Carbohydrate Research 406 (2015) 86–92

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Ruthenium catalyzed synthesis of 2,3-unsaturated *C*-glycosides from glycals

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ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form
12 January 2015
Accepted 20 January 2015
Available online 29 January 2015

Keywords:
Glycal
Ferrier glycosylation
C-glycosides
Stereoselective synthesis
Ruthenium trichloride

ABSTRACT

A highly efficient and convenient C-glycosylation method was developed using ruthenium(III) chloride for the synthesis of 2,3-unsaturated *C*-glycosides. Various nucleophiles such as allyl trimethylsilane, triethylsilane, trimethylsilyl cyanide, trimethylsilyl azide and heterocycles such as thiophene and furan reacted smoothly with glycals in the presence of catalytic amount of ruthenium trichloride under mild reaction conditions.

1. Introduction

The *C*-glycosides are subject of considerable interest due to the role played by them as versatile chiral synthons and key intermediates for the synthesis of several carbohydrate compounds of biological significance.[1] Significantly, the *C*-glycosides are utilized as valuable intermediates in the synthesis of several natural products such as palytoxin, spongistatin, halichondrin,[2] and various functionalized β-*C*-saccharides.[3] Furthermore, they are employed as powerful synthetic tools for the synthesis of modified carbohydrates and analogs of naturally occurring *C*-nucleosides antibiotics[4] and *C*-linked α(2,3)sialylgalactose lactone.[5] Besides, the *C*-glycosides are more stable to hydrolytic cleavage hence utilized as glycosidase inhibitors and served as potential therapeutic agents for understanding the mechanism of carbohydrate-processing enzymes and other critical cellular processes.[6] Particularly, 2,3-unsaturated *C*-glycosides are attractive due to the presence of 2,3-olefinic moiety in pyran rings, which could be further functionalized into other carbohydrates derivatives and useful chiral molecules by using various complexity generating reactions.[7]

As evident, several reagent systems have been evolved to effect the Ferrier glycosylation of glycals to obtain 2,3-unsaturated *C*-glycosides.[8] Another reported procedure for the synthesis of 2,3-unsaturated *C*-glycosides involves a two step process, Tebbe methylenation and thermal Claisen rearrangement[9a] On the other hand, the scope of Pd-mediated glycosylation[9b,c] has been demonstrated in the stereoselective and regioselective construction of glycosidic linkage via a Pd π-allyl intermediate. However, a combination of Pd-catalyst and phosphine ligand with a sub-stoichiometric amount of diethyl zinc as an additive at high temperature is required for the success of these reactions. In a recent report,[9d] Mukherjee and co-worker developed a highly efficient and reliable catalytic system for the C-glycosylation of glycals with unactivated alkynes using a combination of $Cu(OTf)_2$ and ascorbic acid. Similarly, the Ferrier-type C-alkynylations with silylacetylene[9e] and alkynyltrifluoroborates[9f] compounds have been reported using stoichiometric amount of $BF_3 \cdot OEt_2$. However, the indium-mediated C-alkynylation with iodoalkynes using Barbier reaction required refluxing conditions and excess loading of indium metal and iodoalkyne.[9g]

Over the decade, the palladium-catalyzed Heck reaction has been employed for the syntheses of aryl-*C*-glycosides[10] by cross coupling of glycals with aryl halides,[10b,c] aryl boronic acids,[10d,e] and benzoic acids.[10f] More recently, Liu and co-worker demonstrated the synthesis of aryl-*C*-glycosides by a Pd-catalyzed oxidative Heck cross-coupling of inactivated glycals and aryl hydrazines.[10g] However the Heck type C-glycosylation represent a significant approach of aryl-C-glycosylation, with restricted substrate scope, use for expensive and relatively toxic reagents, wherein less stable and

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http://dx.doi.org/10.1016/j.carres.2015.01.009
0008-6215/

moisture sensitive organometallic compounds, use of additives such as strong bases and phosphine ligands,[10b] harsh conditions and tedious work-up remains unsolved issues. Therefore, the development of an efficient and general protocol utilizing nontoxic and environmental friendly reagent system is desirable for the synthesis of *C*-glycosides and carbohydrate intermediates en route to several biologically important sugar molecules.

2. Results and discussion

Recently, we have demonstrated the expeditious synthesis of α-D-mannopyranosides and 2,3-unsaturated O-glycosides from glycal employing ruthenium catalysis.[11b,d] In continuation of our research interest towards developing efficient glycosylation methods,[11] we envisioned that the use of ruthenium(III) chloride as eco-friendly and economical catalyst would be advantage in the carbohydrate chemistry particularly in the *C*-glycosides syntheses. Herein, we report a novel, convenient and efficient method for the C-glycosylation using ruthenium(III) chloride as a versatile and efficient catalyst under mild reaction conditions.

To begin with, the C-glycosylation reactions were optimized using 3,4,6-tri-O-acetyl glucal (**1a**) as the glycal donor and allyl trimethylsilane (**2a**) as the model acceptor in different organic solvents, results are summarized in Table 1. In initial experiments, the C-glycosylation coupling reaction of compound **1a** with **2a** was carried out in the presence of 5 mol % of $RuCl_3$ in dichloromethane at room temperature. Whilst moderate conversion was observed in 8 h, the rate of conversion improved to 80% at 40 °C and the corresponding 4,6-di-O-acetyl-2,3-unsaturated *C*-allylglucoside (**3a**) was obtained in 65% yield with an α/β ratio of 90:10 (Table 1, entry 2). However, no improvement was realized when 1,2-dichloroethane was used as solvent (Table 1, entries 3,4).

