Mild and Regioselective Azol-halogenation of Alkenes

Kai Sun,*a Baixue Luan,a Zhenhua Liu,b Jiali Zhu,a Jikang Du,a Enqi Bai,a Yu Fang,a and Bing Zhangc

a College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, P. R. China

b College of Chemistry, Shandong Normal University, Jinan 250014, P. R. China

c College of Chemistry and Energy, Zhengzhou University, Zhengzhou 450001, P. R. China

Corresponding author: sunk468@nenu.edu.cn

Supporting Information

Table of Contents

I. General remarks .................................................................................................................. S2

II. Synthesis procedure for compounds 3 ............................................................................. S2

III. Analytical data of products obtained in this study......................................................... S3-12

IV. 1H and 13C-NMR spectra for compounds 3 and 4......................................................... S4-S46
I. General remarks.

All reagents were purchased from commercial sources and used without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer in deuterated solvents containing TMS as an internal reference standard. High-resolution mass spectrometry (HRMS) analyses were conducted on a Waters LCT Premier/XE. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All the reactions were monitored by thin-layer chromatography (TLC) using GF254 silica gel-coated TLC plates. Purification by flash column chromatography was performed over SiO$_2$ (silica gel 200–300 mesh).

II. General procedure:

Styrene 1a (0.45 mmol, 46.8 mg), 5-phenyl-1$H$-tetrazole 2a (0.3 mmol, 43.8 mg) and NBS (0.6 mmol, 106.8 mg) were added to an open round-bottom flask. The mixture was stirred at rt. in DCE (2.0 mL) for about 12.0 h. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography over silica gel (EtOAc/petroleum ether = 1:5, v/v) to give compound 3a (87.6 mg) in 89% yield.
III. Analytical data of products obtained in this study

1-(2-bromo-1-phenylethyl)-5-phenyl-1H-tetrazole (3a). White solid (89%, 87.6 mg), melting point: 96-97 °C; ^1H NMR (400 MHz; CDCl₃): δ = 4.02 (q, *J* = 5.2, 1H), 4.47 (t, *J* = 10.8, 1H), 6.22 (q, *J* = 4.8, 1H), 7.40-7.42 (m, 3H), 7.49-7.52 (m, 5H), 8.21 (dd, *J*_₁ = 2.4, 1H, *J*_₂ = 8.0, 2H). ^13C NMR (100 MHz; CDCl₃): δ = 31.8, 69.4, 123.4, 124.3, 126.9, 127.0, 128.8, 129.2, 129.6, 130.4, 135.3, 145.4, 165.3. HRMS (ESI-TOF) Calcd for C₁₅H₁₄BrN₄, [M+H]^+ 329.0404; Found 329.0409.

1-(2-bromo-1-(2-chlorophenyl)ethyl)-5-phenyl-1H-tetrazole (3b). Yellow oil liquid (84%, 91.6 mg), ^1H NMR (400 MHz; CDCl₃): δ = 4.04 (q, *J* = 4.4, 1H), 4.34 (d, *J* = 10.8, 1H), 6.81 (q, *J* = 4.4, 1H), 7.28-7.52 (m, 7H), 8.22 (t, *J* = 5.2, 2H). ^13C NMR (100 MHz; CDCl₃): δ = 30.6, 65.6, 127.0, 127.1, 127.5, 127.7, 128.8, 130.2, 130.5, 130.6, 132.9, 133.1, 165.3. HRMS (ESI-TOF) Calcd for C₁₅H₁₃BrClN₄, [M+H]^+ 363.0012; Found 363.0008.

1-(2-bromo-1-(3-chlorophenyl)ethyl)-5-phenyl-1H-tetrazole (3c). Yellow oil liquid (81%, 88.4 mg), ^1H NMR (400 MHz; CDCl₃): δ = 4.02 (q, *J* = 5.2, 1H), 4.42 (t, *J* = 10.8, 1H), 6.18 (q, *J* = 5.2, 1H), 7.38 (d, *J* = 4.8, 3H), 7.50-7.52 (m, 4H), 8.18-8.21 (m, 2H). ^13C NMR (100 MHz; CDCl₃): δ = 31.4, 68.6, 125.3, 127.0, 127.1, 127.3, 128.9, 129.9, 130.5, 135.2, 137.0, 165.4. HRMS (ESI-TOF) Calcd for C₁₃H₁₃BrClN₄, [M+H]^+ 363.0012; Found 363.0017.

