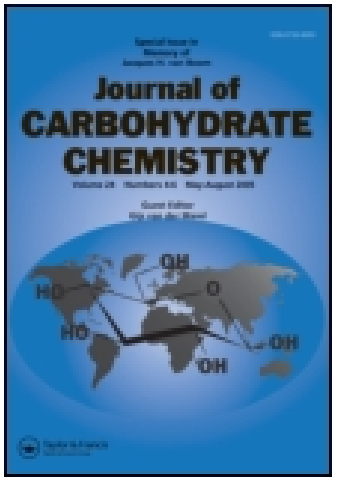

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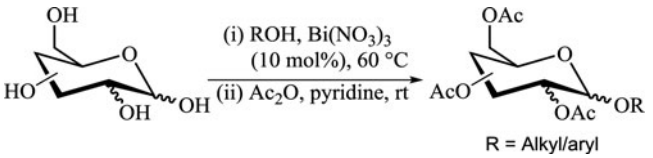
GRAPHICAL ABSTRACT



$Bi(NO_3)_3$, a low-cost, mild, and environmentally green catalyst, has been successfully utilized for Fischer glycosylation for the synthesis of alkyl/aryl glycopyranosides by reacting unprotected sugars, namely, D-glucose, L-rhamnose, D-galactose, D-arabinose, and *N*-acetyl-D-glucosamine with various alcohols in good to excellent yields. The glycosides were formed with high α-selectivity. Further, an expedient separation of α- and β-glycosides using silver nitrate–impregnated silica gel flash liquid chromatography has been developed.

Keywords Fischer glycosylation; Bismuth nitrate; Carbohydrates; Flash chromatography; Separation

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lcar.

