Supporting Information

Organophosphine-Free Copper-Catalyzed Isothiocyanation of Amines with Sodium Bromodifluoroacetate and Sulfur

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1. General Information

Chemicals were either purchased or purified by standard techniques. $^1$H NMR spectra were measured on 500 MHz or 400 MHz spectrometer ($^1$H: 500 MHz or 400 MHz) and $^{13}$C NMR spectra were measured on a 500 MHz ($^{13}$C: 125 MHz), using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in $\delta$ relative to CDCl$_3$ ($^1$H NMR for 7.26 ppm, $^{13}$C NMR for 77.16 ppm), the coupling constants $J$ are given in Hz. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometry. All reactions were conducted under air atmosphere using standard Schlenk techniques. Melting points were measured on X4 melting point apparatus and uncorrected. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

2. Optimization Details

Table 1 Screening Conditions

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ª Reaction conditions: 1a (0.2 mmol), BrCF₂CO₂Na (1.5 equiv), S₈ (1.0 equiv), catalyst (5 mol%), base (2 equiv), solvent 2 mL at 100 °C for 12 h. b isolated yield. c BrCF₂CO₂Na (1.0 equiv). d S₈ 0.75 equiv. e At 80 °C.

3. General Procedure for the Synthesis of Isothiocyanate 2a-2x

\[
\begin{align*}
R-NH₂ + BrCF₂CO₂Na + S₈ & \xrightarrow{\text{Cul 5 mol %, K₃PO₄ 2 equiv}} \xrightarrow{\text{CH₃CN, 100 °C, 12 h}} R-NCS
\end{align*}
\]

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with β-aminonaphthalene 1a (28.6 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), K₃PO₄ (84.9 mg, 2.0 equiv), BrCF₂CO₂Na (59.1 mg, 1.5 equiv) and S₈ (51.2 mg, 1.0 equiv) in CH₃CN (2 mL) under air atmosphere. The reaction mixture was stirred at 100 °C for 12 hours. After the reaction was finished, the mixture was poured into ethyl acetate. Then, the combined organic component was evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired products 2a-2x.

4. Typical Experimental Procedure for the Synthesis of compound 3

\[
\begin{align*}
\text{NH}_2 & \xrightarrow{\text{Standard conditions}} \xrightarrow{\text{With or without S₈}} \text{N}
\end{align*}
\]

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with 3a (21.6 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), K₃PO₄ (84.9 mg, 2.0 equiv) and BrCF₂CO₂Na (59.1 mg, 1.5 equiv) in CH₃CN (2 mL) under air atmosphere. The reaction mixture was stirred at 100 °C for 12 hours. After the reaction was finished, the mixture was poured into ethyl acetate. Then, the combined organic component was evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product 3.

5. Typical Experimental Procedure for the Synthesis of compound 4

\[
\begin{align*}
\text{NH}_2 & \xrightarrow{\text{Standard conditions}} \xrightarrow{\text{With or without S₈}} \text{O}
\end{align*}
\]

4, 71%
To a flame-dried Schlenk tube with a magnetic stirring bar was charged with 4a (21.8 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), K₃PO₄ (84.9 mg, 2.0 equiv) and BrCF₂CO₂Na (59.1 mg, 1.5 equiv) in CH₃CN (2 mL) under air atmosphere. The reaction mixture was stirred at 100 °C for 12 hours. After the reaction was finished, the mixture was poured into ethyl acetate. Then, the combined organic component was evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product 4.

6. Typical Experimental Procedure for the Synthesis of ANTU (5)

\[
\text{2a} + \text{BrCF}_2\text{CO}_2\text{Na} + \text{S}_8 \xrightarrow{1)} \text{standard conditions} \xrightarrow{2)} \text{NH}_3\cdot\text{H}_2\text{O (28-30 wt%)} \xrightarrow{\text{CH}_3\text{CN, 80 °C, 6 h}} \text{5, ANTU, 54%}
\]

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with 2a (28.6 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), K₃PO₄ (84.9 mg, 2.0 equiv), BrCF₂CO₂Na (59.1 mg, 1.5 equiv) and S₈ (51.2 mg, 1.0 equiv) in CH₃CN (2 mL) under air atmosphere. The reaction mixture was stirred at 100 °C for 12 hours. When the reaction was finished, NH₃·H₂O (28%-30% aqueous solution, 1.2 equiv) was added to the reaction mixture and continued to react at 80 °C for 6 hours. After the reaction was finished, saturated aq. NH₄Cl was added and the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product ANTU.

