Pergamon

Tetrahedron 58 (2002) 3579–3588

TETRAHEDRON

Allyl, epoxy and glycosyl perfluoroimidates. One-pot preparation and reaction☆

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Received 28 December 2001; accepted 13 March 2002

Abstract—The one-pot preparation of allyl, epoxy and glycosyl perfluoroimidates and their reaction are described. Volatile perfluoronitriles were generated from perfluoroamides with an 'activated' dimethyl sulfoxide (DMSO) species at −78°C. Allyl, epoxy and glycosyl perfluoroimidates were prepared in 44–92% yield following in situ nucleophilic addition of alcohol and sugar derivatives to nitriles. The obtained trifluoroacetimidates were more stable than the trichloro analogue and were easily purified by SiO_2 column chromatography and/or distillation. The 3,3-sigmatropic rearrangement of allylic analogues, acid-catalyzed cyclization of the epoxy analogues and glycosylation of sugar analogues were studied comparing with their corresponding trichloroacetimidates. The trifluoroacetimidates were considerably less reactive than trichloroacetimidates due to their electron-withdrawing substituents on the imidate carbon.

1. Introduction

In view of their importance as intermediates in organic synthesis, imidates have been documented in the literature.[2] In particular, trichloroacetimidates (X=CCl_3) have been paid great attention[3] and widely used as the precursor for (1) protection of a hydroxy group (R=*tert*-Bu, allyl and benzyl-type),[4] (2) introduction of nitrogen functionality in the molecules via 3,3-sigmatropic rearrangement (R=allyl)[5] or intramolecular cyclization (R=epoxy),[6] and (3) synthesis of glycosides and oligosaccharides (R=sugar derivative).[7] The trichloroacetimidates were widely prepared from trichloroacetonitrile and alcohol by base-catalyzed condensation.[8] Despite the usefulness of these reagents, the high reactivity and poor chemical stability of trichloroacetimidates sometimes gave low yields and nonreproducible results at the isolation, preparation and reaction. There are few practical procedures for stable perfluoro analogues especially for trifluoroacetimidate[9,10] because of the highly volatile and toxic property of trifluoroacetonitrile.[11,12] We have previously succeeded in the one-pot synthesis of benzyl-type perfluoroimidates (X=CF_3, CF_2Cl, CF_3CF_2, and $CF_3CF_2CF_2$), which could serve as a stable reagent for benzyl protection as thermally and chemically stable imidates.[13] Herein, we wish to report in full our observation regarding the one-pot synthesis of allyl, epoxy and glycosyl perfluoroimidates and their reaction comparing with the corresponding trichloroacetimidates (Fig. 1).

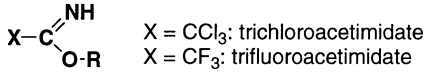

Figure 1. Imidates.

2. Results and discussion

2.1. One-pot preparation of allyl and epoxy trifluoroacetimidates

The one-pot synthesis of the trifluoro analogue of allylic alcohols (**1**–**5**) and their epoxy alcohols (**6**–**8**) is summarized in Table 1. The epoxy alcohols (**6**–**8**) were prepared in optically active forms from the allylic alcohols (**1**–**4**) by Katsuki–Sharpless catalytic asymmetric epoxidation.[14] Volatile trifluoroacetonitrile (bp −64°C) were generated from trifluoroacetamide with an 'activated' dimethyl sulfoxide (DMSO) species under previously reported method[15] and then allyl alcohols were added to the reaction mixture with DBU to afford the desired trifluoroacetimidate (**I**–CF_3 to **IV**–CF_3) in 76–82% yields, respectively (entries 1–4). Although the secondary alcohol was less reactive than primary alcohol, **V**–CF_3 was also produced in 54% yield (entry 5). The 2,3-epoxy trifluoroacetimidates (**VI**–CF_3 to **VIII**–CF_3) were also obtained in 76–92% yields (entries 6–8). The obtained allyl trifluoroacetimidates (**I**–CF_3 to **V**–CF_3) were purified by SiO_2 column chromatography and following bulb-to-bulb distillation. The

☆ For Part 1 see Ref. 1.

Keywords: activated dimethyl sulfoxide; dehydration; perfluoronitrile; perfluoroamide; perfluoroimidate; 3,3-sigmatropic rearrangement; acid-catalyzed cyclization; glycosylation.

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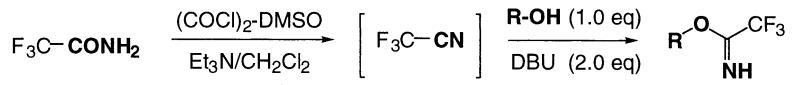
0040–4020/02/$ - see front matter
PII: S0040-4020(02)00305-8

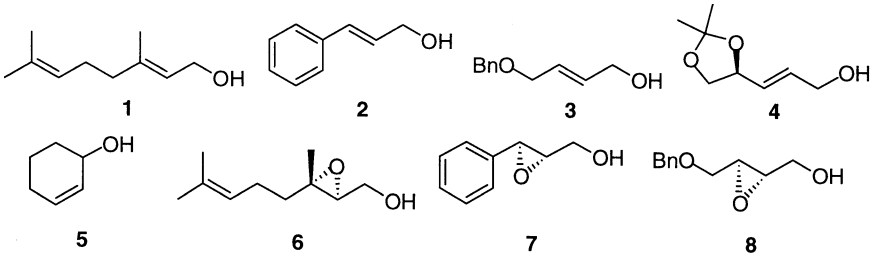
Table 1. One-pot synthesis of allyl and epoxy perfluoroimidates



trifluoroacetamide (3.3 eq) | trifluoroacetonitrile (3 eq) | allyl and epoxy trifluoroacetimidates

Entry	Alcohol	Yield[a]	Imidate
1	**1**	80	**I**–CF_3
2	**2**	76	**II**–CF_3
3	**3**	82	**III**–CF_3
4	**4**	77	**IV**–CF_3
5	**5**	54	**V**–CF_3
6	**6**	79	**VI**–CF_3
7	**7**	76	**VII**–C_3
8	**8**	92	**VIII**–CF_3

[a] Isolation yields after purification by Kugelrohr distillation and/or SiO_2 column chromatography.



boiling points of allyl trifluoroacetimidates were lower than that of the trichloro analogue, they could be easily distilled without 3,3-sigmatropic rearrangement. The epoxy trifluoroacetimidates (**VI**–CF_3 to **VIII**–CF_3) were simply purified by SiO_2 column chromatography in the usual manner. The purified allyl and epoxy trifluoroacetimidates (**I**–CF_3 to **VIII**–CF_3) could be stored for a year in a freezer.

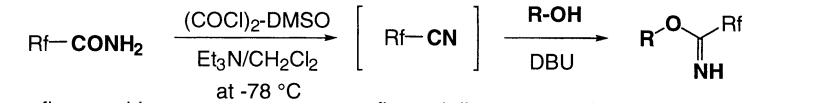
2.2. One-pot preparation of glycosyl perfluoroimidates

One-pot preparation of glycosyl perfluoroimidates was also successfully achieved as shown in Table 2. The 2,3,4,6-tetra-*O*-acetyl-α-D-glucose (**9**) and 2,3,4,6-tetra-*O*-benzyl-α-D-glucose (**10**) were used as the acyl- and ether-protected glucose derivatives. After perfluoronitriles (chlorodifluoroacetonitrile, trifluoroacetonitrile, pentafluoropropionitrile, and heptafluorobutyronitrile)[12] were generated from the corresponding perfluoroamide, these were trapped with **9** to yield the perfluoroimidates (**IX**–CF_3, **IX**–CF_2Cl, **IX**–C_2F_5 and **IX**–C_3F_7) in 44, 52, 29 and 27% yields, respectively (entries 1–4). Although acyl-protected glucose (**9**) afforded only the α-anomer of perfluoroimidates, ether-protected glucose (**10**) provided a 7/1 mixture of α- and β-anomers of trifluoroacetimidates (**X**–CF_3) in 49% yield (entry 5). The obtained α- and β-anomer mixture was separated by SiO_2 column chromatography.

2.3. 3,3-Sigmatropic rearrangement of allyl trifluoroacetimidates

The 3,3-sigmatropic rearrangement of allyl trichloroacetimidate into allyl trichloroacetamide is a widely used

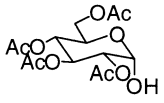
Table 2. One-pot synthesis of glycosyl perfluoroimidates



perfluoroamide (5.3 eq) | perfluoronitrile (5 eq) | glycosyl perfluoroimidate

Entry	R	Rf	Yield[a]	Imidate
1	**9**	CF_3	44	**IX**–CF_3
2	**9**	CF_2Cl	52	**IX**–CF_2Cl
3	**9**	C_2F_5	29	**IX**–C_2F_5
4	**9**	C_3F_7	27	**IX**–C_3F_7
5	**10**	CF_3	49[b]	**X**–CF_3

[a] Isolation yields after purification by SiO_2 column chromatography.
[b] 3 equiv. of trifluoroacetonitrile was generated.



