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# Supporting information Scalable Electrochemical Oxidant- and Metal-Free Dehydrogenative Coupling of S-H/N-H

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#### **General Information**

All materials were purchased from general merchants. The instrument for electrolysis is dual display potentiostat (RXN-1503D) (China). Cyclic voltammograms were obtained on a CHI 660 potentiostat. <sup>1</sup>H NMR and <sup>13</sup>C NMR

were recorded at a Bruker Avance III HD spectrometer (Bremen, Germany) at 400

MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR with CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as the solvent and TMS as the internal standard. High resolution mass spectra (HRMS) were measured on an Agilent 1290-6540 mass spectrometer (Santa Clara, USA). Low resolution mass spectra $\Box$ (LRMS) were recorded under an electron ionization (EI) conditions by using a Shimadzu GCMS-QP2010 Plus mass spectrometer (Kyoto, Japan). The melting points of the products were determined by an X-4 micro-melting point apparatus (Beijing, China). Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A300-10/12 EPR spectrometer.

#### General procedure for small scale electrolysis

With no precautions to exclude air or moisture, a 25 mL sealed glass tube was charged with a stir bar, *tetra*-butylammonium tetrafluoroborate (Bu<sub>4</sub>N•BF<sub>4</sub>) (0.50 mmol, 164.5 mg), thiols (0.3mmol, 1.0 equiv.), amine (3.0 mmol, 10 equiv.) and MeCN (5 mL). The Ni foam anode (area: 2 cm<sup>2</sup>) and Ni foam cathode (area: 2 cm<sup>2</sup>) were inserted to this solution, and the reaction mixture was electrolyzed at a constant current of 5 mA under room temperature for 6 h. The reaction was monitored by TLC. When the reaction was finished, the reaction mixture was transferred to a 25 mL flask and the solvent was removed in vacuo. The residue was subjected to flash column chromatography on silica gel to afford products **3a-3t**.

#### Procedure for gram scale electrolysis

To a 3 L glass tank were added 2-mercaptobenzothiazole (0.24 mol, 40.08 g, 1 equiv.),  $Bu_4N \bullet BF_4$  (0.4 mol, 131.60 g), tert-Butylamine (2.4 mol, 177.60 g, 258 mL, 10 equiv.) and MeCN (4 L). Ni foam anode (area: 280 cm<sup>2</sup>) and Ni foam cathode (area: 280 cm<sup>2</sup>) were inserted to this solution and electrolysis was conducted at a constant current (250 mA). The electrolysis was stopped after 22 h. The reaction mixture was analyzed by HPLC and the product was obtained in 95% yield. The solution was transferred to a round bottom flask and concentrated in vacuo. The solvent MeCN was recycled by rotovap for future use. The resulting residue was passed through a short silicagel plug (hexanes : EtOAc = 3:1) to remove the electrolyte; the filtrate was concentrated in vacuo. The crude material was purified by flash column chromatography (hexanes : EtOAc = 10 : 1) to afford the desired product **3a** in 94% yield.



Figure S1. A 50-gram synthesis of 3a.

#### General procedure for cyclic voltammetry (CV)

Cyclic voltammographs of 0.012 M **1a**, **2m** in CH<sub>3</sub>CN with 0.1 M Bu<sub>4</sub>N $\bullet$ BF<sub>4</sub>, glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode under nitrogen at room temperature. The scan rate is 100 mV/s, ranging from 0 V to 1.8 V.

#### Free radical trapping experiments

#### 1. Free radical trapping of 1a with DMPO

A reaction tube equipped with a stir bar was loaded with **1a** (0.30 mmol), Bu<sub>4</sub>N•BF<sub>4</sub> (0.5 mmol) and DMPO (68  $\mu$ L) in 5.0 mL CH<sub>3</sub>CN. The Ni foam anode (area: 2 cm<sup>2</sup>) and Ni foam cathode (area: 2 cm<sup>2</sup>) were inserted to this solution, and the reaction mixture was electrolyzed at a constant current of 5 mA under room temperature for 2 h. After electrolysis, the reaction mixture sample was analyzed by HMRS. After electrolysis, the reaction mixture sample was analyzed by HMRS. After electrolysis, the reaction mixture sample was analyzed by HMRS. After electrolysis, the reaction mixture sample was analyzed by HMRS. After electrolysis, the reaction mixture sample was analyzed by HMRS. After electrolysis, the reaction mixture sample was analyzed by HMRS. An adduct of thiyl radical from **1a** with DMPO was detected by HRMS analysis (Figure S2). HRMS (ESI): m/z calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>OS<sub>2</sub> [M]<sup>+</sup>, 279.0620; found, 279.0617. The HRMS result suggested that a thiyl radical might be involved in this electrochemical transformation.

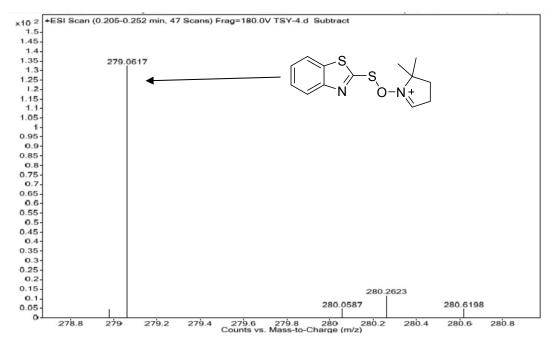


Figure S2. HRMS analysis of the adduct of thiol radical from 1a with DMPO

#### 2. Free radical trapping of 2m with DMPO

A reaction tube equipped with a stir bar was loaded with 2m (3 mmol), Bu<sub>4</sub>N•BF<sub>4</sub> (0.5 mmol) and DMPO (68 µL) in 5.0 mL CH<sub>3</sub>CN. The Ni foam anode (area: 2 cm<sup>2</sup>) and Ni foam cathode (area: 2 cm<sup>2</sup>) were inserted to this solution, and the reaction mixture was electrolyzed at a constant current of 5 mA under room temperature for 2 h. After electrolysis, the reaction mixture sample was analyzed by HMRS. After electrolysis, the reaction mixture sample was analyzed. An adduct of nitrogen radical from 2m with DMPO was detected by HRMS analysis (Figure S3). HRMS (ESI): m/z

calcd for  $C_{13}H_{19}N_2O$  [M]<sup>+</sup>, 219.1492; found, 219.1494. The HRMS result suggested that a nitrogen radical might be involved in this electrochemical transformation.

