Preparation of Sugar-Derived β-Keto Phosphonates and Their Use in the Synthesis of Higher Sugars

K. Narkunan and M. Nagarajan*

School of Chemistry, University of Hyderabad, Hyderabad-500 134, India

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Sugar-derived β-keto phosphonates **5**, **6**, **7**, and **8** were synthesised by the acylation of lithium dimethyl methylphosphonate with the corresponding methyl glycuronates **1**, **2**, and **3** and glyconate **4** in THF at −78 °C, respectively. Wadsworth–Emmons reaction of **5**, **6**, **7**, and **8** with various sugar-derived aldehydes proceeded in good yield to produce higher sugar enones. Similarly, C-2 symmetric bis phosphonate **28** derived from L-tartrate **27** was prepared and condensed with various sugar-derived aldehydes to provide C-2 symmetric bis enones in moderate yields. Treatment of the glucose-derived β-keto phosphonate **5** with various aldehydes and excess Cs_2CO_3 resulted in complete cis elimination of the C-4 benzyl group along with the Wadsworth–Emmons reaction, leading to cross-conjugated dienones.

Introduction

Synthesis of higher sugars containing more than six carbon atoms has been a challenge to the organic chemist since the time of Fischer.[1] In recent years,[2] interest in the synthesis of higher sugars has intensified as these complex chiral structures are components of lincomycins,[3] ezoaminuroic acid,[4] 3-deoxy-D-*manno*-2-octulosonic acid (KDO),[5] and *N*-acetylneuraminic acid (Neu5Ac).[6] Higher sugars also serve as highly functionalized synthons for the preparation of complex natural products exemplified by the macrolide antibiotics erythromycin[7] and streptovaricin.[8]

One of the earliest methods for the synthesis of higher sugars is the Killiani–Fischer reaction, which is used to extend the aldose chain by one carbon from the reducing end.[9] Subsequently, many methodologies were developed which could homologate the sugar unit by two or more carbon atoms at a time, using the Wittig reaction.[10–15] However, the Wadsworth–Emmons reaction has not been used so far in the synthesis of higher sugars and this prompted us to explore its synthetic viability for this purpose. A preliminary communication has already appeared.[16]

Results and Discussion

A thorough search of the literature revealed that only very few β-keto phosphonates derived from sugars are known.[17,18] The required dimethyl ((methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranuronyl)methyl)phosphonate (**5**) was obtained in quantitative yield by the acylation of lithium dimethyl methylphosphonate with the readily available methyl (methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranosid)uronate (**1**)[19] in THF at −78 °C (Scheme 1). Initial attempts at the reaction of **5** with *p*-anisaldehyde employing different bases such as DBU/LiCl,[20] K_2CO_3,[21] and NaH[22] resulted in the required higher sugar enone, as evidenced from the ^1H NMR spectra of the crude product mixtures. However, due to the difficulty in separating the pure enone from the rest of the mixture, we looked for an alternative method for this synthesis. A recent report concerning the use of Cs_2CO_3 in 2-propanol[17] as a satisfactory base solvent combination for the Wadsworth–Emmons reaction prompted

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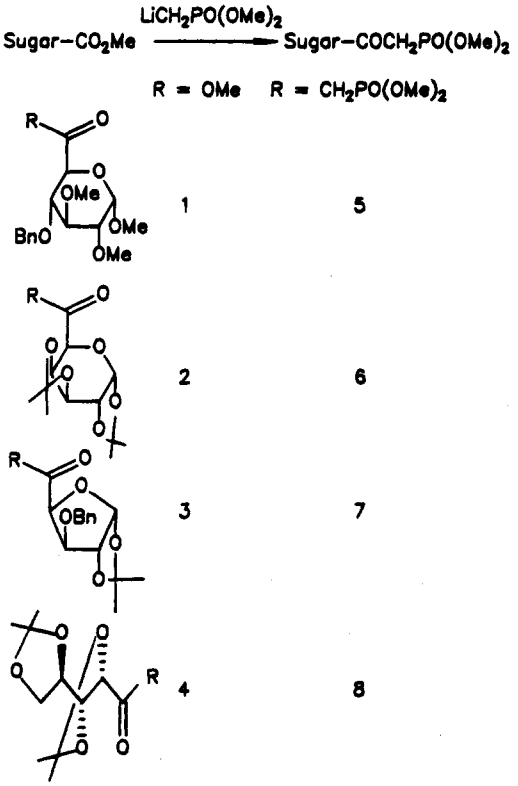
Scheme 1

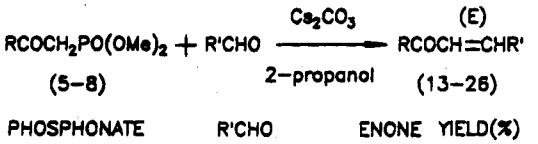


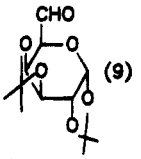
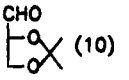
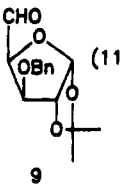
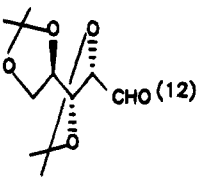
us to explore its application to our system. Gratifyingly, the reaction of **5** with *p*-anisaldehyde proceeded cleanly, giving the desired enone **13** in 88% yield. The trans stereochemistry of the enone double bond in **13** was readily apparent from its ^{1}H NMR spectrum (olefinic coupling of about 16 Hz). Subsequently, the β-keto phosphonate **5** was treated with various aldehydes as shown in Scheme 2, giving the corresponding condensation products in high yields. Encouraged by this, β-keto phosphonates **6**, **7**, and **8** were synthesized from their corresponding glycuronates **2**[23] and **3**, and glyconate **4**[24] in a similar way in quantitative yields (Scheme I). The phosphonates **6**, **7**, and **8** were reacted with various aldehydes derived from aldoses at C1, C5, and C6 to yield the corresponding condensed products in high yields (Scheme 2). In all cases, this reaction provides single, geometrically pure, (*E*) isomer. Of these enones, **19** and **20** have been previously reported in the literature.[15,25] The utility of such enones in the synthesis of higher sugars has been discussed by Jarosz.[15]

