Synthesis of C–N Axially Chiral Biaryls *via* Asymmetric Chan-Lam Coupling

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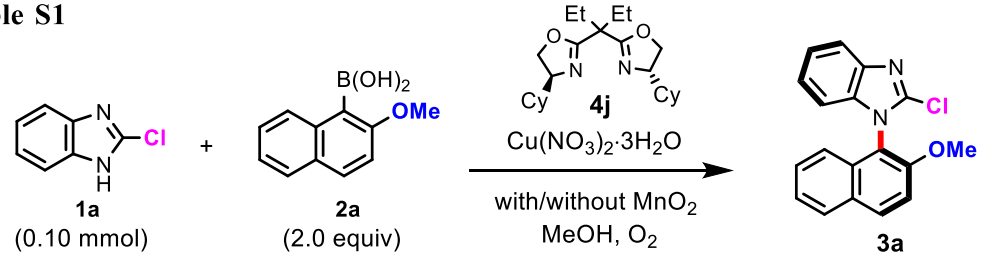
Table of contents

1. The ratio and amount optimizations of copper and ligand **4j**.....S2
2. General considerations.....S3
3. Experimental procedure, spectroscopic and numerical data
   3-1. Synthesis of ligand **4j**.....S5
   3-2. Preparation of optically active catalyst Stock Solution (A).....S7
   3-3. Preparation of none-optically active catalyst Stock Solution (B).....S7
   3-4. Asymmetric coupling between imidazole and boronic acid.....S7
   3-5. Synthesis of racemic coupling product between imidazole and aryl boronic acid.....S7
   3-6. Spectroscopic and numerical data of the coupling product.....S9
   3-7. Large scale synthesis of **3b**.....S13
4. Transformation of coupling product **3b**
   4-1. Recrystallization of **3b**.....S55
   4-2. Suzuki coupling.....S57
   4-3. Sonogashira coupling.....S59
   4-4. Reductive dehalogenation.....S62
   4-5. Metallative methylation.....S64
5. X-Ray Data of **3b**.....S66
6. Rotational barrier of (*S*)-**3w**.....S68
7. Experimental references.....S69
8. ^{1}H, ^{13}C, and ^{19}F NMR spectra of new compounds.....S70

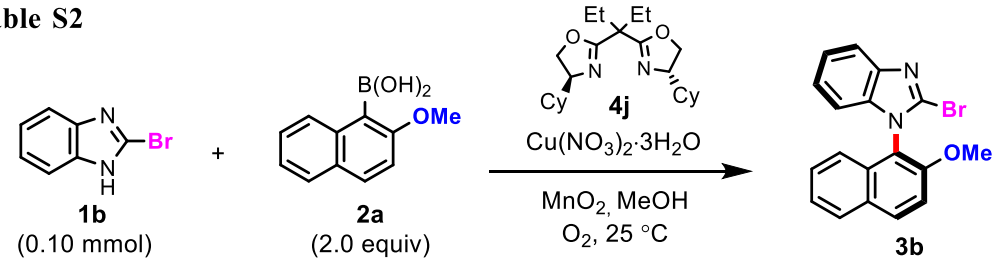
1. The ratio and amount optimizations of copper and ligand 4j:

Table S1



entry	Cu cat. : **4j** (mol%)	temp.	MnO_2	yield (%) of **3a**	ee (%) of **3a**
1	25 : 0	25 °C	+	33	0
2	25 : 0	25 °C	–	9	0
3	25 : 12.5	25 °C	+	95	48
4	25 : 12.5	25 °C	–	16	38
5	25 : 25	25 °C	+	90	66
6	25 : 25	25 °C	–	22	64
7	25 : 50	100 °C	+	89	68
8	25 : 50	75 °C	+	90	72
9	25 : 50	50 °C	+	90	72
10	25 : 50	25 °C	+	94	72
11	25 : 50	25 °C	–	37	78
12	25 : 50	–10 °C	+	12	80

Table S2



entry	Cu cat. : **4j** (mol%)	time	ratio (%) **1b** : **3b**	ee (%) of **3b**
1	25 : 50	1 h	95 : 5	–
2	25 : 50	3 h	69 : 31	86
3	25 : 50	5 h	37 : 63	86
4	25 : 50	7 h	2 : 98	84
5	25 : 50	**9 h**	0 : 100	84
6	50 : 100	22 h	0 : 100	82
7	25 : 50	22 h	0 : 100	86
8	13 : 26	22 h	0 : 100	80
9	8 : 16	22 h	0 : 100	80
10	**4 : 8**	22 h	0 : 100	82
11	2 : 4	22 h	32 : 68	84
12	1 : 2	22 h	95 : 5	86

2. General considerations:

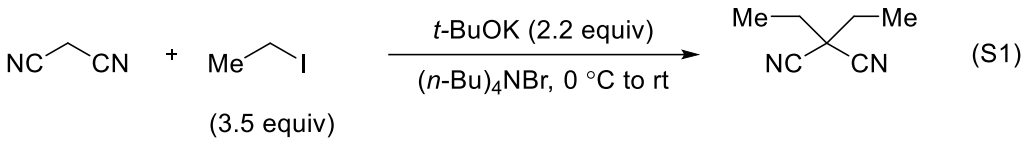
Reagents: A test tube and a septum cap were used for the coupling reaction and the reaction temperature was controlled using Chemist Plaza CP-10 purchased from SIBATA SCIENTIFIC TECHNOLOGY. Anhydrous THF was purchased from Kanto Chemical and purified with a Glass Contour solvent dispensing system (Nikko Hansen) using two packed columns of activated molecular sieves. Wako 1st Grade MeOH was used for the coupling reactions. $Cu(NO_3)_2.3H_2O$, 99.9% and MnO_2, 99.5% were purchased from FUJIFILM Wako Pure Chemical and used without further purification. (4*S*,4'*S*)-2,2'-(propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) **4a** was purchased from Tokyo Chemical Industry and used without further purification. Chiral bisoxazoline ligands ((4S,4'S)-2,2'-(pentane-3,3-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (**4b**),[4,3] (4*S*,4'S)-2,2'-(1,3-diphenylpropane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (**4c**),[4,3] (4*S*,4'*S*)-2,2'-(2,6-dimethylheptane-4,4-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (**4d**),[4,3] (4*S*,4'*S*)-2,2'-(cyclopentane-1,1-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (**4e**),[4,6] (*S*)-4-((*R*)-sec-butyl)-2-(2-((*S*)-4-((*S*)-sec-butyl)-4,5-dihydrooxazol-2-yl)propan-2-yl)-4,5-dihydrooxazole (**4f**),[5,7] (4*S*,4'*S*)-2,2'-(propane-2,2-diyl)bis(4-ethyl-4,5-dihydrooxazole) (**4g**),[5,8] (4*S*,4'*S*)-2,2'-(propane-2,2-diyl)bis(4-cyclohexyl-4,5-dihydrooxazole) (**4h**),[5,9] (*S*)-4-((*R*)-sec-butyl)-2-(3-((*S*)-4-((*S*)-sec-butyl)-4,5-dihydrooxazol-2-yl)pentan-3-yl)-4,5-dihydrooxazole (**4i**)),[5,10] 2-methoxy-1-napthyl boronic acid[11] and 2-methoxymethyl-1-napthyl boronic acid[12–14] were prepared according to the literature. All other reagents were purchased from FUJIFILM Wako Pure Chemical, Tokyo Chemical Industry, Sigma-Aldrich (Merck), NACALAI TESQUE, Kishida Chemical, Chem Impex International, Oakwood Products, and Combi-Blocks and used without further purification. Flash chromatography was performed with silica gel 60N, spherical neutral (40–50 μm), purchased from Kanto Chemical. All reactions were monitored by thin-layer chromatography (TLC) on glass-backed silica gel 60 F^{254}, 0.2 mm plates (Merck), and compounds were visualized under UV light (254 nm) and dipped with TLC stain with ceric ammonium molybdate solution.

Analytical methods: IR spectra were recorded by a Bruker FT-IR ALPHA. High-resolution mass spectra (HRMS) were measured by Waters AQUITY H-class RDa. Melting points were measured by a SANSYO SMP-300 melting point apparatus. Optical rotations were measured by ATAGO AP-300 automatic polarimeter. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a JEOL JMN-ECA-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz, ^{19}F: 470 MHz), a JEOL JMN-ECS-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz). Instrument with chemical shifts reported in ppm relative to the residual deuterated solvent. GC spectra were taken on SHIMADZU GC-2010. Chiral HPLC measurements

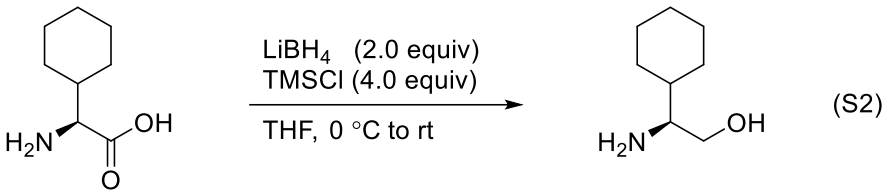
were performed on a Shimadzu system with a quaternary low-pressure LC-20AD pump, an automatic SIL-20A HT injector, a CTO-10AS oven and a SPD-M20 with diode array detector (DAD). The injection volume was 1.0–10 μL, the temperature of the oven set to 30 °C and the concentration of the sample around 0.10–1.0 mg/L. Preparative recycling gel permeation chromatography (GPC) was performed with LaboACE LC-5060 Plus II equipped with JAIGEL-2HR Plus column (chloroform as an eluent). X-ray single crystal diffraction data were recorded on Rigaku XtaLAB mini II. The chromatogram of the racemic compound is on the left, the one of the enantiomerically enriched compound is on the right. "Yield" refers to the isolated yields of compounds showing at most only trace peaks in the ^{1}H NMR spectra that are not attributable to the assigned structure. ^{1}H NMR, ^{13}C NMR and melting points (where applicable) of all known compounds were taken. All new products were further characterized by ^{13}C NMR, IR, and high resolution mass spectrum (HRMS). The absolute stereochemistry of coupling product (*S*)-**3b** was confirmed by a single-crystal X-ray structure analysis.

3. Experimental procedure, spectroscopic and numerical data:

3-1. Synthesis of ligand 4j

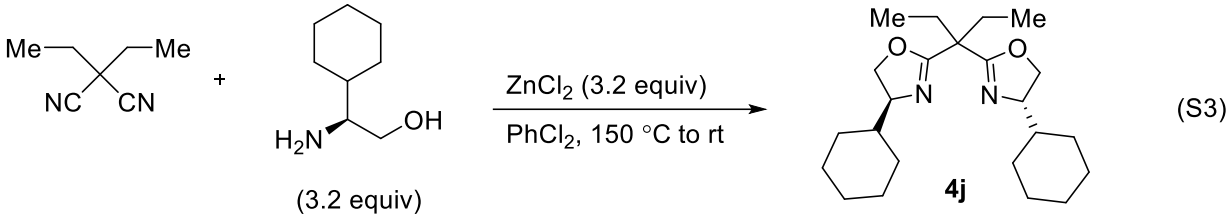


Diethyl malononitrile:[1] Malononitrile (20 g, 0.30 mol), tetra(*n*-butylammonium)bromide (3.9 g, 12 mmol) and iodoethane (142 mL, 1.3 mol) were charged in an oven-dried 1.0 L flask and mixed for 30 min at 0 °C by an overhead stirrer. Potassium *tert*-butoxide (74 g, 0.66 mol) was added in the flask and stirred for 2 days. To the obtained mixture was poured water (ca. 100 mL) and Et_2O (*ca.* 300 mL), and then the aqueous phase was washed three times with Et_2O. The ethereal solution was washed with brain, dried over anhydrous magnesium sulfate, and evaporated to afford the crude product. The crude product was purified by a silica-gel column (Et_2O) to afford the titled compound (7.5 g, 20% yield) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.27 (6 H, t, *J* = 7.5 Hz), 2.07 (4 H, q, *J* = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.8, 31.0, 39.6, 115.4.



(*R*)-2-Amino-2-cyclohexylethan-1-ol:[2] Lithium borohydride (ca. 4 mol/L in THF) (25 mL) and anhydrous THF (25 mL) were charged in a 300 mL three-necked flask. After stirring for 15 min at 0 °C, chlorotrimethylsilane (26 mL, 0.2 mol) was added dropwise into the flask and stirred for 15 min at room temperature. The reaction mixture was cooled to 0 °C. A solution of 2-cyclohexylglycine (7.9 g, 50 mmol) in THF (25 mL) was added dropwisely to the mixture at 0 °C. The mixture was stirred overnight at room temperature, quenched with MeOH (80 mL). To the obtained mixture was poured 2.5 M of saturated sodium hydroxide (40 mL). After evaporation of the reaction mixture, the aqueous phase was washed three times with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, evaporated to afford the titled compound (4.1 g, 58 % yield) as a colorless solid. $[\alpha]_D^{20}$ = +6.4 (c 0.5, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98–1.32 (6 H,

m), 1.66–1.77 (5 H, m), 2.67 (1 H, brs), 3.36–3.41 (1 H, m), 3.52 (2 H, brs), 3.67–3.70 (1 H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.1, 26.3, 29.0, 29.3, 40.7, 57.7, 63.5.



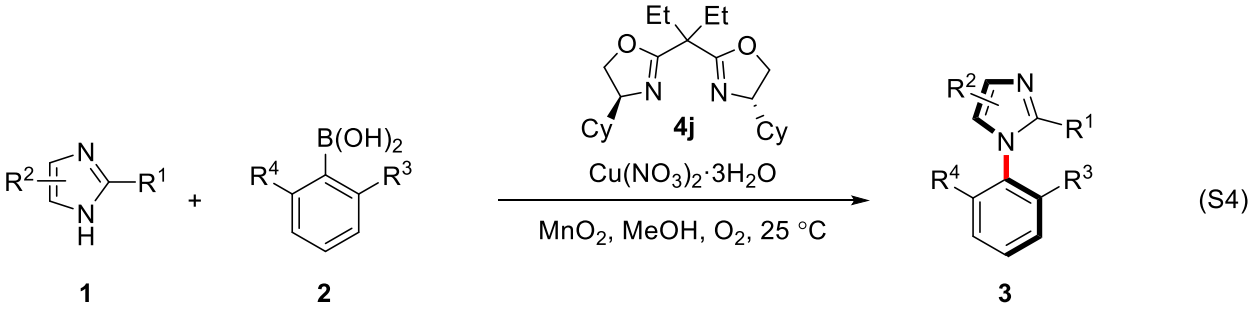
(S3)

(4*S*,4'*S*)-2,2'-(Pentane-3,3-diyl)bis(4-cyclohexyl-4,5-dihydrooxazole) (4j):[3,15] Diethyl malononitrile (0.80 g, 6.5 mmol), zinc chloride (2.8 g, 21 mmol), (*R*)-2-amino-2-cyclohexylethan-1-ol (3.0 g, 21 mmol) and *o*-dichlorobenzene (20 mL) were added to a 300 mL two-necked flask. The reaction mixture was stirred at 150 ºC for 7 h. The reaction mixture was cooled to room temperature. To the reaction mixture were added water (3.0 mL) and ethylenediamine (6.0 mL), and the reaction mixture was stirred at room temperature for 1 h. Water (30 mL) and Et_2O (100 mL) were added to the reaction mixture and the aqueous phase was washed three times with Et_2O. The combined organic phase was washed three times with saturated ammonium chloride, and dried over $MgSO_4$. The mixture was evaporated to afford the titled compound (1.9 g, 80% yield) as a pale yellow oil. $[\alpha]_D^{20}$ = +116.0 (c 1.0, MeOH). IR: 1653, 2921 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81–0.84 (6 H, m), 1.00 (4 H, m), 1.12–1.24 (4 H, m), 1.45 (2 H, m), 1.57–1.82 (12 H, m), 1.94–2.02 (4 H, m), 3.94–3.99 (4 H, m), 4.14–4.19 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.0, 24.9, 25.8, 25.9, 26.3, 28.2, 29.1, 42.2, 46.3, 69.5, 70.7, 166.7.

3-2. Procedure for the preparation of optically active catalyst Stock Solution (A): $Cu(NO_3)_2 \cdot 3H_2O$ (64 mg, 0.25 mmol) and MeOH (10 mL, 0.025 M) were charged in a 10 mL vial. The mixture was added to **4j** (188 mg, 0.50 mmol) in a 20 mL vial. After the sonication for 15 min, the Stock Solution (A) (0.025 M) was capped with septum and evacuated and back-filled with Ar (This operation was repeated three times).

3-3. Procedure for the preparation of none-optically active catalyst Stock Solution (B): $Cu(NO_3)_2 \cdot 3H_2O$ (64 mg, 0.25 mmol) and MeOH (10 mL, 0.025 M) were charged in a 10 mL vial. The mixture was added to TMEDA or (±)-**4j** (188 mg, 0.50 mmol) in a 20 mL vial. After the sonication for 15 min, the Stock Solution (B) (0.025 M) was capped with septum and evacuated and back-filled with Ar (This operation was repeated three times).

3-4. Asymmetric coupling between imidazole 1 and aryl boronic acid 2



(S4)

General Procedure I: To a test tube were added the imidazole **1** (0.20 mmol), the boronic acid **2** (0.40 mmol) and MnO_2 (2.0–20 mmol). After the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was added, the mixture was evacuated and backfilled with O_2 (This operation was repeated three times). The reaction mixture was stirred under an O_2 atmosphere (balloon) at 25 °C for 22 h and passed through Celite with EtOAc. The filtrate was concentrated in vacuo. The purification of the crude product with a silica-gel column chromatography using hexane/EtOAc gave the *N*-arylation product **3**. If required, the product was further purified by GPC. The enantiomeric excess was determined by HPLC (UV detection monitored at 254 nm).

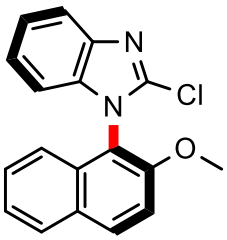
3-5. Synthesis of racemic coupling product between imidazole 1 and aryl boronic acid 2

General Procedure II: To a test tube were added the imidazole **1** (0.20 mmol), the boronic acid **2**

(0.40 mmol) and MnO_2 (2.0–20 mmol). After the Stock Solution (B) [2.0 mL, 0.05 mmol (Cu), 0.1 mmol (TMEDA or (±)-**4j**)] was added, the mixture was evacuated and backfilled with O_2 (This operation was repeated three times). The reaction mixture was stirred under an O_2 atmosphere (balloon) at 25 °C for 22 h and passed through Celite with EtOAc. The filtrate was concentrated in vacuo. The purification of the crude product with a silica-gel column chromatography using hexane/EtOAc gave a mixture of the *N*-arylation product. If required, the product was further purified by GPC. The enantiomeric excess was determined by HPLC (UV detection monitored at 254 nm).

3-6. Spectroscopic and numerical data of the coupling product

1-(2-Methoxynaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole (3a) (Table 2)



3a

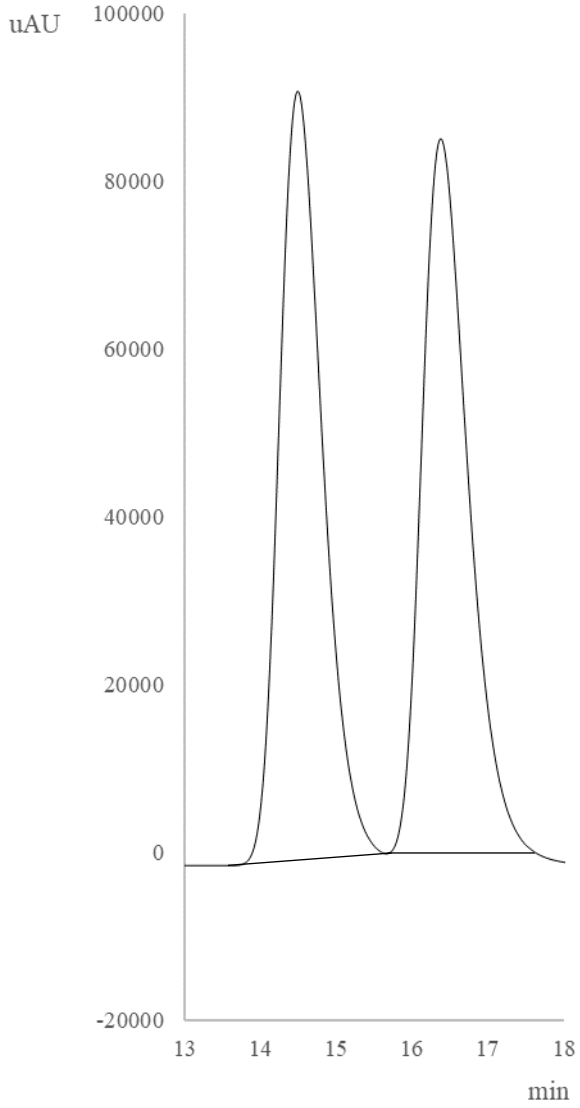
(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole [(*S*)-3a]: Following the General Procedure I, a mixture of 2-chloro-benzimidazole (**1a**) (31 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3a** (65 mg, quant, 74% ee) as a colorless solid. $[\alpha]_D^{20}$ = +61.3 (c 1.0, MeOH). Mp: 139–140 °C. IR: 2838 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.86 (3 H, s), 6.82 (1 H, d, *J* = 8.0 Hz), 7.13–7.20 (2 H, m), 7.32 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.39–7.43 (2 H, m), 7.46 (1 H, d, *J* = 9.0 Hz), 7.82 (1 H, d, *J* = 8.0 Hz), 7.91–7.94 (1 H, m), 8.09 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 57.4, 111.4, 114.2, 116.6, 120.3, 122.2, 123.8, 124.4, 125.5, 129.3, 129.8, 132.4, 132.8, 137.7, 143.0, 143.3, 154.8. HRMS (ESI, TOF) Calcd for $C_{18}H_{14}ClN_2O$ $[M+H]^+$: 309.0795. Found: 309.0784. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/Et_2NH = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 14.20 min (87%), 15.99 min (13%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole [(*rac*)-3a]: Following the General Procedure II, a mixture of 2-chloro-benzimidazole (**1a**) (0.61g, 4.0 mmol), 2-methoxynaphthalen boronic acid (**2a**) (1.6 g, 8.0 mmol) and MnO_2 (3.5 g, 40 mmol) in the Stock Solution (B) [40 mL, 1.0 mmol (Cu), 2.0 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3a** as a colorless solid (1.3 g, 99% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/Et_2NH = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 14.48 min (50%), 16.37 min (50%).

