**Efficient Conversion of Substituted Aryl Thioureas to
2-Aminobenzothiazoles Using
Benzyltrimethylammonium Tribromide
(Supplemental Material)**

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Table of Contents

	Page
Experimental Section. General Methods	3
Preparation of Thiourea Starting Materials	3
6-Bromo-2-(methylamino)benzothiazole (5)	3
Methyl <i>N</i> -(2-Carboxyethyl)aminobenzothiazole (8)	4
2-[2-(Dimethylamino)ethylamino]benzothiazole (10)	5
2-(2-Acetoxyethylamino)benzothiazole (12)	6
2-(2-Hydroxyethylamino)benzothiazole (13)	6
5-Methoxy-2-(methylamino)benzothiazole (15)	7
2-(Methylamino)-5-methylbenzothiazole (17) and 2-(Methylamino)-7-methylbenzothiazole (18)	8
5-Bromo-2-(methylamino)benzothiazole (20) and 7-Bromo-2-(methylamino)benzothiazole (21)	8
2-Methylamino-6-methylbenzothiazole (25).	9
2-(<i>N</i> -Piperidino)benzothiazole (30)	9
2-Methylamino-6-(Trifluoromethoxy)benzothiazole (32)	10
2-Amino-6-bromobenzothiazole (34)	11

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded on an NMR spectrometer at 300 and 75.5 MHz, respectively. Chemical shifts were reported as ppm (δ values) in Hertz (Hz) downfield from tetramethylsilane as the internal reference in DMSO- d_6 . Mass spectra were obtained with a single quadrupole and fitted with an electrospray source. Elemental analyses were within 0.4% of the theoretical value. Melting points were taken in open capillary tube and are uncorrected. Purifications were conducted by preparative thin layer chromatography using 20 x 20 cm tapered silica gel plates or by flash column chromatography on silica gel (230-400 mesh). The progress of reactions was monitored by thin layer chromatography (TLC) on 250- μM precoated silica gel plates. Most reagents and solvents were purchased and used without further purification.

Preparation of Thioureas 3, 6, 7, 9, 11, 14, 16, 19, 22, and 24. Substituted aryl thioureas were prepared as described in the literature¹⁶ or acquired from commercial sources.

6-Bromo-2-(methylamino)benzothiazole (5). *N*-Methyl-*N'*-4-bromophenyl thiourea **6** (150.0mg, 0.600 mmol) was stirred in acetic acid (5 mL) and treated with **1** (240 mg, 0.600 mmol) at ambient temperature. The reaction mixture was stirred for 18h and was slowly poured into ice cold saturated NaHCO_3 and extracted into EtOAc (3 x 40 mL) The organic extracts were dried over MgSO_4 , filtered and concentrated. The crude product was recrystallized from EtOAc/heptane and provided 110 mg (73%) of **5** as a white solid: mp 228°C. ^1H NMR (DMSO- d_6 , 300 MHz) δ 8.07-8.06 (m, 1H, NH), 7.91 (d, *J*

= 1.9 Hz, 1H), 7.33 (m, 2H), 2.90-2.89 (m, 3H); MS MH^+ (rel int) 242.9 (100%), 244.9 (98%). Anal. Calcd for $C_8H_7BrN_2S$: C, 39.52; H, 2.90; Br, 32.87; N, 11.52 S, 13.19. Found: C, 39.51; H, 2.53; Br, 32.56 N, 11.41; S, 12.88.

6-Bromo-2-(methylamino)benzothiazole (5). *N*-Methyl-*N'*-phenyl thiourea **3** (166.4, 1.00 mmol) and **1** (863.2, 2.21 mmol) were stirred in acetic acid (12 mL) at ambient temperature for 18 hr. The reaction mixture was then slowly poured into ice cold saturated $NaHCO_3$ and extracted into EtOAc (100 mL). The organic extracts were washed with water (50 mL), dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by preparative TLC (2% MeOH in $CHCl_3$) and furnished 169.4 mg (70%) of **5** as a white solid: mp 227-228°C. 1H NMR (DMSO- d_6 300 MHz) δ 8.06-8.07 (m, 1H), 7.90-7.91 (m, 1H), 7.29-7.37 (m, 2H), 2.92-2.93 (d, J = 4.7 Hz, 3H); ^{13}C NMR (DMSO- d_6 75.5 MHz) δ 167.318, 151.846, 132.445, 128.281, 123.240, 119.221, 111.964, 30.395. MS MH^+ (rel int) 244 (98%), 242 (100%). Anal. Calcd for $C_8H_7BrN_2S$: C, 39.52; H, 2.90; Br, 32.87; N, 11.52 S, 13.19. Found: C, 39.50; H, 2.68; Br, 33.06 N, 11.57; S, 13.18.

