Supporting Information

Synthesis of 3-Substituted Aryl[4,5]isothiazoles Through an all Heteroatom Wittig-equivalent Process

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Table of Contents

General Methods S2
Synthesis of compounds 1, 3, 5, 6, 7 and 8, 9. S2-S32
1H NMR and 13C NMR Spectra of all compounds S33-S121
References S122
General Methods

All commercially available reagents were used without purification unless otherwise noted. Column chromatography was performed using silica gel (100–200 mesh). Visualization of the compounds was accomplished with UV light (254 nm) or iodine. $^1$H NMR and $^{13}$C NMR spectra were recorded in CDCl$_3$ operating at 400 MHz and 100 MHz, respectively. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent CDCl$_3$ (7.28 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl$_3$ (77.10 ppm). Chemical shifts are reported in δ (parts per million) values. Coupling constants $J$ are reported in Hz. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), and multiple (m). High-resolution mass spectra were recorded on a Liquid Chromatograph Mass Spectrometer (LCMS-IT-TOF).

Synthesis of Compounds 1a-1e, 3a-3k, 3m, 3p, 5a-5k, 5m, 5p, 5q and 6, 7.

General procedure for the preparation of 1a-e. To a solution of Bromo-Ar (1 eq.) in THF at -78°C under nitrogen was added dropwise a solution of n-BuLi (2.5 M in Hexane, 1.5 eq.) and stirred for 30 min. Then the solution of the S-tert-Butyl tert-butylthiosulfinate (1.1 eq.) in THF (20 mL) was added, and the resulting mixture was stirred for another 30 min. Water (30 mL) was added and the mixture was extracted with EtOAc (3 × 30 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (4/1) to afford the desired product 1a-e as a white solid.
**Phenyl tert-butyl sulfoxide (1a):**

\[\text{Phenyl tert-butyl sulfoxide (1a):} \]

\[1a\]

In a 100 mL vial along with a stirring bar, \(n\)-BuLi (2.5 M in Hexane, 30 mmol, 12 mL) was added to Bromo-benzene (3.12 g, 20 mmol) in THF (35 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the S-tert-Butyl tert-butylthiosulfinate (4.27 g, 22 mmol) in THF (20 mL) was added, and the resulting mixture was stirred for another 30 min. Water (30 mL) was added and the mixture was extracted with EtOAc (3 × 30 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (4/1) to afford the desired product 1a (2.58 g, 71% yield, white solid: mp 58 – 59 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 – 7.58 (m, 2H), 7.50 – 7.47 (m, 3H), 1.17 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.9, 131.1, 128.4, 126.3, 55.8, 22.8.

**1-Fluoro-4-(2-methyl-propane-2-sulfinyl)-benzene (1b):**

\[\text{1-Fluoro-4-(2-methyl-propane-2-sulfinyl)-benzene (1b):} \]

\[1b\]

In a 100 mL vial along with a stirring bar, \(n\)-BuLi (2.5 M in Hexane, 15 mmol, 6 mL) was added to 1-Bromo-4-fluoro-benzene (1.74, 10 mmol) in THF (20 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the S-tert-Butyl tert-butylthiosulfinate (2.135 g, 11 mmol) in THF (10 mL) was added, and the resulting mixture was stirred for another 30 min. Water (20 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (4/1) to afford the desired product 1b (1.5 g, 75% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (dd, \(J = 8.2, 5.4\) Hz, 2H), 7.19 (t, \(J = 8.5\) Hz, 2H), 1.16 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.8, 163.3,
135.5, 135.4, 128.4, 128.4, 115.9, 115.6, 55.8, 22.6.

1-Methoxy-4-(2-methyl-propane-2-sulfinyl)-benzene (1c):

\[
\text{\begin{center}
\includegraphics[width=0.1\textwidth]{1c}
\end{center}}
\]

In a 100 mL vial along with a stirring bar, \( n \)-BuLi (2.5 M in Hexane, 15 mmol, 6 mL) was added to 1-Bromo-4-methoxy-benzene (1.85 g, 10 mmol) in THF (20 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the \( \text{S-\text{t}ert} \)-Butyl \( \text{t}ert \)-butylthiosulfinate (2.135 g, 11 mmol) in THF (10 mL) was added, and the resulting mixture was stirred for another 30 min. Water (20 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (4/1) to afford the desired product 1c (1.63 g, 77% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.52 (d, \( J = 8.8 \) Hz, 2H), 7.00 (d, \( J = 8.8 \) Hz, 2H), 3.86 (s, 3H), 1.16 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 162.0, 130.8, 127.9, 113.9, 55.6, 55.5, 22.7.

2-(2-Methyl-propane-2-sulfinyl)-naphthalene (1d):

\[
\text{\begin{center}
\includegraphics[width=0.1\textwidth]{1d}
\end{center}}
\]

In a 100 mL vial along with a stirring bar, \( n \)-BuLi (2.5 M in Hexane, 15 mmol, 6 mL) was added to 2-Bromo-naphthalene (2.05 g, 10 mmol) in THF (20 mL). The mixture was stirred at -78°C for 60 min under nitrogen. Then a solution of the \( \text{S-\text{t}ert} \)-Butyl \( \text{t}ert \)-butylthiosulfinate (2.135 g, 11 mmol) in THF (10 mL) was added, and the resulting mixture was stirred for another 60 min. Water (20 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na\(_2\)SO\(_4\)),
and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (4/1) to afford the desired product 1d (1.63 g, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 (s, 1H), 7.99 – 7.87 (m, 3H), 7.64 (dd, $J = 8.6$, 1.3 Hz, 1H), 7.59 (dd, $J = 8.9$, 5.1 Hz, 2H), 1.24 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.4, 134.6, 132.5, 128.6, 128.2, 128.0, 127.7, 127.1, 126.8, 122.4, 56.3, 22.9.

3-(2-Methyl-propane-2-sulfinyl)-pyridine (1e):

In a 100 mL vial along with a stirring bar, $n$-BuLi (2.5 M in Hexane, 15 mmol, 6 mL) was added to 3-Bromo-pyridine (1.57 g, 10 mmol) in THF (20 mL). The mixture was stirred at -78°C for 60 min under nitrogen. Then a solution of the S-tert-Butyl tert-butylthiosulfinate (2.135 g, 11 mmol) in THF (10 mL) was added, and the resulting mixture was stirred for another 60 min. Water (20 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (4/1) to afford the desired product 1e (1.34 g, 73% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.81 – 8.63 (m, 2H), 8.04 (dt, $J = 7.9$, 1.7 Hz, 1H), 7.51 (dd, $J = 7.9$, 4.8 Hz, 1H), 1.22 (s, 10H).

