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O- and *N*-Glycosidation of D-glycals using Ferrier rearrangement under Mitsunobu reaction conditions. Application to *N*-nucleoside synthesis

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ABSTRACT

We have disclosed the reaction of 3-hydroxy free glycals with *O*- or *N*-nucleophiles under Mitsunobu reaction conditions proceeded to produce 2,3-unsaturated glycosides in good to high yield and moderate stereoselectivity. The reaction would take place via allyloxycarbenium ion.

1. Introduction

O-Glycosidation and *N*-glycosidations are fundamental reactions in carbohydrate synthesis.[1] So far, Koenigs–Knorr and its modified reactions have been used in glycosidation reaction.[2,3] On the other hand, Ferrier reported the glycosidation of 1,2-unsaturated glycals with nucleophiles in the presence of Lewis acids leading to the 2,3-unsaturated glycosides.[4,5] In Ferrier reaction the 3-positional group works as a leaving group.

During the course of our study of the synthesis of allose derivatives,[6] we attempted the inversion of equatorial 3-hydroxy group in D-glucose derivatives using diethyl azodicarboxylate (DEAD), PPh_3, and *p*-nitrobenzoic acid (Mitsunobu reaction conditions) to obtain the allose derivatives, that is, the 3-hydroxygroup inversion in the product. However, the product was not a simple inversion product at 3-position, but O-glycosidation product via the rearrangement of double bond as a mixture of α- and β-isomers. In our cases, 3-hydroxy group works as a leaving group. Here, we report *O*- and *N*-glycosidation under Mitsunobu reaction conditions.

2. Results and discussion

4,6-*O*-Benzylidene D-glucal **1** was prepared as follows: (1) oxidation of allylic hydroxyl group of D-glucal leading to the formation of 1,5-anhydro-D-*erythro*-hex-1-en-3-ulose.[7] (2) 4,6-Benzylidation of 3-ulose.[8] (3) Reduction of 3-keto group. The reaction of 4,6-*O*-benzylidene D-glucal **1** with *p*-nitrobenzoic acid in the presence of DEAD or DMEAD[9,10] and PPh_3 proceeded to give *p*-nitrobenzoyl 4,6-*O*-benzylidene-2,3-deoxy-D-*erythro*-hex-2-enopyranoside **2** in 70% yield. As for the stereochemistry of the products, the reaction of **1** with *p*-nitrobenzoic acid in the presence of DEAD and PPh_3 at 23 °C for 1 h in THF gave the product in the ratio of α/β=75:25 (78% yield). The same reaction carried out in toluene at 25 °C gave the product in α/β=75:25 (83% yield). The reaction at 0 °C afforded the product in α/β=64:36 (79% yield) as shown in Table 1 (entries 1–3). 4,6-Di-*O*-acetyl D-glucal **3** was directly prepared by the reaction of 3,4,6-tri-*O*-acetyl D-glucal with lipase at pH 7.0.[11] For substrate **3**, the ratio of the product was only moderate compared with the case of substrate **1**. That is, α-isomers (**4**–**7**) were slightly predominantly obtained not only for *p*-nitrobenzoic acid, but also *p*-nitrophenol, *o*-nitrophenol, and *p*-isopropylphenol (entries 4–15 in Table 1). It should be noted that the reaction of 4,6-di-*O*-acetyl D-glucal (**3**) with *p*-nitrobenzoic acid did not proceed neither in the presence of $BF_3 \cdot OEt_2$ nor Me_3SiOTf. Sobi and Sulikowski reported similar type of Mitsunobu reaction of glycal with phenolic nucleophiles for three substrates, that is, L-rhamnal, D-glucal, and L-fucal derivatives.[12] They suggested the reaction proceeded in S_N2' manner. However, we propose S_N1 mechanism via allyloxocarbenium ion as shown Scheme 2. The both of the starting material **1** derived from D-glucal and **8** derived from D-allal gave the product in same α/β ratio (α/β=75:25) in Scheme 1. This result will indicate the reaction would proceed via the common intermediate. As for the

