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

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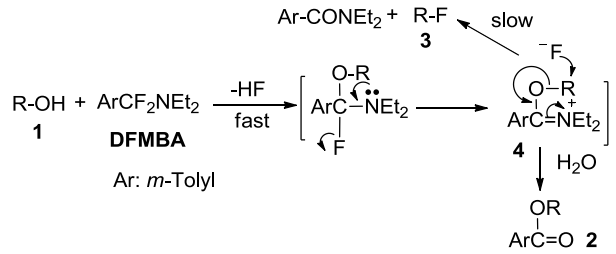
1. Introduction

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 the fluoride (**3b**) or (**3c**) under these conditions.

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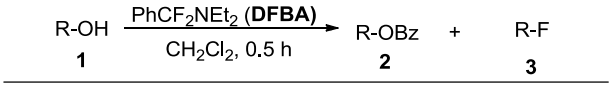
Table 1 Benzoylation of alcohols with **DFBA**[a]

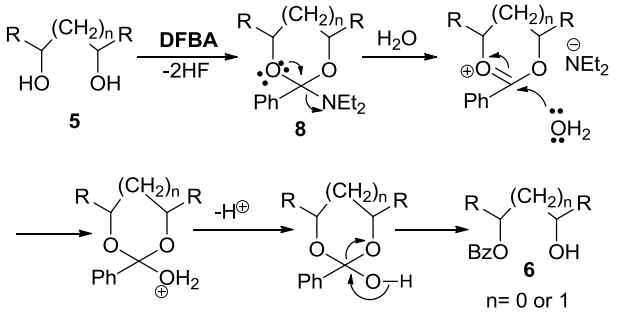


R-OH	Temp.(°C)	DFBA / R-OH	Yield (%) 2[b]	Yield (%) 3[c]
1-decanol **1a**	0	1.1	72	0
	20	1.1	77	5
	40	1.1	74	22
	0	2.0	97	0
4-*tert*-butylphenol **1b**	20[d]	1.5	38 (43)	0
	20[e]	2.0	73 (20)	0
	40[e]	2.0	59 (22)	0
cyclododecanol **1c**	0	1.1	46 (24)	0
	20	1.5	73 (11)	0
	40	2.0	94 (4)	0

[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-benzoates in good yields (Entries 8-10). The reaction of **DFBA** with diols is fast and is applicable to the 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).

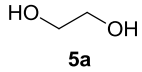
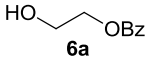
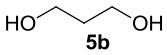
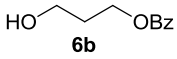
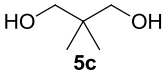
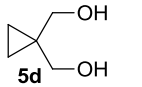
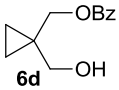
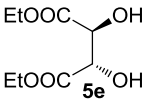
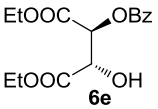
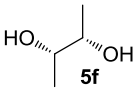
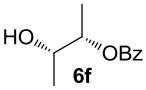
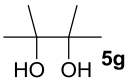
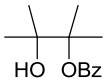
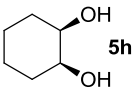
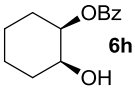
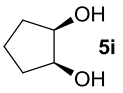
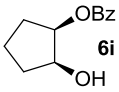
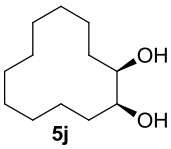
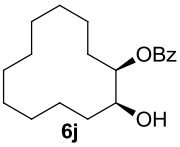
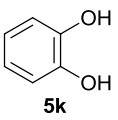
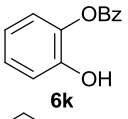
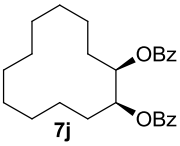


Scheme 2. Reaction mechanism in mono-benzoylation of diols with **DFBA**

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

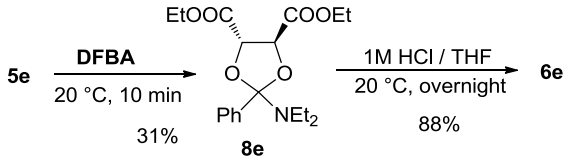
decomposed to inert *N*,*N*-diethylbenzamide by the addition of water. Therefore, the benzoylation of **6** to di-benzoate **7** scarcely occurred during the reaction, and **6** was obtained selectively (Scheme 2).

