Electronic Supplementary Information
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1. General Information

A. Materials:

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity ≥ 99.999%) unless otherwise mentioned. Sodium formate-$^{13}$C (99 atom % $^{13}$C) was purchased from Sigma-Aldrich. All aryl halides and other commercial reagents were purchased from Adamas-beta, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh). The LED lamps were purchased from Kessil (PR160-390 nm, 427 nm, 440 nm, 456 nm, 467 nm, 520 nm). The Photo Reaction Setup was purchased from Anhui kemi machinery technology Co., Ltd.

B. Analytical Methods:

$^1$H-NMR, $^{19}$F-NMR and $^{13}$C-NMR spectra were recorded on Bruker Avance 400 spectrometer or Bruker Avance 500 spectrometer at ambient temperature. Data for $^1$H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for $^{13}$C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data or EI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI or EI source and controlled by Xcalibur software.
2. Preparation of Substrates

**2,4-dichloro-1-(5-chloro-2-((3-iodobenzyl)oxy)phenoxy)benzene (S1):** 4-chloro-2-(2,4-dichlorophenoxy)phenol (1.2 equiv., 12 mmol), 1-(bromomethyl)-3-iodobenzene (1.0 equiv., 10 mmol), K₂CO₃ (1.5 equiv., 15 mmol) were placed in a 100 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, anhydrous DMF (30 mL, 0.4 M) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred at room temperature for 24 h. The mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified via flash column chromatography on silica gel. (Eluent: petroleum ether/ethyl acetate = 20:1).

1H NMR (400 MHz, CDCl₃) δ 7.54 (dt, J = 7.9, 1.4 Hz, 1H), 7.42 (t, J = 1.7 Hz, 1H), 7.37 (d, J = 2.5 Hz, 1H), 7.11 – 7.01 (m, 2H), 7.00 – 6.85 (m, 4H), 6.58 (d, J = 8.8 Hz, 1H), 4.89 (s, 2H).

13C NMR (101 MHz, CDCl₃) δ 152.3, 150.2, 143.3, 138.1, 137.2, 135.8, 130.6, 130.5, 130.2, 128.1, 127.7, 126.1, 124.4, 122.3, 121.9, 117.7, 115.6, 94.5, 70.0.

HRMS (ESI) (m/z): [M+Na]⁺ Calcd for C₁₉H₁₂Cl₁NaO₂⁺, 526.8840; Found 526.8843.

**1-((8S,9S,10R,13S,14S,17S)-3-bromo-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one (S2):** Dione (10 mmol, 1.0 equiv.) was dissolved in glacial acetic acid (0.4 M) and phosphorus tribromide (20 mmol, 2.0 equiv.) was added drop wise to the mixture at room temperature. The dark solution was kept at 8-10 °C for 24 h during which the product got precipitated from the solution. The solid product was filtered and
washed with cold glacial acetic acid, followed by cold water (3 × 50.0 ml). The product was dried under vacuum to afford. (Eluent: petroleum ether).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.19 (d, \(J = 2.3\) Hz, 1H), 5.32 (dd, \(J = 5.0, 2.9\) Hz, 1H), 2.75 (dd, \(J = 8.3, 2.7\) Hz, 1H), 2.61 – 2.47 (m, 1H), 2.43 – 2.35 (m, 1H), 2.13 (t, \(J = 5.4\) Hz, 1H), 2.06 (s, 3H), 1.92 – 1.80 (m, 1H), 1.78 – 1.65 (m, 5H), 1.59 – 1.48 (m, 2H), 1.46 – 1.32 (m, 1H), 1.30 – 1.18 (m, 3H), 1.17 – 1.08 (m, 1H), 0.88 (d, \(J = 1.1\) Hz, 7H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 212.7, 140.9, 131.1, 124.5, 120.7, 61.2, 50.6, 47.4, 45.6, 35.5, 35.0, 34.4, 33.0, 32.9, 31.9, 31.8, 25.9, 24.4, 21.0, 20.7, 18.9.

\[ \text{[Diagram]} \]

4-(5-(4-bromophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide\(^2\) (S3): 1-(4-bromophenyl)-4,4,4-trifluorobutane-1,3-dione (1.20 g, 4.0 mmol) and 4-hydrazonebenzenesulfonamide hydrochloride (1.07 g, 4.8 mmol) were dissolved in 15 mL of EtOH and the mixture heated at reflux for 24 h. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (Eluent: petroleum ether/ethyl acetate = 2:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.3\) Hz, 2H), 7.41 (dd, \(J = 26.6, 8.1\) Hz, 4H), 7.03 (d, \(J = 8.1\) Hz, 2H), 6.71 (s, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.3 (q, \(J = 39.2\) Hz), 144.0, 142.1, 141.8, 132.4, 130.3, 127.7, 127.5, 125.6, 125.1 – 116.0 (m), 124.2, 106.8 (d, \(J = 2.4\) Hz).

\(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -62.44.

\[ \text{[Diagram]} \]

\(N\)-(4-bromophenyl)methacrylamide (S4): To a solution of aniline (10 mmol, 1.0 equiv), triethylamine (20 mmol, 2.0 equiv) in dry DCM (0.3 M) at 0 °C under Ar atmosphere corresponding acyl chloride (11 mmol, 1.1 equiv) was added. The resulting solution was slowly allowed to warm to room temperature over 6 h. After the reaction, water was added, stirred and the layers were separated. The organic layer was washed with water (2 × 30 mL), dried over Na\(_2\)SO\(_4\), filtered and the solvent was removed under
reduced pressure to yield crude product. The product was dried under vacuum to afford. (Eluent: petroleum ether/ethyl acetate = 10:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 (s, 1H), 7.44 – 7.32 (m, 4H), 5.72 (d, \(J = 1.1\) Hz, 1H), 5.40 (d, \(J = 1.6\) Hz, 1H), 1.98 (t, \(J = 1.2\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.6, 140.7, 136.9, 132.0, 121.6, 120.2, 117.0, 18.7.

HRMS (ESI) (m/z): [M+Na]^+ Calcd for C\(_{10}\)H\(_{10}\)BrNNaO^+, 261.9838; Found 261.9841.
3. Investigation of the Key Reaction Parameters

In the air, a 10 mL transparent Schlenk tube equipped with a magnetic stirrer was charged with 4-Iodobiphenyl (1.0 equiv., 0.2 mmol), potassium formate (1.5 equiv., 0.3 mmol), 4DPAIPN (1 mol%, 0.01 equiv.), Ni(PCy\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (5 mol%, 0.05 equiv.), dtbbpy (6 mol%, 0.06 equiv.). The test tube was evacuated and backfilled with argon for three times, then DMA (2 mL) were added and the mixture was stirred under irradiation with 440 nm blue LEDs, maintained at room temperature (28 ± 2 °C) for 20 h.

For methyl esterification: After the reaction was over, the Schlenk tube was charged with 'tBuOK (1.5 equiv., 0.3 mmol). Dry DMSO (2 mL) and methyl iodide (1.5 equiv., 0.3 mmol) were added dropwise over a period of 15 min. The mixture was stirred at room temperature for 15 min, poured into water and extracted with ethyl acetate. Under reduced pressure, the combined organic layers were evaporated. The residue was purified by flash column chromatography on silica gel to give the target product. (Eluent: petroleum ether/ethyl acetate = 10:1).

3.1 Optimization of the Reaction Condition for Aryl Iodide

Table S1: Optimization of the nickel catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ni-cat</th>
<th>3 yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiCl\textsubscript{2}•glyme</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>NiBr\textsubscript{2}•glyme</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>Ni(PCy\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>Ni(acac)\textsubscript{2}</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Ni(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>Ni(PPh\textsubscript{3})\textsubscript{4}</td>
<td>47</td>
</tr>
<tr>
<td>7</td>
<td>Ni(OTf)\textsubscript{2}</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>Ni(cod)\textsubscript{2}</td>
<td>14</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard. n.d. = not detected.
**Table S2: Optimization of photoredox catalysts [PC]**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ni-cat</th>
<th>3 yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4CzPN</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>4DPAIPN</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>4CzTPN</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>4CzIPN</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>Ir[dF(CF\textsubscript{3})(ppy\textsubscript{2})(dtbbpy)]PF\textsubscript{6}</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>Ru(bpy\textsubscript{3})Cl\textsubscript{2}</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard.

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**Table S3: Optimization of different ligands**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>3 yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4DPAIPN 1 (mol%), Ni(PCI\textsubscript{3})Cl\textsubscript{2} 5 (mol%)</td>
<td>98</td>
</tr>
<tr>
<td>ligand (6 mol%), DMA (2 mL), r.t., 20 h, 440 nm Blue LEDs</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard.
Table S4: Optimization of different solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>3 Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMA</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>acetone</td>
<td>n.d.</td>
</tr>
<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>PhCH₃</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>36</td>
</tr>
<tr>
<td>8</td>
<td>CH₃CN</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard.

