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## **Supporting Information**

# High Atomic Utilization Conversion of Ethers to Furancarbaldehydes via Oxidation Iminium-ion Activation Cascade Strategy

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1. General information	
2. Experimental Section	S2
3. Characterization Data	
4. Copies of NMR Spectra	

### **1. General Information**

Commercial reagents were purchased from TCI, Acros, Accela and Adamas and used without further purification unless otherwise stated. Solvents, unless otherwise specified, were reagent grade and distilled once prior to use. <sup>1</sup>H and <sup>13</sup>CNMR spectra were recorded on Bruke Avance-400 (400 MHz), and tetramethylsilane (TMS) was used as a reference. Chromatography was carried out with silica gel (300-400 mesh) using mixtures of petroleum ether (b.p. 60-90 °C) and ethyl acetate as eluents. HRMS were carried out on Micromass GCTTM gas chromatograph-mass spectrometer. Melting points were determined in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected.

#### 2. Experimental Section

#### 2.1 General Procedure for Synthesis of 1a, 1t-1w



The starting phenols (3.0 mmol),  $K_2CO_3$  (7.5 mmol) were dissolved in acetone (20.0 ml), and cinnamyl bromide (3.9 mmol) was added into the mixture, then the reaction was warmed to 60°C for about 20 hours. After the reaction completed, water was added to the reaction mixture, extracted with ethyl acetate, then the organic phase was washed with saturated brine and concentrated under vacuum. The crude product was purified by silica gel chromatography to obtain **1a**, **1t-1w**.

#### 2.2 General Procedure for Synthesis of 1b-1s, 1x-1z



A mixture of NaH (4.5 mmol) in THF (20 mL), S-2 (3.6 mmol) was dropwise added by syringe with ice-bath, then added S-1 (3.0 mmol) and then the reaction was warmed to room temperature for about 1 hour. The resulting mixture was quenched with water and extracted by ethyl acetate. The organic layer was dried with anhydrous  $Na_2SO_4$ , and evaporated under reduced to obtain compound S-3.

DIBAL-H (7.2 mmol) was slowly added to a stirred solution of ester S-3 (3.0 mmol) in DCM (20.0 mL) at 0°C. And the reaction mixture was stirred for about 2 hours at room temperature. After completion, the reaction mixture was poured into cold diluted HCl (0.5 N), and extracted with dichloromethane. The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced to obtain compound S-4.

To a stirred solution of S-4 (3.0 mmol), 1-bromo-2-naphthol (3.6 mmol), and

triphenylphosphane (3.9 mmol) in THF (20 mL) under argon atmosphere was added diethylazodicarboxylate (DEAD, 3.6 mmol) drop-wise at 0°C. The mixture was further stirred at room temperature for about 20 hours. The solvent was evaporated under reduced pressure to give a viscous residue. The residue was purified by silica gel column chromatography to obtain **1b-1s**, **1x-1z**.

#### 2.3 General Procedure for Synthesis of 2

A mixture of **1** (0.50 mmol), DDQ (0.60 mmol),  $H_2O$  (0.60 mmol) in  $CH_2Cl_2$  (5 mL) was stirred at 50°C for about 1 hour, followed by addition of **C5** (0.10 mmol),  $K_2CO_3$  (2.50 mmol) and MeCN (5ml), and heated to 65°C for 24 hours. After the reaction completed, the mixture was filtered, and the filtrate was concentrated under vacuum. The crude product was purified by silica gel chromatography to obtain **2**.

#### 2.4 Optimization of Reaction Conditions

1a

Table S1. Optimization of ether oxidation.

Br		н Н
	a. oxidate, solvent, T	
	b. K <sub>2</sub> CO <sub>3</sub> , <b>C5</b> , CH <sub>3</sub> CN, 65 °C	

2a

Entry	Oxidate	Solvent	H <sub>2</sub> O(equiv.)	Temperature(°C)	Time (h) <sup>c</sup>	Yields(%) <sup>d</sup>
1	IBX	$CH_2Cl_2$	1.2	50	>20	ND <sup>e</sup>
2	DMP	$CH_2Cl_2$	1.2	50	>20	10
3	TEMPO	$CH_2Cl_2$	1.2	50	>20	ND
4	PCC	$CH_2Cl_2$	1.2	50	>20	18
5	BF <sub>4</sub> NO	$CH_2Cl_2$	1.2	50	>20	ND
6	DDQ	$CH_2Cl_2$	1.2	50	1	71
7	DDQ <sup>a</sup>	$CH_2Cl_2$	1.2	50	1	66
8	DDQ	$CH_2Cl_2^b$	-	50	>20	46
9	DDQ	$CH_2Cl_2$	0.8	50	14	65
10	DDQ	$CH_2Cl_2$	1.6	50	1.5	68
11	DDQ	THF	1.2	50	3	58
12	DDQ	CHCl <sub>3</sub>	1.2	50	1.5	65
13	DDQ	DMF	1.2	50	>20	10
14	DDQ	CH <sub>3</sub> CH <sub>2</sub> OH	1.2	50	>20	30
15	DDQ	CH <sub>3</sub> CN	1.2	50	3	45
16	DDQ	toluene	1.2	50	4	25
17	DDQ	DMSO	1.2	50	>20	ND
18	DDQ	dioxane	1.2	50	2	30
19	DDQ	$CH_2Cl_2$	1.2	0	8	57
20	DDQ	$CH_2Cl_2$	1.2	25	2	63
21	DDQ	$CH_2Cl_2$	1.2	40	1.5	65
22	DDQ	$CH_2Cl_2$	1.2	65	0.70	70

Reaction conditions: a mixture of **1a** (0.50 mmol), oxidation (0.60 mmol) and H<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), was stirred at setting temperature for about 1 hour, followed by addition of **C5** (0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (2.50 mmol) and MeCN (5 mL) continued to stir 24 hours at 65°C. <sup>a</sup> 0.75 mmol DDQ used. <sup>b</sup> redistilled CH<sub>2</sub>Cl<sub>2</sub> used. <sup>c</sup> the time when **1a** completely transformed and determined by TLC. <sup>d</sup> by NMR. <sup>e</sup> ND means not determined. **Table S2. Optimization of aromatization reaction.** 