General procedure for the preparation of 3a-k, 3m, 3p, 3q and 6, 7. To a solution of 1 (1 eq.) in THF at -78°C under nitrogen was added dropwise a solution of $n$-BuLi (2.5 M in Hexane, 1.5eq.), and the reaction contents were allowed to stir at this temperature for 30 min. Thereafter, the solution of the S-tert-butylthiosulfinate (1.1eq.) in THF (20 mL) was added, and the resulting mixture was stirred for another 30 min. Water (30 mL) was added and the mixture was extracted with EtOAc (3 × 30 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (4/1) to afford the desired product 3a-m as a white solid.
4-Methyl-N-[[2-(2-methyl-propane-2-sulfinyl)-phenyl]-phenyl-methyl]-benzenesulfonamide (6):

In a 25 mL vial along with a stirring bar, \( n \)-BuLi (2.5 M in Hexane, 3.6 mmol, 1.44 mL) was added to Phenyl tert-butyl sulfoxide\(^{(1)}\) (546 mg, 3 mmol) in THF (6 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the N-Benzylidene-4-methyl-benzenesulfonamide\(^{(2)}\) (854 mg, 3.3 mmol) in THF (5 mL) was added, and the resulting mixture was stirred for another 2 h. Water (10 mL) was added and the mixture was extracted with EtOAc (3 x 20 mL), dried (\( \text{Na}_2\text{SO}_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 6 (806 mg, 61% yield, white solid). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.79 (d, \( J = 7.9 \) Hz, 1H), 7.68 (d, \( J = 6.5 \) Hz, 1H), 7.53 (d, \( J = 7.5 \) Hz, 2H), 7.44 – 7.34 (m, 2H), 7.11 (d, \( J = 7.9 \) Hz, 2H), 7.05 (d, \( J = 6.8 \) Hz, 3H), 6.94 (d, \( J = 6.6 \) Hz, 2H), 6.25 – 6.17 (m, 1H), 6.04 (d, \( J = 6.8 \) Hz, 1H), 2.37 (s, 3H), 1.24 (s, 9H).

3-Phenyl-2-(toluene-4-sulfonyl)-2,3-dihydro-benzo[d]isothiazole 1-oxide (7):

In a 25 mL vial along with a stirring bar, to a mixture of 4-Methyl-N-[[2-(2-methyl-propane-2-sulfinyl)-phenyl]-phenyl-methyl]-benzenesulfonamide (441 mg) and glacial acetic acid (90 mg) in \( \text{CH}_2\text{Cl}_2\) (5 mL) was added N-bromosuccinimide (356 mg) in \( \text{CH}_2\text{Cl}_2\) (4 mL). The mixture was stirred at room temperature for 4 h under nitrogen. The reaction mixture was quenched with a \( \text{NH}_4\text{Cl} \) saturated aqueous solution and extracted with DCM (3 x 10 mL), the organic phase was
washed with brine (3 × 10 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (5/1) to afford the desired product 7 (263 mg, 66% yield, white solid: mp 224 – 227 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, J = 6.0, 2.7 Hz, 1H), 7.64 – 7.53 (m, 4H), 7.35 (dd, J = 6.4, 2.8 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.25 – 7.19 (m, 4H), 6.29 (s, 1H), 2.31 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 145.0, 143.5, 142.0, 138.6, 135.7, 133.5, 130.3, 130.0, 129.0, 128.4, 128.0, 127.5, 125.9, 125.7, 71.7, 21.4. HRMS (ESI) m/z calcd for C₂₀H₁₈NO₃S₂ [M + H]⁺ 384.0723, found 384.0724.

2-Methyl-propane-2-sulfinic acid [(2-(2-methyl-propane-2-sulfinyl)-phenyl)-phenyl-methyl]–amide (3a):

![Diagram](image.png)

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to Phenyl tert-butyl sulfoxide¹ (273 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid benzylideneamide³ (345 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3a (457.5 mg, 78% yield, white solid: mp 127 – 128 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 6.9 Hz, 1H), 7.84 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.33 – 7.30 (m, 4H), 7.27 (dd, J = 5.7, 3.0 Hz, 1H), 6.18 (s, 1H), 3.67 (s, 1H), 1.36 (s, 9H), 1.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 141.1, 140.9, 138.9, 131.4, 129.1, 128.4, 128.1, 127.9, 127.1, 126.9, 57.9, 57.8, 56.2, 23.2, 22.7. HRMS (ESI) m/z calcd for C₂₁H₃₆NO₃S₂ [M + H]⁺ 392.1712, found 392.1715.
2-Methyl-propane-2-sulfinic acid {(4-methoxy-phenyl)-[2-(2-methyl-propane -2-sulfinyl)-phenyl]- methyl}-amide (3b):

![Chemical Structure](image)

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to Phenyl tert-butyl sulfoxide (273 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78℃ for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-methoxy-benzyldeneamide (395 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3b (480 mg, 76% yield, white solid: mp 98 – 100 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 6.12 (s, 1H), 3.77 (s, 3H), 3.60 (s, 1H), 1.35 (s, 9H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 141.4, 138.8, 133.0, 131.4, 129.2, 128.0, 127.1, 126.7, 114.5, 57.7, 57.4, 56.1, 55.3, 23.2, 22.7. HRMS (ESI) m/z calcd for C₂₂H₃₂NO₃S₂ [M + H]⁺ 422.1818, found 422.1815.

2-Methyl-propane-2-sulfinic acid {(4-chloro-phenyl)-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl}-amide (3c):

![Chemical Structure](image)
In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to Phenyl tert-butyl sulfoxide (273 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78 °C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-chloro-benzylideneamide\(^{(3)}\) (401 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3c (452 mg, 71% yield, white solid: mp 81 – 83 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 \((d, J = 7.6\) Hz, 1H), 7.80 \((d, J = 7.5\) Hz, 1H), 7.58 \((t, J = 7.4\) Hz, 1H), 7.52 \((t, J = 7.4\) Hz, 1H), 7.27 \((s, 4\)H), 6.15 \((s, 1\)H), 3.62 \((s, 1\)H), 1.35 \((s, 9\)H), 1.30 \((s, 9\)H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.7, 139.3, 138.7, 134.3, 131.6, 129.4, 129.3, 128.4, 127.3, 126.7, 57.9, 57.5, 56.3, 23.1, 22.7. HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{29}\)ClNO\(_2\)S\(_2\) [M + H]\(^+\) 426.1323, found 426.1319.

2-Methyl-propane-2-sulfinic acid \{[5-fluoro-2-(2-methyl-propane-2-sulfinyl)–phenyl]–phenyl \(-methyl\}\}-amide (3d):

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 1-Fluoro-4-(2-methyl-propane-2-sulfinyl)-benzene\(^{(1)}\) (300 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78 °C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-methoxy-benzylideneamide (345 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3d (386 mg, 63% yield, white solid: mp 129 – 130 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 \((dd, J = 8.7, 8.7\) Hz, 1H), 7.27 \((s, 4H), 6.15 \((s, 1H), 3.62 \((s, 1H), 1.35 \((s, 9H), 1.30 \((s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.7, 139.3, 138.7, 134.3, 131.6, 129.4, 129.3, 128.4, 127.3, 126.7, 57.9, 57.5, 56.3, 23.1, 22.7. HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{29}\)ClNO\(_2\)S\(_2\) [M + H]\(^+\) 426.1323, found 426.1319.
5.7 Hz, 1H), 7.56 (dd, J = 10.1, 2.6 Hz, 1H), 7.40 – 7.25 (m, 4H), 7.19 (ddd, J = 10.5, 8.3, 2.6 Hz, 1H), 6.14 (s, 1H), 3.66 (s, 1H), 1.35 (s, 9H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.0, 163.5, 144.2, 144.1, 140.1, 134.4, 134.3, 129.8, 129.7, 129.3, 129.1, 128.7, 127.9, 115.6, 115.4, 114.3, 114.0, 57.9, 57.5, 56.3, 23.1, 22.7; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -107.19. HRMS (ESI) m/z calcd for C$_{21}$H$_{29}$FNO$_3$S$_2$ [M + H]$^+$ 410.1618, found 410.1621.

