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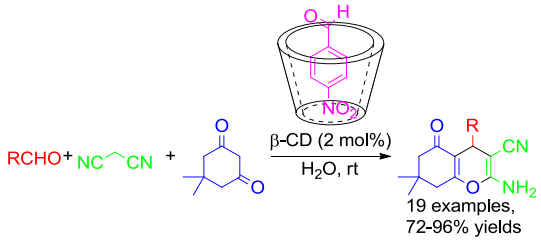
Graphical Abstract



Tetrahydro-4*H*-chromenes were synthesized via an efficient one-pot three-component protocol by supramolecular catalysis with β-cyclodextrin in water.

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ARTICLE

One-pot synthesis of tetrahydro-4*H*-chromenes by supramolecular catalysis in water

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Tetrahydro-4*H*-chromenes were synthesized via a one-pot three-component condensation catalyzed by β-cyclodextrin (β-CD) under mild conditions in water. The supramolecular reaction mechanism was extensively elucidated by spectroscopic analyses. This protocol could provide a unique strategy for the preparation of such biologically important scaffolds in supramolecular-catalyzed mode.

Introduction

Tetrahydro-4*H*-chromenes are important scaffolds existing among natural products and medicinal chemistry.[1] They possess some important biological activities including anticancer,[2] antimicrobial,[3] antioxidant[4] and molluscicidal[5] activities, etc. Thus the synthesis of tetrahydro-4*H*-chromenes has received numerous attentions from chemists. Many synthetic methods were reported.[6] However, most of them suffered from certain drawbacks such as use of toxic reagents or solvents, high temperature, long reaction time and difficulties to general application. So it is still necessary to explore new approach to the synthesis of tetrahydro-4*H*-chromenes.

Among existing catalytic methods in organic synthesis, supramolecular catalysis represents a unique fashion and the closest mode to enzyme catalysis, which could precisely regulate a specific reaction via sophisticated coordination of reaction components by non-covalent interactions.[7] Host-guest models are among essential catalytic systems for supramolecular catalysis. Natural or well-designed artificial supramolecular hosts have been employed in organic synthesis, such as crown ethers, cyclodextrins (CDs), calixarenes, cucurbiturils and cyclophanes, etc. Among those, CDs have attracted special interests ascribing to their unique virtues of readily accessibility, low toxicity, appreciable aqueous solubility and functional fecundity. They are truncated-cone-like cyclic oligosaccharides normally consisted of 6, 7 or 8 D-glucose units, referring to α-, β-, and γ-CD respectively (Fig. 1). β-CD is the most frequently used one in contrast to other CDs for its most readily availability, aqueous solubility and low toxicity. Native and modified β-CDs have been involved in varies of chemical transformations in aqueous media[8] such as oxidation,[9] reduction,[10] addition,[11] substitution[12] and condensation.[13] Recently, a grinding procedure using per-6-NH_2-β-CD was reported.[14] As part of our efforts to the developments of supramolecular chemistry based on CDs, we report here a one-pot three-components synthesis of tetrahydro-4*H*-chromenes by supramulecular catalysis with simple β-CD in water.

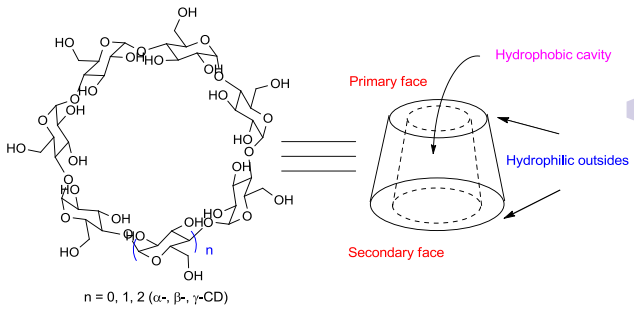

Fig. 1 Structures of α-, β-, and γ-CD.

Results and discussion

Optimization of reaction conditions are performed with a template reaction of 4-Cl-benzaldehyde, malononitrile and dimedone. The results were summarized in Table 1. Only a 23% yield of product was obtained when no catalyst was employed for this reaction (entry 1). It was found that β-CD could efficiently furnish the target molecule with excellent yield (94%) with a 10 mol% of catalyst loading in 5 h (entry 5), superior to other phase-transfer catalysts such as tetrabutyl ammonium chloride (TBAC, entry 2), hexadecyl trimethyl ammonium bromide (HTAB, entry 3) and tetraethyl ammonium iodide (TEAI, entry 4). Levels of yielding were maintained while a 4 or 2 mol% of catalyst loading was employed (entries 6 and 7), in contrast to a significant decline

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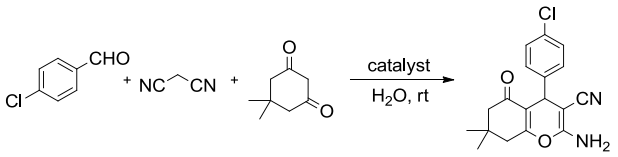
when decreasing to 1 mol% (entry 8). Neither extending the reaction time nor raising the reaction temperature did improve the yield (entries 9, 10 & 11). Besides, another two types of CDs, namely, α- and γ-CD both showed lower efficacy for this reaction (entries 12 & 13).

