New Synthesis of Pyrrolidines *via* Reaction of γ-Halocarbanions with Imines

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Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

γ-Chlorocarbanions of proper nucleophilicity, generated from 3-chloropropyl pentachlorophenyl sulfone (= pentachloro[(3-chloropropyl)sulfonyl]benzene; **1**; Ar = C_6Cl_5), add to electron-deficient formal imines **3a**–**l** to produce anionic adducts that enter intramolecular substitution leading to substituted pyrrolidines. This new and simple synthesis of pyrrolidines mimics a 1,3-dipolar cycloaddition, although it proceeds in two distinct steps.

Substituted pyrrolidine rings are present in numerous alkaloids, pharmaceuticals, plant protecting agents [1], ligands of transition metal catalysts [2], *etc.*, thus, general methods for the synthesis of this ring system are of great interest and demands. There are many routes leading to substituted pyrrolidine rings, based on cationic cyclizations, mainly *via* iminium ions [3], cyclization proceeding *via* free radicals [4], dipolar cycloadditions [5], reactions proceeding *via* carbanions [6], *etc.*

Of particular value and interest is the construction of pyrrolidine and other five-membered heterocyclic rings *via* 1,3-dipolar cycloaddition proceeding according to the concept created and pioneered by *Huisgen* and co-workers [7]. *Huisgen* also formulated basic structural elements of 1,3-dipoles and general mechanistic features of this process [8]. Addition of readily generated azomethine ylides (= iminium ylides) to alkenes is a general route to pyrrolidines [5].

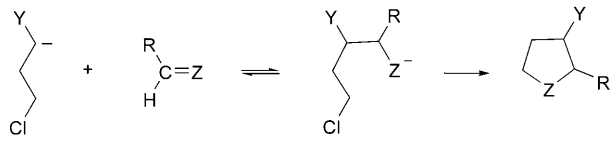
In this paper, we report a simple and efficient protocol of the synthesis of the pyrrolidine ring *via* reactions of γ-halocarbanions with formal imines, that to some extent mimic 1,3-dipolar cycloaddition.

Known reactions of γ-halocarbanions are limited to intramolecular substitution of the halogen atom leading to three-membered rings. Synthesis of cyclopropanes *via* alkylation of 'methylenic' carbanions with 1,2-dihaloalkanes [9] and *via* addition of α-halocarbanions to *Michael* acceptors [10] proceeds *via* intermediate formation of γ-halocarbanions. They are also intermediates in the *Ramberg–Bäcklund* [11] and *Favorski* reactions [12]. Due to the high rate of the intramolecular substitution promoted by the proximity effect, intermolecular reactions of γ-halocarbanions are observed only when structural features decelerate [13] or hinder the intramolecular reaction [14].

On the other hand, γ-halocarbanions containing an electron-deficient C-atom connected to the halogen atom and the nucleophilic carbanion center in a 1,3 relation-

ship can be considered as analogues of 1,3-dipoles, and upon addition to polar double bonds, followed by 1,5-intramolecular substitution, they should form five-membered rings (*Scheme 1*). This reaction shall proceed *via* two distinct time-separated steps.

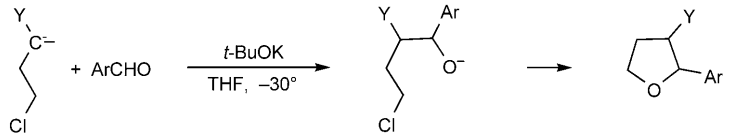
Scheme 1



Z = O, N–R', CH–EWG

Indeed, we have shown recently that γ-halocarbanions generated *via* deprotonation of 3-chloropropyl phenyl sulfone (= [(3-chloropropyl)sulfonyl]benzene), 4-chlorobutanenitrile, and *t*-butyl 4-chlorobutanoate, in spite of very fast intramolecular substitution leading to the corresponding cyclopropanes, can be trapped by active external electrophiles such as aldehydes and ketones. The produced aldol-type anions enter intramolecular substitution to give substituted tetrahydrofurans [15] (*Scheme 2*).

