Supplementary information:

Diastereoselective HOTf-catalyzed three-component one-pot 1,3-dipolar cycloaddition of α-diazo ester, nitrosobenzene and electron-deficient alkene

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**General information:** Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents employed in the reactions were used directly without purification. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on Bruker AMX 500 and Bruker Avance DPX300 spectrophotometer (CDCl$_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as $\delta$ in units of parts per million (ppm) relative to the signal of chloroform-d ($\delta$ 7.26, single) or solvent. Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (double of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a $J$ value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as $\delta$ in units of parts per
High resolution mass spectrometry (HRMS) was recorded on Finnigan MAT 95 × P spectrometer.

Experimental procedures and characterizations:

General procedure for the HOTf catalyzed three component 1,3-dipolar cycloaddition reaction of α-diazo ester, nitrosobenzene and electron deficient alkene

To a solution of nitrosobenzene (0.25 mmol), electron deficient alkene (0.5 mmol) and HOTf (2 mol%) in CH₂Cl₂ (1.0 mL) was added α-diazo ester (0.3 mmol), the resulted solution was stirred at room temperature (23 °C) and monitored by TLC. Upon completion of consumption of nitrosobenze, the solution was concentrated and purified by flush column chromatography using an ethyl acetate/ hexane as eluant on silica gel to afford the desired cycloadduct.

Characterization of the product:

4a

\[ \text{Ph} \quad \text{EtO} - \text{C} - \text{N}=\text{O} \quad \text{''CO}_2\text{Me} \]

\[^{1}H\text{ NMR (CDCl}_{3},\ 500 \text{ MHz}): \delta \ 1.31 (t, J = 7.2 \text{ Hz}, 3 \text{H}), \ 3.52 (s, 3 \text{H}), \ 3.68 (s, 3 \text{H}), \ 4.26-4.34 (m, 3 \text{H}), \ 4.79 (d, J = 7.0 \text{ Hz}, 1 \text{H}), \ 5.01 (d, J = 7.5 \text{ Hz}, 1 \text{H}), \ 6.99 (t, J = 7.5 \text{ Hz}, 1 \text{H}), \ 7.14 (d, J = 8.0 \text{ Hz}, 2 \text{H}), \ 7.26-7.27 (m, 2 \text{H}). \]

\[^{13}C\text{ NMR (CDCl}_{3},\ 125 \text{ MHz}): \delta \ 14.1, \ 52.4, \ 52.7, \ 53.8, \ 62.4, \ 68.1, \ 77.6, \ 114.6, \ 122.7, \ 128.7, \ 150.4, \ 168.4, \ 169.7 \]

HRMS (ESI): Anal. For C_{16}H_{20}NO_{7}^{+1} (M^{+}+1) Calcd.: 338.1240, Found: 338.1236
**H NMR (CDCl₃, 500 MHz)**: δ 3.51 (s, 3H), 3.68 (s, 3H), 3.84 (s, 3H), 4.33 (t, \( J = 7.0 \) Hz, 3H), 4.83 (d, \( J = 7.0 \) Hz, 1H), 5.01 (d, \( J = 7.0 \) Hz, 1H), 6.95 (t, \( J = 7.5 \) Hz, 1H), 7.13 (d, \( J = 8.0 \) Hz, 2H), 7.26-7.29 (m, 2H).

**13C NMR (CDCl₃, 125 MHz)**: δ 52.4, 52.7, 53.3, 53.8, 67.8, 77.7, 114.5, 122.7, 128.8, 150.3, 168.4, 170.2

HRMS (ESI): Anal. For C₁₁H₁₅NO₇⁺ (M⁺+1) Calcd.: 324.1083, Found: 324.1082

![Chemical Structure](image)

**H NMR (CDCl₃, 500 MHz)**: δ 1.30 (t, \( J = 7.2 \) Hz, 3H), 3.56 (s, 3H), 3.68 (s, 3H), 4.26-4.30 (m, 2H), 4.30-4.32 (m, 1H), 4.73 (d, \( J = 6.8 \) Hz, 1H), 4.99 (d, \( J = 7.4 \) Hz, 1H), 7.08 (d, \( J = 9.0 \) Hz, 2H), 7.22 (d, \( J = 9.0 \) Hz, 1H).

