Supporting Information:

Bio-based captodative ligands for redox polymerization of Elium[®] thermoplastic composites under mild conditions

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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 ESI-HRMS 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 or a Bruker Avance 300 spectrometer of the Spectropole: ¹H (400 MHz), ¹H (300 MHz), ¹³C (100 MHz) and ¹³C (75 MHz). The ¹H chemical shifts were referenced to the solvent peak CDCl₃ (7.26 ppm) or (CD₃)₂CO (2.05 ppm) and the

¹³C chemical shifts were referenced to the solvent peak CDCl₃ (77.0 ppm) or $(CD_3)_2CO$ (29.84 ppm and 206.26 ppm). All compounds were prepared with analytical purity up to accepted standards for new organic compounds (> 98%), which was checked by high-field NMR analysis.



Figure S1 : Dose-dependent effect of **LO1-LO12**, **LS1-LS7** and TPO on human liver cell viability. Human liver cells (HepG2) were exposed to increasing concentrations of **LO1-LO12** (A), **LS1-LS7** or TPO (B) (ranging from 0 to 100 μ M) for 48 h before cell viability was measured using a resazurin-based assay. Results are expressed in percentage of cell viability, cells treated with vehicle alone (DMSO) being used as a negative control, giving 100% viability. Data were plotted as mean +/- SD, n=3 using GraphPad Prism.



Chemical Formula: $C_{15}H_{10}O_3$ Molecular Weight: 238,2420

Methyl 2-hydroxybenzoate (**10.00 g**, 65.73 mmol) and 2-bromo-1-phenylethan-1-one (**13.08 g**, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**18.17 g**, 131.45 mmol) was added, and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (48% yield).

¹H NMR (400 MHz, CDCl₃ + **TFA**) δ 8.29 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.37 (ddd, *J* = 7.9, 7.1, 0.8 Hz, 1H).

Compound LO1 was insoluble in conventional deuterated solvents for ¹³C NMR registration.

HRMS (ESI MS) m/z: Calculated: 237.0557 found: 237.0558 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxybenzofuran-2-yl)(phenyl)methanone LO1



Molecular Weight: 364.1385

Methyl 2-hydroxybenzoate (**10.00 g**, 65.73 mmol) and 2-bromo-1-(4-iodophenyl)ethan-1-one (**21.36 g**, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**18.17 g**, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et_2O . The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (51% yield).

¹H NMR (400 MHz, CDCl₃ + **TFA**) δ 8.03 – 7.94 (m, 4H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H).

Compound LO2 was insoluble in conventional deuterated solvents for ¹³C NMR registration ¹³C NMR.

HRMS (ESI MS) m/z: Calculated: 362.9524 found: 362.9517 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxybenzofuran-2-yl)(4-iodophenyl)methanone LO2



Methyl 2-hydroxybenzoate (10.00 g, 65.73 mmol) and 2-bromo-1-(4-bromophenyl)ethan-1one (18.27 g, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (18.17 g, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (48% yield).

¹H NMR (300 MHz, CDCl₃ + **TFA**) δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.67 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H).

Compound LO2 was insoluble in conventional deuterated solvents for ¹³C NMR registration ¹³C NMR.

HRMS (ESI MS) m/z: Calculated: 314.9662 found: 314.9659 ([M-H]⁻ detected).



¹H NMR spectrum of (4-bromophenyl)(3-hydroxybenzofuran-2-yl)methanone LO3



Chemical Formula: C₁₉H₁₂O₃ Molecular Weight: 288.3020

Methyl 2-hydroxybenzoate (**10.00 g**, 65.73 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1one (**16.37 g**, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**18.17 g**, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (56% yield).

¹H NMR of two rotamers (400 MHz, CDCl₃ + **TFA**) δ 8.99 (s, 1H), 8.33 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.08 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.68 – 7.58 (m, 3H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.36 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H).

¹³C NMR of two rotamers (101 MHz, CDCl₃+**TFA**) δ 180.53, 162.69, 156.85, 137.68, 135.92, 133.03, 132.77, 132.49, 132.42, 131.60, 131.29, 130.13, 129.82, 129.38, 129.24, 128.82, 128.78, 128.04, 127.23, 127.16, 125.29, 125.01, 124.81, 123.81, 122.39, 120.05, 113.17.

