New insights into Photochromic Properties of N-Salicylideneaniline Derivatives Using a Co-Crystal Engineering Approach: Supporting Information

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Supporting information 1: XRPD Patterns of Anils for which no SC-XRD experiment was successful (I, J, K and O).

Data are normalized at 100 for highest peak.

Anil I:

Anil J:
Anil K:

Anil O:
Supporting information 2: XRPD Patterns of Anil L for which the structure (hydrate) after crystallization do not corresponded to initial (after grinding) powder.

Data are normalized at 100 for highest peak. Blue pattern is measured powder after grinding while red pattern is simulated spectra from hydrate structure of L. Patterns slightly differ below 20° but completely differ above.
Supporting information 3: XRPD Patterns of cocrystals for which no SC-XRD experiment was successful.


Data are normalized at 100 for highest peak. Blue pattern is measured powder after grinding while red pattern is reference pattern of the Anil (either measured directly or simulated) and green pattern is reference pattern of the coformer (either measured directly or simulated). In some case peaks of either Anil or coformer remain meaning the stoichiometry of cocrystal is likely not 1:1.

C-C4:
C-C16:

C-C20: Three polymorphs available for Coformer C20 and shown here. None of them correspond to the blue pattern (after grinding).
D-C1: Peaks of the Anil seems to be still present (probably not a 1/1 stoichiometry in the cocrystal). Many new peaks and most of the coformer peaks are missing.

D-C2: Peaks of the Anil seems to be still present (probably not a 1/1 stoichiometry in the cocrystal). Many new peaks and most of the coformer peaks are missing.
D-C20: Two polymorphs available for coformer C20 but form I (shown here) present a good match with the blue curve (but not Anil D). Hence it’s probably not a 1/1 stoichiometry.

E-C3:
E-C8:

E-C11:
E-C19: Three polymorphs found for coformer C19. None of them match the blue curve.

E-C20: Three polymorphs found for coformer C20. None of them match the blue curve.
F-C10:

![Graph of F-C10](image)

F-C11:

![Graph of F-C11](image)
G-C3:

G-C5:
H-C1: Anil peaks are still present but with weaker intensities. Probably not 1:1 stoichiometry.

H-C2:
H-C3: Anil peaks are still present but with weaker intensities. Probably not a 1:1 stoichiometry.

H-C4:
J-C8: Quite similar pattern for Co-crystal J-C8 and Anil J but some peaks are missing, there are a few new peaks (around 21° and 32°), some peak are slightly moved, peaks of coformer C9 are not present anymore and intensities do not match for many peaks.

J-C9:
M-C10:

M-C20: Three polymorphs for C-20 but only one shown as it match the powder pattern (which mean there is still C-20 remains after grinding): probably not 1/1 stoichiometry. The existence of the co-crystal is deduced by the absence of the pattern of Anil M alone and the presence of new peaks.
O-C20:

![Graph showing X-ray diffraction patterns for different samples labeled as Co-crystal O-C20, Anil O dop, and Odfomer C20.1.](image)
Supporting information 4: XRPD Patterns of cocrystals for which the structure after crystallization do not corresponded to initial (after grinding) powder (MeCN solvate of E-C12 and hydrates of I-C10 and N-C5).

Data are normalized at 100 for highest peak. Blue pattern is measured powder after grinding while red pattern is simulated spectra from hydrate/solvate structure of cocrystal.

**E-C12:** Similar patterns after grinding and after crystallization but some peaks are shifted either toward right or left. Some peaks are present in only one of the pattern and intensities does not match globally. Furthermore structure found is a stoichiometric solvate with MeCN which is very unlikely to happen during LA-Grinding as only a catalytic amount of MeCN was used.

**I-C10:** The two powder patterns completely differ.
**N-C5**: Similar patterns after grinding and after crystallization but some peaks are shifted either toward right or left. Some peaks are present in only one of the pattern and intensities does not match globally. New peaks don’t match anil N or coformer C5 pattern also. Probably not or less hydrated after grinding than after crystallization.
Supporting Information 5: DRS and Ratio profile of photochromic compounds

Deviations and peaks above 650 nm (especially around 665 nm) are believed to be experimental artifacts and are, to the best of our knowledge, not reported for any states of the Anils. This has been verified and corrected for cocrystal E-C5 which presented such a feature for first sample but not for other samples of the same powder (however this has not been verified all compounds due to lack of time/access to resources). Thus these features are not taken into account in the photochromic/non-photochromic assignment. Criterion chosen were any peak of maximum intensity ≥ 1.5 and peak of max intensity between 1.3 and 1.5 with abrupt change (intensity change of at least 0.3 over 50 nm). Other results were classified as non-photochromic (Section 1.7).

A: Extremely intense change ($I_{\text{max}}$=45 at 535 nm).

A-C20: Average change ($I_{\text{max}}$=2.3 at 553 nm).

B-C4: Weak change ($I_{\text{max}}$=1.6 at 544 nm).
**B-C9**: Weak but well defined change ($I_{\text{max}}=1.7$ at 555 nm).

**B-C10**: Weak but well defined change ($I_{\text{max}}=1.3$ at 545 nm but $\Delta I=0.35$ between 495 and 545 nm) and thus classified as photochromic.

**B-C20**: Weak and not well defined change ($I_{\text{max}}=1.39$ at 537 nm but $\Delta I=0.41$ between 540 and 590 nm) and thus classified as photochromic.
C: Extremely intense change ($I_{max}=9.3$ at 572 nm). Random noise above 650 nm.

C-C8: Weak but well defined change ($I_{max}=1.5$ at 569 nm).

C-C16: Intense change ($I_{max}=2.2$ at 560 nm).
C-C20: Weak but well defined change ($I_{\text{max}}=1.6$ at 569 nm).

C-C21: Intense change ($I_{\text{max}}=3.3$ at 570 nm).

D: Weak change ($I_{\text{max}}=1.6$ at 571 nm). Random noise above 650 nm.
**D-C2:** Average but not well defined change (two peaks, $I_{\text{max}}=2.1$ at 594 nm). Depletion at 665 nm not considered here.