Scheme 2



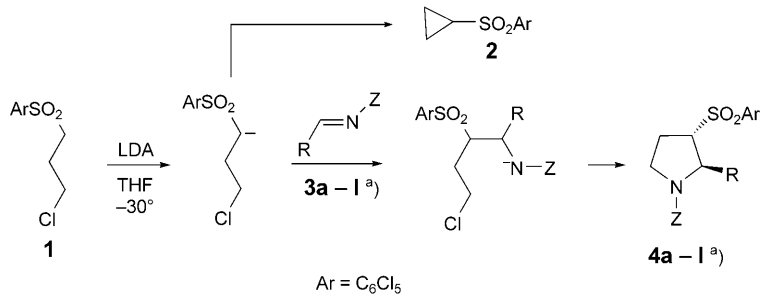
Y = $PhSO_2$, CN, *t*-BuOCO

Our attempts to extend reactions of these γ-halocarbanions to other electrophilic partners containing electron-deficient double bonds, *i.e.*, *Michael* acceptors and imines that should lead to cyclopentanes and pyrrolidines, was initially unsuccessful. Treatment of mixtures of some of these electrophilic partners and the carbanion precursors, shown in *Scheme 2*, with the base gave only cyclopropanes, whereas electrophiles decomposed or polymerized. Obviously, the intramolecular substitution in the γ-halocarbanions was faster than the addition to these moderately active electrophiles. This problem for the reaction with *Michael* acceptors was solved by tuning the acidity of the γ-halocarbanion precursor. We found that carbanions of pentachlorophenyl 3-chloropropyl sulfone (= pentachloro[(3-chloropropyl)sulfonyl]benzene; **1**) are less nucleophilic than the corresponding phenyl sulfone, hence, their lifetimes are sufficiently long for addition to a variety of *Michael* acceptors. Subsequent intramolecular substitution in the anionic adducts results in the formation of substituted cyclopentanes [16].

In spite of the extended lifetimes of carbanions of **1**, the base-promoted reaction of **1** with a simple formal imine, *i.e.*, *N*-benzylideneaniline, gave only (arylsulfonyl)cyclopropane **2**, which is the product of the intramolecular substitution (*Scheme 3*). On the other hand, in the reaction of **1** with the more-electrophilic *N*-tosyl-substituted formal imine **3a**, an *N*-benzylidenesulfonamide, the expected [(3-pentachlorophenyl)-

sulfonyl]-2-phenyl-1-tosyl pyrrolidine (**4a**) was obtained. (Arylsulfonyl)cyclopropane **2** was formed as a minor side product.

Scheme 3



a) For **a**–**l**, see the *Table*.

N-Tosyl-substituted formal imines derived from other aromatic aldehydes, cinnamaldehyde, and pivalaldehyde reacted similarly giving the expected substituted 1-tosylpyrrolidines usually in good yield (*Table*). In all experiments, minor amounts of the cyclopropane **2** were formed.

Table. *Synthesis of Pyrrolidines by the Reaction of Carbanions of* **1** *with Electron-Deficient Imines* (see *Scheme 3*)

Imine	R	Z	Pyrrolidines	Yield [%]	Yield of **2** [%]
3a	Ph	Tol SO_2	**4a**	75	5
3b	4-Me–C_6H_4	Tol SO_2	**4b**	73	9
3c	4-Cl–C_6H_4	Tol SO_2	**4c**	54	10
3d	3-CF_3–C_6H_4	Tol SO_2	**4d**	72	5
3e	PhCH=CH	Tol SO_2	**4e**	60	16
3f	2-furyl	Tol SO_2	**4f**	63	8
3g	*t*-Bu	Tol SO_2	**4g**	52	12
3h	Ph	EtOCO	**4h**	45	a)
3i	Ph	$(EtO)_2PO$	**4i**	68	a)
3j	4-Me–C_6H_4	$(EtO)_2PO$	**4j**	75	a)
3k	Ph	PhSO	**4k**	4	a)
3l	Ph	4-Cl–C_6H_4–SO	**4l**	42	a)

a) Not determined.

