Electronic supplementary information:

Efficient synthesis of tetrazole hemiaminal silyl ethers via three-component hemiaminal silylation

Ming-Sheng Xie,* Xuan Cheng, Yang-Guang Chen, Xiao-Xia Wu, Gui-Rong Qu and Hai-Ming Guo*

Henan Key Laboratory of Organic Functional Molecules and Drug Innovation, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.
E-mail: xiemingsheng@htu.edu.cn; ghm@htu.edu.cn

Contents

1. General information ..................................................................................................................................... S2

2. General procedure for the synthesis of 2,5-disubstituted tetrazole hemiaminal silyl ethers.....................S2

3. Gram-scale synthesis of 2,5-disubstituted tetrazole 4aa ........................................................................S3

4. The release of 5-phenyl tetrazole 1a from 2,5-disubstituted tetrazole hemiaminal silyl ether 4aa ..........S4

5. The X-ray data for tetrazoles 4an and 5aa .............................................................................................S5

6. Synthesis, analytical and spectral characterization data of 5-substituted tetrazoles ...............................S9

7. Copies of NMR spectra of the 5-substituted tetrazoles .........................................................................S13

8. 1H NMR spectroscopy of the crude reaction mixtures. .......................................................................S19

9. The analytical and spectral characterization data for the 2,5-disubstituted tetrazole hemiaminal silyl ethers…S25

10. Copies of NMR spectra of the adducts .................................................................................................S39
1. General information

$^1$H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quaternary, m = multiplet, br = broad), coupling constants (Hz), integration. $^{13}$C NMR data were collected on Bruker Avance III HD 150 spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). CH$_2$Cl$_2$ was distilled over calcium hydride prior to use. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use. 5-Substituted tetrazoles $^{1b,1e,1f,1g,1h,1i,1j,1k}$ are known compounds, and are prepared according to the reported procedures. 5-Substituted tetrazoles $^{1h}$ and $^{1i}$ are prepared according to the reported procedures. 5-Substituted tetrazole $^{1a}$ was purchased from Shaoyuan Technology (Shanghai) Co., Ltd.; 5-Substituted tetrazole $^{1c,1d,1j}$, and $^{1l}$ were purchased from Energy Chemical (Shanghai) Co., Ltd.; 5-Substituted tetrazole $^{1m}$ was purchased from TCI (Shanghai) Co., Ltd.

2. General procedure for the synthesis of 2,5-disubstituted tetrazole hemiaminal silyl ethers

\[
\begin{align*}
\text{R}^1\text{N}^-\text{NH} & \quad \text{O} \\
\text{R}^2\text{H} & \quad \text{R}^3\text{O}^-\text{SiR}^3 \\
\text{P}^\circ\text{EtN}(1.5 \text{ equiv}) & \quad \text{CH}_2\text{Cl}_2, \text{ RT} \\
\text{R}^1\text{N}^-\text{NH} & \quad \text{O} \\
\text{R}^2\text{H} & \quad \text{R}^3\text{O}^-\text{SiR}^3 \\
\end{align*}
\]

In a test tube, 5-phenyl tetrazole $^{1}$ (0.2 mmol) was added in CH$_2$Cl$_2$ (2 mL) at RT. Subsequently, $i$Pr$_2$EtN (0.3 mmol, 1.5 equiv) was added. Then, acetaldehyde $^{2}$ (0.28 mmol, 1.4 equiv) was added to the solution when 5-phenyl tetrazole $^{1}$ was completely dissolved. After that, tert-butyldimethylsilyl trifluoromethanesulfonate $^{3}$ (0.3 mmol, 1.5 equiv) was added and the reaction mixture was stirred at RT for 2-3 h. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash column.
chromatography on silica gel (eluent: petroleum ether/ethylacetate = 10/1) to afford the pure product 4.

3. Gram-scale synthesis of 2,5-disubstituted tetrazole 4aa

In a round flask, 5-phenyl tetrazole 1a (1.46 g, 10 mmol) was added in CH₂Cl₂ (100 mL) at RT. iPr₂EtN (2.6 mL, 15 mmol, 1.5 equiv) was added subsequently. Then, acetaldehyde 2a (0.78 mL, 14 mmol, 1.4 equiv) was added to the solution after 1a is completely dissolved. After that, tert-butyldimethylsilyl trifluoromethanesulfonate 3a (3.5 mL, 15 mmol, 1.5 equiv) were added and the mixture was stirred at RT for 2 h. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash column chromatography on silica gel (eluent: petroleum ether/ethylacetate = 10/1) to afford the product 4aa (2.9550 g, 97% yield) as a colorless oil.
4. The release of 5-phenyl tetrazole 1a from 2,5-disubstituted tetrazole hemiaminal silyl ether 4aa

In a test tube, 2-(1-((tert-butyldimethylsilyl)oxy)ethyl)-5-phenyl-2\(H\)-tetrazole 4aa (61 mg, 0.2 mmol) was added in solvent (2 mL). Then, acid (x equiv) was added and the mixture was stirred at RT. At the end of the reaction, the crude mixture was concentrated on a rotary evaporator and purified by flash column chromatography on silica gel (eluent: petroleum ether/ethylacetate = 1/1) to give the desired product 1a as a white solid.

Table S1. 2,5-disubstituted tetrazole hemiaminal silyl ether 4aa at acid atmosphere

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid(^a)</th>
<th>Solvent</th>
<th>x</th>
<th>t (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_3)COOH</td>
<td>THF</td>
<td>1</td>
<td>8</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>CH(_3)COOH</td>
<td>CH(_3)OH</td>
<td>1</td>
<td>8</td>
<td>NR</td>
</tr>
<tr>
<td>3</td>
<td>CF(_3)COOH</td>
<td>CH(_3)OH</td>
<td>1</td>
<td>8</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>HCl</td>
<td>CH(_3)OH</td>
<td>1</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>HCl</td>
<td>H(_2)O</td>
<td>1</td>
<td>8</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>HCl</td>
<td>CH(_3)OH:H(_2)O = 1:3</td>
<td>1</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>HCl</td>
<td>CH(_3)OH:H(_2)O = 1:1</td>
<td>1</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>8</td>
<td>HCl</td>
<td>CH(_3)OH:H(_2)O = 3:1</td>
<td>1</td>
<td>12</td>
<td>85</td>
</tr>
<tr>
<td>9</td>
<td>HCl</td>
<td>CH(_3)OH</td>
<td>0.1</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>10</td>
<td>HCl</td>
<td>CH(_3)OH</td>
<td>0.05</td>
<td>2</td>
<td>99</td>
</tr>
<tr>
<td>11(^c)</td>
<td>HCl</td>
<td>CH(_3)OH</td>
<td>0.01</td>
<td>12</td>
<td>90</td>
</tr>
</tbody>
</table>

\(^a\) Unless otherwise noted, acids were analytical reagent. \(^b\) Isolated yield based on 4aa. \(^c\) The hydrochloric acid (1.7 µL) used is diluted with 1 mL of analytical reagent hydrochloric acid into 9 mL of distilled water.
5. The X-ray data for tetrazoles 4an and 5aa.