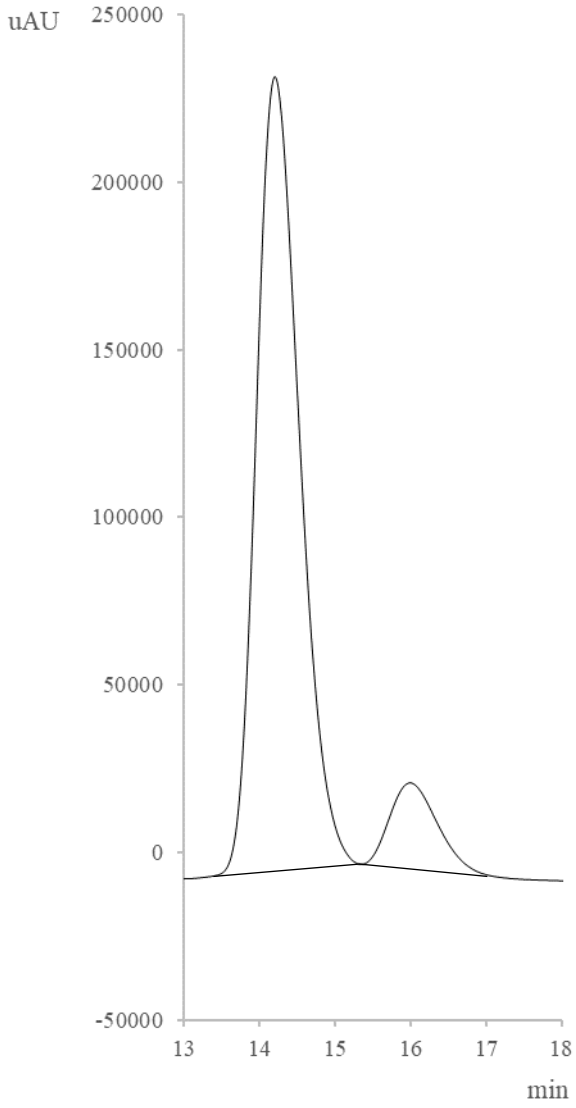
HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole (3a)

【PDA chromatograms】

(*rac*)-**3a**



(*S*)-**3a**

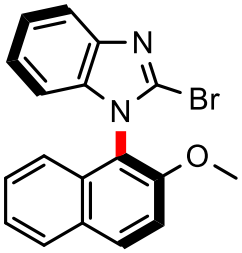


【PDA Table】Monitored at 254 nm

Peak#	Ret.time	Area	Area%
1	14.483	3756545	49.53
2	16.37	3828190	50.47
Total		7584735	100

Peak#	Ret.time	Area	Area%
1	14.198	9821933	86.80
2	15.99	1493828	13.20
Total		11315761	100

1-(2-Methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3b) (Table 3)



3b

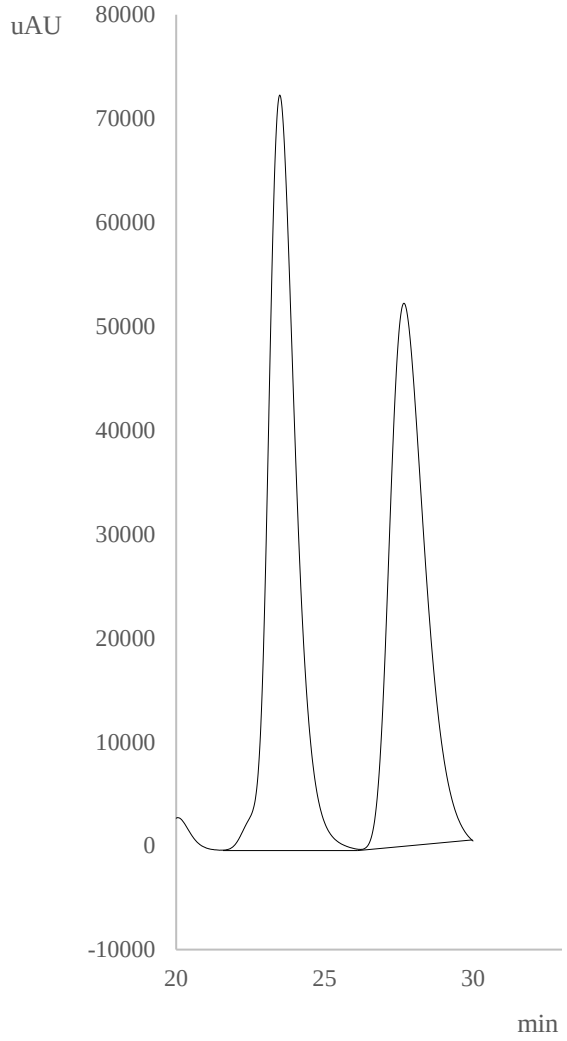
(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole [(*S*)-3b]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3b** (66 mg, 94% isolated yield, 85% ee) as a colorless solid. $[\alpha]_D^{20}$ = +75.7 (c 1.0, MeOH). Mp: 141–143 °C. IR: 2967 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.81 (3 H, s), 6.80 (1 H, d, *J* = 8.0 Hz), 7.08 (1 H, d, *J* = 7.0 Hz), 7.13 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.27 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.33–7.43 (3 H, m), 7.83 (1 H, d, *J* = 8.0 Hz), 7.89 (1 H, d, *J* = 8.0 Hz), 8.06 (1 H, d, *J* = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.3, 110.4, 113.2, 116.3, 119.2, 121.1, 122.6, 123.4, 124.5, 128.2, 128.7, 131.4, 131.8, 137.2, 143.2, 153.7. HRMS (ESI, TOF) Calcd for $C_{18}H_{14}BrN_2O$ $[M+H]^+$: 353.0290. Found: 353.0285. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 5/1, 1.0 mL/min, 30 °C, 254 nm): 23.7 min (92%), 28.4 min (8%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3b]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (0.82 g, 4.0 mmol), 2-methoxynaphthalen boronic acid (**2**) (1.6 g, 8.0 mmol) and MnO_2 (3.5 g, 40 mmol) in the Stock Solution (B) [40 mL, 1.0 mmol (Cu), 2.0 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3b** as a colorless solid (1.0 g, 73% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 5/1, 1.0 mL/min, 30 °C, 254 nm): 23.5 min (52%), 27.6 min (48%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3b)

【PDA chromatograms】

(*rac*)-**3b**



Peak#	Ret. Time	Area	Area%
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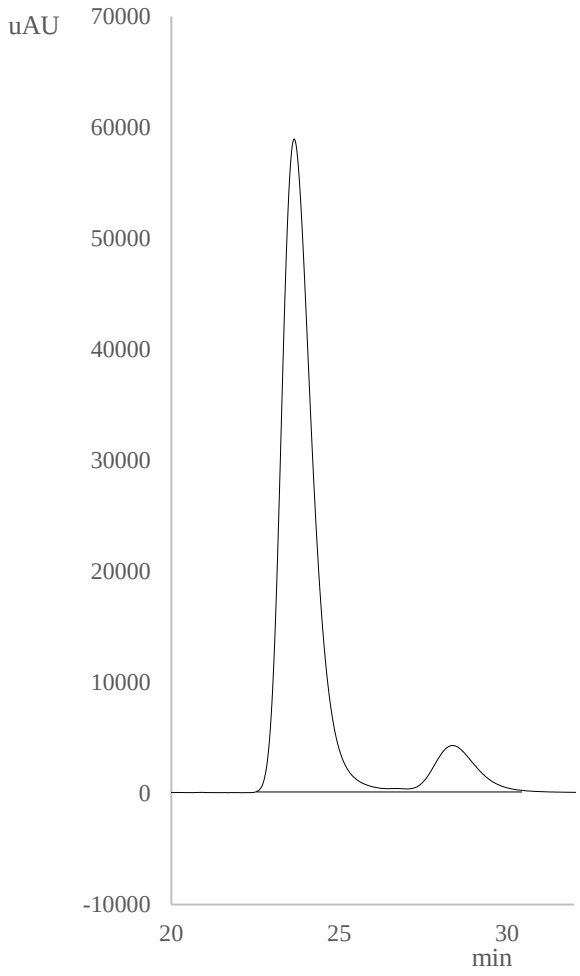
2	27.63	4315837	47.88
total		9014204	100

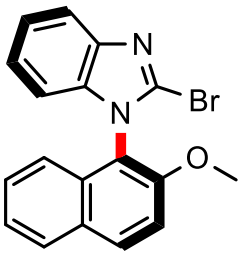
(*S*)-**3b**



Peak#	Ret. Time	Area	Area%
1	23.66	3767734	92.05
2	28.38	325645	8
total		4093379	100

3-7. Large scale synthesis of 3b

1-(2-Methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3b)



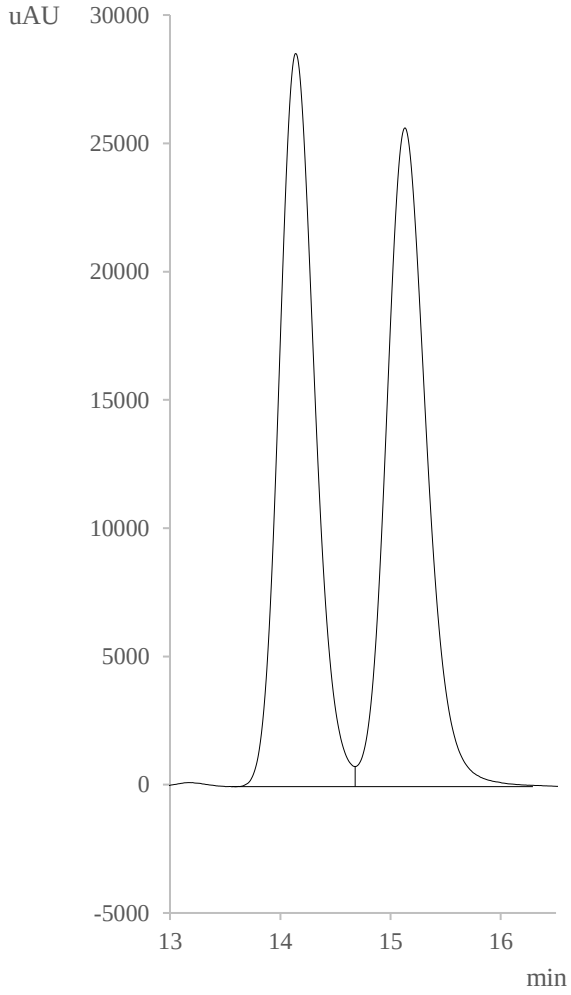
3b

(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole [(*S*)-3b]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (0.49 g, 2.5 mmol), 2-methoxynaphthalene boronic acid (**2a**) (1.0 g, 5.0 mmol) and MnO_2 (2.2 g, 25 mmol) in the chiral Stock Solution (A) [25 mL, 0.63 mmol (Cu), 1.25 mmol (**4j**)] was stirred for 22 h at 25 °C in 100 mL recovery flask. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3b** (0.77 g, 87% isolated yield, 86% ee) as a colorless solid. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 240 nm): 13.98 min (93%), 14.86 min (7%).

HPLC data of 1-(2-Methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3b) prepared in a large scale

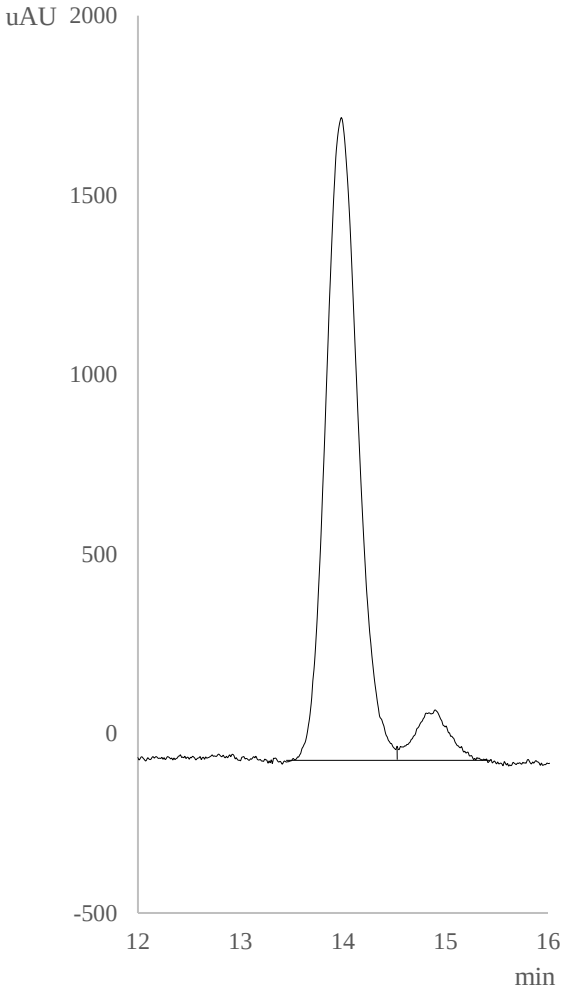
【PDA chromatograms】

(*rac*)-**3b**



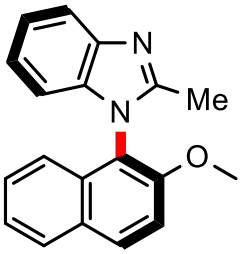
Peak#	Ret. Time	Area	Area%
1	14.134	646813	49.78
2	15.125	652606	50.22
total		1299419	100

(*S*)-**3b**



Peak#	Ret. Time	Area	Area%
1	13.979	38821	92.63
2	14.895	3088	7.37
total		41909	100

1-(2-Methoxynaphthalen-1-yl)-2-methyl-benzo[*d*]imidazole (3c) (Table 3)



3c

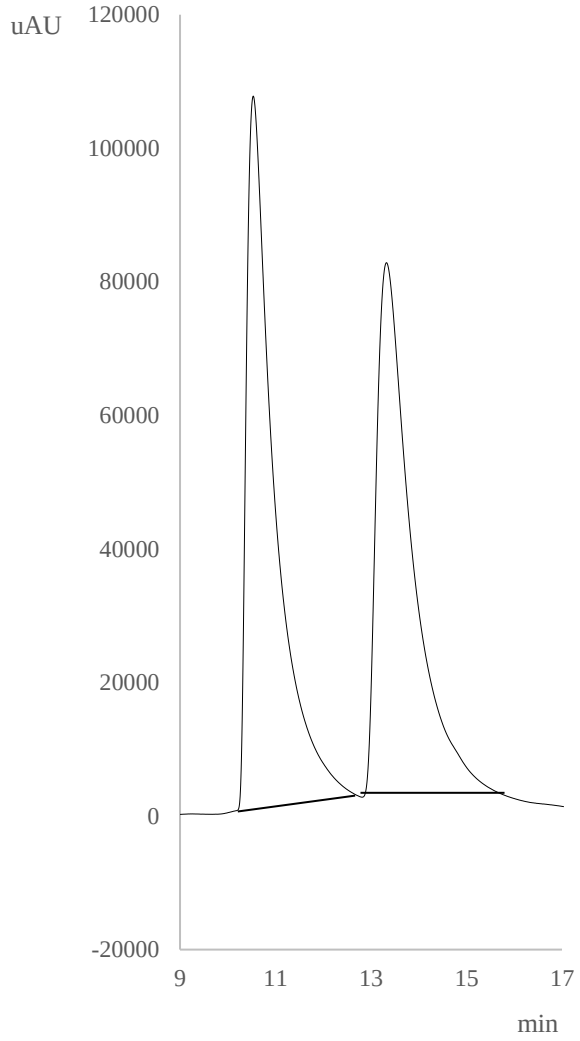
(*R*)-1-(2-Methoxynaphthalen-1-yl)-2-methyl-benzo[*d*]imidazole [(*R*)-3c]: Following the General Procedure I, a mixture of 2-methyl-benzimidazole (**1c**) (27 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*R*)-**3c** (50 mg, 86% isolated yield, 48% ee) as a pale yellow solid. $[\alpha]_D^{20}$ = –137.9 (c 1.0, MeOH). Mp: 124–126 °C. IR: 2936 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.36 (3 H, s), 3.84 (3 H, s), 6.78 (1 H, d, *J* = 8.0 Hz), 7.07 (1 H, d, *J* = 8.0 Hz), 7.12 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.28 (1 H, m), 7.35–7.43 (2 H, m), 7.45 (1 H, d, *J* = 9.0 Hz), 7.83 (1 H, d, *J* = 8.0 Hz), 7.92 (1 H, d, *J* = 8.0 Hz), 8.06 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 56.4, 110.2, 113.3, 116.8, 118.7, 121.4, 122.2, 122.5, 124.5, 128.23, 128.28, 129.0, 131.2, 131.4, 136.4, 142.3, 153.3, 153.4. HRMS (ESI, TOF) Calcd for $C_{19}H_{17}N_2O$ $[M+H]^+$: 289.1341. Found: 289.1330. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 90/10, 1.0 mL/min, 30 °C, 254 nm): 10.47 min (26%), 12.97 min (74%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-methyl-benzo[*d*]imidazole [(*rac*)-3c]: Following the General Procedure II, a mixture of 2-methyl-benzimidazole (**1c**) (0.54 g, 4.0 mmol), 2-methoxynaphthalen boronic acid (**2a**) (1.6 g, 8.0 mmol) and MnO_2 (3.5 g, 40 mmol) in the Stock Solution (B) [40 mL, 1.0 mmol (Cu), 2.0 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3c** as a pale yellow solid (0.72 g, 62% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 90/10, 1.0 mL/min, 30 °C, 254 nm): 10.53 min (50%), 13.32 min (50%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-methyl-benzo[*d*]imidazole (3c)

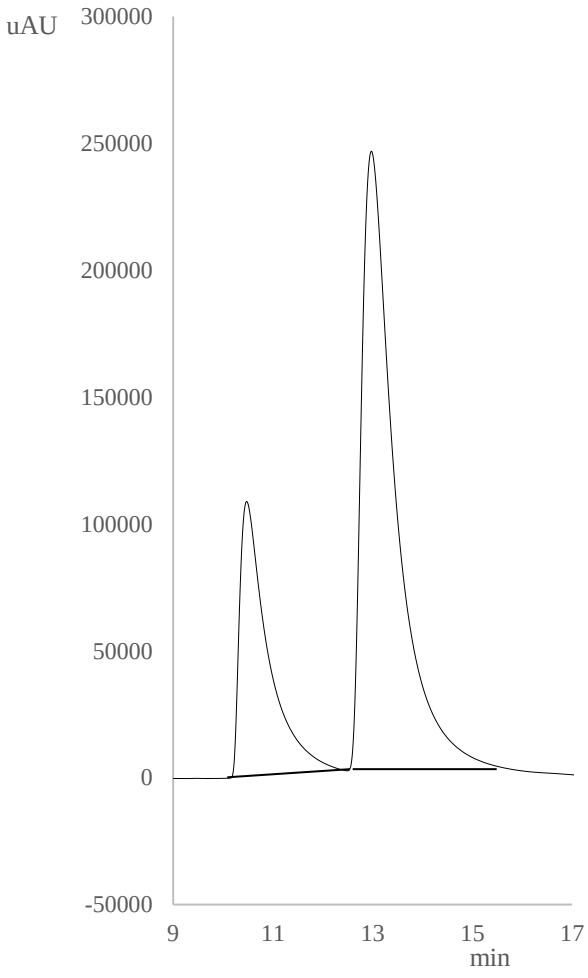
【PDA chromatograms】

(*rac*)-**3c**



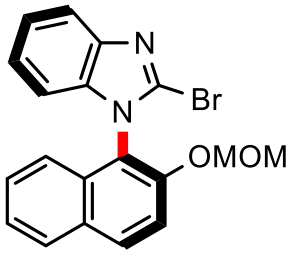
Peak#	Ret. Time	Area	Area%
1	10.53	4591770	49.69
2	13.32	4651237	50.322
total		9243007	100

(*R*)-**3c**



Peak#	Ret. Time	Area	Area%
1	10.47	4160106	26.15
2	12.97	11749153	73.85
total		15909259	100

1-(2-Methoxymethylnaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3d) (Table 3)



3d

(*S*)-1-(2-Methoxymethylnaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole [(*S*)-3d]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-methoxymethylnaphthalene boronic acid (**2b**) (93 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3d** (57 mg, 74% isolated yield, 90% ee) as a colorless solid. $[\alpha]_D^{20}$ = +62.7 (c 1.0, $CHCl_3$). Mp: 144–145 °C. IR: 2941 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.30 (3 H, s), 5.18 (2 H, s), 6.85 (1 H, d, *J* = 8.0 Hz), 7.12 (1 H, d, *J* = 8.0 Hz), 7.17 (1 H, dd, *J* = 7.0, 7.0 Hz), 7.30 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.40–7.48 (2 H, m), 7.63 (1 H, d, *J* = 9.0 Hz), 7.84 (1 H, d, *J* = 8.0 Hz), 7.93 (1 H, d, *J* = 7.5 Hz), 8.07 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.4, 94.6, 110.5, 115.9, 117.6, 119.3, 121.5, 122.8, 123.5, 125.0, 128.2, 129.5, 131.4, 131.7, 135.4, 143.3, 151.7. HRMS (ESI, TOF) Calcd for $C_{19}H_{16}BrN_2O_2$ $[M+H]^+$: 383.0395. Found: 383.0385. Rt: (DAICEL CHIRALPAK® IB-N, hexane/*i*-PrOH = 98/2, 1.0 mL/min, 30 °C, 254 nm): 15.21 min (95%), 17.14 min (5%).

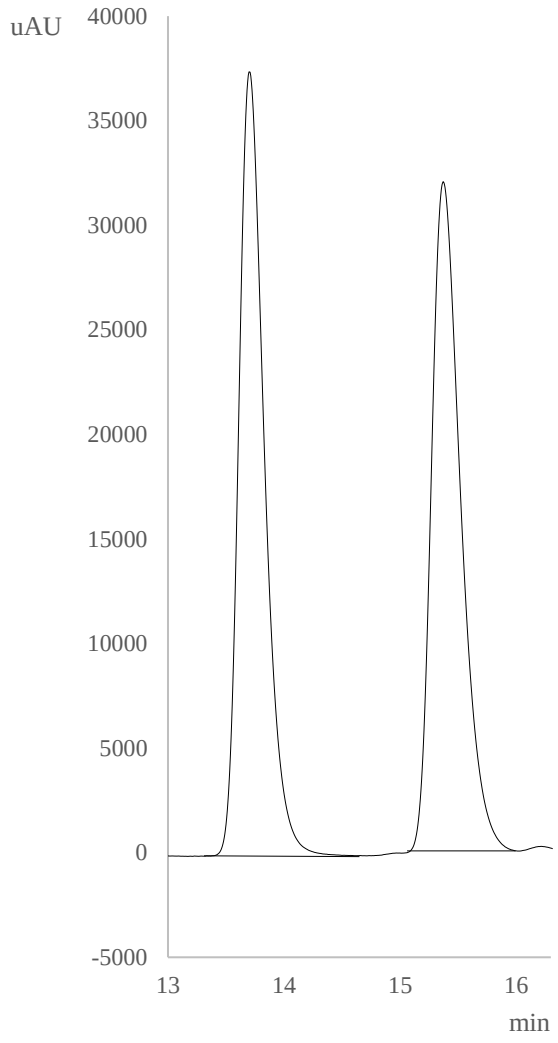
(*rac*)-1-(2-Methoxymethylnaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3d]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (49.3 mg, 0.25 mmol), 2-methoxymethylnaphthalen boronic acid (**2b**) (116 mg, 0.5 mmol) and MnO_2 (0.22 g, 2.5 mmol) in the Stock Solution (B) [2.0 mL, 0.063 mmol (Cu), 0.13 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3d** with impurity (59% GC yield). This mixture was triturated to afford the pure titled compound (*rac*)-**3d** as a colorless solid (11 mg, 12% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK®

IB-N, hexane/*i*-PrOH = 98/2, 1.0 mL/min, 30 °C, 254 nm): 13.7 min (51%), 15.37 min (49%).

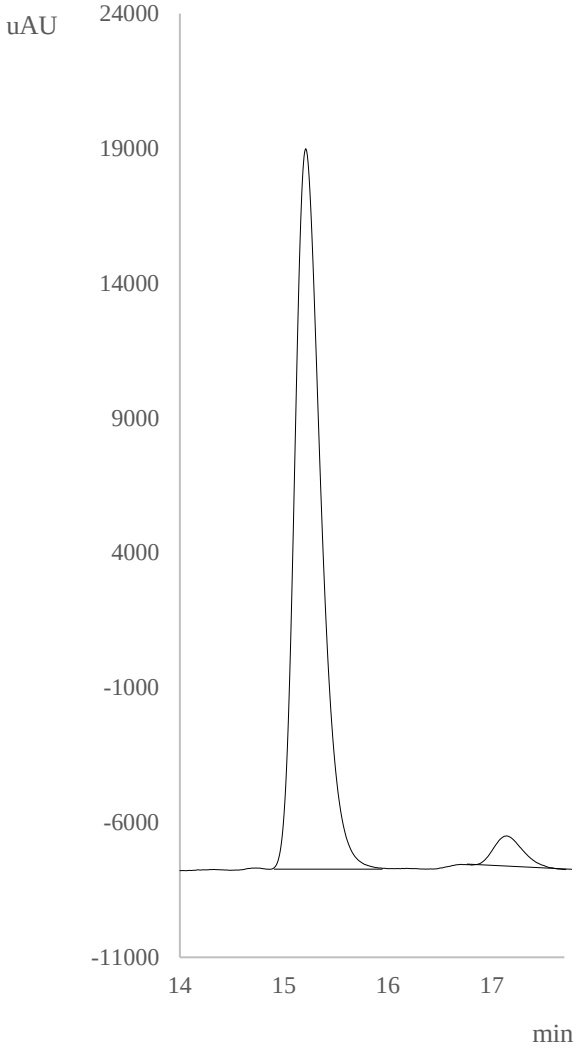
HPLC data of 1-(2-methoxymethylnaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3d)

【PDA chromatograms】

(*rac*)-**3d**



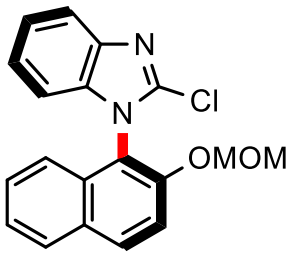
(*S*)-**3d**



Peak#	Ret. Time	Area	Area%
1	13.7	577356	50.52
2	15.37	565517	49.48
total		1142873	100

Peak#	Ret. Time	Area	Area%
1	15.21	469179	95.43
2	17.14	22457	4.57
total		491636	100

1-(2-Methoxymethylnaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole (3e)



3e

(*S*)-1-(2-Methoxymethylnaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole [(*S*)-3e]: Following the General Procedure I, a mixture of 2-chloro-benzimidazole (**1a**) (31 mg, 0.20 mmol), 2-methoxymethylnaphthalene boronic acid (**2b**) (93 mg, 0.40 mmol) and MnO_2 (0.17 g, 20 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3e** (47 mg, 80% isolated yield, 78% ee) as a colorless solid. $[\alpha]_D^{20}$ = +94.8 (c 1.0, $CHCl_3$). Mp: 162–163 °C. IR: 2917 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.29 (3 H, s), 5.18 (2 H, s), 6.83 (1 H, d, *J* = 8.0 Hz), 7.14–7.21 (2 H, m), 7.32 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.40–7.48 (2 H, m), 7.63 (1 H, d, *J* = 9.0 Hz), 7.83 (1 H, d, *J* = 8.0 Hz), 7.93 (1 H, d, *J* = 7.5 Hz), 8.06 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.3, 94.7, 110.4, 115.9, 116.9, 119.4, 121.4, 122.9, 123.5, 125.0, 128.21, 128.27, 129.5, 131.4, 131.7, 136.8, 142.0, 142.2, 151.7. HRMS (ESI, TOF) Calcd for $C_{19}H_{16}ClN_2O_2$ $[M+H]^+$: 339.0900. Found: 399.0891. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 90/10, 1.0 mL/min, 30 °C, 254 nm): 12.16 min (89%), 15.39 min (11%).

