# Rhodium(III)-Catalyzed Directed C-H Naphthylation of Aryl Esters with 7-Oxabenzonorbornadienes

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## **Electronic Supporting Information (ESI)**

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## **Experimental Section**

#### **General information:**

All reactions were carried out under the  $N_2$  atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use (three times). Dry solvents were used for the reaction. Column chromatography purifications were performed using SiO<sub>2</sub> (100-200 mesh ASTM) from Merck if not indicated otherwise. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Starting Materials: Aryl ester,<sup>1</sup> 7-oxabenzonorbornadienes<sup>2</sup> and [Cp\*RhCl<sub>2</sub>]<sub>2</sub><sup>3</sup> was prepared according to literature procedure. Commercially available metal salts and other chemicals were purchased from Sigma-Aldrich and Spectrochem. Pvt. Ltd., India was used without further purification.

# General Procedure for the Synthesis of Aryl esters<sup>1</sup>

To a solution of acids (15 mmol) in MeOH (30 mL) was added  $SOCl_2$  (30 mmol). This mixture was heated to reflux for 3 h before evaporation. The residue was dissolved in DCM (30 mL), washed with aqueous NaHCO<sub>3</sub>, water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The residue was purified by column chromatography (n-hexane/EtOAc).

# General Procedure for the Synthesis of 7-Oxabenzonorbornadienes<sup>2</sup>

Under N<sub>2</sub> a stirred solution of substituted 1,2-dibromobenzene (14.06 mmol) in anhydrous THF 25 mL Furan 30 mL was treated drop wise with 5.8 mL of BuLi (2.4 M in hexane) at -78 °C. The solution was stirred at -78 °C for 1.5 hr. 20 mL distillated water was added to reaction mixture and left to warm up to room temperature, diethyl ether was added to the reaction mixture, separated, extracted and dried over Na<sub>2</sub>SO<sub>4</sub>. The ether was then removed in vacuo and the resulting mixture was purified by flash chromatography (10%~50% ethyl acetate in hexanes) to give the product.

#### **General Procedure for the Synthesis of Compounds 3:**

A 15-mL pressure tube with septum containing  $[Cp*RhCl_2]_2$  (5 mol %, 6.18 mg), and 7oxabenzonorbornadienes **2** (0.4 mmol), AgSbF<sub>6</sub> (20 mol %, 13.74 mg), and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (1 equiv, 0.2 mmol, 40 mg) was evacuated and purged with nitrogen gas three times. To the tube, were then added aryl ester **1** (0.2 mmol) and pivalic acid (2 equiv, 0.4 mmol, 81.6 mg) in 1,2-dichloroethane (2.0 mL) via syringe sequentially and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then the reaction mixture was allowed to stir at 100 °C for 12 h in the oil bath. Then, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), filtered through celite, and the filtrate was concentrated. The crude residue was purified by column chromatography. The crude residue was purified through a silica gel column using n-hexane and ethyl acetate as an eluant to give the pure desired product.

#### Synthesis of 2-(Naphthalen-2-yl)benzoic acid:

A reaction tube with a magnetic stir bar was charged with **3aa** (0.2 mmol), NaOH (10 equiv.) in (MeOH/H<sub>2</sub>O=1/1) (4.0 mL), and the mixture was stirred for 12 h at 70 °C. The reaction solution was then cooled to room temperature. The reaction mixture was poured into water (3  $\times$  20 mL) and extracted with EtOAc (3  $\times$  20 mL). The combined water layer was washed with water (2  $\times$  20 mL), saturated HCl (2  $\times$  20 mL), extracted with EtOAc (3  $\times$  20 mL), brine, and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under vacuum and got the desired product **6aa** (34 mg, 70%).

#### Synthesis of 11H-Benzo[*a*]fluoren-11-one:

A mixture of 2-(2-naphthyl-yl)benzoic acid **6aa** (0.2 mmol) and PPA (3 equiv) was stirred at 75 °C for 4 h under Ar. The color of the reaction mixture turned deep brown-black. The reaction mixture was poured on ice and water and stirred for 1 h. The yellow solid was filtered off, dissolved in  $CH_2Cl_2$ , the solution was washed with aqueous  $Na_2CO_3$  and water. The organic layer was dried on  $Na_2SO_4$ , filtered and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (PE:EtOAc, 95:5) to give **7aa** as an orange powder, yield 52 %.

#### Synthesis of 6H-Dibenzo[*c*,*h*]chromen-6-one:

To a 10 mL Wheaton V-vial substituted 2-(2-naphthyl-yl)benzoic acid **6aa-6ca** (0.2 mmol) and  $K_2S_2O_8$  (0.6 mmol, 3 equiv), followed by  $H_2O/MeCN$  (2 mL, 1:1) were added on air. The reaction mixture was heated for 18 h at 50 °C. Solution of NaHCO<sub>3</sub> (aq. saturated) was added to the reaction mixture, and the product was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated in vacuo. The residue was purified by column chromatography (ethyl acetate/hexanes 5/95 or dichloromethane) to produce the desired product **8aa-8ca** as a solid compound.

#### Synthesis of 1-Benzyl-3-(3-(naphthalen-2-yl)phenyl)pyrrolidine-2,5-dione:

The 2-(Naphthalen-2-yl)benzoic acid (0.2 mmol), 1-benzyl-1H-pyrrole-2,5-dione (1.5 equiv),  $[Ru(p-cymene)Cl_2]_2$  (5 mol %) and sodium bicarbonate (1 equiv) were taken in a dried screw cap reaction tube with a magnetic stir bar under open air. Then, dry DCE (2.0 mL) was added with a syringe, the tube was capped, and the resulting mixture was heated at 100 °C. After completion of the reaction, it was allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane : ethyl acetate = 80:20) to provide pure decarboxylated addition product.

