Supporting Information

A Practical Flow Synthesis of Hydrazine Derivatives from Alcohols

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1. General information

All the reactions were conducted under air conditions unless otherwise noted. All solvents were obtained from commercial suppliers and used without further purification. Reagents were purchased from Energy Chemical, Adamas-beta, and etc. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on a 400 MHz spectrometer in CDCl$_3$ ($\delta$H = 0.0 ppm, $\delta$C = 77.02 ppm as standard). Data for $^1$H NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, 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). High-resolution mass spectra were obtained by ESI on a TOF mass analyzer.

2. Optimization of the deoxygenative hydrazination

2.1 Table S1. Investigation of reaction solvent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of 2a (%)$^b$</th>
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<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$CN</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>DMSO</td>
<td>Trace</td>
</tr>
<tr>
<td>6</td>
<td>Acetone</td>
<td>32</td>
</tr>
</tbody>
</table>

$^a$ Continuous flow conditions: Feed 1: alcohol (1a, 2 mmol, 0.1 M), Ph$_3$P (3 mmol, 1.5 equiv), solvent (10.0 mL); feed 2: DBAD (0.3 mmol, 1.5 equiv, 0.15 M), solvent (10.0 mL), 30 $^\circ$C, 7 mL reactor volume, 1.1 * 1.5 mm, $t_R = 42$ min. $^b$ Isolated yields in 1.0 mmol scale.

2.2 Table S2. The exploration of reaction temperature.
<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>Yield of 2a (%)</th>
</tr>
</thead>
<tbody>
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<td>10</td>
<td>57</td>
</tr>
<tr>
<td>2</td>
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<td>85</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>82</td>
</tr>
</tbody>
</table>

*a Continuous flow conditions: Feed 1: alcohol (1a, 2 mmol, 0.1 M), PPh₃ (3 mmol, 1.5 equiv), solvent (10.0 mL); feed 2: DBAD (0.3 mmol, 1.5 equiv, 0.15 M), solvent (10.0 mL), T °C, 7 mL reactor volume, 1.1 * 1.5 mm, tᵣ = 42 min. * Isolated yields in 1.0 mmol scale.

2.3 Table S3. Investigation of flow rate.

<table>
<thead>
<tr>
<th>Entry</th>
<th>flow rate (mL/h)</th>
<th>tᵣ (min)</th>
<th>Yield of 2a (%)</th>
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<tbody>
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<td>1</td>
<td>40</td>
<td>10.5</td>
<td>46</td>
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<td>2</td>
<td>20</td>
<td>21</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>42</td>
<td>85</td>
</tr>
</tbody>
</table>

*a Continuous flow conditions: Feed 1: alcohol (1a, 2 mmol, 0.1 M), PPh₃ (3 mmol, 1.5 equiv), MeCN (10.0 mL); feed 2: DBAD (0.3 mmol, 1.5 equiv, 0.15 M), MeCN (10.0 mL), T °C, 7 mL reactor volume, 1.1 * 1.5 mm. * Isolated yields in 1.0 mmol scale.

3. General procedure
3.1 General procedure for deoxygenative hydrazination of alcohols.

There are two 10 ml syringes. One was filled with alcohol (2.0 mmol) and PPh₃ (786.9 mg, 3 mmol) in MeCN (10.0 mL). Another was filled with DBAD (690.9 mg, 3 mmol) in MeCN (10.0 mL). Next, the syringes were placed into the syringe driver, and the advancing speed of the device was set at 5.0 mL/h, and the infusion mode was set to single infusion. The tubing (1.1 x 1.5 mm, 5 m, volume = 7.0 mL) was placed into a water bath at 30 °C. Thus, the reaction mixture was at the speed of 10.0 mL/h at 30 °C. After approximately 0.3 h of equilibration, 10.0 mL of the product solution was collected. The organic layers were concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate). In addition, 100.0 mL of the product solution was collected for the gram-reaction.
3.2 General procedure for the synthesis of pharmacologically active compounds on gram-scale

(1) Synthesis of hydrazine derivatives

According to the general procedure, the reaction mixture of octan-2-ol was collected 200.0 mL, the reaction mixture of 2-phenylethan-1-ol was collected 100.0 mL, and the reaction mixture of 4-(benzo[d][1,3]dioxol-5-yl)butan-2-ol was collected 100.0 mL. The finished mixture was concentrated under vacuo and purified by flash column chromatography on silica gel. The responding hydrazine derivative was afforded and used in next steps.

(2) The deprotection of hydrazine derivatives to hydrazinium hydrochloride

The obtained hydrazine derivative was dissolved in MeOH (50.0 mL) and cooled down to 0 °C. Then acetyl chloride (9.54 g for octan-2-ol, 4.77 g for 2-phenylethan-1-ol and 4-(benzo[d][1,3]dioxol-5-yl)butan-2-ol) was slowly added dropwise. Then the mixture was stirred for 2.5 min. Subsequently, 40 mL HCl in MeOH (37%, 200 μL/mL) was added (20 mL for 4-(benzo[d][1,3]dioxol-5-yl)butan-2-ol). The reaction was stirred at room temperature for 2.0 h. The solvent was removed under reduced pressure, then further dried using vacuum drying chamber, to afford the corresponding hydrazine hydrochloride 5a-c.
4. Investigation of the reaction mechanism

4.1 The deuterium-labeled experiments

In order to clarify the origination of the hydrogen atom from hydrazination products \( \textbf{2} \), the deuterium-labeled experiments were conducted. We speculate that the hydrogen atom of products originates from alcohols. Benzyl alcohol-OD (\( \textbf{1e-D} \)) was prepared according to the previous reference (\textit{J. Org. Chem.} 2019, \textbf{84}, 11676). When benzyl alcohol-OD was used under the standard conditions in CD\(_3\)CN, the peak of \( ^1\)H spectrum at 2.16 ppm disappeared and D-\( \textbf{2e} \) was afforded (Figure S2). It suggests that the hydrogen atom might originate from benzyl alcohol. Next, benzyl alcohol-OD and \( \textbf{2e} \) were stirred for 12 h in CD\(_3\)CN. It is found that there is no deuterium exchange between benzyl alcohol-OD and \( \textbf{2e} \). Thus, the hydrogen atom of \( \textbf{2e} \) likely originates from alcohols. Generally, the nucleophile is a relatively acidic compound (pKa \( \leq 15 \)) in Mitsonobu Reaction. However, the pKa value of alcohols is greater than 15 (pKa-\( \textbf{1e} \) = 27 in DMSO). As shown in Figure S4, the formed intermediate \( \textbf{7} \) might contribute to the proton transfer, resulting in the oxypophonium salt \( \textbf{8} \) and the hydrazine anion. In addition, \( \textbf{1f} \) was chosen to examine the possible intermediate. As shown in Figure S5-2, there are three kinds of peaks. A small peak at -115.2 ppm can be assigned to \( \textbf{2f} \). The major peak at 117.1 ppm might be assigned to the relatively stable oxypophonium salt \( \textbf{8} \) while the rest peak at -116.54 ppm might be assigned to the unstable intermediate \( \textbf{7} \).

