A Novel and Effective Procedure for the Preparation of Glucuronides

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Supporting Information Availabe: Experimental procedures and spectroscopic data for 6-phenyl sulfides (**2**, **6**, **8**, **10**, **11**), coupling products (**17**-**23**), and final methyl glucuronates (**24**-**29**).

Supporting Information

General Remarks. Solvents were distilled from the appropriate drying agents before use. Unless stated otherwise, all reactions were carried out under a positive pressure of argon and were monitored by TLC on silica gel HF_{254} (0.5 mm, Qingdao, China). Spots were detected under UV light or by charging with 10% H_2SO_4 in MeOH. Flash column chromatography was carried out on silica gel H (400 mesh, Qingdao, China). Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Mass spectra were recorded on a HP5989A mass spectrometer.

Typical Procedure for Preparation of 6-Phenylsulfides (2, **6**, **8**, **10**, **11)**. To a solution of 6-OH glucopyranoside (2.0 mmol) in dry pyridine (10 mL) was added $(PhS)_2$ (2.0 equiv) and $^nBu_3P$ (2.0 equiv). After being stirred at room temperature for 24 h, the mixture was diluted with EtOAc. The organic layer was washed with brine, and then dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography.

Methyl 2,3,4-tri-*O*-benzoyl-6-phenylthio-6-deoxy-α-D-glucopyranoside (2). Purification by chromatography (petroleum ether-EtOAc, 8:1 to 4:1) gave **2** as a colorless syrup: $[\alpha]_D^{25}$ +49.8 (c 1.33, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 8.01-7.20 (m, 20 H), 6.11 (t, 1 H, J = 9.9), 5.50 (t, 1 H, J = 9.6), 5.28 (dd, 1 H, J = 10.2, 3.6), 5.22 (d, 1 H, J = 3.6), 4.25 (td, 1 H, J = 9.6, 2.5), 3.47 (s, 3 H), 3.26 (dd, 1 H, J = 13.9,

2.6), 3.15 (dd, 1 H, *J* = 14.0, 8.8); EIMS *m/z*: 599, 598, 567, 489, 105. Anal. Calcd for $C_{34}H_{30}O_8S$: C, 68.21; H, 5.05; S, 5.36. Found: C, 67.96, H, 5.10, S, 5.59.

Ethyl 2,3,4-tri-*O*-benzoyl-6-phenylthio-6-deoxy-1-thio-β-D-glucopyranoside (6). Purification by chromatography (petroleum ether-EtOAc,10:1 to 5:1) gave **6** as a colorless syrup: $[\alpha]_D^{19}$ +37.2 (c 1.49, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.96-7.21 (m, 20 H), 5.86 (t, 1 H, *J* = 9.6), 5.53 (t, 2 H, *J* = 9.6), 4.81 (d, 1 H, *J* = 10.2), 3.95 (m, 1 H), 3.30-3.15 (m, 2 H), 2.73 (m, 2 H), 1.28 (t, 3 H, *J* = 7.4); EIMS *m/z*: 628, 567, 415, 105. Anal. Calcd for $C_{35}H_{32}O_7S_2$: C, 66.86; H, 5.13. Found: C, 66.62, H, 5.30.

Methyl 2,3-di-*O*-acetyl-6-phenylthio-6-deoxy-α-D-glucopyranoside (8). Purification by chromatography (petroleum ether-EtOAc 2:1 to 1:1) afforded **7** as a colorless syrup: $[\alpha]_D^{13}$ +117.1 (c 1.19, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.68-7.25 (m, 5 H), 5.24 (tt, 1 H, *J* = 9.5, 1.9), 4.88 (m, 2 H), 3.86 (td, 1 H, *J* = 9.6, 2.5), 3.59 (t, 1 H, *J* = 9.3), 3.54 (dd, 1 H, *J* = 13.6, 2.5), 3.38 (s, 3 H), 3.08 (dd, 1 H, *J* = 13.6, 8.2), 2.10 and 2.08 (each s, each 3 H); EIMS *m/z*: 370, 339, 310, 43. HRMS *m/z* Calcd for $C_{17}H_{22}O_7S$: 370.06366. Found: 370.10795.

