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Synthesis of chlorophyll *a* glycoconjugates using olefin cross-metathesis

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Methods and materials

Solvents were purified and prepared using standard procedures. All reactions were carried out in an argon atmosphere with protection from direct light. Column chromatography was carried out using 40/60 silica gel (Merck). Preparative TLC was performed using silica gel 60 (Merck) and 20×20 cm plates with 1 mm layer thickness. Analytical TLC was carried out using Kieselgel 60 F_{245} plates (Merck). Grubbs Catalyst, 2nd Generation **4** {benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium} [246047-72-3] was purchased from Sigma-Aldrich.

Electronic spectra were recorded using a Jasco-UV 7800 spectrophotometer. NMR spectra were recorded at 257°C on Bruker DPX 300 and Bruker Avance 600 spectrometers. The ^{13}C and ^{1}H scale were calibrated using signals of ^{13}C nuclei and of residual protons in deuterated solvents, respectively. The evolution delay in ^{1}H-^{13}C gHMBC experiments was 60 ms. Mass spectra were obtained on a Bruker Ultraflex TOF/TOF time-of-flight mass spectrometer by the MALDI method, using 2,5-dihydroxybenzoic acid (DHB) as the matrix. The methyl ester of pheophorbide *a* was obtained from chlorophyll *a* using a reported procedure.[2] Purpurin and its methyl ester were obtained by allomerisation of chlorophyll *a* similarly to a reported method.[3] Mesopheophorbid and mesopurpurin were obtained by catalytic hydrogenation of methyl ester of pheophorbide *a* and methyl ester of purpurin Zn complex using the technique reported previously.[4]

Chlorin e_6 trimethyl ester **1**

A solution of pheophorbide *a* methyl ester [2] (200 mg, 0.33 mmol) in dichloromethane (5 ml) was cooled in an ice bath, an 1 M solution of sodium methoxide (330 μl) in dry methanol was added, and the resulting mixture was stirred at 0 °C. After two hours, glacial acetic acid (19 μl) was added, the mixture was washed with water (50 ml), and the resulting mixture was extracted with dichloromethane (2x20 ml). The combined extracts were dried with anhydrous sodium sulfate, concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel using a dichloromethane/methanol system (49:1) as the eluent. The yield was 193 mg (92%).

^{1}H NMR (300 MHz, $CHCl_3$, δ): 9.62 (H, s, 10-H), 9.45 (H, s, 5-H), 8.70 (H, s, 20-H), 7.97 (H, dd, *J* = 17.8, 11.5 Hz 3^1-H), 6.27 (H, dd, *J* = 17.8 Hz, 1.5 Hz), 6.06 (H, dd, *J* = 11.5, 1.5 Hz), 5.37 (2H, d, *J* = 18.8 Hz, 15^1-CH_2^a), 5.21 (2H, d, *J* = 18.8 Hz, 15^1-CH_2^b), 4.42 (2H, m, 18-H, 17-H), 4.24 (3H, s, 13^2-CH_3) 3.75 (3H, s, 15^3-CH_3), 3.74 (2H, q, *J* = 7.3 Hz), 3.56 (3H, s, 17^4-CH_3), 3.55 (3H, s, 12^1-CH_3), 3.40 (3H, s, 2^1-CH_3), 3.19 (3H, s, 7^1-CH_3), 2.56 (H, m, 17^2-CH_2^a), 2.18 (2H, m, 17^1-CH_2^a , 17^2-CH_2^b), 1.75 (H, m, 17^1-CH_2^b), 1.66 (3H, d, *J* = 7.3 Hz), 1.64 (3H, t, *J* = 7.7 Hz), -1.33 (H, s), -1.48 (H, s). UV-VIS ($CHCl_3$), λ, nm (ε, $M^{-1}cm^{-1}$): 404 (142400), 500 (14400), 530 (6300), 558 (1700), 608 (4900), 666 (43000).

