SUPPORTING INFORMATION

Efficient Synthesis of (E)-2-Nitromethylcinnamates via Phosphine-Catalyzed Tandem α-Addition and 1,3-Rearrangement

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1. General Information --------------------------------------------------S2
2. Optimization of Reaction Conditions -----------------------------------S3
3. Preparation of the Substituted Nitromethanes -------------------------S4
4. Representative Procedure for the Tandem Reaction -------------------S5
5. Procedure for the Gram-scale Synthesis and Elaborations ------------S15
6. Mechanism Studies -----------------------------------------------------S18
7. References -------------------------------------------------------------S25
8. NMR Spectra of the Products-------------------------------------------S26
1. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. $^1$H and $^{13}$C NMR spectra were recorded at ambient temperature in CDCl$_3$ or CD$_3$OD on a Bruker Advance (400 MHz). The chemical shifts are reported in parts per million (ppm) relative to CDCl$_3$ ($\delta = 7.26$) and to CD$_3$OD ($\delta = 3.31$) for $^1$H-NMR and relative to the central resonances of CDCl$_3$ ($\delta = 77.16$) and to CD$_3$OD ($\delta = 49.00$) for $^{13}$C-NMR; multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants ($J$) were reported in Hertz (Hz). All high resolution mass (ESI-MS) were obtained on Thermo LTQ mass spectrometer. For thin layer chromatography (TLC) was performed using commercially prepared and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatographic separations were performed on commercially prepared 200-300 mesh silica gel.

All the substituted nitro compounds were synthesized based on known methods reported in literature.$^{[1]}$
2. Optimization of Reaction Conditions

Table S1: Screening of the catalysts<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time [h]</th>
<th>Yield [%]&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
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<td>Ph&lt;sub&gt;3&lt;/sub&gt;P</td>
<td>4</td>
<td>91</td>
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<tr>
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<tr>
<td>3</td>
<td>Cy&lt;sub&gt;3&lt;/sub&gt;P</td>
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<td>4</td>
<td>TEA</td>
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<td>31</td>
</tr>
<tr>
<td>5</td>
<td>DABCO</td>
<td>4</td>
<td>&lt;5</td>
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</tbody>
</table>

<sup>a</sup>Reactions were performed with 1a (0.1 mmol), 2a (0.15 mmol) and catalyst in solvent (1.0 mL) at room temperature. <sup>b</sup>Yields of isolated products. TEA = triethylamine, DABCO = 1,4-diazabicyclo[2.2.2]octane.

Table S2: Screening of the solvent<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>solvent</th>
<th>Time [h]</th>
<th>Yield [%]&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>90</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reactions were performed with 1a (0.1 mmol), 2a (0.15 mmol) and catalyst in solvent (1.0 mL) at room temperature. <sup>b</sup>Yields of isolated products.
Table S3: Screening of the catalyst loading

<table>
<thead>
<tr>
<th>Entry</th>
<th>x mol %</th>
<th>Time [h]</th>
<th>Yield [%]</th>
</tr>
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</tr>
<tr>
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<tr>
<td>5</td>
<td>1</td>
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<td>84</td>
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</tbody>
</table>

*a* Reactions were performed with 1a (0.1 mmol), 2a (0.15 mmol) and catalyst in solvent (1.0 mL) at room temperature. *b* Yields of isolated products. *c* The solvent was toluene.

3. Preparation of the Substituted Nitromethanes

All substituted nitromethanes were synthesized according to the reported procedures.[1]

\[
\begin{align*}
\text{Ph} & \text{NO}_2 + \text{CO}_2\text{Me} & \text{Cy}_3\text{P} (x \text{ mol}%) \\
\begin{array}{c}
\text{Ph} \\
1a
\end{array} & \text{CH}_2\text{Cl}_2, \text{RT} & \begin{array}{c}
\text{P} \\
3a_1
\end{array}
\end{align*}
\]

Scheme S1. Preparation of the substituted nitromethanes.

Silver nitrite (1.154 g, 7.5 mmol) was added to a round bottom flask covered in tin foil containing anhydrous diethyl ether (15 mL). After stirring at room temperature for 15 minutes, the mixture was then cooled at 0 °C. A solution of benzylbromide (5 mmol) in diethyl ether (1.0 mL) was added dropwise via addition funnel. The reaction was stirred at 0 °C for 1 h and then heated to reflux for 4 h. The mixture was filtered over celite using ethyl acetate as eluent. The product was purified by column chromatography on silica gel (eluting with 10:1 hexane/ethyl acetate unless otherwise stated). All nitro substrates were known compounds and listed in Figure S1.
4. Representative Procedure for the Tandem Reaction

To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl)benzene 1a (27.4 mg, 0.2 mmol) and Cy₃P (0.6 mg, 0.002 mmol), followed by the addition of dry CH₂Cl₂ (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate 2a (25.2 mg, 0.3 mmol) in CH₂Cl₂ (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 12 h, and TLC show that the reaction was completed. Then, the CH₂Cl₂ was removed under reduced pressure. The
residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford 3a₁ (41.6 mg, 94% yield) as a yellow oil.

