Electronic Supplementary Information

Practical Synthesis of β-oxo benzo[d]thiazol sulfones: Scope and Limitations

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Table of Contents

Electronic Supplementary Information .................................................................................. 1
Experimental procedures ........................................................................................................... 3
Sulfone synthesis (5) ................................................................................................................ 3
  2-(methylthio)benzo[d]thiazole (5a) .................................................................................. 3
  2-(heptylsulfonyl)benzo[d]thiazole (5b) .......................................................................... 4
  2-(benzylsulfonyl)benzo[d]thiazole (5c) ........................................................................ 5
  Starting from alcohol and BT-SH or PT-SH ................................................................. 6
  2-(tricosanylsulfonyl)benzo[d]thiazole (5d) .................................................................. 6
  2-(hex-3-yn-1-ylsulfonyl)benzo[d]thiazole (5e) ............................................................. 7
  2-(hex-5-en-1-ylsulfonyl)benzo[d]thiazole (5f) ............................................................. 7
  2-((4-((tert-butyldiphenylsilyl)oxy)butyl)sulfonyl)benzo[d]thiazole (5g) ...................... 7
Self-condensation of sulfone 5a .......................................................................................... 8
  2-((benzo[d]thiazol-2-ylmethyl)sulfonyl)benzo[d]thiazole (7) ........................................ 8
α-Heterosulfonyl ketones (4) and esters (11) .................................................................... 8
  2-(benzo[d]thiazol-2-ylsulfonyl)-1-phenylethanone (4a) .............................................. 9
  1-(benzo[d]thiazol-2-ylsulfonyl)propan-2-one (4b) ..................................................... 9
  2-(benzo[d]thiazol-2-ylsulfonyl)-1-cyclohexylctan-1-one (4c) ...................................... 10
  2-(benzo[d]thiazol-2-ylsulfonyl)-1-mesityloctan-1-one (4d) ......................................... 11
3-(benzo[d]thiazol-2-ylsulfonil)-1-phenoxy-2-nonan-2-one (4e) ........................................... 11
ethyl 3-(benzo[d]thiazol-2-ylsulfonil)-2-oxononanoate (4f) .................................................. 12
5-(benzo[d]thiazol-2-ylsulfonil)-1-chloroundecan-4-one (4g) .............................................. 12
2-(benzo[d]thiazol-2-ylsulfonil)-1-cyclohexylethanoate (4h) ............................................. 13
methyl 2-(benzo[d]thiazol-2-ylsulfonil)acetate (11a) ............................................................... 14
allyl 2-(benzo[d]thiazol-2-ylsulfonil)acetate (11b) ................................................................. 14
tert-butyl 2-(benzo[d]thiazol-2-ylsulfonil)acetate (11c) .......................................................... 15
methyl 2-(benzo[d]thiazol-2-ylsulfonil)-2-phenylacetate (11d) .............................................. 16
tert-butyl 2-(benzo[d]thiazol-2-ylsulfonil)-2-phenylacetate (11e) ........................................... 16
methyl 2-(benzo[d]thiazol-2-ylsulfonil)-2-lignocerate (11f) .................................................... 17
methyl 2-(benzo[d]thiazol-2-ylsulfonil)hept-5-ynoate (11g) ..................................................... 18
allyl 2-(benzo[d]thiazol-2-ylsulfonil)hept-5-ynoate (11h) ....................................................... 18
methyl 2-(benzo[d]thiazol-2-ylsulfonil)hept-6-enol (11i) .......................................................... 19
methyl 2-(benzo[d]thiazol-2-ylsulfonil)-5-((tert-butylidiphenylsilyl)oxy)pentanoate (11j) ....... 20
allyl 2-(benzo[d]thiazol-2-ylsulfonil)octanoate (11k) ............................................................... 20
S-ethyl 2-(benzo[d]thiazol-2-ylsulfonil)ethanethioate (11l) ..................................................... 21
2-(benzo[d]thiazol-2-ylsulfonil)-N,N-diethylacetamide (11m) ............................................. 21
Synthesis of 2-(((phenylsulfonyl)methyl)sulfonyl)benzo[d]thiazole (12b) .............................. 22
((iodomethyl)sulfonyl)benzene (S-6) ....................................................................................... 22
2-(((phenylsulfonyl)methyl)thio)benzo[d]thiazole (S-7) ......................................................... 22
2-(((phenylsulfonyl)methyl)sulfonyl)benzo[d]thiazole (12b) .................................................. 23

Computations ............................................................................................................................ 25
Computational details .............................................................................................................. 25
Conformational analysis .......................................................................................................... 25

Litterature .............................................................................................................................. 29
Experimental procedures

Sulfone synthesis (5)

2-(methylthio)benzo[d]thiazole (5a)

Sulfide S-1 synthesis: A solution of BTSH (10.0 g, 59.8 mmol, 1.0 equiv) in THF (240 mL, 0.25M) was cooled to 0°C and NaH (60% in min. oil) (2.63 g, 65.8 mmol, 1.1 equiv) was added portionwise within 10 min. The resulting solution was stirred at 0°C for 30 min, before methyl iodide (4.5 mL, 71.8 mmol, 1.2 equiv) was added dropwise. The cooling bath was removed and the resulting mixture was allowed to warm to rt and stirred for a further 8h. Saturated aqueous NH₄Cl (100 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether:EtOAc = 10:1->4:1) yielding the desired sulfide as a white solid (10.5 g, 99 % yield).

TLC (petroleum ether:EtOAc = 4:1)

Mp = 48-49°C, lit.¹ 48-49°C; ¹H-NMR (300 MHz, CDCl₃): δ = 2.81 (s, 3H, H-1), 7.30 (td, J = 7.6, 1.2 Hz, 1 H), 7.43 (td, J = 8.3, 1.2 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 16.1 (C-1), 121.1, 121.5, 124.2, 126.2, 135.3, 153.5, 168.2 (C-2); IR (film): ν⁻¹ = 3062, 2925, 2851, 1462, 1429, 1311, 1240, 1082, 1007, 964, 908, 756, 727, 675.

Sulfone 5a: A solution of sulfide (10.0 g, 55.2 mmol, 1.0 equiv) in EtOH (276 mL, 0.20M) was cooled to 0°C and Na₂WO₄·2 H₂O (1.82 g, 5.51 mmol, 0.1 equiv) was added. After 5 min at 0°C, 35% aqueous solution of H₂O₂ (21.4 mL, 221 mmol, 4.0 equiv) was added dropwise. The resulting mixture was stirred at 0°C for 30 min, before the cooling bath was removed and the stirring continued at rt for a further 10h. Saturated aqueous Na₂S₂O₃ (100 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether:EtOAc = 4:1->2:1->1:1) yielding the desired sulfone as yellowish crystals (9.88 g, 84 % yield). In some cases, if the reaction was stopped before a full sulfide and/or sulfoxide conversion, sulfoxide S-2 was isolated as a byproduct.
TLC (petroleum ether:EtOAc = 2:1)

Sulfone (5a)
Mp = 91-92°C, lit.² = 92-93°C; ¹H-NMR (300 MHz, CDCl₃): δ = 3.40 (s, 3H, H-1), 7.60 (pd, J = 7.2, 1.4 Hz, 2H), 8.00 (dd, J = 7.2, 1.8 Hz, 1H), 8.19 (dd, J = 7.3, 1.7 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 42.6 (C-1), 122.5, 125.5, 127.8, 128.2, 152.5, 166.5 (C-3); IR (film): ν⁻¹ = 3181, 3023, 3009, 2927, 1699, 1683, 1473, 1425, 1317, 1309, 1151, 1028, 956, 756, 690; MS (APCI), m/z (%): 214 (100) [M⁺+H], 183 (7), 251 (12), 136 (17); El. an. for C₇H₆NO₂S₂, calc. C 45.23, H 3.31, N 6.57, S 30.07; found C 45.23, H 3.24, N 6.82, S 29.88.

Sulfoxide (S-2)
Mp = 69-70°C, lit.³ = 70.5-71.5°C; ¹H-NMR (300 MHz, CDCl₃): δ = 3.08 (d, J = 7.5 Hz, 1H, H-1), 7.48 (td, J = 7.9, 1.9 Hz, 1H), 7.55 (td, J = 8.1, 1.8 Hz, 1H), 7.99 (dd, J = 7.9, 1.4 Hz, 1H), 8.05 (dd, J = 8.1, 1.0 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 43.3 (C-1), 122.5, 124.1, 126.4, 127.1, 136.1, 153.9, 178.5 (C-2); IR (film): ν⁻¹ = 3062, 3000, 2915, 1649, 1578, 1475, 1427, 1338, 1315, 1236, 1153, 1086, 1059, 1003, 953, 758, 725; MS (APCI), m/z (%): 198 (100) [M⁺], 183 (34), 180 (40), 151 (17), 136 (21); El. an. for C₈H₇NOS₂, calc. C 48.71, H 3.58, N 7.10; found C 49.03, H 3.68, N 7.02.

