Asymmetric recognition and sequential ring opening of 2-substituted-*N*-nosylaziridines with $(DHQD)_2AQN$ and TMSNu

Supporting Information

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General methods.

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H-NMR, 270 MHz; ^{13}C-NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were measured with Shimadzu Model GCMS-QP5000 spectrometer and JEOL DX-300 HF mass spectrometer. High-resolution mass spectral data was obtained on a JEOL JMS-DX303HF Spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. High performance liquid chlomatography (HPLC) was performed on HITACHI D-7400 (UV-Detector). Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Flash column chromatography (FCC) was performed using silica gel FL60D (Fuji Silysia Chemical Co.). Preparative gel permeation liquid chromatography (GPLC) was performed on a JAI (Japan Analytical Industry) LC-908 instrument with JAIGEL 1H-2H columns and chloroform as an eluent. Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and spraying with an ethanolic phosphomolybdic acid solution followed by heating.

General procedure for preparation of aziridines.[1] **(starting materials)**

The alkenes (6 mmol) were added to a solution of *N*-chloro-*N*-sodio-2-nitrobenzesulfonamide[2] (0.78 g, 3.0 mmol) and iodine (76 mg, 0.35 mmol) in MeCN (10 mL) at room temperature. The solution was stirred in the dark at room temperature under an atmosphere of nitrogen, quenched with 0.5 N aqueous $Na_2S_2O_3$ (5 mL), extracted with CH_2Cl_2 (25 mL$\times$4). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate).

Procedure for recognition of aziridine 1a with $(DHQD)_2AQN$. (Figure 1)

A slution of aziridine **1a** (0.1 mmol) and $(DHQD)_2AQN$ (0.05 mmol) in MeCN (0.4 mL) was stirred at room temperature for indicated time under an atmosphere of nitrogen. The reaction mixture was then passed through a 15 cm plag of silica gel with *n*-hexane/AcOEt (1/1, 100 mL). The solvent was removed *in vacuo* to give the crude product which was purified by preparative thin-layer chromatography.

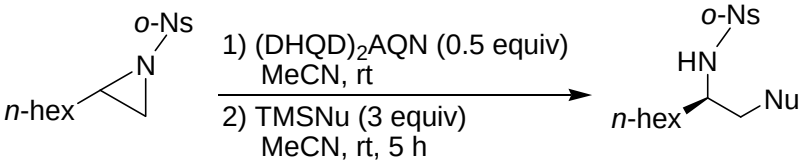
General procedure for asymmetric recognition and sequential ring opening of aziridines. (Schemes 1 and 2, Table 1)

A solution of the aziridine (0.1 mmol) and $(DHQD)_2AQN$ (0.5 mmol) in methylene chloride (0.4 mL) was stirred at room temperature under an atomosphere of nitrogen. After stirring for indicated time, TMSNu was added and the mixture was further stirred for 5 h at the same temperature. The reaction mixture was then passed through a 15 cm plug of silica gel with *n*-hexane/AcOEt (1/1, 100 mL). The solvent was removed *in vacuo* to give the crude product which was purified by preparative thin-layer chromatography.

Transformation of adduct (aziridine 1a－$(DHQD)_2AQN$). (Scheme 3)

To a solution of aziridine－$(DHQD)_2AQN$ adduct in MeCN (1 mL) was added thiophenol (0.18 mmol, 3 equiv) and K_2CO_3 (0.18 mmol, 3 equiv). The mixture was heated to reflux for 12 h under an atomosphere of argon, and then phenylisocyanate (0.6 mmol, 10 equiv) was added to the reflux solution. The solution was further heated to reflux for 12 h under an atomosphere of argon. The reaction mixture was then passed through a 15 cm plug of silica gel with *n*-hexane/AcOEt (1/1, 100mL). The solvent was removed *in vacuo* to give the crude product which was purified by preparative thin-layer chromatography.

Asymmetric Ring Opening of *n*-Hexyl-substituted Aziridine with TMSNu

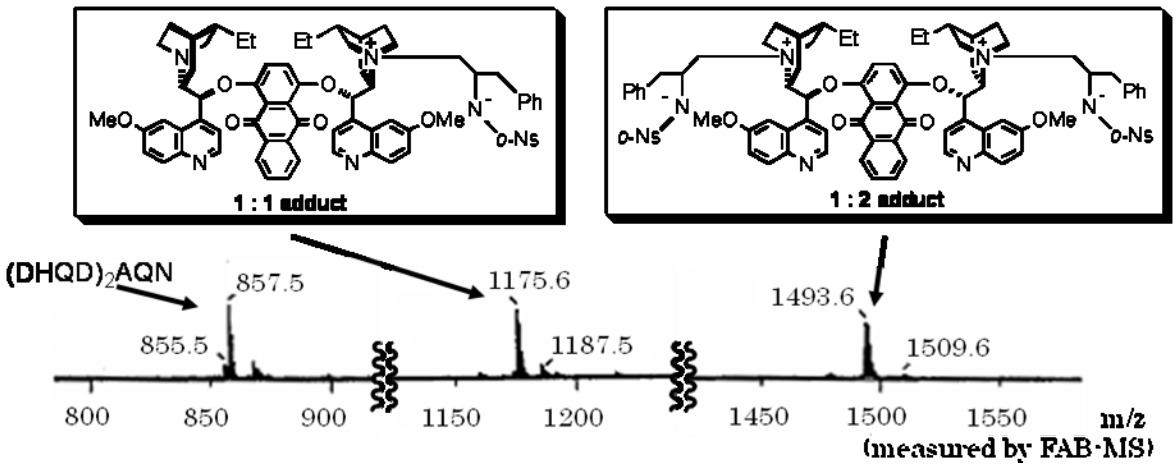


1i **2i-4i**

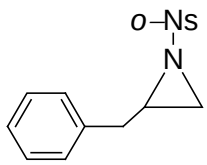
entry	Nu		yield[a] (%)	ee[b] (%)
1	CN	**2i**	68	59
2	N_3	**3i**	70	62
3	I	**4i**	74	54

[a] Isolated yield based on consumption of half amount of aziridine **1i**.
[b] Determined by chiral HPLC.

