Supporting Information

for

Derivatives of tribromomethyl phenyl sulfone

as novel compounds with potential pesticidal activity

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1. General methods

All reactions were set up in air, and undistilled solvents were used, unless stated otherwise. The reagents were purchased from commercial sources and were used without further purification except for Et₃N, which was distilled from potassium hydroxide prior to use. The reported yields refer to pure isolated products, unless stated otherwise. Reactions were monitored by gas chromatography (GC) and/or thin-layer chromatography (TLC) carried out on silica-gel plates by using UV light or p-anisaldehyde solution and heat as visualizing agents. ¹H NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer in CDCl₃, using TMS (tetramethylsilane) as an internal standard; all signals are reported in ppm as (s = singlet, dd = doublet of doublets, m = multiplet, integration). IR spectra were recorded in paraffin oil on a Specord M80 Zeiss Jena spectrophotometer and reported with interpretation of significant bands. Elemental analyses were obtained by means of a Perkin Elmer 2400 apparatus. All melting points (mp) are given uncorrected.

2. Experimental procedures

2-(4-Chlorophenylthio)acetic acid (3)
(Method A)

To a stirred solution of 50% w/w aq NaOH (10.9 mL) and 4-chlorothiophenol (46.0 g, 0.32 mol) sodium chloroacetate (prepared by neutralization of chloroacetic acid (30.2 g, 0.32 mol) with 50% w/w aq NaOH) was added. The mixture was heated under reflux for 2 h. After cooling of the mixture, the precipitate was filtered off, washed with 10% w/w aq NaOH saturated with sodium chloride, then dissolved in hot water and acidified with hydrochloric acid. The resulting precipitate was filtered off, washed with cold water and dried. Product 3 was obtained in 75% yield (48.0 g, 0.24 mol); mp 99–100 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.96 (m, 2H), 7.68–7.62 (m, 2H), 3.24 (s, 2H).
1-Chlorophenyl-4-tribromomethylsulfone (1)  
(Method A)

To 2-(4-chlorophenylthio)acetic acid (3) (10.2 g, 0.05 mol) dissolved in 0.5 M aq NaOH (150 mL), freshly prepared 14% w/w aq sodium hypobromite (250 mL) was added. The solution was stirred at room temperature for 80 hours. The resulting precipitate was filtered off, washed with water, dried and recrystallized from ethanol. Sulfone 1 was obtained in 76% yield (16.2 g, 0.038 mol); mp 144–145 °C; IR ν: 1590 (CHAr), 1360, 1155 (SO2), 550 (CBr3) cm⁻¹; ¹H NMR (400 MHz, CDCl3) δ 8.12–7.98 (m, 2H), 7.87–7.70 (m, 2H).

4-Chlorophenylmethyl sulfide (5)  
(Method B and C)

To a stirred solution of 4-chlorothiophenol (2) (14.2 g, 98.6 mmol) in 10% w/w aq NaOH (49.5 mL) dimethyl sulfate (25.0 g, 0.198 mol) was slowly added dropwise. When the addition was finished, 10% w/w aq NaOH was added to make the mixture alkaline (pH ~8). Next, the mixture was extracted with diethyl ether twice, and the combined organic extracts were dried over Na2SO4 and filtered. Ether was distilled off and the oily residue was distilled under vacuum (bp 70–72 °C / 2.66 × 10⁻³ bar). Sulfide 5 was obtained in 94% yield (14.6 g, 92.4 mmol).

4-Chlorophenyl methyl sulfone (4)  
(Method B and C)
After heating the mixture of sulfide 5 (20.15 g, 0.1275 mol) and glacial acetic acid (95 mL) to its boiling point, 30% w/w aq hydrogen peroxide (40 mL) was slowly added dropwise. The mixture was refluxed for 3 hours, and afterwards the contents of the flask were poured onto ice. The precipitate was filtered off and washed with cold water until the filtrate became neutral. Recrystallization from ethanol afforded the product 4 as a white crystalline solid (23.25 g, 0.1224 mol, 96%); mp 97–98 °C.

