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Synthesis of Aromatic and Olefinic Sodium Sulfonates by Electrophilic Destannylation with Trimethylsilyl Chlorosulfonate

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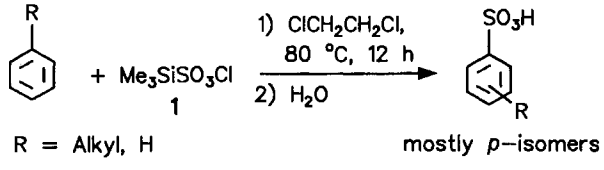
A mild and effective method for the preparation of a variety of aromatic, olefinic, and acetylenic sodium sulfonates is described. The reaction of trialkylaryl- (**2a–k**) and -heteroarylstannanes (**4a–d**), bis-(1-alkenyl)dibutylstannanes (**6a–f**), or trialkylalkynylstannanes with trimethylsilyl chlorosulfonate (**1**) followed by hydrolysis with aqueous $NaHCO_3$ provides the sodium sulfonates in an *ipso*-specific and in the case of vinylic stannanes stereospecific manner. A comparison of the reactivity of stannylated and silylated olefinic compounds **13** and **14** underlines the greater leaving ability of the stannyl moiety. The in situ preparation of the stannanes makes it possible to apply the synthetic method to natural products such as *N*-substituted apocodeine (**17**).

Electrophilic aromatic substitution is one of the most important reactions in synthetic organic chemistry[2]. However, there are still some considerable limitations to this type of reaction. The substitution patterns are determined by the directing effects of substituents already present in the molecule and the use of weak electrophiles is restricted or impossible in some cases. A strategy for obtaining unconventional substitution patterns is provided by the use of the trialkylstannyl moiety as a superior leaving group rather than the conventional proton. Trialkylarylstannanes open an elegant and easy way to introduce electrophiles into an aromatic ring in an *ipso*-specific manner. This has for example been demonstrated for Friedel-Crafts acylations[3], amidations with various isocyanates[4–6], and sulfonations[7]. This type of reaction may also be extended to vinylic stannanes, where electrophilic destannylation can make possible the introduction of keto-[8] or amide-[1] and other functionalities next to the double bond.

The synthesis of aromatic compounds containing sulfofunctions is of considerable interest[9], in particular the introduction of groups which can render organic molecules water soluble. Most methods for generating sulfonic acids and their derivatives involve the use of agressive reagents such as SO_3[10] or chlorosulfonic acid[11]. A milder reagent which has been used for the preparation of aromatic sulfonic acids and their salts is the easily accessible trimethylsilyl chlorosulfonate **1**[12] (Scheme 1); the latter has been reacted with aromatic hydrocarbons[13] and with trimethylarylsilanes (via electrophilic desilylation)[14]. The disadvantages of this method are the long reaction times and high temperatures required; in addition the reactions are often not regiospecific.

Scheme 1



Results and Discussion

Compound **1** reacts under mild conditions (room temperature, no catalyst) in short reaction times (1 h) with trialkylaryl stannanes in an *ipso*-specific manner with the loss of trialkyltin chloride to form trimethylsilyl arenesulfonates. These can easily be hydrolyzed with $NaHCO_3$/water to give the corresponding sodium arenesulfonates (Scheme 2).

The strong directing effects of methyl and even of methoxy groups can be completely overcome by the use of the trialkylstannyl moiety as a leaving group. Only *ipso*-substitution products are formed in good yields (45 to 80%). It is possible to introduce a sulfonate group directly to the 3-position of anisole or toluene via an electrophilic substitution using **1**. Unusual substitution patterns which are not available from classical aromatic substitutions routes can thus be obtained.

This method for synthesizing sodium sulfonates can easily be extended to include poly- and heterocyclic sodium sulfonates (Scheme 3), as demonstrated by a few typical examples.

It is thus possible to obtain thiophene derivatives substituted in the 3-position; these are not readily accessible, since thiophene normally undergoes substitution at the 2-position by electrophiles.

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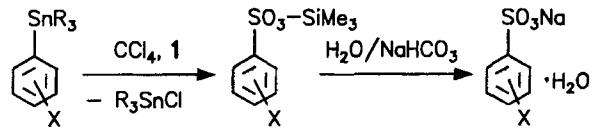
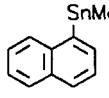
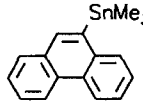
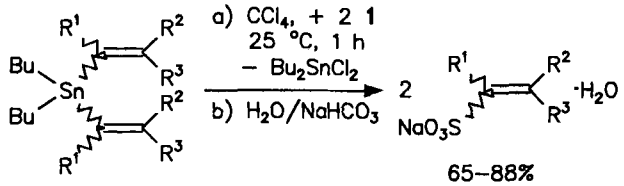
Scheme 2



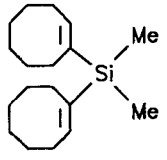
45–79%

2	R	X	3	yield (%)
a	Bu	4–Me	a	61
b	Bu	3–Me	b	73
c	Me	4–OMe	c	45
d	Me	3–OMe	d	79
e	Me	4–Cl	e	45
f	Me	3–Cl	f	62
g	Bu	3–Cl	f	56
h	Me	2–Cl	g	61
i	Bu	2–Cl	g	69
j			h	68
k			i	59



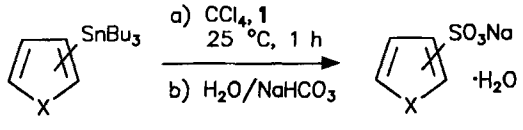
6a–f 7a–f

6	R^1	R^2	R^3	7	yield (%)
a	H	Me	H	a	82
b	Me	Me	H	b	71
c	–[CH2]3–		H	c	80
d	–[CH2]4–		H	d	76
e	–[CH2]6–		H	e	88
f	Ph	H	H	f	65



