Supporting Information

Supported Manganese Catalysts Achieve Highly Efficient C-H Bond Oxidation and Olefin Epoxidation

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1. General information

Commercial reagents were used without further purification, and solvents were dried before use. Melting points were recorded with a micro melting point apparatus and uncorrected. The ¹H NMR spectra were recorded at 400 MHz. The ¹³C NMR spectra were recorded at 100 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. HRMS spectra were recorded on an Agilent 1200HPLC-6210TOFMS using ESI as an ion source. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm). Optical rotations were determined using an AUTOPOL V polarimeter. HPLC analyses were performed on Agilent 1100 and Waters e2695 equipped with OD-H, AD-H, IA-H, IC-H, and OJ-H.

The morphology of samples was observed through a field emission scanning electron microscope (FE-SEM, HITACHI Regulus 8100) at an acceleration voltage of 10 kV. The related elemental distribution was analyzed with energy-dispersive X-ray spectroscopy (EDS, Oxford Ultim Max 65). Transmission electron microscope (TEM) images were performed using a Tecnai G2 F30 S-Twin and Energy spectrum model: Xplore 80. Nitrogen sorption isotherms at the temperature of liquid nitrogen were performed on a Micromeritics system, and the samples were degassed for 10 h at 393 K before the measurements. The specific surface areas were calculated from the adsorption data using Brunauer–Emmett–Teller (BET) methods. The total pore volume at P/Po = 0.995. The pore size distribution curves were obtained from the desorption branches using the nonlocal density functional

theory (NLDFT) method. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (METTLER TOLEDO TGA/DSC 3+), the sample was heated at the rate of 10 k·min⁻¹ from room temperature up to 1073 K under a nitrogen atmosphere.

2. Synthesis and characterization of the catalysts.

2.1 The procedure for the synthesis of Mn(^{Et}PMB)



(1) The synthesis of 6.

A 50 mL reactor was added **Ethylamine** (90 mg, 2.0 mmol), **N**-(*tert*-butoxycarbonyl)-*L*prolinal (398 mg, 2.0 mmol), and DCM (10 mL). The mixture was stirred at 40 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated to dryness under reduced pressure. Then dissolved in MeOH (20 mL) and NaBH₄ (189 mg, 5.0 mmol) was slowly added at 0 °C. The mixture was extracted with DCM (50 mL×3) after 8 hours of reaction. The combined organic phase was dried with anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure to obtain a yellow liquid **6** (416 mg, 1.85 mmol) in 91% yield.

(2) The synthesis of 7.

A 50 mL reactor was added **6** (416 mg, 1.8 mmol) and DCM (20 mL), then TFA (4.15 g, 36.4 mmol) was slowly added at 25° C and stirred for 12 hours. The mixture was concentrated under reduced pressure to remove residual acid and obtained a yellow crude **7** (211 mg, 1.65 mmol) in 90% yield.

(3) The synthesis of 8.

A 100 mL reactor was added **7** (211 mg, 1.65 mmol), **2-(Chloromethyl)-1-methyl-1***H***-benzimidazole** (743 mg, 4.1 mmol), K_2CO_3 (682 mg, 4.9 mmol), and MeCN (30 mL). The mixture was stirred at 60°C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under decompression and purified by silica gel column

chromatography (PE: EA = 1: 1, v/v), then after recrystallization (PE: EA = 5: 1, v/v) to obtain a yellow solid **8** (480 mg, 1.15 mmol) in 70% yield.

(4) The synthesis of **Mn(^{Et}PMB)**.

8 (480 mg, 1.15 mmol) and Mn(OTf)₂ (447 mg, 1.27 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60°C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under a vacuum to obtain a light yellow solid **Mn(^{Et}PMB)** (860 mg, 1.12 mmol) in 97% yield.

2.2 The procedure for the synthesis of Mn(^{Bn}PMB)



(1) The synthesis of 9.

A 50 mL reactor was added **Benzylamine** (214 mg, 2.0 mmol), **N**-(*tert*-butoxycarbonyl)-*L*-prolinal (398 mg, 2.0 mmol), and DCM (10 mL). The mixture was stirred at 40°C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated to dryness under reduced pressure. Then dissolved in MeOH (20 mL) and NaBH₄ (189 mg, 5.0 mmol) was slowly added at 0°C. The mixture was extracted with DCM (50 mL×3) after 8 hours of reaction. The combined organic phase was dried with anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure to obtain a yellow liquid **9** (523 mg, 1.8 mmol) in 90% yield.

(2) The synthesis of **10**.

A 50 mL reactor was added **9** (523 mg, 1.8 mmol) and DCM (20 mL), then TFA (4.11 g, 36.0 mmol) was slowly added at 25° C and stirred for 12 hours. The mixture was concentrated under reduced pressure to remove residual acid and obtained a yellow crude **10** (312 mg, 1.64 mmol) in 91% yield.

(3) The synthesis of **11**.

A 100 mL reactor was added **10** (312 mg, 1.64 mmol), **2-(Chloromethyl)-1-methyl-1***H***benzimidazole** (740 mg, 4.1 mmol), K_2CO_3 (680 mg, 4.9 mmol), and MeCN (30 mL). The mixture was stirred at 60°C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under decompression and purified by silica gel column chromatography (PE: EA = 1: 1, v/v), then after recrystallization (PE: EA = 5: 1, v/v) to obtain a yellow solid **11** (510 mg, 1.07 mmol) in 65% yield.

(4) The synthesis of **Mn(^{Bn}PMB)**.

11 (510 mg, 1.07 mmol) and Mn(OTf)₂ (414 mg, 1.17 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60 °C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under a vacuum to obtain a light yellow solid **Mn(^{Bn}PMB)** (859 mg, 1.03 mmol) in 97% yield.

2.3 The procedure for the synthesis of C1



(1) The synthesis of **12**.

A 100 mL reactor was added (4-vinylbenzyl) Amine (595 mg, 5.0 mmol), *N*-(*tert*butoxycarbonyl)-*L*-prolinal (996 mg, 5.0 mmol), and DCM (10 mL). The mixture was stirred at 40 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated to dryness under reduced pressure. Then dissolved in MeOH (20 mL) and NaBH₄ (908 mg, 24.0 mmol) was slowly added at 0 °C. The mixture was extracted with DCM (50 mL×3) after 8 hours of reaction. The combined organic phase was dried with anhydrous Na₂SO₄, and concentrated to dryness under reduced pressure to obtain a yellow liquid **12** (1.45 g, 4.6 mmol) in 92% yield. (2) The synthesis of 13.

A 100 mL reactor was added **12** (1.0 g, 3.2 mmol) and DCM (20 mL), then TFA (7.21 g, 63.2 mmol) was slowly added at 25° C and stirred for 12 hours. The mixture was concentrated under reduced pressure to remove residual acid and obtained a yellow crude **13** (608 mg, 2.8 mmol) in 88% yield.

(3) The synthesis of L1.

A 100 mL reactor was added **13** (216 mg, 1.0 mmol), **14** (451 mg, 2.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), and MeCN (20 mL). The mixture was stirred at 60 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under decompression and purified by silica gel column chromatography (PE: EA = 1: 1, v/v), then after recrystallization (PE: EA = 5: 1, v/v) to obtain a yellow solid **L1** (318 mg, 0.63 mmol) in 63% yield.

(4) The synthesis of **C1**.

L1 (318 mg, 0.63 mmol) and Mn(OTf)₂ (245 mg, 0.69 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60° C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under vacuum to obtain a light yellow solid **C1** (525 mg, 0.61 mmol) in 97% yield.





(1) The synthesis of L2.

A 100 mL reactor was added **13** (216 mg, 1.0 mmol), **15** (622 mg, 2.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), and MeCN (20 mL). The mixture was stirred at 60 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under decompression and purified by silica gel column chromatography (PE: EA = 1: 1, v/v), then

after recrystallization (PE: EA = 5: 1, v/v) to obtain a yellow solid **L2** (306 mg, 0.48 mmol) in 48% yield.

(2) The synthesis of C2.

L2 (306 mg, 0.48 mmol) and Mn(OTf)₂ (185 mg, 0.53 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60 $^{\circ}$ C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under vacuum to obtain a light yellow solid **C2** (456 mg, 0.46 mmol) in 96% yield.

2.5 The procedure for the synthesis of C3



(1) The synthesis of L3.

A 100 mL reactor was added **13** (216 mg, 1.0 mmol), **16** (487 mg, 2.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), and MeCN (20 mL). The mixture was stirred at 60 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under decompression and purified by silica gel column chromatography (PE: EA = 1: 1, v/v), then after recrystallization (PE: EA = 5: 1, v/v) to obtain a yellow solid **L3** (239 mg, 0.45 mmol) in 45% yield.

(2) The synthesis of C3.

L3 (239 mg, 0.45 mmol) and Mn(OTf)₂ (174 mg, 0.49 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60° C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under vacuum to obtain a light yellow solid **C3** (385 mg, 0.43 mmol) in 97% yield.

2.6 The procedure for the synthesis of C4



(1) The synthesis of L4.

A 100 mL reactor was added **13** (216 mg, 1.0 mmol), **17** (649 mg, 2.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), and MeCN (20 mL). The mixture was stirred at 60 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under decompression and purified by silica gel column chromatography (PE: EA = 1: 1, v/v), then after recrystallization (PE: EA = 5: 1, v/v) to obtain a yellow solid **L4** (216 mg, 0.33 mmol) in 33% yield.

(2) The synthesis of C4.

L4 (216 mg, 0.33 mmol) and Mn(OTf)₂ (127 mg, 0.36 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60° C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under vacuum to obtain a light yellow solid **C4** (315 mg, 0.31 mmol) in 95% yield.

2.7 The procedure for the synthesis of C5



(1) The synthesis of L5.

A 100 mL reactor was added **13** (216 mg, 1.0 mmol), **18** (319 mg, 2.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), and MeCN (20 mL). The mixture was stirred at 60 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under

decompression and purified by silica gel column chromatography (PE: EA = 1: 1, v/v) to obtain a yellow solid **L5** (251 mg, 0.63 mmol) in 63% yield.

(2) The synthesis of **C5**.

L5 (251 mg, 0.63 mmol) and Mn(OTf)₂ (245 mg, 0.69 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60° C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under vacuum to obtain a light yellow solid **C5** (455 mg, 0.61 mmol) in 96% yield.

2.8 The procedure for the synthesis of C6



(1) The synthesis of L6.

A 100 mL reactor was added **19** (306 mg, 1.0 mmol), **14** (451 mg, 2.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), and MeCN (20 mL). The mixture was stirred at 60 °C for 8 hours with a nitrogen atmosphere. Upon completion, the reaction mixture was concentrated under decompression and purified by silica gel column chromatography (PE: EA = 1: 1, v/v), then after recrystallization (PE: EA = 5: 1, v/v) to obtain a yellow solid **L6** (244 mg, 0.41 mmol) in 41% yield.

(2) The synthesis of C6.

L6 (244 mg, 0.41 mmol) and $Mn(OTf)_2$ (159 mg, 0.45 mmol) were dissolved in MeCN (30 mL) at room temperature, then the mixture was stirred at 60 °C for 6 hours in a nitrogen atmosphere. After drying under a vacuum, the result solids were washed thoroughly with PE three times. Then dried under vacuum to obtain a light yellow solid **C6** (373 mg, 0.39 mmol) in 96% yield.

2.9 The procedure for the synthesis of supported Mn catalysts

The synthesis of C1@POP10: C1 (86 mg, 0.1 mmol), DVB (130 mg, 1 mmol), and AIBN (30 mg, 0.18 mmol) were dissolved in THF (10 mL) in a Schlenk reactor. The mixture was stirred at 100° C for 24 hours. When the reaction was completed, the solution was filtered and washed with THF and EtOAc three times respectively. Then dried at 70°C for 24 hours to obtain a yellow solid.

The synthesis C1@POP30, C1@POP60, C2@POP30, C3@POP30, C4@POP30, C5@POP30, C6@POP30: Supported Mn catalysts were synthesized by the same method. The difference is in the ratio of manganese complexes to DVB. Then supported Mn catalysts indicated as C1@POP30 (C1 : DVB = 1 : 30), C1@POP60 (C1 : DVB = 1 : 60), C2@POP30 (C2 : DVB = 1 : 30), C3@POP30 (C3 : DVB = 1 : 30), C4@POP30 (C4 : DVB = 1 : 30), C5@POP30 (C5 : DVB = 1 : 30), C5@POP30 (C5 : DVB = 1 : 30).