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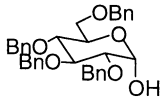

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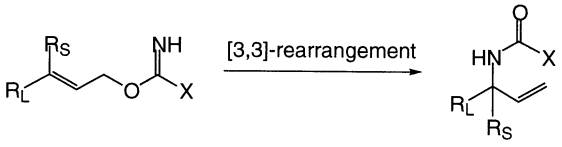
Table 3. 3,3-Sigmatropic rearrangement: allyl trichloroacetimidates vs allyl trifluoroacetimidates



Entry	R_L	R_S	X	Imidate	Conditions	Time (h)	Yield (%)[a]	Amide
1	$Me_2C{=}CHCH_2CH_2$	Me	CCl_3	**I**–CCl_3	A[b]	4	90	**Ia**–CCl_3
2	$Me_2C{=}CHCH_2CH_2$	Me	CF_3	**I**–CF_3	A	16	69	**Ia**–CF_3
3	$Me_2C{=}CHCH_2CH_2$	H	CCl_3	**I**–CCl_3	B[c]	4	66	**Ia**–CCl_3
4	$Me_2C{=}CHCH_2CH_2$	H	CF_3	**I**–CF_3	B	16	19 (38)[d]	**Ia**–CF_3
5	Ph	H	CCl_3	**II**–CCl_3	A	4	92	**IIa**–CCl_3
6	Ph	H	CF_3	**II**–CF_3	A	16	70	**IIa**–CF_3
7	$BnOCH_2$	H	CCl_3	**III**–CCl_3	A	52	86	**IIIa**–CCl_3
8	$BnOCH_2$	H	CF_3	**III**–CF_3	A	68	71	**IIIa**–CF_3
9	2,2-Dimethyl-1,3-dioxolane	Me	CCl_3	**IV**–CCl_3	A	23	61	**IVa**–CCl_3
10	2,2-Dimethyl-1,3-dioxolane	Me	CF_3	**IV**–CF_3	A	96	60 (28)[d]	**Iva**–CF_3

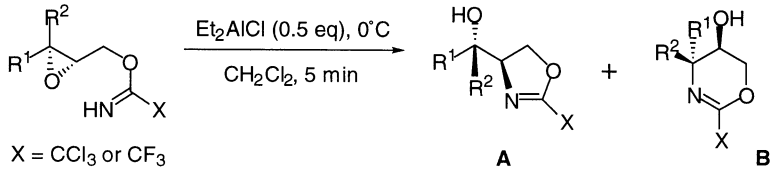
[a] Isolation yields after chromatographic purification.
[b] Condition A: xylene, 150°C in a sealed tube.
[c] Condition B: $PdCl_2(MeCN)_2$, THF, 25°C, in Ar atmosphere.
[d] Parentheses show the recovery yield of the starting material.

method for the introduction of nitrogen functionality in the molecule.[5] However, the deprotection of the trichloroacetamide group required harsh condition and is difficult in the presence of a variety of functional groups. On the other hand, trifluoroacetamide is one of the more easily cleaved amides. We studied here the 3,3-sigmatropic rearrangement of trifluoroacetimidates comparing with trichloroacetimidates under thermal (Condition A)[16] and Pd-catalyzed conditions (Condition B).[17] These results are summarized in Table 3. When geranyl and cinnamyl trichloroacetimidates (**I**–CCl_3 and **II**–CCl_3) were refluxed in xylene (Condition A: 150°C), **I**–CCl_3 and **II**–CCl_3 smoothly rearranged within 4 h to give the trichloroacetamides (**Ia**–CCl_3 and **IIa**–CCl_3) in 90 and 92% yield, respectively (entries 1 and 5). Trifluoroacetimidate also rearranged into trifluoroacetamides (**Ia**–CF_3 and **IIa**–CF_3) after 16 h under Condition A in 69 and 70% yield (entries 2 and 6). In the presence of $PdCl_2(MeCN)_2$ in THF (Condition B), although trichloroacetimidate rearrangement proceeded in 66% yield within 4 h, trifluoroacetimidate rearrangement occurred in only 19% yield and 38% of the starting material was recovered after 16 h (entries 3 and 4). 2(*E*)-Benzyloxybutenyl imidates (**III**–CCl_3 and **III**–CF_3) rearranged to amide in 86 and 71% yield for 52 and 68 h (entries 7 and 8). These results showed the 3,3-sigmatropic rearrangement of trifluoroacetimidate took prolonged reaction time and gave lower product yield than the trichloro analogues. However, trichloroacetimidate gradually decomposed under heating conditions; **IV**–CCl_3 provided only 61% of trichloroacetamide (**IVa**–CCl_3). On the other hand, stable trifluoro analogue (**IV**–CF_3) provided better results to give 60% of product (**IVa**–CF_3) and 28% of the starting material still remained without decomposition (entry 9 vs 10).

2.4. Et_2AlCl-catalyzed cyclization of 2,3-epoxy trifluoroacetimidates

Lewis acid-catalyzed cyclization of 2,3-epoxy trichloroacetimidates is documented to give 5-membered oxazoline (**A**) and 6-membered dihydrooxazoline (**B**) depending on the structure of the imidates and the catalyst (Table 4).[6] On treatment of cinnamyl 2,3-epoxyacetimidates (**VII**–CCl_3 and **VII**–CF_3) with 0.5 equiv. of Et_2AlCl in CH_2Cl_2 at 0°C, cyclization took place at the benzylic position to give dihydrooxazolines (**12B**–CCl_3 and **12B**–CF_3) in 96 and 97% yields, respectively (entries 3 and 4). The geranyl

Table 4. Et_2AlCl-catalyzed cyclization: 2,3-epoxy trichloroacetimidates vs 2,3-epoxy trifluoroacetimidates

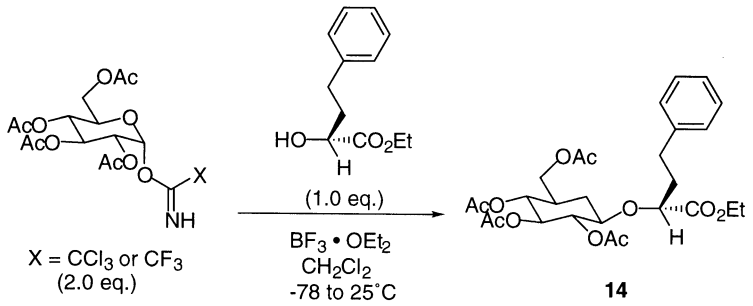


X = CCl_3 or CF_3 **A** **B**

Entry	R^1	R^2	X	Imidate	Products	A/B	Yield (%)[a]
1	$Me_2C{=}CHCH_2CH_2$	Me	CCl_3	**VI**–CCl_3	**11**–CCl_3	10/90	99
2	$Me_2C{=}CHCH_2CH_2$	Me	CF_3	**VI**–CF_3	**11**–CF_3	2/98	92
3	Ph	Me	CCl_3	**VII**–CCl_3	**12**–CCl_3	0/100	96
4	Ph	H	CF_3	**VII**–CF_3	**12**–CF_3	0/100	97
5	$BnOCH_2$	H	CCl_3	**VIII**–CCl_3	**13**–CCl_3	100/0	60
6[b]	$BnOCH_2$	H	CF_3	**VIII**–CF_3	**13**–CF_3	100/0	86

[a] Isolation yields after chromatographic purification.
[b] Reaction runs with 2.5 equiv. of Et_2AlCl for 30 min.

Table 5. $BF_3{\cdot}Et_2O$-catalyzed glycosylation: glycosyl trichloroacetimidates vs glycosyl trifluoroacetimidates



Entry	X	Imidate	$BF_3{\cdot}Et_2O$ (equiv.)	Yield (%)[a]
1	CCl_3	**IX**–CCl_3	0.25	73
2	CCl_3	**IX**–CCl_3	0.5	67
3	CCl_3	**IX**–CCl_3	1.0	64
4	CF_3	**IX**–CF_3	0.25	65
5	CF_3	**IX**–CF_3	0.5	73
6	CF_3	**IX**–CF_3	1.0	57

[a] Isolation yields after chromatographic purification.

2,3-epoxytrichloroacetimidate (**VI**–CCl_3) cyclized with Et_2AlCl (0.5 equiv.) at the quaternary center to afford a mixture of **11A**–CCl_3 and **11B**–CCl_3 in 99% with 10/90 ratio (entry 1). Under the same reaction conditions, trifluoro analogue (**VI**–CF_3) showed much higher regioselectivity to give a mixture of **11A**–CF_3 and **11B**–CF_3 in 92% yield with 2/98 ratio (entry 2). In the case of **VIII**–CCl_3, which has no polarized center at the 3-position, the cyclization took place at the 2-position to produce 5-membered oxazoline (**A**). The oxazoline (**13A**–CCl_3) was selectively obtained in 60% yield. Cyclization of **VIII**–CF_3 required 2.5 equiv. of Et_2AlCl for 30 min, **13A**–CF_3 was produced in 86% yield (entries 5 and 6).

2.5. Glycosylation of glycosyl trifluoroacetimidates

Trichloroacetimidate-mediated glycosylation[7] was announced by Schmidt as an alternative useful method to the classical Koenigs–Knorr[18] procedure and now appears to be one of the most ideal glycosylation protocols. We anticipated the *O*-acetyl-protected trifluoroacetimidate (**IX**–CF_3) was desirable to develop a thermally and chemically more stable glycosyl donor (Table 5). The $BF_3{\cdot}Et_2O$-catalyzed glycosylation of **IX**–CCl_3 and **IX**–CF_3 with alcohol afforded only β-glycosides (**17**) from the neighboring-group participation with typical yields being 57–73%. Since the reactivity of the nitrogen atom is reduced by electron-withdrawing perfluoro substitution on the imidate carbon, the activation of trifluoroacetimidate required twice the amount of catalyst than the trichloro analogues (entries 1–3 vs 4–6).