S. No	Catalyst	Oxidant	Additive 1	Additive 2	Solvent	Temperature °C	Yield (%) <sup>b</sup>
1	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	-	$AgSbF_6$	-	DCE	100	nr
2	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	AgOAc	$AgSbF_6$	PivOH	DCE	100	25
3	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub>	$AgSbF_6$	PivOH	DCE	100	58
4	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	DCE	100	80
5	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	$AgSbF_6$	PivOH	DCE	100	67
6	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	2]2 Ag <sub>2</sub> O Ag		PivOH	DCE	100	trace
7	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	2] <sub>2</sub> Cu(OAc) <sub>2</sub> .H <sub>2</sub> O AgOTf PivOH		PivOH	DCE	100	62
8	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF <sub>6</sub>	AcOH	DCE	100	69
9	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF <sub>6</sub>	1-AdaCOOH	DCE	100	48
10	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF <sub>6</sub> MesCOOH DCE		DCE	100	19
11	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	- DCE		100	nr
12	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	1,4-dioxane	100	Trace
13	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF <sub>6</sub>	PivOH	1,2- dichlorobenzene	100	73
14	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cl <sub>2</sub> ] <sub>2</sub> Cu(OAc) <sub>2</sub> .H <sub>2</sub> O AgSbF <sub>6</sub>		PivOH	TFE	100	59
15	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	THF	100	Trace
16	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	toluene	100	24
17	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	DCE	120	76
18	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	DCE	80	49
19	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	DCE	60	Trace
20	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF <sub>6</sub>	PivOH	DCE	100	61 <sup>c</sup>
21	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	$AgSbF_6$	PivOH	DCE	100	48 <sup>d</sup>
22	[Cp*Rh(MeCN) <sub>3</sub> ](SbF <sub>6</sub> ) <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF <sub>6</sub>	PivOH	DCE	100	62
23	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF6	PivOH	DCE	100	46
24	[Cp*Co(CO)I <sub>2</sub> ]	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF6	PivOH	DCE	100	nr
25	$[Ru(p-cymene)Cl_2]_2$	Cu(OAc) <sub>2</sub> .H <sub>2</sub> O	AgSbF6	PivOH	DCE	100	nr

Table S1: Optimization of the Rhodium(III)-Catalyzed C-H Naphthylation<sup>a</sup>

<sup>a</sup>All reactions were carried out using aryl ester (**1a**) (0.1 mmol), 7-oxabenzonorbornadienes (**2a**) (0.2 mmol), catalyst (5 mol %), oxidant (1 equiv), additive 1 (20 mol %) and additive 2 (0.4 mmol) in solvent (1.0 mL) for 12 h. <sup>b</sup> Isolated yield. <sup>c</sup> with 2.5 mol % of [Cp\*RhCl<sub>2</sub>]<sub>2</sub>, <sup>d</sup> with 1.0 mol % of [Cp\*RhCl<sub>2</sub>]<sub>2</sub>.

## **Mechanistic studies**

#### (a) Deuterium Labeling Experiment for D-1a

A 15-mL pressure tube with septum containing  $[Cp*RhCl_2]_2$  (5 mol %, 6.18 mg), AgSbF<sub>6</sub> (20 mol %, 13.74 mg), and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (1 equiv, 0.1 mmol, 40 mg) was evacuated and purged with nitrogen gas three times. To the tube, were then added methyl benzoate **1a** (0.2 mmol, 27.22 mg) and pivalic acid (2 equiv, 0.4 mmol, 81.6 mg) and D<sub>2</sub>O (10 equiv, 20 mmol) in 1,2-dichloroethane (2.0 mL) via syringe sequentially and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then the reaction mixture was allowed to stir at 100 °C for 4 h in the oil bath. Then, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), filtered through celite, and the filtrate was concentrated. The crude residue was purified by column chromatography. In the reaction, product **D-1a** was observed in 93% yield with 21% of deuterium incorporation at both ortho carbons of methyl benzoate and 42% of deuterium incorporation is a key intermediate in the reaction as well as it is a reversible process.

<sup>1</sup>H Spectra of Compound **D1a** (400 MHz, CDCl<sub>3</sub>)



#### (b) General Procedure for Competition Experiment:

A 15-mL pressure tube with septum containing  $[Cp*RhCl_2]_2$  (5 mol %, 6.18 mg), and 7oxabenzonorbornadienes **2a** (0.4 mmol, 57.66 mg), AgSbF<sub>6</sub> (20 mol %, 13.74 mg), and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (1 equiv, 0.2 mmol, 40 mg) was evacuated and purged with nitrogen gas three times. To the tube, were then added methyl 4-methoxybenzoate **1b** (0.2 mmol, 33.23 mg), methyl 4-(trifluoromethyl)benzoate **1i** (0.2 mmol, 40.82 mg), and pivalic acid (2 equiv, 0.4 mmol, 81.6 mg) in 1,2-dichloroethane (2.0 mL) via syringe sequentially and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then the reaction mixture was allowed to stir at 100 °C for 12 h in the oil bath. Then, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), filtered through celite, and the filtrate was concentrated. The crude residue was purified by column chromatography. The crude residue was purified through a silica gel column using n-hexane and ethyl acetate as an eluant to give the pure desired product **3ba** and **3ia** in 49% (3.1:1) yield.

#### (c) General Procedure for Radical Trapping Experiment:

A 15-mL pressure tube with septum containing  $[Cp*RhCl_2]_2$  (5 mol %, 6.18 mg), and 7oxabenzonorbornadienes **2a** (0.4 mmol, 57.66 mg), AgSbF<sub>6</sub> (20 mol %, 13.74 mg), Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (1 equiv, 0.2 mmol, 40 mg) and TEMPO (1 equiv, 0.2 mmol, 31.25 mg) was evacuated and purged with nitrogen gas three times. To the tube, were then added methyl benzoate (0.2 mmol, 27.22 mg), and pivalic acid (2 equiv, 0.4 mmol, 81.6 mg) in 1,2dichloroethane (2.0 mL) via syringe sequentially and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then the reaction mixture was allowed to stir at 100 °C for 12 h in the oil bath. Then, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), filtered through celite, and the filtrate was concentrated. The crude residue was purified by column chromatography. The crude residue was purified through a silica gel column using n-hexane and ethyl acetate as an eluant to give the pure desired product.

#### (d) General Procedure for KIE Studies:

## i) Competitive Reaction



A 15-mL pressure tube with septum containing  $[Cp*RhCl_2]_2$  (5 mol %, 6.18 mg), and 7oxabenzonorbornadienes **2** (0.4 mmol), AgSbF<sub>6</sub> (20 mol %, 13.74 mg), and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (1 equiv, 0.2 mmol, 40 mg) was evacuated and purged with nitrogen gas three times. To the tube, were then added aryl ester **1a** (0.2 mmol), deuterated aryl ester  $[D_5]$ -**1a** (0.2 mmol) and pivalic acid (2 equiv, 0.4 mmol, 81.6 mg) in 1,2-dichloroethane (2.0 mL) via syringe sequentially and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then the reaction mixture was allowed to stir at 100 °C for 1 h in the oil bath. Then, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), filtered through celite, and the filtrate was concentrated. The crude residue was purified by column chromatography. The crude residue was purified through a silica gel column using n-hexane and ethyl acetate as an eluant to give the pure desired product. The ratio of the compounds was determined by <sup>1</sup>H NMR integration to give an intermolecular kinetic isotopic effect (KIE) value (k<sub>H</sub>/k<sub>D</sub> = 2.42).