**D-C5:** Intense change ($I_{\text{max}}=4.1$ at 577 nm).

**G-C16:** Linear profile up to 550 nm. Small peak at 605 nm ($I_{\text{max}}=1.5$). Peak at 665 nm ($I_{\text{max}}=2.2$) not considered here.
G-C17: Linear profile up to 600 nm. Small peak at 610 nm ($I_{\text{max}}=1.6$). Peak at 662 nm ($I_{\text{max}}=2.2$) not considered here.

![Kubelka-Munk Measurements after/before irradiation](image1)

![Ratio of Kubelka-Munk Measurements after/before irradiation](image2)

G-C18: Linear profile up to 600 nm. Intense peak at 610 nm ($I_{\text{max}}=2.6$). Peak at 660 nm ($I_{\text{max}}=5.5$) not considered here.

![Kubelka-Munk Measurements after/before irradiation](image3)

![Ratio of Kubelka-Munk Measurements after/before irradiation](image4)

H-C1: Weak and not well defined change ($I_{\text{max}}=1.6$ at 562 nm), assigned to photochromic by comparison with Anil H alone (non-photochromic, perfect linear profile, CFR Section 1.7).

![Kubelka-Munk Measurements after/before irradiation](image5)

![Ratio of Kubelka-Munk Measurements after/before irradiation](image6)
**H-C16:** Almost linear profile up to 550 nm. Small peak at 615 nm ($I_{\text{max}}=1.44$) but $\Delta I=0.68$ between 575 nm and 615 nm and thus assigned to photochromic. Peak at 665 nm ($I_{\text{max}}=2.1$) not considered here.

**I-C7:** Weak and not well defined change ($I_{\text{max}}=1.45$ at 521 nm but $\Delta I=0.35$ between 471 nm and 521 nm and thus assigned to photochromic). Also differs a lot from Anil I alone (non-photochromic, perfect linear profile up to 600 nm, CFR Section 1.7).

**I-C12:** Weak but well defined change ($I_{\text{max}}=1.33$ at 499 nm but $\Delta I=0.38$ between 452 and 502 nm) and thus assigned to photochromic. Also differs a lot from Anil I alone (non-photochromic, perfect linear profile up to 600 nm, CFR Section 1.7).
J: Small peak ($I_{\text{max}}$=1.35 at 540 nm) but with $\Delta I=0.46$ between 490 and 540 nm and thus assigned to photochromic.

J-C6: Weak but well defined change ($I_{\text{max}}$=1.43 at 597 nm), assigned to photochromic by comparison with Anil J alone (non-photochromic, perfect linear profile, CFR Section 1.7).

J-C7: Average change ($I_{\text{max}}$=1.9 at 549 nm).
**M:** Intense and well defined change ($I_{\text{max}} = 3.1$ at 575 nm).

**M-C15:** Average and well defined change ($I_{\text{max}} = 2.2$ at 589 nm).

**O:** Average and well defined change ($I_{\text{max}} = 1.9$ at 588 nm).
O-C16: Weak but well defined change ($I_{max}=1.35$ at 572 nm but $\Delta I=0.55$ between 572 nm and 622 nm and thus assigned to photochromic).
Supporting information 6: DRS and Ratio profile of inverted photochromic compounds

For the two compounds presenting a depletion at 550 nm after irradiation (A-C8 and E-C8), the calculated ratio has been inverted (1/ratio) in order to make it easily comparable with other results.

A-C8: Inverted ratio $I_{\text{max}}=23.5$ at 602 nm.

E-C8: Inverted ratio $I_{\text{max}}=3.6$ at 548 nm.
Supporting information 7: DRS and Ratio profile of non-photochromic compounds

B: Noisy but linear profile.

B-C2: Slightly noisy but linear profile.

B-C21: Slightly noisy but linear profile.
C-C4: Perfectly linear profile.

C-C5: Almost perfectly linear profile.

C-C9: Perfectly linear profile.
C-C10: Slightly noisy but linear profile ($I_{\text{max}}=1.25$ at 660 nm; assigned to non-photochromic).

D-C1: Perfectly linear profile, noisy above 600 nm.

D-C11: Perfectly linear profile.
D-C20: Almost perfectly linear profile.

E: Noisy but linear profile ($I_{\text{max}}=1.28$ at 510 nm) up to 600 nm. Upward deviation above 600 nm probably due to experimental artefact; assigned to non-photochromic.

E-C1: Perfectly linear profile.
E-C2: Perfectly linear profile.

E-C3: Almost perfectly linear [small peak but too low intensity: $I_{\text{max}}=1.13$ at 515 nm and thus assigned to non-photochromic].

E-C4: Almost perfectly linear profile.
E-C5: Almost perfectly linear profile, noisy above 600 nm.

E-C6: Almost perfectly linear profile.

E-C9: Almost perfectly linear profile.
E-C10: Almost perfectly linear profile.

E-C11: Perfectly linear profile.

E-C12: Linear profile up to 600 nm. Downward deviation above 600 nm probably due to experimental artefact; assigned to non-photochromic.
E-C13: Perfectly linear profile.

E-C15: Slightly noisy but linear profile [small peak but too low intensity: \( I_{\text{max}} = 1.25 \) at 545 nm and thus assigned to non-photochromic].

E-C19: Linear profile up to 500 nm. Slight upward deviation above 500 nm (\( I_{\text{max}} = 1.24 \) at 550 nm); assigned to non-photochromic.
E-C20: Almost perfectly linear profile. Slight inverted peak but too low intensity: $1/I_{\text{max}} = 1.11$ at 540 nm and thus assigned to non-photochromic.

E-C21: Perfectly linear profile.

F: Linear profile.
**F-C1:** Perfectly linear profile.

**F-C4:** Slightly noisy but linear profile.

**F-C5:** Linear profile.
F-C6: Almost perfectly linear profile.

F-C8: Slightly noisy but linear profile.