50 °Ç

Entry	Catalyst	Base	Solvent	Temperature(°C)	Additive <sup>e</sup>	Yield(%) <sup>f</sup>
1	C1	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	65	_	38
2	<b>C2</b>	$K_2CO_3$	CH <sub>3</sub> CN	65		24
3	<b>C3</b>	$K_2CO_3$	CH <sub>3</sub> CN	65		33
4	<b>C4</b>	$K_2CO_3$	CH <sub>3</sub> CN	65		18
5	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	_	71
6ª	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	_	52
7 <sup>b</sup>	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	_	58
8°	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	_	65
9 <sup>d</sup>	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	_	61
10	C5	$Cs_2CO_3$	CH <sub>3</sub> CN	65	_	34
11	C5	DBU	CH <sub>3</sub> CN	65	_	30
12	C5	DABCO	CH <sub>3</sub> CN	65	_	25
13	C5	CH <sub>3</sub> COONa	CH <sub>3</sub> CN	65	_	$ND^{g}$
14	C5	TEA	CH <sub>3</sub> CN	65		45
15	C5	NaCO <sub>3</sub>	CH <sub>3</sub> CN	65		42
16	C5	$K_2CO_3$	DCM	65	_	15
17	C5	$K_2CO_3$	THF	65	_	ND
18	C5	$K_2CO_3$	CH <sub>3</sub> CH <sub>2</sub> OH	65	_	20
19	C5	$K_2CO_3$	DMF	65	_	13
20	C5	$K_2CO_3$	DMSO	65	_	ND
21	C5	$K_2CO_3$	Toluene	65	_	ND
22	C5	$K_2CO_3$	1,4-dioxane	65	_	ND
23	C5	$K_2CO_3$	CH <sub>3</sub> CN	25	_	50
24	C5	$K_2CO_3$	CH <sub>3</sub> CN	50	_	64
25	C5	$K_2CO_3$	CH <sub>3</sub> CN	75	_	64
26	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	TBAB	53
27	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	18-Crown-6	44
28	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	<i>n</i> -Pentanoic acid	51
29	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	TBAHS	62
30	C5	$K_2CO_3$	CH <sub>3</sub> CN	65	TMAC	56

Reaction conditions: a mixture of **1a** (0.50 mmol), DDQ (0.60 mmol) and  $H_2O$  (0.60 mmol) in the  $CH_2Cl_2$  (5 mL), was stirred at 50 °C for about 1 hour, followed by addition of **Cat.** (0.10 mmol), **Base** (2.50 mmol) and solvent (5 mL) continued to stir 24 hours at setting temperature. <sup>a</sup> **C5** (0.05 mmol, 0.1 equiv.). <sup>b</sup> **C5** (0.20 mmol, 0.4 equiv.). <sup>c</sup> **Base** (2.00 mmol, 4.0 equiv.) <sup>d</sup> **Base** (3.00 mmol, 6.0 equiv.) <sup>e</sup> 0.10 mmol addition used. <sup>f</sup> by NMR. <sup>g</sup> ND means not determined.

#### Table S3. The effect of halogen substitution on the reaction.



Entry	X	Yield(%)
1	Н	-
2	F	-
3	Cl	36
4	Br	71
5	Ι	73

#### 2.5 Control experiments.



1a (0.17 g, 0.5 mmol) in DCM (5.0 mL) was added DDQ (0.14 g, 0.6 mmol) and H<sub>2</sub>O (11 mg, 0.6 mmol), after stirred at 50 °C for 1 h, diphenylprolinol TMS ether C5 (33 mg, 0.1 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.26 g, 2.5 mmol) and CH<sub>3</sub>CN (5.0 mL) were added, then the reaction mixture was stirred at 65 °C for 6 h. After cooling to ambient temperature, the mixture was filtered through the Celite pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1 to 2:1) to afford the intermediate 4a as a yellow solid (70 mg, 51 %, mp 181-182 °C).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.92 (s, 1H), 7.92 (s, 1H), 7.86-7.82 (m 2H), 7.47-7.41 (m, 1H), 7.37-7.31 (m, 2H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.22-7.13 (m, 5H), 5.17 (s, 1H).

#### -9.923 -9.23 -9.23 -7.816 -7.816 -7.816 -7.816 -7.816 -7.450 -7.7500 -7.75000 -7.75000 -7.75000 -7.75000 -7.75000 -7.75000 -7.75000 -7.7



To a solution of 4a (30 mg, 0.1 mmol) in MeCN (3 mL) was added diphenylprolinol TMS ether C5 (7 mg, 0.02 mmol) and K<sub>2</sub>CO<sub>3</sub>(76 mg, 0.5 mmol), then the reaction mixture was stirred at 65 °C for 2 h. After cooling to ambient temperature, the mixture was filtered through the Celite pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography to afford the desired product 2a (28 mg, 94%). **2.6 Gram-scale Reaction.** 



A mixture of **1a** (2.04 g, 6.0 mmol), DDQ (1.63 g, 7.2 mmol), H<sub>2</sub>O (0.13 g, 7.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was stirred at 50°C for about 1 hour, followed by addition of **C5** (0.39 g, 1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (4.15 g, 30.0 mmol) and MeCN (15ml), and heated to 65°C for 24 hours. After the reaction completed, the mixture was filtered, and the filtrate was concentrated under vacuum. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 200:1) to obtain **2a**.

### 3. Characterization Data

### **3.1 Characterization Data for substrates (1)**

1-bromo-2-(cinnamyloxy)naphthalene (1a)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid (0.94 g, 92%); mp. 95-96°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (dd, J = 8.6, 1.0 Hz, 1H), 7.78 (d, J = 3.3 Hz, 1H), 7.76 (d, J = 2.5 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.44 – 7.41 (m, 1H), 7.41 – 7.37 (m, 2H), 7.35 – 7.27 (m, 3H), 7.24 (d, J = 5.0 Hz, 1H), 6.80 (d, J = 16.0 Hz, 1H), 6.46 (dt, J = 16.0, 5.6 Hz, 1H), 4.91 (dd, J = 5.5, 1.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 136.4, 133.3, 133.2, 130.1, 128.9, 128.6(2C), 128.1, 128.0, 127.7, 126.7(2C), 126.3, 124.5, 124.2, 115.7, 110.0, 70.8. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(2-fluorophenyl)allyl)oxy)naphthalene (1b)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a brown solid (0.93g 87%); mp. 110-112°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (d, J = 8.6 Hz, 1H), 7.78 (dd, J = 8.4, 5.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 1.2 Hz, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.24 – 7.15 (m, 1H), 7.14 – 6.91 (m, 3H), 6.56 (dt, J = 16.1, 5.5 Hz, 1H), 4.92 (d, J = 5.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.3, 151.8, 132.1, 128.9, 128.1, 127.8, 127.0, 126.7, 126.6(2C), 125.7, 125.2, 124.5, 123.4, 123.0, 114.7, 114.4, 108.8, 69.6. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(3-fluorophenyl)allyl)oxy)naphthalene (1c)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a brown solid (0.95g, 89%); mp. 93-95°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (d, J = 8.5 Hz, 1H), 7.77 (dd, J = 8.9, 2.9 Hz, 2H), 7.56 (m, 1H), 7.40 (m, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 7.16 (dt, J = 7.7, 1.2 Hz, 1H), 7.10 (dt, J =

