Supporting Information

for

Synthesis of photo- and ionochromic N-acylated 2-(aminomethylene)benzo[b]thiophene-3(2H)-ones with a terminal phenanthroline group


Experimental procedures and characterization data for all new compounds 1, 2a–c and 3a–c
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Synthesis

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

5-Aminophenanthroline (1.95 g, 10 mmol) was dissolved in 50 mL of acetonitrile by means of stirring under reflux conditions. To the resulting hot solution, 1.78 g (10 mmol) of 3-hydroxybenzo[b]thiophene-2-carbaldehyde [1] was added, followed by 3 mL of acetic acid. The obtained mixture was refluxed for 15–20 min and then cooled to room temperature. The precipitate that formed was filtered, washed with acetonitrile (3 × 5 mL) and recrystallized from DMF. Yield 2.63 g (74%), mp 231–234°C (DMF). IR spectrum, ν, cm⁻¹: 1619 (C=O), 1637 (C=O), 3688–3060 (NH). ¹H NMR spectrum (CDCl₃), δ, ppm: 7.31 td (1H Ar, J₁ 7.4 Hz, J₂ 1.0 Hz), 7.40–7.59 m (2H Ar, 2H phen), 7.75 dd (1H phen, J₁ 8.3 Hz, J₂ 4.2 Hz), 7.98 d (1H Ar, J 7.6 Hz), 8.10 s (1H, CH), 8.12 dd (1H phen, J₁ 8.2 Hz, J₂ 1.6 Hz), 8.68 dd (1H phen, J₁ 8.3 Hz, J₂ 1.6 Hz), 9.07 dd (1H phen, J₁ 4.3 Hz, J₂ 1.7 Hz), 9.24 dd (1H phen, J₁ 4.3 Hz, J₂ 1.5 Hz), 13.31 br. s (1H, NH). ¹³C NMR spectrum (CDCl₃), δ, ppm: 108.4, 108.7, 122.0, 123.4, 123.7, 123.9, 124.6, 125.6, 128.5, 129.6, 132.9, 133.1, 134.0, 1354.0, 140.2, 144.2, 145.6, 146.7, 149.4, 151.0, 187.1. HRMS (ESI), m/z: found, 378.0677 [M+Na]⁺. C₂₁H₁₃N₃OS. Calculated, 378.0964 [M+Na]⁺.

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

Compound 1 (0.1 g, 2.5 mmol) was dissolved in 0.5 mL (MeCO)₂O containing 0.1 mL of triethylamine by means of stirring under reflux conditions. The reaction mixture was refluxed for 5–10 min and then cooled to room temperature. The yellow solid that precipitated after cooling to room temperature was filtered, washed with methanol (3 × 1 mL) and recrystallized from acetic anhydride. Yield 0.1 g (89%), mp 302–304°C ((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 (1H Ar, J 8.0 Hz), 7.02 t (1H Ar, J 7.5 Hz), 7.27 t (1H Ar,
\( J \ 6.6 \text{ Hz} \), 7.68 dd (1\(^H\)phen, \( J_1 \ 8.3 \text{ Hz} \), \( J_2 \ 4.3 \text{ Hz} \)), 7.74-7.78 m (2\(^H\)phen), 7.93 s (1H, CH), 8.08 d (1\(^H\)Ar, \( J \ 8.2 \text{ Hz} \)), 8.35 dd (1\(^H\)phen, \( J_1 \ 8.0 \text{ Hz} \), \( J_2 \ 1.5 \text{ Hz} \)), 9.11 br. s (1\(^H\)phen), 9.27 dd (1\(^H\)phen, \( J_1 \ 4.2 \text{ Hz} \), \( J_2 \ 1.6 \text{ Hz} \)), 9.34 dd (1\(^H\)phen, \( J_1 \ 4.3 \text{ Hz} \), \( J_2 \ 1.7 \text{ Hz} \)). \(^{13}\)C NMR spectrum (CDCl\(_3\)), \( \delta_c \), ppm: 22.6, 114.2, 123.2, 124.0, 124.3, 125.1, 126.3, 126.6, 127.4, 128.9, 130.5, 130.7, 132.1, 132.4, 134.6, 136.9, 145.7, 146.8, 146.9, 151.6, 152.3, 170.2, 188.8.

