Electrochemical NaI/NaCl-mediated one-pot synthesis of 2-aminobenzoxazoles and 2-aminobenzothiazoles in aqueous media via tandem addition-cyclization

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**Table S1.** Additional optimization experiments

![Chemical structure](image)

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Reaction conditions: graphite rod ($\#5$ mm, $5$ mm immersion depth, immersed surface area of $2.3$ cm$^2$) as both cathode and anode, current density = 13 mA/cm$^2$, 3a (0.6 mmol), 4a (0.5 mmol), NaI (0.05 mmol), NaCl (0.075 mmol) EtOH 1 mL, water 1 mL, room temperature, 2 hrs., undivided cell.

Faradaic efficiency calculation:

\[
\text{Faradaic efficiency} = \frac{Q_{\text{experimental}}}{Q_{\text{theoretical}}} \times 100
\]

\[
\text{Faradaic efficiency} = \frac{z \times n \times F}{Q_{\text{theoretical}}} \times 100
\]

With \(z\) = number of electron that the reaction used = 2

\(n = \text{mol of product that obtained} = 0.5 \times 95\% = 0.475 \text{ mmol}\)

\(F = \text{Faradaic constant} (96485 \text{ C/mol})\)

\(Q_{\text{theoretical}} \text{ can be calculated from } I \text{ (current, Ampere)} \times t \text{ (reaction time, second)}\)

\[
\text{Faradaic efficiency} = \frac{2 \times 0.475 \times 10^{-3} \times 96485}{0.03 \times 7200} \times 100
\]

\(\text{Faradaic efficiency} = 42\%\)
Experimental Section

Materials and methods

All chemicals and solvents were obtained from commercially available suppliers such as Sigma-Aldrich and TCI (Japan) and were used without further purification, unless otherwise stated. Pyrex reactor ($\phi = 2.0$ cm, Height = $6.2$ cm) was used for electrochemical reaction. Power supply (KORAD, KA3005D) was purchased from Shenzhen Korad Technology CO., LTD. All electrodes such as graphite rod ($\phi = 5$ mm) and platinum plate (5x5x0.1 mm) were purchased from Minihua Store, China. Electrochemical reaction setup was depicted in Figure S1 and S2. Analytical thin layer chromatography (TLC) was performed with precoated Merck silica gel 60 F254 plates (0.25 mm for thick layer) and visualized at 254 nm using an ultraviolet lamp. Column chromatography was performed with Silicycle silica gel 60-200 $\mu$m (70-230 mesh). $^1$H-NMR, $^{13}$C-NMR spectra were obtained with JEOL JNM-ECZ500R/S1 NMR spectrometers operating at 500 MHz for $^1$H or 125 MHz for $^{13}$C nuclei. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) with a MicroTOF Bruker mass spectrometer. Fourier transform infrared spectra were acquired on Nicolet 6700 FTIR spectrometer equipped with a mercury-cadmium telluride (MCT) detector (Nicolet, USA).

General procedure for synthesis of 2-aminobenzoxazoles (General Procedure A)

A mixture of 2-aminophenol (1.2 equiv., 0.600 mmol), isothiocyanate (1.0 equiv., 0.500 mmol), sodium iodide (0.1 equiv., 0.050 mmol) and sodium chloride (0.15 equiv., 0.075 mmol) was dissolved in mixed 1 mL of water with 1 mL of ethanol in a tube. The reaction mixture was electrolysed at a constant current of 30 mA (13 mA/cm$^2$, graphite rods as both cathode and anode) at room temperature for 2 hours. The reaction was extracted with water and ethyl acetate. The organic layer was evaporated under reduced pressure to give the
crude product, which was further purified by column chromatography (eluted with ethyl acetate/hexane) to afford the desired compound.

**General procedure for synthesis of 2-aminobenzothiazoles (General Procedure B)**

A mixture of 2-aminobenzenethiol (1.2 equiv., 0.600 mmol), isothiocyanate (1.0 equiv., 0.500 mmol), sodium iodide (0.1 equiv., 0.050 mmol) and sodium chloride (0.15 equiv., 0.075 mmol) was dissolved in mixed 1 mL of water with 1 mL of ethanol in a tube. The reaction mixture was electrolysed at a constant current of 30 mA (13 mA/cm², graphite rods as both cathode and anode) at room temperature for 2 hours. The reaction was extracted with water and ethyl acetate. The organic layer was evaporated under reduced pressure to give the crude product, which was further purified by column chromatography (eluted with ethyl acetate/hexane) to afford the desired compound.

**N-phenylbenzo[d]oxazol-2-amine (6aa)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6aa (99.8 mg, 0.475 mmol, 95%) as a white solid: ¹H NMR (500 MHz, DMSO) δ ppm 10.62 (s, 1H), 7.78 (d, J = 7.7 Hz, 2H), 7.47 (dd, J = 7.2, 5.7 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.22 (td, J = 7.6, 1 Hz, 1H), 7.12 (td, J = 7.8, 1 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H). ¹³C NMR (125 MHz, DMSO): δ ppm 158.0, 147.1, 142.5, 138.8, 129.2, 124.0, 122.2, 121.7, 117.6, 116.7, 109.0. IR (ATR, cm⁻¹): 3385, 3167, 3039, 2920, 2853, 1635, 1571, 1455, 1240, 736. ESI-MS: m/z: 211.1167 [M+H]⁺ (calcd for [C₁₃H₁₁N₂O]⁺ 211.0871).

