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Supporting Information

of

Divergent Synthesis of Chiral Heterocycles via Sequencing of

Enantioselective Three-Component Reactions and One-Pot

Subsequent Cyclizations

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General Information:

Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly dried solvents. Toluene, dichloromethane and 1,2-dichloroethane were distilled over calcium hydride. Powdered 3 Å molecular sieves were flame-dried under vacuum immediately prior to use. All other commercially obtained reagents were used as received unless specifically indicated. Substituted BINOLs were prepared according to literature procedures.^{1,2} BINOL-Zr-MS complex were prepared according to literature procedures.³⁻⁵ All reactions were monitored by thinlayer chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 (at 400 and 100 MHz, respectively) and reported relative to tetramethylsilane (TMS) as internal standard. Data for ¹H NMR spectra are reported as follows: chemical shift (d ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = troplet, q =quartet, m = nultiplet, br = broad. HRMS were acquired using either a Bruker MicroTOF with positive electrospray ionization (ESI) or a Waters Micromass Q-TOF micro Synapt High Definition Mass Spectrometer with field ionization (FI) of chemical ionization (CI). HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump) with Chiralcel AD, OD, IA or IC columns.

Condition Optimization and Experimental Procedures:

Reaction Condition Optimizations for Rh(II)/Zr(IV)-BINOL Co-Catalyzed Three-Component Reaction of Methyl Phenyldiazoacetate **1a**, Benzyl Alcohol **2a** and *N*arylaldimine **3a**.

Table S1. Condition Optimization of Rh(II)/Zr(IV)-BINOL (*in situ* prepared) Co-Catalytic System^a

E	BnOH 2a + Ph COO 1a	HO N Ph 3a OMe	Rh ₂ (OAc) ₄ (1 mol%) Zr(O ^f Bu) ₄ (20 mol%) 5 (40 mol%) ► toluene, rt ► Ph	HO HN Ph COOMe 4a	Y OH OH Sa: X = Y = H Sb: X = H, Y = Br Sc: X = Br, Y = H Sd: X = I, Y = H
	entry	5	yield $(\%)^b$	dr ^c	ee (%) ^d
•	1	5a	60	78:22	52
	2	5b	75	70:30	62
	3	5c	72	80:20	16
	4	5d	80	87:13	80

^{*a*} Unless otherwise noted, all reactions were conducted in 0.6 mmol scale of **3a**, **1a**:**2a**:**3a** = 1.1:1.2:1. See the 'General procedure' for experimental details. ^{*b*} Isolated yield after column chromatography. ^{*c*} Determined by ¹H NMR of crude mixture. ^{*d*} Determined by chiral HPLC, major diastereomer.

	H BnOH 2a + N ₂ Ph Ph COOMe	O N 3a	Rh ₂ (OAc) ₄ (1 mol%) 5d-ZrMS (X mol%) solvent		Ph OOMe		1
entry	Zr(IV):5d	X	solvent	T (°C)	yield (%) ^b	dr ^c	ee (%) ^d
1	1:2	20	CH ₂ Cl ₂	rt	82	86:14	70
2	1:2	20	PhMe	rt	90	90:10	86
3	1:2	10	PhMe	rt	81	90:10	60
4 ^e	1:2	10	PhMe	rt	77	93:7	86
5 ^e	1:1	10	PhMe	rt	70	94:6	94
6 ^e	1:1	10	CH_2Cl_2	rt	85	95:5	85
7 ^e	1:1	10	DCE	rt	90	95:5	87

Table S2. Condition Optimization of Rh(II)/Zr(IV)-5dMS Co-Catalytic System^a

^{*a*} Unless other noted, all reactions were conducted on a 0.1 mmol scale of **3a**, **1a**:**2a**:**3a** = 3:3:1. **2a** was mixed with $Rh_2(OAc)_4$, **5d-ZrMS** complex and **3a** before **1a** was added via a syringe pump. See the Supporting Information for experimental details. ^{*b*} Isolated yield after column chromatography purification. ^{*c*} Determined by ¹H NMR of crude mixture. ^{*d*} Determined by chiral HPLC, major diastereomer. ^{*e*} **2a** was mixed with **1a** and then added to a mixture of $Rh_2(OAc)_4$, **5d-ZrMS** complex and **3a** via a syringe pump. See the 'General procedure' for experimental details.

General procedure for Table S1:

To a suspension of (S)-3,3'-diiodo-1,1'-binaphthalene-2,2'-diol (86 mg, 0.16 mmol) in toluene (4.0 mL) was added $Zr(OtBu)_4$ (31 mg, 0.08 mmol) at room temperature, and the resulting solution was stirred for 30 min. Benzyl alcohol (16 ul, 0.16 mmol) was added to the above solution, which was stirred for an additional 30 min to form Zr(IV) complex. Then aldimine **3a** (118.2 mg, 0.6 mmol) and $Rh_2(OAc)_4$ (2.7 mg, 1 mol%) were added. The mixture was stirred for 5 min, then a mixture of methyl phenyldiazoacetate 1a (116.2 mg, 0.66 mmol) and benzyl alcohol 2a (65 mg, 0.6 mmol) in 2 mL of toluene were added via a syringe pump over 1 h. After completion of the addition, saturated aqueous NaHCO₃ (10 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The organic layers were combined and dried over anhydrous Na₂SO₄. After filtration and concentration under reduced pressure, and the crude product was subjected to ¹H-NMR analysis to determine the diastereoselectivity. The crude product was purified by flash chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1:9) to give 4a (217 mg, 80% yield). The optical purity was determined by HPLC analysis using a chiral Daicel Chirapak AD-H column.

General procedure for Table S2:

Entries 1 – 3:

To a suspension of the (*S*)-3-I-ZrMS catalyst (5d)₂-ZrMS (60 or 120 mg, containing 0.01 or 0.02 mmol Zr) and Rh₂(OAc)₄ (0.4 mg, 1 mol%) in 1 mL of the corresponding solvent was added 2a (4.3 mg, 0.04 mmol) and stirred for 30 min before aldimine 3a (19.7 mg, 0.1 mmol) in 0.5 mL of the corresponding solvent was added and stirred for another 5 min. Then a mixture of methyl phenyldiazoacetate 1a (52.9 mg, 0.3 mmol) and benzyl alcohol 2a (28.1 mg, 0.26 mmol) in 1 mL of the corresponding solvent was added via a syringe pump over 1 h. After completion of the addition, the reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H-NMR analysis for the determination of diastereoselectivity. The crude product was purified by flash chromatography on

silica gel to give **4a**. The optical purity was determined by HPLC analysis using a chiral Daicel Chirapak AD-H column.

Entries 4 – 7:

To a suspension of the (*S*)-3-I-Zr catalyst **5d-ZrMS** (46 mg, containing 0.01 mmol Zr) and Rh₂(OAc)₄ (0.4 mg, 1 mol%) in toluene (1 mL) was added aldimine **3a** (0.1 mmol) in 0.5 mL of toluene at 30 °C. After stirring for 5 min, methyl phenyldiazoacetate **1a** (52.9 mg, 0.3 mmol) and benzyl alcohol **2a** (0.3 mmol) in 1 mL of toluene were added via a syringe pump over 1 h. After completion of the addition, the reaction mixture was further stirred for 30 min. The reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H-NMR analysis for the determination of diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give **4a**. The optical purities were determined by HPLC analysis using a chiral IA column.