The tetrazole 4an was recrystallized by petroleum/ether (10/1).

CCDC 1835497 (4an) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
### Table S2 Crystal data and structure refinement for 4an.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>cx-20180320</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{24}H_{28}N_{4}OSi</td>
</tr>
<tr>
<td>Formula weight</td>
<td>416.59</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>292.64(10)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pna2₁</td>
</tr>
<tr>
<td>a/Å</td>
<td>11.4816(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.2451(6)</td>
</tr>
<tr>
<td>c/Å</td>
<td>16.6439(9)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2340.0(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.182</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.122</td>
</tr>
<tr>
<td>F(000)</td>
<td>888.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.35 × 0.27 × 0.15</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKa (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>6.902 to 49.958</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-13 ≤ h ≤ 10, -14 ≤ k ≤ 10, -19 ≤ l ≤ 13</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>6796</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3019 [R_{int} = 0.0216, R_{sigma} = 0.0312]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3019/1/276</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.041</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0380, wR₂ = 0.0850</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0538, wR₂ = 0.0911</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.20/-0.17</td>
</tr>
<tr>
<td>Flack parameter</td>
<td>0.08(7)</td>
</tr>
</tbody>
</table>
The tetrazole 5aa was recrystallized by petroleum/ether (1/1).

CCDC 1835498 (5aa) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>cyg-20180315</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₁₅H₂₄N₄OSi</td>
</tr>
<tr>
<td>Formula weight</td>
<td>304.47</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293.0(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.5430(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>10.2385(13)</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.1084(19)</td>
</tr>
<tr>
<td>α/°</td>
<td>71.826(12)</td>
</tr>
<tr>
<td>β/°</td>
<td>83.376(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>78.570(10)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>878.7(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρcalcg/cm³</td>
<td>1.151</td>
</tr>
<tr>
<td>μ/mm l</td>
<td>0.138</td>
</tr>
<tr>
<td>F(000)</td>
<td>328.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.5 × 0.28 × 0.12</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>6.896 to 50</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 ≤ h ≤ 7, -11 ≤ k ≤ 12, -16 ≤ l ≤ 16</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>6596</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3077 [Rint = 0.0377, Rsigma = 0.0627]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3077/0/196</td>
</tr>
<tr>
<td>Goodness-of-fit on F2</td>
<td>1.049</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R1 = 0.0675, wR2 = 0.1548</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R1 = 0.0993, wR2 = 0.1727</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.32/−0.22</td>
</tr>
</tbody>
</table>
6. Synthesis, analytical and spectral characterization data of 5-substituted tetrazoles

Synthesis of 5-substituted tetrazole $1b^1$

To a mixture of nitrile (2 mmol) and NaN$_3$ (2 mmol) in DMSO (6 mL), CuSO$_4$$\cdot$5H$_2$O (2 mol%) was added and the mixture was stirred at 140 °C. After completion of the reaction, the mixture was treated with EtOAc and 4 M HCl and stirred vigorously. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic portion was washed with saturated sodium thiosulfate solution and H$_2$O and subsequently concentrated. The residue was purified by column chromatography (silica gel; hexane-EtOAc) to afford the pure 5-substituted tetrazole $1b$.

Synthesis of 5-substituted tetrazole $1e^2$

To a mixture of nitrile (2 mmol) and NaN$_3$ (5 mmol) in o-xylene (20 mL), Bu$_3$SnCl (5 mmol) was added and the mixture was stirred at reflux for 6 h. Then the reaction mixture was cooled to RT and a solution of NaOH in water was added. After stirring for 1 h at RT, the aqueous layer was diluted with water, cooled to 5-10 ºC and acidified to pH = 2 with 6 N HCl. Finally, the product $1e$ was extracted into EtOAc (3×10 mL) and distilled completely. The residue was purified by column chromatography (silica gel; hexane-EtOAc) to afford the pure 5-substituted tetrazole $1e$.

Synthesis of 5-substituted tetrazoles: $1f^3$, $1h$, $1i$ and $1k^3$

To a mixture of nitrile (2 mmol) and NaN$_3$ (2.5 mmol) in toluene (10 mL), Et$_3$N·HCl (6 mmol) was added and the mixture was stirred at 110 ºC for 18-24 h. After cooling to RT, the mixture was treated with water. To the aqueous layer, 4 M HCl was added dropwise until pH was acidic. After
filtration, the solid was purified by column chromatography (silica gel; hexane-EtOAc) to afford pure 5-substituted tetrazoles.

Synthesis of 5-substituted tetrazole 1g

An oven-dried flask was charged with NaN₃ (3 mmol) and Et₂AlCl (3 mmol, 0.9 M in toluene) in toluene at 0 °C under nitrogen and stirred for 15 min. The mixture was then warmed to room temperature and stirred for 4 h. Then, nitrile (2 mmol) was added at room temperature in two portions. The mixture was gradually heated to 55 °C and stirred for 18 h. Then, the reaction mixture was cooled to 0 °C and added to a solution of NaOH. The pH value was adjusted to 1.5 with 6 M HCl. The solution was extracted with ethyl acetate to afford the crude product, which was purified by column chromatography (silica gel; hexane-EtOAc) to afford pure 5-substituted tetrazole 1g.

5-(m-Tolyl)-2H-tetrazole (1b)

White solid.  
^1H NMR (400 MHz, CD₃OD, δ): 7.85 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 2.45 (s, 3H).

5-Cyclopropyl-2H-tetrazole (1e)

White solid.  
^1H NMR (400 MHz, CD₃OD, δ): 2.18-2.25 (m, 1H), 1.20-1.25 (m, 2H), 1.04-1.08 (m, 2H).

5-(tert-Butyl)-2H-tetrazole (1f)

White solid.  
^1H NMR (400 MHz, CD₃OD, δ): 2.18-2.25 (m, 1H), 1.20-1.25 (m, 2H), 1.04-1.08 (m, 2H).
White solid.  \(^1\)H NMR (400 MHz, CD\(_3\)OD, \(\delta\)): 1.45 (s, 9H)

\((E)-5\)-Styryl-2\(H\)-tetrazole (1g)

Brown solid.

\(^1\)H NMR (400 MHz, CD\(_3\)OD, \(\delta\)): 7.65-7.68 (m, 1H), 7.62-7.65 (m, 2H), 7.36-7.45 (m, 3H), 7.21 (d, \(J = 8.4\) Hz, 1H).

\((E)-5\)-(But-2-en-2-yl)-2\(H\)-tetrazole (1h)

White solid, mp: 144.1-145.6 °C.