Table 1. Optimization of reaction conditions[a]

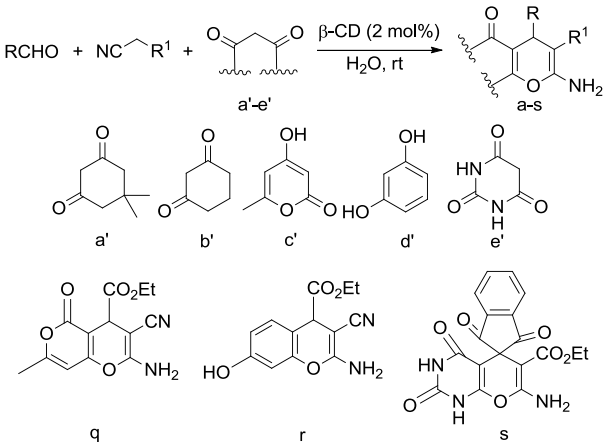


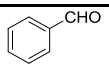
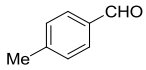
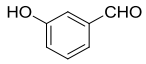
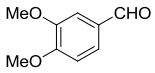
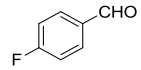
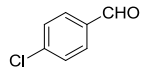
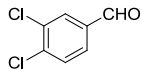
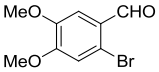
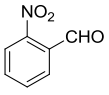
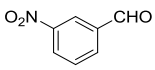
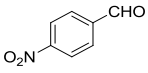
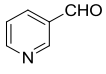
Entry	Catalyst (mol%)	Temperature	Time (h)	Yield (%)[b]
1	None	rt	5	23
2	TBAC (10)	rt	5	81
3	HTAB (10)	rt	5	70
4	TEAI (10)	rt	5	53
5	β-CD (10)	rt	5	94
6	β-CD (4)	rt	5	93
7	β-CD (2)	rt	5	94
8	β-CD (1)	rt	5	82
9	β-CD (2)	rt	7.5	93
10	β-CD (2)	60 °C	2.5	93
11	β-CD (2)	80 °C	1	94
12	α-CD (5)	rt	5	76
13	γ-CD (5)	rt	5	57

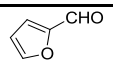
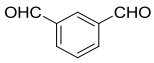
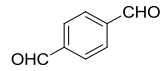
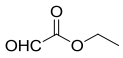
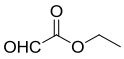
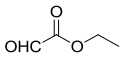
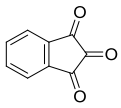
[a] Reaction conditions: 4-Cl-benzaldehyde (1 mmol), malononitrile (1.05 mmol) and dimedone (1.05 mmol) were stirred in water (5 mL) followed by TLC.
[b] Isolated yields.

With the optimized reaction conditions in hand, the substrate scope was investigated subsequently. As summarized in Table 2, benzaldehyde (entry 1) and aldehydes with electron-donating group (Me, OH, OMe, entries 2-4), halogen group (F or Cl, entries 5-7) or hybrid substituent groups (entry 8) all gave excellent yields (≥90%). However, it depended on the substitution position for electron-withdrawing group (NO_2). *m*-Nitro substitution on benzaldehyde maintained a high yield (91%, entry 10) while *o*- or *p*-nitro substitution both decreased the yields (entries 9 & 11). This indicated that electronic properties of substituted groups on the benzene ring might have considerable impacts on the reaction. Heterocyclic aromatic aldehydes, such as 3-pyridylaldehyde and furaldehyde could also give good yields (entries 12 & 13). To our delight, phthalaldehydes (*m*- and *p*-) also reacted smoothly to give dimeric symmetric molecules with satisfactory yields (entries 14 & 15). Ethyl glyoxalate instead of aryl aldehydes could also give the corresponding products with high yields (entries 16-18). When ninhydrin, ethyl cyanoacetate and barbituric acid were involved at one time, the product ethyl-7′-amino-1,2′,3,4′-tetraoxo-1,1′,2′,3,3′,4′-hexahydro-spiro[indene-2,5′-pyrano[2,3-d]pyrimidine]-6′-carboxylate (**s**) was obtained with excellent yield as well (entry 19).

Table 2. Substrate scope[a]



Entry	Aldehyde	R^1	Diketone	Product	Yield (%)
1		CN	a′	**a**	95
2		CN	a′	**b**	96
3		CN	a′	**c**	96
4		CN	a′	**d**	90
5		CN	a′	**e**	91
6		CN	a′	**f**	94
7		CN	a′	**g**	92
8		CN	a′	**h**	94
9		CN	a′	**i**	72
10		CN	a′	**j**	91
11		CN	a′	**k**	77
12		CN	a′	**l**	89

13		CN	a′	**m**	91
14[b]		CN	a′	**n**	83
15[b]		CN	a′	**o**	91
16		CN	b′	**p**	89
17		CN	c′	**q**	87
18		CN	d′	**r**	94
19		CO_2Et	e′	**s**	90

[a] General reaction conditions: aldehyde (1 mmol), malononitrile or ethyl cyanoacetate (1.05 mmol) and dimedone (1.05 mmol) were stirred in water (5 mL) at room temperature for 5 h.
[b] Aldehyde (1 mmol), malononitrile (2.1 mmol) and dimedone (2.1 mmol) were used in these cases.
[c] Isolated yields.