Methyl *N*-(2-Carboxyethyl)aminobenzothiazole (8). Methyl *N*-2-carboxyethyl-*N'*-phenyl thiourea **7** (238.7 mg, 1.002 mmol) was dissolved in acetic acid (5 mL) and treated with **1** (391.5 mg, 1.004 mmol) at ambient temperature. The reaction mixture was stirred for 2h and was slowly poured into ice cold saturated $NaHCO_3$ and extracted into EtOAc (2 x 40 mL) The organic extracts were dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by preparative TLC (2% MeOH in $CHCl_3$) and yielded 197.9 mg (84%) of **8** as a white powder: mp 89°C. 1H NMR (DMSO- d_6 300 MHz) δ 8.09-8.11 (m, 1H, NH), 7.65 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.22 (t, J

= 7.7 Hz, 7.7 Hz, 1H), 7.01 (t, J = 7.5 Hz, 7.5 Hz, 1H), 3.62 (s, 3H), 3.59 (t, J = 6.6 Hz, 6.6 Hz, 2H), 2.68 (t, J = 6.6 Hz, 6.6 Hz, 2H); ^{13}C NMR (DMSO- d_6 75.5 MHz) δ 172.078, 166.162, 152.834, 130.688, 125.866, 121.330, 121.247, 118.466, 51.761, 40.020, 33.694. MS MH^+ (rel int) 237.0 (70%). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 55.91; H, 5.12; N, 11.86; S, 13.57. Found: C, 55.89; H, 5.22; N, 11.78; S, 13.46.

Methyl N-(2-Carboxyethyl)aminobenzothiazole (8). Methyl *N*-2-carboxyethyl-*N'*-phenyl thiourea **7** (238.5 mg, 1.002 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with **1** (390.5 mg, 1.004 mmol) at ambient temperature. The reaction mixture was stirred for 18 h, diluted with CH_2Cl_2 (40 mL) and neutralized with saturated NaHCO_3 . The organic solution was dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by preparative TLC (2% MeOH in CHCl_3) and gave 181.4 mg (77%) of **8** as an off white powder (mp 88-89°C). ^1H NMR (DMSO- d_6 300 MHz) δ 8.11 (m, 1H, NH), 7.65 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.7 Hz, 7.7 Hz, 1H), 7.01 (t, J = 7.5 Hz, 7.5 Hz, 1H), 3.62 (s, 3H), 3.59 (t, J = 6.6 Hz, 6.6 Hz, 2H), 2.68 (t, J = 6.6 Hz, 6.6 Hz, 2H); MS MH^+ (rel int) 237.0 (70%). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 55.91; H, 5.12; N, 11.86; S, 13.57. Found: C, 55.78; H, 4.99; N, 11.84; S, 13.54.

2-[2-(Dimethylamino)ethylamino]benzothiazole (10). *N*-Dimethylaminoethyl-*N'*-phenyl thiourea **9** (223.7 mg, 1.000 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with **1** (390.9 mg, 1.002 mmol) at ambient temperature. The reaction mixture was stirred for 1h and was poured into saturated NaHCO_3 and extracted with additional CH_2Cl_2 (40 mL). The organic extracts were dried over Na_2SO_4 , filtered and concentrated. The isolated residue was purified by preparative TLC (2% MeOH in CHCl_3) and yielded 160.7 mg (81%) of free base **10** as a yellow oil. The free base was dissolved in 15 mL of