N-*Methoxypurpurinimide methyl ester* **2**

Hydroxylamine hydrochloride (185 mg, 2.66 mmol) was added to a solution of purpurin[3] (150 mg, 0.266 mmol) in pyridine (3 ml) and the mixture was stirred for 14 h at room temperature. The reaction mixture was then diluted with water (120 ml), 1 N HCl was added to pH 3.0, and the mixture was stirred for 15 min. The mixture was transferred into a separating funnel and extracted with chloroform (5x20 ml). The combined extracts were washed with water, dried with anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was dissolved in a dichloromethane/methanol mixture (25:1, 10 ml), an ethereal solution of diazomethane (7 ml) was added, and the mixture was stirred for 15 min at room temperature. The reaction mixture was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography in a dichloromethane/methanol system (24:1). The yield was 144 mg (89%).
^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.44 (H, s, 10-H), 9.21 (H, s, 5-H), 8.52 (H, s, 20-H), 7.82 (H, dd, *J* = 17.8 Hz, *J* = 11.6 Hz, 3^1-CH_2), 6.25 (H, dd, *J* = 17.8 Hz, *J* = 1.4 Hz, 3^2-CH_2^E), 6.13 (H, dd, *J* = 11.6 Hz, *J* = 1.4 Hz, 3^2-CH_2^Z), 5.26 (H, m, 17-H), 4.38 (3H, s, $NOCH_3$), 4.35 (H, q, *J* = 7.3 Hz, 18-H), 3.75 (3H, s, 17^4-$COOCH_3$), 3.59 (3H, s, 12-CH_3), 3.53 (2H, q, *J* = 7.6 Hz, 8^1-CH_2), 3.31 (3H, s, 2-CH_3), 3.07 (3H, s, 7-CH_3), 2.82 (H, m, 17^2-CH_2^a), 2.53 (H, m, 17^1- CH_2^a), 2.46 (H, m, 17^2-CH_2^b), 1.96 (H, m, 17^1- CH_2^b), 1.73 (3H, d, *J* = 7.3 Hz, 18-CH_3), 1.61 (3H, t, *J* = 7.6 Hz, 8^2-CH_3), 0.13 (H, NH), 0.04 (H, NH).

Allyl-β-D-galactopyranoside tetraacetate **3**

Tin tetrachloride (0.36 ml, 3.07 mmol) was added to a solution of pentaacetyl-β-D-galactopyranose (1 g, 2.56 mmol) in dry dichloromethane (7 ml) cooled in an ice bath. After a white precipitate was formed, allyl alcohol (0.22 ml, 3.07 mmol) was added; the resulting mixture was heated to room temperature and stirred for 30 min after complete dissolution. The reaction mixture was mixed with a saturated aqueous $NaHCO_3$ solution (100 ml), stirred for 15 min and extracted with dichloromethane (2x20 ml). The combined extracts were washed with water (100 ml), dried with anhydrous sodium sulfate and concentrated *in vacuo*. The residue was

purified by column chromatography on silica gel, using an ethyl acetate/hexane system (1:2) as the eluent. The yield was 0.6 g (60%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.84 (H, m, -CH_2-$\underline{CH}$=CH_2), 5.37 (H, dd, *J* = 3.4, 1.0 Hz, 4-H), 5.25 (H, dq, *J* = 17.2, 1.6 Hz, -CH_2-CH=$\underline{CH_2}^a$), 5.23 (H, dd, *J* = 10.5, 7.9 Hz, 2-H), 5.19 (H, dq, *J* = 10.4, 1.6 Hz, -CH_2-CH=$\underline{CH_2}^b$), 5.00 (H, dd, *J* = 10.5, 3.4 Hz, 3-H), 4.51 (H, d, *J* = 7.9 Hz,1-H), 4.34 (H, ddt, *J* = 13.1, 4.8 Hz, 1.6 Hz, -$\underline{CH_2}^a$-CH=CH_2), 4.18 (H, dd, *J* = 11.2, 6.6 Hz, 6-CH_2^a), 4.11, (H, dd, *J* = 11.2, 6.9 Hz, 6-CH_2^b), 4.09 (H, ddt, *J* = 13.1, 6.2, 1.4 Hz, -$\underline{CH_2}^b$-CH=CH_2), 3.88 (H, td, *J* = 6.7, 1.0 Hz, 5-H), 2.14 (3H, s, -OAs), 2.05 (3H, s, -OAs), 2.04 (3H, s, -OAs), 1.97 (3H, s, -OAs).

Tetraacetylgalactosylchlorin **5**

A solution of catalyst **4** (17 mg, 0.02 mmol) in dichloromethane (0.5 ml) was added to a solution of chlorin e_6 trimethyl ester **1** (50 mg, 0.08 mmol) and allyl-β-D-galactopyranoside peracetate **3** (125 mg, 0.320 mmol) in dichloromethane (2 ml) and the resulting mixture was refluxed for 16 h. The reaction mixture was concentrated *in vacuo* and the residue was purified by preparative thin-layer chromatography in a dichloromethane/methanol system (49:1). The yield was 32 mg (40%).