10.1, 2.1 Hz, 1H), 6.94 (td, J = 8.6, 2.5 Hz, 1H), 6.78 (d, J = 15.8 Hz, 1H), 6.45 (m, 1H), 4.88 (dd, J = 5.4, 1.7 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.3, 152.9, 138.8, 133.2, 131.8, 130.1, 130.0, 128.9, 128.1, 127.8, 126.3, 125.6, 124.6, 122.6, 115.5, 114.8, 113.1, 110.0, 70.4. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(4-fluorophenyl)allyl)oxy)naphthalene (1d)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid (0.96 g, 90%); mp. 149-150°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (dd, J = 8.6, 1.0 Hz, 1H), 7.74 – 7.66 (m, 2H), 7.48 (m, 1H), 7.35 – 7.31 (m, 1H), 7.31 – 7.29 (m, 1H), 7.29 – 7.25 (m, 1H), 7.19 (d, J = 9.0 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.68 (m, 1H), 6.29 (m, 1H), 4.80 (dd, J = 5.6, 1.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.75, 161.3, 152.9, 133.1, 132.5, 132.0, 130.0, 128.9, 128.2, 128.1, 128.0, 127.7, 126.3, 124.5, 123.8, 115.6(2C), 115.4, 109.9, 70.6. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(2-chlorophenyl)allyl)oxy)naphthalene (1e)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid (0.92 g, 82%); mp. 114-116°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d, J = 8.6 Hz, 1H), 7.70 (t, J = 7.4 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.32 (t, J = 7.7 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 9.1 Hz, 1H), 7.17 (d, J = 5.6 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.36 (m, 1H), 4.85 (d, J = 5.4 Hz, 2H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,)  $\delta$  152.9, 134.6, 133.3, 133.2, 130.1, 129.7, 129.4, 129.0, 128.9, 128.1, 127.7, 127.1(2C), 126.9, 126.3, 124.6, 115.6, 110.0, 70.7. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(3-chlorophenyl)allyl)oxy)naphthalene (1f)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale brown solid (0.94 g, 84%); mp. 86-88°C. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d, J = 8.5 Hz, 1H), 7.79 (dd, J = 8.5, 5.8 Hz, 2H), 7.58 (ddd, J = 8.4, 6.9, 1.2 Hz, 1H), 7.41 (ddd, J = 7.9, 5.9, 1.1 Hz, 2H), 7.26 (ddd, J = 11.1, 4.7, 2.3 Hz, 4H), 6.78 (d, J = 16.0 Hz, 1H), 6.48 (dt, J = 16.0, 5.4 Hz, 1H), 4.92 (dd, J = 5.4, 1.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 138.4, 134.7, 133.3, 131.7, 130.2, 130.0, 129.1, 128.2, 128.0, 127.9, 126.7, 126.5, 125.9, 125.0, 124.8, 115.7, 110.1, 70.5. HRMS (EI): *m/z* calcd for C<sub>19</sub>H<sub>14</sub>BrClO [M<sup>+</sup>]: 371.9917, found: 371.9919.

#### 1-bromo-2-((3-(4-chlorophenyl)allyl)oxy)naphthalene (1g)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid (0.98 g, 88%); mp. 154-155°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d, J = 9.0 Hz, 1H), 7.79 (dd, J = 8.5, 5.5 Hz, 2H), 7.64 – 7.51 (m, 1H), 7.42 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.30 (dd, J = 8.6, 2.1 Hz, 3H), 6.78 (d, J = 16.0 Hz, 1H), 6.45 (dt, J = 16.0, 5.5 Hz, 1H), 4.91 (dd, J = 5.5, 1.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 135.0, 133.7, 133.3, 131.9, 130.2, 129.0, 128.9, 128.2, 128.0, 127.9, 126.4, 124.9, 124.7, 115.7, 110.1, 70.7. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

#### 1-bromo-2-((3-(2-bromophenyl)allyl)oxy)naphthalene (1h)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid (1.08 g, 86%); mp. 113-115°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (d, *J* = 8.6 Hz, 1H), 7.79 (t, *J* = 8.3 Hz, 2H), 7.56 (ddd, *J* = 5.3, 4.8, 3.6 Hz, 3H), 7.41 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.28 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.20 (d, *J* = 15.9 Hz, 1H), 7.11 (td, *J* = 7.9, 1.6 Hz, 1H), 6.41 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.95 (dd, *J* = 5.5, 1.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 136.5, 133.3, 133.1, 132.0, 130.2, 129.3, 129.0, 128.2, 127.8, 127.6, 127.4, 127.3, 126.4, 124.7, 123.9, 115.7, 110.1, 70.6. HRMS (EI): *m/z* calcd for C<sub>19</sub>H<sub>14</sub>Br<sub>2</sub>O [M<sup>+</sup>]: 417.9391, found: 417.9395.

1-bromo-2-((3-(3-bromophenyl)allyl)oxy)naphthalene (1i)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale brown solid (1.13 g, 90%); mp. 91-92°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (dd, J = 8.6, 1.0 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.77 – 7.75 (m, 1H), 7.59 – 7.53 (m, 2H), 7.43 – 7.34 (m, 2H), 7.31 (m, 1H), 7.24 (d, J = 0.8 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 6.74 (m, 1H), 6.44 (m, 1H), 4.88 (dd, J = 5.3, 1.7 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 138.7, 133.3, 131.6, 130.9, 130.2, 129.6, 129.1, 128.2, 127.9, 126.5, 125.9, 125.4, 124.8, 122.9, 115.7, 110.1, 70.5. HRMS (EI): *m/z* calcd for C<sub>19</sub>H<sub>14</sub>Br<sub>2</sub>O [M<sup>+</sup>]: 417.9391, found: 417.9393.

1-bromo-2-((3-(4-bromophenyl)allyl)oxy)naphthalene (1j)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid (1.15 g, 92%); mp. 156-157°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d, J = 8.5 Hz, 1H), 7.79 (dd, J = 8.5, 5.1 Hz, 2H), 7.65 – 7.53 (m, 1H), 7.50 – 7.38 (m, 3H), 7.29 (dd, J = 8.7, 2.0 Hz, 3H), 6.77 (d, J = 16.0 Hz, 1H), 6.47 (dt, J = 16.0, 5.4 Hz, 1H), 4.91 (dd, J = 5.4, 1.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 135.5, 133.3, 131.9, 131.9, 130.2, 129.0, 128.3, 128.2, 127.9, 126.5, 125.1, 124.7, 121.9, 115.7, 110.1, 70.7. HRMS (EI): *m/z* calcd for C<sub>19</sub>H<sub>14</sub>Br<sub>2</sub>O [M<sup>+</sup>]: 417.9391, found: 417.9392.





Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid (0.81 g, 76%); mp. 114-116°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (dd, J = 8.6, 1.0 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.47 (m, 1H), 7.38 (dd, J = 5.3, 3.7 Hz, 1H), 7.30 (m, 1H), 7.20 (d, J = 8.9 Hz, 1H), 7.10 – 7.03 (m, 3H), 6.97 (m, 1H), 6.24 (m, 1H), 4.83 (dd, J = 5.5, 1.7 Hz, 2H), 2.24 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 135.7, 135.6, 133.2, 131.1, 130.3, 130.1, 128.9, 128.1, 127.8, 127.7, 126.3, 126.2, 125.8, 125.3, 124.5, 115.7, 110.0, 70.8, 19.8. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(m-tolyl)allyl)oxy)naphthalene (11)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale brown solid (0.90 g, 85%); mp. 91-92°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (dd, J = 8.6, 1.1 Hz, 1H), 7.70 (d, J = 2.5 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.48 (m, 1H), 7.31 (m, 1H), 7.20 (d, J = 8.9 Hz, 1H), 7.15 – 7.11 (m, 3H), 6.99 (m, 1H), 6.69 (m, 1H), 6.36 (m, 1H), 4.82 (dd, J = 5.6, 1.6 Hz, 2H), 2.26 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.0, 137.1, 135.2, 132.2, 132.1, 129.0, 127.8, 127.7, 127.4, 127.0, 126.6, 126.3, 125.2, 123.4, 122.8, 122.7, 114.6, 108.8, 69.7, 20.3. The data is consistent with *Adv*. *Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(p-tolyl)allyl)oxy)naphthalene (1m)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale brown solid (0.96 g, 91%); mp. 149-151°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, J = 8.6 Hz, 1H), 7.65 (d, J = 8.7 Hz, 2H), 7.45 (m, 1H), 7.29 (m, 1H), 7.18 (dd, J = 15.8, 8.4 Hz, 3H), 7.02 (d, J = 7.8 Hz, 2H), 6.66 (d, J = 15.9 Hz, 1H), 6.30 (m, 1H), 4.77 (dd, J = 5.7, 1.6 Hz, 2H), 2.23 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.1, 137.9, 133.6, 133.2(2C), 130.1, 129.4(2C), 128.9, 128.1, 127.7, 126.6(2C), 126.3, 124.5, 123.1, 115.7, 109.9, 70.9, 21.3. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

