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## **Supporting Information**

# for Enantioselective [1,3] O-to-C Rearrangement: Dearomatization of Akyl 2-Allyloxy/Benzyloxy-1/3-naphthoates Catalyzed by a Chiral π–Cu(II) Complex

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## 1. General Remarks

<sup>1</sup>H NMR spectra were recorded on a JEOL ECS400 400 MHz spectrometer or a Bruker 500 MHz spectrometer in CDCl<sub>3</sub>. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quartet, m = multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration). <sup>13</sup>C NMR spectra were recorded on a JEOL ECS400 100 MHz or a Bruker 125 MHz spectrometer in CDCl<sub>3</sub>. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. Enantiomeric ratios were determined by HPLC, using a chiralpak AS-3 column, chiralpak AD-3 column and chiralpak IA-3 column with hexane and *i*-PrOH as solvents. The racemic adducts were attained by using the complex of Cu(OTf)<sub>2</sub> and racemic ligand as the catalyst. The absolute configuration of **21** was determined unequivocally according to the X-ray diffraction analysis, and those of other adducts were deduced on the basis of this result.

## 2. General Procedure for the Synthesis of Ligands



To a solution of *N*-(*tert*-butoxycarbonyl)-L-norvaline (1.08 g, 5.0 mmol) in dichloromethane (DCM, 25 mL) were added 1-hydroxybenzotriazole (HOBt, 743 mg, 5.5 mmol), DCC (1.10 g 5.5 mmol) and butylamine (0.6 mL, 6.0 mmol) at 0 °C. Then the mixture was stirred at room temperature for 16 h before quenched with 10% w/w citric acid. After the mixture was filtered, the organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated under reduced pressure. *tert*-Butyl (*S*)-(1-(butylamino)-1-oxopentan-2-yl)carbamate was obtained and directly used in next step without further purification.

To a solution of the crude *tert*-butyl (*S*)-(1-(butylamino)-1-oxopentan-2-yl)carbamate in DCM (6.4 mL) was added trifliroacetic acid (TFA, 3.2 mL) dropwise at 0 °C. The mixture was then stirred at room temperature for 3 h. The mixture was neutralized with NaOH (1 M). The organic layer was separated, the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated under reduced pressure. (*S*)-2-amino-*N*-butylpentanamide was obtained and directly used in next step without further purification.



To a solution of the crude (*S*)-2-amino-*N*-butylpentanamide and *N*,*N*-diisopropylethylamine (DIPEA, 1.0 mL, 6.0 mmol) in MeCN (20 mL) was added dibenzosuberyl chloride (1.2 g, 5.25 mmol). The mixture was reacted at room tempertaure until the reaction completed (monitored by TLC). The reaction mixture was filtered through a pad of celite and washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane = 1/5, v/v) to afford the ligand L8.

## (S)-N-Butyl-2-[(10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]pentanamide (L8):

60% overall yield; white solid; m.p. = 89.1 °C;  $[α]^{23}_D = -15.9$  (*c* 1.00, CHCl<sub>3</sub>); IR (film) 3304, 2957, 2929, 2871, 1644, 1552, 1445, 760 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.24 – 7.11 (m, 8H), 6.64 (s, 1H), 4.64 (s, 1H), 3.65 (m, 2H), 3.16 (dt, *J* = 20.1, 6.7 Hz, 1H), 3.08 – 2.96 (m, 4H), 1.66 (m, 1H), 1.57 – 1.53 (m, 2H), 1.39 – 1.26 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): β 174.3, 130.4, 130.3, 127.7, 127.6, 126.1, 125.9, 61.4, 38.5, 35.8, 32.8, 32.4, 31.5, 19.9, 19.0, 13.7, 13.6; HRMS (ESI+) *m/z* calcd. for C<sub>24</sub>H<sub>33</sub>N<sub>2</sub>O: 365.2587, found: 365.2589.

The ligands used in screening were synthesized using the same procedure of synthesizing L8. (S)-2-[(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]-1-(pyrrolidin-1-yl)propan-1-one (L1):



57% overall yield; colorless viscous liquid;  $[\alpha]^{25}_{D} = +59.3$  (*c* 0.71, CHCl<sub>3</sub>); IR (neat) 2971, 2874, 1638, 1427, 764 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.34 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.18 – 7.05 (m, 7H), 4.72 (s, 1H), 4.27 (brs, 1H), 3.61 – 3.47 (m, 3H), 3.13 (d, *J* = 6.6 Hz, 1H), 3.06 – 2.99 (m, 1H), 2.93

(t, J = 12.7 Hz, 1H), 2.87 – 2.81 (m, 1H), 2.75 (m, 1H), 2.27 (m, 1H), 1.85 – 1.82 (m, 4H), 1.13 (d, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  173.5, 130.7, 129.5, 127.6, 127.1, 125.6, 125.2, 52.1, 45.4, 45.3, 33.1, 31.3, 25.7, 23.9, 18.7; HRMS (ESI+) m/z calcd. for C<sub>22</sub>H<sub>27</sub>N<sub>2</sub>O: 335.2118, found: 335.2110.

(S)-2-[(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]-1-(pyrrolidin-1-yl)butan-1-one



(L2):

54% overall yield; yellow viscous liquid;  $[\alpha]^{26}_{D} = +57.8$  (*c* 0.71, CHCl<sub>3</sub>); IR (neat) 2967, 2871, 1636, 1424, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33

(d, J = 7.0 Hz, 1H), 7.20 – 7.05 (m, 7H), 4.67 (s, 1H), 4.35 (brs, 1H), 3.63 – 3.47 (m, 3H), 3.08 – 2.74 (m, 5H), 2.17 (m, 1H), 1.85 (m, 4H), 1.47 (td, J = 13.8, 6.9 Hz, 2H), 0.89 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  173.3, 130.9, 129.6, 127.6, 127.2, 125.7, 125.2, 58.5, 45.5, 45.4, 33.2, 31.3, 26.5, 25.8, 24.0, 10.8; HRMS (ESI+) *m*/*z* calcd. for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O: 349.2274, found: 349.2265.

# (S)-2-[(10,11-Dihydro-5*H*-dibenzo[a,d][7]annulen-5-yl)amino]-3-methyl-1-(pyrrolidin-1-yl)but an-1-one (L3):



61% overall yield; white solid; m.p. = 89.8 °C;  $[\alpha]^{26}{}_{D}$  = +74.3 (*c* 0.71, CHCl<sub>3</sub>); IR (film) 2956, 2871, 1637, 1492, 1422, 767 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (d, *J* = 6.8 Hz, 1H), 7.18 – 7.03 (m, 7H), 4.58 (s, 1H), 4.46 (brs, 1H), 3.68 – 3.51 (m, 3H), 3.09 (dt, *J* = 9.6, 6.8 Hz, 1H), 2.91 –

2.72 (m, 4H), 2.23 (m, 1H), 1.89 – 1.84 (m, 4H), 1.71 (s, 1H), 0.93 – 0.82 (m, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  173.2, 131.0, 129.6, 127.8, 127.3, 125.9, 125.3, 62.8, 45.9, 45.5, 33.4, 31.7, 31.2, 26.0, 24.2, 20.0, 18.4; HRMS (ESI+) *m/z* calcd. for C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>NaO: 385.2250, found: 385.2241.

(S)-2-[(10,11-Dihydro-5*H*-dibenzo[a,d][7]annulen-5-yl)amino]-1-(pyrrolidin-1-yl)pentan-1-one (L4):



63% overall yield; yellow viscous liquid;  $[α]^{27}_D$  = +49.8 (*c* 0.71, CHCl<sub>3</sub>); IR (neat) 2956, 2871, 1637, 1493, 1422, 768 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 6.8 Hz, 1H), 7.20 – 7.04 (m, 7H), 4.66 (s, 1H), 4.36 (brs, 1H), 3.63 – 3.50 (m, 3H), 3.06 – 2.84 (m, 4H), 2.73 (m, 1H), 2.21 (m, 1H), 1.84 –

1.78 (m, 4H), 1.51 – 1.27 (m, 4H), 0.75 (t, J = 6.9 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  173.4, 130.8, 129.5, 127.6, 127.1, 125.7, 125.1, 56.4, 45.4, 45.3, 35.3, 33.2, 31.2, 25.8, 23.9, 19.0, 13.4; HRMS (ESI+) m/z calcd. for C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>NaO: 385.2250, found: 385.2247.

## (S)-2-[(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]-1-(pyrrolidin-1-yl)hexan-1-one



(L5):

62% overall yield; yellow viscous liquid;  $[α]^{27}_D$  = +45.6 (*c* 0.71, CHCl<sub>3</sub>); IR (neat) 2952, 2865, 1638, 1421, 765 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 6.9 Hz, 1H), 7.20 – 7.05 (m, 7H), 4.67 (s, 1H), 4.37 (brs, 1H),

3.64 - 3.50 (m, 3H), 3.06 - 3.02 (m, 4H), 2.74 (m, 1H), 2.12 (m, 1H), 1.86 - 1.81 (m, 4H), 1.41 - 1.14 (m, 6H), 0.81 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  173.5, 130.9, 129.5, 127.6, 127.2, 125.8, 125.2, 56.8, 45.5, 45.4, 33.3, 33.0, 31.3, 28.1, 25.9, 24.0, 22.2, 13.8; HRMS (ESI+) *m/z* calcd. for C<sub>25</sub>H<sub>32</sub>N<sub>2</sub>NaO: 399.2407, found: 399.2398.

(*S*)-2-[(10,11-Dihydro-5*H*-dibenzo[a,d][7]annulen-5-yl)amino]-*N*-ethylpentanamide (L6): 58% overall yield; white solid; m.p. = 115.4 °C;  $[\alpha]^{23}_{D} = -14.6$  (*c* 0.71, CHCl<sub>3</sub>); IR (film) 3302, 2903, 2864, 2359, 1646, 1541, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.11 (m, 8H), 6.61



(s, 1H), 4.64 (s, 1H), 3.67 (m, 2H), 3.15 (ddd, J = 21.6, 13.8, 7.2 Hz, 2H), 3.06 (dd, J = 7.7, 5.0 Hz, 1H), 2.96 (m, 2H), 1.95 (m, 1H), 1.69 – 1.62 (m, 1H), 1.53 – 1.50 (m, 1H), 1.40 – 1.24 (m, 2H), 1.03 (t, J = 7.3 Hz, 3H), 0.84 (t, J = 7.3 Hz, 3H); 13C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  174.3, 130.5, 130.4,

127.8, 127.7, 126.2, 126.1, 61.7, 35.9, 33.7, 32.9, 32.6, 19.1, 14.7, 13.8; HRMS (ESI+) *m/z* calcd. for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>NaO: 359.2094, found: 359.2085.

