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

$^1$H NMR spectra were recorded on a JEOL ECS400 400 MHz spectrometer or a Bruker 500 MHz spectrometer in CDCl$_3$. 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). $^{13}$C NMR spectra were recorded on a JEOL ECS400 100 MHz or a Bruker 125 MHz spectrometer in CDCl$_3$. 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)$_2$ and racemic ligand as the catalyst. The absolute configuration of 2l 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$_2$SO$_4$, 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 trifluoroacetic 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$_2$SO$_4$, 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 temperature 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.

(5)-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}^{23} = -15.9 (c 1.00, CHCl3); IR (film) 3304, 2957, 2929, 2871, 1644, 1452, 1445, 760 cm^{-1}; ^1H NMR (500 MHz, CDCl3): 6 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); ^13C NMR (125 MHz, CDCl3): ^13C NMR (125 MHz, CDCl3) δ 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_{24}H_{33}N_{2}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; [α]_{22}^{22} = +59.3 (c 0.71, CHCl3); IR (neat) 2971, 2874, 1638, 1427, 764 cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ 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); ^13C NMR (100 MHz, CDCl3) δ 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_{22}H_{37}N_{2}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; [α]_{22}^{22} = +57.8 (c 0.71, CHCl3); IR (neat) 2967, 2871, 1636, 1424, 762 cm^{-1}; ^1H NMR (400 MHz, CDCl3) δ 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); 13C NMR (100 MHz, CDCl3) δ 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 C23H29N2O: 349.2274, found: 349.2265.

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

61% overall yield; white solid; m.p. = 89.8 °C; [α]26D = +74.3 (c 0.71, CHCl3); IR (film) 2956, 2871, 1637, 1492, 1422, 767 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 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); 13C NMR (125 MHz, CDCl3) δ 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 C23H30N2O: 385.2250, found: 385.2241.

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

63% overall yield; yellow viscous liquid; [α]26D = +49.8 (c 0.71, CHCl3); IR (neat) 2956, 2871, 1637, 1493, 1422, 768 cm⁻¹; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (125 MHz, CDCl3) δ 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 C24H30N2O: 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]27D = +45.6 (c 0.71, CHCl3); IR (neat) 2952, 2865, 1638, 1421, 765 cm⁻¹; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (125 MHz, CDCl3) δ 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 C25H32N2O: 399.2407, found: 399.2398.

(S)-2-[(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)amino]-N-ethylpentanamide (L6):

58% overall yield; white solid; m.p. = 115.4 °C; [α]23D = −14.6 (c 0.71, CHCl3); IR (film) 3302, 2903, 2864, 2359, 1646, 1541, 761 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 7.24 – 7.11 (m, 8H), 6.61
(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]D = −13.4 (c 0.71, CHCl3); IR (film) 3333, 3061, 2964, 2873, 2669, 1651, 1538, 1456, 761 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.22 – 7.11 (m, 8H), 6.79 (s, 1H), 4.69 (s, 1H), 3.66 (m, 2H), 3.11 – 2.98 (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); 13C NMR (125 MHz, CDCl3) δ 174.4, 130.6, 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 C23H30N2O: 373.2250, found: 373.2251.
3. General Procedure for the Synthesis of Methyl 2-Allyloxy- and 2-Benzylxylo-1-naphthoates

The starting naphthols\(^1\) (6 mmol) and Cs\(_2\)CO\(_3\) (9 mmol) were dissolved in acetone (40 mL). Cinnamyl bromide\(^2\) (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\(_2\)SO\(_4\), and concentrated under vacuum. The residue was purified by silica gel chromatography to afford corresponding product.

**Methyl 2-(cinnamylxylo)-1-naphthoate (1a):**

\[
\begin{align*}
\text{CO}_2\text{R} & \quad \text{CS}_2\text{CO}_3 \quad (1.5 \text{ equiv}) \\
\text{R}^1 & \quad \text{Br} \quad \text{Acetone, 60 °C} \\
\text{CO}_2\text{R} & \quad \text{R}^2
\end{align*}
\]

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\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, \(J = 9.1\) Hz, 1H), 7.79 (d, \(J = 8.2\) 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); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 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\(_{21}\)H\(_{18}\)NaO\(_3\): 341.1148; found: 341.1146.

**Methyl (E)-2-\{3-(o-tolyloxy)\}-1-naphthoate (1b):**

\[
\begin{align*}
\text{CO}_2\text{R} & \quad \text{CO}_2\text{R} \quad \text{Ph} \\
\text{R}^1 & \quad \text{R}^2 \quad \text{R}^1 \\
\text{CO}_2\text{R} & \quad \text{CO}_2\text{R}
\end{align*}
\]

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, 1283, 1233, 809, 747 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 9.1\) Hz, 1H), 7.79 (d, \(J = 8.2\) Hz, 1H), 7.76 (d, \(J = 8.5\) Hz, 1H), 7.52 – 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); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 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, 19.6; HRMS (ESI+) \(m/z\) calcd. for C\(_{22}\)H\(_{20}\)NaO\(_3\): 355.1305; found: 355.1298.

**Methyl (E)-2-\{3-(m-tolyloxy)\}-1-naphthoate (1c):**

\[
\begin{align*}
\text{CO}_2\text{R} & \quad \text{CO}_2\text{R} \\
\text{R}^1 & \quad \text{Ph} \\
\text{CO}_2\text{R} & \quad \text{CO}_2\text{R}
\end{align*}
\]

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\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 9.1\) Hz, 1H), 7.79 (d,
$J = 8.2 \text{ Hz, } 1H), 7.76 (d, J = 8.6 \text{ Hz, } 1H), 7.52 \text{ – } 7.48 \text{ (m, } 1H), 7.39 \text{ – } 7.36 \text{ (m, } 1H), 7.31 (d, J = 9.1 \text{ Hz, } 1H), 7.22 \text{ – } 7.20 \text{ (m, } 3H), 7.08 \text{ – } 7.06 \text{ (m, } 1H), 6.71 (d, J = 16.0 \text{ Hz, } 1H), 6.39 (dt, J = 16.0, 5.6 \text{ Hz, } 1H), 4.87 (dd, J = 5.6, 1.5 \text{ Hz, } 2H), 4.04 (s, 3H), 2.34 (s, 3H); ^{13}C \text{ NMR (125 MHz, CDCl}_3 \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; \text{ HRMS (ESI+) m/z calcd. for } C_{22}H_{20}NaO_3: 355.1305; \text{ found: 355.1303.}