EtOAc, and the solution was acidified with 1.0 N HCl in Et₂O to yield 176.6 mg of the dihydrochloride salt. mp 217-222 °C (dec.). ¹H NMR (DMSO-d₆ 300 MHz) δ 10.7 (br s, 1H (exchangeable), 9.9 (br s, 1H (exchangeable), 8.7 (br s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 7.5 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 7.6 Hz, 1H), 3.94 (m, 2H), 3.40-3.41 (m, 2H); ¹³C NMR (DMSO-d₆ 75.5 MHz) δ 167.192, 143.868, 127.116, 126.690, 123.716, 122.730, 116.121, 54.940, 42.736. MS MH⁺ (rel int) 222.1 (100%). Anal. Calcd for C₁₁H₁₅N₃S 2.0 HCl: C, 44.90; H, 5.82; Cl, 24.10; N, 14.28; S, 10.90; Found: C, 45.07; H, 5.72; Cl, 23.87 N, 14.30; S, 10.82.

2-(2-Acetoxyethylamino)benzothiazole (12). *N*-2-Hydroxyethyl-*N'*-phenyl thiourea **11** (196.3mg, 1.000 mmol) was dissolved in acetic acid (5 mL) and treated with **1** (390.2 mg, 1.000 mmol) at ambient temperature. The reaction mixture was stirred for 4h and was slowly poured into ice cold saturated NaHCO₃ and extracted into CHCl₃ (2 x 75 mL) The organic extracts were dried over Na₂SO₄, filtered and concentrated. The crude product was purified by preparative TLC (40% EtOAc in hexane) and yielded 173.3 mg (73%) of **12** as a white powder: mp 89-93 °C. ¹H NMR (DMSO-d₆ 300 MHz) δ 8.16 (t, *J* = 5.4 Hz, 5.4 Hz, 1H, NH), 7.66 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.25-7.20 (m, 1H), 7.05-6.99 (m, 1H), 4.20 (t, *J* = 5.4 Hz, 5.4 Hz, 2H), 3.64-3.59 (m, 2H), 2.02 (s, 3H); ¹³C NMR (DMSO-d₆ 75.5 MHz) δ 170.290, 165.961, 152.329, 130.272, 125.470, 120.955, 120.846, 118.039, 62.222, 42.547, 20.648. MS MH⁺ (rel int) 237.0 (100%). Anal. Calcd for C₁₁H₁₂N₂O₂S: C, 55.91; H, 5.12; N, 11.86; S, 13.57. Found: C, 55.91; H, 4.98; N, 11.77; S, 13.46.

2-(2-Hydroxyethylamino)benzothiazole (13). To a suspension of *N*-2-hydroxyethyl-*N'*-phenyl thiourea **11** (196.6 mg, 1.000 mmol) in CH₂Cl₂ (5 mL) was added

1 (390.5 mg, 1.000 mmol) at ambient temperature. The reaction mixture was stirred for 22 h, diluted with 40 mL of CH₂Cl₂ and was poured into saturated Na₂CO₃. The organic layer was separated, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by preparative TLC (5% MeOH in CHCl₃) and yielded 147.6 mg (76%) of **13** as a white powder: mp 99-101 °C; lit²⁶ 104-105.5°C. ¹H NMR (DMSO-d₆ 300 MHz) δ 8.04 (t, *J* = 5.4 Hz, 5.4 Hz, 1H, NH), 7.64 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.23-7.18 (m, 1H), 7.02-6.97 (m, 1H), 4.81 (t, *J* = 5.3 Hz, 5.3 Hz, 1H), 3.62-3.56 (m, 2H), 3.46-3.40 (m, 2H); ¹³C NMR (DMSO-d₆ 75.5 MHz) δ 166.188, 152.472, 130.212, 125.346, 120.725, 120.654, 117.767, 59.386, 46.465. MS MH⁺ (rel int) 195.1 (100%). Anal. Calcd for C₉H₁₀N₂OS: C, 55.65; H, 5.19; N, 14.42; S, 16.22. Found: C, 55.31; H, 5.02; N, 14.24; S, 16.22.

