



Carbonyllithium chemistry. Intramolecular conversion of an acyllithium via the utilization of an anionic 1,2-stannyl rearrangement[☆]

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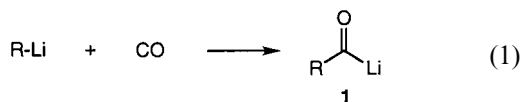
Abstract

The reaction of α -stannylmethylolithium with CO (1 atm) generates the acyllithium that smoothly undergoes anionic 1,2-stannyl rearrangement at -78°C to give the enolate derivative of acyltin. The rearrangement of the stannyl group is much faster than that of the silyl group. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Acyllithium; Intramolecular conversion; α -Stannylmethylolithium; Carbon monoxide; Anionic 1,2-stannyl rearrangement

1. Introduction

It is well known that the reaction of organolithium compounds with carbon monoxide generates carbonyllithium derivatives **1** as initial intermediates (see Eq. (1)). In general, carbonyllithium intermediates are too reactive to undergo selective reactions. Seyferth [1] and others [2] have demonstrated that it is possible to trap the highly reactive carbonyllithium **1** by an electrophile, providing the trapping reagents are present in situ. The authors have devised a different methodology, i.e. intramolecular trapping, for the immediate conversion of carbonyllithium species into more stable ones, such as enolates [3] and ynolates [4].



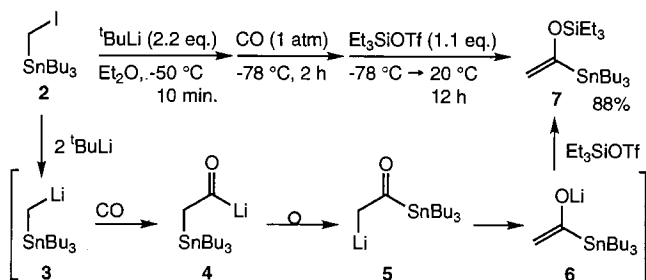
In a previous paper, the authors reported that the reaction of trimethylsilylmethylolithium, $\text{Me}_3\text{SiCH}_2\text{Li}$,

with carbon monoxide gave an acyllithium derivative that then underwent an anionic 1,2-silicon shift [3a]. The intramolecular process allowed the conversion of the highly reactive acyllithium into the more stable lithium enolate of trimethylsilyl methyl ketone. This 1,2-anionic silicon shift was observed only at temperatures above 15°C . At lower temperatures, e.g. at -78°C , a different product was formed, which corresponded to a dimer of the acyllithium.

It would be interesting to determine if an analogous conversion is possible in the case of organotin compounds. No distinct example of an anionic 1,2-migration of an organostannyl group is known, to the authors knowledge. The anionic rearrangement of an organostannyl group would be expected to be much faster than that of an organosilyl group, since it has been firmly established that lithium–tin exchange is much faster than lithium–silicon exchange [5]. It should also be noted that such lithium–metal exchange constitutes a nucleophilic displacement at the tin or silicon atom and can be regarded as an anionic rearrangement in the case of an intramolecular process. This paper reports that the reaction of (tributylstannyl)methylolithium, $\text{Bu}_3\text{SnCH}_2\text{Li}$, with carbon monoxide proceeds in a highly selective manner due to the rapid 1,2-stannyl migration, even at -78°C .

[☆] This paper is dedicated to the memory of the late Professor Rokuro Okawara.

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Scheme 1.

2. Results and discussion

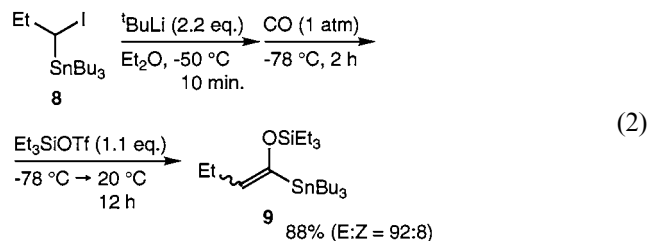
For the generation of α -stannylmethylolithiums, two methods involving lithium–iodine exchange and lithium–tin exchange, reported by Kaufmann [6] and Sato [7], respectively, have been shown to be useful. Because of the efficiency and ready availability of starting materials, the method described by Kaufmann was adopted. However, the *n*-BuLi used in this method gives rise to *n*-BuI as a by-product, which may further react and thus complicate the reaction. For this reason, the authors modified Kaufmann's method and used two equivalents of *t*-BuLi instead of one.

