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Selective mono-acylation of 1,2- and 1,3-diols using $(\alpha, \alpha$ -difluoroalkyl)amines

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1. Introduction

Acylation of alcohols is a fundamental and important organic reaction; that has been frequently used for the protection of alcohols in both simple and complex molecules. Although many acylation methods are already known, a new and more efficient method is required.¹ Recently, we reported the selective fluorination of alcohols using a new fluorination reagent, *N*,*N*-diethyl- α , α -difluoro-*m*-methylbenzylamine (**DFMBA**).² In the reaction, a relatively high temperature was required (>100 °C), and at a lower temperature, a significant amount of an ester (**2**) derived from alcohol (**1**) and **DFMBA** was formed as a by-product. From these results, it can be presumed that the formation of adduct (**4**) in the reaction of **1** and **DFMBA** is fast, but the subsequent fluorination step is slow and **2** is formed by quenching **4** with water. Therefore, we applied α , α -difluoroalkylamines for acylation of the alcohols by carrying out the reaction under mild conditions (Scheme 1).



Scheme 1. Reaction mechanism in the fluorination of alcohols with DFBA

2. Results and discussion

2.1. Benzoylation of alcohols with DFBA

As an acylation reagent, *N*,*N*-diethyl- α , α -difluorobenzylamine (**DFBA**)^{2d,3} was used instead of **DFMBA** because it reacts with alcohols to afford benzoyl esters. Initially, the reaction of **DFBA** with 1-decanol (**1a**) was examined (Table 1). When the reaction was carried out at 0 °C for 30 min using 1.1 eq of **DFBA** to **1a**, decyl benzoate (**2a**) was obtained in 72% yield without the formation of decyl fluoride (**3a**). At 20 °C, the yield of **2a** increased to 77%, but the formation of **3a** (5%) was also observed. At 40 °C, a significant amount of **3a** (22%) was formed. These results suggested that the fluorination of **1a** proceeds at temperatures higher than 0 °C and can be prevented by carrying out the reaction at temperatures below 0 °C. Consequently, **2a** could be obtained in 97 % yield without the formation of **3a** by carrying out the reaction at 0 °C using 2 eq of **DFBA**. The benzoylation of 4-*tert*-butylphenol (**1b**) and cyclododecanol (**1c**) is slow, and a higher reaction temperature (20-40 °C) was required. However, the fluorination of these substrates is non-feasible or slower than that of **1a**, and the corresponding benzoate (**2b**) or (**2c**) was obtained without the formation of these substrates is non-feasible or slower than that of **1a**, and the corresponding benzoate (**2b**) or (**2c**) was obtained without the formation of the fluoride (**3b**) or (**3c**) under these conditions.

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R-OH		R-OBz	+	R-F
1	$CH_2CI_2, 0.$	^{5 n} 2		3
R-OH	Temp (°C)		Yield (%)	
	· opi('0)	BI BAT IN OIL	2 ^b	3 ^c
	٥	1.1	72	0
1-decanol	20	1.1	77	5
1a	<u>)</u> 40	1.1	74	22
, u	ιo	2.0	97	0
	^{20d}	1.5	38 (43)	0
4- <i>tert</i> -butylphe	nol { 20 ^e	2.0	73 (20)	0
1b	40 ^e	2.0	59 (22)	0
	0 ک	1.1	46 (24)	0
cyclododecan	ol { 20	1.5	73 (11)	0
1c	40 ل	2.0	94 (4)	0

 Table 1
 Benzoylation of alcohols with DFBA^a

DACE NET (DEPA)

 a If otherwise not mentioned, the reaction was carried out in CH_2Cl_2 for 0.5 h. b Isolated yield based on 1 used. In parentheses, recovered 1. c GC yield. d The reaction time is 1 h. e The reaction time is 3 h.

2.2. Mono-benzoylation of diols

Selective mono-benzoylation of diols is useful in organic synthesis, and many methods have been reported.⁴ In the fluorination of 1,2- and 1,3-diols with **DFMBA**, selective mono-fluorination occurred through a cyclic intermediate and acylated fluorohydrins were obtained.^{2c} Therefore, we applied **DFBA** to the selective mono-benzoylation of diols.⁵ When *prim*-diols were used, the reaction was completed at 20 °C and the corresponding mono-benzoylated products were obtained in good yields (Entries 1-4 in Table 2). With cyclic diols, the reaction was carried out at 40 °C to afford mono-benzoylation of less-reactive catechol and the sterically hindered pinacol (Entries 7 and 11). Even when 2 eq of **DFBA** to the diols was used, mono-benzoates were obtained selectively (Entries 6-11). Furthermore, from the isolated mono-benzoate (**6j**), the di-benzoate (**7j**) was obtained in good yield under the mono-benzoylation conditions (Entry 12).



Scheme 2. Reaction mechanism in mono-benzoylation of diols with DFBA

Therefore, the selectivity observed in the mono-benzoylation of diols with **DFBA** is not attributed to the steric hindrance generated in the second benzoylation but to the reaction mechanism that includes a cyclic intermediate.⁸ As in the case of the fluorination reaction of diols with **DFMBA**, a cyclic amide acetal (8) must be initially formed in the reaction of diol 5 with **DFBA**.^{2c} The amide acetal 8 exists stably under the conditions and changes to mono-benzoate 6 upon the addition of water while excess **DFBA** is

decomposed to inert N,N-diethylbenzamide by the addition of water. Therefore, the benzoylation of **6** to di-benzoate **7** scarcely occurred during the reaction, and **6** was obtained selectively (Scheme 2).