Table S5: Optimization of different light sources

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light Sources</th>
<th>3 Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>390 nm purple LEDs</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>427 nm purple LEDs</td>
<td>71</td>
</tr>
<tr>
<td>3</td>
<td>440 nm blue LEDs</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>456 nm blue LEDs</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>467 nm blue LEDs</td>
<td>67</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard.
Table S6: Control experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>conditions</th>
<th>3 yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No [PC]</td>
<td>n.d.</td>
</tr>
<tr>
<td>2</td>
<td>No Ni-cat</td>
<td>n.d.</td>
</tr>
<tr>
<td>3</td>
<td>No ligand</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>No light</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard.
3.2 Optimization of the Reaction Condition for Aryl Bromide

Table S7: Optimization of the nickel catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ni-cat</th>
<th>3 yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiCl₂•glyme</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>NiBr₂•glyme</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Ni(PCy₃)₂Cl₂</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Ni(acac)₂</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Ni(PPh₃)₂Cl₂</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>Ni(PPh₃)₄</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>Ni(OTf)₂</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>Ni(cod)₂</td>
<td>16</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard.
Table S8: Control experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>conditions</th>
<th>3 yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiI</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>NaI</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>KI</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>HCOOLi</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>HCOONa</td>
<td>96</td>
</tr>
<tr>
<td>6</td>
<td>HCOOCs</td>
<td>17</td>
</tr>
<tr>
<td>7</td>
<td>No TBAI</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>No TBAI, NiI₂ (5 mol%)</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>Ni(cod)₂ (5 mol%), PPh₃ (10 mol%) instead of Ni(PPh₃)₂Cl₂</td>
<td>59</td>
</tr>
<tr>
<td>10</td>
<td>4-iodobiphenyl instead of 4-bromobiphenyl</td>
<td>85</td>
</tr>
</tbody>
</table>

The yield was determined by GC used bis(4-methoxyphenyl)methanone as internal standard.

Table S9: Unsuccessful Substrates

<table>
<thead>
<tr>
<th>R-Br + HCOOK</th>
<th>4DPAIPN (1 mol%), Ni[PPh₃]₂Cl₂ (5 mol%)</th>
<th>R-CO₂H</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 mmol</td>
<td>0.3 mmol</td>
<td></td>
</tr>
</tbody>
</table>

yield: 0% 0% < 5% < 5%
4. General Procedure and Spectral Data

4.1 General Procedure

**General Procedure A for carboxylation of aryl iodide:** In the air, a 10 mL transparent Schlenk tube equipped with a magnetic stirrer was charged with aryl iodide (1.0 equiv., 0.2 mmol) (if solid), potassium formate (1.5 equiv., 0.3 mmol), 4DPAIPN (1 mol%, 0.01 equiv.), Ni(PCy$_3$)$_2$Cl$_2$ (5 mol%, 0.05 equiv.), dtbbpy (6 mol%, 0.06 equiv.). The test tube was evacuated and backfilled with argon for three times, then aryl iodide (1.0 equiv., 0.2 mmol) (if liquid) and DMA (2 mL) were added and the mixture was stirred under irradiation with 440 nm blue LEDs, maintained at room temperature (28 ± 2 °C) for 20 h. The reaction mixture was diluted with ethyl acetate, washed with 2 N HCl, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the target product.

**General Procedure B for carboxylation of aryl bromide or alkenyl bromide:** In the air, a 10 mL transparent Schlenk tube equipped with a magnetic stirrer was charged with aryl bromide or alkenyl bromide (1.0 equiv., 0.2 mmol) (if solid), sodium formate (1.5 equiv., 0.3 mmol), 4DPAIPN (1 mol%, 0.01 equiv.), Ni(PPh$_3$)$_2$Cl$_2$ (5 mol%, 0.05 equiv.), TBAI (10 mol%, 0.1 equiv.), dtbbpy (6 mol%, 0.06 equiv.). The test tube was evacuated and backfilled with argon for three times, then aryl bromide (1.0 equiv., 0.2 mmol) (if liquid) and DMA (2 mL) were added and the mixture was stirred under irradiation with 440 nm blue LEDs, maintained at room temperature (28 ± 2 °C) for 20 h. The reaction mixture was diluted with ethyl acetate, washed with 2 N HCl, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the target product.

**Reaction Setup**

Figure S1 The photo-reaction setup
4.2 Characterization Data for the Products

[1,1'-biphenyl]-4-carboxylic acid (3)³

Method A: Reaction with 4-iodo-1,1'-biphenyl resulted in 39.0 mg (92% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 20:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 – 7.91 (m, 1H), 7.74 – 7.46 (m, 3H), 7.42 – 7.33 (m, 1H), 7.35 – 7.26 (m, 1H), 3.85 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.0, 145.6, 140.0, 130.1, 128.9, 128.9, 128.1, 127.3, 127.1, 52.1.

4-methylbenzoic acid (4)³

Method A: Reaction with 1-iodo-4-methylbenzene resulted in 26.7 mg (98% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 12.81 (br s, 1H), 7.86 (d, $J$ = 8.3 Hz, 2H), 7.25 (d, $J$ = 8.1 Hz, 2H), 2.32 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 167.8, 143.4, 129.8, 129.5, 128.5, 21.5.

4-(tert-butyl)benzoic acid (5)³

Method A: Reaction with 1-(tert-butyl)-4-iodobenzene resulted in 31.7 mg (89% yield) of the title product obtained as a colorless solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.97 – 7.74 (m, 2H), 7.72 – 7.32 (m, 2H), 1.27 (s, 9H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 172.5, 161.0, 134.4, 133.2, 130.6, 40.0, 36.0.

4-methoxybenzoic acid (6)³

Method A: Reaction with 1-bromo-4-methoxybenzene resulted in 18.2 mg (60% yield) of the title product obtained as a colorless solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 12.65 (br s, 1H), 7.91 (d, $J$ = 8.8 Hz, 2H), 7.02 (d, $J$ = 8.8 Hz, 2H), 3.83 (s, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 167.5, 163.3, 131.8, 123.5, 114.3, 55.9.
3,5-dimethylbenzoic acid (7)\(^3\)

Method A: Reaction with 1-iodo-3,5-dimethylbenzene resulted in 22.2 mg (74% yield) of the title product obtained as a colorless solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.55 (d, \(J = 2.2\) Hz, 2H), 7.22 (d, \(J = 2.1\) Hz, 1H), 2.30 (s, 6H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.6, 137.7, 134.2, 130.7, 127.0, 20.7.

4-bromobenzoic acid (8)\(^3\)

Method A: Reaction with 1-bromo-4-iodobenzene resulted in 37.0 mg (92% yield) of the title product obtained as a colorless solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 13.22 (br s, 1H), 7.88 (d, \(J = 8.4\) Hz, 2H), 7.82 – 7.29 (m, 2H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.1, 132.2, 131.8, 130.4, 127.4.

4-chlorobenzoic acid (9)\(^3\)

Method A: Reaction with 1-chloro-4-iodobenzene resulted in 28.1 mg (90% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.22 (br s, 1H), 7.97 – 7.95 (m, 2H), 7.59 – 7.57 (m, 2H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 166.9, 138.2, 131.6, 130.1, 129.2.

4-fluorobenzoic acid (10)\(^3\)

Method A: Reaction with 1-fluoro-4-iodobenzene resulted in 16.8 mg (60% yield) of the title product obtained as a colorless solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 13.07 (br s, 1H), 8.38 – 7.86 (m, 2H), 7.33 (t, \(J = 8.9\) Hz, 2H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 166.8, 166.6, 164.1, 132.5 (d, \(J = 9.4\) Hz), 127.7 (d, \(J = 3.3\) Hz), 116.2, 116.0.

\(^{19}\)F NMR (377 MHz, DMSO) \(\delta\) -106.90.
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (11)\(^4\)

Method A: Reaction with 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane resulted in 34.7 mg (70% yield) of the title product obtained as a colorless solid. (Eluent: petroleum ether/ethyl acetate = 4:1).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.95 (d, \(J = 8.2\) Hz, 2H), 7.82 – 7.77 (m, 2H), 1.31 (s, 12H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 172.4, 141.4, 139.7, 138.4, 133.8, 89.3, 29.9.

4-(methylthio)benzoic acid (12)\(^5\)

Method A: Reaction with (4-iodophenyl)(methyl)sulfane resulted in 31.9 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 4:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 12.83 (br s, 1H), 7.87 (dd, \(J = 8.5, 1.7\) Hz, 2H), 7.34 (dd, \(J = 8.5, 1.9\) Hz, 2H), 2.53 (s, 3H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.5, 145.3, 130.2, 127.2 125.3, 14.4.

4-formylbenzoic acid (13)\(^3\)

Method A: Reaction with 4-iodobenzaldehyde resulted in 16.8 mg (56% yield) of the title product obtained as a yellow solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 13.45 (br s, 1H), 10.13 (s, 1H), 8.36 – 8.12 (m, 2H), 8.12 – 7.96 (m, 2H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 193.4, 167.0, 139.3, 136.1, 130.4, 130.0.

