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One-pot synthesis of perfluorinated benzenedithiols from perfluoroarenes and thioacetic acid

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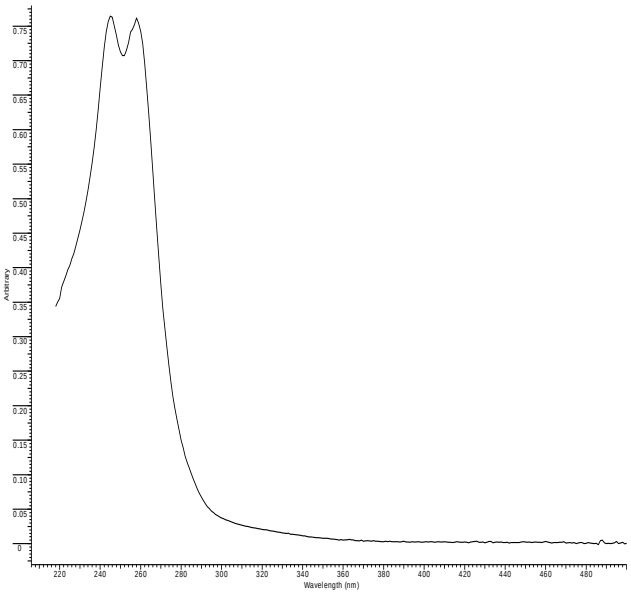
The ^{1}H NMR spectra were measured on a Bruker AV-300 instrument (300.13 MHz) in $CDCl_3$, internal standard HMDS. The ^{13}C NMR spectra were obtained on Bruker AV–300 (75.47 MHz) and Bruker DRX500 (125.78 MHz) spectrometers in $CDCl_3$, internal standard $CDCl_3$. The ^{19}F NMR spectra were run on a Bruker AV-300 spectrometer (282.4 MHz) in $CDCl_3$, internal standard C_6F_6. The IR and UV spectra were obtained on Bruker Vector 22 IR and Cary 5000 instruments, respectively. The molecular weights and elemental compositions were determined on a Thermo Scientific DFS mass spectrometer (EI 70 eV) and an Agilent 7200 Accurate Mass Q-TOF GC/MS system (EI 70 eV, column HP-5MS, injector temperature 280°C, temperature program: hold 2 min at 50°C, ramp 10 K min^{-1} to 280°C, hold 10 min). Gas chromatography–mass spectrometry was performed on a Hewlett–Packard HP 5890 chromatograph coupled with an HP 5971 mass-selective detector and an Agilent 6890N/5973N GC/MS system mass spectrometer; EI 70 eV, HP-5 30 m × 0.25 mm ID × 0.25 μm column, carrier gas He (1 ml min^{-1}), oven temperature 50–280°C, ion source temperature 173°C. Gas chromatography was performed on an LKhM-72 chromatograph with a heat conductivity detector, column 2 mm × 4 mm ID, packing 15% of dimethylpolysiloxane VS-1 or dimethyltrifluoropropylpolysiloxane SKTFT-50 on Chromosorb W-AW-DMCS, carrier gas He (60 ml min^{-1}), injector temperature 280°C, detector temperature 280°C, temperature program: hold 1 min at 50°C, ramp 10 K min^{-1} to 280°C, hold until all components have been eluted. The X-ray diffraction experiments were carried out on a Bruker KAPPA APEX II diffractometer with MoKα radiation.

Hexafluorobenzene (99%) was obtained in an experimental chemical workshop NIOCh SB RAS. Perfluoroindane (98%) was synthesized in the Perm branch of GIPH. Technical mixture of perfluorinated *m*- and *p*-xylenes (98%) was obtained in P&M INVEST.

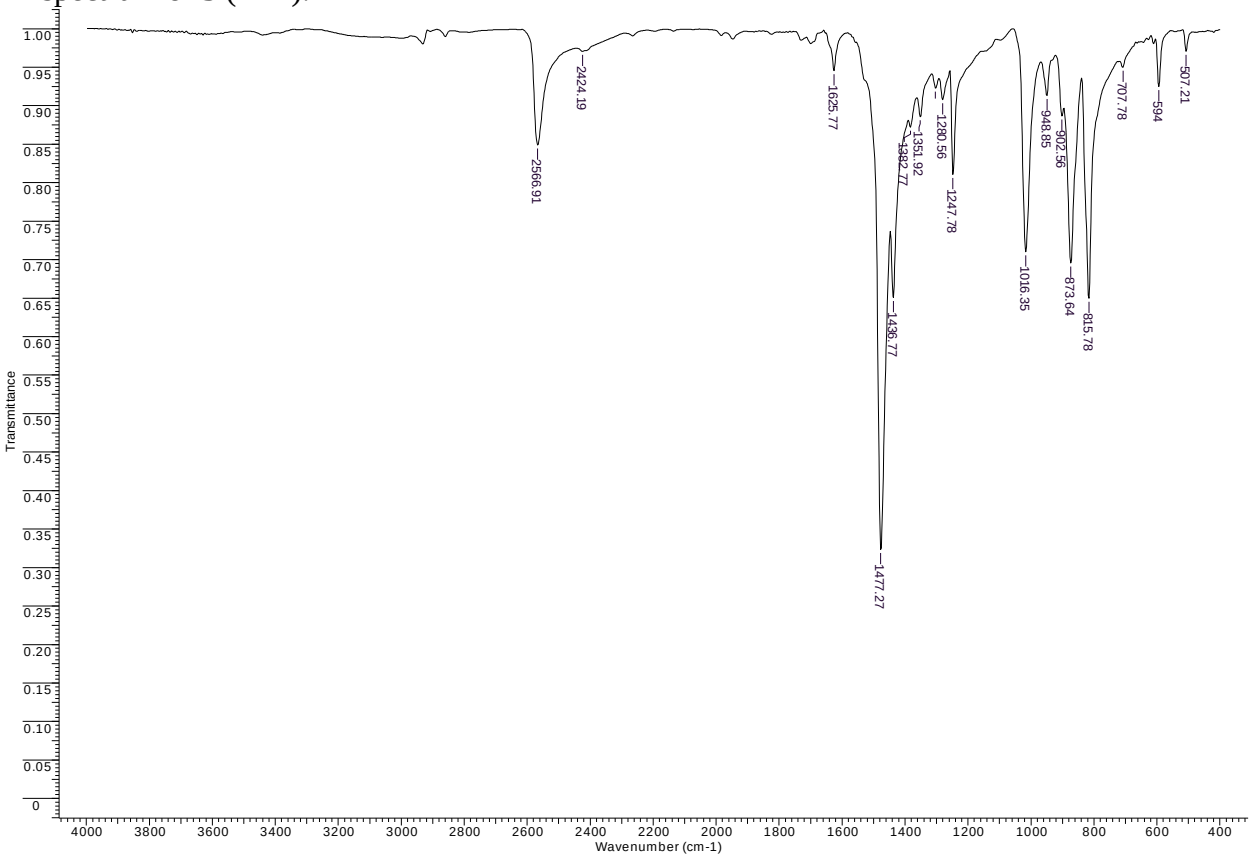
Commercial reagents were used: thioacetic acid (96%) (Sigma-Aldrich), acetyl chloride (98%) (Sigma-Aldrich).

2,3,5,6-Tetrafluorobenzene-1,4-dithiol 3. Thioacetic acid (9.90 g, 130.06 mmol) was added to a mixture of hexafluorobenzene (6.04 g, 32.46 mmol) and Na_2CO_3 (5.53 g, 52.18 mmol) in DMF solution (60 ml), and the resulted mixture was stirred for 5 h. Then additional portion of Na_2CO_3 (1.79 g, 16.89 mmol) was added, and the resulted mixture was stirred for additional 5 h. The progress of reaction was monitored by means of ^{19}F NMR spectroscopy. The reaction mixture was treated with aqueous NaOH solution (3.3 M, 60 ml) and stirred for 16 h, quenched with conc. HCl (60 ml) and subjected to steam-distillation. The product crystallized on cooling. The crystals were separated, dried over $CaCl_2$. Yield 5.01 g (23.25 mmol, 72%) of 99.4% purity. M.p. 71-73°C. IR (KBr), ν, cm^{-1}: 2567, 1477, 1437, 1383, 1352, 1281, 1248, 1016, 949, 903, 874, 816, 708, 594, 507. UV spectrum (hexane), λ_{max}, nm (log ε): 245 (4.18), 248 (4.18). NMR, *δ*, ppm.: 3.65 s (SH). ^{13}C NMR, *δ*, ppm.: 108.2 m, 141.8 m, 145.0 m. ^{19}F NMR, *δ*, ppm.: 24.7 s. Found: M^+ 213.9528, $C_6H_2F_4S_2$. Calculated: M^+ 213.9529.