General procedure for Table 1:

To a suspension of **5d-ZrMS** (34.5 mg, containing 0.015 mmol Zr) and $Rh_2(OAc)_4$ (0.4 mg, 1 mol%) in 1 mL of toluene was added aldimine **3a** (0.1 mmol) in 0.5 mL of toluene at 30 °C. After stirring for 5 min, methyl phenyldiazoacetate **1a** (52.9 mg, 0.3 mmol) and alcohol **2** (0.3 mmol) in 1 mL of toluene were added via a syringe pump over 1 h. After completion of the addition, the reaction mixture was further stirred for 30 min. The reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H-NMR analysis for the determination of diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give **4**. The optical purities were determined by HPLC analysis using a chiral IA column.

Synthesis of α-Hydroxyl-β-Amino Ester and Determination of the Absolute Configuration of 4a:



Scheme S1

Preparation of Compound 4a-DE1 (Scheme S1):

A mixture of compound **4a** (0.47 g, 1 mmol), CH_3I (5.7 g, 40 mmol) and K_2CO_3 (0.8 g) in acetone (12.5 mL) was stirred at room temperature for 8 h. Aqueous NH_4CI was added to quench the reaction. After a usual work up, the free amine product was obtained in 90% yield.

To a solution of PhI(OAc)₂ (300 mg, 0.9 mmol) in methanol (3 mL) was added a solution of the above free amine product (100 mg, 0.21 mmol) in CH₂Cl₂ (0.5 mL) and methanol (1 mL) over 30 min at room temperature. The reaction mixture was stirred for additional 30 min, and followed by the addition of 1 M HCl (10 mL). A white precipitate was formed immediately and then slowly dissolved to afford a yellow solution in 90 min. The organic layer was separated and the aqueous layer was subsequently extracted with CH_2Cl_2 (2 ×15 mL). The combined organic layer was back extracted with 10 mL of 0.1 M HCl. To the combined aqueous layer was added CH₂Cl₂ (10 mL). To this biphasic mixture was added (Boc)₂O (96 µL, 0.42 mmol) with vigorous stirring, and followed by the addition of solid Na₂CO₃ portion wise until the pH was adjusted to 10-11. This mixture was stirred for 90 min with occasional addition of Na_2CO_3 to maintain the pH = 10–11. The two layers were separated and the aqueous layer was further extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layer was dried over anhydrous MgSO₄, filtered and concentrated. The crude product was purified by flash chromatography on silica gel (eluent: EtOAc/light petroleum =1:30) to give **4a-DE1** {42 mg, 40%, $[\alpha]_D^{20} = +12.0^{\circ}$ (c = 0.5, EtOAc)}.

Preparation of Compound 4a-DE2 (Scheme S1):

To a solution of **4a-DE1** (30 mg, 0.065 mmol) in EtOH (2 ml) was added 10% Pd on carbon (100mg). The reaction mixture was charged with an atmosphere of H2 and stirred at r.t. for 24 h. The catalyst was filtered off, and the solvent was removed under reduced pressure. The crudeproduct was purified by flash chromatography on silica gel eluting with EtOAc:light petroleum =1:12 to give α -hydroxyl- β -amino ester **4a-DE2** (20 mg, 83%).



Scheme S2

Preparation of SC2 from compound SC1 (Scheme S2):

To the solution of compound **SC1** (0.1 mmol) in 2.0 mL of methanol was added 0.6 mL of 3 N HCl in 2.0 mL of 1,4-dioxane. The mixture was stirred at room temperature for 2 h, and was then concentrated. To the resulting residue was added 10 mL of saturated aqueous NaHCO₃. The aqueous phase was extracted with EtOAc ($3 \times 10 \text{ mL}$), and the combined organic phase was dried over anhydrous MgSO₄. After filtration, EtOAc was removed to give free amine as colorless oil. The free amine was dissolved in 3.0 mL of menthol containing 10% Et₃N at 50 °C, and 2 equiv. (Boc)₂O was added to the solution with stirring. The crude product was purified by flash chromatography on silica gel (eluent: EtOAc/light petroleum=1:30) to give **SC2** (31 mg, 68% yield in two steps).⁶

Determination of the absolute configuration of 4a

The absolute configuration of the three-component product 4a was assigned as (2S, 3S)

by comparison of the optical rotation of **4a-DE1** $\{[\alpha]_D^{20} = +12.0^\circ (c = 0.5, \text{EtOAc})\}$ (Scheme S1) and compound **SC2** $\{[\alpha]_D^{20} = -14.1^\circ (c = 0.5, \text{EtOAc})\}$, which was synthesized from known compound **SC1** as previously reported (Scheme S2).⁶ The absolute configuration of **SC1** has been determined to be (R,R,R) by single crystal Xray analysis.

General procedure for the sequencing of three-component reaction and subsequent cyclization for the synthesis of chiral morpholines (Table 2):

To a suspension of **5d-ZrMS** (34.5 mg, containing 0.015 mmol Zr) and Rh₂(OAc)₄ (0.4 mg, 1 mol%) in CH₂Cl₂ (1 mL) was added aldimine **3a** (0.1 mmol) in 0.5 mL of CH₂Cl₂ at 30 °C. After stirring for 5 min, methyl phenyldiazoacetate **1a** (52.9 mg, 0.3 mmol) and bromoethanol **2h** (21.6 μ L, 0.3 mmol) in 1 mL of CH₂Cl₂ were added via a syringe pump over 1 h. After completion of the addition, the reaction mixture was further stirred for 30 min. Triethylamine (0.5 mmol) was added in one portion, and the reaction mixture was further stirred at 30 to 40 °C for about 5 hours, when the reaction was finished as monitored by TLC. The reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H-NMR analysis for the determination of diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give **6**. The optical purities were determined by HPLC analysis using a chiral IA column.

Sequencing transformation for the preparation of morpholin-3-one 7.

To a suspension of the air-stable **5d-ZrMS** (20 mol%) in 1 mL of CHCl₃ was added $Rh_2(OAc)_4$ (1 mol%) and *N*-aryl aldimine (**3e**) (0.1 mmol) at 0 °C. The mixture was stirred for 5 min before a mixture of methyl phenyl diazoacetate (**1a**) (0.3 mmol) and 2-phthalimidoethanol (**2i**) (0.3 mmol) in 1 mL of CHCl₃ were added at 0 °C via a syringe pump within 1 h. After completion of the addition, the reaction mixture was further stirred for 3 h at 0 °C. EtOH (2 mL) and hydrazine hydrate (6.8 eq) were sequentially added. The reaction mixture was then heated to 50 °C and reacted

overnight. When the reaction was finished as monitored by TLC, the reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H NMR analysis to determine the diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give morpholin-3-one **7** (62% yield, >95:5 dr, 97% ee). The enantiomeric excess was determined by chiral HPLC analysis.

Sequencing transformation for the preparation of 2,2-disubstituted morpholine 8.

To a suspension of the air-stable **5d-ZrMS** (20 mol%) in 1 mL of CHCl₃ was added Rh₂(OAc)₄ (1 mol%) and *N*-arylaldimine **3a** (0.1 mmol) at 0 °C. The mixture was stirred for 5 min before a mixture of methyl phenyl diazoacetate (**1a**) (0.3 mmol) and (*E*)-ethyl 4-hydroxybut-2-enoate (**2j**) (0.3 mmol) in 1 mL of CHCl₃ were added at 0 °C via a syringe pump within 1 h. After completion of the addition, the reaction mixture was further stirred for 3 h at 0 °C. AlCl₃ (0.2 mmol) was added in one portion, and the reaction mixture was further stirred by TLC, the reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H NMR analysis to determine the diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give compound **8** (51% yield, 95:5 dr, 94% ee). The enantiomeric excess was determined by chiral HPLC analysis.

Sequencing transformation for the preparation of γ-lactam 10.

