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Selective Monobenzoylation of 1,2- and 1,3-Diols Catalyzed by Me_2SnCl_2 in Water (Organic Solvent Free) under Mild Conditions

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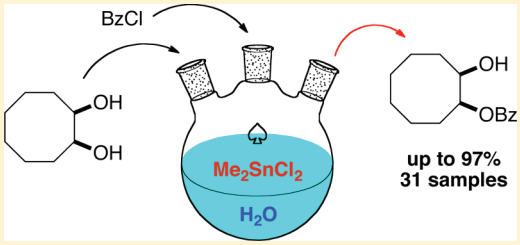
Supporting Information

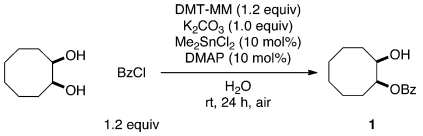
ABSTRACT: We have developed an efficient method for selective monobenzoylation of 1,2- and 1,3-diols in water catalyzed by Me_2SnCl_2. Treatment of 1,2- and 1,3-diols with benzoyl chlorides, DMT-MM, and potassium carbonate in the presence of a catalytic amount of Me_2SnCl_2 and DMAP in water at room temperature gave monobenzoates in up to 97% yield.



Selective functionalization of polyols represents a major current challenge in the efficient preparation of building blocks that target the synthesis of natural products or new drug candidates.[1] In particular, regio- and stereoselective functionalization of nonprotected polyols such as carbohydrates, inositols, and natural products with nonenzymatic catalysts has been an attractive challenge. Over the last several decades, catalytic regioselective acylation of nonprotected monosaccharides[2] and natural products[1a,d−f] has been achieved in the presence of organic and organometal catalysts. These catalytic reactions not only facilitate protection of a particular hydroxy group in polyols, but also realize natural product synthesis in a minimum number of steps. However, the polyols that can be effectively targeted in such reaction sequences are limited because most polyols are not sufficiently soluble in organic solvents. Moreover, organic reactions in water have recently attracted considerable attention from the standpoint of green chemistry,[3] and several acylation methods including the Schotten−Baumann-type reaction have been developed.[4] However, their methods require special conditions such as pH control,[4b] and nonenzymatic methods for the selective acylation of polyols in water (organic solvent free) has not been reported so far. This is because the most fundamental problems are the hydrolysis of the acyl halides and the corresponding ester products and unavoidable overacylation.[1h] To resolve such problems, we began an investigation on catalytic selective monobenzoylation of 1,2- and 1,3-diols in water under mild conditions as the first step for all polyols.

After a series of optimization studies, we found that the monoselective benzoylation of *cis*-cyclooctane-1,2-diol proceeded efficiently in the presence of 10 mol % of Me_2SnCl_2, 10 mol % of *N*,*N*-dimethylaminopyridine (DMAP), 1.0 equiv of potassium catbonate, and 1.2 equiv of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM)[5] in water at room temperature under air atmosphere (entry 1, Table 1; 97% yield and no dibenzoate). Table 1 provides information about the effect of a number of reaction parameters on the efficiency of monoselective benzoylation of *cis*-cyclooctane-1,2-diol. In the absence of Me_2SnCl_2, essentially no reaction was observed

Table 1. Selective Monobenzoylation of *cis*-Cyclooctane-1,2-diol in Water[a]



entry	variation from the "standard" conditions	yield of **1** (%)
1	none	97
2	no Me_2SnCl_2	<1
3	no DMT-MM	63
4	no DMAP	89
5	under Ar, no DMAP	>99
6	1 mol % of Me_2SnCl_2	15
7	Bu_2SnCl_2, instead of Me_2SnCl_2	69
8	Oc_2SnCl_2, instead of Me_2SnCl_2	42
9	Ph_2SnCl_2, instead of Me_2SnCl_2	41
10	Me_2SnBr_2, instead of Me_2SnCl_2	95
11	Me_2SnO, instead of Me_2SnCl_2	72
12	Me_2SnS, instead of Me_2SnCl_2	70
13	$CuCl_2$, instead of Me_2SnCl_2	63
14	BzBr, instead of BzCl	88[b]
15	Bz_2O, instead of BzCl	87
16	BzOH, instead of BzCl	17

[a]All data are the average of two experiments. [b]Dibenzoate was obtained in 2 and 6% yields.

(entry 2, Table 1). In the absence of DMT-MM, the yield was dropped down to 63% (entry 3, Table 1). In addition, the use of DMAP resulted in 89% yield with 5% yield of the known intermediate **34** generated from DMT-MM and benzoic acid (entry 4, Table 1). This reaction without a catalytic amount of DMAP under Ar atmosphere underwent monobenzoylation in

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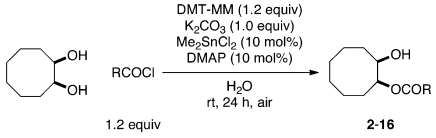
>99% yield (entry 5, Table 1). Use of a smaller amount of Me_2SnCl_2 gave monobenzoate **1** in unsatisfying yield (15% yield; entry 6, Table 1). Me_2SnBr_2 can be employed in place of Me_2SnCl_2 as a catalyst at the expense of a slight erosion in selectivity (entry 10, Table 1), whereas the other Sn catalysts and Cu catalysts did not show impressive activities (entries 7–9 and 11–13, Table 1). Treatment of BzBr in place of BzCl afforded **1** in 79% yield with 6% of the dibenzoate (entry 14, Table 1). Bz_2O reacted with *cis*-cyclooctane-1,2-diol to give **1** in good yield (entry 15, Table 1; 87% yield). BzOH, which is normally generated from BzCl in water, was less reactive under these reaction conditions (entry 16, Table 1; 17% yield).

Further, we examined the scope of this catalytic monoselective benzoylation with respect to electron-donating and electron-withdrawing substituents on the electrophile (Table 2).

