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Synthesis of Thioesters by Simultaneous Activation of Carboxylic Acids and Alcohols Using PPh_3/NBS with Benzyltriethylammonium Tetrathiomolybdate as the Sulfur Transfer Reagent

Purushothaman Gopinath,[a] Ravindran Sasitha Vidyarini,[a] and Srinivasan Chandrasekaran*[a][‡]

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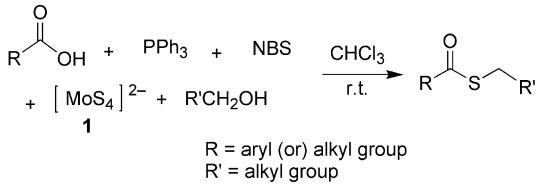
A new and simple route for the synthesis of thioesters starting from carboxylic acids and alcohols is reported by using tetrathiomolybdate as the key sulfur transfer reagent. Triphenylphosphane and *N*-bromosuccinimide were used for the activation of the carboxylic acid and alcohol in the same pot followed by the transfer of sulfur from tetrathiomolybdate. Thioesters were obtained in good to moderate yields. Primary alcohols show excellent reactivity and gave good yields of the corresponding thioesters, whereas secondary alcohols gave moderate yields and tertiary alcohols were very less reactive and gave poor yields of the corresponding thioesters.

Introduction

The thioester unit is an integral component of many natural products[1] and bioactive compounds.[2] The recent advent of organometallic coupling[3] reactions with thioesters as coupling partners has increased the quest for newer methods of thioester synthesis. Thioesters also serve as important intermediates in the biosynthesis of polyketides and nonribosomal polypeptides from fatty acids and amino acids.[4] Additionally, thioesters are used as building blocks for the synthesis of heterocyclic compounds,[5] as substrates in stereoselective aldol reactions,[6] and as intermediates in the synthesis of various natural products[7] and drugs of clinical interest (antihypertensive agents).[8]

Due to these widespread applications, a number of chemical and enzymatic methods have been developed for synthesis of thioesters. General synthetic methods include the direct coupling of an activated carboxylic acid with a thiol[9] or the coupling of thiocarboxylates with arenediazonium salts[10] or alkyl halides.[11] With issues related to handling of thiols and thioacids and the availability of starting materials, a simple and alternative protocol for the synthesis of thioesters is needed.

Recently, we reported a one-pot protocol for the synthesis of thioesters directly from carboxylic acids and alkyl halides[12] by using PPh_3 and *N*-bromosuccinimide (NBS) for activating the carboxylic acid[13] and benzyl triethylammonium tetrathiomolybdate[14] (**1**), as the sulfur transfer reagent. Because alkyl halides are generally synthesized from the corresponding alcohols, we speculated that an alternative protocol with the use of alcohols as starting materials would be an important and more versatile route for the synthesis of thioesters (Scheme 1).



Scheme 1. General reaction scheme.

To the best of our knowledge this is the first report of the synthesis of thioesters starting from carboxylic acids and alcohols without the use of thiols or thioacids as starting materials. The results of this investigation are presented in this paper.

Results and Discussion

It is known from the literature that alcohols can also be activated by using PPh_3 and NBS[15] to form the corresponding bromide. So, we conceived that the simultaneous activation of both the carboxylic acid and the alcohol by using PPh_3 and NBS in the same pot, followed by treatment with reagent **1** could form the corresponding thioester. Accordingly, benzoic acid (**2a**; 1.0 equiv.) and ethanol (1.2 equiv.) were treated with PPh_3 and NBS to form the

[a] Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India
Fax: +91-80-2360-2423
E-mail: scn@orgchem.iisc.ernet.in
[‡] Honorary Professor, Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur, Bangalore

