

Preparation of Amidosulfones

To a solution of methyl phenyl sulfone in THF under an argon atmosphere at 0 °C was added dropwise *n*-BuLi (1.4M in hexane, 2 equiv), and the mixture was stirred for 0.5 h. To this mixture was added dropwise a solution of the carbamate (1 equiv) in THF, and the mixture was stirred at 0 °C for 0.5 h and then at ambient temperature for 6 h. The reaction was quenched with water, the mixture was extracted with EtOAc (twice), and the extract was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed on silica gel, eluting with EtOAc-hexanes, to give pure amidosulfone.

Alkylation of Amidosulfones

To a solution of the amidosulfone in THF under an argon atmosphere at 0 °C was added solid potassium *tert*-butoxide (1 equiv), and the mixture was stirred for 40 min. To this mixture at 0 °C was added solid tetra-*n*-butylammonium iodide (1 equiv) followed by the alkyl bromide (2 equiv), and the mixture was allowed to warm to ambient temperature and stirred for 8 h. The reaction was quenched with saturated, aqueous NaHCO_3 , and the mixture was extracted with EtOAc (twice). The extract was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*, and the residue was chromatographed on silica gel, eluting with EtOAc-hexanes, to give the pure alkylated amidosulfone.

Reductive Desulfonylation of Alkylated Amidosulfones.

(a) With SmI_2

To a stirred solution of the alkylated amidosulfone in anhydrous THF-MeOH (3:1) under an argon atmosphere at -78 °C was added dropwise SmI_2 (0.1M in THF, 0.56 equiv). The color of the solution

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changed immediately from dark blue to green, and the reaction was then quenched with 10% aqueous
 Na_2CO_3 . The mixture was extracted with EtOAc (twice), and the extract was washed with brine, dried
(Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed on silica gel, eluting with
 $\text{MeOH}\text{-CH}_2\text{Cl}_2$, to give the pure amide.

(b) With Na(Hg)

To a solution of the alkylated amidosulfone in anhydrous MeOH at ambient temperature was added Na_2HPO_4 (50 equiv) followed by Na(Hg) (6%, 25 equiv), and the mixture was stirred for 2 h. The mixture was filtered, the filtrate was concentrated *in vacuo*, and the residue was taken up into a mixture of water and EtOAc. The organic phase was separated and the aqueous phase was extracted with EtOAc (twice). The organic extract was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*, and the residue was chromatographed on silica gel, eluting with EtOAc-hexanes, to give the pure amide.

Characterization Data

2: IR (neat) 2973, 2933, 2854, 1699, 1448, 1422, 1366, 1272, 1234, 1183, 1146, 1024, 869, 764
 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.41 (s, 9H), 1.41-1.60 (m, 6H), 3.31 (t, $J = 6$ Hz, 4H); ^{13}C NMR
(75 MHz, CDCl_3) δ 24.6 (2), 25.8 (2), 28.5 (3), 44.5, 79.1, 154.6; MS (FAB) m/z 186 (M+H), 149, 136,
130, 112, 95, 89; HRMS (FAB) m/z 186.1487 (calcd for $\text{C}_{10}\text{H}_{20}\text{NO}_2$: 186.1481).

3: IR (neat) 2977, 2889, 1705, 1416, 1380, 1343, 1237, 1124, 1018, 771 cm^{-1} ; ^1H NMR (300
MHz, CDCl_3) δ 0.92 (t, $J = 7$ Hz, 3H), 1.92 (q, $J = 8$ Hz, 2H), 3.68 (t, $J = 8$ Hz, 4H), 3.77 (q, $J = 7$ Hz,
2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 15.1, 48.7 (2), 59.9, 156.1; MS (FAB) m/z 130 (M+H), 91.

7: IR (neat) 2933, 2809, 1693, 1595, 1435, 1287, 1242, 1127, 1001, 967, 743, 689, 583 cm^{-1} ; ^1H
NMR (300 MHz, CDCl_3) δ 1.17 (t, $J = 7$ Hz, 3H), 2.33-2.40 (m, 4H), 3.07 (d, $J = 7$ Hz, 2H), 3.39-3.45

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(m, 4H), 4.05 (q, J = 7 Hz, 2H), 6.16 (dt, J = 17, 7 Hz, 1H), 6.43 (d, J = 16 Hz, 1H), 7.10-7.32 (m, 5H);

^{13}C NMR (75 MHz, CDCl_3) δ 14.8, 43.8, 53.0 (2), 61.2, 61.4, 126.2, 126.4 (2), 127.7, 128.7 (2), 133.5, 136.9, 155.6; MS (FAB) m/z 275 (M+H), 217, 195, 133, 117; HRMS (FAB) m/z 275.1757 (calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_4$: 275.1760).