Table 2 Mono-benzoylation of diols with **DFBA**[a]

Entry	Substrate	Temp. (°C)	Product	Yield (%)[b]
1	 **5a**	20	 **6a**	84[c] (5)
2[d]	 **5b**	20	 **6b**	82[c] (4)
3	 **5c**	20	 **6c**	94 (4)
4[e]	 **5d**	20	 **6d**	70[c] (12)
5	 **5e**	40	 **6e**	71 (0)
6[f]	 **5f**	40	 **6f**	91 (0)
7[f,g]	 **5g**	20	 **6g**	86 (2)
8[f]	 **5h**	40	 **6h**	92 (3)
9[f]	 **5i**	40	 **6i**	87 (5)
10[f]	 **5j**	40	 **6j**	95 (0)
11[f]	 **5k**	40	 **6k**	89 (4)
12[f]	**6j**	40	 **7j**	99

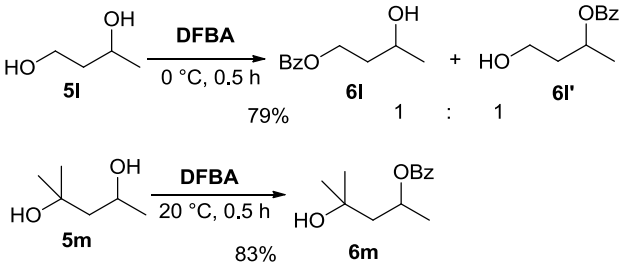
[a] If otherwise not mentioned, the reaction was carried out in CH_2Cl_2 for 0.5 h using 1.1 eq. of **DFBA** to substrate. [b] Isolated yield based on substrate used. In parentheses, yield of dibenzoate obtained by GC. [c] ^{1}H NMR yield. [d] The reaction time is 3 h. [e] The reaction time is 5 h. [f] 2 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).



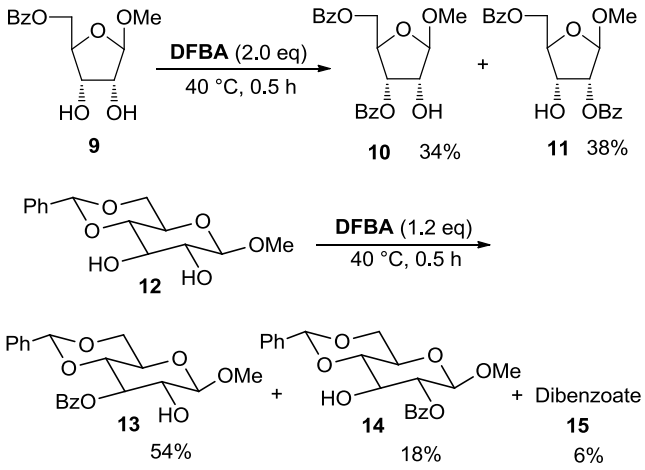
Scheme 3. Isolation and reaction of cyclic amide acetal **8e**

Next, we examined the regioselectivity in the benzoylation of unsymmetrical diols. With 1,3-butandiol (**5l**) having *prim*- and *sec*-alcohol, regioselectivity was not observed, and 3-hydroxybutyl benzoate (**6l**) and 4-hydroxybut-2-yl benzoate (**6l'**) 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).

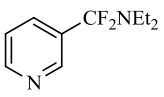
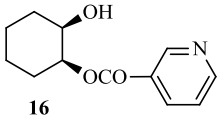
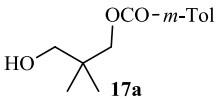
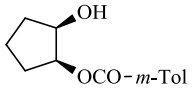
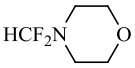
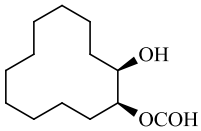
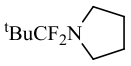
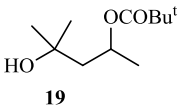
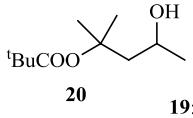