\(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): 6.61 (qq, \(J = 7.2, 1.6\) Hz, 1H), 2.05-2.06 (m, 3H), 1.82-1.85 (m, 3H).

\(^{13}\)C NMR (150 MHz, CD\(_3\)OD, \(\delta\)): 132.8, 122.1, 14.0, 13.6.

HRMS: [M + Na\(^+\)] calcd. for C\(_5\)H\(_8\)N\(_4\)Na, 147.0641; found, 147.0639.

\((Z)-5\)-(But-2-en-2-yl)-2\(H\)-tetrazole (1i)

White solid, mp: 88.2-89.3 °C.

\(^1\)H NMR (400 MHz, (CD\(_3\))\(_2\)SO, \(\delta\)): 6.07 (qq, \(J = 7.2, 1.6\) Hz, 1H), 2.09-2.11 (m, 3H), 1.96 (dq, \(J = 7.2, 1.6\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CD\(_3\)OD, \(\delta\)): 134.2, 121.0, 22.1, 15.7.

HRMS: [M + Na\(^+\)] calcd. for C\(_5\)H\(_8\)N\(_4\)Na, 147.0641; found, 147.0640.

5-Benzhydryl-2\(H\)-tetrazole (1k)

White solid.

\(^1\)H NMR (400 MHz, CD\(_3\)OD, \(\delta\)): 7.35-7.38 (m, 1H), 7.34-7.35 (m, 2H), 7.32-7.33 (m, 1H), 7.28-7.31 (m, 1H), 7.26-7.28 (m, 1H), 7.23-7.24 (m, 2H), 7.18-7.22 (m, 2H), 5.91 (s, 1H).
References:


7. Copies of NMR spectra of the 5-substituted tetrazoles

$^1$H-NMR of 1b

$^1$H-NMR of 1e
$^1$H-NMR of $1h$

$^{13}$C-NMR of $1h$
NOESY of 1h

1H-NMR of 1i
$^{13}$C-NMR of 1i

NOESY of 1i
$^1$H-NMR of 1k
8. $^1$H NMR spectroscopy of the crude reaction mixtures.
1a:2a:3a = 1:1.4:1.5

4aa:5aa >99:1

H₃ no H₄' signal
4ea:5ea = 65:35
Ph\(=\text{N-N}) + \text{H} + \text{PhMe}(1.5\text{ equiv}) \rightarrow \text{CH}_2\text{C}_2\text{RT, 3 h} \rightarrow 4\text{ga:5}\text{ga} = 81:19
$4\text{ja}:5\text{ja} = 82:18$
9. The analytical and spectral characterization data for the 2,5-disubstituted tetrazole hemiaminal silyl ethers

2-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-phenyl-2H-tetrazole (4aa).

\[
\begin{align*}
\text{N} & \text{N} \\
\text{O} & \text{Si-}tBu \\
Ph & \text{N} \\
\end{align*}
\]

Colorless oil (60.4 mg, 99% yield).

\(^1\)H NMR \((600 \text{ MHz, CDCl}_3, \delta)\): 8.19 (d, \(J = 7.8 \text{ Hz, } 2\text{H})\), 7.45-7.50 (m, 3H), 6.25 (q, \(J = 6.0 \text{ Hz, } 1\text{H})\), 1.91 (d, \(J = 6.0 \text{ Hz, } 3\text{H})\), 0.88 (s, 9H), 0.18 (s, 3H), -0.03 (s, 3H).

\(^{13}\)C NMR \((150 \text{ MHz, CDCl}_3, \delta)\): 165.0, 130.4, 129.0, 127.7, 127.1, 83.6, 25.6, 23.3, 18.1, -5.0, -5.3.

HRMS: \([\text{M + Na}^+]\) calcd. for C\(_{15}\)H\(_{24}\)N\(_4\)NaOSi, 327.1612; found, 327.1620.

2-(1-((tert-Butyldimethylsilyl)oxy)propyl)-5-phenyl-2H-tetrazole (4ab).

\[
\begin{align*}
\text{N} & \text{N} \\
\text{O} & \text{Si-}tBu \\
Ph & \text{N} \\
\end{align*}
\]

Colorless oil (61.2 mg, 96% yield).

\(^1\)H NMR \((400 \text{ MHz, CDCl}_3, \delta)\): 8.18-8.20 (m, 2H), 7.45-7.52 (m, 3H), 6.16 (t, \(J = 6.4 \text{ Hz, } 1\text{H})\), 2.20-2.32 (m, 2H), 0.95 (t, \(J = 7.2 \text{ Hz, } 3\text{H})\), 0.86 (s, 9H), 0.16 (s, 3H), -0.09 (s, 3H).

\(^{13}\)C NMR \((150 \text{ MHz, CDCl}_3, \delta)\): 165.1, 130.4, 129.0, 127.7, 127.1, 88.3, 30.2, 25.6, 18.1, 9.2, -5.1, -5.3.

HRMS: \([\text{M + Na}^+]\) calcd. for C\(_{16}\)H\(_{26}\)N\(_4\)NaOSi, 341.1768; found, 341.1776.

2-(1-((tert-Butyldimethylsilyl)oxy)butyl)-5-phenyl-2H-tetrazole (4ac).

\[
\begin{align*}
\text{N} & \text{N} \\
\text{O} & \text{Si-}tBu \\
Ph & \text{N} \\
\end{align*}
\]

Colorless oil (64.3 mg, 97% yield).

\(^1\)H NMR \((600 \text{ MHz, CDCl}_3, \delta)\): 8.19 (d, \(J = 7.8 \text{ Hz, } 2\text{H})\), 7.45-7.50 (m, 3H), 6.25 (t, \(J = 6.0 \text{ Hz, } 2\text{H})\), 2.20-2.32 (m, 2H), 0.95 (t, \(J = 7.2 \text{ Hz, } 3\text{H})\), 0.86 (s, 9H), 0.16 (s, 3H), -0.09 (s, 3H).
1H), 2.23-2.29 (m, 1H), 2.14-2.20 (m, 1H), 1.41-1.52 (m, 1H), 1.24-1.33 (m, 1H), 0.97 (t, J = 7.2 Hz, 3H), 0.86 (s, 9H), 0.16 (s, 3H), -0.10 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 86.8, 38.9, 25.6, 18.1, 13.6, -5.1, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{17}$H$_{28}$N$_4$NaOSi, 355.1925; found, 355.1919.

2-(1-((tert-Butyldimethylsilyl)oxy)pentyl)-5-phenyl-2H-tetrazole (4ad).

<chemistry>
\begin{center}
\includegraphics[width=0.2\textwidth]{image}
\end{center}
</chemistry>

Colorless oil (64.5 mg, 93% yield).