F-C9: Slightly noisy but linear profile.
F-C10: Perfectly linear profile.

F-C11: Perfectly linear profile.

F-C12: Perfectly linear profile.
F-C19: Almost perfectly linear profile.

F-C21: Almost perfectly linear profile.

G: Perfectly linear profile.
**G-C1:** Perfectly linear profile up to 550 nm. Slight upward deviation above 550 nm ($I_{\text{max}} = 1.32$ at 600 nm); Limit case, assigned to non-photochromic by default.

**G-C2:** Perfectly linear profile up to 550 nm. Slight upward deviation above 550 nm ($I_{\text{max}} = 1.42$ at 605 nm); Limit case, assigned to non-photochromic by default.

**G-C3:** Linear profile.
**G-C5:** Linear profile up to 600 nm. Intense peak at 665 nm ($I_{\text{max}}=3.1$) don’t correspond to any reported transition/state: assigned to non-photochromic by default.

**G-C6:** Almost perfectly linear profile, slightly noisy above 600 nm.

**G-C13:** Almost perfectly linear profile, slightly noisy above 600 nm.
**G-C21:** Perfectly linear profile.

[Graph showing intensity vs. wavelength for G-C21 and G-C21_365nm_30min before and after irradiation.]

**H:** Perfectly linear profile.

[Graph showing intensity vs. wavelength for H and H_365nm_30min before and after irradiation.]

**H-C2:** Noisy but linear profile (slight upward deviation above 600 nm).

[Graph showing intensity vs. wavelength for H-C2 and H-C2_365nm_30min before and after irradiation.]
**H-C3:** Linear profile up to 550 nm. Slight upward deviation above 550 nm ($I_{\text{max}}=1.32$ at 610 nm); Limit case, assigned to non-photochromic by default.

**H-C4:** Linear profile up to 550 nm. Slight upward deviation above 550 nm; Noisy above 630 nm.

**H-C6:** Perfectly linear profile up to 600 nm. Slightly noisy above.
**H-C7:** Linear profile up to 500 nm. Noisy above 500 nm ($I_{\text{max}} = 1.3$ at 605 and 660 nm).

**H-C12:** Perfectly linear up to 600 nm. Peak at 665 nm ($I_{\text{max}} = 2.0$) don’t correspond to any reported transition/state: assigned to non-photochromic by default.

**I:** Perfectly linear up to 600 nm. Intense peak at 670 nm ($I_{\text{max}} = 10.0$) don’t correspond to any reported transition/state: assigned to non-photochromic by default.
**I-C8:** Perfectly linear profile.

**I-C9:** Almost perfectly linear profile. Small peak but too low intensity: $I_{\text{max}}=1.14$ at 495 nm and thus assigned to non-photochromic.

**I-C10:** Slightly noisy but linear profile.
I-C11: Slightly noisy but more or less linear profile.

J-C1: Slightly noisy profile.

J-C8: Slightly noisy profile.
J-C9: Almost perfectly linear profile.

J-C10: Slightly noisy but more or less linear profile.

J-C11: Perfectly linear profile.
K: Linear but continuous upward deviation above 550 nm.

K-C3: Perfectly linear profile.

K-C4: Perfectly linear profile.
**K-C5:** Linear profile.

**K-C6:** Perfectly linear profile.

**K-C9:** Perfectly linear profile.
K-C10: Linear profile.

K-C15: Linear profile.

K-C16: Slightly noisy, no abrupt change.
**L:** More or less linear (no abrupt change)

**L-C12:** Linear profile.

**M-CS:** Slightly noisy above 550 nm, no abrupt change.
**M-C10:** More or less linear profile.

**M-C20:** Linear profile.

**N:** Small peak at 573 nm ($I_{\text{max}} = 1.34$) but $\Delta I = 0.26$ between 573 nm and 623 nm and change is thus considered too small to be significant.
**N-C5:** Slightly noisy above 550 nm but linear profile.

**N-C10:** Small peak at 572 nm ($I_{\text{max}}=1.32$). Limit case, assigned to non-photochromic by default.

**N-C21:** Perfectly linear profile.
O-C9: More or less linear profile (small inverted peak at 670 nm discarded).

O-C13: Linear profile.

O-C15: More or less linear profile (small inverted peak at 670 nm discarded).
**O-C17:** Linear profile up to 600 nm. Slight upward deviation above 600 nm.

**O-C20:** More or less linear (slight inverted peak at 565 nm but too low intensity).
Supporting Information 8: H-NMR data of Anils A to O.

NMR analysis. H NMR spectra were recorded on Bruker-300 MHz. H NMR chemical shifts are reported relative to CD$_3$CN (1.94 ppm).

Compound A: δ (ppm): 13.26 (s, 1H); 8.82 (s, 1H); 7.56-7.31 (m, 7H); 7.03-6.98 (dt, 2H, $J_1$=7.8Hz, $J_2$=1.2Hz).

Compound B: δ (ppm): 13.11 (s, 1H); 8.79 (s, 1H); 7.56-7.53 (dd, 1H, $J_1$=7.5Hz, $J_2$=1.5Hz); 7.49-7.43 (m, 2H); 7.05-6.99 (m, 1H); 6.67-6.62 (ddd, 1H, $J_1$=8.7Hz, $J_2$=2.4Hz, $J_2$=1.8Hz); 4.77 (s, 1H).

Compound C: δ (ppm, DMSO): 9.57-9.56 (d, 1H, $J$=3.9Hz); 8.35-8.32 (d, 1H, $J$=8.4Hz); 7.92-7.89 (d, 1H, $J$=9.3Hz).
Compound J: $\delta$ (ppm): 13.46 (s, 1H); 8.66 (s, 1H); 7.70 (s, 1H); 7.40-7.33 (m, 3H); 7.22-7.14 (m, 2H); 6.48-6.44 (dd, 1H, $J_1=8.7$ Hz, $J_2=2.4$ Hz); 6.38-6.37 (d, 1H, $J = 2.4$ Hz).

