A pot-economy and diastereoselective synthesis involving catalyst-free click reaction for fused-triazolobenzodiazepines

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1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. $^1$H NMR (300 or 400 MHz) and $^{13}$C NMR spectra (75 or 101 MHz) were recorded on Agilent NMR spectrometers. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform $\delta$ 7.26; acetonitrile $\delta$ 1.94; DMSO $\delta$ 2.50), carbon (chloroform $\delta$ 77.0; acetonitrile $\delta$ 1.32 and 118.26; DMSO $\delta$ 39.5). 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 were reported in Hertz (Hz).

The high resolution mass (HRMS) spectra were obtained on a Waters Micromass GCT Premier. LC-MS were performed on an Agilent 2100 LC with a 6130 quadrupole MS spectrometer. A C18 column (5.0 μm, 6.0 x 50 mm) was used for the separation. The mobile phases were MeOH and H₂O both containing 0.05% CF₃CO₂H. A linear gradient was used to increase from 25:75 v/v MeOH/H₂O to 100% MeOH over 7.0 min at a flow rate of 0.7 mL/min. UV detections were conducted at 210 nm, 254 nm and 365 nm. Low resolution mass spectra were recorded in APCI (atmospheric pressure chemical ionization). Final products were purified on Angela HP-100 pre-LC system with a Venusil PrepC₁₈ column (10 μm, 120 Å, 21.2 mm x 250 mm).

Synthesis of intermediate 6a

To a solution of alanine methyl ester hydrochloride 2a (1.2 mmol), 2-azidebenzaldehyde 3a (1.1 mmol), and N-Ethylmaleimide 4a (1.0 mmol) in 2.0 mL of CH₃CN was added Et₃N (2.0 mmol). After stirred at 25 °C for 5 min, the reaction mixture was heated under microwaves at 115 °C for 25 min. Upon the completion of the reaction as monitored by LC-MS, propargyl bromide solution (80% in toluene, 5.0 mmol) and K₂CO₃ (1.5 mmol) were added to the reaction mixture and then heated by microwaves at 120 °C for 40 min. The concentrated reaction mixture was isolated on a semi prep-HPLC with C18 column to afford a light yellow solid 6a (71% yield).

$methyl(1R,3S,3aR,6aS)-3-(2-azidophenyl)-5-ethyl-1-methyl-4,6-dioxo-2-(prop-2-yn-1-yl)octahydropyrrolo[3,4-c]pyrrole-1-carboxylate (6a)$:

![Image of chemical structure]

$^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.37 – 7.16 (m, 3H), 7.11 – 6.99 (m, 1H), 4.96 (d, J = 10.0 Hz, 1H), 3.87 – 3.82 (m, 3H), 3.70 (dd, J = 18.7, 2.4 Hz, 1H), 3.60 (dd, J = 10.0, 8.0 Hz, 1H), 3.44 – 3.12 (m, 4H), 2.20 (t, J = 2.5 Hz, 1H), 1.66 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl₃) $\delta$ 175.2, 174.3, 172.2, 138.9, 129.1, 127.7, 127.3, 124.8, 118.2, 79.2, 74.6, 70.1, 57.8, 54.6, 52.3, 46.0, 35.4, 33.7, 18.8, 12.8.

General procedure for one-pot synthesis of triazolobenzodiazepines 1

To a solution of an amino ester 2 (1.2 mmol), 2-azidebenzaldehyde 3 (1.1 mmol), and maleimide 4 (1.0 mmol) in 2.0 mL of CH₃CN was added Et₃N (2.0 mmol). After stirred at 25 °C for 5 min, the reaction mixture was heated under microwaves at 115 °C for 25 min. Upon the completion of the reaction as monitored by LC-MS, propargyl bromide solution (80% in toluene, 5.0 mmol) and K₂CO₃ (1.5 mmol) were added to the reaction mixture and then heated by microwaves at 150 °C for 50 min. The
concentrated reaction mixture was isolated on a semi prep-HPLC with C<sub>18</sub> column to afford purified product 1 as a single diastereomer.

