Supporting Information

Visible-Light-Promoted Oxidative Halogenation of Alkynes
Yiming Li+, Tao Mou+, Lingling Lu, Xuefeng Jiang*

School of Chemistry and Molecular Engineering, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P. R. China.

xfjiang@chem.ecnu.edu.cn

Index

I. General Information ................................................................. S2
II. Conditions Optimization ....................................................... S3
III. Mechanistic Studies .............................................................. S5
IV. The Procedure and Data for Oxyhalogenation of Alkynes ........ S17
V. X-ray Crystallography Analysis of Compound 8 .................... S54
VI. NMR Spectra ................................................................. S55
VII. References ................................................................. S190
**I. General Information**

**NMR Spectrum:**

$^1$H and $^{13}$C spectra were collected on 400 MHz or 500 MHz NMR spectrometers (Bruker AVANCE). Chemical shifts for protons are reported in parts per million (ppm) downfield and are referenced to residual protium in the NMR solvent (CHCl$_3$ = $\delta$ 7.26). Chemical for carbon are reported in parts per million downfield and are referenced to coupling of carbon nucleus on deuterium (CHCl$_3$ = $\delta$ 77.0). Date are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = double, t = triplet, q = quartet, m = multiplet ), coupling constants in Hertz (Hz), integration.

**Mass Spectroscopy:**

Mass spectra were in general recorded on a Waters Synapt G2 (HRMS) and Waters Acquity H (LCMS).

**Chromatography:**

Column chromatography was performed with silica gel (300 – 400 mesh ASTM).

**IR:**

SHIMADZU IR Tracer-100 Spectrometers. TENSOR (27) Series FT-IR Spectrometers.

**Solvent:**

CH$_3$CN was dried with CaH$_2$ and distilled using standard methods. Distilled water was bought and used without further purification.
II. Conditions Optimization

Table S1: Condition optimization of oxybromonation.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>'Br' Source</th>
<th>Acid</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaBr</td>
<td>CH\textsubscript{3}COOH</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>NaBr</td>
<td>CSA</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>NaBr</td>
<td>H\textsubscript{3}PO\textsubscript{4}</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>NaBr</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>89 (85)\textsuperscript{c}</td>
</tr>
<tr>
<td>5</td>
<td>KBr</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>LiBr</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>NH\textsubscript{4}Br</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>77</td>
</tr>
<tr>
<td>8</td>
<td>MgBr\textsubscript{2}</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>64</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The reaction conditions: 1 (0.2 mmol), H\textsubscript{2}O (6.0 mmol), Acid (0.7 mmol), "Br" (0.5 mmol), MeCN (2.0 mL), room temperature, air, 6 W blue LEDs, 8 h. \textsuperscript{b}NMR yield with CH\textsubscript{2}Br\textsubscript{2} as internal standard. \textsuperscript{c}isolated yield.

Table S2: Condition optimization of oxychloronation.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>'Cl' Source</th>
<th>Acid (3.5 equiv.)</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>59\textsuperscript{b}</td>
</tr>
<tr>
<td>2</td>
<td>LiCl</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>KCl</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>63</td>
</tr>
<tr>
<td>4</td>
<td>MgCl\textsubscript{2}</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>NH\textsubscript{4}Cl</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>LiCl</td>
<td>NaHSO\textsubscript{4}, H\textsubscript{2}O (4.0 equiv.)</td>
<td>75 (71)\textsuperscript{c}</td>
</tr>
<tr>
<td>7</td>
<td>LiCl</td>
<td>KHSO\textsubscript{4}</td>
<td>60</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The reaction conditions: 1-\textsubscript{mOMe} (0.2 mmol), H\textsubscript{2}O (6.0 mmol), NaHSO\textsubscript{4}, H\textsubscript{2}O (0.8 mmol), "Cl" (0.6 mmol), MeCN (2.0 mL), room temperature, air, 6 W blue LEDs, 24 h. \textsuperscript{b}NMR yield with CH\textsubscript{2}Br\textsubscript{2} as internal standard. \textsuperscript{c}isolated yield.
**Table S3:** Variation from standard conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variation from standard conditions</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>none&lt;sup&gt;b&lt;/sup&gt;</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>N&lt;sub&gt;2&lt;/sub&gt; instead of air</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>O&lt;sub&gt;2&lt;/sub&gt; instead of air</td>
<td>48</td>
</tr>
<tr>
<td>5</td>
<td>no light</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>no light, 70 °C</td>
<td>NR</td>
</tr>
<tr>
<td>7</td>
<td>no NaBr</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>no NaHSO&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Trace</td>
</tr>
<tr>
<td>9</td>
<td>no H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>only NaBr</td>
<td>Trace</td>
</tr>
<tr>
<td>11</td>
<td>only NaHSO&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>NR</td>
</tr>
<tr>
<td>12</td>
<td>only H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>NR</td>
</tr>
</tbody>
</table>

<sup>a</sup>NMR yield with CH<sub>3</sub>Br<sub>2</sub> as internal standard. <sup>b</sup>the schlenk tube (25 mL) were sealed.
III. Mechanistic Studies

1) Ultraviolet–visible Absorption Experiments
Ultraviolet–visible absorption experiments were performed using a Shimadzu UV-2700 UV-visible spectrophotometer. In each experiment, the varying samples were combined in CH$_3$CN in screw-top 1.0 cm quartz cuvettes.

Figure S1: Ultraviolet–visible absorption of 1.
2) Stern–Volmer Fluorescent Quenching Experiments

Fluorescence quenching studies were performed using a Shimadzu RF-6000 Fluorescence Spectrophotometer. In each experiment, the photocatalyst and varying concentrations of quencher were combined in CH$_3$CN in screw-top 1.0 cm quartz cuvettes. For the emission quenching of phenylacetylene (0.1 M), the solution was irradiated at 299 nm, and the emission intensity was observed at 347 nm.

Figure S2: Quenching experiments of 1 with sat. NaHSO$_4$•H$_2$O (aq).
Figure S3: Quenching experiments of 1 with sat. NaBr (aq).

Figure S4: Quenching experiments of 1 with HBr (aq).
Figure S5: Fluorescent quenching experiments of 1 with different reagents.
3) Radical Trapping Experiments with TEMPO

All reactions were operated under standard conditions with extra TEMPO (2 equiv.). The yields of 2 were determined with NMR.

![Chemical reaction diagram]

4) Radical Clock Experiment

![Chemical reaction diagram]
5) **Control Experiments**

All the reactions were conducted under standard conditions with certain amount of additives. The corresponding yields were calculated by NMR with CH$_2$Br$_2$ as internal standard.

**Table S3**: Control Experiments.

<table>
<thead>
<tr>
<th>Entries</th>
<th>Additives</th>
<th>Function</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaN$_3$ (1 equiv.)</td>
<td>$^1$O$_2$ inhibitor</td>
<td>87%</td>
</tr>
<tr>
<td>2</td>
<td>Ph$_2$C$_5$O (1 equiv.)</td>
<td>$^1$O$_2$ inhibitor, O$_2^-$ inhibitor</td>
<td>83%</td>
</tr>
<tr>
<td>3</td>
<td>tBuOH (1 equiv.)</td>
<td>HO$^-$ inhibitor</td>
<td>88%</td>
</tr>
</tbody>
</table>
6) **Electron paramagnetic resonance experiments**

The electron paramagnetic resonance (EPR) experiments were recorded on an X-band Bruker E500 10/12. A reaction system with $\text{UO}_2(\text{OAc})_2\cdot2\text{H}_2\text{O}$ (0.004 mmol), sulfide 1a (0.2 mmol), DMPO\(^a\) (0.1 mmol), CH\(_3\)CN (1 mL) was irradiated with blue light (2w*3) under oxygen atmosphere with paralleled reactor. After 10 mins, melting-point tube was used to suck certain amount of reaction system, then, both ends were melted by fire. This sample was submitted for the EPR experiments.

\(^a\)DMPO = 5,5-dimethyl-1-pyrroline-1-oxide.

![Figure S6: EPR spectrums.](image)

No obvious $^1\text{O}_2$, HO\(^-\) and $\text{O}_2\cdot$ in standard system
7) Studies on Hydrogen Peroxide

The amount of H$_2$O$_2$ was determined by titration with iodide ion, as described previously in the literature in which the reflux procedures was instead by stirring at room temperature.\cite{1} In an iodometric titration, the formation of I$_3^-$ and the consumption of H$_2$O$_2$ follows a one-to-one ratio as eqs S1-3. The concentration H$_2$O$_2$ can be derived from the concentration of I$_3^-$(Abs@361 nm = εb[I$_3^-$]). All iodometric titrations are conducted anaerobically to avoid the oxidation of I$^-$ to I$_3^-$ by O$_2$.\cite{2}

\[
\begin{align*}
2 \text{H}_2\text{O}_2 + 2 \text{I}^- & \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + \text{I}_2 & \text{(eq S1)} \\
\text{I}_2 + \text{I}^- & \rightarrow \text{I}_3^- & \text{(eq S2)} \\
\text{H}_2\text{O}_2 + 2 \text{I}^- & \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + \text{I}_3^- & \text{(eq S3)}
\end{align*}
\]

**Figure S3:** UV-Vis Absorption of I$_3^-$ Generated by Different Concentration of H$_2$O$_2$.

**Figure S7:** Standard curve of the amount of I$_3^-$ for its quantitative studies.
8) Quantitative Studies of H$_2$O$_2$.

**Table S4:** Control experiments based on the generation of H$_2$O$_2$ under standard oxybromoation conditions.

![Chemical Reaction Diagram](image-url)

<table>
<thead>
<tr>
<th>Entries</th>
<th>Conditions</th>
<th>in-situ generated H$_2$O$_2$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>standard conditions</td>
<td>0.112 mmol</td>
</tr>
<tr>
<td>2</td>
<td>no H$_2$O (O$_2$, sealed)</td>
<td>0.021 mmol</td>
</tr>
<tr>
<td>3</td>
<td>no NaHSO$_4$</td>
<td>0.040 mmol</td>
</tr>
<tr>
<td>4</td>
<td>no NaBr</td>
<td>0.038 mmol</td>
</tr>
</tbody>
</table>
9) Oxygen Labelling Reactions

These reactions are conducted under standard sulfoxidation or sulfonation conditions with $^{18}$O$_2$ instead of O$_2$.

![Diagram 1](image1.png)

**Figure S8:** GCMS spectrum for labelling experiments with O$_2^{18}$.

![Diagram 2](image2.png)

**Figure S9:** Tracking Experiments without H$_2$O
Tracking experiments indicate H$_2$O is necessary due to the low efficiency with only O$_2$.

![Reaction Scheme](image)

**Figure S10:** GCMS spectrum for labelling experiments with different amount of H$_2$O$^{18}$.
Table S5: Results of labelling experiments with different amount of H$_2$O$^{18}$.

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entries</th>
<th>H$_2$O$^{18}$ (x eq)</th>
<th>MS(276)/MS(282)</th>
<th>NMR Yield of 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1/0</td>
<td>32%</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>1/0.23</td>
<td>52%</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>1/3</td>
<td>84%</td>
</tr>
</tbody>
</table>

10) Oxygen-Labelling Experiments

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entries</th>
<th>O$_2$</th>
<th>H$_2$O</th>
<th>MS(276)/MS(282)</th>
<th>2 (NMR Yields)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>H$_2$O (30 equiv.)</td>
<td>-</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>O$_2^{18}$</td>
<td>-</td>
<td>0/1</td>
<td>10%</td>
</tr>
<tr>
<td>3</td>
<td>O$_2^{16}$</td>
<td>H$_2$O$^{18}$ (30 equiv.)</td>
<td>1/3</td>
<td>84%</td>
</tr>
<tr>
<td>4</td>
<td>O$_2^{18}$</td>
<td>H$_2$O$^{18}$ (30 equiv.)</td>
<td>0/1</td>
<td>73%</td>
</tr>
</tbody>
</table>
11) Proposed Mechanism

Radical Trapping Experiment, GCMS
UV-Vis Absorption
Iodometry Experiments
Radical Clock Experiment
H$_2$O$_2$ etc.

Fluorescent Quenching

$\text{X}^- \rightarrow \text{X}$

Quenching Experiments
EPR Experiments
Iodometry Experiments

H$_2$O$_{18}$ Labelling Experiments
IV. The Procedure and Data for Oxyhalogenation of Alkynes

1) The General Procedure

**Condition A:** In a Schlenk tube, **Substrate** (0.2 mmol, 1.0 equiv.), NaBr (0.5 mmol, 2.5 equiv.), NaHSO$_4$$\cdot$H$_2$O (0.7 mmol, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), and the reaction mixture was stirred under 2 W*3 blue LEDs at room temperature for 8 hours, which is opened to air. After the reaction completed, the reaction mixture was purified by column chromatography on silica gel to give desired product.

