Supporting Information

Et₃B-Induced Radical Addition of *N,N*-Dichlorosulfonamide to Alkenes and Pyrrolidine Formation via Radical Annulation

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Table of Contents

Instrumentation and Materials	S2
General Procedures	
Radical Addition of <i>N,N</i> -Dichlorobenzenesulfonamide to 1,3-Dienes	S2
Radical Annulation of Chloroamide 6 with Alkenes	S2
Compound Data	S3

Instrumentation and Materials

^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken in CDCl_3 as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merk Silica gel 60F₂₅₄. Column chromatography was done with silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Triethylborane was purchased from Aldrich and used for reactions as a hexane solution (1.0 M). Benzene and toluene were dried over slices of sodium. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Radical Addition of *N,N*-Dichlorobenzenesulfonamide to 1,3-Dienes

A solution of triethylborane (0.05 mL, 1.0 M hexane solution, 0.05 mmol) was added dropwise to a solution of *N,N*-dichlorobenzenesulfonamide (**1**) (226 mg, 1.0 mmol) and 1,3-butadiene (2.0 mmol) in toluene (5 mL) at $-78\text{ }^\circ\text{C}$. After stirring for 1 h, the solvent was removed under reduced pressure. Purification of the residue by chromatography afforded *N*-(4-chloro-2-butenyl)-*N*-chlorobenzenesulfonamide (**6a**, 266 mg, 0.95 mmol) in 95% yield.

Radical Annulation of Chloroamide **6** with Alkenes

A solution of triethylborane (0.05 mL, 1.0 M hexane solution, 0.05 mmol) was added dropwise to a solution of chloroamide **6a** (140 mg, 0.5 mmol) and styrene (0.11 mL, 1.0 mmol) in benzene (4.0 mL) at room temperature. After stirring for 3 h, the solvent was removed under reduced pressure.

Purification of the residual oil by chromatography afforded 3-(1,2-dichloroethyl)-4-phenyl-1-benzenesulfonylpyrrolidine **8a**, (184 mg, 0.48 mmol) in 96% yield.

Compound Data

***N*-Benzenesulfonyl-3-phenyl-4-vinylpyrrolidine (9a, 76/24 diastereomeric mixture):**

IR (neat) 3030, 2887, 1643, 1603, 1497, 1479, 1346, 1167, 1092, 1030 cm^{-1} ; ^1H NMR (CDCl_3) For major isomer δ 2.73–2.80 (m, 1H), 2.87–3.00 (m, 1H), 3.17 (t, $J = 9.9$ Hz, 1H), 3.31 (t, $J = 9.9$ Hz, 1H), 3.74 (ddd, $J = 7.8, 9.9, 12.9$ Hz, 2H), 4.85–4.96 (m, 2H), 5.52 (ddd, $J = 7.2, 9.9, 17.7$ Hz, 1H), 7.06–7.09 (m, 2H), 7.19–7.30 (m, 3H), 7.55–7.67 (m, 3H), 7.86–7.93 (m, 2H); ^{13}C NMR (CDCl_3) For major isomer δ 49.75, 50.18, 52.74, 54.55, 117.46, 127.26, 127.48, 128.66, 129.16, 132.79, 134.82, 135.59, 136.96, 138.53. Found: C, 68.60; H, 6.17%. Calcd for $\text{C}_{18}\text{H}_{19}\text{SO}_2\text{N}$: C, 68.98; H, 6.11%.

***N*-Benzenesulfonyl-3-methyl-4-phenyl-3-vinylpyrrolidine (9b, 87/13 diastereomeric mixture):**

IR (neat) 3062, 3030, 2885, 1639, 1602, 1585, 1481, 1446, 1346, 1164, 1096 cm^{-1} ; ^1H NMR (CDCl_3) For major isomer δ 0.67 (s, 3H), 3.06 (t, $J = 8.7$ Hz, 1H), 3.34 (dd, $J = 9.9, 15.6$ Hz, 2H), 3.73 (dd, $J = 1.2, 8.7$ Hz, 2H), 4.84 (dd, $J = 0.6, 10.8$ Hz, 1H), 5.01 (dd, $J = 0.6, 10.8$ Hz, 1H), 5.71 (dd, $J = 10.8, 18.0$ Hz, 1H), 7.00–7.03 (m, 2H), 7.21–7.26 (m, 3H), 7.55–7.68 (m, 3H), 7.90–7.93 (m, 2H); ^{13}C NMR (CDCl_3) For major isomer δ 17.99, 47.69, 50.65, 52.69, 58.79, 114.37, 127.21, 127.35, 128.12, 128.37, 129.15, 132.74, 136.45, 137.26, 142.53. Found: C, 69.74; H, 6.28%. Calcd for $\text{C}_{19}\text{H}_{21}\text{SO}_2\text{N}$: C, 69.69; H, 6.46%.

