A green procedure for the regio and chemoselective hydrophosphonylation of organic unsaturated systems using CaO under solventless conditions.

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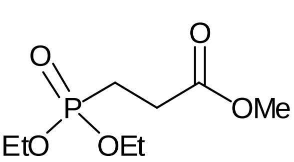
Supporting Information

General Remarks

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian Mercury Plus 400 instrument. ^{1}H (300 and 500 MHz) and ^{13}C (75.5 and 125.8 MHz) NMR spectra were recorded on Bruker Avance-300 and Avance-500 spectrometers. The assignments of ^{1}H and ^{13}C signals were confirmed by homonuclear COSY and heteronuclear 2D correlated spectra, respectively. GC-MS analyses were carried out by using the EI technique (70 eV) with a GC–MS Agilent Technologies 6850 SerieII/5973 Inert instrument. Mass spectra (CI and LSI) were recorded on Micromass AutoSpec-Q mass spectrometers with a resolution of 1,000 or 10,000 (10% valley definition). For LSI spectra, ions were produced by a beam of Cs^+ ions, respectively, using thioglycerol as matrix and NaI as additive. IR spectra were recorded with a Perkin–Elmer Paragon 500 FTIR. TLC was performed on aluminium pre-coated sheets (E. Merck Silica Gel 60 F_{254}); spots were visualized by UV light, by charring with 10% H_2SO_4 in EtOH. Column chromatography was performed using E. Merck Silica Gel 60 (40–63 mm). Calcium oxide (Aldrich) was used as received.



Methyl 3-(diethoxyphosphinyl)propanoate (9).[1] The crude product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **9**: 90 mg, 80%; IR ν_{max} 3461, 2985, 1742, 1394, 1367, 1026, 971 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.08, 4.04 (2 ddq, 2H, $^2J_{H,H}$ = 10.4 Hz, $^3J_{P,H}$ = 8.4 Hz, $^3J_{\mathrm{H,H}}$ = 7.2 Hz, $\mathrm{C}H_2\mathrm{CH}_3$), 3.65 (s, 3H, OMe), 2.55 (m, 2H, CH_2P), 2.03 (m, 2H, CH_2CO), 1.27 (t, 6H, $2\mathrm{CH}_2\mathrm{C}H_3$) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.6 (d, $^3J_{\mathrm{C,P}}$=18.2 Hz, CO), 61.8 (d, $^2J_{\mathrm{C,P}}$=6.5 Hz, $\mathrm{C}H_2\mathrm{CH}_3$), 52.1 (OMe), 27.4 (d, $^2J_{\mathrm{C,P}}$=4.0 Hz,

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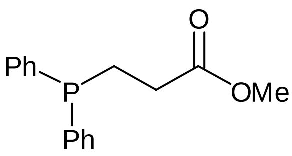
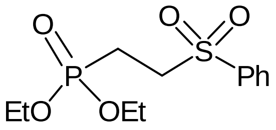
[1] Y. Okamoto and H. Sakurai, *Synthesis* 1982, 497–499.

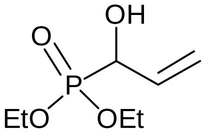
CH_2CO), 21.1 (d, $^{1}J_{C,P}$=143.2 Hz, CH_2P), 16.5 (d, $^{3}J_{C,P}$=5.3 Hz, $2CH_2CH_3$) ppm; GC-MS (70 eV): *m/z*: 224 (M^+), 193, 179, 165, 151, 137 (100), 123, 109, 95.



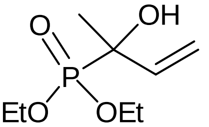
Methyl 3-(diphenylphosphino)propanoate (10).[2] The crude product was purified by column chromatography (2:1 hexane–EtOAc→ 1:2 hexane–EtOAc) to give **10**: 132 mg, 49%; IR ν_{max} 3053, 2950, 2361, 1738, 1434, 1355, 1224, 1166, 739 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.45-7.33 (m, 5H, Ar-H), 3.65 (s, 3H, CH_3), 2.44–2.33 (m, 4H CH_2P, CH_2CO) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.8 (d, $^{3}J_{C,P}$= 15.0 Hz, C=O), 138.0, 132.9, 129.1, 128.8 (Ar), 52.0 (OMe), 30.8 (d, 1C, $^{1}J_{C,P}$= 18.9 Hz, CH_2P), 23.2 (d, $^{2}J_{C,P}$= 12.2 Hz, CH_2CO) ppm; GC-MS (70 eV): *m/z*: 272 (M^+), 257 (100), 241, 201, 183, 152, 133, 107.



