anti-Selective Catalytic Asymmetric Nitroaldol Reaction via a Heterobimetallic Heterogeneous Catalyst

Tatsuya Nitabaru,[1] Akihiro Nojiri,[†] Makoto Kobayashi,[2] Naoya Kumagai, [†,*] and Masakatsu Shibasaki[†,*]

Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Process Chemistry, R&D, Kissei Pharmaceutical Company, Ltd., 197-5 Kamiyoshi, Kubiki-ku, Joetsu, Niigata 942-0145, Japan

mshibasa@mol.f.u-tokyo.ac.jp, nkumagai@mol.f.u-tokyo.ac.jp

Supporting Information

1. General

1-1. General procedures.

Reactions were performed in flame-dried 20 mL test tubes with a magnetic stirring bar unless otherwise noted. The test tubes were fitted with a glass 3-way stopcock and reactions were conducted under argon atmosphere. Air- and moisture-sensitive liquids were transferred via gas-tight syringe and stainless-steel needle. Flash chromatography was performed using silica gel 60 (230-400 mesh) purchased from Merck.

1-2. Materials.

Commercial reagents were purchased from, Kojundo Chemical Co Ltd. ($RE(O^iPr)_3$, $RE_5O(O^iPr)_{13}$: stored and handled in a dry box, contact: http://www.kojundo.co.jp/English/index.html, Fax: +81-49-284-1351, e-mail: sales@kojundo.co.jp.), TCI (aldehydes, nitroethane, nitropropane, nitroethanol), Wako Pure Chemical Co. Ltd. (aldehydes), and Aldrich (NaHMDS (1.0 M/THF)). Aldehydes were purified by distillation or recrystallization. THF was distilled from sodium/benzophenone ketyl or used as received from KANTO Chemical Co. Ltd. (anhydrous).

[1] The University of Tokyo.
[2] Kissei Pharmaceutical Company, Ltd.

1-3. Instrumentation.
^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on JEOL LA-500 or ECX–500 spectrometers (500 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ppm, CD_3OD: δ 3.31 ppm). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Chemical shifts for fluorines are reported in the scale relative to CF_3COOH (–79.0 ppm) as an external reference. Coupling constants are reported in Hertz (Hz). Infrared (IR) spectra were obtained using a JASCO FT/IR 410 spectrophotometer. Melting points were determined on an open capillary apparatus. Optical rotation was measured using a 1 mL cell with a 0.5 dm path length on a JASCO polarimeter P-1010. ESI mass spectral data for new compounds were obtained using a Waters ZQ-4000 mass spectrometer. High-resolution mass spectra (FAB) were obtained using a JEOL JMS-MS700V mass spectrometer. ESI TOF MS spectra of the catalyst was obtained using JEOL Accu TOF JMS T100-LP. ICP analysis of the heterobimetalic catalyst was conducted with Shimadzu ICPS-7510. WDXRF analysis of the heterobimetallic catalyst was conducted with Rigaku ZSX Primus II.

2. Experimental Procedure and Characterization

2-1. Representative procedure for *anti*-selective catalytic asymmetric nitroaldol reaction (for Table 2, entry 12).
To a flame dried test tube (20 mL) equipped with a magnetic stirring bar and 3-way glass stopcock was charged ligand **1b** (5.9 mg, 0.018 mmol) and dried under vacuum at room temperature for 30 min. Ar was backfilled to the test tube, then THF (200 μL) and $Nd(O^iPr)_3$ (45 μL, 0.009 mmol, 0.2 M/THF, transferred by well-dried syringe and needle) were successively added at room temperature. After stirring the resulting solution at the same temperature for 1 h, the mixture was cooled to 0 °C and NaHMDS (18 μL, 0.018 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added dropwise at the same temperature. After stirring the resulting mixture at room temperature for 30 min (white precipitate appeared), nitroethane (**3a**) (72 μL, 1.0 mmol) (clear solution developed), and H_2O (45 μL, 0.009 mmol, 0.2 M/THF) were successively added and the resulting solution (or suspension) was stirred for 1 h at the same temperature (gradually became white suspension). The mixture was diluted with THF (100 μL) and cooled to –40 °C, then benzaldehyde (**2a**) (10 μL, 0.10 mmol) was added dropwise. After stirring at the same temperature for 20 h, 1N HCl aq. was added and the resulting mixture was extracted with diethyl ether (x2). The organic layer was washed with sat. aq. $NaHCO_3$ and brine, then dried over Na_2SO_4. After removal of the organic solvent under reduced pressure, the resulting residue was analyzed by ^{1}H NMR to determine chemical yield (99%, 1,4-dioxane (3.71 ppm) as an internal standard) and diastereomeric ratio (*anti*/*syn* = 40/1, PhC***H***(OH)–: *anti* = 5.39 ppm (major), *syn* = 5.01 ppm (minor)) of **4aa**. The relative configuration was determined by comparison with the reported chemical shift values in the literature (ref 9 in maintext). Enantiomeric excess was determined by HPLC analysis (*anti* = 84% ee, DAICEL CHIRALPAK AD-H (ϕ0.46 cm x 25 cm), 2-propanol/*n*-hexane 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R 8.0 min (*anti* minor-enantiomer: (*1S,2R*)) and 8.8 min (*anti* major-enantiomer: (*1R,2S*))).

2-2. Representative procedure for *anti*-selective catalytic asymmetric nitroaldol reaction with supernatant and precipitates (for Scheme 1).
To a flame dried glass tube (inner diameter 5 mm, length 10 cm, capped with rubber septum) was added ligand **1m** (6.8 mg, 0.018 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar, then THF (200 mL) and $Nd_5O(O^iPr)_{13}$ (45 μL, 0.009 mmol, 0.2 M/THF (based on Nd), transferred by well-dried syringe and needle) were successively added at room temperature. After agitation of the resulting mixture with vortex mixer at the same temperature for 30 sec, the mixture was cooled to 0 °C and NaHMDS (18 μL, 0.018 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added at the same temperature to give white suspension. After agitation of the resulting mixture with vortex mixer at room temperature for 30 sec, nitroethane (**3a**) (60 μL), was added at the same temperature to give a clear solution. After standing at the same temperature, the white precipitates appeared and the whole suspension was transferred to Eppendorf safe-lock tube (size 1.5 mL). The tube was centrifuged (ca. 10^4 rpm, 30 sec). The supernatant was decanted to the flame-dried test tube dried test tube **A** and dry THF (1.0 mL) was added to the precipitate. The tube was agitated by vortex mixer for 30 sec and centrifuged again (washing process). The supernatant was decanted (discarded). The resulting precipitate was agitated with dry THF (1200 μL) and the resulting suspension was transferred to a flame-dried test tube **B** filled with nitroethane (**3a**) (215 μL, 3.0 mmol) via gas-tight syringe. The mixture was cooled to –40 °C, then benzaldehyde (**2a**) (30.5 μL, 0.30 mmol) was added dropwise. After stirring the reaction mixture at the same temperature for 20 h, 1N HCl aq. was added and the resulting mixture was extracted with diethyl ether (x2). The combined organic layers were washed with sat. aq. $NaHCO_3$ and brine, then dried over Na_2SO_4. After removal of volatiles under reduced pressure, the resulting residue was analyzed by ^{1}H NMR to determine chemical yield (96%,

1,4-dioxane (3.71 ppm) as an internal standard) and diastereomeric ratio (*anti*/*syn* = >40/1) of **4aa**. Enantiomeric excess was determined by HPLC analysis (*anti* = 94% ee, DAICEL CHIRALPAK AD-H (ϕ0.46 cm x 25 cm), 2-propanol/*n*-hexane 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R 8.0 min (*anti* minor-enantiomer: (*1S*,*2R*)) and 8.8 min (*anti* major-enantiomer: (*1R*,*2S*))).
The reaction was run by adding **2a** (30.5 μL, 0.30 mmol) and **3a** (215 μL, 3.0 mmol) in test tube **A** (supernatant) under the identical conditions as test tube **B** (precipitates), affording **4aa** (21% yield, *anti*/*syn* = 6.5/1, *anti* = 62% ee).

2-3. Representative procedure for *anti*-selective catalytic asymmetric nitroaldol reaction with heterogeneous heterobimetallic catalyst (for Table 5, entry 1).
To a flame dried glass tube (inner diameter 5 mm, length 10 cm, capped with rubber septum) was added ligand **1m** (6.8 mg, 0.018 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar, then THF (200 mL) and $Nd_5O(O^iPr)_{13}$ (45 μL, 0.009 mmol, 0.2 M/THF (based on Nd), transferred by well-dried syringe and needle) were successively added at room temperature. After agitation of the resulting mixture with vortex mixer at the same temperature for 30 sec, the mixture was cooled to 0 °C and NaHMDS (18 μL, 0.018 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added at the same temperature to give white suspension. After agitation of the resulting mixture with vortex mixer at room temperature for 30 sec, nitroethane (**3a**) (60 μL), was added at the same temperature to give a clear solution. After standing at the same temperature, the white precipitates appeared and the whole suspension was transferred to Eppendorf safe-lock tube (size 1.5 mL). The tube was centrifuged (ca. 10^4 rpm, 30 sec). The supernatant was decanted and dry THF (1.0 mL) was added to the precipitate. The tube was agitated by vortex mixer for 30 sec and centrifuged again (washing process). The supernatant was decanted (discarded). The resulting precipitates were agitated with dry THF (1200 μL) and the resulting suspension was transferred to a flame-dried test tube filled with nitroethane (**3a**) (215 μL, 3.0 mmol) via gas-tight syringe. The mixture was cooled to –40 °C, then benzaldehyde (**2a**) (30.5 μL, 0.30 mmol) was added dropwise. After stirring the reaction mixture at the same temperature for 20 h, 1N HCl aq. was added and the resulting mixture was extracted with diethyl ether (x2). The combined organic layers were washed with sat. aq. $NaHCO_3$ and brine, then dried over Na_2SO_4. After removal of volatiles under reduced pressure, the residue was purified by flash silica gel column chromatography (SiO_2, hexane/ethyl acetate = 10/1) to give the desired product **4aa** as a colorless oil (54.1 mg, 99% yield). Enantiomeric excess was determined by HPLC analysis (*anti* = 92% ee, DAICEL CHIRALPAK AD-H (ϕ0.46 cm x 25 cm), 2-propanol/*n*-hexane 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R 8.0 min (*anti* minor-enantiomer: (*1S*,*2R*)) and 8.8 min (*anti* major-enantiomer: (*1R*,*2S*))).

2-4. Large-scale demonastration of *anti*-selective nitroaldol reaction of 2c and 3a (for Scheme 6).
To a flame-dried 30 mL pear-shaped flask was charged $Nd_5O(O^iPr)_{13}$ (1.11 g, 0.738 mmol, 3.69 mmol based on Nd) in a dry box, and dried under vacuum for 1 h at room temperature. Ar was back-filled and cooled to 0 °C. To the flask was added THF (18.4 mL, distilled from sodium-benzophenone ketyl) to give 0.2 M (based on Nd)/THF solution. The solution was stirred at 0 °C for 1 h and at room temperature for 1 h, then left stand overnight.
To a flame-dried 100 mL pear-shaped flask were added ligand **1m** (1.78 g, 4.71 mmol), THF (21.0 mL, dehydrated, Kanto Chemical Co. Ltd, used as received), and 0.2 M $Nd_5O(O^iPr)_{13}$ (based on Nd) in THF (11.8 mL, 2.36 mmol) at room temperature under Ar. After cooling the resulting mixture to 0 °C, NaHMDS (1.0 M/THF, 4.12 mL, 4.12 mmol, Aldrich, used as received) was added to give white suspension, which was warmed to room temperature. To the suspension was added nitroethane (**3a**) (10.5 g, 140 mmol) and clear solution developed, which turned to white suspension again within 10 min. The suspension was stirred at room temperature for 1 h and left stand for 2 h. Centrifugation (ca. 10^3 rpm, 5 min) of the suspension and decantation of the supernatant gave the white precipitates, to which was added THF and the resulting suspension was agitated with a vortex mixer, then centrifuged again. The supernatant was decanted and the resulting precipitates were agitated with THF (40 mL, dehydrated, Kanto Chemical Co. Ltd, used as received) to give catalyst suspension.

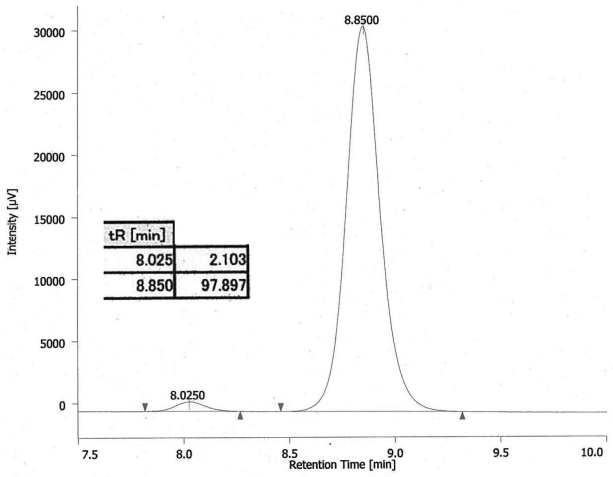
To a oven-dried (120 °C) 3-necked 5 L round-bottom flask equipped with a overhead mechanical stirrer, a digital thermometer and a three-way glass stopcock were charged **2c** (50 g, 235.6 mmol) and dried under vacuum, then back-filled with Ar. To the flask were added THF (850 mL, dehydrated, Kanto Chemical Co. Ltd, used as received), nitroethane (**3a**) (177 g, 2360 mmol, WAKO pure chemical, used as received), and the flask was immersed to cooling bath adjusted at –30 °C (medium: 2-propanol). After cooling the solution to –30.7 °C, the heterogeneous Nd/Na heterobimetallic catalyst (suspension in THF 40 g, 10g rinse) was transferred to the flask dropwise (8 min) via syringe. Upon addition of the catalyst, the internal temperature raised to –27.6 °C. The resulting white suspension was stirred for 24 h, the range of internal temperature was –24.5 ~ –34.7 °C. The reaction was quenched with 1N HCl (23.5 mL) at the same temperature, the gradually warmed to room temperature. Ethyl acetate (500 g) and 10% NaCl aq. (150 g) were added, and the organic layer was separated. Aqueous layer was extracted with ethyl acetate (150 g). The combined

organic layers were washed with sat. $NaHCO_3$ aq. (200 g), 10% NaCl aq. (150 g), and brine (150 g), then dried over Na_2SO_4 for 1 h. After filtration, volatiles were removed under reduced pressure and the resulting residue was analyzed by ^{1}H NMR to determine conversion (85%, determined by integration value of **4ea**/**2e**) and diastereomeric ratio (*anti*/*syn* = >40/1, –C(NO_2)C***H*****$_3$**: *anti* = 1.52 ppm (major), *syn* = 1.30 ppm (minor)) of **4ea**. The relative configuration was determined by comparison with the reported chemical shift values in the literature (ref 10b in maintext). Small aliquot of the residue was purified by preparative thin-layer chromatography and submitted to HPLC analysis for the determination of enantiomeric excess (*anti* = 96.6% ee, DAICEL CHIRALPAK AS-H (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R 29.3 min (*anti* minor-enantiomer: (1*S*,2*R*)) and 35.0 min (*anti* major-enantiomer: (1*R*,2*S*))). To the residue was added ethyl acetate (200 g) and the resulting solution was evaporated at 50 °C under reduced pressure. The residue was re-dissolved with ethyl acetate (100 g). To the solution was added *n*-heptane (250 g) dropwise with gentle stirring (solid material appeared when ca. 100g of *n*-heptane was added). After stirring for 1 h, additional *n*-heptane (1050 g) was added dropwise over 1 h and the resulting suspension was left stand at room temperature for 5 h then at 0 °C for 2 h. The solid material was collected by filtration and washed with ice-cold ethyl acetate/*n*-heptane = 1/13 mixed solvent (140 g x 2), then dried at 35 °C for 8 h under vacuum to give pure **4ca** as a white solid (75.7 g, 51.3 mmol, 76% yield).