HRMS (ESI MS) m/z: Calculated: 287.0714 found: 287.0706 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxy-2,3-dihydrobenzofuran-2-yl)(naphthalen-2-yl)methanone LO4

³C NMR spectrum of (3-hydroxy-2,3-dihydrobenzofuran-2-yl)(naphthalen-2-yl)methanone LO4





Molecular Weight: 266.2960

Methyl 2-hydroxybenzoate (**10.00 g**, 65.73 mmol) and 2-bromo-1-(4-ethylphenyl)ethan-1-one (**14.93 g**, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**18.17 g**, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et_2O . The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (53% yield).

¹H NMR (400 MHz, CDCl₃ + **TFA**) δ 8.24 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.68 (ddd, *J* = 8.5, 7.2, 1.2 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 182.55, 158.00, 154.95, 150.34, 135.78, 132.90, 130.75, 129.86, 128.20, 123.25, 121.51, 119.95, 112.79, 29.12, 15.18.

HRMS (ESI MS) m/z: Calculated: 265.0870 found: 265.0868 ([M-H]⁻ detected).



¹H NMR spectrum of (4-ethylphenyl)(3-hydroxy-2,3-dihydrobenzofuran-2-yl)methanone LO5

¹³C NMR spectrum of (4-ethylphenyl)(3-hydroxy-2,3-dihydrobenzofuran-2-yl)methanone LO5



Synthesis of benzo[d][1,3]dioxol-5-yl(3-hydroxy-2,3-dihydrobenzofuran-2-yl)methanone LO6



Chemical Formula: C₁₆H₁₀O₅ Molecular Weight: 282.2510

Methyl 2-hydroxybenzoate (10.00 g, 65.73 mmol) and 1-(benzo[d][1,3]dioxol-5-yl)-2bromoethan-1-one (15.97 g, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (18.17 g, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (49% yield).

¹H NMR (400 MHz, CDCl₃ + **TFA**) δ 8.06 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.13 (s, 2H).

Compound LO6 was insoluble in conventional deuterated solvents for ¹³C NMR registration ¹³C NMR.

HRMS (ESI MS) m/z: Calculated: 281.0455 found: 281.0458 ([M-H]⁻ detected).

¹*H* NMR spectrum of benzo[d][1,3]dioxol-5-yl(3-hydroxy-2,3-dihydrobenzofuran-2-yl)methanone LO6





Methyl 2-hydroxybenzoate (**10.00 g**, 65.73 mmol) and 4-(2-bromoacetyl)benzonitrile (**14.73 g**, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**18.17 g**, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Purification was achieved by recrystallization in diethyl ether and pure product was then obtained as an orange powder (63% yield).

¹H NMR (400 MHz, CDCl₃ + **TFA**) δ 8.43 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.74 (ddd, *J* = 8.6, 7.2, 1.3 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.37 (m, 1H).

Compound LO7 was insoluble in conventional deuterated solvents for ¹³C NMR registration ¹³C NMR.

HRMS (ESI MS) m/z: Calculated: 262.0510 found: 262.0515 ([M-H]⁻ detected).



¹H NMR spectrum of 4-(3-hydroxybenzofuran-2-carbonyl)benzonitrile LO7



Methyl 2-hydroxybenzoate (**10.00 g**, 65.73 mmol) and 2-bromo-1-(4-methoxyphenyl)ethan-1one (**15.06 g**, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**18.17 g**, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder. The product was purified using column chromatography on silica gel with DCM : pentane (1 ; 1) as eluent (48% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.54 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.30 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 7.04 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 181.74, 163.76, 157.32, 154.65, 135.65, 132.02, 130.47, 128.06, 123.18, 121.36, 119.93, 113.97, 112.68, 55.50.

HRMS (ESI MS) m/z: Calculated: 267.0663 found: 267.0659 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxy-2,3-dihydrobenzofuran-2-yl)(4-methoxyphenyl)methanone LO8

³C NMR spectrum of (3-hydroxy-2,3-dihydrobenzofuran-2-yl)(4-methoxyphenyl)methanone LO8



Synthesis of (6-bromo-9-dodecyl-9H-carbazol-3-yl)(3-hydroxy-2,3-dihydrobenzofuran-2-yl)methanone LO9



Methyl 2-hydroxybenzoate (**5.00 g**, 32.86 mmol) and 2-bromo-1-(6-bromo-9-dodecyl-9Hcarbazol-3-yl)ethan-1-one (**17.59 g**, 32.86 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**9.09 g**, 65.73 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (52% yield).