3. Optimization of the hydroxylation reaction

3.1 Evaluation of axial ligand

Table S1 Evaluation of axial ligand



				CIX@FOF30	
Entry	Х	Cat.(mol%)	Yield(%) ^[b]	ee (%) ^[c]	dr ^[d]
1	OAc	2	57	83.1	>95:5
2	OTf	2	61	93.3	>95:5
3	CI	2	40	75.3	87:13
4	Br	2	52	80.7	>95:5
5	NO ₃	2	54	83.4	>95:5
6	CIO ₄	2	50	89.8	>95:5
7	OTf	1.5	60	93.2	>95:5
8	OTf	1.0	60	93.3	>95:5
9	OTf	0.5	56	93.1	>95:5

	10	OTf	0.2	37	87.6	90:10
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^a**1a** (0.5 mmol), C1X@POP30, and EHA (9 equiv.) were added to in 2 mL of solvent (TFE/DCM = 5:1), then H_2O_2 (1.1 equiv. aqueous solution was diluted in 0.5 mL TFE) was added to the solution dropwise at -20°C, using a syringe pump over 2.5 h and stirred for another 0.5 h. ^bIsolated yields. ^cDetermined by chiral HPLC analysis. ^dDetermined by ¹HNMR.

3.2 Evaluation of oxidant

Table S2 Evaluation of Oxidant^a

	1a	C1@POP30 , Oxid TFE/DCM, -2	dant, EHA 20 °C	O OH Za	
Entry	Oxidant	Usage(equiv.)	Yield(%) ^[c]	ee (%) ^[d]	dr ^[e]
1	H_2O_2	1	57	93.3	>95:5
2 ^b	m-CPBA	1	46	83.0	90:10
3	TBHP	1	52	91.8	>95:5
4 ^b	PhIO	1	49	89.9	>95:5
5	H_2O_2	1.1	60	93.3	>95:5
6	H_2O_2	1.2	55	93.3	>95:5

^a**1a** (0.5 mmol), **C1@POP30** (1 mol%), and EHA (9 equiv.) were added to 2 mL of solvent (TFE/DCM = 5:1), then oxidant (aqueous solution was diluted in 0.5 mL TFE) was added to the solution dropwise at -20°C, using a syringe pump over 2.5 h and stirred for another 0.5 h. ^bOxidant was multiple small additions at -20°C over 2.5 h and stirred for another 0.5 h. ^c Isolated yields. ^d Determined by chiral HPLC analysis. ^eDetermined by ¹HNMR.

3.3 Evaluation of acid additive

Table S3 Evaluation of acid additive^a



7	BA (Butyric Acid)	9	45	77.3	87:13
8	AA (Acetic acid)	9	45	77.1	85:15
9	DMBA (2,2-Dimethylbutyric acid)	7	61	94.8	>95:5
10	DMBA (2,2-Dimethylbutyric acid)	6	60	94.7	>95:5
11	DMBA (2,2-Dimethylbutyric acid)	5	55	91.3	>95:5

^a**1a** (0.5 mmol), **C1@POP30** (1 mol%), and acid were added to 2 mL of solvent (TFE/DMC = 5:1), then H_2O_2 (1.1 equiv. 50% aqueous solution diluted in 0.5 mL TFE) was added to the solution dropwise at -20°C, using a syringe pump over 2.5 h and stirred for another 0.5 h. ^b Isolated yields. ^c Determined by chiral HPLC analysis. ^eDetermined by ¹HNMR.

3.4 Evaluation of temperature

Table S4 Optimization of Mn-catalyzed asymmetric hydroxylation^a



^a **1a** (0.5 mmol), **C1@POP30** (1 mol%), and DMBA (6 equiv.) were added to 2 mL of solvent (TFE/DMC = 5:1), then H_2O_2 (1.1 equiv. 50% aqueous solution diluted in 0.5 mL TFE) was added to the solution dropwise using a syringe pump over 1.5 h and stirred for another 0.5 h. ^bIsolated yields. ^cDetermined by chiral HPLC analysis. ^eDetermined by ¹HNMR.

4. General procedure for reactions and recycling studies.

4.1 General procedure for racemic hydroxylation



Substrate **1** was synthesized by reference.¹ Substrate **1** (0.5 mmol), Cat.0 (1 mol%), AcOH (2.5 mmol, 5 equiv.), and mixed solvent (1 mL) were added in a Schlenk reactor at -40 $^{\circ}$ C. Then oxidant solution (0.25 mmol, 0.5 equiv., 50% H₂O₂ in the 1.0 mL solution) was added

via a syringe pump over 1.5 hours with stirring. Then another Cat.0 (1 mol%) and AcOH (2.5 mmol, 5 equiv.) in the 1 mL solvent were added to the above mixture, and another oxidant solution (0.25 mmol, 0.5 equiv., 50% H₂O₂ in the 1.0 mL solution) was added via a syringe pump over 1.5 hours. The reaction was monitored by TLC. Upon completion, the mixture was quenched with a saturated Na₂SO₃ aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous NaHCO₃, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography to afford the racemic hydroxylation product. (The solvent was mixed with TFE/DCM=5:1)

4.2 General procedure for asymmetric hydroxylation



Substrate **1** (0.5 mmol), Mn catalyst (1 mol%), DMBA (3 mmol, 6 equiv.), and mixed solvent (2 mL) were added in a Schlenk reactor at -40 °C. Then oxidant solution (0.55 mmol, 1.1 equiv., 50% H_2O_2 in the 0.5 mL solution) was added via a syringe pump over 2.5 hours and stirred for another 0.5 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with a saturated Na_2SO_3 aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4 , concentrated under reduced pressure, and purified by silica gel column chromatography to afford the target product. (The solvent was mixed with TFE/DCM=5:1, X-ray-quality crystals were grown by slow diffusion of PE into DCM solutions)

Table S5.	Crystallographic data	and refinements	for product 2a.
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Empirical formula	$C_{18}H_{16}O_2$
Formula weight	264.31
Temperature/K	150.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	5.9260(3)
b/Å	11.6332(6)
c/Å	19.3715(10)

α/°	90
β/°	90
γ/°	90
Volume/Å ³	1335.44(12)
$ ho_{calc}g/cm^3$	1.315
µ/mm⁻¹	0.427
F(000)	560.0
Crystal size/mm ³	$0.4 \times 0.4 \times 0.2$
Radiation	GaKα (λ = 1.34138)
2O range for data collection/°	7.712 to 126.85
Index ranges	-7 ≤ h ≤ 7, -15 ≤ k ≤ 15, - 25 ≤ l ≤ 24
Reflections collected	13849
Independent reflections	3273 [R _{int} = 0.0463, R _{sigma} = 0.0299]
Data/restraints/parameters	3273/0/182
Goodness-of-fit on F ²	1.052
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0308$, $wR_2 = 0.0796$
Final R indexes [all data]	$R_1 = 0.0320$, $wR_2 = 0.0801$
Largest diff. peak/hole / e Å- ³	0.18/-0.17
Flack parameter	-0.03(9)

4.3 General procedure for racemic ketonization



Substrate **1** (0.5 mmol), Cat.0 (1 mol%), AcOH (5.0 mmol, 10 equiv.), and MeCN/DCM (5:1, 2 mL) were added in a Schlenk reactor at -40 $^{\circ}$ C. Then oxidant solution (1.5 mmol, 3.0 equiv., 50% H₂O₂ in the 1.0 mL MeCN) was added via a syringe pump over 3 hours with stirring. The reaction was monitored by TLC. Upon completion, the mixture was quenched with a saturated Na₂SO₃ aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous NaHCO₃, dried over anhydrous Na₂SO₄, concentrated under reduced pressure, and purified by silica gel column

chromatography to afford the racemic oxidation product.





Substrate **1** (0.5 mmol), Mn catalyst (1 mol%), DMBA (3 mmol, 6 equiv.), and MeCN/DCM (5:1, 2 mL) were added in a Schlenk reactor at -40 $^{\circ}$ C. Then oxidant solution (0.55 mmol, 1.1 equiv., 50% H₂O₂ in the 0.5 mL MeCN) was added via a syringe pump over 2.5 hours and stirred for another 0.5 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with a saturated Na₂SO₃ aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous NaHCO₃, dried over anhydrous Na₂SO₄, concentrated under reduced pressure, and then purified by silica gel column chromatography to afford the target products.

4.5 General procedure for racemic epoxidation



Substrate **4** was synthesized by reference.²⁻⁵ Substrate **4** (0.5 mmol), Mn catalyst (2 mol%), acetic acid (5 mmol, 10 equiv.), and MeCN (2 mL) were added in a Schlenk reactor at 0 $^{\circ}$ C. Then 50% H₂O₂ (1.5 mmol, 3 equiv.) was added via a syringe pump over 2 hours and stirred another 2 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with a saturated Na₂SO₃ aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous NaHCO₃, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to afford the racemic epoxides.

4.6 General procedure for asymmetric epoxidation



Substrate **4** (0.25 mmol), Mn catalysts (1 mol%), DMBA (1.25 mmol, 5 equiv.), and MeCN (1 mL) were added in a Schlenk reactor at -40 $^{\circ}$ C. Then H₂O₂ (0.375 mmol, 1.5 equiv., 50%

aqueous solution diluted in 0.5 mL MeCN) was added via a syringe pump over 1.5 hours and stirred another 0.5 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with a saturated Na₂SO₃ aqueous solution and then extracted with DCM. The combined organic layers were washed twice with saturated aqueous NaHCO₃, dried over anhydrous Na₂SO₄, concentrated under reduced pressure, and then purified by silica gel column chromatography to afford the target products.

4.7 Recycling studies

Chalcone (208 mg, 1 mmol), **C1@POP30** (1 mol%) and DMBA (581 mg, 5 mmol) were added to 2 mL MeCN and cooled down to -40 °C. Then, H₂O₂ (81.6 mg, 1.2 mmol, 50% aqueous solution diluted in 0.5 mL MeCN) was added via a syringe pump over 2 hours and stirred another 2 h. After the reaction, the catalyst was separated through centrifugation, and the catalyst was washed with EA, dried and reused in next run. In the 5th cycle, yield was decreased obviously. We surmised that it may be metal loss, so recovered catalyst re-coordination and re-introduced into the reaction after centrifugation and dying. The results are shown in Table S6. Additionally, TEM images indicate that both the freshly prepared and recycled **C1@POP30** exhibit similar morphologies (Fig. S5, S6). This suggests that the catalyst demonstrates significant stability in the oxidation reaction.

Cycle	Yield(%)	ee(%)
1	96	99.3
2	95	99.2
3	93	99.2
4	91	99.3
5	87	99.1
6	95	99.2

Table S6. Cycle results.

4.8 Continuous flow

Grind **C1@POP30** (238 mg) and silica gel (2.0 g) until mixed thoroughly, then fill to the bed-type continuous flow column. Purge the continuous flow system with argon for 30 minutes, and pump MeCN to the continuous flow system to exhaust at 16 μ L/min for 30 minutes with syringe pumps. Prepare a solution of chalcone (2.08 g, 10 mmol), DMBA

(5.81 g, 50 mmol) diluted in MeCN to 36 mL, and a solution of 50%H₂O₂ (816 mg, 12 mmol) diluted in MeCN to 18 mL. Inject the two solutions into the continuous flow system at a flow rate of 40 µL/min and 20 µL/min respectively at -40°C. At the same time, the sampling test is at the planned time. The effluent was poured into the saturated Na₂SO₃ aqueous solution and then extracted with DCM. The combined organic layer was dried with anhydrous Na₂SO₄, concentrated under reduced pressure, and purified by flash column chromatography over silica gel to get asymmetric epoxidation products (2.06 g, 99% conv., 92% yield, 98.9% ee.).

5. Characterization

5.1 The swelling ratio (SR) of C1@POP10, 30 and 60

The swelling ratio (SR) of the samples was determined gravimetrically by immersing a preweighed (Wd) dried sample in 3.5 mL of MeCN for 1 h. The samples were centrifuged (16000 r/min) to remove the solvent and weighed (Ws). The SR of the samples is calculated as follows^{6, 7}:

$$SR(\%) = \frac{Ws - Wd}{Wd} \times 100$$

catalysis	Wd (mg)	Ws (mg)	SR (%)
C1@POP10	50	167	234
C1@POP30	50	187	274
C1@POP60	50	197	294

Table S7. Swelling ratio (SR) of catalysis 10, 30, and 60.

5.2 The XPS results



Figure S1. XPS of Mn 2p. (a) C1@POP30. (b) C1.



Figure S2. XPS of C1@POP30. (a) N 1s. (b) O 1s.

5.3 N2 sorption isotherm and Pore size distribution



Figure S3. a) N_2 sorption isotherm. b) Pore size distribution

5.4 TGA results



5.5 Transmission electron microscope (TEM)



Figure S5. Transmission electron microscope (TEM) fresh. (a) C1@POP30, scale bar 50 nm, (b) 10 nm, (c) Transmission electron microscope (TEM) image and energydispersive X-ray spectroscopy (EDS) mapping of composition elements: (d) Mn, (e)

N, (f) O (scale bar 100 nm).



