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PAPER

Synthesis of hybrid polycycles containing fused hydroxy benzofuran and 1*H*-indazoles via domino cyclization reaction

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Stoichiometry controlled domino cyclization reaction of hydrazone and *p*-benzoquinone to angularly fused 3*H*-benzofuro[3,2-e]indazole core with an embedded oxygenated dibenzofuran framework under mild reaction condition is disclosed. The reaction involves palladium catalyzed 5-hydroxy-1*H*-indazole formation followed by TFA mediated [3+2] annulation between the in situ formed 5-hydroxy-1*H*-indazole and p-benzoquinone. Developed method is attractive because of concomitant formation of two heterocyclic rings with consecutive multiple bond forming events that include two C-C, one C-N and one C-O bonds. The spectroscopic and theoretical studies of the blue emissive benzofuroindazole derivatives has also been described.

Introduction

Development of efficient synthetic routes to construct complex hybrid molecular scaffolds is a prevalent area of research in synthetic organic chemistry due to their diverse biological activities.[1] In fact, hybrid molecules contribute significantly towards the development of polypharmacology. The hybrid molecular scaffolds, usually a combination of two or more biologically relevant molecules, exhibit enhanced performance in their application compared to their individual counterparts.[1b,f] Thus the synthesis of polycyclic hybrid molecules with two or more heterocycles gained much attention in recent years.[2] However, synthesis of hybrid molecules is always challenging as it demands highly atom and step-economical protocols with multiple bond formation in one-pot.[3] The strategy will be more appealing if multiple ring formations occur in a sequential manner during the course of the reaction rather than the direct coupling of individual components. Nitrogen and oxygen containing heterocycles are the key architectural scaffolds in many potent drug molecules because of their omnipresent nature in biologically active molecules and natural products.[4] Their abundance in the pharmaceuticals necessitate the need in the development of step-economic, one-pot strategy for the synthesis of fused hybrid heterocycles containing oxygen and nitrogen.[5]

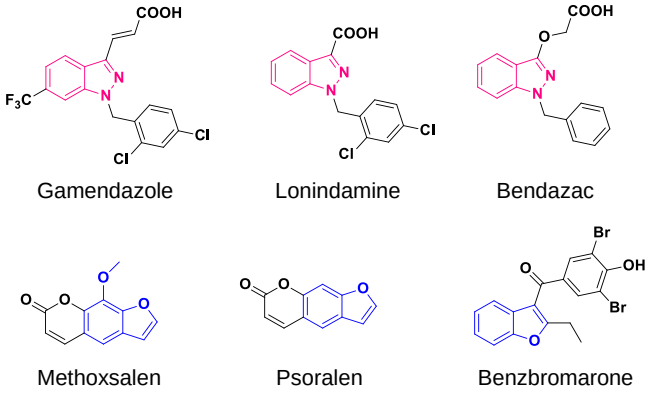

Fig. 1 Representative examples of indazole and benzofuran containing drug molecules.

Indazole and benzofuran are important class of heterocyclic compounds having a wide range of biomedical and pharmaceutical applications (Fig. 1).[6,7] In this context, a hybrid molecule with these two heterocycles - indazole[8] and benzofuran[9] - as key components could be of potential interest. To the best of our knowledge the direct synthesis of such a hybrid molecule, based on readily available substrates, is not yet reported. Domino cyclization reactions, with multiple C-C and C-hetero atom bond formations in one-pot, have attracted the widespread attention in organic synthesis. The

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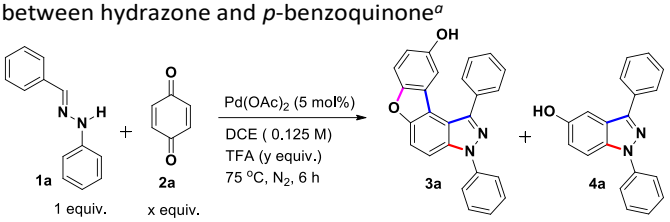
strategy enables to stitch heterocycles of different biological functions in a sequential manner, which left a mark in drug developments. The approach is well used for the construction of complex fused heteroaromatic polycycles.[10] During the last decade domino cyclization reaction strategies were successfully employed for the practical synthesis of many molecules of biological relevance.[11] Furthermore, one-pot bicyclization reactions ensure the bond forming efficiency and realize the formation of new rings in a step-economic manner.[10]

Very recently, we have reported an efficient method towards the synthesis of *N*-protected 5-hydroxy-1*H*-indazoles via modified aza-Nenitzsescu reaction (Table 1).[12] In this approach, palladium(II) catalyzed condensation between *p*-benzoquinone (*p*-BQ) and hydrazone in presence of trifluoroacetic acid (TFA) afforded 5-hydroxy-1*H*-indazoles in good to moderate yield. The method is quite versatile as it affords biologically relevant 3-substituted 5-hydroxy-1*H*-indazoles in one-pot from common reagents such as hydrazones and *p*-BQs. Cyclization of phenols across activated olefins is one of the prominent methods for benzofuran synthesis and both inter and intramolecular strategies have well been studied.[13] Encouraged by our previous work, we assumed the possibility for *in situ* domino annulation of 5-hydroxy-1*H*-indazole across *p*-BQ if excess *p*-BQ and TFA are present in the reaction medium (Table 1). This domino cyclization will lead to a polycyclic hybrid molecule in one-pot with a fused 1*H*-indazole and hydroxy benzofuran moieties with an embedded dibenzofuran framework. Herein, we report an efficient method leading towards the synthesis of a novel polycyclic hybrid molecule containing angularly fused hydroxy benzofuran and 1*H*-indazole with an embedded dibenzofuran framework. Concomitant formation of two potent heterocycles from common precursors such as hydrazones and *p*-BQs is highly noteworthy as the reported methods for the synthesis of hybrid molecules depend on late stage coupling of pre-functionalized substrates.[14] Furthermore, in the present case, the reaction involves the formation of two new C-C, one C-N and one C-O bonds in one-pot under relatively mild conditions leaving behind a free hydroxyl group for further fabrication of the 3*H*-benzofuro[3,2-*e*]indazole core. We also report the photophysical properties of some of the selected benzofuroindazole derivatives.

Results and Discussion

Encouraged by our recent report on the synthesis of 5-hydroxy 1*H*-indazoles[12] and in order to expand the synthetic utility of the reaction, we speculated the possibility to annulate the 1*H*-indazoles across olefin so that potent polycyclic hybrid molecules can be readily accessed. For this, our hypothesis was to annulate the hydroxyl group of 1*H*-indazole *in situ* across the *p*-BQ maintaining its concentration excess in the reaction medium. Keeping this in mind, we commenced our investigation by performing the reaction under the optimized condition[12] with a change in stoichiometry of the reactants, hydrazone:*p*-BQ, as 1:2. Justifying our hypothesis we isolated two fractions, the major one being the 5-hydroxy-1*H*-indazole **4a**, while the other fraction was identified as 1,3-diphenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol **3a** (Table 1, entry 2). This preliminary result encouraged us to pursue the reaction screening in detail and the observations are summarized in Table 1. The compound **3a** formed exclusively in 40% yield when the hydrazone to *p*-BQ stoichiometry enhanced to 1:3 (Table 1, entry 4) and further increase in *p*-BQ did not improve the conversion (Table 1, entry 5). Interestingly, the stoichiometry of TFA was also found to be very crucial (Table 1, entry 6 and 7) and maximum product formation observed when the TFA stoichiometry is 28 equiv. (7 mmol) (Table 1, entry 7). However, loading of more $Pd(OAc)_2$ (10 mol%) did not improve the yield (Table 1, entry 8).