The catalytic mechanism of the reaction was firstly studied through ^{1}H NMR analysis with *p*-nitrobenzaldehyde as a model substrate. A comparison of the ^{1}H NMR spectra (in D_2O) of β-CD (A, in black), β-CD/*p*-nitrobenzaldehyde complex (B, in red), and freeze-dried reaction mixture of β-CD/*p*-nitrobenzaldehyde/dimedone (C, in blue) was shown in Fig. 2. It was obvious that there was an upfield shift of H_3 (0.01 ppm) and a downfield shift of H_5 (0.03 ppm) protons of β-CD in the β-CD/*p*-nitrobenzaldehyde complex comparing to β-CD, which indicated that the *p*-nitrobenzaldehyde was included in the cavity of β-CD. Furthermore, more significant shifts were found between the ^{1}H NMR spectra of freeze-dried reaction mixture of β-CD/*p*-nitrobenzaldehyde/dimedone and β-CD, in which an upfield shift of H_3 (0.04 ppm) and a downfield shift of H_5 (0.02 ppm) occurred.

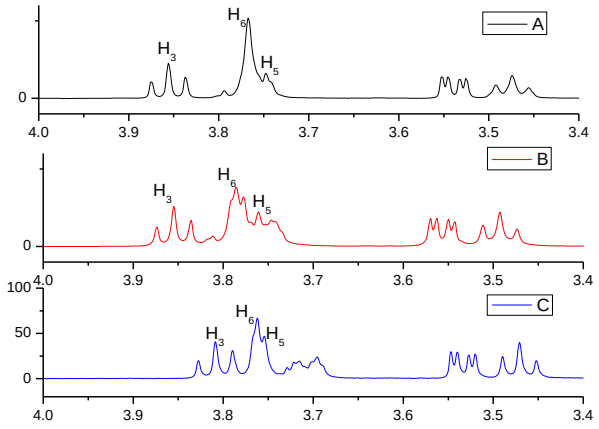


Fig. 2. ^{1}H NMR spectra (500 MHz) of (A) β-CD, (B) β-CD/*p*-nitrobenzaldehyde complex, and (C) freeze-dried reaction mixture of β-CD/*p*-nitrobenzaldehyde/malononitrile/dimedone. The spectra were obtained in D_2O at 25 °C.

In addition, the variation of the ^{1}H chemical shifts of guest substrate (*p*-nitrobenzaldehyde) before and after inclusion complexation with β-CD was recorded in DMSO-d_6/D_2O (Fig. 3). Significant downfield shifts for H_a (0.04), H_o (0.05 ppm) and H_m (0.06 ppm) protons of *p*-nitrobenzaldehyde were observed, further confirming the formation of inclusion complex of *p*-nitrobenzaldehyde with β-CD.

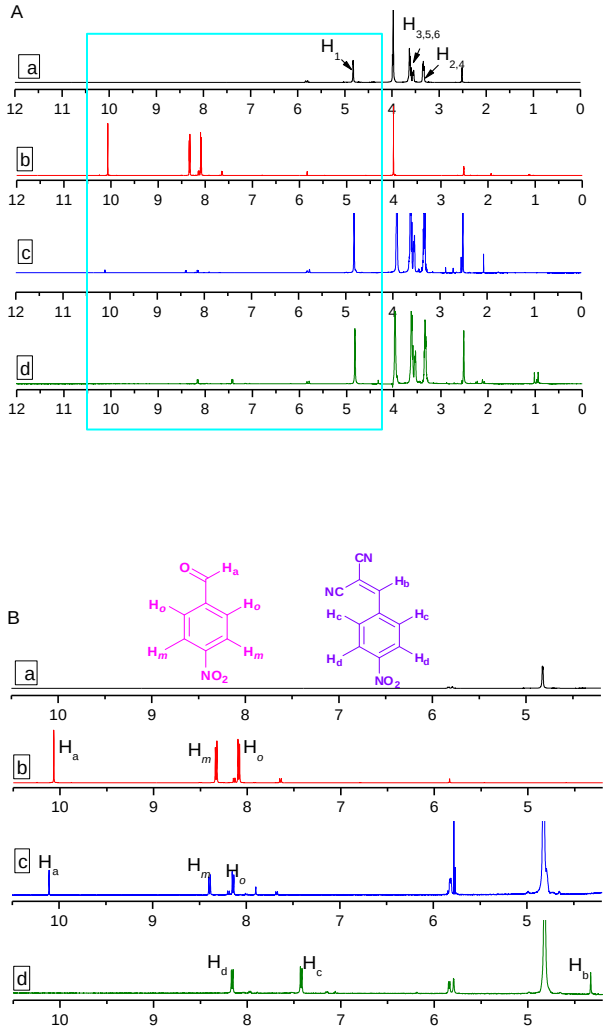


Fig. 3. (A) Complete and (B) enlarged (*δ* 4.2–12 ppm) ^{1}H NMR spectra (500 MHz) of (a) β-CD, (b) *p*-nitrobenzaldehyde, (c) β-CD/*p*-nitrobenzaldehyde complex, and (d) freeze-dried reaction mixture of β-CD/*p*-nitrobenzaldehyde/malononitrile/dimedone. The spectra were obtained in DMSO-d_6/D_2O=4:1 (v:v) at 25 °C.

