

Naphthoquinone-based Imidazolyl Esters as Blue-Light-Sensitive Type I Photoinitiators

Fatima Hammoud^{1,2,3}, Aristeia Pavlou⁴, Alexandros Petropoulos⁴, Bernadette Graff^{1,2}, Michael G. Siskos⁴, Akram Hijazi³, Fabrice Morlet-Savary^{1,2}, Frédéric Dumur^{5*} and Jacques Lalevée^{1,2*}

¹ Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France.

² Université de Strasbourg, France.

³ EDST, Université Libanaise, Campus Hariri, Hadath, Beyrouth, Liban.

⁴ Department of Chemistry, Section of Organic Chemistry and Biochemistry, University of Ioannina, Ioannina, 45110, Greece.

⁵ Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France.

Corresponding authors: Frederic.dumur@univ-amu.fr; jacques.lalevee@uha.fr

Experimental part:

UV-visible absorption and photolysis experiments

UV-visible absorption properties of the different compounds as well as the steady state photolysis were studied using a JASCO V730 UV-visible spectrophotometer.

Photopolymerization kinetics (RT-FTIR)

Experimental conditions for each photosensitive formulation are indicated in the caption of each figure. All polymerization experiments were performed at room temperature and the irradiation was started after $t = 10$ s. The weight of the photoinitiating system was calculated from the monomer content. The conversions of the TA acrylate functions were continuously followed by real time FTIR (RT-FTIR) spectroscopy (JASCO FTIR 4600). Photopolymerization experiments were carried out in laminate (the formulation was sandwiched between two polypropylene films (thickness ~ 25 μ m) to reduce the O₂ inhibition). Decrease of the C=C double bond peak was continuously monitored from 1581 to 1662 cm^{-1} . For the thicker samples (1.4 mm of thickness), formulations were deposited on a polypropylene film inside a 1.4 mm mold under air. Evolution of the C=C bond was continuously followed from 6117 to 6221 cm^{-1} , respectively. The different procedures were described by us in references. The generated CO₂ was detected by real time Fourier transformed infrared

spectroscopy (RT-FTIR) and the infrared spectra of OXE system in the polymerization processes at $t = 0$ s and $t = 30$ s. Obviously, a new absorption peak at 2337 cm^{-1} appears after irradiation and it was assigned to CO_2 .

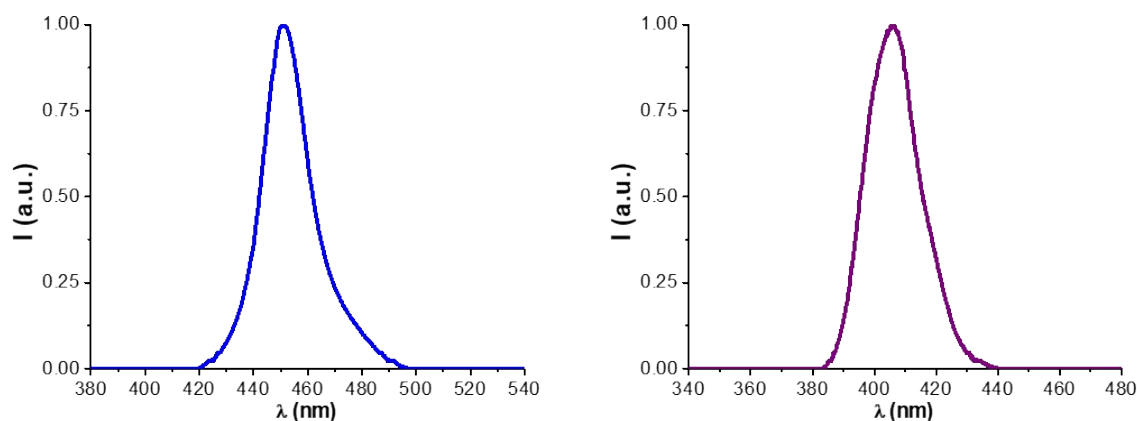


Figure S1. The emission spectra of the LED centered at 405 nm and 455 nm.

Computational procedure

Molecular orbital calculations were carried out using the Gaussian 16 suite of programs. Electronic absorption spectra for the different compounds were calculated with time-dependent density functional theory at the MPW1PW91/6-31G* level of theory on the relaxed geometries calculated at the UB3LYP/6-31G* level of theory. Triplet state energy levels were calculated at this level of theory after full optimization of the excited state.