8: IR (neat) 2968, 2938, 2853, 2807, 2755, 1690, 1456, 1422, 1361, 1240, 1161, 1127, 987, 966, 872, 744 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.45 (s, 9H), 2.43 (t, J = 5 Hz, 4H), 3.15 (dd, J = 7, 1 Hz, 2H), 3.45 (t, J = 5 Hz, 4H), 6.24 (dt, J = 16, 7 Hz, 1H), 6.51 (d, J = 16 Hz, 1H), 7.17-7.40 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 28.5 (3), 43.3, 53.0 (2), 79.6, 126.2, 126.4 (2), 127.6, 128.6 (2), 133.4, 136.8, 154.8; MS (FAB) m/z 303 (M+H), 245, 229, 201, 172, 155, 143, 117, 91; HRMS (FAB) m/z 303.2072 (calcd for $\text{C}_{18}\text{H}_{27}\text{N}_2\text{O}_2$: 303.2072).

9: IR (neat) 2934, 2859, 2363, 1696, 1416, 1313, 1258, 1158, 1112, 1042, 716 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.28 (t, J = 7 Hz, 3H), 1.38-1.75 (m, 4H), 1.85-2.03 (m, 2H), 2.32 (d, J = 14 Hz, 1H), 2.69-2.84 (m, 1H), 4.21 (q, J = 7 Hz, 2H), 5.53 (s, 1H), 7.23-7.33 (m, 1H), 7.48-7.59 (m, 1H), 8.52 (d, J = 11 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.7, 19.3, 25.3, 27.8, 40.3, 51.7, 61.7, 123.5, 134.5, 135.5, 148.0, 148.5, 155.9; MS (FAB) m/z 235 (M+H), 205, 189, 154, 149, 136, 120, 107, 89; HRMS (FAB) m/z 235.1454 (calcd for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}_2$: 235.1447).

10: IR (neat) 3426, 2971, 2931, 1664, 1454, 1398, 1364, 1330, 1253, 1143, 1047, 993, 769, 701 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.23 (d, J = 7 Hz, 3H), 1.53 (s, 9H), 2.50-2.80 (s, 3H), 4.05-4.22 (m, 1H), 7.21-7.39 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.1, 27.8 (3), 30.6, 57.4, 79.5, 85.1, 126.3 (2), 127.3, 128.0 (2), 142.7, 146.7; MS (FAB) m/z 266 (M+H), 210, 192, 158, 148, 136, 102, 91; HRMS (FAB) m/z 266.1753 (calcd for $\text{C}_{15}\text{H}_{24}\text{NO}_3$: 266.1756).

14: IR (neat) 2939, 2853, 1644, 1450, 1307, 1144, 1081, 1012, 747, 690 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.46-1.56 (m, 2H), 1.56-1.66 (m, 4H), 3.45-3.53 (m, 4H), 4.24 (s, 2H), 7.49-7.59 (t, J = 6 Hz, 2H), 7.64 (tt, J = 8, 1 Hz, 1H), 7.88-7.94 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 24.2, 25.4, 26.2,

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43.4, 48.4, 59.8, 128.4 (2), 129.2 (2), 134.2, 139.0, 159.5; MS (FAB) *m/z* 268 (M+H), 203, 181, 169,
141, 126, 112, 97, 91; HRMS (FAB) *m/z* 268.1009 (calcd for C₁₃H₁₈NSO₃: 268.1007).

15: IR (KBr) 2989, 2927, 1658, 1438, 1309, 1295, 1235, 1159, 1077, 1027, 810, 756, 725 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.31 (q, *J* = 8 Hz, 2H), 3.93 (s, 2H), 4.06 (t, *J* = 8 Hz, 2H), 4.34 (t, *J* = 8 Hz, 2H), 7.54-7.63 (m, 2H), 7.64-7.73 (m, 1H), 7.92-7.99 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 15.0, 48.7, 51.3, 58.7, 128.7 (2), 129.3 (2), 134.4, 161.3; MS (FAB) *m/z* 240 (M+H), 219, 186, 149, 136, 107, 89; HRMS (FAB) *m/z* 240.0704 (calcd for C₁₁H₁₄NSO₃: 240.0694).

19: IR (KBr) 2922, 2804, 2350, 1648, 1450, 1432, 1325, 1316, 1158, 1082, 996 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.47 (d, *J* = 3, 4 Hz, 2H), 2.59 (d, *J* = 4 Hz, 2H), 3.17 (d, *J* = 7 Hz, 2H), 3.58-3.69 (m, 4H), 4.22 (s, 2H), 6.15-6.30 (m, 1H), 6.52 (d, *J* = 16 Hz, 1H), 7.17-7.42 (m, 5H), 7.51-7.71 (m, 3H), 7.88-7.97 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 42.5, 47.3, 52.7, 53.1, 60.0, 60.9, 125.8, 126.5, 127.9, 128.6, 128.8, 129.4, 133.8, 134.4, 138.9, 159.7; MS (FAB) *m/z* 385 (M+H), 307, 269, 217, 154, 136, 89; HRMS (FAB) *m/z* 385.1589 (calcd for C₂₁H₂₅N₂O₃S: 385.1586).