Similarly, to facilitate the extension of the carbon chain from both the ends, C-2 symmetric bis phosphonate **28** was prepared from diethyl 2,3-*O*-isopropylidene-L-tartrate (**27**)[26] and was treated with various sugar aldehydes to provide the corresponding C-2 symmetric bis enones in moderate yields as shown in Scheme 3. ^{1}H and ^{13}C NMR spectra immediately indicate the presence of C-2 symmetry in **29**, **30** and **31**.

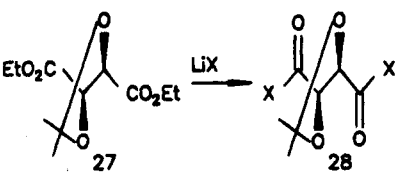
Our earlier observations on the reaction of the phosphonate **5** with various aldehydes showed the formation of trace quantities of eliminated products along with the required condensed products. On careful analysis, we found that if Cs_2CO_3 present in a 2 equiv excess, then

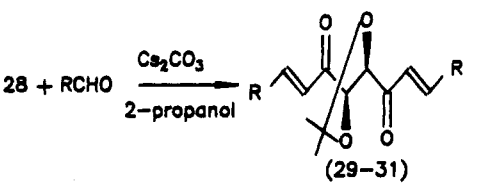
Scheme 2



PHOSPHONATE	R'CHO	ENONE	YIELD(%)
5	p–Anisaldehyde	13	88
5	Benzaldehyde	14	85
5	Isobutyraldehyde	15	84
5	 (9)	16	84
6	p–Anisaldehyde	17	94
6	 (10)	18	70
6	9	19	90
6	 (11)	20	91
7	9	21	75
7	11	22	79
8	9	23	70
8	11	24	91
8	 (12)	25	65
8	10	26	76

Scheme 3





RCHO	DIENONE	YIELD(%)
9	29	54
11	30	44
12	31	54

condensation of **5** with aldehydes leads to complete elimination of the C-4 benzyl group along with the Wadsworth–Emmons reaction (Scheme 4). It is interesting to note that under identical conditions, neither glucophosphonate **5** nor glucuronate **1** gave rise to such elimination. But when the enone **13** was treated with 3 equiv of Cs_2CO_3 in 2-propanol, it led to elimination of the C-4 benzyl group, giving the cross-conjugated dienone **32**.

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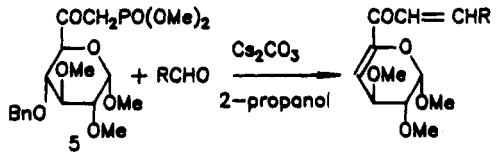
Scheme 4



RCHO	DIENONE	YIELD(%)
p-Anisaldehyde	32	80
Benzaldehyde	33	90
Isobutyraldehyde	34	86

Such cross-conjugated dienones can be subjected to Nazarov-type cyclizations.[27]

In conclusion, the method adopted here provides a simple and convenient route to the synthesis of higher sugar enones of any combination. Problems due to cis and trans isomeric mixtures do not arise. It can be used to extend the carbon chain from either end or both and difficulties due to epimerization do not arise.

Experimental Section

Melting points were determined using a Büchi 510 capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 1310 spectrophotometer. ^{1}H NMR spectra were recorded at 100, 200, and 400 MHz using JEOL FX-100, Bruker ACF 200, and Bruker ACP 400 instruments. ^{13}C NMR spectra were recorded at 25 and 50 MHz using the above first two instruments. ^{31}P NMR spectra were recorded at 40.5 and 81 MHz using JEOL FX-100 and Bruker ACF 200 instruments. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (0.0 ppm) as an internal standard (^{1}H and ^{13}C). Aqueous H_3PO_4 (85%) (0.0 ppm) was used as an external reference in ^{31}P NMR. Data are reported as follows: chemical shifts (multiplicity, coupling constants, integrated intensity). Optical rotations were measured using an Autopol II-automatic polarimeter at 25 °C in a 1 dm cell of 1.2 mL capacity using chloroform as solvent. Elemental analyses were performed using a Perkin-Elmer 240C CHN analyzer.

Materials. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. THF was purified by distillation from sodium–benzophenone and 2-propanol was distilled from anhydrous K_2CO_3 prior to use. All organic extracts were dried over anhydrous $MgSO_4$. Acme silica gel 100–200 mesh was used for column chromatography.

