Quickly FeCl$_3$-catalyzed highly chemo- and stereo- selective [3+2] dipolar cycloaddition of aziridines with isothiocyanates

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General Remarks: All reactions were carried out in oven-dried flask sealed with rubber septa under a positive pressure of dry nitrogen unless otherwise indicated. Reactions were run using Teflon™-coated magnetic stir bars. Aziridines 1a-1j, 1k were prepared following the procedure of M. Komatsu as steps in Scheme SI-1. $^1$H-NMR and $^{13}$C-NMR were recorded on a Bruker AC-300 FT ($^1$H: 300 and 400 MHz, $^{13}$C: 75 and 100 MHz) using TMS as internal reference. The chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000FTIR spectrometer. HRMS were recorded on the TOF-HRMS-EI at the Instruments' Center for Physical Science, University of Science & Technology of China. Nitromethane, 1,2-dichloroethane and dichloromethane were distilled from CaH$_2$ and stored over 4Å molsieves in screw-cap flasks. All commercially available reagents were used as received.

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(Z)-N-(5-phenyl-3-tosylthiazolidin-2-ylidene) aniline

The title compound was a white solid. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 2.47 (3 H, s), 2.04 (1 H, $J$ = 9 Hz, t), 4.58 (1 H, $J$ = 6.3 Hz, q), 4.78 (1 H, $J$ = 6.6 Hz, q), 6.78 (2 H, $J$ = 8.1 Hz, d), 7.07 (1 H, m), 7.25 (2 H, $J$ = 6.9 Hz, d), 7.29 (7 H, m), 7.98 (2 H, $J$ = 8.4 Hz, d). $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) = 21.8, 47.0, 56.9, 120.8, 124.4, 127.5, 128.8, 129.0, 129.1, 129.2, 129.3, 134.8, 136.7, 144.9, 150.1, 152.2. IR (liquid film, cm$^{-1}$): $\nu$ = 3062, 2926, 1643, 1592, 1362, 1172, 1101. m. p.: 136 - 138 °C. HRMS (EI-TOF) calc. C$_{22}$H$_{20}$N$_2$O$_2$S$_2$: 408.5364. Found: 408.1125.

(Z)-N-(5-p-tolyl-3-tosylthiazolidin-2-ylidene)aniline

The title compound was a white solid, $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) = 2.36 (3 H, s), 2.46 (3 H, s), 4.01 (1 H, $J$ = 9.3 Hz, t), 4.56 (1 H, $J$ = 6.6 Hz, q), 4.75 (1 H, $J$ = 6.6 Hz, q), 6.78 (2 H, $J$ = 7.5Hz, d), 7.05 (1 H, $J$ = 7.5 Hz, t), 7.11 (2 H, $J$ = 8.1 Hz, d), 7.24 (4 H, m), 7.34 (2 H, $J$ = 8.1 Hz, d), 7.98 (2 H, $J$ = 8.1 Hz, d); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) = 21.2, 21.8, 46.9, 56.9, 120.8, 124.3, 127.4, 128.9, 129.2, 129.3, 129.7, 133.4, 134.6, 138.7, 144.9, 150.0, 152.4; IR (liquid film, cm$^{-1}$): $\nu$=3029, 2923, 1643, 1592, 1362, 1288, 1248, 1171, 1101. m.p:133 - 134 °C. HRMS (El-TOF) calc. C$_{23}$H$_{22}$N$_2$O$_2$S$_2$: 422.5868. Found: 422.1197.

