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New optically active organotin compounds for heterogeneous bimetallic catalysis [1]

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Abstract

Chiral tin(IV) derivatives with two or three chiral centers adjacent to the metal (−)-Ment$_2$SnMe$_2$, (−)-Ment$_2$SnPh$_2$, (−)-Ment$_3$SnCl, (−)-Ment$_3$SnH; (−)-Ment = (1R,2S,5R)-1-chloro-5-methyl-2-isopropylcyclohexane, R$_2$Sn[CH(Me)(n-Hex)]$_2$ (R = Bu or Ph) have been prepared either by the coupling of menthylmagnesium chloride with tin halides or by the reaction of lithium stannates with optically active (2-octyl)tosylate. The stereospecificity of both processes was remarkably high, leading to new optically pure organotin reagents which have been fully characterized.

Keywords: Tin; Optically active organotin compounds; Heterogeneous bimetallic catalysis; Lithium stannate

1. Introduction

Organotin compounds are valuable and versatile reagents in organic synthesis, either for modifications of functional groups or for carbon–carbon bond formations with regio- and stereoselective controls [1]. Recently, we have demonstrated that it is possible to graft organostannic fragments, namely Sn(n-C$_4$H$_9$)$_x$ onto the surface of Rh particles supported on silica [2]. These organometallic fragments are obtained by partial hydrogenolysis of Sn(n-C$_4$H$_9$)$_4$ on metallic Rh. These new catalytic materials, in which a metallic surface is partially covered by an organotin fragment, exhibit much higher activities and selectivities than conventionally prepared rhodium catalysts [3]. For example, a rhodium surface modified by organotin fragments becomes fully selective for the reduction of the carbonyl function of α,β-unsaturated aldehydes [3]. In principle, by changing the steric and electronic properties of the grafted organometallic fragments, it may be possible to influence and control the chemo-, regio- and stereoselectivity of any catalytic reaction catalyzed by metallic surfaces.

In order to achieve the objective of enantioselective heterogeneous catalysis, it is necessary to develop access to a general family of chiral organotin compounds. Several routes are available to synthesize organotin compounds in which one chiral carbon is directly linked to the metal or remote from it. Hydrostannation of menthylcrotonate followed by reduction steps affords optically active (2-butenyl)triorganotin compounds [4]. Resolution of prochiral ethers or asymmetric reduction of acyltriorganotins followed by etherification leads to optically active α-metallated ethers able to undergo stereospecific transmetallations or condensations with very high enantiomeric excess [5–8]. The coupling of an alkali metal triorganostannate with optically active 2-octyl or 2-butyl tosylate, bromide or chloride affords 2-octyl or 2-butyltriorganotin compounds with varying degrees of optical purity [9]. The use of an optically stable Grignard reagent, menthylmagnesium chloride [10], may lead to organotin compounds with several chiral groups linked to the tin [11]. This publication reports this synthetic access to (−)-Ment$_2$SnR$_2$ with R = CH$_3$, C$_6$H$_5$ and (−)-Ment$_3$SnX with X = Cl, H.

[1] In memory of Professor Takaya.
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However, to get chiral centers as close as possible to the metal, this method is limited to menthyl-type substituents [12]. To solve this problem, we also present here the results of an alternative method leading to the introduction of two secondary chiral groups on the tin [13].

2. Results

In the remainder of this paper we shall designate as R* the chiral group (−)-menthyl. The corresponding Grignard reagent R*MgCl reacts stereospecifically with $SnCl_2Me_2$ and $SnCl_2Ph_2$ to give di(−)-menthyldimethyltin **1** and di(−)-menthyldiphenyltin **2** respectively, which can be isolated as a colorless liquid in good yield (Eq. (1)). No di(+)-neomenthyldimethyltin or di(+)-neomenthyldiphenyltin are formed during this synthesis, which indicates that no inversion at the asymmetric menthyl C_1 atom takes place during the elementary step of C–Sn bond formation.

$$SnCl_2R_2 + R^*MgCl \longrightarrow R_2SnR_2 \quad (1)$$

R* = (−)-menthylchloride, R = Me **1**, Ph **2**

The addition of (−)-menthylmagnesium chloride in THF to a solution of tin tetrachloride in benzene, followed by acidic (HCl) hydrolysis, gave tri(−)-menthyltin chloride **3**. This compound crystallizes in excellent yield from the ethanol solution as white crystals.