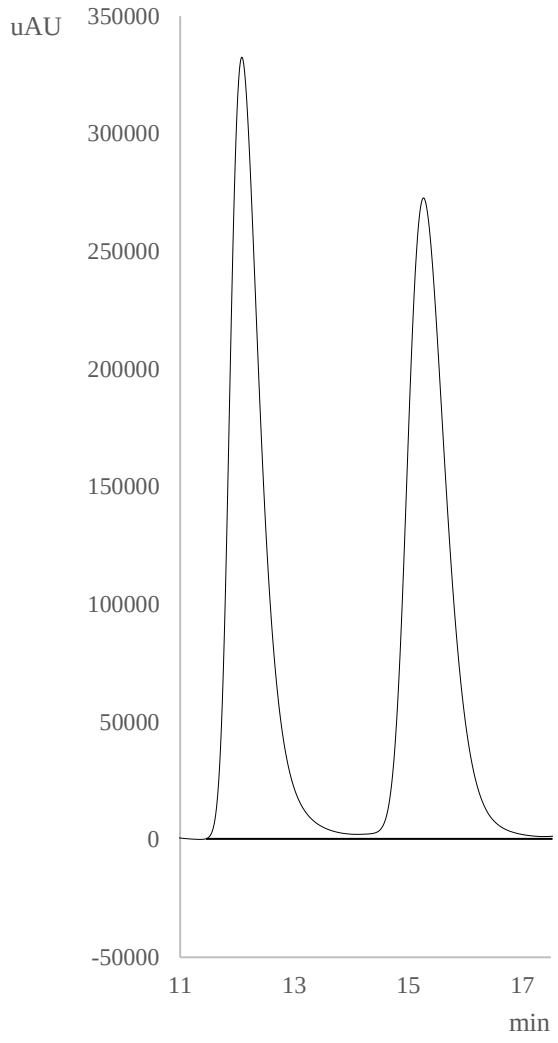
(*rac*)-1-(2-Methoxymethylnaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole [(*rac*)-3e]: Following the General Procedure II, a mixture of 2-chloro-benzimidazole (**1a**) (38 mg, 0.25 mmol), 2-methoxymethylnaphthalen boronic acid (**2b**) (0.11 g, mmol) and MnO_2 (0.22 g, 25 mmol) in the Stock Solution (B) [2.5 mL, 0.063 mmol (Cu), 1.3 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3e** with impurity (47% GC yield). This mixture was triturated to afford the pure titled compound (*rac*)-**3e** as a colorless solid (10 mg, 12% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-

PrOH = 90/10, 1.0 mL/min, 30 °C, 254 nm): 12.08 min (50%), 15.26 min (50%).

HPLC data of 1-(2-methoxymethylnaphthalen-1-yl)-2-chloro-benzo[*d*]imidazole (3e)

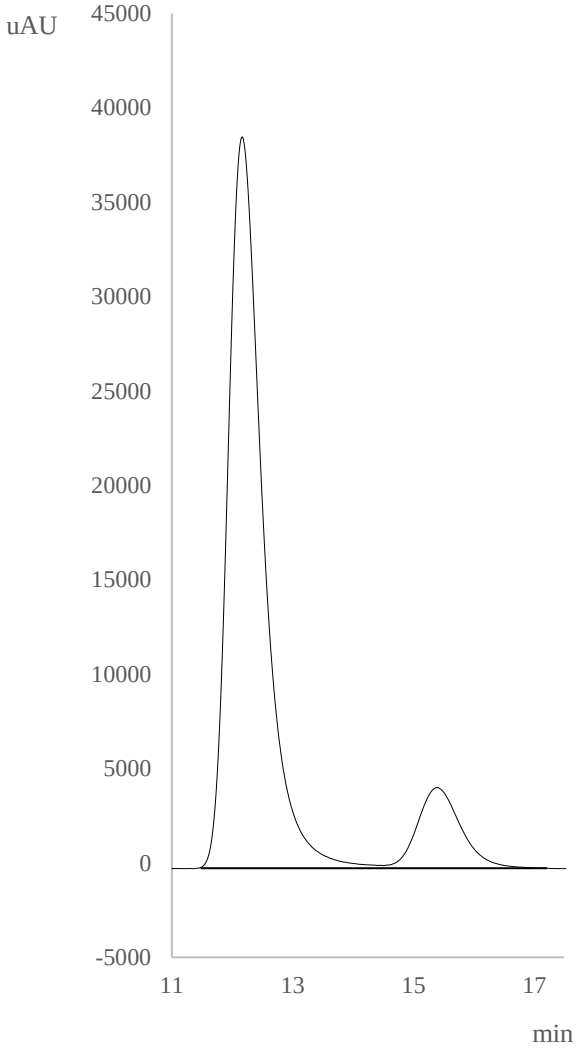
【PDA chromatograms】

(*rac*)-**3e**



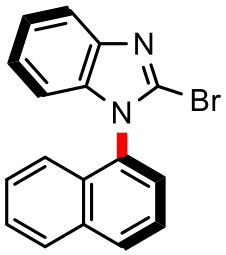
Peak#	Ret. Time	Area	Area%
1	12.08	13141571	49.62
2	15.26	13340674	50.38
total		26482245	100

(*S*)-**3e**



Peak#	Ret. Time	Area	Area%
1	12.16	1538944	88.7
2	15.39	196112	11.3
total		1735056	100

Naphthalen-1-yl-2-bromo-benzo[*d*]imidazole (3f) (Table 3)



3f

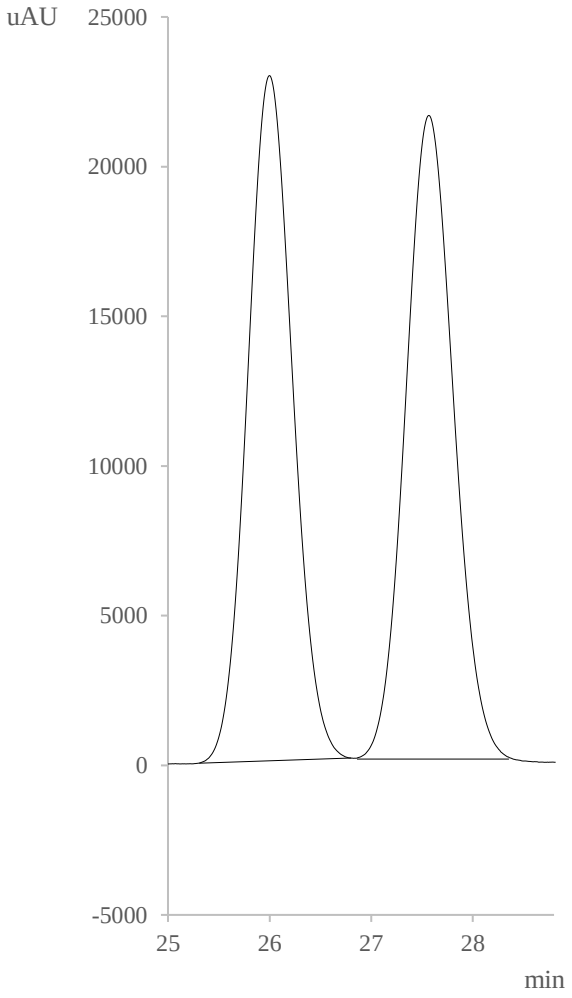
(*R*)-Naphthalen-1-yl-2-bromo-benzo[*d*]imidazole [(*S*)-3f]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 1-naphthalene boronic acid (**2c**) (69 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*R*)-**3f** (65 mg, quant, 52% ee) as a colorless solid. $[\alpha]_D^{20} = -52.9$ (c 1.0, MeOH). Mp: 124–125 °C. IR: 2931 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.86 (1 H, d, *J* = 8.0 Hz), 7.15–7.20 (2 H, m), 7.31 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.43 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.52–7.59 (2 H, m), 7.64 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.86 (1 H, d, *J* = 8.0 Hz), 8.00 (1 H, d, *J* = 8.0 Hz), 8.09 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.5, 119.3, 122.3, 123.0, 123.7, 125.4, 126.9, 127.0, 127.7, 128.5, 130.1, 130.4, 130.9, 131.6, 134.3, 137.9, 143.0. HRMS (ESI, TOF) Calcd for $C_{17}H_{12}BrN_2$ $[M+H]^+$: 323.0184. Found: 323.0175. Rt: (DAICEL CHIRALPAK® IC, hexane/*i*-PrOH = 98/2, 1.0 mL/min, 30 °C, 254 nm): 24.90 min (76%), 26.36 min (24%).

(*rac*)-Naphthalen-1-yl-2-bromo-benzo[*d*]imidazole [(*rac*)-3f]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (0.82 g, 4.0 mmol), 1-naphthalene boronic acid (**2c**) (1.4 g, 8.0 mmol) and MnO_2 (3.5 g, 40 mmol) in the Stock Solution (B) [40 mL, 1.0 mmol (Cu), 2.0 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3f** as a colorless solid (1.0 g, 76% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® IC, hexane/*i*-PrOH = 98/2, 1.0 mL/min, 30 °C, 254 nm): 25.99 min (50%), 27.56 min (50%).

HPLC data of naphthalen-1-yl-2-bromo-benzo[*d*]imidazole (3f)

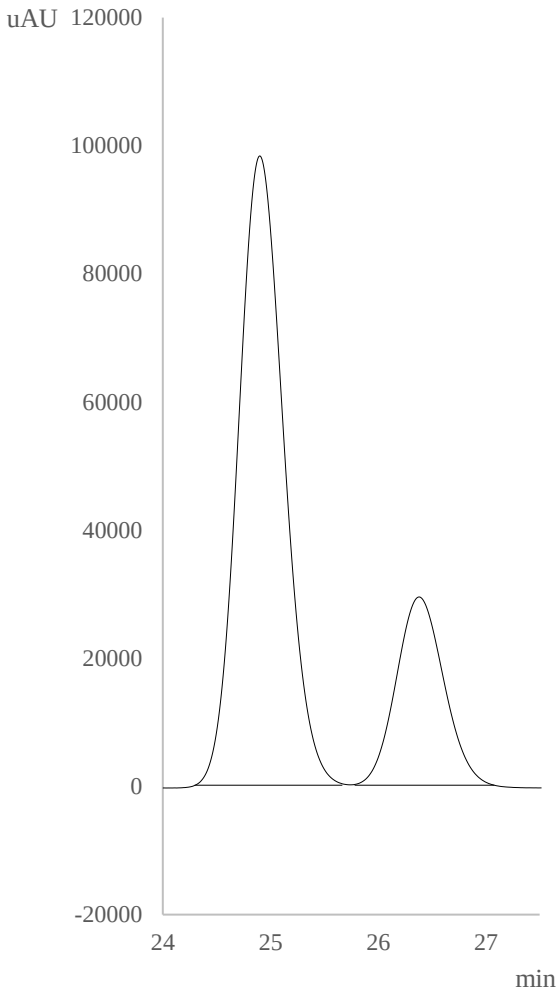
【PDA chromatograms】

(*rac*)-**3f**



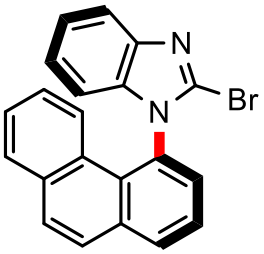
Peak#	Ret. Time	Area	Area%
1	25.993	716328	49.89
2	27.563	719410	50.11
total		1435738	100

(*R*)-**3f**



Peak#	Ret. Time	Area	Area%
1	24.895	2937619	75.77
2	26.375	940091	24.24
total		3877710	100

Phenanthrene-1-yl-2-bromo-benzo[*d*]imidazole (3g) (Table 3)



3g

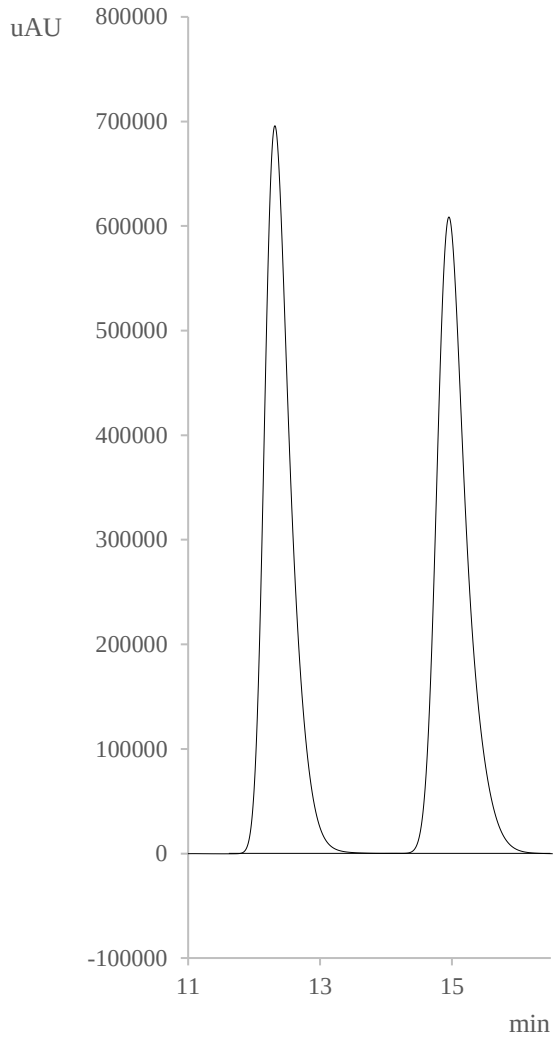
(*R*)-Phenanthrene-1-yl-2-bromo-benzo[*d*]imidazole [(*R*)-3g]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), phenanthrene boronic acid (**2d**) (89 mg, 0.40 mmol) and MnO_2 (0.17 g, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*R*)-**3g** (31 mg, 42% isolated yield, 60% ee) as a colorless solid. $[\alpha]_D^{20}$ = –6.7 (c 0.84, MeOH). Mp: 164–167 °C. IR: 3052 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.77 (1 H, d, *J* = 11.0 Hz), 6.93 (1 H, d, *J* = 10.0 Hz), 7.14–7.20 (2 H, m), 7.35 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.47–7.54 (2 H, m), 7.75 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.83–7.92 (4 H, m), 8.16 (1 H, d, *J* = 10.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.9, 119.5, 123.3, 124.0, 124.3, 126.5, 126.9, 127.2, 127.5, 127.6, 128.1, 128.9, 129.1, 129.8, 130.3, 131.5, 131.8, 133.2, 134.7, 136.7, 143.6. HRMS (ESI, TOF) Calcd for $C_{21}H_{14}BrN_2O$ $[M+H]^+$: 373.0340. Found: 373.0342. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/Et_2NH = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 12.22 min (80%), 14.84 min (20%).

(*rac*)-Phenanthrene-1-yl-2-bromo-benzo[*d*]imidazole [(*rac*)-3g]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (82 mg, 0.4 mmol), phenanthrene boronic acid (**2d**) (0.18 g, 0.80 mmol) and MnO_2 (3.5 g, 40 mmol) in the Stock Solution (B) [4.0 mL, 0.10 mmol (Cu), 0.20 mmol ((±)-**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3g** as a colorless solid (55 mg, 37 % isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/Et_2NH = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 12.31 min (50%), 14.95 min (50%).

HPLC data of phenanthrene -yl-2-bromo-benzo[*d*]imidazole (3g)

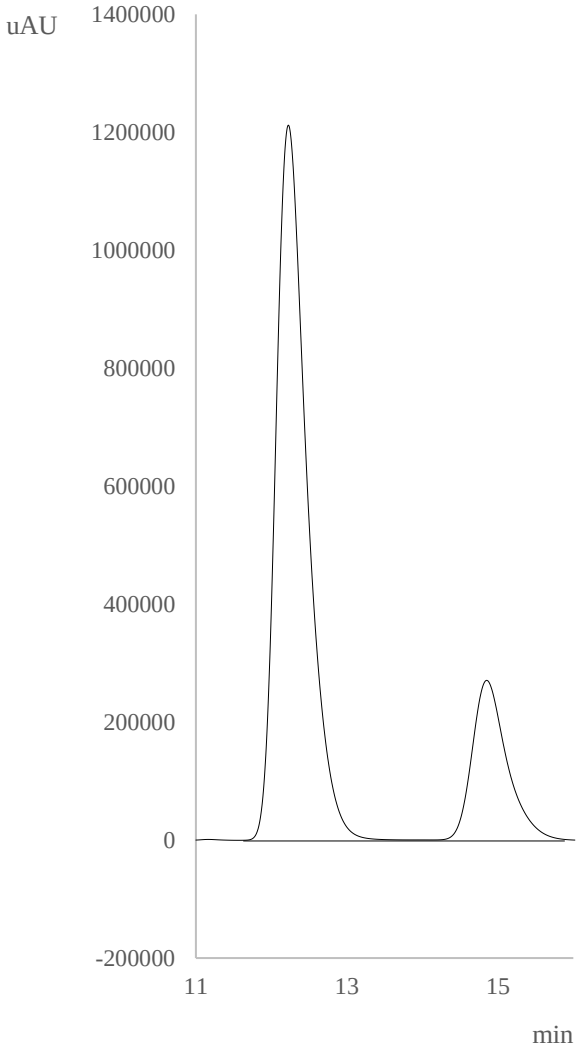
【PDA chromatograms】

(*rac*)-**3g**



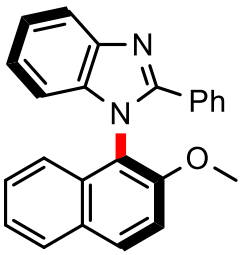
Peak#	Ret. Time	Area	Area%
1	12.31	19664757	50.12
2	14.95	19548723	49.85
total		39213480	100

(*R*)-**3g**



Peak#	Ret. Time	Area	Area%
1	12.22	34585404	79.94
2	14.84	8680964	20.06
total		43266368	100

1-(2-Methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole (3h) (Table 3)



3h

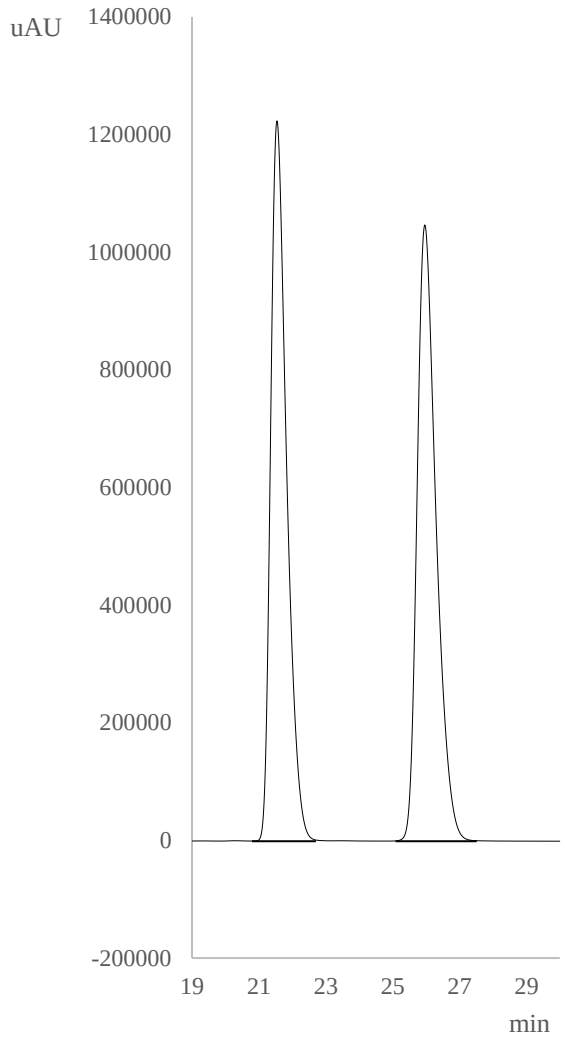
(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole [(*S*)-3h]: Following the General Procedure I, a mixture of 2-phenyl-benzimidazole (**1d**) (39 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3h** (31 mg, 44% isolated yield, 52% ee) as a pale yellow oil. $[\alpha]_D^{20}$ = +47.8 (c 1.0, MeOH). IR: 2929 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.58 (3 H, s), 6.82 (1 H, d, *J* = 8.0 Hz), 7.15–7.19 (3 H, m), 7.24 (1 H, d, *J* = 7.0 Hz), 7.30–7.36 (3 H, m), 7.39–7.44 (2 H, m), 7.54 (2 H, d, *J* = 8.0 Hz), 7.90–7.93 (1 H, m), 7.96 (1 H, d, *J* = 8.0 Hz), 8.01 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.8, 113.6, 118.7, 119.7, 121.8, 122.6, 123.0, 124.5, 128.0, 128.2, 128.3, 129.0, 129.3, 130.5, 131.0, 131.4, 137.4, 143.3, 153.0, 154.3. HRMS (ESI, TOF) Calcd for $C_{24}H_{19}N_2O$ $[M+H]^+$: 351.1497. Found: 351.1498. Rt: (DAICEL CHIRALPAK® IK-3, hexane/*i*-PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm): 21.57 min (24%), 25.94 min (76%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole [(*rac*)-3h]: Following the General Procedure II, a mixture of 2-phenyl-benzimidazole (**1d**) (78 mg, 0.40 mmol), 2-methoxynaphthalen boronic acid (**2a**) (1.6 g, 8.0 mmol) and MnO_2 (0.35 g, 0.80 mmol) in the racemic Stock Solution (B) of [4.0 mL, 0.10 mmol (Cu), 0.20 mmol ((±)-**4j**)]was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3h** as a colorless solid (56 mg, 40% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® IK-3, hexane/*i*-PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm): 21.54 min (50%), 26 min (50%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole (3h)

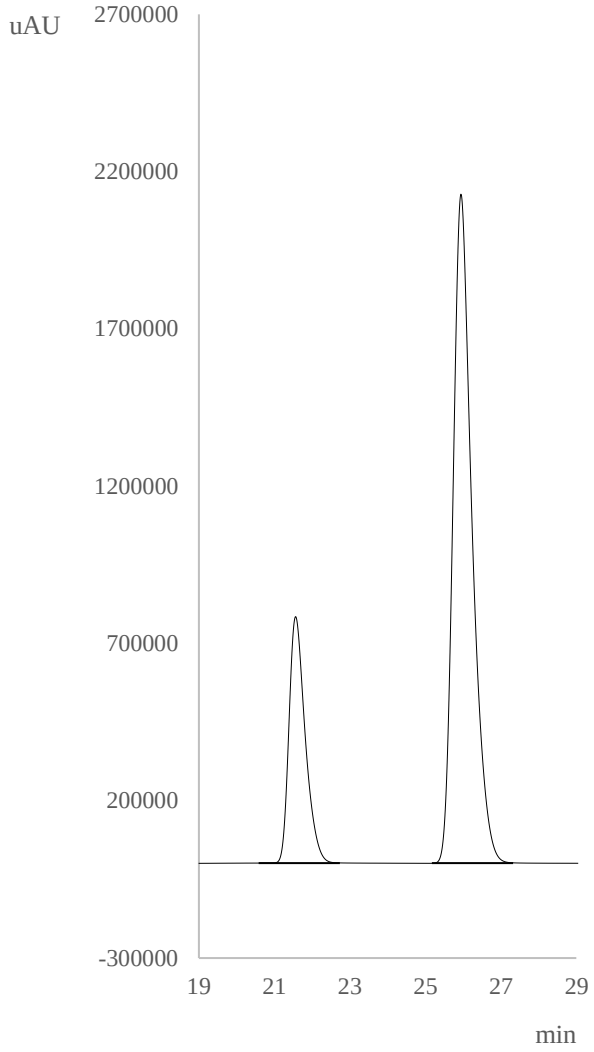
【PDA chromatograms】

(*rac*)-**3h**



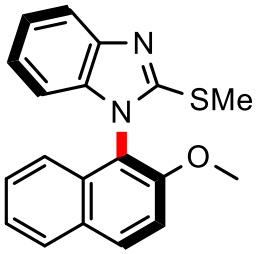
Peak#	Ret. Time	Area	Area%
1	21.54	40655573	49.6
2	26	41391469	50.4
total		82047042	100

(*S*)-**3h**



Peak#	Ret. Time	Area	Area%
1	21.57	23420609	24
2	25.94	74005726	76
total		97426335	100

