Supporting Information for:

Visible-Light Induced Enhancement in Multi-catalytic Activity of Sulfated Carbon dots for Aerobic Carbon-Carbon Bond Formation**

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**Instrumentation:** The powder XRD measurements were carried out by using a Bruker D8 Advance X-ray diffractometer with CuKα source (wavelength= 0.154 nm). TEM images were obtained by using a JEOL JEM- 2100 microscope operated at 200 kV FTIR spectra were recorded with KBr pellets by using a Bruker Tensor 27 instrument. UV-visible measurements were performed using a Varian Cary 100 Bio spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from HoribaYovin (model: FM-100). The samples were excited at different excitation wavelength ranging from 310 to 520 nm. X-ray photoelectron spectra (XPS) were recorded using an ESCA instrument, VSW of UK make. EPR measurements were carried out using a JEOL spectrometer (Model: JES-FA200). $^1$H and $^{13}$C NMR spectra were recorded with Bruker Advance (III) 400 MHz or 100 MHz spectrometers, respectively. Data for $^1$H NMR spectra are reported as chemical shift (δ ppm), multiplicity (s=singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J Hz) and integration and assignment data for $^{13}$C NMR spectra are reported as a chemical shift. High resolutions mass spectral analyses (HRMS) were carried out using ESI-TOF-MS.

**Materials:** Glucose, oleic acid, oleum, catalase, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and all other chemicals were purchased from Sigma–Aldrich, India or Merck, India and used without further purification. We used Millipore water (ultrapure level) throughout the experiments.
Experimental Section

Synthesis of N-phenyl-tetrahydroisoquiniline:

\[
\text{phenyl boronic acid (0.368g, 2 mmol) and Cu(OAc)_2.H_2O (20 mg, 0.1 mmol) in DCM (10 mL) were taken in a flask and the mixture was stirred for 5 minutes at room temperature. To this stirring suspension was added 1,2,3,4 tetrahyroisoquinoline (0.072 g, 99.1 mmol) and stirred under O_2 atmosphere for 24 h. The mixture was extracted with water and DCM. The product was purified using silica gel column chromatography (using 2% ethylacetate/ hexane).}
\]

Synthesis of Thioxanthene:

In the typical synthesis of thioxanthene, 5 mmol of thioxanthenone was dissolved in 40 ml of dry THF and added into it 1.2 equivalent of NaBH_4 and 6 mmol of I_2 at 0 °C. After bringing to room temperature, the reaction mixture was refluxed for 12 h at 60 °C. The reaction mixture was quenched with brine and extracted with ethyl acetate. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (eluting with 2% ethylacetate/ hexane) to provide thioxanthene with 92% yield.
Figure S1: Characterization of s-CD

(a) UV-visible spectra of s-CDs in water; the band at 278 nm signifies $\pi-\pi^*$ transition.
(b) Full scan FTIR spectrum recorded using KBr which shows the presence of $-\text{OH}$, $\text{C=O}$, $\text{C=C}$, $-\text{SO}_3\text{H}$ functionalities on s-CD surface.
(c) Magnified FTIR spectrum of s-CDs, shows peaks at 1703 cm$^{-1}$ ($\text{C=O}$), 1627 cm$^{-1}$ ($\text{C=C}$). Peaks at 1038 cm$^{-1}$ and 1002 cm$^{-1}$ are attributed to the $\text{O=S=O}$ stretching vibrations in $-\text{SO}_3\text{H}$ groups and peak at 1166 cm$^{-1}$ for $-\text{SO}_3\text{H}$ stretching.
Table S1: Elemental analysis of s-CDs

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>S</th>
<th>Adsorbed H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % in s-CD</td>
<td>50.2</td>
<td>4.64</td>
<td>33.6</td>
<td>2.3</td>
<td>9.26</td>
</tr>
<tr>
<td>Atom ratio</td>
<td>4.2</td>
<td>4.64</td>
<td>2.1</td>
<td>0.0718</td>
<td>0.514</td>
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Table S2: Performance of various catalysts for the model coupling reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>3αb Yield (%)</th>
<th>3cα Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>χCH₃COOH (hv)/(Δ)</td>
<td>12</td>
<td>12/7</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>χH₂SO₄(conc) (hv)/(Δ)</td>
<td>12</td>
<td>68/62</td>
<td>Trace</td>
</tr>
<tr>
<td>3</td>
<td>χBenzoic acid (hv)/(Δ)</td>
<td>12</td>
<td>16/14</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>χPTSA (hv)/(Δ)</td>
<td>12</td>
<td>64/69</td>
<td>Trace</td>
</tr>
<tr>
<td>5</td>
<td>dCD (hv)</td>
<td>3</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>χPCA (hv)</td>
<td>3</td>
<td>15</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>dS-CD (hv)</td>
<td>3</td>
<td>91</td>
<td>Trace</td>
</tr>
<tr>
<td>8</td>
<td>dS-CD (Δ)</td>
<td>10</td>
<td>36</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>dGO (Δ)</td>
<td>10</td>
<td>39</td>
<td>32</td>
</tr>
<tr>
<td>10</td>
<td>dS- GO (hv)/(Δ)</td>
<td>10</td>
<td>38/42</td>
<td>22/24</td>
</tr>
<tr>
<td>11</td>
<td>eS- GO (hv)/(Δ)</td>
<td>10</td>
<td>43/48</td>
<td>29/26</td>
</tr>
</tbody>
</table>

Unless otherwise specified, all the reactions were carried out with 2-methoxy xanthene (0.5 mmol) and Cyclohexanone (3 mmol) as the model substrates; using 34 W blue LED lamp (hv = 425 nm) at 25 °C under O₂ environment; Δ= Reaction performed without visible-light illumination at 70 °C; bIsolated yield; c catalyst (7 mol%), d catalyst (5.0 mg); e catalyst (30 mg).
Table S3: Diasteriomer coupling product yield

<table>
<thead>
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<th>Product</th>
<th>Diasteriometric Ratio</th>
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<tbody>
<tr>
<td>3hc</td>
<td>2.9:1</td>
</tr>
<tr>
<td>3ia</td>
<td>0.92:1</td>
</tr>
<tr>
<td>3ib</td>
<td>1.3:1</td>
</tr>
<tr>
<td>3ic</td>
<td>1:1</td>
</tr>
<tr>
<td>3jb</td>
<td>1:1</td>
</tr>
<tr>
<td>6b</td>
<td>1:0.92</td>
</tr>
</tbody>
</table>

Leaching experiment:

The model coupling reaction of xanthene and cyclohexanone was carried out under visible light illumination under optimal reaction conditions. The reaction was stopped after 90 min (approx. 50% conversion) and the s-CD catalyst were removed from the reaction mixture by centrifugation. The reaction was further continued with the supernatant for 10 h under visible light irradiation.

