A typical procedure for the rearrangement and characterization data for the new compounds

Aza-pinacol rearrangement: acid-catalyzed rearrangement of aziridines to imines

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The following is a typical procedure of the rearrangement. The compound numbers given here are the same as those appeared in the text.

To a solution of 150 mg (0.59 mmol) of **1a** in 5 ml of $CHCl_3$ was added 21 μl (0.18 mmol) of BF_3•Et_2O under argon. The mixture was stirred for 2 h at room temperature and poured into aqueous $NaHCO_3$. The organic layer was separated, washed with water, dried over K_2CO_3, and evaporated. The residue was chromatographed on a column of silica gel (20 g). Elution with hexane/AcOEt (6:1) gave 77 mg (51%) of the imine **2a** and then elution with hexane/AcOEt (3:1) gave 36 mg (24%) of the *N*-allyl sulfonamide **3a**. Further elution with hexane/AcOEt (2:1) afforded 16 mg (16%) of *p*-toluenesulfonamide.

The following are characterization data (mp, ^1H and ^{13}C NMR, IR, and HRMS spectra, and elemental analyses) for the new compounds **1**–**4** and **7**–**10**.

Aziridine 1a: Colorless plates (hexane), mp 84–85 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 12H), 2.42 (s, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.2, 21.5, 53.0, 126.8, 129.3, 140.0, 143.0; IR (KBr) 3012, 2972, 2936, 1598, 1472, 1444, 1380, 1316, 1288, 1180, 1152, 1088, 1042, 930, 810, 708 cm^{-1}. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.68; H, 7.58; N, 5.45.

Aziridine 1b: Colorless plates (hexane/CH_2Cl_2), mp 163–165 °C decomp.; ^1H NMR (200 MHz, $CDCl_3$) δ 1.35 (s, 6H), 2.44 (s, 3H), 7.20–7.35 (m, 8H), 7.47-7.51 (m, 4H), 7.94 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.6, 21.7, 53.1, 64.5, 127.3, 127.7, 128.1, 128.4, 129.5, 139.0, 139.1, 143.7; IR (KBr) 3028, 2996, 2932, 1600, 1496,

1446, 1314, 1304, 1292, 1156, 1090, 952, 890, 706 cm^{-1}. Anal. Calcd for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71. Found: C, 73.02; H, 6.12; N, 3.56.

Aziridine 1c: Colorless plates (hexane), mp 120–121 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 6H), 1.64–1.88 (m, 12H), 2.20 (s, 2H), 2.42 (s, 3H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.0, 21.5, 26.5, 26.9, 31.7, 35.5, 36.4, 36.6, 52.8, 64.8, 127.4, 129.2, 139.5, 143.1; IR (KBr) 3008, 2920, 2868, 2848, 1608, 1480, 1456, 1446, 1372, 1306, 1228, 1212, 1182, 1146, 854, 776 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NO_2S$: C, 69.53; H, 7.88; N, 4.05. Found: C, 69.60; H, 7.91; N, 3.93.

Aziridine 1e: Colorless crystals (hexane), mp 128–130 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (d, *J* = 5.4 Hz, 3H), 2.41 (s, 3H), 3.86 (q, *J* = 5.4 Hz, 1H), 7.22–7.37 (m, 12H), 7.68 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.5, 21.6, 44.8, 61.9, 127.4, 127.7, 128.0, 128.1, 128.5, 129.4, 130.4, 136.4, 137.0, 138.8, 143.7; IR (KBr) 3032, 2988, 2928, 1598, 1496, 1452, 1314, 1174, 1162, 1154, 1092, 940, 758, 702 cm^{-1}. Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found: C, 72.72; H, 5.82; N, 3.85.

Aziridine 1f: Colorless crystals (hexane/CH_2Cl_2), mp 131–133 °C partly decomp.; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (d, *J* = 5.9 Hz, 3H), 1.59–2.04 (m, 12H), 2.41 (broad s, 2H), 2.43 (s, 3H), 2.92 (q, *J* = 5.9 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.5, 21.4, 26.9, 27.1, 33.0, 33.7, 35.0, 35.6, 36.0, 36.7, 37.8, 47.6, 65.2, 127.1, 129.3, 138.5, 143.3; IR (KBr) 3000, 2900, 2860, 1596, 1450, 1314, 1302, 1288, 1156, 1132, 1090, 1068, 984, 960, 934, 750 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23. Found: C, 68.93; H, 7.64; N, 4.20.

