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Reactions of 1-alkylsulfanyl- and 1-alkylsulfonyl-2,3,5,6-tetrafluorobenzenes with nitromethane and DBU

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General. The NMR spectra of reaction mixtures or individual compounds were recorded on Bruker AV-300 [300.13 (^{1}H) MHz, 282.4 (^{19}F) MHz], Bruker AV-400 [400.13 (^{1}H) MHz, 100.61 (^{13}C) MHz], Bruker AV-600 [150.95 (^{13}C) MHz] or Bruker DRX-500 [125.76 (^{13}C) MHz] spectrometers for solutions of samples in $CDCl_3$ or CD_3CN. IR spectra were recorded on a Bruker Vector 22 spectrophotometer from pellets with KBr for solids and from films for liquid samples. UV spectra were obtained on a Hewlett Packard 8453 spectrophotometer from solutions in ethanol. The molecular mass was determined from high resolution mass spectra taken on a Thermo Electron Corporation DFS instrument (ionizing electrons energy 70 eV) or on vapor pressure osmometer KNAUER K-7000. GC-MS spectra were measured on a Hewlett-Packard G1081A instrument equipped with a gas chromatograph HP 5890 Series II and a mass-selective detector HP 5971 (EI, 70 eV), capillary column HP-5 (5% of diphenyl-, 95% dimethylsiloxane) 30 m × 0.25 mm × 0.25 μm, carrier gas helium, flow rate 1 mL/min. Injector temperature 280 °C, ion source temperature 173 °C. Scanning rate 1.2 scan/s in mass region 30–650 a.u.m. The melting points were measured on a Mettler Toledo Thermosystem FP-90 apparatus. The elemental analyses were obtained on a Carlo Erba CHN-analyzer with a modified sample combustion tube,[S1] after combustion, sulfur was determined by titration with $BaNO_3$ by the procedure FR.1.31.2010.07509, and fluorine was determined by spectrophotometry.[S2]

Yields of products were determined by ^{19}F NMR spectroscopy using C_6H_5F or CF_3CO_2H as a quantitative internal references.

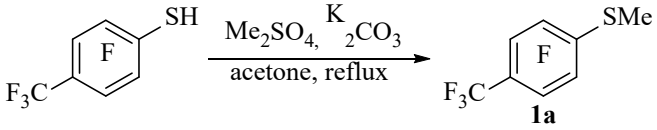
Materials.

Starting compounds were commercially available products of reagent grade and, if necessary, were purified in the usual manner before use.

Acetyl bromide and 100% HNO_3 were obtained according to[S3] and[S4] respectively.

Starting polyfluoroarenes were obtained by following literature methods: 1-(benzylsulfanyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (**1b**),[S5] 1-[(difluoromethyl)sulfanyl]-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (**1c**) and 3-[(difluoromethyl)sulfanyl]-1,2,4,5-tetrafluorobenzene (**1d**),[S6] 1,2,4,5-tetrafluoro-3-methanesulfonylbenzene (**4a**),[S7] 1,2,4,5-tetrafluoro-3-phenylmethanesulfonylbenzene (**4b**), 1,2,4,5-tetrafluoro-3-phenylmethanesulfonyl-6-(trifluoromethyl)benzene (**4d**), 3-difluoromethanesulfonyl-1,2,4,5-tetrafluorobenzene (**4e**), 1-difluoromethanesulfonyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (**4f**).[S8]

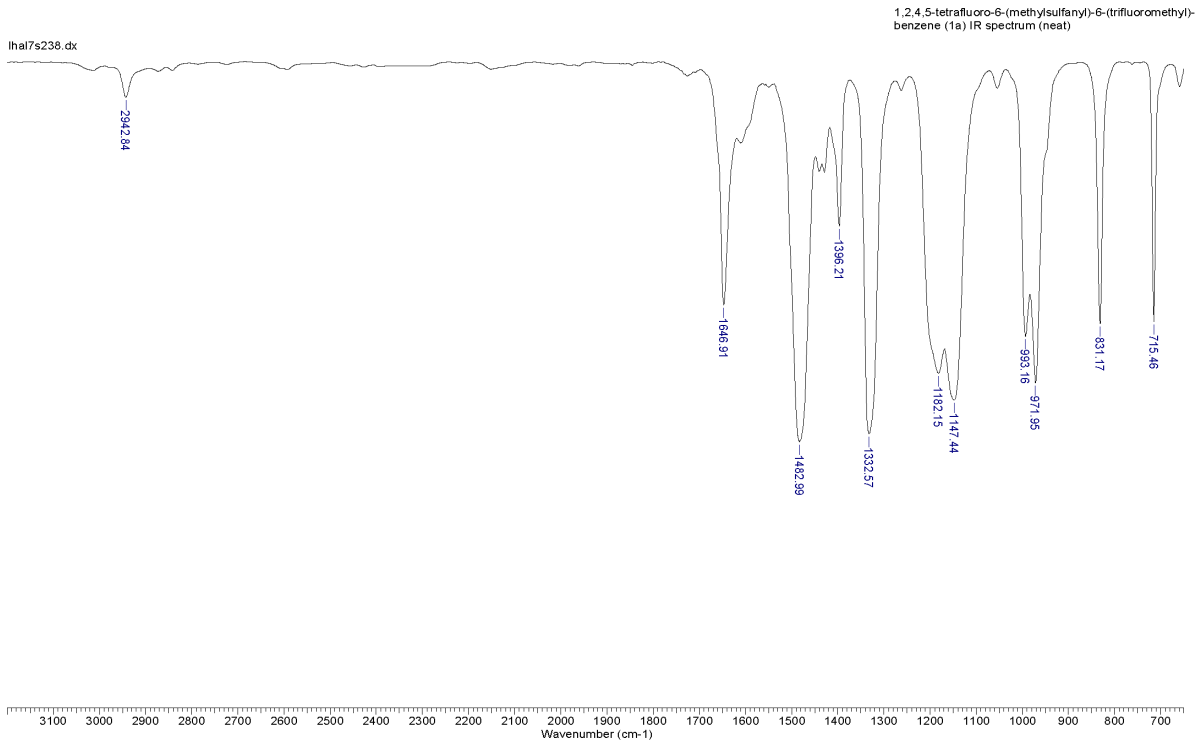
1,2,4,5-Tetrafluoro-3-(methylsulfanyl)-6-(trifluoromethyl)benzene (1a).



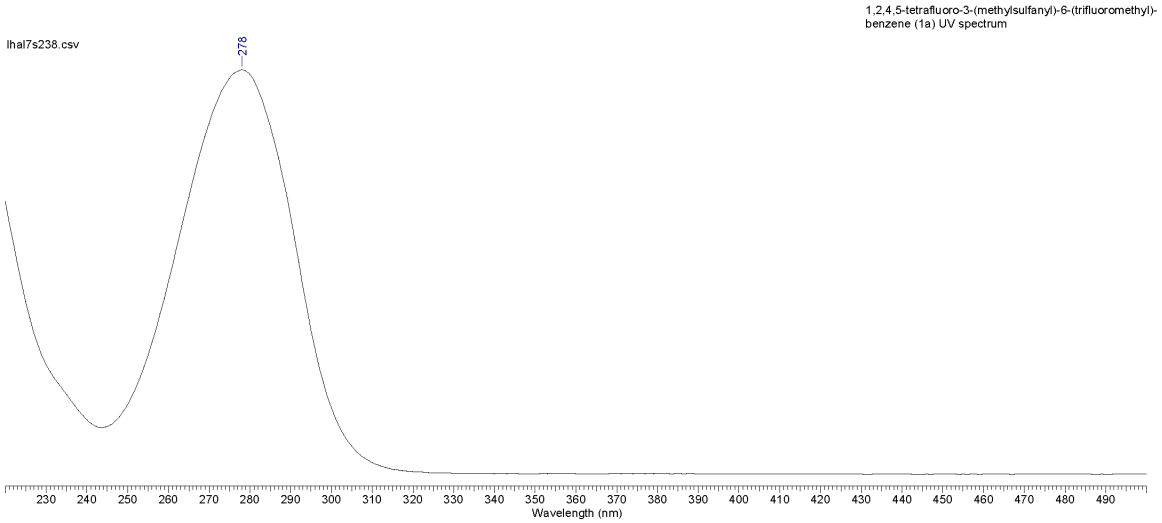
1a

2,3,5,6-Tetrafluoro-4-(trifluoromethyl)benzenethiol (124.92 g, 0.499 mol) was added to the mixture of dimethyl sulfate (69.51 g, 0.551 mol) and K_2CO_3 (75.41 g, 0.546 mol) in acetone (0.5 l) with stirring for 40 min. After completion of the addition, the resulting mixture was refluxed with stirring for 10.5 hours, the progress of the reaction was monitored by ^{19}F NMR. When the reaction was finished, ~1/2 of resulting mixture by volume was distilled off, residue was poured into water (1 l), organic layer was separated and washed with water (2 × 1 l) and was steam distilled. 120.79 g (yield - 92 %) of sulfane **1a** was obtained. Colorless liquid. IR (neat, ν_{max}, cm^{-1}): 2943(w) (CH), 1647(s) (ArF), 1483(vs) (ArF), 1396(m) (CF), 1333(vs) (CF), 1182(s) (CF), 1147(s) (CF), 993(s) (CF), 972(s), 831(s), 715(s) (C-S). UV, λ_{max}, nm (log ε): 278 (3.97). ^1H NMR [$CDCl_3$, 400.13 MHz]: δ_H 2.60 (t, $^5J_{HF}$ 1.3, 3H, C<u>H</u>$_3$S) ppm; ^{13}C NMR [$CDCl_3$, 125.76 MHz]: δ_C 16.8 (t, $^4J_{CF}$ 5.1, <u>C</u>H_3S), 107.8 (qt, $^2J_{CF}$ 34.9, $^2J_{CF}$ 12.9, C-(6)), 122.5 (t, $^2J_{CF}$ 19.0, C-(3)), 120.9 (q, $^1J_{CF}$ 274.2, <u>C</u>F_3), 144.1 (ddd, $^1J_{CF}$ 260.8, $^2J_{CF}$ 17.3, $^3J_{CF}$ 1.4, C-(2,4) or C-(1,5)), 146.3 (ddt, $^1J_{CF}$ ~247, $^2J_{CF}$ ~14, $^{3,4}J_{CF}$ ~4, C-(2,4) or C-(1,5)), ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -141.9 (m, 2F, F-(1,5)), -135.0 (m, 2F, F-(2,4)), -57.5 (t, $^4J_{FF}$ 21.7, 3F, C<u>F</u>$_3$) ppm. Anal. calcd for $C_8H_3F_7S$, %: C 36.37; H 1.14; F 50.34; S 12.14; M^+ 263.9838. Found, %: C 36.48; H 1.45; F 50.33; S 12.22; M^+ 263.9842.

IR spectrum of **1a**.

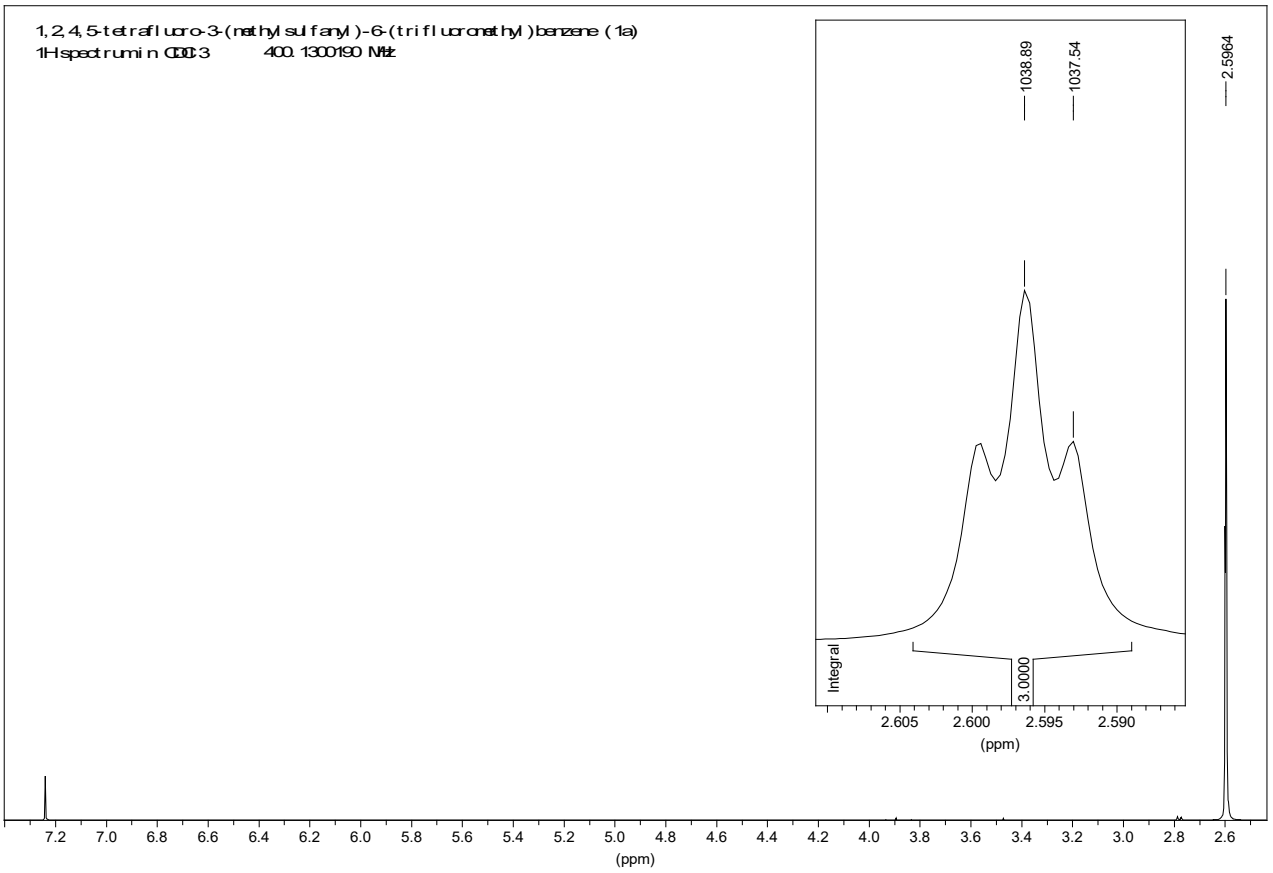


UV spectrum of **1a**.

