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Probing Carbocatalytic Activity of Carbon Nanodots for the Synthesis of Biologically Active Dihydro/Spiro/Glyco Quinazolinones and aza-Michael Adducts

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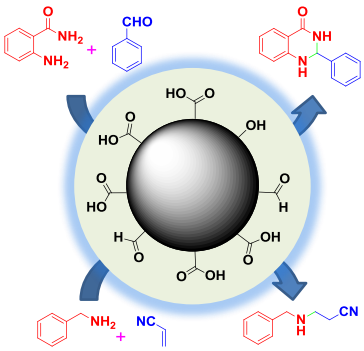


ABSTRACT: Herein, we report the fluorescent carbon dots as an effective and recyclable carbocatalyst for the generation of carbon-hetero atom bond leading to quinazolinone derivatives and aza- Michael adducts under mild reaction conditions. The results establish this nanoscale form of carbon as an alternative carbocatalyst for important acid catalyzed organic transformations. The mild surface acidity of carbon dots imparted by –COOH functionality could effectively catalyze the formation of synthetically challenging spiro/glycoquinazolinones under the present reaction conditions.

INTRODUCTION

Acid catalyzed processes play a key role in modern organic synthesis.[1] Traditional acid catalysts including mineral acids such as sulphuric acid and organic acids such as *p*-toluenesulphonic acid give rise to serious disadvantages like corrosion, toxicity, separation of catalysts from homogeneous reaction mixtures and necessity of neutralization of waste streams which impedes their commercialization.[2] Development of solid acid catalysts with a

possibility to tune the surface properties including acidic functionalities might be important in controlling the yield and selectivity of the products. Carbonaceous materials such as carbon nanotube and graphene oxide have been extensively used as carbocatalysts or as supports for immobilization of catalytically active species.[3] With the emphasis on catalytic materials with extensive environmental footprint towards green and sustainable chemistry, the exploitation of the inherent catalytic activity induced by the surface functionality of the carbonaceous materials is of continuous quest to afford a highly benign and affordable synthesis.[4] For example, the carboxylic acid and epoxide functionalities on graphene oxide (GO) have been exploited as catalytic sites for important organic transformations such as oxidation and hydration reactions,[5] aza-Michael addition reaction,[6] ring-opening reactions,[7] Friedel-Crafts reaction,[8] multi-component coupling reactions[9] etc. However, harsh reaction conditions involving use of strong oxidizing agents such as conc. H_2SO_4 and $KMnO_4$ in the synthesis of GO and possible involvement of trace metals on GO surfaces during catalytic reactions demands designing more environmentally benign alternative carbocatalysts.[10] Carbon nanodots (CND), a fluorescent form of carbon, have attracted tremendous research activities in recent years owing to their ease of synthesis through a metal-free pathway, tunable emission properties, biocompatibility, water-solubility and easy surface functionalization.[11] Depending on the carbon source used for the synthesis of CNDs, tailored surface functionality can be achieved.[12] The presence of –COOH functionality on the CND surface can be exploited for the acid catalysed organic transformations in a recyclable pathway to achieve an efficient and sustainable synthesis of organic feedstocks following green protocols. The photocatalytic activity of CNDs has been exploited for environmental remediation, H_2 production, CO_2 reduction and organic synthesis.[13] CNDs have also been used as surface stabilizing agents for nanoparticles for effective catalytic activities.[14]

However, few studies have focussed on exploring the surface functionality on CNDs as catalytic sites for important organic transformations.[15]

2,3-Dihydroquinazolinones and aza-Michael adducts are important classes of organic compounds as potent building blocks for important natural products and as probes in biological applications.[16-17] These compounds display wide range of biological activities as antitumor, antidefibrillatory, antidepressant, analgesic, diuretic, antihistamine, vasodilating agent, antihypertensive, CNS stimulant, tranquilizer and antianxietic.[16] Several acid catalysts such as β-cyclodextrin,[18] ionic liquids,[19] quaternary ammonium salts,[20] silica sulfuric acid,[21] montmorillonite K-10,[22] cyanuric chloride,[16a] β-cyclodextrin-SO_3H,[23] Cu-CNTs[24] etc. have been developed for generating carbon-heteroatom bonds in aza-Michael adducts and quinazolinones. Although, these catalysts have shown efficacy with respect to yield of the products but several of these catalytic systems suffer from certain disadvantages such as tedious catalyst preparation involving laborious surface modifications, high reaction temperature, prolonged reaction time and extensive work-up procedures. In some cases, catalysts had to be surface passivated using strong acids such as conc. H_2SO_4 to obtain milder reaction conditions. Although carbonaceous nanomaterials such as GO have shown high activity towards acid-catalyzed organic transformations, the catalytic activity of their zero-dimensional counterpart CNDs has not been explored yet. This prompted us to investigate the inherent catalytic ability of –COOH surface functionalized CNDs towards carbon-heteroatom bond formation. β-carotene was employed as the carbon source to generate CNDs. The prime motive to use β-carotene was that unlike most of the carbon sources used to make CNDs,[25] β-carotene doesn't have any oxygen functionality present in it. The catalytic activity of the CNDs is driven only by the surface –COOH groups generated during the carbonization of β-carotene. The ease of synthesis of CNDs from easily available carbon sources through simple microwave or hydrothermal treatment and with their non-toxic and biocompatible properties,

CNDs can overcome numerous intricacies associated with other catalytic systems towards the synthesis of 2, 3-Dihydroquinazolinones and aza-Michael adducts through a mild reaction pathway. Recently, Li *et al*. have shown the photocatalytic activity of sulphated graphene quantum dots in visible light induced ring opening reactions.[26] The efficient catalytic activity of carboxylic acid functionalized CNDs, as reported herein, towards the synthesis of biologically active dihydro/spiroquinazolinones and quinazolinone-glyco- conjugates along with aza-Michael adducts demonstrate the potential of this carbonaceous nanodots as a non-toxic, biocompatible and recyclable acid catalyst for organic transformations of biological relevance.

RESULTS AND DISCUSSION

The CNDs were synthesized by a hydrothermal treatment of β-carotene in water (details in experimental section). It is worth mentioning that β-carotene is totally insoluble in water. However, upon hydrothermal treatment, it resulted in a yellow dispersion of carbon dots. The solution exhibited strong fluorescence under UV light (λ_{ex} = 365 nm) (Fig. S1). The as synthesized CNDs exhibited maximum emission at 468 nm when excited at 370 nm and photoluminescence shifted to longer wavelengths with increasing excitation wavelengths, a typical behaviour of CNDs (Fig. 1a). Transmission electron microscopy (TEM) images showed the formation of well-dispersed spherical nanoparticles with average particle diameter of 3.5 ± 0.8 nm (Fig. 1b). High resolution TEM image showed the formation of highly crystalline CNDs as evidenced by the appearance of lattice fringes signifying the (102) lattice plane of graphitic (sp2) carbon (Fig. S2a). AFM studies validated the formation of CNDs with particle sizes in the range of 3.5-5.5 nm (Fig. 1c) and their contour heights between 1 and 2 nm (Fig. S2c). Further, X-ray photoelectron spectroscopy (XPS) measurements revealed the structural features of C-dots. The C1s core level spectrum of C-dot was fitted into four components with binding energies (BEs) at about 285.1, 286.8, 287.8

and 289.0 eV, which correspond to C-C, C-OH, C=O and O-C=O respectively (Fig. 1d). Powder X-ray diffraction spectra of CNDs showed a broad peak at 2θ = 23°, corresponding to a d-spacing of 3.8 Å (Fig. S2b). The presence of hydroxyl and carboxylic acid functionality on CND surface was further confirmed by FTIR studies (Fig. S4c). To quantify the hydroxyl and carboxyl groups present on the surface of CNDs, base titrations were performed (details in experimental section).

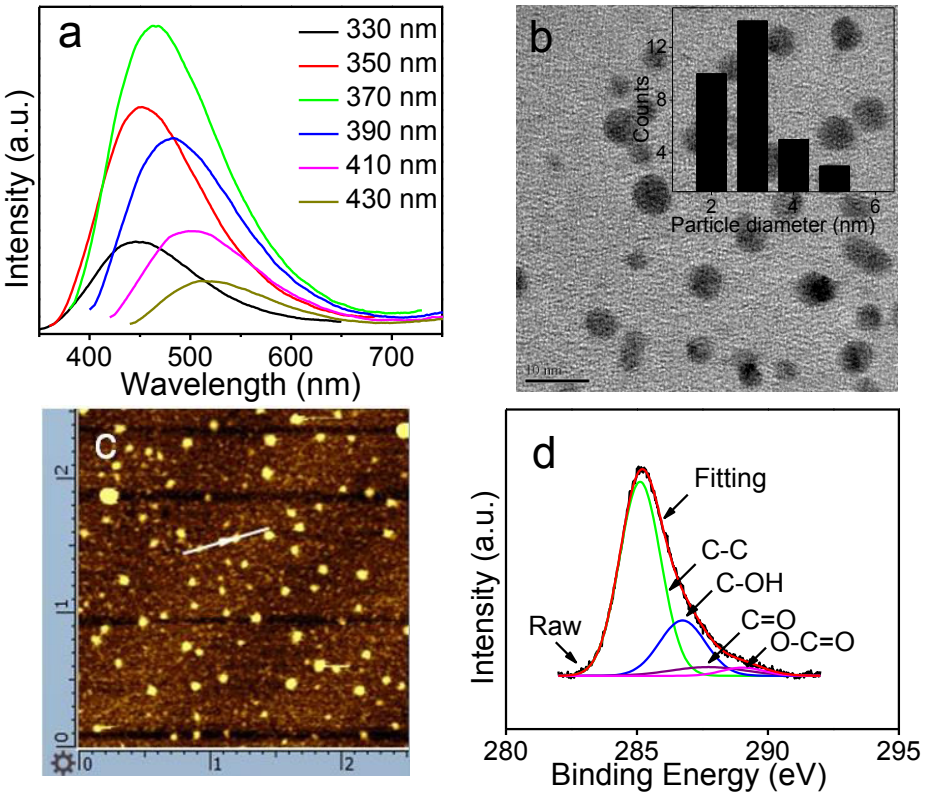
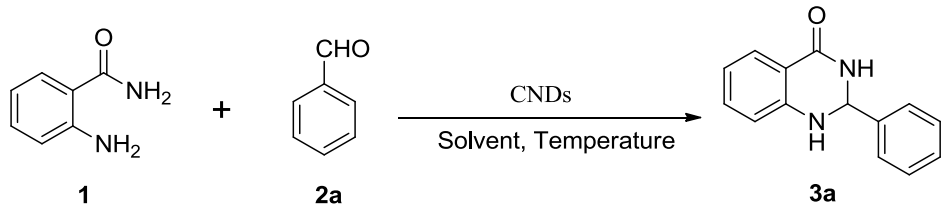