## (S)-2-[(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]-N-propylpentanamide (L7):



61% overall yield; white solid; m.p. = 107.6 °C;  $[α]^{27}_D = -13.4$  (*c* 0.71, CHCl<sub>3</sub>); IR (film) 3298, 2958, 2929, 2871, 1638, 1557, 1444, 1156, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 – 7.11 (m, 8H), 6.66 (s, 1H), 4.65 (s, 1H), 3.64 (brs, 2H), 3.14 (td, *J* = 13.4, 6.8 Hz, 1H), 3.06 – 2.98 (m, 4H), 1.98 (m,

1H), 1.68 – 1.29 (m, 6H), 0.86 (dt, J = 14.3, 7.3 Hz, 6H); 13C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.4, 130.4, 130.3, 127.7, 127.6, 126.1, 126.0, 61.4, 40.5, 35.8, 32.8, 32.4, 22.7, 19.0, 13.7, 11.3; HRMS (ESI+) m/z calcd. for C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>NaO: 373.2250, found: 373.2241.

(S)-2-[(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]-N-neopentylpentanamide (L9):



56% overall yield; white solid; m.p. = 108.3 °C;  $[\alpha]^{28}_{D} = -13.6$  (*c* 0.71, CHCl<sub>3</sub>); IR (film) 3313, 3061, 3016, 2957, 2869, 1651, 757 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.22 – 7.11 (m, 8H), 6.79 (s, 1H), 4.69 (s, 1H), 3.66 (m, 2H), 3.11 – 2.98 (m, 4H), 2.76 (m, 1H), 2.00 (m, 1H), 1.70 – 1.34 (m, 4H),

0.88 - 0.84 (m, 12H); 13C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  174.4, 130.5, 130.4, 127.8, 127.7, 126.2, 126.1, 61.7, 50.1, 36.0, 32.9, 32.6, 31.5, 27.1, 19.1, 13.8; HRMS (ESI+) *m/z* calcd. for C<sub>25</sub>H<sub>34</sub>N<sub>2</sub>NaO: 401.2563, found: 401.2558.

(S)-2-[(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]-N-isopropylpentanamide (L10):



60% overall yield; white solid; m.p. = 114.0 °C;  $[\alpha]^{24}_{D} = -11.2$  (*c* 0.71, CHCl<sub>3</sub>); IR (film) 3301, 2964, 2873, 2360, 1639, 1543, 1456, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.11 (m, 8H), 6.52 (d, *J* = 7.6 Hz, 1H), 4.63 (brs, 1H), 3.96 (ddt, *J* = 13.1, 8.0, 6.6 Hz, 1H), 3.68 (m, 2H), 3.03 –

2.97 (m, 3H), 1.94 (m, 1H), 1.69 – 1.63 (m, 1H), 1.51-1.49 (m, 1H), 1.36 – 1.29 (m, 2H), 1.10 (d, J = 6.6 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H), 0.84 (t, J = 7.3 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  173.5, 130.6, 130.4, 127.8, 127.7, 126.2, 126.0, 61.6, 40.6, 35.9, 32.9, 32.6, 22.8, 22.4, 19.1, 13.8; HRMS (ESI+) *m*/*z* calcd. for C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>NaO: 373.2250, found: 373.2251.

## 3. General Procedure for the Synthesis of Methyl 2-Allyloxy- and

## 2-Benzyloxy-1-naphthoates



The starting naphthols<sup>1</sup> (6 mmol) and  $Cs_2CO_3$  (9 mmol) were dissolved in acetone (40 mL). Cinnamyl bromide<sup>2</sup> (or benzyl bromide) (8 mmol) was added by syringe and the reaction was heated to 60 °C until TLC revealed complete conversion of naphthols. The mixture was diluted with ethyl acetate and water after cooling. The organic layer was washed with brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The residue was purified by silica gel chromatography to afford corresponding product.

## Methyl 2-(cinnamyloxy)-1-naphthoate (1a):



**1a** was isolated by FC on silica gel using pentane/EtOAc 30:1; 86% yield; white solid; m.p. = 114.0 °C; IR (film) 2945, 1725, 1286, 1236, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 8.2

Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.52 – 7.49 (m, 1H), 7.41 – 7.37 (m, 3H), 7.34 – 7.31 (m, 3H), 7.27 – 7.24 (m, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 16.0, 5.6 Hz, 1H), 4.88 (dd, J = 5.5, 1.5 Hz, 2H), 4.04 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 153.5, 136.3, 132.6, 131.5, 130.9, 128.6, 128.5, 128.0, 127.8, 127.5, 126.4, 124.2, 124.1, 123.8, 118.4, 114.8, 70.2, 52.3; HRMS (ESI+) *m*/*z* calcd. for C<sub>21</sub>H<sub>18</sub>NaO<sub>3</sub>: 341.1148; found: 341.1146.

## Methyl (E)-2-{[3-(o-tolyl)allyl]oxy}-1-naphthoate (1b):



**1b** was isolated by FC on silica gel using pentane/EtOAc 30:1; 78% yield; white solid; m.p. = 86.1 °C; IR (film) 3025, 2948, 1726, 1510, 1437, 1284, 1233, 809, 747 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.89

(d, J = 9.1 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.50 (ddd, J = 8.4, 6.9, 1.2 Hz, 1H), 7.45 (dd, J = 5.3, 3.7 Hz, 1H), 7.38 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 7.33 (d, J = 9.1 Hz, 1H), 7.18 – 7.13 (m, 3H), 6.97 (d, J = 15.8 Hz, 1H), 6.28 (dt, J = 15.8, 5.5 Hz, 1H), 4.90 (dd, J = 5.5, 1.6 Hz, 2H), 4.04 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.5, 135.5, 131.4, 130.9, 130.6, 130.2, 128.7, 128.0, 127.7, 127.5, 126.0, 125.7, 125.4, 124.2, 123.8, 118.4, 114.8, 70.3, 52.3, 19.6; HRMS (ESI+) *m/z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1305; found: 355.1298.

## Methyl (E)-2-{[3-(m-tolyl)allyl]oxy}-1-naphthoate (1c):



**1c** was isolated by FC on silica gel using pentane/EtOAc 30:1; 67% yield; yellow liquid; IR (neat) 2941, 1727, 1510, 1283, 1235, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, *J* = 9.1 Hz, 1H), 7.79 (d,

J = 8.2 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.39 – 7.36 (m, 1H), 7.31 (d, J = 9.1 Hz, 1H), 7.22 – 7.20 (m, 3H), 7.08 – 7.06 (m, 1H), 6.71 (d, J = 16.0 Hz, 1H), 6.39 (dt, J = 16.0, 5.6 Hz, 1H), 4.87 (dd, J = 5.6, 1.5 Hz, 2H), 4.04 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.6, 138.1, 136.3, 132.9, 131.5, 131.0, 128.7, 128.4, 128.0, 127.5, 127.2, 124.3, 124.0, 123.8, 123.7, 118.4, 114.8, 70.4, 52.4 21.3; HRMS (ESI+) *m*/*z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1305; found: 355.1303.

#### Methyl (*E*)-2-{[3-(*p*-tolyl)allyl]oxy}-1-naphthoate (1d):



1d was isolated by FC on silica gel using pentane/EtOAc 30:1; 83% yield; white solid; m.p. = 95.5 °C; IR (film) 2950, 1726, 1510, 1283, 1234, 754 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, *J* = 9.1 Hz,

1H), 7.79 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.32 – 7.29 (m, 3H), 7.14 – 7.12 (m, 2H), 6.71 (d, J = 16.0 Hz, 1H), 6.35 (dt, J = 15.9, 5.7 Hz, 1H), 4.87 (dd, J = 5.7, 1.4 Hz, 2H), 4.04 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.6, 137.8, 133.6, 132.8, 131.5, 131.0, 129.3, 128.7, 128.0, 127.5, 126.4, 124.3, 123.8, 123.2, 118.5, 115.0, 70.6, 52.4, 21.2; HRMS (ESI+) m/z calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1305; found: 355.1297.

Methyl (*E*)-2-{[3-(4-bromophenyl)allyl]oxy}-1-naphthoate (1e):

**CO**<sub>2</sub>Me **F Ie** was isolated by FC on silica gel using pentane/EtOAc 30:1; 83% yield; white solid; m.p. = 111.4 °C; IR (film) 2946, 1726, 1510, 1284, 1234, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J =9.1 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.51 (t, J = 8.3 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 9.1 Hz, 1H), 7.27–7.25 (m, 2H), 6.68 (d, J = 16.0 Hz, 1H), 6.39 (dt, J = 16.0, 5.4 Hz, 1H), 4.87 (dd, J = 5.4, 1.5 Hz, 2H), 4.04 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.3, 153.4, 135.3, 131.7, 131.6, 131.4, 131.0, 128.8, 128.0, 128.0, 127.6, 125.1, 124.4, 123.8, 121.7, 118.5, 114.8, 70.1, 52.4; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>BrNaO<sub>3</sub>: 419.0253; found: 419.0244.

