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Note

Synthesis of 1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3-diiodo-1-propene and its reaction with primary amines ☆

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ABSTRACT

Iodination of 1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene affords an *E*/*Z*-mixture of 1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3-diiodo-1-propene. S_N2 displacement of the allylic iodide with primary amines affords an *E*/*Z*-mixture of allylic amines under a variety of conditions. Due to its experimental simplicity and low cost of reagents, this procedure may find wide use in the laboratory for functionalization of sugar allenes.

Carbohydrate-based starting materials are widely used in target-oriented syntheses of optically active compounds.[1] C-Glycosylic compounds ('C-glycosides') with unsaturated aglycones are useful for further functionalization purposes because of their potential for the introduction of new stereogenic centers in the side chain.[2] The addition of iodine to allene is well established;[3–5] however, this type of reaction has not been reported for sugar allenes. In this communication, we report the addition of iodine to 1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**)[6] in a variety of organic solvents and the subsequent S_N2 displacement of the allylic iodide in the diiodo addition products with primary amines. We found that in all cases an *E*/*Z*-mixture of *E*-**2** and *Z*-**2** was formed and that the *E*/*Z* ratio was influenced by the solvent, time, and temperature[7] (Table 1).

In Table 1 EtOH is identified as the best solvent for the reactions studied. The products were formed by addition of iodine to the terminal π-bond of the allene moiety. The other regioisomer resulting from I_2 addition to the internal π-bond of allene (**1**) was not observed. Selectivity for (*Z*)-**2** increased with increasing reaction time and temperature (Table 1, entries 5, 7, and 8), and further studies of this trend are needed. The *E*/*Z*-isomerization of the diiodides is presumed to proceed via a radical mechanism[7] involving excess I_2 (Scheme 1).

The olefin geometry was assigned on the basis of the chemical shift of the vinylic protons in the ^{1}H NMR spectrum of the diiodide reaction mixture. The vinyl proton resonance for the major ***Z*-2** (δ 6.36) is 0.04 ppm upfield from the corresponding resonance for the *E*-isomer ***E*-2** (δ 6.40). This assignment was also confirmed by appropriate NOE experiments (Fig. 1).

Irradiation at the resonance frequency of H_3 in the *Z*-isomer ***Z*-2** (δ 6.36) resulted in an enhancement of the H_4 and H_{1a} resonances of 8.5 and 6.3%, respectively, whilst irradiation at the analogous resonance frequency of the *E*-isomer ***E*-2** (δ 6.40) did not result in any enhancement of H_{1a} or H_{1b} but gave a 5.1% enhancement of H_4.

The crude (1:1.9-*E*/*Z*)-mixture of allylic iodides **2** was subjected to S_N2 displacement with benzylamine nucleophiles **4a, b** varying both solvent (CH_2Cl_2, THF) and base (Et_3N, K_2CO_3). Part of this study is summarized in Table 2.

The geometry of ***E*-5a** and ***Z*-5a** was determined by NOE experiments as shown in Figure 2.

In conclusion, we have established a simple route from 1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) to (*E*/*Z*)-1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3-diiodo-1-propene (**2**) in >95% yield. Regioselective substitution of the allylic diiodide by benzylamines can be achieved in moderate to good yield (Table 2, entries 1 and 6).

1. Experimental

1.1. General methods

All reagents were commercially available and used without purification. Flash column chromatography was performed using

☆ IUPAC nomenclature: (2*E*/2*Z*)-5*S*,6*R*,7*S*,9-tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-1,2-diiodonon-2-enitol.