7. Typical Experimental Procedure for the Synthesis of Chloromethiuron (6)

\[
\text{Cl-} + \text{BrCF}_2\text{CO}_2\text{Na} + \text{S}_8 \xrightarrow{1)} \text{standard conditions} \xrightarrow{2)} \text{dimethylamine} \xrightarrow{\text{CH}_3\text{CN, 80 °C, 6 h}} \text{6, Chloromethiuron, 63%}
\]

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with 1d (28.2 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), K₃PO₄ (84.9 mg, 2.0 equiv), BrCF₂CO₂Na (59.1 mg, 1.5 equiv) and S₈ (51.2 mg, 1.0 equiv) in CH₃CN (2 mL)
under air atmosphere. The reaction mixture was stirred at 100 °C for 12 hours. When the reaction was finished, dimethylamine (2M in THF, 1.2 equiv) was added to the reaction mixture and continued to react at 80 °C for 6 hours. After the reaction was finished, the mixture was extracted with ethyl acetate. Then the residue was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product Chloromethiuron.

8. Typical Experimental Procedure for the Synthesis of compound 7

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with 1m (34.4 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), K3PO4 (84.9 mg, 2.0 equiv), BrCF2CO2Na (59.1 mg, 1.5 equiv) and S8 (51.2 mg, 1.0 equiv) in CH3CN (2 mL) under air atmosphere. The reaction mixture was stirred at 100 °C for 12 hours. When the reaction was finished, dibutylamine (38.7 mg, 1.5 equiv) was added to the reaction mixture and continued to react at 80 °C for 6 hours. Then the residue was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product 7.

9. Typical Experimental Procedure for the Synthesis of compound 8

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with 1x (38.6 mg, 0.2 mmol), CuI (1.9 mg, 5 mol %), K3PO4 (84.9 mg, 2.0 equiv), BrCF2CO2Na (59.1 mg, 1.5 equiv) and S8 (51.2 mg, 1.0 equiv) in CH3CN (2 mL) under air atmosphere. The reaction mixture was stirred at 100 °C for 12 hours. When the reaction was finished, dibutylamine (38.7 mg, 1.5 equiv) was added to the reaction mixture and continued to react at 80 °C for 6 hours. Then the residue was evaporated
under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product 8.

10. Data for All Compounds

2-isothiocyanatonaphthalene (2a):¹ white solid (32.2 mg, 87% yield); m.p. 116-118 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.80 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.53-7.50 (m, 2H), 7.30 (d, J = 8.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 135.8, 133.4, 132.0, 129.8, 128.7, 128.0, 127.6, 127.4, 126.9, 124.0, 123.8; LRMS (EI 70 ev) m/z (%): 185 (M⁺, 100), 153 (11), 127 (39), 126 (12).

I-isothiocyanatonaphthalene (2b):² white solid (30.0 mg, 81% yield); m.p. 53-55 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.78-7.76 (m, 1H), 7.63-7.54 (m, 2H), 7.41-7.40 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 136.2, 134.1, 129.3, 128.5, 127.8, 127.6, 127.4, 127.2, 125.4, 123.5, 122.8; LRMS (EI 70 ev) m/z (%): 185 (M⁺, 100), 153 (17), 127 (25), 126 (14).

isothiocyanatobenzene (2c):³ colorless oil (22.4 mg, 83% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.40 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.29-7.26 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 135.6, 131.4, 129.7, 127.4, 125.8; LRMS (EI 70 ev) m/z (%): 135 (M⁺, 100), 77 (43), 51 (13).

4-chloro-1-isothiocyanato-2-methylbenzene (2d):⁴ white solid (31.5 mg, 86% yield); m.p. 37-38 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (s, 1H), 7.14-7.08 (m, 2H), 2.34 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 136.7, 132.8, 130.9, 130.7, 129.2, 127.14, 127.06,
18.4; LRMS (EI 70 ev) m/z (%): 183 (M⁺, 100), 151 (11), 148 (100), 121 (10), 89 (23).

**1-isothiocyanato-3-methylbenzene (2e):** colorless oil (24.7 mg, 83% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.23 (t, J = 7.6 Hz, 1H), 7.10-7.02 (m, 3H), 2.34 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.8, 135.2, 131.2, 129.4, 128.3, 126.4, 122.8, 21.3; LRMS (EI 70 ev) m/z (%): 149 (M⁺, 100), 117 (8), 91 (49), 65 (12).