4-(methoxycarbonyl)benzoic acid (14)\(^3\)

Method A: Reaction with methyl 4-iodobenzoate resulted in 32.4 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 12.92 (br s, 1H), 7.59 (d, \(J = 2.5\) Hz, 4H), 3.42 (s, 3H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 166.6, 165.6, 134.8, 133.1, 129.6, 129.3, 52.4.
4-acetylbenzoic acid (15)\(^3\)

Method A: Reaction with 1-(4-iodophenyl)ethan-1-one resulted in 24.6 mg (75% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 13.31 (br s, 1H), 8.06 (s, 4H), 2.64 (s, 3H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 198.2, 167.1, 140.3, 134.9, 130.0, 128.8, 27.5.

4-hydroxybenzoic acid (16)\(^6\)

Method A: Reaction with 4-bromophenol resulted in 16.8 mg (56% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 7.80 (d, \(J = 8.7\) Hz, 2H), 6.83 (d, \(J = 8.7\) Hz, 2H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.7, 162.1, 132.0, 121.8, 115.6.

4-carbamoylbenzoic acid (17)\(^7\)

Method A: Reaction with 4-iodobenzamide resulted in 24.8 mg (75% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 1:1).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 13.22 (br s, 1H), 8.15 (s, 1H), 8.08 – 7.86 (m, 4H), 7.57 (s, 1H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.7, 167.3, 138.5, 133.5, 129.6, 128.1.

4-fluoro-3-(trifluoromethyl)benzoic acid (18)

Method A: Reaction with 1-fluoro-4-iodo-2-(trifluoromethyl)benzene resulted in 29.1 mg (70% yield) of the title product obtained as a viscous liquid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.31 (ddd, \(J = 8.7, 5.0, 2.2\) Hz, 1H), 8.22 (dd, \(J = 7.1, 2.2\) Hz, 1H), 7.65 (dd, \(J = 10.5, 8.7\) Hz, 1H).

\(^13\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 165.6, 161.9 (dd, \(J = 260.0, 2.0\) Hz), 136.8 (d, \(J = 10.2\) Hz), 128.6 (qd, \(J = 4.5, 2.5\) Hz), 128.4 (d, \(J = 3.0\) Hz), 122.6 (q, \(J = 272.0\) Hz), 118.3 (d, \(J = 21.4\) Hz), 117.4 (qd, \(J = 33.0, 13.1\) Hz).

\(^19\)F NMR (377 MHz, DMSO-\(d_6\)) \(\delta\) -60.76, -110.02 (q, \(J = 12.4\) Hz).

HRMS (ESI) (m/z): [M-H] Calcd for C\(_8\)H\(_3\)F\(_4\)O\(_2\)^-, 207.0075; Found 207.0080.
3,5-bis(trifluoromethyl)benzoic acid (19)

Method A: Reaction with 1-iodo-3,5-bis(trifluoromethyl)benzene resulted in 38.7 mg (75% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.46 (d, \(J = 2.0\) Hz, 2H), 8.28 (s, 1H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 164.9, 134.1, 131.4 (t, \(J = 33.5\) Hz), 129.7 (q, \(J = 3.8\) Hz), 126.6 – 125.3 (m), 123.2 (q, \(J = 272.7\) Hz).

\(^{19}\)F NMR (377 MHz, DMSO-\(d_6\)) \(\delta\) -62.47.

2-naphthoic acid (20)

Method A: Reaction with 2-iodonaphthalene resulted in 30.6 mg (89% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.18 (br s, 1H), 8.66 (s, 1H), 8.15 (d, \(J = 8.0\) Hz, 1H), 8.13 – 7.91 (m, 3H), 7.83 – 7.35 (m, 2H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 172.7, 140.1, 137.3, 135.8, 134.5, 133.5, 133.4, 133.3, 132.8, 132.0, 130.4.

terephthalic acid (21)

Method A: Reaction with 1,4-diiodobenzene (1.0 equiv., 0.2 mmol), potassium formate (3.0 equiv., 0.6 mmol), 4DPAIPN (1 mol%, 0.01 equiv.), Ni(PC\(_3\))\(_2\)Cl\(_2\) (10 mol%, 0.1 equiv.), dtbbpy (12 mol%, 0.12 equiv.). resulted in 21.6 mg (65% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 1:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 8.11 (s, 4H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.1, 134.9, 129.9.

3-((4-chloro-2-(2,4-dichlorophenoxy)phenoxy)methyl)benzoic acid (22)

Method A: Reaction with 2,4-dichloro-1-(5-chloro-2-((3-iodobenzyl)oxy)phenoxy)benzene resulted in 65.8 mg (78% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 1:1, with 5% AcOH).
\[^1\text{H}\text{ NMR}\ (500 \text{ MHz, DMSO-}d_6) \delta 12.88 \text{ (br s, 1H)}, 7.96 – 7.78 \text{ (m, 2H)}, 7.65 \text{ (t, } J = 2.7 \text{ Hz, 1H)}, 7.52 – 7.34 \text{ (m, 2H)}, 7.30 \text{ (dd, } J = 8.8, 2.5 \text{ Hz, 1H)}, 7.17 \text{ (dd, } J = 8.6, 2.2 \text{ Hz, 1H)}, 7.08 \text{ (dd, } J = 8.5, 2.4 \text{ Hz, 1H}), 6.80 \text{ (dd, } J = 8.9, 2.2 \text{ Hz, 1H}), 5.23 \text{ (d, } J = 2.1 \text{ Hz, 2H}).

\[^{13}\text{C} \text{ NMR}\ (126 \text{ MHz, DMSO-}d_6) \delta 167.5, 152.4, 150.6, 142.9, 137.2, 131.9, 131.4, 130.3, 130.2, 129.3, 129.0, 128.8, 128.5, 127.4, 123.7, 123.0, 121.8, 118.7, 115.8, 70.0.

**[1,1'-biphenyl]-4-carboxylic acid (24)**

Method A: Reaction with 4-iodo-1,1'-biphenyl resulted in 36.4 mg (92% yield) of the title product obtained as a colorless solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\[^1\text{H} \text{ NMR}\ (500 \text{ MHz, DMSO-}d_6) \delta 12.98 \text{ (br s, 1H)}, 8.33 – 7.96 \text{ (m, 2H)}, 7.84 – 7.67 \text{ (m, 4H)}, 7.51 \text{ (dd, } J = 8.4, 6.9 \text{ Hz, 2H}), 7.47 – 7.40 \text{ (m, 1H)}. 

\[^{13}\text{C} \text{ NMR}\ (126 \text{ MHz, DMSO-}d_6) \delta 167.6, 144.8, 139.5, 130.4, 130.1, 129.6, 128.8, 127.4, 127.3.

**4-phenoxybenzoic acid (25)**

Method B: Reaction with 1-bromo-4-phenoxybenzene resulted in 38.5 mg (90% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\[^1\text{H} \text{ NMR}\ (400 \text{ MHz, DMSO-}d_6) \delta 12.80 \text{ (br s, 1H)}, 8.14 – 7.70 \text{ (m, 2H)}, 7.57 – 7.40 \text{ (m, 2H)}, 7.25 \text{ (td, } J = 7.3, 1.1 \text{ Hz, 1H)}, 7.13 \text{ (dt, } J = 8.7, 1.2 \text{ Hz, 2H}), 7.09 – 6.91 \text{ (m, 2H)}.

\[^{13}\text{C} \text{ NMR}\ (126 \text{ MHz, DMSO-}d_6) \delta 172.0, 166.2, 160.3, 136.9, 135.5, 130.5, 129.9, 125.2, 122.4.

**3-morpholinobenzoic acid (26)**

Method B: Reaction with 4-(3-bromophenyl)morpholine resulted in 34.4 mg (83% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\[^1\text{H} \text{ NMR}\ (400 \text{ MHz, DMSO-}d_6) \delta 7.52 – 7.46 \text{ (m, 1H)}, 7.42 \text{ (d, } J = 7.5 \text{ Hz, 1H)}, 7.35 \text{ (t, } J = 7.9 \text{ Hz, 1H)}, 7.20 \text{ (dd, } J = 8.2, 2.4 \text{ Hz, 1H}), 3.75 \text{ (t, } J = 4.8 \text{ Hz, 4H}), 3.14 \text{ (t, } J = 4.8 \text{ Hz, 4H}).
$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 168.1, 151.5, 132.0, 129.6, 120.5, 119.9, 115.6, 66.5, 48.6.

3-(trifluoromethyl)benzoic acid (27)$^3$

Method B: Reaction with 1-bromo-3-(trifluoromethyl)benzene resulted in 36.5 mg (96% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.50 (br s, 1H), 8.45 – 8.14 (m, 2H), 8.02 (d, $J$ = 7.7 Hz, 1H), 7.96 – 7.61 (m, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 166.5, 133.6, 132.4, 130.5, 130.3 – 129.4 (m), 129.9 – 129.7 (m), 126.0 (d, $J$ = 4.2 Hz), 124.2 (q, $J$ = 272.2 Hz).

