I. General methods

Infrared (IR) spectra were recorded on a JASCO FT/IR-300E and Perkin-Elmer 1710 FT spectrometer. Nuclear magnetic resonance (\textsuperscript{1}H-NMR and \textsuperscript{13}C-NMR) spectra were measured on a JEOL JNM-LA 300 [300 MHz (\textsuperscript{1}H), 75 MHz (\textsuperscript{13}C)] spectrometer, JEOL JNM-GSX 400 [400 MHz (\textsuperscript{1}H), 100 MHz (\textsuperscript{13}C)] spectrometer, and Bruker AMX 500 [500 MHz (\textsuperscript{1}H), 125 MHz (\textsuperscript{13}C)] spectrometer, using DMSO-d\textsubscript{6} or CHCl\textsubscript{3}-d as a solvent, and were reported in ppm relative to DMSO (\textsuperscript{\delta} 2.50) or CHCl\textsubscript{3} (\textsuperscript{\delta} 7.24) for \textsuperscript{1}H-NMR and relative to the central DMSO-d\textsubscript{6} (\textsuperscript{\delta} 39.51) or CHCl\textsubscript{3}-d (\textsuperscript{\delta} 77.23) resonance for \textsuperscript{13}C-NMR. Coupling constants (\textit{J}) in \textsuperscript{1}H-NMR are in Hz. Low-resolution mass spectra (MS) were recorded on a VG Trio-2 GC-MS spectrometer, and high-resolution mass spectra (HRMS) were measured on a JEOL JMS-AX 505wA, JEOL JMS-HX 110A spectrometer. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plate (silica gel 60 GF\textsubscript{254}, 0.25 mm) were used. For flash column chromatography, E. Merck Kieselgel 60 (70–230 mesh) was used. All solvents and commercially available chemicals were used without additional purification.
II. Synthetic procedure and Characterization of new compounds

II-1. Preparation of New Substrates

\textit{tert}-Butyl 2-(diphenylmethylene)hydrazinecarboxylate (2).

\[
\begin{align*}
\text{Ph} & \quad \text{O} \\
\text{Ph} & \quad \text{H}_2\text{N} & \quad \text{O} & \quad \text{Ot-Bu} \\
\text{Ph} & \quad \text{N} & \quad \text{H} & \quad \text{O} & \quad \text{Ot-Bu}
\end{align*}
\]

To a solution of \textit{tert}-butyl carbazate (1.00 g, 7.57 mmol) in CH\textsubscript{2}Cl\textsubscript{2} were added benzophenone (1.65 g, 9.08 mmol) and acetic acid (0.52 mL, 9.08 mmol) under argon atmosphere, and the resulting solution was stirred at room temperature. After 20 h, the mixture was neutralized by the addition of a solution of NaHCO\textsubscript{3}. The organic layer was separated, and the aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2}. The combined organic layer and extracts were dried over MgSO\textsubscript{4} and concentrated. The residue was purified by silica gel column chromatography (hexanes:EtOAc = 10:1) to afford 2 (1.80 g, 80% yield) as a white solid. m.p. 148 °C; \textsuperscript{1}H-NMR (300 MHz, DMSO-\textit{d}_6): \(\delta\) 8.60 (s, 1H), 7.60–7.51 (m, 3H), 7.42–7.34 (m, 5H), 7.27–7.24 (m, 2H), 1.41 (s, 9H) ppm; \textsuperscript{13}C-NMR (100 MHz, DMSO-\textit{d}_6): \(\delta\) 152.1, 150.0, 129.5, 128.4, 128.3, 126.8, 80.0, 27.9 ppm; IR (neat): \(\nu\) 3357, 2977, 1746, 1480, 1367, 1321, 1229, 1156, 1065, 869, 766, 699 cm\textsuperscript{-1}; MS (FAB\textsuperscript{+}): \(m/z\) 297 [M+H]\textsuperscript{+}; HRMS (FAB\textsuperscript{+}): calcd for C\textsubscript{18}H\textsubscript{21}N\textsubscript{2}O\textsubscript{2} [M+H]\textsuperscript{+} 297.1603, found: 297.1607.