The two-dimensional NMR (2D-NMR) spectroscopy (ROESY) further confirmed the formation of an inclusion complex between *p*-nitrobenzaldehyde and β-CD. As shown in Fig. 4,

the hydrogen on the aromatic ring of *p*-nitrobenzaldehyde had obvious Nuclear Overhauser Effect (NOE) interactions with H_3 and H_5 protons of β-CD.

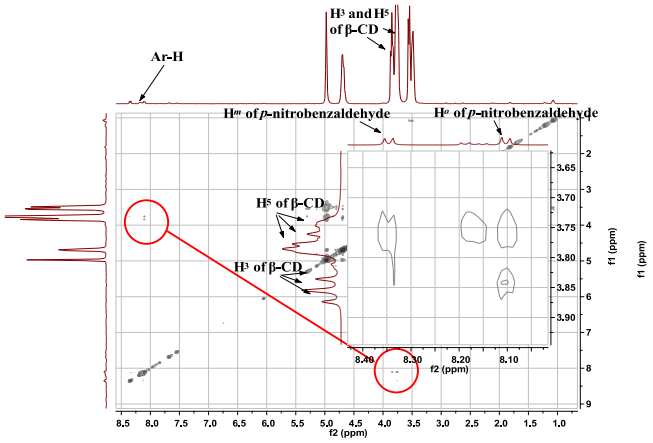


Fig. 4. ROESY of *p*-nitrobenzaldehyde/β-CD complex in D_2O at 25 °C.

The ROESY experiment could also help to elucidate the inclusion mode of β-CD/*p*-nitrobenzaldehyde complex. The spectrum showed sophisticated NOE correlations between aromatic protons of *p*-nitrobenzaldehyde and H_3 and H_5 protons of β-CD. In detail, the H_m protons of *p*-nitrobenzaldehyde correlated with H_5 protons of β-CD, whilst H*o* protons correlated with both H_5 and H_3 protons (see the enlarged view in Fig. 4). So, it seems that the nitro group is placed on the side of the primary face of β-CD, which is near to H_5 protons. The possible inclusion mode for the β-CD/*p*-nitrobenzaldehyde complex is therefore proposed as depicted in Fig. 5.

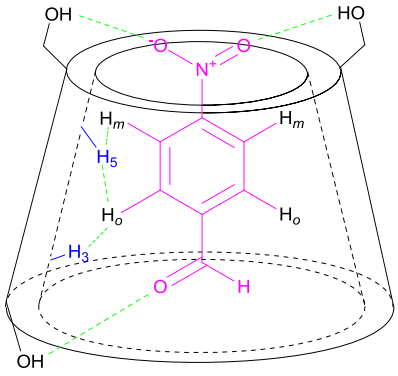


Fig. 5. Possible inclusion mode of β-CD/*p*-nitrobenzaldehyde complex.

Possible reaction mechanism could be further elucidated with the assistant of ROESY of freeze-dried reaction mixture of β-CD/*p*-nitrobenzaldehyde/malononitrile/dimedone in DMSO-d_6/D_2O (Fig. 6). Significant NOE correlations between aromatic protons (H_c) of Knoevenagel adduct of *p*-nitrobenzaldehyde with malononitrile and H_5 of β-CD could prove the inclusion complex of Knoevenagel adduct with β-CD during the reaction, similar to that between the unreacted dimedone and β-CD. So it seemed that β-CD provided hydrogen-bonding interactions with substrates and intermediates with not only its hydroxyl groups but also the interior protons H_3 and H_5 serving as the very catalyst in this reaction as illustrated in Fig. 5.

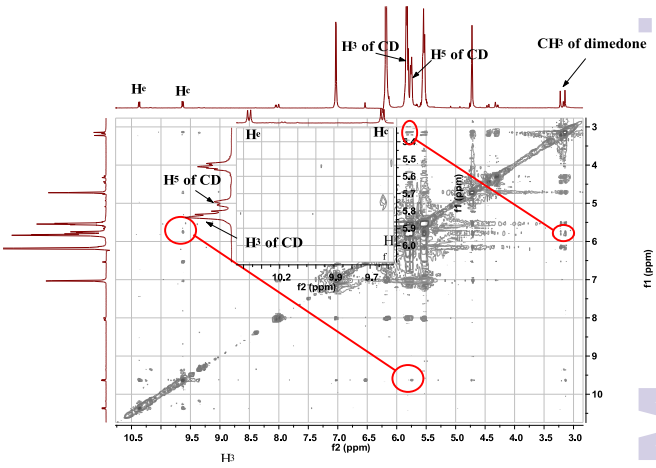


Fig. 6. ROESY of freeze-dried reaction mixture of β-CD/*p*-nitrobenzaldehyde/malononitrile/dimedone in DMSO-d_6/D_2O (4:1, v:v) at 25 °C.

Thus the reaction mechanism could then be proposed concisely based on the above information as follows: At first, a Knoevenagel condensation might take place between malononitrile and *p*-nitrobenzaldehyde. Subsequently, a Michael addition of dimedone to the Knoevenagel adduct followed by cyclization and hydrogen transfer furnished the tetrahydro-4*H*-chromene.