2. Analytical data for Intermediate 6a and Final Products 1

\( \text{methyl}(11R,11aS,14aR,14bS)-13\text{-ethyl}-11\text{-methyl}-12,14\text{-dioxo}-11a,12,13,14,14a,14b\text{-hexahydro}-9H,11H-benzo[ff]pyrrolo[3',4':3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]diazepine-11-carboxylate (1a):} 

\[ \text{Following the general procedure, the title compound 1a was obtained as a white solid (69% yield).} \]

\( ^1\text{H NMR (400 MHz, CD}_3\text{CN)} \delta 8.12 \text{ (dd, } J = 5.6, 4.0 \text{ Hz, } 1\text{H}), 7.69 \text{ – 7.62 (m, } 1\text{H}), 7.50 \text{ – 7.42 (m, } 3\text{H}), 5.13 \text{ (d, } J = 7.1 \text{ Hz, } 1\text{H}), 4.02 \text{ (d, } J = 15.2 \text{ Hz, } 1\text{H}), 3.72 \text{ – 3.57 (m, } 5\text{H}), 3.16 \text{ (dd, } J = 14.3, 7.4 \text{ Hz, } 3\text{H}), 1.52 \text{ (s, } 3\text{H}), 0.74 \text{ (t, } J = 7.2 \text{ Hz, } 3\text{H).} \]

\( ^{13}\text{C NMR (101 MHz, CD}_3\text{CN)} \delta 175.3, 174.6, 171.5, 137.5, 134.5, 132.1, 130.5, 128.2, 127.2, 126.9, 123.8, 70.5, 67.2, 53.5, 51.7, 47.6, 39.0, 33.1, 14.8, 11.7. \)

\( \text{HRMS (EI, m/z): calcd. for C}_{20}\text{H}_{21}\text{N}_5\text{O}_4: 395.1594, \text{Found: 395.1622.} \)

\( \text{methyl}(11R,11aS,14aR,14bS)-11,13\text{-dimethyl}-12,14\text{-dioxo}-11a,12,13,14,14a,14b\text{-hexahydro}-9H,11H-benzo[ff]pyrrolo[3',4':3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]diazepine-11-carboxylate (1b):} 

\( \text{Following the general procedure, the title compound 1b was obtained as a white solid (63% yield).} \]

\( ^1\text{H NMR (400 MHz, CD}_3\text{CN)} \delta 8.20 \text{ – 8.12 (m, } 1\text{H}), 7.71 \text{ – 7.63 (m, } 1\text{H}), 7.50 \text{ – 7.42 (m, } 3\text{H}), 5.11 \text{ (d, } J = 7.1 \text{ Hz, } 1\text{H}), 4.03 \text{ (d, } J = 15.2 \text{ Hz, } 1\text{H}), 3.75 \text{ (t, } J = 7.5 \text{ Hz, } 1\text{H}), 3.66 \text{ – 3.57 (m, } 4\text{H}), 3.18 \text{ (d, } J = 7.8 \text{ Hz, } 1\text{H}), 2.62 \text{ (s, } 3\text{H}), 1.52 \text{ (s, } 3\text{H).} \]

\( ^{13}\text{C NMR (101 MHz, CD}_3\text{CN)} \delta 175.6, 174.9, 171.5, 137.2, 134.3, 132.1, 130.7, 128.2, 127.2, 126.6, 123.6, 70.6, 67.2, 53.5, 51.7, 47.7, 39.4, 24.1, 14.7. \)

\( \text{HRMS (EI, m/z): calcd. for C}_{19}\text{H}_{19}\text{N}_5\text{O}_4: 381.1437, \text{Found: 381.1511.} \)

\( \text{methyl}(11R,11aS,14aR,14bS)-13\text{-isobutyl}-11\text{-methyl}-12,14\text{-dioxo}-11a,12,13,14,14a,14b\text{-hexahydro}-9H,11H-benzo[ff]pyrrolo[3',4':3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]diazepine-11-carboxylate (1c):} 

\( \text{Following the general procedure, the title compound 1c was obtained as a white solid (63% yield).} \]

\( ^1\text{H NMR (400 MHz, CD}_3\text{CN)} \delta 8.13 \text{ – 8.05 (m, } 1\text{H}), 7.64 \text{ (ddd, } J = 12.8, 6.5, 5.0 \text{ Hz, } 1\text{H}), 7.49 \text{ – 7.41 (m, } 3\text{H}), 5.16 \text{ (d, } J = 7.4 \text{ Hz, } 1\text{H}), 4.04 \text{ (d, } J = 15.1 \text{ Hz, } 1\text{H}), 3.72 \text{ – 3.57 (m, } 6\text{H}), 3.13 \text{ (d, } J = 7.6 \text{ Hz, } 1\text{H),} \)
2.96 (dd, J = 13.1, 7.5 Hz, 2H), 1.52 (s, 3H), 0.56 (d, J = 6.7 Hz, 3H), 0.34 (d, J = 6.7 Hz, 3H).