<sup>1</sup>H Spectra of Compound **3aa/D-3aa** (400 MHz, CDCl<sub>3</sub>)



#### ii) Parallel reaction:



A 15-mL pressure tube with septum containing [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (5 mol %, 6.18 mg), and 7oxabenzonorbornadienes **2** (0.4 mmol), AgSbF<sub>6</sub> (20 mol %, 13.74 mg), and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (1 equiv, 0.2 mmol, 40 mg) was evacuated and purged with nitrogen gas three times. To the tube, were then added aryl ester **1a** (0.2 mmol) or deuterated aryl ester [**D**<sub>5</sub>]-**1a** (0.2 mmol) and pivalic acid (2 equiv, 0.4 mmol, 81.6 mg) in 1,2-dichloroethane (2.0 mL) via syringe sequentially and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then the reaction mixture was allowed to stir at 100 °C in the oil bath. For 90 min, an aliquot (0.1 mL) was removed by a syringe every 15 min and directly analyzed by <sup>1</sup>H-NMR. The KIE value was found to be  $k_{\rm H}/k_{\rm D} \approx 2.25$ .



#### (e) General Procedure for the C-H Naphthylation reaction in 3 mmol:

A 60-mL pressure tube with septum containing  $[Cp*RhCl_2]_2$  (5 mol %, 92.71 mg), and 7oxabenzonorbornadienes **2a** (6 mmol, 865 mg), AgSbF<sub>6</sub> (20 mol %, 206.17 mg), and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (1 equiv, 3 mmol, 598.95 mg) was evacuated and purged with nitrogen gas three times. To the tube, were then added methyl benzoate **1a** (3 mmol, 402.52 mg) and pivalic acid (2 equiv, 6 mmol, 612.78 mg) in 1,2-dichloroethane (20 mL) via syringe sequentially and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then the reaction mixture was allowed to stir at 100 °C for 12 h in the oil bath. Then, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL), filtered through celite, and the filtrate was concentrated. The crude residue was purified by column chromatography. The crude residue was purified through a silica gel column using n-hexane and ethyl acetate as an eluant to give the pure desired product **3aa** in 72% yield (566 mg) as a colourless liquid.

# Spectral Data of All Compounds.

Methyl 2-(naphthalen-2-yl)benzoate (3aa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 80% (42 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (tt, *J* = 7.9, 3.8 Hz, 4H), 7.79 (s, 1H), 7.55 (dd, *J* = 7.9, 2.5 Hz, 1H), 7.52 – 7.40 (m, 5H), 3.58 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.2, 142.5, 139.0, 133.3, 132.5, 131.4, 131.1, 131.0, 130.0, 128.1, 127.7, 127.4, 127.3, 127.0, 126.9, 126.2, 126.0, 52.0. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>H 263.1067; Found 263.1062.

Methyl 4-methoxy-2-(naphthalen-2-yl)benzoate (3ba)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 82% (48 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, *J* = 9.3 Hz, 1H), 7.77 (dd, *J* = 11.8, 6.8 Hz, 3H), 7.69 (s, 1H), 7.48 – 7.37 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 3.49 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 161.9, 145.4, 139.4, 133.3, 132.6, 132.6, 128.1, 127.8, 127.2, 127.2, 126.6, 126.2, 126.0, 122.6, 116.7, 112.7, 55.5, 51.7. HRMS (ESI/Q-TOF) m/z: [M + K]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>K 331.0731; Found 331.0727.

## Methyl 4-methyl-2-(naphthalen-2-yl)benzoate (3ca)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 76% (42 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (dd, *J* = 17.2, 9.9 Hz, 5H), 7.55 – 7.45 (m, 2H), 7.41 (d, *J* = 8.4 Hz,

1H), 7.33 – 7.17 (m, 2H), 3.58 (s, 3H), 2.43 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.0, 142.8, 142.0, 139.3, 133.3, 132.5, 132.0, 130.3, 128.1, 128.0, 127.9, 127.7, 127.2, 127.2, 126.7, 126.2, 125.9, 51.9, 21.5. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>H 277.1223; Found 277.1236.

Methyl 4-fluoro-2-(naphthalen-2-yl)benzoate (3da)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 62% (35 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 – 7.82 (m, 4H), 7.78 (s, 1H), 7.51 (d, *J* = 3.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.14 (dd, *J* = 19.9, 9.2 Hz, 2H), 3.59 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.0, 165.4, 162.9, 145.7, 145.6, 137.9, 133.2, 132.7, 132.6, 128.2, 127.8, 127.5, 126.8, 126.7, 126.4, 126.3, 118.3, 118.0, 114.4, 114.2, 52.1. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>FO<sub>2</sub>H 281.0972; Found 281.0977.

Methyl 4-chloro-2-(naphthalen-2-yl)benzoate (3ea)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 67% (40 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, *J* = 11.8 Hz, 4H), 7.78 (s, 1H), 7.50 (dd, *J* = 11.5, 7.8 Hz, 3H), 7.40 (dd, *J* = 11.9, 9.1 Hz, 2H), 3.59 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.1, 144.4, 137.7, 137.5, 133.2, 132.7, 131.6, 131.2, 129.1, 128.2, 127.8, 127.6, 127.5, 126.9, 126.6, 126.4, 126.3, 52.1. HRMS (ESI/Q-TOF) m/z: [M]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>ClO<sub>2</sub> 296.0599; Found 296.0599.

Methyl 4-bromo-2-(naphthalen-2-yl)benzoate (3fa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 52% (36 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, *J* = 8.3 Hz, 3H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.64 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.51 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 3.59 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 144.5, 137.6, 134.1, 133.2, 132.7, 131.6, 130.4, 129.6, 128.2, 127.8, 127.6, 126.9, 126.6, 126.4, 126.3, 126.0, 52.2. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>BrO<sub>2</sub>H 341.0172; Found 341.0180.

#### Methyl 4-iodo-2-(naphthalen-2-yl)benzoate (3ga)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 40% (35 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, *J* = 7.2 Hz, 4H), 7.74 – 7.67 (m, 2H), 7.53 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.43 (q, *J* = 3.9 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 1H), 3.51 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 144.3, 140.0, 137.5, 136.4, 133.2, 132.7, 131.4, 130.2, 128.2, 127.8, 127.6, 126.9, 126.7, 126.4, 126.3, 98.4, 52.2. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>IO<sub>2</sub>H 389.0033; Found 389.0037.

## Methyl 4-(tert-butyl)-2-(naphthalen-2-yl)benzoate (3ha)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 79% (50 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (dd, J = 7.8, 4.9 Hz, 4H), 7.79 (s, 1H), 7.55 – 7.39 (m, 5H), 3.58 (s, 3H), 1.37 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.0, 155.1, 142.5, 139.7, 133.3, 132.5, 130.1, 128.4, 128.1, 127.9, 127.8, 127.3, 127.3, 126.8, 126.2, 125.9, 124.4, 51.9, 35.1, 31.2. HRMS (ESI/Q-TOF) m/z: [M + K]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>K 357.1251; Found 357.1254.