Figure 1: (a) Excitation dependent emission spectrum of CNDs, (b) TEM image of CNDs (scale bar 10 nm), particle size distribution histogram (inset b), (c) AFM image of CNDs and (d) C1s XPS of CNDs.

The activity of –COOH functionalized CNDs in acid catalysed organic transformations was studied for the cyclocondensation reaction between 2-aminobenzamide and aldehydes leading to the formation of 2,3-dihydroquinazolinon-4(*1H*)-one (Scheme 1). The model reaction of condensation between 2-aminobenzamide and benzaldehyde was

studied with respect to temperature, catalyst loading and solvent variation in order to achieve the

Scheme 1: Model cyclocondensation reaction leading to the formation of 2,3-dihydroquinazolinon-4(1H)-one



1 2a 3a

optimized reaction condition (Table 1 and Table 2). The reaction was highly dependent on catalyst loading, as higher conversion was observed with increasing concentration of CNDs.

Table 1: Optimisation with respect to catalyst loading and temperature[a]

Entry	Catalyst loading (mg)	Temp. (°C)	Time (min)	Yield (%)[b]
1	0	25	150	45
2	1.0	25	120	62
3	3.0	25	90	65
4	5.0	25	70	76
5	5.0	40	55	97
6	7.0	40	50	97
7	5.0	40	40	79
8	5.0	40	120	[c]55
9	5.0	40	55	[d]95

[a]All the reactions were carried out using 2-aminobenzamide 1 (1.0 mmol), benzaldehyde 2a (1.0 mmol), in water-acetonitrile (9:1) mixture as solvent (11 ml). The amount of CND in the reaction medium was varied by using a parent solution of 0.6 $mgmL^{-1}$ concentration in water. [b]Isolated yields. [c]The reaction was carried out by using 5 mg rCNDs. [d]The reaction was performed under dark environment.

Although the conversion was moderate at room temperature, increasing the reaction temperature to 40 °C resulted in high yield of the desired product. Further increase in temperature was detrimental for the reaction as several by-products were observed. Although the reaction preceded well using water as the solvent, longer reaction time was required. This can be attributed to the low solubility of the substrates in water. Addition of a small amount of an organic solvent enhanced the yield minimizing the reaction time. From these optimization studies, the best condition for this condensation reaction was found to be 10 mL of CND solution with 0.5 $mgmL^{-1}$ concentration at 40 °C using acetonitrile as a co-solvent. Reduced CNDs resulted in less yield of the desired product even after prolonged reaction time, suggesting the role of –COOH functionality on CNDs in catalyzing the reaction (Table 1, entry 8). Further, the model reaction was performed under a dark environment to ensure that the catalytic activity is due to the surface acidity of the CNDs and

Table 2: Optimisation with respect to co-solvents[a]

Entry	Solvent (mL)	Time (min)	Yield (%)[b]
1	-	75	68[c]
2	Ethanol	85	90
3	Methanol	90	88
4	Acetonitrile	55	97
5	Toluene	120	65
6	THF	60	85
7	DCM	80	81

[a]All the reactions were carried out using 10 mL of carbon dot solution in water (0.5 $mgmL^{-1}$) with co-solvent (1 mL), 2-aminobenzamide 1 (1.0 mmol), benzaldehyde 2a (1.0 mmol) at 40 °C. [b]Isolated yields. [c]Reaction was performed in aqueous carbon dot solution.

not induced by exposed daylight. Indeed, we found excellent result even when the reaction was carried out in dark (Table 1, entry 9). A comparative study was carried out using other carbonaceous materials such as graphene oxide, graphite, multiwall carbon nanotubes and β-cycoldextrin (Table 3) under the optimized reaction condition. The results clearly demonstrated the comparable catalytic activity of CNDs with GO, whereas the others gave moderate yield. For further comparison the model reaction was performed with some common acid catalysts such as conc. H_2SO_4, *p*TSA, benzoic acid and glacial acetic acid (Table 3) where conc. H_2SO_4 and *p*TSA were found to give excellent yields. Although from this comparative study we found GO, conc. H_2SO_4 and *p*TSA to be effective with respect to the product yield, the disadvantages associated with these catalysts as discussed earlier make CNDs a viable alternative for acid-catalyzed reactions.

Table 3: Catalytic activity of different carbon based catalysts and acid catalysts[a]

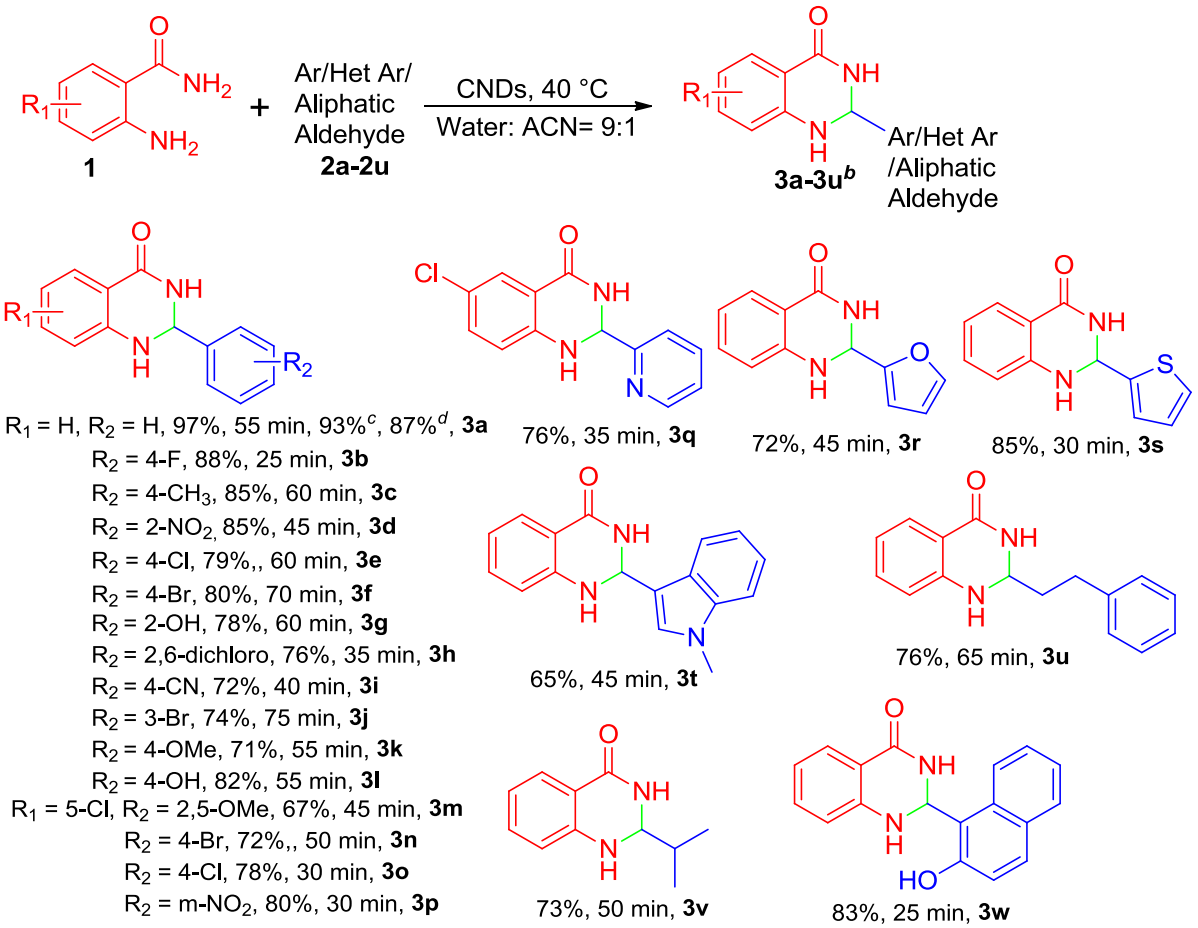
Entry	Catalysts	Yield (%)[b]
1	Graphene Oxide	98
2	Graphite	64
3	MWCNT	55
4	*β*-Cyclodextrin	66
5	CNDs	97
6	Conc. H_2SO_4	92
7	*p*-CH_3-C_6H_4-SO_3H	91
8	C_6H_5-COOH	59
9	CH_3COOH	57

[a]All the reactions were carried out using 2-aminobenzamide 1 (1.0 mmol), benzaldehyde 2a (1.0 mmol), 5 mg catalyst in water-acetonitrile solvent (11 ml) at 40 °C. [b]Isolated yields.