Figure S2. The \( ^1\)H spectrum of the reaction mixture and \( \textbf{2e} \).
Figure S3. The $^1$H spectrum of benzyl alcohol-OD and 2e.

Figure S4. The proposed mechanism.

Figure S5. The $^{19}$F spectrum of reaction mixture.
4.2 The side reaction

We found that the yellow color of DBAD solution disappeared as soon as DBAD was mixed with Ph$_3$P. The byproduct di-tert-butyl hydrazine-1,2-dicarboxylate was collected after purification. In batch, the side reaction will compete with the deoxygenative hydrazination, resulting in a lower yield.

di-tert-butyl hydrazine-1,2-dicarboxylate $^1$H NMR (400 MHz, Chloroform-$_d$) δ 6.66 (s, 2H), 1.39 (s, 18H).
5. Characterization of products

di-tert-butyl 1-(4-phenylbutyl)hydrazine-1,2-dicarboxylate (2a). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 308.9 mg, 85%, purified by flash chromatography, colorless solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.20 (m, 2H), 7.15 (t, J = 7.7 Hz, 3H), 6.29 - 6.08 (br m, 1H), 3.44 (s, 2H), 2.62 (d, J = 7.0 Hz, 2H), 1.59 (q, J = 4.5 Hz, 4H), 1.45 (dd, J = 8.2, 5.1 Hz, 18H).

di-tert-butyl 1-(2-(benzoyloxy)ethyl)hydrazine-1,2-dicarboxylate (2b). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 246.1 mg, 67%, purified by flash chromatography, colorless solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 4.5 Hz, 4H), 7.28 (t, J = 3.9 Hz, 1H), 6.54 – 6.35 (br m, 1H), 4.49 (s, 2H), 3.52 (t, J = 5.8 Hz, 2H), 1.88 (p, J = 6.5 Hz, 2H), 1.45 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 155.2, 155.2, 138.1, 138.1, 128.3, 127.6, 81.0, 81.0, 72.7, 67.3, 48.7, 28.1. HRMS m/z (ESI) calcd for C₁₉H₃₀N₂NaO₅⁺ (M + Na)⁺ 389.2047; found:389.2050.

di-tert-butyl 1-(2-(benzoyloxy)-2-oxoethyl)hydrazine-1,2-dicarboxylate (2c). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 258.5 mg, 68%, purified by flash chromatography, white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.27 (m, 5H), 6.69 (br s, 1H), 5.18 (d, J = 6.5 Hz, 2H), 4.28 (d, J = 35.2 Hz, 2H), 1.46 (s, 18H), ¹³C NMR (101 MHz, CDCl₃) δ 169.7, 155.1, 154.5, 135.2, 128.6, 128.4, 128.2, 81.9, 81.4, 67.0, 51.0, 28.1, 28.0.

di-tert-butyl 1-(2-(naphthalen-1-yl)ethyl)hydrazine-1,2-dicarboxylate (2d). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 266.5 mg, 69%, purified by flash chromatography, white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 1H), 7.78 (dd, J = 47.5, 7.5 Hz, 2H), 7.48 (dd, J = 16.8, 8.9 Hz, 2H), 7.42 – 7.27 (m, 2H), 6.52 – 6.37 (br m, 1H), 3.82 (s, 2H), 3.37 (s,
di-tert-butyl 1-benzylhydrazine-1,2-dicarboxylate\(^2\) (2e). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph\(_3\)P reagent and 1.5 equiv DBAD reagent; 257.6 mg, 80\%, purified by flash chromatography, white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 (dt, \(J = 14.2, 7.0\) Hz, 5H), 6.28 – 6.05 (br m, 1H), 4.64 (s, 2H), 1.48 (s, 9H), 1.44 (s, 9H).

\[ \text{di-tert-butyl 1-(4-fluorobenzyl)hydrazine-1,2-dicarboxylate}^3 \] (2f). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph\(_3\)P reagent and 1.5 equiv DBAD reagent; 248.6 mg, 73\%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, DMSO-d6) \(\delta\) 9.13 (s, 1H), 7.31 (s, 2H), 7.14 (d, \(J = 8.0\) Hz, 2H), 4.43 (s, 2H), 1.40 (d, \(J = 12.7\) Hz, 18H).

\[ \text{di-tert-butyl 1-(4-cyanobenzyl)hydrazine-1,2-dicarboxylate}^3 \] (2g). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph\(_3\)P reagent and 1.5 equiv DBAD reagent; 253.3 mg, 73\%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 (d, \(J = 7.9\) Hz, 2H), 7.44 (d, \(J = 7.9\) Hz, 2H), 6.56 (br s, 1H), 4.68 (s, 2H), 1.48 – 1.43 (m, 18H).

\[ \text{di-tert-butyl 1-(4-(trifluoromethyl)benzyl)hydrazine-1,2-dicarboxylate}^3 \] (2h). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph\(_3\)P reagent and 1.5 equiv DBAD reagent; 281.0 mg, 72\%, purified by flash chromatography, white solid; Rf = 0.4 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 – 7.38 (m, 4H), 6.35 – 6.24 (br m, 1H), 4.68 (s, 2H), 1.46 (d, \(J = 15.4\) Hz, 18H).
di-tert-butyl 1-(3-phenoxymethyl)hydrazine-1,2-dicarboxylate (2i). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph3P reagent and 1.5 equiv DBAD reagent; 302.3 mg, 73%, purified by flash chromatography, white waxy semi-solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.49 - 7.13\) (m, 3H), \(7.12 - 6.71\) (m, 6H), \(6.34 - 6.18\) (br m, 1H), \(4.54\) (s, 2H), \(1.45\) (s, 9H), \(1.39\) (s, 9H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 157.4, 156.9, 155.0, 139.2, 129.7, 129.4, 123.3, 122.7, 118.9, 118.2, 117.7, 110.0, 81.3, 81.3, 52.6, 28.1, 28.1. HRMS m/z (ESI) calcd for C\(_{23}\)H\(_{31}\)N\(_2\)O\(_5\)\(^{+}\) (M + H)\(^+\) 415.2227, found: 415.2225.