5-Methoxy-2-(methylamino)benzothiazole (15). *N*-Methyl-*N'*-3-methoxyphenyl thiourea **14** (196.7 mg, 1.000 mmol) was dissolved in acetic acid (5 mL) and treated with **1** (390.9 mg, 1.002 mmol) at ambient temperature. The reaction mixture was stirred for 30 min and was slowly poured into ice cold saturated NaHCO₃ and extracted into EtOAc (3 x 40 mL) The organic extracts were dried over Na₂SO₄, filtered and concentrated. The isolated residue was purified by preparative TLC eluting with 2% MeOH in CHCl₃ and gave 169.1 mg (87%) of **4** as a white solid: mp 131.5-132.5°C. ¹H NMR (DMSO-d₆ 300 MHz) δ 7.91-7.89 (m, 1H, NH), 7.50 (d, *J* = 8.6 Hz, 1H), 7.05-6.99 (m, 1H), 6.63 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.75 (s, 3H), 2.91 (d, *J* = 4.6 Hz, 3H); ¹³C NMR (DMSO-d₆ 75.5 MHz) δ 168.467, 158.704, 154.327, 122.012, 121.408, 108.898, 103.395, 55.563, 30.683. MS MH⁺ (rel int) 195.1 (100%). Anal. Calcd for C₉H₁₀N₂OS: C, 55.65; H, 5.19; N, 14.42; S, 16.51. Found: C, 55.49; H, 5.03; N, 14.35; S, 16.22.

2-(Methylamino)-5-methylbenzothiazole (17) and 2-(Methylamino)-7-methylbenzothiazole (18). *N*-Methyl-*N'*-3-methylphenyl thiourea **16** (180.4 mg, 1.000 mmol) was dissolved in acetic acid (5 mL) and treated with **1** (390.3 mg, 1.002 mmol) at ambient temperature. The reaction mixture was stirred for 30 min and was slowly poured into ice cold saturated NaHCO₃ and extracted into EtOAc (2 x 80 mL) The organic extracts were dried over Na₂SO₄, filtered and concentrated. The isolated residue was purified by preparative TLC (2% MeOH in CHCl₃) and provided 157.8 mg (88%) of a ca 3:2 inseparable mixture of **17** and **18** as a white solid. ¹H NMR (DMSO-d₆ 300 MHz) δ 7.93-7.91 (m, 0.40 x 1H, NH), 7.87-7.85 (m, 0.60 x 1H), 7.52 – 7.50 (m, 0.60 x 1H), 7.21 (s, 1 H), 7.13 (t, *J* = 7.6 Hz, 0.40 x 1H), 6.85 – 6.82 (m, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.05-6.99 (m, 1H), 2.94-2.92 (m, 3H), 2.92 (s, 0.60 x 3H), 2.90 (s, 0.40 x 3H); ¹³C NMR (DMSO-d₆ 75.5 MHz) δ 167.056 (166.277), 152.937 (152.521), 134.713, 130.336 (130.068), 127.089, 125.552, 121.830 (121.296), 120.369, 118.431, 115.524, 30.445, 21.001 (20.940). MS MH⁺ (rel int) 195.1 (100%). Anal. Calcd for C₉H₁₀N₂S: C, 60.64; H, 5.65; N, 15.72; S, 17.99. Found: C, 60.67; H, 5.27; N, 15.60; S, 17.86.

5-Bromo-2-(methylamino)benzothiazole (20) and 7-Bromo-2-(methylamino)benzothiazole (21). To a suspended solution of *N*-methyl-*N'*-3-bromophenyl thiourea **19** (245.7 mg, 1.000 mmol) was dissolved in acetic acid (5 mL) was added **1** (390.8 mg, 1.002 mmol) at ambient temperature. The reaction mixture was stirred for 18h and was then slowly poured into ice cold saturated NaHCO₃ and extracted into CHCl₃ (2 x 70 mL) The organic extracts were dried over Na₂SO₄, filtered and concentrated. The isolated residue was purified by preparative TLC (3% MeOH in CHCl₃) and yielded 157.8 mg (88%) of a ca 3:2 inseparable mixture of **20** and **21** as a