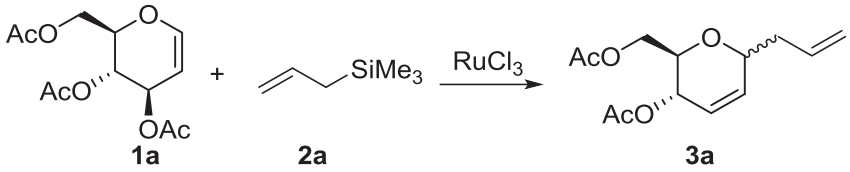
Remarkably, when acetonitrile was employed as the solvent, the reaction proceeded smoothly at room temperature and furnished **3a** in excellent yield (96%) and high selectivity (α:β, 96:4) within 30 min (Table 1, entry 5). On the other hand, solvents such as toluene, THF, diethyl ether could not afford any desired *C*-glycoside. Notably, when the catalytic quantity was further decreased to 2 mol %, reaction was slow and sluggish (Table 1, entries 6,7). Nevertheless, acetonitrile as the solvent in the presence of 5 mol % $RuCl_3$ was found to be optimal requirement for the C-glycosylation of glycals.

The structure and stereochemistry of compound **3a** was established through spectroscopic analysis and correlated with that of literature data.[12a] The ^{1}H NMR spectrum of **3a** revealed the absence of characteristic resonance due to anomeric proton of glucal **1a** at δ 6.47 (d, $J_{1\text{-}2}$=6.2 Hz, 1H), whilst anomeric proton of *C*-glycoside **3a** was observed at δ 4.29 (ddd, *J*=7.7, 5.7, 1.9 Hz, 1H). Furthermore, the ^{13}C spectrum of *C*-glycoside **3a** unambiguously proved the presence of olefinic carbons at δ 133.8, 132.6, 123.5 and 117.4 ppm, whilst all other resonances were in complete agreement with the assigned structure. In addition, compound **3a** gave satisfactory MS/HRMS analysis [HRMS (ESI) *m*/*z* $[M+Na]^+$ calcd for $C_{13}H_{18}O_5Na^+$: 277.10464; found: 277.10428].

Next, we investigated the generality of the current protocol for various silylated *C*-nucleophiles under optimized condition. Accordingly, the C-glycosylation reactions of glycal **1a** with trimethylsilyl cyanide (**2b**) and triethylsilane (**2c**) furnished glycosyl cyanide **3b** and 2,3-unsaturated glycoside **3c**, respectively in excellent yields (Table 2, entry 1,2). Interestingly, the reaction of trimethylsilyl azide (**2d**) as the acceptor with glycal **1a** afforded a mixture of the *C*-3 azido glycal (**3d**) with epimeric ratio of 72:28 and the *C*-1 glycosyl azide (**3d′**) with an α/β ratio of 89:11 (Table 2, entry 3). The anomeric and epimeric ratios were measured by ^{1}H NMR spectroscopy by relative integration of anomeric or separable protons. These results were consistent and with conformity with that of observed by other research groups.[12a,b] The silyl enol ether **2e** worked equally well to obtain the corresponding *C*-glycosides **3e** in 95% yield as stereoisomeric mixture due to prochirality at α-carbon (entry 4). Similarly, the C-glycosylation of β-keto ester **2f** proceeded efficiently to afford the corresponding 2,3-unsaturated *C*-glycoside **3f** in high yield as a stereoisomeric mixture. It is pertinent to mention that the *C*-glycosides such as allyl glycosides, glycosyl azide and glycosyl cyanides offers further synthetic usefulness in the construction of carbon chains into sugar core and the preparation of glycopeptides and glycoconjugates bearing chiral sugar-scaffolds.[13]

Encouraged by these results, we next focused on coupling of heterocycles using present protocol to obtain sugar-heterocycles hybrid *C*-glycosides, since these compounds have significant synthetic utility for the preparation of biologically active molecules with potent antiviral and anticancer activities.[14] Accordingly, the Ferrier C-glycosylation of **1a** with thiophene (**2g**) in the presence of 5 mol % $RuCl_3$ in acetonitrile at ambient temperature resulted the

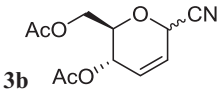
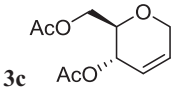
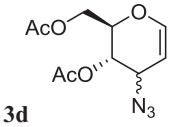
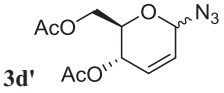
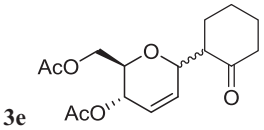
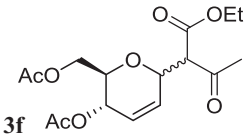
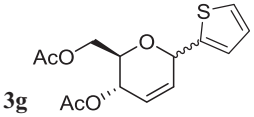
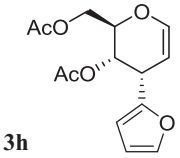
Table 1
$RuCl_3$ catalyzed C-glycosylation of glycal **1a** with allyl trimethylsilane (**2a**) under various conditions[a]



Entry	Solvent	Time (h)	Temp (°C)	Conv. (%)[b]	Yield (%)[c]	α:β ratio[d]
1	CH_2Cl_2	8	rt	60	—	—
2	CH_2Cl_2	16	40	80	65	90:10
3	$C_2H_4Cl_2$	8	rt	40	—	—
4	$C_2H_4Cl_2$	16	40	80	60	90:10
5	**CH_3CN**	**0.5**	**rt**	**100**	**96**	**96:4**
6[e]	CH_3CN	48	rt	10	—	—
7[e]	CH_3CN	16	40	60	52	96:4

Entry 5 represents the best reaction conditions, shown in bold.
[a] Reaction conditions: Glycal **1a** (1 equiv), allyltrimethylsilane (1.2 equiv) and 5 mol% $RuCl_3$.
[b] Progress of reaction was monitored by TLC analysis at given time, rt=room temperature, n. r.=no reaction.
[c] Isolated yields.
[d] The α/β ratios were based on the relative integration of anomeric or separable protons (^{1}H NMR spectrum).
[e] The reactions were performed with 2 mol % of $RuCl_3$.