Table 1 Optimization of the stoichiometry controlled reaction between hydrazone and *p*-benzoquinone[a]



Entry	Hydrazone, **1a** (equiv.)	*p*-BQ, **2a** (equiv.)	TFA (equiv.)	Yield[b]	
				Benzofuro-indazole, **3a**	Indazole, **4a**
1[c]	1	1.2	14	0	69
2	1	2	14	20	30
3	1	2.4	14	35	Trace
4	**1**	**3**	**14**	**40**	**0**
5	1	4	14	40	0
6	1	3	20	53	0
7	**1**	**3**	**28**	**63**	**0**
8[d]	1	3	28	43	0

[a]Unless and otherwise stated all reactions were carried out with **1a** (0.25 mmol), **2a** (1.2-4 equiv.), $Pd(OAc)_2$ (5 mol%) in DCE (0.125 M, 2 mL), TFA (14-28 equiv.) under N_2 at 75 °C for 6 h. [b]Isolated yields after column chromatography, [c]Ref. 12. [d]10 mol% of $Pd(OAc)_2$.

We then performed a series of control experiments to understand the reaction in detail (Scheme 1). Treating the preformed 5-hydroxy-1*H*-indazole **4a** (1 equiv.) and *p*-BQ **2a** (2 equiv.), in the absence of both $Pd(OAc)_2$ (5 mol%) and TFA (14 equiv.), afforded no product at all. Similar result was observed when we repeated the reaction with $Pd(OAc)_2$ in the absence of TFA. However, the expected product, **3a** was isolated in 66% yield when we carried out the reaction in presence of TFA (14

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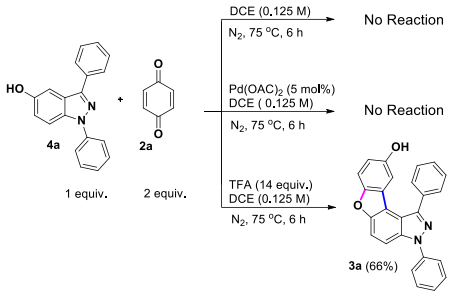
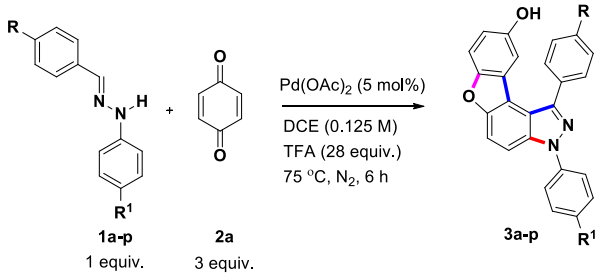
equiv.) alone without $Pd(OAc)_2$. These experiments proved that $Pd(OAc)_2$ has a role of catalyzing the first cyclization to indazole ring and benzofuran ring was formed by TFA mediated [3+2] annulation reaction of 5-hydroxy-1*H*-indazole, **4a** and *p*-BQ.

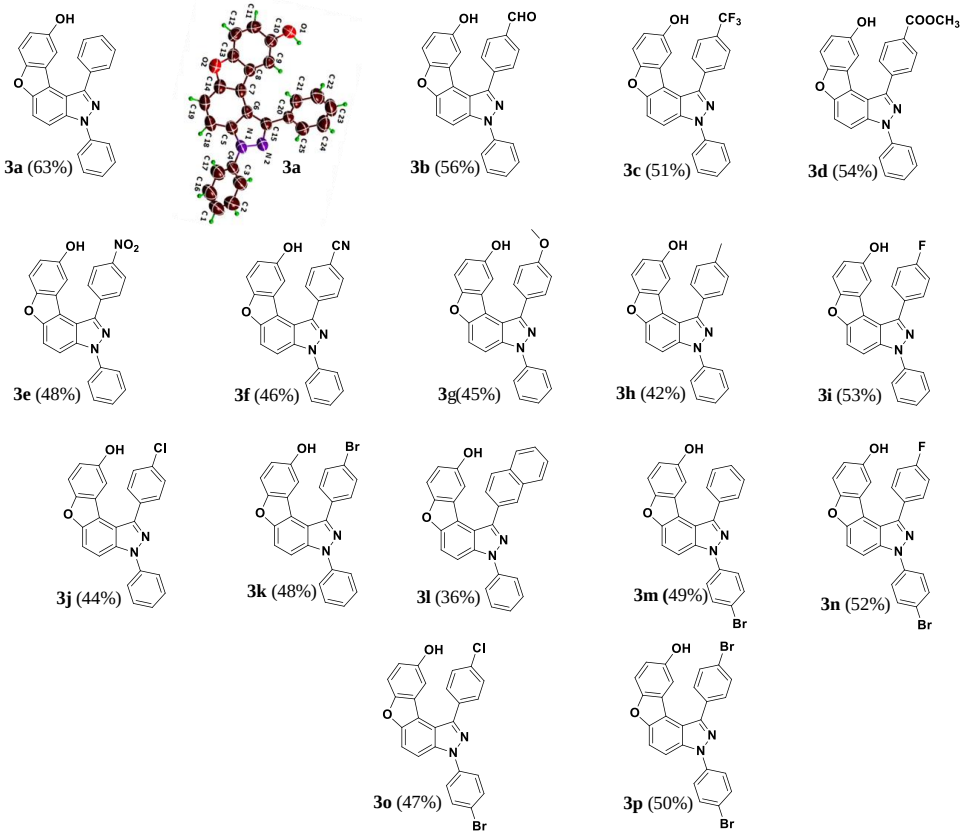


Scheme 1 Control experiment between 5-hydroxy-1*H*-indazole, **4a** and *p*-BQ, **2a.**

Having established the optimal reaction conditions, we further investigated the substrate scope and functional group tolerance of this promising annulation reaction with various substrates (Table 2). Hydrazones of varying electronic nature smoothly afforded the benzofuroindazoles in moderate to good yield. It is interesting to note that a number of acid sensitive functional groups such as –OMe (**3g**), –CN (**3f**), –COOMe (**3d**) and –CHO (**3b**) showed good tolerance to the reaction conditions to afford the hybrid molecule derivatives with these potent functional groups, which will be quite useful for a late stage derivatization. In addition to Cl (**3j**) and Br (**3k**), F (**3i**) as well as CF_3 (**3c**) substituted hydrazones also successfully afforded the product in moderate yield. Employing *p*-nitro derivative of hydrazone in this annulation reaction managed to yield the polycyclic hybrid molecule (**3e**) in 48% yield, while β-naphthaldehyde hydrazone resulted in the similar derivative (**3l**) in 36%. Similarly, *N*-bromophenyl hydrazones also smoothly underwent the reaction to yield respective tetracycles (**3m-p**) in 47-

Table 2 Substrate scope of the reaction[a]





[a] Standard reaction condition: **1a-p** (0.25 mmol), **2a** (0.75 mmol), $Pd(OAc)_2$ (5 mol%), DCE (0.125 M, 2 mL) TFA (28 equiv., 7 mmol), under N_2 at 75 °C for 6 h.