2-5. Characterization of nitroaldol products

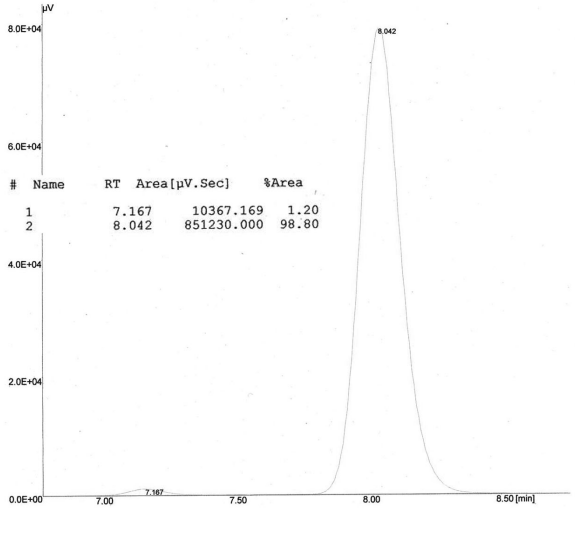
4aa, **4ba**, **4ca**, **4ea**, **4fa**, **4ia**, **4ja**, **4ka**, **4la**, **4ma**, **4ab** are reported compounds [(a) Ooi, T.; Doda, K.; Maruoka, K. *J. Am. Chem. Soc.* **2003**, *125*, 2054. (b) Risgaard, T.; Gothelf, K. V.; Jørgensen, K. A. *Org. Biomol. Chem.* **2003**, *1*, 153. (c) Gruber-Khadjawi, M.; Purkarthofer, T.; Skrane, W.; Griengle, H. *Adv. Synth. Catal.* **2007**, *349*, 1445. (d) Uraguchi, D.; Sakaki, S.; Ooi, T. *J. Am. Chem. Soc.* **2007**, *129*, 12392. (e) Nitabaru, T.; Kumagai, N.; Shibasaki, M. *Tetrahedron Lett.* **2008**, *49*, 272. (f) Handa, S.; Nagawa, K.; Sohtome, Y.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3230]. Relative and absolute configurations of these nitroaldol products were determined by comparing chemical shifts in ^{1}H NMR and reported retention times in HPLC analysis. The relative configuration of the new products was determined by NOE analysis after conversion to the corresponding cyclic carbamates. The absolute configuration of the new products was determined by analogy.

(1*R*,2*S*)-2-Nitro-1-phenylpropan-1-ol (4aa) (4ba)



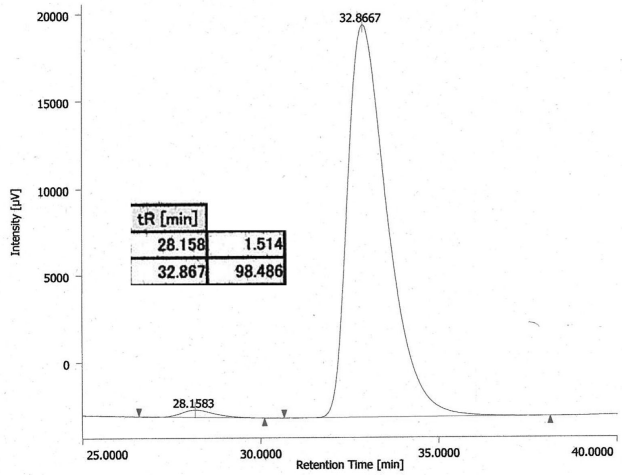
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min
detection 254 nm

(1*R*,2*S*)-1-(2,4-Dimethylphenyl)-2-nitropropan-1-ol (4ba)



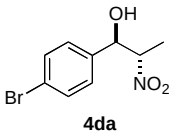
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min
detection 254 nm

(1*R*,2*S*)-1-(4-(Benzyloxy)phenyl)-2-nitropropan-1-ol (4ca)



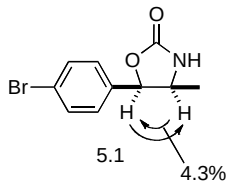
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min
detection 254 nm

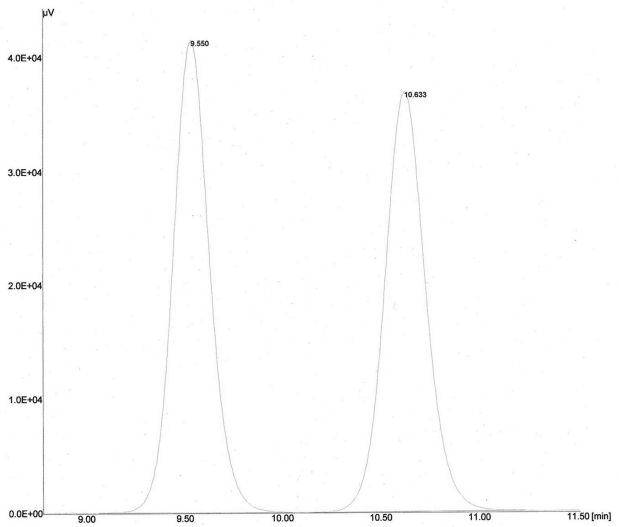
(1*R*,2*S*)-1-(4-Bromophenyl)-2-nitro-1-propanol (4da)

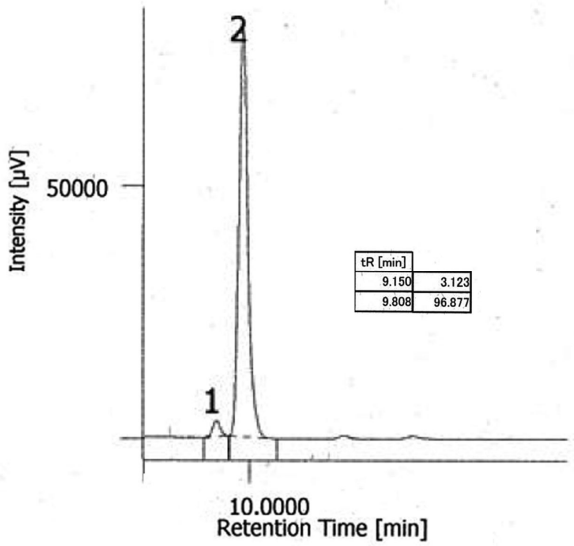


4da

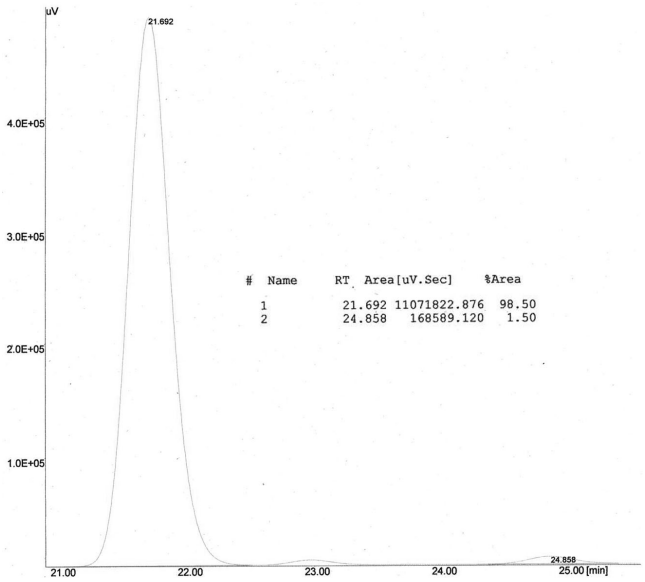
Colorless solid; IR (KBr) ν 3521, 2912, 1547 cm^{-1}; m.p. 83-84 °C; ^1H NMR ($CDCl_3$) δ 1.47 (d, *J* = 6.7 Hz, 3H), 2.77-2.81 (m, 1H), 4.63 (dq, *J* = 3.7, 7.1 Hz, 1H), 5.33-5.36 (m, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 12.0, 73.2, 87.1, 122.5, 127.7, 131.9, 137.4; $[\alpha]_D^{24}$ –1.7 (*c* 0.81, $CHCl_3$, 94% ee sample); ESI-MS *m*/*z* 282 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_9H_{10}N_1O_3BrCs$ *m*/*z* 391.8898 $[M+Cs]^+$, found 391.8894; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection 210 nm, t_R = 9.6 min (minor), 10.6 min (major). Relative configuration was determined after conversion to the corresponding carbamate.





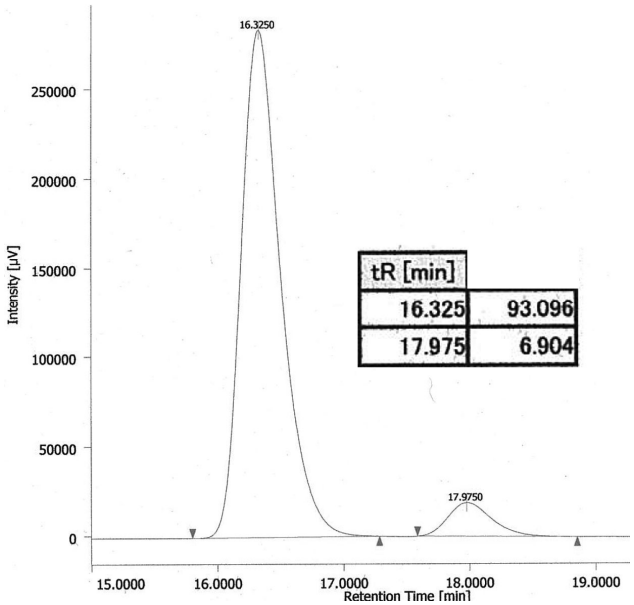


(1*R*,2*S*)-1-(4-Fluorophenyl)-2-nitropropan-1-ol (4ea)



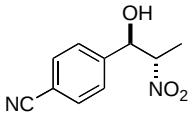
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/EtOH/*n*-hexane = 1/2.3/30, flow rate 0.5 mL/min
detection 220 nm

(1*R*,2*S*)-2-Nitro-1-(4-nitrophenyl)propan-1-ol (4fa)



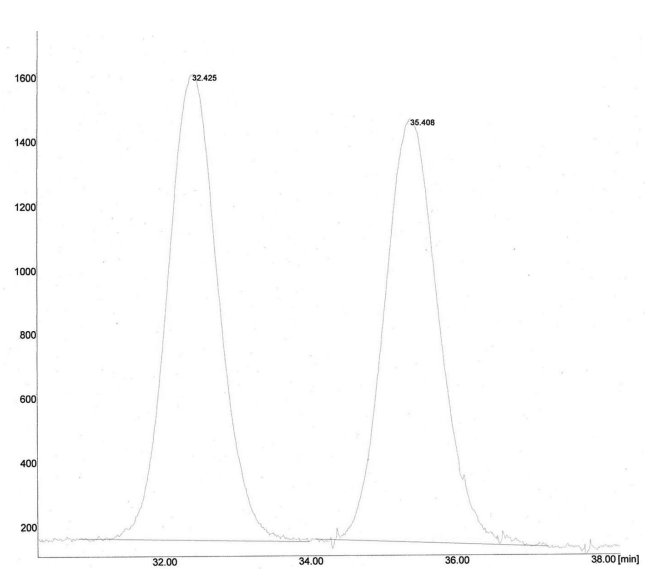
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
+ CHIRALPAK OD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/4, flow rate 1.0 mL/min
detection 254 nm

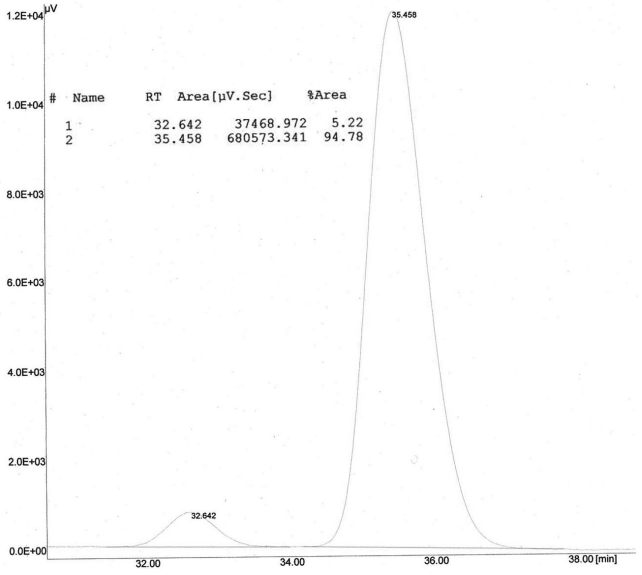
4-((1*R*,2*S*)-1-Hydroxy-2-nitropropyl)benzonitrile (4ga)



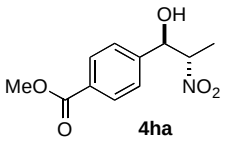
4ga

Colorless solid; IR (KBr) ν 3449, 2234, 1551 cm^{-1}; m.p. 99-100 °C; ^1H NMR ($CDCl_3$) δ 1.47 (d, *J* = 6.9 Hz, 3H), 3.06 (d, *J* = 3.4 Hz, 1H), 4.68 (dq, *J* = 3.5, 6.9 Hz, 1H), 5.49 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.9, 73.0, 86.8, 112.4, 118.3, 126.8, 132.5, 143.7; $[\alpha]_D^{29}$ –2.6 (*c* 0.94, $CHCl_3$, 90% ee sample (ee has been changed by separation of diastereomers by preparative chiral HPLC)); ESI-MS *m*/*z* 229 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{10}H_{10}N_2O_3Cs$ *m*/*z* 338.9746 $[M+Cs]^+$, found 338.9754; CHIRALPAK AS-H (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection 254 nm, t_R = 32.6 min (minor), 35.5 min (major).





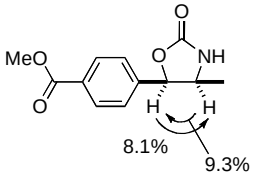
(1*R*,2*S*)-1-(4-Methoxycarbonylphenyl)-2-nitro-1-propanol (4ha)

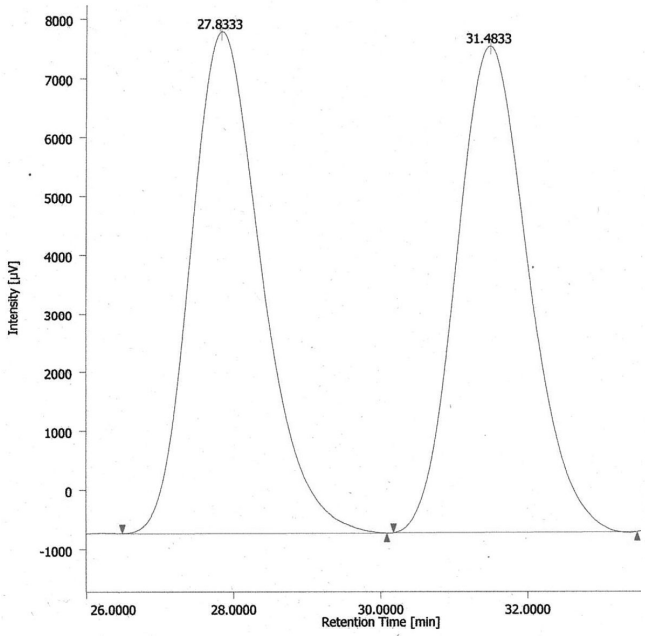


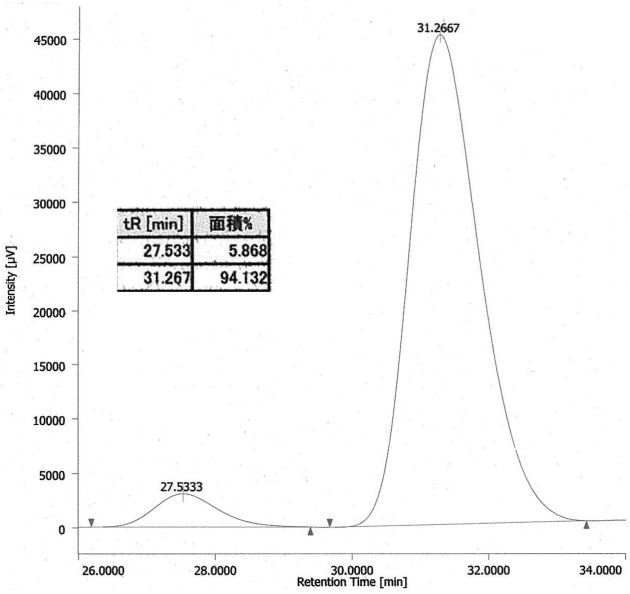
4ha

Colorless oil; IR (neat) ν 3468, 1718, 1701, 1619 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (d, *J* = 7.0 Hz, 3H), 2.86 (d, *J* = 3.7 Hz, 1H), 3.90 (s, 3H), 4.69 (dq, *J* = 3.4, 7.0 Hz, 1H), 5.47 (dd, *J* = 3.4, 3.7 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.8, 52.3, 73.4, 87.0, 126.0, 130.0, 130.3, 143.3, 166.6; $[\alpha]_D^{26}$ –0.6 (*c* 0.37, $CHCl_3$, 89% ee sample); ESI-MS *m*/*z* 262 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{11}H_{13}NO_5Cs$ *m*/*z* 371.9848 $[M+Cs]^+$, found 371.9837; CHIRALPAK AS-H (ϕ 0.46 cm x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection 254 nm, t_R = 27.5 min (minor), 31.3 min (major).