1-bromo-2-((3-(3-methoxyphenyl)allyl)oxy)naphthalene (1n)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid (0.89 g, 80%); mp. 97-99°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (m, 1H), 7.79 – 7.77 (m, 1H), 7.77 – 7.74 (m, 1H), 7.56 (m, 1H), 7.39 (m, 1H), 7.27 (d, *J* = 9.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.00 (m, 1H), 6.95 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.83 – 6.80 (m, 1H), 6.77 (m, 1H), 6.45 (m, 1H), 4.89 (dd, *J* = 5.6, 1.6 Hz, 2H), 3.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.0, 153.1, 138.0, 133.3, 133.2, 130.2, 129.7, 129.0,

128.2, 127.8, 126.5, 124.7, 124.6, 119.4, 115.8, 113.8, 112.1, 110.1, 70.9, 55.4. HRMS (EI): *m/z* calcd for C<sub>20</sub>H<sub>17</sub>BrO<sub>2</sub> [M<sup>+</sup>]: 368.0412, found: 368.0414.

1-bromo-2-((3-(4-methoxyphenyl)allyl)oxy)naphthalene (10)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid (0.93 g, 84%); mp. 151-153°C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (d, J = 8.5 Hz, 1H), 7.79 (t, J = 7.4 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.9 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 15.9 Hz, 1H), 6.37 – 6.32 (m, 1H), 4.90 (d, J = 5.6 Hz, 2H), 3.81 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  159.7, 153.2, 133.3, 133.1, 130.2, 129.3, 129.0, 128.2, 128.0, 127.8, 126.4, 124.6, 122.0, 115.9, 114.1, 110.1, 71.2, 55.4. HRMS (EI): *m/z* calcd for C<sub>20</sub>H<sub>17</sub>BrO<sub>2</sub> [M<sup>+</sup>]: 368.0412, found: 368.0416.

1-bromo-2-((3-(4-ethoxyphenyl)allyl)oxy)naphthalene (1p)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a brown solid (0.92 g, 80%); mp. 147-149°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.23 (dd, J = 8.6, 1.0 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.54 (m, 1H), 7.37 (m, 1H), 7.33 – 7.29 (m, 2H), 7.23 (d, J = 10.8 Hz, 1H), 6.84 – 6.80 (m, 2H), 6.71 (m, 1H), 6.30 (m, 1H), 4.84 (dd, J = 5.8, 1.5 Hz, 2H), 3.99 (q, J = 7.0 Hz, 2H), 1.38 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 153.2, 133.3, 133.2, 130.2, 129.1, 129.0, 128.2, 128.0, 127.8, 126.5, 124.6, 121.8, 115.9, 114.7, 110.1, 71.3, 63.6, 15.0. HRMS (EI): *m/z* calcd for C<sub>21</sub>H<sub>19</sub>BrO<sub>2</sub> [M<sup>+</sup>]: 382.0568, found: 382.0572.





Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale brown solid (0.88 g, 72%); mp. 161-162°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d, *J* = 8.5 Hz, 1H), 7.79 (dd, *J* = 8.6, 4.9 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 3H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 9.1 Hz, 1H), 6.86

(d, J = 16.0 Hz, 1H), 6.55 (m, 1H), 4.92 (d, J = 5.1 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 139.9, 133.2, 131.4, 130.1, 129.7, 129.0, 128.1, 127.8, 126.9, 126.8(3C), 126.3, 125.6 (2C), 124.7, 115.5, 110.0, 70.3. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

#### **3-(3-((1-bromonaphthalen-2-yl)oxy)prop-1-en-1-yl)thiophene (1r)**



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale brown solid (0.74 g, 71%); mp. 134-135°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,)  $\delta$  8.24 (d, J = 8.6 Hz, 1H), 7.79 (dd, J = 8.5, 4.3 Hz, 2H), 7.57 (ddd, J = 8.4, 6.9, 1.2 Hz, 1H), 7.41 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.24 (d, J = 1.2 Hz, 1H), 7.20 (d, J = 2.6 Hz, 1H), 6.81 (d, J = 15.9 Hz, 1H), 6.32 (dt, J = 15.9, 5.7 Hz, 1H), 4.89 (dd, J = 5.7, 1.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.1, 139.2, 133.3, 130.2, 129.0, 128.2, 127.8, 127.6, 126.4, 126.3, 125.2, 124.7, 124.1, 123.06, 115.8, 110.0, 70.8. HRMS (EI): *m/z* calcd for C<sub>17</sub>H<sub>13</sub>BrOS [M<sup>+</sup>]: 343.9870, found: 343.9872.

1-bromo-2-((3-(naphthalen-2-yl)allyl)oxy)naphthalene (1s)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale brown solid (0.79 g, 68%); mp. 137-138°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 11.4, 6.0 Hz, 6H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.44 (tt, *J* = 14.9, 7.4 Hz, 3H), 7.34 (d, *J* = 9.0 Hz, 1H), 6.99 (d, *J* = 15.9 Hz, 1H), 6.61 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.99 (d, *J* = 5.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.1, 133.9, 133.7, 133.4, 133.3, 133.2, 130.2, 129.0, 128.4, 128.2, 127.8, 127.8, 127.0, 126.4, 126.2, 124.7, 124.6, 123.7, 115.8, 110.1, 70.9. HRMS (EI): *m/z* calcd for C<sub>23</sub>H<sub>17</sub>BrO [M<sup>+</sup>]: 388.0463, found: 388.0465.

1,6-dibromo-2-(cinnamyloxy)naphthalene (1t)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid (0.77 g, 61%); mp.  $166-167^{\circ}$ C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 9.0 Hz, 1H), 7.60 (dd, J = 9.1, 2.0 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.35 – 7.30 (m, 3H), 7.28 (d, J = 1.2 Hz, 1H), 6.80 (m, 1H), 6.45 (m, 1H), 4.90 (dd, J = 5.6, 1.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.2, 136.2, 133.3, 131.8, 130.9, 130.8, 129.8, 128.6 (2C), 128.2, 128.0, 127.9, 126.6 (2C), 123.8, 118.4, 116.4, 109.9, 70.7. The data is consistent with *Adv. Synth. Catal.*, 2015, **357**, 2442-2446.