$^{19}$F NMR (377 MHz, DMSO-$d_6$) $\delta$ -61.52.

3-cyanobenzoic acid (28)$^3$

Method B: Reaction with 3-bromobenzonitrile resulted in 23.8 mg (81% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.35 – 8.22 (m, 2H), 8.11 (dt, $J$ = 7.7, 1.5 Hz, 1H), 7.74 (t, $J$ = 7.8 Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 166.2, 136.7, 134.2, 133.2, 132.6, 130.5, 118.5, 112.3.

3-(adamantan-1-yl)-4-methoxybenzoic acid (29)

Method B: Reaction with 1-(5-bromo-2-methoxyphenyl)adamantane resulted in 54.3 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.50 (br s, 1H), 7.81 (d, $J$ = 7.8 Hz, 2H), 7.05 (d, $J$ = 8.4 Hz, 1H), 3.87 (s, 2H), 2.04 (s, 8H), 1.73 (s, 5H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 167.9, 162.5, 137.6, 129.5, 128.0, 122.9, 112.1, 55.8, 40.5, 40.4, 39.4, 36.9, 36.9, 28.8.


4-benzoylbenzoic acid (30)$^3$
Method B: Reaction with (4-bromophenyl)(phenyl)methanone resulted in 37.5 mg (83% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.11 (dd, $J = 8.3$, 1.8 Hz, 2H), 7.86 – 7.81 (m, 2H), 7.80 – 7.76 (m, 2H), 7.75 – 7.70 (m, 1H), 7.59 (m, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 195.9, 167.2, 141.0, 137.0, 134.6, 133.6, 130.2, 130.1, 129.9, 129.2.

4-butoxybenzoic acid (31)$^{12}$

Method B: Reaction with 1-bromo-4-butoxybenzene resulted in 32.2 mg (83% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.61 (br s, 1H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.00 (d, $J = 8.5$ Hz, 2H), 4.03 (t, $J = 6.5$ Hz, 2H), 1.77 – 1.65 (m, 2H), 1.51 – 1.34 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 167.5, 162.8, 131.8, 123.2, 114.6, 67.9, 31.1, 19.1, 14.1.

4-((tetrahydro-2H-pyran-4-yl)oxy)benzoic acid (32)$^{12}$

Method B: Reaction with 1-bromo-4-butoxybenzene resulted in 31.1 mg (70% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.58 (br s, 1H), 7.88 (d, $J = 8.9$ Hz, 2H), 7.06 (d, $J = 8.9$ Hz, 2H), 4.69 (dt, $J = 8.8$, 4.5 Hz, 1H), 3.86 (dt, $J = 11.6$, 4.4 Hz, 2H), 3.50 (ddd, $J = 11.9$, 9.5, 2.8 Hz, 2H), 2.15 – 1.88 (m, 2H), 1.72 – 1.53 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 167.4, 161.1, 131.9, 123.3, 115.7, 72.0, 65.0, 32.1.

3,4,5-trimethoxybenzoic acid (33)$^{13}$
Method B: Reaction with 5-bromo-1,2,3-trimethoxybenzene resulted in 29.7 mg (70% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

H NMR (400 MHz, DMSO-\textit{d}6) δ 7.26 (s, 2H), 3.84 (s, 6H), 3.75 (s, 3H).

\(^{13}\)C NMR (101 MHz, DMSO-\textit{d}6) δ 167.4, 153.1, 141.8, 126.4, 107.0, 60.5, 56.4.

4-(2-((\textit{tert}-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)benzoic acid (34)

Method B: Reaction with methyl 3-(4-bromophenyl)-2-((\textit{tert}-butoxycarbonyl)amino)propanoate resulted in 45.2 mg (70% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 1:1).

\(^1\)H NMR (400 MHz, DMSO-\textit{d}6) δ 12.86 (br s, 1H), 7.86 (d, \(J = 8.1\) Hz, 2H), 7.36 (d, \(J = 8.1\) Hz, 2H), 4.23 (ddd, \(J = 10.2, 8.1, 5.1\) Hz, 1H), 3.62 (s, 3H), 3.08 (dd, \(J = 13.7, 5.0\) Hz, 1H), 2.93 (dd, \(J = 13.7, 10.2\) Hz, 1H), 1.32 (s, 9H).

\(^{13}\)C NMR (101 MHz, DMSO-\textit{d}6) δ 172.8, 167.6, 155.8, 143.4, 129.8, 129.7, 129.4, 78.8, 60.2, 55.2, 52.3, 28.5.

3-hydroxy-4-methoxybenzoic acid (35)

Method B: Reaction with 5-bromo-2-methoxyphenol in 31.9 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\textit{d}6) δ 12.48 (br s, 1H), 9.82 (s, 1H), 7.44 (d, \(J = 7.7\) Hz, 2H), 6.84 (d, \(J = 7.9\) Hz, 1H), 3.80 (s, 3H).

\(^{13}\)C NMR (126 MHz, DMSO-\textit{d}6) δ 167.7, 151.6, 147.7, 123.9, 122.0, 115.5, 113.2, 56.0.

4-(methylsulfonyl)benzoic acid (36)

Method B: Reaction with 1-bromo-4-(methylsulfonyl)benzene resulted in 24.0 mg (60% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1, with 5% AcOH).

\(^1\)H NMR (500 MHz, DMSO-\textit{d}6) δ 8.22 – 8.11 (m, 2H), 8.11 – 7.96 (m, 2H), 3.29 (s, 3H).

\(^{13}\)C NMR (126 MHz, DMSO-\textit{d}6) δ 166.7, 144.6, 136.0, 130.6, 127.7, 43.7.

4-vinylbenzoic acid (37)
Method B: Reaction with 1-bromo-4-vinylbenzene resulted in 28.1 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1, with 5% AcOH).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 12.83 (br s, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 6.24 (s, 1H), 5.96 (s, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 168.2, 142.0, 137.2, 128.6, 128.5, 128.4, 126.5.

4-methacrylamidobenzoic acid (38)$^{16}$

Method B: Reaction with resulted in 28.1 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.10 (s, 1H), 7.96 – 7.87 (m, 2H), 7.81 (d, $J = 8.8$ Hz, 2H), 5.84 (s, 1H), 5.57 (s, 1H), 1.96 (d, $J = 1.7$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 167.7, 167.4, 143.7, 140.6, 133.7, 130.6, 125.7, 121.1, 119.7, 19.1.

2-oxoindoline-5-carboxylic acid (39)$^{17}$

Method B: Reaction with $N$-(4-bromophenyl)methacrylamide resulted in 28.3 mg (80% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 10.75 (s, 1H), 7.84 (d, $J = 1.6$ Hz, 1H), 7.76 (d, $J = 1.6$ Hz, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 3.55 (s, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 177.2, 167.8, 148.4, 130.5, 126.4, 125.9, 124.0, 109.2, 36.0.

quinoline-6-carboxylic acid (40)$^9$

Method B: Reaction with 6-bromoquinoline resulted in 28.0 mg (81% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1)

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 13.31 (br s, 1H), 9.05 (dd, $J = 4.2$, 1.8 Hz, 1H), 8.71 (d, $J = 1.8$ Hz, 1H), 8.60 (dd, $J = 8.5$, 1.7 Hz, 1H), 8.25 (dd, $J = 8.8$, 1.9 Hz, 1H), 8.13 (d, $J = 8.8$ Hz, 1H), 7.65 (dd, $J = 8.3$, 4.2 Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 167.4, 153.1, 149.8, 138.0, 131.4, 129.8, 129.2, 129.0, 127.6, 122.7.
dibenzo[\(b,d\)]furan-2-carboxylic acid (41)\(^{18}\)

Method B: Reaction with 2-bromodibenzo[\(b,d\)]furan resulted in 40.3 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.10 (br s, 1H), 8.81 (d, \(J = 1.7\) Hz, 1H), 8.31 (dd, \(J = 7.8, 1.2\) Hz, 1H), 8.26 – 8.09 (m, 1H), 7.79 (dd, \(J = 17.2, 8.4\) Hz, 2H), 7.67 – 7.50 (m, 1H), 7.47 (t, \(J = 7.5\) Hz, 1H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.7, 158.4, 156.5, 129.5, 128.7, 126.5, 124.3, 124.1, 123.6, 122.2, 112.3, 112.1. (one carbon signal was overlapped).

dibenzo[\(b,d\)]thiophene-2-carboxylic acid (42)\(^{18}\)

Method B: Reaction with 2-bromodibenzo[\(b,d\)]thiophene resulted in 43.8 mg (96% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH)

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 8.94 (d, \(J = 1.7\) Hz, 1H), 8.65 – 8.44 (m, 1H), 8.32 – 8.01 (m, 3H), 7.58 (ddd, \(J = 6.7, 4.3, 1.7\) Hz, 2H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.9, 143.7, 139.4, 135.5, 135.1, 128.1 (2C), 127.9, 125.6, 123.6 (2C), 123.5, 122.9.