FAB mass spectrum of aziridine 1a trapped by $(DHQD)_2AQN$



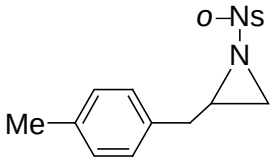
***N*-(2-Nitrobenzenesulfonyl)-2-benzylaziridine (1a)**



1a

White solid; mp 72-73 °C; IR (KBr, cm^{-1}) 1539, 1369, 1327, 1167; ^1H NMR (270 MHz, $CDCl_3$) δ = 2.36 (d, 1H, *J* = 3.2 Hz, H-3,), 2.81 (dd, 1H, *J* = 4.2, 9.7 Hz, C<u>H</u>$_2$Ph,), 2.92-2.99 (m, 2H, C<u>H</u>$_2$Ph and H-3), 3.23-3.28 (m, 1H, H-2), 7.15-7.26 (m, 5H, Ph), 7.64-7.73 (m, 3H, Ar-<u>H</u>), 8.07 (d, 1H, *J* = 5.4 Hz, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 34.95, 37.40, 42.80, 124.22, 126.83, 128.48, 128.90, 131.10, 131.97, 134.32, 136.44; MS (EI) *m*/*z* (relative intensity, %) 318 (M^+, 1), 186 (6), 132 (M^+–*o*-$NsNH_2$, 43), 91 (71), 77 (36), 55 (100); HRMS (CI, isobutane) calcd for $C_{15}H_{14}N_2O_4S$ $(M + H)^+$ 319.0754, found 319.0755; HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 7:3, 0.7 mL/min, 254 nm) t_R = 38.1 min., t_S = 52.4 min.

***N*-(2-Nitrobenzenesulfonyl)-2-(*p*-tolylmethyl)aziridine (1b)**

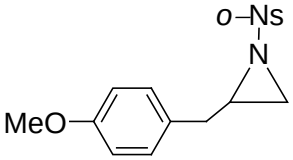


1b

White solid; mp 112-114 °C; IR (KBr, cm^{-1}) 1549, 1365, 1329, 1167; ^1H NMR (270 MHz, $CDCl_3$) δ = 2.28 (s, 3H, Ar-C<u>H</u>$_3$), 2.35 (d, 1H, H-3, *J* = 5.1 Hz), 2.76 (dd, 1H, Ar-C<u>H</u>$_2$, *J* = 6.2, 14.3 Hz), 2.88-2.96 (m, 2H, Ar-C<u>H</u>$_2$ and H-3), 2.95-3.25 (m, 1H, H-2), 6.95-7.08 (m, 4H, Ar-<u>H</u>), 7.61-7.77 (m, 3H, Ar-<u>H</u>), 8.06 (d, 1H, *J* = 7.7 Hz, Ar-<u>H</u>); ^{13}C NMR (68

MHz, $CDCl_3$) δ = 21.11, 35.11, 37.03, 43.04, 124.11, 128.69, 129.06, 131.03, 131.70, 131.82, 133.20, 134.03, 136.20, 148.38; MS (EI) *m/z* (relative intensity, %) 332 (M^+, 22), 186 (17), 146 (M^+–*o*-$NsNH_2$, 100), 119 (96), 105 (78); HRMS (CI, isobutane) calcd for $C_{16}H_{16}N_2O_4S$ $(M + H)^+$ 333.0910, found 333.0900; HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 43.5 and 48.1 min.

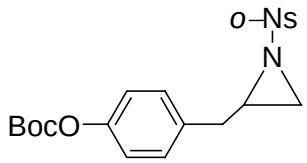
_N_-(2-Nitrobenzenesulfonyl)-2-(_p_-methoxyphenylmethyl)aziridine (1c)



1c

White solid; mp: 105-107 °C; IR (KBr, cm^{-1}) 1549, 1373, 1331, 1251, 1169; ^1H NMR (270 MHz, $CDCl_3$) δ = 2.34 (d, 1H, H-3, *J* = 4.9 Hz), 2.70-2.95 (m, 3H, Ar-C<u>H</u>$_2$ and H-3), 3.15-3.25 (m, 1H, H-2), 3.77 (s, 3H, O-C<u>H</u>$_3$), 6.71 (d, 2H, *J* = 6.5 Hz, Ar-<u>H</u>), 7.06 (d, 2H, *J* = 8.9 Hz, Ar-<u>H</u>), 7.60-8.04 (m, 3H, Ar-<u>H</u>), 8.06 (d, 1H, *J* = 8.9 Hz, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 35.04, 36.55, 43.11, 55.23, 113.78, 124.11, 128.31, 129.83, 131.02, 131.66, 131.83, 134.12, 148.37, 158.25; MS (EI) *m/z* (relative intensity, %) 348 (M^+, 20), 186 (8), 162 (M^+–*o*-$NsNH_2$, 71), 135 (38), 121 (100); Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63; N, 8.04. Found: C, 55.14; H, 4.62; N, 7.87; HPLC (Daicel Chiralpak IA, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 42.2 and 45.6 min.