## Methyl 2-(naphthalen-2-yl)-4-(trifluoromethyl)benzoate (3ia)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 41% (27 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 3H), 7.82 (s, 1H), 7.75 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.53 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 3.62 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 143.0, 137.4, 134.3, 133.2, 132.7, 130.4, 128.2, 127.9, 127.8, 127.1, 126.5, 126.5, 124.1, 121.1, 118.1, 52.4. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub>Na 353.0760; Found 353.0764.

#### Methyl 2-(naphthalen-2-yl)-4-nitrobenzoate (3ja)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 29% (18 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (s, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 3H), 7.84 (s, 1H), 7.54 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 3.64 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.7, 149.2, 143.8, 136.7, 136.4, 133.2, 132.9, 130.9, 128.2, 128.1, 127.8, 127.3, 126.8, 126.1, 125.7, 122.0, 52.6. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>NO<sub>4</sub>NH<sub>4</sub> 325.1183; Found 325.1177.

## Methyl 5-methyl-2-(naphthalen-2-yl)benzoate (3ka)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 75% (42 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (dd, J = 10.3, 6.4 Hz, 4H), 7.77 (s, 1H), 7.69 (s, 1H), 7.53 – 7.45 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.36 (s, 1H), 3.58 (s, 3H), 2.43 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.4, 139.6, 138.9, 137.2, 133.4, 132.4, 132.2, 131.0, 130.7, 130.5, 128.1, 127.7, 127.4, 127.2, 126.8, 126.2, 125.9, 52.0, 21.0. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>Na 299.1043; Found 299.1057.

## Methyl 5-fluoro-2-(naphthalen-2-yl)benzoate (3la)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 28% (16 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 – 7.68 (m, 3H), 7.62 (d, *J* = 0.9 Hz, 1H), 7.47 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.26 (ddd, *J* = 8.4, 7.7, 3.6 Hz, 2H), 7.10 (td, *J* = 8.2, 2.7 Hz, 1H), 3.46 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.8, 162.7, 160.7, 138.7, 138.7, 138.0, 133.3, 132.9, 132.9, 132.6, 132.5, 132.5, 128.1, 128.1, 128.1, 127.8, 127.7, 127.5, 127.1, 127.03, 127.02, 126.99, 126.4, 126.2, 118.5, 118.3, 117.0, 116.8, 52.2. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>FO<sub>2</sub>H 281.0972; Found 281.0959.

## Methyl 5-chloro-2-(naphthalen-2-yl)benzoate (3ma)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 58% (34 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, *J* = 9.2 Hz, 4H), 7.76 (s, 1H), 7.59 – 7.47 (m, 3H), 7.46 – 7.35 (m, 2H), 3.61 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.8, 141.0, 137.7, 133.4, 133.3, 132.6, 132.4, 132.2, 131.4, 129.9, 128.1, 127.7, 127.6, 126.9, 126.8, 126.4, 126.2, 52.3. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>ClO<sub>2</sub>H 297.0677; Found 297.0673.

Methyl 5-bromo-2-(naphthalen-2-yl)benzoate (3na)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 47% (32 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (d, *J* = 2.0 Hz, 1H), 7.91 – 7.83 (m, 3H), 7.76 (s, 1H), 7.68 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.50 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.36 (dd, *J* = 15.0, 8.3 Hz, 2H), 3.61 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.7, 141.4, 137.7, 134.4, 133.3, 132.8, 132.7, 132.5, 128.1, 127.8, 127.6, 126.9, 126.7, 126.4, 126.2, 121.3, 52.3. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>BrO<sub>2</sub>H 341.0172; Found 341.0172.

#### Methyl 2-methyl-6-(naphthalen-2-yl)benzoate (3oa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 73% (40 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 – 7.81 (m, 4H), 7.56 – 7.45 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.22 (m, 1H), 3.53 (s, 3H), 2.43 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.4, 140.1, 138.4, 135.6, 133.3, 132.5, 129.5, 129.3, 128.2, 127.9, 127.7, 127.6, 127.1, 126.5, 126.3, 126.1, 51.9, 19.8. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>Na 299.1043; Found 299.1042.

#### Methyl 2-methoxy-6-(naphthalen-2-yl)benzoate (3pa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 64% (37 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d, *J* = 8.9 Hz, 4H), 7.48 (ddd, *J* = 22.4, 14.1, 9.0 Hz, 4H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 3.59 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 156.6, 141.2, 137.5, 133.3, 132.7, 130.6, 128.2, 128.0, 127.7, 127.2, 126.4, 126.3, 126.2, 123.3, 122.3, 110.0, 56.1, 52.2. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>NH<sub>4</sub> 310.1438; Found 310.1441.

#### Methyl 2-fluoro-6-(naphthalen-2-yl)benzoate (3qa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 38% (21 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 – 7.74 (m, 4H), 7.51 – 7.37 (m, 4H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 8.8 Hz, 1H), 3.56 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.2, 161.1, 158.6, 142.5, 136.8, 133.3, 132.8, 131.4, 131.3, 128.2, 128.2, 127.7, 127.3, 126.5, 126.4, 126.2, 125.8,

125.8, 114.8, 114.6, 52.5. HRMS (ESI/Q-TOF) m/z:  $[M + H]^+$  Calcd for C<sub>18</sub>H<sub>13</sub>FO<sub>2</sub>H 281.0972; Found 281.0973.

Methyl 2-chloro-6-(naphthalen-2-yl)benzoate (3ra)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 42% (25 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 – 7.82 (m, 4H), 7.51 (dd, *J* = 9.0, 6.0 Hz, 4H), 7.47 – 7.37 (m, 2H), 3.64 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.6, 141.7, 136.8, 133.3, 133.2, 132.8, 131.3, 130.3, 128.4, 128.3, 128.2, 127.7, 127.4, 126.5, 126.4, 126.2, 52.4. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>ClO<sub>2</sub>Na 319.0496; Found 319.0489.

## methyl 2-bromo-6-(naphthalen-2-yl)benzoate (3sa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 37% (25 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 – 7.78 (m, 4H), 7.57 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.48 (dd, *J* = 6.2, 3.3 Hz, 3H), 7.40 – 7.34 (m, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 3.61 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 141.8, 136.8, 135.5, 133.2, 132.8, 131.6, 130.7, 129.1, 128.3, 127.8, 127.5, 126.61, 126.56, 126.2, 119.8, 52.5. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>14</sub>BrO<sub>2</sub>H 341.0172; Found 341.0179.

#### Methyl 3-(naphthalen-2-yl)thiophene-2-carboxylate (3ta)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 56% (30 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 – 7.81 (m, 4H), 7.64 – 7.44 (m, 4H), 7.19 (d, *J* = 4.7 Hz, 1H), 3.77 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.6, 148.7, 133.3, 133.0, 132.9, 131.8, 130.4,

128.2, 128.0, 127.7, 127.6, 127.2, 126.3, 126.2, 52.0. HRMS (ESI/Q-TOF) m/z:  $[M + Na]^+$  Calcd for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>SNa 291.0450; Found 291.0443.