Entry	Substrate	Temp. (°C) Product	Yield (%) ^b
1	HO _{OH} 5a	20	HO 6a	84 ^c (5)
2 ^d	HO OF	<mark>1</mark> 20	HO OBz 6b	82 ^c (4)
3		H 20	HO OE 6c	3z 94 (4)
4 ^e	Sd OH	20	6d OBz	70 ^c (12)
5	EtOOC OH EtOOC 5e	40	EtOOC OB EtOOC 6e	z 71 (0)
6 ^f	HO,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	40	HO _{////} OBz	91 (0)
7 ^{f,g}	HO OH 5g	20	HO OBz 6g	86 (2)
8 ^f	OH 5h OH	40	OBz 6h OH	92 (3)
9 ^f	OH 5i OH	40	OBz 6i OH	87 (5)
10 ^f		Н 40 Н		^{3z} 95 (0) H
11 ^f	OH OH 5k	40		89 (4)
12 ^f	6j	40		^{3z} 99 3z

Table 2 Mono-benzoylation of diols with DFBA^a

^a If otherwise not mentioned, the reaction was carried out in CH₂Cl₂ for 0.5 h using 1.1 eq. of **DFBA** to substrate. ^b Isolated yield based on substrate used. In parentheses, yield of dibenzoate obtained by GC. ^{c 1}H NMR yield. ^d The reaction time is 3 h. ^e The reaction time is 5 h. ^f2 eq of **DFBA** to the substrate was used. ^g The reaction time is 1 h.

Generally, after the aqueous work-up, only mono-benzoate **6** was obtained and the presumed cyclic intermediate **8** could not be isolated. However, in the reaction of diethyl tartrate **5e** with **DFBA**, the corresponding amide acetal **8e** was isolated, and it changed to mono-benzoate **6e** under acidic conditions (Scheme 3).



Scheme 3. Isolation and reaction of cyclic amide acetal 8e

Next, we examined the regioselectivity in the benzoylation of unsymmetrical diols. With 1,3-butandiol (51) having *prim*- and *sec*-alcohol, regioselectivity was not observed, and 3-hydroxybutyl benzoate (61) and 4-hydroxybut-2-yl benzoate (61') were obtained as a 1:1 mixture. On the other hand, in the reaction with 4-methyl-2,4-pentandiol (5m) having *sec*- and *tert*-alcohol, the benzoylation selectively occurred at *sec*-alcohol to afford 4-hydroxy-4-methylbut-2-yl benzoate (6m) in 83% yield (Scheme 4).⁹



Scheme 4. Benzoylation of unsymmetrical diols with DFBA

The selective protection of one hydroxy group in sugars is important for their transformation to oligosaccharide.¹⁰ Therefore, we applied the present benzoylation reaction to sugars. When methyl 5-*O*-benzoyl- β -D-ribofuranose (9) was subjected to the reaction with **DFBA**, selective mono-benzoylation occurred to afford methyl 3,5-di-*O*-benzoyl- β -D-ribofuranose (10) and methyl 2,5-di-*O*-benzoyl- β -D-ribofuranose (11) in 34% and 38% yields, respectively. With methyl 4,6-*O*-benzylidene- β -*D*-glucopyranoside (12), methyl 3-benzoyl-4,6-*O*-benzylidene- β -D-glucopyranoside (13) was obtained in 54% yield with minor products of 2-benzoyl-4,6-*O*-benzylidene- β -D-glucopyranoside (14) (18%) and dibenzoate (15) (6%) (Scheme 5).



Scheme 5. mono-Benzoylation of sugars with DFBA

2.3. Acylation of diols with various a,a-difluoroalkylamines

As various difluoroalkylamines can be prepared from amides in two steps,³ the present *mono*-benzoylation reaction of diols can be extended to other acylation reactions. The selective *mono*-nicotinylation, formylation, and pivaloylation as well as 3-methylbenzoylation of diols were achieved by using N-(difluoro(pyridin-3-yl)methyl)-N,N-diethylamine, N-(difluoromethyl)morpholine, N-(1,1-difluoro-2,2-dimethylpropyl)pyrrolidine, and **DFMBA** as shown in Table 3.



Table 3. Acylation of diols with various α, α -difluoroalkylamines^a

^a If otherwise not mentioned, the reaction was carried out in CH₂Cl₂ at 20 °C for 0.5 h using 1.1 eq. of difluoroalkylamine to substrate. ^b Isolated yield based on substrate used. In parentheses, yield of diacylated product. ^c2 eq. of difluoroamine to substrate was used. ^d The reaction was carried out at 40 °C.

