Electronic Supplementary Information for:

**NFSI-participated Intermolecular Aminoazidation of Alkene through Iron Catalysis**

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General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, J&K Chemicals, Adamas-beta, Accela ChemBio and Aladdin Chemicals. FeCl$_2$ was purchased from Alfa-Aesar (99.99% purity, ultra dry, CAS No. 7758-94-3). TMSN$_3$ was purchased from TCI (>95%, CAS No. 4648-54-8). N-Fluorobenzenesulfonimide (NFSI) (98% purity, CAS No. 133745-75-2) and 2,2''-bipyridine (98% purity, CAS No. 366-18-7) were purchased from Accela ChemBio. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Products were purified by flash chromatography on silica gel using petroleum ether, ethyl acetate and dichloromethane as the eluents. $^1$H-NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced with TMS in CDCl$_3$ (0 ppm). $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). High resolution mass spectra were obtained from an Agilent 6520B Q-TOF mass spectrometer with electron spray ionization (ESI) as the ion source.
To a reaction tube charged with FeCl₂ (6.3 mg, 0.05 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of styrene (1a, 57.5 μL, 0.5 mmol), TMSN₃ (98.6 μL, 0.75 mmol) in DCE (2 mL) via a syringe under N₂ (1 atm). The reaction mixture was stirred at 100 °C for indicated time in Table S1. After rapidly cooled by ice, the mixture was diluted with ethyl acetate, filtered through a celite pad, and concentrated in vacuo. The residue was analyzed with ¹H-NMR to determine the yields of 2a through iron-catalysis, using CH₂Br₂ as an internal standard. Similarly, the yields of 2a via copper-catalysis, using the same copper catalyst employed by Zhang and Studer,[1] were determined in the same way. Then the yields of 2a via iron- or copper-catalysis in different times were summarized in Table S1 and Figure S1, accordingly.

Table S1. Detailed Results of Kinetic Studies.

<table>
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<tr>
<th>Time (min)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>180</th>
<th>300</th>
<th>420</th>
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<tr>
<td>FeCl₂</td>
<td>39.8</td>
<td>53.0</td>
<td>64.1</td>
<td>72.7</td>
<td>78.0</td>
<td>82.5</td>
<td>89.8</td>
<td>87.2</td>
<td>85.6</td>
</tr>
<tr>
<td>CuCl</td>
<td>9.7</td>
<td>13.7</td>
<td>15.4</td>
<td>16.3</td>
<td>15.8</td>
<td>14.6</td>
<td>13.6</td>
<td>11.8</td>
<td>9.6</td>
</tr>
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Figure S1. Detailed Results of Kinetic Studies.
From the data in Table S1 and Figure S1, this aminoazidation catalyzed by FeCl$_2$ is remarkably faster than catalyzed by CuCl, which was previously employed by Zhang and Studer$^{[1]}$ while the yields of 2a remained very low, no matter how much the reaction time was, when the reaction was catalyzed by CuCl. These results demonstrated that the iron catalyst, which could achieve this reaction rapidly without any ligand or additive and provide the product in excellent yield after 3 hours, is a competitive alternative to previously used copper catalyst, which could not effectively realize this reaction in absence of certain ligands.$^{[1]}$
Experimental Procedure and Characterization Data

Typical Procedure: To a reaction tube charged with FeCl₂ (6.3 mg, 0.05 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of alkene (1a-u, 0.5 mmol), TMSN₃ (98.6 μL, 0.75 mmol) in DCE (2 mL) via a syringe under N₂ (1 atm). The reaction mixture was stirred at 100 °C for 3 hours. After rapidly cooling by ice, the mixture was diluted with ethyl acetate, filtered through a celite pad, and concentrated in vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silical gel to afford aminoazidated product 2a-u.

N-(2-Azido-2-phenylethyl)-N-(phenylsulfonyl)benzenesulfonamide[H] (2a):

The reaction of 0.5 mmol of styrene (1a) with NFSI and TMSN₃ afforded 187.2 mg of 2a (85%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.07-8.05 (m, 4H), 7.67-7.63 (m, 2H), 7.56-7.52 (m, 4H), 7.40-7.35 (m, 5H), 5.01 (dd, J = 9.6 Hz, 4.2 Hz, 1H), 4.06 (dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.72 (dd, J = 15.6 Hz, 4.2 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 139.22, 136.44, 134.02, 129.12, 129.02, 128.98, 128.57, 127.19, 65.57, 53.18 ppm. HRMS m/z (ESI) calcd for [C₂₀H₁₈N₄O₄S₂Na]⁺ 465.0662, found 465.0669.

