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Regioselective Brønsted Acid Catalyzed Annulation of Cyclopropane Aldehydes with *N*'-Aryl Anthranil Hydrazides: Domino Construction of Tetrahydropyrrolo[1,2-*a*]quinazolin-5(1*H*)ones

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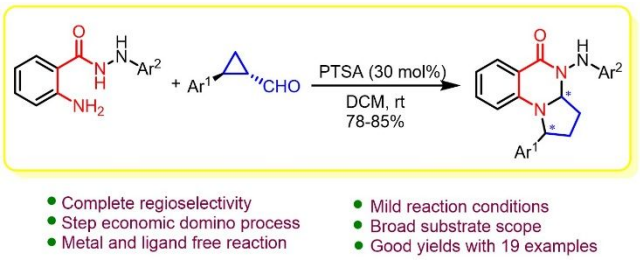
Supporting Information

ABSTRACT: *A highly regioselective synthesis of tetrahydropyrrolo[1,2-a]quinazolin-5(1H)one derivatives was achieved by reacting cyclopropane aldehydes with N'-aryl anthranil hydrazides in the presence of PTSA (p-toluene sulphonic acid). The transformation involves domino imine formation and intramolecular cyclization to form 2-arylcyclopropyl-2,3-dihydroquinolin-4(1H)-one, followed by nucleophilic ring opening of the cyclopropyl ring to form desired tetrahydropyrrolo[1,2-a]quinazolin-5(1H)one in good to excellent yield with complete regioselectivity. This protocol tolerates a great variety of functional groups and thus provides a simple and step efficient method for pyrroloquinazolinones synthesis.*



INTRODUCTION

Over the past few decades, nitrogen-containing heterocycles are among the most remarkable structural motif of pharmaceuticals that have made a significant contribution to drug discovery.[1] These covers around 59% of the USFDA approved drugs.[2] Considerable interest has been paid towards their advancement due to the associated diverse biological and pharmacological activities.[3] Pyrroloquinazolinones and its derivatives have been found as an important core of a variety of natural products and biologically important molecules in the past few years.[4] They often possess a wide array of biological activities like anti-tumor, antihypertensive, and anti-inflammatory activity. In addition, some of them are used as thrombin receptor antagonists also (**Figure 1**).[5] Consequently, synthesis of these interesting nitrogen heterocycles has become a significant segment of synthetic organic and pharmaceutical chemistry.

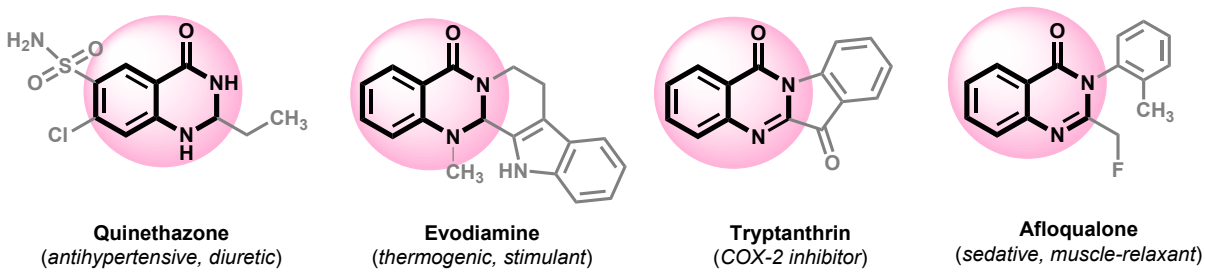


Figure 1. Pharmaceutical molecules having 2,3-dihydroquinazolinone and pyrroloquinazolinones framework.

Over the time, donor acceptor cyclopropanes (DACs) have emerged as an inimitable three carbon building block in the arena of organic synthesis for the synthesis of a variety of carbo- and heterocycles.[6] Owing to their high ring strain and vicinal arrangement of electron releasing and electron accepting groups, easy

cleavage of C-C bond is facilitated. The engendered 1,3-zwitterionic species[7] undergoes various transformation such as cycloaddition reactions, ring opening, rearrangement and ring expansion reactions towards the formation of diverse high-value open-chain and cyclic compounds.[8]

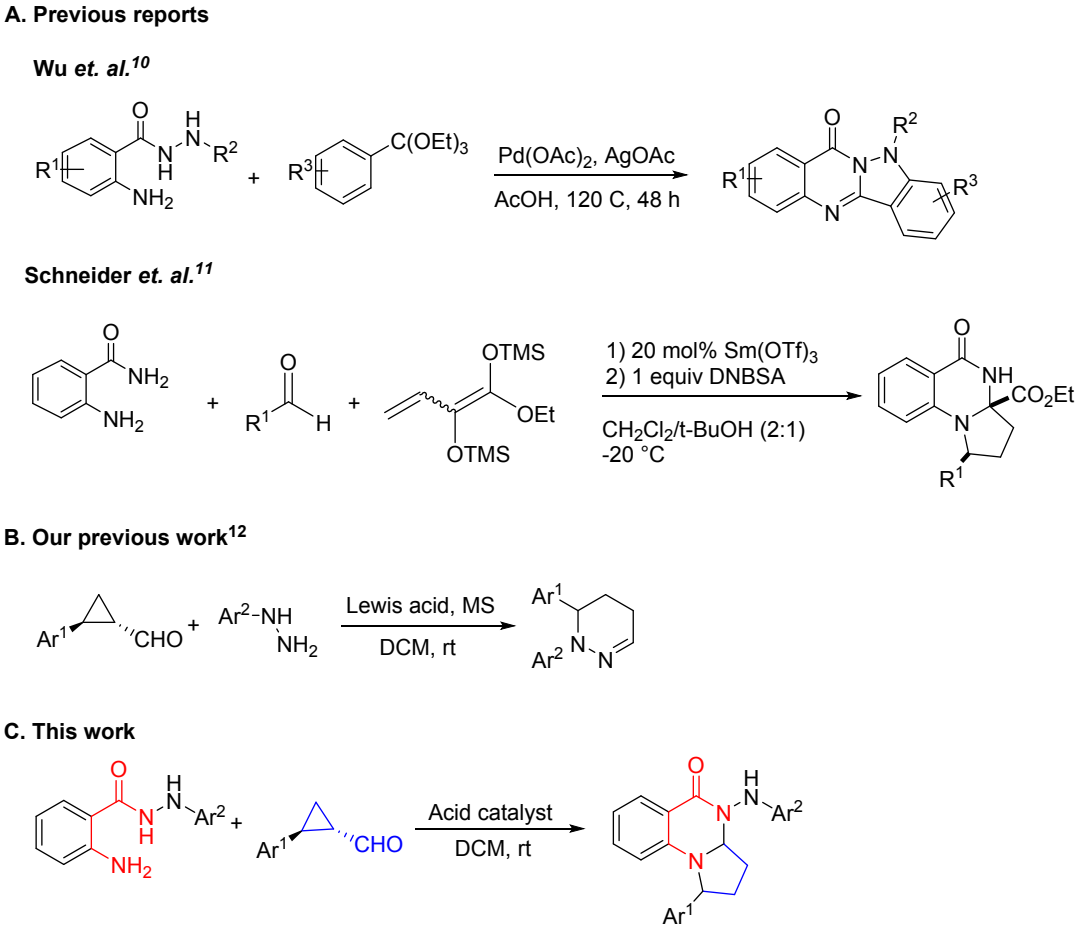
The classical approach for the synthesis of desired quinazolinones is based on the direct acid catalyzed condensation of 2-nitrobenzamides and 2-aminobenzamide with carbonyl compounds.[9] Moreover, in 2014, Wu *et al*. documented the cascade Palladium-catalyzed/C-H activation reaction of 2-amino-*N*′-arylbenzohydrazides with triethyl orthobenzoates for the formation of indazolo[3,2-*b*]quinazolinones.[10] Later, in 2015, Schneider *et. al*. introduced the one pot [3+2] cycloheteroannulation of bis-silyl dienediolate with 2-aminobenzamide-derived imines to furnish highly substituted pyrrolo[1,2-*a*]quinazolinones in good yields (**Scheme 1A**).[11] Recently, our group has reported the annulation of cyclopropane aldehydes (CAs) with various aryl hydrazines towards the formation of tetrahydropyridazine derivatives under Lewis acid catalysis (**Scheme 1B**).[12] Envisioned by our previous work on cyclopropanes[13] and synthetic utility of donor acceptor cyclopropanes (DACs) and hydrazides we thought to utilize cyclopropane aldehydes and *N'*-aryl benzohydrazides as building block for the synthesis of pyrroloquinazoline derivatives using facile reaction conditions (**Scheme 1C**).

In pursuit of discovering a simple and facile route for the synthesis of designed nitrogen heterocycles, the use of domino reactions can particularly be an attractive process. Domino reactions involve several bond-forming reactions in a one-pot operation and allow the highly efficient synthesis of complex molecules starting from simple substrates.[14] They feature operational simplicity, improvement of efficiency, avoidance of toxic reagents and the reduction of waste.[15] The quality and importance

of a domino reaction can be associated with the number of bonds generated and complexity increased in the process.[16] Hence, performing the reaction of CAs with *N'*-aryl anthranil hydrazides in domino fashion can be a useful platform for the simple and efficient construction of designed pyrroloquinazolinone derivatives in step economic manner.

To the best of our knowledge, no previous report for the synthesis of pyrroloquinazolinones through annulation of CAs with hydrazides have been reported so far. Therefore, keeping these reactivities in mind, herein, we report a Bronsted acid catalyzed regioselective annulation of CAs and *N'*-aryl anthranil hydrazides to furnish tetrahydropyrrolo[1,2-*a*]quinazolin-5(1*H*)ones along with a broad substrate scope.

Scheme 1. Reactivity of benzohydrazides/hydrazines with different aldehydes



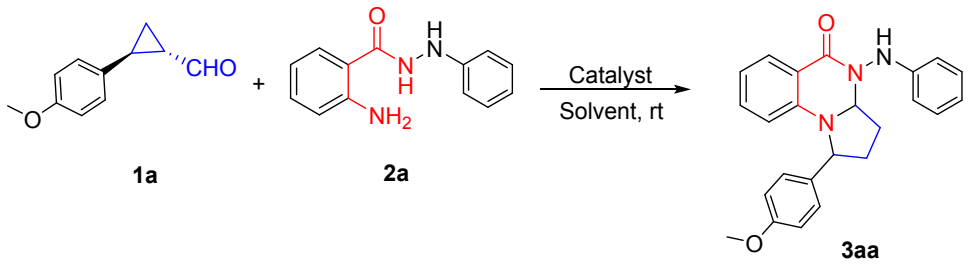
RESULT AND DISCUSSION

To evaluate our hypothesis, we started the investigation with cyclopropane aldehyde **1a** and anthranil hydrazide **2a** as model substrate, and the results are summarized in **Table 1**. Knowledge gained from the success of our recent studies on the reactivity of CAs with *N*-benzyl amines and aryl hydrazine derivatives[12,17] drove us to start this optimization with different Brønsted acids at room temperature. At first, we started with the reaction of **1a** and **2a** in the presence of 30 mol% of acetic acid in ethanol; the desired cycloadduct **3aa** was obtained in 10% yield (**Table 1**, **entry 1**). Different Brønsted acids were then examined for the following transformation in dichloromethane. To our delight, in the presence of 30 mol% of PTSA (*p*-toluene sulphonic acid) reaction got completed in 10 h, affording the final cycloadduct **3aa** with 85% yield (**Table 1**, **entry 2**). When we proceeded to use TFA (trifluoroacetic acid) and triflic acid, the reaction got completed in 8 h and 4 h, respectively. In both cases, the reaction yield got decreased to 70% and 60%, respectively, which may be due to the decomposition of the cyclopropane aldehyde during the reaction (**Table 1**, **entry 3-4**). Further, on moving to CSA (camphor sulphonic acid), reaction yield got increased to 80%. Whereas on using 2,4-DNBSA (2,4-dinitrobenzene sulphonic acid) for the transformation, meagre amount of compound **3aa** was obtained with a yield of 10% (**Table 1**, **entry 5-6**). Conducting the reaction with a catalyst loading of 20% decreased the yield to 75% while increasing the catalyst loading from 50 to 100 mol%, increased the yield of the final product **3aa** to 90% within the same duration of time (10 h) (**Table 1**, **entry 7-9**).

For further optimization, PTSA was chosen as the most promising catalyst for the cycloaddition of **1a** and **2a,** and a variety of solvents were then screened. In the presence of alcoholic solvents like ethanol and methanol, yield got decreased due to

the incomplete conversion of intermediate bicyclic compound **4** to the final cycloadduct **3aa** (**Table 1**, **entry 10-11**). The incomplete conversion was also noticed in the case of ACN, THF, DCE, and toluene, leading to the decreased yield of the final compound **3aa** (**Table 1**, **entry 12-15**). No formation of the final cycloadduct was observed when the **1a** and **2a** were made to react in the absence of catalyst (**Table 1**, **entry 16**). Thereupon, on the basis of the above optimization results, we choose 30 mol% PTSA in DCM solvent at room temperature as an optimal reaction condition for the annulation of **1a** with **2a**.