#### Methyl (*E*)-2-{[3-(4-chlorophenyl)allyl]oxy}-1-naphthoate (1f):

.CI



**1f** was isolated by FC on silica gel using pentane/EtOAc 30:1; 73% yield; white solid; m.p. = 111.8 °C; IR (film) 2947, 1725, 1282, 1234 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (d, *J* = 9.1 Hz, 1H),

7.80 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.51 (t, J = 8.3 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.33 – 7.28 (m, 5H), 6.70 (d, J = 16.0 Hz, 1H), 6.38 (dt, J = 16.0, 5.5 Hz, 1H), 4.88 (dd, J = 5.5, 1.6 Hz, 2H), 4.04 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 153.4, 134.8, 133.4, 131.5, 131.3, 130.9, 128.7, 128.6, 128.0, 127.7, 127.6, 124.9, 124.3, 123.8, 118.4, 114.7, 70.0, 52.3; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>ClNaO<sub>3</sub>: 375.0758; found: 375.0749

## Methyl (*E*)-2-{[3-(naphthalen-1-yl)allyl]oxy}-1-naphthoate (1g):



**1g** was isolated by FC on silica gel using pentane/EtOAc 30:1; 48% yield; light yellow solid; m.p. = 136.3 °C; IR (film) 3095, 2951, 1726, 1510, 1284, 1234, 788 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ

8.08 – 8.07 (m, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.86 – 7.77 (m, 4H), 7.61 (d, J = 7.0 Hz, 1H), 7.54 – 7.37 (m, 7H), 6.43 (dt, J = 15.7, 5.3 Hz, 1H), 5.00 (d, J = 4.4 Hz, 2H), 4.05 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.6, 134.2, 133.5, 131.6, 131.1, 131.0, 129.9, 128.8, 128.4, 128.2, 128.1, 127.6, 127.3, 126.1, 125.8, 125.5, 124.3, 123.9, 123.8, 123.7, 118.5, 114.8, 70.2, 52.4; HRMS (ESI+) *m*/*z* calcd. for C<sub>25</sub>H<sub>20</sub>NaO<sub>3</sub>: 391.1305; found: 391.1296.

#### Methyl (*E*)-2-{[3-(naphthalen-2-yl)allyl]oxy}-1-naphthoate (1h):



**1h** was isolated by FC on silica gel using pentane/EtOAc 30:1; 53% yield; white solid; m.p. = 86.0 °C; IR (film) 3063, 2954, 1726, 1284, 1235, 787 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J =

9.1 Hz, 1H), 7.81 – 7.75 (m, 6H), 7.62 (d, J = 8.6 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 9.1 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H), 6.54 (dt, J = 15.9, 5.5 Hz, 1H), 4.94 (dd, J = 5.5, 1.4 Hz, 2H), 4.06 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.6, 133.8, 133.5, 133.1, 132.8, 131.6, 131.0, 128.7, 128.2, 128.0, 127.9, 127.6, 127.5, 126.7, 126.3, 126.0, 124.6, 124.3, 123.8, 123.4, 118.4, 114.8, 70.4, 52.4; HRMS (ESI+) *m/z* calcd. for C<sub>25</sub>H<sub>20</sub>NaO<sub>3</sub>: 391.1305; found: 391.1295.

## Methyl (*E*)-2-{[3-(furan-3-yl)allyl]oxy}-1-naphthoate (1i):



**1i** was isolated by FC on silica gel using pentane/EtOAc 15:1; 46% yield; yellow viscous liquid; IR (neat) 2950, 1725, 1510, 1438, 1285, 1238, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 9.1 Hz, 1H),

7.79 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.50 (t, J = 7.1 Hz, 1H), 7.43 (s, 1H), 7.40 – 7.37 (m, 2H), 7.29 (d, J = 9.1 Hz, 1H), 6.61.6.54 (m, 2H), 6.13 (dt, J = 15.8, 5.6 Hz, 1H), 4.82 (dd, J = 5.6, 1.4 Hz, 2H), 4.04 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.6, 143.6, 140.8, 131.5, 131.0, 128.7, 128.0, 127.6, 124.3, 123.8, 123.7, 123.4, 122.8, 118.4, 114.9, 107.5, 70.3, 52.4; HRMS (ESI+) *m/z* calcd. for C<sub>19</sub>H<sub>16</sub>NaO<sub>4</sub>: 331.0941; found: 331.0941.

## Methyl (*E*)-2-{[3-(thiophen-3-yl)allyl]oxy}-1-naphthoate (1j):



**1j** was isolated by FC on silica gel using pentane/EtOAc 15:1; 47% yield; light brown solid; m.p. = 96.3 °C; IR (film) 2946, 1726, 1512, 1278, 1234 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 9.1 Hz,

1H), 7.79 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.50 (t, J = 7.0 Hz, 1H), 7.38 (t, J = 7.0 Hz, 1H), 7.30 (d, J = 9.1 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.23 – 7.22 (m, 1H), 7.19 – 7.18 (m, 1H), 6.74 (d, J = 15.9 Hz, 1H), 6.26 (dt, J = 15.9, 5.6 Hz, 1H), 4.85 (dd, J = 5.6, 1.5 Hz, 2H), 4.04 (s, 3H); <sup>13</sup>C

NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.5, 138.9, 131.5, 130.9, 128.6, 128.0, 127.5, 127.0, 126.1, 124.9, 124.2, 124.0, 123.8, 122.7, 118.3, 114.8, 70.2, 52.3; HRMS (ESI+) *m/z* calcd. for C<sub>19</sub>H<sub>16</sub>NaO<sub>3</sub>S: 347.0712; found: 347.0716.

## Methyl (*E*)-2-[(3-phenylbut-2-en-1-yl)oxy]-1-naphthoate (1k):

**Ik** was isolated by FC on silica gel using pentane/EtOAc 30:1; 85% yield; white solid; m.p. = 68.7 °C; IR (film) 2947, 1728, 1510, 1438, 1283, 1234, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 8.3 Hz, 1H), 7.44 – 7.26 (m, 7H), 6.05 (t, *J* = 6.2 Hz, 1H), 4.93 (d, *J* = 6.2 Hz, 2H), 4.03 (s, 3H), 2.14 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ 168.4, 153.6, 142.4, 139.0, 131.4, 130.9, 128.6, 128.2, 128.0, 127.5, 127.4, 125.7, 124.2, 123.7, 122.6, 118.4, 114.8, 67.2, 52.3, 16.3; HRMS (ESI+) *m/z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1310; found: 355.1298.

## Methyl 2-{[3,3-bis(4-chlorophenyl)allyl]oxy}-1-naphthoate (11):



11 was isolated by FC on silica gel using pentane/EtOAc 30:1; 88% yield; white solid; m.p. = 105.8 °C; IR (film) 2950, 1729, 1491, 1283, 1235, 1091, 1014, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 9.1 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 8.2 Hz, 1H), 7.40 – 7.37 (m, 3H), 7.27 – 7.24

(m, 2H), 7.16 – 7.13 (m, 4H), 7.07 (d, J = 9.1 Hz, 1H), 6.32 (t, J = 6.7 Hz, 1H), 4.73 (d, J = 6.7 Hz, 2H), 4.03 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.2, 143.9, 139.5, 136.7, 134.1, 134.0, 131.5, 131.0, 130.9, 128.9, 128.7, 128.5, 128.0, 127.6, 124.4, 124.4, 123.8, 118.7, 114.8, 67.5, 52.4; HRMS (ESI+) m/z calcd. for C<sub>27</sub>H<sub>20</sub>Cl<sub>2</sub>NaO<sub>3</sub>: 485.0682; found: 485.0687.

## Methyl 2-[(3-methylbut-2-en-1-yl)oxy]-1-naphthoate (1m):



**1m** was isolated by FC on silica gel using pentane/EtOAc 30:1; 78% yield; yellow liquid; IR (neat) 2949, 1731, 1510, 1473, 1283, 1234, 1053, 810, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* 

= 8.2 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.49 (t, J = 7.1 Hz, 1H), 7.37 (t, J = 7.1 Hz, 1H), 7.28 (s, 1H), 5.49 – 5.46 (m, 1H), 4.70 (d, J = 6.6 Hz, 2H), 4.02 (s, 3H), 1.77 (s, 3H), 1.74 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.7, 137.7, 131.2, 130.9, 128.4, 127.9, 127.3, 124.0, 123.6, 119.6, 118.3, 114.9, 66.7, 52.1, 25.6, 18.0; HRMS (ESI+) *m*/*z* calcd. for C<sub>17</sub>H<sub>18</sub>NaO<sub>3</sub>: 293.1148; found: 293.1150.

## Methyl 6-bromo-2-(cinnamyloxy)-1-naphthoate (1n):



**1n** was isolated by FC on silica gel using pentane/EtOAc 30:1; 87% yield; a light brown solid; m.p. = 86.5 °C; IR (film) 2947, 1730,1497, 1286, 1233 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, *J* = 1.9 Hz,

1H), 7.79 (d, J = 9.1 Hz, 1H), 7.65 (d, J = 9.1 Hz, 1H), 7.57 – 7.55 (m, 1H), 7.41 – 7.26 (m, 6H), 6.74 (d, J = 16.0 Hz, 1H), 6.39 (dt, J = 16.0, 5.6 Hz, 1H), 4.88 (dd, J = 5.6, 1.4 Hz, 2H), 4.04 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  167.9, 153.9, 136.2, 132.9, 130.8, 130.6, 129.9, 129.6, 129.5, 128.6, 127.9, 126.5, 125.6, 123.9, 118.4, 117.9, 115.8, 70.3, 52.5; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>BrNaO<sub>3</sub>: 419.0253; found: 419.0252.

#### Methyl 3-bromo-2-(cinnamyloxy)-1-naphthoate (1o):

**CO**<sub>2</sub>Me **Io** was isolated by FC on silica gel using pentane/EtOAc 30:1; 78% yield; **i** o was isolated by FC on silica gel using pentane/EtOAc 30:1; 78% yield; **i** o was isolated by FC on silica gel using pentane/EtOAc 30:1; 78% yield; **i** o olorless liquid; IR (neat) 2947, 1731, 1278, 1224, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (s, 1H), 7.76 (d, *J* = 9.4 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.50 – 7.26 (m, 7H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.50 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.81 (dd, *J* = 6.2, 1.3 Hz, 2H), 4.02 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  167.4, 150.7, 136.4, 134.4, 133.7, 131.3, 129.9, 128.6, 127.9, 127.7, 127.2, 126.7, 126.4, 125.7, 124.5, 124.2, 116.8, 75.9, 52.8; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>BrNaO<sub>3</sub>: 419.0253; found: 419.0250.