Arenemethanimines R–CH=NH activated by substitution at the N-atom with some other electron-accepting groups, such as diethoxyphosphoryl and ethoxycarbonyl (see **3h**–**j**), are also sufficiently active electrophiles to trap the carbanion of **1** and subsequently produce substituted 1-(ethoxycarbonyl)- and 1-(diethoxyphosphoryl)-pyrrolidines. Of particular interest in this reaction should be *N*-benzylidenebenzenesulfinamide (**3k**) because phenylsulfinyl- and alkylsulfinyl-substituted compounds can be readily obtained in enantiomerically pure form and are known to be efficient chiral auxiliaries [17]. The benzenesulfinamide **3k** was, however, an insufficiently active electrophile, and in the reaction with the carbanion of **1**, the expected pyrrolidine **4k**

was formed only in minute amounts (see *Table*), the major process being cyclopropane formation. This problem was solved simply by use of the 4-chlorobenzenesulfinamide **3l** that shows a stronger electron-accepting character. Thus the base-promoted reaction of **1** with **3l** gave the expected pyrrolidine **4l** in acceptable yield (see *Table*).

All pyrrolidines obtained according to *Scheme 3* were formed as single diastereoisomers in which the substituent R and the (pentachlorophenyl)sulfonyl group were in *trans* relationship. It should be mentioned that the yields of the pyrrolidines given in the *Table* are not optimized, and the reactions were carried out under standard conditions. From these results, we can conclude that the reaction of γ-halocarbanions of properly tuned nucleophilicity with electron-deficient imines is an efficient and simple new synthesis of functionalized pyrrolidines. Taking into account the facile desulfonylation as well as the formation of sulfonyl-substituted carbanions, these products are attractive for further reactions. For example, in the reaction of pyrrolidine **4b** with ethyl iodoacetate, the product of alkylation is formed in 80% yield, offering rather wide synthetic possibilities. In this connection, an interesting synthesis of pyrrolidines should be mentioned, which proceeds *via* reactions of γ-iodoenolates ($ICH_2CH_2CH{=}C(R){-}O^-$) generated *in situ* by treatment of acylcyclopropanes with MgI_2 or Et_2AlI [18]. Although γ-iodoenolates cyclize rapidly, this is a reversible process, whereas addition to formal imines followed by cyclization to pyrrolidines proceeds irreversibly.

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Experimental Part

General. Pentachlorophenyl 3-chloropropyl sulfone was obtained as described earlier [16]. *N*-Substituted imines **3a**–**l** were synthesized according to literature procedures, *i.e.*, **3a**–**g** [19], **3h** [20], **3i**,**j** [21], **3k**,**l** [22]. Lithium diisopropylamide (LDA) was purchased from *Aldrich*. All reactions were performed in oven-dried glassware under dry Ar. THF was freshly distilled from K/benzophenone. Column chromatography and prep. TLC: *Merck* silica gel *60* and silica gel *60* PF_{254} resp. M.p.: uncorrected. ^{1}H- and ^{13}C-NMR Spectra: *Varian Gemini-200-MHz* and *Varian Mercury-400-MHz* spectrometer; δ in ppm, *J* in Hz. HR-MS: *AMD-604* instrument; in *m/z*.

Reaction of [Pentachloro[(3-chloropropyl)sulfanoyl]benzene (**1**) *with Substituted Imines, Synthesis of* **4a**–**4**: *General Procedure*. To a soln. of **1** (117 mg, 0.3 mmol) and *N*-tosyl-substituted arenemethanimine, (0.4 mmol) in THF (5 ml) at $-30°$, 1.8M LDA (0.27 ml, 0.5 mmol) was added. The mixture was stirred for 5 min, warmed to r.t., quenched with aq. NH_4Cl soln., and extracted and the product purified by CC or prep. TLC (hexane/AcOEt).