Table 1. Optimization of reaction conditions[a]



S. No.	Catalyst[b]	Loading (mol%)	Solvent[c]	Time (h)	*dr* ratio	Yield (%)[d]
1	AcOH	30	EtOH	12	20:80	10
2	PTSA	30	DCM	10	34:66	85
3	TFA	30	DCM	08	33:67	70
4	Triflic acid	30	DCM	04	30:70	60
5	CSA	30	DCM	10	33:67	80
6	2,4-DNBSA	30	DCM	14	20:80	10
7	PTSA	20	DCM	10	32:68	75
8	PTSA	50	DCM	10	34:66	87
9	PTSA	1 equiv	DCM	10	35:65	90
10	PTSA	30	EtOH	12	25:75	45
11	PTSA	30	MeOH	12	25:75	45
12	PTSA	30	ACN	12	25:75	53
13	PTSA	30	THF	12	25:75	50
14	PTSA	30	DCE	12	30:70	60
15	PTSA	30	Toluene	12	25:75	30
16	No catalyst	-	DCM	24	-	0

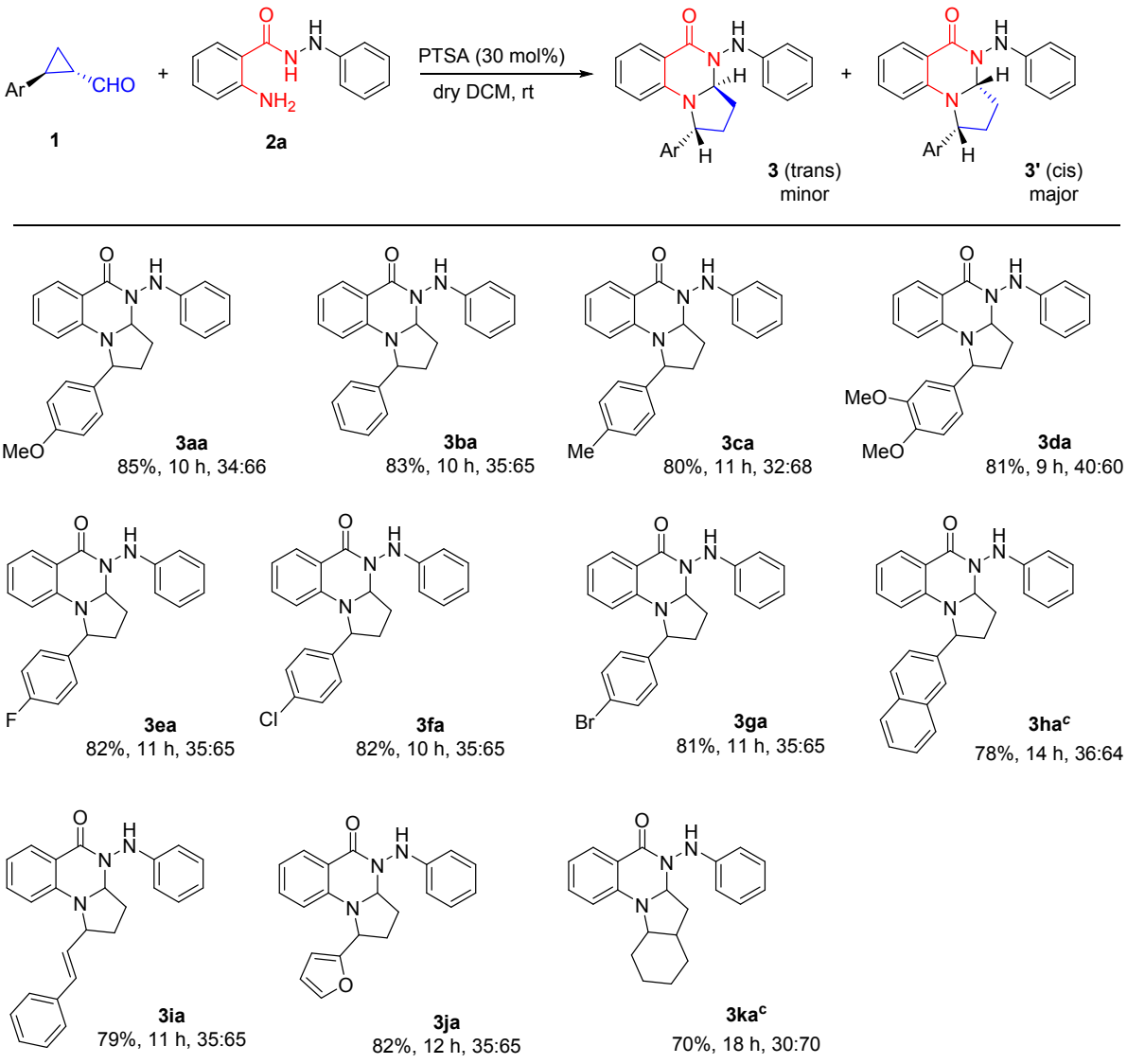
[a]Reactions were carried out with 1.2 equiv of **1a** and 1 equiv of **2a**. [b]AcOH = acetic acid, TFA = trifluoro acetic acid, PTSA = *p*-toluene sulphonic acid, CSA = camphor

sulphonic acid, 2,4-DNBSA = 2,4-dinitro benzenesulphonic acid. [c]DCM = dichloromethane, EtOH = ethanol, MeOH = methanol, ACN = acetonitrile, THF = tetrahydrofuran, DCE = dichloroethane. [d]Isolated yield.

Using the optimized reaction conditions, we further checked the generality of the method with a variety of aryl substituted CAs **1a-k** having different steric and electronic properties with hydrazide **2a** (**Table 2**). Both electron-rich and electron-deficient aromatic groups were found similarly viable for the following transformation, affording the desired product in good to excellent yields (70-85%). Substrates bearing unsubstituted phenyl **1b** and 4-methyl substituents **1c** took a comparatively longer time to complete the annulation as compared to the substrate having 3,4-dimethoxy groups on the phenyl ring **1d** with almost similar yields. Perhaps this may be due to the high electron donating capability of the two methoxy groups, which makes the cyclopropane aldehyde **1d** more active as compared to other carbaldehydes (**1a-1c**). On the contrary, substrates with fluoro **1e**, chloro **1f**, and bromo **1g** substituent at the 4-position of the aryl group displayed a similar reactivity for the ensuing annulation by furnishing the products in good yields. Other aromatic analogs like 2-naphthyl **1h** and cinnamyl **1i** groups with extended π-system were also checked for the reaction. The reaction with 2-naphthyl cyclopropane aldehyde **1h** was done at reflux conditions to afford the desired adduct with slightly lesser yield (78%). In addition, 2-furyl substituted CA **1j** was also examined, it resulted in the construction of final adduct in a longer time but with comparatively good yield. Starting with the fused cyclopropane aldehyde **1k**, octahydroindolo[1,2-*a*]quinazolin-5(6*H*)-one **3ka** with fused [6-6-5-6] tetracyclic framework was obtained at reflux conditions in good yield (70%). In total, we have subjected 11 different CAs for following cycloaddition reaction, thereby demonstrating the good functional group tolerance for the transformation. The geometry of both the

diastereoisomers (*trans* and *cis*) of **3aa** was established on the basis of NOE experiment.

Table 2. Scope investigation with regard to cyclopropane aldehyde[a,b]

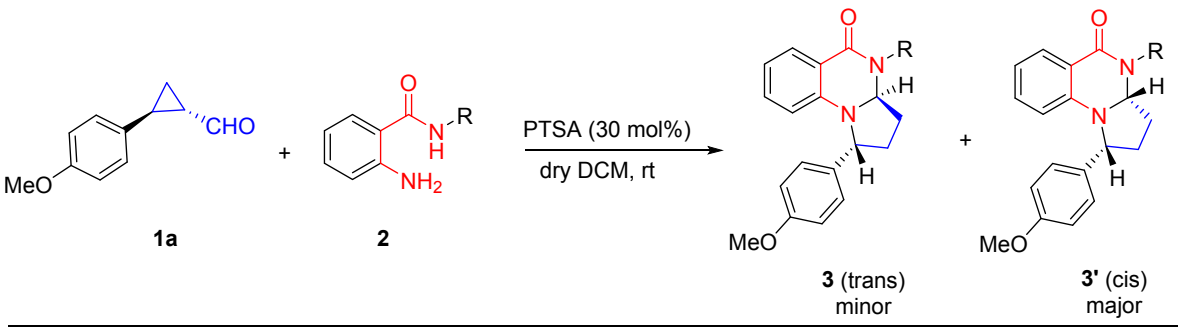


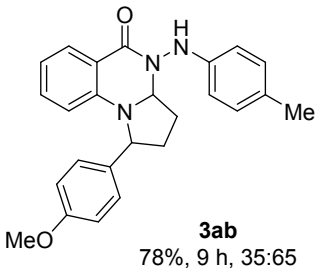
[a]Unless otherwise specified all the reactions were carried out in DCM at rt with 1.2 equiv of **1** and 1 equiv of **2a** in the presence of PTSA (30 mol%). [b]Isolated yield. [c]Reaction was performed at reflux conditions.

Later on, the generality and viability of the reaction was explored with respect to *N'*-aryl substituted anthranil hydrazides/amides **2a-i** by reacting them with 4-

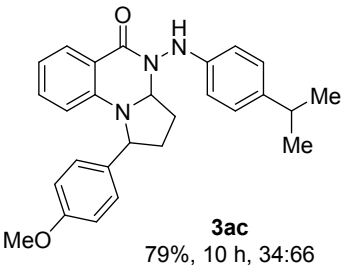
methoxyphenyl cyclopropane aldehyde **1a** (**Table 3**). To our delight, benzohydrazide derivatives bearing electron releasing substituents like 4-methyl **2a** and 4-isopropoyl **2b** on N'-phenyl ring, afforded the cycloadduct with appreciable yields. While anthranil hydrazides having *N'*-phenyl ring substituted with deactivating groups like 4-fluoro **2d**, 4-chloro **2e**, and 4-bromo **2f** rendered in the formation of the final product with good yields. Further, *N*'-benzyl substituted hydrazide **2g** led to the amalgamation of cycloadduct **3ag** with a diastereomeric ratio of 20:80 in 81% yield. The stereochemistry of both the diastereoisomers were fixed on the basis of the single crystal X-ray analysis. In order to check the effect/utility of hydrazides for the following transformation, benzamides **2i** and **2h** were used in place of hydrazides. Both *N*-benzyl anthranilamide (**2h**) and *N*-phenyl anthranilamide (**2i**) resulted in the formation of final tricyclic tetrahydropyrroloquinazolin-5-one derivatives 3**ah** and 3**ai**, respectively, in good yields with a diastereomeric ratio of approximately 3:1. However, the separation of diastereomeric mixture in both the cases was not feasible *via* thin layer and column chromatography and the mixture was isolated as such from the column without separation. The relative configuration of both the diastereomers (*cis* and *trans*) was established on the basis of the NOE experiment data of **3aa** and **3aa**' and was further supported by the X-ray structural analysis of both the diastereomers of **3ag** (see *supporting information* **Figure S1** and **S2**). Therefore, configuration of both the diastereomers for all the synthesized cycloadducts was set on the basis of structural analogy.

Table 3. Scope investigation with regard to anthranil hydrazide[a,b]

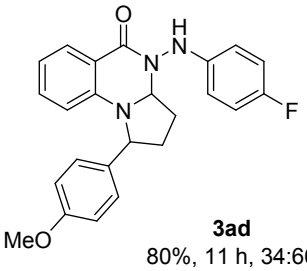




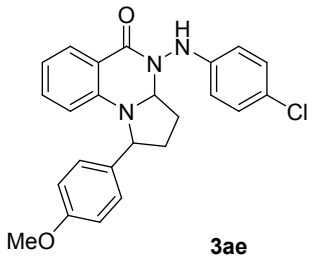
3ab
78%, 9 h, 35:65



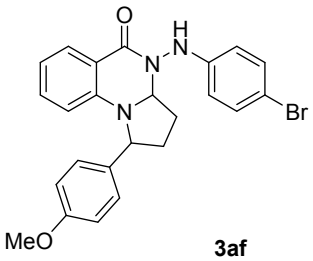
3ac
79%, 10 h, 34:66



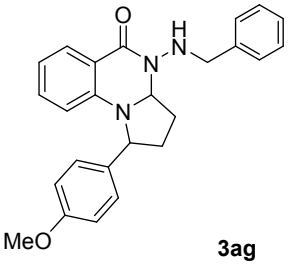
3ad
80%, 11 h, 34:66



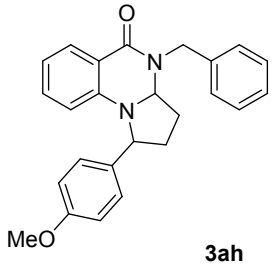
3ae
81%, 10 h, 35:65



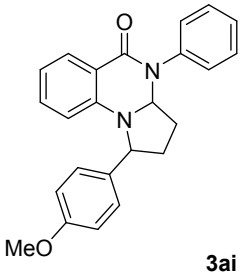
3af
81%, 10 h, 33:67



3ag
81%, 10 h, 20:80



3ah
81%, 8 h, 50:50



3ai
81%, 9 h, 30:70

[a]Unless otherwise specified all the reactions were carried out in DCM at rt with 1.2 equiv of **1a** and 1 equiv of **2** in the presence of PTSA (30 mol%). [b]Isolated yield.

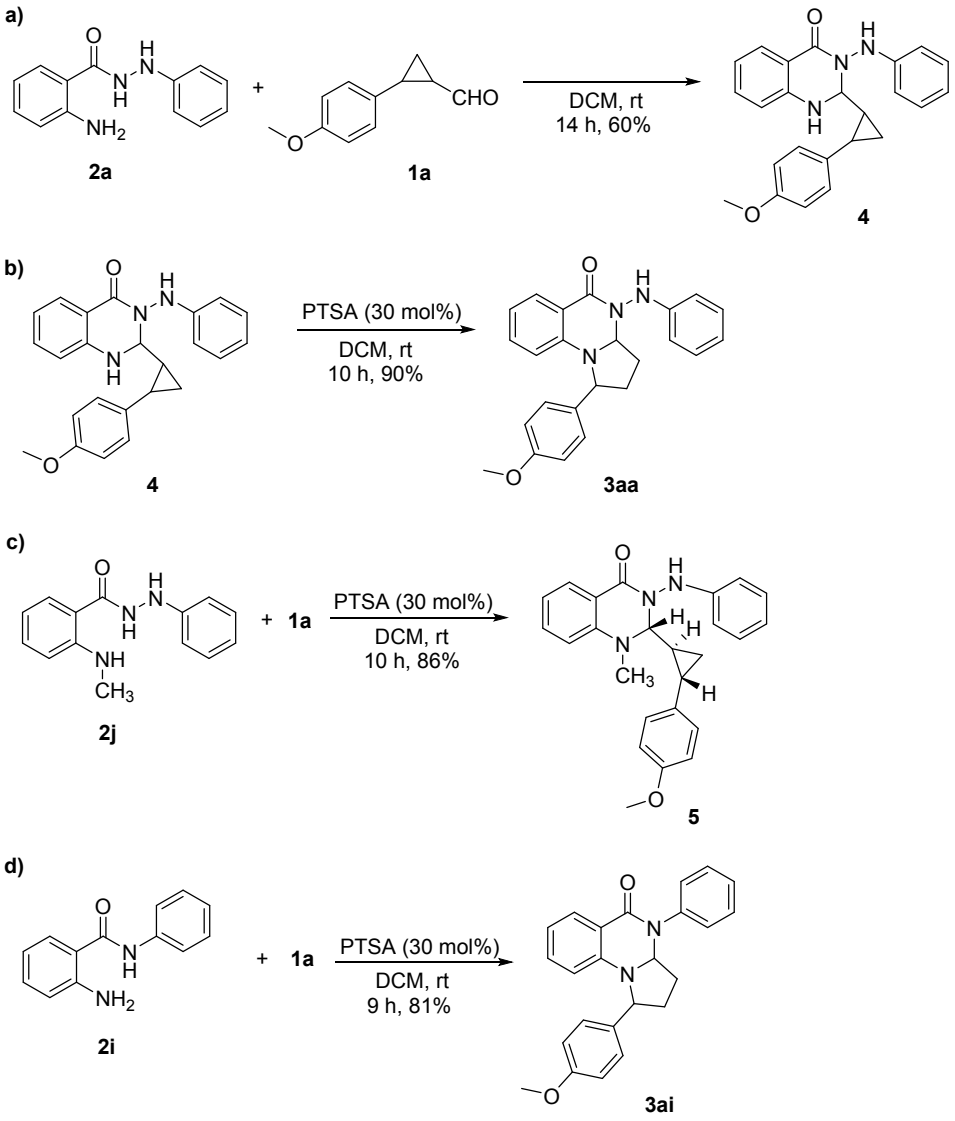
Finally, in order to better understand the proposed annulation mechanistically, several control experiments were carried out. Firstly, to check the inevitability of acid catalyst for the transformation, the annulation reaction of *N*'-phenyl anthranil hydrazide **2a** with 4-methoxyphenyl CA **1a** was executed in the absence of PTSA. The formation

of bicyclic product **4** with diastereomeric ratio of 1:1 with 60% yield was only perceived in 14 h, indicating the importance of acid catalyst for the formation of final cycloadduct (**Scheme 2a**). Further, the obtained dihydroquinazolin-4-one **4** was then treated with PTSA (30 mol%) in DCM for 10 h and led to the construction of tetrahydropyrrolo[1,2-*a*]quinazolin-5(1H)-one **3aa** with 90% yield (**Scheme 2b**). Indicating that the reaction of anthranil hydrazides **1** with cyclopropane aldehydes **2** proceeds through the formation of dihydroquinazoli-4-one intermediate **4** first, followed by the formation of the final tricyclic adduct **3**. Next, to validate the formation of tetrahydropyrrolo[1,2-*a*]quinazolin-5(1H)-ones **3** over hexahydro-10H-pyridazino[6,1-b]quinazolin-10-one **6**, *N*-methyl substituted anthranil hydrazide **2j** made to react with cyclopropane aldehyde **1a** in the presence of PTSA. The following reaction resulted in the formation of bicyclic adduct **5** only, ruling out the possibility of formation [6-6-6] fused tricyclic adduct **6** (**Scheme 2c**). This may be due to the reduced kinetic favourability for the formation of 6-membered ring over the 5-membered ring. The structure and configuration of the formed bicyclic adduct ***5*** was also confirmed by X-ray structure analysis (see *supporting information* **Figure S3**). It was also further supported by the reaction of 2-amino benzamide **2i** with cyclopropane aldehyde **1a**, the construction of final tetrahydropyrrolo[1,2-*a*]quinazolin-5(1H)-ones **3ai** was observed with 81% yield (**Scheme 2d**).