1-(2-Methoxynaphthalen-1-yl)-2-thiomrthyl-benzo[*d*]imidazole (3i) (Table 3)



3i

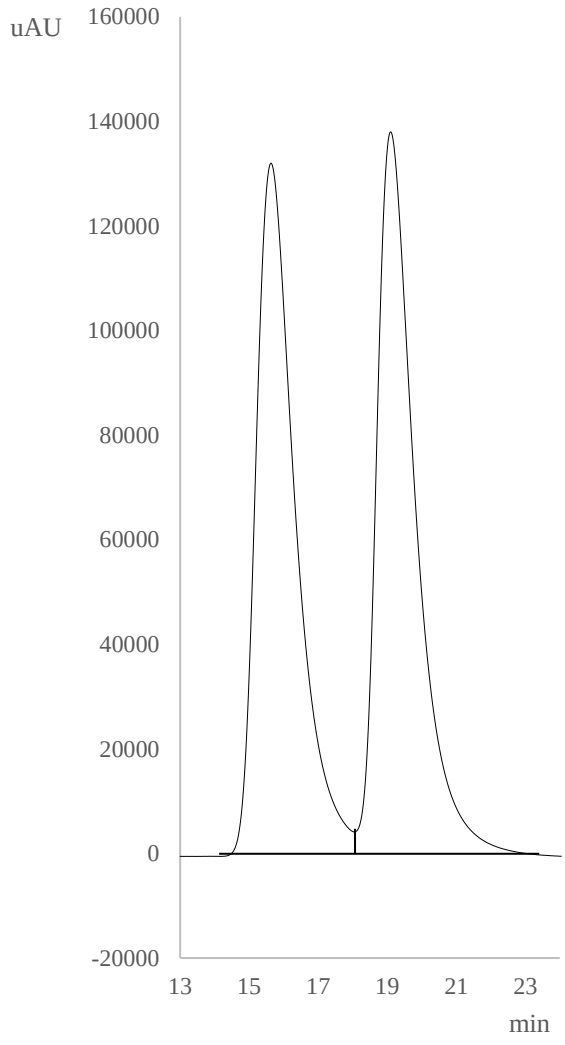
(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-thiomethyl-benzo[*d*]imidazole [(*S*)-3i]: Following the General Procedure I, a mixture of 2-thiomethyl-benzimidazole (**1e**) (34 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3i** (51 mg, 80% isolated yield, 46% ee) as a colorless solid. $[\alpha]_D^{20}$ = +30.1 (c 0.92, MeOH). Mp: 139–142 °C. IR: 2930 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.73 (3 H, s), 3.86 (3 H, s), 6.77 (1 H, d, *J* = 8.0 Hz), 7.07–7.14 (2 H, m), 7.26 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.37–7.43 (2 H, m), 7.45 (1 H, d, *J* = 9.0 Hz), 7.82 (1 H, d, *J* = 8.0 Hz), 7.89–7.92 (1 H, m), 8.06 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.4, 56.6, 109.4, 113.6, 116.0, 118.0, 121.6, 121.9, 122.0, 124.5, 128.0, 128.2, 129.0, 131.6, 131.6, 137.9, 143.8, 154.1, 155.0. HRMS (ESI, TOF) Calcd for $C_{19}H_{17}N_2OS$ $[M+H]^+$: 321.1062. Found: 321.1046. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 90/10, 1.0 mL/min, 30 °C, 254 nm): 16.11 min (27%), 19.66 min (73%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-thiomethyl-benzo[*d*]imidazole [(*rac*)-3i]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1e**) (26 mg, 0.16 mmol), 2-methoxynaphthalen boronic acid (**2a**) (65 mg, 0.32 mmol) and MnO_2 (0.14 g, 1.6 mmol) in the Stock Solution (B) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3i** as a colorless solid (28 mg, 54% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 90/10, 1.0 mL/min, 30 °C, 254 nm): 15.63 min (49%), 19.09 min (51%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-thiomethyl-benzo[*d*]imidazole (3i)

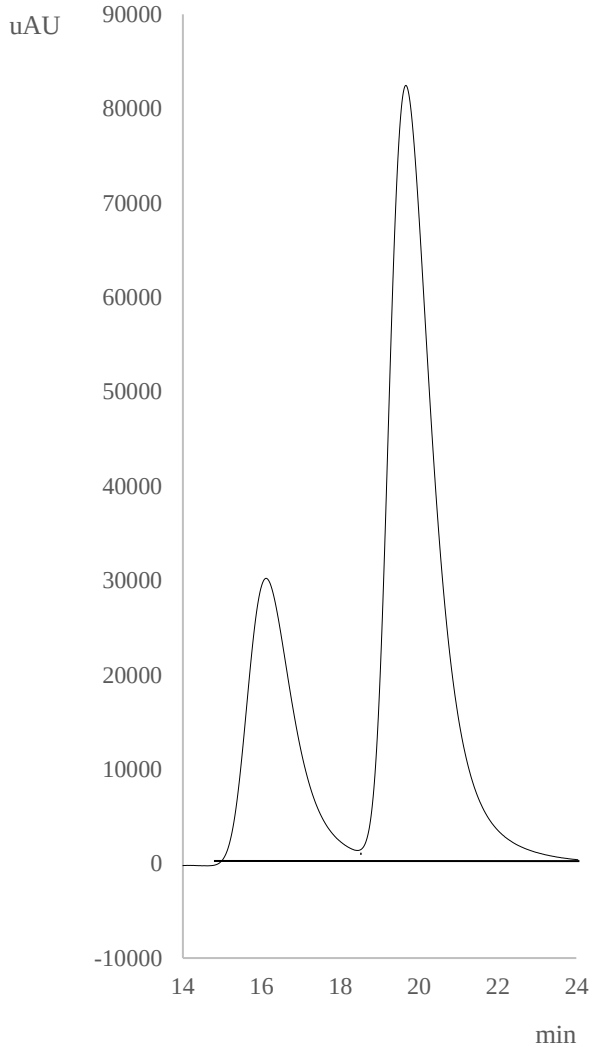
【PDA chromatograms】

(*rac*)-**3i**



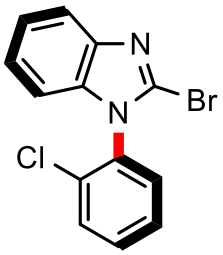
Peak#	Ret. Time	Area	Area%
1	15.63	10585204	49.21
2	19.09	10926354	50.79
total		21511558	100

(*S*)-**3i**



Peak#	Ret. Time	Area	Area%
1	16.11	2584025	27.28
2	19.66	6887329	72.72
total		9471354	100

1-(2-Chlorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3j) (Table 3)



3j

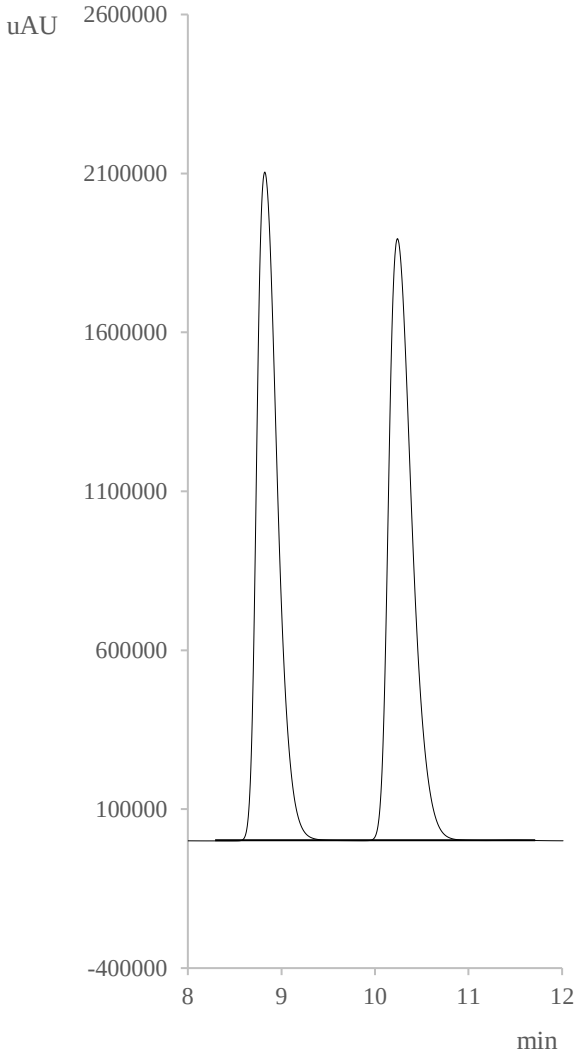
(–)-1-(2-Chlorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(–)-3j]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-chlorophenyl boronic acid (**2e**) (64 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (–)-**3j** (62 mg, quant, 80% ee) as a pale yellow oil. $[\alpha]_D^{20}$ = –11.2 (c 0.98, MeOH). IR: 3059 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.97 (1 H, d, *J* = 8.0 Hz), 7.24 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.30 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.42 (1 H, d, *J* = 8.0 Hz), 7.49 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.55 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.65 (1 H, d, *J* = 8.0 Hz), 7.79 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.1, 119.4, 123.1, 123.8, 128.1, 129.9, 130.5, 130.8, 131.3, 132.9, 133.5, 136.7, 143.0. HRMS (ESI, TOF) Calcd for $C_{13}H_9BrClN_2$ $[M+H]^+$: 306.9638. Found: 306.9634. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 8.9 min (90%), 10.3 min (10%).

(*rac*)-1-(2-Chlorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3j]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2chlorophenyl boronic acid (**2e**) (64 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (B) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3j** (48 mg, 77% isolated yield) as a pale yellow oil. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 8.7 min (50%), 10.01 min (50%).

HPLC data of 1-(2-chlorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3j)

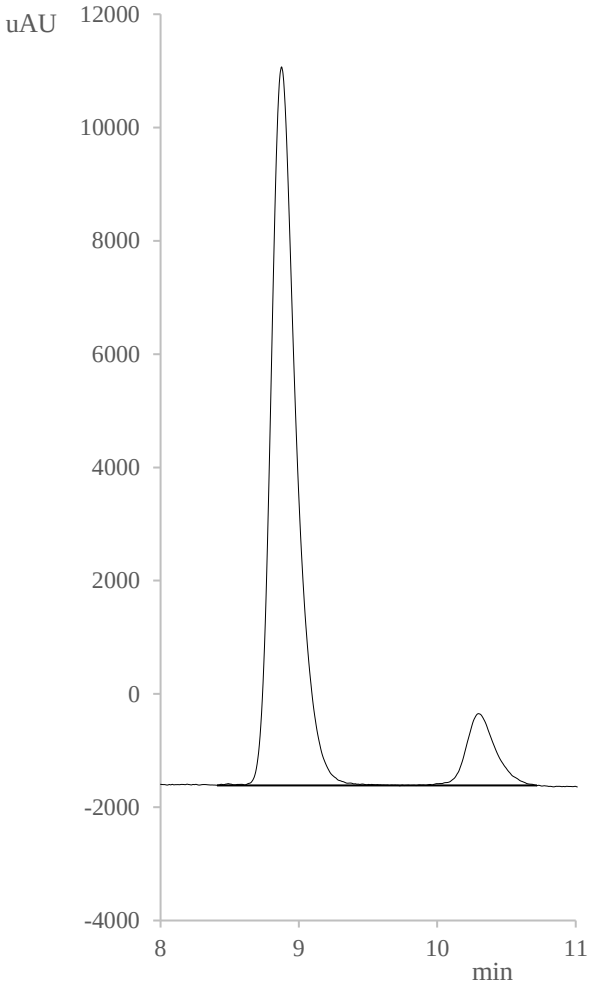
【PDA chromatograms】

(*rac*)-**3j**



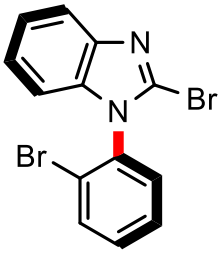
Peak#	Ret. Time	Area	Area%
1	8.82	32316644	49.5
2	10.24	32943357	50.5
total		65260001	100

(–)-**3j**



Peak#	Ret. Time	Area	Area%
1	8.87	158736	89.8
2	10.3	17974	10.2
total		4093379	100

1-(2-Bromophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3k) (Table 3)



3k

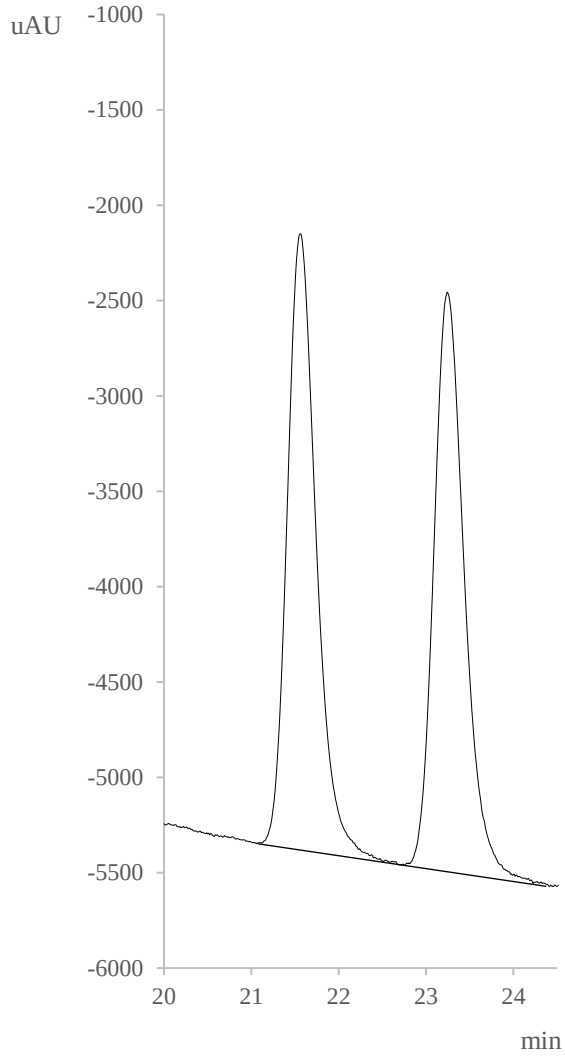
(–)-1-(2-Bromophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(–)-3k]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-bromophenyl boronic acid (**2f**) (80 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (–)-**3k** (70 mg, quant, 80% ee) as a pale yellow oil. $[\alpha]_D^{20} = -12.5$ (c 0.94, MeOH). IR: 3057 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.97 (1 H, d, *J* = 8.0 Hz), 7.25 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.31 (1 H, dd, *J* = 8.5, 8.5 Hz), 7.43(1 H, d, *J* = 8.0 Hz), 7.48 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.55 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.79 (1 H, d, *J* = 8.0 Hz), 7.83 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.2, 119.4, 123.1, 123.5, 123.8, 128.9, 129.8, 130.6, 131.6, 134.0, 134.6, 136.7, 143.0. HRMS (ESI, TOF) Calcd for $C_{13}H_9Br_2N_2$ $[M+H]^+$: 350.9132. Found: 350.9127. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm): 19.67 min (10%), 20.87 min (90%).

(*rac*)-1-(2-Bromophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3k]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-chlorophenyl boronic acid (**2f**) (80 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (B) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3k** (70 mg, quant) as a pale yellow oil. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm): 21.56 min (50%), 23.24 min (50%).

HPLC data of 1-(2-bromophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3k)

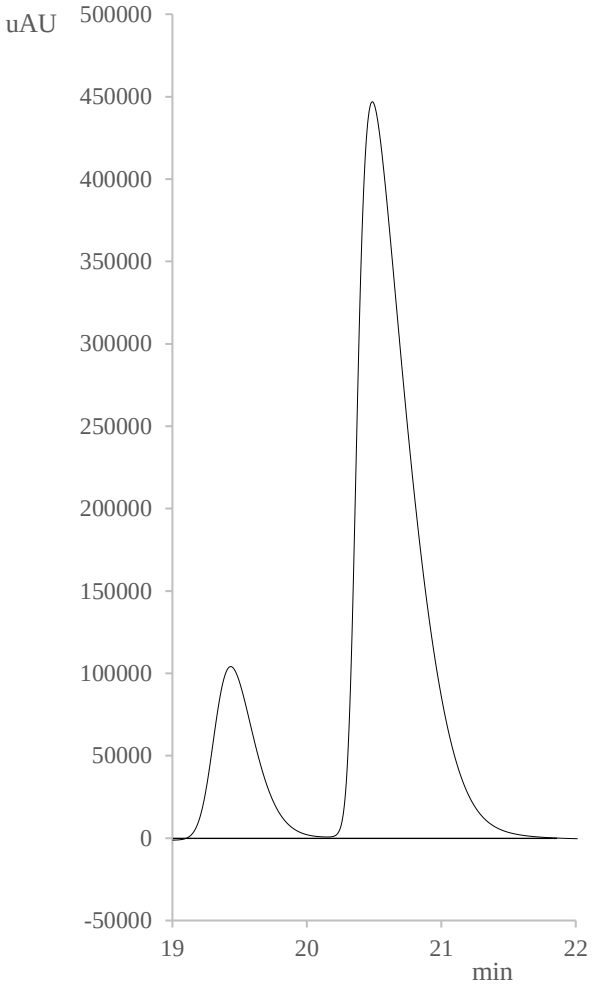
【PDA chromatograms】

(*rac*)-**3k**



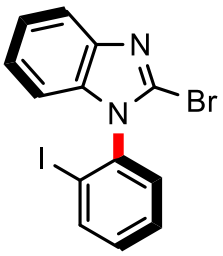
Peak#	Ret. Time	Area	Area%
1	21.56	72682	50.2
2	23.24	71852	49.8
total		144534	100

(–)-**3k**



Peak#	Ret. Time	Area	Area%
1	19.67	664139	9.6
2	20.87	6325033	90.4
total		6989172	100

1-(2-Iodophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3l) (Table 3)



3l

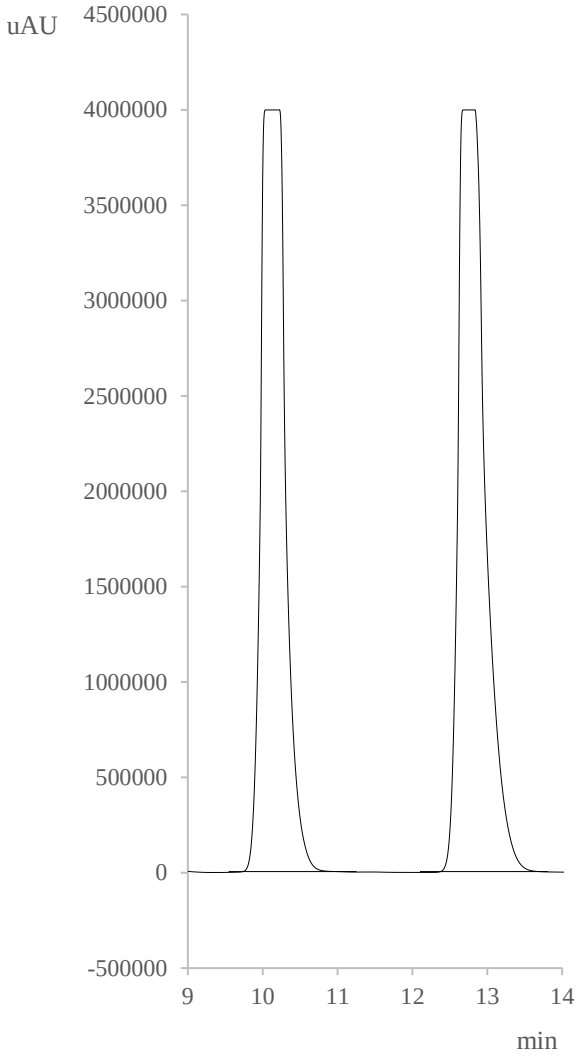
(–)-1-(2-Iodophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(–)-3l]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-iodophenyl boronic acid (**2g**) (101 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (–)-**3l** (80 mg, quant, 80% ee) as a pale yellow oil. $[\alpha]_D^{20} = -19.8$ (c 1.1, MeOH). IR: 3055 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.94 (1 H, d, *J* = 8.0 Hz), 7.24 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.28–7.32 (2 H, m), 7.38 (1 H, d, *J* = 8.0 Hz), 7.57 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.79 (1 H, d, *J* = 8.0 Hz), 8.05 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 98.8, 110.3, 119.4, 123.1, 123.8, 129.5, 129.7, 129.9, 131.5, 136.4, 138.1, 140.3, 142.9. HRMS (ESI, TOF) Calcd for $C_{13}H_9BrIN_2$ $[M+H]^+$: 398.8994. Found: 398.8987. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.5, 1.0 mL/min, 30 °C, 254 nm): 10.17 min (90%), 13.45 min (10%).

(*rac*)-1-(2-Iodophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3l]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-iodophenyl boronic acid (**2e**) (101 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (B) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3l** (80 mg, quant) as a pale yellow oil. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.5, 1.0 mL/min, 30 °C, 254 nm): 10.04 min (51%), 12.68 min (49%).

HPLC data of 1-(2-iodophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3l)

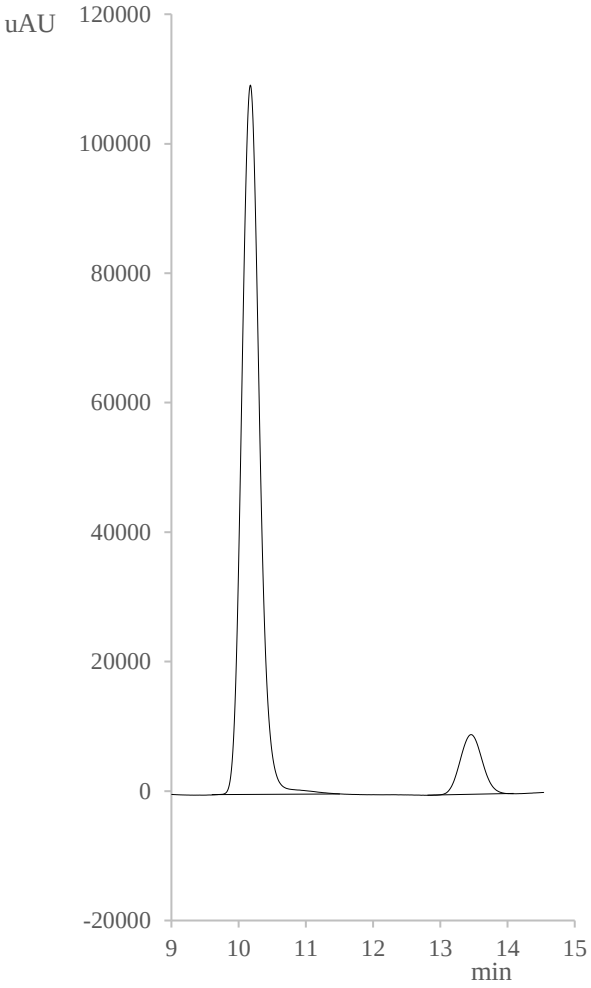
【PDA chromatograms】

(*rac*)-**3l**



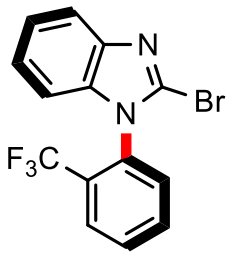
Peak#	Ret. Time	Area	Area%
1	10.04	92422636	50.7
2	12.68	92426787	49.3
total		1.85E+08	100

(–)-**3l**



Peak#	Ret. Time	Area	Area%
1	10.17	2023352	90.4
2	13.45	213448	9.6
total		2236800	100

1-(2-Trifluorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3m) (Table 3)



3m

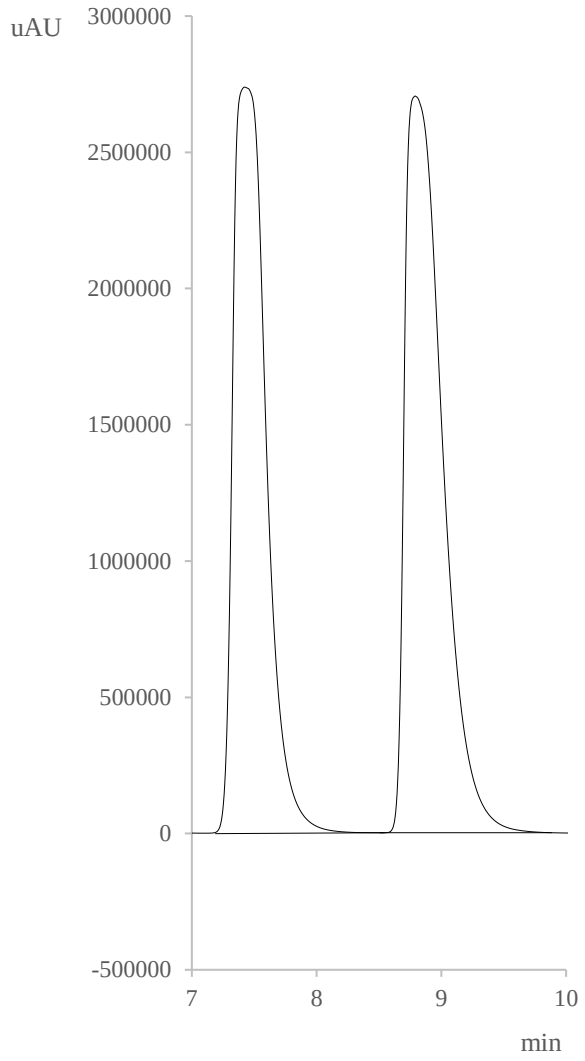
(–)-1-(2-Trifluorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(–)-3m]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-trifluorophenyl boronic acid (**2h**) (78 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (–)-**3m** (16 mg, 23% isolated yield, 86% ee) as a pale yellow oil. $[\alpha]_D^{20}$ = –2.8 (c 0.79, MeOH). IR: 3058 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.85 (1 H, d, *J* = 8.0 Hz), 7.14–7.25 (2 H, m), 7.31 (1 H, d, *J* = 7.5 Hz), 7.67–7.75 (3 H, m), 7.87 (1 H, d, *J* = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 110.4, 119.3, 122.5 (q, *J* = 273.5 Hz), 123.1, 123.8, 127.8 (q, *J* = 5.0 Hz), 129.5 (q, *J* = 31.5 Hz), 130.5, 130.7, 131.7, 133.2, 133.5, 138.2, 142.9. ^{19}F NMR (471 MHz, CDCl3) δ: −60.7. HRMS (ESI, TOF) Calcd for $C_{14}H_9BrF_3N_2$ $[M+H]^+$: 340.9901. Found: 340.9892. Rt: (DAICEL CHIRALPAK® AD-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 7.6 min (7%), 8.99 min (93%).