For gram-scale synthesis: A mixture of 2-aminophenol (1.2 equiv., 9.60 mmol), isothiocyanate (1.0 equiv., 8.00 mmol), sodium iodide (0.1 equiv., 0.80 mmol), and sodium
chloride (0.15 equiv., 1.20 mmol) was dissolved in mixed 16 mL of water with 16 mL of ethanol in a 50 mL three-necked round bottom flask. The reaction mixture was electrolysed at a constant current of 30 mA (13 mA/cm², graphite rods as both cathode and anode) at room temperature for 24 hours. The reaction was extracted with water and ethyl acetate. The organic layer was evaporated under reduced pressure to give the crude product, which was further washed carefully with ethanol and filtered to afford the desired compound (1.179 g, 5.614 mmol, 70%). The ¹H and ¹³C NMR data are identical to above procedure and were shown in figures S64-S65.

6-methyl-N-phenylbenzo[d]oxazol-2-amine (6ba) Synthesized according to the General procedure A using 2-amino-5-methylphenol (73.8 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ba (103.3 mg, 0.461 mmol, 92%) as a white solid: ¹H NMR (500 MHz, DMSO): δ ppm 10.55 (s, 1H), 7.81 (d, J = 7.7 Hz, 2H), 7.37 (t, J = 8 Hz, 2H), 7.33 (d, J = 7.9 Hz, 1H), 7.27 (s, 1H), 7.02 (t, J = 7.3 Hz, 2H), 2.36 (s, 3H). ¹³C NMR (125 MHz, DMSO): δ ppm 157.7, 147.3, 140.2, 138.9, 131.2, 129.0, 124.7, 122.0, 117.5, 116.1, 109.3, 21.1. IR (ATR, cm⁻¹): 3160, 3038, 2920, 2853, 1666, 1597, 1487, 1431, 1372, 1274, 751. ESI-MS: m/z: 225.1014 [M+H]+ (calcd for [C₁₄H₁₃N₂O]+ 225.1028).

5-(tert-butyl)-N-phenylbenzo[d]oxazol-2-amine (6ca) Synthesized according to the General procedure A using 2-amino-4-tert-butylphenol (99.1 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ca (129 mg, 0.485 mmol, 97%) as a white solid: ¹H NMR (500 MHz, DMSO): δ ppm 10.56 (s, 1H), 7.8 (d, J = 8 Hz, 2H), 7.48 (d, J = 1.9 Hz, 1H), 7.36 (m, 3H), 7.12 (dd, J = 8.4, 1.9 Hz, 1H),
7.02 (t, J = 7.4 Hz, 1H), 1.3 (s, 9H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 158.2, 146.9, 145.0, 142.4, 139.0, 129.0, 122.0, 118.6, 117.5, 113.6, 108.0, 34.5, 31.6. IR (ATR, cm$^{-1}$): 3042, 2950, 1672, 1603, 1575, 1495, 1425, 1371, 1264, 1226, 977, 736. ESI-MS: m/z: 267.1492 [M+H]$^+$ (calcd for [C$_{17}$H$_{19}$N$_2$O]$^+$ 267.1497).

5-bromo-N-phenylbenzo[d]oxazol-2-amine (6da) Synthesized according to the General procedure A using 2-amino-4-bromophenol (112.8 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h.) to afford 6da (121.3 mg, 0.420 mmol, 84%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): δ ppm 10.78 (s, 1H), 7.76 (d, J = 8 Hz, 2H), 7.62 (d, J = 2 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.37 (t, J = 7.9 Hz, 2H), 7.24 (dd, J = 8.3, 2.0 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 159.0, 146.3, 144.6, 138.4, 129.0, 124.1, 122.5, 119.2, 117.9, 116.0, 110.6. IR (ATR, cm$^{-1}$): 3036, 2853, 1674, 1591, 1570, 1495, 1457, 1441, 1420, 1366, 1247, 1228, 971, 795, 733. ESI-MS: m/z: 288.9963 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$N$_2$OBr]$^+$ 288.9977).

5-chloro-N-phenylbenzo[d]oxazol-2-amine (6ea) Synthesized according to the General procedure A using 2-amino-4-chlorophenol (86.1 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h.) to afford 6ea (111.8 mg, 0.457 mmol, 91%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): δ ppm 10.78 (s, 1H), 7.76 (d, J = 7.7 Hz, 2H), 7.49 (d, J = 2.2 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.37 (dt, J = 8.3, 7.9 Hz, 2H), 7.11 (dd, J = 8.5, 2.2 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 159.2, 145.9, 144.1, 138.4, 129.0, 128.2, 122.5,
5-methoxy-N-phenylbenzo[d]oxazol-2-amine (6fa) Synthesized according to the General procedure A using 2-amino-4-methoxyphenol (83.0 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6fa (98.0 mg, 0.408 mmol, 82%) as a light pink solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.59 (s, 1H), 7.77 (dd, $J = 8.5$, 0.8 Hz, 2H), 7.36 (m, 3H), 7.07 (d, $J = 2.5$ Hz, 1H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.67 (dd, $J = 8.8$, 2.6 Hz, 1H), 3.76 (s, 3H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 158.8, 156.7, 143.5, 141.5, 138.8, 129.0, 122.1, 117.6, 108.9, 108.0, 101.9, 55.6. IR (ATR, cm$^{-1}$): 3047, 2924, 1656, 1600, 1572, 1499, 1458, 1446, 1249, 1246, 736. ESI-MS: m/z: 241.1071 [M+H]$^+$ (calcd for [C$_{14}$H$_{13}$N$_2$O$_2$]+ 241.1077).$^1$

