Electronic Supplementary Information (ESI)

Chiral Cobalt(II) Complex Catalyzed Friedel-Crafts-Aromatization for Synthesis of Axially Chiral Biaryldiols
Chaoran Xu, Haifeng Zheng, Bowen Hu, Xiaohua Liu*, Lili Lin and Xiaoming Feng*

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, People’s Republic of China

Fax: (+86)28-85418249

E-mail: liuxh@scu.edu.cn, xmfeng@scu.edu.cn

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1. General information

$^1$H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl$_3$, $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. $^{13}$C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl$_3$, $\delta = 77.0$).

Enantiomeric excess (e.e.) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C.

Optical rotations were reported as follows: $[\alpha]_D^{25}$ (c: g/100 mL, in solvent).

HRMS was recorded on a commercial apparatus (ESI Source).

All catalytic reactions were run in dried glassware or test tube.

THF, toluene and diethyl ether (Et$_2$O) were distilled from sodium and benzophenone as indicator.

CH$_3$CN and CH$_2$Cl$_2$ was distilled over CaH$_2$.

Co(ClO$_4$)$_2 \cdot 6$H$_2$O (99%), Ag$_2$O were purchased from Alfa.

All racemic products (3aa-3oa) were obtained by using Co(ClO$_4$)$_2 \cdot 6$H$_2$O (10 mol%) and racemic $N,N'$-dioxide ligand ($L$-RaPr$_2$ 10 mol%) as the catalyst according to general procedure for the catalytic enantioselective Friedel-Crafts- Aromatization reaction.

Quinone substrates (1a-1k) were synthesized by using the literature method (Chen, Y, H. Cheng, D, J. Zhang, J. Wang, Y. Liu, X, Y. Tan, B. J. Am. Chem. Soc. 2015, 137, 15062.). Quinone substrates (1m, 1n, 1o) were synthesized as follow method.

2-nathphol substrates (2a-2e) were purchased from commercial source.

2-nathphol substrates (2f-2v) were obtained by using the literature method as followed (Q. Yin, S. G. Wang, X. W. Liang, D. W. Gao, J. Zheng and S. L. You, Chem. Sci., 2015, 6, 4179.).
The method for the synthesis of quinone substrates

To a solution of benzoquinone (20 mmol, 1.0 equiv) in dichloromethane (100 mL) was added the corresponding boronic acid (30 mmol, 1.5 equiv), water (100 mL), and silver(I) nitrate (680 mg, 4.0 mmol, 0.2 equiv). Potassium persulfate (16.2 g, 60 mmol, 3.0 equiv) was then added and the solution was stirred vigorously at room temperature and monitored by thin-layer chromatography analysis of the organic layer. Upon consumption of quinone (3 – 24 h), the reaction was diluted with dichloromethane (50 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (3 x 30 mL), dried over sodium sulfate, and evaporated in vacuo. The product was used for next step with silica gel quick purification.

To a solution of corresponding substituted benzoquinone in CH$_3$CN (30 mL), trimethylsilyl/bromide (TMSBr, 30 mmol, 4.0 mL) was added, and tetraethylammonium fluoroborate (TBAF, 1.0 M in THF, 1.5 mmol, 1.5 mL) in CH$_3$CN (10 mL) was carefully added, at which time the quinone color was disappeared. The reaction mixture was stirred for 2 hours at room temperature. After removal of solvent in vacuo, the resulted mixture was mixed with water (10 mL) and ethyl acetate (30 mL). The aqueous layer was separated and extracted with ethyl acetate twice (2 x 15 mL). The organic layers were combined and dried over sodium sulfate, filtrated and removal of the solvent in vacuo. Purification was performed by silica gel chromatography to yield the pure product.

To a solution of the corresponding bromo-substituted benzene-1,4-diol (10 mmol) in DMF (15 mL), Pd(dppf)Cl$_2$ (0.75 g, 1.0 mmol), MeOH (6 mL), Bu$_3$N (2.74 mL, 14.8 mmol) was added in sequence. The vessel was purged and pressurized with CO (4.0 MPa) and stirred at 110 °C for 24 h. The reaction was cooled to room temperature, diluted with CH$_2$Cl$_2$ (50 mL), washed with 1N HCl (2 x 35 mL), brine/water (1:1, 35 mL), and brine (35 mL). The organic layers were combined, dried over Na$_2$SO$_4$, and concentrated under reduced pressure to afford a dark purple oil. The residue was purified by flash chromatography (5-10% EtOAc/hexanes) to afford the titled compound as a white solid.

Methyl 4-ethyl-2,5-dihydroxybenzoate

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.29 (s, 1H), 7.18 (s, 1H), 6.79 (s, 1H), 4.62 (s, 1H), 3.91 (s, 3H), 2.63 (q, $J = 7.6$ Hz, 2H), 1.23 (td, $J = 7.6, 1.6$ Hz, 3H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.2, 155.9, 145.9, 140.5, 117.7, 114.2, 109.6, 52.2, 23.4, 13.3.

Methyl 2,5-dihydroxy-4-isopropylbenzoate

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.27 (s, 1H), 7.18 (s, 1H), 6.84 (s, 1H), 4.49 (s, 1H), 3.92 (s, 3H), 3.42 – 3.05 (m, 1H), 1.24 (d, $J = 6.8$ Hz, 6H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.1, 156.3, 145.3, 145.0, 115.3, 114.3, 109.5, 52.2, 27.6, 22.2.

Methyl 2,5-dihydroxy-4-isobutylbenzoate

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.27 (s, 1H), 7.19 (s, 1H), 6.73 (s, 1H), 4.54 (s, 1H), 3.91 (s, 3H), 2.47 (d, $J = 7.2$ Hz, 2H), 2.0 – 1.90 (m, 1H), 1.05 – 0.81 (m, 6H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.2, 155.6, 146.2, 138.2, 119.5, 114.4, 109.9, 52.2, 39.66, 28.6, 22.5.

To a 25 mL round-bottom flask was added 2,5-dihydroxy-benzoic acid methyl ester (1.0 mmol), MgSO$_4$ (dried at 300 °C for 2.0 h before use, 360 mg, 3 mmol), and Et$_2$O (dry, 20 mL). The solution was added Ag$_2$O (700 mg, 3.0 mmol), and then stirred for 2.0 h at room temperature. The reaction mixture was then filtered, washed with 10 mL of Et$_2$O (dry), and concentrated under reduced pressure at room temperature to afford the quinone product. The product was immediately used without further purification. (The product is sensitive to acid, H$_2$O and light, and stable at -20 °C for at least one week without any noticeable polymerization as judged by $^1$H NMR spectroscopy.)
3. The method for the synthesis of naphthalen-2-ol substrates

To a mixture of 6-bromonaphthalen-2-ol (1.1 g, 5 mmol, 1 eq), RB(OH)$_2$ (7.5 mmol, 1.5 eq) and Pd(OAc)$_2$ (45 mg, 0.2 mmol, 0.04 eq) in water (10 mL) was added diisopropylamine (1 mL). After heat to reflux for 10 hours, the mixture was then filtered and washed with 10 mL ethyl acetate 3 times. The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dry over Na$_2$SO$_4$, filtered and then concentrated. The residue was purified by silica gel column chromatograph (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product.

To a solution of 6-alkenylnaphthalen-2-ol (1 mmol, 1 eq) in ethyl acetate (3 mL), 10% Pd/C (20 mg) was added under N$_2$ atmosphere. Then the reaction was charged with 1 atm of hydrogen and stirred at room temperature for 17 hours. The reaction mixture was filtered and washed with ethyl acetate. The filtrate was concentrated under reduce pressure. The crude product was purified by silica gel column (ethyl acetate/petroleum ether = 1/30, v/v) to afford the product.

6-(3,4-dichlorophenyl)naphthalen-2-ol

\[ \delta \]

$^1$H NMR (400 MHz, DMSO) \( \delta \) 9.92 (s, 1H), 8.17 (s, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.82 – 7.66 (m, 4H), 7.20 – 7.17 (m, 1H), 7.16 (dd, J = 8.8, 2.3 Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO) \( \delta \) 156.0, 140.9, 134.3, 131.7, 131.5, 130.9, 130.0, 129.6, 128.2, 127.8, 126.9, 126.6, 125.7, 124.8, 119.3, 108.5.

6-(furan-2-yl)naphthalen-2-ol

\[ \delta \]

$^1$H NMR (400 MHz, DMSO) \( \delta \) 9.84 (s, 1H), 8.09 (s, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 10.6 Hz, 3H), 7.12 (dd, J = 11.2, 1.7 Hz, 2H), 6.97 (d, J = 3.2 Hz, 1H), 6.64 – 6.56 (m, 1H).