After the initial assessment of the optimal reaction conditions, we investigated the scope of the reaction by condensing 2-aminobenzamide with various commercially available aromatic aldehydes having different electronically activating or deactivating substituents to form a

series of dihydroquinazolines (Table 4). It was found that aldehydes with electron withdrawing substituents resulted in better yields compared to the ones with electron donating substituents. This can be attributed to the increased electrophilicity of the carbonyl moiety in the aldehydes with electron-withdrawing substituents. It was observed that

Table 4: Substrate scope of the cyclocondensation reaction with various aromatic/heteroaromatic/aliphatic aldehydes.[a]



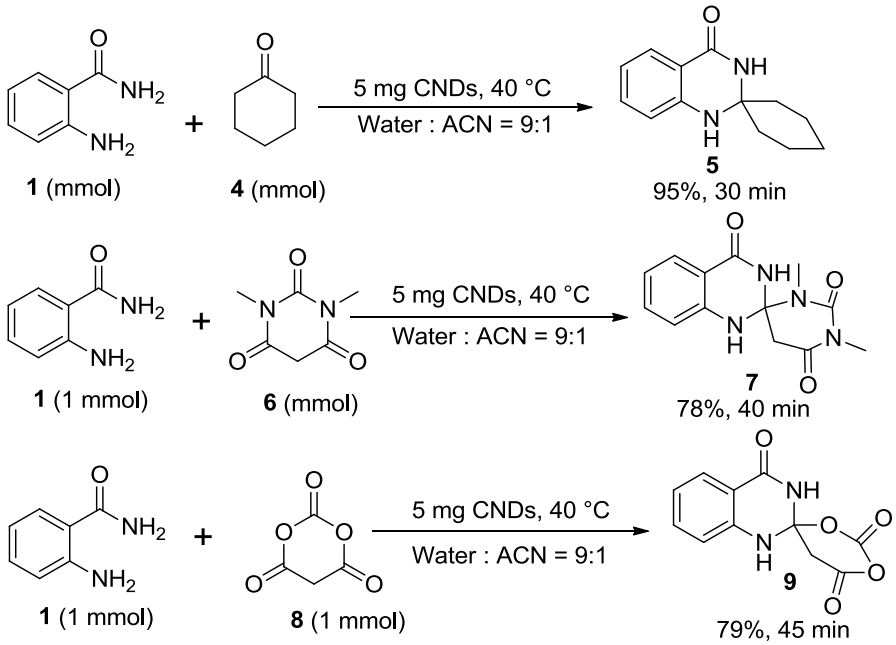
[a]All the reactions were carried out using **1** (1.0 mmol), aldehyde **2a-2u** (1.0 mmol), CND dispersion in water (10 ml)(0.5 mgmL^{-1}) and acetonitrile (1 mL) at 40 °C. [b] Isolated yields. [c,d]2nd and 3rd cycle respectively performed for 1 hr.

heterocyclic aldehydes having pyridine, furan, thiophene and indole moiety (entry 3q-3t, table 4) were equally compatible with the catalytic system and were easily introduced to the

dihydroquinazolinone skeleton with excellent yields. The feasibility of the reaction was also investigated with aliphatic aldehydes that resulted in considerable formation of the dihydroquinazoline derivative (entry 3v, table 4). Aldehydes with fused ring systems were also found to be active under the set of reaction conditions and resulted in adequate yield (entry 3w, table 4). To further expand the scope of the reaction, we performed the condensation reaction of aldehydes with 2-amino-5-chlorobenzamide and the yield of the dihydroquinazoline product was found to be excellent showing the efficient activity of CNDs with substituted 2-aminobenzamide as well.

After the successful exploration of CND catalysis for the condensation reaction with aromatic, aliphatic and heteroaromatic aldehydes, the methodology was further extended for cyclic ketones and cyclic hetrocyclic ketones. It was observed that cyclohexanone and heterocyclic ketones 1, 3-dimethylbarbituric acid and 2, 2-dimethyl-1,3-dioxane-4,5-dione (Meldrum's acid) were easily introduced in the spirocyclized product with considerable yields (Scheme 2). It is worth mentioning that 1, 3-dimethylbarbituric acid and meldrum's

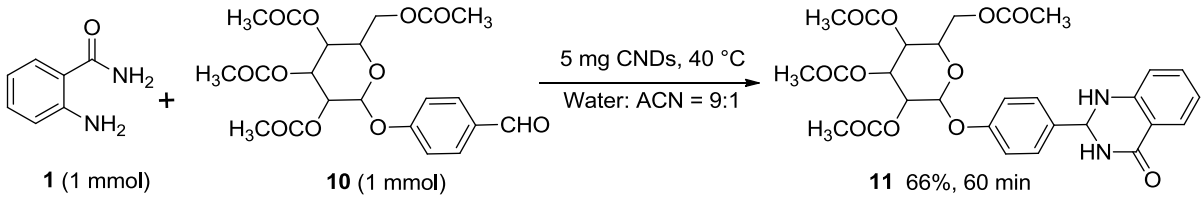
Scheme 2: Synthesis of spirocyclizedquinazolinones:



acid are highly unstable under acidic or basic environment as they are prone to hydrolysis. However, due to mild acidic behavior of CNDs, the hydrolysis did not take place and we could obtain high yield of the spirocyclized product without any noticeable formation of hydrolysed by-products. Thus, the mild acidic behaviour of CND surface could be used as an effective catalyst for structurally perplexing substrates such as spirocyclized products under mild reaction conditions.

Further, we explored the possibility of using CNDs as catalysts for glycosidic bond formation. It is well known that due to high chemical sensitivity of the *O*-glycocydic linkages, synthesis of *O*-aryl glycosides is a challenging task. When 2-aminobenzamide was condensed with the glycoconjugate **10** (4-Formylphenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside) using CNDs as a catalyst, the desired dihydroquinazolinone derivative with glycoside moiety was obtained with a significant isolated yield (Scheme 3).The glycosidic aldehyde **10** synthesized by a reported protocol (experimental section) and glycosidicdihydroquinazolinone **11** were characterised by NMR and Mass spectroscopy.

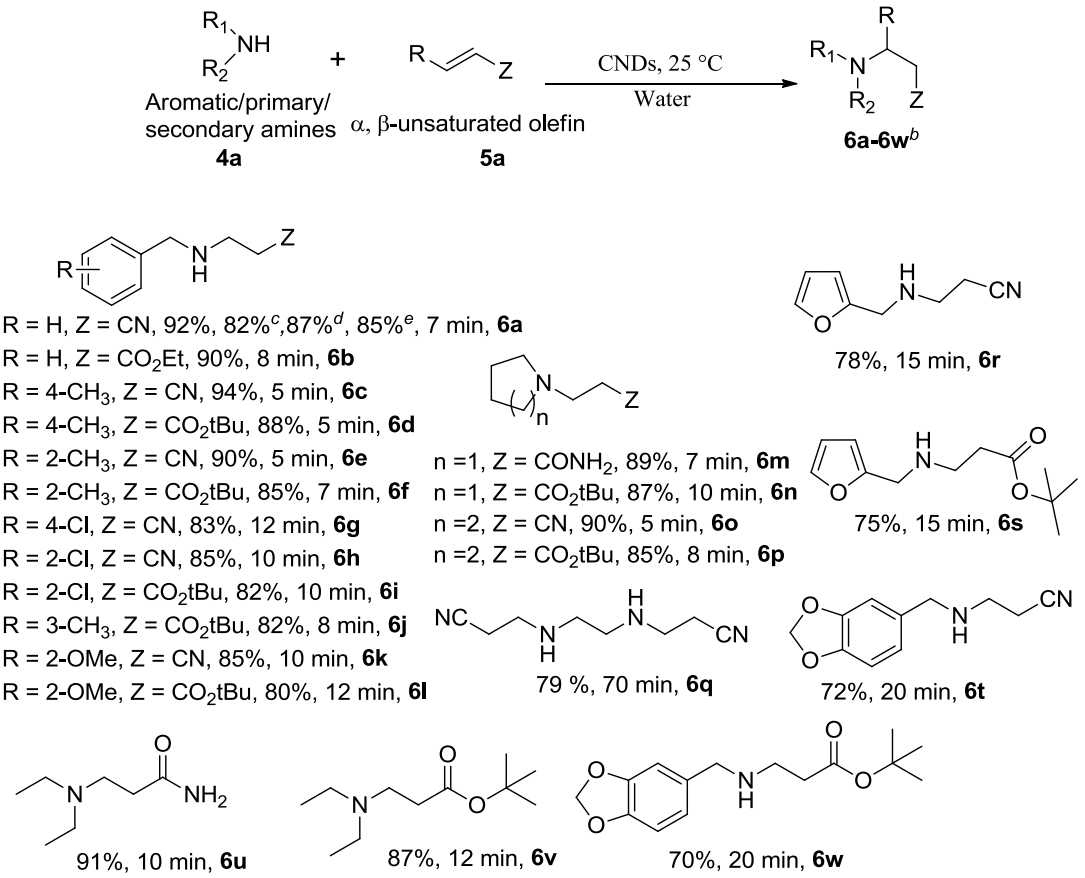
Scheme 3: Synthesis of Glycosidic bond



The catalytic applicability of the carboxylic acid functionalized CNDs for condensation reactions were further evaluated for the aza-Michael addition reaction between benzylamine and acrylonitrile at room temperature. In absence of any catalyst, the reaction required almost an hour to get completed in aqueous medium, as also reported by S. Verma *et.al*[6]. However, in presence of a catalytic amount of CNDs, the rate of this reaction enhanced tremendously as the reaction was completed within a short time (7 min). We extended the substrate scope

using a wide range of amines with various α, β-unsaturated electron deficient systems including ethyl acrylate, acrylamide, tert-butylacrylate (Table 5). A variety of amines including secondary amines, aromatic amines both with electronically activating and deactivating groups as well as aliphatic amines were compatible with the catalytic system and afforded the aza-Michael adducts in excellent yields. As reported in Table 5, most of the reactions got completed in a short reaction time (5-20 min), except for ethylenediamine (entry 6q, table 5), where the reaction took prolonged time (70 min) for completion.

