4-Methyl-N-(2,2,4,4-tetrachloro-3-oxo-8-oxabicyclo[3.2.1]oct-6-en-1-ylmethyl)-benzenesulfonamide

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A mixture of N-furfuryl-p-toluenesulfonamide (1) (2.51 g, 10 mmol) [1] and pentachloroacetone [2] (3.23 g, 14 mmol) was cooled in an ice bath. With magnetic stirring, a 2 molar solution of sodium 2,2,2-trifluoroethoxide in 2,2,2-trifluoroethanol[3] (7 mL, 14 mmol) was added dropwise, over 15 min. Stirring was continued for 15 min at 0 °C and then at room temperature for 2–3 hours[4]. The mixture was allowed to stir for a further 2 hours. Then, the heterogeneous mixture was poured on saturated brine (20 mL). The precipitate was dissolved by adding a little of dichloromethane and water, and the organic layer was separated. The aqueous layer was acidified with hydrochloric acid to pH 4–5 and then extracted with dichloromethane (4 × 20 mL). The combined dichloromethane solutions were washed with saturated brine (20 mL) and dried overnight with magnesium sulfate. After filtration, the solution was concentrated in a rotary evaporator. The remaining yellow mass was recrystallized from dry ethanol (10 mL) to yield 3.60 g (81%) of 2 as a colourless crystalline solid.

Melting Point: 162–163 °C.

TLC (silica, hexane/tert-butylmethyl ether (1:1 v/v)): A pale yellow spot emerged after spraying the sheet with vanillin/sulfuric acid reagent followed by heating with a hot-air gun; \( R_f = 0.27 \). The starting material (1) showed a brownish violet spot at \( R_f = 0.37 \).

\(^1\)H-NMR (250 MHz, CDCl\(_3\)): \( \delta = 2.45 \) (s, 3 H, \( CH_3C_6H_4SO_2 \)); ABX sub-spectrum (14 lines) with \( \delta_A = 3.89 \), \( \delta_B = 3.65 \), \( \delta_X = 5.10 \), \( J_{AB} = (-)14 \) Hz, \( J_{AX} = 9.6 \) Hz, \( J_{BX} = 3.6 \) Hz, 3 H, diastereotopic CH\(_2-\)NH; 5.16 (d, \( J = 1.7 \) Hz, 1 H, H-5), AB sub-spectrum with \( \delta_A = 6.48 \) (H-6), \( \delta_B = 6.46 \) (H-7), \( J_{AB} = 5.5 \) Hz, the lines of the A part are split into doublets with \( J = 1.7 \) Hz; AA’BB’ sub-spectrum with \( \delta_A = 7.76 \), \( \delta_B = 7.35 \), \( J_{AB} = 8.2 \) Hz (H-2/6 and H-3/5 from \( CH_3C_6H_4SO_2 \)).

\(^{13}\)C-NMR/DEPT (62.9 MHz, CDCl\(_3\)): \( \delta = 21.6 \) (+, \( CH_3C_6H_4SO_2 \)); 42.2 (-, \( CH_2-\)N); 81.9 (C\(_q\), C-4); 85.05 (C\(_q\), C-2); 87.9 (+, C-5); 93.3 (C\(_q\), C-1); 127.0 (+, C-2/6 of the tosyl group); 130.0 (+, C-3/5 of the tosyl group); 134.4 (+, C-6); 135.7 (+, C-7); 136.7 (C\(_q\), C-4 of the tosyl group); 144.1 (C\(_q\), C-1 of the tosyl group); 183.9 (C\(_q\), C-3).
IR (CHCl$_3$ film, cm$^{-1}$): 3395, 3280 (N-H); 3110 (=C-H); 1768 with shoulder at 1750 (C=O); 1600 (C=C); 1495 (NH); 1430, 1340 (SO$_2$); 1163 cm$^{-1}$ (SO$_2$).

Elemental Analysis: Calculated for C$_{15}$H$_{13}$Cl$_4$NO$_4$S (445.15): C, 40.47%; H, 2.94%; Cl, 31.86%; N: 3.15%; S, 7.20%. Found: C, 40.24%; H, 3.02%; Cl, 31.63%; N, 3.15%; S, 7.15%.

References and Notes
4. If 1 has not disappeared after that time (check by TLC), more pentachloroacetone (0.7–1.2 g, 3–5 mmol) was added, and the base solution in such amount that a test with wet pH indicator paper showed an alkaline reaction.

Sample Availability: Available from MDPI.

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