2-(heptylsulfonyl)benzo[d]thiazole (5b)

Sulfide S-3 synthesis: A solution of BTSH (8.0 g, 47.8 mmol, 1.0 equiv) in THF (191 mL, 0.25M) was cooled to 0°C and NaH (60% in min. oil) (2.30 g, 57.4 mmol, 1.2 equiv) was added portionwise within 10 min. The resulting solution was stirred at 0°C for 30 min, before heptyl bromide (8.27 mL, 52.6 mmol, 1.1 equiv) was added dropwise. The cooling bath was removed and the resulting mixture was allowed to warm to rt and stirred for a further 8h. Saturated aqueous NH₄Cl (100 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and the solvents were removed under reduced pressure. The crude sulfide was used in the next step without additional purification.

Sulfone 5b: A solution of crude sulfide S-3 in EtOH (214 mL, 0.20M) was cooled to 0°C and Na₂WO₄·2 H₂O (1.82 g, 5.51 mmol) was added. After 5 min at 0°C, 35% aqueous solution of H₂O₂ (21.4 mL, 221 mmol) was added dropwise. The resulting mixture was stirred at 0°C for 30 min, before the cooling bath was removed and the stirring continued at rt for a further 10h. Saturated aqueous Na₂S₂O₃ (100 mL) was
added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and
the combined organic layers were washed with brine (50 mL), dried over MgSO\textsubscript{4}, filtered and the
solvents were removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether:EtOAc = 20:1->10:1) yielding the desired sulfone 5b (13.4 g, 94 % yield).

**TLC (petroleum ether:EtOAc = 10:1)**

\[
\text{Mp} = 38-39^\circ\text{C}; \quad \text{\textsuperscript{1}H-NMR (300 MHz, CDCl}_3\text{): } \delta = 0.85 (t, J = 6.8 Hz, 3H, H-7), 1.16 - 1.37 (m, 6H), 1.44 (dt, J = 14.6, 6.7 Hz, 2H, H-3), 1.88 (dt, J = 12.1, 7.6 Hz, 2H, H-2), 3.51 (dd, J = 9.1, 7.0 Hz, 2H, H-1), 7.63 (pd, J = 7.2, 1.8 Hz, 2H), 8.03 (dd, J = 7.2, 1.7 Hz, 1H), 8.23 (dd, J = 7.3, 1.5 Hz, 1H); \text{\textsuperscript{13}C-NMR (75 MHz, CDCl}_3\text{): } \delta = 14.16 (C-7), 22.43, 22.64, 28.37, 28.75, 31.53 (C-2), 54.90 (C-1), 122.54, 125.63, 127.83, 128.18, 136.95, 152.93, 166.11 (C-8); \text{IR (film): } \nu^{-1} = 3064, 2951, 2924, 2854, 1555, 1472, 1458, 1329, 1317, 1143, 1126, 1024, 912, 853, 762; \text{MS (CI), } m/z (\%): 298 (100) [M\textsuperscript{+}], 299 (19), 250 (14), 234 (17), 183 (17), 136 (14); \text{HRMS (CI), } m/z: \text{calc. 298.0936 for C}_{14}H_{20}NO_2S_2, \text{found 298.0938.}
\]

**2-(benzylsulfonyl)benzo[d]thiazole (5c)**

**Sulfide S-5 synthesis:** A solution of BTSH (6.51 g, 39 mmol, 1.0 equiv) in THF (195 mL, 0.20M) was cooled
to 0°C and NaH (60% in min. oil) (1.86 g, 46.6 mmol, 1.2 equiv) was added portionwise within 10 min.
The resulting solution was stirred at 0°C for 30 min, before benzyl bromide (5.33 mL, 46.6 mmol, 1.2 equiv)
was added dropwise. The cooling bath was removed and the resulting mixture was allowed to
warm to rt and stirred for a further 8h. Saturated aqueous NH\textsubscript{4}Cl (100 mL) was added and resulting
layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and the combined
organic layers were washed with brine (50 mL), dried over MgSO\textsubscript{4}, filtered and the solvents were
removed under reduced pressure. The crude sulfide S-5 was used in the next step without further
purification.

\[
\text{Mp} = 39-40^\circ\text{C}, \text{lit.}^4 = 39^\circ\text{C}; \quad \text{\textsuperscript{1}H-NMR (300 MHz, CDCl}_3\text{): } \delta = 4.61 (s, 2H, H-8), 7.30(m, 5H), 7.41 – 7.49 (m, 2H), 7.76 (d, J = 8.0 Hz, 1H),7.92 (d, J = 8.1 Hz, 1H); \text{\textsuperscript{13}C-NMR (75 MHz, CDCl}_3\text{): } \delta = 37.9 (C-8), 121.2, 121.8, 124.5, 126.3, 128.0, 128.9, 129.3, 135.5, 136.4, 146.6 (C-7); \text{IR (film): } \nu^{-1} = 3060, 3028, 2922, 1600, 1560, 1495, 1454, 1425, 1310, 1275, 1238, 1126, 1074, 993, 916, 852, 754, 725, 698, 667.
\]
Sulfone 5c: A solution of crude sulfide S-5 in EtOH (200 mL, 0.20M) was cooled to 0°C and Na₂WO₄·2H₂O (1.82 g, 5.51 mmol, 0.1 equiv) was added. After 5 min at 0°C, 35% aqueous solution of H₂O₂ (15.2 mL, 156 mmol, 4.0 equiv) was added dropwise. The resulting mixture was stirred at 0°C for 30 min, before the cooling bath was removed. The reaction was stirred at rt for a further 10h. Saturated aqueous Na₂S₂O₃ (100 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (petroleum ether:EtOAc = 10:1→2:1) yielding the desired sulfone 5c (8.94 g, 79 % yield).

TLC (petroleum ether:EtOAc = 4:1)

MP = 112-113°C, lit.⁵ = 112°C; H-NMR (300 MHz, CDCl₃): δ = 4.78 (s, 1H, H-2), 7.23-7.38 (m, 5H), 7.56-7.75 (m, 2H), 7.96 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 7.8 Hz, 1H); C-NMR (75 MHz, CDCl₃): δ = 61.2 (C-2), 122.5, 125.7, 126.5, 127.9, 128.2, 129.1, 129.4, 131.3, 137.3, 152.8, 165.4 (C-1); IR (film): ν₁ = 3063, 2982, 2922, 1549, 1470, 1331, 1198, 1153, 1071, 1026, 914, 874, 853, 762, 729, 696; MS (Cl, m/z (%): 290 (43) [M⁺], 291 (9) [M⁺+1], 289 (23), 274 (22), 225 (37), 224 (100), 91 (97); HRMS (Cl, m/z: calc. 290.0309 for C₁₄H₁₂NO₂S₂, found 290.0313.

Starting from alcohol and BT-SH or PT-SH

General procedure: A solution of BT-SH or PT-SH (1.2 mmol, 1.2 equiv), PPh₃ (1.2 mmol, 1.2 equiv) and alcohol (1.0 mmol, 1.0 equiv) in THF (10 mL, 0.1M) was cooled to 0°C and DEAD (1.2 mmol, 1.2 equiv) was added. The resulting solution was allowed to warm to rt and stirred for 5-8 h.

The resulting solution was diluted with EtOH (25 mL), cooled to 0°C and Na₂WO₄·2H₂O (0.1 mmol, 0.1 equiv) in one portion. After 5 min at 0°C, an aqueous 35% solution of H₂O₂ (10.0 mmol, 10 equiv) was added dropwise with a use of pipette Pasteur. The resulting yellowish solution was allowed to warm to rt and stirred at rt for 10h.

Water (50 mL) was added and the whole mixture was extracted with EtOAc (3x100 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and the solvents were evaporated under reduced pressure. The residue was purified by flash chromatography on SiO₂ using the appropriate eluting system.

2-(tricosanylsulfonyl)benzo[d]thiazole (5d)
Purification by flash chromatography (petroleum ether:EtOAc = 50:1 -> 10:1) gave sulfone 5d (459 mg, 89%).