Diethyl 2-(phenylsulfonyl)ethylphosphonate (11).[3] The crude product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **11**: 279 mg, 91%; IR ν_{max} 3468, 2929, 1150, 1023, 783 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H, Ar-H), 7.70-7.68 (m, 1H, Ar-H), 7.61-7.56 (m, 2H, Ar-H), 4.13-4.00 (m, 4H, $2CH_2CH_3$), 3.31-3.25 (m, 2H, CH_2SO_2), 2.17-2.08 (m, 2H, CH_2P), 1.29 (t, 6H, $^{3}J_{H,H}$= 6.8 Hz, 2 CH_2CH_3) ppm; ^{13}C-RMN (100 MHz, $CDCl_3$) δ 138.3, 134.4, 129.7, 128.4 (Ar-C), 62.3 (d, $^{2}J_{C,P}$= 6.4 Hz, $2CH_2CH_3$), 50.2 (d, $^{2}J_{C,P}$= 3.4 Hz, CH_2SO_2), 19.6 (d, $^{1}J_{C,P}$= 142.5 Hz, CH_2P), 16.3 (d, $^{3}J_{C,P}$= 5.9 Hz, $2CH_2CH_3$) ppm; GC-MS (70 eV): *m/z*: 307 ($[M+H]^+$), 261, 242, 214, 174, 165, 138, 121, 109 (100), 91.



Diethyl (1-hydroxyallyl)phosphonate (12).[4] The crude product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **12**: 160 mg, 82%; IR ν_{max} 3306, 2985, 1239, 1026, 971 cm^{-1}; ^{1}H-RMN (400 MHz, $CDCl_3$) δ 5.98 (m, 1H, H-2), 5.47 (ddt, 1H, $^{4}J_{1,3a}$ = $^{2}J_{3a,3b}$= 1.6 Hz, $^{3}J_{2,3a}$ = 16.8 Hz, $^{4}J_{H3a,P}$= 5.0 Hz, H-3a), 5.28 (ddt, 1H, $^{4}J_{1,3b}$ = 1.6 Hz, $^{2}J_{3b,3a}$= 1.6 Hz, $^{3}J_{2,3b}$ = 10.8 Hz, $^{4}J_{H3b,P}$=3.6 Hz, H-3b), 4.50 (tt, 1H, $^{3}J_{OH,H}$= $^{2}J_{P,H}$= 6.0 Hz, H-1), 4.45 (m, 1H, OH), 4.19–4.11 (m, 4H, $2CH_2CH_3$), 1.30, 1.29 (2t, 3H each, $^{3}J_{H,H}$ = 7.0 Hz, $2CH_2CH_3$) ppm; ^{13}C-RMN (100 MHz, $CDCl_3$) δ 133.0 (d, $^{2}J_{C,P}$= 3.8 Hz, C-2), 117.2 (d, $^{3}J_{C,P}$= 12.9 Hz, C-3), 69.7 (d, $^{1}J_{C,P}$=159.1 Hz, C-1), 63.4 (d, $^{2}J_{C,P}$= 6.8 Hz, $2CH_2CH_3$), 16.7 (d, $^{3}J_{C,P}$= 6.0 Hz, $2CH_2CH_3$) ppm; GC-MS (70 eV): *m/z*: 194 (M^+), 165, 138, 121, 111, 99, 91, 82 (100), 65.