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.18-8.20 (m, 2H), 7.47-7.52 (m, 3H), 6.23 (t, J = 6.4 Hz, 1H), 2.15-2.31 (m, 2H), 1.33-1.42 (m, 3H), 1.19-1.26 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H), 0.86 (s, 9H), 0.16 (s, 3H), -0.10 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.1, 130.4, 129.0, 127.7, 127.1, 87.1, 36.6, 26.8, 25.6, 22.2, 18.1, 14.0, -5.1, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{18}$H$_{30}$N$_4$NaOSi, 369.2081; found, 369.2090.

2-(1-((tert-Butyldimethylsilyl)oxy)hexyl)-5-phenyl-2H-tetrazole (4ae).

<chemistry>
\begin{center}
\includegraphics[width=0.2\textwidth]{image}
\end{center}
</chemistry>

Colorless oil (65.5 mg, 91% yield).

$^1$H NMR (600 MHz, CD$_2$OD, δ): 8.10-8.13 (m, 2H), 7.48-7.53 (m, 3H), 6.33 (t, J = 6.0 Hz, 1H), 2.23-2.29 (m, 1H), 2.15-2.21 (m, 1H), 1.43-1.50 (m, 1H), 1.30-1.38 (m, 4H), 1.22-1.29 (m, 1H), 0.89 (t, J = 7.2 Hz, 3H), 0.85 (s, 9H), 0.18 (s, 3H), -0.10 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.0, 130.4, 129.0, 127.7, 127.1, 87.1, 36.6, 31.2, 25.6, 24.3, 22.5, 18.1, 14.0, -5.1, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{19}$H$_{32}$N$_4$NaOSi, 383.2238; found, 383.2247.
2-(1-((tert-Butyldimethylsilyl)oxy)-2-methylpropyl)-5-phenyl-2H-tetrazole (4af).

\[
\begin{align*}
\text{Colorless oil (61.5 mg, 93% yield).} \\
\text{\textsuperscript{1}H NMR (600 MHz, CDCl}_3, \delta): 8.19-8.20 \text{ (m, 2H), 7.46-7.52 \text{ (m, 3H), 5.87 \text{ (d, } J = 8.4 \text{ Hz, 1H), 2.54-2.60 \text{ (m, 1H), 1.14 \text{ (d, } J = 6.6 \text{ Hz, 3H), 0.86 \text{ (s, 9H), 0.76 \text{ (d, } J = 6.6 \text{ Hz, 3H), 0.13 \text{ (s, 3H), -0.16 \text{ (s, 3H).}}} \\
\text{\textsuperscript{13}C NMR (150 MHz, CDCl}_3, \delta): 165.0, 130.4, 129.0, 127.7, 127.1, 92.0, 35.0, 25.6, 18.2, 18.1, 17.6, -5.3, -5.4.} \\
\text{HRMS: [M + Na\textsuperscript{+}] calcd. for C}_{17}\text{H}_{28}\text{N}_4\text{NaOSi, 355.1925; found, 355.1920.}
\end{align*}
\]

2-(1-((tert-Butyldimethylsilyl)oxy)-3-methylbutyl)-5-phenyl-2H-tetrazole (4ag).

\[
\begin{align*}
\text{Colorless oil (63.7 mg, 92% yield).} \\
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3, \delta): 8.18-8.20 \text{ (m, 2H), 7.45-7.52 \text{ (m, 3H), 6.33 \text{ (t, } J = 7.2 \text{ Hz, 1H), 2.19-2.26 \text{ (m, 1H), 1.99-2.05 \text{ (m, 1H), 1.60-1.71 \text{ (m, 1H), 1.00 \text{ (d, } J = 6.8 \text{ Hz, 3H), 0.95 \text{ (d, } J = 6.8 \text{ Hz, 3H), 0.86 \text{ (s, 9H), 0.16 \text{ (s, 3H), -0.14 \text{ (s, 3H).}}} \\
\text{\textsuperscript{13}C NMR (150 MHz, CDCl}_3, \delta): 165.1, 130.4, 129.0, 127.7, 127.1, 85.7, 45.5, 25.6, 24.2, 22.9, 22.0, 18.1, -5.1, -5.3.} \\
\text{HRMS: [M + Na\textsuperscript{+}] calcd. for C}_{18}\text{H}_{30}\text{N}_4\text{NaOSi, 369.2081; found, 369.2081.}
\end{align*}
\]

2-(1-((tert-Butyldimethylsilyl)oxy)-2-ethylbutyl)-5-phenyl-2H-tetrazole (4ah).

\[
\begin{align*}
\text{Colorless oil (66.3 mg, 92% yield).} \\
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3, \delta): 8.18-8.20 \text{ (m, 2H), 7.45-7.52 \text{ (m, 3H), 6.10 \text{ (d, } J = 8.0 \text{ Hz, 1H),}}
\end{align*}
\]
2.22-2.30 (m, 1H), 1.54-1.74 (m, 2H), 1.10-1.17 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H), 0.86 (s, 9H), 0.81 (t, $J = 7.6$ Hz, 3H), 0.14 (s, 3H), -0.21 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 165.0, 130.4, 129.0, 127.7, 127.1, 89.3, 46.4, 25.6, 20.6, 20.4, 18.1, 10.7, 10.1, -5.3, -5.5.

HRMS: [M + Na]$^+$ calcd. for C$_{19}$H$_{32}$N$_4$NaOSi, 383.2238; found, 383.2239.

2-(((tert-Butyldimethylsilyl)oxy)(cyclohexyl)methyl)-5-phenyl-2$H$-tetrazole (4ai).

[Chemical structure image]

Colorless oil (61.0 mg, 82% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.19-8.21 (m, 2H), 7.45-7.52 (m, 3H), 5.90 (d, $J = 8.4$ Hz, 1H), 2.23-2.33 (m, 2H), 2.13 (d, $J = 12.8$ Hz, 1H), 1.80-1.84 (m, 1H), 1.61-1.71 (m, 2H), 1.24-1.36 (m, 1H), 0.93-1.06 (m, 2H), 0.85 (s, 9H), 0.12 (s, 3H), -0.16 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 165.1, 130.4, 129.0, 127.1, 89.3, 46.4, 25.6, 18.1, -5.27, -5.34.

HRMS: [M + Na]$^+$ calcd. for C$_{20}$H$_{32}$N$_4$NaOSi, 395.2238; found, 395.2241.

2-(1-(((tert-Butyldimethylsilyl)oxy)pent-4-en-1-yl)-5-phenyl-2$H$-tetrazole (4aj).

[Chemical structure image]

Colorless oil (62.4 mg, 91% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.18-8.20 (m, 2H), 7.45-7.52 (m, 3H), 6.26 (t, $J = 6.4$ Hz, 1H), 5.76-5.86 (m, 1H), 5.02-5.08 (m, 2H), 2.25-2.44 (m, 2H), 0.86 (s, 9H), 0.16 (s, 3H), -0.12 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 165.1, 136.5, 130.5, 129.0, 127.6, 127.1, 116.2, 86.3, 35.9, 28.8, 25.6, 18.1, -5.1, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{18}$H$_{28}$N$_4$NaOSi, 367.1925; found, 367.1917.

\[
\text{Ph} - \text{N} - \text{N} \\
\text{Ph} - \text{O} - \text{Bu}
\]

Colorless oil (54.6 mg, 72% yield).