**methyl (E)-2-(nitromethyl)-3-phenylacrylate (3a₁)**

![3a₁](image)

A yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 1H), 7.48-7.41 (m, 3H), 7.36-7.23 (m, 2H), 5.35 (s, 2H), 3.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.20, 147.66, 133.48, 130.20, 129.13, 128.91, 122.00, 71.83, 52.72; HRMS (ESI) m/z calcd for C₁₁H₁₁NO₄ [M+Na]⁺ = 244.0586, found = 244.0568.

**ethyl (E)-2-(nitromethyl)-3-phenylacrylate (3a₂)**

![3a₂](image)

A yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 1H), 7.48-7.41 (m, 3H), 7.36-7.29 (m, 2H), 5.35 (s, 2H), 4.33 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.69, 147.33, 133.58, 130.10, 129.09, 128.89, 122.34, 71.87, 61.83, 14.15; HRMS (ESI) m/z calcd for C₁₂H₁₃NO₄ [M+Na]⁺ = 258.0742, found = 258.0732.

**tert-butyl (E)-2-(nitromethyl)-3-phenylacrylate (3a₃)**

![3a₃](image)

A yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.46-7.40 (m, 3H), 7.34-7.29 (m, 2H), 5.30 (s, 2H), 1.53 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 164.62, 146.41, 133.82, 129.86, 129.04, 128.79, 123.81, 82.52, 72.10, 27.98; HRMS (ESI) m/z calcd for C₁₄H₁₇NO₄ [M+Na]⁺ = 286.1055, found = 286.1029.

**(E)-3-(nitromethyl)-4-phenylbut-3-en-2-one (3a₄)**
A yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (s, 1H), 7.52-7.42 (m, 3H), 7.37-7.30 (m, 2H), 5.34 (s, 2H), 2.55 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.47, 147.10, 133.51, 131.25, 130.34, 129.22, 128.87, 70.63, 25.33; HRMS (ESI) \(m/z\) calcd for C\(_{11}\)H\(_{11}\)NO\(_3\) [M+Na]\(^+\) = 228.0637, found = 228.0628.

**methyl (E)-2-(nitromethyl)-3-(o-tolyl)acrylate (3b)**

A yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25 (s, 1H), 7.32 (dd, \(J = 7.6, 7.6\) Hz, 1H), 7.28-7.20 (m, 3H), 7.10 (d, \(J = 7.6\) Hz, 1H), 5.24 (s, 2H), 3.88 (s, 3H), 2.31 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.97, 147.35, 137.25, 132.82, 130.60, 129.99, 127.79, 126.37, 122.86, 71.69, 52.70, 19.88; HRMS (ESI) \(m/z\) calcd for C\(_{12}\)H\(_{13}\)NO\(_4\) [M+Na]\(^+\) = 258.0742, found = 258.0728.

**methyl (E)-3-(2-fluorophenyl)-2-(nitromethyl)acrylate (3c)**

A yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.15 (s, 1H), 7.47-7.40 (m, 1H), 7.30-7.25 (m, 1H), 7.24-7.19 (m, 1H), 7.19-7.12 (m, 1H), 5.30 (s, 2H), 3.88 (s, 3H); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -112.12; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.70, 160.24 (d, \(J = 249.5\) Hz), 140.54 (d, \(J = 3.2\) Hz), 132.26 (d, \(J = 8.5\) Hz), 129.85 (d, \(J = 2.3\) Hz), 124.79 (d, \(J = 3.7\) Hz), 124.03, 121.44 (d, \(J = 14.0\) Hz), 116.27 (d, \(J = 21.3\) Hz), 71.82 (d, \(J = 1.8\)Hz), 52.84; HRMS (ESI) \(m/z\) calcd for C\(_{11}\)H\(_{10}\)NO\(_4\)F [M+Na]\(^+\) = 262.0492, found = 262.0484.
methyl (E)-3-(2-chlorophenyl)-2-(nitromethyl)acrylate (3d)

![Structure](image)

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (s, 1H), 7.47 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.38 (ddd, $J = 7.6$, 7.6, 1.6 Hz, 1H), 7.32 (ddd, $J = 7.6$, 7.6, 1.6 Hz, 1H), 7.26 (dd, $J = 7.6$, 1.6 Hz, 1H), 5.23 (s, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.63, 144.71, 134.23, 132.23, 131.25, 130.11, 129.42, 127.34, 123.86, 71.79, 52.87; HRMS (ESI) m/z calcd for C$_{11}$H$_{10}$NO$_4$Cl [M+Na]$^+$ = 278.0196, found = 278.0196.

