Photocatalyzed Transfer Hydrogenation and Deuteriation of Cyclic N-Sulfonylimines

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Part I General Method

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous THF (Tetrahydrofuran) and dioxane were distilled from sodium benzophenone ketyl prior to use. Anhydrous CH$_3$CN and DCE (Dichloroethane) was distilled from calcium hydride and stored under argon. Cyclic $N$-sulfonylimines $1a$-$u$ were prepared according to the reported references.$^{[1-4]}$ $^1$HNMR and $^{13}$C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. CDCl$_3$ was used as solvent. Chemical shifts (δ) were reported in ppm with tetramethylsilane as internal standard, and J values were given in Hz. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents.

Part II Procedure for the reactions

Typical procedure for the preparation of cyclic $N$-sulfonylimines$^{[1-3]}$.

![Cyclic N-sulfonylimine reaction](image)

The Grignard reagent was typically prepared using flame-dried magnesium turnings (2.0 equiv) with a few crystals of I$_2$ in anhydrous THF (10 mL). The aryl halide (1.0 equiv) was added to the solution until initiation of the Grignard reagent, after which the remaining aryl halide was added dropwise at 0 °C. The reaction was stirred 2 h at room temperature, then titrated. The Grignard reagent (2.0 equiv) was then slowly added to a solution of saccharin (1.0 equiv) in THF (6 mL) at 0 °C. The reaction was allowed to warm and stirred at 22 °C overnight. The reaction was quenched with saturated aqueous NH$_4$Cl (20 mL) and extracted with EtOAc (3 x 20 mL). The solvent was removed under reduced pressure and the crude product was dissolved in toluene (30 mL), followed by the addition of TsOH (200 mg, 1.2 mmol). The resulting solution was heated to reflux for 2h. The solvent was removed and then a saturated aqueous NH$_4$Cl solution (20 mL) was added. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuum. The product was purified by recrystallization from hot absolute ethanol and chloroform or by flash column chromatography using silica gel to obtain the corresponding $N$-sulfonylimines. Compounds $1a$-$t$ were prepared in similar methods.
Supporting information

Typical procedure for the preparation of N-sulfonylimine 1u\[^{[4]}\]:
A 50 mL Schlenck flask containing CH\(_2\)Cl\(_2\) (30 mL) was charged with benzenesulfinamide (314 mg, 2.0 mmol), acetophenone (1.2 mL, 10 mmol) and Ti(OEt)\(_4\) (1.7 mL, 8.0 mmol). The resulting solution was refluxed and monitored by TLC until complete consumption of benzenesulfinamide. Then, CH\(_3\)OH (6 mL) and a few drops of NaHCO\(_3\) were added. The solution was filtered through anhydrous Na\(_2\)SO\(_4\) and washed with EtOAc. The solvent was removed under reduced pressure and the crude product was dissolved in CH\(_2\)Cl\(_2\) (10 mL) followed by the addition of m-CPBA (0.7 mg, 3.0 mmol). After the completion of the reaction, the solution was washed with saturated solution of NaHCO\(_3\) and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure and the crude product was purified by column chromatography using hexanes and EtOAc (10:1) to obtain the corresponding N-sulfonylimine 1u in 66% yield.

Typical procedure for the transfer hydrogenation of cyclic N-sulfonylimines:
N-Sulfonylimines 1a (24.3 mg, 0.1 mmol), catalyst Ir(ppy)\(_3\) (1.3 mg, 0.02 mmol), PhSSPh (8.7 mg, 0.04 mmol) and 2.0 mL THF were added to a Schlenk tube under argon atmosphere, and then DIEDA (8.7 μL, 0.05 mmol) and H\(_2\)O (180 μL, 10 mmol) was injected using a micro-syringe. The mixture was placed under a 30 W blue LED light source and stirred at room temperature. Upon completion of the reaction, the reaction mixture was concentrated, and the residue was purified by chromatography on a silica gel column to afford the desired product 2a (24.3 mg, 99% yield).