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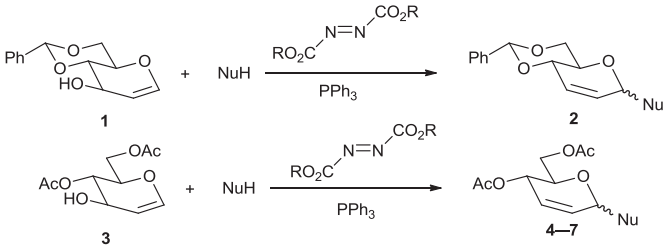
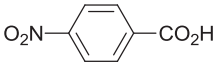
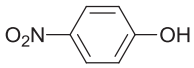
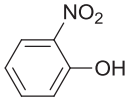
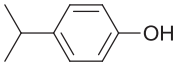
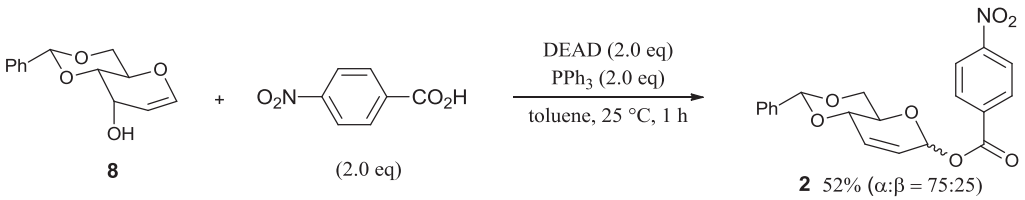
Table 1
Glycosidation of protected D-glucals with oxygen nucleophiles using Mitsunobu reagents[a]



Entry	Substrate	NuH	Dialkyl azodicarboxylate (R)	Solvent	Conditions		Product		
					Temp/°C	Time/h	Yield[b] (%)		α/β[c]
1	**1**		DEAD (Et)	THF	23	1	**2**	78	75:25
2	**1**		DEAD	Toluene	25	1	**2**	83	75:25
3	**1**		DEAD	Toluene	0	1	**2**	79	66:34
4	**3**		DIAD (*i*-Pr)	THF	20	1	**4**	82	53:47
5	**3**		DIAD	Toluene	20	1	**4**	49	63:37
6[d]	**3**		DMEAD ($(CH_2)_2OCH_3$)	THF	20	4	**4**	73	61:39
7[d]	**3**		DMEAD	THF	20	18	**4**	67	58:42
8[e]	**3**		DMEAD	THF	20	5	**4**	78	57:43
9[e]	**3**		DMEAD	THF	20	18	**4**	73	58:42
10[e]	**3**		DMEAD	Toluene	20	3	**4**	74	52:48
11[d]	**3**		DMEAD	THF	20	24	**5**	82	59:41
12[d]	**3**		DMEAD	THF	20	2	**6**	78	64:36
13[e]	**3**		DMEAD	THF	20	24	**7**	49	58:42

[a] All reactions were carried out using 2 equiv of dialkyl azodicarboxylate, PPh_3, and nucleophile unless otherwise noted.
[b] Isolated yield as a mixture of α and β isomer.
[c] ^1H NMR analysis.
[d] Dialkyl azodicarboxylate, PPh_3, and nucleophile (1.5 equiv).
[e] Dialkyl azodicarboxylate, PPh_3, and nucleophile (1.2 equiv).



Scheme 1. Examination using 4,6-benzylidene-D-allal as a substrate.

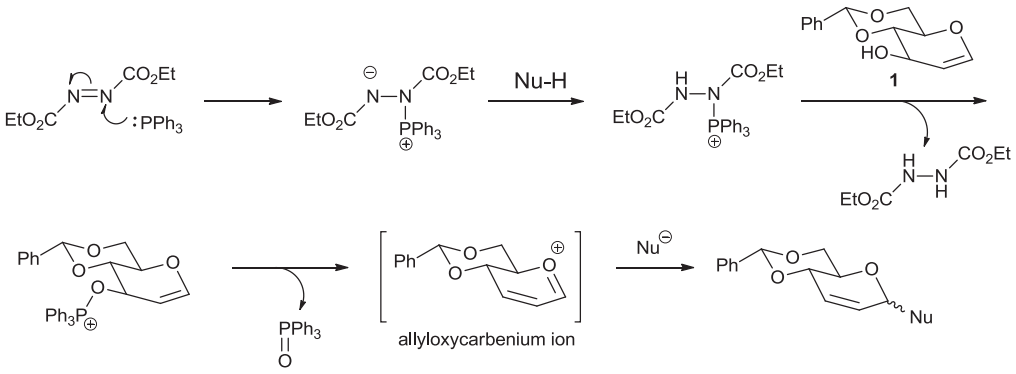
difference of stereoselectivity of the product between the case of substrate **1** (α/β=75:25) and **3** (α/β=66:34 to 52:48), we assume the participation of 4-acetyl group contributed the production of kinetically favored β-isomer.[4e]

