Supporting Information

Syntheses of 2-Aryl Benzothiazoles via Photocatalyzed Oxidative condensation of Amines with 2-Aminothiophenol in the presence of BODIPY Derivatives

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Supporting Information

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1. General Information

Reagents and solvents were purchased as reagent-grade and used without further purification unless otherwise stated. **DCM was freshly distilled**. All ^1H and ^{13}C NMR spectra were recorded in CDCl_3 at room temperature on the spectrometer (400 MHz ^1H NMR, 100 MHz ^{13}C NMR) with tetramethylsilane as the internal standard.

Characterization Data of BODIPYs

BODIPY 1a (203mg, 25%).^[1] ^1H NMR (400 MHz, CDCl_3): δ =7.68 (d, 2H, J = 4.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 5.99 (s, 2H), 2.55 (s, 6H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ =155.9, 142.9, 140.0, 134.0, 132.5, 131.2, 129.8, 123.3, 121.5, 14.5, 13.4; EI-MS: m/z =402[M]⁺.

BODIPY 1b (180mg, 23%).^[1] ^1H NMR (400 MHz, CDCl_3): δ =7.35-7.53 (m, 3H,), 5.99 (s, 2H), 2.55 (s, 6H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ =156.5, 141.8, 134.9, 134.7, 133.0, 131.0, 130.4, 128.2, 121.4, 14.2, 13.3; EI-MS: m/z =392[M]⁺.

BODIPY 2a (77mg, 79%).^[2] ^1H NMR (400 MHz, CDCl_3): δ =7.68 (d, 2H, J = 4.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 6.07 (s, 2H), 2.60 (s, 3H), 2.57 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ =158.4, 152.0, 144.8, 142.9, 140.1, 138.6, 133.6, 132.6, 129.8, 123.6, 121.5, 14.8, 14.7, 13.8, 13.6; EI-MS: m/z =482[M]⁺. Anal Calcd for $\text{C}_{19}\text{H}_{17}\text{BBBr}_2\text{F}_2\text{N}_2$: C, 47.5; H, 3.56; N, 5.81; Found: C, 47.39; H, 3.64; N, 5.76.

BODIPY 2b (64mg, 76%).^[2] ^1H NMR (400 MHz, CDCl_3): δ =7.35-7.53 (m, 3H,), 5.99 (s, 1H), 2.60 (s, 3H), 2.57 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ =158.4, 152.0, 144.8, 142.6, 140.5, 138.8, 133.7, 131.7, 130.9, 129.6, 127.8, 122.3, 110.6, 14.8, 14.7, 13.8, 13.6; EI-MS: m/z =472[M]⁺. Anal Calcd for $\text{C}_{19}\text{H}_{16}\text{BBBrCl}_2\text{F}_2\text{N}_2$: C, 48.5; H, 3.42; N, 5.93; Found: C, 48.49; H, 3.48; N, 5.91.

BODIPY 3a (106mg, 94%). ^1H NMR (400 MHz, CDCl_3): δ =7.68 (d, 6H, 4.0 Hz), 7.16 (d, 2H, 8.0 Hz), 2.61 (s, 6H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ =154.5, 140.4, 138.4, 136.3, 133.4, 131.4, 130.1, 124.0, 122.1, 14.1, 13.7; EI-MS: m/z =561[M]⁺; Anal Calcd for $\text{C}_{19}\text{H}_{16}\text{BBBr}_3\text{F}_2\text{N}_2$: C, 40.8; H, 2.88; N, 4.99; Found: C, 40.65; H, 3.44; N, 4.96.

BODIPY 3b (101.4mg, 92%). ^1H NMR (400 MHz, CDCl_3): δ =7.35-7.53 (m, 3H,), 2.61 (s, 6H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ =154.5, 140.4, 138.4, 133.7, 131.7, 130.9, 129.6, 127.8, 122.3, 110.6, 14.1, 13.7; EI-MS: m/z =551[M]⁺. Anal Calcd for $\text{C}_{19}\text{H}_{15}\text{BBBr}_2\text{Cl}_2\text{F}_2\text{N}_2$: C, 41.6; H, 2.75; N, 5.08. Found: C, 41.48; H, 3.28; N, 5.01.

Characterization Data for Selected Compounds

2-Phenylbenzothiazole (**6a**).^[3] ¹H NMR (400 MHz, CDCl₃): δ=8.06–8.09 (m, 3H), 7.87 (d, J = 7.6 Hz, 1H), 7.45–7.50 (m, 4H), 7.36 (t, J = 7.6 Hz, 1H); ¹³C NMR(100 MHz, CDCl₃): δ=168.0, 154.0, 134.9, 133.5, 130.9, 128.9, 127.5, 126.2, 125.2, 123.1, 121.6; HRMS (EI)m/z calcd for C₁₃H₉NS: 211.0456, found 211.0445; Anal. Calcd for C₁₃H₉NS Elemental Analysis: C, 73.90; H, 4.29; N, 6.63; Found: C, 73.98; H, 4.41; N, 6.50.