**13C NMR (CDCl₃, 125 MHz)**: δ 14.1, 52.6, 52.8, 53.8, 62.5, 68.0, 77.6, 115.9, 127.7, 128.7, 149.0, 168.3, 168.3, 169.3

HRMS (ESI): Anal. For C₁₆H₁₉NO₇ Cl⁺ (M⁺+1) Calcd.: 372.0850, Found: 372.0846

![Chemical Structure](image)

**H NMR (CDCl₃, 500 MHz)**: δ 1.32 (t, \( J = 7.2 \) Hz, 3H), 3.56 (s, 3H), 3.69 (s, 3H), 4.28-4.35 (m, 3H), 4.73 (d, \( J = 6.8 \) Hz, 1H), 4.99 (d, \( J = 7.4 \) Hz, 1H), 6.92-6.95 (m, 1H), 7.97-7.99 (m, 1H), 7.20-7.16 (m, 2H)

**13C NMR (CDCl₃, 125 MHz)**: δ 14.1, 52.6, 52.8, 53.6, 62.6, 67.8, 77.7, 112.2, 114.4, 122.3, 129.9, 134.6, 151.7, 168.2, 168.3, 169.4

HRMS (ESI): Anal. For C₁₆H₁₉NO₇ Cl⁺ (M⁺+1) Calcd.: 372.0850, Found: 372.0853

![Chemical Structure](image)
$^1$H NMR (CDCl$_3$, 500 MHz): δ 1.33 (t, $J = 7.5$ Hz, 3H), 3.58 (s, 3H), 3.70 (s, 3H), 4.29-4.32 (m, 2H), 4.33-4.35 (m, 1H), 4.75 (d, $J = 6.8$ Hz, 1H), 5.01 (d, $J = 7.4$ Hz, 1H), 7.04 (d, $J = 9.0$ Hz, 2H), 7.39 (d, $J = 9.0$ Hz, 1H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 14.7, 52.6, 52.8, 53.7, 62.6, 67.9, 77.6, 115.2, 116.2, 131.6, 149.5, 168.2, 168.3, 169.3

HRMS (ESI): Anal. For C$_{16}$H$_{19}$NO$_7$Br$^+$ (M$^+$+1) Calcd.: 416.0345, Found: 416.0359

$^1$H NMR (CDCl$_3$, 500 MHz): δ 1.33 (t, $J = 7.0$ Hz, 3H), 3.51 (s, 3H), 3.69 (s, 3H), 3.88 (s, 3H), 4.29-4.34 (m, 2H), 4.37 (t, $J = 7.0$ Hz, 1H), 4.88 (d, $J = 7.0$ Hz, 1H), 5.03 (d, $J = 7.0$ Hz, 1H), 7.12 (d, $J = 8.5$ Hz, 2H), 7.60 (d, $J = 8.5$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 14.1, 51.8, 52.6, 52.8, 53.6, 62.7, 67.0, 77.8, 112.8, 123.4, 130.7, 154.0, 166.8, 168.0, 169.1, 169.3

HRMS (ESI): Anal. For C$_{18}$H$_{22}$NO$_9$ (M$^+$+1) Calcd.: 396.1295, Found: 396.1293

$^1$H NMR (CDCl$_3$, 500 MHz): δ 1.31 (t, $J = 7.0$ Hz, 3H), 1.35 (t, $J = 7.0$ Hz, 3H), 3.49 (s, 3H), 3.67 (s, 3H), 4.29-4.35 (m, 5H), 4.86 (d, $J = 6.5$ Hz, 1H), 5.00 (d, $J = 7.5$ Hz, 1H), 7.09 (d, $J = 9.0$ Hz, 2H), 7.94 (d, $J = 9.0$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 14.1, 14.4, 52.6, 52.8, 53.7, 60.7, 62.7, 67.0, 77.8, 112.8, 123.8, 130.7, 154.0, 166.3, 168.1, 168.2, 169.4

HRMS (ESI): Anal. For C$_{19}$H$_{24}$NO$_{9}$ (M$^+$+1) Calcd.: 410.1451, Found: 410.1451
**Supplementary Material (ESI) for Chemical Communications**

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**1H NMR (CDCl₃, 500 MHz):** δ 1.32 (t, J = 7.1 Hz, 3H), 2.30 (s, 3H), 3.59 (s, 3H), 3.70 (s, 3H), 4.26-4.32 (m, 3H), 4.74 (d, J = 7.0 Hz, 1H), 5.02 (d, J = 7.4 Hz, 1H), 7.07-7.11 (m, 4H).

**13C NMR (CDCl₃, 125 MHz):** δ 14.1, 20.7, 52.4, 52.7, 53.9, 62.3, 68.4, 77.5, 115.4, 129.3, 132.5, 147.8, 168.5, 168.6, 169.6

HRMS (ESI): Anal. For C₁₇H₂₂NO₇⁺ (M⁺+1) Calcd.: 352.1396, Found: 352.1397

![4i](image)

**1H NMR (CDCl₃, 500 MHz):** δ 1.01 (t, J = 7.2 Hz, 3H), 2.30 (s, 3H), 3.73 (s, 3H), 3.76 (s, 3H), 3.94-4.01 (m, 2H), 4.21 (dd, J = 8.1, 5.6 Hz, 1H), 4.69 (d, J = 5.6 Hz, 1H), 5.04 (d, J = 8.1 Hz, 1H), 7.09-7.13 (m, 2H), 7.13-7.18 (m, 2H), 7.49 (d, J = 7.8 Hz, 1H).

