Electronic Supplementary Information (ESI) for:

Efficient Metal-free Aminoiiodination of Alkene with N-fluorobenzenesulfonimide under Mild Conditions

Bowen Lei,† Qi Miao,† Lifang Ma,† Ruoqi Fu,† Fangrong Hu,† Ni Ni,† and Ziyuan Li*,†

† Department of Pharmaceutical and Biological Engineering, School of Chemical Engineering, Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu 610065, China

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General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, TCI, Acros, J&K Chemicals and Adamas-beta. NaI (99% purity, CAS No. 7681-82-5), NFSI (98% purity, CAS No. 133745-75-2) and TEMPO (98% purity, CAS No. 2564-83-2) was purchased from Adamas-beta. 1,4-Dioxane (99%, ACS grade, CAS No. 123-91-1) were purchased from J&K Chemicals. 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.
Experimental Procedure and Characterization Data

1) Method A: Transition-metal and additive-free aminoiodination with NaI and NFSI at 40 °C

Typical Procedure: To a reaction tube charged with NaI (150 mg, 1 mmol) and NFSI (315 mg, 1 mmol) was added a solution of alkene (1, 0.5 mmol) in 1,4-dioxane (2 mL) via a syringe. The reaction mixture was stirred at 40 °C in air for 6 hours. After rapidly cooling by ice, the mixture was diluted with ethyl acetate, 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 aminoiodinated product 2 or 3.

2) Method B: TEMPO-assisted aminoiodination with NaI and NFSI at 25 °C

Typical Procedure: To a reaction tube charged with NaI (150 mg, 1 mmol) and NFSI (315 mg, 1 mmol) was added a solution of alkene (1, 0.5 mmol) and TEMPO (78 mg, 0.5 mmol) in 1,4-dioxane (2 mL) via a syringe. The reaction mixture was stirred at 25 °C in air for 3 hours, and then diluted with ethyl acetate, washed with water and brine, dried over Na₂SO₄, 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 aminoiodinated product 2 or 3.

3) Characterization of the aminoiodinated product 2 and 3

Aminoiodination of Styrene (1a):

Method A: The reaction of 0.5 mmol of styrene (1a) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 223.5 mg of 2a (85%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of styrene (1a) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 218.0 mg of 2a (83%) and trace 3a after flash chromatography on silica gel using...
petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**N-(2-Iodo-1-phenylethyl)-N-(phenylsulfonyl)benzenesulfonamide (2a)**

White solid, m.p. 157.0-158.8 °C. 1H NMR (CDCl3, 400 MHz): δ = 7.59-7.44 (m, 11H), 7.38-7.31 (m, 4H), 5.75 (dd, J = 11.8 Hz, 3.0 Hz, 1H), 4.24 (dd, J = 11.8 Hz, 10.5 Hz, 1H), 3.11 (dd, J = 10.5 Hz, 3.0 Hz, 1H) ppm; 13C NMR (CDCl3, 100 MHz): δ = 140.0, 133.8, 132.6, 129.9, 129.0, 128.7, 128.3, 128.1, 65.2, 1.8 ppm. HRMS m/z (ESI) calcd for [C20H18NO4S2+Na]⁺ 549.9614, found 549.9623.

**N-(2-Iodo-2-phenylethyl)-N-(phenylsulfonyl)benzenesulfonamide (3a)**

Colorless oil. 1H NMR (CDCl3, 400 MHz): δ = 7.67-7.59 (m, 6H), 7.46-7.42 (m, 6H), 7.33-7.30 (m, 3H), 5.60 (dd, J = 11.0 Hz, 4.6 Hz, 1H), 4.89 (dd, J = 15.5 Hz, 11.0 Hz, 1H), 4.08 (dd, J = 15.5 Hz, 4.6 Hz, 1H) ppm; 13C NMR (CDCl3, 100 MHz): δ = 139.9, 138.6, 133.9, 129.2, 128.9, 128.9, 128.6, 125.7, 55.6, 28.7 ppm. HRMS m/z (ESI) calcd for [C20H18NO4S2+K]⁺ 565.9354, found 565.9362.

**Aminoidination of 4-tert-Butylstyrene (1b):**

**Method A:** The reaction of 0.5 mmol of 4-tert-butylstyrene (1b) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 235.8 mg of 2b (81%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of 4-tert-butylstyrene (1b) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 176.4 mg of 2b (61%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**N-(1-(4-(Tert-butyl)phenyl)-2-iodoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2b)**

White solid, m.p. 130.3-132.0 °C. 1H NMR (CDCl3, 400 MHz): δ = 8.30-7.50 (m, 6H), 7.41-6.90 (m, 8H), 5.76 (dd, J = 11.8 Hz, 3.0 Hz, 1H), 4.24 (dd, J = 11.8 Hz, 10.6 Hz, 1H), 3.12 (dd, J = 10.6 Hz, 3.0 Hz, 1H), 1.36 (s, 9H) ppm; 13C NMR (CDCl3, 100 MHz): δ = 151.8, 140.1, 133.7, 129.5, 129.4, 128.8, 128.1, 125.1, 65.1, 34.6, 31.4, 2.1 ppm. HRMS m/z (ESI) calcd for [C20H36NO4S2+Na]⁺ 606.0240, found 606.0234.

