Supporting Information

Lewis Acid-Catalyzed Enantioselective Hydroxylation Reactions of Oxindoles and β -Keto Esters Using DBFOX Ligand

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Determination of the absolute configuration of 2a-n

The absolute configuration of **2a** was established to (*R*) by deprotection under TFA treatment to yield the known 3-hydroxy-3-phenyl-2-oxindole (**6**).¹ See experimental section for detail. The absolute configurations of **2b-n** were tentatively determined based on the result of **2a**.

Determination of the absolute configuration of 5a-g

The absolute configurations of **5a-g** were tentatively assigned to (*S*) based on the result of the asymmetric hydroxylation of the benzyl ester **4h,i** to **5h,i** under the same experimental conditions. The absolute configurations of **5h,i** were assigned to (*S*) by the relative retention times of the (*R/S*)-isomers reported in the literature.² See experimental section for detail.

¹ Barroso, S.; Blay, G.; Carbona, L.; Fernández, I.; Garcia, B.; Pedro, J. R. *J. Org. Chem.* **2004**, *69*, 6821.

² (a) Davis, F. A.; Liu, H.; Chen, B.-C.; Zhou, P. *Tetrahedron* **1998**, *54*, 10481. (b) Acocella, M. R.; Mancheño, O. G.; Bella, M.; Jørgensen, K. A. *J. Org. Chem.* **2004**, *69*, 8165.

Optimization of the reaction conditions for Enantioselective Hydroxylation of **4** to **5**

Full date of the optimization of the reaction conditions were summarized in Table SI-1-4.

Table SI-1. Variations of Lewis Acid and Solvent^a

run	Lewis Acid	solvent	time (h)	yield (%)	ee (%)
1	Ni(ClO ₄) ₂ ·6H ₂ O	CH ₂ Cl ₂	0.5	81	91 (+)
2	Zn(ClO ₄) ₂	CH ₂ Cl ₂	2	89	81 (+)
3	Zn(SbF ₆) ₂	CH ₂ Cl ₂	2	99	72 (+)
4	Cu(OTf) ₂	CH ₂ Cl ₂	3	89	19 (+)
5	Ni(OAc) ₂ ·4H ₂ O	CH ₂ Cl ₂	4	70	24 (+)
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6	Ni(ClO ₄) ₂ ·6H ₂ O	THF	0.5	78	13 (+)
7	Ni(ClO ₄) ₂ ·6H ₂ O	Et ₂ O	1	75	56 (+)
8	Ni(ClO ₄) ₂ ·6H ₂ O	EtOH	0.5	91	37 (+)
9	Ni(ClO ₄) ₂ ·6H ₂ O	Toluene	3	85	86 (+)

Ad: 1-adamantyl

^a**4b** (1.0 equiv), **3b** (1.2 equiv), DBFOX (11 mol%) and Lewis Acid (10 mol%) were reacted in solvent in the presence of MS 4A at rt.

Table SI-2. Variation of Reaction Temperature^a

run	temp. (°C)	time (h)	yield (%)	ee (%)
1	-80	15.5	89	35 (+)
2	-40	15.5	83	83 (+)
3	-15	3.5	75	87 (+)
4	0	3.5	73	31 (+)
5	rt	0.5	81	91 (+)
6	40	0.5	92	90 (+)

^a**4b** (1.0 equiv), **3b** (1.2 equiv), DBFOX (11 mol%) and Lewis Acid (10 mol%) were reacted in solvent in the presence of MS 4A at the temperature indicated in the Table.

Table SI-3. Variations of Equivalent of 3b and Temperature^a

run	3b (equiv)	temp.	time (h)	yield (%)	ee (%)
1	3.0	rt	1	99	82 (+)
2	3.0	-15 °C	3	74	73 (+)
3	1.2	rt	0.25	65	90 (+)
4	1.2	rt	0.5	81	91 (+)

^a**4b** (1.0 equiv), **3b** (1.2 -3.0 equiv), DBFOX (11 mol%) and Ni(ClO₄)₂·6H₂O (10 mol%) were reacted in CH₂Cl₂ in the presence of MS 4A at the temperature indicated in the Table.

Table SI-4. Variations of Oxidant^a

run	oxidant	time (h)	yield (%)	ee (%)
1	$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{C}(\text{O})\text{N}(\text{SO}_2\text{Ph})\text{C}(\text{CH}_3)_2$ 3b	0.5	81	91 (+)
2	<i>t</i> BuOOH	48	17	38 (+)
3	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OOH}$	51	75	38 (-)
4	$\text{C}_6\text{H}_5\text{I}=\text{O}$	0.5	38	36 (+)
5	$\text{C}_6\text{H}_4\text{C}(\text{Me})_2\text{N}(\text{SO}_2\text{Ph})\text{C}(\text{O})\text{N}(\text{SO}_2\text{Ph})\text{C}(\text{CH}_3)_2$ 3a	0.5	85	96 (+)

^a**4b** (1.0 equiv), **Oxidant** (1.2 equiv), DBFOX (11 mol%) and Ni(ClO₄)₂·6H₂O (10 mol%) were reacted in CH₂Cl₂ in the presence of MS 4A at rt.

Experimental Section

General Methods

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels through a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silicagel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol/ heat. Column chromatography was carried out on a column packed with silicagel 60N spherical neutral size 63-210 μm . The ^1H -NMR (200 MHz), ^{19}F -NMR (188 MHz), and ^{13}C -NMR (50.3 MHz) spectra for solution in CDCl_3 , CD_3OD or *d*-DMSO were recorded on a Varian Gemini-200. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or CHCl_3 or CH_3OH or DMSO. HPLC analyses were performed on a JASCO PU-2080 Plus or SHIMADZU LC-2010A HT using 4.6 x 250 mm CHIRALPAK AD-H or CHIRALCEL OJ-H or CHIRALCEL OD-H or CHIRALPAK AS-H column and SUMICHIRAL OA-7000 column. GC analyses were performed on a SHIMADZU GC 14B using CP-CHIRASIL-DEX CB and CHIRALDEX G-TA. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/IR-200 spectrometer.

Preparation of Oxindoles 1a-n

Oxindoles **1b**,³ **1c**³ and **1i**⁴ were prepared according to the literature procedures. The other oxindoles **1a**, **1d-h**, **1j-n** were prepared as follows.

N-*t*-Butoxycarbonyl-3-phenyl-2-oxindole (**1a**)

A solution of **6**⁵ (837 mg, 4.0 mmol) and $(\text{Boc})_2\text{O}$ (2.2 g, 10 mmol) in THF (40 ml) was stirred with Na_2CO_3 (3.0 g, 28.3 mmol) for 22 h at room temperature. The solid was filtered and washed with THF. The filtrates were combined and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica-gel (Hexane/AcOEt) to give the product **1a** in 54% yield (663 mg) as white solid. ^1H -NMR (200 MHz, CDCl_3): 1.63 (s, 9H); 4.72 (s, 1H); 7.14-7.33 (m, 8H); 7.91 (d, $J=8.2$ Hz, 1H); MS (EI): m/z 309 (M^+), 209 ($\text{M}^+ - 1 - \text{COO}^t\text{Bu}$); IR (KBr): 2982, 2935, 1727, 1608, 1479, 1465, 1370, 1348, 1291, 1148, 1090, 845, 764.