2-Methyl-propane-2-sulfinic acid [[5-fluoro-2-(2-methyl-propane-2-sulfinyl)-phenyl] -
(4-methoxy-phenyl)-methyl]-amide (3e):

![Chemical Structure](image)

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 1-Fluoro-4-(2-methyl-propane-2-sulfinyl)-benzene (300 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-methoxy-benzylideneamide (395 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3ee (493.8 mg, 75% yield, white solid: mp 58 – 61 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (dd, J = 8.7, 5.7 Hz, 1H), 7.54 (dd, J = 10.1, 2.6 Hz, 1H), 7.22 (d, J = 8.7 Hz, 2H), 7.20 – 7.14 (m, 1H), 6.83 (d, J = 8.8 Hz, 2H), 6.08 (s, 1H), 3.77 (s, 3H), 3.59 (s, 1H), 1.34 (s, 9H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.0, 163.5, 159.7, 144.6, 144.5, 134.2, 134.1, 134.1, 134.0, 132.2, 129.8, 129.7, 129.2, 115.4, 115.2, 114.6, 114.1, 113.8, 57.9, 57.1, 56.3, 55.3, 23.0, 22.7; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -107.28. HRMS (ESI) m/z calcd for C$_{22}$H$_{31}$FNO$_3$S$_2$ [M + H]$^+$ 440.1724, found 440.1728.
2-Methyl-propane-2-sulfinic acid \{(4-chloro-phenyl)\-[5-fluoro-2-(2-methyl-propane-2-sulfinyl)\)-phenyl\]-methyl\}-amide (3f):

![Chemical structure]

In a 25 mL vial along with a stirring bar, \(n\)-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 1-Fluoro-4-(2-methyl-propane-2-sulfinyl)-benzene (300 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at \(-78^\circ\text{C}\) for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-chloro-benzylideneamide (401 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 \(\times\) 20 mL), dried (\(\text{Na}_2\text{SO}_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3f (405 mg, 61% yield, white solid: mp 126 – 127 °C). \(^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.84 \ (dd, J = 8.7, 5.7 \text{ Hz, 1H}), 7.50 \ (dd, J = 9.9, 2.5 \text{ Hz, 1H}), 7.30 – 7.21 \ (m, 4H), 7.18 \ (td, J = 8.5, 2.6 \text{ Hz, 1H}), 6.09 \ (s, 1H), 3.70 \ (d, J = 1.3 \text{ Hz, 1H}), 1.30 \ (s, 9H), 1.27 \ (s, 9H); \(^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \delta 166.0, 163.5, 143.8, 143.7, 138.6, 134.7, 134.3, 134.3, 130.0, 129.9, 129.5, 129.3, 115.8, 115.6, 114.1, 113.9, 58.0, 57.0, 56.4, 23.0, 22.7; \(^{19}\text{F NMR} \ (376 \text{ MHz, CDCl}_3) \delta -106.79. \text{ HRMS (ESI)} \ m/z \text{ calcd for C}_{21}\text{H}_{28}\text{FCINO}_2\text{S}_2 [M + H]^+ 444.1229, \text{ found} 444.1230.

2-Methyl-propane-2-sulfinic acid \([5\text{-methoxy-2-(2-methyl-propane-2-sulfinyl)-phenyl}\]-phenyl\)-methyl\}-amide (3g):

![Chemical structure]
In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 1-Methoxy-4-(2-methyl-propane-2-sulfinyl)-benzene $^{(1)}$ (318 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-methoxy-benzylideneamide (345 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3g (473 mg, 75% yield, white solid: mp 140 – 141 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, $J$ = 8.7 Hz, 1H), 7.38 (d, $J$ = 2.6 Hz, 1H), 7.34 (dd, $J$ = 12.6, 4.4 Hz, 4H), 7.31 – 7.24 (m, 1H), 7.01 (dd, $J$ = 8.8, 2.6 Hz, 1H), 6.14 (s, 1H), 3.89 (s, 3H), 3.63 (s, 1H), 1.34 (s, 9H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.1, 142.9, 140.7, 129.8, 129.1, 129.0, 128.4, 127.9, 113.2, 112.9, 57.7, 57.6, 56.2, 55.4, 23.1, 22.7. HRMS (ESI) m/z calcd for C$_{22}$H$_{32}$NO$_3$S$_2$ [M + H]$^+$ 422.1818, found 422.1818.

2-Methyl-propane-2-sulfinic acid [[5-methoxy-2-(2-methyl-propane-2-sulfinyl)-phenyl]-
(4-methoxy-phenyl)-methyl]-amide (3h):

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 1-Methoxy-4-(2-methyl-propane-2-sulfinyl)-benzene (318 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-methoxy-benzylideneamide (395 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3h (487 mg, 72% yield, white solid: mp 62 – 66 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J$ = 8.7 Hz,
1H), 7.35 (t, J = 6.0 Hz, 1H), 7.24 (d, J = 8.7 Hz, 2H), 7.00 (dd, J = 8.7, 2.6 Hz, 1H), 6.83 (d, J = 8.7 Hz, 2H), 6.09 (s, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 3.56 (s, 1H), 1.33 (s, 9H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 141.4, 138.8, 133.0, 131.4, 129.2, 128.0, 127.1, 126.7, 114.5, 57.7, 57.4, 56.1, 55.3, 23.1, 22.7. HRMS (ESI) m/z calcd for C₂₃H₃₄NO₄S₂ [M + H]⁺ 452.1924, found 452.1923.

2-Methyl-propane-2-sulfinic acid {(4-chloro-phenyl)-[5-methoxy-2-(2-methyl-propane-2-sulfinyl) -phenyl]-methyl}-amide (3i):

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 1-Methoxy-4-(2-methyl-propane-2-sulfinyl)-benzene (318 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-chloro-benzylideneamide (401 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3i (483 mg, 73% yield, white solid: mp 127 – 131 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.7 Hz, 1H), 7.33 (d, J = 2.6 Hz, 1H), 7.29 (d, J = 1.6 Hz, 4H), 7.02 (dd, J = 8.7, 2.6 Hz, 1H), 6.12 (d, J = 1.2 Hz, 1H), 3.89 (s, 3H), 3.57 (s, 1H), 1.33 (s, 9H), 1.32 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 142.5, 139.1, 134.4, 129.8, 129.3, 129.3, 113.2, 112.9, 57.7, 57.1, 56.3, 55.5, 29.70, 23.1, 22.7. HRMS (ESI) m/z calcd for C₂₂H₃₁ClNO₃S₂ [M + H]⁺ 456.1428, found 456.1427.

2-Methyl-propane-2-sulfinic acid {[3-(2-methyl-propane-2-sulfinyl)-naphthalen-2-yl]–phenyl -methyl}-amide (3j):
In a 25 mL vial along with a stirring bar, \( n \)-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 2-(2-Methyl-propane-2-sulfinyl)-naphthalene\(^{(1)} \) (348 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78℃ for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-methoxy-benzylideneamide (345 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (\( \text{Na}_2\text{SO}_4 \)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3j (502 mg, 76% yield, colorless liquid). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.40 (s, 1H), 8.31 (s, 1H), 8.02 – 7.89 (m, 2H), 7.60 (ddd, \( J = 15.9, 14.3, 7.3 \) Hz, 2H), 7.34 – 7.23 (m, 5H), 6.25 (s, 1H), 3.71 (s, 1H), 1.37 (s, 9H), 1.36 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 140.6, 137.1, 137.0, 134.3, 132.2, 129.2, 128.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.2, 126.5, 58.5, 58.3, 56.2, 23.1, 22.7. HRMS (ESI) m/z calcd for \( \text{C}_{25}\text{H}_{32}\text{NO}_2\text{S}_2 \) [M + H]\(^+ \) 442.1869, found 442.1870.