(*rac*)-1-(2-Trifluorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3m]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-trifluorophenyl boronic acid (**2h**) (78 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (B) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3m** (65 mg, 93% isolated yield) as a pale yellow oil. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® AD-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 7.56 min (51%), 9.08 min (49%).

HPLC data of 1-(2-trifluorophenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3m)

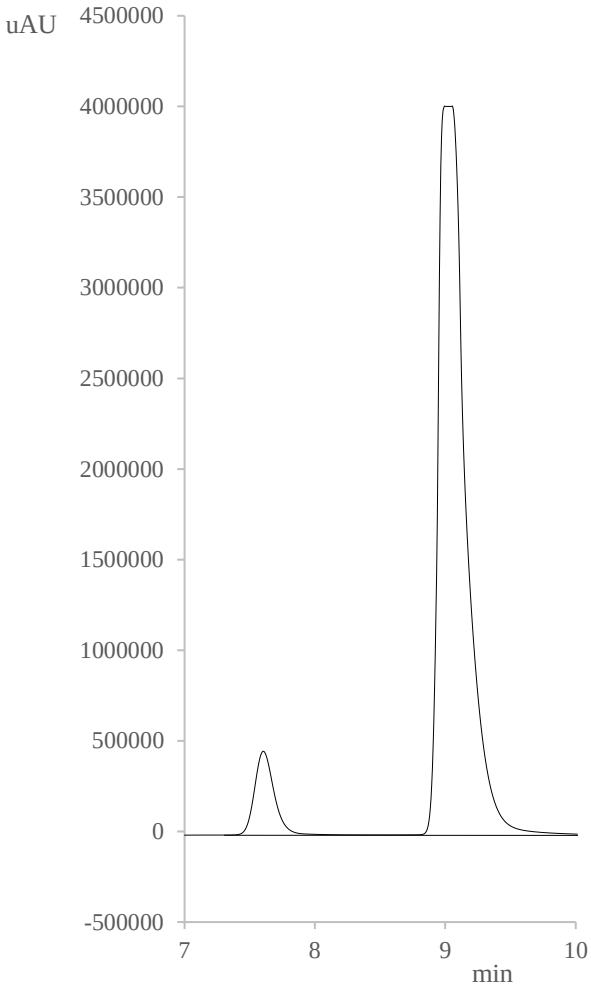
【PDA chromatograms】

(*rac*)-**3m**



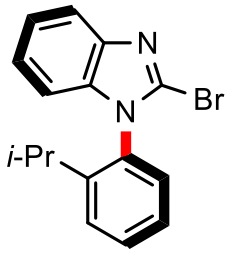
Peak#	Ret. Time	Area	Area%
1	7.59	20137695	50.56
2	9.08	19688170	49.44
total		39825865	100

(–)-**3m**



Peak#	Ret. Time	Area	Area%
1	7.6	4687785	7.4
2	8.99	58073739	92.53
total		62761524	100

1-(2-Isopropylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3n) (Table 3)



3n

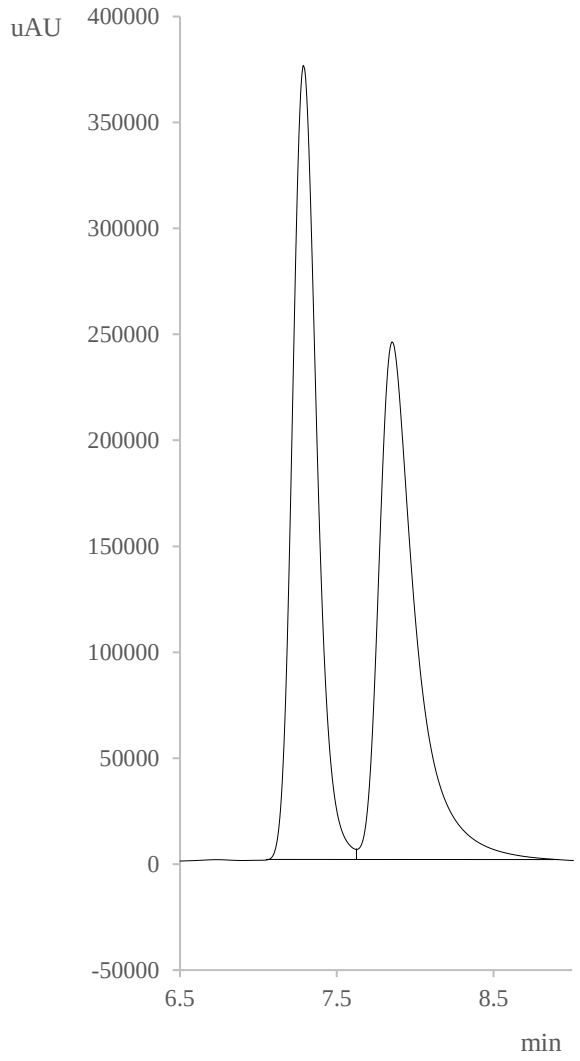
(–)-1-(2-Isopropylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(–)-3n]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-isopropylphenyl boronic acid (**2i**) (67 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (–)-**3n** (28 mg, 44% isolated yield, 80% ee) as a colorless solid. $[\alpha]_D^{20}$ = –30.7 (c 1.0, MeOH). Mp: 87–88 °C. IR: 2960 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.98 (3 H, d, *J* = 7.0 Hz), 1.11 (3 H, d, *J* = 7.0 Hz), 2.36–2.43 (1 H, m), 6.87 (1 H, d, *J* = 8.0 Hz), 7.11–7.24 (3 H, m), 7.30 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.47–7.53 (2 H, m), 7.71 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ:23.4, 24.0, 28.1, 110.3, 119.3, 122.9, 123.6, 127.1, 127.2, 129.0, 130.7, 130.8, 132.7, 137.7, 143.0, 147.5. HRMS (ESI, TOF) Calcd for $C_{13}H_{16}BrN_2$ $[M+H]^+$: 315.0497. Found: 315.0485. Rt: (DAICEL CHIRALPAK® ID-3, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 6.92 min (90%), 7.3 min (10%).

(*rac*)-1-(2-Isopropylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3n]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (21 mg, 0.10 mmol), 2-isopropylphenyl boronic acid (**2i**) (34 mg, 0.20 mmol) and MnO_2 (87 mg, 1.0 mmol) in the Stock Solution (B) [1.0 mL, 0.025 mmol (Cu), 0.05 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3n** (27 mg, 88% isolated yield) as a colorless solid. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® ID-3, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 7.28 min (50%), 7.85 min 50%).

HPLC data of 1-(2-isopropylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3n)

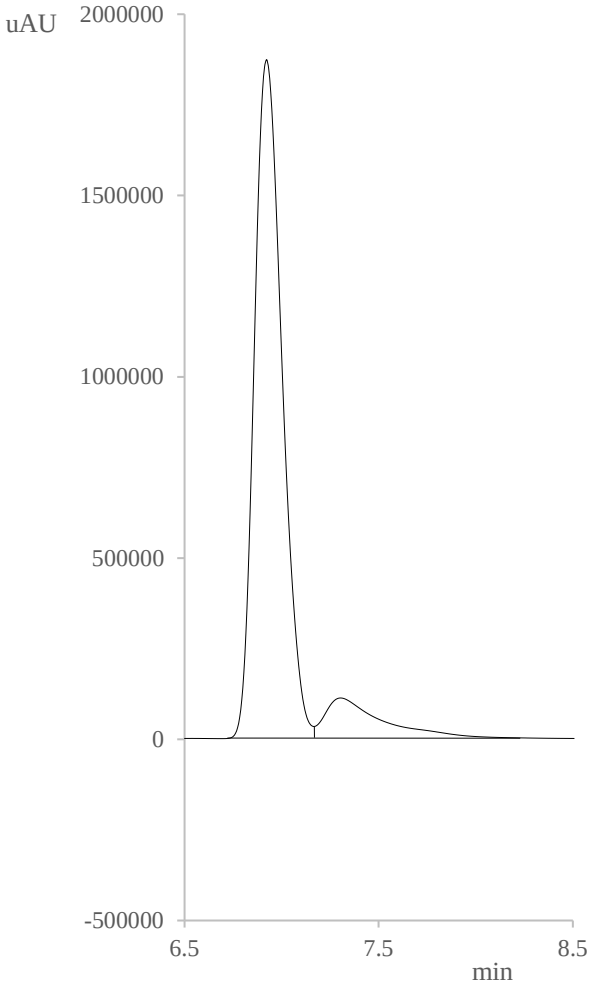
【PDA chromatograms】

(*rac*)-**3n**



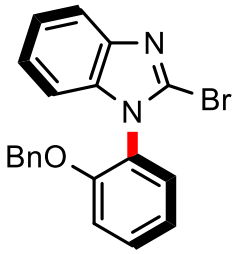
Peak#	Ret. Time	Area	Area%
1	7.28	4135203	50.05
2	7.85	4124595	49.95
total		8259798	100

(–)-**3n**



Peak#	Ret. Time	Area	Area%
1	6.92	18687355	90
2	7.3	2086572	10
total		20773927	100

1-(2-Benzyloxyphenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3o) (Table 3)



3o

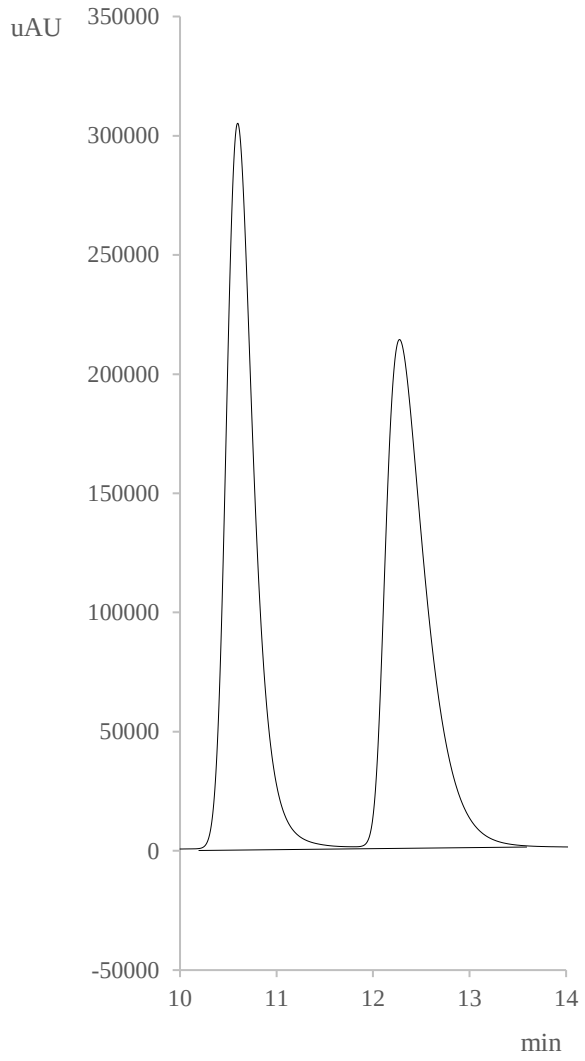
(–)-1-(2-Benzyloxylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(–)-3o]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-benzyloxyphenyl boronic acid (**2j**) (91 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (–)-**3o** (76 mg, quant, 60% ee) as a pale yellow oil. $[\alpha]_D^{20} = -4.91$ (c 0.94, MeOH). IR: 3062 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.96 (1 H, d, *J* = 12.5 Hz), 5.00 (1 H, d, *J* = 12.5 Hz), 6.95 (1 H, d, *J* = 8.0 Hz), 7.02–7.05 (2 H, m), 7.07–7.09 (2 H, m), 7.12–7.22 (5 H, m), 7.28 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.42 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.70 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 70.3, 110.4, 114.1, 119.1, 121.3, 122.7, 123.4, 124.2, 126.7, 127.9, 128.5, 129.8, 130.9, 131.2, 135.9, 137.3, 143.0, 154.5. HRMS (ESI, TOF) Calcd for $C_{20}H_{16}BrN_2$ $[M+H]^+$: 379.0446. Found: 379.0448. Rt: (DAICEL CHIRALPAK® IB-N, hexane/EtOH/DEA = 90/10/0.5, 1.0 mL/min, 30 °C, 254 nm): 10.15 min (80%), 11.87 min (20%).

(*rac*)-1-(2-Benzyloxyphenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3o]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (0.41 g, 2.0 mmol), 2-benzyloxyphenyl boronic acid (**2j**) (0.91 g, 4.0 mmol) and MnO_2 (1.7 g, 20 mmol) in the Stock Solution (B) [20 mL, 0.50 mmol (Cu), 1.0 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3o** (0.28 g, 37% isolated yield) as a pale yellow oil. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® IB-N, hexane/EtOH/DEA = 90/10/0.5, 1.0 mL/min, 30 °C, 254 nm): 10.59 min (50%), 12.27 min (50%).

HPLC data of 1-(2-benzyloxyphenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3o)

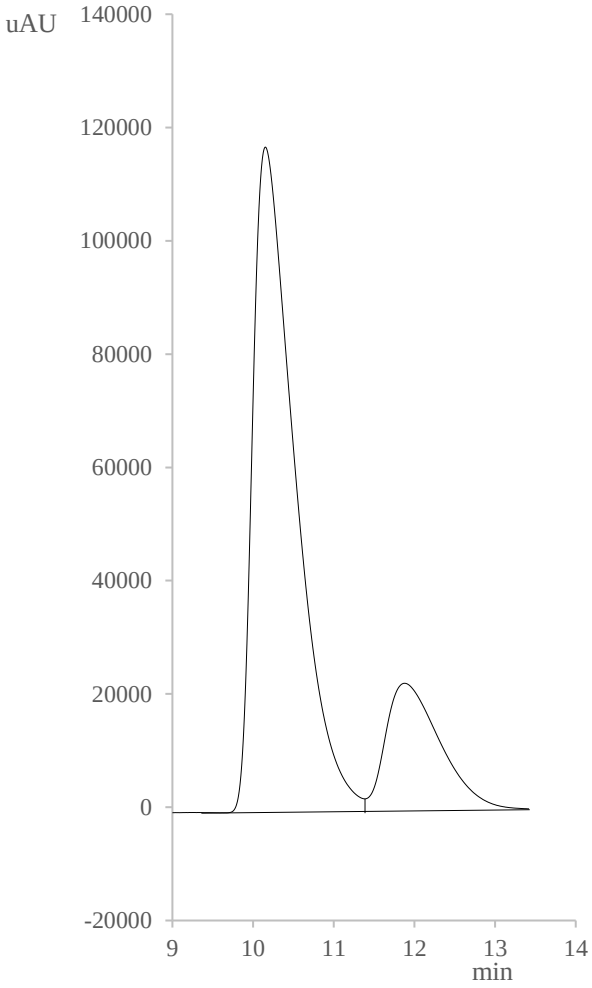
【PDA chromatograms】

(*rac*)-**3o**



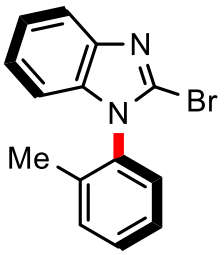
Peak#	Ret. Time	Area	Area%
1	10.59	6285679	49.9
2	12.27	6299147	50.05
total		12584826	100

(–)-**3o**



Peak#	Ret. Time	Area	Area%
1	10.15	4283044	80.3
2	11.87	1051240	19.7
total		5334284	100

1-(2-Methylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3p) (Table 3)



3p

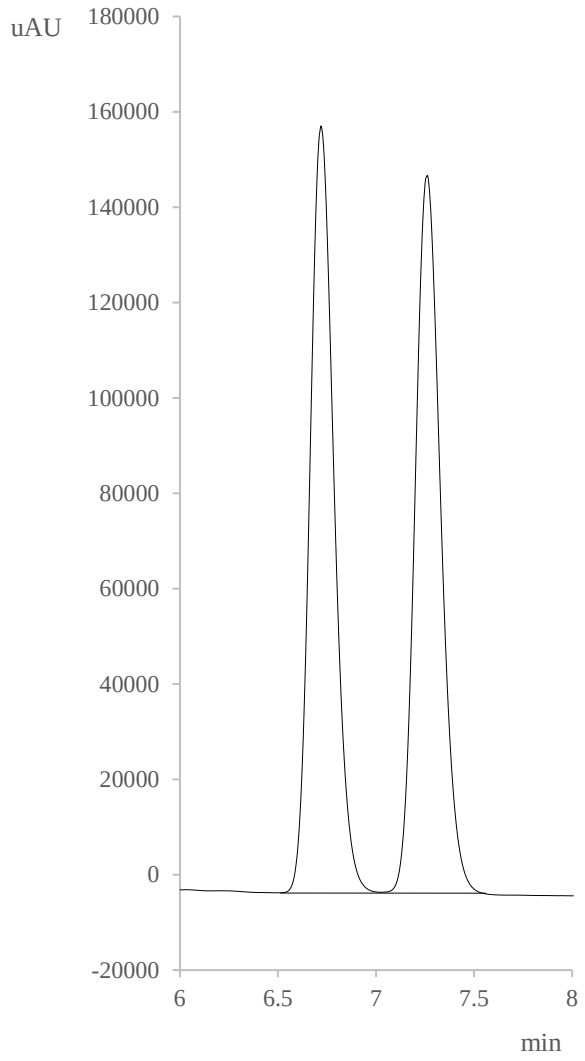
(–)-1-(2-Methylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(–)-3p]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-methylphenyl boronic acid (**2k**) (91 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (–)-**3p** (76 mg, quant, 56% ee) as a pale yellow oil. $[\alpha]_D^{20} = -4.91$ (c 0.94, MeOH). IR: 3054 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.01 (3 H, s), 6.95 (1 H, d, *J* = 8.0 Hz), 7.21–7.31 (3 H, m), 7.38–7.51 (3 H, m), 7.79 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.4, 110.2, 119.3, 122.9, 123.6, 127.3, 128.8, 130.1, 131.4, 134.1, 136.8, 136.9, 143.1. HRMS (ESI, TOF) Calcd for $C_{14}H_{12}BrN_2$ $[M+H]^+$: 287.0184. Found: 287.0174. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 6.96 min (78%), 7.56 min (22%).

(*rac*)-1-(2-Methylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3p]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-methylphenyl boronic acid (**2k**) (91 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (B) [2.0 mL, 0.05 mmol (Cu), 0.1 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3p** (36 mg, 63% isolated yield) as a pale yellow oil. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 6.72 min (50%), 7.26 min (50%).

HPLC data of 1-(2-methylphenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3p)

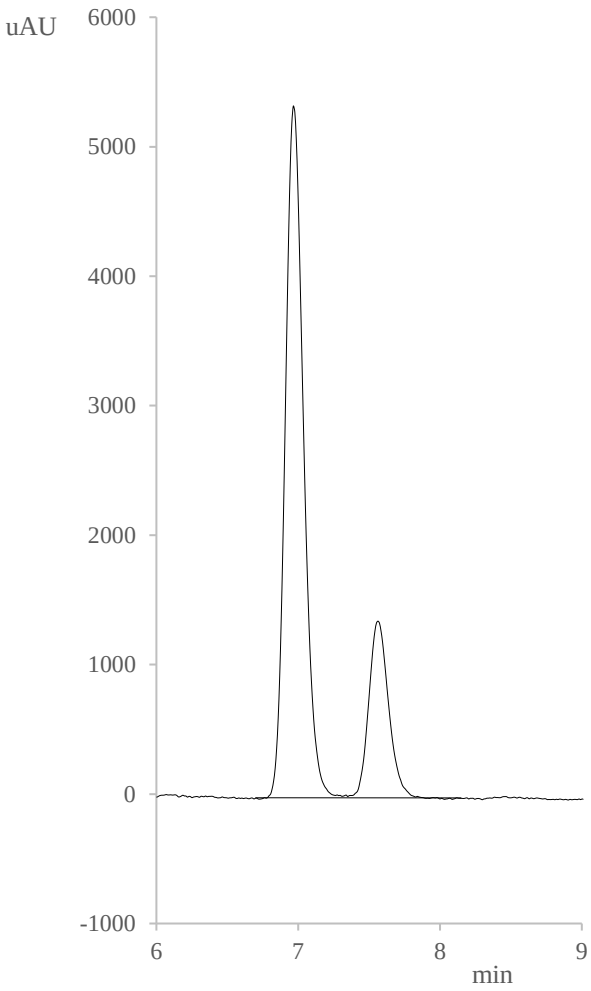
【PDA chromatograms】

(*rac*)-**3p**



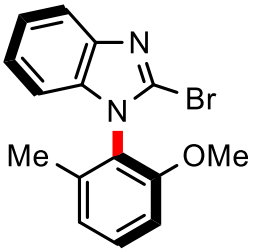
Peak#	Ret. Time	Area	Area%
1	6.72	1374282	49.9
2	7.26	1381787	50.14
total		2756069	100

(–)-**3p**



Peak#	Ret. Time	Area	Area%
1	6.96	47915	78.3
2	7.56	13283	21.7
total		61198	100

1-(2-Methoxy-2-methyl-phenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3q) (Table 3)



3q

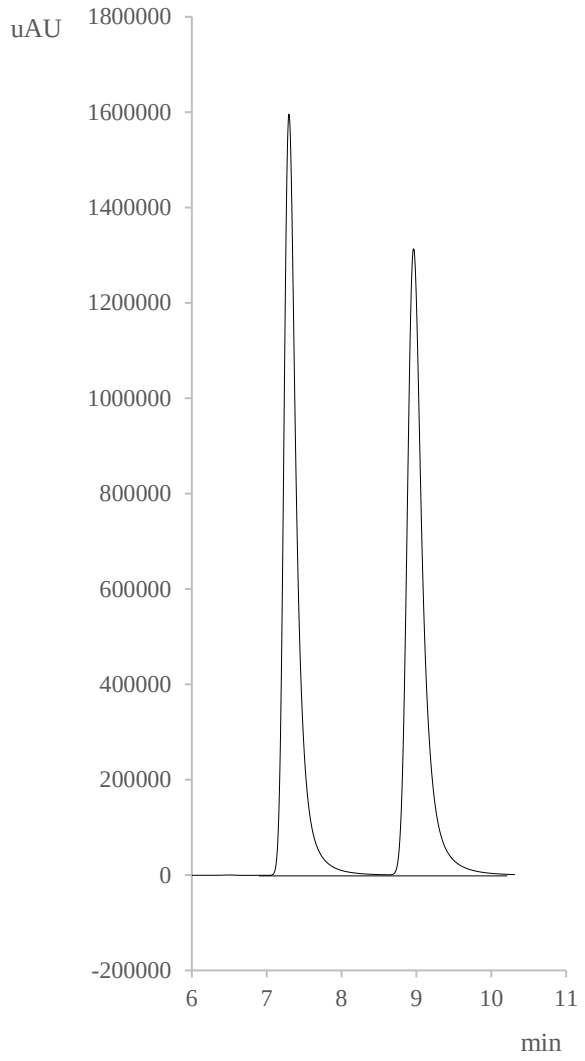
(+)-1-(2-Methoxy-2-methyl-phenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(+)-3q]: Following the General Procedure I, a mixture of 2-bromo-benzimidazole (**1b**) (41 mg, 0.20 mmol), 2-methoxy-2-methyl-phenyl boronic acid (**2l**) (66 mg, 0.40 mmol) and MnO_2 (0.17 g, 20 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (+)-**3q** (63 mg, quant, 70% ee) as a colorless oil. $[\alpha]_D^{20}$ = +11.9 (c 1.1, MeOH). IR: 2938 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.92 (3 H, s), 3.61 (3 H, s), 6.85 (1 H, d, *J* = 8.0 Hz), 6.85 (1 H, d, *J* = 8.0 Hz), 6.92 (1 H, d, *J* = 8.0 Hz), 7.13 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.17–7.21 (2 H, m), 7.35 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.70 (1 H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.4, 55.8, 109.5, 110.0, 119.2, 122.5, 122.7, 123.4, 130.8, 131.0, 136.4, 138.5, 143.3, 156.1. HRMS ESI, TOF) Calcd for $C_{15}H_{14}BrN_2O$ $[M+H]^+$: 317.0290. Found: 317.0278. Rt: (DAICEL CHIRALPAK® AD-H, hexane/*i*-PrOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 7.31 min (85%), 8.98 min (15%).