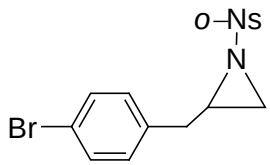
***N*-(2-Nitrobenzenesulfonyl)-2-(*p*-*tert*-butoxycarbonyloxyphenylmethyl)aziridine (1d)**



1d

Colorless oil; IR (neat, cm^{-1}) 1755 (Boc); ^1H NMR (270 MHz, $CDCl_3$) δ = 1.56 (s, 9H, $C(C\underline{H}_3)_3$), 2.35 (d, 1H, *J* = 4.6 Hz, H-3), 2.82-2.94 (m, 3H, Ar-$C\underline{H}_2$ and H-3), 3.13-3.24 (m, 1H, H-2), 6.96 (d, 2H, *J* = 6.8 Hz, Ar-<u>H</u>), 7.13 (d, 2H, *J* = 8.4 Hz, Ar-<u>H</u>), 7.59-8.00 (m, 3H, Ar-<u>H</u>), 8.00 (d, 1H, *J* = 6.8 Hz, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 27.72, 34.68, 36.73, 42.75, 83.50, 121.13, 124.11, 129.69, 130.88, 131.20, 131.88, 133.83, 134.36, 148.24, 149.68, 151.61; MS (CI, isobutane) *m/z* (relative intensity, %) 435 ($[M + H]^+$, 3), 379 (100), 335 (41), 215 (64); HRMS (CI, isobutane) calcd for $C_{20}H_{23}N_2O_7S$ $(M + H)^+$ 435.1226, found 435.1217; HPLC (Daicel Chiralpak AS, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 124.6 and 156.0 min.

***N*-(2-Nitrobenzenesulfonyl)-2-(*p*-bromophenylmethyl)aziridine (1e)**

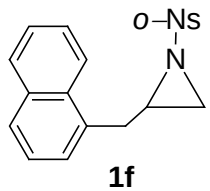


1e

White solid; mp 90-91 °C; IR (KBr, cm^{-1}) 1543, 1363, 1329, 1165; ^1H NMR (270 MHz, $CDCl_3$) δ = 2.36 (d, 1H, *J* = 4.6 Hz, H-3), 2.67-2.87 (dd, 1H, *J* = 7.3, 14.3 Hz Ar-$C\underline{H}_2$), 2.86-2.96 (m, 2H, Ar-$C\underline{H}_2$ and H-3), 3.10-3.22 (m, 1H, H-2), 7.00 (d, 2H, *J* = 8.4 Hz, Ar-<u>H</u>), 7.24

(d, 2H, *J* = 9.2 Hz, Ar-H), 7.58-7.95 (m, 3H, Ar-H), 7.98 (d, 1H, *J* = 7.8 Hz, Ar-H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 34.64, 36.70, 42.57, 120.58, 123.96, 130.44, 130.86, 131.07, 131.23, 131.68, 134.14, 135.26, 148.20; MS (EI) *m/z* (relative intensity, %) 396 (M+, 5), 210 (M^+–*o*-$NsNH_2$, 8), 123 (68), 103 (100); Anal. Calcd for $C_{15}H_{13}BrN_2O_4S$: C, 45.35; H, 3.30; N, 7.05. Found: C, 45.61; H, 3.29; N, 6.94.; HPLC (Daicel Chiralpak IA, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm) *t* = 66.9 and 70.4 min.

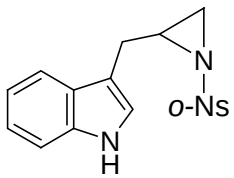
***N*-(2-Nitrobenzenesulfonyl)-2-(1-naphthylmethyl)aziridine (1f)**



1f

Colorless oil; IR (neat, cm^{-1}) 1543, 1335, 1167; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 2.38 (d, 1H, *J* = 4.1 Hz, H-3,), 2.91 (d, 1H, *J* = 6.2 Hz, H-3), 3.27-3.36 (m, 3H, Ar-CH_2 and H-2), 7.27-7.49 (m, 7H, Ar-H), 7.61-7.64 (m, 1H, Ar-H), 7.74-7.76 (m, 2H, Ar-H), 7.91-7.95 (m, 1H, Ar-H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 34.16, 34.73, 42.47, 123.42, 123.71, 125.19, 125.44, 125.94, 127.02, 127.44, 128.41, 130.46, 130.70, 131.42, 131.45, 132.55, 133.38, 134.08, 147.87; MS (EI) *m/z* (relative intensity, %) 368 (M^+, 23), 182 (27), 141 (86), 127 (11); HRMS (EI) calcd for $C_{19}H_{16}N_2O_4S$ $(M)^+$ 368.0832, found 368.0836; HPLC (Daicel Chiralpak IA, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm) *t* = 50.1 and 56.0 min.

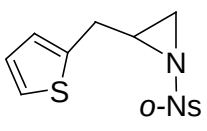
***N*-(2-Nitrobenzenesulfonyl)-2-(1-*H*-3-indolylmethyl)aziridine (1g)**



1g

Yellow solid; mp 119-121 °C (decomp.); IR (KBr, cm^{-1}) 3435 (NH), 1543, 1362, 1327, 1169; ^1H NMR (270 MHz, $CDCl_3$) δ = 2.39 (d, *J* = 4.9 Hz, 1H, H-3), 2.92 (d, *J* = 9.7 Hz, 1H, H-3), 3.00-3.08 (m, 2H, Ar-C<u>H</u>$_2$), 3.28-3.38 (m, 1H, H-2), 7.01-7.10 (m, 2H, Ar-<u>H</u>), 7.12-7.19 (ddd, 1H, *J* = 1.1, 7.0, 7.0 Hz, Ar-<u>H</u>), 7.25-7.33 (m, 1H, Ar-<u>H</u>), 7.48-7.55 (m, 2H, Ar-<u>H</u>), 7.62-7.98 (m, 2H, Ar-<u>H</u>), 7.98-8.02 (m, 2H, Ar-<u>H</u> and N<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 27.17, 35.44, 42.45, 110.61, 111.03, 118.56, 119.45, 121.99, 122.52, 123.93, 127.08, 130.85, 131.52, 131.62, 133.98, 135.89; MS (EI) *m/z* (relative intensity, %) 357 (M^+, 15), 186 (20), 171 (M^+–*o*-$NsNH_2$, 33), 130 (80), 64 (100); HRMS (CI, isobutane) calcd for $C_{17}H_{16}N_3O_4S$ $(M + H)^+$ 358.0862, found 358.0858; HPLC (Daicel Chiralpak AD, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) t_R = 162.2 min, t_S = 187.5 min.