**Condition B:** In a Schlenk tube, **Substrate** (0.2 mmol, 1.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), NaHSO$_4$$\cdot$H$_2$O (0.8 mmol, 4.0 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), and the reaction mixture was stirred under 6 W blue LEDs at room temperature for 24 hours, which is opened to air. After the reaction completed, the reaction mixture was purified by column chromatography on silica gel to give desired product.
2) The Procedure and Data of Table 1 and 2

2,2-dibromo-1-phenylethan-1-one 2: Prepared under outlined condition A as in general procedure using ethynylbenzene (20.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 2 in 85% (47.1 mg) yield as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 8.07 (m, 2H), 7.65 – 7.62 (m, 1H), 7.53 – 7.49 (m, 2H), 6.71 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 185.98, 134.47, 130.88, 129.72, 128.96, 39.71; MS (EI) m/z 276; IR (film) 1693, 1593, 1579, 1448, 1267, 1190, 979, 800, 702, 682, 626, 570 cm⁻¹.

Prepared under outlined condition A as in general procedure using ethynylbenzene (2.04 g, 2.0 mmol, 1.0 equiv.), NaBr (5.14 mg, 2.5 equiv.), NaHSO₄·H₂O (9.67 mg, 3.5 equiv.), H₂O (1.08 g, 30.0 equiv.) were dissolved in CH₃CN (80 mL), the reaction was stirred under 2 W *15 blue LEDs at room temperature for 48 hours with bubbling oxygen using balloon affording compound 2 in 56% (3.113 g) yield as yellow oil.

2,2-dichloro-1-phenylethan-1-one 3: Prepared under outlined condition B as in general procedure using ethynylbenzene (20.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 3 in 63% (24.1 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.01 (m, 2H), 7.65 (dt, J = 8.7, 1.2 Hz, 1H), 7.58 – 7.47 (m, 2H), 6.69 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 185.92, 134.57, 131.36, 129.76, 128.93, 67.80; HRMS (ESI) [M+Na]+ Calcd for C₈H₆Cl₂ONa 210.9693, Found 210.9986; IR (film) 2920, 2850, 1707, 1647, 1469, 1363, 1259, 1082, 1022, 968, 802,
2,2-dibromo-1-(4-fluorophenyl)ethan-1-one 4: Prepared under outlined condition A as in general procedure using 1-ethynyl-4-fluorobenzene (24.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 4 in 72% (42.3 mg) yield as pale yellow oil. 

1H NMR (400 MHz, CDCl₃) δ 8.17 – 8.12 (m, 2H), 8.20 – 8.16 (m, 2H), 6.62 (s, 1H); 13C NMR (101 MHz, CDCl₃) δ 184.57, 166.35 (d, J = 258.9 Hz), 132.69 (d, J = 9.5 Hz), 127.11 (d, J = 2.9 Hz), 116.24 (d, J = 9.5 Hz), 39.36; 19F NMR (282 MHz, CDCl₃) δ -101.83 – -101.91 (m); MS (EI) m/z 294; IR (film) 1697, 1597, 1506, 1413, 1271, 1242, 1190, 1161, 983, 850, 765, 704, 588 cm⁻¹.

2,2-dibromo-1-(4-chlorophenyl)ethan-1-one 5: Prepared under outlined condition A as in general procedure using 1-chloro-4-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 5 in 74% (45.8 mg) yield as pale yellow oil. 

1H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 6.61 (s, 1H); 13C NMR (101 MHz, CDCl₃) δ 184.91, 141.08, 131.22, 129.30, 129.10, 39.24; MS (EI) m/z 310; IR (film) 3037, 1693, 1587, 1402, 1276, 1205, 1093, 989, 844, 765, 729, 665, 565 cm⁻¹.

2,2-dibromo-1-(4-bromophenyl)ethan-1-one 6: Prepared under outlined condition A as in general procedure using 1-bromo-4-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 6 in 73% (50.1 mg) yield as pale yellow oil. 

1H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 7.9 Hz, 2H), 6.63 (s, 1H); 13C NMR (101 MHz, CDCl₃) δ 185.01, 140.95, 131.22, 129.30, 129.10, 39.24; MS (EI) m/z 326; IR (film) 3037, 1693, 1587, 1402, 1276, 1205, 1093, 989, 844, 765, 729, 665, 565 cm⁻¹.
under outlined condition A as in general procedure using 1-bromo-4-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 6 in 88% (62.6 mg) yield as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.94 (m, 2H), 7.69 – 7.61 (m, 2H), 6.61 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 185.12, 132.31, 131.24, 129.91, 129.53, 39.26; MS (EI) m/z 356; IR (film) 3034, 1693, 1581, 1485, 1394, 1271, 1201, 1070, 985, 840, 719, 653, 563 cm⁻¹.

2,2-dibromo-1-(4-nitrophenyl)ethan-1-one 7: Prepared under outlined condition A as in general procedure using 1-ethynyl-4-nitrobenzene (29.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 7 in 56% (35.9 mg) yield as yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, J = 8.9 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H), 6.60 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 184.52, 150.83, 135.63, 131.04, 123.95, 38.78; MS (EI) m/z 321; IR (film) 2920, 1705, 1600, 1521, 1344, 1259, 1190, 987, 866, 854, 785, 713, 657, 565 cm⁻¹.

2,2-dibromo-1-(4-cyanophenyl)ethan-1-one 8: Prepared under outlined condition A as in general procedure using 4-cyanobenzonitrile (25.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 8 in 82% (49.3 mg) yield as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.16 (m,
2H), 7.85 – 7.77 (m, 2H), 6.59 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 184.73, 134.11, 132.93, 132.61, 130.29, 117.53, 38.83; MS (EI) m/z 301; IR (film) 2920, 2231, 1703, 1404, 1261, 1205, 989, 852, 761, 680, 574 cm$^{-1}$.

2,2-dibromo-1-(4-ethylphenyl)ethan-1-one 9: Prepared under outlined condition A as in general procedure using 1-ethyl-4-ethynylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO$_4$·H$_2$O (96.7 mg, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 9 in 80% (48.6 mg) yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, $J$ = 8.1 Hz, 2H), 7.33 (d, $J$ = 8.0 Hz, 2H), 6.71 (s, 1H), 2.73 (q, $J$ = 7.6 Hz, 2H), 1.27 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 185.66, 151.83, 129.96, 128.49, 128.40, 39.92, 29.08, 15.02; MS (EI) m/z 304; IR (film) 2966, 1691, 1604, 1415, 1271, 1182, 981, 848, 686, 761, 592, 570 cm$^{-1}$.

2,2-dibromo-1-(4-(tert-butyl)phenyl)ethan-1-one 10: Prepared under outlined condition A as in general procedure using 1-(tert-butyl)-4-ethynylbenzene (31.7 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO$_4$·H$_2$O (96.7 mg, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 10 in 76% (50.4 mg) yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, $J$ = 8.6 Hz, 2H), 7.52 (d, $J$ = 8.6 Hz, 2H), 6.71 (s, 1H), 1.35 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 185.61, 158.61, 129.75, 128.11, 125.98, 39.93, 35.37, 31.01; MS (EI) m/z 332; IR (film) 2966, 1691, 1604, 1415, 1271, 1182, 981, 848, 686, 761, 592, 570 cm$^{-1}$.
1-([1,1'-biphenyl]-4-yl)-2,2-dibromoethan-1-one 11: Prepared under outlined condition A as in general procedure using 4-ethynyl-1,1'-biphenyl (35.7 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 11 in 72% (50.7 mg) yield as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.46 (dt, J = 24.6, 7.3 Hz, 3H), 6.74 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 185.59, 147.18, 139.37, 130.38, 129.43, 129.09, 128.70, 127.52, 127.34, 39.82; MS (EI) m/z 352; IR (film) 1693, 1600, 1406, 1269, 1190, 983, 854, 779, 746, 694, 624, 570 cm⁻¹.

2,2-dibromo-1-(4-pentylphenyl)ethan-1-one 12: Prepared under outlined condition A as in general procedure using 1-ethynyl-4-pentylbenzene (34.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 12 in 56% (38.7 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.70 (s, 1H), 2.68 (t, J = 7.7 Hz, 2H), 1.72 – 1.60 (m, 2H), 1.33 (d, J = 3.4 Hz, 4H), 0.90 (t, J = 6.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 185.66, 150.66, 129.87, 129.01, 128.38, 39.87, 36.10, 31.43, 30.64, 22.48, 13.98; MS (EI) m/z 346; IR (film) 2927, 1693, 1602, 1415, 1269, 1182, 983, 852, 690, 596, 570 cm⁻¹.

2,2-dibromo-1-(3-fluorophenyl)ethan-1-one 13: Prepared under outlined condition A as in general procedure using 1-
ethynyl-3-fluorobenzene (24.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 13 in 86% (51.7 mg) yield as colorless oil. 

**¹H NMR (400 MHz, CDCl₃)** δ 7.88 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 9.3 Hz, 1H), 7.50 (dd, J = 13.8, 7.8 Hz, 1H), 7.34 (t, J = 8.2 Hz, 1H), 6.63 (s, 1H); 

**¹³C NMR (101 MHz, CDCl₃)** δ 184.85 (d, J = 2.4 Hz), 162.71 (d, J = 249.97 Hz), 132.81 (d, J = 6.7 Hz), 130.61 (d, J = 7.7 Hz), 125.47 (d, J = 3.1 Hz), 121.58 (d, J = 21.5 Hz), 116.70 (d, J = 23.2 Hz), 39.14;  

**¹⁹F NMR (282 MHz, CDCl₃)** δ -101.83 – -101.91 (m);  

**MS (EI)** m/z 294;  

**IR (film)** 1697, 1587, 1485, 1438, 1267, 1153, 875, 752, 700, 671, 624, 582 cm⁻¹.

**2,2-dibromo-1-(3-chlorophenyl)ethan-1-one 14:** 

Prepared under outlined condition A as in general procedure using 1-chloro-3-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 14 in 74% (46.2 mg) yield as pale yellow oil. 

**¹H NMR (400 MHz, CDCl₃)** δ 8.06 (t, J = 1.7 Hz, 1H), 7.98 (dd, J = 7.9, 0.6 Hz, 1H), 7.65 – 7.57 (m, 1H), 7.46 (t, J = 7.9 Hz, 1H), 6.62 (s, 1H);  

**¹³C NMR (101 MHz, CDCl₃)** δ 184.84, 135.30, 134.38, 132.42, 130.19, 129.76, 127.79, 39.13;  

**MS (EI)** m/z 312;  

**IR (film)** 1699, 1570, 1471, 1419, 1253, 1190, 1091, 1076, 798, 736, 669, 624, 572 cm⁻¹.

**2,2-dibromo-1-(3-bromophenyl)ethan-1-one 15:** 

Prepared under outlined condition A as in general procedure using 1-
bromo-3-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 15 in 76% (53.7 mg) yield as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.21 (s, 1H), 8.07 – 7.98 (m, 1H), 7.81 – 7.74 (m, 1H), 7.40 (t, J = 7.9 Hz, 1H), 6.61 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 184.73, 137.28, 132.67, 132.61, 130.40, 128.22, 123.19, 39.04; MS (EI) m/z 354; IR (film) 1699,1566, 1471, 1419, 1251, 1190, 1068, 993, 800, 731, 671, 624, 572 cm⁻¹.

2,2-dibromo-1-(3-methoxyphenyl)ethan-1-one 16:
Prepared under outlined condition A as in general procedure using 1-ethynyl-3-methoxybenzene (26.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 16 in 86% (52.6 mg) yield as white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, J = 8.3 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.17 (dd, J = 8.3, 2.6 Hz, 1H), 6.71 (s, 1H), 3.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 185.88, 160.01, 132.13, 129.88, 121.96, 121.06, 114.08, 55.57, 39.65; HRMS (EI) m/z Calcd for C₉H₈Br₂O₂ 305.8891, Found 305.8894; IR (film) 1693, 1595, 1581, 1485,1427, 1271, 1161, 1041, 875, 798, 748, 677, 626, 588 cm⁻¹.

tert-butyl 3-(2,2-dibromoacetyl)benzoate 17: Prepared under outlined condition A as in general procedure using tert-butyl 3-ethynylbenzoate (40.5 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5
equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 17 in 54% (40.7 mg) yield as colorless oil. 

**¹H NMR (400 MHz, CDCl₃)** δ 8.67 (t, J = 1.6 Hz, 1H), 8.29 – 8.19 (m, 2H), 7.58 (t, J = 7.8 Hz, 1H), 6.71 (s, 1H), 1.62 (s, 9H); 

**¹³C NMR (101 MHz, CDCl₃)** δ 185.45, 164.37, 134.96, 133.32, 132.93, 131.04, 130.57, 129.02, 82.11, 39.36, 28.17; 

**HRMS (ESI)** [M+Na]⁺ Calcd for C₁₃H₁₄Br₂O₃Na 398.9207, Found 398.9227; 

**IR (film)** 2978, 1701, 1602, 1367, 1309, 1247, 1155, 846, 779, 732, 677, 570 cm⁻¹.

**Diphenyl (3-(2,2-dibromoacetyl)phenyl)phosphoramidate 18:** Prepared under outlined condition A as in general procedure using diphenyl (3-ethynylphenyl)phosphoramidate (69.9 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 18 in 72% (75.2 mg) yield as white solid. 