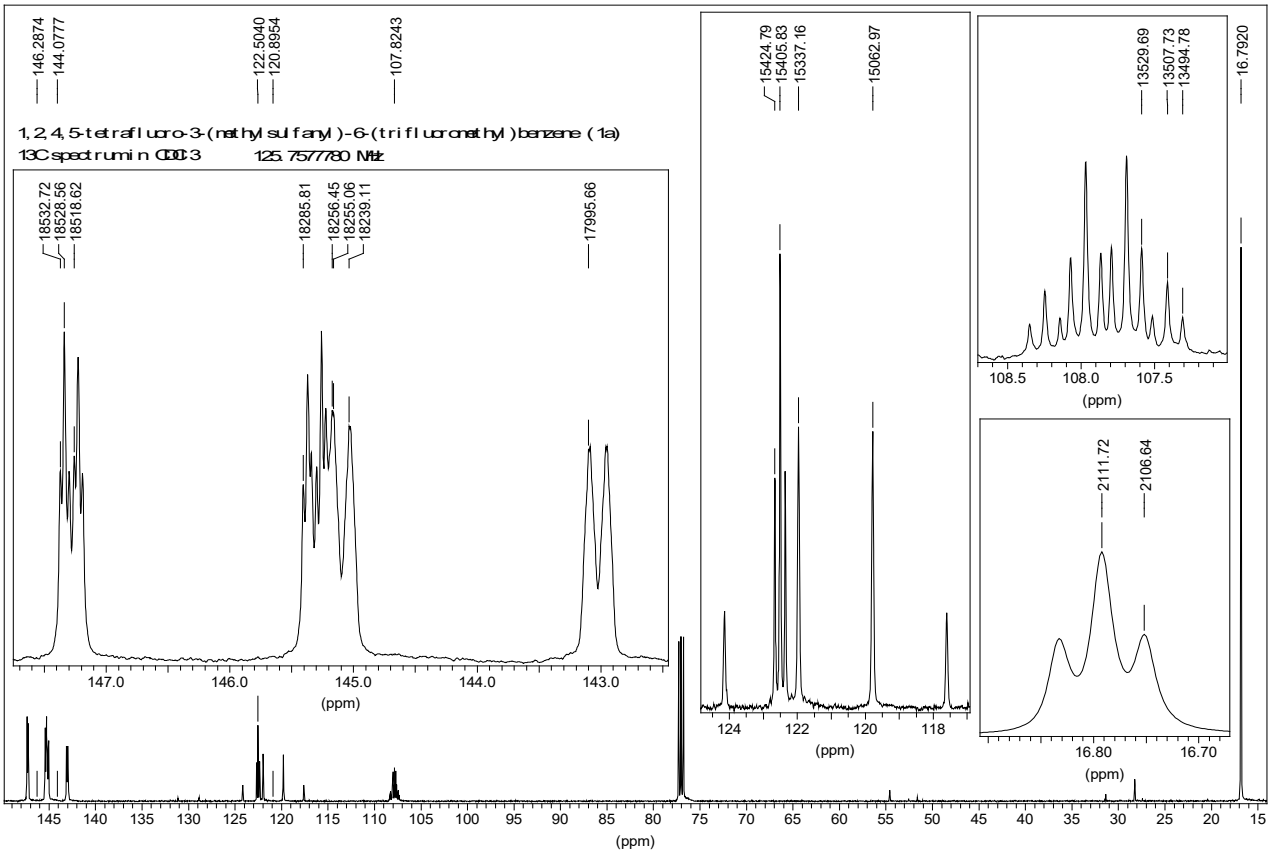


No	nm	A	FWHH	Asym	Intensity
1	278.00	0.966	31.95	-0.21	VS

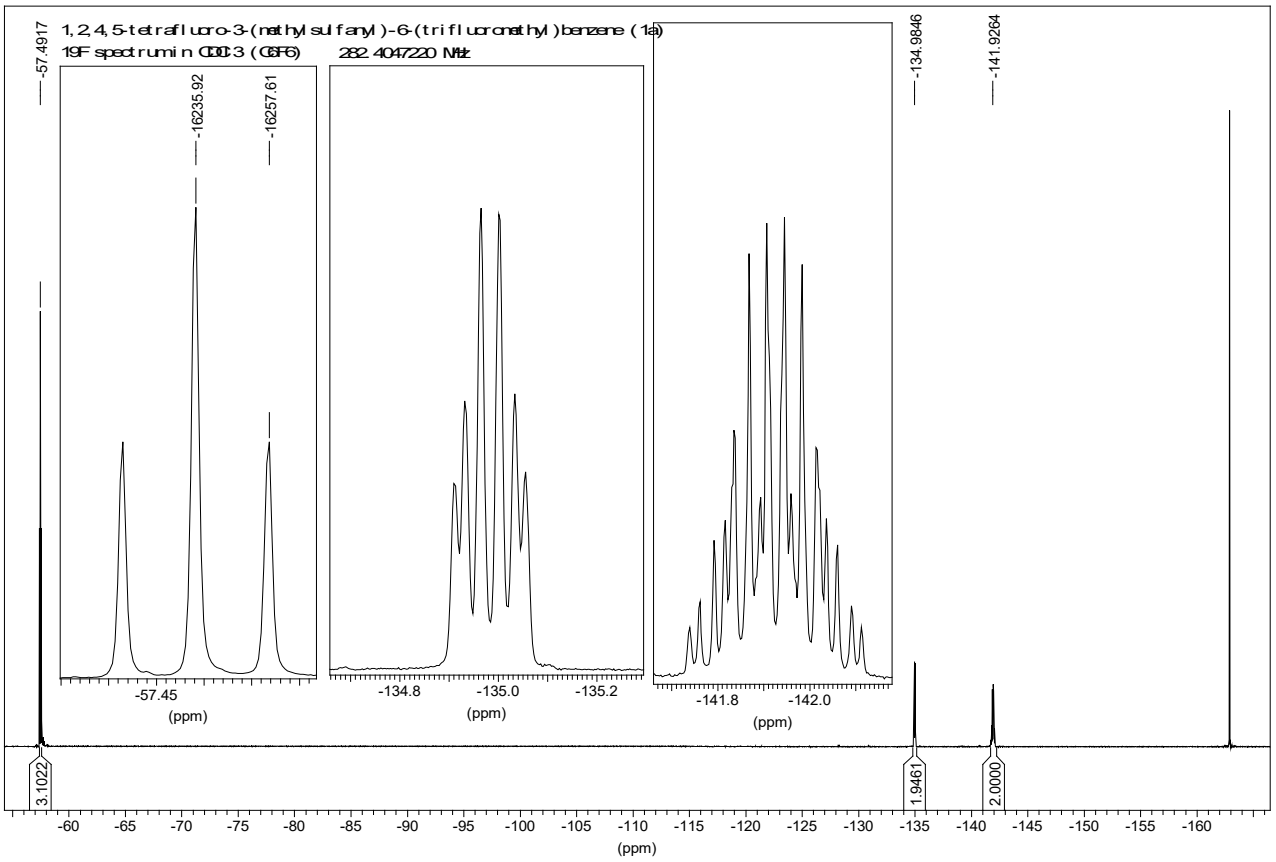
^{1}H NMR spectrum of **1a**.



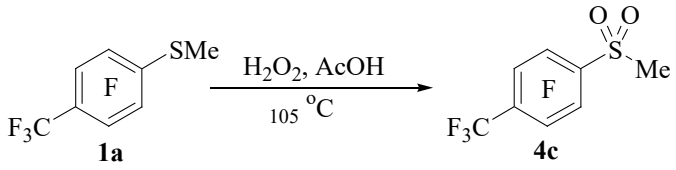
^{13}C NMR spectrum of **1a**.



^{19}F NMR spectrum of **1a**.

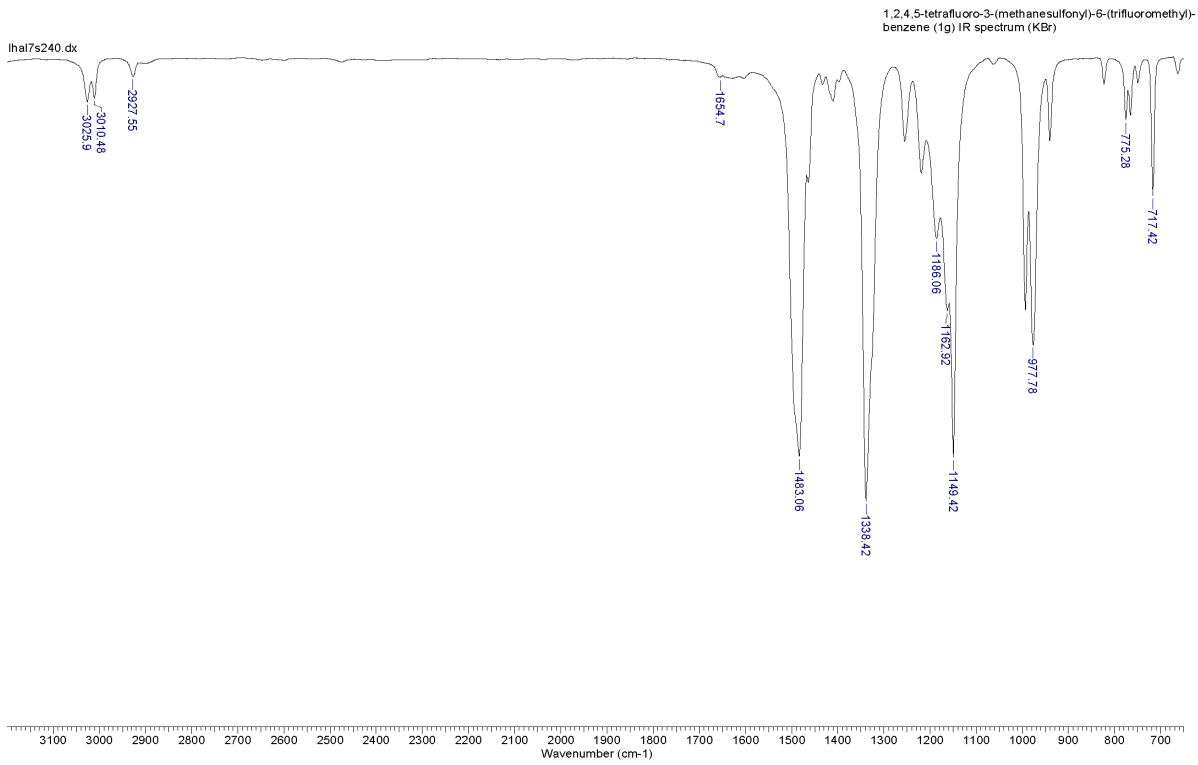


1,2,4,5-Tetrafluoro-3-methanesulfonyl-6-(trifluoromethyl)benzene (4c).

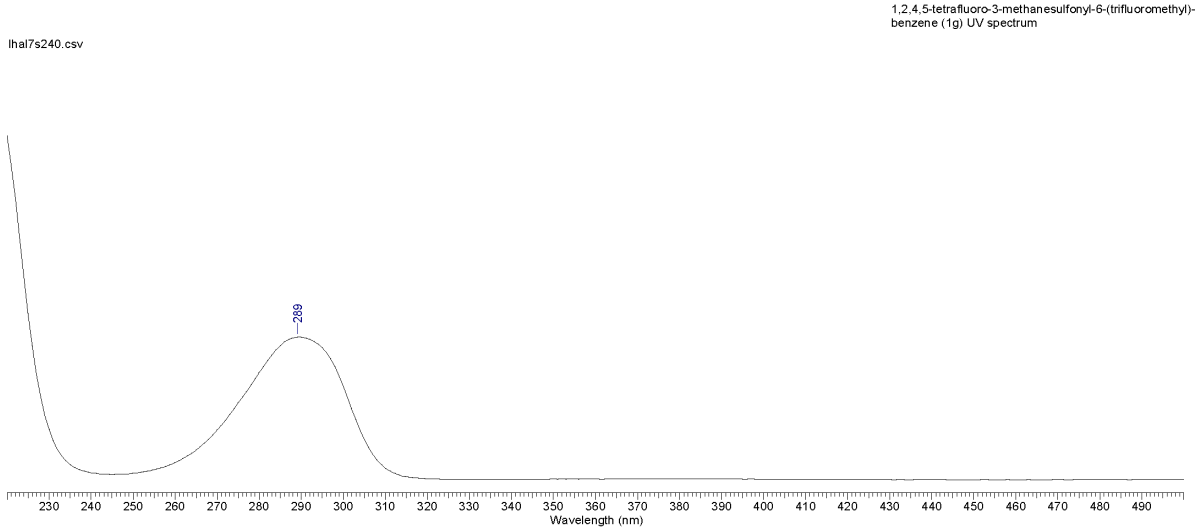


Glacial AcOH (150 ml, *ca* 2.62 mol) was added to the water solution of H_2O_2 (33 %, 150 ml, *ca* 1.64 mol), then sulfane **1a** (45.36 g, 171.71 mmol) was added with stirring. Resulting mixture was stirred at 105 °C for 6 h, progress of reaction was monitored by ^{19}F NMR. After completion of the reaction, the mass was cooled to -20°C, the resulting crystals were filtered and washed first with ice water (100 ml), then with an aqueous solution of Na_2CO_3 (5 %, 2 × 100 ml), then with ice water until neutral, the resulting product was dried in air stream, 47.94 g (yield - 94 %) of arene **4c** was obtained. White crystals. Mp 112-113 °C. IR (KBr, ν_{max}, cm^{-1}): 3026(w) (CH), 3010(vw) (CH), 2928(vw) (CH), 1655(vw) (ArF), 1483(s) (ArF), 1338(s) (SO_2), 1186(m) (CF), 1163(m) (CF), 1149(vs) (SO_2), 978(s) (CF), 775(w) (C-S), 717(m) (C-S). UV, λ_{max}, nm (log ε): 289 (3.49). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 3.37 (s, 3H, C<u>H</u>$_3$SO$_2$) ppm; ^{13}C NMR [$CDCl_3$, 125.76 MHz]: δ_C 45.8 (<u>C</u>H$_3$SO$_2$), 114.6 (qd, $^2J_{CF}$ 35.4, $^2J_{CF}$ 12.5, C-(6)), 120.0 (q, $^1J_{CF}$ ~276, <u>C</u>F$_3$), 123.9 (t, $^2J_{CF}$ 14.8, C-(3)), 143.1 – 145.9 (m, C-(1,2,4,5)) ppm; ^{19}F NMR [$CDCl_3$, 282.40 MHz]: δ_F -137.1 (m, 2F, F-(1,5)), -135.8 (m, 2F, F-(2,4)), -58.0 (t, $^4J_{FF}$ 22.1, 3F, C<u>F</u>$_3$) ppm. Anal. calcd for $C_8H_3F_7O_2S$, %: C 32.44; H 1.02; F 44.90; S 10.83; M^+ 295.9737. Found, %: C 32.30; H 1.36; F 45.22; S 10.70; M^+ 295.9736.

IR spectrum of **4c**.

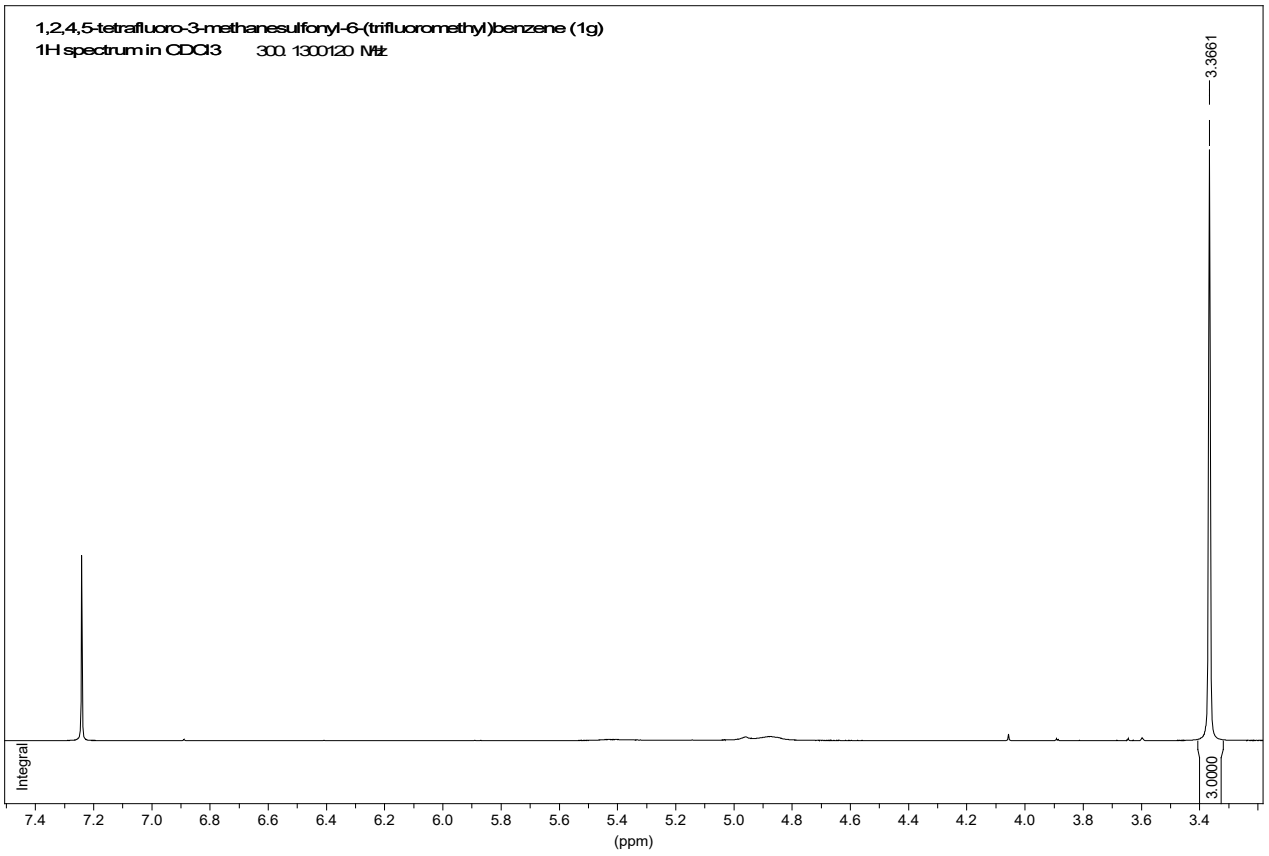


UV spectrum of **4c**.