3. Conclusion

In conclusion, we have described a convenient and simple alternative method for the preparation of perfluoroimidates in high yields. This one-pot procedure does not need special equipment. The overall sequence proceeded cleanly on 10-gram scale and is reproducible. The obtained perfluoroimidates were more stable than the trichloro analogue and were purified by SiO_2 column chromatography and/or distillation. We next studied the reaction of allyl, epoxy and glycosyl perfluoroimidates for 3,3-sigmatropic rearrangement, acid-catalyzed cyclization, and glycosylation. Allyl, epoxy and glycosyl trifluoroacetimidates can serve as an exchangeable precursor for the corresponding trichloro analogues.

4. Experimental

4.1. Apparatus

^1H and ^{13}C NMR spectra were recorded on JEOL JNM EX-400 and JEOL JNM LA-400 instruments (399.65 MHz ^1H, 100.4 MHz ^{13}C, 376.0 MHz ^{19}F) spectrometer in deuterochloroform ($CDCl_3$) with either tetramethylsilane (TMS) (0.00 ppm ^1H, 0.00 ppm ^{13}C), chloroform (7.26 ppm ^1H, 77.00 ppm ^{13}C) or fluorotribromometane (CBr_3F) (7.00 ppm ^{19}F) as an internal reference unless otherwise stated. Data are reported in the following order: chemical shifts are given (d); multiplicities are indicated [br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), exch (exchangeable)]; coupling constants, *J*, are reported (Hz); integration is provided; and assignment is indicated. Infrared spectra were measured with a Shimadzu OR-8000 spectrometer. Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67–100%), m (medium 40–67%), w (weak 20–40%), and br (broad). Low and high resolution Electron Impact (EIMS) was taken with a JEOL JMS AX-500 spectrometer with ionization voltages of 70 and 15 eV. Data are reported in the form of *m/e* (intensity relative to base=100). Measurements of optical rotations were carried out with a Horiba SEPA-300 high sensitivity polarimeter and rotation values are reported as follows: $[\alpha]_{wavelength}^{temperature}$, (concentration in g/100 ml, solvent). Analytical thin-layer chromatography was performed using Merck SiO_2 plates with F-254 indicator. Column chromatography was performed with indicated solvents on Merck SiO_2 60 (230–400 mesh ASTM). Visualization was accomplished by UV light,

iodine, $KMnO_4$, *para*-anisaldehyde or pancardi solution. Melting points (mp) were determined on a Yanaco MP-21 micro melting point apparatus and are uncorrected.

4.2. General procedure for one-pot preparation of perfluoroimidates

In a flame-dried 300 ml three-necked round-bottom flask equipped with a stirring bar, a thermometer, a septum and a nitrogen inlet were introduced perfluoroamide (3.3 mmol), DMSO (15 mmol) and CH_2Cl_2. This solution was cooled down to −75°C (internal) and $(COCl)_2$ (3 mmol) and Et_3N (10 mmol) were slowly added at intervals of 10 min. No rise in temperature was observed during this process. After stirring for 30 min at −78°C, DBU (2 mmol) and alcohol (1 mmol) were added slowly via syringe. The reaction mixture was stirred for 15 min at −78°C, the mixture was allowed to reach room temperature over 10 h. The reaction mixture was quenched by addition of water; the aqueous layer was extracted with EtOAc. The combined organic phases were washed with brine, dried (Na_2SO_4), and then filtered. Concentration and following purification by SiO_2 column chromatography (hexane/EtOAc) and Kugelrohr distillation afforded the indicated yield of products.

4.2.1. Geranyl 2,2,2-trifluoroacetimidate (I–CF_3). Imidate formation was achieved according to the general procedure using geraniol (154 mg, 1 mmol), 2,2,2-trifluoroacetamide (373 mg, 3.3 mmol), DMSO (0.68 ml, 9.6 mmol), $(COCl)_2$ (260 μl, 3.0 mmol), Et_3N (1.25 ml, 9 mmol) and DBU (300 μl, 2.0 mmol) in CH_2Cl_2 (10 ml). SiO_2 column chromatography (hexane/EtOAc) and following Kugelrohr distillation purified the crude product to give 200 mg (80%) of the 2,2,2-trifluoroacetimidate (**I**–CF_3) as a colorless oil: R_f 0.50 (hexane/EtOAc, 20/1); bp 90°C/0.9 mmHg; ^1H NMR ($CfDCl_3$) 8.09 (1H, s, NH), 5.41 (1H, t, J=7.1 Hz), 5.06 (1H, t, J=7.4 Hz), 4.76 (2H, d, J=6.8 Hz), 2.15–2.02 (4H, m), 1.70 (3H, s), 1.67 (3H, s), 1.58 (3H, s); ^{13}C NMR ($CDCl_3$) 158.1 (q, J=38.0 Hz), 143.4, 131.9, 123.6, 117.3, 115.2 (q, J=280 Hz, CF_3), 64.6, 39.5, 26.2, 25.6, 17.6, 16.6; IR (neat, cm^{-1}) 3355 (w), 2971 (w), 2928 (w), 2861 (w), 1784 (w), 1684 (s), 1449 (w), 1377 (w), 1331 (w), 1200 (s), 1167 (s), 1076 (m), 939 (w), 841 (m); EI-MS (70 eV) 250 (4), 249 (M^+, 22), 234 (13), 206 (11), 180 (580), 166 (36), 154 (42), 136 (70), 121 (67), 93 (100), 80 (57); EI-HRMS calcd for $C_{12}H_{18}F_3NO$ (M^+), 249.1340; found, 249.1336.

4.2.2. Cinnamyl 2,2,2-trifluoroacetimidate (II–CF_3). Imidate formation was achieved according to the general procedure using cinnamyl alcohol (296 mg, 2.2 mmol), 2,2,2-trifluoroacetamide (734 mg, 3 mmol), DMSO (1.36 ml, 8.7 mmol), $(COCl)_2$ (0.51 ml, 5.9 mmol), Et_3N (2.5 ml, 18 mmol) and DBU (0.6 ml, 4 mmol) in CH_2Cl_2 (30 ml). SiO_2 column chromatography (hexane/EtOAc) and following Kugelrohr distillation purified the crude product to give 384 mg (76%) of the 2,2,2-trifluoroacetimidate (**II**–CF_3) as a colorless oil: R_f 0.25 (hexane/EtOAc, 10/1); bp 100–105°C/0.9 mmHg; ^1H NMR ($CDCl_3$) 8.23 (1H, s, NH), 7.43–7.40 (2H, m), 7.36–7.32 (2H, m), 7.29–7.26 (1H, m), 6.73 (1H, d, J=16.1 Hz), 6.37 (1H, td, J=6.3, 16.1 Hz), 4.94 (2H, d, J=6.3 Hz); ^{13}C NMR ($CDCl_3$) 157.8 (q, J=38.0 Hz), 136.0, 135.0, 128.6, 128.4, 126.7, 121.9, 115.6 (q, J=280 Hz, CF_3), 68.2; IR (neat, cm^{-1}) 3347 (w), 3087 (w), 3063 (w), 3031 (w), 2950 (w), 2887 (w), 1686 (s), 1356 (m), 1202 (s), 1167 (s), 1117 (m), 1076 (s), 967 (m), 847 (m), 747 (m), 735 (m), 693 (m); EI-MS (70 eV) 230 (5), 229 (M^+, 20), 219 (5), 200 (17), 181 (15), 169 (12), 160 (17), 131 (32), 117 (50), 116 (93), 115 (100); EI-HRMS calcd for $C_{11}H_{10}F_3NO$ (M^+), 229.0714; found, 229.0689.

4.2.3. 4-Benzyloxy-2(*E*)-butenyl 2,2,2-trifluoroacetimidate (III–CF_3). Imidate formation according to the general procedure using 4-benzyloxy-2(*E*)-butene-1-ol (267 mg, 1.5 mmol), 2,2,2-trifluoroacetamide (396 mg, 3.5 mmol), DMSO (0.71 ml, 10 mmol), $(COCl)_2$ (0.26 ml, 3.0 mmol), Et_3N (1.12 ml, 8 mmol) and DBU (0.30 ml, 2.0 mmol) in CH_2Cl_2 (4 ml) afforded a colorless oil, which was purified by SiO_2 column chromatography (hexane/EtOAc, 20/1) to give 335 mg (82%) of the 2,2,2-trifluoroacetimidate (**III**–CF_3) as a colorless oil: R_f 0.20 (hexane/EtOAc, 8/1); ^1H NMR ($CDCl_3$) 8.19 (1H, s, NH), 7.36 (5H, m), 5.98 (1H, td, J=3.9, 15.6 Hz), 5.93 (1H, td, J=3.9, 15.6 Hz), 4.79 (2H, d, J=3.9 Hz), 4.54 (2H, s), 4.07 (2H, d, J=3.9 Hz); ^{13}C NMR ($CDCl_3$) 157.5 (q, J=38.0 Hz), 138.1, 131.9, 128.5, 127.8, 127.7, 125.3, 115.5 (q, J=280 Hz, CF_3), 72.5, 69.7, 67.4; IR (neat, cm^{-1}) 3351 (w), 3067 (w), 2944 (w), 2859 (w), 1686 (s), 1497 (w), 1455 (m), 1354 (m), 1202 (s), 1165 (s), 1098 (m), 1073 (m), 1028 (m), 972 (m), 912 (m), 849 (m); EI-MS (70 eV) 274 (0.4), 273 (M^+, 0.6), 256 (0.9), 166 (15), 105 (28), 91 (100), 79 (20), 69 (13), 65 (21); EI-HRMS calcd for $C_{13}H_{14}F_3NO$ (M^+), 273.0977; found, 273.0989.