Diethyl (1-hydroxy-1-methylallyl)phosphonate (13).[5] The crude product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **13**: 179 mg, 87%. Reaction carried out with 10 mmol of methyl vinyl ketone **4** 10 mmol of diethyl phosphite and 10 mmol of CaO at room temperature for 5 h gave 1.54 g (74%) of **13**. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.99 (ddd, 1H, $^{3}J_{2,3a}$= 17.4 Hz, $^{3}J_{2,3b}$= 10.8 Hz, $^{3}J_{2,P}$= 3.9 Hz, H-2), 5.42 (ddd, 1H, $^{2}J_{3a,3b}$= 1.1 Hz, $^{4}J_{3a,P}$= 5.0 Hz, H-3a), 5.20 (dd, 1H, $^{4}J_{3b,P}$= 3.9 Hz, H-3b), 4.13 (quint, 2H, $^{3}J_{H,H}$= $^{3}J_{H,P}$= 7.1 Hz, CH_2CH_3), 4.12 (quint, 2H, $^{3}J_{H,H}$=

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[2] M. Riondato, D. Camporese, D. Martín, J. Suades, A. Álvarez-Larena and U. Mazzi, *Eur. J. Inorg. Chem.*, 2005, 4048–4055.

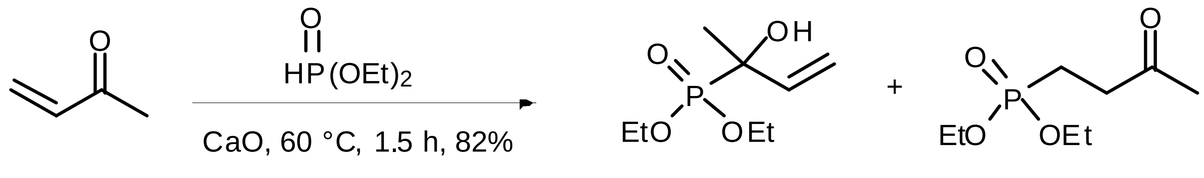
[3] D. R. Marshall, P. J. Thomas, C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1898–909.

[4] G. M. Blackburn and D. E. Kent, *J. Chem. Soc., Perkin Trans. 1*, 1986, 913–917.

[5] G. Keglevich, M. Sipos, D. Takács, I. Greiner, *Heteroatom Chem.* 2007, **18**, 226–229.

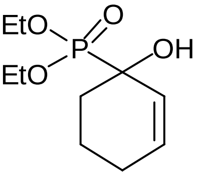
$^{3}J_{\mathrm{H,P}}$= 7.1 Hz, CH_2CH$_3$), 3.77 (bs, 1H, OH), 1.48 (d, 3H, $^{3}J_{\mathrm{H,P}}$= 5.9 Hz, CH$_3$COH), 1.29 (t, 3H, CH$_2$CH_3), 1.28 (t, 3H, CH$_2$CH_3) ppm; ^{13}C-RMN (75.5 MHz, CDCl$_3$) δ 138.3 (C-2), 115.1 (d, $^{3}J_{\mathrm{C,P}}$= 9.8 Hz, C-3), 72.9 (d, $^{1}J_{\mathrm{C,P}}$= 160.3 Hz, C-1), 63.5 (d, $^{2}J_{\mathrm{C,P}}$= 7.4 Hz, CH$_2$CH$_3$), 63.3 (d, $^{2}J_{\mathrm{C,P}}$= 7.5 Hz, CH$_2$CH$_3$), 23.6 (d, $^{2}J_{\mathrm{C,P}}$= 0.9 Hz, CH$_3$C(OH)), 16.6, 16.5 (2d, $^{3}J_{\mathrm{C,P}}$= 5.6 Hz, CH$_2$$CH_3$) ppm; EIMS *m/z* 208 (M$^+$, 1%); HREI-MS *m/z* calcd for $C_8H_{17}O_4P$, M$^+$: 208.0864, found: 208.0862.

Reaction of methyl vinyl ketone 4 and diethyl phosphite at 60 °C.

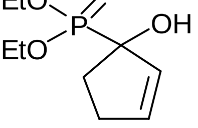


4 **13** 1:4 **21**

To a mixture of compound **4** (1 mmol) and diethyl phosphite (1 mmol) was added calcium oxide (1 mmol). The corresponding mixture was stirred at 60 °C for 1.5 h, and after cooling EtOAc was added, and the suspension was filtered through a Celite pad. The filtrate was concentrated to dryness and purified by column chromatography to give a mixture of compounds **13** and **21** as a 1:4 regioisomeric mixture in 82% yield. ^{1}H-NMR (300 MHz, CDCl$_3$) for **21**[6]: δ 4.10 (m, 4H, CH_2CH$_3$), 2.74 (m, 2H, CH$_2$P), 2.18 (s, 3H, CH$_3$), 2.03 (m, 2H, CH$_2$CO), 1.33 (t, 6H, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, CH$_2$CH_3).