***N*-Benzenesulfonyl-3-phenyl-4-(1-undecenyl)pyrrolidine (9c):**

IR (neat) 2926, 2855, 1447, 1350, 1167, 1092 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, J = 7.2 Hz, 3H), 1.00–1.32 (m, 14H), 1.80–1.86 (m, 2H), 2.67–2.75 (m, 1H), 2.82–2.91 (m, 1H), 3.11 (t, J = 9.9 Hz, 1H), 3.30 (t, J = 10.5 Hz, 1H), 3.71 (ddd, J = 7.5, 10.5, 17.7 Hz, 2H), 5.07 (dd, J = 7.5, 15.6 Hz, 1H), 5.25 (dt, J = 6.3, 15.6 Hz, 1H), 7.04–7.07 (m, 2H), 7.17–7.29 (m, 3H), 7.54–7.65 (m, 3H), 7.86–7.90 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.11, 22.66, 28.84, 29.05, 29.29, 29.40, 29.51, 31.87, 32.34, 48.99, 50.45, 53.23, 54.43, 127.00, 127.08, 127.47, 127.53, 128.54, 129.12, 132.72, 133.99, 136.98, 138.80. Found: C, 73.49; H, 8.59%. Calcd for $\text{C}_{27}\text{H}_{37}\text{SO}_2\text{N}$: C, 73.76; H, 8.48%.

***N*-Benzenesulfonyl-3-(1,11-dodecadienyl)-4-phenylpyrrolidine (9d):**

IR (neat) 2925, 2854, 1639, 1446, 1350, 1166, 1092 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.00–1.40 (m, 12H), 1.84 (dt, J = 6.3, 6.9 Hz, 2H), 2.03 (dt, J = 7.2, 7.2 Hz, 2H), 2.67–2.76 (m, 1H), 2.82–2.92 (m, 1H), 3.11 (t, J = 9.9 Hz, 1H), 3.30 (t, J = 9.9 Hz, 1H), 3.72 (ddd, J = 7.8, 10.2, 18.0 Hz, 2H), 4.91–5.04 (m, 2H), 5.08 (dd, J = 7.2, 15.3 Hz, 1H), 5.26 (dt, J = 15.3, 6.3 Hz, 1H), 5.81 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 7.06 (d, J = 6.6 Hz, 2H), 7.18–7.28 (m, 3H), 7.55–7.69 (m, 3H), 7.88 (d, J = 7.7 Hz, 2H); ^{13}C NMR (CDCl_3) δ 28.82, 28.90, 29.04, 29.08, 29.31, 29.36, 32.33, 33.77, 48.98, 50.46, 53.23, 54.43, 114.11, 127.04, 127.09, 127.48, 127.53, 128.55, 129.12, 132.72, 133.96, 137.04, 138.82, 139.19. Found: C, 74.76; H, 8.54%. Calcd for $\text{C}_{28}\text{H}_{37}\text{SO}_2\text{N}$: C, 74.46; H, 8.26%.

***N*-Benzenesulfonyl-3-trimethylsilylmethyl-4-vinylpyrrolidine (9h, 53/47 diastereomeric mixture):**

IR (neat) 3071, 2953, 2895, 1641, 1479, 1447, 1421, 1348, 1249, 1165, 1094 cm^{-1} ; ^1H NMR (CDCl_3) δ -0.07 (d, J = 0.6 Hz, 4.5H), -0.06 (d, J = 0.6 Hz, 4.5H), 0.13–0.26 (m, 1H), 0.48 (dd, J = 4.8, 14.7 Hz,