$^{13}$C NMR (101 MHz, DMSO) \( \delta \) 155.6, 153.5, 142.5, 133.8, 129.7, 127.6, 126.7, 124.8, 122.4, 121.5, 119.2, 112.1, 108.8, 105.2.

(E)-6-(pent-1-en-1-yl)naphthalen-2-ol

\[ \delta \]

$^1$H NMR (400 MHz, DMSO) \( \delta \) 9.71 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.07 (dd, J = 8.4, 7.2 Hz, 2H), 6.48 (d, J = 16.0 Hz, 1H), 6.43 – 6.15 (m, 1H), 2.19 (dd, J = 14.4, 7.0 Hz, 2H), 1.48 (dd, J = 14.4, 7.2 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) \( \delta \) 155.2, 133.8, 131.8, 130.0, 129.4, 129.2, 127.8, 126.3, 125.0, 123.7, 118.7, 108.7, 34.6, 22.1, 13.6.

6-(2-methylprop-1-en-1-yl)naphthalen-2-ol

\[ \delta \]

$^1$H NMR (400 MHz, DMSO) \( \delta \) 9.70 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.12 – 7.01 (m, 2H), 6.35 (s, 1H), 1.90 (d, J = 6.8 Hz, 6H).

$^{13}$C NMR (101 MHz, DMSO) \( \delta \) 155.10, 134.22, 132.90, 132.36, 129.21, 127.5, 127.6, 126.58, 125.65, 125.01, 118.67, 108.45, 26.73, 19.36.

6-(4-fluorophenyl)naphthalen-2-ol

\[ \delta \]

$^1$H NMR (400 MHz, DMSO) \( \delta \) 9.85 (s, 1H), 8.08 (s, 1H), 7.88 – 7.76 (m, 4H), 7.72 (d, J = 8.8 Hz, 1H), 7.33 (t, J = 8.8 Hz, 2H), 7.22 – 7.11 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO) \( \delta \) 155.56, 136.74 (d, J = 3.1 Hz), 133.77, 133.26, 129.76, 128.49 (d, J = 8.1 Hz), 127.91, 126.72, 125.1, 125.0, 119.10, 115.77, 115.56, 108.43.

6-(o-tolyl)naphthalen-2-ol

\[ \delta \]

$^1$H NMR (400 MHz, DMSO) \( \delta \) 9.80 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 9.6 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.29 (dd, J = 10.8, 1.2 Hz, 4H), 7.19 (s, 1H), 7.14 (d, J = 8.8 Hz, 1H), 2.28 (s, 3H).
6-(benzo[d][1,3]dioxol-5-yl)naphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.79 (s, 1H), 8.01 (s, 1H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.8$ Hz, 1H), 7.35 (s, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.12 (dd, $J = 12.4, 3.6$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 1H), 6.08 (s, 2H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 155.4, 141.3, 135.5, 134.9, 133.4, 130.3, 129.7, 129.5, 127.6, 127.3, 127.1, 125.9, 125.7, 118.9, 108.4, 20.3.

6-(3-methoxyphenyl)naphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.84 (s, 1H), 8.10 (s, 1H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.75 (dt, $J = 8.8, 5.2$ Hz, 2H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.32 (dd, $J = 9.6, 5.2$ Hz, 2H), 7.19 – 7.11 (m, 2H), 6.94 (dd, $J = 8.0, 2.4$ Hz, 1H), 3.85 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 159.8, 155.6, 141.8, 134.2, 134.0, 129.9, 129.8, 127.9, 126.6, 125.3, 125.2, 119.0, 112.62, 112.1, 108.4, 107.0, 101.1.

6-(4-(tert-butyl)phenyl)naphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.80 (s, 1H), 8.04 (s, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.73 – 7.62 (m, 3H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.13 (dd, $J = 13.6, 4.8$ Hz, 2H), 1.32 (s, 9H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 155.4, 149.4, 137.4, 134.2, 133.7, 129.7, 128.0, 126.3, 125.2, 119.0, 112.62, 112.1, 108.5, 34.2, 31.1.

6-phenylnaphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.83 (s, 1H), 8.08 (s, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.81 – 7.66 (m, 4H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.2$ Hz, 1H), 7.23 – 7.05 (m, 2H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 155.6, 140.3, 134.3, 133.9, 129.8, 128.9, 128.0, 127.0, 126.7, 126.6, 125.2, 125.1 119.1, 108.4.

6-(furan-3-yl)naphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.76 (s, 1H), 8.24 (s, 1H), 7.99 (s, 1H), 7.76 (t, $J = 5.2$ Hz, 2H), 7.72 – 7.64 (m, 2H), 7.15 – 7.07 (m, 2H), 7.07 – 7.01 (m, 1H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 155.2, 144.2, 139.0, 133.6, 129.2, 127.9, 126.5, 126.2, 126.0, 124.5, 123.4, 119.0, 108.7.

6-(m-tolyl)naphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.80 (s, 1H), 8.07 (s, 1H), 7.84 (d, $J = 8.8$ Hz, 1H), 7.73 (dt, $J = 8.8, 5.2$ Hz, 2H), 7.59 (s, 1H), 2.43 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 155.5, 141.4, 135.5, 134.9, 133.4, 130.3, 129.7, 129.5, 127.6, 127.3, 127.1, 125.9, 125.7, 118.9, 108.4, 20.3.
7.54 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.22 – 7.06 (m, 3H), 2.40 (s, 3H).
$^1$H NMR (400 MHz, DMSO) $\delta$ 9.77 (s, 1H), 7.84 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.53 (dd, J = 8.8, 1.6 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.15 (d, J = 2.4 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 3.77 (s, 3H).

13C NMR (101 MHz, DMSO) $\delta$ 160.7, 145.5, 143.3, 139.6, 139.1, 135.0, 134.1, 133.2, 132.9, 132.5, 131.9, 130.5, 130.3, 130.2, 129.0, 124.2, 113.7, 26.4.

6-(2-methoxyphenyl)naphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.74 (s, 1H), 7.84 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.53 (dd, J = 8.8, 1.6 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.15 (d, J = 2.4 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 3.77 (s, 3H).

13C NMR (101 MHz, DMSO) $\delta$ 160.7, 145.5, 143.3, 139.6, 139.1, 135.0, 134.1, 133.2, 132.9, 132.5, 131.9, 130.5, 130.3, 130.2, 129.0, 124.2, 113.7, 26.4.

6-(4-ethoxyphenyl)naphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.77 (s, 1H), 7.84 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.53 (dd, J = 8.8, 1.6 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.15 (d, J = 2.4 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 3.77 (s, 3H).

13C NMR (101 MHz, DMSO) $\delta$ 160.7, 145.5, 143.3, 139.6, 139.1, 135.0, 134.1, 133.2, 132.9, 132.5, 131.9, 130.5, 130.3, 130.2, 129.0, 124.2, 113.7, 26.4.

[1,2'-binaphthalen]-6'-ol

$^1$H NMR (400 MHz, DMSO) $\delta$10.00 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.95 (dd, J = 8.0, 4.4 Hz, 2H), 7.91 (s, 1H), 7.86 (dd, J = 8.4, 2.8 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.53 (ddd, J = 8.4, 5.2, 1.3 Hz, 3H), 7.50 – 7.43 (m, 1H), 7.37 (d, J = 2.4 Hz, 1H), 7.27 (dd, J = 8.8, 2.4 Hz, 1H).

13C NMR (101 MHz, DMSO) $\delta$ 155.7, 139.7, 134.3, 133.8, 133.5, 131.1, 129.6, 128.3, 128.2, 127.8, 127.4, 126.2, 126.0, 125.8, 125.5, 119.15, 108.66.

6-isobutylnaphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.64 (s, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.09 (dd, J = 8.8, 2.4 Hz, 1H), 2.57 (d, J = 7.2 Hz, 2H), 1.93 (dt, J = 13.6, 6.8 Hz, 1H), 0.92 (d, J = 6.8 Hz, 6H).

13C NMR (101 MHz, CDCl3) $\delta$ 159.9, 140.5, 138.2, 134.0, 133.2, 133.0, 131.9, 131.0, 123.7, 113.7, 49.8, 34.9, 27.4.

6-pentylnaphthalen-2-ol

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.60 (s, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.27 (dd, J = 8.4, 1.6 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 7.07 (dd, J = 8.8, 2.4 Hz, 1H), 2.75 – 2.64 (m, 2H), 1.71 – 1.60 (m, 2H), 1.33 (dd, J = 6.8, 3.6 Hz, 4H), 0.89 (t, J = 6.8 Hz, 3H).