methyl (E)-3-(2-bromophenyl)-2-(nitromethyl)acrylate (3e)

![Structure](image)

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 (s, 1H), 7.66 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.38 (ddd, $J = 7.6$, 76, 1.2 Hz, 1H), 7.30 (ddd, $J = 7.6$, 76, 1.6 Hz, 1H), 7.25 (dd, $J = 7.6$, 1.6 Hz, 1H), 5.22 (s, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.61, 146.69, 134.14, 133.26, 131.31, 129.47, 127.93, 123.92, 123.58, 71.76, 52.88; HRMS (ESI) m/z calcd for C$_{11}$H$_{10}$NO$_4$Br [M+Na]$^+$ = 321.9691, found = 321.9697.

methyl (E)-2-(nitromethyl)-3-(2-(trifluoromethyl)phenyl)acrylate (3f)

![Structure](image)

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.35-8.30 (m, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 7.61 (dd, $J = 7.2$, 7.2 Hz, 1H), 7.55 (dd, $J = 7.6$, 7.6 Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 5.13 (s, 2H), 3.89 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -60.57; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.30, 144.33, 132.44, 132.03 (q, $J = 1.7$Hz, 129.49 (d, $J = 43.4$ Hz), 128.83 (d, $J = 30.5$ Hz), 128.02 (d, $J = 69.8$ Hz), 126.52 (q, $J = 5.1$ Hz), 124.95,
122.23, 71.48, 52.92; HRMS (ESI) m/z calcd for C_{12}H_{10}NO_{4}F_3 [M-H]^- = 288.0489, found = 288.0493.

**methyl (E)-2-(nitromethyl)-3-(m-tolyl)acrylate (3g)**

![3g](image)

A yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 (s, 1H), 7.36-7.30 (m, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.15-7.08 (m, 2H), 5.36 (s, 2H), 3.87 (s, 3H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.28, 147.91, 138.97, 133.45, 131.01, 129.59, 129.02, 125.94, 121.74, 71.88, 52.71, 21.41; HRMS (ESI) m/z calcd for C$_{12}$H$_{13}$NO$_4$ [M+Na]$^+$ = 258.0742, found = 258.0727.

**methyl (E)-3-(3-fluorophenyl)-2-(nitromethyl)acrylate (3h)**

![3h](image)

A yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (s, 1H), 7.42 (ddd, $J = 8.0, 8.0, 6.0$ Hz, 1H), 7.17-7.08 (m, 2H), 7.06-7.01 (m, 1H), 5.33 (s, 2H), 3.87 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -111.07; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.83, 162.85 (d, $J = 247.0$ Hz), 146.14 (d, $J = 2.2$ Hz), 135.47 (d, $J = 7.7$ Hz), 130.90 (d, $J = 8.3$ Hz), 124.47 (d, $J = 3.1$ Hz), 123.15, 117.16 (d, $J = 21.0$ Hz), 115.78 (d, $J = 22.2$ Hz), 71.59, 52.86; HRMS (ESI) m/z calcd for C$_{11}$H$_{10}$NO$_4$F [M+Na]$^+$ = 262.0492, found = 262.0505.

**methyl (E)-3-(3-chlorophenyl)-2-(nitromethyl)acrylate (3i)**

![3i](image)

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (s, 1H), 7.43-7.35 (m, 2H), 7.33-7.29 (m, 1H), 7.22-7.17 (m, 1H), 5.32 (s, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz,
CDCl$_3$ δ 165.79, 146.00, 135.21, 135.16, 130.46, 130.19, 128.82, 126.70, 123.28, 71.56, 52.89; HRMS (ESI) m/z calcd for C$_{11}$H$_{10}$NO$_4$Cl [M-H] = 254.0226, found = 254.0105.

**methyl (E)-3-(3-bromophenyl)-2-(nitromethyl)acrylate (3j)**

![3j](image)

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.50-7.45 (m, 1H), 7.32 (dd, $J = 8.0$ 7.6, Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 5.31 (s, 2H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.79, 146.00, 135.21, 135.16, 130.46, 130.19, 128.82, 126.70, 123.28, 71.56, 52.89; HRMS (ESI) m/z calcd for C$_{11}$H$_{10}$NO$_4$Cl [M-H] = 254.0226, found = 254.0105.

