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Supporting Information

for

**Synthesis of photo- and ionochromic *N*-acylated 2-aminomethylenebenzo[*b*]thiophene-3(2*Н*)-ones with a terminal phenanthroline group**

Vladimir P. Rybalkin, Sofiya Yu. Zmeeva, Lidiya L. Popova, Irina V. Dubonosova,

Olga Yu. Karlutova, Oleg P. Demidov, Alexander D. Dubonosov and Vladimir A. Bren

**Experimental procedures and characterization data**

**for all novel compounds 1, 2a–c, 3a–c**

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**Synthesis**

(*E*)-2-(((1,10-Phenanthrolin-5-yl)amino)methylene)benzo[*b*]thiophen-3(2*H*)-one **(1)**

5-Aminophenanthroline (1.95 g, 10 mmol) was dissolved by boiling in a minimal amount of acetonitrile. To the resulting hot solution, 1.78 g (10 mmol) of 3-hydroxybenzo[*b*]thiophene-2-carbaldehyde [1S] was added, followed by 3 mL of acetic acid. The obtained mixture was refluxed for 15-20 min, the precipitate that formed was filtered off, washed with acetonitrile and recrystallized from DMF. Yield 2.63 g (74%), mp 231–234°С (DMF). IR spectrum, ν, cm–1: 1619 (C=O), 1637 (C=O), 3688-3060 (NH). 1H NMR spectrum (CDCl3), δ, ppm: 7.31 td (1НAr, *J1* 7.4 Hz, *J2* 1.0 Hz), 7.40-7.59 m (2HAr, 2Hphen), 7.75 dd (1Нphen, *J1* 8.3 Hz, *J2* 4.2 Hz), 7.98 d (1НAr, *J* 7.6 Hz), 8.10 s (1H, CH), 8.12 dd (1Hphen, *J1* 8.2 Hz, *J2* 1.6 Hz), 8.68 dd (1Hphen, *J1* 8.3 Hz, *J2* 1.6 Hz), 9.07dd (1Hphen, *J1* 4.3 Hz, *J2* 1.7 Hz), 9.24 dd (1Hphen, *J1* 4.3 Hz, *J2* 1.5 Hz), 13.31 br. s (1H, NH). 13С NMR spectrum (CDCl3), δC, ppm: 108.41, 108.72, 122.04, 123.44, 123.71, 123.85, 124.59, 125.62, 128.48, 129.62, 132.85, 133.10, 133.98, 134.97, 140.21, 144.16, 145.56, 146.70, 149.36, 150.97, 187.10. HRMS (ESI), *m/z*: found, 378.0677 [*M*+Na]+. C21H13N3OS. Calculated, 378.0964 [*M*+Na]+.

(*Z*)-*N*-((3-Oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-*N*-(1,10-phenanthrolin-5-yl)acetamide **(2a)**

Compound **1** (0.1 g, 2.5 mmol) was dissolved by boiling in (MeCO)2O (0.5 mL) containing 0.1 mL of triethylamine. The yellow solid that precipitated after cooling was filtered off and washed thoroughly with methanol. Yield 0.1 g (89%), mp 302–304°С (MeCO)2O). IR spectrum, ν, cm–1: 1663 (C=O), 1705 (C=O). 1H NMR spectrum (CDCl3), δ, ppm: 2.07 br. s (3H, CH3), 6.84 d (1НAr, *J* 8.0 Hz), 7.02 т (1HAr, *J* 7.5 Hz), 7.27 t (1HAr, *J* 6.6 Hz), 7.68 dd (1Нphen, *J1* 8.3 Hz, *J2* 4.3 Hz), 7.74-7.78 m (2Нphen), 7.93 s (1H, CH), 8.08 d (1HAr, *J* 8.2 Hz), 8.35 dd (1Нphen, *J1* 8.0 Hz, *J2* 1.5 Hz), 9.11 br. s (1Нphen), 9.27 dd (1Нphen, *J1* 4.2 Hz, *J2* 1.6 Hz), 9.34 dd (1Нphen, *J1* 4.3 Hz, *J2* 1.7 Hz). 13С NMR spectrum (CDCl3), δC, ppm: 22.62, 114.22, 123.19, 124.03, 124.30, 125.06, 126.33, 126.63, 127.38, 128.92, 130.54, 130.74, 132.14, 132.43, 134.57, 136.92, 145.74, 146.78, 146.91, 151.61, 152.30, 170.16, 188.82. HRMS (ESI), *m/z*: found, 398.0963 [*M*+H]+. C23H16N3O2S. Calculated, 398.0958 [*M*+H]+.