HRMS (ESI), \( m/z \): found, 398.0963 [\( M+H \)]\(^+\). \( C_{23}H_{16}N_3O_2S \). Calculated, 398.0958 [\( M+H \)]\(^+\).

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

Compound 1 (0.11 g, 2.8 mmol) was dissolved in 0.5 mL (Me\( \text{CH}_2\)CO\(_2\)O containing 0.1 mL of triethylamine by means of stirring under reflux conditions. The reaction mixture was refluxed for 10 min and then cooled to room temperature. The yellow solid that precipitated after cooling was filtered, washed with acetonitrile (3 \( \times \) 5 mL) and recrystallized from propionic anhydride. Yield 0.105 g (83%), mp 309–310°C ((\( C_2\text{H}_5\)CO)\(_2\)O. IR spectrum, \( \nu \), cm\(^{-1}\): 1665 (C=O), 1712 (C=O). \(^1\)H NMR spectrum (CDCl\(_3\)), \( \delta \), ppm: 1.09 t (3H, CH\(_3\)), 2.12 br. s (1H, CH\(_2\)), 2.45 br. s (1H, CH\(_2\)), 6.84 d (1\(^H\)Ar, \( J \ 8.0 \text{ Hz} \)), 7.08 t (1\(^H\)Ar, \( J \ 8.4 \text{ Hz} \)), 7.26 t (1H, Ar, \( J \ 6.5 \text{ Hz} \)), 7.68 dd (1H, Het, \( J_1 \ 8.3 \text{ Hz} \), \( J_2 \ 4.3 \text{ Hz} \)), 7.75-7.78 m (2\(^H\)phen), 7.92 s (1H, CH), 8.06 dd (1\(^H\)phen, \( J_1 \ 8.3 \text{ Hz} \), \( J_2 \ 1.6 \text{ Hz} \)), 8.35 dd (1\(^H\)phen, \( J_1 \ 8.0 \text{ Hz} \), \( J_2 \ 1.7 \text{ Hz} \)), 9.15 br. s (1\(^H\)phen), 9.27 dd (1\(^H\)phen, \( J_1 \ 4.3 \text{ Hz} \), \( J_2 \ 1.6 \text{ Hz} \)), 9.34 dd (1\(^H\)phen, \( J_1 \ 4.3 \text{ Hz} \), \( J_2 \ 1.6 \text{ Hz} \)). \(^{13}\)C NMR spectrum (CDCl\(_3\)), \( \delta_c \), ppm: 8.9, 28.2, 113.9, 123.2, 124.0, 124.3 125.0, 126.3, 126.8, 127.4, 129.0, 130.6, 130.7, 132.1, 132.4, 134.45, 136.9, 145.8, 146.8, 146.9, 151.6, 152.3, 173.7, 188.8. HRMS (ESI), \( m/z \): found, 412.1121 [\( M+H \)]\(^+\). \( C_{24}H_{18}N_3O_2S \). Calculated, 412.1114 [\( M+H \)]\(^+\).
(Z)-N-[(3-Oxobenzo[b]thiophen-2(3H)-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 phenylacetyl chloride was added at room temperature while stirring. The reaction mixture was refluxed for 10–15 min until the precipitate dissolved and then cooled to room temperature. The solution was left at room temperature for 10 h. Gradually, a fine crystalline yellow solid formed. The precipitate was filtered, washed with acetonitrile (3 × 1 mL) and recrystallized from DMF. Yield 0.54 g (68%), mp 301–302°C (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 (1Hₚhen, J₁ 8.3 Hz, J₂ 4.3 Hz), 7.68 s (1Hₚhen), 7.74-7.76 m (1Hₐr, 1Hₚhen), 7.90 br m (1Hₐr), 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). ¹³C NMR spectrum (CDCl₃), δC, ppm: 41.9, 114.5, 123.1, 124.0, 124.1, 125.0, 126.3, 126.7, 127.1, 127.4, 128.6, 128.7, 129.6, 130.4, 130.6, 131.6, 132.3, 132.9, 134.5, 136.88, 145.7, 146.6, 146.7, 151.4, 152.3, 170.7, 188.7. HRMS (ESI), m/z: found, 474.1272 [M+H]⁺. C₂₉H₂₀N₃O₂S. Calculated, 474.1271 [M+H]⁺.