4.2.4. 4,5-*O*-Isopropylidenedioxy-2(*E*)-propenyl 2,2,2-trifluoroacetimidate (IVf–CF_3). Imidate formation was achieved according to the general procedure using 4,5-*O*-isopropyridenedioxy-2(*E*)-propene-1-ol (57 mg, 0.36 mmol), 2,2,2-trifluoroacetamide (130 mg, 1.15 mmol), DMSO (230 μl, 8.7 mmol), $(COCl)_2$ (94 μl, 3.2 mmol), Et_3N (452 μl, 3.2 mmol) and DBU (108 μl, 0.72 mmol) in CH_2Cl_2 (5 ml). SiO_2 column chromatography (hexane/EtOAc) purified the crude product to give 70 mg (77%) of the 2,2,2-trifluoroacetimidate (**IV**–CF_3) as a colorless oil: R_f 0.67 (hexane/EtOAc, 3/1); bp 75–80°C/0.3 mmHg; $[\alpha]_D^{28}$=+29.6 (c=0.99, $CHCl_3$); ^1H NMR ($CDCl_3$) 8.22 (1H, s, NH), 5.96 (1H, td, J=5.6, 15.6 Hz), 5.85 (1H, dd, J=7.1, 15.6 Hz), 4.76 (1H, dd, J=5.6, 13.9 Hz), 4.74 (1H, dd, J=5.6, 13.9 Hz), 4.53 (1H, ddd, J=6.4, 6.8, 7.3 Hz), 4.10 (1H, dd, J=6.4, 8.3 Hz), 3.60 (1H, dd, J=7.3, 8.3 Hz), 1.40 (3H, s), 1.37 (3H, s); ^{13C} NMR ($CDCl_3$) 157.5 (q, J=38.0 Hz), 132.5, 126.4, 115.5 (q, J=280 Hz, CF_3), 109.6, 76.0, 69.2, 66.9, 26.5, 25.7; IR (neat, cm^{-1}) 3299 (m), 2990 (m), 2940 (m), 1690 (s), 1485 (m), 1381 (m), 1374 (s), 1352 (m), 1202 (s), 1161 (s), 1063 (s), 970 (m), 851 (m); EI-MS (70 eV) 253 (M^+, 1.4), 238 (M^+−15, 58), 178 (78), 154 (35), 83 (48), 72 (100), 69 (18); EI-HRMS calcd for $C_9H_{11}F_3NO$ (M^+−15), 238.0691; found, 238.0684.

4.2.5. Cyclohexenyl 2,2,2-trifluoroacetimidate (V–CF_3). Imidate formation was achieved according to the general procedure using cyclohexenol (98 mg, 1 mmol), 2,2,2-trifluoroacetamide (373 mg, 3.3 mmol), DMSO (0.68 ml, 9.6 mmol), $(COCl)_2$ (0.26 ml, 3.0 mmol), Et_3N (1.25 ml, 9 mmol) and DBU (0.3 ml, 2.0 mmol) in CH_2Cl_2 (10 ml). SiO_2 column chromatography (hexane/EtOAc) and

following Kugelrohr distillation purified the crude product to give 104 mg (54%) of the cyclohexenyl 2,2,2-trifluoroacetimidate (**V**–CF_3) as a colorless oil: R_f 0.50 (hexane/EtOAc, 10/1); bp 20°C/16 mmHg; ^{1}H NMR ($CDCl_3$) 8.10 (1H, s, NH), 6.02 (1H, dtd, J=1.3, 3.8, 10.0 Hz), 5.84 (1H, dtd, J=3.9, 2.2, 10.0 Hz), 5.45–5.40 (1H, m), 2.17–2.09 (1H, m), 2.06–1.95 (1H, m), 1.95–1.85 (2H, m), 1.83–1.74 (1H, m), 1.70–1.60 (1H, m); ^{13}C NMR ($CDCl_3$) 157.6 (q, J=38.0 Hz), 133.7, 124.4, 115.6 (q, J=280 Hz), 71.4, 27.6, 24.9, 18.6; IR (neat, cm^{-1}) 3357 (m), 2936 (m), 1682 (s), 1456 (w), 1418 (w), 1395 (w), 1320 (w), 1204 (s), 1165 (s), 1049 (s), 1007 (w), 911 (m), 839 (m); EI-MS (70 eV) 193 (M^+, 6.5), 179 (16), 159 (8), 110 (21), 98 (16), 97 (16), 81 (100), 79 (56), 57 (45); EI-HRMS calcd for $C_8H_{10}F_3NO$ (M^+), 193.0714; found, 193.0750.

4.2.6. (2*S*,3*R*) 6(*E*)-3,7-Dimethyl-2,3-epoxyoctenyl 2,2,2-trifluoroacetimidate (VI–CF_3). Imidate formation was achieved according to the general procedure using (2*S*,3*R*) 6(*E*)-3,7-dimethyl-2,3-epoxyocten-1-ol (426 mg, 2.5 mmol), 2,2,2-trifluoroacetamide (989 mg, 8.75 mmol), DMSO (1.77 ml, 25 mmol), $(COCl)_2$ (0.65 ml, 7.5 mmol), Et_3N (2.1 ml, 15 mmol) and DBU (0.75 ml, 5 mmol) in CH_2Cl_2 (13 ml). SiO_2 column chromatography (hexane/EtOAc, 20/1) purified the crude product to give 522 mg (79%) of the 2,2,2-trifluoroacetimidate as a colorless oil: R_f 0.45 (hexane/EtOAc, 5/1); $[\alpha]_D^{25}$=+24.5 (c=1.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 8.26 (1H, s, NH), 5.05–5.02 (1H, m), 4.39 (1H, dd, J=4.4, 11.9 Hz), 4.25 (1H, J=dd, 6.5, 11.9 Hz), 3.06 (1H, dd, J=4.4, 6.4 Hz), 2.05–1.99 (2H, m), 1.62 (3H, s), 1.56 (3H, s), 1.47–1.40 (2H, m), 1.28 (3H, s); ^{13}C NMR ($CDCl_3$) 157.0 (q, J=38.0 Hz), 132.2, 123.1, 115.4 (q, J=280 Hz), 66.5, 60.4, 59.0, 38.2, 25.5, 23.5, 17.5, 16.7; IR (neat, cm^{-1}) 3310 (w), 2973 (w), 2936 (w), 2863 (w), 2361 (w), 2323 (w), 1686 (s), 1479 (w), 1200 (s), 1165 (s), 1073 (m), 963 (w), 845 (m); FAB-MS 289 ([M+Na]$^+$, 5.8), 267 (2), 266 (MH^+, 13), 248 (2), 176 (15), 154 (43), 133 (68), 105 (61), 91 (59); FAB-HRMS calcd for $C_{12}H_{19}F_3NO_2$ (MH^+), 266.1368; found, 266.1359.

4.2.7. (2*S*,3*R*)-3-Phenyl-2,3-epoxypropyl 2,2,2-trifluoroacetimidate (VII–CF_3). Imidate formation was achieved according to the general procedure using (2*S*,3*R*)-3-phenyl-2,3-epoxypropane-1-ol (375 mg, 2.5 mmol), 2,2,2-trifluoroacetamide (989 mg, 8.75 mmol), DMSO (1.77 ml, 25 mmol), $(COCl)_2$ (0.65 ml, 7.5 mmol), Et_3N (2.1 ml, 15 mmol) and DBU (0.75 ml, 5 mmol) in CH_2Cl_2 (10 ml). SiO_2 column chromatography (hexane/EtOAc, 20/1) purified the crude product to give 466 mg (76%) of the 2,2,2-trifluoroacetimidate (**VII**–CF_3) as a colorless oil: R_f 0.33 (hexane/EtOAc, 10/1); $[\alpha]_D^{25}$=+46.9 (c=1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 8.24 (1H, s, NH), 7.21–7.39 (5H, m), 4.63 (1H, dd, J=3.1, 12.2 Hz), 4.32 (1H, dd, J=5.6, 12.2 Hz), 3.84 (1H, d, J=1.9 Hz), 3.36 (1H, ddd, J=1.9, 3.1, 5.6 Hz); ^{13}C NMR ($CDCl_3$) 157.0 (q, J=38.0 Hz), 132.2, 123.1, 115.4 (q, J=280 Hz), 66.5, 60.4, 59.0, 38.2, 25.5, 23.5, 17.5, 16.7; IR (neat, cm^{-1}) 3310 (w), 2973 (w), 2936 (w), 2863 (w), 2361 (w), 2323 (w), 1686 (s), 1479 (w), 1200 (s), 1165 (s), 1073 (m), 963 (w), 845 (m); FAB-MS 248 (3), 247 (20), 246 (MH^+, 100), 228 (4), 202 (20), 154 (43), 133 (68), 105 (61), 91 (59); FAB-HRMS calcd for $C_{11}H_{11}F_3NO_2$ (MH^+), 246.0742; found, 246.0714.