**methyl (E)-2-(nitromethyl)-3-(3-(trifluoromethyl)phenyl)acrylate (3k)**

![3k](image)

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.62-7.56 (m, 2H), 7.51 (d, $J = 7.6$ Hz, 1H), 5.30 (s, 2H), 3.89 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.94; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.66, 145.87, 135.43, 133.10, 131.71, 130.66, 127.11, 123.32, 123.22, 71.53, 52.89; HRMS (ESI) m/z calcd for C$_{11}$H$_{10}$NO$_4$Br [M-H] = 297.9720, found = 297.8659.

**methyl (E)-2-(nitromethyl)-3-(p-tolyl)acrylate (3l)**

![3l](image)

A yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (s, 1H), 7.19-7.12 (m, 4H), 5.29 (s, 2H), 3.78 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.41, 147.77,
140.83, 130.61, 129.86, 129.12, 120.98, 71.97, 52.66, 21.44; HRMS (ESI) m/z calcd for C_{12}H_{13}NO_4 [M+Na]^+ = 258.0742, found = 258.0730.

**methyl (E)-3-(4-fluorophenyl)-2-(nitromethyl)acrylate (3m)**

![Chemical structure of 3m](image)

A yellow oil; ^1^H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 7.37-7.30 (m, 2H), 7.18-7.11 (m, 2H), 5.34 (s, 2H), 3.87 (s, 3H); ^19^F NMR (376 MHz, CDCl_3) δ -109.01; ^13^C NMR (100 MHz, CDCl_3) δ 166.08, 163.71 (d, J = 250.8 Hz), 146.52, 131.10 (d, J = 8.6 Hz), 129.56 (d, J = 3.4 Hz), 121.87 (d, J = 0.9 Hz), 116.44 (d, J = 21.8 Hz), 71.78, 52.80; HRMS (ESI) m/z calcd for C_{11}H_{10}NO_4F [M-NO_2]^+ = 193.0659, found = 193.0660.

**methyl (E)-3-(4-chlorophenyl)-2-(nitromethyl)acrylate (3n)**

![Chemical structure of 3n](image)

A white solid; ^1^H NMR (400 MHz, CDCl_3) δ 8.13 (s, 1H), 7.47-7.39 (m, 2H), 7.27 (d, J = 8.0 Hz, 3H), 5.32 (s, 2H), 3.88 (s, 3H); ^13^C NMR (100 MHz, CDCl_3) δ 165.94, 146.33, 136.53, 131.83, 130.22, 129.49, 122.49, 71.69, 52.85; HRMS (ESI) m/z calcd for C_{11}H_{10}NO_4Cl [M-NO_2]^+ = 209.0364, found = 209.0444.

**methyl (E)-3-(4-bromophenyl)-2-(nitromethyl)acrylate (3o)**

![Chemical structure of 3o](image)

A white solid; ^1^H NMR (400 MHz, CDCl_3) δ 8.09 (s, 1H), 7.60-7.55 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 5.31 (s, 2H), 3.87 (s, 3H); ^13^C NMR (100 MHz, CDCl_3) δ 165.93, 146.36, 132.44, 132.29, 130.39, 124.80, 122.57, 71.68, 52.85; HRMS (ESI) m/z calcd for C_{11}H_{10}NO_4Br [M-H]^− = 297.9720, found = 297.9742.
**methyl (E)-3-(4-(tert-butyl)phenyl)-2-(nitromethyl)acrylate (3p)**

A yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (s, 1H), 7.48-7.44 (m, 2H), 7.27 (d, $J$ = 9.2 Hz, 2H), 5.39 (s, 2H), 3.86 (s, 3H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.44, 153.93, 147.69, 130.59, 129.04, 126.14, 121.03, 72.00, 52.68, 34.94, 31.13; HRMS (ESI) $m/z$ calcd for C$_{15}$H$_{19}$NO$_4$ [M+Na]$^+$ = 300.1212, found = 300.1201.

**methyl (E)-2-(nitromethyl)-3-(4-(trifluoromethyl)phenyl)acrylate (3q)**

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (s, 1H), 7.71 (d, $J$ = 8.0 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 5.30 (s, 2H), 3.89 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.99; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.63, 145.86, 136.77 (d, $J$ = 1.1 Hz), 131.88 (q, $J$ = 32.7 Hz), 129.03, 126.10 (q, $J$ = 3.7 Hz), 124.01, 123.62 (d, $J$ = 270.7 Hz), 71.47, 52.94; HRMS (ESI) $m/z$ calcd for C$_{12}$H$_{10}$NO$_4$F$_3$ [M-H]$^-$ = 288.0489, found = 288.0499.

**methyl (E)-2-(nitromethyl)-3-(4-nitrophenyl)acrylate (3r)**

A yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, $J$ = 8.8 Hz, 2H), 8.20 (s, 1H), 7.51 (d, $J$ = 8.8 Hz, 2H), 5.29 (s, 2H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.32, 148.45, 144.86, 139.69, 129.64, 124.95, 124.31, 71.34, 53.10; HRMS (ESI) $m/z$ calcd for C$_{11}$H$_{10}$N$_2$O$_6$ [M-H]$^-$ = 265.0466, found = 265.0490.