Table 5: Aza-Michael addition of Amines and α, β-unsaturated compounds using CNDs[a]



[a]All reactions were carried out using 1.0 mmol of amine and 1.2 mmol of α, β-unsaturated compound, catalyst: 10 mL CNDs in water (0.5 mgmL^{-1}). [b]Isolated yields. [c]the reaction was carried out for 55 min in water without any catalyst.[d,e]2nd and 3rd cycle of reaction respectively carried out for 7 min.

For industrial applications through a green chemistry approach, recyclability of the catalysts is highly desirable. We evaluated the reusability of the CNDs for both of the model reactions of 2, 3-dihydroquinazolinone and aza-Michael adducts. The CNDs could be readily recovered and reused for at least three runs without any significant impact on the yield of the products. Most important of all, the catalyst in the aqueous layer could be reused directly after the products were extracted in organic phase without any treatment. The recovered CNDs after the third cycle of reaction did not show any significant morphological or structural changes as observed by TEM (Fig. S4a) and other spectroscopic studies. The surface functional groups present on CNDs have been reported to influence the luminescence as they act as surface energy traps.[27] In our case, we did not observe any shift in the emission peak in the fluorescence spectra of CNDs suggesting that the surface functional groups did not get modified during catalysis (Fig. S4d). This was further confirmed by zeta potential measurements, as the zeta potential value of CNDs before and after reaction did not change significantly (Fig. S4e). C1s core level spectra of the recovered CNDs showed similar features of functional groups as that of the pristine catalyst showing no appreciable surface modification (Fig. S4b). This further validates the activity of CNDs as a mere acid catalyst without undergoing any chemical modifications themselves.[7b]

A plausible mechanism for the formation of 2, 3-dihydroquinazolinone derivatives is shown in scheme 4.

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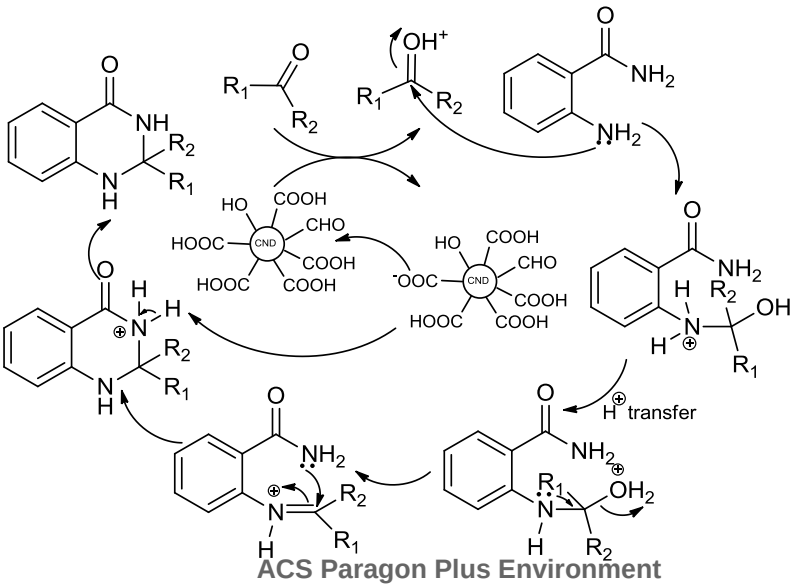

Scheme 4: Plausible mechanism for CNDs catalyzed cyclocondesation reaction of carbonyl compound and 2-aminobenzamide

The inherent surface acidity of CNDs first activates the carbonyl carbon making the carbon centre highly electrophilic for nucleophilic addition of 2-aminobenzamide. Hydrogen transfer resulted in protonated N, O-hemiketal followed by anchimeric assistance by the $–NH_2$ group to give an imine which further undergoes intramolecular cyclization and deprotonation to give the desired quinazolinone product.

In conclusion, carboxylic acid functionalized carbon nanodots can effectively catalyse condensation between 2-aminobenzamide and aldehydes/cyclic ketones leading to biologically relevant dihydro/spiroquinazolinones under mild reaction conditions. The mildly acidic surface behaviour of these dots could be extended towards the catalytic formation of aza-Michael adducts. The proficient catalytic activity of the nanodots for condensation reactions will definitely add up to the already established versatile applicability of these water-soluble, non-toxic and biocompatible fluorescent nanodots in biological, photocatalysis and opto-electronic device applications. Mild reaction conditions, easy work up and good recyclability may fortify carbon nanodots as effective acid catalyst for important organic transformations in a metal-free and green pathway.

EXPERIMENTAL SECTION

Synthesis of carbon nanodots (CNDs):

30 mg of natural carbon source β-carotene was dispersed in 30 mL Mili-Q water by sonication for 5 minutes and then the mixture was transferred to a 50 mL teflon coated autoclave. The heterogeneous mixture was then subjected to hydrothermal treatment at 180 °C for 3 hrs. This resulted in a pale-yellow dispersion of luminescent carbon dots after

filtration. The concentration of CNDs in this dispersion was found to be 0.6 $mgmL^{-1}$. For the reduction of the CNDs (rCNDs), a similar procedure was followed which has been reported for reduction of grapheme oxide.[28] Briefly, a 20 mL CND dispersion (0.6 $mgmL^{-1}$) was taken in a round bottom flask. Hydrazine hydrate (0.5 mL, 10 mmol) was then added and the mixture was heated under reflux conditions in an oil bath at 100 °C for 4 hours. The resultant solution was dialyzed against Milli-Q water for 48 hours to remove excess of reducing agent**.**

The measurement of quantity of total functional groups (-OH and -COOH groups):

The quantitative assessment of –OH and –COOH functional groups on CND surface was carried out following a literature procedure.[29] A CND dispersion (5 mL, 0.5 mg/mL) was first purged with argon for 30 minutes. Then it was titrated with aliquots of sodium hydroxide aqueous solution (0.05 mol/L). The mixture was stirred continuously and the pH was monitored using a pH meter. The titration was carried out until a pH of 10.41 was obtained. The total number of functional groups was calculated from the inflection point of the titration curve which was determined by plotting the ratio $\Delta pH/\Delta V$ against the volume of NaOH added. The experiment was repeated thrice to get precise values. The concentration of functional groups calculated using the equation $N_1V_1 = N_2V_2$ was found to be 1.96×10^{-3} mol/L.

The measurement of quantity of -COOH functional groups:

A CND dispersion (5 mL, 0.5 mg/mL) was first purged with Ar for 30 minutes. Titration was carried out with aliquots of sodium bicarbonate aqueous solution (0.05 mol/L). The mixture was stirred continuously and the pH was monitored using a pH meter. The titration was carried out until a pH of 8.10 was reached. The acidity was calculated from the inflection point of the titration curve which was determined by plotting the ratio $\Delta pH/\Delta V$ against the

volume of $NaHCO_3$ added. The experiment was repeated thrice to get precise values. The concentration of –COOH functional groups calculated to be 1.45 x 10^{-4} mol/L.

General method of synthesis of 2,3-dihydroquinazolinones:

In a typical reaction, 1.0 mmol of 2-aminobenzamide/5-chloro-2-aminobenzamide and 1.0 mmol of aldehydes/cyclic ketones were taken in a 15 mL of reaction vial with 10 mL of CNDs and 1 mL of acetonitrile. The mixture was stirred (900 rpm) at 40 °C for a period of time as mentioned in table 3. The progress of the reactions was monitored by TLC using 25% ethyl acetate and hexane as eluent. After completion of the reaction, the reaction mixture was brought to room temperature where crystallized products were obtained. The crystallized products were filtered and further washed by hexane, dried and evaluated by spectral analysis. Any remaining products in the reaction mixture were further extracted using a hexane/ethyl acetate solvent mixture and subsequent evaporation under reduced pressure.

General method of synthesis of aza-Michael adducts:

In a typical reaction, 1.0 mmol of amine and 1.2 mmol of α, β-unsaturated compound were mixed with 5 mg CND solution in water (10 mL) and stirred at room temperature for specified time as mentioned in table 4. The progress of the reaction was monitored by TLC using 2% methanol-dichloromethane mixture as eluent. After completion of the reaction, the resulting products were extracted using hexane/ethyl acetate solvent mixture. The organic layer was dried over anhydrous sodium sulphate and evaporation of the solvent under reduced pressure gave the final product. The product was further dried under high vacuum and submitted for spectral analysis.

