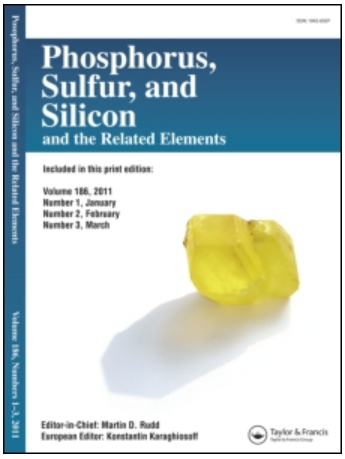

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Regio- and Stereoselective Synthesis of Thioglycosides from 4,5-Diphenyl- and 3,4,5-Triphenylimidazole-2-thione

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Regio- and Stereoselective Synthesis of Thioglycosides from 4,5-Diphenyl- and 3,4,5-Triphenylimidazole-2-thione

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Six new thioglycosides incorporating the 4,5-diphenyl- and 3,4,5-triphenylimidazole moiety have been successfully synthesized under both conventional and microwave conditions by reaction of the corresponding thiones with acetobromosugars in presence of triethylamine as base. Attempted preparation of the bis(glycosyl) derivatives from 4,5-diphenylimidazole-2-thione in the presence of different bases was unsuccessful. Evaluation of the glycosylthioimidazoles as disarmed donors has been investigated using different promoters; NBS/TMSOTf has been found to be an effective promoter for the activation of the anomeric center towards glycosylation reaction.

Keywords 4,5-Diphenylimidazole; glycosylation; microwave irradiation; oligosaccharide; thioglycosides; 3,4,5-triphenylimidazole

INTRODUCTION

One of the main efforts in the field of synthetic carbohydrate chemistry has been focused on the development of new methodologies for the synthesis of 1,2-*cis* or 1,2-*trans* glycosidic bonds with complete stereoselectivity.[1] Among these, thioglycosides are promising candidates for glycoside synthesis due to their easy preparation, sufficient stability under various reaction conditions, and the ability to be readily converted into derivatives containing different protecting groups.[2–4] Moreover, activation of their anomeric center with a variety of promoters makes them excellent glycosyl donors.[5–11]

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Imidazoles are some of the most frequently applied heterocycles in medicinal chemistry, showing antiasthmatic,[12] anti-inflammatory,[13] antiulcerative,[14] antithrombotic,[15] fungicidal,[16] and herbicidal[17] activity. In continuation of our studies on the application of microwave techniques in organic synthesis,[18–27] we present here new thioglycosides incorporating imidazole moieties as heterocycles prepared under both conventional and microwave conditions.

RESULTS AND DISCUSSION

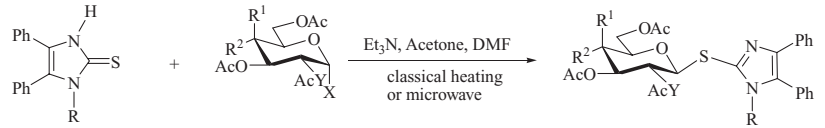
Coupling of imidazoles **1** and **2** with glycosyl halides **3a–c** in dry acetone and in the presence of triethylamine was achieved under microwave conditions to give the thioglycosides **4–9** within 4 to 6 minutes in good yields (88–90%). On the other hand, conventional heating required 16–20 h and resulted in 76–81% yield (Table I); the *N*-nucleoside analogue of **4** was prepared[28] by the reaction of the chloromercury salt of **1** with **3a**.

The formation of the thioglycosides **4–9** proceeds via a S_N2 mechanism and involves the formation of a thiolate anion, generated by proton abstraction in presence of triethylamine. The generated anion acts as a nucleophile in the nucleophilic displacement of the halogen atom of the glycosyl halides **3a–c** to give the β-thioglycosides **4–9**. The identity of the reaction products **4–9** was established by their elemental analysis and spectroscopic data. Attempted preparation of the bis(glycosyl) derivatives of **1** using different basic conditions (K_2CO_3, KOH, or NaH) in acetone, MeCN, or EtOH as solvent was unsuccessful under both conventional and microwave conditions. This indicates that further abstraction of another hydrogen atom from the imidazole ring under such reaction conditions does not take place.