Conclusion

In summary, a one-pot three-component reaction of aldehydes, malononitrile and dimedone to construct the biologically active tetrahydro-4*H*-chromenes was established by supramolecular catalysis using β-CD in water. It provides a highly efficient and environmentally benign protocol of synthesis of 4*H*-chromene frameworks. The reaction mechanism proposed with the aid of spectrometric analysis might derive inspiration for organic synthesis based on supramolecular host-guest inclusions.

Experimental

General information

Melting points (uncorrected) were determined on an RY-1 instrument (Shanghai, China). IR spectra were recorded on a Bio-Rad FTS-40 FTIR spectrometer (Bio-Rad, USA). ^{1}H NMR spectra were measured on a Bruker Avance DRX 500 spectrometer (Bruker, Germany) at 298 K. HRESI-MS data were recorded on a Bruker MicrOTOF-Q-II mass spectrometer (Bruker, Germany). All reagents were of analytical purity and were used as received.

General procedure for preparation of tetrahydro-4*H*-chromenes

Aldehyde (1 mmol) was first added to distilled water（5 mL） in a 25-mL flask and the slurry was stirred to make the solids disperse in aqueous solution. Then β-CD (2% mol), malononitrile (1.05 mmol) and dimedone (1.05 mmol) were added sequentially. The mixture was allowed to stir at room temperature for 5 h (followed by TLC). The resulted precipitate was filtered and washed with water to yield almost pure products, which could be further purified by recrystallization by ethanol or by column chromatography on silica gel eluted by petroleum ether/ethyl acetate system.

2-Amino-3-cyano-7,7-dimethyl-4-phenyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (a). White solid; Yield: 95%; mp: 230-235 °C; IR (KBr, ν_{max}, cm^{-1}): 3403(NH_2), 2962(C-H), 2216(CN), 1677(C=O), 1664(C=C), 1593(C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.27 (t, J = 7.5 Hz, 2H, ArH), 7.19-7.17 (m, 1H, ArH), 7.13 (d, J = 7.2 Hz, 2H, ArH), 6.99 (s, 2H, NH_2), 4.15 (s, 1H), 2.51 (s, 2H, H-8, H-8′), 2.24 (d, J = 16.0 Hz, 1H, H-6), 2.09 (d, J = 16.0 Hz, 1H, H-6′), 1.02 (s, 3H), 0.94 (s, 3H); HRMS (ESI) m/z calcd for $C_{18}H_{18}N_2NaO_2$ ($[M+Na]^+$): 317.1266, found 317.1259.

2-Amino-3-cyano-7,7-dimethyl-4-(4-methylphenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (b). White powder; Yield: 96%; mp: 235 °C; IR (KBr, ν_{max}, cm^{-1}): 3383 (NH_2), 2968 (C-H), 2190 (CN), 1690 (C=O), 1645 (C=C), 1606 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.07 (d, J = 7.9 Hz, 2H, ArH), 7.00 (d, J = 8.1 Hz, 2H, ArH), 6.95 (s, 2H, NH_2), 4.11 (s, 1H), 2.50 (d, J = 8 Hz, 1H, H-8), 2.48 (s, 1H, H-8′), 2.24-2.21 (d, J = 16 Hz, 1H, H-6), 2.23 (s, 3H, CH_3), 2.07 (d, J = 16 Hz, 1H, H-6′), 1.02 (s, 3H), 0.93 (s, 3H); HRMS (ESI) m/z calcd for $C_{19}H_{20}N_2NaO_2$ ($[M+Na]^+$): 331.1422, found 331.1423.

2-Amino-3-cyano-7,7-dimethyl-4-(3-hydroxyphenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (c). White powder; Yield: 96%; mp: 295-300 °C; IR (KBr, ν_{max}, cm^{-1}): 3461 (OH), 3318, 3208 (NH_2), 2203 (CN), 1684 (C=O), 1645 (C=C), 1600(C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.33(s, 1H, OH), 7.04 (t, J = 8.0 Hz, 1H, ArH), 6.96 (s, 2H, NH_2), 6.53 (t, J = 4.1 Hz 3H, ArH), 4.04 (s, 1H), 2.52 (J = 19.0, 1.8 Hz, 1H, H-8), 2.45 (d, J = 17.6 Hz, 1H, H-8′), 2.24 (d, J = 16.1 Hz, 1H, H-6), 2.19 (d, J = 16.1 Hz, 1H, H-6′), 1.02 (s, 3H), 0.95 (s, 3H); HRMS (ESI) m/z calcd for $C_{18}H_{18}N_2NaO_3$ ($[M+Na]^+$): 333.1215, found 333.1191.

2-Amino-3-cyano-7,7-dimethyl-4-(3,4-dimethoxyphenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (d). White powder; Yield: 90%; mp: 206-208 °C; IR (KBr, ν_{max}, cm^{-1}): 3409 (NH_2), 2962 (C-H), 2203 (CN), 1697 (C=O), 1658 (C=C), 1606 (C=C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.96 (s, 2H), 6.87–6.85 (d, 1H, J = 8.4 Hz), 6.69–6.68 (d, J = 2.0 Hz, 1H), 6.66–6.64 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), 4.12 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.52-2.49 (m, 2H), 2.28-2.08 (m, 2H), 1.03 (s, 3H), 0.97 (s, 3H); HRMS (ESI) m/z calcd for $C_{20}H_{22}N_2NaO_4$ ($[M+Na]^+$): 377.1477, found 377.1472.