3. Conclusion

The selective mono-benzoylation of 1,2- or 1,3-diols was achieved by using N,N-diethyl- α,α -difluorobenzylamine (**DFBA**). The reaction was completed under mild conditions in a short reaction time, and *prim-, sec-,* and *tert*-diols and catechol could be converted to the corresponding mono-benzoates. It was shown that the reaction proceeded through a cyclic amide acetal. The selective *mono*-nicotinylation, formylation, and pivaloyation of diols were also performed by using the corresponding difluoroalkylamines.

4. Experimental

4.1. General

The IR spectra were recorded using a JASCO FT/IR-410. The ¹H NMR (400 MHz), and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ on a JEOL JNM-A400II FT NMR and the chemical shift, δ , were referred to TMS. The EI and ESI high-resolution mass spectra were measured on a JEOL JMS-T100GCV. **DFMBA** was donated from Mitsubishi Gas Chemical Company, INC. **DFBA**, *N*-(difluoromethyl)morpholine, and *N*-(1,1-difluoro-2,2-dimethylpropyl)pyrrolidine were prepared according to the previously reported

procedures.³ *N*-(Difluoro(pyridin-3-yl)methyl)-*N*,*N*-diethylamine was prepared from *N*,*N*-diethyl nicotinamide according to the literature (bp 52-54 °C / 0.1 mmHg).³ They were stored in a Teflon bottle under N₂. The small scale reaction can be carried out using glasswares, but use of Teflon wares is recommended.

4.2. Benzoylation of alcohols with DFBA

4.2.1. Decyl benzoate (2a)¹¹

To a CH₂Cl₂ solution (3 mL) of **DFBA** (199 mg, 1.0 mmol) was added at 0 °C under N₂ atmosphere **1a** (79 mg, 0.5 mmol), and the mixture was stirred at 0 °C for 30 min. Then, the mixture was poured into sat. aq NaHCO₃ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:Et₂O = 10:1) gave **2a** (127 mg) in 97% yield; IR (neat) 2925, 1721, 1274 cm⁻¹. ¹H NMR δ 8.06-8.04 (m, 2H), 7.56 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.44 (dd, *J* = 7.5, 7.5 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.80-1.73 (m, 2H), 1.48-1.27 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H). ¹³C NMR δ 166.64, 132.73, 130.49, 129.49 (2C), 128.26 (2C), 65.10, 31.86, 29.50 (2C), 29.27, 29.26, 28.69, 26.02, 22.65, 14.09.

4.2.2. 4-tert-Butylphenyl benzoate (2b)

The reaction was carried out as in the case of **4.2.1**. using **DFBA** (199 mg, 1.0 mmol) and **1b** (75 mg, 0.5 mmol) at 20 °C for 3 h. Purification by column chromatography (silica gel/hexane:Et₂O = 10:1) gave **2b** (93 mg) in 73% yield; white solid. mp 78 °C (lit.¹² 80-82 °C). IR (KBr) 2963, 1734, 1264 cm⁻¹. ¹H NMR δ 8.20 (d, *J* = 6.9 Hz, 2H), 7.65-7.62 (m, 1H), 7.51 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 1.34 (s, 9H). ¹³C NMR δ 165.34, 148.68, 148.56, 133.49, 130.15 (2C), 129.68, 128.52 (2C), 126.39 (2C), 120.98 (2C), 34.49, 31.42 (3C).

4.2.3. Cyclododecyl benzoate (2c)¹³

The reaction was carried out as in the case of **4.2.1.** using **DFBA** (199 mg, 1.0 mmol) and **1c** (92 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane: Et₂O = 10:1) gave **2c** (135 mg) in 94% yield; white solid. mp 38-40 °C. IR (KBr) 2935, 1713, 1276 cm⁻¹. ¹H NMR δ 8.24 (d, *J* = 8.0 Hz, 2H), 7.53 (dd, *J* = 7.6, 7.1 Hz, 1H), 7.42 (dd, *J* = 7.9, 7.4 Hz, 2H), 5.29-5.23 (m, 1H), 1.87-1.79 (m, 2H), 1.69-1.61 (m, 2H), 1.45-1.33 (m, 18H). ¹³C NMR δ 166.19, 132.60, 130.89, 129.45 (2C), 128.20 (2C), 72.85, 29.05(2C), 24.13(2C), 23.91, 23.28 (2C), 23.09 (2C), 20.82 (2C).

4.3. mono-Benzoylation of diols

4.3.1. 2-Hydroxyethyl benzoate (6a)¹⁴

To a CH₂Cl₂ solution (3 mL) of **DFBA** (111 mg, 0.55 mmol) was added at room temperature under N₂ atmosphere **5a** (31 mg, 0.5 mmol), and the mixture was stirred at 20 °C for 30 min. Then, the mixture was poured into sat. aq NaHCO₃ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. The yield of **6a** was determined by ¹H NMR using 1,4-dimethoxybenzene as an internal standard (84%) and the yield of dibenzoate was determined by GC (5%). Pure **6a** was obtained by column chromatography (silica gel/hexane:EtOAc = 2:1); IR (neat) 3424, 2952, 1719, 1277 cm⁻¹. ¹H NMR δ 8.08-8.06 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 4.49-4.47 (m, 2H), 3.99-3.95 (m, 2H), 2.07 (t, *J* = 5.9 Hz, 1H). ¹³C NMR δ 166.93, 133.12, 129.73, 129.60 (2C), 128.33 (2C), 66.56, 61.17.