***tert*-Butyldimethylsilyl 2,3-di-*O*-benzoyl-6-phenylthio-6-deoxy-α/β-D-glucopyranoside (10)**. Compound **10** was inseparable α/β anomers. Its acetylation products (Ac_2O, pyridine, 100%) were separated (α/β 2/1) and characterized. ***tert*-Butyldimethylsilyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-phenylthio-6-deoxy-α-D-glucopyranoside**: $[\alpha]_D^{25}$ +101.0 (c 1.02, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.97-7.21 (m, 15 H), 5.97 (t, 1 H, *J* = 9.9), 5.58 (d, 1 H, *J* = 3.0), 5.29 (t, 1 H, *J* = 9.9), 5.17 (dd, 1 H, *J* = 10.2, 3.0), 4.33 (m, 1 H), 3.21 (dd, 1 H, *J* = 13.7, 3.3), 3.10 (dd, 1 H, *J* = 13.7, 8.0), 1.96 (s, 3 H), 0.85 (s, 9 H); EIMS *m/z*: 619, 579, 505, 105. ***tert*-Butyldimethylsilyl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-phenylthio-6-deoxy-β-D-glucopyranoside**: $[\alpha]_D^{25}$ +67.1 (c 1.02, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.91-7.23 (m, 15 H), 5.62 (t, 1 H, *J* = 9.8), 5.41 (dd, 1 H, *J* = 10.2, 7.6), 5.25 (t, 1 H, *J* = 9.6), 4.95 (d, 1 H, *J* = 7.4), 3.80 (m, 1 H), 3.13 (m, 2 H), 1.96 (s, 3 H), 0.78 (s, 9 H); EIMS *m/z*: 637, 619, 579, 505, 105.

Preparation of 2,3-di-*O*-benzoyl-4-*O*-acetyl-6-phenylthio-6-deoxy-α-D-glucopyranosyl trichloroacetimidate (11). To a solution of the above acetates (637 mg, 1.0 mmol) in dry THF (8 mL), was added HOAc (0.08 mL) and TBAF (2.0 mL, 1 M solution in THF). After being stirred at room temperature for 10 h, the mixture was

diluted with ether and washed with brine. The organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether-EtOAc 4:1) to afford a colorless syrup, which was then dissolved in CH_2Cl_2 (10 mL). $CNCCl_3$ (0.6 mL) and DBU (one drop) were added to the resulting solution. After being stirred at room temperature for 1 h, the solution was concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether-EtOAc with 1% of triethylamine 6:1 to 4:1) to afford **11** (545 mg, 81% from **10**) as a white foam: $[\alpha]_D^{27}$ +92.8 (c 0.99, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 8.60 (s, 1 H), 7.93-7.21 (m, 15 H), 6.73 (s, br, 1 H), 6.02 (t, 1 H, *J* = 9.9), 5.50 (dd, 1 H, *J* = 10.2, 3.6), 5.40 (t, 1 H, *J* = 9.9), 4.35 (m, 1 H), 3.24 (dd, 1 H, *J* = 14.3, 3.6), 3.11 (dd, 1 H, *J* = 14.3, 7.4), 1.99 (s, 3 H).

Procedure for Preparation of 17 and 18. A suspension of thioglycoside donor (**6**, 0.51 mmol), acceptor (**1** or **15**, 0.25 mmol), and 4 Å MS in dry CH_2Cl_2 (8 mL) was stirred at room temperature for 30 min. And MeOTf (0.29 mL) was then added to the reaction. After 10 h, the reaction was quenched with triethylamine (0.1 mL) and filtered. The filtrate was concentrated in vacuo to give a residue, which was purified by flash column chromatography.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-phenylthio-6-deoxy-β-D-glucopyranosyl)-α-D-glucopyranoside (17). Purification by chromatography (petroleum ether-EtOAc 4:1) afforded **17** as a colorless syrup: ^{1}H NMR (300 MHz, $CDCl_3$) 8.00-7.20 (m, 35 H), 6.09 (t, 1 H, *J* = 9.9), 5.84 (t, 1 H, *J* = 9.6), 5.52 (t, 1 H, *J* = 9.9), 5.48 (t, 1 H, *J* = 9.6), 5.34 (t, 1 H, *J* = 10.2), 5.13 (dd, 1 H, *J* = 10.2, 3.6), 5.00 (d, 1 H, *J* = 3.6), 4.88 (d, 1 H, *J* = 8.0), 4.24 (m, 1 H), 4.01 (dd, 1 H, *J* = 11.5, 1.7), 3.92 (m, 1 H), 3.72 (dd, 1 H, *J* = 11.3, 7.4), 3.64 (m, 1 H), 3.20 (m, 4 H); ESIMS *m/z*: 1097 (M + Na + 1).