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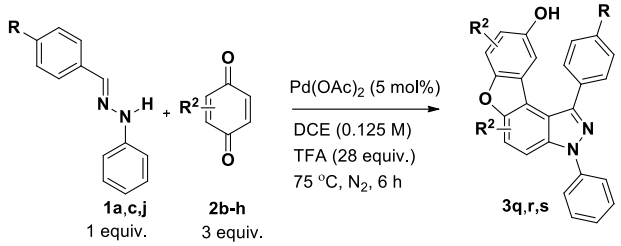
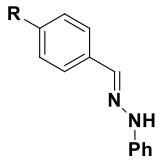
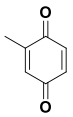
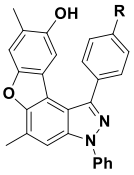
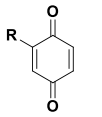
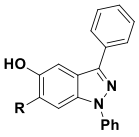
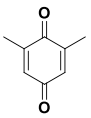
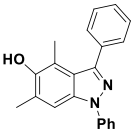
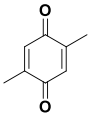
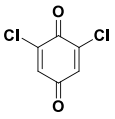
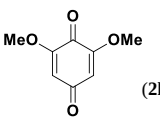
52% yield. Even though the isolated yields of the reaction were moderate to good, it is quite noteworthy that the strategy readily gives access to a complex polycyclic hybrid molecule via multiple bond formation in one-pot and most importantly starting from readily available precursors, the hydrazones and *p*-BQs.

After exploring the versatility of the method towards a number of hydrazones with different electronic and steric nature, we next investigated the scope of different *p*-BQ derivatives. With 2-methyl *p*-benzoquinone, the expected benzofuroindazole derivatives were isolated in good yields. 2,6-dimethyl *p*-benzoquinone could afford only the indazole (**4d**) derivative, which failed to annulate further in presence of TFA. In contrast, 2,5-dimethyl and 2,6-dimethoxy derivatives completely failed in the reaction, neither the indazole nor the fused polycycle were formed. Subsequently, we turned our attention towards haloquinones. 2-chloro *p*-benzoquinone, 2-bromo *p*-benzoquinone and 2,6-dichloro *p*-benzoquinone have been tested in this two-step annulation reaction. With 2-chloro benzoquinone the reaction proceeded up to the indazole level (36%) and the reaction with 2-bromo *p*-benzoquinone yielded the corresponding indazole in trace (confirmed by HRMS†). However, attempts to isolate the pure product was not successful due to the complex reaction mixture. But 2,6-dichloro *p*-benzoquinone did not afford any product (Table 3). We attributed the poor reactivity of substituted quinones to steric and electronic effects.

Interestingly, when a preformed indazole **4a** was treated with 2-chloro *p*-benzoquinone **2c** in presence of TFA, the annulation proceeded smoothly to afford the expected polycycle in 29% yield as a white solid (Scheme 2). In order to ascertain the synthetic utility of the new method, we carried out the reaction with 1 g of **1a** (5.15 mmol) under the optimized conditions and the corresponding

Table 3 Substrate scope of the reaction with substituted *p*-benzoquinones[a]



Hydrazone	*p*-benzoquinone	Benzofuroindazole	Indazole
 R = H (**1a**) R = CF_3 (**1c**) R = Cl (**1j**)	 (**2b**)	 R = H (**3q**: 69%) R = CF_3 (**3r**: 56%) R = Cl (**3s**: 48%)	
1a	 R = Cl (**2c**), Br (**2d**)	[b]NF	 R = Cl (**4b**: 36%) R = Br (**4c**: Trace)
1a	 (**2e**)	NF	 (**4d**: 62%)
1a	 (**2f**)	[c]NR	
1a	 (**2g**)	NR	
1a	 (**2h**)	NR	

[a] Standard reaction condition: **1** (0.25 mmol), **2b - h** (0.75 mmol), $Pd(OAc)_2$ (5 mol%), DCE (0.125 M, 2 mL) TFA (28 equiv., 7 mmol), under N_2 at 75 °C for 6 h. [b]Not formed, [c]No reaction.

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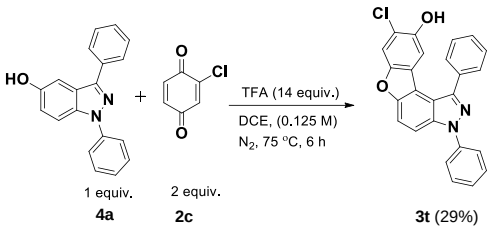
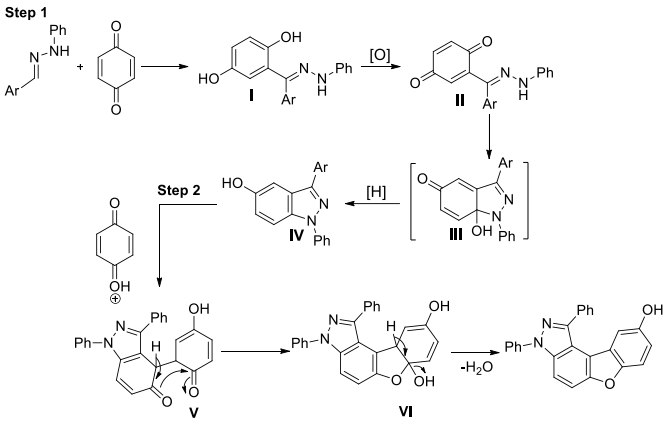
benzofuroindazole **3a** was isolated in 46% yield after column chromatography.



Scheme 2 Reaction between **4a** and **2c**.

On the basis of control experiments a plausible mechanism for the formation of 3*H*-benzofuro[3,2-e]indazole is proposed (Scheme 3). The first step involves the aza-Nenitzescu reaction and we recently reported a modified, Pd(II) catalyzed protocol for this reaction in which 5-hydroxy-1*H*-indazole is obtained from hydrazone and *p*-BQ in presence of TFA.[12] The proposed mechanism for the formation of hydroxy indazole IV, first involves the addition of hydrazone to *p*-BQ to generate a hydroquinone adduct I. This adduct subsequently oxidized by Pd(II) to quinone intermediate II followed by an intramolecular cyclization to afford a carbinolamine intermediate III. Reduction of the carbinolamine intermediate III to hydroxy indazole helps to regenerate Pd(II) in the catalytic cycle.[15] This *in situ* generated hydroxy indazole IV from step 1, subsequently participate in a [3+2] annulation reaction[13a] with excess *p*-BQ in presence of TFA to afford the final product. The benzofuran annulation reaction initiates with the formation of oxacarbenium ion by the activation of *p*-BQ by TFA. Nucleophilic addition of 5-hydroxy-1*H*-indazole to this oxacarbenium intermediate proceed selectively through C_4 carbon of indazole to form the adduct V. Intramolecular cyclization of compound V followed by dehydration readily afford 1,3-diphenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol **3a**.



