Supplementary Material

1 Supplementary Data

2-Amino-3-cyano-7-hydroxy-4-(3-nitrophenyl)-4H-chromene (4b)

Yield: 94%; M.p. 166-168 °C; \(^1\)HNMR (300 MHz, DMSO-d\(_6\)): 4.82 (1H, s, CHAr), 6.19 (1H, d, J=8.8 Hz, ArH), 6.59 (1H, d, J=9.6 Hz, ArH), 6.77 (1H, d, J=9.6 Hz, ArH), 6.97 (2H, s, NH\(_2\)), 7.33 (2H, d, J=9.6 Hz, ArH), 7.86 (2H, d, J=9.6 Hz, ArH), 9.69 (1H, s, OH).

2-Amino-3-cyano-7-hydroxy-4-(4-methylphenyl)-4H-chromene (4c)

Yield: 91%; M.p. 185-187 °C; \(^1\)HNMR (300 MHz, DMSO-d\(_6\)): 2.51 (3H, s, CH\(_3\)), 4.72 (1H, s, CHAr), 6.21 (1H, d, J=9.6 Hz, ArH), 6.70 (1H, d, J=9.6 Hz, ArH), 6.84 (1H, d, J=10.4 Hz, ArH), 7.03 (2H, s, NH\(_2\)), 7.17 (2H, d, J=9.6 Hz, ArH), 7.48 (2H, d, J=9.6 Hz, ArH), 9.63 (1H, s, OH).

2-Amino-3-cyano-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene (4p)
Yield: 88%; M.p. 208-210 °C; $^1$HNMR (300 MHz, DMSO-d$_6$): 3.71 (3H, s, OCH$_3$), 4.53 (1H, s, CHAr), 6.18 (1H, d, $J$=8.8 Hz, ArH), 6.45 (1H, dd, $J$=7.2, 2.4 Hz, ArH), 6.77 (1H, d, $J$=8.4 Hz, ArH), 6.84 (2H, s, NH$_2$), 7.25 (2H, d, $J$=8.4 Hz, ArH), 7.83 (2H, d, $J$=9.2 Hz, ArH), 9.78 (1H, s, OH).

2 Supplementary Figures and Tables

2.1 Supplementary Figures

Supplementary Scheme 1.
Supplementary Scheme 2.
## 2.2 Supplementary Tables

**Table 1.** Optimization table of photocatalyst, solvent and visible-light for the synthesis of 4a\(^a\)

![Chemical Reaction](image)

| Entry | Photocatalyst          | Light Source         | Solvent (3 mL)          | Time (min) | Isolated Yields (%) |
|-------|------------------------|----------------------|-------------------------|------------|---------------------|
| 1     | __                     | White light (18 W)   | H\(_2\)O/EtOH (2:1)     | 15         | 57                  |
| 2     | Na\(_2\) eosin Y (0.2 mol%) | White light (18 W)   | H\(_2\)O/EtOH (2:1)     | 5          | 78                  |
| 3     | Na\(_2\) eosin Y (0.5 mol%) | White light (18 W)   | H\(_2\)O/EtOH (2:1)     | 5          | 93                  |
| 4     | Na\(_2\) eosin Y (1 mol%) | White light (18 W)   | H\(_2\)O/EtOH (2:1)     | 5          | 93                  |
| 5     | Na\(_2\) eosin Y (0.5 mol%) | White light (18 W)   | EtOAc                   | 5          | 67                  |
| 6     | Na\(_2\) eosin Y (0.5 mol%) | White light (18 W)   | EtOH                    | 5          | 63                  |
| 7     | Na\(_2\) eosin Y (0.5 mol%) | White light (18 W)   | MeOH                    | 10         | 52                  |
| 8     | Na\(_2\) eosin Y (0.5 mol%) | White light (18 W)   | H\(_2\)O                 | 5          | 70                  |
| 9     | Na\(_2\) eosin Y (0.5 mol%) | White light (18 W)   | __                      | 10         | 75                  |
|   | Reaction Conditions                                                                 |
|---|------------------------------------------------------------------------------------|
| 10| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | H$_2$O/EtOH (1:1) | 5 | 79 |
| 11| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | H$_2$O/EtOH (1:2) | 5 | 72 |
| 12| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | Toluene | 20 | 46 |
| 13| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | CHCl$_3$ | 25 | 27 |
| 14| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | THF | 25 | 32 |
| 15| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | CH$_2$Cl$_2$ | 25 | 30 |
| 16| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | DMSO | 15 | 42 |
| 17| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | DMF | 25 | 36 |
| 18| Na$_2$ eosin Y (0.5 mol%) | White light (18 W) | CH$_3$CN | 10 | 49 |
| 19| Na$_2$ eosin Y (0.5 mol%) | Green light (18 W) | H$_2$O/EtOH (2:1) | 5 | 81 |
| 20| Na$_2$ eosin Y (0.5 mol%) | Blue light (18 W) | H$_2$O/EtOH (2:1) | 5 | 76 |
| 21| Na$_2$ eosin Y (0.5 mol%) | — | H$_2$O/EtOH (2:1) | 20 | <5 |
| 22| Na$_2$ eosin Y (0.5 mol%) | White light (10 W) | H$_2$O/EtOH (2:1) | 5 | 71 |
| 23| Na$_2$ eosin Y (0.5 mol%) | White light (12 W) | H$_2$O/EtOH (2:1) | 5 | 80 |
| 24| Na$_2$ eosin Y (0.5 mol%) | White light (20 W) | H$_2$O/EtOH (2:1) | 5 | 93 |
| 25| | White light (18 W) | H$_2$O/EtOH (2:1) | 5 | 51 |