5-nitro-N-phenylbenzo[d]oxazol-2-amine (6ga) Synthesized according to the General procedure A using 2-amino-4-nitrophenol (92.5 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h.) to afford 6ga (53.4 mg, 0.209 mmol, 42%) as a yellow solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 11.01 (s, 1H), 8.21 (dd, $J = 2.2$, 1.2 Hz, 1H), 8.06 (ddd, $J = 8.8$, 2.2, 1.2 Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.70 (dd, $J = 8.8$, 0.9 Hz, 1H), 7.4 (t, $J = 7.5$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 160.1, 151.4, 144.6, 143.5, 138.0, 129.1, 122.9, 118.2, 118.1, 111.5, 109.3. IR (ATR, cm$^{-1}$): 3035, 2921, 1688, 1584, 1528, 1495, 1465, 1440, 1341, 1263, 1234, 976, 735, 685. ESI-MS: m/z: 256.0723 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$N$_3$O$_3$]+ 256.0722).$^1$
**N-(m-tolyl)benzo[d]oxazol-2-amine (6ab)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), m-tolyl isothiocyanate (74.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ab (104.3 mg, 0.466 mmol, 93%) as a light brown solid: \(^1\)H NMR (500 MHz, DMSO) \(\delta\) ppm 10.56 (s, 1H), 7.62 (d, \(J = 6\) Hz, 2H), 7.47 (dd, \(J = 10.6, 7.8\) Hz, 2H), 7.23 (m, 2H), 7.11 (td, \(J = 7.8, 1\) Hz, 1H), 6.84 (d, \(J = 7.5\) Hz, 1H), 2.31 (s, 3H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) ppm 158.1, 147.1, 142.6, 138.8, 138.3, 128.9, 124.0, 123.0, 121.6, 118.1, 116.7, 114.9, 108.9, 21.3. IR (ATR, cm\(^{-1}\)): 3046, 2920, 1634, 1606, 1574, 1499, 1487, 1460, 1242, 736. ESI-MS: m/z: 225.1017 [M+H]\(^+\) (calcd for [C\(_{14}\)H\(_{13}\)N\(_2\)O]\(^+\) 225.1028).

**N-(4-ethylphenyl)benzo[d]oxazol-2-amine (6ac)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-ethylphenyl isothiocyanate (81.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ac (105.4 mg, 0.443 mmol, 89%) as a light brown solid: \(^1\)H NMR (500 MHz, DMSO): \(\delta\) ppm 10.52 (s, 1H), 7.69 (d, \(J = 8.6\) Hz, 2H), 7.46 (dd, \(J = 8.8\) Hz, 2H), 7.2 (m, 3H), 7.10 (td, \(J = 8.8, 1\) Hz, 1H), 2.55 (q, \(J = 7.6\) Hz, 2H), 1.15 (t, \(J = 7.6\) Hz, 3H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) ppm 158.2, 147.1, 142.7, 137.6, 136.5, 128.2, 124.0, 121.5, 117.8, 116.5, 108.9, 27.6, 15.8. IR (ATR, cm\(^{-1}\)): 3390, 2965, 1652, 1615, 1574, 1511, 1439, 1339, 1270, 1229, 822, 734. ESI-MS: m/z: 239.1178 [M+H]\(^+\) (calcd for [C\(_{15}\)H\(_{15}\)N\(_2\)O]\(^+\) 239.1184).

**N-(4-methoxyphenyl)benzo[d]oxazol-2-amine (6ad)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-methoxyphenyl
isothiocyanate (82.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ad (86.4 mg, 0.360 mmol, 72%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.42 (s, 1H), 7.69 (dd, $J = 6.9$, 2 Hz, 2H), 7.43 (dd, $J = 7.6$, 4.7 Hz, 2H), 7.19 (t, $J = 7.7$ Hz, 1H), 7.09 (t, $J = 7.8$ Hz, 1H), 6.96 (dd, $J = 7$, 2 Hz, 2H), 3.73 (s, 3H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 158.5, 154.7, 147.2, 142.7, 132.0, 123.9, 121.3, 119.3, 116.4, 114.3, 108.8, 55.2. IR (ATR, cm$^{-1}$): 2837, 2359, 2341, 1672, 1580, 1510, 1459, 1283, 1267, 1163, 1030, 965, 820, 752, 738, 700. ESI-MS: m/z: 241.0971 [M+H]$^+$ (calcd for [C$_{14}$H$_{13}$N$_2$O$_2$]+ 241.0999).$^1$

$\text{N-(3-iodophenyl)benzo[d]oxazol-2-amine (6ae)}$ Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 3-iodophenyl isothiocyanate (130.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ae (105.6 mg, 0.314 mmol, 63%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.75 (s, 1H), 8.25 (s, 1H), 7.73 (dd, $J = 8.2$, 1.8 Hz, 1H), 7.49 (dd, $J = 10.2$, 8 Hz, 2H), 7.37 (d, $J = 7.8$ Hz, 1H), 7.22 (t, $J = 7.7$ Hz, 1H), 7.15 (t, $J = 8.3$ Hz, 2H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 157.4, 147.0, 142.2, 140.2, 131.0, 130.6, 125.5, 124.1, 122.0, 117.0, 109.1, 94.9. IR (ATR, cm$^{-1}$): 3038, 2926, 1673, 1586, 1568, 1488, 1458, 1240, 1224, 735. ESI-MS: m/z: 336.9816 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$IN$_2$O]+ 336.9838).

$\text{N-(4-bromophenyl)benzo[d]oxazol-2-amine (6af)}$ Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-bromophenyl isothiocyanate (107.0 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6af (91.7 mg, 0.317 mmol, 64%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.79 (s,
1H), 7.74 (dd, J = 6.8, 2.1 Hz, 2H), 7.52 (dd, J = 6.9, 1.9 Hz, 2H), 7.46 (dd, J = 7.8, 0.8 Hz, 2H), 7.21 (td, J = 7.6, 0.7 Hz, 1H), 7.12 (td, J = 8.3, 0.8 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 157.7, 147.1, 142.3, 138.2, 131.8, 124.2, 122.0, 119.6, 116.8, 113.7, 109.1. IR (ATR, cm$^{-1}$): 3160, 3029, 2920, 1675, 1592, 1573, 1487, 1458, 1364, 1352, 1248, 1232, 733. ESI-MS: m/z: 288.9960 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$BrN$_2$O]$^+$ 288.9977).