**methyl (E)-2-(nitromethyl)-3-(4-(trifluoromethoxy)phenyl)acrylate (3s)**
A white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 7.40-7.35 (m, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 5.33 (s, 2H), 3.88 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.74; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.37, 150.66 (q, $J = 1.8$ Hz), 146.02, 130.38, 122.82, 121.38 (d, $J = 0.6$ Hz), 120.34 (d, $J = 256.9$ Hz), 71.64, 52.86; HRMS (ESI) $m/z$ calcd for C$_{12}$H$_{10}$NO$_5$F$_3$ [M-H]$^-$ = 304.0438, found = 304.0435.

**methyl (E)-3-(4-chloro-2-fluorophenyl)-2-(nitromethyl)acrylate (3t)**

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (s, 1H), 7.28 (dd, $J = 8.8$, 6.0 Hz, 1H), 7.24 (dd, $J = 8.0$, 2.4 Hz, 1H), 7.06 (ddd, $J = 8.0$, 8.0 2.4 Hz, 1H), 5.22 (s, 2H), 3.89 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -107.57; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.49, 163.34 (d, $J = 253.1$ Hz), 143.69, 135.51 (d, $J = 10.3$ Hz), 130.74 (d, $J = 9.1$ Hz), 128.40 (d, $J = 3.7$ Hz), 124.02, 117.85 (d, $J = 24.9$ Hz), 114.88 (d, $J = 21.3$ Hz), 71.77, 52.94; HRMS (ESI) $m/z$ calcd for C$_{11}$H$_9$NO$_4$FCl [M-NO$_2$]$^-$ = 227.0275, found = 227.0270.

**methyl (E)-3-(3,5-dimethylphenyl)-2-(nitromethyl)acrylate (3v)**

A yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 7.06 (s, 1H), 6.91 (s, 2H), 5.36 (s, 2H), 3.86 (s, 3H), 2.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.35, 148.10, 138.82, 133.44, 131.93, 126.65, 121.52, 71.92, 52.68, 21.29; HRMS (ESI) $m/z$ calcd for C$_{13}$H$_{15}$NO$_4$ [M+Na]$^+$ = 272.0899, found = 272.0888.
**methyl (E)-3-(3,5-dimethoxyphenyl)-2-(nitromethyl)acrylate (3w)**

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (s, 1H), 6.50 (dd, $J = 2.4, 2.4$ Hz, 1H), 6.43 (d, $J = 2.4$ Hz, 2H), 5.36 (s, 2H), 3.87 (s, 3H), 3.78 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.12, 161.19, 147.77, 135.25, 122.44, 106.58, 102.18, 71.93, 55.47, 52.75; HRMS (ESI) m/z calcd for C$_{13}$H$_{15}$NO$_6$ [M+Na]$^+$ = 304.0797, found = 304.0775.

**methyl (E)-3-(3,4-dichlorophenyl)-2-(nitromethyl)acrylate (3x)**

A white solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (s, 1H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.43 (d, $J = 2.0$ Hz, 1H), 7.17 (dd, $J = 8.4, 2.0$ Hz, 1H), 5.30 (s, 2H), 3.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.60, 144.91, 134.67, 133.66, 133.26, 131.22, 130.68, 127.77, 123.60, 71.47, 52.96; HRMS (ESI) m/z calcd for C$_{11}$H$_9$NO$_4$Cl$_2$ [M-H]$^-$ = 287.9836, found = 287.8961.

**methyl (E)-3-(naphthalen-1-yl)-2-(nitromethyl)acrylate (3y)**

A yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.71 (s, 1H), 7.95-7.89 (m, 2H), 7.88-7.83 (m, 1H), 7.60-7.54 (m, 2H), 7.49 (dd, $J = 8.4, 7.2$ Hz, 1H), 7.36 (d, $J = 7.2$ Hz, 1H), 5.27 (s, 2H), 3.93 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.87, 146.51, 133.47, 131.20, 130.80, 130.47, 128.78, 127.21, 126.16, 125.38, 124.26, 124.20, 72.03, 52.82; HRMS (ESI) m/z calcd for C$_{15}$H$_{13}$NO$_4$ [M+Na]$^+$ = 294.0742, found = 294.0713.
methyl (E)-3-(naphthalen-2-yl)-2-(nitromethyl)acrylate (3z)

A yellow solid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.34 (s, 1H), 7.92-7.81 (m, 4H), 7.60-7.52 (m, 2H), 7.40 (dd, $J = 8.4, 1.6$ Hz, 1H), 5.44 (s, 2H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.28, 147.80, 133.71, 133.00, 130.90, 129.26, 129.01, 128.61, 127.81, 127.73, 127.10, 125.58, 121.99, 72.04, 52; HRMS (ESI) $m/z$ calcd for C$_{13}$H$_{11}$NO$_4$ [M+Na]$^+$ = 294.0742, found = 294.0743.