Figure S2: Reaction profile for the model coupling reaction under visible light irradiation (red) and after the s-CDs were removed by centrifugation from the reaction mixture (blue).
Recyclability studies of s-CDs:

To study the recyclability of s-CDs, the model photocatalytic reaction was performed in cycles of reactions under standard photocatalytic reaction conditions. After the completion of the 1st cycle of the reaction, the organic products were extracted using ethyl acetate, while the s-CDs were separated out by centrifugation. The 2nd cycle of the photocatalytic reaction was carried out using the recovered s-CDs as catalyst. The same s-CDs could be reused for at least for four runs with excellent yields. The s-CDs showed efficient recyclability as a photocatalyst and 76% of the desired coupling product could be obtained even after the fourth cycle.

Figure S3: Recyclability test for monitoring the efficiency of s-CDs as a photocatalyst for the coupling reaction in a cycle of reactions.
Figure S4: Characterization of recovered s-CD.

(a) The recovered s-CDs after the fourth cycle were analysed to determine the relationship between the catalytic reactivity and surface functionalities. TEM study revealed that there is no pronounced morphological change.

(b) Normalized fluorescence emission spectra of the pristine of recovered s-CDs. From the emission spectra of the recovered s-CDs, a minor blue shift in the emission peak as well as an enhancement in the fluorescence intensity was observed as compared to the pristine ones.

(c) FTIR spectra of s-CDs and recovered s-CDs after fourth cycle of reactions where the band at 1038 cm\(^{-1}\) associated with O=S=O and the band at 1166 cm\(^{-1}\) corresponding to -SO\(_3\)H groups are reduced significantly.

Table S4: Elemental analysis of Recycled s-CDs

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Sulphur</th>
<th>Adsorbed H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % in Recycled s-CD</td>
<td>52.3</td>
<td>3.7</td>
<td>32.6</td>
<td>2.12</td>
<td>9.28</td>
</tr>
<tr>
<td>Atom ratio</td>
<td>4.36</td>
<td>3.7</td>
<td>2.04</td>
<td>0.066</td>
<td>0.515</td>
</tr>
</tbody>
</table>
Figure S5: Comparative XPS analysis of s-CD and recovered s-CD

(a) The high resolution XPS spectra of S2p region revealed the peaks at 164.7 eV for sulfoxide and 169.7 eV for sulphonic acid and sulphate.

(b) The S2p core level XPS spectra show that the amount of \(\text{SO}_3\text{-H} / \text{SO}_4^2\) functionality (169.7 eV) is reduced in the recovered s-CDs as compared to the pristine ones.
Figure S6: Comparative studies of s-CD and recovered s-CD.

(a) The C 1s region of s-CD is deconvoluted into C=C (284.5 eV), C-C (285.7), C-OH (286.3 eV), -C-O-C, C-S (287.2 eV), and -COOH (288.6 eV) bonds suggesting the presence of hydroxyl, carbonyl, and carboxylic acid groups on s-CD surface.

(b) C 1s core XPS spectra of the recovered s-CDs revealed that there was no significant change in the graphitic content as well as the oxygen functionalities such as in carboxylic group.

(c) The s-CD exhibited two broad peaks at D band 1346.3 cm\(^{-1}\) which attributed to the presence of sp\(^3\) defect in graphitic plane and G band at 1586.2 cm\(^{-1}\) owing to the in plane vibration of sp\(^2\) carbons. The intensity ratio of D and G bands (I\(_D/I_G=0.93\)) in pristine s-CD did not change appreciably after the coupling reaction. This revealed that the graphitic pool of s-CD was not affected by the reaction.
Table S5: Elemental analysis of s-CDs obtained after thermal treatment at 200°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Sulphur</th>
<th>Adsorbed H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % in s-CD</td>
<td>53.6</td>
<td>3.9</td>
<td>31.2</td>
<td>0.93</td>
<td>10.37</td>
</tr>
<tr>
<td>Atom ratio</td>
<td>4.46</td>
<td>3.9</td>
<td>1.95</td>
<td>0.015</td>
<td>0.576</td>
</tr>
</tbody>
</table>

Characterization data for hydroperoxy intermediate:

**9-Hydroperoxy-4-methoxy-9H-xanthene:** Yellowish oil; \(^1\)H NMR (400 MHz, CDCl₃) δ (ppm) 7.6 (d, \(J = 8.7\), 1H), 7.41-7.37 (t, \(J = 8.28\), 1H), 7.34-7.32 (d, \(J = 7.28\), 1H), 7.19-7.17 (t, \(J = 7.52\) Hz, 1H), 7.16-7.14 (d, \(J = 8.28\) Hz, 1H), 7.09-7.07 (t, \(J = 7.8\) Hz, 1H), 6.98-6.96 (d, \(J = 8\) Hz, 1H), 5.95 (s, 1H), 3.95 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ (ppm) 152.5, 147.9, 142.0, 131.3, 129.9, 122.9, 122.9, 122.4, 119.8, 119.0, 116.9, 112.0, 80.3, 56.3; Mass: 244.07, HRMS (ESI): calcd for [C₁₄H₁₂O₄⁺ + Na⁺] 267.0612, found 267.0623.
Figure S7: $^1$H and $^{13}$C NMR spectra for hydroperoxy intermediate.
Detection of hydrogen peroxide in the catalytic reactions

To detect \( \text{H}_2\text{O}_2 \) during the catalytic reaction, a modified iodometric method was employed. After 15 minutes of the reaction between 2-methoxyhydroperoxide intermediate with cyclohexanone under thermal condition (at 50°C), an equal volume of water and dichloromethane was added to extract the formed coupling product. The aqueous layer was acidified with \( \text{H}_2\text{SO}_4 \) to \( \text{pH} \approx 2 \) and 1 mL of a 10% solution of KI and three drops of 3% solution of ammonium molybdate were added. In the presence of hydrogen peroxide \( \Gamma^- \) is oxidised to \( \text{I}_2 \), \( \text{H}_2\text{O}_2 + 2\Gamma^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2 \), and with an excess of iodide ions, the tri-iodide ion is formed according to the reaction \( \text{I}_2 \text{(aq.)} + \Gamma^- \rightarrow \text{I}_3^- \). The formation of \( \text{I}_3^- \) could be monitored by UV-Visible spectroscopy at wavelength 353 nm.

![Absorbance](image)

**Figure S8:** UV/Visible absorption spectra of the tri-iodide formed by \( \text{H}_2\text{O}_2 \) oxidation.

**Radial Scavenging Analysis:** To explore the involvement of various free radicals during the photocatalytic reaction, known radical scavengers were added in the reaction medium and the model photocatalytic C-C coupling reaction was studied in presence of visible-light under standard reaction conditions. Whereas Butylated hydroxytoluene (BHT) was used as a scavenger for studying the involvement of radicals in the mechanism, ascorbic acid (AA) was...
used as a superoxide radical scavenger, \textit{tert}-butyl alcohol (TBA) as \textsuperscript{·}OH radical scavenger, EDTA as hole ($h^+$) scavenger and CuCl$_2$ as electron scavenger.$^2$

\textbf{Table S6: Control experiments of photocatalytic Cross dehydrogenative coupling of xanthene and cyclohexanone with the addition of various radical scavengers}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Scavenger</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BHT</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>$p$-benzoquinone</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>TBA</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>EDTA</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>CuCl$_2$</td>
<td>10</td>
</tr>
</tbody>
</table>

**Figure S9:** Normalized FTIR spectra of fresh s-GO (red) and s-GO after one cycle of reaction (pink).
Figure S10: Stern–Volmer plots for the quenching of luminescence quantum yields (454 nm excitation) of the s-CDs.