13C NMR (101 MHz, DMSO) $\delta$ 159.9, 141.7, 138.2, 133.9, 133.1, 132.7, 131.1, 123.69 (s), 113.7, 40.3, 36.2, 35.9, 27.2, 19.2.
4. Optimization of the reaction conditions

Table 1: Screening the metal salts of the reaction

<table>
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<tr>
<th>Entry[a]</th>
<th>Matel salt</th>
<th>3aa Yield (%)[b]</th>
<th>Ee (%)[c]</th>
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<tr>
<td>1</td>
<td>Cu(OTf)$_2$</td>
<td>87</td>
<td>Race</td>
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<td>2</td>
<td>Mg(OTf)$_2$</td>
<td>62</td>
<td>Race</td>
</tr>
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<td>3</td>
<td>Ni(OTf)$_2$</td>
<td>58</td>
<td>Race</td>
</tr>
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<td>4</td>
<td>Zn(OTf)$_2$</td>
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<td>5</td>
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<td>Co(ClO$_4$)$_2$·6H$_2$O</td>
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<td>Co(BF$_4$)$_2$·6H$_2$O</td>
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<td>60</td>
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<td>13</td>
<td>CoBr$_2$</td>
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<td>Race</td>
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[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (1a, 0.1 mmol), 2-naphthol (2a, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of DCM under N$_2$, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

Table 2: Screening the ligands of the reaction
Table 3: Screening the solvents of the reaction

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<th>Entry[a]</th>
<th>Solvent</th>
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<td>Yield (%)[b]</td>
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<td>3</td>
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[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (1a, 0.1 mmol), 2-naphthol (2a, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of DCM under N$_2$, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.
7    CHCl₃    90    20
8    1,2-dichloroethane    93    20
9    1,1,2-trichloroethane    90    28
10    1,1,2,2-tetrachloroethane    89    31
11    1,1,1-trichloroethane    95    Race

[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (1a, 0.1 mmol), 2-naphthol (2a, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of solvent under N₂, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. EA = ethyl acetate, THF = tetrahydrofuran.

Table 4: Screening the temperature of the reaction

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<th>Yield (%)[b]</th>
<th>Ee (%)[c]</th>
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<td>6[f]</td>
<td>-78</td>
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<td>83</td>
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</table>

[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (1a, 0.1 mmol), 2-naphthol (2a, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of solvent under N₂, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Reaction at -50 °C for 24 h. [e] Reaction at -60 °C for 48 h. [f] Reaction at -78 °C for 60 h.
5. General procedure for the catalytic enantioselective Friedel-Crafts-Aromatization reaction

In an oven dried test tube with a magnetic stirring bar, naphthalen-2-ol (0.1 mmol), \(N,N'\)-dioxide \(L\text{-RaPr}2\) (0.01 mmol) and Co(\(\text{ClO}_4\))2·6H2O (0.01 mmol) in CH2Cl2 (2.0 mL) were stirred at 35 °C for 1h. Then the mixture was cooled to -78 °C, and the quinone (0.1 mmol) dissolved in 0.5 mL DCM was added. The mixture was stirred at -78 °C for 60 h. The reaction mixture was detected by TLC. After completion, 0.8 mg NaBH4 in 0.2 mL MeOH was added to quench the reaction. Then flash column chromatography was carried out to provide the desired product. The products was used immediately for HPLC and NMR analysis.

6. Gram-scale synthesis of the product 3aa

To an oven dried 100 mL round-bottom flask with a magnetic stirring bar were sequentially added naphthalen-2-ol (3.5 mmol), \(N,N'\)-dioxide-metal complex \(L\text{-RaPr}2/\text{Co(\(\text{ClO}_4\))2·6H2O}\) (1:1, 0.35 mmol) and CH2Cl2 (60 mL) under N2 atmosphere. After stirring at 35 °C for 1h, the mixture was cooled to -78 °C, and the quinone (3.5 mmol) dissolved in 20 mL DCM was added. The mixture was stirred at -78 °C for 60 h. The reaction mixture was detected by TLC. After completion, 28 mg NaBH4 in 10 mL MeOH was added, followed by poured into 50 mL of water. The mixture was extract by DCM, and the aqueous layer was washed with DCM (2 x 10 mL). The combined organic phases was washed with brine (20 mL), and dried over Na2SO4. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with DCM/EA = 20:1. The products was used immediately for HPLC and NMR analysis.
7. The analytical and spectral characterization data of the products

methyl (αR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate white solid; 91% yield, 95:5 e.r.; [α]_D^{25} = -22.4 (c 0.54, CH₂Cl₂);
Determined by HPLC analysis [Daicel chiralpakADH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t₁ = 20.97 min, t₂ = 22.87 min];

\[1H\text{ NMR (400 MHz, CDCl}_3\] \(\delta\) 10.79 (s, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.38 – 7.33 (m, 2H), 7.26 (s, 2H), 7.17 (dd, J = 6.0, 3.6 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 5.13 (s, 1H), 4.63 (s, 1H), 3.21 (s, 3H).

\[13C\text{ NMR (101 MHz, CDCl}_3\] \(\delta\) 170.4, 157.1, 151.1, 147.3, 133.0, 130.7, 129.1, 128.2, 127.4, 124.0, 123.9, 123.5, 120.5, 117.9, 117.5, 113.7, 112.6, 52.2.

HRMS (ESI) calcd for [M+H]+, C₁₈H₁₅O₅⁺, m/z: 311.0919, observed: 311.0919.

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ethyl (αR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate white solid; 82% yield, 96:4 e.r.; [α]_D^{25} = -46.3 (c 0.366, CH₂Cl₂);
Determined by HPLC analysis [Daicel chiralpakADH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t₁ = 17.51 min, t₂ = 19.40 min];

\[1H\text{ NMR (400 MHz, CDCl}_3\] \(\delta\) 10.98 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.81 (dd, J = 5.6, 4.0 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 (dd, J = 5.6, 4.0 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H), 5.07 (s, 1H), 4.64 (s, 1H), 3.85 – 3.58 (m, 2H), 0.30 (t, J = 7.2 Hz, 3H).

\[13C\text{ NMR (101 MHz, CDCl}_3\] \(\delta\) 170.0, 157.1, 151.1, 147.3, 133.3, 130.6, 129.2, 128.1, 127.4, 123.9, 123.6, 120.5, 117.8, 117.6, 114.0, 112.6, 61.1, 12.5.

HRMS (ESI) calcd for [M+H]+, C₁₉H₁₇O₅⁺, m/z: 325.1076, observed: 325.1080.
propyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate white solid; 80% yield, 95:5 e.r.; $[\alpha]_D^{25} = -32.1$ (c 0.320, CH2Cl2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/i-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, $t_1 = 10.74$ min, $t_2 = 15.85$ min];

1H NMR (400 MHz, CDCl3) $\delta$ 11.05 (s, 1H), 7.87 (d, $J = 9.2$ Hz, 1H), 7.82 (dd, $J = 6.4$, 3.2 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.27 (dd, $J = 17.2$, 7.6 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.15 (d, $J = 9.2$ Hz, 1H), 4.99 (s, 1H), 4.57 (s, 1H), 3.82 – 3.53 (m, 2H), 0.69 (ddt, $J = 26.4$, 14.0, 7.2 Hz, 2H), 0.26 (t, $J = 7.6$ Hz, 3H).