(*Z*)-*N*-((3-Oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-*N*-(1,10-phenanthrolin-5-yl)propionamide **(2b)**

Compound **1** (0.11 g, 2.8 mmol) was dissolved by boiling in (MeCH2CO)2O (0.5 mL) containing 0.1 mL of triethylamine. The yellow solid that precipitated after cooling was filtered off and thoroughly washed with methanol. Yield 0.105 g (83%), mp 309–310°С (С2Н5CO)2O). IR spectrum, ν, cm–1: 1665 (C=O), 1712 (C=O). 1H NMR spectrum (CDCl3), δ, ppm: 1.09 t (3H, СH3), 2.12 br. s (1H, CH2), 2.45 br. s (1H, CH2), 6.84 d (1НAr, *J* 8.0 Hz), 7.08 t (1HAr, *J* 8.4 Hz), 7.26 t (1H, Ar, *J* 6.5 Hz),7.68 dd (1Н, Het, *J1* 8.3 Hz, *J2* 4.3 Hz), 7.75-7.78 m (2Нphen), 7.92 s (1H, CH), 8.06 dd (1Hphen, *J1* 8.3 Hz, *J2* 1.6 Hz), 8.35 dd (1Hphen, *J1* 8.0 Hz, *J2* 1.7 Hz), 9.15 br. s (1Hphen), 9.27 dd (1Hphen, *J1* 4.3 Hz, *J2* 1.6 Hz), 9.34 dd (1Hphen, *J1* 4.3 Hz, *J2* 1.6 Hz). 13С NMR spectrum (CDCl3), δC, ppm: 8.98, 28.18, 113.87, 123.17, 124.00, 124.29 125.01, 126.30, 126.77, 127.39, 129.01, 130.60, 130.73, 132.09, 132.37, 134.49, 136.90, 145.78, 146.77, 146.89, 151.57, 152.25, 173.69, 188.84. HRMS (ESI), *m/z*: found, 412.1121 [*M*+H]+. C24H18N3O2S. Calculated, 412.1114 [*M*+H]+.

(*Z*)-*N*-((3-Oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)-*N*-(1,10-phenanthrolin-5-yl)-2-phenylacetamide **(2c)**

To a suspension of compound **1** (0.6 g, 1.68 mmol) in 200 mL of acetonitrile containing 1.5 mL of triethylamine, 0.75 mL of phenylacetic acid chloride was added and refluxed until the precipitate dissolved. The yellow solid gradually formed. The precipitate was filtered off, washed with acetonitrile and recrystallized from DMF.

Yield 0.54 g (68%), mp 301–302°С (DMF). IR spectrum, ν, cm–1: 1668 (C=O), 1731 (C=O). 1H NMR spectrum (CDCl3), δ, ppm: 3.40-3.80 br. m (2H, CH2), 6.70-6.90 br. m (3HAr), 7.05-7.18 m (4HAr), 7.26 m (1HAr), 7.54 dd (1Нphen, *J1* 8.3 Hz, *J2* 4.3 Hz), 7.68 s (1Hphen), 7.74-7.76 m (1HAr, 1Hphen), 7.90 br m (1НAr), 8.22 dd (1Hphen, *J1* 8.0 Hz, *J2* 1.6 Hz), 9.15 br. s (1H, CH), 9.22 dd (1Hphen, *J1* 4.3 Hz, *J2* 1.6 Hz), 9.35 dd (1Hphen, *J1* 4.3 Hz, *J2* 1.7 Hz). 13С NMR spectrum (CDCl3), δC, ppm: 41.91, 114.53, 123.13, 123.95, 124.06, 125.02, 126.30, 126.73, 127.11, 127.41, 128.63, 128.74, 129.60, 130.42, 130.62, 131.57, 132.32, 132.90, 134.53, 136.88, 145.71, 146.61, 146.73, 151.41, 152.30, 170.65, 188.74. HRMS (ESI), *m/z*: found, 474.1272 [*M*+H]+. C29H20N3O2S. Calculated, 474.1271 [*M*+H]+.

*O*-Acylated photoproducts **3a-c**

A suspension of yellow solids **2a**, **2b** or **2c** (20 mg) in 1 mL of acetonitrile was refluxed for 10-15 s, then irradiated with a Sweko IP65 led emitter (SUL-S1-20W-230-4000K-WH) for 3-5 min. The procedure was repeated up to 10 times until complete dissolution. Colorless solids of **3a**, **3b** or **3c** gradually precipitated. They were filtered and washed with acetonitrile.