Mp = 35-36°C; ¹H-NMR (300 MHz, CDCl₃): δ = 0.85 (t, J = 6.8 Hz, 3H, H-3), 1.05 - 1.79 (m, 40H), 1.88 (dt, J = 12.1, 7.6 Hz, 2H, H-2), 3.51 (dd, J = 9.1, 7.0 Hz, 2H, H-1), 7.62 (pd, J = 7.2, 1.4 Hz, 2H), 8.03 (dd, J = 7.2, 1.7 Hz, 1H), 8.23 (dd, J = 7.3, 1.5 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 14.3 (C-6), 22.9, 26.4, 27.1, 29.2, 29.3, 29.6, 29.8, 29.9, 31.5, 54.8 (C-1), 122.4, 125.6, 127.8, 128.2, 136.9, 152.9, 166.1 (C-4); IR (film): ν¹ = 3063, 2982, 2922, 1553, 1470, 1456, 1331, 1198, 1153, 1071, 1026, 874, 853, 762, 729, 696; MS (APCI), m/z (%): 522 (100) [M⁺], 324 (25), 134 (27); HRMS (CI), m/z: calc. 521.3361 for C₃₀H₅₁NO₂S₂, found 521.3359.

2-(hex-3-yn-1-ylsulfonyl)benzo[d]thiazole (5e)

Purification by flash chromatography (petroleum ether:EtOAc = 10:1 -> 4:1) gave sulfone 5e (228 mg, 86%).

Mp = 40-41°C; ¹H-NMR (300 MHz, CDCl₃): δ = 1.80 (t, J = 2.3 Hz, 3H, H-6), 2.03 - 2.23 (m, 2H, H-2), 2.38 - 2.52 (m, 2H, H-3), 3.25 (t, J = 8.2 Hz, 2H, H-2), 7.64 (pd, J = 7.2, 1.5 Hz, 2H), 8.03 (dd, J = 7.2, 2.1 Hz, 1H), 8.26 (dd, J = 7.4, 2.0 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 14.4, 21.2, 25.8, 60.6, 75.9, 78.2, 122.5, 125.9, 128.5, 137.4, 152.8, 164.2 (C-1); IR (film): ν¹ = 3062, 2983, 2921, 1555, 1468, 1335, 1197, 1152, 1026, 914, 874, 762, 729; MS (APCI), m/z (%): 280 (100) [M⁺], 281 (29), 199 (31), 145 (24); HRMS (APCI), m/z: calc. 279.0388 for C₁₃H₁₃NO₂S₂, found 279.0389.

2-(hex-5-en-1-ylsulfonyl)benzo[d]thiazole (5f)

Purification by flash chromatography (petroleum ether:EtOAc = 10:1 -> 4:1) gave sulfone 5f (250 mg, 89%).

Mp = 42-43°C; ¹H-NMR (300 MHz, CDCl₃): δ = 1.18 - 1.36 (m, 2H), 1.67 (dt, J = 14.6, 6.7 Hz, 2H), 2.34 (dt, J = 12.1, 7.6 Hz, 2H, H-5), 3.48 (dd, J = 9.3, 7.0 Hz, 2H, H-2), 4.92 - 5.08 (m, 2H, H-7), 5.65 (ddt, J = 16.1, 11.2, 6.4 Hz, 1H, H-6), 7.63 (pd, J = 7.2, 1.3 Hz, 2H), 8.01 (dd, J = 7.2, 1.7 Hz, 1H), 8.22 (dd, J = 7.3, 1.5 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 23.2, 28.7, 31.5 (C-5), 55.6 (C-2), 115.8, 122.54, 125.63, 127.83, 128.18, 133.8, 136.95, 152.93, 166.1 (C-1); IR (film): ν¹ = 3063, 2951, 2924, 2853, 1557, 1471, 1458, 1317, 1144, 1122, 853, 762; MS (APCI), m/z (%): 282 (100) [M⁺], 283 (38), 199 (31), 145 (24); HRMS (APCI), m/z: calc. 281.0544 for C₁₃H₁₃NO₂S₂, found 281.0549.

2-((4-((tert-butyldiphenylsilyl)oxy)butyl)sulfonyl)benzo[d]thiazole (5g)
Purification by flash chromatography (petroleum ether:EtOAc = 20:1 -> 10:1) gave sulfone 5g (449 mg, 88%). Obtained characterization data were in agreement with those published in the literature.6

Self-condensation of sulfone 5a

\[ \text{2-[(benzo[d]thiazol-2-ylmethyl)sulfonyl]benzo[d]thiazole (7)} \]

A solution of sulfone 5a (200 mg, 0.94 mmol, 1.0 equiv) in THF (9.4 mL, 0.10 M) was cooled to -78°C and stirred for 10 min at this temperature. A solution of LiN(TMS)2 in THF (10.3 mL, 1.03 mmol, 1.1 equiv, 1.0M solution in THF) was added dropwise and the resulting mixture was stirred at -78°C for 2h. A 10% solution of HCl in MeOH (10 mL) was added and the resulting mixture was allowed to warm to rt. The whole mixture was extracted with EtOAc (3x20 mL) and the resulting organic layers were combined, washed with brine (15 mL), dried over MgSO4, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on SiO2 (petroleum ether/EtOAc = 10:1 -> 4:1 -> 2:1) yielding compound 7 (99 mg, 30.5% (61% after recalculation)) as yellow crystals.

Mp 182-183°C (lit.5 181-182°C); 1H NMR (CDCl3, 300 MHz): \( \delta = 5.32 \) (s, 2H, H-2), 7.39 – 7.53 (m, 2H), 7.57 – 7.74 (m, 2H), 7.86 (dd, \( J = 7.7, 1.0 \) Hz, 1H), 7.97 (dd, \( J = 13.0, 4.8 \) Hz, 2H), 8.27 (d, \( J = 7.8 \) Hz, 1H); 13C NMR (75 MHz, CDCl3): \( \delta = 59.0 \) (C-2), 121.9, 122.6, 124.0, 126.0, 126.3, 126.8, 128.0, 128.5, 136.5, 137.4, 152.7, 153.0, 155.2 (C-3), 164.3 (C-1); IR (film): \( \nu_{max}/\text{cm}^{-1} = 2986 \) (w), 2923 (w), 2911 (w), 1556 (w), 1504 (m), 1469 (s), 1434 (m), 1421 (w), 1394 (w), 1317 (s), 1280 (w), 1240 (m), 1201 (m), 1155 (s), 1097 (m), 1088 (m), 1064 (w), 1028 (m), 1014 (w), 910 (m), 856 (m), 762 (s), 731 (s); MS (CI), m/z (%,): 347 (M+, 13), 311 (5), 283 (29), 178 (36), 164 (33), 150 (100), 136 (100), 104 (65); HRMS (CI), m/z: calc. 346.9983 for C15H11N2O2S3, found 346.9986; El. an. for C15H11N2O2S3, calc. C 52.00, H 2.91, N 8.09; found C 52.06, H 3.09, N 8.16.

\alpha-\text{Heterosulfonyl ketones (4) and esters (11)}

General procedure

A solution of sulfone (1.0 mmol, 1.0 equiv) in THF (5 mL, 0.20M) was cooled to -78°C and LiHMDS (1.0M sol. in THF) (2.2 mL, 2.2 mmol, 2.2 equiv) was added dropwise. A color of the reaction mixture turned from colorless or slightly yellow to orange/red. Immediately after, a solution of acylating agent (acyl halide, carboxylic acid anhydride or acyl imidazole7) or alkoxy carbonylating agent (alkoxy chloroformate, alkoxy imidazoylformate8 or Boc2O) (1.1 mmol, 1.1 equiv) in THF (0.5 mL)9 was added. The color of the reaction mixture faded within few minutes. The resulting mixture was stirred at -78°C for 30 min, allowed to warm to 0°C within 1h and stirred at 0°C for a further 30 min before sat. aq. sol. of NH4Cl (15 mL) was added. The whole mixture was extracted with EtOAc (3x75 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO4, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography on SiO2.
2-(benzo[d]thiazol-2-ylsulfonyl)-1-phenylethanone (4a)

Starting from sulfone 5a (100 mg, 0.47 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->2:1->1:1):
  - Using BzCl as acylating agent (Table 1, entry 4), the reaction yielded 143 mg (96%) of 4a.
  - Using Bz₂O as acylating agent (Table 1, entry 16), the reaction yielded 137 mg (92%) of 4a.
  - Using Bz-Im as acylating agent (Table 1, entry 17), the reaction yielded 137 mg (92%) of 4a.
  - Using Bz-CN as acylating agent (Table 1, entry 18), the reaction yielded 135 mg (92%) of 4a.