**1-isothiocyanato-4-methoxybenzene (2f):** colorless oil (25.5 mg, 84% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 158.7, 134.3, 127.0, 123.8, 114.9, 55.6; LRMS (EI 70 ev) m/z (%): 165 (M⁺, 100), 150 (78), 122 (60), 63 (11).

**1-(tert-butyl)-4-isothiocyanatobenzene (2g):** colorless oil (31.7 mg, 83% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 1.31 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 150.9, 134.8, 128.5, 126.6, 125.4, 34.9, 31.3; LRMS (EI 70 ev) m/z (%): 191 (M⁺, 39), 177 (13), 176 (100), 148 (32), 136 (15).

**2-isothiocyanato-1,1'-biphenyl (2h):** white solid (36.3 mg, 86% yield); m.p. 67-69 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.49 (m, 4H), 7.45-7.41 (m, 2H), 7.36-7.35 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.7, 137.8, 135.4, 130.7, 129.1, 129.0, 128.7, 128.5, 128.2, 127.6, 127.3; LRMS (EI 70 ev) m/z (%): 211 (M⁺, 100), 179 (14), 178 (79), 152 (30), 151 (29).
(4-isothiocyanatophenyl)(methyl)sulfane (2i):^5 pale yellow oil (25.3 mg, 70% yield); ^1H NMR (400 MHz, CDCl$_3$) δ 7.19 (d, $J = 8.8$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 2.48 (s, 3H); ^13C NMR (125 MHz, CDCl$_3$) δ 138.6, 135.6, 128.1, 127.3, 126.2, 15.9; LRMS (EI 70 ev) m/z (%): 181 (M$^+$, 100), 166 (66), 122 (9), 108 (26).

1-ethynl-4-isothiocyanatobenzene (2j):^4 pale yellow solid (21.3 mg, 67% yield); m.p. 71-73 °C; ^1H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz 2H), 3.16 (s, 1H); ^13C NMR (125 MHz, CDCl$_3$) δ 137.2, 133.5, 131.8, 125.8, 121.3, 82.6, 79.3; LRMS (EI 70 ev) m/z (%): 159 (M$^+$, 100), 101 (33), 75 (22), 74 (11).

1-fluoro-4-isothiocyanatobenzene (2k):^4 colorless oil (22.0 mg, 72% yield); ^1H NMR (400 MHz, CDCl$_3$) δ 7.22-7.18 (m, 2H), 7.07-7.02 (m, 2H); ^13C NMR (125 MHz, CDCl$_3$) δ 161.2 (d, $J_{C-F} = 247.5$ Hz), 136.2, 127.6, 127.5 (d, $J_{C-F} = 8.8$ Hz), 116.8 (d, $J_{C-F} = 23.8$ Hz); LRMS (EI 70 ev) m/z (%): 153 (M$^+$, 100), 95 (39), 75 (17).

1-chloro-3-isothiocyanatobenzene (2l):^4 colorless oil (27.2 mg, 81% yield); ^1H NMR (400 MHz, CDCl$_3$) δ 7.35-7.26 (m, 3H), 7.15 (d, $J = 7.2$ Hz, 1H); ^13C NMR (125 MHz, CDCl$_3$) δ 137.7, 135.2, 132.8, 128.4, 128.3, 127.1; LRMS (EI 70 ev) m/z (%): 169 (M$^+$, 100), 134 (8), 113 (12), 111 (37).

1-bromo-2-isothiocyanatobenzene (2m):^2 colorless oil (36.4 mg, 85% yield); ^1H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, $J = 8.0$ Hz, 1H), 7.34-7.27 (m, 2H), 7.16 (t, $J = 8.0$ Hz, 1H); ^13C NMR (125 MHz, CDCl$_3$) δ 138.1, 133.5, 131.6, 128.4, 128.3, 127.1,
120.9; LRMS (EI 70 ev) m/z (%): 215/213 (M+, 100), 157 (13), 155 (13), 134 (42).