5. Procedure for the Gram-scale Synthesis and Elaborations

A. Gram-scale Synthesis

To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl)benzene 1a (1.371 g, 10 mmol), Cy$_3$P (28.0 mg, 0.1 mmol), and followed by the addition of dry CH$_2$Cl$_2$ (70 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate 2a (1.261 g, 15 mmol) in CH$_2$Cl$_2$ (10 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for overnight, and TLC show that the reaction was completed. Then the CH$_2$Cl$_2$ was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford 3a$_1$ (2.100 g, 95% yield) as a yellow oil.
B. Elaborations of product

\[
\begin{align*}
\text{NO}_2 & \quad \text{CO}_2\text{Me} \quad \text{NaNO}_2 (1.0 \text{ eq.}), \text{I}_2 (0.2 \text{ eq.}) \\
3\text{a}_1 & \quad \text{DMSO (5.0 eq.)}, \text{DMF, RT, 3 h} \\
& \quad \text{(91\%)} \\
& \quad \text{NO}_2 \quad \text{MeO}_2\text{C} \\
5 & \quad \text{H}_2 \quad \text{O}_2 \quad \text{N}
\end{align*}
\]

To a stirred solution of \(3\text{a}_1\) (66.4 mg, 0.3 mmol) in DMF (3.0 mL) was added NaNO\(_2\) (20.7 mg, 0.3 mmol) at room temperature in open air. I\(_2\) (15.2 mg, 0.06 mmol) and DMSO (110 \(\mu\)L, 1.5 mmol) were added to the reaction mixture at the same temperature and the reaction was allowed to continue for 3 h. Thereafter the reaction was quenched by the addition of Na\(_2\)S\(_2\)O\(_3\) (10\% w/w aqueous, 4.2 mL) and the resulting mixture was extracted with ethyl acetate (3 \times 10 mL). The combined organic fractions were dried over Na\(_2\)SO\(_4\), and the solvent was removed under vacuum. The crude product thus obtained was purified chromatography over a column of silica gel using hexane/ethyl acetate (20:1) as eluent to afford the desired product \(5\) (67.5 mg, 91\%) as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04-7.99 (m, 2H), 8.02-8.00 (m, 1H), 7.66-7.60 (m, 1H), 7.59-7.53 (m, 2H), 3.90 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.32, 159.15, 132.99, 129.08, 128.67, 124.85, 102.96, 53.26; HRMS (ESI) \(m/z\) calcd for C\(_{11}\)H\(_8\)N\(_2\)O\(_5\) [M+NH\(_4\)]\(^+\) = 266.0771, found = 266.0490.

\[
\begin{align*}
\text{Ph} & \quad \text{CO}_2\text{Me} \quad \text{Zn (20.0 eq.)}, \text{HCl (20.0 eq.)} \\
3\text{a}_1 & \quad \text{EtOH/H}_2\text{O, 0 °C - RT, 12 h} \\
& \quad \text{(90\%)} \\
& \quad \text{Ph} \quad \text{CO}_2\text{Me} \\
\text{NH}_2 & \quad \text{NH}_2
\end{align*}
\]

The compound 6 was prepared using a modified procedure by Trost et al.\(^\text{[2]}\). \(3\text{a}_1\) (664 mg, 3.0 mmol) was taken in HCl/EtOH/H\(_2\)O (27.5 mL, 3.0 M, 60.0 mmol, EtOH/H\(_2\)O = 1:2) and Zn powder (3.923 g, 60.0 mmol) was introduced to the solution
portionwise. The mixture was stirred for 12 h at ambient temperature. The reaction mixture was diluted with water and the aqueous phase was extracted with ethyl acetate twice. The combined organic extracts were washed with brine and dried over Na₂SO₄. After concentration, the resulting residue was purified by column chromatography on silica gel (eluting with 1:1 hexane/ethyl acetate unless otherwise stated) to afford the corresponding amine 6 in 90% yield (516 mg, 2.7 mmol).