N-(2-Azido-2-(p-tolyl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide[H] (2b):

The reaction of 0.5 mmol of p-methylstyrne (1b) with NFSI and TMSN₃ afforded 178.1 mg of 2b (78%) as white solid (m.p. 133.4-134.8 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.06-8.04 (m, 4H), 7.66-7.62 (m, 2H), 7.55-7.52 (m, 4H), 7.25 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 4.98 (dd, J = 9.6 Hz, 4.3 Hz, 1H), 4.05 (dd, J = 15.6 Hz, 9.6 Hz, 1H), 3.70 (dd, J = 15.6 Hz, 4.3 Hz, 1H), 2.36 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 139.20, 138.95, 133.98, 133.32, 129.75, 128.94, 128.56, 127.15, 65.32, 53.09, 21.16 ppm. HRMS m/z (ESI) calcd for [C₂₁H₂₀N₂O₄S₂Na]⁺ 479.0818,
N-(2-Azido-2-(4-(tert-butyl)phenyl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide\textsuperscript{11} (2c):

The reaction of 0.5 mmol of p-tert-butylstyrene (1c) with NFSI and TMSN\textsubscript{3} afforded 199.4 mg of 2c (80%) as light yellow oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 8.08-8.06\) (m, 4H), 7.65-7.62 (m, 2H), 7.55-7.51 (m, 4H), 7.42 (d, \(J = 8.3\) Hz, 2H), 7.29 (d, \(J = 8.3\) Hz, 2H), 4.98 (dd, \(J = 9.8\) Hz, 3.9 Hz, 1H), 4.08 (dd, \(J = 15.6\) Hz, 9.8 Hz, 1H), 3.71 (dd, \(J = 15.6\) Hz, 3.9 Hz, 1H), 1.32 (s, 9H) ppm; \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta = 152.08\). 139.25. 133.97, 133.36, 128.93, 128.54, 126.84, 125.96, 65.30, 53.11, 34.61, 31.21 ppm. HRMS m/z (ESI) calcd for [C\textsubscript{2}dH\textsubscript{20}N\textsubscript{4}O\textsubscript{2}S\textsubscript{2}+Na]\textsuperscript{+} 521.1293, found 521.1290; calcd for [C\textsubscript{2}dH\textsubscript{20}N\textsubscript{4}O\textsubscript{2}S\textsubscript{2}+K]\textsuperscript{+} 537.1027, found 537.1030.

4-(1-Azido-2-(N-(phenylsulfonyl)phenylsulfonamido)ethyl)phenyl acetate\textsuperscript{11} (2d):

The reaction of 0.5 mmol of 4-vinylphenyl acetate (1d) with NFSI and TMSN\textsubscript{3} afforded 184.3 mg of 2d (74%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (12:1 to 8:1, v/v) as the eluent. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 8.06-8.04\) (m, 4H), 7.66-7.62 (m, 2H), 7.56-7.52 (m, 4H), 7.37 (d, \(J = 8.6\) Hz, 2H), 7.12 (d, \(J = 8.6\) Hz, 2H), 5.02 (dd, \(J = 9.5\) Hz, 4.2 Hz, 1H), 4.03 (dd, \(J = 15.6\) Hz, 9.5 Hz, 1H), 3.72 (dd, \(J = 15.6\) Hz, 4.2 Hz, 1H), 2.29 (s, 3H) ppm; \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta = 169.12, 150.97, 139.02, 134.00, 133.91, 128.95, 128.47, 128.25, 122.26, 64.99, 53.02, 20.97 ppm. HRMS m/z (ESI) calcd for [C\textsubscript{2}dH\textsubscript{20}N\textsubscript{4}O\textsubscript{6}S\textsubscript{2}+Na]\textsuperscript{+} 523.0716, found 523.0720.

