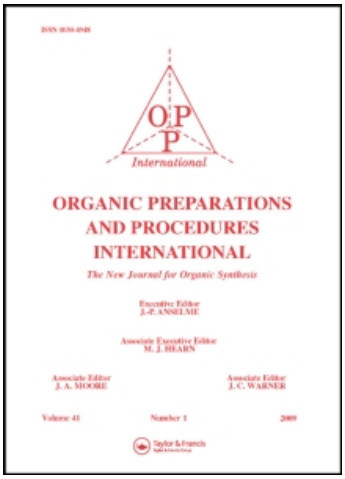


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

Bismuth(III) Triflate Catalyzed Allylation of Cyclic Acetals and Dithianes Followed by *in situ* Derivatization to Generate Highly Functionalized Esters

Scott W. Krabbe[a]; Matthew J. Spafford[a]; Ram S. Mohan[a]
[a] Laboratory for Environmentally Friendly Organic Synthesis, Department of Chemistry, Illinois Wesleyan University, Bloomington, IL, USA

Online publication date: 21 July 2010

To cite this Article Krabbe, Scott W. , Spafford, Matthew J. and Mohan, Ram S.(2010) 'Bismuth(III) Triflate Catalyzed Allylation of Cyclic Acetals and Dithianes Followed by *in situ* Derivatization to Generate Highly Functionalized Esters', Organic Preparations and Procedures International, 42: 4, 363 — 371
To link to this Article: DOI: 10.1080/00304948.2010.495652
URL: http://dx.doi.org/10.1080/00304948.2010.495652

Organic Preparations and Procedures International, 42:363–371, 2010

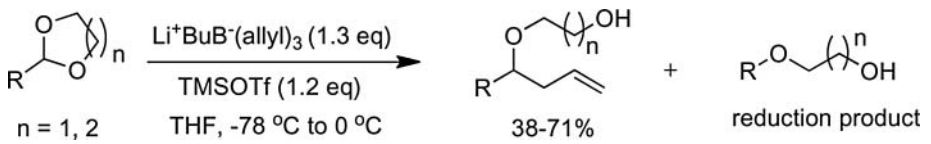
ISSN: 0030-4948 print
DOI: 10.1080/00304948.2010.495652

Bismuth(III) Triflate Catalyzed Allylation of Cyclic Acetals and Dithianes Followed by *in situ* Derivatization to Generate Highly Functionalized Esters

Scott W. Krabbe, Matthew J. Spafford, and Ram S. Mohan

Laboratory for Environmentally Friendly Organic Synthesis, Department of Chemistry, Illinois Wesleyan University, Bloomington, IL, USA

The allylation of acyclic acetals to generate homoallyl ethers has been well documented in the literature. Several catalysts have been developed for this purpose including $TiCl_4$,[1] $AlCl_3$,[2] $BF_3{\cdot}Et_2O$,[3] tritylperchlorate,[4] montmorillonite,[5] $TMSN(SO_2F)_2$,[6] $ISiMe_3$,[7] TMSOTf,[8] $TiCp_2(CF_3SO_3)_2$,[9] tris(*p*-bromophenyl)aminium hexachloroantimonate,[10] triarylpyrilium salts,[11] $TMSNTf_2$,[12] $BiBr_3$,[13] $Sc(OTf)_3$,[14] $Bi(OTf)_3$,[15,16] and CuBr.[17] In contrast, there are far fewer reports in the literature of the corresponding allylation of cyclic acetals. The allylation of a number of 1,3-dioxolanes and 1,3-dioxanes catalyzed by TMSOTf has been reported by Hunter and co-workers[18] (*Scheme 1*).