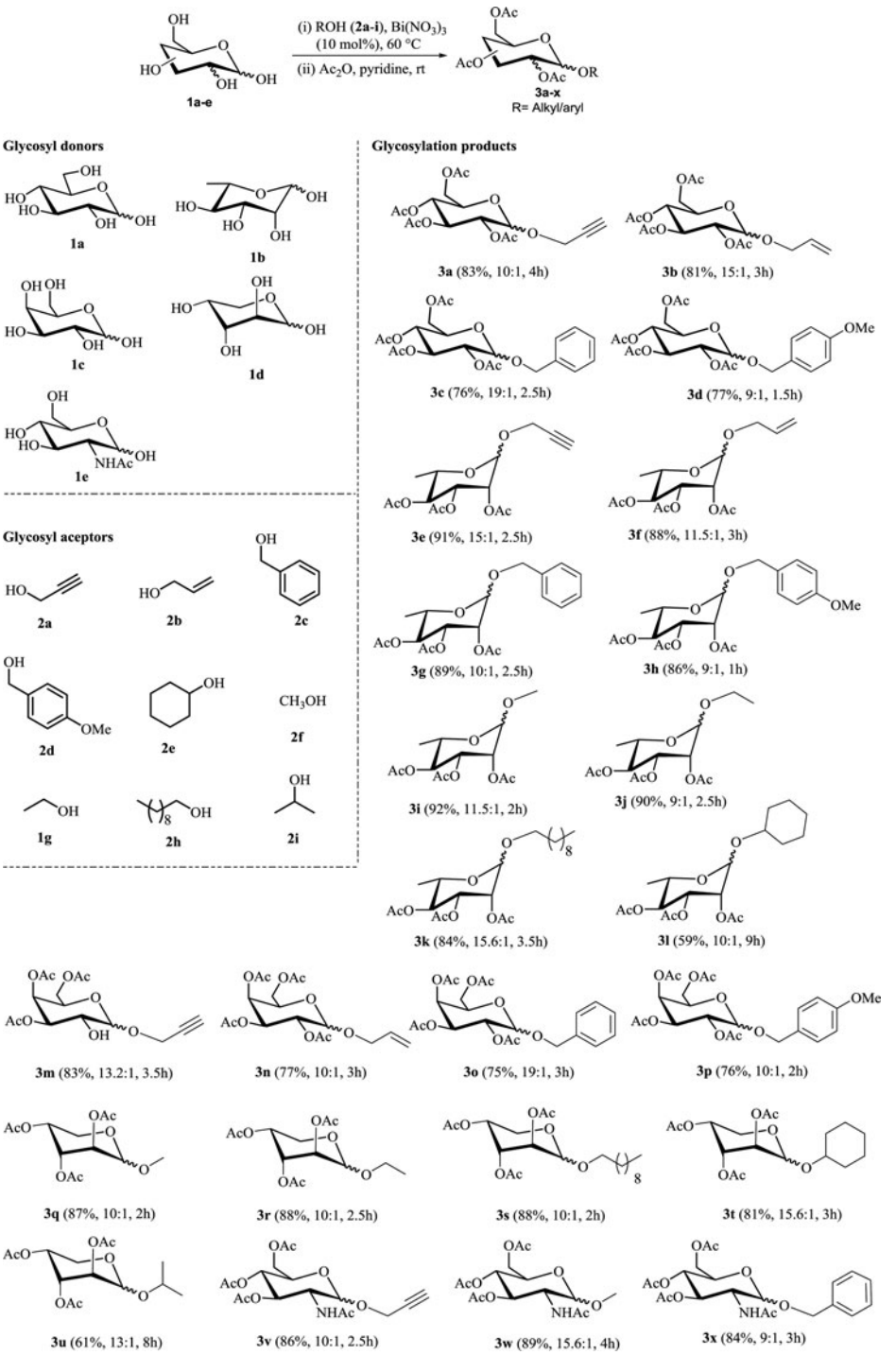
INTRODUCTION

Carbohydrates play an important role in various biological processes (e.g., cell adhesion, cell–cell interaction) and in disease processes such as pathogen infection, tumor metastasis, and inflammation in the precinct as glycosides and glycoconjugates.[1–5] Considering their biological importance, several glycosylation methods have been developed over the years. Beginning with the classical Koenig-Knorr method,[6] several excellent glycosidation methods have been reported, including Schmidt's trichloroacetamidates,[7] glycosyl halides,[8] *n*-pentenyl glycosides,[9] thioglycosides,[10] glycols,[11] phosphates,[12] and phosphites,[13] to name a few. However, Fischer glycosidation,[14] developed in 1893, still remains a favorite for the simple glycoside bond formation as it can be carried out in a single step without bothering with protecting group strategies. Moreover, Fischer-type glycosylation is the preferred method for the synthesis of simple glycosides, namely, *viz*. allyl, methyl, ethyl, benzyl, and *p*-methoxybenzyl glycosides as these temporary protecting groups of the anomeric hydroxyl group can easily undergo deprotection for further utilization in oligosaccharide synthesis.[15] Several synthetic methodologies[] have been explored to improve conventional Fischer glycosylation; however, in general, some of these methodologies suffer from a number of shortcomings: use of strong mineral acids, longer reaction time, use of excess of alcohols, preparation of specific catalysts, and decomposition of the product under reaction conditions.[15] Since Fischer glycosylation is an important reaction for glycoside bond formation, we reasoned that synthesis of glycosides using a green catalyst would still be desirable.

RESULTS AND DISCUSSION

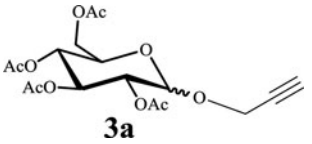
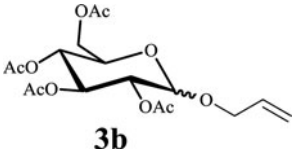
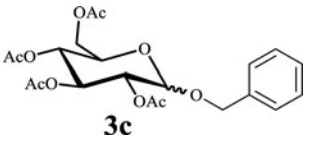
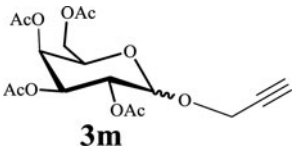
In our quest for an alternative procedure for Fischer glycosylation, we opined that bismuth nitrate could act as an efficient catalyst for the desired glycosylation. In recent times, bismuth salts, especially bismuth nitrate, have been found to be an efficient catalyst[17a–e] in various organic transformations due to their low toxicity,[17f-g] easy availability, and low cost. Herein, we report bismuth nitrate–catalyzed Fischer-type glycosylation of various unprotected and unactivated sugars with a diverse range of alcohols to afford alkyl/aryl glycosides (Sch. 1).