4-Chlorophenyl tribromomethyl sulfone (1)
(Method B)

4-Chlorophenyl methyl sulfone 4 (9.5 g, 0.05 mol) was added to freshly prepared 14% w/w aq sodium hypobromite (150 mL), and the resulting mixture was stirred at 75 °C for 3 hours. After cooling the mixture to ambient temperature, the precipitate was filtered off, washed with water, dried and recrystallized from 2-propanol. Product 1 was obtained in 95% yield (20.3 g, 47.5 mmol); mp 165–167 °C; IR ν: 1590 (CH Ar), 1335, 1125 (SO2), 550 (CBr3) cm⁻¹; ¹H NMR (400 MHz, CDCl3) δ 8.02–7.95 (m, 2H), 7.67–7.60 (m, 2H).

4-Halogenphenyltribromomethylsulfone 1 and 1'
(Method C)

To a solution of KOH (2.8 g, 0.050 mol) in methanol (30 mL), 4-halogenphenyl methyl sulfone 4 (1.91 g, 0.01 mol) or 4' (2.35 g, 0.01 mol) was added. After the stirred mixture was cooled below 20 °C, bromine chloride (3.0 g of a 50% w/w solution in carbon tetrachloride, 0.013 mol) was added dropwise. The mixture was stirred at room temperature for 2 hours. The precipitate was filtered off, washed with hexane, dried and recrystallized from 2-propanol. Sulfone 1 was obtained in 94% yield (4.02 g, 9.41 mmol); mp 165–167 °C.
Sulfone 1 was obtained in 90% yield (4.25 g, 9.01 mmol); mp 174–175 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.99–7.92 (m, 2H), 7.62–7.56 (m, 2H).

4-Halogeno-3-nitrophenyltribromomethylsulfone 6 and 6'

\[
\begin{align*}
\text{SO}_2\text{CB}_{\text{Br}_3}^X & \xrightarrow{\text{HNO}_3, \text{H}_{\text{SO}_4}} \text{SO}_2\text{CB}_{\text{Br}_3}^{X\text{O}_2}\text{N}^* \quad 1 \quad X = \text{Cl} \\
& \quad 1' \quad X = \text{Br} \\
& \quad 6 \quad X = \text{Cl} \\
& \quad 6' \quad X = \text{Br}
\end{align*}
\]

Sulfone 1 (8.55 g, 0.02 mol) or 1' (9.44 g, 0.02 mol) was dissolved in concentrated (min. 95% w/w) sulfuric acid (25 mL). The mixture was heated to 60 °C and concentrated (65% w/w) nitric acid (1.7 mL, 0.025 mol HNO\textsubscript{3}) was added slowly with the temperature kept below 70 °C. When the addition was finished, the mixture was heated at 80 °C for 2 hours. Then, the mixture was cooled down and poured onto crushed ice. The precipitate was filtered off, washed with water and dried. The product was purified by recrystallization from 2-propanol. Nitrophenyl sulfone 6 was obtained in 96% yield (9.08 g); mp 172–173 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.42 (dd, 1H), 8.20–8.12 (m, 2H). Nitrosulfone 6' was obtained in 94% yield (9.72 g); mp 178–180 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.34 (dd, 1H), 8.16–8.10 (m, 2H).

2-Nitro-4-tribromomethylsulfonylaniline 7a

\[
\begin{align*}
\text{SO}_2\text{CB}_{\text{Br}_3}^\text{Cl} \xrightarrow{\text{NH}_3(\text{aq})} \text{NH}_2\text{SO}_2\text{CB}_{\text{Br}_3}^\text{Cl} \quad 6 \\
& \quad 7a
\end{align*}
\]

To a solution of nitrosulfone 6 (23.6 g, 0.05 mol) in dioxane (200 mL) 25% w/w aqueous ammonia (100 mL) was added. After stirring the mixture for two hours at 60 °C, another portion of 25% w/w aqueous ammonia (50 mL) was added. The reaction mixture was maintained for another two hours at 60 °C. The mixture was cooled down to room temperature and concentrated in vacuo. The precipitate was filtered off, washed with water, dried and recrystallized from ethanol. Product 7a was obtained in 95% yield (21.6 g, 47.7 mmol); mp 273–275 °C.
2-Nitro-4-tribromomethylsulfonylethanolhydrazine (7b)