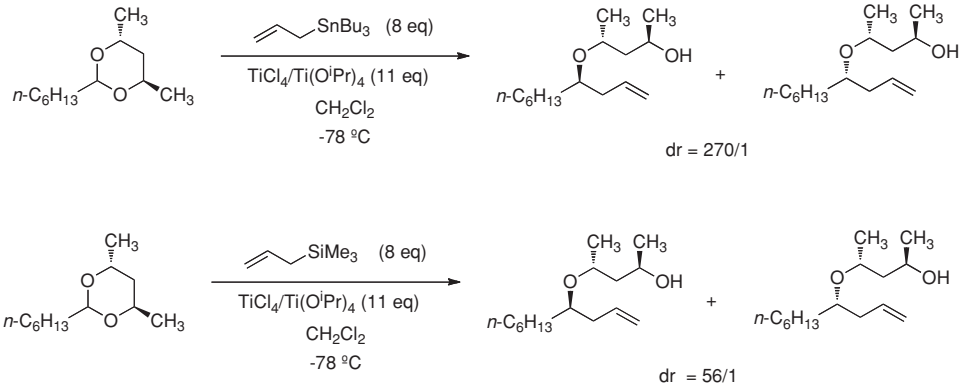


Scheme 1

This method utilized allyl borates as the source of the allyl group. The allyl borate reagents are not commercially available and must be synthesized. A corrosive catalyst (TMSOTf) was employed in stoichiometric quantities and low temperatures were required (−78 °C). In a few cases, an alcohol by-product arising from reduction of the cyclic acetal under the reaction conditions was also isolated in significant yield. Denmark and co-workers have reported one of the few Hosomi-Sakurai protocols utilizing 1,3-dioxanes as substrates[19] (*Scheme 2*). The allylation of 4,6-dimethyl-2-hexyl-1,3-dioxane proceeded with a high degree of diastereoselectivity (270:1) with a stoichiometric loading of $TiCl_4$/$Ti(O\text{-}i\text{-}Pr)_4$ (11 eq) and allyltributyltin (8.0 equivalents) as the allylating agent. The

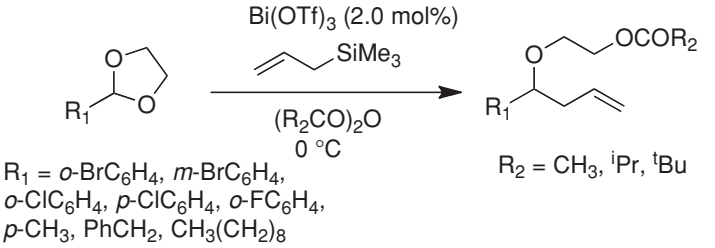
Received January 15, 2010; in final form May 10, 2010.
Address correspondence to: Ram S. Mohan, Laboratory for Environmentally Friendly Organic Synthesis, Department of Chemistry, Illinois Wesleyan University, Bloomington, IL 61701, USA. E-mail: rmohan@iwu.edu

diastereoselectivity was much lower when allyltrimethylsilane was employed (56:1). The use of a corrosive Ti-based catalyst and a toxic organotin compound in excess of stoichiometric amounts detracts from the utility of this method.



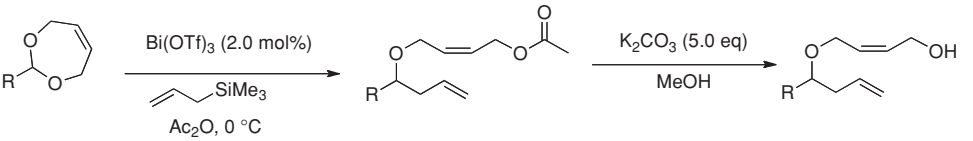
Scheme 2

The lack of a highly catalytic, widely applicable, and environmentally-friendly method for the allylation of cyclic acetals prompted us to explore the bismuth(III) triflate-catalyzed allylation of cyclic acetals. A previous communication reported a highly catalytic and efficient method (*Scheme 3*) for the allylation of dioxolanes followed by *in situ* derivatization with acetic anhydride to generate highly functionalized esters.[20]



Scheme 3

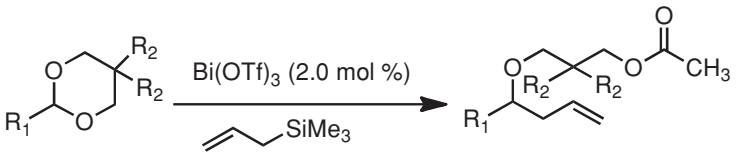
Herein we report detailed procedures for the extension of this methodology to the allylation of dioxanes, dioxepines and dithianes (*Tables 1, 2* and *Scheme 4*). To the best of our knowledge, this is the first report of a highly catalytic method for the allylation of cyclic acetals while there is no report on the allylation of dithianes. The use of a non-toxic



3a R = *p*-ClC_6H_4 **4a** (67%) **5a** (90%)
3b R = $CH_3(CH_2)_8$ **4b** (59%) **5b** (93%)

