

Supporting Information

Benzothiazole Sulfinic Acid Transfer Reagent Under Oxidation Free Conditions

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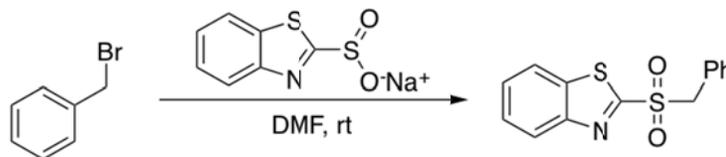
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Materials and methods

Diisopropyl ethyl amine was freshly distilled from calcium hydride. Sodium benzothiazole-2-sulfinate was synthesized as previously described.¹ All other chemicals, reagents, and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. All reactions were carried out under ambient conditions with no effort to maintain desiccated conditions. All reactions were stirred via magnetic Teflon coated stir bars. Each reaction was monitored via thin layer chromatography (TLC), using glass supported silica gel 60 F₂₅₄ plates (Merck, kGaA). All silica flash columns were performed using 230 x 400 mesh silica gel (Sorbent Technologies). All ¹H and ¹³C NMR's were recorded on a Bruker DRX spectrometer at 400 MHz for ¹H and 100 MHz for ¹³C or a Varian VNMRs spectrometer at 600 MHz for ¹H and 150 MHz for ¹³C. All chemical shifts are referenced to residual solvent signals in CDCl₃ (7.26 ppm for ¹H and 77 ppm for ¹³C). Mass Spectrometry (MS) was recorded on Bruker Ultraflex extreme MALDI TOF mass spectrometer.

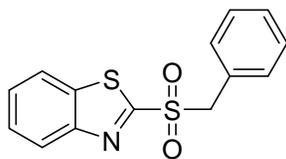
Experimental Procedures

Procedure for Benzothiazolation



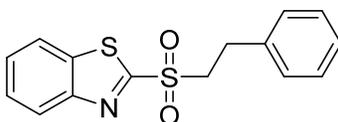
To a 100 mL round bottom flask with magnetic stir bar was added 880 mg (4.0 mmol) BTS and was suspended in 20 mL of DMF and stirred at room temperature. To the stirring slurry, 0.12 mL (170 mg, 1.0 mmol) benzyl bromide was added and allowed to stir at room temperature for 18 hours. The reaction was diluted with 150 mL ethyl acetate and washed with brine (3 x 100 mL), dried over MgSO₄, filtered and concentrated via rotary evaporator. The crude product was purified via silica flash column (9:1 hexane: ethyl acetate mobile phase) yielding the product as a white solid, 285 mg, 99% yield.

2-benzylsulfonyl benzothiazole (1)



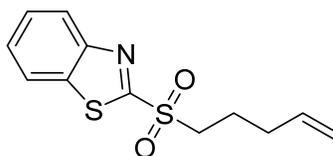
Synthesized according to the general procedure. Isolated as a white solid in 99% yield, 285 mg. M.P.: 112.0-112.9 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.26 (d, J = 12 Hz, 1H), 7.94 (d, J = 12 Hz, 1H), 7.65 (t, J = 6 Hz, 1H), 7.58 (t, J = 6 Hz, 1H), 7.26-7.32 (m, 5H), 4.76 (s, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 165.18, 152.56, 137.04, 131.09, 129.20, 128.88, 127.97, 127.62, 126.33, 125.47, 122.26, 61.00. MS (m/z): Calcd for C₁₄H₁₁NO₂S₂ [M⁺] = 289.0, found: 289.0. All data matches previously reported characterization.²

2-(phenethylsulfonyl) benzothiazole (2)



Synthesized according to the general procedure at 0.1 mmol scale. Isolated as a white solid in 95% yield, 29 mg. M.P.: 85.9-86.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.67 - 7.54 (m, 2H), 7.24 (t, J = 7.0 Hz, 2H), 7.17 (t, J = 7.5 Hz, 3H), 3.84 - 3.75 (m, 2H), 3.25 - 3.15 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 165.63, 152.64, 136.85, 136.75, 128.80, 128.36, 128.05, 127.65, 127.04, 125.45, 122.30, 55.86, 28.44. HRMS (m/z): Calcd for C₁₅H₁₄NO₂S₂ [M+H]⁺ = 304.0466, found: 304.0463.

