

## The synthesis of new 3,4-(bisaryl)-1,8-naphthalimide and 2,3-(bisaryl)-7*H*-benzimidazo[2,1-*a*]benzo[*d*]isoquinolin-7-one compounds and an investigation of their photochromic properties

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**Abstract:** Three new photochromic compounds, 3-(2,5-dimethyl-3-thienyl)-4-(2-phenyl-5-methyl-4-thiazolyl)-1,8-naphthalimide (**1-O**), 2,3-bis(2-phenyl-5-methyl-4-thiazolyl)-7*H*-benzimidazo[2,1-*a*]benzo[*d*]isoquinolin-7-one (**2-O**), and 2,5-dimethyl-3-thienyl)-7*H*-benzimidazo[2,1-*a*]benzo[*d*]isoquinolin-7-one (**3-O**), were synthesized and their photochromic properties were studied. Compound **1-O** was synthesized by two consecutive Suzuki coupling reactions using 2,5-dimethylthiophene-3-boronic acid and 5-methyl-2-phenylthiazole-4-boronic acid. Photochromic compounds **2-O** and **3-O** were prepared by multistep reactions starting with 3-iodo-4-bromo-1,8-naphthalic anhydride and 2,5-dimethylthiophene-3-boronic acid or 2-phenyl-5-methylthiazole-4-boronic acid. All photochromic compounds showed a color change from colorless (or light yellow) to blue-green, purple, or orange colors (depending on the nature of the structures) on exposure to UV light at 365 nm in ethyl acetate solutions. The colored solutions can be reversed to the original colorless (or light yellow) solution by exposure to visible light at 530 nm.

**Key words:** Diarylethene, photochromism, 1,8-naphthalimide, 1,8-naphthalic anhydride, 7*H*-benzimidazo[2,1-*a*]benzo[*d*]isoquinolin-7-one

### 1. Introduction

Photochromic compounds usually have two forms, an open form (form O, generally colorless) and a closed form (form C, often colored). The structural and color changes in the photochromic molecules can be controlled by different wavelengths of light. The UV light is usually used for ring-closure photoreactions, and visible light is usually used for ring-opening photoreactions.<sup>1</sup>

Organic photochromic compounds such as fulgides, diarylethenes, and diarylethene related compounds have some possible industrial applications in actinometry, optical memory systems, information storage at a molecular level, molecular-level switches, etc.

Fulgides and diarylethenes are well-known photochromic compounds that show color change via electrocyclic reaction.<sup>2,3</sup> Diarylethenes are known to be more stable than fulgides with regard to thermal stability and fatigue resistance. They could be used for optical switches and in high-density optical recording materials. For optical recording application, it is very important to develop photochromic diarylethenes with different absorption wavelengths, especially with shorter absorption wavelengths, as the recording capacity is proportional to the wave laser wavelength.<sup>4–6</sup>

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Recently, many research groups studying photochromism have focused on synthesizing new types of photochromic systems that are related to diarylethenes. A major modification to diarylethenes has been made by replacing the ethene part in the diarylethenes with other suitable ring systems that act with ethene-like behavior. Some synthesized examples of recently reported photochromic compounds within this framework include bisarylthiazole/phenylthiazoles, bisarylthiophenes, bisarylindenone/indenols, bisarylcoumarin, bisarylbenz[f]indenones/benz[f]indenols, bisarylcyclopentenones, bisarylnaphthoquinones, bisarylazulene, and bisarylpyridazinone.<sup>7–22</sup>

1,8-Naphthalimide derivatives are of interest due to their promising useful photophysical and biological properties. Most of these properties concern the planar shape and the efficient optimal dimensions. In addition, they are particularly attractive as fluorophores. They have high quantum yields and good photostability, and their fluorescence varies from tunable bluish red to broad spectrum. 1,8-Naphthalimide-derived fluorescent pigments and fluorescent compounds can be used as sensors, for pH determination, and as optical switches for certain metal cations.<sup>23–25</sup>

In this study, three new photochromic compounds, 3-(2,5-dimethyl-3-thiophenyl)-4-(5-methyl-2-phenyl-4-thiazolyl)-1,8-naphthalimide (**1-O**), 2,3-bis(2-phenyl-5-methyl-4-thiazolyl)-7*H* benzimidazo[2,1-a]benzo[d]isoquinolin-7-one (**2-O**), and 2,5-dimethyl-3-thiophenyl-7*H*-benzimidazo[2,1-a]benzo[d]isoquinolin-7-one (**3-O**), were prepared and their photochromic properties were examined.