2-Methyl-propane-2-sulfinic acid \{3-(2-methyl-propane-2-sulfinyl)-pyridin-4-yl]-phenyl-methyl]-amide (3k):

In a 25 mL vial along with a stirring bar, \( n \)-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to 2-(2-Methyl-propane-2-sulfinyl)-naphthalene\(^{(1)} \) (273 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78℃ for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 4-methoxy-benzylideneamide (345 mg, 1.65 mmol) in THF (4 mL)
was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3k (317 mg, 54% yield, white solid: colorless liquid). \(^1\)H NMR (400 MHz, CDCl₃) δ 9.03 (s, 1H), 8.79 (d, J = 5.2 Hz, 1H), 7.63 (d, J = 5.2 Hz, 1H), 7.43 – 7.30 (m, 5H), 6.34 (d, J = 3.6 Hz, 1H), 3.75 (d, J = 3.4 Hz, 1H), 1.21 (s, 9H), 1.07 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 151.4, 150.9, 149.2, 139.0, 135.8, 129.3, 129.1, 128.8, 128.6, 123.3, 58.0, 57.5, 56.4, 23.1, 22.6. HRMS (ESI) m/z calcd for C₂₀H₂₉N₂O₂S₂ [M + H\(^+\)] 393.1665, found 393.1663.

2-Methyl-propane-2-sulfinic acid {[2-(2-methyl-propane-2-sulfinyl)-phenyl]-naphthalen-1-yl-methyl]-amide (3m):

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to (2-Methyl-propane-2-sulfinyl)-benzene (273 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid naphthalen-1-ylmethyleneamide (3) (427 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3m (489 mg, 74% yield, white solid: mp 135 – 137 °C). \(^1\)H NMR (400 MHz, CDCl₃) δ 8.48 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.94 (dd, J = 13.3, 7.9 Hz, 2H), 7.82 (d, J = 8.2 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.68 (t, J = 7.2 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.28 (t, J = 3.8 Hz, 1H), 6.89 (s, 1H), 6.72 (d, J =
2-Methyl-propane-2-sulfinic acid {cyclohexyl-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl}-amide (3p):

In a 25 mL vial along with a stirring bar, \(n\)-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to (2-Methyl-propane-2-sulfinyl)-benzene (273 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid cyclohexylmethyleneamide\(^{(3)}\) (354 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3p (455 mg, 77% yield, white solid: mp 119 – 120 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 – 7.85 (m, 1H), 7.52 – 7.37 (m, 3H), 4.87 (dd, \(J = 4.6, 3.0\) Hz, 1H), 3.56 (d, \(J = 2.3\) Hz, 1H), 1.75 (t, \(J = 11.2\) Hz, 4H), 1.66 – 1.52 (m, 2H), 1.28 (s, 9H), 1.24 (s, 9H), 1.21 – 1.13 (m, 2H), 1.13 – 0.92 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.5, 139.3, 130.7, 127.6, 126.6, 59.1, 57.5, 56.0, 45.6, 30.0 28.0, 26.3, 26.1, 23.2, 22.7. HRMS (ESI) m/z calcd for C\(_{25}\)H\(_{32}\)NO\(_2\)S\(_2\) [M + H]\(^+\) 442.1869, found 442.1870.

2-Methyl-propane-2-sulfinic acid {cyclopropyl-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl}-amide (3q):
In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.8 mmol, 0.72 mL) was added to (2-Methyl-propane-2-sulfinyl)-benzene (273 mg, 1.5 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid cyclopropylmethyleneamide (4) (285 mg, 1.65 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3q (399 mg, 75% yield, white solid: mp 51 – 55 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.55 – 7.40 (m, 2H), 4.39 (d, J = 8.7 Hz, 1H), 3.67 (s, 1H), 1.26 (s, 18H), 1.09 (d, J = 5.6 Hz, 1H), 0.84 – 0.62 (m, 2H), 0.60 – 0.41 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 138.7, 131.5, 127.8, 126.8, 126.7, 58.3, 57.3, 55.9, 23.1, 22.7, 22.5, 21.3. HRMS (ESI) m/z calcd for C₁₈H₃₀NO₂S₂ [M + H]⁺ 356.1712, found 356.1715.

General procedure for the preparation of 5. To a mixture of 3 (1 eq.) and glacial acetic acid (1.5 eq.) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (2 eq.) in CH₂Cl₂ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5.

3-Phenyl-benzo[d]isothiazole (5a):
In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid 
\{[2-(2-methyl-propane-2-sulfinyl)-phenyl]-phenyl-methyl\}-amide (260 mg) and glacial acetic acid 
(60 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (237 mg) in CH₂Cl₂ (3 mL). The mixture 
was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with 
a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was 
washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica 
gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5a as a known 
compound(5) (140.3 mg, 82% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 8.2 Hz, 1H), 8.02 
(d, J = 8.2 Hz, 1H), 7.90 (dd, J = 8.0, 1.4 Hz, 2H), 7.62 – 7.53 (m, 4H), 7.52 – 7.46 (m, 1H); ¹³C 
NMR (100 MHz, CDCl₃) δ 164.4, 153.5, 135.2, 133.8, 129.3, 128.8, 128.7, 127.5, 125.0, 124.9, 
119.9.

3-(4-Methoxy-phenyl)-benzo[d]isothiazole (5b):

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid 
\{(4-methoxy-phenyl)-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl\}-amide (300 mg) and 
glacial acetic acid (65 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (254 mg) in CH₂Cl₂ (3 
ml). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture 
was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the 
organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue 
was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product
5b as a known compound \(^6\) (144.3 mg, 84% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (d, \(J = 8.2\) Hz, 1H), 8.00 (d, \(J = 8.1\) Hz, 1H), 7.91 – 7.80 (m, 2H), 7.56 (t, \(J = 7.3\) Hz, 1H), 7.47 (t, \(J = 7.5\) Hz, 1H), 7.10 (dd, \(J = 9.2, 2.2\) Hz, 2H), 3.92 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.5, 159.9, 153.1, 133.8, 130.0, 128.0, 127.4, 124.9, 124.9, 119.9, 114.2, 55.0.

3-(4-Chloro-phenyl)-benzo[d]isothiazole (5c):

\[ \text{N} \]
\[ \text{S} \]
\[ \text{Cl} \]

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid \{(4-chloro-phenyl)-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl\}-amide (300 mg) and glacial acetic acid (63.5 mg) in CH\(_2\)Cl\(_2\) (3 mL) was added N-bromosuccinimide (251 mg) in CH\(_2\)Cl\(_2\) (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH\(_4\)Cl saturated aqueous solution and extracted with DCM (3 \(\times\) 5 mL), the organic phase was washed with brine (3 \(\times\) 5 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5c (140 mg, 81% yield, white solid: mp 97 – 102 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.17 (d, \(J = 8.2\) Hz, 1H), 8.03 (d, \(J = 8.2\) Hz, 1H), 7.88 – 7.81 (m, 2H), 7.64 – 7.47 (m, 4H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.1, 153.6, 135.5, 133.6, 133.5, 130.0, 129.1, 127.6, 125.2, 124.5, 120.1. HRMS (ESI) m/z calcd for C\(_{13}\)H\(_9\)ClNS [M + H]^+ 246.0139, found 246.0139.