## Benzyl 2-(cinnamyloxy)-1-naphthoate (1p):

**1p** was isolated by FC on silica gel using pentane/EtOAc 30:1; 83% yield; white solid; m.p. = 62.3 °C; IR (film) 3025, 1727, 1510, 1281, 1226, 747  $m^{-1}$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, J = 9.1 Hz, 1H), 7.79 – 7.42 (m, 2H), 7.49 – 7.46 (m, 3H), 7.38 – 7.25 (m, 10H), 6.70 (d, J = 16.0 Hz, 1H), 6.34 (dt, J = 15.9, 5.7 Hz, 1H), 5.51 (s, 2H), 4.85 (d, J = 5.7 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  167.9, 153.6, 136.3, 135.8, 133.0, 131.6, 131.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 126.6, 124.2, 124.1, 123.8, 118.2, 114.7, 70.3, 67.1; HRMS (ESI+) *m/z* calcd. for C<sub>27</sub>H<sub>22</sub>NaO<sub>3</sub>: 417.1461; found: 417.1454.

#### Methyl 2-(cinnamyloxy)-6-(p-tolyl)-1-naphthoate (1q):



**1q** was isolated by FC on silica gel using pentane/EtOAc 30:1; 83% yield; white solid; IR (film) 1722, 1499, 1290, 1248, 813 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, *J* = 1.6 Hz, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.77 (dd, *J* =

8.8, 1.6 Hz, 1H), 7.60 – 7.59 (m, 2H), 7.42 – 7.40 (m, 2H), 7.37 – 7.31 (m, 3H), 7.30 – 7.26 (m, 3H), 6.76 (d, J = 16.0 Hz, 1H), 6.42 (dt, J = 16.0, 5.5 Hz, 1H), 4.90 (dd, J = 5.5, 1.4 Hz, 3H), 4.06 (s, 3H), 2.42 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.6, 137.6, 137.1, 136.9, 136.3, 132.7, 131.8, 130.0, 129.6, 129.0, 128.5, 127.9, 127.2, 127.0, 126.5, 125.4, 124.4, 124.2, 118.2, 115.2, 70.3, 52.4, 21.1; HRMS (ESI+) *m*/*z* calcd. for C<sub>28</sub>H<sub>24</sub>NaO<sub>3</sub>: 431.1618; found: 431.1612.

## Methyl 2-(cinnamyloxy)-6-(phenylethynyl)-1-naphthoate (1r):

**1r** was isolated by FC on silica gel using pentane/EtOAc 30:1; 83% yield; white solid; m.p. = 126.6 °C; IR (film) 2951, 1728, 1597, 1282, 1250, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (s,



1H), 7.86 (d, J = 9.1 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.41 – 7.26 (m, 9H), 6.75 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 16.0, 5.6 Hz, 1H), 4.90 (dd, J = 5.5, 1.2 Hz, 2H), 4.05 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.1, 154.3, 136.2, 132.9,

131.6, 131.5, 130.4, 130.1, 128.6, 128.3, 127.9, 126.5, 124.0, 123.2, 119.0, 118.3, 115.3, 89.8, 89.4, 70.2, 52.5; HRMS (ESI+) *m/z* calcd. for C<sub>29</sub>H<sub>22</sub>NaO<sub>3</sub>: 441.1461; found: 441.1458.

## Methyl 2-[(3,4-dimethoxybenzyl)oxy]-1-naphthoate (1s):



**1s** was isolated by FC on silica gel using pentane/EtOAc 15:1; 78% yield; yellow viscous liquid; IR (neat) 2950, 2835, 1727, 1514, 1238, 1138, 1028, 811 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (d, *J* = 9.1

Hz, 1H), 7.76 (t, J = 8.4 Hz, 2H), 7.49 (t, J = 8.1 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 9.1 Hz, 1H), 7.02 (d, J = 1.7 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 5.19 (s, 2H), 4.00 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.5, 149.0, 148.7, 131.4, 130.9, 129.2, 128.7, 128.0, 127.5, 124.3, 123.7, 119.6, 118.5, 114.9, 110.8, 110.4, 71.4, 55.8, 55.7, 52.3; HRMS (ESI+) *m*/*z* calcd. for C<sub>21</sub>H<sub>20</sub>NaO<sub>5</sub>: 375.1203; found: 375.1199.

#### Methyl 2-[(4-methoxybenzyl)oxy]-1-naphthoate (1t):

OMe



1t was isolated by FC on silica gel using pentane/EtOAc 30:1; 81% yield; yellow solid; m.p. = 79.2 °C; IR (film) 2951, 1728, 1513, 1284, 1245, 812 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.80 (d, J = 9.1 Hz,

1H), 7.76 – 7.74 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.36 – 7.32 (m, 3H), 7.24 (d, J = 9.1 Hz, 1H), 6.88 (d, J = 8.6 Hz, 2H), 5.15 (s, 2H), 3.98 (s, 3H), 3.76 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 159.3, 153.6, 131.4, 130.9, 128.7, 128.6, 128.0, 127.5, 124.2, 123.8, 118.5, 115.0, 113.8, 71.3, 55.2, 52.3; HRMS (ESI+) m/z calcd. for C<sub>20</sub>H<sub>18</sub>NaO<sub>4</sub>: 345.1097; found: 345.1095.

#### Methyl 2-(benzo[d][1,3]dioxol-5-ylmethoxy)-1-naphthoate (1u):

**Lu** was isolated by FC on silica gel using pentane/EtOAc 20:1; 85% yield; yellow viscous liquid; IR (neat) 2950, 1727, 1504, 1445, 1244, 1038, 810 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 6.93 (s, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 5.93 (s, 2H), 5.12 (s, 2H), 4.01 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 153.4, 147.8, 147.3, 131.5, 130.9, 130.5, 128.7, 128.0, 127.6, 124.3, 123.8, 120.8, 118.5, 114.9, 108.1, 107.9, 101.0, 71.5, 52.3; HRMS (ESI+) *m/z* calcd. for C<sub>20</sub>H<sub>16</sub>NaO<sub>5</sub>: 359.0890; found: 359.0884.

## Methyl (*E*)-2-[(2-methyl-3-phenylallyl)oxy]-1-naphthoate (1v):

1v was isolated by FC on silica gel using pentane/EtOAc 30:1; 83% yield; white solid; m.p. = 87.7 °C; IR (film) 2949, 1729, 1510, 1284, 1234, 1136, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

 $\begin{array}{c} & \delta 7.89 \ (d, J = 9.0 \ Hz, 1H), \ 7.80 \ (d, J = 8.2 \ Hz, 1H), \ 7.77 \ (d, J = 8.5 \ Hz, \\ & 1H), \ 7.52 - 7.49 \ (m, 1H), \ 7.40 - 7.28 \ (m, 6H), \ 7.25 - 7.22 \ (m, 1H), \ 6.66 \\ & (s, 1H), \ 4.75 \ (s, 2H), \ 4.04 \ (s, 3H), \ 1.98 \ (s, 3H); \ ^{13}C \ NMR \ (125 \ MHz, \\ CDCl_3) \ \delta \ 168.4, \ 153.6, \ 137.1, \ 133.4, \ 131.5, \ 131.0, \ 128.9, \ 128.6, \ 128.1, \ 128.0, \ 127.5, \ 127.5, \ 126.6, \\ 124.2, \ 123.8, \ 118.2, \ 114.6, \ 75.2, \ 52.3, \ 15.12; \ HRMS \ (ESI+) \ m/z \ calcd. \ for \ C_{22}H_{20}NaO_3; \ 335.1305; \\ found: \ 335.1300. \end{array}$ 



1-allylnaphthalen-2-ol<sup>3</sup> and 1-phenylnaphthalen-2-ol<sup>4</sup> were synthesized according to the literature. 3a and 3b were synthesized base on the literature<sup>5</sup> with a little modification, the modified procedure was shown as bellow.

To a solution of MOMO protected 1-allylnaphthalen-2-ol or 1-phenylnaphthalen-2-ol (5.00 mmol) in Et2O (20.0 mL) was added n-BuLi (6.25 mL, 10.0 mmol, 1.6M in hexane) at 0 oC. The reaction mixture was allowed to room temperature. After stirring for 1 h at room temperature, the reaction was quenched by dry ice (ca. 1 g) slowly, and then solvents were removed in vacuo. To the residue in Acetone (50.0mL) were added iodomethane (0.778 mL, 10.0 mmol) and Cs2CO3 (4.4 g, 12.5 mmol) at room temperature. After stirring for 2 h at 40 oC, the resulting mixture was poured into water and the aqueous layers were extracted with EtOAc (twice). The combined organic layers were washed with brine and dried over anhydrous MgSO4, then the solvents were removed in vacuo .The residue was purified by flash column chromatography on silica gel to give the corresponding ester.

To a solution of the corresponding ester intermidiate in MeOH (0.2 M) was added conc. HCl aq. (a few drops). The reaction mixture was warmed to 50 °C. After stirring for 2 h, water was added to the resulting mixture, and the aqueous layers were extracted with EtOAc. The combined organic layers were washed with brine and dried over anhydrous MgSO4, then the solvents were removed

in vacuo. The residue was directly used in next step without further purification.

Then **3a** and **3b** could be synthesized by using the same procedure for the synthesis of methyl 2-allyloxy- and 2-Benzyloxy-1-naphthoates as we mentioned at the beginning of part 3.

#### Methyl (*E*)-4-phenyl-3-((3-(thiophen-3-yl)allyl)oxy)-2-naphthoate (3a):



**3a** was isolated as yellow solid by FC on silica gel using pentane/EtOAc 30:1; 64% yield; yellow solid; m.p. = 75.3 °C; IR (neat) 2948, 1728, 1446, 1301, 1211, 965, 754 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 (s, 1H), 7.90 (dd, J = 6.5, 2.8 Hz, 1H), 7.58 – 7.43 (m,

8H), 7.21 (dd, J = 4.9, 3.0 Hz, 1H), 7.07 (d, J = 5.0 Hz, 1H), 7.03 (d, J = 2.6 Hz, 1H), 6.27 (d, J = 15.8 Hz, 1H), 5.79 (dt, J = 15.7, 6.4 Hz, 1H), 4.29 (d, J = 6.4 Hz, 2H), 3.97 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  166.9, 151.8, 139.2, 135.6, 135.2, 133.1, 132.2, 131.1, 129.7, 128.9, 128.2, 128.1, 127.5, 127.2, 125.8, 125.5, 125.2, 125.1, 124.7, 122.4, 75.3, 52.4.; HRMS (ESI+) *m/z* calcd. for C<sub>25</sub>H<sub>20</sub>NaO<sub>3</sub>S: 423.1025; found: 423.1017.

