Supporting Information for

**Brønsted acid-catalyzed homogeneous O-H and S-H insertion reactions under metal- and ligand-free conditions**

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1. General considerations

All reactions and manipulations were performed using standard Schlenk techniques. 

$^1$H and $^{13}$C{${^1}$H} NMR spectra were recorded on a Bruker DRX-400 MHz spectrometer and all chemical shift values refer to CDCl$_3$ ($\delta(^1$H), 7.26 ppm; $\delta(^{13}$C), 77.16 ppm), (CD$_3$)$_2$SO ($\delta(^1$H), 2.50 ppm, $\delta(^{13}$C), 39.52 ppm). X-ray Crystallographic analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The GC analysis was obtained on Agilent 7890/5975C. The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds 3a$^1$, 3b-q$^2$, 3v$^3$, 3z$^2$, 3z2-z3$^4$, 3z7$^5$, 3z9-z12$^6$, 3v$^7$, 4a$^7$, 4g$^7$, 5k$^8$, 7a$^{10}$, 10f$^{11}$, 7o$^{10}$, 7p$^{12}$, 7s$^{10}$, 9a$^{13}$ and 11a$^2$ were known and their spectroscopic features were in good agreement with that reported in the literatures.

References

2. Experimental procedures

2.1 Preparation for synthesis of α-diazoesters

\[
\begin{align*}
\text{R}^1\text{O} & \quad \text{R}^2 \\
+ \quad \text{SO}_3\text{N}_3 \\
\text{DBU} & \quad \text{MW (400 W), 40 °C, 1 h} \\
\rightarrow \quad \text{R}^1\text{O} & \quad \text{R}^2
\end{align*}
\]

A typical procedure for the synthesis of α-diazoesters 1 – Synthesis of 1a: DBU (2.24 mL, 15 mmol) was added slowly to a stirred solution of ethyl 2-phenylacetate (sm1a, 1.41 mL, 10.0 mmol) and tosylazide (sm2, 2.42 mL, 11.0 mmol) in the CH\(_3\)CN (20 mL) at 0 °C. After that, it was placed in microwave reactor that was heated to 40 °C (400 W, monitored by IR temperature sensor) and maintained at this temperature for 30 min. After cooling to room temperature, the reaction mixture was quenched with saturated aqueous solution of NH\(_4\)Cl (5 mL), extracted with DCM (3 × 30 mL), washed with brine (3 × 30 mL), dried over anhydrous Na\(_2\)SO\(_4\), and concentrated under reduced pressure to give the product. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/AcOEt, 10:1) to afford the corresponding ethyl-2-diazo-2-phenylacetate 1a as a yellow oil (1.65 g, 87%).

2.2 Screening the optimum reaction conditions for the synthesis of 3a

\[
\begin{align*}
\text{O}_2 & \quad \text{N} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{N}_2 \\
\rightarrow \quad \text{O}_2 \quad \text{N} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{O} \quad \text{N}_2
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>1a:2a (equiv)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
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<td>—</td>
<td>1:1.5</td>
<td>DCE</td>
<td>rt</td>
<td>trace</td>
</tr>
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<td>HCl</td>
<td>1:1.5</td>
<td>DCE</td>
<td>rt</td>
<td>21</td>
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<td>3</td>
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<td>32</td>
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<td>4</td>
<td>H(_3)PO(_4)</td>
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<td>DCE</td>
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<td>6</td>
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<td>DCE</td>
<td>rt</td>
<td>15</td>
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<tr>
<td>7</td>
<td>HCOOH</td>
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<td>DCE</td>
<td>rt</td>
<td>21</td>
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</table>

Table S1. Screening the optimum conditions for the synthesis of 3a
On the outset of this study, we chose ethyl 2-diazo-2-phenylacetate 1a and p-nitrophenol 2a as the model substrates to screen the optimum reaction conditions (Table S1). We found that the O-H insertion reaction hardly occurred in the absence of a catalyst in DCE at room temperature (entry 1). A variety of acids furnished the product 3a (entries 2-10) with low to moderate yield (15-54%). To our delight, when CF$_3$SO$_3$H was chosen as a catalyst, the yield of 3a obviously improved up to 76% in DCE at room temperature for 20 min (entry 11). By contrast, when bases were used as catalysts, the
desired product \(3a\) (entries 12-16) was got in lower yield (26%). Then, we went on to screen other reaction parameters to learn more about this catalytic system. When the amount of the CF\(_3\)SO\(_3\)H was reduced (entries 17-19) or increased (entry 20), affording the product in reduced yield. On the other hand, screening the solvent (entries 21-28) suggested that DCE was the best solvent for this transformation (entry 11). Lowing or elevating the reaction temperatures deteriorated the reaction efficiency, giving the product \(3a\) in diminished yield (entries 29-34). The yield was raised up to 78% when the quantity of \(2a\) (1.4 equiv) was decreased (entry 35), further decreasing or increasing the quantity of \(2a\) could not increase the yield (entry 36-37). Based on the above results, the optimum conditions for the synthesis of \(3a\) were identified as DCE at room temperature for 20 min, CF\(_3\)SO\(_3\)H (20 mol%) as catalyst, \(1a:2a\) (equiv) = 1:1.4 (entry 35).

2.3 Screening the optimum reaction conditions for the synthesis of 5a

\[
\begin{align*}
\text{N} & \quad \text{O} \\
& \quad \text{N} \\
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{N}
\end{align*}
\]

\[
\text{1a} \quad \text{4a} \quad \text{conditions} \quad \text{5a}
\]

**Table S2.** Screening the optimum conditions for the synthesis of 5a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>1a:2a (equiv)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF(_3)SO(_3)H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>CF(_3)SO(_3)H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>40</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>CF(_3)SO(_3)H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>CF(_3)SO(_3)H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>60</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>—</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>HCl</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>H(_2)SO(_4)</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>35</td>
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<td>8</td>
<td>HNO(_3)</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>31</td>
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<td>9</td>
<td>HClO(_4)</td>
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<td>DCE</td>
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<td>71</td>
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<td>10</td>
<td>HAc</td>
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<td>DCE</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>C(_6)H(_5)SO(_3)H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>12</td>
<td>H(_3)PO(_4)</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>Et(_3)N</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>trace</td>
</tr>
<tr>
<td>14</td>
<td>CF(_3)SO(_3)H(^a)</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>15</td>
<td>CF(_3)SO(_3)H(^b)</td>
<td>1:1.4</td>
<td>DCE</td>
<td>50</td>
<td>65</td>
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</table>
Based on the optimized reaction conditions for O-H insertion of phenols, we optimized the reaction conditions for O-H insertion of oximes by employing ethyl 2-diazo-2-phenylacetate 1a and (E)-1-phenylethan-1-one oxime 4a as substrates (Table S2). After screening the temperature (entries 1-4), acid (entries 6-12) and base (entry 13) catalysts, the amount of acid (entries 14-17), solvent (entries 18-20), and material molar ratio (entries 21-22), we found the optimal reaction conditions for the synthesis of 5a in DCE at 50 °C for 30 min, CF$_3$SO$_3$H (20 mol%) as catalyst, 1a:4a (equiv) = 1:1.4 (entry 3).

### 2.4 Screening the optimum reaction conditions for the synthesis of 7a

![Chemical reaction diagram]

**Table S3.** Screening the optimum conditions for the synthesis of 7a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>1a:2a (equiv)</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF$_3$SO$_3$H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>CF$_3$SO$_3$H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>0</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>CF$_3$SO$_3$H</td>
<td>1:1.4</td>
<td>DCE</td>
<td>40</td>
<td>77</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>HCl</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>H$_2$SO$_4$</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>HNO$_3$</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>33</td>
</tr>
<tr>
<td>8</td>
<td>HClO$_4$</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>75</td>
</tr>
<tr>
<td>9</td>
<td>HAc</td>
<td>1:1.4</td>
<td>DCE</td>
<td>rt</td>
<td>28</td>
</tr>
</tbody>
</table>
Based on the optimized reaction conditions for O-H insertion of phenols and oximes, we optimized the reaction conditions for S-H insertion of thiols by employing ethyl 2-diazo-2-phenylacetate 1a and 4-chlorobenzenethiol 6a as substrates (Table S3). After screening the temperature (entries 1-3), acid (entries 5-11) and base (entry 12) catalysts, the amount of acid (entries 13-16), solvent (entries 17-19), and material molar ratio (entries 20-21), the optimum conditions for the synthesis of 7a were identified as DCE at room temperature for 5 min, CF$_3$SO$_3$H (20 mol%) as catalyst, 1a:6a (equiv) = 1:1.4 (entry 1).

2.5 Typical procedure for O-H insertion of phenols and alcohols

A typical procedure for the synthesis of O-H insertion products (3) – Synthesis of 3a: A mixture of CF$_3$SO$_3$H (20 mol%), 4-nitrophenol (2a, 97 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (1a, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under air for 20 min. Then, the crude product was got by removing
solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 3a as a colorless oil (117 mg, 78%).

2.6 Typical procedure for O-H insertion of oximes

A typical procedure for the synthesis of O-H insertion products of oximes (5)

**Synthesis of 5a:** A mixture of CF$_3$SO$_3$H (20 mol%), (E)-1-phenylethan-1-one oxime (4a, 95 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (1a, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at 50 °C under air for 0.5 h. After the reaction mixture was cooled to room temperature, removing solvent under reduced pressure to get the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 5a as a colorless oil (123 mg, 83%).

2.7 Typical procedure for S-H insertion of thiols

A typical procedure for the synthesis of S-H insertion products of thiols (7)

**Synthesis of 7a:** A mixture of CF$_3$SO$_3$H (20 mol%), 4-chlorobenzenethiol (6a, 101 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (1a, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under air for 5 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 7a as a colorless oil (129 mg, 84%).