2-Amino-3-cyano-7,7-dimethyl-4-(4-fluorophenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (e). White solid; Yield: 91%; mp: 196 °C; IR (KBr, ν_{max}, cm^{-1}): 3448 (NH_2), 3046 (C-H), 2242 (CN), 1606 (C=O), 1580 (C=C), 1522 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.19 (d, J = 8.4 Hz, 2H, ArH), 7.07 (d, J = 8.4 Hz, 2H, ArH), 7.04 (s, 2H, NH_2), 4.19 (s, 1H), 2.48 (s, 2H, H-8 H-8′), 2.24 (d, J = 16.1 Hz, 1H, H-6), 2.10 (d, J = 16.1 Hz, 1H, H-6′), 1.01 (s, 3H), 0.93 (s, 3H); HRMS (ESI) m/z calcd for $C_{18}H_{17}FN_2NaO_2$ ($[M+Na]^+$): 335.1172, found 335.1175.

2-Amino-4-(4-chlorophenyl)-3-cyano-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (f). White solid; Yield: 94%; mp: 225 °C; IR (KBr, ν_{max}, cm^{-1}): 3448 (NH_2), 3040 (C-H), 2242 (CN), 1600 (C=O), 1593 (C=C), 1487 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.33 (d, J = 8.4 Hz, 2H, ArH), 7.16 (d, J = 8.4 Hz, 2H, ArH), 7.05 (s, 2H, NH_2), 4.18 (s, 1H), 2.48 (s, 2H, H-8， H-8′), 2.25 (d, J = 16.1 Hz, 1H, H-6), 2.10 (d, J = 16.1 Hz, 1H, H-6′), 1.01 (s, 3H), 0.93 (s, 3H); HRMS (ESI) m/z calcd for $C_{18}H_{18}ClN_2O_2$ ($[M+H]^+$): 329.1051, found 329.1050.

2-Amino-3-cyano-4-(3,4-dichlorophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (g). White solid; Yield: 92%; mp: 225-230 °C; IR (KBr, ν_{max}, cm^{-1}): 3409 (NH_2), 2955 (C-H), 2203 (CN), 1677 (C=O), 1613 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.55 (d, J = 8.3 Hz, 1H, ArH), 7.37 (d, J = 2.1 Hz, 1H, ArH), 7.14 (m, 1H, ArH), 7.12 (s, 2H, NH_2), 4.23 (s, 1H), 2.49 (dd, J = 3.4, 1.7 Hz, 2H, H-8, H-8′), 2.23 (d, J = 16.1 Hz, 1H, H-6), 2.11 (d, J = 16.1 Hz, 1H, H-6′), 1.02 (s, 3H), 0.94 (s, 3H); HRMS (ESI) m/z calcd for $C_{18}H_{17}Cl_2N_2O_2$ ($[M+H]^+$): 363.0662, found 363.0642.

2-Amino-4-(2-bromo-3,4-dimethoxyphenyl)-3-cyano-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (h). White powder; Yield: 94%; mp: 186 °C; IR (KBr, ν_{max}, cm^{-1}): 3487 (NH_2), 2968 (C-H), 2190 (CN), 1671 (C=O), 1638 (C=C), 1593 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.98 (s, 1H, ArH), 6.65 (s, 1H, ArH), 4.77 (s, 1H), 4.66 (s, 2H, NH_2), 3.83 (s, 3H), 3.82 (s, 3H), 2.52-2.39 (dd, J = 14.0, 9.5 Hz, 2H, H-8, H-8′), 2.29 (d, J = 16.1 Hz, 1H H-6), 2.17 (d, J = 16.1 Hz, 1H, H-6′), 1.12 (s, 3H), 1.09 (s, 3H); HRMS (ESI) m/z calcd for $C_{20}H_{21}BrN_2NaO_4$ ($[M+Na]^+$):455.0577, found 455.0577.

2-Amino-3-cyano-7,7-dimethyl-4-(2-nitrophenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (i). Light yellow powder; Yield: 72%; mp: 232-234 °C; IR (KBr, ν_{max}, cm^{-1}): 3481 (NH_2), 2955 (C-H), 2203 (CN), 1697 (C=O), 1677 (C=C), 1606 (C=C), 1541 (NO_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.17 (s, 2H), 4.93 (s, 1H), 2.50 (s, 2H), 2.20 (d, J = 16.1 Hz, 1H), 2.01 (d, J = 16.1 Hz, 1H), 1.01 (s, 3H), 0.88 (s, 3H); HRMS (ESI) m/z calcd for $C_{18}H_{17}N_3NaO_4$ ($[M+Na]^+$): 362.1111, found 362.1101.

2-Amino-3-cyano-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (j). Light yellow powder; Yield: 91%; mp: 206-208 °C; IR (KBr, ν_{max}, cm^{-1}): 3440 (NH_2), 2968 (C-H), 2190 (CN), 1690 (C=O), 1613 (C=C), 1528 (NO_2); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.10-8.04 (m, 2H, ArH), 7.48-7.68 (m, 2H, ArH), 6.04 (brs, 2H, NH_2), 4.53 (s, 1H), 2.48 (d, J = 8 Hz, 2H, H-8, H-8′), 2.29 (d, J = 16.1 Hz, 1H, H-6), 2.17 (d, J = 16.1 Hz, 1H, H-6′), 1.11 (s, 3H), 1.03 (s, 3H); HRMS (ESI) m/z calcd for $C_{18}H_{17}N_3NaO_4$ ($[M+Na]^+$): 362.1111, found 362.1111.