Cholesterol-3-yl 2,3,4-tri-*O*-benzoyl-6-phenylthio-6-deoxy-β-D-glucopyrano-side (18). Purification by chromatography (petroleum ether-EtOAc, 10:1) afforded **18** as a white foam: ^{1}H NMR (300 MHz, $CDCl_3$) 7.98-7.18 (m, 20 H), 5.82 (t, 1 H, *J* = 9.6), 5.48 (m, 2 H), 5.28 (m, 1 H), 4.88 (d, 1 H, *J* = 8.0), 3.93 (m, 1 H), 3.51 (m, 1 H), 3.21 (d, 2 H, *J* = 5.5), 0.93, 0.92, 0.89, 0.87, 0.67 (each s, each 3 H); EIMS *m/z*: 584, 567, 368, 105.

Procedure for Preparation of 19 and 20. A solution of trichloroacetimidate donor (**11**, 0.37 mmol), aglycone (**15** or **16**, 0.74 mmol), and 4 Å MS (1.0 g) in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 30 min and then cooled to -50°C. A solution of TMSOTf (0.93 mL, 0.08 M) in CH_2Cl_2 was slowly added to the reaction. After being stirred for another 30 min, the reaction was quenched with triethylamine (0.1 mL) and filtered. The filtrates were concentrated in vacuo to give a residue, which was purified by flash column chromatography.

Cholesterol-3-yl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-phenylthio-6-deoxy-β-D-glucopyranoside (19). Purification by chromatography (petroleum ether-EtOAc 10:1) afforded **19** as a white foam: $[\alpha]_D^{24}$ +57.3 (c 1.06, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.90-7.20 (m, 15 H), 5.60 (t, 1 H, *J* = 9.6), 5.37 (dd, 1 H, *J* = 9.9, 9.6), 5.22 (m, 2 H), 4.77 (d, 1 H, *J* = 8.0), 3.78 (m, 1 H), 3.45 (m, 1 H), 3.13 (d, 2 H, *J* = 5.5), 1.94 (s, 3 H); Anal. Calcd for $C_{55}H_{70}O_8S$: C, 74.12; H, 7.92. Found: C, 73.75, H, 7.82.

Diosgenin-3-yl 4-*O*-acetyl-2,3-di-*O*-benzoyl-6-phenylthio-6-deoxy-β-D-glucopyranoside (20). Purification by chromatography (petroleum ether-EtOAc 6:1) afforded **20** as a white foam: ^{1}H NMR (300 MHz, $CDCl_3$) 7.92-7.21 (m, 15 H), 5.62 (t, 1 H, *J* = 9.9), 5.39 (t, 1 H, *J* = 9.9), 5.23 (m, 2 H), 4.80 (d, 1 H, *J* = 7.7), 3.81 (m, 1 H), 3.47 (m, 2 H), 3.38 (t, 1 H, *J* = 10.9), 3.15 (d, 2 H, *J* = 5.5), 1.96 (s, 3 H); EIMS *m/z*: 919, 918, 522, 505, 396, 105. Anal. Calcd for $C_{55}H_{66}O_{10}S\cdot H_2O$: C, 70.49; H, 7.31. Found: C, 70.27; H, 7.03.

Procedure for Preparation of 21-23. A suspension of trichloroacetimidate donor (**12-14**, 2.10 mmol), acceptor (**8**, 1.05 mmol) and 4 Å MS (2.0 g) in dry CH_2Cl_2 (15 mL) was stirred at room temperature for 30 min and then cooled to -50°C. A solution of TMSOTf (1.0 mL, 0.21 M) in CH_2Cl_2 was slowly added to the reaction. After being stirred for another 30 min, the reaction was quenched with triethylamine (0.2 mL) and filtered. The filtrates were concentrated in vacuo to give a residue, which was purified by flash column chromatography.

Methyl 2,3-di-*O*-acetyl-6-phenylthio-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (21). Purification by chromatography (petroleum ether-EtOAc, 3:1) afforded **21** as a colorless syrup: $[\alpha]^{13}_D$ +71.5 (c 1.22, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 8.07-7.21 (m, 25 H), 5.72 (t, 1 H, *J* = 9.6), 5.60

(t, 1 H, *J* = 9.6), 5.49 (t, 2 H, *J* = 9.3, 8.2), 4.82 (m, 3 H), 4.64 (dd, 1 H, *J* = 12.1, 3.0), 4.43 (dd, 1 H, *J* = 12.4, 5.5), 3.98 (m, 1 H), 3.88 (m, 2 H), 3.41 (d, 1 H, *J* = 10.2), 3.29 (s, 3 H), 3.11 (dd, 1 H, *J* = 13.5, 5.0), 2.05 and 1.97 (each s, each 3 H); EIMS *m/z*: 948, 826, 579, 370,105. Anal. Calcd for $C_{51}H_{48}O_{16}S$: C, 64.55; H, 5.10. Found: C, 64.30, H, 5.14.