Scheme 4

Table 1
Bismuth(III) Triflate Catalyzed Allylation of 1,3-Dioxanes



1a-j **2a-j**

Entry	R_1	R_2	time	Yield(%)[a]
a	*o*-BrC_6H_4	H	1.5 h	79
b	*p*-BrC_6H_4	H	2 h	65
c	*p*-ClC_6H_4	H	2 h	70
d	*p*-$CH_3C_6H_4$	H	1.5 h	60
e	*m*-$CH_3OC_6H_4$	H	1.5 h	70
f	$CH_3(CH_2)_8$	H	4 h	75
g	$BrCH_2CH_2$	H	2.5 h	70
h	*p*-ClC_6H_4	CH_3	10 min	74[b]
i	*p*-$CH_3C_6H_4$	CH_3	30 min	83
j	$CH_3(CH_2)_8$	CH_3	3.5 h	72

[a]Refers to yield of purified product obtained by filtration of reaction mixture through a silica gel column.
[b]Product was isolated by aqueous work-up followed by flash chromatography.

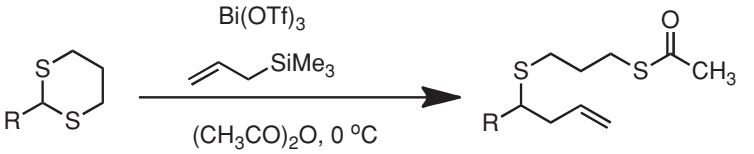
catalyst,[21,22] the solvent-free conditions and the *in situ* derivatization make this method attractive for the generation of highly functionalized esters. In addition, the ester can be hydrolyzed readily to generate the corresponding alcohol. In all cases, no allylation of the acetal was observed in the absence of acetic anhydride. In most cases, allylations were carried out under solvent-free conditions and the product was isolated by filtration of the reaction mixture through a silica gel column, thus eliminating an aqueous waste stream. The results of these studies are summarized in *Tables 1–4*.

The methodology was also applicable to dioxepines (*Scheme 4*). In these cases, the ester product was further hydrolyzed to the corresponding alcohol in excellent yields thus demonstrating that highly functionalized alcohols can also be easily generated by this methodology.

The allylation of 1,3-dithianes proceeded smoothly under mild, solvent-free conditions with low catalyst loadings (2.0–10.0 mol%). Although allylation of dioxolanes and dioxanes proceeded with a 2.0 mol% loading of bismuth(III) triflate, electron-rich aryl dithianes and aliphatic dithianes required more catalyst (4.0–10.0 mol%) for the reactions to proceed to completion. To the best of our knowledge, this procedure represents the first example of the application of 1,3-dithianes as substrates for the Hosomi-Sakurai reaction.

In summary, a robust and highly catalytic method for the allylation and *in situ* derivatization of a number of cyclic acetals (dioxanes, dioxepines and dithianes) has been

Table 2
Bismuth(III) Triflate Catalyzed Allylation of 1,3-Dithianes



6a-d **7a-d**

Entry	R	mol% $Bi(OTf)_3$	t	Yield (%)[a]
a	C_6H_5	2.0[b]	3 h 45 min	78
b	*p*-ClC_6H_4	2.0	2 h 45 min	65
c	*m*-$CH_3C_6H_4$	4.0	4 h 30 min	74
d	$CH_3(CH_2)_8$	10.0	3 h 30 min	63

[a]Refers to yield of purified product obtained by filtration of reaction mixture through a silica gel column.
[b]An additional 2.0 mol% $Bi(OTf)_3$ was added after 3 h.

developed. Most reagents used to date for the allylation of cyclic acetals are highly corrosive or toxic and are often required in stoichiometric amounts.

Experimental Section

Bismuth(III) triflate was purchased from Aldrich Chemical Company and stored under vacuum. Allyltrimethylsilane was purchased from Acros Chemical Company or Aldrich Chemical Company. Acetic anhydride was purchased from Fisher Scientific. Dioxanes and dithianes were prepared following procedures developed in our group or literature protocols.[23,24] Products were analyzed using a JEOL Eclipse NMR Spectrometer at 270 MHz for ^1H NMR and 67.5 MHz for ^{13}C NMR in $CDCl_3$ as the solvent. GC analysis was performed on a Varian CP-3800 Gas Chromatograph equipped with a 30 m silica-packed column with a diameter of 0.25 mm (Conditions: hold at 100°C for 1 min; ramp at 30°C/min until 220°C; hold at 220°C; flow rate; 2.0 mL/min of He). Thin-layer chromatography was performed on silica gel plates. Spots were visualized under UV light (when a UV active chromophore was present) and by spraying the plate with phosphomolybdic acid followed by heating. Purifications were performed by flash chromatography on silica gel. Products were characterized by ^1H NMR, ^{13}C NMR, and GC analysis. Satisfactory combustion analyses were obtained on all new compounds. Several new compounds were also characterized by high resolution mass spectra (70-VSE mass spectrometer). Elemental analyses were performed at Atlantic Microlabs, Atlanta, GA. High Resolution Mass Spectrometry (HRMS) data were obtained at the Mass Spectrometry Laboratory at the University of Illinois Urbana Champaign.