2-Amino-3-cyano-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (k). Light yellow powder; Yield: 77%; mp: 150-153 °C; IR (KBr, ν_{max}, cm^{-1}): 3409 (NH_2), 2962 (C-H), 2196 (CN), 1697 (C=O), 1671 (C=C), 1600 (C=C), 1522(NO_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J = 8.1 Hz, 2H), 7.44 (d,

J = 8.1 Hz, 2H), 7.17 (s, 2H), 4.36 (s, 1H), 2.50 (s, 2H), 2.26 (d, *J* = 15.7 Hz, 1H), 2.11 (d, *J* = 15.7 Hz, 1H), 1.04 (s, 3H), 0.96 (s, 3H); HRMS (ESI) *m/z* calcd for $C_{18}H_{18}N_3O_4$ ($[M+H]^+$): 340.1292, found 340.1272.

2-Amino-3-cyano-7,7-dimethyl-4-(3-pyridinyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (l). Light yellow powder; Yield: 89%; mp: 255-256 °C; IR (KBr, ν_{max}, cm^{-1}): 3325 (NH_2), 2949 (C-H), 2196 (CN), 1690 (C=O), 1671 (C=C), 1600 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.44–8.33 (m, 2H, ArH), 7.53 (dt, *J* = 7.8, 1.9 Hz, 1H, ArH), 7.31(dd, *J* = 7.8, 4.8 Hz, 1H, ArH), 7.11 (s, 2H, NH2), 4.24 (s, 1H), 2.52 (s, 2H, H-8, H-8´), 2.24 (d, *J* = 16.1 Hz, 1H, H-6), 2.11 (d, *J* = 16.1 Hz, 1H, H-6´), 1.02 (s, 3H), 0.94 (s, 3H); HRMS (ESI) *m/z* calcd for $C_{17}H_{18}N_3O_2$ ($[M+H]^+$): 296.1394, found 296.1447.

2-Amino-3-cyano-7,7-dimethyl-4-(2-furyl)-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran (m). White powder; Yield: 91%; mp: 225-226 °C; IR (KBr, ν_{max}, cm^{-1}): 3403 (NH_2), 2955 (C-H), 2196 (CN), 1690 (C=O), 1677 (C=C), 1613 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.48-7.45 (m, 1H, furan-H), 7.06 (s, 2H), 6.31 (dd, *J* = 3.0, 1.9 Hz, 1H, furan-H), 6.04 (d, *J* = 3.2 Hz, 1H, furan-H), 4.31 (s, 1H), 2.51 (d, *J* = 17.6 Hz, 1H , H-8), 2.45 (s, 1H, H-8´), 2.27 (d, *J* = 16.1 Hz, 1H, H-6), 2.15 (d, *J* = 16.1 Hz, 1H, H-6´), 1.03 (s, 3H), 0.97 (s, 3H); HRMS (ESI) *m/z* calcd for $C_{16}H_{16}N_2NaO_3$ ($[M+Na]^+$):307.1053, found 307.1037.

1,3-Bis(2-amino-3-cyano-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran)benzene (n). White powder; Yield: 83%; mp: 300 °C (decomp.); IR (KBr, ν_{max}, cm^{-1}): 3455 (NH_2), 2942 (C-H), 2248 (CN), 1613 (C=O), 1574 (C=C), 1483 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.02-6.92 (m, 4H, ArH), 6.79 (brs, 4H, 2×NH_2), 4.11 (s, 2H), 2.61 (m, 2H, H-8), 2.47 (m, 2H, H-8´), 2.15(d, *J* = 16.1 Hz, 2H, H-6), 2.02 (d, *J* = 16.1 Hz, 2H, H-6´), 1.03 (s, 6H), 0.95 (s, 6H); HRMS (ESI) *m/z* calcd for $C_{30}H_{30}N_4NaO_4$ ($[M+Na]^+$):533.2159, found 533.7487.

1,4-Bis(2-amino-3-cyano-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran)benzene (o). White powder; Yield: 91%; mp: 305 °C; IR (KBr, ν_{max}, cm^{-1}): 3435 (NH_2), 2942 (C-H), 2235 (CN), 1606 (C=O), 1590 (C=C), 1496 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.05 (s, 4H, ArH), 6.97 (s, 4H, 2×NH_2), 4.14 (s, 2H), 2.57-2.52 (m, 2H, H-8), 2.47 (s, 2H, H-8´), 2.24(d, *J* = 16.1 Hz, 2H, H-6), 2.18 (d, *J* = 16.1 Hz, 2H, H-6´), 1.04 (s, 6H), 0.99 (s, 6H); HRMS (ESI) *m/z* calcd for $C_{30}H_{30}N_4NaO_4$ ($[M+Na]^+$):533.2159, found $[M+Na]^+$:533.7909.