**Methyl (E)-2-[[3-(p-tolyl)allyloxy]-1-naphthoate (1d):**

![Structural formula of 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⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 7.87 (d, $J = 9.1 \text{ Hz, } 1H), 7.79 (d, J = 8.2 \text{ Hz, } 1H), 7.76 (d, J = 8.5 \text{ Hz, } 1H), 7.50 (t, J = 7.6 \text{ Hz, } 1H), 7.38 (t, J = 7.5 \text{ Hz, } 1H), 7.32 \text{ – } 7.29 \text{ (m, } 3H), 7.14 \text{ – } 7.12 \text{ (m, } 2H), 6.71 (d, J = 16.0 \text{ Hz, } 1H), 6.35 (dt, J = 15.9, 5.7 \text{ Hz, } 1H), 4.87 (dd, J = 5.7, 1.4 \text{ Hz, } 2H), 4.04 (s, 3H), 2.34 (s, 3H); ^{13}C \text{ NMR (125 MHz, CDCl}_3 \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; \text{ HRMS (ESI+) m/z calcd. for } C_{22}H_{20}NaO_3: 355.1305; \text{ found: 355.1297.}

**Methyl (E)-2-[[3-(4-bromophenyl)allyloxy]-1-naphthoate (1e):**

![Structural formula of 1e]

1e 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⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 7.88 (d, $J = 9.1 \text{ Hz, } 1H), 7.80 (d, J = 8.2 \text{ Hz, } 1H), 7.76 (d, J = 8.5 \text{ Hz, } 1H), 7.51 (t, J = 8.3 \text{ Hz, } 1H), 7.45 \text{ – } 7.43 \text{ (m, } 2H), 7.39 (t, J = 8.0 \text{ Hz, } 1H), 7.29 (d, J = 9.1 \text{ Hz, } 1H), 7.27 \text{ – } 7.25 \text{ (m, } 2H), 6.68 (d, J = 16.0 \text{ Hz, } 1H), 6.39 (dt, J = 16.0, 5.4 \text{ Hz, } 1H), 4.87 (dd, J = 5.4, 1.5 \text{ Hz, } 2H), 4.04 (s, 3H); ^{13}C \text{ NMR (125 MHz, CDCl}_3 \delta 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; \text{ HRMS (ESI+) m/z calcd. for } C_{21}H_{17}BrNaO_3: 419.0253; \text{ found: 419.0244.}

**Methyl (E)-2-[[3-(4-chlorophenyl)allyloxy]-1-naphthoate (1f):**

![Structural formula of 1f]

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⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 7.89 (d, $J = 9.1 \text{ Hz, } 1H), 7.80 (d, J = 8.2 \text{ Hz, } 1H), 7.76 (d, J = 8.5 \text{ Hz, } 1H), 7.51 (t, J = 8.3 \text{ Hz, } 1H), 7.39 (t, J = 8.0 \text{ Hz, } 1H), 7.33 \text{ – } 7.28 \text{ (m, } 5H), 6.70 (d, J = 16.0 \text{ Hz, } 1H), 6.38 (dt, J = 16.0, 5.5 \text{ Hz, } 1H), 4.88 (dd, J = 5.5, 1.6 \text{ Hz, } 2H), 4.04 (s, 3H); ^{13}C \text{ NMR (125 MHz, CDCl}_3 \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; \text{ HRMS (ESI+) m/z calcd. for } C_{21}H_{17}ClNaO_3: 375.0758; \text{ 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⁻¹; ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₃H₂₉NaO₅: 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⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₃H₂₉NaO₅: 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⁻¹; ¹H NMR (500 MHz, CDCl₃) 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 = 7.1 Hz, 1H), 7.43 (s, 1H), 7.40 – 7.37 (m, 2H), 7.29 (d, J = 9.1 Hz, 1H), 6.616.54 (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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₁₉H₁₆NaO₄: 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⁻¹; ¹H NMR (500 MHz, CDCl₃) 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); ¹³C
NMR (125 MHz, CDCl3) δ 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 C19H16NaO2S: 347.0712; found: 347.0716.

Methyl (E)-2-[(3-phenylbut-2-en-1-yl)oxy]-1-naphthoate (1k): 1k 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⁻¹; ¹H NMR (500 MHz, CDCl3) δ 7.88 (d, J = 9.1 Hz, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.54 – 7.26 (m, 7H), 6.05 (t, J = 6.2 Hz, 1H), 4.93 (d, J = 6.2 Hz, 2H), 4.03 (s, 3H), 3.92 (s, 3H); ¹³C NMR (125 MHz, CDCl3) δ 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 C22H20NaO3: 355.1310; found: 355.1298.

Methyl 2-[(3,3-bis(4-chlorophenyl)allyl)oxy]-1-naphthoate (1l): 1l 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⁻¹; ¹H NMR (500 MHz, CDCl3) δ 7.82 (d, J = 8.3 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); ¹³C NMR (125 MHz, CDCl3) δ 168.4, 153.2, 143.9, 139.5, 136.7, 134.1, 134.0, 131.5, 131.0, 128.9, 128.7, 128.5, 128.0, 127.6, 124.4, 123.8, 118.7, 114.8, 67.5, 52.4; HRMS (ESI+) m/z calcd. for C22H18Cl2NaO3: 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⁻¹; ¹H NMR (500 MHz, CDCl3) δ 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); ¹³C NMR (125 MHz, CDCl3) δ 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 C17H18Nao3: 293.1148; found: 293.1150.

Methyl 6-bromo-2-(cinnamyl)oxy]-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⁻¹; ¹H NMR (500 MHz, CDCl3) δ 7.95 (d, J = 1.9 Hz,
Methyl 3-bromo-2-(cinnamyoxy)-1-naphthoate (1o):

1o was isolated by FC on silica gel using pentane/EtOAc 30:1; 78% yield; colorless liquid; IR (neat) 2947, 1731, 1278, 1224, 748 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₁H₁₇BrNaO₃: 419.0253; found: 419.0252.

Benzyl 2-(cinnamyoxy)-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 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₇H₂₂NaO₃: 417.1461; found: 417.1454.

Methyl 2-(cinnamyoxy)-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⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₈H₂₄NaO₃: 431.1618; found: 431.1612.

Methyl 2-(cinnamyoxy)-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⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.00 (s,
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⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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), 3.76 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₁H₂₀NaO₅: 375.1203; found: 375.1199.

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

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⁻¹; ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₁H₁₅NaO₅: 345.1097; found: 345.1095.