The reaction was carried out as follows (see Section 3 for details). To an Et₂O solution of tributylstannylmethyl iodide, **2**, a pentane solution of *t*-BuLi (2.2 equivalents) was added at -50°C . The mixture was exposed to carbon monoxide at atmospheric pressure at -78°C for 2 h. After quenching with triethylsilyl trifluoromethanesulfonate (1.1 equivalents) at -78°C , the reaction mixture was stirred at 20°C for 12 h. After work-up with cold sat. NaHCO₃ (aq), triethyl[[1-(tributylstannyl)ethenyl]oxy]silane (**7**) was isolated in 88% yield by Kugelrohr distillation ($153^{\circ}\text{C}/1\text{ mmHg}$).

The reaction sequence envisaged is shown in Scheme 1. This intramolecular transformation of acyllithium **4** takes place via the anionic 1,2-shift of the organotin group. It is noteworthy that the stannyl group migrates smoothly, even at -78°C . In contrast, it is known that

a silyl group does not migrate at -78°C and the reaction gives an enediol compound [3a]. These results indicate that the migration of the stannyl group is considerably faster than that of the silyl group.

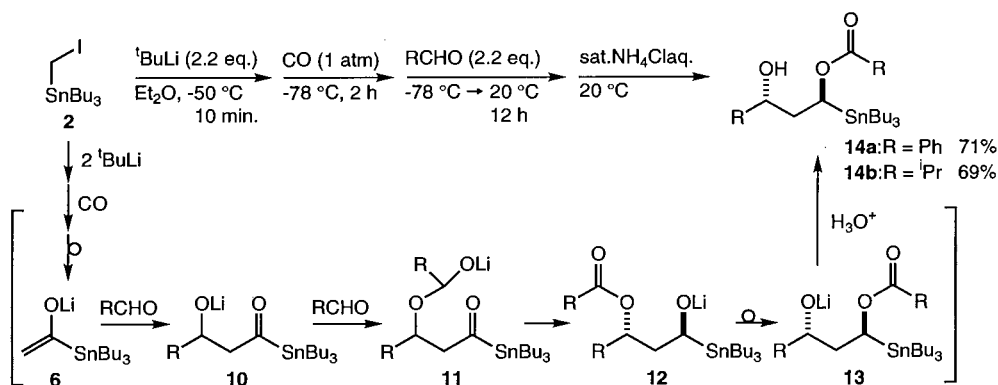
The reaction of 1-(tributylstannyl)propyllithium [8] with CO at -78°C also led to a clean reaction involving intramolecular conversion of the acyllithium via 1,2-stannyl shift (see Eq. (2)).



As observed in the reaction of silylmethylolithium with CO, this reaction also gave a more stable *E*-enolate, predominantly [3a,e]. The ratio of the stereochemistry of the silylated product **9** was determined by ¹H-NMR of vinylic hydrogens [9].

The enolate appears to undergo standard enolate reactions. The reaction of the lithium enolate of acyltin with electrophiles would be expected to give acyltin compounds, which are known to be somewhat difficult to handle because of their lability [10]. The reaction of acyltin enolate with two equivalents of an aldehyde was examined. Reaction with benzaldehyde afforded the *anti*-1,3-diol monoester by the aldol-Tishchenko reaction [11].

An acyltin enolate **6** was treated with two equivalents of RCHO (R = Ph or *i*-Pr) at 20°C for 12 h. After quenching with sat. NH₄Cl (aq), the *anti*-1,3-diol monoester **14** was isolated by column chromatography on silica gel (**14a**, 71%; **14b**, 69%; Scheme 2). The stereochemistries of the products **14** were determined by comparison with similar compounds [12]. Excellent diastereoselection would be expected to proceed via the formation of a six-membered transition state for the case of an intramolecular Tishchenko reduction (Fig. 1)



Scheme 2.

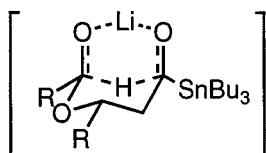


Fig. 1. The six-membered transition state for the case of an intramolecular Tishchenko reduction.