12

Scheme 3



4a–d 5a–d

70–95%

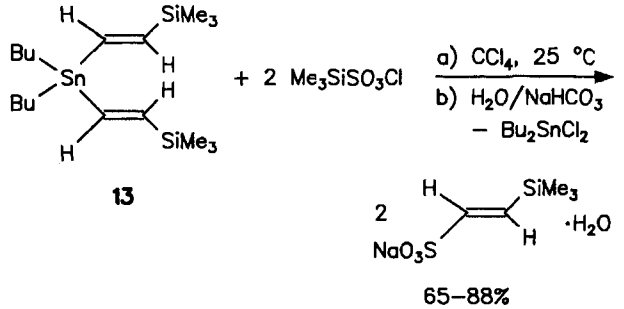
4	X	–$SnBu_3$	5	–SO_3Na	yield (%)
a	O	2–	a	2–	95
b	S	2–	b	2–	90
c	S	3–	c	3–	76
d	NMe	2–	d	2–	70

Vinylstannanes have received considerable interest[15] in electrophilic destannylations. The reaction of bis(1-alkenyl)-dibutylstannanes with **1** at room temperature provides a very simple method for generating sodium salts of vinylic sulfonic acids, these being formed in good yields in an exothermic reaction.

This destannylation by means of **1** proceeds in a regio- and ipso-specific manner without isomerisation at the olefinic double bond. Yields higher than 50% demonstrate that electrophilic substitution occurs at both vinylic residues in the stannane.

The superior leaving ability of the stannyl group is demonstrated by the fact that the corresponding silanes, e.g. bis-(cyclooctene-1-yl)dimethylsilane **12** do not react with **1** under the same conditions as the stannanes.

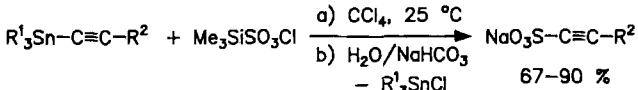
An increase of reaction time and temperature to 24 h and 80°C respectively affords the corresponding desilylation product **7e**, though in much lower yield (42%) than from the stannane **6e** (88%). The selective replacement of the stannyl moiety with an electrophile without reaction at a trimethylsilyl group also attached at the double bond is another piece of evidence for the effectivity of the stannyl group.



13 14

65–88%

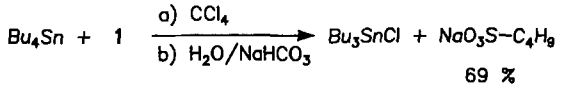
Even trialkylstannyl-substituted alkynes react with **1** to give the corresponding sodium sulfonates in good yields, thus demonstrating that this type of electrophilic destannylation can be easily transferred to practically any unsaturated stannylated system.



8a–d 67–90 % 9a–c

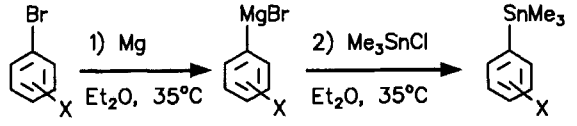
8	R^1	R^2	9	yield (%)
a	Me	Ph	a	90
b	Me	$MeOCH_2$	b	85
c	Bu	$MeOCH_2$	c	67
d	Me	$PhOCH_2$	d	79

This type of reaction is not restricted to a stannyl group attached to an unsaturated carbon atom. Even tetrabutylstannane reacts with **1** to form the corresponding sodium sulfonate in an electrophilic substitution reaction, although electrophilic reactions do not normally occur at sp^3-hybridised carboncentres. This underlines the excellent leaving ability of the trialkylstannyl group.

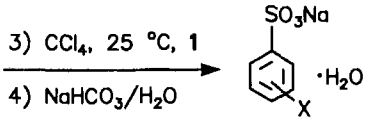


The cleavage of a second alkyl group from the tin by-product Bu_3SnCl by **1** was not observed.

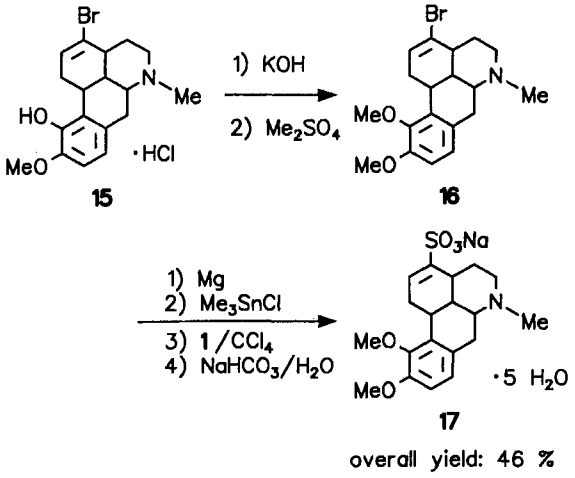
The scope of this procedure can be extended considerably by using a stannane generated in situ from a Grignard reagent and Me_3SnCl.



X	yield (%)
3-Me	76 %
3-OMe	62 %
3-Cl	60 %



Compound **1** was added directly to the stannane thus generated to form the sodium sulfonates in almost the same yields as those obtained from the stannanes which had been isolated. The method of in situ generation of the stannyl reagent and subsequent destannylation with **1** is applicable to natural products such as an *N*-substituted apocodeine[16].



The Grignard compounds used to form the stannanes, themselves also react with **1** (as demonstrated for X = 3-Me) to form the sodium sulfonates after hydrolysis but the yield is reduced to 15%.

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Experimental

Melting points: Gallenkamp F 370. – IR: Shimadzu 3283. – NMR: Varian EM 360 (60 MHz, ^1H), Bruker AC 200 (200 MHz, ^1H), and Bruker AM 300 (300 MHz, ^1H; 75.47 MHz, ^{13}C; 59.63 MHz, ^{29}Si; 111.92 MHz, ^{119}Sn). – MS: Finnigan MAT 8230, 70 eV. – Elementary analyses: Carlo Erba MOD 1106.