di-tert-butyl 1-(3-nitrobenzyl)hydrazine-1,2-dicarboxylate (2j). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph3P reagent and 1.5 equiv DBAD reagent; 312.1 mg, 85%, purified by flash chromatography, light yellow solid; Rf = 0.4 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.71 - 7.30\) (m, 4H), \(6.28 - 6.09\) (br m, 1H), \(4.68\) (s, 2H), \(1.48\) (s, 9H), \(1.45\) (s, 9H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 155.4, 155.0, 148.2, 139.4, 134.6, 129.4, 123.0, 122.5, 81.9, 81.5, 50.5, 28.1, 28.0. HRMS m/z (ESI) calcd for C\(_{17}\)H\(_{25}\)N\(_3\)NaO\(_6\)\(^{+}\) (M + Na)\(^+\) 390.1636, found: 390.1637.

di-tert-butyl 1-(2-chlorobenzyl)hydrazine-1,2-dicarboxylate (2k). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph3P reagent and 1.5 equiv DBAD reagent; 270.9 mg, 76%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta 9.21\) (s, 1H), \(7.42\) (d, \(J = 5.0\) Hz, 2H), \(7.30\) (dd, \(J = 9.6, 5.2\) Hz, 2H), \(4.60\) (s, 2H), \(1.40\) (s, 18H).

di-tert-butyl 1-(3,5-dimethoxybenzyl)hydrazine-1,2-dicarboxylate (2l). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph3P reagent and 1.5 equiv DBAD reagent; 309.7 mg, 81%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.43\) (s, 2H), \(6.39 - 6.36\) (m, 1H), \(6.14\) (s, 1H), \(4.58\) (s, 2H), \(3.77\) (s, 6H), \(1.49\) (s, 9H), \(1.45\) (s, 9H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 160.8, 155.7, 155.1, 139.5, 133.4, 131.0, 128.9, 128.8, 116.7, 115.3, 112.3, 111.9, 112.7, 111.8, 111.2, 110.0, 110.0, 109.9, 109.9, 81.3, 81.3, 52.6, 28.1, 28.1.
106.1, 99.3, 81.2, 81.1, 55.2, 52.9, 28.1, 28.1. HRMS m/z (ESI) calcd for C_{19}H_{31}N_{2}O_{6}^{+} (M + H)^{+} 383.2177, found: 383.2170.

di-tert-butyl 1-(2,4,6-trimethylbenzyl)hydrazine-1,2-dicarboxylate (2m). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 287.6 mg, 79%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 6.84 (s, 2H), 6.07 (s, 1H), 5.10 – 4.35 (m, 2H), 2.27 (d, J = 6.8 Hz, 9H), 1.47 (s, 9H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 155.5, 154.8, 138.5, 138.3, 137.2, 137.0, 129.5, 129.0, 80.9, 80.8, 45.3, 28.2. HRMS m/z (ESI) calcd for C_{20}H_{33}N_{2}O_{4}^{+} (M + H)^{+} 365.2435, found: 365.2438.

di-tert-butyl 1-(naphthalen-1-ylmethyl)hydrazine-1,2-dicarboxylate (2n). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 282.9 mg, 76%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 40.9 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.50 (p, J = 6.6 Hz, 2H), 7.41 (q, J = 6.9 Hz, 2H), 6.07 – 5.87 (br m, 1H), 5.07 (d, J = 41.9 Hz, 2H), 1.51 (s, 9H), 1.43 (s, 9H).

di-tert-butyl 1-(furan-2-ylmethyl)hydrazine-1,2-dicarboxylate (2o). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 209.1 mg, 67%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.34 (m, 1H), 6.36 (br s, 1H), 6.33 – 6.29 (m, 1H), 6.24 – 6.06 (br m, 1H), 4.61 (s, 2H), 1.48 (s, 9H), 1.45 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 155.0, 154.9, 150.7, 142.3, 110.3, 108.6, 81.3, 81.2, 45.7, 28.2. HRMS m/z (ESI) calcd for C_{15}H_{25}N_{2}O_{5}^{+} (M + H)^{+} 313.1758, found: 313.1762.

di-tert-butyl 1-(thiophen-2-ylmethyl)hydrazine-1,2-dicarboxylate (2p). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 236.5 mg, 72%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J = 37.3$ Hz, 1H), 6.92 (d, $J = 14.9$ Hz, 2H), 6.34 - 6.09 (br m, 1H), 4.75 (s, 2H), 1.45 (s, 18H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.9, 154.7, 139.4, 126.9, 126.7, 125.5, 81.5, 81.3, 47.6, 28.2, 28.1. HRMS m/z (ESI) calcd for C$_{15}$H$_{25}$N$_2$O$_4$S$^+$ (M + H)$^+$ 329.1530, found: 329.1530.

di-tert-butyl 1-(benzo[b]thiophen-2-ylmethyl)hydrazine-1,2-dicarboxylate (2q). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph$_3$P reagent and 1.5 equiv DBAD reagent; 332.9 mg, 83%, purified by flash chromatography, white crystalline solid; RF = 0.5 (petroleum ether/ethylacetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J = 7.5$ Hz, 1H), 7.43 (d, $J = 8.1$ Hz, 1H), 7.26 – 7.16 (m, 2H), 6.63 (s, 1H), 6.28 - 6.51 (br m, 1H), 4.77 (s, 2H), 1.49 (s, 9H), 1.45 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.9, 154.6, 153.4, 153.4, 128.2, 124.1, 122.7, 120.8, 111.1, 105.3, 81.6, 81.3, 46.4, 28.1. HRMS m/z (ESI) calcd for C$_{19}$H$_{26}$N$_2$NaO$_4$S$^+$ (M + Na)$^+$ 401.1505, found: 401.1495.

di-tert-butyl 1-(2-(5-ethylpyridin-2-yl)ethyl)hydrazine-1,2-dicarboxylate (2r). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph$_3$P reagent and 1.5 equiv DBAD reagent; 255.9 mg, 70%, purified by flash chromatography, white crystalline solid; RF = 0.4 (petroleum ether/ethylacetate 4:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (s, 1H), 7.50 – 7.37 (m, 1H), 7.14 (s, 1H), 6.52 (br s, 1H), 3.82 (s, 2H), 3.01 (s, 2H), 2.61 (q, $J = 7.6$ Hz, 2H), 1.47 (s, 18H), 1.23 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.4, 155.8, 155.1, 148.7, 136.8, 135.9, 128.2, 124.1, 122.7, 120.8, 111.1, 80.8, 49.0, 35.3, 28.2, 28.1, 25.6, 15.3. HRMS m/z (ESI) calcd for C$_{19}$H$_{32}$N$_3$O$_4^+$ (M + H)$^+$ 366.2387, found: 366.2384.