***N*-(2-Nitrobenzenesulfonyl)-2-(2-thienylmethyl)aziridine (1h)**

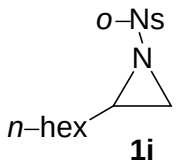


1h

Colorless oil; IR (neat, cm^{-1}) 1545, 1367, 1335, 1167; ^1H NMR (270 MHz, $CDCl_3$) δ = 2.39 (d, 1H, *J* = 4.1 Hz, H-3), 2.93-3.10 (m, 2H, Ar-C<u>H</u>$_2$ and H-3), 3.19-3.30 (m, 2H, Ar-C<u>H</u>$_2$ and H-2), 6.83-6.90 (m, 2H, Ar-<u>H</u>), 7.11

(dd, 1H, *J* = 1.4, 4.9 Hz, Ar-H), 7.60-8.15 (m, 3H, Ar-H), 8.14 (m, 1H, Ar-H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 31.53, 34.95, 42.28, 124.10, 124.25, 125.88, 126.79, 130.93, 131.63, 131.88, 134.16, 137.66, 148.22; MS (EI) *m/z* (relative intensity, %) 324 (M^+, 10), 186 (22), 138 (M^+–*o*-$NsNH_2$, 73), 111 (67), 97 (100); HRMS (CI, isobutane) calcd for $C_{13}H_{13}N_2O_4S_2$ $(M + H)^+$ 325.0318, found 325.0322; HPLC (Daicel Chiralpak AS, hexane/2-propanol, 95:5, 0.25 mL/min, 254 nm) *t* = 188.9 and 193.8 min.

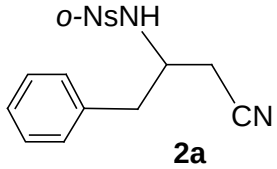
***N*-(2-Nitrobenzenesulfonyl)-2-*n*-hexylaziridine (1i)**



1i

colorless oil; IR (neat, cm^{-1}) 2929, 2858, 1547, 1462, 1367, 1335, 1167; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 0.86 (t, 3H, *J* = 4.6 Hz, *n*-$C_5H_{10}CH_3$), 1.15-1.59 (m, 10H, *n*-$C_5H_{10}CH_3$), 2.29 (d, 1H, *J* = 4.6 Hz, H-3), 2.86-2.88 (d, 1H, *J* = 7.3 Hz, H-3), 2.97-3.06 (m, 1H, H-2), 7.71-7.81 (m, 3H, Ar-H), 8.18-8.22 (m, 1H, Ar-H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 13.94, 22.38, 26.34, 28.61, 31.25, 31.45, 36.01, 42.11, 124.13, 131.01, 131.99, 134.35, 148.45; MS (EI) *m/z* (relative intensity, %); HRMS (CI, isobutane) calcd for $C_{13}H_{13}N_2O_4S_2$ $(M + H)^+$; HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm, 30 ℃) *t* = 26.2 and 30.3 min.

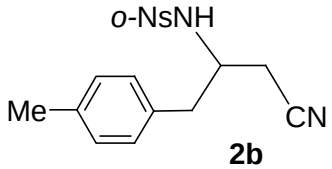
***N*-(2-Cyano-1-benzylethyl)-2-nitrobenzenesulfonamide (2a)**



2a

Pale yellow oil; IR (neat, cm^{-1}) 2252 (CN); ^1H NMR (270 MHz, $CDCl_3$) δ = 2.76-2.86 (m, 3H, C<u>H</u>$_2$CN and C<u>H</u>$_2$Ph), 3.02-3.07 (dd, 1H, C<u>H</u>$_2$Ph, *J* = 3.9, 9.6 Hz), 3.88-3.96 (m, 1H, N-C<u>H</u>), 5.70 (d, 1H, N<u>H</u>, *J* = 4.0 Hz, D_2O exchangeable), 6.99-7.07 (m, 5H, Ph), 7.68-7.79 (m, 3H, Ar-<u>H</u>), 7.97-7.99 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 25.28, 39.83, 53.08, 116.62, 125.83, 127.29, 128.65, 128.82, 130.31, 133.10, 133.27, 133.57, 134.78, 146.94; MS (CI, isobutane) *m/z* (relative intensity, %) 346 ($[M + H]^+$, 100); HRMS (CI, isobutane) *m/z* calcd for $C_{16}H_{16}N_3O_4S$ $(M + H)^+$ 346.0861, found 346.0865; $[\alpha]^{24}_D$ = -43.0 (c = 4.40, $CHCl_3$) (75% ee) HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 7:3, 0.7 mL/min, 254 nm, 30 ℃) t_S = 42.2 min, t_R = 55.8 min.