(a) Electron acceptor 2,4-dinitrotoluene (DNT, 0.9 V vs NHE) in toluene were added to the s-CD aqueous solution. The emission intensity of s-CD at 424 nm was efficiently quenched. The Stern–Volmer quenching constants ($K_{sv} = \tau F^0 k_q$) were calculated from the linear regression and found to be 0.4619 mM$^{-1}$.

(b) Electron donor N, N-diethylaniline (DEA, 0.88 V vs NHE) in methanol were added to the aqueous s-CD solution and the calculated Stern-Volmer quenching constants were found to be 2.53 M$^{-1}$. 
Photocurrent response measurements:

Commercial indium tin oxide (ITO) was used as the substrate for electrode build-up, and cleaned by sonication sequentially for 20 min each in acetone, 10% KOH in ethanol and doubly deionized water. Photo-electrochemical experiments were performed in a conventional three-electrode cell (Pyrex window) with a platinum wire as the auxiliary electrode and an Hg/HgCl$_2$ (saturated KCl) as the reference electrode. The working electrodes were ITO/s-CDs, with the glass side facing the incident light. They were prepared by spreading aqueous slurries over ITO glass substrates. Lithium perchlorate (LiClO$_4$) in acetonitrile was used as a electrolyte in cells. A 34 W blue LED light was used as light source and positioned 4 cm away from the photo-electrochemical cell. The photocurrent signal was recorded with a CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China) connected to a personal computer. All electrochemical experiments were carried out at room temperature.

Figure S11: Transient photocurrent response of s-CDs under visible light.
Figure S12: (a) Band gap of s-CD obtained from UV-Visible spectrum and calculated using Kubelka–Munk theory; (b) Reduction potential of s-CD measured by cyclic voltammetry; (c) HOMO/LUMO band positions of s-CD; (d) Cyclic voltamograms of the s-CDs/ITO electrode in acetonitrile using lithium perchlorate (LiClO₄) as an electrolyte under visible light irradiation or without light irradiation.
Figure S13: Characterization of graphene oxide (GO).

(a) The transmission electron microscopy (TEM) analysis indicated a layered structure of GO.

(b) UV-visible study showed two absorption peaks, a maximum at 230 nm corresponding to $\pi-\pi^*$ transitions of aromatic C–C bonds and a shoulder at 305 nm attributed to $n-\pi^*$ transitions of C–O bonds.

(c) The X-ray diffraction (XRD) pattern showed a characteristic peak at $2\theta$ value of 10.2° with d spacing of 0.865 nm.

(d) Raman spectra of GO showing the D and G band of graphitic carbon.

Table S7: Elemental analysis of s-GO

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Sulphur</th>
<th>Adsorbed H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % in s-GO</td>
<td>48.32</td>
<td>2.49</td>
<td>37.1</td>
<td>2.24</td>
<td>9.85</td>
</tr>
<tr>
<td>Atom ratio</td>
<td>4.03</td>
<td>2.49</td>
<td>2.31</td>
<td>0.07</td>
<td>0.547</td>
</tr>
</tbody>
</table>
References:


$^1$H and $^{13}$C NMR spectra:

3aa

**2-(9H-xanthen-9-yl)cyclopentanone**: colourless solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.29-7.22 (m, 3H), 7.15-7.10 (m, 4H), 7.02 (t, $J$ = 7.4 Hz, 1H), 4.79 (d, $J$ = 2.7 Hz, 1H), 2.47 (td, $J$ = 9.7 Hz, $J$ = 2.2 Hz, 1H), 2.27 (dd, $J$ = 18.5 Hz, $J$ = 7.4 Hz, 1H), 1.84-1.76 (m, 2H), 1.69-1.63 (m, 1H), 1.61-1.51 (m, 1H), 1.44 (ddd, $J$ = 23.3 Hz, $J$ = 11.3 Hz, $J$ = 6.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 199.4, 153.1, 152.5, 129.2, 128.2, 127.8, 124.5, 123.7, 123.5, 121.9; 116.4, 116.3, 59.9, 39.3, 38.0, 24.0, 20.4 HR-MS (ESI positive) m/z: calcd. For C$_{18}$H$_{16}$O$_2$Na$^+$, [M+Na]$^+$: 287.135551; found: 315.135314.

3ab

**2-(9H-xanthen-9-yl)cyclohexanone**: colourless solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.42 (dd, $J$ = 7.52 Hz, 1H), 7.23-7.17 (m, 3H), 7.07-7.0 (m, 4H), 4.93 (s, 1H), 2.52-2.39 (m, 2H), 2.27-2.19 (m, 1H), 1.94-1.91 (m, 1H), 1.77-1.69 (m, 2H), 1.48-1.40 (m, 2H), 1.14-1.04 (m, 1H), 1.55-1.41 (m, 2H), 1.15 (ddd, $J$ = 25.6 Hz, $J$ = 12.8 Hz, $J$ = 3.6 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 210.8, 153.3, 153.0, 130.5, 128.8, 127.8, 127.7, 125.6, 123.5, 123.2, 122.9, 116.3, 116.1, 60.7, 42.1, 36.7, 26.7, 24.8, 23.1; HR-MS (EI) m/z: calcd. for C$_{19}$H$_{18}$O$_2$Na$^+$ [M+Na]$^+$: 301.130678; found: 301.130632.
3ac

9-(2,4-dimethoxyphenyl)-4-methoxy-9H-xanthene: White solid, $^1$H NMR (400 MHz) $\delta$ ppm 7.20 (d, $J= 8.4$ Hz, 1H), 7.13 (dt, $J= 8.4$ Hz, 1H), 7.08 (d, $J= 7.64$ Hz, 1H), 6.91 (dt, $J= 7.6$ Hz, 1H), 6.85 (t, $J= 7.64$ Hz, 1H), 6.82 (d, $J= 8.4$ Hz, 1H), 6.75 (d, $J= 7.64$ Hz, 1H), 6.70 (d, $J= 7.64$ Hz, 1H), 6.43 (s, 1H), 6.32 (dd, $J= 8.4$ Hz, 1H), 5.69 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 210.1, 153.2, 152.9, 147.9, 147.8, 142.8, 142.6, 130.4, 128.7, 127.7, 127.6, 126.6, 125.6, 123.9, 123.7, 123.4, 123.2, 122.8, 122.7, 122.2, 120.4, 116.7, 116.7, 116.6, 110.2, 110.0, 60.5, 56.2, 56.1, 42.13, 42.09, 36.8, 36.7, 29.7, 29.7, 27.8, 27.5, 26.7, 26.6, 24.74, 24.72; HR-MS (EI) m/z: calcd. for C$_{20}$H$_{20}$O$_2$Na$^+$ [M+Na]$^+$: 301.150668; found: 301.150652.