The trialkylaryl- **2a–k**[17,18], trialkyheteroaryl- **4a–d**[19], trialkylalkynylstannanes **8a–d**[20], and bis(1-alkenyl)dibutylstannanes **6a**, **b**, **e**[1] were prepared according to published procedures; in the latter case the (*E*)/(*Z*) ratios were as follows: **6a**: (*E*)/(*Z*) = 1.00:0.66; **6b**: (*E*)/(*Z*) = 1.00:3.50; **6e**: (*E*)/(*Z*) = 0:1.00.

Bis-1-alkenyldibutylstannanes (**6c**, **d**). – *General Procedure I:* A solution of dibutyltin dichloride in anhydrous diethyl ether is added under Ar during 1 h to the alkenyllithium reagent prepared from the corresponding 1-bromo-1-alkene and lithium in anhydrous diethyl ether. After stirring under reflux for 12 h the reaction mixture is hydrolysed with 100 ml of saturated aqueous NH_4Cl. Twofold extraction of the aqueous layer with 100 ml of diethyl ether, drying of the combined organic layers with $MgSO_4$, and removal of the solvent affords the crude product which is then subjected to fractionated distillation.

Dibutylbis(cyclopenten-1-yl)stannane (**6c**): **6c** is obtained according to General Procedure I from 3.74 g (0.54 mol) of lithium, 40.0 g (0.27 mol) of 1-bromo-1-cyclopentene[21] in 250 ml of anhydrous ether, and 24.9 g (0.08 mol) of Bu_2SnCl_2 in 50 ml of anhydrous ether. Yield: 26.2 g (87%), b.p. 105°C/0.02 Torr. – ^1H NMR ($CDCl_3$): δ = 0.93 (t, 6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 1.46 (m, 12H, $CH_{2,Butyl}$), 1.72 (m, 4H, CH_2), 2.27 (m, 8H, $CH_{2,Allyl}$), 5.80 (m, 2H, CH, $^3J_{SnH}$ = 37.5 Hz). – ^{13}C NMR ($CDCl_3$): δ = 9.8 (CH_2, $^1J_{SnC}$ = 366 Hz), 13.7 (CH_3), 23.5 (CH_2, $^2J_{SnC}$ = 41 Hz), 27.3 (CH_2, $^3J_{SnC}$ = 70 Hz), 29.3 (CH_2, $^2J_{SnC}$ = 31 Hz), 34.3 (CH_2, $^3J_{SnC}$ = 70 Hz), 39.5 (CH_2, $^3J_{SnC}$ = 49 Hz), 141.4 (CH, $^2J_{SnC}$ = 41 Hz), 142.4 (C_q, $^1J_{SnC}$ = 418 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = −101.7. – MS; *m/z* (%): 367 (1) [M^+ – H], 311 (100) [M^+ – C_4H_9], 301 (6) [M^+ – Cyclopentenyl], 255 (94) [M^+ – 2 C_4H_9 + H], 245 (7) [M^+ – C_4H_9 – Cyclopentenyl + H], 187 (89) [M^+ – 2 C_4H_9 – Cyclopentenyl], 121 (49) [SnH^+], 67 (45) [Cyclopentenyl$^+$], 57 (20) [$C_4H_9^+$]. – $C_{18}H_{32}Sn$ (367.14): calcd. C 58.89, H 8.79; found C 58.3, H 8.8.

Dibutylbis(cyclohexen-1-yl)stannane (**6d**): **6d** is obtained according to General Procedure I from 2.76 g (0.40 mol) of lithium, 36.0 g (0.22 mol) of 1-bromo-1-cyclohexene[22], and 20.0 g (0.06 mol) of Bu_2SnCl_2. Yield: 25.1 g (96%), b.p. 120°C/0.01 Torr. – ^1H NMR ($CDCl_3$): δ = 0.88 (t, 6H, CH_3, $^3J_{HH}$ = 7.0 Hz), 1.40 (m, 12H, $CH_{2,Butyl}$), 1.60 (m, 8H, CH_2), 2.11 (m, 8H, $CH_{2,Allyl}$), 5.80 (m, 2H, CH, $^3J_{SnH}$ = 69.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = 8.9 (CH_2Sn, $^1J_{SnC}$ = 328 Hz), 13.6 (CH_3), 22.8 (CH_2), 23.8 (CH_2, $^2J_{SnC}$ = 33 Hz), 27.4 (CH_2, $^3J_{SnC}$ = 56 Hz), 27.6 (CH_2, $^3J_{SnC}$ = 56 Hz), 29.2 (CH_2, $^2J_{SnC}$ = 20 Hz), 31.9 (CH_2, $^3J_{SnC}$ = 36 Hz), 137.7 (CH, $^2J_{SnC}$ = 26 Hz), 139.9 (C_q, $^1J_{SnC}$ = 420 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = −89.2. – MS; *m/z* (%): 339 (100) [M^+ – C_4H_9], 315 (10) [M^+ – Cyclohexenyl], 283 (54) [M^+ – C_4H_9 – C_4H_8; (Cyclohexenyl)$_2SnH^+$], 201 (9) [M^+ – Cyclohexenyl – 2 C_4H_9], 162 (4) [(Cyclohexenyl)$_2$], 121 (15) [SnH^+], 81 (16) [Cyclohexenyl], 57 (2) [$C_4H_9^+$]. – $C_{20}H_{36}Sn$ (395.20): calcd. C 60.79, H 9.18; found C 60.9, H 9.2.