[11a,c,e,g–i]. The following intramolecular transfer of the benzoyl group (**12** → **13**) gives the observed product **14** [11b,f,g].

The authors have thus demonstrated that the anionic rearrangement of an organostannyl group in the acyllithium occurred rapidly, even at low temperature (-78°C). To their knowledge, this is a rare example of a 1,2-anionic stannyl rearrangement. The present work, in addition to the one previously reported, indicates that the rearrangement is a key step in the intramolecular conversion of carbonyllithium and should find further applications.

3. Experimental

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a JEOL JNM-EX270 (^1H at 270 MHz, ^{13}C at 67.5 MHz) spectrometer. Mass spectra (MS) were recorded on a Shimadzu GCMS-QP5000 spectrometer. Infrared spectra (IR) were recorded on a Hitachi 270-50 IR spectrometer as neat. Column chromatography was performed using Kiesegel 60 (230–400 mesh, Merck 9385) Diethyl ether (Et_2O) was distilled from sodium benzophenone ketyl immediately prior to use. A 1.54 M pentane solution of *t*-BuLi was purchased from Kanto Chemical Company, and used without titration. Tributylstannylmethyl iodide **2** [13] and 1-(tributylstannyl)propyl iodide **8** [8] were prepared according to literature procedures.

3.1. Synthesis of triethyl[[1-(tributylstannyl)ethenyl]oxy]silane (**7**)

A 50-ml round-bottomed flask equipped with a magnetic stirrer bar, a three-way stopcock, and a nitrogen line was flame-dried under a stream of nitrogen. In the reaction flask, 20 ml of anhydrous Et_2O and 0.862 g (2.0 mmol) of tributylstannylmethyl iodide **2** were placed and the solution was cooled to -50°C with a dry ice/ CH_3CN bath. To the stirred solution, 2.86 ml of a pentane solution of *t*-BuLi (1.54 M, 4.4 mmol) were added by a syringe within 5 s. After stirring for 10 min, the reaction mixture was cooled to -78°C with a dry ice/MeOH bath. The three-way stopcock was then connected to a vacuum line (10 mmHg) and also to a balloon filled with carbon monoxide through a glass

column packed with anhydrous calcium sulfate. After two cycles of evacuation of the nitrogen and filling with carbon monoxide, the reaction mixture was stirred under this atmosphere of carbon monoxide for 2 h. To the reaction mixture was added 0.497 ml (2.2 mmol) of triethylsilyl trifluoromethanesulfonate at -78°C and the reaction mixture was allowed warm to 20°C , and then stirred for 12 h. To the mixture, 10 ml of a cold sat. NaHCO_3 (aq) and 30 ml of ether were added, and the layers were separated. The aqueous layer was extracted with ether (3×15 ml). The organic layers were combined and dried over magnesium sulfate. The solvents were removed under reduced pressure to provide a yellow liquid. Kugelrohr distillation ($153^{\circ}\text{C}/1$ mmHg) of the residue gave pure product **7** as a colorless liquid (0.785 g, 88% yield). $^1\text{H-NMR}$ (CDCl_3) δ 0.67 (q, $J = 8.3$ Hz, 6H, SiCH_2), 0.75–1.05 (m, 24H, SiCH_2CH_3 and $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.2–1.65 (m, 12H, $\text{SnCH}_2\text{CH}_2\text{CH}_2$), 4.23 [s, $J(^1\text{H}-^{119}\text{Sn}) = 27$ Hz, 1H, (*Z*)- $\text{CH}_2=\text{C}$], 4.89 [s, $J(^1\text{H}-^{119}\text{Sn}) = 103$ Hz, 1H, (*E*)- $\text{CH}_2=\text{C}$]; $^{13}\text{C-NMR}$ (CDCl_3) δ 5.32 (SiCH_2), 6.76 (SiCH_2C), 9.85 [$J(^{13}\text{C}-^{119}\text{Sn}) = 336$ Hz, $J(^{13}\text{C}-^{117}\text{Sn}) = 321$ Hz, SnCH_2], 13.70 ($\text{SnCH}_2\text{CH}_2\text{CH}_2\text{C}$), 27.33 [$J(^{13}\text{C}-^{119}\text{Sn}) = 56$ Hz, $\text{SnCH}_2\text{CH}_2\text{C}$], 29.02 [$J(^{13}\text{C}-^{119}\text{Sn}) = 21$ Hz, SnCH_2C], 105.28 [$J(^{13}\text{C}-^{119}\text{Sn}) = 94$ Hz, $\text{SnC}=\text{CH}_2$], 169.67 ($\text{SnC}=\text{CH}_2$); IR (neat) 2960 (s), 1578 (s), 1466 (s), 1417 (m), 1377 (m), 1238 (m), 1173 (s), 1071 (w), 1002 (s), 825 (m), 748 (s), 664 (w) cm^{-1} ; MS m/z (relative intensity) 391 (10, $\text{M}^+ - \text{Bu}$), 365 (12), 309 (23), 307 (13), 305 (10), 253 (17), 251 (16), 249 (13), 234 (11), 223 (18), 221 (15), 195 (15), 193 (12), 179 (18), 177 (22), 175 (16), 123 (11), 121 (26), 120 (12), 119 (18), 117 (11), 115 (16), 87 (62), 59 (100), 58 (10), 57 (17). Anal. Calc. for $\text{C}_{29}\text{H}_{44}\text{OSiSn}$: C, 53.70; H, 9.91. Found: C, 53.65; H, 9.79.