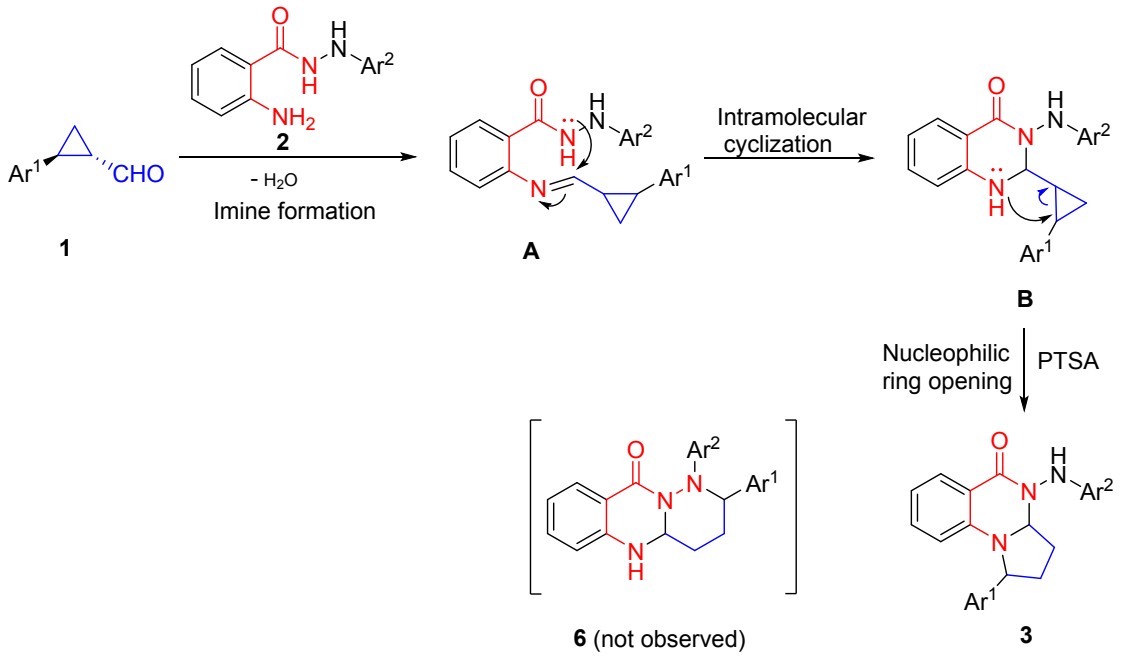
On the basis of the above results, we have proposed a plausible mechanism, as shown in **scheme 3,** for the following annulation reaction. The reaction proceeds through the formation of intermediate imine **A** *via* the reaction of cyclopropane aldehyde **1** with anthranil hydrazide **2**. Formed imine **A** then undergoes intramolecular cyclization with *N*-atom of the hydrazide linkage and leads to the formation of intermediate dihydroquinazolin-4-ones **B** with intact cyclopropane ring. The structure

of the formed bicyclic intermediate **B** is confirmed by ^{1}H and ^{13}C NMR spectra**.** Cyclopropyl ring of the intermediate **B** then undergoes nucleophilic ring opening and cyclization with the *N*-atom of the quinazoline ring rather than *N*'-atom of the phenyl ring, which eventually leads to the construction of the final cycloadduct **3**. The nitrogen atom of *N*'-phenyl group of intermediate **B** does not participate in the final cyclization, eliminating the formation of tricyclic compound **6**.

Scheme 2: Control Experiments

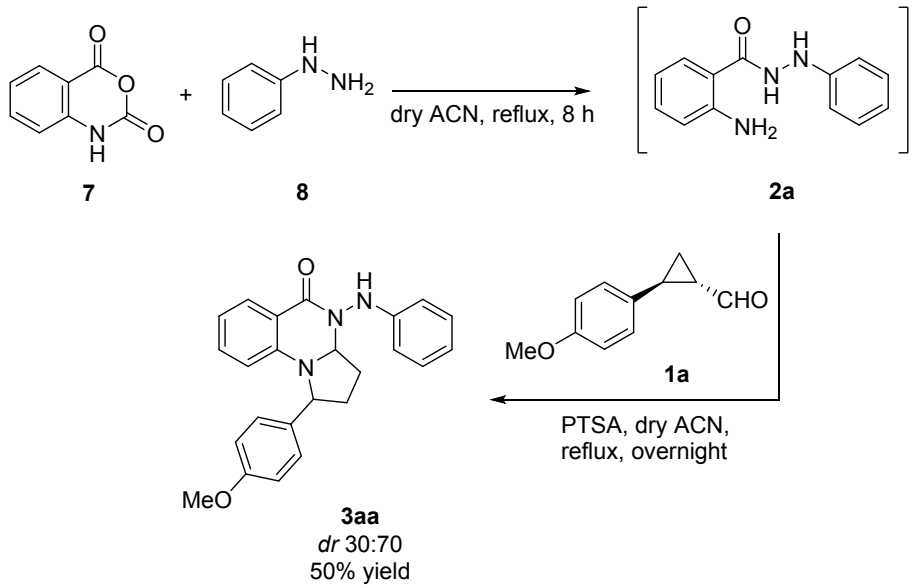


Scheme 3: Proposed Mechanism



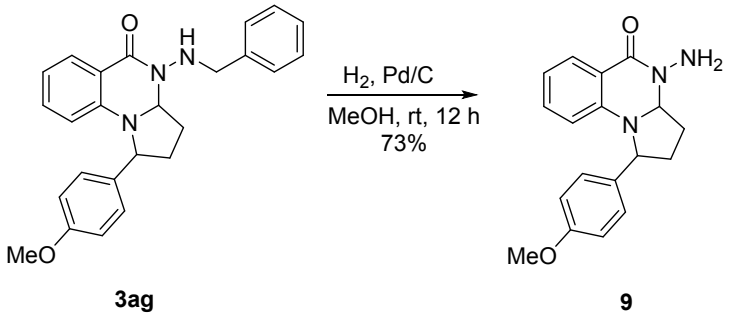
Having plenty of cycloadduct in hand, following cycloaddition was carried out in one pot *via in situ* generations of anthranil hydrazide **2a** in the reaction mixture starting from Isatoic anhydride **7** (1 equiv) and phenyl hydrazine **8** (1 equiv) under reflux conditions in dry ACN. After the complete consumption of phenyl hydrazine **8** in reaction mixture, as observed from thin layer chromatography. CA **1a** (1.1 equiv) and PTSA (30 mol%) were then added to the reaction mixture and refluxed for overnight till completion of reaction. The desired cycloadduct **3aa** was obtained in 50% yield with *dr* 30:70 (**Scheme 4**).

Scheme 4: One pot sequential synthesis of 3aa



Further to check synthetic potentiality of the synthesized tetrahydropyrrolo[1,2-*a*]quinazolin-5(1*H*)one derivates, debenzylation of the compound **3ag** was performed in the presence of H_2 and Pd/C to provide the corresponding 4-amino-tetrahydropyrrolo[1,2-*a*]quinazolin-5(1*H*)-one **9**. The obtained free NH_2 group of compound **9** can be further utilized for post functionalization of the tetrahydropyrrolo quinazolin-5-one derivatives (**Scheme 5**).

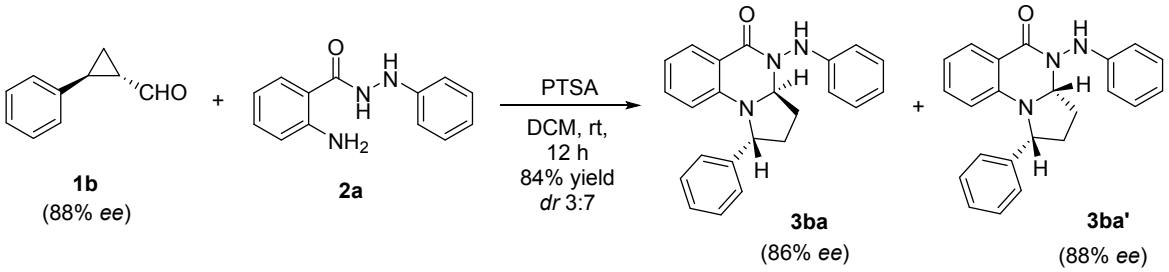
Scheme 5: Debenzylation of 3ag



To investigate the stereospecificity of the ring opening process, an enantioenriched cyclopropane carbaldehyde **1b** was employed in the mentioned reaction (**Scheme 6**). Formation of the enantioenriched annulated product **3ba** and

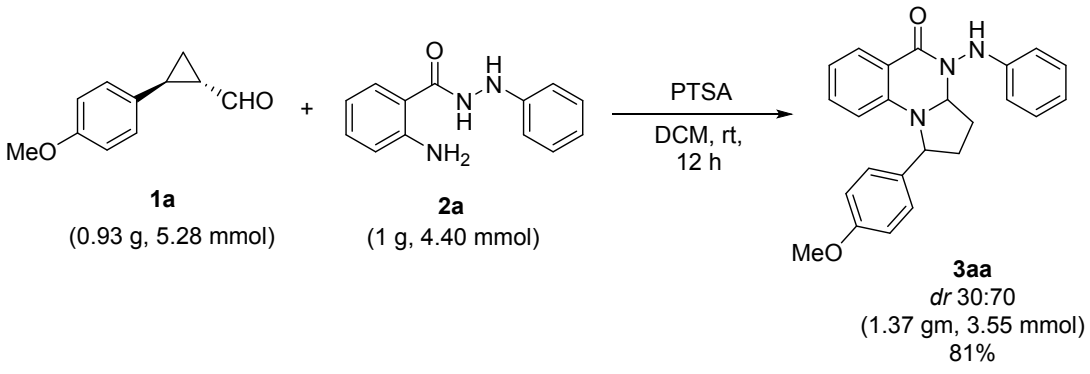
3ba' with 86% and 88% *ee*, respectively, established that the reaction proceeds in a stereospecific manner (see *supporting information pp-S228* for details).

Scheme 6: Stereospecificity of the ring opening



Gram scale synthesis for the proposed annulation using 4-methoxyphenyl cyclopropane aldehyde **1a** and *N*'-phenyl anthranil hydrazide **2a** as substrate was also performed (**Scheme 7**). To our delight final product **3aa** was obtained with excellent yield (81% yield), indicating the importance of proposed protocol for larger scale syntheses.

Scheme 7: Gram scale synthesis



CONCLUSION

In conclusion, we have developed a simple and efficient step economic method for the synthesis of tetrahydropyrrolo[1,2-*a*]quinazolin-5(1*H*)one derivatives by reacting cyclopropane aldehydes and *N*'-aryl anthranil hydrazides with complete

regioselectivity. The reaction follows a domino sequence of imination/intramolecular cyclization/nucleophilic ring opening. A wide range of cyclopropane aldehydes and hydrazides have been screened for the synthesis of highly functionalized pyrroloquinazolinone derivatives with good to excellent yields.

EXPERIMENTAL SECTION

General information. All solvents and reagents were obtained from commercial sources and were purified following the standard procedure prior to use. The developed chromatogram was analyzed by UV lamp (254 nm) or *p*-anisaldehyde solution. Products were purified by flash chromatography on silica gel (mesh size 230–400). Unless otherwise specified, all the ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$. Chemical shifts of ^{1}H NMR and ^{13}C NMR spectra are expressed in parts per million (ppm). All coupling constants are absolute values and are expressed in Hertz. The description of the signals includes the following: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, q = quartet, br = broad, and m = multiplet. All ^{13}C spectra were recorded with broadband proton decoupling.

Isatoic anhydride **7**, *N*-methyl isatoic anhydride, base free phenyl hydrazine derivatives were obtained according to the reported procedures.[18-20]

General Procedure for the preparation of trans-2-arylcyclopropanealdehydes (1a-j)[12,13c,17] For the reaction schemes, see Scheme S1 in the Supporting Information.

1) To a mixture of triethyl phosphonoacetate (22.0 mmol, 1.1 equiv.), DBU (0.70 mmol, 0.035 equiv.), and finely ground K_2CO_3 (40 mmol, 2 equiv.) was added ArCHO (20 mmol, 1 equiv.), and the resulting mixture was stirred using a magnetic stirrer for 4 h at room temperature under argon atmosphere. Ethyl acetate was added to the crude mixture and the solid was filtered off. The solid was rinsed with

ethyl acetate, and the combined filtrate was concentrated. The resulting oil was distilled under reduced pressure using a bulb-to-bulb apparatus (10 mm Hg/240 °C) to give corresponding alkene (yield 84%) (*E*:*Z* =99:1).