4.3.2. 3-Hydroxypropan-1-yl benzoate (6b)¹⁴

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (110 mg, 0.55 mmol) and **5b** (38 mg, 0.5 mmol) at 20 °C for 3 h. The yield of **6b** (82%) was determined by ¹H NMR using 1,4-dimethoxybenzene as an internal standard. Pure **6b** was obtained by column chromatography (silica gel/hexane:EtOAc = 2:1); IR (neat) 3416, 2960, 1718, 1277 cm⁻¹. ¹H NMR δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.59-7.55 (m, 1H), 7.45 (dd, *J* = 7.7, 7.7 Hz, 2H), 4.50 (t, *J* = 6.2 Hz, 2H), 3.78 (dt, *J* = 6.0, 6.0 Hz,

2H), 2.05-1.99 (m, 2H), 1.93 (t, *J* = 5.6 Hz, 1H). ¹³C NMR δ 167.00, 133.04, 130.01, 129.57 (2C), 128.37 (2C), 61.73, 59.10, 31.84.

4.3.3. 3-Hydroxy-2,2-dimethylpropan-1-yl benzoate (6c)¹⁵

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (110 mg, 0.55 mmol) and **5c** (52 mg, 0.5 mmol) at 20 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 3:1) gave **6c** (98 mg) in 94% yield; IR (neat) 3438, 2963, 1720, 1274 cm⁻¹. ¹H NMR δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.57 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.45 (dd, *J* = 6.9, 6.9 Hz, 2H), 4.18 (s, 2H), 3.40 (s, 2H), 1.01 (s, 6H). ¹³C NMR δ 167.07, 133.08, 129.91, 129.55 (2C), 128.37 (2C), 69.68, 68.08, 36.64, 21.51 (2C).

4.3.4. {1-(Hydroxymethyl)cyclopropyl}methyl benzoate (6d)

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (110 mg, 0.55 mmol) and **5d** (51 mg, 0.5 mmol) at 20 °C for 5 h. The yield of **6d** (70%) was determined by ¹H NMR using 1,4-dimethoxybenzene as an internal standard. Pure **6d** was obtained by column chromatography (silica gel/hexane:EtOAc = 2:1); IR (neat) 3423, 2950, 1714, 1274 cm⁻¹. ¹H NMR δ 8.07-8.05 (m 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 4.33 (s, 2H), 3.53 (d, *J* = 5.9 Hz, 2H), 2.16 (t, *J* = 6.1 Hz, 1H), 0.69-0.59 (m, 4H). ¹³C NMR δ 167.10, 133.06, 130.01, 129.62 (2C), 128.37 (2C), 68.65, 66.62, 22.56, 8.93 (2C). HRMS (ESI) calcd for C₁₂H₁₄O₃Na (M⁺+Na) 229.08352, found 229.08335.

4.3.5. (2S, 3S)-Diethyl 2-benzoyloxy-3-hydroxybutandioate (6e)

The reaction was carried out as in the case of **4.3.1** using **DFBA** (110 mg, 0.55 mmol) and **5e** (103 mg, 0.5 mmol) at 40 °C for 30 min. After the reaction, THF (3 mL) and 1M HCl (3 mL) were added and the mixture was stirred at 20 °C overnight. Then, the mixture was poured into sat. aq NaHCO₃ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:EtOAc = 1:1) gave **6e** (110 mg) in 71% yield; white solid. mp 51-53 °C (lit.¹⁶ 56-59 °C). IR (KBr) 3428, 2982, 1763, 1748, 1718, 1265, 1225 cm⁻¹. ¹H NMR δ 8.05-8.03 (m, 2H), 7.59 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.45 (dd, *J* = 7.8, 7.8 Hz, 2H), 5.66 (d, *J* = 2.2 Hz, 1H), 4.86 (dd, *J* = 7.5, 2.4 Hz, 1H), 4.33-4.21 (m, 4H), 3.26 (d, *J* = 7.3 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ¹³C NMR δ 170.87, 166.49, 165.23, 133.63, 129.92 (2C), 128.70, 128.49 (2C), 73.43, 70.66, 62.65, 62.16, 14.06, 14.03.

4.3.6. (2R, 3R)-3-Hydroxybutan-2-yl benzoate (6f)¹⁷

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (199 mg, 1.0 mmol) and **5f** (45 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave **6f** (88 mg) in 89% yield; IR (neat) 3443, 2980, 1714, 1276 cm⁻¹. ¹H NMR δ 8.07-8.05 (m, 2H), 7.60-7.56 (m, 1H), 7.46 (dd, J = 8.0, 8.0 Hz, 2H), 5.07-5.00 (m, 1H), 3.95-3.89 (m, 1H), 2.00 (brs, 1H), 1.36 (d, J = 6.3 Hz, 3H), 1.27 (d, J = 6.3 Hz, 3H). ¹³C NMR δ 166.23, 133.04, 130.21, 129.56 (2C), 128.37 (2C), 75.42, 70.10, 19.00, 16.21.