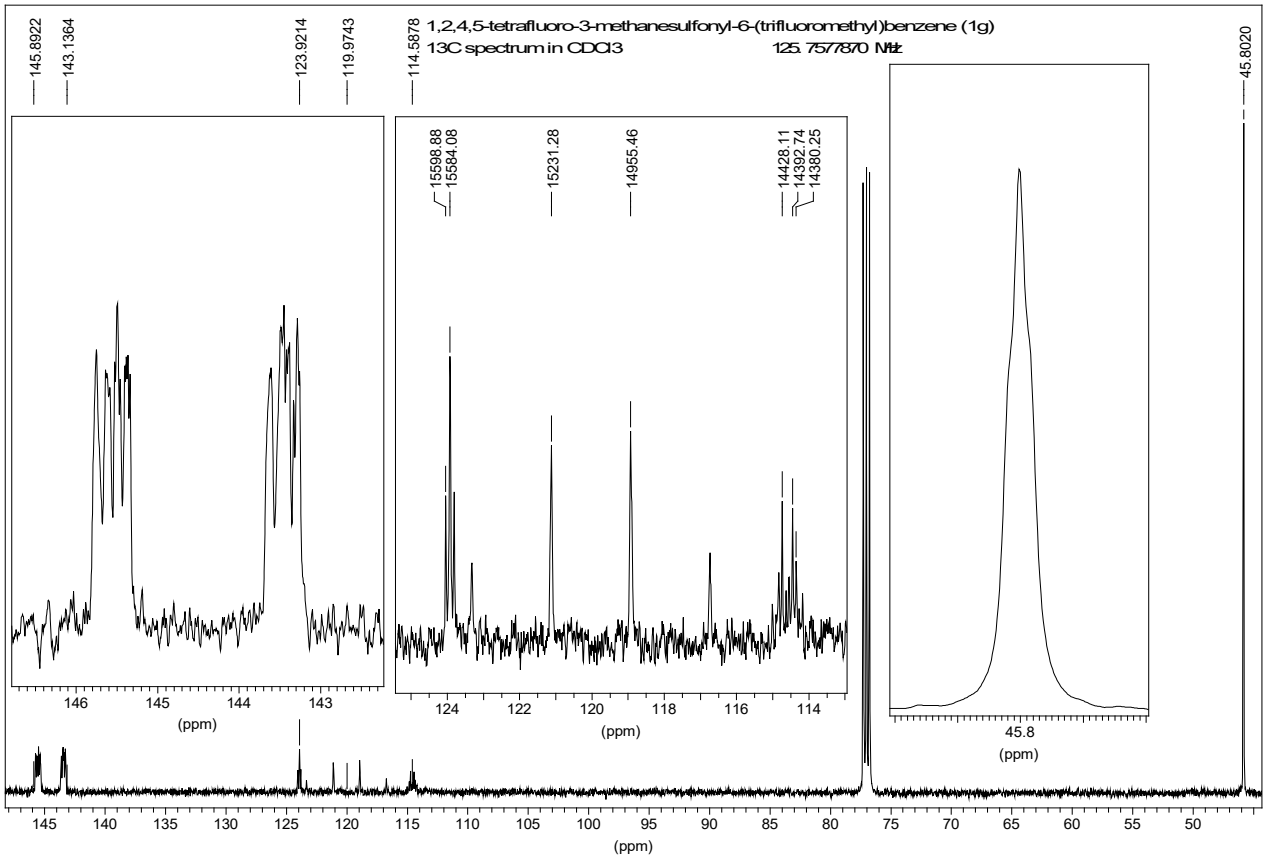


No	nm	A	FWHH	Asym	Intensity
1	289.00	0.312	28.38	-0.16	M

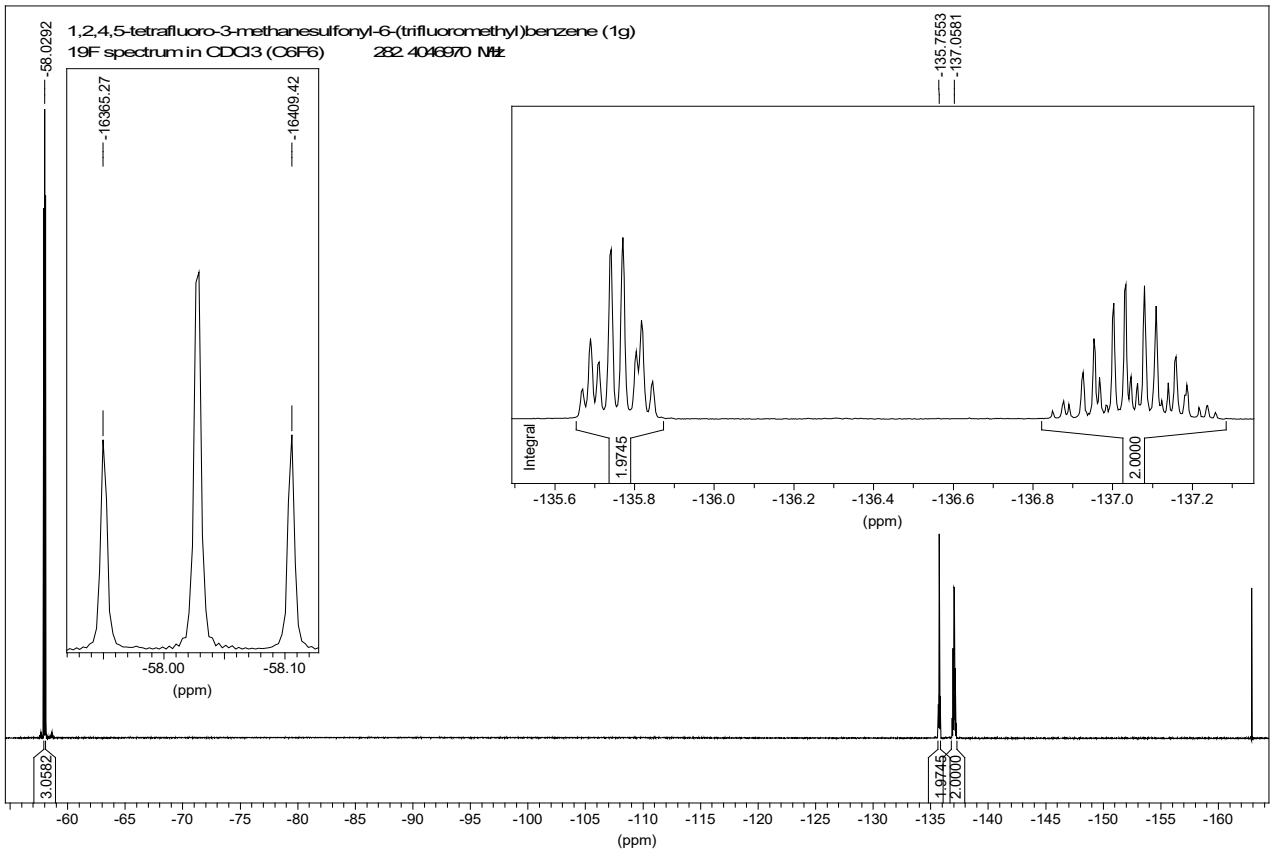
^{1}H NMR spectrum of **4c**.



^{13}C NMR spectrum of **4c**.



^{19}F NMR spectrum of **4c**.



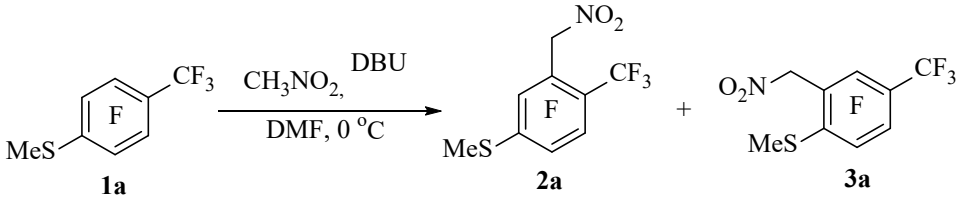
Reactions of 1-alkylsulfanyl and alkylsulfonyl-4-X-2,3,5,6-tetrafluorobenzenes with nitromethane (*general procedure*). To a certain volume of a solution containing DBU (concentration ~2M) and nitromethane (concentration ~13M) in the selected solvent cooled to the reaction temperature, the same volume of ~1M arene solution was added. The addition should be slow to avoid overheating of the reaction mass. The obtained mixture was stirred for the definite time, progress of reaction was monitored by ^{19}F NMR. At the end of the reaction, the mixture was poured into a ~3% aqueous HCl solution containing a 2-fold molar excess relative to DBU and cooled to 0 °C. The mixtures were then processed as shown below:

1) In case of sulfanes **1a-d** and sulfones **4e-f** the mixture was extracted with Et_2O (2×150 ml in case of **1a-b**, **d**, **4e,f**, 2×20 ml in case of **1c**), the combined organic layer was dried $MgSO_4$, the solvent was evaporated, the residue processed as shown in every individual example.

2) In case of sulfones **4a,b**, the mixture consisting of precipitate and aqueous solution was washed with hexane (3×250 ml) with stirring. The organic layer was separated, the residue was cooled to 3 °C, the precipitate was filtered, washed with water and dried in air stream. The hexane solutions were combined, the solvent was evaporated, the residue was analyzed by ^{1}H, ^{19}F NMR and GC-MS.

3) In case of sulfones **4c,d**, the mixture was extracted with hexane (2×400 ml), the combined organic layer was evaporated, the residue was steam distilled, thus, 1,2,4,5-tetrafluoro-3-(nitromethyl)-6-(trifluoromethyl)benzene (**6'**) was obtained. The residue after distillation was separated from water and recrystallized from $CHCl_3$, thus, nitromethyl derivatives were obtained.

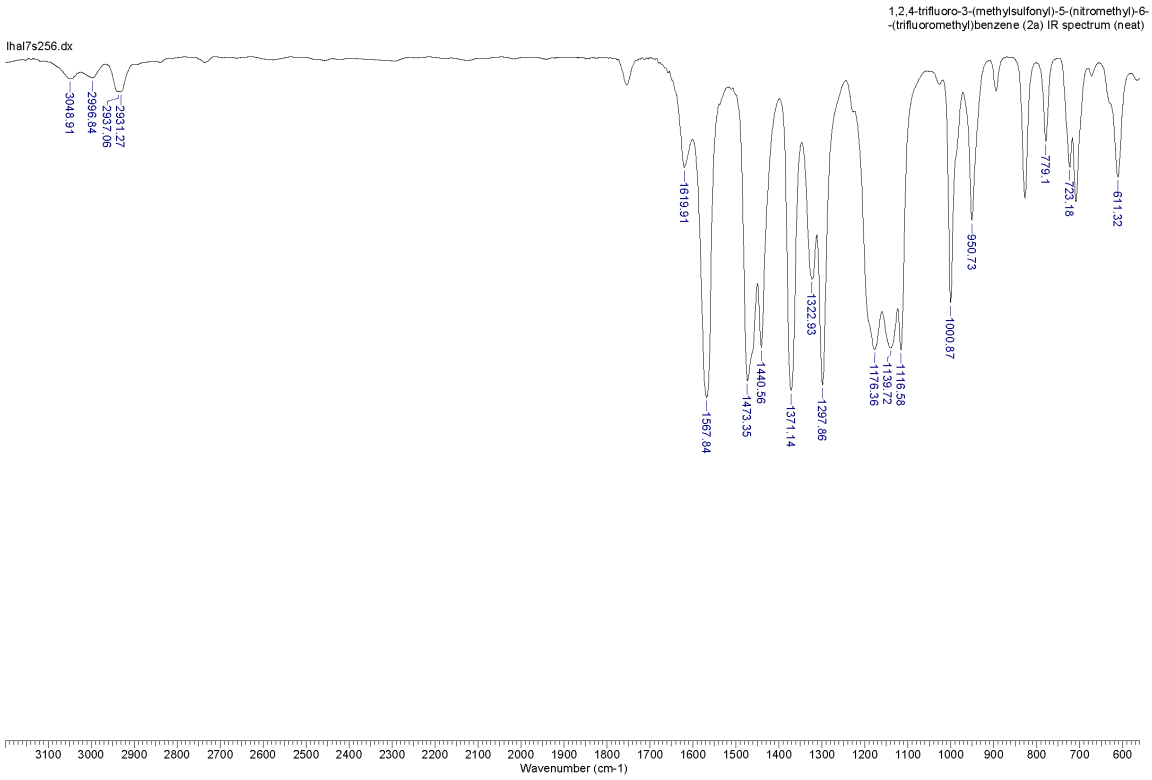
1,2,4-Trifluoro-3-methylsulfanyl-5-nitromethyl-6-(trifluoromethyl)benzene (2a).



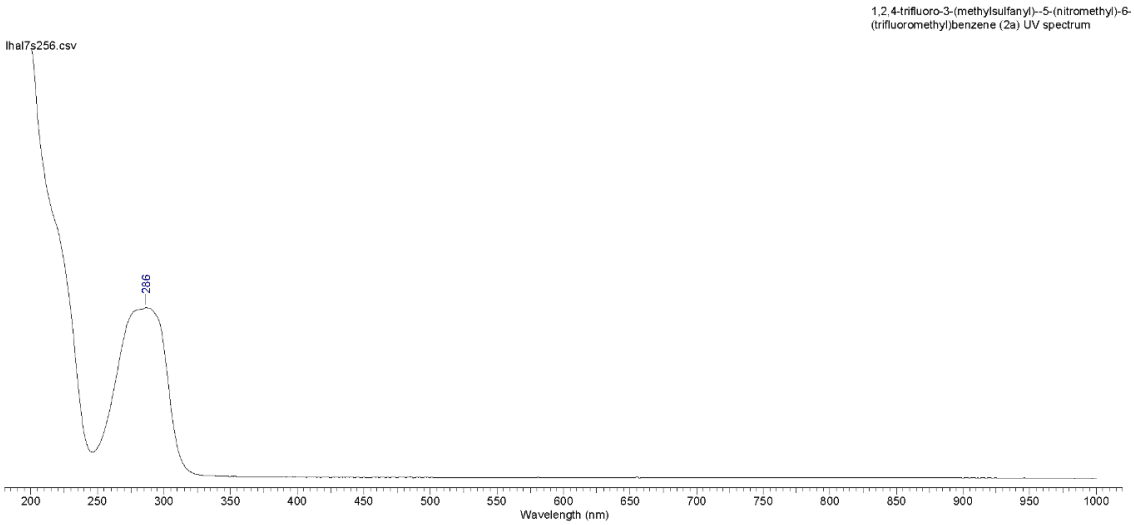
From sulfane **1a** (26.95 g, 102.02 mmol) in DMF (100 ml), nitromethane (82.36 g, 1.35 mol) and DBU (34.45 g, 226.29 mmol) in DMF (100 ml) at 0 °C for 6.5 h, a 30.10 g of mixture was obtained containing compounds **2a** and **3a** with ratio 93 : 7 according to ^{19}F NMR. A 27.60 g of mixture was obtained after distillation under reduced pressure (86-96 °C, 0.17-0.12 mmHg) containing sulfane **2a** according to ^{19}F NMR (PhF) (yield - 82 %). Pale yellow oil. IR (neat, ν_{max}, cm^{-1}): 3049(vw) (CH), 2997(vw) (CH), 2931(w) (CH), 1620(m) (ArF), 1568(vs) (NO_2), 1473(vs) (ArF), 1441(s) (CF), 1371(vs) (NO_2), 1323(s) (CF), 1298(s) (CF), 1176(s) (CF), 1140(s) (CF), 1117(s) (CF), 1001(s) (CF), 951(m) (C-NO_2), 779(w) (C-S), 723(m) (C-S), 611(m) (C-NO_2). UV, λ_{max}, nm (log ε): 286 (3.88). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 2.61 (s, 3H, C$\underline{H}_3$S), 5.64 (s, 2H, C$\underline{H}_2$NO$_2$) ppm; ^{13}C NMR [$CDCl_3$, 150.91 MHz]: δ_C 16.7 (d, $^4J_{CF}$ ~5, $\underline{C}$H$_3$S), 67.8 ($\underline{C}$H$_2$NO$_2$), 110.9 (dd, $^2J_{CF}$ 19.7, $^3J_{CF}$ 3.5, C-(5)), 117.1 (qdd, $^2J_{CF}$ 33.5, $^3J_{CF}$ 9.3, $^3J_{CF}$ 2.3, C-(6)), 121.8 (dd, $^2J_{CF}$ 24.3, $^2J_{CF}$ 17.3, C-(3)), 121.8 (q, $^1J_{CF}$ 275.1, $\underline{C}$F$_3$), 145.7 (dd, $^1J_{CF}$ 261.3, $^2J_{CF}$ 16.2, C-(1)), 151.7 (ddd, $^1J_{CF}$ 254.3, $^2J_{CF}$ 15.0, $^3J_{CF}$ 6.9, C-(2)), 156.5 (dt, $^1J_{CF}$ 247.4, $^{3,4}J_{CF}$ ~4, C-(4)) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -139.9 (qdd, $^4J_{FF}$ 26.3, $^3J_{FF}$ 21.7, $^5J_{FF}$ 13.2, 1F, F-(1)), -123.4 (dd, $^3J_{FF}$ 21.7, $^4J_{FF}$ 6.2, 1F, F-(2)), -110.4 (dd, $^5J_{FF}$ 13.2, $^4J_{FF}$ 6.2, 1F, F-(4)), -56.2 (d, $^4J_{FF}$ 26.3, 3F, C$\underline{F}_3$) ppm. Anal. calcd for $C_9H_5F_6NO_2S$, %: C 35.42; H 1.65; F 37.35; N 4.59; S 10.50; M^+ 304.9940. Found, %: C 35.30; H 1.78; F 37.23; N 4.52; S 10.41; M^+ 304.9937.

The mixture also contained 1,2,4-trifluoro-6-methylsulfanyl-5-nitromethyl-3-(trifluoromethyl)benzene (**3a**) (yield - 6 %, according to ^{19}F NMR (PhF)). ^{1}H NMR (mixture of isomers) [$CDCl_3$, 300.13 MHz]: δ_H 2.54 (s, 3H, C$\underline{H}_3$S), 5.77 (d, $^4J_{HF}$ 2.4, C$\underline{H}_2$NO$_2$) ppm; ^{19}F NMR (mixture of isomers) [$CDCl_3$, 282.4 MHz]: δ_F -132.0 (dd, $^3J_{FF}$ 21.7, $^5J_{FF}$ 14.7, 1F, F-(1)), -130.6 (quint, $^{3,4}J_{FF}$ 21.7, 1F, F-(2)), -116.8 (qdt, $^4J_{FF}$ 21.7, $^5J_{FF}$ 14.7, $^4J_{FH}$ 2.4, 1F, F-(4)), -57.6 (t, $^4J_{FF}$ 21.7, 3F, C$\underline{F}_3$) ppm. Anal. calcd for $C_9H_5F_6NO_2S$: M^+ 305. Found by GC-MS: M^+ 305, 1S.

IR spectrum of **2a**.

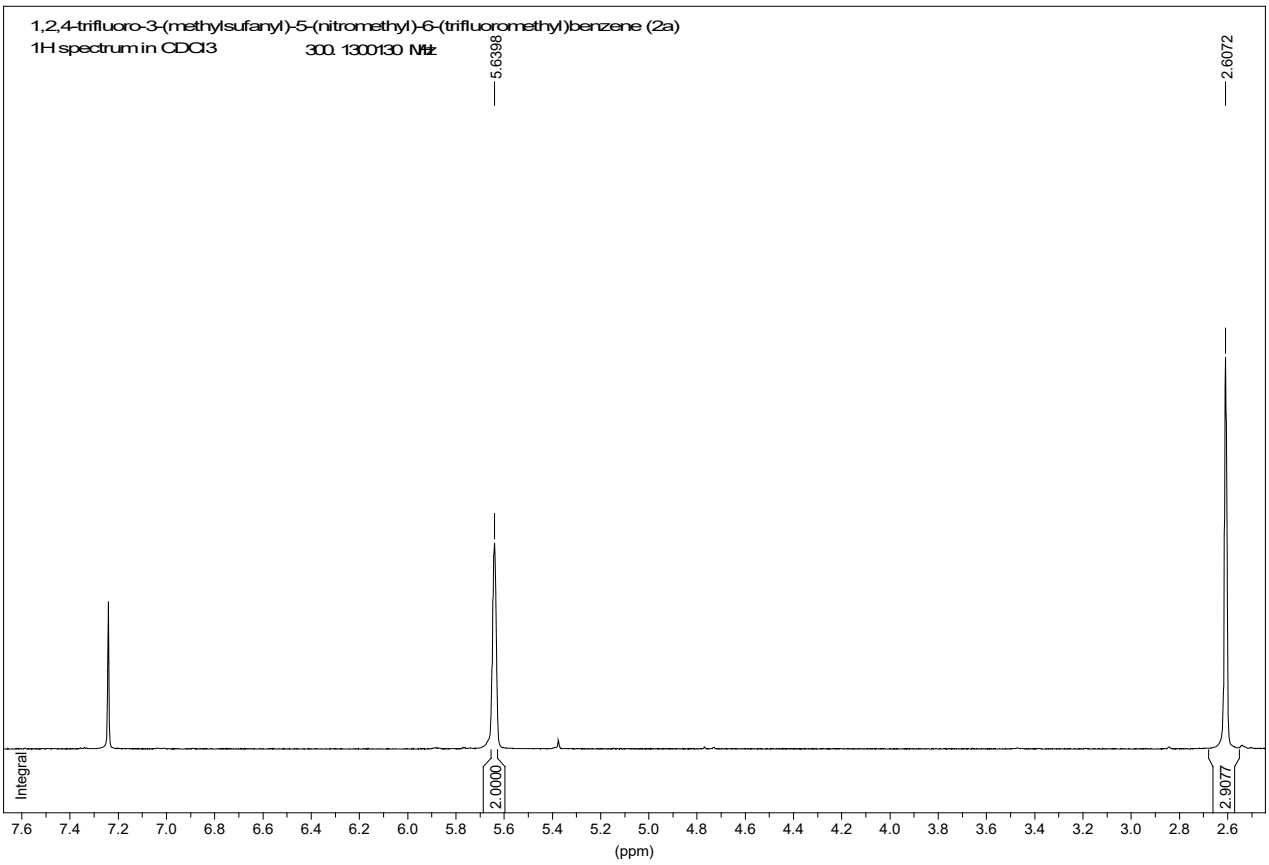


UV spectrum of **2a**.