Initially, D-glucose was reacted with a varied quantity of propargyl alcohol (4–10 equiv.) at 60°C to 100°C under solvent-free reaction conditions catalyzed by $Bi(NO_3)_3$ (5 mol% and 10 mol%). We observed that D-glucose on reaction with propargyl alcohol (5 equiv.) and $Bi(NO_3)_3$ (10 mol%) at 60°C afforded the desired propargyl D-glucoside in an 83% yield in 4 h as a mixture of both anomers (α:β = 10:1). Thus, taking the alcohol (5 equiv.) and $Bi(NO_3)_3$



Scheme 1: Synthesis of alkyl/aryl glycosides.

Table 1: Comparison of $Bi(NO_3)_3{\cdot}5H_2O$ with other catalysts for the Fischer-type glycosylation

Glycoside	Catalyst	Temp. (°C)	Time (h)	Yield[a] (%)	α:β Ratio
 **3a**	Sulfamic acid	80	4	78[16d]	8:1
	H_2SO_4-silica gel	65	6	79[16b]	10:1
	$Bi(NO_3)_3{\cdot}5H_2O$	60	4	83	10:1
 **3b**	Sulfamic acid	80	4	82[16d]	5:1
	H_2SO_4-silica gel	65	6	79[16b]	10:1
	CF_3SO_3H	80	48	67[16e]	-
	$Bi(NO_3)_3{\cdot}5H_2O$	60	3	81	15:1
 **3c**	Sulfamic acid	80	5	81[16d]	6:1
	H_2SO_4-silica gel	65	7	78[16b]	10:1
	$Bi(NO_3)_3{\cdot}5H_2O$	60	2.5	76	19:1
 **3m**	Sulfamic acid	80	4	78[15d]	8:1
	H_2SO_4- silica	65	6	79[15b]	10:1
	$Bi(NO_3)_3{\cdot}5H_2O$	60	3.5	83	13.2:1

[a] References for reported methods.

(10 mol%) at 60°C as the ideal reaction condition, we embarked on generalization of the reaction by reacting various sugars with alcohols to afford a series of alkyl/aryl glycosides in excellent yields. It is pertinent to mention here that in all of the examples, the thermodynamically more stable glycopyranosides[18] were obtained. All of the alkyl/aryl glycoside products formed by the reaction of unprotected and unactivated monosaccharides with varied alcohols are depicted with yield, α/β ratio, and the time taken for completion of the reaction in parentheses. Also, we have carried out a comparison of our method with some of the reported procedures by taking selected substrates (Table 1). The comparative study was carried out with reference to the catalyst used, reaction temperature and time, yield, and the ratio of α- and β-glycosides. The higher selectivity for the formation of α-glycosides was observed in our method as compared to the previous procedures.

In general, all of the reactions proceeded smoothly and afforded the desired alkyl glycopyranosides in good to excellent yields with anomeric selectivity. In order to carry out the detailed characterization of the products formed,

the crude products were acetylated (see Experimental). The ratio of α- and β-anomers formed was deduced by ^{1}H NMR spectral analysis of the acetylated products by comparing the integration values of the peaks and coupling constant. In all cases, the product was formed as a mixture of α/β-anomers, but the thermodynamically more stable α-anomer was found to be predominant. The ratio of anomers formed was also determined by HPLC profiling (SunFire C18 column, 100 Å, 3.5 μm, 4.6 mm $\times$ 150 mm, mobile phase: MeOH: H_2O, 9:1, UV set at 254 or 220 nm) of all the synthesized compounds (see supplementary data).

In all the cases, glycosides are formed in a mixture of α- and β-anomers and the ratio of anomeric mixtures thus formed was practically determined by ^{1}H NMR spectroscopy of the products by comparing anomeric peaks and coupling constants. The isolation of α- and β-glycosides was seldom carried out, as isolation by column chromatography is tedious as well as time consuming. We were interested in the development of a method for the isolation of pure α- and β-glycosides. In this endeavor, we turned our attention to using an automated flash chromatography system equipped with a UV detector and ELSD. The RediSep column cartridge (12 g) was filled with $AgNO_3$-impregnated flash silica gel.[19] The crude reaction mixture was loaded onto the CombiFlash using a solid sample cartridge with slurry made with SiO_2 (230–400 mesh). The detection of peaks was performed with the UV detector set at 254 or 220 nm and ELSD and eluted in gradient mode with petroleum ether/EtOAc at a 20-mL/min flow rate. All glycosides of rhamnose and arabinose were eluted in 8% to 15% EtOAc/petroleum ether, whereas glycosides of glucose, galactose, and *N*-acetyl glucosamine were found to be polar and eluted with 15% to 20% EtOAc/petroleum ether mobile phase. A representative separation of compounds **3l** and **3t** is depicted in Figure 1. All of the aryl/alkyl glycosides were satisfactorily separated to furnish pure α- and β-glycosides using the automated flash chromatography system with $AgNO_3$-impregnated flash silica gel except for the propargyl glycosides, as these formed complex mixtures with $AgNO_3$ and could not be separated. These were separated by flash chromatography/re–flash chromatography (230–400 mesh) under the identical conditions. All of the isolated α- and β-glycosides were identified by their spectral data (see supplementary data).