NMR data are presented in Table 1S. Mass spectrum (MALDI), *m/z*: 999.7 $(M)^+$, 1037 $(M+K)^+$. UV-VIS ($CHCl_3$), λ, nm (ε, M^{-1} cm^{-1}): 404 (140100), 501 (14900), 531 (7900), 610 (5900), 666 (43000).

*17^3,15^2-Dimethylmesochlorin e_6 13^1-*N*-allylamide* **6**

Allylamine (2 ml, 26 mmol) was added to a solution of mesopheophorbide *a* methyl ester[4] (see Scheme 2) (195 mg, 0.32 mmol) in dichloromethane (2 ml) and the mixture was stirred for 16 h at room temperature. After that, the reaction mixture was concentrated *in vacuo*. The target product was purified by column chromatography in a chloroform/methanol system (97:3). The yield was 187 mg (88%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.70 (H, s, 10-H), 9.47 (H, s, 5-H), 8.74 (H, s, 20-H), 6.49 (H, t, *J* = 5.7 Hz, 13^2-NH), 6.14 (H, ddt, *J* = 17.1 Hz, *J* = 10.3 Hz, *J* = 5.9 Hz, 13^4-H), 5.54 (H, d, *J* = 18.9 Hz, 15-CH_2^a), 5.41 (H, dq, *J* = 17.1 Hz, *J* = 1.5 Hz, 13^5-CH_2^E), 5.30 (H, dq, *J* = 10.3 Hz, *J* = 1.3 Hz, 13^5-CH_2^Z), 5.25 (H, d, *J* = 18.9 Hz, 15-CH_2^b), 4.50, (H, dt, *J* = 15.4 Hz, *J* = 5.0 Hz, 13^3-H^a), 4.45 (H, q, *J* = 7.4 Hz, 18-H), 4.35 (H, m, 17-H), 4.24 (H, dt, *J* = 15.4 Hz, *J* = 5.0 Hz, 13^3-H^b), 3.90 (2H, q, *J* = 7.7 Hz, 3^1-CH_2), 3.80 (3H, s, 15^3-$COOCH_3$), 3.79 (2H, q, *J* = 7.7 Hz ,8^1-CH_2), 3.62 (3H, s, 17^4-$COOCH_3$), 3.57 (3H, s, 12-CH_3), 3.38 (3H, s, 2-CH_3), 3.34 (3H, s, 7-CH_3), 2.53 (H, m, 17^2-CH_2^a), 2.22 (H, m, 17^1- CH_2^a), 2.13 (H, m, 17^2-CH_2^b), 1.80 (H, m, 17^1- CH_2^b), 1.76 (3H, t, *J* = 7.7 Hz, 3^2-CH_3), 1.72 (3H, t, *J* = 7.7 Hz, 8^2-CH_3), 1.71 (3H, d, *J* = 7.4 Hz, 18-

CH_3), -1.70 (H, NH), -1.80 (H, NH). Mass spectrum (MALDI), *m/z*: 666.1 $(M)^+$. UV-VIS ($CHCl_3$), λ, nm (ε, M^{-1} cm^{-1}): 395 (113700), 496 (13600), 595 (5200), 650 (38900).