***N*-[2-Cyano-1-(*p*-tolylmethyl)ethyl]-2-nitrobenzenesulfonamide (2b)**

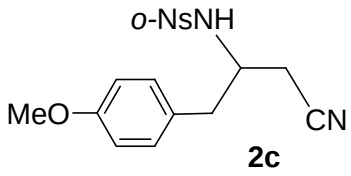


2b

White solid; mp 42-44 °C; IR (KBr, cm^{-1}) 2252 (CN); ^1H NMR (270 MHz, $CDCl_3$) δ = 2.20 (s, 1H, Ar-C<u>H</u>$_3$), 2.70-2.82 (m, 3H, C<u>H</u>$_2$CN and Ar-C<u>H</u>$_2$), 2.97-3.05 (dd, 1H, C<u>H</u>$_2$CN, *J* = 5.2, 14.0 Hz), 3.80-3.90 (m, 1H, N-C<u>H</u>), 5.69 (d, 1H, N<u>H</u>, *J* = 5.2 Hz, D_2O exchangeable), 6.80-6.89 (m, 4H, Ar-<u>H</u>), 7.64-7.80 (m, 3H, Ar-<u>H</u>), 7.93-7.97 (m, 1H,

Ar-H); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 21.08, 25.50, 39.51, 53.32, 116.49, 125.70, 128.63, 129.26, 130.32, 131.48, 132.99, 133.15, 133.43, 136.78, 146.83; MS (EI) *m/z* (relative intensity, %) 359 (M^+, 1), 254 ($M^+CH_2C_6H_4CH_3$, 15), 186 (100), 157 (M^+–*o*-$NsNH_2$, 33), 105 (93); HRMS (CI, isobutane) calcd for $C_{17}H_{17}N_3O_4S$ $(M + H)^+$ 360.1019, found 360.1021; $[\alpha]^{27}_D$ = -65.1 (c = 0.61, $CHCl_3$) (87% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 7:3, 0.5 mL/min, 254 nm) *t* = 43.6 and 61.8 min.

***N*-[2-Cyano-1-(*p*-methoxyphenylmethyl)ethyl]-2-nitrobenzenesulfonamide (2c)**

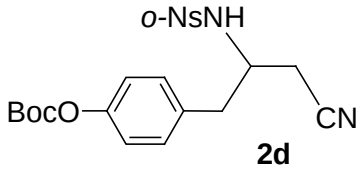


2c

White solid; mp 38-40 °C; IR (KBr, cm^{-1}) 2266 (CN); ^{1}H NMR (270 MHz, $CDCl_3$) δ = 2.69-2.80 (m, 3H, C$\underline{H}_2$CN and Ar-C$\underline{H}_2$), 2.96-3.04 (dd, 1H, *J* = 5.3, 14.1 Hz, C$\underline{H}_2$CN), 3.71 (s, 1H, O-C$\underline{H}_3$), 3.78-3.92 (m, 1H, N-C$\underline{H}$), 5.67 (d, 1H, *J* = 5.3 Hz, N$\underline{H}$, D_2O exchangeable), 6.53 (d, 2H, *J* = 8.4 Hz, Ar-$\underline{H}$), 6.86 (d, 2H, *J* = 8.4 Hz, Ar-$\underline{H}$), 7.63-7.72 (m, 2H, Ar-$\underline{H}$), 7.74-7.81 (m, 1H, Ar-$\underline{H}$), 7.91-7.98 (m, 1H, Ar-$\underline{H}$); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 25.51, 39.07, 53.41, 55.17, 113.93, 116.52, 125.80, 126.48, 129.79, 130.32, 133.01, 133.34, 133.40, 146.80, 158.44; MS (EI) *m/z* (relative intensity, %) 375 (M^+, 2), 186 (7), 173 (M^+–*o*-$NsNH_2$, 2), 121 (100); HRMS (CI,

isobutane) calcd for $C_{17}H_{17}N_3O_5S$ $(M + H)^+$ 376.0968, found 376.0964; $[\alpha]^{28}_D$ = –230.4 (c = 0.909, $CHCl_3$) (80% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 7:3, 0.5 mL/min, 254 nm) *t* = 69.8 and 101.2 min.

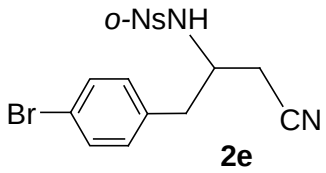
***N*-[2-Cyano-1-(*p-tert*-butoxycarbonyloxyphenylmethyl)ethyl]-2-nitrobenzenesulfon amide (2d)**



2d

Colorless oil; IR (neat, cm^{-1}) 2256 (CN), 1741 (Boc); ^1H NMR (270 MHz, $CDCl_3$) δ = 1.56 (s, 9H, C-($C\underline{H}_3$)$_3$), 2.70-2.87 (m, 3H, $C\underline{H}_2CN$ and Ar-$C\underline{H}_2$), 3.01-3.10 (dd, 1H, *J* = 5.1, 14.3 Hz, $C\underline{H}_2CN$), 3.80-3.95 (m, 1H, N-C<u>H</u>), 5.66 (d, 1H, *J* = 5.9 Hz, N<u>H</u>, D_2O exchangeable), 6.84 (d, 2H, *J* = 8.4 Hz, Ar-<u>H</u>), 6.98 (d, 2H, *J* = 8.4 Hz, Ar-<u>H</u>), 7.63-7.85 (m, 3H, Ar-<u>H</u>,), 7.91-7.98 (m, 1H, Ar-<u>H</u>,); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 25.41, 27.62, 39.16, 52.99, 83.69, 116.27, 121.40, 125.98, 129.54, 129.91, 131.93, 132.71, 132.74, 133.51, 146.86, 149.93, 151.23; MS (CI) *m/z* (relative intensity, %) 362 (M^+ + H –Boc, 100); HRMS (FAB) calcd for $C_{21}H_{24}N_3O_7S$ $(M + H)^+$ 462.1336, found 462.1338; $[\alpha]^{30}_D$ = -56.2 (c = 0.973, $CHCl_3$) (81% ee); HPLC (Daicel Chiralpak IA, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 53.2, 64.2 min.