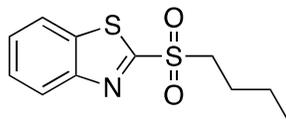
2-(pent-4-en-1-ylsulfonyl) benzothiazole (3)



Synthesized according to the general procedure at 0.5 mmol scale. Isolated as colorless oil in 99% yield, 132 mg. ¹H NMR (400 MHz, CDCl₃) δ 8.18-8.21 (m, 1H), 7.98-8.01 (m, 1H), 7.55-7.64 (m, 2H), 5.65-5.75 (1H, m), 5.02-5.05 (1H, m), 5.00 (t, J = 1.4 Hz, 1H), 3.47-3.51 (m, 2H), 2.19 (q, J = 7.1 Hz, 2H), 1.94-2.01 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 165.76, 152.69,

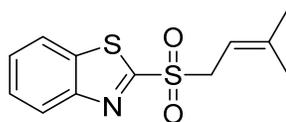
136.72, 135.92, 128.01, 127.64, 125.43, 122.32, 116.79, 53.97, 31.94, 21.43. HRMS (m/z): Calcd for C₁₅H₁₄NO₂S₂ [M+H]⁺ = 268.0466, found: 268.0461.

2-(butylsulfonyl) benzothiazole (4)



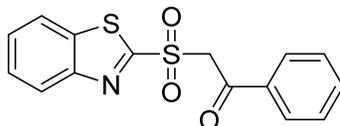
Synthesized according to the general procedure at 0.2 mmol scale. Isolated as colorless oil in 95% yield, 49 mg. ¹H NMR (600 MHz, CDCl₃) δ 8.21 (dt, *J* = 8.3, 0.9 Hz, 1H), 8.01 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.63 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.59 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1H), 3.54 – 3.48 (m, 2H), 1.90 – 1.81 (m, 2H), 1.47 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.91, 152.72, 136.74, 127.97, 127.61, 125.43, 122.33, 54.48, 24.21, 21.53, 13.44. HRMS (m/z): caclcd C₁₁H₁₄NO₂S₂ [M+H]⁺ = 256.0466, found: 256.0461.

2-((3-methylbut-2-en-1-yl) sulfonyl) benzothiazole (5)



Synthesized according to the general procedure at 0.1 mmol scale. Isolated as a white solid in 97% yield, 26 mg. M.P.: 80.8-82.2 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.22 (dt, *J* = 8.3, 1.0 Hz, 1H), 8.01 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.63 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.59 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 5.25 (tp, *J* = 7.9, 1.4 Hz, 1H), 4.22 (d, *J* = 7.9 Hz, 2H), 1.73 (d, *J* = 1.5 Hz, 3H), 1.57 (d, *J* = 1.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.87, 152.69, 144.89, 137.01, 127.89, 127.57, 125.38, 122.26, 108.54, 54.74, 25.97, 18.29. MS (m/z): Calcd for C₁₂H₁₃NO₂S₂ [M]⁺ = 267.0, found: 267.0. All data matches previously reported characterization.³

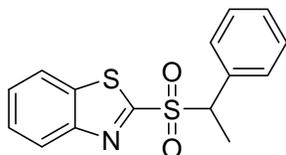
2-(benzothiazol-2-ylsulfonyl)-1-phenylethan-1-one (6)



Synthesized according to the general procedure at 0.1 mmol scale. Isolated as a white solid in 91% yield, 29 mg. M.P.: 120.1-122.3 °C. ¹H NMR (600 MHz, CDCl₃) δ 8.08 (d, *J* = 7.3 Hz, 2H),

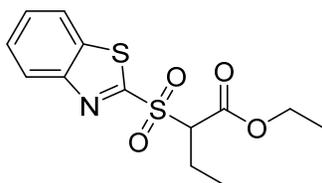
7.81 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 8.2 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 4.97 (s, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 192.94, 165.22, 152.84, 135.51, 133.82, 128.80, 128.58, 126.02, 124.40, 121.49, 121.06, 40.97. MS (m/z): Calcd C₁₅H₁₁NO₃S₂Na [M+Na]⁺ = 340.0, found: 340.0. All data matches previously reported characterization.⁴

