Supporting Information for:

Catalytic Enantioselective Synthesis of Chiral Phthalides by SmI_2 -Mediated Reductive Cyclization of 2-Acylarylcarboxylates

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1. Initial Screen of Achiral Protonating Agent.

entry ^a	achiral protonating agent	^t BuOH (equiv)	yield (%) ^b
1	triphenylmethanol	-	65
2	phenylmethanamine	-	25
3	2,6-diisopropylphenol	-	12
4	diethylamine	-	15
5	diisopropylamine	-	-
6	piperidine	-	12
7	2,2,6,6-tetramethylpiperidine	-	-
8 ^c	diisopropylamine	0.1	75
9 ^c	2,2,6,6-tetramethylpiperidine	0.1	85

^a 1 equiv of achiral protonating agent was employed. ^b Isolated yield. ^c In combination with a catalytic amount of *tert*-butyl alcohol.

2. General procedure for the catalytic enantioselective synthesis of chiral phthalides.

Under nitrogen, a freshly prepared solution of samarium diiodide (1.0 mmol) in THF (5 mL) was cooled to -78°C. A mixture of 0.5 mmol of 2-acylarylcarbonylates (**1**), 0.5 mmol (1 equiv) of 2,2,6,6-tetramethylpiperidine (**4**), and 0.05 mmol (10 mol%) of (4*S*,5*R*)-4,5-diphenyl-oxazolidin-2-one (**3**) in 5 mL of THF was added dropwise. The reaction was kept at this temperature for 0.5 hour and then allowed to warm up slowly to -50°C within 1 hour. After stirring at -50°C for another 1 hour, the reaction was quenched with 5 mL of saturated aqueous Na₂S₂O₃. Extraction with ethyl acetate and purification by flash column chromatography afforded the desired product **2**. The enantiomeric excess was determined by chiral HPLC analysis.

3. Characterization data and chiral HPLC conditions of the obtained optically active phthalides.

2a $[\alpha]_D^{20} +49.5$ (*c* 2.00, CHCl₃) for 98% *ee* [lit.: $[\alpha]_D^{20} -48.6$ (*c* 2.1, CHCl₃) for $\geq 96\%$ *ee* in the *R*-isomer, *Tetrahedron Lett.* **1996**, 37, 2205.]; ¹H NMR (300 MHz, CDCl₃): δ 6.53 (s, 1H), 6.99-7.02 (m, 2H), 7.12-7.40 (m, 4H), 7.58-7.63 (m, 2H), 7.80-7.85 (m, 1H); FT-IR (KBr, cm⁻¹): ν 1747, 1286, 1086; EI-MS (*m/z*, %): 210 (*M*⁺, 26.36), 105 (100.00). HPLC: Daicel Chiralpak AD column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

2b $[\alpha]_D^{20} +18.9$ (*c* 0.36, CHCl₃) for 94% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 2.35 (s, 3H), 6.38 (s, 1H), 7.13-7.19 (m, 4H), 7.32 (d, 1H, *J* = 8.7 Hz), 7.54-7.64 (m, 2H), 7.94 (d, 1H, *J* = 7.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 21.2, 82.8, 122.9, 125.6, 125.7, 127.0, 129.3, 129.7, 133.4, 134.2, 139.30, 149.8, 170.6; FT-IR (KBr, cm⁻¹): ν 1758, 1287, 1066, 975; EI-MS (*m/z*, %): 224 (*M*⁺, 48.27), 119 (100.00); HRMS (EI) for C₁₅H₁₂O₂: calcd. 224.0837, found 224.0827. HPLC: Daicel Chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 9:1.

2c $[\alpha]_D^{20} +8.9$ (*c* 1.15, CHCl₃) for 96% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 3.81 (s, 3H), 6.38 (s, 1H), 7.02-7.18 (m, 4H), 7.32-7.52 (m, 3H), 7.82-7.88 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 55.3, 82.7, 114.4, 122.9, 125.6, 126.0, 128.3, 128.8, 129.3, 134.2, 149.8, 160.4, 170.5; FT-IR (KBr, cm⁻¹): ν 1754, 1287, 1255, 1073; EI-MS (*m/z*, %): 240 (*M*⁺, 100.00); HRMS (EI) for C₁₅H₁₂O₃: calcd. 240.0786, found 240.0798. HPLC: Daicel Chiralpak AS column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