**¹H NMR (400 MHz, CDCl₃)** δ 8.00 (d, J = 10.4 Hz, 1H), 7.87 (d, J = 1.9 Hz, 1H), 7.67 (dt, J = 7.2, 1.6 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.28 – 7.21 (m, 4H), 7.21 – 7.15 (m, 4H), 7.12 (dd, J = 11.0, 4.0 Hz, 2H), 6.63 (s, 1H); 

**¹³C NMR (101 MHz, CDCl₃)** δ 185.73, 150.15, 150.09, 140.11, 131.91, 129.89, 125.59, 123.98, 123.90, 123.29, 120.29, 120.25, 118.81, 118.74, 39.74; 

**³¹P NMR (122 MHz, CDCl₃)** δ -7.30 (d, J = 9.7 Hz); 

**HRMS (ESI)** [M+Na]⁺ Calcd for C₂₀H₁₄Br₂O₃PNa 545.9081, Found 545.9067; 

**IR (film)** 1699, 1589, 1489, 1296, 1184, 979, 948, 763, 688, 628, 586 cm⁻¹.

**2,2-dibromo-1-(o-tolyl)ethan-1-one 21:** Prepared under outlined condition A as in general procedure using 1-ethynyl-2-
methylbenzene (23.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 21 in 84% (49.0 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.64 (m, 1H), 7.45 (td, J = 7.6, 1.1 Hz, 1H), 7.36 – 7.26 (m, 2H), 6.68 (s, 1H), 2.51 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.58, 140.26, 132.71, 132.30, 136.26, 128.10, 125.77, 42.23, 21.10; MS (EI) m/z 292; IR (film) 1699, 1598, 1456, 1253, 1178, 968, 792, 736, 632, 572 cm⁻¹.

2,2-dibromo-1-(2-isopropylphenyl)ethan-1-one 22: Prepared under outlined condition A as in general procedure using 1-ethynyl-2-isopropylbenzene (28.9 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 22 in 84% (53.4 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.45 (m, 3H), 7.24 (ddd, J = 8.2, 6.0, 1.8 Hz, 1H), 6.59 (s, 1H), 3.20 (dt, J = 13.6, 6.8 Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 189.93, 149.63, 133.07, 132.39, 127.07, 126.70, 125.55, 43.02, 30.19, 24.28; HRMS (EI) m/z Calcd for C₁₁H₁₂Br₂O 317.9255, Found 239.0064 [M–Br]; IR (film) 2964, 1707, 1598, 1444, 1249, 1176, 972, 790, 758, 692, 630, 574 cm⁻¹.

2,2-dibromo-1-(2-(trifluoromethoxy)phenyl)ethan-1-one 23: Prepared under outlined condition A as in general procedure using 1-ethynyl-2-(trifluoromethoxy)benzene (37.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6
W blue LEDs at room temperature for 8 hours affording compound 23 in 56% (40.3 mg) yield as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.82 (dd, J = 7.8, 1.7 \text{ Hz}, 1\text{H}), 7.63 (ddd, J = 8.4, 7.5, 1.8 \text{ Hz}, 1\text{H}), 7.43 (td, J = 7.6, 1.0 \text{ Hz}, 1\text{H}), 7.40 – 7.34 (m, 1\text{H}), 6.72 (s, 1\text{H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 186.71, 146.50 (d, J = 1.6 \text{ Hz}), 134.35, 131.97, 127.29, 127.07, 120.66 (d, J = 1.6 \text{ Hz}), 120.25 (q, J = 260.8 \text{ Hz}), 42.05; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta -57.03 (d, J = 1.5 \text{ Hz}); \) HRMS (EI) m/z Calcd for C\(_{11}\)H\(_{12}\)Br\(_2\)O 317.9255, Found 239.0064 [M–Br]; IR (film) 1714, 1602, 1450, 1247, 1161, 983, 781, 758, 630, 617 cm\(^{-1}\).

2,2-dibromo-1-(thiophen-3-yl)ethan-1-one 20: Prepared under outlined condition A as in general procedure using 3-ethynylthiophene (21.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO\(_4\).H\(_2\)O (96.7 mg, 3.5 equiv.), H\(_2\)O (108.0 mg, 30.0 equiv.) were dissolved in CH\(_3\)CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 2 hours affording compound 20 in 64% (36.4 mg) yield as brown yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.37 (dd, J = 2.8, 1.0 \text{ Hz}, 1\text{H}), 7.67 (d, J = 5.1 \text{ Hz}, 1\text{H}), 7.37 (dd, J = 5.1, 2.9 \text{ Hz}, 1\text{H}), 6.43 (d, J = 0.8 \text{ Hz}, 1\text{H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 180.56, 135.34, 134.57, 128.03, 126.80, 40.22; \) MS (EI) m/z 282; IR (film) 1681, 1504, 1409, 1257, 1176, 999, 812, 742, 667, 605 cm\(^{-1}\).

N-(3-(2,2-dibromoacetyl)phenyl)furan-2-carboxamide 24: Prepared under outlined condition A as in general procedure using N-(3-ethynylphenyl)furan-2-carboxamide (42.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO\(_4\).H\(_2\)O (96.7 mg, 3.5 equiv.), H\(_2\)O (108.0 mg, 30.0 equiv.) were dissolved in CH\(_3\)CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 24 in 61% (47.7 mg) yield as white solid.
1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (t, $J = 1.8$ Hz, 1H), 8.28 (s, 1H), 8.07 – 7.96 (m, 1H), 7.89 – 7.81 (m, 1H), 7.58 – 7.47 (m, 2H), 7.28 (d, $J = 3.5$ Hz, 1H), 6.74 (s, 1H), 6.58 (dd, $J = 3.5, 1.7$ Hz, 1H); 13C NMR (101 MHz, CDCl$_3$) $\delta$ 185.67, 156.29, 147.27, 144.63, 138.25, 131.72, 129.79, 125.64, 125.49, 120.62, 116.01, 112.85, 39.57; HRMS (ESI) [M+H]$^+$ Calcd for C$_{13}$H$_{10}$Br$_2$NO$_3$ 385.9027, Found 385.9030; IR (film) 1697, 1662, 1581, 1539, 1433, 1313, 1267, 1161, 1012, 883, 806, 754, 678, 628, 592 cm$^{-1}$.

2-chloro-N-(3-(2,2-dibromoacetyl)phenyl)nicotinamide 25: Prepared under outlined condition A as in general procedure using 2-chloro-N-(3-ethynylphenyl)nicotinamide (51.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO$_4$H$_2$O (96.7 mg, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 25 in 79% (68.2 mg) yield as white solid. 1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (s, 1H), 8.44 (dd, $J = 4.8, 1.9$ Hz, 1H), 8.29 (d, $J = 1.6$ Hz, 1H), 8.08 (dd, $J = 7.6, 1.9$ Hz, 1H), 8.02 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.91 – 7.81 (m, 1H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.35 (dd, $J = 7.6, 4.8$ Hz, 1H), 6.72 (s, 1H); 13C NMR (101 MHz, CDCl$_3$) $\delta$ 185.76, 163.37, 151.39, 147.10, 139.56, 138.22, 131.72, 131.29, 129.86, 126.17, 126.10, 122.95, 121.08, 39.55; HRMS (ESI) [M+H]$^+$ Calcd for C$_{14}$H$_{10}$Br$_2$ClN$_2$O$_2$ 430.8798, Found 430 8788; IR (film) 1662, 1579, 1546, 1487, 1433, 1398, 1271, 1138, 1066, 736, 678, 628 cm$^{-1}$.

N-(3-(2,2-dibromoacetyl)phenyl)-2,2,3,3-tetramethylcyclopropane-1-carboxamide 19: Prepared under outlined condition A as in general
procedure using N-(3-ethynylphenyl)-2,2,3,3-tetramethylcyclopropane-1-carboxamide (48.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 19 in 83% (68.1 mg) yield as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (t, J = 1.8 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.76 – 7.59 (m, 2H), 7.40 (t, J = 8.0 Hz, 1H), 6.74 (s, 1H), 1.32 (s, 6H), 1.21 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 186.00, 170.63, 139.36, 131.48, 129.53, 125.67, 124.51, 120.10, 39.76, 38.50, 30.09, 23.78, 16.71; HRMS (ESI) [M+Na]⁺ Calcd for C₁₆H₁₉Br₂NO₂Na 437.9680, Found 437.9678; IR (film) 2945, 1660, 1591, 1541, 1487, 1431, 1300, 1155, 1112, 806, 702, 628 cm⁻¹.

2,2-dibromo-1-phenylpropan-1-one 26: Prepared under outlined condition A as in general procedure using prop-1-yn-1-ylbenzene (23.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 26 in 83% (48.5 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 2.76 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.30, 133.50, 131.74, 131.38, 127.98, 57.95, 37.51; MS (EI) m/z 292; IR (film) 1680, 1595, 1446, 1377, 1249, 1186, 1062, 952, 800, 717, 684, 650, 574 cm⁻¹.

2,2-dibromo-1-phenylheptan-1-one 27: Prepared under outlined condition A as in general procedure using hept-1-yn-1-ylbenzene (34.5 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were
dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 27 in 76% (52.5 mg) yield as colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.34 (d, $J = 7.6$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 2.71 – 2.63 (m, 2H), 1.79 – 1.68 (m, 2H), 1.49 – 1.32 (m, 4H), 0.93 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.65, 133.19, 132.76, 131.07, 127.91, 67.02, 46.80, 31.17, 27.09, 22.44, 13.97; HRMS (EI) m/z Calcd for C$_{13}$H$_{16}$Br$_2$O 345.9568, Found 345.9568; IR (film) 2929, 1680, 1597, 1446, 1232, 1186, 974, 810, 711, 686, 655, 607, 570 cm$^{-1}$.

2,2-dibromo-2-cyclopropyl-1-phenylethan-1-one 28: Prepared under outlined condition A as in general procedure using (cyclopropylethynyl)benzene (28.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO$_4$·H$_2$O (96.7 mg, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 28 in 57% (35.8 mg) yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (d, $J = 7.8$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 2.01 – 1.85 (m, 1H), 0.99 – 0.83 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.43, 133.12, 132.87, 131.09, 127.92, 71.35, 25.35, 7.58; HRMS (EI) m/z Calcd for C$_{11}$H$_{10}$Br$_2$O 315.9098, Found 315.9096; IR (film) 1680, 1595, 1446, 1232, 1136, 1022, 947, 839, 804, 736, 686, 653, 613 cm$^{-1}$.

2,2-dibromo-3-chloro-1-phenylpropan-1-one 29: Prepared under outlined condition A as in general procedure using (3-chloroprop-1-yn-1-yl)benzene (30.1 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO$_4$·H$_2$O (96.7 mg, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was
stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 29 in 68% (44.1 mg) yield as white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (d, \(J = 7.6\) Hz, 2H), 7.60 (t, \(J = 7.4\) Hz, 1H), 7.48 (t, \(J = 7.7\) Hz, 2H), 4.49 (s, 2H); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 186.97, 133.78, 132.00, 130.93, 128.12, 60.91, 53.68; MS (EI) m/z 324; IR (film) 1685, 1678, 1595, 1446, 1251, 1186, 935, 817, 767, 686, 607, 586 cm\(^{-1}\).

\[\begin{array}{c}
\text{2,2-dibromo-1,4-diphenylbutan-1-one 30: Prepared under outlined condition A as in general procedure using but-1-yne-1,4-diyl dibenzene (41.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO}_4\cdot\text{H}_2\text{O (96.7 mg, 3.5 equiv.), H}_2\text{O (108.0 mg, 30.0 equiv.) were dissolved in CH}_3\text{CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 30 in 63% (48.0 mg) yield as white solid.} \\
\text{\(^1\)H NMR (400 MHz, CDCl}_3\text{) \(\delta\) 8.41 (d, \(J = 7.8\) Hz, 2H), 7.62 (t, \(J = 7.2\) Hz, 1H), 7.51 (t, \(J = 7.8\) Hz, 2H), 7.38 – 7.33 (m, 2H), 7.29 (dd, \(J = 12.8, 8.2\) Hz, 3H), 3.12 – 3.05 (m, 2H), 3.05 – 2.98 (m, 2H); \(^1\)C NMR (126 MHz, CDCl}_3\text{) \(\delta\) 188.36, 140.25, 133.40, 132.53, 131.16, 128.70, 128.62, 128.01, 126.36, 65.47, 48.81, 33.89; HRMS (ESI) [M+Na]^+ Calcd for C\(_{16}\)H\(_{14}\)Br\(_2\)ONa 402.9309, Found 402.9316; IR (film) 2920, 2850, 1728, 1645, 1469, 1261, 1080, 966, 800, 700 cm\(^{-1}\).} 
\end{array}\]
stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 31 in 72% (56.7 mg) yield as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01 (dd, \(J = 7.8, 0.9\) Hz, 1H), 7.30 (td, \(J = 7.6, 1.3\) Hz, 1H), 7.27 – 7.12 (m, 7H), 2.96 – 2.85 (m, 4H), 2.28 (s, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 194.26, 139.97, 137.37, 135.97, 131.22, 130.81, 128.67, 128.66, 128.18, 126.47, 124.97, 67.78, 48.44, 34.03, 20.57; HRMS (EI) m/z Calcd for C\(_{17}\)H\(_{16}\)Br\(_2\)O 393.9568, Found 315.0377 [M–Br]; IR (film) 1695, 1600, 1496, 1454, 1234, 808, 748, 725, 698, 563 cm\(^{-1}\).