TABLE I Comparison of the Data for the Synthesis of Compounds 4–9 Using Conventional and Microwave Methods

	Conventional method		Microwave Method	
	Time (h)	Yield (%)	Time (min)	Yield (%)
4	16	76	4.0	88
5	16	80	4.5	90
6	17	78	5.0	89
7	18	80	4.0	90
8	20	78	6.0	92
9	20	81	6.0	91

The regioselective formation of thioglycosides **4**, **5**, and **8** rather than the respective *N*-glycosides or bis(glycosides) was confirmed by the presence of a characteristic signal in the ^{1}H NMR spectra at $\delta_H = 9.93$–11.39 ppm due to the NH proton. The signal of the anomeric proton appears as a doublet in the range $\delta_H = 4.78$–5.52 ppm with a coupling constant of 9.9–10.7 Hz, confirming the β-configuration. 2D NMR spectra facilitated the assignment of the signals for the sugar and imidazole moieties of compound **4**. Thus, in the ^{1}H,^{1}H-COSY spectrum, the signal of H-1′ correlates with the doublet of doublets due to H-2′ at $\delta_H = 5.06$ ppm. The ^{13}C NMR signals of the respective carbon atoms appear at $\delta_C = 83.6$ and 70.2 ppm. The signals of both H-3′ and H-4′ were assigned as doublet of doublets at $\delta_H = 5.25$ and 5.06 ppm, respectively. They correlate with the signal of the corresponding carbon atoms at $\delta_C = 73.6$ and 67.9. The signal of H-5′ appears as a multiplet at $\delta_H = 3.71$–3.75 ppm and correlates with the doublet of doublets of H-6′ and H-6″ at $\delta_H = 4.07$ and 4.35 ppm, respectively. The respective carbon atoms resonate at $\delta_C = 76.2$ and 61.5 ppm. The structures of compounds **5–9** were established similarly (Scheme 1).



1 R = H
2 R = Ph

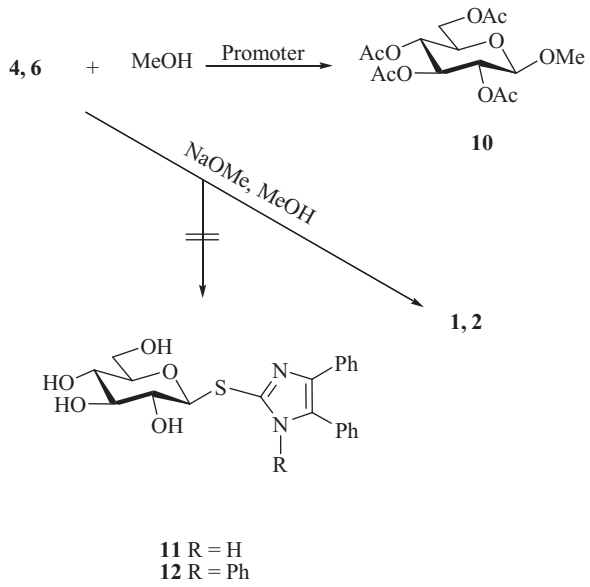
3a Y = O, X = Br, R^1 = H, R^2 = OAc
3b Y = NH, X = Cl, R^1 = H, R^2 = OAc
3c Y = O, X = Br, R^1 = OAc, R^2 = H

4 R = H, Y = O, R^1 = H, R^2 = OAc
5 R = H, Y= NH, R^1 = H, R^2 = OAc
6 R = Ph, Y = O, R^1 = H, R^2 = OAc
7 R = Ph, Y= NH, R^1 = H, R^2 = OAc
8 R = H, Y = O, R^1 = OAc, R^2 = H
9 R = Ph, Y = O, R^1 = OAc, R^2 = H

SCHEME 1

The formation of 1,2-*cis* or 1,2-*trans* glycosidic linkages is dependent particularly on the protecting groups of the sugar moiety and the promoters that activate the anomeric center. Disarmed donors protected with acetyl groups result in the formation of 1,2-*trans* glycosides, while armed donors containing benzyl groups give the respective 1,2-*cis* glycosides.