2d $[\alpha]_D^{20} +42.4$ (*c* 0.48 CHCl₃) for 97% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 6.39 (s, 1H), 7.04-7.10 (m, 2H), 7.23-7.32 (m, 3H), 7.55-7.70 (m, 2H), 7.96 (d, 1H, *J* = 7.8 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 81.9, 115.8, 116.1, 122.7, 125.7, 128.9, 129.1, 129.5, 132.2, 134.4, 149.3, 161.5, 164.8, 170.3; ¹⁹F NMR (282 MHz, CDCl₃): δ -112.08; FT-IR (KBr, cm⁻¹): ν 1757, 1510, 1291, 1230; EI-MS (*m/z*, %): 228 (*M*⁺, 35.97), 105 (100.00); HRMS (EI) for C₁₄H₉O₂FNa (*M*⁺+Na): calcd. 251.0484, found 251.0479. HPLC: Daicel Chiralpak AD column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

2e $[\alpha]_D^{20} +68.0$ (*c* 0.33, CHCl₃) for 92% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 6.37 (s, 1H), 7.15-7.18 (m, 2H), 7.30-7.34 (m, 1H), 7.51-7.68 (m, 4H), 7.96-7.99 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 81.9, 122.8, 123.5, 125.5, 125.6, 125.81,

125.84, 128.6, 129.6, 132.3, 134.5, 135.6, 149.2, 170.2; FT-IR (KBr, cm^{-1}): ν 1760, 1286, 1065, 1002; EI-MS (m/z , %): 289 (M^+ , 9.59), 105 (100.00); HRMS (EI) for $\text{C}_{14}\text{H}_9\text{O}_2\text{BrNa}$ ($M^+ + \text{Na}$): calcd. 310.9684, found 310.9678. HPLC: Daicel Chiralpak AD column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

2f $[\alpha]_D^{20} +30.5$ (*c* 0.62, CHCl_3) for 97% *ee*; ^1H NMR (300 MHz, CDCl_3): δ 2.24 (d, 6H, $J = 5.4$ Hz), 6.35 (s, 1H), 6.99-7.01 (m, 2H), 7.12-7.34 (m, 2H), 7.55-7.65 (m, 2H), 7.95-7.97 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 19.6, 19.7, 82.9, 122.9, 124.6, 125.6, 127.1, 128.2, 129.2, 130.1, 133.8, 134.2, 137.4, 138.0, 150.0, 170.6; FT-IR (KBr, cm^{-1}): ν 1751, 1286, 1068, 966, 733; EI-MS (m/z , %): 238 (M^+ , 3.87), 75 (100.00); HRMS (EI) for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Na}$ ($M^+ + \text{Na}$): calcd. 261.0893, found 261.0886. HPLC: Daicel Chiralpak AD column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol 9:1.

2g $[\alpha]_D^{20} +15.2$ (*c* 0.56, CHCl_3) for 97% *ee*; ^1H NMR (300 MHz, CDCl_3): δ 3.80 (s, 3H), 3.88 (s, 3H), 6.37 (s, 1H), 6.68 (s, 1H), 6.87 (s, 2H), 7.32-7.35 (m, 1H), 7.56-7.67 (m, 2H), 7.97 (d, 1H, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 55.90, 55.93, 82.8, 110.0, 111.8, 120.0, 122.9, 125.6, 125.8, 128.6, 129.3, 134.2, 149.4, 149.6, 149.9, 170.4; FT-IR (KBr, cm^{-1}): ν 1743, 1516, 1259, 1067, 709; EI-MS (m/z , %): 270 (M^+ , 16.20), 269 (100.00); HRMS (EI) for $\text{C}_{16}\text{H}_{14}\text{O}_4$: calcd. 270.0892, found 270.0894. HPLC: Daicel Chiralpak AD column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 7:3.

2h $[\alpha]_D^{20} +25.1$ (*c* 0.92, CHCl_3) for 95% *ee*; ^1H NMR (300 MHz, CDCl_3): δ 6.56 (s, 1H), 7.21-7.25 (m, 1H), 7.34 (d, 1H, $J = 4.2$ Hz), 7.49-7.65 (m, 4H), 7.81-7.86 (m, 4H), 7.99 (d, 1H, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 82.2, 122.9, 123.8, 125.68, 126.7, 126.8, 127.8, 128.1, 129.1, 129.4, 133.1, 133.6, 133.7, 134.4, 149.7, 170.5; FT-IR (KBr, cm^{-1}): ν 1759, 1288, 1067, 728; EI-MS (m/z , %): 260 (M^+ , 100.00); HRMS (EI) for $\text{C}_{18}\text{H}_{12}\text{O}_2$: calcd. 260.0837, found 260.0835. HPLC: Daicel Chiralpak AD column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 9:1.