2,2-dibromo-1-(2-isopropylphenyl)-4-phenylbutan-1-one 32: Prepared under outlined condition A as in general procedure using 1-isopropyl-2-(4-phenylbut-1-yn-1-yl)benzene (49.7 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO\(_4\)H\(_2\)O (96.7 mg, 3.5 equiv.), H\(_2\)O (108.0 mg, 30.0 equiv.) were dissolved in CH\(_3\)CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 32 in 68% (57.4 mg) yield as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 – 7.74 (m, 1H), 7.42 – 7.31 (m, 2H), 7.29 – 7.20 (m, 2H), 7.20 – 7.10 (m, 4H), 3.02 – 2.91 (m, 2H), 2.88 (ddd, \(J = 10.0, 5.4, 2.2\) Hz, 2H), 2.78 (hept, \(J = 6.8\) Hz, 1H), 1.19 (d, \(J = 6.8\) Hz, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 195.76, 147.35, 139.88, 135.99, 130.69, 128.69, 128.66, 127.27, 126.49, 126.17, 125.03, 68.41, 48.19, 33.98, 31.47, 24.21; HRMS (EI) m/z Calcd for C\(_{19}\)H\(_{20}\)Br\(_2\)O 421.9881, Found 343.0698 [M–Br]; IR (film) 2964, 1699, 1496, 1454, 1234, 1201, 1033, 943, 758, 698, 653, 624 cm\(^{-1}\).

tert-butyl 3-(2,2-dibromo-4-phenylbutanoyl)benzoate 33: Prepared under outlined condition A as in general procedure using
tert-butyl 3-(4-phenylbut-1-yn-1-yl)benzoate (61.3 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 33 in 54% (51.9 mg) yield as colorless oil. 

**1H NMR (400 MHz, CDCl₃)** δ 8.99 (s, 1H), 8.54 (d, J = 7.9 Hz, 1H), 8.20 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.36 – 7.21 (m, 5H), 3.08 – 3.05 (m, 2H), 3.01 – 2.98 (m, 2H), 1.63 (s, 9H); 

**13C NMR (101 MHz, CDCl₃)** δ 187.74, 164.70, 140.14, 134.65, 133.95, 132.69, 132.18, 132.11, 128.68, 128.63, 128.01, 126.38, 81.79, 65.09, 48.63, 33.85, 28.20; 

**HRMS (ESI)** [M+Na]⁺ Calcd for C₂₁H₂₂Br₂O₃Na 502.9833, Found 502.9855; **IR** (film) 1714, 1683, 1600, 1454, 1367, 1307, 1224, 1157, 1124, 848, 729, 698, 615, 578 cm⁻¹.

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2,2-dibromo-3-methoxy-1-(3-methoxyphenyl)propan-1-one 34: Prepared under outlined condition A as in general procedure using 1-methoxy-4-(3-methoxyprop-1-yn-1-yl)benzene (54.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 34 in 86% (48.5 mg) yield as colorless oil.

**1H NMR (400 MHz, CDCl₃)** δ 7.95 (d, J = 7.8 Hz, 1H), 7.77 (s, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 4.22 (s, 2H), 3.85 (s, 3H), 3.56 (s, 3H); 

**13C NMR (101 MHz, CDCl₃)** δ 187.71, 159.12, 133.61, 128.93, 123.40, 119.88, 115.47, 79.85, 61.45, 59.94, 55.46; 

2-(2,2-dibromo-4-chlorobutanoyl)benzyl 2,2-dichloroacetate 35: Prepared under outlined condition A as in general procedure using 2-(4-chlorobut-1-yn-1-yl)benzyl 2,2-dichloroacetate (61.1 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO$_4$H$_2$O (96.7 mg, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 35 in 68% (65.1 mg) yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 7.8$ Hz, 1H), 7.63 – 7.55 (m, 2H), 7.48 – 7.42 (m, 1H), 5.98 (s, 1H), 5.43 (s, 2H), 3.93 – 3.86 (m, 2H), 3.22 – 3.14 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.11, 164.01, 135.52, 133.14, 132.49, 130.22, 129.78, 127.77, 66.65, 64.13, 61.92, 48.69, 41.28; HRMS (ESI) [M+Na]$^+$ Calcd for C$_{11}$H$_8$Br$_2$Cl$_2$O$_2$Na 500.8038, Found 500.8032; IR (film) 2924, 1768, 1724, 1602, 1465, 1288, 1155, 1029, 763, 727 cm$^{-1}$.

methyl (3-(2,2-dibromo-4-chlorobutanoyl)benzoyl)-L-valinate 36: Prepared under outlined condition A as in general procedure using methyl (3-(4-chlorobut-1-yn-1-yl)benzoyl)-L-valinate (64.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO$_4$H$_2$O (96.7 mg, 3.5 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 36 in 51% (50.9 mg) yield as colorless syrup. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (s, 1H), 8.53 (d, $J = 7.8$ Hz, 1H), 8.03 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 6.73 (d, $J = 8.1$ Hz, 1H), 4.78 (dd, $J = 8.3$, 5.0 Hz, 1H), 3.94 – 3.84 (m, 2H), 3.78 (s, 4H), 3.23 – 3.14 (m, 2H), 2.30 (dq, $J = 12.5$, 6.4 Hz, 1H), 1.01 (t, $J = 7.2$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.74, 172.49, 166.08, 134.38, 134.13, 132.20, 131.95, 129.70, 128.50, 60.51, 57.62, 52.37, 49.03,
2,2-dichloro-1-(2-(trifluoromethoxy)phenyl)ethan-1-one 37:
Prepared under outlined condition B as in general procedure using 1-ethynyl-2-(trifluoromethoxy)benzene (37.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 37 in 59% (32.3 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 6.71 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 186.72, 146.73, 134.52, 131.81, 127.46, 127.22, 121.55, 120.52, 69.70; ¹⁹F NMR (282 MHz, CDCl₃) δ -57.04 (d, J = 1.5 Hz); HRMS (EI) m/z Calcd for C₁₇H₂₀Br₂ClNO₄Na 517.9345, Found 517.9349; IR (film) 2962, 1739, 1645, 1529, 1228, 1155, 1001, 821, 682, 588 cm⁻¹.

2,2-dichloro-1-(2-isopropylphenyl)ethan-1-one 38: Prepared under outlined condition B as in general procedure using 1-ethynyl-2-isopropylbenzene (28.9 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 38 in 54% (25.6 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.43 (m, 3H), 7.24 (d, J = 5.3 Hz, 1H), 6.54 (s, 1H), 3.30 – 3.12 (m, 1H), 1.24 (d, J = 6.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 190.05, 149.82, 133.33, 132.42, 127.08, 126.91, 125.51, 69.50, 30.05, 24.18; HRMS (EI) m/z Calcd for C₁₁H₁₂Cl₂O 230.0265 Found 194.0493 [M–
HCl; IR (film) 2966, 1716, 1598, 1444, 1265, 1217, 1033, 977, 810, 758, 723, 648, 599 cm⁻¹.

**2,2-dichloro-1-(2-fluorophenyl)ethan-1-one 39:** Prepared under outlined condition B as in general procedure using 1-ethynyl-2-fluorobenzene (24.0 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 39 in 59% (24.6 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (td, J = 7.6, 1.8 Hz, 1H), 7.63 (ddddd, J = 8.3, 7.2, 5.2, 1.8 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.20 (ddddd, J = 11.4, 8.4, 0.7 Hz, 1H), 6.82 (d, J = 2.0 Hz, 1H): ¹³C NMR (101 MHz, CDCl₃) δ 184.39 (d, J = 4.1 Hz), 161.16(d, J = 255.9 Hz), 136.26 (d, J = 9.4 Hz), 132.27 (d, J = 2.0 Hz), 125.18 (d, J = 3.2 Hz), 121.08 (d, J = 12.4 Hz), 116.81 (d, J = 23.8 Hz), 70.26 (d, J = 11.9 Hz); ¹⁹F NMR (282 MHz, CDCl₃) δ -108.44 – -108.51 (m); MS (EI) m/z 205; IR (film) 2920, 2850, 1710, 1645, 1423, 1365, 1230, 1093, 968, 680, 646 cm⁻¹.

**2,2-dichloro-1-(2-chlorophenyl)ethan-1-one 40:** Prepared under outlined condition B as in general procedure using 1-chloro-2-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 40 in 62% (27.6 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 7.7 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.39 (t, J = 7.0 Hz, 1H), 6.78 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 188.81, 134.39, 133.12, 131.34, 130.61, 130.58, 127.21, 69.33; HRMS (ESI) [M+Na]⁺ Calcd for C₈H₅Cl₂ONa 244.9298, Found 244.0289; IR (film) 1724, 1589,
1-(2-bromophenyl)-2,2-dichloroethan-1-one 41: Prepared under outlined condition B as in general procedure using 1-bromo-2-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 41 in 66% (35.3 mg) yield as yellow oil. 

**1H NMR (400 MHz, CDCl₃)** δ 7.71 – 7.62 (m, 1H), 7.55 (dd, J = 7.4, 1.7 Hz, 1H), 7.36 – 7.46 (m, 2H), 6.73 (s, 1H); 

**13C NMR (101 MHz, CDCl₃)** δ 189.36, 136.71, 133.66, 132.91, 130.33, 127.60, 119.28, 68.85; 

**MS (EI) m/z 266; IR (film) 2924, 1726, 1587, 1429, 1288, 1207, 1055, 983, 802, 719, 669, 636 cm⁻¹.**

2,2-dichloro-1-(3-methoxyphenyl)ethan-1-one 42: Prepared under outlined condition B as in general procedure using 1-ethynyl-3-methoxybenzene (26.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 42 in 71% (31.5 mg) yield as colorless oil. 

**1H NMR (400 MHz, CDCl₃)** δ 7.65 (ddd, J = 7.7, 1.5, 0.9 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.19 (ddd, J = 8.3, 2.6, 0.8 Hz, 1H), 6.69 (s, 1H), 3.87 (s, 3H); 

**13C NMR (101 MHz, CDCl₃)** δ 185.80, 159.99, 132.64, 129.88, 122.05, 121.16, 114.06, 67.73, 55.56; 

**HRMS (ESI) [M+Na]⁺ Calcd for C₉H₇Cl₂O₂Na 240.9794, Found 240.9788; IR (film) 1703, 1597, 1581, 1487, 1429, 1282, 1255, 1163, 1045, 877, 808, 736, 682 cm⁻¹.**

2,2-dichloro-1-(3-chlorophenyl)ethan-1-one 43: Prepared...
under outlined condition B as in general procedure using 1-chloro-3-ethynylbenzene (27.3 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 43 in 62% (27.6 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (t, J = 1.9 Hz, 1H), 7.98 (ddd, J = 7.9, 1.6, 1.1 Hz, 1H), 7.62 (ddd, J = 8.0, 2.1, 1.0 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 6.60 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 184.86, 135.30, 134.49, 132.82, 130.18, 129.80, 127.83, 67.68; MS (EI) m/z 222; IR (film) 1707, 1571, 1471, 1423, 1284, 1220, 1080, 999, 812, 700, 678, 651 cm⁻¹.

2,2-dichloro-1-(4-ethylphenyl)ethan-1-one 44: Prepared under outlined condition B as in general procedure using 1-ethyl-4-ethynylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 44 in 55% (23.0 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.98 (m, 2H), 7.35 (t, J = 7.4 Hz, 2H), 6.68 (s, 1H), 2.74 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 185.60, 151.95, 129.99, 128.95, 128.47, 67.85, 29.09, 15.00; MS (EI) m/z 216; IR (film) 2968, 1701, 1604, 1415, 1280, 1224, 1178, 989, 852, 798, 740, 634 cm⁻¹.

