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Carbohydrate Research 341 (2006) 1948–1953
Carbohydrate RESEARCH

Note

O-Isopropylidenation of carbohydrates catalyzed by vanadyl triflate

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Received 12 December 2005; received in revised form 27 March 2006; accepted 2 April 2006
Available online 15 May 2006

Abstract—Vanadyl triflate has been identified as a mild and efficient catalyst for the chemoselective *O*-isopropylidenation of functionalized carbohydrates with acetone and acetone equivalents. The current protocol is compatible with a diverse array of protecting groups and the products can be readily isolated by simple aqueous wash.

Keywords: *O*-Isopropylidenation; Vanadyl triflate; Saccharides; Acetonides; Chemoselectivity

The protection of 1,2- and 1,3-diols as *O*-isopropylidene derivatives (acetonides) is important in multi-step syntheses in organic, medicinal, and carbohydrate chemistry.[1] Although many approaches have been displayed for protecting diols and, particularly, polyols with contiguous hydroxyl groups, *O*-isopropylidenation constitutes one of the most important tactics during the synthesis of oligosaccharides.[2,3] The *O*-isopropylidenation of a diol is typically performed by using acetone under anhydrous conditions in the presence of an acid catalyst—generally *p*-toluenesulfonic acid (TsOH) at elevated temperature. In addition, this condensation reaction can be performed by using other acetonide-forming agents, including 2,2-dimethoxypropane (DMP) and 2-methoxypropene (MP) in anhydrous solvents such as *N*,*N*-dimethylformamide (DMF) or dimethylsulfoxide with acid catalysis. So far, a diverse array of catalysts have been employed in the isopropylidenation of saccharides preferably by using the latter approach, including pyridinium *p*-toluenesulfonate (PPTS),[4] TESOTf,[5] HBF_4,[6] di-*p*-nitrophenyl hydrogen phosphate,[7] Lewis acidic metal salts (e.g., $ZnCl_2$,[8] $AlCl_3$,[9] ceric ammonium nitrate (CAN),[10] $CuSO_4$,[11] $FeCl_3$,[12] $SnCl_2$,[13] and PdX_2[14]), iodine,[15] and heterogeneous media (e.g., ion exchange resins,[16] morillonite clay,[17] zeolites,[18] and hetero-polyacids (HPA)[19]). However, the aforementioned reagents are either moisture sensitive or sluggish in terms of reactivity at ambient temperature. Therefore, dried solvents, harsher reaction conditions, or cumbersome workup and purification are sometimes required during synthetic manipulation, Thus, an ideal neutral and water tolerant catalyst that meets the demands of offering greater safety, re-usability, functional substrate compatibility, and, most importantly, chemoselectivity remains to be explored.

The synthetic utility of vanadium-containing compounds has been widely explored and utilized as reagents or catalysts for redox-type C–C bond forming reactions[20,21] and oxidation processes when combined with suitable co-oxidants.[22] For the past five years, we have identified several water-tolerant vanadyl and other oxometallic species as recoverable, amphoteric catalysts for nucleophilic acyl substitutions (NAS) of anhydrides,[23a,b] methyl esters,[23c] and carboxylic acids[23d] with protic nucleophiles with high functional group

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doi:10.1016/j.carres.2006.04.001

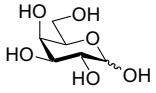
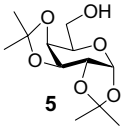
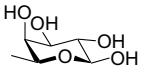
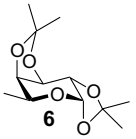
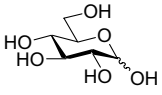
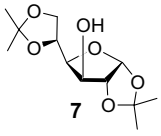
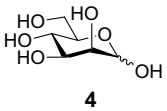
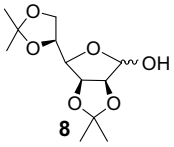
compatibility and chemoselectivity and the direct atom-efficient benzylidenation[24] of saccharides with equimolar aldehydes. In continuation of our related works in catalysis[25] and as part of an ongoing effort to explore vanadyl triflate as a neutral, water-tolerant, and recoverable reagent in new catalytic reactions, we report herein a handy and efficient method for chemoselective *O*-isopropylidenation of carbohydrates catalyzed by vanadyl triflate ($VO(OTf)_2 \cdot xH_2O$) at ambient temperature.