Aziridine 1h: Colorless crystals (hexane), mp 126–129 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.78–2.02 (m, 12H), 2.22–2.28 (m, 2H), 2.40 (s, 2H), 2.44 (s, 3H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.6, 26.8, 27.1, 35.1, 35.4, 37.0, 37.1, 40.9, 62.2, 127.4, 129.4, 137.9, 143.6; IR (KBr) 2900, 2848, 1454, 1306, 1290, 1256, 1156, 1122, 1100, 1088, 974, 876, 806, 744 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO_2S$: C, 68.10; H, 7.30; N, 4.41. Found: C, 68.07; H, 7.41; N, 4.24.

Imine 2a: Colorless needles (hexane), mp 86–87 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (s, 9H), 2.43 (s, 3H), 2.55 (s, 3H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.6, 21.5, 27.2, 43.1, 126.9. 129.3, 138.8, 143.2, 195.2; IR (KBr) 2968, 2928, 1610, 1428, 1370, 1304, 1300, 1160, 1144, 1096, 812, 766 cm^{-1}. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.69; H, 7.61; N, 5.47.

Imine 2b: Colorless crystals (hexane/CH_2Cl_2), mp 123–125 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.84 (s, 3H), 2.42 (s, 3H), 2.45 (s, 3H), 7.17–7.38 (m, 12H), 7.78 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5, 23.2, 27.9, 60.4, 126.9, 127.1, 128.4, 128.5, 129.3, 138.7, 143.3, 143.6, 191.4; IR (KBr) 3056, 2984, 2936, 1608, 1496, 1452, 1316, 1300, 1148, 1090, 1074, 1030, 868, 772, 702 cm^{-1}. Anal. Calcd for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71. Found: C, 73.15; H, 6.19; N, 3.63.

Imine 2c: Colorless needles (hexane), mp 139–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 3H), 1.58–2.08 (m, 14H), 2.42 (s, 3H), 2.55 (s, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.7, 21.5, 23.9, 27.0, 27.1, 32.7, 33.3, 34.6, 38.0, 51.8, 126.7, 129.3, 139.0, 143.1, 195.9; IR (KBr) 2920, 2864, 1610, 1454, 1424, 1374, 1306, 1212, 1146, 1090, 990, 854, 734 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NO_2S$: C, 69.53; H, 7.88; N, 4.05. Found: C, 69.34; H, 7.91; N, 4.01.

Imine 2f: Colorless crystals (hexane), mp 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49–1.91 (m, 12H), 2.31 (broad s, 2H), 2.43 (s, 3H), 2.55 (s, 3H), 2.58 (broad s, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5, 22.4, 27.5, 27.6, 29.8, 32.5, 37.4, 38.7, 56.4, 126.8, 129.4, 139.0, 143.2, 191.2; IR (KBr) 3064, 2908, 2852, 1614, 1574, 1456, 1368, 1354, 1304, 1206, 1146, 1094, 816, 730, 716 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23. Found: C, 68.57; H, 7.60; N, 4.08.

Imine 2f': Colorless crystals (hexane), mp 104–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 3H), 1.62–2.03 (m, 14H), 2.47 (s, 3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 8.54 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.8, 22.4, 26.8, 27.1, 31.9, 33.7, 34.5, 37.7, 46.3, 127.6, 129.8, 134.1, 144.6, 186.6; IR (KBr) 2984, 2916, 2856, 1628, 1454, 1322, 1292, 1158, 1092, 816, 782, 718, 674 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23. Found: C, 68.50; H, 7.58; N, 4.29.

***N*-Allyl sulfonamide 3a**: Colorless crystals (hexane), mp 57–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55–1.58 (m, 9H), 2.43 (s, 3H), 3.53 (d, *J* = 5.9 Hz, 2H), 4.28 (t, *J* = 5.9 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.9, 20.0, 20.7, 21.5, 45.9, 122.6, 127.1, 129.5, 130.6, 137.1, 143.2; IR (KBr) 3280, 3052, 2920, 2864, 1598, 1456, 1416, 1318, 1290, 1158, 1094, 1048, 1032, 882, 822, 722 cm^{-1}. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.59; H, 7.57; N, 5.46.