Attempted glycosylation of the disarmed thioglucoside **6** with methanol using different promoters such as MeI, AgOTs, and TMSOTf under inert nitrogen atmosphere at 0°C or even at room temperature was unsuccessful. However, the activation is successful using the combination of NBS/TMSOTf and gives the glucoside **10** in 48% yield, with complete retention of the β-configuration.



11 R = H
12 R = Ph

SCHEME 2

In order to obtain the benzylated derivatives of **11** and **12** as armed glycosyl donors deprotection of **4** and **6** with sodium methoxide is required (Scheme 2). However, the deacetylation of **4** and **6** did not give **11** and **12**, but the products were identified to be **1** and **2**, respectively. More studies are required to prepare the respective benzylated derivatives.

In conclusion, a number of glycosylthioimidazoles has been synthesized under both conventional and microwave conditions. Preliminary results on the use of one of the new compounds as glucosyl donor under activation with NBS/TMSOTf prove to be successful.

EXPERIMENTAL

Melting points were determined with a Melt-temp apparatus and are uncorrected. TLC was performed on Baker-Flex silica gel 1B-F plates using ethyl acetate-hexane as eluent, and the spots were detected by UV light absorption. Irradiation was achieved in a domestic microwave oven EM-230M. The oven was adjusted on the defrost mode with the fixed output power (1200 Watt output). Irradiation was done, unless otherwise stated, in a closed Teflon cylindrical vessel, which was placed at the center of a rotating plate inside the oven. The vessel was supported by a frame for safety. The vessel had an

outside diameter of 6.5 cm and a length of 6.0 cm, while inside it was 3.0 cm wide and 2.0 cm long. Additional 2.0 cm of the length inside the vessel was used for the screw of the cover in order to be tight. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Jeol spectrometer DELTA2_NMR, operating at 500 MHz (^{1}H) and 127.5 MHz (^{13}C). The assignment of ^{1}H NMR signals was based on ^{1}H, ^{1}H-DQF-COSY spectra, while the assignment of the ^{13}C NMR signals was based on HMQC experiments. Chemical shifts are given in ppm relative to the signal of TMS as internal standard. Elemental analyses were performed in the unit of Microanalyses at Faculty of Science, Cairo University.

Preparation of Thioglycosides 4–9: General Procedure

Method A. A solution of compounds **1** or **2** (1 mmol) and triethylamine (1 mmol) in dry acetone (10 mL) and few drops of dry DMF was stirred for 1 h, then glycosyl halides **3a–c** (1.1 mmol) were added. Stirring was continued overnight. Then the reaction mixture was refluxed for 1–4 h and then filtered. From the solution, the solvent was evaporated under reduced pressure, and the product was recrystallized from ethanol or purified by column chromatography.

Method B. A solution of compounds **1** or **2** (0.5 mmol), triethylamine (0.5 mmol), and glycosyl halides **3a–c** (0.55 mmol) in dry acetone (5 mL) and few drops of dry DMF in a closed Teflon vessel was irradiated by microwave for 4–6 min. The reaction mixture was cooled and processed as described above.

*(4,5-Diphenylimidazol-2-yl)-(2′,3′,4′,6′-tetra-*O*-acetyl-1-thio)-β-*D*-glucopyranoside (4)*