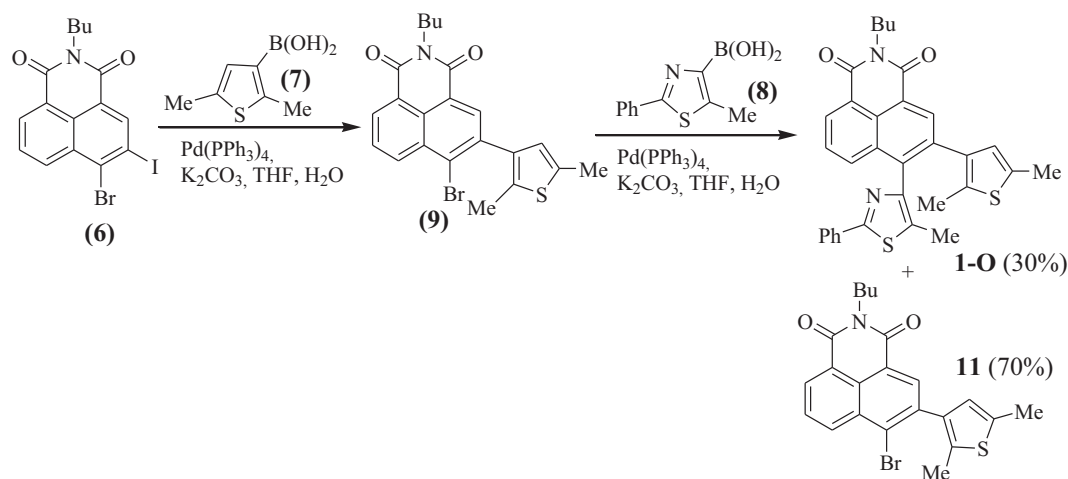
Photochromic 2,3-(bisaryl)-7*H*-benzimidazo[2,1-a]benzo[d]isoquinolin-7-one (**2-O** and **3-O**) compounds have not yet been reported; however, similar bisaryl-1,8-naphthalimide compounds that present symmetrical aryl groups, such as 3,4-bis(2,5-dimethyl-3-thiophenyl or 5-(4-methoxyphenyl)-2-methyl-3-thiophenyl)-1,8-naphthalimide, have already been reported.<sup>26,27</sup>

## 2. Results and discussion

3-Iodo-4-bromo-1,8-naphthalic anhydride (**5**)<sup>27</sup>, 3-iodo-4-bromo-1,8-naphthalimide (**6**)<sup>27</sup>, 2,5-dimethylthiophene-3-boronic acid (**7**)<sup>26,27</sup>, and (5-methyl-2-phenyl-4-thiazole-4-boronic acid (**8**)<sup>18–20</sup> were prepared together by a multistage reaction using procedures in the published literature.

In order to produce 3,4-(bisaryl)-1,8-naphthalimide (**1-O**), which presents different aryl groups such as 2,5-dimethyl-3-thienyl and 2-phenyl-5-methyl-4-thiazolyl groups, a two-step Suzuki coupling reaction was used (Figure 1). In the first Suzuki coupling reaction, an intermediate compound (**9**) was prepared via a reaction between 3-iodo-4-bromo-1,8-naphthalimide (**6**) and 2,5-dimethyl-3-thienyl boronic acid (**7**) in a medium containing palladium catalysts (e.g., Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd<sub>2</sub>(dba)<sub>3</sub>). In order to stop the reaction at the intermediate stage, the reaction was monitored by thin-layer Chromatography (TLC). The intermediate adduct (**9**) was obtained using simple purification by liquid–liquid extraction, and the crude product (**9**) was then used in the second Suzuki coupling reaction with 2-phenyl-5-methylthiazole-4-boronic acid and the necessary palladium catalyst (e.g., Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd<sub>2</sub>(dba)<sub>3</sub>) to give photochromic compound **1-O**. **1-O** was isolated from the reaction together with side product **11**. TLC results showed that compound **1-O** and its intermediate product (**11**) have very close retention times on the TLC plate, and, as a result, complete separation is almost impossible with flash column chromatography.

Synthesis of 2,3-(bisaryl)-7*H*-benzimidazo[2,1-a]benzo[de]isoquinolin-7-one (**2-O**) uses a multistep reaction (Figure 2). All attempts to obtain **12** via a one-pot Suzuki coupling reaction using excess boronic acid and a palladium catalyst failed. Thus, two consecutive Suzuki coupling reactions were used to get **12**. First of