Table 2. Selective Monobenzoylation of *cis*-Cyclooctane-1,2-diol in Water[a]



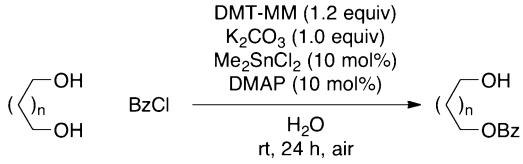
entry	R	product	yield (%)
1	2-Me-Ph	**2**	65
2	3-Me-Ph	**3**	93
3	4-Me-Ph	**4**	90
4	2-MeO-Ph	**5**	15
5	3-MeO-Ph	**6**	95
6	4-MeO-Ph	**7**	80
7	2-Cl-Ph	**8**	70
8	3-Cl-Ph	**9**	92
9	4-Cl-Ph	**10**	93
10[b]	1-Nap	**11**	57
11	2-Nap	**12**	83
12	2-Thienyl	**13**	84
13	$PhCH_2$	**14**	64
14	$PhCH_2CH_2$	**15**	44
15	$PhCH_2CH_2CH_2$	**16**	44

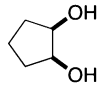
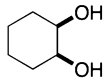
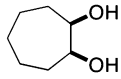
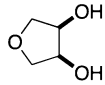
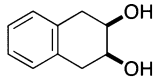
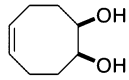
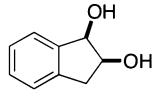
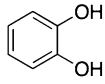
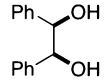
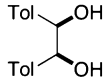
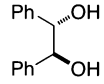
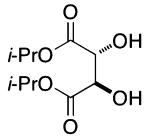
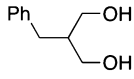
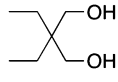
[a]All data are the average of two experiments. [b]Dibenzoate was obtained in 12% yield.

In the case of the benzoyl chlorides with electron-danating groups at meta and para positions, the benzoylation proceeded in 80–95% yields with no formation of dibenzoates (entries 2, 3, 5 and 6, Table 2). Similarly, use the benzoyl chlorides with electron-withdrawing groups at meta and para positions afforded the corresponding monobenzoates **9** and **10** in 92 and 93% yield, respectively (entries 8 and 9, Table 2). On the other hand, the benzoyl chlorides with these substituents at ortho position gave relatively poor yields in this catalytic monobenzoylation (entries 1, 4 and 7, Table 2; 65, 15, and 69% yield, respectively). This trend can be attributed to the effect of steric hindrance at the ortho position. We have also demonstrated the monoselective protection of *cis*-cyclooctane-1,2-diol using the other acyl reagents in water. 2-Naphthoyl chloride afforded the monoacylate **12** in 82% yield, whereas 1-naphthoyl chloride afforded a lower yield of the monoprotected product **11** with 12% yield of the diacylate (entries 10 and 11, Table 2). Reaction of 2-thiophenecarbonyl chloride with *cis*-cyclooctane-1,2-diol yielded in 84% of the monothionyl product **13** (entry 12, Table 2). Moreover, the catalytic selective monoprotection using homologues of benzoyl chloride shown in entries 13–15 (Table 2) yielded the corresponding products in 44–64% yields.

With these achievements in hand, this catalytic system was used in selective monobenzoylation with a wide range of commercially available 1,2- and 1,3-diols (Table 3). All *meso*-1,2-diols containing

Table 3. Selective Monobenzoylation of 1,2- and 1,3-diols in Water[a]



entry	1,2- and 1,3-diols	product	yield (%)
1		**17**	81
2		**18**	61
3		**19**	90
4		**20**	52
5		**21**	75
6		**22**	50
7		**23a-b**	93 (α:β=1:2)[b]
8		**24**	30
9		**25**	76
10		**26**	71
11		**27**	75
12		**28**	67
13		**29**	51
14		**30**	48

[a]All data are the average of two experiments. [b]The ratio was calculated by ^1H NMR.

cyclic or acyclic diols were also monobenzoylated in good yields (entries 1–6, 9, and 10, Table 3). However, the catalytic

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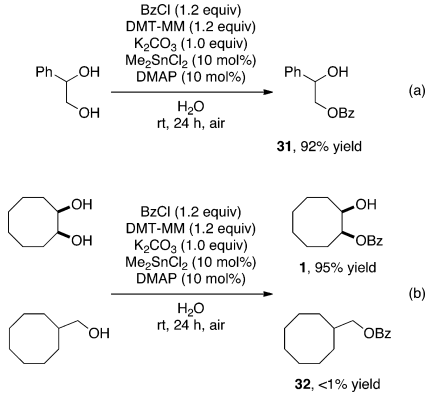
monobenzoylation using *trans*-cyclic-1,2-diols did not give any isolatable products because of the instability of coordination intermediate resulting from Me_2SnCl_2 and *trans*-cyclic-1,2-diols. In the case of *cis*-1,2-dihydroxyindan (entry 7, Table 3), the catalytic reaction afforded the two regioisomers in a 1:2 ratio with 93% overall yield. Using one of the less active diols, catechol, the reaction with 1.2 equiv of BzCl served the corresponding monobenzoate in 30% yield (entry 8, Table 3). Furthermore, *rac*-acyclic diols (entries 11 and 12, Table 3) and 1,3-diols (entries 13 and 14, Table 3) were also converted to the corresponding monobenzoates in moderate yields.

Next, we demonstrated selective monobenzoylation of 1,2-diols in the presence of primary and secondary hydroxy groups. When *rac*-phenylethane-1,2-diol was treated under these catalytic conditions, the primary hydroxy group of *rac*-phenylethane-1,2-diol was selectively benzoylated in 92% yield (Scheme 1a).

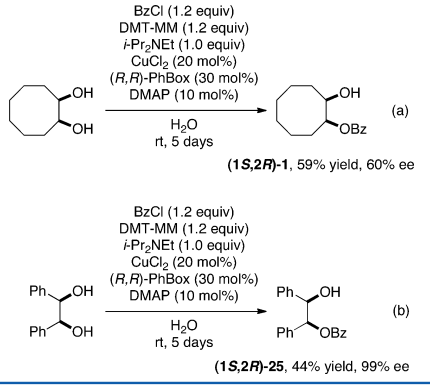
Scheme 1. Selective and Competitive Monobenzoylation in Water



Furthermore, competitive benzoylation between *cis*-cyclooctane-1,2-diol and *rac*-cyclooctane-methanol gave **1** selectively in 95% yield with no detection of **32** (Scheme 1b).

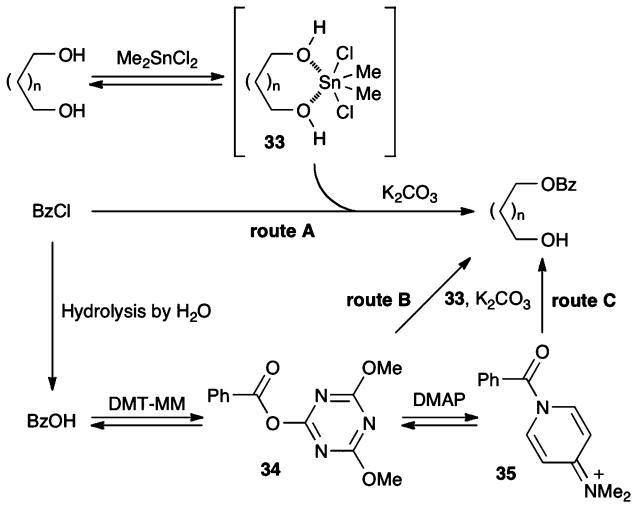
In addition, we briefly investigated the asymmetric benzoylation of *meso*-1,2-diols. Using catalytic amount of several Sn catalysts with (*R*,*R*)-PhBox,[6] the catalytic reaction provided the desired products with no enantiomeric excess. After Sn catalyst was replaced to $CuCl_2$, the enantiomeric excess was improved to provide (**1***S*,**2***R*)-**1** and (**1***S*,**2***R*)-**25** with 60 and 99% ee, respectively (Scheme 2a and 2b).