Fluorescence experiments

Steady state fluorescence. Fluorescence spectra were acquired in a quartz cell at room temperature using a JASCO FP-750 spectrofluorometer.

Time correlated single photon counting (TCSPC). Fluorescence excited state lifetimes were determined using a time correlated single-photon counting system, a HORIBA DeltaFlex with a HORIBA PPD-850 as detector. The excitation source was a HORIBA nanoLED-370 with an excitation wavelength of 367 nm and a pulse duration inferior to 1.4 ns. The fluorescence intensity decay profiles were recorded in acetonitrile in a quartz cell. A silica colloidal solution LUDOX was used to evaluate the impulse response function (IRF) of the apparatus.

ESR spin-trapping (ESR-ST) experiments

ESR-ST experiments were carried out using an X-band spectrometer (Bruker EMX-plus). A LED@405 nm was used as the irradiation source for the bond cleavage and generation of radicals at room temperature under N₂ atmosphere in toluene. The free radicals generated were trapped by phenyl-*N-tert*-butylnitron (PBN) based on a procedure described in the literature. After the end of the experiment, some ESR simulations were carried out using the PEST WINSIM program.

Direct Laser Write

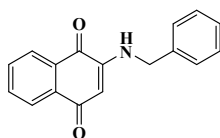
For direct laser write experiments, a laser diode @405 nm (spot size around 50 μm) was used for the spatially controlled irradiation. The photosensitive resin was polymerized under air and the generated 3D patterns were analyzed using a numerical optical microscope (DSX-HRSU from Olympus Corporation) as presented in the references.

Synthesis of the investigated naphthoquinone-esters

General information

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ¹H and ¹³C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ¹H (400 MHz) and ¹³C (100 MHz). The ¹H chemical shifts were referenced to the solvent peak CDCl₃ (7.26 ppm) and the ¹³C chemical shifts were referenced to the solvent peak CDCl₃ (77.0 ppm). All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.

Synthesis of 2-(benzylamino)naphthalene-1,4-dione



Chemical Formula: C₁₇H₁₃NO₂
Molecular Weight: 263.2960

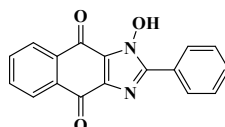
Benzylamine (0.47 g, 0.48 mL, 4.40 mmol, M = 107.15 g/mol, d = 0.981) was added in 30 mL of absolute ethanol containing 1 equivalent of 1,4-naphthaquinone (0.7 g, 4.40 mmol, M = 158.16 g/mol). The reaction mixture was stirred at room temperature overnight. During these hours, a change in the color of the reaction mixture was observed from yellow to red. A precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum (1.06 g, 92% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.08 (ddd, *J* = 10.8, 7.7, 1.2 Hz, 2H), 7.73 (td, *J* = 7.5, 1.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.3 Hz, 1H), 7.42 – 7.29 (m, 5H), 6.20 (s, 1H), 5.79 (s, 1H), 4.38 (d, *J* = 5.8 Hz, 2H)

¹³C NMR (75 MHz, CDCl₃) δ 183.05, 181.87, 147.75, 135.93, 134.75, 133.58, 132.05, 130.53, 129.02, 128.13, 127.64, 126.28, 126.22, 101.78, 46.81

HRMS (ESI MS) *m/z*: theor: 263.0946 found: 263.0948 (M⁺ detected).

Synthesis of 1-hydroxy-2-phenyl-1H-naphtho[2,3-d]imidazole-4,9-dione



Chemical Formula: C₁₇H₁₀N₂O₃
Molecular Weight: 290.2780

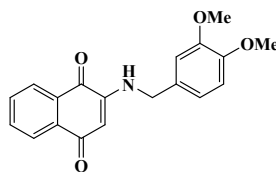
A mixture of 1.5 mL of 60% nitric acid and 2.5 mL of 94% sulfuric acid was added dropwise to 2-(benzylamino)naphthalene-1,4-dione (1.32 g, 5.02 mmol, M = 263.29 g/mol) in 30 mL of acetic acid, and the mixture was stirred at room temperature overnight. The mixture was then poured onto 250 g of ice. The yellow–orange precipitate was filtered off, washed with water, and dried (0.98 g, 67% yield).

