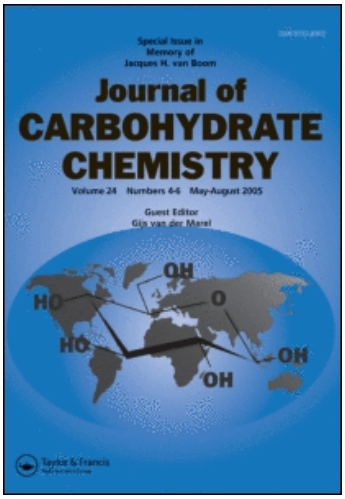


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# An Efficient Approach to the 2-Nonulosonic Acid Skeleton Through a Hetero-Diels-Alder Reaction

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# AN EFFICIENT APPROACH TO THE 2-NONULOSONIC ACID SKELETON THROUGH A HETERO-DIELS-ALDER REACTION

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## ABSTRACT

The hetero-Diels-Alder reaction of 1,3-diene-polyols with glyoxylates is an expeditious way to build up the skeleton of ulosonic acids. This paper reports an efficient means to improve the yields and the stereoselectivity associated with the hetero-cycloaddition of the activated 1,3-diene, 2*S*,3*S*-4*E*-1-*O*-Benzyl-2,3-*O*-isopropylidene-6-*tert*-butyldimethylsilyloxyhepta-4,6-diene-1,2,3-triol (**3**) with the dienophile ethyl glyoxylate. The effects of temperature, catalyst, and solvent on the outcome of the Diels-Alder reaction were investigated. The cycloaddition can proceed smoothly even at -78 °C and the complex bis [3-(heptafluorobutyryl)camphorato]oxovanadium (**8**) was found to be a very efficient catalyst for the cycloaddition reaction. The satisfactory selectivity (*endo/exo*: 97:3 and *re/si*: 82:18) observed in this catalytic reaction shows that there is a match effect between the substrate and catalyst.

## INTRODUCTION

Ulosonic acids have attracted much attention in recent years as the scope of their biological importance widens. Excellent reviews have covered this topic in depth.[1] In

view of their interesting biological properties and stereochemical complexity, ulosonic acids, especially sialic acid and its analogs, present challenging synthetic targets. In this respect, the strategy based on the hetero-Diels-Alder cycloaddition is likely to provide a straightforward access to these target molecules.

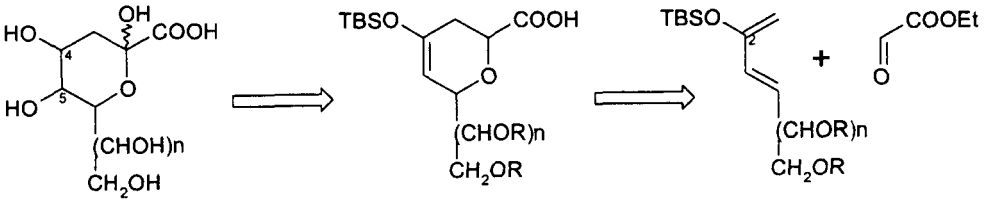
Using an inverse electron demand hetero-Diels-Alder reaction of chiral oxabutadiene, Tietze et al.[2] succeeded in the stereoselective synthesis of the dihydropyran moiety of a ulosonic acid. On the other hand, Lubineau et al.[3] reported the normal hetero- Diels-Alder reaction of 2*S*,3*E*-hexa-3,5-diene-1,2-diol and sodium glyoxylate for the synthesis of 2-deoxy KDO and KDO (3-deoxy-D-manno-2-octulosonic acid). An inseparable mixture of cycloadducts in the proportion of 42/32/19/7 was obtained in a 54% total yield in this water-promoted hetero-Diels-Alder reaction. Recently it was also reported that the cycloaddition of *E*-penta-2,4-dienol to sodium glyoxylate in water gave a 1.5/1 product mixture in 71% yield,[4] and the cycloaddition of 2*R*,3*S*,4*E*-hepta-4,6-diene-1,2,3-triol gave a mixture (*endo: exo* = 44:56, *re*:*si* = 41:59) in 67% yield.[5] In the absence of water, the hetero cycloaddition of 2*R*,3*S*,4*E*-hepta-4,6-diene-1,2,3-triol triacetate to methyl glyoxylate proceeded with low selectivity (*endo: exo* = 65:35, *re*:*si* = 40:60) in low yield (25%), even at elevated temperature (140 °C) for 4 h.