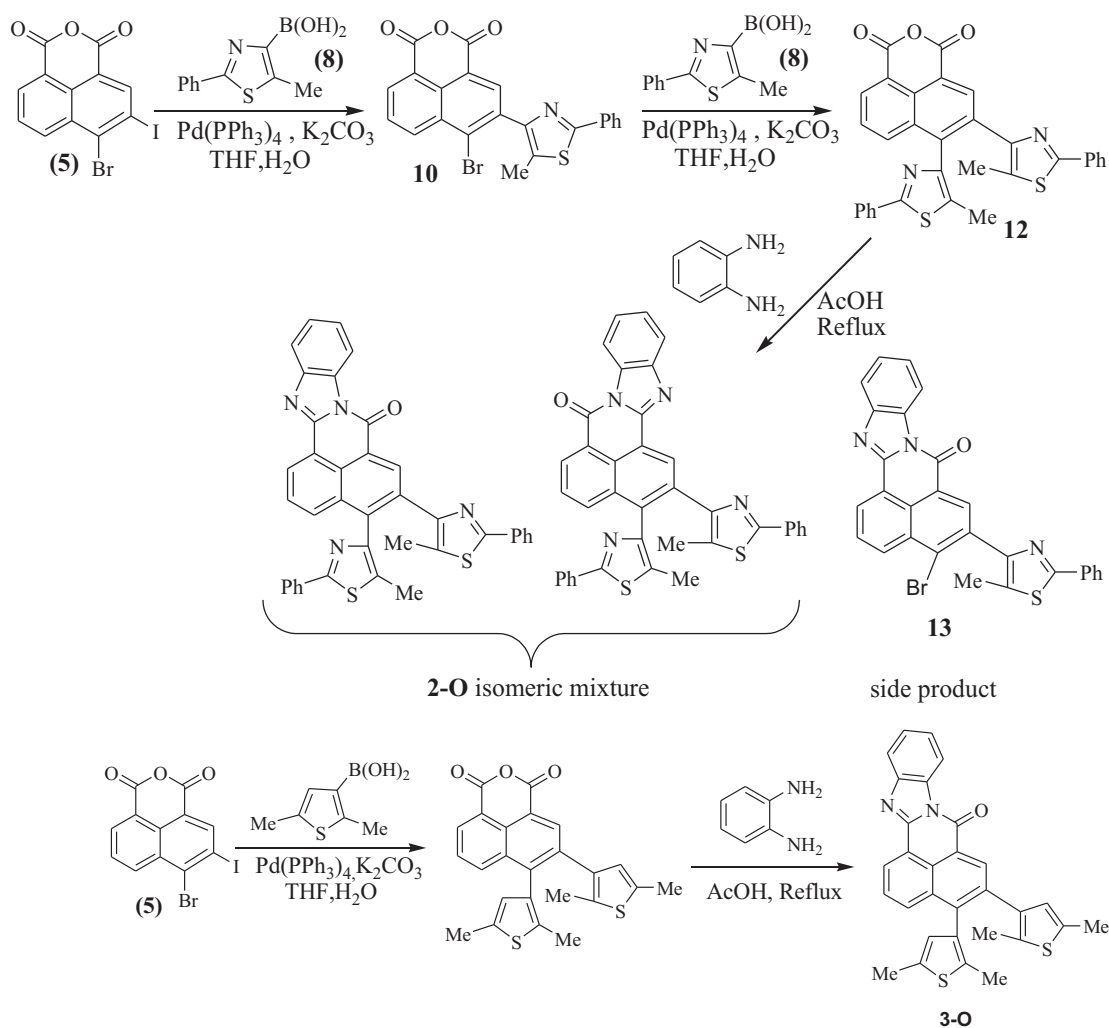


**Figure 1.** Synthesis of 3,4-(bisaryl)-1,8-naphthalimide (**1-O**).

all, a reaction between 3-iodo-4-bromo-1,8-naphthalic anhydride (**5**) and 5-methyl-2-phenylthiazole-4-boronic acid (**8**) was used to give a semicoupled product (**10**). After simple liquid–liquid extraction that gave the crude product (**10**), the second Suzuki coupling reaction yielded compound **12**. After extraction of the organic component from the reaction mixture, the crude product **12** was refluxed with *o*-phenylenediamine in the presence of glacial acetic acid under a dry nitrogen atmosphere. The reaction was monitored using TLC. After 1 day of reflux, the reaction mixture was subjected to flash column chromatography to give photochromic isomers. A condensation reaction between **12** and *o*-phenylenediamine resulted in two photochromic isomers whose retention times were very close to each other on the TLC plate. The <sup>1</sup>H NMR spectrum showed that the photochromic mixture consisted of two isomers of **2-O** and a side product (**13**). Many attempts to separate these isomers using classic flash column chromatography have failed. On the other hand, photochromic isomers were also proven by LC–MS analysis where [M+H] appeared at 617.16 m/z (the calculated molecular weight for **2-O** was 616.14 g/mol). Photochromic compound **3-O**, which is an isomeric mixture that presents 2,5-dimethyl-3-thienyl groups instead of 2-phenyl-5-methyl-4-thiazolyl groups, was also similarly synthesized. An investigation of the structure of **3-O** was carried out by LC–MS analysis (ESI-491.13 (M+H)) (calculated for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>OS<sub>2</sub>: 490.12).