Nitrosulfone 6 (4.72 g, 0.01 mol) and triethylamine (1.4 mL, 0.01 mol) was dissolved in tetrahydrofuran (20 mL). Hydrazine hydrate (40% w/w N\textsubscript{2}H\textsubscript{4}, 1.5 mL, ca 0.05 mmol) was slowly added, with the temperature kept below 20 °C. The resulting mixture was stirred for 1.5 hours at room temperature. The solvent was evaporated and the precipitate dissolved in dichloromethane (50 mL). The solution was consecutively washed with 10% w/w aq HCl, water, saturated aq NaHCO\textsubscript{3} and water. The organic layer was dried over MgSO\textsubscript{4}, filtered and concentrated in vacuo. Recrystallization from ethanol afforded product 7b (4.41 g, 9.43 mmol, 94% yield); mp 218–220 °C.

2-Nitroaniline derivatives (7c–7h)
(General procedure)

Nitrosulfone 6 (4.72 g, 0.01 mol), the appropriate nonaromatic amine (0.01 mol) and potassium carbonate (2 g, 0.015 mmol) were mixed in toluene (30 mL). The mixture was heated under reflux for 6 hours. After cooling, diethyl ether (50 mL) was added. The mixture was consecutively washed with 10% w/w aq HCl, water, saturated aq NaHCO\textsubscript{3} and water. The organic layer was dried over MgSO\textsubscript{4}, filtered and concentrated in vacuo. The product was recrystallized from 2-propanol.
2-Nitroaniline derivatives (7i–7k)
(General procedure)

![Chemical structure]

Nitrosulfone 6 (4.72 g, 0.01 mol), the appropriate aromatic amine (0.01 mol) and triethylamine (1.4 mL, 0.01 mol) were dissolved in ethanol (35 mL). The mixture was heated under reflux for 6 hours. After cooling, ethanol was evaporated under reduced pressure, and the precipitate was dissolved in dichloromethane (40 mL). The mixture was consecutively washed with 10% w/w aq HCl, water, saturated aq NaHCO₃ and water. The organic layer was dried over MgSO₄, filtered and concentrated in vacuo. The product was recrystallized from 2-propanol.

Diphenyl ether derivatives (7l–7o)
(General procedure)

![Chemical structure]

Nitrosulfone 6 (4.72 g, 0.01 mol), appropriate phenol (0.01 mol) and 10% w/w aqueous sodium hydroxide (50 mL) was stirred and heated under reflux for 3 hours. After cooling to room temperature, the precipitate was filtered off, washed with water, dried and recrystallized from 2-propanol or ethanol.
2-Nitro-4-tribromomethylsulfonylphenylhydrazones (8a–8l)

(General procedure)

To the solution of 2-nitro-4-(tribromomethylsulfonyl)phenylhydrazone (7b) (4.68 g, 0.01 mol) in dioxane (15 mL), concentrated (min. 95% w/w) sulfuric acid (0.2 mL) was added dropwise. The mixture was stirred for a few minutes at room temperature and the appropriate ketone or aldehyde (0.01 mol) was added. After stirring for 30 minutes, the precipitate was filtered off, washed with water (until the water after filtration achieved a pH of 7), dried and recrystallized from 2-propanol.

4-Tribromomethylsulfonyl-1,2-phenylenediamine (9)

The stirred mixture of 2-nitro-4-(tribromomethylsulfonyl)aniline (7a) (22.65 g, 0.05 mol), anhydrous stannous chloride (66.3 g, 0.35 mol) and ethanol (200 mL) was heated to 70 °C. Then 250 mL of concentrated (35–38% w/w) hydrochloric acid was slowly added dropwise, with the temperature kept within the range of 70–75 °C. After cooling to room temperature, the precipitate was filtered off and treated with 15% w/w aqueous sodium hydroxide. The resulting residue was separated, washed with water, dried and recrystallized from ethanol. Phenylenediamine 9 was isolated in 60% yield (12.7 g, 0.03 mol); mp 164–165 °C. After concentrating and cooling the filtrate, pale yellow crystals of 4-dibromomethylsulfonyl-1,2-phenylenediamine (10) were obtained in 30% yield (5.2 g, 0.015 mol); mp 148–150 °C.
5-Tribromomethylsulfonylbenzimidazole derivatives (11a–11e)
(General procedure)

The suspension of 4-tribromomethylsulfonyl-1,2-phenylenediamine (9) (4.23 g, 0.01 mol) and the appropriate carboxylic acid (0.01 mol) in 4 M aqueous hydrochloric acid (30 mL) was stirred and heated under reflux for three hours (or six hours, in the case of the preparation of 11d and 11e). The suspension was neutralized by aqueous ammonia, filtered off, washed with water, dried and recrystallized from ethanol.