Compound K: $\delta$ (ppm, DMSO): 13.23 (s, 1H); 12.91 (s, 1H); 10.36 (s, 1H); 8.85 (s, 1H); 7.99 (ddd, 2H, $J_1=8.7$Hz, $J_2=2.1$Hz, $J_3=1.8$Hz); 7.48-7.45 (d, 1H, $J=8.7$Hz); 7.44-7.40 (ddd, 2H, $J_1=8.7$Hz, $J_2=2.1$Hz, $J_3=1.8$Hz); 6.43-6.40 (dd, 1H, $J_1=8.5$ Hz, $J_2=2.3$ Hz); 6.31-6.30 (d, 1H, $J = 2.3$ Hz).

Compound L: $\delta$ (ppm, DMSO): 13.35 (s, 1H); 10.33 (s, 1H); 8.84 (s, 1H); 7.98-7.92 (dd, 3H, $J_1=8.7$Hz, $J_2=8.4$Hz); 7.47-7.44 (d, 1H, $J=8.4$Hz); 7.41-7.38 (d, 2H, $J=8.7$Hz); 7.35 (s, 1H); 6.43-6.40 (dd, 1H, $J_1=8.7$ Hz, $J_2=2.4$ Hz); 3.82 (s, 3H).

Compound M: $\delta$ (ppm, DMSO): 13.26 (s, 1H); 8.95 (s, 1H); 7.49-7.39 (m, 4H); 7.31-7.28 (tt, 1H, $J_1=6.9$Hz, $J_2=7.2$Hz, $J_3=0.9$Hz, $J_4=1.5$Hz); 7.26-7.23 (dd, 1H, $J_1=7.8$Hz, $J_2=1.2$Hz); 7.14-7.11 (dd, 1H, $J_1=8.1$Hz, $J_2=1.2$Hz); 6.93-6.88 (t, 1H, $J_1=8.1$Hz); 3.82 (s, 3H).

Compound N: (ppm, DMSO): 13.06 (s, 1H); 8.94 (s, 1H); 7.52-7.45 (m, 2H); 7.34-7.27 (tt, 2H, $J_1=8.7$Hz, $J_2=3.6$Hz, $J_4=2.1$Hz); 7.25-7.22 (dd, 1H, $J_1=8.1$Hz, $J_2=1.5$Hz); 7.15-7.12 (dd, 1H, $J_1=8.1$Hz, $J_2=1.5$Hz); 6.93-6.88 (dd, 1H, $J_1=8.1$Hz, $J_2=7.8$Hz); 3.82 (s, 3H).

Compound O: $\delta$ (ppm, DMSO): 12.87 (s, 2H); 9.00 (s, 1H); 8.04-8.0 (dt, 2H, $J_1=8.7$Hz, $J_2=2.1$Hz); 7.51-7.47 (dt, 2H, $J_1=8.7$Hz, $J_2=2.1$Hz); 7.30-7.27 (dd, 1H, $J_1=8.1$Hz, $J_2=1.5$Hz); 7.18-7.15 (dd, 1H, $J_1=8.1$Hz, $J_2=1.5$Hz); 6.96-6.91 (t, 1H, $J_1=8.1$Hz); 3.83 (s, 3H).
### Supporting information 9: Structural data and Ortep representation of new photochromic compounds D, C-C16, C-C20 and M-C15

#### Table S1: Structural data of photochromic compounds

<table>
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<tr>
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<th>Anil D</th>
<th>Cocrystal C-C16</th>
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<td><strong>V [Å³]</strong></td>
<td>1171.35(9)</td>
<td>1751.00(19)</td>
<td>816.39(19)</td>
<td>1500.52(18)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>ρcalcd [Mgm⁻³]</strong></td>
<td>1.362</td>
<td>1.378</td>
<td>1.799</td>
<td>1.272</td>
</tr>
<tr>
<td><strong>μ [mm⁻¹]</strong></td>
<td>0.093</td>
<td>0.098</td>
<td>1.997</td>
<td>0.090</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>504</td>
<td>760</td>
<td>430</td>
<td>608</td>
</tr>
<tr>
<td><strong>Crystal size [mm]</strong></td>
<td>0.45 x 0.38 x 0.09</td>
<td>0.30 x 0.16 x 0.02</td>
<td>0.17 x 0.06 x 0.02</td>
<td>0.30 x 0.25 x 0.04</td>
</tr>
<tr>
<td><strong>Theta range for data collection [°]</strong></td>
<td>3.677 to 25.337</td>
<td>3.275 to 25.167</td>
<td>2.935 to 25.240</td>
<td>2.991 to 25.686</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>8263</td>
<td>3056</td>
<td>12704</td>
<td>10984</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>2099 [R(int) = 0.0298]</td>
<td>3056 [R(int) = 0.000]</td>
<td>2950 [R(int) = 0.0614]</td>
<td>5327 [R(int) = 0.0548]</td>
</tr>
</tbody>
</table>

1 Data appeared to be twinned and were refined against an hklf5 formatted reflection file, this imposes merge 0, suppressing the calculation of R_int.
<table>
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<tr>
<th>Completeness to θ_max [%]</th>
<th>98.7</th>
<th>98.1</th>
<th>99.5</th>
<th>98.6</th>
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<tr>
<td>Max. and min. transmission</td>
<td>1.00000 and 0.93611</td>
<td>1.00000 and 0.68941</td>
<td>1.00000 and 0.92674</td>
<td>1.00000 and 0.94617</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2099 / 0 / 172</td>
<td>3056 / 0 / 250</td>
<td>2950 / 0 / 219</td>
<td>5327 / 2 / 396</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.061</td>
<td>1.042</td>
<td>1.031</td>
<td>1.053</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0523, wR₂ = 0.1512</td>
<td>R₁ = 0.0919, wR₂ = 0.1938</td>
<td>R₁ = 0.0404, wR₂ = 0.0977</td>
<td>R₁ = 0.0461, wR₂ = 0.1304</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0577, wR₂ = 0.1575</td>
<td>R₁ = 0.1155, wR₂ = 0.2109</td>
<td>R₁ = 0.0485, wR₂ = 0.1045</td>
<td>R₁ = 0.0516, wR₂ = 0.1340</td>
</tr>
<tr>
<td>Largest diff. Peak/hole [e Å⁻³]</td>
<td>0.159 and -0.192</td>
<td>0.283 and -0.252</td>
<td>0.676 and -0.711</td>
<td>0.139 and -0.105</td>
</tr>
</tbody>
</table>