Part III Characterization Data of the products

3-phenyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2a)\[^{[2]}\]

![Image of 3-phenyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide](image)

White solid, 99% yield, Mp 128-131 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.84 (dd, J = 5.8, 3.0 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.40 (s, 5H), 7.16 (dd, J = 5.3, 2.9 Hz, 1H), 5.74 (d, J = 4.1 Hz, 1H), 5.14 (d, J = 3.2 Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) 61 39.8, 138.7, 134.7, 133.4, 129.5, 129.3, 129.1, 127.6, 125.4, 121.2, 61.4.

3-(p-tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2b)\[^{[2]}\]

![Image of 3-(p-tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide](image)
White solid, 98% yield, Mp 168-170°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 5.7$, 3.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.30 – 7.24 (m, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.15 (dd, $J = 5.4$, 2.9 Hz, 1H), 5.71 (d, $J = 3.6$ Hz, 1H), 5.01 (s, 1H), 2.37 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.1, 139.1, 135.8, 134.8, 133.4, 129.9, 129.4, 127.6, 125.4, 121.1, 61.2, 21.2.

3-(4-ethylphenyl)-2,3-dihydrobenzo[d]isothazole 1,1-dioxide (2c)

White solid, 89% yield, Mp 120-123°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 7.1$ Hz, 1H), 7.55 – 7.40 (m, 2H), 7.19 (d, $J = 7.1$ Hz, 2H), 7.14 (d, $J = 7.7$ Hz, 2H), 7.07 (d, $J = 6.6$ Hz, 1H), 5.62 (d, $J = 3.7$ Hz, 1H), 4.91 (d, $J = 2.3$ Hz, 1H), 2.57 (q, $J = 7.5$ Hz, 2H), 1.15 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.4, 140.1, 135.9, 134.9, 133.3, 129.4, 128.8, 127.6, 125.4, 121.1, 61.3, 28.6, 15.4. HRMS calcd for C$_{15}$H$_{15}$NO$_2$S [M]$^+$ : 273.0824. Found: 273.0827.

3-(4-(tert-butyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2d)

White solid, 98% yield, Mp 128-130°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 – 7.80 (m, 1H), 7.58 – 7.50 (m, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.30 – 7.24 (m, 2H), 7.16 (d, $J = 7.0$ Hz, 1H), 5.70 (d, $J = 3.9$ Hz, 1H), 5.04 (d, $J = 3.6$ Hz, 1H), 1.30 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.3, 140.1, 135.6, 134.9, 133.3, 129.4, 127.4, 126.2, 125.5, 121.1, 61.2, 34.7, 31.3. HRMS calcd for C$_{17}$H$_{19}$NO$_2$S [M]$^+$ : 301.1137. Found: 301.1140.

3-(m-tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2e)$^2$
White solid, 98% yield, Mp 155-158 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J = 7.2$ Hz, 1H), 7.59 – 7.49 (m, 2H), 7.27 (dd, $J = 9.7$, 5.6 Hz, 1H), 7.16 (t, $J = 9.9$ Hz, 4H), 5.68 (d, $J = 3.7$ Hz, 1H), 5.05 (d, $J = 2.1$ Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.9, 138.2, 137.5, 133.7, 132.3, 128.9, 128.4, 128.1, 127.1, 124.4, 123.7, 120.1, 60.4, 20.37.

3-($o$-tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2f)$^{[2]}$

$\text{\includegraphics[width=2cm]{image}}$

White solid, 98% yield, Mp 67-69 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 – 7.83 (m, 1H), 7.65 – 7.54 (m, 2H), 7.30 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 6.03 (d, $J = 4.5$ Hz, 1H), 4.86 (d, $J = 4.1$ Hz, 1H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.1, 136.8, 136.2, 135.7, 133.3, 131.3, 129.5, 129.1, 128.1, 127.1, 125.2, 121.3, 58.3, 19.4.