³ Hamashima, Y.; Suzuki, T.; Takano, H.; Simura, Y.; Sodeoka, M. *J. Am. Chem. Soc.* **2005**, *127*, 10164.

⁴ Rajeswaran, W. G.; Cohen, L. A. *Tetrahedron* **1998**, *54*, 11375.

⁵ Wolff, J.; Taddei, M. *Tetrahedron*, **1986**, *42*, 4267; Clark, R. D.; Muchowski, J. M.; Fisher, L. E.; Flippin, L. A.; Repke, D. B.; Souchet, M. *Synthesis*, **1991**, 871; Fleming, I.; Loreto, M. A.; Wallace, I. H. M. *J. Chem. Soc., Perkin Transactions I*, **1986**, 349.

N-*t*-Butoxycarbonyl-5-methyl-3-(4-methylphenyl)-2-oxindole (**1d**)

The compound **1d** was prepared according to the reported procedure by Sodeoka³ as follows: A solution of *p*-TolMgBr in ether (0.9 M, 10.3 ml, 9.31 mmol) was added to a stirred cold ($-40\text{ }^{\circ}\text{C}$) suspension of 5-methylisatin (750 mg, 4.65 mmol) in THF (21 ml) under nitrogen atmosphere. The mixture was allowed to room temperature and stirred for 5 h. The reaction mixture was diluted with ether, and quenched with 1N HCl. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine and then dried over MgSO_4 . After the removal of solvent, purification by silica-gel column chromatography (Hexane/Acetone) was carried out to give **8** in 84% yield (985 mg) [Pale orange solid; $^1\text{H-NMR}$ (200 MHz, CD_3OD): 2.26 (s, 3H); 2.29 (s, 3H); 6.82 (d, $J=7.8\text{ Hz}$, 1H); 6.92-6.97 (m, 1H); 7.05-7.12 (m, 3H); 7.21-7.25 (m, 2H); MS (EI): m/z 253 (M^+); IR (KBr): 3420, 3200, 3086, 3025, 2916, 1702, 1625, 1493, 1336, 1207, 1148, 1057, 820, 775]. To a solution of **8** (870 mg, 3.43 mmol) in dichloromethane (34 ml), DMAP (42 mg, 0.343 mmol), and $(\text{Boc})_2\text{O}$ (1.65 g, 7.56 mmol) was added at room temperature, and the mixture was stirred for 20 min. After the removal of solvent, the crude product was purified by column chromatography on silica-gel (Hexane/ AcOEt) to give **9** in 99% yield (1.56 g) [Pale yellow foam; $^1\text{H-NMR}$ (200 MHz, CDCl_3): 1.38 (s, 1H); 1.59 (s, 1H); 2.31 (s, 3H); 2.34 (s, 3H); 7.07-7.25 (m, 6H); 7.82 (d, $J=8.4\text{ Hz}$, 1H); MS (EI): m/z 453 (M^+), 353 ($\text{M}^++1-\text{COO}^t\text{Bu}$); IR (KBr): 2980, 2932, 2870, 1790, 1753, 1726, 1494, 1371, 1338, 1293, 1253, 1147, 1123, 797, 734]. To a solution of **9** (1.55 g, 3.42 mmol) in MeOH, Pd/C (150 mg) was added and resulting mixture was stirred under hydrogen atmosphere for 11 h at room temperature. The reaction mixture was filtered through Celite to remove Pd/C . After removal of the solvent, **1d** was obtained in 95% yield (1.10 g) as pale yellow oil. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 1.61 (s, 9H); 2.30 (s, 3H); 2.32 (s, 3H); 4.63 (s, 1H); 6.94 (s, 1H); 7.03-7.15 (m, 5H); 7.78 (d, $J=8.4\text{ Hz}$, 1H); MS (EI): m/z 337 (M^+), 237 ($\text{M}^++1-\text{COO}^t\text{Bu}$); IR (neat): 2981, 2925, 1768, 1729, 1488, 1369, 1339, 1300, 1281, 1252, 1155, 1104, 1023, 818, 756.

N-*t*-Butoxycarbonyl-5-methyl-3-phenyl-2-oxindole (**1e**)

Oxindole **1e** was prepared from 5-methylisatin according to a described procedure to prepare **1d**. Pale yellow solid; $^1\text{H-NMR}$ (200 MHz, CDCl_3): 1.62 (s, 9H); 2.31 (s, 3H); 4.67 (s, 1H); 6.95 (s, 1H); 7.11-7.34 (m, 6H); 7.78 (d, $J=8.2\text{ Hz}$, 1H); MS (EI): m/z 323 (M^+), 223 ($\text{M}^++1-\text{COO}^t\text{Bu}$); IR (KBr): 2975, 2934, 2872, 1762, 1726, 1486, 1369, 1337, 1298, 1153, 1104, 1047, 1026, 1001, 849, 725.

N-t-Butoxycarbonyl-3-(4-fluorophenyl)-5-methyl-2-oxindole (1f)

Oxindole **1f** was prepared from 5-methylisatin according to a described procedure to prepare **1d**. Yellow oil; ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 9H); 2.32 (s, 3H); 4.66 (s, 1H); 6.94 (s, 1H); 7.04 (d, *J*=8.6 Hz, 2H); 7.12-7.19 (m, 3H); 7.78 (d, *J*=8.4 Hz, 1H); ¹⁹F-NMR (188 MHz): -114.1- -113.9 (m, 1F); MS (EI): *m/z* 341 (M⁺), 241 (M⁺+1-COO^tBu); IR (neat): 3078, 3008, 2979, 2921, 1730, 1604, 1509, 1489, 1374, 1338, 1281, 1224, 1152, 1109, 1048, 1022, 857, 741.

N-t-Butoxycarbonyl-5-methoxy-3-phenyl-2-oxindole (1g)

Oxindole **1g** was prepared from 5-methoxyisatin according to a described procedure to prepare **1d**. White solid; ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 9H); 3.76 (s, 3H); 4.69 (s, 1H); 6.71 (d, *J*=2.4 Hz, 1H); 6.87 (dd, *J*=8.9, 2.6 Hz, 1H); 7.17-7.34 (m, 3H); 7.83 (d, *J*=9.0 Hz, 1H); MS (EI): *m/z* 339 (M⁺), 239 (M⁺+1-COO^tBu); IR (KBr): 3051, 2984, 2936, 2839, 1766, 1723, 1598, 1489, 1455, 1353, 1302, 1159, 1035, 847, 720.

N-t-Butoxycarbonyl-3-(4-fluorophenyl)-5-methoxy-2-oxindole (1h)

Oxindole **1h** was prepared from 5-methoxyisatin according to a described procedure to prepare **1d**. White solid; ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 1H); 3.77 (s, 3H); 4.67 (s, 1H); 6.69 (d, *J*=1.8 Hz, 1H); 6.88 (dd, *J*=8.9, 2.9 Hz, 1H); 7.02 (t, *J*=8.6 Hz, 2H); 7.13-7.20 (m, 2H); 7.83 (d, *J*=8.8 Hz, 1H); ¹⁹F-NMR (188 MHz): -113.9-113.8 (m, 1F); MS (EI): *m/z* 357 (M⁺), 257 (M⁺+1-COO^tBu); IR (KBr): 2932, 1766, 1722, 1597, 1512, 1489, 1352, 1302, 1282, 1230, 1157, 856, 805.