Figure S6. Transmission electron microscope (TEM) (a) used C1@POP30, scale bar 50 nm, (b) 10 nm, (c) Transmission electron microscope (TEM) image and energydispersive X-ray spectroscopy (EDS) mapping of composition elements: (d) Mn, (e) N, (f) O (scale bar 100 nm).

6. Spectra data

(*S*)-*N*-((1-methyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)-*N*-((1-((1-methyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)ethanamine (^{Et}PMB):



Yellow solid; m.p.= 79.1-80.7 °C;¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.67 (m, 2H), 7.33 – 7.18 (m, 6H), 4.22 (d, *J* = 13.2 Hz, 1H), 3.86 (d, *J* = 13.2 Hz, 1H), 3.83 (s, 3H), 3.74 (d, *J* = 13.6 Hz, 1H), 3.70 – 3.52 (m, 4H), 2.74 (ddd, *J* = 9.2, 6.8, 2.4 Hz, 1H), 2.67 – 2.51 (m, 4H), 2.42 (dd, *J* = 12.8, 8.0 Hz, 1H), 2.30 (td, *J* = 9.2, 7.2 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.67 – 1.50 (m, 2H), 1.50 – 1.36 (m, 1H), 1.06 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.37, 152.16, 142.14, 142.10, 136.26, 136.17, 122.55, 122.39, 121.91, 121.80, 119.49, 119.44, 109.09, 62.30, 58.84, 54.94, 52.39, 52.27, 48.84, 30.42, 30.07, 29.87, 22.52, 11.55; HRMS-ESI (m/z): calcd for C₂₅H₃₃N₆ [M + H]⁺: 417.2761, found: 417.2765.

(*S*)-*N*-benzyl-1-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[*d*]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (^{Bn}PMB):



Yellow solid; m.p.= 83.5-85.1 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 (tdd, *J* = 8.8, 3.6, 2.4 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.25 – 7.18 (m, 7H), 4.20 (dd, *J* = 13.2, 1.2 Hz, 1H), 3.75 (qd, *J* = 13.2, 1.2 Hz, 2H), 3.65 – 3.57 (m, 3H), 3.56 (s, 3H), 3.46 (s, 3H), 2.76 – 2.65 (m, 3H), 2.56 – 2.46 (m, 1H), 2.27 (td, *J* = 9.2, 7.2 Hz, 1H), 2.01 – 1.92 (m, 1H), 1.63 – 1.53 (m, 1H), 1.53 – 1.35 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.29, 151.75, 142.19, 142.15, 138.41, 136.20, 129.60, 128.35, 127.46, 122.60, 122.36, 121.95, 121.78, 119.53, 119.46, 109.10, 109.08, 62.38, 60.19, 59.41, 54.78, 52.35, 52.09, 30.50, 29.92, 29.71, 22.36; HRMS-ESI (m/z): calcd for C₃₀H₃₅N₆ [M + H]⁺: 479.2918, found: 479.2922.

(*S*)-1-(1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L1):



Yellow solid; m.p.= 84.2-85.9 °C;¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.67 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 8H), 6.68 (dd, *J* = 17.6, 3.2 Hz, 1H), 5.72 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.23 (dd, *J* = 11.2, 1.2 Hz, 1H), 4.20 (d, *J* = 13.6 Hz, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.67 – 3.56 (m, 5H), 3.55 – 3.52 (m, 1H), 3.48 (s, 3H), 2.77 – 2.64 (m, 3H), 2.50 (dd, *J* = 12.4, 7.2 Hz, 1H), 2.28 (td, *J* = 9.2, 7.2 Hz, 2H), 2.02 – 1.91 (m, 1H), 1.67 – 1.46 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.27, 151.72, 142.17, 142.12, 137.98, 136.80, 136.42, 136.20, 129.77, 126.17, 122.63, 122.38, 121.97, 121.80, 119.53, 119.46, 113.87, 109.12, 109.10, 62.33, 59.85, 59.38, 54.82, 52.38, 52.10, 30.49, 30.00, 29.72, 22.37; HRMS-ESI (m/z): calcd for C₃₂H₃₇N₆ [M + H]⁺: 505.3074, found: 505.3073.

(S)-1-(1-cyclohexyl-1H-benzo[d]imidazol-2-yl)-N-((1-((1-cyclohexyl-1H-

benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L2):



Yellow solid; m.p.= 89.7-90.9 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.67 (m, 2H), 7.59 – 7.48 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.15 (m, 4H), 6.70 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.43 (tdt, *J* = 12.0, 7.6, 4.0 Hz, 2H), 4.11 (d, *J* = 13.2 Hz, 1H), 3.94 (d, *J* = 13.2 Hz, 1H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.69 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 13.2 Hz, 1H), 3.44 (d, *J* = 13.2 Hz, 1H), 2.79 – 2.67 (m, 2H), 2.67 – 2.48 (m, 2H), 2.37 – 2.19 (m, 2H), 2.17 – 2.00 (m, 3H), 1.98 – 1.84 (m, 5H), 1.81 – 1.72 (m, 3H), 1.56 – 1.47 (m, 1H), 1.36 – 1.20 (m, 5H), 1.17 – 1.05 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 151.77, 150.90, 143.08, 142.94, 138.05, 136.86, 136.44, 134.11, 134.09, 129.60, 126.33, 122.04, 121.83, 121.45, 121.27, 119.96, 119.84, 113.80, 112.43, 112.27, 62.22, 59.93, 59.21, 56.16, 55.62, 54.34, 52.85, 52.48, 31.40, 31.34, 31.31, 31.10, 30.76, 26.20, 25.95, 25.83, 25.76, 25.47, 25.40, 22.59; HRMS-ESI (m/z): calcd for $C_{42}H_{53}N_6$ [M + H]⁺: 641.4326, found: 641.4325.

(S)-1-(1,5-dimethyl-1H-benzo[d]imidazol-2-yl)-N-((1-((1,5-dimethyl-1H-

benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L3):



Yellow solid; m.p.= 84.7-86.1 °C;¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.14 – 7.02 (m, 4H), 6.68 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.17 (d, *J* = 13.2 Hz, 1H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.71 (d, *J* = 3.6 Hz, 1H), 3.62 (d, *J* = 4.4 Hz, 1H), 3.59 – 3.57 (m, 4H), 3.54 (d, *J* = 4.0 Hz, 1H), 3.48 (s, 3H), 2.74 – 2.54 (m, 5H), 2.46 (s, 6H), 2.34 – 2.13 (m, 4H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.19, 151.62, 142.45, 142.40, 138.06, 136.78, 136.45, 134.34, 134.33, 131.56, 131.38, 129.74, 126.14, 124.06, 123.82, 119.28, 119.23, 113.79, 108.62, 108.59, 62.35, 59.86, 59.36, 54.76, 52.32, 52.16, 30.49, 30.00, 29.76, 22.40, 21.52; HRMS-ESI (m/z): calcd for C₃₄H₄₁N₆ [M + H]⁺: 533.3387, found: 533.3387.

(*S*)-1-(5-bromo-1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((5-bromo-1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L4):



Yellow solid; m.p.= 85.3-87.2 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.80 (m, 2H), 7.38 – 7.27 (m, 4H), 7.25 – 7.18 (m, 2H), 7.12 – 7.08 (m, 1H), 7.06 – 7.02 (m, 1H), 6.68 (ddd, *J* = 18.0, 11.2, 2.8 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.18 – 4.10 (m, 1H), 3.81 - 3.72 (m, 1H), 3.71 - 3.58 (m, 3H), 3.53 - 3.48 (m, 7H), 2.70 (t, *J* = 8.4 Hz, 2H), 2.63 - 2.54 (m, 2H), 2.50 - 2.45 (m, 1H), 2.32 - 2.22 (m, 1H), 2.11 - 1.87 (m, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 153.35, 152.87, 143.37, 137.72, 136.92, 136.35, 135.14, 135.08, 129.73, 126.18, 125.66, 125.46, 122.31, 122.23, 114.96, 114.83, 113.96, 110.35, 110.32, 62.33, 59.88, 59.37, 54.83, 52.21, 51.83, 30.43, 30.11, 29.97, 22.43; HRMS-ESI (m/z): calcd for $C_{32}H_{35}Br_2N_6$ [M + H]⁺: 661.1284, found: 661.1283. (S)-1-(pyridin-2-yl)-*N*-((1-(pyridin-2-ylmethyl)pyrrolidin-2-yl)methyl)-*N*-(4-

vinylbenzyl)methanamine (L5):



Yellow solid; m.p.= 74.0-76.1 °C;¹H NMR (400 MHz, Chloroform-*d*) δ 8.52 – 8.48 (m, 2H), 7.64 – 7.56 (m, 2H), 7.55 – 7.49 (m, 1H), 7.39 – 7.24 (m, 5H), 7.16 – 7.06 (m, 2H), 6.68 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.20 (d, *J* = 11.2 Hz, 1H), 4.37 – 4.10 (m, 1H), 3.82 – 3.68 (m, 2H), 3.68 – 3.39 (m, 3H), 2.82 – 2.37 (m, 3H), 2.25 – 2.14 (m, 1H), 2.10 – 1.83 (m, 2H), 1.76 – 1.50 (m, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 160.22, 148.92, 148.78, 139.04, 136.66, 136.37, 136.35, 136.32, 129.19, 126.09, 123.07, 123.00, 121.89, 121.79, 113.35, 62.35, 61.30, 61.16, 59.44, 59.02, 54.87, 30.11, 22.57; HRMS-ESI (m/z): calcd for C₂₆H₃₁N₄ [M + H]⁺: 399.2543, found: 399.2540.

(S)-N-((1-methyl-1H-benzo[d]imidazol-2-yl)methyl)-N-((1-((1-methyl-1Hbenzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-2-(4'-vinyl-[1,1'-biphenyl]-4yl)ethan-1-amine (L6):



Yellow solid; m.p.= 135.5-137.9 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 1H), 7.39 – 7.32 (m, 4H), 7.31 (s, 1H), 7.25 – 7.20 (m, 3H), 6.71 (dd, *J* = 17.6, 11.2 Hz,

1H), 5.75 (d, J = 17.6 Hz, 0H), 5.26 (d, J = 10.8 Hz, 0H), 4.62 (s, 1H), 4.24 (d, J = 13.2 Hz, 1H), 3.83 – 3.71 (m, 1H), 3.69 (d, J = 13.6 Hz, 1H), 3.65 (d, J = 13.6 Hz, 1H), 3.61 (s, 3H), 3.56 (d, J = 13.2 Hz, 1H), 3.51 (s, 3H), 2.77 – 2.66 (m, 3H), 2.53 (dd, J = 12.8, 7.2 Hz, 1H), 2.35 – 2.24 (m, 1H), 2.02 – 1.94 (m, 1H), 1.63 – 1.56 (m, 1H), 1.54 – 1.47 (m, 1H), 1.45 – 1.38 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 152.19, 151.71, 141.82, 141.70, 137.96, 137.49, 136.81, 136.42, 136.07, 136.02, 129.77, 128.75, 128.60, 128.42, 126.18, 122.74, 122.52, 122.11, 121.98, 119.42, 119.33, 113.88, 109.16, 62.32, 59.85, 59.39, 54.76, 52.03, 51.91, 46.30, 30.48, 30.03, 29.76, 22.38; HRMS-ESI (m/z): calcd for C₃₂H₃₇N₆ [M + H]⁺: 595.3544, found: 595.3540.

(1*R*,2*S*)-1-hydroxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2a):



White solid; m.p.= 129.1-130.7 °C;⁸ 64% yield, 99.1% *ee*, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.33 – 7.24 (m, 4H), 7.15 (d, *J* = 7.2 Hz, 1H), 5.13 (d, *J* = 8.4 Hz, 1H), 3.47 (d, *J* = 16.0 Hz, 1H), 3.40 (s, 1H), 3.15 (t, *J* = 6.0 Hz, 2H), 2.96 (d, *J* = 16.4 Hz, 1H), 2.56 (dt, *J* = 13.6, 7.2 Hz, 1H), 2.23 (dt, *J* = 13.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.90, 144.42, 143.28, 138.68, 133.74, 131.72, 128.72, 128.33, 128.01, 127.40, 126.87, 124.83, 123.75, 82.79, 58.06, 39.30, 33.24, 26.50; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254nm, *t* (major) = 11.225 min, *t* (minor) = 15.045 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₇O₂ [M + H]⁺: 265.1223, found: 265.1224.