4.2.8. (2*S*,3*R*)-4-Benzyloxy-2,3-epoxybutyl 2,2,2-trifluoroacetimidate (VIII–CF_3). Imidate formation was achieved according to the general procedure using (2*S*,3*R*)-4-benzyloxy-2,3-epoxybutane-1-ol (170 mg, 0.875 mmol), 2,2,2-trifluoroacetamide (318 mg, 2.82 mmol), DMSO (0.91 ml, 12.8 mmol), $(COCl)_2$ (0.22 ml, 2.6 mmol), Et_3N (1.19 ml, 8.53 mmol) and DBU (0.26 ml, 1.71 mmol) in CH_2Cl_2 (5 ml). SiO_2 column chromatography (hexane/EtOAc, 5/1) purified the crude product to give 233 mg (92%) of the 2,2,2-trifluoroacetimidate (**VIII**–CF_3) as a colorless oil: R_f 0.33 (hexane/EtOAc, 5/1); $[\alpha]_D^{27}$=−18.5 (c=1.03, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 8.28 (1H, s, NH), 7.38–7.28 (5H, m), 4.60 (1H, d, J=12.0 Hz), 4.56 (1H, d, J=12.0 Hz), 4.56 (1H, dd, J=3.0, 12.2 Hz), 4.21 (1H, dd, J=5.8, 12.2 Hz), 3.77 (1H, dd, J=2.9, 11.4 Hz), 3.56 (1H, dd, J=5.1, 11.4 Hz), 3.28 (1H, ddd, J=2.2, 3.0, 5.8 Hz), 3.19 (1H, ddd, J=2.2, 2.9, 5.1 Hz); ^{13}C NMR ($CDCl_3$) 157.6 (q, J=38.8 Hz), 136.0, 128.6, 128.5, 125.6, 115.4 (q, J=279.2 Hz, CF_3), 67.2, 58.6, 56.3; IR (neat, cm^{-1}) 3335 (w), 3033 (w), 2959 (w), 2874 (w), 2863 (w), 1690 (s), 1466 (w), 1410 (w), 1362 (w), 1202 (s), 1165 (s), 1088 (s), 885 (m), 847 (m), 750 (m), 698 (m); FAB-MS 312 ([M+Na]$^+$, 10), 291 (6), 290 (MH^+, 34), 176 (17), 154 (50), 136 (38), 91 (100); FAB-HRMS calcd for $C_{18}H_{15}F_3NO_3$ (MH^+), 290.1004; found, 290.1027.

4.2.9. *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl) trifluoroacetimidate (IX–CF_3). Imidate formation was achieved according to the general procedure using 2,3,4,6-tetra-*O*-acetyl-α-D-glucose (2.3 g, 6.6 mmol), 2,2,2-trifluoroacetamide (4.13 g, 36.4 mmol), DMSO (7.0 ml, 99.2 mmol), $(COCl)_2$ (2.1 ml, 33.1 mmol), Et_3N (9.0 ml, 66.1 mmol) and DBU (1.96 ml, 13.2 mmol) in CH_2Cl_2 (8 ml). SiO_2 column chromatography (hexane/EtOAc, 2/1) purified the crude product to give 1.29 g (44%) of the (2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl) 2,2,2-trifluoroacetimidate (**IX**–CF_3) as a colorless oil: R_f 0.30 (hexane/EtOAc, 2/1); $[\alpha]_D^{23}$=+86.7 (c=1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 8.74 (1H, s, NH), 6.49 (1H, d, J=3.7 Hz, HC(1)), 5.42 (1H, t, J=9.9 Hz, HC(3)), 5.09 (1H, t, J=9.9 Hz, HC(4)), 5.05 (1H, dd, J=3.8, 10.4 Hz, HC(2)), 4.20 (1H, dd, J=3.9, 12.4 Hz, HC(6)), 4.05–4.00 (2H, m, HC(5) and HC(6)), 1.99 (3H, s, Me), 1.96 (3H, s, Me), 1.94 (3H, s, Me), 1.93 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 170.4, 169.8, 169.6, 169.3, 157.7 (t, J=39.6 Hz), 115.1 (t, J=280.0 Hz), 91.6 (C(1)), 69.8 (C(5)), 69.60 (C(3)), 69.2 (C(2)), 67.5 (C(4)), 61.1 (C(6)), 20.4 (×2), 20.3, 20.2; ^{19}F NMR ($CDCl_3$) −74.6; IR (neat, cm^{-1}) 3312 (m), 2967 (m), 1755 (s), 1705 (s), 1435 (w), 1370 (m), 1221 (s), 1165 (s), 1078 (m), 1040 (s), 959 (w), 926 (m), 899 (m), 756 (w), 711 (w); FAB-MS 444 (MH^+, 4), 439 (5), 384 (15), 331 (100), 289 (20), 271 (18), 229 (17), 211 (12), 169 (100), 139 (25), 127 (47); FAB-HRMS calcd for $C_{16}H_{21}F_3NO_{10}$ (MH^+), 444.1118; found, 444.1089.

4.2.10. *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl) 2-chloro-2,2-difluoroacetimidate (IX–CF_2Cl). Imidate formation was achieved according to the general procedure using 2,3,4,6-tetra-*O*-acetyl-α-D-glucose (280 mg, 0.81 mmol), 2-chloro-2,2-difluoroacetamide (572 mg, 4.4 mmol), DMSO (0.86 ml, 12.1 mmol), $(COCl)_2$ (0.35 ml, 4.0 mmol), Et_3N (1.1 ml, 8.1 mmol) and DBU (0.24 ml, 1.62 mmol) in CH_2Cl_2 (8 ml). SiO_2 column chromatography (hexane/EtOAc, 2/1) purified the crude product

to give 194 mg (52%) of the *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl) 2-chloro-2,2-difluoroacetimidate (**IX**–CF_2Cl) as a colorless oil: R_f 0.38 (hexane/EtOAc, 2/1); $[\alpha]_D^{26}=+54.7$ (c=1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) 8.52 (1H, s, NH), 6.50 (1H, d, J=3.6 Hz, HC(1)), 5.45 (1H, t, J=10.2 Hz, HC(3)), 5.09 (1H, t, J=10.2 Hz, HC(4)), 5.08 (1H, dd, J=3.6, 10.2 Hz, HC(2)), 4.21 (1H, dd, J=3.6, 12.2 Hz, HC(6)), 4.11–4.02 (2H, m, HC(5) and HC(6)), 2.01 (3H, s, Me), 1.98 (3H, s, Me), 1.96 (3H, s, Me), 1.95 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 170.4, 169.8, 169.6, 169.3, 157.9 (t, J=33.4 Hz), 117.1 (t, J=293.2 Hz, CF_2Cl), 91.8 (C(1)), 69.8 (C(5)), 69.60 (C(3)), 69.3 (C(2)), 67.6 (C(4)), 61.2 (C(6), 20.4 (×2), 20.3, 20.2; ^{19}F NMR ($CDCl_3$) −62.3 (d, J=175 Hz), −62.7 (d, J=175 Hz); IR (neat, cm^{-1}) 3312 (m), 3211 (w), 2964 (m), 2259 (w), 2120 (w), 1732 (s), 1696 (s), 1651 (m), 1435 (m), 1371 (s), 1320 (m), 1225 (s), 1146 (s), 1078 (s), 1040 (s), 976 (s), 924 (s), 901 (s); EI-MS (70 eV) 462 (0.2), 460 (0.6), 459 (M^+, 0.2), 446 (1), 331 (32), 288 (5), 271 (6), 242 (13), 200 (20), 169 (100), 157 (57), 145 (25), 127 (28), 115 (94), 109 (63), 103 (32), 98 (92), 97 (57), 81 (31), 73 (42); EI-HRMS calcd for $C_{16}H_{20}ClF_2NO_{10}$ (M^+), 459.0744; found, 459.0777.

4.2.11. *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl) 2,2,3,3,3-pentafluoropropionimidate (IX–C_2F_5). Imidate formation was achieved according to the general procedure using 2,3,4,6-tetra-*O*-acetyl-α-D-glucose (156 mg, 0.45 mmol), 2,2,3,3,3-pentafluoroacetamide (404 mg, 2.48 mmol), DMSO (0.48 ml, 6.75 mmol), $(COCl)_2$ (0.20 ml, 2.25 mmol), Et_3N (0.62 ml, 4.50 mmol) and DBU (135 μl, 0.9 mmol) in CH_2Cl_2 (10 ml). SiO_2 column chromatography (hexane/EtOAc, 4/1 to 2/1) purified the crude product to give 64 mg (29%) of the *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl) 2,2,2,3,3-pentafluoropropionimidate (**IX**–C_2F_5) as a colorless oil: R_f 0.23 (hexane/EtOAc, 4/1); $[\alpha]_D^{23}=+75.7$ (c=1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) 8.84 (s, NH), 6.60 (1H, d, J=3.7 Hz, HC(1)), 5.43 (1H, t, J=9.9 Hz, HC(3)), 5.13 (1H, t, J=9.8 Hz, HC(4)), 5.10 (1H, dd, J=3.7, 9.9 Hz, HC(2)), 4.24 (1H, dd, J=4.3, 12.6 Hz, HC(6)), 4.11–4.03 (2H, m, HC(5) and HC(6)), 2.06 (3H, s, Me), 2.02 (3H, s, Me), 1.99 (3H, s, Me), 1.96 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 170.4, 169.8, 169.6, 169.4, 156.1 (t, J=29.8 Hz), 117.7 (tq, J=35.5, 286.6 Hz, CF_3), 106.1 (qt, J=39.7, 256.0 Hz, CF_2), 91.8 (C(1)), 70.1 (C(5)), 69.5 (C(3)), 69.3 (C(2)), 67.5 (C(4)), 61.2 (C(6)), 20.5, 20.4, 20.1; ^{19}F NMR ($CDCl_3$) −82.9, −120.9; IR (neat, cm^{-1}); 3312 (m), 2963 (m), 2261 (w), 2112 (w), 1767 (s), 1748 (s), 1696 (s), 1435 (m), 1371 (s), 1318 (s), 1221 (s), 1171 (s), 1078 (s), 1044 (s), 1017 (s), 920 (s), 854 (m); EIMS (70 eV); 493 (M^+, 0.2), 475 (2), 431 (9), 331 (18), 271 (16), 248 (8), 236 (5), 218 (5), 204 (15), 202 (15), 169 (100), 157 (25), 145 (19), 127 (29), 115 (55), 109 (67), 101 (45), 98 (38), 73 (22); FAB-MS 494 (MH^+, 0.8), 423 (5), 331 (100), 289 (15), 271 (12), 229 (25), 211 (16), 169 (100), 145 (30), 127 (100), 109 (100), 81 (56); FAB-HRMS calcd for $C_{17}H_{21}F_5NO_{10}$ (MH^+), 494.1086; found, 494.1063.