\textit{tert}-Butyl 2-(4-chlorobenzyl)hydrazinecarboxylate (3).

\[
\begin{align*}
\text{Cl} & \quad \text{CHO} \\
\text{H}_2\text{N} & \quad \text{O} & \quad \text{Ot-Bu} \\
\text{Cl} & \quad \text{N} & \quad \text{H} & \quad \text{O} & \quad \text{Ot-Bu}
\end{align*}
\]

To a stirred solution of 4-chlorobenzaldehyde (2.00 g, 14.23 mmol) in THF was added a solution of \textit{tert}-butyl carbazate (2.26 g, 17.07 mmol) in THF at room temperature. After stirring for 48 h, EtOAc and water were added, and the organic layer was separated. The aqueous layer was extracted with EtOAc, and the combined organic layer was dried over MgSO\textsubscript{4}, concentrated. The residue was purified by silica gel column chromatography (hexanes:EtOAc = 10:1) to afford 3 (2.99 g, 82% yield) as a white solid. m.p. 171 °C; \textsuperscript{1}H-NMR (300 MHz, DMSO-\textit{d}_6): \(\delta\) 10.97 (s, 1H), 7.97 (s, 1H), 7.62–7.59 (m, 2H), 7.46–7.44 (m, 2H), 1.45 (s, 9H) ppm; \textsuperscript{13}C-NMR (100 MHz, DMSO-\textit{d}_6): \(\delta\)
II-2. Aza-Michael Reaction

**General Procedure**
To a solution of *tert*-butyl benzyloxy carbamate (5, 2.0 equiv.) and tetra-*n*-butylammonium bromide (0.1 equiv.) was added 50% KOH (1.2 equiv.) and enone (6, 1.0 equiv.) successively. The resulting mixture was stirred at room temperature until the starting enone disappeared on TLC. After the reaction was completed, EtOAc and brine were added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic solution was dried over MgSO₄ and concentrated. The residue was purified by silica gel column chromatography to afford the aza-Michael adduct 7.

**tert-Butyl benzyloxy(3-oxocyclohexyl)carbamate (7a)**

![Chemical Structure](image)

Colorless oil. $^1$H-NMR (300 MHz, CDCl₃): $\delta$ 7.39–7.29 (m, 5H), 4.80 (s, 2H), 4.22–4.11 (m, 1H), 2.69–2.60 (m, 1H), 2.49–2.43 (m, 1H), 2.32–2.12 (m, 2H), 2.06–1.82 (m, 3H), 1.60–1.52 (m, 1H), 1.49 (s, 9H) ppm; $^{13}$C-NMR (100 MHz, CDCl₃): $\delta$ 208.9, 156.3, 135.0, 129.2, 128.5, 128.3, 81.8, 78.5, 58.1, 44.6, 40.3, 28.1, 27.8, 21.8 ppm; IR (neat): $\nu$ 2970, 1710, 1455, 1370, 1322, 1257, 1165, 1113, 856, 750, 700 cm$^{-1}$; MS (FAB$^-$): m/z 320 [M+H]$^-$; HRMS (FAB$^-$): calcd for C₁₈H₂₆NO₄ [M+H]$^-$ 320.1862, found 320.1865.

**tert-Butyl benzyloxy(3-oxocycloheptyl)carbamate (7b)**

![Chemical Structure](image)

Colorless oil. $^1$H-NMR (300 MHz, CDCl₃): $\delta$ 7.39–7.31 (m, 5H), 4.81 (dd, $J$=9.54, 12.27 Hz, 2H), 4.12 (s, 1H), 3.00 (dd, $J$=11.37, 14.46 Hz, 1H), 2.61–2.34 (m, 3H),
2.01–1.79 (m, 4H), 1.62–1.35 (m, 2H), 1.50 (s, 9H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 211.6, 156.8, 135.3, 129.2, 128.5, 128.4, 81.9, 78.5, 75.4, 47.6, 43.8, 34.4, 28.2, 27.1, 23.8 ppm; IR (neat): ν 2932, 1702, 1454, 1369, 1256, 1163, 1070, 856, 748, 700 cm$^{-1}$; MS (FAB$^+$): m/z 334 [M+H]$^+$; HRMS (FAB$^+$): calcd for C$_{19}$H$_{27}$NO$_4$ [M+H]$^+$ 334.2018, found: 334.2028.