#### 5-bromo-6-(cinnamyloxy)-2-naphthonitrile (1u)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid (0.67 g, 61%); mp. 149-151°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d, *J* = 8.9 Hz, 1H), 8.16 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.45 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.98 (d, *J* = 5.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.4, 136.1, 134.7, 134.2, 133.7, 129.5, 128.7(2C), 128.5, 128.2, 128.0, 127.6, 126.7(2C), 123.3, 119.0, 116.4, 109.5, 107.8, 70.5. HRMS (EI): *m/z* calcd for C<sub>20</sub>H<sub>14</sub>BrNO [M<sup>+</sup>]: 363.0259, found: 363.0265.

1-bromo-2-(cinnamyloxy)-3-methoxynaphthalene (1v)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid (0.72 g, 65%); mp. 182-184°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 – 8.13 (m, 1H), 7.70 – 7.66 (m, 1H), 7.44 – 7.38 (m, 4H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.13 (s, 1H), 6.72 (m, 1H), 6.57 (m, 1H), 4.79 (dd, *J* = 6.3, 1.3 Hz, 2H), 3.97 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.5, 146.0, 136.6, 133.5, 131.5, 128.5(2C), 127.9, 127.8, 126.8, 126.7, 126.6(2C), 126.0, 125.1, 125.0, 116.9, 106.8, 74.1, 55.9. HRMS (EI): *m/z* calcd for C<sub>20</sub>H<sub>17</sub>BrO<sub>2</sub> [M<sup>+</sup>]: 368.0412, found: 368.0418.

### 1-bromo-2-(cinnamyloxy)-4-methoxybenzene (1w)



Following the general procedure, the compound was purified by flash chromatography

(petroleum ether/ethyl acetate = 200:1) as a colorless oil in 87% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (d, *J* = 7.0 Hz, 3H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.59 (s, 1H), 6.46 (d, *J* = 9.3 Hz, 2H), 4.79 (d, *J* = 4.5 Hz, 2H), 3.83 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 155.8, 136.5, 133.3(2C), 128.7(2C), 128.1, 126.8(2C), 126.8, 123.9, 106.5, 103.2, 101.7, 69.8, 55.7. HRMS (EI): *m/z* calcd for C<sub>16</sub>H<sub>15</sub>BrO<sub>2</sub> [M<sup>+</sup>]: 318.0255, found: 318.0263.

4-(3-(2-bromo-5-methoxyphenoxy)prop-1-en-1-yl)-*N*,*N*-dimethylaniline (1x)



Following the general procedure, the compound was obtained as a pale-yellow oil in 71% crude yield. Due to the instability of 1x, we failed to get the pure NMR spectra of 1x. Crude 1x was directly used for the next reaction.

#### 1-bromo-4-methoxy-2-((3-(3-(trifluoromethyl)phenyl)allyl)oxy)benzene (1y)



#### ÓMe

Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a colorless oil in 74% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 (s, 1H), 7.40 (dd, *J* = 23.0, 7.7 Hz, 2H), 7.35 – 7.22 (m, 2H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 6.37 – 6.26 (m, 2H), 4.66 – 4.51 (m, 2H), 3.64 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 155.5, 137.3, 133.4, 131.3, 131.0, 129.8, 129.1, 125.9, 124.5, 124.2, 123.3, 106.5, 103.1, 101.5, 69.2, 55.6. HRMS (EI): *m/z* calcd for C<sub>17</sub>H<sub>14</sub>BrF<sub>3</sub>O<sub>2</sub> [M<sup>+</sup>]: 386.0129, found: 386.0135.

1-bromo-2-((3-(4-fluorophenyl)allyl)oxy)-4-methoxybenzene (1z)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a colorless oil in 84% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d, J = 8.7 Hz, 1H), 7.38 (dd, J = 8.6, 5.5 Hz, 2H), 7.02 (t, J = 8.7 Hz, 2H), 6.75 (d, J = 16.0 Hz, 1H), 6.53 (d, J = 2.7 Hz, 1H), 6.42 (dd, J = 8.7, 2.7 Hz, 1H), 6.33 (dt, J = 15.9,

5.6 Hz, 1H), 4.80 – 4.65 (m, 2H), 3.79 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.7, 160.2, 155.7, 133.4, 132.5, 132.1,128.4, 128.3, 123.6, 115.8, 115.5, 106.5, 103.3, 101.7, 69.7, 55.7. HRMS (EI): *m/z* calcd for C<sub>16</sub>H<sub>14</sub>BrFO<sub>2</sub> [M<sup>+</sup>]: 336.0161, found: 336.0169.

**3.1 Characterization Data for products (2)** 

2-phenylnaphtho[2,1-b]furan-1-carbaldehyde (2a)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 71% yield, 97 mg; mp. 125-126°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.30 (s, 1H), 9.54 (dd, J = 8.5, 1.2 Hz, 1H), 7.93 (d, J = 8.1, 0.9 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 7.79 (m, 2H), 7.70 – 7.65 (m, 2H), 7.59 – 7.54 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 167.1, 152.6, 131.4, 130.9, 129.9, 129.0, 128.7, 128.6, 128.5, 128.2, 127.8, 126.9, 125.5, 120.4, 120.2, 111.7. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(2-fluorophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2b)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 47% yield, 68 mg; mp. 141-142°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.05 (d, *J* = 3.6 Hz, 1H), 9.44 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.60 (dd, *J* = 8.3, 5.9 Hz, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.21 – 7.13 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  185.2 (d, *J* = 4.8 Hz), 160.2, 157.8, 152.3, 131.9 (d, *J* = 8.4 Hz), 131.1 (d, *J* = 1.6 Hz), 130.4, 127.6, 127.4, 127.3, 126.8, 126.0, 124.5, 123.6 (d, *J* = 3.8 Hz), 120.7, 118.7, 116.0 (d, *J* = 13.6 Hz), 115.6 (d, *J* = 21.8 Hz), 110.7. HRMS (EI): *m/z* calcd for C<sub>19</sub>H<sub>11</sub>FO<sub>2</sub>[M<sup>+</sup>]: 290.0743, found: 290.0745. **2-(3-fluorophenyl)naphtho[2,1-***b***]furan-1-carbaldehyde (2c)** 



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid in 51% yield, 74 mg; mp. 151-152°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.36 (s, 1H), 9.51 (d, J = 8.4 Hz, 1H), 8.00 – 7.94 (m, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.63 – 7.53 (m, 4H), 7.33 – 7.26 (m, 1H). <sup>13</sup>C NMR

(100 MHz, CDCl<sub>3</sub>)  $\delta$  186.3, 164.9 (d, J = 253.8 Hz), 152.7, 131.5, 130.7 (d, J = 8.0 Hz), 128.7 (d, J = 3.3 Hz), 128.6, 128.4, 127.7, 127.1, 125.8, 125.6, 120.9, 120.1, 118.0, 117.8 (d, J = 21.4 Hz), 116.7 (d, J = 23.4 Hz), 116.5, 111.6. HRMS (EI): m/z calcd for C<sub>19</sub>H<sub>11</sub>FO<sub>2</sub>[M<sup>+</sup>]: 290.0743, found: 290.0741.