5-Tribromomethylsulfonylbenzimidazole derivatives (11f–11g)
(General procedure)

To a solution of the appropriate carboxylic acid (0.01 mol) in dry xylene (20 mL), titanium tetrachloride (1.1 mL, 0.01 mol) was added under a nitrogen atmosphere. The solution was stirred and diamine 9 (4.23 g, 0.01 mol) was added. The reaction mixture was heated at 130 °C for 2 hours. After cooling to room temperature, the reaction mixture was neutralized with a saturated aqueous solution of sodium bicarbonate. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water, dried over Na₂SO₄ and concentrated in vacuo. The residue was recrystallized from ethanol.

5-Tribromomethylsulfonyl-2-mercaptobenzimidazole (11h)
A mixture of 4-tribromomethylsulfonyl-1,2-phenylenediamine (9) (4.23 g, 0.01 mol), carbon disulfide (1.14 g, 0.015 mol), potassium hydroxide (0.84 g, 0.015 mol) in water (10 mL) and ethanol (20 mL) was heated under reflux for 5 hours. The reaction mixture was concentrated under reduced pressure and water (20 mL) was added to the residue. The mixture was acidified with acetic acid. The precipitate was separated, washed with water and recrystallized from ethanol. Mercaptobenzimidazole 11h was obtained in 80% yield (3.72 g, 8 mmol); mp 276–278 °C.

Benzimidazolethiocarbamate derivatives (11i-11j)
(General procedure)

A mixture of 5-tribromomethylsulfonyl-2-mercaptobenzimidazole (11h) (0.01 mol) and the appropriate isocyanate (0.01 mol) in dry dioxane (15 mL) was heated under reflux for 3 hours. After cooling the reaction mixture to ambient temperature, the precipitate was filtered off and purified by washing with hot chloroform.
**Table 1.** Derivatives of 2-nitroaniline, 2-nitrophenylhydrazine and diphenyl ether.