The reaction performed with 2.0 g (9.4 mmol) of sulfone 5a and 1.31 mL (11.4 mmol) of BzCl\(^{10}\) gave 2.89 g (97%) of 4a.

TLC (petroleum ether:EtOAc = 2:1)

\begin{center}
\begin{tabular}{c}
\text{BzCl (UV, KMnO}_4\text{)}
\text{11a (UV, KMnO}_4\text{)}
\text{sulfone (UV, KMnO}_4\text{)}
\end{tabular}
\end{center}

Mp = 123-124°C, lit.\(^{11}\) 122°C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.22\) (s, 2H, H-2), 7.43 – 7.53 (m, 2H), 7.55 – 7.69 (m, 3H), 7.94 (dd, \(J = 8.4, 1.2\) Hz, 2H), 8.01 (dd, \(J = 7.0, 2.2\) Hz, 1H), 8.20 (dd, \(J = 7.2, 2.1\) Hz, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 61.4\) (C-2), 122.6, 125.7, 127.9, 128.4, 129.17, 129.19, 134.9, 135.6, 137.3, 152.6, 165.5 (C-1), 187.3 (C-3); IR (film): \(\nu \text{ cm}^{-1} = 3063\) (w), 2959 (w), 2925 (w), 2921 (w), 2919 (w), 1683 (s), 1598 (m), 1471 (m), 1338 (s), 1155 (s), 991 (m), 760 (s), 731 (s), 688 (s); MS (APCI), \(m/z\) (%): 318 (100) [M\(^+\)+1], 319 (20), 236 (9), 105 (11); El. an. for C\(_{15}\)H\(_{11}\)NO\(_3\)S\(_2\), calc. C 56.76, H 3.49, N 4.41; found C 56.78, H 3.11, N 4.67.

1-(benzo[d]thiazol-2-ylsulfonyl)propan-2-one (4b)

Starting from sulfone 5a (100 mg, 0.47 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->2:1->1:1):
  - Using AcCl as acylating agent (Table 5, entry 1), the reaction yielded 108 mg (90%) of 4b.
  - Using Ac₂O as acylating agent (Table 5, entry 2), the reaction yielded 110 mg (92%) of 4b.
  - Using Ac-Im as acylating agent (Table 5, entry 3), the reaction yielded 107 mg (89%) of 4b.

The reaction performed with 2.0 g (9.4 mmol) of sulfone 5a and 0.8 mL (11.4 mmol) of AcCl\(^{12}\) gave 2.15 g (90%) of 4b.
TLC (petroleum ether:EtOAc = 2:1)

\[ \text{UV, KMnO}_4 \] 4b

sulfone (UV, KMnO4)

MP = 126-127°C, lit.13 125-127°C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 2.46 \) (s, 3H, H-4), 4.60 (s, 2H, H-2), 7.57 – 7.71 (m, 2H), 8.03 (dd, \( J = 8.0, 1.4 \) Hz, 1H), 8.22 (dd, \( J = 6.7, 1.5 \) Hz, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 31.7 \) (C-4), 65.6 (C-2), 122.6, 125.8, 128.0, 128.5, 137.1, 152.6, 165.0 (C-1), 194.8 (C-3); IR (film): \( \nu^1 = 2990 \) (w), 2952 (w), 2925 (w), 2853 (w), 1726 (s), 1556 (w), 1471 (m), 1334 (s), 1159 (s), 1028 (m), 854 (m), 762 (s); MS (APCI), \( m/z \) (%): 256 (100) [M\(^+\)+1], 258 (15), 214 (27), 136 (13); El. an. for C\(_{10}\)H\(_9\)NO\(_3\)S\(_2\), calc. C 46.82, H 3.35, N 5.49; found C 46.82, H 3.35, N 5.12.

2-(benzo[d]thiazol-2-ylsulfonyl)-1-cyclohexyloctan-1-one (4c)

Starting from sulfone 5b (100 mg, 0.34 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1):
- Using AcCl as acylating agent (Table 5, entry 4), the reaction yielded 114 mg (83%) of 4c.
- Using Ac-Im as acylating agent (Table 5, entry 5), the reaction yielded 126 mg (92%) of 4c.

TLC (petroleum ether:EtOAc = 4:1)

\[ \text{UV, KMnO}_4 \] 4c

sulfone (UV, KMnO4)

MP = 132-133°C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.82 \) (t, \( J = 6.7 \) Hz, 3H, H-13), 1.06 – 1.56 (m, 13H), 1.59 – 2.09 (m, 6H), 2. 12 – 2.33 (m, 1H), 2.78 (tt, \( J = 11.3, 3.3 \) Hz, 1H, H-4), 4.73 (dd, \( J = 10.7, 3.5 \) Hz, 1H, H-2), 7.64 (pd, \( J = 7.2, 1.6 \) Hz, 1H), 7.65 (p, \( J = 7.2 \) Hz, 1H), 8.01 (dd, \( J = 7.2, 1.8 \) Hz, 1H), 8.25 (dd, \( J = 7.4, 1.9 \) Hz, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \( \delta = 14.1 \) (C-13), 22.6, 25.2, 25.8, 26.0, 27.1, 27.3, 27.6, 28.5, 29.0, 31.4, 52.8 (C-4), 72.7 (C-2), 122.5, 125.9, 127.9, 128.4, 137.4, 152.8, 164.2 (C-1), 204.1 (C-3); IR (film): \( \nu^1 = 2991 \) (w), 2952 (w), 2927 (w), 2852 (w), 1728 (s), 1554 (w), 1475 (m), 1161 (s), 1029 (m), 853 (m), 761 (s); MS (APCI), \( m/z \) (%): 408 (100) [M\(^+\)], 409 (21), 105 (40); El. an. for C\(_{21}\)H\(_{29}\)NO\(_3\)S\(_2\), calc. C 61.88, H 7.17, N 3.44; found C 62.03, H 7.29, N 3.13.
2-(benzo[d]thiazol-2-ylsulfonyl)-1-mesityloctan-1-one (4d)

Starting from sulfone 5b (100 mg, 0.34 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1) yielding 112 mg (89%) of 4d (Table 5, entry 6).

TLC (petroleum ether:EtOAc = 4:1) 

Mp = 145-146°C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.86\) (t, \(J = 6.7\) Hz, 3H, H-13), 1.20 – 1.31 (m, 4H), 1.36 (dt, \(J = 14.6, 7.3\) Hz, 2H, H-10), 1.51 (tt, \(J = 12.1, 6.2\) Hz, 2H, H-15), 1.98 (s, 3H, H-15), 2.29 (s, 6H, H-14, partial overlap), 5.38 (t, \(J = 6.5\) Hz, 1H, H-2), 6.55 (s, 2H, H-6), 7.50 – 7.64 (m, 2H), 7.92 (d, \(J = 7.7\) Hz, 1H), 8.12 (dd, \(J = 7.6, 0.8\) Hz, 1H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)): \(\delta = 14.16\) (C-13), 20.6 (C-14), 21.0 (C-15), 22.6, 24.9, 27.6, 29.3, 31.4, 74.2 (C-2), 122.2, 125.3, 127.6, 128.0, 129.4, 135.5, 136.0, 137.2, 140.6, 152.4, 165.9 (C-1), 197.3 (C-3); IR (film): \(\nu^\prime = 3063\) (w), 3059 (w), 2958 (w), 2925 (w), 2920 (w), 1681 (s), 1597 (m), 1471 (m), 1331 (s), 1156 (s), 990 (m), 761 (s), 730 (s), 689 (s); MS (APCI), \(m/z\) (%): 444 (100) [M\(^+\)], 445 (26), 324 (51); El. an. for C\(_{24}\)H\(_{29}\)NO\(_3\)S\(_2\), calc. C 64.98, H 6.59, N 3.16; found C 65.21, H 6.23, N 3.19.

3-(benzo[d]thiazol-2-ylsulfonyl)-1-phenoxynonan-2-one (4e)

Starting from sulfone 5b (100 mg, 0.34 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1->4:1) yielding 125 mg (86%) of 4e as yellowish oil (Table 5, entry 7).

TLC (petroleum ether:EtOAc = 4:1)
ethyl 3-(benzo[d]thiazol-2-ylsulfonyl)-2-oxononanoate (4f)

Starting from sulfone 5b (100 mg, 0.34 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->2:1) yielding 104 mg (78%) of 4f as yellow oil (Table 5, entry 8).

TLC (petroleum ether:EtOAc = 2:1)

Keto/enol forms of 11f = ~1:1. Peaks belonging to enol form are marked with *.