(1'*R*,2*R*)-1'-hydroxy-1',3'-dihydro-2,2'-spirobi[inden]-1(3*H*)-one (2b):



White solid; m.p.= 127.4-128.8 °C; 42% yield, 99.0% *ee*, 10:1 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.63 (td, *J* = 7.6, 1.2 Hz, 1H), 7.48 – 7.38 (m, 3H),

7.34 – 7.27 (m, 3H), 5.03 (d, J = 5.2 Hz, 1H), 3.62 (d, J = 15.6 Hz, 1H), 3.29 (d, J = 16.8 Hz, 2H), 3.10 (d, J = 17.2 Hz, 1H), 2.89 (d, J = 15.6 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 208.36, 152.86, 143.38, 141.66, 136.46, 135.32, 128.90, 127.85, 127.43, 126.49, 125.02, 124.83, 124.37, 83.50, 77.39, 77.07, 76.76, 60.37, 41.54, 41.52; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254nm, t (major) = 13.826 min, t (minor) = 21.649 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₅O₂ [M + H]⁺: 251.1067, found: 251.1069.

(1'*R*,6*S*)-1'-hydroxy-1',3',8,9-tetrahydrospiro[benzo[7]annulene-6,2'-inden]-5(7*H*)one (2c):



White solid; m.p.= 129.9-131.4 °C; 38% yield, 46.6% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.34 (m, 2H), 7.31 – 7.20 (m, 4H), 7.18 – 7.14 (m, 2H), 5.03 (d, *J* = 8.4 Hz, 1H), 3.50 (d, *J* = 9.2 Hz, 1H), 3.41 (d, *J* = 16.4 Hz, 1H), 3.04 – 2.94 (m, 1H), 2.92 – 2.80 (m, 2H), 2.18 – 2.07 (m, 1H), 2.06 – 1.97 (m, 2H), 1.98 – 1.88 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 213.80, 143.56, 140.91, 140.02, 137.83, 131.18, 128.85, 128.53, 127.49, 127.28, 126.74, 124.84, 124.63, 83.04, 62.55, 40.77, 34.63, 33.41, 23.93; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 254nm, *t* (major) = 11.670 min, *t* (minor) = 18.850 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₉O₂ [M + H]⁺: 279.1380, found: 279.1379.

(1*R*,2*S*)-7'-chloro-1-hydroxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2d):



White solid; m.p.= 139.5-140.8 °C; 59% yield, 98.0% *ee*, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 2.4 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.34 – 7.19 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 5.14 (d, *J* = 11.2 Hz, 1H), 3.48 (d, *J* = 16.0 Hz, 1H), 3.27 – 3.00 (m, 3H), 2.93 (d, *J* = 16.4 Hz, 1H), 2.52 (ddd, *J* = 14.0, 8.8, 5.6 Hz, 1H), 2.36 – 2.10 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 199.47, 143.97, 141.43, 138.60, 133.58, 133.09, 133.02,

130.27, 128.50, 127.68, 127.49, 124.86, 123.81, 82.53, 57.99, 39.28, 33.02, 25.92; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 80:20, flow rate=1 mL/min, wavelength = 254nm, t (major) = 12.906 min, t (minor) = 13.992 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₆ClO₂ [M + H]⁺: 299.0833, found: 299.0830.

(1*R*,2*S*)-7'-bromo-1-hydroxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2e):



White solid; m.p.= 178.4-179.3 °C;⁸ 66% yield, 97.7% *ee*, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.42 (d, *J* = 6.8 Hz, 1H), 7.33 – 7.20 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.13 (d, *J* = 10.4 Hz, 1H), 3.48 (d, *J* = 16.4 Hz, 1H), 3.25 – 2.98 (m, 3H), 2.91 (d, *J* = 16.4 Hz, 1H), 2.50 (ddd, *J* = 13.6, 8.8, 5.2 Hz, 1H), 2.23 (dt, *J* = 13.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 199.33, 143.92, 141.94, 138.68, 136.40, 133.32, 130.72, 130.56, 128.51, 127.48, 124.86, 123.85, 120.87, 82.47, 57.98, 39.31, 32.96, 25.98; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 80:20, flow rate=1 mL/min, wavelength = 254nm, *t* (major) = 10.969 min, *t* (minor) = 15.069 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₆BrO₂ [M + H]⁺: 343.0328, found: 343.0330.

(1*R*,2*S*)-7'-fluoro-1-hydroxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2f):



White solid; m.p.= 152.3-154.2 °C; 65% yield, 99.2% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.36 – 7.13 (m, 5H), 5.15 (d, *J* = 11.2 Hz, 1H), 3.49 (d, *J* = 16.0 Hz, 1H), 3.25 – 3.00 (m, 3H), 2.94 (d, *J* = 16.0 Hz, 1H), 2.52 (ddd, *J* = 13.6, 8.4, 5.2 Hz, 1H), 2.24 (dt, *J* = 13.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 199.65, 199.64, 162.91, 160.46, 144.03, 138.97, 138.94, 138.66, 133.37, 133.31, 130.57, 130.50, 128.48, 127.47, 127.42, 124.86, 123.80, 123.77, 121.22, 121.00, 113.88, 113.66, 82.53, 57.91, 39.27, 33.26, 25.78; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 80:20, flow rate=1 mL/min,

wavelength = 254nm, t (major) = 11.369 min, t (minor) = 13.156 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₆FO₂ [M + H]⁺: 283.1129, found: 283.1134.

(1R,2S)-1-hydroxy-7'-methoxy-1,3,3',4'-tetrahydro-1'H-spiro[indene-2,2'-

naphthalen]-1'-one (2g):



White solid; m.p.= 118.5-119.1 °C;⁸ 69% yield, 99.1% *ee*, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.33 – 7.20 (m, 2H), 7.17 (t, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.47 (d, *J* = 16.0 Hz, 1H), 3.34 (s, 1H), 3.08 (t, *J* = 5.6 Hz, 2H), 2.96 (d, *J* = 16.0 Hz, 1H), 2.53 (dt, *J* = 14.0, 7.2 Hz, 1H), 2.22 (dt, *J* = 13.2, 5.2 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.85, 158.50, 144.41, 138.69, 135.84, 132.43, 129.93, 128.32, 127.38, 124.83, 123.72, 122.27, 109.75, 82.66, 58.00, 55.44, 39.25, 33.42, 25.68; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 254nm, *t* (major) = 24.059 min, *t* (minor) = 21.024 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₉O₃ [M + H]⁺: 295.1329, found: 295.1332.

(1R,2S)-1-hydroxy-6'-methoxy-1,3,3',4'-tetrahydro-1'H-spiro[indene-2,2'-

naphthalen]-1'-one (2h):



White solid; m.p.= 125.7-128.1°C; 65% yield, 99.1% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.20 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 3H), 3.57 – 3.50 (m, 1H), 3.44 (d, *J* = 16.0 Hz, 1H), 3.12 – 3.08 (m, 2H), 2.96 (d, *J* = 16.4 Hz, 1H), 2.61 – 2.48 (m, 1H), 2.19 (dt, *J* = 13.6, 5.2 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 199.81, 163.92, 145.83, 144.62, 138.77, 130.51, 128.23, 127.32, 125.20, 124.77, 123.70, 113.51, 112.42, 82.94, 57.62, 55.50, 39.56, 33.43, 26.93; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 254nm, *t* (major) = 20.135 min, *t* (minor) = 28.245 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₉O₃ [M + H]⁺: 295.1329, found: 295.1333.

(1*R*,2*S*)-1-hydroxy-7'-methyl-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2i):



White solid; m.p.= 137.8-139.4 °C; 67% yield, 99.0% *ee*, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.36 – 7.20 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 2H), 5.11 (d, *J* = 10.4 Hz, 1H), 3.46 (d, *J* = 16.4 Hz, 1H), 3.39 (d, *J* = 10.8 Hz, 1H), 3.16 – 3.06 (m, 2H), 2.96 (d, *J* = 16.0 Hz, 1H), 2.63 – 2.46 (m, 1H), 2.35 (s, 3H), 2.21 (dt, *J* = 13.6, 4.8 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 201.22, 144.43, 140.35, 138.71, 136.53, 134.77, 131.45, 128.64, 128.29, 128.06, 127.36, 124.81, 123.75, 82.74, 58.01, 39.28, 33.32, 26.07, 20.98; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 254nm, *t* (major) = 11.932 min, *t* (minor) = 14.825 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₉O₂ [M + H]⁺: 279.1380, found: 279.1387.

(1*R*,2*S*)-1-hydroxy-4'-methyl-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2j):



White solid; m.p.= 140.7-142.4 °C; 52% yield, 99.0% *ee*, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.56 (td, *J* = 7.6, 1.6 Hz, 1H), 7.44 – 7.23 (m, 6H), 5.27 (d, *J* = 9.6 Hz, 1H), 3.92 (d, *J* = 16.4 Hz, 1H), 3.64 – 3.21 (m, 1H), 2.67 (d, *J* = 16.4 Hz, 1H), 2.33 – 2.20 (m, 2H), 2.05 (dd, *J* = 14.0, 10.4 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.08, 147.65, 142.44, 141.58, 133.70, 132.17, 128.98, 127.79, 127.25, 126.91, 126.68, 125.02, 124.93, 81.22, 58.29, 42.40, 41.34, 29.46, 21.23; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 80:20, flow rate=1 mL/min, wavelength = 254nm, *t* (major) = 14.341 min, *t* (minor) = 17.683 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₉O₂ [M + H]⁺: 279.1380, found: 279.1383. **((15,25)-1-hydroxy-2,3-dihydro-1***H***-inden-2-yl)(phenyl)methanone (2k):**



White solid; m.p.= 105.3-106.7 °C;⁸ 66% yield, 98.0% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.31 – 7.28 (m, 3H), 5.50 (t, *J* = 6.0 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 1H), 3.60 (dd, *J* = 16.0, 7.6 Hz, 1H), 3.24 – 2.97 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.64, 143.36, 141.67, 136.90, 133.41, 128.98, 128.83, 128.38, 127.30, 125.00, 124.66, 77.26, 51.33, 33.31; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 29.460 min, *t* (minor) = 35.160 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₅O₂ [M + H]⁺: 239.1067, found: 239.1074.

(3-chlorophenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2m):



White solid; m.p.= 142.3-144.5 °C; 63% yield, 95.6% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 2.4 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.57 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.33 – 7.22 (m, 3H), 5.49 (d, *J* = 6.0 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 1H), 3.63 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.11 (ddd, *J* = 16.4, 8.4 Hz, 1H), 2.73 (s, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 198.96, 142.99, 141.55, 138.54, 135.16, 133.24, 130.14, 129.17, 128.46, 127.38, 126.39, 125.06, 124.67, 77.27, 51.73, 32.88; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 21.710 min, *t* (minor) = 24.695 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₄ClO₂ [M + H]⁺: 273.0677, found: 273.0684.

(4-chlorophenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2n):



White solid; m.p.= 161.0-161.9 °C;⁸ 65% yield, 98.1% *ee*, 14:1 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.92 (m, 2H), 7.52 – 7.46 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.33 – 7.27 (m, 3H), 5.49 (d, *J* = 6.4 Hz, 1H), 4.30 (q, *J* = 7.6, 1H), 3.61 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.12 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.80 (s, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 199.16,

143.10, 141.53, 139.83, 135.25, 129.75, 129.14, 129.12, 129.06, 128.71, 127.38, 125.04, 124.64, 77.29, 51.45, 33.07; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, t (major) = 22.000 min, t (minor) = 24.061 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₄ClO₂ [M + H]⁺: 273.0677, found: 273.0681.

(4-bromophenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2o):

White solid; m.p.= 141.7-142.9 °C;⁸ 66% yield, 98.1% ee, 5:1 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.44 – 7.40 (m, 1H), 7.32 – 7.24 (m, 3H), 5.49 (t, *J* = 6.4 Hz, 1H), 4.29 (td, *J* = 8.0, 6.4 Hz, 1H), 3.61 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.12 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.80 (d, *J* = 7.6 Hz, 1H);¹³C NMR (100 MHz, Chloroform-*d*) δ 199.33, 143.07, 141.53, 135.67, 132.14, 129.84, 129.14, 128.55, 127.38, 125.04, 124.64, 77.28, 51.47, 33.02; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 23.600 min, *t* (minor) = 25.364 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₄BrO₂ [M + H]⁺: 317.0172, found: 317.0177.

(4-fluorophenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1H-inden-2-yl)methanone (2p):



White solid; m.p.= 105.9-106.8 °C;⁸ 57% yield, 96.6% *ee*, 5:1 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.08 (m, 2H), 7.49 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.27 – 7.20 (m, 2H), 5.55 (dd, *J* = 8.0, 6.0 Hz, 1H), 4.36 (td, *J* = 8.0, 6.0 Hz, 1H), 3.66 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.18 (dd, *J* = 16.4, 8.4 Hz, 1H), 3.07 – 2.83 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 198.86, 167.19, 164.65, 143.17, 141.53, 133.32, 133.29, 131.05, 130.96, 129.09, 127.36, 125.02, 124.63, 116.06, 115.84, 77.30, 51.29, 33.22; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 85:15, flow rate=0.8 mL/min, wavelength = 254 nm, *t* (major) = 19.379 min, *t* (minor) = 21.443 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₄FO₂ [M + H]⁺: 257.0972, found: 257.0970.