4.2.12. *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl) 2,2,3,3,4,4,4-heptafluorobutyrimidate (IX–C_3F_7). Imidate formation according to the general procedure was achieved using 2,3,4,6-tetra-*O*-acetyl-α-D-glucose (156 mg, 0.45 mmol), 2,2,2,3,3,4,4-heptafluoroacetamide (529 mg, 2.48 mmol), DMSO (0.48 ml, 6.75 mmol), $(COCl)_2$ (0.20 ml, 2.25 mmol), Et_3N (0.62 ml, 4.50 mmol) and DBU (135 μl, 0.9 mmol) in CH_2Cl_2 (10 ml). SiO_2 column chromatography (hexane/EtOAc, 4/1 to 2/1) purified the crude product to give 63 mg (27%) of the *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl) 2,2,2,3,3,4,4-heptafluoropropionimidate (**IX**–C_3F_7) as a colorless oil: R_f 0.21 (hexane/EtOAc, 4/1); $[\alpha]_D^{23}=+78.9$ (c=1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) 8.82 (1H, s, NH), 6.61 (1H, d, J=3.8 Hz, HC(1)), 5.45 (1H, t, J=9.9 Hz, HC(3)), 5.13 (1H, t, J=9.6 Hz, HC(4), 5.11 (1H, dd, J=3.8, 9.9 Hz, H(2)), 4.25 (1H, dd, J=4.5, 12.8 Hz, HC(6)), 4.11–4.041 (2H, m, HC(5) and HC(6)), 2.06 (3H, s, Me), 2.03 (3H, s, Me), 2.01 (3H, s, Me), 1.98 (3H, s, Me); ^{13}C NMR ($CDCl_3$) 170.5, 169.8, 169.7, 169.4, 156.2 (t, J=29.8 Hz, CF_3), 117.5 (tq, J=34.8, 288.7 Hz, CF_2), 112.0–105.0 (m, CF_2), 108.1 (tt, J=33.1, 277.0 Hz, CF_2) 92.0 (C(1)), 70.1 (C(5)), 69.6 (C(3)), 69.3 (C(2)), 67.5 (C(4)), 61.3 (C(6)), 20.6 (×2), 20.5, 20.2; ^{19}F NMR (376 MHz, $CDCl_3$) −80.9 (t, J=9.4 Hz), −118.4 (sextet, J=9.4 Hz), −126.8 (t, J=9.4 Hz); IR (neat, cm^{-1}) 3310 (w), 2965 (w), 1761 (s), 1752 (s), 1696 (s), 1435 (m), 1372 (s), 1314 (m), 1229 (s), 1163 (s), 1125 (s), 1080 (s), 1042 (s), 967 (m), 922 (m), 899 (m); EI-MS (70 eV) 544 (1.4), 543 (M^+, 0.2), 484 (4), 423 (5), 331 (68), 321 (55), 298 (34), 280 (10), 268 (17), 250 (10), 242 (11), 238 (15), 211 (14), 200 (13), 169 (100), 157 (56), 145 (41), 127 (50), 115 (81), 109 (86), 98 (58), 84 (42), 73 (30); FAB-MS 544 (MH^+, 0.9), 484 (5), 423 (3), 331 (100), 289 (12), 271 (15), 229 (21), 211 (14), 169 (100), 139 (48), 127 (96), 109 (100), 97 (68), 81 (62); FAB-HRMS calcd for $C_{18}H_{24}F_7NO_{10}$ (MH^+), 544.1054; found, 544.1082.

4.2.13. *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl) 2,2,2-trifluoroacetimidate and *O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl) 2,2,2-trifluoroacetimidate (X–CF_3). Imidate formation was achieved according to the general procedure using 2,3,4,6-tetra-*O*-benzyl-α-D-glucose (541 mg, 1.0 mmol), 2,2,2-trifluoroacetamide (362 mg, 3.2 mmol), DMSO (0.43 ml, 6.0 mmol), $(COCl)_2$ (262 μl, 3.0 mmol), Et_3N (1.25 ml, 9.0 mmol) and DBU (0.30 ml, 2.0 mmol) in CH_2Cl_2 (12 ml). The crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc, 1/6) to give 274 mg (43%) of α-anomer of **X**–CF_3 as a colorless oil from the first fraction. The β-anomer (40 mg, 6%) was obtained from the second fraction as a colorless oil: Data for α-**X**–CF_3: R_f 0.60 (hexane/EtOAc, 3/1); $[\alpha]_D^{27.2}=+57.2$ (c=1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) 8.48 (1H, s, NH), 7.32–7.26 (18H, m, HC(Ar)), 7.15–7.13 (2H, m, HC(Ar)), 6.53 (1H, d, J=3.4 Hz, HC(1)), 4.96 (1H, d, J=11.0 Hz), 4.85 (1H, d, J=10.5 Hz), 4.83 (1H, d, J=11.0 Hz), 4.72 (1H, d, J=12.0 Hz), 4.68 (1H, d, J=12.0 Hz), 4.59 (1H, d, J=12.0 Hz), 4.51 (1H, d, J=10.5 Hz), 4.46 (1H, d, J=12.0 Hz), 4.00 (1H, dd, J=9.0, 9.5 Hz, HC(3)), 3.89 (1H, dt, J=2.0, 9.0 Hz, HC(5)), 3.79 (1H, t, J=9.0 Hz, HC(4)), 3.77 (1H, dd, J=2.0, 11.0 Hz, HC(6)), 3.74 (1H, dd, J=3.4, 9.5 Hz, HC(2)), 3.65 (1H, dd, J=2.0, 11.0 Hz, HC(6)); ^{13}C NMR ($CDCl_3$) 156.4 (q, J=38.0 Hz), 138.6, 138.0, 137.7, 137.6, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9 (×2), 127.8, 127.7 (×2), 127.6, 115.4 (q, J=280.0 Hz), 93.1, 81.4, 79.0, 76.7, 75.7, 75.3, 73.4, 73.1, 72.9, 67.9; IR (neat, cm^{-1}) 3330 (w), 3032 (w), 2921 (m), 2869 (m), 1696 (m), 1456 (m), 1362 (m), 1200 (s), 1166 (s), 1109 (s), 1073 (s), 1001 (m), 735 (s), 698 (s); FAB-MS 659 (5.4), 658 ($[M+Na]^+$, 12), 415 (8), 271 (5), 202 (9), 181

(41), 91 (100); FAB-HRMS calcd for $C_{36}H_{36}F_3NO_6Na$ ($[M+Na]^+$), 658.2392; found, 658.2404. Data for β-**X**–CF_3: R_f 0.54 (hexane/EtOAc, 3/1); $[\alpha]_D^{27.2}=+27.2$ (c=0.31, CH_2Cl_2); ^1H NMR ($CDCl_3$) 8.60 (1H, s, NH), 7.35–7.27 (18H, m, HC(Ar)), 7.17–7.15 (2H, m, HC(Ar)), 5.81 (1H, d, J=7.5 Hz, HC(1)), 4.94 (1H, d, J=11.0 Hz), 4.84 (1H, d, J=11.0 Hz), 4.83 (1H, d, J=10.7 Hz), 4.82 (1H, d, J=10.8 Hz), 4.75 (1H, d, J=10.8 Hz), 4.64 (1H, d, J=12.0 Hz), 4.56 (1H, d, J=10.7 Hz), 4.53 (1H, d, J=12.0 Hz), 3.78–3.72 (5H, m), 3.65–3.62 (1H, m); ^{13}C NMR ($CDCl_3$) 156.4 (q, J=38.8 Hz), 138.4, 137.9 (×2), 137.7, 128.5, 128.4 (×2), 128.1, 128.0, 127.9, 127.8 (×3), 127.7, 115.4 (q, J=280.0 Hz), 96.9, 84.5, 80.7, 77.1, 75.73, 75.66, 75.04, 75.00, 73.4, 68.1; IR (neat, cm^{-1}) 3326 (w), 3032 (w), 2915 (m), 2870 (m), 1698 (m), 1497 (m), 1455 (m), 1362 (m), 1200 (s), 1165 (s), 1092 (s), 1069 (s), 1028 (s), 735 (m), 698 (s); FAB-MS 659 (19), 658 ($[M+Na]^+$, 39), 415 (13), 271 (23), 202 (48), 181 (100), 91 (100); FAB-HRMS calcd for $C_{36}H_{36}F_3NO_6Na$ ($[M+Na]^+$), 658.2392; found, 658.2404.

4.3. General procedure for 3,3-sigmatropic rearrangement

In a sealed tube, allyl imidates were heated at reflux temperature (bath temperature 150°C) under a nitrogen atmosphere. This solution was cooled down to room temperature and the reaction mixture was evaporated in vacuo. Concentrated of crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc) and Kugelrohr distillation to afford the trifluoroacetamide.