1H-NMR (300 MHz, CDCl3): δ = 0.84 (t, J = 6.7 Hz, 3H, H-10). 0.98 – 1.57 (m, 8H), 2.08 – 2.38 (m, 2H), 4.12 (q, J = 7.2 Hz, 2H, H-11*), 4.30 (q, J = 7.2 Hz, 2H, H-11), 5.55 (t, J = 7.2 Hz, 1H, H-2), 7.51 – 7.72 (m, 2H), 7.93 – 8.07 (m, 1H), 8.14 – 8.27 (m, 1H); 13C-NMR (75 MHz, CDCl3): δ = 14.1 (C-10*), 14.4 (C-10), 21.23, 22.56, 26.18, 26.87, 28.06, 28.91, 31.24, 31.37, 60.6 (C-11), 63.8 (C-11*), 68.6 (C-2*), 122.6, 125.7, 128.0, 127.8, 128.6, 137.2, 152.3, 160.3, 164.3, 171.3 (C-4), 185.1 (C-3); IR (film): ν⁻¹ = 3320 (w), 2955 (m), 2928 (s), 2856 (m), 1731 (s), 1705 (s), 1674 (s), 1470 (s), 1330 (m), 1150 (s), 1020 (m), 852 (m), 762 (m), 729 (s); MS (APCI), m/z (%): 398 (100) [M⁺], 399 (22), 370 (48), 334 (31), 298 (30), 281 (58), 199 (14), 136 (11); El. an. for C₁₈H₂₃NO₅S₂, calc. C 54.39, H 5.83, N 3.52; found C 54.42, H 5.89, N 3.58.

5-(benzo[d]thiazol-2-ylsulfonyl)-1-chloroundecan-4-one (4g)

Starting from sulfone 5b (100 mg, 0.34 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1->4:1) yielding 110 mg (81%) of 4g as yellow oil (Table 5, entry 9).
TLC (petroleum ether:EtOAc = 4:1)

1H-NMR (300 MHz, CDCl3): δ = 0.83 (t, J = 6.7 Hz, 3H, H-12), 1.12 – 1.37 (m, 8H), 2.31 – 1.99 (m, H-5 and H-7), 2.89 (dt, J = 10.7, 3.9 Hz, 1H, H-2), 7.63 (pd, J = 7.2, 1.4 Hz, 2H), 8.02 (dd, J = 7.1, 1.9 Hz, 1H); 13C-NMR (75 MHz, CDCl3): δ = 14.10 (C-12), 22.6, 26.2, 26.8, 27.0, 28.9, 31.4, 41.6, 44.0, 74.6 (C-2), 122.5, 125.9, 128.0, 128.5, 137.3, 152.7, 164.0 (C-1), 200.3 (C-3); IR (film): ν1 = 2955 (m), 2928 (s), 2856 (m), 1720 (s), 1467 (s), 1330 (s), 1315 (s), 1144 (m), 1022 (m), 852 (m), 762 (m), 729 (s); MS (APCI), m/z (%): 402 (11) [M+], 404 (7), 366 (100), 302 (40); El. an. for C18H24ClNO3S2, calc. C 53.78, H 6.02, N 3.48; found C 53.92, H 5.91, N 3.69.

2-(benzo[d]thiazol-2-ylsulfonyl)-1-cyclohexylethanoic (4h)

Starting from sulfone 5a (200 mg, 0.94 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->2:1) yielding sulfone 4h (252 mg, 83%) as slightly yellow crystals (Table 4, entry 3).

TLC (petroleum ether:EtOAc = 2:1)

Keto/enol forms of 4h = ~9:1. Peaks belonging to enol form are marked with *.
Mp = 87-88°C; 1H-NMR (300 MHz, CDCl3): δ = 1.12 – 1.42 (m, 6H), 1.61 – 2.01 (m, 4H), 2.55 – 2.70 (ddd, J = 14.0, 7.5, 3.4 Hz, 1H, H-4), 4.68 (s, 2H, H-2), 5.30 (s, 1H, H-2*), 7.41 – 7.54 (m, 2H), 8.01 (dd, J = 7.8, 1.5 Hz, 1H), 8.19 (dd, J = 7.5, 1.3 Hz, 1H); 13C-NMR (75 MHz, CDCl3): δ = 25.4, 25.7, 27.9, 51.8 (C-4), 62.7 (C-2), 122.6, 125.6, 127.9, 128.3, 137.1, 152.5, 165.5 (C-1), 200.5 (C-3); IR (film): ν1 = 2940 (m), 2932 (m), 2925 (m), 2909 (w), 2894 (w), 2857 (m), 1716 (m), 1706 (s), 1473 (s), 1450 (m), 1336 (s), 1317 (s), 1294 (m), 1278 (m), 1157 (s), 1147 (s), 1128 (s), 1088 (m), 1062 (m), 1028 (m), 999 (s), 902 (m), 856 (s), 760 (s), 731 (s), 708 (s), 692 (s); MS (APCI), m/z (%): 324 (100) [M+], 198 (60), 134 (29); El. an. for C15H17NO3S2, calc. C 55.70, H 5.30, N 4.33; found C 55.79, H 5.18, N 4.11.
methyl 2-(benzo[d]thiazol-2-ylsulfonyl)acetate (11a)

Starting from sulfone 5a (100 mg, 0.34 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->2:1->1:1):
- Using ClCOOMe as alkoxycarbonylating agent (Table 6, entry 1), the reaction yielded 120 mg (94%) of 11a.
- Using Im-COOMe as alkoxycarbonylating agent (Table 6, entry 2), the reaction yielded 113 mg (89%) of 11a.
- Using NC-COOMe as alkoxycarbonylating agent (Table 6, entry 3), the reaction yielded 116 mg (91%) of 11a.

The reaction performed with 3.0 g (14.1 mmol) of sulfone 5a and 1.3 mL (16.9 mmol) of ClCOOMe gave 3.74 g (98%) of 11a.

TLC (petroleum ether:EtOAc = 2:1)

Keto/enol forms of 11a = ~7:1. Peaks belonging to enol form are marked with *.

Mp = 69-70°C; 1H-NMR (300 MHz, CDCl3): δ = 3.66 (s, 3H, H-4), 3.73 (s, 3H, H-4*), 4.59 (s, 2H, H-2), 5.31 (s, 1H, H-2*), 7.54 – 7.71 (m, 2H), 8.02 (dd, J = 7.1, 2.1 Hz, 1H), 8.21 (dd, J = 7.3, 2.2 Hz, 1H); 13C-NMR (75 MHz, CDCl3): δ = 52.4 (C-4*), 53.5 (C-4), 58.7 (C-2), 122.6, 125.7, 127.9, 128.4, 137.1, 152.6, 162.3 (C-1), 165.0 (C-3); IR (film): ν = 2992 (w), 2984 (w), 2938 (w), 1803 (m), 1741 (s), 1471 (s), 1342 (s), 1155 (s), 1122 (s), 762 (s), 729 (s); MS (APCI), m/z (%): 272 (100) [M⁺], 240 (35), 214 (7); El. an. for C_{10}H_{9}NO_{4}S_{2}, calc. C 44.27, H 3.34, N 5.16; found C 44.67, H 3.12, N 4.97.

allyl 2-(benzo[d]thiazol-2-ylsulfonyl)acetate (11b)

Starting from sulfone 5a (100 mg, 0.47 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->1:1) yielding 132 mg (95%) of 11b (Table 6, entry 34).

The reaction performed with 1.0 g (4.69 mmol) of sulfone 13a and 0.598 mL (5.63 mmol) of ClCOOCH_{2}CH=CH gave 1.31 g (94%) of 11b.
TLC (petroleum ether:EtOAc = 2:1)

Keto/enol forms of 11b = ~7:1. Peaks belonging to enol form are marked with *.