Dibutylbis(1-phenyl-1-ethenyl)stannane (**6f**): A solution of the Grignard reagent, prepared from 73.2 g (0.40 mol) of 1-bromo-1-

phenylethene and 9.36 g (0.40 mol) of magnesium in 100 ml of THF is added to a suspension of 25.0 g (0.10 mol) of dibutyltinoxide in 100 ml of anhydrous *n*-heptane at 70–80 °C during 1 h. After stirring under reflux for 3 h the reaction mixture is hydrolyzed with 100 ml of saturated aqueous NH_4Cl. The aqueous layer is extracted with 150 ml of diethyl ether and dried with $MgSO_4$. After removal of the solvent and distillation 35.5 g (81%) of **6f** is obtained, b.p. 160 °C/0.01 Torr. – ^1H NMR ($CDCl_3$): δ = 0.89 (t, 6H, CH_3, $^3J_{HH}$ = 6.5 Hz), 1.19–1.64 (m, 12H, CH_2), 5.45 (d, 2H, CH, $^2J_{HH}$ = 3.0 Hz), 6.23 (d, 2H, CH, $^2J_{HH}$ = 3.0 Hz), 7.34 (m, 10H, H_{aromat}). – ^{13}C NMR ($CDCl_3$): δ = 11.5 (CH_2, $^1J_{SnC}$ = 343 Hz), 13.6 (CH_3), 27.1 (CH_2, $^3J_{SnC}$ = 61 Hz), 28.7 (CH_2, $^2J_{SnC}$ = 20 Hz), 126.4 (CH_{aromat}, $^3J_{SnC}$ = 20 Hz), 127.9 (CH_2, $^2J_{SnC}$ = 101 Hz), 128.2 (CH), 128.4 (CH), 145.6 ($C_{q,aromat}$, $^1J_{SnC}$ = 36 Hz), 153.8 (C_q, $^1J_{SnC}$ = 374 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = −69.2. – MS; *m/z* (%): 440 (8) [M^+], 383 (65) [$M^+ - C_4H_9$], 337 (22) [M^+ – Ph–C=CH_2], 327 (20) [$M^+ - 2\,C_4H_9 + H$], 281 (22) [$M^+ - C_4H_9$ – Ph–C=CH_2], 223 (67) [$M^+ - 2\,C_4H_9$ – Ph–C=CH_2], 206 (44) [(Ph–C=CH)$_2^+$], 197 (51) [$PhSn^+$], 177 (13) [$SnC_4H_9^+$], 127 (78) [SnH^+], 103 (100) [Ph–C=CH_2^+], 91 (48) [Ph–CH_2^+], 77 (78) [$C_6H_5^+$], 51 (45) [$C_4H_3^+$], 42 (79) [$C_3H_6^+$]. – $C_{24}H_{32}Sn$ (439.21): calcd. C 65.63, H 7.34; found C 67.2, H 7.4.

Dibutylbis[(E)-2-trimethylsilylethenyl]stannane (**13a**): A mixture of 4.91 g (50.0 mmol) of trimethylsilylethyne[23] and 4.70 g (20.0 mmol) of dibutyltindihydride[24] is heated in the presence of AIBN for 5 h at 40 °C. After distillation 6.2 g (72%) of **13a** is obtained, b.p. 140 °C/0.4 Torr. – ^1H NMR ($CDCl_3$): δ = 0.07 (s, 18H, $SiMe_3$, $^2J_{SiH}$ = 36.0 Hz), 0.88 (t, 6H, CH_3, $^3J_{HH}$ = 6.9 Hz), 0.96 (m, 4H, CH_2), 1.31 (m, 4H, CH_2), 1.51 (m, 4H, CH_2), 6.64 (d, 2H, $^3J_{HH}$ = 22.6 Hz, $^2J_{SnH}$ = 103.6 Hz), 6.95 (d, 2H, CH, $^3J_{HH}$ = 22.6 Hz, $^3J_{SnH}$ = 105.6 Hz, $^2J_{SiH}$ = 11.0 Hz). – ^{13}C NMR ($CDCl_3$): δ = −1.4 (CH_3, $SiMe_3$, $^1J_{SiC}$ = 49 Hz), 10.1 (CH_2, $^1J_{SnC}$ = 352 Hz), 13.8 (CH_3), 27.2 (CH_2, $^3J_{SnC}$ = 53 Hz), 29.0 (CH_2, $^2J_{SnC}$ = 20 Hz), 148.8 (CH, $^1J_{SnC}$ = 389 Hz), 155.8 (CH, $^2J_{SnC}$ = 61 Hz, $^1J_{SiC}$ = 23 Hz). – ^{119}Sn NMR ($CDCl_3$): δ = −104.0 ($^3J_{SnSi}$ = 97.6 Hz). – ^{29}Si NMR ($CDCl_3$): δ = −9.1 ($^3J_{SnSi}$ = 97.6 Hz). – MS; *m/z* (%): 432 (2) [M^+], 375 (100) [$M^+ - C_4H_9$], 333 (6) [M^+ – Me_3SiC=CH], 319 (32) [M^+ – Me_3SiCH=CH – CH_3 + H], 277 (26) [M^+ – Me_3SiCH=CH – C_4H_9 + H], 221 (20) [$HSnC_4H_9C_3H_7^+$], 177 (12) [$SnC_4H_9^+$], 135 (5) [$SnMe^+$], 121 (6) [SnH], 73 (59) [$SiMe_3^+$]. – $C_{18}H_{40}Si_2Sn$ (431.38): calcd. C 50.12, H 9.35; found C 49.8, H 9.5.

Sodium Sulfonates (**3a–i**, **5a–d**, **7a–f**, **9a–c**). – *General Procedure II:* The stannane is slowly added to a solution of **1** in 20 ml of anhydrous CCl_4 under Ar at room temperature. After 1 h the exothermic reaction is complete and the reaction mixture is hydrolyzed with 30 ml of saturated aqueous $NaHCO_3$ and stirred for 20 min. The layers are separated and the aqueous layer washed three times with 10 ml of ether. The water is removed from the aqueous layer in vacuo and the residue is digested with 70 ml of boiling ethanol and filtered off. The ethanol is evaporated and the solid residue is washed twice with 20 ml of *n*-pentane and dried in vacuo at 80 °C. The compounds are obtained as hygroscopic solids.

Sodium 4-Toluenesulfonate Hydrate (**3a**): **3a** is obtained according to General Procedure II from 1.90 g (5.00 mmol) of **2a** and 0.94 g (5.00 mmol) of **1**. Yield: 0.65 g (61%), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3485, 1188, 1047 cm^{-1}. – ^1H NMR (D_2O): δ = 2.40 (s, 3H, CH_3), 7.27–7.77 (2 d, 4H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 23.3 (CH_3), 128.2, 132.2 (all CH), 142.3, 145.2 (all C_q). – $C_7H_7NaO_3S \cdot H_2O$ (212.20): calcd. C 39.62, H 4.27; found C 39.1, H 4.0.