N-(2-Azido-2-(4-fluorophenyl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide\textsuperscript{11} (2e):

The reaction of 0.5 mmol of p-fluorostyrene (1e) with NFSI and TMSN\textsubscript{3} afforded 185.3 mg of 2e (81%) as white solid (m.p. 104.7-105.9 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 8.06-8.03\) (m, 4H), 7.67-7.63 (m, 2H), 7.56-7.52 (m, 4H), 7.34-7.31 (m, 2H), 7.09-7.04 (m, 2H), 5.01 (dd, \(J = 9.3\) Hz, 4.5 Hz, 1H), 4.02 (dd, \(J = 15.6\) Hz, 9.3 Hz, 1H), 3.71 (dd, \(J = 15.6\) Hz, 4.5 Hz, 1H) ppm; \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta = 162.91\). 139.12, 134.06, 132.27 (d, \(J = 3.0\) Hz), 129.06, 128.99, 128.51, 116.09 (d, \(J = 21.4\) Hz), 64.86, 53.16 ppm. HRMS m/z (ESI) calcd for [C\textsubscript{2}dH\textsubscript{17}F\textsubscript{4}N\textsubscript{4}O\textsubscript{6}S\textsubscript{2}+Na]\textsuperscript{+} 587.0316, found 587.0318.
483.0567, found 483.0569.

**N-(2-Azido-2-(3-fluorophenyl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide**

The reaction of 0.5 mmol of m-fluorostyrene (1e) with NFSI and TMSN₃ afforded 190.2 mg of 2f (83%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 12:1, v/v) as the eluent. **¹H NMR (CDCl₃, 400 MHz):** δ = 8.07-8.05 (m, 4H), 7.66-7.63 (m, 2H), 7.56-7.52 (m, 4H), 7.38-7.32 (m, 1H), 7.14-7.13 (m, 1H), 7.07-7.02 (m, 2H), 5.01 (dd, J = 9.5 Hz, 4.2 Hz, 1H), 4.04 (dd, J = 15.6 Hz, 9.5 Hz, 1H), 3.71 (dd, J = 15.6 Hz, 4.2 Hz, 1H) ppm; **¹³C NMR (CDCl₃, 100 MHz):** δ = 162.95 (d, J = 246.5 Hz), 139.08, 138.95 (d, J = 7.1 Hz), 134.04, 130.74 (d, J = 8.1 Hz), 129.00, 128.48, 122.74 (d, J = 2.9 Hz), 115.95 (d, J = 21.0 Hz), 114.13 (d, J = 22.1 Hz), 112.70 ppm (J = 15.6 Hz, 9.5 Hz, 1H), 65.02 (d, J = 1.2 Hz), 53.16 ppm. **HRMS m/z (ESI) calcd for [C₂₀H₁₇FN₄O₄S₂+Na⁺]** 483.0567, found 483.0570.

**N-(2-Azido-2-(4-chlorophenyl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide**

The reaction of 0.5 mmol of p-chlorostyrene (1g) with NFSI and TMSN₃ afforded 188.0 mg of 2g (79%) as white solid (m.p. 144.8-146.0 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. **¹H NMR (CDCl₃, 400 MHz):** δ = 8.04-8.01 (m, 4H), 7.66-7.62 (m, 2H), 7.55-7.51 (m, 4H), 7.34 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 5.01 (dd, J = 9.1 Hz, 4.8 Hz, 1H), 3.99 (dd, J = 15.6 Hz, 9.1 Hz, 1H), 3.73 (dd, J = 15.6 Hz, 4.8 Hz, 1H) ppm; **¹³C NMR (CDCl₃, 100 MHz):** δ = 138.99, 134.89, 134.86, 134.84, 129.26, 128.97, 128.58, 128.45, 64.83, 52.98 ppm. **HRMS m/z (ESI) calcd for [C₂₀H₁₅ClN₄O₄S₂+K⁺]** 499.0278, found 499.0278, calcd for [C₂₀H₁₅ClN₄O₄S₂+Na⁺]** 515.0011, found 515.0017.

**N-(2-Azido-2-(3-chlorophenyl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide (2h):**

The reaction of 0.5 mmol of m-chlorostyrene (1h) with NFSI and TMSN₃ afforded 177.9 mg of 2h (75%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. **¹H NMR (CDCl₃, 400 MHz):** δ = 8.07-8.05 (m, 4H), 7.67-7.63 (m, 2H), 7.56-7.52 (m, 4H), 7.33-7.31 (m, 3H), 7.25-7.23 (m, 1H), 4.99 (dd, J = 9.4 Hz, 4.3 Hz, 1H), 4.03 (dd, J = 15.6 Hz, 9.4 Hz, 1H), 3.71 (dd, J = 15.6 Hz, 4.3 Hz, 1H) ppm; **¹³C NMR (CDCl₃, 100 MHz):** δ = 139.06, 138.51, 134.96, 134.08, 130.39, 129.16, 129.00, 128.48, 127.29, 125.25, 64.99, 53.14 ppm. **HRMS**
**m/z (ESI) calcld for [C_{20}H_{17}ClN_{3}O_{3}S_{2}+Na]^+ 499.0272, found 499.0278.**