N-t-Butoxycarbonyl-3-isopropyl-2-oxindole (1j)

Oxindole **1j** was prepared from isatin according to a described procedure to prepare **1d**. Colorless oil; ¹H-NMR (200 MHz, CDCl₃): 0.95 (d, *J*=6.8 Hz, 3H); 1.07 (d, *J*=6.8 Hz, 3H); 1.64 (s, 9H); 2.43-2.58 (m, 1H); 3.46 (d, *J*=3.2 Hz, 1H); 7.09-7.16 (m, 1H); 7.25-7.32 (m, 2H); 7.80 (d, *J*=8.0 Hz, 1H); MS (EI): *m/z* 275 (M⁺), 175 (M⁺+1-COO^tBu); IR (neat): 2966, 2933, 2875, 1791, 1762, 1731, 1607, 1480, 1465, 1369, 1356, 1290, 1253, 1150, 1092, 912, 847, 734.

N-t-Butoxycarbonyl-3-pentafluorophenyl-2-oxindole (1n)

Oxindole **1n** was prepared from isatin according to a described procedure to prepare **1d**. Green oil; ¹H-NMR (200 MHz, CDCl₃): 1.66 (s, 9H); 5.10 (s, 1H); 7.02 (d, *J*=7.4 Hz, 1H); 7.14 (dd, *J*=7.4, 7.6 Hz, 1H); 7.36 (dd, *J*=7.7, 7.9 Hz, 1H); 7.90 (d, *J*=7.9 Hz, 1H); ¹⁹F-NMR (188 MHz): -160.1-159.9 (m, 2F); -152.5 (t, *J*=21.1 Hz, 1F); -143.5 (s, 1F); -138.0 (s, 1F); MS (EI): *m/z* 399 (M⁺); IR (neat): 2984, 2936, 1732, 1657, 1608, 1505, 1467, 1371, 1345, 1289, 1250, 1150, 1092, 1049, 1001, 841, 756.

N-t-Butoxycarbonyl-3-(4-bromobenzyl)-2-oxindole (1k)

To a solution of **10**⁶ (2.0 g, 6.66 mmol) in CH₃CN (50 ml), DMAP (814 mg, 6.66 mmol) and (Boc)₂O (1.98 g, 7.00 mmol) were added at room temperature, and then mixture was stirred for 30 min. After removal of the solvent, the crude product was purified by column chromatography on silica-gel eluting with Hexane/AcOEt to give **11** in 96% yield (2.57 g) [Yellow solid; ¹H-NMR (200 MHz, CDCl₃): 6.99 (t, *J*=7.8 Hz, 1H); 7.27-7.38 (m, 1H); 7.46-7.61 (m, 5H); 7.74 (s, 1H); 7.88-8.09 (m, 1H); MS (EI): *m/z* 399, 401 (*M*⁺), 299, 301 (*M*⁺+1-COO^tBu); IR (KBr): 2984, 2870, 1728, 1590, 1494, 1464, 1336, 1292, 1255, 1153, 1077, 1003, 823, 779, 749]. To a solution of **11** (2.3 g, 5.75 mmol) in THF (57 ml), Pd/C (230 mg) was added, and resulting mixture was stirred under hydrogen atmosphere for 16 h at room temperature. This reaction mixture was filtered through Celite to remove Pd/C. After removal of the solvent, the crude product was purified by column chromatography on silica-gel eluting with Hexane/AcOEt to give **1k** (724 mg, 31%) as pale yellow solid. ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 9H); 2.99 (dd, *J*=13.8, 8.4 Hz, 1H); 3.39 (dd, *J*=13.6, 4.6 Hz, 1H); 3.79 (dd, *J*=8.4, 4.6 Hz, 1H); 6.82 (d, *J*=7.4 Hz, 1H); 6.96-7.02 (m, 2H); 7.03-7.07 (m, 1H); 7.20-7.28 (m, 1H); 7.31-7.36 (m, 2H); 7.70 (d, *J*=8.0 Hz, 1H); MS (EI): *m/z* 401, 403 (*M*⁺), 301, 303 (*M*⁺+1-COO^tBu); IR (KBr): 2981, 2930, 2899, 1772, 1605, 1480, 1350, 1295, 1253, 1147, 1091, 1072, 1009, 993, 839, 734.

***N*-t-Butoxycarbonyl-3-(4-chlorobenzyl)-2-oxindole (1l)**

Oxindole **1l** was prepared from 3-(4-chlorobenzylidene)indolin-2-one^{6, 7} according to a described procedure to prepare **1k**. Yellow oil; ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 1H); 3.01 (dd, *J*=13.7, 8.4 Hz, 1H); 3.41 (dd, *J*=13.9, 4.6 Hz, 1H); 3.80 (dd, *J*=8.4, 4.6 Hz, 1H); 6.82 (d, *J*=7.4 Hz, 1H); 7.00-7.07 (m, 3H); 7.18-7.29 (m, 3H); 7.71 (d, *J*=7.6 Hz, 1H); MS (EI): *m/z* 357 (*M*⁺), 257 (*M*⁺+1-COO^tBu); IR (neat): 2980, 2923, 1794, 1765, 1730, 1613, 1479, 1454, 1352, 1297, 1253, 1149, 1092, 1013, 847, 753.

***N*-t-Butoxycarbonyl-3-(4-methoxybenzyl)-2-oxindole (1m)**

Oxindole **1m** was prepared from 3-(4-methoxybenzylidene)indolin-2-one^{6, 7} according to a described procedure to prepare **1k**. Yellow oil; ¹H-NMR (200 MHz, CDCl₃): 2.92 (dd, *J*=13.8, 9.0 Hz, 1H); 3.43 (dd, *J*=13.8, 4.6 Hz, 1H); 3.73-3.80 (m, 1H); 3.77 (s, 3H); 6.75-6.81 (m, 3H), 6.96-7.06 (m, 3H); 7.18-7.26 (m, 1H); 7.71 (d, *J*=8.2 Hz, 1H); MS (EI): *m/z* 353 (*M*⁺), 253 (*M*⁺+1-COO^tBu); IR (neat): 2980, 2933, 2837, 1730, 1610, 1513, 1479, 1353, 1297, 1252, 1148, 1093, 842, 756.

⁶ Huang, A.; Kodanko, J. J.; Overman, L. E. *J. Am. Chem. Soc.* **2004**, *126*, 14043; Villemin, D; Martin, B. *Synthetic Communications* **1998**, *28*, 3201; Sun, L.; Tran, N.; Tang, F.; App, H.; Hirth, P.; McMahon, G.; Tang, C. *J. Med. Chem.* **1998**, *41*, 2588.

⁷ Coda, A. C.; Invernizzi, A. G.; Righetti, P. P.; Tacconi, G.; Gatti, G. *J. Chem. Soc. Perkin Transactions 2*, **1984**, 615; Yun, Y. K.; Labadie, J. *Chimica Oggi*. **2000**, *18*, 11. Wang, X.-S.; Zeng, Z.-S.; Li, Y.-L.; Shi, D.-Q.; Tu, S.-J.; Wei, X.-Y.; Zong, Z.-M. *Youji Huaxue*, **2005**, *25*, 1598.