1-(2-bromo-1-(3-bromophenyl)ethyl)-5-phenyl-1H-tetrazole (3d). White solid
1-(2-bromo-1-(4-fluorophenyl)ethyl)-5-phenyl-1H-tetrazole (3e). Colourless liquid (89%, 92.6 mg), ¹H NMR (400 MHz; CDCl₃): δ = 4.05 (q, J = 4.8, 1H), 4.41 (t, J = 10.5, 1H), 6.61 (q, J = 5.2, 1H), 7.16-7.20 (m, 2H), 7.38-7.51 (m, 7H), 8.19 (dd, J₁ = 3.6, 1H, J₂ = 8.0, 2H). ¹³C NMR (100 MHz; CDCl₃): δ = 30.8, 62.2, 116.0, 116.2, 122.6, 122.7, 124.9, 127.0, 127.1, 127.8, 127.9, 130.5, 131.3, 131.4, 138.4, 160.9, 165.3. HRMS (ESI-TOF) Calcd for C₁₅H₁₃BrFN₄, [M+H]⁺ 347.0307; Found 347.0312.

1-(2-bromo-1-(4-chlorophenyl)ethyl)-5-phenyl-1H-tetrazole (3f). Yellow oil liquid (93%, 101.4 mg), ¹H NMR (400 MHz; CDCl₃): δ = 4.01 (q, J = 5.6, 1H), 4.41 (t, J = 10.8, 1H), 6.23 (q, J = 5.6, 1H), 7.38-7.51 (m, 7H), 8.19 (dd, J₁ = 3.6, 1H, J₂ = 8.0, 2H). ¹³C NMR (100 MHz; CDCl₃): δ = 31.5, 68.6, 126.1, 126.8, 127.0, 127.1, 128.5, 128.8, 128.9, 129.5, 130.5, 133.6, 135.8, 165.4. HRMS (ESI-TOF) Calcd for C₁₅H₁₃BrClN₄, [M+H]⁺ 363.0012; Found 363.0018.

1-(2-bromo-1-(4-nitrophenyl)ethyl)-5-phenyl-1H-tetrazole (3g). Yellow oil liquid (62%, 69.6 mg), ¹H NMR (400 MHz; CDCl₃): δ = 4.08 (q, J = 5.6, 1H), 4.41 (t, J = 10.6, 1H), 6.33 (m, 1H), 7.51 (dd, J₁ = 1.2, 1H, J₂ = 4.4, 3H), 7.70 (d, J = 8.8, 2H), 8.17 (dd, J₁ = 4.0, 1H, J₂ = 6.8, 2H), 8.27 (d, J = 8.8, 2H). ¹³C NMR (100 MHz;
CDCl$_3$): $\delta = 30.8, 68.1, 123.8, 124.3, 126.8, 127.0, 127.1, 128.4, 128.9, 130.7, 140.5, 148.6, 165.7$. HRMS (ESI-TOF) Calcd for C$_{15}$H$_{13}$BrN$_3$O$_2$, [M+H]$^+$ 374.0252; Found 374.0258.

1-(2-bromo-1-(p-tolyl)ethyl)-5-phenyl-1$H$-tetrazole (3h). Yellow oil liquid (91%, 93.6 mg), $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 2.35$ (s, 1H), 3.99 ($J = 5.2$, 1H), 4.46 (t, $J = 10.8$, 1H), 6.20 ($q$, $J = 5.2$, 1H), 7.20 (d, $J = 6.8$, 2H), 7.38 (d, $J = 8.0$, 2H), 7.48-7.51 (m, 3H), 8.19 (dd, $J_1 = 2.4$, 1H, $J_2 = 8.0$, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 21.1, 32.0, 69.3, 127.0, 127.3, 128.8, 129.7, 165.2$. HRMS (ESI-TOF) Calcd for C$_{16}$H$_{16}$BrN$_4$, [M+H]$^+$ 343.0558; Found 343.0561.