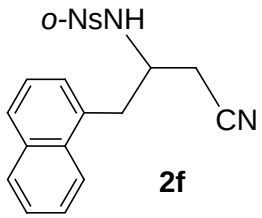
***N*-[2-Cyano-1-(*p*-bromophenylmethyl)ethyl]-2-nitrobenzenesulfonamide (2e)**



2e

White solid; mp 144-145 °C; IR (KBr, cm^{-1}) 2251 (CN); ^{1}H NMR (270 MHz, $CDCl_3$) δ = 2.70-2.85 (m, 3H, C<u>H</u>$_2$CN and Ar-C<u>H</u>$_2$), 2.98-3.01 (dd, 1H, *J* = 4.6, 14.0 Hz, C<u>H</u>$_2$CN,), 3.83-3.98 (m, 1H, N-C<u>H</u>), 5.71 (brs, 1H, N<u>H</u>, D_2O exchangeable), 6.87 (d, 2H, *J* = 8.4 Hz, Ar-<u>H</u>), 7.07 (d, 2H, *J* = 8.4 Hz, Ar-<u>H</u>), 7.76-7.80 (m, 4H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 29.13, 39.38, 53.55, 116.3, 121.36, 125.79,129.99, 130.46, 131.51, 133.01, 133.24, 133.47, 133.92, 146.77; MS (CI, isobutane) *m/z* (relative intensity, %) 426 ($[M+1]^+$, 100), 424 ($[M + H]^+$, 98), 254 (15), 224 ($[M + H]^+$ –*o*-$NsNH_2$, 11), 222 ($[M + H]^+$ –*o*-$NsNH_2$, 10), 186 (31); HRMS (CI, isobutane) *m/z* calcd for $C_{16}H_{15}BrN_3O_4S$ $(M + H)^+$ 423.9968, found 423.9978; $[\alpha]^{31}_D$ = -76.7 (c = 0.64, $CHCl_3$) (86% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 7:3, 0.25 mL/min, 254 nm) *t* = 137.2 and 180.6 min.

***N*-[2-Cyano-1-(1-naphtylmethyl)ethyl]-2-nitrobenzenesulfonamide (2f)**

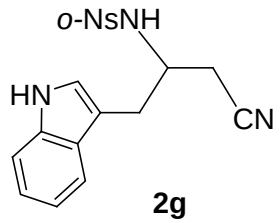


2f

Colorless oil; IR (neat, cm^{-1}) 2251 (CN) ; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 2.80-3.00 (m, 2H, Ar-C<u>H</u>$_2$), 3.09-3.19 (dd, 1H, *J* = 10.3, 14.3 Hz, C<u>H</u>$_2$CN), 3.58-3.70 (dd, 1H, *J* = 4.9, 14.3 Hz

C$\underline{H}_2$CN), 4.06-4.12 (m, 1H, N-C$\underline{H}$), 5.76 (d, 1H, *J* = 5.7 Hz, N$\underline{H}$, D_2O exchangeable), 7.10-7.74 (m, 11 H, Ar-$\underline{H}$); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 26.3, 37.7, 51.8, 116.6, 122.7, 125.1, 125.3, 125.7, 126.6, 128.4, 128.5, 129.0, 129.4, 130.4, 130.7, 132.2, 132.5, 133.0, 133.4, 145.9; MS (EI) *m/z* (relative intensity, %) 395 (M^+, 6), 193 (M^+–*o*-$NsNH_2$, 6), 186 (51), 141 (100); HRMS (CI, isobutane) *m/z* calcd for $C_{20}H_{18}N_3O_4S$ $(M + H)^+$ 396.1019, found 396.1029; $[\alpha]^{31}_D$ = -46.1 (c = 0.84, $CHCl_3$) (82% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 7:3, 0.5 mL/min, 254 nm) *t* = 44.8 and 66.7 min.

***N*-[2-Cyano-1-(1-*H*-3-indolylmethyl)ethyl]-2-nitrobenzenesulfonamide (2g)**

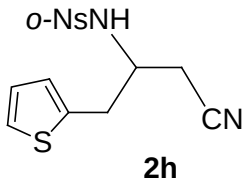


2g

Yellow solid; mp 93-95 °C (decom); IR (KBr, cm^{-1}) 2254 (CN); ^{1}H NMR (270 MHz, CD_3CN) δ = 1.91-3.07 (m, 4H, Ar-C$\underline{H}_2$ and C$\underline{H}_2$CN), 3.88-4.02 (m, 1H, N-C$\underline{H}$), 6.08 (brs, 1H, N$\underline{H}$, D_2O exchangeable), 6.84 (dd, 1H, *J* = 7.6, 7.6 Hz, Ar-$\underline{H}$), 6.96-7.03 (m, 2H, Ar-$\underline{H}$), 7.13 (d, 1H, Ar-$\underline{H}$, *J* = 8.1 Hz), 7.19-7.27 (m, 2H, Ar-$\underline{H}$), 7.38-7.51 (m, 3H, Ar-$\underline{H}$), 8.82 (brs, 1H, N$\underline{H}$, D_2O exchangeable); ^{13}C NMR (68 MHz, CD_3CN) δ = 26.30, 30.49, 52.91, 109.63, 112.38, 118.43, 118.83, 119.82, 122.17, 125.30, 125.63, 127.34, 130.17, 132.89, 133.26, 134.33, 137.04, 146.97; MS (EI) *m/z* (relative intensity, %) 384 (M^+, 3),

186 (2), 182 (M^+–*o*-$NsNH_2$, 2), 130 (100); Anal. Calcd for $C_{18}H_{18}N_4O_4S$: C, 56.24; H, 4.20; N, 14.57. Found: C, 55.96; H, 4.46; N, 14.71.; $[\alpha]^{23}_D$ = –17.3 (c = 0.51, acetone) (75% ee); HPLC (Daicel Chiralpak IA, hexane/2-propanol, 9:1, 0.7 mL/min, 254 nm, 30 °C) t_S = 111.4 min, t_R = 140.3 min.