*N-(2-Azido-2-(2-chlorophenyl)ethyl)-N-(phenylsulfonfyl)benzenesulfonamide (2i):*  

The reaction of 0.5 mmol of 2-chlorostyrene (1i) with NFSI and TMSN₃ afforded 189.4 mg of 2i (80%) as white solid (m.p. 133.1-134.5 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.15-8.14 (m, 4H), 7.69-7.65 (m, 2H), 7.59-7.55 (m, 4H), 7.52-7.49 (m, 1H), 7.40-7.27 (m, 3H), 5.51 (dd, J = 10.5 Hz, 3.8 Hz, 1H), 4.05 (dd, J = 15.6 Hz, 10.5 Hz, 1H), 3.69 (dd, J = 15.6 Hz, 3.8 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 139.17, 134.54, 134.06, 132.92, 130.03, 129.96, 129.02, 128.65, 128.33, 127.70, 61.82, 51.57 ppm. HRMS m/z (ESI) calcld for [C_{20}H_{17}ClN_{3}O_{3}S_{2}+Na]^+ 499.0272, found 499.0276.

*N-(2-Azido-2-(4-bromophenyl)ethyl)-N-(phenylsulfonfyl)benzenesulfonamide (2j):*  

The reaction of 0.5 mmol of p-bromostyrene (1j) with NFSI and TMSN₃ afforded 214.5 mg of 2j (83%) as white solid (m.p. 122.1-123.7 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.03-8.01 (m, 4H), 7.67-7.63 (m, 2H), 7.56-7.49 (m, 6H), 7.22 (d, J = 8.4 Hz, 2H), 5.00 (dd, J = 9.0 Hz, 4.8 Hz, 1H), 3.98 (dd, J = 15.6 Hz, 9.0 Hz, 1H), 3.73 (dd, J = 15.6 Hz, 4.8 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 139.01, 135.46, 134.08, 132.27, 129.01, 128.92, 128.51, 123.10, 64.95, 52.93 ppm. HRMS m/z (ESI) calcld for [C_{20}H_{17}BrN_{3}O_{3}S_{2}+Na]^+ 542.9767, found 542.9776.

*N-(2-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)-N-(phenylsulfonfyl)benzenesulfonamide (2k):*  

The reaction of 0.5 mmol of 4-vinyl-1,1'-biphenyl (1k) with NFSI and TMSN₃ afforded 153.9 mg of 2k (60%) as light yellow solid (m.p. 132.0-133.7 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.07-8.05 (m, 4H), 7.65-7.58 (m, 6H), 7.54-7.50 (m, 4H), 7.47-7.35 (m, 5H), 5.07 (dd, J = 9.4 Hz, 4.5 Hz, 1H), 4.08 (dd, J = 15.6 Hz, 9.4 Hz, 1H), 3.79 (dd, J = 15.6 Hz, 4.5 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 141.95, 140.15, 139.17, 135.31, 134.01, 128.97, 128.87, 128.56, 127.75, 127.71, 127.67, 127.03, 65.32, 53.06 ppm. HRMS m/z (ESI) calcld for [C_{26}H_{22}N_{4}O_{4}S_{2}+Na]^+ 541.0975, found 541.0977.
**N-(2-Azido-2-(naphthalen-2-yl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide**

The reaction of 0.5 mmol of 2-vinylnaphthalene (1I) with NFSI and TMSN₃ afforded 105.1 mg of 2I (43%) as light yellow solid (m.p. 125.2-126.8 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, 1/1) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.01-7.99 (m, 4H), 7.90-7.79 (m, 4H), 7.60-7.42 (m, 9H), 5.21 (dd, J = 8.8 Hz, 5.0 Hz, 1H), 4.10 (dd, J = 15.6 Hz, 8.8 Hz, 1H), 3.88 (dd, J = 15.6 Hz, 5.0 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 139.03, 133.96, 133.65, 133.42, 133.11, 129.18, 128.09, 127.74, 127.12, 126.73, 126.66, 124.22, 65.73, 52.94 ppm. HRMS m/z (ESI) calcd for [C₈H₈N₂O₃S₂+Na]⁺ 515.0818, found 515.0825; calcd for [C₈H₈N₂O₃S₂+K]⁺ 531.0563, found 531.0566.