Typical Procedure

A homogeneous mixture of 2-(2-bromophenyl)-1,3-dioxane (0.2450 g, 1.008 mmol), allyltrimethylsilane (0.2723 mL, 0.1958 g, 1.713 mmol, 1.7 eq), and acetic anhydride

Table 3
Preparation of Highly Functionalized Esters by Allylation of Dioxanes, Dioxepines and Dithianes followed by *in situ* Derivatization with Acetic Anhydride

Cmpd	^{1}H NMR (δ)	^{13}C NMR (δ)
2a	1.84–1.89 (m, 2 H), 1.99 (s, 3 H), 2.39–2.44 (m, 2 H), 3.34–3.38 (m, 2 H), 4.13–4.18 (t, 2 H, $J = 6.43$ Hz), 4.68–4.71 (m, 1 H), 5.00–5.07 (m, 2 H), 5.80–5.86 (m, 1 H). 7.10–7.51 (m, 4 H)	(15 peaks) 171.0, 141.2, 134.4 132.6, 128.7, 127.6, 127.6, 122.9, 117.0, 80.2, 65.4, 61.6, 41.1, 28.9, 20.9.
2b	1.82–1.86 (m, 2 H), 1.98 (s, 3 H), 2.32–2.50 (m, 2 H), 3.31–3.34 (m, 2 H), 4.10–4.15 (m, 3 H), 4.96–5.02 (m, 1 H), 5.65–5.76 (m, 1 H), 7.11–7.14 (d, 2 H, $J = 8.15$ Hz), 7.42–7.45 (d, 2 H, $J = 8.15$ Hz).	(13 peaks) 171.0, 141.1, 134.2, 131.4, 128.3, 121.3, 117.2, 81.5, 65.0, 61.6, 42.4, 28.9, 20.9.
2c	1.82–1.89 (m, 2 H), 1.98 (s, 3 H), 2.32–2.54 (m, 2 H), 3.31–3.34 (m, 2 H), 4.11–4.20 (m, 3 H), 4.97–5.03 (m, 2 H), 5.66–5.76 (m, 1 H), 7.17–7.31 (m, 4 H).	(13 peaks) 171.0, 140.6, 134.2, 133.1, 128.4, 128.0, 117.2, 81.4, 65.0, 61.5, 42.4, 28.9, 20.9.
2d	1.82–1.89 (m, 2 H), 1.98 (s, 3 H), 2.33 (s, 3 H), 2.37–2.56 (m, 2 H), 3.29–3.35 (m, 2 H), 4.11–4.16 (m, 3 H), 4.97–5.05 (m, 2 H), 5.70–5.76 (m, 1 H). 7.11–7.17 (m, 4 H).	(14 peaks) 171.1, 139.0, 137.2, 135.0, 129.0, 126.6, 116.7, 82.0, 64.8, 61.8, 42,6, 29.0, 21.1, 20.9.
2e	1.83–1.87 (m, 2 H), 1.98 (s, 3 H), 2.35–2.52 (m, 2 H), 3.30–3.38 (m, 2 H), 3.79 (s, 3 H), 4.11–4.16 (m, 3 H), 4.97–5.05 (m, 2 H), 5.70–5.80 (m, 1 H), 6.78–6.85 (m, 3 H), 7.20–7.26 (m, 1 H).	(16 peaks) δ 171.1, 159.7, 143.8, 134.8, 129.3, 119.0, 116.8, 112.9, 111.9, 82.0, 65.0, 61.7, 55.1, 42.5, 28.9, 20.9
2f	0.85 (t, 3 H, $J = 6.91$ Hz), 1.24 (s, 14 H), 1.39–1.43 (m, 2 H), 1.80–1.89 (m, 2 H), 2.02 (s, 3 H), 2.22 (t, 2 H, $J = 6.18$ Hz), 3.20–3.29 (m, 1 H), 3.40–3.57 (m, 2 H), 4.14 (t, 2 H, $J =$ 6.42 Hz), 5.00–5.06 (m, 2 H), 5.71–5.86 (m, 1 H).	(18 peaks) δ 171.1, 135.1, 116.7, 79.3, 65.2, 61.8, 38.3, 33.8, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 25.4, 22.7, 21.0, 14.1.
2g	1.83–1.96 (m, 4 H), 2.03 (s, 3 H), 2.24–2.29 (m, 2 H), 3.45–3.51 (m, 4 H), 3.60–3.66 (m, 1 H), 4.11–4.16 (m, 2 H), 5.04–5.10 (m, 2 H), 5.71–5.81 (m, 1 H).	(11 peaks) 171.1, 133.9, 117.6, 76.5, 65.6, 61.6, 37.9, 37.3, 30.4, 29.2, 21.0.