Scheme 2. Asymmetric Benzoylation of *meso*-1,2-Diols in Water



Finally, we proposed that the catalytic monobenzoylation results from the domination of three competitive pathways: (i) route A, where an active intermediate generated by deprotonation of the stannylene complex **33** reacts directly with benzoyl chloride; (ii) route B, where **33** reacts with an active intermediate **34** generated by the condensation of BzOH with DMT-MM; and (iii) route C, where **33** reacts with the acyl pyridinium intermediate **35** generated from **34** with DMAP (Scheme 3). Considering from the results of entries 3, 4, and 15

Scheme 3. Proposal Mechanism of Catalytic Monobenzoylation in Water



in Table 1, about 65% of monobenzoate **1** is generated from route A. Also, about 25 and 10% of **1** are obtained through route B and C, respectively.

In conclusion, a catalytic process for the benzoylation of 1,2- and 1,3-diols in water (organic solvent free) with high monoselectivity under mild conditions has been developed. The catalytic reaction can be conveniently carried out and widely applied in water because it does not require toxic and flammable organic solvents. The method will provide not only a new approach to an environmentally benign process for esterification, but also useful selective protection techniques of a hydroxy group in polyols in a minimum number of steps.

EXPERIMENTAL SECTION

General Procedure for Selective Monobenzoylation of 1,2- and 1,3-Diols in Water. K_2CO_3 (138 mg, 1.0 mmol), DMT-MM (including 15.6% water, 393 mg, 1.2 mmol), 4-dimethylaminopyridine (12.2 mg, 0.10 mmol), and benzoyl chloride (139 mL, 1.2 mmol) were added to a suspension of a mixture of *meso*-1,2-cyclooctanediol (144 mg, 1.0 mmol) and Me_2SnCl_2 (22.0 mg, 0.10 mmol) in purified water (6.0 mL) at room temperature under air. After stirring for 24 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with water and brine, dried with $MgSO_4$, filtrated, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography (*n*-hexane/ethyl acetate = 10/1) to give *cis*-2-hydroxycyclooctyl benzoate **1** (240.2 mg, 97%) as colorless oil.

cis-2-Hydroxycyclooctyl Benzoate (1).[7e,f] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.03 (m, 2H), 7.59−7.42 (m, 3H), 5.32 (dt, J = 9.3, 2.4 Hz, 1H), 4.15−4.08 (m, 1H), 2.32 (br s, 1H), 2.31−2.10 (m, 1H), 2.00−1.20 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 133.0, 130.3, 129.6 (2), 128.4 (2), 77.7, 71.9, 30.6, 27.9, 26.9, 25.6, 24.2, 22.0; IR (neat) 3460, 2920, 1709, 1271, 1109 cm^{-1}; MS m/z (rel intensity) 248 (M^+, 15), 205 (60), 143 (40), 105 (100), 77 (45); HRMS calcd for $C_{15}H_{20}O_3$ (M^+) 248.1412, found 248.1400.

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*cis-2-Hydroxycyclooctyl 2-Methylbenzoate (**2**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 8.2, 1.3 Hz, 1H), 7.39 (td, J = 7.4, 1.3 Hz, 1H), 7.30−7.20 (m, 2H), 5.30 (dt, J = 8.9, 2.3 Hz, 1H), 4.08 (ddd, J = 8.9, 4.3, 2.6 Hz, 1H), 2.60 (s, 3H), 2.36 (br s, 1H), 2.30−2.10 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 140.0, 131.9, 131.6, 130.4, 129.8, 125.7, 77.4, 71.8, 30.5, 27.9, 26.9, 25.6, 24.3, 22.0, 21.7; IR (neat) 3418, 2924, 1709, 1252, 1076 cm^{-1}; MS m/z (rel intensity) 262 (M^+, 35), 219 (20), 143 (40), 119 (100), 91 (80); HRMS calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1549.

*cis-2-Hydroxycyclooctyl 3-Methylbenzoate (**3**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.83 (m, 2H), 7.39−7.30 (m, 2H), 5.31 (dt, J = 9.1, 2.2 Hz, 1H), 4.10 (ddd, J = 9.1, 4.3, 2.6 Hz, 1H), 2.40 (s, 3H), 2.30−2.10 (m, 1H), 2.25 (br s, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 138.2, 133.8, 130.3, 130.1, 128.3, 126.7, 77.6, 71.9, 30.5, 27.9, 26.9, 25.6, 24.2, 22.0, 21.2; IR (neat) 3458, 2920, 1707, 1277, 1107 cm^{-1}; MS m/z (rel intensity) 262 (M^+, 70), 219 (100), 143 (60), 119 (85), 91 (75); HRMS calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1560.

*cis-2-Hydroxycyclooctyl 4-Methylbenzoate (**4**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 5.29 (dt, J = 9.0, 2.2 Hz, 1H), 4.08 (ddd, J = 9.0, 4.1, 2.4 Hz, 1H), 2.48 (br s, 1H), 2.40 (s, 3H), 2.25−2.10 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 143.7, 129.6 (2), 129.0 (2), 127.6, 77.5, 71.9, 30.5, 27.9, 26.8, 25.6, 24.2, 22.0, 21.6; IR (neat) 3429, 2922, 1694, 1273, 1107 cm^{-1}; MS m/z (rel intensity) 262 (M^+, 15), 219 (45), 143 (20), 119 (100), 91 (45); HRMS calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1549.

*cis-2-Hydroxycyclooctyl 2-Methoxybenzoate (**5**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.7, 1.8 Hz, 1H), 7.48 (ddd, J = 8.7, 7.0, 1.4 Hz, 1H), 7.04−6.97 (m, 2H), 5.30 (dt, J = 9.8, 2.5 Hz, 1H), 4.10−4.00 (m, 1H), 3.90 (s, 3H), 2.94 (br s, 1H), 2.23−2.10 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 158.6, 133.5, 131.8, 120.6, 120.5, 111.9, 77.8, 71.6, 56.0, 29.7, 27.4, 26.7, 25.3, 25.0, 22.3; IR (neat) 3507, 2916, 1680, 1277, 1099 cm^{-1}; MS m/z (rel intensity) 278 (M^+, 5), 235 (10), 152 (5), 135 (100), 98 (15); HRMS calcd for $C_{16}H_{22}O_4$ (M^+) 278.1518, found 278.1520.