4.3.1. 2,2,2-Tifluoro-*N*-(3,7-dimethyl-1,6-octadien-3-yl)-acetamide (Ia–CF_3). 3,3-Sigmatropic rearrangement was achieved according to the general procedure using geranyl 2,2,2-trifluoroacetimidate (**I**–CF_3, 75 mg, 0.3 mmol) in xylene (0.6 ml) for 16 h. The crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc, 20/1) to give 51.3 mg (69%) of (**Ia**–CF_3) as a colorless oil: R_f 0.28 (hexane/EtOAc, 20/1); ^1H NMR ($CDCl_3$) 6.36 (1H, s, NH), 5.87 (1H, dd, J=10.7, 17.3 Hz), 5.18 (1H, d, J=10.7 Hz), 5.11–5.07 (1H, m), 5.09 (1H, d, J=17.3 Hz), 2.02–1.95 (2H, m), 1.84–1.75 (2H, m), 1.66 (3H, s), 1.58 (3H, s), 1.50 (3H, s); ^{13}C NMR ($CDCl_3$) 155.9 (q, J=35.4 Hz), 140.7, 133.4, 123.3, 115.7 (q, J=289.1 Hz), 113.7, 58.8, 39.1, 25.6, 24.0, 17.6; IR (neat, cm^{-1}) 3441 (w), 3328 (w), 2975 (m), 2920 (m), 2861 (m), 1713 (s), 1549 (m), 1455 (m), 1414 (w), 1379 (m), 1206 (s), 1184 (s), 1159 (s), 922 (w), 881 (w); EI-MS (70 eV) 250 (0.7), 249 (M^+, 3.2), 234 (2), 206 (3), 166 (27), 136 (42), 121 (32), 93 (100), 80 (41); EI-HRMS calcd for $C_{12}H_{18}F_3NO$ (M^+), 249.1340; found, 249.1339.

4.3.2. 2,2,2-Trifluoro-*N*-(3-phenyl-1-pentene-3-yl) acetamide (IIa–CF_3). 3,3-Sigmatropic rearrangement was achieved according to the general procedure using cinnamyl 2,2,2-trifluoroacetimidate (**II**–CF_3, 64 mg, 0.28 mmol) in xylene (0.6 ml) for 16 h. The crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc, 20/1) to give 45.0 mg (70%) of (**IIa**–CF_3) as the white solid: R_f 0.38 (hexane/EtOAc, 5/1); mp 75–76°C; ^1H NMR ($CDCl_3$) 7.44–7.29 (5H, m, HC(Ar)), 6.58 (1H, s, NH), 6.03 (1H, ddd, J=5.6, 10.5, 17.1 Hz, HC(2)), 5.63 (1H, ddd, J=1.0, 5.6, 7.0 Hz, HC(3)), 5.35 (1H, dd, J=1.0, 10.5 Hz, HC(1)), 5.27 (1H, dd, J=1.0, 17.1 Hz, HC(1)); ^{13}C NMR ($CDCl_3$) 156.5 (q, J=37.2 Hz), 138.4, 135.2, 129.1, 129.1, 127.2, 117.3, 116.0 (q, J=287.8 Hz), 55.7; IR (KBr, cm^{-1}) 3312 (s), 3088 (m), 3034 (w), 1701 (s), 1551 (s), 1456 (s), 1341 (s), 1405 (s), 1360 (s), 1350 (s), 1082 (m), 997 (m), 935 (s), 924 (m), 889 (m), 756 (s), 725 (s), 700 (s); EI-MS (70 eV) 230 (12), 229 (M^+, 76), 160 (91), 117 (57), 116 (79), 115 (100); FAB-MS 252 ($[M+Na]^+$, 11), 231 (4), 230 (MH^+, 30), 176 (15), 117 (100); FAB-HRMS calcd for $C_{11}H_{11}F_3NO$ (MH^+), 230.0793; found, 230.0811.

4.3.3. 2,2,2-Trifluoro-*N*-(4-benzyloxy-1-buten-3-yl) acetamide (IIIa–CF_3). 3,3-Sigmatropic rearrangement was achieved according to the general procedure using 4-benzyloxy-2(*E*)-butenyl 2,2,2-trifluoroacetimidate (**III**–CF_3, 61 mg, 0.22 mmol) in xylene (0.6 ml) for 68 h. The crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc, 20/1) to give 43.1 mg (71%) of (**IIIa**–CF_3) as the colorless prisms: R_f 0.30 (hexane/EtOAc, 5/1); mp 42.5–43.0°C; ^1H NMR ($CDCl_3$) 7.38–7.29 (5H, m), 6.76 (1H, s, NH), 5.85 (1H, ddd, J=5.8, 10.5, 17.1 Hz), 5.26 (1H, dd, J=1.4, 17.1 Hz), 5.25 (1H, dd, J=1.4, 10.5 Hz), 4.64 (1H, m), 4.56 (1H, d, J=11.9 Hz), 4.52 (1H, d, J=11.9 Hz), 3.60 (1H, dd, J=3.9, 9.8 Hz), 3.57 (1H, dd, J=4.1, 9.7 Hz); ^{13}C NMR ($CDCl_3$) 156.6 (q, J=37.2 Hz), 137.3, 133.6, 129.4, 128.0, 127.7, 117.6, 115.8 (q, J=287.4 Hz), 73.3, 70.5, 51.9; IR (KBr, cm^{-1}) 3422 (w), 3302 (m), 2867 (m), 1705 (s), 1559 (m), 1362 (m), 1210 (s), 1183 (s), 1115 (m), 1105 (s), 737 (m), 698 (m); EI-MS (70 eV) 274 (5), 273 (M^+, 9), 243 (17), 167 (39), 152 (99), 130 (99), 107 (42), 91 (100); EI-HRMS calcd for $C_{13}H_{14}F_3NO$ (M^+), 273.0977; found, 273.0996.

4.3.4. Mixture of (3*R*,4*S*)-4,5-diisopropylidenedioxy-3-trifluoroacetylaminoprop-2-ene and (3*S*,4*S*)-4,5-diisopropylidenedioxy-3-trifluoroacetylaminoprop-2-ene (IVa–CF_3). 3,3-Sigmatropic rearrangement was achieved according to the general procedure using 4-benzyloxy-2(*E*)-butenyl 2,2,2-trifluoroacetimidate (**IV**–CF_3, 75.0 mg, 0.3 mmol) in xylene (0.6 ml) for 96 h. The crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc, 8/1) to recover 21 mg (28%) of starting material (**IV**–CF_3) from the first fraction. The 1/1 mixture of **IVa**–CF_3 (45 mg, 60%) was obtained from the second fraction as a colorless oil: R_f 0.27 (hexane/EtOAc, 5/1); ^1H NMR ($CDCl_3$) 6.69 and 6.64 (1H, br s, NH), 5.84–5.75 (1H, m), 5.34–5.11 (2H, m), 4.54–4.50 (1H, m), 4.28–4.23 (1H, m), 4.06 (0.5H, dd, J=6.9, 8.8 Hz), 4.04 (0.5H, dd, J=6.8, 9.0 Hz), 3.78 (0.5H, dd, J=5.1, 9.0 Hz), 3.64 (0.5H, dd, J=6.1, 8.8 Hz), 1.413 and 1.408 (3H, s), 1.38 and 1.31 (3H, s); ^{13}C NMR ($CDCl_3$) 157.1 and 156.7 (q, J=37.1 Hz), 133.5 and 131.1, 119.8 and 118.2, 115.8 and 115.7 (q, J=283.3 Hz), 110.2 and 110.0, 76.3 and 76.0, 66.4 and 65.5, 54.5 and 53.1, 26.1 and 25.9, 24.66 and 24.59; IR (neat, cm^{-1}) 3302 (m), 3090 (w), 2992 (m), 1705 (s), 1557 (s), 1379 (s), 1211 (s), 1182 (s), 1161 (s), 1069 (s), 992 (m), 934 (m), 857 (m), 723 (m); EI-MS (70 eV) 238 (M^+-15, 27), 196 (10), 178 (25), 101 (100); EI-HRMS calcd for $C_9H_{11}F_3NO$ (M^+-15), 238.0691; found, 238.0697.

4.4. General procedure for Et_2AlCl-catalyzed cyclization

0.5 equiv. of Et_2AlCl (1.0 M in hexane) was added to an ice-cooled solution of epoxy trifluoroacetimidate in CH_2Cl_2. This solution was stirred for 5 min at room temperature and the reaction mixture was quenched with sat. aqueous $NaHCO_3$. The reaction mixture was diluted with CH_2Cl_2, washed with brine, dried over Na_2SO_4 and evaporated in vacuo. Concentrated crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc) to afford the product.