Colorless plates; mp: 130–131°C. TLC, $\mathbf{R}_f$: 0.47 (hexane-EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.77$ (s, 3H, OAc), 1.99 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.11 (s, 3H, OAc), 3.71–3.75 (m, 1H, H-5′), 4.07 (dd, $J_{6',5'} = 4.6$, $J_{6',6''} = 13.0$ Hz, 1H, H-6′), 4.35 (dd, $J_{6'',5'} = 2.3$, $J_{6'',6'} = 13.0$ Hz, 1H, H-6″), 4.81 (d, $J_{1',2'} = 10.0$ Hz, 1H, H-1′), 5.06, (t, $J_{2',3'} = 9.2$ Hz, 1H, H-2′), 5.09 (t, $J_{4',3'} = 9.9$ Hz, 1H, H-4′), 5.25 (dd, $J_{3',2'} = 9.2$, $J_{3',4'} = 10.0$ Hz, 1H, H-3′), 7.24–7.31 (m, 6H, arom-H), 7.51 (d, $J = 7.7$ Hz, 4H, arom-H), 9.93 (s, 1H, D_2O exchangeable, NH). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta =$ 20.5, 20.7, 20.9 (CH_3CO), 61.5 (C-6′), 67.9 (C-4′), 70.2 (C-2′), 73.6 (C-3′), 76.2 (C-5′), 83.6 (C-1′), 127.8, 127.9, 128.3, 128.6, 129.9, 133.7, 169.5, 170.0, 170.1 (CH_3CO). Anal. Calcd. for $C_{29}H_{30}N_2O_9S$ (582.17): C, 59.78; H, 5.19; N, 4.81. Found: C, 59.82; H, 5.59; N, 4.49%.

(4,5-Diphenylimidazol-2-yl)(2′-acetamido-3′,4′,6′-tri-O-acetyl-2′-deoxy-1-thio)-β-D-glucopyranoside (5)

Colorless crystals; mp: 148°C. TLC, $\mathbf{R}_f$: 0.34 (hexane-EtOAc 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.85 (s, 3H, NAc), 2.00 (s, 6H, OAc), 2.01 (s, 3H, OAc), 3.70–3.73 (m, 1H, H-5′), 4.06 (dd, $J_{2',1'}$ = 10.7, $J_{2',3'}$ = 9.9 Hz, 1H, H-2′), 4.09 (dd, $J_{6',5'}$ = 7.7, $J_{6',6''}$ = 13.0 Hz, 1H, H-6′), 4.27 (dd, $J_{6'',5'}$ = 2.3, $J_{6'',6'}$ = 13.0 Hz, 1H, H-6″), 4.78 (d, $J_{1',2'}$ =10.7 Hz, 1H, H-1′), 4.98 (t, $J_{3',2'}$ = 9.9 Hz, 1H, H-3′), 5.25 (t, $J_{4',3'}$ = 9.9 Hz, 1H, H-4′), 6.87 (d, $J_{NH,2'}$ = 8.4 Hz, 1H, D_2O exchangeable, N*H*Ac), 7.25–7.31 (m, 6H, arom-H), 7.51–7.53 (m, 4H, arom-H), 11.39 (s, 1H, D_2O exchangeable, NH imidazole). Anal. Calcd. for $C_{29}H_{31}N_3O_8S$ (581.18): C, 59.88; H, 5.37; N, 7.22. Found: C, 59.87; H, 5.76; N, 6.84%.

(3,4,5-Triphenylimidazol-2-yl)-(2′,3′,4′,6′-tetra-O-acetyl-1-thio)-β-D-glucopyranoside (6)

Colorless crystals; mp: 182–184°C. TLC, $\mathbf{R}_f$: 0.42 (hexane-EtOAc 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.98 (s, 3H, OAc), 1.99 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.07 (s, 3H, OAc), 3.83 (ddd, $J_{5',4'}$ = 9.9, $J_{5',6'}$ = 2.3, $J_{5',6''}$ = 5.3 Hz, 1H, H-5′), 4.14 (dd, $J_{6',5'}$ = 2.3, $J_{6',6''}$ = 12.3 Hz, 1H, H-6′), 4.24 (dd, $J_{6'',5'}$ = 5.3, $J_{6'',6'}$ = 12.3 Hz, 1H, H-6″), 5.13 (t, $J_{2',1'}$ = 10.7, 1H, H-2′), 5.15 (t, $J_{2',3'}$ = 9.9 Hz, 1H, H-4′), 5.28 (t, $J_{3',2'}$ = 9.9 Hz, 1H, H-3′), 5.51 (d, $J_{1',2'}$ = 10.7 Hz, 1H, H-1′), 7.07–7.10 (m, 4H, arom-H), 7.17–7.32 (m, 9H, arom-H), 7.53–7.54 (m, 2H, arom-H). Anal. Calcd. for $C_{35}H_{34}N_2O_9S$ (658.20): C, 63.82; H, 5.20; N, 4.25. Found: C, 63.72; H, 5.26; N, 4.19%.