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

1u 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⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₀H₁₆NaO₅: 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⁻¹; ¹H NMR (500 MHz, CDCl₃)
δ 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\(_3\)) δ 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.

1-allylnaphthalen-2-ol\(^3\) and 1-phenynaphthalen-2-ol\(^4\) were synthesized according to the literature. 3a and 3b were synthesized base on the literature\(^5\) with a little modification, the modified procedure was shown as bellow.

To a solution of MOMO protected 1-allylnaphthalen-2-ol or 1-phenynaphthalen-2-ol (5.00 mmol) in Et\(_2\)O (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 Cs\(_2\)CO\(_3\) (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 MgSO\(_4\), 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 intermediate 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 MgSO\(_4\), 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-Benzylxy-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⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₅H₂₀NaO₃S: 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, 1306, 1219, 1159, 964, 752 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.32 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.1 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 C₂₂H₂₀NaO₃S: 387.1025; found: 387.1029.

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

L₈ (0.0165 mmol) and Cu(OTf)₂ (0.015 mmol) were stirred in 0.4 mL of DCM at room temperature 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)$_2$. 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 substrates$^a$

$^a$All reactions were carried out with 0.15 mmol of 1 in 0.75 mL of DCM.
As shown in Table S2, dichloromethane was the best solvent. 1,2-Dichloroethane was also available. However, Et₂O 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•L₁₁ or Cu(OTf)₂•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•L₁₁ (cf. Table 1).

**Table S1: Ligand screening**

| Ligand | R = | Conv. b | Ee of 2a c | 2a : 2a’ d |
|--------|-----|---------|------------|------------|
|        |     | 99%     | 99%        | 68%        | 38%        | 100% d |
|        |     | 99% ee  | 2% ee      | rac        | 45% ee     | 50% ee  |
|        |     | 67:33   | 72:28      | 66:35      | 68:22      | 21:79   |

*All reactions were carried out with 0.15 mmol of 1a in 0.75 mL of DCM. bBased on NMR. cDetermined by HPLC analysis. dThe reaction was carried out at 30 °C.*
6. Spectral Characterization Data for the Products

**Methyl (S)-1-cinnamyl-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2a):**

Yield (90%); colorless viscous liquid; IR (neat) 3026, 2950, 1742, 1663, 1222, 746 cm\(^{-1}\); \([\alpha]_D^{26} = +111.9\) (c 1.50, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 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\(_{21}\)H\(_{18}\)NaO\(_3\): 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); \(t_e = 6.83\) and 8.65 min.

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

Yield (90%); colorless viscous liquid; \([\alpha]_D^{26} = +76.2\) (c 0.84, CHCl\(_3\)); IR (neat) 3023, 2952, 1742, 1663, 1222, 967, 750 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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, \(J = 15.4, 7.6\) Hz, 1H), 3.64 (s, 3H), 3.32 (ddd, \(J = 13.5, 7.8\) Hz, 1H), 3.17 (ddd, \(J = 13.5, 7.4\) Hz, 1H), 2.06 (s, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 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_{22}H_{20}NaO_3: 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, λ = 272 nm); t_r = 6.24 and 6.74 min.

**Methyl (S,E)-2-oxo-1-[3-(m-toly)allyl]-1,2-dihyronaphthalene-1-carboxylate (2c):**

Yield (91%); colorless viscous liquid; [α]^28_D = +93.8 (c 0.83, CHCl_3); IR (neat) 3024, 2951, 1743, 1663, 1223, 764 cm^{-1}; ^1H NMR (500 MHz, CDCl_3) δ 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); ^13C NMR (125 MHz, CDCl_3) δ 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_{22}H_{20}NaO_3: 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, λ = 254 nm); t_r = 6.56 and 8.02 min.

**Methyl (S,E)-2-oxo-1-[3-(p-toly)allyl]-1,2-dihyronaphthalene-1-carboxylate (2d):**

Yield (87%); colorless viscous liquid; [α]^28_D = +93.1 (c 0.85, CHCl_3); IR (neat) 3034, 2951, 1742, 1664, 1223, 764 cm^{-1}; ^1H NMR (500 MHz, CDCl_3) δ 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); ^13C NMR (125 MHz, CDCl_3) δ 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_{22}H_{20}NaO_3: 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, λ = 254 nm); t_r = 6.67 and 10.29 min.

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

Yield (76%); yellow viscous liquid; [α]^29_D = +98.1 (c 0.84, CHCl_3); IR (neat) 3026, 2951, 1742, 1663, 1487, 1223, 761 cm^{-1}; ^1H NMR (500 MHz, CDCl_3) δ 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), ^1H 3.27 (ddd, J = 13.6, 8.1, 0.9 Hz, 1H), 3.11 (ddd, J = 13.6, 7.0, 1.2 Hz, 1H); ^13C NMR (125 MHz, CDCl_3) δ 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_{21}H_{17}BrNaO_3: 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, λ = 254 nm); \( t_r = 8.05 \) and 11.36 min.

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

Yield (78%); colorless viscous liquid; [\( \alpha \)] \(_{D}^{29} \) = +113.7 (c 0.83, CHCl\(_3\)); IR (neat) 3038, 2952, 1742, 1663, 1224, 761 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 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); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 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\(_{21}\)H\(_{17}\)ClNaO\(_3\): 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); \( t_r \) = 7.78 and 10.73 min.

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

Yield (95%); colorless viscous liquid; [\( \alpha \)] \(_{D}^{30} \) = +40.5 (c 0.84, CHCl\(_3\)); IR (neat) 3038, 2951, 1742, 1662, 1224, 761 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 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); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 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\(_{32}\)H\(_{23}\)ClNaO\(_3\): 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); \( t_r \) = 7.60 and 8.35 min.

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

Yield (86%); colorless viscous liquid; [\( \alpha \)] \(_{D}^{20} \) = +120.0 (c 0.85, CHCl\(_3\)); IR (neat) 3022, 2951, 1742, 1662, 1224, 757 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 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); \(^1\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 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, 125.3, 125.7, 125.3, 123.4, 122.7, 62.8, 52.9, 44.11; HRMS (ESI+) \( m/z \) calcd. for C\(_{25}\)H\(_{20}\)NaO\(_3\): 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, λ = 254 nm); t_r = 8.77 and 13.43 min.