D-Galactose was first selected as a test mono-saccharide substrate in the *O*-isopropylidenation (Table 1, entry 1) by using acetone and common acetonide-forming agents (DMP and MP) in the presence of a catalytic amount of $VO(OTf)_2$. The test reaction procedure involved mixing 1 mmol of a given sugar with 5 mL of acetone or 10 equiv of DMP or MP (as a 0.1 M solution in CH_3CN) in the presence of 5 mol % of $VO(OTf)_2$ at ambient temperature for 2–10 h. Of these three acetonating reagents examined, 1,2:5,6-di-*O*-isopropylidene-galactopyranoside—**5** was the only isolable product with yields in the range of 85–93%. The same chemoselective acetonide-protection product—**6** was formed in high yields (92–95%) when L-fucose was used as the starting sugar (entry 2). Interestingly, the isopropylidenation of D-glucose and mannose led to only thermodynamically favored di-isopropylidene-protected furanosides **7** and **8**,[26] regardless of the acetonating reagents used (entries 3 and 4). As noted in entries 1 and 3 of Table 1, the straight acetone and $VO(OTf)_2$ recipe normally requires a longer reaction time to afford similarly good yields of products **5** and **7** presumably due to the poorer solubility of the starting materials **1** and **3** in acetone. Additionally, the current new catalytic protocol poses a very simple workup and purification procedure. Simple extraction of the water-quenched reaction mixture by ethyl acetate led to direct separation of the product from the water-soluble catalyst. And the catalyst can be readily recovered from the aqueous phase after concentration in vacuo.

To expand the substrate scope, a series of monosaccharides with sulfur-(S–Ar) and oxygen-(OMe and OPh) containing substituents at the anomeric position were further examined with the optimal catalytic protocol (Table 2, entries 1–6). In general, isopropylidenations by using DMP and MP led to better yields with shorter reaction time than those by using acetone. Notably, glucopyranosides **9**–**11** (entries 1–3) furnished the corresponding 4,6-*O*-isopropylidene derivatives **15**–**17** exclusively due to slower rate of *trans* ring-fused acetonide formation. Whereas only 3,4-*O*-isopropylidene derivatives **18** and **19** were obtained starting from galactopyranosides **12** and **13** (entries 4 and 5), respectively. On the other hand, using a slight excess (1.2 equiv) of MP in the case of benzylidene-protected **14** provided *trans*-2,3-isopropylidene glucopyranoside **20** in moderate yield (Table 2, 64%, entry 6). However, the *trans*-isopropylidene of **20** was unstable and easily decomposed.

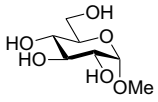
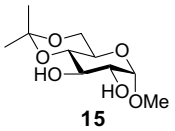
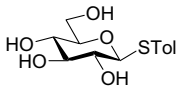
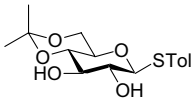
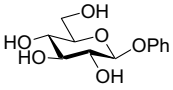
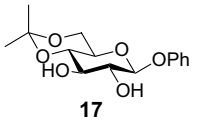
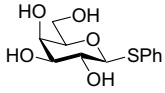
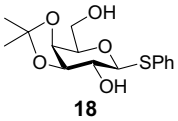
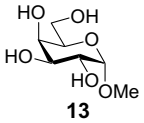
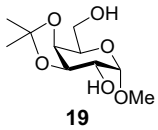
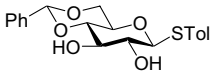
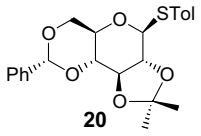
With the preliminary success on the use of vanadyl triflate in the chemoselective isopropylidenation of simple monosaccharides, the generality of the protocol was further extended to more complexed carbohydrates. As shown in Table 3, chemoselective isopropylidenations of functionalized monosaccharides (**21**, **24**, and **26**) and disaccharides (**22**, **23**, and **25**) also proceeded

Table 1. Protection of free sugar acetonide with $VO(OTf)_2$

Entry	Substrate	Product	Reagent[a]	Time (h)	Yield (%)
1	 **1**	 **5**	DMP	2	93
			MP	2	89
			Acetone	10	85
2	 **2**	 **6**	DMP	2	95
			MP	2	92
			Acetone	3	92
3	 **3**	 **7**	DMP	2	90
			MP	2	90
			Acetone	10	89
4	 **4**	 **8**	DMP	2	93
			MP	2	92
			Acetone	3	92

[a] DMP/MP 10 equiv or acetone 5 mL in CH_3CN.