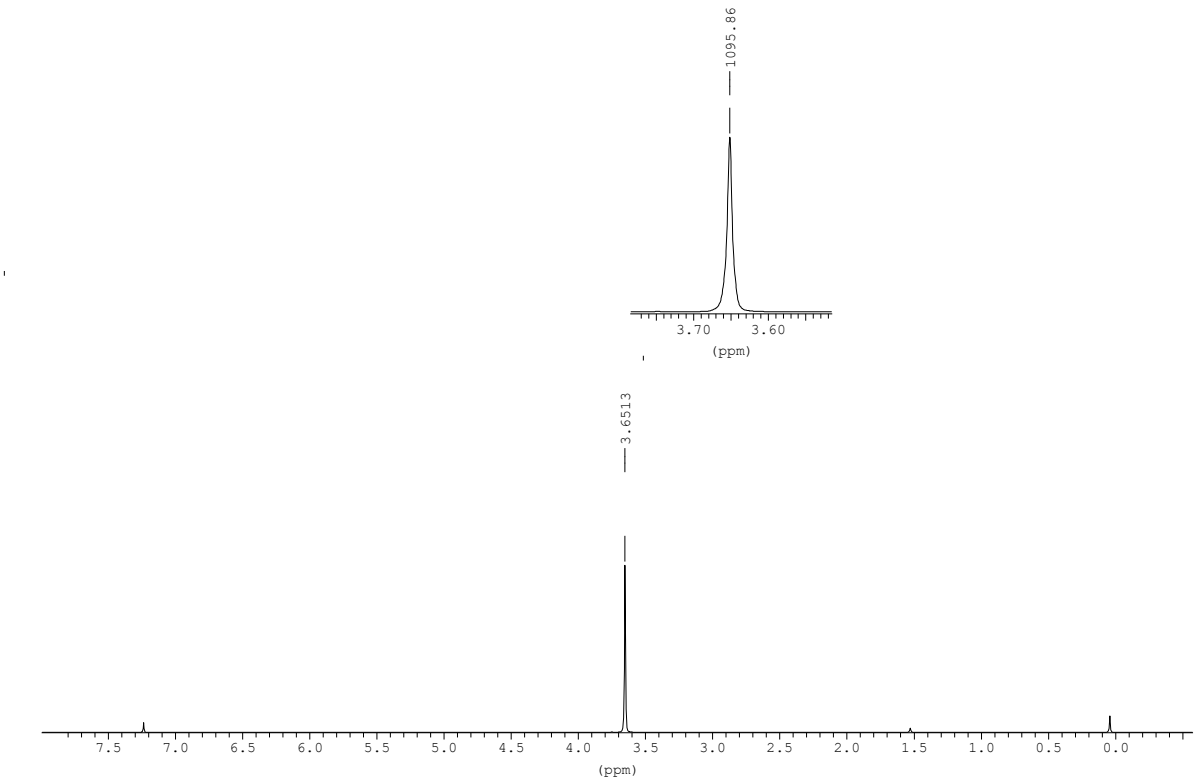
UV spectra of **3** (hexane).



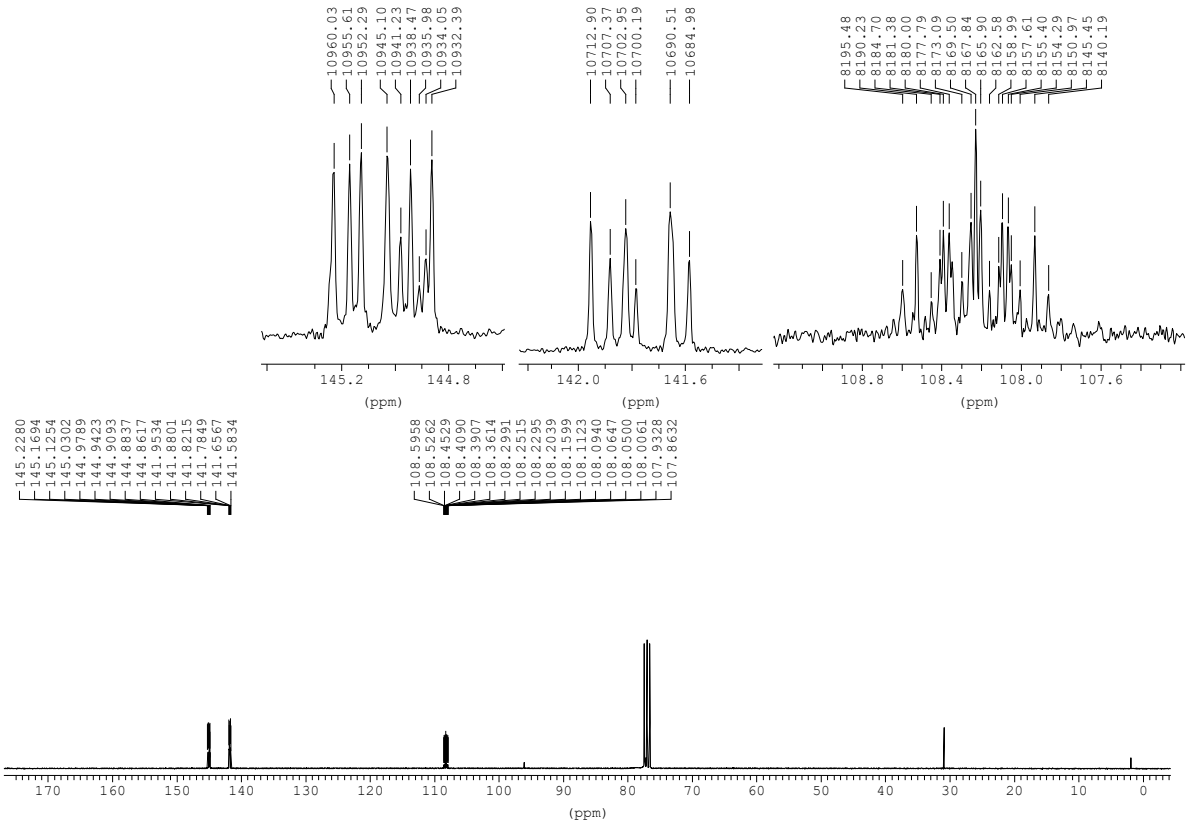
IR spectrum of **3** (KBr).



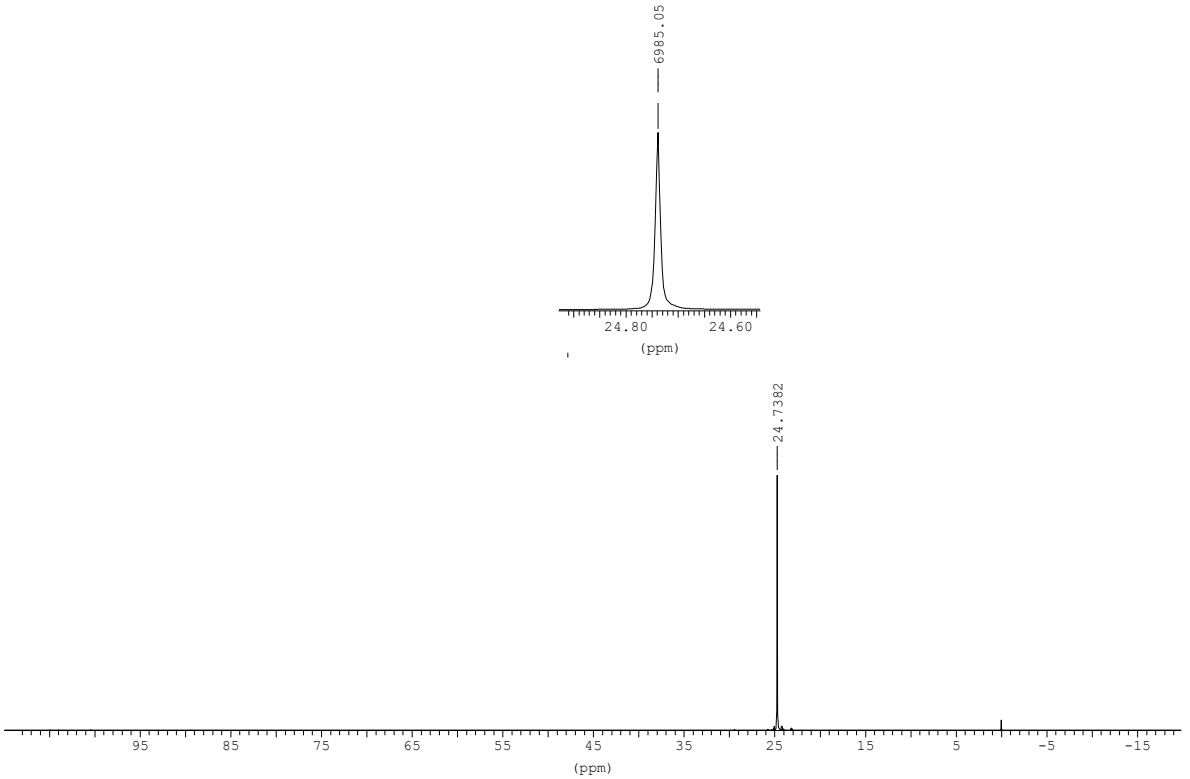
^{1}H NMR spectrum ($CDCl_3$, HMDS δ_H =0.04 ppm) Bruker Avance – 300 (300.13 MHz) of **3.**



^{13}C NMR spectrum ($CDCl_3$, δ_C =77.0 ppm) Bruker Avance – 300 (75.47 MHz) of **3.**

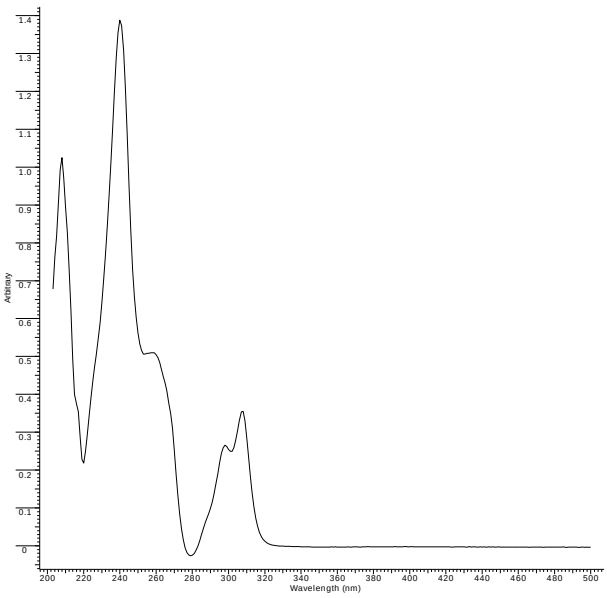


^{19}F NMR spectrum ($CDCl_3$, C_6F_6 δ_F =0.0 ppm) Bruker Avance – 300 (282.40 MHz) of **3.**