4.3.7. 3-Hydroxy-2,3-dimethylbutan-2-yl benzoate (6g)¹⁸

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (199 mg, 1.0 mmol) and **5g** (59 mg, 0.5 mmol) at 20 °C for 1 h. Purification by column chromatography (silica gel/hexane:EtOAc = 3:1) gave **6g** (95 mg) in 86 % yield; IR (neat) 3439, 2988, 1714, 1287 cm⁻¹. ¹H NMR δ 7.99 (d, J = 7.0 Hz, 2H), 7.55 (dd, J = 7.3, 7.3 Hz, 1H), 7.44 (dd, J = 7.8, 7.8 Hz, 2H), 3.78 (s, 1H), 1.64 (s, 6H), 1.31 (s, 6H). ¹³C NMR δ 166.48, 132.84, 131.15, 129.40 (2C), 128.28 (2C), 89.89, 74.73, 25.13(2C), 21.78 (2C).

4.3.8. cis-2-Hydroxycyclohexyl benzoate (6h)¹⁹

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (199 mg, 1.0 mmol) and **5h** (58 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave **6h** (101 mg) in 92% yield; IR (neat) 3469, 2939, 1716, 1279 cm⁻¹. ¹H NMR δ 8.06 (d, *J* = 7.0 Hz, 2H), 7.58 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.46 (dd, *J* = 7.9, 7.9 Hz, 2H), 5.24-5.21 (m, 1H), 3.97 (brs, 1H), 2.06-1.38 (m, 8H). ¹³C NMR δ 166.23, 133.06, 130.37, 129.60 (2C), 128.41 (2C), 74.61, 69.64, 30.40, 27.37, 21.81, 21.52.

4.3.9. cis-2-Hydroxycyclopentyl benzoate (6i)¹⁹

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (199 mg, 1.0 mmol) and **5i** (51 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave **6i** (90 mg) in 87% yield; IR (neat) 3468, 2970, 1715, 1278 cm⁻¹. ¹H NMR δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.58 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.45 (dd, *J* = 7.7, 7.7 Hz, 2H), 5.26-5.22 (m, 1H), 4.34-4.30 (m, 1H), 2.17-1.60 (m, 6H). ¹³C NMR δ 166.39, 133.04, 130.07, 129.57 (2C), 128.34 (2C), 77.36, 73.30, 30.78, 28.12, 19.41.

4.3.10. cis-2-Hydroxycyclododecyl benzoate (6j)

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (199 mg, 1.0 mmol) and **5j** (100 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave **6j** (144 mg) in 95% yield; white solid. mp 111 °C (lit²⁰ 112.5-113.5 °C). IR (KBr) 3523, 2926, 1700, 1276 cm⁻¹. ¹H NMR δ 8.07-8.05 (m, 2H), 7.59-7.55 (m, 1H), 7.45 (dd, *J* = 7.8, 7.4 Hz, 2H), 5.32 (t, *J* = 6.0 Hz, 1H), 4.00 (d, *J* = 5.2 Hz, 1H), 1.88-1.36 (m, 20H). ¹³C NMR δ 166.70, 133.02, 130.25, 129.61 (2C), 128.36 (2C), 71.46, 71.42, 28.89-21.31 (10C).

4.3.11. 2-Hydroxyphenyl benzoate (6k)

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (199 mg, 1.0 mmol) and **5k** (55 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 3:1) gave **6k** (95 mg) in 89% yield; white solid: mp 130 °C (lit.²¹ 130°C). IR (KBr) 3411, 1715, 1273 cm⁻¹. ¹H NMR δ 8.24-8.22 (m, 2H), 7.68 (dd, J = 7.5, 7.5 Hz, 1H), 7.54 (dd, J = 7.7, 7.7 Hz, 2H), 7.22-7.17 (m, 2H), 7.09-7.07 (m, 1H), 7.01-6.97 (m, 1H), 5.43 (s, 1H). ¹³C NMR δ 165.07, 147.25, 138.77, 134.04, 130.38 (2C), 128.73, 128.71 (2C), 127.18, 122.50, 121.12, 118.06.

4.3.12. cis-1,2-Dibenzoyloxycyclododecane (7j)

The reaction was carried out as in the case of **4.3.6**. using **DFBA** (199 mg, 1.0 mmol) and **6j** (152 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 5:1) gave **7j** (205 mg) in 99% yield; IR (neat) 2935, 1715, 1259 cm⁻¹. ¹H NMR δ 8.01 (d, J = 7.7 Hz, 4H), 7.55 (dd, J = 7.6, 7.3 Hz, 2H), 7.42 (dd, J = 7.7, 7.6 Hz, 4H), 5.50 (t, J = 6.3 Hz, 2H), 2.01-1.83 (m, 4H), 1.59-1.25 (m, 16H). ¹³C NMR δ 166.11 (2C), 132.86 (2C), 130.37 (2C), 129.60 (4C), 128.29 (4C), 73.62, 73.44, 26.18-21.45 (10C). HRMS (ESI) calcd for C₂₆H₃₂O₄Na (M⁺+Na) 431.21928, found 431.22011.