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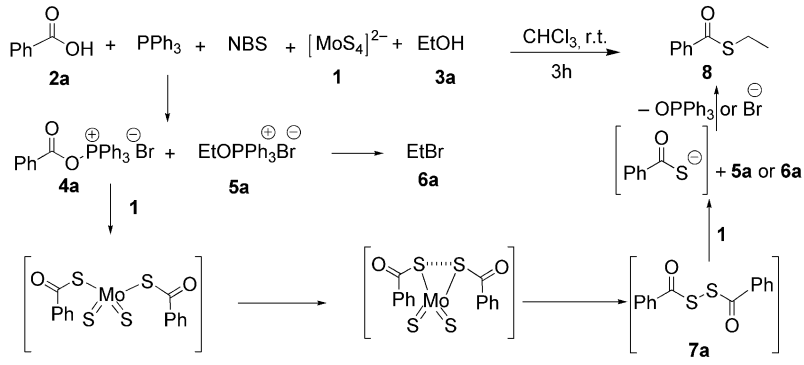


Scheme 2. Synthesis of ethyl thiobenzoate by simultaneous activation protocol.

corresponding activated intermediates followed by the addition of reagent **1** (2.0 equiv.) to give the corresponding thioester **8** in 74% yield (Scheme 2). We speculated that tetrathiomolybdate **1** would react with benzoyloxy phosphonium salt **4a** (as it is more reactive than **5a** or **6a**) to form the corresponding dibenzoyl disulfide (**7a**), followed by reductive cleavage to generate the thiobenzoate ion. The thiobenzoate ion may then react with the alkoxy phosphonium intermediate **5a** or bromide **6a** to give ethyl thiobenzoate (**8**).

In order to test the generality of this methodology, the reaction was then carried out with other alcohols and benzoic acid as the standard. The results of this study are summarized in Table 1. Under these conditions the reaction of primary alcohols (Table 1, Entries 1–3) gave very good yields of products in short reaction times (1–3 h). However, the reaction of allylic alcohols and secondary alcohols (Table 1, Entries 4–6) gave only moderate yield of the product. The reaction of a tertiary alcohol (Table 1, Entry 7) gave very poor yield and required a longer reaction time (12 h). These results could be rationalized on the basis of the steric crowding around the reaction center (carbon attached to the OH group), which offers hindrance to nucleophilic substitution by the thioaroylate ion.

Interestingly, the reaction of benzyl alcohol (Table 1, Entry 8) gave the corresponding disulfide instead of the expected thioester. This is because benzyloxy phosphonium intermediate **5h** or benzyl bromide (**6h**) reacts with reagent **1** in preference to benzoyloxy phosphonium intermediate **4a** (Scheme 3).

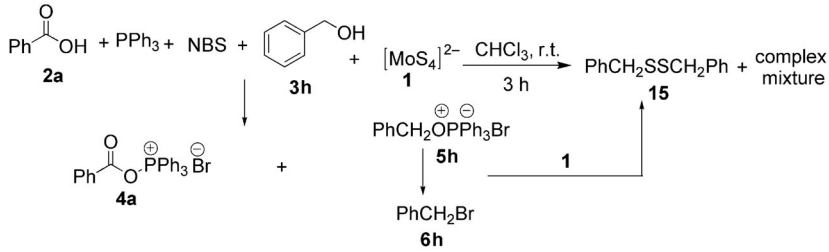
When the reaction was carried out with other carboxylic acids, the reactivity profile and the yields were very similar to those obtained earlier. Phenyl acetic acid (aliphatic acid) and *p*-methoxy benzoic acid (aromatic acid) both gave almost similar yields of their corresponding thioesters. The results of this study with various carboxylic acids and primary alcohols are summarized in Table 2.

Thioester derivatives of carbohydrates also play a key role in several synthetic transformations. We first studied the reactivity of anomeric alcohols to show the generality of the methodology. Thus, anomeric alcohol[16] **24**, synthesized from D-(+)-mannose, iodine, and acetone, was treated with benzoic acid, PPh_3, NBS, and reagent **1** to form the corresponding β-thioglycoside **25** in 60% yield (Scheme 4). Similarly, phenyl acetic acid gave the corresponding β-thioglycoside **26** in 55% yield.