To a suspension of (*R*)-**5d-ZrMS** (20 mol%) in 1 mL of CHCl₃ was added $Rh_2(OAc)_4$ (2–3mol%) and *N*-aryl aldimine (**3e**) (0.1 mmol) at 0 °C. The mixture was stirred for 5 min before a mixture of dimethyl 2-diazosuccinate (**1e**) (0.3 mmol) and benzyl alcohol (**2a**) (0.3 mmol) in 1 mL of CHCl₃ were added at 0 °C via a syringe pump within 1 h. After completion of the addition, the reaction mixture was further stirred for 3 h at 0 °C. The reaction mixture was then warmed to room temperature and TFA (5 mol%) was added and reacted for 5 h. The reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H NMR

analysis to determine the diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give γ -Lactam **10** (65% yield, >95:5 dr, 90% ee). The enantiomeric excess was determined by chiral HPLC analysis.

Sequencing transformation for the preparation of 1,4-dioxine compound 12.

To a suspension of (*R*)-**5d-ZrMS** (6 mol%) in 1 mL of CH_2Cl_2 was added $Rh_2(OAc)_4$ (1 mol%) and 4-bromobenzaldehyde (**11**) (0.1 mmol) at room temperature. The mixture was stirred for 3 min before a mixture of methyl phenyl diazoacetate (**1a**) (0.2 mmol) and propargyl alcohol (**2k**) (0.2 mmol) in 1 mL of CH_2Cl_2 were added at 0 °C via a syringe pump within 1 h. After completion of the addition, the reaction mixture was further stirred for 3 h at 0 °C. Then 20 mol% PtCl₂ was added to the reaction mixture and stirred for 48h at room temperature. When the reaction was finished as monitored by TLC, the reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H NMR analysis to determine the diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give product **12** (56% yield, 94:6 dr, 97% ee). The enantiomeric excess was determined by chiral HPLC analysis.

Sequencing transformation for the preparation of 2*H*-pyran compound 14.

To a suspension of (*R*)-5d-ZrMS (6 mol%) in 1 mL of CH_2Cl_2 was added $Rh_2(OAc)_4$ (1 mol%) and cinnamaldehyde (13) (0.1 mmol) at room temperature. The mixture was stirred for 3 min before a mixture of methyl phenyl diazoacetate (1a) (0.2 mmol) and allylic alcohol (2d) (0.2 mmol) in 1 mL of CH_2Cl_2 were added at 0 °C via a syringe pump within 1 h. After completion of the addition, the reaction mixture was further stirred for 3 h at 0 °C. Then 8 mol% Grubbs II reagent was added to the reaction mixture and stirred for 48 h at 40 °C. When the reaction was finished as monitored by TLC, the reaction mixture was filtered through a cotton plug, concentrated under reduced pressure and subjected to ¹H NMR analysis to determine the diastereoselectivity. The crude product was purified by flash chromatography on silica gel to give product 14 (70% yield, 95:5 dr, 99% ee). The enantiomeric excess

was determined by chiral HPLC analysis.

X-Ray Crystal Analysis Data

X-ray diffraction parameters and data for *rac*-6a (CCDC: 975762)



Bond precision: $C-C = 0.003$.0035	5 A	W	avelength=0.71073	
Cell:	a=9.9379	(6)	b=10	.0008(6)	c=10.82	276(6)
	alpha=96	.918(2)	beta	=104.753(2)	gamma=9	99.920(2)
Temperature:	296 K				-	
		Calculate	d			Reported
Volume		1009.72(1	0)			1009.72(10)
Space group		P -1				P-1
Hall group		-P 1				?
Moiety formu	ıla	C24 H23 N	04			?
Sum formula		C24 H23 N	04			C24 H23 N O4
Mr		389.43				389.43
Dx,g cm-3		1.281				1.281
Z		2				2
Mu (mm-1)		0.087				0.087
F000		412.0				412.0
F000'		412.20				
h,k,lmax		11,11,12				11,11,12
Nref		3551				3528
Tmin,Tmax		0.973,0.9	81			0.964,0.981
Tmin'		0.964				
Correction m	nethod= M	ULTI-SCAN				
Data complet	eness= 0	.994		Theta(max) =	25.000	
R(reflection	s)= 0.04	50(2240)		wR2(refle	ctions)=	= 0.1226(3528)
S = 1.008		Npar=	262			

X-ray diffraction parameters and data for *rac-9* (CCDC: 975764)



Bond precision: $C-C = 0.003$		= 0.0036 A	Wavelength=0.71073
Cell:	a=9.1316(14)	b=11.5658(17)	c=12.884(2)
	alpha=87.471(5)) beta=84.937(5)	gamma=78.960(5)
Temperature	:296 K		
	Calcul	ated	Reported
Volume	1329.8	(4)	1329.9(3)
Space group	P -1		P-1
Hall group	-P 1		?
Moiety formu	ıla C26 H2	5 N 06, C2 O	?
Sum formula	C28 H2	5 N 07	C28 H25 N O7
Mr	487.49		487.49
Dx,g cm-3	1.217		1.217
Z	2		2
Mu (mm-1)	0.088		0.088
F000	512.0		512.0
F000'	512.28		
h,k,lmax	10,13,	15	10,13,15
Nref	4696		4654
Tmin,Tmax	0.975,	0.990	0.961,0.990
Tmin'	0.960		
Correction r	nethod= MULTI-SC	CAN	
Data complet	eness= 0.991	Theta(max)=	= 25.010
R(reflection	ns) = 0.0476(320)	04) wR2(ref	lections)= 0.1464(4654)
S = 1.020	Npa	r= 325	

X-ray diffraction parameters and data for *rac*-10 (CCDC: 975763)



Sond precision: $C-C = 0.0048$		0.0048 A	Wavelength=0.71073
Cell:	a=9.6542(8)	b=10.7705(9)	c=12.1323(9)
	alpha=87.694(2)	beta=71.902(2)	gamma=69.127(2)
Temperature:	296 K		
	Calcula	ted	Reported
Volume	1116.89	(16)	1116.89(16)
Space group	P -1		P-1
Hall group	-P 1		?
Moiety formu	ıla C25 H22	Br N 05	?
Sum formula	C25 H22	Br N O5	C25 H22 Br N 05
Mr	496.34		496.35
Dx,g cm-3	1.476		1.476
Z	2		2
Mu (mm-1)	1.877		1.877
F000	508.0		508.0
F000'	507.66		
h,k,lmax	11,12,1	4	11,12,14
Nref	3942		3902
Tmin,Tmax	0.459,0	.713	0.506,0.729
Tmin'	0.450		
Correction m	nethod= MULTI-SCA	AN	
Data complet	ceness= 0.990	Theta(max)=	25.010
R(reflection	ns)= 0.0318(3380)) wR2(refl	ections)= 0.0887(3902)
S = 1.081	Npar	= 289	

Characterization Data of Products:



Compound **4a**: yield 70%; 94% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: $t_{major} = 13.56$ min, $t_{minor} = 32.54$ min); ¹H NMR (300 MHz, CDCl₃) δ 7.54 (m, 2H), 7.27–7.53 (m, 8H), 7.18 (m, 3H), 7.08 (m, 2H), 6.63–6.81 (m, 4H), 5.93 (br, 1H), 5.20 (s, 1H), 4.71(br, 1H), 4.58 (d, J = 11.8 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.8 Hz, 1H), 4.71(br, 1H), 4.58 (d, J = 11.8 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.8 Hz, 1H), 3.74 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.6, 145.7, 138.1, 137.8, 134.7, 134.4, 129.1, 128.6, 128.4, 128.2, 127.7, 127.4, 127.3, 127.2, 127.0, 120.7, 119.6, 116.4, 114.5, 87.7, 67.8, 65.3, 52.2; HRMS: calcd for C₂₉H₂₇NO₄ (M+Na)⁺ 454.2013; found: 454.2013.