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

Yield (63%); colorless viscous liquid; [α]_D^{27} = +59.4 (c 0.95, CHCl_3); IR (neat) 3026, 1742, 1661, 1225, 759 cm⁻¹; **1H NMR** (500 MHz, CDCl_3) δ 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 (dd, J = 13.6, 8.2, 0.9 Hz, 1H), 3.08 (dd, J = 13.6, 7.0, 1.2 Hz, 1H); **13C NMR** (125 MHz, CDCl_3) δ 197.6, 171.2, 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_{19}H_{16}NaO_4: 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, λ = 254 nm); t_r = 7.69 and 10.62 min.

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

Yield (85%); colorless liquid; [α]_D^{27} = +107.1 (c 1.14, CHCl_3); IR (neat) 2959, 1741, 1661, 1224, 765 cm⁻¹; **1H NMR** (500 MHz, CDCl_3) δ 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 (dd, J = 13.6, 7.0, 1.1 Hz, 1H); **13C NMR** (125 MHz, CDCl_3) δ 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_{19}H_{16}NaO_3: 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, λ = 254 nm); t_r = 8.48 and 13.16 min.

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

Yield (92%); colorless viscous liquid; [α]_D^{28} = +81.0 (c 0.84, CHCl_3); IR (neat) 3022, 2951, 1743, 1663, 1224, 760 cm⁻¹; **1H NMR** (500 MHz, CDCl_3) δ 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); **13C NMR** (125 MHz, CDCl_3) δ 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_{23}H_{20}NaO_3: 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, λ = 254 nm); t_r = 6.67 and
9.22 min.

**Methyl (S)-1-[3,3-bis(4-chlorophenyl)allyl]-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2l):**

![Image of compound 2l]

Yield (89%); white solid; m.p. = 99.5 °C; [α]^{24}_D = +109.16 (c 0.85, CHCl₃); IR (neat) 3027, 2952, 1743, 1664, 1490, 1224, 1092, 830, 759 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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), 3.03 (dd, J = 14.3, 8.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 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 calced. for C_{27}H_{26}Cl_{2}NaO₃: 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, λ = 254 nm); tᵣ = 8.02 and 10.86 min.

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

![Image of compound 2m]

Yield (58%); colorless liquid; [α]^{29}_D = −3.8 (c 0.83, CHCl₃); IR (neat) 2952, 2913, 1742, 1664, 1227, 828, 762 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 9.9 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.35 – 7.34 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 6.19 (d, J = 9.9 Hz, 1H), 4.64 (tdd, J = 7.0, 2.8, 1.4 Hz, 1H), 3.62 (s, 3H), 3.14 (dd, J = 14.1, 8.1 Hz, 1H), 2.91 (dd, J = 14.1, 7.0 Hz, 1H), 1.47 (s, 3H), 1.35 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 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 calced. for C_{17}H_{18}NaO₃: 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, λ = 290 nm); tᵣ = 5.63 and 6.08 min.

**Methyl (S)-6-bromo-1-cinnamyl-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2n):**

![Image of compound 2n]

Yield (95%); yellow viscous liquid; [α]^{26}_D = +115.7 (c 0.84, CHCl₃); IR (neat) 3027, 2950, 1743, 1667, 1224, 748 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 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); ¹³C NMR (125 MHz, CDCl₃) δ 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 calced. for C_{21}H_{17}BrNaO₃: 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, λ = 254 nm); tᵣ = 7.32 and 9.04
**Methyl (S)-3-bromo-1-cinnamyl-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2o):**

![Structure](image)

Yield (95%); yellow viscous liquid; [α]$_D^{27}$ = +0.9 (c 0.84, CHCl$_3$); IR (neat)
3027, 2952, 1745, 1675, 1229, 748 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.87 (s, 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 (dd, $J$ = 13.5, 7.1, 0.7 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) 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$_{21}$H$_7$BrNaO$_3$: 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, λ = 254 nm); $t_e$ = 7.91 and 16.81 min.

**Benzyl (S)-1-cinnamyl-2-oxo-1,2-dihyronaphthalene-1-carboxylate (2p):**

![Structure](image)

Yield (82%); colorless viscous liquid; [α]$_D^{28}$ = +32.5 (c 0.85, CHCl$_3$); IR (neat)
3029, 1742, 1663, 1214, 744 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 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); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 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$_{27}$H$_{23}$NaO$_3$: 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, λ = 254 nm); $t_e$ = 13.4 and 15.15 min.

**Methyl (S)-1-cinnamyl-2-oxo-6-(p-toly)-1,2-dihyronaphthalene-1-carboxylate (2q):**

![Structure](image)

Yield (95%); colorless viscous liquid; [α]$_D^{31}$ = +120.4 (c 0.84, CHCl$_3$); IR (neat) 3034, 2951, 1742, 1665, 1234, 815, 751 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 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); $^{13}$C NMR (125 MHz, CDCl$_3$) 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$_{28}$H$_{24}$NaO$_3$: 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, λ = 254 nm); $t_e$ = 8.93 and
Methyl (S)-1-cinnamyl-2-oxo-6-(phenylethynyl)-1,2-dihyronaphthalene-1-carboxylate (2r):

Yield (94%); colorless viscous liquid; [α]_D^20 = +226.6 (c 0.84, CHCl₃);
IR (neat) 3027, 2947, 1743, 1666, 1222, 757 cm⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 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); ^13C NMR (125 MHz, CDCl₃) δ 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 C₂₀H₂₂NaO₃: 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, λ = 254 nm); tᵣ = 8.71 and 9.98 min.

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

Yield (96%); light yellow solid; m.p. = 140.1 °C; [α]_D^25 = +96.1 (c 0.61, CHCl₃); IR (neat) 2953, 2841, 1742, 1661, 1516, 1236, 1028, 763 cm⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 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); ^13C NMR (125 MHz, CDCl₃) δ 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 C₂₀H₂₀NaO₃: 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, λ = 300 nm); tᵣ = 10.79 and 18.18 min.

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

Yield (92%); yellow solid; m.p. = 88.0 °C; [α]_D^25 = +87.8 (c 0.61, CHCl₃); IR (film) 2952, 2837, 1742, 1661, 1513, 1246, 1034, 754 cm⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 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); ^13C NMR (125 MHz, CDCl₃) 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 C₂₀H₁₈NaO₄: 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, λ = 254 nm); tᵣ.
Methyl (S)-1-(benzo[d][1,3]dioxol-5-ylmethyl)-2-oxo-1,2-dihydropththalene-1-carboxylate (2u):

Yield (95%); yellow solid; m.p. = 131.3 °C; [α]^{23}_{D} = +110.4 (c 0.61, CHCl₃); IR (film) 2938, 2890, 1742, 1658, 1487, 1443, 1224, 1038, 930 cm⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 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); ^13C NMR (125 MHz, CDCl₃) δ 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 C₂₀H₁₆NaO₅: 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, λ = 300 nm); tᵣ = 9.42 and 12.12 min.