13C NMR (101 MHz, CDCl3) 170.3, 157.5, 151.0, 147.2, 133.1, 130.7, 129.3, 128.2, 127.4, 123.9, 123.9, 123.6, 120.6, 117.6, 113.9, 112.6, 67.2, 20.7, 9.8.

butyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 83% yield, 95:5 e.r.; [α]D 25 = -36.6 (c 0.204, CH2Cl2);
Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t1 = 14.91 min, t2 = 22.95 min];
1H NMR (400 MHz, CDCl3) δ 11.07 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.82 (dd, J = 5.6, 4.0 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.31 – 7.24 (m, 2H), 7.20 (dd, J = 5.6, 4.0 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 5.05 (s, 1H), 4.58 (s, 1H), 3.73 (td, J = 5.6, 2.4 Hz, 2H), 0.71 – 0.40 (m, 7H).
13C NMR (101 MHz, CDCl3) δ 170.4, 157.5, 151.0, 147.2, 133.1, 130.6, 129.2, 128.2, 127.4, 124.0, 123.6, 120.6, 117.6, 117.6, 113.9, 112.6, 65.5, 29.5, 18.6, 13.5.

isopropyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 60% yield, 97:3 e.r.; [α]D 25 = -60.5 (c 0.376, CH2Cl2);
Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t1 = 11.03 min, t2 = 15.36 min];
1H NMR (400 MHz, CDCl3) δ 11.06 (s, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.39 – 7.32 (m, 2H), 7.26 (d, J = 9.2 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.13 (d, J = 9.2 Hz, 1H), 5.03 (s, 1H), 4.75 (dt, J = 12.4, 6.2 Hz, 1H), 4.64 (s, 1H), 0.65 (d, J = 6.4 Hz, 3H), 0.19 (d, J = 6.4 Hz, 3H).
isobutyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 80% yield, 95:5 e.r.; [α]D25 = -30.7 (c 0.502, CH2Cl2);
Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t1 = 10.01 min, t2 = 23.00 min];

**1H NMR (400 MHz, CDCl3)** δ 11.09 (s, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.38 – 7.32 (m, 2H), 7.27 (s, 2H), 7.21 (dd, J = 5.6, 4.0 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 5.07 (s, 1H), 4.55 (s, 1H), 3.52 (ddd, J = 29.6, 10.8, 6.8 Hz, 2H), 0.87 (dd, J = 13.6, 6.8 Hz, 1H), 0.38 (d, J = 6.8 Hz, 3H), 0.18 (d, J = 6.8 Hz, 3H).

**13C NMR (101 MHz, CDCl3)** δ 170.4, 157.5, 151.0, 147.2, 133.0, 130.7, 129.6, 128.2, 127.5, 124.0, 123.6, 120.6, 117.7, 117.6, 113.9, 112.6, 72.1, 26.8, 18.6, 18.4.


**Retention Time** | **Area**      | **% Area**
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benzyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 96% yield, 90:10 e.r.; [α]D25 = -20.5 (c 0.650, CH2Cl2);
Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/
i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t1 = 9.08 min, t2 = 25.38
min];
1H NMR (400 MHz, CDCl3) δ 10.95 (s, 1H), 7.71 (dd, J = 7.6, 2.0 Hz,
1H), 7.59 (d, J = 9.2 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.23 (s, 1H), 7.15 (d, J = 9.2 Hz, 2H), 7.09
(d, J = 9.2 Hz, 1H), 7.04 (t, J = 7.6 Hz, 2H), 7.00 (d, J = 9.2 Hz, 1H), 6.56 – 6.37 (m, 2H),
5.06 (s, 1H), 4.73 – 4.63 (m, 2H), 4.57 (s, 1H).
13C NMR (101 MHz, CDCl3) δ 170.0, 157.5, 151.0, 147.3, 133.7, 133.0, 130.7, 129.1, 128.4,
128.3, 128.2, 127.3, 124.1, 123.8, 123.5, 120.5, 117.9, 117.4, 113.6, 112.4,
67.5.
HRMS (ESI) calcd for [M+H]+, C24H19O5+
+ m/z: 387.1232, observed: 387.1231.

2-bromobenzyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)
benzoate
white solid; 70% yield, 93:7 e.r.; [α]D25 = 5.1 (c 0.652, CH2Cl2);
Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/
i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t1 = 8.89 min, t2 = 17.22 min];
1H NMR (400 MHz, CDCl3) δ 10.97 (s, 1H), 7.62 – 7.57 (m, 1H), 7.43 (d, J = 9.2 Hz, 1H),
7.35 – 7.26 (m, 4H), 7.18 – 7.12 (m, 2H), 7.07 (td, J = 7.6, 1.6 Hz, 1H), 6.94 (ddd, J = 9.2, 6.8,
2.8 Hz, 2H), 6.32 (dd, J = 7.6, 1.6 Hz, 1H), 5.05 – 4.52 (m, 4H).
13C NMR (101 MHz, CDCl3) δ 169.8, 157.5, 151.0, 147.3, 133.1, 132.8, 132.5, 130.6, 130.3,
129.7, 129.0, 128.3, 127.3, 127.2, 124.2, 123.9, 123.7, 123.5, 120.6, 118.0, 117.3, 113.4,
112.1, 67.0.
HRMS (ESI) calcd for [M+Na]+, C24H17O5BrNa+, m/z: 487.0157, 489.0137, observed:
3-bromobenzyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 92% yield, 92.5:7.5 e.r.; [α]D25 = -35.9 (c 0.674, CH2Cl2); Determined by HPLC analysis [Daicel chiralpakADH, n-hexane/ i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t1 = 10.83 min, t2 = 19.20 min];

1H NMR (400 MHz, CDCl3) δ 10.87 (s, 1H), 7.74 – 7.67 (m, 1H), 7.62 (d, J = 9.2 Hz, 1H), 7.31 (dd, J = 6.8, 2.8, 2.0 Hz, 3H), 7.25 (s, 1H), 7.11 (d, J = 9.2 Hz, 2H), 7.02 (d, J = 9.2 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.66 (t, J = 1.6 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H), 5.14 – 4.96 (m, 1H), 4.61 (s, 3H).

13C NMR (101 MHz, CDCl3) δ 169.8, 157.5, 150.9, 147.3, 153.7, 132.9, 131.6, 131.4, 130.7, 129.8, 129.0, 128.3, 127.4, 127.2, 124.3, 123.4, 122.2, 120.5, 118.0, 117.3, 113.5, 112.2, 66.5.


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4-bromobenzyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 93% yield, 92:8 e.r.; $[\alpha]_D^{25} = -44.5$ (c 0.802, CH$_2$Cl$_2$); Determined by HPLC analysis [Daicel chiralpakADH, n-hexane/ i-PrOH = 70/30, 1.0 mL/min, $\lambda$ = 254 nm, $t_1 = 10.97$ min, $t_2 = 26.31$ min];

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.89 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 9.2 Hz, 1H), 7.31 (td, J = 7.2, 1.6 Hz, 2H), 7.25 (d, J = 2.8 Hz, 1H), 7.12 (dd, J = 12.0, 8.8 Hz, 4H), 7.01 (d, J = 9.2 Hz, 1H), 6.29 (d, J = 8.4 Hz, 2H), 5.03 (s, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.8, 157.6, 150.9, 147.3, 132.9, 132.6, 131.4, 130.6, 130.0, 129.1, 128.4, 127.4, 124.3, 123.9, 123.5, 122.3, 120.6, 117.8, 117.4, 113.6, 113.2, 66.6.

HRMS (ESI) calcd for [M+Na]$^+$, C$_{24}$H$_{17}$O$_5$BrNa$^+$, m/z: 487.0157, 489.0137, observed: 487.0153, 489.0150.

cyclopentyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 55% yield, 98:2 e.r.; $[\alpha]_D^{25} = -53.7$ (c 0.264, CH$_2$Cl$_2$);
Determined by HPLC analysis [Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t₁ = 11.23 min, t₂ = 22.06 min];

^1^H NMR (400 MHz, CDCl₃) δ 1.19 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.36 (dd, J = 6.0, 3.2 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.14 (d, J = 9.2 Hz, 1H), 4.95 (dd, J = 5.6, 3.2 Hz, 3H), 1.52 – 1.30 (m, 2H), 1.05 (ddd, J = 46.8, 13.6, 6.8 Hz, 4H), 0.81 (dd, J = 9.6, 4.4 Hz, 2H), 0.56 (ddd, J = 17.6, 13.6, 6.4 Hz, 2H).

^1^C NMR (101 MHz, CDCl₃) δ 170.0, 157.5, 150.9, 147.2, 133.2, 130.6, 129.3, 128.2, 127.4, 124.1, 123.8, 123.7, 120.6, 117.6, 117.5, 114.1, 112.8, 78.8, 31.9, 31.8, 23.3, 23.2.

HRMS (ESI) calcd for [M+Na]^+ , C_{22}H_{20}O_{5}Na^+, m/z: 387.1208, observed: 387.1214.

methyl (aR)-3,6-dihydroxy-2-(2-hydroxy-6-methoxynaphthalen-1-yl)benzoate

white solid; 91% yield, 95.5:4.5 e.r.; [α]D²⁵ = -63.4 (c 0.404, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t₁ = 18.43 min, t₂ = 31.43 min];

^1^H NMR (400 MHz, CDCl₃) δ 10.75 (s, 1H), 7.75 (d, J = 9.2 Hz, 1H), 7.26 (d, J = 10.4 Hz, 2H), 7.18 – 7.07 (m, 3H), 7.03 (dd, J = 9.2, 2.4 Hz, 1H), 4.68 (s, 2H), 3.90 (s, 3H), 3.24 (s, 3H).