Compound **4a-DE1**: yield 40% (3 steps), ¹H NMR (300 MHz, CDCl₃) δ 7.33–7.57 (m, 10H), 7.22 (m, 5H), 5.54 (d, J = 10.4 Hz, 1H), 5.35 (d, J = 10.4 Hz, 1H), 4.73 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 3.63 (s, 3H), 1.31 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 171.0, 154.6, 138.4, 135.5, 128.9, 128.3(overlap), 128.0(overlap), 127.6, 127.4, 127.2, 87.5, 79.5, 68.1, 61.5, 51.9, 28.3; HRMS: calcd for C₂₈H₃₁NO₅ (M+Na)⁺ 484.2094; found: 484.2083. [α]²⁰_D = + 12.0° (c = 0.5, EtOAc).



Compound **4a-DE2**, yield 83% from **9**; ¹H NMR (300 MHz, CDCl₃) δ 7.78 (m, 2H), 7.29–7.41 (m, 8H), 5.64 (d, J = 9.8Hz, 1H), 5.46 (d, J = 9.8Hz, 1H), 3.86 (s, 3H), 3.61 (s, 3H), 1.22 (s, 9H); ¹³C NMR (75MHz, CDCl₃) δ 173.3, 155.0, 138.3(overlap),

138.0, 128.2, 128.0, 126.6, 81.1, 79.5, 59.2, 53.3, 28.1; HRMS: calcd for C₂₁H₂₅NO₅ (M+Na)⁺ 394.1625; found: 394.1638. $[\alpha]_D^{20} = -42.1^{\circ}(c = 0.5, \text{EtOAc}).$

Compound **SC2**: $[\alpha]_D^{20} = -14.1^{\circ}(c = 0.5, \text{ EtOAc}).$



Compound **4b**: yield 66%; 96% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm; Retention time: $t_{major} = 19.82$ min, $t_{minor} = 9.62$ min); ¹H NMR (300 MHz, CDCl₃) δ 6.92–7.38 (m, 10H), 6.46–6.71 (m, 4H), 5.81 (s, 1H), 4.99 (br, 1H), 4.41 (br, 1H), 3.76 (s, 3H), 3.33–3.76 (m, 2H), 1.61 (m, 2H), 1.39 (m, 2H), 0.91(m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.8, 146.5, 137.9, 135.3, 134.3, 129.5, 129.0, 128.6, 128.2, 128.0, 127.6, 127.3, 127.2, 120.7, 120.3, 117.7, 114.7, 87.3, 65.6, 65.4, 52.1, 32.0, 19.2, 13.9; HRMS: calcd for C₂₆H₂₉NO₄ (M+Na)⁺ 442.1989; found: 442.1982.



Compound 4c: yield 52%; 95% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm; Retention time: t_{major} = 20.75 min, t_{minor} = 8.38 min); ¹H NMR (300 MHz, CDCl₃) δ 7.27–7.38 (m, 5H), 7.14 (m, 3H), 6.99 (m, 2H), 6.43–6.61 (m, 4H), 5.88 (br, 1H), 5.12 (s, 1H), 4.69(br, 1H), 3.93 (m, 1H), 3.71 (s, 3H), 1.22 (d, *J* = 6.1 Hz, 3H), 1.02 (d, *J* = 6.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.6, 145.7, 138.1, 136.4, 134.5, 129.2, 128.9, 128.2,

127.4, 127.2, 127.1, 120.9, 119.4, 116.4, 114.6, 86.9, 68.8, 64.5, 51.9, 23.8, 23.1; HRMS: calcd for C₂₅H₂₇NO₄ (M+Na)⁺ 428.1832; found: 428.1821.



Compound **4d**, yield 82%, 94% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm; Retention time: $t_{\text{major}} = 21.91$ min, $t_{\text{minor}} = 10.18$ min); ¹H NMR (300 MHz, CDCl₃) δ 6.97–7.42 (m, 10H), 6.48-6.89 (m, 4H), 5.89 (m, 1H), 5.70 (s, 1H), 5.36 (m, 1H), 5.19 (m, 1H), 5.02(br, 1H), 4.52 (br, 1H), 3.95–4.03 (m, 2H), 3.75 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.6, 146.3, 137.6, 134.9, 134.2, 129.1, 128.4, 128.3, 127.7, 127.4, 127.2, 120.8, 120.3, 117.57, 115.9, 114.6, 87.6, 66.9, 65.5, 52.2; HRMS: calcd for C₂₅H₂₅NO₄ (M+Na)⁺ 426.1676; found: 426.1685.



Compound **4e**: yield 89%, 93% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.5 mL/min; hexane / EtOH = 20 : 1; 254 nm; Retention time: $t_{\text{major}} = 40.35$ min, and $t_{\text{minor}} = 27.67$ min); ¹H NMR (400 MHz, CDCl₃) δ 7.44 (dd, J = 7.7, 1.7 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.15 (m, 3H), 7.08 (s, 2H), 6.71 (d, J = 6.7 Hz, 1H), 6.62 – 6.51 (m, 2H), 6.42 (d, J = 6.8 Hz, 1H), 5.13 (s, 1H), 4.99 (s, 1H), 3.66 (s, 3H), 3.56 – 3.24 (m, 4H), 1.46 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.39, 156.37, 145.55, 138.28, 135.05, 134.87, 128.96, 128.61, 128.50, 127.91, 127.59, 127.46, 120.70, 119.07, 115.34, 114.69, 87.54, 79.55, 65.16, 65.02, 52.17, 40.91, 28.52. HRMS: calcd for C₂₉H₃₄N₂O₆ (M+Na)⁺ 529.2315; found: 529.2341.



Compound **4f**: yield 83%, 92% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / EtOH = 30 : 1; 254 nm; Retention time: $t_{major} = 45.77$ min, $t_{minor} = 26.14$ min); ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 6.4 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.17 – 7.10 (m, 3H), 7.06 (s, 2H), 6.73 (dd, J = 7.4, 1.2 Hz, 1H), 6.62 – 6.49 (m, 2H), 6.41 (d, J = 7.1 Hz, 1H), 5.04 (s, 1H), 5.00 (s, 1H), 3.68 (s, 3H), 3.49 – 3.26 (m, 4H), 1.74 (m, 2H), 1.45 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 171.47, 156.40, 145.29, 138.29, 135.49, 128.92, 128.72, 128.42, 127.87, 127.54, 127.44, 120.78, 118.73, 114.91, 87.44, 79.45, 65.36, 63.21, 52.07, 37.73, 29.94, 28.50. HRMS: calcd for C₃₀H₃₆N₂O₆ (M+Na)⁺ 543.2471; found: 543.2499.



Compound **4g**: yield 83%, 95% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / EtOH = 20 : 1; 254 nm; Retention time: t_{major} = 33.60 min, t_{minor} = 20.20 min); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, J = 7.1, 2.1 Hz, 2H), 7.42 (s, 1H), 7.33 (m, 3H), 7.19 – 7.07 (m, 3H), 7.02 (d, J = 6.6 Hz, 2H), 6.67 (d, J = 7.4 Hz, 1H), 6.58 (m, 2H), 6.41 (d, J = 7.5 Hz, 1H), 6.38 – 6.32 (m, 1H), 6.29 (d, J = 3.0 Hz, 1H), 5.58 (s, 1H), 4.94 (s, 1H), 4.60 (d, J = 12.3 Hz, 1H), 4.45 (s, 1H), 4.42 (d, J = 12.3 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.36, 151.60, 146.48, 142.60, 137.91, 134.90, 134.23, 129.11, 128.63, 128.53, 127.92, 127.47, 127.35, 120.75, 120.43, 117.65, 114.65, 110.31, 108.70, 87.92, 65.96, 60.95, 52.24. HRMS: calcd for C₂₇H₂₅NO₅ (M+Na)⁺ 466.1630; found: 466.1615.