$$R^*MgCl + SnCl_4 \xrightarrow{-MgCl_2} \underset{3}{R_3SnCl} + MgCl_2 \quad (2)$$

The corresponding tri(−)-menthyltin hydride **4** is obtained by reduction with lithium aluminium hydride.

$$R_3SnCl \xrightarrow{LiAlH_4} \underset{4}{R_3SnH} \quad (3)$$

Optically active dibutyl- and diphenyldi(2-octyl)tin were obtained via the one pot stepwise metallation–alkylation process between dibutyl- and diphenyltin hydrides, two equivalents of lithium diisopropylamide and two equivalents of 2-octyl tosylate. The reaction proceeded first through the formation of a hydrodiorganostannyllithium which was alkylated with one equivalent of tosylate. The resulting (2-octyl)diorganotin hydride was then lithiated with the second equivalent of lithium diisopropylamide and alkylated with the remaining equivalent of tosylate. With (−)-(R)-2-octyl tosylate (ee = 96%) and dibutyltindihydride, (+)-(S,S)-di(2-octyl)dibutyltin (ee ≥ 96%) was recovered in 47% yield.

$$R_2SnH_2 \xrightarrow[2MeCH(OTs)n\text{-}Hex]{2^iPrN_2Li} R_2Sn[CH(Me)(n\text{-}Hex)]_2 \quad (4)$$

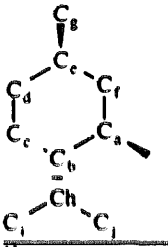
R = Bu, yield 47%, $[\alpha]_D^{18}$ 17.1°, ee > 96%R = Ph, yield 47%, $[\alpha]_D^{18}$ −30.2°, ee > 96%

3. Discussion

The spectroscopic data, including ^{13}C, ^1H, ^{119}Sn NMR and infrared, of compounds **1–4** are summarized in Tables 1, 2 and 3.

The assignment of the 10 resonances of the menthyl ligand(s) is based on the analysis of multiplicity by means of DEPT experiments and by comparison with the chemical shifts of (−)menthyltrimethyltin already fully characterized by Schuman and coworkers [11]. The analysis of the $^{13}C\{^1H\}$ NMR spectra of these compounds reveals in fact a retention of the configuration of the C_1 atom of the (−)menthylmagnesium chloride during the alkylation process. As already reported [11], there is a strong stereospecificity of the Grignard reaction during the formation of the bond between the menthyl ligand and the tin.

Table 1
$^{13}C\{^1H\}$, ^1H and ^{119}Sn NMR data of compounds **1–4**



^{13}C	1	2	3	4
[a] δ [b] (J_{Sn-C})	$(Men)_2SnMe_2$	$(Men)_2SnPh_2$	$(Men)_3SnCl$	$(Men)_3SnH$
a	41.7	42.65	43.7	34.4
^1J	(371.2/355)	(355)	(329)	(339)
b	47.0	46.9	46.7	47.7
^2J	(14.8)	(13.6)	(11)	(16)
c	26.7	26.87	27.4	27.2
^3J	(57.7)	(30.0)	(67)	(53)
d	33.9	35.2	35.3	36.0
e	35.3	35.6	35.6	37.8
			(65)	(60.5)
f	35.9	37.6	40.9	43.8
^2J	(17.6)		(17.6)	(16.8)
g	22.9	22.4	22.8	23
h	33.5	34	35.3	33.8
	(18.3)			(18)
i	22.3	21.7	22.3	22
j	16.1	15.7	17	16.3
Me	−11.5	128.2; 137.5		
^1J	267.5/255.5			
[a] δ_{Sn}	−16.2		93.6	−102.9
[a] δ_{Sn-H}				5.23

[a] δ, chemical shifts in ppm;
[b] J_{Sn-C}, ^{13}C–$^{117/119}Sn$ coupling constants in Hz.