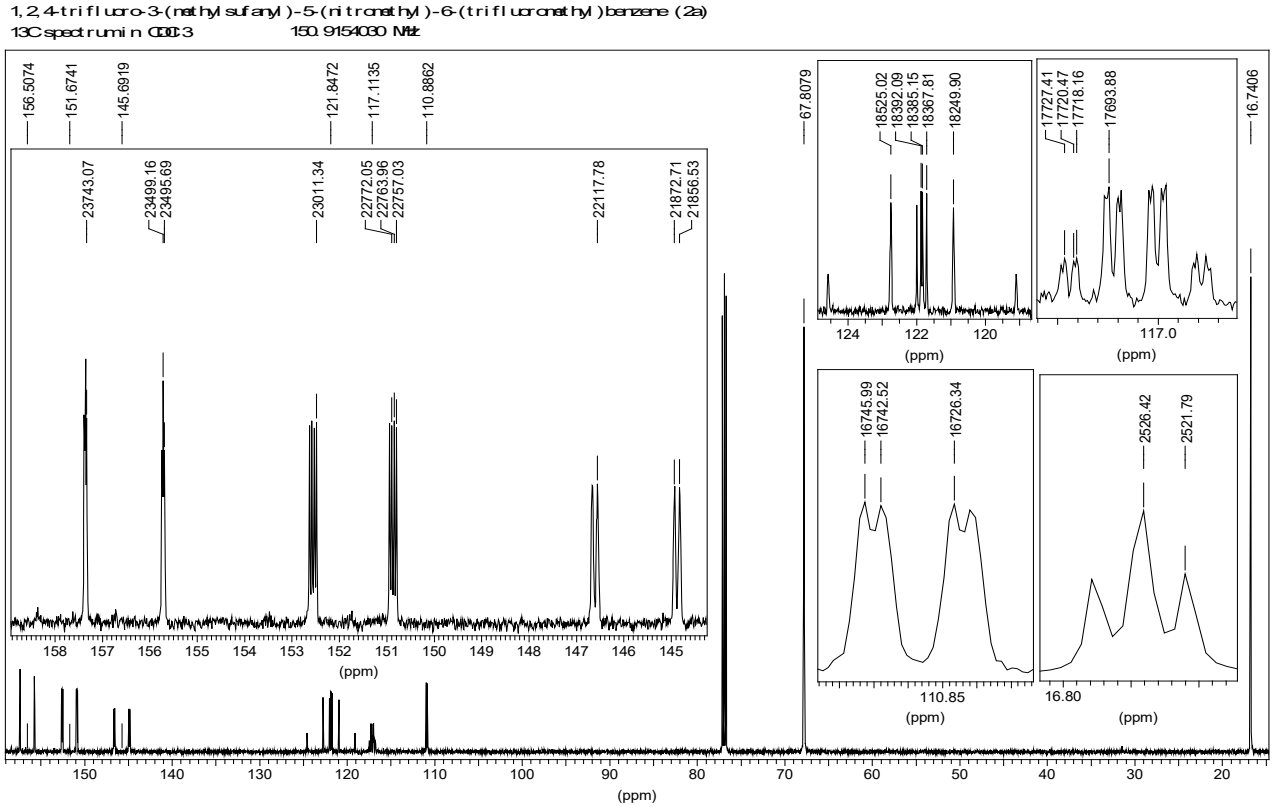


No	nm	A	FWHH	Asym	Intensity
1	286.00	0.390	42.19	-0.35	M

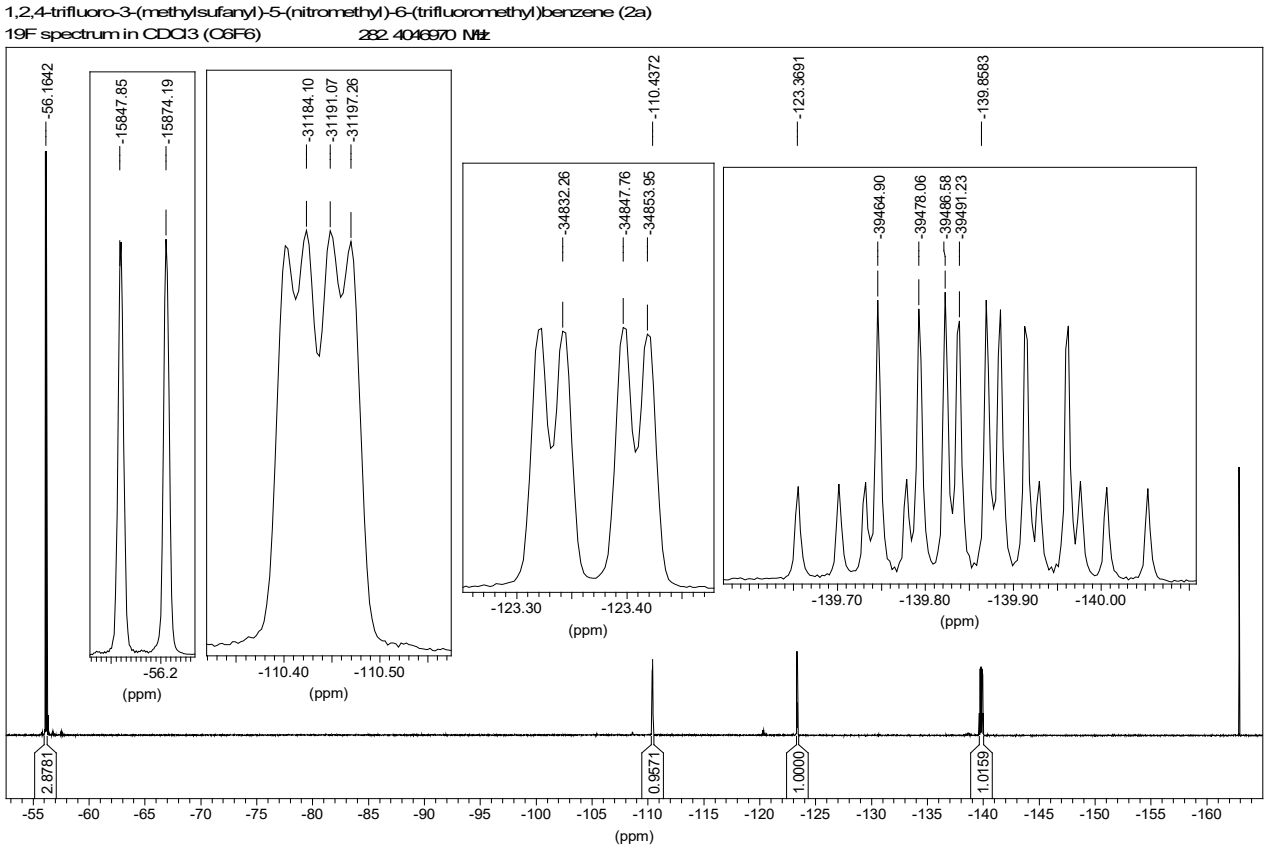
^{1}H NMR spectrum of **2a**.



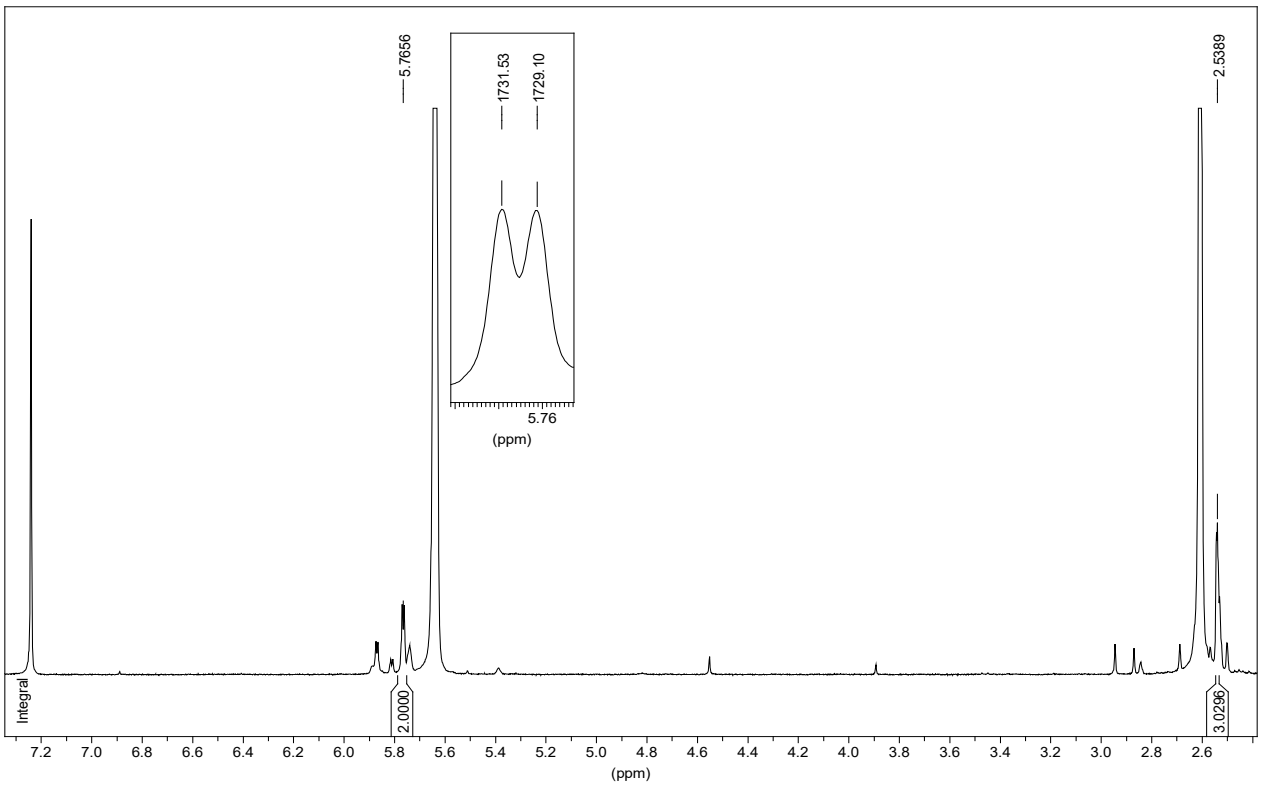
^{13}C NMR spectrum of **2a**.



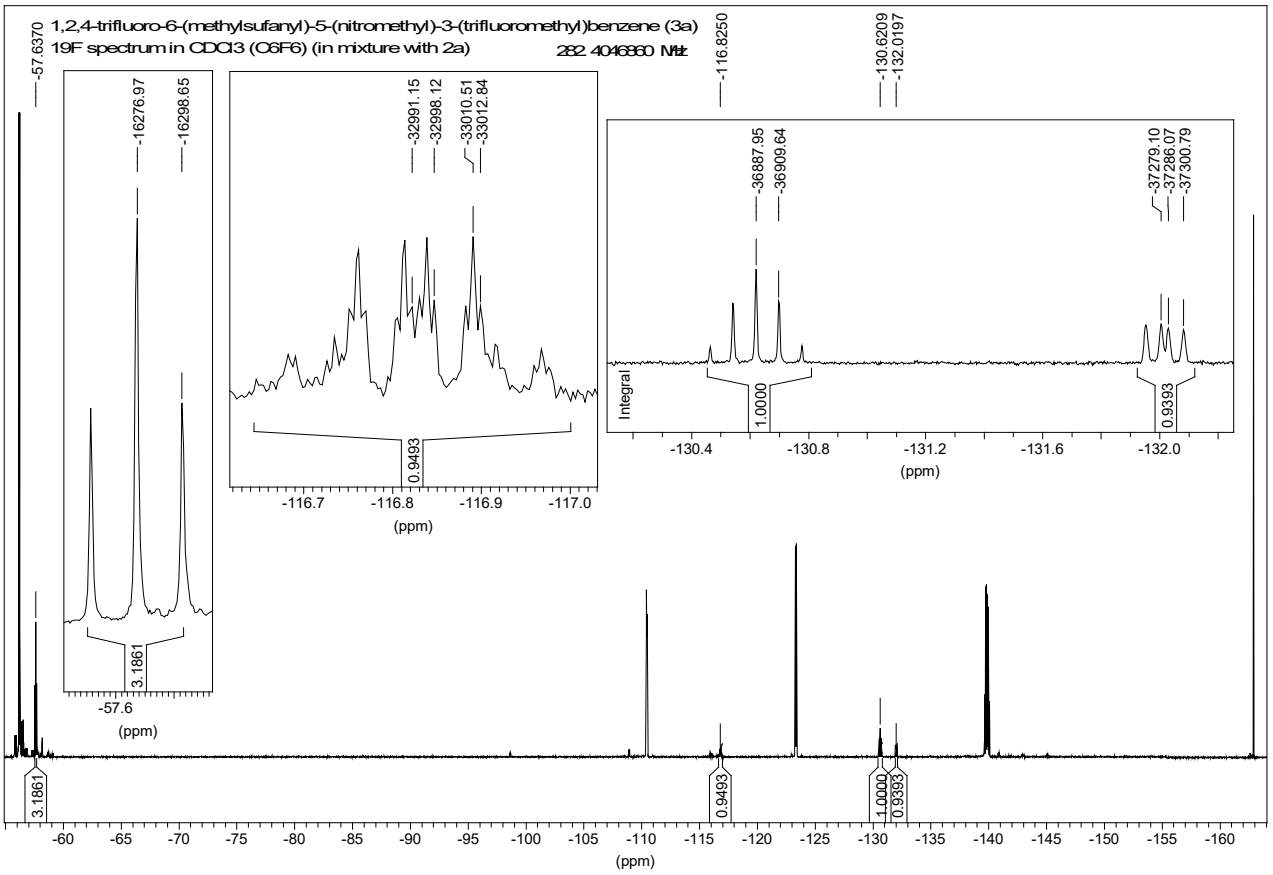
^{19}F NMR spectrum of **2a**.



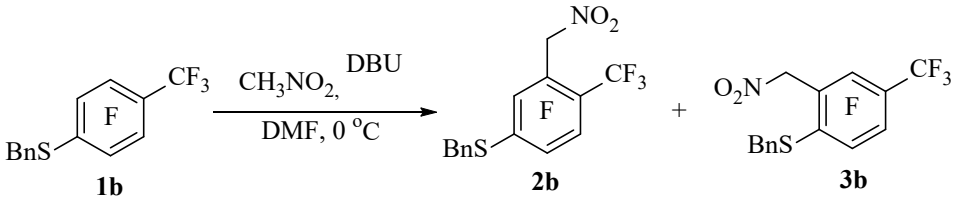
^{1}H NMR spectrum of **3a**.



^{19}F NMR spectrum of **3a**.



1-(Benzylsulfanyl)-2,3,6-trifluoro-5-nitromethyl-4-(trifluoromethyl)benzene (2b).