General procedure for the Enantioselective Catalytic Hydroxylation of oxindoles:

Zn(OAc)₂ (10 mol%) and the (*R,R*)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenyloxazoline) (11 mol%) were stirred under vacuum for 2 h at room temperature. Dry dichloromethane (1 ml) and MS 4A (substrate/ MS 4A=1: 500 mol/ g) were added under nitrogen atmosphere and stirred for 1 h. Then a solution of oxindole **1** (0.10–0.25 mmol) in dry dichloromethane (2 ml) was added to the catalyst solution. After stirring for another 30 min, oxidant **3**⁸ (1.2 equiv) was added directly to the mixture. The reaction was stirred at the temperature for 1 h to 28 h with monitoring by TLC, it was stopped by the addition of water. The reaction mixture was then diluted with dichloromethane, washed with saturated aqueous sodium bicarbonate solution, brine, dried over MgSO₄ and the solvent was evaporated under reduced pressure. The purified by column chromatography on silica gel eluting with Hexane/AcOEt to give **2**. The ee of the product **2** was determined by chiral HPLC on CHIRALPAK AD-H or CHIRALCEL OJ-H or CHIRALPAK AS-H column.

(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-phenyl-2-oxindole (**2a**)

Colorless oil; ¹H-NMR (200 MHz, CDCl₃): 1.63 (s, 9H); 3.29 (s, 1H); 7.15-7.42 (m, 8H); 7.93 (d, *J*=8.0 Hz, 1H); ¹³C-NMR (50.3 MHz, CDCl₃): 175.4, 148.7, 139.5, 139.4, 130.0, 128.4, 128.3, 125.3, 125.1, 124.9, 115.3, 84.8, 77.6, 28.2; HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 0.5 ml/ min, 254 nm) *t*_R (major)=25.9 min, *t*_R (minor) =51.5 min; [α]_D²⁶ +52.3 (*c*=0.43, CHCl₃ 93% ee); MS (EI): *m/z* 325 (M⁺), 225 (M⁺+1–COO^tBu); IR (neat): 3453, 2981, 1789, 1734, 1608, 1479, 1370, 1343, 1286, 1250, 1148, 1102, 1009, 839, 754, 628.

(*R*)-3-Hydroxy -3-phenyl-2-oxindole (**6**)

To dry dichloromethane (1.0 ml) solution of **2a** (0.059 mmol) was added TFA (0.35 mmol) at room temperature, and stirred for 17h⁴. The reaction mixture was diluted with ethyl acetate, and then saturated aqueous sodium bicarbonate under ice-bath cooling. The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with brine. After dried over MgSO₄, then removal of solvent gave (*R*)-3-hydroxy-3-phenyl-2-oxindole (**6**) as a colorless solid quantitatively. ¹H-NMR (200 MHz, DMSO): 6.58 (s, 1H); 6.86 (d, *J*=7.8 Hz, 1H); 6.92 (t, *J*=7.8 Hz, 1H); 7.06 (d, *J*=7.6Hz, 1H); 7.18-7.25 (m, 6H), 10.4 (s, 1H); [α]_D²⁷ –13.5 (*c*=0.26, CH₃OH), lit.¹ [α]_D²⁵ –12.3 (*c*=0.91, CH₃OH).

(*R*)-*N*-*t*-Butoxycarbonyl-3-(4-methylphenyl)-3-hydroxy-2-oxindole (**2b**)

White foam; ¹H-NMR (200 MHz, CDCl₃): 1.63 (s, 9H); 2.32 (s, 3H); 3.21 (s, 1H); 7.11-7.33 (m, 6H); 7.39 (td, *J*=8.2, 1.6 Hz, 1H); 7.92 (d, *J*=8.0 Hz, 1H); ¹³CNMR (50.3 MHz, CDCl₃): 175.5, 148.7, 139.3, 138.1, 136.6, 130.0, 129.8, 129.0, 125.3, 125.0, 124.8, 115.1, 84.7, 77.5, 28.2, 21.3; HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 1.0 ml/ min, 210 nm) *t*_R (major)=13.7 min, *t*_R (minor) =22.2 min; [α]_D²⁶ +45.3 (*c*=0.67, CHCl₃ 94% ee); MS (EI): *m/z* 339 (M⁺), 239 (M⁺+1–COO^tBu); IR (KBr): 3457, 2981, 2931, 1780, 1733, 1608, 1480, 1466, 1370, 1344, 1287, 1251, 1148, 1101, 1009, 840, 753.

⁸ (a) Davis, F. A.; Towson, J. C.; Vashi, D. B.; ThimmaReddy, R.; McCauley, J. P.; Harakal, M. E.; Gosciniak, D. J. *J. Org. Chem.* **1990**, *55*, 1254. (b) Oppolzer, W.; Wills, M.; Starkemann, C.; Bernardinetti, G. *Tetrahedron Lett.* **1990**, *31*, 4117. (c) Davis, F. A.; Chen, B.-C. *Chem. Rev.* **1992**, *92*, 919.

(R)-N-*t*-Butoxycarbonyl-3-hydroxy-3-(4-fluorophenyl)-2-oxindole (2c)

Colorless oil; ¹H-NMR (200 MHz, CDCl₃): 1.63 (s, 9H); 3.19 (s, 1H); 7.01 (t, *J*=8.8 Hz, 2H); 7.21 (t, *J*=7.6 Hz, 2H); 7.28-7.45 (m, 3H); 7.93 (d, *J*=8.4 Hz, 1H); ¹⁹F-NMR (188 MHz): -112.8—112.7 (m); ¹³C-NMR (50.3 MHz, CDCl₃): 175.2, 162.5 (d, *J*=247.0 Hz), 148.6, 139.3, 135.2 (d, *J*=2.8 Hz), 130.2, 129.7, 127.4 (d, *J*=8.4 Hz), 125.2, 124.8, 115.4, (d, *J*=21.5 Hz), 115.3, 85.0, 77.2, 28.2; HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 1.0 ml/ min, 210 nm) *t*_R (major)=11.1 min, *t*_R (minor) =17.9 min; [α]_D²⁶ +20.2 (*c*=0.59, CHCl₃ 91% ee); MS (EI): *m/z* 343 (M⁺), 243 (M⁺+1-COO^tBu); IR (neat): 3447, 2983, 2933, 1793, 1735, 1607, 1507, 1479, 1467, 1371, 1343, 1287, 1252, 1148, 1096, 1011, 834.

(R)-N-*t*-Butoxycarbonyl-3-hydroxy-5-methyl-3-(4-methylphenyl)-2-oxindole (2d)

White foam; ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 9H); 2.31 (s, 3H); 2.32 (s, 3H); 3.19 (s, 1H); 7.10-7.25 (m, 6H); 7.79 (d, *J*=8.4 Hz, 1H); ¹³C-NMR (50.3 MHz, CDCl₃): 175.7, 148.8, 138.1, 136.9, 136.7, 134.7, 130.3, 130.0, 129.0, 125.2, 115.0, 77.6, 84.5, 28.2, 21.3, 21.2; HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 1.0 ml/ min, 254 nm) *t*_R (major)=15.9 min, *t*_R (minor) =23.5 min; [α]_D²⁶ +19.2 (*c*=0.64, CHCl₃ 93% ee); MS (EI): *m/z* 353 (M⁺), 253 (M⁺+1-COO^tBu); IR (KBr): 3455, 2981, 2926, 1781, 1732, 1590, 1488, 1370, 1334, 1300, 1279, 1245, 1153, 1011, 821, 735.