**Aminoidination of 4-vinylphenyl acetate (1c):**

**Method A:** The reaction of 0.5 mmol of 4-vinylphenyl acetate (1c) with NaI (1 mmol) and NFSI (1 mmol)
at 40 °C afforded 247.3 mg of 2c (85%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of 4-vinylphenyl acetate (1c) with NaI (1.5 mmol), NFSI (1.5 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 227.5 mg of 2c (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**4-(2-Iodo-1-(N-((phenylsulfonyl)phenylsulfonamido)ethyl)phenyl acetate (2c)**

White solid, m.p. 149.1-151.3 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.30-7.30\) (m, 12H), 7.05 (d, \(J = 8.6\) Hz, 2H), 5.72 (dd, \(J = 11.8\) Hz, 3.0 Hz, 1H), 4.21 (t, \(J = 11.2\) Hz, 1H), 3.08 (dd, \(J = 10.6\) Hz, 3.0 Hz, 1H), 2.34 (s, 3H) ppm; \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 169.2, 150.9, 139.9, 134.0, 131.1, 130.3, 129.1, 128.1, 121.7, 64.7, 21.1, 1.7\) ppm. HRMS \(m/z\) (ESI) calcd for [C\(_{22}\)H\(_{30}\)NO\(_5\)S\(_2\)+Na\(^+\)]\(^+\) 607.9669, found 607.9677.

**Aminoiiodination of 4-vinyl-1,1'-biphenyl (1d):**

**Method A:** The reaction of 0.5 mmol of 4-vinyl-1,1'-biphenyl (1d) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 240.6 mg of 2d (80%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of 4-vinyl-1,1'-biphenyl (1d) with NaI (1.5 mmol), NFSI (1.5 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 204.5 mg of 2d (68%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**N-((1,1'-biphenyl)-4-yl)-2-iodoethyl)-N-((phenylsulfonyl)benzenesulfonamide (2d)**

White solid, m.p. 160.1-162.1 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.40-7.60\) (m, 7H), 7.53-7.46 (m, 8H), 7.41-7.20 (m, 4H), 5.82 (dd, \(J = 11.8\) Hz, 3.0 Hz, 1H), 4.27 (t, \(J = 11.2\) Hz, 1H), 3.15 (dd, \(J = 10.5\) Hz, 3.0 Hz, 1H) ppm; \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 141.5, 140.3, 140.0, 133.8, 131.5, 130.4, 128.9, 128.1, 127.7, 127.1, 126.9, 65.0, 1.8\) ppm. HRMS \(m/z\) (ESI) calcd for [C\(_{26}\)H\(_{32}\)NO\(_4\)S\(_2\)+Na\(^+\)]\(^+\) 625.9927, found 625.9930.

**Aminoiiodination of 4-fluorostyrene (1e):**

**Method A:** The reaction of 0.5 mmol of 4-fluorostyrene (1e) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 181.5 mg of 2e (67%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

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Method B: The reaction of 0.5 mmol of 4-fluorostyrene (1e) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 170.8 mg of 2e (63%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-(1-(4-Fluorophenyl)-2-idoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2e)

White solid, m.p. 138.1-139.5 °C. 1H NMR (CDCl₃, 400 MHz): δ = 8.20-7.20 (m, 12H), 7.01 (t, J = 8.6 Hz, 2H), 5.70 (dd, J = 11.9 Hz, 3.0 Hz, 1H), 4.18 (dd, J = 11.9 Hz, 10.6 Hz, 1H), 3.09 (dd, J = 10.6 Hz, 3.0 Hz, 1H) ppm; 13C NMR (CDCl₃, 100 MHz): δ = 162.7 (d, J = 247.6 Hz), 139.9, 134.0, 131.8 (d, J = 8.3 Hz), 129.1, 128.6 (d, J = 3.5 Hz), 128.0, 115.2 (d, J = 21.6 Hz), 64.6, 1.8 ppm. HRMS m/z (ESI) calcd for [C₂₀H₁₇FNO₅S₂+Na]⁺ 567.9520, found 567.9526.

Aminoiodination of 3-fluorostyrene (1f):

Method A: The reaction of 0.5 mmol of 3-fluorostyrene (1f) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 173.8 mg of 2f (64%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of 3-fluorostyrene (1f) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 160.1 mg of 2f (59%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-(1-(3-Fluorophenyl)-2-idoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2f)

White solid, m.p. 140.1-141.6 °C. 1H NMR (CDCl₃, 400 MHz): δ = 8.40-7.40 (m, 10H), 7.33-7.25 (m, 2H), 7.19-7.16 (m, 1H), 7.08-7.03 (m, 1H), 5.69 (dd, J = 11.8 Hz, 3.0 Hz, 1H), 4.16 (dd, J = 11.8 Hz, 10.6 Hz, 1H), 3.09 (dd, J = 10.6 Hz, 3.0 Hz, 1H) ppm; 13C NMR (CDCl₃, 100 MHz): δ = 162.6 (d, J = 245.4 Hz), 139.8, 135.3 (d, J = 7.3 Hz), 134.1, 129.7 (d, J = 8.0 Hz), 129.1, 128.0, 125.5 (d, J = 2.9 Hz), 117.0 (d, J = 22.6 Hz), 115.7 (d, J = 21.0 Hz), 64.6 (d, J = 1.2 Hz), 1.4 ppm. HRMS m/z (ESI) calcd for [C₂₀H₁₇FNO₅S₂+Na]⁺ 567.9520, found 567.9521.