(Continued on next page)

Table 3
Preparation of Highly Functionalized Esters by Allylation of Dioxanes, Dioxepines and Dithianes followed by *in situ* Derivatization with Acetic Anhydride *(Continued)*

Cmpd	^{1}H NMR (δ)	^{13}C NMR (δ)
2h	0.87 (s, 3H), 0.89 (s, 3 H), 1.98 (s, 3 H), 2.24–2.53 (m, 2 H), 2.95–3.05 (q, 2 H, $J = 8.64$ Hz), 3.84–3.93 (dd, 2 H, $J = 10.63, 2.21$ Hz), 4.11–4.16 (m, 1 H), 4.96–5.02 (m, 2 H), 5.66–5.81 (m, 1 H), 7.15–7.18 (m, 2 H), 7.26–7.30 (m, 2 H).	(14 peaks) 171.2, 140.9, 134.5, 133.0, 128.4, 127.9, 117.0, 81.7, 74.4, 69.7, 42.6, 35.3, 21.9, 20.9.
2i	0.88 (s, 3 H), 0.90 (s, 3 H), 1.99 (s, 3 H), 2.26–2.56 (m, 2 H), 2.33 (s, 3 H), 2.94–3.09 (dd, 2 H, $J = 17.08$, 8.64 Hz), 3.85–3.94 (t, 2 H, 10.58 Hz), 4.11–4.13 (m, 1 H), 4.96–5.00 (m, 2 H). 5.73–5.84 (m, 1 H), 7.13 (s, 4 H).	(15 peaks) 171.0, 139.3, 136.9, 135.1, 128.8, 126.4, 116.4, 82.1, 74.1, 69.7, 42.8, 35.3, 21.9, 21.0, 20.8.
2j	0.85–0.89 (m, 9 H), 1.24–1.41 (m, 16 H), 2.03 (s, 3 H), 2.19 (t, 2 H, $J =$ 6.91 Hz), 3.08–3.22 (m, 3 H), 3.86 (s, 2 H), 4.97–5.01 (m, 2 H), 5.72–5.83 (m, 1 H).	(19 peaks) 171.0, 135.30, 116.48, 79.34, 74.53, 69.91, 38.29, 35.52, 33.80, 31.96, 29.81, 29.69, 29.65, 29.39, 25.36, 22.73, 22.05, 20.91, 14.15.
4a	2.02 (s, 3 H), 2.30–2.59 (m, 2 H), 3.84–3.97 (m, 2 H), 4.24–4.29 (t, 1 H, $J = 6.67$ Hz), 4.49–4.52 (d, 2 H, $J = 5.94$ Hz), 4.98–5.04 (m, 2 H), 5.60–5.78 (m, 3 H), 7.19–7.25 (m, 2 H), 7.28–7.32 (m, 2 H).	(14 peaks) 170.8, 140.2, 134.3, 133.5, 130.7, 128.7, 128.2, 126.7, 117.5, 81.0, 64.3, 60.4, 42.5, 21.0.
4b	0.82–0.87 (t, 3 H, $J = 6.68$ Hz), 1.22–1.45 (m, 16 H), 2.02 (s, 3 H), 2.21–2.25 (t, 2 H, $J = 6.55$ Hz), 3.25–3.34 (quintet, 1 H), 3.99–4.14 (m, 2 H), 4.59–4.61 (d, 2 H, $J =$ 6.18 Hz), 4.99–5.07 (m, 2 H), 5.57–5.86 (m, 3 H).	(19 peaks) 170.8, 135.0, 131.7, 125.91, 116.9, 79.0, 64.5, 60.4, 38.4, 33.9, 32.0, 29.8, 29.7, 29.6, 29.4, 25.4, 22.7, 21.0, 14.2.
5a	2.29–2.57 (m, 2 H), 2.67–2.73 (broad doublet, 1 H, $J = 15.3$ Hz), 3.78–3.91 (m, 2 H), 4.00–4.03 (d, 2 H, $J =$ 6.18 Hz), 4.24–4.29 (t, 1 H, $J = 6.68$ Hz), 4.96–5.02 (m, 2 H), 5.56–5.77 (m, 3 H), 7.18–7.21 (d, 2 H, $J = 8.42$ Hz), 7.27–7.30 (d, 2 H, $J = 8.40$ Hz).	(12 peaks) 140.1, 134.2, 133.5, 132.5, 128.7, 128.2, 128.0, 117.6, 80.9, 64.3, 58.5, 42.5.