2-((1-phenylethyl) sulfonyl) benzothiazole (7)



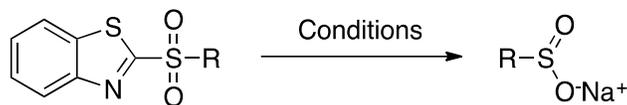
Synthesized according to the general procedure at 0.1 mmol scale. Isolated as a colorless oil in 98% yield, 30 mg. ¹H NMR (600 MHz, CDCl₃) δ 8.23 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.62 (td, J = 8.3, 7.7, 1.2 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.33 – 7.23 (m, 5H), 4.85 (q, J = 7.2 Hz, 1H), 1.90 (d, J = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.00, 152.61, 137.17, 132.15, 129.64, 129.23, 128.71, 127.86, 127.51, 125.45, 122.16, 65.28, 14.06. HRMS (m/z): Calcd for C₁₅H₁₄NO₂S₂ [M+H]⁺ = 304.0466, found: 304.0463.

ethyl 2-(benzothiazol-2-ylsulfonyl) butanoate (8)



Synthesized according to the general procedure at 1.0 mmol scale. Isolated as a colorless oil in 95% yield, 297 mg. ¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.68 – 7.57 (m, 2H), 4.37 (dd, J = 9.6, 5.1 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.32 – 2.25 (m, 2H), 1.13 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.5 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.68, 152.61, 137.11, 128.18, 127.69, 125.65, 122.25, 122.24, 71.09, 62.56, 19.96, 13.80, 11.46. HRMS (m/z): Calcd for C₁₃H₁₆NO₄S₂ [M+H]⁺ = 314.0521, found: 314.0518.

Benzothiazole Removal



Procedure A

In a 10 mL round bottom flask with magnetic stir bar, 56 mg (0.20 mmol) 2-benzylsulfonyl benzothiazole **1** was dissolved in 2 mL of ethanol at room temperature. To this solution, 15 mg (0.4 mmol) NaBH₄ was added and allowed to stir for two hours. The solution was concentrated via rotary evaporator. 4 mL hexanes was added to the crude product revealing the product as a white solid, which was filtered and washed with additional hexanes, then dried under high vacuum. The product was obtained in almost quantitative yield, 36 mg.

Procedure B

To a 10 mL round bottom flask with magnetic stir bar was added 28 mg (0.10 mmol) 2-benzylsulfonyl benzothiazole **1** and suspended in 0.5 mL of acetonitrile and 0.25 mL of water and stirred vigorously at room temperature. To this solution, 0.084 mL of NaOH solution in water (2.3 M) was added. Within 10 minutes, the reaction had become homogeneous and was monitored by TLC. After 30 hours, TLC showed no starting material remaining. The solution was diluted to 10 mL of water, and washed with DCM (4 x 20 mL). The aqueous layer was concentrated on a rotary evaporator yielding the product as a white solid. 16 mg, 89 % yield.

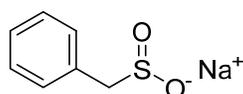
Procedure C

In a 10 mL round bottom flask with magnetic stir bar, 58 mg (0.20 mmol) 2-benzylsulfonyl benzothiazole **1** was suspended in 0.5 mL acetonitrile and 0.5 mL water and stirred vigorously at room temperature. To this solution 11 mg (0.22 mmol) NaHS • H₂O was added. After 3 hours, the reaction became totally homogeneous and was monitored by TLC. After 12 hours, TLC showed no starting material remaining. The solution was diluted to 10 mL with water and washed by DCM (4 x 20 mL). The aqueous layer was concentrated on a rotary evaporator yielding the product as a white solid. 27 mg, 75 % yield.

Procedure D

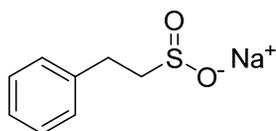
In a 10 mL round bottom flask with magnetic stir bar, 32 mg (0.30 mmol) Na_2CO_3 was suspended in 2 mL DCM and stirred vigorously at room temperature. To this, 30 μL (30 mg, 0.24 mmol) freshly distilled benzyl mercaptan was added and stirred for 10 minutes. To the solution was added 58 mg (0.20 mmol) 2-benzylsulfonyl benzothiazole **1** and the reaction was monitored by TLC over 18 hours. The reaction was diluted with 10 mL water then washed with DCM (3 x 20 mL). The aqueous layer was concentrated on a rotary evaporator yielding the product as a white solid. 32 mg. 91 % yield.