#### Methyl (*E*)-4-allyl-3-((3-(thiophen-3-yl)allyl)oxy)-2-naphthoate (3b):



**3b** was isolated as yellow viscous liquid by FC on silica gel using pentane/EtOAc 30:1; 42% yield; yellow viscous liquid; IR (neat) 2948, 1726, 1446, 1219, 1159, 964, 752 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.57 (t,

J = 7.6 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.20 (s, 1H), 6.74 (d, J = 15.8 Hz, 1H), 6.36 (dt, J = 15.8, 6.1 Hz, 1H), 6.10 (ddd, J = 22.6, 10.6, 5.6 Hz, 1H), 5.07 (d, J = 10.2 Hz, 1H), 4.97 (d, J = 17.2 Hz, 1H), 4.62 (d, J = 6.1 Hz, 2H), 3.96 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  167.0, 152.4, 139.3, 136.7, 135.0, 131.9, 129.9, 129.5, 128.6, 128.2, 127.2, 126.0, 125.3, 125.1, 124.8, 124.6, 124.5, 122.7, 116.0, 75.9, 52.4, 29.8; HRMS (ESI+) m/z calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>S: 387.1025; found: 387.1029.

# 4. General Procedure for Catalytic Asymmetric [1,3] Rearrangement of Methyl 2-Allyloxy- and 2-Benzyloxy-1-naphthoates

L8 (0.0165 mmol) and  $Cu(OTf)_2$  (0.015 mmol) were stirred in 0.4 mL of DCM at room tempertaure for 0.5 h, then the reaction system was cooled to specific temperature. Naphthyl ethers 1 (0.15 mmol) was dissolved in 0.35 mL DCM and added to the system. The mixture was stirred at the same temperature until reaction completed. Then the solvent was removed, and the residue was purified by flash chromatography on silica gel (products 2s, 2t, 2u, 4a and 4b were purified using diol silica gel) to give the product 2, which was then directly analyzed by HPLC to determine the enantiomeric excess.

#### 5. Prospect for Appropriate Substrate and Optimization of the Reaction Conditions

As shown in Scheme S1, compounds 1 are appropriate substrates for the [1,3] rearrangement. 1-Methoxycarbonyl moiety of 1 was important for chelation with Cu(OTf)<sub>2</sub>. 3-Aryl substituent on the allyl moiety of 1 was also important for [1,3] rearrangement because of the stability of the tight ion-pair transition state. Secondary allylic ether 1F was decomposed to 2-hydroxy-1-naphthoate without giving 2F under the same conditions.



Scheme S1: Prospect for appropriate substrastes<sup>a</sup>

<sup>a</sup>All reactions were carried out with 0.15 mmol of 1 in 0.75 mL of DCM.

#### Table S1: Ligand screening<sup>a</sup>



<sup>a</sup>All reactions were carried out with 0.15 mmol of **1a** in 0.75 mL of DCM. <sup>b</sup>Based on NMR. <sup>c</sup>Determined by HPLC analysis. <sup>d</sup>The reaction was carried out at 30 °C.

As shown in Table S2, dichloromethane was the best solvent. 1,2-Dichloroethane was also available. However, Et<sub>2</sub>O reduced the reactivity and the ee value. More polar solvents like ethers, esters and methanol were less effective because Lewis acidity of the catalyst was seriously decreased in polar solvents. In addition, the rearrangement did not occur in less polar toluene even at 30 °C. Judging from these experimental results, polarity of halogenated solvents may be effective to stabilize the tight ion pair transition state. Moreover, available solvents are also limited due to the solubility of ligands and substrates.

It was noted that this rearrangement more cleanly occurred in the presence of  $Cu(OTf)_2 \cdot L11$  or  $Cu(OTf)_2 \cdot L8$ , although  $Cu(OTf)_2$  was active for this rearrangement (cf. Scheme S1). Moreover, L11 was inferior to L8 with regard to the enantioselectivity, regioselectivity (2a:2a') and catalytic activity, probably due to some undesired steric hindrance of  $Cu(OTf)_2 \cdot L11$  (cf. Table 1).

Table S2: Solvent effect<sup>a</sup>



solvent. <sup>b</sup>Based on NMR. <sup>c</sup>Determined by HPLC analysis.

## 6. Spectral Characterization Data for the Products

#### Methyl (S)-1-cinnamyl-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2a):

Ph Yield (90%); colorless viscous liquid; IR (neat) 3026, 2950, 1742, 1663, 1222, 746 cm<sup>-1</sup>;  $[\alpha]^{26}_{D} = +111.9$  (*c* 1.50, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 - 7.43 (m, 2H), 7.38 - 7.34 (m, 3H), 7.20 - 7.17 (m, 2H), 7.16 - 7.14 (m, 1H), 7.09 - 7.07 (m, 2H), 6.20 - 6.17 (m, 2H), 5.68 - 5 .62 (m, 1H), 3.65 (s, 3H), 3.28 (ddd, *J* = 13.6, 8.1, 1.0 Hz, 1H), 3.14 (ddd, *J* = 13.6, 7.0, 1.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.4, 170.9, 146.0, 139.2, 136.9, 134.0, 130.4, 129.7, 129.5, 128.2, 128.1, 127.2, 126.9, 126.0, 125.2, 122.1, 62.6, 52.9, 43.9; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>18</sub>NaO<sub>3</sub>: 341.1148; found: 341.1154; The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm); *t*<sub>r</sub> = 6.83 and 8.65 min.

#### Methyl (*S*,*E*)-2-oxo-1-[3-(*o*-tolyl)allyl]-1,2-dihydronaphthalene-1-carboxylate (2b):



Yield (90%); colorless viscous liquid;  $[\alpha]^{28}{}_{D} = +76.2$  (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3023, 2952, 1742, 1663, 1222, 967, 750 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.46-7.43 (m, 2H), 7.39 – 7.32 (m, 3H), 7.05 – 7.00 (d, *J* = 25.3 Hz, 4H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.19 (d, *J* = 9.9 Hz, 1H), 5.51 (dt, *J* =

L11

15.4, 7.6 Hz, 1H), 3.64 (s, 3H), 3.32 (dd, J = 13.5, 7.8 Hz, 1H), 3.17 (dd, J = 13.5, 7.4 Hz, 1H), 2.06 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.4, 170.9, 146.1, 139.3, 136.3, 135.1, 132.5, 130.4, 129.9, 129.7, 129.6, 128.1, 127.2, 127.0, 125.8, 125.6, 125.3, 123.7, 62.8, 52.9, 44.2, 19.5; HRMS

(ESI+) m/z calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1305; found: 355.1306; The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 272 nm);  $t_r$  = 6.24 and 6.74 min.

#### Methyl (*S*,*E*)-2-oxo-1-[3-(*m*-tolyl)allyl]-1,2-dihydronaphthalene-1-carboxylate (2c):



Yield (91%); colorless viscous liquid;  $[\alpha]^{28}_{D} = +93.8$  (*c* 0.83, CHCl<sub>3</sub>); IR (neat) 3024, 2951, 1743, 1663, 1223, 764 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 – 7.42 (m, 2H), 7.38 – 7.33 (m, 3H), 7.09 – 7.06 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.90 – 6.98 (m, 2H), 6.19 (d, *J* = 9.9 Hz, 1H), 6.14 (d, *J* = 15.7

Hz, 1H), 5.64 (dt, J = 15.4, 7.6 Hz, 1H), 3.64 (s, 3H), 3.28 (dd, J = 13.6, 8.1 Hz, 1H), 3.13 (dd, J = 13.6, 7.1 Hz, 1H), 2.25 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.4, 171.0, 146.0, 139.3, 137.8, 136.9, 134.2, 130.4, 129.7, 129.6, 128.2, 128.1, 128.0, 127.0, 126.9, 125.3, 123.1, 122.0, 62.8, 52.9, 44.0, 21.2; HRMS (ESI+) *m*/*z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1305; found: 355.1301. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_{\rm r} = 6.56$  and 8.02 min.

#### Methyl (*S*,*E*)-2-oxo-1-[3-(*p*-tolyl)allyl]-1,2-dihydronaphthalene-1-carboxylate (2d):



Yield (87%); colorless viscous liquid;  $[\alpha]^{28}{}_{D}$  = +93.1 (*c* 0.85, CHCl<sub>3</sub>); IR (neat) 3034, 2951, 1742, 1664, 1223, 764 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 – 7.41 (m, 2H), 7.36 – 7.31 (m, 3H), 7.00 – 6.96 (m, 4H), 6.17 (d, *J* = 9.9 Hz, 1H), 6.14 (d, *J* = 15.8 Hz, 1H), 5.60 (dt, *J* = 15.5, 7.6

Hz, 1H), 3.63 (s, 3H), 3.27 (dd, J = 13.5, 8.1 Hz, 1H), 3.13 (dd, J = 13.5, 7.0 Hz, 1H), 2.25 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.5, 171.0, 146.0, 139.3, 137.0, 134.2, 133.9, 130.3, 129.7, 129.6 129.0, 128.0, 126.9, 125.9, 125.3, 121.1, 62.8, 52.9, 44.0, 21.0; HRMS (ESI+) *m/z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1305; found: 355.1306. The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$ = 254 nm); *t*<sub>r</sub> = 6.67 and 10.29 min.

## Methyl (*S*,*E*)-1-[3-(4-bromophenyl)allyl]-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2e):



Yield (76%); yellow viscous liquid;  $[\alpha]^{29}{}_{D}$  = +98.1 (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3026, 2951, 1742, 1663, 1487, 1223, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 – 7.43 (m, 2H), 7.38 – 7.33 (m, 3H), 7.30 – 7.29 (m, 2H), 6.94 – 6.93 (m, 2H), 6.18 (d, *J* = 9.9 Hz, 1H), 6.11 (d, *J* = 15.7

Hz, 1H), 5.69 – 5.62 (m, 1H), 3.64 (s, 3H), <sup>1</sup>H 3.27 (ddd, J = 13.6, 8.1, 0.9 Hz, 1H), 3.11 (ddd, J = 13.6, 7.0, 1.2 Hz, 1H)); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.2, 170.8, 146.0, 139.1, 135.8, 132.9, 131.4, 130.4, 129.8, 129.5, 128.2, 127.6, 126.9, 125.2, 123.2, 121.0, 62.6, 52.9, 43.8; HRMS (ESI+) m/z calcd. for C<sub>21</sub>H<sub>17</sub>BrNaO<sub>3</sub>: 419.0253; found: 419.0251. The product was analyzed by HPLC to

determine the enantiomeric excess: 91% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 8.05$  and 11.36 min.