Diethyl (1-hydroxycyclohex-2-enyl)phosphonate (14).[7] The mixture was stirred for 48 h, and the product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **14**: 182 mg, 78%; ^{1}H-RMN (300 MHz, CDCl$_3$) δ 6.08 (dt, 1H, $^{3}J_{\mathrm{H2,H3}}$ = 10.0 Hz, $^{3}J_{\mathrm{H,P}}$= 3.8 Hz, H-2), 5.85 (ddt, 1H, $^{3}J_{\mathrm{H3,H4}}$= 2.0 Hz, $^{4}J_{\mathrm{H,P}}$= 9.4 Hz, H-3), 4.19 (m, 4H, 2CH_2CH$_3$), 3.38 (d, 1H, $^{3}J_{\mathrm{OH,P}}$= 4.1 Hz, OH), 2.13-1.70 (m, 6H, 3CH$_2$), 1.34, 1.32 (2t, 3H each, $^{3}J_{\mathrm{H,H}}$= 7.0 Hz, 2CH$_2$CH_3) ppm; ^{13}C-RMN (75.5 MHz, CDCl$_3$) δ 134.5 (d, $^{2}J_{\mathrm{C2,P}}$= 11.1 Hz, C-2), 125.5 (s, C-3), 69.5 (d, $^{1}J_{\mathrm{C1,P}}$= 165.8 Hz, C-1), 63.3 (d, $^{2}J_{\mathrm{C,P}}$= 7.3 Hz, 2CH$_2$CH$_3$), 31.1 (d, $^{2}J_{\mathrm{C,P}}$= 3.0 Hz, C-6), 25.1 (d, $^{4}J_{\mathrm{C,P}}$= 1.0 Hz, C-4), 17.7 (d, $^{3}J_{\mathrm{C,P}}$= 7.3 Hz, C-5), 16.7 (d, $^{3}J_{\mathrm{C,P}}$= 5.3 Hz, 2CH$_2$$CH_3$) ppm; LSIMS *m/z* 257 ([M+Na]$^+$, 8%); HRLSI-MS *m/z* calcd for $C_{10}H_{19}O_4PNa$, [M+Na]$^+$: 257.0919, found: 257.0906.



Diethyl (1-hydroxycyclopent-2-enyl)phosphonate (15).[4] The crude product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **15**: 148 mg, 67%. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 6.05 (m, 1H, H-2), 5.74 (dt, 1H, $^{3}J_{\mathrm{H2,H3}}$= 7.7, $^{3}J_{\mathrm{H,H}}$= 2.1 Hz, H-3), 4.18-4.02 (m, 4H, 2CH_2CH$_3$), 3.86 (bs, 1H, OH), 2.59-2.44 (m, 2H, 2CH), 2.41-2.27 (m, 1H, CH), 1.93-1.79 (m, 1H, CH), 1.26 (t, 3H, $^{3}J_{\mathrm{H,H}}$= 7.0 Hz, 2CH$_2$CH_3), 1.24 (t, 3H, $^{3}J_{\mathrm{H,H}}$= 7.0 Hz, 2CH$_2$CH_3) ppm; ^{13}C-RMN (75.5 MHz, CDCl$_3$) δ 138.0 (d, $^{2}J_{\mathrm{C,P}}$= 13.3 Hz, C-2), 130.9 (d, $^{3}J_{\mathrm{C,P}}$= 1.3 Hz, C-3), 83.5 (d, $^{1}J_{\mathrm{C,P}}$= 169.9 Hz, C-

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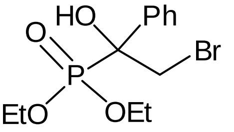
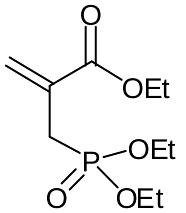
[6] C. A. Verbicky and C. K. Zercher, *J.Org.Chem.* 2000, **65**, 5615–5622.

[7] M. Attolini, F. Bouguir, G. Iacazio, G. Peiffera and M. Maffei, *Tetrahedron* 2001, **57**, 537–543.