**N-(2-Azido-2-phenylpropyl)-N-(phenylsulfonyl)benzenesulfonamide**

The reaction of 0.5 mmol of prop-1-en-2-ylbenzene (1m) with NFSI and TMSN₃ afforded 144.8 mg of 2m (64%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, 1/1) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.11-8.09 (m, 4H), 7.65-7.61 (m, 2H), 7.57-7.53 (m, 4H), 7.44-7.30 (m, 5H), 4.17 (d, J = 15.8 Hz, 1H), 3.99 (d, J = 15.8 Hz, 1H), 1.67 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 141.43, 140.58, 133.73, 128.90, 128.85, 128.43, 128.27, 125.82, 66.92, 58.85, 21.54 ppm. HRMS m/z (ESI) calcd for [C₂₁H₂₀N₄O₃S₂+Na]⁺ 479.0818, found 479.0823.

**N-(1-Azido-1-phenylpropan-2-yl)-N-(phenylsulfonyl)benzenesulfonamide**

The reaction of 0.5 mmol of (E)-prop-1-en-1-ylbenzene (1n) with NFSI and TMSN₃ afforded 173.6 mg of 2n (76%, dr > 94:6) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, 1/1) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 7.64-7.61 (m, 4H), 7.57-7.53 (m, 2H), 7.40-7.24 (m, 9H), 5.21 (d, J = 9.7 Hz, 1H), 4.37 (dq, J = 9.7 Hz, 6.7 Hz, 1H), 1.51 (d, J = 6.8, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 135.87, 133.69, 129.13, 128.81, 128.73, 128.67, 128.41, 127.56, 69.71, 61.48, 17.94 ppm. HRMS m/z (ESI) calcd for [C₂₁H₂₀N₄O₃S₂+Na]⁺ 479.0818, found 479.0818; calcd for [C₂₁H₂₀N₄O₃S₂+K]⁺ 495.0558, found 495.0559.

**N-(1-Azido-1,2,3,4-tetrahydronaphthalen-2-yl)-N-(phenylsulfonyl)benzenesulfonamide**

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The reaction of 0.5 mmol of 1,2-dihyronaphthalene (1o) with NFSI and TMSN₃ afforded 85.6 mg of 2o (37%, dr > 97:3) as light yellow oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. \( ^1 \)H NMR (CDCl₃, 400 MHz): \( \delta = 8.14-8.12 \) (m, 4H), 7.70-7.66 (m, 2H), 7.60-7.56 (m, 4H), 7.41 (d, \( J = 7.5 \) Hz, 1H), 7.27-7.20 (m, 2H), 7.08 (d, \( J = 7.2 \) Hz, 1H), 5.38 (d, \( J = 10.0 \) Hz, 1H), 4.36-4.29 (m, 1H), 2.82-2.78 (m, 2H), 2.63-2.52 (m, 1H), 1.89-1.83 (m, 1H) ppm; \( ^{13} \)C NMR (CDCl₃, 100 MHz): \( \delta = 135.66, 134.08, 134.00, 129.02, 128.69, 128.56, 128.04, 127.94, 126.83, 64.97, 62.78, 29.99, 28.44 \) ppm. HRMS m/z (ESI) calcd for \([C_{22}H_{24}N_{6}O_{5}S_{2}+Na]^+\) 491.0818, found 491.0826.

**N-(2-Azido-2-cyclohexylethyl)-N-(phenylsulfonfyl)benzenesulfonamide (2p):**

In presence of 2,2'-bipyridine (3.9 mg, 0.025 mmol), the reaction of 0.5 mmol of vinyl cyclohexane (1p) with NFSI and TMSN₃ at 80°C for 6 hours afforded 104.2 mg of 2p (47%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. \( ^1 \)H NMR (CDCl₃, 400 MHz): \( \delta = 8.12-8.09 \) (m, 4H), 7.68-7.65 (m, 2H), 7.59-7.55 (m, 4H), 3.89 (dd, \( J = 15.8 \) Hz, 10.5 Hz, 1H), 3.65-3.61 (m, 2H), 1.77-1.75 (m, 3H), 1.67-1.64 (m, 2H), 1.51-1.43 (m, 1H), 1.26-1.12 (m, 5H) ppm; \( ^{13} \)C NMR (CDCl₃, 100 MHz): \( \delta = 139.33, 133.97, 129.04, 128.40, 67.49, 50.80, 41.10, 29.80, 28.03, 26.00, 25.90, 25.73 \) ppm. HRMS m/z (ESI) calcd for \([C_{20}H_{24}N_{6}O_{5}S_{2}+K]^+\) 487.0871, found 487.0880.