1-(2-bromo-1-(4-methoxyphenyl)ethyl)-5-phenyl-1$H$-tetrazole (3i). Yellow oil liquid (84%, 90.5 mg), $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 3.80$ (s, 1H), 3.97 (q, $J = 4.8$, 1H), 4.44 (t, $J = 10.8$, 1H), 6.16 (q, $J = 4.8$, 1H), 6.91 (d, $J = 8.8$, 2H), 7.44-7.51 (m, 5H), 8.17 (d, $J = 1.6$, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 32.0, 55.3, 69.0, 114.5, 126.9, 127.3, 128.5, 128.8, 130.3, 160.5, 165.2$. HRMS (ESI-TOF) Calcd for C$_{16}$H$_{16}$BrON$_4$, [M+H]$^+$ 359.0508; Found 359.0514.

1-(2-bromo-1-(4-tert-butyl)phenyl)ethyl)-5-phenyl-1$H$-tetrazole (3j). Yellow oil liquid (85%, 98.2 mg), $^1$H NMR (400 MHz; CDCl$_3$): $\delta = 1.31$ (s, 9H), 4.01 (q, $J = 4.8$, 1H), 4.49 (t, $J = 10.8$, 1H), 6.22 (q, $J = 4.4$, 1H), 7.41-7.52 (m, 7H), 8.22 (t, $J = 7.6$, 2H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta = 31.2, 34.7, 69.3, 126.2, 126.8, 127.0, 127.3, 128.8, 130.4, 132.3, 152.8, 165.2$. HRMS (ESI-TOF) Calcd for C$_{19}$H$_{22}$BrN$_4$, [M+H]$^+$ 385.1030; Found 385.1025.
1-(2-bromo-1-(4-(chloromethyl)phenyl)ethyl)-5-phenyl-1H-tetrazole (3k).

Yellow oil liquid (77%, 87.2 mg), \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 3.99\) (q, \(J = 5.2, 1\)H), 4.44 (t, \(J = 10.8, 1\)H), 4.56 (s, 1H), 6.22 (q, \(J = 5.2, 1\)H), 7.42-7.51 (m, 7H), 8.18 (dd, \(J_1 = 2.8, J_2 = 8.0, 2\)H). \(^13\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 31.7, 45.3, 68.9, 127.0, 127.1, 127.5, 128.9, 129.4, 130.5, 135.3, 139.1, 165.3, 169.0\). HRMS (ESI-TOF) Calcd for C\(_{16}\)H\(_{15}\)BrClN\(_4\) [M+H]\(^+\) 377.0171; Found 377.0176.

4-(2-bromo-1-(5-phenyl-1H-tetrazol-1-yl)ethyl)phenyl acetate (3l). White solid (80%, 92.9 mg), melting point: 108-109 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 2.30\) (s, 1H), 3.98 (q, \(J = 4.8, 1\)H), 4.44 (t, \(J = 10.8, 1\)H), 6.21 (q, \(J = 4.8, 1\)H), 7.14 (d, \(J = 8.4, 2\)H), 7.49-7.55 (m, 5H), 8.18 (dd, \(J_1 = 2.4, J_2 = 7.8, 2\)H). \(^13\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 21.0, 31.7, 68.8, 122.4, 127.0, 128.4, 128.8, 130.4, 132.7, 151.5, 165.3, 169.0\). HRMS (ESI-TOF) Calcd for C\(_{17}\)H\(_{16}\)BrO\(_2\)N\(_4\) [M+H]\(^+\) 387.0457; Found 387.0461.

1-(1-bromo-2-phenylpropan-2-yl)-5-phenyl-1H-tetrazole (3m). Yellow oil liquid (87%, 89.5 mg), \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 2.41\) (s, 1H), 4.14 (d, \(J = 6.8, 1\)H), 4.66 (d, \(J = 6.8, 1\)H), 7.09 (dd, \(J_1 = 2.4, J_2 = 6.8, 2\)H), 7.34 (dd, \(J_1 = 3.2, J_2 = 6.0, 3\)H), 7.49 (dd, \(J_1 = 3.2, J_2 = 6.0, 3\)H), 8.21 (dd, \(J_1 = 2.4, J_2 = 7.8, 2\)H). \(^13\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 25.4, 39.7, 70.5, 125.0, 125.8, 127.0, 127.4, 128.7, 128.8, 128.9, 130.3, 140.6, 164.9\). HRMS (ESI-TOF) Calcd for C\(_{16}\)H\(_{16}\)BrN\(_4\) [M+H]\(^+\) 343.0559; Found 343.0552.