Methyl 2,3-di-*O*-acetyl-6-phenylthio-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-glucopyranoside (22). Purification by chromatography (petroleum ether-EtOAc, 2:1) afforded **22** as a colorless syrup: $[\alpha]^{25}_{D}$ +86.3 (c 0.86, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.41-7.18 (m, 5 H), 5.51 (d, 1 H, *J* = 2.5), 5.29 (m, 3 H), 5.10 (dd, 1 H, *J* = 9.9, 4.9), 4.82 (m, 2 H), 4.71 (m, 1 H), 4.25 (dd, 1 H, *J* = 12.1, 4.4), 4.12 (dd, 1 H, *J* = 12.1, 2.7), 3.86 (m, 1 H), 3.59 (m, 2 H), 3.36 (s, 3 H), 2.96 (dd, 1 H, *J* = 14.2, 8.4); EIMS *m/z*: 700, 370, 353, 331, 169. Anal. Calcd for $C_{31}H_{40}O_{16}S$: C, 53.14; H, 5.75. Found: C, 52.85, H, 5.96.

Methyl 2,3-di-*O*-acetyl-6-phenylthio-6-deoxy-4-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (23). Purification by chromatography (petroleum ether-EtOAc, 4:1 to 3:1) afforded **23** as a colorless syrup: ^{1}H NMR (300 MHz, $CDCl_3$) 7.46-7.19 (m, 5 H), 5.44 (t, 1 H, *J* = 9.3), 5.22 (dd, 1 H, *J* = 10.2, 3.0), 5.15 (m, 1 H), 5.04 (t, 1 H, *J* = 9.9, 10.2), 4.86 (m, 2 H), 4.80 (dd, 1 H, *J* = 10.2, 3.7), 3.98 (m, 1 H), 3.86 (dd, 1 H, *J* = 9.9, 6.3), 3.73 (t, 1 H, *J* = 9.6), 3.52 (dd, 1 H, *J* = 13.5, 2.5), 3.39 (s, 3 H), 3.12 (dd, 1 H, *J* = 13.5, 7.7), 2.14, 2.06, 2.05, 2.00 (each s, each 3 H), 1.15 (d, 3 H, *J* = 6.3). Anal. Calcd for $C_{29}H_{38}O_{14}S$: C, 54.19; H, 5.96. Found: C, 53.87, H, 6.14.

Representative Procedure for the Conversion of 6-Phenylsulfides to Methyl Glucuronides. To a solution of **23** (436 mg, 0.68 mmol) in CCl_4 (10 mL) at 0°C were added pyridine (0.11 mL) followed by slow addition of SO_2Cl_2 (0.11 mL). The resulting solution was stirred at this temperature for 5 h, and then diluted with CH_2Cl_2. The mixture was washed with water, dried over $MgSO_4$, and concentrated in vacuo to give a residue, which was used in the next step without any purification. The above crude material was dissolved in MeOH-H_2O-CH_2Cl_2 (2:1:1, 10 mL), and then $HgCl_2$ (1.8 g) was added. After the mixture was stirred for 48 h at room temperature, the solvent was evaporated and the residue was dissolved in EtOAc-Et_2O (1:1, 50 mL). The resulting

solution was then washed with half saturated NaCl solution, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether-EtOAc 3:1) to afford **29** (349 mg, 89%) as a white foam.

Methyl [methyl (2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)uronate]-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (24): ^{1}H NMR (300 MHz, $CDCl_3$) 7.99-7.22 (m, 30 H), 6.09 (t, 1 H, *J* = 9.9), 5.93 (t, 1 H, *J* = 9.3), 5.68 (t, 1 H, *J* = 9.3), 5.59 (t, 1 H, *J* = 9.3), 5.34 (t, 1 H, *J* = 9.9), 5.11 (dd, 1 H, *J* = 10.2, 3.6), 5.00 (d, 1 H, *J* = 7.7), 4.92 (d, 1 H, *J* = 3.6), 4.35 (d, 1 H, *J* = 9.6), 4.23 (m, 1 H), 4.16 (m, 1 H), 3.79 (dd, 1 H, *J* = 11.5, 8.2), 3.67 (s, 3 H), 3.10 (s, 3 H); ESIMS *m/z*: 1033 (M + Na + 1).