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.21 (s, 1H), 8.16 (ddd, *J* = 13.6, 8.2, 4.6 Hz, 4H), 7.93 – 7.83 (m, 2H), 7.65 – 7.53 (m, 3H)

¹³C NMR (75 MHz, DMSO-*d*₆) δ 178.01, 173.86, 147.66, 137.99, 134.02, 133.86, 132.99, 132.60, 130.64, 128.81, 128.18, 127.15, 126.43, 126.06

HRMS (ESI MS) m/z: theor: 290.0691 found: 290.0698 (M⁺ detected)

Synthesis of 2-((3,4-dimethoxybenzyl)amino)naphthalene-1,4-dione



Chemical Formula: C₁₉H₁₇NO₄
Molecular Weight: 323.3480

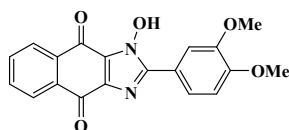
3,4-Dimethoxybenzylamine (0.73 g, 0.66 mL, 4.40 mmol, M = 167.21 g/mol, d = 1.109) was added in 30 mL of absolute ethanol containing 1 equivalent of 1,4-naphthaquinone (0.7 g, 4.40 mmol, M = 158.16 g/mol). The reaction mixture was stirred at room temperature overnight. During these hours, a change in the color of the reaction mixture was observed from yellow to red. A precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum (1.21 g, 85% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.07 (dd, *J* = 18.7, 7.6 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 6.85 (dd, *J* = 14.3, 6.0 Hz, 3H), 6.15 (s, 1H), 5.82 (s, 1H), 4.30 (d, *J* = 4.6 Hz, 2H), 3.88 (s, 6H)

¹³C NMR (75 MHz, CDCl₃) δ 183.02, 181.81, 149.50, 149.04, 147.78, 134.81, 133.55, 132.09, 130.50, 128.26, 126.33, 126.27, 120.26, 111.53, 111.00, 101.55, 56.00, 46.81

HRMS (ESI MS) m/z: theor: 323.1158 found: 323.1153 (M⁺ detected).

Synthesis of 2-(3,4-dimethoxyphenyl)-1-hydroxy-1H-naphtho[2,3-d]imidazole-4,9-dione



Chemical Formula: C₁₉H₁₄N₂O₅
Molecular Weight: 350.3300

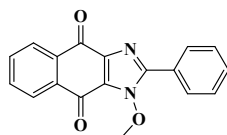
A mixture of 1.5 mL of 60% nitric acid and 2.5 mL of 94% sulfuric acid was added dropwise to 2-((3,4-dimethoxybenzyl)amino)naphthalene-1,4-dione (1.62 g, 5.02 mmol, M = 323.35 g/mol) in 30 mL of acetic acid, and the mixture was stirred at room temperature overnight. The mixture was then poured onto 250 g of ice. The yellow–orange precipitate was filtered off, washed with water, and dried under vacuum (1.48 g, 84% yield).

^1H NMR (400 MHz, DMSO- d_6) δ 13.16 (s, 1H), 8.13 (s, 2H), 7.90 (d, J = 3.4 Hz, 2H), 7.79 (d, J = 9.9 Hz, 2H), 7.34 (s, 1H), 3.97 (s, 6H)

Anal. Calc. for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_5$: C, 65.1; H, 4.0; O, 22.8; Found: C, 65.3; H, 3.6; O, 22.4 %

HRMS (ESI MS) m/z : theor: 350.0903 found: 350.0907 (M^+ detected).

Synthesis of 1-methoxy-2-phenyl-1H-naphtho[2,3-d]imidazole-4,9-dione (1)



Chemical Formula: $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3$
Molecular Weight: 304.3050