di-tert-butyl 1-((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)hydrazine-1,2-dicarboxylate (2s). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph$_3$P reagent and 1.5 equiv DBAD reagent; 259.2 mg, 68%, purified by flash chromatography, colorless solid; RF = 0.5 (petroleum ether/ethylacetate 3:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (d, $J = 3.8$ Hz, 1H), 7.30-7.17 (br m, 1H), 4.69 (s, 2H), 3.74 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H), 1.56 – 1.40 (m, 18H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.8, 156.1, 154.5, 154.5, 148.7, 124.8, 123.9, 81.0, 80.4, 59.8, 51.9, 28.1, 28.1, 13.0, 10.2. HRMS m/z (ESI) calcd for C$_{19}$H$_{32}$N$_3$O$_5^+$ (M + H)$^+$ 382.2336, found: 382.2335.
di-tert-butyl 1-((6-(methoxycarbonyl)pyridin-3-yl)methyl)hydrazine-1,2-dicarboxylate (2t). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 285.9 mg, 75%, purified by flash chromatography, white crystalline solid; Rf = 0.5 (petroleum ether/ethylacetate 3:1); ¹H NMR (400 MHz, CDCl₃) δ 9.12 (s, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 6.99 - 6.72 (br m, 1H), 4.84 (s, 2H), 3.95 (s, 3H), 1.46 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 165.6, 161.7, 155.5, 154.7, 150.4, 137.6, 124.6, 121.6, 81.6, 81.0, 54.9, 52.3, 28.1, 28.0. HRMS m/z (ESI) calcd for C₁₈H₂₈N₃O₆⁺ (M + H)⁺ 382.1973, found: 382.1979.

di-tert-butyl 1-((2-bromothiazol-4-yl)methyl)hydrazine-1,2-dicarboxylate (2u). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 276.9 mg, 68%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 3:1); ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, J = 32.9 Hz, 1H), 6.8 - 6.57 (br m, 1H), 4.73 (s, 2H), 1.47 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 155.0, 154.7, 152.9, 135.5, 119.9, 81.5, 81.1, 49.4, 28.0, 28.0. HRMS m/z (ESI) calcd for C₁₄H₂₃BrN₃O₄S⁺ (M + H)⁺ 408.0587, found: 408.0590.

di-tert-butyl 1-((4-bromothieno[2,3-c]pyridin-2-yl)methyl)hydrazine-1,2-dicarboxylate (2v). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 358.7 mg, 79%, purified by flash chromatography, white solid; Rf = 0.5 (petroleum ether/ethylacetate 3:1); ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 1H), 8.52 (s, 1H), 7.33 - 6.47 (br m, 1H), 4.93 (s, 2H), 1.52 (s, 9H), 1.47 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 154.1, 148.8, 144.6, 144.0, 142.5, 136.6, 122.1, 114.2, 82.0, 81.3, 48.8, 28.1. HRMS m/z (ESI) calcd for C₁₆H₂₃BrN₃O₃S⁺ (M + H)⁺ 458.0744; found: 458.0748.
\begin{align*}
&\text{di-tert-butyl 1-((1-tert-butoxycarbonyl)-1H-indol-3-yl)methyl} & \text{hydrazine-1,2-dicarboxylate (2w).}\notag \\
&\text{According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph}_3\text{P reagent and 1.5 equiv} \\
&\text{DBAD reagent; 341.4 mg, 74\%, purified by flash chromatography, off-white solid; Rf = 0.5} \\
&\text{(petroleum ether/ethylacetate 3:1); } & \text{1H NMR (400 MHz, CDCl}_3) & \delta 8.13 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 9.3 Hz, 2H), 7.32 (t, J = 7.7 Hz, 1H), 6.96 – 6.18 (br m, 1H), 4.77 (s, 2H), 1.67 (s, 9H), 1.50 (s, 9H), 1.45 (s, 9H).} \\
&\text{13C NMR (101 MHz, CDCl}_3) & \delta 155.2, 155.2, 149.6, 135.6, 129.8, 125.3, 124.5, 122.7, 119.5, 115.2, 83.8, 81.3, 43.7, 28.2, 28.2. \notag \\
&\text{HRMS m/z (ESI) calcd for C}_{24}\text{H}_{36}\text{N}_3\text{O}_6^+ (M + H)^+ 462.2599, found: 462.2592.} \\
\end{align*}

\begin{align*}
&\text{di-tert-butyl 1-((1H-benzo[d][1,2,3]triazol-1-yl)methyl} & \text{hydrazine-1,2-dicarboxylate (2x).}\notag \\
&\text{According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph}_3\text{P reagent and 1.5 equiv} \\
&\text{DBAD reagent; 284.2 mg, 78\%, purified by flash chromatography, off-white solid; Rf = 0.5} \\
&\text{(petroleum ether/ethylacetate 2:1); } & \text{1H NMR (400 MHz, CDCl}_3) & \delta 7.93 (d, J = 68.6 Hz, 1H), 7.50 (t, J = 10.4 Hz, 1H), 7.43 – 7.26 (m, 1H), 6.92 – 6.67 (m, 1H), 6.51 (br s, 1H), 6.24 (s, 2H), 1.48 (s, 9H), 1.46 (s, 9H).} \\
&\text{13C NMR (101 MHz, CDCl}_3) & \delta 155.8, 154.5, 145.9, 132.6, 127.7, 124.1, 119.5, 110.5, 81.6, 81.2, 60.6, 28.0, 27.9. \notag \\
&\text{HRMS m/z (ESI) calcd for C}_{17}\text{H}_{26}\text{N}_5\text{O}_4^+ (M + H)^+ 364.1979, found: 364.1984.} \\
\end{align*}