(3,4,5-Triphenylimidazol-2-yl)-(2′-acetamido-3′,4′,6′-tri-O-acetyl-2′-deoxy-1-thio)-β-D-glucopyranoside) (7)

Colorless crystals; mp: 168–170°C. TLC, $\mathbf{R}_f$: 0.30 (hexane-EtOAc 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.94 (s, 3H, NAc), 2.01 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.31 (s, 3H, OAc), 3.77 (ddd, $J_{5',4'}$ = 10.0, $J_{5',6'}$ = 2.3, $J_{5',6''}$ = 5.3 Hz, 1H, H-5′), 4.11 (dd, $J_{6',5'}$ = 2.3, $J_{6',6''}$ = 12.2 Hz, 1H, H-6′), 4.17 (dd, $J_{2',1'}$ = 10.7, $J_{2',3'}$ = 9.2 Hz, 1H, H-2′), 4.21 (dd, $J_{6'',5'}$ = 5.3, $J_{6'',6'}$ = 12.2 Hz, 1H, H-6″), 5.10 (dd, $J_{3',2'}$ = 9.2, $J_{3',4'}$ = 9.9 Hz, 1H, H-3′), 5.32 (t, $J_{4',5'}$ = 10.0 Hz, 1H, H-4′), 5.48 (d, $J_{1',2'}$ =10.7 Hz, 1H, H-1′), 6.92 (d, $J_{NH,2'}$ = 8.4 Hz, 1H, D_2O exchangeable, N*H*Ac), 7.05–7.10 (dd, J = 6.1, J = 6.9, 4H, arom-H), 7.17–7.30 (m, 9H, arom-H), 7.48 (d, J = 6.9, 2H, Ar-H). Anal. Calcd. for $C_{35}H_{35}N_3O_8S$ (657.73): C, 63.91; H, 5.36; N, 6.39. Found: C, 63.53; H, 5.57; N, 6.20%.

*(4,5-Diphenylimidazol-2-yl)-(2′,3′,4′,6′-tetra-*O*-acetyl-1-thio)-β-*D*-galactopyranoside (8)*

Colorless plates; mp: 160–162°C. TLC, $\mathbf{R}_f$: 0.40 (hexane-EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.76$ (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.97 (s, 3H, OAc), 2.13 (s, 3H, OAc), 3.94–3.97 (m, 1H, H-5′), 4.08 (dd, $J_{6',5'} = 4.6$, $J_{6',6''} = 11.5$ Hz, 1H, H-6′), 4.25 (dd, $J_{6'',5'} = 7.6$, $J_{6'',6'} = 11.5$ Hz, 1H, H-6″), 4.82 (d, $J_{1',2'} = 9.9$ Hz, 1H, H-1′), 5.08 (dd, $J_{3',2'} = 9.9$, $J_{3',4'} = 3.1$Hz, 1H, H-3′), 5.26 (t, $J_{2',1'} = 9.9$ Hz, 1H, H-2′), 5.41 (d, $J_{4',3'} = 3.1$ Hz, 1H, H-4′), 7.25–7.57 (m, 10H, arom-H), 10.09 (s, 1H, D_2O exchangeable, NH imidazole). Anal. Calcd. for $C_{29}H_{30}N_2O_9S$ (582.17): C, 59.78; H, 5.19; N, 4.81. Found: C, 59.39; H, 5.39; N, 4.52%.