3ad

2-(2-hydroxy-9H-xanthen-9-yl)cyclohexanone: Yellow solid, $^1$H NMR (400 MHz) $\delta$ ppm 7.42 (dd, $J= 7.52$ Hz, 1H), 7.23-7.17 (m, 3H), 7.07-7.0 (m, 2H), 6.99-6.92 (m,3H), 4.93 (s, 1H), 2.52-2.39 (m, 2H), 2.27-2.19 (m, 1H), 1.94-1.91 (m, 1H), 1.77-1.69 (m, 2H), 1.48-1.40 (m, 2H), 1.14-1.04 (m, 1H), 1.55-1.41 (m, 2H), 1.15 (ddd, $J= 25.6$ Hz, $J= 12.8$ Hz, $J= 3.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 210.8, 153.3, 153.0, 130.5, 128.8, 127.8, 127.7, 125.6, 123.5, 123.2, 122.9, 116.3, 116.1, 60.7, 42.1, 36.7, 26.7, 24.8, 23.1; HR-MS (EI) m/z: calcd. for C$_{19}$H$_{18}$O$_3$Na$^+$ [M+Na]$^+$: 317.120568; found: 317.120343.
3ae

2-(9H-xanthen-9-yl)cycloheptanone: colourless solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.26-7.20 (m, 3H), 7.10-7.04 (m, 4H), 7.01 (t, $J = 7.3$ Hz, 1H), 4.64 (d, $J = 3.9$ Hz, 1H), 2.5 (d, $J = 11.4$ Hz, 1H), 2.36-2.32 (m, $J = 12.4$ Hz, 1H), 2.16-2.06 (m, 1H), 1.74-1.72 (br m, 3H), 1.38-1.12 (m, 4H), 1.05-0.99 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 216.4, 153.2, 153.0, 129.1, 128.7, 128.1, 127.9, 124.5, 123.6, 123.1, 121.9, 116.6, 116.3, 62.4, 44.7, 42.1, 29.9, 28.5, 25.1, 24.8. HR-MS (ESI positive) m/z: calcd. For C$_{20}$H$_{20}$NaO$_2$ [M+Na]$^+$: 315.135551; found: 315.135314.

3ba

2-(9H-thioxanthen-9-yl)cyclohexanone: Light yellow solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.63 (dd, $J = 7.56$ Hz, $J = 1.68$ Hz, 1H), 7.42-7.36 (m, 2H), 7.24-7.10 (m, 6H), 4.69 (d, $J = 9.52$ Hz, 1H), 3.14-3.07 (m, 1H), 2.35-2.30 (m, 1H), 2.22-2.14 (m, 1H), 2.01-1.94 (m, 1H), 1.76-1.69 (m, 1H), 1.63-1.50 (m, 3H), 1.40-1.32 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 212.1, 141.9, 138.6, 136.6, 133.7, 132.7, 130.9, 130.2, 127.2, 126.6, 126.4, 126.2, 50.4, 47.3, 43.2, 33.9, 29.8, 28.9, 25.3; HR-MS (ESI positive) m/z: calcd. For C$_{19}$H$_{18}$NaOS [M+Na]$^+$: 317.095651; found: 315.09311.

3bb

2-(9H-thioxanthen-9-yl)cycloheptanone: White solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.42-7.36 (m, 1H), 7.28-7.27 (m, 1H), 7.24-7.10 (m, 5H), 4.50 (d, $J = 10.2$ Hz, 1H), 2.31-2.23 (m, 1H), 2.10-2.04 (m, 1H), 2.16-2.06 (m, 1H), 1.76-1.66 (br m, 3H), 1.50-1.44 (m, 1H), 1.38-1.34 (m, 1H), 1.24 (br s, 3H); $^{13}$C NMR (100 MHz,
(CDCl$_3$): $\delta$ ppm 214.5, 136.9, 135.8, 132.6, 130.5, 130.3, 127.3 (t), 127.0, 126.7, 126.45, 126.41, 126.1, 50.9, 50.0, 43.7, 29.7, 28.4, 27.8, 23.6; HR-MS (ESI positive) m/z: calcd. For C$_{20}$H$_{20}$NaOS [M+Na]$^+$: 332.115851; found: 332.114113.

![Diagram](image_url)

**3ca**

**3-(9H-xanthen-9-yl)pentan-2-one**: Brown oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.27-7.21 (m, 2H), 7.15-7.02 (m, 6H), 4.08 (d, $J = 8.5$ Hz, 1H), 2.69 (t, $J = 10.8$ Hz, 1H), 1.76 (s, 3H), 1.62-1.55 (m, 1H), 1.39-1.33 (m, 1H), 0.73 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 212.2, 153.2, 129.6, 128.8, 128.1, 127.9, 124.7, 124.1, 123.5, 123.1, 116.7, 61.0, 42.8, 33.4, 22.9, 12.0; HR-MS (EI) m/z: calcd. for C$_{18}$H$_{18}$O$_2$ [M+Na]$^+$: 289.120678; found: 266.120632.

![Diagram](image_url)

**3cb**

**1-phenyl-2-(9H-xanthen-9-yl)ethanone**: White solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.79 (d, $J = 5.4$ Hz, 2H), 7.48 (t, $J = 8.04$ Hz, 1H), 7.37-7.30 (m, 4H), 7.19 (t, $J = 7.8$ Hz, 2H), 7.1 (d, $J = 6.84$ Hz, 2H), 7.02 (t, $J = 5.6$ Hz, 2H), 4.85 (t, $J = 4.4$ Hz, 1H), 3.34 (d, $J = 5.1$ Hz, 2H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ ppm 197.2, 152.3, 129.5, 128.8, 128.5, 128.1, 127.9, 126.3, 125.5, 123.5, 116.6, 57.1, 43.3; HR-MS (ESI positive) m/z: calcd. for C$_{21}$H$_{16}$NaO$_2$ [M+Na]$^+$: 323.104136; found: 323.104250.
3cc

1-phenyl-2-(9H-xanthen-9-yl)propan-1-one: Pale yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 7.67 (d, $J = 7.28$ Hz, 2H), 7.41 (t, $J = 7.52$ Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 2H), 7.19 (td, $J = 8.5$ Hz, $J = 1.5$ Hz, 1H), 7.11 (d, $J = 7.5$ Hz, 1H), 7.09-6.96 (m, 5H), 6.85 (td, $J = 7.5$ Hz, $J = 2.0$ Hz, 1H), 4.32 (d, $J = 7.7$ Hz, 1H), 3.64-3.57 (m, 1H), 1.18 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 203.4, 153.4, 153.1, 137.1, 129.9, 129.0, 128.6, 128.2, 127.9, 125.2, 123.6, 116.58, 116.62, 68.4, 48.6, 42.8, 29.8, 14.6 HRMS (ESI positive) m/z: calcd. for C$_{22}$H$_{18}$NaO$_2$ [M+Na]$^+$: 337.119729; found: 337.119576.