Aminoiodination of 4-chlorostyrene (1g):

Method A: The reaction of 0.5 mmol of 4-chlorostyrene (1g) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 226.2 mg of 2g (81%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of 4-chlorostyrene (1g) with NaI (1 mmol), NFSI (1 mmol) and
TEMPO (0.5 mmol) at 25 °C afforded 192.7 mg of 2g (69%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**N-(1-(4-Chlorophenyl)-2-iodoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2g)**

White solid, m.p. 131.2-132.8 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.30$-7.39 (m, 12H), 7.28 (d, $J = 8.6$ Hz, 2H), 5.69 (dd, $J = 11.8$ Hz, 3.0 Hz, 1H), 4.16 (dd, $J = 11.8$ Hz, 10.6 Hz, 1H), 3.08 (dd, $J = 10.6$ Hz, 3.0 Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 139.8, 134.7, 134.0, 131.3, 131.3, 129.1, 128.4, 128.4, 64.5, 1.4$ ppm. HRMS m/z (ESI) calcd for [C$_{20}$H$_7$ClINO$_2$S$_2$+Na]$^+$ 583.9224, found 583.9224.

**Aminoiodination of 3-chlorostyrene (1h):**

**Method A:** The reaction of 0.5 mmol of 3-chlorostyrene (1h) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 212.7 mg of 2h (76%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of 3-chlorostyrene (1h) with NaI (1.5 mmol), NFSI (1.5 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 184.4 mg of 2h (66%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**N-(1-(3-Chlorophenyl)-2-iodoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2h)**

White solid, m.p. 157.6-159.2 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.20$-7.37 (m, 12H), 7.33-7.24 (m, 2H), 5.68 (dd, $J = 11.8$ Hz, 3.0 Hz, 1H), 4.15 (t, $J = 11.2$ Hz, 1H), 3.10 (dd, $J = 10.6$ Hz, 3.0 Hz, 1H) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 139.7, 134.7, 134.3, 134.1, 130.1, 129.5, 129.0, 128.8, 128.0, 127.8, 64.4, 1.3$ ppm. HRMS m/z (ESI) calcd for [C$_{20}$H$_7$ClINO$_2$S$_2$+Na]$^+$ 583.9224, found 583.9229.

**Aminoiodination of 2-chlorostyrene (1i):**

**Method A:** The reaction of 0.5 mmol of 2-chlorostyrene (1i) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 156.6 mg of 2i (56%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of 2-chlorostyrene (1i) with NaI (1.5 mmol), NFSI (1.5 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 153.5 mg of 2i (55%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.
**N-(1-(2-Chlorophenyl)-2-iodoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2i)**

White solid, m.p. 197.1-198.7 °C. \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.90-7.70\) (m, 4H), 7.61-7.52 (m, 3H), 7.38-7.28 (m, 5H), 7.14-7.10 (m, 1H), 6.85-6.83 (m, 1H), 6.19 (dd, \(J = 12.0\) Hz, 3.8 Hz, 1H), 4.15 (dd, \(J = 12.0\) Hz, 10.6 Hz, 1H), 3.80 (dd, \(J = 10.6\) Hz, 3.8 Hz, 1H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 140.0, 136.8, 133.5, 132.6, 130.3, 129.7, 128.7, 128.6, 128.0, 126.9, 61.5, 2.5\) ppm. HRMS m/z (ESI) calcd for \([C_{20}H_{17}ClINO_5S_2]+\) 583.9224, found 583.9232.

**Aminoiodination of 4-bromostyrene (1j):**

**Method A:** The reaction of 0.5 mmol of 4-bromostyrene (1j) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 238.1 mg of 2j (79%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of 4-bromostyrene (1j) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 201.8 mg of 2j (67%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**N-(1-(4-Bromophenyl)-2-iodoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2j)**

White solid, m.p. 148.5-149.8 °C. \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.20-7.42\) (m, 1H), 7.34-7.20 (m, 3H), 5.67 (dd, \(J = 11.8\) Hz, 3.0 Hz, 1H), 4.16 (dd, \(J = 11.8\) Hz, 10.6 Hz, 1H), 3.08 (dd, \(J = 10.6\) Hz, 3.0 Hz, 1H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 139.8, 134.0, 131.8, 131.6, 131.41, 129.1, 128.0, 122.9, 64.5, 1.4\) ppm. HRMS m/z (ESI) calcd for \([C_{20}H_{17}BrINO_5S_2]+\) 627.8719, found 627.8730.