Table 2
C-glycosylation of glucal **1a** with various acceptors under optimized condition[a]

Entry	Nucleophile	Glycoside	Time (min)	Yield (%)[b]	α:β ratio[c]
1	**2b**	 **3b**	20	90	60:40
2	**2c**	 **3c**	40	98	—
3	**2d**	 **3d**	20	47	72:28
		 **3d'**	20	35	89:11
4	**2e**	 **3e**	60	95	83:17
5	**2f**	 **3f**	20	96	88:12
6	**2g**	 **3g**	20	88	54:46
7	**2h**	 **3h**	40	68	α

[a] All reactions were performed with glucal **1a** (1 mmol), 1.2 equiv of acceptor with 5 mol % of $RuCl_3$ in acetonitrile at room temperature.
[b] Isolated and un-optimized yields.
[c] The α:β and epimeric ratios were examined by ^1H NMR spectroscopy.

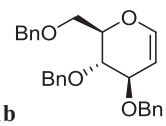
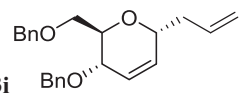
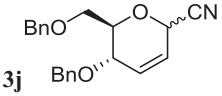
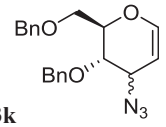
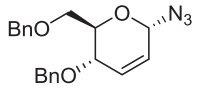
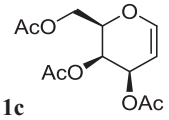
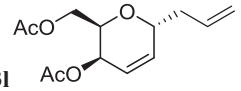
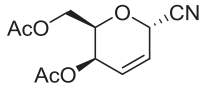
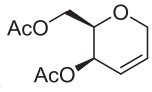
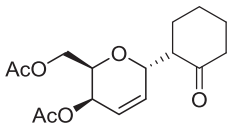
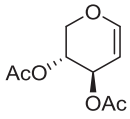
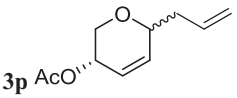
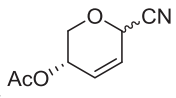
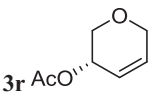
corresponding *C*-glycosyl heteroaromatic (**3g**) in good yield in a mixture of α/β ratio 1:1 (Table 2, entry 6). In contrast, the furan (**2h**) underwent regioselective C-glycosylation with glucal **1a** under identical conditions to afford *C*-3-substituted glycal (**3h**) as the major product along with a trace amount of the 2,3-unsaturated *C*-1-glycoside (Table 2, entry 7).[12c]

We next attempted the activation of 3,4,6-tri-O-benzyl glucal (**1b**) under ruthenium-mediated C-glycosylation. Accordingly, the glucal **1b** was reacted with allyltrimethylsilane (**2a**) to obtained the corresponding *C*-allyl glucoside (**3i**) in 96% yield with high anomeric selectivity (Table 3, entry 1). On the other hand, the C-glycosylation of the trimethylsilyl cyanide (**2b**) with **1b** provided the corresponding glycoside (**3j**) as mixture of α:β ratio 60:40 (Table 3, entry 2). Similarly, the glycosylation reaction of **1b** with trimethylsilyl azide (**2d**) proceeded smoothly to afford the corresponding C-3 glycal azide (**3k**) as major product in 80% yields along with *C*-1 epimer (**3k′**) in 16% yield with exclusive α selectivity (Table 3, entry 3). However, relatively faster reaction rate was observed in case of per-acetylated glucal **1a** than the benzylated glucal **1b**, which explain that the acetyl group behaves as better leaving group than benzyl ether.

We next examined the scope and efficiency of current C-glycosylation method in the context of other glycals. Thus, the C-glycosylation reaction of 3,4,6-tri-O-acetyl galactal (**1c**) with silylated *C*-nucleophiles (**2a**–**2c**) and silyl enol ether (**2e**) furnished the desired 2,3-unsaturated *C*-galactosides (**3l**–**3o**) in high yields with exclusive α-selectivity (Table 3, entries 4–7). Similarly, the Ferrier C-glycosylation of 3,4-di-O-acetyl xylal (**1d**) was performed with silylated nucleophiles (**2a**–**2c**) under similar conditions to obtain the corresponding 2,3-unsaturated *C*-xylosides (**3p**–**3r**) in good yield with high anomeric selectivity in favor of α-anomer (Table 3, entries 8–10).

The predominant formation of axial *C*-glycosides in the case of galactal could be attributed to a vinylogous anomeric effect, an allylic effect demonstrate a preferred quasi-axial orientation of the C3-OAc group in per-acetylated glycals and depends on

Table 3
$RuCl_3$ catalyzed C-glycosylation of glycals[a]

Entry	Glycal	Nucleophile	Glycoside	Time (min)	Yield (%)[b]	α:β ratio[c]
1	 **1b**	**2a**	 **3i**	30	96	α only
2	**1b**	**2b**	 **3j**	40	92	60:40
3	**1b**	**2d**	 **3k**	40	80	67:33
			 **3k'**	40	16	α only
4	 **1c**	**2a**	 **3l**	10	94	α only
5	**1c**	**2b**	 **3m**	40	82	α only
6	**1c**	**2c**	 **3n**	20	94	—
7	**1c**	**2e**	 **3o**	60	90	α only
8	 **1d**	**2a**	 **3p**	10	92	95:5
9	**1d**	**2b**	 **3q**	10	82	89:11
10	**1d**	**2c**	 **3r**	30	88	—

[a] All reactions were performed with glycal (1 mmol), 1.2 equiv of acceptor with 5 mol % of $RuCl_3$ in acetonitrile at room temperature.
[b] Isolated and un-optimized yields.
[c] The α:β and epimeric ratios were examined by ^1H NMR spectroscopy.

conformational equilibrium between $^4H_5 \leftrightarrow {}^5H_4$, two opposite half-chair confirmations.[12d-f]

3. Conclusions

In summary, we have demonstrated an efficient, convenient and highly catalytic system for the C-glycosylation of glycals to access *C*-glycosides under mild reaction conditions. In addition, the utility and flexibility of the current reagent system was successfully demonstrated for a wide range of substrates to achieve various functionalized 2,3-unsaturated *C*-glycosides of significant synthetic value. In the present C-glycosylation protocol, the use of environmental friendly reagent system and the easy availability of starting materials are added advantages. We believe that Ru-catalyzed glycosylation would find its applicability and contribute in advancing glycochemistry.