1-(2-bromo-1,1-diphenylethyl)-5-phenyl-1H-tetrazole (3n). White solid (90%, 109.4 mg), melting point: 123-124 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 4.88\) (s, 2H),
7.34-7.40 (m, 10H), 7.47-7.50 (m, 3H), 8.17 (dd, \( J_1 = 2.0, J_2 = 7.6, 2H \)). 13C NMR (100 MHz; CDCl3): \( \delta = 38.5, 76.4, 127.0, 127.3, 128.2, 128.5, 128.7, 128.8, 130.4, 139.3, 164.6 \). HRMS (ESI-TOF) Calcd for C_{21}H_{18}BrN_{4}, [M+H]^+ 405.0718; Found 405.0713.

1-(2-bromocyclooctyl)-5-phenyl-1H-tetrazole (3o). Yellow oil liquid (71%, 71.3 mg), 1H NMR (400 MHz; CDCl3): \( \delta = 1.70-1.87 \) (m, 2H), 2.01-2.22 (m, 2H), 2.26-2.29 (m, 3H), 2.30-2.33 (m, 4H), 2.52-2.56 (m, 1H), 5.00-5.05 (m, 1H), 5.37-5.42 (m, 1H), 7.47-7.51 (m, 3H), 8.17 (dd, \( J_1 = 2.0, J_2 = 8.0, 2H \)). 13C NMR (100 MHz; CDCl3): \( \delta = 24.6, 25.0, 25.6, 25.7, 32.3, 32.9, 55.9, 71.0, 126.9, 127.5, 128.8, 130.2, 165.0 \). HRMS (ESI-TOF) Calcd for C_{15}H_{20}BrN_{4}, [M+H]^+ 335.0871; Found 335.0876.

1-(4-bromotetrahydrofuran-3-yl)-5-phenyl-1H-tetrazole (3p). Yellow oil liquid (76%, 67.3 mg), 1H NMR (400 MHz; CDCl3): \( \delta = 1.70-1.87 \) (m, 2H), 2.01-2.22 (m, 2H), 2.26-2.29 (m, 3H), 2.30-2.33 (m, 4H), 2.52-2.56 (m, 1H), 5.00-5.05 (m, 1H), 5.37-5.42 (m, 1H), 7.47-7.51 (m, 3H), 8.17 (dd, \( J_1 = 2.0, J_2 = 8.0, 2H \)). 13C NMR (100 MHz; CDCl3): \( \delta = 46.5, 71.1, 71.2, 75.8, 126.8, 126.9, 128.9, 130.6, 165.6 \). HRMS (ESI-TOF) Calcd for C_{11}H_{12}BrON_{4}, [M+H]^+ 295.0195; Found 295.0198.

1-(2-iodo-1-phenylethyl)-5-phenyl-1H-tetrazole (3q). White solid (84%, 94.7 mg), melting point: 123-124 °C; 1H NMR (400 MHz; CDCl3): \( \delta = 3.88 \) (q, \( J = 5.6, 1H \), 4.25 (t, \( J = 10.6, 1H \), 6.17 (q, \( J = 5.2, 1H \), 7.40 (t, \( J = 5.2, 3H \), 7.49-7.51 (m, 5H), 8.19 (dd, \( J_1 = 2.4, 1H, J_2 = 8.0, 2H \)). 13C NMR (100 MHz; CDCl3): \( \delta = 3.83, 70.0, 126.9, 127.3, 128.8, 129.2, 129.5, 130.4, 136.1, 165.2 \). HRMS (ESI-TOF) Calcd for
C_{15}H_{16}IN_{4}, [M+H]^+ 377.0265; Found 377.0262.

**1-(1-iodo-2-phenylpropan-2-yl)-5-phenyl-1H-tetrazole (3r).** Yellow oil liquid (86%, 100.6 mg), ^1^H NMR (400 MHz; CDCl\_3): δ = 2.41 (s, 3H), 4.08 (d, J = 6.8, 1H), 4.49 (d, J = 6.8, 1H), 7.10 (dd, J\_1 = 2.4, 1H, J\_2 = 7.6, 2H), 7.33-7.52 (m, 6H), 8.23 (dd, J\_1 = 1.6, 1H, J\_2 = 8.0, 2H). ^1^C NMR (100 MHz; CDCl\_3): δ = 14.9, 27.7, 69.9, 125.0, 127.0, 127.4, 128.6, 128.9, 129.0, 130.4, 140.3, 164.9. HRMS (ESI-TOF) Calcd for C_{15}H_{16}IN_{4}, [M+H]^+ 391.0420; Found 391.0426.