2.8 The synthesis of MBX-102 acid 3v'
**Synthesis of 3v':** A mixture of 3v (172 mg, 0.5 mmol) and NaOH (36 mg, 0.9 mmol) in EtOH (5 mL) was stirred at 90 °C reflux for 8 h. After the reaction was judged to be completed by TLC, adding slowly the 1 M HCl until the PH of reaction mixture reached 3-4. Then, 15 mL H2O was added to the mixture. The aqueous layer was extracted with ethyl acetate (3 × 20 mL), washed with brine (3 × 20 mL), dried over anhydrous Na2SO4, concentrated under reduced pressure to give the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (2:1) to afford the corresponding 3v' as a white syrup (137 mg, 83%).

**2.9 A gram-scale experiment**

1 gram-scale experiment for the synthesis of 3t: A mixture of CF$_3$SO$_3$H (20 mol%), 4-nitrophenol (2a, 0.93 g, 6.7 mmol) and methyl 2-(4-chlorophenyl)-2-diazoacetate (1l, 1.00 g, 4.8 mmol) in DCE (48 mL) was stirred at room temperature under air for 30 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 3t as a white solid (1.26 g, 82%).
1 gram-scale experiment for the synthesis of 5i: A mixture of CF₃SO₃H (20 mol%), (E)-1-phenylethan-1-one oxime (4a, 0.90 g, 6.7 mmol) and methyl 2-(4-chlorophenyl)-2-diazoacetate (1l, 1.00 g, 4.8 mmol) in DCE (48 mL) was stirred at 50 °C under air for 1 h. After the reaction mixture was cooled to room temperature, removing solvent under reduced pressure to get the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 5i as a white solid (1.23 g, 81%).

1 gram-scale experiment for the synthesis of 7a: A mixture of CF₃SO₃H (20 mol%), 4-chlorobenzenethiol (6a, 1.07 g, 7.4 mmol) and ethyl 2-diazo-2-phenylacetate (1a, 1.00 g, 5.3 mmol) in DCE (53 mL) was stirred at room temperature under air for 20 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 7a as a colorless oil (1.30 g, 80%).

2.10 A typical procedure for the synthesis of N-H insertion product 9a

Synthesis of 9a: A mixture of CF₃SO₃H (20 mol%), aniline (8a, 65 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (1a, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at 80 °C under air for 2 h. After the reaction mixture was cooled to room temperature, removing solvent under reduced pressure to get the crude product. The crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 9a as a colorless oil (77 mg, 60%).

2.11 A typical procedure for the synthesis of C-H insertion product 11a
Synthesis of 11a: A mixture of CF$_3$SO$_3$H (20 mol%), 4-allyl-2-methoxyphenol (10a, 115 mg, 0.7 mmol) and ethyl 2-diazo-2-phenylacetate (1a, 95 mg, 0.5 mmol) in DCE (5 mL) was stirred at room temperature under air for 0.5 h. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford the corresponding 11a as a colorless oil (99 mg, 61%).

3. Control experiments

As Shown in Scheme S1, ketoximes and aldoximes are prone to rearrangement and give amide products (including N-substituted amide and primary amide) (Scheme S1a). Based on the control experiments, acid-free, ketoxime 4a and aldoxime 4g did not give the rearrangement products (Scheme S1b). Under the standard conditions, 4g was easy to rearrange and furnish the primary amide product 4g'' in 19% yield (Scheme S1c). Furthermore, increasing the temperature to 80 °C and prolonging the reaction time to 2 h, 4a could provide the Beckmann rearrangement product 4a' (N-substituted amide) in 13% yield, and 4g afforded the primary amide product 4g'' in 27% yield (Scheme S1d). Significantly, the N-substituted amide product 4a' and the primary amide product 4g'' both could not afford the N-H insertion products 5a' or 5q'' in this catalytic system (Scheme S1e-f). Combined with the above results, we could infer that the rearrangement of aldoximes lead to the O-H insertion in reduced yield.
Scheme S1 Control experiments

References

Copies of NMR spectra

ZZP-547-8

ZZP-551-8
4. X-Ray crystallographic studies

Single crystals of compounds 3t and 5l were grown in petroleum ether (60-90 °C)/CH₂Cl₂ (v/v, 5/1) at 25 °C and their X-ray diffraction studies were carried out on a
SMART APEX diffractometer with graphite-monochromated Mo radiation ($\lambda = 0.71073 \text{ Å}$). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1975821 for 3t and CCDC 1996648 for 5l Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

![Molecular structure of compound 3t](image)

**Figure S1.** Molecular structure of compound 3t

**Table S4.** Crystal data and structure refinement for 3t

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<tr>
<th>Property</th>
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<td>Empirical formula</td>
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<tr>
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</tr>
<tr>
<td>Temperature</td>
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</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>P 21/c</td>
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<tr>
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<tr>
<td></td>
<td>$b = 8.7483(6)$ Å, $\beta = 102.690(3)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 10.4253(8)$ Å, $\gamma = 90^\circ$</td>
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Table S5. Crystal data and structure refinement for 5l

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</tr>
<tr>
<td>□γ</td>
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</table>

Figure S2. Molecular structure of compound 5l
5. Kinetic isotope effect of the O-H insertion reaction

A mixture of phenol (2q, 18.8 mg, 0.2 mmol, 2q-D1, 95.1 mg, 1 mmol), CF₃SO₃H (20 mol%), 4 Å M.S. (100 mg) and ethyl 2-diazo-2-phenylacetate (1a, 163.5 mg, 0.86 mmol) in DCE (5 mL, freshly distilled) was stirred at room temperature under N₂ for 20 min. Then, the crude product was got by removing solvent under reduced pressure. Finally, the crude product was purified by flash chromatography with petroleum ether (60-90 °C)/AcOEt (10:1) to afford corresponding insertion product and conducted a ¹H NMR analysis to determine the H/D ratio.
6. NMR titration experiments

**Figure S3.** $^1$H NMR spectra of the phenol and ($E$)-1-phenylethan-1-one oxime signals in CDCl$_3$. (a) phenol (0.35 mmol), (b) phenol (0.35 mmol) with CF$_3$SO$_2$H (10 mol%). (c) ($E$)-1-phenylethan-1-one oxime (0.35 mmol), (d) ($E$)-1-phenylethan-1-one oxime (0.35 mmol) with CF$_3$SO$_2$H (10 mol%).
\(^1\)H-NMR titration experiments.

The preparation of mother liquor: (a) phenol (0.35 mmol), (b) phenol (0.35 mmol) with CF\(_3\)SO\(_3\)H (10 mol%), (c) (E)-1-phenylethan-1-one oxime (0.35 mmol), (d) (E)-1-phenylethan-1-one oxime (0.35 mmol) with CF\(_3\)SO\(_3\)H (10 mol%) were added in CDCl\(_3\) (2.5 mL), respectively and stirred at room temperature under 0.1 Mpa air for 20 min. Then, the mother liquor of (a) 100 \(\mu\)L, (b) 100 \(\mu\)L, (c) 100 \(\mu\)L, (d) 100 \(\mu\)L were moved in CDCl\(_3\) (0.5 mL), respectively. Last, conducted a \(^1\)H NMR analysis to show the \(^1\)H of OH in phenol and (E)-1-phenylethan-1-one oxime, as shown in Fig. S3.

7. Analytical Data for known compounds

Ethyl 2-(4-nitrophenoxy)-2-phenylacetate (3a): Colorless oil; 78% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25–8.11 (m, 2H), 7.57 (dd, \(J = 7.6, 1.8\) Hz, 2H), 7.46–7.36 (m, 3H), 7.07–6.96 (m, 2H), 5.72 (s, 1H), 4.32–4.12 (m, 2H), 1.21 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C\(^{\{\text{1}H\}}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.79, 162.15, 142.26, 134.29, 129.50, 129.05, 127.15, 125.95, 115.46, 78.90, 77.48, 77.16, 76.84, 62.14, 14.05.

Ethyl 2-phenyl-2-(4-(trifluoromethyl) phenoxy) acetate (3b): Colorless oil; 80% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (dd, \(J = 7.6, 1.3\) Hz, 2H), 7.54 (d, \(J = 8.6\) Hz, 2H), 7.46–7.36 (m, 3H), 7.02 (d, \(J = 8.6\) Hz, 2H), 5.67 (s, 1H), 4.30–4.14 (m, 2H), 1.22 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C\(^{\{\text{1}H\}}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.40, 159.78, 134.88, 129.36, 129.03, 128.41, 127.19, 127.14, 127.10, 124.37 (q, \(J = 271.3\) Hz), 124.04 (q, \(J = 32.8\) Hz), 120.33, 115.50, 78.71, 62.03, 14.13.
Ethyl 2-(4-fluorophenoxy)-2-phenylacetate (3c): Yellow oil; 74% yield; $^1$H NMR (400 MHz, CDCl$_3$) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (dd, $J = 7.7$, 1.4 Hz, 2H), 7.45–7.34 (m, 3H), 7.00–6.87 (m, 4H), 5.55 (s, 1H), 4.27–4.13 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 169.90, 157.95 (d, $J = 239.7$ Hz), 153.52 (d, $J = 2.3$ Hz), 135.44, 129.16, 128.93, 127.18, 116.98 (d, $J = 8.1$ Hz), 116.10 (d, $J = 23.3$ Hz), 79.57, 61.83, 14.16.

Ethyl 2-(4-chlorophenoxy)-2-phenylacetate (3d): Colorless oil; 77% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (dd, $J = 7.6$, 1.4 Hz, 2H), 7.44–7.34 (m, 3H), 7.22 (d, $J = 9.0$ Hz, 2H), 6.89 (d, $J = 9.0$ Hz, 2H), 5.57 (s, 1H), 4.27–4.12 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 169.70, 155.98, 135.19, 129.59, 129.22, 128.96, 127.17, 126.88, 116.97, 79.04, 61.90, 14.15.