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}, \(\delta\)): 8.23-8.26 (m, 2H), 7.50-7.57 (m, 3H), 7.28-7.35 (m, 5H), 6.42 (dd, \(J = 7.6\), 5.6 Hz, 1H), 3.49-3.63 (m, 2H), 0.81 (s, 9H), -0.03 (s, 3H), -0.12 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}, \(\delta\)): 165.1, 135.2, 130.5, 129.9, 129.0, 128.7, 127.6, 127.4, 127.1, 87.7, 43.5, 25.5, 18.0, -5.3, -5.6.

\textbf{HRMS:} [M + Na]\textsuperscript{+} calcd. for C\textsubscript{21}H\textsubscript{28}N\textsubscript{4}NaOSi, 403.1925; found, 403.1915.

2-(1-(((\textit{tert}-Butyldimethylsilyl)oxy)-3-phenylpropyl)-5-phenyl-2H-tetrazole (4al).

\[
\text{Ph} - \text{N} - \text{N} \\
\text{Ph} - \text{O} - \text{Bu}
\]

Colorless oil (67.1 mg, 85% yield).

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}, \(\delta\)): 8.19-8.22 (m, 2H), 7.46-7.53 (m, 3H), 7.29-7.33 (m, 2H), 7.19-7.23 (m, 3H), 6.26 (t, \(J = 6.0\) Hz, 1H), 2.65-2.81 (m, 2H), 2.51-2.64 (m, 2H), 0.88 (s, 9H), 0.16 (s, 3H), -0.12 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (150 MHz, CDCl\textsubscript{3}, \(\delta\)): 165.2, 140.2, 130.5, 129.0, 128.7, 128.5, 127.6, 127.1, 126.5, 86.2, 38.4, 30.9, 25.6, 18.1, -5.1, -5.3.

\textbf{HRMS:} [M + Na]\textsuperscript{+} calcd. for C\textsubscript{22}H\textsubscript{30}N\textsubscript{4}NaOSi, 417.2081; found, 417.2090.


\[
\text{Ph} - \text{N} - \text{N} \\
\text{Ph} - \text{O} - \text{Bu}
\]

White solid (52.2 mg, 71% yield). mp: 53.8-54.5 °C.

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}, \(\delta\)): 8.15-8.17 (m, 2H), 7.58-7.60 (m, 3H), 7.39-7.44 (m, 3H), 7.36 (s, 1H), 0.95 (s, 9H), 0.23 (s, 3H), 0.00 (s, 3H).
$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.4, 137.5, 130.4, 129.5, 128.9, 128.7, 127.5, 127.1, 126.3, 87.1, 25.6, 18.2, -5.2, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{26}$H$_{26}$N$_4$NaOSi, 389.1768; found, 389.1770.

2-(((tert-Butyldimethylsilyl)oxy)(naphthalen-1-yl)methyl)-5-phenyl-$2H$-tetrazole (4an).

White solid (40.1 mg, 48% yield). mp: 140.1-140.9 °C.

$^1$H NMR (600 MHz, CDCl$_3$, δ): 8.27 (d, $J = 7.2$ Hz, 1H), 8.08-8.10 (m, 2H), 7.98 (s, 1H), 7.93-7.95 (m, 2H), 7.88-7.89 (m, 1H), 7.64 (t, $J = 7.8$ Hz, 1H), 7.45-7.47 (m, 2H), 7.42-7.44 (m, 3H), 0.95 (s, 9H), 0.29 (s, 3H), 0.06 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.4, 133.8, 132.0, 130.5, 130.4, 129.9, 129.2, 128.9, 127.5, 127.2, 127.1, 126.0, 125.5, 122.2, 84.6, 25.7, 18.3, -5.0, -5.2.

HRMS: [M + Na]$^+$ calcd. for C$_{24}$H$_{28}$N$_4$NaOSi, 439.1925; found, 439.1929.

2-(1-((tert-Butyldimethylsilyl)oxy)-2-methylallyl)-5-phenyl-$2H$-tetrazole (4ao).

Colorless oil (40.1 mg, 61% yield).

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.18-8.20 (m, 2H), 7.45-7.51 (m, 3H), 6.60 (s, 1H), 5.51 (s, 1H), 5.20-5.24 (m, 1H), 1.76 (s, 3H), 0.90 (s, 9H), 0.20 (s, 3H), -0.04 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 165.2, 140.7, 130.4, 129.0, 127.6, 127.2, 115.9, 88.3, 25.6, 18.2, 17.5, -5.0, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{17}$H$_{26}$N$_4$NaOSi, 353.1768; found, 353.1773.
2-(1-((Trimethylsilyl)oxy)ethyl)-5-phenyl-2H-tetrazole (4ap).

Colorless oil (20.8 mg, 40% yield).

$^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 8.18-8.20 (m, 2H), 7.46-7.54 (m, 3H), 6.43 (q, $J = 6.0$ Hz, 1H), 1.91 (d, $J = 6.0$ Hz, 3H), 0.12 (s, 9H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 165.1, 130.5, 129.0, 127.7, 127.1, 83.2, 23.4, -0.3.

HRMS: [M + Na]$^+$ calcd. for C$_{12}$H$_{18}$N$_4$NaOSi, 285.1142; found, 285.1151.

2-(1-((Triethylsilyl)oxy)ethyl)-5-phenyl-2H-tetrazole (4aq).

Colorless oil (43.5 mg, 71% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.18-8.20 (m, 2H), 7.46-7.52 (m, 3H), 6.44 (q, $J = 6.0$ Hz, 1H), 1.91 (d, $J = 6.0$ Hz, 3H), 0.90 (t, $J = 8.0$ Hz, 9H), 0.56-0.67 (m, 6H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 165.1, 130.4, 129.0, 127.7, 127.1, 88.3, 23.5, 6.5, 4.4.

HRMS: [M + Na]$^+$ calcd. for C$_{15}$H$_{24}$N$_4$NaOSi, 327.1612; found, 327.1612.

2-(1-((Triisopropylsilyl)oxy)ethyl)-5-phenyl-2H-tetrazole (4ar).

Colorless oil (63.8 mg, 92% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.17-8.20 (m, 2H), 7.44-7.52 (m, 3H), 6.55 (q, $J = 6.0$ Hz, 1H), 1.92 (d, $J = 5.6$ Hz, 3H), 1.09-1.17 (m, 3H), 1.05(d, $J = 7.2$ Hz, 9H), 0.98(d, $J = 7.2$ Hz, 9H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 165.0, 130.4, 129.0, 127.7, 127.1, 83.6, 23.8, 17.9, 17.7, 12.1.