Reusability of the catalyst:

After removing the crystallized organic products from the reaction mixture by filtration, the filtrate was further extracted with hexane/ethyl acetate solvent mixture (3 times) to remove any organic products present. The aqueous layer containing the carbon dots was further used for the next cycles of reaction.

Synthesis of 4-formylphenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside:

Acetobromo-α-D-galactose (0.5 g) and 4-hydroxybenzaldehyde (0.25g) were dissolved in 2.5 mL chloroform. An aqueous solution (2 mL) of sodium carbonate (0.3 g) and TBAB (tetrabutylammoniumbromide) (0.1 g) were added to the mixture.[30] The mixture was heated to reflux under vigorous stirring overnight. The mixture was cooled, ethyl acetate was added and the organic layer was washed with 1 N NaOH solution to remove remaining phenol. Further, the organic layer was dried over sodium sulphate and evaporation of the solvent under reduced pressure. Repeated washing with ethanol and hexane gave the purified target product in 65% yield (0.38 g).

Characterisation data:

2-phenyl-2,3-dihydroquinazolin-4(1H)-one (3a)[23]: Colorless crystal (217 mg, 97%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.76 Hz, 1H), 7.60 (m, 2H), 7.44 (m, 3H), 7.33 (t, *J* = 7.52 Hz, 1H), 6.90 (t, *J* = 7.76 Hz, 1H), 6.67 (d, *J* = 8.04 Hz, 1H), 5.90 (s, 1H), 5.88 (br, 1H, NH), 4.35 (br, 1H, NH), ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.0, 148.3, 142.1, 133.8, 128.9, 128.8, 127.8, 127.3, 117.6, 115.4, 114.8, 67.0. Mass: 224.00. HRMS (ESI): calcd for [$C_{14}H_{12}N_2O + Na^+$] 247.0842, found 247.0864.

2-(4-fluorophenyl)-2,3-dihydroquinazolin-4(1H)-one (3b)[24]: Colorless crystal (212 mg, 88%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 (br, 1H, NH), 7.67 (d, *J* = 7.56 Hz, 1H), 7.58 (m, 2H), 7.46-7.50 (m, 1H), 7.38 (s, 1H), 7.16 (t, *J* = 8.52 Hz, 1H), 6.97 (t, *J* = 8.8 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 5.74 (s, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 164.6, 148.0, 133.6, 129.3, 129.2,

127.8, 118.0, 115.5, 115.28, 115.20, 114.8, 67.3. Mass: 242.2483, HRMS (ESI): calcd for $[C_{14}H_{11}FN_2O + Na^+]$ 265.0748, found 265.0771.

2-(*p*-tolyl)-2,3-dihydroquinazolin-4(1H)-one (3c)[16a]: Colorless crystal (202 mg, 85%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20 (br, 1H, NH), 7.57(d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.76 Hz, 2H), 7.22 (t, *J* = 7.52 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.03 (s, 1H), 6.71 (d, *J* = 8.28 Hz, 1H), 6.65 (t, *J* = 7.52 Hz, 1H), 5.69 (s, 1H, NH), 2.28 (s, 3H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.1, 148.4, 139.1, 138.2, 133.7, 129.7, 129.3, 128.1, 127.8, 127.2, 117.5, 115.4, 114.8. Mass: 238.2845, HRMS (ESI): calcd for $[C_{15}H_{14}N_2O + Na^+]$ 261.0998, found 261.1016.

2-(2-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (3d)[33]: Orange crystal (228 mg, 85%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.82 (1H, NH), 8.13-8.16 (m, 2H), 7.88-7.92 (m, 2H), 7.78-7.82 (m, 2H), 7.53-7.57 (m, 2H), 7.36 (t, *J* = 7.28 Hz, 1H), 7.17 (d, *J* = 7.76 Hz, 1H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.0, 158.7, 149.7, 149.2, 134.4, 132.8, 132.2, 130.3, 130.2, 129.9, 129.7, 127.0, 125.1, 119.7, , Mass: 269.2554, HRMS (ESI): calcd for $[C_{14}H_{11}N_3O_3 + Na^+]$ 292.0693, found 292.0715.

2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (3e)[23]: Colorless crystal (203 mg, 79%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.33 (s, 1H, NH), 7.61 (d, *J* = 6.76 Hz, 1H), 7.45-7.52 (m, 4H), 7.26 (t, *J* = 8.28 Hz, 1H), 7.14 (s, 1H), 6.74 (d, *J* = 8.04 Hz, 1H), 6.69 (t, *J* = 7.24 Hz, 1H), 5.78 (s, 1H, NH), ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.9, 148.1, 141.1, 133.9, 133.4, 129.2, 128.7, 127.8, 117.7, 115.4, 114.9, 66.2.

2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (3f)[31]: Colorless crystal (241 mg, 80%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.26 (br, s, 1H, NH), 7.60 (d, *J* = 7.52 Hz, 1H), 7.52 (d, *J* = 8.52 Hz, 2H), 7.41 (d, *J* = 8.28 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.06 (s, 1H), 6.7 (d, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 7.28 Hz, 1H), 5.72 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$ +DMSO-d_6): δ 163.9, 148.0, 141.4, 133.7, 131.6, 129.4, 127.8, 122.0, 117.6, 115.3, 114.9, 66.4, Mass: 303.1539, HRMS (ESI): calcd for $[C_{14}H_{11}BrN_2O + Na^+]$ 324.9947 & 326.9927, found 324.9965 & 326.9951.

2-(2-hydroxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (3g)[31]: Colorless solid (187 mg, 78%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.83 (s, 1H), 7.90 (s, 1H, NH), 7.59 (d, *J* = 7.76 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.04 Hz, 1H), 7.13 (t, *J* = 6.76 Hz, 1H), 6.83 (d, *J* = 8.04 Hz, 1H), 6.78 (d, *J* = 7.52 Hz, 1H), 6.75 (t, *J* = 8.28 Hz, 1H), 6.71 (s, 1H), 6.64 (t, *J* = 7.52 Hz, 1H), 5.98 (s, 1H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.4, 155.0, 148.5, 133.6, 129.7, 127.7, 127.68, 127.63, 119.2, 117.4, 115.8, 115.2, 115.0, 61.6. Mass: 240.2573, HRMS (ESI): calcd for [$C_{14}H_{12}N_2O_2$ + Na^+] 263.0791, found 263.0803.

2-(2,6-dichlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (3h)[40]: Pale-yellow crystal (221 mg, 76%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.81 (s, 1H), 8.14 (br, 1H, NH), 7.91 (d, *J* = 7.24 Hz, 1H), 7.52-7.64 (m, 5H), 7.41 (t, *J* = 7.28 Hz, 1H), 7.24 (d, *J* = 7.76 Hz, 1H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.2, 158.8, 134.7, 133.0, 132.6, 131.6, 130.4, 130.0, 128.7, 127.5, 119.6, 97.9. . Mass: 293.1480, HRMS (ESI): calcd for [$C_{14}H_{10}cl_2N_2O$ + Na^+] 315.0062, found 315.0080.

4-(4-oxo-1,2,3,4-tetrahydroquinazolin-2yl)benzonitrile (3i)[16a]: Pale-yellow crystal (179 mg, 72%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 (br, s, 1H, NH), 7.84 (d, *J* = 8.28 Hz, 2H), 7.63 (d, *J* = 8.04 Hz, 2H), 7.58 (d, *J* = 7.52 Hz, 1H), 7.26 (s, 1H), 7.23 (t, *J* = 7.28 Hz, 1H), 6.73 (d, *J* = 8.04 Hz, 1H), 6.67 (t, *J* = 7.28 Hz, 1H), 5.83 (s, 1H, NH), ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.8, 147.8, 147.7, 134.0, 132.8, 128.1, 127.8, 117.9, 115.3, 114.9, 111.5, 65.9 . Mass: 249.2673, HRMS (ESI): calcd for [$C_{15}H_{11}N_3O$ + Na^+] 272.0794, found 272.0811.

2-(3-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (3j)[16a]: Colorless crystal (223 mg, 74%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.36 (br, s, 1H, NH), 7.65 (s, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 8.04 Hz, 1H), 7.45 (d, *J* = 7.76 Hz, 1H), 7.33 (t, *J* = 8.00 Hz, 1H), 7.24 (t, *J* = 8.56 Hz, 1H), 7.19 (s, 1H), 6.73 (d, *J* = 8.04 Hz, 1H), 6.67 (t, *J* = 7.52 Hz, 1H), 5.75 (1H, NH), ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.8, 147.9, 145.1, 133.9, 131.6, 131.0, 130.1, 127.8, 126.2, 122.0, 117.8, 115.3, 114.9, 65.9. Mass: 303.1539, HRMS (ESI): calcd for [$C_{14}H_{11}BrN_2O$ + Na^+] 324.9947, found 324.9961.