Methyl (3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-xylofuranosid)uronate (3). To a stirred mixture of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**11**)[28] (557 mg, 2 mmol) and $NaHCO_3$ (3.36 g, 40 mmol) in a 9:1 methanol–water mixture (4 mL) was added a solution of Br_2 (1.6 g, 10 mmol) in a 9:1 methanol–water mixture (5 mL) dropwise.[29] After 5 h, excess Br_2 was quenched with powdered $Na_2S_2O_3$ and the contents were diluted with 10 mL of water and extracted with 30 mL of ether. The ether extract was dried and evaporated and the residue purified by column chromatography on silica gel using 10% ethyl acetate in hexane to afford 524 mg of oily **3** (85%): IR (neat) 1750, 1730 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35–7.20 (m, 5H), 6.09 (d, J = 3.58 Hz, 1H), 4.83 (d, J = 3.64 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 3.61 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.26 (d, J = 3.68 Hz, 1H), 3.75 (s, 3H), 1.47 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (25 MHz) 168.3, 137.0, 128.4 (2C), 128.0, 127.7 (2C), 112.4, 105.7, 82.7, 81.7, 79.5, 72.2, 52.0, 26.8, 26.2; [α]$^{25}_D$ −45° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.21; H, 6.58.

Methyl 2,3:4,5-di-*O*-isopropylidene-D-arabinonate (4)[24] was prepared from 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**12**)[30] in 75% yield using the same procedure as described for **3**.

Preparation of β-keto Phosphonates 5, 6, 7, 8, and 28. To a stirred solution of dimethyl methylphosphonate (744 mg, 6 mmol) in 10 mL of THF at −78 °C was added *n*-butyllithium (5.5 mmol) dropwise. After 15 min, a solution of the glycuronate or glyconate (**1**,[19] **2**,[23] **3**, **4**,[24] or **27**;[26] 5 mmol) in 5 mL of THF was added dropwise. After warming to room temperature over 2 h, the reaction mixture was quenched with 12 mL of 5% aqueous citric acid and extracted with 50 mL of CH_2Cl_2. The CH_2Cl_2 extracted was dried and evaporated to give the corresponding phosphonate (**5**, **6**, **7**, **8**, or **28**) in quantitative yields. Phosphonates **5**, **6**, **7**, **8**, and **28** can be used as such for the Wadsworth–Emmons reaction without any purification.

Dimethyl ((methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranuronyl)methyl)phosphonate (5) was prepared from methyl (methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranosid)uronate (**1**).[19] **5**: syrup; IR (neat) 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 5H), 4.88 (d, J = 3.53 Hz, 1H), 4.82 (d, J = 10.7 Hz, 1H), 4.65 (d, J = 10.7 Hz, 1H), 4.33 (d, J = 9.82 Hz, 1H), 3.76 (d, J = 11.3 Hz, 3H), 3.74 (d, J = 11.13 Hz, 3H), 3.67 (d, J = 9.02 Hz, 1H), 3.64 (s, 3H), 3.57 (d, J = 9.75 Hz, 1H), 3.53 (s, 3H), 3.48 (s, 3H), 3.30 (dd, J = 14, 22.54 Hz, 1H), 3.24 (dd, J = 3.42, 9.52 Hz, 1H), 3.20 (dd, J = 14, 22.42 Hz, 1H); ^{13}C NMR (25 MHz) 199.9, 139.9, 129.6, 129.4, 129.1, 99.2, 84.7, 82.7, 79.8, 79.7, 74.9, 62.2, 60.2, 56.8, 54.0 (m), 40.5 (d, J = 129 Hz); ^{31}P NMR (40.5 Hz) 21.8; [α]$^{25}_D$ +98.5° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{19}H_{29}O_9P$: C, 52.77; H, 6.76. Found: C, 52.72; H, 6.78.

Dimethyl ((1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranuronyl)methyl)phosphonate (6) was prepared from methyl (1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosid)uronate (**2**).[23] **6**: syrup; IR (neat) 1720 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.64 (d, J = 4.9 Hz, 1H), 4.64 (dd, J = 2.3, 7.8 Hz, 1H), 4.59 (dd, J = 1.9, 7.8 Hz, 1H), 4.36 (dd, J = 4.9, 2.3 Hz, 1H), 4.32 (d, J = 1.9 Hz, 1H), 3.82 (d, J = 11.22 Hz, 3H), 3.79 (d, J = 11.24 Hz, 3H), 3.64 (dd, J = 15.14, 20.45 Hz, 1H), 3.07 (dd, J = 15.15, 21.7 Hz, 1H), 1.51 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (25 MHz) 200.1 (d, J = 5.9 Hz), 109.4, 108.8, 96.0, 73.2 (d, J = 2.95 Hz), 71.8, 70.2, 70.0, 52.0 (m), 37.1 (d, J = 134 Hz), 25.4 (2C), 24.4, 23.7; ^{31}P NMR (40.5 MHz) 22.68; [α]$^{25}_D$ −126.3° (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{15}H_{25}O_9P$: C, 47.37; H, 6.63. Found: C, 47.25; H, 6.60.

Dimethyl ((3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranuronyl)methyl)phosphonate (7) was prepared from methyl (3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranosid)uronate (**3**). **7**: syrup; IR (neat) 1720 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40–7.20 (m, 5H), 6.08 (d, J = 3.57 Hz, 1H), 4.73 (d, J = 3.7 Hz, 1H), 4.59 (d, J = 3.59 Hz, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.47 (d, J = 11.7 Hz, 1H), 4.29 (d, J = 3.72 Hz, 1H), 3.78 (d, J = 11.2 Hz, 3H), 3.75 (d, J = 11.24 Hz, 3H), 3.50 (dd, J = 15.3, 20.38 Hz, 1H), 3.02 (dd, J = 15.4, 21.3 Hz, 1H), 1.47 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (25 MHz) 200.3, 136.7, 128.7 (2C), 128.3, 127.9 (2C), 112.7, 106.1, 85.3 (d, J = 3 Hz), 83.7, 81.8, 72.5, 53.0 (m), 38.1 (d, J = 135.3 Hz), 26.9, 26.3; ^{31}P NMR (81 MHz) 21.95; [α]$^{25}_D$ −72.78° (*c* 3.1, $CHCl_3$). Anal. Calcd for $C_{18}H_{25}O_8P$: C, 53.99; H, 6.29. Found: C, 53.88; H, 6.25.