Forward and reverse photoreactions of photochromes **1-O**, **2-O**, and **3-O** in solution were carried out at different light wavelengths. After irradiation of **1-O** in ethyl acetate by UV light at 365 nm, a light yellow to blue-green color change was observed owing to the occurrence of C-forms (**1-C**), which reverse upon exposure to visible light at 530 nm. The C-form ( $\lambda_{\text{max}} = 656 \text{ nm}$ ) showed a bathochromic shift of 315 nm compared to the O-form ( $\lambda_{\text{max}} = 341 \text{ nm}$ ) due to the large conjugated systems in the C-forms. The ring-closure and ring-opening isomerization at different wavelengths of light is general behavior in most organic photochromic compounds, especially in fulgide, diarylethenes, and diarylethenes related to photochromic molecules. Figure 3 shows the photoreaction and absorption spectral changes for **1-O** in ethyl acetate before and after irradiation with UV light.

Likewise, irradiation of a nearly colorless ethyl acetate solution of **2-O** ( $\lambda_{\text{max}} = 337 \text{ nm}$ ) underwent photocyclization to form purple-colored photochrome **2-C** ( $\lambda_{\text{max}} = 555 \text{ nm}$ ), which can then change back to **2-O** upon exposure to light at 530 nm. From the photoreaction of **2-O**, bathochromic shifts of 218 nm were



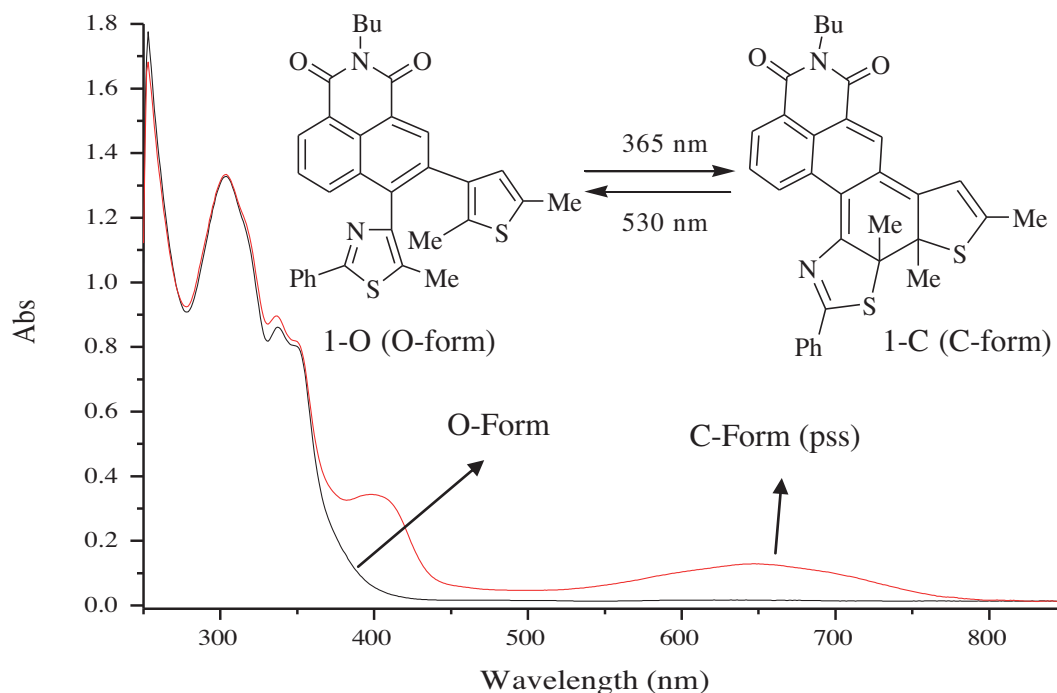
**Figure 2.** Synthesis of **2-O** and **3-O**.

observed, which are attributed to the longer conjugation of the C-form compared to the O-form. Figure 4 shows the photoreaction and absorption spectral changes for **2-O** in ethyl acetate before and after irradiation with UV light.

A photochromic reaction was also conducted for **3-O**, whereby it produced a reversible color change from light yellow ( $\lambda_{\text{max}} = 351 \text{ nm}$ ) to an orange color ( $\lambda_{\text{max}} = 545 \text{ nm}$ ) upon exposure to UV (365 nm) and visible (530 nm) light, respectively. The UV-Vis spectra and the photoreaction for **3-O** can be seen in Figure 5.