0.5H), 0.75 (dd, $J = 3.0, 14.7$ Hz, 0.5H), 1.58–1.68 (m, 0.5H), 2.05–2.15 (m, 1H), 2.57–2.65 (m, 0.5H), 2.74 (t, $J = 9.9$ Hz, 0.5H), 2.85 (t, $J = 9.0$ Hz, 0.5H), 2.99 (t, $J = 9.9$ Hz, 0.5H), 3.24 (dd, $J = 3.6, 9.9$ Hz, 0.5H), 3.37–3.52 (m, 1.5H), 3.61 (dd, $J = 7.5, 9.9$ Hz, 0.5H), 4.88–5.06 (m, 2H), 5.31–5.47 (m, 1H), 7.51–7.61 (m, 3H), 7.81–7.85 (m, 2H); ^{13}C NMR (CDCl_3) δ –1.12, 15.34, 18.10, 38.42, 40.89, 47.38, 51.99, 52.19, 52.68, 53.28, 54.64, 117.15, 117.73, 127.33, 127.34, 129.02, 129.05, 132.56, 132.61, 135.29, 136.54, 137.15. Found: C, 59.47; H, 7.60%. Calcd for $\text{C}_{16}\text{H}_{25}\text{SO}_2\text{NSi}$: C, 59.40; H, 7.79%.

***N*-Benzenesulfonyl-3-vinyl-1,2,3,3a,8,8a-hexahydro-1-azacyclopentia[*a*]indene (9i, 70/30 diastereomeric mixture):**

IR (nujol) 2929, 2855, 1447, 1340, 1159, 1094 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.60–2.70 (m, 0.3H), 2.78–2.88 (m, 0.7H), 3.02–3.11 (m, 1H), 3.28–3.44 (m, 2.7H), 3.51–3.58 (m, 1H), 3.80 (t, $J = 7.5$ Hz, 0.3H), 4.35–4.42 (m, 0.7H), 4.49–4.55 (m, 0.3H), 4.95–5.11 (m, 2H), 5.47 (ddd, $J = 8.1, 10.2, 18.0$ Hz, 0.7H), 5.74 (ddd, $J = 8.1, 10.2, 18.0$ Hz, 0.3H), 7.10–7.22 (m, 4H), 7.53–7.68 (m, 3H), 7.86–7.91 (m, 2H); ^{13}C NMR (CDCl_3) δ 40.68, 40.75, 46.42, 48.70, 52.39, 53.98, 54.86, 55.63, 63.85, 64.26, 116.72, 117.33, 123.56, 124.97, 125.19, 126.02, 126.22, 126.82, 127.30, 127.56, 127.65, 127.75, 129.05, 129.17, 132.70, 132.75, 135.15, 136.79, 137.21, 138.52, 139.15, 141.49, 141.86, 143.04. Found: C, 70.09; H, 6.01%. Calcd for $\text{C}_{19}\text{H}_{19}\text{SO}_2\text{N}$: C, 70.13; H, 5.88%

***N*-Benzenesulfonyl-2-methyl-3-phenyl-4-vinylpyrrolidine (9j, 77/23 diastereomeric mixture):**

IR (neat) 3064, 3030, 2900, 1643, 1602, 1496, 1446, 1348, 1166, 1092 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.38 (d, $J = 6.0$ Hz, 2.31H), 1.50 (d, $J = 6.3$ Hz, 0.69H), 2.22–2.35 (m, 1H), 2.59 (dd, $J = 8.7, 11.1$ Hz, 0.77H), 2.88–2.96 (m, 0.23H), 3.04–3.70 (m, 3H), 3.87 (dd, $J = 7.5, 11.1$ Hz, 0.77H), 3.94–4.02 (m,

0.23H), 4.73–4.92 (m, 2.23H), 5.44 (ddd, $J = 7.2, 10.5, 17.4$ Hz, 0.77H), 6.55 (d, $J = 6.9$ Hz, 0.46H), 6.85 (dd, $J = 1.5, 7.2$ Hz, 1.54H), 7.03–7.27 (m, 3H), 7.58–7.71 (m, 3H), 7.92–7.96 (m, 2H); ^{13}C NMR (CDCl_3) For major isomer δ 20.68, 49.00, 53.41, 60.15, 63.86, 117.34, 127.31, 127.47, 127.84, 128.69, 129.19, 129.23, 132.79, 135.08, 138.27. Found: C, 69.49; H, 6.41%. Calcd for $\text{C}_{19}\text{H}_{21}\text{SO}_2\text{N}$: C, 69.69; H, 6.46%.