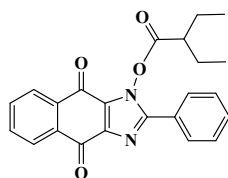
1-Hydroxy-2-phenyl-1H-naphtho[2,3-d]imidazole-4,9-dione (0.69 g, 2.38 mmol, M = 290.28 g/mol) was dissolved in **DMF** (50 mL) and potassium *tert*-butoxide (0.32 g, 2.86 mmol, 1.2 eq., M = 112.21 g/mol) was added. Then, iodomethane (0.68 g, 0.30 mL, 4.78 mmol, M = 141.94 g/mol, d = 2.28) was added. The solution was stirred at room temperature overnight. Water was added. The solvent was removed under reduced pressure. The residue was dissolved in water and DCM was added. The organic phase was washed several times with water. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The solid was suspended in a minimum of acetone and diethyl ether was added. A yellow precipitate formed. It was filtered off, washed several times with ether and dried under vacuum (0.64 g, 88% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.21 – 8.11 (m, 4H), 7.94 – 7.88 (m, 2H), 7.64 (dd, J = 6.8, 2.8 Hz, 3H), 4.19 (s, 3H)

^{13}C NMR (75 MHz, CDCl_3) δ 178.06, 173.40, 146.39, 138.15, 134.21, 134.09, 132.70, 132.23, 131.17, 129.61, 129.17, 127.84, 126.43, 126.31, 126.16, 67.50, 54.42, 54.36, 54.31

HRMS (ESI MS) m/z : theor: 304.0848 found: 304.0844 (M^+ detected).

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl hexanoate (2)



Chemical Formula: C₂₃H₂₀N₂O₄
Molecular Weight: 388.4230

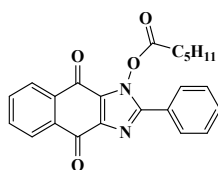
1-Hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.16 g, 4 mmol, M = 290.28 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, 2-ethylbutyryl chloride (0.54 g, V = 0.55 mL, 4 mmol, d = 0.982, M = 134.60 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.21 g, 78% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.35 – 8.22 (m, 1H), 8.21 – 8.10 (m, 1H), 8.06 – 7.93 (m, 2H), 7.84 – 7.66 (m, 2H), 7.58 – 7.42 (m, 3H), 2.71 – 2.60 (m, 1H), 1.96 (td, *J* = 14.4, 7.4 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H)

¹³C NMR (75 MHz, CDCl₃) δ 178.51, 174.20, 171.73, 149.03, 138.73, 134.02, 133.61, 132.95, 132.91, 131.29, 129.92, 128.84, 128.75, 127.36, 126.48, 126.01, 46.00, 24.09, 23.82, 11.43, 11.24

HRMS (ESI MS) *m/z*: theor: 388.1423 found: 388.1426 (M⁺ detected).

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl hexanoate (3)



Chemical Formula: C₂₃H₂₀N₂O₄
Molecular Weight: 388.4230

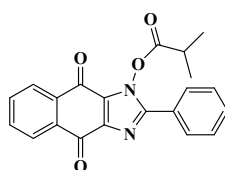
1-Hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.16 g, 4 mmol, M = 290.28 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, hexanoyl chloride (0.54 g, V = 0.56 mL, 4 mmol, d = 0.963, M = 134.60 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.27 g, 82% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.26 – 8.21 (m, 1H), 8.10 – 8.05 (m, 1H), 8.00 – 7.93 (m, 2H), 7.73 – 7.68 (m, 2H), 7.49 – 7.44 (m, 3H), 3.34 – 3.27 (m, 2H), 1.77 (dd, $J = 14.2, 7.1$ Hz, 2H), 1.60 (dd, $J = 10.1, 5.0$ Hz, 2H), 1.35 – 1.32 (m, 2H), 0.85 (t, $J = 5.1$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 178.39, 174.23, 172.90, 148.47, 138.59, 134.09, 133.65, 132.88, 131.33, 128.87, 128.46, 127.37, 126.38, 33.08, 30.96, 23.93, 22.13, 13.78

HRMS (ESI MS) m/z : theor: 388.1423 found: 388.1425 (M^+ detected)

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl hexanoate (4)



Chemical Formula: $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_4$
Molecular Weight: 360.3690