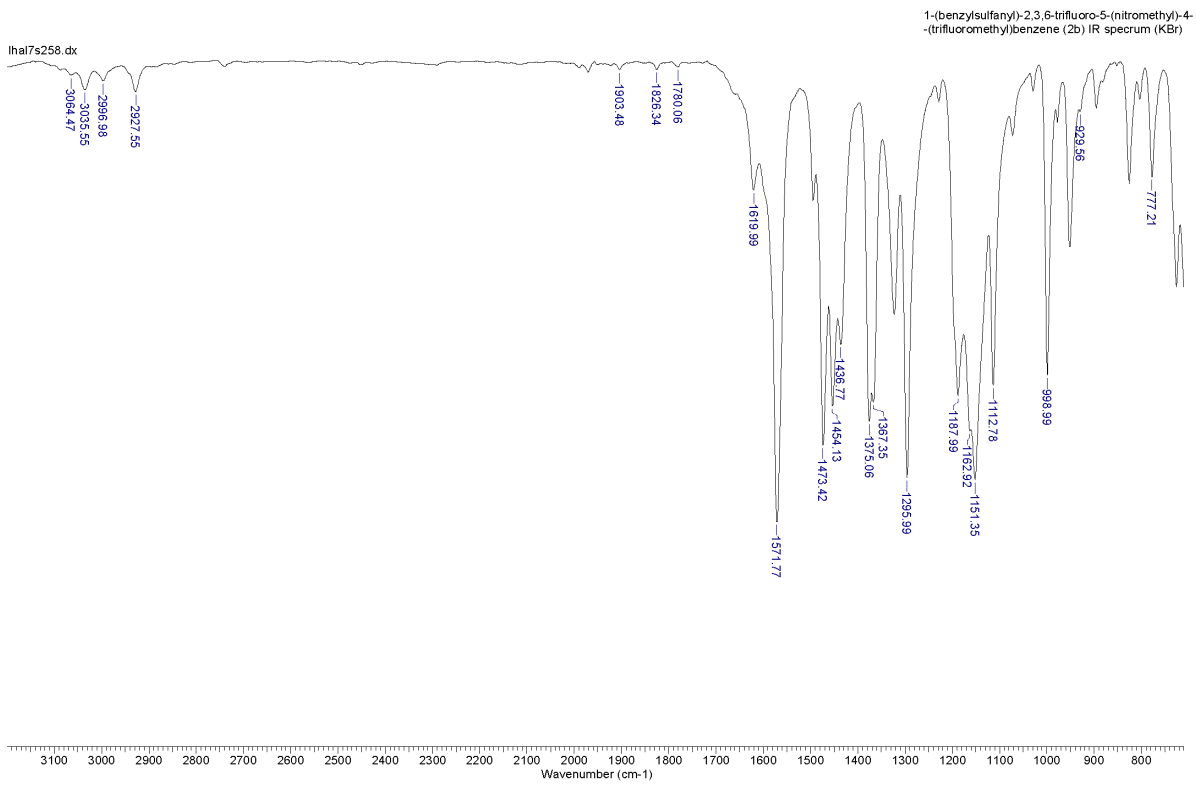


From sulfane **1b** (34.76 g, 102.16 mmol) in DMF (100 ml), nitromethane (82.58 g, 1.35 mol) and DBU (34.70 g, 227.93 mmol) in DMF (100 ml) at 0 °C for 7 h, a 37.78 g of mixture was obtained containing sulfane **2b** (yield - 87 %, according to ^{19}F NMR (CF_3CO_2H)). Crystallization from hexane/benzene (v/v 6 : 1) gave 30.66 g of pure sulfane **2b**. Pale-yellow solid. Mp 37-38 ºC. IR (KBr, ν_{max}, cm^{-1}): 3064(vw) (CH), 3036(vw) (CH), 2997(vw) (CH), 2928(w) (CH), 1903(vw), 1826(vw), 1780 (vw), 1620(w) (ArF), 1572(vs) (NO_2), 1473(s) (ArF), 1454(s) (CF), 1437(s) (CF), 1375(s) (NO_2), 1367(s) (CF), 1296(vs) (CF), 1188(s) (CF), 1163(s) (CF), 1151(vs) (CF), 1113(s) (CF), 999(s) (CF), 930(w) (C-NO_2), 777(w) (C-S), 710(m) (C-S), 667(w) (C-NO_2). UV, λ_{max}, nm (log ε): 292 (3.86). ^{1}H NMR [CD_3CN, 300.13 MHz]: δ_H 4.23 (s, 2H, PhC$\underline{H}_2$S), 5.77 (s, 2H, C$\underline{H}_2NO_2$), 7.12-7.41 (m, 5H, Ph) ppm; ^{13}C NMR [$CDCl_3$, 125.76 MHz]: δ_C 38.4 (t, $^4J_{CF}$ 3.4, Ph$\underline{C}H_2$S), 67.9 ($\underline{C}H_2NO_2$), 111.0 (dd, $^2J_{CF}$ 20.1, $^3J_{CF}$ 3.7, C-(5)), 118.2 (qdd, $^2J_{CF}$ ~33, $^2J_{CF}$ ~9, $^3J_{CF}$ ~2, C-(4)), 119.3 (dd, $^2J_{CF}$

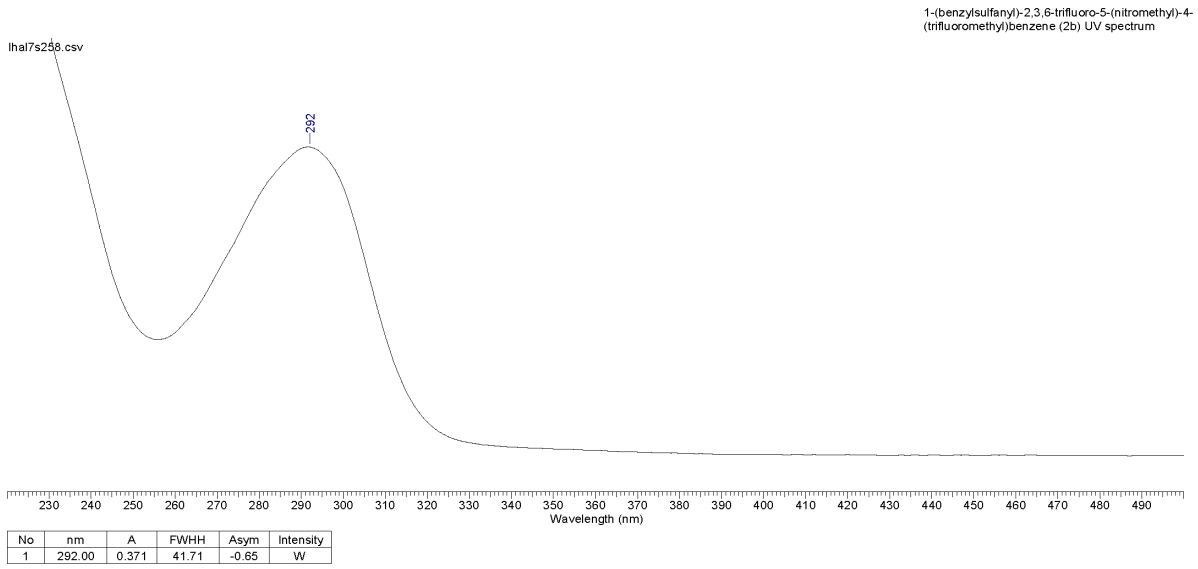
25.7, $^{2}J_{CF}$ 18.7, C-(1)), 121.8 (qd, $^{1}J_{CF}$ 275.6, $^{3}J_{CF}$ 1.4, $\underline{C}F_3$), 128.0 (C-(4')), 128.7 (C-(2',6') or C-(3',5')), 128.8 (C-(2',6') or C-(3',5')), 135.7 (C-(1')), 145.7 (ddd, $^{1}J_{CF}$ 261.8, $^{2}J_{CF}$ 16.8, $^{4}J_{CF}$ 1.5, C-(3)), 152.5 (ddd, $^{1}J_{CF}$ 254.8, $^{2}J_{CF}$ 14.6, $^{3}J_{CF}$ 6.7, C-(2)), 157.5 (dt, $^{1}J_{CF}$ 248.1, $^{3,4}J_{CF}$ 3.5, C-(6)) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -139.6 (qdd, $^{4}J_{FF}$ 26.3, $^{3}J_{FF}$ 22.5, $^{5}J_{FF}$ 13.9, 1F, F-(3)), -120.9 (dd, $^{3}J_{FF}$ 22.5, $^{4}J_{FF}$ 5.4, 1F, F-(6)), -108.8 (dd, $^{5}J_{FF}$ 13.9, $^{4}J_{FF}$ 5.4, 1F, F-(2)), -56.3 (d, $^{4}J_{FF}$ 26.3, 3F, $C\underline{F}_3$) ppm. Anal. calcd for $C_{15}H_9F_6NO_2S$, %: C 47.25; H 2.38; F 29.90; N 3.67; S 8.41; M^+ 381.0253. Found, %: C 47.25; H 2.31; F 30.25; N 3.45; S 8.22; M^+ 381.0260.

The mixture before crystallization also contained of 1-(benzylsulfanyl)-2,3,5-trifluoro-6-(nitromethyl)-4-(trifluoromethyl)benzene (**3b**) (yield - 6 %). From mixture of isomers were found: ^{1}H NMR [CD_3CN, 300.13 MHz]: δ_H 4.18 (s, 2H, PhC$\underline{H}_2$S), 5.63 (d, $^{4}J_{HF}$ 2.3, C$\underline{H}_2NO_2$), 7.12-7.41 (m, 5H, Ph) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -130.7 (dq, $^{3}J_{FF}$ 22.5, $^{4}J_{FF}$ 22.5, 1F, F-(3)), -130.0 (dd, $^{3}J_{FF}$ 22.5, $^{5}J_{FF}$ 15.5, 1F, F-(2)), -116.2 (qdt, $^{4}J_{FF}$ 22.5, $^{5}J_{FF}$ 14.7, $^{4}J_{FH}$ 2.3, 1F, F-(5)), -57.7 (t, $^{4}J_{FF}$ 22.5, 3F, $C\underline{F}_3$) ppm. Anal. calcd for $C_{15}H_9F_6NO_2S$: M^+ 381. Found by GC-MS: M^+ 381, 1S.

IR spectrum of **2b**.

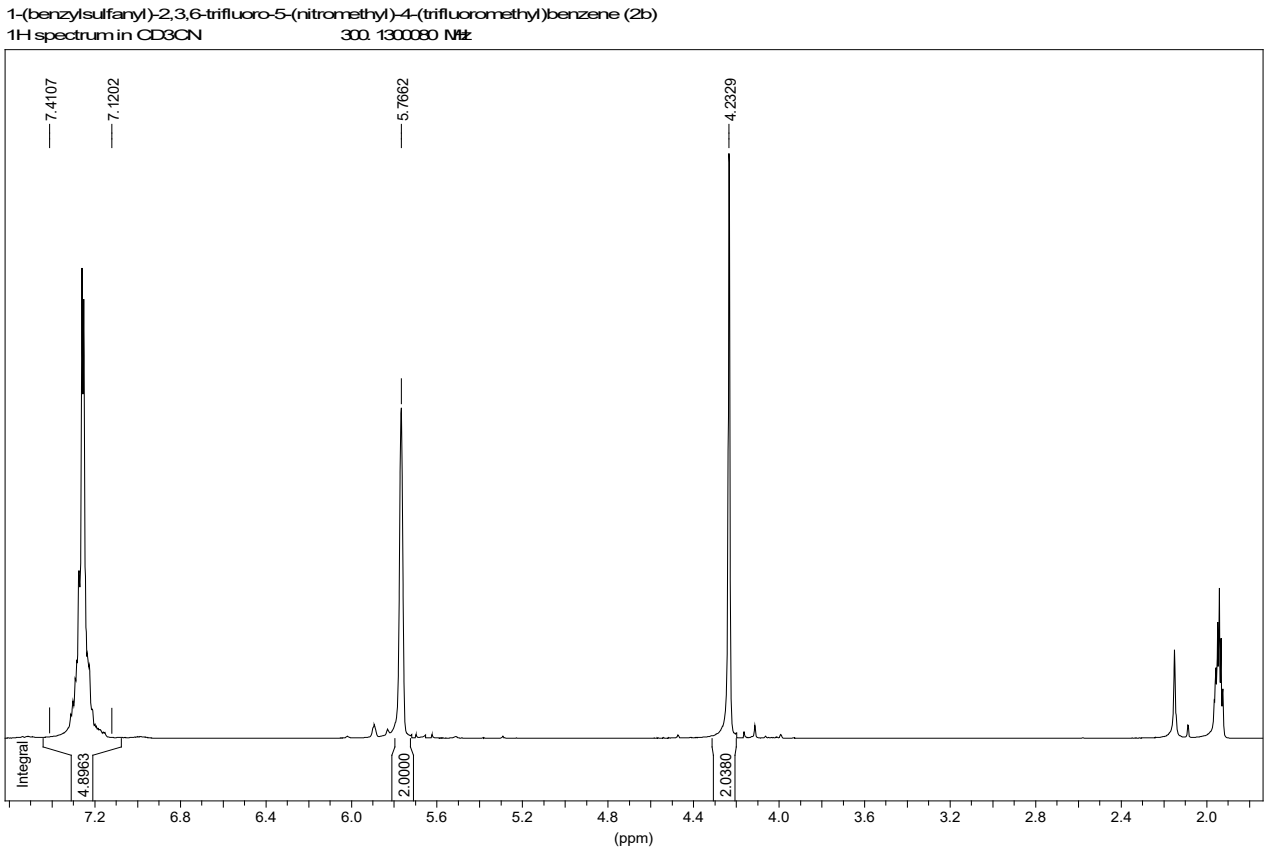


UV spectrum of **2b**.

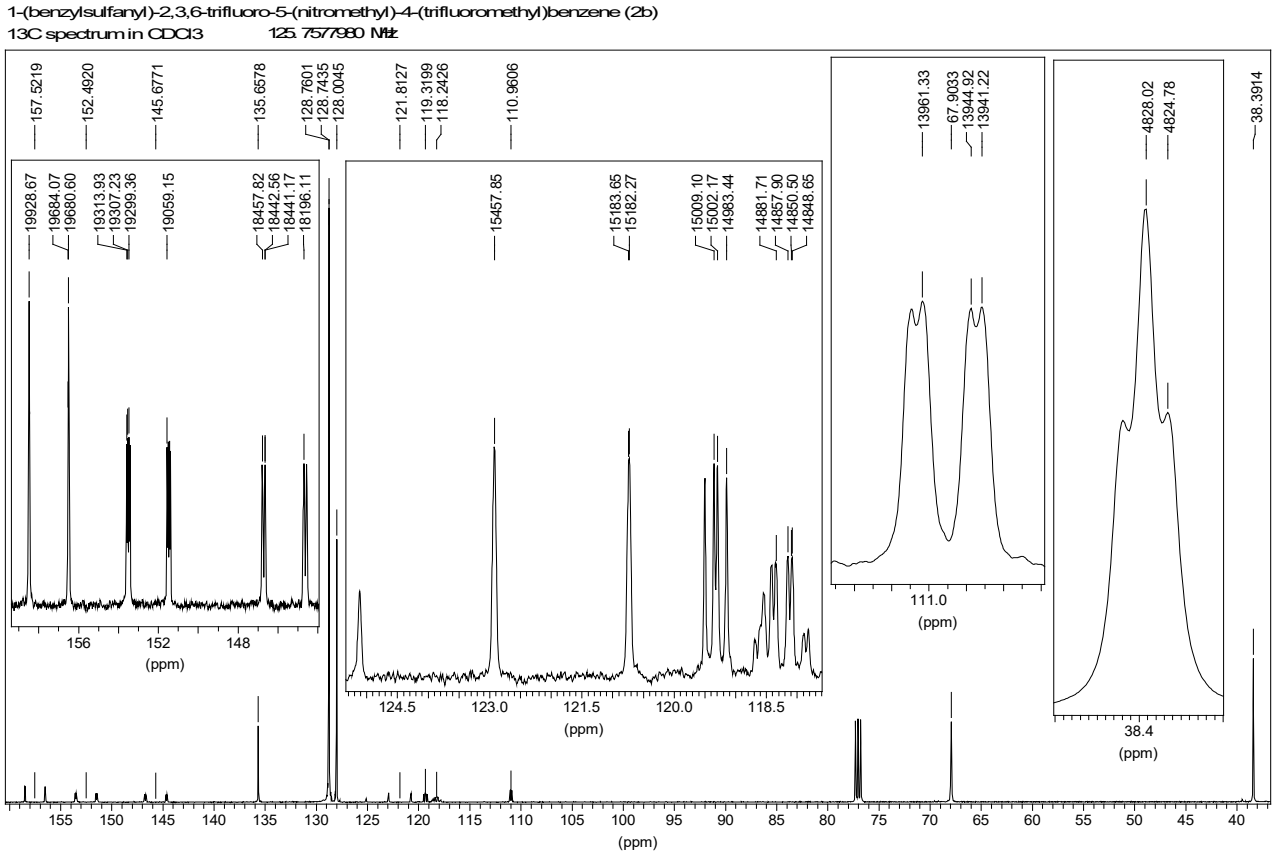


No	nm	A	FWHH	Asym	Intensity
1	292.00	0.371	41.71	-0.65	W

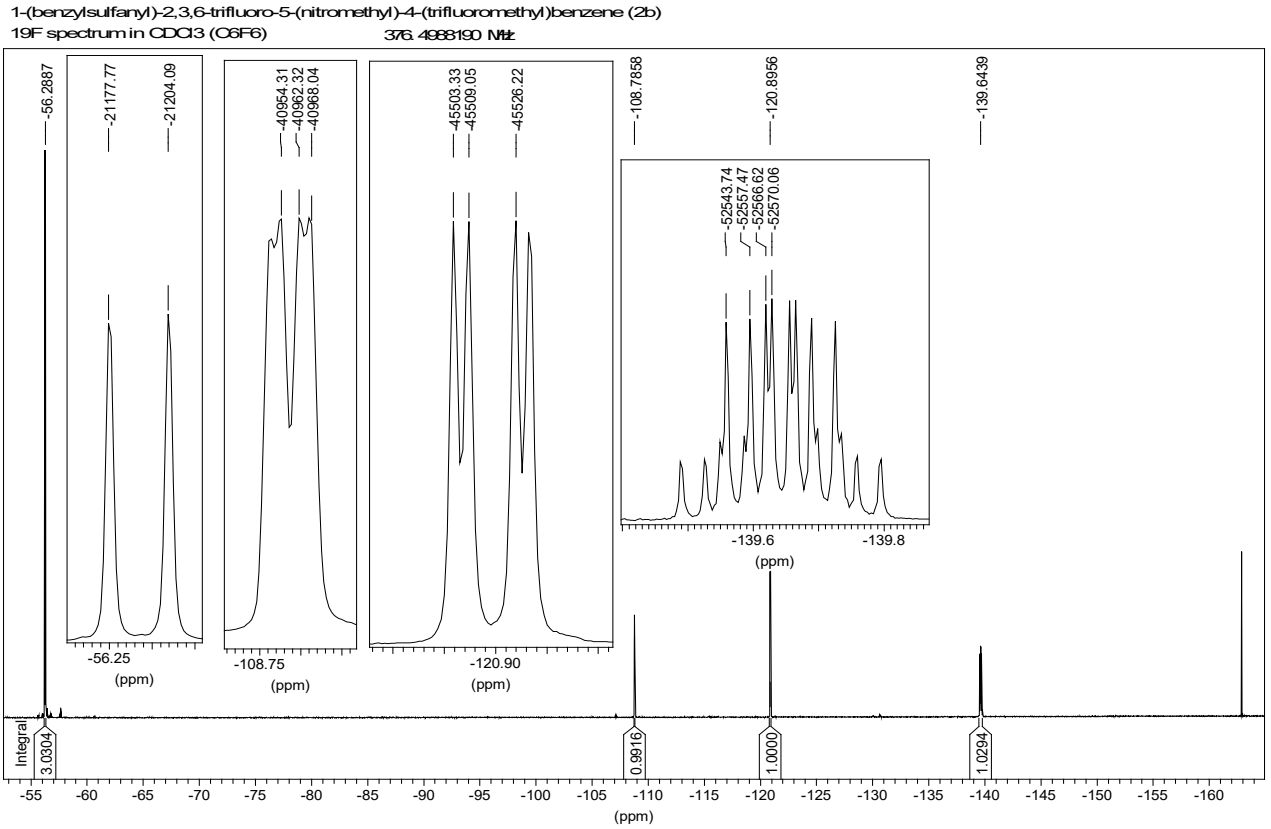
^{1}H NMR spectrum of **2b**.