The formation of triphenylphosphine oxide will be the driving force to produce allyloxocarbenium ion. This method can be applied for nitrogen nucleophiles, such as phthalimide, pyrimidinone, and pyrimidin-thione also worked that led to the novel *N*-nucleosides (Table 2). In these reactions the products (**9**–**11**) were obtained in moderate yield (40–68%) and selectivity (57:43 to 63:37) (Table 2).

The reaction would proceed via the same intermediate with the conventional Ferrier reaction, that is, allyloxocarbenium ion. It should be mentioned that dihydropyrimidinone having non-aromatic structure did not work as a nucleophile. This may be attributed to the importance of acidity of nucleophile (Nu–H) in Scheme 2.

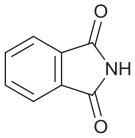
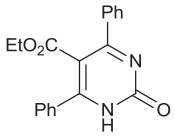
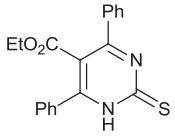
3. Conclusion

In conclusion, we have revealed *O*- and *N*-glycosidation of D-glycals under Mitsunobu reaction conditions. Application to the

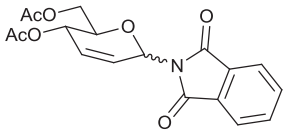


Scheme 2. Possible mechanism of glycosidation using Mitsunobu reagents.

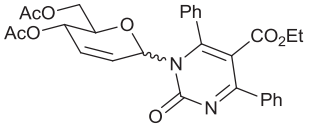
Table 2
Glycosidation of protected D-glucals with nitrogen nucleophiles using Mitsunobu reagents[a]

Entry	Substrate	NuH	Dialkyl azodicarboxylate	Conditions		Product		
				Temp/°C	Time/h	Yield[b] (%)		α/β[c]
1[d]	**3**		DMEAD	0	6	**9**	40	57:43
2	**3**		DMEAD	50	1	**10**	68	63:37
3	**3**		DMEAD	20	24	**11**	40	60:40

[a] All reactions were carried out using 1.2 equiv of dialkyl azodicarboxylate, PPh_3, and nucleophile unless otherwise noted.
[b] Isolated yield as a mixture of α and β isomer.
[c] ^1H NMR analysis.
[d] Dialkyl azodicarboxylate, PPh_3, and nucleophile (1.5 equiv).



9



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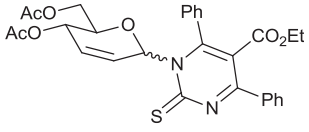

11

novel *N*-nucleosides synthesis has been also disclosed. Further study for the synthesis of novel *N*-nucleosides is now under investigation.

4. Experimental section

4.1. General

All reactions were carried out in an oven-dried glassware with magnetic stirring. All starting materials were obtained from commercial sources. ^1H and ^{13}C NMR spectra (400 and 100.6 MHz, respectively) were recorded using Me_4Si as the internal standard (0 ppm). Some of the peaks of ^{13}C NMR are overlapped especially in aromatic regions. The following abbreviations are used: s=singlet, d=doublet, m=multiplet.

4.2. General procedure

4.2.1. Method A. (using DEAD or DIAD). To a mixture of nucleophile (0.6 mmol), triphenylphosphine (0.6 mmol) substrate (**1** or **3**) (0.5 mmol), and solvent (2.0 mL) was added DEAD (or DIAD) (0.6 mmol) slowly. After the completion of the reaction, satd $NaHCO_3$ was added. Extraction with ethyl acetate and the combined organic layers were dried over Na_2SO_4, and evaporated. The residue was silica gel column chromatographed to give the product as a mixture of α- and β-isomers.