(*E*)-2(((1,10-Phenanthrolin-5-yl)imino)methyl)benzo[*b*]thiophen-3-yl acetate (**3a)**

Yield 16 mg (80%), mp 219–221°С (СН3CN). IR spectrum, ν, cm–1: 1757 (C=O). 1H NMR spectrum (CDCl3), δ, ppm: 2.47 s (3H, OMe), 7.31 s (1Нphen) 7.41 t (1HAr, *J* 7.6 Hz), 7.47 t (1HAr, *J* 7.4 Hz), 7.56-7.61 m (2Нphen), 7.65 dd (1Нphen, *J1* 8.2 Hz, *J2* 4.2 Hz), 7.83 d (1HAr, *J* 8.0 Hz), 8.20 dd (1Hphen, *J1* 8.0 Hz, *J2* 1.2 Hz), 8.73 dd (1Hphen, *J1* 8.2 Hz, *J2* 1.4 Hz), 8.77 s (1H, CH), 9.10 dd (1Hphen, *J1* 4.1 Hz, *J2* 1.3 Hz) 9.20 dd (1Hphen, *J1* 4.1 Hz, *J2* 1.4 Hz). 13С NMR spectrum (CDCl3), δC, ppm: 20.59, 110.91, 121.70, 122.97, 123.25, 123.36, 125.07, 126.03, 127.76, 128.73, 128.86, 132.63, 132.82, 135.77, 138.67, 144.51, 145.48, 146.33, 147.08, 149.51, 150.79, 151.35, 168.28. HRMS (ESI), *m/z*: found, 398.0962 [*M*+H]+. C23H16N3O2S. Calculated, 398.0958 [*M*+H]+.

(*E*)-2(((1,10-Phenanthrolin-5-yl)imino)methyl)benzo[*b*]thiophen-3-yl propionate **(3b)**

Yield 15 mg (75%), mp 225–227°С (СН3CN). IR spectrum, ν, cm–1: 1764 (C=O). 1H NMR spectrum (CDCl3), δ, ppm: 1.36 t (3H, Me, *J* 7.6 Hz), 2.79 q (2H, OCH2, *J* 7.6 Hz), 7.31 s (1Нphen), 7.41 t (1HAr, *J* 7.6 Hz), 7.47 t (1HAr, J 7.7 Hz), 7.57-7.60 m (2Нphen), 7.65 dd (1Нphen, *J1* 8.2 Hz, *J2* 4.3 Hz), 7.83 d (1HAr, *J* 8.1 Hz), 8.22 dd (1Hphen, *J1* 8.0 Hz, *J2* 1.6 Hz), 8.74 dd (1Hphen, *J1* 8.2 Hz, *J2* 1.7 Hz), 8.76 s (1H, CH), 9.11 dd (1Hphen, *J1* 4.3 Hz, *J2* 1.7 Hz) 9.21dd (1Hphen, *J1* 4.3 Hz, *J2* 1.7 Hz). 13С NMR spectrum (CDCl3), δC, ppm: 9.25, 27.45, 110.87, 121.70, 122.97, 123.24, 123.36, 125.04, 126.03, 127.73, 128.75, 128.80, 132.71, 132.83, 135.75, 138.71, 144.67, 145.51, 146.36, 147.18, 149.52, 150.82, 151.38, 171.89. HRMS (ESI), *m/z*: found, 412.1119 [*M*+H]+. C24H18N3O2S. Calculated, 412.1114 [*M*+H]+.

(*E*)-2(((1,10-Phenanthrolin-5-yl)imino)methyl)benzo[*b*]thiophen-3-yl phenylacetate (**3c)**

Yield 17 mg (85%), mp 221–224°С (СН3CN). IR spectrum, ν, cm–1: 1750 (C=O). 1H NMR spectrum (CDCl3), δ, ppm: 4.00 s (2H, OCH2), 7.09 s (1Нphen), 7.16-7.46 м (8HAr), 7.60-7.66 m (2HAr), 7.80 d (1HAr, *J* 8.1 Hz), 8.19 dd (1Hphen, *J1* 8.0 Hz, *J2* 1.5 Hz), 8.45 s (1H, CH), 8.71 dd (1Hphen, *J1* 8.2 Hz, *J2* 1.7 Hz), 9.13 dd (1Hphen, *J1* 4.3 Hz, *J2* 1.6 Hz), 9.20 dd (1Hphen, *J1* 4.2 Hz, *J2* 1.4 Hz). 13С NMR spectrum (CDCl3), δC, ppm: 41.39, 110.87, 121.64, 122.95, 123.21, 123.30, 125.07, 126.05, 127.70, 127.83, 128.66, 128.89, 128.99, 129.28, 132.58, 132.80, 132.96, 135.70, 138.65, 144.55, 145.51, 146.31, 146.91, 149.52, 150.77, 151.15, 168.99. HRMS (ESI), *m/z*: found, 474.1273 [*M*+H]+. C29H20N3O2S. Calculated, 474.1271 [*M*+H]+.

**Reference**

1S. Bren; V. A., Usacheva, V. I.; Minkin, V. I. *Chem. Heterocycl. Compd.* **1972**, *8*, 836-840. doi: 10.1007/BF00475214