**1-(1-iodo-3-phenylpropan-2-yl)-5-phenyl-1H-tetrazole (3s).** Pink oil liquid (91%, 106.5 mg), ^1^H NMR (400 MHz; CDCl\_3): δ = 3.27-3.29 (m, 1H), 3.47 (t, J = 6.8, 1H), 3.71 (t, J = 8.4, 1H), 4.95-5.09 (m, 2H), 7.12 (d, J = 6.8, 1H), 7.24-7.35 (m, 4H), 7.51 (d, J = 5.6, 3H), 8.17 (s, 2H). ^1^C NMR (100 MHz; CDCl\_3): δ = 27.7, 43.7, 67.1, 126.9, 127.4, 127.5, 128.7, 128.9, 129.0, 130.4, 130.5, 135.1, 137.8, 165.3. HRMS (ESI-TOF) Calcd for C_{15}H_{16}IN_{4}, [M+H]^+ 391.0420; Found 391.0427.

**1-(1-iodopentan-2-yl)-5-phenyl-1H-tetrazole (3t).** Yellow oil liquid (61%, 62.6 mg), ^1^H NMR (400 MHz; CDCl\_3): δ = 0.90-0.94 (m, 3H), 1.42-1.46 (m, 1H), 1.59-1.65 (m, 2H), 1.75-1.81 (m, 1H), 4.56-4.60 (m, 1H), 4.93-5.08 (m, 2H), 7.48 (dd, J\_1 = 3.6, J\_2 = 6.0, 3H), 8.16-8.18 (m, 2H). ^1^C NMR (100 MHz; CDCl\_3): δ = 13.0, 22.4, 28.1, 38.7, 60.3, 126.9, 127.2, 128.9, 130.4, 165.2. HRMS (ESI-TOF) Calcd for C_{12}H_{16}IN_{4}, [M+H]^+ 343.0421; Found 343.0415.

**1-(4-iodotetrahydrofuran-3-yl)-5-phenyl-1H-tetrazole (3u).** Yellow oil liquid
(77%, 79.0 mg), \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 4.22 (q, J = 5.2, 1H), 4.36 (q, J = 6.4, 1H), 7.50 (q, J = 6.8, 1H), 4.60 (t, J = 10.4, 1H), 4.79 (t, J = 4.0, 1H), 5.67 (t, J = 3.2, 1H), 7.47-7.49 (m, 3H), 8.12 (q, J = 4.0, 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 18.8, 71.0, 72.7, 77.5, 126.9, 128.9, 130.6, 165.5.\) HRMS (ESI-TOF) Calcd for C\(_{11}\)H\(_{12}\)ION\(_4\), [M+H]\(^+\) 343.0057; Found 343.0053.

1-(3-iodobicyclo[2.2.1]heptan-2-yl)-5-phenyl-1\(H\)-tetrazole (3v). White solid (81%, 88.9 mg), melting point: 123-124 \(^\circ\)C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 1.49 (t, J = 6.8, 2H), 1.82-1.91 (m, 2H), 2.36 (t, J = 8.8, 1H), 2.62 (s, 1H), 3.39 (t, J = 6.8, 1H), 3.68 (d, J = 4.0, 1H), 3.85 (s, 1H), 4.57 (q, J = 4.8, 1H), 7.47 (t, J = 7.6, 3H), 8.18 (dd, \(J_1 = 1.6, J_2 = 8.0, 2H\)). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 25.8, 26.4, 26.6, 36.2, 44.7, 47.9, 66.0, 126.8, 127.7, 128.8, 130.0, 164.4.\) HRMS (ESI-TOF) Calcd for C\(_{14}\)H\(_{16}\)IN\(_4\), [M+H]\(^+\) 367.0420; Found 367.0424.