20: IR (neat) 2932, 2856, 2351, 1645, 1441, 1313, 1158, 1085, 1012, 686 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.10-1.30 (m, 2H), 1.75-2.00 (m, 1H), 2.40 (d, *J* = 15 Hz, 2H), 3.10-3.33 (m, 1H), 3.96 (d, *J* = 14 Hz, 1H), 4.39 (ABq, *J* = 40, 14 Hz, 2H), 7.26-7.38 (m, 1H), 7.50-7.72 (m, 4H), 7.90-8.01 (m, 2H), 8.53 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 19.1, 24.9, 26.0, 27.4, 29.9, 39.0, 44.3, 50.2, 60.1, 128.6(2), 129.4(2), 134.7, 135.1, 148.2, 161.3; MS (FAB) *m/z* 345 (M+H), 30.7, 259, 235, 219, 136, 107, 89; HRMS (FAB) *m/z* 345.1267 (calcd for C₁₈H₂₁N₂O₃S: 345.1273).

21: IR (neat) 3440, 3064, 2984, 2941, 2870, 2248, 1655, 1443, 1414, 1311, 1150, 1079, 910, 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃ rotamers) δ 1.13 and 1.36 (d, *J* = 7 Hz, 3H), 2.66 and 2.95 (s, 3H), 2.79 and 3.31 (m, 1H), 4.15 (d, *J* = 4 Hz, 2H), 4.36-4.50 and 4.59-4.66 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 11.3, 14.9, 29.2, 33.8, 57.4, 59.2, 59.4, 60.3, 75.2, 76.0, 126.1, 126.2, 127.6, 127.9, 128.2,

348 (M+H), 330, 240, 217, 148, 136, 100, 89; HRMS (FAB) *m/z* 348.1275 (calcd for C₁₈H₂₂NO₄S: 348.1270).

22: IR (neat) 2998, 2940, 2852, 2344, 1653, 1481, 1420, 1397, 1315, 1145, 1079, 1016, 899, 761, 684 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.25 (t, *J* = 6 Hz, 2H), 4.31 (s, 2H), 4.33 (t, *J* = 6 Hz, 2H), 7.08 (t, *J* = 5 Hz, 1H), 7.20 (q, *J* = 6 Hz, 2H), 7.59 (t, *J* = 6 Hz, 2H), 7.70 (t, *J* = 5 Hz, 1H), 7.96 (d, *J* = 6 Hz, 2H), 8.10 (d, *J* = 6 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 28.1, 49.5, 62.7, 117.7 (2), 124.9, 125.0, 127.7, 128.8 (2), 129.4 (2), 132.0, 134.5, 142.4; MS (FAB) *m/z* 302 (M+H), 288, 257, 243, 235, 219, 201, 183, 161, 136, 118, 107, 89; HRMS (FAB) *m/z* 302.0846 (calcd for C₁₆H₁₆NO₃S: 302.0851).

25: [α]_D²³ +28.0 (c 0.30, CHCl₃); IR (neat) 3064, 2964, 2927, 2890, 2855, 1651, 1471, 1442, 1414, 1326, 1253, 1153, 1079, 999, 864, 836, 779, 693 cm⁻¹; ¹H NMR (300 MHz, DMSO, 120 °C) δ -0.22 (s, 3H), 0.03 (s, 3H), 0.87 (s, 9H), 1.11-1.25 (m, 2H), 2.85 (s, 6H), 4.27 (m, 2H), 7.28 (m, 5H), 7.47-7.85 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ -5.0, -4.5, -2.8, 12.2, 15.8, 18.2, 18.3, 25.8, 25.9, 26.0, 29.2, 59.2, 60.4, 61.0, 76.3, 126.4, 126.7, 127.6, 128.1, 128.4, 128.5, 128.7, 129.1, 129.2, 134.1, 134.2, 139.1, 142.0; MS (FAB) *m/z* 462 (M+H), 404, 330, 270, 240, 221, 148, 100; HRMS (FAB) *m/z* 462.2136 (calcd for C₂₄H₃₆NO₄SSi: 462.2134).