In pursuing these studies further, we decided to study the reactivity of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranuronic acid[17] (**27**), a sugar carboxylic acid synthesized from glucuronic acid by acetylation with the use of acetic anhydride,

Table 1. Reaction of benzoic acid with various alcohols.

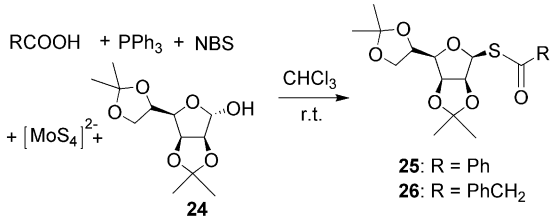
Entry	Acid	Alcohol	Product	Time [h]	Yield [%]
1	PhCOOH	EtOH **3a**	**8**	3	74
2	PhCOOH	OH **3b**	**9**	3	81
3	PhCOOH	OH **3c**	**10**	1	90
4	PhCOOH	OH **3d**	**11**	4	50
5	PhCOOH	Ph OH **3e**	**12**	3.5	52
6	PhCOOH	OH **3f**	**13**	6	40
7	PhCOOH	OH **3g**	**14**	12	15
8	PhCOOH	OH **3h**	**15** (70%) + other products	1	–



Scheme 3. Reaction of benzyl alcohol with reagent **1**.

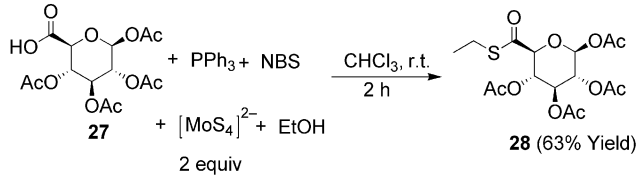
Table 2. Reaction of various carboxylic acids with alcohols.

Entry	Acid	Alcohol	Product	Time [h]	Yield [%]
1	**2b**	EtOH **3a**	**16**	3	80
2	**2b**	**3c**	**17**	4	72
3	**2c**	**3c**	**18**	4.5	70
4	**2c**	**3i**	**19**	5	66
5	**2c**	EtOH **3a**	**20**	4	75
6	**2c**	**3b**	**21**	3.5	82
7	**2d**	EtOH **3a**	**22**	4	65
8	**2e**	**3b**	**23**	3	80



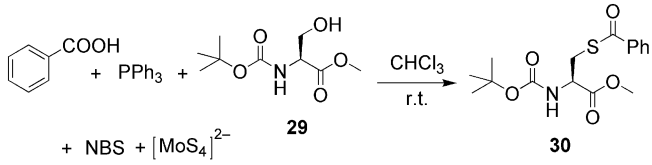
Scheme 4. Synthesis of β-thioglycosides **25** and **26**.

iodine, and methanol. Carboxylic acid **27**, when treated with PPh_3, NBS, reagent **1**, and ethanol ($CHCl_3$, 28 °C, 2 h) afforded the corresponding ethyl thioester **28** in 63% yield (Scheme 5).



Scheme 5. Synthesis of glucuronic acid based thioester **28**.

Cysteine is an important structural and functional component of many proteins and enzymes. Although it is more commonly synthesized through biotransformation, the chemical synthesis is still a challenge to the synthetic organic chemist. One of the most common methods for its preparation is starting from *N*-Boc serine ester, which is tosylated first followed by nucleophilic displacement with the corresponding thioacid or thioacetate.[18] It seemed logical to attempt a one-pot conversion of *N*-Boc serine into *S*-protected cysteine by using our methodology involving reagent **1**. Accordingly, the reaction of *N*-Boc-L-serine methyl ester[19] (**29**) with benzoic acid and reagent **1** under the reaction conditions ($CHCl_3$, 28 °C, 2 h) led to the formation of cysteine derivative **30** in 70% yield (Scheme 6).