1-(2-bromo-1-phenylethyl)-1\(H\)-benzo[\(d\)]imidazole (3w). White solid (80%, 72.0 mg), melting point: 35-36 \(^\circ\)C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 4.14-4.19 (m, 2H), 5.77 (t, J = 6.0, 1H), 7.25-7.30 (m, 5H), 7.37 (d, J = 4.4, 3H), 7.84 (d, J = 7.2, 1H), 8.20 (s, 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 31.8, 61.2, 110.2, 120.5, 122.7, 123.3, 126.6, 129.1, 129.3, 133.3, 136.4, 141.3, 143.5.\) HRMS (ESI-TOF) Calcd for C\(_{15}\)H\(_{14}\)BrN\(_2\), [M+H]\(^+\) 301.0340; Found 301.0345.

2-(2-bromo-1-phenylethyl)-2\(H\)-benzo[\(d\)][1,2,3]triazole (3x). White solid (42.6%, 38.5 mg), melting point: 103-104 \(^\circ\)C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 4.07 (q, J = 4.8, 1H), 4.62 (t, J = 10.4, 1H), 6.22 (q, J = 5.2, 1H), 7.36-7.42 (m, 5H), 7.50 (d, J = 6.0, 1H).
1H), 7.90 (dd, J = 3.2, 1H, J = 6.8, 2H). 13C NMR (100 MHz; CDCl3): δ = 32.6, 72.1, 118.3, 126.6, 127.0, 129.0, 129.3, 136.5, 144.3. HRMS (ESI-TOF) Calcd for C14H13BrN3, [M+H]+ 302.0293; Found 302.0287.

1-(2-bromo-1-phenylethyl)-1H-benzo[d][1,2,3]triazole (3x'). White solid (28.4%, 25.6 mg), melting point: 133-134 °C; 1H NMR (400 MHz; CDCl3): δ = 4.15 (q, J = 5.2, 1H), 4.64 (t, J = 10.4, 1H), 6.01 (q, J = 5.6, 1H), 7.34-7.43 (m, 8H), 8.08 (d, J = 8.0, 1H). 13C NMR (100 MHz; CDCl3): δ = 32.7, 64.8, 109.3, 120.1, 124.2, 126.9, 127.6, 129.2, 133.1, 136.6, 146.0. HRMS (ESI-TOF) Calcd for C14H13BrN3, [M+H]+ 302.0293; Found 302.0289.

2-(2-bromo-1-phenylethyl)-5-methyl-2H-benzo[d][1,2,3]triazole (3y). White solid (48%, 45.5 mg), melting point: 79-80 °C; 1H NMR (400 MHz; CDCl3): δ = 2.50 (s, 3H), 4.05 (q, J = 5.2, 1H), 4.60 (t, J = 10.8, 1H), 6.19 (q, J = 4.8, 1H), 7.23 (d, J = 8.8, 1H), 7.35 (d, J = 6.8, 3H), 7.48 (dd, J = 1.6, J = 7.6, 2H), 7.65 (s, 1H), 7.78 (d, J = 8.8, 1H). 13C NMR (100 MHz; CDCl3): δ = 22.0, 32.7, 71.9, 116.5, 117.7, 127.0, 129.0, 129.2, 129.5, 136.6, 136.7, 143.0, 144.8. HRMS (ESI-TOF) Calcd for C15H15BrN3, [M+H]+ 316.0449; Found 316.0455.

2-(2-bromo-1-phenylethyl)-5-methyl-2H-benzo[d][1,2,3]triazole (3y'). Yellow oil liquid (32%, 37.9 mg), 1H NMR (400 MHz; CDCl3): δ = 2.48 (s, 3H), 4.13-1.18 (m, 1H), 4.62-4.68 (m, 1H), 5.97-6.02 (m, 1H), 7.20 (s, 1H), 7.29-7.39 (m, 7H), 7.41 (d, J = 5.2, 1H). 13C NMR (100 MHz; CDCl3): δ = 21.4, 32.7, 64.8, 108.4, 108.8, 119.0, 119.5, 126.9, 129.1, 129.7, 134.2, 136.7, 146.6. HRMS (ESI-TOF) Calcd for
C_{13}H_{13}BrN_{3}, [M+H]^+ 316.0449; Found 316.0452.