## Methyl (*S*,*E*)-1-[3-(4-chlorophenyl)allyl]-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2f):



Yield (78%); colorless viscous liquid;  $[\alpha]^{29}{}_{D} = +113.7$  (*c* 0.83, CHCl<sub>3</sub>); IR (neat) 3038, 2952, 1742, 1663, 1224, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 – 7.43 (m, 2H), 7.38 – 7.34 (m, 3H), 7.15 – 7.13 (m, 2H), 7.01 – 6.99 (m, 2H), 6.18 (d, *J* = 9.9 Hz, 1H), 6.13 (d, *J* = 15.8 Hz, 1H),

5.67-5.61 (m, 1H), 3.64 (s, 3H), 3.27 (ddd, J = 13.6, 8.1, 1.0 Hz, 1H), 3.11 (ddd, J = 13.6, 7.0, 1.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.3, 170.8, 146.0, 139.2, 135.4, 132.9, 130.4, 129.8, 129.5, 128.5, 128.2, 127.2, 126.9, 125.3, 123.1, 62.7, 52.9, 43.8; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>ClNaO<sub>3</sub>: 375.0758; found: 375.0760. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm); *t*<sub>r</sub> = 7.78 and 10.73 min.

#### Methyl (*S*,*E*)-1-[3-(naphthalen-1-yl)allyl]-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2g):



Yield (95%); colorless viscous liquid;  $[\alpha]^{30}_{D} = +40.5$  (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3038, 2951, 1742, 1662, 1224, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 - 7.75 (m, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.50 - 7.47 (m, 1H), 7.44 - 7.29 (m, 7H), 7.20 (d, *J* = 7.1 Hz, 1H), 6.85 (d, *J* 

= 15.5 Hz, 1H), 6.21 (d, J = 9.9 Hz, 1H), 5.66 (dt, J = 15.3, 7.6 Hz, 1H), 3.67 (s, 3H), 3.42 (dd, J = 13.4, 7.8 Hz, 1H), 3.26 (dd, J = 13.4, 7.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.5, 170.9, 146.1, 139.4, 135.0, 133.3, 132.1, 130.9, 130.5, 129.8, 129.7, 128.2, 128.1, 127.6, 127.0, 125.8, 125.6, 125.5, 125.4, 125.3, 123.9, 123.7, 62.8, 53.0, 44.3; HRMS (ESI+) *m/z* calcd. for C<sub>25</sub>H<sub>20</sub>NaO<sub>3</sub>: 391.1305; found: 391.1310. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm); *t*<sub>r</sub> = 7.60 and 8.35 min.

## Methyl (*S*,*E*)-1-[3-(naphthalen-2-yl)allyl]-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2h):



Yield (86%); colorless viscous liquid;  $[\alpha]^{20}{}_{D} = +120.0$  (*c* 0.85, CHCl<sub>3</sub>); IR (neat) 3022, 2951, 1742, 1662, 1224, 757 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 – 7.68 (m, 2H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.46 – 7.31 (m, 8H), 7.26 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.19 (d, *J* 

= 9.9 Hz, 1H), 5.79 (dt, J = 15.4, 7.6 Hz, 1H), 3.64 (s, 3H), 3.34 (dd, J = 13.6, 8.1 Hz, 1H), 3.18 (dd, J = 13.6, 7.1 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.4, 171.0, 146.0, 139.3, 134.4, 134.2, 133.4, 132.7, 130.4, 129.8, 129.6, 128.1, 127.9, 127.8, 127.5, 127.0, 126.1, 125.8, 125.7, 125.3, 123.4, 122.7, 62.8, 52.9, 44.11; HRMS (ESI+) m/z calcd. for C<sub>25</sub>H<sub>20</sub>NaO<sub>3</sub>: 391.1305; found:

391.1303. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm);  $t_r$  = 8.77 and 13.43 min.

#### Methyl (*S*,*E*)-1-[3-(furan-3-yl)allyl]-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2i):



Yield (63%); colorless viscous liquid;  $[\alpha]^{27}{}_{D} = +59.4$  (*c* 0.95, CHCl<sub>3</sub>); IR (neat) 3026, 1742, 1661, 1225, 759 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.46 - 7.42 (m, 2H), 7.38 - 7.34 (m, 3H), 7.23 - 7.19 (m, 2H), 6.22 (d, J =1.6 Hz, 1H), 6.19 (d, J = 9.9 Hz, 1H), 6.03 (d, J = 15.7 Hz, 1H), 5.40 -

5.34 (m, 1H), 3.64 (s, 3H), 3.23 (ddd, J = 13.6, 8.2, 0.9 Hz, 1H), 3.08 (ddd, J = 13.6, 7.0, 1.2 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.4, 171.0, 146.0, 143.1, 140.0, 139.3, 130.4, 129.7, 129.6, 128.1, 127.0, 125.4, 123.8, 121.8, 107.4, 62.8, 52.9, 43.8; HRMS (ESI+) *m*/*z* calcd. for C<sub>19</sub>H<sub>16</sub>NaO<sub>4</sub>: 331.0941; found: 331.0950. The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm); *t*<sub>r</sub> = 7.69 and 10.62 min.

#### Methyl (*S*,*E*)-2-oxo-1-[3-(thiophen-3-yl)allyl]-1,2-dihydronaphthalene-1-carboxylate (2j):



Yield (85%); colorless liquid;  $[\alpha]^{27}{}_{\rm D}$  = +107.1 (*c* 1.14, CHCl<sub>3</sub>); IR (neat) 2959, 1741, 1661, 1224, 765 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 – 7.42 (m, 2H), 7.38 – 7.34 (m, 3H), 7.13 – 7.11 (m, 1H), 6.90 – 6.89 (m, 2H), 6.20 – 6.17 (m, 2H), 5.53–5.47 (m, 1H), 3.63 (s, 3H), 3.25 (dd, *J* = 13.6, 8.2 Hz,

1H), 3.10 (ddd, J = 13.6, 7.0, 1.1 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.4, 170.9, 146.0, 139.6, 139.3, 130.4, 129.7, 129.6, 128.3, 128.1, 126.9, 125.6, 125.3, 124.9, 122.1, 121.5, 62.7, 52.9, 43.8; HRMS (ESI+) *m*/*z* calcd. for C<sub>19</sub>H<sub>16</sub>NaO<sub>3</sub>S: 347.0712; found: 347.0720. The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 8.48$  and 13.16 min.

#### Methyl (*S*,*E*)-2-oxo-1-[3-phenylbut-2-en-1-yl]-1,2-dihydronaphthalene-1-carboxylate (2k):



Yield (92%); colorless viscous liquid;  $[\alpha]^{28}{}_{\rm D}$  = +81.0 (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3022, 2951, 1743, 1663, 1224, 760 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (d, *J* = 9.9 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.36 – 7.34 (m, 3H), 7.21 – 7.13 (m, 3H), 7.08 – 7.06 (m, 2H), 6.22 (d, *J* = 9.9 Hz, 1H), 5.25 – 5.20 (m, 1H), 3.65 (s, 3H),

3.34 (dd, J = 14.2, 8.2 Hz, 1H), 3.14 (dd, J = 14.2, 7.2 Hz, 1H), 1.77 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.6, 171.2, 146.0, 143.6, 139.5, 138.9, 130.3, 129.7, 128.1, 128.0, 127.7, 127.1, 126.7, 125.7, 125.3, 119.9, 62.6, 52.9, 39.7, 16.0; HRMS (ESI+) *m*/*z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1310; found: 355.12306. The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm); *t*<sub>r</sub> = 6.67 and

9.22 min.

## Methyl (S)-1-[3,3-bis(4-chlorophenyl)allyl]-2-oxo-1,2-dihydronaphthalene-1-carboxylate (21):



Yield (89%); white solid; m.p. = 99.5 °C;  $[\alpha]^{24}{}_{D}$  = +109.16 (*c* 0.85, CHCl<sub>3</sub>); IR (neat) 3027, 2952, 1743, 1664, 1490, 1224, 1092, 830, 759 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 (d, *J* = 9.9 Hz, 1H), 7.40–7.30 (m, 3H), 7.27 – 7.25 (m, 2H), 7.13 – 7.12 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.27 (d, *J* = 9.9 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.65 (t, *J* = 7.6 Hz, 1H), 5.65 (t, J = 7.6 Hz

1H), 3.03 (dd, J = 14.3, 8.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.1, 170.8, 146.2, 143.0, 140.2, 139.1, 137.0, 133.2, 133.2, 131.0, 130.6, 129.7, 129.4, 128.5, 128.4, 128.2, 128.2, 127.1, 125.2, 122.5, 62.5, 53.0, 40.2; HRMS (ESI+) m/z calcd. for C<sub>27</sub>H<sub>20</sub>Cl<sub>2</sub>NaO<sub>3</sub>: 485.0682; found: 485.0678. The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak AD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 8.02$  and 10.86 min.

#### Methyl (S)-1-(3-methylbut-2-en-1-yl)-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2m):



14.1, 8.1 Hz, 1H), 2.91 (dd, J = 14.1, 7.0 Hz, 1H), 1.47 (s, 3H), 1.35 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.8, 171.3, 145.8, 139.7, 135.9, 130.2, 129.7, 129.5, 127.8, 127.0, 125.4, 116.2, 62.6, 52.8, 39.2, 25.6, 17.7; HRMS (ESI+) *m*/*z* calcd. for C<sub>17</sub>H<sub>18</sub>NaO<sub>3</sub>: 293.1148; found: 293.1152. The product was analyzed by HPLC to determine the enantiomeric excess: 68% ee (Chiralpak AS-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 290 nm); *t*<sub>r</sub> = 5.63 and 6.08 min.