1-(4-(tert-butyl)phenyl)-2,2-dichloroethan-1-one 45: Prepared under outlined condition B as in general procedure using 1-(tert-butyl)-4-ethynylbenzene (31.7 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the
reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 45\(^{12}\) in 59\% (27.2 mg) yield as colorless oil. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.08 – 7.98\) (m, 2H), 7.58 – 7.51 (m, 2H), 6.67 (s, 1H), 1.36 (s, 9H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 185.56, 158.73, 129.78, 128.63, 125.95, 67.85, 35.37, 30.98\); MS (EI) m/z 229; IR (film) 2964, 1705, 1604, 1463, 1409, 1365, 1278, 1222, 1109, 989, 854, 792, 702, 628 cm\(^{-1}\).

1-([1,1'-biphenyl]-4-yl)-2,2-dichloroethan-1-one 46
Prepared under outlined condition B as in general procedure using 4-ethynyl-1,1'-biphenyl (35.7 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO\(_4\) \(\cdot\) \(\text{H}_2\)\(_2\)O (110.4 mg, 4.0 equiv.), H\(_2\)O (108.0 mg, 30.0 equiv.) were dissolved in CH\(_3\)CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 46\(^9\) in 75\% (40.2 mg) yield as white solid. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.24 – 8.12\) (m, 2H), 7.80 – 7.70 (m, 2H), 7.68 – 7.61 (m, 2H), 7.55 – 7.46 (m, 2H), 7.46 – 7.41 (m, 1H), 6.71 (s, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 185.57, 147.30, 139.37, 130.41, 129.92, 129.10, 128.72, 127.50, 127.34, 67.91\); MS (EI) m/z 264; IR (film) 2920, 1707, 1647, 1423, 1367, 1232, 1093, 904, 729, 669 cm\(^{-1}\).

2,2-dichloro-1-(4-chlorophenyl)ethan-1-one 47: Prepared under outlined condition B as in general procedure using 1-chloro-4-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO\(_4\) \(\cdot\) \(\text{H}_2\)\(_2\)O (110.4 mg, 4.0 equiv.), H\(_2\)O (108.0 mg, 30.0 equiv.) were dissolved in CH\(_3\)CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 47\(^{13}\) in 63\% (28.2 mg) yield as colorless oil. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.10 – 8.02\)
(m, 2H), 7.54 – 7.46 (m, 2H), 6.59 (s, 1H): $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.94, 141.25, 131.24, 129.50, 129.30, 67.78; MS (EI) m/z 222; IR (film) 2924, 1710, 1589, 1489, 1402, 1274, 1219, 1093, 1014, 848, 788, 713 cm$^{-1}$.

1-(4-bromophenyl)-2,2-dichloroethan-1-one 48: Prepared under outlined condition B as in general procedure using 1-bromo-4-ethynylbenzene (36.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO$_4$.H$_2$O (110.4 mg, 4.0 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 48 in 63% (34.7 mg) yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 – 7.92 (m, 2H), 7.71 – 7.64 (m, 2H), 6.58 (s, 1H): $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 185.17, 132.30, 131.26, 129.30, 67.75; MS (EI) m/z 268; IR (film) 1705, 1583, 1487, 1398, 1273, 1217, 1072, 1010, 987, 844, 783, 619, 588 cm$^{-1}$.

1-(4-acetylphenyl)-2,2-dichloroethan-1-one 49: Prepared under outlined condition B as in general procedure using 1-(4-ethynylphenyl)ethan-1-one (28.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO$_4$.H$_2$O (110.4 mg, 4.0 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 49 in 53% (25.0 mg) yield as white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J = 8.3$ Hz, 2H), 8.07 (d, $J = 8.2$ Hz, 2H), 6.65 (s, 1H), 2.66 (s, 3H): $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.10, 185.46, 141.08, 134.52, 130.08, 128.56, 67.83, 26.92; MS (EI) m/z 230; IR (film) 1699, 1680, 1504, 1402, 1265, 1226, 962, 862, 790, 715, 651 cm$^{-1}$.

4-(2,2-dichloroacetyl)benzonitrile 50: Prepared under
outlined condition B as in general procedure using 4-ethynylbenzonitrile (25.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 50 in 63% (26.9 mg) yield as white solid. \(^1\)H NMR (400 MHz, CDCl₃) δ 8.25 – 8.19 (m, 2H), 7.85 – 7.80 (m, 2H), 6.57 (s, 1H); \(^13\)C NMR (101 MHz, CDCl₃) δ 184.83, 134.35, 132.58, 130.32, 117.69, 117.48, 67.72; HRMS (ESI) [M-H]⁺ Calcd for C₉H₄Cl₂NO 211.9670, Found 211.9644; IR (film) 2922, 2233, 1712, 1606, 1406, 1282, 1220, 958, 802, 732, 626 cm⁻¹.

2,2-dichloro-1-(thiophen-3-yl)ethan-1-one 51: Prepared under outlined condition B as in general procedure using 3-ethynylthiophene (21.6 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 51 in 45% (16.9 mg) yield as pale yellow oil. \(^1\)H NMR (400 MHz, CDCl₃) δ 8.38 (dd, J = 2.9, 1.2 Hz, 1H), 7.68 (dd, J = 5.1, 1.2 Hz, 1H), 7.39 (dd, J = 5.1, 2.9 Hz, 1H), 6.42 (s, 1H); \(^13\)C NMR (101 MHz, CDCl₃) δ 180.36, 135.50, 134.97, 127.96, 126.73, 68.63; MS (EI) m/z 194; IR (film) 3109, 1693, 1508, 1411, 1280, 1224, 881, 821, 721, 680, 651 cm⁻¹.

2,2-dichloro-1-phenylpropan-1-one 52: Prepared under outlined condition B as in general procedure using prop-1-yn-1-ylbenzene (23.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 52 in 62% (25.0 mg) yield as
colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.41 – 8.23 (m, 2H), 7.64 – 7.55 (m, 1H), 7.47 (dd, $J = 10.8, 4.8$ Hz, 2H), 2.36 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 188.12, 133.61, 131.31, 131.19, 128.13, 82.74, 34.30; MS (EI) m/z 202; IR (film) 1689, 1597, 1448, 1379, 1255, 1074, 960, 808, 686, 640 cm$^{-1}$.

2,2-dichloro-2-cyclopropyl-1-phenylethan-1-one 53: Prepared under outlined condition B as in general procedure using (cyclopropylethynyl)benzene (28.4 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO$_4$$\cdot$H$_2$O (110.4 mg, 4.0 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 53 in 52% (24.3 mg) yield as colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.29 (dt, $J = 8.6, 1.5$ Hz, 2H), 7.63 – 7.54 (m, 1H), 7.51 – 7.43 (m, 2H), 2.01 (tt, $J = 8.1, 5.3$ Hz, 1H), 0.94 – 0.82 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 188.31, 133.33, 132.23, 130.95, 128.09, 89.95, 23.04, 4.66; HRMS (EI) m/z Calcd for C$_{11}$H$_{10}$Cl$_2$O 228.0109 Found 193.0418 [M–Cl]; IR (film) 2920, 2848, 1716, 1633, 1365, 1230, 1093, 1024, 954, 690, 569 cm$^{-1}$.

2,2-dichloro-1,4-diphenylbutan-1-one 54: Prepared under outlined condition B as in general procedure using but-1-ynediyl dibenzene (41.2 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO$_4$$\cdot$H$_2$O (110.4 mg, 4.0 equiv.), H$_2$O (108.0 mg, 30.0 equiv.) were dissolved in CH$_3$CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 54 in 48% (25.0 mg) yield as colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 – 8.20 (m, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.39 – 7.19 (m, 5H), 3.14 – 2.98 (m, 2H), 2.91 – 2.72 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 188.20, 140.30, 133.54, 131.94, 131.00, 128.61, 128.15, 126.33, 86.69, 46.42, 31.29; HRMS (EI) Calcd for C$_{16}$H$_{14}$Cl$_2$O 292.0422, Found 292.0420; IR (film)
2,2,3-trichloro-1-phenylpropan-1-one 55: Prepared under outlined condition B as in general procedure using (3-chloroprop-1-yn-1-yl)benzene (30.1 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 55 in 63% (30.0 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (dt, J = 8.6, 1.6 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.54 – 7.46 (m, 2H), 4.33 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 186.89, 134.00, 131.39, 130.84, 128.30, 83.41, 52.27; HRMS (EI) m/z Calcd for C₉H₇Cl₃O 235.9562 Found 200.9874 [M–Cl]; IR (film) 1689, 1597, 1448, 1413, 1259, 1186, 937, 840, 804, 686, 651, 557 cm⁻¹.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-(2,2-dibromoacetyl)benzoate 56: Prepared under outlined condition A as in general procedure using (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-ethynylnylbenzoate (56.9 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 56 in 83% (76.4 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.72 (s, 1H), 8.33 – 8.24 (m, 2H), 7.60 (t, J = 7.8 Hz, 1H), 6.71 (s, 1H), 4.97 (td, J = 10.9, 4.3 Hz, 1H), 2.13 (d, J = 11.9 Hz, 1H), 1.94 (dt, J = 13.8, 6.9 Hz, 1H), 1.74 (d, J = 11.1 Hz, 2H), 1.57 (d, J = 11.1 Hz, 2H), 1.19 – 1.08 (m, 2H), 0.93 (t, J = 5.8 Hz, 7H), 0.80 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 185.33, 164.78, 135.07, 133.62, 131.80, 131.13, 129.15, 129.15,
(1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-(2,2-dibromoacetyl)benzoate 57: Prepared under outlined condition A as in general procedure using (1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-ethynylbenzoate (56.5 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 57 in 77% (70.4 mg) yield as colorless syrup. ¹H NMR (400 MHz, CDCl₃) δ 8.79 (t, J = 1.6 Hz, 1H), 8.30 (tt, J = 7.7, 1.3 Hz, 2H), 7.62 (t, J = 7.8 Hz, 1H), 6.67 (s, 1H), 5.15 (ddd, J = 9.9, 3.3, 2.3 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.18 – 2.08 (m, 1H), 1.90 – 1.73 (m, 2H), 1.51 – 1.39 (m, 1H), 1.33 (ddd, J = 12.4, 9.5, 4.4 Hz, 1H), 1.14 (dd, J = 13.8, 3.4 Hz, 1H), 0.95 (d, J = 19.4 Hz, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 185.30, 165.49, 134.98, 133.71, 131.73, 131.09, 130.82, 129.22, 81.40, 49.19, 47.97, 44.99, 39.30, 36.91, 28.10, 27.43, 19.73, 18.93, 13.65; HRMS (ESI) [M+Na]⁺ Calcd for C₁₉H₂₄Br₂O₃Na 480.9990, Found 480.9998; IR (film) 2954, 1705, 1602, 1456, 1298, 1242, 1188, 1099, 960, 779, 723, 675, 630 cm⁻¹.

methyl (3-(2,2-dibromoacetyl)benzoyl)-L-phenylalaninate 58: Prepared under outlined condition A as in general procedure using methyl (3-ethynylbenzoyl)-L-phenylalaninate (61.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.),
H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 58 in 67% (64.7 mg) yield as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.37 (t, J = 1.7 Hz, 1H), 8.26 – 8.16 (m, 1H), 7.98 – 7.90 (m, 1H), 7.55 (td, J = 7.8, 2.7 Hz, 1H), 7.33 – 7.23 (m, 3H), 7.17 – 7.11 (m, 2H), 6.76 – 6.56 (m, 2H), 5.08 (dt, J = 7.6, 5.8 Hz, 1H), 3.78 (s, 3H), 3.26 (qd, J = 13.9, 5.8 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 185.26, 171.94, 165.47, 135.66, 134.79, 132.73, 132.65, 131.24, 129.40, 129.30, 128.79, 128.18, 127.39, 53.68, 52.61, 39.33, 37.83; HRMS (ESI) [M+H]⁺ Calcd for C₁₉H₁₇Br₂NO₄Na 503.9422, Found 503.9423; IR (film) 1739, 1701, 1647, 1535, 1435, 1261, 1203, 995, 702, 632 cm⁻¹. (3aR,3bS,6R,6aS,7aR)-2,2-dimethyl-5-oxohexahydrofuro[2′,3′:4,5]furo[2,3-d][1,3]dioxol-6-yl 4-(2,2-dibromoacetyl)benzoate 59: Prepared under outlined condition A as in general procedure using (3aR,3bS,6R,6aS,7aR)-2,2-dimethyl-5-oxohexahydrofuro[2′,3′:4,5]furo[2,3-d][1,3]dioxol-6-yl 4-ethynylbenzoate (78.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), NaHSO₄·H₂O (96.7 mg, 3.5 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 8 hours affording compound 59 in 59% (61.6 mg) yield as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.08 (m, 4H), 6.65 (s, 1H), 6.02 (d, J = 3.5 Hz, 1H), 5.33 – 5.09 (m, 2H), 4.94 (d, J = 3.6 Hz, 1H), 4.90 (d, J = 3.5 Hz, 1H), 1.49 (s, 3H), 1.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃)
δ 185.24, 170.34, 164.06, 135.26, 132.48, 130.51, 129.91, 113.33, 106.23, 85.47, 82.16, 81.42, 73.62, 39.16, 27.15, 26.60; HRMS (ESI) [M+Na]+ Calcd for C_{18}H_{16}Br_2O_8Na 540.9110. Found 540.9105; IR (film) 2922, 2850, 1797, 1730, 1705, 1261, 1180, 1105, 1074, 1024, 867, 736, 682, 563 cm⁻¹.