Figure 1: ORTEP representation of Anil D (a), cocrystal C-C16 (b), cocrystal C-C20 (c) and cocrystal M-C15 (d).
Supporting Information 10: Synthesis of Anils A to O

Compound A (N-Salicylideneaniline) was prepared by hand grinding (ten minutes) of salicylaldehyde (10 mmol) with aniline (10 mmol) in presence of a catalytic amount of acetic acid (1 drop) and dried for 48 h at 45 °C and used as such (yield: 98%, purity: 99%).

Compound B (4-fluoro-Salicylideneaniline) was prepared by hand grinding (5 minutes) of salicylaldehyde (10 mmol) with 4-fluoro-aniline (10 mmol) and dried for 48 h at 45°C and used as such (yield: 98%, purity: 99%).

Compound C (p-(Salicylideneamino)benzoic acid) was prepared by hand grinding of salicylaldehyde (10 mmol) with 4-aminobenzoic acid (10 mmol) until appearance of an orange-pink solid (5 minutes). 10 ml of acetonitrile where added and the solution was heated to 70 °C, yielding an orange precipitate after 5 minutes. The solution was left to evaporate and the solid was dried for 48 h at 45°C and used as such (yield: 96%, purity: 95-99%).

Compound D (p-(Salicylideneamino)benzamide) was prepared by dissolution of 4-aminobenzamide (10 mmol) in 5 ml of acetonitrile at 70 °C. To this solution were added 1 drop of pure acetic acid and salicylaldehyde (10 mmol) and the solution was stirred regularly with a spatula until appearance of a yellow solid (after +/- 30 minutes). The solution was left to evaporate and the solid was dried for 48 h at 45°C and used as such (yield: 98%, purity: 99%).

Compound E (2-Hydroxy-1-naphthalaniline) was prepared by dissolution of hydroxy-1-naphthaldehyde (5 mmol) in 5 ml of acetonitrile at 50 °C. Benzamine (5mmol) was added to this solution and the solution was stirred regularly with a spatula. Precipitate started to appear after 10 minutes. The solution was then left to evaporate and the yellow solid was dried for 48 h at 45°C and used as such (yield: 98%, purity: 97%).

Compound F (2-Hydroxy-1-naphthalidene-p-fluoroaniline) was prepared by dissolution of hydroxy-1-naphthaldehyde (5 mmol) in 5 ml of acetonitrile at 45 °C. To this solution were

\[ \text{The photochromically active polymorph of this compound was obtained using this procedure.} \]
added 1 drop of pure acetic acid and 4-fluoro-benzamine (5 mmol) and the solution was stirred regularly with a spatula. Precipitate started to appear after 2 minutes. The solution was left to evaporate and the yellow solid obtained was dried for 48 h at 45°C and used as such (yield: 98%, purity: 97-99%).

Compound **G** (4-[(2-Hydroxy-1-naphthalenyl)methylene]amino]benzoic acid) was prepared by dissolution of hydroxy-1-naphthaldehyde (10 mmol) in 5 ml of acetonitrile at 60 °C. To this solution was added 4-aminobenzoic acid (10 mmol) and the solution was stirred regularly with a spatula. A yellow precipitate started to appear after 1 minute and the solution was left to evaporate at 60°C. Then 10 ml of ethyl-acetate were added and the solution was heated to 75 °C and left at this temperature until complete evaporation of solvent. The yellow solid was then dried for 48 h at 45°C and used as such (yield: 98%, purity: 99%).

Compound **H** (4-[(2-hydroxy-1-naphthalenyl)methylene]amino]-benzamide) was prepared by dissolution of hydroxy-1-naphthaldehyde (10 mmol) and 4-amino-benzamide (10 mmol) in 10 ml of boiling ethanol (79 °C). To this solution was added 1 drop of pure acetic acid and the solution stirred regularly with a spatula. An orange precipitate started to appear after 10 minutes. The solution was kept boiling until complete evaporation and the orange solid was dried for 48 h at 45°C and used as such (yield: 98%, purity: 99%).

Compound **I** (4-[(Phenylimino)methyl]-1,3-benzenediol) was prepared by addition of benzamine (10 mmol) to a mixture of 2,4-dihydroxy-benzaldehyde (10 mmol) and 10 ml of acetonitrile. The solution was kept at 60 °C overnight and led to a red gel. This gel was triturated with pure hexane and led to a yellow precipitate. The solution was left to evaporate and the yellow solid was dried for 48 h at 45°C and used as such (yield: 98%, purity: 99%).

Compound **J** (4-[(4-Fluorophenyl)imino]methyl]-1,3-benzenediol) was prepared by addition of 4-fluoro-benzamine (10 mmol) to a mixture of 2,4-dihydroxy-benzaldehyde (10 mmol) and 10 ml of acetonitrile. The solution was kept at 60 °C overnight and led to a red gel.
This gel was triturated with pure hexane and led to a yellow precipitate. The solution was left to evaporate and the yellow solid was dried for 48 h at 45°C and used as such (yield: 98%, purity: 99%).

Compound K (4-[[2,4-Dihydroxyphenyl)methylene]amino]benzoic acid) was prepared by addition of 4-amino-benzoic acid (10 mmol) to a mixture of 2,4-dihydroxy-benzaldehyde (10 mmol) and 10 ml of acetonitrile at 60 °C. The solution quickly turned yellow and a yellow precipitate started to appear after 2 minutes. The solution was left to evaporate and the yellow solid was dried for 48 h at 45°C and used as such (yield: 98%, purity: 97%).