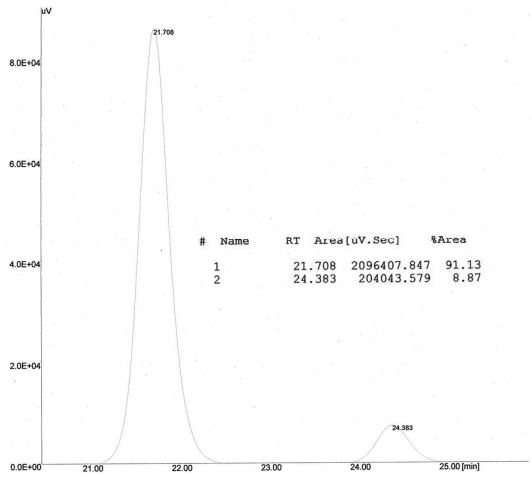
Relative configuration was determined after conversion to the corresponding carbamate.





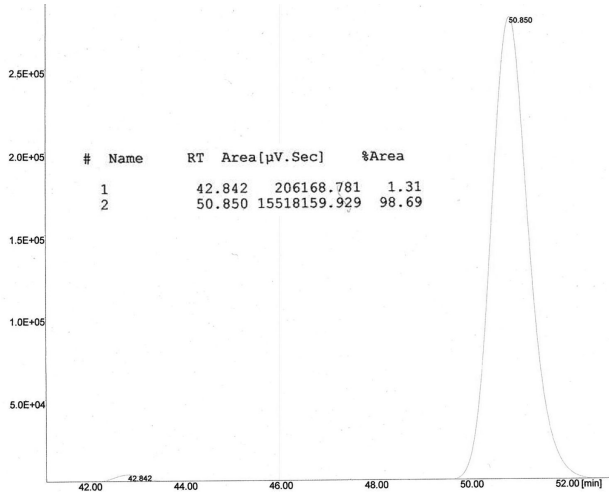


(1*S*,2*S*)-1-(Furan-2-yl)-2-nitropropan-1-ol (4ia)



CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)

(3*R*,4*S*,*E*)-4-Nitro-1-phenylpent-1-en-3-ol (4ja)

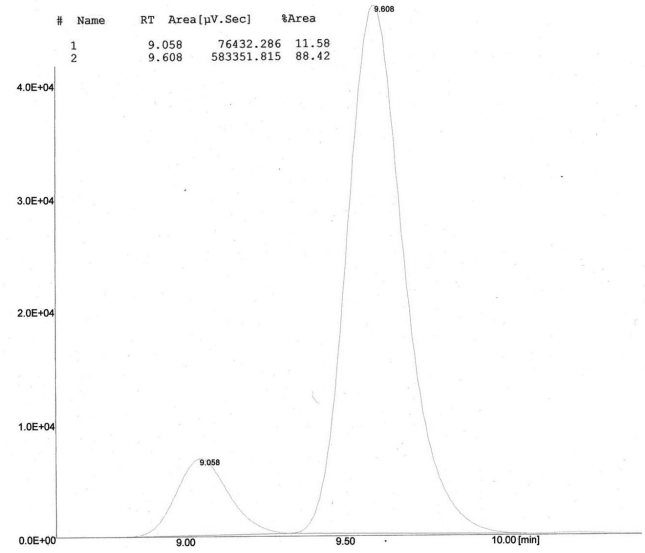


CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)

2-propanol/EtOH/*n*-hexane = 1/1/18, flow rate 0.5 mL/min
detection 254 nm

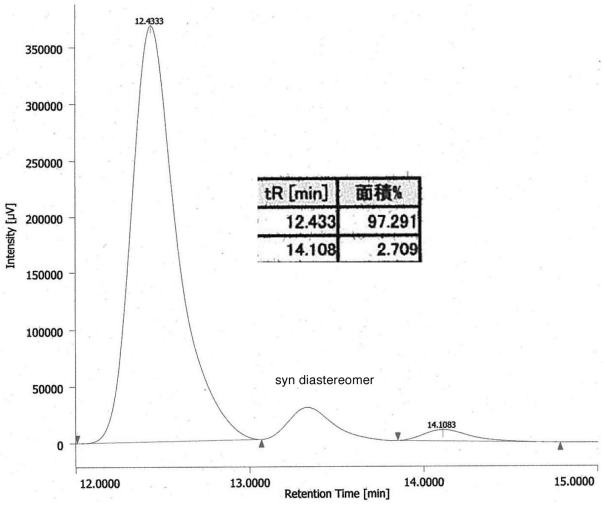
2-propanol/*n*-hexane = 1/20, flow rate 0.5 mL/min
detection 254 nm

(3*R*,4*S*)-4-Nitro-1-phenylpentan-3-ol (4ka)



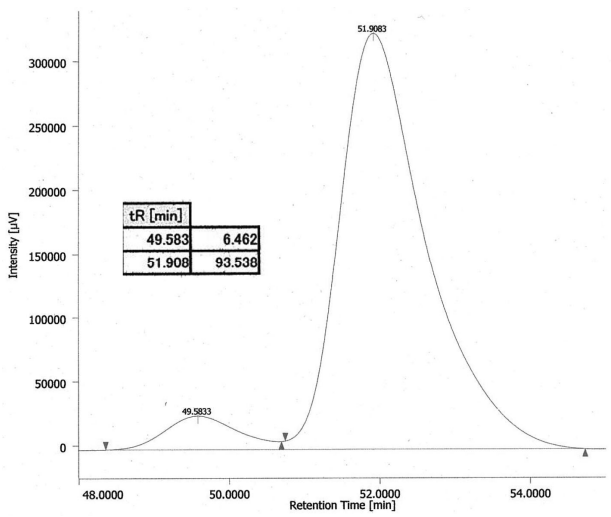
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min
detection 254 nm

(1*R*,2*S*)-1-Cyclohexyl-2-nitropropan-1-ol (4la)



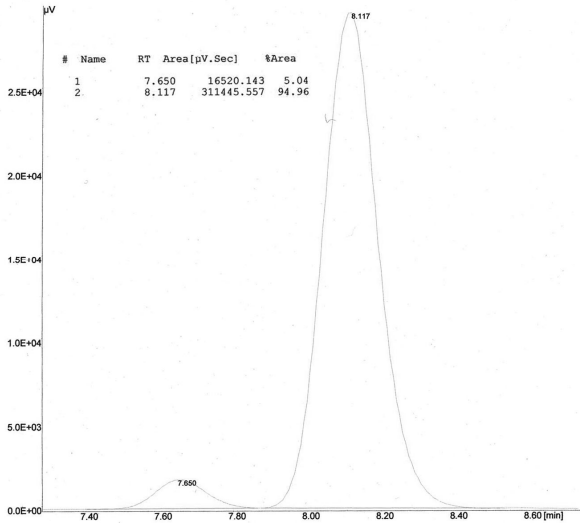
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/20, flow rate 1.0 mL/min
detection 210 nm

(2*S*,3*R*)-2-Nitroundecan-3-ol (4ma)



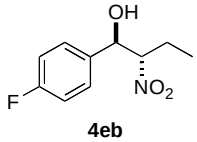
CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/99, flow rate 0.5 mL/min
detection 210 nm

(1*R*,2*S*)-2-Nitro-1-phenylbutan-1-ol (4ab)



CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm)
2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min
detection 254 nm

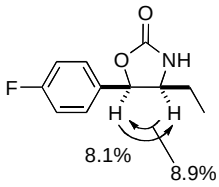
(1*R*,2*S*)-1-(4-Fluorophenyl)-2-nitro-1-butanol (4eb)

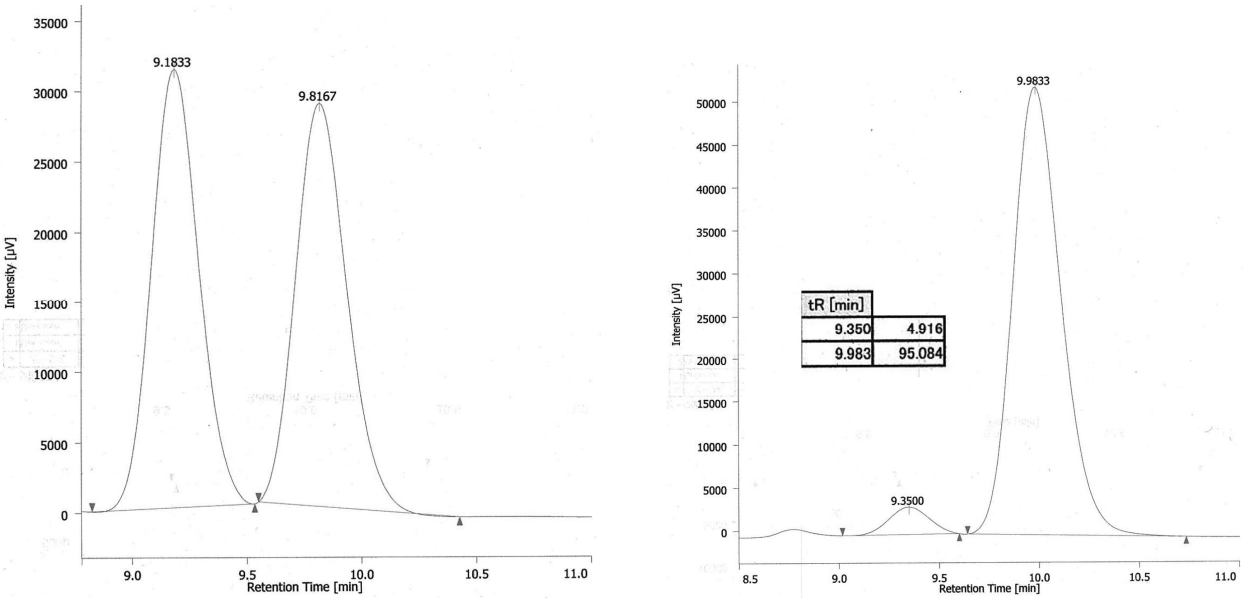


4eb

Colorless oil; IR (neat) ν 3446, 1610, 1548, 1509 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.85-1.93 (m, 1H), 2.08-2.17 (m, 1H), 2.72 (d, *J* = 3.1 Hz, 1H), 4.52 (ddd, *J* = 3.4, 5.2, 10.7 Hz, 1H), 5.13 (dd, *J* = 2.8, 4.9 Hz, 1H), 7.04 (dd, *J* = 8.6, 8.9 Hz, 2H), 7.33 (dd, *J* = 5.2, 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) d 10.3, 21.5, 73.6, 94.6, 115.7 (d, *J* = 21.7 Hz), 128.0 (d, *J* = 8.3 Hz), 134.3 (d, *J* = 3.1 Hz), 162.8 (d, *J* = 247.0 Hz); $[\alpha]_D^{25}$ +7.1 (*c* 0.65, $CHCl_3$, 90% ee sample); ESI-MS *m*/*z* 236 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{10}H_{12}NO_3FCs$ *m*/*z* 345.9856 $[M+Cs]^+$, found 345.9852; CHIRALPAK AS-H (0.46 cm ϕ x 25 cm), 2-propanol/*n*-hexane = 1/9, 1.0 mL/min, detection 254 nm, t_R = 9.4 min

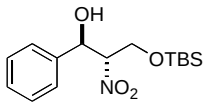
(minor), 9.8 min (major).
Relative configuration was determined after conversion to the corresponding carbamate.





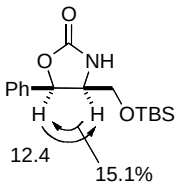
(1*R*,2*S*)-1-Phenyl-2-nitro-3-(*tert*-butyldimethylsilyloxy)-1-propanol (4ac)

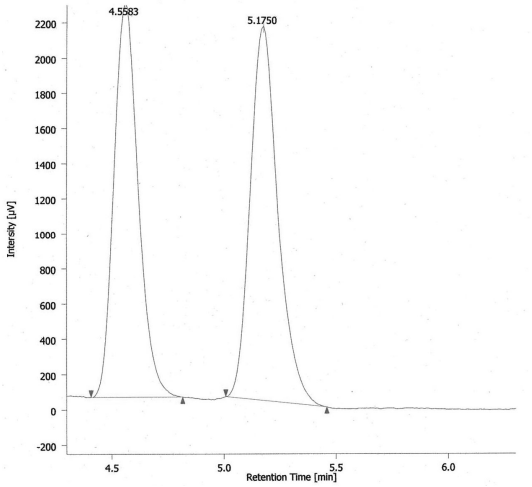
Anti and *syn* diastereomers were separated by preparative chiral stationary phase HPLC (CHIRALPAK AS-H (ϕ 2.0 cm x 20 cm), 2-propanol/*n*-hexane = 1/9, flow rate 5.0 mL/min, detection 254 nm)

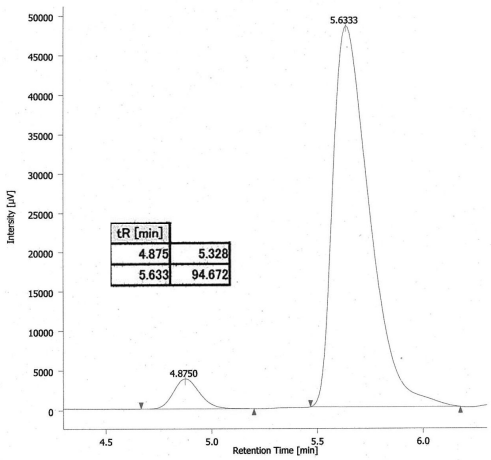


4ac

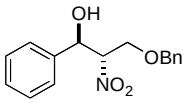
Colorless oil; IR (neat) ν 3456, 2933, 2363, 1556 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 3H), 0.03 (s, 3H), 0.84 (s, 9H), 3.09 (brd, 1H), 4.11 (dd, *J* = 3.7, 11.6 Hz, 1H), 4.22 (dd, *J* = 7.7, 11.6 Hz, 1H), 4.73 (ddd, *J* = 3.4, 5.5, 8.8 Hz, 1H), 5.28 (dd, *J* = 4.3, 5.5 Hz, 1H), 7.30-7.35 (m, 1H), 7.35-7.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –5.8, -5.7, 18.0, 25.6, 61.0, 92.6, 126.0, 128.8, 128.8, 138.5; $[\alpha]_D^{26}$ –14.6 (*c* 0.75, $CHCl_3$, 90% ee sample); ESI-MS *m*/*z* 334 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{15}H_{25}NO_4SiCs$ *m*/*z* 444.0607 $[M+Cs]^+$, found 444.0606; CHIRALPAK AS-H (0.46 cm ϕ x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection 254 nm, t_R = 4.9 min (minor), 5.6 min (major).
Relative configuration was determined after conversion to the corresponding carbamate.







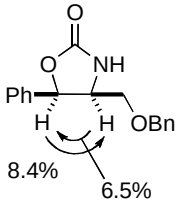
(1*R*,2*S*)-1-Phenyl-2-nitro-3-(benzyloxy)-1-propanol (4ad)

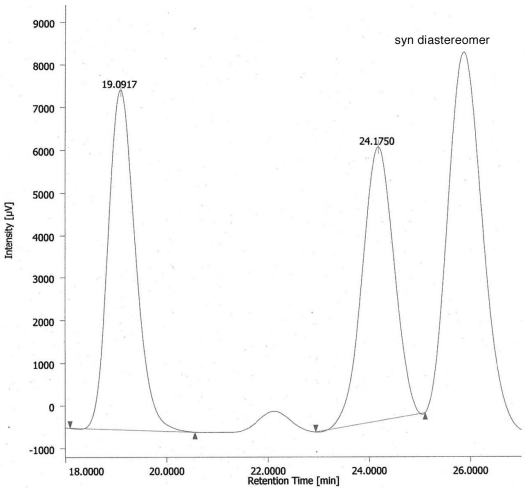


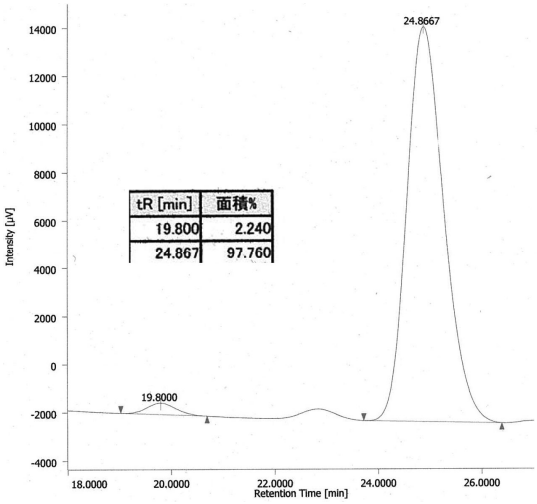
4ad

Colorless oil; IR (neat) ν 3442, 2921, 1553 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.94 (d, J = 4.3 Hz, 1H), 3.94 (dd, J = 3.1, 11.0 Hz, 1H), 4.13 (dd, J = 8.3, 11.0 Hz, 1H), 4.49 (d, J = 11.9 Hz, 1H), 4.53 (d, J = 11.9 Hz, 1H), 4.88 (ddd, J = 3.1, 5.2, 8.3 Hz, 1H), 5.30 (dd, J = 4.3, 5.2 Hz, 1H), 7.24-7.27 (m, 2H), 7.28-7.40 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 66.8, 73.2, 73.6, 91.1, 126.0, 127.7, 128.0, 128.5, 128.8, 128.8, 136.8, 138.2; $[\alpha]_D^{26}$ –17.7 (*c* 0.87, $CHCl_3$, >99% ee sample (ee has been changed by separation of diastereomers by preparative chiral HPLC)); ESI-MS *m/z* 310 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{16}H_{17}NO_4Cs$ *m/z* 420.0212 $[M+Cs]^+$, found 420.0214; CHIRALPAK AS-H (0.46 cm ϕ x 25 cm), 2-propanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection 254 nm, t_R = 19.1 min (minor), 24.2 min (major).