Mp = 72-73°C; 1H-NMR (300 MHz, CDCl3): δ = 4.60 (td, J = 2.7, 1.3 Hz, 2H, H-4), 4.61 (s, 2H, H-2), 4.65 – 4.70 (m, 1H, H-2*), 5.18 (ddd, J = 10.5, 2.2, 1.1 Hz, 1H, H-6), 5.24 (ddd, J = 17.3, 2.8, 1.4 Hz, 1H, H-6), 5.31 – 5.42 (m, 2H, H-6*), 5.77 (ddt, J = 22.2, 10.4, 5.9 Hz, 1H, H-5), 5.85 – 6.00 (m, 1H, H-5*), 7.58 – 7.69 (m, 2H), 8.02 (dd, J = 7.0, 1.9 Hz, 1H), 8.22 (dd, J = 7.4, 2.1 Hz, 1H); 13C-NMR (75 MHz, CDCl3): δ = 58.8 (C-4), 67.3 (C-2), 119.8, 122.6, 125.7, 128.0, 128.5, 130.6, 132.7, 152.6, 161.5 (C-1), 165.0 (C-3); IR (film): ν1 = 3089 (w), 3073 (w), 2992 (w), 2984 (w), 2938 (w), 1803 (m), 1741 (s), 1650 (w), 1554 (w), 1519 (m), 1471 (s), 1423 (m), 1471 (s), 1342 (s), 1317 (s), 1300 (s), 1276 (s), 1240 (s), 1195 (s), 1155 (s), 1122 (s), 1088 (s), 1028 (s), 987 (s), 935 (s), 854 (s), 796 (s), 762 (s), 729 (s), 710 (s), 694 (s), 652 (m), 644 (s), 633 (s), 625 (s), 617 (s), 609 (m); MS (APCI), m/z (%): 298 (100) [M]+, 240 (24); El. an. for C12H11NO3S2, calc. C 48.47, H 3.73, N 4.71; found C 48.82, H 3.65, N 4.38.

tert-butyl 2-(benzo[d]thiazol-2-ylsulfonyl)acetate (11c)

Starting from sulfone 5a (100 mg, 0.47 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1):
- Using Boc2O as alkoxy carbonylating agent (Table 6, entry 5), the reaction yielded 138 mg (94%) of 11c.
- Using Im-COOtBu as alkoxy carbonylating agent (Table 6, entry 6), the reaction yielded 144 mg (89%) of 11c.

The reaction performed with 2.0 g (9.38 mmol) of sulfone 5a and 2.46 g (11.3 mmol) of Boc2O gave 2.88 g (98%) of 11c.

TLC (petroleum ether:EtOAc = 4:1)

Keto/enol forms of 11c = ~6:1. Peaks belonging to enol form are marked with *.

Mp = 75-76°C; 1H-NMR (300 MHz, CDCl3): δ = 1.13 (s, 9H, H-5), 1.48 (s, 9H, H5*), 4.49 (s, 2H, H-2), 7.63 (p, J = 7.2, 1.5 Hz, 2H), 8.03 (dd, J = 7.1, 1.8 Hz, 1H), 8.23 (dd, J = 7.2, 1.7 Hz, 1H); 13C-NMR (75 MHz, CDCl3): δ = 27.8 (C-5), 28.2 (C-5*), 60.1 (C-2), 84.6 (C-4), 122.6, 125.7, 127.9, 128.4, 137.0, 152.7, 160.6 (C-1), 165.4
(C-3); IR (film): ν⁻¹ = 2977 (w), 2935 (w), 1794 (m), 1732 (s), 1471 (m), 1339 (s), 1144 (s), 1088 (s), 761 (s), 629 (s); MS (ESI), m/z (%): 336 (33) [M+Na⁺], 258 (100), 240 (19); El. an. for C₁₃H₁₅NO₄S₂, calc. C 49.82, H 4.82, N 4.47; found C 50.13, H 4.98, N 4.75.

**methyl 2-(benzo[d]thiazol-2-ylsulfonyl)-2-phenylacetate (11d)**

Starting from sulfone 5c (100 mg, 0.35 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->1:1):

- Using CICOOMe as alkoxy carbonylating agent (Table 6, entry 7), the reaction yielded 106 mg (88%) of 11d.
- Using Im-COOOMe as alkoxy carbonylating agent (Table 6, entry 8), the reaction yielded 113 mg (94%) of 11d.
- Using NC-COOMe as alkoxy carbonylating agent (Table 6, entry 9), the reaction yielded 110 mg (92%) of 11d.

TLC (petroleum ether:EtOAc = 2:1)

Mp = 115-116°C; ¹H-NMR (300 MHz, CDCl₃): δ = 3.78 (s, 3H, H-4), 5.77 (s, 1H, H-2), 7.30 – 7.42 (m, 3H), 7.50 – 7.55 (m, 2H), 7.62 – 7.68 (m, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.24 (d, J = 7.6 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 53.7 (C-4), 73.6 (C-2), 122.5, 125.7, 126.4, 127.9, 128.4, 129.2, 130.3, 130.9, 137.4, 152.5, 164.4, 164.7; IR (film): ν⁻¹ = 3072 (s), 2963 (m), 2937 (w), 1740 (s), 1472 (s), 1341 (s), 1144 (s), 1121 (s), 762 (s), 729 (s); MS (APCI), m/z (%): 348 (100) [M⁺], 284 (26), 224 (12), 149 (7); El. an. for C₁₆H₁₃NO₄S₂, calc. C 55.32, H 3.77, N 4.03; found C 55.67, H 3.60, N 3.99.

**tert-butyl 2-(benzo[d]thiazol-2-ylsulfonyl)-2-phenylacetate (11e)**

Starting from sulfone 5c (100 mg, 0.35 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 4:1->2:1):

- Using Boc₂O as alkoxy carbonylating agent (Table 6, entry 10), the reaction yielded 124 mg (91%) of 11.
- Using Im-COOtBu as alkoxy carbonylating agent (Table 6, entry 11), the reaction yielded 134 mg (98%) of 11e.
TLC (petroleum ether:EtOAc = 4:1)

Keto/enol forms of 11e = ~5:1. Peaks belonging to enol form are marked with *.

Mp = 121-122°C; 1H-NMR (300 MHz, CDCl₃): δ = 1.38 (s, 9H, H-5), 1.49 (s, J = 5.5 Hz, 9H, H-5*), 5.71 (s, 1H, H-2), 7.33 – 7.43 (m, 3H), 7.51 – 7.69 (m, 4H), 7.96 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H); 13C-NMR (75 MHz, CDCl₃): δ = 27.7 (C-5), 28.04 (C-5*), 74.2 (C-4), 122.3, 125.5, 126.6, 127.7, 128.1, 128.9, 130.0, 130.8, 137.1, 152.4, 162.6 (C-2), 165.1 (C-3); IR (film): ν¹ = 3071 (s), 3062 (m), 2995 (w), 2938 (w), 1805 (w), 1742 (s), 1471 (s), 1332 (s), 1143 (s), 1112 (s), 761 (s), 728 (s); MS (APCI), m/z (%): 390 (100) [M⁺]+, 200 (31); El. an. for C₁₉H₁₉NO₄S₂, calc. C 58.59, H 4.92, N 3.60; found C 58.21, H 5.02, N 3.83.

methyl 2-(benzo[d]thiazol-2-ylsulfonyl)-2-lignocerate (11f)

Starting from sulfone 5d (100 mg, 0.19 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 20:1->10:1):

- Using ClCOOMe as alkoxy carbonylating agent (Table 6, entry 12), the reaction yielded 98 mg (88%) of 11f.
- Using Im-COOMe as alkoxy carbonylating agent (Table 6, entry 13), the reaction yielded 104 mg (94%) of 11f.
- Using NC-COOMe as alkoxy carbonylating agent (Table 6, entry 14), the reaction yielded 103 mg (93%) of 11f.

TLC (petroleum ether:EtOAc = 10:1)

Keto/enol forms of 11f = ~8:1. Peaks belonging to enol form are marked with *.

Mp = 111-112°C; 1H-NMR (300 MHz, CDCl₃): δ = 0.88 (t, J = 6.7 Hz, 3H, H-6), 1.05 – 1.71 (m, 40H), 2.14 – 2.34 (m, 2H, H-5), 3.64 (t, J = 6.7 Hz, 2H, H-5*), 3.74 (s, 3H, H-4), 4.44 (dd, J = 8.8, 6.0 Hz, 1H, H-2), 5.30 (s, 1H*), 7.58 – 7.71 (m, 2H), 8.03 (dd, J = 7.1, 1.9 Hz, 1H), 8.26 (dd, J = 7.2, 1.8 Hz, 1H); 13C-NMR (75 MHz, CDCl₃): δ = 14.3 (C-6), 22.9, 26.4, 27.1, 29.2, 29.3, 29.6, 29.8, 29.9, 32.1, 53.5 (C-4), 70.0 (C-2), 122.5, 125.9, 127.9, 128.4, 137.4, 152.8, 164.5 (C-1), 165.6 (C-3); IR (film): ν¹ = 3061 (w), 2996 (s), 2929 (s), 2859 (w), 1473 (s), 1243 (m), 1160 (s), 967 (s), 728 (s), 696 (s), 670 (s).
1801 (w), 1744 (s), 1472 (m), 1331 (s), 1143 (s), 1122 (s), 761 (s), 727 (s); MS (APCI), m/z (%): 580 (100) [M⁺], 581 (37); El. an. for C₃₂H₅₃NO₄S₂, calc. C 66.28, H 9.21, N 2.42; found C 66.49, H 9.17, N 2.57.

methyl 2-(benzo[d]thiazol-2-ylsulfonyl)hept-5-ynoate (11g)

Starting from sulfone 5e (100 mg, 0.19 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1->4:1->2:1->1:1):
- Using ClCOOMe as alkoxy carbonylating agent (Table 6, entry 15), the reaction yielded 112 mg (88%) of 11g as yellowish oil.
- Using Im-COOMe as alkoxy carbonylating agent (Table 6, entry 16), the reaction yielded 118 mg (93%) of 11g as yellowish oil.
- Using NC-COOMe as alkoxy carbonylating agent (Table 6, entry 17), the reaction yielded 119 mg (94%) of 11g as yellowish oil.