**N-(2-Azidooctyl)-N-(phenylsulfonfyl)benzenesulfonamide (2q):**

In presence of 2,2'-bipyridine (3.9 mg, 0.025 mmol), the reaction of 0.5 mmol of 1-octene (1q) with NFSI and TMSN₃ at 80°C afforded 116.0 mg of 2q (52%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. \( ^1 \)H NMR (CDCl₃, 400 MHz): \( \delta = 8.10-8.08 \) (m, 4H), 7.68-7.64 (m, 2H), 7.58-7.55 (m, 4H), 3.86 (dd, \( J = 15.1 \) Hz, 9.2 Hz, 1H), 3.75-3.69 (m, 1H), 3.57 (dd, \( J = 15.1 \) Hz, 3.9 Hz, 1H), 1.50-1.42 (m, 2H), 1.32-1.23 (m, 8H), 0.89 (t, \( J = 6.9 \) Hz, 3H) ppm; \( ^{13} \)C NMR (CDCl₃, 100 MHz): \( \delta = 139.40, 134.01, 129.06, 128.41, 62.00, 52.15, 32.29, 31.52, 28.86, 25.80, 22.47, 13.99 \) ppm. HRMS m/z (ESI) calcd for \([C_{20}H_{24}N_{6}O_{5}S_{2}+Na]^+\) 473.1288, found 473.1298.

**N-(2-Azidodecyl)-N-(phenylsulfonfyl)benzenesulfonamide (2r):**
In presence of 2,2′-bipyridine (3.9 mg, 0.025 mmol), the reaction of 0.5 mmol of 1-decene (1r) with NFSI and TMSN₃ at 80°C afforded 94.3 mg of 2r (40%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.10-8.08 (m, 4H), 7.68-7.64 (m, 2H), 7.58-7.54 (m, 4H), 3.86 (dd, J = 15.1 Hz, 9.3 Hz, 1H), 3.75-3.69 (m, 1H), 3.56 (dd, J = 15.1 Hz, 3.9 Hz, 1H), 1.50-1.43 (m, 2H), 1.32-1.26 (m, 12H), 0.89 (t, J = 6.9 Hz, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 139.31, 133.99, 129.02, 128.35, 61.96, 52.09, 32.23, 31.71, 29.25, 29.15, 25.79, 22.56, 14.03 ppm. HRMS m/z (ESI) calcd for [C₂₂H₃₃N₅O₅S₂+Na]⁺ 501.1606, found 501.1607; calcd for [C₂₂H₃₃N₅O₅S₂+Na]⁺ 501.1601, found 501.1607.

N-(2-Azido-2-(1,3-dioxoisooindolin-2-yl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide (2s):

In presence of 2,2′-bipyridine (3.9 mg, 0.025 mmol), the reaction of 0.5 mmol of N-vinylphthalimide (1s) with NFSI and TMSN₃ at 80°C afforded 172.5 mg of 2s (68%) as white solid (m.p. 177.3-178.6 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 3:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.05-8.03 (m, 4H), 7.90-7.88 (m, 2H), 7.77-7.75 (m, 2H), 7.67-7.63 (m, 2H), 7.57-7.53 (m, 4H), 6.04 (dd, J = 7.3 Hz, 4.9 Hz, 1H), 4.42-4.30 (m, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 166.97, 138.34, 134.60, 134.29, 131.35, 129.14, 128.62, 123.91, 65.30, 47.32 ppm. HRMS m/z (ESI) calcd for [C₂₂H₁₇N₅O₅S₂+K]⁺ 550.0252, found 550.0258.