**Aminoiodination of 2-vinylnaphthalene (1k):**

**Method A:** The reaction of 0.5 mmol of 2-vinylnaphthalene (1k) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 236.7 mg of 2k (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**N-(2-Iodo-1-(naphthalen-2-yl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide (2k)**

Colorless oil. \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.91-7.80\) (m, 5H), 7.70 (d, \(J = 8.6\) Hz, 1H), 7.55-7.00 (m, 11H), 5.94 (dd, \(J = 11.8\) Hz, 3.0 Hz, 1H), 4.37 (dd, \(J = 11.8\) Hz, 10.6 Hz, 1H), 3.22 (dd, \(J = 10.6\) Hz, 3.0 Hz, 1H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 139.9, 133.8, 133.1, 132.7, 129.7, 129.4, 128.9, 128.4, 128.0, 127.9, 127.4, 127.1, 126.8, 126.4, 65.3, 1.9\) ppm. HRMS m/z (ESI)
Aminoiodination of allylbenzene (II):

**Method A:** The reaction of 0.5 mmol of allylbenzene (II) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 211.3 mg of 3l (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of allylbenzene (II) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 39.3 mg of 2l (14.5%) and 181.8 mg of 3l (67.2%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-(1-Iodo-3-phenylprop-2-yl)-N-(phenylsulfonyl)benzenesulfonamide (2l)

\[
\text{N}^{\text{S}(\text{SO}_2)\text{Ph})_2^l \quad \text{Colorless oil.} 
\]

\[
\begin{align*}
\text{δ} & = 8.20-7.80 \text{ ppm (m, 4H)},
7.66-7.63 \text{ ppm (m, 2H)},
7.56-7.52 \text{ ppm (m, 4H)},
7.25-7.22 \text{ ppm (m, 3H)},
7.11-7.09 \text{ ppm (m, 2H)},
4.55-4.48 \text{ ppm (m, 1H)},
3.66 \text{ ppm (dd, } J = 10.7 \text{ Hz, 7.8 Hz, 1H)},
3.48-3.40 \text{ ppm (m, 2H)},
3.27 \text{ ppm (dd, } J = 14.0 \text{ Hz, 5.7 Hz, 1H}) \text{ ppm;}
\end{align*}
\]

\[
\begin{align*}
\text{1^C NMR (CDCl}_3, 100 \text{ MHz}): \delta & = 137.1, 134.1, 134.0, 129.1, 129.1, 128.9, 128.8, 127.1, 67.0, 40.0, 4.3 \text{ ppm.}
\end{align*}
\]

HRMS m/z (ESI) calcd for [C\textsubscript{24}H\textsubscript{20}INO\textsubscript{2}S\textsubscript{2}+Na\textsuperscript{+}]\textsuperscript{+} 563.9771, found 563.9763.

N-(2-Iodo-3-phenylpropyl)-N-(phenylsulfonyl)benzenesulfonamide (3l)

\[
\text{N}^{\text{S}(\text{SO}_2)\text{Ph})_2^l \quad \text{White solid, m.p. 114.0-115.8 °C.} 
\]

\[
\begin{align*}
\text{δ} & = 8.02-8.00 \text{ ppm (m, 4H)},
7.67 \text{ ppm (t, } J = 7.5 \text{ Hz, 2H)},
7.54 \text{ ppm (t, } J = 7.8 \text{ Hz, 4H)},
7.27-7.24 \text{ ppm (m, 3H)},
6.94-6.92 \text{ ppm (m, 2H)},
4.51-4.44 \text{ ppm (m, 1H)},
4.35 \text{ ppm (dd, } J = 15.1 \text{ Hz, 5.6 Hz, 1H)},
4.19 \text{ ppm (dd, } J = 15.1 \text{ Hz, 9.8 Hz, 1H)},
3.22 \text{ ppm (dd, } J = 14.8 \text{ Hz, 4.2 Hz, 1H)},
2.94 \text{ ppm (dd, } J = 14.8 \text{ Hz, 11.0 Hz, 1H}) \text{ ppm;}
\end{align*}
\]

\[
\begin{align*}
\text{1^C NMR (CDCl}_3, 100 \text{ MHz): } \delta & = 139.2,
139.0, 134.2, 129.2, 128.7, 128.4, 128.4, 126.9, 56.2, 42.9, 31.9 \text{ ppm.} 
\end{align*}
\]

HRMS m/z (ESI) calcd for [C\textsubscript{26}H\textsubscript{20}INO\textsubscript{2}S\textsubscript{2}+Na\textsuperscript{+}]\textsuperscript{+} 563.9771, found 563.9778.

Aminoiodination of vinylcyclohexane (1m):

**Method A:** The reaction of 0.5 mmol of vinylcyclohexane (1m) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 51.2 mg of 2m (19.2%) and 175.2 mg of 3m (65.7%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of vinylcyclohexane (1m) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 196.3 mg of 3m (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.
**N-(1-Cyclohexyl-2-iodoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2m)**

White solid, m.p. 176.1-177.7 °C. 1H NMR (CDCl₃, 400 MHz): δ = 8.16-8.11 (m, 4H), 7.70-7.54 (m, 6H), 4.39-4.34 (m, 1H), 3.54 (dd, J = 11.3 Hz, 7.2 Hz, 1H), 3.30 (dd, J = 11.3 Hz, 3.2 Hz, 1H), 2.15-2.07 (m, 2H), 1.85-1.82 (m, 1H), 1.65-1.45 (m, 3H), 1.26-1.09 (m, 3H), 0.95-0.89 (m, 2H) ppm; 13C NMR (CDCl₃, 100 MHz): δ = 140.7, 139.5, 134.1, 133.8, 129.2, 128.9, 128.8, 128.7, 71.1, 42.4, 31.9, 31.7, 26.6, 25.8, 25.5, 4.8 ppm. HRMS m/z (ESI) calcd for [C₂₀H₂₄INO₅S₂+Na]⁺ 556.0084, found 556.0086.