1-(2-bromo-1-phenylethyl)-5-chloro-1H-benzo[d][1,2,3]triazole (3z). Yellow oil liquid (48.1%, 48.5 mg), \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 4.01\) (q, \(J = 4.8, 1\)H), 4.47 (t, \(J = 10.4, 1\)H), 6.24 (q, \(J = 4.8, 1\)H), 7.38-7.43 (m, 5H), 7.49 (dd, \(J_1 = 2.0, J_2 = 7.6, 2\)H), 8.09 (d, \(J = 6.8, 1\)H), 8.21 (s, 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 31.9, 69.6, 125.0, 127.0, 127.1, 129.0, 129.3, 129.8, 130.2, 130.4, 134.9, 135.1, 164.1\). HRMS (ESI-TOF) Calcd for C\(_{14}\)H\(_{12}\)BrClN\(_3\), [M+H]^+ 335.9905; Found 335.9909.

1-(2-bromo-1-phenylethyl)-5-chloro-1H-benzo[d][1,2,3]triazole (z'). Yellow oil liquid (28.9%, 29.1 mg), \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 4.12-4.17\) (m, 1H), 4.65 (t, \(J = 10.4, 1\)H), 5.92-5.97 (m, 1H), 7.35-7.43 (m, 7H), 8.02 (d, \(J = 8.8, 1\)H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 32.5, 65.1, 109.1, 110.2, 119.5, 121.1, 125.4, 126.9, 128.6, 129.3, 134.2, 136.2, 146.5\). HRMS (ESI-TOF) Calcd for C\(_{14}\)H\(_{12}\)BrClN\(_3\), [M+H]^+ 335.9905; Found 335.9901.

2-(2-bromo-1-phenylethyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (3aa). White solid (81%, 135.6 mg), melting point: 113-114 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 4.12\) (q, \(J = 7.2, 1\)H), 4.52 (q, \(J = 9.2, 1\)H), 5.45 (q, \(J = 7.2, 1\)H), 7.38 (q, \(J = 6.8, 3\)H), 7.61 (d, \(J = 6.8, 2\)H), 7.80-7.87 (m, 3H), 8.03 (d, \(J = 7.2, 1\)H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 29.8, 58.4, 120.9, 125.3, 126.9, 128.4, 128.8, 129.2, 134.4, 134.9, 135.2, 137.3, 158.7\). HRMS (ESI-TOF) Calcd for C\(_{15}\)H\(_{13}\)BrSNO\(_3\), [M+H]^+ 365.9801; Found 365.9805.
\(N\)-(2-bromo-1-phenylethyl)-\(N\)-(phenylsulfonyl)benzenesulfonamide \((3ab)\).

White solid (96%, 138.2 mg), melting point: 153-155 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 3.31\) (q, \(J = 3.6\), 1H), 4.46 (t, \(J = 10.8\), 1H), 5.79 (q, \(J = 3.2\), 1H), 7.32-7.60 (m, 15H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 29.8, 64.5, 128.1, 128.4, 128.6, 128.9, 129.6, 132.6, 133.9, 139.8\). HRMS (ESI-TOF) Calcd for C\(_{20}\)H\(_{19}\)BrS\(_2\)NO\(_4\), [M+H]\(^+\) 479.9940; Found 479.9936.

5-phenyl-1-(1-phenylvinyl)-1\(^H\)-tetrazole (4). White solid, melting point: 164-165 °C; \(^1\)H NMR (400 MHz; CDCl\(_3\)): \(\delta = 5.70\) (s, 1H), 6.12 (d, \(J = 0.8\), 1H), 7.45-7.52 (m, 8H), 8.21 (q, \(J = 4.0\), 1H). \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta = 110.9, 127.1, 127.8, 128.5, 128.9, 129.8, 130.5, 133.3, 143.6, 164.9\).
IV. $^1$H and $^{13}$C-NMR spectra for compounds 3 and 4

Compound 3a
Compound 3b
Compound 3c
Compound 3f
Compound 3g
Compound 3h
Compound 3i
Compound 3k
Compound 3l
Compound 3m
Compound 3n
Compound 3o
Compound 3q
Compound 3r
Compound 3s
Compound 3t
Compound 3u
Compound 3v
Compound 3w
Compound 3x
Compound 3x'
Compound 3y’
Compound 3z
Compound 3z'
Compound 3aa
Compound 3ab