Scheme 3 Plausible mechanism for the formation of 3*H*-benzofuro[3,2-*e*]indazole.

The synthesized benzofuroindazole derivatives are found to be fluorescent in the solution state. In chloroform, all compounds showed absorption maxima around 340 nm (339-342 nm) and fluorescence emission with maxima ranging from 392-445 nm (Figure 2). The longer wavelength absorption bands except in **3b** can be assigned to the π-π^* transitions centered on benzofuroindazole moiety. In the case of **3b**, the lower energy absorption band can be attributed to the intramolecular charge transfer (CT) transitions from benzofuroindazole moiety to formyl group attached C_3-phenyl ring. From the emission spectra, it is clear that substituents at C_3-phenyl ring did not have a significant effect on the spectral characteristics of benzofuroindazole derivatives except when it is having a formyl group. In the latter case it resulted in a red shift of 53 nm in the emission maximum (λ_{em} = 445 nm) compared to the unsubstituted 1,3-diphenyl-3*H*-benzofuro[3,2-e]indazo-9-ol **3a** (λ_{em} = 392 nm), which can be correlated to a D-A characteristics in the molecule owing to the presence of formyl group. The fluorescence quantum yield of **3a-n** were measured by comparative method[16] using quinine sulfate in 0.1 M H_2SO_4 as the quantum yield standard (Φ_F = 0.54). Most of the compounds showed quantum yield values in the range of 0.11 to 0.29 except **3b** (Φ_F = 0.02), **3m** (Φ_F = 0.07) and **3n** (Φ_F = 0.07) having high non-radiative decay rate constants (Table S1†). Time resolved fluorescence decay of compounds **3a-n** were measured by time-correlated single photon counting method using an excitation wavelength of 340 nm (Fig. S1†) and the obtained lifetime values are summarized in Table S1†.

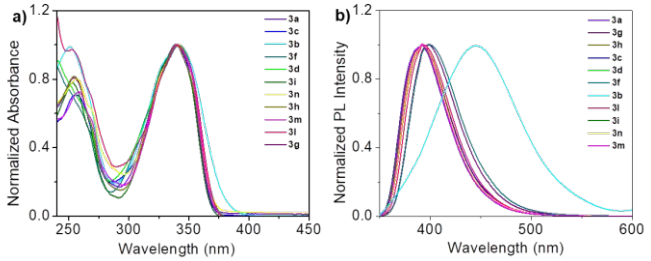


Fig. 2 The absorption (a) and photoluminescence (b) spectra of **3a-n** $CHCl_3$. All the studies were carried out at a concentration of 1 x 10^{-5} M.

In order to get insight into ground state geometry, energy and nature of frontier molecular orbital (FMO) of benzofuroindazole based fluorophores, density functional theory (DFT) of representative derivatives (**3a**, **3b** and **3g**) was carried out using Gaussian 09 program.[17] The ground state geometries were optimized in gas phase at B3LYP level theory in conjunction with 6-311+g(d,p) basis set. In the case of model derivative **3a** the MO coefficient of density in highest occupied molecular orbital (HOMO) was distributed over 3*H*-benzofuro[3,2-*e*]indazole with a lesser extent of distribution over C_3-phenyl ring compared to the *N*-phenyl ring. In compound **3g**, due to the presence of an electron donating methoxy group, C_3-phenyl ring also exhibited a small but sufficient distribution of MO coefficient density in HOMO. In the case of compounds **3a** and **3g**, the MO coefficient of density of LUMO was distributed over benzofuran and indazole framework. Since MO coefficient density of HOMO and LUMO was distributed throughout the entire molecule, these molecules lack ICT characteristics. On the other hand, in the presence of formyl group at C_3-phenyl ring, the

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situation is changed. The coefficient density of LUMO of D-A type molecule **3b** was shifted from benzofuran fused indazole frameworks and mainly localized over formyl group substituted C_3-phenyl ring (Figure 3). To calculate the electronic transitions and the respective absorption spectra, time-dependent DFT (TD-DFT) calculations were carried out with electronically optimized ground state structures in solution state employing polarizable continuum (PCM) model applying self-consistent reaction field (SCRF) in $CHCl_3$. The PBE1PBE functional gave a comparable correlation with the experimentally observed UV/Vis absorption spectral bands. From TD-DFT results (Table S2 and Fig. S2†) it is undoubtedly confirmed that transitions from ground state (S_0) to first excited state (S_1) having a substantial contribution from H → L transition and is responsible for the appearance lowest energy band in the absorption spectrum of these molecules. In the case of **3b**, a transition corresponding H → L + 1 is also found to contribute in the absorption spectrum (Table S2 and Fig. S2†).

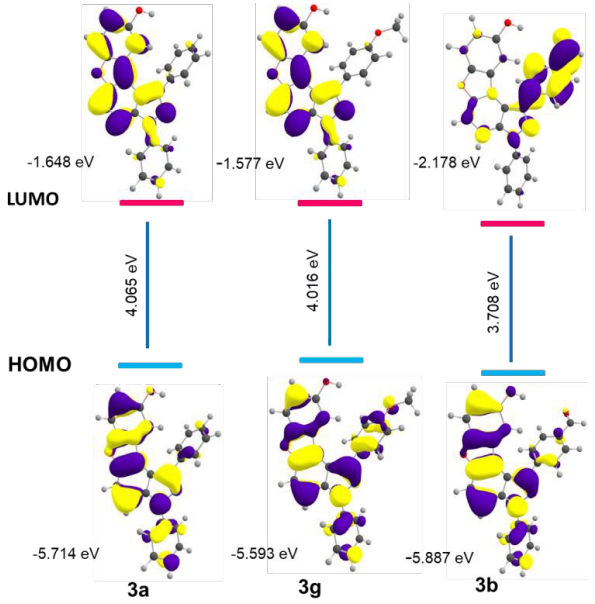

Fig. 3 Calculated molecular orbitals (HOMO and LUMO) and energy levels of benzofuroindazole derivatives **3a**, **3b** and **3g**.

Conclusions

In conclusion, a versatile approach towards the synthesis of a new skeletally diverse angular polycyclic hybrid heterocycle with embedded oxygenated dibenzofuran framework having fused hydroxy benzofuran and indazole unit has been demonstrated. The developed method is operationally simple, works under relatively mild conditions and proceeds via sequential one-pot strategy. Furthermore, the method is highly step-economical constructing four new bonds in one-pot and the starting materials are easily available and cheap. The reaction showed excellent functional group tolerance so that number of derivatives with free potent functional groups has been synthesized and it offers possibility for further chemistry. The π-extended hybrid heterocycles are found to be fluorescent and their spectral characteristics were evaluated with the help of theoretical support. This highly atom and step economical method towards a new class of polycyclic hybrid molecule that contains an angularly fused hydroxy benzofuran and indazole can open up further promising chemistry.

Experimental

General Remarks

Unless and otherwise stated all reactions were carried out in Schlenk tube under nitrogen atmosphere. All the reagents including catalysts were brought from commercial suppliers and used as such without additional purification. All the solvents were dried by standard methods and distilled prior to use. The crude reaction mixture was purified with silica gel (60-120 mesh) column chromatography using hexane-ethyl acetate solvent mixture as eluent. Isolated compounds were characterized by ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy and high-resolution mass spectrometry (HRMS).