1-iodo-2-isothiocyanatobenzene (2n):\(^2\) colorless oil (31.3 mg, 60% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79 (d, \(J = 8.0\) Hz, 1H), 7.32 (t, \(J = 8.0\) Hz, 1H), 7.24 (d, \(J = 8.0\) Hz, 1H), 6.97 (t, \(J = 8.0\) Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 139.5, 136.9, 135.0, 129.2, 128.4, 127.0, 94.2; LRMS (EI 70 ev) m/z (%): 261 (M+, 100), 134 (32), 90 (12).

methyl 4-isothiocyanatobenzoate (2o):\(^3\) white solid (30.5 mg, 79% yield); m.p. 42-43 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 (d, \(J = 8.4\) Hz, 2H), 7.26 (d, \(J = 7.6\) Hz, 2H), 3.91 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 166.0, 138.2, 135.8, 131.2, 128.8, 125.8, 52.5; LRMS (EI 70 ev) m/z (%): 193 (M+, 69), 162 (100), 134 (40), 90 (13).

1-(4-isothiocyanatophenyl)ethan-1-one (2p):\(^2\) white solid (18.4 mg, 52% yield); m.p. 77-78 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94 (d, \(J = 8.4\) Hz, 2H), 7.29 (d, \(J = 8.4\) Hz, 2H), 2.59 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 196.5, 138.3, 136.0, 135.6, 129.9, 126.0, 26.7; LRMS (EI 70 ev) m/z (%): 177 (M+, 55), 162 (100), 134 (52), 90 (13).

1-isothiocyanato-4-(trifluoromethyl)benzene (2q):\(^2\) white solid (24.8 mg, 61% yield); m.p. 42-43 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 (d, \(J = 8.8\) Hz, 2H), 7.31 (d, \(J = 8.8\) Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 138.7, 135.2, 129.2 (q, \(J_{C,F} = 32.5\) Hz), 127.0 (q, \(J_{C,F} = 3.8\) Hz), 126.1, 123.7 (q, \(J_{C,F} = 271.3\) Hz); LRMS (EI 70 ev) m/z (%): 203 (M+, 100), 184 (17), 145 (39).
1-isothiocyanato-4-nitrobenzene (2r): yellow solid (16.6 mg, 46% yield); m.p. 107-108 °C; 1H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 9.2 Hz, 2H), 7.34 (d, J = 9.2 Hz, 2H); 13C NMR (125 MHz, CDCl₃) δ 145.9, 140.3, 137.9, 126.4, 125.3; LRMS (EI 70 ev) m/z (%): 180 (M⁺, 100), 150 (35), 134 (41), 122 (24), 90 (34).

4-isothiocyanato-1H-indole (2s): colorless oil (24.7 mg, 71% yield); 1H NMR (400 MHz, CDCl₃) δ 8.40 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.32-7.31 (m, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.77-6.76 (m, 1H); 13C NMR (125 MHz, CDCl₃) δ 136.7, 136.0, 125.4, 125.3, 122.8, 122.2, 116.7, 111.0, 100.2; LRMS (EI 70 ev) m/z (%): 174 (M⁺, 100), 142 (17), 116 (20), 89 (12).

(isothiocyanatomethyl)benzene (2t): colorless oil (21.5 mg, 72% yield); 1H NMR (400 MHz, CDCl₃) δ 7.44-7.40 (m, 2H), 7.38-7.36 (m, 1H), 7.34-7.32 (m, 2H), 4.71 (s, 2H); 13C NMR (125 MHz, CDCl₃) δ 134.3, 132.5, 129.0, 128.4, 126.9, 48.7; LRMS (EI 70 ev) m/z (%): 149 (M⁺, 23), 91 (100), 65 (14).

(2-isothiocyanatoethyl)benzene (2u): colorless oil (19.9 mg, 61% yield); 1H NMR (400 MHz, CDCl₃) δ 7.40 (t, J = 7.6 Hz, 2H), 7.35-7.31 (m, 1H), 7.27 (d, J = 7.6 Hz, 2H), 3.78 (t, J = 7.0 Hz, 2H), 3.04 (t, J = 7.0 Hz, 2H); 13C NMR (125 MHz, CDCl₃) δ 137.0, 131.0, 128.8, 128.7, 127.2, 46.5, 36.7; LRMS (EI 70 ev) m/z (%): 163 (M⁺, 45), 105 (13), 91 (100), 65 (11).