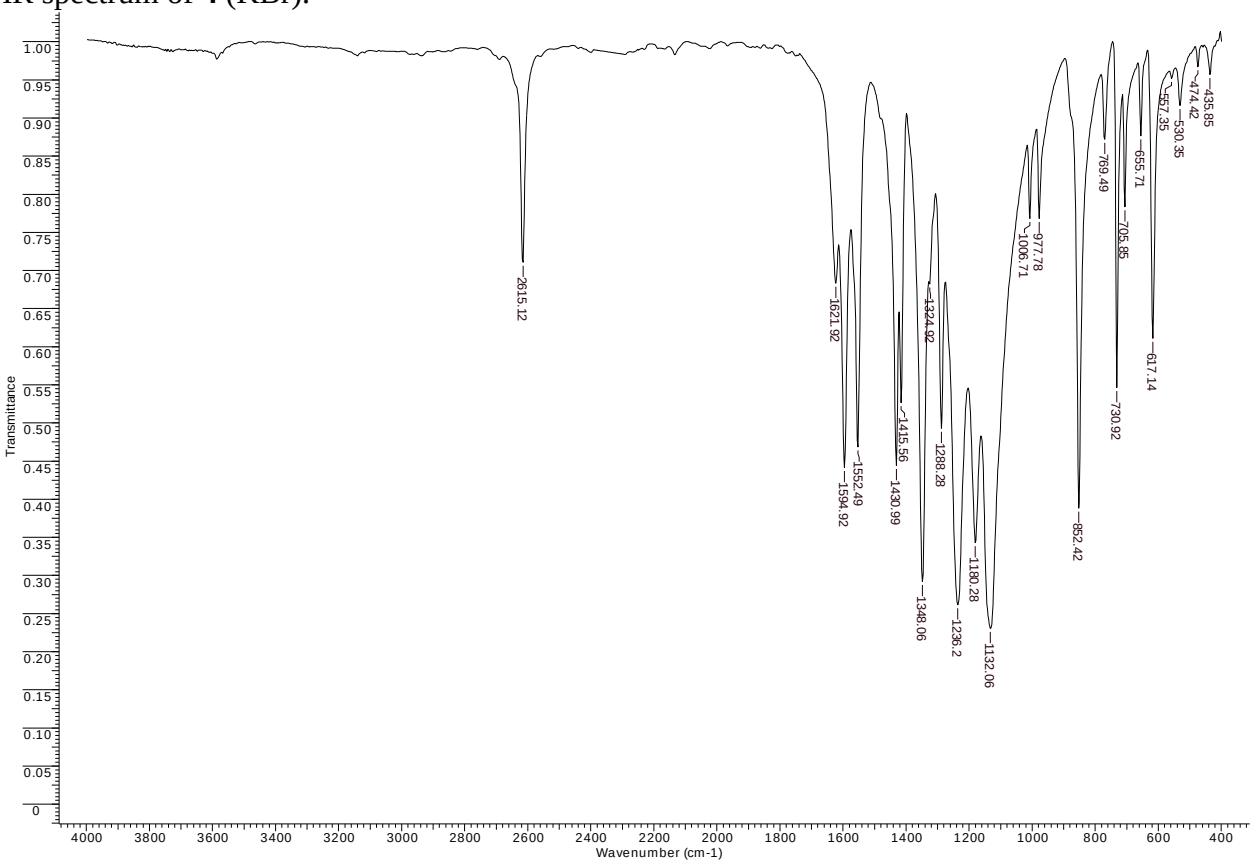


2,5-Difluoro-4,6-bis(trifluoromethyl)benzene-1,3-dithiol 4. Solid Na_2CO_3 (12.72 g, 120.01 mmol) and thioacetic acid (18.82 g, 247.24 mmol) were added to a 72:28 (^{19}F NMR) mixture of perfluorinated *m*- and *p*-xylenes (39.86 g, 139.34 mmol) in DMF (250 ml), and the resulted mixture was stirred for 5 h. The reaction mixture was treated with aqueous NaOH solution (2 M, 300 ml) and stirred for 16 h, quenched with conc. HCl (150 ml) and subjected to steam-distillation. At this operation, unreacted perfluoro-*p*-xylene was separated from the desired product. The product crystallized on cooling. The crystals were separated, dried over $CaCl_2$. Yield 23.25 g (72.29 mmol, 72%) of 97.7% purity (GC). M.p. 66-67°C. IR (KBr), ν, cm^{-1}: 2615, 1622, 1595, 1553, 1431, 1416, 1348, 1325, 1288, 1236, 1180, 1132, 1007, 978, 852, 769, 731, 706, 656, 617, 557, 530, 474, 436. UV spectrum (hexane), λ_{max}, nm (log ε): 208 (4.30), 240 (4.44), 258 (4.00), 298 (3.72), 308 (3.84). ^{1}H NMR δ, ppm.: 4.36 d.q (SH, *J* 10, *J* 8.5 Hz). ^{13}C NMR, δ, ppm.: 113.5 q.d.d ($^{4(6)}$C, ^2J ~34 Hz, ^2J 16, ^3J 2 Hz), 121.2 q.d.d (<u>C</u>F_3, ^1J (CF) 277, *J* ~2.5, *J* ~1 Hz), 122.8 d ($^{1(3)}$C, ^2J 28 Hz), 147.9 d.d (^{2}C, ^1J (CF) 231, ^4J 4 Hz), 155.4 d.m (^{5}C, ^1J (CF) ~270 Hz). ^{19}F NMR, δ, ppm.: 47.2 septet d (1F, F^5, *J* 27, *J* 15 Hz), 59.3 m (1F, F^2), 105.8 dd (6F, 4,6-CF_3, *J* 27, *J* 8.5). Found, %: C 30.16; H 0.51; F 48.33; S 20.05. M^+ 313.9472, $C_8H_2F_8S_2$. Calculated, %: C 30.58; H 0.64; F 48.37; S 20.41. M^+ 313.9465.

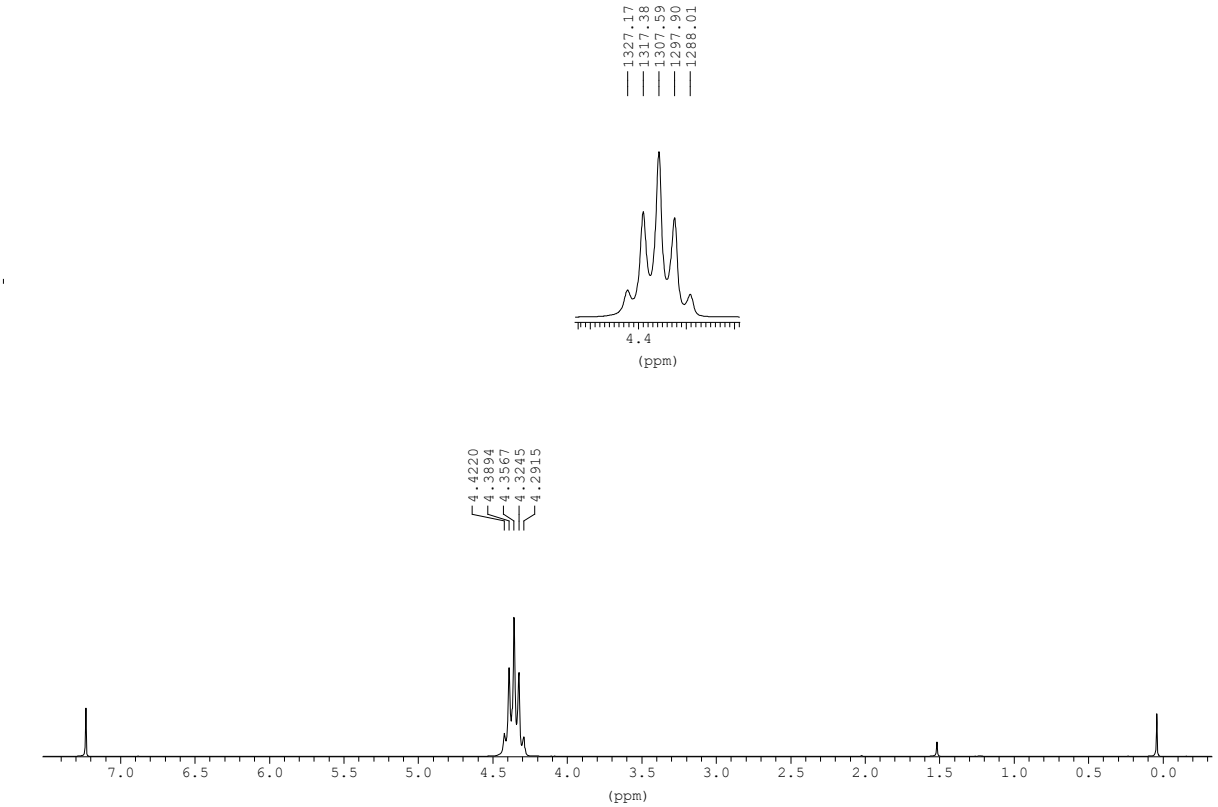
UV spectrum of **4** (hexane).