Melting points were determined using calibrated digital melting point apparatus (Stuart melting point apparatus SMP30). Infrared spectra were recorded on JASCO FTIR-4100 using KBr pellet and only intense peaks were reported. ^1H NMR (400 and 500 MHz) and ^{13}C NMR (100 and 125 MHz) spectra were recorded in $CDCl_3$, DMSO-d_6 and Acetone-d_6 on Bruker Avance III 400 MHz, Bruker AMX 500 spectrophotometer with tetramethylsilane (TMS; δ_H = 0 ppm) as internal standard and chemical shifts were reported in ppm relative to TMS. HRMS were recorded on Thermo Scientific Exactive mass spectrometer using ESI method with orbitrap mass analyzer.

General procedure for the synthesis of hydrazones: Hydrazones were synthesized according to a reported procedure.[18] To a stirred solution of phenyl hydrazine (1 equiv.) in methanol at room temperature, the corresponding aldehyde (1 equiv.) was added (liquid aldehydes were added dropwise while solid aldehydes in small portions) and the stirring was continued (2-16 h depending on the electronic nature of the aldehyde). After the completion of reaction, the hydrazone was precipitated with ice-cold water and filtered. The precipitate obtained was dissolved in dichloromethane, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The product thus obtained was dried in the vacuum oven and used without any further purification.

General procedure for the synthesis of 1,3-diphenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol: To a stirred solution of hydrazone (0.25 mmol; 1 equiv.), *p*-BQ (0.75 mmol; 3 equiv.) and $Pd(OAc)_2$ (0.0125 mmol; 0.05 equiv.) in dry DCE (0.125 M, 2 mL) in an oven dried Schlenk tube under nitrogen atmosphere, TFA (7 mmol, 28 equiv.) was added and the mixture was heated at 75 °C under nitrogen atmosphere for 6 h. Then the reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered through a Celite pad. The filtrate is neutralized with saturated $NaHCO_3$ solution. The organic layer was then extracted with ethyl acetate. The combined organic layer was finally washed with brine solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was then subjected to silica gel column chromatography using hexane and ethyl acetate as eluent.

Characterization of 1,3-diphenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol derivatives.

1,3-diphenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3a): Following the general procedure, reaction of 1-benzylidene-2-phenylhydrazine **1a** (0.25 mmol, 49 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3a** (59.5 mg) as an off-white solid in 63% yield; m.p. 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.83-7.77 (m, 5H), 7.68 (d, *J* = 9.2 Hz 1H), 7.58-7.54 (m, 5H), 7.43 (t, *J* = 8 Hz, 2H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.19 (d, *J* = 2.8 Hz, 1H), 4.74 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 151.3, 151.0, 146.5, 139.9, 137.4, 134.6, 130.6 (2C), 129.5 (2C), 128.8, 128.4 (2C), 127.2, 124.2, 123.7 (2C), 117.7, 115.2, 114.8, 112.8, 111.8, 109.9, 109.6 ppm; FT-IR (KBr): ν_{max} = 3419, 1592, 1496, 1350, 1198, 1134 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{17}N_2O_2$ $[M+H]^+$ 377.1285 found 377.1295.

4-(9-hydroxy-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-1-yl)benzaldehyde (3b): Following the general procedure, reaction of 4-((2-phenylhydrazono)methyl)benzaldehyde **1b** (0.25 mmol, 56 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3b** (56.6 mg) as a white solid in 56% yield; m.p. 240-242 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 10.23 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 2H), 8.11 (s, 1H), 8.05 (d, *J* = 8 Hz, 2H), 7.98 (d, *J* = 9 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 9.5 Hz, 1H), 7.67 (t, *J* = 8 Hz, 2H), 7.54-7.49 (m, 2H), 7.01 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.57 (d, *J* = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 191.9, 153.3, 152.9, 150.6, 145.0, 140.3, 139.9, 137.7, 136.9, 130.8 (2C), 129.6, 129.5, 127.4, 123.9, 123.5 (2C), 116.9, 115.4, 115.3, 114.8, 113.0, 111.8, 110.2, 109.4, 109.3 ppm; FT-IR (KBr): ν_{max} = 3407, 2859, 1689, 1595, 1499, 1345, 1169 1139 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{17}N_2O_3$ $[M+H]^+$ 405.1234 found 405.1237.

3-phenyl-1-(4-(trifluoromethyl)phenyl)-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3c): Following the general procedure, reaction of 1-phenyl-2-(4-(trifluoromethyl)benzylidene)hydrazine **1c** (0.25 mmol, 66 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3c** (56.7 mg) in 51% yield as weightless white compound; m.p. 261-263 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.24 (s, 1H), 8.07 (d, *J* = 8Hz, 2H), 8.00 (d, *J* = 9 Hz, 3H), 7.91 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.84 (d, *J* = 9.5 Hz, 1H), 7.70 (t, *J* = 8Hz, 2H), 7.54-7.50 (m, 2H), 7.03 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.51 (d, *J* = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 153.3, 153.1, 150.6, 144.7, 139.8, 138.6, 137.7, 130.8 (2C), 130.3, 129.6 (2C), 127.4, 125.3 (q)(-CF_3), 123.9 123.5, 116.9 (2C), 115.4, 115.3, 114.8, 113.0, 111.7, 110.2, 109.5, 109.4 ppm; FT-IR (KBr): ν_{max} = 3414, 1616, 1499, 1406, 1329, 1171, 1110 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{16}F_3N_2O_2$ $[M+H]^+$ 445.1158 found 445.1165.

Methyl-4-(9-hydroxy-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-1-yl)benzoate (3d): Following the general procedure, reaction of methyl 4-((2-phenylhydrazono)methyl)benzoate **1d** (0.25 mmol, 63.5 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3d** (58.6 mg) as an off-white solid in 54% yield; m.p. 230-232 °C; ^{1}H NMR (400 MHz, Acetone-d_6, TMS): δ = 8.38 (s, 1H), 8.15 (d, *J* = 8 Hz, 2H), 7.87-7.83 (m, 3H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.54 (t, *J* = 8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.88 (dd, *J* = 9, 2.6 Hz, 1H), 6.42 (d, *J* = 2.8 Hz, 1H), 3.85 (s, 3H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 167.3, 154.2, 154.1, 151.4, 146.1, 140.8, 140.1, 138.6, 131.4, 131.2 (2C), 130.5 (2C), 130.3 (2C), 128.3, 124.4 (2C), 117.8, 116.5, 116.3, 115.8, 113.9, 112.6, 111.1, 110.3, 52.6 ppm; FT-IR (KBr): ν_{max} = 3408, 1701, 1595, 1496, 1286, 1192, 1124 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{19}N_2O_4$ $[M+H]^+$ 435.1339 found 435.1351.