3-(4-methoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2g)$^{[2]}$

$\text{\includegraphics[width=2cm]{image}}$

White solid, 98% yield, Mp 150-153 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 – 7.76 (m, 1H), 7.65 – 7.47 (m, 2H), 7.30 – 7.19 (m, 2H), 7.13 (d, $J = 6.7$ Hz, 1H), 6.89 (d, $J = 8.6$ Hz, 2H), 5.68 (d, $J = 3.9$ Hz, 1H), 5.00 (d, $J = 3.5$ Hz, 1H), 3.80 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.2, 140.3, 135.0, 133.3, 130.6, 129.4, 129.0, 125.4, 121.1, 114.6, 61.0, 55.4.

3-(2-methoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2h)$^{[6]}$

$\text{\includegraphics[width=2cm]{image}}$

White solid, 93% yield, Mp 168-170 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (dd, $J = 6.5$, 2.1 Hz, 1H), 7.53 (m, 2H), 7.34 (m, 1H), 7.25 (ddd, $J = 8.3$, 7.0, 2.2 Hz, 2H), 6.99 – 6.92 (m, 2H), 5.98 (d, 2H), 5.00 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.7, 141.2, 138.5, 137.6, 128.8, 128.3, 125.6, 121.0, 114.8, 61.2, 55.5.
6.15 (d, \( J = 5.0 \) Hz, 1H), 5.14 (d, \( J = 4.7 \) Hz, 1H), 3.85 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.0, 140.4, 135.3, 133.1, 130.2, 129.2, 128.7, 126.4, 125.2, 121.3, 112.1, 111.1, 56.4, 55.6.

3-(3-methoxyphenyl)-2,3-dihydrobenzo[\( d \)]isothiazole 1,1-dioxide (2i)

White solid, 94% yield, Mp 133-135 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.87 – 7.78 (m, 1H), 7.62 – 7.49 (m, 2H), 7.33 – 7.25 (m, 1H), 7.18 (t, \( J = 6.3 \) Hz, 1H), 6.96 (d, \( J = 7.5 \) Hz, 1H), 6.93 – 6.86 (m, 2H), 5.69 (d, \( J = 3.9 \) Hz, 1H), 5.10 (d, \( J = 3.0 \) Hz, 1H), 3.78 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 160.3, 140.2, 139.7, 138.7, 133.4, 130.3, 129.5, 125.4, 121.2, 119.7, 114.6, 112.9, 61.3, 55.4. HRMS calcd for C\(_{14}\)H\(_{13}\)NO\(_3\)S [M\(^+\)]: 275.0616. Found: 275.0609.

3-(3,4,5-trimethoxyphenyl)-2,3-dihydrobenzo[\( d \)]isothiazole 1,1-dioxide (2j)

Yellow solid, 78% yield, Mp 189-191 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.89 – 7.75 (m, 1H), 7.68 – 7.49 (m, 2H), 7.24 – 7.15 (m, 1H), 6.57 (s, 2H), 5.63 (d, \( J = 2.3 \) Hz, 1H), 5.24 (s, 1H), 3.81 (d, \( J = 3.2 \) Hz, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 153.8, 139.6, 138.3, 134.7, 134.3, 133.4, 129.6, 125.3, 121.2, 104.4, 61.6, 60.8, 56.2.

3-(4-phenoxyphenyl)-2,3-dihydrobenzo[\( d \)]isothiazole 1,1-dioxide (2k)

White solid, 91% yield, Mp 91-93 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.94 – 7.82 (m, 1H), 7.67 – 7.53 (m, 2H), 7.41 – 7.30 (m, 4H), 7.17 (dd, \( J = 14.9, 7.4 \) Hz, 2H), 7.09 – 6.95 (m, 4H), 5.74 (d, \( J = 3.9 \) Hz, 1H), 5.03 (d, \( J = 3.5 \) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 158.3, 156.4, 139.9, 134.9, 133.4, 133.1, 129.9, 129.6, 129.2, 125.4, 123.9, 121.2, 119.4, 119.0, 60.9. HRMS calcd for C\(_{19}\)H\(_{15}\)NO\(_3\)S [M\(^+\)]: 337.0773. Found: 337.0781.
S7 - (4-fluorophenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2l)²