Ethyl 2-(4-bromophenoxy)-2-phenylacetate (3e): Colorless oil; 72% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (dd, $J = 7.6$, 1.6 Hz, 2H), 7.42–7.35 (m, 5H), 6.92–6.79 (m, 2H), 5.58 (s, 1H), 4.29–4.13 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 169.66, 156.50, 135.16, 132.54, 129.24, 128.97, 127.18, 117.46, 114.25, 78.96, 61.93, 14.17.
Ethyl 2-(4-formylphenoxy)-2-phenylacetate (3f): Colorless oil; 61% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.88 (s, 1H), 7.83 (d, $J$ = 8.8 Hz, 2H), 7.58 (dd, $J$ = 7.6, 1.5 Hz, 2H), 7.45–7.37 (m, 3H), 7.06 (d, $J$ = 8.7 Hz, 2H), 5.71 (s, 1H), 4.28–4.15 (m, 2H), 1.21 (t, $J$ = 7.1 Hz, 3H). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 190.88, 169.23, 162.24, 134.69, 132.12, 130.83, 129.44, 129.07, 127.21, 115.73, 78.70, 62.11, 14.15.

Ethyl 2-phenyl-2-(p-tolyloxy) acetate (3g): Colorless oil; 60% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (dd, $J$ = 7.9, 1.5 Hz, 2H), 7.42–7.33 (m, 3H), 7.07 (d, $J$ = 8.3 Hz, 2H), 6.90–6.83 (m, 2H), 5.59 (s, 1H), 4.28–4.12 (m, 2H), 2.27 (s, 3H), 1.21 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.21, 155.37, 135.81, 131.21, 130.11, 128.97, 128.85, 127.19, 115.54, 79.02, 61.69, 20.63, 14.17.

Ethyl 2-(4-methoxyphenoxy)-2-phenylacetate (3h): Colorless oil; 51% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (dd, $J$ = 7.8, 1.4 Hz, 2H), 7.43–7.33 (m, 3H), 6.95–6.89 (m, 2H), 6.84–6.78 (m, 2H), 5.55 (s, 1H), 4.28–4.13 (m, 2H), 3.75 (s, 3H), 1.21 (t, $J$ = 7.1 Hz, 3H). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 170.19, 154.69, 151.55, 135.86, 128.94, 128.79, 127.16, 116.98, 114.72, 79.80, 61.62, 55.69, 14.12.

Ethyl 2-(4-allylphenoxy)-2-phenylacetate (3i): Colorless oil; 90% yield; $^1$H NMR (400 MHz, CDCl$_3$) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (dd, $J$ = 7.8, 1.4 Hz, 2H), 7.43–7.34 (m, 3H), 7.09 (d, $J$ = 8.7 Hz, 2H), 6.93–6.87 (m, 2H), 5.94 (dd, $J$ = 17.7, 9.3 Hz, 1H), 5.60 (s, 1H), 5.09–5.05 (m, 1H), 5.03 (t, $J$ = 1.4 Hz, 1H), 4.28–4.13 (m, 2H), 3.32
(d, \( J = 6.7 \) Hz, 2H), 1.21 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C\[^{1}\]H NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.13, 155.88, 137.76, 135.75, 133.40, 129.70, 128.99, 128.85, 127.18, 115.71, 115.61, 78.96, 61.71, 39.45, 14.16.

### Ethyl 2-(3-fluorophenoxy)-2-phenylacetate (3j):
Colorless oil; 72% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (dd, \( J = 7.8, 1.4 \) Hz, 2H), 7.43–7.37 (m, 3H), 7.21 (dd, \( J = 15.1, 8.2 \) Hz, 1H), 6.77–6.71 (m, 1H), 6.71–6.65 (m, 2H), 5.59 (s, 1H), 4.26–4.13 (m, 2H), 1.21 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C\[^{1}\]H NMR (100 MHz, CDCl\(_3\)) \( \delta \) 169.64, 163.61 (d, \( J = 245.9 \) Hz), 158.67 (d, \( J = 10.9 \) Hz), 135.13, 130.49 (d, \( J = 9.9 \) Hz), 129.24, 128.97, 127.19, 111.15 (d, \( J = 3.0 \) Hz), 108.81 (d, \( J = 21.3 \) Hz), 103.58 (d, \( J = 25.1 \) Hz), 78.92, 61.93, 14.15.

### Ethyl 2-phenyl-2-(m-tolyloxy) acetate (3k):
Colorless oil; 59% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.60 (dd, \( J = 7.8, 1.3 \) Hz, 2H), 7.44–7.34 (m, 3H), 7.16 (t, \( J = 7.8 \) Hz, 1H), 6.81 (d, \( J = 8.1 \) Hz, 2H), 6.75 (dd, \( J = 8.3, 2.2 \) Hz, 1H), 5.63 (s, 1H), 4.29-4.13 (m, 2H), 2.32 (s, 3H), 1.22 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C\[^{1}\]H NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.17, 157.47, 139.77, 135.71, 129.36, 128.99, 128.85, 127.17, 122.73, 116.56, 112.19, 78.67, 61.71, 21.63, 14.16.

### Ethyl 2-(2-fluorophenoxy)-2-phenylacetate (3l):
Colorless oil; 66% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.59 (dd, \( J = 7.7, 1.6 \) Hz, 2H), 7.44–7.35 (m, 3H), 7.13–7.06 (m, 1H), 7.03–6.92 (m, 3H), 5.64 (s, 1H), 4.25–4.16 (m, 2H), 1.20 (t, \( J = 7.1 \) Hz, 3H).

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$^{13}$C$^{1}H$ NMR (100 MHz, CDCl$_3$) δ 169.66, 153.42 (d, $J = 246.9$ Hz), 145.31 (d, $J = 10.6$ Hz), 135.29, 129.19, 128.87, 127.28, 124.36 (d, $J = 3.9$ Hz), 122.94 (d, $J = 7.0$ Hz), 117.78, 116.79 (d, $J = 18.4$ Hz), 80.26, 61.81, 14.12.

![Structure of 2-(2-ethoxy-2-oxo-1-phenylethoxy) benzoic acid (3m)](structure1.png)

2-(2-ethoxy-2-oxo-1-phenylethoxy) benzoic acid (3m): Colorless oil; 90% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 10.44 (s, 1H), 7.99 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.58 (dd, $J = 7.3$, 2.2 Hz, 2H), 7.51–7.41 (m, 4H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.94–6.88 (m, 1H), 6.14 (s, 1H), 4.30–4.16 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}$C$^{1}H$ NMR (100 MHz, CDCl$_3$) δ 169.42, 168.45, 161.96, 136.40, 133.63, 130.45, 129.60, 129.06, 127.76, 119.50, 117.78, 111.91, 75.28, 62.11, 14.14.

![Structure of Ethyl 2-phenyl-2-(o-tolyloxy) acetate (3n)](structure2.png)

Ethyl 2-phenyl-2-(o-tolyloxy) acetate (3n): Colorless oil; 57% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (dd, $J = 7.9$, 1.2 Hz, 2H), 7.44-7.35 (m, 3H), 7.18 (dd, $J = 7.3$, 0.7 Hz, 1H), 7.14-7.06 (m, 1H), 6.94-6.87 (m, 1H), 6.76 (d, $J = 8.1$ Hz, 1H), 5.65 (s, 1H), 4.26-4.10 (m, 2H), 2.38 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C$^{1}H$ NMR (100 MHz, CDCl$_3$) δ 170.25, 155.70, 136.02, 131.17, 128.91, 128.80, 127.86, 127.03, 126.78, 121.59, 112.17, 78.78, 61.64, 16.57, 14.12.

![Structure of Ethyl 2-(2-bromo-4-(trifluoromethyl) phenoxy)-2-phenylacetate (3o)](structure3.png)

Ethyl 2-(2-bromo-4-(trifluoromethyl) phenoxy)-2-phenylacetate (3o): White solid, m.p.: 71-73 °C; 64% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, $J = 1.8$ Hz, 1H), 7.65 (dd, $J = 7.7$, 1.6 Hz, 2H), 7.51–7.37 (m, 4H), 6.87 (d, $J = 8.6$ Hz, 1H), 5.72 (s, 1H), 4.27–4.14 (m, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C$^{1}H$ NMR (100 MHz, CDCl$_3$) δ 168.83,
156.43, 134.40, 131.14 (q, \( J = 7.4, 3.7 \) Hz), 129.43, 129.03, 127.06, 125.86 (q, \( J = 3.8 \) Hz), 125.18 (q, \( J = 33.4 \) Hz), 123.45 (q, \( J = 271.9 \) Hz), 113.69, 113.30, 79.45, 62.17, 14.11.

**Ethyl 2-((5,5'-diallyl-2'-hydroxy-[1,1'-biphenyl]-2-yl) oxy)-2-phenylacetate (3p):**

White solid, m.p.: 74-76 °C.; 88% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.49 (dd, \( J = 6.5, 3.0 \) Hz, 2H), 7.33 (dd, \( J = 5.0, 1.6 \) Hz, 3H), 7.20–7.09 (m, 3H), 7.03 (d, \( J = 8.5 \) Hz, 2H), 6.86 (d, \( J = 8.4 \) Hz, 1H), 6.01 (dd, \( J = 13.3, 6.1 \) Hz, 1H), 5.96 (dd, \( J = 13.4, 6.1 \) Hz, 1H), 5.75 (s, 1H), 5.20–4.97 (m, 4H), 4.30–4.11 (m, 2H), 3.40 (d, \( J = 6.7 \) Hz, 2H), 3.36 (d, \( J = 6.7 \) Hz, 2H), 1.20 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.93, 152.47, 151.80, 138.06, 137.43, 134.27, 133.27, 132.02, 131.26, 129.48, 129.26, 129.12, 128.91, 128.06, 127.29, 125.79, 117.40, 116.12, 115.57, 78.06, 62.55, 39.56, 39.47, 14.07.