Compound **6a**: yield 63%; 94% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.6 mL/min; hexane / isopropanol = 18 : 1; 254 nm, Retention time: t_{major} = 17.26 min, and t_{minor} = 15.64 min); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.42 (m, 3H), 7.33 – 7.22 (m, 3H), 7.03 (td, J = 7.8, 1.4 Hz, 1H), 6.96 (dd, J = 8.1, 1.4 Hz, 1H), 6.61 – 6.49 (m, 2H), 6.06 (dd, J = 7.9, 1.2 Hz, 1H), 4.85 (s, 1H), 4.29 – 4.16 (m, 2H), 3.70 – 3.61 (m, 1H), 3.27 (s, 3H), 2.41 (d, J = 11.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.64, 151.86, 137.17, 135.44, 133.93, 130.97, 129.32, 128.64, 127.99, 127.55, 126.90, 126.66, 125.04, 119.29, 114.33, 83.02, 65.01, 62.86, 52.24, 44.79; HRMS (ESI) calcd for C₂₄H₂₃NO₄ (M+Na)⁺412.1519, found 412.1563.



Chemical Formula: C25H25NO4

Compound **6b**: yield 69%; 93% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.5 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: $t_{major} = 22.49$ min, and $t_{minor} = 20.69$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 6.9 Hz, 1H), 7.18 (s, 2H), 6.94 (m, 3H), 6.84 (d, J = 8.0 Hz, 1H), 6.54 – 6.40 (m, 2H), 5.99 (d, J = 7.8 Hz, 1H), 4.71 (s, 1H), 4.20 – 4.05 (m, 2H), 3.55 (m, 1H), 3.17 (s, 3H), 2.30 – 2.27 (d, J = ? Hz, 1H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 151.89, 137.57, 137.27, 135.54, 130.91, 130.82, 129.30, 128.59, 128.26, 126.83, 126.68, 125.17, 119.26, 114.24, 83.11, 64.68, 62.86, 52.24, 44.77, 21.15;HRMS (ESI) calcd for C₂₅H₂₅NO₄ (M+Na)⁺ 426.1676, found 426.1657.



Compound **6c**: yield 71%; 85% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 26.96 min, and t_{minor} = 14.79 min.); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.7 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.30 (s, 1H), 7.02 (t, J = 7.7 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.77 (d, J = 8.6 Hz, 2H), 6.55 (dd, J = 15.8, 8.1 Hz, 2H), 6.08 (d, J = 7.8 Hz, 1H), 4.77 (s, 1H), 4.24 – 4.14 (m, 2H), 3.80 (s, 3H), 3.74 (m, 1/2H), 3.62 (td, J = 11.4, 4.4 Hz, 1H), 3.27 (s, 3H), 2.37 (d, J = 11.8 Hz, 1H), 1.85 (m, 1/2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.64, 159.11, 151.85, 137.15, 135.42, 132.14, 129.24, 128.53, 126.82, 126.60, 126.01, 125.15, 119.22, 114.17, 112.76, 83.11, 67.92, 64.29, 62.79, 55.05, 52.23, 44.70, 25.56; HRMS (ESI) calcd for C₂₅H₂₅NO₅ (M+Na)+442.1625, found 442.1652.



Compound **6d**: yield 83%; 92% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 15.55 min, and t_{minor} = 12.37 min.); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.7 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.37 (s, 2H), 7.08 – 7.01 (m, 1H), 6.96 (dd, J = 11.5, 4.9 Hz, 3H), 6.57 (td, J = 7.8, 1.5 Hz, 1H), 6.53 (s, 1H), 6.09 (dd, J = 7.9, 1.1 Hz, 1H), 4.83 (s, 1H), 4.26 – 4.17 (m, 2H), 3.58 (ddd, J = 12.0, 9.6, 5.5 Hz, 1H), 3.31 (s, 3H), 2.44 (d, J = 11.9 Hz, 1H); ¹³CNMR (100 MHz, CDCl₃) δ 170.54, 163.71, 161.25, 151.83, 136.95, 135.26, 132.63, 132.56, 129.86, 129.82,

129.33, 128.72, 127.03, 126.58, 124.81, 119.40, 114.56, 114.47, 114.35, 83.04, 64.47, 62.85, 52.33, 44.86; HRMS (ESI) calcd for $C_{24}H_{22}FNO_4$ (M+Na)⁺430.1425, found 430.1462.



Compound **6e**: yield 63%; 94% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 18.08 min, and t_{minor} = 12.50 min.); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.37 (d, J = 8.2 Hz, 2H), 7.24 (s, 1H), 7.03 (t, J = 7.7 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.57 (t, J = 7.6 Hz, 1H), 6.45 (s, 1H), 6.09 (d, J = 7.8 Hz, 1H), 4.79 (s, 1H), 4.25 – 4.15 (m, 2H), 3.74 (t, J = 6.2 Hz, 1/2H), 3.58 – 3.49 (m, 1H), 3.30 (s, 3H), 2.42 (d, J = 11.9 Hz, 1H), 1.85 (t, J = 6.3 Hz, 1/2H); ¹³C NMR (126 MHz, DMSO) δ 170.43, 151.67, 136.75, 135.10, 132.84, 132.45, 130.67, 129.32, 128.73, 127.02, 126.50, 124.69, 122.32, 119.47, 114.49, 82.85, 67.93, 62.79, 52.40, 44.81, 25.57; HRMS (ESI) calcd for C₂₄H₂₂BrNO₄ (M+Na)⁺ 490.0624, found 490.0612.



Compound **6f**: yield 80%; 93% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 16.60 min, and t_{minor} = 12.43 min.); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.32 (s, 2H), 7.24 (d, *J* = 8.7 Hz, 2H),

7.08 – 7.01 (m, 1H), 6.96 (dd, J = 8.0, 1.3 Hz, 1H), 6.59 (td, J = 7.7, 1.3 Hz, 1H), 6.48 (s, 1H), 6.11 (d, J = 7.9 Hz, 1H), 4.82 (s, 1H), 4.28 – 4.16 (m, 2H), 3.56 (ddd, J = 12.1, 9.2, 5.9 Hz, 1H), 3.33 (s, 3H), 2.45 (d, J = 11.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.48, 151.76, 136.85, 135.19, 134.04, 132.45, 132.20, 129.35, 128.76, 127.75, 127.07, 126.56, 124.75, 119.49, 114.53, 82.97, 62.85, 52.40; HRMS (ESI) calcd for C₂₄H₂₃NO₄ (M+Na)⁺ 446.1130, found 446.1137.



Compound **6g**: yield 65%; 92% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 37.63 min, and t_{minor} = 18.42 min.); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.6 Hz, 3H), 7.43 (t, J = 7.3 Hz, 1H), 7.03 (t, J = 7.7 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.55 (t, J = 7.6 Hz, 1H), 6.40 (s, 1H), 6.07 (d, J = 7.7 Hz, 1H), 4.94 (s, 1H), 4.28 – 4.20 (m, 2H), 3.74 (t, J = 6.2 Hz, 1/2H), 3.53 – 3.42 (m, 1H), 3.34 (s, 3H), 2.54 (d, J = 11.9 Hz, 1H), 1.85 (t, J = 6.4 Hz, 1/2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.25, 151.53, 147.42, 141.41, 136.38, 134.82, 131.54, 129.36, 128.96, 127.26, 126.40, 123.98, 122.47, 119.72, 114.90, 82.80, 67.93, 62.88, 52.53, 25.57; HRMS (ESI) calcd for C₂₄H₂₂N₂O₆ (M+Na)⁺ 457.1370, found 457.1391.