Sodium 3-Toluenesulfonate Hydrate (**3b**): **3b** is obtained according to General Procedure II from 1.90 g (5.00 mmol) of **2b** and 0.94 g (5.00 mmol) of **1**. Yield: 0.77 g (73), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3535, 1169, 1047 cm^{-1}. – ^1H NMR (D_2O): δ = 2.35 (s, 3H, CH_3), 7.17–7.58 (m, 4H, CH_{aromat}). – ^{13}C NMR (D_2O): δ = 23.3 (CH_3), 126.2, 128.5, 131.7, 134.9 (all CH), 142.2, 145.1 (all C_q). – $C_7H_7NaO_3S \cdot H_2O$ (212.20): calcd. C 39.62, H 4.27; found C 39.5, H 4.3.

Sodium 4-Methoxyphenylsulfonate Hydrate (**3c**): **3c** is obtained according to General Procedure II from 1.35 g (5.00 mmol) of **2c** and 0.94 g (5.00 mmol) of **1**. Yield: 0.51 g (45), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3460, 1183, 1050 cm^{-1}. – ^1H NMR (D_2O): δ = 3.87 (s, 3H, CH_3), 6.95–7.80 (2 d, 4H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 58.3 (CH_3), 117.0, 130.4 (all CH), 137.8, 164.0 (all C_p). – $C_7H_7NaO_4S \cdot H_2O$ (228.20): calcd. C 36.84, H 3.98; found C 36.1, H 3.8.

Sodium 3-Methoxyphenylsulfonate Hydrate (**3d**): **3d** is obtained according to General Procedure II from 1.35 g (5.00 mmol) of **2d** and 0.94 g (5.00 mmol) of **1**. Yield 0.75 g (66%), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3540, 1169, 1050 cm^{-1}. – ^1H NMR (D_2O): 3.80 (s, 3H, CH_3), 6.83–7.48 (m, 4H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 58.5 (CH_3), 113.8, 120.1, 120.9, 133.2 (CH), 146.7, 161.8 (C_q). – $C_7H_7NaO_4S \cdot H_2O$ (228.20): calcd. C 36.84, H 3.98; found C 36.2, H 3.90.

Sodium 4-Chlorophenylsulfonate Hydrate (**3e**): **3e** is obtained according to General Procedure II from 1.38 g (5.00 mmol) of **2e** and 0.94 g (5.00 mmol) of **1**. Yield: 0.52 g (45%), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3450, 1179, 1042 cm^{-1}. – ^1H NMR (D_2O): 7.40–7.83 (2 d, 4H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 129.9, 130.8 (all CH), 139.7, 140.9 (all C_q). – $C_6H_4ClNaO_3S \cdot H_2O$ (232.61): calcd. C 30.98, H 2.60; found C 29.90, H 2.50.

Sodium 3-Chlorophenylsulfonate Hydrate (**3f**): **3f** is obtained according to General Procedure II from 1.38 g (5.00 mmol) of **2f** and 0.94 g (5.00 mmol) of **1**, yield: 0.72 g (62%); or from 2.00 g (5.00 mmol) of **2g** and 0.94 g (5.00 mmol) of **1**, yield: 0.65 g (56%), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3435, 1196, 1052 cm^{-1}. – ^1H NMR (D_2O): 7.37–7.83 (m, 4H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 126.6, 128.2, 133.5, 135.2 (all CH), 137.0, 146.8 (all C_q). – $C_6H_4ClNaO_3S \cdot H_2O$ (232.61): calcd. C 30.98, H 2.60; found C 30.6, H 2.4.

Sodium 2-Chlorophenylsulfonate Hydrate (**3g**): **3g** is obtained according to General Procedure II from 1.38 g (5.00 mmol) of **2h** and 0.94 g (5.00 mmol) of **1**, yield: 0.71 g (61%); or from 2.00 g (5.00 mmol) of **2i** and 0.94 g (5.00 mmol) of **1**, yield: 0.80 g (69%), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3445, 1139, 1046 cm^{-1}. – ^1H NMR (D_2O): 7.27–8.07 (m, 4H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 130.0, 131.7 (all CH), 133.4 (C_q), 134.2, 135.6 (all CH), 142.4 (all C_q). – $C_6H_4ClNaO_3S \cdot H_2O$ (232.61): calcd. C 30.98, H 2.60; found C 30.5, H 2.7.

Sodium 1-Naphthalenesulfonate Hydrate (**3h**): **3h** is obtained according to General Procedure II from 1.45 g (5.00 mmol) of **2j** and 0.94 g (5.00 mmol) of **1**. Yield: 0.84 g (68%), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3440, 1193, 1024 cm^{-1}. – ^1H NMR (D_2O): δ = 7.20–8.73 (m, 7H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 127.3, 127.7, 128.8, 129.4, 130.4 (all CH), 130.7 (C_q), 131.6, 135.3 (all CH), 136.6, 140.7 (all C_q). – $C_{10}H_7NaO_3S \cdot H_2O$ (248.23): calcd. C 48.39, H 3.65; found C 48.4, H 3.5.

Sodium 9-Anthracenesulfonate Hydrate (**3i**): **3i** is obtained according to General Procedure II from 1.70 g (5.00 mmol) of **2k** and 0.94 g (5.00 mmol) of **1**. Yield: 0.88 g (59%), m.p. >320 °C. – IR (KBr): $\tilde{\nu}$ = 3455, 1184, 1047 cm^{-1}. – ^1H NMR (D_2O): 7.80–8.12 (m, 6H, H_{aromat}), 8.42 (s, 1H, H_{aromat}), 8.91–9.06 (m, 3H, H_{aromat}). – ^{13}C NMR (D_2O): δ = 122.7, 122.8, 125.4, 126.3, 126.5, 127.1, 127.7, 128.1, 128.6, 129.4, 130.3, 130.4 (all CH), 142.2

(C_q). – $C_{14}H_9NaO_3S \cdot H_2O$ (298.29): calcd. C 56.37, H 3.72; found C 56.0, H 3.7.