| Comp. No. | R            | Mol. Formula   | Mol. Wt. [g/mol] | M.P. [°C] | Yield [%] | Elemental analyses | IR cm⁻¹ |
|-----------|--------------|----------------|------------------|-----------|-----------|-------------------|---------|
| 7a        | NH₂          | C₆H₄Br₂N₂O₅S  | 452.90           | 273-275   | 93        | % C: 18.56, % H: 1.11, % N: 6.19 | NH₂: 3450, 3350, N₂O: 1540, 1370, SO₂: 1340, 1160, C-Br: 540 |
| 7b        | NH₂N₂H₂      | C₆H₄Br₂N₂O₅S  | 468.92           | 218-220   | 94        | % C: 17.93, % H: 1.50, % N: 8.96 | NH₂: 3380, 3325, N₂O: 1555, 1365, SO₂: 1345,1160, C-Br: 540 |
| 7c        | NHCH₃        | C₆H₄Br₂N₂O₅S  | 466.93           | 228-230   | 95        | % C: 20.58, % H: 1.51, % N: 6.00 | NH₂: 3360, N₂O: 1565, 1370, SO₂: 1355,1150, C-Br: 550 |
| 7d        | NHC₆H₄     | C₆H₄Br₂N₂O₅S  | 535.05           | 194-195   | 87        | % C: 29.18, % H: 2.83, % N: 5.24 | NH₂: 3360, N₂O: 1550, 1370, SO₂: 1355,1160, C-Br: 550 |
| 7e        | NHCH₂CH₂CH₃ | C₆H₄Br₂N₂O₅S  | 494.98           | 185-186   | 92        | % C: 24.27, % H: 2.24, % N: 5.66 | NH₂: 3370, N₂O: 1555, 1365, SO₂: 1345,1160, C-Br: 550 |
| 7f        | NHCH₂CH(CH₃)₂| C₆H₄Br₂N₂O₅S  | 509.01           | 154-135   | 94        | % C: 25.96, % H: 2.57, % N: 5.50 | NH₂: 3350, N₂O: 1555, 1365, SO₂: 1355,1150, C-Br: 550 |
| 7g        | N(C₃H₃)₂     | C₆H₄Br₂N₂O₅S  | 510.02           | 175-176   | 94        | % C: 25.91, % H: 2.77, % N: 5.49 | NO₂: 1560, 1360, SO₂: 1345,1150, C-Br: 545 |
| 7h        | N(CH₂CH₂CH(CH₄)₂)₂| C₆H₄Br₂N₂O₅S  | 565.11           | 147-149   | 92        | % C: 31.88, % H: 3.75, % N: 4.96 | NO₂: 1555, 1365, SO₂: 1350,1160, C-Br: 550 |
| 7i        | NH-Cl        | C₆H₄ClBr₂N₂O₅S | 563.44           | 196-197   | 96        | % C: 27.71, % H: 1.43, % N: 4.97 | NH₂: 3345, N₂O: 1560, 1360, SO₂: 1345,1155, C-Br: 540 |
| 7j        | NH-CH₃       | C₆H₄ClBr₂N₂O₅S | 543.02           | 184-186   | 88        | % C: 30.97, % H: 2.04, % N: 5.16 | NH₂: 3330, N₂O: 1520, 1380, SO₂: 1350,1175, C-Br: 550 |
| 7k        | NH-CH₃      | C₆H₄ClBr₂N₂O₅S | 559.02           | 173-174   | 86        | % C: 30.08, % H: 1.98, % N: 5.01 | NH₂: 3330, N₂O: 1540, 1360, SO₂: 1350,1160, C-Br: 555 |
| 7l        | O-Cl        | C₆H₄Br₂NO₅S   | 529.98           | 144-145   | 91        | % C: 29.46, % H: 1.52, % N: 2.64 | NO₂: 1555, 1365, SO₂: 1355,1150, C-O-C: 1250, C-Br: 550 |
| 7m        | O-Cl        | C₆H₄ClBr₂NO₅S | 564.43           | 148-149   | 92        | % C: 27.66, % H: 1.25, % N: 2.48 | NO₂: 1550, 1365, SO₂: 1355,1155, C-O-C: 1250, C-Br: 550 |
| 7n        | O-Cl        | C₆H₄ClBr₂NO₅S | 598.87           | 154-156   | 92        | % C: 26.07, % H: 1.01, % N: 2.34 | NO₂: 1550, 1365, SO₂: 1360,1160, C-O-C: 1250, C-Br: 550 |
| 7o        | O-Cl        | C₆H₄Br₂NO₅S   | 648.16           | 167-168   | 90        | % C: 40.77, % H: 2.80, % N: 2.16 | NO₂: 1550, 1365, SO₂: 1355,1155, C-O-C: 1260, C-Br: 550 |
Table 2. 2-Nitro-4-tribromomethylsulfonylphenylhydrazones.