Table 3
Preparation of Highly Functionalized Esters by Allylation of Dioxanes, Dioxepines and Dithianes followed by *in situ* Derivatization with Acetic Anhydride *(Continued)*

Cmpd	^{1}H NMR (δ)	^{13}C NMR (δ)
5b	0.82–0.86 (t, 3 H, $J = 6.55$ Hz), 1.23 (broad s, 14 H), 1.29–1.45 (m, 2 H), 2.21–2.26 (m, 2 H), 2.56 (s, 1 H), 3.27–3.36 (quintet, 1 H), 3.96–4.10 (m, 2 H), 4.13–4.15 (m, 2 H), 5.00–5.08 (m, 2 H), 5.60–5.85 (m, 3 H).	(17 peaks) 134.9, 131.9, 128.8, 117.1, 79.2, 64.6, 58.6, 38.3, 33.8, 32.0, 29.8, 29.67, 29.65, 29.4, 25.4, 22.7, 14.2.
7a	1.67–1.73 (m, 2 H), 2.27–2.37 (m, 5 H), 2.56–2.61 (t, 2 H, $J = 7.43$ Hz), 2.80–2.88 (m, 2 H), 3.78–3.84 (t, 1 H, $J = 7.43$ Hz), 4.95–5.05 (m, 2 H), 5.64–5.74 (m, 1 H), 7.24–7.30 (m, 5 H).	(13 peaks) 195.5, 141.9, 135.2, 128.4, 127.8, 127.1, 116.9, 49.4, 40.8, 30.5, 29.7, 29.0, 28.0.
7b	1.68–1.73 (m, 2 H), 2.26–2.31 (m, 5 H), 2.51–2.58 (m 2 H), 2.75–2.91 (m, 2 H), 3.75–3.81 (t, 3 H, $J = 7.40$ Hz), 4.96–5.03 (m, 2 H), 5.60–5.70 (m, 1 H), 7.24–7.26 (m, 4 H).	(13 peaks) 195.6, 140.5, 134.8, 132.7, 129.2, 128.6, 117.3, 48.8, 40.8, 30.6, 29.7, 29.0, 28.0.
7c	1.66–1.76 (m, 2 H), 2.28 (S, 3 H), 2.33 (s, 3 H), 2.52–2.61 (t, 2 H, $J = 14.34$ Hz), 2.76–2.94 (m, 2 H), 3.74–3.79 (t, 1 H, $J = 7.37$ Hz), 4.96–5.06 (m, 2 H), 5.64–5.74 (m, 1 H). 7.01–7.25 (m, 4 H).	(16 peaks) 195.6, 141.9, 138.1, 135.4, 128.4, 128.3, 128.0, 124.9, 116.9, 49.5, 40.9, 30.6, 29.8, 29.0, 28.0, 21.5.
7d	0.83–0.88 (t, 3 H, $J = 6.67$ Hz), 1.24 (s, 14 H), 1.39–1.58 (m, 3 H), 1.79–1.85 (m, 2 H), 2.27–2.32 (m, 4 H), 2.51–2.64 (m, 3 H), 2.92–2.98 (t, 2 H, $J = 7.15$ Hz), 5.02–5.08 (m, 2 H), 5.77–5.87 (m, 1 H).	(15 peaks) 195.6, 135.7, 116.8, 45.3, 39.3, 34.2, 31.9, 30.6, 29.6, 29.3, 29.2, 28.1, 26.7, 22.7, 14.1.