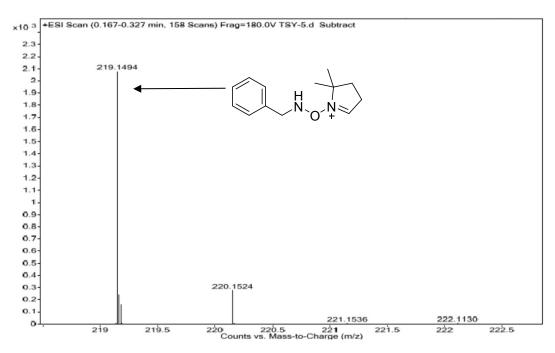
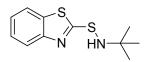
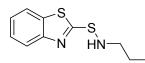


Figure S3. HRMS analysis of the adduct of nitrogen radical from 2m with DMPO.

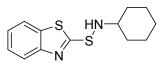
#### **Characterization Data of all products**



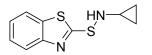
**N-tert-Butyl-2-benzothiazolesulfenamide (3a)**<sup>[1]</sup>. White solid (67.9 mg, 95% yield) (hexane : EtOAc = 10 : 1 as eluent). 105-106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.82-7.74 (m, 2H), 7.41-7.35 (m, 1H), 7.28-7.22 (m, 1H), 3.42 (s, 1H), 1.28 (s, 9H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  = 181.14, 155.14, 134.94, 125.78, 123.45, 121.48, 120.93, 55.55, 29.04. LRMS (EI): m/z calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub> [M]<sup>+</sup>, 238; found, 238.



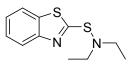
*N*-propyl-2-benzothiazolesulfenamide (3b)<sup>[1]</sup>. Light yellow oil (63.9 mg, 95% yield) (hexane: EtOAc = 10:1 as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.77-7.69 (m, 2H), 7.35-7.29 (m, 1H), 7.21-7.16 (m, 1H), 3.23 (t, *J* = 5.4 Hz, 1H), 3.07-2.97 (m, 2H), 1.63-1.52 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 178.69, 154.96, 135.02, 125.88, 123.63, 121.57, 121.07, 54.87, 23.80, 11.28. LRMS (EI): m/z calcd for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub> [M]<sup>+</sup>, 224; found, 224.



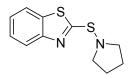
*N*-cyclohexyl-2-benzothiazolesulfenamide (3c)<sup>[1]</sup>. White solid (57.8 mg, 73% yield) (hexane: EtOAc = 10 : 1 as eluent). 98-100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.75-7.66 (m, 2H), 7.32-7.26 (m, 1H), 7.19-7.13 (m, 1H), 3.19 (d, *J* = 5.5 Hz, 1H), 2.86-2.72 (m, 1H), 2.03-1.92 (m, 2H), 1.73-1.59 (m, 2H), 1.56-1.47 (m, 1H), 1.21-1.07 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 180.06, 155.11, 134.99, 125.82, 123.53, 121.51, 121.00, 60.29, 33.73, 25.64, 24.90. LRMS (EI): m/z calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub> [M]<sup>+</sup>, 264; found, 264.



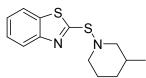
**N-cyclopropyl-2-benzothiazolesulfenamide (3d).** Colorless oil (40.0 mg, 51% yield) (hexane : EtOAc = 10 : 1 as eluent). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  = 8.00 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.09 (s, 1H), 2.79-2.70 (m, 1H), 0.66-0.52 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$  = 179.90, 155.04, 134.76, 126.55, 124.15, 122.15, 121.49, 33.55, 8.36. HRMS (ESI) m/z calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 223.0358, found 223.0357.



*N*,*N*-diethyl-2-Benzothiazolesulfenamide (3e)<sup>[1]</sup>. Light yellow oil (60.0 mg, 84% yield) (hexane: EtOAc = 10:1 as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.83-7.73 (m, 2H), 7.40-7.34 (m, 1H), 7.27-7.21 (m, 1H), 3.15 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 179.21, 155.21, 135.03, 125.79, 123.50, 121.50, 120.93, 52.50, 13.51. LRMS (EI) m/z calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub>[M]<sup>+</sup>: 238, found 238.

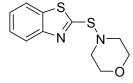


**2-(1-pyrrolidinylthio)-Benzothiazole (3f).** Colorless oil (61.6 mg, 87% yield) (hexane: EtOAc = 10:1 as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.76-7.68 (m, 2H), 7.33-7.28 (m, 1H), 7.21-7.15 (m, 1H), 3.26 (t, *J* = 6.5 Hz, 4H), 1.94-1.82 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 177.14, 154.12, 134.00, 124.74, 122.52, 120.54, 119.96, 54.67, 25.17. HRMS (ESI) m/z calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>[M+H]<sup>+</sup>: 237.0515, found 237.0516.

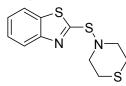


**2-[(3-methyl-1-piperidinyl)thio]-Benzothiazole (3g)**<sup>[1]</sup>. Light yellow oil (55.5 mg, 70% yield) (hexane: EtOAc = 10:1 as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.84-

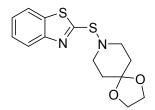
7.77 (m, 2H), 7.41-7.36 (m, 1H), 7.29-7.23 (m, 1H), 3.33-3.21 (m, 2H), 3.12-3.00 (m, 1H), 2.76 (t, J = 11.0 Hz, 1H), 1.92-1.82 (m, 1H), 1.81-1.70 (m, 3H), 1.05-0.93 (m, 1H), 0.91 (d, J = 6.7 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 177.39$ , 155.21, 135.12, 125.68, 123.46, 121.56, 120.89, 64.81, 57.37, 32.58, 31.56, 26.60, 19.14. LRMS (EI) m/z calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>[M]<sup>+</sup>: 264, found 264.