**Erythrosin B (0.5 mol%)**

|   | Reaction Conditions |
|---|---------------------|
| 26| White light (18 W) | H$_2$O/EtOH (2:1) | 5 | 53 |
Phenanthrenequinone (0.5 mol%)

27

Rhodamine B (0.5 mol%)

28

Acenaphthenequinone (0.5 mol%)

29

Riboflavin (0.5 mol%)

30

9H-Xanthen-9-one (0.5 mol%)

31
Fluorescein (0.5 mol%)

32

White light (18 W)  H₂O/EtOH (2:1)  5  68

Rose bengal (0.5 mol%)

*Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), resorcinol (1 mmol) in visible-light, various solvents and photocatalysts at rt.

**Supplementary Table 1.**

**Table 2.** Photoexcited Na₂ eosin Y as photocatalyst for synthesis of 2-amino-4H-chromene scaffolds.
| Compound | Reaction Time | Yield | Melting Point |
|----------|---------------|-------|---------------|
| 4a       | 5 min         | 93%   | 234-236 °C    |
|          |               |       | Lit. 232-234 °C [27] |
| 4b       | 5 min         | 94%   | 166-168 °C    |
|          |               |       | Lit. 168-170 °C [32] |
| 4c       | 3 min         | 91%   | 185-187 °C    |
|          |               |       | Lit. 186-188 °C [28] |
| 4d       | 10 min        | 88%   | 223-225 °C    |
|          |               |       | Lit. 222-224 °C [24] |
| 4e       | 7 min         | 91%   | 179-181 °C    |
|          |               |       | Lit. 180-182 °C [33] |
| 4f       | 5 min         | 95%   | 192-194 °C    |
|          |               |       | Lit. 190-192 °C [32] |
| 4g       | 10 min        | 84%   | 249-251 °C    |
|          |               |       | Lit. 250-252 °C [23] |
| 4h       | 5 min         | 86%   | 187-189 °C    |
|          |               |       | Lit. 189-191 °C [27] |
| 4i       | 5 min         | 92%   | 194-196 °C    |
|          |               |       | Lit. 194-196 °C [24] |
| Compound | Reaction Time | Yield | Melting Point | Literature Melting Point |
|----------|---------------|-------|---------------|--------------------------|
| 4j       | 9 min         | 87%   | 200-202 °C    | 198-200 °C [35]          |
| 4k       | 5 min         | 92%   | 211-213 °C    | 210-212 °C [24]          |
| 4l       | 3 min         | 93%   | 146-148 °C    | 148-150 °C [29]          |
| 4m       | 7 min         | 89%   | 175-177 °C    | 176-178 °C [35]          |
| 4n       | 3 min         | 94%   | 227-229 °C    | 228-231 °C [25]          |
| 4o       | 3 min         | 96%   | 227-229 °C    | 228-231 °C [25]          |
| 4p       | 7 min         | 88%   | 208-210 °C    | 210-212 °C [29]          |
| 4q       | 10 min        | 83%   | 259-261 °C    | 257-259 °C [27]          |
| 4r       | 3 min         | 96%   | 160-162 °C    | 162-163 °C [34]          |
Table 3. The comparison between the catalytic capacity of some catalysts in this work$^a$

| Entry | Catalyst             | Conditions    | Time/Yield (%) | References |
|-------|----------------------|---------------|----------------|------------|
| 1     | glycine              | H$_2$O, sonication | 9 min/94       | [22]       |
| 2     | mesolite             | EtOH, reflux  | 30 min/93      | [23]       |
| 3     | potassium phthalimide | H$_2$O, reflux | 12 min/94      | [24]       |
| No. | Catalyst/Reactant                  | Reaction Conditions          | Time | Ref. |
|-----|-----------------------------------|------------------------------|------|------|
| 4   | MgFe$_2$O$_4$NPs                  | EtOH, 65 °C                  | 12 min/74 | [25] |
| 5   | POM@Dy-PDA                        | EtOH/H$_2$O, reflux          | 15 min/95 | [26] |
| 6   | P4VPy-CuI                         | H$_2$O, reflux               | 15 min/94 | [27] |
| 7   | nanozeolite clinoptilolite        | H$_2$O, reflux               | 15 min/92 | [28] |
| 8   | WELFSA                            | H$_2$O, rt                   | 1.5 h/88 | [29] |
| 9   | tungstic acid functionalized SBA-15 | H$_2$O, 100 °C            | 12 min/86 | [30] |
| 10  | MIL-101(Cr)-SO$_3$H               | H$_2$O, 100 °C               | 180 min/82 | [31] |
| 11  | [Et$_2$NH(CH$_2$)$_2$CO$_2$H][AcO] | solvent-free, 60 °C         | 12 min/92 | [32] |
| 12  | {[4,4′-BPyH][C(CN)$_3$]$_2$}      | solvent-free, 80 °C         | 15 min/90 | [33] |
| 13  | DBU                               | EtOH, MW, 50 °C             | 3 min/94 | [34] |
| 14  | hydrotalcite                      | H$_2$O, 60 °C               | 4 h/95  | [35] |
| 15  | Na$_2$ eosin Y                    | visible light irradiation, H$_2$O/EtOH (2:1), rt | 5 min/93 | This work |

$^a$ Based on the three-component reaction of benzaldehyde, malononitrile and resorcinol.

Supplementary Table 3.