**N-(2-Cyclohexyl-2-iodoethyl)-N-(phenylsulfonyl)benzenesulfonamide (3m)**

White solid, m.p. 121.8-123.2 °C. 1H NMR (CDCl₃, 400 MHz): δ = 8.04-8.02 (m, 4H), 7.66 (t, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 4H), 4.44-4.40 (m, 1H), 4.24-4.10 (m, 2H), 1.86-1.60 (m, 4H), 1.29-1.02 (m, 6H), 0.61-0.58 (m, 1H) ppm; 13C NMR (CDCl₃, 100 MHz): δ = 139.5, 134.1, 129.1, 128.2, 53.8, 41.7, 38.6, 33.5, 30.4, 26.0, 25.8, 25.3 ppm. HRMS m/z (ESI) calcd for [C₂₀H₂₄INO₅S₂+Na]⁺ 556.0084, found 556.0087.

**Aminoiiodination of cyclohexene (1n):**

**Method A:** The reaction of 0.5 mmol of cyclohexene (1n) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 193.7 mg of 2n (77%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of cyclohexene (1n) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 191.4 mg of 2n (76%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**N-(trans-2-Iodocyclohexyl)-N-(phenylsulfonyl)benzenesulfonamide (2n)**

White solid, m.p. 164.7-166.3 °C. 1H NMR (CDCl₃, 400 MHz): δ = 8.25 (s, 2H), 7.93 (s, 2H), 7.70-7.50 (m, 6H), 4.96-4.89 (m, 1H), 4.04-3.97 (m, 1H), 2.66-2.62 (m, 1H), 2.31-2.21 (m, 1H), 2.04-1.77 (m, 3H), 1.51-1.48 (m, 1H), 1.32-1.26 (m, 2H) ppm; 13C NMR (CDCl₃, 100 MHz): δ = 141.3, 138.5, 134.2, 133.8, 129.4, 129.0, 128.5, 128.2, 70.4, 42.0, 32.8, 30.8, 28.0, 26.2 ppm. HRMS m/z (ESI) calcd for [C₁₀H₂₀INO₅S₂+Na]⁺ 527.9771, found 527.9775.

**Aminoiiodination of cyclopentene (1o):**

**Method A:** The reaction of 0.5 mmol of cyclopentene (1o) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C
afforded 173.4 mg of 2o (71%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of cyclopentene (1o) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 175.8 mg of 2o (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-(trans-2-Iodocyclopentyl)-N-(phenylsulfonyl)benzenesulfonamide (2o)

**Method A:** The reaction of 0.5 mmol of cyclopentene (1o) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 175.8 mg of 2o (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of cyclopentene (1o) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 175.8 mg of 2o (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

Aminoisodination of (E)-3-hexene (1p):

**Method A:** The reaction of 0.5 mmol of (E)-3-hexene (1p) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 163.8 mg of 2p (65%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of (E)-3-hexene (1p) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 184.6 mg of 2p (73%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-(3S,4R)- or (3R,4S)-4-Iodohexan-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (2p)

**Aminoisodination of (Z)-3-hexene (1q):**

**Method A:** The reaction of 0.5 mmol of (Z)-3-hexene (1q) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 186.7 mg of 2q (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.
Method B: The reaction of 0.5 mmol of (Z)-3-hexene (1q) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 199.7 mg of 2q (79%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-((3S,4S)- or (3R,4R)-4-IodoheXan-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (2q)

Colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.12-8.07\) (m, 4H), 7.64 (t, \(J = 7.4\) Hz, 2H), 7.54 (t, \(J = 7.6\) Hz, 4H), 4.61-4.56 (m, 1H), 4.41-4.36 (m, 1H), 2.16-1.97 (m, 3H), 1.74-1.66 (m, 1H), 1.05 (t, \(J = 7.1\) Hz, 3H), 0.71 (t, \(J = 7.4\) Hz, 3H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 141.3, 138.7, 134.1, 133.8, 133.7, 129.3, 129.0, 128.7, 72.3, 42.1, 30.1, 23.6, 14.8, 12.2\) ppm. HRMS m/z (ESI) calcd for \([C_{18}H_{23}INO_{4}S_{2}+Na]^{+}\) 529.9927, found 529.9932.

Aminoiiodination of (E)-4-octene (1r):

Method A: The reaction of 0.5 mmol of (E)-4-octene (1r) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 122.3 mg of 2r (46%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of (E)-4-octene (1r) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 154.6 mg of 2r (58%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-((4S,5R)- or (4R,5S)-5-Iodoctan-4-yl)-N-(phenylsulfonyl)benzenesulfonamide (2r)

Colorless oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.15-8.11\) (m, 4H), 7.70-7.64 (m, 2H), 7.61-7.55 (m, 4H), 4.44 (td, \(J = 10.3\) Hz, 2.8 Hz, 1H), 4.35-4.29 (m, 1H), 2.45-2.35 (m, 1H), 2.06-2.01 (m, 1H), 1.45-1.26 (m, 3H), 1.14-1.03 (m, 2H), 0.75 (t, \(J = 7.3\) Hz, 3H), 0.63 (t, \(J = 7.3\) Hz, 3H), 0.60-0.50 (m, 1H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 141.1, 138.9, 134.2, 133.8, 129.2, 129.1, 128.8, 128.8, 70.7, 42.4, 38.6, 34.7, 23.3, 20.1, 13.4, 12.8\) ppm. HRMS m/z (ESI) calcd for \([C_{20}H_{26}INO_{4}S_{2}+NH_{4}]^{+}\) 553.0686, found 553.0688.