tert-Butyl benzyloxy(3-oxobutyl)carbamate (7c)

[Chemical structure image]

Colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.37–7.28 (m, 5H), 4.77 (s, 2H), 3.68 (d, $J=6.9$ Hz, 2H), 2.65 (t, $J=6.9$ Hz, 2H), 2.09 (s, 3H), 1.47 (s, 9H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 207.0, 156.3, 135.2, 129.4, 128.5, 128.3, 81.5, 76.7, 44.5, 40.7, 30.1, 28.2 ppm; IR (neat): ν 2926, 1712, 1367, 1252, 1162, 1104, 1028, 857, 750, 700 cm$^{-1}$; MS (FAB$^+$): m/z 294 [M+H]$^+$; HRMS (FAB$^+$): calcd for C$_{16}$H$_{24}$NO$_4$ [M+H]$^+$ 294.1750, found: 294.1703.

tert-Butyl benzyloxy(4-oxohexan-2-yl)carbamate (7d)

[Chemical structure image]

Colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.40–7.28 (m, 5H), 4.80 (s, 2H), 4.55–4.43 (m, 1H), 2.62 (m, 2H), 2.38 (q, $J=7.32$ Hz, 2H), 1.49 (s, 9H), 1.19 (d, $J=6.78$ Hz, 3H), 1.00 (t, $J=7.32$ Hz, 3H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 209.2, 156.8, 135.5, 129.3, 128.4, 128.3, 81.6, 78.2, 52.3, 46.2, 36.1, 28.2, 17.5, 7.6 ppm; IR (neat): ν 2977, 2936, 1712, 1455, 1368, 1318, 1167, 1104, 1018, 856, 750, 700 cm$^{-1}$; MS (FAB$^+$): m/z 322 [M+H]$^+$; HRMS (FAB$^+$): calcd for C$_{18}$H$_{28}$NO$_4$ [M+H]$^+$ 322.2018, found: 322.2028.

tert-Butyl benzyloxy(3-oxo-3-phenylpropyl)carbamate (7e)

[Chemical structure image]

Colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.89–7.86 (m, 2H), 7.55–7.27 (m, 8H), 4.83 (s, 2H), 3.86 (t, $J=7.20$ Hz, 2H), 3.20 (t, $J=7.20$ Hz, 2H), 1.48 (s, 9H) ppm; $^{13}$C-
NMR (100 MHz, CDCl₃): δ 198.4, 156.4, 136.6, 135.4, 133.1, 129.5, 128.5, 128.4, 128.0, 81.6, 76.8, 45.2, 35.8, 28.2 ppm; IR (neat): ν 2928, 1689, 1451, 1367, 1252, 1212, 1161, 856, 745, 696 cm⁻¹; MS (FAB⁺): m/z 356 [M+H]⁺; HRMS (FAB⁺): calcd for C₂₁H₂₆NO₄ [M+H]⁺ 356.1862, found: 356.1869.

**tert-Butyl benzyloxy(1-oxo-1-phenylpentan-3-yl)carbamate (7f)**

![Structure of tert-Butyl benzyloxy(1-oxo-1-phenylpentan-3-yl)carbamate (7f)](image)

Colorless oil. ¹H-NMR (300 MHz, CDCl₃): δ 7.90–7.87 (m, 2H), 7.56–7.27 (m, 8H), 4.85 (s, 2H), 4.52–4.47 (m, 1H), 3.26–3.03 (m, 2H), 1.83–1.53 (m, 2H), 1.47 (s, 9H), 0.97 (t, J=7.32 Hz, 3H) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 198.0, 157.0, 136.8, 135.8, 133.0, 129.2, 128.5, 128.3, 128.1, 81.4, 78.4, 58.6, 41.5, 28.2, 25.3, 11.1 ppm; IR (neat): ν 2967, 1702, 1454, 1367, 1322, 1256, 167, 1115, 856, 752, 696 cm⁻¹; MS (FAB⁺): m/z 384 [M+H]⁺; HRMS (FAB⁺): calcd for C₂₃H₃₀NO₄ [M+H]⁺ 384.2175, found: 384.2165.