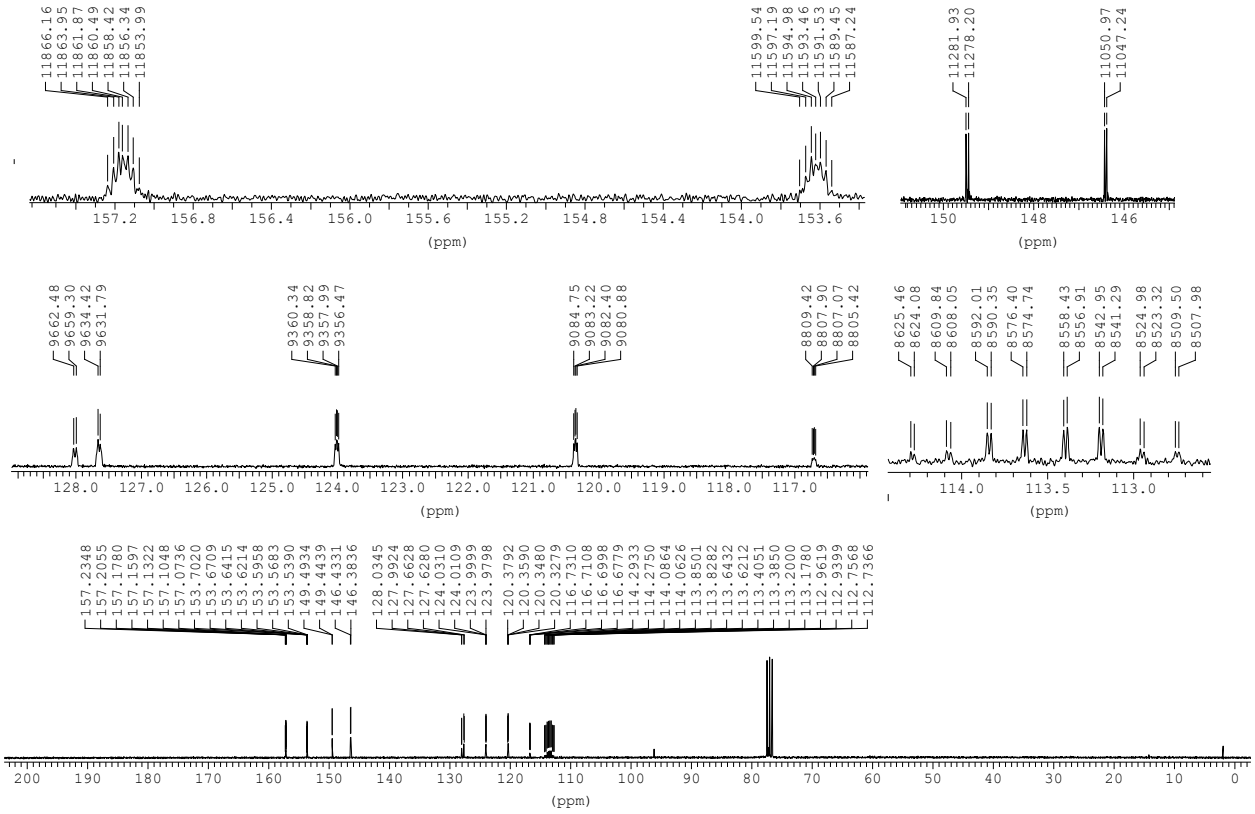
IR spectrum of **4** (KBr).



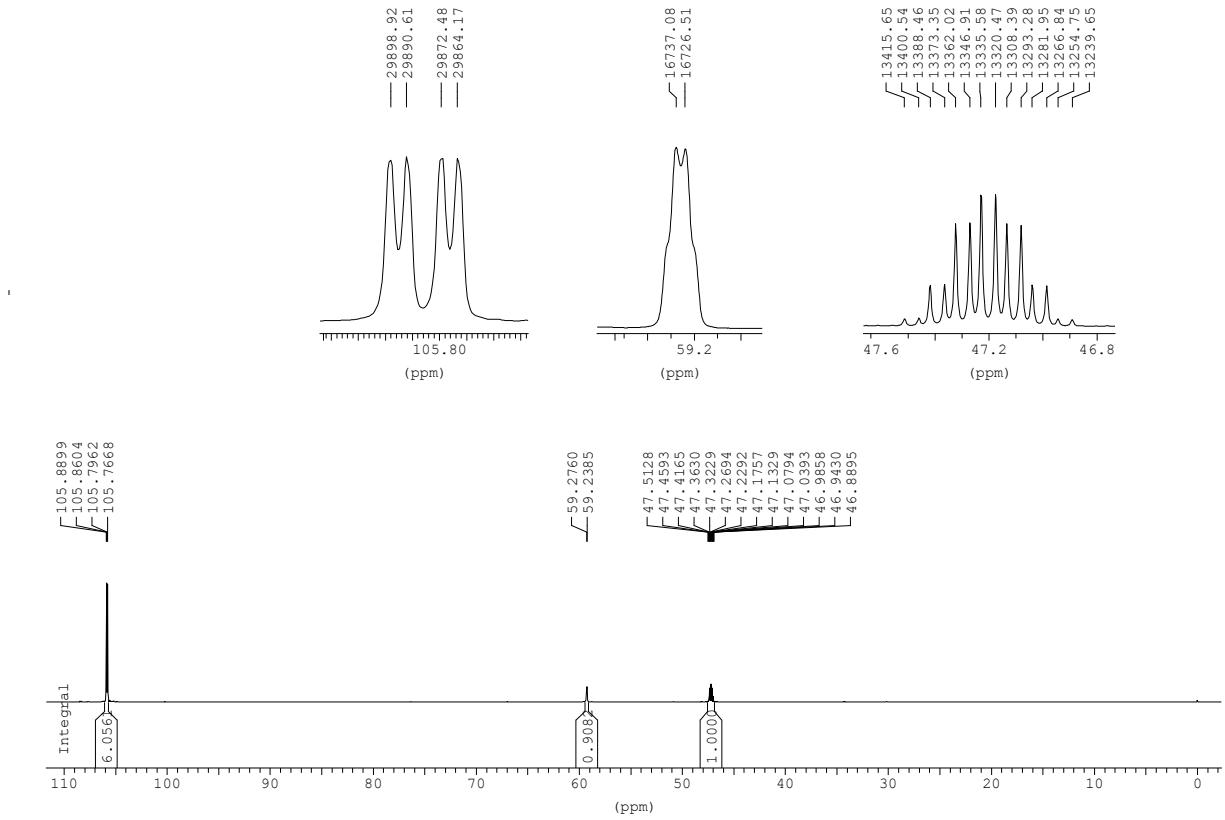
^{1}H NMR spectrum ($CDCl_3$, HMDS δ_H =0.04 ppm) Bruker Avance – 300 (300.13 MHz) of **4.**



^{13}C NMR spectrum ($CDCl_3$, δ_C =77.0 ppm) Bruker Avance – 500 (75.47 MHz) of **4.**

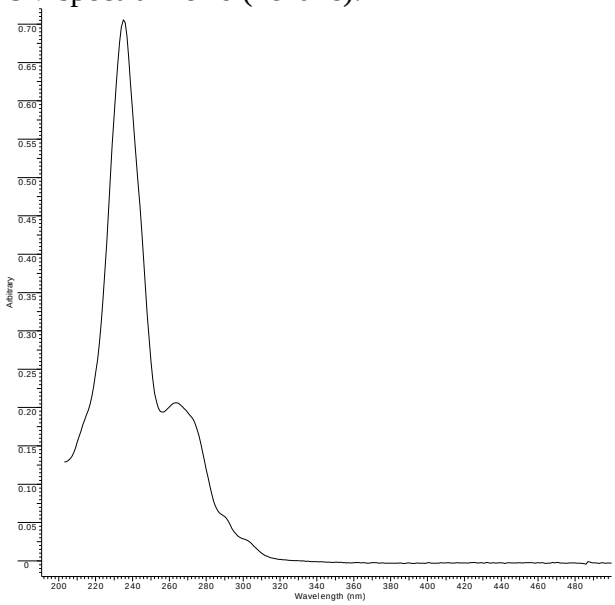


^{19}F NMR spectrum ($CDCl_3$, C_6F_6 δ_F =0.0 ppm) Bruker Avance – 300 (282.36 MHz) of **4.**