4.2.2. Method B. (using DMEAD). To a mixture of nucleophile (0.6 mmol), triphenylphosphine (0.6 mmol), substrate (**1** or **3**) (0.5 mmol), and solvent (2.0 mL) was added DMEAD (0.6 mmol) slowly. After the completion of the reaction, satd $NaHCO_3$ was

added. Organic layers were evaporated and residue was extracted with diethyl ether and the combined organic layers were dried over Na_2SO_4, and evaporated. The residue was silica gel column chromatographed to give the product as a mixture of α- and β-isomers.

*4.2.3. p-Nitrobenzoyl 4,6-O-benzylidene-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranoside (**2**).* White solids (73%, α/β=75:25); IR (KBr) 695, 716, 1096, 1527, 1533, 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 3.8–4.1 (m, 2H, H5; H6); 4.3–4.4 (m, 2H, *H*4; *H*6′); 5.64 (s, 75/100H, PhC*H*); 5.65 (s, 25/100H, PhC*H*); 5.8–5.9 (m, 1H, *H*2); 6.39 (d, *J*=9.6 Hz, 1H, *H*3); 6.59 (s, 75/100H, *H*1); 6.76 (s, 25/100H, *H*1); 7.3–7.6 (m, 5H, Ph*H*); 8.2–8.4 (m, 4H, *p*-$NO_2C_6H_4$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.2; 69.0; 71.3; 74.3; 74.5; 89.7; 96.0; 102.3; 123.6; 124.3; 126.2; 128.4; 129.3; 131.0; 131.1; 133.0; 135.1; 136.7; 163.6. Anal. Calcd for $C_{20}H_{17}NO_7$: C, 62.66; H, 4.47; N, 3.65. Found: C, 62.45; H, 4.55; N, 3.77. MS [ESI^+]: *m*/*z*: 406.1 $[M+Na]^+$.

*4.2.4. p-Nitrobenzoyl 4,6-di-O-acetyl-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranoside (**4**).* White solids (73%, α/β=58:42); IR (KBr) 1241, 1738, 2969 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 1.95 (s, 42/100×3H, *OAc*); 2.06 (s, 58/100×3H, *OAc*); 2.0–2.2 (m, 3H, *OAc*); 4.2–4.4 (m, 3H, *H*5; *H*6; *H*6′); 5.19 (dd, *J*=4.8, 2.0 Hz, 42/100H, *H*4); 5.46 (dd, *J*=9.6, 1.6 Hz, 58/100H, *H*4); 5.9–6.1 (m, 58/100H, *H*2); 6.14 (d, 1H, *H*3); 6.2–6.3 (dd, 42/100H, *H*2); 6.59 (s, 58/100H, *H*1); 6.68 (s, 42/100H, *H*1); 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7; 20.9; 62.3; 62.7; 63.1; 64.5; 69.4; 73.0; 88.4; 89.6; 97.0; 123.6; 125.2; 126.6; 127.7; 130.9; 131.5; 135.0; 150.7; 163.4; 169.9; 170.3; 170.5; 170.7. Anal. Calcd for $C_{17}H_{17}NO_9$: C, 53.83; H, 4.52; N, 3.69. Found: C, 53.53; H, 4.52; N, 3.78. MS [ESI^+]: *m*/*z*: 402.0 $[M+Na]^+$.

*4.2.5. p-Nitrophenyl 4,6-di-O-acetyl-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranoside (**5**).* White solids (82%, α/β=59:41); IR (KBr) 1231, 1342, 1592, 1743, 2958 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 1.83 (s, 41/100×3H, *OAc*); 1.97 (s, 59/100×3H, *OAc*); 2.0–2.2 (m, 3H, *OAc*); 4.1–4.4 (m, 3H, *H*5; *H*6; *H*6′); 5.15 (dd, *J*=5.0, 2.2 Hz, 41/100H, *H*4); 5.42 (d, *J*=9.6 Hz, 59/100H, *H*4); 5.82 (s, 59/100H, *H*1); 5.90 (s, 41/100H, *H*1); 6.0–6.3 (m, 2H, *H*2; *H*3); 7.1–7.2 (m, 2H, Ar*H*); 8.1–8.3 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9; 62.4; 62.9; 63.1; 64.7; 68.3; 72.9; 91.4; 92.6; 115.6; 116.3; 116.6; 125.7; 125.8; 126.1; 128.2; 131.1; 161.6; 161.8; 170.0; 170.1. Anal. Calcd for $C_{16}H_{17}NO_8$: C, 54.70; H, 4.88; N, 3.99. Found: C, 54.70; H, 4.88; N, 4.07. MS [ESI^+]: *m*/*z*: 374.1 $[M+Na]^+$.