2-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (3k)[16a]: Colorless crystal (180 mg, 71%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.16 (s, 1H, NH), 7.58 (d, J = 6.76 Hz, 1H), 7.38 (d, J = 8.72 Hz, 2H), 7.22 (t, J = 7.04 Hz, 1H), 6.98 (s, 1H), 6.92 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.04 Hz, 1H), 6.65 (t, J = 7.24 Hz, 1H), 5.68 (s, 1H, NH), 3.73 (s, 3H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.1, 159.9, 148.4, 133.9, 133.7, 128.6, 127.8, 117.5, 115.4, 114.8, 114.1, 66.7, 55.6. Mass: 254.2839, HRMS (ESI): calcd for [$C_{15}H_{14}N_2O_2$ + Na^+] 277.0947, found 277.0974.

2-(4-hydroxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (3l)[31]: Brown solid (196 mg, 82%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.49 (s, 1H, -OH), 8.06 (s, 1H, NH), 7.58 (d, J = 7.0 Hz, 1H), 7.27 (d, J = 8.52 Hz, 2H), 7.21 (t, J = 6.76 Hz, 1H), 6.91 (s, 1H), 6.73 (d, J = 8.52 Hz, 2H), 6.70 (d, J = 8.28 Hz, 1H), 6.65 (t, J = 7.52 Hz, 1H), 5.63 (s, 1H, NH), ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.2, 158.1, 148.6, 133.6, 132.0, 128.7, 127.8, 117.5, 115.42, 115.40, 114.8, 67.1. Mass: 240.2573, HRMS (ESI): calcd for [$C_{14}H_{12}N_2O_2$ + Na^+] 263.0791, found 263.0813.

6-chloro-2-(2,5-dimethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (3m): Colorless solid (213 mg, 67%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19 (br, 1H, NH), 7.53 (d, 1H), 7.23-7.26 (dd, 1H), 7.01 (s, 1H), 6.96 (m, 1H), 6.89 (s, 1H), 6.86-6.90 (m, 1H), 6.77 (d, 1H), 5.97 (s, 1H), 3.76 (s, 3H), 3.65 (s, 3H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.1, 153.3, 150.9, 147.1, 133.5, 129.9, 126.8, 121.1, 116.9, 116.2, 114.1, 113.8, 112.7, 61.4, 56.5, 55.8. Mass: 318.7549, HRMS (ESI): calcd for [$C_{16}H_{15}ClN_2O_3$ + Na^+] 341.0663, found 341.0678.

2-(4-bromophenyl)-6-chloro-2,3-dihydroquinazoli-4(1H)-one (3n)[34]: Pale-yellow solid (241 mg, 72%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.59 (s, 1H), 8.11 (br, 1H, NH), 7.87 (d, J = 8.52 Hz, 2H), 7.79 (d, 1H), 7.75 (d, J = 8.28 Hz, 2H), 7.73 (br, 1H, NH), 7.58 (dd, J = 8.52, 1H), 7.27-7.29 (d, 1H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.6, 162.4, 148.3, 135.0, 132.5, 131.8, 131.3, 130.89, 130.8, 129.5, 126.4, 121.9. Mass: 337.5990, HRMS (ESI): calcd for [$C_{14}H_{10}BrClN_2O$ + Na^+] 358.9557, found 358.9568.

6-chloro-2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (3o)[41]: Colorless crystal (227 mg, 78%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.49 (br, 1H, NH), 7.43-7.51(m, 5H), 7.34 (s, 1H), 7.26-7.28

(d, 1H), 6.75 (d, *J* = 8.76 Hz, 1H), 5.78 (br, 1H, NH), ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.8, 146.8, 140.7, 133.63, 133.6, 129.1, 128.8, 126.8, 121.4, 116.9, 116.4, 66.0. Mass: 293.1480, HRMS (ESI): calcd for [$C_{14}H_{10}Cl_2N_2O + Na^+$] 315.0062, found 315.0084.

6-chloro-2-(3-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (3p): Pale-yellow solid (242 mg, 80%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.76 (s, 1H), 8.73 (s,1H), 8.36-8.42 (m,2H), 8.00 (br, 1H, NH), 7.85 (t, *J* = 7.76 Hz, 1H), 7.75 (d, 1H), 7.72 (br, 1H, NH), 7.59-7.63 (m, 1H), 7.30-7.32 (d, *J* = 8.52 Hz, 1H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.8, 161.5, 148.7, 147.8, 137.5, 135.3, 131.7, 131.6, 131.15, 131.12, 129.2, 126.7, 123.8, 121.9, Mass: 303.7005, HRMS (ESI): calcd for [$C_{14}H_{10}ClN_3O_3 + Na^+$] 326.0303, found 316.0322.

6-chloro-2-(pyridin-2-yl)-2,3-dihydroquinazolin-4(1H)-one (3q): Colorless crystal (196 mg, 76%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 11 (br, 1H, NH), 8.68 (d, 1H), 8.55 (d, 1H), 8.31 (d, 1H), 7.93 (t, *J* = 7.8 Hz, 1H), 7.71-7.78 (m, 2H), 7.41-7.52 (m, 1H), 7.26 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 149.1, 148.8, 148.2, 148.1, 147.6, 137.6, 135.0, 129.6, 126.4, 126.2, 123.5, 122.0, 77.2. Mass: 259.6910, HRMS (ESI): calcd for [$C_{13}H_{10}ClN_3O + Na^+$] 282.0405, found 282.0420.

2-(furan-2-yl)-2,3-dihydroquinazolin-4(1H)-one (3r)[21]: Light orange crystal (154 mg, 72%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 6.52 Hz, 1H), 7.04 (d, 1H), 7.32 (t, *J* = 8.76 Hz, 1H), 6.88 (t, *J* = 7.24 Hz, 1H), 6.68 (d, *J* = 8.00 Hz, 1H), 6.43 (d, 1H), 6.34-6.35 (m, 1H), 6.32 (br, 1H, NH), 5.92 (t, 1H), 4.65 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 152.0, 146.1, 143.2, 134.0, 128.6, 119.9, 115.8, 115.0, 110.6, 108.3, 62.0. Mass: 214.2200, HRMS (ESI): calcd for [$C_{12}H_{10}N_2O_2 + Na^+$] 237.0634, found 237.0651.

2-(thiophen-2-yl)-2,3-dihydroquinazolin-4(1H)-one (3s)[31]: Light-brown solid (195 mg, 85%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.42 (br, s, 1H, NH), 7.59 (d, *J* = 7.76 Hz, 1H), 7.43 (d, *J* = 5.04 Hz, 1H), 7.24 (t, *J* = 8.04 Hz, 1H), 7.23 (s, 1H), 7.10 (d, *J* = 3.00 Hz, 1H), 6.96 (t, *J* = 4.04 Hz, 1H), 6.73 (d, *J* = 8.28 Hz, 1H), 6.68 (t, *J* = 7.52 Hz, 1H), 6.0 (s, 1H, NH), ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.5, 147.7, 146.9, 133.8, 127.7, 126.9, 126.3, 126.1, 117.9, 115.5, 115.1, 63.0. Mass: 230.2856, HRMS (ESI): calcd for [$C_{12}H_{10}N_2OS + Na^+$] 253.0406, found 253.0430.

2-(1-methyl-1*H*-indol-3-yl)-2,3-dihydroquinazolin-4(1H)-one (3t): Colorless crystal (180 mg, 65%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 9.04 Hz, 1H), 7.88 (d, *J* = 7.76 Hz, 1H), 7.30-7.37 (m, 3H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.04 Hz, 1H), 6.65 (d, *J* = 8.04 Hz, 1H), 6.19 (s, 1H), 5.88 (br, 1H, NH), 4.47 (br, 1H, NH), 3.81 (s, 3H), 3.48 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 137.4, 133.8, 128.8, 128.4, 122.7, 120.17, 120.12, 119.5, 116.0, 114.6, 111.9, 109.7, 62.8, 33.0. Mass: 274.2753, HRMS (ESI): calcd for [$C_{17}H_{15}N_3O + Na^+$] 300.1107, found 300.1121.

2-phenethyl-2,3-dihydroquinazolin-4(1H)-one (3u)[18b]: Pale-yellow crystal (191 mg, 76%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.01 (br, s, 1H, NH), 7.57 (d, *J* = 7.56 Hz, 1H), 7.21-7.29 (m, 5H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.72 (d, *J* = 8.04 Hz, 1H), 6.66 (t, *J* = 7.28 Hz, 2H), 4.72 (t, *J* = 5.04 Hz, 1H), 2.72-2.76 (q, *J* = 8.04 Hz, 2H), 1.88-1.94 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 149.0, 142.1, 133.6, 128.8, 128.7, 127.9, 126.2, 117.5, 115.5, 114.9, 64.4, 37.1, 31.1. Mass: 252.3110, HRMS (ESI): calcd for [$C_{16}H_{16}N_2O + Na^+$] 275.1155, found 275.1172.

2-isopropyl-2,3-dihydroquinazolin-4(1*H*)-one (3v)[32]: Colorless crystal (138 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 9.32 Hz, 1H), 7.28 (t, *J* = 8.28 Hz, 1H), 6.82 (t, *J* = 7.04 Hz, 1H), 6.63 (d, *J* = 8.04 Hz, 1H), 6.0 (br, 1H, NH), 4.68 (d, *J* = 4.76 Hz, 1H), 4.17 (br, 1H, NH), 1.91-1.99 (m, 1H), 1.02-1.05 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 147. 4, 133.8, 128.5, 119.1, 115.5, 114.5, 70.2, 32.8, 17.0, 16.8. Mass: 190.2417, HRMS (ESI): calcd for [$C_{11}H_{14}N_2O + Na^+$] 213.0998, found 213.1013.