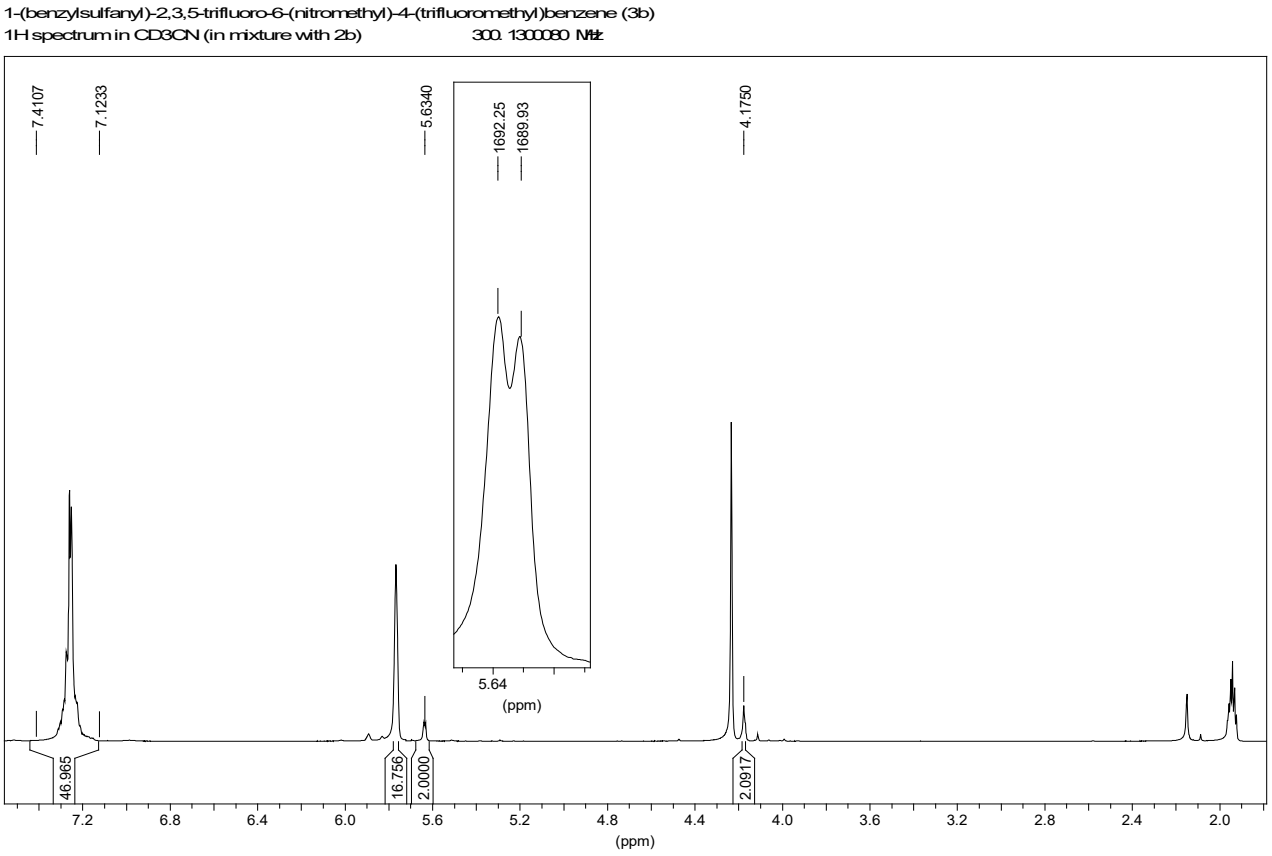
^{13}C NMR spectrum of **2b**.



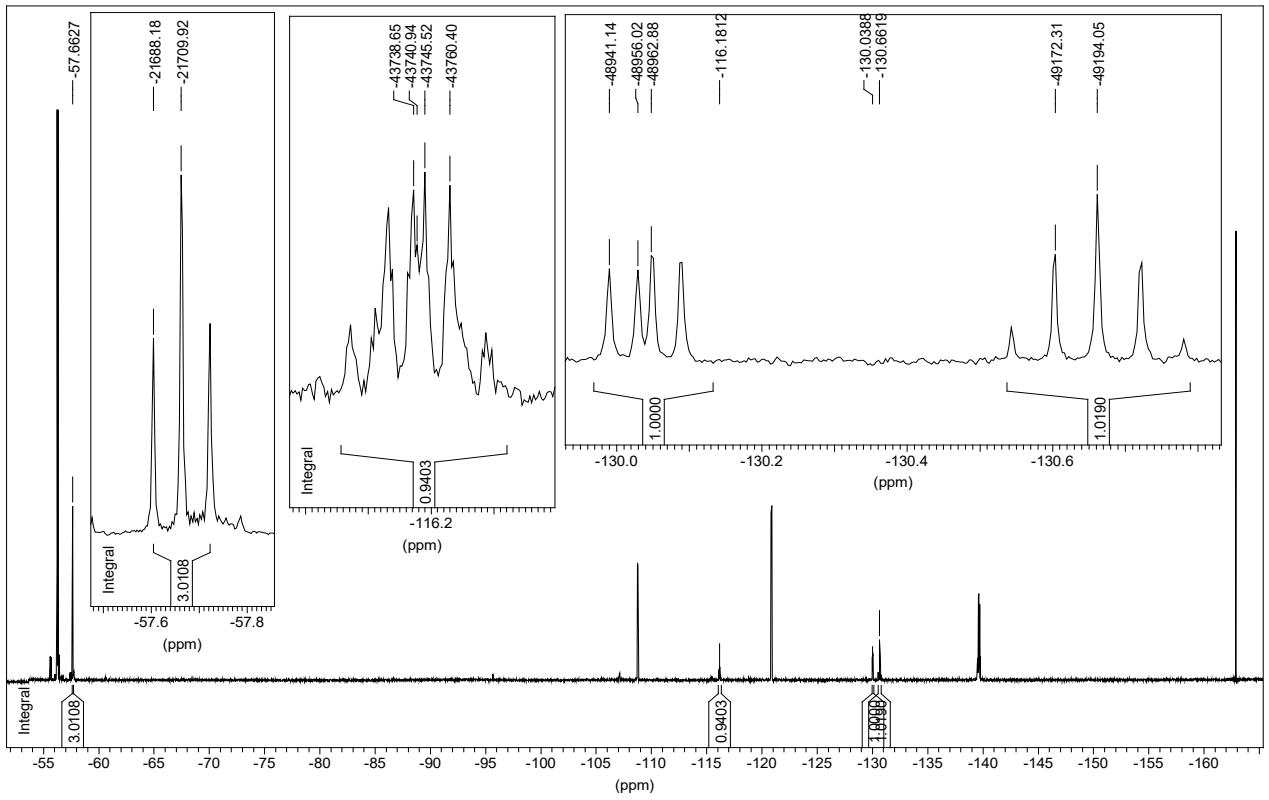
^{19}F NMR spectrum of **2b**.



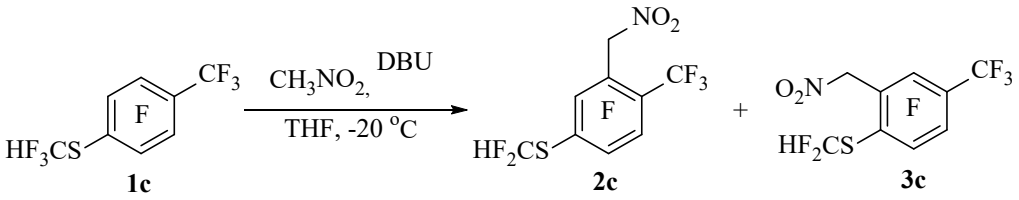
^{1}H NMR spectrum of **3b**.



^{19}F NMR spectrum of **3b**.



Reaction of 1c with nitromethane.

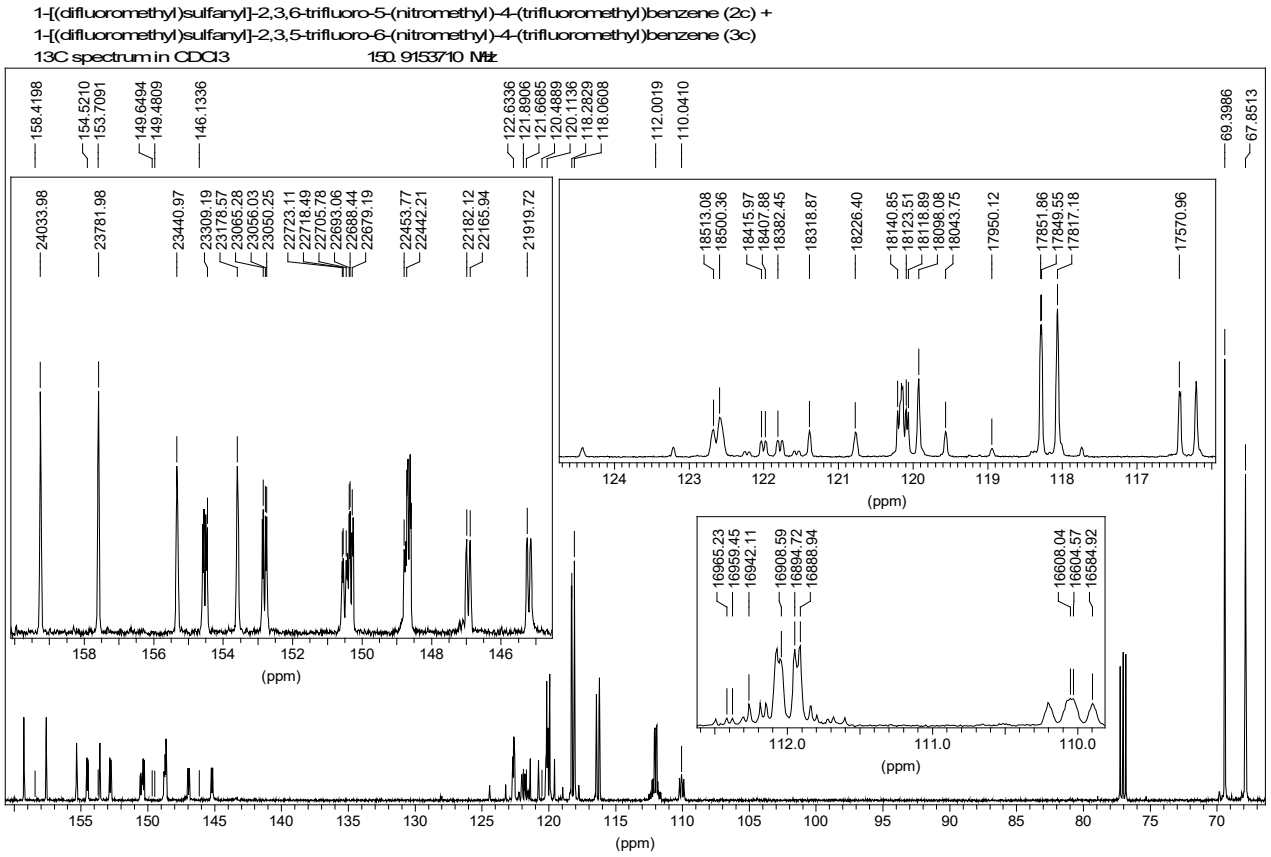


From sulfane (**1c**) (0.94 g, 3.13 mmol) in THF (3 ml), nitromethane (2.29 g, 37.52 mol) and DBU (0.95 g, 6.24 mmol) in THF (3 ml) at -20 ºC for 5 h, a 1.07 g of mixture of sulfanes **2c** and **3c** was obtained with ratio 51 : 49 respectively according to ^{19}F NMR. Sublimation (0.83-0.63 mmHg, 90-86 °C) gave 0.99 g of mixture contained sulfane **2c** (yield - 47 %) and of sulfane **3c** (yield - 45 %) according to ^{19}F NMR (PhF). ^{13}C NMR [$CDCl_3$, 150.91 MHz] (mixture of isomers): δ_C 67.9 ($\underline{C}H_2NO_2$), 69.4 ($\underline{C}H_2NO_2$), 110.0 (dd, $^2J_{CF}$ 23.1, $^2J_{CF}$ 19.7, C_{Ar}), 112.0 (dd, $^2J_{CF}$ 19.7, J_{CF} 5.8, C_{Ar}), 112.0 (qdd, $^2J_{CF}$ 34.7, $^2J_{CF}$ 17.3, $^2J_{CF}$ 11.6, C-(4)), 118.1 (t, $^1J_{CF}$ 280.9, $\underline{C}F_2H$), 118.3 (t, $^1J_{CF}$ 280.9, $^4J_{CF}$ 2.3, $\underline{C}F_2H$), 120.1 (dd, $^2J_{CF}$ 22.0, J_{CF} 4.6, C_{Ar}), 120.5 (q, $^1J_{CF}$ 275.1, $\underline{C}F_3$), 121.7 (q, $^1J_{CF}$ 276.3, $\underline{C}F_3$), 121.9 (qd, $^2J_{CF}$ 33.5, $^2J_{CF}$ 8.1, C-(4)), 122.6 (d, $^2J_{CF}$ 12.7, C_{Ar}), 146.1 (dd, $^1J_{CF}$ 262.4, $^2J_{CF}$ 16.2, C_{FAr}), 149.5 (ddd, $^1J_{CF}$ 250.9, $^2J_{CF}$ 13.3, J_{CF} 3.0, C_{FAr}), 149.6 (ddd, $^1J_{CF}$ 270.5, $^2J_{CF}$ 18.5, J_{CF} 5.8, C_{FAr}), 153.7 (ddd, $^1J_{CF}$ 258.9, $^2J_{CF}$ 14.5, J_{CF} 5.2, C_{FAr}), 154.5 (d, $^1J_{CF}$ 262.4, C_{FAr}), 158.4 (d, $^1J_{CF}$ 252.0, C_{FAr}) ppm; Anal. calcd for $C_9H_3F_8NO_2S$, %: C 31.68; H 0.89; F 44.55; N 4.11; S 9.40; M^+ 340.9751, $(M-F)^+$ 321.9761. Found, %: C 31.60; H 1.03; F 44.82; N 4.37; S 9.19; $(M-F)^+$ 321.9767, M 342 (KNAUER K-7000).

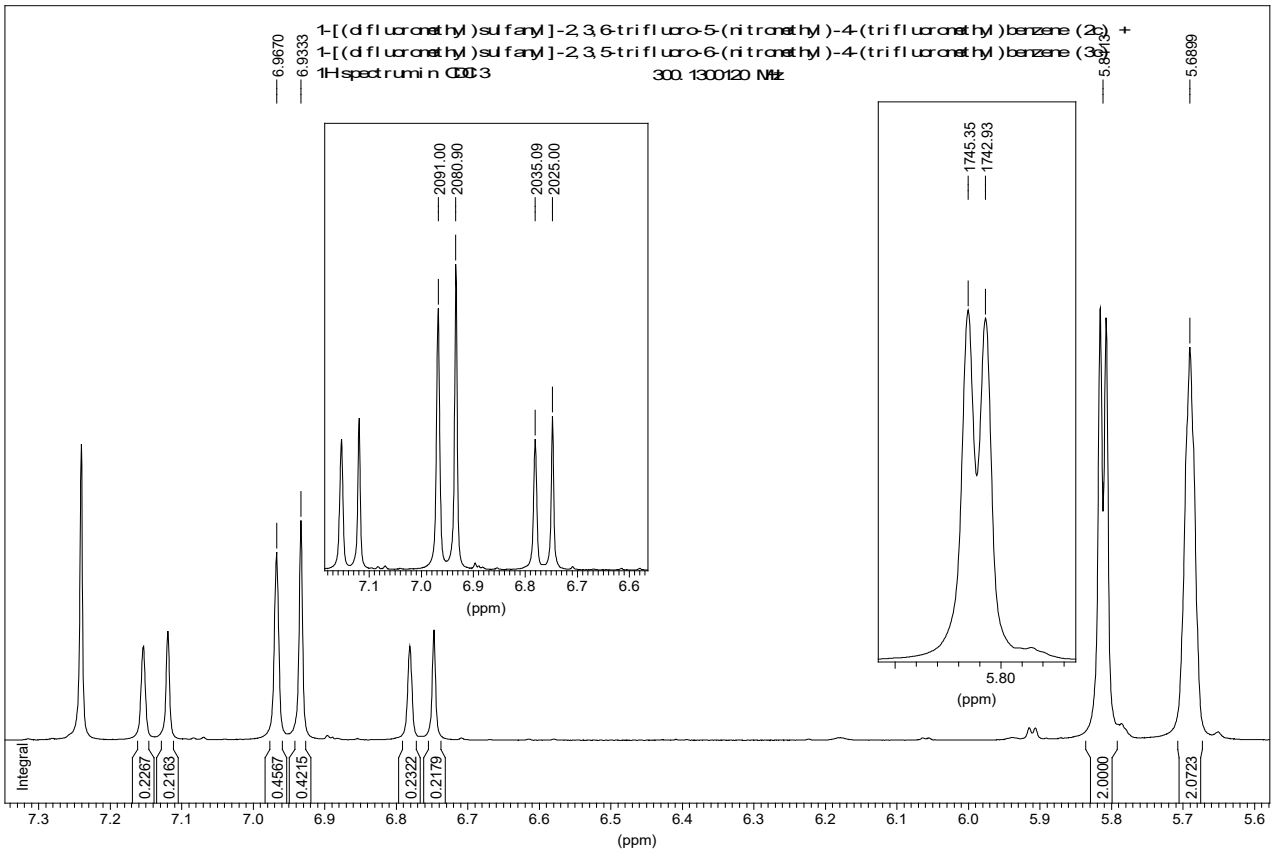
1-[(Difluoromethyl)sulfanyl]-2,3,6-trifluoro-5-nitromethyl-4-(trifluoromethyl)benzene (**2c**) (from mixture of isomers). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 5.69 (s, 2H, $C\underline{H}_2NO_2$), 6.97 (t, $^2J_{HF}$ 55.8, 1H, $SCF_2\underline{H}$) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -137.6 (qdd, $^4J_{FF}$ 26.3, $^3J_{FF}$ 22.5, $^5J_{FF}$ 14.7, 1F, F-(3)), -116.9 (dtd, $^3J_{FF}$ 22.5, $^5J_{FF}$ 5.4, $^4J_{FF}$ 4.6, 1F, F-(2)), -106.2 (m, 1F, F-(6)), -91.6 (dt, $^2J_{FH}$ 55.8, $^5J_{FF}$ 5.4, 2F, $C\underline{F}_2H$), -56.7 (d, $^4J_{FF}$ 26.3, 3F, $C\underline{F}_3$) ppm.