Aminoiiodination of (Z)-4-octene (1s):

Method A: The reaction of 0.5 mmol of (Z)-4-octene (1s) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 151.4 mg of 2s (57%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of (Z)-4-octene (1s) with NaI (1 mmol), NFSI (1 mmol) and TEMPO
(0.5 mmol) at 25 °C afforded 207.8 mg of 2s (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-((4S,5S)- or (4R, 5R)-5-Iodoctan-4-yl)-N-(phenylsulfonyl)benzenesulfonamide (2s)

2s  

Colorless oil. 1H NMR (CDCl3, 400 MHz): δ = 8.20-8.00 (m, 4H), 7.65 (t, J = 7.4 Hz, 2H), 7.54 (t, J = 7.7 Hz, 4H), 4.57-4.44 (m, 2H), 2.06-2.00 (m, 1H), 1.94-1.83 (m, 2H), 1.73-1.58 (m, 2H), 1.40-1.31 (m, 1H), 1.13-1.08 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H), 0.72 (t, J = 7.3 Hz, 3H) ppm; 13C NMR (CDCl3, 100 MHz): δ = 141.4, 138.9, 134.1, 133.7, 129.4, 128.8, 128.7, 71.1, 40.0, 38.8, 32.7, 23.5, 21.1, 13.7, 13.0 ppm. HRMS m/z (ESI) calcd for [C26H26NO6S2+Na]⁺ 558.0240, found 558.0248.

Aminoiodination of 2-vinylisoindoline-1,3-dione (1t):

Method A: The reaction of 0.5 mmol of 2-vinylisoindoline-1,3-dione (1t) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 213.8 mg of 2t (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 6:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of 2-vinylisoindoline-1,3-dione (1t) with NaI (1.5 mmol), NFSI (1.5 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 127.5 mg of 2t (43%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 6:1, v/v) as the eluent.

N-(1-(1,3-Dioxoisindolin-2-yl)-2-idoethyl)-N-(phenylsulfonyl)benzenesulfonamide (2t)

2t  

White solid, m.p. 199.6-201.5 °C. 1H NMR (CDCl3, 400 MHz): δ = 8.16-8.14 (m, 4H), 7.80 (dd, J = 5.5 Hz, 3.0 Hz, 2H), 7.73 (dd, J = 5.5 Hz, 3.0 Hz, 2H), 7.59-7.47 (m, 6H), 6.74 (dd, J = 12.4 Hz, 4.1 Hz, 1H), 4.75 (dd, J = 12.4 Hz, 10.0 Hz, 1H), 3.51 (dd, J = 12.4 Hz, 4.1 Hz, 1H) ppm; 13C NMR (CDCl3, 100 MHz): δ = 166.9, 140.1, 134.6, 134.1, 131.0, 129.1, 128.9, 128.7, 127.8, 123.8, 68.2, 1.6 ppm. HRMS m/z (ESI) calcd for [C22H17IN2O5S2+Na]⁺ 618.9465, found 618.9472.

Aminoiodination of vinyl benzoate (1u):

Method A: The reaction of 0.5 mmol of vinyl benzoate (1u) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 244.6 mg of 2u (86%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 10:1, v/v) as the eluent.

Method B: The reaction of 0.5 mmol of vinyl benzoate (1u) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 218.9 mg of 2u (77%) after flash chromatography on silica gel using...
petroleum ether and ethyl acetate (10:1, v/v) as the eluent.

2-Iodo-1-(N-(phenylsulfonyl)phenylsulfonamido)ethyl benzoate (2u)

White solid, m.p. 116.7-118.2 °C. \[^1\text{H}\text{ NMR (CDCl}_3, 400 MHz): \delta = 8.05 (d, J = 0.76 Hz, 4H), 7.83-7.81 (m, 2H), 7.59-7.51 (m, 3H), 7.44-7.37 (m, 6H), 7.07 (t, J = 7.1 Hz, 1H), 4.00 (dd, J = 10.6 Hz, 7.7 Hz, 1H), 3.86 (dd, J = 10.6 Hz, 6.6 Hz, 1H) ppm; \[^{13}\text{C}\text{ NMR (CDCl}_3, 100 MHz): \delta = 164.0, 139.5, 134.1, 133.8, 130.0, 129.0, 128.7, 128.4, 127.9, 82.9, 2.2 ppm. HRMS m/z (ESI) calcd for [C\text{21}H\text{18}INO\text{6}S\text{2}+Na]^+ 593.9512, found 593.9518.]

Aminoiiodination of trimethyl(vinyl)silane (1v):

**Method A:** The reaction of 0.5 mmol of trimethyl(vinyl)silane (1v) with NaI (1 mmol) and NFSI (1 mmol) at 40 °C afforded 174.3 mg of 3v (67%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, v/v) as the eluent.

**Method B:** The reaction of 0.5 mmol of trimethyl(vinyl)silane (1v) with NaI (1 mmol), NFSI (1 mmol) and TEMPO (0.5 mmol) at 25 °C afforded 208.4 mg of 3v (80%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1, v/v) as the eluent.