| Comp. No | R          | Mol. Formula | Mol. Wt. [g/mol] | M.P. [°C] | Yield [%] | Calcd. % C | Calcd. % H | Calcd. % N | Found % C | Found % H | Found % N | IR cm⁻¹                                                                 |
|----------|------------|--------------|------------------|-----------|-----------|------------|------------|------------|-----------|-----------|------------|------------------------------------------------------------------------|
| 8a       | N=CCH₂C₃H₇ | C₁₂H₃Br₂N₂O₂S | 536.03           | 168-170   | 96        | 26.89      | 2.63       | 7.84       | 26.94     | 2.55      | 7.75       | NH 3330, NO₂ 1555, 1350, SO₂ 1355, 1165, C-Br₅ 555                   |
| 8b       |            | C₁₂H₃Br₂N₂O₂S | 534.02           | 197-199   | 87        | 26.99      | 2.26       | 7.89       | 26.56     | 2.08      | 7.75       | NH 3320, NO₂ 1550, 1350, SO₂ 1355, 1160, C-Br₅ 555                   |
| 8c       |            | C₁₂H₃Br₂N₂O₂S | 548.04           | 212-214   | 89        | 28.49      | 2.57       | 7.67       | 28.38     | 2.38      | 7.56       | NH 3330, NO₂ 1550, 1350, SO₂ 1355, 1160, C-Br₅ 555                   |
| 8d       |            | C₁₄H₃Br₂Cl₂N₂O₂S | 624.91         | 225-227   | 93        | 26.91      | 1.29       | 6.72       | 26.76     | 1.32      | 6.64       | NH 3335, NO₂ 1550, 1350, SO₂ 1355, 1160, C-Br₅ 555                   |
| 8e       |            | C₁₅H₁₀Br₂Cl₂N₂O₂S | 638.94         | 174-175   | 90        | 28.20      | 1.58       | 6.58       | 28.31     | 1.46      | 6.44       | NH 3335, NO₂ 1550, 1350, SO₂ 1355, 1155, C-Br₅ 555                   |
| 8f       | N=C(C₆H₅)₂ | C₁₃H₁₀Br₂N₂O₂S | 632.12           | 243-244   | 92        | 38.00      | 2.23       | 6.65       | 37.87     | 2.18      | 6.56       | NH 3335, NO₂ 1550, 1350, SO₂ 1350, 1155, C-Br₅ 555                   |
| 8g       | N=CHCH₃   | C₁₂H₃Br₂N₂O₄S | 493.95           | 195-197   | 85        | 21.88      | 1.63       | 8.51       | 21.76     | 1.45      | 8.38       | NH 3325, NO₂ 1550, 1350, SO₂ 1350, 1155, C-Br₅ 555                   |
| 8h       |            | C₁₂H₃Br₂N₂O₄S | 522.01           | 181-182   | 89        | 25.31      | 2.32       | 8.05       | 25.12     | 2.24      | 7.98       | NH 3325, NO₂ 1550, 1350, SO₂ 1350, 1155, C-Br₅ 555                   |
| 8i       |            | C₁₃H₁₀Cl₂N₂O₄S | 519.99           | 202-204   | 91        | 25.41      | 1.94       | 8.08       | 25.33     | 1.76      | 7.97       | NH 3325, NO₂ 1550, 1350, SO₂ 1350, 1165, C-Br₅ 555                   |
| 8j       |            | C₁₂H₃Br₂N₂O₄S | 550.06           | 144-145   | 88        | 28.39      | 2.93       | 7.64       | 28.43     | 2.78      | 7.57       | NH 3325, NO₂ 1550, 1350, SO₂ 1350, 1155, C-Br₅ 555                   |
| 8k       |            | C₁₄H₃Br₂ClN₂O₂S | 590.47           | 284-286   | 92        | 28.48      | 1.54       | 7.12       | 28.37     | 1.44      | 7.04       | NH 3325, NO₂ 1550, 1350, SO₂ 1350, 1160, C-Br₅ 555                   |
| 8l       |            | C₁₄H₃Br₂FN₂O₂S | 574.01           | 246-247   | 94        | 29.29      | 1.58       | 7.32       | 29.08     | 1.48      | 7.24       | NH 3325, NO₂ 1565, 1350, SO₂ 1350, 1155, C-Br₅ 555                   |
| Comp. No. | R       | Mol. Formula | Mol. Wt. [g/mol] | M.P. [°C] | Yield [%] | Elemental analyses | IR                  |
|-----------|---------|--------------|------------------|----------|-----------|--------------------|---------------------|
| 11a       | CH₃     | C₆H₃Br₂N₂S₂S | 446.94           | 187-189  | 86        | 24.19 1.58 6.27   | 24.34 1.72 6.18     | NH 3330, SO₂ 1335,1130, CBr₃ 550 |
| 11b       | CF₃     | C₆H₃Br₂F₂N₂S₂S | 500.91           | 241-243  | 93        | 21.58 0.80 5.59   | 22.12 0.88 5.46     | NH 3300, SO₂ 1330,1120, CBr₃ 555 |
| 11c       | CH₂C₅H₅ | C₁₅H₁₄Br₃N₂O₂S₂ | 523.04           | 234-235  | 57        | 34.45 2.12 5.36   | 34.25 1.97 5.27     | NH 3360, SO₂ 1335,1130, CBr₃ 550 |
| 11d       | C₆H₅Cl  | C₁₅H₁₄BrCl₃N₂O₂S₂ | 607.93           | 238-239  | 81        | 29.64 1.49 4.61   | 29.45 1.37 4.43     | NH 3350, SO₂ 1325,1145, CBr₃ 550 |
| 11e       | C₆H₄Cl⁻ | C₁₅H₁₄BrCl₃N₂O₂S₂ | 573.48           | 227-229  | 77        | 31.42 1.76 4.88   | 31.30 1.55 4.76     | NH 3330, SO₂ 1330,1140, CBr₃ 555 |
| 11f       | C₆H₅   | C₁₄H₉Br₃N₂O₂S | 509.01           | 267-269  | 79        | 33.04 1.78 5.50   | 32.78 1.57 5.38     | NH 3300, SO₂ 1330,1125, CBr₃ 550 |
| 11g       | C₆H₄-4-Cl | C₁₅H₁₄Cl₃N₂O₂S | 385.65           | 270-272  | 65        | 34.26 2.87 14.53  | 34.40 2.92 14.46    | NH 3360, SO₂ 1335,1155, CBr₃ 550 |
| 11h       | SH      | C₂H₃Br₂N₂O₂S₂ | 464.97           | 276-278  | 80        | 20.67 1.08 6.02   | 20.46 1.15 5.94     | NH 3400, SO₂ 1335, 1150, CBr₃ 555 |
| 11i       | C₅H₄N₂H | C₁₅H₁₀Br₃N₂O₂S₂ | 584.09           | 340 (d)  | 92        | 30.85 1.73 7.19   | 30.62 1.56 7.12     | NH 3350, C=O 1715, SO₂ 1340, 1150, CBr₃ 555 |
| 11j       | C₅H₄N₂Cl | C₁₅H₁₀Br₃N₂O₂S₂ | 618.54           | 325-326  | 76        | 29.13 1.47 6.79   | 29.02 1.26 6.74     | NH 3360, C=O 1710, SO₂ 1340, 1150, CBr₃ 550 |