N-(2-Azido-2-butoxyethyl)-N-(phenylsulfonyl)benzenesulfonamide (2t):

In presence of 2,2′-bipyridine (3.9 mg, 0.025 mmol), the reaction of 0.5 mmol of 1-(vinyloxy)butane (1t) with NFSI and TMSN₃ at 80°C for 6 hours afforded 111.2 mg of 2t (51%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.11-8.09 (m, 4H), 7.69-7.65 (m, 2H), 7.59-7.55 (m, 4H), 4.81 (t, J = 6.0 Hz, 1H), 3.93 (dd, J = 15.7 Hz, 6.1 Hz, 1H), 3.80 (dd, J = 15.7 Hz, 5.8 Hz, 1H), 3.67 (dt, J = 9.5 Hz, 6.9 Hz, 1H), 3.40 (dt, J = 9.5 Hz, 6.6 Hz, 1H), 1.50-1.43 (m, 2H), 1.34-1.26 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 139.17, 134.03, 128.97, 128.55, 90.33, 69.82, 50.54, 31.19, 19.00, 13.73 ppm. HRMS m/z (ESI) calcd for [C₁₈H₂₃N₅O₅S₂+Na]⁺ 461.0924, found 461.0930.

1-Azido-2-(N-(phenylsulfonyl)phenylsulfonamido)ethyl benzoate (2u):
In presence of 2,2’-bipyridine (3.9 mg, 0.025 mmol), the reaction of 0.5 mmol of vinyl benzoate (1u) with NFSI and TMSN₃ at 80°C for 6 hours afforded 142.3 mg of 2u (59%) as colorless oil, after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 8.06-8.02 (m, 6H), 7.62-7.58 (m, 3H), 7.50-7.43 (m, 6H), 6.42 (t, J = 6.3 Hz, 1H), 3.80 (dq, J = 15.5 Hz, 6.3 Hz, 2H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 165.66, 139.11, 134.14, 133.87, 130.09, 129.13, 128.52, 128.35, 128.24, 83.39, 49.56 ppm. HRMS m/z (ESI) calcd for [C₂₁H₁₈N₄O₆S₂+K]⁺ 525.0299, found 525.0309.
Control Experiments

1) TEMPO-suppressed Control Experiment

Typical Procedure: To a reaction tube charged with FeCl₂ (6.3 mg, 0.05 mmol), NFSI (236.5 mg, 0.75 mmol) and TEMPO (156.3 mg, 1 mmol) was added a solution of styrene (1a, 57.5 μL, 0.5 mmol), TMSN₃ (98.6 μL, 0.75 mmol) in DCE (2 mL) via a syringe under N₂ (1 atm). The reaction mixture was stirred at 100 °C for 3 hours. After rapidly cooling by ice, the mixture was diluted with ethyl acetate, filtered through a celite pad, and concentrated in vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silical gel to afford aminoazidated product 2a (15.1 mg, 7%) and TEMPO-captured product 4a (43.4 mg, 16%).

N-(2-Phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-N-(phenylsulfonyl)benzenesulfonamide (4a):

The reaction of 0.5 mmol of styrene (1a) under standard conditions, adding 1 mmol of TEMPO afforded 43.4 mg of 4a (16%) as white solid (m.p. 132.3-133.7 °C), after flash chromatography on silica gel using petroleum ether and ethyl acetate (20:1 to 15:1, v/v) as the eluent. ¹H NMR (CDCl₃, 400 MHz): δ = 7.60-7.56 (m, 6H), 7.43-7.39 (m, 4H), 7.36-7.30 (m, 5H), 5.23 (dd, J = 11.0 Hz, 4.7 Hz, 1H), 4.39 (dd, J = 14.9 Hz, 11.0 Hz, 1H), 4.03 (dd, J = 14.9 Hz, 4.7 Hz, 1H), 1.51-1.39 (m, 5H), 1.27-1.24 (m, 4H), 1.11-0.97 (m, 6H), 0.88-0.70 (m, 3H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 139.90, 138.49, 133.58, 129.28, 128.62, 128.12, 127.83, 84.10, 59.95, 50.09, 40.50, 34.90, 34.23, 20.22, 17.11 ppm. HRMS m/z (ESI) calcd for [C₂₀H₂₈N₅O₅S₂⁺]⁺ 557.2138, found 557.2144.

