

## Crystal structure of co-crystals

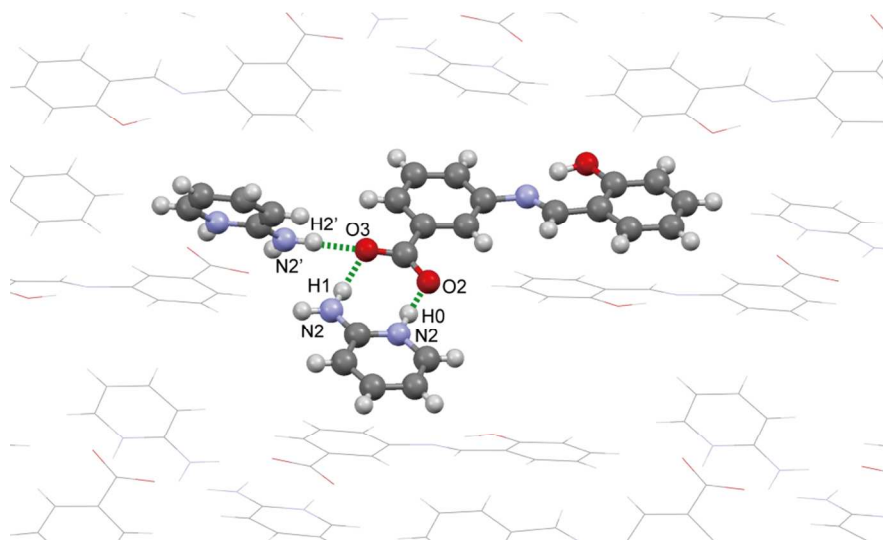


Figure S1. Crystal structure of **1a**

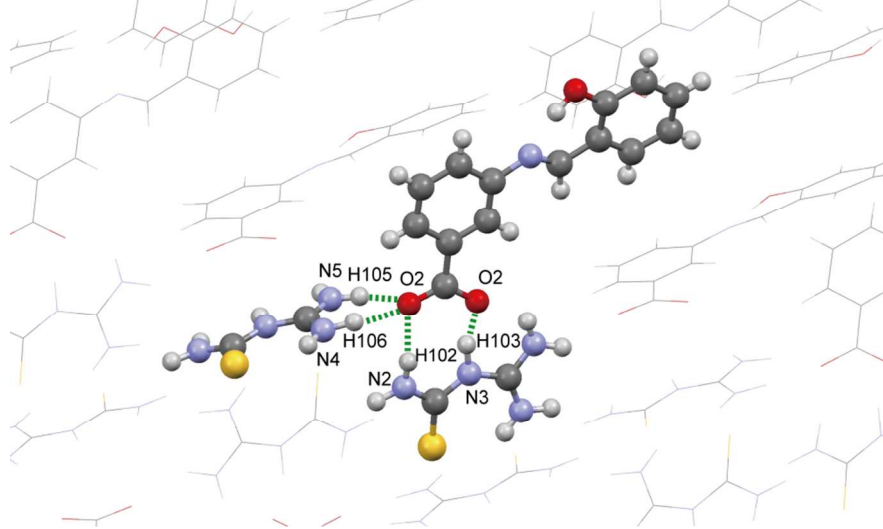


Figure S2. Crystal structure of **1b**

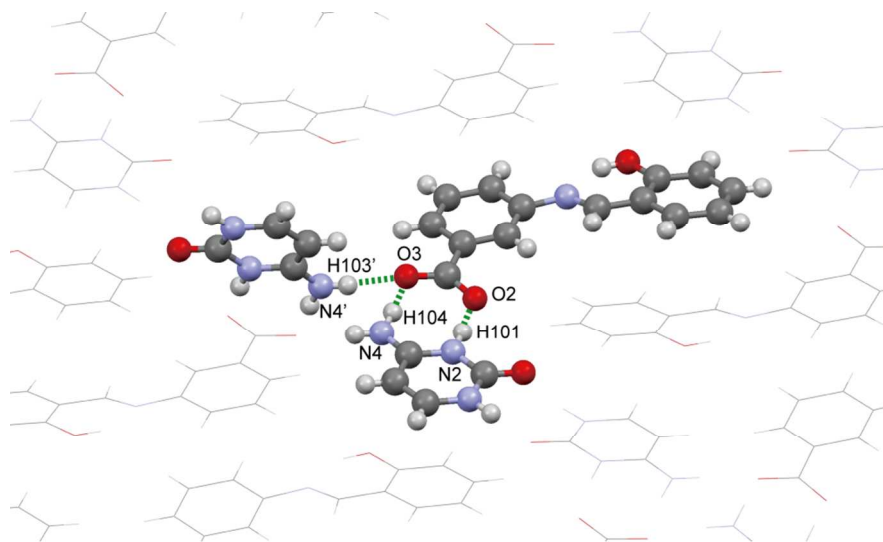


Figure S3. Crystal structure of **1c**