**13C NMR (CDCl₃, 125 MHz):** δ 13.7, 17.9, 52.6, 52.7, 54.0, 61.7, 67.4, 76.7, 120.5, 126.4, 126.6, 130.4, 132.7, 145.0, 168.4, 168.9, 169.4

HRMS (ESI): Anal. For C₁₇H₂₂NO₇⁺ (M⁺+1) Calcd.: 352.1396, Found: 352.1393

![5a](image)

**1H NMR (CDCl₃, 500 MHz):** δ 1.01 (t, J = 7.5 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H), 3.82-4.00 (m, 2H), 4.09-4.13 (m, 2H), 4.21-4.30 (m, 2H), 4.31-4.34 (m, 1H), 4.77 (d, J = 7.1 Hz, 1H), 4.96 (d, J = 7.4 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 8.7 Hz, 2H), 7.24 (dt, J = 8.7, 7.4 Hz, 2H).

**13C NMR (CDCl₃, 125 MHz):** δ 13.5, 13.9, 14.1, 54.1, 61.7, 61.8, 62.4, 68.2, 77.9, 114.4, 122.5, 128.8, 150.9, 167.9, 167.9, 169.9

HRMS (ESI): Anal. For C₁₈H₂₄NO₇⁺ (M⁺+1) Calcd.: 366.1553, Found: 366.1551

![5b](image)

**1H NMR (CDCl₃, 500 MHz):** δ 1.30 (t, J = 7.2 Hz, 3H), 3.59 (s, 3H), 3.84 (s, 3H), 4.25-4.29 (m, 2H), 4.33 (dd, J = 5.3, 3.6 Hz, 1H), 4.79 (d, J = 3.6 Hz, 1H), 5.11 (d, J = 5.3 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 2H), 7.26-7.29 (m, 2H).

**13C NMR (CDCl₃, 125 MHz):** δ 14.1, 52.9, 53.0, 54.2, 62.4, 70.4, 78.0, 115.4, 123.5, 129.0, 148.9, 168.8, 169.0, 169.9
HRMS (ESI): Anal. For $\text{C}_{18}\text{H}_{20}\text{NO}_7^{+1}$ (M$^+$+1) Calcd.: 338.1240, Found: 338.1237

![Chemical Structure](image1)

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.08 (t, $J = 7.2$ Hz, 3H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H), 4.02 (q, $J = 7.2$ Hz, 2H), 4.26-4.29 (m, 4H), 4.30-4.33 (m, 1H), 4.82 (d, $J = 3.4$ Hz, 1H), 5.10 (d, $J = 5.4$ Hz, 1H), 7.00 (t, $J = 7.4$ Hz, 1H), 7.09 (d, $J = 7.8$ Hz, 2H), 7.26 (m, 2H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 13.9, 14.1, 14.1, 54.5, 62.1, 62.4, 70.6, 78.2, 115.3, 123.4, 129.0, 149.1, 168.3, 169.1, 169.4

HRMS (ESI): Anal. For $\text{C}_{18}\text{H}_{20}\text{NO}_7^{+1}$ (M$^+$+1) Calcd.: 366.1553, Found: 366.1549

![Chemical Structure](image2)

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.31 (t, $J = 6.9$ Hz, 3H), 4.29-4.38 (m, 2H), 4.98 (d, $J = 5.1$ Hz, 1H), 5.03 (dd, $J = 8.7$, 5.1 Hz, 1H), 5.30 (d, $J = 8.7$ Hz, 1H), 7.02 (t, $J = 7.2$ Hz, 1H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.27-7.36 (m, 7H), 7.44-7.52 (m, 3H), 7.64 (d, $J = 7.2$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 14.1, 62.3, 62.4, 71.9, 84.4, 114.3, 122.4, 127.4, 128.6, 128.8, 128.9, 129.1, 129.2, 133.8, 135.9, 136.0, 150.4, 170.8, 195.9

HRMS (ESI): Anal. For $\text{C}_{18}\text{H}_{22}\text{NO}_8^{+1}$ (M$^+$+1) Calcd.: 402.1705, Found: 402.1709

![Chemical Structure](image3)

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 1.33 (t, $J = 7.2$ Hz, 3H), 4.31-4.39 (m, 2H), 4.87 (d, $J = 4.8$ Hz, 1H), 4.96 (dd, $J = 8.1$, 4.8 Hz, 1H), 5.58 (d, $J = 8.1$ Hz, 1H), 7.05 (t, $J = 7.2$ Hz, 1H), 7.13 (d, $J = 8.7$ Hz, 2H), 7.31-7.41 (m, 4H), 7.54-7.57 (m, 1H), 7.64-7.71 (m, 4H), 8.22 (d, $J = 8.7$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 14.1, 62.1, 62.7, 71.8, 82.2, 114.4, 123.0, 124.0, 128.1, 128.7, 128.9, 129.3, 134.2, 135.7, 143.9, 148.2, 149.7, 170.3, 195.4