A significant improvement[5] in the yield of the nonaqueous hetero-Diels-Alder reaction was observed with diethyl ketomalonate instead of methyl glyoxylate as the dienophile, however, the diastereoselectivity was still unsatisfactory. These results prompted us to consider a new strategy for control of the reactivity and stereoselectivity of this type of hetero-Diels-Alder cycloaddition in connection with our efforts to synthesize ulosonic acid.

## RESULTS AND DISCUSSION

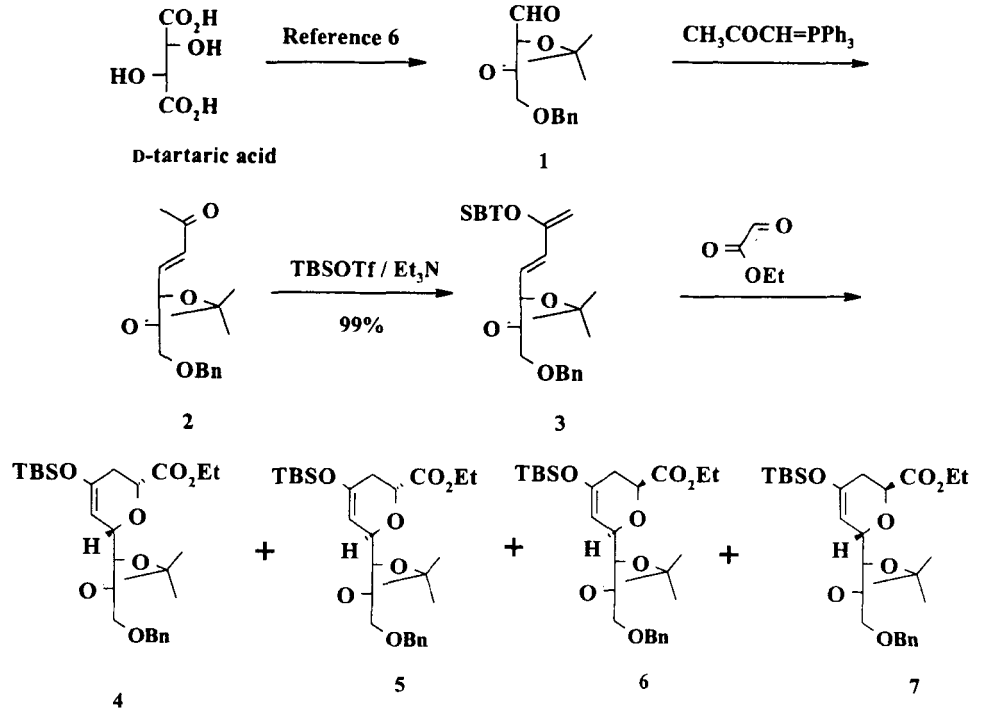
Our general approach to the synthesis of ulosonic acid is shown in **Scheme 1**, with the hetero-Diels-Alder reaction of 2-silyloxyalka-1,3-dienepolyol and ethyl glyoxylate as the key step. Introduction of a 2-silyloxy group for the activation of the diene was demonstrated efficient in the hetero-Diels-Alder reactions in an earlier synthesis of sialic acid described by Danishefsky.[6] It seems that ulosonic acid would be easily accessible through a similar approach, if the 2-silyloxy-1,3-diene carried the proper

substituent at position 4, and if the aforementioned issues of yield and stereoselectivity could be resolved.