**Ethyl 3-[benzyloxy(tert-butoxycarbonyl)amino]propanoate (7g)**

![Structure of Ethyl 3-[benzyloxy(tert-butoxycarbonyl)amino]propanoate (7g)](image)

Colorless oil. ¹H-NMR (300 MHz, CDCl₃): δ 7.38–7.31 (m, 5H), 4.80 (s, 2H), 4.07 (q, J=7.14 Hz, 2H), 3.71 (t, J=7.14 Hz, 2H), 2.55 (t, J=7.14 Hz, 2H), 1.47 (s, 9H), 1.19 (t, J=7.14 Hz, 3H) ppm; ¹³C-NMR (100 MHz, CDCl₃): δ 171.6, 156.3, 135.2, 129.4, 128.5, 128.3, 81.6, 60.4, 45.4, 32.1, 28.2, 14.0 ppm; IR (neat): ν 2978, 1733, 1453, 1369, 1253, 1161, 1096, 1024, 856, 749, 700 cm⁻¹; MS (FAB⁺): m/z 324 [M+H]⁺; HRMS (FAB⁺): calcd for C₁₇H₂₆NO₅ [M+H]⁺ 324.1811, found: 324.1805.

**Methyl 3-[benzyloxy(tert-butoxycarbonyl)amino]butanoate (7h)**

![Structure of Methyl 3-[benzyloxy(tert-butoxycarbonyl)amino]butanoate (7h)](image)

Colorless oil. ¹H-NMR (300 MHz, CDCl₃): δ 7.38–7.26 (m, 5H), 4.77 (s, 2H), 3.81–3.50 (m, 2H), 3.57 (s, 3H), 2.86–2.75 (m, 1H), 1.47 (s, 9H), 1.12 (d, J=7.14 Hz, 3H)
ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 175.3, 156.1, 135.2, 129.3, 128.4, 128.2, 81.4, 76.5, 51.8, 51.6, 37.9, 28.1, 14.6 ppm; IR (neat): v 2976, 1736, 1456, 1368, 1249, 1298, 1248, 857, 751, 700, 616 cm$^{-1}$; MS (FAB$^+$): $m/z$ 324 [M+H]$^+$; HRMS (FAB$^+$): calcd for C$_{17}$H$_{26}$NO$_5$ [M+H]$^+$ 324.1811, found: 324.1813.

tert-Butyl 3-amino-3-oxopropyl(benzyloxy)carbamate (7i)

White solid. m.p. 189 °C; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.39–7.29 (m, 5H), 5.82 (s, 1H), 5.64 (s, 1H), 4.81 (s, 2H), 3.73 (t, $J$=6.77 Hz, 2H), 2.46 (t, $J$=6.77 Hz, 2H), 1.47 (s, 9H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 173.4, 156.4, 135.1, 129.5, 128.6, 128.4, 81.9, 76.9, 45.6, 33.4, 28.2 ppm; IR (neat): v 3346, 2976, 2673, 1450, 1369, 1292, 1252, 1162, 1024, 855, 750, 700 cm$^{-1}$; MS (FAB$^+$): $m/z$ 295 [M+H]$^+$; HRMS (FAB$^+$): calcd for C$_{15}$H$_{23}$N$_2$O$_4$ [M+H]$^+$ 295.1658, found: 295.1654.

tert-Butyl benzyloxy(2-cyanoethyl)carbamate (7j)

Colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.40–7.30 (m, 5H), 4.85 (s, 2H), 3.62 (t, $J$=6.87 Hz, 2H), 2.50 (t, $J$=6.87 Hz, 2H), 1.49 (s, 9H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 156.0, 135.0, 129.4, 128.7, 128.5, 117.6, 82.5, 77.4, 45.9, 28.0, 15.6 ppm; IR (neat): v 2977, 1705, 1454, 1369, 1253, 1216, 1162, 1104, 1022, 854, 750, 700 cm$^{-1}$; MS (FAB$^+$): $m/z$ 277 [M+H]$^+$; HRMS (FAB$^+$): calcd for C$_{15}$H$_{21}$N$_2$O$_3$ [M+H]$^+$ 277.1552, found: 277.1559.

tert-Butyl benzyloxy[2-(phenylsulfinyl)ethyl]carbamate (7k)

Colorless oil. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 7.59–7.47 (m, 5H), 7.36–7.30 (m, 5H), 4.82 (d, $J$=2.91 Hz, 2H), 3.93–3.84 (m, 1H), 3.62–3.53 (m, 1H), 3.07–2.94 (m, 1H), 2.94–2.85 (m, 1H), 1.46 (s, 9H) ppm; $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 156.1, 143.3,
135.0, 131.0, 129.4, 129.2, 128.6, 128.4, 123.9, 77.0, 53.9, 43.3, 28.1 ppm; IR (neat): ν 3741, 2926, 1704, 1251, 1369, 1285, 1157, 1044, 749, 685 cm⁻¹; MS (FAB⁺): \( m/z \) 376 [M+H]⁺; HRMS (FAB⁺): calcd for C₂₀H₂₆NO₄S [M+H]⁺ 376.1583, found: 376.1578.

tert-Butyl benzyloxy[2-(phenylsulfonyl)ethyl]carbamate (7l)

\[
\begin{align*}
\text{Colorless oil. } & \text{H-NMR (300 MHz, CDCl₃): } \delta 7.86–7.84 (m, 2H), 7.66–7.51 (m, 3H), 7.32–7.30 (m, 5H), 4.73 (s, 2H), 3.70–4.07 (m, 2H), 3.30–3.25 (m, 2H), 1.42 (s, 9H) \text{ ppm; } \\
\text{13C-NMR (100 MHz, CDCl₃): } & \delta 155.9, 138.8, 135.0, 133.8, 129.4, 129.3, 128.6, 128.4, 127.9, 82.2, 77.1, 52.3, 43.9, 28.0 \text{ ppm; IR (neat): } \nu 2927, 1705, 1449, 1368, 1315, 1152, 1085, 1000, 749, 694, 616 \text{ cm}^{-1}; \text{ MS (FAB⁺): } \frac{m}{z} 391 [M]; \text{ HRMS (FAB⁺): calcd for } C_{20}H_{25}NO_{5}S [M] 391.1435, \text{ found: 391.1451.}
\end{align*}
\]

II-3. Deprotection of the Aza-Michael Adduct

tert-Butyl 3-oxobutylcarbamate (8c)

\[
\begin{align*}
\text{To a solution of } 7c (64 mg, 0.218 mmol) \text{ in EtOAc (1 mL) was added a catalytic amount of acetone-washed (5×1 mL) Raney-Ni (4200; slurry in water; active catalyst; Aldrich). The reaction mixture was stirred under hydrogen atmosphere at room temperature. After stirring for 1 h, the mixture was filtered through Celite pad, and washed with EtOAc. The filtrate and washings were combined and concentrated. The residue was purified by silica gel column chromatography (hexanes:EtOAc = 3:1) to afford } 8c (37 mg, 90\% \text{ yield) as colorless oil. H-NMR (300 MHz, CDCl₃): } \delta 4.95 (br s, 1H), 3.31 (m, 2H), 2.63 (t, } J=5.85 \text{ Hz, 2H), 2.12 (s, 3H), 1.39 (s, 9H) \text{ ppm; } \text{13C-NMR (100 MHz, CDCl₃): } \delta 208.13, 155.84, 79.27, 43.49, 35.78, 30.14, 28.35 \text{ ppm; IR (neat): } \nu 3365, 2976, 2931, 1712, 1518, 1455, 1366, 1275, 1251, 1168, 866 \text{ cm}^{-1} ; \text{ MS (FAB⁺): } \frac{m}{z} 210 [M+Na]^+; \text{ HRMS (FAB⁺): calcd for } C_{9}H_{17}NO_{3}Na [M+Na]^+ 210.1106, \text{ found: 210.1109.}
\end{align*}
\]
**tert-Butyl hydroxyl(3-oxobutyl)carbamate (9c)**