(Z)-N-(5-o-tolyl-3-tosylthiazolidin-2-ylidene)aniline
The title compound was a white solid, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 2.35 (3 H, s), 2.49 (3 H, s), 4.09 (1 H, $J$ = 8.4 Hz, q), 4.55 (1 H, $J$ = 6.4 Hz, q), 5.02 (1 H, $J$ = 6.4 Hz, q), 6.77 (1 H, $J$ = 7.2 Hz, d), 7.05 (1 H, t), 7.15 (3 H, m), 7.21 (4 H, m), 7.34 (2 H, m), 7.44 (1 H, m), 8.05 (2 H, $J$ = 9.2 Hz, d); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 19.6, 21.8, 43.2, 55.8, 60.5, 120.9, 124.4, 126.6, 126.9, 128.5, 129.1, 129.4, 130.9, 134.6, 136.2, 145.0, 150.2. IR (liquid film, cm$^{-1}$): $\nu$ = 3029, 2925, 1735, 1641, 1358, 1169, 1095. m.p.: 147-148 °C. HRMS (EI-TOF) calc. C$_{23}$H$_{22}$N$_2$O$_2$S$_2$: 422.5868. Found: 422.1197.

(Z)-N-(5-methyl-5-phenyl-3-tosylthiazolidin-2-ylidene)aniline

The title compound was a white solid, $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) = 1.89 (3 H, s), 2.46 (3 H, s), 4.37 (2 H, $J$ = 10.2 Hz, q), 6.75 (2 H, $J$ = 7.5 Hz, d), 7.07 (1 H, $J$ = 8.1 Hz, t), 7.30 (10 H, m), 7.93 (2 H, $J$ = 8.1 Hz, d); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) = 21.8, 29.8, 55.2, 61.8, 120.9, 124.4, 126.0, 127.2, 128.1, 128.4, 128.8, 128.9, 129.1, 129.2, 134.9, 134.9, 141.8, 144.9, 150.1, 151.9; IR (liquid film, cm$^{-1}$): $\nu$ = 2925, 1642, 1592, 1362, 1171, 1087, 662. m. p.: 103 - 104 °C; HRMS (EI-TOF) calc. C$_{23}$H$_{22}$N$_2$O$_2$S$_2$: 422.5868. Found: 422.1197.

(Z)-N-(5-(4-fluorophenyl)-3-tosylthiazolidin-2-ylidene)aniline
The title compound was a white solid, $^1$H-NMR (300 MHz, CDCl$_3$) δ (ppm) = 2.45 (3 H, s), 4.02 (1 H, $J = 8.4$ Hz, q), 4.54 (1 H, $J = 6.3$ Hz, q), 4.74 (1 H, $J = 6.9$ Hz, t), 6.77 (2 H, $J = 7.2$ Hz, d), 7.02 (3 H, m), 7.31 (6 H, m), 7.97 (2 H, $J = 8.1$ Hz, d).

$^{13}$C-NMR (75 MHz, CDCl$_3$) δ (ppm) = 21.8, 46.3, 56.9, 115.9, 116.3, 120.8, 124.5, 129.1, 129.3, 129.4, 129.4, 132.6, 124.7, 145.1, 150.1, 151.9, 161.2, 164.4; IR (liquid film, cm$^{-1}$): $\nu$ = 3066, 2981, 1735, 1643, 1593, 1592, 1491, 1368, 1293, 1170, 1098. m. p.: 119 - 120 °C. HRMS (EI-TOF) calc. C$_{22}$H$_{19}$FN$_2$O$_2$S$_2$: 426.5269. Found: 426.0944.

(Z)-N-(5-(3-chlorophenyl)-3-tosylthiazolidin-2-ylidene)aniline

![3fa](image)

The title compound was a white solid, $^1$H-NMR (300 MHz, CDCl$_3$) δ (ppm) = 2.48 (3 H, s), 4.04 (1 H, $J = 8.1$ Hz, q), 4.58 (1 H, $J = 6.1$ Hz, q), 4.74 (1 H, $J = 6.6$ Hz, t), 6.78 (2 H, $J = 7.8$ Hz, d), 7.07 (1 H, $J = 7.2$ Hz, t), 7.30 (8 H, m), 7.96 (2 H, $J = 7.8$ Hz, d). $^{13}$C-NMR (75 MHz, CDCl$_3$) δ (ppm) = 22.5, 46.3, 56.7, 120.8, 124.5, 125.9, 127.7, 129.1, 129.3, 129.4, 130.5, 134.6, 135.0, 139.0, 145.2, 150.1. IR (liquid film, cm$^{-1}$): $\nu$ = 3061, 2927, 1735, 1643, 1592, 1491, 1368, 1293, 1170, 1098. m. p.: 125 - 127 °C. HRMS (EI-TOF) calc. C$_{22}$H$_{19}$ClN$_2$O$_2$S$_2$: 442.9815. Found: 442.0649.