2) A suspension of TMSOI (16.8 mmol, 1.2 equiv.) and NaH (21 mmol, 1.5 equiv.) in anhydrous DMSO (15 mL) was stirred for 1 h. A DMSO solution (15 mL) of alkene (14 mmol, 1 equiv.) was added at 0 °C. The reaction mixture was stirred at 55 °C for 24 h. Another suspension of TMSOI (4.2 mmol, 0.3 equiv.) and NaH (4.2 mmol, 0.3 equiv.) in DMSO (10 mL) was added to the reaction mixture and reaction was stirred at 65°C for 84 h. The solution was poured into a brine solution and extracted with ethyl acetate. The combined organic layer was washed with water and dried over MgSO4, concentrated and purified by silica gel column to afford corresponding cyclopropane derivative as a white solid (60-80%yield).
3) To a stirred solution of LAH (1.35 mmol, 1.5 equiv.) in 7 mL diethyl ether was added dropwise a solution of cyclopropane ester (0.90 mmol, 1equiv.) in 3 mL diethyl ether under N_2 atmosphere. After the addition was completed the reaction mixture was refluxed for another 6 h. The reaction mixture was then cooled to rt, and the excess LAH was destroyed by ethyl acetate. 15 mL of 10% H_2SO4 and 8 mL of ether was added, and the aqueous layer was extracted several times with diethyl ether. The combined organic layer was washed with water and 5% $NaHCO_3$, dried over $MgSO_4$ and concentrated in a rotary evaporator (90-95% yield). Without any further purification, the crude material (a colorless oil) was used for the next step.
4) To a solution of cyclopropane alcohol (6.8 mmol, 1 equiv.) in dry DCM (14 mL), PCC (13.6 mmol, 2 equiv.) was added in a portion-wise manner through a solid addition tube under N_2 atmosphere. After 3h reaction mixture was filtered through a small plug of celite and concentrated in vacuo. The crude mixture was purified

by silica gel column chromatography using ethyl acetate in hexane as an eluent. Starting from aryl aldehyde the 2-arylcyclopropanecarbaldehydes was obtained in 40-50% overall yield.

*trans-2-(4-Methoxyphenyl)cyclopropane-1-carbaldehyde (**1a**).*[12] 4-Methoxy benzaldehyde (1.0 g, 7.35 mmol), **1a** (0.62 g, 3.53 mmol), 48% overall yield, white solid. ^{1}H NMR (400 MHz): δ 9.30 (d, *J* = 4.9 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H),3.79 (s, 3H), 2.62-2.55 (m, 1H), 2.12-2.06 (m, 1H), 1.73-1.67 (m, 1H), 1.51-1.45 (m, 1H).

*trans-2-Phenylcyclopropane-1-carbaldehyde (**1b**).*[12] Benzaldehyde (1.0 g, 9.43 mmol), **1b** (0.69 g, 4.72 mmol), 50% overall yield, white solid. ^{1}H NMR (400 MHz): δ 9.32 (d, *J* = 4.5 Hz, 1H), 7.32-7.27 (m, 2H), 7.25-7.20 (m, 1H), 7.13-7.09 (m, 2H), 2.66-2.60 (m, 1H), 2.20-2.14 (m, 1H), 1.76-1.71 (m, 1H), 1.56-1.51 (m, 1H).

*trans-2-(p-Tolyl)cyclopropane-1-carbaldehyde (**1c**).*[17] 4-Methylbenzaldehyde (1.0 g, 8.32 mmol), **1c** (0.64g, 3.99 mmol), 48% overall yield, white solid. ^{1}H NMR (400 MHz): δ 9.30 (d, *J* = 4.5 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 2.63-2.57 (m, 1H), 2.32 (s, 3H), 2.16-2.10 (m, 1H), 1.74-1.68 (m, 1H), 1.54-1.48 (m, 1H).

*trans-2-(3,4-Dimethoxyphenyl)cyclopropane-1-carbaldehyde (**1d**).*[12] 3,4-Dimethoxy benzaldehyde (1.0 g, 6.02 mmol), **1d** (0.53 g, 2.59 mmol), 43% overall yield, white solid. ^{1}H NMR (400 MHz): δ 9.31 (d, *J* = 4.5 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.69-6.64 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 2.63−2.58 (m, 1H), 2.15−2.08 (m, 1H), 1.73−1.67 (m, 1H), 1.53−1.47 (m, 1H).

*trans-2-(4-Fluorophenyl)cyclopropane-1-carbaldehyde (**1e**).*[12] 4-Fluorobenzaldehyde (1.0 g, 8.06 mmol), **1e** (0.66 g, 4.03 mmol), 50% overall yield, white solid. ^{1}H NMR

(400 MHz): δ 9.33 (d, *J* = 4.5 Hz, 1H), 7.11−7.05 (m, 2H), 7.01-6.95 (m, 2H), 2.65−2.58 (m, 1H), 2.15−2.09 (m, 1H), 1.75−1.69 (m, 1H), 1.51−1.45 (m, 1H).

*trans-2-(4-Chlorophenyl)cyclopropane-1-carbaldehyde (**1f**).*[17] 4-Chlorobenzaldehyde (1.0 g, 7.11 mmol), **1e** (0.70 g, 3.88 mmol), 55% overall yield, white solid. ^{1}H NMR (400 MHz): δ 9.33 (d, *J* = 4.5 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 2.62-2.56 (m, 1H), 2.17-2.11 (m, 1H), 1.76-1.70 (m, 1H), 1.52-1.46 (m, 1H).

*trans-2-(4-Bromophenyl)cyclopropane-1-carbaldehyde (**1g**).*[13c] 4-Bromo benzaldehyde (1.0 g, 5.40 mmol), **1g** (0.8 g, 3.57 mmol), 66% overall yield, white solid. ^{1}H NMR (400 MHz): δ 9.31 (d, *J* = 4.3 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 2.6-2.54 (m, 1H), 2.16-2.09 (m, 1H), 1.75-1.69 (m, 1H), 1.50-1.45 (m, 1H).

*trans-2-(Naphthalen-2-yl)cyclopropane-1-carbaldehyde (**1h**).*[12] 2-Naphthaldehyde (1.0 g, 6.40 mmol), **1h** (0.65 g, 3.31 mmol), 52% overall yield, off white solid. ^{1}H NMR (400 MHz): δ 9.37 (d, *J* = 4.5 Hz, 1H), 7.81-7.74 (m, 3H), 7.58 (s, 1H), 7.49-7.41 (m, 2H),7.20 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.82-2.76 (m, 1H), 2.30-2.23 (m, 1H), 1.83-1.77 (m, 1H), 1.69-1.62 (m, 1H).

*trans-2-Styrylcyclopropane-1-carbaldehyde (**1i**).*[17] *trans*-Cinnamaldehyde (1.0 g, 7.56 mmol), **1i** (0.62 g, 3.60 mmol), 47% overall yield, off white solid. ^{1}H NMR (400 MHz): δ 9.24 (d, *J* = 4.58 Hz, 1H), 7.32-7.29 (m, 4H), 6.56 (d, *J* = 15.57 Hz, 1H), 5.76 (dd, *J* = 15.57, 8.52 Hz, 1H), 2.33-2.25 (m, 1H), 2.08-2.01 (m, 1H), 1.66-1.60 (m, 1H), 1.34-1.28 (m, 1H).

*trans-2-(Furan-2-yl)cyclopropane-1-carbaldehyde (**1j**).*[12] Furan-2-carbaldehyde (1.0 g, 10.41 mmol), **1j** (0.64 g, 4.69 mmol), 45% overall yield, pale yellow oil. ^{1}H NMR (400 MHz): δ 9.36 (d, *J* = 4.3 Hz, 1H), 7.27−7.25 (m, 1H), 6.30−6.28 (m, 1H), 6.10 (d, *J* =

3.3 Hz, 1H), 2.65−2.59 (m, 1H), 2.32−2.26 (m, 1H), 1.69−1.64 (m, 1H), 1.62−1.56 (m, 1H).

*General procedure for preparation of bicyclo[4.1.0]heptane-7-carbaldehyde (**1k**).*[17] For the reaction scheme, see Scheme S2 in the Supporting Information. To a suspension of cyclohexene (2.36 g, 28.7 mmol) and $Rh_2(OAc)_4$ (40 mg, 0.09 mmol) in CH_2Cl_2 (10 mL) at room temperature was added ethyl diazoacetate (3.28 g, 28.7 mmol) *via* syringe pump and over the course of 12 hours. Once the addition was complete, the green mixture was stirred for another 12 hours, and then filtered through a short pad of celite. The filtrate was concentrated in a rotary evaporator. The crude mixture was separated by flash chromatography using ethyl acetate/hexane as eluent.

The reduction of cyclopropane carboxylate to cyclopropyl methanol and the oxidation of cyclopropyl methanol to cyclopropane aldehyde was carried out following the general procedure described in the preparation of *trans*-2-aryl cyclopropane aldehydes.

*Bicyclo[4.1.0]heptane-7-carbaldehyde (**1k**).*[17] Cyclohexene (2.36 g, 28.7 mmol), **1k** (1.60 g, 12.9 mmol), 45% overall yield, colorless oil. ^{1}H NMR (400 MHz): δ 9.00 (d, *J* = 5.49 Hz, 1H), 1.96-1.84 (m, 2H), 1.77-1.64 (m, 4H), 1.38 (t, *J* = 4.36 Hz, 1H), 1.34-1.24 (m, 2H), 1.23-1.14 (m, 2H).

General Procedure for the preparation of anthranil hydrazides (2a-j)[21c] For the reaction scheme, see Scheme S3 in the Supporting Information. To a mixture of isatoic anhydride/N-methyl isatoic anhydride (0.61 mmol, 1 equiv.) and hydrazine/aniline derivatives (0.67 mmol, 1.1 equiv.) in ethanol (5 mL), catalytic amount of glacial acetic acid (2 drops) was added. The mixture was heated under reflux for 2 hours, concentrated to its half volume, and then cooled. The separated solid was filtered and

crystallized from aqueous ethanol to give the titled compounds in 75-85% yield. Solid obtained was used as such for further reaction.

*2-Amino-N'-phenylbenzohydrazide (**2a**):*[10] Isatoic anhydride (0.20 g, 1.22 mmol), phenylhydrazine (0.14 g, 1.34 mmol), **2a** (0.25 g, 1.10 mmol), 82% yield, yellow solid. ^{1}H NMR (400 MHz): δ 7.76 (s, 1H), 7.48 (d, *J* = 8.18 Hz, 1H), 7.30-7.22 (m, 3H), 6.96-6.89 (m, 3H), 6.74-6.66 (m, 2H), 6.27 (s, 1H), 5.56 (s, 2H).

*2-amino-N'-(p-tolyl)benzohydrazide (**2b**)* [10] Isatoic anhydride (0.10 g, 0.61 mmol), 4-methylphenylhydrazine (0.081 g, 0.67 mmol), **2b** (0.12 g, 0.50 mmol), 82% yield, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.47 (d, *J* = 8.37 Hz, 1H), 7.29-7.23 (m, 1H), 7.05 (d, *J* = 8.28 Hz, 2H), 6.85 (d, *J* = 8.28 Hz, 2H), 6.72-6.66 (m, 2H), 5.86 (s, 2H), 2.26 (s, 3H).

*2-amino-N'-(4-isopropylphenyl)benzohydrazide (**2c**):*[10] Isatoic anhydride (0.10 g, 0.61 mmol), 4-isopropoylphenylhydrazine (0.11 g, 0.67 mmol), **2b** (0.14 g, 0.52 mmol), 85% yield, yellow solid. ^{1}H NMR (400 MHz): δ 7.72 (s, 1H), 7.46 (dd, *J* = 8.25, 1.34 Hz, 1H), 7.28-7.23 (m, 2H), 7.10 (d, *J* = 8.46 Hz, 2H), 6.87 (d, *J* = 8.49 Hz, 2H), 6.71-6.66 (m, 2H), 5.56 (s, 2H), 2.86-2.76 (m, 1H), 1.19 (d, *J* = 6.86 Hz, 6H).

*2-amino-N'-(4-fluorophenyl)benzohydrazide (**2d**):*[10] Isatoic anhydride (0.10 g, 0.61 mmol), 4-fluorophenylhydrazine (0.085 g, 0.67 mmol), **2d** (0.11 g, 0.44 mmol), 74% yield, yellow solid. ^{1}H NMR (400 MHz): δ 7.80 (s, 1H), 7.47 (d, *J* = 7.92 Hz, 1H), 7.30-7.27 (m, 1H), 6.98-6.86 (m, 4H), 6.73-6.67 (m, 2H), 6.26 (s, 1H), 5.57 (s, 2H).

*2-amino-N'-(4-chlorophenyl)benzohydrazide (**2e**):*[10] Isatoic anhydride (0.10 g, 0.61 mmol), 4-chlorophenylhydrazine (0.096 g, 0.67 mmol), **2e** (0.13 g, 0.49 mmol), 82% yield, yellow solid. ^{1}H NMR (400 MHz): δ 7.72 (s, 1H), 7.48 (dd, *J* = 8.49, 1.30 Hz, 1H),

7.31-7.26 (m, 1H), 7.20 (d, *J* = 8.70 Hz, 2H), 6.88 (d, *J* = 8.70 Hz, 2H), 6.73-6.68 (m, 2H), 5.59 (s, 2H).

*2-amino-N'-(4-bromophenyl)benzohydrazide (**2f**):*[21a] Isatoic anhydride (0.10 g, 0.61 mmol), 4-bromophenylhydrazine (0.12 g, 0.67 mmol), **2f** (0.14 g, 0.46 mmol), 75% yield, yellow solid. ^{1}H NMR (400 MHz): δ 7.72 (s, 1H), 7.48 (d, *J* = 8.39 Hz, 1H), 7.37-7.27 (m, 1H), 6.83 (d, *J* = 8.72 Hz, 2H), 6.73-6.68 (m, 2H), 6.24 (s, 1H), 5.54 (s, 2H).

*2-amino-N'-benzylbenzohydrazide (**2g**):*[10] Isatoic anhydride (0.40 g, 2.45 mmol), benzylhydrazine (0.33 g, 2.69 mmol), **2g** (0.50 g, 2.07 mmol), 85% yield, white solid. ^{1}H NMR (400 MHz): δ 7.60 (s, 1H), 7.42-7.24 (m, 6H), 7.22-7.15 (m, 2H), 6.67 (d, *J* = 8.07 Hz, 1H), 6.59 (t, *J* = 7.57 Hz, 1H), 5.39 (s, 2H), 4.04 (s, 2H).

*2-amino-N-benzylbenzamide (**2h**):*[21b] Isatoic anhydride (0.10 g, 0.61 mmol), benzylamine (0.072 g, 0.67 mmol), **2h** (0.12 g, 0.53 mmol), 87% yield, white solid. ^{1}H NMR (400 MHz): δ 7.37-7.27 (m, 6H), 7.20 (t, *J* = 7.78 Hz, 1H), 6.69 (d, *J* = 8.29 Hz, 1H), 6.63 (t, *J* = 7.78 Hz, 1H), 6.33 (s, 1H), 5.57 (s, 2H), 4.60 (s, 2H).