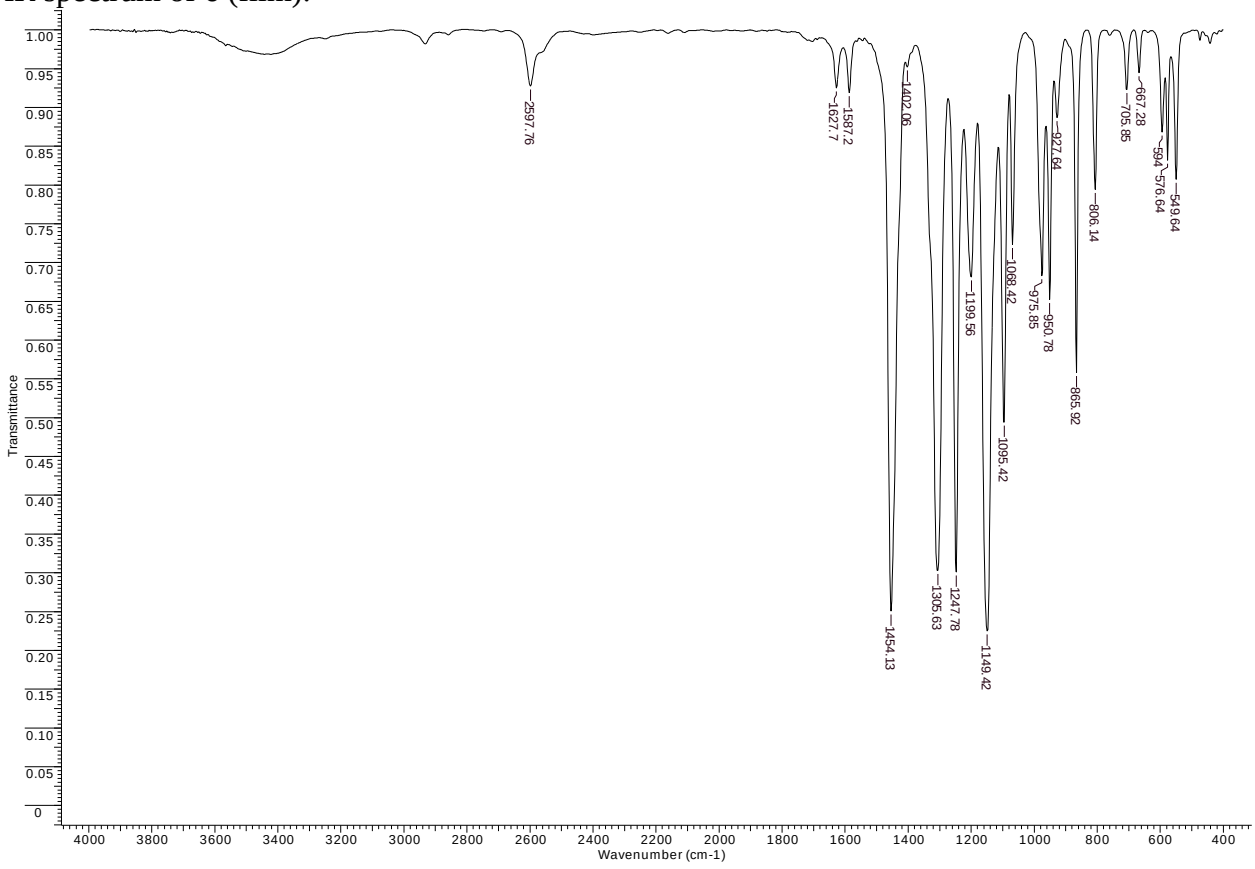


Octafluoroindane-5,6-dithiol 6. Thioacetic acid (6.86 g, 90.12 mmol) was added to a mixture of perfluoroindane (12.02 g, 40.32 mmol) and Na_2CO_3 (4.69 g, 44.25 mmol) in DMF solution (120 ml), and the resulted mixture was stirred for 6 h. Then aqueous NaOH solution (1.7 M, 200 ml) was added, and the reaction mixture was stirred for 2 h and quenched with conc. HCl (100 ml). The resulted solution was extracted with $CHCl_3$ (3×20 ml). The organic phase was separated, dried with $CaCl_2$. The solvent was removed under reduced pressure to give 2.60 g of the crude product, which was purified by sublimation at 150ºC and 0.04 Torr to give 0.44 g of **8** of 73.3% purity (GC). The aqueous phase was treated with conc. HCl (40 ml) and then extracted with $CHCl_3$ (3×20 ml), the organic solution was separated, dried with $CaCl_2$, and the solvent was removed to give 10.01 g of the crude product. The sublimation at 120ºC and 0.8 Torr gave 3.56 g with content of compounds **6** and **7** 75.8% and 17.0% (GC), respectively. Recrystallization from hexane (3 ml) gave 2.01 g (6.15 mmol) of dithiol **6**. Colorless liq. IR (film), ν, cm^{-1}: 2598, 1628, 1587, 1454, 1306, 1248, 1200, 1149, 1095, 1068, 976, 951, 928, 866, 806, 706, 667, 594, 577, 550. UV spectrum (hexane), λ_{max}, nm (log ε): 235 (4.45), 264 (3.91). ^{1}H NMR, *δ*, ppm: 4.28 s (SH). ^{13}C NMR, *δ*, ppm: 112.7 t. quintet (2-CF_2, ^1J 276, ^2J 25 Hz), 113.8 t.t ((1(3)-CF_2), ^1J 262, ^2J ~26 Hz), 120.7 m, 130.3 m, 151.2 d.d ($^{4(7)}$C, ^1J 264, J 6 Hz). ^{19}F NMR, *δ*, ppm: 32.3 quintet (2F, 2-CF_2, J 5 Hz), 49.2 m (2F, $F^{4,7}$), 54.7 m (4F, 1,3-CF_2). Found, %: C 33.40; H 0.74; F 46.53; S 19.98. M^+ 325.9463. $C_9H_2F_8S_2$. Calculated, %: C 33.14; H 0.62; F 46.59; S 19.66. M^+ 325.9465.

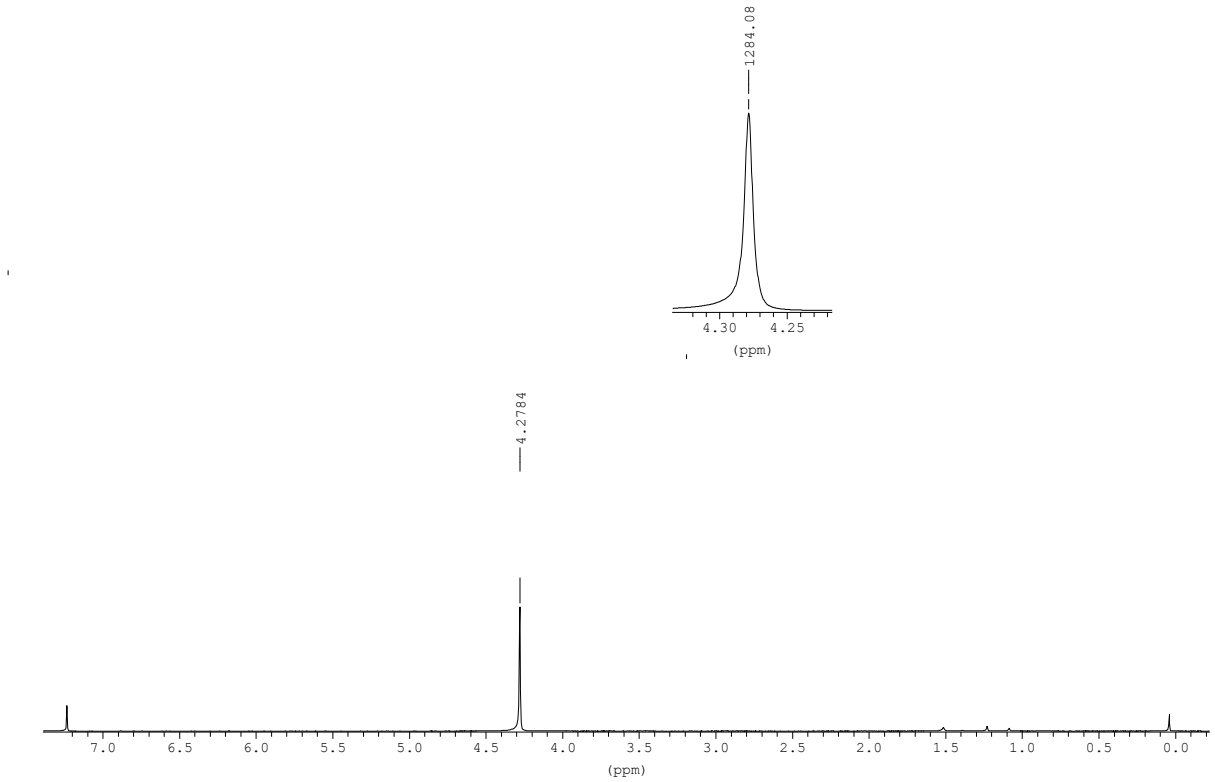
UV spectrum of **6** (hexane).



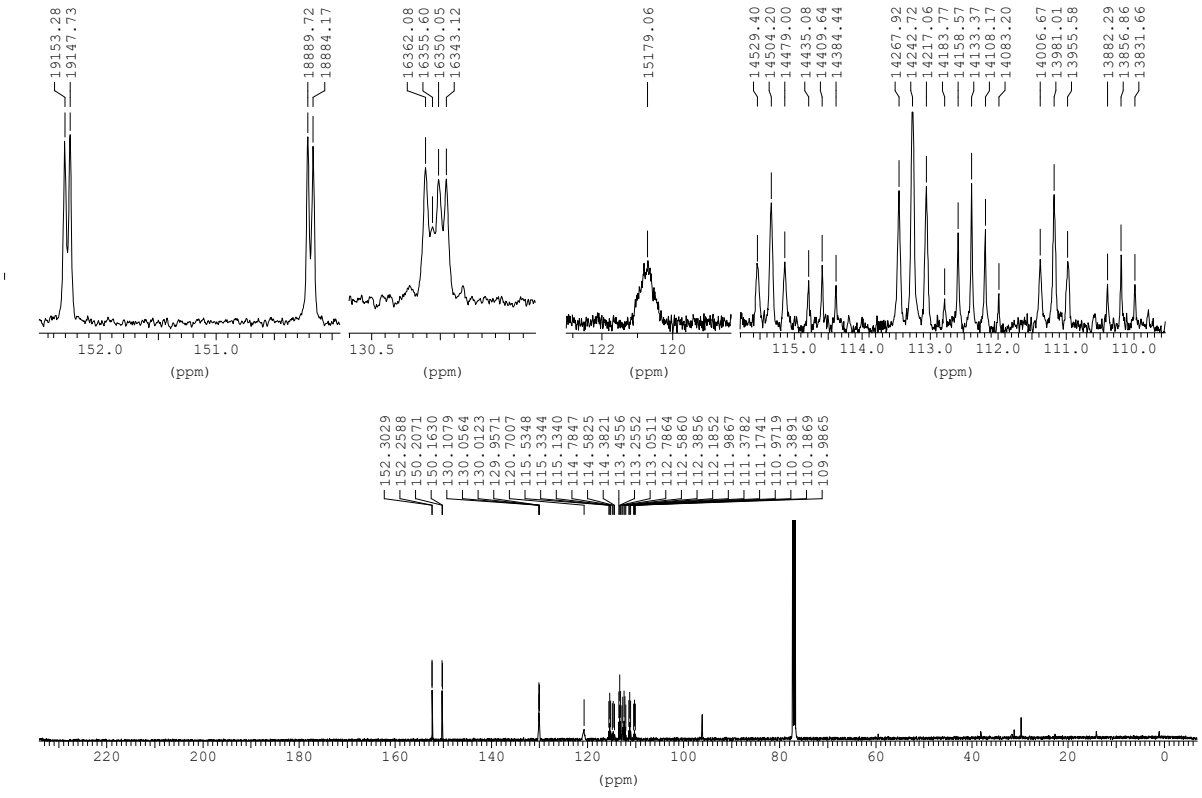
IR spectrum of **6** (film).