Compound **6h**: yield 58%; 90% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / Ethanol = 10 : 1; 254 nm, Retention time: $t_{major} = 10.31$

min, and $t_{\text{minor}} = 8.84 \text{ min.}$; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 7.6 Hz, 2H), 7.51 (m, 7H), 7.10 – 7.02 (m, 1H), 6.97 (dd, J = 8.1, 1.4 Hz, 1H), 6.57 (td, J = 7.7, 1.5 Hz, 1H), 6.44 (s, 1H), 6.06 (dd, J = 7.9, 1.0 Hz, 1H), 4.92 (s, 1H), 4.29 – 4.22 (m, 2H), 3.55 (ddd, J = 12.1, 8.6, 6.3 Hz, 1H), 3.32 (s, 3H), 2.49 (d, J = 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.43, 151.70, 137.94, 136.69, 135.05, 131.13, 129.40, 128.86, 127.15, 126.53, 124.51 , 124.42, 124.38, 119.58, 114.69, 82.87, 62.88, 52.44; HRMS (ESI) calcd for C₂₅H₂₂F₃NO₄ (M+Na)⁺480.1393, found 480.1415.



Compound **6i**: yield 70%; 90% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 29.65 min, and t_{minor} = 23.45 min.); ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 7.7 Hz, 2H), 7.54 (dd, J = 12.4, 4.5 Hz, 4H), 7.45 (t, J = 7.3 Hz, 3H), 7.09 – 7.02 (m, 1H), 6.97 (dd, J = 8.1, 1.4 Hz, 1H), 6.58 (td, J = 7.7, 1.4 Hz, 1H), 6.42 (s, 1H), 6.08 (d, J = 7.7 Hz, 1H), 4.88 (s, 1H), 4.24 (dd, J = 7.2, 2.8 Hz, 2H), 3.54 – 3.44 (m, 1H), 3.35 (d, J = 8.0 Hz, 3H), 2.54 (d, J = 12.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.31, 151.63, 139.39, 136.50, 134.91, 131.42, 131.20, 129.39, 128.96, 127.29, 126.46, 124.15, 119.68, 118.58, 114.87, 111.91, 82.87, 62.92, 52.51; HRMS (ESI) calcd for C₂₅H₂₂N₂O₄ (M+Na)⁺437.1472, found 1501.



Compound **6j**: yield 67%; 90% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.7 mL/min; hexane / ethanol = 80 : 1; 254 nm, Retention time: $t_{major} = 28.55$

min, and $t_{\text{minor}} = 32.45$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.06 (dd, J = 10.7, 4.6 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.59 (dd, J = 10.7, 4.5 Hz, 1H), 6.46 (s, 1H), 6.11 (d, J = 7.8 Hz, 1H), 4.82 (s, 1H), 4.28 – 4.16 (m, 2H), 3.64 – 3.53 (m, 1H), 3.34 (d, J = 2.4 Hz, 3H), 2.45 (d, J = 10.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.45, 151.71, 136.81, 135.93, 135.08, 133.55, 130.76, 129.39, 129.12, 128.79, 128.75, 128.20, 127.15, 126.54, 124.75, 119.45, 114.59, 82.86, 64.73, 62.80, 52.43, 44.82; HRMS (ESI) calcd for C₂₄H₂₂ClNO₄ (M+Na)⁺446.1130, found 446.1151.



Compound **6k**: yield 56%; 91% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.35 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 30.60 min, and t_{minor} = 27.74 min.); ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 6.7 Hz, 2H), 7.27 (d, *J* = 13.4 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 6.43 (s, 1H), 6.08 (d, *J* = 7.9 Hz, 1H), 4.78 (s, 1H), 4.26 – 4.15 (m, 2H), 3.74 (t, *J* = 6.2 Hz, 1/2H), 3.55 (td, *J* = 11.4, 4.2 Hz, 1H), 3.32 (s, 3H), 2.42 (d, *J* = 11.9 Hz, 1H), 1.85 (t, *J* = 6.3 Hz, 1/2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.41, 151.62, 136.72, 136.10, 134.98, 133.58, 131.07, 129.35, 129.01, 128.76, 127.12, 126.48, 124.71, 121.70, 119.40, 114.55, 82.78, 67.93, 64.64, 62.74, 52.42, 44.69, 25.57; HRMS (ESI) calcd for C₂₄H₂₂BrNO₄ (M+Na)⁺ 490.0624, found 490.0625.



Compound **61**: yield 64%; 92% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.35 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: t_{major} = 28.64 min, and t_{minor} = 26.20 min.); ¹H NMR (400 MHz, CDCl₃) δ 8.31 (t, J = 7.4 Hz, 1H), 7.84 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.7 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.88 (t, J = 9.1 Hz, 1H), 6.56 (t, J = 7.5 Hz, 2H), 6.17 (d, J = 7.9 Hz, 1H), 5.44 (s, 1H), 4.29 – 4.16 (m, 2H), 3.66 (td, J = 11.3, 4.4 Hz, 1H), 3.30 (s, 3H), 2.45 (d, J = 12.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.39, 152.19, 136.80, 135.39, 130.94, 129.83, 129.74, 129.37, 128.75, 127.20, 126.60, 123.55, 123.41, 123.38, 122.06, 121.93, 119.44, 115.11, 114.87, 114.37, 82.96, 77.25, 62.86 (s), 52.32; HRMS (ESI) calcd for C₂₄H₂₂FNO₄ (M+Na)⁺430.1425, found 430.1404.



Compound **6m**: yield51%; 89% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.5 mL/min; hexane / ethanol = 20 : 1; 254 nm, Retention time: $t_{major} = 19.09$ min, and $t_{minor} = 17.53$ min.); ¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 6.9 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 7.7 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.57 (s, 1H), 6.52 (t, J = 7.6 Hz, 1H), 6.05 (d, J = 7.8 Hz, 1H), 5.69 (s, 1H), 4.22 (dt, J = 23.1, 9.9 Hz, 2H), 3.75 (td, J = 11.7, 3.4 Hz, 1H), 3.23 (s, 3H), 2.39 (d, J = 11.9 Hz, 1H); ¹³C NMR (100 MHz,) δ 170.27, 152.62, 136.73, 134.62, 133.73, 132.89, 130.96, 129.47, 128.79, 128.69, 127.38, 126.88, 126.66, 124.45, 119.41, 114.28, 82.91, 62.74,

60.77, 52.18, 44.40; HRMS (ESI) calcd for $C_{24}H_{22}BrNO_4$ (M+Na)⁺ 490.0624, found 490.0612.



Compound **6n**: yield 59%; 76% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / ethanol = 10 : 1; 254 nm, Retention time: $t_{major} = 24.09$ min, and $t_{minor} = 16.84$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.77 (m, 2H), 7.55 (m, 2H), 7.42 (t, J = 6.9 Hz, 1H), 7.04 (m, 2H), 6.94 (dd, J = 8.1, 1.4 Hz, 1H), 6.74 (s, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.64 – 6.56 (m, 1H), 6.53 (s, 1H), 6.19 (d, J = 7.9 Hz, 1H), 5.96 (s, 2H), 4.76 (s, 1H), 4.19 (m, 2H), 3.74 – 3.60 (m, 1H), 3.34 (s, 3H), 2.40 (d, J = 12.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.61, 151.83, 147.19, 146.93, 137.13, 135.38, 129.32, 128.64, 127.68, 126.96, 126.61, 125.12, 125.01, 119.35, 114.34, 111.13, 107.34, 101.01, 83.12, 64.59, 62.77, 52.36, 44.71; HRMS (ESI) calcd for C₂₅H₂₃NO₆ (M+Na)⁺ 456.1418, found 456.1430.