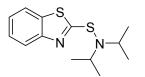
**2-(4-morpholinylthio)-Benzothiazole (3h)**<sup>[1]</sup>. White solid (65.0 mg, 86% yield) (hexane: EtOAc = 10:1 as eluent). 80-82 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.80-7.71 (m, 2H), 7.37-7.31 (m, 1H), 7.25-7.19 (m, 1H), 3.76(t, *J* = 4.7 Hz, 4H), 3.22 (t, *J* = 4.7 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 174.86, 155.05, 135.02, 126.01, 123.95, 121.89, 121.05, 67.90, 56.59. LRMS (EI) m/z calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>OS<sub>2</sub>[M]<sup>+</sup>: 252, found 252.



**2-(4-thiomorpholinylthio)-Benzothiazole (3i)**<sup>[1]</sup>. White solid (74.8 mg, 93% yield) (hexane : EtOAc = 10 : 1 as eluent). 63-65 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.86-7.77 (m, 2H), 7.44-7.37 (m, 1H), 7.31-7.25 (m, 1H), 3.55 (t, *J* = 4.9 Hz, 4H), 2.79 (t, *J* = 5.0 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 175.75, 155.18, 135.02, 126.00, 123.90, 121.87, 121.06, 58.65, 28.58. LRMS (EI) m/z calcd. for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>S<sub>3</sub> [M]<sup>+</sup>: 268, found 268.

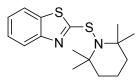


**8-(2-benzothiazolylthio)-1,4-Dioxa-8-azaspiro**[**4.5**]**decane** (**3j**)<sup>[1]</sup>. White solid (134.0 mg, 69% yield) (hexane: EtOAc = 10:1 as eluent). 109-111 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.85-7.76 (m, 2H), 7.50-7.32 (m, 1H), 7.33-7.19 (m, 1H), 3.97 (s, 4H), 3.38 (t, *J* = 5.6 Hz, 4H), 1.89 (t, *J* = 5.6 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 176.83, 155.29, 135.20, 125.86, 123.68, 121.75, 121.04, 105.82, 64.42, 55.22, 36.13. LRMS (EI) m/z calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> [M]<sup>+</sup>: 308, found 308.

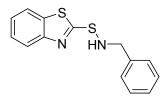


*N*,*N*-bis(1-methylethyl)-2-Benzothiazolesulfenamide (3k)<sup>[1]</sup>. White solid (16.0 mg, 20% yield) (hexane: EtOAc = 10:1 as eluent). 56-58 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.81-7.72 (m, 2H), 7.40-7.33 (m, 1H), 7.28-7.20 (m, 1H), 3.51-3.41(m, 2H), 1.26

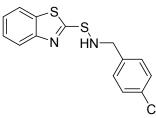
(d, J = 6.5 Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 182.28$ , 155.11, 134.77, 125.75, 123.39, 121.38, 120.85, 55.71, 22.50, 21.69. LRMS (EI) m/z calcd for C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>[M]<sup>+</sup>: 266, found 266.



**2-[(2,2,6,6-tetramethyl-1-piperidinyl)thio]-Benzothiazole (31)**<sup>[1]</sup>. White solid (18.0 mg, 20% yield) (hexane: EtOAc = 10:1 as eluent). 135-137 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.74-7.64 (m, 2H), 7.34-7.27 (m, 1H), 7.20-7.14 (m, 1H), 1.77-1.60 (m, 5H), 1.54-1.43 (m, 1H), 1.34 (s, 6H), 1.20 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 182.21, 154.56, 134.63, 125.74, 123.36, 121.37, 120.76, 61.09, 40.76, 32.52, 24.90, 17.30. LRMS (EI) m/z calcd for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>S<sub>2</sub>[M]<sup>+</sup>: 306, found 306.



*N*-(**phenyImethyl**)-2-Benzothiazolesulfenamide (3m) <sup>[1]</sup>. White solid (74.3 mg, 91% yield) (hexane: EtOAc = 10:1 as eluent).117-119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.80-7.72 (m, 2H), 7.38-7.27 (m, 5H), 7.28-7.19 (m, 2H), 4.20 (d, *J* = 6.0 Hz, 2H), 3.49 (t, *J* = 5.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 177.39, 154.83, 138.49, 135.04, 128.76, 128.48, 128.03, 125.98, 123.81, 121.67, 121.16, 57.08. LRMS (EI) m/z calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>[M]<sup>+</sup>: 272, found 272.

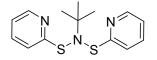


*N*-[(4-chlorophenyl)methyl]-2-Benzothiazolesulfenamide(3n). White solid (38.6 mg, 42% yield) (hexane: EtOAc = 10:1 as eluent). 116-117 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.87-7.79 (m, 2H), 7.45-7.39 (m, 1H), 7.35 (s, 4H), 7.32-7.27 (m, 1H), 4.25 (d, *J* = 5.8 Hz, 2H), 3.60 (t, *J* = 5.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 176.47, 154.67, 136.86, 135.01, 133.85, 129.87, 128.88, 126.04, 123.92, 121.71, 121.17, 56.18. HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 307.0125, found 307.0126.

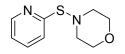
#### N-[bis(phenyl)-methyl]-2-Benzothiazolesulfenamide (30). White solid (46.0 mg, 44%

yield) (hexane: EtOAc = 10:1 as eluent). 138-140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 

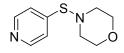
= 7.80-7.72 (m, 2H), 7.38-7.27 (m, 8H), 7.25-7.16 (m, 4H), 5.35 (d, J = 5.6 Hz, 1H), 4.00 (d, J = 5.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 176.20$ , 154.57, 141.80, 135.12, 128.74, 127.88, 127.75, 126.00, 123.88, 121.71, 121.18, 69.11. HRMS (ESI) m/z calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>S<sub>2</sub> [M+H]<sup>+</sup>: 349.0828, found 349.0829.



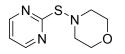
*N*-(1,1-dimethylethyl)-*N*-(2-pyridinylthio)-2-Pyridinesulfenamide (3p). White solid (48.9 mg, 56% yield) (hexane: EtOAc = 10:1 as eluent). 110-112 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.48-8.40 (m, 2H), 7.67-7.59 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.02-6.94(m, 2H), 1.42 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 164.80, 149.30, 136.45, 119.64, 118.10, 67.07, 29.62. HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>S<sub>2</sub>[M+H]<sup>+</sup>: 292.0937, found 292.0939.