$^{N}$-(2-fluorophenyl)benzo[d]oxazol-2-amine (6ag) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 2-fluorophenyl isothiocyanate (76.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ag (102.9 mg, 0.45 mmol, 90%) as a white solid: $^1$H NMR (400 MHz, DMSO): δ ppm 10.42 (s, 1H), 8.27 (t, J = 7.9 Hz, 1H), 7.46 (t, J = 9.0 Hz, 2H), 7.24 (m, 3H), 7.12 (t, J = 7.6 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO): δ ppm 158.5, 154.0, 152.1, 147.5, 142.2, 126.6 (d, J = 11.3 Hz), 124.7 (d, J = 2.5 Hz), 124.1 (d, J = 6.3 Hz). 121.9 (d, J = 16.3 Hz), 116.8, 115.6 (d, J = 17.5 Hz), 109.1. IR (ATR, cm$^{-1}$): 3141, 3002, 1644, 1573, 1504, 1459, 1366, 1282, 1243, 1197, 1100, 737. ESI-MS: m/z: 229.0764 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$FN$_2$O]$^+$ 229.0777).

$^{N}$-(4-chlorophenyl)benzo[d]oxazol-2-amine (6ah) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-chlorophenyl isothiocyanate (84.8 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ah (88.7 mg, 0.363 mmol, 73%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): δ ppm 10.78 (s, 1H), 7.8 (d, J = 7.3 Hz, 2H), 7.47 (t, J = 7.3 Hz, 2H), 7.42 (d, J = 7 Hz, 2H), 7.22 (t, J = 7.7 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 157.7, 147.0, 142.2, 137.8, 128.9, 125.7, 124.1, 121.9, 119.1, 116.8, 109.1. IR (ATR, cm$^{-1}$): 3378, 2924, 1653, 1598,
N-(4-hydroxyphenyl)benzo[d]oxazol-2-amine (6ai) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-hydroxyphenyl isothiocyanate (75.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ai (82.4 mg, 0.365 mmol, 73%) as a light orange solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.25 (s, 1H), 9.21 (s, 1H), 7.55 (dd, $J = 6.7$, 2.2 Hz, 2H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.39 (d, $J = 7.7$ Hz, 1H), 7.18 (t, $J = 7.7$ Hz, 1H), 7.07 (t, $J = 7.7$ Hz, 1H), 6.80 (dd, $J = 6.7$, 2.2 Hz, 2H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 158.7, 152.9, 147.2, 142.8, 130.5, 123.9, 121.2, 119.6, 116.3, 115.5, 108.8. IR (ATR, cm$^{-1}$): 3261, 3176, 3069, 1632, 1571, 1540, 1505, 1457, 1235, 1219, 1007, 817, 745. ESI-MS: m/z: 227.08188 [M+H]$^+$ (calcd for [C$_{13}$H$_{11}$N$_2$O$_2$]$^+$ 227.08205).

N-(3-hydroxyphenyl)benzo[d]oxazol-2-amine (6aj) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 3-hydroxyphenyl isothiocyanate (75.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6aj (76.8 mg, 0.340 mmol, 68%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.50 (s, 1H), 9.50 (s, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.44 (dd, $J = 7.8$, 0.7 Hz, 1H), 7.36 (t, $J = 1.9$ Hz, 1H), 7.21 (td, $J = 7.6$, 1.2 Hz, 1H), 7.12 (m, 3H), 6.44 (dt, $J = 7.2$, 2.1 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 158.0, 147.0, 142.6, 139.8, 129.7, 124.1, 121.7, 116.6, 109.5, 109.0, 108.6, 104.8. IR (ATR, cm$^{-1}$): 3321, 3176, 3069, 2919, 1651, 1615, 1504, 1461, 1352, 1249, 1157, 944, 764, 737. ESI-MS: m/z: 227.08213 [M+H]$^+$ (calcd for [C$_{13}$H$_{11}$N$_2$O$_2$]$^+$ 227.08205).
**N-(4-(trifluoromethyl)phenyl)benzo[d]oxazol-2-amine (6ak)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-(trifluoromethyl)phenyl isothiocyanate (101.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h) to afford 6ak (107.5 mg, 0.387 mmol, 77%) as a white solid: $^1$H NMR (500 MHz, DMSO): δ ppm 11.07 (s, 1H), 7.97 (d, $J = 8.6$ Hz, 2H), 7.72 (d, $J = 8.7$ Hz, 2H), 7.50 (dd, $J = 7.8$, 2.3 Hz, 2H), 7.24 (t, $J = 7.7$ Hz, 1H), 7.16 (t, $J = 7.7$ Hz, 1H). $^{13}$C NMR (100 MHz, DMSO): δ ppm 157.4, 147.0, 142.4, 142.1, 126.3, 125.7, 124.2, 123.5, 122.2, 122.0, 117.4, 117.0, 109.2. IR (ATR, cm$^{-1}$): 2359, 1615, 1574, 1486, 1459, 1325, 1282, 1235, 1160, 1106, 1069, 1014, 978, 829, 737. ESI-MS: m/z: 279.0750 [M+H]$^+$ (calcd for [C$^{14}$H$^{10}$F$^3$N$^2$O]$^+$ 279.0745).$^1$