Scheme 6. Synthesis of *N*-Boc-L-cysteine derivative **30**.

Conclusions

In conclusion, a variety of substituted thioesters and thioglycosides were synthesized from carboxylic acids and alcohols by using benzyltriethylammonium tetrathiomolybdate as a sulfur transfer reagent via acyloxy and alkoxy phosphonium salts as intermediates. We have also shown a one-pot protocol for the synthesis of a cysteine derivative from serine.

Experimental Section

General Procedure for the Synthesis of Thioesters 8–23: To a well-stirred solution of the corresponding carboxylic acid (1.0 mmol), PPh_3 (2.8 mmol), alcohol (1.2 mmol), and NBS (2.8 mmol) in $CHCl_3$ (5 mL) (stirred for 10 min) was added benzyltriethylammonium tetrathiomolybdate (**1**; 2.0 mmol). After completion of the reaction, diethyl ether (20 mL) was added to the reaction mixture, and it was filtered through a pad of Celite. The residue was again extracted with CH_2Cl_2 (5 mL) followed by extraction with diethyl ether (20 mL) and filtered again through a pad of Celite. The combined extract was evaporated, and the residue was purified by column chromatography on silica gel to give the corresponding thioesters.

Compound 10: Colorless liquid. Yield: 0.218 g, 90%. IR (neat): $\tilde{\nu}$ = 1662, 1207, 912 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.96 (m, 2 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.45 (t, J = 8.0 Hz, 2 H), 7.34–7.22 (m, 5 H), 3.32 (t, J = 8.0 Hz, 2 H), 2.98 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 140.1, 137.1, 133.3, 128.6, 128.5, 127.2, 126.5, 35.9, 30.4 ppm. HRMS: calcd. for $C_{15}H_{14}OSNa^+$ [M + Na^+] 265.0663; found 265.0662.

Compound 17: Colorless liquid. Yield: 0.184 g, 72%. IR (neat): $\tilde{\nu}$ = 1686, 1163 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.17 (m, 10 H), 3.82 (s, 2 H), 3.10 (t, J = 8.0 Hz, 2 H), 2.84 (t, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.2, 139.9, 133.6, 129.5, 128.7, 128.5, 127.4, 126.5, 50.6, 35.7, 30.6 ppm. HRMS: calcd. for $C_{16}H_{16}OSNa^+$ [M + Na^+] 279.0820; found 279.0807.

Compound 18: Colorless liquid. Yield: 0.190 g, 70%. IR (neat): $\tilde{\nu}$ = 1658, 1601, 1167 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 9.0 Hz, 2 H), 7.35–7.21 (m, 5 H), 6.92 (d, J = 9.0 Hz, 2 H), 3.86 (s, 3 H), 3.29 (t, J = 7.8 Hz, 2 H), 2.96 (t, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 163.7, 140.2, 129.4, 128.6, 113.7, 55.5, 36.1, 30.3 ppm. HRMS: calcd. for $C_{16}H_{16}O_2SNa^+$ [M + Na^+] 295.0769; found 295.0769.

Compound 19: Colorless liquid. Yield: 0.189 g, 66%. IR (neat): $\tilde{\nu}$ = 1654, 1597, 1163 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.4 Hz, 2 H), 7.18–7.11 (m, 4 H), 6.92 (d, J = 8.4 Hz, 2 H), 3.86 (s, 3 H), 3.27 (t, J = 7.5 Hz, 2 H), 2.92 (t, J = 7.5 Hz, 2 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.4, 163.7, 137.1, 136.0, 130.1, 129.4, 129.2, 128.5, 113.7, 55.5, 35.6, 30.4, 21.0 ppm. HRMS: calcd. for $C_{17}H_{18}O_2SNa^+$ [M + Na^+] 309.0925; found 309.0903.