Dimethyl ((2,3:4,5-di-*O*-isopropylidene-D-arabinonyl)methyl)phosphonate (8) was prepared from methyl 2,3:4,5-di-*O*-isopropylidene-D-arabinonate (**4**).[24] **8**: solid, mp 66–68 °C (hexane–chloroform); IR (KBr) 1740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.54 (d, J = 5.4 Hz, 1H), 4.23–4.15 (m, 2H), 4.12 (dd, J = 8.5, 6.18 Hz, 1H), 3.95 (dd, J = 4.56, 8.5 Hz, 1H), 3.81 (d, J = 11.3 Hz, 3H), 3.80 (d, J = 11.22 Hz, 3H), 3.46 (dd, J = 14.3, 22.43 Hz, 1H), 3.35 (dd, J = 14.23, 22.36 Hz, 1H), 1.46 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (25 MHz) 200.8 (d, J = 6 Hz), 111.7, 110.0, 83.1 (d,

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J = 3 Hz), 78.2, 76.6, 66.8, 53.1 (m), 37.4 (d, J = 130.75 Hz), 27.1, 26.5, 26.2, 25.2; ^{31}P NMR (81 MHz) 21.27; $[\alpha]^{25}_D$ −2.76° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{14}H_{25}O_8P$: C, 47.72; H, 7.15. Found: C, 47.65; H, 7.14.

Tetramethyl (2,3-*O*-isopropylidene-L-tartaroyl)bis(methylphosphonate) (28) was prepared from diethyl 2,3-*O*-isopropylidene-L-tartrate (**27**).[26] **28**: syrup; IR (neat) 1720 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 4.76 (s, 2H), 3.78 (d, J = 11 Hz, 6H), 3.76 (d, J = 11 Hz, 6H), 3.60−3.00 (m, 4H), 1.40 (s, 6H); ^{13}C NMR (25 MHz), 200.2 (d, J = 5.9 Hz), 112.9, 81.2 (d, J = 2.95 Hz), 52.9 (m), 36.7 (d, J = 130.9 Hz), 25.8; ^{31}P NMR (81 MHz) 20.96; $[\alpha]^{25}_D$ +30° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{13}H_{24}O_{10}P_2$: C, 38.81; H, 6.01. Found: C, 38.90; H, 5.98.

General Procedure for Wadsworth−Emmons Reaction. To a stirred mixture of Cs_2CO_3 (325 mg, 1 mmol) in 3 mL of 2-propanol at 0 °C was added the β-keto phosphonate (**5**, **6**, or **8**, 1 mmol) in 2 mL of 2-propanol. After 5 min, the aldehyde (1.2 mmol) in 2 mL of 2-propanol was added and the mixture allowed to warm up to rt over 8 h (procedure A) or 4 h (procedure B). When the bis phosphonate **28** was employed, the amounts of Cs_2CO_3 and the aldehyde used were doubled (procedure C). Procedure D is identical to procedure A except for the use of a 3-fold excess of Cs_2CO_3. The reaction mixture was then quenched with an excess of 5% aqueous citric acid and extracted with CH_2Cl_2. The CH_2Cl_2 extract was dried and evaporated to obtain the crude product which was purified by column chromatography using 10% ethyl acetate in hexane.

(*E*)-1-(4-Methoxyphenyl)-2-(methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranuronyl)ethylene (13) was obtained by the condensation of β-keto phosphonate **5** and *p*-anisaldehyde (procedure A). **13**: syrup; IR (neat), 1680, 1660 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.72 (d, J = 15.7 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.22 (s, 5H), 6.90 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 15.7 Hz, 1H), 4.95 (d, J = 4 Hz, 1H), 4.78 (d, J = 11 Hz, 1H), 4.54 (d, J = 11 Hz, 1H), 4.46 (d, J = 9.3 Hz, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.57 (s, 3H), 3.49 (s, 3H), 3.80−3.24 (m, 3H); ^{13}C NMR (25 MHz) 194.1, 160.8, 142.8, 136.5, 129.3 (2C), 127.1 (4C), 126.5, 125.8, 120.2, 113.2, 96.8, 82.3, 80.3, 74.5, 73.8, 72.0, 60.0, 57.8, 54.4, 54.1; $[\alpha]^{25}_D$ +107.2° (*c* 0.7, $CHCl_3$). Anal. Calcd for $C_{25}H_{30}O_7$: C, 67.85; H, 6.83. Found: C, 67.75; H, 6.80.