**Ethyl 2-phenoxy-2-phenylacetate (3q):** Colorless oil; 68% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.54 (dd, \( J = 7.8, 1.4 \) Hz, 2H), 7.38–7.29 (m, 3H), 7.24–7.20 (m, 2H), 6.99–6.82 (m, 3H), 5.58 (s, 1H), 4.20–4.07 (m, 2H), 1.15 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.06, 157.40, 135.59, 129.65, 129.02, 128.86, 127.16, 121.87, 115.55, 78.71, 61.74, 14.13.
Methyl 2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetate (3v): White solid; m.p.: 84-86 °C; 78% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55–7.49 (m, 2H), 7.43–7.36 (m, 3H), 7.26 (t, $J = 3.9$ Hz, 1H), 7.20 (s, 1H), 7.08 (dd, $J = 8.2$, 2.4 Hz, 1H), 5.64 (s, 1H), 3.75 (s, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 169.60, 157.25, 135.46, 133.38, 132.29 (q, $J = 3.9$ Hz), 118.94 (q, $J = 3.9$ Hz), 118.62, 112.90 (q, $J = 3.9$ Hz), 78.18, 53.04.

2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetic acid (3v'): White syrup; 83% yield; $^1$H NMR (400 MHz, (CD$_3$)$_2$SO) $\delta$ 13.57 (s, 1H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.57–7.49 (m, 3H), 7.31 (t, $J = 9.1$ Hz, 3H), 6.11 (s, 1H). $^{13}$C{$^1$H} NMR (100 MHz, (CD$_3$)$_2$SO) $\delta$ 170.34, 157.27, 134.78, 133.58, 130.88, 130.37 (q, $J = 31.8$ Hz), 129.29, 128.77, 123.95 (q, $J = 272.4$ Hz), 119.50, 118.00 (q, $J = 3.7$ Hz), 111.92 (q, $J = 3.7$ Hz), 76.56.

Ethyl 2-isopropoxy-2-phenylacetate (3z): Colorless oil; 54% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (dd, $J = 8.0$, 1.4 Hz, 2H), 7.38–7.29 (m, 3H), 4.97 (s, 1H), 4.22–4.11 (m, 2H), 3.74–3.62 (m, 1H), 1.26–1.23 (m, 3H), 1.23–1.17 (m, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.68, 137.46, 128.60, 128.49, 127.22, 78.67, 71.05, 61.20, 22.21, 22.19, 14.20.

Ethyl 2-(cyclohexyloxy)-2-phenylacetate (3z3): Colorless oil; 47% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (dd, $J = 7.9$, 1.1 Hz, 2H), 7.37–7.27 (m, 3H), 5.03 (s, 1H),
4.23–4.09 (m, 2H), 3.41–3.32 (m, 1H), 2.05–1.94 (m, 1H), 1.94–1.85 (m, 1H), 1.82–1.67 (m, 2H), 1.58–1.21 (m, 6H), 1.19 (t, \( J = 7.1 \) Hz, 3H). \( ^{13}C\{^1H\} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.82, 137.69, 128.61, 128.46, 78.38, 77.65, 61.19, 32.45, 25.85, 24.31, 14.26.

**Ethyl 2-(benzyloxy)-2-phenylacetate (3z7):** Colorless oil; 51% yield; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.49 (dd, \( J = 7.7, 1.6 \) Hz, 2H), 7.41–7.30 (m, 8H), 4.94 (s, 1H), 4.62 (s, 2H), 4.26–4.11 (m, 2H), 1.22 (t, \( J = 7.1 \) Hz, 3H). \( ^{13}C\{^1H\} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.89, 137.33, 136.53, 128.74, 128.69, 128.54, 128.15, 128.00, 127.47, 79.80, 71.25, 61.30, 14.18.

**Ethyl 2-hydroxy-2-phenylacetate (3z9):** Colorless oil; 50% yield; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.43 (dd, \( J = 8.0, 1.2 \) Hz, 2H), 7.40–7.29 (m, 3H), 5.16 (d, \( J = 5.8 \) Hz, 1H), 4.31–4.11 (m, 2H), 3.57 (d, \( J = 5.8 \) Hz, 1H), 1.22 (t, \( J = 7.1 \) Hz, 3H). \( ^{13}C\{^1H\} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 173.78, 138.53, 128.66, 128.49, 126.63, 72.99, 62.33, 14.12.

**Ethyl 2-(4-chlorophenyl)-2-hydroxyacetate (3z10):** White solid, 62% yield; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.36 (d, \( J = 8.6 \) Hz, 2H), 7.31 (d, \( J = 8.5 \) Hz, 2H), 5.12 (d, \( J = 5.4 \) Hz, 1H), 4.31–4.10 (m, 2H), 3.75–3.63 (m, 1H), 1.21 (t, \( J = 7.1 \) Hz, 3H). \( ^{13}C\{^1H\} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 173.35, 136.97, 134.30, 128.77, 127.98, 72.28, 62.50, 14.08.
**Ethyl 2-(4-bromophenyl)-2-hydroxyacetate (3z11):** White solid, 65% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51–7.43 (m, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 5.10 (d, $J = 5.4$ Hz, 1H), 4.30–4.09 (m, 2H), 3.79–3.69 (m, 1H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 173.22, 137.47, 131.69, 128.28, 122.44, 72.31, 62.48, 14.06.

**Benzyl 2-hydroxy-2-phenylacetate (3z12):** White solid, 71% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48–7.42 (m, 2H), 7.41–7.31 (m, 6H), 7.26–7.19 (m, 2H), 5.27–5.24 (m, 2H), 5.15 (d, $J = 12.4$ Hz, 1H), 3.67 (d, $J = 5.8$ Hz, 1H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 173.53, 138.27, 135.08, 128.64, 128.61, 128.54, 128.48, 128.00, 126.67, 73.06, 67.65.

**2-(4-chlorophenyl)-2-(3-(trifluoromethyl) phenoxy) acetic acid (3v'):** White syrup; 83% yield; $^1$H NMR (400 MHz, (CD$_3$)$_2$SO) $\delta$ 13.57 (s, 1H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.57–7.49 (m, 3H), 7.31 (t, $J = 9.1$ Hz, 3H), 6.11 (s, 1H). $^{13}$C{$^1$H} NMR (100 MHz, (CD$_3$)$_2$SO) $\delta$ 170.34, 157.27, 134.78, 133.58, 130.88, 130.37 (q, $J = 31.8$ Hz), 129.29, 128.77, 123.95 (q, $J = 272.4$ Hz), 119.50, 118.00 (q, $J = 3.7$ Hz), 111.92 (q, $J = 3.7$ Hz), 76.56.
Ethyl (E)-2-(((1-phenylethylidene) amino) oxy) acetate (5k): Colorless oil; 50% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.69–7.59 (m, 2H), 7.40–7.32 (m, 3H), 4.74 (s, 2H), 4.24 (q, \(J = 7.1\) Hz, 2H), 2.32 (s, 3H), 1.29 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C \(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta 170.25, 156.71, 136.29, 129.46, 128.51, 126.41, 70.98, 60.98, 14.34, 13.23.

Ethyl 2-((4-chlorophenyl) thio)-2-phenylacetate (7a): Colorless oil; 84% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.42 (dd, \(J = 7.7, 1.8\) Hz, 2H), 7.35–7.28 (m, 5H), 7.25–7.21 (m, 2H), 4.86 (s, 1H), 4.19–4.09 (m, 2H), 1.18 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C \(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta 170.24, 135.48, 134.43, 134.34, 132.23, 129.20, 128.83, 128.63, 128.52, 61.96, 56.58, 14.12.

Ethyl 2-phenyl-2-(p-tolylthio) acetate (7c): Colorless oil; 91% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.46 (dd, \(J = 7.9, 1.6\) Hz, 2H), 7.35–7.28 (m, 5H), 7.08 (d, \(J = 7.9\) Hz, 2H), 4.86 (s, 1H), 4.19–4.08 (m, 2H), 2.32 (s, 3H), 1.18 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C \(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta 170.59, 138.38, 135.95, 133.41, 130.12, 129.79, 128.68, 128.63, 128.27, 61.72, 56.88, 21.23, 14.08.

Ethyl 2-(ethylthio)-2-phenylacetate (7f): Colorless oil; 60% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.48 (dd, \(J = 8.2, 1.3\) Hz, 2H), 7.33 (dt, \(J = 7.3, 6.5\) Hz, 3H), 4.59 (s,
1H), 4.24–4.15 (m, 2H), 2.61–2.46 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) δ 171.00, 136.38, 129.30, 128.68, 128.54, 128.11, 61.70, 52.13, 26.01, 14.19, 14.17.

**Ethyl 2-(4-methoxyphenyl)-2-(p-tolythio) acetate (7o):** Colorless oil; 65% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45–7.39 (m, 2H), 7.32 (dd, J = 6.8, 5.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.91–6.87 (m, 2H), 4.85 (s, 1H), 4.20–4.11 (m, 2H), 3.84 (s, 3H), 2.36 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) δ 170.84, 159.62, 138.33, 133.38, 129.86, 129.81, 127.91, 114.13, 61.68, 56.22, 55.40, 21.28, 14.13.

**Methyl 2-phenyl-2-(p-tolythio) acetate (7p):** Colorless oil; 85% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (dd, J = 9.2, 3.1 Hz, 2H), 7.33–7.30 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 4.86 (s, 1H), 3.68 (s, 3H), 2.32 (s, 3H). $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) δ 171.09, 138.51, 135.89, 133.47, 130.01, 129.86, 128.74, 128.64, 128.35, 56.89, 52.74, 21.26.