Sodium phenylmethanesulfinate (10)



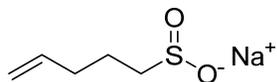
Synthesized according to procedure A at 0.1 mmol scale. White solid in 98% yield, 17 mg. ^1H NMR (600 MHz, CD_3OD) δ 7.31 – 7.24 (m, 4H), 7.23 – 7.17 (m, 1H), 3.51 (s, 2H). ^{13}C NMR (151 MHz, CD_3OD) δ 133.32, 129.52, 127.80, 126.22, 69.52. MS (m/z) Calcd for $\text{C}_7\text{H}_7\text{O}_2\text{S} [\text{M}-\text{Na}]^- = 155.0$, found: 155.0. All data matches previously reported characterization.⁵

Sodium 2-phenylethane-1-sulfinate (11)



Synthesized according to procedure A at 0.25 mmol scale. The product was isolated as a white solid in 98% yield, 47 mg. ^1H NMR (400 MHz, CD_3OD) δ 7.28 – 7.18 (m, 4H), 7.18 – 7.08 (m, 1H), 2.90 – 2.84 (m, 2H), 2.55 – 2.46 (m, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ 141.03, 128.01, 127.99, 125.46, 63.16, 28.31. MS (m/z): Calcd $\text{C}_8\text{H}_9\text{O}_2\text{S} [\text{M}-\text{Na}]^- = 169.0$, found: 169.0. All data matches previously reported characterization.⁶

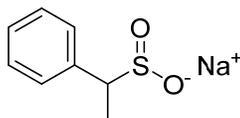
Sodium pent-4-ene-1-sulfinate (12)



Synthesized according to procedure A at 0.25 mmol scale. Isolated as a white solid in 95% yield, 37 mg. Matches previously reported NMR data.² ^1H NMR (400 MHz, D_2O) δ 5.74 (ddt, $J = 17.0$, 10.2, 6.6 Hz, 1H), 5.00 – 4.84 (m, 2H), 2.26 – 2.17 (m, 2H), 2.01 (q, $J = 7.2$ Hz, 2H), 1.52 (p, $J =$

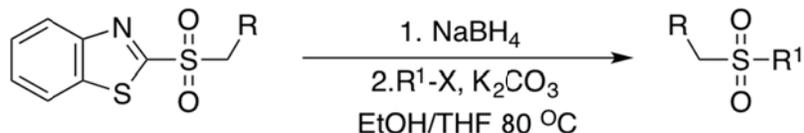
7.5 Hz, 2H). ^{13}C NMR (101 MHz, D_2O) δ 138.64, 114.95, 60.05, 32.25, 20.95. MS (m/z): Calcd for $\text{C}_5\text{H}_9\text{O}_2\text{S}$ $[\text{M}-\text{Na}]^- = 133.0$, found: 133.0. All data matches previously reported characterization.⁷

Sodium 1-phenylethane-1-sulfinate (13)



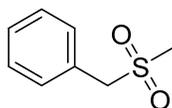
Synthesized according to procedure A at 0.25 mmol scale. The product was isolated as a white solid in 75% yield, 36 mg. ^1H NMR (600 MHz, Methanol- d_4) δ 7.30 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 3.15 (q, $J = 7.2$ Hz, 1H), 1.46 (d, $J = 7.2$ Hz, 3H). HRMS Calcd for $\text{C}_8\text{H}_9\text{O}_2\text{S}$ $[\text{M}-\text{Na}]^- = 169.0329$, found: 169.0331.

General Procedure for the Trans-sulfurization of Benzothiazole Sulfones



To a 50 mL round bottom with a magnetic stir bar, 590 mg (2.0 mmol) of **1** was dissolved in 10 mL ethanol and 10 mL THF and stirred at room temperature. To the stirring solution 150 mg (4.0 mmol) of NaBH_4 was added and allowed to stir for one hour. TLC showed no starting material remaining. Then, 550 mg (4.0 mmol) K_2CO_3 was added to the solution followed by 0.19 mL (3.0 mmol) iodomethane, heated to 80°C , and allowed to stir overnight. The reaction solution was cooled to room temperature and diluted to 150 mL with ethyl acetate, then washed with 3 x 150 mL of brine, dried over MgSO_4 , and concentrated. The crude product was purified via column chromatography (9:1 Hexane: ethyl acetate mobile phase) yielding 340 mg of a white solid, 99% yield.