(R)-N-*t*-Butoxycarbonyl-3-hydroxy-5-methyl-3-phenyl-2-oxindole (2e)

White foam; ¹H-NMR (200 MHz, CDCl₃): 1.63 (s, 9H); 2.32 (s, 3H); 3.19 (s, 1H); 7.10 (s, 1H); 7.18 (dd, *J*=8.2, 1.4 Hz, 1H); 7.31-7.37 (m, 5H); 7.80 (d, *J*=8.4 Hz, 1H); ¹³C-NMR (50.3 MHz, CDCl₃): 175.6, 148.8, 139.7, 137.0, 134.8, 130.4, 129.9, 128.4, 128.3, 125.3, 115.0, 84.6, 77.8, 28.2, 21.2; HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 1.0 ml/ min, 254 nm) *t*_R (major)=14.2 min, *t*_R (minor) =22.7 min; [α]_D²⁶ +26.9 (*c*=0.58, CHCl₃ 90% ee); MS (EI): *m/z* 339 (M⁺), 239 (M⁺+1-COO^tBu); IR (KBr): 3449, 2980, 2922, 1783, 1733, 1490, 1448, 1370, 1335, 1300, 1279, 1249, 1153, 1011, 820, 720.

(R)-N-*t*-Butoxycarbonyl-3-(4-fluorophenyl)-3-hydroxy-5-methyl-2-oxindole (2f)

White foam; ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 9H); 2.33 (s, 3H); 3.13 (s, 1H); 7.00-7.06 (m, 2H); 7.08-7.09 (m, 1H); 7.17-7.22 (m, 1H); 7.29-7.36 (m, 2H); 7.80 (d, *J*=8.4 Hz, 1H); ¹⁹F-NMR (188 MHz): -112.9—112.8 (m); ¹³C-NMR (50.3 MHz, CDCl₃): 175.4, 162.4 (d, *J*=247.0 Hz), 148.7, 136.9, 135.4 (d, *J*=3.2 Hz), 135.0, 130.6, 129.6, 127.4 (d, *J*=8.4 Hz), 125.2, 115.4 (d, *J*=21.6 Hz), 84.8, 77.3, 28.2, 21.2; HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 1.0 ml/ min, 254 nm) *t*_R (major)=12.1 min, *t*_R (minor) =16.4 min; [α]_D²⁶ +5.6 (*c*=0.65, CHCl₃ 90% ee); MS (EI): *m/z* 357 (M⁺), 257 (M⁺+1-COO^tBu); IR (KBr): 3454, 2982, 2936, 1781, 1734, 1600, 1601, 1508, 1490, 1334, 1301, 1278, 1245, 1153, 1011, 848.

(R)-N-*t*-Butoxycarbonyl-3-hydroxy-5-methoxy-3-phenyl-2-oxindole (2g)

White foam; ¹H-NMR (200 MHz, CDCl₃): 1.62 (s, 9H); 3.28 (s, 1H); 3.76 (s, 3H); 6.84 (d, *J*=2.8 Hz, 1H); 6.91 (dd, *J*=8.9, 2.8 Hz, 1H); 7.31-7.36 (m, 5H); 7.85 (d, *J*=8.8 Hz, 1H); ¹³C-NMR (50.3 MHz, CDCl₃): 175.5, 157.0, 148.8, 139.4, 132.6, 131.1, 128.4, 128.3, 125.3, 116.3, 115.4, 110.2, 84.6, 77.9, 55.7, 28.2; HPLC: (AD-H, hexane/ⁱPrOH=95/

5, 1.0 ml/ min, 254 nm) t_R (major)=22.9 min, t_R (minor) =38.6 min; $[\alpha]_D^{26} +8.0$ ($c=0.64$, CHCl_3 97% ee); MS (EI): m/z 355 (M^+), 255 ($M^++1-\text{COO}^t\text{Bu}$); IR (KBr): 3449, 2980, 2929, 1782, 1731, 1600, 1490, 1371, 1336, 1298, 1278, 1250, 1152, 1005, 845.

(*R*)-*N*-*t*-Butoxycarbonyl-3-(4-fluorophenyl)-3-hydroxy-5-methoxy-2-oxindole (2h)

White foam; $^1\text{H-NMR}$ (200 MHz, CDCl_3): 1.61 (s, 9H); 3.41 (s, 1H); 3.76 (s, 3H); 6.82 (d, $J=2.4$ Hz, 1H); 6.89-7.06 (m, 3H); 7.28-7.35 (m, 2H); 7.84 (d, $J=9.0$ Hz, 1H); $^{19}\text{F-NMR}$ (188 MHz): -112.8—112.7 (m); $^{13}\text{C-NMR}$ (50.3 MHz, CDCl_3): 175.3, 162.5 (d, $J=247.0$ Hz), 157.1, 148.7, 135.2 (d, $J=3.2$ Hz), 132.5, 130.8, 127.4 (d, $J=8.4$ Hz), 116.4, 115.6, 115.4 (d, $J=21.5$ Hz), 110.2, 84.8, 77.4, 55.7, 29.9, 28.2; HPLC: (AD-H, hexane/ $^i\text{PrOH}=95/5$, 1.0 ml/ min, 254 nm) t_R (major)=19.6 min, t_R (minor) =31.0 min; $[\alpha]_D^{26} -9.5$ ($c=0.64$, CHCl_3 91% ee); MS (EI): m/z 373 (M^+), 273 ($M^++1-\text{COO}^t\text{Bu}$); IR (KBr): 3428, 2983, 2938, 1774, 1723, 1600, 1459, 1369, 1349, 1297, 1274, 1248, 1162, 1007, 844.

(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-methyl-2-oxindole (2i) and 3-Hydroxy-3-methyl-2-oxindole (7)

$\text{Zn}(\text{OAc})_2$ (1.8 mg, 0.011 mmol) and the (*R,R*)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenyloxazoline) (5.7 mg, 0.012 mmol) were stirred under vacuum for 2 h at room temperature. Dry dichloromethane (1 ml) and MS 4A (56 mg) were added under nitrogen atmosphere and stirred for 1 h. Then a solution of *N*-*t*-Butoxycarbonyl-3-methyl-2-oxindole (26.2 mg, 0.113 mmol) in dry dichloromethane (2 ml) was added to the catalyst solution. After stirring for another 30 min, oxidant **3a** (26.8 mg, 0.136 mmol) was added directly to the mixture. The reaction was stirred at the temperature for 19 h. It was stopped by the addition of water. The reaction mixture was then diluted with dichloromethane, washed with saturated aqueous sodium bicarbonate solution, brine, dried over MgSO_4 and the solvent was evaporated under reduced pressure to furnish a crude **2i**, which was go for next step without purification. **Deprotection of 2i: 3-Hydroxy-3-methyl-2-oxindole (7):** To dry dichloromethane (0.5 ml) solution of crude (*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-methyl-2-oxindole (**2i**) was added TFA (35 μl , 0.41 mmol) at room temperature, and stirred for 4 h. The reaction mixture was diluted with ethyl acetate, and then saturated aqueous sodium bicarbonate under ice-bath cooling. The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with brine. After dried over MgSO_4 , then removal of solvent gave **7** in 68% yield as a colorless solid. $^1\text{H-NMR}$ (200 MHz, CD_3OD): 1.40 (s, 3H); 6.77 (dt, $J=7.8, 0.8$ Hz, 1H); 6.93 (td, $J=7.5, 1.0$ Hz, 1H); 7.13 (td, $J=7.6, 1.2$ Hz, 1H), 7.23 (dq, $J=7.4, 0.8\text{Hz}$, 1H); $^{13}\text{C-NMR}$ (50.3 MHz, CD_3OD): 182.0, 141.7, 134.1, 130.0, 124.2, 123.4, 111.0, 74.6, 24.8; HPLC: (OJ-H, hexane/ $^i\text{PrOH}=90/10$, 1.0 ml/ min, 254 nm) t_R (minor)=12.4min, t_R (major) =15.9 min; $[\alpha]_D^{26} +32.5$ ($c=0.20$, CHCl_3 84% ee); MS (EI): m/z 163 (M^+); IR (KBr): 3370, 3182, 3088, 2975, 1705, 1625, 1473, 1351, 1196, 1147, 946, 656.