## Methyl (S)-6-bromo-1-cinnamyl-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2n):

Ph Yield (95%); yellow viscous liquid;  $[\alpha]^{26}{}_{D} = +115.7$  (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3027, 2950, 1743, 1667, 1224, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (dd, J = 8.3, 1.8 Hz, 1H), 7.49 (d, J = 1.6 Hz, 1H), 7.36 (d, J = 9.9 Hz, 1H), 7.25 - 7.14 (m, 4H), 7.11 - 7.09 (m, 2H), 6.23 - 6.19 (m, 2H), 5.64 (dt, J = 15.4, 7.6 Hz, 1H), 3.64 (s, 3H), 3.28 (dd, J = 13.6, 8.2 Hz, 1H), 3.11 (dd, J = 13.6, 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  196.7, 170.4, 144.3, 137.8, 136.7, 134.4, 133.1, 132.2, 131.4, 128.6, 128.3, 127.4, 126.4, 126.1, 121.9, 121.7, 62.4, 53.1, 43.6; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>BrNaO<sub>3</sub>: 419.0253; found: 419.0251. The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 7.32$  and 9.04 min.

## Methyl (S)-3-bromo-1-cinnamyl-2-oxo-1,2-dihydronaphthalene-1-carboxylate (20):

MeO<sub>2</sub>C, Ph Yield (95%); yellow viscous liquid;  $[\alpha]^{27}_{D} = +0.9$  (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3027, 2952, 1745, 1675, 1229, 748 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 (s, Br 20 1H), 7.48 – 7.45 (m, 1H), 7.38 – 7.35 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.12 (m, 3H), 7.09–7.07 (m, 2H), 6.19 (d, *J* = 15.7 Hz, 1H), 5.60 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.63 (s, 3H), 3.31 (dd, *J* = 13.6, 8.1 Hz, 1H), 3.15 (ddd, *J* = 13.5, 7.1, 0.7 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 190.4, 170.2, 147.3, 138.6, 136.8, 134.7, 130.7, 130.0, 129.3, 128.4, 128.3, 127.4, 126.9, 126.1, 121.5, 121.4, 64.1, 53.1, 44.3; HRMS (ESI+) *m/z* calcd. for C<sub>21</sub>H<sub>17</sub>BrNaO<sub>3</sub>: 419.0253; found: 419.0253. The product was analyzed by HPLC to determine the enantiomeric excess: 81% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm); *t*<sub>r</sub> = 7.91 and 16.81 min.

## Benzyl (S)-1-cinnamyl-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2p):

Ph Yield (82%); colorless viscous liquid;  $[\alpha]^{28}{}_{D} = +32.5$  (*c* 0.85, CHCl<sub>3</sub>); IR (neat) 3029, 1742, 1663, 1214, 744 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d, J =9.9 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.29 – 7.24 (m, 4H), 7.20 – 7.12 (m, 3H), 7.08 – 7.07 (m, 4H), 6.20 – 6.17 (m, 2H), 5.69 – 5.63 (m, 1H), 5.14 – 5.08 (m, 2H), 3.31 (dd, J = 13.6, 8.1 Hz, 1H), 3.14 (dd, J = 13.7, 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.3, 170.1, 146.0, 139.1, 137.0, 135.4, 134.1, 130.3, 129.7, 129.6, 128.3, 128.1, 127.9, 127.4, 127.2, 127.0, 126.1, 125.3, 122.3, 67.1, 62.9, 43.7; HRMS (ESI+) *m/z* calcd. for C<sub>27</sub>H<sub>22</sub>NaO<sub>3</sub>: 417.1461; found: 417.1462. The product was analyzed by HPLC to determine the enantiomeric excess: 89% ee (Chiralpak AD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 13.4$  and 15.15 min.

#### Methyl (S)-1-cinnamyl-2-oxo-6-(p-tolyl)-1,2-dihydronaphthalene-1-carboxylate (2q):



Yield (95%); colorless viscous liquid;  $[\alpha]^{31}_{D} = +120.4$  (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3034, 2951, 1742, 1665, 1234, 815, 751 cm<sup>-1</sup>;<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.54 - 7.49 (m, 4H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.28 - 7.27 (m, 2H), 7.19 - 7.09 (m, 5H),

6.25 – 6.21 (m, 2H), 5.70 (dt, J = 15.3, 7.5 Hz, 1H), 3.66 (s, 3H), 3.31 (dd, J = 13.6, 8.2 Hz, 1H), 3.18 (dd, J = 13.6, 6.9 Hz, 1H), 2.41 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.4, 170.9, 146.0, 141.0, 137.8, 137.6, 137.0, 136.6, 134.1, 130.0, 129.6, 128.7, 128.3, 128.0, 127.4, 127.2, 126.8, 126.1, 125.6, 122.3, 62.5, 52.9, 43.8, 21.1; HRMS (ESI+) m/z calcd. for C<sub>28</sub>H<sub>24</sub>NaO<sub>3</sub>: 431.1618; found: 431.1611. The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 8.93$  and 9.76 min.

#### Methyl (S)-1-cinnamyl-2-oxo-6-(phenylethynyl)-1,2-dihydronaphthalene-1-carboxylate (2r):



Yield (94%); colorless viscous liquid;  $[\alpha]^{30}{}_{D}$  = +226.6 (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3027, 2947, 1743, 1666, 1222, 757 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.41 (d, *J* = 9.9 Hz, 1H), 7.36 – 7.34 (m, 4H), 7.20 – 7.15 (m, 2H), 7.15 – 7.09 (m,

3H), 6.23 – 6.20 (m, 2H), 5.66 (dt, J = 15.5, 7.6 Hz, 1H), 3.64 (s, 3H), 3.30 (dd, J = 13.6, 8.2 Hz, 1H), 3.15 (dd, J = 13.6, 7.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  196.9, 170.6, 145.1, 138.9, 136.8, 134.3, 133.1, 132.5, 131.6, 129.8, 128.6, 128.4, 128.3, 127.3, 127.1, 126.1, 126.0, 123.4, 122.6, 121.9, 90.8, 87.9, 62.7, 53.0, 43.7; HRMS (ESI+) *m*/*z* calcd. for C<sub>29</sub>H<sub>22</sub>NaO<sub>3</sub>: 441.1461; found: 441.1454. The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak IA-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm);  $t_r = 8.71$  and 9.98 min.

#### Methyl (S)-1-(3,4-dimethoxybenzyl)-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2s):



Yield (96%); light yellow solid; m.p. = 140.1 °C;  $[\alpha]^{25}{}_{D}$  = +96.1 (*c* 0.61, CHCl<sub>3</sub>); IR (neat) 2953, 2841, 1742, 1661, 1516, 1236, 1028, 763 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.50–7.44 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 9.9 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H),

6.25 (dd, J = 8.2, 1.9 Hz, 1H), 5.93–5.91 (m, 2H), 3.74 (s, 3H), 3.68 (d, J = 13.5 Hz, 1H), 3.66 (s, 3H), 3.47 (s, 3H), 3.46 (d, J = 13.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.8, 171.1, 147.6, 145.6, 139.6, 130.1, 130.0, 129.6, 128.0, 127.2, 126.6, 125.5, 122.1, 112.5, 110.2, 63.6, 55.5, 55.3, 52.9, 46.3; HRMS (ESI+) *m*/*z* calcd. for C<sub>21</sub>H<sub>20</sub>NaO<sub>5</sub>: 375.1203; found: 375.1201. The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AS-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 300 nm);  $t_r$  = 10.79 and 18.18 min.

## Methyl (S)-1-(4-methoxybenzyl)-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2t):



Yield (92%); yellow solid; m.p. = 88.0 °C;  $[\alpha]^{25}{}_{D}$  = +87.8 (*c* 0.61, CHCl<sub>3</sub>); IR (film) 2952, 2837, 1742, 1661, 1513, 1246, 1034, 754 cm<sup>-1</sup>;<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 – 7.42 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 10.0 Hz, 1H), 6.50 – 6.46 (m, 4H), 5.93 (d, *J* 

= 10.0 Hz, 1H), 3.68 (d, *J* = 13.5 Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.46 (d, *J* = 13.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.9, 171.2, 158.3, 145.7, 139.5, 130.7, 130.1, 130.0, 129.5, 128.0, 127.2, 126.2, 125.4, 112.9, 63.6, 55.0, 52.9, 45.8; HRMS (ESI+) *m*/*z* calcd. for C<sub>20</sub>H<sub>18</sub>NaO<sub>4</sub>: 345.1097; found: 345.1094. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak AD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm); *t*<sub>r</sub>

= 8.06 and 8.99 min.

# Methyl (S)-1-(benzo[d][1,3]dioxol-5-ylmethyl)-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2u):



Yield (95%); yellow solid; m.p. = 131.3 °C;  $[\alpha]^{23}_{D}$  = +110.4 (*c* 0.61, CHCl<sub>3</sub>); IR (film) 2938, 2890, 1742, 1658, 1487, 1443, 1224, 1038, 930 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 10.0 Hz, 1H),

6.42 (d, J = 8.0 Hz, 1H), 6.07 (dd, J = 8.0, 1.7 Hz, 1H), 6.03 (d, J = 1.7 Hz, 1H), 5.97 (d, J = 10.0 Hz, 1H), 5.79 (s, 2H), 3.66 (d, J = 13.5 Hz, 1H), 3.65 (s, 3H), 3.43 (d, J = 13.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  197.7, 171.1, 146.7, 146.2, 145.7, 139.3, 130.2, 129.9, 129.6, 128.2, 127.9, 127.1, 125.4, 123.0, 110.0, 107.5, 100.6, 63.5, 52.9, 46.2; HRMS (ESI+) *m/z* calcd. for C<sub>20</sub>H<sub>16</sub>NaO<sub>5</sub>: 359.0890; found: 359.0883. The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 300$  nm);  $t_r = 9.42$  and 12.12 min.

#### Methyl (*S*,*E*)-1-(2-methyl-3-phenylallyl)-2-oxo-1,2-dihydronaphthalene-1-carboxylate (2v):

Ph Yield (71%); colorless viscous liquid;  $[\alpha]^{25}{}_{D} = +40.5$  (*c* 0.84, CHCl<sub>3</sub>); IR (neat) 3022, 2951, 1742, 1663, 1223, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.42 (m, 2H), 7.40 – 7.35 (m, 3H), 7.22 – 7.18 (m, 2H), 7.13 – 7.10 (m, 1H), 6.90 – 6.88 (m, 2H), 6.22 (d, *J* = 9.9 Hz, 1H), 5.89 (s, 1H), 3.63 (s, 3H), 3.39 (d, *J* = 13.3 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 1.36 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.8, 171.2, 145.9, 139.6, 137.7, 132.2, 130.2, 129.74, 129.72, 128.6, 128.1, 127.8, 127.4, 126.1, 125.7, 62.8, 53.0, 50.5, 19.3; HRMS (ESI+) *m/z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 335.1305; found: 335.1308. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralpak AS-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda = 254$  nm); *t*<sub>r</sub> = 6.81 and 8.00 min.