Compound L (4-[[2,4-dihydroxyphenyl)methylene]amino]-benzamide) was prepared by addition of 4-amino-benzamide (10 mmol) to a mixture of 2,4-dihydroxy-benzaldehyde (10 mmol) 25 ml of ethanol and 5 ml of acetonitrile at 75 °C. The solution quickly turned yellow and a yellow precipitate started to appear after 10 minutes. The solution was left to evaporate and the yellow solid was dried for 48 h at 60°C and used as such (yield: 98%, purity: 98%).

Compound M (3'-Methoxysalicylideneaniline) was prepared by dissolution of ortho-vanilin (10 mmol) in 2 ml of acetonitrile at 50 °C. To this solution was added benzamine (10 mmol) and 5 ml of ethanol and the solution was stirred regularly with a spatula for 30 minutes. The solution was left to evaporate and led to a red gel. This gel was triturated with pure hexane and led to a red precipitate. The solution was left to evaporate and the red solid was dried for 48 h at 50°C and used as such (yield: 98%, purity: 99%).

Compound N (2-[[4-Fluorophenyl]imino]methyl)-6-methoxyphenol) was prepared by dissolution of ortho-vanilin (10 mmol) in 2 ml of acetonitrile at 50 °C. To this solution was added 4-fluoro-benzamine (10 mmol) and 5 ml of ethanol and the solution was stirred regularly with a spatula for 30 minutes. The solution was left to evaporate and led to a red gel. This gel was triturated with pure hexane and led to a red precipitate. Solution evaporation led to a yellow solid, which was dried for 48 h at 50°C and used as such (yield: 98%, purity: 99%).
Compound $O$ (4-[(2-hydroxy-3-methoxyphenyl)methylene]amino]-benzoic acid) was prepared by dissolution of ortho-vanilin (10 mmol) in 2 ml of acetonitrile at 50 °C. To this solution was added 4-amo-benzoic acid (10 mmol) and 10 ml of ethanol and the solution was left to stir regularly with a spatula. The solution slowly turned red and a clear-pink precipitate appeared after 5 minutes. The solution was left to evaporate and the yellow solid was dried for 48 h at 50°C and used as such (yield: 98%, purity: 99%).
Supporting Information 11: Starting Materials

Carboxylic acids, amides and halogenated benzene derivatives used as co-formers, solvents and starting materials for synthesis were all purchased and used as such. Product codes are given in the brackets. From Alfa Aesar: 4-aminobenzoic acid (10177463). From Accros Organic: 2,4-dihydroxybenzaldehyde (173640250); 2,5-dihydroxybenzoic acid (165200500); 4-aminobenzamide (351640250); 4-fluoro-aniline (119290250); 4-hydroxybenzoic acid (120995000); Acetylsalicylic acid (158185000); Biurea (402700050); Maleic acid (125230010); Nicotinamide (128271000); Ortho-vanilin (153071000); Oxalic acid (186432500); Tartaric acid D (137871000); Urea (424585000). From Fisher Chemicals: Acetone (200-662-2). From Fluorochem: 1,2-diodo-tetrafluoro-benzene (010455); 1,3,5-trifluoro-triiodo-benzene (044647); 1,4-diiodo-tetrafluoro-benzene (010456). From J.T.Baker: n-butanol (71-36-3). From Janssen Chimica: Acetic acid (14.893.52). From Sigma Aldrich: 2,3-dihydroxybenzoic acid (206-135-5); 2,4-dihydroxybenzoic acid (101527441); 3,4-dihydroxybenzoic acid (100986520); 3,5-dihydroxybenzoic acid (202-730-7); 4-nitrobenzamide (101156988); Benzamide (101247421); Dimethylsulfoxide (101306263); Salicylaldehyde (101669521); Salicylamide (101235208). From U.C.B. s.a.: Salicylic acid (4388); Aniline (1163-4944). From TCI: Citraconic acid (207-858-7); hydroxy-1-naphtaldehyde (708-06-5). From VWR Chemicals: Acetonitrile (200-835-2); Chloroform (83626.320); Diethyl ether (200-467-2); Ethanol (200-578-6); Ethyl acetate (205-500-4); Hexane (203-777-6); Methanol (20847.307); Tetrahydrofuran (28551.321).
Supporting information 12: measured number of short contacts.

Table S2: total cumulated average amount of neighbor atoms of each moiety and type of compounds as a function of interatomic distance and the corresponding standard deviations.

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<th>VdW radii + length (Å)</th>
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<th>+0.1</th>
<th>+0.05</th>
<th>+0</th>
<th>-0.05</th>
<th>-0.1</th>
<th>-0.2</th>
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</thead>
<tbody>
<tr>
<td>Photochromic compounds (N=8)</td>
<td>7.31</td>
<td>4.25</td>
<td>2.31</td>
<td>0.88</td>
<td>0.44</td>
<td>0.25</td>
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<tr>
<td>Standard deviations</td>
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<td>1.49</td>
<td>1.10</td>
<td>0.64</td>
<td>0.62</td>
<td>0.46</td>
<td>0.46</td>
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<tr>
<td>Non-photochromic compounds (N=20)</td>
<td>7.65</td>
<td>5.10</td>
<td>3.48</td>
<td>2.73</td>
<td>1.85</td>
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<tr>
<td>Standard deviations</td>
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<td>Photochromic compounds (N=8)</td>
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<td>1.69</td>
<td>0.88</td>
<td>0.38</td>
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<tr>
<td>Standard deviations</td>
<td>2.13</td>
<td>2.24</td>
<td>1.21</td>
<td>1.22</td>
<td>0.64</td>
<td>0.52</td>
<td>0.46</td>
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<tr>
<td>Non-photochromic compounds (N=20)</td>
<td>12.23</td>
<td>6.68</td>
<td>4.28</td>
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<td>1.80</td>
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<tr>
<td>Standard deviations</td>
<td>2.43</td>
<td>2.51</td>
<td>1.82</td>
<td>2.07</td>
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<td>1.32</td>
<td>0.59</td>
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Table S3: Corresponding CCDC number, name, formula and Unit Cell parameters for all submitted structure.