3cd

1-(p-tolyl)-2-(9H-xanthen-9-yl)propan-1-one: Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 7.66 (d, $J = 7.7$ Hz, $J = 1.4$ Hz, 2H), 7.26 (t, $J = 9.0$ Hz, 1H), 7.19-7.03 (m, 8H), 6.92 (td, $J = 6.4$ Hz, $J = 1.5$ Hz, 1H), 4.40 (d, $J = 7.6$ Hz, 1H), 3.68-3.61 (m, 1H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 202.1, 173.5, 165.4, 159.4, 157.3, 151.5, 130.8, 129.5, 128.1, 127.5, 125.1, 123.0, 123.3, 116.7, 104.9, 98.8, 55.6, 55.3, 36.4, 31.0 HRMS (ESI positive) m/z: calcd. for C$_{23}$H$_{20}$NaO$_2$ [M+Na]$^+$: 351.139789; found: 333.139578.
**3da**

**1-phenyl-2-(9H-thioxanthen-9-yl)ethanone:** Colourless oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.80 (d, $J = 5.3$ Hz, 2H), 7.49 (t, $J = 8.01$ Hz, 1H), 7.36-7.32 (m, 4H), 7.20 (t, $J = 7.8$ Hz, 2H), 7.1 (d, $J = 6.84$ Hz, 2H), 7.03 (t, $J = 5.6$ Hz, 2H), 4.86 (t, $J = 4.4$ Hz, 1H), 3.34 (d, $J = 5.1$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 198.1, 152.2, 129.4, 128.6, 128.4, 127.7, 126.3, 125.5, 123.5, 116.5, 57.1, 43.3; HRMS (ESI positive) m/z: calcd. for C$_{21}$H$_{16}$NaOS [M+Na]$^+$: 339.073724; found: 339.070572.

**3ea**

**dimethyl 2-(9H-xanthen-9-yl)malonate:** Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.30 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 2H), 7.25 (td, $J = 8.1$ Hz, $J = 1.7$ Hz, 2H), 7.15 (dd, $J = 8.2$ Hz, $J = 1.1$ Hz, 2H), 7.05 (td, $J = 7.4$ Hz, $J = 1.2$ Hz, 2H), 4.82 (d, $J = 9.0$ Hz, 1H), 3.6 (d, $J = 9.0$ Hz, 1H), 3.55 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 167.6, 152.7, 129.4, 128.9, 123.4, 122.7, 116.9, 60.0, 52.5, 39.9; HR-MS (ESI positive) m/z: calcd. for C$_{18}$H$_{16}$NaO$_5$ [M+Na]$^+$: 335.088992; found: 335.088817.
**diethyl 2-(9H-xanthen-9-yl)malonate:** Brown oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.32 (dd, $J = 7.6$ Hz, $J = 1.5$ Hz, 2H), 7.26-7.22 (m, 2H), 7.14 (dd, $J = 8.2$ Hz, $J = 1.04$ Hz, 2H), 7.05 (td, $J = 7.4$ Hz, $J = 1.2$ Hz, 2H), 4.81 (d, $J = 8.9$ Hz, 1H), 4.06-3.94 (m, 2H), 3.59 (d, $J = 8.9$ Hz, 1H), 1.08 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 167.5, 153.2, 129.0, 128.5, 123.4, 122.9, 116.7, 61.6, 60.3, 39.7, 13.5; HR-MS (ESI positive) m/z: calcd. for C$_{20}$H$_{20}$NaO$_5$ [M+Na]$^+$: 363.117982; found: 335.117812.

**ethyl 3-oxo-2-(9H-xanthen-9-yl)butanoate:** Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.33 (dd, $J = 7.7$ Hz, $J = 1.4$ Hz, 1H), 7.27-7.24 (m, 3H), 7.14 (ddd, $J = 8.5$ Hz, $J = 4.1$ Hz, $J = 1.3$ Hz, 2H), 7.04 (m, 2H), 4.85 (d, $J = 9.2$ Hz, 1H), 4.03-3.94 (m, 2H), 3.79 (d, $J = 9.2$ Hz, 1H), 1.90 (s, 3H), 1.09 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 201.8, 167.4, 153.4, 153.3, 129.7, 129.3, 128.49, 128.47, 123.6 (t), 123.5, 123.4, 123.3, 116.9, 116.7, 63.9, 60.3, 39.5, 32.9, 13.9; HRMS (ESI positive) m/z: calcd. for C$_{19}$H$_{18}$NaO$_4$ [M+Na]$^+$: 333.109729; found: 333.109576.

**dimethyl 2-(9H-thioxanthen-9-yl)malonate:** Light yellow solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.44-7.42 (m, 2H), 7.40-7.38 (m, 2H), 7.20-7.19 (m, 4H), 4.91 (d, $J = 9.04$ Hz, 1H), 4.2 (d, $J = 9.04$ Hz, 1H), 3.47 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 167.7, 153.2, 134.3, 133.5, 130.0, 127.3, 126.5, 52.4, 51.4, 48.7; HR-MS (ESI positive) m/z: calcd. for C$_{18}$H$_{16}$NaO$_4$S [M+Na]$^+$: 351.078972; found: 351.078816.
**diethyl 2-(9H-thioxanthen-9-yl)malonate:** Light yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.44-7.41 (m, 4H), 7.20-7.18 (m, 4H), 4.82 (d, $J = 8.9$ Hz, 1H), 4.91 (d, $J = 8.8$ Hz, 1H), 4.16 (d, $J = 8.9$ Hz, 1H), 3.99-3.87 (m, 4H) 1.03 (t, $J = 5.84$, 3H) ; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 167.5, 153.4, 134.5, 133.6, 130.2, 127.2, 126.5, 61.3, 51.5, 48.7, 13.8; HRMS (ESI positive) m/z: calcd. For C$_{20}$H$_{20}$NaO$_4$S [M+Na]$^+$: 379.097282; found: 363.097132.

**methyl 3-oxo-2-(9H-thioxanthen-9-yl)butanoate:** White solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.43-7.40 (m, 3H), 7.34 (m, 1H), 7.20-7.18 (m, 4H), 4.93 (d, $J = 11.0$ Hz, 1H), 4.46 (d, $J = 10.76$ Hz, 1H), 3.97-3.88 (m, 2H), 1.82 (s, 3H), 1.05 (t, $J = 7.01$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 201.9, 167.4, 134.7, 134.4, 133.9, 133.44, 133.39, 130.6, 130.2, 127.3, 127.2, 127.1, 126.8, 126.6, 61.4, 57.5, 48.4, 31.2, 13.9; HRMS (ESI positive) m/z: calcd. for C$_{18}$H$_{16}$NaO$_3$S [M+Na]$^+$: 335.068572; found: 333.0684576.