¹H NMR (400 MHz, CDCl₃, + **TFA**) δ 9.11 (s, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.29 (d, *J* = 1.9 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.32 (m, 3H), 4.32 (t, *J* = 7.2 Hz, 2H), 1.91 (t, *J* = 7.2 Hz, 3H), 1.44 – 1.23 (m, 27H), 0.92 – 0.85 (m, 4H).

Compound LO9 was insoluble in conventional deuterated solvents for ¹³C NMR registration ¹³C NMR.

HRMS (ESI MS) m/z: Calculated: 574.1791 found: 574.1780 ([M-H]⁻ detected).

¹H NMR spectrum of (6-bromo-9-dodecyl-9H-carbazol-3-yl)(3-hydroxy-2,3dihydrobenzofuran-2-yl)methanone LO9





Methyl 2-hydroxybenzoate (**10.00 g**, 65.73 mmol) and 2-bromo-1-(p-tolyl)ethan-1-one (**14.00 g**, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**18.17 g**, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et_2O . The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was obtained as a yellow powder (50% yield).

¹H NMR (400 MHz, CDCl₃ + **TFA**) δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.61 (ddd, *J* = 8.4, 7.0, 1.2 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 2.48 (s, 3H).

Compound LO10 was insoluble in conventional deuterated solvents for ¹³C NMR registration ¹³C NMR.

HRMS (ESI MS) m/z: Calculated: 251.0714 found: 251.0710 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxybenzofuran-2-yl)(p-tolyl)methanone LO10



Chemical Formula: C₁₈H₁₆O₆ Molecular Weight: 328,3200

Methyl 2-hydroxybenzoate (10.00 g, 65.73 mmol) and 2-bromo-1-(2,4,5trimethoxyphenyl)ethan-1-one (19.00 g, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (18.17 g, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. The product was purified using column chromatography on silica gel with DCM : pentane (1 ; 1) as eluent (51% yield).

¹H NMR (400 MHz, Acetone_D6) δ 7.81 (dt, J = 7.9, 1.0 Hz, 1H), 7.59 (ddd, J = 8.5, 7.1, 1.3 Hz, 1H), 7.50 (dt, J = 8.5, 0.9 Hz, 1H), 7.36 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H), 7.23 (s, 1H), 6.89 (s, 1H), 3.96 (s, 3H), 3.89 (s, 3H).

¹³C NMR (101 MHz, Acetone_D6) δ 185.16, 154.23, 154.06, 153.92, 153.03, 143.43, 136.11, 130.19, 123.17, 120.75, 120.23, 117.68, 113.54, 112.54, 98.38, 56.32, 56.06, 55.54.

HRMS (ESI MS) m/z: Calculated: 327.0874 found: 327.0872 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxybenzofuran-2-yl)(2,4,5-trimethoxyphenyl)methanone LO11

¹³C NMR spectrum of (3-hydroxybenzofuran-2-yl)(2,4,5-trimethoxyphenyl)methanone LO11





Molecular Weight: 328,3200

Methyl 2-hydroxybenzoate (10.00 g, 65.73 mmol) and 2-bromo-1-(3,4,5trimethoxyphenyl)ethan-1-one (19.00 g, 65.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (18.17 g, 131.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et_2O . The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (56% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.82 (m, 1H), 7.72 (s, 2H), 7.57 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.47 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.33 (ddd, *J* = 7.9, 7.1, 0.9 Hz, 1H), 4.00 (s, 6H), 3.98 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 181.86, 157.84, 154.75, 153.17, 142.95, 135.69, 130.81, 130.27, 123.39, 121.55, 119.84, 112.68, 107.37, 61.05, 56.37.