Ketone 4f: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60–1.91 (m, 12H), 2.14 (s, 3H), 2.38 (broad s, 2H), 2.49 (broad s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.5,

27.6, 29.2, 33.3, 37.2, 38.3, 57.7, 211.0; IR (neat) 2904, 2852, 1706, 1454, 1352, 1258, 1188, 1168, 1100, 952 cm^{-1}; HRMS calcd for $C_{12}H_{18}O$ (M^+) 178.1358, found 178.1365.

Cycloadduct 7: Colorless needles (hexane/Et_2O), mp 97–98 °C partly decomp.; ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 3H), 1.49–1.93 (m, 19H), 2.13 (broad d, *J* = 13.4 Hz, 1H), 2.40 (s, 3H), 3.39 (broad d, *J* = 18.5 Hz, 1H), 3.86 (broad d, *J* = 18.5 Hz, 1H), 4.26-4.31 (m, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.8, 18.8, 21.5, 27.6, 28.0, 28.3, 29.4, 29.5, 31.3, 31.6, 38.1, 38.9, 39.2, 43.0, 44.7, 51.4, 120.9, 123.0, 126.9, 129.2, 138.3, 142.7; IR (KBr) 2988, 2908, 2844, 1598, 1456, 1440, 1350, 1340, 1160, 1138, 1090, 1024, 918, 816, 756, 684 cm^{-1}. Anal. Calcd for $C_{24}H_{33}NO_2S$: C, 72.14; H, 8.32; N, 3.51. Found: C, 71.92; H, 8.38; N, 3.41.

Fluoride 8: Colorless crystals (hexane), mp 114–116 °C, ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 6H), 1.33 (d, J_{HF} = 22.2 Hz, 6H), 2.42 (s, 3H), 4.92 (s, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.5, 22.2 (d, $^3J_{CF}$ = 3.8 Hz), 22.3 (d, $^2J_{CF}$ = 24.6 Hz), 61.6 (d, $^2J_{CF}$ = 20.0 Hz), 100.1 (d, $^1J_{CF}$ = 172.5 Hz), 127.1, 129.5, 140.1, 143.0; IR (KBr) 3268, 2992, 2948, 1456, 1432, 1400, 1376, 1318, 1312, 1152, 1096, 940, 858, 664 cm^{-1}; Anal. Calcd for $C_{13}H_{20}FNO_2S$: C, 57.12; H, 7.37; N, 5.12. Found: C, 57.40; H, 7.41; N, 4.97.

***N*-Allyl sulfonamide 9**: Colorless crystals (hexane), mp 73–75 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 6H), 1.65 (s, 3H), 2.42 (s, 3H), 4.57 (s, 1H), 4.80 (s, 1H), 4.95 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.7, 21.5, 27.3, 59.4, 111.6, 127.2, 129.3, 139.9, 142.9, 148.5; IR (KBr) 3288, 3096, 2984, 2924, 1600, 1430, 1404, 1324, 1290, 1166, 1144, 1094, 996, 814, 664 cm^{-1}. Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53. Found: C, 61.48; H, 7.62; N, 5.38.

Aminoalcohol 10: Colorless crystals (hexane/CH_2Cl_2), mp 163–165 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 6H), 2.43 (s, 3H), 2.75 (s, 1H), 5.19 (broad s, 1H), 7.23–7.28 (m, 8H), 7.48–7.51 (m, 4H), 7.72 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.5, 24.1, 63.0, 82.9, 127.3, 127.4, 127.7, 128.6, 129.5, 140.0, 143.1, 143.8; IR (KBr) 3504, 3328, 3064, 3024, 2996, 1598, 1450, 1410, 1392, 1330, 1184, 1148, 1050, 816, 708, 664 cm^{-1}. Anal. Calcd for $C_{23}H_{25}NO_3S$: C, 69.85; H, 6.37; N, 3.54. Found: C, 69.68; H, 6.36; N, 3.44.