N-(2-Iodo-2-(trimethylsilyl)ethyl)-N-(phenylsulfonyl)benzenesulfonamide (3v)

White solid, m.p. 119.8-121.4 °C. \[^1\text{H}\text{ NMR (CDCl}_3, 400 MHz): \delta = 8.09-8.07 (m, 4H), 7.68-7.64 (m, 2H), 7.58-7.54 (m, 4H), 4.18 (dd, J = 15.5 Hz, 11.7, 1H), 3.93 (dd, J = 15.5 Hz, 3.8 Hz, 1H), 3.55 (dd, J = 11.7 Hz, 3.8 Hz, 1H), 0.19 (s, 9H) ppm; \[^{13}\text{C}\text{ NMR (CDCl}_3, 100 MHz): \delta = 139.6, 134.0, 129.0, 128.6, 52.9, 15.5, -2.0 ppm. HRMS m/z (ESI) calcd for [C\text{17}H\text{18}INO\text{4}S\text{2}Si+K]^+ 561.9436, found 561.9434.
Single Crystal X-ray Diffractometry Structure of 2n

Figure S1. Single crystal X-ray diffractometry structure of 2n

CCDC Deposition Number: 1857005
Control Experiments

1) Control experiments proving NFSI can oxidize I⁻ to I⁺

Typical Procedure: To a reaction tube charged with NaI (150 mg, 1 mmol) and NFSI (315 mg, 1 mmol) was added a solution of N-(quinolin-8-yl)acetamide (93 mg, 0.5 mmol) in 1,4-dioxane (2 mL) via a syringe. The reaction mixture was stirred at 25 °C in air for 6 hours. After diluted with ethyl acetate, the reaction mixture was concentrated in vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (6:1, v/v) as the eluent on silical gel to afford the C5-iodinated product 152.7 mg (98%). White solid, m.p. 144.3-145.6 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 9.77 (s, 1H), 8.75 (dd, J = 4.2 Hz, 1.5 Hz, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.34 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.51 (dd, J = 8.5 Hz, 4.2 Hz, 1H), 2.34 (s, 3H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 168.8, 148.6, 140.7, 138.8, 138.2, 135.4, 129.5, 123.1, 117.7, 89.2, 25.1 ppm. HRMS m/z (ESI) calcd for [C₁₁H₉IN₂O+Na]⁺ 334.9652, found 334.9654.

1) Control experiments proving TEMPO cannot oxidize I⁻ to I⁺

Typical Procedure: To a reaction tube charged with NaI (150 mg, 1 mmol) was added a solution of N-(quinolin-8-yl)acetamide (93 mg, 0.5 mmol) and TEMPO (156 mg, 1 mmol) in 1,4-dioxane (2 mL) via a syringe. The reaction mixture was stirred at 25 °C in air for 6 hours, and TLC suggested that no iodinated product was generated. After diluted with ethyl acetate, the reaction mixture was concentrated in vacuo to recover the substrate N-(quinolin-8-yl)acetamide 86.7 mg (93%). White solid, m.p. 100.5-101.4 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 9.78 (s, 1H), 8.79-8.75 (m, 2H),
8.14 (dd, $J = 8.3$ Hz, 1.7 Hz, 1H), 7.54-7.47 (m, 2H), 7.43 (dd, $J = 8.3$ Hz, 4.2 Hz, 1H), 2.34 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 168.7, 148.0, 138.2, 136.3, 134.5, 127.9, 127.3, 121.5, 121.4, 116.3, 25.1 ppm.
Gram-scale Aminoiiodination of Alkene with NaI and NFSI

**Method A:** To a reaction tube charged with NaI (3.00 g, 20 mmol) and NFSI (6.31 g, 20 mmol) was added a solution of alkenes 1 (10 mmol) in 1,4-dioxane (30 mL) dropwise. The reaction mixture was stirred at 40 °C in air for 10 hours. After cooling by iced water, the reaction mixture was diluted with ethyl acetate, washed with water and brine, dried over Na₂SO₄, and concentrated in vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent on silical gel to afford corresponding aminoiiodinated products 2 or 3.

**Method B:** To a reaction tube charged with NaI (3.00 g, 20 mmol) and NFSI (6.31 g, 20 mmol) cooled by iced water was added a solution of alkenes 1 (10 mmol) and TEMPO (1.56 g, 10 mmol) in 1,4-dioxane (30 mL) dropwise. The reaction mixture was stirred at 25 °C in air for 3 hours, and then diluted with ethyl acetate, washed with water and brine, dried over Na₂SO₄, and concentrated in vacuo to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent on silical gel to afford corresponding aminoiiodinated products 2 or 3.

**Gram-scale Aminoiiodination of Styrene (1a):**

**Method A:** The reaction of 10 mmol of styrene (1a) with NaI (20 mmol) and NFSI (20 mmol) at 40 °C afforded 4.10 g of 2a (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent.

**Method B:** The reaction of 10 mmol of styrene (1a) with NaI (20 mmol), NFSI (20 mmol) and TEMPO (10 mmol) at 25 °C afforded 3.93 g of 2a (75%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent.

**Gram-scale Aminoiiodination of vinylcyclohexane (1m):**

**Method A:** The reaction of 10 mmol of vinylcyclohexane (1m) with NaI (20 mmol) and NFSI (20 mmol)
at 40 °C afforded 1.74 g of 2m (32.6%) and 2.73 g of 3m (51.2%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1 to 6:1, v/v) as the eluent.