4. Experimental

4.1. General synthesis information, methods and materials

Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Reactions were run in screw capped glass vials (4 mL) stirred with Teflon®-coated magnetic stir bars. Moisture and air-sensitive reactions were performed in flame-dried round bottom flasks, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen. Moisture and air-sensitive liquids or solutions were transferred via nitrogen-flushed syringe. Concentration of solvents was accomplished by rotary evaporation using a Büchi rotary evaporator at temperatures between 35 °C and 50 °C. Analytical TLC was performed using Whatman 250 micron aluminum backed UV F254 precoated silica gel flexible plates. Subsequent to elution, ultraviolet illumination at 254 nm allowed for visualization of UV active materials. Staining with p-anisaldehyde, basic potassium permanganate solution, or Molisch's reagents allowed for further visualization. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Avance 300 or Avance 500 MHz nuclear magnetic resonance spectrometers. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) relative to tetramethylsilane (δ 0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d (δ 7.26, singlet). The number of protons (n) for a given resonance is indicated by nH. IR spectra were recorded on Bruker Alpha spectrometer and mass analyses (ESI): were performed using a Finnegan MAT 1020 mass spectrometer operating at 70 eV.

4.2. General procedure for the $RuCl_3$-catalyzed C-glycosylation

To a stirred solution of glycal (1 equiv) and acceptor or carbon nucleophile (1.2 equiv) in anhydrous acetonitrile (2 mL/mmol) under an atmosphere of argon was added $RuCl_3$ (5 mol %) at room temperature. The reaction mixture was stirred until the complete consumption of the starting material (glycal). The solvent was concentrated in vacuo, the crude residue was re-dissolved in dichloromethane and loaded on a silica gel column. The product was purified by silica gel chromatography using Hexane/EtOAc to afford the 2,3-unsaturated-*C*-glycosides in excellent yields. All the products were confirmed by IR, ^{1}H NMR, ^{13}C NMR and MS/HRMS spectroscopy, and overall spectroscopic data were in complete agreement with assigned structures and also compared with literature data.

4.2.1. Compound (**3a**)

Colorless viscous oil; $[\alpha]_D^{25}$ +120.37 (*c* 2.7, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2923, 2852, 1737, 1435, 1369, 1222, 1044, 971, 913, 750, 666; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.95–5.78 (m, 3H, H-3, H-2, C*H*=CH_2), 5.14–5.11 (m, 3H, H-4, CH=C*H*$_2$), 4.28 (m, 1H, H-1), 4.22 (dd, *J*=11.9, 6.4 Hz, 1H, H_a-6), 4.16 (dd, *J*=11.9, 3.6 Hz, 1H, H_b-6), 3.97 (td, *J*=6.2, 3.6 Hz, 1H, H-5), 2.51–2.29 (m, 2H, H_{ab}-1), 2.09 (s, 6H, 2×C*H*$_3$COO); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 170.1, 133.8, 132.6, 123.5, 117.4, (74.1-β), (74.0-β), 71.1, 69.5, (65.4-β), 64.8, (63.5-β), 62.7, 37.6, 20.8, 20.6; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{13}H_{18}O_5Na^+$: 277.10464; found: 277.10428.

4.2.2. Compound (**3b**-**α**)

Semi solid; $[\alpha]_D^{25}$ +150.00 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2954, 2922, 2852, 1745, 1462, 1372, 1217, 1044, 973, 910, 770, 667; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.04 (dt, *J*=10.2, 2.0 Hz, 1H, H-3), 5.90 (ddd, *J*=6.7, 2.0 Hz, 1H, H-2), 5.35 (dq, *J*=9.2, 2.0 Hz, 1H, H-4), 5.08 (dt, *J*=3.4, 1.7 Hz, 1H, H-1), 4.26 (d, *J*=4.0 Hz, 2H, H_{ab}-6), 4.04 (dt, *J*=9.2, 4.0 Hz, 1H, H-5), 2.12 (s, 3H, C*H*$_3$COO), 2.11 (s, 3H, C*H*$_3$COO); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.0, 129.7, 123.5, 115.5, 72.0, 63.7, 62.6, 62.2, 20.8, 20.7; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{11}H_{13}O_5Na^+$: 262.06859; found: 262.06813.

4.2.3. Compound (**3b**-**β**)

Semi solid; $[\alpha]_D^{25}$ +277.27 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2954, 2922, 2852, 1745, 1462, 1372, 1217, 1044, 973, 910, 770, 667; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.05 (dt, *J*=10.4, 2.6 Hz, 1H, H-3), 5.93 (dt, *J*=10.2, 1.8 Hz, 1H, H-2), 5.32 (dq, *J*=8.3, 2.0 Hz, 1H, H-4), 5.12 (dd, *J*=2.8, 2.0 Hz, 1H, H-1), 4.28 (dd, *J*=9.5, 2.8 Hz, 1H, H_a-6), 4.20 (dd, *J*=9.5, 2.8 Hz, 1H, H_b-6), 3.82 (ddd, *J*=6.0, 2.8 Hz, 1H, H-5), 2.12 (s, 3H, C*H*$_3$COO), 2.10 (s, 3H, C*H*$_3$COO); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 170.0, 128.7, 124.2, 115.7, 74.4, 63.5, 62.9, 62.5, 20.8, 20.7; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{11}H_{13}O_5Na^+$: 262.06859; found: 262.06813.