Geometrical information can be obtained from the $^1J(^{13}C-^{117/119}Sn)$ and $^3J(^{13}C-^{117/119}Sn)$ values. The coupling constants $^3J(^{13}C-^{117/119}Sn)$ of the menthyl carbon in γ position to tin C_c, C_h, C_e have the same magnitude as those reported by Schuman and coworkers [11]. From the Karplus-type relationship existing between $^3J(^{13}C-Sn)$ and the dihedral angle of the coupling nuclei [14], it could be deduced that the Me_2Sn group is in equatorial position, as shown in Fig. 1.

The values of the coupling constants $^1J(^{13}C^{117/119}Sn)$ have been related to the C–Sn–C bond angle by Eq. (5) established for the dimethyltin(IV) compounds [15]:

$$^1J(^{13}C-Sn) = 10.5\theta - 810 \quad (5)$$

The calculated angles, using Eq. (5), for an Me_2SnR_2 series are listed in Table 2 and seem reasonable: cyclohexyl and (−)menthyl groups have a similar steric requirement and give the same values for θ.

The physical properties of the organotin hydride **4** are listed in Tables 1–3. The Sn–H bond shows a strong and sharp infrared absorption corresponding to a ν(Sn–H) vibration at 1786 cm^{-1}.

As shown in Table 3, the substitution of a methyl group on the tin atom by a bulkier alkyl group [^{i}Pr, ^{t}Bu, (−)-Ment] leads to a shift to lower frequency of the Sn–H vibration [11]. The value of the frequency of the Sn–H vibration is sensitive to the steric hindrance in the coordination sphere of the tin atom. These remarks lead to the conclusion that cyclohexyl and (−)menthyl groups have a similar steric requirement.

In a previous work we showed that treatment of diorganotin dihydrides by lithium diisopropylamide and alkylating agents such as primary halides, aldehydes or epoxides gave the expected dialkylated diorganotins via stepwise metallation–alkylations [13]. To extend this method to enantioselective synthesis of tetraorganotins with two chiral carbons linked to the metal, the reaction of diorganotin hydrides, lithium diisopropylamide and chiral secondary halides was studied. Despite good results when lithium trimethyl- or triphenylstannate was opposed to secondary organic chlorides or bromides [9], extensive decomposition of lithium dibutylstannate was only observed with 2-chloro- and 2-bromo-octane. It led to tetrabutyltin, cyclo(polydibutyltins) and only very little of the expected product. However, when 2-octyl tosylate was used, the expected product, di(2-octyl)dibutyltin, was satisfactorily recovered in a 47% yield, which showed that dialkylation was possible with tosylates. Futhermore, with (−)-(R)-2-octyl tosylate [17], prepared from (−)-(R)-2-octanol (ee 96%) [18], di(2-octyl)dibutyltin **5** showed an optical rotation of +17.1°. The configuration and optical purity of **5** were established by ^{119}Sn NMR spectroscopy. This sensitive technique allowed the identification of the three diastereomers of tetra(2-butyl)tin [19] and showed that the spectrum of a mixture of di(2-octyl)dibutylstannanes, prepared from racemic chloro(2-octyl)magnesium and dichlorodibutylstannane, consisted of two peaks of equal intensity at −18.0 and −18.4 ppm attributed to the expected diastereomers [20]. The ^{119}Sn NMR spectrum of (+)-di(2-octyl)dibutyltin showed only one signal at 18.2 ppm (Table 4), indicating that only one diastereomer was formed during the reaction. As the product

Table 3
Values of ν(Sn–H) vibrations of related tin-hydride derivatives

(−)-MentSnMe$_2$H	ν(Sn–H) = 1798	Ref. [11]
(−)-MentSn^{i}PrMeH	ν(Sn–H) = 1786	Ref. [11]
(−)-MentSn^{t}BuMeH	ν(Sn–H) = 1722	Ref. [11]
(−)-Ment$_2$SnH	ν(Sn–H) = 1786	This work
Chex$_2$SnH	ν(Sn–H) = 1782	Ref. [16]

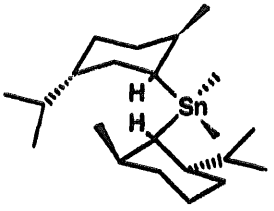
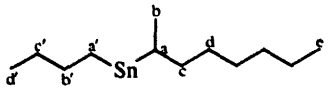


Fig. 1. Di(-)menthyldimethyltin **1**.