Table 2. Protection of sugar acetonide with $VO(OTf)_2$

Entry	Substrate	Product	Reagent[a]	Time (h)	Yield (%)
1	 **9**	 **15**	DMP MP Acetone	1 4 11	92 90 85
2[d]	 **10**	 **16**	DMP MP Acetone	4 6 24	89 82 50[b]
3	 **11**	 **17**	DMP MP Acetone	4 6 24	88 86 50[b]
4	 **12**	 **18**	DMP MP Acetone	4 6 24	92 94 50[b]
5	 **13**	 **19**	DMP MP Acetone	1 6 11	91 87 80
6[c,d]	 **14**	 **20**	DMP MP	20 4	Trace 64

[a] DMP/MP 1.5 equiv or acetone 5 mL in CH_3CN.
[b] 50% starting material was recovered.
[c] DMP: 10 equiv and MP: 1.2 equiv in 0.5 M CH_3CN.
[d] Tol = *p*-methyl phenyl.

smoothly within 6 h and in good yields. Functional groups such as NHTroc (Troc: $C(O)O(CH)_2CCl_3$, entry 1), alkene (entry 3), NHTFA (TFA: $C(O)CF_3$, entries 4 and 5), azido, *tert*-butyl ester, and Fmoc (a carbamate, entry 5) remained intact under optimal $VO(OTf)_2$-catalyzed conditions. Notably, chemoselective formations of the thermodynamically favored 1,2-acetonides (**30** and **31**) over the corresponding 1,3- or 2,3-acetonides were observed at the terminal triol side chain of sialic acids (entries 4 and 5). Strikingly, in the case of azido-galactoside-**26** (entry 6), 74% of the expected 3,4-*O*-isopropylidene **32** was formed along with 4,6-*O*-isopropylidene protected side product (15%).

In summary, a new versatile and neutral protocol for the chemoselective *O*-isopropylidenation of functionalized carbohydrates has been demonstrated, which involves water-tolerant vanadyl triflate as the recoverable catalyst. The current system offers an efficient and alternative variant over existing methods in terms of operational simplicity and compatibility to diversed functional groups, auguring well for its potential applications in organic and carbohydrate synthesis.

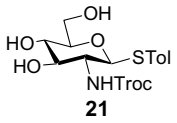
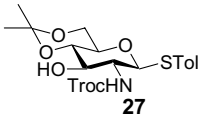
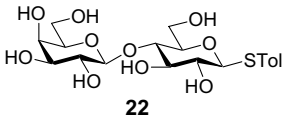
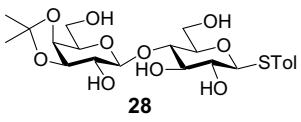
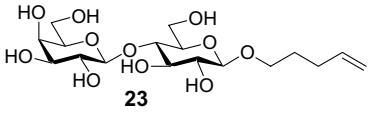
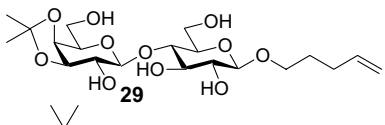
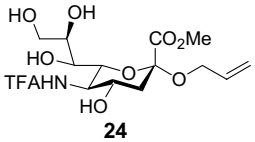
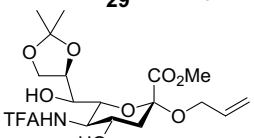
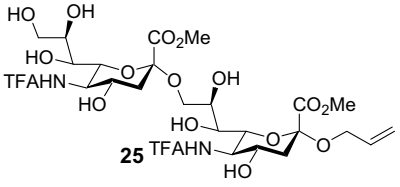
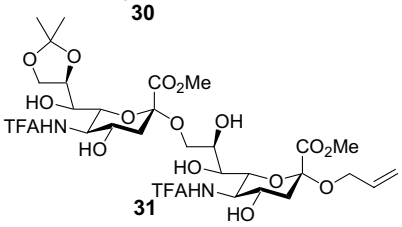
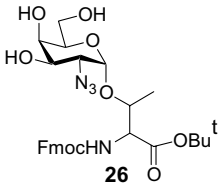
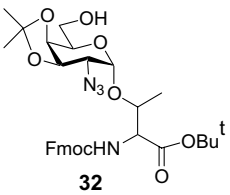
1. Experimental