*2-amino-N-phenylbenzamide (**2i**):*[21b] Isatoic anhydride (0.10 g, 0.61 mmol), aniline (0.063 g, 0.67 mmol), **2i** (0.11 g, 0.51 mmol), 85% yield, white solid. ^{1}H NMR (400 MHz): δ 7.75 (s, 1H), 7.56 (d, *J* = 8.20 Hz, 2H), 7.47 (d, *J* = 8.25 Hz, 1H), 7.40-7.34 (m, 2H), 7.28=7.23 (m, 1H), 7.15 (t, *J* = 7.46 Hz, 1H), 6.74-6.66 (m, 2H), 5.49 (s, 2H).

*2-(methylamino)-N'-phenylbenzohydrazide (**2j**):*[21c] *N*-Methylisatoic anhydride (0.10 g, 0.56 mmol), phenylhydrazine (0.067 g, 0.62 mmol), **2j** (0.11 g, 0.45 mmol), 81% yield, white solid. ^{1}H NMR (400 MHz): δ 7.29 (s, 1H), 7.50 (dd, *J* = 8.03, 1.57 Hz, 1H), 7.45-7.36 (m, 2H), 7.28-7.22 (m, 2H), 6.96-6.89 (m, 3H), 6.70 (d, *J* = 8.39 Hz, 1H), 6.63 (t, *J* = 7.70 Hz, 1H) 6.23 (s, 1H), 2.84 (d, *J* = 4.22 Hz, 3H).

Representative procedure for the Bronsted acid catalysed annulation of cyclopropanealdehydes (1) and anthranil hydrazides (2). For the reaction scheme, see Scheme S4 in the Supporting Information. A round bottom flask equipped with magnetic stirrer bar was charged with PTSA (0.066 mmol, 0.3 equiv). A solution of cyclopropane carbaldehyde (0.26 mmol, 1.2 equiv), and anthranil hydrazides/benzamides (0.22 mmol, 1 equiv) in DCM (1 mL) was added to it, and the mixture was stirred at room temperature till the completion of reaction (as monitered by TLC). The excess of the solvent was evaporated on a rotary evaporator. The crude mixture obtained was further purified by column chromatography on silica gel using ethyl acetate/hexane as eluent.

In case of aldehydes **3h** and **3k** reaction was done at reflux conditions using DCM as solvent at 50 °C (oil bath temperature).

*1-(4-Methoxyphenyl)-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3aa** and **3aa'**):* Reaction time: 10 h, **1a** (46.48 mg, 0.26 mmol), **2a** (50 mg, 0.22 mmol), **3aa** and **3aa'** (72 mg, 0.187 mmol), 85% yield.

3aa: white crystalline solid, 24.5 mg, R_f = 0.60 (EtOAc:Hexane = 2.5:7.5), mp 129-131 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.84, 1.23 Hz, 1H), 7.27-7.15 (m, 5H), 6.98-6.88 (m, 5H), 6.81 (t, *J* = 7.22 Hz, 1H), 6.44 (s, 1H), 6.40 (d, *J*= 8.25 Hz, 1H), 5.58 (dd, *J* = 6.19, 2.68 Hz, 1H), 5.02 (dd, *J* = 7.63, 2.27 Hz, 1H), 3.82 (s, 3H), 2.76-2.63 (m, 1H), 2.50-2.40 (m, 1H), 2.32-2.21 (m ,1H), 1.93-1.84 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz): δ 158.8, 148.3, 146.2, 146.1, 135.2, 134.2, 129.29, 129.2, 126.7, 121.6, 118.8, 115.5, 114.6, 114.2, 114.1, 77.05, 66.4, 55.4, 34.0, 29.1; IR (neat): 3053, 2928, 1666, 1605, 1492, 1378, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{24}N_3O_2$ 386.1863; Found 386.1865.

3aa': white crystalline solid, 47.5 mg, R_f = 0.50 (EtOAc:Hexane = 2.5:7.5), mp 132-133 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.66, 1.39 Hz, 1H), 7.38-7.33 (m, 2H), 7.28-7.18 (m, 4H), 7.07-7.01 (m, 2H), 6.95-6.88 (m, 3H), 6.78 (t, *J* = 7.49 Hz, 1H), 6.50 (s, 1H), 6.34 (d, *J* = 8.36 Hz, 1H), 5.28-5.20 (m, 1H), 4.85 (dd, *J* = 9.2, 1.91 Hz, 1H), 3.80 (s, 3H), 2.54-2.32 (m, 2H), 2.30-2.22 (m, 1H), 2.00-1.93 (m ,1H); ^{13}C{^{1}H} NMR (100 MHz): δ 158.9, 146.2, 134.8, 134.2, 129.6, 129.2, 127.1, 121.5, 118.2, 115.6, 114.3, 114.2, 113.0, 111.3, 77.5, 60.6, 55.3, 32.6, 28.7; IR (neat): 3053, 2954, 1667, 1605, 1492, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{24}N_3O_2$ 386.1863; Found 386.1860.

*1-Phenyl-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ba** and **3ba'**):* Reaction time: 10 h, **1b** (38.56 mg, 0.26 mmol), **2a** (50 mg, 0.22 mmol), **3ba** and **3ba'** (65 mg, 0.182 mmol), 83% yield.

3ba: white crystalline solid, 23 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5), mp 139-141 °C. ^{1}H NMR (400 MHz): δ 7.95 (d, *J* = 7.70 Hz, 1H), 7.41-7.35 (m, 2H), 7.33-7.17 (m, 6H), 6.99-6.90 (m, 3H), 6.82 (t, *J* = 7.52 Hz, 1H), 6.45 (s, 1H), 6.39 (d, *J* = 8.16 Hz, 1H), 5.64-5.57 (m, 1H), 5.07 (d, *J* = 7.20 Hz, 1H), 2.81-2.68 (m, 1H), 2.51-2.42 (m, 1H), 2.33-2.21 (m ,1H), 1.97-1.88 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz): δ 148.3, 146.1, 143.2, 134.3, 129.2, 128.9, 127.3, 125.6, 121.6, 118.9, 115.5, 114.6, 114.1, 77.1, 66.9, 33.9, 29.1; IR (neat): 3054, 1661, 1603, 1491, 1382, 1264, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{22}N_3O$ 356.1757; Found 356.1749.

3ba': white crystalline solid, 42 mg, R_f = 0.41 (EtOAc:Hexane = 2.5:7.5), mp 140-141 °C. ^{1}H NMR (400 MHz): δ 7.96 (d, J = 7.91 Hz, 1H), 7.48-7.43 (m, 2H), 7.41-7.35 (m, 2H), 7.32-7.18 (m, 4H), 7.08-7.02 (m, 2H), 6.92 (t, *J* = 7.41 Hz, 1H), 6.78 (t, *J* = 7.59 Hz, 1H), 6.54 (s, 1H), 6.34 (d, *J* = 8.27 Hz, 1H), 5.31-5.21 (m, 1H), 4.90 (d, *J* = 9.10

Hz, 1H), 2.58-2.31 (m, 2H), 2.31-2.24 (m, 1H), 2.06-1.97 (m ,1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 148.3, 146.2, 142.8, 134.2, 129.7, 129.2, 128.9, 127.5, 126.0, 121.5, 118.3, 115.6, 114.2, 113.0, 77.6, 61.1, 32.5, 28.7; IR (neat): 3054, 1664, 1603, 1491, 1378, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{22}N_3O$ 356.1757; Found 356.1764.

*4-(Phenylamino)-1-(p-tolyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ca** and **3ca'**):* Reaction time: 11 h, **1c** (84.58 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3ca** and **3ca'** (130 mg, 0.35 mmol), 80% yield.

3ca: light yellow semisolid, 42 mg, R_f = 0.65 (EtOAc:Hexane = 2.5:7.5). ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.84, 1.79 Hz, 1H), 7.27-7.12 (m, 7H), 6.98-6.89 (m, 3H), 6.81 (t, *J* = 7.32 Hz, 1H), 6.42 (s, 1H), 6.40 (d, *J* = 8.22 Hz, 1H), 5.58 (dd, *J* = 6.29, 2.82 Hz, 1H), 5.04 (dd, *J* = 7.84, 2.18 Hz, 1H), 2.76-2.63 (m, 1H), 2.48-2.39 (m, 1H), 2.38-2.20 (m ,4H), 1.93-1.85 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 148.3, 146.2, 140.2, 137.0, 134.2, 129.6, 129.28, 129.25, 125.5, 121.6, 118.7, 115.4, 114.5, 114.1, 77.07, 66.6, 34.0, 29.1, 21.1; IR (neat): 3270, 2922, 1658, 1602, 1490, 1381, 1264, 734; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{24}N_3O$ 370.1914; Found 370.1912.

3ca': light yellow semisolid, 88 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5). ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.75, 1.59 Hz, 1H), 7.35-7.31 (m, 2H), 7.28-7.16 (m, 7H), 7.07-7.01 (m, 2H), 6.92 (t, *J* = 7.41 Hz, 1H), 6.77 (t, *J* = 7.80 Hz, 1H), 6.49 (s, 1H), 6.34 (d, *J* = 8.29 Hz, 1H), 5.29-5.20 (m, 1H), 4.87 (d, *J* = 9.10 Hz, 1H), 2.53-2.22 (m, 6H), 2.01-1.94 (m ,1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 146.2, 139.8, 137.2, 134.2, 129.6, 129.2, 125.9, 121.5, 118.2, 114.2, 113.0, 77.3, 60.9, 32.5, 28.7, 21.1; IR (neat): 3054, 1664, 1604, 1491, 1381, 1264, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{24}N_3O$ 370.1914; Found 370.1928.

*1-(3,4-Dimethoxyphenyl)-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a] quinazolin-5(1H)-one (**3da** and **3da'**):* Reaction time: 09 h, **1d** (108.9 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), ***3da*** *and* ***3da'*** (148 mg, 0.356 mmol), 81% yield.

3da: white solid, 59 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5), mp 164-165 °C. ^{1}H NMR (400 MHz): δ 7.95 (d, *J* = 7.70 Hz, 1H), 7.25-7.19 (m, 3H), 6.99-6.89 (m, 3H), 6.88-6.74 (m, 4H), 6.43 (d, *J* = 8.16 Hz, 1H), 6.40 (s, 1H), 5.58 (d, *J* = 6.68 Hz, 1H), 5.00 (d, *J* = 7.20 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.77-2.63 (m, 1H), 2.51-2.40 (m, 1H), 2.34-2.21 (m ,1H), 1.98-1.85 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ 149.4, 148.2, 146.2, 146.1, 135.7, 134.3, 129.3, 129.2, 121.6, 119.0, 117.6, 115.6, 114.8, 114.1, 111.3, 108.7, 77.3, 77.1, 66.8, 56.0, 34.0, 29.1. IR (neat): 3054, 2930, 1658, 1603, 1491, 1263, 733; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_3$ 416.1969; Found 416.1982.

3da': white solid, 89 mg, R_f = 0.54 (EtOAc:Hexane = 2.5:7.5), mp 165-166 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.78, 1.35 Hz, 1H), 7.24-7.18 (m, 3H), 7.06-7.01 (m, 2H), 7.01-6.94 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 5.26-5.19 (m, 1H), 4.82 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.86 (s, 3H), 2.53-2.34 (m, 2H), 2.30-2.23 (m, 1H), 2.01-1.94 (m ,1H). ^{13}C{^{1}H} NMR (100 MHz): δ 149.4, 148.4, 148.3, 146.2, 135.4, 134.2, 129.6, 129.2, 121.6, 118.3, 118.0, 115.5, 114.2, 113.0, 111.3, 108.7, 77.5, 77.3, 60.9, 55.8, 32.5, 28.7. IR (neat): 3057, 2834, 1660, 1603, 1491, 1257, 753; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_3$ 416.1969; Found 416.1967.

*1-(4-Fluorophenyl)-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H) -one (**3ea** and **3ea'**):* Reaction time: 11 h, **1e** (86.68 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3ea** and **3ea'** (135 mg, 0.36 mmol), 82% yield.

3ea: off white solid, 47 mg, R_f = 0.56 (EtOAc:Hexane = 2.5:7.5), mp 157-159 °C. ^{1}H NMR (400 MHz): δ 7.96 (dd, *J* = 7.73, 1.34 Hz, 1H), 7.27-7.19 (m, 5H), 7.10-7.03 (m, 2H), 6.97-6.90 (m, 3H), 6.84 (t, *J* = 7.42 Hz, 1H), 6.44 (s, 1H), 6.37 (d, *J* = 8.19 Hz, 1H), 5.57 (dd, *J* = 6.22, 2.74 Hz, 1H), 5.04 (brd, *J* = 7.56 Hz, 1H), 2.78-2.67 (m, 1H), 2.51-2.43 (m, 1H), 2.30-2.19 (m ,1H), 1.92-1.84 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ 163.3, 160.8, 146.0, 138.9, 134.3, 129.3, 129.2, 127.2, 127.1, 121.6, 119.1, 115.9, 115.7, 114.6, 114.1, 77.0, 66.4, 34.0, 29.0. IR (neat): 3269, 3049, 2873, 1658, 1602, 1491, 1222, 750; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}FN_3O$ 374.1663; Found 374.1667.

3ea': off white solid, 88 mg, R_f = 0.50 (EtOAc:Hexane = 2.5:7.5), mp 160-161 °C. ^{1}H NMR (400 MHz): δ 7.96 (dd, *J* = 7.74, 1.34 Hz, 1H), 7.44-7.37 (m, 2H), 7.28-7.19 (m, 3H), 7.10-7.00 (m, 4H), 6.93 (t, *J* = 7.37 Hz, 1H), 6.80 (t, *J* = 7.46 Hz, 1H), 6.49 (s, 1H), 6.30 (d, *J* = 8.40 Hz, 1H), 5.28-5.20 (m, 1H), 4.88 (dd, *J* = 9.20, 1.70 Hz, 1H), 2.57-2.45 (m, 1H), 2.42-2.24 (m, 2H), 2.00-1.93 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz): δ 163.3, 160.9, 146.0, 138.4, 134.2, 129.7, 129.3, 127.5, 127.5, 121.6, 118.5, 115.9, 115.7, 114.2, 112.9, 77.5, 60.5, 32.5, 28.6. IR (neat): 3275, 3049, 2873, 1663, 1604, 1492, 1223, 752; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}FN_3O$ 374.1663; Found 374.1666.

*1-(4-Chlorophenyl)-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3fa** and **3fa'**):* Reaction time: 10 h, **1f** (93.61 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3fa** and **3fa'** (140 mg, 0.36 mmol), 82% yield.