3.2. Synthesis of triethyl[[1-(tributylstannyl)butenyl]oxy]silane (**9**)

In a manner similar to that described for the tin compound **2**, 0.918 g (2.0 mmol) of **8** in 20 ml of Et_2O was reacted with *t*-BuLi (1.54 M in pentane, 4.4 mmol, 2.86 ml) at -50°C and CO at -78°C , triethylsilyl trifluoromethanesulfonate (2.2 mmol) at -78°C followed by stirring at 20°C for 12 h. After work-up and purification by Kugelrohr distillation (160 – $165^{\circ}\text{C}/0.75$ mmHg) of the product mixture gave the acyltin enolate **9** as a colorless liquid (0.853 g, 88% yield, *E/Z* = 92/8). Spectral data were obtained from a mixture of *E*- and *Z*-isomers. In the $^{13}\text{C-NMR}$ spectrum of the mixture of *E*- and *Z*-isomers, the resonances arising from the *Z*-isomer could not be observed. $^1\text{H-NMR}$ (CDCl_3) δ (*E*-isomer) 0.66 (q, $J = 7.9$ Hz, 6H, SiCH_2), 0.80–1.05 (m, 27H, SiCH_2CH_3 and $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}=\text{CHCH}_2\text{CH}_3$), 1.20–1.60 (m, 12H, $\text{SnCH}_2\text{CH}_2\text{CH}_2$), 2.13 (qn, $J = 7.3$ Hz, 2H, $\text{C}=\text{CHCH}_2$), 4.61 (t, $J = 6.6$

Hz, 1H, C=CH), (*Z*-isomer) (partial) 1.8 (qn, $J = 7.8$ Hz, C=CHCH₂), 5.47 (t, $J = 7.8$ Hz, C=CH); ¹³C-NMR (CDCl₃) (*E*-isomer) 5.36 (SiC), 6.92 (SiCH₂C), 10.12 [$J(^{13}\text{C}-^{119}\text{Sn}) = 331$ Hz, $J(^{13}\text{C}-^{117}\text{Sn}) = 316$ Hz, SnCH₂], 13.66 (SnCH₂CH₂CH₂C), 14.32 (C=CHCH₂CH₃), 18.64 (C=CHCH₂), 27.39 [$J(^{13}\text{C}-^{119}\text{Sn}) = 57$ Hz, SnCH₂CH₂C], 29.00 [$J(^{13}\text{C}-^{119}\text{Sn}) = 18$ Hz, SnCH₂C], 129.61 (SnC=CH), 156.53 (SnC=CH); IR (neat) (mixture of *E*- and *Z*-isomers) 2960 (s), 2930 (s), 2878 (s), 1605 (m), 1463 (s), 1417 (m), 1377 (m), 1326 (m), 1283 (m), 1238 (m), 1136 (s), 1073 (s), 1004 (s), 961 (m), 900 (w), 875 (w), 838 (m), 768 (m), 741 (s) cm⁻¹; MS m/z (relative intensity) 419 (11, M⁺-Bu), 365 (13), 309 (26), 308 (10), 305 (10), 253 (14), 251 (20), 249 (12), 223 (23), 221 (18), 195 (22), 193 (16), 191 (11), 179 (20), 177 (23), 175 (13), 165 (12), 149 (11), 123 (14), 121 (31), 120 (16), 119 (28), 117 (17), 115 (21), 91 (16), 87 (70), 75 (16), 69 (10), 59 (100), 58 (14), 57 (31), 56 (10), 55 (14). Anal. (mixture of *E*- and *Z*-isomers) Calc. for C₂₂H₄₈O₂SiSn: C, 55.58; H, 10.18. Found: C, 55.42; H, 10.08.