*4.2.6. o-Nitrophenyl 4,6-di-O-acetyl-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranoside (**6**).* Yellow oil (78%, α/β=64:36); IR (KBr) 1221, 1525, 1592, 1737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 1.89 (s, 36/100×3H, *OAc*); 1.97 (s, 64/100×3H, *OAc*); 2.12 (s, 36/100×3H, *OAc*); 2.13 (s, 64/100×3H, *OAc*); 4.1–4.3 (m, 3H, *H*5; *H*6; *H*6′); 5.17 (s, 36/100H, *H*4); 5.40 (d, *J*=9.2 Hz, 64/100H, *H*4); 5.74 (s, 64/100H, *H*1); 5.86 (s, 36/100H, *H*1); 6.0–6.1 (m, 1H, *H*2); 6.22 (d, *J*=2.0 Hz, 1H, *H*3); 7.1–7.2 (m, 1H, Ar*H*); 7.4–7.6 (m, 2H, Ar*H*); 7.8–7.9 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4; 20.7; 20.9; 62.5; 63.0; 64.7; 68.3; 73.1; 92.9; 95.0; 118.2; 120.0; 122.2; 122.9; 125.1; 125.9; 126.0; 128.3; 131.0; 133.7; 133.8; 150.2; 170.1; 170.2; 170.3; 170.6. Anal. Calcd for $C_{16}H_{17}NO_8$: C, 54.70; H, 4.88; N, 3.99. Found: C, 54.70; H, 4.91; N, 4.08. MS [ESI^+]: *m*/*z*: 374.1 $[M+Na]^+$.

*4.2.7. p-Isopropylphenyl 4,6-di-O-acetyl-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranoside (**7**).* White paste (49%, α/β=58:42); IR (KBr) 1228, 1744, 2961 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 1.1–1.3 (m, 6H, $CH(CH_3)_2$); 1.85 (s,42/100×3H, *OAc*); (s, 58/100×3H, *OAc*); 2.1–2.2 (m, 3H, *OAc*); 2.8–2.9 (m, 1H, $CH(CH_3)_2$); 4.1–4.4 (m, 3H, *H*5; *H*6; *H*6′); 5.16 (s, 42/100H, *H*4); 5.39 (d, *J*=10.0 Hz, 58/100H, *H*4); 5.66 (s, 58/100H, *H*1); 5.78 (s, 42/100H, *H*1); 5.9–6.1 (m, 1H, *H*2); 6.1–6.3 (m, 1H, *H*3) 7.0–7.2 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4; 20.6; 21.0; 24.1; 33.3; 33.4; 62.7; 63.4; 63.5; 65.1; 67.7; 72.8; 91.9; 93.2; 116.1; 117.0; 125.3; 127.22; 127.24; 129.7; 143.0; 154.9; 155.1; 170.3; 170.6; 170.7. Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.34; H, 7.01. MS [ESI^+]: *m*/*z*: 371.1 $[M+Na]^+$.

*4.2.8. 1-{4,6-Di-O-acetyl-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranosyl}-phthalimide (**9**).* White solids (40%, α/β=57:43); IR (KBr) 719, 1221, 1773 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 2.06 (s, 57/100×3H, *OAc*); 2.07 (s, 43/100×3H, *OAc*); 2.12 (s, 43/100×3H, *OAc*); 2.14 (s, 57/100×3H, *OAc*); 4.1–4.2 (m, 37/100H, *H*5); 4.1–4.3 (m, 2H, *H*6; *H*6′); 4.3–4.4 (m, 57/100H, *H*5); 5.43 (dd, *J*=9.2, 1.1 Hz, 57/100H, *H*4); 5.52 (dd, *J*=9.0, 2.2 Hz, 43/100H, *H*4); 5.8–6.2 (m, 3H, *H*1; *H*2; *H*3); 7.6–7.8 (m, 2H, Ar*H*); 7.8–8.0 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7; 20.9; 21.0; 62.6; 63.0; 64.6; 70.4; 72.2; 74.3; 74.8; 123.6; 123.7; 125.0; 127.4; 128.7; 129.5; 131.6; 131.7; 134.4; 134.5; 166.6; 167.7; 170.0; 170.3; 170.8. HRMS [ESI^+]: *m*/*z* calcd for $C_{18}H_{17}NO_7Na$: 382.0903 $[M+Na]^+$. Found: 382.0915 $[M+Na]^+$.