4.4.1. 2-((4*R*)-2′-Trifluoromethyl(1′,3′-oxazolin-4′-yl)(2*S*)-6-methylhept-5-en-2-ol (11A–CF_3) and (4*R*,5*R*)-4-methyl-2-trifluoromethyl-4-(4-methylpent-3-enyl)-5*H*,6*H*-1,3-oxazin-5-ol (11B–CF_3). Et_2AlCl-catalyzed cyclization was achieved according to the general procedure using (2*S*,3*R*) 6(*E*)-3,7-dimethyl-2,3-epoxyoctenyl 2,2,2-trifluoroacetimidate (**VI**–CF_3, 169.5 mg, 0.64 mmol) and Et_2AlCl (0.32 ml, 0.32 mmol) in CH_2Cl_2 (5.0 ml). The mixture of oxazoline and dihydrooxazine were separated by SiO_2 column chromatography (hexane/EtOAc, 10/1) to give 152 mg (90%) of oxazoline (**11B**–CF_3) and 3.8 mg (2%) of dihydrooxazoline (**11A**–CF_3) as a colorless oil: data for **11A**–CF_3: R_f 0.19 (hexane/EtOAc, 5/1); $[\alpha]_D^{27}=-34.3$ (c=1.03, $CHCl_3$); ^1H NMR ($CDCl_3$) 5.14–5.10 (1H, m), 4.55 (1H, dd, -J=9.0, 10.3 Hz), 4.50 (1H, dd, J=9.0, 10.3 Hz), 4.28 (1H, qt, J=1.7, 9.0 Hz), 2.21–2.02 (2H, m), 1.69 (3H, s), 1.63 (3H, s), 1.54–1.46 (2H, m), 1.29 (3H, s); ^{13}C NMR ($CDCl_3$) 156.0 (q, J=40.5 Hz), 132.6, 123.8, 116.4 (q, J=274.3 Hz), 74.6, 73.2, 70.8, 38.6, 25.6, 23.3, 22.1, 17.7; IR (neat, cm^{-1}) 3424 (m), 2945 (m), 2928 (m), 2854 (m), 1715 (m), 1402 (m), 1210 (s), 1163 (s), 1130 (s); EI-MS (70 eV) 265 (M^+, 11), 134 (38), 109 (93), 69 (100); EI-HRMS calcd for $C_{12}H_{18}F_3NO_2$ (M^+), 265.1290; found, 265.1285. Data for **11B**–CF_3: R_f 0.18 (hexane/EtOAc, 5/1); $[\alpha]_D^{27}=+22.9$ (c=0.81, $CHCl_3$); ^1H NMR ($CDCl_3$) 5.08–5.04 (1H, m), 4.28 (1H, dd, J=3.9, 11.3 Hz), 4.07 (1H, dd, J=6.6, 11.3 Hz), 3.03 (1H, ddd, J=1.7, 3.9, 6.6 Hz), 2.30–2.23 (1H, m), 2.14–1.94 (2H, m), 1.65 (3H, s), 1.57 (3H, s), 1.56–1.44 (2H, m), 1.22 (3H, s); ^{13}C NMR ($CDCl_3$) 144.9 (q, J=38.8 Hz), 132.4, 123.6, 116.6 (q, J=276.7 Hz), 66.3, 66.1, 56.3, 40.5, 25.6, 21.8, 21.5, 17.5; IR (neat, cm^{-1}) 3386 (m), 2975 (m), 2930 (m), 1694 (s), 1455 (m), 1387 (s), 1350 (s), 1209 (s), 1154 (s), 1092 (s), 878 (w), 822 (w), 735 (w); EI-MS (70 eV) 266 (MH^+, 3), 265 (M^+, 8), 222 (87), 183 (76), 133 (22), 154 (37), 109 (44), 69 (100); EI-HRMS calcd for $C_{12}H_{18}F_3NO_2$ (M^+), 265.1290; found, 265.1283.

4.4.2. (4*R*,5*R*)-2-Trifluoromethyl-4-phenyl-4*H*,5*H*,6*H*-1,3-oxazin-5-ol (12B–CF_3). Et_2AlCl-catalyzed cyclization was achieved according to the general procedure using (2*S*,3*R*)-3-phenyl-2,3-epoxypropyl 2,2,2-trifluoroacetimidate (**VII**–CF_3, 245.2 mg, 1.0 mmol) and Et_2AlCl (0.5 ml, 0.5 mmol) in CH_2Cl_2 (10.0 ml). The crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc, 2/1) to give 237.7 mg (97%) of (**12B**–CF_3) as the white solid: mp 95–97°C; $[\alpha]_D^{21}=94.4$ (c=1.04, $CHCl_3$); ^1H NMR ($CDCl_3$) 7.40–7.30 (3H, m), 7.16–6.95 (2H, m), 4.48 (1H, br s, NH), 4.18 (1H, dd, J=3.1, 11.2 Hz), 4.08 (1H, ddd, J=1.7, 5.8, 11.2 Hz), 3.87–3.78 (1H, m), 2.73 (1H, br s, OH); ^{13}C NMR ($CDCl_3$) 147.9 (q, J=38.7 Hz), 138.7, 128.9, 128.0, 126.9, 116.6, 67.1, 66.5, 61.8; IR (KBr, cm^{-1}) 3297 (s), 2942 (w), 1698 (s), 1543 (w), 1543 (w), 1453 (w), 1391 (w), 1335 (m), 1215 (s), 1165 (s), 1105 (m), 1044 (w), 885 (w), 752 (w), 698 (w); FAB-MS 247 (17), 246 (MH^+, 100), 227 (2), 91 (14); FAB-HRMS calcd for $C_{11}H_{11}F_3NO_3$ (MH^+), 246.0742; found, 246.0734.

4.4.3. (4*R*,5*R*)-2-Trifluoromethyl-4-phenyl-4*H*,5*H*,6*H*-1,3-oxazin-5-ol (13A–CF_3). Et_2AlCl-catalyzed cyclization was achieved for 30 min according to the general procedure using (2*S*,3*R*)-4-benzyloxy-2,3-epoxybutyl 2,2,2-trifluoroacetimidate (**VIII**–CF_3, 81 mg, 0.28 mmol) and Et_2AlCl (0.70 ml, 0.70 mmol) in CH_2Cl_2 (3.0 ml). The crude mixture was purified by SiO_2 column chromatography (hexane/EtOAc, 3/1) to give 69.5 mg (86%) of **13A**–CF_3 as a colorless oil: R_f=0.30 (hexane/EtOAc, 5/1); $[\alpha]_D^{21.5}=-38.7$ (c=0.75, $CHCl_3$); ^1H NMR ($CDCl_3$) 7.40–7.30 (5H, m), 4.60–4.45 (4H, m), 4.40–4.35 (1H, m), 3.95–3.82 (1H, m), 3.67 (1H, dd, J=3.9, 9.7 Hz), 3.60 (1H, dd, J=5.8, 9.7 Hz), 2.67 (1H, br s, OH); ^{13}C NMR ($CDCl_3$) 156.3 (q, J=40.5 Hz), 137.5, 128.9, 128.0, 127.8, 116.3, (q, J=274.3 Hz), 73.6, 71.6, 71.3, 71.0, 68.5; IR (neat, cm^{-1}) 3600–3250 (m), 3915 (w), 2869 (m), 1742 (m), 1690 (m), 1404 (m), 1210 (s), 1163 (s), 1132 (s), 909 (m), 745 (m), 700 (m); FAB-MS 291 (5), 290 (6), 290 (MH^+, 30), 185 (19), 154 (50), 91 (100); FAB-HRMS calcd for $C_{13}H_{15}F_3NO_3$ (MH^+), 290.1004; found, 290.1009.

4.5. Ethyl *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl) (*R*)-2-hydroxy-4-phenylbutyrate (14)

A solution of **IX**–CF_3 (99.0 mg, 0.22 mmol) and ethyl (*R*)-2-hydroxy-4-phenylbutyrate (22 mg, 0.11 mmol) in CH_2Cl_2 (5 ml) was cooled to 0°C. $BF_3{\cdot}OEt_2$ (13 μl, 0.05 mmol) was added to this solution, and the reaction mixture was stirred for 15 min and then warmed to room temperature over 3 h. The reaction was quenched by adding sat. aqueous NH_4Cl and partitioned between EtOAc. The aqueous layer was extracted three times with EtOAc, and the combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was purified by SiO_2 column chromatography (hexane/EtOAc, 3/1) to give 43.0 mg (73%) of the β-glycoside (**14**) as a colorless oil: R_f: 0.18 (hexane/EtOAc, 3/1); $[\alpha]_D^{29}=+10.4$ (c=1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) 7.22 (5H, m, HC(Ar)), 5.20 (1H, t, J=9.3 Hz, HC(3′)), 5.12 (1H, dd, J=7.8, 9.5 Hz, HC(2′)), 5.07 (1H, dd, J=9.3, 10.0 Hz, HC(4′), 4.57 (1H, d, J=7.8 Hz, HC(1′)), 4.17 (1H, dd, J=5.1, 12.2 Hz, HC(6′)), 4.15 (2H, q, J=7.1 Hz, H_2C), 4.04 (1H, dd, J=5.1, 12.2 Hz, HC(6′)), 3.91 (1H, dd, J=4.4, 9.0 Hz, HC(2)), 3.64 (1H, ddd, J=2.4, 5.2, 10.0 Hz, HC(5′)), 2.66 (2H, m, H_2C(4)), 2.05 (6H, s, Me), 2.01 (3H, s, Me), 2.00 (3H, s, Me), 2.03 (2H, m, H_2C(3)), 1.25 (3H, t, J=7.1 Hz, Me); ^{13}C NMR ($CDCl_3$) 171.5, 170.6, 170.3, 169.3, 169.0, 140.5, 128.6, 128.4, 126.2, 101.3 (C(1′)), 79.2 (C(2)), 72.8 (C(3′)), 71.9 (C(5′)), 71.3 (C(2′)), 68.2 (C(4′)), 61.8 (C(6′)), 61.0, 34.1 (C(3)),30.9 (C(4)), 20.6, 20.6, 20.6, 20.5, 14.0; IR (neat, cm^{-1}) 3063 (w), 2982 (w), 2870 (w), 2257 (w), 1759 (s), 1509 (w), 1456 (w), 1433 (w), 1370 (m), 1229 (s), 1171 (m), 1136 (w), 1067 (m), 1040 (s), 982 (w), 912 (m), 735 (m), 702 (w), 648 (w), 600 (w); FAB-MS 539 (MH^+, 3), 331 (100), 289 (20), 271 (9), 229 (15), 169 (100), 145 (22), 127

(45), 109 (100), 91 (56); FAB-HRMS calcd for $C_{26}H_{35}O_{12}$ (MH^+), 539.2129; found, 539.2175.

Acknowledgements

Partial financial support of this research under the Biodesign Research Program of the Institute of Physical and Chemical Research (RIKEN) and Dainippon Ink & Chemicals, Inc Award in Synthetic Organic Chemistry, Japan is gratefully acknowledged.

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