4.3.13. (4S, 5S)-Diethyl 2-(diethylamino)-2-phenyl-1,3-dioxolane-4,5-dicarboxylate (8e)

To a CH₂Cl₂ solution (3 mL) of **DFBA** (199 mg, 1.0 mmol) was added at 20 °C under N₂ atmosphere **5e** (206 mg, 1.0 mmol), and the mixture was stirred for 10 min. Then, the mixture was poured into sat. aq NaHCO₃ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:Et₂O = 2:1) gave **8e** (112 mg) in 31% yield. To a THF solution (3 mL) of **8e** (112 mg, 0.31 mmol) was added 1 M aq HCl (3 mL) and the mixture was stirred at 20 °C overnight. The mixture was poured into sat. aq NaHCO₃ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:EtOAc = 1:1) gave **6e** (54 mg) in 88% yield. **8e**; IR (neat) 2981, 1748, 1117 cm⁻¹. ¹H NMR δ 7.63-7.60 (m, 2H), 7.34-7.32 (m, 3H), 4.73 (d, *J* = 6.2 Hz, 1H), 4.59 (d, *J* = 6.2 Hz, 1H), 4.28 (q, *J* = 7.0 Hz, 2H), 4.08-3.91 (m, 2H), 2.77 (q, *J* = 7.1 Hz, 4H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = Hz, 6H). ¹³C NMR δ 169.26, 169.02, 139.02, 128.67, 127.71 (2C), 127.55 (2C), 123.48, 75.91, 75.13, 61.74, 61.49, 40.28 (2C), 14.08, 13.99 (2C), 13.90. HRMS (EI) calcd for C₁₉H₂₈O₆N 366.19111, found 366.19214.

4.3.14. 3-Hydroxybutyl benzoate (6l)²² and 4-hydroxybut-2-yl benzoate (6l')²²

The reaction was carried out as in the case of **4.3.6** using **DFBA** (149 mg, 0.75 mmol) and **51** (45 mg, 0.5 mmol) at 0 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 1:1) gave a mixture of **61** and **61'** (77 mg) in 79% yield (inseparable). From ¹H NMR spectra, **61** and **61'** were found to be formed in 1:1 ratio; ¹H NMR δ 8.06-8.03 (m, 2H), 7.59-7.55 (m, 1H), 7.47-7.43 (m, 2H),

5.43-5.34 (m, 0.5H, **6l**'), 4.64-4.58 (m, 0.5H, **6l**), 4.41-4.36 (m, 0.5H, **6l**), 3.98-3.97 (m, 0.5H, **6l**), 3.70-3.66 (m, 1H, **6l**'), 2.53 (brs, 0.5H), 2.14 (brs, 1H), 1.99-1.80 (m, 2H), 1.38 (t, J = 0.7Hz, 1.5H, **6l**'), 1.25 (t, J = 0.8 Hz, 1.5H, **6l**).

4.3.15. 4-Hydroxy-4-methylpentan-2-yl benzoate (6m)²³

The reaction was carried out as in the case of **4.3.1**. using **DFBA** (199 mg, 1.0 mmol) and **51** (59 mg, 0.5 mmol) at 20 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave **6m** (92 mg) in 83% yield. IR (neat) 3480, 2975, 1714, 1281 cm⁻¹. ¹H NMR δ 8.06-8.02 (m, 2H), 7.59-7.39 (m, 3H), 5.48-5.37 (m, 1H), 2.07 (dd, J = 14.8, 8.7 Hz, 1H), 1.77 (dd, J = 14.9, 3.3 Hz, 1H), 1.39 (d, J = 6.3 Hz, 3H), 1.28 (s, 3H), 1.26 (s, 3H). ¹³C NMR δ 166.17, 132.94, 130.44, 129.46 (2C), 128.37 (2C), 70.00, 69.36, 49.02, 29.91, 29.68, 21.76.

4.3.16. Methyl 3,5-di-*O*-benzoyl-β-D-ribofuranoside (10) and methyl 2,5-di-*O*-benzoly-β-D-ribofuranoside (11)

The reaction was carried out as in the case of **4.3.6** using 2.0 eq of **DFBA** (199 mg, 1.0 mmol) at 40 °C for 30 min. The yields of **10** (34%) and **11** (38%) were determined by ¹HNMR using 1,4-dimethoxybenzene as an internal standard, respectively. Pure **10** and **11** were obtained by column chromatography (silica gel/CHCl₃:acetone = 20:1); **10**²⁴; IR (neat) 3469, 2936, 1724, 1273 cm⁻¹. ¹H NMR δ 8.04 (d, J = 7.9 Hz, 4H), 7.60 (dd, J = 7.6, 7.4 Hz, 1H), 7.54 (dd, J = 7.5, 7.4 Hz, 1H), 7.45 (dd, J = 7.8, 7.8 Hz, 2H), 7.38 (dd, J = 7.8, 7.7 Hz, 2H), 5.54 (dd, J = 6.3, 4.8 Hz, 1H), 4.98 (s, 1H), 4.67-4.46 (m, 4H), 3.38 (s, 3H). ¹³C NMR δ 166.25, 165.71, 133.62, 133.09, 129.78 (2C), 129.71, 129.68 (2C), 128.91, 128.52 (2C), 128.32 (2C), 108.48, 78.35, 74.71, 74.30, 64.95, 55.26. **11**; white solid. mp 136 °C (lit.²⁴ 132-133 °C). IR (KBr) 3409, 2943, 1723, 1274 cm⁻¹. ¹H NMR δ 8.04 (d, J = 7.9 Hz, 4H), 7.60 (dd, J = 7.6, 7.4 Hz, 1H), 7.45 (dd, J = 7.8, 7.7 Hz, 2H), 5.54 (dd, J = 7.8, 7.7 Hz, 2H), 5.54 (dd, J = 7.9 Hz, 4H), 7.60 (dd, J = 7.6, 7.4 Hz, 1H), 7.55, 55.26. **11**; white solid. mp 136 °C (lit.²⁴ 132-133 °C). IR (KBr) 3409, 2943, 1723, 1274 cm⁻¹. ¹H NMR δ 8.04 (d, J = 7.9 Hz, 4H), 7.60 (dd, J = 7.6, 7.4 Hz, 1H), 7.54 (dd, J = 7.5, 7.4 Hz, 1H), 7.45 (dd, J = 7.8, 7.7 Hz, 2H), 5.54 (dd, J = 6.3, 4.8 Hz, 1H), 4.98 (s, 1H), 4.67-4.46 (m, 4H), 3.38 (s, 3H). ¹³C NMR δ 166.48, 166.10, 133.53, 133.11, 129.81 (2C), 129.75, 129.68 (2C), 129.08, 128.46 (2C), 128.34 (2C), 105.94, 80.78, 77.09, 71.11, 64.56, 55.14.