((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)(3-methoxyphenyl)methanone (2q):



White solid; m.p.= 103.7-104.7 °C;⁸ 71% yield, 98.0% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 1H), 7.55 (dd, *J* = 2.4, 1.6 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.32 – 7.24 (m, 3H), 7.18 – 7.10 (m, 1H), 5.48 (d, *J* = 6.0 Hz, 1H), 4.31 (td, *J* = 8.0, 6.4 Hz, 1H), 3.85 (s, 3H), 3.61 (dd, *J* = 16.4, 8.0 Hz, 1H), 3.14 (td, *J* = 16.0, 8.4 Hz, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.33, 160.00, 143.29, 141.71, 138.26, 129.79, 128.99, 127.28, 125.00, 124.67, 120.93, 119.84, 112.73, 77.33, 55.48, 51.54, 33.24; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 25.665 min, *t* (minor) = 19.359 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₇O₃ [M + H]⁺: 269.1172, found: 269.1176.

((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)(4-methoxyphenyl)methanone (2r):

MeO HO

White solid; m.p.= 153.3-154.7 °C;⁸ 70% yield, 98.4% *ee*, >95:5 dr; H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.47 – 7.42 (m, 1H), 7.29 – 7.27 (m, 3H), 7.02 – 6.94 (m, 2H), 5.48 (d, *J* = 6.0 Hz, 1H), 4.29 (ddd, *J* = 8.4, 7.6, 6.0 Hz, 1H), 3.89 (s, 3H), 3.56 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.35 (s, 1H), 3.15 (dd, *J* = 16.0, 8.4 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.46, 144.34, 143.49, 141.67, 134.36, 129.52, 128.90, 128.52, 127.26, 124.96, 124.63, 77.27, 51.01, 33.55, 21.72; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 22.620 min, *t* (minor) = 25.238 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₇O₃ [M + H]⁺: 269.1172, found: 269.1170.

((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)(*p*-tolyl)methanone (2s):



White solid; m.p.= 120.6-121.9 °C;⁸ 74% yield, 98.1% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.39 (m, 1H), 7.33 – 7.26 (m, 5H), 5.49 (d, *J* = 6.4 Hz, 1H), 4.31 (td, *J* = 8.0, 6.0 Hz, 1H), 3.58 (dd, *J* = 16.0, 7.6 Hz, 1H), 3.22 (s, 1H), 3.14 (dd, *J* = 16.0, 8.4 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.46,

144.34, 143.49, 141.67, 134.36, 129.52, 128.90, 128.52, 127.26, 124.96, 124.63, 77.27, 51.01, 33.55, 21.72; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 80:20, flow rate=1 mL/min, wavelength = 254 nm, t (major) = 20.769 min, t (minor) = 22.726 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₇O₂ [M + H]⁺: 253.1223, found: 253.1227.

(3,4-dimethylphenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2t):

White solid; m.p.= 106.1-107.0 °C;⁸ 68% yield, 96.5% ee, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.77 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.36 – 7.22 (m, 4H), 5.48 (d, *J* = 4.0 Hz, 1H), 4.32 (td, *J* = 8.0, 6.0 Hz, 1H), 3.57 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.34 – 3.02 (m, 2H), 2.35 (s, 6H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.78, 143.54, 143.12, 141.72, 137.22, 134.75, 130.04, 129.52, 128.87, 127.24, 126.13, 124.96, 124.62, 77.28, 50.94, 33.65, 20.10, 19.89; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 80:20, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 25.815 min, *t* (minor) = 24.217 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₉O₂ [M + H]⁺: 267.1380, found: 267.1380.

(4-ethylphenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2u):

White solid; m.p.= 94.3-95.2 °C;⁸ 57% yield, 97.3% *ee*, >95:5 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.93 (m, 2H), 7.49 – 7.39 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.23 (m, 3H), 5.48 (d, *J* = 6.0 Hz, 1H), 4.46 – 4.16 (m, 1H), 3.58 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.23 (s, 1H), 3.14 (ddd, *J* = 16.4, 8.4, 2.8 Hz, 1H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 200.43, 150.46, 143.51, 141.71, 134.58, 128.89, 128.64, 128.35, 127.25, 124.97, 124.65, 77.27, 51.06, 33.52, 29.02, 15.21; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 80:20, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 18.938 min, *t* (minor) = 21.016 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₉O₂ [M + H]⁺: 267.1380, found: 267.1385.

((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)(4-(trifluoromethyl)phenyl)methanone (2v):



White solid; m.p.= 188.5-189.4 °C;⁸ 64% yield, 92.5% ee, 4:1 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.27 (m, 3H), 5.52 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.36 (td, *J* = 8.0, 6.4 Hz, 1H), 3.67 (dd, *J* = 16.4, 7.6 Hz, 1H), 3.13 (dd, *J* = 16.4, 8.4 Hz, 1H), 2.58 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 199.19, 142.85, 141.55, 139.77, 134.69, 134.37, 129.29, 128.61, 127.44, 125.93, 125.90, 125.86, 125.82, 125.11, 124.67, 77.26, 52.06, 32.66; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 92:8, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 15.646 min, *t* (minor) = 19.006 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₄FO₂ [M + H]⁺: 307.0940, found: 307.0938.

Ethyl (1S,2S)-1-hydroxy-2,3-dihydro-1H-indene-2-carboxylate (2w):



Colorless oil; 34% yield, 78.5% ee, 94:6 dr; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.40 (m, 1H), 7.32 – 7.22 (m, 3H), 5.34 (d, *J* = 5.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.50 – 3.32 (m, 2H), 3.10 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.91 (s, 1H), 1.32 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 173.11, 142.68, 141.83, 129.08, 127.21, 125.02, 124.90, 75.85, 60.94, 49.47, 32.89, 14.27; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 85:15, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 13.066 min, *t* (minor) = 15.404 min]; HRMS-ESI (m/z): calcd for C₁₂H₁₅O₃ [M + H]⁺: 207.1016, found: 207.1012.

(S)-3',4'-dihydro-1'H-spiro[indene-2,2'-naphthalene]-1,1'(3H)-dione (3a):



White solid; m.p.= 110.5-111.3 °C;⁹ 85% yield, 97.0% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.64 (td, *J* = 7.6, 1.2 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.29 (m, 2H), 3.86 (d, *J* =

17.2 Hz, 1H), 3.51 (ddd, J = 17.2, 8.8, 4.8 Hz, 1H), 3.15 – 2.95 (m, 2H), 2.57 (ddd, J = 14.0, 6.8, 5.2 Hz, 1H), 2.33 (ddd, J = 13.6, 8.8, 4.8 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 204.11, 196.41, 152.93, 144.29, 135.26, 135.21, 133.86, 131.47, 128.83, 128.17, 127.83, 126.81, 126.48, 124.68, 61.10, 38.01, 32.20, 25.50; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 16.618 min, *t* (minor) = 22.762 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₅O₂ [M + H]⁺: 263.1067, found: 263.1064.

(*R*)-2,2'-spirobi[indene]-1,1'(3*H*,3'*H*)-dione (3b):



White solid; m.p.= 171.4-172.3 °C;¹⁰ 71% yield, 96.0% *ee*; ¹H NMR (400 MHz, Chloroform*d*) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.65 (td, *J* = 7.6, 1.2 Hz, 2H), 7.56 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.46 – 7.37 (m, 2kH), 3.73 (d, *J* = 17.2 Hz, 2H), 3.19 (d, *J* = 16.8Hz, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 202.72, 153.86, 135.47, 135.30, 127.82, 126.38, 124.93, 65.35, 38.09; Determined by HPLC analysis [Daicel chiralpak IC, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 19.288 min, *t* (minor) = 34.535 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₃O₂ [M + H]⁺: 249.0910, found: 249.0906.

(S)-8,9-dihydrospiro[benzo[7]annulene-6,2'-indene]-1',5(3'H,7H)-dione (3c):



White solid; m.p.= 157.1-159.4 °C;79% yield, 45.0% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 (p, *J* = 7.2 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 3.64 (d, *J* = 16.8 Hz, 1H), 3.22 (d, *J* = 16.8 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.90 – 2.74 (m, 1H), 2.53 – 2.25 (m, 1H), 2.10 – 1.93 (m, 2H), 1.79 (dt, *J* = 14.8, 4.4 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 209.77, 204.97, 153.49, 140.14, 137.43, 135.22, 134.92, 132.03, 128.41, 127.81, 127.54, 127.15, 126.50, 124.91, 64.41, 36.66, 31.42, 30.04, 22.44; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254

nm, t (major) = 21.517 min, t (minor) = 26.959 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₇O₂ [M + H]⁺: 277.1223, found: 277.1228.

(S)-7'-bromo-3',4'-dihydro-1'H-spiro[indene-2,2'-naphthalene]-1,1'(3H)-dione (3e):



White solid; m.p.= 139.7-142.1 °C; 84% yield, 95.1% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 3.86 (d, *J* = 16.8 Hz, 1H), 3.45 (ddd, *J* = 17.2, 9.6, 5.2 Hz, 1H), 3.00 (d, *J* = 16.8 Hz, 1H), 2.92 (dt, *J* = 17.2, 5.6 Hz, 1H), 2.50 (dt, *J* = 13.6, 5.6 Hz, 1H), 2.31 (ddd, *J* = 14.4, 9.6, 5.2 Hz, 1H); ¹³ C NMR (100 MHz, Chloroform-*d*) δ 203.46, 195.03, 152.84, 143.07, 136.55, 135.39, 134.88, 132.93, 130.84, 130.68, 127.93, 126.51, 124.75, 120.75, 60.85, 37.88, 32.07, 25.01; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 28.432 min, *t* (minor) = 40.066 min]; HRMS-ESI (m/z): calcd for C₁₈H₁₄BrO₂ [M + H]⁺: 341.0172, found: 341.0177.

(S)-7'-methyl-3',4'-dihydro-1'H-spiro[indene-2,2'-naphthalene]-1,1'(3H)-dione (3i):



White solid; m.p.= 117.3-119.4 °C;87% yield, 97.0% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.2, 1.2 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 3.81 (d, *J* = 17.2 Hz, 1H), 3.41 (ddd, *J* = 17.2, 8.8, 4.8 Hz, 1H), 3.03 (d, *J* = 17.2 Hz, 1H), 2.95 (ddd, *J* = 16.8, 6.8, 4.8 Hz, 1H), 2.52 (ddd, *J* = 13.6, 6.8, 4.8 Hz, 1H), 2.36 (s, 3H), 2.27 (ddd, *J* = 13.6, 8.8, 4.8 Hz, 1H); ¹³ C NMR (100 MHz, Chloroform-*d*) δ 204.23, 196.67, 152.96, 141.41, 136.46, 135.30, 135.17, 134.89, 131.25, 128.75, 128.18, 127.79, 126.49, 124.64, 61.12, 37.98, 32.35, 25.12, 20.98; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 15.386 min, *t* (minor) = 24.238 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₇O₂ [M + H]⁺: 277.1223, found: 277.1225.

4-([1,1'-biphenyl]-4-yl)-4-oxobutanoic acid (3x):


White solid; m.p.= 185.1-187.2 °C;¹¹ 74% yield; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.18 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 1H), 3.29 (t, *J* = 6.0 Hz, 2H), 2.62 (dd, *J* = 6.8, 5.6 Hz, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 198.51, 174.32, 145.01, 139.37, 135.72, 129.58, 129.06, 128.86, 127.46, 127.38, 33.60, 28.36; HRMS-ESI (m/z): calcd for C₁₆H₁₅O₃ [M + H]⁺: 255.1016, found: 255.1020.

(2R,3S)-3-Phenyloxiran-2-yl)-phenylmethanone (5aa):



White solid; m.p.= 78.2-82.9 °C;¹² 96% yield, 99.3% *ee;* ¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 7.75 (m, 2H), 7.65 – 7.60 (m, 1H), 7.49 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.45 – 7.35 (m, 5H), 4.30 (d, *J* = 2.0 Hz, 1H), 4.08 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.12, 135.49, 134.04, 129.10, 128.92, 128.81, 128.39, 125.82, 61.05, 59.43; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 15.366min, *t* (minor) = 13.802min]; HRMS-ESI (m/z): calcd for C₁₅H₁₃O₂ [M + H]⁺: 225.0910, found: 225.0911.

(2R,3S)-3-(2-Chlorophenyl)oxiran-2-yl)-phenylmethanone (5ab):



Colorless oil; 94% yield, 98.1% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.40 (m, 2H), 7.36 – 7.31 (m, 2H), 4.41 (d, *J* = 1.6 Hz, 1H), 4.17 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.81, 135.37, 134.10, 133.80, 133.33, 129.79, 129.36, 128.90, 128.43, 127.29, 126.15, 60.07, 57.19; Determined by HPLC analysis [Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 95:5, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 23.604 min, *t* (minor) = 25.076 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂ClO₂ [M + H]⁺: 259.0520, found: 259.0519.