\begin{align*}
&\text{di-tert-butyl 1-((1,1’-biphenyl-4-yl)ethyl} & \text{hydrazine-1,2-dicarboxylate (2y).}\notag \\
&\text{According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph}_3\text{P reagent and 1.5 equiv DBAD reagent;} \\
&\text{280.2 mg, 68\%, purified by flash chromatography, off-white solid; Rf = 0.5} \\
&\text{(petroleum ether/ethylacetate 5:1); } & \text{1H NMR (400 MHz, CDCl}_3) & \delta 7.56 (t, J = 8.2 Hz, 4H), 7.47 – 7.37 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 6.09 – 6.01 (br m, 1H), 5.65 – 5.54 (m, 1H), 1.57 (d, J = 6.6 Hz, 3H), 1.47 (s, 18H).} \\
&\text{13C NMR (101 MHz, CDCl}_3) & \delta 155.4, 154.5, 140.8, 140.4, 140.3, 128.7, 127.6, 127.2, 127.1, 127.0, 81.3, 80.9, 54.4, 29.7, 28.3, 28.2. \notag \\
&\text{HRMS m/z (ESI) calcd for C}_{23}\text{H}_{38}\text{N}_3\text{O}_6^+ (M + H)^+ 413.2435, found: 413.2447.} \\
\end{align*}
di-tert-butyl 1-(1-phenoxypinan-2-yl)hydrazine-1,2-dicarboxylate (2z). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 261.2 mg, 71%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.23 (m, 2H), 6.94 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 7.6 Hz, 2H), 6.12 (br s, 1H), 4.61 (d, J = 48.6 Hz, 1H), 3.93 (d, J = 51.2 Hz, 2H), 1.25 (d, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.5, 155.7, 154.7, 129.3, 120.8, 114.5, 81.3, 81.0, 68.6, 51.5, 28.1, 28.1, 14.1. HRMS m/z (ESI) calcd for C₁₉H₃₀N₂O₅⁺ (M + Na)⁺ 389.2047, found: 389.2055.

di-tert-butyl 1-(1-benzylpiperidin-4-yl)hydrazine-1,2-dicarboxylate (2ab). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 284.3 mg, 70%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 3:1); ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 4.2 Hz, 4H), 7.24 (dd, J = 9.0, 4.4 Hz, 1H), 6.09 – 5.83 (br m, J = 104.6 Hz, 1H), 4.04 (s, 1H), 3.48 (s, 2H), 2.93 (d, J = 11.0 Hz, 2H), 2.03 (t, J = 12.7 Hz, 2H), 1.87 – 1.60 (m, 4H), 1.46 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 156.2, 155.6, 138.3, 129.2, 128.2, 127.0, 81.1, 80.8, 63.1, 54.4, 52.9, 29.2, 28.2, 28.2. HRMS m/z (ESI) calcd for C₂₂H₃₆N₃O₄⁺ (M + H)⁺ 406.2700, found: 406.2713.

di-tert-butyl (Z)-1-(3-phenylallyl)hydrazine-1,2-dicarboxylate (2ac). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 257.9 mg, 74%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.33 (m, 2H), 7.30 (dt, J = 9.7, 4.6 Hz, 2H), 7.26 – 7.19 (m, 1H), 6.52 (d, J = 4.3 Hz, 1H), 6.48 (d, J = 4.4 Hz, 1H), 6.29 – 6.14 (m, 1H), 4.22 (s, 2H), 1.49 (d, J = 4.9 Hz, 9H), 1.45 (d, J = 4.8 Hz, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 155.3, 155.2, 136.6, 133.0, 128.5, 127.6, 126.4, 124.4, 81.2, 81.1, 51.8, 28.2, 28.1. HRMS m/z (ESI) calcd for C₁₉H₂₈N₂NaO₄⁺ (M + Na)⁺ 371.1941, found: 371.1950.
di-tert-butyl 1-(6-bromohexyl)hydrazine-1,2-dicarboxylate (2ad). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 272.1 mg, 69%, purified by flash chromatography, white semi-solid; Rf = 0.7 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 6.34 - 6.14 (br m, 1H), 3.40 (t, J = 6.8 Hz, 4H), 1.86 (p, J = 6.9 Hz, 2H), 1.57 (p, J = 7.4 Hz, 2H), 1.47 (m, 20H), 1.32 (dt, J = 15.6, 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.6, 155.4, 81.0, 80.9, 49.2, 33.7, 32.7, 28.2, 28.2, 27.8, 27.3, 25.8. HRMS m/z (ESI) calcd for C₁₆H₃₂BrN₂O₄⁺ (M + H)⁺ 395.1540, found: 395.1545.

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

di-tert-butyl 1-(hex-5-en-1-yl)hydrazine-1,2-dicarboxylate (2ae). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 226.4 mg, 72%, purified by flash chromatography, white semi-solid; Rf = 0.7 (petroleum ether/ethylacetate 5:1). ¹H NMR (400 MHz, CDCl₃) δ 6.35 (br m, 1H), 5.88 – 5.62 (m, 1H), 5.17 – 4.78 (m, 2H), 3.44 (s, 2H), 2.07 (q, J = 7.3 Hz, 2H), 1.57 (p, J = 7.3 Hz, 2H), 1.47 (d, J = 5.3 Hz, 18H), 1.43 – 1.36 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.4, 155.1, 138.5, 114.6, 81.0, 80.8, 49.1, 33.4, 28.2, 28.1, 26.8, 25.9. HRMS m/z (ESI) calcd for C₁₆H₃₀N₂NaO₄⁺ (M + Na⁺) 337.2098, found: 337.2093.

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

di-tert-butyl 1-(hex-5-en-1-yl)hydrazine-1,2-dicarboxylate (2af). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 243.6 mg, 67%, purified by flash chromatography, white semi-solid; Rf = 0.7 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 6.32 – 6.09 (br m, 1H), 3.44 (s, 2H), 2.07 (q, J = 7.3 Hz, 2H), 1.95 (t, J = 2.5 Hz, 1H), 1.68 (t, J = 7.4 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.48 (s, 9H), 1.46 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 157.9, 155.5, 84.2, 81.1, 81.0, 68.5, 48.8, 28.2, 26.6, 25.6, 18.1. HRMS m/z (ESI) calcd for C₁₆H₃₀N₂O₄⁺ (M + H⁺) 313.2122, found: 313.2114.