2-Amino-3-cyano-4-ethyl formate-5-oxo-4*H*-5,6,7,8-tetrahydroenzopyran (p). White powder; Yield: 89%; mp: 155-156 °C; IR (KBr, ν_{max}, cm^{-1}): 3370 (NH_2), 2983, 2899 (C-H), 2196 (CN), 1654 (C=O); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.25 (s, 2H, NH_2), 4.07 (m, *J* = 7.0 Hz, 2H, CH_2), 3.78 (s, 1H, CH), 2.57 (m, 2H, CH_2), 2.34 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 1.17 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR(126 MHz, DMSO-d_6) δ 196.46, 171.57, 165.41, 159.88, 119.05, 110.25, 61.04, 51.71, 36.33, 36.15, 26.57, 20.25, 14.42; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}N_2NaO_4$ ($[M+Na]^+$): 285.0851, found 285.0847.

2-Amino-4-ethyl formate-7-methyl-5-oxo-4,5-dihydropyrano [4,3-b]pyran-3-carbonitrile (q). White powder; Yield: 87%; mp: 195-197 °C; IR (KBr, ν_{max}, cm^{-1}): 3389, 3360 (NH_2), 3084 (=CH), 2989, 2885 (C-H), 2206 (CN), 1726 (C=O); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.45 (s, 2H, NH_2), 6.28 (s, 1H, -CH=), 4.13 (m, *J* 7.0 Hz, 2H, CH_2), 3.96 (s, 1H, CH), 2.27 (s, 3H, CH_3), 1.19 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR(126 MHz, DMSO-d_6) δ 171.02, 163.94, 162.05, 159.57, 159.17, 118.63, 98.18, 97.09, 61.51, 51.60, 36.97, 19.71, 14.41; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_2NaO_5$ ($[M+Na]^+$): 299.0644, found 299.0643.

2-Amino-3-cyano-4-ethyl formate-7-hydroxy-4*H*-chromene (r). White powder; Yield: 94%; mp: 201-202 °C; IR (KBr, ν_{max}, cm^{-1}): 3480, 3320 (NH_2), 2996 (C-H), 2205 (CN), 1696 (C=O), 1652, 1614, 1588 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.82 (s, 1H, OH), 7.08 (d, *J* = 8.2 Hz, 1H, ArH), 7.06 (S, 2H, NH_2), 6.59 (dd, *J* = 8.3, 1.6 Hz, 1H, ArH), 6.42 (d, *J* = 1.6 Hz, 1H, ArH), 4.32 (s, 1H, CH), 4.09 (q, *J* = 7.0 Hz, 2H, CH_2), 1.16 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR(126 MHz, DMSO-d_6) δ 172.44, 161.73, 158.36, 149.81, 129.57, 120.41, 112.68, 108.45, 102.93, 61.30, 50.90, 40.99, 14.41; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_2NaO_4$ ($[M+Na]^+$): 283.0695, found 283.0694.

Ethyl-7′-amino-1,2′,3,4′-tetraoxo-1,1′,2′,3,3′,4′-hexahydrospiro[indene-2,5′-pyrano[2,3-d]pyrimidine]-6′-carboxylate (s). Light yellow powder; Yield: 90%; mp: 278-279 °C; IR (KBr, ν_{max}, cm^{-1}): 3604 (NH), 3385, 3275 (NH_2), 2985 (C-H), 1730, 1699, 1672 (C=O), 1512, 1447, 1415 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.47 (s, 1H, NH), 11.15 (s, 1H,NH), 8.16 (s, 2H, NH_2), 7.91 (dt, *J* = 6.8, 3.5 Hz, 2H, ArH), 7.87 (dt, *J* = 6.8, 3.5 Hz, 2H, ArH), 3.57 (q, *J* = 7.1 Hz, 2H, CH_2), 0.31 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR(126 MHz, DMSO-d_6) δ 202.79, 166.95, 162.70, 160.09, 153.96, 149.41, 142.19, 135.39, 122.08, 88.10, 74.06, 59.81, 51.61, 12.69; HRMS (ESI) *m/z* calcd for $C_{18}H_{14}N_3O_7$ ($[M+H]^+$): 384.0832, found 384.0829.

Preparation of β-CD/*p*-nitrobenzaldehyde inclusion complex.

β-CD (0.1 mmol) was dissolved in water (5 mL) and the mixture was allowed to stir constantly to form a clear solution with the evolution of heat (the solution temperature reached approximately 50 °C. Then *p*-nitrobenzaldehyde (0.1 mmol) in methanol (0.3 mL) was added dropwise. After addition finished the mixture was cooled to room temperature and then was placed in an ice bath for 12 h. It was filtered to remove any insolubles. Finally, the inclusion complex was obtained as dried solid by rotary evaporation *in vacuo*.

Preparation of freeze-dried reaction mixture of β-CD/*p*-nitrobenzaldehyde/malononitrile/dimedone

β-CD (0.1 mmol) was dissolved in water (5 mL) with constant stirring, followed by the dropwise addition of a methanol solution (0.3 mL) of *p*-nitrobenzaldehyde (0.1 mmol), malononitrile (0.1 mmol) and dimedone (0.1 mmol). The resultant mixture was stirred for 15 min. Then it was cooled to room temperature and was placed in an ice bath for 12 h followed by filtration to remove any insolubles. Finally, the freeze-dried powder was obtained by freeze-drying.

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Notes and references

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