1.1. General methods

^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 or 500 MHz. Assignment of ^1H NMR spectra was achieved using 2D methods (COSY). Chemical shifts were expressed in parts per million using residual $CHCl_3$ as reference. High-resolution mass spectra were obtained by means of a Micromass (Autospec) mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254). Silica gel 60 (E. Merck Co.) was employed for all flash chromatography. All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen unless indicated otherwise. All solvents were dried and distilled by standard techniques.

Compounds **5**,[27] **7**,[28] **8**,[29] **15**,[30] **18**,[31] **19**,[32] **20**,[24] **27**,[33] **29**,[34] and **32**[35] have previously been reported and the NMR spectral data are in good agreement with the literature data.

Table 3. Protection of sugar acetonide with DMP[a]/$VO(OTf)_2$

Entry	Substrate	Time (h)	Product	Yield (%)
1[b]	 **21**	5	 **27**	91
2[b]	 **22**	5	 **28**	89
3	 **23**	6	 **29**	88
4	 **24**	6	 **30**	92
5	 **25**	6	 **31**	89
6	 **26**	5	 **32**	74

[a] DMP: 10 equiv in 0.5 N CH_3CN.
[b] Tol = *p*-methyl phenyl.

1.2. General procedure for the acetonation

A 50 mL two-necked round bottomed flask, under dry nitrogen atmosphere, was charged with the vanadyl triflate, $VO(OTf)_2$ (0.05 mmol), followed by addition of anhydrous acetonitrile (10 mL). To the above solution of catalyst, DMP (10 mmol), MP (10 mmol), and acetone (5 mL) were slowly added at ambient temperature and the resulting solution was stirred for 10 min. The starting sugar (1.0 mmol) was then added to the above green solution and the resulting mixture was stirred at ambient temperature for a period of time. The reaction was monitored by TLC. After completion of the reaction, to the reaction mixture were sequentially added 0.5 mL triethylamine and cold saturated sodium bicarbonate solution. The reaction mixture was extracted with 30 mL ethyl acetate. The organic layer was washed with brine solution, dried over magnesium sulfate, and filtered. The organic solvent was removed in vacuo and the crude product was purified by flash chromatography.

1.2.1. 1,2:3,4-Di-*O*-isopropylidine-1-thio-L-fucopyranose (6). Syrup; ^1H NMR (500 MHz, $CDCl_3$): 5.52 (d, 1H, $J = 4.8$ Hz), 4.59 (dd, 1H, $J = 8.0$ Hz, $J = 2.4$ Hz), 4.29 (dd, 1H, $J = 5.2$ Hz, $J = 2.4$ Hz), 4.08 (dd, 1H, $J = 8.0$ Hz, $J = 2.0$ Hz), 3.94–3.89 (m, 1H), 1.53 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.26 (d, 3H, $J = 6.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 108.83, 108.12, 96.45, 73.44, 70.86, 70.27, 63.38, 25.94, 25.93, 24.80, 24.34, 15.82; TLC: $R_f = 0.25$ (EtOAc/hexane, 1/3); HRMS (FAB) calcd for $C_{12}H_{21}O_5$ $[M+H]^+$: 245.1382. Found: 245.1389.

1.2.2. 4-Methyl phenyl-3,4-*O*-isopropylidine-1-thio-β-D-glucopyranoside (16). Syrup; ^1H NMR (400 MHz, $CDCl_3$): 7.41 (d, 2H, $J = 8$ Hz), 7.14 (d, 2H, $J = 8$ Hz), 4.58 (d, 1H, $J = 9.6$ Hz), 3.94 (dd, 1H, $J = 10.4$ Hz, $J = 5.2$ Hz), 3.76 (t, 1H, $J = 10.8$ Hz), 3.68 (t, 1H, $J = 8.4$ Hz), 3.51 (t, 1H, $J = 9.6$ Hz), 3.41–3.27 (m, 2H), 3.10 (br, 1H, OH), 2.90 (br, 1H, OH), 2.61 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.42 (s, 3H,

CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): 138.68, 133.43, 129.84, 127.50, 99.80, 88.80, 74.91, 72.89, 72.66, 71.52, 61.97, 28.94, 21.12, 19.10; TLC: $R_f = 0.20$ (ethyl acetate/hexane, 1/2); EI MS (70 eV) calcd for $C_{16}H_{22}O_5S$: 326. Found: 326 (M^+, 24), 202 (28), 122 (100), 91 (89), 69 (34). Anal. Calcd for $C_{16}H_{22}O_5S$: C, 58.87; H, 6.79. Found: C, 58.49, H, 6.47.