HRMS: [M + Na]$^+$ calcd. for C$_{18}$H$_{30}$N$_4$NaOSi, 369.2081; found, 369.2071.
2-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-(m-toly)-2H-tetrazole (4ba).

Colorless oil (62.5 mg, 98% yield).

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.02 (s, 1H), 7.98 (d, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 7.6$ Hz, 1H), 7.28 (d, $J = 7.6$ Hz, 1H), 6.42 (q, $J = 6.0$ Hz, 1H), 2.44 (s, 3H), 1.91 (d, $J = 5.6$ Hz, 3H), 0.87 (s, 9H), 0.18 (s, 3H), -0.04 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, δ): 165.1, 138.7, 131.2, 128.9, 127.6, 127.5, 124.2, 83.5, 25.6, 23.3, 21.5, 18.1, -5.0, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{16}$H$_{26}$N$_4$NaOSi, 341.1768; found, 347.1765.

2-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-(4-bromophenyl)-2H-tetrazole (4ca).

Colorless oil (48.9 mg, 64% yield).

$^1$H NMR (400 MHz, CDCl$_3$, δ): 8.05-8.07 (m, 2H), 7.61-7.63 (m, 2H), 6.41 (q, $J = 6.0$ Hz, 1H), 1.90 (d, $J = 5.6$ Hz, 3H), 0.86 (s, 9H), 0.18 (s, 3H), -0.04 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 164.2, 132.3, 128.6, 126.7, 124.5, 83.7, 25.6, 23.3, 18.1, -5.0, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{15}$H$_{23}$BrN$_4$NaOSi, 405.0717; found, 405.0720.

2-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-methyl-2H-tetrazole (4da).

Colorless oil (13.2 mg, 27% yield).

$^1$H NMR (400 MHz, CDCl$_3$, δ): 6.33 (q, $J = 6.0$ Hz, 1H), 2.55 (s, 3H), 1.82 (d, $J = 6.0$ Hz, 3H), 0.85 (s, 9H), 0.15 (s, 3H), -0.08 (s, 3H).
$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 162.9, 83.1, 25.6, 23.3, 18.1, 11.1, -5.0, -5.3.

**HRMS:** [M + Na]$^+$ calcd. for C$_{10}$H$_{22}$N$_4$NaOSi, 265.1455; found, 265.1445.

2-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-cyclopropyl-2$H$-tetrazole (4ea).

![Chemical Structure](image)

Colorless oil (18.8 mg, 35% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 6.28 (q, $J = 6.0$ Hz, 1H), 2.15-2.24 (m, 1H), 1.80 (d, $J = 5.6$ Hz, 3H), 1.06-1.08 (m, 4H), 0.84 (s, 9H), 0.13 (s, 3H), -0.09 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 168.7, 83.1, 25.6, 23.2, 18.1, 8.71, 8.65, 6.8, -5.1, -5.4.

**HRMS:** [M + Na]$^+$ calcd. for C$_{12}$H$_{24}$N$_4$NaOSi, 291.1612; found, 291.1612.

2-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-(tert-butyl)-2$H$-tetrazole (4fa).

![Chemical Structure](image)

Colorless solid (16.5 mg, 29% yield). mp: 157.8-158.9 °C.

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 6.31 (q, $J = 6.0$ Hz, 1H), 1.84 (d, $J = 6.0$ Hz, 3H), 1.43 (s, 9H), 0.83 (s, 9H), 0.12 (s, 3H), -0.11 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 174.3, 83.1, 31.7, 29.7, 25.6, 23.1, 18.0, -5.2, -5.3.

**HRMS:** [M + Na]$^+$ calcd. for C$_{13}$H$_{28}$N$_4$NaOSi, 307.1925; found, 307.1917.

(E)-2-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-styryl-2$H$-tetrazole (4ga).

![Chemical Structure](image)

Colorless oil (45.6 mg, 69% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.77 (d, $J = 16.8$ Hz, 1H), 7.55-7.58 (m, 2H), 7.31-7.42 (m, 3H), 7.17 (d, $J = 16.8$ Hz, 1H), 6.39 (q, $J = 6.0$ Hz, 1H), 1.88 (d, $J = 6.0$ Hz, 3H), 0.87 (s, 9H), 0.17 (s,
(E)-2-\((\text{tert-Butyldimethylsilyl\text{oxy}})\text{ethyl}\)-5-(but-2-en-2-yl)\(-2H\)-tetrazole (4ha).

\[
\text{\includegraphics[width=1cm]{image}}
\]

Colorless oil (50.1 mg, 90% yield).

\(^1\text{H NMR}\ (400 \text{ MHz, CDCl}_3, \delta):\ 6.83 (\text{qq, } J = 7.2, 1.6 \text{ Hz, } 1\text{H}), \ 6.32 (\text{q, } J = 6.0 \text{ Hz, } 1\text{H}), \ 2.11-2.12 \text{ (m, } 3\text{H}), \ 1.83-1.87 \text{ (m, } 6\text{H}), \ 0.85 (\text{s, } 9\text{H}), \ 0.14 (\text{s, } 3\text{H}), \ -0.08 (\text{s, } 3\text{H}).
\]

\(^{13}\text{C NMR}\ (150 \text{ MHz, CDCl}_3, \delta):\ 167.1, \ 128.7, \ 123.9, \ 83.2, \ 25.6, \ 23.2, \ 18.1, \ 13.9, \ 13.5, \ -5.0, \ -5.3.
\]

\text{HRMS: } [\text{M + Na}]^+ \text{ calcd. for C}_{13}\text{H}_{26}\text{N}_{4}\text{NaOSi, 305.1768; found, 305.1767.}

(Z)- 2-\((\text{tert-Butyldimethylsilyl\text{oxy}})\text{ethyl}\)-5-(but-2-en-2-yl)-\(-2H\)-tetrazole (4ia).

\[
\text{\includegraphics[width=1cm]{image}}
\]

Colorless oil (51.2 mg, 91% yield).