(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-isopropyl-2-oxindole (2j)

Colorless oil; $^1\text{H-NMR}$ (200 MHz, CDCl_3): 0.80 (d, $J=6.8$ Hz, 3H); 1.06 (d, $J=6.8$ Hz, 3H); 1.63 (s, 3H); 2.24 (sept, $J=6.8$ Hz, 1H); 2.67 (s, 1H); 7.18 (td, $J=7.5, 1.0$ Hz, 1H); 7.31-7.40 (m, 2H); 7.83 (dd, $J=7.9, 1.0$ Hz, 1H); $^{13}\text{C-NMR}$ (50.3 MHz, CDCl_3): 177.1, 148.5, 139.6, 129.5, 127.2, 124.4, 114.8, 84.5, 78.9, 37.4, 28.2, 16.5, 16.0; HPLC: (OD-H hexane/ $^i\text{PrOH}=95/5$, 0.5 ml/ min, 254 nm) t_R (major) =19.7 min, t_R (minor) =28.1 min; $[\alpha]_D^{26} +55.8$ ($c=0.40$, CH_3OH

83% ee); MS (EI): m/z 291 (M^+), 191 ($M^+ + 1 - \text{COO}^t\text{Bu}$); IR (neat): 3430, 1777, 1731, 1640, 1466, 1369, 1343, 1289, 1251, 1150, 753.

(*R*)-*N*-*t*-Butoxycarbonyl-3-(4-bromobenzyl)-3-hydroxy-2-oxindole (2k)

Colorless crystals; mp: 135–136 °C (recrystallization from hexane–CH₂Cl₂); ¹H-NMR (200 MHz, CDCl₃): 1.58 (s, 9H); 2.77 (s, 1H); 3.08 (d, $J=12.8$ Hz, 1H); 3.22 (d, $J=13.0$ Hz, 1H); 6.78 (d, $J=8.2$ Hz, 2H); 7.14–7.19 (m, 2H); 7.22–7.35 (m, 3H); 7.64 (d, $J=8.2$ Hz, 1H); ¹³C-NMR (50.3 MHz, CDCl₃): 176.3, 148.1, 138.9, 132.1, 131.7, 130.8, 129.9, 127.5, 124.5, 124.0, 121.1, 114.9, 84.7, 76.8, 45.4, 28.2; HPLC: (AS-H, hexane/ⁱPrOH=95/ 5, 1.0 ml/ min, 254 nm) t_R (major)=16.0 min, t_R (minor) =23.1 min; $[\alpha]_D^{26} +54.7$ ($c=0.70$, CHCl₃ 86% ee); MS (EI): m/z 417, 419 (M^+), 316, 317 ($M^+ - \text{COO}^t\text{Bu}$), 317, 319 ($M^+ + 1 - \text{COO}^t\text{Bu}$); IR (KBr): 3424, 2973, 2925, 1797, 1713, 1613, 1466, 1345, 1307, 1276, 1252, 1146, 1011, 841, 752.

(*R*)-*N*-*t*-Butoxycarbonyl-3-(4-chlorobenzyl)-3-hydroxy-2-oxindole (2l)

Colorless crystals; mp: 133–134 °C (recrystallization from hexane–CH₂Cl₂); ¹H-NMR (200 MHz, CDCl₃): 1.58 (s, 9H); 2.93 (s, 1H); 3.10 (d, $J=12.8$ Hz, 1H); 3.24 (d, $J=12.8$ Hz, 1H); 6.83 (d, $J=8.2$ Hz, 2H); 7.07–7.20 (m, 4H); 7.27–7.34 (m, 1H); 7.63 (d, $J=8.0$ Hz, 1H); ¹³C-NMR (50.3 MHz, CDCl₃): 176.3, 148.1, 138.9, 132.9, 131.6, 131.3, 129.8, 127.9, 127.5, 124.5, 124.0, 114.9, 84.6, 76.9, 45.3, 28.2; HPLC: (AS-H, hexane/ⁱPrOH=95/ 5, 0.8 ml/ min, 210 nm) t_R (major)=12.1 min, t_R (minor) =15.7 min; $[\alpha]_D^{26} +57.4$ ($c=0.60$, CHCl₃ 86% ee); MS (EI): m/z 373 (M^+), 273 ($M^+ + 1 - \text{COO}^t\text{Bu}$); IR (KBr): 3420, 2976, 2925, 1797, 1714, 1613, 1467, 1345, 1308, 1276, 1253, 1146, 844, 753.

(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-(4-methoxybenzyl)-2-oxindole (2m)

Yellow oil; ¹H-NMR (200 MHz, CDCl₃): 1.58 (s, 9H); 2.81 (s, 1H); 3.07 (d, $J=13.0$ Hz, 1H); 3.21 (d, $J=13.2$ Hz, 1H); 3.73 (s, 3H); 6.66 (d, $J=8.6$ Hz, 2H); 6.83 (d, $J=8.6$ Hz, 2H); 7.13–7.19 (m, 2H); 7.27–7.33 (m, 1H); 7.64 (d, $J=8.2$ Hz, 1H); ¹³C-NMR (50.3 MHz, CDCl₃): 176.6, 158.3, 148.2, 138.9, 132.9, 131.1, 129.6, 128.0, 125.0, 124.3, 124.1, 114.8, 113.2, 84.3, 55.2, 45.2, 28.2; HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 0.8 ml/ min, 254 nm) t_R (major)=24.0 min, t_R (minor) =30.6 min; $[\alpha]_D^{26} +54.7$ ($c=0.73$, CHCl₃ 85% ee); MS (EI): m/z 369 (M^+), 268 ($M^+ - \text{COO}^t\text{Bu}$); IR (neat): 3452, 2979, 2837, 1790, 1731, 1612, 1513, 1468, 1347, 1291, 1250, 1149, 1006, 839, 756.

(*R*)-*N*-*t*-Butoxycarbonyl-3-hydroxy-3-pentafluorophenyl-2-oxindole (2n)

Colorless solid; ¹H-NMR (200 MHz, CDCl₃): 1.66 (s, 9H); 3.59 (s, 1H); 7.19 (t, $J=7.4$ Hz, 1H); 7.38–7.45 (m, 2H); 7.92 (d, $J=8.8$ Hz, 1H); ¹⁹F-NMR (188 MHz): –159.6 (dd, $J=24.3$, 19.1 Hz, 2F); –152.0 (t, $J=21.1$ Hz, 1F); –138.0 (d, $J=18.4$ Hz, 2F); HPLC: (AD-H, hexane/ⁱPrOH=95/ 5, 1.0 ml/ min, 254 nm) t_R (major)=7.6 min, t_R (minor) =9.4 min; $[\alpha]_D^{26} +73.0$ ($c=0.26$, CHCl₃ 36% ee); MS (EI): m/z 415 (M^+), 315 ($M^+ + 1 - \text{COO}^t\text{Bu}$); IR (KBr): 3431, 2982, 1766, 1739, 1607, 1525, 1496, 1339, 1287, 1256, 1152, 986, 954, 653.