![Chemical Structure](image1)

White solid, 98% yield, Mp 163-166 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (m, 1H), 7.62 – 7.49 (m, 2H), 7.41 – 7.29 (m, 2H), 7.15 – 7.10 (m, 1H), 7.06 (t, J = 8.6 Hz, 2H), 5.72 (d, J = 4.1 Hz, 1H), 5.22 (d, J = 3.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 164.3, 161.8, 139.6, 134.7, 134.6, 134.6, 133.5, 129.7, 129.5, 129.4, 125.3, 121.2, 116.4, 116.2, 60.6.

3-(4-chlorophenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2m)⁵

![Chemical Structure](image2)

Light yellow solid, 98% yield, Mp 179-181 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.79 (m, 1H), 7.61 – 7.53 (m, 2H), 7.40 – 7.28 (m, 4H), 7.17 – 7.02 (m, 1H), 5.71 (d, J = 3.9 Hz, 1H), 5.18 (d, J = 3.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.2, 137.3, 135.1, 134.6, 133.5, 129.8, 129.5, 128.9, 125.3, 121.3, 60.6.

3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2n)

![Chemical Structure](image3)

Yellow solid, 98% yield, Mp 134-136 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, J = 5.2, 2.0 Hz, 1H), 7.68 – 7.50 (m, 6H), 7.18 – 7.09 (m, 1H), 5.81 (s, 1H), 5.42 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 142.8, 138.7, 134.4, 133.6, 129.9, 127.9, 126.3, 126.2, 125.3, 121.4, 60.6. HRMS calcd for C₁₃H₁₀F₃NO₂S [M⁺]: 313.0384. Found: 313.0382.

3-(naphthalen-2-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2o)
White solid, 90% yield, Mp 135-138°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 – 7.70 (m, 5H), 7.45 (dd, $J = 8.7$, 3.5 Hz, 4H), 7.28 (d, $J = 8.5$ Hz, 1H), 7.11 – 6.99 (m, 1H), 5.80 (d, $J = 3.9$ Hz, 1H), 5.11 (d, $J = 3.1$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.7, 135.9, 134.8, 133.5, 133.4, 133.1, 129.6, 127.9, 127.3, 126.9, 126.8, 125.5, 124.4, 121.2, 61.59. HRMS calcd for C$_{17}$H$_{13}$NO$_2$S [M]$^+$: 295.0667. Found: 295.0670.

3-((1,1'-biphenyl)-4-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide 

(2p)

White solid, 94% yield, Mp 203-205 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.80 (m, 1H), 7.61 – 7.51 (m, 6H), 7.43 (dd, $J = 11.8$, 5.1 Hz, 4H), 7.36 (t, $J = 7.3$ Hz, 1H), 7.18 (d, $J = 7.2$ Hz, 1H), 5.76 (d, $J = 4.0$ Hz, 1H), 5.22 (d, $J = 3.9$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.0, 140.2, 139.8, 137.7, 134.7, 133.5, 129.7, 129.6, 128.9, 128.1, 127.9, 127.8, 127.5, 127.1, 126.9, 125.5, 121.2, 61.1. HRMS calcd for C$_{19}$H$_{15}$NO$_2$S [M]$^+$: 321.0824. Found: 321.0820.

3-(3-(hydroxymethyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2q)$^{[2]}$

Colorless oil, 95% yield, $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (dd, $J = 5.7$, 3.1 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.26 (s, 1H), 7.23 – 7.14 (m, 3H), 7.05 (dd, $J = 5.7$, 2.7 Hz, 1H), 5.61 (d, $J = 3.5$ Hz, 1H), 5.58 (d, $J = 3.7$ Hz, 1H), 4.51 (s, 2H), 2.76 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$)
δ 142.11, 139.7, 139.1, 134.5, 133.4, 129.5, 129.3, 127.6, 126.7, 125.9, 125.4, 121.1, 64.6, 61.3.