\(^1\text{H NMR}\ (400 \text{ MHz, CDCl}_3, \delta):\ 6.36 (\text{qq, } J = 6.0 \text{ Hz, } 1\text{H}), \ 5.97 (\text{qq, } J = 7.2, 1.6 \text{ Hz, } 1\text{H}), \ 2.17-2.18 \text{ (m, } 3\text{H}), \ 2.07 (\text{dq, } J = 7.2, 1.6 \text{ Hz, } 3\text{H}), \ 1.86 (\text{d, } J = 5.6 \text{ Hz, } 3\text{H}), \ 0.85 (\text{s, } 9\text{H}), \ 0.14 (\text{s, } 3\text{H}), \ -0.07 \text{ (s, } 3\text{H}).
\]

\(^{13}\text{C NMR}\ (150 \text{ MHz, CDCl}_3, \delta):\ 165.4, \ 130.8, \ 123.1, \ 83.3, \ 25.6, \ 23.2, \ 22.2, \ 18.1, \ 15.8, \ -5.0, \ -5.3.
\]

\text{HRMS: } [\text{M + Na}]^+ \text{ calcd. for C}_{13}\text{H}_{26}\text{N}_{4}\text{NaOSi, 305.1768; found, 305.1769.}

2-(1-\((\text{tert-Butyldimethylsilyl\text{oxy}})\text{ethyl}\))-benzyl-\(-2H\)-tetrazole (4ja).

\[
\text{\includegraphics[width=1cm]{image}}
\]
Colorless oil (19.6 mg, 31% yield).

\[ ^1\text{H NMR} \ (600 \text{ MHz, CDCl}_3, \delta) \ : \ 7.28-7.32 \ (m, 4\text{H}), \ 7.21-7.24\text{(m, 1H)}, \ 6.33\text{(q, } J = 6.0 \text{ Hz, 1H)}, \ 4.26\ (s, 2\text{H}), \ 1.83\ (d, J = 5.4 \text{ Hz, 3H}), \ 0.83\ (s, 9\text{H}), \ 0.12\ (s, 3\text{H}), -0.12\ (s, 3\text{H}). \]

\[ ^{13}\text{C NMR} \ (150 \text{ MHz, CDCl}_3, \delta) : \ 165.5, \ 136.9, \ 128.9, \ 128.7, \ 126.9, \ 83.3, \ 32.0, \ 25.5, \ 23.2, \ 18.0, \ -5.1, -5.4. \]

\textbf{HRMS:} [M + Na]^+ calcd. for C_{16}H_{26}N_{4}NaOSi, 341.1768; found, 341.1772.

2-(1-((tert-Butyldimethylsilyloxy)ethyl)-5-benzhydryl-2\textit{H}-tetrazole (4ka).

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

Colorless oil (43.4 mg, 55% yield).

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3, \delta) : \ 7.34-7.35 \ (m, 2\text{H}), \ 7.31-7.32 \ (m, 3\text{H}), \ 7.27-7.30 \ (m, 3\text{H}), \ 7.21-7.25 \ (m, 2\text{H}), \ 6.35\ (q, J = 6.0 \text{ Hz, 1H}), \ 5.84\ (s, 1\text{H}), \ 1.85\ (d, J = 6.0 \text{ Hz, 3H}), \ 0.83\ (s, 9\text{H}), \ 0.12\ (s, 3\text{H}), -0.12\ (s, 3\text{H}). \]

\[ ^{13}\text{C NMR} \ (150 \text{ MHz, CDCl}_3, \delta) : \ 167.8, \ 140.92, \ 140.91, \ 128.89, \ 128.87, \ 128.65, \ 128.64, \ 127.09, \ 127.07, \ 83.5, \ 48.8, \ 25.5, \ 23.2, \ 18.0, -5.1, -5.3. \]

\textbf{HRMS:} [M + Na]^+ calcd. for C_{22}H_{30}N_{4}NaOSi, 417.2081; found, 417.2079.

2-(1-((tert-Butyldimethylsilyloxy)ethyl)-5-(benzylthio)-2\textit{H}-tetrazole (4la).

\[
\begin{align*}
\text{Ph} & \quad \text{S} \quad \text{N} \quad \text{N}
\end{align*}
\]

Colorless oil (39.3 mg, 56% yield).

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3, \delta) : \ 7.38-7.41 \ (m, 2\text{H}), \ 7.22-7.31 \ (m, 3\text{H}), \ 6.30\ (q, J = 6.0 \text{ Hz, 1H}), \ 4.43\ (s, 2\text{H}), \ 1.82\ (d, J = 6.0 \text{ Hz, 3H}), \ 0.85\ (s, 9\text{H}), 0.13\ (s, 3\text{H}), -0.10\ (s, 3\text{H}). \]

\[ ^{13}\text{C NMR} \ (150 \text{ MHz, CDCl}_3, \delta) : 163.7, \ 136.8, \ 129.2, \ 128.7, \ 127.7, \ 83.7, \ 36.7, \ 25.6, \ 23.2, \ 18.0, \ -5.0, -5.3. \]

\textbf{HRMS:} [M + Na]^+ calcd. for C_{16}H_{26}N_{4}NaOSSi, 373.1489; found, 373.1491.
Ethyl 2-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2H-tetrazol-5-yl)acetate (4ma).

Colorless oil (23.3 mg, 51% yield).

$^1$H NMR (400 MHz, CDCl$_3$, δ): 6.36 (q, $J = 6.0$ Hz, 1H), 4.19 (q, $J = 6.0$ Hz, 2H), 3.98 (s, 2H), 1.85 (d, $J = 5.6$ Hz, 3H), 1.25 (t, $J = 6.8$ Hz, 3H), 1.91 (d, $J = 6.0$ Hz, 3H), 0.85 (s, 9H), 0.15 (s, 3H), -0.08 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 168.4, 160.1, 83.6, 61.7, 32.1, 25.6, 23.3, 18.0, 14.2, -5.1, -5.4.

HRMS: [M + Na]$^+$ calcd. for C$_{13}$H$_{26}$N$_4$NaO$_3$Si, 337.1666; found, 337.1660.

1-(1-((tert-butyldimethylsilyl)oxy)ethyl)-5-phenyl-1H-tetrazole (5aa).

White solid. mp: 75.0-75.7 °C.

$^1$H NMR (600 MHz, CDCl$_3$, δ): 7.86-7.88 (m, 2H), 7.52-7.59 (m, 3H), 6.36 (q, $J = 6.0$ Hz, 1H), 1.76 (d, $J = 6.0$ Hz, 3H), 0.84 (s, 9H), 0.01 (s, 3H), -0.09 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 153.9, 131.4, 129.6, 129.1, 124.7, 80.4, 25.5, 23.2, 17.9, -4.8, -5.1.

HRMS: [M + Na]$^+$ calcd. for C$_{15}$H$_{24}$N$_4$NaOSi, 327.1612; found, 327.1621.

1-(1-((tert-butyldimethylsilyl)oxy)ethyl)-5-methyl-1H-tetrazole (5da).

Colorless oil (12.2 mg, 25% yield).

$^1$H NMR (400 MHz, CDCl$_3$, δ): 6.33 (q, $J = 6.0$ Hz, 1H), 2.67 (s, 3H), 1.73 (d, $J = 6.0$ Hz, 3H), 0.86 (s, 9H), 0.11 (s, 3H), -0.07 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 150.8, 80.8, 25.6, 23.9, 18.0, 10.0, -5.0, -5.3.
HRMS: [M + Na]$^+$ calcd. for C$_{16}$H$_{22}$N$_4$NaOSi, 265.1455; found, 265.1451.

1-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-cyclopropyl-1$H$-tetrazole (5ea).