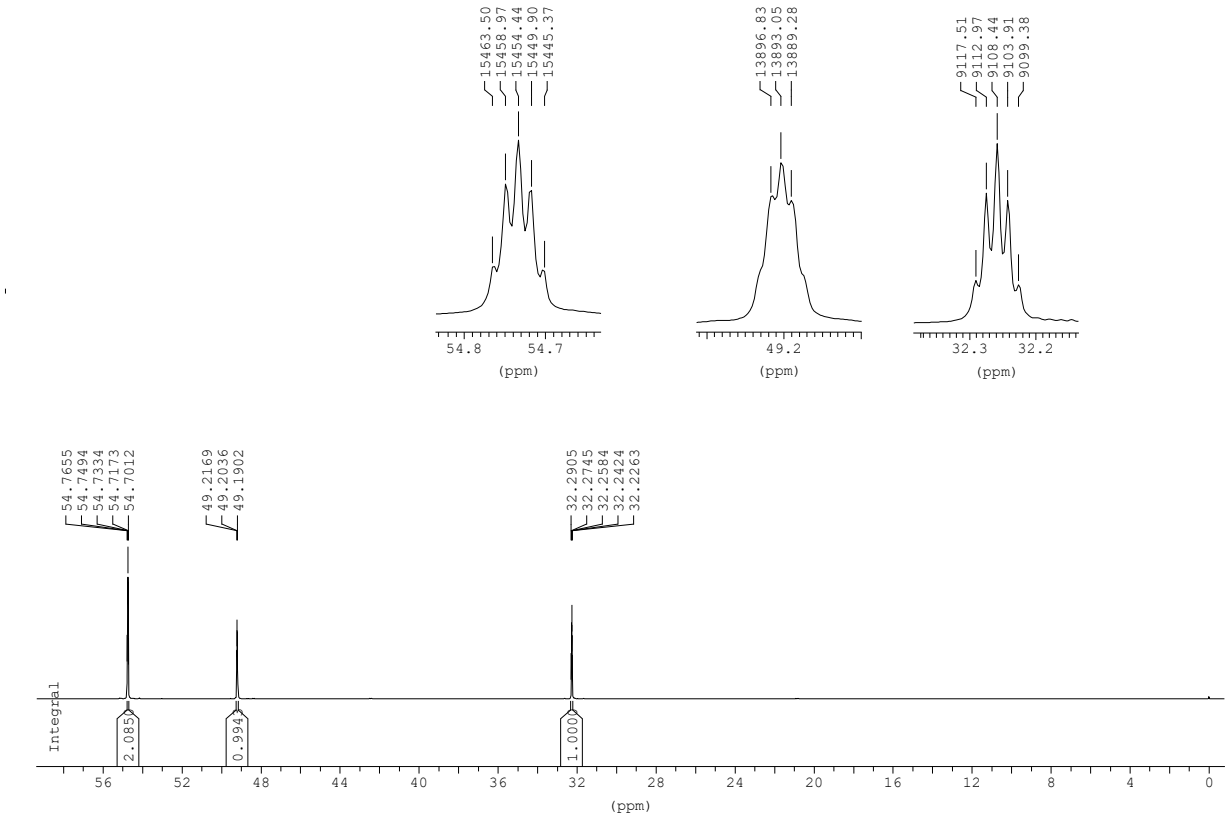
^{1}H NMR spectrum ($CDCl_3$, HMDS δ_H =0.04 ppm) Bruker Avance – 300 (300.13 MHz) of **6.**



^{13}C NMR spectrum ($CDCl_3$, δ_C =77.0 ppm) Bruker DRX– 500 (125.76 MHz) of **6.**

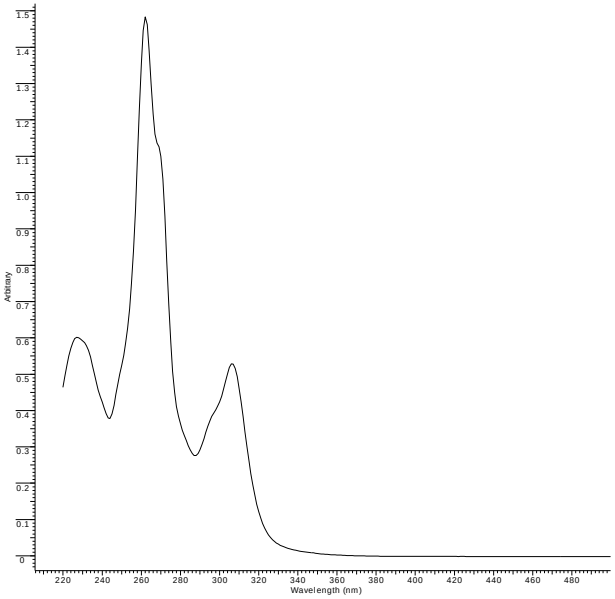


^{19}F NMR spectrum ($CDCl_3$, C_6F_6 δ_F =0.0 ppm) Bruker Avance – 300 (282.36 MHz) of **6.**



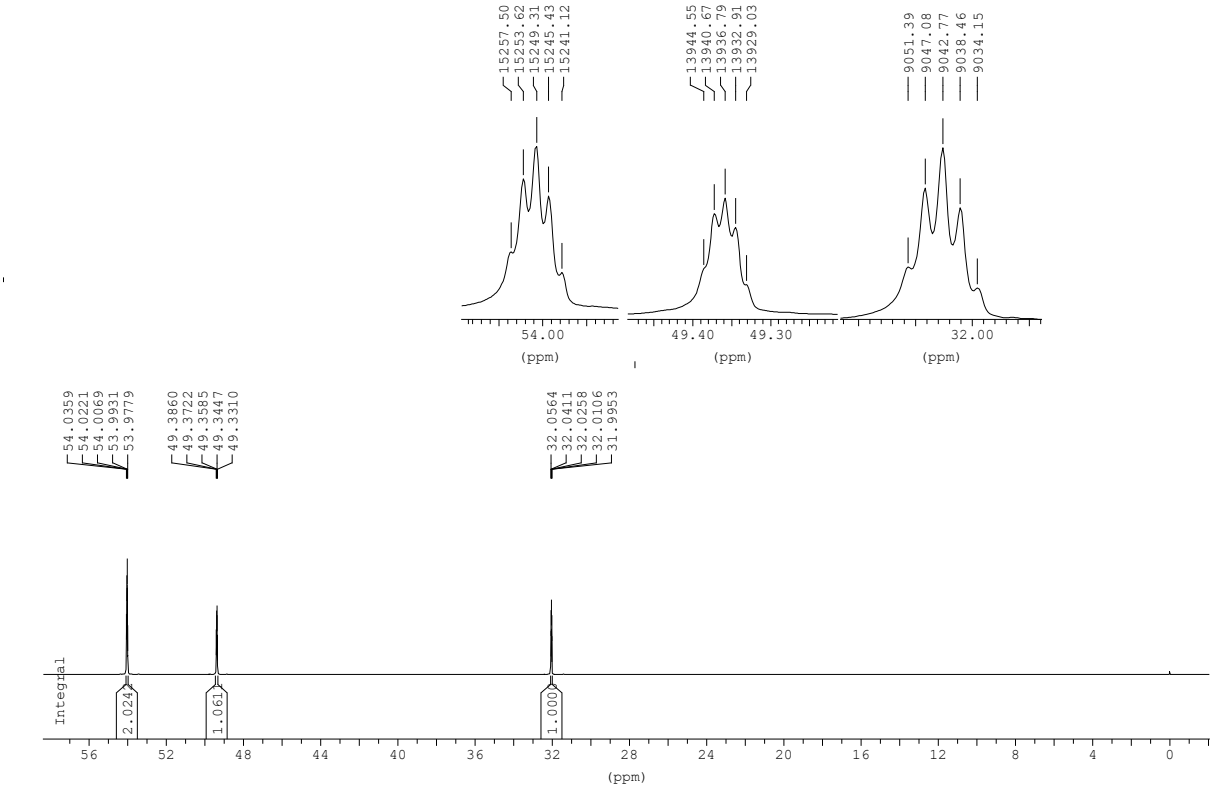
Hexadecafluoro-2,12-dithiapentacyclo[11.7.0.0^{3,11}.0^{5,9}.0^{15,19}]icosa-1(13),3,5(9),10,14,19-hexaene 8. A solution of compound **9** (338.0 mg, 0.95 mmol) in DMF (3 ml) was added to a mixture of solution of thiol **7** (294.9 mg, 0.94 mmol) in DMF (3 ml) and Na_2CO_3 (111.8 mg, 1.05 mmol). The reaction mixture was stirred for 3 h at room temperature and was poured into 15% aq. HCl (6 ml). The mixture was extracted with DCM (3×2 ml), the combined extract was separated, dried with $CaCl_2$ and the solvent was removed *in vacuo* to give 538.3 mg (98.4% HPLC) of the crude product which was purified by recrystallization from hexane-$CHCl_3$ mixture. Yield 90%. M.p. 153-155ºC. IR (KBr), ν, cm^{-1}: 2926, 2854, 1591, 1458, 1439, 1331, 1306, 1248, 1213, 1159, 1092, 1065, 951, 895, 706, 675, 600, 579, 554. UV spectrum (hexane), λ_{max}, nm (log ε): 235 (4.45), 264 (3.91).227 (4.08), 262 (4.47), 306 (4.02). ^{13}C NMR, *δ*, ppm:112.4 t.quintet (7,17-$\underline{C}F_2$, ^1J 276.5, ^2J 25 Hz), 113.2 t.t (6,8,16,18- $\underline{C}F_2$, ^1J 262, ^2J ~26 Hz), 120.7 m, 130.0 m, 151.2 d.d (^{4,10,14,20}C ^1J 264, J 6 Hz). ^{19}F NMR, *δ*, ppm: 32.0 quintet (4F, 7,17-CF_2, J 4.5 Hz), 49.4 m (4F, $F^{4,10,14,20}$), 54.0 m (8F, 6,8,16,18-CF_2). Found, %: C 37.22; F 52.04; S 10.92. M^+ 583.9184. $C_{18}F_{16}S_2$. Calculated, %: C 37.00; F 52.02; S 10.98. M^+ 583.9180.