2-(2-Fluorophenyl)benzothiazole (**6b**).^[4] ¹H NMR (400 MHz, CDCl₃): δ=8.44(t, 1H, J = 7.6 Hz), 8.13 (d, 1H, J = 8.0 Hz), 7.95 (d, 1H, J = 8.0 Hz), 7.42–7.54 (m, 3H), 7.27 (t, 1H, J = 7.6 Hz), 7.24 (d, 1H, J = 7.6 Hz); ¹³C NMR(100 MHz, CDCl₃): δ=161.7, 161.0, 159.2, 152.5, 135.7, 135.6, 132.2, 132.1, 129.7, 126.3, 125.3, 124.7, 124.6, 123.2, 121.4, 116.5, 116.3; EI-MS:m/z, calcd for C₁₃H₈NFS: 229.0361, found 229.0361; Anal. Calcd for C₁₃H₈NFS. Elemental Analysis: C, 68.10; H, 3.52; N, 6.11; Found: C, 68.22; H, 3.61; N, 6.00.

2-(2-Methylphenyl) benzothiazole (**6c**).^[4] ¹H NMR (400 MHz, CDCl₃): δ=8.13 (d, 1H, J = 8.8 Hz), 7.94 (d, 1H, J = 8.8 Hz), 7.78 (d, 1H, J = 8.8 Hz), 7.51 (t, 1H, J = 9.2 Hz), 7.33–7.44 (m, 4H), 2.69 (s, 3H); ¹³C NMR(100 MHz, CDCl₃): δ=167.9, 153.7, 137.2, 135.5, 133.0, 131.5, 130.5, 129.9, 126.1, 126.0, 125.0, 123.3, 121.3, 21.3; EI-MS:m/z, calcd for C₁₄H₁₁NS: 225.0612, found 225.0606; Anal. Calcd for C₁₄H₁₁NS; Elemental Analysis: C, 74.63; H, 4.92; N, 6.22; Found: C, 74.75; H, 5.01; N, 6.02.

2-(2-Methoxyphenyl)benzothiazole (**6d**).^[3] ¹H NMR (400 MHz, CDCl₃): δ=8.50 (d, 1H, J = 8.8 Hz), 8.06 (d, J = 8.4 Hz, 1H), 7.89 (d, 1H, J = 8.4 Hz), 7.43–7.47 (m, 2H), 7.33 (t, 1H, J = 8.0 Hz), 7.10 (t, 1H, J = 7.6 Hz), 7.01 (d, 1H, J = 8.4 Hz), 4.00 (s, 3H); ¹³C NMR(100 MHz, CDCl₃): δ=163.1, 157.1, 152.0, 136.0, 131.7, 129.4, 125.8, 124.5, 122.7, 122.1, 121.2, 121.1, 111.5, 55.6; EI-MS:m/z, calcd for C₁₄H₁₁NOS: 241.0561, found 241.0552.

2-(2-Ethoxyphenyl)benzothiazole (**6e**).^[4] ¹H NMR (400 MHz, CDCl₃): δ=8.57 (d, 1H, J = 9.6 Hz), 8.10 (d, 1H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.49 (t, 1H, J = 9.2 Hz), 7.42 (t, 1H, J = 8.8 Hz), 7.39 (t, 1H, J = 8.0 Hz), 7.12 (t, 1H, J = 7.6 Hz), 7.04 (d, 1H, J = 8.0 Hz), 4.29 (q, 2H, J = 6.8 Hz), 1.65 (t, 3H, J = 6.8 Hz); ¹³C NMR(100 MHz, CDCl₃): δ=163.2, 156.6, 152.0, 136.1, 131.7, 129.4, 125.8, 124.5, 122.7, 122.2, 121.2, 120.9, 112.2, 64.9, 14.9; EI-MS:(m/z)=255 (M⁺)

2-(3-Chlorophenyl)benzothiazole (**6f**).^[4] ¹H NMR (400 MHz, CDCl₃): δ=8.07–8.11 (t, 2H), 7.89–7.94 (t, 2H), 7.51 (t, 1H, J = 6.0 Hz), 7.40–7.48 (m, 3H); ¹³C NMR(100 MHz, CDCl₃): δ=166.2, 153.9, 135.2, 135.1, 135.0, 130.8, 130.2, 127.3, 126.5, 125.6, 125.5, 123.4, 121.7; EI-MS: m/z, calcd for C₁₃H₈ClNS: 245.0066, found 245.0060.