Compound 21: Colorless liquid. Yield: 0.172 g, 82%. IR (neat): $\tilde{\nu}$ = 1657, 1603, 1259, 1167 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.7 Hz, 2 H), 6.92 (d, J = 8.7 Hz, 2 H), 3.86 (s, 3 H), 3.04 (t, J = 7.2 Hz, 2 H), 1.76–1.64 (m, 2 H), 1.03 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.6, 163.6, 130.2, 129.3, 113.7, 55.5, 30.8, 23.1, 13.4 ppm. HRMS: calcd. for $C_{11}H_{14}O_2SH^+$ [M + H^+] 211.0793; found 211.0793.

Compound 23: Colorless liquid. Yield: 0.155 g, 80%. IR (neat): $\tilde{\nu}$ = 1661, 1206, 914 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 3.04 (t, J = 7.2 Hz, 2 H), 2.40 (s, 3 H), 1.73–1.64 (m, 2 H), 1.03 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 144.0, 134.7, 129.2, 127.2, 30.8, 23.0, 21.6, 13.4 ppm. HRMS: calcd. for $C_{11}H_{14}OSNa^+$ [M + Na^+] 217.0663; found 217.0661.

(1*S*)-Benzoyl-2,3:5,6-di-*O*-isopropylidene-1-thio-β-D-mannofuranose (25): To a well-stirred mixture of benzoic acid (0.122 g, 1.0 mmol), PPh_3 (0.734 g, 2.8 mmol), 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (0.312 g, 1.2 mmol), and NBS (0.498 g, 3.0 mmol) in $CHCl_3$ (8 mL) was added tetrathiomolybdate (**1**; 1.2 g, 2.0 mmol). The reaction mixture was stirred for 2 h at room temperature (28 °C). Diethyl ether (30 mL) was added to the reaction mixture, and it was filtered through a pad of Celite. The residue was again extracted with CH_2Cl_2 (8 mL) followed by extraction with diethyl ether (30 mL) and filtered again through a pad of Celite. The combined extract was evaporated, and the residue was purified by column chromatography on silica gel to give **25** as a colorless liquid (0.209 g, 60%). $[\alpha]_D^{26}$ = +10.8 (c = 2.5, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2915, 1682, 1235, 868 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.0 Hz, 2 H), 7.62–7.43 (m, 3 H), 5.64 (d, J = 3.6 Hz, 1 H), 4.94–4.86 (m, 2 H), 4.89–4.23 (m, 1 H), 4.12–4.10 (m, 2 H), 3.66 (dd, J = 3.3, 5.4 Hz, 1 H), 1.56 (s, 3 H), 1.47 (s, 3 H), 1.39 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.3, 136.3, 133.8, 128.6, 127.5, 113.4, 109.3, 83.3, 81.9, 80.7, 80.2, 72.8, 67.1, 27.0, 25.8, 25.2, 24.8 ppm. HRMS: calcd. for $C_{19}H_{24}O_6SNa^+$ [M + Na^+] 403.1191; found 403.1197.

2,3:5,6-Di-*O*-isopropylidene-(1*S*)-phenylacetyl-1-thio-β-D-mannofuranose (26): The same procedure as that used for compound **25** was followed. Colorless liquid. Yield: 0.200 g, 55%. $[\alpha]_D^{27}$ = –9.9 (c = 1.1, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 2920, 1690, 1230, 862 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 5 H), 5.38 (d, J = 3.2 Hz, 1 H), 4.82–4.77 (m, 2 H), 4.42–4.38 (m, 1 H), 4.10–4.03 (m, 2 H), 3.87 (s, 2 H), 3.55 (dd, J = 2.8, 8.4 Hz, 1 H), 1.49 (s, 3 H), 1.44 (s, 3 H), 1.36 (s, 3 H), 1.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.9, 132.7, 129.6, 128.7, 127.6, 113.3, 109.4, 83.3, 81.7, 81.6, 80.2, 72.7, 67.1, 50.5, 27.1, 25.8, 25.1, 24.7 ppm. HRMS: calcd. for $C_{20}H_{26}O_6SNa^+$ [M + Na^+] 417.1348; found 417.1331.