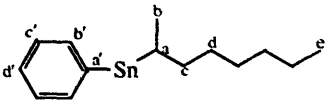
Table 2
Calculated dimethyltin angle Θ = C–Sn–C deduced from Eq. (4) and using the values of ^{13}C NMR chemical shift and coupling constants in Me_2SnR_2 and (−)-menthylSn derivatives

Compound	δ	$^1J^{119}_{Sn-^{117}Sn-Me}$	δ	$^1J^{119}_{Sn-^{117}Sn-C_1}$	Calc. Θ °
Me_4Sn	9.1	340/321	–	–	109°
Me_2SnBu_2	−11.5	300/287	10.2	350/330	106°
Me_2SnNp_2	−6.6	297/284	32.0	346/331	105°
$Me_2SnChex_2$	−14.0	272/262	25.5	371/354	103°
$Me_2Sn^tBu_2$	−14.4	250/239	24.8	388/377	101°
Me_2Sn(−)-Ment$_2$	−11.1	267/255	30.3	371/355	103°
Me_3Sn(−)-Ment	−10.5	301/287	31.6	412/394	106°
Me_2HSn(−)-Ment	−12.6	300/314	32.2	424	107°
	−12.8	300/314			
$Me_2{}^tBuSn$(−)-Ment	−11.7	248/301	33.6	345/361	105°
	−12.2	288/301			

Table 4
$^{13}C\{^1H\}$ and ^{119}Sn NMR data of compounds 5 and 6



5



6

$^{13}C\{^1H\}$ and ^{119}Sn NMR	5	6
	δ [a], $\{J_{Sn-C}\}$ [b]	δ [a], $\{J_{Sn-C}\}$ [b]
a, ^1J	20.2 {322}	22.5 {382}
b, ^2J	18.9 {15}	19.1 {17}
c, ^2J	36.4 {13}	36.2 {17}
d, ^3J	29.7 {38}	30.1 {38}
e	14.1	14.2
	22.7	22.8
	29.4	29.8
	31.9	31.9
	7.9 {290}	
a', ^1J	29.4	137.5 {29}
b', ^2J	27.7 {52}	128.3 {41}
c', ^3J	13.6	140.4
[a] δ_{Sn}	−18.2	−77.8

[a] δ, chemical shifts in ppm;
[b] $\{J_{Sn-C}\}$; $^{13}C-^{119}Sn$ coupling constants in Hz.

had a high optical activity, unlikely to be due to an impurity, it could not be the inactive (R,S)-diastereomer. Thus, as lithium stannates are known to react with tosylates with inversion of the configuration at carbon, the (S,S) configuration was attributed to the isolated stereomer. The stereoselectivity of the coupling was very high, better than 96%.

As phenyl groups can be cleaved and replaced by other functionalities, it was of interest to demonstrate the validity of our method with diphenyl compounds. Indeed, it worked quite well as, with (+)-(S)-2-octyl tosylate (ee 80%), diphenyltin dihydride gave a dialkylation product in 57% yield with an optical rotation of −30.2°. The enantiomeric excess was determined as above by ^{119}Sn NMR where two peaks at −77.8 and −78.1 ppm in an 86/14 ratio were respectively attributed to (−)-(R,R)- and (+)-(S,S)-di(2-octyl)diphenyltin **6** and to (R,S)-di(2-octyl)diphenyltin (Table 4). As for a total stereoselectivity with a tosylate of ee = 80%, the expected value for the ratio of optically active versus optically inactive isomers was 82/18; the reaction occurred with a very high selectivity. The slightly better experimental ratio (86/14) than the theoretical one might indicate some asymmetric induction in the second alkylating step, as the intermediate tin hydride was linked to a chiral 2-octyl group. However, the theoretical value being within experimental error (4%), this hypothesis seems unlikely.

Pure nucleophilic substitution (SN_2), metal–halogen exchange, free radical and electron-transfer mechanisms can be involved in the coupling of the alkali metal organostannates with halides or tosylates, depending on the reaction conditions (solvent, temperature, order of addition of reagents) and the nature of the reagents (leaving group, substituents of the metal, counterion, presence of additives) [9]. However, only pure nucleophilic substitution leads to enantiomerically pure products. In the present study it has been shown that two stepwise deprotonations of diorganotin dihydrides with LDA was compatible with very high enantioselectivity, which is indicative of a pure SN_2 reaction. Furthermore, the presence of butyl groups on the tin, favoring racemizing electron-transfer or metal–halogen exchange mechanisms [21], proved not to be unfavorable to an inversion mechanism, despite earlier findings showing that sodium triphenylstannate is more selective than sodium trimethylstannate [9].