$^{13}$C NMR (101 MHz, CD$_3$CN) δ 175.7, 174.8, 171.4, 132.2, 128.2, 127.1, 126.8, 123.8, 70.5, 67.4, 53.3, 51.5, 47.4, 45.2, 39.0, 26.3, 18.8, 18.2, 14.5.

HRMS (EI, m/z): calcd. for C$_{22}$H$_{25}$N$_5$O$_4$: 423.1907, Found: 423.2022.

$methyl(11R,11aS,14aR,14bS)$-$11$-methyl-$12,14$-dioxo-$13$-phenyl-$11a,12,13,14a,14b$-hexahydro-$9H,11H$-benzo[f]pyrrolo[3′,4′:3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]$diazipine-$11$-carboxylate ($1d$):

Following the general procedure, the title compound $1d$ was obtained as a white solid (46% yield).

$^1$H NMR (300 MHz, CD$_3$CN) δ 8.13–8.05 (m, 3.5 Hz, 1H), 7.73–7.66 (m, 1H), 7.52–7.10 (m, 6H), 6.89–6.72 (m, 2H), 5.19 (d, J = 6.9 Hz, 1H), 4.05 (d, J = 15.2 Hz, 1H), 3.83–3.50 (m, 4H), 3.29 (d, J = 7.7 Hz, 1H), 1.55 (s, 3H).

$^{13}$C NMR (75 MHz, CD$_3$CN) δ 175.8, 175.2, 172.5, 138.5, 135.4, 133.1, 133.1, 131.5, 129.9, 129.3, 128.2, 127.8, 127.4, 124.7, 71.9, 68.3, 54.7, 52.8, 49.1, 39.9, 15.9.

HRMS (EI, m/z): calcd. for C$_{24}$H$_{21}$N$_5$O$_4$: 443.1594, Found: 443.1684.

$methyl(11R,11aS,14aR,14bS)$-$13$-benzyl-$11$-methyl-$12,14$-dioxo-$11a,12,13,14a,14b$-hexahydro-$9H,11H$-benzo[f]pyrrolo[3′,4′:3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]$diazipine-$11$-carboxylate ($1e$):

Following the general procedure, the title compound $1e$ was obtained as a white solid (66% yield).

$^1$H NMR (300 MHz, CD$_3$CN) δ 8.14–7.93 (m, 1H), 7.70–7.48 (m, 2H), 7.13–7.00 (m, 3H), 6.72 (d, J = 7.0 Hz, 2H), 5.19 (d, J = 7.3 Hz, 1H), 4.36 (s, 2H), 4.05 (d, J = 15.1 Hz, 1H), 3.77 (t, J = 7.5 Hz, 1H), 3.72–3.56 (m, 1H), 3.30 (s, 3H), 3.21 (d, J = 7.7 Hz, 1H), 1.52 (s, 3H).

$^{13}$C NMR (75 MHz, CD$_3$CN) δ 176.3, 175.7, 172.2, 138.5, 136.1, 135.4, 133.2, 131.5, 129.2, 128.8, 128.1, 127.6, 126.6, 124.7, 71.6, 68.4, 54.5, 52.3, 48.5, 42.1, 40.1, 15.4.

HRMS (EI, m/z): calcd. for C$_{25}$H$_{23}$N$_5$O$_4$: 457.1750, Found: 457.1872.

$methyl(11R,11aS,14aR,14bS)$-$13$-methyl-$12,14$-dioxo-$11a,12,13,14a,14b$-hexahydro-$9H,11H$-benzo[f]pyrrolo[3′,4′:3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]$diazipine-$11$-carboxylate ($1f$):

Following the general procedure, the title compound $1f$ was obtained as a white solid (58% yield).