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<th>CCDC Number</th>
<th>Name</th>
<th>Formula</th>
<th>Unit Cell parameters</th>
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<tbody>
<tr>
<td>1903903</td>
<td>Anil D</td>
<td>C_{14}H_{12}N_{2}O_{2}</td>
<td>a 5.0689(2); b 5.2132(2); c 44.382(2); P21/c</td>
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<tr>
<td>1903904*</td>
<td>Anil G</td>
<td>C_{18}H_{13}NO_{3}</td>
<td>a 5.7867(4); b 5.0636(2); c 47.218(3); P21/n</td>
</tr>
<tr>
<td>1903905</td>
<td>Anil L Hydrate</td>
<td>C_{14}H_{12}N_{2}O_{3}, H_{2}O</td>
<td>a 3.8746(3); b 12.8553(13); c 24.1167(17); P21/c</td>
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<tr>
<td>1903906</td>
<td>Cocrystal A-C20</td>
<td>C_{13}H_{11}NO, C_{6}F_{4}I_{2}</td>
<td>a 5.2253(2); b 5.9554(4); c 15.1232(10); P1</td>
</tr>
<tr>
<td>1903907</td>
<td>Anil D Hydrate</td>
<td>C_{14}H_{12}N_{2}O_{2}, H_{2}O</td>
<td>a 12.3086(9); b 4.6341(3); c 41.505(3); P21/n</td>
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<tr>
<td>1903908</td>
<td>Cocrystal C-C20</td>
<td>2(C_{14}H_{11}NO), C_{6}F_{4}I_{2}</td>
<td>a 4.8147(6); b 6.1302(9); c 27.836(3); P-1</td>
</tr>
<tr>
<td>1903909</td>
<td>Anil N</td>
<td>C_{14}H_{12}FNO_{2}</td>
<td>a 11.351(2); b 12.0862(17); c 9.3991(17); P21/c</td>
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<td>1903910</td>
<td>Cocrystal D-C1</td>
<td>C_{14}H_{12}N_{2}O_{2}, C_{7}H_{6}O_{4}</td>
<td>a 10.7763(3); b 11.1516(2); c 17.3530(4); P21/c</td>
</tr>
<tr>
<td>1903911</td>
<td>Anil E Dihydrate</td>
<td>C_{17}H_{13}NO, 2(H_{2}O)</td>
<td>a 4.9439(2); b 16.2432(8); c 18.1103(8); P212121</td>
</tr>
<tr>
<td>1903912</td>
<td>Cocrystal E-C1</td>
<td>2(C_{17}H_{13}NO), C_{7}H_{6}O_{4}</td>
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</tr>
<tr>
<td>1903913</td>
<td>Cocrystal E-C4</td>
<td>2(C_{17}H_{13}NO), C_{7}H_{6}O_{4}</td>
<td>a 10.8294(12); b 11.5570(14); c 13.989(2); P-1</td>
</tr>
<tr>
<td>1903914</td>
<td>Anil H</td>
<td>C_{18}H_{14}N_{2}O_{2}</td>
<td>a 5.7580(6); b 5.0485(4); c 46.553(4); P21/n</td>
</tr>
<tr>
<td>1903915</td>
<td>Cocrystal E-C6</td>
<td>2(C_{17}H_{13}NO), C_{7}H_{6}O_{3}</td>
<td>a 7.4238(5); b 21.9484(12); c 22.6133(10); P212121</td>
</tr>
<tr>
<td>1903916*</td>
<td>Cocrystal E-C8</td>
<td>C_{17}H_{13}NO, C_{7}H_{6}O_{4}</td>
<td>a 4.9438(5); b 16.2432(8); c 18.1103(8); P212121</td>
</tr>
<tr>
<td>1903917</td>
<td>Cocrystal E-C2</td>
<td>2(C_{17}H_{13}NO), C_{7}H_{6}O_{4}</td>
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</tr>
<tr>
<td>1903918</td>
<td>Anil E</td>
<td>C_{17}H_{13}NO</td>
<td>a 12.1011(7); b 14.1663(6); c 7.3898(3); P21/c</td>
</tr>
<tr>
<td>1903919</td>
<td>Cocrystal E-C9</td>
<td>C_{17}H_{14}NO^{+}, C_{6}H_{14}O_{4}</td>
<td>a 5.6859(3); b 20.2627(7); c 7.9800(4); P21</td>
</tr>
<tr>
<td>1903920*</td>
<td>Cocrystal C-C16</td>
<td>C_{14}H_{11}NO_{3}, C_{6}H_{6}N_{2}O</td>
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</tr>
<tr>
<td>1903921</td>
<td>Cocrystal E-C11</td>
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</tr>
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<td>1903922*</td>
<td>Cocrystal E-C5</td>
<td>2(C_{17}H_{13}NO), C_{7}H_{6}O_{4}</td>
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</tr>
<tr>
<td>1903923</td>
<td>Cocrystal M-C15</td>
<td>C_{14}H_{13}NO_{2}, CH_{4}N_{3}O</td>
<td>a 16.5139(12); b 12.0736(8); c 7.5359(5); Pc</td>
</tr>
<tr>
<td>Structure ID</td>
<td>Crystalline Form</td>
<td>Chemical Formula</td>
<td>Crystallographic Parameters</td>
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<tr>
<td>1903924</td>
<td>Cocrystal F-C5</td>
<td>3(C\textsubscript{17}H\textsubscript{12}FNO\textsubscript{2}), 2(C\textsubscript{7}H\textsubscript{6}O\textsubscript{4})</td>
<td>a 10.6896(3); b 23.7848(8); c 21.5387(7); P\textsubscript{21}/n</td>
</tr>
<tr>
<td>1903925</td>
<td>Cocrystal I-C10 Hydrate</td>
<td>C\textsubscript{13}H\textsubscript{12}NO\textsubscript{2}\textsubscript{2}\textsuperscript{+}, C\textsubscript{2}H\textsubscript{6}O\textsubscript{4}\textsuperscript{-}, H\textsubscript{2}O</td>
<td>a 7.6543(6); b 9.5179(6); c 10.7618(8); P-1</td>
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<tr>
<td>1903926*</td>
<td>Cocrystal O-C13 Hydrate</td>
<td>C\textsubscript{13}H\textsubscript{13}NO\textsubscript{4}, C\textsubscript{7}H\textsubscript{6}N\textsubscript{2}O\textsubscript{3}</td>
<td>a 26.4610(17); b 7.2777(5); c 43.334(5); I2/a</td>
</tr>
<tr>
<td>1903927</td>
<td>Cocrystal F-C9</td>
<td>2(C\textsubscript{17}H\textsubscript{12}FNO\textsubscript{2}), C\textsubscript{4}H\textsubscript{4}O\textsubscript{4}</td>
<td>a 3.88889(14); b 32.5630(11); c 11.8170(4); P\textsubscript{21}/c</td>
</tr>
<tr>
<td>1903928*</td>
<td>Cocrystal N-C5 Hydrate</td>
<td>2(C\textsubscript{14}H\textsubscript{12}FNO\textsubscript{2}), C\textsubscript{7}H\textsubscript{6}O\textsubscript{4}, H\textsubscript{2}O</td>
<td>a 9.4810(6); b 17.4577(8); c 19.5354(15); P\textsubscript{21}/n</td>
</tr>
<tr>
<td>1903929</td>
<td>Cocrystal F-C4 Hydrate</td>
<td>2(C\textsubscript{17}H\textsubscript{12}FNO\textsubscript{2}), 2(C\textsubscript{7}H\textsubscript{6}O\textsubscript{4}), H\textsubscript{2}O</td>
<td>a 26.5472(10); b 5.5127(2); c 28.2059(12); C2/c</td>
</tr>
<tr>
<td>1903930</td>
<td>Cocrystal E-C12 Solvate</td>
<td>2(C\textsubscript{17}H\textsubscript{13}NO), C\textsubscript{4}H\textsubscript{6}O\textsubscript{5}, C\textsubscript{2}H\textsubscript{2}N</td>
<td>a 37.7706(6); b 5.23850(7); c 16.7696(2); P\textsubscript{ca21}</td>
</tr>
</tbody>
</table>