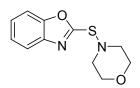
**4-(2-pyridinylthio)-Morpholine (3q).** Light yellow oil (36.5 mg, 62% yield) (hexane: EtOAc = 3:1 as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.40-8.29 (m, 1H), 7.57-7.51 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 6.96-6.86 (m, 1H), 3.70 (t, *J* = 4.8 Hz, 4H), 3.18(t, *J* = 4.8 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 164.21, 149.45, 136.56, 119.57, 118.11, 67.95, 56.17. HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>:197.0743, found 197.0744.



**4-(4-pyridinylthio)-Morpholine (3r).** Colorless oil (35.9 mg, 61% yield) (hexane: EtOAc = 3:1 as eluent). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.45-8.40 (m, 2H), 7.23-7.20 (m, 2H), 3.82-3.75 (m, 4H), 3.12-3.06 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 152.27, 149.32, 117.03, 77.36, 77.04, 76.72, 67.75, 56.19. HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>:197.0743, found 197.0744.



**4-(2-pyrimidinylthio)-Morpholine (3s).** White solid(49.0 mg, 83% yield) (hexane: EtOAc = 3:1 as eluent). 57-58 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.46 (d, *J* = 4.8 Hz, 2H), 6.88 (t, *J* = 4.9 Hz, 1H), 3.75 (s, 4H), 2.65 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 176.81, 157.04, 116.77, 57.06, 29.08. HRMS (ESI) m/z calcd for C<sub>8</sub>H<sub>11</sub>N<sub>3</sub>OS [M+H]<sup>+</sup>:198.0696, found 198.0697.

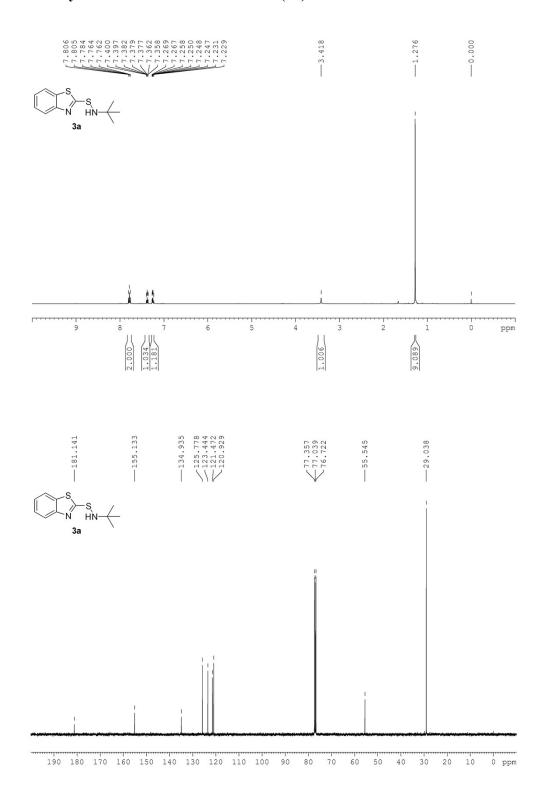


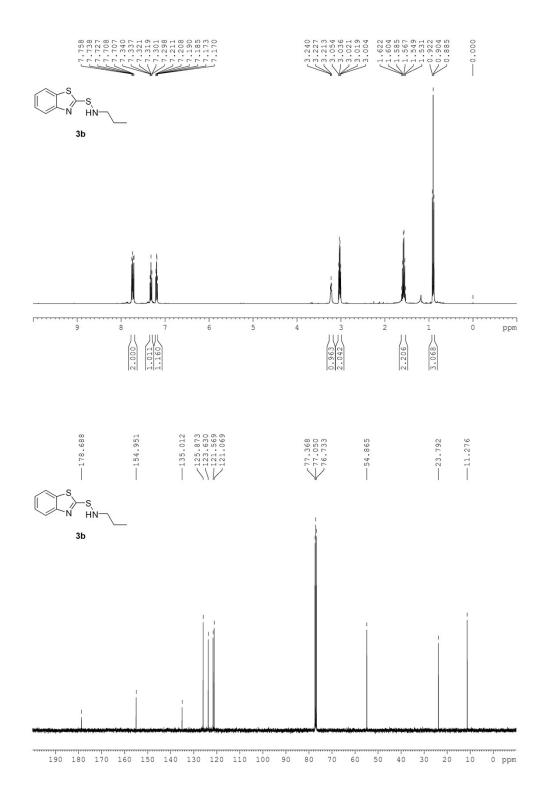
**2-(4-morpholinylthio)-Benzoxazole (3t).** White solid(53.9 mg, 76% yield) (hexane: EtOAc = 10:1 as eluent). 36-38 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.61-7.56 (m, 1H), 7.44-7.39 (m, 1H), 7.27-7.18 (m, 2H), 3.69 (t, *J* = 4.7 Hz, 4H), 3.37 (t, *J* = 4.8 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.18, 151.37, 141.66, 124.45, 124.35, 119.19, 110.19, 67.75, 55.79. HRMS (ESI) m/z calcd for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup>:237.0692, found 237.0692.

#### References

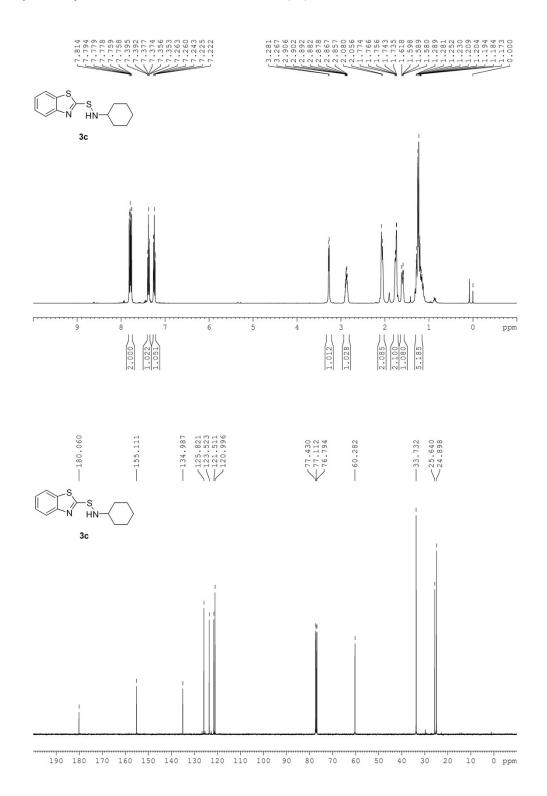
[1]Y. Dou, X. Huang, H. Wang, L. Yang, H. Li, B. Yuan, G. Yang, *Green Chem.* **2017**, *19*, 2491-2495.