1.2.3. Phenyl 4,6-*O*-isopropylidine-β-D-glucopyranoside (17). Syrup; ^1H NMR (400 MHz, $CDCl_3$): 7.32–7.27 (m, 2H), 7.08–7.01 (m, 3H), 4.96 (d, 1H, $J = 7.32$ Hz), 3.94 (dd, 1H, $J = 10.5$ Hz, $J = 5.4$ Hz), 3.79 (t,1H, $J = 10.4$ Hz), 3.75 (dd, 1H, $J = 10.8$ Hz, $J = 5.4$ Hz), 3.66 (dd, 1H, $J = 7.32$ Hz, $J = 6.1$ Hz), 3.49 (br, 1H, OH), 3.41–3.35 (m, 2H), 1.90 (br, 1H, OH), 1.51 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.85, 129.57, 123.13, 116.85, 101.15, 99.93, 74.36, 73.50, 72.97, 67.41, 61.97, 28.96, 19.04; TLC: $R_f = 0.16$ (ethyl acetate/hexane, 1/2). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.92; H, 6.58.

1.2.4. 4-Methyl phenyl *O*-(3,4-*O*-isopropylidine-β-D-galactopyranosyl)-(1→4)-1-thio-β-D-glucopyranoside (28). White solid; mp 189–191 °C; ^1H NMR (400 MHz, MeOD): 7.49 (d, 2H, $J = 8.4$ Hz), 7.16 (d, 2H, $J = 8.0$ Hz), 4.55 (d, 1H, $J_{1,2} = 10$ Hz, H-1), 4.39 (d, 1H, $J_{1,2} = 8.4$ Hz, H-1′), 4.21 (dd, 1H, $J = 5.6$ Hz, $J = 2.4$ Hz, H-4′), 4.07 (dd, 1H, $J = 7.8$ Hz, $J = 5.6$ Hz, H-3′), 3.97–3.75 (m, 5H, H-5′, H-6′a, H-6′b, H-6a, H-6b), 3.57–3.56 (m, 2H, H-3, H-4), 3.49–3.43 (m, 2H, H-5, H-2′), 3.27 (dd, 1H, $J = 10$ Hz, $J = 7.8$ Hz, H-2), 2.31 (s, 3H), 1.47 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, MeOD): 137.46, 132.35, 129.38, 129.08, 109.63, 102.58, 87.89, 79.38, 78.99, 78.96, 76.40, 73.89, 73.60, 72.98, 71.98, 60.96, 60.49, 26.94, 25.03, 19.65; TLC: $R_f = 0.25$ (MeOH/$CHCl_3$, 1/3); HRMS (FAB) calcd for $C_{22}H_{32}O_{10}S$ $[M+H]^+$: 489.1794. Found 489.1787.