(2R,3S)-3-(3-Chlorophenyl)oxiran-2-yl)-phenylmethanone (5ac):



White solid; m.p.= 68.9-74.1 °C;¹² 95% yield, 99.4% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 4.25 (s, 1H), 4.06 (s, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.76, 135.38, 134.99, 134.15, 134.06, 129.06, 128.96, 128.38, 127.15, 60.96, 58.72; Determined by HPLC analysis [Daicel chiralpak OD-H, 25 °C, hexane/ isopropanol 98:2, flow rate=0.8 mL/min, wavelength = 254 nm, *t* (major) = 27.918 min, *t* (minor) = 25.883 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂ClO₂ [M + H]⁺: 259.0520, found: 259.0520.

(2R,3S)-3-(4-Chlorophenyl)oxiran-2-yl)-phenylmethanone (5ad):



White solid; m.p.= 113.3-115.7 °C;¹² 96% yield, 99.2% *ee*; ¹H NMR (400 MHz, Chloroform*d*) δ 8.02 – 7.97 (m, 2H), 7.65 – 7.60 (m, 1H), 7.53 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 4.25 (d, *J* = 2.0 Hz, 1H), 4.06 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.75, 135.38, 134.97, 134.14, 134.07, 129.05, 128.96, 128.37, 127.15, 60.94, 58.71; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 13.716 min, *t* (minor) = 12.597min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂ClO₂ [M + H]⁺: 259.0520, found: 259.0519.

(2R,3S)-3-(2-Methoxyphenyl)oxiran-2-yl)-phenylmethanone (5ae):

Colorless oil; 80% yield, 99.0% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.94 (m, 2H), 7.68 – 7.56 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.33 (ddd, *J* = 16.0, 8.0 1.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.39 (d, *J* = 1.6 Hz, 1H), 4.19 (d, *J* = 2.0 Hz, 1H), 3.84 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.69, 158.22, 135.70, 133.79, 129.69, 128.76, 128.42, 125.55, 124.26, 120.81, 110.33, 60.50, 55.77, 55.38. Determined

by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 93:7, flow rate=1 mL/min, wavelength = 254 nm, t (major) = 18.616 min, t (minor) = 16.328 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₅O₃ [M + H]⁺: 255.1016, found: 255.1016.

(2R,3S)-3-(3-Methoxyphenyl)oxiran-2-yl)-phenylmethanone (5af):



Colorless oil; 88% yield, 93.1% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.65 – 7.60 (m, 1H), 7.52 – 7.47 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 6.97 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.94 – 6.89 (m, 2H), 4.28 (d, *J* = 2.0 Hz, 1H), 4.06 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.05, 160.08, 137.16, 135.47, 134.05, 129.92, 128.92, 128.39, 118.24, 114.78, 110.85, 60.97, 59.34, 55.36; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 93:7, flow rate=1 mL/min, wavelength = 254 n *t* (major) = 21.998 min, *t* (minor) = 23.609 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₅O₃ [M + H]⁺: 255.1016, found: 255.1016.

(2R,3S)-3-(4-Bromophenyl)oxiran-2-yl)-(phenyl)methanone (5ag):



White solid; m.p.= 90.3-92.7 °C;¹² 96% yield, 99.3% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.58 – 7.48 (m, 4H), 7.31 – 7.23 (m, 2H), 4.27 (s, 1H), 4.07 (s, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.72, 135.37, 134.61, 134.16, 132.00, 128.97, 128.38, 127.45, 123.10, 60.91, 58.77; Determined by HPLC analysis [Daicel chiralpak OD-H, 25 °C, hexane/ isopropanol 92:8, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 17.376 min, *t* (minor) = 15.541 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂BrO₂ [M + H]⁺: 303.0015, found: 303.0016.

(2R,3S)-3-(4-Trifluorophenyl)oxiran-2-yl)-phenylmethanone (5ah):



White solid; m.p.= 107.2-110.2 °C;¹² 97% yield, 99.1% *ee*; ¹H NMR (400 MHz, Chloroform*d*) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.66 (m, 3H), 7.57 – 7.45 (m, 4H), 4.28 (s, 1H), 4.15 (s, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.48, 139.60, 135.31, 134.25, 131.38, 131.05, 129.00, 128.40, 126.13, 125.88, 125.84, 125.80, 125.77, 125.25, 122.54, 60.91, 58.48; Determined by HPLC analysis [Daicel chiralpak OD-H, 25 °C, hexane/ isopropanol 92:8, flow rate=1 mL/min, wavelength = 254 nm, t (major) = 15.051 min, t (minor) = 13.435 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₂F₃O₂[M + H] ⁺: 293.0784, found: 293.0784.

4-((2S,3R)-3-benzoyloxiran-2-yl)benzonitrile (5ai):

White solid; m.p.= 93.5-97.2 °C;¹³ 95% yield, 91.6% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.95 (m, 2H), 7.73 – 7.62 (m, 3H), 7.55 – 7.46 (m, 4H), 4.25 (d, *J* = 1.6 Hz, 1H), 4.15 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.20, 140.88, 135.24, 134.34, 132.64, 129.03, 128.49, 128.42, 126.48, 118.34, 112.89, 60.86, 58.24; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 21.439 min, *t* (minor) = 19.222 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₂NO₂[M + H] ⁺: 250.0863, found: 250.0863.

[(2R,3S)-3-[1,1'-biphenyl]-4-yloxiranyl]phenylmethanone (5aj):



White solid; m.p.= 127.2-132.5 °C; 95% yield, 98.3% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m, 2H), 7.66 – 7.59 (m, 5H), 7.53 – 7.44 (m, 6H), 7.41 – 7.36 (m, 1H), 4.36 (d, *J* = 1.6 Hz, 1H), 4.14 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.07, 142.13, 140.42, 135.51, 134.47, 134.06, 128.94, 128.91, 128.41, 127.68, 127.56, 127.14, 126.31, 61.09, 59.32; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 23.449 min, *t* (minor) = 24.980 min]; HRMS-ESI (m/z): calcd for C₂₁H₁₇O₂ [M+H]⁺: 301.1223, found 301.1220.

[(2R,3S)-3-(2-Naphthalenyl)-2-oxiranyl]phenylmethanone (5ak):



White solid; m.p.= 82.5-84.3 °C;¹³ 70% yield, 96.0% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.90 – 7.85 (m, 4H), 7.66 – 7.59 (m, 1H), 7.55 – 7.46 (m, 4H), 7.43

(dd, J = 8.4, 1.6 Hz, 1H), 4.40 (d, J = 1.6 Hz, 1H), 4.25 (d, J = 1.6 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.04, 134.02, 132.91, 128.92, 128.82, 128.38, 127.92, 127.87, 126.71, 126.63, 125.88, 122.46, 61.22, 59.67; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 22.504 min, *t* (minor) = 18.546 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₅O₂ [M+H]⁺: 275.1067, found 275.1066.

(2-Chlorophenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5al):

Colorless oil; 85% yield, 96.6% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.38 – 7.33 (m, 6H), 4.15 (d, *J* = 2.0 Hz, 1H), 4.09 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 196.32, 136.52, 135.28, 133.13, 132.19, 130.49, 130.17, 129.09, 128.74, 127.23, 125.87, 62.94, 60.47; Determined by HPLC analysis [Daicel chiralpak OJ-H, 25 °C, hexane/ isopropanol 98:2, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 35.370 min, *t* (minor) = 27.406 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂ClO₂ [M+H]⁺: 259.0520, found 259.0522.

(3-Chlorophenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5am):

CI

White solid; m.p.= 90.7-92.8 °C;¹⁴ 90% yield, 93.0% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (t, *J* = 2.0 Hz, 1H), 7.89 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.59 (m, 1H), 7.48 – 7.34 (m, 6H), 4.24 (d, *J* = 2.0 Hz, 1H), 4.08 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.14, 136.88, 135.31, 135.17, 133.96, 130.26, 129.23, 128.86, 128.42, 126.54, 125.83, 61.04, 59.55; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 13.657 min, *t* (minor) = 15.185 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂ClO₂ [M+H]⁺: 259.0520, found 259.0520.

(4-Chlorophenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5an):



White solid; m.p.= 92.5-94.7 °C;¹⁵ 87% yield, 92.8% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.94 (m, 2H), 7.49 – 7.45 (m, 2H), 7.43 – 7.34 (m, 5H), 4.23 (d, *J* = 2.0 Hz, 1H), 4.08 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 192.08, 140.65, 135.26, 133.71, 129.83, 129.28, 129.19, 128.85, 125.80, 61.10, 59.41; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 20.777 min, *t* (minor) = 17.564 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂ClO₂ [M+H]⁺: 259.0520, found 259.0520.

(2-Methoxyphenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5ao):



Yellow oil; 90% yield, 98.9% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.8, 7.6, 2.0 Hz, 1H), 7.44 – 7.31 (m, 5H), 7.05 (td, *J* = 7.6, 0.8 Hz, 1H), 6.93 (dd, *J* = 8.4, 0.8 Hz, 1H), 4.31 (d, *J* = 2.0 Hz, 1H), 4.01 (d, *J* = 2.0 Hz, 1H), 3.60 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 194.88, 159.58, 136.50, 134.90, 130.72, 128.70, 128.57, 125.98, 125.79, 121.04, 111.56, 64.56, 59.83, 55.60; Determined by HPLC analysis [Daicel chiralpak OJ-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 34.107 min, *t* (minor) = 31.814 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₅O₃ [M+H]⁺: 255.1016, found 255.1015.

(3-Methoxyphenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5ap):



Yellow oil; 94% yield, 99.0% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.60-7.57 (m, 1H), 7.53 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.43-7.35 (m, 6H), 7.16 (ddd, *J* = 8.0, 2.4, 0.8 Hz, 1H), 4.28 (d, *J* = 2.0 Hz, 1H), 4.08 (d, *J* = 2.0 Hz, 1H), 3.85 (s, 3H); ¹³C NMR (10 MHz, Chloroform-*d*) δ 192.92, 160.02, 136.77, 135.48, 129.91, 129.09, 128.80, 125.82, 121.03, 120.64, 112.42, 61.06, 59.49, 55.54; Determined by HPLC analysis [Daicel chiralpak OJ-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 29.026 min, *t* (minor) = 26.457 min]; HRMS-ESI (m/z): calcd for $C_{16}H_{15}O_3$ [M+H]⁺: 255.1016, found 255.1015.

(4-Methoxyphenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5aq):



White solid; m.p.= 68.2-71.0 °C;¹⁵ 93% yield, 98.2% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.92 (m, 2H), 7.38 (d, *J* = 4.8 Hz, 5H), 7.01 – 6.91 (m, 2H), 4.25 (s, 1H), 4.06 (s, 1H), 3.87 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 191.37, 164.26, 135.71, 130.79, 129.00, 128.77, 128.60, 125.82, 114.13, 60.88, 59.21, 55.59; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 92:8, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 57.452 min, *t* (minor) = 50.788 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₅O₃ [M+H]⁺: 255.1016, found 255.1015.

(4-Fluorophenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5ar):



White solid; m.p.= 93.9-96.1 °C;¹³ 88% yield, 98,2% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.44 – 7.33 (m, 5H), 7.16 (t, *J* = 8.4 Hz, 2H), 4.24 (s, 1H), 4.07 (s, 1H);¹³C NMR (100 MHz, Chloroform-*d*) δ 191.63, 167.54, 164.99 (d, *J* = 255 Hz), 135.33, 131.91, 131.88 (d, *J* = 3 Hz), 131.25, 131.15 (d, *J* = 10 Hz), 129.17, 128.84, 125.81, 116.27, 116.05 (d, *J* = 22 Hz), 61.08, 59.34; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 92:8, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 17.036 min, *t* (minor) = 20.576 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₂FO₂ [M+H]⁺: 243.0816, found 243.0816.

(Naphthalen-1-yl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5as):



White solid; m.p.= 120.1-121.8 °C;¹⁵ 80% yield, 94.0% *ee*; ¹H NMR (400 MHz, Chloroform*d*) δ 8.67 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.98 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.58 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.51 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.47 – 7.36 (m, 5H), 4.26 (d, *J* = 1.6 Hz, 1H), 4.15 (d, J = 2.0 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 196.26, 135.45, 133.92, 133.82, 133.01, 130.29, 129.10, 128.89, 128.80, 128.59, 128.49, 126.84, 125.87, 125.51, 124.35, 62.66, 59.70; Determined by HPLC analysis [Daicel chiralpak IA-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 20.242 min, *t* (minor) = 17.410 min]; HRMS-ESI (m/z): calcd for C₁₉H₁₅O₂ [M+H]⁺: 275.1067, found 275.1067.