*4.2.9. 1-{4,6-Di-O-acetyl-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranosyl}-5-(ethoxycarbonyl)-4,6-diphenyl-pyrimidin-2(1H)-one (**10**).* White solids (68%, α/β=63:37); IR (KBr) 1231, 1729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 0.95 (t, *J*=7.2 Hz, 3H, $CO_2CH_2CH_3$); 1.95 (s, 37/100×3H, *OAc*); 2.03 (s, 63/100×3H, *OAc*); 2.10 (s, 3H, *OAc*); 4.0–4.5 (m, 5H, *H*5; *H*6; *H*6′; $CO_2CH_2CH_3$); 5.20 (d, *J*=3.6 Hz, 37/100H, *H*4); 5.52 (d, *J*=9.6 Hz, 63/100H, *H*4); 6.0–6.2 (m, 2H, *H*2; *H*3); 6.92 (s, 63/100H, *H*1); 6.96 (s, 37/100H, *H*1); 7.4–7.5 (m, 6H, Ar*H*); 7.6–7.8 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4; 20.7; 20.9; 61.9; 62.0; 62.5; 63.3; 64.8; 68.8; 72.9; 89.6; 90.8; 120.7; 122.6; 125.7; 126.0; 128.36; 128.41; 128.44; 128.7; 130.27; 130.34; 130.6; 136.8; 137.1; 162.7; 167.3; 167.4; 167.7; 168.1; 170.2; 170.3; 170.7. HRMS [ESI^+]: *m*/*z* calcd for $C_{29}H_{28}N_2O_8Na$: 555.1743 $[M+Na]^+$. Found: 555.1709 $[M+Na]^+$.

*4.2.10. 1-{4,6-Di-O-acetyl-2,3-dideoxy-α/β-D-erythro-hex-2-enopyranosyl}-5-(ethoxycarbonyl)-4,6-diphenyl-pyrimidin-2(1H)-thione (**11**).* Yellow oil (40%, α/β=60:40); IR (KBr) 1213, 1515, 1728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$); δ 0.9–1.0 (m, 3H, $CO_2CH_2CH_3$); 2.00 (s, 60/100×3H, *OAc*); 2.02 (s, 40/100×3H, *OAc*); 2.10 (s, 60/100×3H, *OAc*); 2.11 (s, 40/100×3H, *OAc*); 4.0–4.4 (m, 5H, *H*5; *H*6; *H*6′; $CO_2CH_2CH_3$); 5.3–5.4 (m, 60/100H, *H*4); 5.46 (dd, *J*=9.0, 1.8 Hz, 40/100H, *H*4); 5.8–6.2 (m, 2H, *H*2; *H*3); 6.81 (d, *J*=2.0 Hz, 60/100H, *H*1); 6.99 (d, *J*=2.0 Hz, 40/100H, *H*1); 7.4–7.6 (m, 6H, Ar*H*); 7.6–7.8 (d, *J*=6.8 Hz, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7; 20.9; 21.0; 62.6; 63.0; 64.6; 70.4; 72.2; 74.3; 74.80; 123.6; 123.7; 125.0; 127.4; 128.7; 129.5; 131.6; 131.7; 134.4; 134.5; 166.6; 167.7; 170.0; 170.3; 170.8. Anal. Calcd for $C_{29}H_{28}N_2O_7S$: C, 63.49; H, 5.11; N, 5.14. Found: C, 63.78; H, 5.11; N, 5.43. MS [ESI^+]: *m*/*z*: 533.1 $[M+H]^+$; 555.2 $[M+Na]^+$.

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