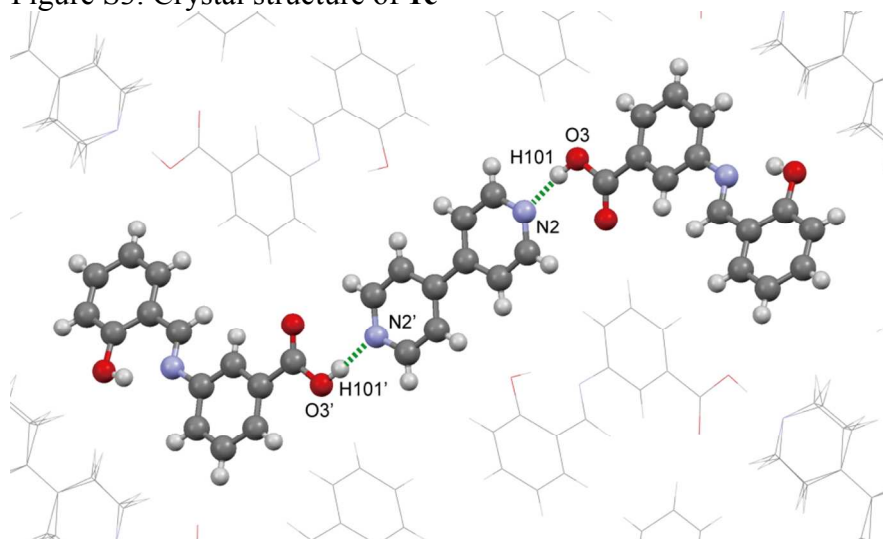


Figure S4. Crystal structure of **1d**

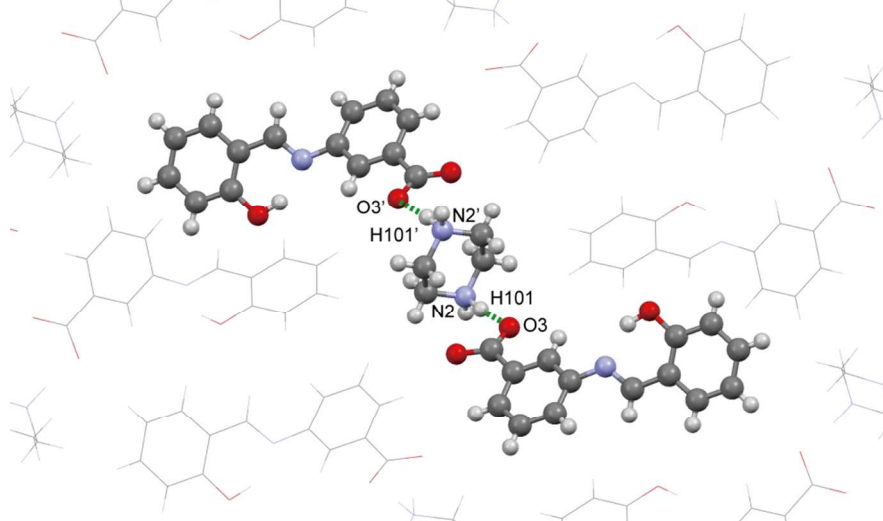


Figure S5. Crystal structure of **1e**

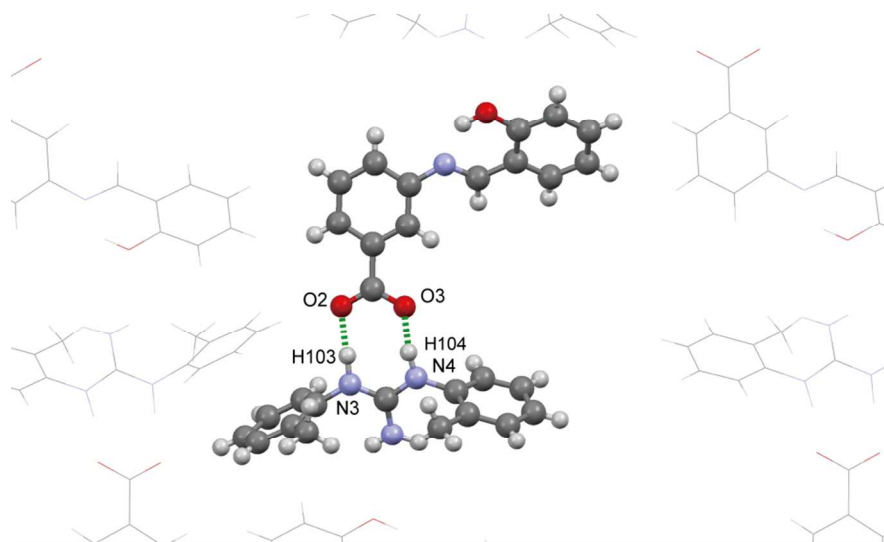


Figure S6. Crystal structure of **1f**

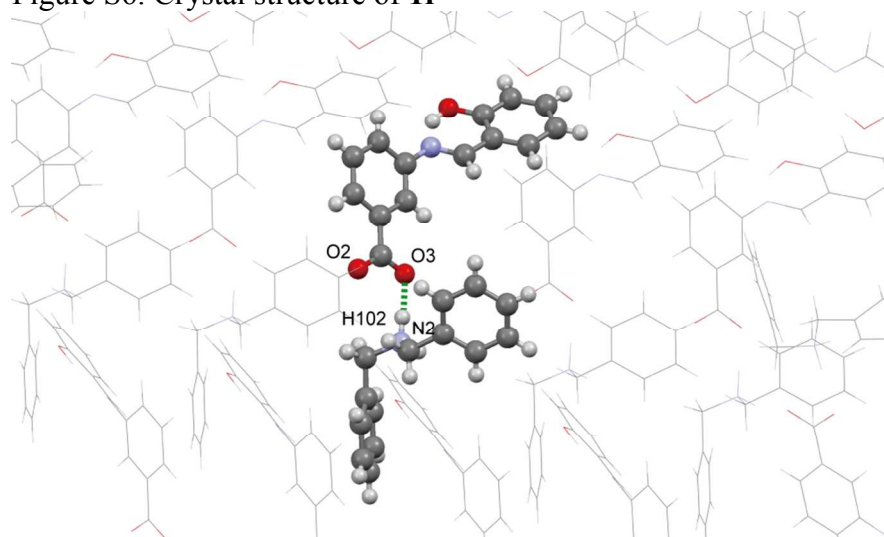
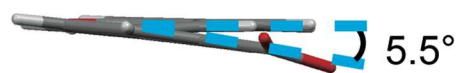


Figure S7. Crystal structure of **1g**

## UV/vis spectra of co-crystals (a)



(b)

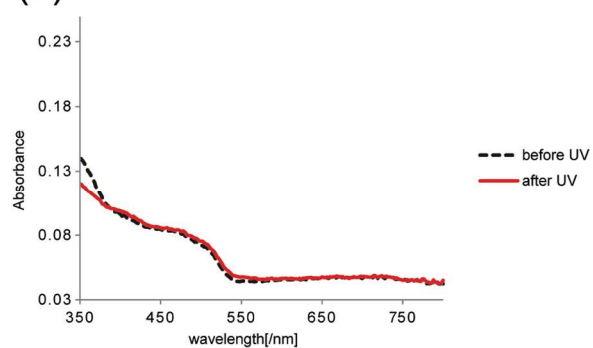


Figure S8. The molecular structures (top) and UV/Vis spectra (bottom) of SA derivatives **1a**.