*(3,4,5-Triphenylimidazol-2-yl)-(2′,3′,4′,6′-tetra-*O*-acetyl-1-thio)-β-*D*-galactopyranoside (9)*

Colorless crystals; mp: 100–102°C; TLC, $\mathbf{R}_f$: 0.45 (hexane-EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.95$ (s, 3H, OAc), 1.97 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.10 (s, 3H, OAc), 4.02–4.05 (m, 1H, H-5′), 4.10-4.15 (m, 2H, H-6′, H-6″), 5.11 (dd, $J_{3',2'} = 9.9$, $J_{3',4'} = 3.4$ Hz, 1H, H-3′), 5.32 (t, $J_{2',1'} = 9.9$ Hz, 1H, H-2′), 5.45 (d, $J_{4',3'} = 3.1$ Hz, 1H, H-4′), 5.52 (d, $J_{1',2'} = 9.9$ Hz, 1H, H-1′), 7.07–7.10 (m, 4H, arom-H), 7.17–7.31 (m, 9H, arom-H), 7.54–7.55 (m, 2H, arom-H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta =$ 20.7, 20.9 (CH_3CO), 61.5 (C-6′), 67.2 (C-4′), 67.4 (C-2′), 72.0 (C-3′), 74.8 (C-5′), 85.5 (C-1′), 126.9, 127.2, 128.2, 128.3, 128.5, 128.8, 129.0, 130.1, 130.6, 131.9, 134.1, 135.6, 139.1, 139.2, 169.8 (CH_3CO), 170.1 (CH_3CO), 170.3 (CH_3CO), 170.5 (CH_3CO). Anal. Calcd. for $C_{35}H_{34}N_2O_9S$ (658.20): C, 63.82; H, 5.20; N, 4.25. Found: C, 63.57; H, 5.57; N, 3.99%.

Procedure for Glycosylation

A mixture of (3,4,5-triphenylimidazol-2-yl)-2-(2′,3′,4′,6′-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside) (**6**) (1.1 mmol, 0.723 g), the acceptor methanol (1 mmol, 0.043 mL), and freshly activated molecular sieve (3 Å, 200 mg) in dry dichloromethane (10 mL) was stirred under nitrogen. The solution was cooled to 0°C, the promoter (2.2 mmol) was added, and the mixture was stirred until completion of the reaction (monitored by TLC). The reaction mixture, in the case of using NBS-TMSOTf, was diluted with dichloromethane (10 mL); the solid was filtered off and washed with dichloromethane (10 mL). The combined filtrate was washed with 20% $NaHCO_3$ solution in water (20 mL). The organic phase was dried and concentrated under reduced pressure. The residue was purified by column chromatography to give **10**.

Methyl (2,3,4,6-tetr-a-O-acetyl)-β-D-glucopyranoside (10)

Colorless crystals (48%); mp: 98–99°C; Lit[29] mp: 104–105°C. TLC, $\mathbf{R}_f$: 0.4 (hexane-EtOAc 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.99$ (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.08 (s, 3H, OAc), 3.39 (s, 3H, OCH_3), 3.95–3.98 (m, 1H, H-5), 4.10 (dd, $J_{6',5'} = 2.3$, $J_{6',6''} = 12.2$ Hz, 1H, H-6′), 4.26 (dd, $J_{6'',5'} = 4.6$, $J_{6'',6'} = 12.3$ Hz, 1H, H-6″), 4.90 (dd, $J_{2',1'} = 10.2$, $J_{2',1'} = 9.9$ Hz, 1H, H-2′), 4.94 (d, $J_{1',2'} = 10.2$ Hz, 1H, H-1′), 5.05 (t, $J_{3',4'}$ =9.9 Hz, 1H, H-3′), 5.46 (t, $J_{4',3'}$ =9.9 Hz, 1H, H-4′). Anal. Calcd. for $C_{15}H_{22}O_{10}$ (362.12): C, 49.72; H, 6.12. Found C, 49.61; H, 6.49%.

Procedure for Deacetylation

Compound **4** or **6** (5 mmol) in dry methanol (15 mL) containing a catalytic amount of sodium methoxide (50 mg, Na metal in 5 mL of methanol) was kept at room temperature overnight. The reaction mixture was neutralized with IR 120 H^+ resin. The resin was filtered off, and the solvent was removed under reduced pressure to give **1** or **2**, respectively.

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