*cis-2-Hydroxycyclooctyl 3-Methoxybenzoate (**6**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (ddd, J = 7.9, 1.5, 1.0 Hz, 1H), 7.56 (dd, J = 2.7, 1.5 Hz, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.10 (ddd, J = 7.9, 2.7, 1.0 Hz, 1H), 5.31 (dt, J = 9.0, 2.3 Hz, 1H), 4.10 (ddd, J = 9.0, 4.2, 2.4 Hz, 1H), 3.85 (s, 3H), 2.34 (br s, 1H), 2.23−2.13 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.5, 131.7, 129.4, 121.9, 119.2, 114.3, 77.9, 71.9, 55.4, 30.6, 27.9, 26.8, 25.7, 24.1, 22.0; IR (neat) 3431, 2922, 1709, 1275, 1101 cm^{-1}; MS m/z (rel intensity) 278 (M^+, 15), 235 (10), 152 (20), 135 (100), 98 (15); HRMS calcd for $C_{16}H_{22}O_4$ (M^+) 278.1518, found 278.1503.

*cis-2-Hydroxycyclooctyl 4-Methoxybenzoate (**7**).* White solid: mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 1H), 5.30−5.26 (m, 1H), 4.15−4.05 (m, 1H), 3.86 (s, 3H), 2.33 (br s, 1H), 2.24−2.12 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.4, 131.6 (2), 122.7, 113.6 (2), 77.4, 72.0, 55.4, 30.6, 28.1, 26.9, 25.7, 24.2, 22.1; IR (neat) 3505, 2916, 1680, 1279, 1099 cm^{-1}; MS m/z (rel intensity) 278 (M^+, 5), 235 (15), 152 (20), 135 (100), 98 (15); HRMS calcd for $C_{16}H_{22}O_4$ (M^+) 278.1518, found 278.1508.

*cis-2-Hydroxycyclooctyl 2-Chlorobenzoate (**8**).* White solid: mp 67−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.7, 1.9 Hz, 2H), 7.40 (dd, J = 8.7, 1.9 Hz, 2H), 5.30 (dt, J = 9.2, 2.0 Hz, 1H), 4.12−4.07 (m, 1H), 2.37 (br s, 1H), 2.30−2.10 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.5, 130.9 (2), 128.8, 128.7 (2), 78.0, 71.8, 30.7, 27.9, 26.8, 25.7, 24.1, 22.0; IR (neat) 3422, 2922, 1713, 1290, 1115 cm^{-1}; MS m/z (rel intensity) 282 (M^+, 10), 239 (45), 157 (30), 139 (100), 126 (40); HRMS calcd for $C_{15}H_{19}ClO_3$ (M^+) 282.1023, found 282.1007.

*cis-2-Hydroxycyclooctyl 3-Chlorobenzoate (**9**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.7, 1.6 Hz, 1H), 7.50−7.39 (m, 2H), 7.38−7.30 (m, 1H), 5.35−5.30 (m, 1H), 4.13−4.08 (m, 1H), 2.33 (br s, 1H), 2.30−2.15 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 133.2, 132.6, 131.5, 131.0, 130.5, 126.7, 78.7, 71.6, 30.1, 27.5, 27.0, 25.3, 24.7, 21.8; IR (neat) 3422, 2922, 1713, 1290, 1115 cm^{-1}; MS m/z (rel intensity) 282 (M^+, 10), 239 (40), 157 (35), 139 (100), 126 (35); HRMS calcd for $C_{15}H_{19}ClO_3$ (M^+) 282.1023, found 282.1017.

*cis-2-Hydroxycyclooctyl 4-Chlorobenzoate (**10**).* White solid: mp 67−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5, 2H), 7.42 (d, J = 8.5, 2H), 5.31 (dt, J = 9.3, 2.0 Hz, 1H), 4.10 (ddd, J = 9.3, 4.1, 2.4 Hz, 1H), 2.30−2.00 (m, 2H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.5, 131.0 (2), 128.8, 128.8 (2), 78.1, 71.9, 30.7, 27.9, 26.9, 25.7, 24.1, 22.1; IR (neat) 3421, 2922, 1715, 1273, 1105 cm^{-1}; MS m/z (rel intensity) 282 (M^+, 10), 239 (30), 157 (25), 139 (100), 126 (35); HRMS calcd for $C_{15}H_{19}ClO_3$ (M^+) 282.1023, found 282.1017.

*cis-2-Hydroxycyclooctyl 1-Naphthoate (**11**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 7.3 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 5.41 (dt, J = 9.4, 2.3 Hz, 1H), 4.20−4.10 (m, 1H), 2.42 (br s, 1H), 2.33−2.17 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 133.8, 133.3, 131.2, 129.9, 128.5, 127.7, 127.4, 126.2, 125.6, 124.4, 77.7, 71.8, 30.5, 27.9, 26.9, 25.6, 24.4, 22.0; IR (neat) 3447, 2922, 1701, 1240, 1134 cm^{-1}; MS m/z (rel intensity) 298 (M^+, 25), 172 (35), 155 (100), 127 (35), 98 (25); HRMS calcd for $C_{19}H_{22}O_3$ (M^+) 298.1569, found 298.1568.

*cis-2-Hydroxycyclooctyl 2-Naphthoate (**12**).* White solid: mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.04 (dd, J = 8.7, 1.6 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.59−7.49 (m, 1H), 5.37 (dt, J = 9.1, 2.3 Hz, 1H), 4.14 (ddd, J = 9.1, 3.8, 2.5 Hz, 1H), 2.52 (br s, 1H), 2.30−2.18 (m, 1H), 2.00−1.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 135.4, 132.4, 131.0, 129.2, 128.2, 128.1, 127.7, 127.5, 126.6, 125.1, 77.8, 71.8, 30.6, 27.9, 26.9, 25.6, 24.2, 22.0; IR (neat) 3534, 2920, 1697, 1229, 1132 cm^{-1}; MS m/z (rel intensity) 298 (M^+, 50), 172 (70), 155 (100), 127 (90), 98 (50); HRMS calcd for $C_{19}H_{22}O_3$ (M^+) 298.1569, found 298.1561.