(a)



(b)

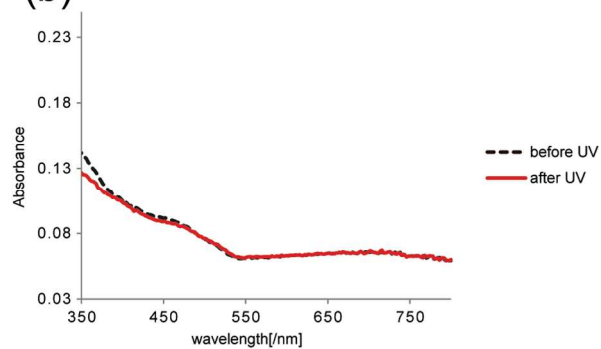
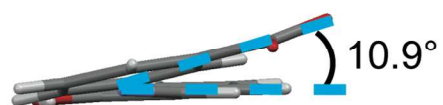


Figure S9. The molecular structures (top) and UV/Vis spectra (bottom) of SA derivatives **1b**.

(a)



(b)

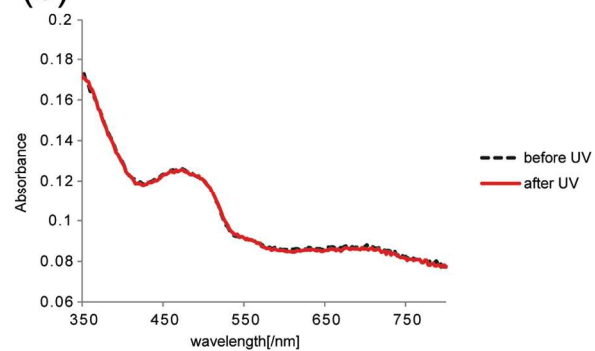
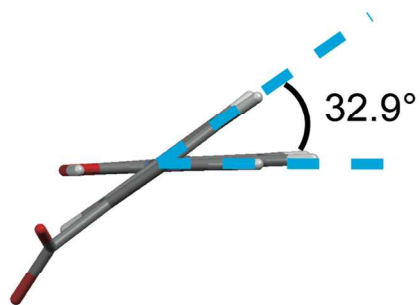


Figure S10. The molecular structures (top) and UV/Vis spectra (bottom) of SA derivatives **1c**.

(a)



(b)

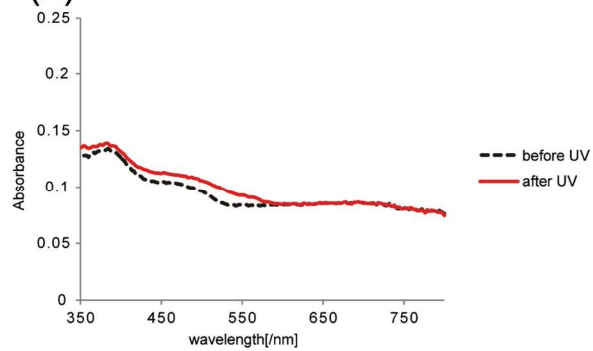


Figure S11. The molecular structures (top) and UV/Vis spectra (bottom) of SA derivatives **1e**.

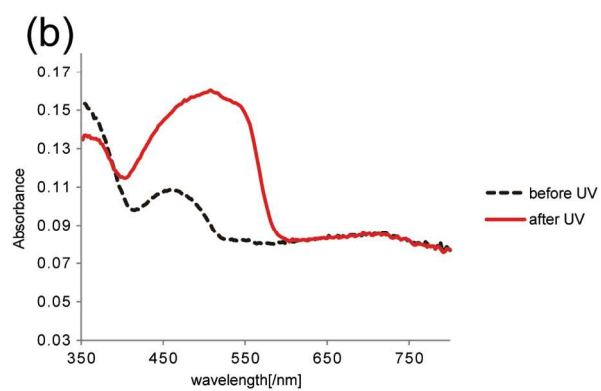
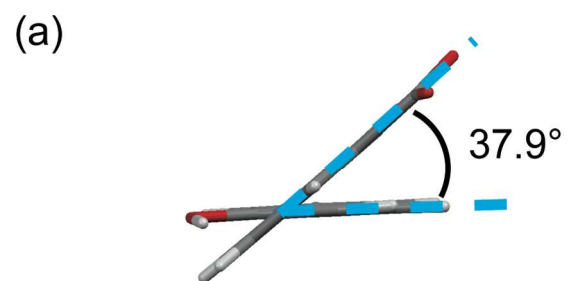


Figure S12. The molecular structures (top) and UV/Vis spectra (bottom) of SA derivatives **1f**.