2-methoxypyrimidine-5-carboxylic acid (43)\(^{19}\)

Method B: Reaction with 2-bromodibenzo[\(b,d\)]thiophene resulted in 43.8 mg (96% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 1:1)

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 9.04 (s, 2H), 4.00 (s, 3H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 161.6, 133.6, 132.7, 132.5 (2C), 55.9.

benzo[\(b\)]thiophene-5-carboxylic acid (44)\(^{3}\)

Method B: Reaction with 5-bromobenzo[\(b\)]thiophene resulted in 30.3 mg (79% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1)

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 13.00 (br s, 1H), 8.54 (d, \(J = 1.5\) Hz, 1H), 8.13 (d, \(J = 8.4\) Hz, 1H), 8.06 – 7.77 (m, 2H), 7.63 (d, \(J = 5.5\) Hz, 1H).

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 168.1, 143.8, 139.8, 129.4, 127.6, 125.7, 125.1, 124.9, 123.2.
3-phenylacrylic acid (45)\(^3\)

\[
\text{Method B: Reaction with (2-bromovinyl)benzene (Z/E = 16:84) resulted in 23.7 mg (79% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 5:1)}
\]

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 12.51 (br s, 1H), 7.77 – 7.63 (m, 2.42H), 7.66 – 7.55 (m, 1H), 7.47 – 7.40 (m, 1.36H), 7.40 – 7.28 (m, 2H), 6.91 (d, \(J = 12.7\) Hz, 1H) (\(E\)), 6.54 (d, \(J = 16.0\) Hz, 0.43H) (\(Z\)), 5.97 (d, \(J = 12.7\) Hz, 1H) (\(E\)). (\(Z/E = 30:70\)).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 168.1, 168.0, 144.4, 140.7, 135.3, 134.7, 130.7, 130.0, 129.4, 129.2, 128.7, 128.5, 121.6, 119.7.

1\(H\)-indene-2-carboxylic acid (46)\(^3\)

\[
\text{Method B: Reaction with 2-bromo-1\(H\)-indene resulted in 30.4 mg (95% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1)}
\]

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 12.52 (br s, 1H), 7.70 (d, \(J = 2.1\) Hz, 1H), 7.60 (dd, \(J = 5.5, 3.2\) Hz, 1H), 7.55 (dd, \(J = 5.3, 3.3\) Hz, 1H), 7.35 (dd, \(J = 5.6, 3.1\) Hz, 2H), 3.64 (d, \(J = 1.9\) Hz, 2H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 166.2, 145.1, 143.1, 140.6, 138.9, 127.7, 127.2, 124.8, 123.8, 38.6.

cyclohex-1-ene-1-carboxylic acid (47)\(^3\)

\[
\text{Method B: Reaction with 1-bromocyclohex-1-ene resulted in 20.2 mg (80% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1)}
\]

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 12.07 (br s, 1H), 6.86 (q, \(J = 3.0, 2.2\) Hz, 1H), 2.29 – 1.93 (m, 4H), 1.77 – 1.34 (m, 4H).

\(^13\)C NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 168.7, 139.2, 130.8, 25.6, 24.3, 22.2, 21.5.

1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-carboxylic acid (48)\(^3\)

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S25
Method B: Reaction with 1-bromocyclohex-1-ene resulted in 20.2 mg (80% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1)

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 12.17 (br, 1H), 7.35 – 7.17 (m, 5H), 6.98 – 6.92 (m, 1H), 2.84 – 2.68 (m, 1H), 2.49 – 2.15 (m, 4H), 1.97 – 1.85 (m, 1H), 1.79 – 1.60 (m, 1H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 168.5, 146.5, 138.9, 130.6, 128.8, 127.2, 126.6, 38.9, 33.6, 29.6, 25.0.

(8$S$,9$S$,10$R$,13$S$,14$S$,17$R$)-17-acetyl-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthrene-3-carboxylic acid (49)

Method B: Reaction with 1-((8$S$,9$S$,10$R$,13$S$,14$S$,17$R$)-3-bromo-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-17-yl)ethan-1-one resulted in 53.4 mg (75% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 12.09 (br s, 1H), 6.97 (d, $J$ = 2.3 Hz, 1H), 5.87 (t, $J$ = 3.9 Hz, 1H), 3.00 – 2.78 (m, 1H), 2.43 (dd, $J$ = 18.3, 5.3 Hz, 1H), 2.31 (dt, $J$ = 19.6, 5.4 Hz, 1H), 1.97 (d, $J$ = 1.5 Hz, 3H), 1.92 – 1.59 (m, 9H), 1.46 (qd, $J$ = 13.2, 4.0 Hz, 1H), 1.35 – 1.16 (m, 3H), 1.14 – 1.03 (m, 2H), 0.97 (d, $J$ = 1.6 Hz, 3H), 0.89 (d, $J$ = 1.6 Hz, 3H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 212.2, 168.9, 141.0, 137.8, 131.5, 126.4, 60.6, 50.9, 47.7, 45.3, 34.9, 34.6, 33.4, 32.9, 32.6, 31.7, 25.9, 24.3, 21.9, 21.5, 21.0, 20.7, 19.1.

HRMS (ESI) (m/z): [M+H]$^+$ Calcd for C$_{22}$H$_{31}$O$_3$, 343.2268; Found 343.2275.

4-(N,N-dipropylsulfamoyl)benzoic acid (56)$^{24}$

Method A: Reaction with 4-bromo-N,N-dipropylbenzenesulfonamide resulted in 49.6 mg (87% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.04 (br s, 1H), 7.57 (dd, $J$ = 105.6, 7.9 Hz, 4H), 2.60 (t, $J$ = 7.5 Hz, 4H), 1.01 (q, $J$ = 7.5 Hz, 4H), 0.35 (t, $J$ = 7.3 Hz, 6H).
$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 166.2, 143.2, 134.3, 130.2, 127.0, 49.6, 21.6, 11.0.

**4-(1-(4-sulfamoylphenyl)-3-(trifluoromethyl)-1H-pyrazol-5-yl)benzoic acid (57)**

Method A: Reaction with 4-bromo-$N,N$-dipropylbenzenesulfonamide resulted in 49.6 mg (87% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.16 (br s, 1H), 7.98 – 7.93 (m, 1H), 7.91 – 7.86 (m, 2H), 7.61 – 7.51 (m, 3H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.37 (s, 1H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 167.1, 144.6 (d, $J = 6.0$ Hz), 143.4 – 142.1 (m), 141.5 – 141.2 (m), 132.7, 131.8, 130.4, 130.1, 129.6, 127.4, 126.5, 123.0, 107.5.

$^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -60.89.

**3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)benzoic acid (58)**

Method A: Reaction with 3-(3-bromophenyl)-5-(2-fluorophenyl)-1,2,4-oxadiazole resulted in 43.7 mg (77% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1).

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.34 (t, $J = 1.9$ Hz, 1H), 8.24 – 7.98 (m, 2H), 7.98 – 7.74 (m, 1H), 7.67 – 7.45 (m, 2H), 7.43 – 6.77 (m, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 177.2, 164.8, 162.5, 160.5, 137.0, 135.4, 133.6 (d, $J = 8.6$ Hz), 132.3, 131.1, 127.6, 126.9 (d, $J = 9.2$ Hz), 124.4 (d, $J = 3.8$ Hz), 122.2, 117.3, 117.1.

$^{19}$F NMR (471 MHz, DMSO-$d_6$) δ -111.98.

**2-(3,5-dichlorophenyl)benzo[d]oxazole-6-carboxylic acid (59)**

Method A: Reaction with 6-bromo-2-(3,5-dichlorophenyl)benzo[d]oxazole resulted in 49.8 mg (65% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.30 (d, $J = 1.5$ Hz, 1H), 8.18 (d, $J = 1.9$ Hz, 2H), 8.04 (d, $J = 1.5$ Hz, 1H), 8.00 – 7.91 (m, 2H).

$^{13}$C NMR (126 MHz, DMSO) δ 170.1, 167.1, 162.6, 150.6, 145.2, 135.7, 133.6, 132.8, 126.4, 120.5, 112.7. (one carbon signal was overlapped).
5. Gram-Scale Reactions

A. Synthesis of [1,1'-biphenyl]-4-carboxylic acid:

\[
\begin{align*}
\text{Ph} & \quad \text{Br} & + & \text{HCOONa} & \underset{4\text{DPAIPN (0.5 mol%), Ni(PPh}_3\text{)_2Cl}_2 (5 \text{ mol%})}{\text{dtbbpy (6 mol%), TBAI (10 mol%)}} \\
10 \text{ mmol} & & 15 \text{ mmol} & & \text{DMA (100 mL), r.t., 24 h} \\
\text{Ph} & \quad \text{COOH} & & & \text{92%, 1.82 g}
\end{align*}
\]

In the air, a 200 mL transparent Schlenk tube equipped with a magnetic stirrer was charged with 4-bromo-1,1'-biphenyl (1.0 equiv., 10 mmol), sodium formate (1.5 equiv., 15 mmol), 4DPAIPN (0.5 mol%), Ni(PPh$_3)_2$Cl$_2$ (5 mol%), TBAI (10 mol%), dtbbpy (6 mol%). The test tube was evacuated and backfilled with argon for three times, then DMA (100 mL) were added. The reaction was irradiated with 3 of the 440 nm Kessil lamps and 1 fans for 24 h. The reaction mixture was diluted with ethyl acetate, washed with 2 N HCl, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the target product.