General procedure for the Enantioselective Catalytic Hydroxylation of β -Keto Esters 4:

Ni(ClO₄)₂·6H₂O (10 mol%) and the (*R,R*)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenyloxazoline) (11 mol%) were stirred

under vacuum for 2 h at room temperature. Dry dichloromethane (1 ml) and MS 4A (substrate/ MS 4A=1: 500 mol/ g) were added under nitrogen atmosphere and stirred for 1 h. Then a solution of β -keto ester **4** (0.10–0.20 mmol) in dry dichloromethane (2 ml) was added to the catalyst solution. After stirring for another 30 min, oxidant (1.2 equiv) was added directly to the mixture. The reaction was stirred at the temperature for 0.5 h to 18 h with monitoring by TLC, it was stopped by the addition of water. The reaction mixture was then diluted with dichloromethane, washed with saturated aqueous sodium bicarbonate solution, brine, dried over MgSO_4 and the solvent was evaporated under reduced pressure. The purified by column chromatography on silica gel eluting with Hexane/AcOEt to give **5**. The ee of the product **5** was determined by chiral HPLC on CHIRALPAK AD-H or CHIRALCEL OJ-H or CHIRALCEL OD-H or SUMICHIRAL OA-7000 column and chiral GC on CP-CHIRASIL-DEX CB or CHIRALDEX G-TA.

***tert*-Butyl 2-Hydroxy-1-oxo-indan-2-carboxylate (5a)**

Colorless solid; $^1\text{H-NMR}$ (200 MHz, CDCl_3): 1.36 (s, 9H); 3.21 (d, $J=17.2$ Hz, 2H); 3.65 (d, $J=17.2$ Hz, 2H); 4.00 (s, 1H); 7.36–7.49 (m, 2H); 7.64 (td, $J=7.5, 1.2$ Hz, 1H); 7.78 (d, $J=7.8$ Hz); $^{13}\text{C-NMR}$ (50.3 MHz, CDCl_3): 200.9, 170.2, 152.0, 135.6, 133.7, 127.7, 126.1, 124.9, 83.9, 80.5, 39.6, 27.8; HPLC: (OJ-H, hexane/ $^i\text{PrOH}$ =95 / 5, 0.8 ml/ min, 254 nm) t_R (major)=13.0 min, t_R (minor)=30.8 min; $[\alpha]_D^{26} +34.1$ ($c=0.42$, CHCl_3 89% ee); MS (EI): m/z 248 (M^+), 147 ($\text{M}^+ - \text{COO}^t\text{Bu}$); IR (neat): 3418, 2983, 2929, 1738, 1712, 1604, 1467, 1370, 1335, 1292, 1254, 1212, 1153, 1130, 926, 837, 767.

1-Adamantyl 2-Hydroxy-1-oxo-indan-2-carboxylate (5b)

Yellow oil; $^1\text{H-NMR}$ (200 MHz, CDCl_3): 1.59 (s, 6H); 1.97 (s, 6H); 2.11 (s, 3H); 3.21 (d, $J=17.2$ Hz, 2H); 3.65 (d, $J=17.2$ Hz, 2H); 4.00 (s, 1H); 7.36–7.47 (m, 2H); 7.63 (td, $J=7.5, 1.0$ Hz, 1H); 7.78 (d, $J=7.8$ Hz); $^{13}\text{C-NMR}$ (50.3 MHz, CDCl_3): 201.0, 169.8, 152.0, 135.6, 133.7, 127.7, 126.0, 124.8, 83.9, 80.5, 41.0, 39.7, 36.0, 30.9; HPLC: (AD-H, hexane/ $^i\text{PrOH}$ =95 / 5, 2.0 ml/ min, 254 nm) t_R (major)=13.9 min, t_R (minor) =22.6 min; $[\alpha]_D^{26} +19.7$ ($c=0.60$, CHCl_3 91% ee); MS (EI): m/z 326 (M^+); IR (neat): 3474, 2913, 2853, 1739, 1608, 1456, 1248, 1196, 1104, 1048, 964, 837, 754.

***tert*-Butyl 2-Hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5c)**

Colorless solid; $^1\text{H-NMR}$ (200 MHz, CDCl_3): $^1\text{H-NMR}$ (200 Hz): 1.39 (s, 9H); 2.22 (ddd, $J=13.8, 7.2, 7.2$ Hz, 1H); 2.65 (ddd, $J=13.6, 5.3, 5.4$ Hz, 1H); 3.08–3.14 (m, 2H); 4.23 (s, 1H); 7.25 (d, $J=7.6$ Hz, 1H); 7.33 (t, $J=7.6$ Hz, 1H); 7.51 (td, $J=7.4, 1.4$ Hz, 1H); 8.03 (dd, $J=7.8, 1.4$ Hz, 1H); $^{13}\text{C-NMR}$ (50.3 MHz, CDCl_3): 194.4, 169.6, 143.5, 133.8, 130.4, 128.6, 127.7, 126.7, 83.3, 77.7, 32.9, 27.9, 25.8; HPLC: (OA-7000, 20 mM phosphate buffer/ CH_3CN =60 / 40, 0.5 ml/ min, 254 nm) t_R (major)=36.4 min, t_R (minor) =41.1 min; $[\alpha]_D^{26} -7.1$ ($c=0.39$, CHCl_3 88% ee); MS (EI): m/z 262 (M^+); IR (neat): 3464, 2986, 2951, 2926, 1719, 1682, 1599, 1458, 1371, 1277, 1161, 1092, 919, 842, 743.

1-Adamantyl 2-Hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (5d)

Yellow solid; $^1\text{H-NMR}$ (200 MHz, CDCl_3): 1.61 (s, 6H); 2.01 (s, 6H); 2.12 (s, 3H); 2.22 (ddd, $J=14.0, 6.8, 6.9$ Hz, 1H); 2.64 (ddd, $J=13.4, 5.1, 5.0$ Hz, 1H); 3.09–3.15 (m, 2H); 4.23(s, 1H); 7.25 (d, $J=7.8$ Hz, 1H); 7.33 (t, $J=7.6$ Hz, 1H);

7.51 (td, $J=7.4$, 1.4 Hz, 1H); 8.03 (dd, $J=7.8$, 1.4 Hz, 1H); ^{13}C -NMR (50.3 MHz, CDCl_3): 194.4, 169.3, 143.5, 133.8, 130.5, 128.6, 127.7, 126.7, 83.4, 77.8, 41.1, 36.0, 33.0, 30.9, 25.9; HPLC: (AD-H, hexane/ $^i\text{PrOH}$ =95 / 5, 2.0 ml/ min, 254 nm) t_{R} (major)=9.6 min, t_{R} (minor)=15.3 min; $[\alpha]_{\text{D}}^{26}$ -3.7 ($c=0.40$, CHCl_3 82% ee); MS (EI): m/z 340 (M^+) IR (neat): 3457, 2905, 2846, 1738, 1684, 1603, 1455, 1259, 1197, 1097, 1050, 969, 742.