UV spectrum of **8** (hexane).

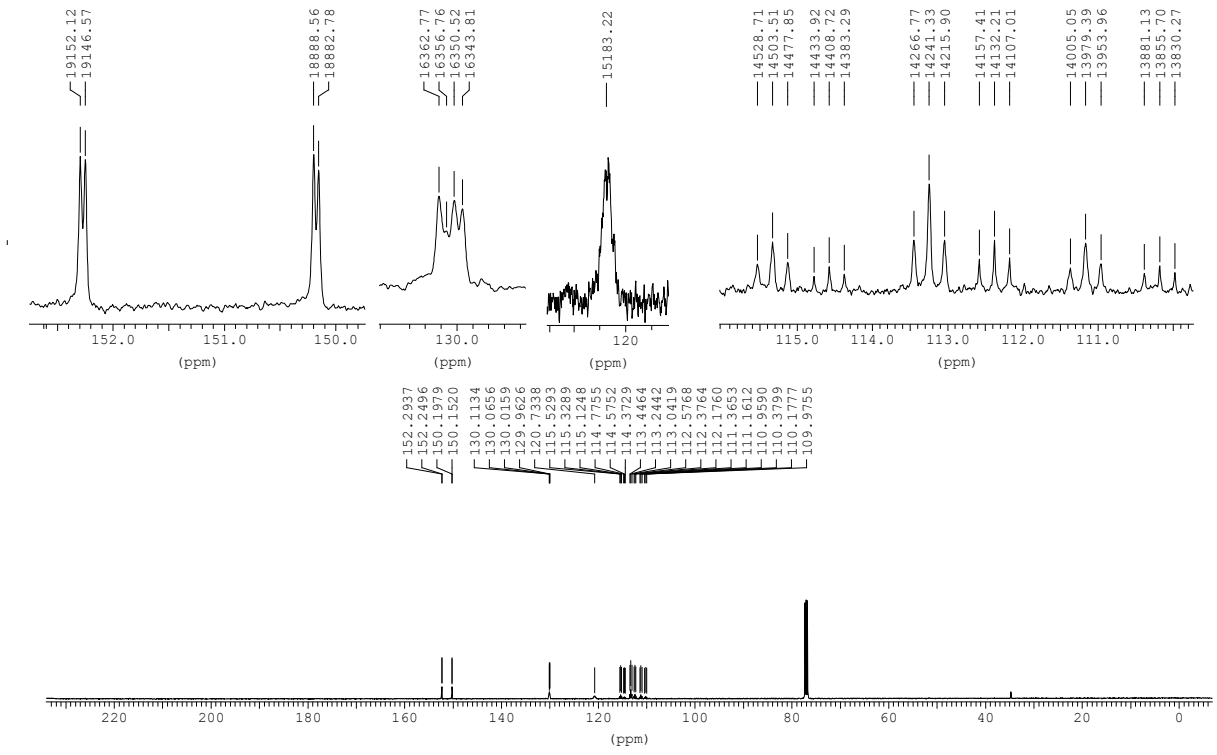


IR spectrum of **8** (KBr).

^{19}F NMR spectrum ($CDCl_3$, C_6F_6 δ_F =0.0 ppm) Bruker Avance – 300 (282.36 MHz) of **8.**

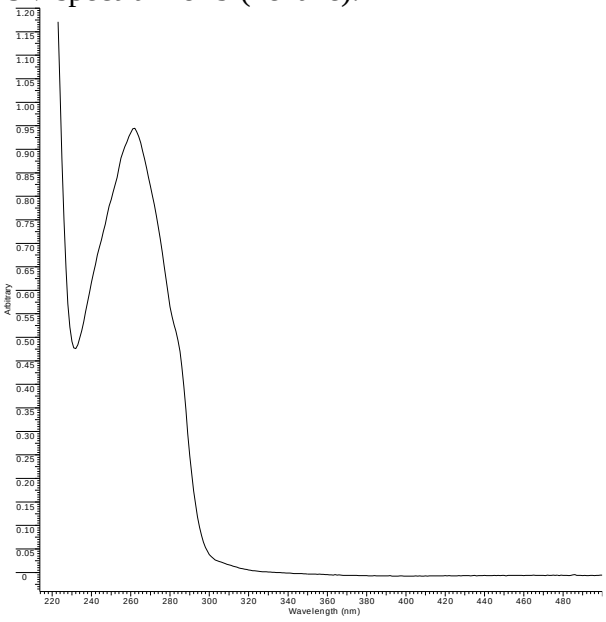


^{13}C NMR spectrum ($CDCl_3$, δ_C =77.0 ppm) Bruker DRX– 500 (125.78 MHz) of **8.**