3fa: off white solid, 49 mg, R_f = 0.70 (EtOAc:Hexane = 2.5:7.5), mp 154-155 °C. ^{1}H NMR (400 MHz): δ 7.95 (dd, *J* = 7.76, 1.39 Hz, 1H), 7.37-7.31 (m, 2H), 7.27-7.18 (m, 5H), 6.97-6.89 (m, 3H), 6.85 (t, *J* = 7.24 Hz, 1H), 6.41 (s, 1H), 6.36 (d, *J* = 8.05 Hz,

1H), 5.57 (dd, *J* = 6.36, 2.63 Hz, 1H), 5.02 (dd, *J* = 5.93, 2.26 Hz, 1H), 2.79-2.67 (m, 1H), 2.52-2.43 (m, 1H), 2.30-2.18 (m ,1H), 1.91-1.83 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 148.2, 145.9, 141.8, 134.3, 133.1, 129.34, 129.3, 127.0, 121.6, 119.2, 115.7, 114.6, 114.1, 113.6, 77.0, 66.5, 33.9, 29.0; IR (neat): 3270, 3049, 2872, 1658, 1602, 1488, 1264, 733; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}ClN_3O$ 390.1368; Found 390.1375.

3fa': off white solid, 91 mg, R_f = 0.60 (EtOAc:Hexane = 2.5:7.5), mp 158-159 °C. ^{1}H NMR (400 MHz): δ 7.96 (dd, *J* = 7.77, 1.56 Hz, 1H), 7.40-7.32 (m, 4H), 7.28-7.20 (m, 3H), 7.05-6.99 (m, 2H), 6.93 (t, *J* = 7.36 Hz, 1H), 6.81 (t, *J* = 7.36 Hz, 1H), 6.49 (s, 1H), 6.29 (d, *J* = 8.12 Hz, 1H), 5.28-5.21 (m, 1H), 4.87 (dd, *J* = 9.34, 1.68 Hz, 1H), 2.56-2.46 (m, 1H), 2.42-2.24 (m, 2H), 2.00-1.92 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 148.2, 145.9, 141.3, 134.2, 133.2, 129.8, 129.3, 129.1, 127.4, 121.6, 118.6, 115.8, 114.2, 112.9, 77.6, 60.5, 32.4, 28.6; IR (neat): 3271, 3049, 2877, 1660, 1603, 1489, 1298, 751; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}ClN_3O$ 390.1368; Found 390.1370.

*1-(4-Bromophenyl)-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ga** and **3ga'**):* Reaction time: 11 h, **1g** (118.36 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3ga** and **3ga'** (154 mg, 0.356 mmol), 81% yield.

3ga: light yellow solid, 54 mg, R_f = 0.65 (EtOAc:Hexane = 2.5:7.5), mp 155-157 °C. ^{1}H NMR (400 MHz): δ 7.95 (dd, *J* = 7.78, 1.34 Hz, 1H), 7.50 (d, *J* = 8.48 Hz, 2H), 7.27-7.21 (m, 3H), 7.15 (d, *J* = 8.48 Hz, 2H), 6.97-6.90 (m, 3H), 6.85 (t, *J* = 7.68 Hz, 1H), 6.42 (s, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 5.56 (dd, *J* = 6.27, 2.61 Hz, 1H), 5.01 (dd, *J* = 7.94, 2.64 Hz, 1H), 2.78-2.67 (m, 1H), 2.51-2.43 (m, 1H), 2.29-2.18 (m ,1H), 1.91-1.83 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 148.2, 145.9, 142.4, 134.3, 132.0, 129.34, 129.3,

127.4, 121.6, 121.1, 119.3, 115.7, 114.6, 114.1, 77.0, 66.6, 33.8, 29.0; IR (neat): 3053, 1661, 1604, 1489, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}BrN_3O$ 434.0863; Found 434.0891.

3ga': light yellow solid, 100 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5), mp 156-157 °C. ^1H NMR (400 MHz): δ 7.96 (dd, *J* = 7.79, 1.36 Hz, 1H), 7.50 (d, *J* = 8.15 Hz, 2H), 7.32 (d, *J* = 8.20 Hz, 2H), 7.28-7.19 (m, 3H), 7.01 (d, *J* = 8.02 Hz, 2H), 6.93 (t, *J* = 7.33 Hz, 1H), 6.81 (t, *J* = 7.47 Hz, 1H), 6.54 (s, 1H), 6.29 (d, *J* = 8.20 Hz, 1H), 5.29-5.19 (m, 1H), 4.85 (dd, *J* = 9.20, 1.45 Hz, 1H), 2.57-2.45 (m, 1H), 2.41-2.24 (m, 2H), 2.00-1.92 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz): δ 148.2, 145.9, 141.9, 134.2, 132.1, 129.8, 129.3, 127.7, 121.6, 121.3, 118.6, 115.8, 114.1, 112.9, 77.5, 60.5, 32.3, 28.6; IR (neat): 3053, 2986, 1667, 1605, 1490, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}BrN_3O$ 434.0863; Found 434.0856.

*1-(Naphthalen-2-yl)-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ha** and **3ha'**):* Reaction time: 14 h, **1h** (103.6 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3ha** and **3ha'** (139 mg, 0.34 mmol), 78% yield.

3ha: yellow solid, 50 mg, R_f = 0.45 (EtOAc:Hexane = 2.5:7.5) , mp 149-150 °C. ^1H NMR (400 MHz): δ 7.96 (dd, *J* = 7.82, 1.58 Hz, 1H), 7.89-7.78 (m, 3H), 7.68 (s, 1H), 7.51-7.45 (m, 2H), 7.38 (dd, *J* = 8.56, 1.54 Hz, 1H), 7.27-7.22 (m, 3H), 7.20-7.15 (m, 1H), 6.99-6.89 (m, 3H), 6.82 (t, *J* = 7.58 Hz, 1H), 6.42 (t, *J* = 4.41 Hz, 1H), 5.68 (dd, *J* = 6.25, 2.53 Hz, 1H), 5.23-5.19 (m, 1H), 2.84-2.72 (m, 1H), 2.53-2.44 (m, 1H), 2.35-2.24 (m ,1H), 2.03-1.95 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz): δ 148.3, 146.2, 140.6, 134.3, 132.8, 129.3, 129.0, 127.9, 127.8, 126.5, 126.0, 124.1, 123.9, 121.6, 119.0, 115.6, 114.8, 114.1, 77.2, 67.2, 33.7, 29.1; IR (neat): 3053, 1661, 1603, 1491, 1384, 1264, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{24}N_3O$ 406.1914; Found 406.1927.

3ha': yellow solid, 89 mg, R_f = 0.35 (EtOAc:Hexane = 2.5:7.5) , mp 152-153 °C. ^{1}H NMR (400 MHz): δ 7.97 (dd, *J* = 7.74, 1.40 Hz, 1H), 7.91-7.79 (m, 4H), 7.56-7.43 (m, 3H), 7.29-7.23 (m, 2H), 7.16 (t, *J* = 7.80 Hz, 1H), 7.12-7.06 (m, 2H), 6.92 (t, *J* = 7.17 Hz, 1H), 6.77 (t, *J* = 7.38 Hz, 1H), 6.52 (s, 1H), 6.38 (d, *J* = 8.43 Hz, 1H), 5.34-5.26 (m, 1H), 5.06 (d, *J* = 9.28 Hz, 1H), 2.62-2.38 (m, 2H), 2.34-2.26 (m ,1H), 2.09-2.02 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz): δ 148.4, 146.2, 140.1, 134.2, 133.4, 132.9, 129.7, 129.3, 129.0, 127.9, 127.8, 126.5, 126.0, 124.6, 124.2, 121.6, 121.3, 118.3, 115.7, 114.2, 113.0, 77.6, 61.2, 32.9, 28.6; IR (neat): 3053, 1664, 1603, 1491, 1381, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{24}N_3O$ 406.1914; Found 406.1906.

*(E)-4-(Phenylamino)-1-styryl-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ia** and **3ia'**):* Reaction time: 11 h, **1i** (90.93 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3ia** and **3ia'** (132.5 mg, 0.347 mmol), 79% yield.

3ia: off white solid, 46.5 mg, R_f = 0.70 (EtOAc:Hexane = 2.5:7.5), mp 159-161 °C. ^{1}H NMR (400 MHz): δ 7.95 (dd, *J* = 7.81, 1.43 Hz, 1H), 7.43-7.38 (m, 2H), 7.37-7.31 (m, 3H), 7.29-7.20 (m, 3H), 6.98-6.89 (m, 3H), 6.88-6.81 (m, 2H), 6.54 (d, *J* = 15.83 Hz, 1H), 6.43 (s, 1H), 6.29 (dd, *J* = 15.84, 5.47 Hz, 1H), 5.43 (dd, *J* = 6.74, 1.85 Hz, 1H), 4.69-4.69-4.62 (m, 1H), 2.58-2.41 (m, 2H), 2.37-2.25 (m ,1H), 1.91-1.83 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz): δ 148.3, 146.4, 136.4, 134.3, 130.2, 130.1, 129.2, 128.7, 127.8, 126.5, 121.5, 118.9, 115.7, 114.7, 114.1, 76.4, 64.9, 30.7, 28.9; IR (neat): 3053, 1660, 1603, 1490, 1382, 1264, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{24}N_3O$ 382.1914; Found 382.1923.

3ia': off white solid, 86 mg, R_f = 0.60 (EtOAc:Hexane = 2.5:7.5), mp 161-162 °C. ^{1}H NMR (400 MHz): δ 7.95 (d, *J* = 7.74 Hz, 1H), 7.42-7.37 (m, 2H), 7.36-7.30 (m, 3H), 7.28-7.19 (m, 3H), 7.04-6.98 (m, 2H), 6.90 (t, *J* = 7.30 Hz, 1H), 6.81 (t, *J* = 7.45 Hz,

1H), 6.73-6.65 (m, 2H), 6.46 (s, 1H), 6.30 (dd, *J* = 15.79, 6.42 Hz, 1H), 5.23-5.15 (m, 1H), 4.57-4.51 (m, 1H), 2.44-2.26 (m, 3H), 2.08-1.98 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 148.4, 146.3, 136.4, 134.2, 130.9, 129.9, 129.7, 129.2, 128.7, 127.8, 126.5, 121.5, 118.2, 115.6, 114.1, 112.9, 77.2, 59.1, 29.9, 28.8; IR (neat): 3025, 1659, 1604, 1491, 1382, 749, 693; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{24}N_3O$ 382.1914; Found 382.1920.

*1-(Furan-2-yl)-4-(phenylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ja** and **3ja'**):* Reaction time: 12 h, **1j** (71.88 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3ja** and **3ja'** (124.5 mg, 0.36 mmol), 82% yield.

3ja: Dark brown sticky solid, 43.5 mg, R_f = 0.65 (EtOAc:Hexane = 2.5:7.5). ^{1}H NMR (400 MHz):δ 7.94 (dd, *J* = 7.80, 1.78 Hz, 1H), 7.39 (dd, *J* = 1.83, 0.90 Hz, 1H), 7.32 (t, *J* = 7.78 Hz, 1H), 7.25-7.20 (m, 2H), 6.96-6.83 (m, 4H), 6.70 (d, *J* = 8.25 Hz, 1H), 6.41 (s, 1H), 6.34 (dd, *J* = 3.23, 1.85 Hz, 1H), 6.22 (d, *J* = 3.18 Hz, 1H), 5.46 (dd, *J* = 6.17, 2.73 Hz, 1H), 5.04 (d, *J* = 7.18 Hz, 1H), 2.62-2.33 (m, 3H), 2.17-2.10 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 155.0, 148.3, 145.9, 142.3, 134.3, 129.2, 121.6, 119.3, 116.0, 114.6, 114.0, 110.3, 106.6, 76.4, 60.1, 30.1, 29.1; IR (neat): 3052, 1660, 1603, 1490, 1264, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{20}N_3O_2$ 346.1550; Found 346.1561.

3ja': Dark brown sticky solid, 81 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5). ^{1}H NMR (400 MHz): δ 7.92 (dd, *J* = 7.82, 1.37 Hz, 1H), 7.37 (d, *J* = 1.06 Hz, 1H), 7.30 (t, *J* = 7.99 Hz, 1H), 7.24-7.18 (m, 2H), 7.02-6.97 (m, 2H), 6.89 (t, *J* = 7.49 Hz, 1H), 6.80 (t, *J* = 7.58 Hz, 1H), 6.57 (d, *J* = 8.22 Hz, 1H), 6.43 (s, 1H), 6.31 (dd, *J* = 3.20, 1.85 Hz, 1H), 6.26 (d, *J* = 3.07 Hz, 1H), 5.21 (dd, *J* = 7.88, 3.00 Hz, 1H), 4.99 (d, *J* = 7.72 Hz, 1H), 2.55-2.42 (m, 1H), 2.40-2.28 (m, 2H), 2.24-2.16 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz):

δ 154.7, 148.4, 145.6, 142.2, 134.1, 129.7, 129.2, 121.5, 118.4, 114.1, 112.7, 110.3, 106.8, 76.7, 55.0, 29.5, 29.3; IR (neat): 3272, 2923, 1658, 1603, 1490, 1389, 1236, 750; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{20}N_3O_2$ 346.1550; Found 346.1554.

*6-(Phenylamino)-6a,7,7a,8,9,10,11,11a-octahydroindolo[1,2-a]quinazolin-5(6H)-one (**3ka** and **3ka'**):* Reaction time: 18 h, **1k** (65.56 mg, 0.52 mmol), **2a** (100 mg, 0.44 mmol), **3ka** and **3ka'** (103 mg, 0.30 mmol), 70% yield.

3ka: off white solid, 31 m, R_f = 0.70 (EtOAc:Hexane = 2.5:7.5), mp 155-156 °C. ^{1}H NMR (400 MHz):δ 7.89 (dd, *J* = 7.83, 1.30 Hz, 1H), 7.34 (td, *J* = 7.46, 1.39 Hz, 1H), 7.24-7.18 (m, 2H), 6.94-6.86 (m, 3H), 6.78-6.68 (m, 2H), 6.36 (s, 1H), 5.26 (d, *J* = 7.39 Hz, 1H), 3.89-3.81 (m, 1H), 2.76 (bs, 1H), 2.39-2.30 (m, 1H), 2.26-2.10 (m, 2H), 1.77-1.67 (m ,3H), 1.56-1.50 (m, 1H), 1.38-1.16 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz): δ 148.3, 146.2, 140.6, 134.3, 132.8, 129.3, 129.0, 127.9, 127.8, 126.5, 126.0, 124.1, 123.9, 121.6, 119.0, 115.6, 114.8, 114.1, 77.2, 67.2, 33.7, 29.1; IR (neat): 2930, 1657, 1603, 1492, 1381, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{24}N_3O$ 334.1914; Found 334.1924.