**N-(naphthalen-1-yl)benzo[d]oxazol-2-amine (6al)** Synthesized according to the General procedure A using 2-aminophenol (65.0 mg, 0.600 mmol), 1-naphthyl isothiocyanate (92.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h) to afford 6al (56.6 mg, 0.218 mmol, 44%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): δ ppm 10.49 (s, 1H), 8.31 (d, $J = 7.3$ Hz, 1H), 8.16 (d, $J = 7.5$ Hz, 1H), 7.95 (dd, $J = 6.7$, 2.7 Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.57 (m, 3H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.42 (d, $J = 7.7$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.12 (t, $J = 7.7$ Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 159.8, 147.6, 142.5, 133.9, 128.3, 126.7, 126.2, 126.0, 125.9, 124.3, 124.0, 122.4, 121.5, 118.6, 116.5, 109.0. IR (ATR, cm$^{-1}$): 2900, 2359, 1627, 1580, 1515, 1462, 1401, 1353, 1274, 1241, 956, 774, 731. ESI-MS: m/z: 261.1025 [M+H]$^+$ (calcd for [C$^{17}$H$^{13}$N$^2$O]$^+$ 261.1020).$^1$
N-(pyridin-3-yl)benzo[d]oxazol-2-amine (6am) Synthesized according to the General procedure A using 2-aminophenol (65.0 mg, 0.600 mmol), 3-pyridyl isothiocyanate (68.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h) to afford 6am (69.0 mg, 0.327 mmol, 65%) as a yellow solid: \(^1\)H NMR (500 MHz, DMSO): \(\delta\) ppm 10.89 (s, 1H), 8.88 (d, \(J = 2.6\) Hz, 1H), 8.28 (dd, \(J = 8.4, 2.4\) Hz, 1H), 8.25 (dd, \(J = 4.6, 1.2\) Hz, 1H), 7.49 (dd, \(J = 11.7, 7.9\) Hz, 2H), 7.41 (d, \(J = 8.3, 4.7\) Hz, 1H), 7.23 (t, \(J = 7.4\) Hz, 1H), 7.14 (t, \(J = 7.7\) Hz, 1H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) ppm 157.8, 147.2, 143.1, 142.2, 139.6, 135.7, 124.3, 124.2, 123.9, 122.1, 116.9, 109.2. IR (ATR, cm\(^{-1}\)): 3380, 2359, 1640, 1594, 1568, 1460, 1430, 1332, 1300, 1235, 1168, 981, 824, 735. ESI-MS: m/z: 212.0828 [M+H]\(^+\) (calcd for \([\text{C}_{12}\text{H}_{10}\text{N}_{3}\text{O}]^+\) 212.0824).

N-(4-nitrophenyl)benzo[d]oxazol-2-amine (6an) Synthesized according to the General procedure A using 2-aminophenol (3a) (65.4 mg, 0.600 mmol), 4-nitrophenyl isothiocyanate (4i) (90.1 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol) and sodium chloride (4.4 mg, 0.075 mmol in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 8h) to afford 6an (16.0 mg, 0.065 mmol, 13%) as a yellow solid: \(^1\)H NMR (500 MHz, DMSO): \(\delta\) ppm 11.44 (s, 1H), 8.29 (dd, \(J = 11.9, 2.8\) Hz, 2H), 7.97 (dd, \(J = 12, 2.9\) Hz, 2H), 7.55 (dd, \(J = 7.7, 5.3\) Hz, 2H), 7.28 (t, \(J = 7.7\) Hz, 1H), 7.21 (t, \(J = 7.7\) Hz, 1H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) ppm 156.9, 147.2, 145.0, 141.7, 141.3, 125.4, 124.4, 122.7, 117.4, 117.2, 109.5. IR (ATR, cm\(^{-1}\)): 2922, 2359, 1671, 1585, 1518, 1457, 1328, 1307, 1239, 1183, 1109, 731. ESI-MS: m/z: 256.0710 [M+H]\(^+\) (calcd for \([\text{C}_{13}\text{H}_{10}\text{N}_{3}\text{O}_3]^+\) 256.0722).

N-(3-nitrophenyl)benzo[d]oxazol-2-amine (6ao) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 3-nitrophenyl
isothiocyanate (90.1 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ao (38.8 mg, 0.152 mmol, 30%) as a light yellow solid: \(^1\)H NMR (500 MHz, DMSO): \(\delta\) ppm 11.17 (s, 1H), 8.77 (t, \(J = 2.2\) Hz, 1H), 8.08 (ddd, \(J = 8.2, 2.1, 0.7\) Hz, 1H), 7.87 (ddd, \(J = 8.2, 2.2, 0.7\) Hz, 1H), 7.65 (t, \(J = 8.2\) Hz, 1H), 7.53 (m, 1H), 7.26 (td, \(J = 7.7, 1.1\) Hz, 1H), 7.18 (td, \(J = 7.8, 1.2\) Hz, 1H).

\(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) ppm 157.4, 148.4, 147.0, 141.9, 140.0, 130.4, 124.3, 123.6, 122.4, 117.1, 116.6, 111.5, 109.3. IR (ATR, cm\(^{-1}\)): 3156, 3100, 3075, 2915, 1674, 1530, 1490, 1457, 1348, 1235, 984, 817, 727. ESI-MS: m/z: 256.07176 [M+H]\(^+\) (calcd for [C\(_{13}\)H\(_{10}\)N\(_3\)O\(_3\)]\(^+\) 256.07222).