5-Fluoro-3-phenyl-benzo[d]isothiazole (5d):

\[ \text{F} \]
\[ \text{N} \]

S19
In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid ([5-fluoro-2-(2-methyl-propane-2-sulfanyl)-phenyl]-phenyl -methyl]-amide (300 mg) and glacial acetic acid (66 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (261 mg) in CH₂Cl₂ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5d (131 mg, 78% yield, white solid: mp 62 – 68 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (dd, J = 8.9, 4.6 Hz, 1H), 7.90 – 7.81 (m, 3H), 7.62 – 7.51 (m, 3H), 7.37 (td, J = 8.6, 2.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.9, 162.2, 160.0, 149.3, 134.8, 129.6, 129.0, 128.5, 121.2, 121.1, 117.3, 117.0, 110.0, 109.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -117.33. HRMS (ESI) m/z calcd for C₁₃H₉FNS [M + H]⁺ 230.0434, found 230.0434.

5-Fluoro-3-(4-methoxy-phenyl)-benzo[d]isothiazole (5e):

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid [[5-fluoro-2-(2-methyl-propane-2-sulfanyl)-phenyl]-(4-methoxy-phenyl)-methyl]-amide (300 mg) and glacial acetic acid (62 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (243 mg) in CH₂Cl₂ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5e (131 mg, 74% yield, white solid: mp 125 – 127 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (dd, J = 8.8, 4.6 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.35 (td, J = 8.6, 2.3 Hz, 1H), 7.15 – 7.06 (m,
2H), 3.92 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.3, 162.0, 160.5, 159.5, 149.0, 134.9, 134.8, 134.7, 129.7, 127.3, 121.2, 121.1, 117.0, 116.6, 114.2, 110.0, 109.7, 55.3; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -117.63. HRMS (ESI) m/z calcd for C$_{14}$H$_{11}$FNOS [M + H]$^+$ 260.0540, found 260.0542.

3-(4-Chloro-phenyl)-5-fluoro-benzo[d]isothiazole (5f):

![3-(4-Chloro-phenyl)-5-fluoro-benzo[d]isothiazole (5f)](image)

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid {[(4-chloro-phenyl)-[5-fluoro-2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl]-amide (300 mg) and glacial acetic acid (61 mg) in CH$_2$Cl$_2$ (3 mL) was added N-bromosuccinimide (241 mg) in CH$_2$Cl$_2$ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH$_4$Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5f (137 mg, 77% yield, white solid: mp 125 – 128 ºC). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (dd, $J = 8.9, 4.6$ Hz, 1H), 7.81 (tt, $J = 7.0, 2.3$ Hz, 3H), 7.60 – 7.52 (m, 2H), 7.38 (td, $J = 8.6, 2.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.6, 162.5, 162.3, 159.9, 149.4, 135.8, 134.7, 134.6, 133.2, 129.8, 129.2, 121.4, 121.3, 117.4, 117.2, 109.7, 109.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -116.95. HRMS (ESI) m/z calcd for C$_{13}$H$_8$ClFNS [M + H]$^+$ 264.0045, found 264.0042.

5-Methoxy-3-phenyl-benzo[d]isothiazole (5g):

![5-Methoxy-3-phenyl-benzo[d]isothiazole (5g)](image)

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid
{[5-methoxy-2-(2-methyl-propane-2-sulfinyl)-phenyl]-phenyl-methyl}-amide (300 mg) and glacial acetic acid (65 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (253 mg) in CH₂Cl₂ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5g (144 mg, 84% yield, white solid: mp 73 – 75 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.82 (m, 3H), 7.63 – 7.48 (m, 4H), 7.25 (dd, J = 8.9, 2.3 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 157.8, 143.8, 135.2, 134.5, 129.1, 128.9, 128.8, 128.5, 126.9, 120.0, 118.9, 99.5, 55.7. HRMS (ESI) m/z calcd for C₁₄H₁₁NOS [M + H]^+ 242.0634, found 242.0637.

5-Methoxy-3-(4-methoxy-phenyl)-benzo[d]isothiazole (5h):

![5-Methoxy-3-(4-methoxy-phenyl)-benzo[d]isothiazole](image)

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid [[[5-methoxy-2-(2-methyl-propane-2-sulfinyl)-phenyl]-(4-methoxy-phenyl)-methyl]-amide (300 mg) and glacial acetic acid (60 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (237 mg) in CH₂Cl₂ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5h (148 mg, 82% yield, white solid: mp 80 – 84 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.77 (m, 3H), 7.55 (d, J = 2.2 Hz, 1H), 7.23 (dd, J = 8.8, 2.3 Hz, 1H), 7.10 (dd, J = 9.2, 2.3 Hz, 2H), 3.92 (s, 3H), 3.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 160.4, 158.0, 146.6, 135.0, 129.8, 128.1, 120.6, 118.9, 114.3, 105.4, 55.7, 55.4. HRMS (ESI) m/z calcd for C₁₅H₁₄NO₂S [M + H]
3-(4-Chloro-phenyl)-5-methoxy-benzo[d]isothiazole (5i):

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid \([\text{[5-methoxy-2-(2-methyl-propane-2-sulfinyl)-phenyl]-(4- methoxy-phenyl)-methyl]}\)-amide (300 mg) and glacial acetic acid (59 mg) in CH\(_2\)Cl\(_2\) (3 mL) was added N-bromosuccinimide (235 mg) in CH\(_2\)Cl\(_2\) (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH\(_4\)Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na\(_2\)SO\(_4\)), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5i (146 mg, 81% yield, white solid: mp 125 – 130 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, \(J = 8.9\) Hz, 1H), 7.85 – 7.79 (m, 2H), 7.59 – 7.52 (m, 2H), 7.49 (d, \(J = 2.2\) Hz, 1H), 7.26 (dd, \(J = 8.9, 2.3\) Hz, 1H), 3.91 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.4, 158.2, 146.8, 135.3, 134.8, 133.9, 132.6, 129.8, 129.1, 120.7, 119.1, 105.0, 55.7. HRMS (ESI) m/z calcd for C\(_{14}\)H\(_{11}\)ClNOS [M + H]\(^+\) 276.0244, found 276.0245.

3-Phenyl-naphtho[2,3-d]isothiazole (5j):

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid \{[3-(2-methyl-propane-2-sulfinyl)-naphthalen-2-yl]–phenyl-methyl\}-amide (300 mg) and glacial
acetic acid (61 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (243 mg) in CH₂Cl₂ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5j (147 mg, 83% yield, colorless liquid).¹H NMR (400 MHz, CDCl₃) δ 7.97 (dt, J = 20.9, 6.9 Hz, 4H), 7.67 (dd, J = 6.5, 3.0 Hz, 2H), 7.63 – 7.57 (m, 3H), 7.54 (t, J = 7.6 Hz, 1H), 7.40 (dd, J = 11.3, 4.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 154.6, 138.4, 131.8, 129.7, 129.3, 129.1, 129.0, 128.9, 128.8, 127.1, 126.0, 123.6, 117.5, 53.4. HRMS (ESI) m/z calcd for C₁₇H₁₂NS [M + H]⁺ 262.0685, found 262.0683.