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

di-tert-butyl 1-(2-((tert-butyldimethylsilyl)oxy)ethyl)hydrazine-1,2-dicarboxylate (2ag). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 277.1 mg, 71%, purified by flash chromatography, light yellow solid; Rf = 0.7 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 6.47 - 6.17 (br m, 1H), 3.75 (s, 2H), 3.56 (s, 2H), 1.47 (s, 18H), 0.89 (s, 9H), 0.13 - 0.01 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 155.2, 154.8, 81.3, 80.9, 60.7, 51.4, 28.2, 28.1, 25.8, 18.1, -5.4. HRMS m/z (ESI) calcd for C₁₈H₄₂N₂O₅Si⁺ (M + NH₄⁺) 408.2888, found: 408.2893.
di-tert-butyl 1-((1R,4S)-bicyclo[2.2.1]heptan-2-yl)methyl)hydrazine-1,2-dicarboxylate  (2ah). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 241.5 mg, 71%, purified by flash chromatography, white semi-solid; Rf = 0.6 (petroleum ether/ethylacetate 5:1); ¹H NMR (400 MHz, CDCl₃) δ 6.30 – 6.07 (br m, 1H), 3.45 (s, 2H), 2.25 – 2.10 (m, 2H), 1.79 (s, 1H), 1.70 (ddd, J = 15.8, 9.4, 3.4 Hz, 1H), 1.60 – 1.52 (m, 2H), 1.47 (d, J = 3.7 Hz, 18H), 1.31 (d, J = 15.2 Hz, 3H), 1.16 – 1.08 (m, 1H), 0.75 – 0.63 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 155.9, 155.4, 81.3, 80.9, 51.3, 39.8, 38.9, 36.9, 36.5, 30.0, 22.7. HRMS m/z (ESI) calcd for C₁₈H₃₃N₂O₄+ (M + H)+ 341.2435, found: 341.2435.

di-tert-butyl 1-(2-((3r,5r,7r)-adamantan-1-yl)ethyl)hydrazine-1,2-dicarboxylate  (2ai). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 260.3 mg, 66%, purified by flash chromatography, white solid; Rf = 0.6 (petroleum ether/ethylacetate 5:1). ¹H NMR (400 MHz, CDCl₃) δ 6.28 – 6.02 (br m, 1H), 3.45 (s, 2H), 1.94 (s, 2H), 1.66 (dt, J = 22.5, 11.9 Hz, 8H), 1.50 (s, 5H), 1.47 (d, J = 5.4 Hz, 18H), 1.37 – 1.31 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.4, 155.2, 80.9, 46.0, 42.3, 41.2, 37.1, 31.6, 28.6, 28.2, 28.2. HRMS m/z (ESI) calcd for C₂₂H₃₉N₂O₄+ (M + H)+ 395.2904, found: 395.2905.

di-tert-butyl 1-((1-((benzyloxy)carbonyl)piperidin-4-yl)methyl)hydrazine-1,2-dicarboxylate  (2aj). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent; 310.3 mg, 67%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 3:1); ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 4.1 Hz, 4H), 7.30 (dd, J = 8.8, 4.6 Hz, 1H), 6.47 – 6.39 (br m, 1H), 5.12 (s, 2H), 4.13 (dt, J = 14.3, 9.3 Hz, 2H), 3.32 (s, 2H), 2.78 (s, 2H), 2.04 (s, 1H), 1.70 (d, J = 12.5 Hz, 2H), 1.47 (s, 9H), 1.45 (s, 9H), 1.21 – 1.07 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.5, 155.4, 136.8, 128.4, 127.8, 127.7, 81.3, 81.0, 66.9, 55.0, 43.8, 34.7, 29.6, 28.1. HRMS m/z (ESI) calcd for C₂₄H₃₈N₃O₆+ (M + H)+ 464.2755, found: 464.2754.

di-tert-butyl 1-((1-(benzoyloxy)carbonyl)piperidin-4-yl)methyl)hydrazine-1,2-dicarboxylate  (2aj). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph₃P reagent and 1.5 equiv DBAD reagent;
270.5 mg, 73%, purified by flash chromatography, white solid; Rf = 0.6 (petroleum ether/ethylacetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.31 - 6.10 (br m, 1H), 5.09 (d, $J$ = 6.6 Hz, 1H), 3.47 (s, 2H), 1.99 (dp, $J$ = 22.1, 7.2, 6.3 Hz, 2H), 1.84 (s, 1H), 1.69 (d, $J$ = 4.9 Hz, 3H), 1.60 (s, 2H), 1.49 (d, $J$ = 6.5 Hz, 18H), 1.40 – 1.29 (m, 3H), 1.24 – 1.08 (m, 2H), 0.91 (t, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.6, 150.3, 126.2, 119.6, 76.1, 75.8, 42.5, 31.9, 29.1, 25.1, 23.2, 23.2, 20.7, 20.4, 14.4, 12.6.

HRMS m/z (ESI) calcd for C$_{20}$H$_{39}$N$_2$O$_4$ $^+$ (M + H)$^+$ 371.2904, found: 371.2902.

di-tert-butyl 1-(3,7-dimethylethyl)hydrazine-1,2-dicarboxylate (4b). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph$_3$P reagent and 1.5 equiv DBAD reagent; 271.8 mg, 73%, purified by flash chromatography, off-white solid; Rf = 0.6 (petroleum ether/ethylacetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.33 - 6.10 (br m, 1H), 3.46 (s, 2H), 1.61 – 1.50 (m, 2H), 1.48 (s, 18H), 1.44 (s, 3H), 1.39 – 1.30 (m, 4H), 1.28 – 1.18 (m, 8H), 1.16 – 1.09 (m, 3H), 1.08 – 0.97 (m, 4H), 0.83 (t, $J$ = 7.2 Hz, 12H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.4, 155.0, 81.0, 80.8, 47.5, 39.2, 37.1, 34.3, 30.5, 28.2 (d, $J$ = 3.2 Hz), 27.9, 24.6, 22.7, 22.6, 19.5. HRMS m/z (ESI) calcd for C$_{20}$H$_{41}$N$_2$O$_4$ $^+$ (M + H)$^+$ 373.3061, found: 373.3061.

di-tert-butyl (E)-1-(3,7,11,15-tetramethylhexadec-2-en-1-yl)hydrazine-1,2-dicarboxylate (4c). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph$_3$P reagent and 1.5 equiv DBAD reagent; 385.6 mg, 76%, purified by flash chromatography, off-white solid; Rf = 0.6 (petroleum ether/ethylacetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.33 - 6.11 (br m, 1H), 5.23 – 5.11 (m, 1H), 4.05 (s, 2H), 1.95 (p, $J$ = 9.0, 8.5 Hz, 2H), 1.61 (s, 3H), 1.44 (s, 18H), 1.39 – 1.30 (m, 4H), 1.28 – 1.18 (m, 8H), 1.16 – 1.09 (m, 3H), 1.08 – 0.97 (m, 4H), 0.83 (t, $J$ = 7.2 Hz, 12H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.4, 155.0, 81.0, 80.8, 46.3, 39.2, 37.1, 34.3, 30.5, 28.2 (d, $J$ = 3.2 Hz), 27.9, 24.6, 22.7, 22.6, 19.7, 19.7, 16.0. HRMS m/z (ESI) calcd for C$_{30}$H$_{59}$N$_2$O$_4$ $^+$ (M + H)$^+$ 511.4469, found: 511.4470.