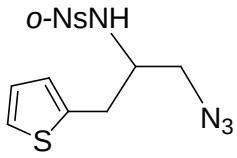
_N_-[2-Cyano-1-(2-thienylmethyl)ethyl]-2-nitrobenzenesulfonamide (2h)



2h

Colorless oil; IR (neat, cm^{-1}) 2251 (CN) ; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 2.78 (d, 2H, *J* = 5.7 Hz), 3.10-3.27 (m, 2H), 3.84-3.96 (m, 1H, N-C<u>H</u>), 5.75 (d, 1H, *J* = 5.9 Hz, N<u>H</u>, D_2O exchangeable), 6.74-6.77 (m, 2H, Ar-<u>H</u>), 6.99 (d, 1H, *J* = 4.9 Hz, Ar-<u>H</u>), 7.70-7.87 (m, 3H, Ar-<u>H</u>), 8.04-8.08 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 24.92, 34.17, 52.88, 116.21, 125.40, 125.85, 127.16, 127.54, 130.50, 133.13, 133.19, 133.68, 136.11, 147.07; MS (EI) *m/z* (relative intensity, %) 351 (M^+, 1), 186 (80), 149 (M^+–*o*-$NsNH_2$, 27), 97 (100); HRMS (CI, isobutane) *m/z* calcd for $C_{14}H_{14}N_3O_4S_2$ $(M + H)^+$ 352.0427, found 352.0432; $[\alpha]^{31}_D$ = –37.6 (c = 0.87, $CHCl_3$) (95% ee); HPLC (Daicel Chiralpak AS, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 82.5 and 108.4 min.

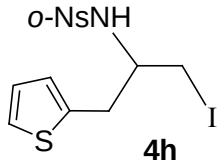
***N*-[2-Azide-1-(2-thienylmethyl)ethyl]-2-nitrobenzenesulfonamide (3h)**



3h

Colorless oil; IR (neat, cm^{-1}) 2108 (N_3); ^1H NMR (270 MHz, $CDCl_3$) δ = 2.97-3.15 (m, 2H), 3.35 (d, 2H, *J* = 5.1 Hz), 3.72-3.88 (m, 1H, N-C<u>H</u>), 5.75 (brs, 1H, N<u>H</u>, D_2O exchangeable), 6.75-6.79 (m, 2H, Ar-<u>H</u>), 7.01 (dd, 1H, *J* = 1.8, 4.9 Hz, Ar-<u>H</u>), 7.63-7.80 (m, 2H, Ar-<u>H</u>), 7.80-7.91 (m, 1H, Ar-<u>H</u>), 8.04-8.09 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 32.81, 54.31, 55.69, 124.89, 125.62, 126.99, 127.02, 130.34, 133.01, 133.38, 134.09, 137.37, 147.20; MS (EI) *m/z* (relative intensity, %); HRMS (CI, isobutane) *m/z* calcd for $C_{13}H_{14}N_5O_4S_2$ $(M + H)^+$ 368.0489, found 368.0482; $[\alpha]^{23}_D$ = –12.0 (c = 1.22, $CHCl_3$) (81% ee); HPLC (Daicel Chiralpak IA, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 46.3 and 54.7 min.

***N*-[2-Iode-1-(2-thienylmethyl)ethyl]-2-nitrobenzenesulfonamide (4h)**

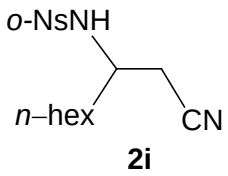


4h

Colorless oil; IR (neat, cm^{-1}) 1167 (CH_2I); ^1H NMR (270 MHz, $CDCl_3$) δ = 3.03-3.21 (m, 2H), 3.30-3.32 (m, 2H), 3.53-3.65 (m, 1H, N-C<u>H</u>), 5.72 (d, 1H, *J* = 7.6 Hz, N<u>H</u>, D_2O exchangeable), 6.75-6.82 (m, 2H, Ar-<u>H</u>), 7.03 (dd, 1H, *J* = 1.4, 4.9 Hz, Ar-<u>H</u>), 7.68-7.77 (m, 2H, Ar-<u>H</u>), 7.80-7.89 (m, 1H, Ar-<u>H</u>), 8.05-8.10 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 11.62, 35.51,

55.27, 124.94, 125.65, 127.02, 130.24, 133.07, 133.45, 134.25, 137.11, 147.24; MS (EI) *m/z* (relative intensity, %); HRMS (CI, isobutane) *m/z* calcd for $C_{13}H_{14}IN_2O_4S_2$ (M + H)$^+$ 452.9441, found 452.9440; $[\alpha]^{23}_D$ = –9.9 (c = 1.64, $CHCl_3$) (82% ee); HPLC (Daicel Chiralpak IA, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 40.8 and 49.2 min

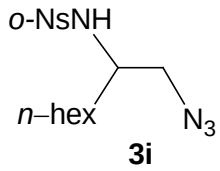
***N*-(1-Cyanooct-2-yl)-2-nitrobenzenesulfonamide (2i)**



2i

Pale yellow oil; IR (neat, cm^{-1}) 2252 (CN); ^{1}H NMR (270 MHz, $CDCl_3$) δ = 0.82 (t, 3H, *J* = 6.2 Hz, *n*-$C_5H_{10}C\underline{H}_3$), 0.88-1.67 (m, 10H, *n*-$C_5\underline{H}_{10}CH_3$), 2.61-2.76 (m, 2H, $C\underline{H}_2CN$), 3.65-3.68 (m, 1H, N-C<u>H</u>), 5.48 (br d, 1H, *J* = 7.3 Hz, N<u>H</u>, D_2Oexchangeable), 7.63-7.93 (m, 3H, Ar-<u>H</u>), 8.09-8.17 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 14.03, 22.42, 25.29, 25.43, 28.43 31.42, 34.07, 51.41, 116.45, 125.52, 130.41, 133.00, 133.85, 147.55; MS (CI, methane) *m/z* (relative intensity, %) 340 ([M + H]$^+$, 100); HRMS (CI, methane) *m/z* calcd for $C_{15}H_{22}N_3O_4S$ (M + H)$^+$ 340.1331, found 340.1328; $[\alpha]^{23}_D$ = –22.2 (c = 1.15, $CHCl_3$) (59% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 57.2 and 72.3 min.