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

Yield (71%); colorless viscous liquid; [α]^{25}_{D} = +40.5 (c 0.84, CHCl₃); IR (neat) 3022, 2951, 1742, 1663, 1223, 762 cm⁻¹; ^1H NMR (500 MHz, CDCl₃) 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); ^13C NMR (125 MHz, CDCl₃) 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 C₂₂H₂₀NaO₅: 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, λ = 254 nm); tᵣ = 6.81 and 8.00 min.

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

Yield (52%); light yellow viscous liquid; [α]^{21}_{D} = +61.7 (c 1.20, CHCl₃); IR (neat) 3020, 2949, 1734, 1216, 756 cm⁻¹; ^1H NMR (500 MHz, CDCl₃) δ 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, 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); ^13C NMR (125 MHz, CDCl₃) δ 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<sub>23</sub>H<sub>20</sub>NaO<sub>3</sub>S: 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, λ = 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-dihyronaphthalene-2-carboxylate (4b):

Yield (56%); light yellow viscous liquid; [α]<sup>23</sup> = -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>) δ 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>) δ 198.0, 165.3, 150.5, 145.2, 139.6, 132.2, 131.8, 131.6, 129.2, 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, λ = 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 (1.2 equiv) CH<sub>3</sub>OH, –78 oC , 2 h 92% ee, 88% yield, 92% ee, 96:4 dr

Methyl (1S,2R)-1-cinnamyl-2-hydroxy-1,2-dihyronaphthalene-1-carboxylate (5):

Yield (88%); colorless viscous liquid; [α]<sup>23</sup> = +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>) δ 7.28 – 7.18 (m, 8H), 7.11 (d, J = 6.8 Hz,
1H), 6.46 (d, J = 9.7 Hz, 1H), 6.34 – 6.26 (m, 2H), 6.08 (dd, J = 9.6, 3.5 Hz, 1H), 5.10 (d, J = 6.2 Hz, 1H), 3.75 (s, 3H), 3.03 (dd, J = 13.5, 5.6 Hz, 1H), 2.96 (dd, J = 13.5, 5.6 Hz, 1H), 1.86 (d, J = 8.1 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 174.4, 137.4, 134.9, 132.8, 132.1, 130.7, 128.4, 127.8, 127.4, 127.1, 127.1, 126.8, 126.1, 70.4, 57.2, 52.4, 35.0; HRMS (ESI+) m/z calcd. for C$_{21}$H$_{20}$NaO$_3$: 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, λ = 254 nm); $t_r$ = 6.78 and 8.15 min.
8. SX-ray Structure of Product (S)-2l and Cu(II) Complex

Crystal data for (S)-2l: C<sub>27</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>3</sub>, \( T = 123 \) K, Orthorhombic, space group \( P2_12_12_1 \)(#19), \( a = 7.6102(8) \), \( b = 10.7051(11) \), \( c = 27.326(3) \) Å, \( V = 2226.2(4) \) Å<sup>3</sup>, \( Z = 4 \), \( \lambda(\text{MoK\textalpha}) = 0.71073 \) Å, 4973 reflections collected, and 294 parameters were used for the solution of the structure, final \( R_1 = 0.0256 \) and \( wR_2 = 0.0671 \), GOF = −0.005(9), CCDC 1865509 contains the supplementary crystallographic data for this paper.

**Figure S1.** X-ray structure of (S)-2l
Figure S2. X-ray structure of Cu(II) complex

Crystal data for Cu(II) complex: C_{50}H_{64} Cu F_{6} N_{4} O_{5} S_{2}, T = 123 K, orthorhombic, space group
$P2_1212_1$, $a = 14.293(3)$, $b = 16.823(3)$, $c = 21.700(5)$ Å, $V = 5217.8(19)$ Å$^3$, $Z = 4$, $\lambda$(MoKα) = 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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2. Tayama, E.; Naganuma, N.; Iwamoto, H.; Hasegawa, E. Chem. Comm. 2014, 50, 6860–6862.
3. M. Amézquita-Valencia, H. Alper, Org. Lett. 2014, 16, 5827-5829.
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5. M. Uyanik, N. Sahara, K. Ishihara, Eur. J. Org. Chem., DOI: 10.1002/ejoc.201801063
10. $^1$H NMR and $^{13}$C NMR Spectra
\[ \text{CO}_2\text{Me} - \text{OMe} - \text{OMe} \]

S86
$\text{MeO}_2\text{C}-\text{\(\text{C}_{104}\)}\text{O}$

2d

-197.473

-170.955

145.962
139.285
136.987
134.174
133.916
130.344
129.677
129.585
128.969
128.051
126.916
125.945
125.271
121.081

77.254
77.000
76.746

-130.344
-129.677
-129.585
-128.969
-128.051
-126.916
-125.945
-125.271

-126.916
-125.945
-125.271

-82.761
-52.857
-43.968
-21.027
H-H COSY
11. HPLC Chromatograms

![HPLC Chromatogram](image)

--- Shimadzu LabSolutions ---

Sample: 
Data Name: LY-5-3a-macked
Method Name: C6-20-80-1-15m h.kn
Batch Name: LY-5-3a-kb
Vol: 1-20 µL
Sample Volume: 1 µL
Acquisition Date: 2017/10/05 16:23:57
Modified Date: 2017/10/05 16:30:21

--- Table ---

| Peak No. | RI (m) | Area  | Height | % Area |
|----------|--------|-------|--------|--------|
| 1        | 6.915  | 982288| 94320  | 49.510 |
| 2        | 8.732  | 589463| 79701  | 50.491 |
| Total    |        | 1571741| 174021 | 100.000 |

--- UV Spectra ---

Retention Time: 6.915 min
Retention Time: 8.732 min

--- Image ---

D:\data\LY\data\LY-5-3a-macked
MeO₂C
\[ \text{2c} \]

--- Shimadzu LabSolutions ---

Sample:

Data Name: LY-5-3c.kd
Method Name: 4-20-80-1-15m in km
Batch Name: LY-5-3c.kb
Yi: 1-19
Injection: 1 μl
Acquisition Date: 2017/10/04 18:40:25
Modified Date: 2017/10/04 19:27:42