4.3.17. Methyl 3-benzoyl-4,6-*O*-benzylidene- β -D-glucopyranoside (13) and methyl 2-benzoyl-4,6-*O*-benzylidene- β -D-glucopyranoside (14)

The reaction was carried out as in the case of **4.3.6** using **DFBA** (120 mg, 0.6 mmol) and **12** (141 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave **13** (104 mg) in 54% yield and **14** (35 mg) in 18% yield, and **15** (15 mg) in 6% yield, respectively. **13**; white solid. mp 180-182 °C (lit.²² 183-184 °C). IR (KBr) 3423, 2866, 1725, 1276, 1080cm⁻¹. ¹H NMR δ 8.10-8.08 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46-7.41 (m, 4H), 7.32-7.30 (m, 3H), 5.55 (brs, 1H), 5.48 (t, *J* = 9.4 Hz, 1H), 4.47 (d, *J* = 7.5 Hz, 1H), 4.42 (dd, *J* = 8.5, 4.9 Hz, 1H), 3.87-3.80 (m, 2H), 3.75-3.70 (m, 1H), 3.64-3.58 (m, 1H), 3.63 (s, 3H), 2.73 (d, *J* = 3Hz, 1H). ¹³C NMR δ 166.63, 136.78, 133.27, 129.92 (2C), 129.55, 129.00, 128.34 (2C), 128.17 (2C), 126.04 (2C), 104.57, 101.41, 78.55, 74.36, 73.60, 68.63, 66.45, 57.68. **14**; white solid. mp 201-203 °C (lit.²⁵ 202-203 °C). IR (KBr) 3552, 2871, 1710, 1281, 1096 cm⁻¹. ¹H NMR δ 8.09 (d, *J* = 7.1 Hz, 2H), 7.61-7.38 (m, 8H), 5.60 (s, 1H), 5.19 (dd, *J* = 9.0, 8.0 Hz, 1H), 4.62 (d, *J* = 7.8 Hz, 1H), 4.42 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.07 (dt, *J* = 3.2, 9.1 Hz, 1H), 3.86 (t, *J* = 10.2 Hz, 1H), 3.58-3.54 (m, 1H), 3.52 (s, 3H), 2.63 (d, *J* = 3.3 Hz, 1H). ¹³C NMR δ 165.91, 136.84, 133.32, 129.94 (2C), 129.56, 129.33, 128.40 (2C), 128.36 (2C), 126.25 (2C), 102.37, 101.91, 80.90, 74.66, 72.42, 68.61, 66.16, 57.26. **15**²⁵; ¹H NMR δ 7.97-7.94 (m, 4H), 7.54-7.31 (m, 10H), 5.79 (t, *J* = 9.5 Hz, 1H), 5.56 (s, 1H), 5.47 (dd, *J* = 8.0, 9.6 Hz, 1H), 4.71 (d, *J* = 7.8 Hz, 1H), 4.45 (dd, *J* = 4.9, 10.4 Hz, 1H), 3.54 (s, 3H).

4.3.18. cis -2-Hydroxycyclohexyl nicotinate (16)

The reaction 4.3.1. was carried out in the case of using as N-(difluoro(pyridin-3-yl)methyl)-N,N-diethylamine (200 mg, 1.0 mmol) and **5h** (58 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave 16 (97) mg) in 88% yield; IR (neat) 3393, 2939, 1720, 1288 cm⁻¹. ¹H NMR δ 9.24 (s, 1H), 8.78 (d, J = 4.7 Hz, 1H), 8.31 (dd, J = 8.0, 3.2 Hz, 1H), 7.40 (dd, J = 7.8, 4.9 Hz, 1H), 5.28-5.26 (m, 1H), 4.01 (s, 1H), 2.21-1.41 (m, 8H). ¹³C NMR δ 164.78, 153.14, 150.61, 137.16, 126.38, 123.30, 75.21, 69.25, 30.35, 27.36, 21.61, 21.57. HRMS (ESI) calcd for $C_{12}H_{15}O_3NNa$ (M⁺+Na) 244.09441, found 244.09473.