3-Phenyl-isothiazolo[4,5-b]pyridine (5k):

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid {[3-(2-methyl-propane-2-sulfinyl)-pyridin-4-yl]-phenyl-methyl}-amide (300 mg) and glacial acetic acid (69 mg) in CH₂Cl₂ (3 mL) was added N-bromosuccinimide (273 mg) in CH₂Cl₂ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH₄Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na₂SO₄), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5k (128 mg, 79% yield, white solid: mp 88 – 91 °C).¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 1H), 8.66 (d, J = 5.6 Hz, 1H), 8.10 (d, J = 5.5 Hz, 1H), 7.91 (dd, J = 7.8, 1.5 Hz, 2H), 7.68 – 7.49 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 143.6, 143.3, 138.2, 134.2, 129.9, 129.1, 128.5, 118.2. HRMS (ESI) m/z calcd for C₁₂H₉N₂S [M + H]⁺ 213.0481, found 213.0478.
3-Naphthalen-1-yl-benzo[d]isothiazole (5m):

![Structure](image)

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid ([2-(2-methyl-propane-2-sulfinyl)-phenyl]-naphthalen-1-yl-methyl}-amide (300 mg) and glacial acetic acid (61 mg) in CH$_2$Cl$_2$ (3 mL) was added N-bromosuccinimide (242 mg) in CH$_2$Cl$_2$ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH$_4$Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5m (131 mg, 74% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (dd, $J = 8.1$, 5.3 Hz, 2H), 7.98 (dd, $J = 15.7$, 8.3 Hz, 2H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.75 (dd, $J = 7.0$, 0.9 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.58 (dd, $J = 8.0$, 7.1 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.38 (t, $J = 7.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.4, 152.9, 135.7, 134.0, 132.5, 132.0, 129.8, 128.5, 128.0, 127.8, 126.7, 126.3, 125.9, 125.3, 125.1, 125.0, 119.9.

3-Cyclohexyl-benzo[d]isothiazole (5p):

![Structure](image)

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid {cyclohexyl-[2-(2-methyl-propane-2-sulfinyl)-phenyl]–methyl}-amide (300 mg) and glacial acetic acid (69 mg) in CH$_2$Cl$_2$ (3 mL) was added N-bromosuccinimide (273 mg) in CH$_2$Cl$_2$ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH$_4$Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded
on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5p (143 mg, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (d, $J$ = 8.1 Hz, 1H), 7.94 (d, $J$ = 8.1 Hz, 1H), 7.52 (t, $J$ = 7.5 Hz, 1H), 7.44 (t, $J$ = 7.5 Hz, 1H), 3.27 (tt, $J$ = 11.7, 3.3 Hz, 1H), 2.10 (d, $J$ = 12.2 Hz, 2H), 2.00 – 1.89 (m, 2H), 1.80 (dt, $J$ = 15.7, 6.1 Hz, 3H), 1.58 – 1.35 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.8, 152.6, 134.1, 127.4, 124.2, 123.3, 120.0, 40.9, 31.9, 26.6, 26.2.

3-Cyclopropyl-benzo[d]isothiazole (5q):

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid {cyclopropyl-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl}-amide (300 mg) and glacial acetic acid (76 mg) in CH$_2$Cl$_2$ (3 mL) was added N-bromosuccinimide (300 mg) in CH$_2$Cl$_2$ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH$_4$Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5q (120 mg, 81% yield, colorless liquid). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J$ = 8.0 Hz, 1H), 7.92 (d, $J$ = 8.1 Hz, 1H), 7.58 – 7.50 (m, 1H), 7.50 – 7.41 (m, 1H), 2.48 (dq, $J$ = 8.3, 4.9 Hz, 1H), 1.30 – 1.24 (m, 2H), 1.15 – 1.09 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 152.5, 135.1, 127.6, 124.4, 123.3, 119.9, 11.8, 8.7. HRMS (ESI) m/z calcd for C$_{10}$H$_{10}$NS [M + H]$^+$ 176.0528, found 176.0530.

Synthesis of Compounds 3l, 3n, 3o, 5l, 5n, 5o and 8, 9.
**2-(2-Methyl-propane-2-sulfinyl)-benzaldehyde (8):**

In a 100 mL vial along with a stirring bar, \( n \)-BuLi (6 mL, 2.5M in hexane, 15 mmol) was added dropwise to a solution of Phenyl tert-butyl sulfoxide (1.82 g, 10 mmol) and TMEDA (3.1 mL, 20 mmol) in THF (35 mL). The resulting mixture was stirred for 1.0 h at –78 °C and DMF (1.6 mL, 20 mmol) was added. After that, the reaction was allowed to warm to rt. and stirred overnight. The resulting mixture was quenched with sat. \( \text{NH}_4 \)Cl, after removing the solvents, the residue was dissolved in EtOAc (100 mL), the organic phase was separated and aqueous layer was extracted with EtOAc (3 x 30 ml). The combined organic layer was dried over anhydrous \( \text{Na}_2\text{SO}_4 \) and concentrated. Flash chromatography of the crude material with petroleum/EtOAc afforded the desired product 8 (1.34 g, 64% yield, yellow oil). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.30 (s, 1H), 8.11 (dd, \( J = 7.9, 0.8 \) Hz, 1H), 7.95 (dd, \( J = 7.6, 1.2 \) Hz, 1H), 7.78 (td, \( J = 7.7, 1.4 \) Hz, 1H), 7.65 (td, \( J = 7.5, 0.9 \) Hz, 1H), 1.16 (s, 9H).

**2-Methyl-propane-2-sulfonic acid 2-(2-methyl-propane-2-sulfinyl)-benzylideneamide (9):**
A solution of Ti(OEt)$_4$ (2.28 g, 10 mmol) and 2-(2-Methyl-propane-2-sulfinyl)-benzaldehyde$^7$(1.05 g, 5 mmol) in DCM was prepared under a N$_2$ atmosphere. Then, (R)-tert-butanesulfinamidine (0.73 g, 6 mmol) was added. The reaction solution was stirred overnight at rt. While rapidly stirring, the reaction was quenched by adding an equal volume of brine. The mixture was diluted with EtOAc and stirred vigorously for 20 min. The resulting mixture was filtered through a pad of Celite, and the pad of celite was washed with EtOAc. The filtrate was transferred to a separatory funnel and washed with brine. The brine was then washed with a small amount of EtOAc. The combined organic layers were dried over Na$_2$SO$_4$ and concentrated. Flash chromatography of the crude material with petroleum/EtOAc afforded the desired product 9 (1.35 g, 86% yield, yellow oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.01 (s, 1H), 8.15 – 8.09 (m, 1H), 8.05 (dd, J = 7.9, 0.8 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.63 – 7.55 (m, 1H), 1.27 (s, 6H), 1.17 (s, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.4, 142.4, 133.5, 132.1, 131.2, 131.1, 127.4, 126.7, 58.3, 58.1, 23.1, 22.7. HRMS (ESI) m/z calcd for C$_{15}$H$_{24}$NO$_2$S$_2$ [M + H]$^+$ 314.1243, found 314.1245.