^1^C NMR (101 MHz, CDCl₃) δ 170.4, 157.1, 156.3, 149.4, 147.3, 130.1, 129.4, 128.1, 125.1, 123.9, 120.5, 119.7, 118.0, 117.9, 114.0, 112.5, 106.7, 55.4, 52.2.

HRMS (ESI) calcd for [M+H]^+ , C_{19}H_{17}O_{6}^+, m/z: 341.1025, observed: 341.1024.
methyl (αR)-3,6-dihydroxy-2-(2-hydroxy-7-methoxynaphthalen-1-yl)benzoate
white solid; 89% yield, 90.5:9.5 e.r.; \([\alpha]_D^{25} = -90.8\) (c 0.254, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpak ADH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, \(\lambda = 254\) nm, \(t_1 = 17.31\) min, \(t_2 = 25.58\) min];

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 10.75 (s, 1H), 7.72 (dd, \(J = 15.6, 9.2\) Hz, 2H), 7.29 (s, 1H), 7.09 (dd, \(J = 13.6, 9.2\) Hz, 2H), 7.00 (dd, \(J = 9.2, 2.4\) Hz, 1H), 6.44 (d, \(J = 2.4\) Hz, 1H), 5.07 (s, 1H), 4.77 (s, 1H), 3.68 (s, 3H), 3.24 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl₃) \(\delta\) 170.5, 159.0, 157.0, 151.7, 147.3, 134.4, 130.4, 129.8, 124.5, 123.9, 120.4, 118.2, 115.9, 114.9, 112.9, 112.5, 102.5, 55.2, 52.2.

HRMS (ESI) calcd for [M+Na]^+, C₁₉H₁₆O₆Na^+, m/z: 363.0845, observed: 363.0842

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methyl (αR)-2-(6-bromo-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate
white solid; 71% yield, 97.5:2.5 e.r.; \([\alpha]_D^{25} = -44.8\) (c 0.358, CH₂Cl₂);
Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, \( \lambda = 254 \) nm, \( t_1 = 9.38 \) min, \( t_2 = 12.58 \) min];

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.78 (s, 1H), 7.98 (d, \( J = 1.6 \) Hz, 1H), 7.77 (d, \( J = 9.2 \) Hz, 1H), 7.42 (dd, \( J = 9.2, 1.6 \) Hz, 1H), 7.29 (dd, \( J = 9.2, 1.6 \) Hz, 2H), 7.15 (d, \( J = 9.2 \) Hz, 1H), 7.06 (d, \( J = 9.2 \) Hz, 1H), 5.09 (s, 1H), 4.53 (s, 1H), 3.24 (s, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 170.2, 157.3, 151.3, 147.3, 131.6, 130.6, 130.2, 129.7, 125.4, 124.2, 120.9, 118.7, 117.7, 117.1, 114.2, 112.4, 52.3.

HRMS (ESI) calcd for [M+K]\(^+\), C\(_{18}\)H\(_{13}\)O\(_5\)BrK, m/z: 426.9583, 428.9563, observed: 426.9584, 428.9570.

\[
\text{Retention Time} \quad \text{Area} \quad \% \text{Area}
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methyl (a\(R\))-2-(7-bromo-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 53% yield, 96.5:3.5 e.r.; [\( \alpha \)]\(_D\)\(^{25} \) = -25.7 (c 0.384, CH\(_2\)Cl\(_2\));

Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, \( \lambda = 254 \) nm, \( t_1 = 10.60 \) min, \( t_2 = 12.92 \) min];

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.83 (s, 1H), 7.82 (d, \( J = 9.2 \) Hz, 1H), 7.69 (d, \( J = 8.8 \) Hz, 1H), 7.43 (dd, \( J = 8.8, 1.8 \) Hz, 1H), 7.31 (s, 1H), 7.27 (dd, \( J = 9.2, 3.6 \) Hz, 2H), 7.15 (d, \( J = 9.2 \) Hz, 1H), 5.14 (s, 1H), 4.56 (s, 1H), 3.25 (s, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 170.2, 157.4, 151.9, 147.3, 134.3, 130.6, 129.9, 127.5, 127.4, 125.6, 124.3, 122.0, 121.0, 118.0, 116.9, 113.3, 112.2, 52.3.

HRMS (ESI) calcd for [M+K]\(^+\), C\(_{18}\)H\(_{13}\)O\(_5\)BrK, m/z: 426.9583, 428.9563, observed: 426.9584, 428.9570.
methyl (aR)-3,6-dihydroxy-2-(2-hydroxy-6-methoxynaphthalen-1-yl)benzoate
white solid; 74% yield, 96.5:3.5 e.r.; \([\alpha]_D^{25} = -74.6\) (c 0.556, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t₁ = 12.76 min, t₂ = 17.23 min];
¹H NMR (400 MHz, CDCl₃) δ 10.80 (s, 1H), 8.02 (d, J = 1.6 Hz, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.62 (dd, J = 8.8, 1.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.27 (dd, J = 8.8, 3.2 Hz, 3H), 7.14 (d, J = 9.2 Hz, 1H), 4.97 (d, J = 74.8 Hz, 2H), 3.25 (s, 3H).
¹³C NMR (101 MHz, CDCl₃) δ 170.4, 157.1, 151.2, 147.4, 140.7, 136.6, 132.2, 131.0, 129.4, 128.9, 127.3, 127.2, 127.0, 126.1, 124.1, 124.1, 120.6, 118.0, 118.0, 113.8, 112.6, 52.3.
white solid; 88% yield, 93.5:6.5 e.r.; \([\alpha]_D^{25} = -74.0\) (c 0.602, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, \(\lambda = 254\) nm, \(t_1 = 10.19\) min, \(t_2 = 13.88\) min];

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 10.80 (s, 1H), 8.01 (d, \(J = 1.6\) Hz, 1H), 7.89 (d, \(J = 9.2\) Hz, 1H), 7.61 (dd, \(J = 8.8, 2.0\) Hz, 1H), 7.52 – 7.44 (m, 2H), 7.36 (t, \(J = 7.6\) Hz, 1H), 7.28 (dd, \(J = 9.2, 7.6\) Hz, 2H), 7.22 (s, 1H), 7.18 (d, \(J = 7.6\) Hz, 1H), 7.13 (d, \(J = 9.2\) Hz, 1H), 5.16 (s, 1H), 4.67 (s, 1H), 3.25 (s, 3H), 2.44 (s, 3H).

\(^13\)C NMR (101 MHz, CDCl₃) \(\delta\) 170.4, 157.1, 151.1, 147.4, 140.7, 138.5, 136.8, 132.1, 131.0, 129.4, 128.8, 128.1, 128.0, 127.1, 126.4, 124.1, 120.6, 118.0, 117.9, 113.7, 112.6, 52.3, 21.6.

HRMS (ESI) calcd for \([M+K]^+\), C\(_{25}\)H\(_{20}\)O\(_5\)K\(^+\), m/z: 439.0948, observed: 439.0948.

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methy C\(_{25}\)H\(_{20}\)O\(_6\)Na\(^+\), m/z: 439.1158, observed: 439.1159.
methyl (aR)-2-(6-(furan-3-yl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate
white solid; 88% yield, 94.5:5.5 e.r.; [a]D^25 = -134.7 (c 0.284, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t₁ = 12.91 min, t₂ = 18.02 min];

^1H NMR (400 MHz, CDCl₃) δ 10.79 (s, 1H), 7.84 (dd, J = 24.8, 16.0 Hz, 3H), 7.49 (dd, J = 11.2, 1.2 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.15 (dd, J = 18.0, 9.2 Hz, 2H), 6.79 (s, 1H), 5.14 (s, 1H), 4.66 (s, 1H), 3.23 (s, 3H).

^13C NMR (101 MHz, CDCl₃) δ 170.4, 157.1, 151.0, 147.3, 143.9, 138.7, 132.0, 130.6, 129.4, 128.0, 126.2, 1256.0, 124.5, 124.2, 124.0, 120.6, 118.1, 117.8, 113.9, 112.5, 108.8, 52.3 .