Ethyl 2-(naphthalen-2-yl)benzoate (3ua)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 77% (43 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 – 7.71 (m, 4H), 7.68 (s, 1H), 7.47 – 7.41 (m, 2H), 7.41 – 7.29 (m, 4H), 3.96 (q, *J* = 7.1 Hz, 2H), 0.78 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.8, 142.4, 139.1, 133.3, 132.5, 131.5, 131.2, 131.0, 129.9, 128.1, 127.7, 127.4, 127.3, 127.2, 127.2, 127.2, 127.01, 126.98, 126.2, 126.0, 60.9, 13.7. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>NH<sub>4</sub> 294.1489; Found 294.1486.

#### Isopropyl 2-(naphthalen-2-yl)benzoate (3va)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 56% (33 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 – 7.80 (m, 4H), 7.77 (s, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.39 (m, 5H), 4.95 (dt, *J* = 12.5, 6.2 Hz, 1H), 0.91 (d, *J* = 6.3 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 142.2, 139.1, 133.2, 132.5, 132.0, 131.0, 130.9, 129.7, 128.0, 127.7, 127.5, 127.3, 127.2, 127.1, 126.2, 125.9, 68.6, 21.4. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>NH<sub>4</sub> 308.1645; Found 308.1647.

#### Phenyl 2-(naphthalen-2-yl)benzoate (3wa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 61% (40 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.90 – 7.80 (m, 4H), 7.72 – 7.37 (m, 6H), 7.19 (td, *J* = 8.3, 7.9, 1.7 Hz, 2H), 7.07 (td, *J* = 7.3, 1.4 Hz, 1H), 6.83 – 6.75 (m, 2H). <sup>13</sup>C

NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 150.7, 142.9, 138.8, 133.3, 132.6, 131.9, 131.3, 130.5, 129.3, 128.1, 127.8, 127.8, 127.5, 127.2, 126.4, 126.2, 125.7, 121.3. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>16</sub>O<sub>2</sub>H 325.1223; Found 325.1222.

#### Benzyl 2-(naphthalen-2-yl)benzoate (3xa)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 63% (43 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J = 7.6 Hz, 1H), 7.82 (ddd, J = 16.9, 9.8, 4.0 Hz, 4H), 7.59 – 7.37 (m, 6H), 7.12 (t, J = 7.3 Hz, 1H), 6.98 (t, J = 7.4 Hz, 2H), 6.78 (d, J = 7.5 Hz, 2H), 5.03 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.7, 142.5, 139.1, 135.1, 133.4, 132.6, 131.4, 131.1, 130.1, 128.2, 128.1, 128.1, 128.0, 127.8, 127.6, 127.4, 127.1, 127.0, 126.3, 126.0, 67.0. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>2</sub>Na 361.1199; Found 361.1206.

## Methyl 2,3-dimethoxy-6-(naphthalen-2-yl)benzoate (5aa)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 69% (45 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 – 7.80 (m, 4H), 7.53 – 7.42 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 3.93 (d, *J* = 10.4 Hz, 6H), 3.62 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 152.1, 146.3, 137.3, 133.4, 132.6, 132.5, 129.1, 128.1, 128.0, 127.7, 127.1, 126.6, 126.3, 126.0, 125.7, 113.7, 61.8, 56.1, 52.2. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>NH<sub>4</sub> 340.1543; Found 340.1545.

Methyl 5-(naphthalen-2-yl)benzo[d][1,3]dioxole-4-carboxylate (5ba)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 73% (45 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (t, *J* = 6.8 Hz, 3H), 7.76 (s, 1H), 7.58 – 7.45 (m, 2H), 7.39 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.94 (s, 2H), 6.11 (s, 2H), 3.58 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.2, 147.6, 147.3, 138.1, 135.3, 133.4, 132.4, 128.1, 127.7, 127.6, 126.9, 126.8, 126.3, 126.0, 124.0, 114.3, 110.2, 102.2, 52.1. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>14</sub>O<sub>4</sub>Na 329.0784; Found 329.0782.

## Methyl 4,5-dimethyl-2-(naphthalen-2-yl)benzoate (5ca)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 76% (44 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (dd, *J* = 9.9, 5.3 Hz, 3H), 7.76 (s, 1H), 7.69 (s, 1H), 7.52 – 7.43 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.22 (s, 1H), 3.57 (s, 3H), 2.33 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.1, 140.7, 140.4, 139.2, 135.9, 133.4, 132.5, 132.4, 131.3, 128.1, 128.0, 127.7, 127.4, 127.2, 126.7, 126.1, 125.8, 51.8, 19.9, 19.3. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>Na 313.1199; Found 313.1197.

## Methyl 4,5-dimethoxy-2-(naphthalen-2-yl)benzoate (5da)



Colourless oil; eluent (15% ethyl acetate in hexane). Isolated yield is 68% (44 mg). <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.92 – 7.80 (m, 3H), 7.76 (s, 1H), 7.56 – 7.45 (m, 3H), 7.40 (dd, J = 8.4, 1.5 Hz, 1H), 6.89 (s, 1H), 3.96 (d, J = 19.0 Hz, 6H), 3.57 (s, 3H). 13C NMR (101 MHz, CDCl3)  $\delta$  168.2, 151.3, 147.9, 139.4, 137.4, 133.3, 132.4, 128.0, 127.7, 127.5, 127.1, 126.6, 126.2, 125.9, 122.0, 114.0, 113.0, 56.2, 56.1, 51.8. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>NH<sub>4</sub> 340.1543; Found 340.1550.

## Methyl [2,2'-binaphthalene]-3-carboxylate (5ea)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 51% (32 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.45 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.84 (m, 6H), 7.62 – 7.53 (m, 2H), 7.53 – 7.47 (m, 3H), 3.65 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.1, 139.2, 138.8, 134.5, 133.4, 132.5, 131.7, 131.3, 130.2, 129.1, 128.7, 128.4, 128.1, 127.9, 127.8, 127.4, 127.3, 126.9, 126.9, 126.3, 126.0, 52.2. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>NH<sub>4</sub> 330.1489; Found 330.1489.

#### Methyl 6-(naphthalen-2-yl)benzo[d][1,3]dioxole-5-carboxylate (5fa)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 46% (47 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 – 7.74 (m, 3H), 7.72 (s, 1H), 7.53 – 7.41 (m, 2H), 7.42 – 7.32 (m, 2H), 6.87 (s, 1H), 6.04 (s, 2H), 3.54 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.1, 150.2, 146.9, 139.2, 139.0, 133.3, 132.4, 128.1, 127.7, 127.3, 126.7, 126.2, 126.0, 123.9, 111.3, 110.1, 102.0, 51.9. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>14</sub>O<sub>4</sub>NH<sub>4</sub> 324.1230; Found 324.1233.