(*E*)-1-Phenyl-2-(methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranuronyl)ethylene (14) was obtained by the condensation of β-keto phosphonate **5** and benzaldehyde (procedure A). **14**: syrup; IR (neat) 1690, 1670 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.70 (d, J = 16 Hz, 1H), 7.60−7.10 (m, 10H), 6.96 (d, J = 16 Hz, 1H), 4.96 (d, J = 4 Hz, 1H), 4.77 (d, J = 10 Hz, 1H), 4.52 (d, J = 10 Hz, 1H), 4.48 (d, J = 9 Hz, 1H), 3.80−3.20 (m, 3H), 3.69 (s, 3H), 3.57 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (25 MHz) 195.3, 144.0, 137.6, 134.3, 130.8, 128.8 (2C), 128.6 (2C), 128.3 (4C), 127.7, 123.5, 98.0, 83.5, 81.4, 79.4, 75.0, 73.1, 61.1, 59.0, 55.6; $[\alpha]^{25}_D$ +108.8° (*c* 1.52, $CHCl_3$). Anal. Calcd for $C_{24}H_{28}O_6$: C, 69.88; H, 6.84. Found: C, 69.75; H, 6.80.

(*E*)-1-(1-Methylethyl)-2-(methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranuronyl)ethylene (15) was obtained by the condensation of β-keto phosphonate **5** and isobutyraldehyde (procedure A). **15**: syrup; IR (neat) 1690, 1675, 1620 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.26 (s, 5H), 6.96 (dd, J = 6.5, 15.7 Hz, 1H), 6.26 (dd, J = 1.8, 15.7 Hz, 1H), 4.88 (d, J = 4 Hz, 1H), 4.74 (d, J = 10 Hz, 1H), 4.52 (d, J = 10 Hz, 1H), 4.35 (d, J = 8.9 Hz, 1H), 3.63 (s, 3H), 3.53 (s, 3H), 3.44 (s, 3H), 3.70−3.20 (m, 3H), 2.56−2.26 (m, 1H), 1.03 (d, J = 6.4 Hz, 6H); ^{13}C NMR (25 MHz) 195.6, 155.6, 137.9, 128.1 (2C), 128.0 (2C), 127.6, 125.0, 98.0, 83.3, 81.4, 79.3, 74.7, 72.1, 61.0, 58.9, 55.5, 31.0, 20.8 (2C); $[\alpha]^{25}_D$ +115.3° (*c* 1.1, $CHCl_3$). Anal. Calcd for $C_{21}H_{30}O_6$: C, 66.64; H, 7.99. Found: C, 66.58; H, 7.95.

6,7-Dideoxy-7-(methyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranuronyl)-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hept-6(*E*)-enopyranose (16) was obtained by the condensation of β-keto phosphonate **5** and 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**9**)[31] (procedure A). **16**: syrup: IR (neat) 1690, 1630 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.26 (s, 5H), 6.96 (dd, J = 3.6, 15.7 Hz, 1H), 6.64 (dd, J = 15.7, 1.8 Hz, 1H), 5.56 (d, J = 4.9 Hz, 1H), 4.86 (d, J = 4 Hz, 1H), 4.66−4.16 (m, 7H), 3.60 (s, 3H), 3.52 (s, 3H), 3.44 (s, 3H), 3.66−3.16 (m, 3H), 1.50 (s, 3H), 1.34 (s, 6H), 1.30 (s, 3H); ^{13}C NMR (25 MHz) 215.2, 143.7, 134.1, 129.8 (2C), 128.3, 127.2 (2C), 121.8, 109.4, 108.5, 97.8, 96.2, 72.7, 70.6, 67.4, 61.0, 58.8, 56.2, 51.4, 50.7, 46.5, 35.7, 35.0, 33.1, 26.0 (2C), 24.1, 23.8; $[\alpha]^{25}_D$ +3.6° (*c* 2.6, $CHCl_3$). Anal. Calcd for $C_{29}H_{40}O_{11}$: C, 61.68; H, 7.14. Found: C, 61.56; H, 7.15.

(*E*)-1-(4-Methoxyphenyl)-2-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranuronyl)ethylene (17) was obtained by the condensation of β-keto phosphonate **6** and *p*-anisaldehyde (procedure A). **17**: syrup; IR (neat) 1680, 1595 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.70 (d, J = 15.9 Hz, 1H), 7.54 (d, J = 9.2 Hz, 2H), 7.12 (d, J = 15.9 Hz, 1H), 6.88 (d, J = 9.2 Hz, 2H), 5.70 (d, J = 5 Hz, 1 H), 4.66 (d, J = 1.8 Hz, 1H), 4.46−4.26 (m, 3H), 3.84 (s, 3H), 1.52 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (25 MHz), 196.7, 161.8, 143.7, 130.6, 127.6, 119.0, 114.4, 109.7, 109.0, 96.5, 73.4, 72.5, 70.7, 70.5, 55.3, 25.9, 24.8, 24.2; $[\alpha]^{25}_D$ −180.5° (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{21}H_{26}O_7$: C, 64.6; H, 6.71. Found: C, 64.35; H, 7.00.

1,2-Dideoxy-1-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranuronyl)-3,4-*O*-isopropylidene-D-*glycero*-tetr-1-enose (18) was obtained by the condensation of β-keto phosphonate **6** and 2,3-*O*-isopropylidene-D-glyceraldehyde (**10**)[32] (procedure A). **18**: syrup; IR (neat) 1695, 1640 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.90−6.84 (m, 2H), 5.66 (d, J = 4.9 Hz, 1H), 4.76−4.56 (m, 3H), 4.40−4.25 (m, 2H), 4.17 (dd, J = 8, 6.5 Hz, 1H), 3.67 (dd, J = 7.1, 8 Hz, 1H), 1.50 (s, 3H), 1.41 (s, 9H), 1.34 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (25 MHz) 196.2, 143.4, 125.0, 109.3, 108.5, 107.8, 95.0, 75.0, 73.0, 72.0, 70.2, 70.0, 68.3, 26.0, 25.5(3C), 24.4, 23.8; $[\alpha]^{25}_D$ −99.3° (*c* 0.73, $CHCl_3$). Anal. Calcd for $C_{19}H_{28}O_8$: C, 59.36; H, 7.34. Found: C, 59.18; H, 7.25.