HRMS (ESI) calcd for [M+Na]^+, C_{22}H_{16}O_{6}Na^+, m/z: 399.0845, observed: 399.0845.
methyl (aR)-2-(6-(furan-2-yl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate
white solid; 84% yield, 96:4 e.r.; [α]D 25 = -83.6 (c 0.560, CH2Cl2);
Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t1 = 11.00 min, t2 = 16.04 min];
1H NMR (400 MHz, CDCl3) δ 10.80 (s, 1H), 8.12 (d, J = 1.6 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.63 (dd, J = 8.8, 1.6 Hz, 1H), 7.50 (d, J = 1.2 Hz, 1H), 7.27 (d, J = 2.0 Hz, 2H), 7.18 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H), 6.70 (dd, J = 3.2, 0.4 Hz, 1H), 6.50 (dd, J = 3.2, 1.6 Hz, 1H), 5.16 (s, 1H), 4.67 (s, 1H), 3.22 (s, 3H).
13C NMR (101 MHz, CDCl3) δ 170.4, 157.1, 153.8, 151.2, 147.3, 142.2, 132.2, 126.6, 124.1, 124.0, 123.9, 122.5, 120.6, 118.2, 117.8, 114.1, 112.5, 111.8, 105.3, 52.3.

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methyl (aR)-2-(6-(4-fluorophenyl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate
white solid; 63% yield, 97:3 e.r.; [α]D 25 = -102.0 (c 0.278, CH2Cl2);
Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t1 = 11.00 min, t2 = 16.05 min];
1H NMR (400 MHz, CDCl3) δ 10.80 (s, 1H), 7.97 (d, J = 1.6 Hz, 1H), 7.63 (dd, J = 8.8, 5.2 Hz, 2H), 7.57 (dd, J = 8.8, 1.6 Hz, 1H), 7.30 (dd, J = 9.2, 4.0 Hz, 2H), 7.23 (s, 1H), 7.19 – 7.12 (m, 3H), 5.13 (s, 1H), 4.63 (s, 1H), 3.26 (s, 3H).
13C NMR (101 MHz, CDCl3) δ 170.4, 163.7, 161.3, 157.2, 151.2, 147.3, 143.6, 136.8, 136.8, 135.7, 132.1, 130.9, 129.4, 128.8, 128.7, 126.8, 126.0, 124.2, 124.1, 120.7, 118.1, 117.7, 115.9.
115.7, 113.8, 112.5, 52.3.

HRMS (ESI) calcd for [M+K]^+, C_{24}H_{17}O_{5}FK^+, m/z: 443.0697, observed: 443.0693.

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methyl (aR)-2-(6-(4-(tert-butyl)phenyl)-2-hydroxynaphthal en-1-yl)-3,6-dihydroxybenzoate white solid; 95% yield, 95:5 e.r.; [α]_D^{25} = -60.8 (c 0.522, CH₂Cl₂); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t₁ = 8.21 min,t₂ = 10.72 min];

\[\begin{align*}
\text{HO} & \quad \text{MeO} \quad \text{C} \\
\text{HO} & \quad \text{OH} \\
\text{OMe} & \quad \text{C} \\
\text{OH} & \quad \text{OH} \\
\end{align*}\]

1H NMR (400 MHz, CDCl₃) δ 10.80 (s, 1H), 8.01 (d, J = 1.6 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 3H), 7.50 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 9.2 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 5.09 (s, 1H), 4.65 (s, 1H), 3.25 (s, 3H), 1.37 (s, 9H).

13C NMR (101 MHz, CDCl₃) δ 170.4, 157.2, 151.1, 150.4, 147.4, 137.8, 136.5, 132.0, 131.0, 129.5, 127.0, 126.8, 125.9, 125.8, 124.0, 120.6, 117.9, 117.9, 113.7, 112.5, 52.3, 34.6, 31.4, 29.7.

HRMS (ESI) calcd for [M+K]^+, C_{28}H_{26}O_{5}K^+, m/z: 481.1417, observed: 481.1412.

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methyl (aR)-2-((6-(3,4-dichlorophenyl)-2-hydroxy)naphthalen-1-yl)-3,6-dihydroxybenzoate
white solid; 80% yield, 95:5 e.r.; $[\alpha]_D^{25} = -73.7$ (c 0.590, CH$_2$Cl$_2$); Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, $\lambda$ = 254 nm, $t_1 = 12.51$ min, $t_2 = 19.16$ min];

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 170.3, 157.2, 151.6, 147.3, 140.8, 134.2, 133.0, 132.5, 131.4, 131.0, 130.8, 129.2, 129.0, 126.4, 126.3, 126.3, 124.5, 124.1, 120.8, 118.4, 117.5, 113.9, 112.5, 52.3.


methyl (aR)-3,6-dihydroxy-2-(2-hydroxy-6-(2-methylprop-1-en-1-yl)naphthalen-1-yl)benzoate
white solid; 88% yield, 95:5 e.r.; $[\alpha]_D^{25} = -79.4$ (c 0.478, CH$_2$Cl$_2$);
Determined by HPLC analysis\(^1\) [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, \(\lambda = 254 \text{ nm}, t_1 = 7.26 \text{ min}, t_2 = 9.42 \text{ min} \); 
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.78 (s, 1H), 7.79 (d, \(J = 9.2 \text{ Hz}, 1\)H), 7.64 (s, 1H), 7.25 (dd, \(J = 4.8, 1.6 \text{ Hz}, 2\)H), 7.22 (d, \(J = 9.2 \text{ Hz}, 1\)H), 7.11 (dd, \(J = 8.8, 5.2 \text{ Hz}, 2\)H), 6.35 (s, 1H), 5.07 (s, 1H), 4.68 (s, 1H), 3.23 (s, 3H), 1.93 (dd, \(J = 8.4, 0.8 \text{ Hz}, 6\)H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.4, 157.1, 150.8, 147.3, 135.9, 134.4, 131.2, 130.6, 129.1, 129.0, 127.4, 124.7, 123.9, 123.1, 120.4, 118.0, 117.6, 113.6, 112.6, 52.2, 27.0, 19.6 .
HRMS (ESI) calcd for [M+K]\(^+\), \(C_{22}H_{20}O_5K^+\), m/z: 403.0948, observed: 403.0948.

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methyl (\(aR\))-(E)-3,6-dihydroxy-2-(2-hydroxy-6-(pent-1-en-1-yl)naphthalen-1-yl)benzoate white solid; 86% yield, 93:7 e.r.; \([\alpha]_D^{25} = -81.5 \text{ (c 0.464, CH}_2\text{Cl}_2\); Determined by HPLC analysis\(^1\) [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, \(\lambda = 254 \text{ nm}, t_1 = 7.45 \text{ min}, t_2 = 10.42 \text{ min} \); 
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.79 (s, 1H), 7.78 (d, \(J = 9.2 \text{ Hz}, 1\)H), 7.66 (d, \(J = 1.2 \text{ Hz}, 1\)H), 7.44 (dd, \(J = 8.8, 1.6 \text{ Hz}, 1\)H), 7.27 (d, \(J = 9.2 \text{ Hz}, 1\)H), 7.21 (d, \(J = 9.2 \text{ Hz}, 1\)H), 7.11 (dd, \(J = 10.4, 9.2 \text{ Hz}, 2\)H), 6.50 (d, \(J = 15.6 \text{ Hz}, 1\)H), 6.29 (dt, \(J = 15.6, 6.8 \text{ Hz}, 1\)H), 5.05 (s, 1H), 4.63 (s, 1H), 3.22 (s, 3H), 2.22 (td, \(J = 8.0, 1.2 \text{ Hz}, 2\)H), 1.52 (dd, \(J = 14.8, 7.6 \text{ Hz}, 2\)H), 0.97 (t, \(J = 7.6 \text{ Hz}, 3\)H).
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.4, 157.1, 150.8, 147.3, 133.6, 132.0, 131.2, 130.6, 129.6, 129.4, 125.6, 125.2, 124.0, 123.7, 120.5, 117.9, 117.7, 113.9, 112.5, 52.2, 35.2, 22.6, 13.8 .
HRMS (ESI) calcd for [M+K]\(^+\), \(C_{23}H_{22}O_5K^+\), m/z: 417.1104, observed: 417.1102.
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white solid; 94% yield, 94:6 e.r.; [α]_D^{25} = -79.3 (c 0.440, CH₂Cl₂); Determined by HPLC analysis (Daicel chiralpakODH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t₁ = 8.68 min, t₂ = 14.37 min);

^1^H NMR (400 MHz, CDCl₃) δ 10.80 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.35 (dd, J = 8.8, 1.6 Hz, 1H), 7.29 (dd, J = 6.0, 3.2 Hz, 5H), 7.24 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H), 5.17 (s, 1H), 4.70 (s, 1H), 3.27 (s, 3H), 2.29 (s, 3H).