Relative configuration was determined after conversion to the corresponding carbamate.







3. Synthesis of Ligand 1

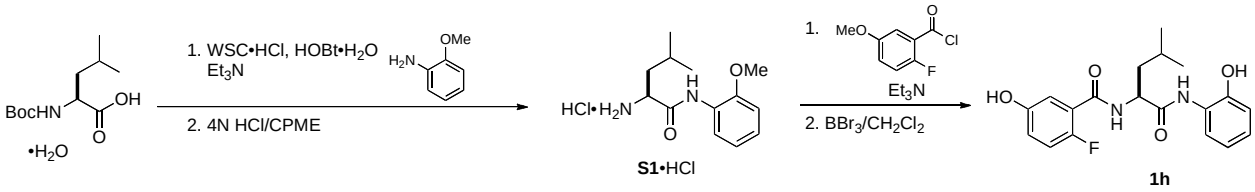
Synthesis of **1a**, **1b**, **1g** was reported in the literature;

Reg #; **1a**: 952656-51-8, **1b**: 1006060-01-0, **1g**: 1006060-05-4.

Synthesis of **1a** and **1g** was reported in ref in ref 10a in maitext and ref s1, respectively. **1b**, **1c-f** were synthesized by

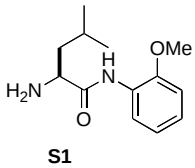
following the procedure reported in these references.

Synthesis of ***1h***



(*S*)-2-Amino-*N*-(2-methoxyphenyl)-4-methylpentanamide (S1)

To a stirred solution of 2-methoxyaniline (5.4 mL, 48 mmol) in CH_2Cl_2 (480 mL) were added Boc-L-Leu-OH•H_2O (10 g, 40 mmol), Et_3N (6.7 mL, 48 mmol), WSC•HCl (8.1 g, 42 mmol), and HOBt•H_2O (1.8 g, 12 mmol) at 0 °C. After stirring at room temperature for 25 h, the reaction mixture was quenched with 1N HCl aq. and extracted with ether. The combined organic layers were washed with 1N HCl aq. and brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was recrystallized from ether/*n*-hexane to give amide (5.15 g, y. 38%) as a white solid. To a stirred solution of the amide (5.0 g, 15 mmol) in CH_2Cl_2 (5.0 mL) was added 4N HCl/CPME (15 mL) at 0 °C. After stirring at room temperature overnight, volatiles were removed under reduced pressure and the resulting residue was recrystallized from CH_2Cl_2/ether to give **S1•HCl** (4.1 g, quantative yield) as a colorless solid. Free amine **S1** was obtained by partition with ethyl acetate/$NaHCO_3$ aq.



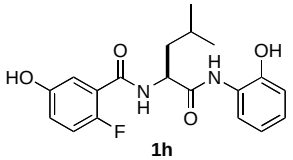
Colorless solid; IR (KBr) ν 3386, 3259, 2962, 1666, 1599 cm^{-1}; m.p. 93-94 °C; ^{1}H NMR (CD_3OD) δ 0.97 (d, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 7.5 Hz, 3H), 1.40-1.47 (m, 1H), 1.63-1.69 (m, 1H), 1.76-1.84 (m, 1H), 3.50 (dd, *J* = 4.6, 9.2 Hz, 1H), 3.88 (s, 3H), 6.91 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 7.08 (dd, *J* = 7.4, 8.1 Hz, 1H), 8.10-8.14 (m, 1H); ^{13}C NMR (CD_3OD) δ 22.1, 23.7, 25.9, 45.4, 55.3, 56.3, 111.6, 121.6, 121.8, 125.7, 128.2, 150.9, 176.8; $[\alpha]_D^{25}$ –13.9 (*c* 1.2, MeOH); ESI-MS *m*/*z* 259 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{13}H_{20}N_2O_2Cs$ *m*/*z* 369.0579 $[M+Cs]^+$, found 369.0579.

2-Fluoro-5-methoxybenzoyl chloride

To a CH_2Cl_2 solution (400 mL) of 2-fluoro-5-methoxybenzoic acid[s2] (19.0 g, 111 mmol) was added oxalyl chloride (13.4 mL, 156 mmol) and dry DMF (100 μL) at 0 °C and the resulting mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, and the resulting solid residue was dissolved in CH_2Cl_2 to give 1.0 M/CH_2Cl_2 solution containing the title compound, which was used in the following procedures.

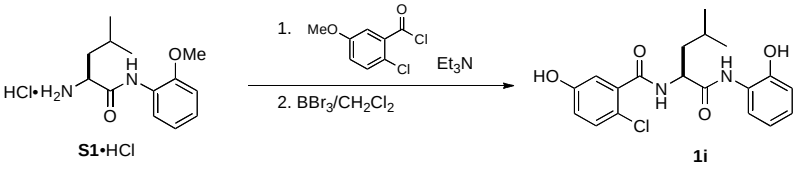
(*S*)-2-Fluoro-5-hydroxy-*N*-(1-(2-hydroxyphenylamino)-4-methyl-1-oxopentan-2-yl)benzamide (1h)

To a stirred solution of **S1**•HCl (272 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) were added Et_3N (350 μL, 2.5 mmol) and 2-fluoro-5-methoxybenzoyl chloride (1.0 M/CH_2Cl_2, 1.0 mL, 1.0 mmol) at 0 °C and the resulting mixture was stirred at room temperature for 1 h. Volatiles were removed under reduced pressure and the resulting residue was partitioned with 1N HCl aq. and ethyl acetate. Organic layer was washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4. Filtration and removal of organic solvent under reduced pressure gave the brown residue, which was purified by silica gel column chromatography to give diamide (390 mg) as a colorless solid. To the CH_2Cl_2 solution (10 mL) of diamide (390 mg) was added BBr_3 (1.0 M/CH_2Cl_2, 6.0 mL, 6.0 mmol) at 0 °C and the resulting solution was stirred at the same temperature for 5 h. H_2O was added at 0 °C and the resulting biphasic mixture was extracted with CH_2Cl_2 twice, and the combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was recrystallized from CH_2Cl_2/*n*-hexane to give **1h** (190 mg, y. 53% from **S1**•HCl) as a colorless solid.



Colorless solid; IR (KBr) ν 3288, 2958, 1647, 1597 cm^{-1}; m.p. 63-64 °C; ^{1}H NMR (CD_3OD) δ 1.02 (d, *J* = 6.3 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H), 1.76-1.84 (m, 3H), 4.78-4.81 (m, 1H), 6.78-6.86 (m, 2H), 6.91 (ddd, *J* = 4.1, 7.5, 7.5 Hz, 1H), 6.98 (ddd, *J* = 1.1, 7.4, 8.1 Hz, 1H), 7.05 (dd, *J* = 8.6, 9.8 Hz, 1H), 7.12 (dd, *J* = 3.4, 5.8 Hz, 1H), 7.82 (dd, *J* = 1.2, 8.1 Hz, 1H); ^{13}C NMR (CD_3OD) δ 21.9, 23.5, 26.1, 41.8, 54.6, 116.5, 116.9 (d, *J* = 2.1 Hz), 117.9 (d, *J* = 24.8 Hz), 120.6 (d, *J* = 3.1 Hz), 120.6 (d, *J* = 5.2 Hz), 123.0, 124.0 (d, *J* = 15.5 Hz), 126.5, 126.8, 149.2, 154.9 (d, *J* = 237.6 Hz), 155.0, 167.0, 172.9; ^{19}F NMR (CD_3OD) δ –129.0; $[\alpha]_D^{26}$ –20.0 (*c* 2.3, MeOH); ESI-MS *m*/*z* 383 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{19}H_{21}N_2O_4Cs$ *m*/*z* 493.0540 $[M+Cs]^+$, found 493.0528.

Synthesis of ***1i***

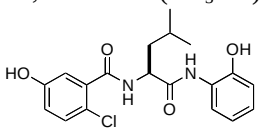


2-Chloro-5-methoxybenzoyl chloride

To a CH_2Cl_2 solution (6.0 mL) of 2-chloro-5-methoxybenzoic acid (258 mg, 1.35 mmol) was added oxalyl chloride (227 μL, 2.71 mmol) and dry DMF (1 drop) at 0 °C and the resulting mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure, and the resulting residue was dissolved in CH_2Cl_2 (6.0 mL) and used in the following procedures.

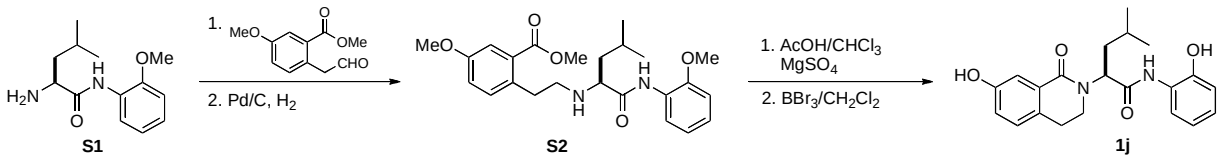
(*S*)-2-Chloro-5-hydroxy-*N*-(1-(2-hydroxyphenylamino)-4-methyl-1-oxopentan-2-yl)benzamide (1i)

To a stirred solution of **S1**•HCl (336 mg, 1.23 mmol) in CH_2Cl_2 (6.0 mL) were added Et_3N (430 μL, 3.1 mmol) and 2-chloro-5-methoxybenzoyl chloride prepared in the procedure described above at 0 °C. After stirring at room temperature overnight, 1N HCl aq. was added and the resulting mixture was extracted with ethyl acetate twice. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4. Filtration and removal of organic solvent under reduced pressure gave the crude diamide as a brown residue. To the CH_2Cl_2 solution (5.4 mL) of the crude diamide was added BBr_3 (1.0 M/CH_2Cl_2, 2.7 mL, 2.7 mmol) at 0 °C and the resulting solution was stirred at the same temperature for 1 h. After stirring at room temperature for 2 h, H_2O was added at 0 °C and the resulting biphasic mixture was extracted with ethyl acetate twice, and the combined organic layers were washed with brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was recrystallized from $CHCl_3$ to give **1i** (135 mg, 29% yield from **S1**•HCl) as a colorless solid.



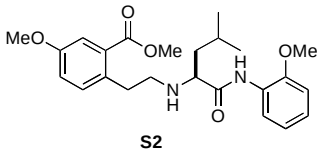
Colorless solid; IR (KBr) ν 3369, 3259, 2956, 1676, 1641, 1540, 1460 cm^{-1}; m.p. 147-148 °C; ^1H NMR (CD_3OD) δ 1.01 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 1.76-1.79 (m, 2H), 1.83-1.89 (m, 1H), 4.74 (d, *J* = 6.7, 8.6 Hz, 1H), 6.81 (ddd, *J* = 1.5, 7.9, 7.9 Hz, 1H), 6.84 (dd, *J* = 6.7, 8.6 Hz, 1H), 6.93 (d, *J* = 3.1 Hz, 1H), 6.93 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.86 (dd, *J* = 1.5, 7.9 Hz, 1H); ^{13}C NMR (CD_3OD) δ 21.7, 23.5, 26.0, 41.4, 54.4, 116.4, 116.6, 119.2, 120.6, 121.4, 122.7, 126.4, 126.9, 131.8, 137.8, 149.0, 157.7, 170.3, 172.7; $[\alpha]_D^{26}$ –67.1 (*c* 1.4, MeOH); ESI-MS *m*/*z* 399 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{19}H_{21}N_2O_4ClCs$ *m*/*z* 509.0244 $[M+Cs]^+$, found 509.0250.

*Synthesis of **1j***



(*S*)-*N*-(2-Hydroxyphenyl)-2-(3-hydroxybenzoylamino)-4-methylpentanamide (S4)

To a stirred solution of (4-methoxy-2-methoxycarbonylbenzyl)acetaldehyde (10 mg, 0.048 mmol, Reg #: 959631-90-4) in MeOH (0.5 mL) were added **S1** (10 mg, 0.042 mmol) and Pd/C (3.0 mg, 10 wt%) at room temperature and the resulting suspension was stirred under hydrogen atmosphere. After stirring for 2.5 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4) to give **S2** as a colorless oil (13.1 mg, 72% yield).

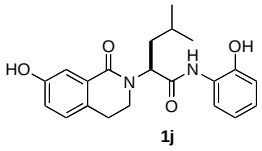


Colorless oil; IR (neat) ν 3307, 2954, 1720, 1680, 1523 cm^{-1}; ^1H NMR (CD_3OD) δ 0.94 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 1.46 (ddd, *J* = 6.1, 8.6, 13.1 Hz, 1H), 1.58 (ddd, *J* = 5.5, 8.3, 13.7 Hz, 1H), 1.70-1.78 (m, 1H), 2.76 (ddd, *J* = 6.7, 8.6, 15.0 Hz, 1H), 2.84 (ddd, *J* = 6.4, 8.2, 14.3 Hz, 1H), 3.05-3.14 (m, 1H), 3.23 (dd, *J* = 5.5, 8.6 Hz, 1H), 3.77 (s, 3H), 3.80 (s, 3H), 3.86 (s, 3H), 6.91 (ddd, *J* = 1.3, 7.6, 7.9 Hz, 1H), 6.98-7.04 (m, 2H), 7.09 (ddd, *J* = 1.5, 7.6, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 2.8 Hz, 1H), 8.05 (dd, *J* = 1.5, 7.9 Hz, 1H); ^{13}C NMR (CD_3OD) δ 22.6, 23.5, 26.2, 35.1, 44.1, 51.5, 52.5, 55.8, 56.3, 63.3, 111.6, 116.5, 119.1, 121.5, 121.9, 125.8, 128.0, 131.8, 133.6, 134.4, 151.0, 159.3, 169.3, 176.0; $[\alpha]_D^{26}$ –56.0 (*c* 0.2, MeOH); ESI-MS *m*/*z* 451 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{24}H_{32}N_2O_5Cs$ *m*/*z* 561.1366 $[M+Cs]^+$, found 561.1371.

(*S*)-2-(7-Hydroxy-1-oxo-3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(2-hydroxyphenyl)-4-methylpentanamide (1j)

To a stirred solution of **S2** (256 mg, 0.6 mmol) in $CHCl_3$ (10 mL) were added AcOH (10 drops) and $MgSO_4$ (1.0 g) at

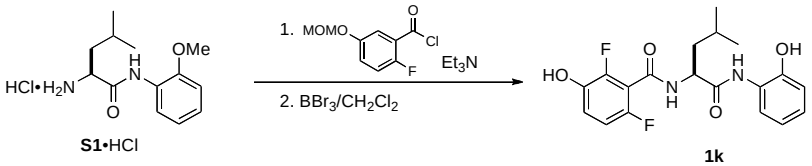
room temperature. After stirring at room temperature for 12 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4) to give lactam (231 mg, 97% yield) as a colorless oil. To the CH_2Cl_2 solution (2.3 mL) of the lactam was added BBr_3 (1.0 M/CH_2Cl_2, 2.3 mL, 2.3 mmol) at 0 °C and the resulting solution was stirred at the same temperature for 2 h. After stirring at room temperature for 2 h, H_2O was added at 0 °C and the resulting biphasic mixture was extracted with ethyl acetate twice, and the combined organic layers were washed with brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/3 to 1/1) to give **1j** (144 mg, 87% yield, 2 steps) as a colorless solid.



1j

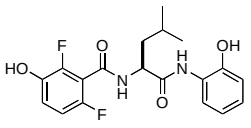
Colorless oil; IR (KBr) ν 3290, 2957, 1601, 1533, 1455, 1318, 751 cm^{-1}; m.p. 83-84 °C; ^1H NMR ($CDCl_3$) δ 0.91 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 1.51-1.58 (m, 1H), 1.76-1.89 (m, 1H), 2.49 (brs, 1H), 2.78-2.88 (m, 2H), 3.53 (ddd, *J* = 5.5, 7.6, 13.1 Hz, 1H), 3.61 (ddd, *J* = 5.5, 7.6, 12.8 Hz, 1H), 5.51 (dd, *J* = 6.7, 8.8 Hz, 1H), 6.77 (dd, *J* = 7.2, 8.7 Hz, 1H), 6.90 (dd, *J* = 2.4, 8.2 Hz, 1H), 6.93 (dd, *J* = 1.2, 8.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.99 (ddd, *J* = 1.2, 7.2, 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.96 (brs, 1H), 8.74 (brs, 1H), 8.91 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.0, 13.0, 24.9, 27.1, 36.5, 42.0, 55.2, 114.9, 118.3, 120.3, 120.5, 122.3, 125.7, 126.5, 128.4, 129.0, 129.9, 147.8, 155.4, 166.2, 170.1; $[\alpha]_D^{25}$ –173 (*c* 0.29, $CHCl_3$); ESI-MS *m/z* 391 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{21}H_{24}N_2O_4Cs$ *m/z* 501.0791 $[M+Cs]^+$, found 501.0808.