Results concerning applications of these compounds in heterogenous enantioselective catalysis will be reported in due course [22].

4. Experimental

All reactions were carried out under a nitrogen atmosphere. THF was distilled from benzophenoneketyl prior use. Diisopropylamine was distilled on KOH. Dibutylstannane, diphenylstannane [23], (−)-(R)-, (+)-(S)-2-octanols [18], (−)-(R)-, (+)-(S)-2-octyl tosylates [17] were prepared according to known procedures. Optical rotations of (−)-(R)-, (+)-(S)-2-octanols were $[\alpha]_D^{18}$ −9.5° and $[\alpha]_D^{18}$ +7.9° respectively. ^1H NMR and ^{13}C

NMR spectra were recorded on a Brucker AC-250 spectrometer (solvent $CDCl_3$, internal reference Me_4Si) and ^{119}Sn NMR spectra were recorded on a Brucker AC-200 spectrometer (solvent C_6D_6, internal reference Me_4Sn). Optical rotations were measured on a Perkin-Elmer 241 polarimeter using a 1 dm cell.

4.1. Di(−)menthyldimethyltin 1

A solution of 3.14 g (14 mmol) of dimethyltin dichloride in 16 ml of dried THF was added dropwise over a period of 1 h at 0 °C to a vigorously stirred solution of a Grignard reagent prepared from 10 g (57 mmol) of (−)menthylchloride and 1.52 g (62 mmol) of magnesium in 25 ml of THF. After stirring for 48 h at room temperature under argon, the solution was treated dropwise with 10 ml of water at 0 °C., stirred for a further 30 min at room temperature and dried over anhydrous magnesium sulfate. Removal of the solvents in vacuo and fractionated distillation (90 °C/40 mbar) yielded **1** (2.95 g, 48.2%) as a colorless liquid. Anal. Found: C, 61.6; H, 10.2; Sn, 27.8. Calc.: C, 61.9; H, 10.3; Sn, 27.8%. $[\alpha]_D^{20} = -33.11°$, benzene. MS (70 eV, 250 °C) m/z: $427(M)^+\cdot$, $412(M-CH_3)^+$, $288(M-C_{10}H_{19})^+$, $274(M-C_{11}H_{22})^+$, $150(C_2H_6-Sn)^+$, $139(C_{10}H_{19})^+$, $83(C_6H_{11})^+$, $55(C_4H_7)^+$.

4.2. Di(−)-menthyldiphenyltin 2

In analogy to the synthesis of **1**, diphenyltin dichloride (7.79 g, 23 mmol) was reacted with menthylMgCl (11.3 g, 57 mmol) in 20 ml of THF. After stirring for 48 h at room temperature under argon, the solution was treated dropwise with 50 ml of water at 0 °C, and stirred for a further 30 min at room temperature. After addition of ether (130 ml), the organic layer was decanted, washed with water, then dried with anhydrous $MgSO_4$. Removal of the solvents in vacuo and distillation in a Buchi GKR 51 micro-oven at 150–180 °C under 10^{-2} mmHg yielded **2** as a colorless oil; yield 3.20 g, 49%. Anal. Found: C, 66.0; H, 8.4; Sn, 21.78. Calc.: C, 69.2; H, 9.4; Sn, 21.4%. $[\alpha]_D^{20} = -30.45°$, benzene.