Methyl 4-(naphthalen-2-yl)benszo[d][1,3]dioxole-5-carboxylate (5fa')



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 15% (9 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (dd, J = 11.9, 8.4 Hz, 4H), 7.59 (d, J = 8.2 Hz, 1H), 7.54 – 7.37 (m, 3H), 6.86 (d, J = 8.2 Hz, 1H), 6.01 (s, 2H), 3.55 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.8, 150.3, 146.2, 133.1, 132.7, 132.4, 128.2, 127.8, 127.5, 127.2, 126.2, 126.1, 126.0,

124.5, 124.5, 107.2, 101.8, 51.9. HRMS (ESI/Q-TOF) m/z:  $[M + NH_4]^+$  Calcd for  $C_{19}H_{14}O_4NH_4$  324.1230; Found 324.1232.

Methyl 3,5-dimethyl-2-(naphthalen-2-yl)benzoate (5ga)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 26% (15 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, *J* = 8.0 Hz, 2H), 7.82 – 7.75 (m, 1H), 7.55 (d, *J* = 12.7 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.23 (s, 1H), 3.42 (s, 3H), 2.38 (s, 3H), 2.06 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.0, 139.0, 138.1, 137.4, 137.0, 134.0, 133.4, 132.4, 131.8, 128.0, 127.8, 127.8, 127.7, 127.4, 127.2, 126.0, 125.8, 51.8, 21.0, 20.8. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>NH<sub>4</sub> 308.1645; Found 308.1646.

Methyl 3,4,5-trimethoxy-2-(naphthalen-2-yl)benzoate (5ha)



Colourless oil; eluent (15% ethyl acetate in hexane). Isolated yield is 19% (13 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 – 7.79 (m, 3H), 7.69 (s, 1H), 7.50 – 7.43 (m, 2H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 2.7 Hz, 1H), 3.96 (d, *J* = 12.0 Hz, 6H), 3.54 (s, 3H), 3.45 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 152.5, 151.8, 145.5, 134.4, 133.2, 132.4, 130.5, 128.2, 128.1, 128.0, 127.7, 127.0, 126.7, 125.9, 125.8, 109.1, 61.0, 56.2, 51.9. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>5</sub>Na 375.1203; Found 375.1212.

## (1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 2-(naphthalen-2-yl)benzoate (5ia)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 34% (26 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (dq, J = 9.2, 5.8 Hz, 4H), 7.75 (d, J = 1.8 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.50 – 7.38 (m, 5H), 4.66 (td, J = 10.8, 4.4 Hz, 1H), 1.85 (dtd, J = 12.0, 4.0, 1.9 Hz, 1H), 1.51 (dddd, J = 19.8, 13.4, 6.3, 3.3 Hz, 2H), 1.43 – 1.27 (m, 2H), 1.04 (ddt, J = 13.9, 10.8, 3.1 Hz, 1H), 0.96 – 0.80 (m, 2H), 0.73 (d, J = 6.6 Hz, 3H), 0.59 (d, J = 7.0 Hz, 3H), 0.54 (d, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 142.1, 139.1, 133.3, 132.6, 132.4, 130.9, 130.9, 129.4, 128.1, 127.7, 127.6, 127.2, 127.2, 127.1, 126.2, 126.0, 75.1, 46.7, 40.3, 34.1, 31.2, 25.7, 23.1, 21.9, 20.7, 15.9. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>30</sub>O<sub>2</sub>H 387.2324; Found 387.2334.

## (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-

2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(naphthalen-2-yl)benzoate (5ja)



Colourless oil; eluent (5% ethyl acetate in hexane). Isolated yield is 28% (34 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 – 7.78 (m, 4H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.55 – 7.46 (m, 1H), 7.45 – 7.37 (m, 5H), 5.13 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.52 (tt, *J* = 11.4, 4.7 Hz, 1H), 1.95 (ddd, *J* = 12.9, 4.9, 2.4 Hz, 2H), 1.90 – 1.74 (m, 3H), 1.68 – 1.48 (m, 5H), 1.45 – 1.17 (m, 9H), 1.18 – 0.73 (m, 18H), 0.70 (s, 3H), 0.62 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 142.4, 139.6, 139.2, 133.3, 132.5, 131.9, 131.1, 130.9, 129.9, 128.0, 127.7, 127.5, 127.3, 127.2, 127.1, 126.3, 126.0, 122.5, 74.9, 56.7, 56.2, 50.0, 42.3, 39.7, 39.6, 37.4, 36.8, 36.5, 36.3, 35.9, 31.9, 31.8, 28.3, 28.1, 27.2, 24.3, 23.9, 22.9, 22.7, 21.0, 19.0, 18.8, 11.9. HRMS (ESI/Q-TOF) m/z: [M + NH<sub>4</sub>]<sup>+</sup> Calcd for C<sub>44</sub>H<sub>56</sub>O<sub>2</sub>NH<sub>4</sub> 634.4619; Found 634.4627.

#### Methyl 2-(6,7-dimethylnaphthalen-2-yl)-4-methylbenzoate (5cb)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 69% (42 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.61 (d, *J* = 3.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.25 (dd, *J* = 12.7, 6.0 Hz, 1H), 3.56 (s, 3H), 2.44 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.3, 142.9, 141.8, 138.3, 135.9, 135.7, 132.2, 131.9, 131.4, 130.2, 128.0, 127.8, 127.6, 127.2, 126.3, 126.2, 125.8, 51.9, 21.5, 20.3. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>H 305.1536; Found 305.1538.

Methyl 2-(6,7-dimethoxynaphthalen-2-yl)benzoate (5ac)



Colourless oil; eluent (20% ethyl acetate in hexane). Isolated yield is 46% (30 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d, *J* = 7.4 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.57 (s, 1H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.27 – 7.16 (m, 1H), 7.07 (s, 2H), 3.93 (d, *J* = 4.0 Hz, 6H), 3.52 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.5, 149.8, 149.6, 142.6, 137.3, 131.3, 131.1, 131.0, 129.8, 129.0, 128.3, 127.1, 126.0, 125.5, 125.2, 106.5, 106.2, 55.9, 52.0. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>Na 345.1097; Found 345.1100.

## Methyl 2-(5,8-dimethoxynaphthalen-2-yl)benzoate (5ad)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 36% (23 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.11 (d, *J* = 9.8 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.21 (m, 4H), 6.58 (s, 2H), 3.82 (d, *J* = 10.6 Hz, 6H), 3.46 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.4, 149.7, 149.5, 142.7, 138.9, 131.4, 131.2, 131.0, 129.9, 127.2, 126.9, 126.2, 125.3, 121.5, 121.1, 103.6, 103.4, 55.8, 55.7, 52.0. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>H 323.1278; Found 323.1278.