HRMS (ESI MS) m/z: Calculated: 327.0874 found: 327.0875 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxybenzofuran-2-yl)(3,4,5-trimethoxyphenyl)methanone LO12

³C NMR spectrum of (3-hydroxybenzofuran-2-yl)(3,4,5-trimethoxyphenyl)methanone LO12

1





Methyl 2-mercaptobenzoate (**10.00 g**, 59.45 mmol) and 2-bromo-1-phenylethan-1-one (**11.83 g**, 59.45 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**16.43 g**, 118.90 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (54% yield).

¹H NMR (400 MHz, CDCl₃) δ 13.45 (s, 1H), 8.10 – 8.03 (m, 3H), 7.74 (d, J = 8.2 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.58 – 7.51 (m, 3H), 7.44 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 191.79, 165.44, 140.84, 138.29, 132.64, 130.34, 130.18, 128.73, 128.43, 124.76, 124.03, 122.99, 109.65.

HRMS (ESI MS) m/z: Calculated: 253.0329 found: 253.0322 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxybenzo[b]thiophen-2-yl)(phenyl)methanone LS1

¹³C NMR spectrum of (3-hydroxybenzo[b]thiophen-2-yl)(phenyl)methanone LS1





Methyl 2-mercaptobenzoate (**5.00 g**, 29.72 mmol) and 2-bromo-1-(4-iodophenyl)ethan-1-one (**9.66 g**, 29.72 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**8.22 g**, 59.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et_2O . The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (60% yield).

¹H NMR (400 MHz, CDCl₃) δ 13.36 (s, 1H), 8.06 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 3H), 7.73 (dt, *J* = 8.2, 0.9 Hz, 2H), 7.57 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 190.63, 165.79, 140.71, 138.00, 137.48, 130.42, 130.21, 129.83, 124.87, 124.10, 123.00, 109.29, 100.25.

HRMS (ESI MS) m/z: Calculated: 378.9295 found: 378.9300 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxybenzo[b]thiophen-2-yl)(4-iodophenyl)methanone LS2

¹³C NMR spectrum of (3-hydroxybenzo[b]thiophen-2-yl)(4-iodophenyl)methanone LS2





Methyl 2-mercaptobenzoate (**5.00 g**, 29.72 mmol) and 2-bromo-1-(4-bromophenyl)ethan-1-one (**8.26 g**, 29.72 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**8.22 g**, 59.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Purification was achieved by recrystallization in diethyl ether and pure product was then obtained as a yellow powder (61% yield).

¹H NMR (400 MHz, CDCl₃) δ 13.36 (s, 1H), 8.07 (ddd, J = 8.1, 1.2, 0.8 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.74 (dt, J = 8.2, 0.9 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.57 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.44 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 190.45, 165.79, 140.73, 136.97, 132.05, 130.43, 130.24, 129.97, 127.71, 124.90, 124.12, 123.02, 109.32.

HRMS (ESI MS) m/z: Calculated: 332.9414 found: 332.9417 ([M-H]⁻ detected).



¹H NMR spectrum of (4-bromophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanone LS3

³C NMR spectrum of (4-bromophenyl)(3-hydroxybenzo[b]thiophen-2-yl)methanone LS3

1



Synthesis of (3-hydroxy-2,3-dihydrobenzo[b]thiophen-2-yl)(naphthalen-2-yl)methanone LS4



Chemical Formula: C₁₉H₁₂O₂S Molecular Weight: 304.3630

Methyl 2-mercaptobenzoate (**5.00 g**, 29.72 mmol) and 2-bromo-1-(naphthalen-2-yl)ethan-1one (**7.40 g**, 29.72 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**8.22 g**, 59.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H_2O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et_2O . The organic phase was washed with H_2O , dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (46% yield).

¹H NMR (400 MHz, CDCl₃) δ 13.55 (s, 1H), 8.63 (d, J = 1.8 Hz, 1H), 8.12 – 8.06 (m, 2H), 8.00 (dd, J = 14.7, 7.9 Hz, 2H), 7.92 (d, J = 7.3 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.66 – 7.54 (m, 3H), 7.45 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 191.58, 165.49, 140.85, 135.53, 135.27, 132.46, 130.37, 130.18, 129.85, 129.50, 128.73, 128.47, 127.88, 127.00, 124.77, 124.38, 124.04, 122.98, 109.83.

HRMS (ESI MS) m/z: Calculated: 303.0485 found: 303.0482 ([M-H]⁻ detected).