#### The NMR Spectra of all products N-tert-Butyl-2-benzothiazolesulfenamide (3a):

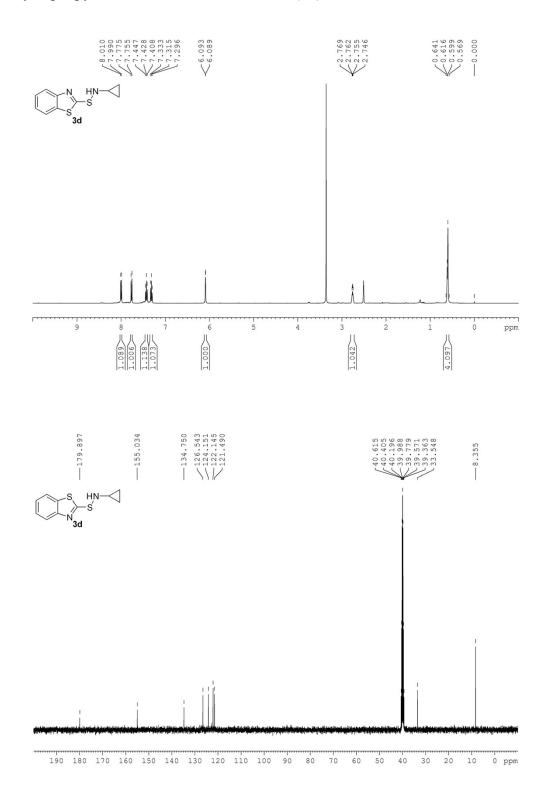




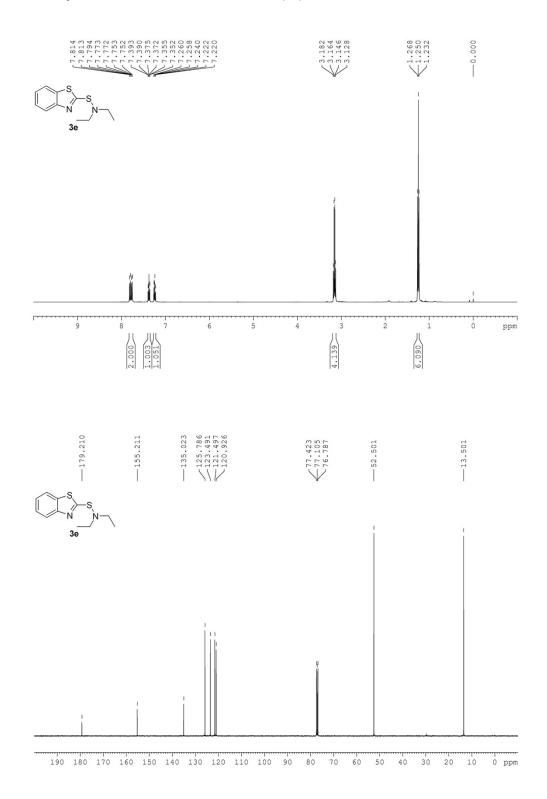
### *N*-cyclohexyl-2-benzothiazolesulfenamide (3c):



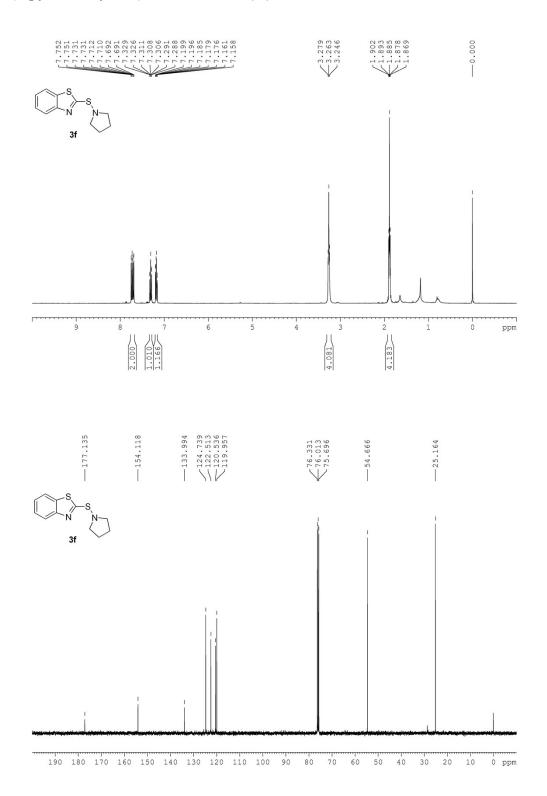
### N-cyclopropyl-2-benzothiazolesulfenamide (3d):