6,7-Dideoxy-7-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranuronyl)-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hept-6(*E*)-enopyranose (21) was obtained by the condensation of β-keto phosphonate **7** and 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**9**)[31] (procedure B). **21**: syrup; IR (neat) 1695, 1630 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$), δ 7.35−7.15 (m, 5H), 6.96 (dd, J = 3.9, 15.72 Hz, 1H), 6.80 (dd, J = 1.5, 15.73 Hz, 1H), 6.08 (d, J = 3.6 Hz, 1H), 5.59 (d, J = 5 Hz, 1H), 4.83 (d, J = 3.5 Hz, 1H), 4.61 (dd, J = 2.45, 7.76 Hz, 1H), 4.57 (d, J = 3.6 Hz, 1H), 4.50 (s, 2H), 4.48−4.42 (m, 1H), 4.34 (d, J = 2.5 Hz, 1H), 4.32 (d, J = 3.46 Hz, 1H), 4.26 (dd, J = 2.06, 7.77 Hz, 1H), 1.49 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (50 MHz) 194.9, 142.0, 137.1, 128.4 (2C), 127.8, 127.7 (2C), 126.1, 112.3, 109.7, 108.7, 105.9, 96.4, 85.1, 83.7, 82.3, 72.8, 72.7, 70.9, 70.6, 67.8, 27.0, 26.4, 26.1, 25.9, 24.9, 24.4; $[\alpha]^{25}_D$ −100.6° (*c* 1.6, $CHCl_3$). Anal. Calcd for $C_{28}H_{36}O_{10}$: C, 63.14; H, 6.81. Found: C, 63.24; H, 6.85.

5,6-Dideoxy-6-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranuronyl)-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5(*E*)-enofuranose (22) was obtained by the condensation of β-keto phosphonate **7** and 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**11**)[28] (procedure B). **22**: syrup; IR (neat) 1690, 1625 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40−7.15 (m, 10H), 6.98 (dd, J = 4.6, 15.8 Hz, 1H), 6.83 (dd, J = 1.13, 15.85 Hz, 1H), 6.09 (d, J = 3.63 Hz, 1H), 5.99 (d, J = 3.71 Hz, 1H), 4.79 (d, J = 3.58 Hz, 1H), 4.80−4.75 (m, 1H), 4.62 (d, J = 3.96 Hz, 1H), 4.58 (d, J = 3.66 Hz, 1H), 4.49 (s, 2H), 4.45 (d, J = 2.47 Hz, 1H), 4.38 (d, J = 2.45 Hz, 1H), 4.29 (d, J = 3.66 Hz, 1H), 3.95 (d, J = 3.28 Hz, 1H); ^{13}C NMR (50 MHz) 195.0, 140.3, 137.1, 136.9, 128.5 (2C), 128.4 (2C), 128.0, 127.9, 127.8 (2C), 127.7 (2C), 127.1, 112.3, 111.9, 105.9, 105.1, 85.1, 83.3, 83.1, 82.9, 82.1, 79.9, 72.2, 26.9, 26.4, 26.3; $[\alpha]^{25}_D$ −55.7° (*c* 1.3, $CHCl_3$). Anal. Calcd for $C_{31}H_{36}O_9$: C, 67.37; H, 6.57. Found: C, 67.45; H, 6.62.

6,7-Dideoxy-7-(2,3:4,5-di-*O*-isopropylidene-D-arabinonyl)-1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hept-6-(*E*)-enopyranose (23) was obtained by the condensation of

(31) Garegg, P. J.; Samuelsson, B. *Carbohydr. Res.* **1978**, *67*, 267.

(32) Daumas, M.; Vo-Quang, Y.; Vo-Quang, L.; Le Goffic, F. *Synthesis* **1989**, 64.

β-keto phosphonate **8** and 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**9**)[31] (procedure A). **23**: solid, mp 128 °C (hexane); IR (KBr) 1700, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, J = 3.96, 15.6 Hz, 1H), 6.85 (dd, J = 1.91, 15.65 Hz, 1H), 5.60 (d, J = 5.03 Hz, 1H), 4.65 (dd, J = 2.47, 7.77 Hz, 1H), 4.56 (d, J = 5.32 Hz, 1H), 4.49 (ddd, J = 1.999, 1.967, 3.966 Hz, 1H), 4.36 (dd, J = 2.42, 4.99 Hz, 1H), 4.31 (dd, J = 2.16, 7.84 Hz, 1H), 4.28 (dd, J = 5.4, 7.06 Hz, 1H), 4.19 (ddd, J = 5.07, 6.32, 7.08 Hz, 1H), 4.12 (dd, J = 6.28, 8.49 Hz, 1H), 3.97 (dd, J = 4.89, 8.52 Hz, 1H), 1.55 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.35 (s, 6H), 1.32 (s, 3H); ^{13}C NMR (25 MHz), 197.6, 143.6, 126.1, 112.0, 110.3, 110.1, 109.1, 96.8, 83.0, 78.8, 77.5, 73.0, 71.2; 70.9, 68.1, 67.1, 27.6, 26.8, 26.7, 26.4, 26.2, 25.5, 25.1, 24.8; $[\alpha]^{25}_D$ −65.04° (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{24}H_{36}O_{10}$: C, 59.49; H, 7.49. Found: C, 59.56; H, 7.54.