**Benzyl 2-phenyl-2-(p-tolythio) acetate (7s):** Colorless oil; 75% yield; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 (dd, J = 7.7, 1.8 Hz, 2H), 7.37–7.29 (m, 8H), 7.25–7.21 (m, 2H), 7.07 (d, J = 7.9 Hz, 2H), 5.19–5.05 (m, 2H), 4.95 (s, 1H), 2.34 (s, 3H). $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) δ 170.49, 138.42, 135.62, 135.43, 133.47, 130.01, 129.93, 129.83, 128.70, 128.67, 128.52, 128.35, 128.29, 128.21, 67.30, 56.76, 21.24.
Ethyl 2-phenyl-2-(phenylamino) acetate (9a): Colorless oil; 60% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.1$ Hz, 2H), 7.41–7.30 (m, 3H), 7.15 (dd, $J = 8.5$, 7.4 Hz, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 7.7$ Hz, 2H), 5.11 (d, $J = 5.3$ Hz, 1H), 5.02 (s, 1H), 4.32–4.08 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.91, 146.08, 137.81, 129.31, 128.90, 128.30, 127.29, 118.10, 113.48, 61.90, 60.86, 14.12.

Ethyl 2-(2-allyl-5-hydroxy-4-methoxyphenyl)-2-phenylacetate (11a): Colorless oil; 61% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17–7.12 (m, 2H), 7.08 (dd, $J = 8.7$, 7.3 Hz, 3H), 6.71 (s, 1H), 6.51 (s, 1H), 5.77 (dd, $J = 17.0$, 10.2 Hz, 1H), 5.32 (s, 1H), 5.02 (s, 1H), 4.93 (dd, $J = 10.1$, 1.5 Hz, 1H), 4.86 (dd, $J = 17.1$, 1.7 Hz, 1H), 4.04 (q, $J = 7.1$ Hz, 2H), 3.70 (s, 3H), 3.17 (dd, $J = 5.8$, 4.3 Hz, 2H), 1.10 (d, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 172.88, 145.74, 144.07, 138.70, 137.06, 129.92, 129.63, 128.82, 128.63, 127.16, 116.13, 115.40, 112.45, 61.27, 56.00, 52.66, 37.12, 14.28.

8. Analytical Data for unknown compounds

Ethyl 2-(4-nitrophenoxy)-2-(p-tolyl) acetate (3r): Light yellow oil; 78% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.23–8.14 (m, 2H), 7.44 (d, $J = 8.1$ Hz, 2H), 7.23 (d, $J =
7.9 Hz, 2H), 7.03–6.97 (m, 2H), 5.67 (s, 1H), 4.28–4.15 (m, 2H), 2.37 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 168.98, 162.29, 142.28, 139.63, 131.37, 129.81, 127.18, 126.01, 115.52, 78.91, 62.13, 21.37, 14.14. HRMS (ESI) calcd for C17H13NO5Na [M+Na]+: 338.0999; Found: 338.1001.

**Ethyl 2-(3,5-difluorophenyl)-2-(4-nitrophenoxo) acetate (3s):** Yellow oil, 68% yield; 1H NMR (400 MHz, CDCl3) δ 8.23–8.17 (m, 2H), 7.44–7.34 (m, 1H), 7.11–7.04 (m, 2H), 6.98 (t, J = 8.2 Hz, 2H), 6.10 (s, 1H), 4.34–4.25 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 167.65, 162.28, 161.32 (d, J = 250.6 Hz), 161.25 (d, J = 250.7 Hz), 142.64, 132.06 (d, J = 10.5 Hz), 131.90, 126.02, 115.77, 112.19 (d, J = 5.5 Hz), 112.03 (d, J = 13.3 Hz), 69.08, 62.67, 14.12. HRMS (ESI) calcd for C16H13F2NO5Na [M+Na]+: 360.0654; Found: 360.0653.

**Methyl 2-(4-chlorophenyl)-2-(4-nitrophenoxo) acetate (3t):** White solid, m.p.: 134-137 °C.; 85% yield; 1H NMR (400 MHz, CDCl3) δ 8.19 (d, J = 9.2 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 9.2 Hz, 2H), 5.70 (s, 1H), 3.76 (s, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 168.97, 161.83, 142.50, 135.69, 132.70, 129.40, 128.54, 126.10, 115.46, 78.13, 53.20. HRMS (APCI) calcd for C15H11NClO5 [M-H]-: 320.0331; Found: 320.0330.

**Allyl 2-(4-nitrophenoxo)-2-phenylacetate (3u):** Colorless oil; 75% yield; 1H NMR (400 MHz, CDCl3) δ 8.21–8.13 (m, 2H), 7.58 (dd, J = 7.6, 1.8 Hz, 2H), 7.47–7.37 (m,
3H), 7.06–6.98 (m, 2H), 5.82 (dd, $J = 17.4$, 10.2 Hz, 1H), 5.76 (s, 1H), 5.23–5.20 (m, 1H), 5.18 (dd, $J = 2.0$, 1.3 Hz, 1H), 4.70–4.60 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 168.46, 162.08, 142.31, 134.19, 131.08, 129.60, 129.10, 127.19, 125.99, 119.17, 115.49, 78.86, 66.39. HRMS (ESI) calcd for C$_{17}$H$_{15}$NO$_5$Na [M+Na]$^+$: 336.0842; Found: 336.0850.

Ethyl 2-butoxy-2-phenylacetate (3w): Colorless oil; 71% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.39–7.29 (m, 3H), 4.85 (s, 1H), 4.26–4.09 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.41 (m, 1H), 1.67–1.61 (m, 2H), 1.46–1.36 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.24, 137.03, 128.63, 128.58, 127.23, 81.26, 69.83, 61.22, 31.79, 19.38, 14.22, 13.97. HRMS (ESI) calcd for C$_{14}$H$_{20}$O$_3$Na [M+Na]$^+$: 259.1305; Found: 259.1316.

Ethyl 2-(octyloxy)-2-phenylacetate (3x): Colorless oil; 67% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, $J = 7.9$, 1.3 Hz, 2H), 7.37–7.28 (m, 3H), 4.85 (s, 1H), 4.26–4.07 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.40 (m, 1H), 1.71–1.60 (m, 2H), 1.40–1.33 (m, 2H), 1.27 (d, $J = 3.4$ Hz, 8H), 1.20 (t, $J = 7.1$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.08, 136.95, 128.50, 128.46, 127.12, 81.17, 70.04, 61.06, 31.84, 29.63, 29.39, 29.25, 26.07, 22.67, 14.10. HRMS (ESI) calcd for C$_{18}$H$_{28}$O$_3$Na [M+Na]$^+$: 315.1931; Found: 315.1945.

Ethyl 2-(octadecyloxy)-2-phenylacetate (3y): White solid; m.p.: 37-38 °C, 65% yield;
1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (dd, $J = 8.0, 1.3$ Hz, 2H), 7.38–7.28 (m, 3H), 4.85 (s, 1H), 4.24–4.10 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.39 (m, 1H), 1.70–1.62 (m, 2H), 1.35–1.27 (m, 30 H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.89 (t, $J = 6.8$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.63, 137.96, 128.47, 128.34, 127.07, 78.61, 78.20, 61.07, 48.53, 40.34, 34.52, 31.58, 25.32, 23.21, 22.39, 21.30, 16.25, 14.15. HRMS (ESI) calcd for C$_{28}$H$_{48}$O$_3$Na [M+Na]$^+$: 455.3496; Found: 455.3503.

Ethyl 2-(isopentyloxy)-2-phenylacetate (3z1): Colorless oil; 55% yield; 1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 6.5$ Hz, 2H), 7.37–7.29 (m, 3H), 4.85 (s, 1H), 4.22–4.12 (m, 2H), 3.62–3.55 (m, 1H), 3.53–3.36 (m, 1H), 1.83–1.70 (m, 1H), 1.67–1.43 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H), 0.92-0.87 (m, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.21, 136.98, 128.60, 128.56, 127.18, 81.26, 68.46, 61.20, 38.47, 25.08, 22.70, 22.66, 14.20. HRMS (ESI) calcd for C$_{15}$H$_{22}$O$_3$Na [M+Na]$^+$: 273.1461; Found: 273.1473.

Ethyl 2-((2-isopropyl-5-methylcyclohexyl) oxy)-2-phenylacetate (3z4): Colorless oil; 47% yield; 1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (dd, $J = 7.9, 1.2$ Hz, 2H), 7.36–7.29 (m, 3H), 5.09 (s, 1H), 4.22–4.11 (m, 2H), 3.33 (td, $J = 10.5, 4.2$ Hz, 1H), 2.60–2.47 (m, 1H), 2.13–2.02 (m, 1H), 1.70–1.62 (m, 2H), 1.40–1.29 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.07–0.98 (m, 1H), 0.96 (d, $J = 7.1$ Hz, 2H), 0.94–0.77 (m, 9H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.82, 137.69, 128.61, 128.46, 127.21, 78.38, 77.65, 61.19, 32.45, 32.30, 25.85, 24.31, 14.26. HRMS (ESI) calcd for C$_{20}$H$_{30}$O$_3$Na [M+Na]$^+$: 341.2087; Found: 341.2094.
Ethyl 2-(but-3-en-1-yloxy)-2-phenylacetate (3z5): Colorless oil; 75% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, $J = 7.9$, 1.5 Hz, 2H), 7.38–7.28 (m, 3H), 5.84 (dd, $J = 17.1$, 10.3 Hz, 1H), 5.10 (dd, $J = 17.2$, 1.7 Hz, 1H), 5.06–5.00 (m, 1H), 4.87 (s, 1H), 4.26–4.11 (m, 2H), 3.66–3.56 (m, 1H), 3.54–3.45 (m, 1H), 2.48–2.37 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.92, 136.72, 134.77, 128.55, 127.15, 116.62, 81.15, 69.20, 61.15, 34.08, 14.11. HRMS (ESI) calcd for C$_{14}$H$_{18}$O$_3$Na [M+Na]$^+$: 257.1148; Found: 257.1147.