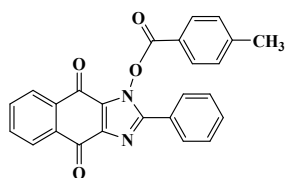
1-Hydroxy-2-phenyl-1H-naphtho[2,3-d]imidazole-4,9-dione (1.16 g, 4 mmol, $M = 290.28$ g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, isobutyryl chloride (0.42 g, $V = 0.42$ mL, 4 mmol, $d = 1.017$, $M = 106.55$ g/mol) was added. The flask was then stirred at room temperature overnight under N_2 atmosphere. The solution was subsequently washed with water and dried over Na_2SO_4 . Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.02 g, 71% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.33 – 8.27 (m, 1H), 8.16 – 8.10 (m, 1H), 8.04 – 7.97 (m, 2H), 7.80 – 7.69 (m, 2H), 7.56 – 7.46 (m, 3H), 3.03 (dt, $J = 14.0, 7.0$ Hz, 1H), 1.47 (d, $J = 7.0$ Hz, 3H), 1.37 (d, $J = 7.0$ Hz, 3H)

^{13}C NMR (75 MHz, CDCl_3) δ 178.44, 174.24, 172.52, 148.56, 138.69, 134.06, 133.62, 132.93, 132.89, 131.33, 129.69, 128.82, 128.54, 127.39, 126.40, 126.03, 32.16, 18.49, 18.46

HRMS (ESI MS) m/z : theor: 360.1110 found: 360.1113 (M^+ detected)

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl 4-methyl benzoate (5)



Chemical Formula: C₂₅H₁₆N₂O₄
Molecular Weight: 408.4130

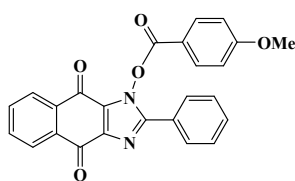
1-Hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.16 g, 4 mmol, M = 290.28 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, 4-methylbenzoyl chloride (0.618 g, 0.53 mL, 4 mmol, M = 154.59 g/mol, d = 1.169) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.37 g, 84% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.35 – 8.25 (m, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.09 – 8.04 (m, 1H), 8.01 – 7.95 (m, 2H), 7.79 – 7.69 (m, 1H), 7.49 – 7.37 (m, 2H), 7.25 (dd, *J* = 7.7, 4.0 Hz, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.31 (s, 3H)

¹³C NMR (75 MHz, CDCl₃) δ 172.01, 171.22, 162.84, 146.85, 144.27, 139.39, 134.09, 133.65, 131.32, 130.74, 130.17, 130.01, 129.12, 129.02, 128.95, 128.71, 128.40, 127.39, 126.94, 126.43, 126.18, 122.06, 21.23

HRMS (ESI MS) *m/z*: theor: 408.1110 found: 408.1111 (M⁺ detected)

Synthesis of 4,9-Dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl 4-methoxybenzoate (6)



Chemical Formula: C₂₅H₁₆N₂O₅
Molecular Weight: 424.4120

1-Hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.16 g, 4 mmol, M = 290.28 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, 4-methoxybenzoyl chloride (680 mg, 4 mmol, M = 170.59 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a

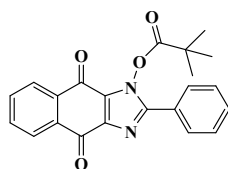
yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.44 g, 85% yield).

^1H NMR (400 MHz, DMSO) δ 8.24 (ddd, $J = 9.0, 7.5, 2.0$ Hz, 3H), 8.12 (dd, $J = 5.6, 3.4$ Hz, 1H), 8.04 (dd, $J = 6.1, 2.7$ Hz, 1H), 7.93 – 7.89 (m, 1H), 7.88 – 7.81 (m, 2H), 7.60 – 7.52 (m, 4H), 7.28 – 7.21 (m, 1H), 3.95 (s, 3H)

^{13}C NMR (75 MHz, CDCl_3) δ 174.30, 170.31, 165.42, 146.74, 134.08, 133.66, 133.34, 133.05, 132.31, 131.28, 128.93, 128.50, 128.42, 128.34, 127.43, 127.28, 126.44, 126.13, 116.86, 116.20, 114.69, 55.75

HRMS (ESI MS) m/z : theor: 424.1059 found: 424.1062 (M^+ detected)

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl pivalate (7)



Chemical Formula: $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_4$
Molecular Weight: 374.3960