Replacement of the 2,5-dimethylthienyl groups with the 2-phenyl-5-methylthiazolyl groups at the 3,4-position of benzimidazo[2,1-a]benzo[d]isoquinolin-7-one caused bathochromic shifts of 10 nm when compared to their C-forms. For example, the  $\lambda_{\text{max}}$  of **3-C** in ethyl acetate was recorded at 545 nm, whereas the  $\lambda_{\text{max}}$  of **2-C** in ethyl acetate was recorded at 555 nm. A slight red shift may be connected to the greater conjugation of the C-form of **2-O** due to the phenyl groups in the thiazole rings.

In conclusion, two new photochromic compounds of 2,3-(bisaryl)-7*H*-benzimidazo[2,1-a]benzo[de]isoquinolin-7-one were synthesized using a Suzuki coupling reaction, starting from 4-bromo-3-iodo-1,8-naphthalic



**Figure 3.** Photoreaction and absorption spectral changes for **1-O** in ethyl acetate ( $\sim 1 \times 10^{-4}$  mol dm $^{-3}$ ) when irradiated by 365 nm UV light.

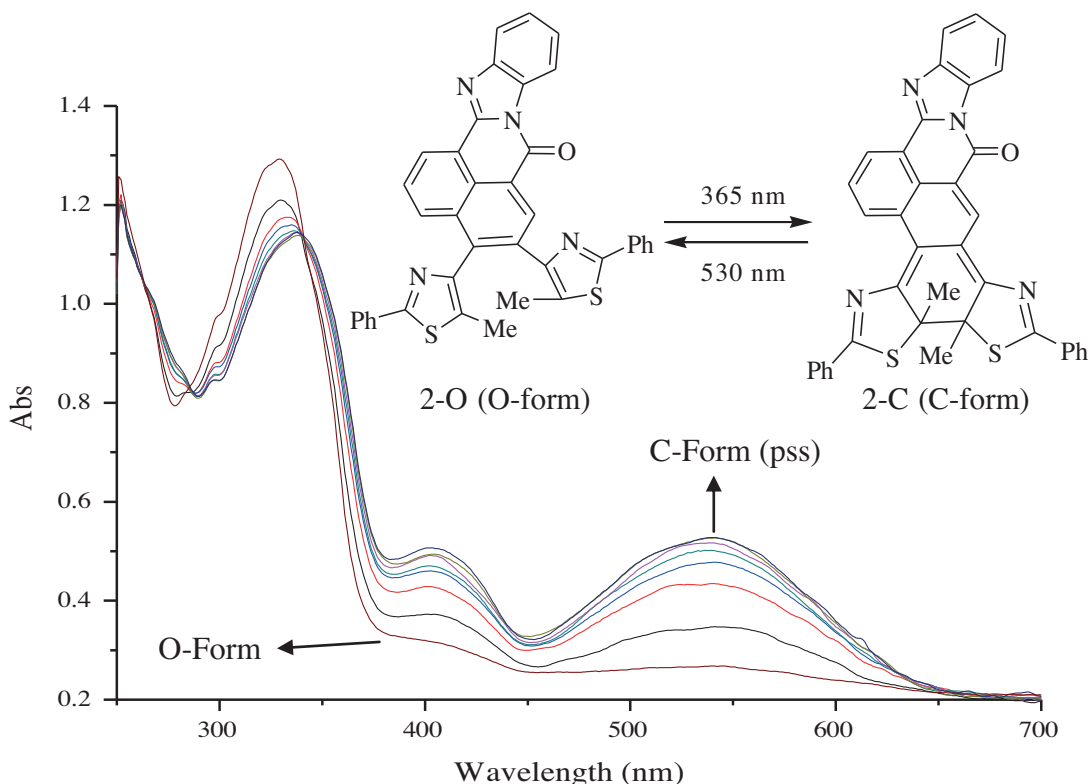
anhydride using (2,5-dimethylthiophen-3-yl) boronic acid or (2-phenyl 5-methyl thiazol-4-yl) boronic acid. Besides these two compounds, a new cross-coupled photochromic 3,4-(bisaryl)-1,8-naphthalimide was also prepared starting from 3-iodo-4-bromo-1,8-naphthalimide (**6**) employing two consecutive Suzuki coupling reactions using (2,5-dimethyl-3-thiophenyl) boronic acid (**7**) and (2-phenyl-5-methyl-4-thiazolyl) boronic acid (**8**). All the compounds in solutions exhibited reversible photoreactions when exposed to UV or visible light.