[(2R,3S)-3-(4-Fluorophenyl)-2-oxiranyl](4-methylphenyl)methanone (5at):



White solid; m.p.= 77.8-82.6 °C; 93% yield, 98.6% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.21 (m, 4H), 7.09 (t, *J* = 8.0 Hz, 2H), 4.24 (s, 1H), 4.06 (s, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 192.41, 164.40, 161.94 (d, *J* = 246 Hz), 145.21, 133.00, 131.42, 131.39 (d, *J* = 3 Hz), 129.62, 128.49, 127.63, 127.55 (d, *J* = 5 Hz), 115.97, 115.75 (d, *J* = 22 Hz), 60.88, 58.73, 21.82; Determined by HPLC analysis [Daicel chiralpak OD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 34.340 min, *t* (minor) = 29.951 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₄FO₂ [M+H]⁺: 257.0972, found 257.0971.

(2R,3S)-4-Methylphenyl-3-(4-methylphenyl)-2-oxiran-methanone (5au):



White solid; m.p.= 103.0-105.8 °C;¹² 90% yield, 98.6% *ee*; ¹H NMR (400 MHz, Chloroform*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.26 (d, *J* = 2.0 Hz, 1H), 4.02 (d, *J* = 1.6 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H).¹³C NMR (100 MHz, Chloroform*d*) δ 192.74, 145.02, 139.00, 133.11, 132.63, 129.56, 129.46, 128.48, 125.80, 60.99, 59.39, 21.79, 21.28; Determined by HPLC analysis [Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 34.340 min, *t* (minor) = 29.951 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₇O₂ [M+H]⁺: 253.1223, found 253.1222.

(4-Fluorophenyl) ((2*R*,3*S*)-3-(4-fluorophenyl)-oxiran-2-yl)-methanone (5av):



White solid; m.p.= 81.5-83.7 °C;¹³ 95% yield, 99.2% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.03 (m, 2H), 7.38 – 7.31 (m, 2H), 7.22 – 7.13 (m, 2H), 7.13 – 7.05 (m, 2H), 4.20 (d, *J* = 2.0 Hz, 1H), 4.06 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 191.42, 166.30 (d, *J* = 256 Hz), 163.23 (d, *J* = 247 Hz), 131.85 (d, *J* = 3 Hz), 131.20 (d, *J* = 9 Hz), 131.12 (d, *J* = 4 Hz), 127.58 (d, *J* = 9 Hz), 116.18 (d, *J* = 20 Hz), 115.91 (d, *J* = 21 Hz), 61.02, 58.70; Determined by HPLC analysis [Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 18.494 min, *t* (minor) = 20.132 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₁F₂O₂ [M+H]⁺: 261.0722, found 261.0722.

(4-Chlorophenyl) ((2R,3S)-3-(4-fluorophenyl)-oxiran-2-yl)-methanone (5aw):



White solid; m.p.= 112.6-115.7 °C; 91% yield, 99.0% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.92 (m, 2H), 7.51 – 7.43 (m, 2H), 7.38 – 7.30 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 4.19 (d, *J* = 2.0 Hz, 1H), 4.06 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 191.88, 163.25 (d, *J* = 246 Hz), 140.72, 133.66, 131.04 (d, *J* = 3 Hz), 129.82, 129.30, 127.59 (d, *J* = 9 Hz), 115.93 (d, *J* = 26 Hz), 61.04, 58.78; Determined by HPLC analysis [Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 18.629 min, *t* (minor) = 21.850 min]; HRMS-ESI (m/z): calcd for C₁₅H₁₁CIFO₂ [M+H]⁺: 277.0426, found 277.0427.

(1a*R*,7b*R*)-2,2-dimethyl-1a,7b-dihydro-2*H*-oxireno[2,3-c]chromene-6-carbonitrile (5ax):

NC

White solid; m.p.= 143.8-146.4 °C;¹⁶ 95% yield, 91.4% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 1H), 7.55 – 7.45 (m, 1H), 6.90 – 6.78 (m, 1H), 3.90 (dd, *J* = 4.4, 2.4 Hz, 1H), 3.53 (dd, *J* = 4.4, 2.4 Hz, 1H), 1.60 – 1.55 (m, 3H), 1.30 – 1.22 (m, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 156.51, 134.41, 133.83, 121.16, 119.04, 118.77,

104.25, 74.70, 62.31, 49.88, 25.50, 23.02. Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 99:1, flow rate=1 mL/min, wavelength = 254 nm, t (major) = 13.337 min, t (minor) = 16.282 min]; HRMS-ESI (m/z): calcd for C₁₂H₁₁NO₂ [M+H]⁺: 201.0790, found 201.0790.

(2R,3'S)-3'-Phenyl-3,4-dihydro-1H-spiro[naphthalene-2,2'-oxiran]-1-one (5ay):

White solid; m.p.= 104.1-107.0 °C; 80% yield, 89.0% ee;¹⁷ ¹H NMR (400 MHz, Chloroform*d*) δ 8.12 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (td, *J* = 7.6, 1.6 Hz, 1H), 7.42 – 7.33 (m, 6H), 7.22 (d, *J* = 7.6 Hz, 1H), 4.36 (s, 1H), 2.91 – 2.70 (m, 2H), 2.54 – 2.33 (m, 1H), 1.86 (dt, *J* = 13.6, 4.4 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 193.62, 143.38, 134.26, 134.16, 132.71, 128.77, 128.39, 128.35, 127.67, 127.02, 126.66, 64.34, 64.11, 27.35, 25.35; Determined by HPLC analysis [Daicel chiralpak AD-H, 25 °C, hexane/ isopropanol 90:10, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 15.607 min, *t* (minor) = 19.754 min]; HRMS-ESI (m/z): calcd for C₁₇H₁₅O₂ [M+H]⁺: 251.1067, found 251.1067.

(2R,3S)-3-Phenyloxirane-2-carboxamide (5ba):

White solid; m.p.= 68.8-70.7 °C; 94% yield, 93.0% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42-7.36 (m, 3H), 7.33 – 7.27 (m, 2H), 6.22 (s, 1H), 5.65 (s, 1H), 3.99 (d, *J* = 2.0 Hz, 1H), 3.53 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 170.06, 134.76, 129.14, 128.71, 125.80, 58.96, 58.62; Determined by HPLC analysis[Daicel chiralpak OJ-H, 25 °C, hexane/ isopropanol 95:5, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 25.630 min, *t* (minor) = 23.086 min]; HRMS-ESI (m/z): calcd for C₉H₁₀NO₂ [M+H]⁺: 164.0706, found 164.0706.

(2R,3S)-N-Methyl-3-phenyloxirane-2-carboxamide (5bb):

White solid; m.p.= 72.5-75.5 °C; 90% yield, 91.8% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 4.8, 1.6 Hz, 3H), 7.29-7.26 (m, 2H), 6.31 (s, 1H), 3.90 (d, *J* = 2.0 Hz, 1H),

3.55 (d, J = 2.0 Hz, 1H), 2.89 (d, J = 5.2 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.06, 134.92, 129.04, 128.66, 125.78, 59.11, 59.03, 25.62; Determined by HPLC analysis[Daicel chiralpak OJ-H, 25 °C, hexane/ isopropanol 95:5, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 31.043 min, *t* (minor) = 22.543 min]; HRMS-ESI (m/z): calcd for C₁₀H₁₂NO₂ [M+H]⁺: 178.0863, found 178.0863.

(2R,3S)-N, N-Diethyl-3-phenyloxirane-2-carboxamide (5bc):

White solid; m.p.= 77.8-80.2 °C; 92% yield, 94.5% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.30 (m, 5H), 4.09 (d, *J* = 2.0 Hz, 1H), 3.58 (d, *J* = 1.6 Hz, 1H), 3.49 – 3.39 (m, 4H), 1.19 (dt, *J* = 16.8, 6.4 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.71, 135.83, 128.73, 128.67, 125.72, 57.64, 57.22, 41.53, 40.94, 14.95, 13.01; Determined by HPLC analysis[Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 36.214 min, *t* (minor) = 28.099 min]; HRMS-ESI (m/z): calcd for C₁₃H₁₈NO₂ [M+H]⁺: 220.1332, found 220.1334.

(2R,3S)-N-Methyl-N-phenyl-3-diphenyloxirane-2-carboxamide (5bd):

White solid; m.p.= 83.3-86.7 °C; 94% yield, 96.5% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 4H), 7.25 – 7.21 (m, 2H), 7.16 – 7.11 (m, 2H), 4.16 (d, *J* = 2.0 Hz, 1H), 3.38 (s, 3H), 3.24 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.56, 142.14, 135.41, 129.89, 128.60, 128.48, 128.15, 126.85, 125.74, 58.24, 56.75, 37.75; Determined by HPLC analysis[Daicel chiralpak OD-H, 25 °C, hexane/ isopropanol 92:8, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 25.063 min, *t* (minor) = 29.935 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₆NO₂ [M+H]⁺: 254.1176, found 254.1176.

(2R,3S)-N, N, 3-triphenyloxirane-2-carboxamide (5be):

White solid; m.p.= 107.1-111.2 °C; 93% yield, 94.8% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.26 (m, 13H), 7.18 (m, 2H), 4.22 (d, *J* = 2.0 Hz, 1H), 3.35 (d, *J* = 2.0 Hz, 1H). ¹³C

NMR (100 MHz, Chloroform-*d*) δ 166.53, 135.22, 128.75, 128.55, 125.80, 58.71, 57.77; Determined by HPLC analysis[Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 70:30, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 38.222 min, *t* (minor) = 61.380 min]; HRMS-ESI (m/z): calcd for C₂₁H₁₈NO₂ [M+H]⁺: 316.1332, found 316.1332.

(2R,3S)-Methyl-3-phenyloxirane-2-carboxylate (5ca):

White solid; m.p.= 87.5-90.3 °C; 87% yield, 89.0% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 - 7.34 (m, 3H), 7.29 - 7.27 (m, 2H), 4.10 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 3.52 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.66, 134.91, 129.05, 128.70, 125.83, 58.00, 56.66, 52.63; Determined by HPLC analysis[Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 93:7, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 17.445 min, *t* (minor) = 15.414 min]; HRMS-ESI (m/z): calcd for C₁₀H₁₁O₃ [M+H]⁺: 179.0703, found 179.0703.

(2R,3S)-Ethyl-3-phenyloxirane-2-carboxylate (5cb):

Colorless oil; 93% yield, 91.6% ee; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 3H), 7.30 (dd, *J* = 7.6, 2.4 Hz, 2H), 4.34 – 4.23 (m, 2H), 4.11 (d, *J* = 2.0 Hz, 1H), 3.52 (d, *J* = 2.0 Hz, 1H)1.33 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.22, 135.02, 128.99, 128.66, 125.85, 61.78, 57.92, 56.79, 14.13; Determined by HPLC analysis[Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 93:7, flow rate=1 mL/min, wavelength = 254 nm, *t* (major) = 16.888 min, *t* (minor) = 14.547 min]; HRMS-ESI (m/z): calcd for C₁₁H₁₃O₃ [M+H]⁺: 193.0859, found 193.0859.

Isopropyl (2R,3S)-3-phenyloxirane-2-carboxylate (5cc):

Corlorless oil; 88% yield, 90.1% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.31 (m, 3H), 7.35 – 7.25 (m, 2H), 5.19 – 5.10 (m, 1H), 4.07 (d, *J* = 2.0 Hz, 1H), 3.48 (d, *J* = 2.0 Hz, 1H), 1.31 (dd, *J* = 7.6, 6.4 Hz, 6H).¹³C NMR (100 MHz, Chloroform-*d*) δ 167.74, 135.11,

128.98, 128.66, 125.88, 69.61, 57.85, 56.99, 21.81, 21.73; Determined by HPLC analysis [Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 93:7, flow rate=1 mL/min, wavelength = 254 nm, t (major) = 14.038 min, t (minor) = 12.055 min]; HRMS-ESI (m/z): calcd for $C_{12}H_{15}O_3$ [M+H]⁺: 207.1016, found 207.1015.

Benzyl (2*R*,3*S*)-3-phenyloxirane-2-carboxylate (5cd):

White solid; m.p.= 103.1-106.0 °C; 90% yield, 89.9% *ee*; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.34 (m, 8H), 7.31 – 7.28 (m, 2H), 5.27 (q, *J* = 12.4 Hz, 2H), 4.13 (d, *J* = 1.6 Hz, 1H), 3.57 (d, *J* = 2.0 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 168.12, 135.02, 134.89, 129.07, 128.73, 128.70, 128.68, 128.55, 125.88, 67.48, 58.08, 56.78; Determined by HPLC analysis [Daicel chiralpak IC-H, 25 °C, hexane/ isopropanol 85:15, flow rate=1 mL/min, wavelength = 220 nm, *t* (major) = 11.436 min, *t* (minor) = 10.641 min]; HRMS-ESI (m/z): calcd for C₁₆H₁₅O₃ [M+H]⁺: 255.1016, found 255.1018.