(*rac*)-1-(2-Methoxy-2-methyl-phenyl-1-yl)-2-bromo-benzo[*d*]imidazole [(*rac*)-3q]: Following the General Procedure II, a mixture of 2-bromo-benzimidazole (**1b**) (51 mg, 0.25 mmol), 2-methoxy-2-methyl-phenyl boronic acid (**2l**) (83 mg, 0.5 mmol) and MnO_2 (0.22 g, 25 mmol) in the Stock Solution (B) [2.5 mL, 0.063 mmol (Cu), 0.13 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3q** (67 mg, 84% isolated yield) as a colorless oil. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® AD-H, hexane/*i*-PrOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 7.29 min (50%), 8.96 min (50%).

HPLC data of 1-(2-methoxy-2-methyl-phenyl-1-yl)-2-bromo-benzo[*d*]imidazole (3q)

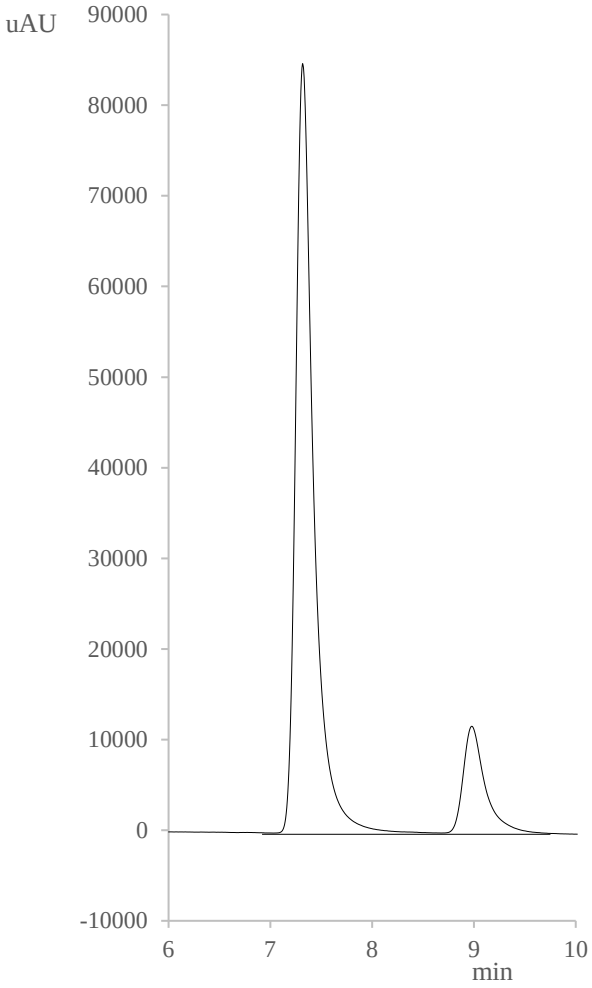
【PDA chromatograms】

(*rac*)-**3q**



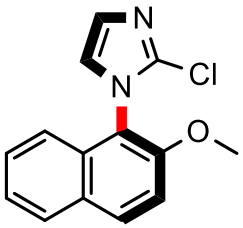
Peak#	Ret. Time	Area	Area%
1	7.29	19967645	50
2	8.96	19961343	50
total		39928988	100

(+)-**3q**



Peak#	Ret. Time	Area	Area%
1	7.31	1035292	85.4
2	8.98	177527	14.6
total		1212819	100

1-(2-Methoxynaphthalen-1-yl)-2-chloro-[*d*]imidazole (3r) (Table 3)



3r

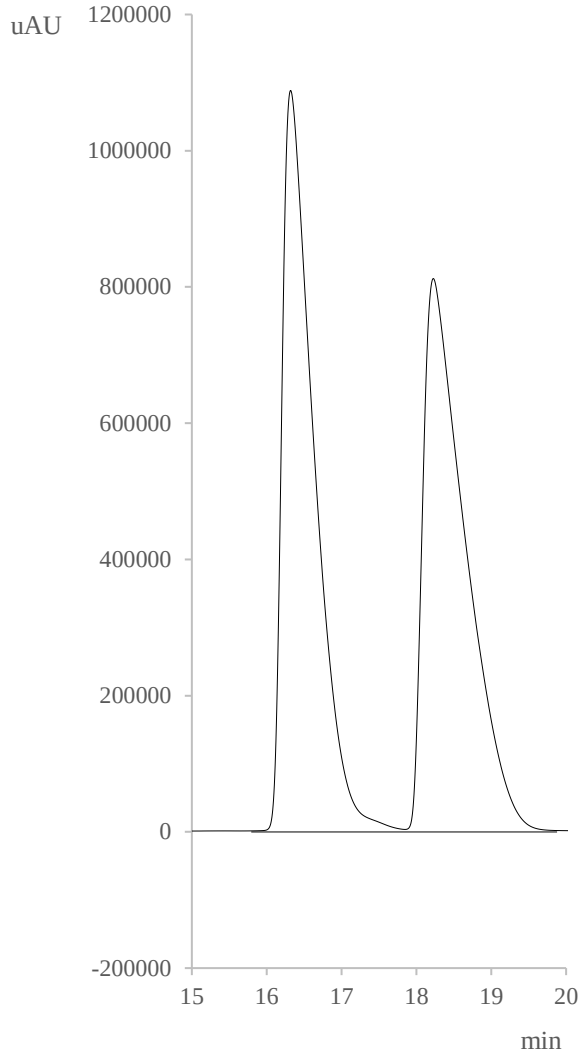
(+)-1-(2-Methoxynaphthalen-1-yl)-2-chloro-[*d*]imidazole [(+)-3r]: Following the General Procedure I, a mixture of 2-chloro-imidazole (**1f**) (21 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (+)-**3r** (52 mg, quant, 62% ee) as a colorless solid. $[\alpha]_D^{20}$ = +24.2 (c 1.0, MeOH). Mp: 72–75 °C. IR: 2940 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.92 (3 H, s), 7.03 (1 H, brd, *J* = 1.0 Hz), 7.21–7.24 (2 H, m), 7.38–7.44 (2 H, m), 7.48 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.87 (1 H, d, *J* = 8.0 Hz), 8.01 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.3, 113.0, 117.6, 120.8, 123.3, 124.3, 127.9, 128.1, 128.4, 128.5, 131.2, 131.3, 133.8, 152.8. HRMS (ESI, TOF) Calcd for $C_{14}H_{12}ClN_2O$ $[M+H]^+$: 259.0638. Found: 259.0625. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.5, 1.0 mL/min, 30 °C, 254 nm): 17.59 min (81%), 20.34 min (19%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)- 2-chloro-[*d*]imidazole [(*rac*)-3r]: Following the General Procedure II, a mixture of 2-chloro-imidazole (**1f**) (0.21 g, 2.0 mmol), 2-methoxynaphthalene boronic acid (**2a**) (0.81 g, 4.0 mmol) and MnO_2 (1.74 g, 20 mmol) in the Stock Solution (B) [20 mL, 0.50 mmol (Cu), 1.0 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (*rac*)-**3r** (0.20 g, 38% isolated yield) as a colorless solid. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.5, 1.0 mL/min, 30 °C, 254 nm): 16.31 min (50%), 18.22 min (50%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-chloro-[*d*]imidazole (3r)

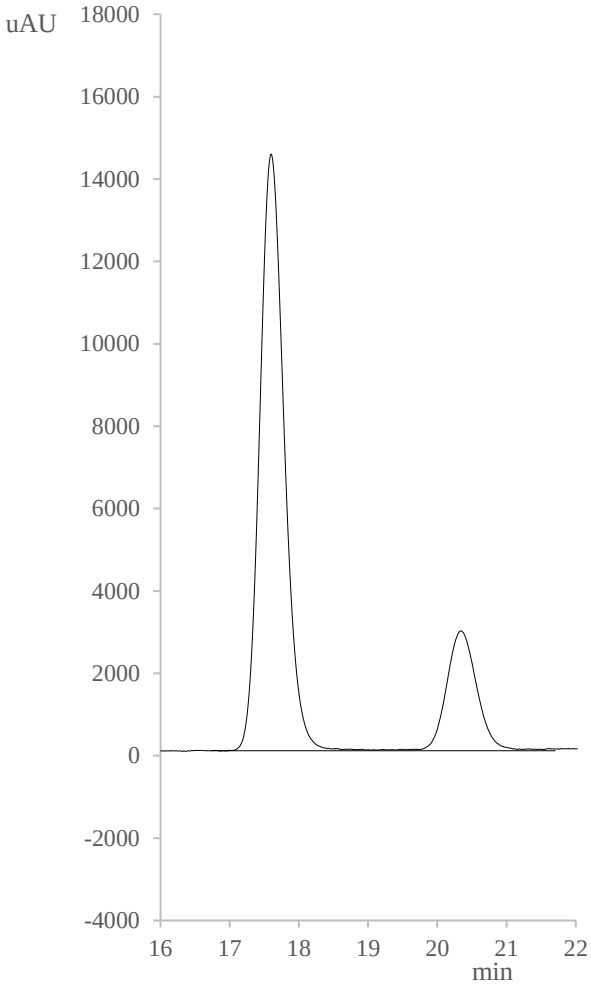
【PDA chromatograms】

(*rac*)-**3r**



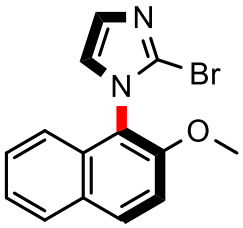
Peak#	Ret. Time	Area	Area%
1	16.31	32399460	50.3
2	18.22	31961138	49.7
total		64360598	100

(+)-**3r**



Peak#	Ret. Time	Area	Area%
1	17.59	353744	81.4
2	20.34	84519	18.6
total		438263	100

1-(2-Methoxynaphthalen-1-yl)-2-bromo-[*d*]imidazole (3s) (Table 3)



3s

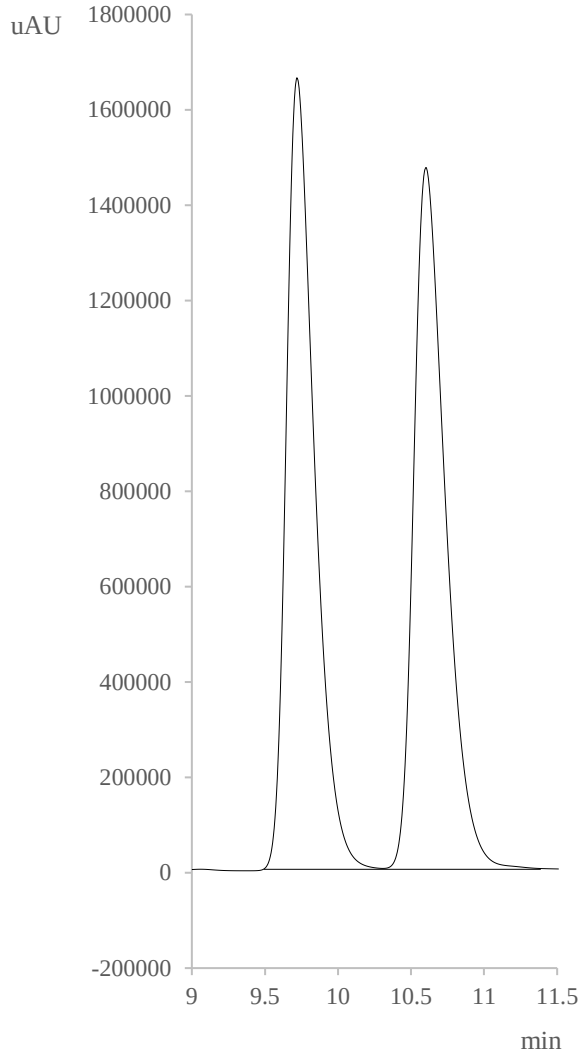
(+)-1-(2-Methoxynaphthalen-1-yl)-2-bromo-[*d*]imidazole [(+)-3s]: Following the General Procedure I, a mixture of 2-bromo-imidazole (**1g**) (30 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (+)-**3s** (59 mg, 97% isolated yield, 76% ee) as a pale yellow solid. $[\alpha]_D^{20}$ = +15.6 (c 1.0, MeOH). Mp: 104–105 °C. IR: 2941 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.91 (3 H, s), 7.08 (1 H, brs), 7.18 (1 H, dd, *J* = 8.5 Hz), 7.26 (1 H, brs), 7.37–7.43 (2 H, m), 7.47 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.86 (1 H, d, *J* = 8.0 Hz), 8.01 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.5, 113.1, 118.6, 121.1, 121.8, 124.4, 124.5, 128.0, 128.2, 128.5, 130.3, 131.4, 152.9. HRMS (ESI, TOF) Calcd for $C_{14}H_{12}BrN_2O$ $[M+H]^+$: 303.0133. Found: 303.0121. Rt: (DAICEL CHIRALPAK® AD-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 9.65 min (88%), 10.6 min (12%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-bromo-[*d*]imidazole [(*rac*)-3s]: Following the General Procedure II, a mixture of 2-bromo-imidazole (**1g**) (30 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (B) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (*rac*)-**3s** (38 mg, 63% isolated yield) as a pale yellow solid. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® AD-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 9.71 min (50%), 10.6 min (50%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-bromo-[*d*]imidazole (3s)

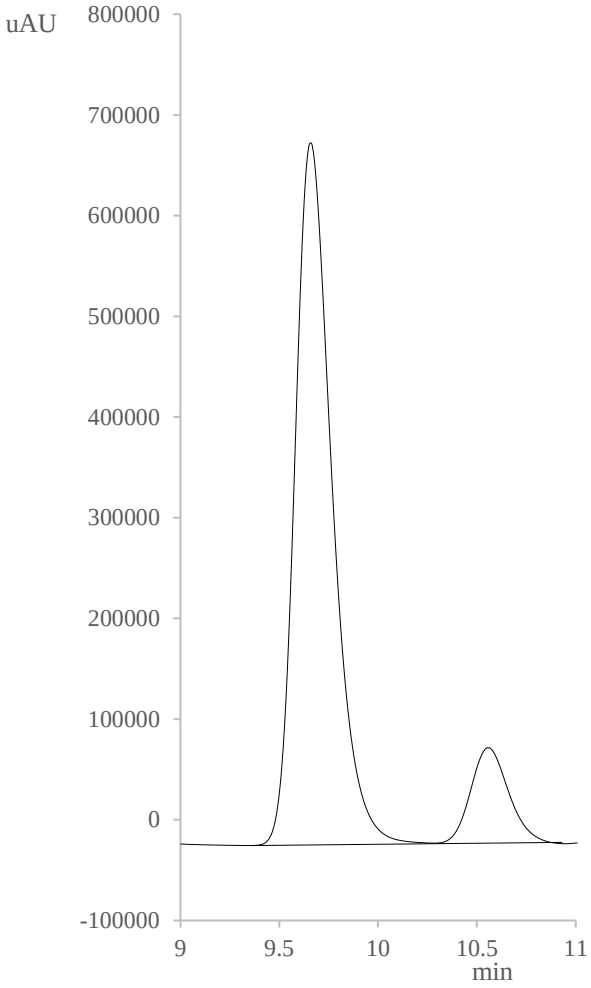
【PDA chromatograms】

(*rac*)-**3s**



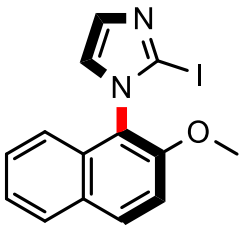
Peak#	Ret. Time	Area	Area%
1	9.71	22494445	49.9
2	10.6	22614362	50.1
total		45108807	100

(+)-**3s**



Peak#	Ret. Time	Area	Area%
1	9.65	9124535	87.6
2	10.55	1297545	12.4
total		10422080	100

1-(2-Methoxynaphthalen-1-yl)-2-iodo-[*d*]imidazole (3t) (Table 3)



3t

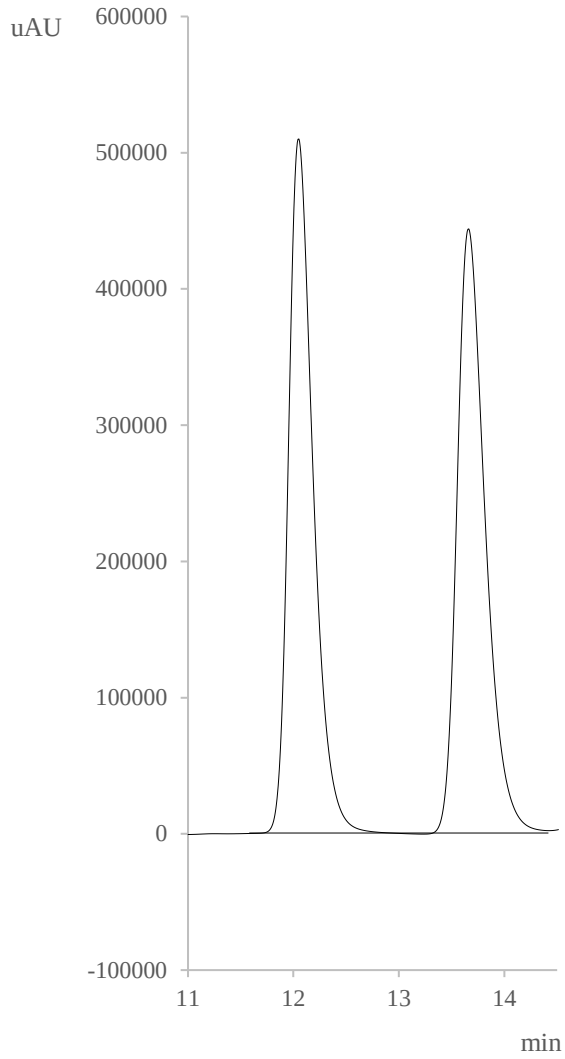
(+)-1-(2-Methoxynaphthalen-1-yl)-2-iodo-[*d*]imidazole [(+)-3t]: Following the General Procedure I, a mixture of 2-iodo-imidazole (**1h**) (40 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (0.17 g, 20 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (+)-**3t** (64 mg, 91% isolated yield, 62% ee) as a pale yellow solid. $[\alpha]_D^{20}$ = +12.2 (c 1.0, MeOH). Mp: 124–127 °C. IR: 2936 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.92 (3 H, s), 7.12 (1 H, d, *J* = 8.0 Hz), 7.15 (1 H, brs), 7.32 (1 H, brs), 7.38–7.41 (2 H, m), 7.47 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.87 (1 H, d, *J* = 8.0 Hz), 8.03 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.5, 93.0, 113.1, 119.9, 121.3, 124.5, 125.5, 128.0, 128.2, 128.5, 131.4, 131.6, 132.7, 153.0. HRMS (ESI, TOF) Calcd for $C_{14}H_{12}IN_2O$ $[M+H]^+$: 350.9994. Found: 350.9982. Rt: (DAICEL CHIRALPAK® AD-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 12 min (81%), 13.69 min (19%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-iodo-[*d*]imidazole [(*rac*)-3t]: Following the General Procedure II, a mixture of 2-iodo-imidazole (**1h**) (40 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (B) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (*rac*)-**3t** (11 mg, 16% isolated yield) as a pale yellow solid. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® AD-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 12.04 min (50%), 13.66 min (50%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-iodo-[*d*]imidazole (3t)

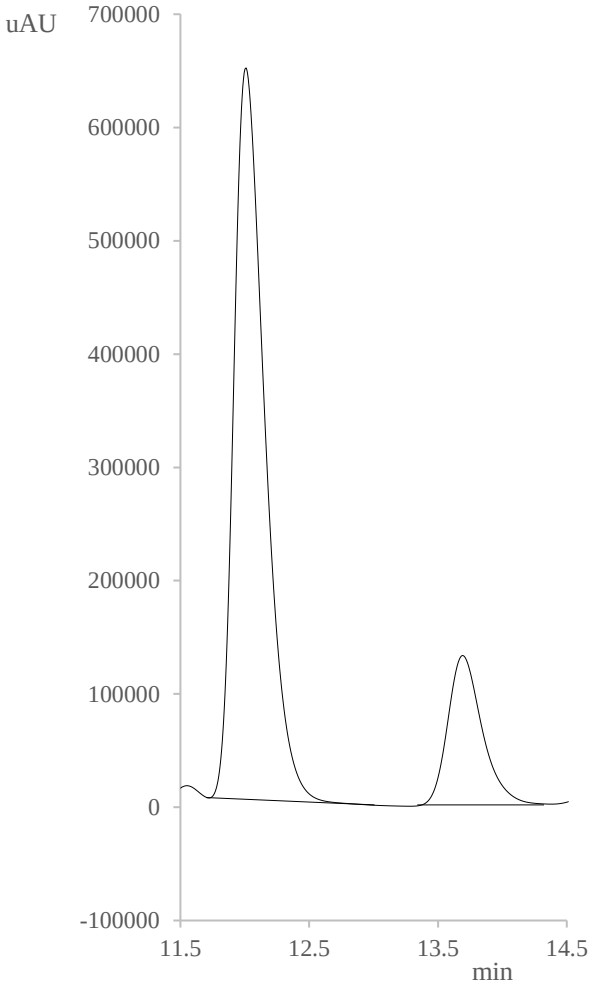
【PDA chromatograms】

(*rac*)-**3t**



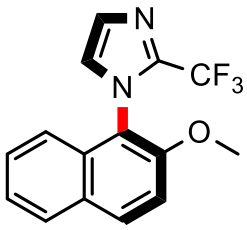
Peak#	Ret. Time	Area	Area%
1	12.04	8405501	50.2
2	13.66	8343629	49.8
total		16749130	100

(+)-**3t**



Peak#	Ret. Time	Area	Area%
1	12	10832802	81.5
2	13.69	2416992	18.5
total		13249794	100

1-(2-Methoxynaphthalen-1-yl)-2-trifluoro-[*d*]imidazole (3u)



3u

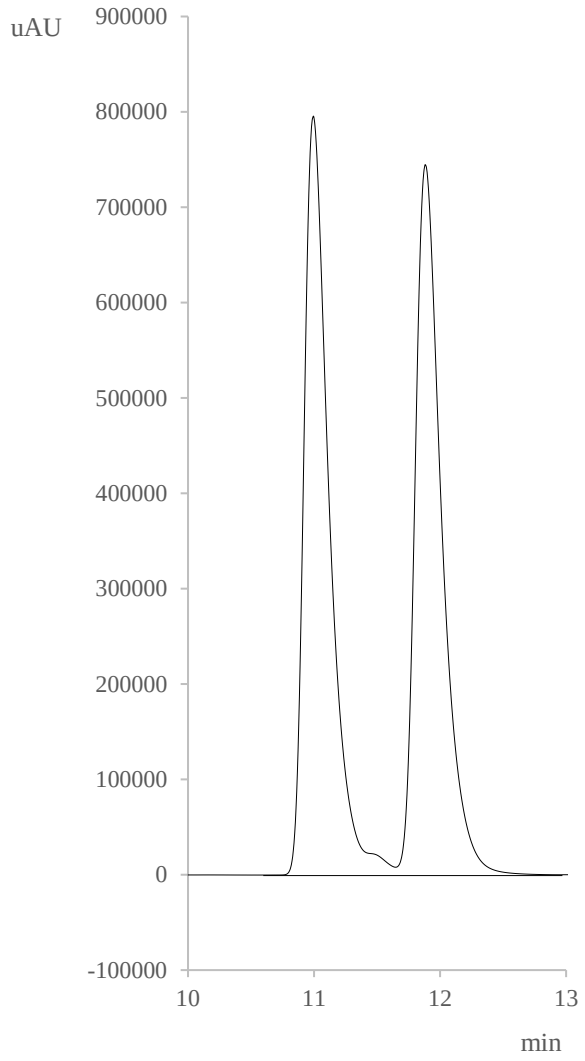
(+)-1-(2-Methoxynaphthalen-1-yl)-2-trifluoro-[*d*]imidazole [(+)-3u]: Following the General Procedure I, a mixture of 2-trifluoro-imidazole (**1i**) (28 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (+)-**3u** (64 mg, 91% isolated yield, 64% ee) as a pale yellow solid. $[\alpha]_D^{20}$ = +13.0 (c 1.0, MeOH). Mp: 78–79 °C. IR: 2944 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.91 (3 H, s), 7.08 (1 H, brd, *J* = 1.5 Hz), 7.11 (1 H, d, *J* = 8.0 Hz), 7.37–7.44 (3 H, m), 7.48 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.87 (1 H, d, *J* = 8.0 Hz), 8.02 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.3, 112.7, 117.7, 118.6 (q, *J* = 270.0 Hz), 120.7, 124.5, 1225.5, 127.9, 128.3, 129.1, 131.4, 131.7, 137.4 (q, *J* = 39.5 Hz), 152.8. ^{19}F NMR (471 MHz, CDCl3) δ: −62.7. HRMS (ESI, TOF) Calcd for $C_{15}H_{12}F_3N_2O$ $[M+H]^+$: 293.0902. Found: 293.0892. Rt: (DAICEL CHIRALPAK® IB-N, hexane/EtOH/DEA = 98/2/0.1, 1.0 mL/min, 30 °C, 254 nm): 11.1 min (82%), 12.0 min (18%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-iodo-[*d*]imidazole [(*rac*)-3u]: Following the General Procedure II, a mixture of 2-iodo-imidazole (**1h**) (68 mg, 0.50 mmol), 2-trifluoro-imidazole (**1i**) (0.20 g, 1.0 mmol) and MnO_2 (0.44 g, 5.0 mmol) in the Stock Solution (B) [5.0 mL, 0.13 mmol (Cu), 0.25 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 1:1) to afford the titled compound (*rac*)-**3u** (150 mg, 85% isolated yield) as a pale yellow solid. ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® IB-N, hexane/EtOH/DEA = 98/2/0.1, 1.0 mL/min, 30 °C, 254 nm): 10.99 min (50%), 11.88 min (50%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)- 2-trifluoro-[*d*]imidazole (3u)