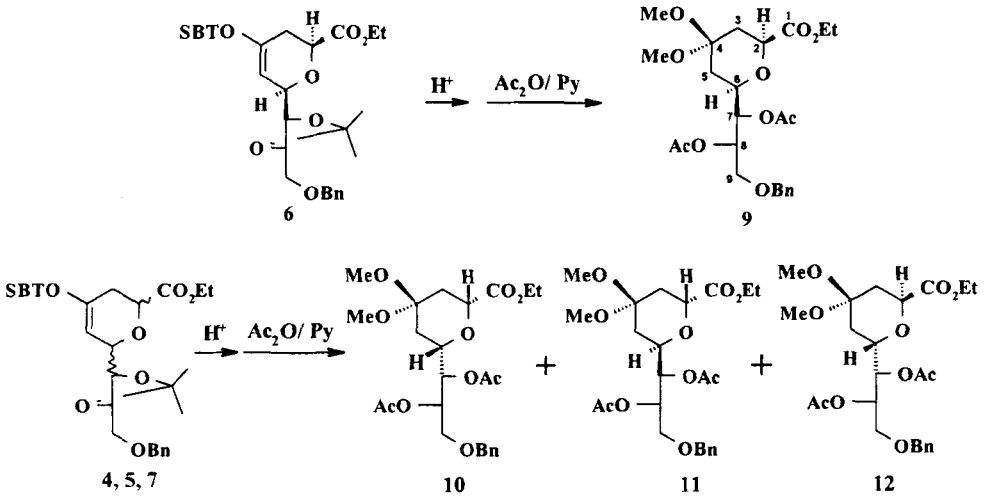
**Scheme 1**

To test this strategy, 2-silyoxy-1,3-diene **3** was synthesized as shown in **Scheme 2**. Aldehyde **1**, prepared[7] from D-tartaric acid in 5 steps, was treated with acetonylidene triphenylphosphorane in THF to give 5*S*,6*S*-3*E*-7-benzyloxy-5,6-*O*-isopropylidenehepta-3-en-2-one **2**, which was in turn transformed to **3** with TBSOTf.



**Scheme 2**

The uncatalyzed thermal reaction (60 °C, 2 h) of diene **3** with ethyl glyoxylate produced a mixture of the four possible Diels-Alder adducts, which could be separated on silica gel and assayed by HPLC analysis (reversed phase C-18 column, eluting with 75% acetonitrile and 25% water). Unfortunately, only the major component of the mixture could be separated by careful chromatography on silica gel. It was not possible to identify compound **6** directly by NMR techniques. In order to ascertain the structure of each of the four adducts produced in the reaction, compound **6** was treated with ion-exchange resin Amberlyst 15 ($H^+$) in methanol followed by acetylation to give **9** (**Scheme 3**). The mixture of compounds **4**, **5** and **7** was subjected to the same conditions to give **10** and **11** in high yields. The minor product **12**, however, could not be obtained in pure form.




**Scheme 3**

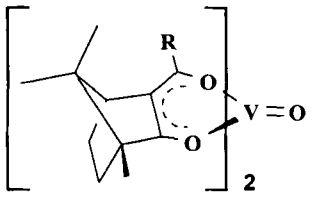
The assignment of the configuration of **6** is based on the following observations. The coupling constant for H-6/H-7 in **9** ($J_{6,7}$=3.6 Hz) is consistent with the general trends observed in this type of structure; namely, that KDN or sialic acid exhibit a small $J_{6,7}$ (0-3.8 Hz), whereas KDO shows a large $J_{6,7}$ (6-10 Hz).[8] The absolute configuration at C-6 was therefore assigned as *R*. The coupling constant in the $^1$H NMR spectrum of **9** ($J_{2,3}$ = 13.2 Hz, 2.4 Hz; $J_{6,7}$ = 3.6 Hz) suggests that this compound was formed from an *endo*, *re*

transition state. The absolute configuration of the minor *trans* diastereomers **4** and **5** could also be deduced from the corresponding J values similarly.[8]