Sodium 2-Furanesulfonate Hydrate (**5a**): **5a** is obtained according to General Procedure II from 1.78 g (5.00 mmol) of **4a** and 0.94 g (5.00 mmol) of **1**. Yield: 0.82 g (95%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3475, 1224, 1142 cm^{-1}. – ^1H NMR (D_2O): δ = 6.63 (m, 1H, CH), 6.96 (m, 1H, CH), 7.70 (m, 1H, CH). – ^{13}C NMR (D_2O): δ = 113.6, 114.6, 147.6 (all CH), 153.9 (C_q). – $C_4H_3NaO_4S \cdot H_2O$ (188.13): calcd. C 25.54, H 2.68; found C 23.8, H 2.4.

Sodium 2-Thiophenesulfonate Hydrate (**5b**): **5b** is obtained according to General Procedure II from 1.86 g (5.00 mmol) of **4b** and 0.94 g (5.00 mmol) of **1**. Yield: 0.84 g (90%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3520, 1216, 1102 cm^{-1}. – ^1H NMR (D_2O): δ = 7.11 (m, 1H, CH), 7.53 (m, 1H, CH), 7.67 (m, 1H, CH). – ^{13}C NMR (D_2O): δ = 130.0, 131.9, 132.5 (all CH), 146.6 (C_q). – $C_4H_3NaO_3S_2 \cdot H_2O$ (204.19): calcd. C 23.53, H 2.47; found C 23.2, H 2.2.

Sodium 3-Thiophenesulfonate Hydrate (**5c**): **5c** is obtained according to General Procedure II from 0.74 g (2.00 mmol) of **4c** and 0.38 g (2.00 mmol) of **1**. Yield: 0.28 g (76%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3450, 1238, 1189 cm^{-1}. – ^1H NMR (D_2O): δ = 7.41 (m, 1H, CH), 7.60 (m, 1H, CH), 7.96 (m, 1H, CH). – ^{13}C NMR (D_2O): δ = 127.7, 130.1, 131.1 (all CH), 145.3 (C_q). – $C_4H_3NaO_3S_2 \cdot H_2O$ (204.19): calcd. C 23.53, H 2.47; found C 23.9, H 2.3.

Sodium 1-Methylpyrrole-2-sulfonate Hydrate (**5d**): **5d** is obtained according to General Procedure II from 1.85 g (5.00 mmol) of **4d** and 0.94 g (5.00 mmol) of **1**. Yield: 0.64 g (70%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3465, 1184, 1094 cm^{-1}. – ^1H NMR (D_2O): δ = 3.51 (s, 3H, CH_3), 6.23 (m, 1H, CH), 6.60 (m, 1H, CH), 6.99 (m, 1H, CH). – ^{13}C NMR (D_2O): δ = 35.2 (CH_3), 105.4, 122.7, 124.3 (all CH), 125.6 (C_q). – $C_5H_6NNaO_3S \cdot H_2O$ (201.17): calcd. C 29.85, H 4.01, N 6.96; found C 29.5, H 3.8, N 6.4.

Sodium (E)- and (Z)-1-Propenesulfonate Hydrate (**7a**): **7a** is obtained according to General Procedure II from 1.00 g (3.00 mmol) of **6a** and 1.13 g (6.00 mmol) of **1**. Yield: 0.80 g (82%) (60% *E*- and 40% *Z* isomer), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3490, 1639, 1194, 1061 cm^{-1}. – ^1H NMR (D_2O): *E* isomer: δ = 2.05 (dvd, 3H, CH_3, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.5 Hz), 6.28 (sextett, 1H, CH, $^3J_{HH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz), 6.41 (dvd, 1H, CH, $^3J_{HH}$ = 17.0 Hz, $^4J_{HH}$ = 1.5 Hz). *Z* isomer: δ = 1.90 (dvd, 3H, CH_3, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.6 Hz), 6.35 (dvd, 1H, CH, $^3J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz), 6.62 (sextett, 1H, CH, $^3J_{HH}$ = 12.0 Hz). – ^{13}C NMR (D_2O): *E* isomer: δ = 16.4 (CH_3), 133.6, 139.8 (all CH), *Z* isomer δ = 17.0 (CH_3), 133.2, 139.5 (all CH). – $C_3H_5NaO_3S \cdot H_2O$ (186.16): calcd. C 32.26, H 3.79; found C 32.0, H 3.6.

Sodium (E)- and (Z)-1-Methyl-1-propenesulfonate Hydrate (**7b**): **7b** is obtained according to General Procedure II from 1.00 g (3.00 mmol) of **6b** and 1.13 g (6.00 mmol) of **1**. Yield: 0.80 g (71%) (20% *E* and 80% *Z* isomer), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3540, 1626, 1202, 1051 cm^{-1}. – ^1H NMR (D_2O): *E* isomer: δ = 2.82 (d, 3H, CH_3, $^3J_{HH}$ = 8.0 Hz), 2.85 (s, 3H, CH_3), 5.41 (q, 1H, CH, $^3J_{HH}$ = 8.0 Hz), *Z* isomer: δ = 2.96 (d, 3H, CH_3, $^3J_{HH}$ = 7.0 Hz), 2.85 (s, 3H, CH_3), 5.41 (q, 1H, CH, $^3J_{HH}$ = 7.0 Hz). – ^{13}C NMR (D_2O): *E* isomer: δ = 12.4, 14.0 (all CH_3), 130.9 (CH), 138.6 (C_q), *Z* isomer δ = 15.6, 21.6 (all CH_3), 132.4 (CH), 138.2 (C_q). – $C_4H_7NaO_3S \cdot H_2O$ (176.16): calcd. C 27.27, H 5.15; found C 26.8, H 4.9.