*Synthesis of **1k***



(*S*)-2,6-Difluoro-3-hydroxy-*N*-(1-(2-hydroxyphenylamino)-4-methyl-1-oxopentan-2-yl)benzamide (1k)

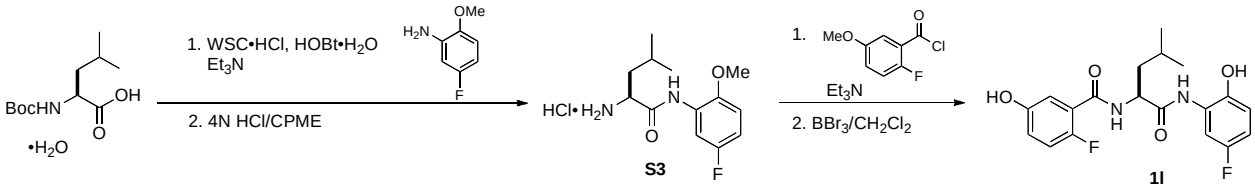
To a stirred solution of 2,6-difluoro-3-(methoxymethoxy)benzoic acid[S3] (220 mg, 1.01 mmol) in $CHCl_3$ (3.5 mL) were added **S1•HCl** (275 mg, 1.01 mmol), Et_3N (153 μL, 1.11 mmol), DCC (250 mg, 1.21 mmol), and DMAP (12 mg, 0.10 mmol) at room temperature. After stirring at the same temperature for 12 h, the reaction mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4 to 1/1) to give diamide (423 mg, 97% yield) as a colorless oil. To the CH_2Cl_2 solution (2.0 mL) of the lactam was added BBr_3 (1.0 M/CH_2Cl_2, 5.0 mL, 5.0 mmol) at 0 °C and the resulting solution was stirred at the same temperature for 2 h. MeOH (10 mL) and H_2O (5.0 mL) were successively added at 0 °C. After stirring at room temperature for 2 h, volatiles were removed under reduced pressure. The residue was take up with H_2O and extracted with ethyl acetate twice, and the combined organic layers were washed with H_2O and brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4 to 1/1) to give **1k** (388 mg, y. 89%, 2 steps) as a colorless solid.



1k

Colorless solid; IR (KBr) ν 3276, 2960, 1653, 1537 cm^{-1}; m.p. 73-74 °C; ^1H NMR (CD_3OD) δ 1.02 (d, *J* = 6.7 Hz, 6H), 1.75-1.88 (m, 3H), 4.78-4.82 (m, 1H), 6.79-6.89 (m, 3H), 6.96-7.01 (m, 2H), 7.84 (dd, *J* = 1.5, 7.9 Hz, 1H); ^{13}C NMR (CD_3OD) δ 21.7, 23.5, 25.9, 41.6, 54.4, 112.1 (dd, *J* = 2.4, 22.6 Hz), 115.9 (dd, *J* = 19.1, 22.6 Hz), 116.5, 119.9 (d, *J* = 8.3 Hz), 120.6, 122.8, 126.4, 126.9, 143.0 (dd, *J* = 2.4, 11.9 Hz), 149.1, 149.1 (dd, *J* = 8.3, 246.8 Hz), 153.1 (dd, *J* = 4.8, 242.0 Hz), 163.8, 172.5; ^{19}F NMR (CD_3OD) δ –138.8, –138.7; $[\alpha]_D^{26}$ –20.3 (*c* 1.9, MeOH); ESI-MS *m/z* 401 $[M+Na]^+$. HRMS (FAB) Anal. calcd. for $C_{19}H_{20}N_2O_4F_2Cs$ *m/z* 511.0445 $[M+Cs]^+$, found 511.0449.

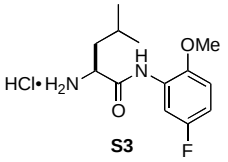
*Synthesis of **1l***



(*S*)-2-Amino-*N*-(5-fluoro-2-methoxyphenyl)-4-methylpentanamide hydrochloride (S3)

To a stirred solution of 5-fluoro-2-methoxyaniline (564 mg, 4.0 mmol) in CH_2Cl_2 (20 mL) were added

Boc-L-Leu-OH•H_2O (1.5 g, 6.0 mmol), Et_3N (1.11 mL, 8.0 mmol), WSC•HCl (1.15 g, 6.0 mmol), and HOBt•H_2O (612 mg, 4.0 mmol) at 0 °C. After stirring at room temperature for 11 h, the reaction mixture was quenched with 1N HCl aq. and extracted with ethyl acetate. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/10 to 1/3) to give amide (600 mg, 42% yield) as a colorless solid. To a stirred solution of the amide (600 mg) in CH_2Cl_2 (2.0 mL) was added 4N HCl/CPME (6.0 mL) at 0 °C. After stirring at room temperature overnight, volatiles were removed under reduced pressure and the resulting residue was recrystallized from MeOH/ether to give **S3** (192 mg, 66% yield, 2 steps) as a colorless solid.

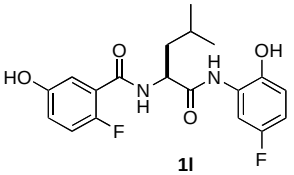


S3

Colorless solid; IR (KBr) ν 3410, 2960, 2048, 1701, 1541, 1502 cm^{-1}; m.p. 88-89 °C (free amine); ^1H NMR (CD_3OD) δ 1.03 (d, *J* = 5.7 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H), 1.73-1.83 (m, 3H), 3.90 (s, 3H), 4.23-4.27 (m, 1H), 6.87 (ddd, *J* = 2.9, 9.7, 9.7 Hz, 1H), 7.02 (dd, *J* = 5.2, 9.2 Hz, 1H), 7.92 (dd, *J* = 2.9, 10.3 Hz, 1H); ^{13}C NMR (CD_3OD) δ 22.3, 23.1, 25.6, 41.8, 53.6, 56.9, 110.3 (d, *J* = 28.6 Hz), 111.9 (d, *J* = 22.6 Hz), 112.6 (d, *J* = 8.3 Hz), 128.4 (d, *J* = 10.7 Hz), 147.7 (d, *J* = 2.4 Hz), 157.8 (d, *J* = 236.1 Hz), 169.1; ^{19}F NMR (CD_3OD) d –124.8; $[\alpha]_D^{25}$ +16.8 (*c* 1.4, MeOH); ESI-MS *m*/*z* 277 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{13}H_{19}N_2O_2FCs$ *m*/*z* 387.0485 $[M+Cs]^+$, found 387.0474.

(*S*)-2-Fluoro-*N*-(1-(5-fluoro-2-hydroxyphenylamino)-4-methyl-1-oxopentan-2-yl)-5-hydroxybenzamide (1l)

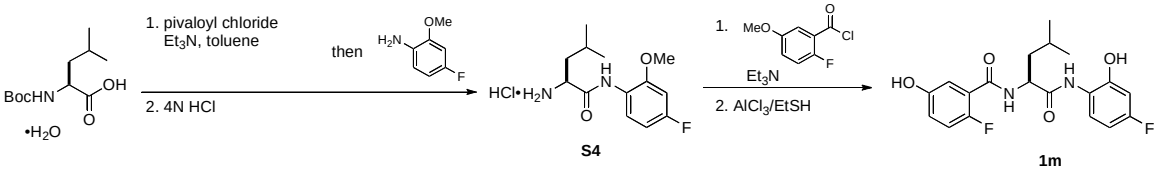
To a stirred solution of **S3** (36.5 mg, 0.125 mmol) in CH_2Cl_2 (1.5 mL) were added Et_3N (52 μL, 0.375 mmol) and 2-fluoro-5-methoxybenzoyl chloride (0.163 mmol/1.0 mL CH_2Cl_2) at 0 °C and the resulting mixture was stirred at room temperature for 20 min. The resulting mixture was partitioned with 1N HCl aq. and ethyl acetate, and organic layer was washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4. Filtrate was concentrated under reduced pressure to give crude diamide. To the CH_2Cl_2 solution (1.5 mL) of the diamide (53.4 mg) was added BBr_3 (1.0 M/CH_2Cl_2, 625 μL, 0.625 mmol) at 0 °C and the resulting solution was stirred at room temperature overnight. H_2O was added at 0 °C and the resulting biphasic mixture was extracted with ethyl acetate, and the combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4 to 1/1) to give **1l** (21.5 mg, 45% yield , 2 steps) as a colorless solid.



1l

Colorless solid; IR (KBr) ν 3290, 2960, 1628, 1534 cm^{-1}; m.p. 70-71 °C; ^1H NMR (CD_3OD) δ 1.00 (d, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H), 1.77-1.85 (m, 3H), 4.78-5.00 (m, 1H), 6.68 (ddd, *J* = 3.1, 8.8, 8.9 Hz, 1H), 6.79 (dd, *J* = 5.2, 8.9 Hz, 1H), 6.89-6.93 (m, 1H), 7.04 (dd, *J* = 9.2, 10.4 Hz, 1H), 7.13 (dd, *J* = 3.1, 5.5 Hz, 1H), 7.81 (dd, *J* = 3.1, 10.7 Hz, 1H); ^{13}C NMR (CD_3OD) δ 21.8, 23.5, 26.1, 41.5, 54.7, 109.1 (d, *J* = 28.6 Hz), 111.4 (d, *J* = 22.7 Hz), 116.1 (d, *J* = 9.5 Hz), 116.9, 117.9 (d, *J* = 25.0 Hz), 120.6 (d, *J* = 8.3 Hz), 124.0 (d, *J* = 15.5 Hz), 127.8 (d, *J* = 10.7 Hz), 144.6, 154.9 (d, *J* = 240.8 Hz), 155.0, 157.2 (d, *J* = 234.9 Hz), 167.2, 172.8; ^{19}F NMR (CD_3OD) δ –128.9, –126.0; $[\alpha]_D^{25}$ –18.2 (*c* 1.8, MeOH); ESI-MS *m*/*z* 401 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{19}H_{24}N_2O_4F_2Cs$ *m*/*z* 511.0445 $[M+Cs]^+$, found 511.0458.

*Synthesis of **1m***



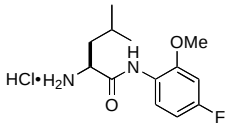
4-Fluoro-2-methoxyaniline

To a solution of 5-fluoro-2-nitrophenol (44.5 g, 283.3 mmol) in acetone (550 mL) added K_2CO_3 (54.8 g, 396.5 mmol) at room temperature. To the suspension was added MeI (48.2 g, 339.6 mmol) and the resulting suspension was stirred at room temperature for 9 h and refluxed for 3 h. Volatiles were removed under reduced pressure and the residue was taken up with H_2O (260 g) and ethyl acetate (360 g). The organic layer was washed with H_2O and brine (100 g), then dried over Na_2SO_4. Filtrate was concentrated and dried under vacuum to give 2-methoxy-4-fluoronitrobenzene (48.3 g, 99% yield) as a yellow solid. To a solution of 2-methoxy-4-fluoronitrobenzene (47.9 g, 279.9 mmol) in ethanol (300 mL, dissolved upon warming to ca. 40 °C) was added Pd/C (9.6 g, 10% w/w Merck) and the resulting suspension was stirred under hydrogen atmosphere at room temperature. After stirring for 18 h, small quantity of 2-methoxy-4-fluoronitrobenzene remained. Hydrogen was replaced with Ar and Pd/C in ethanol (100 mL) was added via syringe and the resulting suspension was stirred under hydrogen. After stirring for 6 h, the reaction mixture was

passed through a pad of Celite, and the filtrate was concentrated to give 4-fluoro-2-methoxyaniline (37.5 g, 95% yield) as a red oil. Reg # 450-91-9.

(*S*)-2-Amino-*N*-(4-fluoro-2-methoxyphenyl)-4-methylpentanamide hydrochloride (S4)

To a stirred suspension of Boc-L-Leu-OH•H_2O (82.9 g, 332.5 mmol) in toluene (420 mL) was successively added Et_3N (36.4 mL, 359.7 mmol) and pivaloyl chloride (40.1 mL, 332.6 mmol) at 0 °C. After stirring the resulting mixture at room temperature for 1.5 h, the resulting white suspension was filtrated and washed with toluene (50 mL x2). To the filtrate was added 4-fluoro-2-methoxyaniline (37.5 g, 265.7 mmol). After stirring the resulting mixture at room temperature for 30 min and at 40 °C for 1 h, the reaction mixture was diluted with ethyl acetate (500 g) and washed with 10% NaCl aq. (200g), 20% K_2CO_3 aq. (200g x2), sat. $NaHCO_3$ aq. (200 g), 10% NaCl aq. (200 g), and brine (100 g), then dried over Na_2SO_4. After filtration and removal of the organic solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 (200 mL) and 4N HCl (340 mL, (150 mL in 1,4-dioxane, 190 mL in CPME)) was added to the resulting solution at 0 °C. After stirring at room temperature overnight, the resulting white suspension was filtered to collect the white solid and washed with CH_2Cl_2 (200 mL). The white solid (177.7 g) was dissolved in warm MeOH (200 mL) and ether was added slowly (200 mL portion, total 1800 mL) and the resulting saturated solution/suspension was left stand at room temperature. The white solid was collected by filtration to give **S4** (63.4 g, 82% yield, 2 steps) as a white solid.



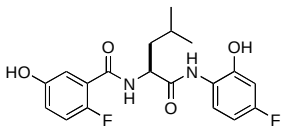
S4

Colorless solid; IR (KBr) ν 3409, 2868, 2067, 1699, 1585, 1539, 1495 cm^{-1}; m.p. 179-180 °C; ^1H NMR (CD_3OD) δ 1.02 (d, *J* = 6.4 Hz, 3H), 1.04 (d, *J* = 6.4 Hz, 3H), 1.76-1.83 (m, 3H), 3.87 (s, 3H), 4.20 (dd, *J* = 6.7, 7.6 Hz, 1H), 6.66 (ddd, *J* = 2.5, 8.6, 8.8 Hz, 1H), 6.85 (dd, *J* = 2.5, 10.4 Hz, 1H), 7.81 (dd, *J* = 6.4, 8.8 Hz, 1H); ^{13}C NMR (CD_3OD) δ 22.5, 23.0, 25.5, 41.9, 53.5, 56.7, 100.6 (d, *J* = 26.9 Hz), 107.2 (d, *J* = 22.7 Hz), 123.2 (d, *J* = 3.1 Hz), 125.7 (d, *J* = 10.3 Hz), 154.0 (d, *J* = 10.3 Hz), 162.3 (d, *J* = 242.9 Hz), 169.4; ^{19}F NMR (CD_3OD) δ –118.7; $[\alpha]_D^{25}$ +1.8 (*c* 1.0, MeOH); ESI-MS *m*/*z* 255 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{13}H_{19}N_2O_2FCs$ *m*/*z* 387.0485 $[M+Cs]^+$, found 387.0474.

(*S*)-2-fluoro-*N*-(1-(4-fluoro-2-hydroxyphenylamino)-4-methyl-1-oxopentan-2-yl)-5-hydroxybenzamide (1m)

To a stirred suspension of the **S4** (63.4 g, 218.0 mmol) in CH_2Cl_2 (200 mL) were added Et_3N (48.6 g, 480.3 mmol) and 2-fluoro-5-methoxybenzoyl chloride (prepared by following the procedure described above, 38.9 g, 228.6 mmol in CH_2Cl_2 (80 mL)) at 0 °C. After stirring the resulting solution at room temperature overnight (>8 h), the resulting mixture was washed with 1N HCl aq., sat. $NaHCO_3$ aq., and brine, then dried over Na_2SO_4. After filtration and removal of the organic solvent, the resulting residue was purified by flash silica gel column chromatography (ethyl acetate/*n*-hexane = 7/3 to 1/1) to give diamide (84.2 g, 95% yield) as a white solid. To a stirred solution of the diamide (660 mg, 1.62 mmol) in *n*-PrSH (8.0 mL) was added $AlCl_3$ (2.1 g, 15.7 mmol) at 0 °C and the resulting suspension was stirred at 0 °C for 6 h. After addition of CH_2Cl_2 (10 mL) and MeOH (10 mL) at the same temperature, volatiles were removed under reduced pressure. The residue was partitioned with H_2O and ethyl acetate, and the organic layer was washed with sat. $NaHCO_3$ aq. (x 2) and brine, then dried over Na_2SO_4. After filtration and removal of the organic solvent under reduced pressure, the residue was recrystallized from $CHCl_3$ to give **1m** as a colorless solid (407 mg, 66% yield, 1st crop).