Prepared under outlined condition A as in general procedure using ((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(2,2-dibromoacetyl)benzoate 60:

1H NMR (400 MHz, CDCl₃) δ 8.23 – 8.05 (m, 4H), 6.66 (s, 1H), 5.56 (d, J = 5.0 Hz, 1H), 4.65 (dd, J = 7.9, 2.5 Hz, 1H), 4.51 (dd, J = 19.3, 11.6, 6.2 Hz, 2H), 4.33 (ddd, J = 9.7, 6.4, 2.2 Hz, 2H), 4.22 – 4.14 (m, 1H), 1.51 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 185.46, 165.18, 134.93, 134.29, 130.08, 129.70, 109.81, 108.85, 96.34, 71.12, 70.77, 70.49, 66.08, 64.59, 39.35, 26.04, 25.98, 24.96, 24.51; HRMS (ESI) [M+Na]+ Calcd for C_{21}H_{24}Br_2O_8Na 584.9736. Found 584.9707; IR (film) 2987, 1722, 1705, 1382, 1263, 1211, 1103, 1068, 1004, 896, 869, 734, 655 cm⁻¹.

2-chloro-N-(3-(2,2-dichloroacetyl)phenyl)nicotinamide 61: Prepared under outlined condition B as in general procedure
using 2-chloro-N-(3-ethynylphenyl)nicotinamide (51.3 mg, 0.2 mmol, 1.0 equiv.), LiCl (25.4 mg, 3.0 equiv.), NaHSO₄·H₂O (110.4 mg, 4.0 equiv.), H₂O (108.0 mg, 30.0 equiv.) were dissolved in CH₃CN (2.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 61 in 80% (54.9 mg) yield as colorless syrup. ¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 8.48 (d, J = 3.9 Hz, 1H), 8.31 (s, 1H), 8.14 (d, J = 7.0 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.38 (dd, J = 7.4, 4.8 Hz, 1H), 6.70 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 185.59, 163.17, 151.51, 147.02, 139.81, 138.12, 132.24, 131.09, 129.86, 129.26, 126.20, 122.99, 121.09, 67.70; HRMS (ESI) [M+Na]⁺ Calcd for C₁₄H₉Cl₃N₂O₂Na 364.9627, Found 364.0628; IR (film) 1664, 1579, 1548, 1487, 1435, 1400, 1319, 1139, 1066, 813, 756, 682, 659 cm⁻¹.

1-(2-allylphenyl)-2,2-dibromoethan-1-one 70: Prepared under outlined condition A as in general procedure using 1-allyl-2-ethynylbenzene (14.2 mg, 0.1 mmol, 1.0 equiv.), NaBr (25.7 mg, 2.5 equiv.), NaHSO₄·H₂O (43.8 mg, 3.5 equiv.), H₂O (54.0 mg, 30.0 equiv.) were dissolved in CH₃CN (1.0 mL), the reaction was stirred under 6 W blue LEDs at room temperature for 24 hours affording compound 70 in 30% (9.5 mg) yield as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 7.8 Hz, 1H), 7.49 (dd, J = 7.6, 1.3 Hz, 1H), 7.37 – 7.29 (m, 2H), 6.64 (s, 1H), 6.03 – 5.94 (m, 1H), 5.10 – 5.00 (m, 2H), 3.58 (d, J = 6.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 188.96, 141.52, 136.60, 132.75, 132.52, 131.57, 128.15, 128.24, 116.58, 42.15, 37.89; HRMS (EI) m/z Calcd for C₁₁H₁₀Br₂O 315.9098, Found 315.9095; IR (film) 2924, 2850, 1712, 1571, 1436, 1363, 1255, 1220, 974, 920, 794, 634 cm⁻¹.
3) Procedure for Synthesis of Mitotane and analog

In schlenk tube, 2, 2-dichloro-1-(2-chlorophenyl)ethan-1-one 40 (150.0 mg, 0.67 mmol) was dissolved in methanol (3.0 mL) and evacuated and refilled with nitrogen (three cycles). The reaction mixture was stirred in ice bath for 10 min, then NaBH$_4$ (12.7 mg, 0.5 equiv.) was added into the mixture. The reaction mixture was quenched by 1N HCl aqueous after stirred at room temperature for 20 min. The mixture was purified by column chromatography on silica gel to give colorless oil in 80% yield (95.6 mg). Subsequently, the product (12.4 mg, 0.055 mmol) was dissolved in chlorobenzene (0.5 mL) and concentrated H$_2$SO$_4$ (0.25 mL) was added dropwise into the mixture and stirred at room temperature for 10 min, then quenched by saturated NaHCO$_3$ aqueous and extracted with DCM (5 mL*3). The organic layer was purified by column chromatography on silica gel to give Mitotane 63 colorless syrup in 89% yield (15.0 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 – 7.18 (m, 9H), 6.37 (d, $J$ = 8.7 Hz, 1H), 5.20 (d, $J$ = 8.7 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.22, 136.79, 134.25, 133.66, 130.30, 128.84, 128.82, 128.44, 127.16, 73.79, 57.23; HRMS (EI) m/z Calcd for C$_{14}$H$_{10}$Cl$_4$ 317.9537, Found 317.9542; IR (film) 1490, 1422, 1409, 1093, 1037, 1014, 879, 771, 750, 734, 686, 609 cm$^{-1}$. 

1 \text{NaBH}_4 (1.5 \text{ equiv.}), \text{MeOH}
2 \text{H}_2\text{SO}_4/\text{PhCl (v/v = 1:2)}

2 steps 71%
In schlenk tube, 2,2-dichloro-1-(2-fluorophenyl)ethan-1-one (30.0 mg, 0.14 mmol) was dissolved in methanol (1.0 mL) and evacuated and refilled with nitrogen (three cycles).

The reaction mixture was stirred in ice path for 10 min, then NaBH₄ (2.6 mg, 0.5 equiv.) was added into the mixture. The reaction mixture was quenched by 1N HCl aqueous after stirred at room temperature for 20 min. The mixture was purified by column chromatography on silica gel to give colorless oil in 72% yield (21.8 mg). Subsequently, the product (21.8 mg, 0.1 mmol) was dissolved in chlorobenzene (0.5 mL) and H₂SO₄ (0.25 mL) was added dropwise into the mixture and stirred at room temperature for 10 min, then quenched by saturated NaHCO₃ aqueous and extracted with DCM (5 mL*3).

The organic layer was purified by column chromatography on silica gel to give F-Mitotane 62 colorless syrup in 90% yield (27.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.23 (m, 6H), 7.14 (t, J = 7.5 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.45 (d, J = 9.2 Hz, 1H), 4.82 (d, J = 9.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 160.23 (d, J = 247.17), 137.30, 133.66, 129.87 (d, J = 1.4 Hz), 129.46 (d, J = 8.6 Hz), 129.33 (d, J = 4.0 Hz), 128.94, 127.02 (d, J = 13.8 Hz), 124.51 (d, J = 3.5 Hz), 116.12 (d, J = 22.7 Hz), 73.45, 56.57; HRMS (EI) m/z Calcd for C₁₄H₁₀Cl₃F 301.9832, Found 301.9835; IR (film) 2926, 1712, 1490, 1365, 1232, 1093, 1014, 823, 761, 750, 607 cm⁻¹.
In schlenk tube, 1-(2-bromophenyl)-2,2-dichloroethan-1-one (90.0 mg, 0.336 mmol) was dissolved in methanol (1.0 mL) and evacuated and refilled with nitrogen (three cycles). The reaction mixture was stirred in ice path for 10 min, then NaBH$_4$ (6.3 mg, 0.5 equiv.) was added into the mixture. The reaction mixture was quenched by 1N HCl aqueous after stirred at room temperature for 20 min. The mixture was purified by column chromatography on silica gel to give colorless oil in 72% yield (65.0 mg). Then 3I' (15.0 mg, 0.055 mmol) was dissolved in chlorobenzene (0.5 mL) and H$_2$SO$_4$ (0.25 mL) was added dropwise into the mixture and stirred at room temperature for 10 min, then quenched by saturated NaHCO$_3$ aqueous and extracted with DCM (5 mL*3). The organic layer was purified by column chromatography on silica gel to give Br-Mitotane 64 colorless syrup in 90% yield (18.1 mg).  

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.43 (dd, $J$ = 7.9, 1.6 Hz, 1H), 7.37 – 7.29 (m, 5H), 7.15 (td, $J$ = 7.8, 1.6 Hz, 1H), 6.36 (d, $J$ = 8.6 Hz, 1H), 5.21 (d, $J$ = 8.6 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.81, 136.74, 133.66, 133.63, 130.34, 129.13, 128.81, 128.60, 73.90, 59.60; HRMS (EI) m/z Calcd for C$_{14}$H$_{10}$BrCl$_3$ 361.9031, Found 361.9037; IR (film) 2922, 2852, 1490, 1469, 1438, 1409, 1095, 1014, 769, 748, 705, 663, 609 cm$^{-1}$
V. X-ray Crystallography Analysis of Compound 8

![Compound 8](image)

**CCDC 1915404**

- **Empirical formula**: \( \text{C}_9\text{H}_5\text{Br}_2\text{NO} \)
- **Formula weight**: 302.96
- **Temperature/K**: 293 (2)
- **Crystal system**: monoclinic
- **Space group**: \( \text{P}2_1/n \)
- **\( a/\AA \)**: 8.40930 (10)
- **\( b/\AA \)**: 9.09290 (10)
- **\( c/\AA \)**: 13.3012 (2)
- **\( \alpha/\degree \)**: 90
- **\( \beta/\degree \)**: 104.1410 (10)
- **\( \gamma/\degree \)**: 90
- **Volume/\( \AA^3 \)**: 986.26 (2)
- **\( Z \)**: 4
- **\( \rho \text{calcg/cm}^3 \)**: 2.040
- **\( \mu/\text{mm}^{-1} \)**: 10.094
- **\( F(000) \)**: 576.0
- **\( F(000) \)**: 0.46 \( \times \) 0.45 \( \times \) 0.42
- **\( \text{CuK}\alpha (\lambda = 1.54184) \)**
- **Radiation**: 11.332 to 134.058
- **\( 2\theta \text{ range for data collection}/\degree \)**: -9 \( \leq \) \( h \leq \) 10, -10 \( \leq \) \( k \leq \) 10, -15 \( \leq \) \( l \leq \) 15
- **Index ranges**: 19779
- **Reflections collected**: 1733 [\( R_{\text{int}} = 0.1818, R_{\text{sigma}} = 0.0614 \)]
- **Independent reflections**: 1733/0/119
- **Data/restraints/parameters**: 1.066
- **Goodness-of-fit on \( F^2 \)**: \( R_1 = 0.0487, wR_2 = 0.1264 \)
- **Final R indexes [\( I\geq2\sigma (I) \)]**: \( R_1 = 0.0497, wR_2 = 0.1280 \)
- **Final R indexes [all data]**: 0.79/-1.43
- **Largest diff. peak/hole / e \( \text{Å}^{-3} \)**
VI. NMR Spectra

$^1$H NMR of 2

![Chemical Structure]

$^1$H NMR of 2
$^{13}$C NMR of 2

![NMR spectrum of 2 with chemical shifts and peaks labeled]
$^1$H NMR of 3

![NMR Spectrum](image-url)
$^{13}$C NMR of 3

![Chemical structure of compound 3](image)

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>128.934</td>
</tr>
<tr>
<td>129.760</td>
</tr>
<tr>
<td>131.361</td>
</tr>
<tr>
<td>134.568</td>
</tr>
<tr>
<td>185.924</td>
</tr>
</tbody>
</table>

**Formula:** $\text{C}_8\text{H}_7\text{Cl_2}$
$^1$H NMR of 4

[Diagram of a molecule with structural formula 4, showing signals at 4.178, 2.041, 1.935, and 1.031 ppm]
$^{13}$C NMR of 4

![Chemical Structure of 4](image)

Chemical shifts:
- 184.50 ppm
- 76.96 ppm
- 68.96 ppm
- 127.76 ppm
- 122.15 ppm
- 111.37 ppm
- 30.98 ppm
$^{19}$F NMR of 4