Ethyl 2-phenyl-2-(undec-10-en-1-yloxy) acetate (3z6): Colorless oil; 72% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.39–7.29 (m, 3H), 4.85 (s, 1H), 4.26–4.09 (m, 2H), 3.59–3.51 (m, 1H), 3.48–3.41 (m, 1H), 1.67–1.61 (m, 2H), 1.46–1.36 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.05, 136.98, 128.49, 128.45, 127.12, 81.19, 70.04, 61.04, 32.00, 29.78, 29.73, 29.67, 29.63, 29.48, 29.44, 26.11, 22.75, 14.15, 14.11. HRMS (ESI) calcd for C$_{21}$H$_{32}$O$_3$Na [M+Na]$^+$: 355.2244; Found: 355.2247.

Allyl 2-ethoxy-2-phenylacetate (3z8): Colorless oil; 67% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (dd, $J = 7.9$, 1.3 Hz, 2H), 7.38–7.29 (m, 3H), 5.83 (dd, $J = 17.2$, 10.5 Hz, 1H), 5.21–5.11 (m, 2H), 4.90 (s, 1H), 4.66–4.55 (m, 2H), 3.64–3.48 (m, 2H), 1.27 (t, $J = 7.0$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.68, 136.70, 131.66, 128.61, 128.58, 127.19, 118.30, 80.91, 65.49, 65.30, 15.12. HRMS (ESI) calcd for C$_{13}$H$_{16}$O$_3$Na

Ethyl (E)-2-phenyl-2-(((1-phenylethylidene) amino) oxy) acetate (5a): Colorless oil; 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71–7.62 (m, 2H), 7.57 (dd, $J$ = 7.7, 1.7 Hz, 2H), 7.44–7.33 (m, 6H), 5.75 (s, 1H), 4.28–4.14 (m, 2H), 2.38 (s, 3H), 1.25 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.92, 156.91, 136.26, 135.37, 129.46, 128.96, 128.69, 128.47, 127.71, 126.41, 83.77, 61.22, 14.24, 13.35. HRMS (ESI) calcd for C$_{18}$H$_{19}$NO$_3$Na [M+Na]$^+$: 320.1257; Found: 320.1249.

Ethyl (E)-2-(((1-(4-nitrophenyl) ethylidene) amino) oxy)-2-phenylacetate (5b): White solid; 61% yield; m.p 86-88 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (d, $J$ = 8.9 Hz, 2H), 7.82 (d, $J$ = 8.9 Hz, 2H), 7.54 (dd, $J$ = 7.3, 2.0 Hz, 2H), 7.45–7.38 (m, 3H), 5.75 (s, 1H), 4.30–4.16 (m, 2H), 2.39 (s, 3H), 1.24 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.54, 154.90, 148.35, 142.20, 134.83, 129.25, 128.83, 127.79, 127.18, 123.74, 84.18, 77.48, 77.16, 76.84, 61.46, 14.26, 13.16. HRMS (APCI) calcd for C$_{18}$H$_{19}$N$_2$O$_5$ [M+H]$^+$: 343.1288; Found: 343.1281.

Ethyl (E)-2-(((1-(4-methoxyphenyl) ethylidene) amino) oxy)-2-phenylacetate (5c): Colorless oil; 70% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66–7.53 (m, 4H), 7.46–7.36 (m, 3H), 6.89 (d, $J$ = 8.8 Hz, 2H), 5.72 (s, 1H), 4.27–4.16 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H), 1.24 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.04, 160.71, 156.43, 135.46, 128.90, 128.76, 128.67, 127.75, 127.69, 113.82, 83.67, 61.17, 55.39,

**Ethyl (E)-2-phenyl-2-(((1-(p-tolyl) ethylidene) amino) oxy) acetate (5d):** Colorless oil; 63% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60–7.52 (m, 4H), 7.45–7.38 (m, 3H), 7.18 (d, \(J = 8.1\) Hz, 2H), 5.73 (s, 1H), 4.28–4.18 (m, 2H), 2.37 (d, \(J = 3.0\) Hz, 6H), 1.25 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.01, 156.86, 139.51, 135.39, 133.42, 129.16, 128.93, 128.68, 127.70, 126.30, 83.69, 61.20, 21.40, 14.25, 13.31. HRMS (ESI) calcd for C_{19}H_{22}NO_{3} [M+H]^+: 312.1594; Found: 312.1589.

**Ethyl (E)-2-phenyl-2-(((1-(m-tolyl) ethylidene) amino) oxy) acetate (5e):** Colorless oil; 45% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.57 (dd, \(J = 7.6, 1.7\) Hz, 2H), 7.48–7.38 (m, 5H), 7.27 (t, \(J = 7.6\) Hz, 1H), 7.19 (d, \(J = 7.5\) Hz, 1H), 5.75 (s, 1H), 4.29–4.17 (m, 2H), 2.38 (d, \(J = 3.2\) Hz, 6H), 1.25 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.97, 157.17, 138.09, 136.21, 135.36, 130.25, 128.95, 128.70, 128.38, 127.70, 127.03, 123.60, 83.71, 61.22, 21.57, 14.25, 13.51. HRMS (ESI) calcd for C_{19}H_{22}NO_{3}Na [M+Na]^+: 334.1414; Found: 334.1409.

**Ethyl (E)-2-phenyl-2-(((1-(o-tolyl) ethylidene) amino) oxy) acetate (5f):** Light yellow oil; 27% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (dd, \(J = 7.6, 1.8\) Hz, 2H), 7.45–7.34 (m, 3H), 7.26–7.15 (m, 4H), 5.69 (s, 1H), 4.27–4.11 (m, 2H), 2.33 (d, \(J = 5.6\) Hz, 6H), 1.23 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.98, 157.19,

Ethyl (E)-2-(((1-phenylethylidene) amino) oxy)-2-(4-(trifluoromethyl) phenyl) acetate (5g): Colorless oil; 60% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.70–7.61 (m, 6H), 7.37 (dd, J = 5.1, 1.9 Hz, 3H), 5.79 (s, 1H), 4.29–4.17 (m, 2H), 2.39 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^13C{^1H} NMR (100 MHz, CDCl_3) δ 170.18, 157.44, 139.43, 136.04, 131.07 (q, J = 32.5 Hz), 129.67, 128.55, 127.94, 126.45, 125.68 (q, J = 3.8 Hz), 124.12 (q, J = 272.3 Hz), 83.10, 61.60, 14.23, 13.40. HRMS (ESI) calcd for C_{19}H_{18}F_3NO_3Na [M+Na]^+: 388.1131; Found: 388.1136.

Ethyl (E)-2-((4-fluorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5h): Colorless oil; 83% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, J = 6.7, 3.0 Hz, 2H), 7.58–7.50 (m, 2H), 7.37 (dd, J = 5.0, 1.7 Hz, 3H), 7.14–7.05 (m, 2H), 5.70 (s, 1H), 4.28–4.17 (m, 2H), 2.36 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^13C{^1H} (100 MHz, CDCl_3) δ 170.78, 163.16 (d, J = 247.6 Hz), 157.09, 136.18, 131.31 (d, J = 3.2 Hz), 129.64, 129.56, 128.51, 126.43, 115.81, 115.59, 83.03, 61.35, 14.25, 13.37. HRMS (ESI) calcd for C_{18}H_{13}FNO_3Na [M+Na]^+: 338.1163; Found: 338.1158.
Ethyl \((E)\)-2-(4-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5i):  
Colorless oil; 81% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.64 (dd, \(J = 6.8, 3.0 \text{ Hz, } 2\text{H}\)), 7.49 (d, \(J = 8.4 \text{ Hz, } 2\text{H}\)), 7.40–7.35 (m, 5H), 5.70 (s, 1H), 4.28–4.15 (m, 2H), 2.36 (s, 3H), 1.24 (t, \(J = 7.1 \text{ Hz, } 3\text{H}\)). \(^{13}\)C\(^{\text{\textsuperscript{1}}}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta \) 170.51, 157.17, 136.13, 134.91, 134.00, 129.58, 129.06, 128.93, 128.51, 126.42, 83.02, 61.41, 14.24, 13.36. HRMS (ESI) calcd for C\(_{18}\)H\(_{18}\)ClNO\(_3\)Na [M+Na\(^+\)]: 354.0867; Found: 354.0867.

![Chemical Structure](image)

Ethyl \((E)\)-2-(4-bromophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5j):  
Light yellow oil; 76% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.68–7.61 (m, 2H), 7.53 (d, \(J = 8.5 \text{ Hz, } 2\text{H}\)), 7.43 (d, \(J = 8.4 \text{ Hz, } 2\text{H}\)), 7.40–7.33 (m, 3H), 5.68 (s, 1H), 4.28–4.14 (m, 2H), 2.36 (s, 3H), 1.24 (t, \(J = 7.1 \text{ Hz, } 3\text{H}\)). \(^{13}\)C\(^{\text{\textsuperscript{1}}}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta \) 170.43, 157.19, 136.11, 134.51, 131.88, 129.58, 129.35, 128.51, 126.42, 123.12, 83.06, 61.43, 14.24, 13.36. HRMS (ESI) calcd for C\(_{18}\)H\(_{18}\)BrNO\(_3\)Na [M+Na\(^+\)]: 398.0362; Found: 398.0362.

![Chemical Structure](image)

Methyl \((E)\)-2-(4-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5l):  
White solid; 85% yield; m.p 84-86 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.63 (dd, \(J = 6.5, 3.2 \text{ Hz, } 2\text{H}\)), 7.48 (d, \(J = 8.4 \text{ Hz, } 2\text{H}\)), 7.40–7.35 (m, 5H), 5.71 (s, 1H), 3.75 (s, 3H), 2.36 (s, 3H). \(^{13}\)C\(^{\text{\textsuperscript{1}}}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta \) 171.03, 157.28, 136.07, 135.02, 133.84, 131.64, 129.63, 129.09, 128.99, 128.53, 126.45, 82.93, 52.48, 13.40. HRMS (ESI) calcd for C\(_{17}\)H\(_{16}\)ClNO\(_3\)Na [M+Na\(^+\)]: 340.0711; Found: 340.0721.