**N-cyclohexylbenzo[d]oxazol-2-amine (6ap)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), cyclohexyl isothiocyanate (70.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ap (27.2 mg, 0.126 mmol, 25%) as a white solid: \(^1\)H NMR (500 MHz, DMSO): \(\delta\) ppm 7.85 (d, \(J = 7.8\) Hz, 1H), 7.3 (dd, \(J = 7.8, 2.6\) Hz, 1H), 7.22 (dd, \(J = 7.6, 2.5\) Hz, 1H), 7.08 (td, \(J = 7.6, 2.8\) Hz, 1H), 6.94 (td, \(J = 7.7, 2.6\) Hz, 1H), 3.54 (m, 1H), 1.96 (s, 2H), 1.71 (s, 2H), 1.32-1.13 (m, 6H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) ppm 161.7, 147.9, 143.4, 123.5, 119.9, 115.3, 108.4, 51.6, 32.4, 25.2, 24.6. IR (ATR, cm\(^{-1}\)): 3372, 3021, 2915, 2873, 1662, 1581, 1499, 1455, 1336, 1245. ESI-MS: m/z: 217.1012 [M+H]\(^+\) (calcd for [C\(_{13}\)H\(_{17}\)N\(_2\)O\(^-\) 217.1340).

**Ethyl 4-(benzo[d]oxazol-2-ylamino)benzoate (6aq)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-ethylbenzoate isothiocyanate (103.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h)
to afford 6aq (76.5 mg, 0.271 mmol, 54%) as a white solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 11.07 (s, 1H), 7.97 (d, $J$ = 8.7 Hz, 2H), 7.88 (d, $J$ = 8.8 Hz, 2H), 7.51 (d, $J$ = 8.4 Hz, 2H), 7.25 (t, $J$ = 7.8 Hz, 1H), 7.17 (dd, $J$ = 8.3, 7.5 Hz, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 1.31 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 165.5, 157.3, 147.0, 143.1, 142.1, 130.6, 124.2, 123.1, 122.3, 117.1, 116.9, 109.2, 60.4, 14.3. IR (ATR, cm$^{-1}$): 3279, 3137, 2954, 2923, 1692, 1645, 1600, 1565, 1440, 1425, 1367, 1280, 848, 727. ESI-MS: m/z: 305.0903 [M+Na]$^+$ (calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}$]$^+$ 305.0902).

$N$-($\text{(4-(tert-butyldimethylsilyl)oxy)phenyl}$benzo[d]oxazol-2-amine)  (6ar)

Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), tert-butyl(4-isothiocyanatophenoxy)dimethylsilane (132.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 6ar (80 mg, 0.235 mmol, 47%) as a white-orange solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.44 (s, 1H), 7.64 (dd, $J$ = 6.7, 2.2 Hz, 2H), 7.44 (d, $J$ = 7.7 Hz, 1H), 7.41 (dd, $J$ = 7.7, 0.5 Hz, 1H), 7.19 (td, $J$ = 7.7, 1.1 Hz, 1H), 7.09 (td, $J$ = 7.8, 1.2 Hz, 1H), 6.86 (dd, $J$ = 6.7, 2.2 Hz, 2H), 0.93 (s, 9H), 0.16 (s, 6H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 158.3, 150.1, 147.1, 142.7, 132.7, 123.9, 121.4, 120.1, 119.1, 116.4, 108.8, 25.6, 17.9, -4.6. IR (ATR, cm$^{-1}$): 3044, 2954, 2929, 2890, 2857, 1686, 1577, 1507, 1457, 1353, 1250, 1229, 1007, 972, 914, 824, 778, 737. ESI-MS: m/z: 341.16960 [M+H]$^+$ (calcd for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}_2\text{Si}$]$^+$ 341.16853).

$N$-phenylbenzo[d]thiazol-2-amine  (8aa) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 8aa (77.2 mg, 0.342 mmol, 68%)
as a light brown solid: $^1$H NMR (500 MHz, DMSO) $\delta$ ppm 10.51 (s, 1H), 7.82 (d, $J = 8.1$ Hz, 2H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.15 (t, $J = 7.4$ Hz, 1H), 7.02 (t, $J = 7.3$ Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 161.6, 152.2, 140.7, 130.1, 129.0, 125.9, 122.3, 122.1, 121.1, 119.3, 117.8. IR (ATR, cm$^{-1}$): 3234, 3189, 3125, 3057, 2931, 1620, 1597, 1562, 1499, 1443, 1225, 1019, 922, 741, 686, 667. ESI-MS: m/z: 227.06358 [M+H]$^+$ (calcd for [C$_{13}$H$_{11}$N$_2$S]$^+$ 227.06429).$^9$

$N$-(m-tolyl)benzo[d]thiazol-2-amine ($8ab$) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), m-tolyl isothiocyanate (74.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford $8ab$ (67.6 mg, 0.282 mmol, 56%) as a light brown solid: $^1$H NMR (500 MHz, DMSO) $\delta$ ppm 10.42 (s, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.65 (d, $J = 8.1$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.58 (s, 1H), 7.32 (t, $J = 7.7$ Hz, 1H), 7.25 (t, $J = 7.8$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 7.5$ Hz, 1H), 2.32 (s, 3H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 161.7, 152.2, 140.6, 138.2, 130.0, 128.9, 125.9, 122.9, 122.2, 121.0, 119.2, 118.3, 115.1, 21.4. IR (ATR, cm$^{-1}$): 3234, 3195, 3137, 3055, 2919, 2851 1620, 1591, 1571, 1488, 1445, 1274, 1245, 879, 743, 719, 671. ESI-MS: m/z: 241.07868 [M+H]$^+$ (calcd for [C$_{14}$H$_{13}$N$_2$S]$^+$ 241.07994).$^9$

$N$-(3-iodophenyl)benzo[d]thiazol-2-amine ($8ae$) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), 3-iodophenyl isothiocyanate (130.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford $8ae$ (83.5 mg, 0.237 mmol, 47%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.60 (s, 1H), 8.29 (t, $J = 1.8$ Hz, 1H), 7.82 (dd, $J = 7.9$, 0.8 Hz, 1H), 7.75 (ddd, $J = 8.2$, 2.0, 0.7 Hz,
1H), 7.64 (d, J = 7.7 Hz, 1H), 7.35 (m, 2H), 7.16 (m, 2H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 161.2, 151.9, 142.0, 131.1, 130.5, 130.1, 126.1 125.7, 122.7, 121.2, 119.6, 117.0, 95.0. IR (ATR, cm$^{-1}$): 3226, 3160, 3096, 2997, 2919, 2845, 1581, 1552, 1445, 1328, 1328, 1241, 988, 926, 745, 714. ESI-MS: m/z: 352.9609 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$IN$_2$S]$^+$ 352.9618).