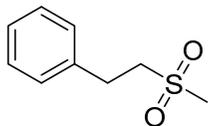
Benzyl methyl sulfone (14)



Synthesized according to the general procedure at 2.0 mmol scale. Isolated as a white solid in 99% yield, 340 mg, M.P.: $126\text{--}127^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 7.41 (s, 5H), 4.25 (s, 2H),

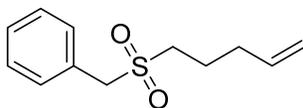
2.75 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 130.50, 129.12, 128.31, 61.31, 39.00. MS (m/z): Calcd for $\text{C}_8\text{H}_{10}\text{O}_2\text{S}$ $[\text{M}+\text{H}] = 171.0$, found: 171.0. All data matches previously reported characterization.⁸

(2-(methylsulfonyl) ethyl) benzene (15)



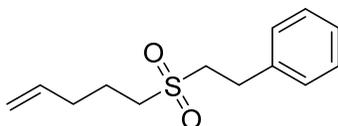
Synthesized according to the general procedure at 0.2 mmol scale. Isolated as a white solid in 99% yield, 36 mg. M.P.: 79.3-80 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.33 (t, $J = 7.5$ Hz, 2H), 7.31 – 7.21 (m, 3H), 3.33 – 3.27 (m, 2H), 3.20 – 3.14 (m, 2H), 2.81 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 137.37, 128.99, 128.41, 127.16, 56.20, 41.00, 28.58. MS (m/z): Calcd for $\text{C}_9\text{H}_{12}\text{O}_2\text{S}$ $[\text{M}^+] = 184.0$, found: 184.0. All data matches previously reported characterization.⁹

((pent-4-en-1-ylsulfonyl) methyl) benzene (16)



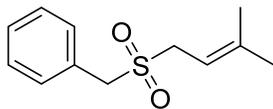
Synthesized according to the general procedure at 0.2 mmol scale. Isolated as a white solid in 73% yield, 34 mg. M.P.: 82.5-84.5 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.40 (s, 5H), 5.70 (ddt, $J = 18.0, 9.5, 6.7$ Hz, 1H), 5.03 (dq, $J = 6.0, 1.5$ Hz, 1H), 5.00 (t, $J = 1.4$ Hz, 1H), 4.21 (s, 2H), 2.85 – 2.77 (m, 2H), 2.18 – 2.07 (m, 2H), 1.94 – 1.85 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 136.17, 130.50, 129.05, 128.07, 116.53, 59.54, 50.29, 32.13, 29.68, 20.92. HRMS (m/z): Calcd for $\text{NaC}_{12}\text{H}_{16}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+ = 247.0769$, found: 247.0764.

(2-(pent-4-en-1-ylsulfonyl) ethyl) benzene (17)



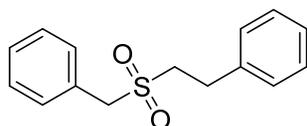
Synthesized according to the general procedure at 0.2 mmol scale. Isolated as a colorless oil in 79% yield, 38 mg. ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.30 (m, 2H), 7.30 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 5.71 (ddt, $J = 16.2, 10.7, 6.7$ Hz, 1H), 5.08 – 5.04 (m, 1H), 5.03 (t, $J = 1.4$ Hz, 1H), 3.26 – 3.21 (m, 2H), 3.17 – 3.11 (m, 2H), 2.89 – 2.83 (m, 2H), 2.19 – 2.12 (m, 2H), 1.95 – 1.86 (m, 2H). HRMS (m/z): Calcd for $\text{NaC}_{13}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+ = 261.0925$, found: 261.0934.