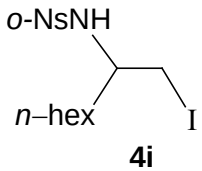
***N*-(1-Azideoct-2-yl)-2-nitrobenzenesulfonamide (3i)**



3i

Pale yellow oil; IR (neat, cm^{-1}) 2104 (N_3); ^1H NMR (270 MHz, $CDCl_3$) δ = 0.84 (t, 3H, *J* = 6.2 Hz, *n*-$C_5H_{10}C\underline{H}_3$), 1.05-1.40 (m, 10H, *n*-$C_5\underline{H}_{10}CH_3$), 3.36-3.38 (m, 2H, $C\underline{H}_2N_3$), 3.53-3.63 (m, 1H, N-C<u>H</u>), 5.41 (br d, 1H, *J* = 8.1 Hz, N<u>H</u>, D_2O exchangeable), 7.72-7.79 (m, 2H, Ar-<u>H</u>), 7.87-7.92 (m, 1H, Ar-<u>H</u>), 8.12-8.17 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 14.07, 22.49, 25.46, 28.74, 31.53, 31.74, 54.60, 55.31, 125.38, 130.25, 132.86, 133.43, 134.75, 147.53; MS (CI, methane) *m/z* (relative intensity, %) 340 ($[M + H]^+$, 100); HRMS (CI, methane) *m/z* calcd for $C_{15}H_{22}N_3O_4S$ $(M + H)^+$ 340.1331, found 340.1328; $[\alpha]^{23}_D$ = –22.2 (c = 1.15, $CHCl_3$) (59% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 57.2 and 72.3 min.

***N*-(1-iodeoct-2-yl)-2-nitrobenzenesulfonamide (4i)**

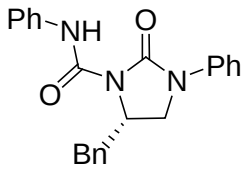


4i

Pale yellow oil; IR (neat, cm^{-1}) 1167 (CH_2I); ^1H NMR (270 MHz, $CDCl_3$) δ = 0.84 (t, 3H, *J* = 6.5 Hz, *n*-$C_5H_{10}C\underline{H}_3$), 1.05-1.30 (m, 10H, *n*-$C_5\underline{H}_{10}CH_3$), 3.24-3.35 (m, 3H, $C\underline{H}_2I$ and N-C<u>H</u>), 5.49 (br d, 1H, , *J* = 7.6 Hz, N<u>H</u>, D_2O exchangeable), 7.75-7.79 (m, 2H, Ar-<u>H</u>), 7.90-7.93 (m, 1H, Ar-<u>H</u>), 8.11-8.17 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 13.02, 13.98, 22.40, 25.17,

28.57, 31.45, 35.46, 54.34, 125.38, 130.03, 132.83, 133.37, 134.86, 147.48; MS (CI, methane) *m/z* (relative intensity, %) 340 ($[M + H]^+$, 100); HRMS (CI, methane) *m/z* calcd for $C_{15}H_{22}N_3O_4S$ $(M + H)^+$ 340.1331, found 340.1328; $[\alpha]^{23}_D$ = –22.2 (c = 1.15, $CHCl_3$) (59% ee); HPLC (Daicel Chiralcel OJ, hexane/2-propanol, 9:1, 0.5 mL/min, 254 nm) *t* = 57.2 and 72.3 min.

5-Benzyl-2-oxo-3-phenylimidazolidine-1-(*N*-phenylcarboxamide) (5)



5

Pale yellow solid; IR (KBr, cm^{-1}) 1722, 1681, 1599, 1556, 1500; ^1H NMR (270 MHz, CD_3CN) δ = 2.92 (dd, 1H, *J* = 8.9, 13.2 Hz), 3.42 (dd, 1H, *J* = 3.1, 13.2 Hz), 3.58 (dd, 1H, *J* = 2.3, 9.6 Hz), 3.92 (dd, 1H, *J* = 9.0, 9.0 H), 4.72-4.80 (m, 1H), 7.05-7.19 (m, 2H), 7.21-7.39 (m, 11H), 7.58 (dd, 2H, *J* = 0.9, 8.5 H), 10.46 (brs, 1H, N<u>H</u>, D_2O exchangeable); ^{13}C NMR (68 MHz, $CDCl_3$) δ = 38.89, 48.01, 52.89, 121.18, 123.39, 123.91, 127.00, 127.31, 127.91, 128.76, 129.14, 129.47, 129.59, 129.67, 130.50, 132.53, 143.26, 135.08, 135.87, 150.15, 155.06; MS (EI) *m/z* (relative intensity, %) 371 (M^+, 14), 186 (80), 161 (100); Anal. ; $[\alpha]^{31}_D$ = +14.8 (c = 0.48, $CHCl_3$) (83% ee); HPLC (Daicel Chiralpak IA, hexane/2-propanol, 95:5, 0.5 mL/min, 254 nm) *t* = 37.0, 62.4 min.

References

1. T. Ando, D. Kano, S. Minakata, I. Ryu, M. Komatsu, *Tetrahedron* 1998, **54**, 13485-13494.

2. G. Li, H.-X. Wei, S. H. Kim, *Tetrahedron* 2001, **57**, 8407-8411.