3ka': off white solid, 72 mg, R_f = 0.65 (EtOAc:Hexane = 2.5:7.5), mp 155-157 °C. ^{1}H NMR (400 MHz): δ 7.89 (dd, *J* = 7.71, 1.13 Hz, 1H), 7.33 (t, *J* = 7.56 Hz, 1H), 7.26-7.19 (m, 2H), 6.95-6.86 (m, 3H), 6.73 (t, *J* = 7.48 Hz, 1H), 6.67 (d, *J* = 8.32 Hz, 1H), 6.34 (s, 1H), 5.30-5.18 (m, 1H), 3.97-3.88 (m, 1H), 2.53-2.42 (m, 1H), 2.41-2.27 (m, 2H), 2.19-2.11 (m, 1H), 1.80-1.66 (m ,3H), 1.57-1.50 (m, 1H), 1.47-1.15(m, 3H); ^{13}C{^{1}H} NMR (100 MHz): δ 148.4, 146.2, 140.1, 134.2, 133.4, 132.9, 129.7, 129.3, 129.0, 127.9, 127.8, 126.5, 126.0, 124.6, 124.2, 121.6, 121.3, 118.3, 115.7, 114.2, 113.0, 77.6, 61.2, 32.9, 28.6; IR (neat): 2932, 1655, 1603, 1492, 1382, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{24}N_3O$ 334.1914; Found 334.1913.

*1-(4-Methoxyphenyl)-4-(p-tolylamino)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ab** and **3ab'**):* Reaction time: 09 h, **1a** (87.63 mg, 0.49 mmol), **2b** (100 mg, 0.41 mmol), **3ab** and **3ab'** (128 mg, 0.32 mmol), 78% yield.

3ab: light yellow solid, 45 mg, R_f = 0.60 (EtOAc:Hexane = 2.5:7.5), mp 150-151 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.85, 1.56 Hz, 1H), 7.24-7.14 (m, 3H), 7.04 (d, *J* = 8.46 Hz, 2H), 6.92-6.78 (m, 5H), 6.42-6.36 (m, 2H), 5.56 (dd, *J* = 6.43, 2.74 Hz, 1H), 5.01 (dd, *J* = 7.85, 2.60 Hz, 1H), 3.81 (s. 3H), 2.73-2.62 (m, 1H), 2.48-2.40 (m, 1H), 2.31-2.20 (m ,4H), 1.91-1.83 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.8, 146.2, 145.8, 135.2, 134.2, 131.0, 129.7, 129.2, 126.7, 118.8, 115.5, 114.5, 114.3, 114.2, 77.03, 66.4, 55.4, 34.0, 29.1, 20.6; IR (neat): 3270, 2835, 1662, 1608, 1510, 1382, 1246, 1173, 813, 750; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_2$ 400.2020; Found 400.2016.

3ab': light yellow solid, 83 mg, R_f = 0.57 (EtOAc:Hexane = 2.5:7.5), mp 151-153 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.77, 1.42 Hz, 1H), 7.35 (d, *J* = 8.68 Hz, 2H), 7.20 (t, *J* = 7.77 Hz, 1H), 7.06 (d, *J* = 8.40 Hz, 2H), 6.98-6.87 (m, 4H), 6.77 (t, *J* = 7.37 Hz, 1H), 6.44 (s, 1H), 6.33 (d, *J* = 8.28 Hz, 1h), 5.23 (dd, *J* = 9.03, 4.97 Hz, 1H), 4.85 (dd, *J* = 8.57, 1.88 Hz, 1H), 3.80 (s. 3H), 2.52-2.32 (m, 2H), 2.30-2.21 (m ,4H), 1.99-1.92 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.9, 146.2, 145.9, 134.8, 134.1, 131.0, 129.7, 129.6, 127.1, 118.1, 115.7, 114.5, 114.3, 113.0, 77.5, 60.6, 55.3, 32.6, 28.7, 20.6; IR (neat): 3274, 2949, 1663, 1609, 1510, 1490, 1386, 1245, 813, 752; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_2$ 400.2020; Found 400.2016.

*4-((4-Isopropylphenyl)amino)-1-(4-methoxyphenyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ac** and **3ac'**):* Reaction time: 10 h, **1a** (78.35 mg, 0.44 mmol), **2c** (100 mg, 0.37 mmol), **3ac** and **3ac'** (125 mg, 0.29 mmol), 79% yield.

3ac: light yellow solid, 42.5 mg, R_f = 0.80 (EtOAc:Hexane = 2.5:7.5), mp 152-153 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, J = 7.75, 1.61 Hz, 1H), 7.24-7.16 (m, 3H), 7.09 (d, *J* = 8.46 Hz, 2H), 6.93-6.86 (m, 4H), 6.81 (t, *J* = 7.59 Hz, 1H), 6.42-6.37 (m, 2H), 5.57 (dd, *J* = 5.84, 2.55 Hz, 1H), 5.01 (dd, *J* = 7.72, 2.01 Hz, 1H), 3.81 (s, 3H), 2.87-2.79 (m, 1H), 2.75-2.64 (m, 1H), 2.52-2.42 (m, 1H), 2.31-2.21 (m ,1H), 1.92-1.83 (m, 1H), 1.20 (d, *J* = 6.90 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz): δ 158.8, 146.2, 146.1, 142.1, 135.3, 134.2, 129.2, 127.1, 126.7, 118.8, 115.6, 114.5, 114.28, 114.23, 77.02, 66.4, 55.4, 34.0, 33.4, 29.1, 24.2; IR (neat): 2958, 1662, 1608, 1382, 1264, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{30}N_3O_2$ 428.2333; Found 428.2343.

3ac': light yellow solid, 82.5 mg, R_f = 0.70 (EtOAc:Hexane = 2.5:7.5), mp 154-155 °C. ^{1}H NMR (400 MHz): δ 7.94 (d, *J* = 8.00 Hz, 1H), 7.35 (d, *J* = 8.52 Hz, 1H), 7.20 (t, *J* = 8.13 Hz, 1H), 7.11 (d, *J* = 8.30 Hz, 2H), 6.97 (d, *J* = 8.17 Hz, 2H), 6.90 (d, *J* = 8.73 Hz, 2H), 6.77 (t, *J* = 7.57 Hz, 1H), 6.45 (s, 1H), 6.33 (d, *J* = 8.17 Hz, 1H), 5.26-5.20 (m, 1H), 4.85 (d, *J* = 8.31 Hz, 1H), 3.80 (s, 3H), 2.87-2.79 (m, 1H), 2.53-2.33 (m, 2H), 2.30-2.23 (m, 1H), 1.99-1.93 (m ,1H), 1.20 (d, *J* = 6.89 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz): δ 158.9, 146.2, 142.1, 134.8, 134.1, 129.6, 127.2, 127.1, 118.1, 114.3, 113.0, 111.3, 77.3, 60.6, 55.3, 33.4, 32.6, 28.7, 24.2; IR (neat): 2923, 1664, 1609, 1491, 1379, 1245, 752; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{30}N_3O_2$ 428.2333; Found 428.2337.

*4-((4-Fluorophenyl)amino)-1-(4-methoxyphenyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a] quinazolin-5(1H)-one (**3ad** and **3ad'**):* Reaction time: 11 h, **1a** (60.34 mg, 0.34 mmol), **2d** (70 mg, 0.28 mmol), **3ad** and **3ad'** (90 mg, 0.22 mmol), 80% yield.

3ad: off white solid, 31 mg, R_f = 0.58 (EtOAc:Hexane = 2.5:7.5), mp 157-158 °C. ^{1}H NMR (400 MHz): δ 7.92 (dd, *J* = 7.78, 1.61 Hz, 1H), 7.21 (t, *J* = 7.71 Hz, 1H), 7.15 (d, *J* = 8.65 Hz, 2H), 6.96-6.86 (m, 6H), 6.80 (t, *J* = 7.58 Hz, 1H), 6.41-6.35 (m, 2H), 5.54

(dd, *J* = 6.30, 3.02 Hz, 1H), 5.00 (dd, *J* = 7.92, 2.68 Hz, 1H), 3.80 (s, 3H), 2.69-2.59 (m, 1H), 2.42-2.34 (m, 1H), 2.30-2.19 (m ,1H), 1.91-1.83 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 159.4, 158.9, 146.2, 144.3, 135.1, 134.3, 129.2, 126.7, 118.8, 115.9, 115.7, 115.6, 115.3, 114.6, 114.3, 77.05, 66.3, 55.4, 34.0, 29.1; IR (neat): 3054, 1665, 1608, 1421, 1381, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}FN_3O_2$ 404.1769; Found 404.1776.

3ad': off white solid, 59 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5), mp 157-159 °C. ^{1}H NMR (400 MHz): δ 7.94 (d, *J* = 8.00 Hz, 1H), 7.35 (d, *J* = 8.52 Hz, 1H), 7.20 (t, *J* = 8.13 Hz, 1H), 7.11 (d, *J* = 8.30 Hz, 2H), 6.97 (d, *J* = 8.17 Hz, 2H), 6.90 (d, *J* = 8.73 Hz, 2H), 6.77 (t, *J* = 7.57 Hz, 1H), 6.45 (s, 1H), 6.33 (d, *J* = 8.17 Hz, 1H), 5.26-5.20 (m, 1H), 4.85 (d, *J* = 8.31 Hz, 1H), 3.80 (s, 3H), 2.87-2.79 (m, 1H), 2.53-2.33 (m, 2H), 2.30-2.23 (m, 1H), 1.99-1.93 (m ,1H). $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 159.4, 159.0, 146.2, 134.7, 134.3, 129.6, 127.0, 118.2, 115.9, 115.8, 115.76, 115.70, 114.3, 113.0, 77.3, 60.6, 55.3, 32.6, 28.7; IR (neat): 3271, 2873, 1663, 1607, 1506, 1386, 1246, 754; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}FN_3O_2$ 404.1769; Found 404.1766.

*4-((4-Chlorophenyl)amino)-1-(4-methoxyphenyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a] quinazolin-5(1H)-one (**3ae** and **3ae'**):* Reaction time: 10 h, **1a** (80.93 mg, 0.45 mmol), **2e** (100 mg, 0.38 mmol), **3ae** and **3ae'** (129 mg, 0.30 mmol), 81% yield.

3ae: off white solid, 45 mg, R_f = 0.57 (EtOAc:Hexane = 2.5:7.5), mp 160-161 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.81, 1.32 Hz, 1H), 7.25-7.14 (m, 5H), 6.92-6.86 (m, 4H), 6.82 (t, *J* = 7.58 Hz, 1H), 6.43-6.38 (m, 2H), 5.55 (dd, *J* = 5.68, 2.64 Hz, 1H), 5.01 (d, *J* = 7.29 Hz, 1H), 3.81 (s, 3H), 2.71-2.60 (m, 1H), 2.43-2.33 (m, 1H), 2.31-2.20 (m ,1H), 1.93-1.84 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 158.9, 147.0, 146.2, 135.0, 134.4,

129.26, 129.0, 126.7, 126.3, 118.9, 115.4, 115.2, 114.6, 114.3, 77.02, 66.3, 55.4, 34.0, 29.1; IR (neat): 3263, 2835, 1658, 1606, 1488, 1382, 1244, 750; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}ClN_3O_2$ 420.1473; Found 420.1483.

3ae': off white solid, 84 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5), mp 161-162 °C. ^1H NMR (400 MHz): δ 7.94 (dd, *J* = 7.77, 1.60 Hz, 1H), 7.33 (d, *J* = 8.45 Hz, 2H), 7.24-7.17 (m, 3H), 7.00-6.94 (m, 2H), 6.90 (d, *J* = 8.75 Hz, 2H), 6.78 (t, *J* = 7.38 Hz, 1H), 6.52 (s, 1H), 6.35 (d, *J* = 8.21 Hz, 1H), 5.25-5.15 (m, 1H), 4.85 (d, *J* = 9.28 Hz, 1H), 3.80 (s, 3H), 2.54-2.42 (m, 1H), 2.38-2.21 (m, 2H), 2.00-1.93 (m ,1H); $^{13}C\{^1H\}$ NMR (100 MHz): δ 159.0, 147.0, 146.2, 134.6, 134.3, 129.6, 129.2, 127.0, 126.3, 118.3, 115.5, 114.3, 113.8, 113.1, 77.5, 60.6, 55.4, 32.5, 28.6; IR (neat): 3053, 2837, 1666, 1608, 1490, 1378, 1263, 731; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}ClN_3O_2$ 420.1473; Found 420.1470.

*4-((4-Bromophenyl)amino)-1-(4-methoxyphenyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a] quinazolin-5(1H)-one (**3af** and **3af'**):* Reaction time: 10 h, **1a** (69.27 mg, 0.39 mmol), **2f** (100 mg, 0.33 mmol), **3af** and **3af'** (124 mg, 0.27 mmol), 81% yield.

3af: white solid, 42 mg, R_f = 0.53 (EtOAc:Hexane = 2.5:7.5), mp 153-154 °C. ^1H NMR (400 MHz): δ 7.91 (dd, *J* = 7.75, 1.37 Hz, 1H), 7.31 (d, *J* = 8.69 Hz, 2H), 7.24-7.19 (m, 1H), 7.15 (d, *J* = 8.69 Hz, 2H), 6.89 (d, *J* = 8.74 Hz, 2H), 6.84-6.78 (m, 3H), 6.41-6.34 (m, 2H), 5.53 (dd, *J* = 5.67, 2.22 Hz, 1H), 5.00 (dd, *J* = 7.75, 1.70 Hz, 1H), 3.80 (s, 3H), 2.70-2.59 (m, 1H), 2.40-2.32 (m, 1H), 2.29-2.19 (m ,1H), 1.91-1.84 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz): δ 158.9, 146.2, 135.0, 134.4, 132.1, 129.2, 126.7, 126.3, 118.9, 155.9, 115.4, 115.2, 114.3, 113.6, 77.04, 66.3, 55.4, 34.0, 29.1; IR (neat): 3266, 2834, 1660, 1607, 1487, 1379, 1244, 752; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}BrN_3O_2$ 464.0968; Found 464.0966.

3af': white solid, 82 mg, R_f = 0.50 (EtOAc:Hexane = 2.5:7.5), mp 156-157 °C. ^{1}H NMR (400 MHz): δ 7.92 (dd, *J* = 7.82, 1.34 Hz, 1H), 7.36-7.29 (m, 4H), 7.21 (t, *J* = 7.82 Hz, 1H), 6.95-6.85 (m, 4H), 6.77 (t, *J* = 7.43 Hz, 1H), 6.48 (s, 1H), 6.33 (d, *J* = 8.16 Hz, 1H), 5.26-5.12 (m, 1H), 4.84 (dd, *J* = 9.16, 1.39 Hz, 1H), 3.79 (s, 3H), 2.53-2.41 (m, 1H), 2.36-2.19 (m, 2H), 1.99-1.92 (m ,1H); ^{13}C{^{1}H} NMR (100 MHz): δ 159.0, 146.2, 134.6, 134.3, 132.1, 129.6, 127.0, 118.3, 115.9, 114.3, 113.6, 113.1, 77.5, 60.6, 55.4, 32.5, 28.6; IR (neat): 3053, 1664, 1607, 1487, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}BrN_3O_2$ 464.0968; Found 464.0963.