B. Synthesis of [1,1'-biphenyl]-4-carboxylic acid:

\[
\begin{align*}
\text{Et}_2\text{N}-\text{SO}_3 & \quad \text{HBr} & + & \text{HCOONa} & \underset{4\text{DPAIPN (0.5 mol%), Ni(PPh}_3\text{)_2Cl}_2 (5 \text{ mol%})}{\text{dtbbpy (6 mol%), TBAI (10 mol%)}} \\
5 \text{ mmol} & & 7.5 \text{ mmol} & & \text{DMA (50 mL), r.t., 24 h} \\
\text{Et}_2\text{N}-\text{SO}_3 & \quad \text{COOH} & & & \text{Et}_2\text{N}-\text{SO}_3 \text{Probencid} & \text{1.12g, 80%}
\end{align*}
\]

In the air, a 100 mL transparent Schlenk tube equipped with a magnetic stirrer was charged with 4-bromo-N,N-dipropylbenzenesulfonamide (1.0 equiv., 5 mmol), sodium formate (1.5 equiv., 7.5 mmol), 4DPAIPN (0.5 mol%), Ni(PPh$_3)_2$Cl$_2$ (5 mol%), TBAI (5 mol%), dtbbpy (6 mol%). The test tube was evacuated and backfilled with argon for three times, then DMA (50 mL) were added. The reaction was irradiated with 3 of the 440 nm Kessil lamps and 1 fans for 24 h. The reaction mixture was diluted with ethyl acetate, washed with 2N HCl, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the target product.
6. \(^{13}\text{C}\)-Labeling Experiments

**General Procedure C for Carboxylation of \(^{13}\text{C}\)-labeling:** In the air, a 10 mL transparent Schlenk tube equipped with a magnetic stirrer was charged with aryl bromide (1.0 equiv., 0.2 mmol) (if solid), sodium formate-\(^{13}\text{C}\) (1.5 equiv., 0.3 mmol), 4DPAIPN (1 mol%, 0.01 equiv.), Ni(PPh\(_3\))\(_2\)Cl\(_2\) (5 mol%, 0.05 equiv.), TBAI (10 mol%, 0.1 equiv.), dtbbpy (6 mol%, 0.06 equiv.). The test tube was evacuated and backfilled with argon for three times, then aryl bromide (1.0 equiv., 0.2 mmol) (if liquid) and DMA (2 mL) were added and the mixture was stirred under irradiation with 440 nm blue LEDs, maintained at room temperature (28 ± 2 °C) for 20 h. The reaction mixture was diluted with ethyl acetate, washed with 2 N HCl, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the target product.

**4-((\text{tert-butoxycarbonyl})(\text{methyl})amino)benzoic acid-\(^{13}\text{C}\) (50)**\(^{21}\)

\[
\text{Boc} - \text{N}^{13}\text{C} - \text{OH}
\]

Method C: Reaction with \text{tert}-butyl (4-bromophenyl)carbamate resulted in 36.2 mg (76% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1).

\(^1\text{H}\) NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 12.18 (br s, 1H), 9.30 (s, 1H), 7.68 – 7.28 (m, 2H), 7.12 (d, \(J = 8.3\) Hz, 2H), 1.03 (s, 9H).

\(^{13}\text{C}\) NMR (126 MHz, DMSO-\(d_6\)) \(\delta\) 167.1, 152.6, 143.8, 130.38 (d, \(J = 3.0\) Hz), 123.94 (d, \(J = 73.4\) Hz), 117.21 (d, \(J = 4.3\) Hz), 79.7, 28.0.

**4-amino-3,5-dichlorobenzoic acid-\(^{13}\text{C}\) (51)**

\[
\text{Cl} - \text{N}^{13}\text{C} - \text{OH}
\]

Method C: Reaction with 4-bromo-2,6-dichloroaniline resulted in 24.0 mg (61% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1).

\(^1\text{H}\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.78 (s, 1H), 7.72 (d, \(J = 4.0\) Hz, 2H), 6.32 (s, 2H).

\(^{13}\text{C}\) NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 166.0, 145.6, 131.9 (d, \(J = 9.7\) Hz), 129.2 (d, \(J = 11.8\) Hz), 119.3, 118.6, 117.6 (d, \(J = 6.6\) Hz).

HRMS (ESI) (m/z): [M-H] \text{Calcd for C}_6\text{H}_5\text{Cl}_2\text{NO}_2\text{,} 204.9658; \text{Found} 204.9662.

**3,4-dimethoxybenzoic acid-\(^{13}\text{C}\) (52)**\(^{22}\)
Method C: Reaction with 4-bromo-1,2-dimethoxybenzene and sodium formate-$^{13}$C resulted in 28.5 mg (78% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1 with 5% AcOH).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 7.56 (m, 1H), 7.44 (dd, $J = 4.2$, 2.0 Hz, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 3.81 (d, $J = 12.6$ Hz, 6H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 167.8, 165.1, 152.9, 148.7, 123.5, 112.3 (d, $J = 3.6$ Hz), 111.4 (d, $J = 5.3$ Hz), 56.1, 55.9.

2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylic acid-$^{13}$C (53)$^{23}$

Method C: Reaction with 6-bromo-2,3-dihydrobenzo[b][1,4]dioxine and sodium formate-$^{13}$C resulted in 28.6 mg (79% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 7.75 – 7.20 (m, 2H), 6.94 (dd, $J = 8.4$, 1.6 Hz, 1H), 4.64 – 3.88 (m, 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 172.1, 152.6, 148.2 (2C), 128.1, 123.3 (d, $J = 2.7$ Hz), 122.2 (d, $J = 5.1$ Hz), 69.6, 69.1.

6-bromo-2-naphthoic acid-$^{13}$C (54)

Method A: Reaction with 2,6-dibromonaphthalene resulted in 40.5 mg (81% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1, with 5% AcOH).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.64 (d, $J = 4.7$ Hz, 1H), 8.32 (d, $J = 1.9$ Hz, 1H), 8.11 (d, $J = 8.7$ Hz, 1H), 8.02 (s, 2H), 7.74 (dd, $J = 8.8$, 1.9 Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 167.6, 136.5, 131.9, 131.2, 131.2, 131.0 (d, $J = 2.6$ Hz), 130.3, 130.1, 127.9 (d, $J = 4.3$ Hz), 126.8 (d, $J = 2.9$ Hz), 122.3.

HRMS (ESI) (m/z): [M-H]$^-$ Calcd for C$_{10}^{13}$CH$_6$BrO$_2^-$, 249.9590; Found 249.9593.

4-(3,3-dimethylbutanamido)-3,5-difluorobenzoic acid-$^{13}$C (55)$^{23}$

Method A: Reaction with N-(4-bromo-2,6-difluorophenyl)-3,3-dimethylbutanamide resulted in 40.3 mg (74% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1).
$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.85 (s, 1H), 8.26 – 6.48 (m, 2H), 2.26 (s, 2H), 1.05 (s, 9H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 170.1, 165.7, 158.8, 156.3, 131.9 (d, $J = 9.8$ Hz), 129.2 (d, $J = 12.0$ Hz), 119.3 (t, $J = 17.3$ Hz), 113.0 (d, $J = 24.0$ Hz), 48.8, 31.1, 29.9.

$^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ -115.38.

4-bromobenzoic acid -$^{13}$C (61)$^8$

Method C: Reaction with 1-bromo-4-iodobenzene resulted in 32.8 mg (82% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 3:1).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 13.19 (br s, 1H), 8.03 – 7.79 (m, 2H), 7.72 (d, $J = 8.4$ Hz, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 167.1, 132.2, 132.1, 131.7 (d, $J = 2.8$ Hz), 130.7, 130.2, 127.4.