beige solid: ^1H NMR (DMSO- d_6 300 MHz) δ 8.19-8.14 (q, J = 4.8 Hz, 1H, NH), 7.62 (d, J = 8.3 Hz, 0.50 x 1H), 7.55-7.54 (m, 0.50 x 1H), 7.39-7.36 (m, 0.50 x 1H), 7.22-7.14 (m, 1.50 x 1H), 2.93 (d, J = 4.6 Hz, 3H); ^{13}C NMR (DMSO- d_6 75.5 MHz) δ 168.624 (166.177), 154.671 (153.320), 132.990, 129.984, 127.612, 123.651, 123.508, 122.905, 120.589, 118.693, 117.248, 112.664, 30.893 (30.825). MS MH^+ (rel int) 243.0 (98%) and 245.0 (100%). Calcd for $\text{C}_8\text{H}_7\text{BrN}_2\text{S}$: C, 39.52; H, 2.90; Br, 32.87; N, 11.52; S, 13.19. Found: C, 39.60; H, 2.67; Br, 33.00; N, 11.42; S, 13.01.

2-Methylamino-6-methylbenzothiazole (25). *N*-Methyl-*N'*-4-methylphenyl thiourea **24** (240 mg, 1.30 mmol) was stirred in acetic acid (5 mL) and treated with **1** (530 mg, 1.30 mmol) at ambient temperature. The reaction mixture was stirred for 18 hr and was slowly poured into ice cold saturated NaHCO_3 and extracted into EtOAc (3 x 40 mL). The organic extracts were dried over MgSO_4 , filtered and concentrated. The crude product was recrystallized from EtOAc/ heptane and provided 160 mg (67%) of **5** as a white solid: mp 153°C; ^1H NMR (DMSO- d_6 300 MHz) δ 7.80-7.78 (m, 1H, NH), 7.45 (s, 1H), 7.26 (d, J = 8.1 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 2.90 (d, J = 4.7 Hz, 3H); 2.30 (s, 3H); ^{13}C NMR (DMSO- d_6 75.5 MHz) δ 167.337, 151.864, 132.465, 128.294, 123.244, 119.233, 111.998, 30.417. MS MH^+ (rel int) 179.1 (100%). Anal. Calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{S}$: C, 60.64; H, 5.65; N, 15.72; S, 17.99. Found: C, 60.24; H, 5.57; N, 15.68; S, 17.95.

2-(*N*-Piperidino)benzothiazole (30). A mixture of phenyl isocyanate (120 μL , 1.00 mmol) and piperidine (99 μL , 1.00 mmol) was dissolved in CH_2Cl_2 (5 mL), stirred for 1 hr then treated with **1** (390.5 mg, 1.00 mmol) at room temperature. The reaction mixture was stirred overnight. The reaction was diluted with CH_2Cl_2 (25 mL) and neutralized was

with aqueous NaHCO_3 . The organic layer was washed with H_2O , dried over Na_2SO_4 , filtered and concentrated to provide a residue. The crude product was purified by Tapered preparative TLC (2% MeOH in CHCl_3) and gave 150.4 mg (69%) of **30** as an off-white solid: mp 92.5-93.5°C; lit²⁷ 93-94°C. ^1H NMR (DMSO-d_6 300 MHz) δ 7.73 (d, J = 7.7 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 3.55 (s, 4H), 1.62 (s, 6H). ^{13}C NMR (DMSO-d_6 75.5 MHz) δ 167.870, 152.654, 130.285, 125.774, 120.918, 120.825, 118.256, 49.029, 24.760, 23.608. MS MH^+ (rel int) 219.0 (100%). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{S}$: C, 66.02; H, 6.46; N, 12.83; S, 14.69. Found: C, 65.78; H, 6.63; N, 12.78; S, 14.76.