4.3. Tri(−)menthyltin chloride 3

A similar experimental procedure to that for the preparation of hexa(−)menthylditin [11] was followed with 1.74 g (6.7 mmol) of $SnCl_4$ and menthylmagnesium chloride from 10 g (57 mmol) of (−)menthylchloride and 1.66 g (68.7 mmol) of Mg. But a large excess of HCl was added (ca. 1.4 ml of a 30% solution). After addition of ether the organic layer was decanted, washed with water, then dried with anhydrous magnesium sulfate. The solvent was removed and the crude product recrystallized from ethanol, yielding 2 g of tri(−)menthyltin chloride **3** as a white crystalline solid (T = 131.2–131.6 °C). Anal. Found: C, 63.5; H, 10.5; Sn, 21.78. Calc.: C, 62.9; H, 9.97; Sn, 20.8%. MS (70 ev, 250 °C) m/z: $571(M)^+$, $539(M-Cl)^+$, $434(M-C_{10}H_{19})^+$, $276(S_nC_{10}H_{19}Cl)^+$, $260(SnC_{10}H_{19})^+$, $139(C_{10}H_{19})^+$, $138(C_{10}H_{18})^+$, $135(CH_3Sn)^+$, $120(Sn)^+$, $97(C_7H_{13})^+$, $95(C_7H_{11})^+$, $83(C_6H_{11})^+$, $81(C_6H_9)^+$, $69(C_5H_9)^+$, $67(C_5H_7)^+$, $57(C_4H_9)^+$, $55(C_4H_7)^+$, $41(C_3H_5)^+$. $[\alpha]_D^{20} = -80.9°$ (c = 1.25 in C_6H_6).

4.4. Tri(−)menthyltin hydride 4

A similar experimental procedure to the preparation of (−)menthyldimethylstannane [11] was used with 1.94 g (3.39 mmol) **3** in ether and 3.41 g (3.41 mmol) $LiAlH_4$ reacting to form **4**. Distillation in a Buchi GKR 51 micro-oven at 150–180 °C under 10^{-2} mmHg enabled **4** to be isolated as a colorless liquid; yield 1.17 g (64%). Anal. Found: C, 67.8; H, 9.67. Calc.: C, 67; H, 10.8; Sn, 22.2%. $[\alpha]_D^{20} = -95.5$(C.1.05 in C_6D_6)°. MS (70 eV, 250 °C) m/z: $538(M)^+$, $399(M-C_{10}H_{19})^+$, $259(SnC_{10}H_{19})^+$, $138(C_{10}H_{18})^+$, $120(Sn)^+$, $95(C_7H_{11})^+$, $81(C_6H_9)$, $67(C_5H_7)^+$, $55(C_4H_7)^+$, $43(C_3H_7)^+$.

4.5. (+)-(S,S)-di(2-octyl)dibutyltin 5

4.7 g (20 μmol) of dibutylstannane was slowly added to a THF (10 ml)/hexane (16 ml) solution of lithium diisopropylamide (42 mmol) at −50 °C. After 30 min at this temperature, the solution was golden yellow. Then, 11.9 g (42 mmol) of (−)-(R)-2-octyl tosylate, prepared from (−)-(R)-2-octanol (ee 96%), was added, and the mixture was allowed to reach 0 °C. After hydrolysis and the usual work-up, the tetraorganotin was recovered in 47% yield as an oil after chromatography on silica gel (eluant petroleum ether). Analytically pure samples were obtained by reversed phase HPLC (C_{18}, 20m, eluant MeOH/^{i}PrOH 80/20). $[\alpha]_D^{18}$ = 17.1°, benzene. High resolution MS m/z: 403.2371 (M–Bu), calc.: 403.239.

4.6. (−)-(R,R)-di(2-octyl)diphenyltin 6

5.5 g (20 μmol) of diphenylstannane was slowly added to a THF (10 ml)/hexane (20 ml) solution of lithium diisopropylamide (42 mmol) at −50 °C. After 30 min at this temperature, the solution was golden yellow. Then, 12.5 g (44 mmol) of (+)-(S)-2-octyl tosylate was added, and the mixture was allowed to reach 0 °C. After hydrolysis and the usual work-up, the tetraorganotin was recovered in 57% yield as an oil after chromatography on silica gel (eluant petroleum ether). Analytically pure samples of a mixture of (−)-(R,R)-di(2-octyl)diphenyltin **6** (86%) and (R,S)-di(2-octyl)diphenyltin (14%) were obtained by reversed phase HPLC (C_{18}, 20m, eluant MeOH/^{i}PrOH 80/20). $[\alpha]_D^{18}$

= −30.2°, benzene. ^{1}H NMR δ: 8.85 (6H, t), 1.10–1.85 (28H, m), 7.15 (6H, m), 7.25 (4H, m). High resolution MS *m/z*: 423.2068 (M–Ph), calc.: 423.208.

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