Procedure for the Synthesis of **4h**: To a soln. of **1** (117 mg, 0.3 mmol) in THF (5 ml) at $-70°$ 1.8M LDA (0.27 ml, 0.5 mmol) was added. After 2 s, ethyl benzylidenecarbamate (**3h**; 70.8 mg, 0.4 mmol) in THF (0.5 ml) was added, then the procedure as above was followed.

3-[(Pentachlorophenyl)sulfonyl]-2-phenyl-1-tosylpyrrolidine (**4a**): M.p. 164° ($CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.25–2.41 (*m*, 2 H); 2.43 (*s*, 3 H); 3.76 (*dt*, ^3J(H,H) = 2.20, 6.78, 1 H); 4.30–4.35 (*m*, 2 H); 5.02 (*d*, ^3J(H,H) = 5.50, 1 H); 7.10–7.62 (m, 9 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.58; 24.57; 48.44; 63.03; 70.62; 126.38; 127.75; 127.84; 128.02; 128.19; 128.50; 128.66; 129.65; 129.73; 133.81; 134.06; 134.34; 135.06; 139.21; 139.38; 143.94. HR-EI-MS 610.91177 ($C_{23}H_{18}Cl_5NO_4S_2^+$; calc. 610.91199).

2-(4-Methylphenyl)-3-[(pentachlorophenyl)sulfonyl]-1-tosylpyrrolidine (**4b**): M.p. 173° (EtOH). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.27 (*s*, 3 H); 2.28–2.41 (*m*, 2 H); 2.43 (*s*, 3 H); 3.72–3.76 (*m*, 2 H); 3.32–4.39 (*m*, 1 H); 4.86 (*d*, ^3J(H,H) = 6.32, 1 H); 6.95 (*s*, 4 H); 7.26–7.59 (*m*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.02; 21.55; 24.23; 48.30; 63.12; 70.13; 126.37; 126.42; 127.69; 128.99; 129.59; 129.67; 133.68; 134.07; 134.28; 134.96; 135.69; 138.33; 139.26; 143.87. Anal. calc. for $C_{24}H_{20}Cl_5NO_4S_2$ (627.81): C 45.92, H 3.21, N 2.23, S 10.21; found: C 45.91, H 3.43, N 2.38, S 10.23.

2-(4-Chlorophenyl)-3-[(pentachlorophenyl)sulfonyl]-1-tosylpyrrolidine (**4c**): Oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.23–2.36 (*m*, 2 H); 2.44 (*s*, 3 H); 3.68–3.79 (*m*, 2 H); 4.21–4.26 (*m*, 1 H); 5.02 (*d*, ^3J(H,H) = 5.22, 1 H); 7.10–7.72 (*m*, 8 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.56; 24.73; 48.38; 62.15; 70.55; 133.59; 133.66; 133.74; 134.16; 134.22; 134.30; 134.88; 135.12; 136.73; 137.99; 139.59; 141.28; 143.56; 144.18. HR-ESI-MS: 667.8657 ($C_{23}H_{17}Cl_5NNaO_4S_2^+$ [M + Na]$^+$; calc. 667.8622).

3-[(Pentachlorophenyl)sulfonyl]-2-[3-(trifluoromethyl)phenyl]-1-tosylpyrrolidine (**4d**): M.p. 103° (EtOH). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.29–2.41 (*m*, 2 H); 2.43 (*s*, 3 H); 3.77–3.82 (*m*, 2 H); 4.25 (*dt*, ^3J(H,H) = 5.37, 7.02, 1 H); 5.15 (*d*, ^3J(H,H) = 5.22, 1 H); 7.27–7.81 (*m*, 8 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.55; 24.82; 48.62; 62.28; 70.76; 122.91;126.36; 127.00; 127.70; 129.21; 129.61; 129.72; 129.76; 130.19; 133.78; 134.18; 135.24; 139.73; 140.60; 144.35. HR-ESI-MS: 679.9054 ($C_{24}H_{18}Cl_5FNO_4S_2^+$, [$M$ + H]$^+$; calc. 679.9067).