**2-(isochroman-1-yl)cyclopentanone:** Yellow oil, $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ ppm 7.34-7.20 (m, 4H), 4.35 (d, $J = 7.6$, 1H), 3.75 (m, 2H), 2.77-2.70 (m, 3H), 2.10-1.85 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm 211.8, 137.1, 136.3, 127.5, 125.8, 125.7, 125.5, 77.5, 62.6,
54.7, 38.9, 28.6, 21.2, 14.1, HRMS (EI) m/z calcd for C_{14}H_{16}O_{2} [M+Na]^+ 239.09380, found 231.09326.

3gb

2-(isochroman-1-yl)cyclohexanone: Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.23-7.14 (m, 3H), 7.13-7.09 (m, 1H), 7.01 (d, J=7.0 Hz, 1H), 5.48 (s, 1H), 4.16 (dd, J=11.0, 5.4 Hz, 1H), 3.75 (t, J=11.3 Hz, 1H), 3.05-2.97 (m, 1H), 2.75 (dd, J=11.1, 5.6 Hz, 1H), 2.62-2.53 (m, 2H), 2.3-2.30 (m, 1H), 1.99 (dd, J=8.2, 4.8 Hz, 1H), 1.89-1.82 (m, 1H), 1.76 (ddd, J=32.4, 20.4, 12.8 Hz, 2H), 1.64 (d, J=7.1 Hz, 1H), 1.54 (t, J=12.5 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 210.8, 136.6, 135.5, 128.9, 126.3, 126.2, 123.9, 73.7, 64.3, 55.7, 42.0, 29.3, 26.1, 25.2, 24.5 HRMS (EI) m/z calcd for C_{15}H_{18}NaO_{2} [M+Na]^+ 253.1180, found 253.1163.

3gc

2-(isochroman-1-yl)cycloheptanone: Yellow oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ ppm 7.33 (m, 2H), 7.23 (m, 2H), 4.4 (d, J=10.9, 1H), 3.75-3.65 (m, 2H), 3.05 (m, 1H), 2.71 (m, 2H), 2.52-2.4 (m, 2H), 1.66-1.41.0 (m, 8H), $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ ppm 214.6, 137.1, 136.3, 127.6, 125.8, 125.7, 125.5, 78.0, 62.6, 54.6, 42.4, 29.5, 28.6, 26.7, 24.2, 22.7; HRMS (EI) m/z calcd for C_{15}H_{18}NaO_{2} [M+Na]^+ 253.1180, found 253.1163.
**2-(isochroman-1-yl)-1-phenylethanone:** Pale yellow, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ ppm 8.04 (d, $J$=7.17 Hz, 2H), 7.60-7.45 (m, 3H), 7.26-7.13 (m, 4H), 5.54 (d, $J$=8.7 Hz, 1H), 4.16-4.09 (m, 1H), 3.86-3.78 (m, 1H), 3.67-3.59 (m, 1H), 3.36-3.30 (m 1H), 3.08-2.98 (m, 1H), 2.76-2.69 (m, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ ppm 198.1, 137.5, 137.1, 134.0, 133.1, 129.0, 128.5, 128.3, 126.5, 126.2, 124.5, 72.6,63.4, 45.4, 28.8; HRMS (EI) m/z calcd for C$_{17}$H$_{16}$NaO$_2$ [M+Na]$^+$ 275.0923, found 275.0912.

**2-(isochroman-1-yl)-1-phenylpropan-1-one:** Yellow solid, $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ ppm 7.99-7.91 (m, 2H), 7.58-7.40 (m, 3H), 7.25-7.01 (m, 4H), 5.28-5.21 (m, 1H), 4.13-4.0 (m, 2H), 3.68-3.53 (m, 1H), 3.06-2.95 (m, 1H), 2.65-2.54 (m, 1H), 1.20-1.06 (m, 3H); $^{13}$C NMR (CDCl$_3$,75 MHz) $\delta$ ppm 201.8, 177.2, 136.6, 135.8, 135.0, 132.7 (two peaks), 129.1, 128.7, 128.6, 128.5, 128.3, 126.6, 126.5, 126.3, 125.8, 124.5, 77.4, 76.6, 63.9, 63.3, 47.2, 46.7, 29.6, 28.8,13.6, 9.7; HRMS (EI) m/z calcd for C$_{18}$H$_{18}$NaO$_2$ [M+Na]$^+$ 289.11760, found 289.11742.
3hc

2-(isochroman-1-yl)-1-(p-tolyl)propan-1-one: Light yellow solid, Diastereomeric ratio 2.9:1, $^{1}$H NMR (400 MHz) δ ppm 7.87 (d, $J$= 8.4 Hz, 2H), 7.26 (d, $J$= 8.4 Hz, 2H), 7.16-7.08 (m, 4H), 5.26 (d, $J$= 3.8, 1H), 4.12-4.06 (m, 1H), 4.00-3.91 (m, 1H), 3.61-3.55 (m, 1H), 3.02-2.94 (m, 1H), 2.60-2.53 (m, 1H), 2.39 (s, 3H), 1.07 (d, $J$= , 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ ppm 201.5, 143.5, 143.4, 136.4, 135.1, 134.3, 129.4,129.2, 128.6, 126.6, 126.4, 124.6, 72.1, 70.4, 65.3, 64.0, 46.8, 34.3, 31.9, 29.5, 29.4, 29.3, 29.2, 28.9, 25.0, 22.7, 21.6, 14.2, 10.2; HRMS (EI) m/z calcd for C$_{19}$H$_{20}$NaO$_2$ [M+Na]$^+$ 303.1380, found 303.1382.

3ia

2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclopentanone: Dark brown soild, Diastereomeric ratio 6.9:1, $^{1}$H NMR (400 MHz) δ ppm 7.29-7.15 (m, 4H), 7.11-7.07 (m, 1H), 7.02 (d, $J$= 8. Hz, 2H), 6.92 (d, $J$= 7.6 Hz, 1H), 6.77 (t, $J$= 7.64 Hz, 1H), 5.58 (s, 1H), 3.57-3.46 (m, 2H), 3.04-2.89 (m, 2H), 2.74-2.69 (m, 1H), 2.30-2.23 (m, 1H), 2.08-2.02 (m, 2H), 1.85-1.75 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 202.9, 153.4, 153.1, 143.7, 134.6, 129.9, 129.3, 129.0, 128.3, 128.1, 127.8, 125.3, 123.4, 123.0, 116.52, 116.48, 48.5, 42.7, 32.0, 31.0, 29.8, 21.6, 14.6; HRMS (EI) m/z calcd for C$_{20}$H$_{21}$NNaO [M+Na]$^+$ 314.1462, found 314.1451.
3ib

2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone: Yellow oil diastereomeric ratio = 1.3 : 1; Isolated major isomer, $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.23 (dd, $J$ = 12.8, 7.1 Hz, 3H), 7.19 – 7.10 (m, 4H), 6.93 (d, $J$ = 8.1 Hz, 2H), 5.63 (d, $J$ = 4.5 Hz, 1H), 3.82 – 3.67 (m, 1H), 3.64 – 3.47 (m, 2H), 2.93 – 2.85 (m, 2H), 2.47 (t, $J$ = 9.9 Hz, 2H), 2.30 (ddd, $J$ = 25.7, 15.3, 9.7 Hz, 2H), 1.86 (d, $J$ = 6.3 Hz, 2H), 1.68 – 1.59 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm, 214.5, 149.3, 140.3, 135.9, 134.6, 129.3, 128.7, 127.9, 125.8, 118.1, 116.4, 114.9, 112.3, 59.3, 56.5, 54.9, 54.0, 42.6, 41.4, 32.8, 30.2, 28.7, 27.7, 27.0, 25.7, 23.8; HRMS (EI) m/z calcd for C$_{21}$H$_{23}$NNaO$_2$ [M+Na]$^+$ 328.1680, found 327.1676.