*cis-2-Hydroxycyclooctyl 2-Thiophenecarboxylate (**13**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 2.7, 1.2 Hz, 1H), 7.58−7.55 (m, 1H), 7.13−7.09 (m, 1H), 5.28−5.25 (m, 1H), 4.09−4.06 (m, 1H), 2.31 (br s, 1H), 2.25−2.10 (m 1H), 2.00−2.50 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 133.9, 133.4, 132.4, 127.7, 78.0, 71.8, 30.4, 27.8, 26.8, 25.6, 24.1, 22.0; IR (neat) 3485, 2922, 1694, 1260, 1092 cm^{-1}; MS m/z (rel intensity) 255 (M + H^+, 50), 237 (20), 154 (15), 111 (100), 69 (50); HRMS calcd for $C_{13}H_{19}O_3S$ (M + H^+) 255.1049, found 255.1064.

*cis-2-Hydroxycyclooctyl Phenylacetylate (**14**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.24 (m, 5H), 5.05 (dt, J = 9.3, 2.4 Hz, 1H), 3.93−3.88 (m, 1H), 3.65 (s, 2H), 2.10−1.40 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 134.0, 129.1 (2), 128.6 (2), 127.2, 77.5, 71.7, 41.7, 30.1, 27.6, 26.9, 25.3, 24.5, 21.7; IR (neat) 3474, 2922, 1724, 1256, 1159 cm^{-1}; MS m/z (rel intensity) 263 (M + H^+, 25), 245 (10), 154 (100), 136 (70), 91 (55); HRMS calcd for $C_{16}H_{23}O_3$ (M + H^+) 263.1642, found 263.1660.

*cis-2-Hydroxycyclooctyl Phenylpropanoate (**15**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.15 (m, 5H), 5.03 (dt, J = 9.3, 2.4 Hz, 1H), 3.90−3.80 (m, 1H), 2.96 (t, J = 7.6 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.10−1.40 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 140.3, 128.5 (2), 128.2 (2), 126.3, 77.0, 71.5, 36.0, 31.0, 30.1, 27.5, 26.9, 25.4, 24.4, 21.7; IR (neat) 3478, 2922, 1724, 1260, 1161 cm^{-1}; MS m/z (rel intensity) 277 (M + H^+, 10), 259 (10), 151 (30), 133 (40), 55 (100); HRMS calcd for $C_{17}H_{25}O_3$ (M + H^+) 277.1778, found 277.1813.

*cis-2-Hydroxycyclooctyl Phenylbutanoate (**16**).* Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.10 (m, 5H), 5.05 (dt, J = 9.3, 2.4 Hz, 1H), 4.00−3.88 (m, 1H), 2.66 (t, J = 7.6 Hz, 2H), 2.34 (t, J = 7.6 Hz, 2H), 2.17 (br s, 1H), 2.10−1.90 (m, 3H), 1.90−1.40 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 141.2, 128.4 (2), 128.3 (2), 126.0, 76.7, 71.6, 35.0, 33.8, 30.2, 27.7, 26.9, 26.5, 25.3, 24.4, 21.8; IR (neat) 3487, 2922, 1724, 1246, 1144 cm^{-1}; MS m/z (rel intensity)

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291 (M + H$^+$, 10), 273 (10), 165 (25), 147 (100), 109 (40), 55 (40); HRMS calcd for $C_{18}H_{27}O_3$ (M + H$^+$) 291.1955, found 291.1988.

cis-2-Hydroxycyclopentyl Benzoate (**17**).[7c−f] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.00 (m, 2H), 7.60−7.50 (m, 1H), 7.50−7.40 (m, 2H), 5.30−5.20 (m, 1H), 4.40−4.25 (m, 1H), 2.20−1.50 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 133.1, 130.1, 129.6 (2), 128.4 (2), 77.4, 73.4, 30.9, 28.2, 19.5; IR (neat) 3449, 2968, 1697, 1271, 1115 cm^{-1}; MS *m*/*z* (rel intensity) 206 (M$^+$, 5), 188 (25), 123 (70), 105 (100), 77 (95), 55 (75); HRMS calcd for $C_{12}H_{14}O_3$ (M$^+$) 206.0943, found 206.0941.

cis-2-Hydroxycyclohexyl Benzoate (**18**).[7a−f] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20−8.00 (m, 2H), 7.70−7.30 (m, 3H), 5.30−5.10 (m, 1H), 4.66 (br s, 1H), 4.10−3.90 (m, 1H), 2.10−1.93 (m, 1H), 1.93−1.55 (m, 5H), 1.55−1.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 132.9, 130.3, 129.5 (2), 128.3 (2), 74.4, 69.5, 30.2 (2), 27.3, 21.6; IR (neat) 3420, 2938, 1695, 1271, 1109 cm^{-1}; MS *m*/*z* (rel intensity) 221 (M$^+$, 5), 135 (2), 105 (100), 77 (90), 70 (40); HRMS calcd for $C_{13}H_{16}O_3$ (M$^+$) 220.1099, found 220.1086.

cis-2-Hydroxycycloheptyl Benzoate (**19**). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.04 (m, 2H), 7.58−7.53 (m, 1H), 7.46−7.27 (m, 2H), 5.25 (dt, *J* = 8.3, 2.4 Hz, 1H), 4.09−4.05 (m, 1H), 2.54 (br s, 1H), 2.15−2.00 (m, 1H), 1.90−1.24 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 133.0, 130.3, 129.6 (2), 128.4 (2), 78.6, 72.8, 31.7, 28.0, 26.9, 22.8, 22.1; IR (neat) 3424, 2930, 1709, 1271, 1113 cm^{-1}; MS *m*/*z* (rel intensity) 235 (M + H$^+$, 80), 154 (20), 105 (100), 77 (30), 55 (20); HRMS calcd for $C_{14}H_{19}O_3$ (M + H$^+$) 235.1329, found 235.1348.

cis-3-Benzoyloxy-4-hydroxytetrahydrofuran (**20**).[7f,g] White solid: mp 82−83 °C (lit.[7f] mp 80−81 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.47 (dd, *J* = 7.3, 7.1 Hz, 2H), 5.40 (ddd, *J* = 5.9, 5.6, 4.2 Hz, 1H), 4.59 (ddd, *J* = 5.9, 5.6, 5.4 Hz, 1H), 4.19 (dd, *J* = 10.3, 5.9 Hz, 1H), 4.06 (dd, *J* = 9.4, 5.9 Hz, 1H), 4.01 (dd, *J* = 10.3, 4.2 Hz, 1H), 3.81 (dd, *J* = 9.4, 5.4 Hz, 1H), 2.24 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 133.5, 129.8 (2), 128.5 (3), 74.3, 72.4, 71.2, 70.6; IR (neat) 3424, 2953, 1715, 1269, 1117 cm^{-1}; MS *m*/*z* (rel intensity) 208 (M$^+$, 5), 165 (15), 122 (85), 105 (100), 77 (75), 51 (25); HRMS calcd for $C_{11}H_{12}O_4$ (M$^+$) 208.0736, found 208.0726.