2-(2-hydroxynaphthalene-1-yl)-2,3-dihydroquinazolin-4(1*H*)-one (3w)[42]: Orange solid (240 mg, 83%), ^{1}H NMR (400 MHz, CD_3OD): δ 9.35 (s, 1H), 8.18 (d, *J* = 8.56 Hz, 1H), 7.75 (d, *J* = 9.28 Hz, 1H), 7.66 (d, *J* = 8.28 Hz, 1H), 7.61 (d, *J* = 7.76 Hz, 2H), 7.56 (t, *J* = 8.04 Hz, 1H), 7.45 (t, *J* = 8.28 Hz, 1H), 7.22-7.30 (m, 2H), 6.82 (d, *J* = 9.28 Hz, 1H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 172.6, 169.6, 154.2, 142.4, 137.8, 134.0, 131.6, 129.5, 129.4, 128.8, 128.6, 127.0, 126.0, 123.9, 123.5, 120.7, 119.5, 109.2. Mass: 274.2753, HRMS (ESI): calcd for [$C_{18}H_{14}N_2O_2 + Na^+$] 313.0947, found 313.0961.

1'*H*-spiro[cyclohexane-1,2'-quinazolin]-4'(3'*H*)-one (5)[23]: Colorless crystal (205 mg, 95%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.04 Hz, 1H), 6.81 (t, *J* = 7.8 Hz,

1H), 6.62 (d, *J* = 8.04 Hz, 1H), 5.93 (br, 1H, NH), 4.29 (br, 1H, NH), 1.83 (br, 4H), 1.43-1.61 (m, 6H), ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 168.9, 151.3, 138.2, 132.4, 122.2, 119.6, 73.0, 42.3, 29.5, 26.3. Mass: 216.2789, HRMS (ESI): calcd for [$C_{13}H_{16}N_2O$ + Na^+] 239.1155, found 239.1166.

1,3-dimethyl-1*H*, 1'*H*-spiro[pyrimidine-4,2'-quinazoline]-2,4',6(3*H*,3'*H*,5*H*)-trione (7): Light orange solid (213 mg, 78%), ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.68 (br, 1H, NH), 7.49 (d, *J* = 8.04 Hz, 1H), 7.10 (t, *J* = 8.04 Hz, 1H), 7.01 (br, 1H, NH), 6.64 (d, *J* = 8.28 Hz, 1H), 6.45 (t, *J* = 7.28 Hz, 1H), 3.68 (s, 2H), 3.09 (s, 6H), ^{13}C NMR (100 MHz, DMSO-d_6): δ 207.0, 171.7, 166.4, 152.8, 150.6, 132.3, 129.2, 116.8, 114.8, 114.1, 31.1, 28.2. Mass: 274.2753, HRMS (ESI): calcd for [$C_{13}H_{14}N_4O_3$ + Na^+] 297.0958, found 297.0980.

2,2-dimethyl-1'*H*-spiro[[1,3]dioxane-4,2'-quinazoline]-4',6(3'*H*)-dione (9): Orange crystal (195 mg, 79%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.76 Hz, 1H), 7.29 (t, *J* = 8.8 Hz, 1H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.66 (br, 1H, NH), 6.59 (d, *J* = 8.04 Hz, 1H), 3.44-3.52 (m, 1H), 2.15 (s, 1H), 1.54 (s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 164.8, 145.9, 134.1, 128.4, 118.9, 114.7, 114.3, 67.6, 30.9, 29.6. Mass: 248.1916, HRMS (ESI): calcd for [$C_{11}H_8N_2O_5$ + Na^+] 271.0325, found 271.0348.

4-Formylphenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (10)[30]: Orange liquid (293 mg, 65%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.83 (d, *J* = 8.52 Hz, 2H), 7.09 (d, *J* = 8.76 Hz, 2H), 5.46-5.53 (m, 2H), 5.10-5.16 (m, 2H), 4.10-4.22 (m, 3H), 2.18 (s, 3H), 2.15 (s, 6H), 2.01 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 170.3, 170.1, 170.0, 169.3, 161.3, 131.8, 116.7, 98.6, 71.3, 70.6, 68.4, 66.7, 61.3, 20.7, 20.66, 20.64, 20.57. Mass: 452.4087, HRMS (ESI): calcd for [$C_{21}H_{24}O_{11}$ + Na^+] 475.1211, found 475.1222.

2-(acetoxymethyl)-6-(4-(4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (11)[16a]: Colorless solid (376 mg, 66%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.52 Hz, 1H), 7.51 (d, *J* = 8.76 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 8.76 Hz, 2H), 6.89 (t, *J* = 7.52 Hz, 1H), 6.64 (d, *J* = 8.04 Hz, 1H), 5.86 (s, 1H), 5.72 (br, 1H, NH), 5.45-5.51 (m, 2H), 5.10 (dd, *J* = 7.04 Hz, 1H), 5.06 (d, *J* = 7.76 Hz, 1H), 4.32 (br, 1H, NH), 4.13-4.24 (m, 2H), 4.07 (t, *J* = 6.52 Hz, 1H), 2.17 (s, 3H), 2.01-2.06 (m, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1,

169.3, 164.7, 158.08, 158.06, 147.1, 134.1, 133.47, 133.46, 128.9, 128.7, 119.8, 117.3, 115.6, 114.6, 99.38, 99.36, 71.2, 70.7, 68.56, 68.55, 66.8, 61.3, 20.75, 20.71, 20.67, 20.6. Mass: 570.5446, HRMS (ESI): calcd for [$C_{28}H_{30}N_2O_{11}$ + Na^+] 593.1791, found 593.1810.

3-(benzylamino)propanenitrile (6a)[18a]: Yellow liquid (147 mg, 92%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.29 (m, 5H), 3.76 (s, 2H), 2.86 (t, *J* = 6.52 Hz, 2H), 2.45 (t, *J* = 6.76 Hz, 2H), 2.18 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.35, 128.64, 128.55, 128.06, 127.47, 127.26, 118.67, 53.14, 44.29, 18.72.

Ethyl 3-(benzylamino)propanoate (6b)[35]: Yellow liquid (186 mg, 90%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.35 (m, 5H), 4.10-4.18(q, 2H), 3.83 (s, 2H), 2.92(t, *J* = 6.52 Hz, 2H), 2.56 (t, *J* = 6.52 Hz, 2H), 1.99 (br, 1H, NH), 1.27 (t, *J* = 7.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.81, 139.98, 128.71, 128.45, 128.23, 128.14, 127.03, 60.49, 53.76, 44.47, 34.72, 14.25.

3-((4-methylbenzyl)amino)propanenitrile (6c)[39]: Yellow liquid (163 mg, 94%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.20 (d, *J* = 8 Hz, 2H), 7.12-7.14 (d, *J* = 8 Hz, 2H), 3.78 (s, 2H), 2.91 (t, *J* = 6.52 Hz, 2H), 2.50 (t, *J* = 6.52 Hz, 2H), 2.33 (s, 3H), 1.84 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.98, 136.39, 129.28, 128.08, 118.67, 52.86, 44.34, 21.08, 18.77.

***tert*-butyl 3-((4-methylbenzyl)amino)propanoate (6d)**: Yellow liquid (219 mg, 88%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.21 (d, *J* = 8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 2H), 3.75 (s, 2H), 2.84 (t, *J* = 6.52 Hz, 2H), 2.45 (t, *J* = 6.52 Hz, 2H), 2.31 (s, 3H), 2.0 (br, 1H, NH), 1.42 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.12, 136.80, 129.14, 128.19, 80.58, 53.47, 44.63, 44.58, 35.76, 28.17, 21.11. Mass: 249.3486, HRMS (ESI): calcd for [$C_{15}H_{23}NO_2$ + Na^+] 272.1621, found 272.1649.

3-((2-methylbenzyl)amino)propanenitrile (6e): Yellow liquid (156 mg, 90%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.19 (m, 4H), 3.74 (s, 2H), 2.90 (t, *J* = 6.52 Hz, 2H), 2.46 (t, *J* = 6.52 Hz, 2H), 2.29 (s, 3H), 1.56 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.37, 136.52, 130.49, 128.49, 127.37, 126.01, 118.77, 51.08, 44.77, 18.98, 18.83. Mass: 174.2423, HRMS (ESI): calcd for [$C_{11}H_{14}N_2$ + Na^+] 197.1049, found 197.1065.

***tert*-butyl 3-((2-methylbenzyl)amino)propanoate (6f)**: Yellow liquid (211 mg, 85%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 1H), 7.15-7.18 (m, 3H), 3.76 (s, 2H), 2.89 (t, *J* = 6.28 Hz, 2H), 2.46 (t, *J* = 6.24 Hz, 2H), 2.34 (s, 3H), 1.80 (br, 1H, NH), 1.44 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.07, 137.82, 136.37, 130.28, 128.52, 127.07, 125.93, 80.51, 51.41, 45.11, 35.84, 28.14, 18.93. Mass: 249.3486, HRMS (ESI): calcd for [$C_{15}H_{23}NO_2 + Na^+$] 272.1621, found 272.1641.

3-((4-chlorobenzyl)amino)propanenitrile (6g)[39]: Yellow liquid (161 mg, 83%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.33 (m, 4H), 3.82 (s, 2H), 2.94 (t, *J* = 6.52 Hz, 2H), 2.52 (t, *J* = 6.52 Hz, 2H), 1.63 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.02, 132.96, 129.41, 128.67, 118.69, 52.43, 44.30, 18.84.