4-bromo-$N$-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)benzamide -$^{13}$C (62)$^5$

Under an atmosphere of argon, 5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-amine (1.0 equiv., 1.0 mmol) was dissolved in CH$_2$Cl$_2$ (0.1 M) before N-methyl morpholine (4.0 equiv., 4.0 mmol), HOBt•H$_2$O (2.0 equiv., 2.0 mmol), EDC (2.0 equiv. 2.0 mmol) and lastly [$^{13}$C]-4-bromoenzoic acid (1.0 equiv., 1.0 mmol) were added. The mixture was stirred at room temperature for 20 hours, at which point TLC analysis indicated full conversion of the amine. Diethyl ether (50 mL) and hydrochloric acid (0.5 M) was added and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 50 mL) before the combined organic phases were dried over MgSO$_4$, filtered and concentrated in vacuo to leave a solid crude. The pure product was obtained as a colorless solid (293.4 mg, 76%) by flash column chromatography (petroleum ether/ethyl acetate = 10:1).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 7.91 (dd, $J = 8.5$, 3.7 Hz, 2H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.67 (t, $J = 2.9$ Hz, 1H), 7.56 (s, 1H), 7.28 (d, $J = 8.6$ Hz, 1H), 1.64 (s, 4H), 1.24 (d, $J = 6.2$ Hz, 12H).
$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 164.6 (d, $J = 10.9$ Hz), 145.0, 140.5, 136.8, 131.8 (d, $J = 3.9$ Hz), 130.2 (d, $J = 2.8$ Hz), 126.9, 125.7, 118.7 (d, $J = 13.0$ Hz), 118.6, 118.5, 35.1, 35.0, 34.5, 34.0, 32.1 (2C), 32.1 (2C).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 167.3, 165.0, 145.0, 140.5, 136.9, 133.5, 132.5 (d, $J = 3.0$ Hz), 129.7, 128.3 (2C), 127.0, 118.7 (d, $J = 25.9$ Hz), 37.9, 35.1, 35.0 (2C), 34.5, 34.0, 32.1 (2C).

4-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ylcarbamoyl)benzoic acid-$[^{13}\text{C}_2]$ (63)$^5$

Method C: Reaction with 4-bromo-N-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)benzamide-$^{13}$C (63) resulted in 56.5 mg (80% yield) of the title product obtained as a white solid. (Eluent: petroleum ether/ethyl acetate = 2:1)

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 10.09 (s, 1H), 7.84 (dd, $J = 8.6, 3.6$ Hz, 2H), 7.65 (t, $J = 2.9$ Hz, 1H), 7.55 (dt, $J = 8.5, 2.9$ Hz, 1H), 7.25 (d, $J = 8.6$ Hz, 1H), 6.86 (dd, $J = 8.8, 2.5$ Hz, 2H), 1.64 (s, 4H), 1.23 (d, $J = 6.4$ Hz, 12H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 167.3, 165.0, 145.0, 140.5, 136.9, 133.5, 132.5 (d, $J = 3.0$ Hz), 129.7, 128.3 (2C), 127.0, 118.7 (d, $J = 25.9$ Hz), 37.9, 35.1, 35.0 (2C), 34.5, 34.0, 32.1 (2C).
7. Preliminary mechanistic studies

7.1 Reactions in Different Gas Atmospheres

A. The reaction under CO$_2$ atmosphere

In the air, a 10 mL transparent Schlenk tube equipped with a magnetic stirrer was charged with 4-iodo-1,1'-biphenyl (1.0 equiv., 0.2 mmol), sodium formate-$^{13}$C (1.5 equiv., 0.3 mmol), 4DPAIPN (1 mol%, 0.01 equiv.), Ni(PCy$_3$)$_2$Cl$_2$ (5 mol%, 0.05 equiv.), dtbbpy (6 mol%, 0.06 equiv.). The test tube was evacuated and backfilled with CO$_2$ for three times, then DMA (2 mL) were added and the mixture was stirred under irradiation with 440 nm blue LEDs, maintained at room temperature (28 ± 2 °C) for 20 h. The reaction mixture was diluted with ethyl acetate, washed with 2 N HCl, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford white solid in 87% yield. The $^{13}$C-content was determined to be 99% by HRMS (ESI).

[1,1'-biphenyl]-4-carboxylic acid-$^{13}$C (24)

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 13.02 (s, 1H), 8.07 (dd, $J = 8.3, 3.9$ Hz, 2H), 7.96 – 7.61 (m, 4H), 7.48 (dt, $J = 30.8, 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 167.6, 144.8, 139.5, 130.4 (d, $J = 2.8$ Hz), 129.7, 129.5, 128.7, 127.4, 127.3 (d, $J = 4.4$ Hz).

Figure S2. HRMS (ESI) spectra
B. The reaction under CO atmosphere

![Reaction Diagram]

**Figure S3.** HRMS (ESI) spectra
7.2 Radical Trap Experiments

![Reaction Scheme]

**Figure S4.** HRMS (ESI) spectra of the mixture reaction system (7.2-C)

**Figure S5.** $^1$H NMR spectra of 65

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65 - H$^+$ Detected by ESI-HRMS
Calculated (m/z): 225.0921
Found (m/z): 225.0919
Figure S6. The crude NMR spectra of the mixture reaction system (7.2-C) using diphenylmethane as an internal standard.

7.2 Stoichiometric Reaction of Isolated Ni(II) Complex

A. Preparation of the complex 66. 29

B. Stoichiometric reaction of isolated Ni(II) complex

7.3 Stern-Volmer Emission Quenching
Fluorescence quenching experiments were measured on a F-4600 FL Spectrophotometer with a 4 mL quartz cuvette with a cap. Anhydrous DMA was degassed by Ar bubbling before using. 4DPAIPN was irradiated at 435 nm and the emission intensity at about 525 nm was observed. In a typical experiment, the emission spectrum of a 2.5*10^{-5} M solution of 4DPAIPN in DMA was collected.

4-Iodobiphenyl 1: A stock solution of 1 (0.1 M) was prepared. Then, different amounts of this stock solution were added to 2 mL of 4DPAIPN in DMA (2.5*10^{-5} M).

HCOONH₄: A stock solution of HCOONH₄ (0.15 M) was prepared. Then, different amounts of this stock solution were added to 2 mL of 4DPAIPN in DMF (2.5*10^{-5} M).

1 + Ni(PCy₃)₂Cl₂ + dtbbpy: A stock solution of 1 (56 mg, 0.2 mmol) with Ni(PCy₃)₂Cl₂ (6.9 mg, 5 mmol%) and dtbbpy (3.2 mg, 6 mol%) in 2 mL of DMA was prepared. Then, different amounts of this stock solution were added to 2 mL of 4DPAIPN in DMA (5*10^{-5} M).

Note: TBA-formate was used instead of Na-formate because of poor solubility of the sodium counter ion.

Figure S7: Steady-state Stern–Volmer experiment of 1.
Figure S8: Steady-state Stern–Volmer experiment of HCOONH₄.

Figure S9: Steady-state Stern–Volmer experiment of 1 + Ni(PCy₃)₂Cl₂ + dtbbpy.
Figure S10: Stern-Volmer plots in comparison.

**Comment**: the data in Figures show that HCOONH$_4$ can quench the fluorescence of the 4DPAIPN species, whereas 4-Iodobiphenyl 1 does not significantly modify the emission profile of the photocatalyst.
8. References
8. NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) spectra of 1-((3-bromobenzyl)oxy)-4-chloro-2-(2,4-dichlorophenoxy)benzene (S1)

$^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 1-((3-bromobenzyl)oxy)-4-chloro-2-(2,4-dichlorophenoxy)benzene (S1)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) spectra of 1-((8S,9S,10R,13S,14S,17S)-3-bromo-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1\(H\)-cyclopenta[a]phenanthren-17-yl)ethan-1-one\(^1\) (S2)

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) spectra of 1-((8S,9S,10R,13S,14S,17S)-3-bromo-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1\(H\)-cyclopenta[a]phenanthren-17-yl)ethan-1-one (S2)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of 4-(5-(4-bromophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (S3)

$^{13}$C NMR (101 MHz, CDCl$_3$) spectra of 4-(5-(4-bromophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (S3)
$^{19}$F NMR (377 MHz, CDCl$_3$) spectra of 4-(5-(4-bromophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (S3)

$^1$H NMR (400 MHz, CDCl$_3$) spectra of N-(4-bromophenyl)methacrylamide (S4)
$^{13}$C NMR (101 MHz, CDCl$_3$) spectra of $N$-(4-bromophenyl)methacrylamide (S4)

$^1$H NMR (400 MHz, CDCl$_3$) spectra of methyl [1,1'-biphenyl]-4-carboxylate (3)
$^{13}$C NMR (101 MHz, CDCl$_3$) spectra of methyl [1,1'-biphenyl]-4-carboxylate (3)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-methylbenzoic acid (4):
$^{13}$C NMR (126 MHz, DMSO-d$_6$) spectra of 4-methylbenzoic acid (4):

$^1$H NMR (400 MHz, DMSO-d$_6$) spectra of 4-(tert-butyl)benzoic acid (5):
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-$(tert$-butyl)benzoic acid (5)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-methoxybenzoic acid (6)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-methoxybenzoic acid (6)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 3,5-dimethylbenzoic acid (7)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3,5-dimethylbenzoic acid (7)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-bromobenzoic acid (8)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-bromobenzoic acid (8)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-chlorobenzoic acid (9)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-chlorobenzoic acid (9)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-fluorobenzoic acid (10)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-fluorobenzoic acid (10)