27: IR (neat) 2979, 2941, 2853, 2350, 1732, 1647, 1450, 1370, 1307, 1252, 1147, 1092, 1009, 838, 723, 692 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.37 (s, 9H), 1.42-1.59 (m, 4H), 1.65-1.72 (m, 2H), 2.84-3.07 (m, 2H), 3.44-3.66 (m, 4H), 4.80 (dd, *J* = 11, 7 Hz, 1H), 7.55 (t, *J* = 8 Hz, 2H), 7.67 (t, *J* = 7 Hz, 1H), 7.82 (d, *J* = 7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 24.5, 25.7, 26.0, 28.1 (3), 44.1, 48.2, 61.9, 81.9, 129.1 (2), 129.8 (2), 134.5, 136.5, 162.3, 169.1; MS (FAB) *m/z* 382 (M+H), 326, 240, 184, 166, 140, 125, 107; HRMS (FAB) *m/z* 382.1682 (calcd for C₁₉H₂₈O₅NS: 382.1688).

NMR (300 MHz, CDCl₃) δ 1.88-2.04 (m, 4H), 2.27 (q, J = 8 Hz, 2H), 3.79 (dd, J = 9, 5 Hz, 1H), 3.50-4.21 (m, 3H), 4.38 (q, J = 8 Hz, 1H), 5.03 (t, J = 10 Hz, 2H), 5.61-5.79 (m, 1H), 7.50-7.21 (m, 3H), 7.85-7.92 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 15.1, 26.3, 30.9, 48.5, 50.8, 65.2, 116.7, 128.9 (2), 130.0 (2), 134.3, 136.7, 161.1, 163.6; MS (FAB) m/z 294 (M+H), 235, 219, 155, 136, 120, 107, 89; HRMS (FAB) m/z 294.1167 (calcd for C₁₅H₂₀NO₃S: 294.1164).

29: IR (neat) 2928, 2854, 2351, 2320, 1732, 1649, 1461, 1380, 1255, 1075, 1018 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.24 (m, 14H), 1.50-1.70 (m, 2H), 1.70-1.92 (m, 2H), 2.30 (t, J = 8 Hz, 4H), 3.67 (s, 3H), 3.74 (dd, J = 11, 4, 1H), 3.95-4.23 (m, 3H), 4.41 (q, J = 8 Hz, 1H), 7.56 (t, J = 8 Hz, 2H), 7.68 (t, J = 7 Hz, 1H), 7.88 (d, J = 2H); ¹³C NMR (75 MHz, CDCl₃) δ 15.0, 24.0, 25.1, 26.0, 27.1, 28.9, 29.2, 29.3, 29.5, 29.6, 30.3, 34.2, 34.5, 48.4, 50.9, 51.6, 64.5, 66.2, 76.4, 128.7, 128.9, 130.0, 134.0, 134.2, 136.8, 164.0, 174.4; MS (FAB) m/z 438 (M+H), 406, 359, 341, 327, 296, 239, 219, 195, 136, 112, 89; HRMS (FAB) m/z 438.2319 (calcd for C₂₃H₃₆NO₅S: 438.2314).

34: IR (neat) 3065, 3019, 2956, 2927, 2856, 2804, 2758, 1655, 1446, 1302, 1237, 1194, 1145, 1084, 993, 833, 741, 692 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, J = 6 Hz, 3H), 1.09-1.33 (m, 4H), 1.86-2.01 (m, 2H), 2.38-2.62 (m, 4H), 3.18 (d, J = 7 Hz, 2H), 3.48-3.85 (m, 4H), 4.28 (dd, J = 9, 5 Hz, 1H), 6.23 (dt, J = 16, 7 Hz, 1H), 6.54 (d, J = 16 Hz, 1H), 7.21-7.42 (m, 5H), 7.61 (m, 3H), 7.85 (d, J = 8 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 13.8, 22.3, 27.8, 29.0, 42.6 (2), 46.6, 52.8, 53.0, 60.7 (2), 65.8, 125.8, 126.4, 127.7, 128.6 (2), 128.8, 129.8, 133.6, 134.1, 136.7, 163.1; MS (FAB) m/z 441 (M+H), 337, 299, 255, 201, 154, 117, 91; HRMS (FAB) m/z 441.2208 (calcd for C₂₅H₃₃N₂O₃S: 441.2212).

35: ¹H NMR (300 MHz, CDCl₃) δ 0.87 (t, J = 5 Hz, 6H), 1.45-1.75 (m, 1H), 1.97 (td, J = 9, 3 Hz, 2H), 3.19 (d, J = 5 Hz, 2H), 3.47-3.87 (m, 4H), 4.38 (dd, J = 8, 2 Hz, 1H), 6.25 (dt, J = 12, 5 Hz, 1H), 6.55 (d, J = 12 Hz, 1H), 7.25 (s, 1H), 7.33 (t, J = 5 Hz, 2H), 7.39 (d, J = 5 Hz, 2H), 7.56 (t, J = 6 Hz,