Sodium 1-Cyclopentenesulfonate Hydrate (**7c**): **7c** is obtained according to General Procedure II from 1.18 g (3.00 mmol) of **6c** and 1.13 g (3.00 mmol) of **1**. Yield: 0.90 g (90%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3475, 1638, 1219, 1039 cm^{-1}. – ^1H NMR (D_2O): δ = 1.94 (m, 2H, CH_2), 2.39 (m, 2H, $CH_{2,allylic}$), 2.51 (m, 2H, $CH_{2,allylic}$), 6.28 (s, 1H, CH). – ^{13}C NMR (D_2O): δ = 26.3, 34.0, 34.9 (all CH_2), 139.8 (CH), 140.0 (C_q). – $C_5H_7NaO_3S \cdot H_2O$ (188.17): calcd. C 31.91, H 4.82; found C 31.0, H 4.7.

Sodium 1-Cyclohexenesulfonate Hydrate (**7d**): **7d** is obtained according to General Procedure II from 1.20 g (3.00 mmol) of **6d** and 1.13 g (3.00 mmol) of **1**. Yield: 1.10 g (76%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3450, 1631, 1202, 1052 cm^{-1}. – ^1H NMR (D_2O): δ = 1.52 (m, 4H, CH_2), 2.11 (m, 2H, $CH_{2,allylic}$), 6.40 (m, 1H, CH). – ^{13}C NMR (D_2O): δ = 22.2, 23.1, 24.7, 25.9 (all CH_2), 133.1 (CH), 140.9 (C_q). – $C_6H_9NaO_3S \cdot H_2O$ (202.20): calcd. C 35.64, H 5.48; found C 35.4, H 5.4.

Sodium 1-Cyclooctenesulfonate Hydrate (**7e**): **7e** is obtained according to General Procedure II from 1.40 g (3.00 mol) of **6e** and 1.13 g (3.00 mmol) of **1**. Yield: 1.18 g (88%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3450, 1639, 1202, 1052 cm^{-1}. – ^1H NMR (D_2O): δ = 1.45 (m, 8H, CH_2), 2.11 (m, 2H, $CH_{2,allylic}$), 2.36 (m, 2H, $CH_{2,allylic}$), 6.42 (t, 1H, CH, $^3J_{HH}$ = 8.0 Hz). – $C_8H_{13}NaO_3S \cdot H_2O$ (230.25): calcd. C 41.73, H 6.57; found C 41.3, H 6.4.

Sodium 1-Phenylethenylsulfonate Hydrate (**7f**): **7f** is obtained according to General Procedure II from 2.20 g (5.00 mmol) of **6f** and 1.88 g (10.0 mmol) of **1**. Yield: 1.34 g (65%), m.p. 191/192°C. – IR (KBr): $\tilde{\nu}$ = 3450, 1630, 1196, 1060, 759, 698 cm^{-1}. – ^1H NMR (D_2O): δ = 5.66 (d, 1H, $^2J_{HH}$ = 2.5 Hz), 6.05 (d, 1H, CH, $^2J_{HH}$ = 2.5 Hz), 7.32 (m, 5H, $H_{aromatic}$). – ^{13}C NMR (D_2O): δ = 79.4 (CH_2), 137.6, 138.1, 138.4 (all $CH_{aromatic}$), 138.6 ($C_{q,aromatic}$), 140.3 (C_q). – $C_8H_7NaO_3S \cdot H_2O$ (224.21): calcd. C 42.86, H 4.05; found C 42.3, H 3.8.

Sodium 2-Phenyl-1-ethynylsulfonate Hydrate (**9a**): **9a** is obtained according to General Procedure II from 1.32 g (5.00 mmol) of **8a** and 0.94 g (5.00 mmol) of **1**. Yield: 0.92 g (90%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3460, 2210, 1256, 1059, 751, 680 cm^{-1}. – ^1H NMR (D_2O): δ = 7.38 (m, 5H, $H_{aromatic}$). – ^{13}C NMR (D_2O): δ = 84.2 (C_q), 86.7 (C_q), 116.1, 121.3, 131.5 (all CH), 152.3 ($C_{q,aromatic}$). – $C_8H_5NaO_3S \cdot H_2O$ (222.19): calcd. C 43.25, H 3.18; found C 43.0, H 3.3.

Sodium 3-Methoxy-1-propynylsulfonate Hydrate (**9b**): **9b** is obtained according to General Procedure II from 1.42 g (6.10 mmol) of **8b** and 1.15 g (6.10 mmol) of **1**, yield: 0.86 g (83%); or from 1.66 g (4.60 mmol) of **8c** and 1.07 g (4.60 mmol) of **1**, yield: 0.53 g (67%); m.p. 193/194°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3455, 2220, 1223, 1070, 1016 cm^{-1}. – ^1H NMR (D_2O): δ = 3.35 (s, 3H, CH_3), 4.23 (s, 2H, CH_2). – ^{13}C NMR (D_2O): δ = 60.9 (CH_3), 62.0 (CH_2), 83.4 (C_q), 86.4 (C_q). – $C_4H_5NaO_4S \cdot H_2O$ (190.15): calcd. C 25.27, H 3.71; found C 25.4, H 3.5.

Sodium 3-Phenoxy-1-propynylsulfonate Hydrate (**9c**): **9c** is obtained according to General Procedure II from 1.76 g (6.00 mmol) of **8d** and 1.13 g (6.00 mmol) of **1**. Yield: 1.11 g (79%), m.p. 199°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3470, 2225, 1202, 1059, 755, 695 cm^{-1}. – ^1H NMR (D_2O): δ = 4.62 (s, 2H, CH_2), 7.00 (m, 5H, $H_{aromatic}$). – ^{13}C NMR (D_2O): δ = 52.0 (CH_2), 80.7 (C_q), 85.3 (C_q), 116.5, 123.9, 131.3 (all CH), 158.1 (C_q). – $C_9H_7NaO_4S \cdot H_2O$ (252.22): calcd. C 42.86, H 3.60; found C 42.3, H 3.4.