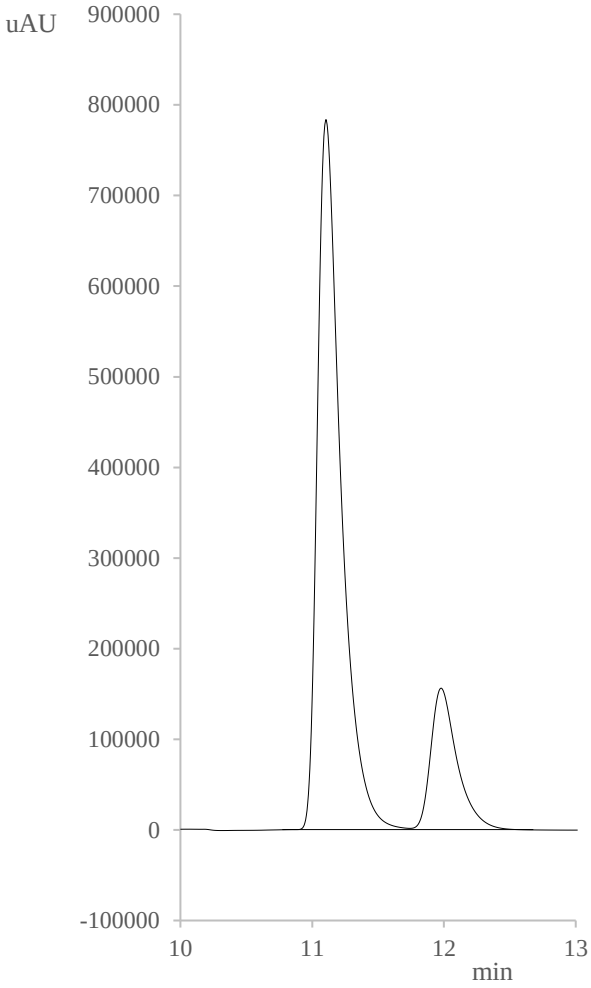
【PDA chromatograms】

(*rac*)-**3u**



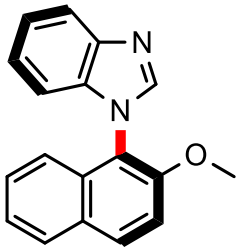
Peak#	Ret. Time	Area	Area%
1	10.99	11139901	50.4
2	11.88	10967077	49.6
total		22106978	100

(+)-**3u**



Peak#	Ret. Time	Area	Area%
1	11.1	9808099	81.7
2	12	2204107	18.3
total		12012206	100

1-(2-Methoxynaphthalen-1-yl)-benzo[*d*]imidazole (3w)



3w

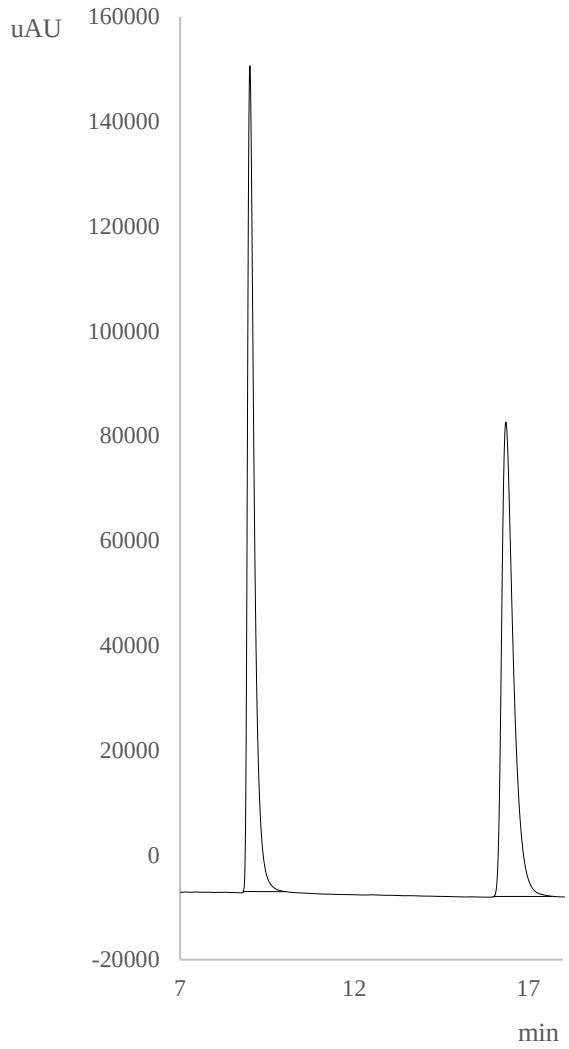
(*S*)-1-(2-Methoxynaphthalen-1-yl)-benzo[*d*]imidazole [(*S*)-3w]: Following the General Procedure I, a mixture of benzimidazole (**1**) (24 mg, 0.20 mmol), 2-methoxynaphthalene boronic acid (**2a**) (81 mg, 0.40 mmol) and MnO_2 (174 mg, 2.0 mmol) in the Stock Solution (A) [2.0 mL, 0.050 mmol (Cu), 0.10 mmol (**4j**)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*S*)-**3w** (53 mg, quant, 6% ee) as a colorless solid. $[\alpha]_D^{20}$ = +16.7 (c 1.0, MeOH). Mp: 155–156 °C. IR: 2931 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.84 (3 H, s), 6.96 (1 H, d, *J* = 8.0 Hz), 7.19–7.24 (2 H, m), 7.34 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.37–7.42 (2 H, m), 7.45 (1 H, d, *J* = 9.0 Hz), 7.91 (1 H, d, *J* = 8.0 Hz), 7.95 (1 H, d, *J* = 8.0 Hz), 8.03–8.06 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.5, 110.8, 113.3, 117.3, 120.2, 121.6, 122.3, 123.2, 124.5, 128.0, 128.1, 128.8, 131.0, 131.5, 135.2, 143.3, 144.7, 153.2. HRMS (ESI, TOF) Calcd for $C_{18}H_{15}N_2O$ $[M+H]^+$: 275.1184. Found: 275.1182. Rt: (DAICEL-CHIRALPAK® IB-N, hexane/*i*-PrOH = 5/1, 1.0 mL/min, 30 °C, 254 nm): 8.9 min (53%), 15.8 min (47%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-benzo[*d*]imidazole [(*rac*)-3w]: Following the General Procedure II, a mixture of benzimidazole (**1**) (0.48 g, 4.0 mmol), 2-methoxynaphthalen boronic acid (**2a**) (1.6 g, 8.0 mmol) and MnO_2 (3.5 g, 40 mmol) in the Stock Solution (B) [4.0 mL, 0.10 mmol (Cu), 0.20 mmol (TMEDA)] was stirred for 22 h at 25 °C. The crude material was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford the titled compound (*rac*)-**3w** as a colorless solid (1.1 g, 99% isolated yield). ^1H NMR spectra was identical with chiral one shown above. Rt: (DAICEL CHIRALPAK® IB-N, hexane/*i*-PrOH = 5/1, 1.0 mL/min, 30 °C, 254 nm): 9.0 min (5%), 16.4 min (47%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-benzo[*d*]imidazole (3w)

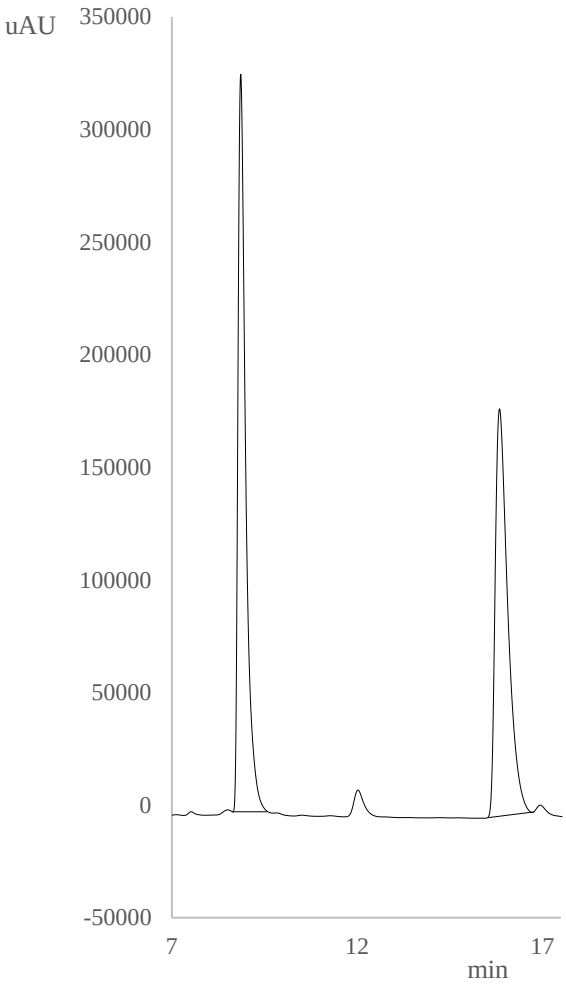
【PDA chromatograms】

(*rac*)-**3w**



Peak#	Ret. Time	Area	Area%
1	9	2156844	50.27
2	16.35	2133319	49.73
total		4290163	100

(*S*)-**3w**



Peak#	Ret. Time	Area	Area%
1	8.86	4753528	52.55
2	15.84	4292947	47.45
total		9046475	100

4. Transformation of 1-(2-methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3b) prepared by the asymmetric Chan-Lam coupling

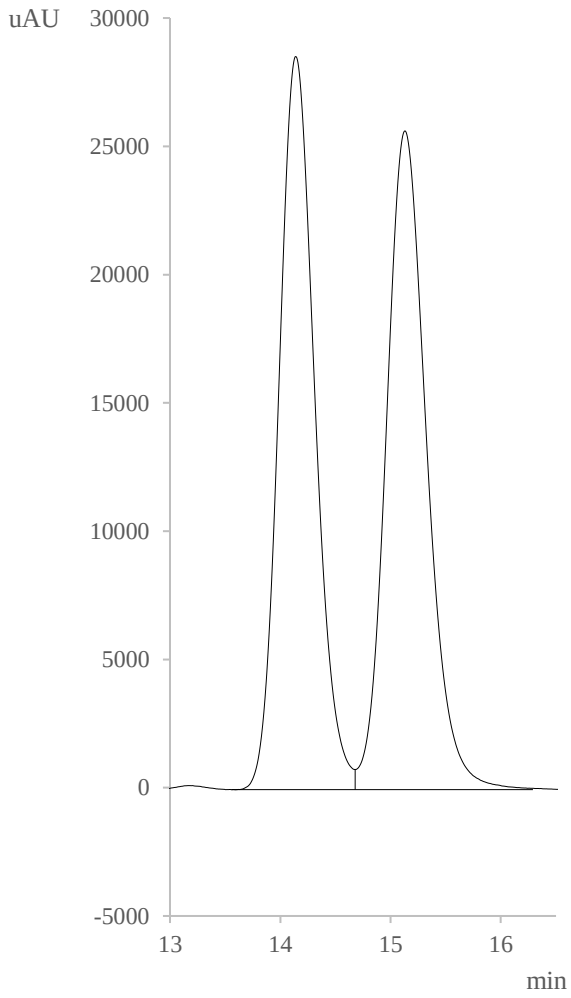
4-1. Recrystallization of 1-(2-methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole (3b):

3b, 85% ee (0.77 g, 2.2 mmol) and hexane (20 mL) were charged in a 50 mL recovery flask. The suspension was heated at 70 ºC and EtOAc (10 mL) was added dropwise into the flask at 70 ºC until the suspension became a clear solution. The mixture was gradually cooled to room temperature and left overnight. The mixture was filtered to afford **3b**, >99% ee (0.42 mg, 55%) as a colorless solid.

HPLC data of (*S*)-1-(2-methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole, [(*S*)-3b] after the recrystallization

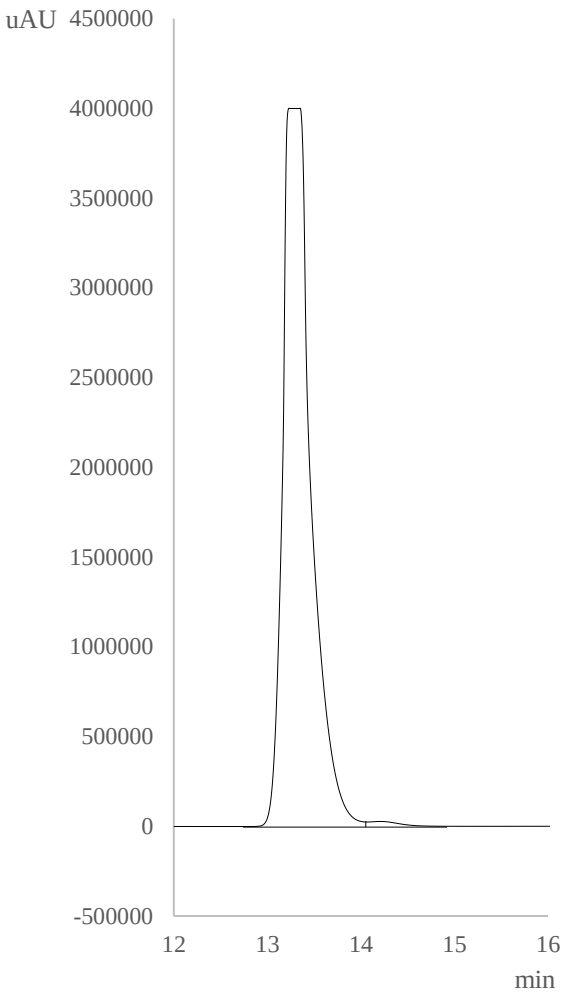
【PDA chromatograms】

(*rac*)-**3b**



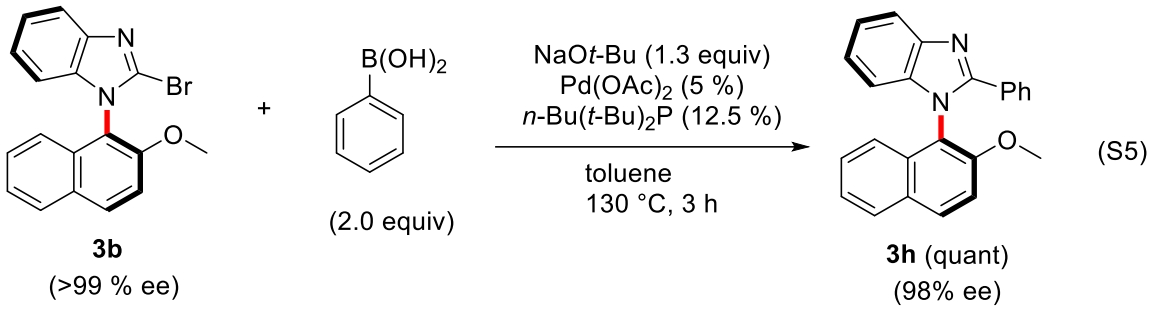
Peak#	Ret. Time	Area	Area%
1	14.134	646813	49.78
2	15.125	652606	50.22
total		1299419	100

(*S*)-**3b**



Peak#	Ret. Time	Area	Area%
1	13.344	84199384	99.86
2	14.202	115010	0.14
total		84314394	100

4-2. Suzuki coupling



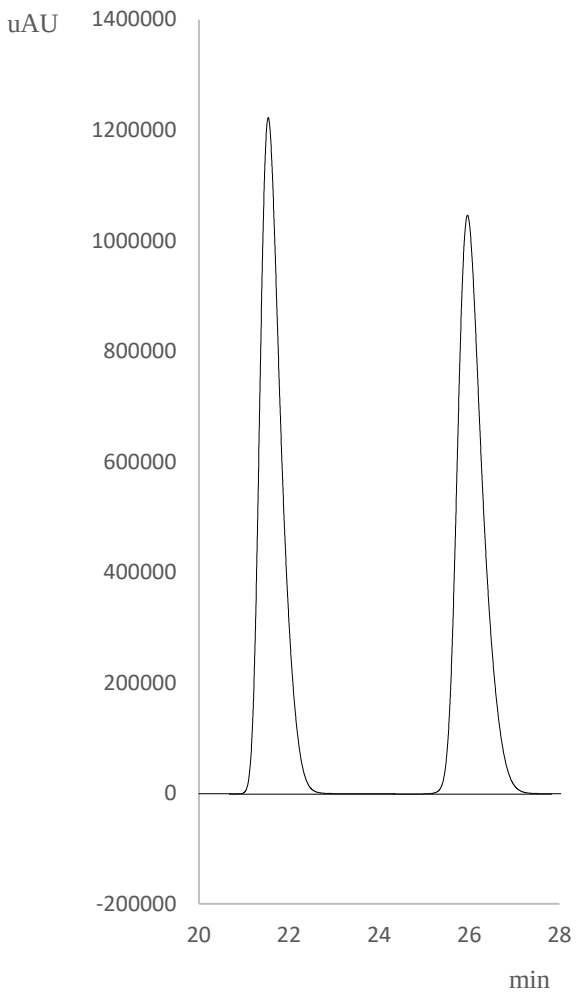
(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole [(*S*)-3h]:

(*S*)-**3b**, >99% ee (35 mg, 0.10 mmol), phenyl boronic acid (24 mg, 0.20 mmol), $Pd(OAc)_2$ (1.1 mg, 5.0 %), *n*-Bu(*t*-Bu)$_2$P·HBF_4 (3.6 mg, 12.5 %) and *t*-BuONa (13 mg, 0.15 mmol) were added to an oven-dried Schlenk flask. The flask was equipped with a rubber septum and evacuated and back-filled with nitrogen (this process was repeated three times). After anhydrous toluene (1.0 mL) was added via a syringe, the septum was replaced with a Teflon screw cap under a flow of nitrogen and the cap was tightly closed. The reaction mixture was stirred for 3 h at 130 °C and passed through Celite with EtOAc. The filtrate was concentrated in vacuo. The purification of the crude product with a silica gel (hexane/EtOAc = 1:1) to afford the titled compound (*S*)-**3h** (43 mg, quant, 98% ee) as colorless solid. $[\alpha]_D^{20}$ = +68.7 (c 1.0, MeOH). Mp: 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.57 (3 H, s), 6.81 (1 H, d, *J* = 8.0 Hz), 7.14–7.18 (3 H, m), 7.22–7.26 (1 H, m), 7.29–7.35 (3 H, m), 7.39–7.43 (2 H, m), 7.53 (2 H, d, *J* = 7.5 Hz), 7.89–7.92 (1 H, m), 7.95 (1 H, d, *J* = 8.0 Hz), 8.00 (1 H, d, *J* = 9.0 Hz). Rt: (DAICEL CHIRALPAK® IK-3, hexane/*i*-PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm): 21.5 min (0.9%), 25.9 min (99.1%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole (3h) prepared by the Suzuki coupling

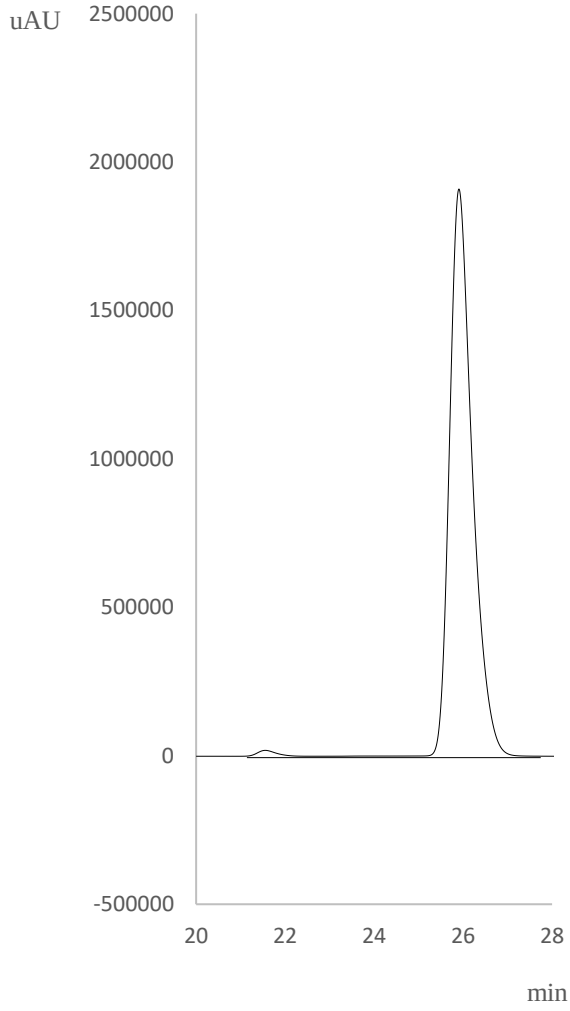
【PDA chromatograms】

(*rac*)-**3h**



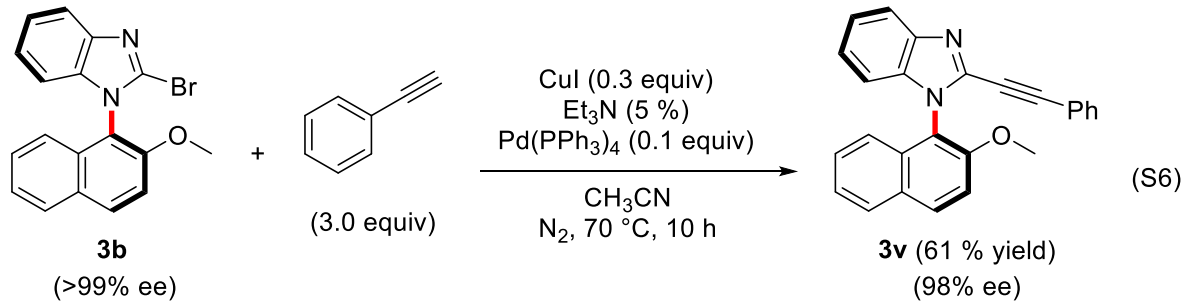
Peak#	Ret. Time	Area	Area%
1	21.54	40655573	49.55
2	25.963	41391469	50.45
total		82047042	100

(*S*)-**3h**



Peak#	Ret. Time	Area	Area%
1	21.55	612369	0.85
2	25.907	67792268	99.15
total		68404637	100

4-3. Sonogashira coupling



(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole [(*S*)-3v]:

(*S*)-**3b**, >99% ee (71 mg, 0.20 mmol), CuI (11 mg, 0.060 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) were charged in an oven-dried Schlenk flask. The flask was equipped with a rubber septum and evacuated and back-filled with nitrogen (this process was repeated three times). After ethynyl benzene (66 µL, 0.60 mmol), triethylamine (83 µL, 0.60 mmol) and anhydrous CH_3CN (1.0 mL) was added to the flask, the septum was replaced with a Teflon screw cap under a flow of nitrogen and the cap was tightly closed. The reaction mixture was stirred for 10 h at 70 °C and passed through Celite with EtOAc. The filtrate was concentrated in vacuo. The purification of the crude product with a silica gel (hexane/EtOAc = 4:1) to afford the titled compound (*S*)-**3v** (46 mg, 61% isolated yield, >99% ee) as colorless solid. $[\alpha]_D^{20} = -56.3$ (c 0.84, MeOH). Mp: 95–97 °C. IR: 2218, 2924 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.85 (3 H, s), 6.92 (1 H, d, *J* = 8.0 Hz), 7.06–7.08 (2 H, m), 7.17–7.20 (2 H, m), 7.22–7.27 (3 H, m), 7.34–7.43 (3 H, m), 7.48 (1 H, d, *J* = 9.0 Hz), 7.92–7.94 (2 H, m), 8.09 (1 H, d, *J* = 9.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.5, 79.5, 93.6, 110.7, 113.4, 117.0, 120.1, 121.2, 121.8, 123.0, 124.1, 124.4, 127.9, 128.1, 128.2, 128.8, 129.2, 131.3, 131.5, 131.7, 135.8, 138.7, 143.1, 153.6. HRMS (ESI, TOF) Calcd for $C_{26}H_{19}N_2O$ $[M+H]^+$: 375.1497. Found: 375.1497. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 8.5 min (<0.5%), 10.2 min (>99.5%).