3ic

2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cycloheptanone: Light brown solid, Diastereomeric ratio 1:1, $^1$H NMR (400 MHz) δ ppm 7.21 (d, $J$ = 8.36 Hz, 1H), 7.20 (d, $J$ = 9.16 Hz, 1H), 7.11-7.02 (m, 4H), 6.90 (d, $J$ = 8.4 Hz, 2H), 6.68 (t, $J$ = 7.64 Hz, 1H), 5.41 (d, $J$ = 8.4, 1H), 3.55 (t, $J$ = 6.12 Hz, 2H), 3.06-2.97 (m, 2H), 2.87-2.80 (m, 1H), 2.43-2.35 (m, 1H), 2.25-2.19 (m, 1H), 2.11-2.06 (m, 1H), 1.87-1.78 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm, 215.4, 149.8, 138.7, 134.3, 129.2, 128.3, 127.1, 126.7, 126.2, 117.0, 113.3, 70.3, 65.1, 63.4, 59.5, 57.9, 44.3, 43.0, 31.9, 29.6, 29.4, 29.0, 28.2, 27.2, 24.8, 23.5, 22.6, 14.0; HR-MS (ESI positive) m/z: calcd. for C$_{22}$H$_{25}$NNaO [M+Na]$^+$: 342.181672; found: 342.181517.
3ja

1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone: Yellow solid, $^1$H NMR (400 MHz, CDCl$_3$): δ ppm  7.84 (d, $J$ = 7.0 Hz, 2H), 7.53 (t, $J$ = 7.7 Hz, 1H), 7.41 (t, $J$ = 7.5 Hz, 2H), 7.25 (t, $J$ = 7.0 Hz, 3H), 7.14-7.10 (m, 3H), 6.96 (d, $J$ = 8 Hz, 2H), 6.75 (t, $J$ = 7.2 Hz, 1H), 5.67 (t, $J$=5.4 Hz, 1H), 3.64-3.54 (m, 3H), 3.41 (dd, $J$ = 16.7, 7.0 Hz, 1H), 3.13-3.07 (m, 1H), 2.93 (d, $J$ = 16.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 198.6, 148.7, 138.5, 137.2, 134.5, 133.1, 129.3, 128.5, 128.3, 128.1, 127.1, 126.8, 126.2, 117.9, 114.3, 55.0, 45.3, 42.1, 27.6; HR-MS m/z: calcd for C$_{23}$H$_{21}$NNaO[M+Na]$^+$: 350.1515; found: 350.1511.

3jb

1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-1-one: Light yellow oil, Diastereomeric ratio 1:1, $^1$H NMR (400 MHz) δ ppm 7.63 (d, $J$=7.64 Hz, 2H), 7.41 (t, $J$=7.64 Hz, 1H), 7.28 (t, $J$=7.6 Hz, 2H), 7.20 (t, $J$= 8.4 Hz, 2H), 7.03 (t, $J$= 6.88 Hz, 2H), 6.99 (d, $J$= 9.16 Hz, 2H), 6.88 (t, $J$= 6.88 Hz, 1H), 6.84 (t, $J$= 7.64 Hz, 1H), 6.68 (t, $J$= 7.64 Hz, 1H), 5.39 (d, $J$= 9.16 Hz, 1H), 3.99-3.94 (m, 1H), 3.63-3.59 (m, 2H), 3.05-2.99 (m, 1H), 2.92-2.87 (m, 1H), 1.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm, 204.5, 137.5, 134.4, 132.9, 129.2, 128.1, 127.3, 126.9, 126.0, 113.4, 70.3, 65.2, 63.4, 48.3, 34.2, 31.9, 29.7, 24.9, 22.7, 16.6, 14.1; HR-MS (ESI positive) m/z: calcd. for C$_{24}$H$_{23}$NNaO [M+Na]$^+$: 364.168792; found: 364.168681.
**3jc**

**2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-(p-tolyl)propan-1-one:** Brown solid, Diastereomeric ratio 1:1, $^1$H NMR (400 MHz) $\delta$ ppm 7.44 (d, $J$= 8.4 Hz, 2H), 7.11-7.07 (m, 3H), 6.98 (d, $J$=8.4 Hz, 2H), 6.93-6.85 (m, 4H), 6.77 (t, $J$= 8.4 Hz, 1H), 6.73 (t, $J$= 6.88 Hz, 1H), 6.56 (t, $J$= 7.64 Hz, 1H), 5.29 (d, $J$= 9.16 Hz, 1H), 3.87-3.79 (m, 1H), 3.50 (t, $J$ = 6.08 Hz, 1H), 2.95-2.88 (m, 1H), 2.81-2.74 (m, 1H), 2.18 (s, 3H), 1.13 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ ppm 205.6, 137.6, 134.6, 133.1, 130.2, 128.1, 127.4, 126.5, 126.3, 114.1, 71.3, 65.2, 63.6, 48.2, 34.3, 31.7, 29.5, 24.7, 22.5, 16.7, 13.3 14.1; HR-MS (ESI positive) m/z: calcd. for C$_{25}$H$_{25}$NNaO $[M+Na]^+$: 378.178982; found: 378.178817.