cis-3-Hydroxyl-2-tetralinyl Benzoate (**21**).[7f] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.25−7.00 (m, 4H), 5.54−5.50 (m, 1H), 4.38−4.35 (m, 1H), 3.31−3.07 (m, 4H), 2.36 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 133.2, 132.8, 132.4, 130.0, 129.7 (2), 129.2, 129.0, 128.4 (2), 126.4, 126.3, 73.0, 67.9, 34.8, 31.7; IR (neat) 3422, 2930, 1713, 1271, 1113 cm^{-1}; MS *m*/*z* (rel intensity) 269 (M + H$^+$, 45), 165 (10), 147 (70), 105 (85), 69 (100); HRMS calcd for $C_{17}H_{17}O_3$ (M + H$^+$) 269.1172, found 269.1173.

cis-2-Hydroxycyclooct-5-enyl Benzoate (**22**). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.06 (m, 2H), 7.61−7.56 (m, 1H), 7.49−7.44 (m, 2H), 5.85−5.70 (m, 2H), 5.29 (dd, *J* = 7.5, 3.5 Hz, 1H), 4.20−4.10 (m, 1H), 3.04 (br s, 1H), 2.75−2.50 (m, 2H), 2.20−1.95 (m, 3H), 1.95−1.70 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 133.2, 130.7, 130.0, 130.0, 129.7 (2), 128.4 (2), 81.3, 73.6, 33.5, 30.3, 22.0, 21.6; IR (neat) 3402, 2934, 1694, 1269, 1113 cm^{-1}; MS *m*/*z* (rel intensity) 247 (M + H$^+$, 45), 154 (10), 123 (35), 105 (100), 77 (20); HRMS calcd for $C_{15}H_{19}O_3$ (M + H$^+$) 247.1329, found 247.1329.

cis-1-hydroxy-2,3-dihydro-1H-inden-2-yl Benzoate (**23a**).[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.01 (m, 1H), 7.57−7.40 (m, 1H), 7.40−7.20 (m, 2H), 6.20 (d, *J* = 5.1 Hz, 1H), 4.72 (q, *J* = 5.8 Hz, 1H), 3.30−3.00 (m, 2H), 2.84 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 141.1, 138.2, 133.0, 129.7, 129.7 (2), 129.4, 128.3 (2), 127.1, 126.1, 124.9, 78.0, 72.9, 38.6; IR (neat) 3358, 3063, 1717, 1271, 1099 cm^{-1}; MS *m*/*z* (rel intensity) 255 (M + H$^+$, 5), 237 (50), 154 (30), 105 (95), 77 (35), 55 (60); HRMS calcd for $C_{16}H_{15}O_3$ (M + H$^+$) 255.1016, found 255.1008.

2-Hydroxy-2,3-dihydro-1H-inden-1-yl Benzoate (**23b**).[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.95 (m, 1H), 7.57−7.40 (m, 1H), 7.40−7.20 (m, 2H), 5.67−5.62 (m, 1H), 5.28 (d, *J* = 5.1 Hz, 1H), 3.30−3.00 (m, 2H), 2.84 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 141.7, 139.1, 133.1, 129.7, 129.6 (2), 128.7, 128.2 (2), 127.2, 125.1, 124.7, 76.3, 75.1, 35.6; IR (neat) 3358, 3063, 1717, 1271, 1099 cm^{-1}; MS *m*/*z* (rel intensity) 255 (M + H$^+$, 5), 237 (50), 154 (30), 105 (95), 77 (35), 55 (60); HRMS calcd for $C_{16}H_{15}O_3$ (M + H$^+$) 255.1016, found 255.1008.

2-Benzoyloxyphenol (**24**).[9] White solid: mp 132−133 °C (lit.[9] mp 132−133 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.3 Hz, 2H), 7.69−7.64 (m, 1H), 7.55−7.50 (m, 3H), 7.20−7.13 (m, 2H), 7.03−6.95 (m, 2H), 5.95 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 147.3, 138.7, 134.0, 130.4 (2), 128.7, 128.7 (2), 127.1, 122.5, 121.0, 117.9; IR (neat) 3408, 2803, 1713, 1595, 710 cm^{-1}; MS *m*/*z* (rel intensity) 214 (M$^+$, 10), 105 (100), 77 (50), 51 (10); HRMS calcd for $C_{13}H_{10}O_3$ (M$^+$) 214.0630, found 214.0627.

anti-2-Benzoyloxy-1,2-diphenylethanol (**25**).[7c,e,f] White solid: mp 162−164 °C (lit.[7c] mp 161−163 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.40 (dd, *J* = 7.3, 7.1 Hz, 2H), 7.31−7.10 (m, 10H), 6.15 (d, *J* = 5.9 Hz, 1H), 5.14 (dd, *J* = 5.9, 3.6 Hz, 1H), 2.30 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 139.5, 136.5, 133.1, 130.0, 129.6 (2), 128.4 (2), 128.4 (2), 128.3 (2), 128.1 (2), 127.6 (2), 127.0 (2), 79.5, 76.6; IR (neat) 3524, 3046, 1697, 1275, 1117 cm^{-1}; MS *m*/*z* (rel intensity) 318 (M$^+$, 5), 212 (55), 107 (45), 105 (100), 77 (40), 51 (5); HRMS calcd for $C_{21}H_{18}O_3$ (M$^+$) 318.1256, found 318.1248.

anti-2-Benzoyloxy-1,2-ditolunylethanol (**26**). White solid: mp 158−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.07 (m, 2H), 7.58−7.51 (m, 1H), 7.45−7.41 (m, 2H), 7.13−7.00 (m, 8H), 6.06 (d, *J* = 7.3 Hz, 1H), 5.02 (d, *J* = 7.3 Hz, 1H), 2.70 (br s, 1H), 2.27 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 137.8, 137.6, 136.1, 133.9, 133.1, 130.1, 129.7 (2), 128.9 (2), 128.8 (2), 128.4 (2), 127.2 (2), 127.0 (2), 80.4, 76.9, 21.1 (2); IR (neat) 3493, 2922, 1717, 1273, 1111 cm^{-1}; MS *m*/*z* (rel intensity) 318 (M + H$^+$, 5), 329 (10), 225 (85), 105 (100), 77 (30), 55 (45); HRMS calcd for $C_{23}H_{23}O_3$ (M + H$^+$) 347.1642, found 347.1666.