(*S*)-2-fluoro-*N*-(1-(4-fluoro-2-hydroxyphenylamino)-4-methyl-1-oxopentan-2-yl)-5-hydroxybenzamide (1m)



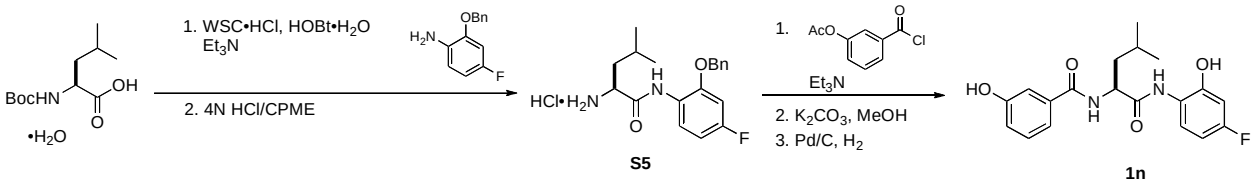
1m

Colorless solid; IR (KBr) ν 3201, 1649, 1532 cm^{-1}; ^1H NMR (CD_3OD) δ 1.00 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.3 Hz, 3H), 1.73-1.85 (m, 3H), 4.78 (dd, *J* = 5.5, 9.5 Hz, 1H), 6.54 (ddd, *J* = 2.9, 8.6, 8.6 Hz, 1H), 6.59 (dd, *J* = 2.9, 9.7 Hz, 1H), 6.90 (ddd, *J* = 3.4, 4.0, 9.2 Hz, 1H), 7.03 (dd, *J* = 9.2, 10.3 Hz, 1H), 7.11 (dd, *J* = 3.4, 5.7 Hz, 1H), 7.75 (dd, *J* = 6.3, 9.2 Hz, 1H); ^{13}C NMR (CD_3OD) δ 21.9, 23.5, 26.1, 41.8, 54.5, 103.7 (d, *J* = 20.9 Hz), 106.5 (d, *J* = 22.6 Hz), 116.9 (d, *J* = 2.4 Hz), 117.9 (d, *J* = 25.0 Hz), 120.6 (d, *J* = 8.3 Hz), 123.1 (d, *J* = 3.6 Hz), 124.0 (d, *J* = 15.5 Hz), 124.5 (d, *J* = 10.7 Hz), 151.1 (d, *J* = 11.9 Hz), 154.9 (d, *J* = 239.6 Hz), 155.5 (d, *J* = 2.4 Hz), 161.7 (d, *J* = 242.0 Hz), 167.0 (d, *J* = 2.4 Hz), 173.0; ^{19}F NMR (CD_3OD) δ –131.3, –121.2; $[\alpha]_D^{27}$ –20.7 (*c* 1.05, MeOH); ESI-MS *m*/*z* 401 $[M+Na]^+$; HRMS calcd. for $C_{19}H_{20}N_2O_4F_2Cs$ $[M+Cs]^+$ 511.0446, found 511.0466.

ent-**1m** was prepared by the analogous procedure.

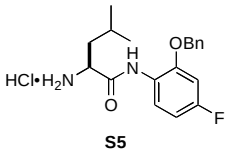
HPLC: DAICEL CHIRALPAK AS-H (0.46 cm ϕ x 25 cm), *n*-hexane/2-propanol = 4/1, column oven 30 °C, flow rate 1.0 mL/min, detection at 254 nm, t_R 9.09 min (**1m** (*S*)) and 36.7 min (*ent*-**1m** (*R*)).

*Synthesis of **1n***



(*S*)-2-Amino-*N*-(2-(benzyloxy)-4-fluorophenyl)-4-methylpentanamide (S5)

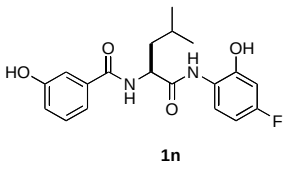
To a stirred solution of 4-fluoro-2-benzyloxyaniline (2.17 g, 10 mmol) in CH_2Cl_2 (50 mL) were added Boc-L-Leu-OH•H_2O (3.74 g, 15 mmol), Et_3N (2.23 mL, 16 mmol), WSC•HCl (3.07 g, 16 mmol), and HOBt•H_2O (460 mg, 3.0 mmol) at 0 °C. After stirring at room temperature for 24 h, the reaction mixture was quenched with 1N HCl aq. and extracted with ethyl acetate. The combined organic layers were washed with brine, then dried over Na_2SO_4. Filtrate was concentrated and the resulting residue was recrystallized from MeOH/Et_2O to give amide (1.96 g, 45% yield) as a white solid. To a stirred solution of the amide (1.96 g) in CH_2Cl_2 (2.0 mL) was added 4N HCl/CPME (8.0 mL) at 0 °C. After stirring at the same temperature for 2 h, volatiles were removed under reduced pressure and the resulting residue was recrystallized from MeOH/ether to give **S5** (1.42 g, 39% yield, 2 steps) as a colorless solid.



Colorless solid; IR (KBr) ν 3409, 1699, 1540, 1497, 1216 cm^{-1}; m.p. 180-181 °C; ^{1}H NMR (CD_3OD) δ 0.90 (d, *J* = 9.8 Hz, 3H), 0.91 (d, *J* = 9.2 Hz, 3H), 1.65-1.74 (m, 3H), 4.10 (dd, *J* = 6.9, 6.9 Hz, 1H), 5.12 (s, 2H), 6.69 (ddd, *J* = 2.9, 8.9, 8.9 Hz, 1H), 6.94 (dd, *J* = 2.9, 10.9 Hz, 1H), 7.33-7.40 (m, 3H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.66 (dd, *J* = 6.3, 8.9 Hz, 1H); ^{13}C NMR (CD_3OD) δ 22.4, 22.9, 25.4, 41.9, 53.3, 72.0, 101.9 (d, *J* = 27.4 Hz), 107.6 (d, *J* = 22.6 Hz), 122.9 (d, *J* = 2.4 Hz), 127.1 (d, *J* = 9.5 Hz), 129.1, 129.3, 129.7, 137.6, 153.8 (d, *J* = 9.5 Hz), 162.5 (d, *J* = 244.4 Hz), 169.5; ^{19}F NMR (CD_3OD) δ –119.0; $[\alpha]_D^{26}$ +1.3 (*c* 4.39, MeOH); ESI-MS *m*/*z* 331 $[M+H]^+$; HRMS (FAB) Anal. calcd. for $C_{19}H_{23}CsN_2O_2F$ *m*/*z* 463.0798 $[M+Cs]^+$, found 463.0815.

(*S*)-*N*-(4-Fluoro-2-hydroxyphenyl)-2-(3-hydroxybenzoylamino)-4-methylpentanamide (1n)

To a stirred solution of 3-acetoxybenzoyl chloride (prepared by 3-acetoxybenzoic acid (270 mg, 1.5 mmol) with oxalyl chloride (214 μL, 2.5 mmol) and DMF (1 drop)) in CH_2Cl_2 (5.0 mL) were added of **S5** (458 mg, 1.25 mmol) and Et_3N (522 μL, 3.75 mmol) 0 °C. After stirring the resulting solution at room temperature for 20 min, the resulting mixture concentrated under reduced pressure. To the resulting residue were added MeOH (12 mL) and K_2CO_3 (258 mg, 1.875 mmol) and the resulting suspension was stirred at room temperature for overnight. The reaction was quenched with 1N HCl aq. and extracted with ethyl acetate. The combined organic layers were washed with sat. $NaHCO_3$ aq. and brine, then dried over Na_2SO_4. After filtration, volatiles were removed under reduced pressure and the resulting residue was dissolved in MeOH (12 mL) and stirred over Pd/C (70 mg, Merck 10 wt%) under hydrogen atmosphere at room temperature for 11 h. The resulting suspension was filtered through a pad of celite and the filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/4 to 1/2) to give **1n** (445 mg, 98% yield, 3 steps) as a colorless solid as a colorless solid.



Colorless solid; IR (KBr) ν 3290, 1641, 1529 cm^{-1}; m.p. 72-73 °C; ^{1}H NMR (CD_3OD) δ 1.00 (d, *J* = 5.8 Hz, 3H), 1.02 (d, *J* = 5.7 Hz, 3H), 1.74-1.88 (m, 3H), 4.78 (dd, *J* = 4.6, 9.8 Hz, 1H), 6.54 (ddd, *J* = 2.9, 8.6, 8.6 Hz, 1H), 6.59 (dd, *J* = 2.9, 10.3 Hz, 1H), 6.95-7.00 (m, 1H), 7.24-7.30 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 6.3, 9.2 Hz, 1H); ^{13}C NMR (CD_3OD) δ 21.9, 23.5, 26.3, 41.5, 54.5, 103.7 (d, *J* = 25.0 Hz), 106.5 (d, *J* = 22.6 Hz), 115.5, 119.4, 119.9, 123.2 (d, *J* = 3.6 Hz), 124.2 (d, *J* = 9.5 Hz), 130.6, 136.6, 150.9 (d, *J* = 10.7 Hz), 158.8, 161.5 (d, *J* = 242.0 Hz), 170.8, 173.3; ^{19}F NMR (CD_3OD) δ –119.0; $[\alpha]_D^{24}$ –7.8 (*c* 1.5, MeOH); ESI-MS *m*/*z* 383 $[M+Na]^+$; HRMS (FAB) Anal. calcd. for $C_{19}H_{21}N_2O_4FCs$ *m*/*z* 493.0540 $[M+Cs]^+$, found 493.0550.

4. ICP Analysis of Nd/1m/Na and Sm/1m/Na Heterobimetallic Catalyst

4-1. ICP analysis of Nd/**1m**/Na catalyst.

Preparation of Nd standard solution.

1006 mg/L $Nd(NO_3)_3$/standard solution (for chemical analysis, in 1N HNO_3 aq.) was diluted with 1N HNO_3 aq. (spectroscopic grade) to give 2, 4, 6, 10 ppm standard solution.

Preparation of the catalyst sample

To a flame dried glass tube (inner diameter 5 mm, length 10 cm, capped with rubber septum) was added ligand **1m** (20.4 mg, 0.054 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar,

then THF (600 μL) and $Nd_5O(O^iPr)_{13}$ (135 μL, 0.027 mmol, 0.2 M/THF (based on Nd), transferred by well-dried syringe and needle) were successively added at room temperature. After agitation of the resulting mixture with vortex mixer at the same temperature for 30 sec, the mixture was cooled to 0 °C and NaHMDS (54 μL, 0.054 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added at the same temperature to give white suspension. After agitation of the resulting mixture with vortex mixer at room temperature for 30 sec, nitroethane (**3a**) (180 μL), was added at the same temperature to give a clear solution. After standing at the same temperature, the white precipitates appeared and the whole suspension was transferred to Eppendorf safe-lock tube (size 1.5 mL). The tube was centrifuged (ca. 10^4 rpm, 30 sec). The supernatant was decanted to 30 mL flask and dry THF (1.0 mL) was added to the precipitate. The tube was agitated by vortex mixer for 30 sec and centrifuged again (washing process). The supernatant was decanted to the flask. The washing process was conducted twice and washings were combined, evaporated and well dried under vacuum and dissolved in 1N HNO_3 aq. (final volume 50.0 mL) to give a supernatant sample. The precipitates were well dried under vacuum for 5 h and dissolved in 1N HNO_3 aq. (final volume 50.0 mL) to give a precipitates sample.

Analytical curve was created by ICP analysis of standard Nd solutions. Nd and Na content of the catalyst (precipitates and supernatant samples) were determined with the analytical curve.

4-2. ICP analysis of Sm/**1m**/Na catalyst.

Preparation of Sm rtandard solution.

1006 mg/L $Sm(NO_3)_3$/standard solution (for chemical analysis, in 1N HNO_3 aq.) was diluted with 1N HNO_3 aq. (spectroscopic grade) to give 2, 4, 6, 10 ppm standard solution.

Preparation of the catalyst sample

To a flame dried glass tube (inner diameter 5 mm, length 10 cm, capped with rubber septum) was added ligand **1m** (20.4 mg, 0.054 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar, then THF (600 μL) and $Sm_5O(O^iPr)_{13}$ (135 μL, 0.027 mmol, 0.2 M/THF (based on Sm), transferred by well-dried syringe and needle) were successively added at room temperature. After agitation of the resulting mixture with vortex mixer at the same temperature for 30 sec, the mixture was cooled to 0 °C and NaHMDS (54 μL, 0.054 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added at the same temperature to give white suspension. After agitation of the resulting mixture with vortex mixer at room temperature for 30 sec, nitroethane (**3a**) (180 μL), was added at the same temperature to give a clear solution. After standing at the same temperature, the white precipitates appeared and the whole suspension was transferred to Eppendorf safe-lock tube (size 1.5 mL). The tube was centrifuged (ca. 10^4 rpm, 30 sec). The supernatant was decanted to 30 mL flask and dry THF (1.0 mL) was added to the precipitate. The tube was agitated by vortex mixer for 30 sec and centrifuged again (washing process). The supernatant was decanted to the flask. The washing process was conducted twice and washings were combined, evaporated and well dried under vacuum and dissolved in 1N HNO_3 aq. (final volume 50.0 mL) to give a supernatant sample. The precipitates were well dried under vacuum for 5 h and dissolved in 1N HNO_3 aq. (final volume 50.0 mL) to give a precipitates sample.

Analytical curve was created by ICP analysis of standard Nd solutions. Nd and Na content of the catalyst (precipitates and supernatant samples) were determined with the analytical curve.

5. XRF analysis of of Nd/1m/Na Heterobimetallic Catalyst

To a flame dried 100 mL flask was added ligand **1m** (1.5 g mg, 4.0 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar, then THF (20 mL) and $Nd_5O(O^iPr)_{13}$ (10 mL, 2.0 mmol, 0.2 M/THF (based on Nd), transferred by well-dried syringe and needle) were successively added at room temperature. After stirring the resulting solution at the same temperature for 10 min, the mixture was cooled to 0 °C and NaHMDS (4.0 mL, 4.0 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added at the same temperature to give white suspension. After stirring the resulting mixture at room temperature for 10, nitroethane (**3a**) (8.5 mL), was added at the same temperature to give a clear solution. After standing at the same temperature, the white precipitates appeared and the whole suspension was transferred to two corning tubes (size 50 mL). The tubes were centrifuged (ca. 10^3 rpm, 5 min). The supernatant was decanted and dry THF (40 mL) was added to the resulting precipitates. The tube was agitated by vortex mixer for 30 sec and centrifuged again (washing process). The supernatant was decanted and the precipitates were collected and dried under vacuum to give heterogeneous catalyst sample 1.504 g for XRD analysis.

0.864 g of 1.504 g sample was taken and well grinded, then pressed to the sampler (40 kN). The sample was submitted to semi-quantitative (SQX) analysis conducted with a Rigaku ZSX Primus II WDXRF spectrometer. Mass% of F, Na, Nd was determined as 3.91, 4.23, and 16.2, respectively. These data corresponded that the 1.504 g of heterogeneous catalyst contained 1.69 mmol of Nd, 1.55 mmol of **1m**, and 2.77 mmol of Na.

6. ESI TOF MS Analysis of the Nd/1m/Na Heterobimetallic Catalyst

*Preparation of MS sample for $Nd_5(O^iPr)_{13}$/**1m** = 1/2 solution in THF (Figure 6(a))*

To a flame dried glass tube (inner diameter 5 mm, length 10 cm, capped with rubber septum) was added ligand **1m** (6.8 mg, 0.018 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar, then THF (200 mL) and $Nd_5O(O^iPr)_{13}$ (45 μL, 0.009 mmol, 0.2 M/THF (based on Nd), transferred by well-dried syringe and needle) were successively added at room temperature. After agitation of the resulting mixture with vortex mixer at the same temperature, the solution was diluted with THF (4.5 mL) to give the sample (final concentration 2 mM).

*Preparation of MS sample for $Nd_5(O^iPr)_{13}$/**1m**/NaHMDS = 1/2/2 solution in THF (Figure 6(b))*

To a flame dried glass tube (inner diameter 5 mm, length 10 cm, capped with rubber septum) was added ligand **1m** (6.8 mg, 0.018 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar, then THF (200 mL) and $Nd_5O(O^iPr)_{13}$ (45 μL, 0.009 mmol, 0.2 M/THF (based on Nd), transferred by well-dried syringe and needle) were successively added at room temperature. After agitation of the resulting mixture with vortex mixer at the same temperature for 30 sec, NaHMDS (18 μL, 0.018 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added at the same temperature to give white suspension. After agitation of the resulting mixture with vortex mixer at room temperature for 30 sec, the suspension was diluted with THF (4.5 mL) to give the slightly cloudy sample solution (final concentration 2 mM). The sample was injected after filtration through 200 μm mesh membrane filter.