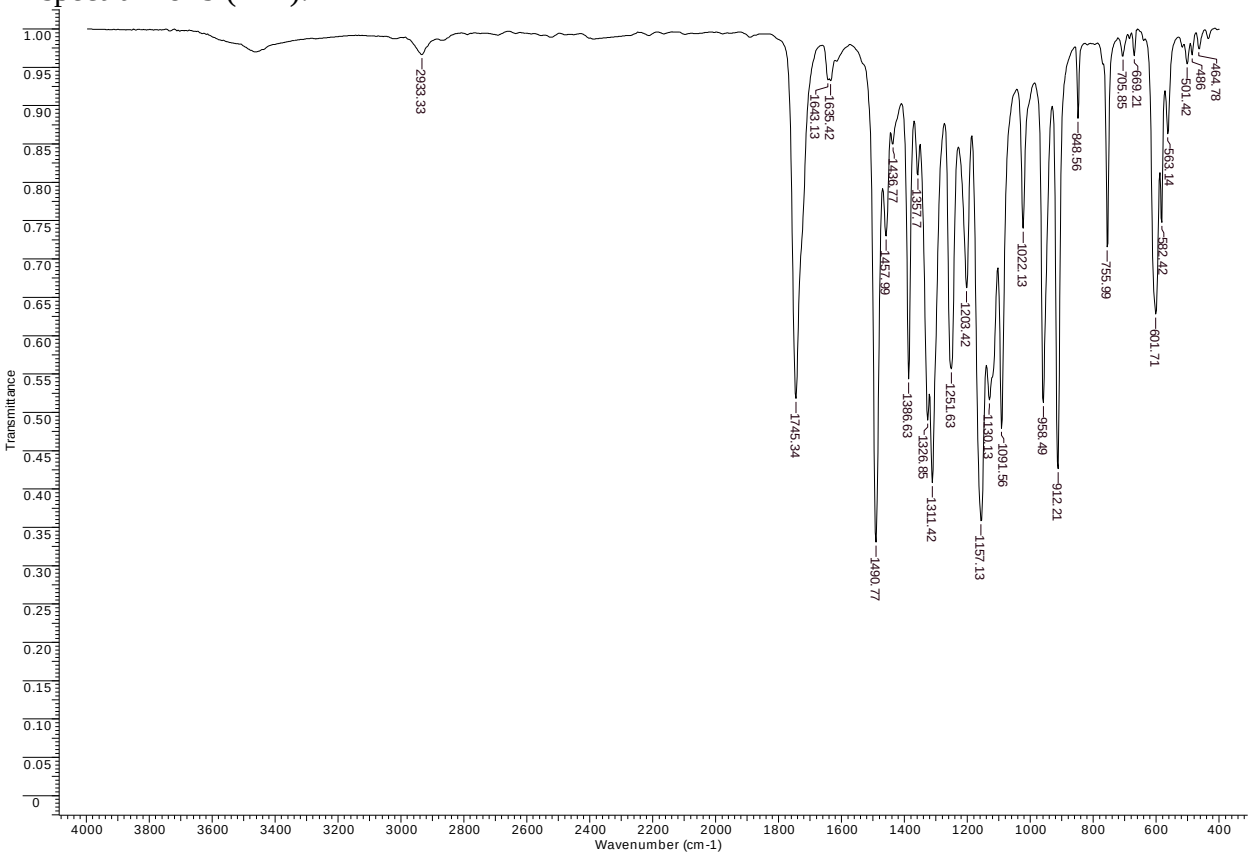


1-(Nonafluoroindane-5-sulfanyl)ethan-1-one 9. Solid K_2CO_3 (0.45 g, 3.26 mmol) and acetyl chloride (0.50 g, 6.37 mmol) were added to a solution of nonafluoroindane-5-thiol **7** (0.95 g, 3.04 mmol) in $CHCl_3$ (5 ml) and the reaction mixture were stirred for 16 h. Then the reaction mixture was diluted with H_2O (10 ml), the organic phase was separated, dried with $CaCl_2$ and the solvent was removed under reduced pressure to give 1.01 g of compound **9** (2.81 mmol) of 98.7% purity (GC). Yield 92%. IR (film), ν, cm^{-1}: 2933, 1745, 1643, 1635, 1491, 1458, 1437, 1387, 1358, 1327, 1311, 1252, 1203, 1157, 1130, 1092, 1022, 958, 912, 849, 756, 706, 669, 602, 582, 563. Colorless liq. UV spectrum (hexane), λ_{max}, nm (log ε): 262 (3.98). ^{1}H NMR, δ, ppm: 2.52 s (CH_3). ^{13}C NMR δ, ppm: 30.0 s (CH_3), 112.4 t.quintet (2-CF_2, ^1J 276, ^2J 25 Гц), 113.5 t.t ((1(3)-CF_2), ^1J ~262, ^2J ~25 Гц), 115.3-116.0 group of signals, 123.2 m, 143.5 d.d.d (^1J 264, ^2J ~16, J 5 Гц), 153.9 d.d.d.t (^1J 262, ^2J 12, J 3, J ~1 Гц), 154.3 d.t (^1J 262, J 3 Гц), 187.0 s (CO). ^{19}F NMR, δ, ppm: 22.1 d.d.t (1F, F^7, $J_{F^7\text{-}F^6}$ 22, $J_{F^7\text{-}F^4}$ ~20, $J_{F^7\text{–}1\text{-}CF_2}$ 7 Hz), 32.1 quintet (2F, 2-CF_2, $J_{2\text{-}CF_2\text{–}1,3\text{-}CF_2}$ ~5 Hz), 49.8 br.d (1F, F^6, $J_{F^6\text{-}F^7}$ 22 Hz), 54.3 m (2F, 1(3)-CF_2), 55.1 m (2F, (1(3)-CF_2), 55.2 br.m (1F, F^4). Found, %: C 37.34; H 0.95; F 48.23; S 9.30. [*M*-F]$^+$ 334.9775. $C_{11}H_3F_9OS$. Calculated, %: C 37.30; H 0.85; F 48.27; S 9.05. [*M*-F]$^+$ 334.9771.

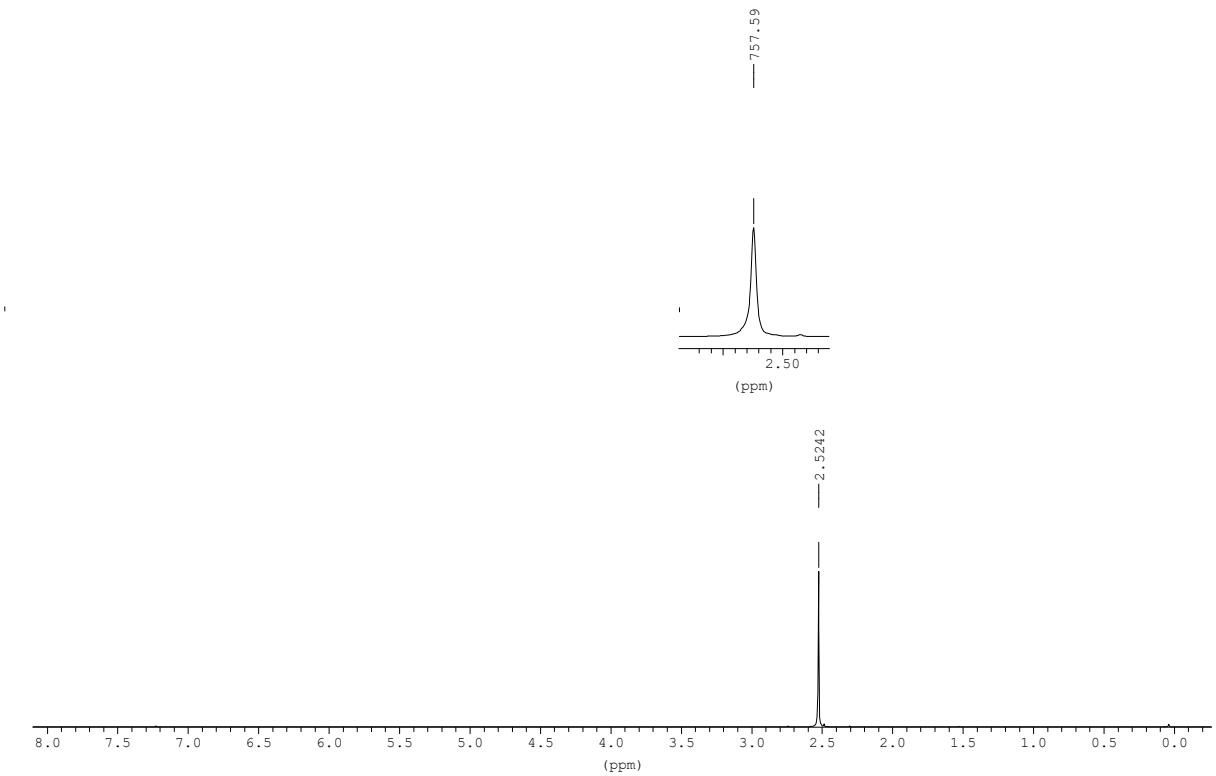
UV spectrum of **9** (hexane).



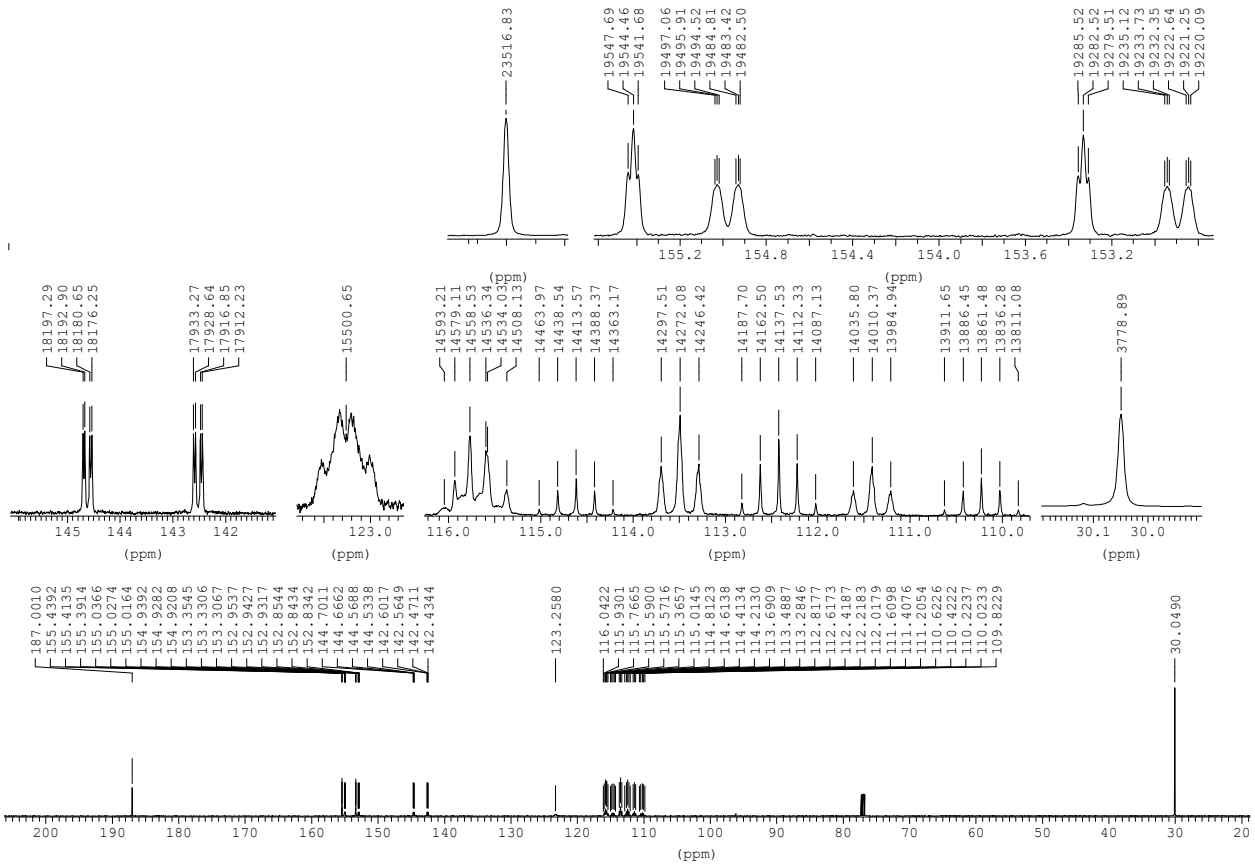
IR spectrum of **9** (film).



^{1}H NMR spectrum ($CDCl_3$, HMDS δ_H =0.04 ppm) Bruker Avance – 300 (300.13 MHz) of **9.**



^{13}C NMR spectrum ($CDCl_3$, δ_C =77.0 ppm) Bruker DRX– 500 (125.78 MHz) of **9.**



^{19}F NMR spectrum ($CDCl_3$, CF_6 δ_F =0.0 ppm) Bruker Avance – 300 (282.40 MHz) of **9.**