The Diels-Alder reaction of **2** with ethyl glyoxylate was then attempted in the presence of Lewis acids in an effort to improve the yield and stereoselectivity. It appears from the results in **Table 1** that zinc chloride, aluminum chloride, diethyl aluminum chloride are better catalysts in terms of yield, but the selectivity was still poor. However, bis-(3-acylcamphorato)oxovanadium complex (-)-**8** as catalyst[9] showed a high degree of double stereodifferentiation. The result clearly indicated that (-)-**8** matched diene **3**, giving rise to the formation of **6** with high *endo*- and *re* facial selectivity.

**Table 1. Reaction of diene 2 with glyoxylate in the presence of Lewis acids**

| Entry | Catalyst | Temp(°C) | Yield(%) | **4 : 5 : 6 : 7** | *endo/exo* | *re/ si* |
|---|---|---|---|---|---|---|
| 1 | none | -78 | 40 | 25 : 8 : 55 : 12 | 80 : 20 | 63 : 37 |
| 2 | none | 0 | 60 | 21 : 9 : 50: 20 | 71 : 29 | 59 : 41 |
| 3 | 1equiv, $ZnCl_2$ | -78 | 70 | 35 : 10 : 50 : 5 | 85 : 15 | 60 : 40 |
| 4 | 1equiv, $AlCl_3$ | -78 | 86 | 40 : 11 : 37 : 12 | 77 : 23 | 48 : 52 |
| 5 | 1equiv,$Et_2AlCl$ | -78 | 77 | 30 : 12 : 42 : 16 | 72 : 28 | 54 : 46 |
| 6 | 5 mol%, **8** | -78 | 65 | 17 : 2 : 80 : 1 | 97 : 3 | 82 : 18 |




**2**

**R=$CF_2CF_2CF_3$**

**8**

It appears from the results in **Table 2** that reducing the temperature from 60 °C to -78 °C leads to a slight increase in the yield of **6** and a significant increase in *endo*-selection. At 60 °C, the *endo* : *exo* ratio is 71: 29, while at -78 °C, it is 97 : 3.

**Table 2. Reaction of diene 2 with glyoxylate and 8 at different temperatures**

| Entry | Temp.(°C) | Time (h) | Yield (%) | **4 : 5 : 6 : 7** | *endo/ exo* | *re / si* |
|---|---|---|---|---|---|---|
| 1 | 60 | 2 | 85 | 30 : 20 : 41: 9 | 71 : 29 | 61 : 39 |
| 2 | 30 | 2 | 70 | 25 : 12 : 45 : 18 | 70 : 30 | 57 : 43 |
| 3 | 0 | 2 | 66 | 21 : 9 : 50 : 20 | 71 : 29 | 59 : 41 |
| 4 | -30 | 4 | 67 | 23 : 7 : 62 : 8 | 85 : 15 | 69 : 31 |
| 5 | -78 | 8 | 65 | 17 : 2 : 80: 1 | 97 : 3 | 82 : 18 |

**Table 3. Reaction of diene 2 with glyoxylate in different solvents**

| Entry | Solvent | Temp. (°C) | Yield(%) | **4 : 5 : 6 : 7** | *endo/exo* | *re/si* |
|---|---|---|---|---|---|---|
| 1 | toluene | -78 | 40 | 25: 12 : 55 : 8 | 80 : 20 | 67 : 32 |
| 2 | $CH_2Cl_2$ | -78 | 35 | 23 : 12 : 52 : 13 | 75 : 25 | 64 : 36 |
| 3 | $Et_2O$ | -78 | 34 | 26 : 6 : 51 : 17 | 77 : 23 | 57 : 43 |
| 4 | THF | -78 | 32 | 24 : 10 : 42 : 24 | 66 : 34 | 52 : 48 |



Varying the reaction solvent at -78 °C did not influence the chemical yield, the *endo/exo* selectivity or the *re/si* selectivity significantly (**Table 3**).