2-Methyl-propane-2-sulfinic acid {[2-(2-methyl-propane-2-sulfinyl)-phenyl]-pyridin-3-yl-methyl}-amide (3l):

In a 25 mL vial along with a stirring bar, 3-Pyridylmagnesium Bromide ( 2.0 M in THF, 3 mmol, 1.5 mL ) was added to 2-Methyl-propane-2-sulfinic acid 2-(2-methyl-propane-2-sulfinyl)-benzylideneamidine$^2$(313 mg, 1 mmol) in THF ( 4 mL ). The mixture was stirred at -50°C for 30 min under nitrogen. After that, the reaction was allowed to warm to rt and stirred for another 6 h. Water (10 mL) was added and the mixture was extracted with EtOAc ( 3 × 20 mL ), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (1/1) to afford the desired product 3l (243 mg, 62% yield, white solid: mp 86 – 89 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.01 (s, 1H), 8.15 – 8.09 (m, 1H), 8.05 (dd, J = 7.9, 0.8 Hz, 1H), 7.75 – 7.67 (m, 1H), 7.63 – 7.55 (m, 1H), 1.27 (s, 6H), 1.17 (s, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.4, 142.4, 133.5, 132.1, 131.2, 131.1, 127.4, 126.7, 58.3, 58.1, 23.1, 22.7. HRMS (ESI) m/z calcd for C$_{15}$H$_{24}$NO$_2$S$_2$ [M + H]$^+$ 314.1243, found 314.1245.
MHz, CDCl$_3$) $\delta$ 8.62 (d, $J$ = 42.3 Hz, 2H), 7.87 (dd, $J$ = 17.8, 7.7 Hz, 2H), 7.67 (d, $J$ = 7.8 Hz, 1H), 7.60 (t, $J$ = 7.2 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.28 (s, 1H), 6.17 (d, $J$ = 19.1 Hz, 1H), 3.78 (s, 1H), 1.35 (s, 9H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.3, 149.1, 140.0, 138.8, 136.0, 131.8, 128.6, 127.4, 126.7, 58.0, 56.5, 56.2, 23.1, 22.7. HRMS (ESI) m/z calcd for C$_{20}$H$_{29}$N$_2$O$_2$S$_2$ [M + H]$^+$ 393.1665, found 393.1667.

3-[(2-Methyl-propane-2-sulfinylamino)-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl]-3H-indene-1-carboxylic acid tert-butyl ester (3n):

In a 25 mL vial along with a stirring bar, n-BuLi (2.5 M in Hexane, 1.5 mmol, 0.6 mL) was added to 3-Bromo-3H-indene-1-carboxylic acid tert-butyl ester$^{(8)}$ (3533 mg, 1.2 mmol) in THF (4 mL). The mixture was stirred at -78°C for 30 min under nitrogen. Then a solution of the 2-Methyl-propane-2-sulfinic acid 2-(2-methyl-propane-2-sulfinyl)-benzylideneamide (313 mg, 1.0 mmol) in THF (4 mL) was added, and the resulting mixture was stirred for another 30 min. After that, the reaction was allowed to warm to rt. and stirred overnight. Water (10 mL) was added and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (1/1) to afford the desired product 3n (489 mg, 74% yield, colorless liquid). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J$ = 7.7 Hz, 1H), 7.94 (dt, $J$ = 5.4, 2.6 Hz, 1H), 7.90 (t, $J$ = 7.3 Hz, 2H), 7.65 – 7.53 (m, 2H), 7.41 – 7.30 (m, 2H), 6.89 (s, 1H), 6.40 (s, 1H), 3.80 (s, 1H), 1.62 (s, 9H), 1.36 (s, 9H), 1.28 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.4, 140.4, 139.0, 135.7, 131.3, 128.4, 127.9, 127.2, 127.1, 126.1, 125.1, 123.3, 121.1, 119.0, 115.5, 84.3, 57.7, 56.0, 50.1, 28.1, 23.2, 22.6. HRMS (ESI) m/z calcd for C$_{28}$H$_{39}$N$_2$O$_4$S$_2$ [M + H]$^+$ 531.2346, found 531.2346.
2-Methyl-propane-2-sulfinic acid {2-methyl-1-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-propyl}-amide (3o):

In a 25 mL vial along with a stirring bar, Isopropylmagnesium Bromide (2.0 M in THF, 3 mmol, 1.5 mL) was added to 2-Methyl-propane-2-sulfinic acid 2-(2-methyl-propane-2-sulfinyl)-benzylideneamide (313 mg, 1 mmol) in THF (4 mL). The mixture was stirred at -50°C for 30 min under nitrogen. After that, the reaction was allowed to warm to rt and stirred for another 6 h. Water (10 mL) was added and the mixture was extracted with EtOAc (3 x 20 mL), dried (Na2SO4), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (2/1) to afford the desired product 3o (207 mg, 58% yield, colorless liquid). 1H NMR (400 MHz, CDCl3) δ 7.91 (dd, J = 5.6, 3.1 Hz, 1H), 7.53 – 7.42 (m, 3H), 4.91 (dd, J = 4.3, 2.7 Hz, 1H), 3.50 (s, 1H), 2.15 (td, J = 13.5, 6.8 Hz, 1H), 1.30 (s, 9H), 1.27 (s, 9H), 1.02 (d, J = 6.9 Hz, 2H), 0.90 (d, J = 6.7 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 141.5, 130.8, 127.7, 127.4, 126.8, 59.0, 56.0, 35.5, 23.2, 22.7, 22.4, 19.7, 17.0. HRMS (ESI) m/z calcd for C18H32NO2S2 [M + H]+ 358.1869, found 358.1869.

3-Pyridin-3-yl-benzo[d]isothiazole (5l):

In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid {[2-(2-methyl-propane-2-sulfinyl)-phenyl]-pyridin-3-yl-methyl}-amide (150 mg) and glacial acetic acid (35 mg) in CH2Cl2 (3 mL) was added N-bromosuccinimide (137 mg) in CH2Cl2 (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was
quenched with a NH$_4$Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5l (58 mg, 71% yield, colorless liquid).$^1$H NMR (400 MHz, CDCl$_3$) δ 9.19 (s, 1H), 8.80 (s, 1H), 8.26 (d, $J$ = 7.9 Hz, 1H), 8.20 (d, $J$ = 8.2 Hz, 1H), 8.06 (d, $J$ = 8.2 Hz, 1H), 7.63 (t, $J$ = 7.5 Hz, 1H), 7.54 (t, $J$ = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.1, 153.7, 150.0, 149.1, 136.3, 133.6, 127.8, 125.5, 124.2, 120.1. HRMS (ESI) m/z calcd for C$_{12}$H$_9$N$_2$S [M + H]$^+$ 213.0481, found 213.0477.

3-Benzof[d]isothiazol-3-yl-indole-1-carboxylic acid tert-butyl ester (5n):

In a 25 mL vial along with a stirring bar, to a mixture of 3-{(2-Methyl-propane-2-sulfinyl lamino)-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-methyl}-3H-indene-1-carboxylic acid tert-butyl ester (300 mg) and glacial acetic acid (51 mg) in CH$_2$Cl$_2$ (3 mL) was added N-bromosuccinimide (202 mg) in CH$_2$Cl$_2$ (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH$_4$Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na$_2$SO$_4$), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5n (146 mg, 74% yield, colorless liquid).$^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 – 8.21 (m, 4H), 8.04 (d, $J$ = 8.1 Hz, 1H), 7.61 (t, $J$ = 7.1 Hz, 1H), 7.52 (t, $J$ = 7.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.38 (dd, $J$ = 11.0, 4.0 Hz, 1H), 1.76 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.1, 152.9, 149.7, 135.4, 134.4, 129.1, 127.6, 125.3, 125.1, 124.1, 123.5, 121.9, 120.0, 116.1, 115.2, 84.4, 28.2. HRMS (ESI) m/z calcd for C$_{20}$H$_{19}$N$_2$O$_2$S [M + H]$^+$ 351.1162, found: 351.1166.
3-Isopropyl-benzo[d]isothazole (5o):