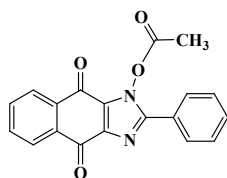
1-Hydroxy-2-phenyl-1H-naphtho[2,3-d]imidazole-4,9-dione (1.16 g, 4 mmol, $M = 290.28$ g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, trimethylacetyl chloride (0.48 g, $V = 0.49$ mL, 4 mmol, $d = 0.979$, $M = 120.58$ g/mol) was added. The flask was then stirred at room temperature overnight under N_2 atmosphere. The solution was subsequently washed with water and dried over Na_2SO_4 . Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.32 g, 88% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.33 – 8.27 (m, 1H), 8.16 – 8.10 (m, 1H), 8.02 – 7.94 (m, 2H), 7.80 – 7.69 (m, 2H), 7.51 (d, $J = 6.7$ Hz, 3H), 1.47 (s, 9H)

^{13}C NMR (75 MHz, CDCl_3) δ 178.53, 174.24, 173.83, 148.84, 138.78, 134.05, 133.63, 132.93, 131.33, 129.83, 128.74, 128.71, 127.41, 126.43, 126.00, 38.57, 26.95

HRMS (ESI MS) m/z : theor: 374.1267 found: 374.1269 (M^+ detected)

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl acetate (8)



Chemical Formula: C₁₉H₁₂N₂O₄
Molecular Weight: 332.3150

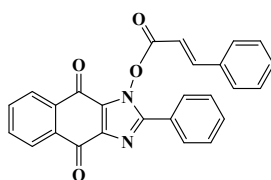
1-Hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.16 g, 4 mmol, M = 290.28 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, acetyl chloride (310 mg, 0.29 mL, 4 mmol, d = 1.104, M = 78.49 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.01 g, 76% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.30 (dd, *J* = 7.2, 1.7 Hz, 1H), 8.12 (dd, *J* = 7.2, 1.7 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.75 (ddd, *J* = 7.3, 5.0, 1.7 Hz, 2H), 7.54 – 7.48 (m, 3H), 2.50 (s, 3H)

¹³C NMR (75 MHz, CDCl₃) δ 178.50, 174.34, 163.06, 148.80, 136.59, 134.12, 133.68, 133.27, 131.35, 129.79, 129.28, 128.98, 128.52, 128.44, 128.02, 127.48, 126.45, 124.96, 15.24

HRMS (ESI MS) *m/z*: theor: 332.0797 found: 332.0799 (M⁺ detected)

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl cinnamate (9)



Chemical Formula: C₂₆H₁₆N₂O₄
Molecular Weight: 420.4240

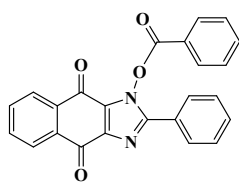
1-Hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.16 g, 4 mmol, M = 290.28 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, cinnamoyl chloride (0.67 g, 4 mmol, M = 166.60 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.28 g, 76% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.28 (dtd, $J = 8.7, 7.4, 1.4$ Hz, 3H), 8.13 – 8.11 (m, 1H), 8.07 – 8.00 (m, 2H), 7.80 – 7.70 (m, 3H), 7.64 (d, $J = 1.8$ Hz, 1H), 7.50 – 7.42 (m, 5H), 6.74 (d, $J = 16.0$ Hz, 1H)

^{13}C NMR (75 MHz, CDCl_3) δ 178.46, 174.32, 163.00, 151.49, 148.64, 138.67, 134.13, 133.70, 133.24, 132.93, 132.07, 131.35, 129.21, 128.97, 128.60, 128.54, 128.46, 127.44, 126.46, 126.01, 110.83

HRMS (ESI MS) m/z : theor: 420.1110 found: 420.1113 (M^+ detected)

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl benzoate (10)



Chemical Formula: $\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_4$
Molecular Weight: 394.3860

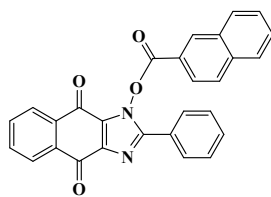
1-Hydroxy-2-phenyl-1H-naphtho[2,3-d]imidazole-4,9-dione (1.16 g, 4 mmol, $M = 290.28$ g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, benzoyl chloride (560 mg, 0.47 mL, 4 mmol, $d = 1.211$, $M = 140.57$ g/mol) was added. The flask was then stirred at room temperature overnight under N_2 atmosphere. The solution was subsequently washed with water and dried over Na_2SO_4 . Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.28 g, 81% yield).