Sample Type: Unknown

--- Chromatogram ---

PDA Chart 254nm

| Peak No. | RT (s) | Area  | Height | % Area |
|----------|--------|-------|--------|-------|
| 1        | 0.022  | 1563230 | 137710 | 92.569 |
| Total    |        | 1629911 | 1399661 | 100.000 |

Retention Time: 16.564 min

--- UV Spectrum ---

Retention Time: 20.022 min

---
シハイドリットラボソリューションズ

サンプルタイプ：Unknown

インジェクション：1 ul

PDA Chromatogram

| Peak No. | RT (min) | Area   | Height | % Area  |
|---------|----------|--------|--------|---------|
| 1       | 11.378   | 20920  | 49.944 | 100.000 |
| Total   | 725226   | 54720  | 100.000 |

保持時間：11.378 min

UV Spectrum

保持時間：18.054 min
Sample:  
Data Name:  
Method Name:  
Batch Num:  
Yield:  
Inj Vol:  
Acq Date: 2018/05/25 16:09:55  
Modified Date: 2018/05/25 16:29:59  
Sample Type: Unknown  
Analyst: System Administrator

--- Shimadzu LabSolutions ---

![Chemical Structure](image)

**PDA Chart 254nm**

| Peak No. | RT (min) | Area   | Height | % Area |
|----------|----------|--------|--------|--------|
| 1        | 8.349    | 49800  | 100    | 100.00 |
| Total    |          | 49800  |        | 100.00 |

**Wavelengths**

- UV Spectrum: 204.4 nm
- Retention Time: 3.349 min

---
Sample:  
Data Name: LY-5-3Ild 
Method Name: 安定化C-4-20-80-1-20h 
Batch Name: LY-5-3Ild 
Vol.: 1-22 
Inj. Volume: 1 ul 
Acquisition Date: 2018/05/25 15:49:37 
Modified Date: 2018/05/25 16:09:40 

サンプルタイプ: Unknown
分析者: System Administrator
解析者: System Administrator

--- Shimadzu LabSolutions ---

![Graph](image)

| Peak No. | RT (min) | Area  | Height | % Area |
|----------|----------|-------|--------|--------|
| 1        | 5.005    | 32519 | 1327   | 4.162  |
| 2        | 8.348    | 39411 | 27474  | 95.833 |
| Total    | 566.770  | 28831 | 100.000|

保持時間: 17.405 min
UVスペクトル: 228.04 nm

保持時間: 3.348 min
UVスペクトル: 254.39 nm

G: LY-5-3Ild
--- Shimadzu LabSolutions ---

Sample: 
Data Name: LY-5-3m001.kd
Method Name: 4-20-80-1-20m in km
Batch No.: LY-5-3m.kb
Val.: 1
Inj.Vol.: 1 ul
Acquisition Date: 2018/03/02 02436
Modified Date: 2018/03/02 04439

Sample Type: Unknown

--- Chromatogram ---

--- Peaks Summary ---

| Peak No. | RT (in) | Area   | Height | % Area |
|----------|---------|--------|--------|--------|
| 1        | 2.5     | 44827  | 43.01  | 75.64  |
| 2        | 13.122  | 732448 | 59927  | 50.736 |
| Total    |         | 700981 | 40720  | 100.000|

Retention Time: 13.122 min
UV Spectrum: 274.51 nm

--- UV Spectrum ---

--- Peak 274.29 ---

--- Peak 274.51 ---
Shimadzu LabSolutions

Sample: 

Data Name: LB-5-3m-mac001.kvd
Method Name: 4-20-00-1-20m.mkm
Batch Name: LB-5-3m-kb
Vial: 1-64
Injection: 1 ul
Acquisition Date: 2018/03/02 00:52
Modified Date: 2018/03/12 15:26:22

サンプルタイプ: Unknown
分析者: System Administrator
解析者: System Administrator

nAU

0.0 2.5 5.0 7.5 10.0 12.5 15.0 17.5

min

PDA Ch1 254nm

Peak No. RT (min) Area Height % Area
1 218.58 240.08
2 217.00 216.02
Total 1164.56 5058.5 100.000

保持時間: 13.16min
UVスペクトル: 274, 499nm

S168
Shimadzu LabSolutions

Sample

Data Name: LY-5-1a-rac.kd
Method Name: 3-80-20-1m4-20min.kn
Batch Name: LY-5-3k.kb
Vol: 1-18
Inj. Volume: 1 ul
Acquisition Date: 2017/10/11 21:42:39
Modified Date: 2017/10/11 22:02:42

サンプルタイプ: Unknown

分析者: System Administrator
解析者: System Administrator

PDA Chart 254nm

| Peak No. | RT (min) | Area   | Height | % Area |
|----------|----------|--------|--------|--------|
| 1        | 0.189    | 310694 | 335479 | 49.177 |
| Total    |          | 638565 | 542831 | 100.000|

保持時間: 16.654 min
UVスペクトル: 29.389 min

D:30DataLYdataLY-5-1a-rac.kd
== Shimadzu LabSolutions ==

Sample: 

Data Name: LY-S-1a.kd
Method Name: 3-80-20-1m in 20m in.kn
Batch Num: LY-S-3a.kh
Vol: 1-19
Injection: 3 ul
Acquisition Date: 2017/10/11 22:03:05
Modified Date: 2017/10/11 22:23:08

Sample Type: Unknown

---

PDA Chart 254nm

| Peak No. | RT (in)  | Area     | Height | % Area |
|----------|----------|----------|--------|--------|
| 1        | 0.218    | 877644   | 6644   | 96.344 |
| Total    |          | 900173   | 69191  | 100.000|

Retention Time: 56.66s el

LC Chart 254nm

Retention Time: 19.218s el

---

DataLYdataLY-S-1a.kd

S170
S171
=== Shimadzu LabSolutions ===

Sample: D
Data Name: 1Y-5-1d-rac.kd
Method Name: S-20-80-1-20m in km
Batch Num: 1Y-5-1d-1kb
Unit: 1-18
Injection: 3.0 ul
Acquisition Date: 2017/11/20 22:32:38
Modified Date: 2017/11/20 22:53:01
Sample Type: Unknown
Analyst: System Administrator

--- PDA Chromatogram 290nm ---

| Peak No. | RT (min) | Area     | Height | % Area |
|---------|---------|----------|--------|--------|
| 1       | 2.30    | 227451   | 122722 | 49.36% |
| Total   |         | 445395   | 364261 | 100.00%|