### 3. Experimental

#### 3.1. General

3-Iodo-4-bromo-1,8-naphthalic anhydride (**5**)<sup>23,27</sup>, 3-iodo-4-bromo-1,8-naphthalimide (**6**)<sup>26,27</sup>, 2,5-dimethylthienyl-3-boronic acid (**7**),<sup>26,27</sup> and (2-phenyl-5-methylthiazole-4-boronic acid (**8**))<sup>18–20</sup> were prepared together with the procedures in the published literature.

The  $^1\text{H}$ NMR spectra of the samples in  $\text{CDCl}_3$  were detected on a Bruker 400 MHz spectrometer. The signals were detected as ppm downfield compared to tetramethylsilane, which operates as an internal standard ( $\delta$ -value) for measuring chemical shifts. Mass spectra were measured by an AB Sciex 4000 Q TRAP LCMS/MS. UV–Vis spectra were measured on an Agilent Cary 60 UV–Vis spectrophotometer. Photochemical reactions in organic solvents were measured over a 10-mm path length quartz cell using an 8-W three-way UV lamp (Cole-Parmer) at 365 nm and a green light source (Obelux CR9 Forensic Lights) at 530 nm. Solutions in the UV cell were mixed throughout the photoreactions. Melting points were determined with a Büchi Melting Point B-540. Flash column chromatographic separation was achieved using a Merck Kieselgel 60 (70 to 230 mesh) with a particle size from 0.06 to 0.200 mm using ethyl acetate and hexane as the eluent. Preparative TLC was

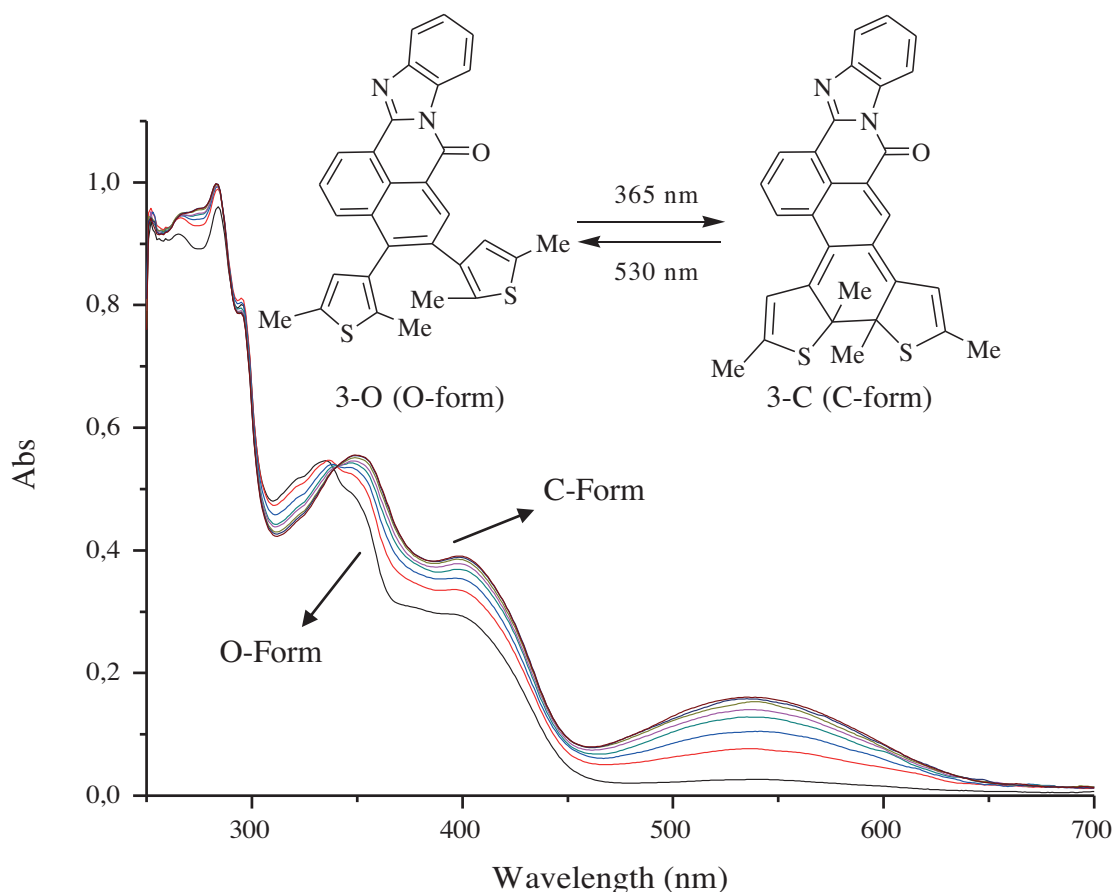


**Figure 4.** Photoreaction and absorption spectral changes for **2-O** in ethyl acetate ( $\sim 1 \times 10^{-4}$  mol dm $^{-3}$ ) when irradiated by 365 nm UV light.

performed on silica gel 60 from Merck with a particle size from 5 to 40  $\mu\text{m}$ . Analytical TLC was carried out on Merck precoated silica gel 60 GF-254 using 0.25-mm-thick TLC plates.