3-((3-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2r)[2]

Yellow solid, 95% yield, Mp 57-59°C. 1H NMR (400 MHz, CDCl3) δ 7.90 – 7.78 (m, 1H), 7.55 (dd, J = 6.1, 2.7 Hz, 2H), 7.34 (t, J = 10.9 Hz, 3H), 7.26 – 7.22 (m, 1H), 7.18 – 7.07 (m, 1H), 5.72 (d, J = 4.0 Hz, 1H), 5.00 (d, J = 3.9 Hz, 1H), 4.73 (s, 2H), 0.91 (s, 9H), 0.08 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 142.8, 142.2, 139.8, 139.1, 138.6, 134.8, 133.3, 129.4, 127.6, 126.7, 126.2, 125.9, 125.4, 125.1, 121.1, 64.6, 25.9, 18.6, -3.6, -5.3.

3-benzyl-2,3-dihydrobenzo[d]isothazole 1,1-dioxide (2s)[2]

White solid, 25% yield, Mp 145-148 oC 1H NMR (400 MHz, CDCl3) δ 7.75 (d, J = 7.7 Hz, 1H), 7.60 – 7.48 (m, 2H), 7.35 – 7.22 (m, 6H), 4.84 (dt, J = 9.3, 4.5 Hz, 1H), 4.64 (s, 1H), 3.23 (dd, J = 13.8, 4.8 Hz, 1H), 2.96 (dd, J = 13.8, 9.6 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 139.4, 136.4, 135.6, 133.0, 129.6, 129.4, 129.0, 127.5, 124.4, 121.5, 58.8, 42.4.

3-phenyl-2,3-dihydrobenzo[d]isothazole 1,1-dioxide (3a)

1H NMR (400 MHz, CDCl3) δ 7.93 – 7.80 (m, 1H), 7.65 – 7.52 (m, 2H), 7.48 – 7.33 (m, 5H), 7.23 – 7.08 (m, 1H), 5.09 (s, 1H). 13C NMR (101 MHz, CDCl3) δ 139.8, 138.7, 134.8, 133.4, 129.6, 129.3, 129.1, 127.6, 125.4, 121.2, 61.3, 60.1 (t, J = 22 Hz).

3-(p-tolyl)-2,3-dihydrobenzo[d]isothazole 1,1-dioxide (3b)[2]
1H NMR (400 MHz, CDCl₃) δ 7.90 – 7.77 (m, 1H), 7.61 – 7.49 (m, 2H), 7.28 – 7.22 (m, 2H), 7.19 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.6 Hz, 1H), 4.95 (s, 1H), 2.35 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 140.1, 139.2, 135.6, 134.9, 133.4, 129.9, 129.5, 127.6, 125.4, 121.1, 60.9 (t, J = 22 Hz), 21.2.

3-(4-ethylphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3c)

1H NMR (400 MHz, CDCl₃) δ 7.79 – 7.70 (m, 1H), 7.48 (ddd, J = 6.3, 5.3, 1.0 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.09 – 7.04 (m, 1H), 4.90 (s, 1H), 2.57 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H). 13C NMR (101 MHz, CDCl₃) δ 145.4, 140.1, 135.8, 135.0, 133.3, 129.4, 128.8, 127.6, 125.4, 121.1, 60.9 (t, J = 23Hz), 28.6, 15.4.

3-(4-tert-butylphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3d)

1H NMR (400 MHz, CDCl₃) δ 7.82 (dd, J = 6.2, 2.7 Hz, 1H), 7.54 (ddd, J = 5.9, 5.2, 3.4 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.19 – 7.12 (m, 1H), 5.02 (s, 1H), 1.30 (s, 9H). 13C NMR (101 MHz, CDCl₃) δ 152.2, 140.0, 135.6, 135.0, 133.3, 129.4, 127.4, 126.2, 125.5, 121.1, 60.8 (t, J = 22Hz), 34.7, 31.3.