1.2.5. Methyl-(2-allyl-3,5-dideoxy-3,5-dideoxy-5-trifluoroacetamido-8,9-*O*-methylethyliden-α-D-galacto-non-2-ulopyranosid)onate (30). Syrup; ^1H NMR (400 MHz, MeOD): 5.87 (dddd, 1H, $J = 17.2$ Hz, $J = 10.5$ Hz, $J = 5.4$ Hz, $J = 5.4$ Hz), 5.24 (dddd, 1H, $J = 17.2$ Hz, $J = 1.7$ Hz, $J = 1.7$ Hz, $J = 1.7$ Hz), 5.12 (dddd, 1H, $J = 10.5$ Hz, $J = 1.7$ Hz, $J = 1.4$ Hz, $J = 1.4$ Hz), 4.28 (dddd, 1H, $J = 12.8$ Hz, $J = 5.4$ Hz, $J = 1.7$ Hz, $J = 1.4$ Hz), 4.23 (ddd, 1H, $J = 6.3$ Hz, $J = 6.3$ Hz, $J = 6.3$ Hz, H-8), 4.10 (m, 1H), 4.08 (dd, 1H, $J = 8.4$ Hz, $J = 6.3$ Hz, H-9a), 4.00 (dd, 1H, $J = 8.4$ Hz, $J = 6.3$ Hz, H-9b), 3.97 (dd, 1H, $J = 10.2$ Hz, $J = 10.0$ Hz, H-5), 3.80 (s, 3H), 3.78 (dd, 1H, $J = 10.2$ Hz, $J = 1.1$ Hz, H-6), 3.71 (ddd, 1H, $J = 12.3$ Hz, $J = 10.0$ Hz, $J = 4.7$ Hz, H-4), 3.53 (dd, 1H, $J = 6.3$ Hz, $J = 1.1$ Hz, H-7), 2.67 (dd, 1H, $J = 12.3$ Hz, $J = 4.7$ Hz, H-3e), 1.75 (dd, 1H, $J = 12.3$ Hz, $J = 12.3$ Hz, H-3a), 1.36 (s, 3H, CH_3), 1.35 (s, 3H, CH_3); ^{13}C NMR (100 MHz, MeOD): 170.19, 159.50, 135.65, 118.05, 117.02, 110.11, 100.50, 77.66, 74.46, 70.52, 68.31, 67.46, 66.48, 54.09, 54.04, 41.75, 27.21, 25.92; TLC: $R_f = 0.63$ (EtOAc/hexane, 1/1+15% MeOH); HRMS (FAB) calcd for $C_{18}H_{26}F_3NO_9$ $[M+H]^+$: 458.1638. Found: 458.1640.

1.2.6. Methyl-(2-allyl-3,5-dideoxy-9-*O*-(methyl-3,5-dideoxy-5-trifluoroacetamido-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-5-trifluoroacetamido-D-glycero-α-D-galacto-non-2-ulopyranoside) onate (31). Syrup; ^1H NMR (400 MHz, MeOD): 5.86 (dddd, 1H, $J = 17.2$ Hz, $J = 10.4$ Hz, $J = 5.2$ Hz, $J = 5.2$ Hz), 5.24 (dddd, 1H, $J = 17.2$ Hz, $J = 1.6$ Hz, $J = 1.6$ Hz, $J = 1.6$ Hz), 5.11 (dddd, 1H, $J = 10.4$ Hz, $J = 1.6$ Hz, $J = 1.6$ Hz, $J = 1.6$ Hz), 4.29 (dddd, 1H, $J = 12.8$ Hz, $J = 5.2$ Hz, $J = 1.6$ Hz, $J = 1.6$ Hz), 4.22 (dd, 1H, $J = 13.2$ Hz, $J = 6.0$ Hz), 4.08 (dd, 1H, $J = 8.4$ Hz, $J = 6.0$ Hz), 4.02–3.94 (m, 5H), 3.92–3.83 (m, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.77–3.70 (m, 1H), 3.72–3.68 (m, 2H), 3.53 (dd, 1H, $J = 8.8$ Hz, $J = 1.2$ Hz), 3.47 (d, 1H, $J = 7.2$ Hz), 2.69 (dd, 1H, $J = 12.0$ Hz, $J = 4.4$ Hz), 2.68 (dd, 1H, $J = 12.0$ Hz, $J = 4.4$ Hz), 1.78 (t, 1H, $J = 12.0$ Hz), 1.75 (t, 1H, $J = 12.0$ Hz), 1.34 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, MeOD): 170.73, 170.10, 159.78, 159.77, 135.46, 118.97, 118.96, 117.10, 110.14, 100.19, 100.09, 73.73, 73.68, 72.62, 71.22, 70.17, 69.65, 68.54, 68.51, 68.37, 66.38, 64.78, 53.95, 53.91, 53.40, 53.38, 41.65, 41.57, 27.25, 25.96; TLC: $R_f = 0.38$ (EtOAc/hexane, 1/1+10% MeOH); HRMS (FAB) calcd for $C_{30}H_{43}N_2F_6O_{17}$ $[M+H]^+$: 817.2466. Found 817.2451.

Acknowledgment

This research was supported by the Academia Sinica, National Taiwan Normal University and National Science Council in Taiwan.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.04.001.

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