*These structures have been found to be twinned and refined against HKLF5.
Supporting information 14: DRS and TGA of photochromic compounds A-C20, C-C16, C-C20, D, D-C5, J-C7 and M-C15.

The thermal stability of photochromic compounds discussed in the main text with their structural analysis (A-C20, C-C16, C-C20, D and M-C15) or with their photochromic intensity (D-C5 and J-C7) has been studied with TGA and DSC. Differential Scanning Calorimetry (DSC) measurements were performed from 30 to 200°C at a scanning rate of 2°C/min on a “Mettler Toledo DSC821e”. Solid samples (weight of 5-15mg) were placed in an aluminum crucible with pierced sealed lids and nitrogen was used as purge gas with a flow rate of 50mL/min. Indium is used as a reference. Thermogravimetric analysis (TGA) was performed from 30 to 500°C at a scanning rate of 10°C/min on a “Mettler Toledo TGA-STDA 851e”. Solid samples (weight of 5-15mg) were placed in aluminum oxide crucible and nitrogen was used as purge gas with a flow rate of 50mL/min.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>DSC</th>
<th>TGA (5% mass loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-C20</td>
<td>78 °C (melting)</td>
<td>146 °C (Boiling/Deg.)</td>
</tr>
<tr>
<td>C-C16</td>
<td>167 °C (melting)</td>
<td>226 °C (Deg.)</td>
</tr>
<tr>
<td>C-C20</td>
<td>102°C (melting/ peritectic), 158 °C (Deg.)</td>
<td>128 °C (Deg.)</td>
</tr>
<tr>
<td>D</td>
<td>229 °C (melting)</td>
<td>285 °C (Deg.)</td>
</tr>
<tr>
<td>D-C5</td>
<td>181 °C (melting)</td>
<td>237 °C (Deg.)</td>
</tr>
<tr>
<td>J-C7</td>
<td>130 °C (melting), 141 °C (recrystallization)</td>
<td>167 °C (Deg.)</td>
</tr>
<tr>
<td>M-C15</td>
<td>114°C (melting/ peritectic), 134 °C (melting).</td>
<td>182 °C (Deg.)</td>
</tr>
</tbody>
</table>

* Small excess of coformer C16 (mp: 130 °C) is believed to be responsible of small eutectic points at around 130 °C.
* In case of cocrystals C-C20 and M-C15, observed behavior is believed to be due to a peritectic transition (however this would require extensive analysis and would be out of the scope of the article). In both case the second peak correspond to the melting point of coformer.

In both case the second peak correspond to the melting point of coformer.
Supporting information 14: Hirshfeld surface and 2D molecular fingerprints of non-photochromic compounds H, E-C1, E-C2, E-C4, E-C5, E-C6, E-C9, E-C11, F-C4, F-C5, F-C9.

Anil H: displaced towards keto form.

Cocrystal E-C1: displaced towards keto form, strong interactions involving the moving moiety.

Cocrystal E-C2: displaced towards keto form.
Cocrystal E-C4: two different molecules of E in crystal cell, one is disordered and thus not shown.

Cocrystal E-C5: two differents of E in crystal cell, both in keto form and presenting strong short contact involving the oxygen atom of keto moiety.

Cocrystal E-C6: two different of E in crystal cell, both in keto form (second one is disordered) and presenting strong short contact involving the oxygen atom of keto moiety.
Cocrystal E-C8: displaced towards keto form, strong interactions involving the moving moiety.

Cocrystal E-C9: displaced towards keto form.

Cocrystal E-C11: displaced towards keto form.
Cocrystal F-C4: displaced towards keto form.

Cocrystal F-C5: displaced towards keto form.

Cocrystal F-C9: displaced towards keto form.