2-(3-fluorophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2d)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid in 72% yield, 104 mg; mp. 157-158°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.26 (s, 1H), 9.49 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.67 (dd, J = 8.7, 6.7 Hz, 2H), 7.55 (m, 1H), 7.28 (d, J = 8.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.3, 165.8, 164.3 (d, J = 252.9 Hz), 152.5, 131.9 (d, J = 8.7 Hz) (2C), 131.5, 128.6, 128.4 (d, J = 3.3 Hz), 128.3, 127.7, 127.0, 125.5, 124.9 (d, J = 3.3 Hz), 120.2, 120.1, 116.3 (d, J = 22.0 Hz) (2C), 111.6. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(2-chlorophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (2e)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid in 34% yield, 52 mg; mp. 144-145°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.95 (s, 1H), 9.47 (dd, J = 8.5, 1.1 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.64 (m, 2H), 7.58 – 7.52 (m, 2H), 7.51 – 7.48 (m, 1H), 7.46 (dd, J = 8.0, 1.8 Hz, 1H), 7.40 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  185.1, 163.5, 152.2, 133.8, 132.1, 131.1, 130.4, 129.5, 127.6, 127.4, 127.3, 126.9, 126.8, 126.0, 125.9, 124.6, 121.1, 118.4, 110.8. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(3-chlorophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2f)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid in 54% yield, 83 mg; mp. 160-161°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.31 (s, 1H), 9.48 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H),

7.86 (d, J = 8.9 Hz, 1H), 7.82 (t, J = 1.9 Hz, 1H), 7.69 (q, J = 2.9, 1.6 Hz, 2H), 7.68 – 7.66 (m, 1H), 7.60 – 7.47 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.2, 164.8, 152.7, 135.2, 131.5, 130.8, 130.3, 130.2, 129.6, 128.8, 128.7, 128.4, 128.0, 127.7, 127.1, 125.6, 120.9, 120.0, 111.6. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(4-chlorophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2g)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid in 73% yield, 112 mg; mp. 165-166°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.24 (s, 1H), 9.45 – 9.40 (m, 1H), 7.91 – 7.87 (m, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.62 (dd, J = 8.5, 6.4 Hz, 2H), 7.53 – 7.47 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.2, 165.4, 152.7, 137.3, 131.5, 131.0 (2C), 129.4 (2C), 128.7, 128.5, 128.4, 127.7, 127.1, 127.0, 125.6, 120.7, 120.1, 111.6. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(2-bromophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (2h)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid in 28% yield, 49 mg; mp. 149-151°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.99 (s, 1H), 9.55 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.42 – 7.35 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.1, 166.0, 153.1, 133.6, 133.3, 132.3, 131.5, 130.0, 128.7, 128.5, 128.4, 127.9, 127.5, 127.1, 125.6, 124.4, 121.9, 119.4, 111.8. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938. **2-(3-bromophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2i)** 



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 53% yield, 93 mg; mp. 162-164°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.33 (s, 1H), 9.50 (dd, J = 8.6, 1.1 Hz, 1H), 7.99 (t, J = 1.8 Hz, 1H), 7.98 – 7.94 (m, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.76 – 7.67 (m, 4H), 7.57 (ddd, J =

8.1, 6.9, 1.2 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.2, 164.7, 152.8, 133.8, 132.4, 131.5, 130.6, 130.4, 128.7(2C), 128.5, 128.4, 127.7, 127.1, 125.7, 123.1, 121.0, 120.1, 111.6. HRMS (EI): m/z calcd for C<sub>19</sub>H<sub>11</sub>BrO<sub>2</sub> [M<sup>+</sup>]: 349.9942, found: 349.9939. **2-(4-bromophenyl)naphtho**[2,1-*b*]furan-1-carbaldehyde (2j)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 66% yield, 116 mg; mp. 170-171°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.32 (s, 1H), 9.50 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.94 (m, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.75 – 7.72 (m, 3H), 7.72 – 7.68 (m, 3H), 7.58 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.3, 165.5, 152.7, 132.3(2C), 131.5, 131.2(2C), 128.7, 128.6, 128.4, 127.7, 127.6, 127.1, 125.7, 125.6, 120.7, 120.2, 111.7. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(o-tolyl)naphtho[2,1-b]furan-1-carbaldehyde (2k)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid in 36% yield, 54 mg; mp. 139-141°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.91 (s, 1H), 9.50 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.9 Hz, 1H), 7.62 (dt, J = 8.4, 3.2 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.43 – 7.39 (m, 2H), 7.34 – 7.27 (m, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.7, 168.7, 152.8, 138.7, 132.2, 131.5, 131.0, 130.9, 128.6, 128.4, 128.1, 128.0, 127.9, 126.9, 125.8, 125.5, 121.6, 119.6, 111.7, 20.3. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(*m*-tolyl)naphtho[2,1-*b*]furan-1-carbaldehyde (2l)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 52% yield, 74 mg; mp. 122-123°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.32 (s, 1H), 9.57 (dd, J = 8.5, 1.1 Hz, 1H), 7.99 – 7.91 (m, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.64 – 7.59 (m, 2H), 7.57 (m, 1H), 7.50 – 7.44 (m, 1H), 7.40 (m, 1H), 2.49 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.9, 167.5, 152.5,

138.9, 131.7, 131.4, 130.4, 128.8, 128.6, 128.5, 128.4, 128.1, 127.8, 127.2, 126.8, 125.4, 120.3, 120.2, 111.6, 21.4. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938. **2-(p-tolyl)naphtho[2,1-***b***]furan-1-carbaldehyde (2m)** 



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 73% yield, 105 mg; mp. 153-155°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.29 (s, 1H), 9.55 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.66 (m, 4H), 7.57 – 7.52 (m, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 167.6, 152.5, 141.4, 131.4, 129.8 (2C), 129.7 (2C), 128.6, 128.5, 128.1, 127.9, 126.8, 125.9, 125.4, 120.3, 120.1, 111.7, 21.6. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(3-methoxyphenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (2n)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 48% yield, 73 mg; mp. 120-121°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.26 (s, 1H), 9.47 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.51 – 7.46 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.04 (dd, *J* = 8.3, 2.6 Hz, 1H), 3.83 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 166.9, 159.9, 152.6, 131.5, 130.1, 129.8, 128.6, 128.5, 128.3, 127.8, 126.9, 125.5, 122.6, 120.5, 120.2, 116.8, 114.9, 111.7, 55.6. HRMS (EI): *m/z* calcd for C<sub>20</sub>H<sub>14</sub>O<sub>3</sub>[M<sup>+</sup>]: 302.0943, found: 302.0939.