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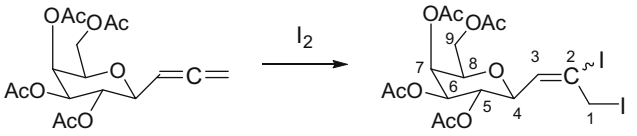
Table 1
The reaction of β-C-galactose allene (**1**) with iodine[a]



1 **2**

Entry	Solvent	Temperature[b] (°C)	Time[c] (h)	Yield[d] (%)	*E*/*Z*[e]
1	CH_2Cl_2	rt	48	20	1:2.3
2	CH_2Cl_2	40	24	25	1:1.7
3	MeOH	rt	24	30	1:1.9
4	MeOH	70	3	40	1:2.3
5	EtOH	80	3	92	1:1.9
6	MeC_6H_5	90	3	22	1:1.5
7	EtOH	Reflux	3	96	1:3.2
8	EtOH	Reflux	1.5	97	1:1.7
9	CH_3CN	Reflux	1.5	81	1:4.1

[a] Compound **1** (0.540 mmol), I_2 (0.594 mmol), and 20 mL of solvent were used.
[b] Oil bath temperature except where noted.
[c] TLC monitoring to 100% completion.
[d] Isolated yield.
[e] Ratios were determined by ^{1}H NMR.

Silica Gel 60 (230–400 mesh). Optical rotations were measured on an AA-100 polarimeter at room temperature and are given in 10^{-1} deg cm^2 g^{-1}. Accurate molecular masses were recorded on a Bruker micrOTOF instrument. Infrared spectra were recorded using a Perkin–Elmer FTIR spectrometer. The IR samples were prepared as thin films by evaporation of a solution of the compound in CH_2Cl_2 onto a germanium plate. Nuclear magnetic resonance spectra were determined at 500 MHz (^{1}H) and at 75 MHz (^{13}C) on Bruker spectrometers. Chemical shift values are quoted in parts per million (ppm) downfield from TMS, and coupling constants are in hertz. Chemical shift multiplicities are reported as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad, and br s = broad singlet, app. t = apparent triplet. 1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) was prepared according to a literature method.[6]

1.2. (2*E*)-5*S*,6*R*,7*S*,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-1,2-diiodonon-2-enitol (*E*-2) and (2*Z*)-5*S*,6*R*,7*S*,9-Tetra-*O*-acetyl-4,8-anhydro-1,2,3-trideoxy-1,2-diiodonon-2-enitol (*Z*-2)

Iodine (0.754 g, 2.970 mmol) was added to a stirred solution of the 1-*C*-(tetra-*O*-acetyl-β-D-galactopyranosyl)allene (**1**) (1.0 g, 2.7 mmol) in EtOH (200 mL).The resulting mixture was stirred and heated under reflux for 3 h. The solvent was then removed, the residue was dissolved in Et_2O (100 mL), and the solution was sequentially washed with satd sodium thiosulfate (100 mL), satd $NaHCO_3$ (100 mL), and satd brine (100 mL). The organic layer was separated, dried (Na_2SO_4), and filtered, and the filtrate evaporated under reduced pressure. Purification of the residue by flash column chromatography, eluting with 2:1 hexane–Et_2O, gave a 1:3.2 mixture of *E*- and *Z*-**2** as a pale-yellow gum (1.61 g, 2.59 mmol, 96%).

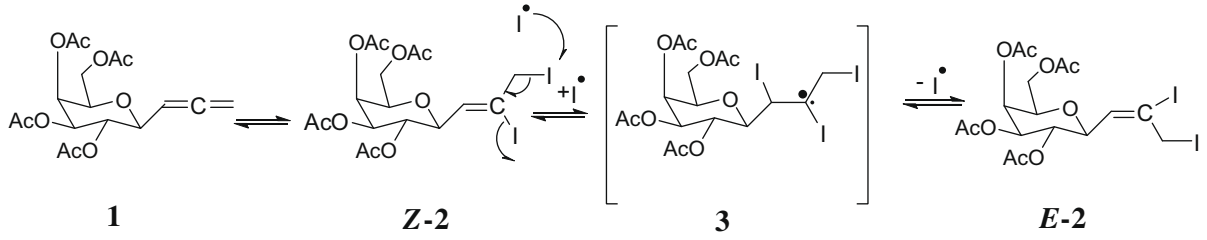
Gradient flash column chromatography of the mixture of *E*- and *Z*-**2** with 3:1 to 2:1 hexane–Et_2O afforded partial separation of *E*- and *Z*-**2** with some fractions containing mixtures of *E*- and *Z*-**2**.