Sodium Butylsulfonate Hydrate (**11**): **11** is obtained according to General Procedure II from 1.07 g (3.00 mmol) of tetrabutylstannane and 2.26 g (12.0 mmol) of **1**. Yield: 0.33 g (69%), m.p. >320°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3450, 1205, 1189 cm^{-1}. – ^1H NMR (D_2O): δ = 0.94 (t, 3H, CH_3, $^3J_{HH}$ = 7.2 Hz), 1.48 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 2.95 (t, 2H, CH_2, $^3J_{HH}$ = 5.8 Hz). – ^{13}C NMR (D_2O): δ = 15.7 (CH_3), 23.9, 28.9, 53.6 (all CH_2).

Sodium (E)-2-(Trimethylsilyl)ethenylsulfonate Hydrate (**14**): **14** is obtained according to General Procedure II from 1.72 g (4.00 mmol) of **13** and 1.51 g (8.00 mmol) of **1**. Yield: 1.22 g (88%), m.p. >320°C (decomp.). – IR (KBr): $\tilde{\nu}$ = 3495, 1617, 1227, 1044 cm^{-1}. – ^1H NMR (D_2O): δ = −0.01 (s, 9H, $SiMe_3$, $^2J_{SiH}$ = 43.4 Hz), 6.52 (d, 1H, CH, $^3J_{HH}$ = 18.4 Hz), 6.64 (d, 1H, CH, $^3J_{HH}$ = 18.4 Hz). – ^{13}C NMR (D_2O): δ = 0.0 (CH_3, $^1J_{SiC}$ = 46 Hz), 142.3 (CH, $^1J_{SiC}$ = 41 Hz), 143.8 (CH, $^2J_{SiC}$ = 13 Hz). – ^{29}Si NMR (D_2O): δ = −2.6. – $C_5H_{11}NaSSiO_3 \cdot H_2O$ (220.29): calcd. C 27.26, H 5.95; found C 27.0, H 6.2.

Sodium Sulfonates. – General Procedure III: The aryl bromide is added to a solution of magnesium in 10 ml of anhydrous ether and the mixture heated under reflux for 2 h. After adding a solution of trimethyltin chloride in 5 ml of anhydrous ether the mixture is heated for a further 2 h under reflux. After removal of the solvent 10 ml of anhydrous CCl_4 and **1** are added. After 1 h stirring at room temperature the reaction mixture is hydrolyzed with 30 ml of a saturated $NaHCO_3$ solution and stirred for 30 min. The layers are separated and the aqueous layer is washed three times with 10 ml of ether. The water is removed in vacuo and the solid residue digested with 100 ml of boiling ethanol and filtered off. The ethanol is evaporated in vacuo and the residue washed twice with *n*-pentane and dried in vacuo at 80°C.

Sodium 3-Toluenesulfonate Hydrate (**3b**): From 0.85 g (5.00 mmol) of 3-bromotoluene, 0.12 g (5.00 mmol) of magnesium and 0.94 g (5.00 mmol) of **1**. Yield: 0.16 g (15%) of **3b** is obtained according to General Procedure III, m.p. >320°C.

Sodium 3-Methoxyphenylsulfonate Hydrate (**3d**): From 0.93 g (5.00 mmol) of 3-bromomethoxybenzene, 0.12 g (5.00 mmol) of magnesium, 0.99 g (5.00 mmol) of Me_3SnCl, and 0.94 g (5.00 mmol) of **1**. Yield: 0.70 (62%) of **3d** is obtained according to General Procedure III, m.p. >320°C.

Sodium 3-Chlorophenylsulfonate Hydrate (**3f**): From 0.96 g (5.00 mmol) of 3-bromochlorobenzene, 0.12 g (5.00 mmol) of magnesium, 0.99 g (5.00 mmol) of Me_3SnCl, and 0.94 g (5.00 mmol) of **1**. Yield: 0.70 (60%) of **3f** is obtained according to General Procedure III, m.p. >320°C.

Sodium 3-Toluenesulfonate Hydrate (**3b**): From 0.85 g (5.00 mmol) of 3-bromotoluene, 0.12 g (5.00 mmol) of magnesium, 0.99 g (5.00 mmol) of Me_3SnCl, and 0.94 g (5.00 mmol) of **1**. Yield: 0.80 (76%) of **3b** is obtained according to General Procedure III, m.p. >320°C.

Sodium Sulfonate of the N-Substituted Apocodeine (**17**): A solution of 1.34 g (3.40 mmol) of **15**, 0.48 g (8.50 mmol) of KOH, and 1.07 g (8.50 mmol) of dimethyl sulfate in 25 ml ethanol is heated under reflux for 8 h. After hydrolysis and extraction of the aqueous layer with ether, the organic layer is dried with $MgSO_4$ and the solvent is evaporated. From **16**, 0.08 g (3.40 mmol) of magnesium, 0.68 g (3.40 mmol) of Me_3SnCl, and 0.53 g (3.40 mmol) of **1** 0.45 g (46%) of **17** is obtained according to General Procedure III, m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3450, 1157, 1047 cm^{-1}. – ^1H NMR (D_2O): δ = 3.13 (s, 3H, NCH_3), 3.39 (s, 3H, OCH_3), 3.72–3.90 (m, 7H, CH, CH_2), 6.90–7.04 (m, 2H, $H_{aromatic}$), 7.39 (d, 1H, $H_{aromatic}$), 7.84 (d, 1H, $H_{aromatic}$). – ^{13}C NMR (D_2O): δ = 25.4, 30.4 (CH_2), 55.8, 57.5, 57.8 (CH_3), 63.2 (CH_2), 115.1, 126.5, 131.3, 132.9 (CH), 124.3, 126.1, 126.9, 128.1, 135.2, 144.7, 154.1 (C_q). – $C_{19}H_{20}NaNO_3S \cdot 5\ H_2O$ (487.50): calcd. C 46.81, H 6.20, N 2.87; found C 46.7, H 6.1, N 2.5.

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