(0.1620 mL, 0.1749 g, 1.713 mmol, 1.7 eq) was stirred at 0°C under N_2 in a flame-dried three-neck round bottom flask as bismuth(III) triflate (0.0132 g, 0.0202 mmol, 2.0 mol%) was added. The reaction mixture immediately acquired a light yellow color. The progress of the reaction was monitored by gas chromatography. After 1.5 h, the reaction mixture was loaded onto 65 g of silica gel and eluted with EtOAc/heptane (5/95, v/v). The column was eluted with 100 mL of the solvent and then fifty-eight fractions (8 mL) were collected. Fractions 20 to 51 were combined and concentrated to yield 0.2569 g (79%) of a

Table 4
Combustion Analysis Data for **2a-j**, **4a-b**, **5a-b** and **7a-d**

Cmpd[a]	Calcd for	Combustion Analyses (Found)			
		C	H	X	S
2a	$C_{15}H_{19}BrO_3$	55.06 (55.33)	5.85 (6.03)	24.42[b] (24.14)	
2b	$C_{15}H_{19}BrO_3$	55.06 (55.25)	5.85 (6.01)	24.42[b] (24.17)	
2c	$C_{15}H_{19}ClO_3 \cdot 0.20\ H_2O$	62.91 (63.19)	6.83 (6.81)	12.38[c] (12.15)	
2d	$C_{16}H_{22}O_3$	73.25 (73.08)	8.45 (8.45)		
2e	$C_{16}H_{22}O_4$	69.04 (68.83)	7.97 (7.94)		
2f	$C_{18}H_{34}O_3$	72.44 (72.55)	11.48 (11.63)		
2g	$C_{11}H_{19}BrO_3$	47.33 (47.57)	6.86 (6.94)	28.62[b] (28.48)	
2h	$C_{17}H_{23}ClO_3 \cdot 0.25\ H_2O$	64.75 (64.66)	7.51 (7.21)	11.24[c] (11.07)	
2i	$C_{18}H_{26}O_3$	74.45 (74.15)	9.02 (9.08)		
2j	$C_{20}H_{38}O_3$	73.57 (73.66)	11.74 (11.94)		
4a	$C_{16}H_{19}ClO_3$	65.19 (65.40)	6.50 (6.59)	12.03[c] (12.07)	
4b	$C_{19}H_{34}O_3 \cdot 0.5\ H_2O$	71.43 (71.65)	11.04 (10.95)		
5a	$C_{14}H_{17}ClO_2 \cdot 0.06\ H_2O$	66.25 (65.98)	6.80 (6.84)	13.97[c] (14.27)	
5b	$C_{17}H_{32}O_2 \cdot 0.1\ H_2O$	75.56 (75.48)	12.01 (12.04)		
7a	$C_{15}H_{20}OS_2$	64.24 (64.48)	7.19 (7.24)		22.87 (22.63)
7b	$C_{15}H_{19}ClOS_2$	57.21 (57.39)	6.08 (6.08)	11.26[c] (11.29)	20.37 (20.18)
7c	$C_{16}H_{22}OS_2$	65.26 (65.41)	7.53 (7.56)		21.78 (21.62)
7d	$C_{18}H_{34}OS_2$	65.40 (65.15)	10.37 (10.15)		19.40 (17.20)

[a]All compounds were isolated as clear, colorless liquids after flash chromatography.
[b]X = Bromine.
[c]X = Chlorine.

Table 5
High Resolution Mass Spectra

Cmpd	HRMS (found) calcd for (M^+)	
2a	$C_{15}H_{19}BrO_3Na$	349.0415 (349.0423)
2b	$C_{15}H_{19}BrO_3Na$	349.0415 (349.0417)
2c	$C_{15}H_{19}ClO_3Na$	305.0920 (305.0913)
2f	$C_{18}H_{34}O_3Na$	321.2406 (321.2416)
2g	$C_{11}H_{20}BrO_3$	279.0596 (279.0598)
2h	$C_{17}H_{23}ClO_3Na$	333.1233 (333.1247)
2j	$C_{20}H_{38}O_3Na$	349.2719 (349.2735)
4a	$C_{16}H_{20}ClO_3$	295.1101 (295.1094)
4b	$C_{19}H_{35}O_3$	311.2586 (311.2586)
5a	$C_{14}H_{17}ClO_2$	253.0995 (253.0993)
5b	$C_{17}H_{33}O_2$	269.2481 (269.2479)
7a	$C_{15}H_{20}OS_2$	280.0956 (280.0952)
7b	$C_{15}H_{19}ClOS_2$	314.0566 (314.0564)
7c	$C_{16}H_{22}OS_2Na$	317.1010 (317.1028)
7d	$C_{18}H_{34}OS_2Na$	353.1949 (353.1963)