1.2.1. Data for *E*-2

Pale-yellow gum; $[\alpha]_D^{24}$ +238.5 (*c* 0.218, $CHCl_3$); IR (film): 2971, 2121, 1737, 1615, 1423, 1366, 753, 600, 542 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.4 (1H, d, *J* 6.4, 3-H), 5.42–5.44 (1H, m, 7-H), 5.3 (1H, dd, *J* 10.7 and 6.0, 5-H), 5.17 (1H, dd, *J* 10.7 and 3.0, 6-H), 4.8 (1H, app t, *J* 6.0 and 5.95, 4-H), 4.56 and 4.37 (2H, 2 × d, *J* 10.25, 1-H), 4.0–4.2 (3H, m, 8-H and 2 × 9-H), 2.1, 2.08, 2.03 and 2.01 (12H, 4 × s, 4 × OCOMe); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 169.1, 169.0, 168.8, 134.2, 129.2, 107.4, 69.7, 68.0, 67.0, 66.4, 65.7, 60.2, 20.9, 19.8, 19.7, 19.6; ESIMS (positive-ion): *m*/*z* 625 (MH^+, 100); HRMS: calcd for $C_{17}H_{22}I_2NaO_9$ (M + Na): 646.9245; found: 646.9255.

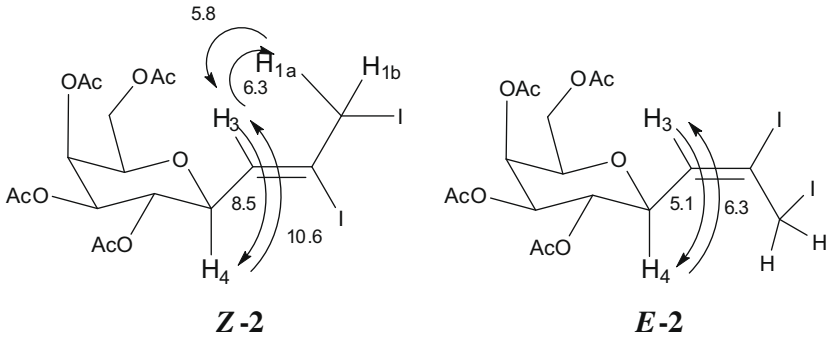
1.2.2. Data for *Z*-2

Pale-yellow gum; $[\alpha]_D^{24}$ +253.5 (*c* 0.493, $CHCl_3$); IR (film): 2971, 2121, 1737, 1615, 1423, 1366, 753, 600, 542 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.36 (1H, d, *J* 7.7, 3-H), 5.42–5.46 (1H, m, 7-H), 5.36 (1H, dd, *J* 10.25 and 6.0, 5-H), 5.18 (1H, dd, *J* 10.25 and 3.0, 6-H), 4.78 (1H, app. t, *J* 6.85 and 6.4, 4-H), 4.50 and 4.45 (2H,



1 ***Z*-2** **3** ***E*-2**

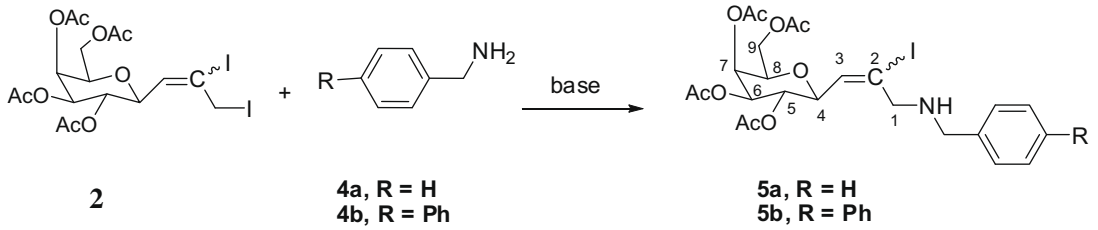
Scheme 1. Proposed *E*/*Z* isomerization mechanism.



***Z*-2** ***E*-2**

Figure 1. NOE data for ***E*-2** and ***Z*-2**.