**Method B:** The reaction of 10 mmol of vinylcyclohexane (1m) with NaI (20 mmol), NFSI (20 mmol) and TEMPO (10 mmol) at 25 °C afforded 0.64 g of 2m (12.0%) and 3.94 g of 3m (73.9%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (25:1 to 6:1, v/v) as the eluent.

**Gram-scale Aminoidination of cyclohexene (1o):**

**Method A:** The reaction of 10 mmol of cyclohexene (1o) with NaI (20 mmol) and NFSI (20 mmol) at 40 °C afforded 4.02 g of 2o (80%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent.

**Method B:** The reaction of 10 mmol of cyclohexene (1o) with NaI (20 mmol), NFSI (20 mmol) and TEMPO (10 mmol) at 25 °C afforded 4.08 g of 2o (81%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent.

**Gram-scale Aminoidination of vinyl benzoate (1v):**

**Method A:** The reaction of 10 mmol of vinyl benzoate (1v) with NaI (20 mmol) and NFSI (20 mmol) at 40 °C afforded 4.66 g of 2v (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 6:1, v/v) as the eluent.

**Method B:** The reaction of 10 mmol of vinyl benzoate (1v) with NaI (20 mmol), NFSI (20 mmol) and TEMPO (10 mmol) at 25 °C afforded 4.55 g of 2v (80%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (10:1 to 6:1, v/v) as the eluent.

**Gram-scale Aminoidination of trimethyl(vinyl)silane (1w):**

**Method A:** The reaction of 10 mmol of trimethyl(vinyl)silane (1w) with NaI (20 mmol) and NFSI (20 mmol) at 40 °C afforded 3.23 g of 3w (62%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent.

**Method B:** The reaction of 10 mmol of trimethyl(vinyl)silane (1w) with NaI (20 mmol), NFSI (20 mmol) and TEMPO (10 mmol) at 25 °C afforded 3.88 g of 3w (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1 to 6:1, v/v) as the eluent.
**A Preliminary Attempt on Aminobromination of Styrene**

**General Procedure:** To a reaction tube charged with NaBr (155 mg, 1.5 mmol) and NFSI (473 mg, 1.5 mmol) was added a solution of styrene 1a (52 mg, 0.5 mmol) and TEMPO (78 mg, 0.5 mmol) in 1,4-dioxane (2 mL) via a syringe. The reaction mixture was stirred at 40 °C in air for 6 hours. After cooling by iced water, the reaction mixture was diluted with ethyl acetate, washed with water and brine, dried over Na₂SO₄, 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 silical gel to afford 64.8 mg of the aminobrominated products 4a (27%).

* N-(2-Bromo-1-phenylethyl)-N-(phenylsulfonyl)benzenesulfonamide (4a)

White solid, m.p. 148.5-149.5 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.58-7.43 (m, 10H), 7.35-7.32 (m, 5H), 5.79 (dd, J = 10.9 Hz, 3.6 Hz, 1H), 4.44 (t, J = 10.8 Hz, 1H), 3.32 (dd, J = 10.7 Hz, 3.7 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 139.9, 133.9, 132.7, 129.6, 128.9, 128.6, 128.4, 128.2, 64.6, 29.8 ppm. HRMS *m/z* (ESI) calcd for [C₂₀H₁₈BrNOS₂+Na]⁺ 501.9753, found 501.9758.
**S22**

**Image Description:**
- The image contains a chemical structure labeled as 2a, which appears to be a compound with a benzene ring and a nitrogen atom attached to it. The structure is labeled with a chemical formula, suggesting it may be a part of a molecular analysis or a chemical reaction.

**Technical Information:**
- The image includes a spectrum graph with various peaks, indicating a chemical analysis result.
- There are annotations and values that likely correspond to chemical shifts and other spectroscopic data, although the specific details are not clearly visible in the image.

**Additional Notes:**
- The image contains a logo forBruker, a company known for its work in chemical analysis and spectroscopy.
- The presence of peaks and labels suggests this is a part of a report or document discussing chemical analysis methods or results.

**Context:**
- This image is likely from a scientific or technical report, possibly related to chemistry, materials science, or a related field where such analysis tools are used.

**Analysis:**
- The structure 2a and the spectrum suggest a detailed analysis of a chemical compound, possibly for the purposes of identification, purity assessment, or reaction monitoring.
- The presence of a Bruker logo indicates the use of advanced equipment or software for the analysis, reinforcing the accuracy and precision of the results presented.

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**Technical Details:**
- The spectrum includes various markers and labels that are typical in such chemical analyses, such as ppm values, which are crucial for identifying the chemical structure and its purity.
- The peaks and their corresponding values are essential for interpreting the chemical composition and its properties.

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**Conclusion:**
- The image is a valuable resource for understanding the chemical properties and analysis methods used in scientific research.
- It highlights the importance of technology in modern chemical analysis and the role of detailed documentation in scientific communication.

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**Further Reading:**
- For a deeper understanding of chemical analysis, one might explore textbooks on spectroscopy, particularly nuclear magnetic resonance (NMR) spectroscopy, or materials science literature that uses such techniques to study chemical compounds.
- Online resources and databases like PubChem or the Chemical Abstracts Service (CAS) can provide additional context and related literature on specific chemical structures and their analyses.
\[ \text{3v} \]

NISO₂Ph₂