1-isothiocyanatohexane (2v): colorless oil (10.9 mg, 38% yield); 1H NMR (400 MHz, CDCl₃) δ 3.49-3.46 (m, 2H), 1.69-1.62 (m, 2H), 1.41-1.27 (m, 6H), 0.87-0.84 (m, 3H);
\(^{13}\text{C} \text{NMR} \text{ (125 MHz, CDCl}_3\text{)} \delta 129.9, 45.1, 31.0, 30.0, 26.2, 22.4, 13.9; \text{ LRMS (EI 70 ev) m/z (\%): 115 (M}^+, 100), 114 (19), 110 (29), 100 (18), 72 (41).\)

iso(thiocyanatocyclohexane) (2w):\(^4\) colorless oil (12.4 mg, 44\% yield); \(^1\text{H} \text{NMR} \text{ (400 MHz, CDCl}_3\text{)} \delta 3.61 \text{ (s, 1H)}, 1.80 \text{ (m, 2H)}, 1.62-1.55 \text{ (m, 4H)}, 1.41-1.33 \text{ (m, 4H)}; \(^{13}\text{C} \text{NMR} \text{ (125 MHz, CDCl}_3\text{)} \delta 130.1, 55.3, 33.1, 24.9, 23.1; \text{ LRMS (EI 70 ev) m/z (\%): 141 (M}^+, 91), 98 (8), 83 (70), 82 (29), 55 (100).\)

\(1\)-iso(thiocyanato-2-(phenylethynyl)benzene) (2x):\(^2\) white solid (28.2 mg, 60\% yield); m.p. 52-53 °C; \(^1\text{H} \text{NMR} \text{ (400 MHz, CDCl}_3\text{)} \delta 7.69-7.67 \text{ (m, 2H)}, 7.56-7.54 \text{ (m, 1H)}, 7.40-7.38 \text{ (m, 3H)}, 7.31-7.23 \text{ (m, 2H)}, 7.18-7.16 \text{ (m, 1H)}; \(^{13}\text{C} \text{NMR} \text{ (125 MHz, CDCl}_3\text{)} \delta 138.2, 132.7, 131.8, 129.1, 129.0, 128.5, 127.1, 124.8, 123.0, 122.7, 97.1, 85.1; \text{ LRMS (EI 70 ev) m/z (\%): 235 (M}^+, 100), 203 (11), 189 (19).\)

\(1\)-(difluoromethyl)-1H-benzo[d]imidazole (3):\(^7\) yellow oil (14.4 mg, 43\% yield); \(^1\text{H} \text{NMR} \text{ (400 MHz, CDCl}_3\text{)} \delta 8.12 \text{ (s, 1H)}, 7.85-7.83 \text{ (m, 1H)}, 7.62-7.60 \text{ (m, 1H)}, 7.48-7.33 \text{ (m, 3H)}; \(^{13}\text{C} \text{NMR} \text{ (125 MHz, CDCl}_3\text{)} \delta 144.1, 139.2, 130.7, 124.9, 124.3, 121.1, 111.2, 109.1 \text{ (t, } J_{\text{C-F}} = 248.8 \text{ Hz}); \(^{19}\text{F} \text{NMR} \text{ (470 MHz, CDCl}_3\text{)} \delta -93.8 \text{ (s, 2F)}; \text{ LRMS (EI 70 ev) m/z (\%): 168 (M}^+, 100), 149 (21), 118 (47), 91 (9).\)

benzo[d]oxazole (4):\(^8\) colorless liquid (14.9 mg, 71\% yield); \(^1\text{H} \text{NMR} \text{ (400 MHz, CDCl}_3\text{)} \delta 8.09 \text{ (s, 1H)}, 7.79-7.77 \text{ (m, 1H)}, 7.58-7.55 \text{ (m, 1H)}, 7.37-7.34 \text{ (m, 2H)}; \(^{13}\text{C} \text{NMR} \text{ (125 MHz, CDCl}_3\text{)} \delta 152.6, 150.0, 140.0, 125.7, 124.7, 120.6, 111.0; \text{ LRMS (EI 70 ev) m/z (\%): 119 (M}^+, 100), 91 (54), 64 (32), 63 (37), 62 (10).\)
1-(naphthalen-1-yl)thiourea (5): grey white solid (21.8 mg, 54% yield); m.p. 190-192 °C; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.80 (s, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.60-7.48 (m, 4H), 7.39-6.95 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 182.4, 134.4, 133.9, 129.6, 128.1, 126.8, 126.20, 126.16, 125.7, 125.0, 122.8; LRMS (EI 70 ev) m/z (%): 202 (M$^+$, 6), 201 (13), 200 (100), 173 (12), 172 (24), 114 (10), 100 (10).