^1H NMR (300 MHz, CDCl_3) δ 8.32 (dd, $J = 7.6, 1.3$ Hz, 4H), 8.24 (dd, $J = 8.4, 1.2$ Hz, 1H), 8.08 (ddd, $J = 9.6, 7.7, 1.6$ Hz, 15H), 7.80 – 7.70 (m, 16H), 7.63 (d, $J = 8.1$ Hz, 6H), 7.50 – 7.43 (m, 11H), 7.33 (s, 10H)

^{13}C NMR (75 MHz, CDCl_3) δ 178.47, 174.31, 162.86, 148.75, 138.77, 135.44, 134.13, 133.91, 133.69, 133.20, 132.98, 132.91, 131.35, 130.69, 129.28, 128.97, 128.42, 128.31, 128.27, 127.47, 127.26, 126.44, 126.13, 125.00

HRMS (ESI MS) m/z : theor: 394.0954 found: 394.0958 (M^+ detected)

Synthesis of 4,9-dioxo-2-phenyl-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl 2-naphthoate (11)



Chemical Formula: C₂₈H₁₆N₂O₄
Molecular Weight: 444.4460

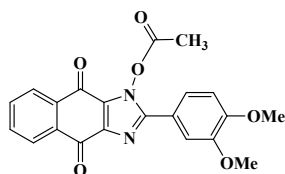
1-Hydroxy-2-phenyl-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.16 g, 4 mmol, M = 290.28 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, 2-naphthoyl chloride (760 mg, 4 mmol, M = 190.02 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.69 g, 95% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.87 (s, 1H), 8.34 – 8.30 (m, 1H), 8.27 – 8.23 (m, 1H), 8.17 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.13 – 8.06 (m, 3H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.66 (m, 4H), 7.44 (dd, *J* = 8.9, 3.4 Hz, 4H)

¹³C NMR (75 MHz, CDCl₃) δ 178.36, 174.34, 166.42, 148.39, 138.62, 134.17, 133.82, 133.69, 133.24, 132.93, 132.84, 131.39, 130.37, 129.48, 128.97, 128.52, 128.42, 128.37, 127.47, 127.19, 126.37, 126.16, 125.96

HRMS (ESI MS) *m/z*: theor: 444.1110 found: 444.1108 (M⁺: detected)

Synthesis of 2-(3,4-dimethoxyphenyl)-4,9-dioxo-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl acetate (12)



Chemical Formula: C₂₁H₁₆N₂O₆
Molecular Weight: 392.3670

2-(3,4-Dimethoxyphenyl)-1-hydroxy-1*H*-naphtho[2,3-*d*]imidazole-4,9-dione (1.40 g, 4 mmol, M = 350.33 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, acetyl chloride (310 mg, 0.29 mL, 4 mmol, d = 1.104, M = 78.49 g/mol)

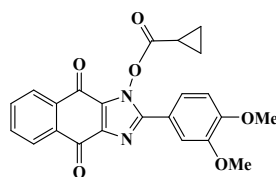
was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.22 g, 78% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.33 – 8.30 (m, 1H), 8.15 – 8.12 (m, 1H), 7.77 (pd, *J* = 7.5, 1.6 Hz, 3H), 7.72 (s, 1H), 7.18 (s, 1H), 4.04 (s, 3H), 4.00 (s, 3H), 2.32 (s, 3H)

¹³C NMR (75 MHz, CDCl₃) δ 178.18, 174.28, 166.32, 153.18, 150.89, 146.10, 141.14, 138.58, 134.34, 133.79, 132.93, 132.72, 129.23, 127.52, 126.51, 114.55, 114.14, 107.75, 56.92, 56.67, 17.55

HRMS (ESI MS) *m/z*: theor: 392.1008 found: 392.1010 (M⁺ detected)

Synthesis of 2-(3,4-dimethoxyphenyl)-4,9-dioxo-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl cyclopropanecarboxylate (13)



Chemical Formula: C₂₃H₁₈N₂O₆
Molecular Weight: 418.4050

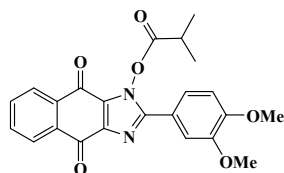
2-(3,4-Dimethoxyphenyl)-1-hydroxy-1H-naphtho[2,3-d]imidazole-4,9-dione (1.40 g, 4 mmol, M = 350.33 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, cyclopropanecarbonyl chloride (0.42 g, V = 0.36 mL, 4 mmol, d = 1.152, M = 104.53 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.47 g, 88% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.33 – 8.29 (m, 1H), 8.17 – 8.13 (m, 1H), 7.79 – 7.73 (m, 4H), 7.17 (s, 1H), 4.05 (s, 3H), 4.00 (s, 3H), 1.81 (td, *J* = 7.6, 4.0 Hz, 1H), 1.21 (t, *J* = 7.0 Hz, 4H)