2-(4-methoxyphenyl)naphtho[2,1-b]furan-1-carbaldehyde (20)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 66% yield, 99 mg; mp. 131-133°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.29 (s, 1H), 9.56 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.68 (t, *J* = 8.9 Hz, 2H), 7.56 (t, *J* =

7.9 Hz, 1H), 7.09 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 167.5, 161.8, 152.3, 131.5(2C), 131.4, 128.6, 128.4, 127.9, 127.8, 126.8, 125.4, 121.1, 120.3, 119.6, 114.5(2C), 111.6, 55.5. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938. **2-(4-ethoxyphenyl)naphtho[2,1-b]furan-1-carbaldehyde (2p)** 



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid in 75% yield, 119 mg; mp. 129-131°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.27 (d, J = 1.2 Hz, 1H), 9.55 (dd, J = 8.5, 1.2 Hz, 1H), 7.94 (dd, J = 8.1, 1.3 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.76 – 7.71 (m, 2H), 7.70 – 7.65 (m, 2H), 7.54 (m, 1H), 7.08 – 7.03 (m, 2H), 4.11 (qd, J = 7.0, 6.5, 2.8 Hz, 2H), 1.47 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 167.6, 161.2, 152.3, 131.5 (2C), 131.4, 128.6, 128.4, 127.9, 127.8, 126.7, 125.4, 120.9, 120.3, 119.5, 115.0 (2C), 111.6, 63.8, 14.7. HRMS (EI): *m/z* calcd for C<sub>21</sub>H<sub>16</sub>O<sub>3</sub> [M<sup>+</sup>]: 316.1099, found: 316.1096.

1-bromo-2-(cinnamyloxy)-3-ethoxynaphthalene (2q)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid in 44% yield, 75 mg; mp. 153-154°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.30 (s, 1H), 9.44 (dd, J = 8.5, 1.2 Hz, 1H), 7.93 (dd, J = 8.3, 1.3 Hz, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 3.4 Hz, 2H), 7.81 (s, 1H), 7.70 – 7.64 (m, 2H), 7.56 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  185.8, 164.0, 152.7, 132.0 (q, J = 33.0 Hz), 131.8, 131.2, 129.8(2C), 128.6, 128.5, 128.1, 127.3, 126.9, 125.7 (q, J = 3.7 Hz), 125.5, 124.9 (q, J = 272.5 Hz), 122.1, 121.1, 119.8, 111.4. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(thiophen-3-yl)naphtho[2,1-b]furan-1-carbaldehyde (2r)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 58% yield, 81 mg; mp. 174-

176°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.57 (s, 1H), 9.40 (d, J = 8.5 Hz, 1H), 7.91 – 7.9 (m, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.75 (m, 1H), 7.71 – 7.63 (m, 3H), 7.54 (dd, J = 8.1, 5.1, 1.3 Hz, 1H), 7.25 (d, J = 3.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  185.5, 160.1, 152.3, 131.5, 130.8, 130.4, 130.2, 128.7, 128.4, 128.3, 128.2, 127.5, 127.0, 125.5, 120.3, 119.7, 111.5. HRMS (EI): m/z calcd for C<sub>17</sub>H<sub>10</sub>O<sub>2</sub>S [M<sup>+</sup>]: 278.0402, found: 278.0399.

2-(naphthalen-2-yl)naphtho[2,1-b]furan-1-carbaldehyde (2s)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 62% yield, 100 mg; mp. 181-182°C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  10.44 (s, 1H), 9.59 (d, *J* = 8.4 Hz, 1H), 8.30 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.95 (t, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.60-7.58 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  187.0, 167.1, 152.8, 134.1, 132.9, 131.5, 130.7, 128.9, 128.8, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.3, 126.9, 126.0, 125.8, 125.5, 120.6, 120.3, 111.7. HRMS (EI): *m/z* calcd for C<sub>23</sub>H<sub>14</sub>O<sub>2</sub> [M<sup>+</sup>]: 322.0994, found: 322.0997.

7-bromo-2-phenylnaphtho[2,1-*b*]furan-1-carbaldehyde (2t)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a white solid in 49% yield, 86 mg; mp. 179-180°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.29 (s, 1H), 9.46 (d, *J* = 9.0 Hz, 1H), 8.09 (d, *J* = 3.7 Hz, 1H), 8.07 (d, *J* = 3.2 Hz 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.81 (m, 1H), 7.74 (d, *J* = 7.7 Hz 1H), 7.72 (d, *J* = 4.8 Hz, 1H), 7.62 (d, *J* = 2.7 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.7, 167.6, 152.5, 151.6, 132.7, 131.7, 131.1, 130.5, 129.9(2C), 129.1, 128.4, 128.1, 127.2, 120.1, 119.4, 118.2, 112.8, 111.0. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

1-formyl-2-phenylnaphtho[2,1-*b*]furan-7-carbonitrile (2u)



NC

Following the general procedure, the compound was purified by flash chromatography

(petroleum ether/ethyl acetate = 100:1) as a yellow solid in 35% yield, 52 mg; mp. 218-220°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.30 (s, 1H), 9.86 – 9.49 (m, 1H), 8.31 (d, *J* = 3.9 Hz, 1H), 7.94 – 7.88 (m, 1H), 7.83 (d, *J* = 7.7 Hz, 4H), 7.63 (d, *J* = 4.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.5, 168.1, 153.8, 134.3, 131.4, 130.4, 130.3, 130.0(2C), 129.3, 129.2(2C), 128.3, 128.1, 127.5, 120.5, 120.0, 119.2, 113.7, 109.0. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

4-methoxy-2-phenylnaphtho[2,1-b]furan-1-carbaldehyde (2v)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 61% yield, 92 mg; mp. 206-207°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.31 (s, 1H), 9.45 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 6.1 Hz, 3H), 7.60 – 7.52 (m, 5H), 7.20 (s, 1H), 4.13 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 167.4, 144.9, 144.3, 132.5, 130.9, 130.1 (2C), 128.9 (2C), 128.5, 127.5, 127.3, 125.9, 124.6, 123.9, 122.0, 120.5, 105.5, 56.0. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

6-methoxy-2-phenylbenzofuran-3-carbaldehyde (2w)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a yellow solid in 64% yield, 81 mg; mp. 117-119°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.30 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.55 (q, *J* = 3.7 Hz, 3H), 7.07 (d, *J* = 2.1 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.88 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 164.7, 159.2, 155.3, 130.9, 129.2(2C), 129.0(2C), 128.9, 123.0, 118.7, 117.7, 113.6, 95.9, 55.9. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938.

2-(4-(dimethylamino)phenyl)-6-methoxybenzofuran-3-carbaldehyde (2x)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) as a yellow solid in 61% yield, 90 mg; mp. 107-109°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.28 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 2.1 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.08 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  186.8, 166.5, 158.6, 154.8, 152.1, 130.2(2C), 122.5, 119.4, 116.1, 115.6, 112.8, 112.0(2C), 96.0, 55.9, 40.3(2C). HRMS (ESI): *m/z* calcd for C<sub>18</sub>H<sub>18</sub>NO<sub>3</sub> [M + H]<sup>+</sup>: 296.1282, found: 296.1286.

6-methoxy-2-(3-(trifluoromethyl)phenyl)benzofuran-3-carbaldehyde (2y)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 51% yield, 82 mg; mp. 106-107°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.33 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 2.1 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.90 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  186.0, 162.0, 159.7, 155.5, 132.0, 131.9, 129.9, 129.8, 127.3, 125.6, 123.8, 123.2, 118.5(2C), 114.1, 95.9, 55.9. HRMS (EI): *m/z* calcd for C<sub>17</sub>H<sub>11</sub>F<sub>3</sub>O<sub>3</sub> [M<sup>+</sup>]: 320.0660, found: 320.0663.