$^1$H NMR (400 MHz, CD$_3$CN) δ 8.18 (d, J = 9.7 Hz, 1H), 7.80 (dd, J = 6.9, 2.5 Hz, 1H), 7.54 (d, J = 0.5 Hz, 1H), 7.52–7.44 (m, 2H), 4.53 (d, J = 6.9 Hz, 1H), 4.15 (d, J = 15.1 Hz, 1H), 3.82–3.72 (m, 3H),
3.66 (d, J = 15.1 Hz, 1H), 3.55 (t, J = 8.1 Hz, 1H), 3.29 (d, J = 5.3 Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) δ 176.0, 175.6, 169.4, 136.3, 134.3, 132.3, 132.1, 128.7, 127.7, 126.3, 123.3, 118.5, 70.2, 66.8, 52.2, 47.4, 46.0, 42.5, 25.1, 1.6.

methyl(11R,11aS,14aR,14bS)-13-ethyl-12,14-dioxo-11a,12,13,14,14a,14b-hexahydro-9H,11H-benzo[f]pyrrolo[3’,4’:3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]diazepine-11-carboxylate (Ig):

Following the general procedure, the title compound Ig was obtained as a white solid (65% yield).

$^1$H NMR (400 MHz, CD$_3$CN) δ 8.15 (dd, J = 5.2, 4.5 Hz, 1H), 7.78 (s, 1H), 7.56 – 7.44 (m, 3H), 4.54 (d, J = 6.8 Hz, 1H), 4.20 – 4.02 (m, 2H), 3.80 – 3.62 (m, 5H), 3.56 – 3.47 (m, 1H), 3.34 – 3.19 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, CD$_3$CN) δ 175.4, 174.7, 169.0, 131.6, 131.2, 128.5, 127.4, 126.1, 123.5, 70.2, 66.6, 51.6, 47.2, 45.8, 41.7, 33.3, 11.8.

methyl(11R,11aS,14aR,14bS)-13-isobutyl-12,14-dioxo-11a,12,13,14,14a,14b-hexahydro-9H,11H-benzo[f]pyrrolo[3’,4’:3,4]pyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]diazepine-11-carboxylate (Ih):

Following the general procedure, the title compound Ih was obtained as a white solid (61% yield).

$^1$H NMR (400 MHz, CD$_3$CN) δ 8.14 – 8.08 (m, 1H), 7.76 – 7.65 (m, 1H), 7.57 – 7.32 (m, 3H), 4.63 (d, J = 7.0 Hz, 1H), 4.20 (d, J = 14.9 Hz, 1H), 3.82 – 3.61 (m, 5H), 3.50 (t, J = 7.8 Hz, 1H), 3.01 (dd, J = 13.1, 7.4 Hz, 3H), 1.66 – 1.50 (m, 1H), 0.58 (d, J = 6.8 Hz, 3H), 0.44 (d, J = 6.7 Hz, 3H).

$^{13}$C NMR (101 MHz, CD$_3$CN) δ 175.8, 175.0, 169.0, 136.9, 136.6, 134.5, 131.7, 130.9, 128.4, 127.3, 126.1, 123.6, 70.6, 66.7, 51.5, 47.2, 45.9, 45.4, 41.4, 26.5, 18.8, 18.5.


Following the general procedure, the title compound Ii was obtained as a white solid (63% yield).

$^1$H NMR (400 MHz, CD$_3$CN) δ 8.12 (dd, J = 6.0, 3.7 Hz, 1H), 7.74 (d, J = 5.8, 3.8 Hz, 1H), 7.62 (d, J = 0.7 Hz, 1H), 7.44 (dd, J = 6.1, 3.5 Hz, 2H), 7.14 (d, J = 7.4 Hz, 1H), 7.04 (dd, J = 10.7, 4.5 Hz, 2H), 6.88 – 6.80 (m, 2H), 4.71 (d, J = 7.1 Hz, 1H), 4.52 – 4.23 (m, 4H), 3.88 – 3.76 (m, 2H), 3.73 – 3.58 (m, 4H).

$^{13}$C NMR (101 MHz, CD$_3$CN) δ 175.5, 174.7, 168.8, 136.8, 135.1, 131.7, 131.0, 128.4, 128.2, 127.3, 126.8, 125.8, 123.5, 70.8, 66.8, 51.5, 47.3, 46.2, 41.7, 41.3.
Following the general procedure, the title compound 1a was obtained as a white solid (61% yield).