- **d** - decomposition

Table 3. 5-Tribromomethylsulfonylbenzimidazole derivatives.
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature: Mercury-400S "Mercury"

PULSE SEQUENCE
Pulse 37.5 degrees
Acq. time 4.88 sec
Width 7000 Hz
48 repetitions
Observe 1H, 560.02502 kHz
Data Processing
FT 6120 65536
Total time 26 min, 42 sec

1H NMR
Pulse Sequence: se2pal
Solvent: CDCl3
Ambient temperature
Mercury-10065 "mercury"

PHASE SEQUENCE
Pulse 25.6 degrees
Acq. time 1.000 sec
Width 30155.3 Hz
100 repetitions

OBSERVE C13, 150.605157 MHz
DECouple H1, 400.1065706 MHz
Power 60 W
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 39 hr., 6 min., 35 sec

13C NMR
S16

Pulse Sequence: EZpu1
Solvent: CDCl3
Ambient Temperature
Mercury 400 MHz "mercury"

PULSE SEQUENCE
Pulse 37.5 degrees
Acq. time 4.000 sec
Width 7460.9 Hz
444 repetitions
REVERE H1, 403.105×25 MHz
DATA PROCESSING
FT size 65536
Total time 36 min, 42 sec

7m
1H NMR

Ethanol
H2O

8.586

5.11

0.81

12.29 16.55

1.84
1.31

1.93

1.00 1.570

1.570
BRC7ac

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400B "mercury"

PULSE SEQUENCE
Pulse 90.0 degrees
Acq. time 1.65 sec
Width 30106.2 Hz
2900 repetitions
Observe C13, 100.606508 MHz
Decompo H1, 406.1069706 MHz
Power 82 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.0 Hz
FT size 85536
Total time 38 hr, 8 min, 35 sec

13C NMR

7m