Compound **60**: yield 77%; 91% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 10 : 1; 254 nm, Retention time: $t_{major} = 20.69$ min, and $t_{minor} = 14.16$ min.); ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.84 (dd, J = 8.9, 4.8 Hz, 2H), 7.70 (d, J = 8.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.54 – 7.43 (m, 3H), 7.31 (s, 1H), 7.02 (ddd, J = 15.5, 8.1, 3.9 Hz, 2H), 6.58 (s, 1H), 6.49 – 6.43 (m, 1H), 6.01 (d, J = 7.9 Hz, 1H), 5.04 (s, 1H), 4.30 (dtd, J = 22.7,

11.5, 2.9 Hz, 2H), 3.73 (td, J = 11.5, 4.1 Hz, 1H), 3.22 (s, 3H), 2.45 (d, J = 11.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.66, 151.84, 137.17, 135.42, 132.84, 132.65, 131.62, 129.38, 128.71, 128.56, 127.45, 127.45, 126.96, 126.83, 126.65, 126.18, 125.94, 125.09, 119.36, 114.37, 83.22, 65.04, 62.98, 52.33; HRMS (ESI) calcd for C₂₈H₂₅NO₄ (M+Na)⁺462.1676, found 430.1679.



Chemical Formula: C₂₄H₂₁Br₂NO₄

Compound **6p**: yield 59%; 75% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / ethanol = 10 : 1; 254 nm, Retention time: $t_{major} = 10.96$ min, and $t_{minor} = 19.83$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.57 (s, 4H), 7.29 (d, J = 8.4 Hz, 2H), 7.13 (s, 2H), 6.96 (t, J = 7.7 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.50 (t, J = 7.6 Hz, 1H), 6.33 (s, 1H), 6.02 (d, J = 7.8 Hz, 1H), 4.65 (s, 1H), 4.08 (m, 2H), 3.45 (td, J = 11.6, 3.4 Hz, 1H), 3.24 (s, 3H), 2.38 (d, J = 11.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.03, 151.58, 136.03, 135.05, 132.59, 130.50, 130.45, 130.78, 128.44, 127.16, 124.62, 123.10, 122.52, 119.66, 114.61, 82.66, 77.26, 64.66, 62.94, 52.58, 44.97; HRMS (ESI) calcd for C₂₈H₂₅NO₄ (M+Na)⁺567.9730, found 567.9736.



Chemical Formula: C₂₄H₂₁Br₂NO₄

Compound **6q**: yield 57%; 70% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / ethanol = 10 : 1; 254 nm, Retention time: $t_{major} = 24.91$ min, and $t_{minor} = 10.22$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.38 (m, 3H), 7.20 (s, 2H), 7.03 (t, J = 7.6 Hz,

1H), 6.95 (d, J = 7.9 Hz, 1H), 6.57 (t, J = 7.5 Hz, 1H), 6.40 (s, 1H), 6.10 (d, J = 7.8 Hz, 1H), 4.73 (s, 1H), 4.27 – 4.09 (m, 2H), 3.52 (td, J = 11.6, 3.2 Hz, 1H), 3.33 (s, 3H), 2.47 (d, J = 11.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.95, 151.58, 139.36, 135.06, 132.53, 132.43, 131.96, 130.81, 130.77, 129.91, 127.10, 125.22, 124.52, 123.69, 122.52, 119.66, 114.72, 82.51, 64.71, 63.00, 52.63, 44.98. HRMS (ESI) calcd for C₂₈H₂₅NO₄ (M+Na)⁺ 567.9730, found 567.9714.



Compound **6r**: yield 58%; 87% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.6 mL/min; hexane / ethanol = 40 : 1; 254 nm, Retention time: $t_{\text{major}} = 21.68$ min, and $t_{\text{minor}} = 16.15$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 9.3 Hz, 2H), 7.10 (s, 1H), 6.99 (dd, J = 22.5, 7.7 Hz, 3H), 6.90 (d, J = 7.9 Hz, 1H), 6.59 (t, J = 7.5 Hz, 1H), 6.44 (d, J = 7.7 Hz, 1H), 4.47 (m, 1H), 4.15 – 3.91 (m, 4H), 3.22 (m, 1H), 2.88 – 2.71 (m, 1H), 1.69 (s, 3H), 1.00 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.37, 151.65, 135.83, 133.92, 131.43, 130.67, 126.74, 123.38, 122.02, 119.84, 114.40, 78.64, 69.36, 62.89, 60.98, 49.79, 22.51, 13.76. HRMS: calcd for C₁₉H₂₀BrNO₄ (M+Na)⁺ 442.0630; found: 442.0652.



Compound 7: yield 62%; 97% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / isopropanol = 5 : 1; 254 nm, Retention time: $t_{\text{major}} = 25.46$ min, and $t_{\text{minor}} = 19.33$ min.);¹H NMR (400 MHz, DMSO) δ 9.25 (s, 1H), 8.00 – 7.82

(m, 3H), 7.55 - 7.41 (m, 4H), 7.36 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 6.49 (t, J = 11.6 Hz, 1H), 6.37 (t, J = 7.3 Hz, 1H), 6.26 (t, J = 7.1 Hz, 1H), 6.17 (d, J = 7.6 Hz, 1H), 5.10 - 4.97 (m, 2H), 3.90 (d, J = 11.4 Hz, 1H), 3.71 (t, J = 9.2 Hz, 1H), 3.02 - 2.92 (m, 1H), 2.86 (t, J = 9.3 Hz, 1H); 13 C NMR (100 MHz, Acetone) δ 169.36, 145.04, 140.30, 139.84, 136.70, 132.86, 131.16, 128.77, 128.35, 127.51, 120.82, 117.17, 114.25, 112.00, 65.19, 62.02, 42.17. HRMS: calcd for C₂₅H₂₂BrNO₅ (M+Na)⁺ 475.0633; found: 475.0626.



CO₂Me Chemical Formula: C₂₈H₂₉NO₆

Compound 8: yield 51%; 94% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / ethanol = 50 : 1; 254 nm, Retention time: $t_{major} = 13.14$ min, and $t_{minor} = 15.19$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.15 – 7.07 (m, 1H), 7.04 (t, J = 7.4 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.86 – 6.65 (m, 7H), 6.46 (td, J = 7.7, 1.3 Hz, 1H), 4.29 (d, J = 8.5 Hz, 1H), 4.23 (s, 1H), 3.89 (dd, J = 16.3, 7.2 Hz, 2H), 3.78 – 3.68 (m, 5H), 2.23 (dd, J = 16.2, 3.9 Hz, 1H), 2.17 – 2.06 (m, 1H), 1.08 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.74, 170.70 , 154.57, 138.12, 134.47, 132.72, 130.88, 128.06, 127.72, 127.56, 127.35, 126.85, 126.12, 124.49, 119.80, 113.93, 85.37, 78.70, 69.14, 60.74, 60.18, 52.39, 34.54, 14.04. HRMS: calcd for C₂₈H₂₉NO₆ (M+Na)⁺498.1893; found: 498.1897.