2-(4-fluorophenyl)-6-methoxybenzofuran-3-carbaldehyde (2z)



Following the general procedure, the compound was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) as a pale-yellow solid in 63% yield, 85 mg; mp. 126-127°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.17 (s, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.73 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.90 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.79 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  186.4, 164.4, 163.4, 159.3, 155.2, 131.0, 130.9, 125.1, 122.9, 118.6, 117.5, 116.6, 114.4, 113.6, 95.9, 55.9. The data is consistent with *Chem. Commun.*, 2018, **54**, 4935-4938

## 4. Copies of NMR Spectra

## 4.1 Copies of Substrates NMR Spectra



75 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 f1 (ppm)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-(cinnamyloxy)naphthalene (1a)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(2-fluorophenyl)allyl)oxy)naphthalene (1b)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(3-fluorophenyl)allyl)oxy)naphthalene (1c)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(4-fluorophenyl)allyl)oxy)naphthalene (1d)

![](_page_28_Figure_0.jpeg)

![](_page_28_Figure_1.jpeg)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(2-chlorophenyl)allyl)oxy)naphthalene

(1e)

![](_page_29_Figure_0.jpeg)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(3-chlorophenyl)allyl)oxy)naphthalene (1f)

![](_page_30_Figure_0.jpeg)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of -1-bromo-2-((3-(4-chlorophenyl)allyl)oxy)naphthalene (1g)

#### 

![](_page_31_Figure_1.jpeg)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)of 1-bromo-2-((3-(2-bromophenyl)allyl)oxy)naphthalene (1h)

 $\begin{array}{c} 8.828 \\ 8.828$ 

![](_page_32_Figure_1.jpeg)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(3-bromophenyl)allyl)oxy)naphthalene (1i)

# (232) (2005)

![](_page_33_Figure_1.jpeg)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(4-bromophenyl)allyl)oxy)naphthalene (1j)

![](_page_34_Figure_0.jpeg)

![](_page_35_Figure_0.jpeg)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(*m*-tolyl)allyl)oxy)naphthalene (11)


S37





0



(10)

 $\begin{array}{c} 7,7,5\\ 7,$ 8.24 8.24 8.21 8.21 8.21 7.75 7.75 7.75



<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(4-ethoxyphenyl)allyl)oxy)naphthalene (1p)

### 





yl)thiophene (1r)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-((3-(naphthalen-2-yl)allyl)oxy)naphthalene (1s)

88.11 10.10 10



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1, 6-dibromo-2-(cinnamyloxy)naphthalene (1t)

# $\begin{bmatrix} 8.3.28\\ 8.3.06\\ 8.3.06\\ 7.3.867\\ 7.3.867\\ 7.7.867\\ 7.7.867\\ 7.7.845\\ 7.7.845\\ 7.7.359\\ 7.$





<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **5-bromo-6-(cinnamyloxy)-2-naphthonitrile (1u)** 

88.16 88.15 88.15 88.15 88.14



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-(cinnamyloxy)-3-methoxynaphthalene (1v)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 1-bromo-2-(cinnamyloxy)-4-methoxybenzene (1w)

### 7,131 7,1337



### 1,144 1,142 1,



## 4.2 Copies of Product NMR Spectra

110.31 110.30 110.30 110.30 110.30 110.30 110.20



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2-phenylnaphtho**[2,1-b]furan-1-carbaldehyde (2a)







HRMS spectra of 2-(2-fluorophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2b)



(2c)





HRMS spectra of 2-(3-fluorophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2c)

 $\begin{array}{c} g_{0} \\ g_{0} \\$ 

 ${}^1\mathrm{H}\ \mathrm{NMR}\ (400\ \mathrm{MHz},\ \mathrm{CDCl}_3)\ \mathrm{of}\ \mathbf{2-(4-fluorophenyl)naphtho}\\ [\mathbf{2,1-}b]\ furan-\mathbf{1-carbaldehyde}$ 



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 f1 (ppm)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2-(4-fluorophenyl)naphtho**[**2,1-***b*]furan-1-carbaldehyde

(2d)





(2e)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2-(3-chlorophenyl)naphtho[2,1-***b***]furan-1-carbaldehyde** 



(2f)



 ${}^1\mathrm{H}\ \mathrm{NMR}\ (400\ \mathrm{MHz}, \mathrm{CDCl}_3)\ \mathrm{of}\ \mathbf{2-(4-chlorophenyl)naphtho}\\ [\mathbf{2,1-}b]\ furan-1-carbaldehyde$ 



20 195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 6ξ f1 (ppm)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 2-(4-chlorophenyl)naphtho[2,1-b]furan-1-carbaldehyde

(2g)





<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2-(2-bromophenyl)naphtho**[**2,1-***b*]furan-**1-carbaldehyde** 

(2h)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of **2-(3-bromophenyl)naphtho**[**2,1-***b*]furan-1-carbaldehyde

(2i)



HRMS spectra of 2-(3-bromophenyl)naphtho[2,1-b]furan-1-carbaldehyde (2i)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2-(4-bromophenyl)naphtho**[**2,1-***b*]furan-1-carbaldehyde

(2j)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2-(***o***-tolyl)naphtho[2,1-***b***]furan-1-carbaldehyde (2k)** 



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2-(***m***-tolyl)naphtho[2,1-***b***]furan-1-carbaldehyde (2l)** 



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2-(*p*-tolyl)naphtho[2,1-*b*]furan-1-carbaldehyde (2m)



<sup>(2</sup>n)



HRMS spectra of 2-(3-methoxyphenyl)naphtho[2,1-b]furan-1-carbaldehyde (2n)



S66





<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2-(4-ethoxyphenyl)naphtho**[**2,1-***b*]furan-**1-carbaldehyde** 



(2p)



HRMS spectra of 2-(4-ethoxyphenyl)naphtho[2,1-b]furan-1-carbaldehyde (2p)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 1-bromo-2-(cinnamyloxy)-3-ethoxynaphthalene (2q)



S69





HRMS spectra of 2-(thiophen-3-yl)naphtho[2,1-b]furan-1-carbaldehyde (2r)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of 2-(naphthalen-2-yl)naphtho[2,1-*b*]furan-1-carbaldehyde (2s)



HRMS spectra of 2-(naphthalen-2-yl)naphtho[2,1-b]furan-1-carbaldehyde (2s)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 7-bromo-2-phenylnaphtho[2,1-b]furan-1-carbaldehyde (2t)


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 1-formyl-2-phenylnaphtho[2,1-*b*]furan-7-carbonitrile (2u)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **4-methoxy-2-phenylnaphtho**[**2,1-***b*]furan-1-carbaldehyde

(2v)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 6-methoxy-2-phenylbenzofuran-3-carbaldehyde (2w)







HRMS spectra of 2-(4-(dimethylamino)phenyl)-6-methoxybenzofuran-3-carbaldehyde

(2x)



<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) of 6-methoxy-2-(3-(trifluoromethyl)phenyl)benzofuran-3carbaldehyde (2y)



HRMS spectra of 6-methoxy-2-(3-(trifluoromethyl)phenyl)benzofuran-3-carbaldehyde



(2z)