## CONCLUSIONS

The effects of catalyst, temperature, and solvent on the outcome of the hetero Diels-Alder reaction of diene **3** with glyoxylate were investigated. The adducts were isolated and characterized by NMR spectroscopy. Bis-[3-(heptafluorobutyryl)camphorato]oxo-vanadium (**8**) was found to be an effective catalyst for the Diels-Alder reaction leading to adduct **6** in high yield and stereoselectivity. Compound **6** is the desired precursor for an approach to the synthesis of KDN and sialic acid and their analogs.

## EXPERIMENTAL

**General methods.** The $^1H$ and $^{13}C$ NMR spectra were recorded on a Brucker AMX-600 operating at 600 MHz for $^1H$ (some $^1H$ spectra were taken on a Bruker AM-

300) and 150 MHz for $^{13}C$, respectively. Chemical shifts are given in ppm downfield from internal tetramethylsilane; signal multiplicity is indicated as follows: s for singlet, d for doublet, t for triplet, q for quadruplet, m for multiplet and br for broadened. Mass spectra were taken on HP 5989A or Finnigan 4021 instrument. IR spectra were recorded on a Bruker FT instrument. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. Flash chromatography was performed on 10-40 μm silica gel.

**5*S*,6*S*-3*E*-7-Benzyloxy-5,6-*O*-isopropylidenehepta-3-en-2-one (2).** To a solution of aldehyde **1** (2.5 g, 10 mmol, freshly prepared from D-tartaric acid) in THF (150 mL) was added 3.82 g (12 mmol) of acetonylidene triphenylphosphorane. This solution was refluxed for 24 h. After cooling, the reaction mixture was passed through a short pad of silica gel (10% ethyl acetate-hexane as eluate) to remove the triphenylphosphine oxide. The filtrate was concentrated and subjected to flash chromatography with 10% ethyl acetate-petroleum as the eluate to give 2.78 g (9.6 mmol) of desired enone **2** as a thick, clear, slightly yellow oil. $[\alpha]_D^{20}$ -11.9° (*c* 1.39, $CHCl_3$); IR (neat): 2967, 2068, 1680, 1454, 1371, 1251, 1095, 730, 690 $cm^{-1}$; $^1H$ NMR (300 MHz, $CD_3COCD_3$): δ 7.34 (5H, m, PhH), 6.41 (1H, dd, J = 11.6, 1.1Hz), 6.04 (1H, dd, J = 11.6, 8.4Hz), 5.19 (1H, dt, J = 8.4, 1.1Hz), 4.56 (1H, s), 4.54 (1H, s), 3.92 (1H, ddd, J = 8.4, 6.2, 3.1Hz), 3.71 (1H, dd, 10.8, 3.1Hz), 3.62 (1H, dd, J = 10.8, 6.2Hz), 2.18 (3H, s), 1.36 (3H, s), 1.34 (3H, s); EIMS (*m/z*): 275 (M-15, 9.13), 188 (1.36), 169 (6.34), 141 (6.41), 12.6 (11.49), 111 (10.53), 97 (13.41), 91 (100.00), 82 (48.66), 65 (12.59), 55 (8.08), 43 (44.69).

**2*S*,3*S*-4*E*-1-*O*-Benzyl-2,3-*O*-isopropylidene-6-*tert*-butyldimethylsilyloxyhepta-4,6-diene-1,2,3-triol (3).** To an ice-cooled solution of **2** (2.90 g, 10 mmol) in ether (100 mL) was added dropwise triethylamine (2.17 mL, 15.7 mmol) and *tert*-butyldimethylsilyl triflate (3.43 g, 13 mmol). After stirring for 5 min, the cooling bath was removed, and the two-phase system was stirred at room temperature for 15 min and then at 20 °C for 1 h. This mixture was concentrated and passed through a short pad of silica gel (ether as the eluate) to give 3.98 g (10 mmol, 100% yield) of a thick, yellow oil. $[\alpha]_D^{20}$ -17.3° (*c* 1.02, $CHCl_3$); IR (neat): 2956, 2858, 1471, 1379, 1369, 1215, 1168, 1134, 1022, 879, 627 $cm^{-1}$; $^1H$ NMR (300 MHz, $CCl_4$): δ 7.44(5H, m), 6.28(1H, d, J =