Table 2
The reaction of diiodide **2** with primary amines under different reaction conditions[a]



Entry	Nucleophile	Base (mol equiv)	Solvent	Temperature (°C)	Time[b] (h)	Product, yield[c] (%)	*E*:*Z*
1	**4a**	Et_3N (1.1)	CH_2Cl_2	rt	24	**5a** (45)	1:1.25
2	**4a**	Et_3N (2)	CH_2Cl_2	rt	24	**5a** (27)	1:1.25
3	**4a**	Et_3N (1.1)	CH_2Cl_2	40	12	**5a** (22)	1:1.2
4	**4b**	Et_3N (1.1)	CH_2Cl_2	rt	24	**5b** (53)	1:1.3
5	**4b**	Et_3N (1.1)	THF	rt	24	**5b** (25)	1:1.5
6	**4b**	K_2CO_3 (5)	CH_2Cl_2	Reflux	24	**5b** (79)	1:2.16
7	**4a**	K_2CO_3 (5)	CH_2Cl_2	Reflux	24	**5a** (25)	1:1.5

[a] Compound **2** (1: 1.9-*E*/*Z*-mixture) (0.33 mmol), nucleophile (1.1 mol equiv), and 5 mL of solvent were used.
[b] Reaction monitored by TLC.
[c] Isolated yield.

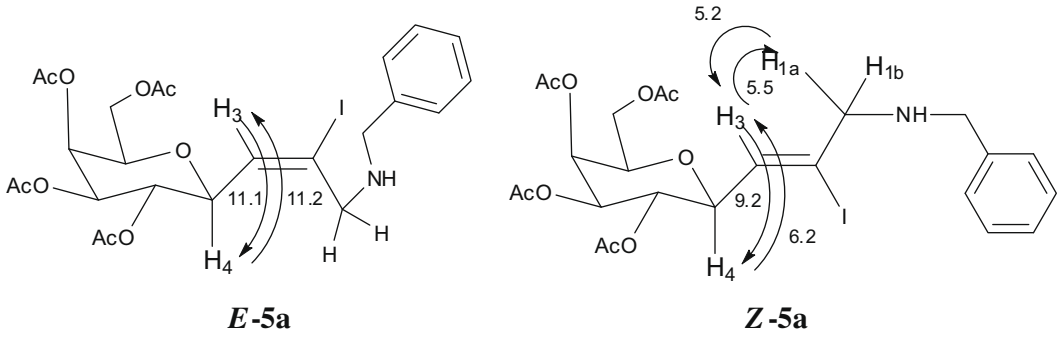


Figure 2. NOE data for ***E*-5a** and ***Z*-5a**.

2 × d, *J* 10.25, 1-H), 4.05–4.15 (2H, m, 2 × 9-H), 4.02 (1H, app t, *J* 6.0 and 5.1), 2.1, 2.06 and 2.03 (12H, 4 × s, 4 × OCOMe); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 170.56, 170.52, 170.2, 130.6, 76.6, 69.9, 69.0, 67.8, 67.5, 62.0, 21.2, 21.1, 21.0; ESIMS (positive-ion): *m*/*z* 625 (MH^+, 100); HRMS: calcd for $C_{17}H_{22}I_2NaO_9$ (M+Na): 646.9245; found: 646.9255.

1.3. General procedure for the reaction of 2 with primary amines

A 1:1.9 mixture of *E*- and *Z*-**2** (0.33 mmol) was dissolved in CH_2Cl_2 (5 mL), and K_2CO_3 (5.0 mol equiv) or Et_3N (1.1 mol equiv), and amine (1.1 mol equiv) were added. The resulting mixture was stirred and heated under reflux for 24 h, cooled, poured into water, and extracted with CH_2Cl_2 (2 × 20 mL). The organic layer was separated and washed with water (2 × 50 mL), dried (Na_2SO_4), and filtered, and the filtrate was evaporated. Purification of the residue by flash column chromatography afforded the product.