3-[(Pentachlorophenyl)sulfonyl]-2-(2-phenylethenyl)-1-tosylpyrrolidine (**4e**): M.p. 180° (dec.; EtOH). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.25 (*m*, 2 H); 2.42 (*s*, 3 H); 3.57–3.67 (*m*, 2 H); 4.20–4.25 (*m*, 1 H); 4.48–4.52 (*m*, 1 H); 5.84 (*dd*, ^3J(H,H) = 8.26, 15.59, 1 H); 6.20 (*d*, ^3J(H,H) = 15.77, 1 H); 7.09–7.71 (*m*, 9 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.55; 24.26; 47.79; 62.13; 67.87; 125.67; 125.99; 126.37; 127.85; 128.48; 128.60; 129.75; 133.44; 133.81; 134.31; 134.79; 135.18; 139.68; 144.08. HR-ESI-MS, 659.9167 ($C_{25}H_{20}Cl_5NNaO_4S_2^+$ [M + Na]$^+$; found 659.9169)

2-Furan-2-yl-3-[(pentachlorophenyl)sulfonyl]-1-tosylpyrrolidine (**4f**): M.p. 166° (EtOH). ^{1}H-NMR (200 MHz, $CDCl_3$): 2.29–2.41 (*m*, 2 H); 2.42 (*s*, 3 H); 3.56–3.65 (*m*, 1 H); 3.37–3.81 (*m*, 1 H); 4.62 (*dt*, ^3J(H,H) = 6.33, 7.70, 1 H); 5.15 (*d*, ^3J(H,H) = 6.19, 1 H); 6.13 (*dd*, ^3J(H,H) = 1.78, 3.30, 1 H); 6.14–6.16 (*m*, 1 H); 7.09–7.12 (*m*, 1 H); 7.28 (*d*, ^3J(H,H) = 7.96, 2 H); 7.58 (*d*, ^3J(H,H) = 8.24, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.55; 24.69; 47.71; 56.58; 66.93; 109.55; 110.36; 127.48; 129.59; 129.66; 133.87; 134.52; 135.00; 139.34; 142.77; 143.87; 149.99. Anal. calc. for $C_{21}H_{16}Cl_5NO_5S_2$ (603.75): C 41.78, H 2.67, N 2.32, S 10.62; found: C 41.96, H 2.50, N 2.33, S 10.75.

*2-(*tert*-Butyl)-3-[(pentachlorophenyl)sulfonyl]-1-tosylpyrrolidine* (**4g**): M.p. 217° (EtOH). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.06 (*s*, 9 H); 1.70–1.78 (*m*, 1 H); 1.81–1.91 (*m*, 1 H); 2.45 (*s*, 3 H); 3.26 (*ddd*, ^3J(H,H) = 6.33, 10.45, 12.38, 1 H); 3.70–3.76 (*m*, 1 H); 4.25 (*dt*, ^3J(H,H) = 4.13, 8.66, 1 H); 4.56 (*d*, ^3J(H,H) = 3.98, 1 H); 7.33 (*d*, ^3J(H,H) = 7.98, 2 H); 7.85 (*d*, ^3J(H,H) = 8.25, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 21.54; 27.29; 28.10; 36.89; 48.25; 65.18; 67.94; 128.66; 129.54; 133.77; 135.09; 135.52; 135.73; 138.20; 143.65. Anal. calc. for $C_{21}H_{22}Cl_5NO_4S_2$ (593.79): C 42.48, H 3.73, N 2.36, S 10.80; found: C 42.48, H 3.72, N 2.36, S 10.72.

Ethyl 3-[(Pentachlorophenyl)sulfonyl]-2-phenylpyrrolidine-1-carboxylate (**4h**): M.p. 204° ($CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.15 (*t*, ^3J(H,H) = 7.17, 3 H); 2.60–2.67 (*m*, 1 H); 2.97–3.11 (*m*, 1 H); 4.14 (*q*, ^3J(H,H) = 7.02, 2 H); 4.54 (*ddd*, ^3J(H,H) = 6.56, 8.54, 10.52, 1 H); 4.64–4.73 (*m*, 2 H); 4.97 (*dt*, ^3J(H,H) = 1.67, 8.69, 1 H); 7.25–7.38 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.44; 26.79; 62.70; 64.45; 73.85; 128.75; 129.45; 131.92; 132.27; 133.18; 133.61; 134.74; 136.42; 137.22; 154.34. HR-ESI-MS: 551.9112 ($C_{19}H_{16}Cl_5NNaO_4S^+$ [M + Na]$^+$; calc. 551.9135).