15.0Hz), 6.05 (1H, dd, J = 15.0, 6.0Hz), 4.72 (2H, s), 4.50 (1H, m), 4.43 (2H, s), 3.93 (2H, m), 3.72 (2H, m), 1.55 (6H, s), 1.17 (9H, s), 0.36 (6H, s); EIMS(*m/z*): 405 ($M^+$+1, 2.00), 389 (1.50), 313 (6.92), 283 (2.61), 255 (5.63), 225 (10.07), 211 (14.14), 183 (8.58), 127 (9.49), 91 (100.00), 73 (34.24), 43 (9.67). HRMS Calcd for $C_{19}H_{36}O_7Si$: 404.2230, Found: 404.2194.

**Ethyl 2,3,5-trideoxy-4-*O*-*tert*-butyldimethylsilyl-7,8-*O*-isopropylidene-9-*O*-benzyl-L-*ribo*-non-4-en-2-ulosonate (6).**

**Thermal Diels-Alder Reactions**

A mixture of diene **3** (398 mg, 1.0 mmol) and ethyl glyoxylate (112 mg, 1.1 mmol) was heated at 60 °C in an autoclave for 4 h. The reaction mixture was cooled and passed through a silica gel column, eluting with 5% ethyl acetate-petroleum to give **6** and the mixture of **4**, **5**, **7** in 80% yield. Compound **6:** $[\alpha]_D^{20}$ +12.6° (*c* 0.74, $CHCl_3$); IR(neat): 2730, 2360, 1731, 1365, 1255, 1083, 701, 669 $cm^{-1}$; $^1H$ NMR (600 MHz, $CD_3COCD_3$): δ 7.36-7.31 (5H, m), 4.99 (1H, d, J = 3.3 Hz, $H_5$), 4.60 (1H, d, J =12.1 Hz, $OCH_2Ph$), 4.56 (1H, d, J = 12.1 Hz, $OCH_2Ph$), 4.29 (1H, d, J = 6.6 Hz, $H_6$), 4.28 (1H, dd, J = 10.9, 3.8 Hz, $H_2$), 4.22 (1H, ddd, J = 7.8, 5.9, 2.5 Hz, $H_8$), 4.16 (2H, q, J = 7.2 Hz, $OCH_2CH_3$), 3.81 (1H, dd, J = 10.8, 2,5 Hz, $H_9$), 3.73 (1H, dd, J = 7.8, 6.6 Hz, $H_7$), 3.63 (1H, dd, J = 10.8, 5.9 Hz, $H_9$), 2.21 (1H, ddd, J = 16.5, 10.9, 3.3 Hz, $H_3$), 2.10 (1H, dd, J = 16.5, 3.8 Hz, $H_3$), 1.38 (3H, s, $CH_3$), 1.35 (3H, s, $CH_3$), 1.22 (3H, t, J = 7.2 Hz), 0.92 (9H, s), 0.18 (3H, s), 0.16 (3H, s); $^{13}C$ NMR (150 MHz, $CD_3COCD_3$): δ 170.71, 154.62, 149.36, 139.68, 128.97, 128.18, 128.08, 110.14, 103.76, 79.98, 79.77, 79.44, 76.39, 73.24, 73.41, 71.99, 61.43, 33.37, 27.53, 27.21, 25.87, 18.44, 14.36, -4.24, -4.50; EIMS (*m/z*): 505 (M-1, 0.70), 449 (0.54), 431 (2.92), 323 (3.02), 285 (100.00), 211 (4.17), 155 (2.21), 91 (18.54), 73 (8.31), 43 (1.09). HRMS Calcd for $C_{27}H_{42}O_7Si$: 506.2700, Found: 506.2697.