1.3.1. (2*E*)-5*S*,6*R*,7*S*,9-Tetra-*O*-acetyl-4,8-anhydro-1-(benzylamino)-1,2,3-trideoxy-2-iodonon-2-enitol (*E*-5a) and (2*Z*)-5*S*,6*R*,7*S*,9-tetra-*O*-acetyl-4,8-anhydro-1-(benzylamino)-1,2,3-trideoxy-2-iodonon-2-enitol (*Z*-5a)

Compounds *E*-**5a** and *Z*-**5a** were prepared by the general procedure from 1:1.9-*E*/*Z*-**2** (0.400 g, 0.641 mmol) in CH_2Cl_2 (7 mL), K_2CO_3 (0.442 g, 3.205 mmol), and benzylamine (**4a**) (0.075 g, 0.705 mmol) under reflux for 24 h. Purification of the residue by gradient elution flash column chromatography with 1:1 to 1:2 hexane–EtOAc afforded ***E*-5a** (0.096 g, 0.160 mmol, 25%) and ***Z*-5a** (0.208 g, 0.346 mmol, 54%) as pale-yellow gums.

1.3.1.1. Data for E-5a. $[\alpha]_D^{24}$ −190.7 (*c* 1.206, $CHCl_3$); IR (film): 3473, 2970, 1739, 1624, 1489, 1434, 1365, 1217, 701, 538 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.33 (5H, m, Ar-H),6.6 (1H, d, *J* 6.8, 3-H), 5.41–5.42 (1H, m, 7-H), 5.2–5.26 (2H, m, 5-H and 6-H), 4.9 (1H, app t, *J* 6.3 and 6.2, 4-H), 4.4.0–4.1 (3H, m, 8-H and 2 × 9-H), 3.7 and 3.6 (2H, 2d, *J* 12.9, NCH_2Ph), 3.5 and 3.4(2H, 2d, *J* 14.8, 2 × 1-H), 2.1, 2.06, 2.01 and 1.96 (12H, 4 × s, 4 × OCOMe); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 170.6, 170.5, 170.2, 139.2, 135.4, 128.9, 128.7, 127.1, 117.5, 70.9, 69.2, 68.4, 68.1, 67.5, 62.1, 54.2, 52.1, 21.6, 21.2; ESIMS (positive-ion): *m*/*z* 604 (MH^+, 100); HRMS: calcd for $C_{24}H_{31}INO_9$ (M+H): 604.1049; found: 604.1070.

1.3.1.2. Data for Z-5a. $[\alpha]_D^{24}$ +107.2 (*c* 1.212, $CHCl_3$); IR (film): 3473, 2970, 1739, 1624, 1489, 1434, 1365, 1217, 701, 538 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34–7.35 (5H, m, Ar-H), 6.2 (1H, d, *J* 7.7, 3-H), 5.44 (1H, dd, J 3.3 and 1.6, 7-H), 5.41 (1H, dd, *J* 10.3 and 5.9, 5-H), 5.2 (1H, dd, *J* 10.3 and 3.3, 6-H), 4.78 (1H, dd, *J* 7.7 and 5.9, 4-H), 4.0–4.2 (3H, m, 6-H and 2 × 9-H), 3.7 and 3.68 (2H, 2d, *J*,13.0, 2 × 1-H), 3.57 and 3.53 (2H, 2d, *J* 15.5, NCH_2Ph), 2.1, 2.04 and 2.02 (12H, 4 × s, 4 × OCOMe); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 170.6, 170.5, 170.2, 139.7, 129.0, 128.7, 128.2,

127.7, 119.5, 76.5, 69.7, 69.0, 67.9, 67.6, 62.1, 61.0, 51.4, 21.3, 21.2, 21.1, 21.0; ESIMS (positive-ion): *m/z* 604 (MH^+, 100); HRMS: calcd for $C_{24}H_{31}INO_9$ (M+H): 604.1049; found: 604.1070.