![Chemical Structure]

$\text{F}$

$\text{Br}$

$\text{Br}$

$\text{4}$
$^1$H NMR of 5

![NMR Spectrogram]

The NMR spectrum shows peaks at the following chemical shifts (ppm):
- 8.081
- 7.485
- 7.475
- 6.606

The structure of 5 is shown below:

5

The structure includes:
- A chlorine (Cl) on the left
- A benzene ring
- A ketone group (O) with two bromine (Br) atoms attached

The peaks correspond to the following functionalities:
- 8.081 ppm: Likely associated with the bromine on the other side of the benzene ring.
- 7.485 ppm: Likely associated with the aromatic hydrogens.
- 7.475 ppm: Likely associated with the aromatic hydrogens.
- 6.606 ppm: Likely associated with the bromine on the same side of the benzene ring.
13C NMR of 5

![13C NMR Spectrogram](image)

- Chemical shifts and peaks for compound 5.
$^1$H NMR of 6
$\text{Br}$

$\text{13C NMR of 6}$

- 39.260 ppm
- 129.527 ppm
- 129.909 ppm
- 131.241 ppm
- 132.307 ppm
- 185.123 ppm

$\text{Br}$$\text{Br}$

$\text{Br}$

$\text{O}$

$\text{Br}$
$^1$H NMR of 7

[Diagram of 7 with chemical shift values]
$^{13}$C NMR of 7

![Chemical structure of compound 7]

- 104.617
- 131.038
- 127.965
- 30.703
**$^1$H NMR of 8**

![NMR spectrum of compound 8](image)

Compound 8 is a molecular structure with the following features:

- A benzene ring
- An ester group (O)相连
- Two bromine (Br) atoms
- A cyano (CN) group

The NMR spectrum shows the chemical shifts of various protons at different ppm values.
$^{13}$C NMR of 8

![Chemical Structure](image)

- 38.829
- 117.534
- 130.290
- 132.610
- 132.932
- 134.114
- 184.726

O

Br

Br

NC
$^1$H NMR of 9

![Chemical Structure of 9]

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.017</td>
<td>2.01</td>
<td>1.00</td>
<td>2.03</td>
<td>2.00</td>
</tr>
<tr>
<td>7.996</td>
<td>7.317</td>
<td>7.337</td>
<td>2.704</td>
<td>2.723</td>
</tr>
<tr>
<td>6.708</td>
<td>2.742</td>
<td>2.761</td>
<td>1.252</td>
<td>1.271</td>
</tr>
</tbody>
</table>

Et  Br  Br

9
$^{13}$C NMR of 9
$^1$H NMR of 10

![Chemical structure of 10](image)

- 0.05 ppm
- 0.13 ppm
- 1.80 ppm
- 2.00 ppm
- 2.04 ppm
- 2.37 ppm
- 4.09 ppm
- 7.10 ppm
$^{13}$C NMR of 10

![Chemical structure of compound 10 with peaks at 106.610, 159.013, 129.753, 128.113, 125.978, 39.934, 35.366, 31.011 ppm]
\[ ^1H \text{NMR of 11} \]

\[ \text{Ph} \]

\[ \text{Br} \]

\[ \text{Br} \]

11

\[ 1.00 \]

\[ 3.12 \]

\[ 2.09 \]

\[ 2.07 \]

\[ 2.02 \]

\[ 6.737 \]

\[ 7.451 \]

\[ 7.476 \]

\[ 7.495 \]

\[ 7.633 \]

\[ 7.652 \]

\[ 7.718 \]

\[ 7.739 \]

\[ 8.158 \]

\[ 8.179 \]

S73
$^{13}$C NMR of 11

![Chemical Structure of 11](image_url)

Chemical shifts (ppm):
- 39.818
- 127.339
- 127.521
- 128.697
- 129.095
- 129.432
- 130.386
- 139.375
- 147.185
- 185.590

Note: The image shows a chemical structure of compound 11, along with its $^{13}$C NMR spectrum. The spectrum displays various peaks corresponding to the chemical shifts of the compound's carbon atoms.
$^1$H NMR of 12

**Chemical Shifts:**
- 8.009 ppm
- 7.986 ppm
- 7.317 ppm
- 7.287 ppm
- 7.071 ppm
- 6.701 ppm
- 5.691 ppm
- 2.682 ppm
- 2.663 ppm
- 1.682 ppm
- 1.663 ppm
- 1.646 ppm
- 1.628 ppm
- 1.609 ppm
- 1.339 ppm
- 1.331 ppm
- 1.313 ppm
- 0.897 ppm
- 0.888 ppm
- 0.879 ppm
- 0.870 ppm

**Chemical Structure:**

\[
\begin{array}{c}
\text{C}_{9}\text{H}_{11} \\
\text{O} \\
\text{Br} \\
\text{Br} \\
\end{array}
\]

**Formula:**
- $\text{C}_{9}\text{H}_{11}\text{OBr}_2$
$\text{C NMR of 12}$

$\begin{array}{l}
13.979 \\
22.478 \\
30.641 \\
31.429 \\
36.100 \\
39.869 \\
128.384 \\
129.013 \\
129.867 \\
150.662 \\
185.657 \\
\end{array}$

$C_9H_{11}$

12
\textbf{\textsuperscript{1}H NMR of 13}

\begin{center}
\includegraphics[width=0.5\textwidth]{s77}
\end{center}
$^{13}$C NMR of 13

![Chemical structure of compound 13](image)

The chemical shifts are as follows:

- 39.13 ppm
- 116.53 ppm
- 116.76 ppm
- 121.48 ppm
- 121.70 ppm
- 125.45 ppm
- 125.48 ppm
- 130.57 ppm
- 130.65 ppm
- 132.78 ppm
- 132.84 ppm
- 161.47 ppm
- 163.95 ppm

The chemical structure of compound 13 is shown with the following atoms:

- F
- O
- Br
- Br

The spectrum is plotted with the chemical shifts on the x-axis and the intensity on the y-axis.
$^{19}$F NMR of 13

\[
\begin{array}{c}
\text{F} \\
\text{O} \\
\text{Br} \\
\text{Br} \\
\end{array}
\]

13
$\text{H NMR of 14}$

$$\text{Cl} \quad \text{O} \quad \text{Br}$$

14
$^{13}$C NMR of 14

14

Cl

O

Br

Br

14
$^1$H NMR of 15

![NMR Spectrum of 15](image-url)
$^{13}$C NMR of 15

![Chemical Structure](image-url)
$^{13}$C NMR of 16

![Chemical structure of 16](image)

- $f_1$ (ppm): 39.646
- 55.573
- 114.078
- 121.061
- 121.964
- 129.881
- 132.131
- 160.009
- 185.879

MeO-$\text{Br}$
$^1$H NMR of 17

![NMR spectrum of compound 17](image)
$^{13}$C NMR of 17

$$
\begin{array}{cccc}
28.168 & 39.362 & 82.113 & 129.025 \\
134.959 & 131.044 & 130.570 & 129.025 \\
185.449 & 121.113 & & \\
\end{array}
$$

![Chemical Structure of 17]
$^1$H NMR of 18

![Image of NMR spectrum]

**Formula:**

$\begin{align*}
\text{H}_2\text{NMR of 18} & \\
\text{1.00} & \\
\text{2.02} & \\
\text{4.16} & \\
\text{4.05} & \\
\text{2.08} & \\
\text{1.00} & \\
\text{1.03} & \\
\text{1.01} & \\
\end{align*}$
$^{13}$C NMR of 18

![Chemical Structure of 18](image)

<table>
<thead>
<tr>
<th>ppm</th>
<th>39.747</th>
<th>118.740</th>
<th>118.817</th>
<th>120.251</th>
<th>120.298</th>
<th>123.296</th>
<th>123.902</th>
<th>123.982</th>
<th>125.588</th>
<th>129.895</th>
<th>131.913</th>
<th>140.114</th>
<th>150.092</th>
<th>150.158</th>
<th>185.729</th>
</tr>
</thead>
</table>

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
$^{31}$P NMR of 18

![Diagram of 18](image-url)
$^1$H NMR of 19

![NMR spectrum of 19](image)

Chemical shifts and spin multiplicities:

- 3.01 ppm (s, 1H)
- 1.00 ppm (d, 3H)
- 1.01 ppm (d, 3H)
- 1.00 ppm (d, 3H)
- 2.51 ppm (s, 3H)
- 7.26 ppm (m, 1H)
- 7.28 ppm (m, 1H)
- 7.30 ppm (m, 1H)
- 7.31 ppm (m, 1H)
- 7.33 ppm (m, 1H)
- 7.43 ppm (m, 1H)
- 7.43 ppm (m, 1H)
- 7.45 ppm (m, 1H)
- 7.45 ppm (m, 1H)
- 7.47 ppm (m, 1H)
- 7.47 ppm (m, 1H)
- 7.66 ppm (m, 1H)
- 7.66 ppm (m, 1H)
- 7.68 ppm (m, 1H)

Structural formula of 19:

![Structural formula](image)
$^{13}$C NMR of 19

![Chemical Structure of 19]

- Me
- O
- Br

19

- 140.29
- 132.715
- 132.299
- 132.715
- 128.097
- 132.261
- 132.772
- 21.097
- 42.230
- 188.582
$^{13}$C NMR of 20

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.282</td>
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</tr>
<tr>
<td>30.187</td>
<td></td>
</tr>
<tr>
<td>43.021</td>
<td></td>
</tr>
<tr>
<td>125.555</td>
<td></td>
</tr>
<tr>
<td>126.701</td>
<td></td>
</tr>
<tr>
<td>127.074</td>
<td></td>
</tr>
<tr>
<td>132.393</td>
<td></td>
</tr>
<tr>
<td>133.070</td>
<td></td>
</tr>
<tr>
<td>149.626</td>
<td></td>
</tr>
<tr>
<td>189.932</td>
<td></td>
</tr>
<tr>
<td>24.282</td>
<td></td>
</tr>
<tr>
<td>30.187</td>
<td></td>
</tr>
<tr>
<td>43.021</td>
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<tr>
<td>125.555</td>
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<td>126.701</td>
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<td>127.074</td>
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<td>132.393</td>
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<tr>
<td>149.626</td>
<td></td>
</tr>
<tr>
<td>189.932</td>
<td></td>
</tr>
</tbody>
</table>
$^{1}$H NMR of 21
$^{13}$C NMR of 21

- 42.055
- 116.364
- 118.955
- 120.655
- 120.671
- 121.546
- 124.138
- 127.066
- 127.297
- 131.974
- 134.348
- 146.494
- 146.510
- 150.066
- 154.813
- 160.655
- 163.655
- 186.713

21

#NMR of 21
$^{19}$F NMR of 21
$^1$H NMR of 22

![Chemical structure of 22](image)

<table>
<thead>
<tr>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
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<tr>
<td>9.00</td>
</tr>
<tr>
<td>9.50</td>
</tr>
<tr>
<td>10.00</td>
</tr>
</tbody>
</table>

S98
$^{13}$C NMR of 22

![Chemical structure of compound 22]

- 10.381 ppm
- 13.345 ppm
- 13.975 ppm
- 12.975 ppm
- 26.799 ppm
- 40.221 ppm

- Chemical shifts for compound 22.
$^1$H NMR of 23

![Chemical Structure of 23](image)

The peaks at various ppm values are indicated on the graph.
$^{13}$C NMR of 23

![Chemical Structure of 23](23.png)

<table>
<thead>
<tr>
<th>f1 (ppm)</th>
<th>39.573</th>
</tr>
</thead>
<tbody>
<tr>
<td>125.494</td>
<td></td>
</tr>
<tr>
<td>125.644</td>
<td></td>
</tr>
<tr>
<td>131.720</td>
<td></td>
</tr>
<tr>
<td>135.658</td>
<td></td>
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<tr>
<td>138.248</td>
<td></td>
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<td>144.628</td>
<td></td>
</tr>
<tr>
<td>147.273</td>
<td></td>
</tr>
<tr>
<td>156.292</td>
<td></td>
</tr>
<tr>
<td>160.892</td>
<td></td>
</tr>
<tr>
<td>162.683</td>
<td></td>
</tr>
<tr>
<td>166.268</td>
<td></td>
</tr>
<tr>
<td>170.584</td>
<td></td>
</tr>
<tr>
<td>179.014</td>
<td></td>
</tr>
<tr>
<td>185.668</td>
<td></td>
</tr>
</tbody>
</table>

23
$^1$H NMR of 24

![Chemical Structure of 24](image)

The spectrum shows the proton resonances at various ppm values.
$^{13}$C NMR of 24

![Chemical Structure of 24](image)