N-(2-fluorophenyl)benzo[d]thiazol-2-amine (8ag) Synthesized according to the General procedure B using 2-aminophenol (75.0 mg, 0.600 mmol), 2-fluorophenyl isothiocyanate (76.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 8ag (89.6 mg, 0.367 mmol, 73%) as a white solid: $^1$H NMR (400 MHz, DMSO): δ ppm 10.34 (s, 1H), 8.56 (t, J = 8.2 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.34-7.22 (m, 3H), 7.16 (t, J = 7.6 Hz, 1H), 7.07 (dd, J = 7.8, 1.0 Hz, 1H). $^{13}$C NMR (100 MHz, DMSO): δ ppm 162.2, 153.3, 151.6, 151.4, 130.6, 128.5 (d, J = 10.0 Hz), 125.9, 124.7 (d, J = 3.8 Hz), 123.4 (d, J = 7.5 Hz). 122.5, 121.4, 121.1 119.4, 115.4 (d, J = 18.8 Hz). ESI-MS: m/z: 229.0764 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$FN$_2$O]$^+$ 229.0777).

N-(4-chlorophenyl)benzo[d]thiazol-2-amine (8ah) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), 4-chlorophenyl isothiocyanate (84.8 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 8ah (56.4 mg, 0.217 mmol, 43%) as a light brown solid: $^1$H NMR (500 MHz, DMSO): δ ppm 10.64 (s, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.33 (dd, J = 8.0, 1.0 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H). $^{13}$C NMR (125 MHz, DMSO): δ ppm 161.3, 152.0, 139.6, 130.0, 128.9, 126.0, 125.4, 122.5, 121.1, 119.4, 119.2. IR (ATR, cm$^{-1}$): 3239, 3174, 3116, 3066, 2961, 2850, 1619, 1565, 1492, 1442, 1272, 1245, 1224, 822, 747, 724. ESI-MS: m/z: 261.02457 [M+H]$^+$ (calcd for [C$_{13}$H$_{10}$ClN$_2$S]$^+$ 261.02432).
**Ethyl 4-(benzo[d]thiazol-2-ylamino)benzoate (8aq)** Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), 4-ethylbenzoate isothiocyanate (103.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford 8aq (76.5 mg, 0.271 mmol, 54%) as a white solid: $^1$H NMR (500 MHz, DMSO): $\delta$ ppm 10.91 (s, 1H), 7.97 (dd, $J = 6.9$, 2.0 Hz, 2H), 7.93 (dd, $J = 7.0$, 2.0 Hz, 2H), 7.84 (dd, $J = 7.9$, 0.7 Hz, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.36 (td, $J = 7.7$, 1.2 Hz, 1H), 7.2 (td, $J = 7.6$, 1.1 Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.3 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ ppm 165.5, 161.0, 151.8, 144.8, 130.6, 130.3, 126.1, 122.9, 122.8, 121.3, 119.8, 117.0, 60.4, 14.3. IR (ATR, cm$^{-1}$): 3283, 3192, 3126, 3090, 2952, 1677, 1594, 1531, 1438, 1416, 1361, 1332, 1283, 1257, 1243, 1166, 1103, 1012, 921, 846. ESI-MS: m/z: 299.08674 [M+H]$^+$ (caled for [C$_{16}$H$_{15}$N$_2$O$_2$S]$^+$ 305.08542).
Figure S1. Reactors set up

Figure S2. Electrodes a) Carbon and b) Platinum

Figure S3. Gram scale set up
Figure S4: \(^1\)H NMR spectra of 6aa ((CD\(_3\))\(_2\)SO)
Figure S5 $^{13}$C NMR spectra of 6aa ((D$_2$)$_2$SO)

Figure S6 $^1$H NMR spectra of 6ba ((D$_2$)$_2$SO)
Figure S7 $^{13}$C NMR spectra of 6ba ((CD$_3$)$_2$SO)

Figure S8 $^1$H NMR spectra of 6ca ((CD$_3$)$_2$SO)
Figure S9 $^{13}$C NMR spectra of 6ca ((CD$_3$)$_2$SO)

Figure S10 $^1$H NMR spectra of 6da ((CD$_3$)$_2$SO)
Figure S11 $^{13}$C NMR spectra of 6da ((CD$_3$)$_2$SO)

Figure S12 $^1$H NMR spectra of 6ea ((CD$_3$)$_2$SO)
Figure S13 $^{13}\text{C}$ NMR spectra of 6ea ((CD$_3$)$_2$SO)
Figure S14 $^1$H NMR spectra of 6fa ((CD$_3$)$_2$SO)

Figure S15 $^{13}$C NMR spectra of 6fa ((CD$_3$)$_2$SO)
Figure S16 $^1$H NMR spectra of 6ga ((CD$_3$)$_2$SO)

![Figure S16](image)

Figure S17 $^{13}$C NMR spectra of 6ga ((CD$_3$)$_2$SO)

![Figure S17](image)
Figure S18: $^1$H NMR spectra of 6ab ((CD$_3$)$_2$SO)
Figure S19 $^{13}$C NMR spectra of $6ab ((\text{CD}_3)_2\text{SO})$
Figure S21 $^{13}$C NMR spectra of 6ac ((CD$_3$)$_2$SO)