***N*-Benzenesulfonyl-3-butyl-4-vinylpyrrolidine (9k, 53/47 diastereomeric mixture):**

IR (neat) 3070, 2929, 2858, 1641, 1446, 1346, 1166, 1094 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80–0.87 (m, 3H), 0.96–1.30 (m, 5.5H), 1.41–1.46 (m, 0.5H), 1.67–1.75 (m, 0.5H), 1.98–2.06 (m, 0.5H), 2.16–2.28 (m, 0.5H), 2.63–2.72 (m, 0.5H), 2.85 (t, $J = 9.6$ Hz, 0.5H), 2.92–3.03 (m, 1H), 3.23 (dd, $J = 3.6, 9.9$ Hz, 0.5H), 3.37–3.59 (m, 2H), 4.92–5.04 (m, 2H), 5.34–5.56 (m, 1H), 7.51–7.65 (m, 3H), 7.82–7.86 (m, 2H); ^{13}C NMR (CDCl_3) δ 13.88, 13.92, 22.64, 22.69, 27.88, 30.06, 30.11, 31.16, 42.40, 44.26, 45.44, 49.22, 51.55, 52.47, 52.70, 53.26, 116.80, 117.19, 127.33, 127.40, 129.00, 129.02, 132.55, 132.60, 135.06, 137.01. Found: C, 65.25; H, 7.80%. Calcd for $\text{C}_{16}\text{H}_{23}\text{SO}_2\text{N}$: C, 65.49; H, 7.90%.

***N*-Benzenesulfonyl-3,3-diethyl-4-vinylpyrrolidine (9l):**

IR (neat) 2966, 2939, 2882, 1447, 1346, 1161, 1097 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.69 (t, $J = 7.5$ Hz, 3H), 0.73 (t, $J = 7.5$ Hz, 3H), 0.98–1.36 (m, 4H), 2.45 (q, $J = 8.4$ Hz, 1H), 3.05–3.18 (m, 3H), 3.43–3.55 (m, 1H), 4.92–5.01 (m, 2H), 5.50 (ddd, $J = 8.7, 10.5, 16.8$ Hz, 1H), 7.53–7.64 (m, 3H), 7.80–7.86 (m, 2H); ^{13}C NMR (CDCl_3) δ 8.19, 8.31, 23.59, 26.79, 47.46, 50.08, 51.58, 55.32, 116.94, 127.27, 128.96, 132.56, 135.40, 136.95. Found: C, 65.22; H, 7.90%. Calcd for $\text{C}_{16}\text{H}_{23}\text{SO}_2\text{N}$: C, 65.49; H, 7.90%.

***N*-Benzenesulfonyl-3-vinyl-2,3,3a,8a-tetrahydro-1*H*-8-oxa-1-azacyclopentia[*a*]indene (9m,**

52/48 diastereomeric mixture):

IR (neat) 2876, 1643, 1595, 1479, 1462, 1447, 1348, 1202, 1165, 1096 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.77 (dd, $J = 9.6, 11.4$ Hz, 0.5H), 2.90–2.96 (m, 0.5H), 3.17 (dd, $J = 6.0, 9.9$ Hz, 0.5H), 3.10–3.30 (m, 0.5H), 3.47 (dd, $J = 2.1, 9.6$ Hz, 0.5H), 3.67 (dd, $J = 6.9, 10.2$ Hz, 0.5H), 3.91 (d, $J = 6.9$ Hz, 0.5H), 4.15 (t, $J = 7.8$ Hz, 0.5H), 5.12–5.23 (m, 2H), 5.64 (ddd, $J = 8.4, 9.9, 17.7$ Hz, 0.5H), 5.87 (ddd, $J = 7.8, 10.2, 17.7$ Hz, 0.5H), 6.44 (d, $J = 6.3$ Hz, 1H), 6.53 (d, $J = 6.6$ Hz, 0.5H), 6.64 (t, $J = 7.5$ Hz, 0.5H), 6.81 (t, $J = 7.5$ Hz, 0.5H), 6.87 (t, $J = 7.2$ Hz, 0.5H), 7.06–7.15 (m, 2H), 7.46–7.60 (m, 3H), 7.95–8.00 (m, 2H); ^{13}C NMR (CDCl_3) δ 47.02, 48.73, 49.61, 50.55, 51.10, 52.77, 95.34, 95.85, 109.32, 109.69, 116.15, 118.79, 120.54, 121.35, 122.70, 124.14, 126.43, 126.62, 127.66, 127.70, 128.78, 128.98, 129.09, 132.72, 133.48, 137.68, 139.41, 139.61, 158.49, 159.45. Found: C, 65.78; H, 5.40%. Calcd for $\text{C}_{18}\text{H}_{17}\text{SO}_3\text{N}$: C, 66.03; H, 5.23%