(*rac*)-1-(2-Methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole [(*rac*)-3v]:

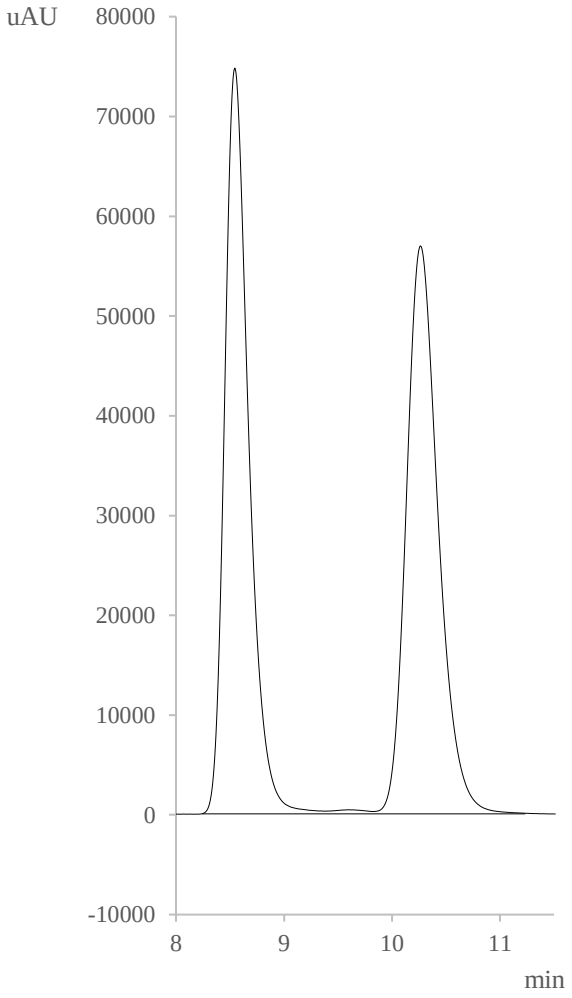
(*rac*)-**3b** (71 mg, 0.20 mmol), CuI (11 mg, 0.060 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) were added to an oven-dried Schlenk flask. The flask was equipped with a rubber septum and evacuated

and back-filled with nitrogen (this process was repeated three times). After ethynyl benzene (66 µL, 0.60 mmol), triethylamine (83 µL, 0.60 mmol) and anhydrous CH_3CN (1.0 mL) was added to the flask, the septum was replaced with a Teflon screw cap under a flow of nitrogen and the cap was tightly closed. The reaction mixture was stirred for 10 h at 70 °C and passed through Celite with EtOAc. The filtrate was concentrated in vacuo. The purification of the crude product with a silica gel (hexane/EtOAc = 4:1) to afford the titled compound (*rac*)-**3v** (46 mg, 61% isolated yield) as colorless solid. Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm): 8.5 min (50%), 10.2 min (50%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-phenyl-benzo[*d*]imidazole (3v) prepared by the Sonogashira coupling

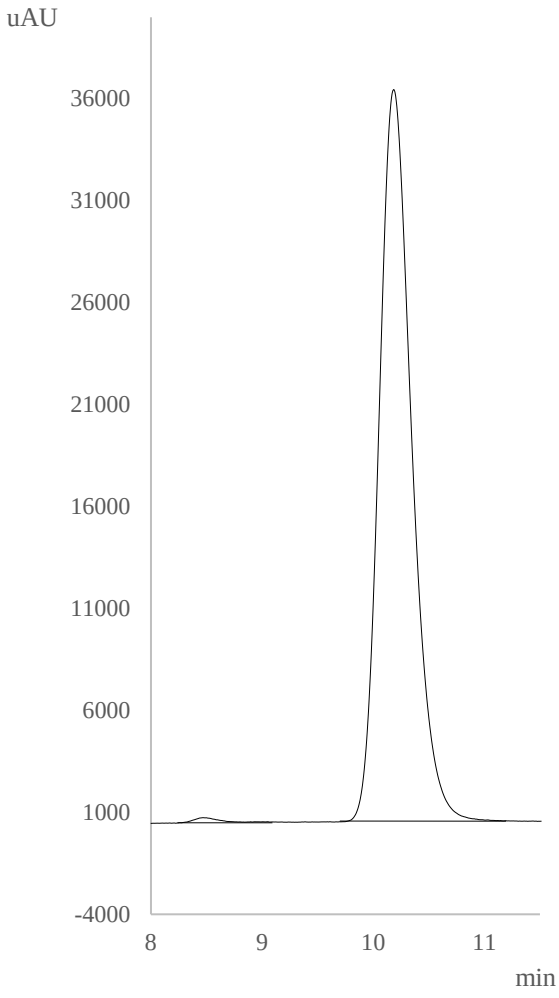
【PDA chromatograms】

(*rac*)-**3v**



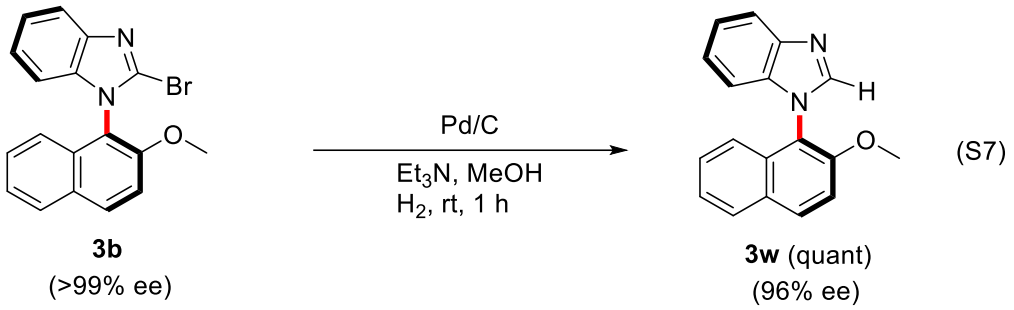
Peak#	Ret. Time	Area	Area%
1	9.573	26810	49.86
2	11.768	26963	50.14
total		53773	100

(*S*)-**3v**



Peak#	Ret. Time	Area	Area%
1	8.465	3466	0.47
2	10.18	731848	99.53
total		3877710	100

4-4. Reductive dehalogenation



3b
(>99% ee)

3w (quant)
(96% ee)

(S7)

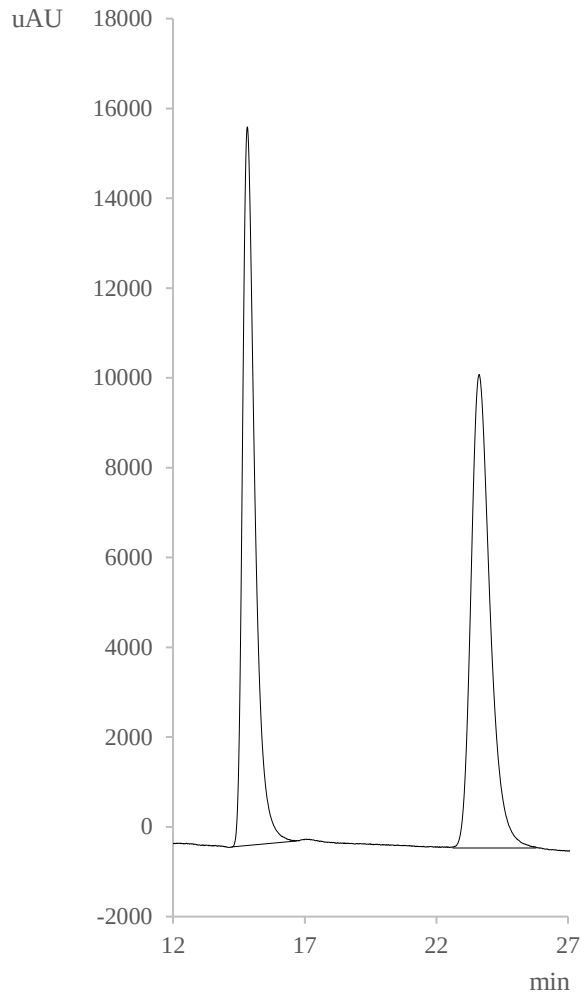
(*S*)-1-(2-Methoxynaphthalen-1-yl)-benzo[*d*]imidazole [(*S*)-3w]:

To a test tube were added (*S*)-**3b**, >99% ee (35 mg, 0.10 mmol), 10% Pd/C (7.1 mg, 10wt%, 0.060 mmol), triethylamine (84 μL, 0.60 mmol). After MeOH (2.0 mL) was added to the test tube, the mixture was evacuated and backfilled with H_2 (This operation was repeated three times). The reaction mixture was stirred under H_2 atmosphere (balloon) at 25 °C for 1 h and passed through Celite with EtOAc. To the obtained mixture was poured water (ca. 10 mL) and EtOAc (*ca.* 40 mL), and then the aqueous phase was washed three times with EtOAc. The EtOAc solution was washed with brain, dried over anhydrous magnesium sulfate, and evaporated to afford the titled compound (*S*)-**3w** (64 mg, quant, 96% ee) as a colorless solid. $[\alpha]_D^{20}$ = +95.5 (c 1.0, MeOH). Mp: 158–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.84 (3 H, s), 6.96 (1 H, d, *J* = 8.0 Hz), 7.19–7.24 (2 H, m), 7.34 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.37–7.43 (2 H, m), 7.45 (1 H, d, *J* = 9.0 Hz), 7.91 (1 H, d, *J* = 8.0 Hz), 7.95 (1 H, d, *J* = 8.0 Hz), 8.03–8.05 (2 H, m). Rt: (DAICEL CHIRALCEL® OJ-H, hexane/*i*-PrOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 14.9 min (98%), 23.9 min (2%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-benzo[*d*]imidazole (3w) prepared by the reductive debromination using Pd/C

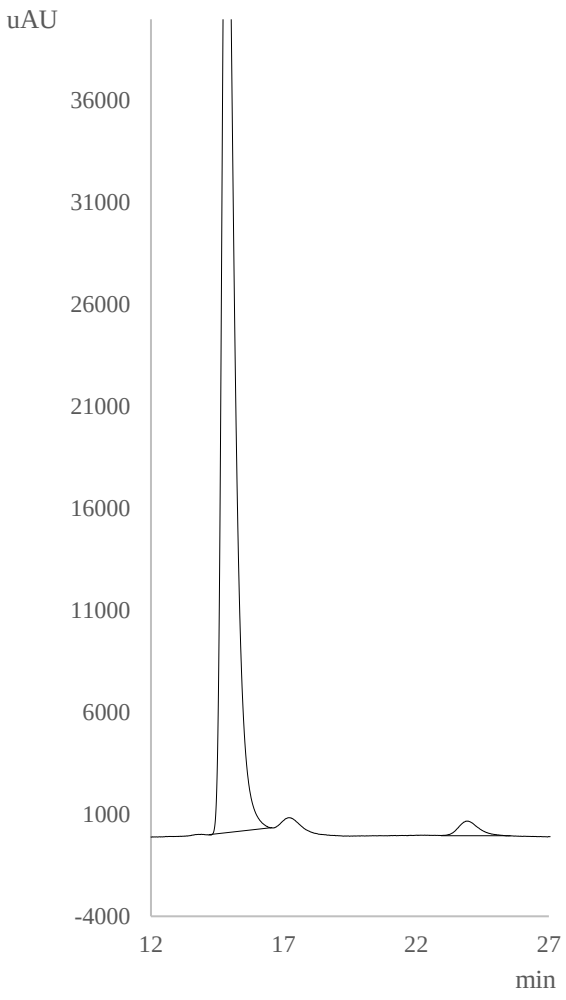
【PDA chromatograms】

(*rac*)-**3w**



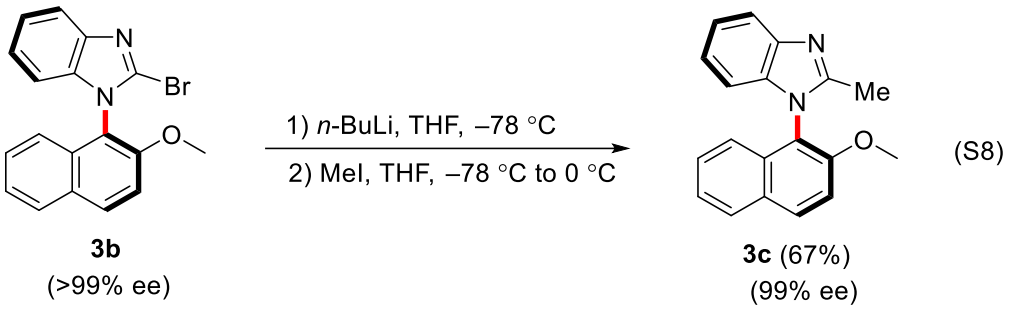
Peak#	Ret. Time	Area	Area%
1	14.811	522735	50.16
2	23.619	519433	49.84
total		1042168	100

(*S*)-**3w**



Peak#	Ret. Time	Area	Area%
1	14.846	1747584	98.4
2	23.87	28538	1.6
total		3877710	100

4-5. Metallative methylation



3b
(>99% ee)

3c (67%)
(99% ee)

(S8)

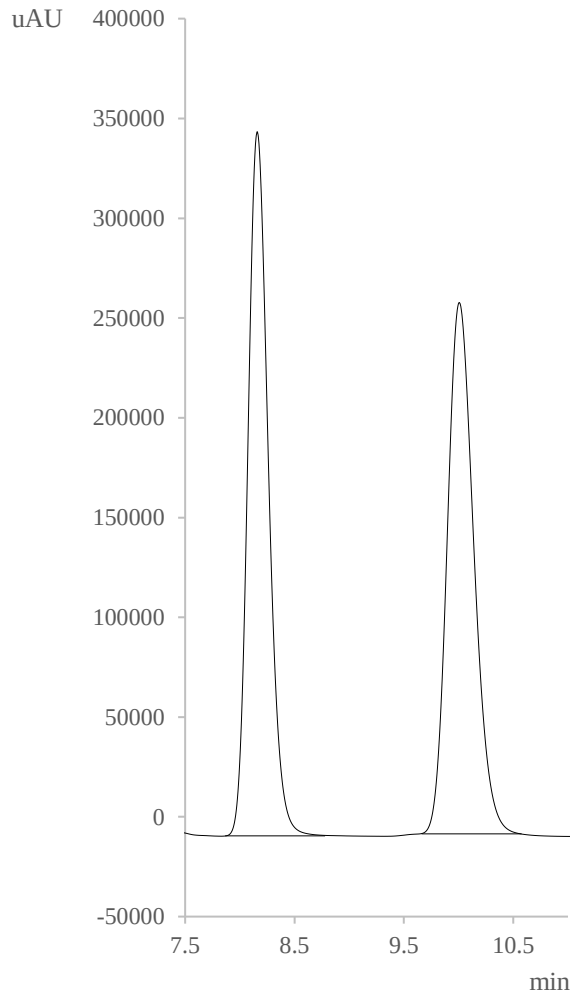
(*S*)-1-(2-Methoxynaphthalen-1-yl)-2-methyl-benzo[*d*]imidazole [(*S*)-3c]:

(*S*)-**3b**, >99% ee (26 mg, 0.075 mmol) and anhydrous THF (1.0 mL) were charged in a 20 mL flask. After stirring for 15 min at –78 °C, *n*-butyllithium (ca. 2.6 mol/L in hexane) (34 µL, 0.090 mol) was added dropwise into the flask and stirred for 1 h at –78 °C. Iodomethane (11 µL, 0.11 mmol) was added dropwisely to the mixture at –78 °C and stirred overnight at room temperature. To the reaction mixture was added water (0.50 mL) and ethylenediamine (0.50 mL), and the reaction mixture was stirred at room temperature for 15 min. To the obtained mixture was poured EtOAc (10 mL), and then the aqueous phase was washed three times with EtOAc. The combined organic phases was washed with brain and evaporated. The purification of the crude product with a silica gel (hexane/EtOAc = 2:1) to afford the titled compound. The mixture was evaporated to afford the titled compound (*S*)-**3c** (14 mg, 67 % isolated yield, 99% ee) as a colorless solid. $[\alpha]_D^{20}$ = +115.2 (c 0.60, MeOH). Mp: 29–30 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.36 (3 H, s), 3.85 (3 H, s), 6.78 (1 H, d, *J* = 8.0 Hz), 7.08 (1 H, d, *J* = 8.5 Hz), 7.13 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.28 (1 H, dd, *J* = 8.0, 8.0 Hz), 7.37–7.44 (2 H, m), 7.47 (1 H, d, *J* = 9.0 Hz), 7.83 (1 H, d, *J* = 8.0 Hz), 7.93 (1 H, d, *J* = 8.5 Hz), 8.07 (1 H, d, *J* = 8.5 Hz). Rt: (DAICEL CHIRALCEL® OJ-H, hexane/EtOH/DEA = 90/10/0.1, 1.0 mL/min, 30 °C, 254 nm): 8.2 min (>99%), 10.14 min (<0.5%).

HPLC data of 1-(2-methoxynaphthalen-1-yl)-2-methyl-benzo[*d*]imidazole (3c) prepared by the metallative methylation

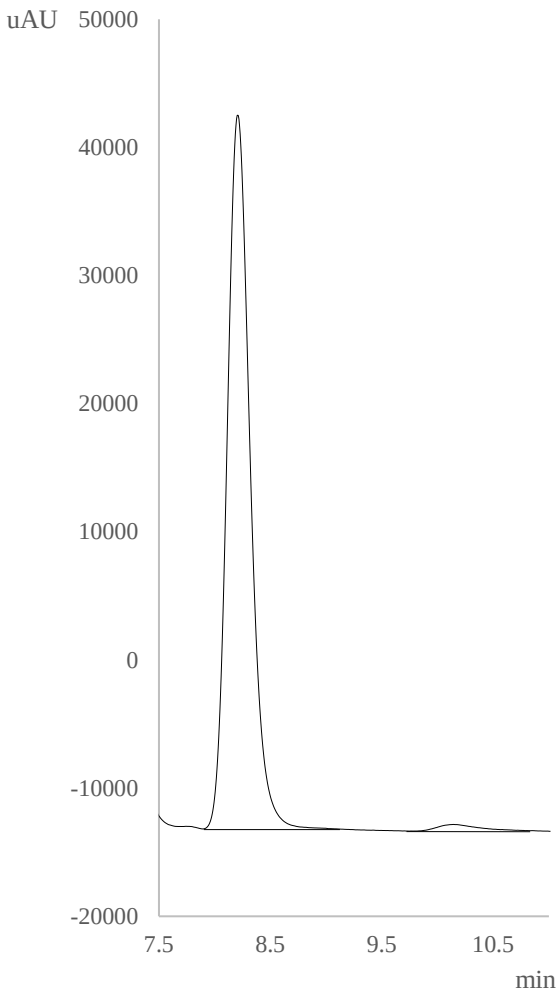
【PDA chromatograms】

(*rac*)-**3c**



Peak#	Ret. Time	Area	Area%
1	8.16	4600260	50.02
2	10	4596214	49.98
total		9196474	100

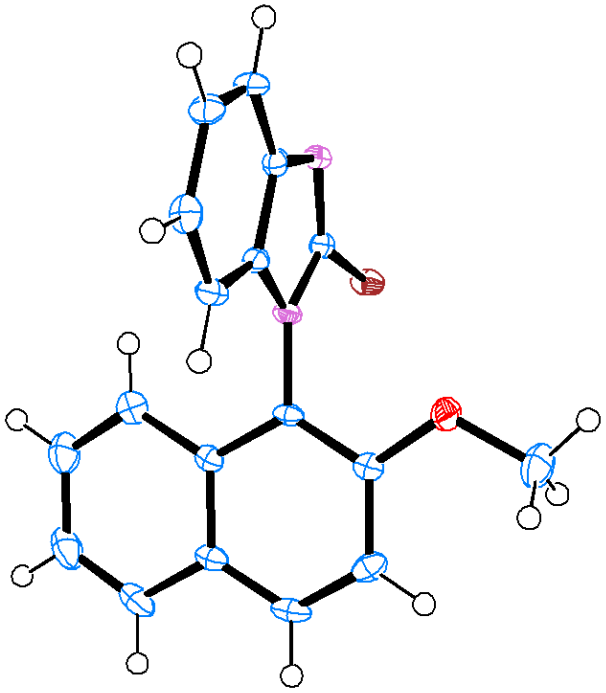
(*S*)-**3c**



Peak#	Ret. Time	Area	Area%
1	8.2	800337	98.53
2	10.14	11978	1.47
total		812315	100

5. X-ray data of (*S*)-1-(2-methoxynaphthalen-1-yl)-2-bromo-benzo[*d*]imidazole, (*S*)-3b:

X-ray diffraction data of (*S*)-**3b** was collected on a Rigaku XtaLAB P100 diffractometer diffratomter employing graphite-monochromated Mo Kα radiation and. The structures was solved by direct method with SIR-92 program[15] and refined with SHELXL program.[16] The structural models were drawn with ORTEP-3 program.[17] Further information on the crystal structure determinations have been deposited with the Cambridge Crystallographic Data Center [(*S*)-**3b**: CCDC 2296508]. Figure S1 shows the ORTEP drawing of (*S*)-**3b**.



(*S*)-**3b**

Fig. S1 X-ray structure of compound (*S*)-**3b** (thermal ellipsoid plot at the 50% probability level)

Table S3. Crystallographic data and structural refinement for compound (*S*)-**3b**

Compound	(*S*)-**3b**
Empirical formula	$C_{18}H_{13}BrN_2O$
Formula weight	353.22
Temperature (K)	100
Crystal system	*orthorhombic*
Space group	$P2_12_12_1$
a (Å)	7.0262 (11)
b (Å)	9.2338 (14)
c (Å)	24.100 (4)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	1563.5 (4)
Z	4
D_{calcd} (g/cm^3)	1.500
R_1	0.0277
wR_2	0.0543
Goodness-of-fit	0.922

6. Rotational barrier of (*S*)-3w

Equation 1. $\Delta G = -RT \ln(kh/k_BT)$

Equation 2. $t_{1/2} = \ln(2)/k$

Equation 3. $k = k_{rac}/2$

Fig. S2 Formula of rotational barrier

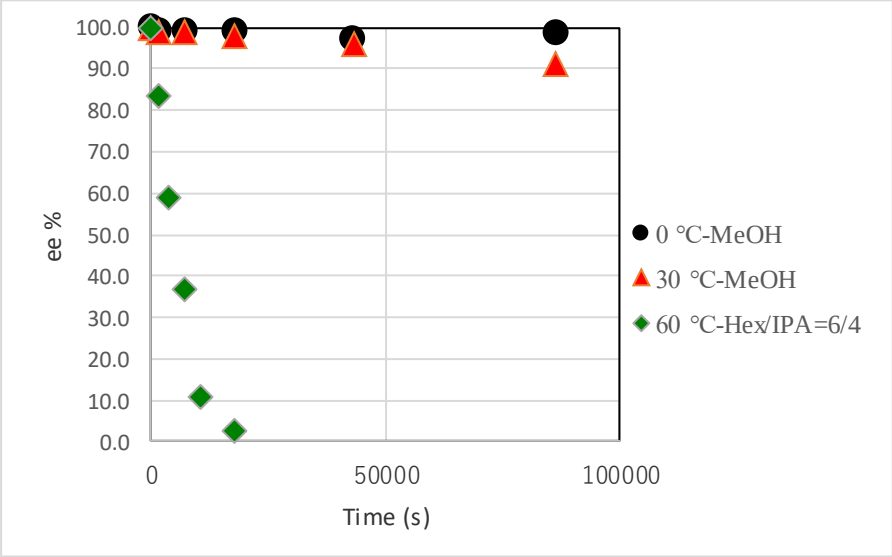
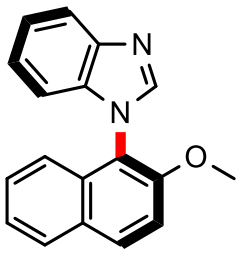


Fig. S3 Decay of ee (%) in (*S*)-**3w**



3w

Rotational barrier: 27.6 kcal/mol

7. Experimental references:

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