TLC (petroleum ether:EtOAc = 2:1)

Keto/enol forms of 11g = ~8:1. Peaks belonging to enol form are marked with *.

¹H-NMR (300 MHz, CDCl₃): δ = 1.73 (t, J = 2.3 Hz, 3H, H-9), 2.13 – 2.33 (m, 1H), 2.34 – 2.49 (m, 3H), 2.67 – 2.87 (m, 2H, H-6*), 3.74 (s, 3H, H-4), 4.70 (dd, J = 7.8, 6.1 Hz, 1H, H-2), 5.31 (s, 1H*), 5.39 – 5.55 (m, 1H), 7.49 – 7.37 (m, 1H*), 7.63 (p, J = 7.2 Hz, 1H), 7.65 (p, J = 7.2 Hz, 1H), 7.94 – 7.80 (m, 2H*), 8.03 (dd, J = 7.2, 2.1 Hz, 1H), 8.26 (dd, J = 7.4, 2.0 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 3.6, 14.4, 16.7, 21.2, 25.8, 53.6, 60.6, 68.9, 75.8, 78.6, 122.5, 125.9, 128.0, 128.5, 137.4, 152.8, 164.2 (C-1), 165.2 (C-3); IR (film): ν₁ = 2954 (w), 2917 (w), 1739 (s), 1471 (m), 1436 (m), 1336 (s), 1149 (s), 1024 (m), 854 (m), 764 (s), 731 (s), 694 (m), 640 (m); MS (APCI), m/z (%): 338 (100) [M⁺], 339 (12), 306 (16); El. an. for C₁₅H₁₅NO₄S₂, calc. C 53.40, H 4.48, N 4.15; found C 53.71, H 4.63, N 4.25.

allyl 2-(benzo[d]thiazol-2-ylsulfonyl)hept-5-ynoate (11h)

Starting from sulfone 5e (100 mg, 0.36 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1->4:1); the reaction yielded 116 mg (89%) of 11h as yellow oil (Table 6, entry 18).
Keto/enol forms of 11h = ~7:1. Peaks belonging to enol form are marked with *.

\[^1\text{H-NMR}\ (300\ \text{MHz, CDCl}_3): \delta = 1.75\ (t, J = 2.3\ \text{Hz, 3H, H-11}), 2.17 – 2.67\ (m, 4H), 3.95 – 4.23\ (m, 2H*), 4.61\ (dd, J = 5.8, 1.2\ \text{Hz, 2H, H-4}), 4.72\ (dd, J = 7.6, 6.3\ \text{Hz, 1H, H-2}), 5.14\ (dd, J = 10.4, 1.1\ \text{Hz, 1H, H-6}), 5.22\ (dd, J = 17.2, 1.3\ \text{Hz, 1H, H-6}), 5.29 – 5.41\ (m, 2H, H-6*), 5.61\ (dd, J = 8.1\ \text{Hz, 1H*}), 7.37\ (t, J = 7.7\ \text{Hz, 1H*}), 7.63\ (p, J = 7.2\ \text{Hz, 1H}), 7.65\ (p, J = 7.2\ \text{Hz, 1H}), 7.89\ (d, J = 8.0\ \text{Hz, 1H*}), 7.98\ (d, J = 7.0, 1.8\ \text{Hz, 1H}), 8.02\ (dd, J = 7.2, 1.8\ \text{Hz, 1H}); \[^{13}\text{C-NMR}\ (75\ \text{MHz, CDCl}_3): \delta = 3.7, 16.7, 25.8, 67.3, 68.9, 75.9, 78.6, 119.6, 122.5, 126.0, 127.9, 128.5, 130.8, 137.4, 152.9, 164.2, 164.5; \text{IR (film): } \nu = 3071\ (w), 3063\ (w), 2934\ (w), 2919\ (w), 2855\ (w), 1739\ (s), 1677\ (w), 1650\ (w), 1554\ (w), 1471\ (s), 1149\ (s), 1024\ (s), 941\ (s), 854\ (s), 764\ (s), 731\ (s); \text{MS (APCI), } m/z\ (%): 364\ (100) [\text{M}^+], 365\ (17), 306\ (7); \text{El. an. for } C_{17}H_{17}NO_4S_2, \text{calc. } C 56.18, H 4.71, N 3.85; \text{found } C 55.82, H 4.83, N 3.95.

methyl 2-(benzo[d]thiazol-2-ylsulfonyl)hept-6-enoate (11i)

Starting from sulphone 5f (100 mg, 0.36 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1-4:1):
- Using CICOOOMe as alkoxy carbonylating agent (Table 6, entry 19), the reaction yielded 105 mg (87%) of 11i (yellow oil).
- Using Im-COOOMe as alkoxy carbonylating agent (Table 6, entry 20), the reaction yielded 115 mg (95%) of 11i (yellow oil).
- Using NC-COOOMe as alkoxy carbonylating agent (Table 6, entry 21), the reaction yielded 113 mg (94%) of 11i (yellow oil).

TLC (petroleum ether:EtOAc = 2:1)

Keto/enol forms of 11i = ~11:1. Peaks belonging to enol form are marked with *.

\[^1\text{H-NMR}\ (300\ \text{MHz, CDCl}_3): \delta = 1.58 – 1.45\ (m, 2H), 2.11\ (dt, J = 14.2, 4.7\ \text{Hz, 2H}), 2.20 – 2.32\ (m, 2H), 3.73\ (s, 3H, H-4), 4.47\ (td, J = 7.9, 5.4\ \text{Hz, 1H, H-2}), 4.95\ (dd, J = 10.5, 1.3\ \text{Hz, 1H, H-9}), 5.05\ (dt, J = 3.0, 1.5\ \text{Hz, 1H, H-9}), 5.73\ (ddt, J = 16.9, 10.2, 6.7\ \text{Hz, 1H, H-8}), 7.64\ (pd, J = 7.2, 1.5\ \text{Hz, 2H}), 8.03\ (dd, J = 7.2, 2.1\ \text{Hz, 2H}); \text{calc. } C 56.18, H 4.71, N 3.85; \text{found } C 55.82, H 4.83, N 3.95.
Starting from sulfone 5g (100 mg, 0.20 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1->1:4):

- Using ClCOOMe as alkoxy carbonylation agent (Table 6, entry 22), the reaction yielded 99 mg (89%) of 11j (yellow oil).
- Using Im-COOMe as alkoxy carbonylation agent (Table 6, entry 23), the reaction yielded 104 mg (93%) of 11j (yellow oil).
- Using Im-COOMe as alkoxy carbonylation agent (Table 6, entry 24), the reaction yielded 102 mg (91%) of 11j (yellow oil).

Keto/enol forms of 11j = ~6:1. Peaks belonging to enol form are marked with*.

Starting from sulfone 5b (100 mg, 0.34 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1->4:1); the reaction yielded 118 mg (92%) of 11k as yellow oil (Table 6, entry 25).

Keto/enol forms of 11k = >20:1. Peaks belonging to enol form are marked with*.
Starting from sulfone 5a (200 mg, 0.94 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 10:1→4:1); the reaction yielded 266 mg (94%) of 11l as yellow oil (Table 7, entry 2).

Keto/enol forms of 11l = 8:1. Peaks belonging to enol form are marked with *.

Starting from sulfone 5a (200 mg, 0.94 mmol), the crude material was purified by flash chromatography (petroleum ether:EtOAc = 2:1→1:1); the reaction yielded 185 mg (63%) of 11m as white solid (Table 7, entry 3).