1-[(Difluoromethyl)sulfanyl]-2,3,5-trifluoro-6-nitromethyl-4-(trifluoromethyl)benzene (**3c**) (from aixture of isomers) ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 5.81 (d, $^4J_{HF}$ 2.3, 2H, $C\underline{H}_2NO_2$), 6.93 (t, $^2J_{HF}$ 55.8, 1H, $SCF_2\underline{H}$) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -128.0 (qvint, $^{3,4}J_{FF}$ 22.5, 1F, F-(3)), -125.8 (ddt, $^3J_{FF}$ 22.5, $^5J_{FF}$ 15.5, $^5J_{FF}$ 6.2, 1F, F-(2)), -114.3 (qdt, $^4J_{FF}$ 22.5, $^5J_{FF}$ 15.5, $^4J_{FH}$ 2.3, 1F, F-(5)), -91.7 (dt, $^2J_{FH}$ 55.8, $^5J_{FF}$ 6.2, 2F, $C\underline{F}_2H$), -57.9 (t, $^4J_{FF}$ 22.5, 3F, $C\underline{F}_3$) ppm.

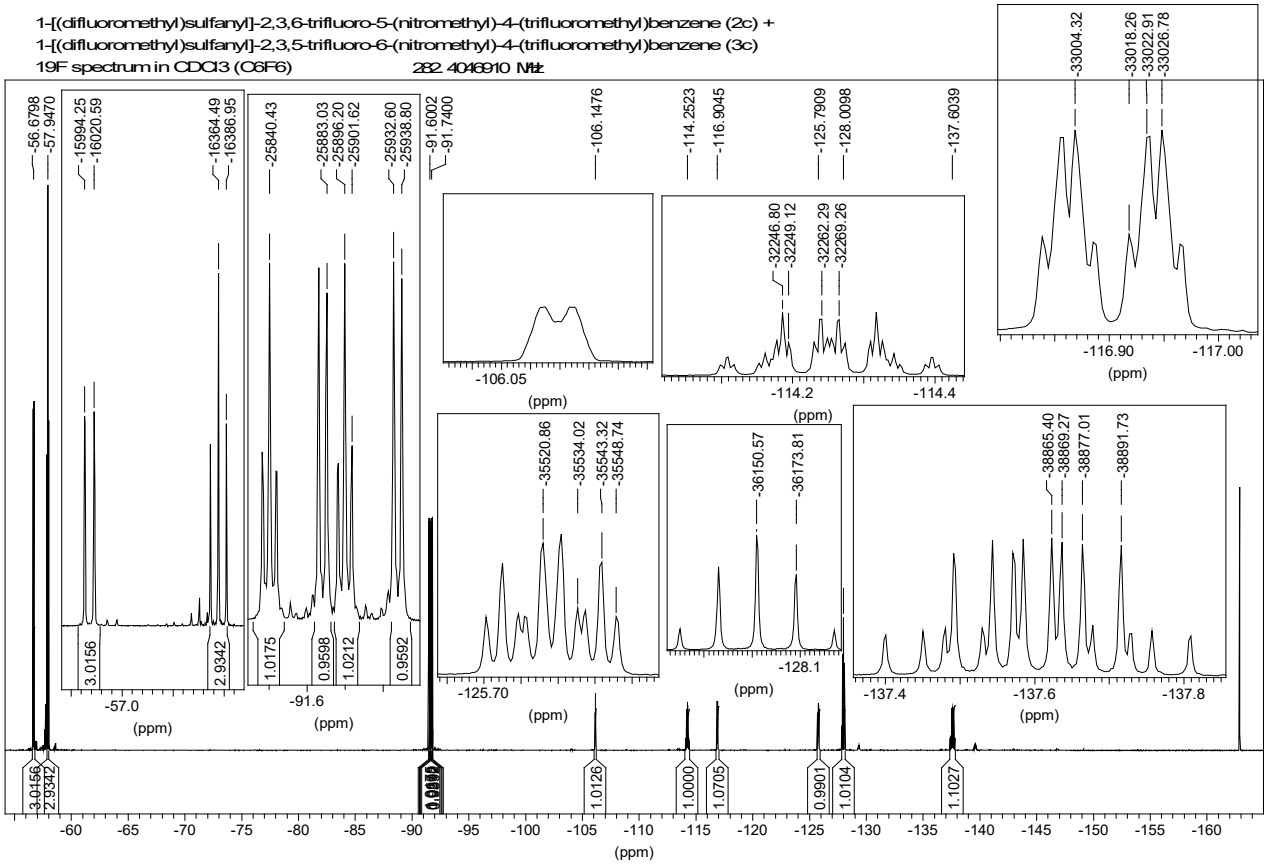
^{13}C NMR spectrum of **2c+3c**.



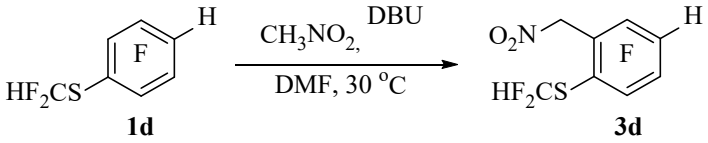
^{1}H NMR spectrum of **2c+3c**.



^{19}F NMR spectrum of **2c+3c**.



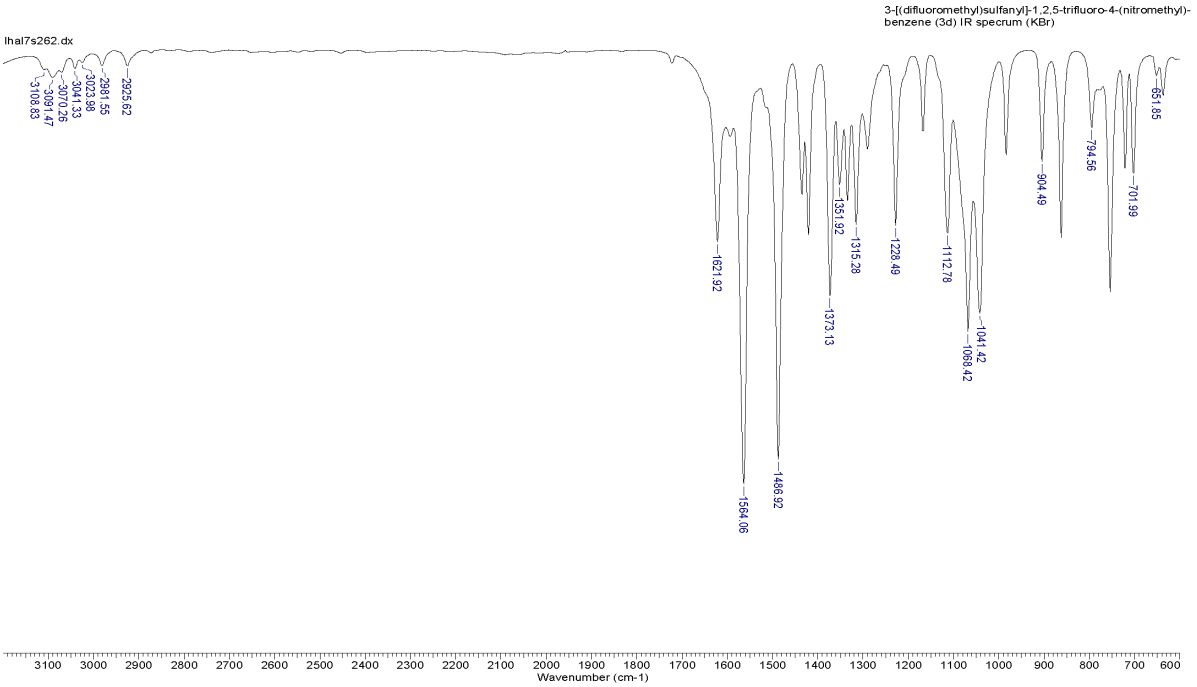
3-[(Difluoromethyl)sulfanyl]-1,2,5-trifluoro-4-(nitromethyl)benzene (**3d**).



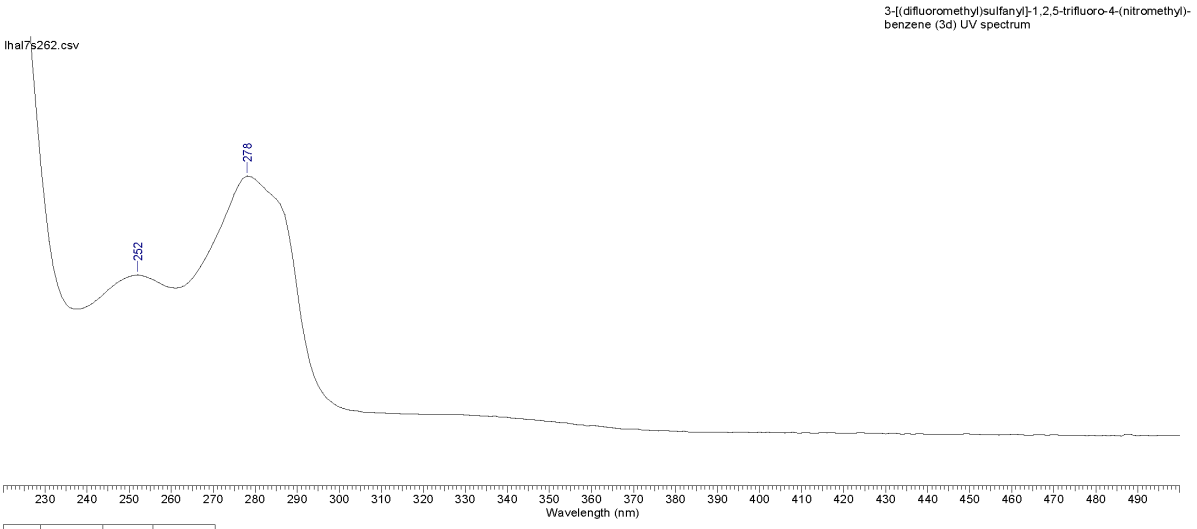
From sulfane **1d** (23.60 g, 101.66 mmol) in DMF (100 ml), nitromethane (82.64 g, 1.35 mol) and DBU (34.21 g, 224.71 mmol) in DMF (100 ml) at 30 °C for 16 h, a 26.11 g of crude product was obtained. Distillation (0.20-0.24 mmHg, 99-101 °C) gave 23.69 g of pure sulfane **3d** (yield - 85 %). IR (KBr, ν_{max}, cm^{-1}): 3109(vw) (CH), 3091(vw) (CH), 3070(vw) (CH), 3041(vw) (CH), 3024(vw) (CH), 2982(vw) (CH), 2926(vw) (CH), 1622(m) (ArF), 1564(vs) (NO_2), 1487(vs) (ArF), 1373(m) (NO_2), 1352(s) (CF), 1315(m) (CF), 1228(m) (CF), 1113(m) (CF), 1068(s) (CF), 1041(s) (CF), 904(w) (C-NO_2), 795(w) (C-S), 702(w) (C-S), 652(vw) (C-NO_2). UV, λ_{max}, nm (log ε): 252 (3.30), 278 (3.51). ^{1}H NMR [CD_3CN, 400.13 MHz]: δ_H 5.88 (d, $^4J_{HF}$ 1.9, 2H, C$\underline{H}_2$NO$_2$), 7.05 (t, $^2J_{HF}$ 55.2, 1H, CF$_2\underline{H}$S), 7.50 (td, $^3J_{HF}$ 9.7, $^4J_{HF}$ 6.7, 1H, H-(6)) ppm; ^{13}C NMR [$CDCl_3$, 150.91 MHz]: δ_C 69.8 ($\underline{C}H_2NO_2$), 108.9 (dd, $^2J_{CF}$ 27.7, $^2J_{CF}$ 22.0, C-(6)), 118.1 (dq, $^2J_{CF}$ 18.5, $^3J_{CF}$ 3.5, C-(3)), 118.5 (td, $^1J_{CF}$ 279.7, $^4J_{CF}$ 2.3, C$\underline{F}_2$H), 118.9 (dd, $^2J_{CF}$ 16.2, $^3J_{CF}$ 3.5, C-(4)), 149.2 (ddd, $^1J_{CF}$ 248.5, $^2J_{CF}$ 12.7, $^4J_{CF}$ 3.5, C-(2)), 151.8 (ddd, $^1J_{CF}$ 260.1, $^2J_{CF}$ 16.2, $^3J_{CF}$ 13.9, C-(1)), 157.3 (ddd, $^1J_{CF}$ 253.2, $^3J_{CF}$ 10.4, $^4J_{CF}$ 3.5, C-(5)) ppm; ^{19}F NMR [CD_3CN, 376.4 MHz]: δ_F -128.6 (m, 1F, F-(2)), -127.8 (ddd, $^3J_{FF}$ 22.9, $^3J_{FH}$ 9.7, $^4J_{FF}$ 5.2, 1F, F-(1)), -111.8 (m, 1F, F-(5)), -91.2 (dd, $^2J_{FH}$ 55.2, $^5J_{FF}$ 5.7, 2F, SC$\underline{F}_2$H) ppm. Anal. calcd for $C_8H_4F_5NO_2S$,

%: C 35.17; H 1.48; F 34.77; N 4.86; S 11.74; M^+ 272.9877, $(M\text{-}NO_2)^+$ 226.9950. Found, %: C 35.51; H 1.24; F 34.81; N 4.86; S 12.09; $(M\text{-}NO_2)^+$ 226.9948, M 269 (KNAUER K-7000).

IR spectrum of **3d**.

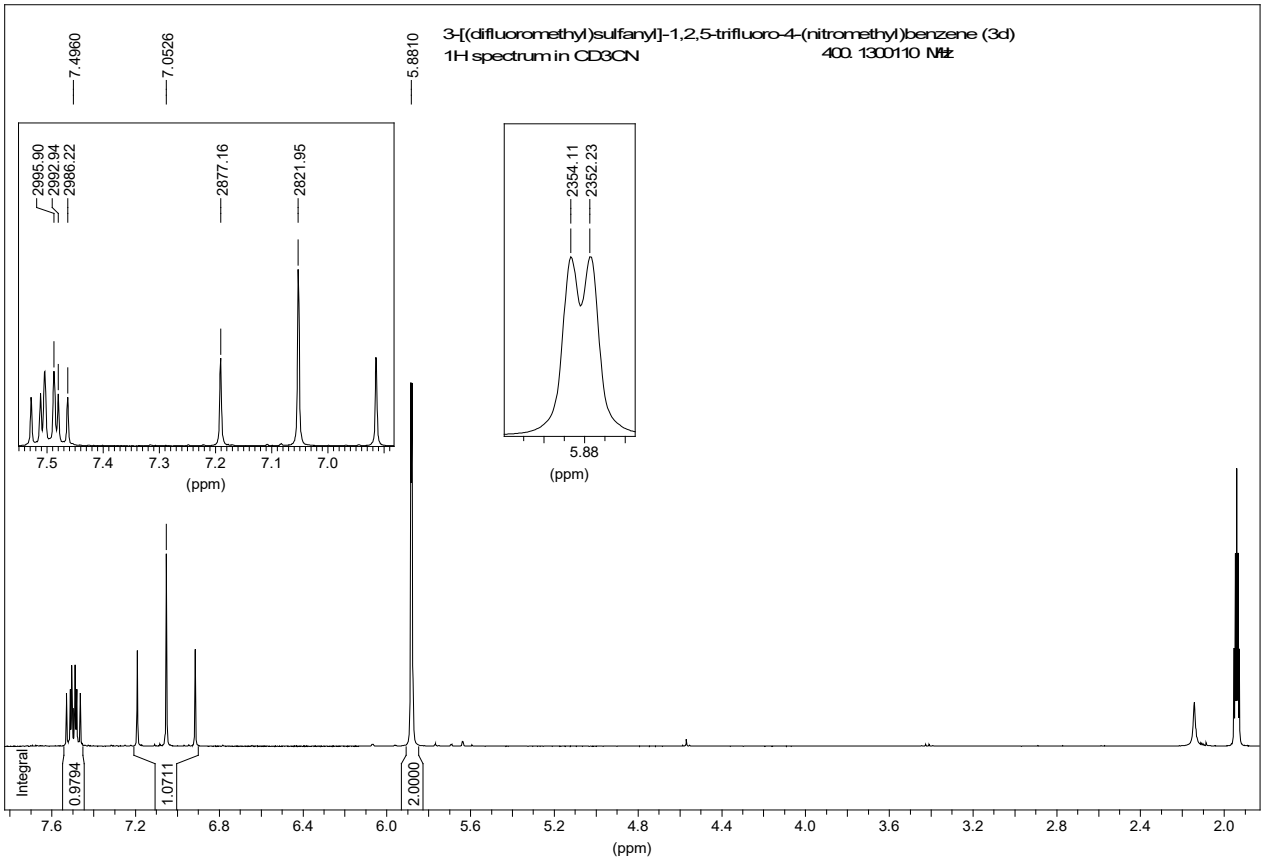


UV spectrum of **3d**.