syn-2-Benzoyloxy-1,2-diphenylethanol (**27**).[10] White solid: mp 144−145 °C (lit.[10] mp 146−148 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.57 (td, *J* = 7.3, 1.2 Hz, 1H), 7.45 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.30−7.15 (m, 10H), 6.11 (d, *J* = 7.3 Hz, 1H), 5.07 (dd, *J* = 7.3, 2.4 Hz, 1H), 2.73 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 139.0, 136.8, 133.2, 129.7, 128.4 (2), 128.2 (2), 128.2 (2), 128.1 (2), 128.1 (2), 127.2 (2), 127.1 (2), 80.5, 77.3; IR (neat) 3480, 3032, 1692, 1277, 1117 cm^{-1}; MS *m*/*z* (rel intensity) 319 (M + H$^+$, 15), 197 (30), 154 (100), 136 (70), 105 (60), 77 (25); HRMS calcd for $C_{21}H_{19}O_3$ (M + H$^+$) 319.1329, found 319.1338.

syn-Diisopropyl 2-Benzoyloxytartrate (**28**). White solid: mp 67−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 7.8, 7.4 Hz, 2H), 5.65 (d, *J* = 2.2 Hz, 1H), 5.16 (sep, *J* = 6.3 Hz, 1H), 5.09 (sep, *J* = 6.3 Hz, 1H), 4.83 (d, *J* = 2.2 Hz, 1H), 3.42 (br s, 1H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 166.0, 165.2, 133.5, 129.9 (2), 128.7, 128.4 (2), 73.5, 70.7, 70.7, 70.1, 21.7, 21.6, 21.5, 21.4; IR (neat) 3451, 2982, 1717, 1227, 1099 cm^{-1}; MS *m*/*z* (rel intensity) 339 (M + H$^+$, 50), 297 (15), 255 (20), 154 (10), 105 (100), 77 (10); HRMS calcd for $C_{17}H_{23}O_7$ (M + H$^+$) 339.1438, found 339.1447.

rac-2-Benzyl-3-hydroxypropyl Benzoate (**29**).[11] Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.02 (m, 2H), 7.60−7.55 (m, 1H), 7.47−7.43 (m, 2H), 7.33−7.19 (m, 5H), 4.45 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.33 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.69 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.60 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.20 (br s, 1H), 2.78 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.73 (dd, *J* = 13.7, 7.7 Hz, 1H), 2.32−2.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 139.3, 133.1, 129.9, 129.6 (2), 129.0 (2), 128.5 (2), 128.4 (2), 126.2, 64.2, 62.0, 42.7, 34.4; IR (neat) 3483, 3063, 1717, 1271, 1113 cm^{-1}; MS *m*/*z* (rel intensity) 271 (M + H$^+$, 60), 253 (35), 154 (45), 105 (100), 91 (50); HRMS calcd for $C_{17}H_{19}O_3$ (M + H$^+$) 271.1329, found 271.1336.

rac-2-Diethyl-3-hydroxybutyl Benzoate (**30**). Colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.59−7.54 (m, 1H), 7.47−7.42 (m, 2H), 4.22 (s, 2H), 3.41 (s, 2H), 2.47 (br s, 1H),

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1.50−1.25 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 133.1, 130.0, 129.6 (2), 128.4 (2), 66.3, 64.1, 41.5, 22.3 (2), 7.0 (2); IR (neat) 3420, 2965, 1699, 1269, 1113 cm^{-1}; MS m/z (rel intensity) 237 (M + H$^+$, 95), 219 (15), 123 (65), 105 (100), 77 (15); HRMS calcd for $C_{14}H_{21}O_3$ (M + H$^+$) 237.1485, found 237.1476.

*rac-2-Hydroxy-2-phenylethyl Benzoate (**31**).*[12] White solid: mp 67−68 °C (lit.[12] mp 65−67 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.01 (m, 2H), 7.60−7.50 (m, 1H), 7.50−7.28 (m, 7H), 5.07 (dd, J = 8.0, 3.7 Hz, 1H), 4.49 (dd, J = 11.5, 3.7 Hz, 1H), 4.40 (dd, J = 11.5, 3.7 Hz, 1H), 2.96 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 139.9, 133.1, 129.7, 129.6 (2), 128.5 (2), 128.4 (2), 128.1, 126.1 (2), 72.4, 69.7; IR (neat) 3294, 2913, 1717, 1263, 1090 cm^{-1}; MS m/z (rel intensity) 243 (M + H$^+$, 20), 154 (30), 137 (30), 105 (100), 77 (25), 69 (10); HRMS calcd for $C_{15}H_{15}O_3$ (M + H$^+$) 243.1016, found 243.1035.

General Procedure for Asymmetric Benzoylation of 1,2-Diols in Water. $CuCl_2$ (26.9 mg, 0.20 mmol) and (*R*,*R*)-PhBox (100.3 mg, 0.30 mmol) were mixed in purified water at room temperature for 1 h under Ar atmosphere. Then, *meso*-1,2-cyclooctanediol (144 mg, 1.0 mmol) and Me_2SnCl_2 (22.0 mg, 0.10 mmol) were added. After the suspension was stirred for 10 min, K_2CO_3 (138 mg, 1.0 mmol), DMT-MM (including 15.6% water, 393 mg, 1.2 mmol), 4-dimethylaminopyridine (12.2 mg, 0.10 mmol), and benzoyl chloride (139 mL, 1.2 mmol) were added to a suspension at room temperature under Ar atmosphere. After stirring for 5 days, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with water and brine, dried with $MgSO_4$, filtrated, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography (*n*-hexane/ethyl acetate = 10/1) to give *cis*-2-hydroxycyclooctyl benzoate (**1*S*,2*R*)-1** (146.5 mg, 59%, 60% ee) as colorless oil.

*(1*S*,2*R*)-2-Hydroxycyclooctyl Benzoate (**1*S*,2*R*)-1*.[7f] HPLC: OJ-H column, *n*-hexane/isopropanol = 98:2, wavelength = 254 nm, flow rate = 1.0 mL/min, retention time = 13.7 min (major), 16.9 min. $[\alpha]_D^{25}$ = +5.9 (60% ee, c = 1.00, $CHCl_3$), lit.[7f] $[\alpha]_D^{20}$ = +8 (77% ee, c = 0.90, CH_2Cl_2).