4.2.4. Compound (**3c**)

Colorless oil; $[\alpha]_D^{25}$ +62.50 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3020, 1736, 1371, 1215, 1046, 1027, 744, 621; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.96 (dt, *J*=11.9, 1.7 Hz, 1H, H-3), 5.76 (dt, *J*=12.5, 2.1 Hz, 1H, H-2), 5.27 (m, 1H, H-4), 4.26–4.15 (m, 4H, H_{ab}-1, H_{ab}-6), 3.74 (ddd, *J*=8.5, 5.7, 3.2 Hz, 1H, H-5), 2.11 (s, 3H, C*H*$_3$COO), 2.09 (s, 3H, C*H*$_3$COO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 170.2, 129.3, 124.1, 73.7, 65.1, 65.0, 63.1, 20.9, 20.7; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{10}H_{14}O_5Na^+$: 237.07334; found: 237.07311.

4.2.5. Compound (**3d** *C-3 isomer*)/(**3d′** *C-1 isomer*)

Colorless oil; IR ($CHCl_3$, cm^{-1}): 3020, 2928, 2103, 1742, 1646, 1370, 1217, 1088, 1049, 910, 771, 667; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.54 (d, *J*=6.0 Hz,1H, H-1, C-3, α), 6.51 (dd, *J*=6.0, 1.8 Hz, 0.4H, H-1, C-3, β), 6.04 (ddd, *J*=10.4, 3.2 Hz, 0.09H, H-2, C-1, β), 5.95 (dt, *J*=10.2, 1.5 Hz, 0.74H, H-3, C-1, α), 5.86 (dt, *J*=10.0, 1.0 Hz, 0.09H, H-3, C-1, β), 5.78 (ddd, *J*=7.3, 2.9 Hz, 0.74H, H-2, C-1, α), 5.57 (br s, 0.74H, H-1, C-1, α), 5.33 (dq, *J*=9.6, 1.7 Hz, 0.74H, H-4, C-1, α), 5.28 (m, 0.09H, H-1, C-1, β), 5.17 (dd, *J*=9.0, 7.3 Hz, 0.4H, H-2, C-3, β), 5.09 (dd, *J*=10.5, 4.3 Hz, 1H, H-2, C-3,α), 5.01–4.97 (m, 0.09H, H-4, C-1, β), 4.90 (t, *J*=6.0 Hz, 1H, H-4, C-3, α), 4.81 (dd, *J*=6.1, 2.6 Hz, 0.4H, H-4, C-3, β), 4.38 (dd, *J*=12.5, 4.9 Hz, 1.4H, H_a-6, C-3), 4.32 (dd, *J*=12.4, 2.3 Hz, 1.4H, H_b-6, C-3), 4.29–4.06 (m, 4H, H_{ab}-6, C-1, H-5), 4.02–3.99 (m, 0.09H, H-5, C-1, β), 2.15–2.09 (s, 3H, 4 isomers, C*H*$_3$COO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 170.5, 170.1, 169.6, 146.9 (C-3 major), 145.7 (C-3 minor), 129.6, 126.3, 98.1 (C-3 minor), 96.5 (C-3 major), 84.9 (C-1 major), 74.3 (C-3 minor), 70.6 (C-3 major), 68.8 (C-1 major), 68.0 (C-3 major), 67.5 (C-3 minor), 64.5 (C-1 major), 62.5 (C-1 major), 61.8 (C-3 major), 61.4 (C-3 minor), 57.6 (C-3 minor), 53.3 (C-3 major), 20.9, 20.7, 20.6, 20.5; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{10}H_{13}N_3O_5Na^+$: 278.07474; found: 278.07431.

4.2.6. Compound (**3e**)

Colorless oil; $[\alpha]_D^{25}$ +87.50 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3019, 2933, 1736, 1370, 1214, 748, 667; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.14 (dt, *J*=10.5, 1.5 Hz, 1H, H-3, major), 6.04 (d, *J*=10.5 Hz, 1H, H-3, minor), 5.93 (ddd, *J*=4.1, 1.8 Hz, 1H, H-2, minor), 5.78 (ddd, *J*=2.6, 2.1 Hz, 1H, H-2, major), 5.13 (m,1H, H-4, major), 4.99 (br s, 1H, H-1, minor), 4.76 (m, 1H, H-4, minor), 4.46 (dd, *J*=8.9, 1.9 Hz, 1H, H-1, major), 4.29–4.06 (m, 5H, H_{ab}-6, H-5, minor), 3.85 (m, 1H, H-5, major), 2.76 (m, 0.65H), 2.63 (m, 1H), 2.46–2.31 (m, 4H), 2.17 (m, 1H), 2.11–2.08 (3H, 2 isomers, C*H*$_3$COO), 2.04–1.90 (m, 3H), 1.74–1.45 (m, 5H), 0.90–0.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 210.9 (major), 210.5 (minor), 170.6, 170.4, 170.2, 132.9 (major), 132.0 (minor), 123.4 (major), 122.8 (minor), 71.7 (minor), 70.1 (major), 69.9 (major), 68.3 (minor), 64.8 (major), 64.3 (minor), 62.7 (major), 61.8 (minor), 53.6 (minor), 53.2 (major), 42.6 (major), 41.7, 30.1 (major), 28.5 (minor), 27.8 (major), 27.4 (minor), 24.5, 24.0,

20.9, 20.7; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{22}O_6Na^+$: 333.13086; found: 333.13018.