***S*-Ethyl 1,2,3,4-Tetra-*O*-acetyl-β-D-glucopyranoside Uronthioate (28):** To a well-stirred mixture of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranuronic acid (0.362 g, 1.0 mmol), PPh_3 (0.734 g, 2.8 mmol), ethanol (0.05 g, 1.2 mmol), and NBS (0.498 g, 2.8 mmol) in $CHCl_3$ (8 mL) was added tetrathiomolybdate (**1**; 1.2 g, 2.0 mmol). The reaction mixture was stirred for 2 h at room temperature (28 °C). Diethyl ether (30 mL) was added to the reaction mixture, and it was filtered through a pad of Celite. The residue was again extracted with CH_2Cl_2 (8 mL) followed by extraction with diethyl ether (30 mL) and filtered again through a pad of Celite. The combined extract was evaporated, and the residue was purified by column chromatography on silica gel to give **28** as a colorless liquid (0.256 g, 63%). $[\alpha]_D^{27}$ = +5.7 (c = 0.6, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 1760, 1682, 1216, 1040 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.79 (d, J = 7.6 Hz, 1 H), 5.31–5.24 (m, 2 H), 5.17–5.13 (m, 1 H), 4.18 (dd, J = 2.5, 6.5 Hz, 1 H), 2.87 (q, J = 7.4 Hz, 2 H), 2.14 (s, 3 H), 2.05 (s, 6 H), 2.03 (s, 3 H), 1.24 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.0, 170.0, 169.2, 168.8, 91.3, 77.9, 72.1, 68.9, 23.0, 20.8, 20.6, 20.5, 14.1 ppm. HRMS: calcd. for $C_{16}H_{22}O_{10}SNa^+$ [M + Na^+] 429.0831; found 429.0835.

***S*-Benzoyl,*N*-Boc-L-Cysteine Methyl Ester (30):** To a well-stirred mixture of benzoic acid (0.122 g, 1.0 mmol), PPh_3 (0.734 g, 2.8 mmol), *N*-Boc-L-Serine methyl ester (0.438 g, 1.2 mmol), and NBS (0.498 g, 2.8 mmol) in $CHCl_3$ (8 mL) was added tetrathiomolybdate (**1**; 1.2 g, 2.0 mmol). The reaction mixture was stirred for 2 h at room temperature (28 °C). Diethyl ether (30 mL) was added to the reaction mixture, and it was filtered through a pad of Celite. The residue was again extracted with CH_2Cl_2 (8 mL) followed by extraction with diethyl ether (30 mL) and filtered again through a pad of Celite. The combined extract was evaporated, and the residue was purified by column chromatography on silica gel to give **30** as a colorless liquid (0.237 g, 70%). $[\alpha]_D^{26}$ = +38.2 (c = 2.0, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3575, 1747, 1718, 1670, 1165 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.97–7.95 (m, 2 H), 7.62–7.57 (m, 1 H), 7.49–7.43 (m, 2 H), 5.35 (d, J = 7.5 Hz, 1 H), 4.66–4.60 (m, 1

H), 3.78 (s, 3 H), 3.58–3.54 (m, 2 H), 1.43 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8, 171.1, 155.1, 136.4, 133.7, 128.6, 127.4, 80.2, 53.2, 52.7, 31.1, 28.2 ppm. HRMS: calcd. for $C_{16}H_{21}NO_5SNa^+$ [M + Na^+] 362.1038; found 362.1025.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra for all new compounds; compounds **8**,[20] **9**,[21] **11**,[22] **12**,[23] **13**,[24] **14**,[25] **16**,[26] **20**,[27] and **22**[28] are reported, their ^{1}H NMR spectra are attached for confirmation.

Acknowledgments

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