*(1*S*,2*R*)-2-Benzoyloxy-1,2-diphenylethanol (**1*S*,2*R*)-25*.[7b] HPLC: OJ column, *n*-hexane/isopropanol = 5:1, wavelength = 254 nm, flow rate = 1.0 mL/min, retention time = 10.2 min, 15.7 min (major). 99% ee. $[\alpha]_D^{25}$ = −36.2 (c = 1.00, $CHCl_3$), lit.[7b] $[\alpha]_D^{24}$ = −35.3 (94% ee, c = 1.00, $CHCl_3$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) For exsamples, see: (a) Lewis, C. A.; Miller, S. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 5616−5619. (b) Français, A.; Urban, D.; Beau, J.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8662−8665. (c) Wang, C.-C.; Lee, J.-C.; Luo, S.-Y.; Kulkarni, S. S.; Huang, Y.-W.; Lee, C.-C.; Chang, K.-L.; Hung, S.-C. *Nature* **2007**, *446*, 896−899. (d) Lewis, C. A.; Merkel, J.; Miller, S. J. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 6007−6011. (e) Lewis, C. A.; Longcore, K. E.; Miller, S. J.; Wender, P. A. *J. Nat. Prod.* **2009**, *72*, 1864−1869. (f) Yoshida, K.; Furuta, T.; Kawabata, T. *Tetrahedron Lett.* **2010**, *51*, 4830−4832. (g) Afagh, N. A.; Yudin, A. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 262−310. (h) Yoshida, K.; Furuta, T.; Kawabata, T. *Angew. Chem., Int. Ed.* **2011**, *123*, 4990−4994.

(2) (a) Nishino, S.; Ishido, Y. *Carbohydr. Res.* **1986**, *155*, 161−174. (b) Kurahashi, T.; Mizutani, T.; Yoshida, J. *J. Chem. Soc., Perkin Trans. 1* **1999**, 465−474. (c) Kurahashi, T.; Mizutani, T.; Yoshida, J. *Tetrahedron* **2002**, *58*, 8669−8677. (d) Griswold, K. S.; Miller, S. J. *Tetrahedron* **2003**, *59*, 8869−8875. (e) Kawabata, T.; Muramatsu, W.; Nishio, T.; Shibata, T.; Schedel, H. *J. Am. Chem. Soc.* **2007**, *129*, 12890−12895. (f) Kawabata, T.; Muramatsu, W.; Nishio, T.; Shibata, T.; Uruno, Y.; Stragies, R. *Synthesis* **2008**, 747−753. (g) Demizu, Y.; Kubo, Y.; Miyoshi, H.; Maki, T.; Matsumura, Y.; Moriyama, N.; Onomura, O. *Org. Lett.* **2008**, *10*, 5075−5077. (h) Ueda, Y.; Muramatsu, W.; Mishiro, K.; Furuta, T.; Kawabata, T. *J. Org. Chem.* **2009**, *74*, 8802−8805. (i) Dhiman, R. S.; Kluger, R. *Org. Biomol. Chem.* **2010**, *8*, 2006−2008. (j) Lee, D.; Taylor, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 3724−3727.

(3) (a) Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997. (b) Grieco, P., Ed.; *Organic Reactions in Water*; Blackie Academic & Professional: London, 1998. (c) Knochel, P.; Houk, K. N.; Keddler, H., Eds.; *Modern Solvents In Organic Synthesis*; Springer: Berlin, 1999; Topics in Current Chemistry, Vol *206*. (d) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023−2035. (e) Kobayashi, S. *Adv. Synth. Catal.* **2002**, *344*, 219. (f) Sinou, D. *Adv. Synth. Catal.* **2002**, *344*, 221−237.

(4) For great method for acylation in water, see: (a) Cameron, L. L.; Wang, S. C.; Kluger, R. *J. Am. Chem. Soc.* **2004**, *126*, 10721−10726. (b) Nakatsuji, H.; Morita, J.; Misaki, T.; Tanabe, Y. *Adv. Synth. Catal.* **2006**, *348*, 2057−2062.

(5) For examples, see: (a) Kaminski, Z. J.; Paneth, P.; Rudzinski, J. *J. Org. Chem.* **1998**, *63*, 4248−4255. (b) Kunishima, M.; Kawachi, C.; Iwasaki, F.; Terao, K.; Tani, S. *Tetrahedron Lett.* **1999**, *40*, 5327−5330. (c) Kunishima, M.; Morita, J.; Kawachi, C.; Iwasaki, F.; Terao, K.; Tani, S. *Synlett* **1999**, 1255−1256. (d) Kunishima, M.; Kawachi, C.; Morita, J.; Terao, K.; Iwasaki, F.; Tani, S. *Tetrahedron* **1999**, *55*, 13159−13170. (e) Falchi, A.; Giacomelli, G.; Porcheddu, A.; Taddei, M. *Synlett* **2000**, 275−277. (f) Demarcus, M.; Ganadu, M. J.; Mura, G. M.; Porcheddu, A.; Quaranta, L.; Reginato, G.; Taddei, M. *J. Org. Chem.* **2001**, *66*, 697. (g) Meloni, M. M.; Taddei, M. *Org. Lett.* **2001**, *3*, 337.

(6) (*R*,*R*)-2,2′-Isopropylidene-bis(4-phenyl-2-oxazoline).

(7) (a) Kawabata, T.; Nagato, M.; Takasu, K.; Fuji, K. *J. Am. Chem. Soc.* **1997**, *119*, 3169−3170. (b) Matsumura, Y.; Maki, T.; Murakami, S.; Onomura, O. *J. Am. Chem. Soc.* **2003**, *125*, 2052−2053. (c) Mizuta, S.; Sadamori, M.; Fujimoto, T.; Yamamoto, I. *Angew. Chem., Int. Ed.* **2003**, *42*, 3383−3385. (d) Mazet, C.; Kohler, V.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4888−4891. (e) Nakamura, D.; Kakiuchi, K.; Koga, K.; Shirai, R. *Org. Lett.* **2006**, *8*, 6139−6142. (f) Kündig, E. P.; Garcia, A. E.; Lomberget, T.; Garcia, P. P.; Romanens, P. *Chem. Commun.* **2008**, 3519−3521. (g) Recuero, V.; Brieva, R.; Gotor, V. *Tetrahedron: Asymmetry* **2008**, *19*, 1684−1688.

(8) Mitsunobu, O.; Kimura, J.; Iiizumi, K.; Yanagisa, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 510−513.

(9) Bredikhin, A. A.; Bredikhina, Z. A.; Zakharychev, D. V.; Konoshenko, L. V. *Tetrahedron: Asymmetry* **2007**, *18*, 1964−1970.

(10) Gissibl, A.; Finn, M. G.; Reiser, O. *Org. Lett.* **2005**, *7*, 2325−2328.

(11) Trost, B. M.; Malhotra, S.; Mino, T.; Rajapaksa, N. S. *Chem.—Eur. J.* **2008**, *14*, 7648−7657.

(12) Ciuffreda, P.; Alessandrini, L.; Terraneo, G.; Santaniello, E. *Tetrahedron: Asymmetry* **2003**, *14*, 3197−3201.