*4.2.7. Compound (**3f**)*

Yellowish oil; $[\alpha]_D^{25}$ +66.00 (*c* 3.0, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): 2981, 2928, 1738, 1717, 1445, 1221, 1037, 772, 604; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.04 (m, 1H, H-2, major), 5.95 (dt, *J*=10.5, 1.7 Hz, 1H, H-2, minor), 5.91–5.83 (m, 1H, H-3, major), 5.81–5.77 (m, 1H, H-3 minor), 5.26 (m, 1H, H-1 major), 5.18–5.11 (m, 1H, H-1, minor), 4.92–4.79 (m, 2H, H-4, both isomer), 4.32–4.05 (m, 6H, H-5, $-OCH_2CH_3$, both isomer), 3.94–3.88 (m, 4H, H_{ab}-6, both isomer), 3.76–3.71 (m, 2H, H-1′, both isomer), 2.32 (s, 3H, CH_3, minor), 2.30 (s, 3H, CH_3, major), 2.09–2.06 (s, 3H, 4 isomers, CH_3COO), 1.30–1.27 (m, 4H, CH_3, both isomer); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.1, 200.0, 170.5, 170.1, 166.6, 166.5, 130.1, 129.9, 129.7, 129.6, 126.6, 126.8, 125.5, 125.4, 74.3, 74.2, 73.5, 73.0, 70.2, 70.0, 64.8, 64.7, 64.4, 64.3, 63.3, 63.1, 63.0, 62.9, 62.8, 62.4, 62.4, 61.6, 61.4, 20.8, 20.5, 13.9; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{16}H_{22}O_8Na^+$: 365.12069; found: 365.12014.

*4.2.8. Compound (**3g** α/β)*

Yellowish oil; $[\alpha]_D^{25}$ +121.73 (*c* 2.3, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3019, 1738, 1431, 1214, 1047, 742, 667; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, *J*=6.1 Hz, 1H, *Ph*, α), 7.30 (d, *J*=6.1 Hz, 0.85H, *Ph*, β), 7.05 (d, *J*=3.5 Hz, 0.85H, *Ph*, β), 7.03 (d, *J*=3.2 Hz, 1H, *Ph*, α), 7.02–7.00 (m, 1H, *Ph*, α), 6.99–6.97 (m, 0.85H, *Ph*, β), 6.21 (ddd, *J*=10.4, 3.4 1.8 Hz, 1H, H-2, α), 6.00 (dt, *J*=10.2, 1.7 Hz, 0.85H, H-2, β), 5.97 (dt, *J*=10.2, 2.0 Hz, 1H, H-3, α), 5.86 (dt, *J*=10.2, 2.1 Hz, 0.85H, H-3, β), 5.54 (d, *J*=2.1 Hz, 1H, H-1, α), 5.50 (d, *J*=1.5 Hz, 0.85H, H-1, β), 5.41 (dq, *J*=9.0, 2.8 Hz, 0.85H, H-4, β), 5.35 (dq, *J*=8.5, 2.0 Hz, 1H, H-4, α), 4.29 (dd, *J*=12.2, 2.4 Hz, 0.85H, H_a-6, β), 4.24 (dd, *J*=12.2, 5.5 Hz, 1H, H_a-6, α), 4.19 (dd, *J*=12.2, 6.0 Hz, 0.85H, H_b-6, β), 4.11 (dd, *J*=12.1, 2.6 Hz, 1H, H_b-6, α), 3.93 (ddd, *J*=8.9, 6.0, 2.4 Hz, 0.85H, H-5, β), 3.87 (ddd, *J*=8.4, 5.5, 2.8 Hz, 1H, H-5, α), 2.11–2.08 (s, 3H, 2 isomers, CH_3COO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9 (β), 170.7 (α), 170.3 (α), 170.2 (β), 142.8 (β), 141.9 (α), 131.8 (β), 130.1 (α), 126.9 (α), 126.7 (α), 126.5 (β), 126.4 (α), 126.2 (α), 125.9 (β), 125.6 (β), 125.4 (β), 74.8 (α), 72.6 (β), 70.0 (α), 68.5 (β), 65.2 (β), 65.0 (α), 63.5 (β), 62.9 (α), 21.0, 20.8, 20.7; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{14}H_{16}O_5SNa^+$: 319.06107; found: 365.06035.

*4.2.9. Compound (**3h**)*

Brownish oil; $[\alpha]_D^{25}$ +504.16 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2923, 2852, 1740, 1653, 1369, 1220, 1050, 771, 744, 602; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J*=1.1 Hz, 1H, *Ph*), 6.53 (dd, *J*=6.0, 1.5 Hz, 1H, H-1), 6.34 (dd, *J*=3.1, 1.8 Hz, 1H, *Ph*), 6.14 (d, *J*=3.2 Hz, 1H, *Ph*), 5.06 (dd, *J*=9.9, 16.1 Hz, 1H, H-4), 4.81 (t, *J*=5.7 Hz, 1H, H-2), 4.31–4.29 (m, 2H, H_{ab}-6), 4.15 (ddd, *J*=9.9, 4.6, 2.8 Hz, 1H, H-5), 4.03 (dt, *J*=6.3, 1.4 Hz, 1H, H-3), 2.09 (s, 3H, CH_3COO), 1.99 (s, 3H, CH_3COO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 169.9, 153.3, 143.9, 142.4, 110.2, 109.0, 98.3, 70.7, 67.7, 62.7, 33.7, 20.7, 20.7; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{14}H_{16}O_6Na^+$: 303.08391; found: 303.08327.

*4.2.10. Compound (**3i**)*

Colorless oil; $[\alpha]_D^{25}$ +73.529 (*c* 3.4, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3064, 3030, 2924, 2859, 1729, 1453, 1363, 1305, 1213, 1092, 994, 914, 737, 698; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.24 (m, 10H, *Ph*), 5.94–5.77 (m, 3H, H-3, H-2, $HC{=}CH_2$), 5.14–5.05 (m, 2H, $HC{=}CH_2$), 4.59 (dd, 2H, *J*=12.1, 5.9 Hz, 2H, CH_2Ph), 4.52 (dd, 2H, *J*=13.8, 11.7 Hz, 2H, CH_2Ph), 4.24 (dt, *J*=7.7, 5.9, 1.9 Hz, 1H, H-1), 4.00 (dd, *J*=7.2, 1.5 Hz, 1H, H-4), 3.82 (m, 1H, H-5), 3.69–3.65 (m, 2H, H_{ab}-6), 2.48 (m, 1H, H_a-1′), 2.33 (m, 1H, H_b-1′); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 134.5, 131.1, 138.3, 128.3, 127.9, 127.8, 127.7, 127.5, 125.6, 117.2, 73.3, 72.0, 71.3, 71.0, 69.9, 69.2, 38.0; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{23}H_{26}O_3Na^+$: 373.17796; found: 373.17721.