## methyl 2-(naphtho[2,3-d][1,3]dioxol-6-yl)benzoate (5ae)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 41% (25 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.59 (s, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (dd, *J* = 19.4, 8.0 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.10 (s, 2H), 5.98 (s, 2H), 3.59 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.4, 147.9, 147.8, 142.4, 137.4, 131.4, 131.0, 130.4, 129.9, 129.6, 127.2, 126.6, 126.2, 125.4, 104.1, 103.8, 101.1, 52.1. HRMS (ESI/Q-TOF) m/z: [M + K]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>14</sub>O<sub>4</sub>K 345.0524; Found 345.0529.

#### Methyl 2,3-dimethoxy-6-(naphtho[2,3-d][1,3]dioxol-6-yl)benzoate (5ie)



Colourless oil; eluent (20% ethyl acetate in hexane). Isolated yield is 17% (13 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.04 (s, 2H), 6.96 (d, *J* = 8.3 Hz, 1H), 5.96 (s, 2H), 3.86 (d, *J* = 4.0 Hz, 6H), 3.57 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.2, 151.9, 147.9, 147.8, 146.2, 135.8, 132.7, 130.5, 129.5, 129.0, 127.0, 126.3, 125.6, 125.0, 113.7, 104.0, 103.7, 101.1, 61.7, 56.1, 52.2. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>18</sub>O<sub>6</sub>Na 389.0996; Found 389.0996.

Methyl 2-(6,7-difluoronaphthalen-2-yl)benzoate (5af)



Colourless oil; eluent (10% ethyl acetate in hexane). Isolated yield is 28% (17 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (dd, J = 7.7, 1.0 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.62 (s, 1H), 7.56 – 7.44 (m, 3H), 7.42 – 7.30 (m, 3H), 3.54 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.6, 150.4, 150.2, 150.2, 150.0, 148.4, 148.2, 148.2, 148.0, 141.1, 138.5, 130.5, 130.0, 129.7, 129.1, 129.1, 129.0, 128.2, 128.2, 126.6, 126.47, 126.46, 125.7, 125.6, 125.10, 125.06, 112.8,

112.7, 112.5, 112.4, 50.9. HRMS (ESI/Q-TOF) m/z:  $[M + NH_4]^+$  Calcd for  $C_{18}H_{12}F_2O_4NH_4$  316.1144; Found 316.1142.

## 2-(Naphthalen-2-yl)benzoic acid (6aa)



White solid; eluent (20% ethyl acetate in hexane). Isolated yield is 70% (35 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.83 – 7.75 (m, 2H), 7.57 (td, *J* = 7.5, 1.4 Hz, 1H), 7.48 (dt, *J* = 6.3, 3.5 Hz, 2H), 7.43 (td, *J* = 8.7, 1.5 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl3)  $\delta$  173.0, 143.4, 138.8, 133.3, 132.6, 132.2, 131.6, 130.8, 129.4, 128.2, 127.7, 127.4, 127.3, 127.2, 127.0, 126.2, 126.1, 126.0. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>12</sub>O<sub>2</sub>Na 271.0730; Found 271.0732.

## 11H-Benzo[*a*]fluoren-11-one (7aa)



White solid; eluent (10% ethyl acetate in hexane). Isolated yield is 52% (24 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 (d, *J* = 8.4 Hz, 1H), 7.90 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.54 (td, *J* = 7.8, 7.3, 1.9 Hz, 3H), 7.39 (tt, *J* = 6.9, 2.0 Hz, 3H), 7.22 (td, *J* = 7.3, 3.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  195.2, 146.1, 143.9, 135.8, 134.6, 134.4, 134.1, 130.2, 129.3, 129.2, 128.5, 126.9, 126.4, 124.3, 123.7, 119.9, 118.0. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>10</sub>ONa 253.0624; Found 253.0621.

## 6H-Dibenzo[*c*,*h*]chromen-6-one (8aa)



White solid; eluent (10% ethyl acetate in hexane). Isolated yield is 79% (39 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.40 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.10 (d, *J* 

= 8.0 Hz, 1H), 7.96 (dd, J = 8.8, 2.7 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.69 (d, J = 8.7 Hz, 1H), 7.64 – 7.49 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  161.2, 147.1, 135.3, 134.9, 134.2, 130.6, 128.6, 127.8, 127.8, 127.6, 127.6, 127.1, 124.5, 123.8, 122.3, 122.0, 121.1, 119.1, 112.9. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>10</sub>O<sub>2</sub>H 247.0754; Found 247.0764.

## 6H-Dibenzo[c,h]chromen-6-one (8ba)



White solid; eluent (15% ethyl acetate in hexane). Isolated yield is 70% (36 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.58 – 8.45 (m, 1H), 8.32 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.22 (d, *J* = 9.1 Hz, 1H), 7.82 – 7.71 (m, 1H), 7.72 – 7.48 (m, 4H), 7.39 (t, *J* = 7.7 Hz, 1H), 2.87 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.6, 147.0, 139.2, 134.8, 134.2, 133.3, 129.0, 128.0, 127.8, 127.1, 126.7, 123.7, 123.2, 123.2, 122.5, 122.5, 114.5, 25.4. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>12</sub>O<sub>2</sub>H 261.0910; Found 261.0914.

#### 8,9-Dimethoxy-6H-dibenzo[c,h]chromen-6-one (8ca)



White solid; eluent (20% ethyl acetate in hexane). Isolated yield is 74% (46 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (d, *J* = 8.1 Hz, 0H), 7.82 (dd, *J* = 20.5, 8.3 Hz, 1H), 7.71 (s, 0H), 7.65 (d, *J* = 8.7 Hz, 0H), 7.63 – 7.50 (m, 1H), 7.37 (s, 0H), 4.08 (s, 1H), 4.00 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.0, 155.1, 149.9, 146.6, 133.7, 130.5, 127.6, 127.5, 127.0, 124.2, 123.8, 122.1, 118.8, 114.3, 112.9, 110.4, 102.8, 56.3. HRMS (ESI/Q-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>14</sub>O<sub>4</sub>H 307.0965; Found 307.0970.

## 1-Benzyl-3-(3-(naphthalen-2-yl)phenyl)pyrrolidine-2,5-dione (9aa)



White solid; eluent (20% ethyl acetate in hexane). Isolated yield is 72% (56 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (dd, J = 10.9, 1.9 Hz, 1H), 7.85 – 7.76 (m, 3H), 7.66 – 7.53 (m, 2H), 7.51 – 7.33 (m, 6H), 7.31 – 7.15 (m, 3H), 7.07 (dt, J = 7.7, 1.4 Hz, 1H), 4.82 – 4.46 (m, 2H), 3.95 (dd, J = 9.6, 4.7 Hz, 1H), 3.09 (ddd, J = 18.5, 9.6, 4.7 Hz, 1H), 2.77 (ddd, J = 18.5, 9.2, 4.8 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  177.5, 175.9, 142.2, 138.1, 137.9, 136.0, 133.7, 132.8, 129.7, 128.9, 128.9, 128.8, 128.6, 128.3, 128.1, 128.0, 127.7, 127.1, 126.5, 126.5, 126.3, 126.2, 126.0, 125.5, 46.0, 42.8, 37.3. HRMS (ESI/Q-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>21</sub>NO<sub>2</sub>Na 414.1470; Found 414.1481.