CONCLUSIONS

In conclusion, we have demonstrated that Fischer glycosylation of unprotected and unactivated sugars with a diverse range of alcohols catalyzed by environmentally benign catalyst $Bi(NO_3)_3$ afforded alkyl/aryl glycosides in good to excellent yields. It is pertinent to mention here that in all of the

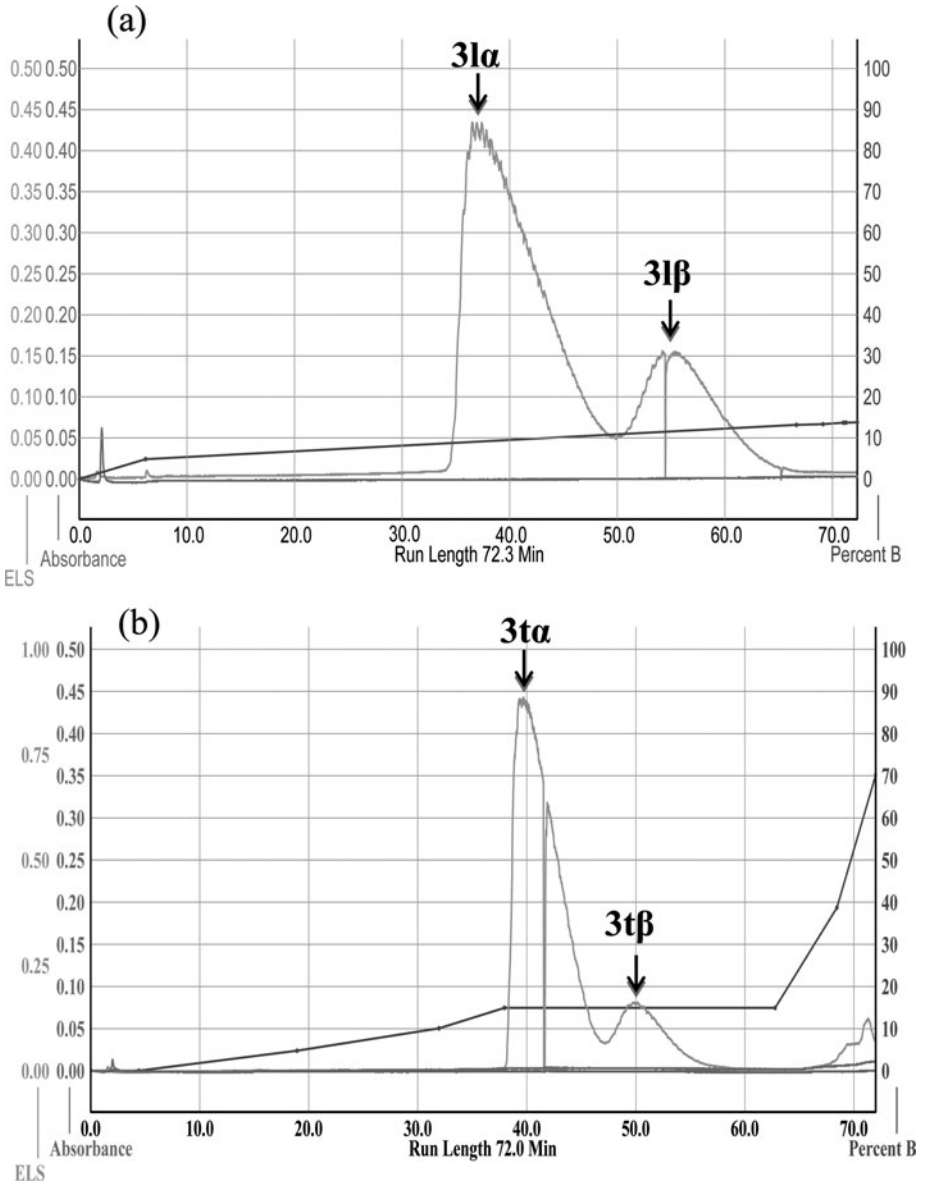


Figure 1: Separation of α- and β-glycosides by $AgNO_3$-impregnated silica gel using automated flash chromatography system equipped with UV detector and ELSD: (a) compound **3l**; (b) compound **3t**.