$^1$H NMR (400 MHz, $CD_3CN$) δ 8.18 – 7.99 (m, 1H), 7.72 – 7.55 (m, 1H), 7.55 – 7.35 (m, 3H), 5.21 (d, $J = 7.4$ Hz, 1H), 4.32 (d, $J = 15.2$ Hz, 1H), 3.86 (d, $J = 15.1$ Hz, 1H), 3.75 – 3.53 (m, 4H), 3.20 (d, $J = 7.8$ Hz, 1H), 2.58 (s, 3H), 2.07 – 1.96 (m, 2H), 1.09 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, $CD_3CN$) δ 175.7, 174.8, 170.9, 137.8, 134.6, 132.1, 130.4, 128.3, 127.3, 127.0, 123.8, 73.3, 66.8, 52.5, 51.6, 48.0, 39.5, 24.5, 24.0, 9.5.

Following the general procedure, the title compound 1k was obtained as a white solid (60% yield).

$^1$H NMR (400 MHz, $CD_3CN$) δ 8.08 (d, $J = 8.9$ Hz, 1H), 8.00 (d, $J = 2.1$ Hz, 1H), 7.63 (dd, $J = 8.9$, 2.3 Hz, 1H), 7.53 (s, 1H), 4.52 (d, $J = 6.8$ Hz, 1H), 4.15 (d, $J = 15.1$ Hz, 1H), 3.81 – 3.62 (m, 6H), 3.52 (t, $J = 8.0$ Hz, 1H), 3.25 (q, $J = 7.2$ Hz, 2H), 0.83 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, $CD_3CN$) δ 175.2, 174.8, 168.9, 136.3, 134.2, 134.0, 131.4, 128.3, 125.3, 120.4, 69.7, 66.5, 51.7, 47.1, 45.8, 41.7, 33.3, 11.8.

Following the general procedure, the title compound 1a was obtained as a white solid (33% yield).

$^1$H NMR (400 MHz, $CH_3CN$) δ 8.19 – 8.11 (m, 1H), 7.85 – 7.77 (m, 1H), 7.60 – 7.55 (m, 1H), 7.52 – 7.32 (m, 5H), 6.98 – 6.90 (m, 2H), 4.64 (d, $J = 6.5$ Hz, 1H), 4.21 (d, $J = 15.1$ Hz, 1H), 3.93 – 3.85 (m, 2H), 3.78 – 3.65 (m, 5H).

$^{13}$C NMR (101 MHz, $CH_3CN$) δ 175.0, 174.3, 169.2, 136.3, 134.7, 132.1, 131.5, 131.2, 128.9, 128.5, 127.5, 126.4, 126.1, 123.6, 70.3, 67.0, 51.8, 47.8, 46.2, 41.6.
trimethyl(11R,12S,13R,13aS)-11-methyl-11,12,13,13a-tetrahydro-9H-benzof[fpyrrolo[1,2-d][1,2,3]triazolo[1,5-a][1,4]diazepine-11,12,13-tricarboxylate (1m):

Following the general procedure, the title compound 1a was obtained as a off-white solid (55% yield).

$^1$H NMR (300 MHz, CD$_3$CN) δ 7.82 – 7.67 (m, 3H), 7.63 – 7.54 (m, 2H), 4.28 – 4.15 (m, 3H), 3.68 (s, 3H), 3.52 (s, 3H), 3.45 – 3.28 (m, 4H), 3.28 (s, 1H), 1.60 (s, 3H).

$^{13}$C NMR (75 MHz, CD$_3$CN) δ 173.1, 172.8, 171.6, 145.2, 137.2, 134.7, 132.4, 130.1, 128.9, 124.4, 70.0, 62.6, 56.7, 52.9, 52.2, 45.7, 37.1, 22.1.
3. X-Ray Report of 1a

![Diagram of molecule 1a](image)

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Crystallographic data (excluding structural factors) for compound 1a has been deposited at the Cambridge Crystallographic Data Centre under the deposition number CCDC1454972.
4. NMR Spectra of Intermediate 6a and Products 1