3-(4-chloro-2-methylphenyl)-1,1-dimethylthiourea (6): white solid (28.7 mg, 63% yield); m.p. 173-175 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19 (s, 1H), 7.16-7.08 (m, 2H), 6.85 (s, 1H), 3.30 (s, 6H), 2.22 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 182.7, 137.2, 136.5, 132.2, 130.6, 128.9, 126.7, 41.5, 18.2; LRMS (EI 70 ev) m/z (%): 228 (M$^+$, 34), 226 (100), 211 (46), 184 (25), 148 (22).

$N,N$-dibutylbenzo[d]thiazol-2-amine (7): colorless liquid (35.6 mg, 68% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (dd, $J = 13.6$, 8.0 Hz, 2H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 3.52-3.48 (m, 4H), 1.72-1.65 (m, 4H), 1.42-1.37 (m, 4H), 0.98 (t, $J = 7.6$ Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 168.0, 153.5, 130.8, 125.8, 120.7, 120.5, 118.7, 51.1, 29.8, 20.2, 14.0; LRMS (EI 70 ev) m/z (%): 262 (M$^+$, 22), 177 (41), 163 (100), 136 (19).
(Z)-4-benzylidene-N,N-dibutyl-4H-benzo[d][1,3]thiazin-2-amine (8):<sup>11</sup> yellow liquid (37.9 mg, 52% yield); <sup>1</sup>H NMR (400 MHz, CDCl3) δ 7.52-7.50 (m, 3H), 7.43-7.39 (m, 2H), 7.32-7.28 (m, 2H), 7.15-7.04 (m, 3H), 3.51 (t, J = 7.2 Hz, 4H), 1.65-1.57 (m, 4H), 1.38-1.32 (m, 4H), 0.95 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl3) δ 152.2, 145.4, 136.3, 129.62, 129.56, 128.2, 127.3, 126.2, 125.5, 124.2, 123.2, 120.4, 48.9, 30.7, 20.3, 14.0; LRMS (EI 70 ev) m/z (%): 364 (M<sup>+</sup>, 100), 331 (49), 307 (46), 275 (45), 265 (76).

\[ \text{[Ring Structure]} \]

2-isocyanonaphthalene (9):<sup>12</sup> white solid (16.8 mg, 55% yield); m.p. 61-63 °C; <sup>1</sup>H NMR (400 MHz, CDCl3) δ 7.88-7.82 (m, 4H), 7.59-7.55 (m, 2H), 7.42 (d, J = 8.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl3) δ 164.4, 133.0, 132.9, 129.8, 128.08, 128.06, 127.8, 127.7, 125.9, 123.5; LRMS (EI 70 ev) m/z (%): 153 (M<sup>+</sup>, 100), 126 (23), 125 (4), 100 (3).

11. References

12. NMR Spectra for All Compounds

$^1$H NMR: 2-isothiocyanatonaphthalene (2a)

$^1$C NMR: 2-isothiocyanatonaphthalene (2a)

$^{13}$C NMR: 2-isothiocyanatonaphthalene (2a)
$^1$H NMR: 1-isothiocyanatonaphthalene (2b)

$^{13}$C NMR: 1-isothiocyanatonaphthalene (2b)
$^1$H NMR: isothiocyanatobenzene (2c)

$^{13}$C NMR: isothiocyanatobenzene (2c)
$^1$H NMR: 4-chloro-1-isothiocyanato-2-methylbenzene (2d)

$^{13}$C NMR: 4-chloro-1-isothiocyanato-2-methylbenzene (2d)
$^1$H NMR: 1-isothiocyanato-3-methylbenzene (2e)

$^{13}$C NMR: 1-isothiocyanato-3-methylbenzene (2e)
$^1$H NMR: 1-isothiocyanato-4-methoxybenzene (2f)

$^{13}$C NMR: 1-isothiocyanato-4-methoxybenzene (2f)
$^1$H NMR: 1-(tert-butyl)-4-isothiocyanatobenzene (2g)

$^{13}$C NMR: 1-(tert-butyl)-4-isothiocyanatobenzene (2g)
$^1$H NMR: 2-isothiocyanato-1,1'-biphenyl (2h)

$^{13}$C NMR: 2-isothiocyanato-1,1'-biphenyl (2h)
$^1$H NMR: (4-isothiocyanatophenyl)(methyl)sulfane (2i)

$^{13}$C NMR: (4-isothiocyanatophenyl)(methyl)sulfane (2i)
$^1$H NMR: 1-ethynyl-4-isothiocyanatobenzene (2j)