^13^C NMR (101 MHz, CDCl₃) δ 170.4, 157.1, 151.1, 147.4, 141.5, 137.6, 135.6, 131.8, 130.8, 130.4, 130.0, 129.2, 129.0, 128.1, 127.4, 125.9, 124.0, 123.2, 120.6, 118.0, 117.9, 113.7, 112.6, 52.3, 20.6.

HRMS (ESI) calcd for [M+Na]^+, C_{25}H_{20}O_{5}Na^+, m/z: 423.1208, observed: 423.1208.

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methyl (aR)-2-(6-(benzo[d][1,3]dioxol-5-yl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate
white solid; 93% yield, 95:5 e.r.; [\alpha]_D^{25} = -127.8 (c 0.352, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 75/25, 1.0 mL/min, \lambda = 254 nm, t₁ = 9.28 min, t₂ = 18.35 min];

\[^{1}\text{H} \text{NMR (400 MHz, CDCl}_3\text{) \delta} 10.79 \text{ (s, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.53 (dd, J = 8.8, 2.0 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.17 – 7.09 (m, 3H), 6.90 (d, J = 8.4 Hz, 1H), 5.99 (s, 2H), 5.13 (s, 1H), 4.66 (s, 1H), 3.25 (s, 3H).}

\[^{13}\text{C NMR (101 MHz, CDCl}_3\text{) \delta} 170.4, 157.1, 151.1, 148.2, 147.3, 147.1, 136.4, 135.1, 131.9, 130.9, 129.4, 126.9, 125.6, 124.1, 124.1, 120.7, 120.6, 118.0, 117.9, 113.7, 112.5, 108.7, 107.6, 101.2, 52.3 .

HRMS (ESI) calcd for [M+K]⁺, C_{25}H_{18}O_7K⁺, m/z: 469.0690, observed: 469.0687.

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methyl (aR)-3,6-dihydroxy-2-(2-hydroxy-6-(3-methoxyphenyl)naphthalen-1-yl)benzoate
white solid; 91% yield, 95.5:4.5 e.r.; [\alpha]_D^{25} = -73.0 (c 0.634, CH₂Cl₂); Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, \lambda = 254 nm, t₁ = 14.82 min, t₂ = 19.89 min];

\[^{1}\text{H NMR (400 MHz, CDCl}_3\text{) \delta} 10.79 \text{ (s, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.61 (dd, J = 8.8, 1.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.26 (dd, J = 13.2, 8.8 Hz, 4H), 7.20 (s, 1H), 7.13 (d, J = 9.2 Hz, 1H), 6.91 (dd, J = 8.0, 2.4 Hz, 1H), 4.88 (s, 2H), 3.87 (s, 3H), 3.25 (s, 3H).}

\[^{13}\text{C NMR (101 MHz, CDCl}_3\text{) \delta} 170.4, 160.0, 157.2, 151.2, 147.4, 142.2, 136.5, 132.2, 131.0, 129.9, 129.4, 127.0, 126.2, 124.1, 124.1, 120.6, 119.7, 118.0, 117.8, 113.8, 113.0, 112.7, 112.5, 55.4, 52.3 .
HRMS (ESI) calcd for [M+K]+, C_{25}H_{20}O_{6}K+, m/z: 455.0897, observed: 455.0891.

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methyl (aR)-2-(6-(4-ethoxyphenyl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 33% yield, 96.5:3.5 e.r.; [α]_D^{25} = -107.1 (c 0.160, CH_{2}Cl_{2}); Determined by HPLC analysis[Daiel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t₁ = 13.50 min, t₂ = 16.14 min);

^1^H NMR (400 MHz, CDCl₃) δ 10.81 (s, 1H), 7.97 (d, J = 1.6 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.69 – 7.51 (m, 3H), 7.29 (dd, J = 13.6, 9.2 Hz, 2H), 7.22 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 9.2 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 5.03 (s, 1H), 4.63 (s, 1H), 4.09 (q, J = 7.2 Hz, 2H), 3.26 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H).

^13^C NMR (101 MHz, CDCl₃) δ 170.4, 158.6, 157.2, 150.9, 147.3, 136.3, 133.0, 131.7, 130.9, 129.5, 128.2, 126.8, 125.3, 124.0, 120.6, 117.9, 117.8, 114.9, 113.6, 112.5, 63.6, 52.3, 14.9.

HRMS (ESI) calcd for [M+K]^+, C_{26}H_{22}O_{6}K^+, m/z: 469.1053, observed: 469.1055.

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<td>2</td>
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<td>95.47</td>
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32
Retention Time | Area      | % Area  
--- | --- | ---  
1 | 13.141 | 525530 | 3.52  
2 | 16.495 | 14423843 | 96.48  

methyl (aR)-3,6-dihydroxy-2-(6'-hydroxy-[1,2'-binaphthalen]-5'-yl)benzoate  
white solid; 98% yield, 94:6 e.r.; $[\alpha]_D^{25} = -68.4$ (c 0.886, CH$_2$Cl$_2$); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, $\lambda = 254$ nm, $t_1 = 12.39$ min,$t_2 = 15.17$ min];  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.74 (s, 1H), 7.90 – 7.75 (m, 5H), 7.48 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 7.23 (dd, $J = 9.2$, 1.2 Hz, 3H), 7.16 (s, 1H), 7.07 (d, $J = 9.2$ Hz, 1H), 5.20 (s, 2H), 3.24 (s, 3H).  
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.5, 157.2, 151.3, 147.4, 139.8, 136.4, 133.9, 132.1, 131.7, 130.9, 130.0, 129.2, 129.1, 128.4, 127.8, 127.3, 126.2, 126.0, 125.9, 125.5, 124.1, 123.4, 120.6, 118.0, 118.0, 113.8, 112.6, 52.4 .  
HRMS (ESI) calcd for [M+K]$^+$, C$_{28}$H$_{20}$O$_5$K$^+$, m/z: 475.0948, observed: 475.0949.

Retention Time | Area      | % Area  
--- | --- | ---  
1 | 11.744 | 17725251 | 50.67  
2 | 14.677 | 17253255 | 49.33  

methyl (aR)-3,6-dihydroxy-2-(2-hydroxy-6-pentylnaphthalen-1-yl)benzoate  
white solid; 80% yield, 95.5:4.5 e.r.; $[\alpha]_D^{25} = -37.7$ (c 0.718, CH$_2$Cl$_2$); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, $\lambda = 254$ nm, $t_1 = 6.70$ min,$t_2 = 8.44$ min];  
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.77 (s, 1H), 7.77 (d, $J = 9.2$ Hz, 1H), 7.58 (s, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 7.24 – 7.17 (m, 2H), 7.11 (d, $J = 9.2$ Hz, 1H), 7.08 (d, $J = 8.4$ Hz, 1H), 5.04 (s, 1H), 4.63 (s, 1H), 3.22 (s, 3H), 2.79 – 2.64 (m, 2H), 1.75 – 1.62 (m, 2H), 1.40 – 1.29 (m, 4H),
0.89 (t, J = 6.8 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.5, 157.0, 150.4, 147.3, 138.5, 131.3, 130.2, 129.3, 128.9, 126.7, 123.9, 123.4, 120.4, 118.2, 117.4, 113.6, 112.6, 52.2, 35.7, 31.6, 31.0, 22.6, 14.1. HRMS (ESI) calcd for [M+K]$^+$, C$_{23}$H$_{24}$O$_5$K$^+$, m/z: 419.1261, observed: 419.1260.

\[
\begin{array}{cccc}
\text{Retention Time} & \text{Area} & \% \text{Area} \\
1 & 6.650 & 3356553 & 49.90 \\
2 & 8.440 & 3370092 & 50.10 \\
\end{array}
\]

methyl (aR)-3,6-dihydroxy-2-(2-hydroxy-6-isobutyl)naphthalen-1-yl)benzoate
white solid; 86% yield, 95.5:4.5 e.r.; $[\alpha]_D^{25}$ = -48.1 (c 0.606, CH$_2$Cl$_2$); Determined by HPLC analysis [Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, $\lambda$ = 254 nm, $t_1$ = 6.64 min, $t_2$ = 8.20 min];