3-(m-tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3e)
1H NMR (400 MHz, CDCl₃) δ 7.89 – 7.80 (m, 1H), 7.63 – 7.50 (m, 2H), 7.29 (d, J = 7.8 Hz, 1H), 7.15 (m, 4H), 4.92 (s, 1H), 2.34 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 139.9, 139.3, 138.5, 134.9, 133.4, 129.9, 129.5, 129.2, 128.1, 125.4, 124.7, 121.1, 61.1 (t, J = 22 Hz), 21.4.

3-(o-tolyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3f)

1H NMR (400 MHz, CDCl₃) δ 7.85 (dd, J = 5.5, 3.3 Hz, 1H), 7.57 (dd, J = 6.1, 2.6 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.12 (d, J = 7.0 Hz, 2H), 4.86 (s, 1H), 2.45 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 140.0, 136.8, 136.2, 135.7, 133.4, 131.3, 129.5, 129.1, 128.1, 127.1, 125.3, 121.3, 57.9 (t, J = 24 Hz), 19.4.

3-(4-methoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (4g)

1H NMR (400 MHz, CDCl₃) δ 7.95 – 7.73 (m, 1H), 7.66 – 7.49 (m, 2H), 7.33 – 7.20 (m, 2H), 7.13 (d, J = 6.3 Hz, 1H), 6.89 (dd, J = 8.6, 1.9 Hz, 2H), 5.02 (s, 1H), 3.81 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 160.2, 140.2, 135.1, 133.3, 130.6, 129.4, 128.9, 125.4, 121.1, 114.6, 60.7 (t, J = 22 Hz), 55.4.

3-(2-methoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3h)

1H NMR (400 MHz, CDCl₃) δ 7.77 – 7.71 (m, 1H), 7.51 – 7.40 (m, 2H), 7.31 – 7.23 (m, 1H), 7.19 (d, J = 1.8 Hz, 1H), 7.17 – 7.12 (m, 1H), 6.91 – 6.83 (m, 2H), 4.97 (s, 1H), 3.77 (s,
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 – 7.71 (m, 1H), 7.63 – 7.51 (m, 2H), 7.30 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.99 – 6.93 (m, 1H), 6.93 – 6.86 (m, 2H), 5.06 (s, 1H), 3.78 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.8, 156.4, 139.8, 135.0, 133.4, 133.0, 129.9, 129.6, 129.2, 125.4, 123.9, 121.2, 119.0, 60.5 (t, $J$ = 17Hz).

3-(3-methoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3i)

3-(3,4,5-trimethoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3j)

3-(4-phenoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3k)

3-(4-fluorophenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3l)
\[ \text{Supporting information} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 7.83 (dd, } J = 5.9, 2.4 \text{ Hz, 1H), 7.62 – 7.51 (m, 2H), 7.44 – 7.31 (m, 2H), 7.22 – 6.95 (m, 3H), 5.16 (s, 1H).} \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 164.3, 161.8, 139.5, 134.7, 134.6, 134.5, 133.5, 129.7, 129.5, 129.4, 125.3, 121.2, 116.4, 116.2, 60.4 (t, } J = 23 \text{ Hz).} \]

\[ \text{3-(4-chlorophenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3m)} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 7.86 – 7.77 (m, 1H), 7.59 – 7.50 (m, 2H), 7.33 (ddd, } J = 17.9, 5.0, 1.5 \text{ Hz, 4H), 7.16 – 7.04 (m, 1H), 5.05 (s, 1H).} \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 139.2, 137.2, 135.1, 134.7, 133.5, 129.8, 129.5, 128.9, 125.3, 121.3, 60.4 (t, } J = 46 \text{ Hz).} \]