**Catalyzed Diels-Alder Reactions**

A solution of the catalyst (0.1 mmol) was added to ethyl glyoxylate (1.1 mmol, 112 mg) in toluene (2 mL). The mixture was stirred at a particular temperature (see Table 2) for 10 min. Then diene **3** (1.0 mmol, 398 mg) was added and the resulting solution was stirred until TLC showed the completion of the reaction. Water (2 drops) was added to

destroy the Lewis acid complex and the mixture was stirred for 10 min. The solution was filtered with suction through Celite and the filter cake was washed several times with dichloromethane. The filtrate was dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography.

**Solvent Effects**

A solution of diene **3** (1.0 mmol, 398 mg) in a particular solvent (2 mL) (see Table 3) was added to a stirred solution of ethyl glyoxylate (1.1 mmol, 112 mg) in the same solvent at -78 °C. The reaction mixture was stirred for 6 h until the completion of reaction and then allowed to warm to room temperature. The reaction mixture was then worked up as described above.



**Ethyl 2,3,5-trideoxy-4,4-dimethoxy-7,8-*O*-acetyl-9-*O*-benzyl-L-*ribo*-non-2-ulsonate (9).** Compound **4** (506 mg, 1.0 mmol) and Amberlyst 15 (100 mg) in methanol (10 mL) was heated at 60 °C for 3 h. The mixture was then cooled, diluted with $CH_2Cl_2$ and washed with water (2×2 mL). After evaporation of the solvent, acetylation of the residue with a mixture of acetic anhydride and pyridine (1:1.1, 4 mL) produced compound **9** (458 mg, 0.95 mmol) in 95% yield. $[\alpha]_D^{20}$: +10.5° (*c* 1.0, $CHCl_3$); IR (neat): 2954, 2873, 1747, 1498, 1455, 1439, 1373, 1223, 1158, 1098, 742, 700, 604 $cm^{-1}$; $^1H$ NMR (300 MHz, $CD_3COCD_3$): δ 7.32 (5H, m), 5.43 (1H, m, H-8), 5.29 (1H, dd, J = 6.9, 3.6 Hz, H-7), 4.53 (1H, d, J = 12.0 Hz, $OCH_2Ph$), 4.59 (1H, d, J = 12.0 Hz, $OCH_2Ph$), 4.17 (2H, q, J = 7.1 Hz, $CO_2C\mathbf{H_2}CH_3$), 3.97 (1H, dd, J = 11.8, 2.4 Hz, $H_2$), 3.82 (1H, ddd, J = 12.2, 3.6, 2.0 Hz, $H_6$), 3.69 (2H, m, $H_9$), 3.12(6H, s, $OCH_3$), 2.25 (1H, dd, J = 13.4, 2.0 Hz, $H_5$), 2.04 (3H, s, $COCH_3$), 2.02 (3H, s, $COCH_3$), 1.9 2 (1H, dd, J = 13.2, 2.4 Hz, $H_3$), 1.45 (1H, dd, J = 13.4, 12.2 Hz, $H_5$), 1.37 (1H, dd, J = 13.2, 11.8 Hz, $H_3$), 1.26 (3H, t, J = 7.1 Hz); EIMS (*m/z*): 423 (4.00), 199 (2.79), 188 (2.39), 176 (5.68), 157 (4.69), 145 (4.74), 127 (4.22), 117 (10.01), 113 (6.39), 91 (100.00), 43 (66.22).

Anal. Calcd for $C_{24}H_{34}O_{10}$: C, 59.72; H, 7.11, Found: C, 59.77; H, 6.79.