5,6-Dideoxy-6-(2,3:4,5-di-*O*-isopropylidene-D-arabinonyl)-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-(*E*)-enofuranose (24) was obtained by the condensation of β-keto phosphonate **8** and 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**11**)[28] (procedure A). **24**: syrup; IR (neat) 1680, 1625 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.32–7.16 (m, 5H), 6.96–6.88 (m, 2H), 5.94 (d, J = 4 Hz, 1H), 4.84–4.76 (m, 1H), 4.68–4.44 (m, 4H), 4.38–3.88 (m, 5H), 1.48 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (25 MHz) 197.0, 141.7, 137.1, 128.6 (2C) 128.1, 127.8 (2C), 126.5, 112.0, 111.6, 109.9, 105.0, 82.9, 82.8, 82.4, 79.9, 78.3, 76.7, 72.3, 66.8, 27.3, 26.9, 26.6, 26.4 (2C), 25.3; $[\alpha]^{25}_D$ −10.96° (*c* 1.1, $CHCl_3$). Anal. Calcd for $C_{27}H_{36}O_9$: C, 64.27; H, 7.19. Found: C, 64.62; H, 7.187.

1,2-Dideoxy-1-(2,3:4,5-di-*O*-isopropylidene-D-arabinonyl)-3,4:5,6-di-*O*-isopropylidene-D-*arabino*-hex-1(*E*)-enose (25) was obtained by the condensation of β-keto phosphonate **8** and 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**12**)[30] (procedure A). **25**: solid; mp 90–91 °C (hexane); IR (KBr) 1700, 1630 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, J = 4.3, 15.5 Hz, 1H), 6.86 (dd, J = 1.5, 15.6 Hz, 1H), 4.58 (ddd, J = 1.4, 4.2, 7.8 Hz, 1H), 4.53 (d, J = 5.6 Hz, 1H), 4.30 (dd, J = 5.2, 6.7 Hz, 1H), 4.20 (m, 1H), 4.14–4.08 (m, 2H), 4.12 (d, J = 5.6 Hz, 1H), 3.97 (dd, J = 8.8, 4.88 Hz, 1H), 3.94 (dd, J = 3.3, 7.77 Hz, 1H), 3.68 (dd, J = 7.77, 7.77 Hz, 1H), 1.47 (s, 3H), 1.44 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (25 MHz) 197.3, 145.1, 125.0, 110.8, 110.0, 109.8 (2C), 82.2, 81.2, 79.3, 78.2, 77.0, 76.5, 67.5, 66.7, 27.1, 26.8, 26.6 (3C), 26.4, 25.1 (2C); $[\alpha]^{25}_D$ +7.07° (*c* 1.4, $CHCl_3$). Anal. Calcd for $C_{23}H_{36}O_9$: C, 60.5; H, 7.95. Found: C, 60.345; H, 7.98.

1,2-Dideoxy-1-(2,3:4,5-di-*O*-isopropylidene-D-arabinonyl)-3,4-*O*-isopropylidene-D-*glycero*-tetr-1(*E*)-enose (26) was obtained by the condensation of β-keto phosphonate **8** and 2,3-*O*-isopropylidene-D-glyceraldehyde (**10**)[32] (procedure A). **26**: syrup; IR (neat) 1700, 1630 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 6.91–6.78 (m, 2H), 4.67 (dt, J = 4, 6.6 Hz, 1H), 4.50 (d, J = 5 Hz, 1H), 4.31–3.81 (m, 4H), 3.65 (dd, J = 7.7 Hz, 2H), 1.43 (s, 6H), 1.39 (s, 6H), 1.32 (s, 6H); ^{13}C NMR (25 MHz) 197.4, 144.8, 125.5, 111.5, 110.2, 109.8, 82.2, 78.2, 76.4, 75.1, 68.6, 66.6, 27.0, 26.3 (2C), 26.1, 25.5, 25.0; $[\alpha]^{25}_D$ +26.85° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{18}H_{28}O_7$: C, 60.66; H, 7.92. Found: C, 60.55; H, 7.85.

Dienone 29 was obtained by the condensation of β-keto phosphonate **28** and 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**9**)[31] (procedure C). **29**: solid; mp 194 °C (hexane–chloroform); IR (KBr) 1690, 1660 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.02 (dd, J = 4.15, 15.65 Hz, 2H), 6.15 (dd, J = 1.94, 15.64 Hz, 2H), 5.61 (d, J = 5.01 Hz, 2H), 4.65 (dd, J = 5.28, 7.74 Hz, 2H), 4.51–4.45 (m, 2H), 4.36 (dd, J = 2.5, 5.02 Hz, 2H), 4.31 (dd, J = 2.09, 7.77 Hz, 2H), 1.52 (s, 6H), 1.43 (s, 6H), 1.35 (s, 6H), 1.33 (s, 6H); ^{13}C NMR (50 MHz) 170.9, 145.5, 121.7, 109.9, 108.9, 96.5, 72.7, 71.0, 70.6, 67.5, 26.1, 26.0, 24.9, 24.6; $[\alpha]^{25}_D$ −128° (*c* 0.8, $CHCl_3$). Anal. Calcd for $C_{33}H_{46}O_{14}$: C, 59.45; H. 6.95. Found: C, 59.32; H, 6.90.