4.3.19. 3-Hydroxy-2,2-dimethylpropan-1-yl 3-methylbenzoate (17a)

The reaction was carried out as in the case of **4.3.6** using **DFMBA** (213 mg, 1.0 mmol) and **5e** (51 mg, 0.5 mmol) at 40 °C for 30 min.. Purification by column chromatography (silica gel/hexane:EtOAc = 3:1) gave **17a** (96 mg) in 87% yield; IR (neat) 3447, 2962, 1719, 1279 cm⁻¹. ¹H NMR δ 7.85-7.83 (m, 2H), 7.40-7.32 (m, 2H), 4.18 (s, 2H), 3.38 (d, *J* = 5.2 Hz, 2H), 2.41 (s, 2H), 2.32 (brs, 1H), 1.02 (s, 6H). ¹³C NMR δ 167.26, 138.16, 133.84, 130.08, 129.83, 128.25, 126.69, 69.60, 68.07, 36.69, 21.51 (2C), 21.21. HRMS (ESI) calcd for C₁₃H₁₈O₃Na (M⁺+Na) 245.11482, found 245.11487.

4.3.20. cis-2-Hydroxycyclopentyl 3-methylbenzoate (17b)

The reaction was carried out as in the case of **4.3.6**. using **DFMBA** (213 mg, 1.0 mmol) and **5i** (51 mg, 0.5 mmol) at 40 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 3:1) gave **17b** (97 mg) in 87% yield; IR (neat) 3470, 2968, 1714, 1280 cm⁻¹. ¹H NMR δ 7.86-7.84 (m, 2H), 7.40-7.32 (m, 2H), 5.25-5.21 (m, 1H), 4.33-4.29 (m, 1H), 2.41 (s, 3H), 2.13-1.62 (m, 6H). ¹³C NMR δ 166.57, 138.18, 133.85, 130.08, 129.97, 128.26, 126.72, 77.30, 73.33, 30.83, 28.13, 21.24, 19.45. HRMS (ESI) calcd for C₁₃H₁₆O₃Na (M⁺+Na) 243.09917, found 243.09905.

4.3.21. cis-2-Hydroxycyclodocecyl formate (18)

The reaction was carried out as in the case of **4.3.1**. using *N*-(difluoromethyl)morpholine (75 mg, 0.55 mmol) and **5j** (100 mg, 0.5 mmol) at 20 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 2:1) gave **18** (93 mg) in 82% yield; IR (neat) 3379, 2947, 1727, 1200 cm⁻¹. ¹H NMR δ 8.14 (s, 1H), 5.21 (t, *J* = 6.1 Hz, 1H), 3.90-3.88 (m, 1H), 1.79-1.35 (m, 20H). ¹³C NMR δ 161.11, 75.51, 71.48, 29.02, 24.65, 24.51, 24.41, 23.65, 23.52, 21.78, 21.74 (2C), 21.15. HRMS (ESI) calcd for C₁₃H₂₄O₃Na (M⁺+Na) 251.16177, found 251.16185.

4.3.22. (4-Hydroxy-4-methylpentan-2-yl) pivalate (19) and (4-hydroxy-2-methylpentan-2-yl) pivalate (20)

The reaction was carried out as in the case of 4.3.6. using N-(1,1-difluoro-2,2-dimethylpropyl)pyrrolidine (177 mg, 1.0 mmol) and **5m** (59 mg, 0.5 mmol) at 20 °C for 30 min. Purification by column chromatography (silica gel/hexane:EtOAc = 3:1) gave 19 (72 mg) in 71% yield and **20** (36 mg) in 18% yield, respectively. **19**; IR (neat) 3446, 2974, 1725, 1169 cm⁻¹. ¹H NMR δ 5.17-5.10 (m, 1H), 2.22 (brs, 1H), 1,90 (dd, J = 14.9, 9.0 Hz, 1H), 1.66 (dd, J = 14.9, 3.1 Hz, 1H), 1.25-1.22 (m, 6H), 1.19 (s, 9H). ¹³C NMR δ 178.11, 69.91, 68.56, 48.75, 38.55, 29.70, 29.52, 26.97 (3C), 21.46. HRMS (ESI) calcd for C₁₁H₂₂O₃Na 225.14612, found 225.14613. 20; IR (neat) 3446, 2972, 1724, 1136 cm⁻¹. ¹H NMR δ 4.12-4.09 (m, 1H), 2.20 (brs, 1H), 1,96 (dd, J = 14.9, 9.2 Hz, 1H), 1.75 (dd, J = 14.8, 2.2 Hz, 1H), 1.53 (d, J = Hz, 3H), 1.23-1.19 (m, 6H), 1.17 (s, 9H). ¹³C NMR δ 177.69, 82.28, 64.76, 50.05, 39.25, 27.14 (3C), 26.84, 25.64, 24.56. HRMS (ESI) calcd for $C_{11}H_{22}O_3Na$ (M⁺+Na) 225.14612, found 225.14614.

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