(Z)-N-(5-(4-bromophenyl)-3-tosylthiazolidin-2-ylidene)aniline

![3ga](image)

The title compound was a white solid, $^1$H-NMR (300 MHz, CDCl$_3$) δ (ppm) = 2.48 (3 H, s), 4.03 (1 H, $J = 8.1$ Hz, q), 4.55 (1 H, $J = 8.8$ Hz, q), 4.72 (1 H, $J = 8.8$ Hz, t), 6.78 (2 H, $J = 7.2$ Hz, d), 7.07 (1 H, $J = 7.8$ Hz, t), 7.24 (4 H, m), 7.35 (m, $J =$
7.8 Hz, d), 7.44 (2 H, J = 7.8 Hz, d), 7.96 (2 H, J = 8.2 Hz, d); ^{13}\text{C-NMR (100 MHz, CDCl}_3) \delta (ppm) = 21.8, 46.3, 56.7, 120.8, 122.8, 124.5, 129.1, 129.2, 129.4, 132.2, 134.5, 135.9, 145.2, 150.0, 151.8. IR (liquid film, cm\(^{-1}\)): \nu = 3063, 2925, 1644, 1592, 1170, 1099, 908. m.p.: 137 - 138 °C. HRMS (El-TOF) calc. C\(_{22}\)H\(_{19}\)N\(_3\)O\(_4\)S\(_2\): 487.4325. Found: 486.0144.

\((Z)-\text{N-(5-(4-nitrophenyl)-3-tosylthiazolidin-2-ylidene)aniline}\)

\(3\text{ha}\)

The title compound was a yellow solid, \(^1\text{H-NMR (300 MHz, CDCl}_3) \delta (ppm) = 2.48 (3 H, s), 4.15 (1 H, J = 6.9 Hz, q), 4.58 (1 H, J = 6.6 Hz, q), 4.84 (1 H, J = 6.6 Hz, t), 6.78 (2 H, J = 7.2 Hz, d), 7.08 (1 H, J = 7.5 Hz, t), 7.26 (2 H, m), 7.36 (2 H, J = 7.4 Hz, d), 7.50 (2 H, J = 8.7 Hz, q), 7.68 (2 H, J = 8.1 Hz, d), 7.97 (2 H, J = 8.4 Hz, d). ^{13}\text{C-NMR (75 MHz, CDCl}_3) \delta (ppm) = 21.8, 45.8, 56.2, 120.69, 124.0, 124.3, 124.7, 127.0, 128.6, 129.2, 129.4, 129.9, 134.4, 144.8, 145.8, 145.4, 147.9, 149.8, 151.04. IR (liquid film, cm\(^{-1}\)): \nu = 2924, 1644, 1592, 1348, 1170, 1101. m.p.: 177-179 °C; HRMS (El-TOF) calc. C\(_{22}\)H\(_{19}\)N\(_3\)O\(_4\)S\(_2\): 453.5310. Found: 452.4719.

\((Z)-\text{N-(5-(4-nitrophenyl)-3-tosylthiazolidin-2-ylidene)aniline}\)

\(3\text{ia}\)

The title compound was a white solid, \(^1\text{H-NMR (400 MHz, CDCl}_3) \delta (ppm) = 2.49 (3 H, s), 4.19 (1 H, J = 6 Hz, q), 4.52 (1 H, J = 6.4 Hz, q), 5.14 (1 H, J = 1.6 Hz, t), 6.79 (2 H, J = 7.2 Hz, d), 7.05 (1 H, J = 7.2 Hz, t), 7.27 (2 H, m), 7.36 (2 H, J = 8 Hz, d), 7.42 (2 H, m), 7.56 (1 H, J = 4 Hz, d), 7.64(1 H, J = 8 Hz, d), 7.89 (2 H, J = 8.4 Hz, d). ^{13}\text{C-NMR (100 MHz, CDCl}_3) \delta (ppm) = 21.9, 41.5, 41.5, 56.8, 120.8,