*4.2.11. Compound (**3j**)*

Colorless viscous oil; $[\alpha]_D^{25}$ +44.737 (*c* 3.8, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2922, 2853, 1724, 1453, 1360, 1272, 1097, 908, 741, 698; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.22 (m, 17H, *Ph*), 6.17–6.11 (m, 1.7H, H-3), 5.79 (dt, *J*=10.2, 1.8 Hz, 0.7H, H-2, β), 5.79 (ddd, *J*=6.7, 3.5, 1.7 Hz, 1H, H-2, α), 5.03 (dd, *J*=2.6, 2.1 Hz, 0.7H, H-1, β), 5.02 (m, 1H, H-1, α), 4.68–4.45 (m, 6H, CH_2Ph), 4.23 (ddd, *J*=10.8, 9.0, 1.8 Hz, 1H, H-4, α), 4.05 (m, 0.7H, H-4, β), 3.85 (dt, *J*=8.9, 2.8 Hz, 1H, H-5, α), 3.76–3.70 (m, 2.4H, H_a-6, H-5, β), 3.67 (dd, *J*=7.8, 5.3 Hz, 1H, H_b-6, α), 3.65 (dd, *J*=5.5, 2.0 Hz, 0.7H, H_b-6, β); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.6, 137.3, 131.3, 130.0, 128.5–127.6, 122.8, 121.9, 116.3, 116.2, 77.2, 74.2, 73.5, 73.4, 71.8, 68.7, 67.9, 63.2, 62.9; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{21}H_{21}NO_3Na^+$: 358.14191; found: 358.14095.

*4.2.12. Compound (**3k** C-3 isomer)/**3k′** C-1 isomer)*

Semi solid; IR ($CHCl_3$, cm^{-1}): 2919, 2864, 2097, 1645, 1452, 1363, 1233, 1107, 734, 696; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.23 (m, 18H, *Ph*), 6.52 (d, *J*=5.6 Hz, 1H, H-1, C-3, α), 6.48 (dd, *J*=6.0, 1.7 Hz, 0.5H, H-1, C-3, β), 6.12 (dt, *J*=10.0, 1.3 Hz, 0.3H, H-3, C-1, α), 5.70 (ddd, *J*=10.2, 2.6, 0.6 Hz, 1H, H-2, C-1, α), 5.33 (br s, 0.3H, H-1, C-1, α), 4.84 (d, *J*=10.8 Hz, 0.5H, H-2, C-3, b), 4.79 (t, *J*=5.6 Hz, 1H, H-2, C-3, a), 4.71–4.43 (m, 6.3H, CH_2Ph), 4.21 (ddd, *J*=9.5, 3.6, 1.7 Hz, 0.5H, H-4, C-3, b), 4.11–4.04 (m, 3.3H, H-4), 3.97–3.92 (m, 1.8H, H_a-6), 3.82–3.73 (m, 4H, H_b-6, H-5); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.3, 146.0, 137.8, 137.2, 131.3, 128.4, 128.4, 128.4, 128.3, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 124.8, 98.2, 95.8, 84.9, 77.1, 74.5, 74.2, 73.4, 75.5, 73.4, 73.2, 73.2, 72.0, 71.3, 71.1, 69.4, 68.3, 68.0, 60.7, 53.4; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{20}H_{21}N_3O_3Na^+$: 374.14751; found: 374.14733.

*4.2.13. Compound (**3l**)*

Colorless viscous oil; $[\alpha]_D^{25}$ −145.00 (*c* 4.0, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2966, 2931, 1744, 1373, 1252, 1165, 1072, 1037, 846. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.06 (dd, *J*=10.4, 2.9 Hz, 1H, H-3), 6.06 (ddd, *J*=10.2, 5.0, 2.0 Hz, 1H, H-2), 5.89–5.81 (m, 1H, $HC{=}CH_2$), 5.16–5.11 (m, 2H, $CH{=}CH_2$), 5.08 (dd, *J*=5.0, 2.6 Hz, 1H, H-4), 4.36 (ddd, *J*=10.7, 5.3, 2.3 Hz, 1H, H-1), 4.20 (dd, *J*=5.7, 2.9 Hz, 2H, H_{ab}-6), 4.15–4.12 (m, 1H, H-5), 2.44 (m, 1H, H_a-1′), 2.30 (m, 1H, H_b-1′), 2.08 (s, 3H, CH_3COO), 2.07 (s, 3H, CH_3COO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 170.3, 134.7, 133.8, 121.9, 117.5, 72.1, 67.9, 63.7, 62.8, 36.6, 20.8, 20.7; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{13}H_{18}O_5Na^+$: 277.10464; found: 277.10470.

*4.2.14. Compound (**3m**)*

Semi solid; $[\alpha]_D^{25}$ −356.66 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2966, 2931, 1744, 1373, 1072, 1037, 846; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.27 (ddd, *J*=10.0, 5.7, 2.1 Hz, 1H, H-3), 6.06 (dd, *J*=10.0, 3.8 Hz, 1H, H-2), 5.17–5.14 (m, 2H, H-4, H-1), 4.20 (m, 3H, H_{ab}-6, H-5), 2.11 (s, 3H, CH_3COO), 2.09 (s, 3H, CH_3COO); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 169.7, 126.3, 125.9, 115.1, 71.6, 62.4, 61.9, 61.9, 20.4, 20.4; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{11}H_{13}O_5Na^+$: 262.06859; found: 262.06812.