\[
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In a 25 mL vial along with a stirring bar, to a mixture of 2-Methyl-propane-2-sulfinic acid {2-methyl-1-[2-(2-methyl-propane-2-sulfinyl)-phenyl]-propyl}-amide (150 mg) and glacial acetic acid (38 mg) in CH\textsubscript{2}Cl\textsubscript{2} (3 mL) was added N-bromosuccinimide (150 mg) in CH\textsubscript{2}Cl\textsubscript{2} (3 mL). The mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was quenched with a NH\textsubscript{4}Cl saturated aqueous solution and extracted with DCM (3 × 5 mL), the organic phase was washed with brine (3 × 5 mL), dried (Na\textsubscript{2}SO\textsubscript{4}), and concentrated. The residue was loaded on a silica gel using petroleum ether / ethyl acetate (10/1) to afford the desired product 5o as a known compound\textsuperscript{(9)} (65 mg, 88% yield). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.02 (d, \(J = 8.1\) Hz, 1H), 7.95 (d, \(J = 8.1\) Hz, 1H), 7.57 – 7.49 (m, 1H), 7.44 (dd, \(J = 11.1, 3.9\) Hz, 1H), 3.62 (hept, \(J = 6.9\) Hz, 1H), 1.50 (s, 3H), 1.49 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 171.4, 152.7, 134.0, 127.4, 124.3, 123.4, 120.0, 31.0, 21.5.
$^1$H NMR(400M, CDCl$_3$) of 1a

![NMR spectrum diagram]
$^{13}$C NMR (100M, CDCl$_3$) of 1a
$^1\text{H NMR}(400\text{M, CDCl}_3) \text{ of 1b}$
$^{13}$C NMR(100M, CDCl$_3$) of 1b
$^1$H NMR(400M, CDCl$_3$) of 1e
$^{13}$C NMR (100M, CDCl$_3$) of 1c
$^1$H NMR(400M, CDCl$_3$) of 1d
$^{13}$C NMR (100M, CDCl$_3$) of 1d
$^1$H NMR(400M, CDCl$_3$) of 1e
$^1$H NMR(400M, CDCl$_3$) of 6
$^1$H NMR (400M, CDCl$_3$) of 7
$^{13}$C NMR(100M, CDCl$_3$) of 7
$^1$H NMR(400M, CDCl$_3$) of 3a
$^{13}$C NMR(100M, CDCl$_3$) of 3a
$^1$H NMR (400M, CDCl$_3$) of 3b
$^{13}$C NMR(100M, CDCl$_3$) of 3b
$^{1}H$ NMR(400M, CDCl$_3$) of 3c
$^{13}$C NMR (100M, CDCl$_3$) of 3c
$^1$H NMR(400M, CDCl$_3$) of 3d
$^{13}$C NMR(100M, CDCl$_3$) of 3d
$^{19}$F NMR (376 MHz, CDCl$_3$) of 3d
$^1$H NMR(400M, CDCl$_3$) of 3e
$^{13}$C NMR (100M, CDCl$_3$) of 3e
$^{19}$F NMR (376 MHz, CDCl$_3$) of 3e
$^1$H NMR(400M, CDCl$_3$) of 3f
$^{13}$C NMR(100M, CDCl$_3$) of 3f
$^{19}$F NMR (376 MHz, CDCl$_3$) of 3f
$^1$H NMR(400M, CDCl$_3$) of 3g
$^{13}$C NMR (100M, CDCl$_3$) of 3g
$^1$H NMR(400M, CDCl$_3$) of 3h
$^{13}$C NMR(100M, CDCl$_3$) of 3h
$^1$H NMR (400M, CDCl$_3$) of 3i
$^{13}$C NMR (100M, CDCl$_3$) of 3i
$^{1}$H NMR(400M, CDCl$_3$) of 3j
$^{13}\text{C} \text{ NMR}(100\text{M, CDCl}_3) \text{ of 3j}$
$^1$H NMR(400M, CDCl$_3$) of 3k
$^{13}$C NMR(100M, CDCl$_3$) of 3k
$^1$H NMR(400M, CDCl$_3$) of 3l
$^{13}$C NMR (100M, CDCl$_3$) of 31
$^1$H NMR (400M, CDCl$_3$) of 3m
$^{13}$C NMR(100M, CDCl$_3$) of 3m
^1H NMR (400M, CDCl$_3$) of 3n
$^{13}$C NMR(100M, CDCl$_3$) of 3n
$^1$H NMR(400M, CDCl$_3$) of 3o
$^{13}$C NMR (100M, CDCl$_3$) of 3o
$^1$H NMR(400M, CDCl$_3$) of 3p
$^{13}$C NMR(100M, CDCl$_3$) of 3p
$^1$H NMR(400M, CDCl$_3$) of 3q
$^{13}$C NMR (100M, CDCl$_3$) of 3q
$^1$H NMR(400M, CDCl$_3$) of 5a
$^{13}$C NMR (100M, CDCl$_3$) of 5a
$^1$H NMR (400 M, CDCl$_3$) of 5b
$^{13}$C NMR(100M, CDCl$_3$) of 5b
$^1$H NMR(400M, CDCl$_3$) of 5c
$^{13}$C NMR (100M, CDCl$_3$) of 5c
$^1$H NMR(400M, CDCl$_3$) of 5d
$^{13}\text{C NMR}(100\text{M}, \text{CDCl}_3)$ of 5d
$^{19}$F NMR (376 MHz, CDCl$_3$) of 5d
$^1$H NMR(400M, CDCl$_3$) of 5e
$^{13}$C NMR(100M, CDCl$_3$) of 5e
$^{19}$F NMR (376 MHz, CDCl$_3$) of 5e
$^1$H NMR(400M, CDCl$_3$) of 5f
$^{13}$C NMR (100M, CDCl$_3$) of 5f
$^{19}$F NMR (376 MHz, CDCl$_3$) of 5f
$^1$H NMR(400M, CDCl$_3$) of 5g
$^{13}$C NMR(100M, CDCl$_3$) of 5g
$^1$H NMR(400M, CDCl$_3$) of 5h
$^{13}$C NMR (100M, CDCl$_3$) of 5h
$^1$H NMR(400M, CDCl$_3$) of 5i
$^{13}$C NMR(100M, CDCl$_3$) of $5i$
$^1$H NMR (400M, CDCl$_3$) of 5j
$^{13}$C NMR(100M, CDCl$_3$) of $5j$
$^1$H NMR(400M, CDCl$_3$) of 5k
$^{13}$C NMR (100M, CDCl$_3$) of 5k

![Carbon-13 NMR spectrum of 5k](image)
$^1$H NMR(400M, CDCl$_3$) of 51
$^{13}$C NMR(100M, CDCl$_3$) of 5I
$^1$H NMR (400M, CDCl$_3$) of 5m
$^{13}$C NMR (100M, CDCl$_3$) of 5m
$^1$H NMR (400 MHz, CDCl$_3$) of 5n
$^{13}$C NMR (100M, CDCl$_3$) of 5n
$^1$H NMR(400M, CDCl$_3$) of 50
$^{13}$C NMR(100M, CDCl$_3$) of 5o
$^1$H NMR(400M, CDCl$_3$) of 5p
$^{13}$C NMR (100M, CDCl$_3$) of 5p
$^1$H NMR(400M, CDCl$_3$) of 5q
$^{13}$C NMR(100M, CDCl$_3$) of 5q
$^1$H NMR(400M, CDCl$_3$) of 8
$^1$H NMR (400M, CDCl$_3$) of 9
$^{13}$C NMR (100M, CDCl$_3$) of 9
References