7. NMR Spectra and HPLC chromatograms

(S)-N-((1-methyl-1H-benzo[d]imidazol-2-yl)methyl)-N-((1-((1-methyl-1H-

benzo[*d*]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)ethanamine (^{Et}PMB)



 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3

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11111 4.02 2.95 1.00-2.96 1.00 1.10 1.01-2.00 5.0 4.5 4.0 f1 (ppm) 8.0 6.5 5.5 .0 9.5 9.0 8.5 7.0 6.0 2.5 2.0 1.0 0.5 0.0 7.5 3.5 3.0 1.5 -0 ¹H NMR (400 MHz) in CDCl₃ CYR240228-1.2.fid $\begin{array}{c} 152.29\\ 151.75\\ 142.19\\ 142.15\\ 133.41\\ 133.41\\ 123.60\\ 123.60\\ 122.60\\ 122.60\\ 122.60\\ 122.36\\$ 62.38 60.19 59.41 54.78 52.35 52.35 30.50 29.92 29.71 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 f1 (ppm) 0 -10 10

(S)-N-benzyl-1-(1-methyl-1H-benzo[d]imidazol-2-yl)-N-((1-((1-methyl-1H-

benzo[*d*]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)methanamine (^{Bn}PMB)

 ^{13}C NMR (100 MHz) in CDCl_3

(*S*)-1-(1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1-methyl-1*H*-benzo[d]imidazol-2yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L1)



¹³C NMR (100 MHz) in CDCl₃

(S)-1-(1-cyclohexyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1-cyclohexyl-1*H*-

benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L2)



¹³C NMR (100 MHz) in CDCl₃

(S)-1-(1,5-dimethyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((1,5-dimethyl-1*H*-

benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L3)



¹³C NMR (100 MHz) in CDCl₃

(*S*)-1-(5-bromo-1-methyl-1*H*-benzo[d]imidazol-2-yl)-*N*-((1-((5-bromo-1-methyl-1*H*-benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-*N*-(4-vinylbenzyl)methanamine (L4)



¹³C NMR (100 MHz) in CDCl₃

(S)-1-(pyridin-2-yl)-N-((1-(pyridin-2-ylmethyl)pyrrolidin-2-yl)methyl)-N-(4-





¹³C NMR (100 MHz) in CDCl₃

(S)-N-((1-methyl-1H-benzo[d]imidazol-2-yl)methyl)-N-((1-((1-methyl-1H-

benzo[d]imidazol-2-yl)methyl)pyrrolidin-2-yl)methyl)-2-(4'-vinyl-[1,1'-biphenyl]-4-



¹³C NMR (100 MHz) in CDCl₃



(1R,2S)-1-hydroxy-1,3,3',4'-tetrahydro-1'H-spiro[indene-2,2'-naphthalen]-1'-one (2a)

¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	11.263	1108640	56767	50.92
2	15.098	1068591	41525	49.08



Peak#	Ret. Time	Area	Height	Area %
1	11.225	1936354	102702	99.57
2	15.045	8434	424	0.43



(1'R,2R)-1'-hydroxy-1',3'-dihydro-2,2'-spirobi[inden]-1(3H)-one (2b)





Peak#	Ret. Time	Area	Height	Area %
1	13.302	1181498	59308	50.00
2	20.512	1181607	36825	50.00







¹³C NMR (100 MHz) in CDCl₃







(1*R*,2*S*)-7'-chloro-1-hydroxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2d)



¹³C NMR (100 MHz) in CDCl₃



(1*R*,2*S*)-7'-bromo-1-hydroxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2e).



 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3





Peak#	Ret. Time	Area	Height	Area %
1	11.143	875696	49040	50.42
2	15.240	860987	37290	49.58



Peak#	Ret. Time	Area	Height	Area %
1	10.969	2370918	134983	98.86
2	15.069	27413	1361	1.14

(1*R*,2*S*)-7'-fluoro-1-hydroxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2f)





 $^{19}\mathsf{F}$ NMR (376 MHz) in CDCI_3







(1*R*,2*S*)-1-hydroxy-7'-methoxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'naphthalen]-1'-one (2g)

¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	21.268	590825	14946	49.76
2	24.347	596602	13237	50.24



Peak#	Ret. Time	Area	Height	Area %
1	21.024	9366	338	0.47
2	24.059	1990530	44964	99.53
(1*R*,2*S*)-1-hydroxy-6'-methoxy-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'naphthalen]-1'-one (2h)



¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	20.141	570390	15417	50.37
2	28.261	561987	10870	49.63



Peak#	Ret. Time	Area	Height	Area %
1	20.135	3172803	87274	99.54
2	28.245	14708	397	0.46

(1*R*,2*S*)-1-hydroxy-7'-methyl-1,3,3',4'-tetrahydro-1'*H*-spiro[indene-2,2'-naphthalen]-1'-one (2i)



¹³C NMR (100 MHz) in CDCl₃







¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	14.291	965448	42306	49.97
2	17.607	966704	34449	50.03





((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)(phenyl)methanone (2k)

¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	29.460	4547788	95335	99.00
2	35.160	45729	970	1.00



(3-chlorophenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2m)

S80





Peak#	Ret. Time	Area	Height	Area %
1	22.127	1167907	23440	48.98
2	24.888	1216688	22855	51.02



Peak#	Ret. Time	Area	Height	Area %
1	21.710	2815824	57869	97.79
2	24.695	63702	1202	2.21



(4-chlorophenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2n)







(4-bromophenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2o)

¹³C NMR (100 MHz) in CDCl₃





Peak#	Ret. Time	Area	Height	Area %
1	23.782	1888358	47544	50.11
2	25.512	1880022	45903	49.89



Peak#	Ret. Time	Area	Height	Area %
1	23.600	2793433	71376	99.04
2	25.364	27173	846	0.96



¹³C NMR (100 MHz) in CDCl₃











Peak#	Ret. Time	Area	Height	Area %
1	19.359	190856	6520	1.02
2	25.665	18522483	386271	98.98



S90





Peak#	Ret. Time	Area	Height	Area %
1	21.243	2182173	59020	50.34
2	23.429	2152457	53513	49.66



Peak#	Ret. Time	Area	Height	Area %
1	22.620	16139196	391512	99.18
2	25.238	132716	3644	0.82











(3,4-dimethylphenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)methanone (2t)







(4-ethylphenyl)((1S,2S)-1-hydroxy-2,3-dihydro-1H-inden-2-yl)methanone (2u)



((1S,2S)-1-hydroxy-2,3-dihydro-1*H*-inden-2-yl)(4-(trifluoromethyl)phenyl)methanone (2v)



 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3



 $^{19}\mathsf{F}$ NMR (376 MHz) in CDCI_3



Peak#	Ret. Time	Area	Height	Area %
1	14.989	2255408	53644	50.19
2	17.757	2238683	43395	49.81



Peak#	Ret. Time	Area	Height	Area %
1	15.646	6028494	139327	96.23
2	19.006	235906	4496	3.77











(*R*)-2,2'-spirobi[indene]-1,1'(3*H*,3'*H*)-dione (3b)



(S)-8,9-dihydrospiro[benzo[7]annulene-6,2'-indene]-1',5(3'H,7H)-dione (3c)










(S)-7'-bromo-3',4'-dihydro-1'*H*-spiro[indene-2,2'-naphthalene]-1,1'(3*H*)-dione (3e)





(S)-7'-methyl-3',4'-dihydro-1'H-spiro[indene-2,2'-naphthalene]-1,1'(3H)-dione (3i)







4-([1,1'-biphenyl]-4-yl)-4-oxobutanoic acid (3x):

 ^{13}C NMR (100 MHz) in DMSO- d_6





 ^{13}C NMR (100 MHz) in CDCl_3



Peak#	Ret. Time	Area	Height	Area %
1	13.913	14348095	473114	49.96
2	15.692	14370696	422730	50.04



Peak#	Ret. Time	Area	Height	Area %
1	13.802	69123	2658	0.37
2	15.366	18382481	555452	99.63



¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	23.943	67515	2488	50.47
2	25.283	66262	2353	49.53







 $^{\rm 13}C$ NMR (100 MHz) in CDCl_3







 ^{13}C NMR (100 MHz) in CDCl_3



Peak#	Ret. Time	Area	Height	Area %
1	12.601	12056921	480523	49.93
2	13.729	12092617	422049	50.07



Peak#	Ret. Time	Area	Height	Area %
1	12.597	95209	4182	0.38
2	13.716	24641026	857298	99.62



 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3





Peak#	Ret. Time	Area	Height	Area %
1	16.328	82605	4011	0.52
2	18.616	15695772	592933	99.48



¹³C NMR (100 MHz) in CDCl₃







(2R,3S)-3-(4-Bromophenyl)oxiran-2-yl)-(phenyl)methanone (5ag)

¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	15.587	5204493	161591	50.04
2	17.793	5195729	132336	49.96









 ^{19}F NMR (376 MHz) in CDCl_3





351612

49.48

10834014

2

14.927



 $^{\rm 13}C$ NMR (100 MHz) in CDCl_3



1	19.008	1256910	48528	50.27
2	21.181	1243613	43525	49.73
	·			



51946

95.80

1515154

2

21.439



[(2R,3S)-3-[1,1'-biphenyl]-4-yloxiranyl]phenylmethanone (5aj)

¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	23.800	7056340	288759	49.95
2	25.343	7069831	270545	50.05





¹³C NMR (100 MHz) in CDCl₃







(2-Chlorophenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5al)

 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3







¹³C NMR (100 MHz) in CDCl₃





Peak#	Ret. Time	Area	Height	Area %
1	13.657	8755432	550062	96.51
2	15.185	316484	16121	3.49



(4-Chlorophenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5an)

 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3







¹³C NMR (100 MHz) in CDCl₃






¹³C NMR (100 MHz) in CDCl₃









 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3







(4-Fluorophenyl)((2R,3S)-3-phenyloxiran-2-yl)-methanone (5ar)





$^{19}\mathsf{F}$ NMR (376 MHz) in CDCI_3







¹³C NMR (100 MHz) in CDCl₃







[(2R,3S)-3-(4-Fluorophenyl)-2-oxiranyl](4-methylphenyl)methanone (5at)

 $^{\rm 13}C$ NMR (100 MHz) in CDCl_3











(2R,3S)-4-Methylphenyl-3-(4-methylphenyl)-2-oxiran-methanone (5au)

 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3







¹³C NMR (100 MHz) in CDCl₃



 $^{19}\mathsf{F}$ NMR (376 MHz) in CDCI_3







(4-Chlorophenyl) ((2R,3S)-3-(4-fluorophenyl)-oxiran-2-yl)-methanone (5aw)

 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3









260500

50.21

21.988

Peak#	Ret. Time	Area	Height	Area %
1	18.629	42303600	1133632	99.52
2	21.850	204637	5890	0.48



(5ax)









Peak#	Ret. Time	Area	Height	Area %
1	13.337	6376749	186278	95.68
2	16.282	288702	7853	4.32



(2*R*,3'S)-3'-Phenyl-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5ay)

¹³C NMR (100 MHz) in CDCl₃







(2R,3S)-3-Phenyloxirane-2-carboxamide (5ba)

 $^{\rm 13}C$ NMR (100 MHz) in CDCl_3





(2R,3S)-N-Methyl-3-phenyloxirane-2-carboxamide (5bb)

 $^{\rm 13}C$ NMR (100 MHz) in CDCl_3







(2R,3S)-N, N-Diethyl-3-phenyloxirane-2-carboxamide (5bc)

¹³C NMR (100 MHz) in CDCl₃



Peak#	Ret. Time	Area	Height	Area %
1	28.099	134417	3460	2.75
2	36.214	4759888	84681	97.25



(2R,3S)-N-Methyl-N-phenyl-3-diphenyloxirane-2-carboxamide (5bd)

 ^{13}C NMR (100 MHz) in CDCl_3





Peak#	Ret. Time	Area	Height	Area %
1	25.063	4601040	62703	98.23
2	29.935	82783	1227	1.77



 $^{\rm 13}{\rm C}$ NMR (100 MHz) in ${\rm CDCI}_{\rm 3}$





Peak#	Ret. Time	Area	Height	Area %
1	38.222	10359158	169693	97.40
2	61.380	276001	3182	2.60



¹³C NMR (100 MHz) in CDCl₃














 $^{\rm 13}\text{C}$ NMR (100 MHz) in CDCl_3





Peak#	Ret. Time	Area	Height	Area %
1	12.055	28822	2247	4.97
2	14.038	551516	34942	95.03



 $^{\rm 13}C$ NMR (100 MHz) in CDCl_3





Peak#	Ret. Time	Area	Height	Area %
1	10.641	578717	48306	5.06
2	11.436	10859766	780023	94.94

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