### 3.2. 3-(2,5-Dimethyl-3-thiophenyl)-4-(2-phenyl-5-methyl-4-thiazolyl)-1,8-naphthalimide (**1-O**)

A mixture of 2,5-dimethylthienyl-3-boronic acid (**7**) (0.31 g, 1.97 mmol), 3-iodo-4-bromo-1,8-naphthalimide (**6**) (0.3 g, 0.654 mmol), potassium carbonate (0.91 g, 6.54 mmol), tetrakis(triphenylphosphine)palladium(0) (0.091 g,  $7.86 \times 10^{-2}$  mmol), and a catalytic proportion of tris(dibenzylideneacetone)dipalladium(0) in THF (30 mL) and H $_2$ O (5 mL) was stirred for 2 h at room temperature and then the reaction mixture was refluxed for 3 h. After the solvent was removed under reduced pressure, the residue was extracted using DCM/H $_2$ O, dried over Na $_2$ SO $_4$ , and filtered. The crude intermediate compound (**9**) (0.025 g) was dissolved in THF (4 mL) and H $_2$ O (1 mL). Then 5-methyl-2-phenylthiazole-4-boronic acid (**8**) (0.037 g, 0.17 mmol), Pd(PPh $_3$ ) $_4$  (0.01 g,  $6.78 \times 10^{-3}$  mmol), and K $_2$ CO $_3$  (0.91 g, 0.565 mmol) were added to the mixture and stirred. The crude reaction mixture was stirred for 4 h at room temperature and then refluxed for 4 h. Afterwards the solvent was removed under reduced pressure and the residue was extracted using DCM/H $_2$ O, dried over Na $_2$ SO $_4$ , and filtered. The remaining precipitate was purified with flash column chromatography on silica gel using ethyl acetate and hexane as the eluents. From these purifications, compound **1-O** was isolated together with side product **11**. Although two flash column chromatography procedures and one preparative TLC procedure were repeatedly carried out, **1-O** and side product **11** could not be separated.



**Figure 5.** Photoreaction and absorption spectral changes for **3-O** in ethyl acetate ( $\sim 1 \times 10^{-4}$  mol dm $^{-3}$ ) irradiated with 365 nm UV light.

The resulting product was a mixture of a yellow solid (0.017 g) containing **1-O** (30%) and side product **11** (70%).

The  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm) spectrum for **1-O** was recorded as follows:  $\delta$  1.01 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.49 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.76 (m, 2H,  $\text{CH}_2\text{CH}_2$ ), 2.02 (s, 3H,  $\text{CH}_3$ ), 2.22 (s, 3H,  $\text{CH}_3$ ), 2.44 (s, 3H,  $\text{CH}_3$ ), 4.23 (t, 2H, N- $\text{CH}_2$ ), 6.55 (s, 1H, thiophene-H), 7.86, 8.16, 8.76 (m, 4H, Ar-H), and 7.45 (m, 5H, Ph).

Photochromic compound **1-O** was calculated for  $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$  as follows: **536.16**; ESI-**537.2** (M+H).

Compound **11** was recorded as follows:  $\delta$  1.01 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.49 (m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.76 (m, 2H,  $\text{CH}_2\text{CH}_2$ ), 2.45 ppm (s, 3H,  $\text{CH}_3$ ), 4.23 (t, 2H, N- $\text{CH}_2$ ),  $\delta$  7.46, 7.98, 8.73, 8.77 (m, 9H, Ph, Ar-H).

### 3.3. 4-Bromo-3-(5-methyl-2-phenyl-4-thiazolyl)-1,8-naphthalic anhydride (**10**)

A mixture of 5-methyl-2-phenylthiazole-4-boronic acid (**8**) (0.44 g, 1.99 mmol), 4-bromo-3-iodo-1,8-naphthalic anhydride (**5**) (0.2 g, 0.497 mmol), potassium carbonate (0.69 g, 4.97 mmol), tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.0597 mmol), and a catalytic proportion of Tris (dibenzylideneacetone) dipalladium(0) in

THF (10 mL) and H<sub>2</sub>O (2 mL) was stirred for 2 h at 45 °C and then the reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure and the mixture was poured onto crushed ice/water and acidified with 5 M HCl. The organic phase was extracted (2 × V) using DCM, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered, leaving a brown solid that was recrystallized by diethyl ether/ethyl acetate to give intermediate compound **10** as a brown solid (0.203 g, 80%). The <sup>1</sup>H NMR (400 MHz, DMSO, ppm) was recorded as follows: δ 2.43 (s, 3H, CH<sub>3</sub>), 7.51 (m, 5H, Ph), 7.9–8.67 (m, 4H, Ar-H).