(((3-methylbut-2-en-1-yl) sulfonyl) methyl) benzene (18)



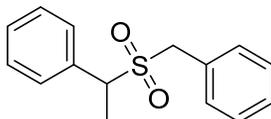
Synthesized according to the general procedure at 0.2 mmol scale. Isolated as a white solid in 94% yield, 46 mg. M.P.: 79.2-79.8 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.39 (s, 5H), 5.32 – 5.25 (m, 1H), 4.18 (s, 2H), 3.57 (d, J = 7.7 Hz, 2H), 2.16 (s, 2H), 1.83 (s, 3H), 1.65 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 142.81, 130.65, 128.93, 128.90, 127.90, 110.05, 58.15, 51.65, 26.04, 18.54. HRMS (m/z): Calcd for NaC₁₅H₁₆O₂S [M]⁺ = 247.0768, found: 247.0767.

(2-(benzylsulfonyl) ethyl) benzene (19)



Synthesized according to the general procedure at 0.2 mmol scale. Isolated as a white solid in 92% yield, 48 mg. M.P.: 123.5-124.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.19 (m, 8H), 7.15 (dd, J = 7.0, 1.8 Hz, 2H), 4.17 (s, 2H), 3.08 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 137.55, 130.50, 129.10, 129.08, 128.90, 128.49, 127.86, 127.08, 59.97, 52.55, 28.00. HRMS (m/z): Calcd for NaC₁₅H₁₆O₂S [M+Na]⁺ = 283.0768, found: 283.0766.

(1-(benzylsulfonyl) ethyl) benzene (20)

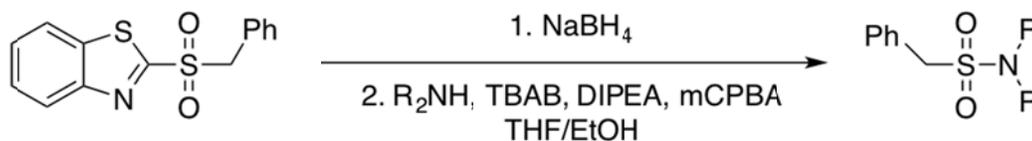


Synthesized according to the general procedure at 0.2 mmol scale. Isolated as a white solid in 70% yield, 38 mg. M.P.: 99-101 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.48 – 7.38 (m, 5H), 7.36 (dt, J = 4.5, 2.9 Hz, 3H), 7.32 – 7.28 (m, 2H), 4.10 (q, J = 7.2 Hz, 1H), 4.00 (d, J = 2.9 Hz, 2H), 1.76 (d, J = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 153.85, 134.37, 130.87, 129.22, 129.07, 128.97, 128.76, 127.41, 62.18, 56.43, 14.40. HRMS (m/z): Calcd for NaC₁₅H₁₆O₂S [M+Na]⁺ = 283.0768, found: 283.0765.

Results of using secondary alkyl halides

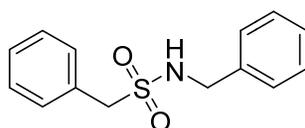
Isopropyl bromide, isopropyl iodide, bromocyclohexane, and 2-butyl bromide were all attempted to react in sulfinic acid exchange (Table 4). However, even at high temperatures (up to 80 °C), no isolatable products were seen via TLC or crude NMR for any reaction. Some trace product may have been formed when using 2-butyl bromide and benzyl sulfinate but after several attempts to repeat the reaction no meaningful amount of product could be isolated. This reaction has not been carried out before to the best of our knowledge. These results are somewhat consistent with other reactions between secondary halides and sulfinic acid derivatives. There are few reactions reported with generally poor yields, at higher temperature than THF and ethanol can provide, and often using aryl sulfinate.¹⁰

Representative Procedure for the One Pot Sulfonamidation of Benzothiazole Sulfones



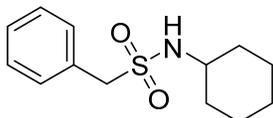
In a 50 mL round bottom with a magnetic stir bar, 590 mg (2.0 mmol) **1** was dissolved in 10 mL ethanol and 10 mL THF and stirred at room temperature. To the stirring solution was added 150 mg (4.0 mmol) NaBH₄ and allowed to stir for one hour. TLC showed no starting material remaining, then 0.2 mL (150 mg, 2.0 mmols) of n-butylamine, 520 μL (390 mg, 3.0 mmols) of DIPEA, 970 mg (3.0 mmol) of tetrabutyl ammonium bromide (TBAB), and 1480 mg (6.0 mmol) of mCPBA were added sequentially and allowed to stir for 18 hours. The reaction was diluted with 150 mL of ethyl acetate and washed with 100 mL of saturated Na₂S₂O₃, followed by saturated NaHCO₃ (2 x 150 mL), and brine (3 x 150 mL), dried over MgSO₄ and concentrated. The crude product was purified flash column chromatography yielding 190 mg of N-butyl-1-phenylmethanesulfonamide as a white solid. 42% yield.