To a solution of amine 6 (310 mg, 1.6 mmol) and Et₃N (0.44 mL, 3.2 mmol) anhydrous CH₂Cl₂ (15.0 mL) was slowly added a solution of p-toluenesulfonyl chloride (366 mg, 1.92 mmol) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 10 h. Water was added and the organic layer was separated. The aqueous phase was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers was washed with brine and dried over Na₂SO₄. Solvent was removed under reduced pressure and the residue was purified column chromatography on silica gel using hexane/ethyl acetate (15:1) as an eluent to afford 7 (514 mg, 93% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.70-7.64 (m, 2H), 7.38 (s, 5H), 7.25 (d, J = 8.0 Hz, 2H), 5.32 (s, 1H), 3.94 (d, J = 6.4 Hz, 2H), 3.74 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.68, 143.52, 143.47, 136.50, 133.92, 129.66, 129.53, 128.77, 127.28, 126.48, 52.32, 40.53, 21.54.

The single crystal confirmed the structure of compound 7, and CCDC 1886135 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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6. Mechanism Studies

A. Control experiments

In this study, we performed further experiments to gain a better understanding of our reaction. A few common electrophiles were examined in their reactions with phenyl nitromethane 1a (Scheme S2). When alkyne 2e and 2f were used as acceptors, the reactions could not be initiated and turned out to be no reaction. On the contrary, once alkyne was changed to alkene or allene, the rearrangement didn’t take place and only additive products were observed. These results imply that terminal alkyynes are crucial for the reactivity as well as rearrangement process.
Scheme S2. Control experiments

**ethyl 4-nitro-4-phenylbutanoate (8)**

\[
\text{Ph} - \text{NO}_2 + \text{MeO}_2\text{C} - \equiv - \text{CO}_2\text{Me} \xrightarrow{\text{Cy}_3\text{P} (5 \text{ mol\%})} \text{CH}_2\text{Cl}_2, \text{RT}, 24 \text{ h} \quad \text{no reaction} \quad (1)
\]

\[
\text{Ph} - \text{NO}_2 + \text{Ph} - \equiv - \text{CO}_2\text{Et} \xrightarrow{\text{Cy}_3\text{P} (5 \text{ mol\%})} \text{CH}_2\text{Cl}_2, \text{RT}, 24 \text{ h} \quad \text{no reaction} \quad (2)
\]

\[
\text{Ph} - \text{NO}_2 + \equiv - \text{CO}_2\text{Et} \xrightarrow{\text{Cy}_3\text{P} (5 \text{ mol\%})} \text{CH}_2\text{Cl}_2, \text{RT}, 24 \text{ h} \quad (3)
\]

\[
\text{Ph} - \text{NO}_2 + \equiv - \text{CO}_2\text{Bn} \xrightarrow{\text{Cy}_3\text{P} (5 \text{ mol\%})} \text{CH}_2\text{Cl}_2, \text{RT}, 24 \text{ h} \quad (4)
\]

A colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49-7.43 (m, 2H), 7.43-7.38 (m, 3H), 5.58 (dd, $J = 6.8, 6.4$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 2.82-2.71 (m, 1H), 2.49-2.38 (m, 1H), 2.35 (dd, $J = 6.8, 7.2$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.83, 134.01, 130.04, 129.16, 127.68, 90.07 (d, $J = 1.4$ Hz), 60.90, 30.34, 28.91, 14.17.

**benzyl (E)-5-nitro-5-phenylpent-2-enoate (9)**

\[
\text{Ph} - \text{NO}_2 - \equiv - \text{CO}_2\text{Bn} \xrightarrow{\text{Cy}_3\text{P} (5 \text{ mol\%})} \text{CH}_2\text{Cl}_2, \text{RT}, 24 \text{ h} \quad (87\%)
\]

A colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48-7.41 (m, 5H), 7.38-7.32 (m, 5H), 6.87-6.78 (m, 1H), 6.00 (ddd, $J = 15.6, 1.6, 1.2$ Hz, 1H), 5.54 (dd, $J = 8.8, 6.0$ Hz, 1H), 5.16 (s, 2H), 3.44-3.34 (m, 1H), 3.02-2.93 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$)
δ 165.35, 141.21, 135.70, 133.45, 130.30, 128.61, 128.35, 128.30, 127.59, 125.29, 89.34 (d, J = 1.8 Hz), 66.47, 36.09.

B. Isotope labelling experiments

Next, isotope labelling experiments were also performed for gaining further understanding of the reaction mechanism, and the results were shown in Scheme S3. When reaction between 1a and 2a was conducted in the solvent of deuterated methanol, deuterium incorporation into both β-position (60% of D) and β'-position (91% of D) of the Tandem product was observed (eq. 1). When the deuterium-labelling substrate d-1a was used, we also obtained the similar product with containing D-atom at both β- and β'-positions in high yield (eq. 2). Notably, the reaction of 13C-labeled phenyl-nitromethane c-1a and methyl propiolate 2a afforded the corresponding Tandem product c-3a1 with only incorporating 13C-atom at its β’-position (eq. 3 and Figure S2). These results demonstrated the desired products was constructed via a α-umpolung/1,3-rearrangement sequence.