The MS spectrum in negative ion detection mode was shown in Figure S1. Isotopic pattern of identified peaks is matched with those of theoretical pattern.

*Preparation of MS sample for $Nd_5(O^iPr)_{13}$/**1m**/NaHMDS = 1/2/2 solution in THF (Figure 6(c))*

To a flame dried glass tube (inner diameter 5 mm, length 10 cm, capped with rubber septum) was added ligand **1m** (6.8 mg, 0.018 mmol) and dried under vacuum at room temperature for 10 min. To the test tube was back-filled Ar, then THF (200 mL) and $Nd_5O(O^iPr)_{13}$ (45 μL, 0.009 mmol, 0.2 M/THF (based on Nd), transferred by well-dried syringe and needle) were successively added at room temperature. After agitation of the resulting mixture with vortex mixer at the same temperature for 30 sec, the mixture was cooled to 0 °C and NaHMDS (18 μL, 0.018 mmol, 1.0 M/THF, purchased from Aldrich and stored in pear-shaped flask with tight glass 3-way stopcock, transferred by well-dried syringe and needle) was added at the same temperature to give white suspension. After agitation of the resulting mixture with vortex mixer at room temperature for 30 sec, nitroethane (**3a**) (60 μL), was added at the same temperature to give a clear solution. After standing at the same temperature, the white precipitates appeared and the whole suspension was transferred to Eppendorf safe-lock tube (size 1.5 mL). The tube was centrifuged (ca. 10^4 rpm, 30 sec). The supernatant was decanted and dry THF (1.0 mL) was added to the precipitates. The tube was agitated by vortex mixer for 30 sec and centrifuged again (washing process). The supernatant was decanted and the resulting precipitates were diluted with THF (9.0 mL) and DMSO (90 μL) to give clear solution (final concentration 1 mM). The sample was injected after filtration through 200 μm mesh membrane filter.

The MS spectrum in negative ion detection mode was shown in Figure S2. Isotopic pattern of identified peaks is matched with those of theoretical pattern.

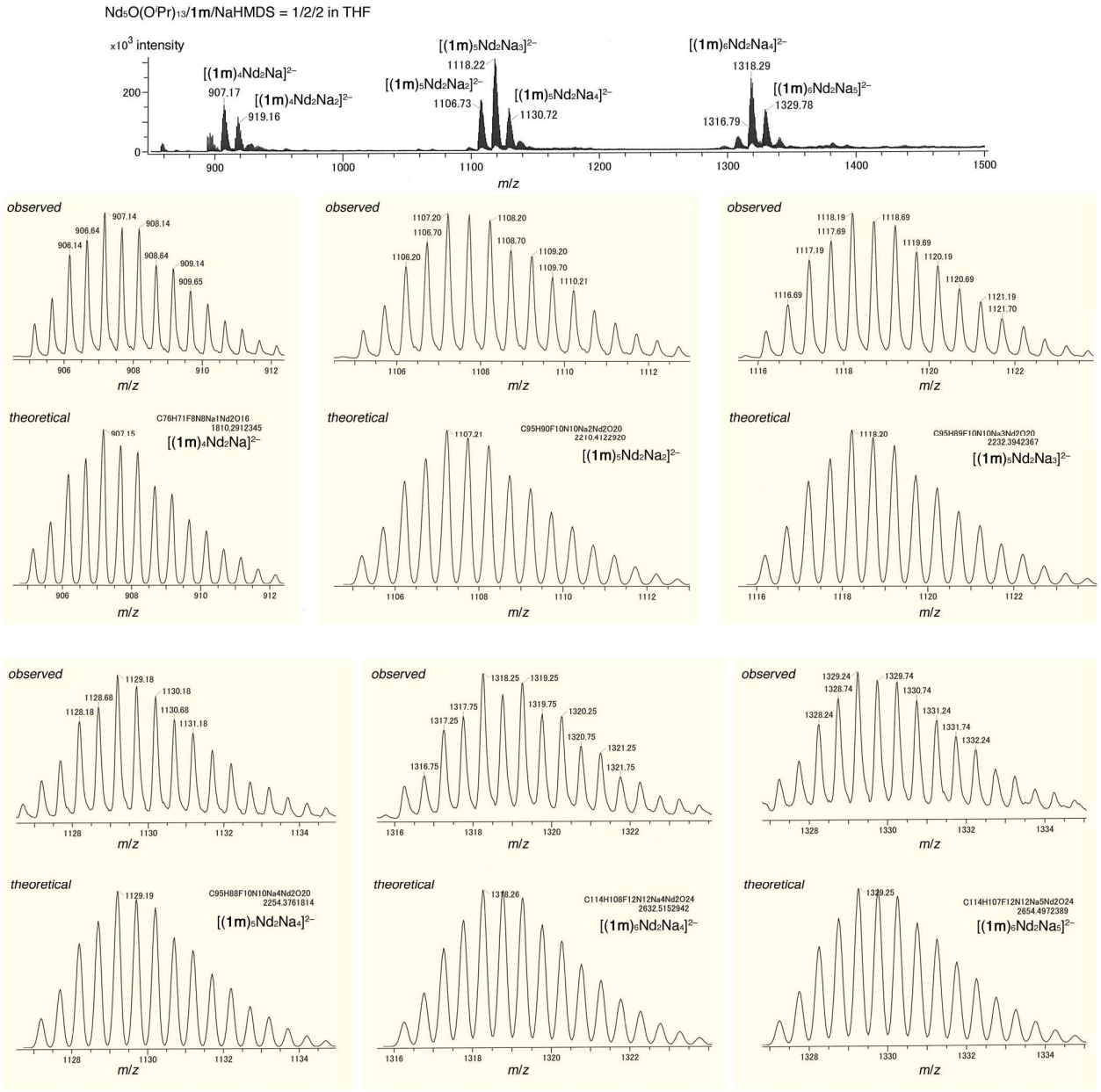


Figure S1. ESI TOF MS spectrum of $Nd_5(O^iPr)_{13}$/**1m**/NaHMDS = 1/2/2 solution.

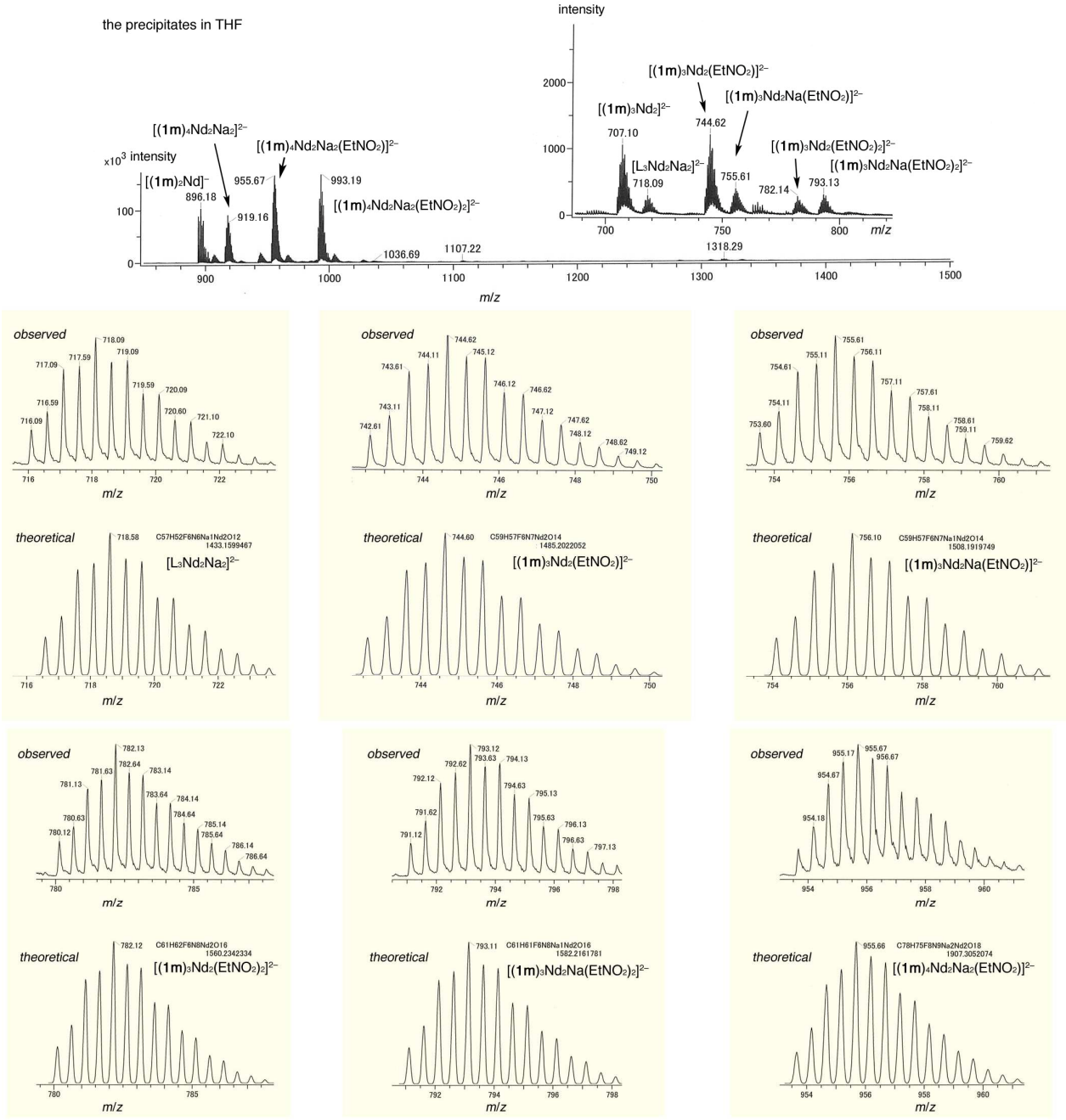
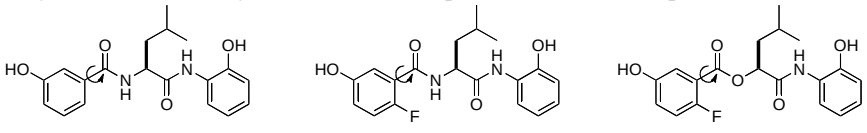


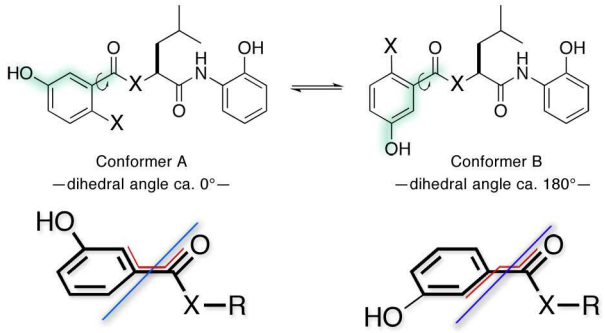
Figure S2. ESI TOF MS spectrum of the precipitates.

7. Conformational Analysis of ligand 1g and 1h

Energy profile of rotational conformers along C-C single bond between *m*-hedroxybenzoyl group and amide carbonyl in ligand **1g**, **1h**, and an ester analog was investigated with the aid of DFT calculation. Calculations were performed on Jaguar version 7.0 released in 2007 (Jaguar version 7.0, Schrödinger, LLC, New York, NY, 2007) using the B3LYP level of density functional theory.[s4] The 6-311G(d,p)++ basis set of Pople and coworkers was used.[s5]



1g **1h** ester analog



The conformation of each ligand was optimized by DFT calculation at B3LYP/6-311G(d,p)++ level of theory. As to the C-C single bond of bond between *m*-hedroxybenzoyl group and amide carbonyl, dihedral angle was ca. 0° in the optimized geometry in each ligand. Input geometry and optimized geometry was shown in the following.

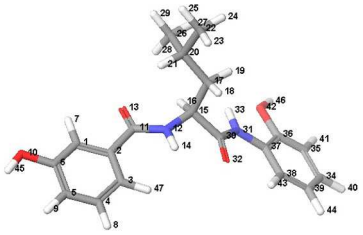
Ligand **1g**—
Input geometry:

		angstroms	
atom	x	y	z
C1	-4.1353210000	1.0899740000	0.5363150000
C2	-4.3319330000	0.4820040000	-0.7232710000
C3	-4.9098490000	-0.8081090000	-0.7844930000
C4	-5.3040860000	-1.4662920000	0.3970970000
C5	-5.1173620000	-0.8465500000	1.6474070000
C6	-4.5298260000	0.4317820000	1.7167760000
H7	-3.6819770000	2.0703470000	0.5936700000
H10	-5.7472020000	-2.4512000000	0.3449650000
H11	-5.4244480000	-1.3648030000	2.5454750000
O11	-4.3384060000	1.0383120000	2.9229510000
C12	-3.8885270000	1.1908410000	-1.9694280000
N13	-3.3800900000	0.4104440000	-2.9274850000
O14	-4.0420810000	2.4070780000	-2.1008160000
H15	-3.3770890000	-0.5841260000	-2.7613920000
C16	-2.9626840000	0.8686070000	-4.2522450000
H18	-2.4602630000	1.8341600000	-4.1714820000
C19	-2.0131590000	-0.1847170000	-4.8743020000
H20	-2.5533300000	-1.1274460000	-4.9831860000
H21	-1.7557790000	0.1191710000	-5.8909120000
C22	-0.7061660000	-0.4436140000	-4.0885290000
H24	-0.9611370000	-0.7176520000	-3.0637230000
C25	0.0585600000	-1.6328670000	-4.6895620000
H26	-0.5509980000	-2.5373990000	-4.6883910000
H27	0.3576010000	-1.4362550000	-5.7199130000
H28	0.9620270000	-1.8513940000	-4.1188480000
C28	0.2000950000	0.7975640000	-4.0302090000
H29	0.4575800000	1.1525030000	-5.0288770000
H30	-0.2741340000	1.6199930000	-3.4946830000
H31	1.1324430000	0.5782540000	-3.5084520000
C31	-4.1929840000	1.0103340000	-5.1693630000
N32	-4.1154720000	1.9768590000	-6.0957050000
O33	-5.1539310000	0.2470810000	-5.0315780000
H34	-3.2623320000	2.5219950000	-6.0991750000
C35	-6.7227830000	3.3862390000	-9.1323430000
C36	-5.4611330000	3.9710710000	-8.9140380000

C37	-4.6220320000	3.4758400000	-7.8963710000
C38	-5.0387670000	2.3939410000	-7.0901850000
C39	-6.3093270000	1.8095310000	-7.3148720000
C40	-7.1454490000	2.3069120000	-8.3336740000
H41	-7.3666010000	3.7664420000	-9.9135690000
H42	-5.1481510000	4.7994680000	-9.5341520000
O43	-3.3954830000	4.0417080000	-7.6824730000
H44	-6.6702040000	0.9813630000	-6.7251740000
H45	-8.1147340000	1.8578260000	-8.5019930000
H46	-4.6383680000	0.5112730000	3.6581030000
H47	-3.2137710000	4.7619250000	-8.2780770000
H48	-5.0474230000	-1.3067990000	-1.7344230000

final geometry:

		angstroms	
atom	x	y	z
C1	-3.6005036032	0.5915892162	0.6424403757
C2	-4.1766280079	0.4061495604	-0.6137000665
C3	-5.4096417120	-0.2498967070	-0.7266205808
C4	-6.0441444417	-0.7233506980	0.4175274153
C5	-5.4626901097	-0.5563332845	1.6720426978
C6	-4.2375228139	0.1048310096	1.7812490278
H7	-2.6604436397	1.1204349345	0.7295857524
H10	-7.0034724629	-1.2210688011	0.3363784157
H11	-5.9621499681	-0.9310964335	2.5605846638
O11	-3.6147957244	0.3069373779	2.9826666658
C12	-3.4282049125	0.9684972981	-1.7948356793
N13	-3.6936506718	0.3906388695	-3.0008928755
O14	-2.6123273282	1.8733107489	-1.6641031564
H15	-4.4207990493	-0.3050258921	-3.0836195781
C16	-3.1973570570	0.9228781053	-4.2581605273
H18	-2.7750037840	1.9057546018	-4.0417168259
C19	-2.1258909885	0.0126847260	-4.9054544161
H20	-2.5856605711	-0.9670530748	-5.0769492186
H21	-1.8760916762	0.4176330105	-5.8943391455
C22	-0.8299828037	-0.1628990142	-4.0932318181
H24	-1.1084317447	-0.4898564354	-3.0850331833
C25	0.0303656420	-1.2668285668	-4.7251657350
H26	-0.5095059358	-2.2168946773	-4.7773904203
H27	0.3306509623	-0.9966425119	-5.7437373974
H28	0.9422708078	-1.4311903316	-4.1444481476
C28	-0.0361233385	1.1443000811	-3.9663550405
H29	0.2325409079	1.5352357393	-4.9549672917
H30	-0.5969071576	1.9083728273	-3.4246106032
H31	0.8937157608	0.9753738557	-3.4159501206
C31	-4.3960070555	1.0441769042	-5.2150113025
N32	-4.2879721098	2.0562275551	-6.1260713129
O33	-5.3281680728	0.2560907303	-5.1568178699
H34	-3.4883103832	2.6681997043	-6.0393483033
C35	-6.7436100955	3.2171728751	-9.3422459114
C36	-5.5729560494	3.9104601458	-9.0338516959
C37	-4.7874791957	3.4993748215	-7.9663684844
C38	-5.1556675279	2.3879549093	-7.1859050978
C39	-6.3292881224	1.6998183400	-7.5025680454
C40	-7.1147338691	2.1170194847	-8.5771422108
H41	-7.3552894379	3.5411184503	-10.1755832921
H42	-5.2696484905	4.7709826873	-9.6225948593