3.3. Reaction of acyltin enolate **6** with two equivalents of benzaldehyde (**14a**)

To a diethyl ether solution of acyltin enolate **6**, prepared from (tributylstannyl)methylolithium **3** with CO vide supra, 0.467 g (4.4 mmol) of benzaldehyde at -78°C were added and the mixture was stirred at 20°C for 12 h. The mixture was then quenched with 10 ml of sat. NH₄Cl (aq), 30 ml of Et₂O were added, and the layers were separated. The aqueous layer was extracted with ether (3 × 15 ml). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to afford a yellow oil. The residue was subjected to column chromatography on silica gel using hexane/EtOAc = 7/1 as the eluent ($R_f = 0.26$) to give **14a** as a colorless oil (0.780 g, 71% yield). ¹H-NMR (CDCl₃) δ 0.85 (t, $J = 7.3$ Hz, 9H, CH₃), 0.92–1.56 (m, 18H, SnCH₂CH₂CH₂), 2.03 (ddd, $J = 3.0$ Hz, 10.2 Hz, 14.9 Hz, 1H, CHH), 2.40 (ddd, $J = 2.6$ Hz, 12.5 Hz, 14.9 Hz, 1H, CHH), 3.09 (d, $J = 3.6$ Hz, 1H, OH), 4.69 (ddd, $J = 3.0$ Hz, 3.6 Hz, 10.2 Hz, 1H, PhCH), 5.56 (dd, $J = 2.6$ Hz, 12.5 Hz, 1H, SnCH), 7.20–7.60 (m, 8H, Ar-H), 8.01 (d, $J = 7.6$ Hz, 2H, Ar-H); ¹³C-NMR (CDCl₃) δ 9.44 [$J(^{13}\text{C}-^{119}\text{Sn}) = 325$ Hz, $J(^{13}\text{C}-^{117}\text{Sn}) = 310$ Hz, SnCH₂], 13.59 (SnCH₂CH₂CH₂C), 27.33 [$J(^{13}\text{C}-^{119}\text{Sn}) = 56$ Hz, SnCH₂CH₂C], 28.97 [$J(^{13}\text{C}-^{119}\text{Sn}) = 20$ Hz, SnCH₂C], 44.36 (CH₂), 67.60 [$J(^{13}\text{C}-^{119}\text{Sn}) = 337$ Hz, $J(^{13}\text{C}-^{117}\text{Sn}) = 322$ Hz, SnCHOH], 70.66 [$J(^{13}\text{C}-^{119}\text{Sn}) = 39$ Hz, PhCH], 125.61 (Ar), 127.22 (Ar), 128.34 (Ar), 128.37 (Ar), 129.45 (Ar), 130.21 (Ar), 132.85 (Ar), 144.35 (Ar), 167.87 (C=O); IR (neat) 3486 (br), 3066 (w), 3032 (w), 2960 (s), 2928 (s), 2874 (s), 2854 (s), 1699 (s), 1604 (w), 1585 (w), 1542 (w), 1495 (w), 1454 (s),

1420 (m), 1376 (m), 1315 (s), 1265 (s), 1198 (w), 1174 (m), 1115 (s), 1068 (s), 1046 (m), 1025 (s), 998 (m), 961 (w), 912 (w), 875 (w), 844 (w), 805 (w), 757 (m), 712 (s) cm⁻¹; MS m/z (relative intensity) 545 (M⁺, 0.44), 489 (18), 487 (15), 179 (26), 177 (28), 176 (10), 175 (18), 123 (13), 121 (31), 120 (14), 119 (23), 118 (15), 117 (71), 115 (12), 105 (100), 79 (17), 77 (59), 51 (18). Anal. Calc. for C₂₈H₄₂O₃Sn: C, 61.67; H, 7.76. Found: C, 61.78; H, 7.64.