![Chemical Structure](image)
Methyl (E)-2-(3-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5m):
Colorless oil; 70% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (dd, $J = 6.5$, 3.2 Hz, 2H), 7.55 (s, 1H), 7.46–7.41 (m, 1H), 7.39–7.30 (m, 5H), 5.72 (s, 1H), 3.76 (s, 3H), 2.38 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.82, 157.38, 137.26, 136.05, 134.66, 130.02, 129.64, 129.21, 128.53, 127.78, 126.46, 125.83, 82.98, 52.52, 13.44. HRMS (ESI) calcd for C$_{17}$H$_{17}$ClNO$_3$ [M+H]$^+$: 318.0891; Found: 318.0898.

Methyl (E)-2-(2-chlorophenyl)-2-(((1-phenylethylidene) amino) oxy) acetate (5n):
White solid; 60% yield; m.p 55-57 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67–7.63 (m, 2H), 7.62–7.58 (m, 1H), 7.46–7.42 (m, 1H), 7.37 (dd, $J = 4.3$, 2.4 Hz, 3H), 7.33–7.29 (m, 2H), 6.24 (s, 1H), 3.77 (s, 3H), 2.35 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.75, 157.08, 136.13, 134.12, 133.57, 130.18, 129.89, 129.54, 129.43, 128.48, 127.17, 126.46, 80.21, 52.45, 13.31. HRMS (ESI) calcd for C$_{17}$H$_{17}$ClNO$_3$ [M+H]$^+$: 318.0891; Found: 318.0902.

Allyl (E)-2-phenyl-2-(((1-phenylethylidene) amino) oxy) acetate (5o):
Yellow oil; 72% yield; $^1$H NMR (400 MHz, CDCl$_3$) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68–7.63 (m, 2H), 7.57 (dd, $J = 7.6$, 1.7 Hz, 2H), 7.43–7.35 (m, 6H), 5.87 (dd, $J = 17.2$, 10.5 Hz, 1H), 5.79 (s, 1H), 5.25 (dd, $J = 17.2$, 1.5 Hz, 1H), 5.18 (dd, $J = 10.5$, 1.3 Hz, 1H), 4.67 (dt, $J = 5.5$, 1.4 Hz, 2H), 2.38 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.61, 157.01, 136.22, 135.23, 131.85, 129.50, 129.06, 128.74, 128.48, 127.76, 126.44,
118.22, 83.77, 65.61, 13.37. HRMS (ESI) calcd for C_{19}H_{20}NO_{3} [M+H]^+: 310.1438; Found: 310.1449.

Isobutyl (E)-2-phenyl-2-(((1-phenylethylidene) amino) oxy) acetate (5p): Colorless oil; 79% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.68–7.63\) (m, 2H), \(7.57\) (dd, \(J = 7.7, 1.6\) Hz, 2H), \(7.42–7.35\) (m, 6H), \(5.76\) (s, 1H), \(4.00–3.90\) (m, 2H), \(2.38\) (s, 3H), \(1.97–1.87\) (m, 1H), \(0.86\) (dd, \(J = 6.7, 1.3\) Hz, 6H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta 171.01, 156.85, 136.28, 135.52, 129.46, 128.95, 128.68, 128.47, 127.69, 126.41, 83.89, 71.16, 27.89, 19.02, 19.01, 13.33. HRMS (ESI) calcd for C_{20}H_{24}NO_{3} [M+H]^+: 326.1751; Found: 326.1764.

Ethyl (E)-2-((benzylideneamino)oxy)-2-phenylacetate (5q): Colorless oil; 63% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.28\) (s, 1H), \(7.64–7.57\) (m, 2H), \(7.55\) (dd, \(J = 7.6, 1.8\) Hz, 2H), \(7.43–7.36\) (m, 6H), \(5.73\) (s, 1H), \(4.35–4.16\) (m, 2H), \(1.26\) (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta 170.66, 150.70, 134.93, 131.78, 130.31, 129.13, 128.78, 127.83, 127.48, 83.90, 61.38, 14.24. HRMS (ESI) calcd for C_{17}H_{18}NO_{3} [M+H]^+: 284.1281; Found: 284.1275.

Ethyl (E)-2-(((4-nitrobenzylidene) amino) oxy)-2-phenylacetate (5r): White solid; 57% yield; m.p 101-104 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.32\) (s, 1H), \(8.23\) (d, \(J = 8.9\) Hz, 2H), \(7.78–7.72\) (m, 2H), \(7.55–7.49\) (m, 2H), \(7.42–7.40\) (m, 2H), \(7.36–7.32\) (m, 1H), \(5.75\) (s, 1H), \(4.29–4.19\) (m, 2H), \(1.25\) (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta 170.72, 150.14, 134.94, 132.31, 130.23, 129.10, 128.79, 127.82, 127.48, 83.89, 61.38, 14.24. HRMS (ESI) calcd for C_{17}H_{18}NO_{3} [M+H]^+: 300.1139; Found: 300.1135.
Ethyl (E)-2-(((4-fluorobenzylidene) amino) oxy)-2-phenylacetate (5s): Colorless oil; 68% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (s, 1H), 7.60–7.51 (m, 4H), 7.44–7.36 (m, 3H), 7.09–7.02 (m, 2H), 5.70 (s, 1H), 4.30–4.15 (m, 2H), 1.25 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.62, 164.01 (d, $J$ = 250.6 Hz), 149.51, 134.87, 133.67 (d, $J$ = 8.5 Hz), 129.39, 129.30, 129.18, 128.80, 128.02 (d, $J$ = 3.2 Hz), 116.07, 115.85, 83.92, 61.41, 14.24. HRMS (ESI) calcd for C$_{17}$H$_{17}$FNO$_3$ [M+H]$^+$: 302.1187; Found: 302.1181.

Ethyl (E)-2-(((4-chlorobenzylidene) amino) oxy)-2-phenylacetate (5t): Colorless oil; 59% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 (s, 1H), 7.52 (dd, $J$ = 8.3, 2.0 Hz, 4H), 7.43–7.37 (m, 3H), 7.36–7.32 (m, 2H), 5.70 (s, 1H), 4.29–4.18 (m, 2H), 1.25 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.56, 149.53, 136.25, 134.79, 130.31, 129.23, 129.11, 128.83, 128.67, 127.85, 84.00, 61.46, 14.26. HRMS (ESI) calcd for C$_{17}$H$_{16}$ClNO$_3$ [M+Na]$^+$: 340.0711; Found: 340.0709.

Ethyl (E)-2-(((2-nitrobenzylidene) amino) oxy)-2-phenylacetate (5u): Colorless oil; 31% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.84 (s, 1H), 8.06 (dd, $J$ = 8.2, 1.2 Hz, 1H), 7.94 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.66–7.60 (m, 1H), 7.58–7.51 (m, 3H), 7.42–7.39 (m,
(m, 3H), 7.36–7.30 (m, 1H), 5.73 (s, 1H), 4.28–4.18 (m, 2H), 1.25 (t, \( J = 7.1 \text{ Hz}, 3\text{H})

\[ ^{13}\text{C}\{^{1}\text{H}\} \text{ NMR (100 MHz, CDCl}_3 \delta 170.56, 149.53, 136.25, 134.80, 130.32, 129.22, 129.11, 128.83, 128.67, 127.85, 84.01, 61.46, 14.26. \]

HRMS (ESI) calcd for \( \text{C}_{17}\text{H}_{16}\text{N}_{2}\text{O}_{5}\text{Na} [\text{M+Na}^+]: 351.0951 \); Found: 351.0950.

Methyl (E)-2-((benzylideneamino)oxy)-2-(4-chlorophenyl) acetate (5v): White solid; 55% yield; m.p 50-52°C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \( \delta 8.26 (s, 1\text{H}), 7.58 (d d, J = 7.4, 2.2 \text{ Hz}, 2\text{H}), 7.49–7.45 (m, 2\text{H}), 7.41–7.34 (m, 5\text{H}), 5.70 (s, 1\text{H}), 3.77 (s, 3\text{H}). \)

\[ ^{13}\text{C}\{^{1}\text{H}\} \text{ NMR (100 MHz, CDCl}_3 \delta 170.73, 151.03, 135.17, 133.47, 131.57, 130.47, 129.16, 129.04, 128.82, 127.53, 83.03, 52.56. \]

HRMS (ESI) calcd for \( \text{C}_{16}\text{H}_{14}\text{ClNO}_{3}\text{Na} [\text{M+Na}^+]: 326.0554 \); Found: 326.0556.

Ethyl 2-((3,4-dichlorophenyl) thio)-2-phenylacetate (7b): Colorless oil; 79% yield; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \( \delta 7.47–7.40 (m, 3\text{H}), 7.36–7.30 (m, 4\text{H}), 7.17 (d d, J = 8.4, 2.1 \text{ Hz}, 1\text{H}), 4.90 (s, 1\text{H}), 4.22–4.10 (m, 2\text{H}), 1.20 (t, \( J = 7.1 \text{ Hz}, 3\text{H}). \)

\[ ^{13}\text{C}\{^{1}\text{H}\} \text{ NMR (100 MHz, CDCl}_3 \delta 169.96, 135.04, 133.99, 133.97, 132.86, 132.39, 131.70, 130.68, 128.91, 128.70, 128.60, 62.10, 56.23, 14.11. \]

HRMS (APCI) calcd for \( \text{C}_{16}\text{H}_{13}\text{Cl}_{2}\text{O}_{2}\text{S} [\text{M-H}^-]: 339.0019 \); Found: 339.0015.