*4.2.15. Compound (**3n**)*

Colorless oil; $[\alpha]_D^{25}$ −33.33 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3020, 1736, 1371, 1215, 1088, 1048, 744, 666; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.11 (ddd, *J*=11.8, 3.7, 1.5 Hz, 1H, H-3), 6.04–5.98 (m, 1H, H-2), 5.11 (dt, *J*=85.3, 2.1 Hz, 1H, H-4), 4.34 (ddd, *J*=17.2, 3.5, 1.8 Hz, 1H, H_a-1), 4.26–4.17 (m, 3H, H_b-1, H_{ab}-6), 3.89 (ddd, *J*=7.3, 5.0, 2.3 Hz, 1H, H-5), 2.09 (s, 3H, CH_3COO), 2.09 (s, 3H, CH_3COO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 170.4, 132.3, 122.0, 73.6, 65.6, 64.2, 63.2, 20.7, 20.7; HRMS (ESI): *m/z* [M+Na]$^+$ calcd for $C_{10}H_{14}O_5Na^+$: 237.07334; found: 237.07347.

4.2.16. Compound (**3o**)

Colorless oil; $[\alpha]_D^{25}$ +88.42 (*c* 3.3, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3020, 1737, 1371, 1215, 1047, 744, 667; ^1H NMR (300 MHz, $CDCl_3$): δ 6.29 (dd, *J*=10.4, 3.2 Hz, 1H, H-3, major), 6.04 (dd, *J*=11.9, 1.5 Hz, 1H, H-3, minor), 5.97–5.90 (m, 2H, H-2), 5.21 (br s, 1H, H-1, minor), 5.07 (m, 1H, H-1, major), 4.80 (d, *J*=6.6 Hz, 1H, H-4, minor), 4.49 (d, *J*=9.8 Hz, 1H, H-4, major), 4.26–4.18 (m, 5H, H_{ab}-6, H-5), 401–3.96 (m, 1H, H-5, major), 2.78–2.60 (m, 2H), 2.51–2.26 (m, 5H), 2.13–2.02 (s, 12H, 2 isomers, C*H*$_3$COO), 1.98–1.55 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.0, 210.3, 170.7, 170.5, 170.4, 170.3, 134.7, 131.4, 123.4, 121.6, 71.1, 69.5, 69.1, 68.5, 64.0, 63.7, 62.9, 61.6, 53.4, 52.4, 42.6, 41.3, 30.6, 28.8, 27.9, 27.5, 24.4, 23.4, 20.8, 20.8, 20.7, 20.6; HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{16}H_{22}O_6Na^+$: 333.13086; found: 333.13085.

4.2.17. Compound (**3p**)

Colorless viscous oil; $[\alpha]_D^{25}$ +125.00 (*c* 1.6, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2984, 2924, 2853, 1743, 1373, 1222, 1070, 1045, 1004, 917, 891, 864, 772; ^1H NMR (500 MHz, $CDCl_3$): δ 6.02 (d, *J*=11.9 Hz, 0.06H, H-3, β), 5.92 (dt, *J*=10.4, 1.2 Hz, 1H, H-3), 5.87–5.79 (m, 2H, H-2, C*H*=CH_2), 5.25 (m, 1H, H-4), 5.15–5.09 (m, 2H, CH=C*H*$_2$), 5.00 (m, 0.06H, H-4, β), 4.31 (m, 0.06H, H-1, β), 4.20–4.17 (m, 1H, H-1), 4.13 (dd, *J*=11.4, 5.0 Hz, 1H, H_a-5), 3.76 (dd, *J*=10.9, 1.8 Hz, 0.06H, H_b-5, β), 3.54 (dd, *J*=11.4, 6.7 Hz, 1H, H_b-5), 2.38–2.26 (m, 2H, H_{ab}-1′), 2.09 (s, 0.18H, C*H*$_3$COO, β), 2.07 (s, 3H, C*H*$_3$COO); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 133.8, 133.4, 124.4, 117.5, 73.0, 65.1, 64.9, 38.6, 21.0.

4.2.18. Compound (**3q**)

Colorless oil; $[\alpha]_D^{25}$ +184.00 (*c* 1.6, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 3020, 2922, 2851, 1739, 1463, 1373, 1215, 750, 667; ^1H NMR (500 MHz, $CDCl_3$): δ 6.22 (ddd, *J*=10.0, 7.2, 1.5 Hz, 1H, H-3), 6.11 (dt, *J*=10.4, 2.3 Hz, 0.12H, H-3, β), 6.06 (dd, *J*=10.6, 3.8 Hz, 1H, H-2), 5.94 (ddd, *J*=11.8, 6.1, 2.5 Hz, 0.12H, H-2, β), 5.28 (m, 0.12H, H-1, β), 5.09–5.05 (m, 2H, H-4, H-1), 4.97 (m, 0.12H, H-4, β), 4.10–4.08 (m, 2H, H_{ab}-5), 3.83 (dd, *J*=9.7, 5.7 Hz, 0.12H, H_b-5), 2.10 (s, 3H, C*H*$_3$COO); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 126.5, 125.8, 115.4, 65.3, 62.2, 61.5, 20.7.

4.2.19. Compound (**3r**)

Colorless oil; $[\alpha]_D^{25}$ +69.44 (*c* 1.8, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): 2920, 2851, 1725, 1462, 1378, 1283, 1215, 1123, 1074, 754, 667; ^1H NMR (300 MHz, $CDCl_3$): δ 6.08 (dt, *J*=10.2, 2.1 Hz, 1H, H-3), 5.96–5.90 (m, 1H, H-2), 5.09 (m, 1H, H-4), 4.21 (dt, *J*=17.0, 1.8 Hz, 1H, H_a-1), 4.09 (dd, *J*=17.0, 2.1 Hz, 1H, H_b-1), 3.95 (dd, *J*=12.5, 1.7 Hz, 1H, H_a-5), 3.81 (dd, *J*=12.5, 3.2 Hz, 1H, H_b-5), 2.10 (s, 3H, C*H*$_3$COO); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 132.2, 122.4, 67.7, 65.0, 64.8, 21.2.

Acknowledgments

This research is supported by Department of Science and Technology, New Delhi (GAP0397 & 0471). The authors are grateful to the Director CSIR-IICT for providing necessary infrastructure. B.S acknowledges a UGC Fellowship.

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