¹³C NMR (75 MHz, CDCl₃) δ 178.25, 174.21, 170.52, 153.13, 150.82, 146.23, 141.20, 138.56, 134.25, 133.74, 132.91, 132.77, 129.45, 127.47, 126.55, 114.72, 114.15, 107.73, 56.91, 56.67, 10.50, 10.39

HRMS (ESI MS) *m/z*: theor: 418.1165 found: 418.1161 (M⁺ detected)

Synthesis of 2-(3,4-dimethoxyphenyl)-4,9-dioxo-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl isobutyrate (14)



Chemical Formula: C₂₃H₂₀N₂O₆
Molecular Weight: 420.4210

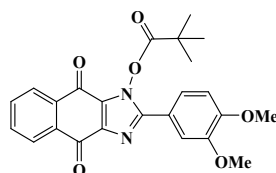
2-(3,4-Dimethoxyphenyl)-1-hydroxy-1H-naphtho[2,3-d]imidazole-4,9-dione (1.40 g, 4 mmol, M = 350.33 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, isobutyryl chloride (0.42 g, V = 0.42 mL, 4 mmol, d = 1.017, M = 106.55 g/mol) was added. The flask was then stirred at room temperature overnight under N₂ atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.41 g, 84% yield)

¹H NMR (300 MHz, CDCl₃) δ 8.32 (dd, J = 7.2, 1.7 Hz, 1H), 8.16 – 8.11 (m, 1H), 7.82 – 7.74 (m, 2H), 7.18 (s, 1H), 4.04 (s, 3H), 4.00 (s, 3H), 2.83 (dt, J = 14.0, 7.0 Hz, 1H), 1.25 (s, 6H)

¹³C NMR (75 MHz, CDCl₃) δ 178.24, 174.18, 172.45, 153.17, 150.84, 146.22, 141.14, 138.63, 134.26, 133.74, 132.91, 132.77, 129.45, 127.47, 126.54, 114.67, 114.17, 107.57, 56.93, 56.69, 31.93, 18.37

HRMS (ESI MS) m/z: theor: 420.1321 found: 420.1322 (M⁺ detected)

Synthesis of 2-(3,4-dimethoxyphenyl)-4,9-dioxo-4,9-dihydro-1H-naphtho[2,3-d]imidazol-1-yl pivalate (15)



Chemical Formula: C₂₄H₂₂N₂O₆
Molecular Weight: 434.4480

2-(3,4-Dimethoxyphenyl)-1-hydroxy-1H-naphtho[2,3-d]imidazole-4,9-dione (1.40 g, 4 mmol, M = 350.33 g/mol) and 3 mL of dry triethylamine were dissolved in 100 mL of anhydrous dichloromethane. Then, trimethylacetyl chloride (0.48 g, V = 0.49 mL, 4 mmol, d = 0.979, M = 120.58 g/mol) was added. The flask was then stirred at room temperature overnight under N₂

atmosphere. The solution was subsequently washed with water and dried over Na₂SO₄. Upon evaporation of the solvent, a yellow precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (1.39 g, 80% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.31 (dd, *J* = 7.2, 1.7 Hz, 1H), 8.13 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.76 (tt, *J* = 7.2, 5.1 Hz, 4H), 7.17 (s, 1H), 4.03 (s, 3H), 4.00 (s, 3H), 1.27 (s, 9H)

¹³C NMR (75 MHz, CDCl₃) δ 178.27, 174.15, 173.80, 153.23, 150.83, 146.36, 141.05, 138.68, 135.71, 134.23, 133.73, 132.91, 132.78, 127.46, 126.54, 114.78, 114.23, 107.50, 56.95, 56.71, 38.62, 26.67

HRMS (ESI MS) *m/z*: theor: 434.1478 found: 434.1472 (M⁺ detected)