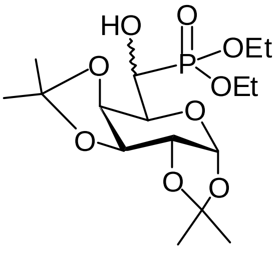
1), 63.2 (d, $^2J_{C,P}$= 7.1 Hz, CH_2CH_3), 63.1 (d, $^2J_{C,P}$= 7.3 Hz, CH_2CH_3), 34.9 (d, $J_{C,P}$= 7.1 Hz, CH_2), 32.1 (d, $J_{C,P}$= 5.1 Hz, CH_2), 16.7 (d, $^3J_{C,P}$= 1.0 Hz, CH_2CH_3), 16.6 (d, $^3J_{C,P}$= 1.0 Hz, CH_2CH_3) ppm; CI-MS *m/z* 221 ($[M+H]^+$, 15%); HRCI-MS *m/z* calcd for $C_9H_{18}O_4P$, $[M+H]^+$: 221.0943, found: 221.0946.



Diethyl (2-bromo-1-hydroxy-1-phenylethyl)phosphonate (16).[8] The crude product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **16**: 290 mg, 86%; ^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H, Ar-H), 7.43-7.31 (m, 3H, Ar-H), 4.20-4.08 (m, 4H, CH_2CH_3, CH_2Br), 3.96 (ddq, 1H, $^2J_{H,H}$= 10.1 Hz, $^3J_{H,P}$=8.0 Hz, $^3J_{H,H}$= 7.1 Hz, CH^ACH_3), 3.79 (ddq, 1H, $^3J_{H,H}$= 7.1 Hz, $^3J_{H,P}$= 8.2 Hz, CH^BCH_3), 3.45 (d, 1H, $^3J_{OH,P}$= 15.2 Hz, OH), 1.29, 1.16 (2t, 3H each, $2CH_2CH_3$) ppm; ^{13}C-RMN (75.5 MHz, $CDCl_3$) δ 137.4, 128.4, 126.4(x2) (Ar), 75.3 (d, $^1J_{C,P}$=112.7 Hz, C-1), 64.3 (d, $^2J_{C,P}$= 7.5 Hz CH_2CH_3), 64.0 (d, $^2J_{C,P}$=7.6 Hz, CH_2CH_3), 40.7 (d, $^2J_{C,P}$= 15.3 Hz, CH_2Br), 16.5, 16.4 (2d, $^3J_{C,P}$= 5.7 Hz, 2 CH_2CH_3) ppm; LSIMS *m/z* 359 ($[M+Na]^+$, 100 %); HRLSI-MS *m/z* calcd for $C_{12}H_{18}BrNaO_4P$, $[M+Na]^+$: 359.0024, found: 359.0020.



Methyl 2-[(diethoxyphosphinyl)methyl]acrylate (17).[9] The crude product was purified by column chromatography (2:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **17**: 225 mg, 90%; IR ν_{max} 3480, 2984, 1633, 1257, 1027, 966 cm^{-1}; ^{1}H-RMN (400 MHz, $CDCl_3$) δ 6.25 (dt, 1H, $^2J_{H,H}$= 5.6 Hz, $J_{1,3a}$= 0.8 Hz, H-3a), 5.75 (dt, 1H, $J_{1,3b}$= 0.8 Hz, H-3b), 4.12 (q, 2H, $^3J_{H,H}$ = 6.8 Hz, CH_2OCO), 3.99 (m, 4H, $2CH_2OP$), 2.84 (dt, $^2J_{H,P}$= 22.0 Hz, CH_2P), 1.21, 1.19 (x2) (4t, 3H each, $^3J_{H,H}$ = 7.2 Hz, $4CH_3$) ppm; ^{13}C-RMN (100 MHz, $CDCl_3$) δ 166.1 (d, $^3J_{C,P}$= 5.7 Hz, CO), 131.5 (d, $^2J_{C\text{-}P}$= 10.6 Hz, C-2), 128.5 (d, $^3J_{C,P}$= 9.9 Hz, C-3), 62.0 (d, $^2J_{C,P}$= 6.0 Hz, $2CH_2OP$), 61.2 (s, CH_2OCO), 28.4 (d, $^1J_{C,P}$= 138.6 Hz, C-1), 16.3 (d, $^3J_{C,P}$= 6 Hz, $2CH_3CH_2OP$), 14.2 (s, CH_3CH_2OCO) ppm; GC-MS (70 eV): *m/z*: 250 (M^+), 221, 205, 193, 177, 149, 121, 109, 81, 68 (100).