clear, colorless liquid product that was determined to be 97% pure by GC analysis, and ^{1}H & ^{13}C NMR spectroscopy.

Acknowledgements

The authors wish to thank the National Science Foundation for an NSF-RUI (Research in Undergraduate Institutions) grant (RUI Grant # 0650682) awarded to RSM.

References

1. A. Hosomi, M. Endo and H. Sakurai, *Chemistry Lett.*, 941 (**1976**).
2. I. Ojima and M. Kumagai, *Chemistry Lett.*, 575 (**1978**).
3. A. Hosomi, M. Endo and H. Sakurai, *Chemistry Lett.*, 499 (**1978**).
4. T. Mukaiyama, H. Nagaoka, M. Murakami and M. Ohshima, *Chemistry Lett.*, 977 (**1985**).
5. M. Kawai, M. Onaka and Y. Izumi, *Chemistry Lett.*, 381 (**1986**).
6. A. Trehan, A. Vij, M. Walia, G. Kaur, R.D. Verma and S. Trehan, *Tetrahedron Lett.*, **34**, 7335 (1993).
7. H. Sakurai, K. Sasaki and A. Hosomi, *Tetrahedron Lett.*, **22**, 745 (1981).
8. T. Tsunoda, M. Suzuki and R. Noyori, *Tetrahedron Lett.*, **21**, 71 (1980).
9. T. K. Hollis, N. P. Robinson, J. Whelan and B. Bosnich, *Tetrahedron Lett.*, **34**, 4309 (1993).
10. M. Kamata, Y. Yokoyama, N. Karasawa, M. Kato and E. Hasegawa, *Tetrahedron Lett.*, **37**, 3483 (1996).
11. M. Kamata, S. Nagai, M. Kato and E. Hasegawa, *Tetrahedron Lett.*, **37**, 7779 (1996).
12. A. Ishii, O. Kotera, T. Saeki and K. Mikami, *Synlett*, 1145 (**1997**).
13. N. Komatsu, M. Uda, H. Suzuki, T. Takahashi, T. Domae and M. Wada, *Tetrahedron Lett.*, **38**, 7215 (1997).
14. J. S. Yadav, B. V. Subba Reddy and P. Srihari, *Synlett*, 673 (**2001**).
15. P. W. Anzalone, A. R. Baru, E. M. Danielson, P. D. Hayes, M. P. Nguyen, A. F. Panico, R. C. Smith and R. S. Mohan, *J. Org. Chem.*, **70**, 2091 (2005).
16. L. C. Weiland, H. M. Zerth and R. S. Mohan, *Tetrahedron Lett*., **43**, 4597 (2002).
17. M. E. Jung and A. Maderna, *J. Org. Chem.*, **69**, 7755 (2004).
18. R. Hunter, J. P. Michael and G. D. Tomlinson, *Tetrahedron*, **50**, 871 (1994).
19. S. E. Denmark and N. G. Almstead, *J. Org. Chem.*, **56**, 6458 (1991).
20. M. J. Spafford, J. E. Christensen, M. G. Huddle, J. R. Lacey and R. S. Mohan, *Australian. J. Chem.*, **61**, 419 (2008).
21. H. Gaspard-Iloughmane and C. Le Roux, *Eur. J. Org. Chem.*, 2517 (**2004**).
22. N. M. Leonard, L. C. Wieland and R. S. Mohan, *Tetrahedron*, **58**, 8373 (2002).
23. T. W. Greene and P. G. M. Wuts, *"Protective Groups in Organic Synthesis"*, 4th ed., John Wiley and Sons, Inc., NJ, 2007.
24. D. M. Podgorski, S. W. Krabbe, L. Le, P. S. Sierszulski and R. S. Mohan, *Synthesis*, In Press (**2010**).