2-(4-Fluorophenyl)benzothiazole (**6g**).^[3] ¹H NMR (400 MHz, CDCl₃): δ=8.05–8.09 (m, 3H), 7.89 (d, 1H, J = 7.6 Hz), 7.49 (t, 1H, J = 7.6 Hz), 7.39 (t, 1H, J = 8.4 Hz), 7.15–7.17 (d, 2H, J = 8.8 Hz); ¹³C NMR(100 MHz, CDCl₃): δ=166.7, 165.6, 163.1, 154.0, 135.0, 129.8, 129.4, 129.4, 126.3, 125.2, 123.1, 121.5, 116.2, 116.1; EI-MS:m/z, calcd for C₁₃H₈NFS: 229.0361, found 229.0366.

2-(4-Methylphenyl)benzothiazole (**6h**). ^[4] ¹H NMR (400 MHz, CDCl₃): δ=8.07 (d, 1H, J = 8.0 Hz), 8.00 (t, 2H, J = 8.0 Hz), 7.89 (d, 1H, J = 8.4 Hz), 7.49 (t, 1H, J = 9.6 Hz), 7.38 (t, 1H, J = 8.4 Hz), 7.30 (d, 2H, J = 7.6 Hz), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=168.2, 154.1, 141.4, 134.9, 130.9, 129.7 (2C), 127.4 (2C), 126.2, 125.0, 123.0, 121.5, 21.5; EI-MS: m/z, calcd for C₁₄H₁₁NS: 225.0612, found 225.0606.

2-(4-Bromophenyl)benzothiazole (**6i**). ^[4] ¹H NMR (400 MHz, CDCl₃): δ=8.07 (d, 1H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.8 Hz), 7.90 (d, 1H, J = 8.8 Hz), 7.61 (d, 2H, J = 8.8 Hz), 7.50 (t, 1H, J = 8.0 Hz), 7.40 (t, 1H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ=166.7, 154.0, 135.0, 132.4, 132.2, 128.8, 126.5, 125.4, 123.2, 121.6; EI-MS (m/z)=289 (M⁺).

2-(4-Chlorophenyl)benzothiazole (**6j**). ^[3] ¹H NMR (400 MHz, CDCl₃): δ=8.07 (d, 1H, J = 8.8 Hz), 8.00 (d, 2H, J = 8.4 Hz), 7.90 (d, 1H, J = 8.8 Hz), 7.50 (d, 2H, J = 8.8 Hz), 7.45 (t, 1H, J = 8.8 Hz), 7.40 (t, 1H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ=166.6, 154.0, 137.0, 135.0, 132.0, 129.2, 128.7, 126.5, 125.4, 123.2, 121.6; EI-MS :m/z, calcd for C₁₃H₈ClNS: 245.0066, found 245.0061.

2-(2, 4-Dimethylphenyl)benzothiazole (**6k**). ^[5] ¹H NMR (400 MHz, CDCl₃): δ=8.12 (d, 1H, J = 8.0 Hz), 7.93 (t, 1H, J = 8.0 Hz), 7.71 (d, 1H, J = 7.6 Hz), 7.51 (t, 1H, J = 7.6 Hz), 7.41 (t, 1H, J = 7.6 Hz), 7.18 (s, 1H), 7.09 (d, 1H, J=8.0 Hz), 2.68 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=168.1, 153.7, 140.1, 137.0, 135.4, 132.3, 130.5, 130.2, 126.8, 126.0, 124.8, 123.1, 121.2, 21.3, 21.2; EI-MS: m/z, calcd for C₁₅H₁₃NS: 239.0769, found 239.0764.

2-(2, 4-Dimethoxyphenyl)benzothiazole (**3l**). ^[4] ¹H NMR (400 MHz, CDCl₃): δ=8.48 (d, 1H, J = 8.4 Hz), 8.06 (d, 1H, J = 8.0 Hz), 7.91 (d, 1H, J = 8.0 Hz), 7.47 (t, 1H, J = 7.6 Hz), 7.31 (t, 1H, J = 7.2 Hz), 6.67 (d, 1H, J = 8.8 Hz), 6.57 (s, 1H), 4.02 (s, 3H), 3.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ=163.2, 162.8, 158.5, 152.1, 135.6, 130.7, 125.7, 124.1, 122.2, 121.1, 115.5, 105.8, 98.4, 55.6, 55.5; EI-MS (m/z)=271 (M⁺).