$^{13}$C NMR: 1-ethynyl-4-isothiocyanatobenzene (2j)
**H NMR: 1-fluoro-4-isothiocyanatobenzene (2k)**

![H NMR spectrum of 1-fluoro-4-isothiocyanatobenzene (2k)](image)

**C NMR: 1-fluoro-4-isothiocyanatobenzene (2k)**

![C NMR spectrum of 1-fluoro-4-isothiocyanatobenzene (2k)](image)
$^1$H NMR: 1-chloro-3-isothiocyanatobenzene (2I)

$^{13}$C NMR: 1-chloro-3-isothiocyanatobenzene (2I)
$^1$H NMR: 1-bromo-2-isothiocyanatobenzene (2m)

$^{13}$C NMR: 1-bromo-2-isothiocyanatobenzene (2m)
\[ ^1H\text{ NMR: } 1\text{-iodo-2-isothiocyanatobenzene (2n)} \]

\[ ^{13}C\text{ NMR: } 1\text{-iodo-2-isothiocyanatobenzene (2n)} \]
$^{1}$H NMR: methyl 4-isothiocyanatobenzoate (2o)

$^{13}$C NMR: methyl 4-isothiocyanatobenzoate (2o)
$^1$H NMR: 1-(4-isothiocyanatophenyl)ethan-1-one (2p)

$^{13}$C NMR: 1-(4-isothiocyanatophenyl)ethan-1-one (2p)
\[ ^1H \text{ NMR: } 1\text{-isothiocyanato-4-(trifluoromethyl)benzene (2q)} \]

\[ ^{13}C \text{ NMR: } 1\text{-isothiocyanato-4-(trifluoromethyl)benzene (2q)} \]
$^{1}H$ NMR: 1-isothiocyanato-4-nitrobenzene (2r)

$^{13}C$ NMR: 1-isothiocyanato-4-nitrobenzene (2r)
$^1$H NMR: 4-isothiocyanato-1H-indole (2s)

$^{13}$C NMR: 4-isothiocyanato-1H-indole (2s)
$^{1}H$ NMR: (isothiocyanatomethyl)benzene (2t)

$^{13}C$ NMR: (isothiocyanatomethyl)benzene (2t)
$^1$H NMR: (2-isothiocyanatoethyl)benzene (2u)

$^{13}$C NMR: (2-isothiocyanatoethyl)benzene (2u)
$^1$H NMR: 1-isothiocyanatoxexane (2v)

$^{13}$C NMR: 1-isothiocyanatoxexane (2v)
$^1$H NMR: isothiocyanatocyclohexane (2w)

$^{13}$C NMR: isothiocyanatocyclohexane (2w)
$^1$H NMR: 1-isothiocyanato-2-(phenylethynyl)benzene (2x)

$^{13}$C NMR: 1-isothiocyanato-2-(phenylethynyl)benzene (2x)
\(^1\)H NMR: 1-(difluoromethyl)-1H-benzo[d]imidazole (3)

\(^{13}\)C NMR: 1-(difluoromethyl)-1H-benzo[d]imidazole (3)
$^{19}$F NMR: 1-(difluoromethyl)-1H-benzo[d]imidazole (3)

$^{1}$H NMR: benzo[d]oxazole (4)
$^{13}$C NMR: benzo[d]oxazole (4)

$^1$H NMR: 1-(naphthalen-1-yl)thiourea (5)
$^{13}$C NMR: 1-(naphthalen-1-yl)thiourea (5)

$^1$H NMR: 3-(4-chloro-2-methylphenyl)-1,1-dimethylthiourea (6)
$^{13}$C NMR: 3-(4-chloro-2-methylphenyl)-1,1-dimethylthiourea (6)

$^1$H NMR: N,N-dibutylbenzo[d]thiazol-2-amine (7)
$^{13}$C NMR: $N,N$-dibutylbenzo[d]thiazol-2-amine (7)

$^1$H NMR: (Z)-4-benzylidene-$N,N$-dibutyl-4H-benzo[d][1,3]thiazin-2-amine (8)
$^{13}$C NMR: (Z)-4-benzylidene-\( \text{N,N-dibutyl-4H-benzo[d][1,3]thiazin-2-amine} \) (8)

$^1$H NMR: 2-isocyanonaphthalene (9)
$^{13}$C NMR: 2-isocyanonaphthalene (9)