Retention Time: 15.606 min
UV Spectra:
Retention Time: 16.056 min

--- 3D Data LYdataLY-5-1d-rac.kd ---
=== Shimadzu LabSolutions ===

Sample: 

Data Name: LY-5-130a.kdd
Method Name: 4:20:80-1:20m in.km
Batch Name: LY-5-130a.kb
Vol: 1.19
Inj Volume: 1 ul
Acquisition Date: 2017/11/06 11:32:29
Modified Date: 2017/11/06 11:32:31

| Peak No. | RT (min) | Area     | Height   | % Area |
|----------|----------|----------|----------|--------|
| 1        | 7.21     | 108106   | 9406     | 3.447  |
| 2        | 9.36     | 3028153  | 167708   | 96.553 |
| Total    |          | 3139260  | 172113   | 100.000|

保留時間: 7.321min   UVスペクトル保持時間: 9.36min

S176
MeO₂C
≡Ph

=== Shimadzu LabSolutions ===

Sample:

Data Name: LY-5-1306-rac.kcd
Method Name: 1.4-20-80-1-20m nlm
Batch Name: LY-5-1306.kbd

Vol: 1-18
Inj Volume: 1 ul
Acquisition Date: 2017/12/14 16:04:51
Modified Date: 2017/12/14 17:04:45

Sample Type: Unknown

RBA Ch1 254nm

| Peak No. | RT (s) | Area   | Height | % Area |
|----------|--------|--------|--------|--------|
| 1        | 7.88s  | 311886 | 24040  | 50.43% |
| 2        | 16.96s | 306499 | 17278  | 34.56% |
| Total    |        | 618444 | 41318  | 100.00%|

Retention Time: 17.883 m h

UV Spectrophotometry

Retention Time: 16.962 m h

S177
BnO₂C

Ph

2p

--- Shimadzu LabSolutions ---

Sample Name: Y-5-130g-rac.kd
Method Name: Y-5-130g
Batch Name: Y-5-130g.kb
Vol: 1.18 μl
Inj Volume: 1 μl
 Acquisition Date: 2017/12/23 16:37:31
Modified Date: 2017/12/23 16:37:33

Sample Type: Unknown
Analyzer: System Administrator
Polarimeter: System Administrator

| Peak No. | RT (min) | Area   | Height | % Area |
|----------|----------|--------|--------|--------|
| 1        | 15.988   | 1114174| 53.05  | 49.935 |
| 2        | 15.988   | 1114834| 44.06  | 50.065 |
| Total    | 29.976   | 222890 | 97.11  | 100.00 |

Retention Time: 13.983 m h
UV Spectrum: 15.000 m h

--- Data-Y5data-Y5-130g-rac.kd ---

S179
Sample Information:
- Sample Name: Unknown
- Method Name: Unknown
- Volume: 1 μL
- Acquisition Date: 2017/12/15 12:42:33
- Modified Date: 2017/12/15 13:36:27

**Chromatogram:**

**PDA Chromatogram:**
- Peak No.
- retention time (min)
- Area
- Height
- % Area

| Peak No. | RT (min) | Area   | Height | % Area |
|----------|----------|--------|--------|--------|
| 1        | 9.708    | 534715 | 41390  | 49.71% |
| Total    |          | 1766524| 83177  | 100.00%|

**UV Spectrum:**
- Retention time: 9.708 min

**Table:**
- Sample Information:
  - Sample Name: Unknown
  - Method Name: Unknown
  - Volume: 1 μL
  - Acquisition Date: 2017/12/15 12:42:33
  - Modified Date: 2017/12/15 13:36:27

**Chromatogram:**

**PDA Chromatogram:**
- Peak No.
- retention time (min)
- Area
- Height
- % Area

| Peak No. | RT (min) | Area   | Height | % Area |
|----------|----------|--------|--------|--------|
| 1        | 9.708    | 534715 | 41390  | 49.71% |
| Total    |          | 1766524| 83177  | 100.00%|

**UV Spectrum:**
- Retention time: 9.708 min
スクリプトのためのラベル

サンプルタイプ: Unknown

結果:

ピークNo. | RT (分) | 区域 | 高さ | % 区域
|--------|--------|------|------|------|
| 1      | 4.263  | 59869| 4330 | 3.533|
| Total  | 161190 | 114737| 100.000%

保持時間: 29.763分

UVスペクトル

ピーク: 208.25, 265.31

ピーク: 208.25, 265.31
Sample: LY-S-5-130c-rac.kd
Method Name: 14-20-80-1-20m in. km
Batch Num: LY-S-5-130c.kd
Vol: 1-18
Injection: 3 ul
Acquisition Date: 2017/12/14 20:59:44
Revised Date: 2017/12/14 21:39:46
Sample Type: Unknown
Analyzer: System Administrator

PDA Chart 254nm
| Peak No. | RT (min) | Area   | Height | % Area |
|---------|----------|--------|--------|--------|
| 1       | 8.602    | 109284.1 | 66996.1 | 50.576 |
| Total   |          | 20962.38 | 118475.1 | 100.000 |

保留時間: 8.692 min  UVスペクトル: 29.717 min

S183
Shimadzu LabSolutions

Sample: 
Data Name: LY-5-130c.kcd
Method Name: 4-20-80-1-20m in.km
Batch Num: LY-5-130c.kkb
Vol: 1-19
Inj Volume: 3 ul
Acquisition Date: 2017/12/14 21:20:09
Modified Date: 2017/12/14 21:40:31

Sample Type: Unknown
Analyzer: System Administrator
Preparer: System Administrator

PDA Chromatogram

| Peak No. | RT (min) | Area   | Height | % Area |
|---------|---------|--------|--------|--------|
| 1       | 0.984   | 1980226| 96241  | 96.546 |
| **Total** | 2051668 | 101656 | 100.000|

Retention Time: 19.984 min
UV Spectrum: 273.82 nm

S185

--- Shimadzu LabSolutions ---

Sample: 
Method Name: Z-20-B0-1-20m in km
Batch No.: LY-6-102c-kb
Yield: 1.61
Injection Date: 2018/06/12 22:39:37
Modified Date: 2018/06/13 10:01:41

Sample Type: Unknown
Analyzer: System Administrator

--- Chromatogram ---

--- Peak Table ---

| Peak No. | RT (min) | Area  | Height | % Area |
|----------|----------|-------|--------|--------|
| 1        | 18.130   | 368849| 44213  | 49.67%
| Total    |          | 359926| 17062  | 100.00% |