1-(4-nitrophenyl)-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3e): Following the general procedure, reaction of 1-(4-nitrobenzylidene)-2-phenylhydrazine **1e** (0.25 mmol, 60.3 mg) with *p*-BQ **2a** (0.75 mmol, 81mg) yielded the desired product **3e** (50.6 mg) in 48% yield as a yellow solid; m.p. 270-272 °C; ^{1}H NMR (400 MHz, Acetone-d_6, TMS): δ = 8.40 (d, *J* = 8.4 Hz, 2H), 8.37 (s, 1H), 7.98 (d, *J*= 8.8 Hz, 2H), 7.89-7.86 (m, 1H), 7.79-7.72 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.43-7.38 (m, 2H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 154.3, 154.1, 151.5, 149.1, 145.0, 142.0, 140.6, 138.7, 132.0 (2C), 130.6 (2C), 128.5, 124.7, 124.6 (2C), 124.5 (2C), 117.7, 116.5, 115.6, 114.2, 112.8, 111.2, 110.0 ppm; FT-IR (KBr): ν_{max} = 3418, 1627, 1509, 1454, 1342, 1175 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{16}N_3O_4$ $[M+H]^+$ 422.1135 found 422.1145.

4-(9-hydroxy-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-1-yl)benzonitrile (3f): Following the general procedure, reaction of 4-((2-phenylhydrazono)methyl)benzonitrile **1f** (0.25 mmol, 55.3 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3f** (46.2 mg) in 46% yield as an white solid; m.p. 306-308 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.52 (s, 1H), 7.96-7.90 (m, 4H), 7.87 (d, *J* = 8 Hz, 1H), 7.79-7.76 (m, 2H), 7.73 (d, *J* = 8 Hz, 1H), 7.56 (t, J = 8 Hz, 2H), 7.41 (d, *J* = 8 Hz, 2H), 6.90 (dd, *J* = 8, 4 Hz, 1H), 6.39 (d, *J* = 2.4, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 154.2, 154.1, 151.4, 145.4, 140.6, 140.1, 138.6, 133.2 (2C), 131.8 (2C), 130.6 (2C), 128.5, 124.7 (2C), 124.5, 119.5, 117.7, 116.4, 115.6, 114.1, 113.3, 112.7, 111.2, 110.1 ppm; FT-IR (KBr): ν_{max} = 3396, 2234, 1591, 1501, 1348, 1188, 1132 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{16}N_3O_2$ $[M+H]^+$ 402.1237 found 402.1252.

1-(4-methoxyphenyl)-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3g): Following the general procedure, reaction of 1-(4-methoxybenzylidene)-2-phenylhydrazine **1g** (0.25 mmol, 56.5 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3g** (47.5 mg) as a white solid in 45% yield; m.p. 218-220 °C; ^{1}H NMR (400 MHz, Acetone-d_6, TMS): δ = 8.46 (s, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.73 (dd, *J* = 8.2, 1 Hz, 2H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.56 (dd, *J* = 6.8, 2 Hz, 2H), 7.50 (t, *J* = 8 Hz, 2H), 7.33-7.30 (m, 2H), 7.04 (dd, *J* =6.6, 1.8 Hz, 2H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.41 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): δ = 161.3, 154.0, 153.9, 151.4, 147.1, 141.0, 138.2, 132.3 (2C), 130.4 (2C), 127.9, 127.6, 125.0 (2C), 124.1, 118.4, 116.2 (2C), 116.1, 114.7, 113.6, 112.3, 110.8, 110.6, 55.8 ppm; FT-IR (KBr): ν_{max} = 3419, 1615, 1500, 1350, 1233,1183, 1132 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{19}N_2O_3$ $[M+H]^+$ 407.1390 found 407.1399.

3-phenyl-1-(*p*-tolyl)-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3h): Following the general procedure, reaction of 1-(4-methylbenzylidene)-2-phenylhydrazine **1h** (0.25 mmol, 52.6 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3h** (41mg) in 42% yield as an off-white solid; m.p. 204-

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206 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.06 (s, 1H), 7.95 (d, *J* = 9.5 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 9 Hz, 1H), 7.68 (d, *J* = 8 Hz, 2H), 7.64 (t, *J* = 7.7 Hz, 2H), 7.49-7.46 (m, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 6.99 (dd, *J* = 8.7, 2.2, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 2.51 (s, 3H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 154.8, 154.7, 154.6, 152.4, 148.2, 141.9, 140.4, 139.2, 131.9, 131.3 (2C), 130.7 (2C), 128.8 (2C), 125.0, 119.3, 117.0 (2C), 116.9, 114.4, 113.2, 111.8, 111.7, 111.6, 22.4 ppm; FT-IR (KBr): ν_{max} = 3419, 1594, 1500, 1347, 1193, 1142 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{19}N_2O_2$ $[M+H]^+$ 391.1441 found 391.1455.

1-(4-fluorophenyl)-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3i): Following the general procedure, reaction of 1-(4-fluorobenzylidene)-2-phenylhydrazine **1i** (0.25 mmol, 53.5 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3i** (52.3 mg) in 53% as an weightless white solid; m.p. 262-264 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.32 (s, 1H), 7.98 (d, *J* = 9 Hz, 1H), 7.89 (dd, *J* = 8.5, 1 Hz, 2H), 7.86-7.81 (m, 3H), 7.66 (t, *J* = 8Hz, 2H), 7.52-7.48 (m, 2H), 7.41 (t, *J* = 9 Hz, 2H), 7.01 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.50 (d, *J* = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 163.4 (C-F, *J* = 244 Hz), 153.2, 153.1, 150.6, 145.3, 140.0, 137.4, 132.2, 132.1, 131.0, 130.9 (2C), 129.6, 127.2, 124.0 (2C), 123.3, 117.3, 115.3, 115.2, 115.0, 112.8, 111.6, 110.1, 109.3 ppm; FT-IR (KBr): ν_{max} = 3409, 1594, 1501, 1345, 1177, 1142 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{16}FN_2O_2$ $[M+H]^+$ 395. 1190 found 395.1198.

1-(4-chlorophenyl)-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3j): Following the general procedure, the reaction of 1-(4-chlorobenzylidene)-2-phenylhydrazine **1j** (0.25 mmol, 57.5mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3j** (45.1 mg) in 44% yield as an ivory white solid; m.p. 237-239 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.34 (s, 1H), 7.99 (d, *J* = 9Hz, 1H), 7.90 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.86-7.82 (m, 3H), 7.69-7.65 (m, 4H), 7.53-7.49 (m, 2H), 7.02 (dd, *J* = 9, 2.5 Hz, 1H), 6.61 (d, *J* = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 153.2, 153.1, 150.6, 145.0, 139.9, 137.6, 134.5, 133.4, 131.7 (2C), 129.6 (2C), 128.5 (2C), 127.3, 124.0, 123.4 (2C), 117.0, 115.4, 114.9, 112.9, 111.7, 110.1, 109.4 ppm; FT-IR (KBr): ν_{max} = 3410, 1592, 1497, 1344, 1186, 1134 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{16}ClN_2O_2$ $[M+H]^+$ 411.0895 found 411.0906.