***tert*-Butyl 1-Cyclopentanone-2-hydroxy-2-carboxylate (5e)**

Colorless oil; ^1H -NMR (200 MHz, CDCl_3): 1.48 (s, 9H); 1.99-2.17 (m, 3H); 2.35-2.50 (m, 3H); 3.70 (s, 1H) ^{13}C -NMR (50.3 MHz, CDCl_3): 213.3, 170.4, 83.9, 79.7, 36.0, 35.0, 28.0, 18.6; GC: (CP-CHIRASIL-DEX CB, 25 m x 0.25 mm, 120 °C) t_{R} (major)=31.4 min, t_{R} (minor)=35.2 min; $[\alpha]_{\text{D}}^{26}$ -4.8 ($c=0.23$, CHCl_3 93% ee); MS (EI): m/z 200 (M^+); IR (neat): 3480, 2978, 1756, 1730, 1459, 1396, 1371, 1259, 1148.

***tert*-Butyl 1-Cyclohexanone-2-hydroxy-2-carboxylate (5f)**

Yellow oil; ^1H -NMR (200 MHz, CDCl_3): 1.48 (s, 9H); 1.61-1.89 (m, 4H); 1.96-2.10 (m, 1H); 2.44-2.71 (m, 3H); 4.26 (s, 1H); ^{13}C -NMR (50.3 MHz, CDCl_3): 207.1, 168.8, 83.0, 81.0, 39.1, 37.6, 28.0, 27.2, 22.3; GC: (CHIRALDEX G-TA, 30 m x 0.25 mm, 120 °C) t_{R} (major)=36.7 min, t_{R} (minor)=42.4 min; $[\alpha]_{\text{D}}^{26}$ -79.7 ($c=0.30$, CHCl_3 86% ee); MS (EI): m/z 214 (M^+), 113 ($\text{M}^+ - \text{COO}^t\text{Bu}$); IR (neat): 3461, 2941, 2869, 1720, 1452, 1370, 1278, 1254, 1146, 1115, 841.

***t*-Butyl 2-Hydroxy-2-methyl-3-oxo-3-phenylpropionate (5g)**

Yellow oil; ^1H -NMR (200 MHz, CDCl_3): 1.36 (s, 9H); 1.68 (s, 3H); 4.30 (s, 1H); 7.39-7.56 (m, 3H); 7.94-7.98 (m, 2H); 7.96 (d, $J=7.7$ Hz); ^{13}C -NMR (50.3 MHz, CDCl_3): 195.4, 171.3, 133.4, 133.2, 129.1, 128.3, 83.5, 79.7, 27.7, 23.5; HPLC: (OJ-H, hexane/ $^i\text{PrOH}$ =95/ 5, 1.0 ml/ min, 254 nm) t_{R} (major)=7.0 min, t_{R} (minor)=9.7 min; $[\alpha]_{\text{D}}^{26}$ $+2.2$ ($c=0.10$, CHCl_3 93% ee); MS (EI): m/z 149 ($\text{M}^+ - \text{COO}^t\text{Bu}$); IR (neat): 3473, 2981, 2935, 1732, 1696, 1450, 1371, 1285, 1239, 1146, 944, 842, 704.

(*S*)-Methyl 2-Hydroxy-1-oxo-indan-2-carboxylate (5h)²

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (4.5 mg, 0.012 mmol) and the (*R,R*)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenyloxazoline) (6.2 mg, 0.014 mmol) were stirred under vacuum for 2 h at room temperature. Dry dichloromethane (1 ml) and MS 4A (62 mg) were added under nitrogen atmosphere and stirred for 1 h. Then a solution of β -keto ester **4h** (23.4 mg, 0.123 mmol) in dry dichloromethane (2 ml) was added to the catalyst solution. After stirring for another 30 min, oxidant **3b** (29.2 mg, 0.148 mmol) was added directly to the mixture. The reaction was stirred at the temperature for 3 h. It was stopped by the addition of water. The reaction mixture was then diluted with dichloromethane, washed with saturated aqueous sodium bicarbonate solution, brine, dried over MgSO_4 and the solvent was evaporated under reduced pressure. Purification by column chromatography on silica gel eluting with Hexane/ AcOEt gave **5h** (22.7 mg, 90% yield; white solid). ^1H -NMR (200 MHz, CDCl_3): 3.25 (d, $J=17.2$ Hz, 1H); 3.73 (d, $J=17.2$ Hz, 1H); 3.73 (s, 3H); 4.00 (s, 1H); 7.39-7.55 (m, 2H); 7.63-7.71 (m, 1H); 7.79 (d, $J=7.6$ Hz, 1H); HPLC: (OD-H, hexane/ $^i\text{PrOH}$ =90/ 10, 1.0 ml/ min, 254 nm) t_{R} (*S*)=12.9 min, t_{R} (*R*)=15.4 min (33% ee); lit.² (OD-H, hexane/ $^i\text{PrOH}$ =90/ 10, 1.0 ml/ min, 254 nm) t_{R} (*S*)=18.8

min, $t_R(R)$ = 22.4 min. (68% ee).

(S)-Benzyl 2-Hydroxy-1-oxo-indan-2-carboxylate (5i)²

Ni(ClO₄)₂·6H₂O (3.6 mg, 0.010 mmol) and the (*R,R*)-4,6-Dibenzofurandiyl-2,2'-bis(4-phenyloxazoline) (5.0 mg, 0.011 mmol) were stirred under vacuum for 2 h at room temperature. Dry dichloromethane (1 ml) and MS 4A (49 mg) were added under nitrogen atmosphere and stirred for 1 h. Then a solution of β-keto ester **4i** (26.2 mg, 0.098 mmol) in dry dichloromethane (2 ml) was added to the catalyst solution. After stirring for another 30 min, oxidant **3a** (23.3 mg, 0.118 mmol) was added directly to the mixture. The reaction was stirred at the temperature for 3 h. It was stopped by the addition of water. The reaction mixture was then diluted with dichloromethane, washed with saturated aqueous sodium bicarbonate solution, brine, dried over MgSO₄ and the solvent was evaporated under reduced pressure. Purification by column chromatography on silica gel eluting with Hexane/ AcOEt gave the **5i** (23.4 mg, 84% yield; colorless oil). ¹H-NMR (200 MHz, CDCl₃): 3.24 (d, *J*=17.4 Hz, 1H); 3.72 (d, *J*=17.4 Hz, 1H); 3.99 (s, 1H); 5.10 (d, *J*=12.4 Hz, 1H); 5.22 (d, *J*=12.4 Hz, 1H); 7.11-7.18 (m, 2H); 7.26-7.30 (m, 3H); 7.38-7.49 (m, 2H); 7.65 (td, *J*=7.5, 1.0 Hz, 1H); 7.79 (d, *J*=7.5 Hz, 1H); HPLC: (OD-H, hexane/ⁱPrOH=90/ 10, 1.0 ml/ min, 254 nm) $t_R(S)$ =14.0 min, $t_R(R)$ = 16.4 min (67% ee); lit.² (OD-H, hexane/ⁱPrOH=90/ 10, 1.0 ml/ min, 254 nm) $t_R(S)$ =15.2 min, $t_R(R)$ = 18.1 min. (68% ee); $[\alpha]_D^{26}$ +16.3 (*c*=0.65, CHCl₃ 67% ee); lit.² $[\alpha]_D^{21}$ -34 (*c*=1.04, CHCl₃ 73% ee).