di-tert-butyl(2-(2-(4-chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl)hydrazine-1,2-dicarboxylate (4d). According to the general procedure in 1.0 mmol scale using 1.5 equiv Ph$_3$P reagent and 1.5 equiv DBAD reagent; 375.9 mg, 65%, purified by flash chromatography, off-white solid; Rf = 0.5 (petroleum ether/ethylacetate 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.07 (m, 10H), 6.80 (t, $J$ = 11.4 Hz, 2H), 6.54 (d, $J$ = 8.5 Hz, 2H), 6.46 – 6.24 (br m, 1H), 3.98 (s, 2H), 2.82, 2.79, 25.1, 24.8, 24.5, 22.7, 22.6, 19.7, 19.7, 16.0. HRMS m/z (ESI) calcd for C$_{30}$H$_{59}$N$_2$O$_4$ $^+$ (M + H)$^+$ 511.4469, found: 511.4470.
3.77 (s, 2H), 3.42 (tt, J = 7.5, 4.6 Hz, 2H), 2.93 (ddt, J = 10.1, 7.5, 4.5 Hz, 2H), 1.54 – 1.32 (m, 18H); 13C NMR (101 MHz, CDCl3) δ 156.7, 155.1, 154.9, 142.8, 141.6, 140.8, 135.1, 135.0, 131.7, 129.4, 129.3, 128.3, 128.2, 126.9, 126.5, 113.3, 81.2, 81.1, 64.9, 48.9, 42.8, 38.5, 28.1. HRMS m/z (ESI) calcd for C34H42ClN2O5+ (M + H)+ 593.2777, found: 593.2779.

octan-2-ylhydrazine hydrochloride (5a). According to the general procedure in 20 mmol scale; 2.56 g, 71%, white solid; 1H NMR (400 MHz, CD3OD) δ 3.24 – 3.14 (m, 1H), 1.79 (ddt, J = 14.5, 10.0, 4.6 Hz, 1H), 1.46 (dd, J = 14.7, 9.9 Hz, 1H), 1.41 – 1.31 (m, 8H), 1.29 (d, J = 6.6 Hz, 3H), 0.96 – 0.86 (m, 3H). 13C NMR (101 MHz, CD3OD) δ 58.9, 32.7, 32.7, 30.2, 26.4, 23.6, 15.4, 14.4.

phenethylhydrazine hydrochloride (5b). According to the general procedure in 10 mmol scale; 1.08 g, 63%, white solid; 1H NMR (400 MHz, CD3OD) δ 7.43 – 7.11 (m, 5H), 3.31 (dt, J = 3.3, 1.6 Hz, 1H), 3.29 – 3.25 (m, 1H), 2.96 (ddd, J = 9.1, 6.8, 1.5 Hz, 2H); 13C NMR (101 MHz, CD3OD) δ 138.4, 129.9, 129.8, 128.1, 53.6, 32.6.

(4-(benzo[d][1,3]dioxol-5-yl)butan-2-yl)hydrazine hydrochloride (5c). According to the general procedure in 10 mmol scale; 1.61 g, 66%, white solid. 1H NMR (400 MHz, CD3OD) δ 6.78 – 6.75 (m, 1H), 6.75 – 6.67 (m, 2H), 5.89 (d, J = 2.3 Hz, 2H), 3.29 – 3.17 (m, 1H), 2.76 – 2.65 (m, 1H), 2.64 – 2.55 (m, 1H), 2.16 – 2.06 (m, 1H), 1.82 – 1.68 (m, 1H), 1.36 (d, J = 6.6 Hz, 3H); 13C NMR (101 MHz, Methanol-d4) δ 149.2, 147.4, 135.7, 122.3, 109.7, 109.1, 102.1, 58.2, 34.8, 32.2, 15.4.
6. NMR spectra of products

di-tert-butyl 1-(4-phenylbutyl)hydrazine-1,2-dicarboxylate (2a)

\[
\begin{align*}
\text{H} & \quad \text{Boc}^- \\
\text{N} & \quad \text{N} \\
\text{Boc} & \quad \text{Boc}
\end{align*}
\]

di-tert-butyl 1-(2-(benzylxoy)ethyl)hydrazine-1,2-dicarboxylate (2b)

\[
\begin{align*}
\text{\textbf{O}} & \quad \text{\textbf{H}} \\
\text{\textbf{N}} & \quad \text{\textbf{Boc}} \\
\text{\textbf{Boc}} & \quad \text{\textbf{Boc}}
\end{align*}
\]
di-tert-butyl 1-(2-(benzyloxy)-2-oxoethyl)hydrazine-1,2-dicarboxylate (2c)
di-tert-butyl 1-(2-(naphthalen-1-yl)ethyl)hydrazine-1,2-dicarboxylate (2d)
di-tert-butyl 1-benzylhydrazine-1,2-dicarboxylate (2e)
di-tert-butyl 1-(4-fluorobenzyl)hydrazine-1,2-dicarboxylate (2f)

di-tert-butyl 1-(4-cyanobenzyl)hydrazine-1,2-dicarboxylate (2g)
di-tert-butyl 1-(4-(trifluoromethyl)benzyl)hydrazine-1,2-dicarboxylate (2h)

\[
\begin{align*}
\text{H} & \quad \text{F}_3\text{C} \\
\text{N} & \quad \text{Boc} \\
\end{align*}
\]

\[
\begin{align*}
\text{\textbf{H}} & \quad \text{\textbf{F}}_3\text{C} \\
\text{\textbf{Boc}} & \quad \text{\textbf{Boc}} \\
\end{align*}
\]

\[
\begin{align*}
\text{\textbf{1.46}} & \quad \text{\textbf{-0.00}} \\
\end{align*}
\]

di-tert-butyl 1-(3-phenoxybenzyl)hydrazine-1,2-dicarboxylate (2i)