2-(Naphthalen-1-yl)benzothiazole (**3m**). ^[6] ¹H NMR (400 MHz, CDCl₃): δ=8.97 (d, 1H, J = 8.4 Hz); 8.23 (d, 1H, J = 8.0 Hz), 7.98 (t, 2H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.0 Hz), 7.63 (t, 1H, J = 6.8 Hz), 7.57–7.60 (m, 3H), 7.47 (t, 1H, J = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ=167.6, 154.1, 135.4, 133.9, 131.0, 130.7, 130.5, 129.3, 128.4, 127.6, 126.5, 126.2, 125.8, 125.2, 124.9, 123.5, 121.3; EI-MS: m/z, calcd for C₁₇H₁₁NS: 261.0612, found 261.0604.

2-(Thiophen-2-yl)benzothiazole (**3n**). ^[3] ¹H NMR (400 MHz, CDCl₃): δ=8.03 (d, 1H, J = 8.0 Hz), 7.85 (d, 1H, J = 8.0 Hz), 7.66 (d, 1H, J = 2.8 Hz), 7.51 (d, 1H, J = 4.0 Hz), 7.48 (t, 1H, J = 8.0 Hz), 7.38 (t, 1H, J = 7.6 Hz), 7.14 (t, 1H, J = 4.4 Hz); ¹³C NMR (100 MHz, CDCl₃): δ=161.4, 153.6, 137.3, 134.6, 129.3, 128.6, 128.0, 126.4, 125.2, 122.9, 121.4; EIMS: m/z, calcd for C₁₁H₇NS₂: 217.0020, found 217.0030; Anal. Calcd for C₁₁H₇NS₂ Elemental Analysis: C, 60.80; H, 3.25; N, 6.45; Found: C, 60.92; H, 3.34; N, 6.32.

2. ^1H and ^{13}C NMR Spectra

^1H and ^{13}C NMR Spectra for 3a

^1H and ^{13}C NMR Spectra for 2a

^1H and ^{13}C NMR Spectra for 6a

^1H and ^{13}C NMR Spectra for 6b

^1H and ^{13}C NMR Spectra for 6c

^1H and ^{13}C NMR Spectra for 6d

^1H and ^{13}C NMR Spectra for 6e

Chemical structure: Clc1ccc(cc1)-c2nc3ccccc3s2

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (7.2-8.2 ppm). Integration values are provided below the peaks: 1.81, 1.89, 1.08, and 2.88.

^1H and ^{13}C NMR Spectra for 6g

¹H and ¹³C NMR Spectra for 6h

Brc1ccc(cc1)-c2nc3ccccc3s2

¹H NMR spectrum (CDCl₃) of 2-(4-bromophenyl)benzothiazole. The spectrum displays aromatic signals in the range of 7.2–8.1 ppm and aliphatic signals in the range of 1.0–2.0 ppm. Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
8.077	1.00
8.058	2.03
7.962	2.19
7.957	1.00
7.934	1.00
7.907	1.00
7.889	
7.631	
7.629	
7.616	
7.604	
7.525	
7.507	
7.504	
7.421	
7.401	
7.399	
7.383	
7.380	
7.261	
1.079	
1.057	
0.962	
0.945	
0.940	
0.907	
0.889	
0.857	
0.831	
0.826	
0.810	
0.794	
0.769	
0.525	
0.507	
0.504	
0.483	
0.471	
0.418	
0.399	
0.380	
0.261

^1H and ^{13}C NMR Spectra for 6j

^1H and ^{13}C NMR Spectra for 6k

^1H and ^{13}C NMR Spectra for 6l

^1H and ^{13}C NMR Spectra for 6m

^1H and ^{13}C NMR Spectra for 6n

REFERENCES

1. Jiao, L.J.; Yu, C.; Li, J.; Wang, Z.; Wu, M.; Hao, E. *J. Org. Chem.* **2009**, *74*, 525-528.
2. Ye, J. H.; Wang, G. P.; Huang, C. M.; Hu, Z. J.; Zhang, W. C.; Zhang, Y. *Synthesis*. **2012**, *44*, 104-110.
3. Canivet, J.; Yamaguchi, J.; Ban, I.; Itami, K. *Org. Lett.* **2009**, *11*, 1733-1736.
4. Yang, Z. Y.; Chen, X.; Wang, S. Z.; Liu, J. D.; Xie, K.; Wang, A. W.; Tan, Z. *J. Org. Chem* **2012**, *77*, 7086-7091.
5. Cheng, Y. N.; Yang, J.; Qu, Y.; Li, P. X. *Org. Lett.* **2012**, *14*, 98-101.
6. Zhao, X.; Wu, G. J.; Zhang, Y.; Wang, J. B. *J. Am. Chem. Soc.* **2011**, *133*, 3296-3299.