HRMS (ESI): Anal. For $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_6^{+1}$ (M$^+$+1) Calcd.: 447.1556, Found: 447.1551
\[ \text{5f} \]

\[ ^1\text{H NMR (CDCl}_3, 300\text{ MHz}) : \delta 1.31\ (t, J = 7.2 Hz, 3H), 4.28-4.39\ (m, 2H), 4.93\ (d, J = 6.0 Hz, 1H), 4.97\ (dd, J = 8.4, 6.0 Hz, 1H), 5.33\ (d, J = 8.4 Hz, 1H), 7.03\ (t, J = 7.5 Hz, 1H), 7.15\ (d, J = 7.8 Hz, 2H), 7.30-7.42\ (m, 8H), 7.53\ (t, J = 7.5 Hz, 1H), 7.67\ (d, J = 7.2 Hz, 2H). \]

\[ ^{13}\text{C NMR (CDCl}_3, 75\text{ MHz}) : \delta 14.1, 62.2, 62.5, 71.8, 83.4, 114.3, 122.6, 128.7, 128.8, 129.0, 129.2, 132.5, 134.0, 134.7, 134.9, 135.8, 150.1, 170.7, 195.8 \]

HRMS (ESI): Anal. For C\(_{25}\)H\(_{23}\)NO\(_4\)Cl\(^+\) (M\(^+\)+1) Calcd.: 436.1316, Found: 436.1317

\[ \text{5g} \]

\[ ^1\text{H NMR (CDCl}_3, 300\text{ MHz}) : \delta 1.36\ (t, J = 7.2 Hz, 3H), 2.00\ (s, 3H), 4.22\ (dd, J = 9.3, 5.7 Hz, 1H), 4.31-4.36\ (m, 2H), 4.94\ (d, J = 5.7 Hz, 1H), 5.03\ (d, J = 9.3 Hz, 1H), 7.00\ (t, J = 7.2 Hz, 1H), 7.15\ (d, J = 7.8 Hz, 2H), 7.26-7.34\ (m, 2H), 7.40-7.46\ (m, 3H), 7.53-7.56\ (m, 2H). \]

\[ ^{13}\text{C NMR (CDCl}_3, 75\text{ MHz}) : \delta 14.2, 30.3, 62.3, 67.7, 70.2, 83.3, 114.2, 122.4, 127.7, 129.0, 129.2, 129.5, 135.7, 150.4, 170.8, 203.0 \]

HRMS (ESI): Anal. For C\(_{20}\)H\(_{22}\)NO\(_4\)\(^+\) (M\(^+\)+1) Calcd.: 340.1549, Found: 340.1553

\[ \text{5h} \]

\[ ^1\text{H NMR (CDCl}_3, 300\text{ MHz}) : \delta 1.12\ (t, J = 7.2 Hz, 3H), 1.34\ (t, J = 7.2 Hz, 3H), 4.04-4.11\ (m, 3H), 4.29-4.36\ (m, 2H), 4.96\ (d, J = 4.8 Hz, 1H), 5.48\ (d, J = 8.4 Hz, 1H), 7.01\ (t, J = 7.2 Hz, 1H), 7.17\ (d, J = 7.8 Hz, 2H), 7.29-7.34\ (m, 2H), 7.36-7.44\ (m, 3H), 7.51-7.55\ (m, 2H). \]

\[ ^{13}\text{C NMR (CDCl}_3, 75\text{ MHz}) : \delta 14.0, 14.2, 59.3, 61.7, 62.3, 71.1, 83.1, 114.4, 122.5, 127.4, 128.7, 129.0, 129.2, 136.2, 150.1, 170.0, 170.3 \]

HRMS (ESI): Anal. For C\(_{21}\)H\(_{24}\)NO\(_5\)\(^+\) (M\(^+\)+1) Calcd.: 370.1654, Found: 370.1663

All the above cycloaddition products are liquid except products 4a and 5e, which X-ray crystal structures were determined as CCDC 755558 (4a: zgf43.cif) and CCDC 755559 (5e: zgf51.cif).
References:


Table Effect of solvents\(^a\)

<table>
<thead>
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<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)(^b)</th>
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<tr>
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<td>2</td>
<td>CHCl(_3)</td>
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\(^a\) Reaction conditions: HOTf/1a/2a/3a = 0.02:1.2:1:2 at room temperature (23 °C). \(^b\) Isolated yield.
NMR spectra:
Supplementary Material (ESI) for Chemical Communications
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![NMR spectra images](image_url)