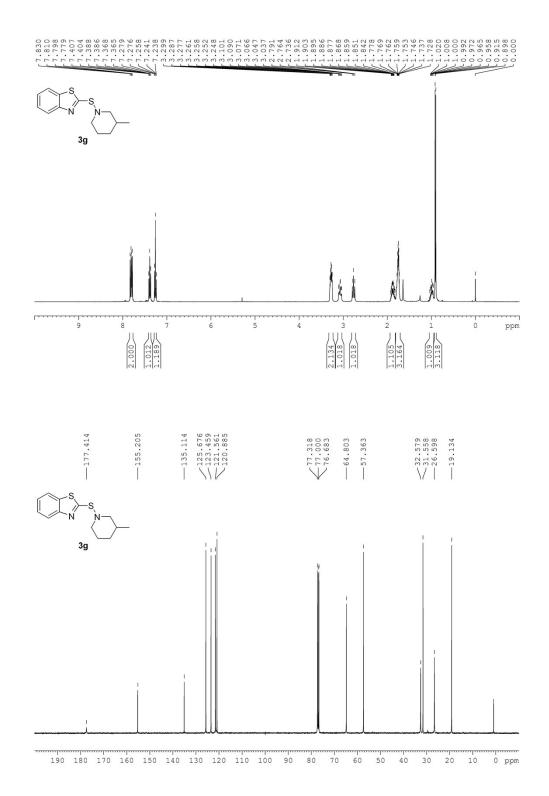
### *N*,*N*-diethyl-2-Benzothiazolesulfenamide (3e):



### 2-(1-pyrrolidinylthio)-Benzothiazole (3f):

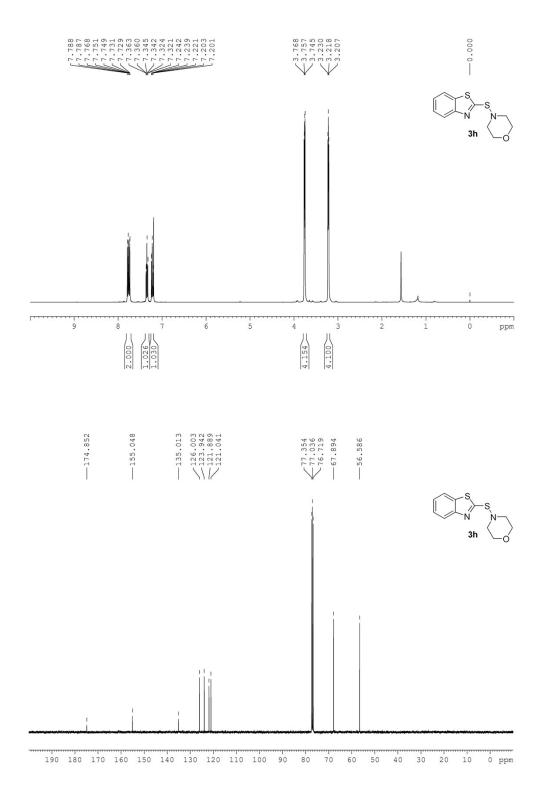


### 2-[(3-methyl-1-piperidinyl)thio]-Benzothiazole (3g):



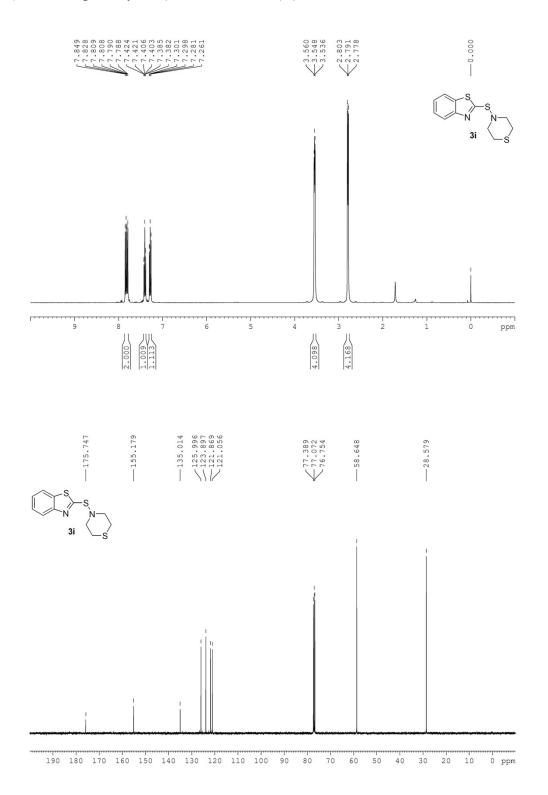
S17

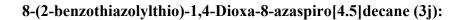
### 2-(4-morpholinylthio)-Benzothiazole (3h):

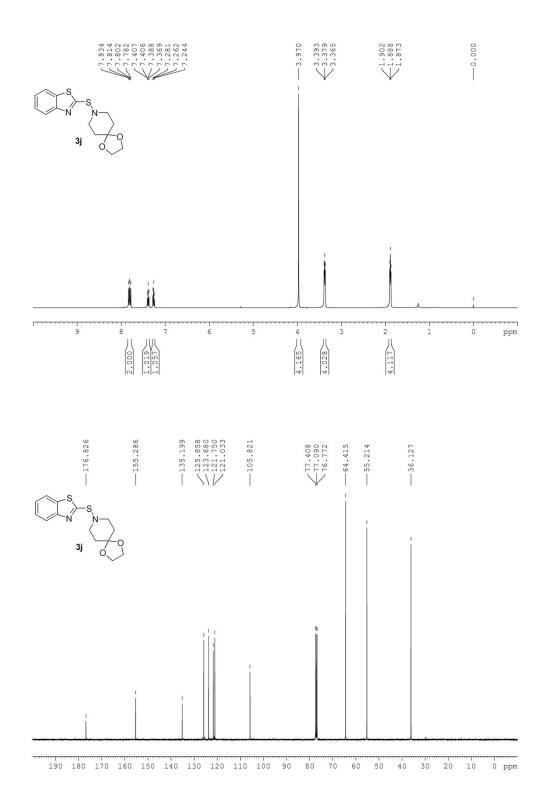


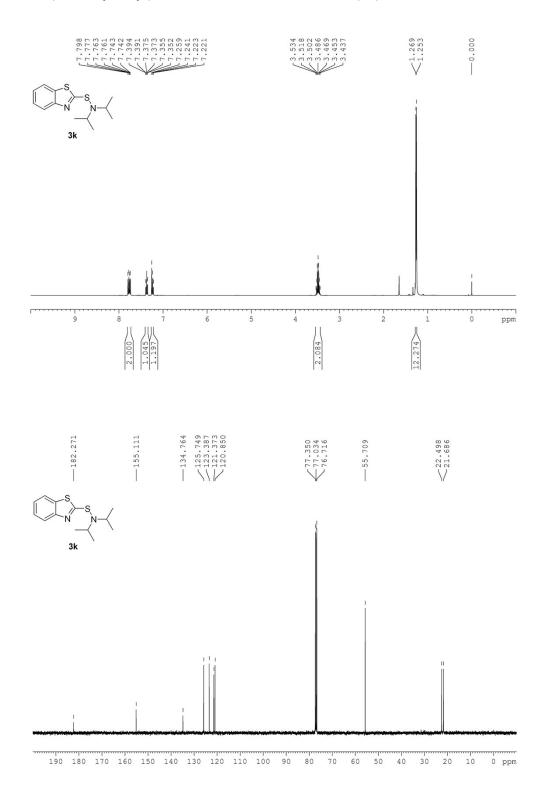
S18

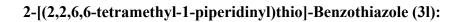
### 2-(4-thiomorpholinylthio)-Benzothiazole (3i):