2i $[\alpha]_D^{20} = +16.9$ (*c* 1.12, CHCl_3) for 96% *ee*; ^1H NMR (300 MHz, CDCl_3): δ 6.68 (s, 1H), 7.01-7.05 (m, 1H), 7.15-7.16 (m, 1H), 7.26-7.49 (m, 2H), 7.58-7.95 (m, 2H), 7.98-7.99 (m, 1H); FT-IR (KBr, cm^{-1}): ν 2925, 2853, 1731, 1464, 1261, 1080; EI-MS (m/z , %): 200 (M^+ , 13.59), 57 (100.00). HPLC: Daicel Chiralcel OJ column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 7:3. [For racemic, lit: Starling, S. M.; Raslan, Delio S.; Oliveira, Alaide B. de; Zani, C. L. *Synth. Commun.*, **1998**, 28, 3567.]

2j $[\alpha]_D^{20} +12.1$ (*c* 0.51, CHCl₃) for 97% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 6.68 (s, 1H), 7.02-7.04 (m, 1H), 7.14-7.16 (m, 1H), 7.36-7.39 (m, 1H), 7.46-7.49 (m, 1H), 7.58-7.69 (m, 1H), 7.71-7.74 (m, 1H), 7.97 (d, 1H, *J* = 7.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 77.9, 123.1, 125.7, 126.0, 127.1, 127.5, 127.9, 129.8, 134.3, 139.0, 148.7, 169.7; FT-IR (KBr, cm⁻¹): ν 1749, 1289, 1069, 943, 710; EI-MS (*m/z*, %): 218 (*M*⁺+2, 5.82), 217 (*M*⁺+1, 16.66), 216 (*M*⁺, 84.47), 104 (100.00); HRMS (EI) for C₁₂H₈O₂S: calcd. 216.0245, found 216.0247. HPLC: Daicel Chiralpak AD column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 7:3.

2k $[\alpha]_D^{20} +46.0$ (*c* 0.51, CHCl₃) for 97% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 6.32 (s, 1H), 7.13-7.21 (m, 3H), 7.46-7.55 (m, 2H), 7.67-8.08 (m, 2H); FT-IR (KBr, cm⁻¹): ν 1752, 1290, 1072, 79; EI-MS (*m/z*, %): 370 (*M*⁺+2, 15.64), 369 (*M*⁺+1, 7.07), 368 (*M*⁺, 31.66), 287 (100.00); Anal. for C₁₄H₁₈O₂Br₂: Calcd. C 45.69, H 2.19; Found C 45.70, H 2.19. HPLC: Daicel Chiralpak AD column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

2l $[\alpha]_D^{20} +17.7$ (*c* 0.67, CHCl₃) for 95% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 3.81 (s, 3H), 6.39 (s, 1H), 6.90 (d, 2H, *J* = 7.5 Hz), 7.18 (d, 2H, *J* = 7.2 Hz), 7.32 (d, 2H, *J* = 7.5 Hz), 7.56-7.69 (m, 1H), 7.97 (d, 1H, *J* = 7.8 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 55.4, 82.8, 114.3, 123.0, 125.6, 125.9, 128.3, 128.8, 129.3, 134.3, 149.8, 160.4, 170.6; FT-IR (KBr, cm⁻¹): ν 1757, 1298, 1063, 978; EI-MS (*m/z*, %): 240 (*M*⁺, 65.38), 104 (100.00); HRMS (EI) for C₁₅H₁₂O₃: calcd. 240.0786, found 240.0785. HPLC: Daicel Chiralpak AD column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

2m $[\alpha]_D^{20} +29.7$ (*c* 0.75, CHCl₃) for 98% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 2.36 (s, 1H), 6.55 (s, 1H), 7.21-7.26 (m, 4H), 7.58-7.64 (m, 2H), 7.74 (s, 1H), 7.86 (d, 1H, *J* = 7.5 Hz), 8.07 (d, 1H, *J* = 7.8 Hz), 8.54 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 21.2, 82.8, 121.9, 123.7, 126.9, 127.1, 127.2, 128.3, 129.0, 129.7, 129.9, 131.3, 134.3, 136.4, 139.3, 146.7, 170.4; FT-IR (KBr, cm⁻¹): ν 2923, 1757, 1292, 1168, 975, 764; EI-MS (*m/z*, %): 274 (*M*⁺, 11.83), 40 (100.00); HRMS (EI) for C₁₉H₁₄O₂Na (*M*⁺+Na): calcd. 297.0886, found 297.0895. HPLC: Daicel Chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 95:5.