Compound 10 [prepared with (*R*)-**5d-ZrMS** derived from (*R*)-BINOL]: yield 65%; 90% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / ethanol = 5 : 1; 254 nm, Retention time: $t_{major} = 17.41$ min, and $t_{minor} = 22.94$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.10 (dd, J = 15.5, 7.8 Hz, 3H), 7.00 (d, J = 8.1 Hz, 1H), 6.92 – 6.81 (m, 3H), 6.74 (t, J = 7.6 Hz, 1H), 5.65 (s, 1H), 4.38 (d, J = 2.4 Hz, 2H), 3.87 (s, 3H), 3.34 (d, J = 17.2 Hz, 1H), 3.09 (d, J = 17.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 172.04, 172.01, 151.33, 136.87, 132.53, 131.51, 130.24, 128.80, 128.32, 127.76, 126.58, 125.27, 124.09, 122.87, 120.87, 120.21, 82.21, 70.82, 68.50, 53.45, 39.15. HRMS: calcd for C₂₅H₂₂BrNO₅ (M+Na)⁺ 518.0579; found: 518.0585.



Compound **12** [prepared with (*R*)-**5d-ZrMS** derived from (*R*)-BINOL]: yield 56%; 97% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.5 mL/min; hexane / ethanol = 15 : 1; 220 nm, Retention time: $t_{major} = 12.6$ min, and $t_{minor} = 19.6$ min.); ¹H NMR (400 MHz, CDCl₃) δ 7.39 (ddd, J = 11.4, 9.2, 2.3 Hz, 7H), 7.16 (d, J = 8.2 Hz, 2H), 6.07 (s, 1H), 5.40 (s, 1H), 3.60 (s, 3H), 1.66 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 169.04, 136.40, 135.39, 134.20, 130.86, 130.21, 128.84, 128.50, 126.46, 122.54, 120.19, 80.76, 78.56, 52.62, 15.44. HRMS: calcd for C₁₉H₁₇BrO₄ (M+Na)⁺ 411.0208; found: 411.0190.



Compound 14 [prepared with (*R*)-5d-ZrMS derived from (*R*)-BINOL]: yield 70%; 99% ee, determined by HPLC (Daicel Chirapak IA, flow rate: 0.8 mL/min; hexane / ethanol = 10 : 1; 220 nm, Retention time: $t_{major} = 14.2 \text{ min}$, and $t_{minor} = 19.3 \text{ min}$.); ¹H NMR (400 MHz, CDCl₃+D₂O 1d) δ 7.68 – 7.59 (m, 2H), 7.40 (dd, *J* = 11.6, 4.5 Hz, 2H), 7.36 – 7.29 (m, 1H), 6.25 – 6.15 (m, 1H), 6.01 – 5.92 (m, 1H), 4.81 (d, *J* = 5.5

Hz, 1H), 4.76 (s, 1H), 4.68 – 4.42 (m, 2H), 3.71 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.22, 137.54, 129.39, 128.55, 128.24, 125.77, 125.56, 82.28, 65.02, 63.89, 52.61; HRMS: calcd for C₁₃H₁₄NO₄ (M+Na)⁺ 257.0790; found: 257.0779.

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S32

100

150

ppm

50





























S48



















S57











S61



S62

HPLC Spectra

Compound *rac*-4a:

Sample Name: TM298 (1-6)-meso

Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 4a: Sample Name: TM298-5



Compound *rac*-4b: Sample Name: TM298-13-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm



Compound 4b: Sample Name: TM298-13



Compound *rac*-4c: Sample Name: TM298-12-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8mL/min; 254 nm; chiral IA



Compound 4c:

Sample Name: TM298-12



Compound *rac*-4d: Sample Name: TM298-11-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 4d:

Sample Name: TM298-11



Compound *rac*-4e: Sample Name: TM1000-89-2 Condition: Hexane/ EtOH = 20/ 1; 0.5 mL/min; 254 nm; chiral IA



Compound 4e: Sample Name: TM1000-84-2



Compound *rac*-4f: Sample Name: TM1000-89-1-1 Condition: Hexane/ EtOH = 30/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 4f: Sample Name: TM1000-83-2-1



Compound *rac*-4g: Sample Name: TM1000-88-1-meso-1 Condition: Hexane/ EtOH = 20/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 4g: Sample Name: TM1000-88-1



Compound *rac-*6a: Sample Name: TM298-18-meso Condition: Hexane/ EtOH = 18/ 1; 0.6 mL/min; 254 nm; chiral IA



Compound 6a: Sample Name: TM298-20



Compound *rac*-6b: Sample Name: TM298-30-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.5 mL/min; 254 nm; chiral IA



Compound 6b:

Sample Name: TM298-42



Compound *rac*-6c: Sample Name: TM298-43-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6c: Sample Name: TM298-43


Compound *rac*-6d: Sample Name: TM298-52-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6d:

Sample Name: TM298-52



Compound *rac*-6e: Sample Name: TM298-11-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6e: Sample Name: TM298-21



Compound *rac*-6f: Sample Name: TM298-53-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6f: Sample Name: TM298-53



Compound *rac*-6g: Sample Name: TM298-26-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6g: Sample Name: TM298-26



Compound *rac*-6h: Sample Name: TM298-56-meso Condition: Hexane/ EtOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6h:

Sample Name: TM298-56



Compound *rac*-6i: Sample Name: TM298-57-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6i: Sample Name: TM298-57



Compound *rac-*6j: Sample Name: TM298-55-meso Condition: Hexane/ EtOH = 80/ 1; 0.7 mL/min; 254 nm; chiral IA



Compound 6j: Sample Name: TM298-55



Compound *rac*-6k: Sample Name: TM298-24-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.35 mL/min; 254 nm; chiral IA



Compound 6k: Sample Name: TM298-44



Compound *rac*-61: Sample Name: TM298-54-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.35 mL/min; 254 nm; chiral IA



Compound 61: Sample Name: TM298-54



Compound *rac-*6m: Sample Name: TM298-27-meso Condition: Hexane/ EtOH = 20/ 1; 0.5 mL/min; 254 nm; chiral IA



Compound 6m:





Compound *rac*-6n: Sample Name: TM298-32-meso Condition: Hexane/ EtOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6n:



S83

Compound *rac*-60: Sample Name: TM298-61-meso Condition: Hexane/ *i*-PrOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 60:

Sample Name: TM298-61



Compound *rac*-6p: Sample Name: TM298-34-meso Condition: Hexane/ EtOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6p: Sample Name: TM298-34



Compound *rac*-6q: Sample Name: TM298-36-meso Condition: Hexane/ EtOH = 10/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 6q: Sample Name: TM298-36



Compound *rac*-6r: Sample Name: TM1000-94-7-meso-130527 Condition: Hexane/ EtOH = 40/ 1; 0.6 mL/min; 254 nm; chiral IA



Compound 6r:

Sample Name: TM1000-94-7-130527



Compound *rac*-7: Sample Name: cmq-51031A-130725 Br-IA(xiaoxuan) Condition: Hexane/ *i*-PrOH = 5/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 7: Sample Name: cmq-51272-130725 Br-IA(cat)



Compound *rac*-8: Sample Name: TM1000-85-5-zhong-jiuzhi-131021 Condition: Hexane/ EtOH = 50/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 8: Sample Name: TM1000-93-3



Compound *rac*-10: Sample Name: TM1000-120-4-6B-131021 Condition: Hexane/ EtOH = 5/ 1; 0.8 mL/min; 254 nm; chiral IA



Compound 10: Sample Name: TM1000-120-37B-131021



Compound *rac*-12: Sample Name: TM1000-226-7-B Condition: Hexane/ EtOH = 15/1; 0.5 mL/min; 220 nm; chiral IA



Compound 12: Sample Name: TM1000-226-8



Compound *rac*-14: Sample Name: TM3000-50-0-A-1 Condition: Hexane/ EtOH = 10/ 1; 0.8 mL/min; 220 nm; chiral IA



Compound 14:

Sample Name: TM3000-50-3