2) Competition Experiment between Electron-rich/-deficient Styrenes
To a reaction tube charged with FeCl₂ (6.3 mg, 0.05 mmol) and NFSI (126.1 mg, 0.4 mmol) was added a solution of p-methylstyrene (1b, 32.9 μL, 0.25 mmol), p-fluorostyrene (1e, 29.8 μL, 0.25 mmol), TMSN₃ (52.6 μL, 0.4 mmol) in DCE (2 mL) via a syringe under N₂ (1 atm). The reaction mixture was stirred at 100 °C for 3 hours. After rapidly cooling by ice, the mixture was diluted with ethyl acetate, filtered through a celite pad, and concentrated in vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1, v/v) on silical gel to afford 116.0 mg of the combined methyl- and fluoro-aminoazidated product 2b and 2e. The average ratio of 2b/2e was determined by ¹H-NMR as 1 : 0.35, as shown in Figure S2. Herein, this competition reaction afforded 0.188 mmol of 2b and 0.066 mmol of 2e.

![Figure S2. ¹H-NMR of the competition experiment between styrenes 1b and 1e.](image)

3) C-H Amination of 1,1-disubstituted Alkenes with NFSI

![3H2.png](image)

**Typical Procedure:** To a reaction tube charged with FeCl₂ (6.3 mg, 0.05 mmol) and NFSI (236.5 mg, 0.75 mmol) was added a solution of 1,1-diphenylethylene (1v, 88.3 μL, 0.5 mmol) and TMSN₃ (98.6 μL, 0.75 mmol, or 0 μL, 0 mmol) in DCE (2 mL) via a syringe under N₂ (1 atm). The reaction mixture was stirred at
100 °C for 3 hours. After rapidly cooling by ice, the mixture was diluted with ethyl acetate, filtered through a celite pad, and concentrated in vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (15:1, v/v) as the eluent on silica gel to afford C-H aminated product 3v (117.8 mg, 50% with TMSN₃, or 128.2 mg, 50% without TMSN₃) as white solid (m.p. 170.5-171.9 °C).

_N-(2,2-Diphenylvinyl)-N-(phenylsulfonyl)benzenesulfonamide (3v):

¹H NMR (CDCl₃, 400 MHz): δ = 7.71-7.69 (m, 4H), 7.58-7.55 (m, 2H), 7.41-7.36 (m, 4H), 7.34-7.20 (m, 10H), 6.13 (s, 1H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 152.25, 139.82, 138.63, 136.73, 133.78, 129.87, 129.07, 128.76, 128.69, 128.64, 128.35, 128.23, 128.13, 116.26 ppm. HRMS m/z (ESI) calcd for [C₉₈H₂₁NO₄S₂+Na⁺] 498.0810, found 498.0818.
References

$\text{Cl} - \text{N} = \text{N(}$\text{SO}_2\text{Ph)}_2$

$2h$
$\text{N}_2$

$\text{Ni(SO}_3\text{Ph)}_2$

$2n$

(dr > 94.6)
N3 \cdot \text{Ni(SO}_2\text{Ph}_2\text{)}

(\text{dr} > 97.3)
\[ \text{N}^2 \text{N(SO}_2\text{Ph)}_2 \]

(dr > 97:3)
\[
\text{\textbf{N}}_3 \quad \text{\textbf{N}}(\text{SO}_2\text{Ph})_2
\]

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**Bruker**

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**PROCEDURE:** 1  
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**PREPARED:** 5 mm PAMPO BR/  
**POLYPMO:** 1  
**DILUTION:** 1  
**SOLVENT:** CDCl3  
**NS:** 12  
**DF:** 0  
**DHW:** 8012.820 Hz  
**FTRES:** 0.122266 Hz  
**AQ:** 60894966 sec  
**AC:** 24.4  
**DR:** 42.400 ussec  
**DE:** 4.55 ussec  
**TE:** 380.0 ussec  
**DI:** 100000000 sec  
**TDC:** 1  

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**CHANNEL 1**

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\[
\text{2r}
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**NMR Spectroscopy Parameters**
- **Name:** 2017-11-21 leikuwea-162
- **Date:** 20171121
- **Time:** 11.17 h
- **Instrument:** Bruker
- **Sample Name:** 2116098_0001
- **Solute:** TCO
- **Solvent:** CDCl3
- **Sample:** 256 mg
- **PPM:** 240.38 Hz
- **FTOADS:** 0.7350 Hz
- **A0:** 1.3451 Hz
- **D0:** 20.000 Hz
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- **P1:** 10.00 Hz
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- **FWHM:** 0 Hz
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