**Scheme S3.** Isotope labelling experiments.
To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl)benzene 1a (27.4 mg, 0.2 mmol) and Cy₃P (2.8 mg, 0.01 mmol), followed by the addition of CD₃OD (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate 2a (25.2 mg, 0.3 mmol) in CD₃OD (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 10 h, and TLC show that the reaction was completed. Then, the CD₃OD was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford d₁-3a₁ (41.6 mg, 94% yield) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (s, 0.09H), 7.46-7.42 (m, 3H), 7.35-7.30 (m, 2H), 5.37-5.33 (m, 0.81H), 3.87 (s, 3H).

To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl-d₂)benzene d-1a (27.8 mg, 0.2 mmol) and Cy₃P (0.6 mg, 0.002 mmol), followed by the addition of CH₂Cl₂ (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate 2a (25.2 mg, 0.3 mmol) in CH₂Cl₂ (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 12 h, and TLC show that the reaction was completed. Then, the CH₂Cl₂ was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford d₂-3a₁ (41.0 mg, 92%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 1H), 7.46-7.40 (m, 3H), 7.35-7.29 (m, 2H), 5.36-5.33 (m, 2H), 3.87 (s, 3H).
To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl-$^{13}$C)benzene c-1a (27.6 mg, 0.2 mmol) and Cy$_3$P (0.6 mg, 0.002 mmol), followed by the addition of CH$_2$Cl$_2$ (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate 2a (25.2 mg, 0.3 mmol) in CH$_2$Cl$_2$ (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 12 h, and TLC show that the reaction was completed. Then, the CH$_2$Cl$_2$ was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford c-3a$_1$ (42.5 mg, 96% yield) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, $J$ = 158.8 Hz, 1H), 7.48–7.41 (m, 3H), 7.36–7.28 (m, 2H), 5.35 (d, $J$ = 4.0 Hz, 2H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.22 (d, $J$ = 1.7 Hz), 147.70, 133.55 (dd, $J$ = 141.6, 104.2 Hz), 130.22, 129.14 (d, $J$ = 4.2 Hz), 128.92 (d, $J$ = 2.2 Hz), 121.92 (d, $J$ = 73.2 Hz), 71.84, 52.77; HRMS (ESI) m/z calcd for C$_{10}^{13}$H$_{11}$NO$_4$ [M+Na]$^+$ = 245.0619, found = 245.0583.

Figure S2. $^{13}$C NMR spectra of the products 3a$_1$ and c-3a$_1$. 
C. In situ $^{31}$P NMR and ESI-HRMS studies

To gain further insight of the reaction mechanism, we then employed $^{31}$P NMR and ESI-MS techniques for characterization of this catalytic system (Scheme S4). Accordingly, the room-temperature $^{31}$P NMR spectra of reaction mixtures were taken, respectively. As compared with the spectra of catalyst PPh$_3$ ($\delta$ -5.45 ppm, spectrum A) and intermediate A ($\delta$ 32.80 ppm, spectrum B) generated from mixing the PPh$_3$ and alkyne 2a, the $^{31}$P NMR spectrum of the reaction mixture after stirring 25 minutes (spectrum C) exhibited some characteristic phosphorus signals for the possible reaction intermediates; for
instance, the well-resolved phosphorus signals at δ 22.11 and 23.90 ppm suggested the existence of the intermediate \( G \) and possible \( D/E \) in the reaction mixture. Furthermore, the ESI-HRMS spectrum of this reaction mixture was also collected in positive-ion mode and shown the existence of this intermediate \( G \) (Scheme S4b).

**D. Proposed reaction cycle**

According to the preliminary mechanism studies, we proposed the reaction mechanism for this Tandem reaction. As shown in Figure S3, the first conjugate addition of phosphine to electron-deficient alkyne \( 2a \) generates zwitterion \( A \), which deprotonates the incoming nucleophile \( 1a \), resulting in the formation of an ion pair that consists of the cationic form of the phosphonium intermediate \( B \) and nucleophile \( C \). The next \( \alpha \)-selective addition of \( C \) to the intermediate \( B \) leads to intermediate \( D \), and then 1,2-proton shift to give \( E \). Subsequently, \( \beta \)-elimination of the phosphine catalyst may occur to generate the \( \alpha \)-umpolung adduct \( F \). Under the phosphine catalytic conditions, 1,3-rearrangement process of the nitro group takes place via allyl phosphonium intermediate \( G \) to afford the final Tandem product \( 3a_1 \) and complete the catalytic cycle.

![Figure S3. Plausible mechanism.](image)

S24
7. References

8. NMR Spectra of the Products