2n $[\alpha]_D^{20} +40.0$ (*c* 0.39, CHCl₃) for 97% *ee*; ¹H NMR (300 MHz, CDCl₃): δ 2.37 (s, 3H), 6.32 (s, 1H), 7.12 (d, 2H, *J* = 8.4 Hz), 7.20 (d, 3H, *J* = 8.4 Hz), 8.03 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 21.3, 82.1, 125.1, 126.1, 127.0, 127.2, 129.9, 134.5,

136.0, 139.4, 140.0, 148.9, 170.9; FT-IR (KBr, cm^{-1}): ν 1765, 1387, 1284, 1165; EI-MS (m/z , %): 296 ($M^+ + 4$, 1.84), 294 ($M^+ + 2$, 12.83), 292 (M^+ , 17.52), 119 (100.00); HRMS (EI) for $\text{C}_{15}\text{H}_{10}\text{O}_2\text{Cl}_2$: calcd. 292.0058, found 292.0055. HPLC: Daicel Chiralcel OD column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

2o $[\alpha]_{\text{D}}^{20} +21.0$ (c 0.42, CHCl_3) for 99% *ee*; ^1H NMR (300 MHz, CDCl_3): δ 2.37 (s, 3H), 2.44 (s, 3H), 6.32 (s, 1H), 7.10 (s, 1H), 7.18 (s, 3H), 7.35 (d, 2H, $J = 7.8$ Hz), 7.84 (d, 1H, $J = 8.4$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 21.3, 22.1, 82.5, 123.1, 123.2, 125.4, 127.0, 129.6, 130.5, 133.7, 139.3, 145.6, 150.5, 170.7; FT-IR (KBr, cm^{-1}): ν 1752, 1296, 1062, 759; EI-MS (m/z , %): 238 (M^+ , 31.71), 119 (100.00); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2$ 238.0994, found 238.0996. HPLC: Daicel Chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 9:1.

2p $[\alpha]_{\text{D}}^{20} +26.1$ (c 0.32, CHCl_3) for 97% *ee*; ^1H NMR (300 MHz, CDCl_3): δ 2.34 (s, 3H), 2.70 (s, 3H), 6.22 (s, 1H), 7.06 (d, 1H, $J = 7.5$ Hz), 7.15 (d, 1H, $J = 7.8$ Hz), 7.20-7.28 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 17.6, 21.3, 82.0, 123.6, 128.1, 129.6, 130.5, 131.3, 132.7, 135.3, 136.7, 139.4, 148.0, 171.0; FT-IR (KBr, cm^{-1}): ν 1753, 1100, 819; EI-MS (m/z , %): 238 (M^+ , 1.95), 133 (100.00); HRMS (EI) for $\text{C}_{16}\text{H}_{14}\text{O}_2$: calcd. 238.0994, found 238.0985. HPLC: Daicel Chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol 8:2.

4. Preparation of deuterated 2,2,6,6-tetramethylpiperidine.

Under nitrogen, to a 5 mL Schlenk flask charged with 0.5 mmol of 2,2,6,6-tetramethylpiperidine was added 0.3 mL (7.4 mmol) of MeOD. After shaking the mixture for 2 minutes, the remained MeOD and newly formed MeOH were carefully removed under vacuum. The above procedure was repeated for 3 times to maximize deuteration of 2,2,6,6-tetramethylpiperidine (according to the ^1H NMR, it seems that over/about 90% of NH proton is deuterated). The obtained deuterated 2,2,6,6-tetramethylpiperidine was next used as achiral protonating agent in the reductive cyclization of ethyl 2-benzoylbenzoate (**1a**).

5. ^1H NMR spectrum of 4, 4-*d*, 2a and 2a-*d*.