O-Acylated photoproducts 3a–c

A suspension of a yellow solid 2a–c (20 mg) in 1 mL of acetonitrile was refluxed for 10–15 s and then irradiated with a Sweko IP65 led emitter (SUL-S1-20W-230-4000K-WH) for 3–5 min. This procedure was repeated up to 10 times until the starting material was completely dissolved. The colorless solid 3a–c gradually precipitated. Then the solid was filtered and washed with acetonitrile (3 × 0.5 mL).
(E)-2(((1,10-Phenanthrolin-5-yl)imino)methyl)benzo[b]thiophen-3-yl acetate (3a)

Yield 16 mg (80%), mp 219–221°C (CH₃CN). IR spectrum, ν, cm⁻¹: 1757 (C=O). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.47 s (3H, OMe), 7.31 s (1Hphen) 7.41 t (1HAr, J 7.6 Hz), 7.47 t (1HAr, J 7.4 Hz), 7.56-7.61 m (2Hphen), 7.65 dd (1Hphen, 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). ¹³C NMR spectrum (CDCl₃), δC, ppm: 20.6, 110.9, 121.7, 123.0, 123.3, 123.4, 125.0, 126.0, 127.8, 128.7, 128.9, 132.6, 132.8, 135.8, 138.7, 144.5, 145.5, 146.3, 147.1, 149.5, 150.79, 151.4, 168.3. 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°C (CH₃CN). 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 (1Hphen), 7.41 t (1HAr, J 7.6 Hz), 7.47 t (1HAr, J 7.7 Hz), 7.57-7.60 m (2Hphen), 7.65 dd (1Hphen, 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) 9.21 dd (1Hphen, J₁ 4.3 Hz, J₂ 1.7 Hz). ¹³C NMR spectrum (CDCl₃), δC, ppm: 9.3, 27.5, 110.9, 121.7, 123.0, 123.2, 123.4, 125.0, 126.0, 127.7, 128.8, 128.8, 132.7, 132.8, 135.8, 138.7, 144.7, 145.5, 146.4, 147.2, 149.5, 150.8, 151.4, 171.9. 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°C (CH₃CN). IR spectrum, ν, cm⁻¹: 1750 (C=O). ¹H NMR spectrum (CDCl₃), δ, ppm: 4.00 s (2H, OCH₂), 7.09 s (1Hphen), 7.16-7.46 m (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 (1H phen, J1 8.2 Hz, J2 1.7 Hz), 9.13 dd (1H phen, J1 4.3 Hz, J2 1.6 Hz), 9.20 dd (1H phen, J1 4.2 Hz, J2 1.4 Hz). $^{13}$C NMR spectrum (CDCl$_3$), δC, ppm: 41.4, 110.9, 121.6, 123.0, 123.2, 123.3, 125.1, 126.1, 127.7, 127.8, 128.7, 128.9, 129.0, 129.3, 132.6, 132.8, 133.0, 135.7, 138.7, 144.6, 145.5, 146.3, 146.9, 149.5, 150.8, 151.2, 169.0. HRMS (ESI), m/z: found, 474.1273 [M+H]$^+$. C$_{29}$H$_{20}$N$_3$O$_2$S. Calculated, 474.1271 [M+H]$^+$.  

References