Methyl (cholesterol-3-yl 4-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranoside) uronate (25): $[\alpha]^{24}_D$ +18.4 (c 1.17, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.95-7.35 (m, 10 H), 5.70 (d, 1 H, *J* = 9.6), 5.47 (t, 1 H, *J* = 9.6), 5.43 (m, 1 H), 4.89 (d, 1 H, *J* = 7.7), 4.25 (m, 3 H), 1.96 (s, 3 H); EIMS *m/z*: 825, 441, 402, 366, 105.

Methyl (diosgenin-3-yl 4-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranoside) uronate (26): $[\alpha]^{26}_D$ -38.5 (c 1.12, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 7.94-7.36 (m, 10 H), 5.70 (t, 1 H, *J* = 9.6), 5.45 (m, 2 H), 4.88 (d, 1 H, *J* = 7.7), 4.39 (m, 1 H), 4.24 (m, 3 H), 3.80 (s, 3 H), 3.46 (m, 1 H), 3.37 (t, 1 H, *J* = 10.2), 1.95 (s, 3 H); EIMS *m/z*: 853, 441, 105.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-(methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside)uronate (27): $[\alpha]^{26}_D$ +26.2 (c 1.13, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 8.10-7.25 (m, 20 H), 5.90 (t, 1 H, *J* = 9.6), 5.64 (t, 1 H, *J* = 9.6), 5.51 (m, 1 H), 5.44 (dd, 1 H, *J* = 9.6, 8.0), 5.07 (d, 1 H, *J* = 8.0), 4.90 (d, 1 H, *J* = 3.8), 4.81 (dd, 1 H, *J* = 10.2, 3.8), 4.64 (dd, 1 H, *J* = 12.2, 2.9), 4.45 (dd, 1 H, *J* = 12.2, 5.8), 4.15 (m, 3 H), 3.40 and 3.38 (each s, each 3 H), 2.05 and 1.98 (each s, each 3 H); EIMS *m/z*: 853, 793, 579, 105. Anal. Calcd for $C_{46}H_{44}O_{18}$: C, 62.44; H, 5.01. Found: C, 62.03; H, 5.01.

Methyl 2,3,4,6-tetra-*O*-acetyl-α-L-mannopyranosyl-(1→4)-(methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside)uronate (28): $[\alpha]^{26}_D$ +89.0 (c 0.98, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 5.49 (d, 1 H, *J* = 2.2), 5.37 (t, 1 H, *J* = 9.8), 5.23 (t, 1 H, *J* = 9.9), 5.17 (dd, 1 H, *J* = 9.9, 3.9), 4.96 (d, 1 H, *J* = 3.8), 4.90 (dd, 1 H, *J* = 10.2, 3.8), 4.52 (m, 1 H), 4.26 (d, 1 H, *J* = 9.9), 4.20 (m, 1 H), 4.12 (dd, 1 H, *J* = 12.4, 2.5), 3.84 (s, 1

H), 3.69 (t, 1 H, *J* = 9.3), 3.65 (m, 1 H), 3.40 (s, 3 H); EIMS *m/z*: 605, 545, 331, 43. Anal. Calcd for $C_{26}H_{36}O_{18}\cdot 0.5H_2O$: C, 48.37; H, 5.78. Found: C, 48.25; H, 5.63.

Methyl 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-(methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside)uronate (29): $[\alpha]^{26}_{D}$ +43.1 (c 1.11, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 5.46 (t, 1 H, *J* = 9.6), 5.12 (dd, 1 H, *J* = 10.2, 3.3), 5.03 (m, 1 H), 4.99 (t, 1 H, *J* = 10.2), 4.92 (d, 1 H, *J* = 3.6), 4.78 (dd, 1 H, *J* = 10.2, 3.6), 4.77 (m, 1 H), 4.26 (d, 1 H, *J* = 9.9), 3.97 (t, 1 H, *J* = 9.6), 3.83 (m, 4 H), 3.44 (s, 3 H), 1.12 (d, 3 H, *J* = 6.1); EIMS *m/z*: 547, 487, 273, 43. Anal. Calcd for $C_{24}H_{34}O_{16}\cdot H_2O$: C, 48.32; H, 6.09. Found: C, 48.15; H, 5.69.