Ethyl 2-phenyl-2-(m-tolylthio) acetate (7d): Colorless oil; 78% yield; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \( \delta 7.49 (d d, J = 7.9, 1.5 \text{ Hz}, 2\text{H}), 7.38–7.29 (m, 3\text{H}), 7.24–7.13 (m, 3\text{H}), 7.08 (d d, J = 7.3, 0.6 \text{ Hz}, 1\text{H}), 4.93 (s, 1\text{H}), 4.26–4.05 (m, 2\text{H}), 2.31 (s, 3\text{H}), 1.19 (t, \( J = 7.1 \text{ Hz}, 3\text{H}). \)
= 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.57, 138.76, 135.80, 133.67, 133.18, 129.51, 128.83, 128.79, 128.70, 128.60, 128.32, 61.74, 56.33, 21.29, 14.07. HRMS (ESI) calcd for C$_{17}$H$_{19}$O$_2$S [M+H]$^+$: 287.1100; Found: 287.1090.

**Ethyl 2-phenyl-2-(o-tolylthio) acetate (7e):** Colorless oil; 67% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (dd, $J$ = 7.7, 1.7 Hz, 2H), 7.38–7.28 (m, 4H), 7.20–7.14 (m, 2H), 7.13–7.06 (m, 1H), 4.84 (s, 1H), 4.19–4.04 (m, 2H), 2.39 (s, 3H), 1.16 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.61, 140.57, 135.84, 133.28, 133.13, 130.49, 128.77, 128.64, 128.40, 128.16, 126.59, 61.82, 55.64, 20.73, 14.10. HRMS (ESI) calcd for C$_{17}$H$_{18}$O$_2$SNa [M+Na]$^+$: 309.0920; Found: 309.0913.

**Ethyl 2-(octylthio)-2-phenylacetate (7g):** Colorless oil; 65% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J$ = 7.0 Hz, 2H), 7.38–7.26 (m, 3H), 4.56 (s, 1H), 4.28–4.10 (m, 2H), 2.61–2.42 (m, 2H), 1.63–1.45 (m, 2H), 1.36–1.19 (m, 13H), 0.87 (t, $J$ = 6.8 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 171.05, 136.43, 128.66, 128.55, 128.10, 61.70, 52.39, 32.04, 31.87, 29.21, 29.20, 29.06, 28.90, 22.73, 14.19. HRMS (ESI) calcd for C$_{18}$H$_{28}$O$_2$SNa [M+Na]$^+$: 331.1702; Found: 331.1699.

**Ethyl 2-((4-chlorobenzyl) thio)-2-phenylacetate (7h):** Colorless oil; 76% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (dd, $J$ = 7.9, 1.5 Hz, 2H), 7.37–7.27 (m, 5H), 7.22 (d, $J$ = 8.4 Hz, 2H), 4.39 (s, 1H), 4.23–4.09 (m, 2H), 3.75 (d, $J$ = 13.6 Hz, 1H), 3.59 (d, $J$ = 13.6 Hz, 1H), 1.25 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.63,
135.88, 135.78, 133.14, 130.50, 128.83, 128.80, 128.70, 128.36, 61.90, 51.73, 35.58, 14.20. HRMS (ESI) calcd for C_{17}H_{18}ClO_{2}S [M+H]^+: 321.0711; Found: 321.0716.

Ethyl 2-phenyl-2-(thiophen-2-ylthio) acetate (7i): Colorless oil; 61% yield; ^1H NMR (400 MHz, CDCl$_3$) δ 7.42–7.36 (m, 3H), 7.35–7.29 (m, 3H), 7.06 (dd, $J = 3.6, 1.2$ Hz, 1H), 6.94 (dd, $J = 5.3, 3.6$ Hz, 1H), 4.77 (s, 1H), 4.22–4.11 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}$C{^1H} NMR (100 MHz, CDCl$_3$) δ 170.15, 136.34, 135.38, 131.30, 131.23, 128.74, 128.71, 128.49, 127.62, 61.93, 59.20, 14.14. HRMS (ESI) calcd for C$_{14}$H$_{18}$NO$_2$S$_2$ [M+NH$_4$]$^+$: 296.0773; Found: 296.0763.

Ethyl 2-((p-tolylthio)-2-(4-(trifluoromethyl) phenyl) acetate (7j): Colorless oil; 62% yield; ^1H NMR (400 MHz, CDCl$_3$) δ 7.65–7.53 (m, 4H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 4.88 (s, 1H), 4.26–4.07 (m, 2H), 2.35 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). $^{13}$C{^1H} NMR (100 MHz, CDCl$_3$) δ 169.97, 140.19, 138.98, 133.88, 130.41 (q, $J = 32.5$ Hz), 129.97, 129.29, 129.12, 125.60 (q, $J = 3.7$ Hz), 124.11 (q, $J = 272.2$ Hz), 62.06, 56.50, 21.26, 14.08. HRMS (ESI) calcd for C$_{18}$H$_{17}$F$_3$O$_2$SNa [M+Na]$^+$: 377.0794; Found: 377.0806.

Ethyl 2-(4-chlorophenyl)-2-((p-tolylthio) acetate (7k): Colorless oil; 85% yield; ^1H NMR (400 MHz, CDCl$_3$) δ 7.43–7.38 (m, 2H), 7.31 (dd, $J = 8.3, 6.8$ Hz, 4H), 7.11 (d,
$J = 7.9$ Hz, 2H), 4.82 (s, 1H), 4.23–4.10 (m, 2H), 2.35 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 3H).

$^{13}$C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 170.22, 138.74, 134.62, 134.19, 133.73, 130.04, 129.89, 129.54, 128.84, 61.90, 56.21, 21.27, 14.09. HRMS (ESI) calced for C\textsubscript{17}H\textsubscript{18}ClO\textsubscript{2}S [M+H]\textsuperscript{+}: 321.0711; Found: 321.0716.

**Ethyl 2-(4-bromophenyl)-2-(\textit{p}-tolylthio) acetate (7l):** Colorless oil; 81% yield; $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.46–7.40 (m, 2H), 7.32–7.23 (m, 4H), 7.07 (d, $J = 7.9$ Hz, 2H), 4.76 (s, 1H), 4.19–4.05 (m, 2H), 2.31 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}$C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 170.10, 138.72, 135.13, 133.70, 131.77, 130.34, 129.88, 129.49, 122.36, 61.89, 56.25, 21.26, 14.07. HRMS (ESI) calced for C\textsubscript{17}H\textsubscript{17}BrO\textsubscript{2}SNa [M+Na]\textsuperscript{+}: 387.0025; Found: 387.0028.

**Ethyl 2-(4-iodophenyl)-2-(\textit{p}-tolylthio) acetate (7m):** Colorless oil; 70% yield; $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.66–7.61 (m, 2H), 7.28–7.24 (m, 4H), 7.07 (d, $J = 7.9$ Hz, 2H), 4.75 (s, 1H), 4.21–4.03 (m, 2H), 2.32 (s, 3H), 1.18 (t, $J = 7.1$ Hz, 3H). $^{13}$C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 170.10, 138.72, 135.13, 133.70, 131.77, 130.34, 129.88, 130.55, 129.90, 129.52, 94.11, 61.92, 56.39, 21.28, 14.09. HRMS (ESI) calced for C\textsubscript{17}H\textsubscript{17}IO\textsubscript{2}SNa [M+Na]\textsuperscript{+}: 434.9886; Found: 434.9886.

**Ethyl 2-(\textit{p}-tolyl)-2-(\textit{p}-tolylthio) acetate (7n):** Colorless oil; 80% yield; $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.35 (d, $J = 8.1$ Hz, 2H), 7.33–7.28 (m, 2H), 7.14 (d, $J = 8.0$ Hz, 2H),
7.09 (d, $J = 7.9$ Hz, 2H), 4.84 (s, 1H), 4.19–4.06 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.75, 138.24, 138.10, 133.22, 132.87, 130.37, 129.78, 129.41, 128.49, 61.66, 56.58, 21.24, 14.09. HRMS (ESI) calcd for C$_{18}$H$_{20}$O$_2$SNa [M+Na]$^+$: 323.1076; Found: 323.1081.

![Methyl 2-(3-chlorophenyl)-2-(p-tolylthio) acetate (7q):](image)

**Methyl 2-(3-chlorophenyl)-2-(p-tolylthio) acetate (7q):** Colorless oil; 78% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 1.8$ Hz, 1H), 7.38–7.27 (m, 5H), 7.13 (d, $J = 8.0$ Hz, 2H), 4.84 (s, 1H), 3.73 (s, 3H), 2.37 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.50, 138.88, 137.87, 134.49, 133.77, 129.94, 129.87, 129.32, 128.77, 128.50, 126.86, 56.31, 52.86, 21.25. HRMS (ESI) calcd for C$_{16}$H$_{15}$ClO$_2$SNa [M+Na]$^+$: 329.0373; Found: 329.0386.

![Methyl 2-(2-chlorophenyl)-2-(p-tolylthio) acetate (7r):](image)

**Methyl 2-(2-chlorophenyl)-2-(p-tolylthio) acetate (7r):** Colorless oil; 70% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (dd, $J = 7.5$, 2.0 Hz, 1H), 7.34 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.26–7.19 (m, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 5.40 (s, 1H), 3.68 (s, 3H), 2.31 (s, 3H). $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 170.64, 138.76, 133.88, 133.84, 133.77, 130.29, 129.88, 129.64, 129.53, 129.38, 127.23, 52.89, 52.78, 21.29. HRMS (ESI) calcd for C$_{16}$H$_{15}$ClO$_2$SNa [M+Na]$^+$: 329.0373; Found: 329.0385.
9. Copies of NMR spectra

FYF-1

[Image of NMR spectrum for 3a]

FYF-1-2

[Image of NMR spectrum for 3a]
ZZP-1-\text{H1}

ZZP-1-\text{C13}
ZZP-551-8

5r

ZZP-551-8

5r