**6a**

**9-(2,4-dimethoxyphenyl)-9H-xanthene:** White solid, $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ ppm 7.20 (td, $J$ = 8.2 Hz, $J$ = 1.4 Hz, 2H), 7.12-7.08 (m, 4H), 6.97 (td, $J$ = 7.7 Hz, $J$ = 1.3 Hz, 2H), 6.86 (d, $J$ = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, $J$ = 8.4 Hz, $J$ = 2.4 Hz, 1H ), 5.72 (s, 1H), 3.84 (s, 3H), 3.75(s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ ppm 159.3, 157.1, 151.5, 130.7, 129.3, 128.1, 127.6, 125.1, 123.0, 116.2, 104.8, 98.7, 55.6, 55.2, 36.4; HRMS: calcd for C$_{21}$H$_{18}$NaO$_3$ $[M+Na]^+$ 341.1153, found: 341.1141.
9-(2,4-dimethoxyphenyl)-4-methoxy-9H-xanthene: white solid, Diastereomeric ratio 1:1.3, ^1^H NMR (400 MHz) δ ppm 7.20 (d, J= 8.4 Hz, 1H), 7.13 (dt=8.4 Hz, 1H), 7.08 (d, J= 7.64 Hz, 1H), 6.91 (dt, J= 7.6 Hz, 1H), 6.85 (t, J= 7.64 Hz, 1H), 6.82 (d, J= 8.4 Hz, 1H), 6.75 (d, J= 7.64 Hz, 1H), 6.70 (d, J= 7.64 Hz, 1H), 6.43 (s, 1H), 6.32 (dd, J= 8.4 Hz, 1H), 5.69 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H); ^1^C NMR (100 MHz, CDCl$_3$) δ ppm, 160.3, 159.7, 159.3, 158.4, 157.0, 151.2, 149.6, 147.7, 141.0, 137.5, 132.9, 130.6, 130.1, 129.5, 129.3, 128.4, 128.0, 127.3, 126.6, 126.4, 126.3, 125.9, 124.9, 123.2, 122.5, 122.2, 121.1, 119.6, 116.5, 116.1, 110.3, 109.7, 104.8, 104.0, 103.7, 100.2, 98.8, 98.7, 95.5, 95.2, 55.2, 45.6, 36.2, 31.9, 29.6, 22.6, 14.1; C$_{22}$H$_{20}$NaO$_3$ [M+Na]$^+$ calcd for 371.1288, found: 317.1280.

6c

9-(2,4-dimethoxyphenyl)-9H-thioxanthene: Light yellow solid, ^1^H NMR (CDCl$_3$, 400 MHz) δ (ppm): 7.39-7.34 (m, 4H), 7.16-7.14 (m, 4H), 6.98 (d, J = 8.28 Hz, 1H), 6.46 (s, 1H), 6.34 (d, J = 8.5 Hz, 1H ), 5.64 (s, 1H), 3.84 (s, 3H), 3.73(s, 3H); ^1^C NMR (CDCl$_3$, 100 MHz) δ (ppm): 159.7, 157.5, 137.6, 133.0, 130.2, 130.1, 129.9, 129.6, 126.9, 126.7, 126.5, 126.4, 126.0, 124.6, 122.3, 106.2, 104.0, 98.8, 55.3, 45.7, 29.8. HRMS: calcd for C$_{21}$H$_{18}$O$_2$S [M+Na]$^+$ 357.0972, found: 357.0969.
6d

4-methyl-3-(9H-xanthen-9-yl)phenol: Light yellow solid, $^1$H NMR (CDCl$_3$, 400 MHz) δ (ppm): 11.71 (s, 1H), 7.48-7.35 (m, 4H), 7.19-7.04 (m, 3H), 7.02-6.97 (m, 2H), 6.89-6.84 (m, 1H), 6.73 (dd, $J = 6.6$ Hz, $J = 2.0$ Hz, 1H), 5.28 (s, 1H), 4.90 (s, 1H), 2.24 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm): 161.8, 155.8, 149.0, 142.6, 138.7, 133.3, 132.5, 130.1, 128.3, 126.5, 122.7, 122.3, 120.0, 119.2, 118.5, 117.7, 117.3, 115.1, 29.8, 20.5. HRMS: calcd for C$_{20}$H$_{16}$NaO$_2$ [M+Na]$^+$ 311.1067, found: 311.1064.
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Chemical Shift (ppm)

Chemical shift

100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780 800 820 840 860 880 900 920 940 960 980 1000 1020 1040 1060 1080 1100 1120 1140 1160 1180 1200 1220 1240 1260 1280 1300 1320 1340 1360 1380 1400 1420 1440 1460 1480 1500 1520 1540 1560 1580 1600 1620 1640 1660 1680 1700 1720 1740 1760 1780 1800 1820 1840 1860 1880 1900 1920 1940 1960 1980 2000 2020 2040 2060 2080 2100 2120 2140 2160 2180 2200 2220 2240 2260 2280 2300 2320 2340 2360 2380 2400 2420 2440 2460 2480 2500 2520 2540 2560 2580 2600 2620 2640 2660 2680 2700 2720 2740 2760 2780 2800 2820 2840 2860 2880 2900 2920 2940 2960 2980 3000 3020 3040 3060 3080 3100 3120 3140 3160 3180 3200 3220 3240 3260 3280 3300 3320 3340 3360 3380 3400 3420 3440 3460 3480 3500 3520 3540 3560 3580 3600 3620 3640 3660 3680 3700 3720 3740 3760 3780 3800 3820 3840 3860 3880 3900 3920 3940 3960 3980 4000 4020 4040 4060 4080 4100 4120 4140 4160 4180 4200 4220 4240 4260 4280 4300 4320 4340 4360 4380 4400 4420 4440 4460 4480 4500 4520 4540 4560 4580 4600 4620 4640 4660 4680 4700 4720 4740 4760 4780 4800 4820 4840 4860 4880 4900 4920 4940 4960 4980 5000 5020 5040 5060 5080 5100 5120 5140 5160 5180 5200 5220 5240 5260 5280 5300 5320 5340 5360 5380 5400 5420 5440 5460 5480 5500 5520 5540 5560 5580 5600 5620 5640 5660 5680 5700 5720 5740 5760 5780 5800 5820 5840 5860 5880 5900 5920 5940 5960 5980 6000 6020 6040 6060 6080 6100 6120 6140 6160 6180 6200 6220 6240 6260 6280 6300 6320 6340 6360 6380 6400 6420 6440 6460 6480 6500 6520 6540 6560 6580 6600 6620 6640 6660 6680 6700 6720 6740 6760 6780 6800 6820 6840 6860 6880 6900 6920 6940 6960 6980 7000 7020 7040 7060 7080 7100 7120 7140 7160 7180 7200 7220 7240 7260 7280 7300 7320 7340 7360 7380 7400 7420 7440 7460 7480 7500 7520 7540 7560 7580 7600 7620 7640 7660 7680 7700 7720 7740 7760 7780 7800 7820 7840 7860 7880 7900 7920 7940 7960 7980 8000 8020 8040 8060 8080 8100 8120 8140 8160 8180 8200 8220 8240 8260 8280 8300 8320 8340 8360 8380 8400 8420 8440 8460 8480 8500 8520 8540 8560 8580 8600 8620 8640 8660 8680 8700 8720 8740 8760 8780 8800 8820 8840 8860 8880 8900 8920 8940 8960 8980 9000 9020 9040 9060 9080 9100 9120 9140 9160 9180 9200 9220 9240 9260 9280 9300 9320 9340 9360 9380 9400 9420 9440 9460 9480 9500 9520 9540 9560 9580 9600 9620 9640 9660 9680 9700 9720 9740 9760 9780 9800 9820 9840 9860 9880 9900 9920 9940 9960 9980 10000

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