\[
\begin{align*}
\text{\textbf{8.48}} & \quad \text{\textbf{8.48}} \\
\text{\textbf{3.24}} & \quad \text{\textbf{5.76}} \\
\text{\textbf{1.66}} & \quad \text{\textbf{1.66}} \\
\text{\textbf{6.91}} & \quad \text{\textbf{6.24}} \\
\text{\textbf{0.95}} & \quad \text{\textbf{0.95}} \\
\text{\textbf{7.55}} & \quad \text{\textbf{7.75}} \\
\text{\textbf{7.53}} & \quad \text{\textbf{7.54}} \\
\text{\textbf{7.50}} & \quad \text{\textbf{7.47}} \\
\text{\textbf{7.48}} & \quad \text{\textbf{7.49}} \\
\text{\textbf{7.43}} & \quad \text{\textbf{7.43}} \\
\text{\textbf{6.34}} & \quad \text{\textbf{6.34}} \\
\text{\textbf{7.24}} & \quad \text{\textbf{7.24}} \\
\text{\textbf{7.25}} & \quad \text{\textbf{7.25}} \\
\text{\textbf{7.25}} & \quad \text{\textbf{7.25}} \\
\text{\textbf{7.00}} & \quad \text{\textbf{7.00}} \\
\text{\textbf{6.98}} & \quad \text{\textbf{6.98}} \\
\text{\textbf{6.16}} & \quad \text{\textbf{6.16}} \\
\text{\textbf{4.54}} & \quad \text{\textbf{4.54}} \\
\text{\textbf{1.45}} & \quad \text{\textbf{1.39}} \\
\text{\textbf{-0.00}} & \\
\end{align*}
\]
di-tert-butyl 1-(3-nitrobenzyl)hydrazine-1,2-dicarboxylate (2j)
di-tert-butyl 1-(2-chlorobenzyl)hydrazine-1,2-dicarboxylate (2k)
di-tert-butyl 1-(3,5-dimethoxybenzyl)hydrazine-1,2-dicarboxylate (21)

\[
\text{MeO} \quad \begin{array}{c}
\text{H} \\
\text{N} \\
\text{N} \\
\text{Me} \\
\text{Me}
\end{array} \\
\text{OMe}
\]

\[
\text{MeO} \\
\text{H} \\
\text{N} \\
\text{N} \\
\text{Me} \\
\text{Me}
\]

\[
\begin{array}{c}
\text{MeO} \\
\text{H} \\
\text{N} \\
\text{N} \\
\text{Me} \\
\text{Me}
\end{array} \\
\text{OMe}
\]
**di-tert-butyl 1-(2,4,6-trimethylbenzyl)hydrazine-1,2-dicarboxylate (2m)**

![Chemical Structure Image]

**NMR Spectra**

**1H NMR (400 MHz, CDCl3)**

- 6.84
- 6.07
- 4.99
- 4.78
- 4.75
- 4.71
- 4.83
- 4.80
- 2.27
- 2.28
- 1.47
- 1.43
- 0.00

- 2.00
- 0.89
- 2.09
- 0.28
- 0.74

**13C NMR (100 MHz, CDCl3)**

- 155.53
- 154.76
- 138.71
- 139.25
- 137.03
- 129.48
- 128.86
- 80.93
- 79.79
- 77.79
- 77.02
- 77.10
- 45.26
- 28.17
- 28.09
- 20.88
- 19.57

**Additional Structural Information**

- Me (Methyl)
- Boc ( tert-Butyloxycarbonyl)

S30
di-tert-butyl 1-(naphthalen-1-ylmethyl)hydrazine-1,2-dicarboxylate (2n)

[Chemical structure image]

di-tert-butyl 1-(furan-2-ylmethyl)hydrazine-1,2-dicarboxylate (2o)

[Chemical structure image]
di-tert-butyl 1-(thiophen-2-ylmethyl)hydrazine-1,2-dicarboxylate (2p)
di-tert-butyl 1-(benzo[b]thiophen-2-ylmethyl)hydrazine-1,2-dicarboxylate (2q)
di-tert-butyl 1-(2-(5-ethylpyridin-2-yl)ethyl)hydrazine-1,2-dicarboxylate (2r)
di-tert-butyl 1-((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)hydrazine-1,2-dicarboxylate (2s)
di-tert-butyl 1-((6-(methoxycarbonyl)pyridin-3-yl)methyl)hydrazine-1,2-dicarboxylate (2t)
di-tert-butyl 1-((2-bromothiazol-4-yl)methyl)hydrazine-1,2-dicarboxylate (2u)
di-tert-butyl 1-((4-bromothieno[2,3-c]pyridin-2-yl)methyl)hydrazine-1,2-dicarboxylate (2v)
di-tert-butyl 1-((1-(tert-butoxycarbonyl)-1H-indol-3-yl)methyl)hydrazine-1,2-dicarboxylate (2w)
di-tert-butyl 1-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)hydrazine-1,2-dicarboxylate (2x)
di-tert-butyl 1-((1,1'-biphenyl)-4-yl)ethyl)hydrazine-1,2-dicarboxylate (2y)
di-tert-butyl 1-(1-phenoxypropan-2-yl)hydrazine-1,2-dicarboxylate (2z)
di-tert-butyl 1-(1-benzylpiperidin-4-yl)hydrazine-1,2-dicarboxylate (2ab)
di-tert-butyl (Z)-1-(3-phenylallyl)hydrazine-1,2-dicarboxylate (2ac)
di-tert-butyl 1-(6-bromohexyl)hydrazine-1,2-dicarboxylate (2ad)
di-tert-butyl 1-(hept-6-en-1-yl)hydrazine-1,2-dicarboxylate (2ae)
di-tert-butyl 1-(hex-5-yn-1-yl)hydrazine-1,2-dicarboxylate (2af)
di-territ-buty 1-(2-((tert-butyldimethylsilyl)oxy)ethyl)hydrazine-1,2-dicarboxylate (2ag)

\[
\text{HN-\text{Boc}} \quad \frac{\text{N}}{\text{Boc}}
\]
di-tert-butyl 1-(((1R,4S)-bicyclo[2.2.1]heptan-2-yl)methyl)hydrazine-1,2-dicarboxylate (2ah)
di-tert-butyl 1-((3r,5r,7r)-adamantan-1-yl)ethyl)hydrazine-1,2-dicarboxylate (2ai)
di-tert-butyl 1-((1-((benzyloxy)carbonyl)piperidin-4-yl)methyl)hydrazine-1,2-dicarboxylate (2aj)
di-tert-butyl 1-(3,7-dimethyloct-6-en-1-yl)hydrazine-1,2-dicarboxylat (4a)
**di-tert-butyl 1-(3,7-dimethyloctyl)hydrazine-1,2-dicarboxylate (4b)**
di-tert-butyl (E)-1-(3,7,11,15-tetramethylhexadec-2-en-1-yl)hydrazine-1,2-dicarboxylate (4c).
di-tert-butyl(Z)-1-(2-(4-(4-chloro-1,2-diphenylbut-1-en-1-yl)phenoxy)ethyl)hydrazine-1,2-dicarboxylate (4d)
octan-2-ylhydrazine hydrochloride (5a)
phenethylhydrazine hydrochloride (5b)
(4-(benzo[d][1,3]dioxol-5-yl)butan-2-yl)hydrazine hydrochloride (5c)
7. Reference