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<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3aa** (500 MHz, CDCl<sub>3</sub>)





110 100 f1 (ppm) 90 DEPT (135) NMR Spectrum of Compound 3aa (126 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3ba** (400 MHz, CDCl<sub>3</sub>)

DEPT (135) NMR Spectrum of Compound 3ba (101 MHz, CDCl<sub>3</sub>)







## DEPT (135) NMR Spectrum of Compound 3ca (101 MHz, CDCl<sub>3</sub>)



· · · ·																
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	
								f1 (ppm)								





DEPT (135) NMR Spectrum of Compound 3da (101 MHz, CDCl<sub>3</sub>)



· · · ·																
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								




DEPT (135) NMR Spectrum of Compound 3ea (101 MHz, CDCl<sub>3</sub>)



							1								· · · ·	
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	
								f1 (ppm)								









															(	
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								





## DEPT (135) NMR Spectrum of Compound 3ga (126 MHz, CDCl<sub>3</sub>)



-													· · · ·			
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								

















													·	1 1	·	
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	
								f1 (ppm)								





DEPT (135) NMR Spectrum of Compound 3ja (101 MHz, CDCl<sub>3</sub>)



60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	-
								f1 (ppm)								





## DEPT (135) NMR Spectrum of Compound 3ka (101 MHz, CDCl<sub>3</sub>)



60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	
								f1 (ppr	n)							

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3la** (400 MHz, CDCl<sub>3</sub>)



f1 (ppm) 













1									· · · ·							
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								





## DEPT (135) NMR Spectrum of Compound 3na (101 MHz, CDCl<sub>3</sub>)



-																
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppn	ו)							





# DEPT (135) NMR Spectrum of Compound 30a (101 MHz, CDCl<sub>3</sub>)



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60	150	140	)	130	120	110	100	90	80	70	60	50	40	30	20	10	(
									f1 (ppr	n)							





# DEPT (135) NMR Spectrum of Compound 3pa (101 MHz, CDCl<sub>3</sub>)



														_		
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppr	n)							





# DEPT (135) NMR Spectrum of Compound 3qa (101 MHz, CDCl<sub>3</sub>)



I			·	· · · ·	· · · · ·	· · · · ·		· · · ·			· · · ·			· · · ·		
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								





# DEPT (135) NMR Spectrum of Compound 3ra (101 MHz, CDCl<sub>3</sub>)



· · ·																т
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								





DEPT (135) NMR Spectrum of Compound 3sa (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3ta** (400 MHz, CDCl<sub>3</sub>)



f1 (ppm) 





Se	58
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<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3ua** (500 MHz, CDCl<sub>3</sub>)











f1 (ppm) 

# DEPT (135) NMR Spectrum of Compound 3va (101 MHz, CDCl<sub>3</sub>)


<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3wa** (400 MHz, CDCl<sub>3</sub>)

# 



# DEPT (135) NMR Spectrum of Compound 3wa (101 MHz, CDCl<sub>3</sub>)



( f1 (ppm) 

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **3xa** (400 MHz, CDCl<sub>3</sub>)



# DEPT (135) NMR Spectrum of Compound 3xa (101 MHz, CDCl<sub>3</sub>)















DEPT (135) NMR Spectrum of Compound 5ba (101 MHz, CDCl<sub>3</sub>)







# DEPT (135) NMR Spectrum of Compound 5ca (101 MHz, CDCl<sub>3</sub>)







# DEPT (135) NMR Spectrum of Compound 5da (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ea** (400 MHz, CDCl<sub>3</sub>)

8.45
7.96
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7.5





# DEPT (135) NMR Spectrum of Compound 5ea (101 MHz, CDCl<sub>3</sub>)



					1											
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								







110 100 f1 (ppm)









# DEPT (135) NMR Spectrum of Compound 5fa' (101 MHz, CDCl<sub>3</sub>)





<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ga** (400 MHz, CDCl<sub>3</sub>)

# DEPT (135) NMR Spectrum of Compound 5ga (101 MHz, CDCl<sub>3</sub>)







- 168.19 152.51 151.78 133.14 133.14 133.14 133.50 125.95 125.95 125.75 125.







#### 





# DEPT (135) NMR Spectrum of Compound 5ia (101 MHz, CDCl<sub>3</sub>)

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **5ja** (500 MHz, CDCl<sub>3</sub>)

#### 7, 288





# DEPT (135) NMR Spectrum of Compound 5ja (126 MHz, CDCl<sub>3</sub>)





DEPT (135) NMR Spectrum of Compound 5cb (101 MHz, CDCl<sub>3</sub>)



· · ·		· · ·					1		1 1					· · ·		
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								





# DEPT (135) NMR Spectrum of Compound 5ac (101 MHz, CDCl<sub>3</sub>)



	· · ·		· · ·				1					' '		· · · · ·		
60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
00	100	110	150	120	110	100	50	00	,,,	00	50	10	50	20	10	•
								f1 (npm)								
								Tra (ppin)								





# DEPT (135) NMR Spectrum of Compound 5ad (101 MHz, CDCl<sub>3</sub>)















DEPT (135) NMR Spectrum of Compound 5ie (126 MHz, CDCl<sub>3</sub>)






<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **6aa** (500 MHz, CDCl<sub>3</sub>)





<sup>110 100</sup> f1 (ppm) -: 

DEPT (135) NMR Spectrum of Compound 6aa (126 MHz, CDCl<sub>3</sub>)

## 132.06 131.48 130.76 130.76 127.68 127.68 127.29 127.28 12



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60	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	(
								f1 (ppm)								

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **7aa** (500 MHz, CDCl<sub>3</sub>)

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-195.24 146.07 143.85 133.78 134.10 134.10 134.10 134.10 134.10 134.10 134.10 134.10 124.28 126.35 1126.35 1126.35 1126.35



DEPT (135) NMR Spectrum of Compound 7aa (126 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound 8aa (500 MHz, CDCl<sub>3</sub>)





- 161.18 - 135.29 135.29 134.51 134.51 133.55 133.55 127.59 127.5



DEPT (135) NMR Spectrum of Compound 8aa (126 MHz, CDCl<sub>3</sub>)



S115

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **8ba** (400 MHz, CDCl<sub>3</sub>)



## DEPT (135) NMR Spectrum of Compound 8ba (101 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **8ca** (400 MHz, CDCl<sub>3</sub>)









## <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compound **9aa** (500 MHz, CDCl<sub>3</sub>)

## 7,2917







-f1 (ppm)