The mixture of compound **4**, **5** and **7** was subjected to the same conditions as above, **10** and **11** were obtained in 85% yield, while the pure minor product **12** could not be obtained due to contamination by impurities. Compound **10**: $[\alpha]_D^{20}$: -25.4° (*c* 1.11, $CHCl_3$); IR (neat): 2954, 1747, 1455, 1373, 1223, 1164, 1049, 700, 603 $cm^{-1}$; $^1H$ NMR

(300 MHz, $CD_3COCD_3$): δ 7.39 (m, 5H), 5.49 (1H, ddd, J = 5.9, 3.6, 2.2 Hz, $H_8$), 5.36 (1H, dd, J = 7.0, 3.6 Hz, $H_7$), 4.56 (2H, s, $OCH_2Ph$), 4.43 (1H, dd, J = 12.1, 3.5 Hz, $H_2$), 4.08 (2H, q, J = 7.1 Hz, $OC\mathbf{H_2}CH_3$), 4.05 (1H, m, $H_6$), 3.81 (6H, s, $OCH_3$), 3.63 (2H, m, $H_9$), 2.65 (1H, dd, J = 15.1, 12.1 Hz, $H_3$), 2.53 (1H, dd, J = 15.0, 3.5 Hz, $H_5$), 2.51 (1H, dd, J = 15.1, 3.5 Hz, $H_3$), 2.37 (1H, dd, J = 15.0, 2.9 Hz, $H_5$), 2.01 (3H, s, $COCH_3$), 2.00 (3H, s, $OCH_3$), 1.23 (3H, t, J = 7.1 Hz, $OCH_2C\mathbf{H_3}$); EIMS (*m/z*): 394 (10.00), 361 (10.20), 287 (2.54), 255 (3.61), 199 (5.88), 171 (22.41), 159 (10.39), 143 (11.34), 117 (15.35), 111 (10.21), 91 (100.00), 71 (9.33), 57 (12.60), 43 (65.39).

Anal. Calcd for $C_{24}H_{34}O_{10}$: C, 59.72; H, 7.11, Found: C, 59.75; H, 6.76.

Compound **11**: $[\alpha]_D^{20}$: +36.1° (*c* 0.2, $CHCl_3$); IR(neat): 2953, 2920, 1749, 1455, 1439, 1373, 1220, 1172, 1102, 1028, 740, 700 $cm^{-1}$; $^1H$ NMR (300MHz, $CD_3COCD_3$): δ 7.38 ( 5H, m), 5.42 (1H, m, $H_8$), 5.32 (1H, dd, J = 7.7, 2.5 Hz, $H_2$), 4.60 (2H, s, $OCH_2Ph$), 4.54 (1H, dd, J = 6.9, 2.5 Hz, $H_7$), 4.42 (1H, dd, J = 12.0, 2.5, 2.0 Hz, $H_6$), 4.29 (1H, dd, J = 11.2, 4.5 Hz, $H_9$), 4.20 (2H, q, J = 7.1 Hz, $OC\mathbf{H_2}CH_3$), 3.84 (1H, dd, J = 11.2, 2.3 Hz, $H_9$), 3.18 (3H, s, $OCH_3$), 3.07 (3H, s, $OCH_3$), 2.53 (1H, 13.7, 2.0 Hz, $H_5$), 1.83 (1H, dd, J = 13.7, 2.5 Hz, $H_3$), 2.06 ( 3H, s, $COCH_3$), 2.03 (3H, s, $COCH_3$), 1.89 (1H, dd, J = 13.7, 7.7 Hz, $H_3$), 1.40 (1H, dd, J = 13.7, 12.0 Hz, $H_5$), 1.28 (3H, t, J = 7.1 Hz, $OCH_2C\mathbf{H_3}$); EIMS (*m/z*): 361 (1.71), 319 (4.94), 259 (4.60), 216 (12.91), 201 (11.31), 171 (3.39), 160 (2.86), 146 (12.77), 114 (16.57), 105 (8.58), 91 (100.00), 55 (10.24), 43 (68.96).

Anal. Calcd for $C_{24}H_{34}O_{10}$: C, 59.72; H, 7.11, Found: C, 59.73; H, 6.77.



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