N-*Allylmesopurpurinimide methyl ester* **7**

Allylamine (2.5 ml, 32.5 mmol) was added to a solution of mesopurpurin methyl ester[4] (see Scheme 2) (105 mg, 0.181 mmol) in dichloromethane (3 ml) and the mixture was stirred for 30 min at room temperature. The reaction mixture was concentrated *in vacuo*, the residue was dissolved in dichloromethane (15 ml), an ethereal solution of diazomethane (3 ml) was added, and the resulting solution was stirred for 10 min at room temperature. The reaction mixture was concentrated *in vacuo*, the residue was dissolved in dichloromethane (7 ml), a 0.4 M solution of potassium hydroxide in methanol (0.5 ml) was added, and the resulting solution was stirred for 5 min at room temperature. The reaction mixture was diluted with dichloromethane (10 ml), water (150 ml) was added, and the mixture was extracted with dichloromethane (3x20 ml). The combined organic extracts were dried with anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using a dichloromethane/methanol system (49:1) as the eluent. The yield was 95 mg (85%).
^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.42 (H, s, 10-H), 9.07 (H, s, 5-H), 8.50 (H, s, 20-H), 6.31 (H, ddt, *J* = 17.1, 10.2, 5.5 Hz, 13^4-H), 5.55 (H, dq, *J* = 17.0, 1.6 Hz, 13^5-CH_2^E), 5.40 (H, m, 17-H), 5.34 (H, dq, *J* = 10.2, 1.5 Hz, 13^5-CH_2^Z), 5.15 (2H, dt, *J* = 5.3, 1.5 Hz, 13-CH_2), 4.36 (H, q, *J* = 7.3 Hz, 18-H), 3.74 (3H, s, 17^4-$COOCH_3$), 3.69 (2H, q, *J* = 7.7 Hz, 3^1-CH_2), 3.59 (3H, s, 12-CH_3), 3.50 (2H, q, *J* = 7.7 Hz, 8^1-CH_2), 3.23 (3H, s, 2-CH_3), 3.08 (3H, s, 7-CH_3), 2.73 (H, m, 17^2-CH_2^a), 2.46 (H, m, 17^1- CH_2^a), 2.36 (H, m, 17^2-CH_2^b), 2.03 (H, m, 17^1- CH_2^b), 1.79 (3H, d, *J* = 7.3 Hz, 18-CH_3), 1.68 (3H, t, *J* = 7.7 Hz, 3^2-CH_3), 1.61 (3H, t, *J* = 7.7 Hz, 8^2-CH_3), -0.01 (H, NH), -1.80 (H, NH). Mass spectrum (MALDI), *m/z*: 620.1 $(M)^+$, 642.1 $(M+Na)^+$. UV-VIS ($CHCl_3$), λ, nm (ε, M^{-1} cm^{-1}): 416 (133800), 477 (7300), 507 (10000), 545 (20500), 640 (7700), 698 (39400).

Tetraacetylgalactosylchlorin **8**

A solution of catalyst **4** (2.55 mg, 0.003 mmol) in dichloromethane (0.5 ml) was added to a solution of 17^3,15^2-dimethylmesochlorin e_6 13^1-*N*-allylamide **6** (40 mg, 0.06 mmol) and allyl-β-D-galactopyranoside peracetate **3** (117 mg, 0.30 mmol) in dichloromethane (2 ml) and the resulting mixture was refluxed. After 8 h, the reaction mixture was concentrated *in vacuo* and the residue was recrystallised from a chloform-hexane mixture in order to remove excess allyl-β-D-galactopyranoside. The residue was purified by preparative thin-layer chromatography in a dichloromethane/methanol system (19:1). The product was obtained as a mixture of *E/Z* isomers

(5:1) in 49 mg (80%) yield. The major *E*-isomer was isolated in 39 mg yield (64%) by means of preparative thin-layer chromatography, using 100% dichloromethane as the eluent.
NMR data are presented in Table 1S. Mass spectrum (MALDI), *m/z*: 1026 $(M)^+$. UV-VIS ($CHCl_3$), λ, nm (ε, M^{-1} cm^{-1}): 394 (114000), 495 (13300), 595 (5000), 650 (39000).

Tetraacetylgalactosylchlorin **9**

A solution of catalyst **4** (2.55 mg, 0.0033 mmol) in dichloromethane (0.5 ml) was added to a solution of *N*-allylmesopurpurinimide methyl ester **7** (40 mg, 0.065 mmol) and allyl-β-D-galactopyranoside peracetate **3** (127 mg, 0.0033 mmol) in dichloromethane (2 ml) and the resulting mixture was refluxed. After 16 h, the reaction mixture was concentrated *in vacuo* and the residue was recrystallised from a chloform-hexane mixture in order to remove excess allyl-β-D-galactopyranoside. The residue was purified by preparative thin-layer chromatography in a dichloromethane/methanol system (19:1). The product was obtained as a mixture of *E/Z* isomers (6:1) in 47 mg (75%) yield. The major *E*-isomer was isolated in 39 mg yield (62%) by means of preparative thin-layer chromatography, using 100% dichloromethane as the eluent.
NMR data are presented in Table 1S. Mass spectrum (MALDI), *m/z*: 980.2 $(M)^+$, 1003 $(M+Na)^+$. UV-VIS ($CHCl_3$), λ, nm (ε, $M^{-1}cm^{-1}$): 416 (133600), 477 (7000), 507 (9800), 545 (20200), 640 (7500), 697 (39100).