\[ \text{3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2n)} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 7.87 – 7.81 (m, 1H), 7.64 (d, } J = 8.2 \text{ Hz, 2H), 7.60 – 7.51 (m, 4H), 7.17 – 7.11 (m, 1H), 5.31 (s, 1H).} \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta 142.7, 138.7, 134.5, 133.6, 129.9, 127.9, 126.3, 126.2, 125.3, 121.4, 60.3 (t, } J = 23 \text{ Hz).} \]

\[ \text{3-(naphthalen-2-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3o)} \]
\( ^1 \text{H NMR (400 MHz, CDCl}_3 \text{)} \) \( \delta 7.83 \) (dd, \( J = 12.8, 8.3 \text{ Hz, 5H} \)), \( 7.51 \) (m, 4H), \( 7.33 \) (d, \( J = 8.5 \text{ Hz, 1H} \)), \( 7.11 \) (dd, \( J = 4.8, 2.3 \text{ Hz, 1H} \)), \( 5.03 \) (s, 1H).\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \text{)} \) \( \delta 139.6, 135.8, 134.8, 133.5, 133.1, 133.0, 129.7, 128.0, 127.9, 127.3, 126.9, 126.9, 125.5, 124.4, 121.3, 61.7. \)

**3-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3p)**

\( ^1 \text{H NMR (400 MHz, CDCl}_3 \text{)} \) \( \delta 7.87 – 7.80 \) (m, 1H), \( 7.60 – 7.53 \) (m, 6H), \( 7.47 – 7.41 \) (m, 4H), \( 7.39 – 7.34 \) (m, 1H), \( 7.21 – 7.14 \) (m, 1H), \( 5.17 \) (s, 1H).\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \text{)} \) \( \delta 142.1, 140.2, 139.7, 137.6, 134.8, 133.5, 132.9, 129.6, 128.9, 128.1, 127.9, 127.8, 127.5, 127.1, 126.9, 125.5, 121.2, 60.8 (t, \( J = 22 \text{ Hz} \)). \)

**3-(3-(hydroxymethyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3q)**

\( ^1 \text{H NMR (400 MHz, CDCl}_3 \text{)} \) \( \delta 7.75 – 7.67 \) (m, 1H), \( 7.50 – 7.42 \) (m, 2H), \( 7.22 \) (ddd, \( J = 16.9, 8.9, 2.5 \text{ Hz, 4H} \)), \( 7.10 – 7.02 \) (m, 1H), \( 5.45 \) (s, 1H), \( 4.54 \) (s, 2H), \( 2.54 \) (s, 1H).\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \text{)} \) \( \delta 142.1, 139.6, 139.0, 134.6, 133.4, 129.6, 129.4, 127.6, 126.8, 125.9, 125.4, 121.2, 64.6, 60.9 (t, \( J = 28 \text{ Hz} \)). \)

**3-(3-(((tert-butyl dimethylsilyl)oxy)methyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (3r)**
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 6.2$, 2.8 Hz, 1H), 7.56 (dd, $J = 9.1$, 4.9 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.25 (dd, $J = 7.7$, 5.7 Hz, 1H), 7.17 – 7.11 (m, 1H), 4.98 (s, 1H), 4.73 (s, 2H), 0.91 (s, 9H), 0.08 (s, 6H).<ref>
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.2, 139.6, 139.0, 133.4, 129.6, 129.4, 127.6, 126.7, 125.9, 125.4, 121.2, 64.7, 61.1 (t, $J = 17$Hz), 25.9, 25.7, 17.9, -3.6, -5.3.
</ref>

Notes and references:
Part IV NMR spectra

2a

2a
Supporting information

**Figure 1**: 
NMR spectra of compound 2c.

- **Top spectrum**: 1H NMR spectrum showing peaks at various chemical shifts.
- **Bottom spectrum**: 13C NMR spectrum showing peaks at various chemical shifts.
Supporting information
Supporting information

\[ \text{2s} \]

\[ \text{2s} \]
$^1$H-NMR of the reaction mixtures that using THF-$d_8$ as solvent instead of THF after 24 hours

$^1$H-NMR of the products that using the mixture of H$_2$O and D$_2$O as reductant after 2 hours