$^{13}$F NMR (377 MHz, DMSO-$d_6$) spectra of 4-fluorobenzoic acid (10)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (11)

$^{13}$C NMR (126 MHz, DMSO) spectra of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (11)
$^1\text{H}$ NMR (500 MHz, DMSO-$d_6$) spectra of 4-(methylthio)benzoic acid (12)

$^{13}\text{C}$ NMR (126 MHz, DMSO-$d_6$) spectra of 4-(methylthio)benzoic acid (12)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-formylbenzoic acid (13)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-formylbenzoic acid (13)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-(methoxycarbonyl)benzoic acid (14)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-(methoxycarbonyl)benzoic acid (14)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-acetylbenzoic acid (15)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-acetylbenzoic acid (15)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-hydroxybenzoic acid (16)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-hydroxybenzoic acid (16)
\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) spectra of 4-carbamoylbenzoic acid (17)

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) spectra of 4-carbamoylbenzoic acid (17)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-fluoro-3-(trifluoromethyl)benzoic acid (18)

$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-fluoro-3-(trifluoromethyl)benzoic acid (18)
$^{19}\text{F NMR (377 MHz, DMSO-$d_6$) spectra of 4-fluoro-3-(trifluoromethyl)benzoic acid (18)}$

$^{1}\text{H NMR (500 MHz, DMSO-$d_6$) spectra of 3,5-bis(trifluoromethyl)benzoic acid (19)}$
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3,5-bis(trifluoromethyl)benzoic acid (19)

$^{19}$F NMR (377 MHz, DMSO-$d_6$) spectra of 3,5-bis(trifluoromethyl)benzoic acid (19)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 2-naphthoic acid (20)

$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 2-naphthoic acid (20)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of terephthalic acid (21)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of terephthalic acid (21)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 3-((4-chloro-2-(2,4-dichlorophenoxy)phenoxy)methyl)benzoic acid (22)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3-((4-chloro-2-(2,4-dichlorophenoxy)phenoxy)methyl)benzoic acid (22)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of [1,1'-biphenyl]-4-carboxylic acid (24)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of [1,1'-biphenyl]-4-carboxylic acid (24)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of [1,1'-biphenyl]-4-carboxylic acid-$^{13}$C (24)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of [1,1'-biphenyl]-4-carboxylic acid-$^{13}$C (24)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-phenoxbenzoic acid (25)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-phenoxbenzoic acid (25)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 3-morpholinobenzoic acid (26)

$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 3-morpholinobenzoic acid (26)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 3-(trifluoromethyl)benzoic acid (27)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3-(trifluoromethyl)benzoic acid (27)
$^{19}$F NMR (377 MHz, DMSO-$d_6$) spectra of 3-(trifluoromethyl)benzoic acid (27)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 3-cyanobenzoic acid (28)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 3-cyanobenzoic acid (28)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 3-((3r,5r,7r)-adamantan-1-yl)-4-methoxybenzoic acid (29)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3-((3$r$,5$r$,7$r$)-adamantan-1-yl)-4-methoxybenzoic acid (29)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-benzoylbenzoic acid (30)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-benzoylbenzoic acid (30)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-butoxybenzoic acid (31)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-butoxybenzoic acid (31)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-((tetrahydro-2H-pyran-4-yl)oxy)benzoic acid (32)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-((tetrahydro-2H-pyran-4-yl)oxy)benzoic acid (32)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 3,4,5-trimethoxybenzoic acid (33)
$^{13}\text{C} \text{ NMR (101 MHz, DMSO-$d_6$)}$ spectra of 3,4,5-trimethoxybenzoic acid (33)

$^1\text{H} \text{ NMR (400 MHz, DMSO-$d_6$)}$ spectra of 4-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)benzoic acid (34)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)benzoic acid (34)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 3-hydroxy-4-methoxybenzoic acid (35)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3-hydroxy-4-methoxybenzoic acid (35)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-(methylsulfonyl)benzoic acid (36)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-(methylsulfonyl)benzoic acid (36)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-vinylbenzoic acid (37)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-vinylbenzoic acid (37)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-methacrylamidobenzoic acid (38)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-methacrylamidobenzoic acid (38)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 2-oxoindoline-5-carboxylic acid (39)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 2-oxoindoline-5-carboxylic acid (39)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of quinoline-6-carboxylic acid (40)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of quinoline-6-carboxylic acid (40)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of dibenzo[b,d]furan-2-carboxylic acid (41)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of dibenzo[$b,d$]furan-2-carboxylic acid (41)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of dibenzo[$b,d$]thiophene-2-carboxylic acid (42)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of dibenzo[$b,d$]thiophene-2-carboxylic acid (42)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 2-methoxypyrimidine-5-carboxylic acid (43)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 2-methoxypyrimidine-5-carboxylic acid (43)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of benzo[b]thiophene-5-carboxylic acid (44)
$^{13}$C NMR (126 MHz, DMSO) spectra of benzo[b]thiophene-5-carboxylic acid (44)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 3-phenylacrylic acid (45)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3-phenylacrylic acid (45)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 1H-indene-2-carboxylic acid (46)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of $^1H$-indene-2-carboxylic acid (46)

\[\text{[Graph of $^{13}$C NMR spectrum]}\]

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of cyclohex-1-ene-1-carboxylic acid (47)

\[\text{[Graph of $^1$H NMR spectrum]}\]
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of cyclohex-1-ene-1-carboxylic acid (47)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-carboxylic acid (48)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-carboxylic acid (48)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of (8S,9S,10R,13S,14S,17R)-17-acetyl-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthrene-3-carboxylic acid (49)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of (8S,9S,10R,13S,14S,17R)-17-acetyl-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthrene-3-carboxylic acid (49)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-((tert-butoxycarbonyl)(methyl)amino)benzoic acid-$^{13}$C (50)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-((tert-butoxycarbonyl)(methyl)amino)benzoic acid-$^{13}$C (50)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-amino-3,5-dichlorobenzoic acid-$^{13}$C (51)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-amino-3,5-dichlorobenzoic acid-$^{13}$C (51)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 3,4-dimethoxybenzoic acid-$^{13}$C (52)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3,4-dimethoxybenzoic acid-$^{13}$C (52)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylic acid-$^{13}$C (53)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylic acid-$^{13}$C (53)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 6-bromo-2-naphthoic acid-$^{13}$C (54)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 6-bromo-2-naphthoic acid-$^{13}$C (54)

$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoic acid-$^{13}$C (55)
$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoic acid.$^{13}$C (55)

$^{19}$F NMR (377 MHz, DMSO-$d_6$) spectra of 4-(3,3-dimethylbutanamido)-3,5-difluorobenzoic acid.$^{13}$C (55)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-($N,N$-dipropylsulfamoyl)benzoic acid (56)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-($N,N$-dipropylsulfamoyl)benzoic acid (56)
$^1$H NMR (400 MHz, DMSO-$d_6$) spectra of 4-(1-(4-sulfamoylphenyl)-3-(trifluoromethyl)-1H-pyrazol-5-yl)benzoic acid (57)

$^{13}$C NMR (101 MHz, DMSO-$d_6$) spectra of 4-(1-(4-sulfamoylphenyl)-3-(trifluoromethyl)-1H-pyrazol-5-yl)benzoic acid (57)
$^{19}$F NMR (377 MHz, DMSO-$d_6$) spectra of 4-(1-(4-sulfamoylphenyl)-3-(trifluoromethyl)-1H-pyrazol-5-yl)benzoic acid (57)

$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)benzoic acid (58)
$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)benzoic acid (58)

$^{19}$F NMR (471 MHz, DMSO-$d_6$) spectra of 3-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)benzoic acid (58)
$^1$H NMR (500 MHz, DMSO-$_d_6$) spectra of 2-(3,5-dichlorophenyl)benzo[\textit{d}]oxazole-6-carboxylic acid (59)

$^{13}$C NMR (126 MHz, DMSO-$_d_6$) spectra of 2-(3,5-dichlorophenyl)benzo[\textit{d}]oxazole-6-carboxylic acid (59)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-bromobenzoic acid -$^{13}$C (61)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-bromobenzoic acid -$^{13}$C (61)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 4-bromo-N-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)benzamide.$^{13}$C (62)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 4-bromo-N-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl)benzamide.$^{13}$C (62)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of $4$-($5,5,8,8$-tetramethyl-$5,6,7,8$-tetrahydronaphthalen-2-ylcarbamoyl)benzoic acid-[$^{13}$C$_2$] (63)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of $4$-($5,5,8,8$-tetramethyl-$5,6,7,8$-tetrahydronaphthalen-2-ylcarbamoyl)benzoic acid-[$^{13}$C$_2$] (63)
$^1$H NMR (500 MHz, DMSO-$d_6$) spectra of 3,3-diphenylpropanoic acid (65)

$^{13}$C NMR (126 MHz, DMSO-$d_6$) spectra of 3,3-diphenylpropanoic acid (65)