Figure S22 $^1$H NMR spectra of 6ad ((CD$_3$)$_2$SO)
Figure S23 $^{13}$C NMR spectra of 6ad ((CD$_3$)$_2$SO)

Figure S24 $^1$H NMR spectra of 6ae ((CD$_3$)$_2$SO)
Figure S25 $^{13}$C NMR spectra of 6ae ((CD$_3$)$_2$SO)

Figure S26 $^1$H NMR spectra of 6af ((CD$_3$)$_2$SO)
Figure S27 $^1$C NMR spectra of 6af ((CD$_3$)$_2$SO)

Figure S28 $^1$H NMR spectra of 6ag ((CD$_3$)$_2$SO)
Figure S29 $^{13}$C NMR spectra of 6ag ((CD$_3$)$_2$SO)

Figure S30 $^1$H NMR spectra of 6ah ((CD$_3$)$_2$SO)
Figure S31 $^{13}$C NMR spectra of 6ah ((CD$_3$)$_2$SO)
Figure S32 ¹H NMR spectra of 6ai ((CD$_3$)$_2$SO)

Figure S33 ¹³C NMR spectra of 6ai ((CD$_3$)$_2$SO)
Figure S34 ^1^H NMR spectra of 6aj ([CD)_3SO)
Figure S35 $^{13}$C NMR spectra of 6aj ((CD$_3$)$_2$SO)

Figure S36 $^1$H NMR spectra of 6ak ((CD$_3$)$_2$SO)
Figure S37 $^{13}$C NMR spectra of 6ak ((CD$_3$)$_2$SO)

Figure S38 $^1$H NMR spectra of 6al ((CD$_3$)$_2$SO)
Figure S39 $^{13}$C NMR spectra of 6al ((CD$_3$)$_2$SO)

Figure S40 $^1$H NMR spectra of 6am ((CD$_3$)$_2$SO)
**Figure S41** $^{13}$C NMR spectra of 6am (CD$_3$SO)

**Figure S42** $^1$H NMR spectra of 6an (CD$_3$SO)
Figure S43 $^{13}$C NMR spectra of 6an ((CD$_3$)$_2$SO)
Figure S44 $^1$H NMR spectra of 6ao ((CD$_3$)$_2$SO)

Figure S45 $^{13}$C NMR spectra of 6ao ((CD$_3$)$_2$SO)
Figure S46 $^1$H NMR spectra of 6ap (DMSO)

Figure S47 $^{13}$C NMR spectra of 6ap (DMSO)
Figure S48 ¹H NMR spectra of 6aq ((CD₃)₂SO)
Figure S49 $^{13}$C NMR spectra of 6aq ((CD$_3$)$_2$SO)

Figure S50 $^1$H NMR spectra of 6ar ((CD$_3$)$_2$SO)
Figure S51 $^{13}$C NMR spectra of 6ar ((CD$_3$)$_2$SO)

Figure S52 $^1$H NMR spectra of 8aa ((CD$_3$)$_2$SO)
Figure S53 $^{13}$C NMR spectra of 8aa ((CD$_3$)$_2$SO)
Figure S54 $^1$H NMR spectra of 8ab ((CD$_3$)$_2$SO)

Figure S55 $^{13}$C NMR spectra of 8ab ((CD$_3$)$_2$SO)
Figure S56 $^1$H NMR spectra of 8ae ((CD$_3$)$_2$SO)

Figure S57 $^{13}$C NMR spectra of 8ae ((CD$_3$)$_2$SO)
Figure S58 \( ^1H \) NMR spectra of 8ag ((CD\(_3\))\(_2\)SO)

Figure S59 \( ^13C \) NMR spectra of 8ag ((CD\(_3\))\(_2\)SO)
Figure S60 $^1$H NMR spectra of 8ah ((CD$_3$)$_2$SO)
Figure S61 $^{13}$C NMR spectra of $8\text{ah}$ ((CD$_3$)$_2$SO)

Figure S62 $^1$H NMR spectra of $8\text{aq}$ ((CD$_3$)$_2$SO)
Figure S63 $^{13}$C NMR spectra of 8aq ((CD$_3$)$_2$SO)

Figure S64 $^1$H NMR spectra of 6aa (gram-scale) ((CD$_3$)$_2$SO)
Figure S65 $^{13}$C NMR spectra of 6aa (gram-scale) ($(CD_3)_2SO$)
Figure S66 Mass spectrum of 6aa
Figure S67 Mass spectrum of 6ba
Figure S68 Mass spectrum of 6ca
Figure S69 Mass spectrum of 6da
Figure S70 Mass spectrum of 6ea
Figure S71 Mass spectrum of 6fa
Figure S72 Mass spectrum of $6_{ga}$
Figure S73 Mass spectrum of 6ab
Figure S74 Mass spectrum of 6ac
Figure S75 Mass spectrum of 6ad
Figure S76 Mass spectrum of 6ae
Figure S77 Mass spectrum of 6af
Figure S78 Mass spectrum of 6ag
Figure S79 Mass spectrum of 6ah
Figure S80 Mass spectrum of 6ai
Figure S81 Mass spectrum of 6aj
**Figure S82** Mass spectrum of 6ak
Figure S83 Mass spectrum of 6al
Figure S84 Mass spectrum of 6am
**Figure S85** Mass spectrum of 6an
Figure S86 Mass spectrum of 6ao
Figure S87 Mass spectrum of 6ap
Figure S88 Mass spectrum of 6aq
Figure S89 Mass spectrum of 6ar
Figure S90 Mass spectrum of 8aa
Figure S91 Mass spectrum of 8ab
Generic Display Report

Figure S92 Mass spectrum of 8ae
Figure S93 Mass spectrum of 8ag
Figure S94 Mass spectrum of 8ah
Figure S95 Mass spectrum of 8aq
References