3.4. Reaction of acyltin enolate **6** with two equivalents of isobutyraldehyde (**14b**)

To a diethyl ether solution of acyltin enolate **6**, prepared from (tributylstannyl)methylolithium **3** with CO vide supra, 0.317 g (4.4 mmol) of isobutyraldehyde were added at -78°C and the mixture was stirred at 20°C for 12 h. The mixture was then quenched with 10 ml of sat. NH₄Cl (aq), 30 ml of Et₂O were added, and the layers were separated. The aqueous layer was extracted with ether (3 × 15 ml). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated under reduced pressure to afford a yellow oil. The residue was subjected to column chromatography on silica gel using hexane/EtOAc = 9/1 as the eluent ($R_f = 0.20$) to give **14b** as a colorless oil (0.608 g, 69% yield). ¹H-NMR (CDCl₃) δ 0.75–1.05 [m, 21H, (CH₃)₂CHO and SnCH₂CH₂CH₂CH₃], 1.16 [dd, $J = 1.3$ Hz, 6.9 Hz, 6H, (CH₃)₂CHC=O], 1.20–1.75 [m, 14H, (CH₃)₂CHC=O and SnCH₂CH₂CH₂], 2.02 (ddd, $J = 2.6$ Hz, 12.2 Hz, 14.2 Hz, 1H, CHH), 2.55 (hept, $J = 6.9$ Hz, 1H, CHC=O), 2.64 (d, $J = 4.0$ Hz, 1H, OH), 3.15–3.25 (m, 1H, *i*-PrCHOH), 5.19 (dd, $J = 2.6$ Hz, 12.2 Hz, 1H, SnCHO); ¹³C-NMR (CDCl₃) δ 9.19 [$J(^{13}\text{C}-^{119}\text{Sn}) = 325$ Hz, $J(^{13}\text{C}-^{117}\text{Sn}) = 310$ Hz, SnCH₂], 13.59 (SnCH₂CH₂CH₂C), 17.79 (CH₃CHCHOH), 18.76 (CH₃CHCHOH), 19.09 (CH₃CHC=O), 19.19 (CH₃CHC=O), 27.35 [$J(^{13}\text{C}-^{119}\text{Sn}) = 55$ Hz, SnCH₂CH₂C], 28.95 [$J(^{13}\text{C}-^{119}\text{Sn}) = 21$ Hz, SnCH₂C], 33.43 (CHCHOH), 34.27 (CHC=O), 38.65 (CH₂CHOH), 66.74 [$J(^{13}\text{C}-^{119}\text{Sn}) = 354$ Hz, $J(^{13}\text{C}-^{117}\text{Sn}) = 337$ Hz, SnCHO], 72.53 [$J(^{13}\text{C}-^{119}\text{Sn}) = 38$ Hz, *i*-PrCHOH], 178.44 (C=O); IR (neat) 3506 (br), 2962 (s), 2932 (s), 2876 (s), 2856 (s), 1714 (s), 1469 (s), 1420 (m), 1387 (m), 1377 (m), 1340 (m), 1290 (m), 1256 (m), 1197 (s), 1161 (s), 1071 (m), 1041 (m), 998 (m), 961 (m), 877 (m), 765 (w) cm⁻¹; MS m/z (relative intensity) 477 (1.0, M⁺), 425 (16), 423 (13), 422 (18), 421 (93), 420 (37), 419 (76), 418 (26), 417 (40), 321 (31), 319 (19), 317 (12), 235 (25), 233 (29), 231 (18), 207 (50), 206 (13), 205 (40), 204 (16), 203 (27), 183 (14), 181 (15), 179 (82), 178 (28), 177 (100), 176 (34), 175 (68), 174 (13), 173 (21), 149 (15), 147 (16), 145 (10), 137 (48), 136 (14), 135 (44), 134 (13), 133 (28), 125 (18), 123 (38), 122 (11), 121 (96), 120 (43), 119 (73), 118 (33), 117 (38), 116 (12), 99 (23), 81 (14), 73 (19), 71 (71), 57 (41),

56 (16), 55 (92). Anal. Calc. for $C_{22}H_{46}O_3Sn$: C, 55.36; H, 9.71. Found: C, 55.35; H, 9.54.

Acknowledgements

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