General method for the deacylation of galactosyl-containing glycoconjugates **5**, **8**, **9**

A 1 M solution of sodium methoxide (120 μl) in anhydrous methanol was added to a solution of the corresponding glycoconjugate (0.03 mmol) in dichloromethane (2 ml) and the mixture was stirred for 1 h at room temperature. After that, glacial acetic acid (7 μl) was added, the mixture was washed with water (20 ml) and extracted with dichloromethane (5x10 ml). The combined extracts were dried with anhydrous sodium sulfate, concentrated *in vacuo*, and chromatographed on a plate using a 10% methanol/dichloromethane system as the eluent.

Galactosylchlorin – deacylated **5**

Yield 83%. Mass spectrum (MALDI), *m/z*: 832.2 (M^+), 853.2 $(M+Na)^+$. UV-VIS (H_2O/1% Cremophore), λ, nm (ε, M^{-1} cm^{-1}): 404 (142000), 505 (15000), 531 (8000), 610 (6000), 666 (43500).

Galactosylchlorin – deacylated **8**

Yield 85%. Mass spectrum (MALDI), *m/z*: 858.3 (M^+), $(M+Na)^+$ 880.3, 896.3 $(M+K)^+$. UV-VIS (H_2O/1% Cremophore), λ, nm (ε, M^{-1} cm^{-1}): 395 (114000), 497 (13300), 598 (5100), 650 (40000).

Galactosylchlorin – deacylated **9**

Yield 65%. Mass spectrum (MALDI), *m/z*: 812.4 (M^+), 834.3 $(M+Na)^+$, 850.4 $(M+K)^+$. UV-VIS (H_2O/1% Cremophore), λ, nm (ε, M^{-1} cm^{-1}): 415 (134000), 480 (7000), 510 (10000), 545 (20000), 640 (7500), 698 (40000).

Table 1S ^1H and ^{13}C NMR data for galactosylchlorins **5, 8** and **9**.

Chlorin e_6/p_6 ("**Chl**")							
^{13}C	δ			^1H	δ, multiplicity,* *J*, Hz		
	5	**8**	**9**		**5**	**8**	**9**
				NH(A)	-1.28, s	-1.60, s	0.10, s
				NH(B)	-1.46, s	-1.68, s	-0.09, s
C-1	139.3	130.1	143.9				
C-2	130.3	139.9	131.1				
C-2^1 (-CH_3)	12.3	10.9	10.7	H-2^1	3.46, s	3.37, s	3.23, s
C-3	133.4	140.8	136.8				
C-3^1	124.5	19.3	19.2	H-3^1	7.94, **dt,** *16.2, 1.6*	3.90, q, *7.7*	3.74, q, *7.7*
C-3^2	131.9	17.1	16.8	H-3^2	6.81, **dt,** *16.2, 5.5*	1.76, t, *7.7*	1.69, t, *7.7*
C-3^3	70.5			H-3^{3a} H-3^{3b}	4.95, **ddd,** *13,5, 5.2, 1.6* 4.67, **ddd,** *13.5, 5.8, 1.6*		
C-4	135.3	135.7	143.3				
C-5 (-CH=)	98.5	97.5	101.2	H-5	9.53, s	9.46, s	9.17, s
C-6	154.7	154.3	155.5				
C-7	136.0	135.6	135.8				
C-7^1 (-CH_3)	11.3	11.3	11.1	H-7^1	3.33, s	3.34, s	3.16, s
C-8	145.0	144.9	145.6				
C-8^1	19.6	19.7	19.3	H-8^1	3.80, q, *7.7*	3.81, q, *7.7*	3.62, q, *7.7*
C-8^2	17.6	17.7	17.4	H-8^2	1.73, t, *7.7*	1.72, t, *7.7*	1.66, t, *7.7*
C-9	149.0	148.5	149.4				
C-10 (-CH=)	102.1	101.7	107.0	H-10	9.71, s	9.70, s	9.55, s
C-11	129.4	129.3	138.9				
C-12	136.6	134.3	131.3				
C-12^1 (-CH_3)	12.4	12.0	12.4	H-12^1	3.59, s	3.57, s	3.79, s
C-13	123.5	127.3	115.3				
C-13^1 (>C=O)	170.4	169.5	163.1				
C-13^2	53.0			H-13^2	4.27, s	6.58, t, *5.4*	
C-13^3		42.0	41.1	H-13^3		4.53 (-) 4.22 (-)	5.12, m
C-13^4		129.0	129.8	H-13^4		6.03, **dt,** *15.6, 6.2*	6.18, **dt,** *15.7, 6.1*
C-13^5		128.5	127.8	H-13^5		5.59, **dt,** *15.6, 5.9*	6.02, **dt,** *15.7, 6.0*
C-13^6		69.0	69.0	H-13^{6a} H-13^{6b}		4.40, **dd,** *13.2, 5.2* 4.18, (-)	4.42, **dd,** *13.6, 5.2* 4.24, **dd,** *13.6, 6.7*
C-14	135.5	134.5	137.3				
C-15	102.3	101.8	97.3				
C-15^1	38.5	37.9	167.2	H-15^{1a} H-15^{1b}	5.37, **d,** *19.0* 5.25, **d,** *19.0*	5.52, **d,** *19.2* 5.26 **d,** *19.2*	
C-15^2 (>C=O)	172.9	174.0					
C-15^3 (-CH_3)	52.1	52.1		H-15^4	3.78, s	3.79, s	
C-16	167.0	166.1	176.6				
C-17	52.9	52.9	54.6	H-17	4.42, m	4.36, m	5.35, m
C-17^1 (-CH_2-)	29.5	29.7	31.3	H-17^{1a} H-17^{1b}	2.22, m 1.78, m	2.21, m 1.81, m	2.43, m 2.00, m
C-17^2 (-CH_2-)	31.0	31.1	32.3	H-17^{2a} H-17^{2b}	2.57, m 2.19, m	2.54, m 2.12, m	2.67, m 2.32, m