cases, the glycosides were formed with high α-selectivity. Also, we have developed an expedient separation method for α- and β-glycosides using silver nitrate–impregnated silica gel flash liquid chromatography, which could be used for the large-scale separations.

EXPERIMENTAL

Typical Experimental Procedure

To a mixture of sugar (1 mmol) and alcohol (5 mmol), $Bi(NO_3)_3{\cdot}5H_2O$ (10 mol%) was added with stirring at rt in a round-bottom flask fitted with a condenser, and the reaction mixture was then allowed to stir at 60°C under nitrogen for an appropriate time until the completion (TLC) of the reaction. The alcohol was removed in vacuo and the resulting crude product was passed through a short bed of Celite and eluted with DCM-MeOH (95:5) to furnish corresponding alkyl/aryl glycosides. Alternatively, the crude reaction product was acetylated with Ac_2O and pyridine (2:1), and usual workup resulted in the crude acetylate product, which was purified by flash chromatography. All of the products were characterized by spectral analysis. The spectral data of all new compounds are given below, and the spectral data of selected known compounds are given as supplementary data.

Spectral Data of New Compounds

Compound **3l*α***: Semisolid; υ_{max} ($CHCl_3$)/cm^{-1} 2934, 1744, 1369, 1216, 1071, 734; δ_H (400 MHz, $CDCl_3$, TMS): 5.33 (dd, J = 3.4, 3.4 Hz, 1H), 5.18 (dd, J = 1.7, 1.4 Hz, 1H), 5.05 (t, J = 9.8 Hz, 1H), 4.87 (brs, 1H), 3.99–3.92 (m, 1H), 3.62–3.55 (m, 1H), 2.15, 2.05, 1.98, 1.88–1.81 (m, 2H), 1.74–1.68 (m, 2H), 1.53–1.41 (m, 2H), 1.34–1.24 (m, 4H), 1.21 (d, J = 6.4 Hz, 3H); δ_C (100 MHz, $CDCl_3$, TMS): 170.1, 169.9, 169.4, 95.5, 75.9, 71.4, 70.5, 69.2, 66.2, 33.1, 31.3, 25.5, 24.0, 23.7, 20.9, 20.7, 20.7, 17.3; HRMS (ESI): calcd for $C_{18}H_{28}O_8Na$ 395.1676, found 395.1669.

Compound **3l*β***: Semisolid; δ_H (500 MHz, $CDCl_3$, TMS) 5.41 (brs, 1H), 5.07–5.01 (m, 2H), 4.73 (brs, 1H), 3.66 (brs, 1H), 3.52 (d, J = 6.1 Hz, 1H), 2.18, 2.05, 1.98, 1.86–1.81 (m, 2H), 1.70 (brs, 2H), 1.50–1.40 (m, 2H), 1.29–1.26 (m, 7H); δ_C (125 MHz, $CDCl_3$, TMS) 170.6, 170.2, 169.8, 96.1, 77.0, 71.3, 70.8, 70.4, 69.8, 33.0, 31.4, 25.5, 23.8, 23.7, 20.9, 20.8, 20.6, 17.5.

Compound **3t*α***: Semisolid; υ_{max} ($CHCl_3$)/cm^{-1} 2932, 1742, 1445, 1216, 1050, 747; δ_H (400 MHz, $CDCl_3$, TMS) 5.41–5.35 (m, 1H), 5.23–5.11 (m, 1H), 4.99–4.94 (m, 1H), 4.44–4.39 (m, 1H), 4.26–4.21 (m, 1H), 4.10–4.04 (m, 1H), 3.66–3.56 (m, 1H), 2.10, 2.09, 2.07, 1.88–1.81 (m, 2H), 1.74–1.68 (m, 2H), 1.54–1.48 (m, 2H), 1.33–1.22 (m, 4H); δ_C (100 MHz, $CDCl_3$, TMS) 170.7, 170.2, 169.7, 103.7, 78.4, 69.3, 67.4, 65.9, 63.4, 33.3, 31.5, 25.5, 23.9, 23.6, 21.0, 20.8, 20.6;HRMS (ESI): calcd for $C_{17}H_{26}O_8Na$ 381.1520, found 395.1512.