Dienone 30 was obtained by the condensation of β-keto phosphonate **28** and 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (**11**)[28] (procedure C). **30**: syrup; IR (neat) 1690, 1630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40–7.20 (m, 10H), 7.08 (dd, J = 4.75, 15.81 Hz, 2H), 6.82 (dd, J = 1.58, 15.81 Hz, 2H), 6.01 (d, J = 3.77 Hz, 2H), 4.88 (s, 2H), 4.88–4.80 (m, 2H), 4.65 (d, J = 3.92 Hz, 2H), 4.60 (d, J = 12.6 Hz, 2H), 4.47 (d, J = 12.04 Hz, 2H), 4.01 (d, J = 3.24 Hz, 2H), 1.50 (s, 6H), 1.36 (s, 6H), 1.33 (s, 6H); ^{13}C NMR (50 MHz) 196.1, 142.5, 137.2, 128.6 (2C), 128.1, 127.8 (2C), 126.6, 113.0, 112.1, 105.2, 83.4, 83.0, 81.1, 80.0, 72.4, 26.9, 26.4, 26.3; $[\alpha]^{25}_D$ −33° (*c* 0.65, $CHCl_3$). Anal. Calcd for $C_{39}H_{46}O_{12}$: C, 66.27; H, 6.56. Found: C, 66.35; H, 6.58.

Dienone 31 was obtained by the condensation of β-keto phosphonate **28** and 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**12**)[30] (procedure C). **31**: solid; mp 120–23 °C (hexane); IR (KBr) 1620, 1665 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.12 (dd, J = 4.3, 15.64 Hz, 2H), 6.18 (dd, J = 1.67, 15.68 Hz, 2H), 4.57 (ddd, J = 1.69, 4.32, 7.86 Hz, 2H), 4.18–4.05 (m, 4H), 4.02–3.92 (m, 2H), 3.68 (dd, J = 7.82 Hz, 2H), 1.43 (s, 6H), 1.41 (s, 12H), 1.35 (s, 6H); ^{13}C NMR (50 MHz) 171.2, 147.8, 120.7, 110.6, 110.0, 81.3, 79.1, 77.1, 67.7, 27.0, 26.8, 26.7, 25.2; $[\alpha]^{25}_D$ −6.9° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{31}H_{46}O_{12}$: C, 60.97; H, 7.59. Found: C, 60.85; H, 7.55.

Cross-conjugated enone 32 was obtained by the condensation of β-keto phosphonate **5** and *p*-anisaldehyde (procedure D). **32**: syrup; IR (neat) 1660, 1625 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.80 (d, J = 15.8 Hz, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.25 (d, J = 15.46 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.17 (d, J = 3.06 Hz, 1H), 5.17 (d, J = 2.45 Hz, 1H), 4.16 (dd, J = 3.02, 7.34 Hz, 1H), 3.88 (s, 3H), 3.60 (s, 6H), 3.57 (d, J = 2.43 Hz, 1H), 3.54 (s, 3H); ^{13}C NMR (25 MHz) 184.8, 162.0, 151.0, 148.0, 145.1, 130.5 (2C), 127.4, 117.6, 114.4 (2C), 107.8, 99.1, 78.8, 74.6, 58.8, 56.8 (2C), 55.3; $[\alpha]^{25}_D$ +158.09° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: C, 64.45; H, 6.62.

Cross-conjugated enone 33 was obtained by the condensation of β-keto phosphonate **5** and benzaldehyde (procedure D). **33**: syrup; IR (neat) 1660, 1630, 1600 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.77 (d, J = 15.5 Hz, 1H), 7.62–7.54 (m, 2H), 7.39–7.35 (m, 3H), 7.32 (d, J = 15.5 Hz, 1H), 6.14 (d, J = 3.05 Hz, 1H), 5.12 (d, J = 2.48 Hz, 1H), 4.12 (dd, J = 3.06, 7.1 Hz, 1H), 3.55 (s, 3H), 3.54 (s, 3H), 3.51 (d, J = 2.45 Hz, 1H), 3.48 (s, 3H); ^{13}C NMR (50 MHz) 184.6, 147.8, 145.0, 134.7, 130.8, 129.0 (2C), 128.6 (2C), 120.1, 108.2, 99.2, 77.9, 74.7, 58.9, 57.1, 56.9; $[\alpha]^{25}_D$ +169° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.85; H, 6.59.

Cross-conjugated enone 34 was obtained by the condensation of β-keto phosphonate **5** and isobutyraldehyde (procedure D). **34**: syrup; IR (neat) 1670, 1615 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.05 (dd, J = 6.4, 15.5 Hz, 1H), 6.68 (dd, J = 15.5, 1.5 Hz, 1H), 6.07 (d, J = 3.4 Hz, 1H), 5.12 (d, J = 2.3 Hz, 1H), 4.12 (dd, J = 3.4, 7.2 Hz, 1H), 3.60 (s, 3H), 3.59 (s, 3H), 3.52 (s, 3H), 3.60–3.45 (m, 1H), 2.68–2.36 (m, 1H), 1.17 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (50 MHz) 185.0, 156.3, 147.6, 121.0, 108.2, 99.0, 77.8, 74.6, 58.8, 57.1, 56.8, 31.4, 21.2 (2C); $[\alpha]^{25}_D$ +187° (*c* 0.75, $CHCl_3$). Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.15; H, 8.18.

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