C-17[3] (>C=O)	173.5	173.5	173.8				
C-17[4] (-CH_3)	51.6	51.5	51.4	H-17[5]	3.64, s	3.61, s	3.55, s
C-18	49.3	49.3	49.2	H-18	4.46, q, *7.3*	4.46, q, *7.3*	4.34, q, *7.4*
C-18[1] (-CH_3)	22.9	22.9	23.8	H-18[1]	1.77, **d,** *7.3*	1.74, **d,** *7.3*	1.75, **d,** *7.4*
C-19	169.4	169.4	175.7				
C-20 (-CH=)	93.6	93.0	94.2	H-20	8.76, s	8.73, s	8.49, s

β-D-galactopyranose **("Gal")**							
^{13}C	δ			^{1}H	δ, multiplicity,* *J*, Hz		
	5	**8**	**9**		**5**	**8**	**9**
C-1	100.7	100.3	99.6	H-1	4.88, **d,** *8.1*	4.54, **d,** *8.0*	4.62, **d,** *8.1*
C-2	69.0	68.8	68.9	H-2	5.50, **dd,** *10.5, 8.1*	5.26, **dd,** *10.4, 8.2*	5.23, **dd,** *104, 8.1*
C-3	71.0	70.9	71.1	H-3	5.20, **dd,** *10.5, 3.5*	5.04, **dd,** *10.4, 3.3*	5.05, **dd,** *10.4, 3.5*
C-4	67.1	67.1	67.2	H-4	5.52, **dd,** *3.5, 1.1*	5.40, **d,** *3.5*	5.37, **d,** *3.7*
C-5	70.9	70.7	70.6	H-5	4.10, **td,** *6.6, 1.1*	3.89, (-)	3.92, t, ***6.7***
C-6	61.4	61.2	61.3	H-6[a]	4.34, **dd,** *11.2, 6.4*	4.19, **dd,** *11.2, 6.4*	4.14, **dd,** *11.2, 6.4*
				H-6[b]	4.28, **dd,** *11.2, 7.0*	4.13, **dd,** *11.2, 7.0*	4.11, **dd,** *11.2, 7.0*
OAc (CO)	169.4-170.2	169.4-170.3	169.5-170.3				
OAc (CH_3)	20.6-20.9	20.5-20.8	20.5-20.7	OAc	2.06-2.24, s	1.99-2.16, s	1.96-2.12, s

* (-) signals with unidentified multiplicity

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