Scheme 5. mono-Benzoylation of sugars with **DFBA**

2.3. Acylation of diols with various α,α-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]

Alcohol	R_2NCF_2R'	Product	Yield (%)[b]
5h		 **16**	88 (0)[cd]
5c	 **DFMBA**	 **17a**	92 (8)[cd]
5i	**DFMBA**	 **17b**	87 (4)[cd]
5j		 **18**	82 (4)
5m		 **19**  **20** **19**:**20** = 4:1	89 (0)[c]

[a] If otherwise not mentioned, the reaction was carried out in CH_2Cl_2 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. [c] 2 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 ^{1}H NMR (400 MHz), and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ 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 N_2. 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 CH_2Cl_2 solution (3 mL) of **DFBA** (199 mg, 1.0 mmol) was added at 0 °C under N_2 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 $NaHCO_3$ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:Et_2O = 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). ^{13}C 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:Et_2O = 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). ^{13}C 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: Et_2O = 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). ^{13}C 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 CH_2Cl_2 solution (3 mL) of **DFBA** (111 mg, 0.55 mmol) was added at room temperature under N_2 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 $NaHCO_3$ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over $MgSO_4$ 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). ^{13}C 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). ^{13}C 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}. ^{1}H 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). ^{13}C 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 ^{1}H 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}. ^{1}H 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). ^{13}C 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 $C_{12}H_{14}O_3Na$ (M^++Na) 229.08352, found 229.08335.

4.3.5. (2*S*, 3*S*)-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 $NaHCO_3$ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over $MgSO_4$ 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}. ^{1}H 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). ^{13}C 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. (2*R*, 3*R*)-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}. ^{1}H 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). ^{13}C 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}. ^{1}H 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). ^{13}C 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}. ^{1}H 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). ^{13}C 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). ^{13}C 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 (lit[20] 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). ^{13}C 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). ^{13}C 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). ^{13}C 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 $C_{26}H_{32}O_4Na$ (M^++Na) 431.21928, found 431.22011.

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

To a CH_2Cl_2 solution (3 mL) of **DFBA** (199 mg, 1.0 mmol) was added at 20 °C under N_2 atmosphere **5e** (206 mg, 1.0 mmol), and the mixture was stirred for 10 min. Then, the mixture was poured into sat. aq $NaHCO_3$ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (silica gel/hexane:Et_2O = 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 $NaHCO_3$ (20 mL) and extracted with diethyl ether (20 mL X 3). The combined organic layer was dried over $MgSO_4$ 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). ^{13}C 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 $C_{19}H_{28}O_6N$ 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 **5l** (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 **6l** and **6l'** (77 mg) in 79% yield (inseparable). From ^1H NMR spectra, **6l** and **6l'** 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 **5l** (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}. ^{1}H 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). ^{13}C 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 $^{1}HNMR$ using 1,4-dimethoxybenzene as an internal standard, respectively. Pure **10** and **11** were obtained by column chromatography (silica gel/$CHCl_3$:acetone = 20:1); **10**[24]; IR (neat) 3469, 2936, 1724, 1273 cm^{-1}. ^{1}H 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). ^{13}C 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}. ^{1}H 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). ^{13}C 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}. ^{1}H 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). ^{13}C 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}. ^{1}H 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). ^{13}C 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]; ^{1}H 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), 3.96-3.88 (m, 2H), 3.74-3.68 (m, 1H), 3.54 (s, 3H).

4.3.18. cis -2-Hydroxycyclohexyl nicotinate (16)

The reaction was carried out as in the case of **4.3.1**. using *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}. ^{1}H 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). ^{13}C 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}. ^{1}H 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). ^{13}C 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 $C_{13}H_{18}O_3Na$ (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}. ^{1}H 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). ^{13}C 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 $C_{13}H_{16}O_3Na$ (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}. ^{1}H 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). ^{13}C 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 $C_{13}H_{24}O_3Na$ (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}. ^{1}H 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). ^{13}C 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 $C_{11}H_{22}O_3Na$ 225.14612, found 225.14613. **20**; IR (neat) 3446, 2972, 1724, 1136 cm^{-1}. ^{1}H 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). ^{13}C 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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