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.77 (s, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.55 (s, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.22 (d, J = 9.2 Hz, 1H), 7.17 (dd, J = 8.8, 1.6 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 7.08 (d, J = 8.8 Hz, 1H), 5.03 (s, 1H), 4.65 (s, 1H), 3.21 (s, 3H), 2.59 (d, J = 7.2 Hz, 2H), 1.93 (dt, J = 13.6, 6.8 Hz, 1H), 0.92 (dd, J = 6.8, 0.8 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.5, 157.0, 150.4, 147.3, 137.3, 131.4, 130.2, 129.4, 129.2, 127.6, 123.9, 123.2, 120.4, 118.2, 117.4, 113.5, 112.6, 52.2, 45.2, 30.2, 22.5, 22.4. HRMS (ESI) calcd for [M+K]$^+$, C$_{22}$H$_{24}$O$_5$K$^+$, m/z: 405.1104, observed: 405.1107.

\[
\begin{array}{cccc}
\text{Retention Time} & \text{Area} & \% \text{Area} \\
1 & 6.579 & 6549990 & 49.67 \\
2 & 8.187 & 6636025 & 50.33 \\
\end{array}
\]
methyl (aR)-3,6-dihydroxy-2-(2-hydroxy-6-methoxynaphthalen-1-yl)-4-methoxybenzoate
white solid; 84% yield, 92.5:7.5 e.r.; \([\alpha]_D^{25} = -4.0\) (c 0.602, CH₂Cl₂); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 75/25, 1.0 mL/min, \(\lambda = 254\) nm, \(t_1 = 19.38\) min, \(t_2 = 32.00\) min];

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 11.40 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.99 (dd, J = 9.2, 2.8 Hz, 1H), 6.65 (s, 1H), 5.14 (s, 2H), 3.95 (s, 3H), 3.88 (s, 3H), 3.18 (s, 3H).

\(^{13}\)C NMR (101 MHz, CDCl₃) \(\delta\) 171.0, 158.9, 155.8, 153.1, 148.6, 137.6, 129.8, 128.3, 125.4, 119.1, 118.9, 117.9, 116.2, 106.5, 104.7, 100.6, 56.3, 55.3, 51.9.


methyl (aR)-4-ethyl-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate
white solid; 71% yield, 90:10 e.r.; \([\alpha]_D^{25} = 9.8\) (c 0.430, CH₂Cl₂); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, \(\lambda = 254\) nm, \(t_1 = 11.97\) min, \(t_2 = 15.63\) min];
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.88 (s, 1H), 7.86 (d, $J = 9.2$ Hz, 1H), 7.84 – 7.78 (m, 1H), 7.40 – 7.31 (m, 2H), 7.27 (d, $J = 9.2$ Hz, 1H), 7.21 – 7.14 (m, 1H), 7.04 (s, 1H), 4.64 (d, $J = 98.4$ Hz, 2H), 3.19 (s, 3H), 2.73 (q, $J = 7.6$ Hz, 2H), 1.28 (t, $J = 7.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.5, 157.2, 151.2, 145.5, 140.8, 133.1, 130.7, 129.1, 128.2, 127.3, 123.9, 123.6, 119.4, 117.5, 116.7, 114.0, 109.8, 52.0, 23.8, 13.1.

HRMS (ESI) calcd for [M+K]$^+$, C$_{20}$H$_{18}$O$_5$K$, m/z$: 377.0791, observed: 377.0789.

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<td>2</td>
<td>16.287</td>
<td>49.98</td>
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methyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)-4-isopropylbenzoate

white solid; 47% yield, 87.5:12.5 e.r.; $[\alpha]_{D}^{25} = 18.3$ (c 0.284, CH$_2$Cl$_2$); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/i-PrOH = 85/15, 1.0 mL/min, $\lambda = 254$ nm, $t_1 = 7.94$ min, $t_2 = 14.10$ min];

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.87 (s, 1H), 7.86 (d, $J = 9.2$ Hz, 1H), 7.83 (dd, $J = 5.6, 3.6$ Hz, 1H), 7.36 (dd, $J = 5.6, 3.6$ Hz, 2H), 7.28 (d, $J = 9.2$ Hz, 1H), 7.20 – 7.15 (m, 1H), 7.09 (s, 1H), 5.02 (s, 1H), 4.66 (s, 1H), 3.33 (dt, $J = 13.6, 6.8$ Hz, 1H), 3.19 (s, 3H), 1.28 (d, $J = 6.8$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.4, 157.4, 151.2, 145.3, 140.5, 133.1, 130.7, 129.2, 128.2, 127.4, 123.9, 123.6, 117.4, 117.1, 116.8, 114.0, 109.7, 52.0, 28.0, 22.1.

HRMS (ESI) calcd for [M+K]$^+$, C$_{21}$H$_{20}$O$_5$K$, m/z$: 391.0948, observed: 391.0948.
methyl (aR)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)-4-isobutylenzoate
white solid; 92% yield, 91.5:8.5 e.r.; $[\alpha]_D^{25} = 20.7$ (c 0.702, CH$_2$Cl$_2$); Determined by HPLC analysis [Daicel chiralpak ADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, $\lambda = 254$ nm, t$_1 = 8.81$ min, t$_2 = 18.10$ min];

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.83 (s, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.39 – 7.31 (m, 2H), 7.26 (d, J = 9.2 Hz, 1H), 7.16 (dd, J = 5.2, 4.4 Hz, 1H), 6.98 (s, 1H), 5.29 – 4.03 (m, 2H), 3.19 (s, 3H), 2.58 (dd, J = 9.2, 7.2 Hz, 2H), 2.01 (dt, J = 13.6, 6.8 Hz, 1H), 0.95 (dd, J = 6.8, 4.4 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.5, 156.8, 151.2, 145.9, 138.6, 133.0, 130.7, 129.2, 128.2, 127.3, 123.9, 123.5, 121.2, 117.5, 116.9, 114.1, 110.1, 52.0, 39.9, 28.6, 22.6, 22.5.

HRMS (ESI) calcd for [M+K]$^+$, C$_{22}$H$_{22}$O$_5$K$^+$, m/z: 405.1104, observed: 405.1106.
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<th>Retention Time</th>
<th>Area</th>
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</tr>
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8. X-ray crystals structure of the product 3da:

Empirical formula \( \text{C}_{21}\text{H}_{20}\text{O}_{5} \)
Formula weight 352.37
Temperature/K 290.64(10)
Crystal system monoclinic
Space group P21
a/Å 8.0345(2)
b/Å 12.6015(4)
c/Å 9.2114(3)
\( \alpha^\circ \) 90
\( \beta^\circ \) 107.576(3)
\( \gamma^\circ \) 90
Volume/Å\(^3\) 889.10(5)
Z 2
\( \rho_{\text{calc}} \)/cm\(^3\) 1.316
\( \mu \)/mm\(^{-1}\) 0.770
F(000) 372.0
Crystal size/mm\(^3\) 0.6 × 0.6 × 0.5
Radiation CuK\( \alpha \) (\( \lambda = 1.54184 \))
2\( \Theta \) range for data collection/° 10.072 to 134.048
Index ranges -8 \( \leq h \leq 9, -15 \leq k \leq 13, -10 \leq l \leq 11 \)
Reflections collected 8560
Independent reflections 2889 [Rint = 0.0347, Rsigma = 0.0282]
Data/restraints/parameters 2889/1/239
Goodness-of-fit on F\(^2\) 1.043
Final R indexes [I>=2\( \sigma \) (I)] R1 = 0.0513, wR2 = 0.1314
Final R indexes [all data] R1 = 0.0521, wR2 = 0.1330
Largest diff. peak/hole / e Å\(^3\) 0.52/-0.46
Flack parameter -0.06(13)
9. X-ray crystal structure of \( L\)-RaPr\(_2\)/Co(ClO\(_4\))\(_2\) complex.

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<td>Temperature/K</td>
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<td>Crystal system</td>
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<td>( \alpha/\degree )</td>
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<tr>
<td>( \beta/\degree )</td>
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<tr>
<td>( \gamma/\degree )</td>
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<td>Volume/(\AA^3)</td>
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<td>( Z )</td>
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<tr>
<td>( \rho \text{calc/cm}^3 )</td>
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<td>( \mu/\text{mm}^{-1} )</td>
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<td>( F(000) )</td>
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<tr>
<td>( \text{Crystal size/mm}^3 )</td>
<td>(0.35 \times 0.3 \times 0.25)</td>
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<tr>
<td>Radiation</td>
<td>MoK(\alpha\ (\lambda=0.71073))</td>
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<td>( 2\Theta \text{ range for data collection/\degree} )</td>
<td>5.872 to 52.74</td>
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<td>Index ranges</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Goodness-of-fit on F(_2)</td>
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<td>Final ( R ) indexes ([I&gt;=2\sigma(I)])</td>
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<td>Largest diff. peak/hole / e (\AA^{-3})</td>
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10. NMR spectra