3-((2-chlorobenzyl)amino)propanenitrile (6h): Yellow liquid (165 mg, 85%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.43 (m, 2H), 7.24-7.30 (m, 2H), 3.96 (s, 2H), 2.96 (t, *J* = 6.52 Hz, 2H), 2.56 (t, *J* = 6.76 Hz, 2H), 2.23 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.80, 133.74, 130.10, 129.67, 128.69, 127.0, 118.60, 50.57, 44.36, 18.82. Mass: 194.6607, HRMS (ESI): calcd for [$C_{10}H_{11}ClN_2 + Na^+$] 217.0503, found 217.0520.

***tert*-butyl 3-((2-chlorobenzyl)amino)propanoate (6i)**: Yellow liquid (220 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.45 (m, 2H), 7.20-7.28 (m, 2H), 3.93 (s, 2H), 2.91 (t, *J* = 6.52 Hz, 2H), 2.50 (t, *J* = 6.52 Hz, 2H), 2.30 (br, 1H, NH), 1.46 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.00, 137.17, 133.76, 130.15, 129.50, 128.41, 126.87, 80.64, 51.05, 44.65, 35.79, 28.13. Mass: 269.7671, HRMS (ESI): calcd for [$C_{11}H_8N_2O_5 + Na^+$] 292.1075, found 292.1102.

***tert*-butyl 3-((3-methylbenzyl)amino)propanoate (6j)**: Yellow liquid (204 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.52 Hz, 1H), 7.12 (s, 1H), 7.09-7.11 (d, *J* = 7.52 Hz, 1H), 7.03-7.05 (d, *J* = 8.04 Hz, 1H) 3.74 (s, 2H), 2.84 (t, *J* = 6.52 Hz, 2H), 2.44 (t, *J* = 6.52 Hz, 2H), 2.32 (s, 3H), 1.88 (br, 1H, NH), 1.43 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.21, 140.04, 138.05, 128.96, 128.33, 127.73, 125.21, 80.56, 53.86, 44.80, 35.85, 28.16, 21.41. Mass: 249.3486, HRMS (ESI): calcd for [$C_{15}H_{23}NO_2 + Na^+$] 272.1621, found 272.1639.

3-((2-methoxybenzyl)amino)propanenitrile (6k): Yellow liquid (161 mg, 85%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.31 (m, 2H), 6.90-6.97 (m, 2H), 3.87 (s, 3H), 3.85 (s, 2H), 2.91 (t, *J* = 6.52 Hz, 2H), 2.54 (t, *J* = 6.76 Hz, 2H), 1.93 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.65, 129.94, 128.72, 127.31, 120.54, 118.79, 110.39, 55.31, 48.75, 44.29, 18.66. Mass: 190.2417, HRMS (ESI): calcd for [$C_{11}H_{14}N_2O + Na^+$] 213.0998, found 213.1019.

***tert*-butyl 3-((2-methoxybenzyl)amino)propanoate (6l)**: Yellow liquid (212 mg, 80%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.24 (m, 2H), 6.83-6.91 (m, 2H), 3.82 (s, 3H), 3.78 (s, 2H), 2.82 (t, *J* = 6.52 Hz, 2H), 2.44 (t, *J* = 6.76 Hz 2H), 1.95 (br, 1H, NH), 1.42 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.15, 157.62, 129.81, 128.28, 128.05, 120.43, 110.25, 80.43, 55.26, 49.12, 44.73, 35.99, 28.14. Mass: 265.3480, HRMS (ESI): calcd for [$C_{15}H_{23}NO_3 + Na^+$] 288.1570, found 288.1589.

3-(pyrrolidin-1-yl)propanamide (6m)[6]: Yellow liquid (126 mg, 89%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (br, 1H, NH), 5.73 (br, 1H, NH), 2.71 (t, *J* = 5.76 Hz, 2H), 2.52-2.55 (m, 4H), 2.38 (t, *J* = 6.28 Hz, 2H), 1.74-1.80 (m, 4H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.49, 53.43, 51.63, 34.12, 23.52.

***tert*-butyl 3-(pyrrolidin-1-yl)propanoate (6n)**: Yellow liquid (173 mg, 87%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.71 (t, *J* = 7.52 Hz, 2H), 2.49 (t, *J* = 6.56 Hz, 4H), 2.42 (t, *J* = 7.76 Hz, 2H), 1.75 (m, 4H), 1.41 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 80.3, 54.0, 51.4, 35.3, 28.1, 23.5. Mass: 199.2899, HRMS (ESI): calcd for [$C_{11}H_{21}NO_2 + Na^+$] 222.1465, found 222.1483.

3-(piperidin-1-yl)propanenitrile (6o)[18a]: Yellow liquid (124 mg, 90%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (t, *J* = 6.76 Hz, 2H), 2.51 (t, *J* = 7.24 Hz, 2H), 2.43 (t, *J* = 5.00 Hz, 4H), 1.56-1.61 (m, 4H), 1.39-1.45 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.97, 54.12, 54.01, 25.70, 24.0, 15.59.

***tert*-butyl 3-(piperidin-1-yl)propanoate (6p)**[36]: Yellow liquid (181 mg, 85%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.64 (t, *J* = 7.76 Hz, 2H), 2.42-2.45 (m, 6H), 1.55-1.61 (m, 6H), 1.42 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.99, 80.42, 54.31, 54.19, 33.27, 28.11, 25.73, 24.15.

3,3′-(ethane-1,2-diylbis(azanediyl))dipropanenitrile (6q)[37]: Yellow liquid (131 mg, 79%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.90 (t, *J* = 6.52 Hz, 4H), 2.72 (s, 4H), 2.48 (t, *J* = 6.52 Hz, 4H), 1.67 (br, 2H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.81, 48.41, 44.98, 18.87.

3-((furan-2-ylmethyl)amino)propanenitrile (6r)[38]: Yellow liquid (117 mg, 78%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.36 (m, 1H), 6.29-6.31 (m, 1H), 6.19 (m, 1H), 3.81 (s, 2H), 2.90 (t, *J* = 6.76 Hz, 2H), 2.49 (t, *J* = 6.76 Hz, 2H), 1.74 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.91, 142.20, 118.60, 110.27, 107.48, 45.49, 44.12, 18.70.

***tert*-butyl 3-((furan-2-ylmethyl)amino)propanoate (6s)**: Yellow liquid (169 mg, 75%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 1H), 6.28-6.29 (m, 1H), 6.16-6.17 (m, 1H), 3.77 (s, 2H), 2.82 (t, *J* = 6.52 Hz, 2H), 2.42 (t, *J* = 6.28 Hz, 2H), 1.91 (br, 1H, NH), 1.42 (s, 9H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.10, 153.62, 141.88, 110.13, 107.01, 80.66, 46.13, 44.47, 35.70, 28.13. Mass: 225.2842, HRMS (ESI): calcd for [$C_{12}H_{19}NO_3 + Na^+$] 248.1257, found 248.1283.

3-((benzo[*d*][1,3]dioxol-5-ylmethyl)amino)propanenitrile (6t): Yellow liquid (147 mg, 72%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 1H), 6.75 (s, 2H), 5.94 (s, 2H), 3.73 (s, 2H), 2.90 (t, *J* = 6.52 Hz, 2H), 2.51 (t, *J* = 6.52 Hz, 2H), 1.73 (br, 1H, NH), ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.87, 146.78, 133.37, 121.23, 118.75, 108.57, 108.19, 101.02, 52.98, 44.16, 18.81. Mass: 204.2252, HRMS (ESI): calcd for [$C_{11}H_{12}N_2O_2 + Na^+$] 227.0791, found 227.0812.

3-(diethylamino)propanamide (6u)[6]: Yellow liquid (131 mg, 91%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (br, 1H, NH), 2.64 (t, *J* = 7.52 Hz, 2H), 2.49-2.52 (q, 4H), 2.32(t, *J* = 7.84 Hz, 2H), 0.99 (t, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 48.7, 46.0, 32.5, 11.3.

***tert*-butyl 3-(diethylamino)propanoate (6v)**[36]: Yellow liquid (175 mg, 87%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (t, *J* = 7.76 Hz, 2H), 2.50-2.55 (q, 4H), 2.37 (t, *J* = 7.8 Hz, 2H), 1.42 (s, 9H), 1.03 (t, 6H).

***tert*-butyl 3-((benzo[*d*][1,3]dioxol-5-ylmethyl)amino)propanoate (6w)**: Yellow liquid (195 mg, 70%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 1H), 6.75 (s, 2H), 5.92 (s, 2H), 3.69 (s, 2H), 2.82 (t, *J* =

6.56 Hz, 2H), 2.43 (t, J = 6.52 Hz, 2H), 1.97 (br, 1H, NH), 1.43 (s, 9H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.21, 147.71, 146.53, 134.03, 121.27, 108.72, 108.11, 100.90, 80.61, 53.61, 44.52, 35.77, 28.16. Mass: 279.3315, HRMS (ESI): calcd for [$C_{15}H_{21}NO_4 + Na^+$] 302.1363, found 302.1384.

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ASSOCIATED CONTENT

Supporting Information

"This material is available free of charge via the internet http://pubs.acs.org." Related figures and copies of ^{1}H and ^{13}C NMR spectra of the products are available in ESI.

NOTES

The authors declare no competing financial interest.

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