To a solution of 7c (52 mg, 0.177 mmol) in EtOH was added a catalytic amount of Pd/C (10% on activated carbon) The reaction mixture was stirred under hydrogen atmosphere at room temperature. After stirring for 20 min, the reaction mixture was filtered through Celite pad, and washed with EtOH. The filtrate and washings were combined and concentrated. The residue was purified by silica gel column chromatography (hexanes:EtOAc = 3:1) to afford 9c (25 mg, 72% yield) as colorless oil. $^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta$ 8.06 (br s, 1H), 3.83 (t, $J=6.78$ Hz, 2H), 2.43 (t, $J=6.78$ Hz, 2H), 1.63 (s, 3H), 1.42 (s, 9H) ppm, $[\text{Minor Lactol (9c')} \delta$ 5.0 (br, 1H), 3.92–4.02 (m, 1H), 3.25–3.31 (m, 1H), 1.58 (s, 3H), 1.53–1.58 (m, 1H), 1.42 (s, 9H) ppm]; $^{13}$C-NMR (75 MHz, C$_6$D$_6$): $\delta$ 205.6, 157.2, 81.3, 47.7, 40.6, 29.5, 28.2 ppm, $[\text{Minor Lactol (9c')} \delta$ 159.9, 105.1, 81.3, 45.9, 39.3, 27.9, 23.1 ppm]; MS (FAB$^+$): m/z 226 [M+Na]$^+$; HRMS (FAB$^+$): calcd for C$_9$H$_{18}$NO$_4$ [M+H]$^+$ 204.1236, found: 204.1243.

**4-(Benzyloxyamino)butan-2-one (10c)**

To a solution of 7c (64 mg, 0.218 mmol) in CH$_2$Cl$_2$ (1 mL) was added trifluoroacetic acid (0.5 mL) in water bath. After stirring for 1 h at room temperature, the reaction mixture was diluted with CH$_2$Cl$_2$ (10 mL), washed with saturated aqueous NaHCO$_3$ solution (2×1 mL) and then back-extracted with CH$_2$Cl$_2$ (2×5 mL). The combined organic layer was dried and concentrated to afford 9c (39 mg, 92% yield) as colorless oil. $^1$H-NMR (300 MHz, C$_6$D$_6$): $\delta$ 7.36–7.11(m, 5H), 4.65 (s, 2H), 2.99 (t, $J=6.15$, 2H), 2.11 (t, $J=6.15$, 2 H), 1.58 (s, 3H) $^{13}$C-NMR (75 MHz, C$_6$D$_6$): $\delta$ 206.0, 138.9, 130.0, 128.7, 128.5, 128.4, 76.2, 47.0, 40.7, 29.4 ppm; MS (FAB$^+$): m/z 194 [M+H]$^+$; HRMS (CI$^-$): calcd for C$_{11}$H$_{16}$NO$_2$ [M+H]$^+$ 194.1181, found: 194.1183.
III. $^1$H and $^{13}$C-NMR spectra of the new compounds
Cl

N

H

O
t-Bu

O

Or-Bu
$\text{NO} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{Bu}$

$7a$
\[
\text{O} \quad \text{N} \quad \text{O}
\]

\[
\text{t-Bu}
\]

7b
O

7g
The image contains a chemical structure and a set of NMR spectra. The chemical structure is labeled as 71.
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