***N*-Benzenesulfonyl-3-methyl-3-phenyl-4-vinylpyrrolidine (9n, 72/28 diastereomeric mixture):**

IR (nujol) 2854, 1340, 1161, 1094 cm^{-1} ; ^1H NMR (CDCl_3) For major isomer δ 1.12 (s, 3H), 2.94 (ddd, $J = 7.8, 8.1, 9.6$ Hz, 1H), 3.31 (dd, $J = 9.6, 9.9$ Hz, 1H), 3.52 (s, 2H), 3.58 (dd, $J = 8.1, 9.9$ Hz, 1H), 4.98 (d, $J = 16.5$ Hz, 1H), 5.08 (d, $J = 9.9$ Hz, 1H), 5.61 (ddd, $J = 7.8, 9.9, 16.5$ Hz, 1H), 7.20–7.31 (m, 5H), 7.53–7.63 (m, 3H), 7.86–7.89 (m, 2H); ^{13}C NMR (CDCl_3) For major isomer δ 20.85, 47.73, 50.95, 51.58, 60.59, 118.42, 125.77, 126.65, 127.31, 128.42, 129.11, 132.71, 133.84, 137.05, 144.32. Found: C, 69.78; H, 6.51%. Calcd for $\text{C}_{19}\text{H}_{21}\text{SO}_2\text{N}$: C, 69.69; H, 6.46%.

***N*-Benzenesulfonyl-3-ethoxy-4-vinylpyrrolidine (9o, 78/22 diastereomeric mixture):**

IR (neat) 2978, 2885, 1641, 1447, 1346, 1167, 1096 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.92 (t, J = 6.9 Hz, 0.66H), 1.01 (t, J = 6.9 Hz, 2.34H), 2.68–2.76 (m, 1H), 3.12–3.55 (m, 6H), 3.65 (q, J = 4.5 Hz, 0.78H), 3.76 (q, J = 2.7 Hz, 0.22H), 5.03–5.12 (m, 2H), 5.59 (ddd, J = 7.5, 10.5, 17.4 Hz, 0.78H), 5.75 (ddd, J = 7.5, 10.5, 17.4 Hz, 0.22H), 7.50–7.65 (m, 3H), 7.81–7.86 (m, 2H); ^{13}C NMR (CDCl_3) For major isomer δ 15.25, 47.88, 50.54, 51.64, 64.92, 81.85, 116.96, 127.41, 128.86, 132.55, 135.79, 136.46. Found: C, 59.69; H, 6.91%. Calcd for $\text{C}_{14}\text{H}_{19}\text{SO}_3\text{N}$: C, 59.76; H, 6.81%.

2-[2-(*N*-Benzenesulfonyl-4-phenylpyrrolidin-3-yl)-2-chloroethyl]-2-chloromalonacid Dimethyl ester (8g):

^1H NMR (CDCl_3) δ 2.35–2.74 (m, 3H), 3.13–3.44 (m, 3H), 3.62–3.84 (m, 8H), 4.05–4.21 (m, 1H), 7.08–7.17 (m, 2H), 7.21–7.35 (m, 3H), 7.56–7.79 (m, 3H), 7.85–7.94 (m, 2H); ^{13}C NMR (CDCl_3) δ 43.30, 43.63, 44.51, 45.60, 46.12, 46.91, 48.36, 48.54, 50.17, 50.96, 52.05, 52.75, 54.03, 54.08, 54.16, 54.63, 55.54, 55.64, 56.37, 56.80, 67.87, 68.07, 68.15, 127.19, 127.38, 127.43, 127.56, 127.68, 128.22, 128.56, 128.91, 128.99, 129.12, 129.29, 132.88, 132.94, 135.80, 136.36, 137.00, 137.72, 138.01, 139.65, 165.97, 166.16, 166.34, 166.38, 166.45. We could not obtain an analytically pure sample.