6-*C*-(Diethoxyphosphinyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (20). The crude product was purified by column chromatography (1:1 hexane–EtOAc → 1:2 hexane–EtOAc) to give **20**: 277 mg, 70%; ^{1}H-RMN (500 MHz, $CDCl_3$) major diastereoisomer δ 5.54 (d, 1H, $J_{1,2}$= 5.0 Hz, H-1), 4.63 (m, 2H, H-3, H-4), 4.31 (dd, 1H, $J_{2,3}$= 2.0 Hz, H-2), 4.21, 4.18 (2 quint, 2H each, $2CH_2CH_3$), 4.15 (m, 1H, $^2J_{6,P}$= 6.5 Hz, H-6), 4.11 (t, 1H, $J_{5,6}$= $^3J_{H5,P}$= 6.0 Hz, H-5), 3.60 (t, 1H, $J_{OH,H\text{-}6}$= 6.5 Hz, $^3J_{OH,P}$=5.2 Hz, OH), 1.53, 1.47, 1.35, 1.31 (4 s, 3H each, 4 CH_3C), 1.33, 1.32 (2t, 3H each, $^3J_{H,H}$= 6.9 Hz, $2CH_2CH_3$) ppm; minor diastereoisomer δ 5.57 (d, 1H, $J_{1,2}$= 5.0 Hz, H-1), 4.60 (dd, 1H, $J_{2,3}$ =2.2 Hz, $J_{3,4}$= 7.6 Hz, H-3), 4.43 (bd, 1H, H-4), 4.26 (dd, 1H, $J_{5,6}$= 4.8 Hz, $^2J_{6,P}$= 9.1 Hz, H-6), 4.27, 4.11 (2m, 2H each, $2CH_2$), 4.21 (m, 1H, H-5), 3.28 (d, 1H, $J_{OH,P}$ = 24.0 Hz, OH), 1.56, 14.6 (2s, 3H each, 2 CH_3C), 1.35-1.31 (m, 6H, $2CH_2CH_3$) ppm; ^{13}C-RMN (75.5 MHz, $CDCl_3$) major diastereoisomer δ 109.8, 109.1 (Me_2C), 96.6 (C-1), 72.0 (d, $^3J_{C,P}$= 6.4 Hz, C-4), 70.9 (C-3), 70.6 (C-2), 69.0 (d, $^1J_{C,P}$= 161.7 Hz, C-6), 65.9 (d, $^2J_{C,P}$= 7.8 Hz, C-5), 63.2 (d, $^2J_{C,P}$= 6.9 Hz,

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CH$_2$CH$_3$), 62.8 (d, $^2J_{C,P}$= 6.9 Hz, CH$_2$CH$_3$), 26.1, 26.0, 25.1, 24.4 ((CH$_3$)$_2$C), 16.6 (d, $^3J_{C,P}$= 5.7 Hz, 2CH$_2$$CH_3$) ppm; minor diastereoisomer δ 109.8 (Me$_2$$C$), 96.5 (C-1), 73.4 (d, $^3J_{C,P}$= 8.8 Hz, C-4), 71.0 (C-3), 70.9 (C-2), 68.4 (d, $^1J_{C,P}$= 169.5 Hz, C-6), 66.0 (d, $^2J_{C,P}$= 2.9 Hz, C-5), 63.6 (d, $^2J_{C,P}$= 6.2 Hz, CH$_2$CH$_3$), 62.6 (d, $^2J_{C,P}$= 6.1 Hz, CH$_2$CH$_3$), 26.1, 26.0 ((CH$_3$)$_2$C), 16.5 (d, $^3J_{C,P}$= 6.4 Hz, 2 CH$_2$CH$_3$) ppm; LSIMS *m/z* 419 ([M+Na]$^+$, 100%), 397 ([M+H]$^+$, 50%); HRLSI-MS *m/z* calcd for $C_{16}H_{29}O_9NaP$ [M+Na]$^+$: 419.1447, found: 419.1466.