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{O-Si-Bu} & \\
\end{align*}
\]

Colorless oil (10.1 mg, 19% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 6.36 (q, $J = 6.0$ Hz, 1H), 2.23-2.29 (m, 1H), 1.80 (d, $J = 6.0$ Hz, 3H), 1.38-1.42 (m, 1H), 1.15-1.25 (m, 3H), 0.87 (s, 9H), 0.11 (s, 3H), -0.07 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 156.7, 80.7, 25.6, 24.1, 17.9, 10.3, 9.3, 5.1, -5.0, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{12}$H$_{24}$N$_4$NaOSi, 291.1612; found, 291.1614.

$(E)$-1-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-styryl-1$H$-tetrazole (5ga).

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

Colorless oil (8.0 mg, 12% yield).

$^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.95 (d, $J = 16.4$ Hz, 1H), 7.55-7.58 (m, 2H), 7.37-7.45 (m, 3H), 7.23 (d, $J = 16.4$ Hz, 1H), 6.44 (q, $J = 6.0$ Hz, 1H), 1.78 (d, $J = 6.0$ Hz, 3H), 0.89 (s, 9H), 0.13 (s, 3H), -0.06 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, $\delta$): 151.9, 140.1, 135.2, 130.1, 129.2, 127.7, 108.8, 81.4, 25.6, 24.8, 18.0, -5.0, -5.3.

HRMS: [M + Na]$^+$ calcd. for C$_{17}$H$_{26}$N$_4$NaOSi, 353.1768; found, 353.1756.

1-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-benzyl-1$H$-tetrazole (5ja).

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

White solid (30.5 mg, 48% yield). mp: 95.2-95.8 °C.

$^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 7.31-7.33 (m, 2H), 7.25-7.28 (m, 1H), 7.22-7.23 (m, 2H), 6.25(q,
\( J = 6.0 \text{ Hz, } 1H \), 4.41 (dd, \( J = 21.0, 16.2 \text{ Hz, } 2H \)), 1.54 (d, \( J = 6.0 \text{ Hz, } 3H \)), 0.86 (s, 9H), 0.07 (s, 3H), -0.07 (s, 3H).

\( ^{13}C \) NMR (150 MHz, CDCl\(_3\), \( \delta \)): 152.8, 134.5, 129.1, 128.8, 127.6, 81.0, 30.0, 25.6, 24.2, 18.0, -4.9, -5.2.

HRMS: \([\text{M} + \text{Na}]^+\) calcd. for C\(_{16}\)H\(_{26}\)N\(_4\)NaOSi, 341.1768; found, 341.1766.

1-(1-((tert-Butyldimethylsilyl)oxy)ethyl)-5-(benzylthio)-1H-tetrazole (5la).

Colorless oil (19.6 mg, 28% yield).

\( ^1H \) NMR (400 MHz, CDCl\(_3\), \( \delta \)): 7.39-7.42 (m, 2H), 7.27-7.34 (m, 3H), 6.14 (q, \( J = 6.0 \text{ Hz, } 1H \)), 4.58 (s, 2H), 1.67 (d, \( J = 6.0 \text{ Hz, } 3H \)), 0.84 (s, 9H), 0.06 (s, 3H), -0.09 (s, 3H).

\( ^{13}C \) NMR (150 MHz, CDCl\(_3\), \( \delta \)): 152.5, 135.9, 129.3, 128.9, 128.1, 80.6, 37.4, 25.6, 23.2, 18.0, -5.0, -5.2.

HRMS: \([\text{M} + \text{Na}]^+\) calcd. for C\(_{16}\)H\(_{26}\)N\(_4\)NaOSSi, 373.1489; found, 373.1487.
10. Copies of NMR spectra of the adducts

$^1$H-NMR of 4aa

$^{13}$C-NMR of 4aa
$^1$H-NMR of 4ab

$^{13}$C-NMR of 4ab
$^1$H-NMR of 4ac

1H-NMR Spectrogram

$^{13}$C-NMR of 4ac

13C-NMR Spectrogram
$^1$H-NMR of 4ad

$^{13}$C-NMR of 4ad
\textbf{\textsuperscript{1}H-NMR of 4ae}

\textbf{\textsuperscript{13}C-NMR of 4ae}
$^1$H-NMR of 4af

$^{13}$C-NMR of 4af
\[ {^1}H\text{-NMR of 4ag} \]

\[ {^{13}}C\text{-NMR of 4ag} \]
\textsuperscript{1}H-NMR of 4ah

\textsuperscript{13}C-NMR of 4ah
$^1$H-NMR of 4ai

$^{13}$C-NMR of 4ai
$^1$H-NMR of 4aj

$^{13}$C-NMR of 4aj
$^1$H-NMR of 4ak

$^{13}$C-NMR of 4ak
$^1$H-NMR of 4al

$^{13}$C-NMR of 4al
$^1$H-NMR of 4am

$^{13}$C-NMR of 4am
$^1$H-NMR of 4an

$^{13}$C-NMR of 4an
$^1$H-NMR of 4ao

$^{13}$C-NMR of 4ao
$^1$H-NMR of 4ap

$^{13}$C-NMR of 4ap
$^1$H-NMR of 4aq

$^{13}$C-NMR of 4aq
$^1$H-NMR of 4ar

$^{13}$C-NMR of 4ar
$^1$H-NMR of 4ba

$^{13}$C-NMR of 4ba
$^1$H-NMR of 4ca

$^{13}$C-NMR of 4ca
$^1$H-NMR of 4da

$^{13}$C-NMR of 4da
$^1$H-NMR of 4fa

$^{13}$C-NMR of 4fa
$^1$H-NMR of 4ga

$^{13}$C-NMR of 4ga

S62
$^1$H-NMR of 4ha

$^{13}$C-NMR of 4ha

S63
$^1$H-NMR of 4ia

$^{13}$C-NMR of 4ia
$^{1}$H-NMR of 4ja

$^{13}$C-NMR of 4ja
$^1$H-NMR of 4ka

$^{13}$C-NMR of 4ka
\textbf{\(^1\)H-NMR of 4la}

\begin{center}
\includegraphics[width=\textwidth]{1H-NMR.png}
\end{center}

\textbf{\(^{13}\)C-NMR of 4la}

\begin{center}
\includegraphics[width=\textwidth]{13C-NMR.png}
\end{center}
$^1$H-NMR of 4ma

$^{13}$C-NMR of 4ma
**$^1$H-NMR of 5da**

![$^1$H-NMR of 5da](image)

**$^{13}$C-NMR of 5da**

![$^{13}$C-NMR of 5da](image)
\(^1\)H-NMR of 5ea

\(^{13}\)C-NMR of 5ea
$^1$H-NMR of 5ga

$^{13}$C-NMR of 5ga
$^1$H-NMR of 5ja

$^{13}$C-NMR of 5ja
$^1$H-NMR of 5la

$^{13}$C-NMR of 5la