N-benzyl-1-phenylmethanesulfonamide (**23**)



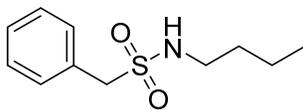
The general procedure for sulfonamidation was followed to give the product as a white solid in 52% yield, 30 mg (in 0.2 mmol scale). M.P.: 142.0-145.2 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.25 (m, 10H), 4.47 (t, *J* = 6.0 Hz, 1H), 4.20 (s, 2H), 4.13 (d, *J* = 5.8 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 136.80, 130.63, 128.82, 128.80, 128.75, 128.09, 128.03, 127.96, 59.40, 47.66. MS (m/z): Calcd for NaC₁₄H₁₅NO₂S [M⁺] = 284.0721, found: 284.0725.

N-cyclohexyl-1-phenylmethanesulfonamide (24)



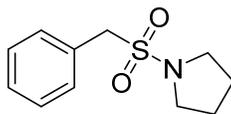
The general procedure for sulfonamidation was followed. The product was obtained as a white solid in 48% yield, 24 mg (in 0.2 mmol scale). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.32 (m, 5H), 4.23 (d, *J* = 1.2 Hz, 2H), 3.90 (d, *J* = 7.7 Hz, 1H), 3.11 (m, 1H), 1.90 (dd, *J* = 12.6, 3.8 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.24 – 1.04 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 130.68, 129.55, 128.67, 128.63, 60.06, 53.32, 34.55, 25.12, 24.77. HRMS (m/z): Calcd for NaC₁₃H₁₉NO₂S [M+Na]⁺ = 276.1033, found: 276.1033.

N-butyl-1-phenylmethanesulfonamide (25)



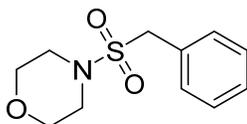
The general procedure for sulfonamidation was followed. The product was isolated as a white solid in 42% yield, 95 mg (in 1.0 mmol scale). M.P.: 77.5- 79.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (s, 5H), 4.23 (s, 2H), 4.08 (q, *J* = 6.4 Hz, 1H), 2.96 (q, *J* = 6.8 Hz, 2H), 1.45 (m, 2H), 1.34 – 1.26 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 130.54, 129.46, 128.79, 128.68, 58.62, 43.43, 32.31, 19.62, 13.53. HRMS (m/z): Calcd for C₁₁H₁₇NO₂SNa [M+Na]⁺ = 248.0728, found: 248.0721.

1-(benzylsulfonyl) pyrrolidine (26)



The general procedure for sulfonamidation was followed. The product was obtained as a white solid in 50% yield, 23 mg (in 0.2 mmol scale). M.P.: 75.0-76.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.30 (m, 5H), 4.25 (s, 2H), 3.15 (t, *J* = 6.7 Hz, 4H), 1.83 – 1.78 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 130.59, 129.47, 128.65, 128.56, 56.47, 48.10, 25.84. MS (m/z): Calcd for C₁₁H₁₅NO₂S [M⁺] = 225.0, found: 225.0. All data matches previously reported characterization.¹¹

4-(benzylsulfonyl)morpholine (27)



The general procedure for sulfonamidation was followed. The product was obtained as a white solid in 48% yield, 23 mg (in 0.2 mmol scale). M.P.: 170.1-172.0 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.39 (m, 5H), 4.23 (s, 2H), 3.63 – 3.58 (m, 4H), 3.12 – 3.07 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 130.70, 128.87, 128.84, 128.53, 66.69, 56.71, 46.10. HRMS (m/z): Calcd for NaC₁₁H₁₅NO₃S [M+Na]⁺ = 264.0670, found: 264.0668.

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