¹H NMR spectrum of (3-hydroxy-2,3-dihydrobenzo[b]thiophen-2-yl)(naphthalen-2-yl)methanone LS4

C NMR spectrum of (3-hydroxy-2,3-dihydrobenzo[b]thiophen-2-yl)(naphthalen-2-yl)methanone LS4



Synthesis of (4-ethylphenyl)(3-hydroxy-2,3-dihydrobenzo[b]thiophen-2-yl)methanone LS5



Chemical Formula: C₁₇H₁₄O₂S Molecular Weight: 282.3570

Methyl 2-mercaptobenzoate (**5.00 g**, 29.72 mmol) and 2-bromo-1-(4-ethylphenyl)ethan-1-one (**6.75 g**, 29.72 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**8.22 g**, 59.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Pure product was then obtained as a yellow powder (42% yield).

¹H NMR (400 MHz, CDCl₃) δ 13.57 (s, 1H), 8.07 (dt, J = 8.0, 1.1 Hz, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.74 (dt, J = 8.2, 0.9 Hz, 1H), 7.55 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H), 7.43 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H), 7.37 (d, J = 8.6 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 191.40, 165.39, 149.69, 140.71, 135.76, 130.38, 130.05, 128.72, 128.25, 124.69, 123.94, 122.95, 109.56, 29.01, 15.18.

HRMS (ESI MS) m/z: Calculated: 281.0642 found: 281.0642 ([M-H]⁻ detected).



¹*H NMR* spectrum of (4-ethylphenyl)(3-hydroxy-2,3-dihydrobenzo[b]thiophen-2-yl)methanone LS5

³C NMR spectrum of (4-ethylphenyl)(3-hydroxy-2,3-dihydrobenzo[b]thiophen-2yl)methanone LS5





Chemical Formula: C₁₆H₁₀O₄S Molecular Weight: 298,3120

Methyl 2-mercaptobenzoate (4.40 g, 26.16 mmol) and 1-(benzo[d][1,3]dioxol-5-yl)-2bromoethan-1-one (6.36 g, 26.16 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (7.23 g, 52.32 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Purification was achieved by recrystallization in diethyl ether and pure product was then obtained as a yellow powder (58% yield).

¹H NMR (400 MHz, $CDCl_3 + TFA$) δ 8.06 (dt, J = 7.8, 1.1 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.59 – 7.52 (m, 2H), 7.43 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.09 (s, 2H).

¹³C NMR (101 MHz, CDCl₃ + **TFA**) δ 191.64, 167.41, 152.43, 148.40, 142.54, 131.44, 130.97, 129.87, 125.36, 125.21, 124.85, 124.51, 122.98, 108.66, 108.50, 102.22.

HRMS (ESI MS) m/z: Calculated: 297.0227 found: 297.0225 ([M-H]⁻ detected).



¹H NMR spectrum of benzo[d][1,3]dioxol-5-yl(3-hydroxybenzo[b]thiophen-2-yl)methanone LS6

³C NMR spectrum of benzo[d][1,3]dioxol-5-yl(3-hydroxybenzo[b]thiophen-2-yl)methanone LS6





Methyl 2-mercaptobenzoate (**5.00 g**, 29.72 mmol) and 4-(2-bromoacetyl)benzonitrile (**6.66 g**, 29.73 mmol) were poured into a flask containing 200 mL of acetone. Then, potassium carbonate (**8.22 g**, 59.45 mmol) was added and the mixture was stirred under reflux overnight. The reaction was quenched by the addition of H₂O (20 mL) and acetone was removed under vacuum. The mixture was extracted with Et₂O. The organic phase was washed with H₂O, dried over MgSO₄, and the solvent was evaporated. Purification was achieved by recrystallization in diethyl ether and pure product was then obtained as an orange powder (47% yield).

¹H NMR (400 MHz, CDCl₃ + **TFA**) δ 8.14 – 8.08 (m, 3H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.63 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H).

Compound LS7 was insoluble in conventional deuterated solvents for ¹³C NMR registration.

HRMS (ESI MS) m/z: Calculated: 278.0281 found: 278.0281 ([M-H]⁻ detected).



¹H NMR spectrum of 4-(3-hydroxybenzo[b]thiophene-2-carbonyl)benzonitrile LS7