O43	-3.6191492387	4.1304845987	-7.6030816648
H44	-6.6137371429	0.8502508159	-6.9015045890
H45	-8.0226738253	1.5738260576	-8.8096838638
H46	-4.1486458867	-0.0623392950	3.6938101673
H47	-3.4607838604	4.8906255244	-8.1714398236
H48	-5.8992712183	-0.3649900122	-1.6860698486

2092.851610593 hartrees

Ligand **1h**—
Input geometry:

		angstroms	
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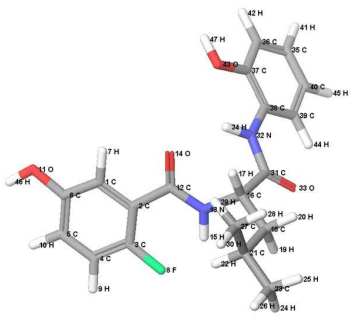
C1	-2.1956440000	-0.0338340000	-0.2937260000
C2	-2.1970620000	0.9776990000	-1.2816970000
C3	-2.7277220000	0.6799650000	-2.5641130000
C4	-3.2558950000	-0.5980960000	-2.8320610000
C5	-3.2571360000	-1.5931150000	-1.8371370000
C6	-2.7239950000	-1.3094910000	-0.5661130000
H7	-1.7862730000	0.1739170000	0.6852840000
F8	-2.7443720000	1.6063170000	-3.5550880000
H10	-3.6612110000	-0.8147510000	-3.8096300000
H11	-3.6669090000	-2.5674430000	-2.0636180000
O11	-2.7141130000	-2.2641490000	0.4066830000
C12	-1.6010020000	2.3186400000	-0.9485430000
N13	-2.0307890000	3.3619360000	-1.6657690000
O14	-0.8088530000	2.4432650000	-0.0102940000
H15	-2.6926990000	3.1705850000	-2.4045580000
C16	-1.6784260000	4.7606540000	-1.4204410000
H18	-0.6191610000	4.8371910000	-1.1692490000
C19	-1.9950200000	5.5923820000	-2.6876310000
H20	-3.0635950000	5.5180920000	-2.8996140000
H21	-1.8151200000	6.6491600000	-2.4804280000
C22	-1.2023390000	5.1952420000	-3.9548320000
H24	-1.3467280000	4.1295120000	-4.1394830000
C25	-1.7451410000	5.9381310000	-5.1851290000
H26	-2.8043370000	5.7281490000	-5.3389670000
H27	-1.6330470000	7.0181680000	-5.0817070000
H28	-1.2208330000	5.6361330000	-6.0926240000
C28	0.3077110000	5.4461870000	-3.8055440000
H29	0.5191340000	6.4911590000	-3.5754580000
H30	0.7433090000	4.8350440000	-3.0151600000
H31	0.8392610000	5.1975190000	-4.7249130000
C31	-2.5164810000	5.3190290000	-0.2537320000
N32	-1.9241910000	6.2733770000	0.4787990000
O33	-3.6618810000	4.8990500000	-0.0615980000
H34	-0.9983250000	6.5533190000	0.1799680000
C35	-3.1120930000	8.5838730000	3.8334210000
C36	-1.9031700000	8.8345610000	3.1572590000
C37	-1.5410160000	8.0467300000	2.0467430000
C38	-2.3866240000	7.0065480000	1.6029070000
C39	-3.5986460000	6.7550150000	2.2912570000
C40	-3.9573780000	7.5444120000	3.4014630000
H41	-3.3895970000	9.1883820000	4.6859700000
H42	-1.2614050000	9.6338260000	3.5007790000
O43	-0.3652330000	8.2852900000	1.3902830000
H44	-4.2695610000	5.9634270000	1.9954980000

H45	-4.8840240000	7.3496630000	3.9238720000
H46	-3.0928520000	-3.0921520000	0.1249300000
H47	0.1273900000	9.0070340000	1.7682850000

final geometry:

		angstroms	
atom	x	y	z
C1	-1.5097072121	0.6487746986	-0.1753939232
C2	-2.1280533262	1.5192878096	-1.0774496837
C3	-3.1400330232	0.9897140948	-1.8821304816
C4	-3.5323403007	-0.3334285149	-1.8097000221
C5	-2.9028478392	-1.1820941240	-0.9040192253
C6	-1.8867807992	-0.6871036899	-0.0843538064
H7	-0.7231947310	1.0392017775	0.4568913732
F8	-3.7905517830	1.7810896555	-2.7916627513
H10	-4.3227630029	-0.6890424610	-2.4581340635
H11	-3.2055306139	-2.2222742161	-0.8405679621
O11	-1.2250771919	-1.4629497882	0.8269026495
C12	-1.6254461807	2.9434555562	-1.0760942502
N13	-2.2252603629	3.8284162023	-1.9086861797
O14	-0.6996778939	3.2708093083	-0.3369776091
H15	-3.0202864724	3.5360523542	-2.4557066190
C16	-1.7846471428	5.2210494334	-2.0149387770
H18	-0.7213700063	5.2283010673	-1.7693058372
C19	-2.0166054577	5.7546054600	-3.4303508553
H20	-3.0932866139	5.7540358831	-3.6278097186
H21	-1.7185705263	6.8082751951	-3.4415983280
C22	-1.2752010996	5.0008587521	-4.5507659371
H24	-1.5622204544	3.9432455738	-4.5035067523
C25	-1.7176531150	5.5386525408	-5.9187794705
H26	-2.7999817998	5.4518047961	-6.0507451581
H27	-1.4528680990	6.5957727739	-6.0284314343
H28	-1.2349939973	4.9890714499	-6.7318309576
C28	0.2512451324	5.0772433182	-4.4045894787
H29	0.5923769201	6.1184300344	-4.4168350596
H30	0.6031633662	4.6194802163	-3.4765740547
H31	0.7450330385	4.5577074793	-5.2306437448
C31	-2.5317958601	6.0810217962	-0.9609583069
N32	-2.0368594997	5.9237073107	0.3055990495
O33	-3.4731208839	6.7956099688	-1.2614361247
H34	-1.2761761905	5.2573535816	0.4159399335
C35	-3.3272742834	7.5199206173	3.9865536978
C36	-2.1713651051	6.7451064508	3.8950341431
C37	-1.7682595552	6.2398850983	2.6660875815
C38	-2.5171705104	6.4952025705	1.5005725530
C39	-3.6706984409	7.2786433596	1.6035197801
C40	-4.0689019302	7.7849081157	2.8409643935
H41	-3.6369273864	7.9121186075	4.9477801959
H42	-1.5766689091	6.5350401854	4.7789759832
O43	-0.6381223459	5.4782464872	2.5036447905
H44	-4.2411842105	7.4833535762	0.7111541571
H45	-4.9665627942	8.3886683779	2.9000528113
H46	-1.5682870119	-2.3622037321	0.8078318318
H47	-0.2465781353	5.2771497319	3.3590479248



2312.810924585 hartrees

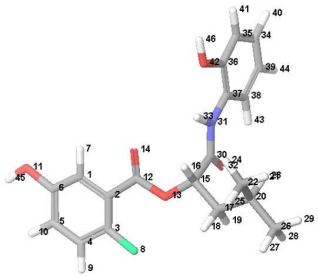
Ester analog—
Input geometry:

		angstroms	
atom	x	y	z
C1	-3.0514090000	-0.0750770000	2.3447460000
C2	-3.8358280000	0.6064140000	1.3829380000
C3	-4.7337610000	-0.1506030000	0.5807290000
C4	-4.8329240000	-1.5454880000	0.7540180000
C5	-4.0486610000	-2.2069730000	1.7159960000
C6	-3.1557970000	-1.4681350000	2.5123930000
H7	-2.3597580000	0.4753770000	2.9675390000
F8	-5.5108090000	0.4226790000	-0.3713290000
H10	-5.5168670000	-2.1117430000	0.1385430000
H11	-4.1414660000	-3.2779260000	1.8301420000
O11	-2.3871880000	-2.0928630000	3.4487260000
C12	-3.6639860000	2.0871900000	1.2713730000
O13	-4.4478450000	2.6627400000	0.3325220000
O14	-2.8766700000	2.7293230000	1.9745530000
C16	-4.4515290000	4.0762380000	0.1140470000
H18	-3.4184460000	4.4175360000	0.0230150000
C19	-5.1826510000	4.3224030000	-1.2268080000
H20	-4.7086330000	3.7156480000	-1.9993110000
H21	-6.1996720000	3.9363770000	-1.1378450000
C22	-5.2448760000	5.7915090000	-1.7112620000
H24	-5.7212840000	6.3973260000	-0.9387280000
C25	-3.8517840000	6.3852080000	-1.9817810000
H26	-3.9267490000	7.4005210000	-2.3730170000
H27	-3.2502050000	6.4434970000	-1.0748520000
H28	-3.2989900000	5.7922310000	-2.7113350000
C28	-6.1234450000	5.9061910000	-2.9666880000
H29	-5.7102360000	5.3330830000	-3.7977650000
H30	-7.1324520000	5.5369080000	-2.7790110000
H31	-6.2152380000	6.9430590000	-3.2928030000
C31	-5.1423650000	4.7890810000	1.2971100000
N32	-4.4551400000	5.7971400000	1.8546820000
O33	-6.2527370000	4.4059010000	1.6766890000
H34	-3.5736040000	6.0320920000	1.4160170000
C35	-5.2921500000	8.5399360000	4.9795650000
C36	-4.2126460000	8.7367530000	4.0975150000
C37	-3.9642460000	7.8050350000	3.0703790000
C38	-4.7972700000	6.6758860000	2.9145050000
C39	-5.8761900000	6.4779830000	3.8099790000
C40	-6.1208300000	7.4105640000	4.8369900000
H41	-5.4816850000	9.2541640000	5.7688970000
H42	-3.5815140000	9.6058540000	4.2198680000
O43	-2.9131530000	7.9888160000	2.2152730000
H44	-6.5253930000	5.6189480000	3.7385910000
H45	-6.9458370000	7.2567080000	5.5190900000
H46	-2.5300060000	-3.0345290000	3.4851780000
H47	-2.4189920000	8.7805180000	2.4040680000

final geometry:

		angstroms	
atom	x	y	z
C1	-3.0048080709	0.2169627682	2.3290560138
C2	-3.7891876906	0.7385008320	1.2911303878
C3	-4.6169914976	-0.1435428398	0.5852976509

C4	-4.6767570392	-1.4914499341	0.9135903467
C5	-3.9017620583	-1.9883910873	1.9582969128
C6	-3.0575491886	-1.1311642008	2.6673544677
H7	-2.3533753759	0.8857295370	2.8754184276
F8	-5.3724945890	0.2742848204	-0.4515099020
H10	-5.3309014891	-2.1400793728	0.3445722044
H11	-3.9552617978	-3.0419451885	2.2149806893
O11	-2.2642875095	-1.5540557576	3.7011437259
C12	-3.6652456270	2.2101113124	1.0511625164
O13	-4.5878722588	2.6953924612	0.2059821573
O14	-2.8114102774	2.8949538781	1.5744247643
C16	-4.5469476738	4.1244880145	-0.0149075925
H18	-3.5000293520	4.4160854751	-0.1072275090
C19	-5.3399259120	4.3616843646	-1.3029670620
H20	-4.9131691955	3.7180185088	-2.0798961617
H21	-6.3611615141	4.0156277658	-1.1231069613
C22	-5.3686798648	5.8239563055	-1.7933367204
H24	-5.7413281434	6.4559786980	-0.9776315707
C25	-3.9786866412	6.3393970234	-2.1919677062
H26	-4.0377555047	7.3696285961	-2.5540288517
H27	-3.2728264575	6.3296793742	-1.3565013611
H28	-3.5553184771	5.7283097890	-2.9963743925
C28	-6.3512459223	5.9608719592	-2.9663952317
H29	-6.0368699396	5.3416441234	-3.8138276896
H30	-7.3582411652	5.6479143544	-2.6779053149
H31	-6.4070539256	6.9965234191	-3.3148347174
C31	-5.2369959137	4.8270733478	1.1712710095
N32	-4.4340789491	5.7025365395	1.8477386875
O33	-6.4055215979	4.6058659352	1.4311841157
H34	-3.4448638327	5.6614551211	1.6420861111
C35	-5.2720675119	8.3365484353	5.0271762834
C36	-3.9807799705	8.2071120271	4.5107801468
C37	-3.7384206436	7.3245413191	3.4660663856
C38	-4.7804754068	6.5474643930	2.9208283998
C39	-6.0696248972	6.6860308115	3.4445588947
C40	-6.3079150050	7.5782425748	4.4906649221
H41	-5.4579747483	9.0269756125	5.8415404493
H42	-3.1625863361	8.7956122064	4.9162072253
O43	-2.4937238770	7.1457470022	2.9046573028
H44	-6.8703632287	6.0990522431	3.0225986963
H45	-7.3129784566	7.6732845019	4.8841040620
H46	-2.3933679416	-2.4957664794	3.8548708186
H47	-1.8274460954	7.6107268648	3.4207967495



2302.088190184 hartrees

Coordination scan of dihedral angle between *m*-hydroxybenzoyl plane and carbonyl plane (step: 10 degree) was performed on these three ligands at B3LYP/6-311G(d,p)+ level of theory. The obtained energy profiles were shown in Figure S3. In contrast to ligand **1g**, ligand **1h** bearing *o*-fluoro substituent exhibited strong preferences for the conformer A (dihedral angle ca. 20°). This is not the case with the ester anolog bearing *o*-fluoro substituent, suggesting that the observed preference in ligand **1h** is mainly due to hydrogen bonding interaction between C-F•••H-N. Electrostatic repulsion between fluoro substituent and carbonyl oxygen would not be a primary cause.

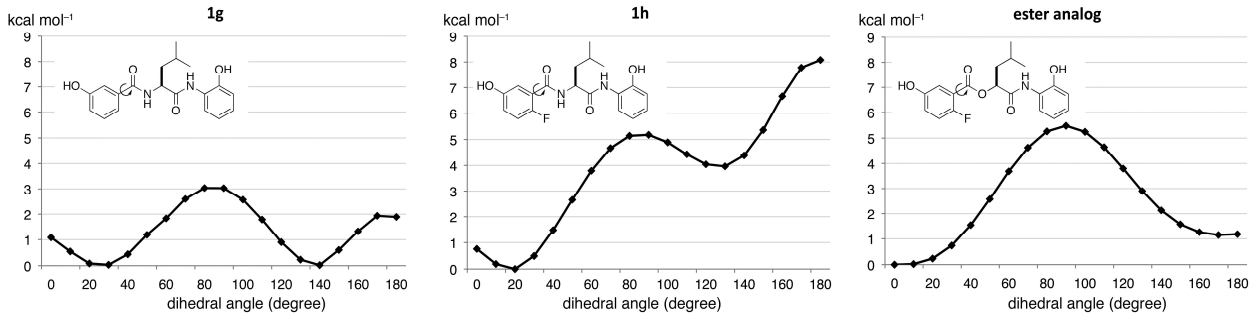


Figure S3. Energy profile of rotational conformers of **1g**, 1**h,** and ester analog.

8. Storage of the Heterogeneous Heterobimetallic Catalyst

The heterogeneous catalyst was prepared in the same procedure as described in the section 2-3, and the catalyst in the eppendorf tube (washed THF was decanted, not doried) was stored under Ar atomosphere at –20 °C. The reaction was performed after aging for the specified period. The eppendorf tube was warmed up to room temperature and used as catalyst.

9. References

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s2 Bridges, A. J.; Lee, A.; Maduakor, E. C.; Schwartz, C. E. *Tetrahedron Lett.* **1992**, *33*, 7495.

s3 Marzi, E.; Gorecka, J.; Schlosser, M. *Synthesis* **2004**, 1609.

s4 B3LYP = Becke-3-Lee-Yang-Parr density functional theory. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

s5 (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Ragué Schleyer, P. *J. Comput. Chem.* **1983**, *4*, 294. (d) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.