((4R, 5S, Z)-5-phenyl-2-(phenylimino)-3-tosylthiazolidin-4-yl)methanol

The title compound was a light yellow oil, ¹H-NMR (300 MHz, CDCl₃) δ (ppm) = 2.48 (3 H, s), 3.76 (2 H, m), 5.03 (1 H, J = 5.1 Hz, d), 5.18 (1 H, J = 6.3 Hz, d), 6.78 (2 H, J = 7.5 Hz, d), 7.08 (1 H, J = 7.5 Hz, t), 7.28 (2 H, J = 7.8 Hz, t), 7.74 (7 H, m), 8.07 (2 H, J = 7.8 Hz, d). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) = 21.7, 51.5, 61.2, 65.9, 120.7, 124.4, 127.6, 127.8, 128.2, 128.7, 129.0, 129.2, 129.3, 129.8, 132.7, 136.1, 144.8, 149.9, 151.5; IR (liquid film, cm⁻¹) : ν = 3519, 3064, 3031, 2925, 2250, 1937, 1642, 1592, 1489, 1450, 1384, 1306, 1237, 1167, 1106, 1089, 909, 813, 764, 732, 697, 663, 596. m. p.: 177 - 178°C; HRMS (EI-TOF) calc. C₂₃H₂₂N₂O₃S₂: 438.5624. Found: 438.1144.

(Z)-N-(naphthalen-1-yl)-5-phenyl-3-tosylthiazolidin-2-imine

The title compound was a light yellow oil, ¹H-NMR (300 MHz, CDCl₃) δ (ppm) = 2.49 (3 H, s), 3.76 (2 H, m), 4.16 - 4.21 (1 H, J = 9 Hz, t), 4.68 - 4.71 (1 H, J = 9 Hz, t), 4.79 - 4.83 (1 H, J = 8 Hz, t), 6.83 (1 H, J = 6 Hz, d), 7.31 (9 H, m), 7.44 (2 H, m), 7.47 (1 H, J = 6 Hz, d), 7.55 (1 H, J = 6 Hz, d), 7.62 (1 H, J = 6 Hz, d). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) = 21.9, 47.0, 57.0, 114.9, 124.02, 124.6, 125.4, 126.3, 127.6, 127.8, 128.9, 129.2, 129.3, 129.64, 134.2, 135.6, 136.7, 144.9, 146.9,

5-phenyl-3-tosylthiazolidine-2-thione

The title compound was a light yellow oil,¹H-NMR (300 MHz, CDCl₃) δ (ppm) 2.45 (3 H, s), 3.44 (2 H, m), 4.78 (1 H, J = 6.3 Hz, t), 4.87 (1 H, J = 6 Hz, q), 7.31 (7 H, m), 7.72 (2 H, J = 6 Hz, d);¹³C-NMR (75 MHz, CDCl₃) δ (ppm) = 21.9, 48.8, 63.7, 127.5, 128.6, 128.9, 129.2, 129.4, 129.6, 129.9, 131.1. IR (liquid film, cm⁻¹): ν = 3286, 2925, 1721, 1598, 1494, 1330, 1161. HRMS (EI-TOF) calc. C₁₆H₁₅NO₂S₃: 349.4810. Found: 349.9874.

(Z)-N-(5-phenyl-3-tosylthiazolidin-2-ylidene)cyclohexanamine

The title compound was a white solid,¹H-NMR (300 MHz, CDCl₃) δ (ppm) = 1.39 (5 H, m), 1.63 (5 H, m), 2.44 (3 H, s), 2.79 (1 H, m), 3.87 (1 H, J = 9 Hz, t), 4.46 (1 H, J = 6.3 Hz, q), 4.76 (1 H, J = 6.9 Hz, t), 7.29 (7 H, m), 7.91 (2 H, J = 8.1 Hz, d);¹³C-NMR (75 MHz, CDCl₃) δ (ppm) = 21.7, 24.5, 25.7, 33.4, 33.6, 46.9, 56.1, 65.5, 127.6, 128.7, 128.9, 129.1, 129.3, 135.1, 137.2, 144.4, 147.2. IR (liquid film, cm⁻¹): ν = 2925, 1639, 1356, 1166, 1100, 661. m. p.: 177 – 178 °C. HRMS (EI-TOF) calc. C₂₂H₂₆N₂O₂S₂: 414.5840. Found: 414.1508.