## The $\Delta pK_a$ values of base molecules

	pKa	$\Delta pK_a$ with <b>1</b>
2-aminopyridine ( <b>a</b> )	6.66	2.75
guanyltiourea ( <b>b</b> )	10.65	6.74
cytosine ( <b>c</b> )	6.43	2.52
4,4'-bipyridyl ( <b>d</b> )	4.82(pKa <sub>1</sub> ), 3.17(pKa <sub>2</sub> )	0.91, -0.74
piperazine anhydrous ( <b>e</b> )	9.69	5.78
1,3-di-o-tolylguanidine ( <b>f</b> )	9.92	6.01
dibenzylamine ( <b>g</b> )	8.91	5.00

As for the basic molecule for the co-crystal former, guanyltiourea (**b**), piperazine anhydrous (**e**), 1,3-di-o-tolylguanidine (**f**), dibenzylamine (**g**) was selected because of the  $\Delta pK_a$  [=pKa (conjugate acid of base)- pKa (acid)] between co-crystal former **a** and SA derivative **1**. In the pharmaceutical industry, there is a widely accepted guideline that a proton transfer ionic co-crystal can be formed if the  $\Delta pK_a$  is greater than 2 or 3. The pKas of conjugate acid of **b**, **e**, **f**, and **g** are 10.65, 9.69, 9.92, and 8.91 respectively and the pKas of SA derivatives **1** are 3.91. Thus the  $\Delta pK_a$ s between **b**, **e**, **f**, **g** and **3-1** are 6.74, 5.78, 6.01, and 5.00 respectively which are sufficient for proton transfer. 2-aminopyridine (**a**), cytosine (**c**), 4,4'-bipyridyl (**d**) were selected because it is commonly used as a co-crystal former and supramolecular heterosynthons between carboxylic acids and aromatic N atoms are often observed. With respect to carboxylic acids and pyridine groups, there is a reliable indicator of co-crystal formation based on  $\Delta pK_a$  value, in which neutral co-crystals tend to form when the  $\Delta pK_a < 0$  and proton transfer ionic co-crystals tend to form when the  $\Delta pK_a$  is greater than 3. When  $0 < \Delta pK_a < 3$ , neutral or ionic co-crystals can exist. The pKas of **a** and **c** are 6.66 and 6.43. The  $\Delta pK_a$ s between **1** and **a**, **c** are 2.75, 2.52 which are  $0 < \Delta pK_a < 3$ , indicating a neutral or an ionic co-crystal. The pKa<sub>1</sub> and pKa<sub>2</sub> of the conjugate acid of **d** are 4.82 and 3.17 respectively. The  $\Delta pK_a$ s between **1** and **d** is 0.91 which are  $0 < \Delta pK_a < 3$ , indicating a neutral or an ionic co-crystal. For the  $\Delta pK_a$ <sub>2</sub>, it is -0.74, respectively which gives a less clear prediction.

## The generation of trans-keto form from enol form

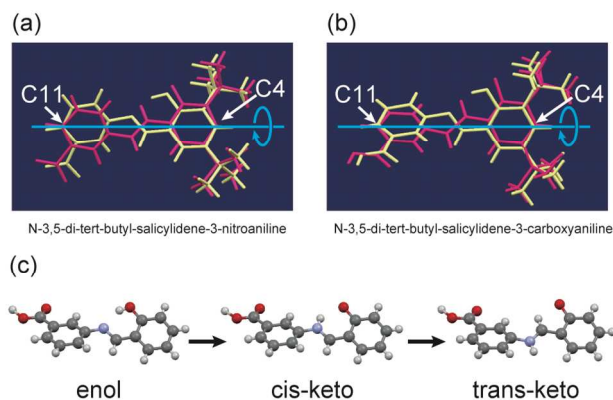


Figure S13 The enol and trans-keto form experimentally observed of *N*-di-3,5-*tert*-butylsalicylidene-3-nitroaniline (a) and *N*-di-3,5-*tert*-butylsalicylidene-3-carboxyaniline (b) <sup>16,19</sup>. (c) At first, cis-keto form was virtually generated from enol form by SHELXL. Subsequently, as the pedal motion was seemed to occur around the axis made by connecting between C4 and C11 atoms. So the atoms relate to the pedal motion were turned over 180 degrees around the axis. And the other atoms were shifted depending on the shift of these atoms.