Keto/enol forms of 11m = 8:1. Peaks belonging to enol form are marked with *.
(7); HRMS (ES), m/z: calc. 335.0500 for C_{13}H_{16}N_{2}O_{3}S_{2}Na, found 335.0483; El. an. for C_{13}H_{16}N_{2}O_{3}S_{2}, calc. C 49.98, H 5.16, N 8.97; found C 50.03, H 5.15, N 8.94.

**Synthesis of 2-(((phenylsulfonyl)methyl)sulfonyl)benzo[d]thiazole (12b)**

A solution of sodium benzenesulfinate (10.0 g, 60.92 mmol, 1.0 equiv) in DMF (250 mL, 0.25M) was stirred at RT for 15 min. Diiodomethane (6.0 mL, 75.06 mmol, 1.2 equiv) was added dropwise and the solution was stirred for a further 17h at RT. H_{2}O (100 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and the combined organic layers were washed with brine (50 mL), dried over MgSO_{4}, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (Petroleum Ether:EtOAc = 10:1->4:1->2:1) yielding the desired iodo-sulfone S-6 as a yellow oil (12.0 g, 70 % yield).

TLC (Petroleum Ether:EtOAc = 2:1)

\[
\text{CH}_{2}I_{2} \hspace{1cm} \text{Iodo- sulfate(UV,KMnO}_{4} \hspace{1cm} \text{Salt (UV,KMnO}_{4} \\
\]

\[\delta = 2.47 \ (s, 2H, H-1), 7.59 \ (t, J = 7.5 \ Hz, 2 H), 7.43 \ (t, J = 7.2 \ Hz, 1H), 7.98 \ (d, J = 7.5 \ Hz, 2H) ; \delta = 16.9 \ (C-1), 129.0, 129.4, 134.6, 135.9; IR (film): \nu^{-1} = 3016, 2948, 1583, 1477, 1446, 1369, 1307, 1211, 1157, 1134, 1080, 1024, 999, 931, 906, 844, 790, 769, 736, 707, 684, 671, 617; MS (APCI), m/z (%) : 283 (100) [M^{+}H], 141 (7), 125 (12).

**2-(((phenylsulfonyl)methyl)thio)benzo[d]thiazole (S-7)**

A solution of BT-SH (14.23 g, 85.08 mmol, 1.0 equiv) in DMF (450 mL, 0.20M) was cooled to 0°C and NaH (60% in min. oil) (3.6 g, 89.33 mmol, 1.05 equiv) was added portionwise within 10 min. The resulting solution was stirred at 0°C for 30 min, before ((iodomethyl)sulfonyl)benzene (S-6) (12.0 g, 42.5 mmol, 0.5 equiv) was added dropwise. The cooling bath was removed and the resulting mixture was stirred at 75°C for a further 18h.
The resulting mixture was cooled to rt and saturated aqueous NH₄Cl (200 mL) was added. Resulting layers were separated and the aqueous layer was extracted with EtOAc (3x400 mL). The combined organic layers were washed with brine (100 mL), dried over MgSO₄, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (Petroleum Ether:EtOAc = 10:1->4:1->2:1) yielding the desired sulfide-sulfone S-7 (8.3 g, 82 % yield) as yellowish crystals.

TLC (Petroleum Ether:EtOAc = 2:1)

\[
\text{Mp} = 142-143^\circ C, \text{lit.}^{17} = 144^\circ C ; \quad ^1\text{H-NMR} (300 \text{ MHz, CDCl}_3): \delta = 5.05 (s, 2H, H-1), 7.34-7.40 (m, 5 H), 7.71 (t, J = 7.5 Hz, 2H), 7.97 (dd, J = 7.7 Hz, 1.6 Hz, 2H); \quad ^{13}\text{C-NMR} (75 \text{ MHz, CDCl}_3): \delta = 54.9 (C-1), 121.1, 121.8, 124.9, 126.2, 128.7, 129.2, 134.0, 135.5, 137.0, 151.9, 161.5 (C-2); \quad \text{IR (film): } \nu^{-1} = 3060, 2995, 2916, 1583, 1446, 1427, 1307, 1238, 1207, 1149, 1124, 1081, 999, 829, 756, 727, 715, 688; \quad \text{MS (APCI), } m/z (\%) : 322 (86) [M^{+}+H], 292 (70), 167.(100)
\]

2-(((phenylsulfonyl)methyl)sulfonyl)benzo[d]thiazole (12b)

A solution of sulfone-sulfide S-7 (12.0 g, 37.3 mmol, 1.0 equiv) in EtOH (200 mL, 0.19M) was cooled to 0°C and (NH₄)₆Mo₇O₂₄·4H₂O (4.6 g, 3.7 mmol, 0.1 equiv) was added. After 5 min at 0°C, 35% aqueous solution of H₂O₂ (36.2 mL, 373.0 mmol, 10.0 equiv) was added. The resulting mixture was stirred at 0°C for 30 min, before the cooling bath was removed and the stirring continued at RT for a further 18h. Saturated aqueous Na₂S₂O₃ (200 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3x250 mL) and the combined organic layers were washed with brine (150 mL), dried over MgSO₄, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (Petroleum Ether:EtOAc = 4:1->2:1->1:1) yielding the desired bis-sulfone as yellowish crystals (10.26 g, 78 % yield)\(^{18}\).
TLC (Petroleum Ether:EtOAc = 2:1)

Mp = 144°C; ^1H-NMR (300 MHz, CDCl$_3$): δ = 5.25 (s, 2H, H-1), 7.50-7.58 (m, 2H), 7.60-7.73 (m, 3H), 7.94-8.10 (m, 3H), 8.21 (dd, J = 7.5, 1.6 Hz, 1H); ^13C-NMR (75 MHz, CDCl$_3$): δ = 72.5 (C-1), 122.6, 125.9, 128.1, 128.7, 129.3, 129.6, 135.2, 138.1, 152.5 (C-2); IR (film): v$^{-1}$ = 2952, 2896, 2844, 1583, 1552, 1467, 1448, 1419, 1330, 1315, 1217, 1164, 1145, 1080, 1026, 999, 854, 827, 759, 827, 759, 748, 729, 648, 617; MS (APCI), m/z (%): 322 (86) [M+H$^+$], 292 (70), 167 (100).

Characteristic peaks that belongs to sulfoxide-sulfone (S-8) by-product:

^1H-NMR (300 MHz, CDCl$_3$): δ = 4.71 (d, J = 13.9 Hz, 1H, H-1), 4.98 (d, J = 13.9 Hz, 1H, H-1').
Computations

Computational details
Geometry optimisation has been carried out using the Jaguar 7.5 pseudospectral program package. These calculations used density functional theory (DFT) with the B3LYP functional and the 6-31+G* basis set on all atoms. All the optimization calculations were carried out using the Poisson-Boltzmann polarizable continuum method as incorporated in Jaguar, and parameters for tetrahedron solvent (THF), i.e. a dielectric constant of 7.43, and a solvent probe radius of 2.5221 Å.

Gas phase electronic energies were obtained by single point calculations at the SCS-MP2 level of theory using ORCA program. The 'aug-cc-pVTZ' basis used is the standard aug-cc-pVTZ basis on all C, N, O and S atoms, the cc-(p)VTZ basis on H atoms, and the 6-311+G** basis on lithium atom.

Solvation energies were obtained by single point calculations using the Poisson-Boltzmann polarisable continuum method as implemented in Jaguar 7.5 program package, at the B3LYP/cc-pVTZ level, using the parameters appropriate for THF.

NBO analysis has been performed at the B3LYP/cc-pVTZ level of theory using the Jaguar 7.5 program package. Reported charges are NPA charges.

Conformational analysis
Energies are given in kcal/mol relative to the most stable isomer.

![Chemical structure](image)

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Litterature

9 If the reaction was performed on 2 mmol scale of sulfone (or bigger), acylating or alkoxy carbonylating agents in THF were pre-cooled to -78°C prior to their addition.
10 A solution of BzCl in THF (5 mL) was cooled to -78°C prior to its addition.
12 A solution of AcCl in THF (5 mL) was cooled to -78°C prior to its addition.
14 A solution of CICOOHMe in THF (10 mL) was cooled to -78°C prior to its addition.
15 A solution of CICOOallyl in THF (2 mL) was cooled to -78°C prior to its addition.
16 A solution of Boc₂O in THF (10 mL) was cooled to -78°C prior to its addition.
17 Product obtained as 99:1 mixture of (PhO₂S)CH₂ and PhO₂S-CH₂-S(O)Ph.
18 At 144°C product sublimates.
24 F. Neese, ORCA, An Ab Initio, DFT, and Semiempirical Electronic Structure Package, version, 2.7.0, Universitäts Bonn, Germany, 2010