(Z)-N-phenyl-3-tosylhexahydrobenzo[d]thiazol-2(3H)-imine
The title compound was a white solid, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 1.50 (4H, m), 1.74 (1H, m), 1.84 (1H, m), 2.02 (2H, m), 2.46 (3H, s), 3.18 (1H, m), 3.64 (1H, m), 6.56 (2H, $J = 8.4$ Hz, q), 7.05 (1 H, m), 7.23 (3 H, m), 7.32 (2 H, $J = 8$ Hz, d), 7.90 (2 H, $J = 7.2$ Hz, d); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 21.8, 24.6, 25.4, 29.6, 29.8, 32.9, 49.3, 70.7, 120.7, 124.4, 129.0, 129.1, 129.3, 135.5, 144.6, 150.2, 154.9. IR (liquid film, cm$^{-1}$): $\nu$ = 2939, 2862, 1639, 1594, 1320, 1156, 1090, 964, 667, 574. m. p.: 126-128 $^\circ$C. HRMS (EI-TOF) calc. C$_{20}$H$_{22}$N$_2$O$_2$S$_2$: 386.5309. Found: 386.1195.

The title compound was a light yellow oil, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 1.25 (5 H, m), 1.53 (2 H, m), 1.61 (2 H, $J = 6.8$ Hz, d), 2.04 (1 H, $J = 4.8$ Hz, d), 2.42 (1 H, s), 2.49 (3 H, s), 3.38 (1 H, m), 4.82 (1 H, $J = 4.8$ Hz, d), 4.88 (1 H, $J = 4.8$ Hz, d), 7.35 (2 H, $J = 8$ Hz, d), 7.69 (2 H, $J = 8$ Hz, d); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 21.7, 23.5, 24.1, 24.5, 28.1, 29.3, 29.7, 29.8, 63.9, 81.2, 83.9, 128.1, 130.0, 132.9, 144.2. IR (liquid film, cm$^{-1}$): $\nu$ = 2939, 2870, 1724, 1598, 1448, 1347, 1165, 983, 669. HRMS (EI-TOF) calc. C$_{14}$H$_{17}$NO$_2$S$_3$: 392.5785. Found: 392.1437.

(Z)-N-cyclohexyl-3-tosylhexahydrobenzo[d]thiazol-2(3H)-imine

$^{3}$ka

$^{3}$kb

$^{3}$kc
The title compound was a light yellow oil, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 1.19 (4 H, m), 1.24 (2 H, m), 1.39 (2 H, m), 1.48 (1 H, m), 1.52 (2 H, m), 1.64 (4 H, m), 1.89 (2 H, $J$ = 5.2 Hz, q), 2.41 (3 H, s), 2.75 (1 H, m), 3.14 (1 H, m), 3.19 (1 H, m), 3.49 (1 H, m), 7.26 (2 H, $J$ = 8 Hz, d), 7.83 (2 H, $J$ = 8 Hz, d); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 21.7, 24.5, 24.6, 24.7, 25.7, 29.9, 32.8, 33.3, 49.0, 65.4, 69.6, 128.9, 129.1, 136.0, 143.9, 149.5. IR (liquid film, cm$^{-1}$): v = 2930, 2855, 1649, 1448, 1362, 1170, 1085. m. p.: 113 - 115$^\circ$C. HRMS (EI-TOF) calc. C$_{20}$H$_{28}$N$_2$O$_2$S$_2$: 392.5785. Found: 392.1661.

The spectral data of all products

3aa
3da
3ha
3ab
3kc