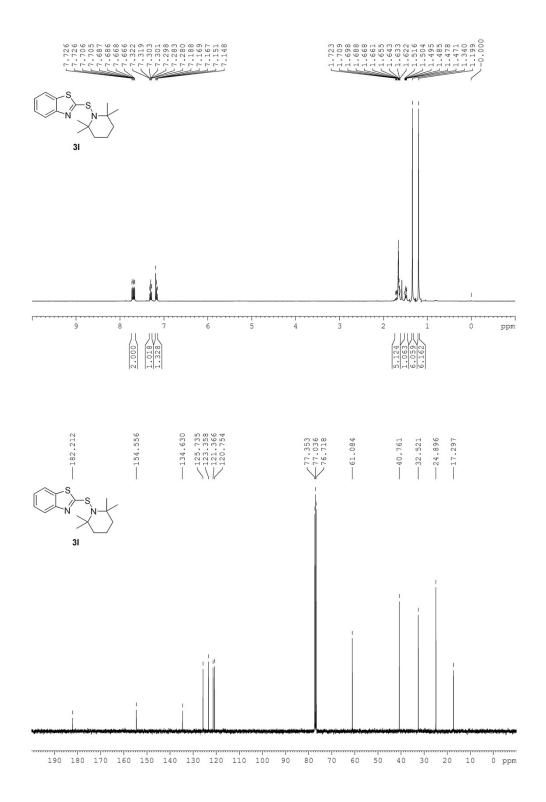




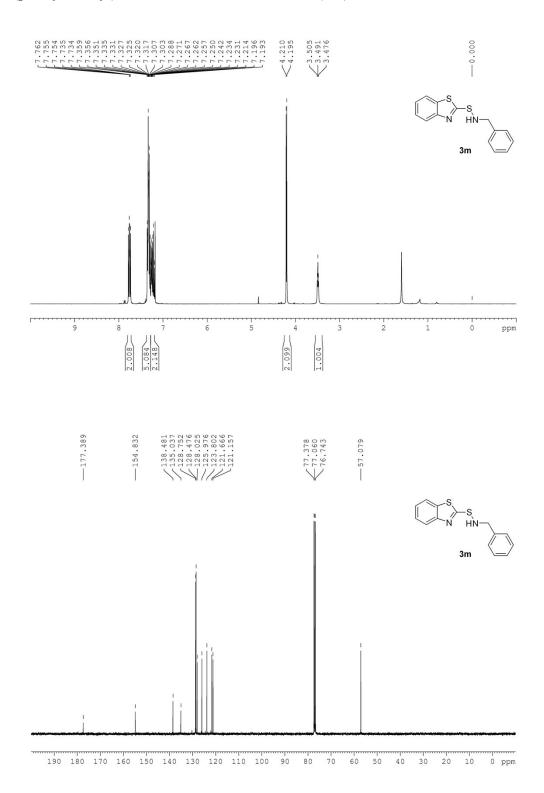




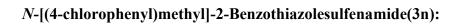


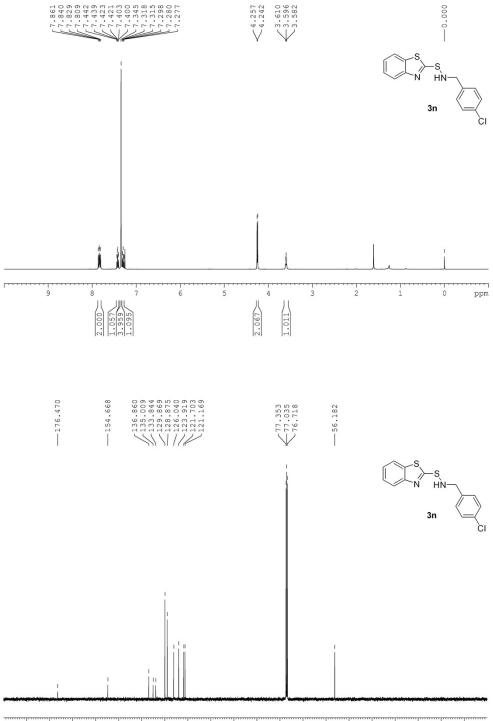


# *N*-(phenylmethyl)-2-Benzothiazolesulfenamide (3m):



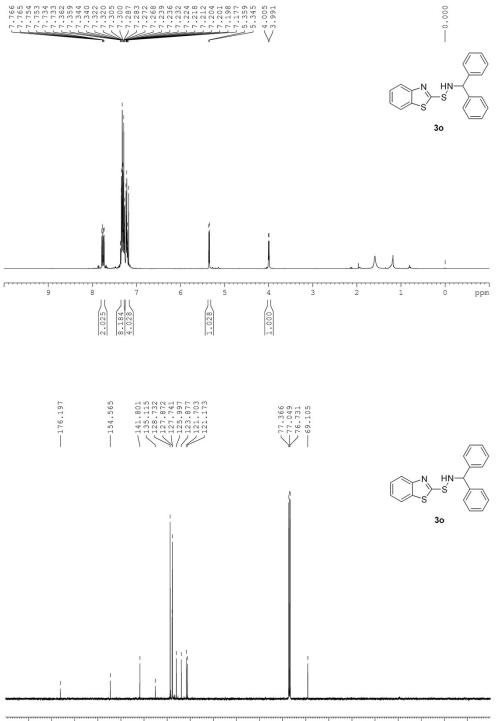
S23





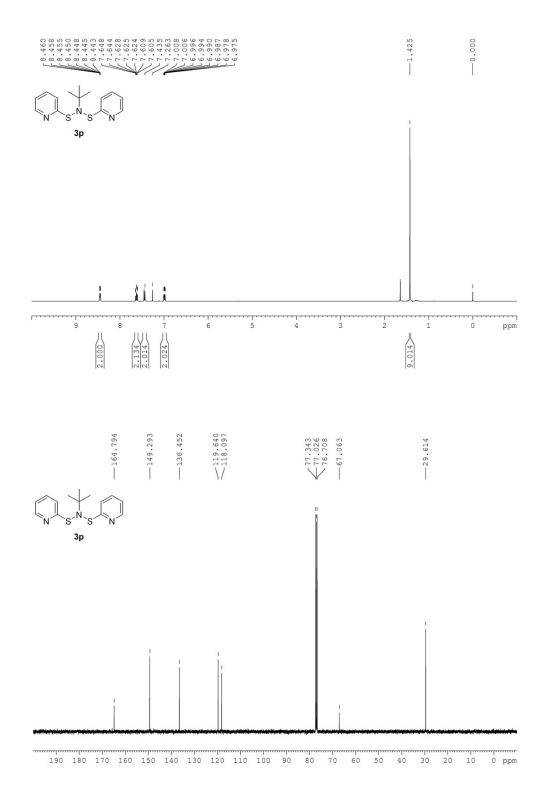
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm





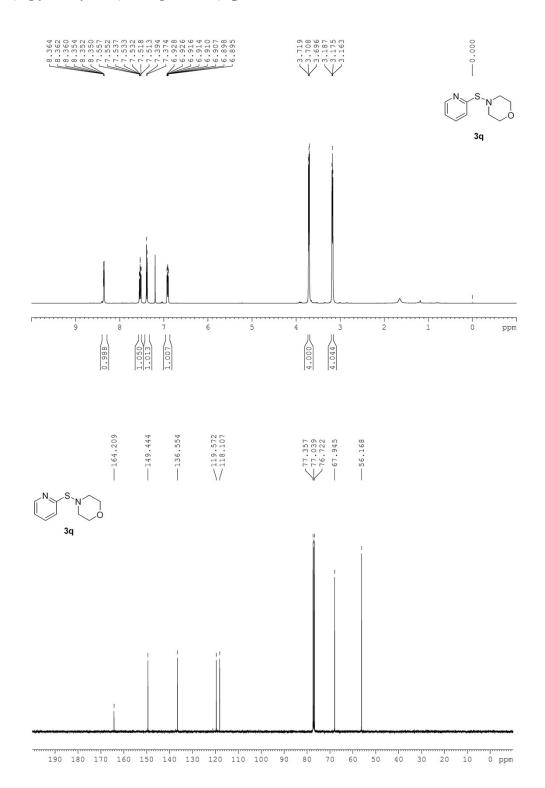
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm





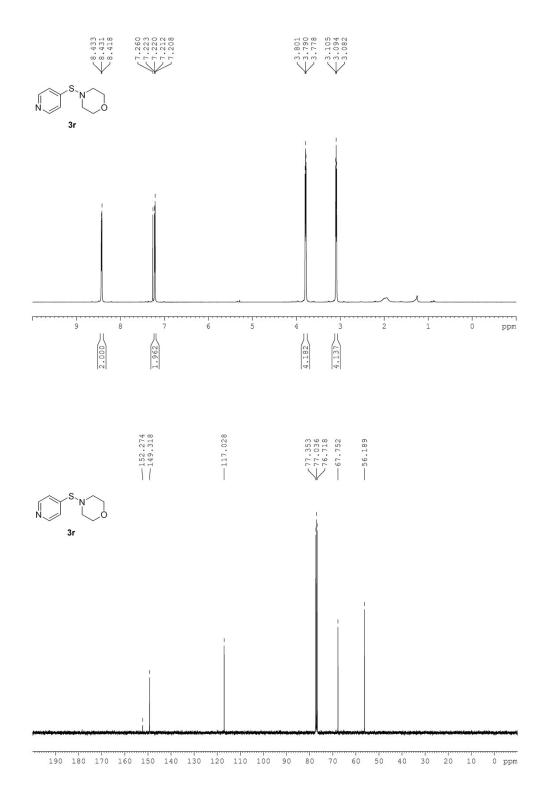
S26

#### 4-(2-pyridinylthio)-Morpholine (3q):

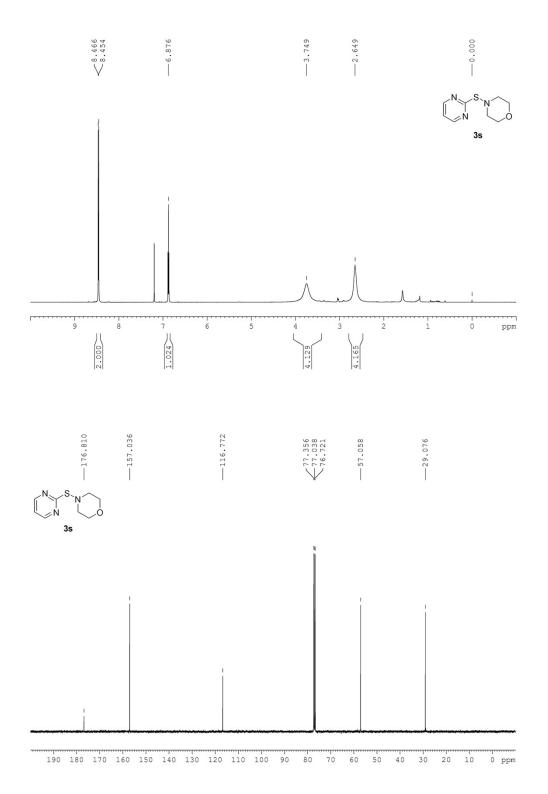


S27

### 4-(4-pyridinylthio)-Morpholine (3r):



## 4-(2-pyrimidinylthio)-Morpholine (3s):



### 2-(4-morpholinylthio)-Benzoxazole (3t):