Methyl (+)-(*R*,*E*)-3-oxo-4-phenyl-4-(3-(thiophen-3-yl)allyl)-3,4-dihydronaphthalene-2carboxylate (4a):



Yield (52%); light yellow viscous liquid;  $[\alpha]^{23}{}_{D} = +61.7$  (*c* 1.20, CHCl<sub>3</sub>); IR (neat) 3020, 2949, 1734, 1216, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (s, 1H), 7.50 (t, *J* = 6.8 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.26 - 7.21 (m, 3H), 7.12 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.34 (d, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.34 (dd, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.34 (dd, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 15.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 7.7, 3.7 Hz, 2H), 6.91 (dd, *J* = 7.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.8 Hz, 1H), 5.74 - 5.52 (m, 2H), 6.91 (dd, *J* = 7.8 Hz, 1H), 7.8 (dd, J) = 7.8 Hz, 1H), 7.8 (dd, J

1H), 3.81 (s, 3H), 3.77 (dd, J = 13.9, 7.3 Hz, 1H), 3.06 (dd, J = 13.6, 7.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  196.3, 165.0, 150.5, 145.8, 141.9, 139.7, 131.9, 131.5, 129.6, 129.3, 128.6, 128.1, 127.6, 127.4, 125.7, 125.6, 124.9, 124.3, 121.3, 61.6, 52.3, 42.4; HRMS (ESI+) *m/z* calcd. for

 $C_{25}H_{20}NaO_3S$ : 423.1025; found: 423.1026; The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AS-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm); t<sub>r</sub> = 11.08 and 14.26 min. The absolute configuration of **4a** was speculated based on the proposed transition state shown in Figure 1b.

## Methyl (-)-(*S*,*E*)-4-allyl-3-oxo-4-(3-(thiophen-3-yl)allyl)-3,4-dihydronaphthalene-2carboxylate (4b):

Yield (56%); light yellow viscous liquid;  $[\alpha]^{22}_{D} = -14.3$  (*c* 1.20, CHCl<sub>3</sub>); IR (neat) 3006, 2950, 1734, 1676, 1217, 759 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 8.12 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.13 – 7.12 (m, 1H), 6.91 (d, *J* = 4.0 Hz, 2H), 6.22 (d, *J* = 15.7 Hz, 1H), 5.57 – 5.51 (m, 1H), 5.35 – 5.27 (m, 1H), 4.87 (d, *J* = 17.0 Hz, 1H), 4.82 (d, *J* = 10.2 Hz, 1H), 3.86 (s, 3H), 3.04 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.98 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.68 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.61 (dd, *J* = 13.6, 7.2 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 198.0, 165.3, 150.5, 145.2, 139.6, 132.2, 131.8, 131.6, 129.2, 127.8, 127.3, 126.3, 125.6, 124.9, 123.7, 121.3, 118.6, 57.8, 52.3, 45.5, 44.7; HRMS (ESI+) *m/z* calcd. for C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub>: 355.1310; found: 355.12306; The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralpak OD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm); t<sub>r</sub> = 9.09 and 11.97 min. The absolute configuration of **4b** was speculated based on the proposed transition state shown in Figure 1b.

## 7. Synthetic Application of 2a



To 1 mL of MeOH were added **2a** (63.6 mg, 0.2 mmol, 92% ee) and CeCl<sub>3</sub>•7H<sub>2</sub>O (1.1 mg, 0.22 mmol), then the reaction system was cooled to -78 °C. After which NaBH<sub>4</sub> (8.4 mg, 0.22 mmol) was added slowly to the solution. After stirring at -78 °C temperature for 2 h, the solvent was evaporated and the residue was purified by column chromatography to give **5** in 88% yield, which was then directly analyzed by HPLC to determine the enantiomeric excess.

## Methyl (1*S*,2*R*)-1-cinnamyl-2-hydroxy-1,2-dihydronaphthalene-1-carboxylate (5):

Yield (88%); colorless viscous liquid;  $[\alpha]^{23}{}_{D}$  = +69.0 (*c* 0.73, CHCl<sub>3</sub>); IR (neat) 3447, 3024, 2950, 1730, 1224, 967, 744 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.18 (m, 8H), 7.11 (d, *J* = 6.8 Hz,

 $\begin{array}{c} \begin{tabular}{ll} \begin{tabular}{ll}$ 

127.1, 126.8, 126.1, 70.4, 57.2, 52.4, 35.0; HRMS (ESI+) m/z calcd. for C<sub>21</sub>H<sub>20</sub>NaO<sub>3</sub>: 343.1305; found: 343.299. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-3, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min,  $\lambda$  = 254 nm);  $t_r$  = 6.78 and 8.15 min.







8. SX-ray Structure of Product (S)-2l and Cu(II) Complex



Figure S1. X-ray structure of (S)-21

Crystal data for (*S*)-**21**: C<sub>27</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>3</sub>, *T* = 123 K, Orthorhombic, space group *P212121*(#19), *a* = 7.6102(8), *b* = 10.7051(11), *c* = 27.326(3) Å, *V* = 2226.2(4) Å<sup>3</sup>, *Z* = 4,  $\lambda$ (MoK $\alpha$ )= 0.71073 Å, 4973 reflections collected, and 294 parameters were used for the solution of the structure, final *R*<sub>1</sub> = 0.0256 and *wR*<sub>2</sub> = 0.0671, GOF = -0.005(9), CCDC 1865509 contains the supplementary crystallographic data for this paper.

## a) bottom-up view



b) top view



c) side view-1



d) side view-2



Figure S2. X-ray structure of Cu(II) complex

Crystal data for Cu(II) complex: C<sub>50</sub> H<sub>64</sub> Cu F<sub>6</sub> N<sub>4</sub> O<sub>8</sub> S<sub>2</sub>, T = 123 K, orthorhombic, space group

*P212121*, a = 14.293(3), b = 16.823(3), c = 21.700(5) Å, V = 5217.8(19) Å<sup>3</sup>, Z = 4,  $\lambda$ (MoK $\alpha$ )= 0.71075 Å, 11938 reflections collected, and 648 parameters were used for the solution of the structure, final  $R_1 = 0.0834$  and  $wR_2 = 0.1397$ , GOF = 1.107, CCDC 1865510 contains the supplementary crystallographic data for this paper.

#### 9. References

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- 5. M. Uyanik, N. Sahara, K. Ishihara, Eur. J. Org. Chem., DOI: 10.1002/ejoc.201801063

## 10. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra




















S38
































































































S86





















S96



































































































H-H COSY



#### H-H NOESY



# **11. HPLC Chromatograms**



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#### Sample D Data Name ELY-6-5%cat.kd Method Name Expet(C 4-20-80-1-20m in.km Batch Nam LY-6-5%cat.kb Vial 1-21 hj Volume Acquisition Date 2018/05/28 10:13:55 分析者 System Adm inistrator Mod ified Date 2018/05/28 10:33:58 解析者 System Adm inistrator







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# === Shim adzu LabSolutions ===

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#### Sample D Data Name Method Name Batch Nam Vial hj Volume Acquisition Date Modified Date : LY-5-1b.kd :C3-80-20-1m H-20m in.km :LY-5-1b.kb :1-19 :1 uL :2017/11/01 142633 :2017/11/01 150556 サンプルタイプ :Unknown :System Administrator :System Administrator 分析者 解析者 mAU 8.016 50-25-10.860 0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 0.0 m'n PDA Ch1 254nm Peak No. (m in) 8.016 10.860 rea 881458 44399 925857 RT Height 689 A re 3003 71977 4.795 Tota UVスペクトレ 保持時間 保持時間 :10.860 m h :8.016 m h m AU 150 <u>1</u>20∳ m A U 8.0 206,01 239.80 7.0 -233**.24**0.30 222.39 6.0 -5.0 -100-219.52 4.0 50 286.00 3.0 283.18 2.0 200 210 220 230 240 250 260 270 280 290 200 210 220 230 240 250 260 270 280 290 nm n۳

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#### Sam ple D Data Nam e Method Nam e Batch Nam Vial hi Volum e Acquisition Date Modified Date : LY-5-130g-rac.kd :C3-80-20-1m H20m in.km :LY-5-130g.kb :1-18 :1 uL :2017/12/23 16:17:31 :2017/12/23 16:37:33 サンプルタイプ :Unknown 分析者 解析者 :System Administrator :System Administrator mAU 15.088 13.383 50-25 0 2.5 5.0 7.5 10.0 12.5 15.0 17.5 0.0 m'n PDA Ch1 254nm Peak No. Height 63605 56507 120112 (m in) 13.383 15.088 A rea 49.935 50.065 100.000 <u>A rea</u> 1184174 1187247 2371421 Tota UVスペクトレ 保持時間 :15.088 m h 保持時間 :13.383 m h m A U m A U 206.9 206.8 100 239.97 239.94 100 222.96 222.96 50

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#### Sam ple D Data Nam e Method Nam e Batch Nam Vial hi Volum e Acquisition Date Modified Date : LY-5-110-rac.kd :C3-80-20-1m H20m in.km :LY-5-110.kb :1-32 :1 uL :2018/02/02 1102 21 :2018/02/02 1122 24 サンプルタイプ :Unknown 分析者 解析者 ∶System Administrator ∶System Administrator mAU 6.7 29 8.050 100-75-50-7.299 9.034 25-0-2.5 5.0 7.5 10.0 12.5 15.0 0.0 17.5 m'n PDA Ch1254nm PeakNo. (m in) 6.729 7.299 8.050 9.034 A rea 41.099 9.389 40.730 A rea 1211638 276803 1200750 258889 2948081 eight 111252 23681 97013 19230 251176 8.782 100.000 4 Tota UVスペク♭レ 保持時間 保持時間 :6.729 m h :7.299 m h AU AU 40 226675 30 255.52 234.19 15 0 200 210 220 230 240 250 260 270 280 290 m A U 206.96 150 255.37 100 233.26 50 -0<sup>-1</sup> 200 210 220 230 240 250 260 270 280 290 nm nm

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