1.3.2. (2*E*)-5*S*,6*R*,7*S*,9-Tetra-*O*-acetyl-4,8-anhydro-1-[(biphenyl-4-ylmethyl)amino]-1,2,3-trideoxy-2-iodonon-2-enitol (*E*-5b) and (2*Z*)-5*S*,6*R*,7*S*,9-tetra-*O*-acetyl-4,8-anhydro-1-[(biphenyl-4-ylmethyl)amino]-1,2,3-trideoxy-2-iodonon-2-enitol (*Z*-5b)

Compounds *E*/*Z* **5b** were prepared by the general procedure from 1:1.9-*E*/*Z*-**2** (0.400 g, 0.641 mmol) in CH_2Cl_2 (7 mL), Et_3N (0.071 g, 0.705 mmol) and 1-biphenyl-4-ylmethanamine (**4b**) (0.128 g, 0.705 mmol) at room temperature for 24 h. Workup, followed by gradient elution flash column chromatography with 1:1 to 1:2 hexane–EtOAc, afforded ***E*-5b** (0.088 g, 0.147 mmol, 23%) and ***Z*-5b** (0.116 g, 0.192 mmol, 30%) as pale-yellow gums.

1.3.2.1. Data for *E*-5b. $[\alpha]_D^{24}$ −110.7 (*c* 0.659, $CHCl_3$); IR (film): 3474, 3003, 2970, 1742, 1488, 1435, 1366, 1228, 1217, 1084, 1053, 911, 765, 700, 530 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.5 and 7.6 (4H, 2d, *J* 7.7, Ar-H), 7.3–7.45 (5H, m, Ar-H), 6.6 (1H, d, *J* 6.8, 3-H), 5.4–5.45 (1H, m, 7-H), 5.26 (1H, dd, *J* 10.6 and 5.6, 5-H), 5.2 (1H, dd, *J* 10.3 and 3, 6-H), 4.95 (1H, app t, *J* 6.4 and 6.0, 4-H), 4.0–4.1 (3H, m, 8-H and 2 × 9-H), 3.76 and 3.68 (2H, 2d, *J* 13.25, 2 × 1-H), 3.5 and 3.4 (2H, 2d, *J* 14.6, NCH_2Ar), 2.1, 2.07, 2.0 and 1.97 (12H, 4 × s, 4 × OCOMe); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 170.6, 170.5, 170.2, 141.2, 140.6, 138.9, 135.4, 129.2, 129.1, 127.7, 127.6, 127.4, 117.8, 71.0, 69.1, 68.4, 68.1, 67.5, 62.1, 54.3, 51.8, 21.3, 21.2, 21.0; ESIMS (positive-ion): *m/z* 680 (MH^+, 100); HRMS: calcd for $C_{30}H_{35}INO_9$ (M+H): 680.1351; found: 680.1365.

1.3.2.2. Data for (*Z*-5b). $[\alpha]_D^{24}$ +234.9 (*c* 0.166, $CHCl_3$); IR (film): 3474, 3003, 2970, 1742, 1488, 1435, 1366, 1228, 1217, 1084, 1053, 911, 765, 700, 530 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.6 (4H, app t, *J* 7.7 and 6.8, Ar-H), 7.4–7.45 (4H, m, 4 × Ar-H), 7.34 (1H, t, *J* 7.25, Ar-H), 6.25 (1H, d, *J* 7.7, 3-H), 5.43–5.45 (1H, m, 7-H), 5.41 (1H, dd, *J* 10.3 and 5.95, 5-H), 5.2 (1H, dd, *J* 10.3 and 3.0, 6-H), 4.95 (1H, app t, *J* 6.8 and 6.4, 4-H), 4.05–4.17 (3H, m, 8-H and 2 × 9-H), 3.75 and 3.72 (2H, 2d, *J* 13.25, 2 × 1-H), 3.59 and 3.55 (2H, 2d, *J* 15.8, NCH_2Ar), 2.17, 2.15, 2.03 and 2.02 (12H, 4 × s, 4 × OCOMe); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 170.1, 170.0, 169.7, 140.8, 140.2, 138.4, 128.7, 127.9, 127.3, 127.2, 127.0, 119.1, 76.1, 69.3, 68.5, 68.3, 67.5, 67.2, 61.7, 60.5, 50.7, 20.9, 20.8, 20.7, 20.6; ESIMS (positive-ion): *m/z* 680 (MH^+, 100); HRMS: calcd for $C_{30}H_{35}INO_9$ (M+H): 680.1351; found: 680.1365.

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