2-Methylamino-6-(Trifluoromethoxy)benzothiazole (32). To a mixture of 4-trifluoromethoxyaniline (140.0 μL , 1.035 mmol) and tetrabutylammonium thiocyanate (331.8 mg, 1.037 mmol) in CH_2Cl_2 (6 mL) was added **1** (404.5 mg, 1.037 mmol) at ambient temperature. The reaction mixture was stirred for 18 h. The reaction mixture was neutralized with aqueous NaHCO_3 and extracted with CH_2Cl_2 (40 mL). The organic solution was washed with H_2O (50 mL), dried over Na_2SO_4 , filtered and concentrated to provide a residue. The crude product was purified by Tapered preparative TLC (50% EtOAc in heptane) and provided 166.0 mg (74%) of **32** as an off white crystalline solid: mp 118°C; lit²⁵ 119°C. ^1H NMR (DMSO-d_6 300 MHz) δ 7.77 (s, 1H.), 7.65 (s, 2H, 2NH), 7.37 (d, J = 8.7 Hz, 1H), 7.20-7.17 (m, 1H), ^{13}C NMR (DMSO-d_6 75.5 MHz) δ 168.077, 152.336, 142.485, 142.462, 132.310, (125.698, 122.318, 118.936, 115.557 quartet for CF_3O group), 119.243, 118.299, 114.702. MS MH^+ (rel int) 235.0 (100%). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$: C, 41.03; H, 2.15; N, 11.96; S, 13.69. Found: C, 41.18; H, 2.03; N, 11.95; S, 13.44.

This material was also prepared using CH_3CN as solvent as described. To a mixture of 4-trifluoromethoxyaniline (140.0 μL , 1.035 mmol) and ammonium thiocyanate (80.0 mg, 1.00 mmol) in CH_3CN (6 mL) was added **1** (390.0 mg, 1.00 mmol) at ambient temperature. The reaction mixture was stirred for 1 d, and then neutralized with aqueous NaHCO_3 and extracted with CH_2Cl_2 (40 mL). The organic solution was washed with H_2O (50 mL), dried over Na_2SO_4 , filtered and concentrated to provide a residue. The crude product was purified by tapered preparative TLC (50% EtOAc in heptane) and gave 144.0 mg (64%) of **32** as an off white crystalline solid: mp 113-114°C. ^1H NMR ($\text{DMSO}-d_6$ 300 MHz) δ 7.78 (s, 1H.), 7.66 (s, 2H, 2NH), 7.37 (d, J = 8.6 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), MS MH^+ (rel int) 235.0 (100%). Anal. Calcd for $\text{C}_8\text{H}_5\text{F}_3\text{N}_2\text{OS}$: C, 41.03; H, 2.15; F, 24.34; N, 11.96; S, 13.69. Found: C, 41.25; H, 2.07; F, 24.22; N, 11.85; S, 13.50.

2-Amino-6-bromobenzothiazole (34). To a mixture of 4-bromoaniline (176.2 mg, 1.02 mmol) and tetrabutylammonium thiocyanate (307.8 mg, 1.02 mmol) in CH_2Cl_2 (5 mL) was added **1** (399.6 mg, 1.02 mmol) at ambient temperature. The reaction mixture was stirred for 1d. The reaction mixture was diluted with CH_2Cl_2 (40 mL), neutralized with aqueous NaHCO_3 and the organic layer was washed with H_2O (50 mL), dried over Na_2SO_4 , filtered and concentrated to provide a residue. The crude product was purified by Tapered preparative TLC (40% EtOAc in hexane) and provided 93.3 mg (41%) of **34** as an off white crystalline solid: mp 215-217°C. ^1H NMR ($\text{DMSO}-d_6$ 300 MHz) δ 7.89-7.88 (m, 1H), 7.60 (s, 2H, 2NH), 7.35-7.23 (m, 1H), 7.24 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($\text{DMSO}-d_6$ 75.5 MHz) δ 167.499, 152.425, 133.473, 128.622, 123.604, 119.442, 112.422. MS MH^+ (rel int) 228.8 (98%) 230.8 (100%). Anal. Calcd for $\text{C}_7\text{H}_5\text{BrN}_2\text{S}$: C, 36.70; H, 2.20; Br, 34.88; N, 12.23; S, 14.00. Found: C, 36.92; H, 1.95; Br, 34.50; N, 12.04; S, 13.80.