--- UV Spectrum ---

UV Spectral Range: 200-700 nm
Wavelength Range: 200-700 nm
Retention Time: 18.130 min

--- Additional Information ---

Data File: LY-6-102c-rac.kd
--- Shimadzu LabSolutions ---

Sample: ...
Data Name: LY-6-102b-rac001.kd
Method Name: 3-80-20-1m 20m in km
Batch Num: LY-6-102b.kd
Vf: 1-48
Injection: 3 ul
Acquisition Date: 2018/06/14 18:42:48
Modified Date: 2018/06/14 20:38:46

Sample Type: Unknown
Analyzer: System Administrator

--- PDA Ch1 254nm ---

| Peak No | RT (min) | Area | Height | % Area |
|---------|----------|------|--------|--------|
| 1       | 0.019    | 107981 | 94.86 | 59.2%  |
| Total   |          | 147574 | 181381 | 100.0% |

Retention Time: 19.03 min
UV Spectrum: 200-350 nm

--- PDA Ch2 254nm ---

Retention Time: 19.03 min
UV Spectrum: 200-350 nm
Sample:  
Date:  
Method Name: [LY-6-102b001.kcd]  
Batch Name: [LY-6-102b.kkb]  
Vial: 1-49  
Inj. Volume: 1.0 ul  
Acquisition Date: 2018/06/14 19:01:33  
Modified Date: 2018/06/14 20:39:28

--- Shimadzu LabSolutions ---

| Peak No. | RT (min) | Area | Height | % Area |
|----------|----------|------|--------|--------|
| 2        | 0.089    | 10915| 974    | 6.131  |
| Total    |          | 178028| 15730 | 100.000|

| 設定時間 | 18.060 min | UVスペクトル | 18.089 min |
|----------|-------------|-------------|------------|

D:\data\LY\dataLY-6-102b001.kcd
== Shimadzu LabSolutions ==

Sample:  

Data Name: LY-5-1c-nc001.kd  
Method Name: Z-20-80-1-20m in.km  
Batch Num: LY-5-1c.kb  
Vial: 1-18  
Injection: 1 ul  
Acquisition Date: 2017/11/13 19:38:03  
Modified Date: 2017/11/13 20:22:38  

サンプルタイプ: Unknown  
分析者: System Administrator  

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**PDA Ch1 254nm**

| Peak No. | RT (min) | Area   | Height | % Area |
|----------|----------|--------|--------|--------|
| 2        | 7.987    | 534,496| 3387   | 49.851 |
| Total    |          | 600,919| 396,861| 100.000|

保持時間: 15.811 min  
UVスペクトラム: 7.987 min

---

D:\data\LY\data\LY-5-1c-nc001.kd
Shimadzu LabSolutions

Sample ID:
Data Name: LY-7-75-RAC.kd
Method Name: C-20-B0-1-30m in:kra
Batch Name: LY-7-75.kb
Vial: 1-61
Hij Volume: 1 ul
Acquisition Date: 2018/10/26 18:36:38
Modified Date: 2018/10/26 21:22:32

Sample Type: Unknown

PDA Ch1 254nm

| Peak No. | IT [s] | Area | Height | % Area |
|----------|-------|------|--------|--------|
| 1        | 11.081| 80779| 8659   | 50.688 |
| 2        | 14.105| 94159| 6753   | 49.312 |
| Total    |       | 597299| 14912  | 100.000 |

Retention Time: 11.081 min
UV Spectrum:
Retention Time: 14.105 min

S193
== Shimadzu LabSolutions ==

*Sample*

**Data Name:** LY-7-75-92EE.kd  
**Method Name:** C2-20-80-1-20m in km  
**Batch Name:** LY-7-75.kb  
**Vial:** 1  
**Sample Type:** Unknown  
**Acquisition Date:** 2018/11/07 15:58:23  
**Modified Date:** 2018/11/07 16:20:04  
**Analyzer:** System Administrator  
**Preparer:** System Administrator

---

**Graph**

- **PDA (Ch1 254nm)**
  - Peak No.: 1  
  - RT (min): 11.079  
  - Area: 59233  
  - Height: 1760  
  - % Area: 96.150
  - Peak No.: 2  
  - RT (min): 14.263  
  - Area: 25933  
  - Height: 525  
  - % Area: 5.850
  - **Total:** 620964  
  - **100.000**

---

**UV Spectrum**

- **Retention Time:** 11.079 min  
- **UV Spectrum:** 14.263 min

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**Notes**

- **Data:** DataLY-dataLY-7-75-92EE.kd
Shimadzu LabSolutions

Sample D
Data Name: LY-5-110-rsc.kd
Method Name: 13-00-20-1m F-20m n,km
Batch Num: LY-5-110.kb
Vol: 1.52
Inj Volume: 1 ul
Acquisition Date: 2018/02/02 11:22:21
Modified Date: 2018/02/02 11:22:24
Sample Type: Unknown

Detector: UV 254nm

| Peak No. | RT (min) | Area   | Height | % Area |
|----------|----------|--------|--------|--------|
| 1        | 0.034    | 298889 | 39230  | 8.787  |
| 2        | 0.293    | 376885 | 29687  | 9.389  |
| 3        | 0.489    | 190759 | 97013  | 40.770 |
| 4        | 0.679    | 121638 | 117252 | 41.099 |
| Total    |          | 2948081| 2511761| 100.000|

Retention Time: 0.679 min
UV Wavelength: 254 nm

At 254 nm:
20.486
255.37
235.26
255.52

At 290 nm:
20.462
255.52
234.19
255.52
== Shimadzu LabSolutions ==

Sample:  
Detector: D:
Data Name: 5-110.kd
Method Name: 3-80-20-1in 1-20n in
Batch Name: 5-110.kb
Vial: 1-33
Injection Volume: 1 ul
Acquisition Date: 2018/02/02 11:22:47
Modified Date: 2018/02/02 11:42:50

Sample Type: Unknown
Analyser: System Administrator

---

**PDA Chromatogram**

| Peak No. | RT (min) | Area     | Height | % Area |
|----------|----------|----------|--------|--------|
| 1        | 6.192    | 208517   | 100    | 95.803 |
| 2        | 8.153    | 91177    | 73.21  | 4.197  |
| Total    |          | 217694   |        | 100.000|

---

**UV Spectra**

**Hold Time:** 56.783 min

**UV**

- 205.12 nm 233.14 nm 285.36 nm

**Hold Time:** 18.753 min

**UV**

- 206.26 nm 231.07 nm 254.85 nm

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S198