1-(4-bromophenyl)-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3k): Following the general procedure, reaction of 1-(4-bromobenzylidene)-2-phenylhydrazine **1k** (0.25 mmol, 68.5 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) yielded the desired product **3k** (54.5 mg) as an ivory white solid in 48% yield; m.p. 256-258 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.35 (s, 1H), 7.97 (d, *J* = 9 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.83-7.82 (m, 3H), 7.81-7.77 (m, 2H), 7.66 (t, *J* = 8 Hz, 2H), 7.53-7.48 (m, 2H), 7.02 (dd, *J* = 9, 2.5 Hz, 1H), 6.62 (d, J = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 153.2, 153.1, 150.6, 145.0, 139.8, 137.6, 133.8, 132.0 (2C), 131.5 (2C), 129.6 (2C), 127.3, 124.0, 123.4 (2C), 122.7, 117.0, 115.4, 114.9, 112.9, 111.7, 110.2, 109.5 ppm; FT-IR (KBr): ν_{max} = 3416, 1591, 1496, 1343, 1187, 1134 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{16}{}^{81}BrN_2O_2$ $[M+H]^+$ 457.0375 found 457.0384.

1-(naphthalen-1-yl)-3-phenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3l): Following the general procedure, the reaction of 1-(naphthalen-2-ylmethylene)-2-phenylhydrazine **1l** (0.25mmol, 61.5 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3l** (38.4 mg) as light pink colored solid in 36% yield; m.p. 201-203 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.37 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8 Hz, 1H), 8.04-7.96 (m, 4H), 7.93 (d, *J* = 8 Hz, 2H), 7.84 (d, *J* = 9 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.64-7.60 (m, 2H), 7.52-7.48 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.67 (s, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 155.1, 154.7, 152.4, 148.0, 141.9, 139.5, 135.4, 135.0, 133.8, 131.4 (2C), 131.1, 130.1 (2C), 129.8, 129.6, 129.0, 128.4, 128.3, 126.0 (2C), 125.2, 119.0, 117.1, 117.0, 114.6, 113.3, 111.9, 111.5 ppm; FT-IR (KBr): ν_{max} = 3330, 1594, 1502, 1352, 1172, 1134 cm^{-1}; HRMS (ESI) calcd. for $C_{29}H_{19}N_2O_2$ $[M+H]^+$ 427.1441 found 427.1461.

3-(4-bromophenyl)-1-phenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3m): Following the general procedure, reaction of 1-benzylidene-2-(4-bromophenyl)hydrazine **1m** (0.25 mmol, 68.5 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3m** (55.7 mg) as an off-white solid in 49% yield; m.p. 206-208 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.13 (s, 1H), 7.96 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.86-7.84 (m, 2H), 7.81-7.77 (m, 5H), 7.63-7.62 (m, 3H), 7.48 (d, *J* = 9 Hz, 1H), 7.00 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.44 (d, *J* = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 153.1, 150.6, 146.8, 139.3, 137.2, 134.4, 132.6 (2C), 130.2 (2C), 129.0, 128.3 (2C), 124.9 (2C), 124.0, 119.7, 117.6, 115.4, 115.3, 112.9, 111.5, 109.9, 109.7, 109.6 ppm; FT-IR (KBr): ν_{max} = 3384, 1585, 1492, 1344, 1179 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{16}BrN_2O_2$ $[M+H]^+$ 455.0390 found 455.0404.

3-(4-bromophenyl)-1-(4-fluorophenyl)-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3n): Following the general procedure, reaction of 1-(4-bromophenyl)-2-(4-fluorobenzylidene)hydrazine **1n** (0.25 mmol, 73.3 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3n** (61.4 mg) as an off-white solid in 52% yield; m.p. 241-243 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.22 (s, 1H), 7.98 (d, *J* = 9.5 Hz, 1H), 7.87-7.84 (m, 3H), 7.82-7.80 (m, 4H), 7.51 (d, *J* = 9 Hz, 1H), 7.40 (t, *J* = 8.7 Hz, 2H), 7.01 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.48 (d, *J* = 2.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 163.4 (C-F, *J* = 245 Hz), 153.2, 153.1, 153.0, 150.6, 145.8, 139.3, 137.3, 132.6, 132.2 (2C), 132.1, 124.9, 123.9 (2C), 119.8, 117.5, 155.5, 115.4, 115.2, 115.1, 113.0, 110.0, 109.3, 109.2 ppm; FT-IR (KBr): ν_{max} = 3416, 1619, 1493, 1341, 1190, 1135 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{15}BrFN_2O_2$ $[M+H]^+$ 473.0295 found 473.0308.

3-(4-bromophenyl)-1-(4-chlorophenyl)-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3o): Following the general procedure, the reaction of 1-(4-bromophenyl)-2-(4-chlorobenzylidene)hydrazine **1o** (0.25 mmol, 77.4 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) afforded the desired product **3o** (57.8 mg) in 47% yield as an pale yellow solid; m.p. 254-256 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.23 (s, 1H), 8.01 (dd, *J* = 9, 2 Hz, 1H), 7.89-7.87 (m, 2H), 7.85-7.82 (m, 5H), 7.68 (dd, *J* = 8.5, 2 Hz, 2H), 7.53 (dd, *J* = 9, 1.5 Hz, 1H), 7.02 (dd, *J* = 9, 2 Hz, 1H), 6.60 (t, *J* = 2, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 155.0, 152.4, 147.3, 141.0, 139.2, 136.4, 135.0, 134.4 (2C), 133.5 (2C), 130.3 (2C), 126.8 (2C), 125.7, 121.7, 119.1, 117.2, 116.8, 114.9, 113.5, 111.8, 111.2, 111.1 ppm; FT-IR (KBr): ν_{max}

= 3424, 1631, 1490, 1264, 1169,1135cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{15}BrClN_2O_2$ [M+H]$^+$ 489.0000 found 489.0009.

1,3-bis(4-bromophenyl)-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3p): Following the general procedure, reaction of 1-(4-bromobenzylidene)-2-(4-bromophenyl)hydrazine **1p** (0.25 mmol, 88.5 mg) with *p*-BQ **2a** (0.75 mmol, 81 mg) yielded the desired product **3p** (68.5 mg) in 50% yield as an off-white solid; m.p. 260-262 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.47 (s, 1H), 7.90-7.86 (m, 1H), 7.76-7.69 (m, 7H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.42 (d, *J* = 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 154.2, 154.1, 151.5, 146.4, 140.1, 138.3, 134.5, 133.5 (2C), 132.9 (2C), 132.4, (2C), 126.0 (2C), 124.7, 123.8, 120.8, 118.1, 116.4, 115.9, 114.1, 112.5, 110.9, 110.3 ppm; FT-IR (KBr): ν_{max} = 3418, 1627, 1509, 1454, 1342, 1175 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{15}Br_2N_2O_2$ [M+H]$^+$ 532.9495 found 532.9493.

5,8-dimethyl-1,3-diphenyl-3*H*-benzofuro[3,2-*e*]indazol-9-ol (3q): Following the general procedure, reaction of 1-benzylidene-2-phenylhydrazine **1a** (0.25 mmol, 49 mg) with 2-methylcyclohexa-2,5-diene-1,4-dione **2b** (0.75 mmol, 92 mg) afforded the desired product **3q** (69.7 mg) in 69% yield as a light brown solid; m.p. 207-209 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 7.93 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 6 Hz, 2H), 7.75 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.59-7.56 (m, 3H), 7.46-7.44 (m, 2H), 6.59 (d, *J* = 2 Hz, 1H), 2.69 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 153.7, 152.7, 152.4, 148.0, 142.1, 139.5, 136.5, 131.7, 131.2 (2C), 130.5, 130.0 (2C), 128.6, 127.2, 127.1 (2C), 125.2, 125.1, 123.7, 117.3, 116.2, 114.2, 110.9, 110.8, 18.1, 17.2 ppm; FT-IR (KBr): ν_{max} = 3414, 1594, 1492, 1459, 1369, 1185, 1130 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{21}N_2O_2$ [M+H]$^+$ 405.1598 found 405.1613.