Compound (**3t*β***): Semisolid; δ_H (400 MHz, $CDCl_3$, TMS) 5.25 (brs, 1H), 5.17 (dd, J = 7.6, 7.1 Hz, 1H), 5.04 (dd, J = 3.4, 3.4 Hz, 1H), 4.51 (d, J = 7.1 Hz, 1H), 4.03 (dd, J = 2.9, 3.2 Hz, 1H), 3.62 (dd, J = 1.2, 1.2 Hz, 2H), 2.14, 2.06, 2.02, 1.88–1.78 (m, 2H), 1.72–1.68 (m, 2H), 1.50–1.46 (m, 2H), 1.33–1.24 (m,

4H); δ_C (100 MHz, $CDCl_3$, TMS) 170.4, 170.2, 169.4, 99.5, 77.4, 70.4, 69.4, 67.9, 63.2, 33.3, 31.5, 25.5, 23.7, 23.5, 20.9, 20.8, 20.7.

Compound **3uα**: Semisolid; υ_{max} ($CHCl_3$)/cm^{-1} 2975, 1742, 1433, 1216, 1047, 746; δ_H (500 MHz, $CDCl_3$, TMS) 5.25 (brs, 1H), 5.16 (dd, $J = 7.2$, 7.2 Hz, 1H), 5.04 (dd, $J = 3.4$, 3.8 Hz, 1H), 4.46 (d, $J = 7.3$ Hz, 1H), 4.03 (dd, $J = 2.7$, 3.1 Hz, 1H), 3.94–3.90 (m, 1H), 3.62 (dd, $J = 1.5$, 1.5 Hz, 1H), 2.14, 2.06, 2.02, 1.24 (d, $J = 6.5$ Hz, 3H), 1.15 (d, $J = 6.1$ Hz, 3H); δ_C (125 MHz, $CDCl_3$, TMS) 170.4, 170.2, 169.4, 99.9, 72.4, 70.4, 69.4, 67.9, 63.3, 23.3, 21.8, 20.9, 20.8, 20.7; HRMS (ESI): calcd for $C_{14}H_{22}O_8Na$ 341.1207, found 341.1200.

Compound **3uβ**: Solid; m.p. 130–132°C; δ_H (500 MHz, $CDCl_3$, TMS) 5.37–5.35 (m, 2H), 5.20 (d, $J = 3.4$ Hz, 1H), 5.12 (dd, $J = 3.1$, 3.8 Hz, 1H), 4.05 (d, $J = 12.9$ Hz, 1H), 3.89–3.84 (m, 1H), 3.66 (d, $J = 13.4$ Hz, 1H), 2.16, 2.08, 2.02, 1.24 (d, $J = 6.1$ Hz, 3H), 1.12 (d, $J = 6.1$ Hz, 3H); δ_C (125 MHz, $CDCl_3$, TMS) 170.5, 170.4, 170.1, 94.7, 70.6, 69.3, 68.6, 67.3, 60.4, 23.2, 21.5, 21.0, 20.8, 20.7.

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SUPPLEMENTAL MATERIAL

Electronic Supplementary Information (ESI) available: Full experimental procedures; spectral data of all new and selected known compounds; copies of ^1H, ^{13}C NMR, and DEPT spectra; LCMS and HRMS spectra of all the compounds; and HPLC chromatograms. These materials are available on request from the corresponding author.

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19. *Preparation[20] of $AgNO_3$-impregnated flash silica gel*: The $AgNO_3$-impregnated flash silica gel (230–400 mesh) for column chromatography was prepared by adding the silica gel to a methanolic silver nitrate solution (5%, w/v). The slurry was then dried under reduced pressure on a rotary evaporator to remove MeOH followed by drying in a hot-air oven at 80°C for approximately 1 h to afford dry $AgNO_3$-impregnated flash silica gel for flash column chromatography.

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