<table>
<thead>
<tr>
<th>f1 (ppm)</th>
<th>39.552</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.386</td>
<td>138.222</td>
</tr>
<tr>
<td>61.386</td>
<td>129.858</td>
</tr>
<tr>
<td>41.268</td>
<td>131.290</td>
</tr>
<tr>
<td>42.268</td>
<td>131.722</td>
</tr>
<tr>
<td>47.268</td>
<td>138.586</td>
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<td>77.268</td>
<td>151.386</td>
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<td>182.268</td>
<td>163.371</td>
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<td>183.268</td>
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</tr>
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<td>221.268</td>
<td>226.178</td>
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<td>225.268</td>
<td>228.301</td>
</tr>
<tr>
<td>226.268</td>
<td>221.081</td>
</tr>
</tbody>
</table>

The chemical structure of 24 shows a combination of chlorine, nitrogen, and bromine atoms in its molecular structure.
'$^1$H NMR of 25

![Chemical Structure of 25]

| f1 (ppm) | 6.07 | 6.19 | 1.00 | 1.03 | 2.02 | 1.01 | 1.01 | 6.740 | 7.382 | 7.402 | 7.422 | 7.669 | 7.707 | 7.727 | 7.905 | 7.925 | 8.072 | 8.077 | 8.081 |
|----------|------|------|------|------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|

25
$^{13}$C NMR of 25

![Chemical Structure](image)
$^1$HNMR of 26

![Chemical structure of compound 26](image)

- Peak at 8.41 ppm
- Peak at 7.597 ppm
- Peak at 7.489 ppm
- Peak at 7.489 ppm
- Peak at 7.489 ppm
- Peak at 7.489 ppm
- Peak at 7.489 ppm
- Peak at 2.01 ppm
- Peak at 2.00 ppm
- Peak at 1.00 ppm
- Peak at 2.00 ppm
- Peak at 8.396 ppm
- Peak at 8.415 ppm
- Peak at 7.450 ppm
- Peak at 7.469 ppm
- Peak at 7.488 ppm
- Peak at 7.560 ppm
- Peak at 7.578 ppm
- Peak at 7.597 ppm
- Peak at 3.12 ppm
$^{13}$C NMR of 26

![Chemical Structure Image]

- 37.746 ppm
- 57.945 ppm
- 127.982 ppm
- 131.377 ppm
- 131.737 ppm
- 133.500 ppm
- 188.303 ppm

Chemical Shifts
$^1$H NMR of 27

![Chemical Structure of 27]

<table>
<thead>
<tr>
<th>$f_1$ (ppm)</th>
<th>3.08</th>
<th>4.17</th>
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<th>2.04</th>
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<td>1.403</td>
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<td>1.419</td>
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<td>7.544</td>
<td>7.563</td>
<td>7.581</td>
<td>8.332</td>
<td>8.351</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
$^{13}$C NMR of 27

![Chemical Structure](image)

S109
\[ \text{\textsuperscript{1}H NMR of 28} \]
$^{13}$C NMR of 28

Chemical shifts (ppm):
- 138.431
- 133.123
- 132.074
- 127.921
- 125.395
- 71.346
- 7.576
1H NMR of 29

The 1H NMR spectrum of compound 29 is shown, with various chemical shifts indicated. The compound contains a benzene ring with substituents at the 2,3-positions. The peaks at 8.32 ppm, 7.69 ppm, and 7.48 ppm are notable in the spectrum.
\[ ^{13}\text{C NMR of 29} \]

![Diagram of 29]

- 166.970
- 153.789
- 132.800
- 128.119
- 60.912
- 53.894

- 53.684
- 60.912
- 128.119
- 130.932
- 132.000
- 133.783
- 186.970
**\(^1\)H NMR of 30**

![Chemical structure of 30]

**Chemical Structure**

- **Formula**: O
- **Substructure**: 
  - Benzene ring
  - Two bromine atoms
  - Ethyl group

**NMR Details**

- **f1 (ppm)**:
  - 8.419
  - 7.600
  - 7.528
  - 7.371
  - 7.312
  - 7.265
  - 7.280
  - 7.242
  - 7.208
  - 7.489
  - 7.600
  - 7.618
  - 7.636
  - 8.399
  - 8.419

**Integration and Multiplicity**

- **1.98 Hz**
- **1.00 Hz**
- **3.12 Hz**
- **2.05 Hz**
- **2.05 Hz**
$^{13}$C NMR of 30

30

\[
\begin{align*}
\text{f1 (ppm)}: & \quad 33.888 \\
& \quad 48.808 \\
& \quad 65.472 \\
& \quad 126.357 \\
& \quad 128.011 \\
& \quad 128.628 \\
& \quad 128.702 \\
& \quad 131.162 \\
& \quad 132.534 \\
& \quad 133.399 \\
& \quad 140.246 \\
& \quad 188.360
\end{align*}
\]
$^1$H NMR of 31

31

Me O C H  Ph
Br Br Ph

1.00 1.05 7.18
2.285 2.863 2.867 2.878 2.884 2.905 2.928 2.933 2.944 2.948
$^1$H and $^13$C NMR of Compound 31

**$^1$H NMR of 31:**

- 1.94 (s, 3H, Me)
- 2.09 (m, 4H, CH$_2$)
- 4.15 (t, 2H, CH$_2$)
- 7.15-7.45 (m, 5H, Ph)

**$^13$C NMR of 31:**

- 20.570
- 34.028
- 48.443
- 67.777
- 124.972
- 126.469
- 128.175
- 128.653
- 130.806
- 131.220
- 135.974
- 137.366
- 139.915
- 194.261

**Chemical Structure of 31:**

- Benzene ring
- Carbonyl group
- Two bromines
- Phenyl group
$^1$H NMR of 32

![NMR spectrum of compound 32](image)

**Chemical Shifts:**
- 7.89 ppm (Ar-H)
- 7.87 ppm (Ar-H)
- 7.53 ppm (Ar-H)
- 7.32 ppm (Ar-H)
- 2.10 ppm (CH3)
- 1.05 ppm (CH3)
- 4.18 ppm (CH)

**Structure of Compound 32:**
- Benzene ring
- Two bromine atoms
- One methoxy group
- One phenyl ring
- Two methyl groups
$^{13}$C NMR of 32

![Chemical Structure of 32](image)

- 24.210
- 31.468
- 33.977
- 48.188
- 68.408
- 125.026
- 126.167
- 126.494
- 127.272
- 128.661
- 128.694
- 130.686
- 135.988
- 139.885
- 147.354
- 195.758

- 106.798
- 115.818
- 124.818
- 125.028
- 125.818
- 126.494
- 127.272
- 128.661
- 128.94
- 130.686
- 135.988
- 139.885
- 147.354
- 195.758
$^1$H NMR of 33

![Chemical structure of 33]
$^{13}$C NMR of 33

$^{13}$BuOOC$_{\text{Ph}}$Br$_2$Br

33
$^1$H NMR of 34

![NMR Spectrum](image_url)
$^{13}$C NMR of 34

![Chemical Structure of 34](image)

S123
1H NMR of 35
$^{13}$C NMR of 35

![Chemical Structure](image)

**Chemical Structure**

- Br-Br
- Br-Cl
- Cl-Cl

**NMR Spectrum**

The NMR spectrum shows the chemical shifts for various carbon atoms in the compound, ranging from 210 ppm to -10 ppm.
$\text{H NMR of 36}$

![Chemical structure of 36](image)

36

S126
$^1$H NMR of

![Chemical Structure](image)

F$_3$CO

O

Cl

Cl

37

F

3

CO

37
$^{13}$C NMR of 37

![Chemical structure of 37](image)

- 186.73
- 166.73
- 114.59
- 111.05
- 77.22
- 67.22
- 21.45
- 12.63
$^{19}$F NMR of 37
\(^1\text{H} \text{ NMR of 38}\)

![NMR spectrum diagram](image-url)
$^{13}$C NMR of 38

![Chemical Structure](image)
$\text{H NMR of 39}$

![Diagram of molecule 39](image)

$\text{F} \quad \text{O} \quad \text{Cl}$

$\text{Cl}$

$\text{39}$

$6.816 \quad 6.822 \quad 7.170 \quad 7.172 \quad 7.191 \quad 7.193 \quad 7.198 \quad 7.200 \quad 7.219 \quad 7.221 \quad 7.298 \quad 7.301 \quad 7.319 \quad 7.336 \quad 7.339 \quad 7.623 \quad 7.625 \quad 7.640 \quad 7.643 \quad 7.963 \quad 7.967 \quad 7.982 \quad 7.986 \quad 8.001 \quad 8.005$
$^{13}$C NMR of 39
$^{19}$F NMR of 39
$^1$H NMR of 40
$^{13}$C NMR of 40

![Chemical Structure](image)

**S137**
$^1$H NMR of 41

[Chemical structure image of 41]

[S138]
$^{13}$C NMR of 41

![Chemical Structure](image)

S139
$^1$H NMR of 42

MOMO

42

H NMR of 42
\textbf{13C NMR of 42}

![Chemical Structure of 42](image)

- \( f_1 (\text{ppm}) \):
  - 185.795
  - 159.990
  - 143.820
  - 125.986
  - 114.990
  - 67.732
  - 55.563

\[ \text{MeO} - \text{C} - \text{Cl} \]

42
$^1$H NMR of 43

![Chemical structure of 43]
$^{13}$C NMR of 43

[Chemical structure of 43 with relevant chemical shifts]
$^1$H NMR of 44

![Chemical Structure](image)

![NMR Spectrum](image)
$^{13}$C NMR of 44
$^1$H NMR of 45

\[
\begin{array}{c}
\text{45} \\
\text{'Bu} \\
\end{array}
\]
$^{13}$C NMR of 45

45

![Chemical structure of 45 with NMR spectrum]
$^1$H NMR of 46
$^{13}$C NMR of 46

![Chemical structure of 46]
$^1$H NMR of 47
1H NMR of 48
$^{13}$C NMR of 48
$^1$H NMR of 49

![Chemical Structure of 49](image)

- 8.194, 8.173, 8.057 ppm
- 6.648, 8.057, 8.077 ppm
- 8.173, 8.194, 8.057 ppm
- 2.659 ppm
$^{13}$C NMR of 49

49

5155
$^1$H NMR of 50

50
$^{13}\text{C} \text{NMR of 50}$

![Chemical structure of 50](image)

**Chemical Formulas**

- C: 67.721
- N: 117.481
- O: 117.689
- Cl: 130.317
- Cl: 132.581
- Cl: 134.349
- NC: 136.833

**Graphical Representation**

A graph showing the NMR spectrum of compound 50 with peaks at various ppm values.
$^1$H NMR of 51

![NMR spectrum of compound 51](image)
\( ^{13} \text{C NMR of 51} \)
'H NMR of 52

52
$^{13}$C NMR of 52

![Chemical Structure of 52](image)

S161
$^{13}$C NMR of 53

![Chemical Structure of 53](image-url)
$^1$H NMR of 54

![Chemical structure of compound 54]
$^{13}$C NMR of 54

54
$^1$H NMR of 55

![NMR Spectrum of Compound 55]

Chemical shift values (ppm):
- 8.270
- 8.269
- 2.080
- 1.028
- 0.002
$^{13}$C NMR of 55

![Chemical structure of 55](image)

- 52.267 ppm
- 83.408 ppm
- 128.296 ppm
- 130.836 ppm
- 131.391 ppm
- 133.995 ppm
- 186.894 ppm
$^1$H NMR of 56

[Chemical structure diagram]

Table of NMR data:

- ppm values for various protons
- Integration and coupling constants

[Graph showing NMR spectrum with peaks labeled]
$^{13}$C NMR of 56
$^1$H NMR of 57
$^1$H NMR of 58

MeOOC

NH

O

O

Br

Br

58
$^{13}$C NMR of 58

![Chemical structure of 58](image)

<table>
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<th>Chemical Shift (ppm)</th>
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<td>185.263</td>
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58
$^1$H NMR of 59

![Chemical Structure of 59](image_url)
$^{13}$C NMR of 59

![Chemical structure of 59](image)

- 185.262
- 170.341
- 164.096
- 137.493
- 136.094
- 129.907
- 113.335
- 110.228
- 85.473
- 81.164
- 73.621
- 38.161
- 27.159
- 26.603
\textbf{\textsuperscript{1}H NMR of 60}

![NMR spectrum of compound 60](image-url)
$^{13}$C NMR of 60

![Structural formula of 60](image)
$^1$H NMR of 61
$^{13}$C NMR of 61

![Chemical Structure of 61]

**Chemical Structure of 61**

- Compound 61 contains elements O, N, Cl, C, and H.

**S179**
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$^{13}$C NMR of 62
$^{19}$F NMR of 62

![Chemical Structure of 62](image)

S182
$^1$H NMR of 63
$^{13}$C NMR of 63

![Chemical structure of compound 63 with NMR spectrum]
$^{1}H$ NMR of 64
$^{13}$C NMR of 64

![Chemical Structure Image]

64
$^1$H NMR of 70
$^{13}$C NMR of 70
VI. References