1068, 996, 870, 815, 750, 642; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H = 8.41 (d, 1H, J = 1.5 Hz), 8.23 (d, 1H, J = 8.3 Hz), 7.96 (d, 1H, J = 8.8 Hz), 7.58−7.54 (m, 1H), 7.50−7.43 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 152.3 (s, −CO−), 149.5 (s, Ar−C), 142.4 (s, Ar−C), 131.2 (s, Ar−C), 129.3 (d, Ar−CH), 129.0 (d, Ar−CH), 127.1 (d, Ar−CH), 124.2 (s, Ar−C), 123.0 (s, Ar−C), 120.6 (d, Ar−CH), 119.2 (d, Ar−CH), 118.6 (d, Ar−CH), 118.3 (s, Ar−C), 117.1 (d, Ar−CH); HR-MS (ESI+) m/z calculated for $[C_{14}H_8ClN_2O_2]^+ = [M + H]^+$ 271.0269, found 271.0269.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00048.

Experimental procedures and characterization for all new compounds, copies of NMR spectra. (PDF)

Crystal data for **5a**. (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +91(40) 2301 7058. Fax: +91(40) 2301 6032. E-mail: sharada@iith.ac.in.

Notes

The authors declare no competing financial interest.

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