*4-(Benzylamino)-1-(4-methoxyphenyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a] quinazolin-5(1H)-one (**3ag** and **3ag'**):* Reaction time: 10 h, **1a** (43.81 mg, 0.24 mmol), **2g** (50 mg, 0.20 mmol), **3ag** and **3ag'** (65 mg, 0.16 mmol), 81% yield.

3ag: white crystalline solid, 13 mg, R_f = 0.65 (EtOAc:Hexane = 2.5:7.5), mp 139-141 °C. ^{1}H NMR (400 MHz): δ 7.95 (dd, *J* = 7.81, 1.51 Hz, 1H), 7.46-7.42 (m, 2H), 7.38-7.27 (m, 3H), 7.19-7.12 (m, 3H), 6.88 (d, *J* = 8.70 Hz, 2H), 6.81 (t, *J* = 7.67 Hz, 1H), 6.32 (d, *J* = 8.16 Hz, 1H), 5.36 (dd, *J* = 5.98, 3.16 Hz, 1H), 5.09 (dd, *J* = 8.30, 4.38 Hz, 1H), 4.83 (dd, *J* = 7.77, 3.52 Hz, 1H), 4.19 (dd, *J* = 11.42, 4.11 Hz, 1H), 3.93 (dd, *J* = 11.15, 8.56 Hz, 1H), 3.81 (s, 3H), 2.53-2.41 (m, 2H), 2.33-2.23 (m, 1H), 1.83-1.73 (m ,1H); ^{13}C{^{1}H} NMR (100 MHz): δ 158.7, 146.0, 137.4, 135.7, 133.8, 129.4, 128.7, 128.6, 127.8, 126.7, 118.7, 115.7, 114.5, 114.2, 77.3, 76.5, 66.3, 56.2, 55.4, 33.6, 29.9; IR (neat): 3274, 2858, 1645, 1605, 1491, 1381, 1245, 744; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_2$ 400.2020; Found 400.2014.

3ag': white crystalline solid, 52 mg, R_f = 0.60 (EtOAc:Hexane = 2.5:7.5), mp 141-142 °C. ^{1}H NMR (400 MHz): δ 7.94 (dd, *J* = 7.78, 1.69 Hz, 1H), 7.46-7.42 (m, 2H), 7.37-7.27 (m, 3H), 7.21 (d, *J* = 8.70 Hz, 2H), 7.16 (t, *J* = 7.74 Hz, 1H), 6.84 (d. *J* = 8.70 Hz,

2H), 6.75 (t, *J* = 7.47 Hz, 1H), 6.25 (d, *J* = 8.24 Hz, 1H), 5.23-5.11 (m, 1H), 5.01 (dd, *J* = 9.13, 5.04 Hz, 1H), 4.77 (d, *J* = 9.21 Hz, 1H), 4.25 (dd, *J* = 11,52, 3.93 Hz, 1H), 4.06 (dd *J* = 11.63, 7.51 Hz, 1H), 3.78 (s, 3H), 2.45-2.34 (m, 1H), 2.31-2.23 (m, 2H), 2.22-2.10 (m ,1H), 1.90-1.83 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 158.8, 145.7, 137.6, 134.9, 133.8, 129.5, 129.1, 128.5, 127.8, 127.1, 117.8, 115.6, 114.1, 112.8, 77.3, 76.8, 60.5, 56.5, 55.3, 32.5, 29.2; IR (neat): 3054, 2986, 1653, 1607, 1491, 1378, 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_2$ 400.2020; Found 400.2018.

As mentioned in the cycloaddition reaction, two diastereomers (cis and trans) have been formed. These diastereomers are very close in polarity in case of **3ah** and **3ai**, thus difficult to separate from column. So, the diastereomeric mixture was separated from the column as such. ^{1}H NMR of the mixture have been reported herein.

*4-Benzyl-1-(4-methoxyphenyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ah** and **3ah'**):* Reaction time: 08 h, **1a** (93.44 mg, 0.52 mmol), **2h** (100 mg, 0.44 mmol), **3ah** and **3ah'** (139 mg, 0.36 mmol), 82% yield.

3ah and **3ah':** light yellow semisolid, 139 mg, R_f = 0.56 (EtOAc:Hexane = 2.5:7.5). ^{1}H NMR (400 MHz): δ 8.03 (d, *J* = 7.87 Hz, 2H), 7.38-7.26 (m, 9H), 7.24-7.08 (m, 7H), 6.87-6.74 (m, 6H), 6.29 (d, *J* = 8.20 Hz, 1H), 6.25 (d, *J* = 8.37 Hz, 1H), 5.39 (t, *J* = 5.69 Hz, 1H), 5.19 (d, *J* = 15.49 Hz, 1H), 5.04-4.97 (m, 2H), 4.79 (dd, *J* = 7.95, 5.69 Hz, 1H), 4.72 (d, *J* = 8.79 Hz, 1H), 4.65 (d, *J* = 15.58 Hz, 1H), 4.60 (d, *J* = 15.66 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.50-2.31 (m, 2H), 2.29-2.04 (m, 4h), 1.90-1.83 (m, 1H), 1.73-1.64 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 165.7, 164.2, 158.8, 158.7, 145.7, 145.5, 137.5, 137.3, 135.8, 134.9, 133.6, 133.5, 129.7, 129.3, 128.7, 128.6, 127.7, 127.6, 127.4, 127.3, 127.0, 126.6, 118.0, 116.7, 115.2, 114.3, 114.1, 113.5, 112.6, 73.98, 73.92, 64.7, 59.6, 55.37, 55.34, 46.7, 46.6, 33.6, 32.5, 31.4, 28.7; IR (neat):

2929, 1712, 1649, 1605, 1511, 1493, 1247, 753; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{25}N_2O_2$ 383.1765; Found 383.1761.

*1-(4-Methoxyphenyl)-4-phenyl-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**3ai** and **3ai'**):* Reaction time: 09 h, **1a** (89.63 mg, 0.50 mmol), **2i** (90 mg, 0.42 mmol), **3ai** and **3ai'** (124 mg, 0.33 mmol), 80% yield.

3ai and **3ai':** light yellow semisolid, 124 mg, R_f = 0.50 (EtOAc:Hexane = 2.5:7.5). ^{1}H NMR (400 MHz): δ 8.03-7.97 (m, 1H), 7.46-7.40 (m, 2H), 7.35-7.17 (m, 5H), 6.92-6.75 (m, 4H), 6.35 (d, J = 8.34 Hz, 1H), 5.49 (dd, J = 9.11, 5.09 Hz, 1H), 4.85 (d, J = 9.73 Hz, 1H), 3.77 (s, 3H), 2.48-2.36 (m, 1H), 2.10-1.92 (m, 1H), 1.91-1.79 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz): δ 165.6, 158.9, 145.8, 139.2, 134.9, 133.8, 133.7, 129.8, 129.5, 129.3, 128.0, 127.7, 127.1, 126.9, 119.0, 118.1, 117.2, 115.0, 114.2, 112.8, 75.4, 75.1, 66.0, 60.3, 55.4, 55.3, 33.7, 32.6, 30.7, 30.3.; IR (neat): 3053, 2836, 1723, 1652, 1605, 1491, 1389, 1246, 731; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{23}N_2O_2$ 371.1754; Found 371.1767.

Representative procedure for the reaction of cyclopropane aldehyde (1a) and anthranil hydrazide (2a). A round bottom flask equipped with magnetic stirrer bar was charged with 4-methoxyphenyl cyclopropane aldehyde **1a** (0.26 mmol, 1.2 equiv) and anthranil hydrazide **2a** (0.22 mmol, 1 equiv), to which DCM (1 mL) was added, and the mixture was stirred at room temperature till the completion of reaction (as monitered by TLC). The excess of the solvent was evaporated on a rotary evaporator. The crude mixture obtained was further purified by column chromatography on silica gel using ethyl acetate/hexane as eluent.

As mentioned in the cycloaddition reaction, two diastereomers (cis and trans) have been formed. These diastereomers are very close in polarity, thus difficult to separate

from column. Thus, the diastereomeric mixture was separated from the column as such. ^{1}H NMR of the mixture (1:1) have been reported herein.

*2-(2-(4-methoxyphenyl)cyclopropyl)-3-(phenylamino)-2,3-dihydroquinazolin-4(1H)-one (**4**):* Reaction time: 14 h, **1a** (46.48 mg, 0.26 mmol), **2a** (50 mg, 0.22 mmol), **4** (51 mg, 0.13 mmol), 60% yield.

4: off white solid, 51 mg, R_f = 0.50 (EtOAc:Hexane = 2.5:7.5), mp 169-170 °C. ^{1}H NMR (400 MHz): δ 7.93-7.88 (m, 2H), 7.38-7.29 (m, 2H), 7.24-7.19 (m, 4H), 7.00-6.83 (m, 12H), 6.79-6.68 (m, 8H), 4.71 (bs, 1H), 4.70 (bs, 1H), 4.38 (dd, *J* = 7.76, 2.29 Hz, 1H), 4.34 (dd, *J* = 8.71, 1.89 Hz, 1H), 3.75 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 2.18-2.10 (m, 1H), 1.82-1.67 (m, 3H), 1.02-0.95 (m, 1H), 0.90-0.76 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz): δ 163.7, 163.5, 158.1, 147.1, 146.9, 146.2, 146.1, 134.2, 134.1, 132.9, 132.7, 129.3, 128.9, 128.8, 127.3, 121.5, 119.4, 114.9, 114.7, 113.9, 113.93, 113.8, 76.9, 76.8, 55.4, 25.3, 25.2, 21.3, 19.2, 13.6, 10.6; IR (neat): 3305, 2928, 1645, 1609, 1513, 1492. 1246, 1032, 753; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{24}N_3O_2$ 386.1863; Found 386.1859.

Representative procedure for the reaction of cyclopropanealdehyde (1a) and *N*-methyl anthranil hydrazide (2j). A round bottom flask equipped with magnetic stirrer bar was charged with PTSA (0.06 mmol, 0.3 equiv). A solution of 4-methoxyphenyl cyclopropane aldehyde **1a** (0.24 mmol, 1.2 equiv) and *N*-methyl anthranil hydrazide **2j** (0.22 mmol, 1 equiv) in DCM (1 mL) was added to it, and the mixture was stirred at room temperature till the completion of reaction (as monitered by TLC). The excess of the solvent was evaporated on a rotary evaporator. The crude mixture obtained was further purified by column chromatography on silica gel using ethyl acetate/hexane as eluent.

*2-(2-(4-methoxyphenyl)cyclopropyl)-1-methyl-3-(phenylamino)-2,3-dihydroquinazolin-4(1H)-one (**5**):* Reaction time: 10 h, **1c** (39.83 mg, 0.24 mmol), **2j** (50 mg, 0.20 mmol), **5** (69 mg, 0.172 mmol), 86% yield.

5: white crystalline solid, 69 mg, R_f = 0.55 (EtOAc:Hexane = 2.5:7.5), mp 174-176 °C. ^{1}H NMR (400 MHz): δ 7.96 (dd, *J* = 7.77, 1.42 Hz, 1H), 7.40 (td, J = 7.93, 1.85 Hz, 1H), 7.28-7.22 (m, 2H), 6.98-6.85 (m, 6H), 6.80 (s, 1H), 6.76 (d, *J* = 8.72 Hz, 2H), 6.66 (d, *J* = 8.35 Hz, 1H), 4.19 (d, *J* = 9.14 Hz, 1H), 3.75 (s, 1H), 3.08 (s, 1H), 1.85-1.79 (m, 1H), 1.32-1.24 (m, 2H), 0.98-0.89 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz): δ 158.0, 147.2, 146.6, 134.3, 132.7, 129.4, 128.9, 127.0, 121.6, 118.5, 115.5, 114.0, 113.7, 112.4, 83.3, 77.3, 55.3, 36.5, 22.4, 20.6, 11.0; IR (neat): 3261, 3053, 1657, 1603, 1492. 1263, 732; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N_3O_2$ 400.2020; Found 400.2028.

*Procedure for the sequential One-Pot Synthesis of **3aa**.* A round-bottom flask equipped with a magnetic stir bar was charged with Isatoic anhydride **7** (0.30 mmol, 1 equiv) and phenyl hydrazine **8** (0.30 mmol, 1 equiv) and dry ACN (2 mL) was added to it under nitrogen atmosphere. Reaction was stirred under reflux for 8 hours till formation of the anthranil hydrazide **2a.** After full consumption of the starting materials (as monitored by TLC), a ACN (0.5 mL) solution of 4-methoxyphenyl cyclopropane aldehyde **1a** (0.33 mmol mg, 1.1 equiv) and p-TSA (0.061 mmol, 30 mol%) was added, and the mixture was refluxed overnight until completion of the reaction (as monitored by TLC). The excess of the solvent was evaporated on a rotary evaporator. The crude mixture obtained was further purified by column chromatography on silica gel using ethyl acetate/hexane as eluent to afford the required compound **3aa** with 50% yield.

*Procedure for the debenzylation of **3ag**.*[13f] To the solution of **3ag** (0.050 g, 0.12 mmol) in methanol (3 ml) was added 10% Pd/C and then hydrogenated at 45 psi. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered over a bed of celite, washed with methanol (5 ml) and concentrated in vacuo. The crude product was further purified by column chromatography on silica gel (60–120 mesh) using 30% ethyl acetate/hexane (3:7 *v/v*) as eluent to afford **9**.

*4-amino-1-(4-methoxyphenyl)-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazolin-5(1H)-one (**9**):* Reaction time: 12 h, **3ag** (0.050 g, 0.12 mmol), **9** (0.028 g, 0.097 mmol), Yield: 73%, Nature: White sticky solid, R_f = 0.25 (ethyl acetate/hexane 40:60), ^{1}H NMR (400 MHz): δ 7.92 (dd, *J* = 7.74, 1.79 Hz, 1H), 7.20-7.12 (m, 3H), 6.92-6.86 (m, 2H), 6.78 (t, *J* = 7.51 Hz, 1H), 6.31 (d, *J* = 8.34 Hz, 1H), 5.43 (t, *J* = 4.99 Hz, 1H), 4.85 (dd, *J* = 8.00, 4.13 Hz, 1H), 4.36 (s, 2H), 3.81 (s, 3H), 2.63-2.54 (m, 1H), 2.49-2.28 (m, 2H), 1.89-1.80 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz): δ 165.7, 163.5, 158.8, 145.8, 135.7, 133.7, 128.6, 126.8, 126.7, 118.6, 115.2, 114.3, 76.6, 66.1, 55.4, 33.4, 30.7; IR (neat): 3027, 2927, 1651, 1608, 1510, 1492, 1378, 1264, 895, 733 cm^{-1}, HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{20}N_3O_2$ 310.1550; Found 310.1552.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information contains ^{1}H NMR, ^{13}C NMR, IR spectra, and mass data of all new compounds (PDF), single crystal X-ray data and images for **3ag, 3ag'** and **5** (**CIF**).

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Notes

The authors declare no competing financial interests.

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