5,8-dimethyl-3-phenyl-1-(4-(trifluoromethyl)phenyl)-3H-benzofuro[3,2-e]indazol-9-ol (3r): Following the general procedure, reaction of 1-phenyl-2-(4-(trifluoromethyl)benzylidene)hydrazine **1c** (0.25 mmol, 66.1 mg) with 2-methylcyclohexa-2,5-diene-1,4-dione **2b** (0.75 mmol, 92 mg) afforded the desired product **3r** (66.1 mg) as an very light pink colored solid in 56% yield; m.p. 234-236 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.03 (d, *J* = 8 Hz, 2H), 7.96-7.93 (m, 3H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.75 (s, 1H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.46 (s, 1H), 6.67 (s, 1H), 2.69 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 152.1, 151.1, 150.6, 144.6, 140.0, 138.6, 138.0, 130.4 (2C), 130.1, 129.8, 129.5 (2C), 127.1, 125.7, 125.5, 125.3 (q) (-CF_3), 123.7, 123.4 (2C), 121.7, 115.0, 114.1, 112.6, 109.2, 109.0, 16.2, 15.4 ppm; FT-IR (KBr): ν_{max} = 3419, 1596, 1501, 1468, 1329, 1190, 1156 cm^{-1}; HRMS (ESI) calcd. for $C_{28}H_{20}F_3N_2O_2$ [M+H]$^+$ 473.1471 found 473.1485.

1-(4-chlorophenyl)-5,8-dimethyl-3-phenyl-3H-benzofuro[3,2-e]indazol-9-ol (3s): Following the general procedure, reaction of 1-(4-chlorobenzylidene)-2-phenylhydrazine **1j** (0.25 mmol, 57.65 mg) with 2-methylcyclohexa-2,5-diene-1,4-dione **2b** (0.75 mmol, 92 mg) afforded the desired product **3s** (52.7 mg) as an white solid in 48% yield; m.p. 240-242 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 8.08 (s, 1H), 7.88-7.80 (m, 4H), 7.76-7.72 (m, 1H), 7.64-7.61 (m, 4H), 7.49-7.44 (m, 2H), 6.74 (s, 1H), 2.68 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 152.0, 151.1, 150.6, 144.8, 140.1, 137.9, 134.3 (2C), 133.4 (2C), 131.4 (2C), 129.5, 128.4, 127.0, 125.3 (2C), 123.5, 123.3, 121.8, 115.1, 114.2, 112.6, 109.1, 108.8, 16.3, 15.4 ppm; FT-IR (KBr): ν_{max} = 3398, 1598, 1499, 1488, 1346, 1182, 1133 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{20}ClN_2O_2$ [M+H]$^+$ 439.1208 found 439.1221.

6-chloro-1,3-diphenyl-1*H*-indazol-5-ol (4b): Following the general procedure, reaction of 1-benzylidene-2-phenylhydrazine **1a** (0.25 mmol, 49 mg) with 2-chlorocyclohexa-2,5-diene-1,4-dione **2c** (0.75 mmol, 106.9 mg) afforded the desired product **4b** (29 mg) in 36% yield as a light pink colored solid; m.p. 138-140 °C; FT-IR (KBr): ν_{max}= 3394, 2962, 1594, 1498, 1249, 1116 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.91-7.90 (m, 2H), 7.73 (s, 1H), 7.67 (dd, *J* = 8.5, 1 Hz, 2H), 7.59 (s, 1H), 7.50-7.43 (m, 4H), 7.37-7.34 (m, 1H), 7.33-7.29 (m, 1H), 5.45 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.7, 145.5, 139.9, 135.7, 132.8, 129.7 (2C), 129.0, 128.5 (2C), 127.6, 127.0 (2C), 122.9, 122.8 (2C), 122.8, 110.8, 105.8 ppm; HRMS (ESI) calcd. for $C_{19}H_{14}ClN_2O$ [M+H]$^+$ 321.0789 found 321.0799.

4,6-dimethyl-1,3-diphenyl-1*H*-indazol-5-ol (4d): Following the general procedure, reaction of 1-benzylidene-2-phenylhydrazine **1a** (0.25 mmol, 49 mg) with 2,6-dimethylcyclohexa-2,5-diene-1,4-dione **2e** (0.75 mmol, 102.2 mg) afforded the desired product **4d** (48.7 mg) as an off-white solid in 62% yield; m.p. 160-162 °C; ^{1}H NMR (500 MHz, Acetone-d_6, TMS): δ = 7.83 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 6.5 Hz, 2H), 7.60-7.57 (m, 3H), 7.54-7.46 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.25 (s, 1H), 2.44 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (125 MHz, Acetone-d_6): δ = 148.4, 146.8, 140.6, 135.3, 135.2, 130.2 (2C), 129.3 (2C), 128.5, 127.9, 127.8 (2C), 125.9, 122.4, 122.2 (2C), 114.7, 108.5, 17.4, 12.4 ppm; FT-IR (KBr): ν_{max} = 3412, 1589, 1492, 1281, 1179, 1117 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{19}N_2O$ [M+H]$^+$ 315.1492 found 315.1497.

8-chloro-1,3-diphenyl-3H-benzofuro[3,2-e]indazol-9-ol (3t): Following the general procedure, reaction of 1,3-diphenyl-1*H*-indazol-5-ol **4a** (0.25 mmol, 71.3 mg) and 2-chloro *p*-BQ **2c** (0.50 mmol, 71.3 mg) in the presence of TFA (14 equiv., 3.5 mmol) afforded the desired product **3t** (29.8 mg) as an white solid in 29% yield; m.p. 233-235 °C; ^{1}H NMR (500 MHz, $CDCl_3$ TMS): δ = 7.87 (d, *J* = 9 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 6.5 Hz, 2H), 7.70 (d, *J* = 9 Hz, 1H), 7.67-7.59 (m, 6H), 7.45 (t, *J* = 7.2 Hz, 1H), 6.45 (s, 1H), 5.31 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4, 150.5, 146.9, 146.5, 139.9, 137.5, 134.2, 130.4 (2C), 129.5 (2C), 129.1, 128.5 (2C), 127.3, 123.7 (2C), 123.6, 118.9, 117.7, 114.9, 112.6, 111.4, 110.4, 110.1 ppm; FT-IR (KBr): ν_{max} = 3409, 1593, 1502, 1461, 1328, 1171, 1130 cm^{-1}; HRMS (ESI) calcd. for $C_{25}H_{16}ClN_2O_2$ [M+H]$^+$ 411.0895 found 411.0928.

Conflicts of interest

There are no conflicts to declare.

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Trifluoroacetic acid mediated [3+2] annulation reaction between the 5-hydroxy-1*H*-indazoles - generated *in situ* - and *p*-benzoquinones has been reported.