#### 3.4. 2,3-Bis(2-phenyl-5-methyl-4-thiazolyl)-7H-benzimidazo[2,1-a] benzo[d]isoquinolin-7-one (2-O)

A mixture of 5-methyl-2-phenylthiazole-4-boronic acid (**8**) (0.33 g, 1.49 mmol), 4-bromo-3-(5-methyl-2-phenyl-4-thiazolyl)-1,8-naphthalic anhydride (**10**) (0.22 g, 0.497 mmol), potassium carbonate (0.49 g, 3.49 mmol), tetrakis(triphenylphosphine)palladium(0) (0.07 g, 0.096 mmol) and a catalytic proportion of Tris (dibenzylideneacetone) dipalladium(0) in THF (10 mL) and H<sub>2</sub>O (2 mL) was stirred for 2 h at 45 °C and then the mixture was refluxed for 2 h. The solvent was removed under reduced pressure and the mixture was poured onto crushed ice/water and acidified with 5 M HCl. The organic phase was extracted (2 × V) using DCM, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The residue was dissolved in glacial acetic acid (8 mL) and *o*-phenylenediamine (0.063 g, ~1.2 eq.) was added. The mixture was refluxed overnight under a nitrogen atmosphere. After removing the solvent, the residue was washed with NaHCO<sub>3</sub> (10%), extracted with DCM (3 × V), dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The reaction mixture was purified with flash column chromatography on silica gel using ethyl acetate/hexane (5% to 30%) as the eluents to give **2-O** as an isomeric mixture as a greenish solid (0.055 g). The <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>, ppm) recorded isomers of **2-O** as follows: δ 2.08 (s, 3H, CH<sub>3</sub>), 2.32 (s, 3H, CH<sub>3</sub>), (2.55 (s, 3H, CH<sub>3</sub>), 2.65 (s, 3H, CH<sub>3</sub>), 7.40–7.52 (m, 5 × Ph), 7.91–8.96 (m, Ar-H). Calculated for C<sub>38</sub>H<sub>24</sub>N<sub>4</sub>OS<sub>2</sub>: 616,14; ESI-617.16 (M+H).

The <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>, ppm) recorded side product **13** as follows: 2.47(s, CH<sub>3</sub>), 7.40–7.52 (m, Ph), 7.91–8.96 (m, Ar-H).

#### 3.5. 2,3-Bis(2,5-dimethyl-3-thienyl)-7H-benzimidazo[2,1-a] benzo[d]isoquinolin-7-one (3-O)

4-Bromo-3-iodo-1,8-naphthalic anhydride (0.3 g, 0.75 mmol), a mixture of 2,5-dimethylthiophene-4-boronic acid (0.35 g, 2.23 mmol), potassium carbonate (1.0 g, 7.46 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1 g, 0.090 mmol), and a catalytic proportion of Tris (dibenzylideneacetone) dipalladium(0) in THF (10 mL) and H<sub>2</sub>O (2 mL) was stirred for 2 h at 45 °C and then the mixture was refluxed for 2 h. The solvent was removed under reduced pressure and the mixture was poured onto crushed ice/water and acidified with 5 M HCl. The organic phase was extracted (2 × V) using DCM, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The residue was dissolved in glacial acetic acid (8 mL) and *o*-phenylenediamine (0.1 g, ~1.2 eq.) was added. The mixture was refluxed overnight under a nitrogen atmosphere. After removing the solvent, the residue was washed with NaHCO<sub>3</sub> (10%), extracted with DCM (3 × V), dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The reaction mixture was purified with flash column chromatography on silica gel using ethyl acetate/hexane (5% to 30%) as the eluents to give **3-O** as an isomeric mixture as a yellow solid (0.058 g). The <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>, ppm) recorded isomers of **3-O** as follows: δ 2.21 (s, 3H, CH<sub>3</sub>), 2.23 (s, 3H, CH<sub>3</sub>), 2.33 (s, 3H, CH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 6.34 (s, 1H, thienyl), 6.39 (s, 1H, thienyl), 7.31–8.66 (m, Ar-H). Calculated for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>OS<sub>2</sub>: 490,12; ESI-491.13 (M+H).



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