Diethyl {3-[(Pentachlorophenyl)sulfonyl]-2-phenylpyrrolidin-1-yl}phosphonate (**4i**): Oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.01 (*dt*, ^3J(H,H) = 0.91, 7.02, 3 H); 1.31 (*dt*, ^3J(H,H) = 0.76, 7.02, 3 H); 2.38–2.45 (*m*, 1 H); 2.52–2.61 (*m*, 1 H); 3.59–3.69 (*m*, 2 H); 3.82–3.94 (*m*, 2 H); 3.98–4.05 (*m*, 2 H); 4.36–4.41 (*m*, 1 H); 5.11 (*t*, ^3J(H,H) = 5.19, 1 H); 7.11–7.24 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.68; 15.76; 16.12; 16.18; 25.89; 25.96; 47.69; 47.74; 62.25; 62.31; 62.33; 62.39; 62.52; 62.58; 71.25; 71.35; 126.19; 127.87; 128.40; 133.88; 134.81; 135.05; 139.20; 140.97. HR-ESI-MS: 593.9381 ($C_{20}H_{22}Cl_5NO_5PS^+$, M^+; calc. 593.9393).

Diethyl {2-(4-Methylphenyl)-3-[(pentachlorophenyl)sulfonyl]pyrrolidin-1-yl}phosphonate (**4j**): M.p. 126° (EtOH). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.00 (*dt*, ^3J(H,H) = 0.83, 7.01, 3 H); 1.30 (*dt*, ^3J(H,H) = 0.69, 7.01, 3 H); 2.27 (*s*, 3 H); 2.38–2.46 (*m*, 1 H); 2.53–2.61 (*m*, 1 H); 3.57–3.66 (*m*, 2 H); 3.80–3.93 (*m*, 2 H); 3.95–4.02 (*m*, 2 H); 4.41 (*dt*, ^3J(H,H) = 5.77, 7.43, 1 H); 4.97 (*t*, ^3J(H,H) = 5.50, 1 H); 6.95–7.00 (*m*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 15.67; 15.75; 16.11; 16.18; 20.97; 25.71; 25.78; 47.60; 47.65; 62.22; 62.28; 62.41; 62.47; 70.89; 70.98; 126.25; 128.91; 133.80; 134.76; 134.97; 137.57; 137.88; 139.10. Anal calc. for $C_{21}H_{23}Cl_5NO_5PS$ (609.72): C 41.37, H 3.80, N 2.30, S 5.26; found: C 41.48, H 3.92, N 2.30, S 5.47.

1-(4-Chlorophenylsulfinyl)-3-[(pentachlorophenyl)sulfonyl]-2-phenylpyrrolidine (**4l**): M.p. 165° (dec.; EtOH). ^{1}H-NMR (200 MHz, $CDCl_3$): 2.65–2.98 (*m*, 2 H); 3.59 (*ddd*, ^3J(H,H) = 5.38, 7.91, 10.91, 1 H); 3.79–3.91 (*m*, 1 H); 4.54–4.66 (*m*, 1 H); 5.84 (*d*, ^3J(H,H) = 7.91, 1 H); 6.94–7.57 (*m*, 9 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 25.61; 47.62; 62.27; 69.42; 120.46; 127.15; 127.25; 127.49; 128.11; 128.16; 128.67; 129.02; 136.98; 137.12; 140.92. HR-ESI-MS: 637.8532 ($C_{22}H_{15}Cl_6NNaO_3S_2^+$, [$M$ + Na]$^+$; calc. 637.8517).

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