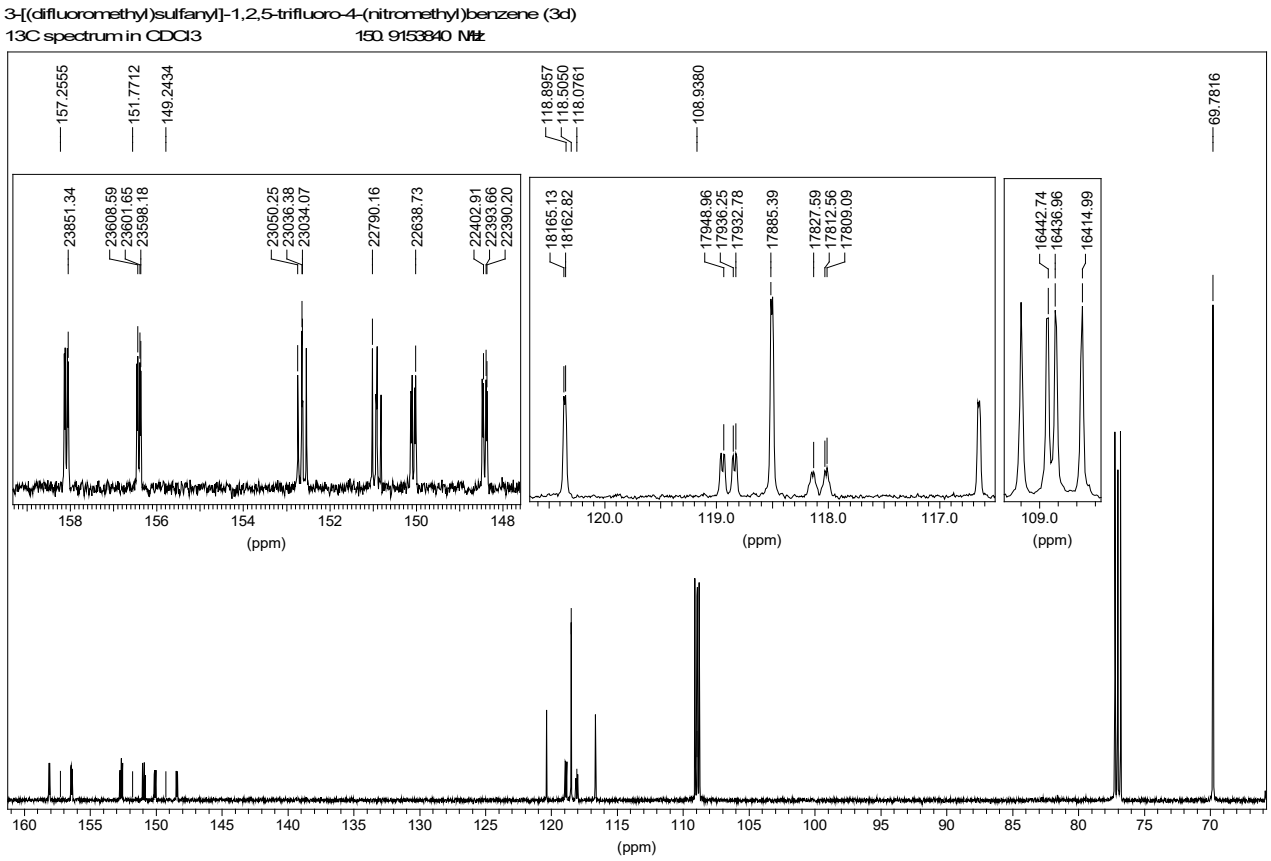


No	nm	A	Intensity
1	252.00	0.101	VW
2	278.00	0.163	W

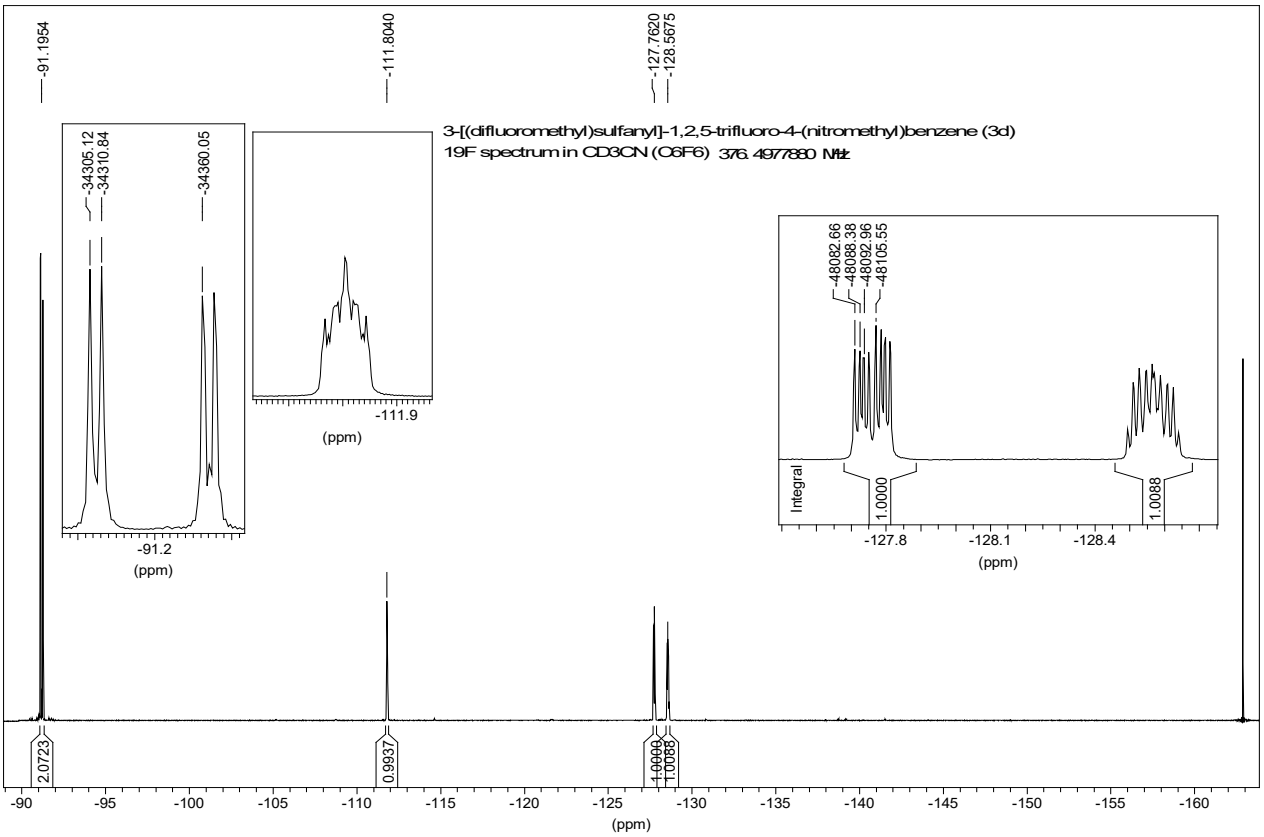
^{1}H NMR spectrum of **3d**.



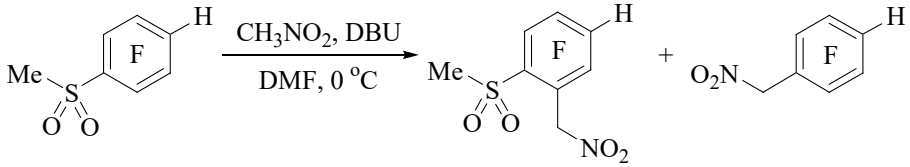
^{13}C NMR spectrum of **3d**.



^{19}F NMR spectrum of **3d**.



1,2,5-Trifluoro-3-methanesulfonyl-4-(nitromethyl)benzene (**5a**).



4a **5a** **6**

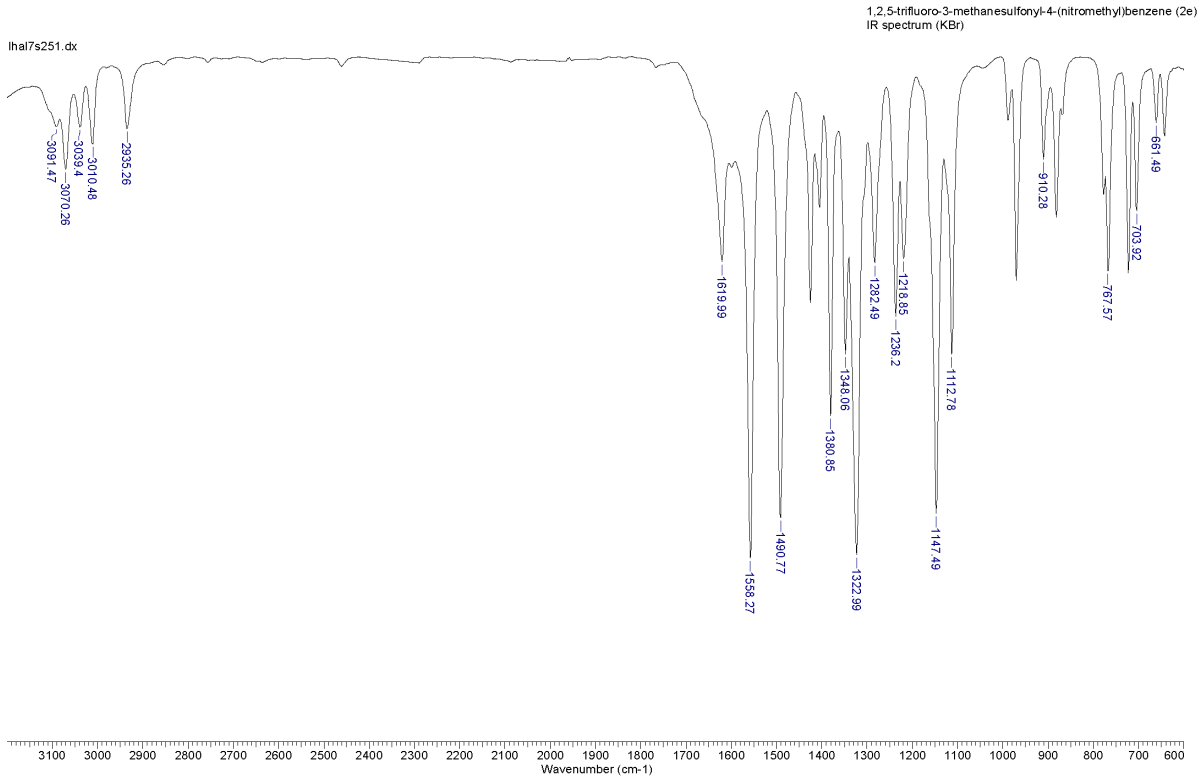
a) From sulfone **4a** (0.100 g, 0.438 mmol) in THF (0.5 ml), nitromethane (0.358 g, 5.865 mmol) and DBU (0.137 g, 0.900 mmol) in THF (0.5 ml) at 0 °C for 4 h, a mixture of **5a** and **6** was obtained with ratio 91 : 9 respectively according to ^{19}F NMR.

b) From sulfone **4a** (29.25 g, 128.20 mmol) in DMF (130 ml), nitromethane (102.88 g, 1.69 mol) and DBU (42.96 g, 282.19 mmol) in DMF (130 ml) at 0 °C for 3 h, a mixture of **5a** and **6** was obtained with ratio 93 : 7 respectively according to ^{19}F NMR. 29.74 g (yield - 86 %) of nitromethyl derivative **5a** obtained after treatment. White solid. Mp 108-109 °C. IR (KBr, ν_{max}, cm^{-1}): 3091(w) (CH), 3070(w) (CH), 3039(w) (CH), 3010(w) (CH), 2935(w) (CH), 1620(m) (ArF), 1558(vs) (NO_2), 1491(vs) (ArF), 1381(s) (NO_2), 1348(m) (CF), 1323(vs) (SO_2), 1282(m) (CF), 1236(m) (CF), 1219(m) (CF), 1147(vs) (SO_2), 1113(m) (CF), 910(w) (C-NO_2), 768(m) (C-S), 704(m) (C-S), 661(w) (C-NO_2). UV, λ_{max}, nm (log ε): 281 (3.61), 315 (2.34), 330 (2.30). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 3.29 (d, $^5J_{HF}$ 0.7, 3H, C$\underline{H}_3SO_2$), 6.06 (d, $^4J_{HF}$ 1.5, C$\underline{H}_2NO_2$), 7.36 (td, $^3J_{HF}$ 8.6, $^4J_{HF}$ 6.7, 1H, H-

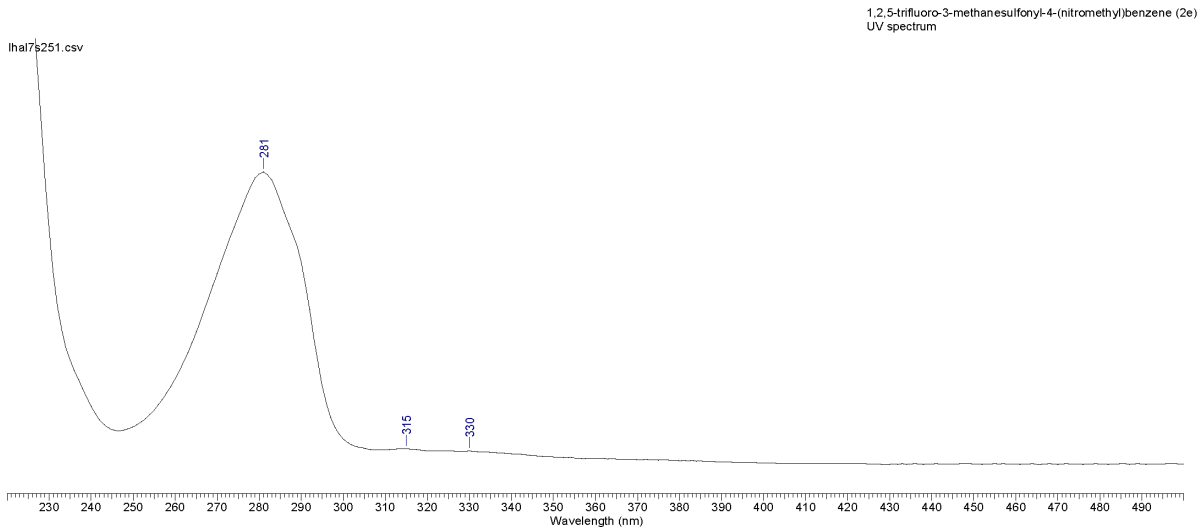
(6)) ppm; ^{13}C NMR [$CDCl_3$, 125.76 MHz]: δ_C 44.5 (d, $^4J_{CF}$ 2.3, $\underline{C}H_3SO_2$), 66.2 (d, $^3J_{CF}$ 4.9, $\underline{C}H_2NO_2$), 111.0 (dd, $^2J_{CF}$ 29.4, $^2J_{CF}$ 20.8, C-(6)), 113.1 (dd, $^2J_{CF}$ 17.1, $^3J_{CF}$ 4.4, C-(4)), 130.6 (d, $^2J_{CF}$ 12.5, C-(3)), 146.6 (dd, $^1J_{CF}$ 255.0, $^2J_{CF}$ 14.8, C-(2)), 151.9 (dt, $^1J_{CF}$ 262.2, $^{2,3}J_{CF}$ 14.6, C-(1)), 156.7 (dd, $^1J_{CF}$ 253.2, $^3J_{CF}$ 7.6, C-(5)) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -134.0 (ddd, $^3J_{FF}$ 23.2, $^5J_{FF}$ 13.9, $^3J_{HF}$ 6.7, 1F, F-(2)), -125.5 (ddd, $^3J_{FF}$ 23.2, $^3J_{HF}$ 8.6, $^4J_{FF}$ 6.2, 1F, F-(1)), -113.4 (m, 1F, F-(5)) ppm. Anal. calcd for $C_8H_6F_3NO_4S$, %: C 35.69; H 2.25; F 21.17; N 5.20; S 11.91; M^+ 223.0035. Found, %: C 35.70; H 2.60; F 21.27; N 4.98; S 11.80; M^+ 223.0033.

Residue (1.69 g) from hexane solutions contained 82% of **1,2,4,5-tetrafluoro-3-(nitromethyl)benzene** (**6**) (yield - 5 %) according to NMR (PhF). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 5.60 (s, 2H, $C\underline{H}_2NO_2$), 7.23 (tt, $^3J_{HF}$ 9.4, $^4J_{HF}$ 7.5, 1H, H-(6)), ppm. ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -142.4 (m, 2F, F-(2,4)), -138.5 (m, 2F, F-(1,5)) ppm. Anal. calcd for $C_7H_3F_4NO_2$: M^+ 209.0094. Found: M^+ 209.0092.

IR spectrum of **5a**.

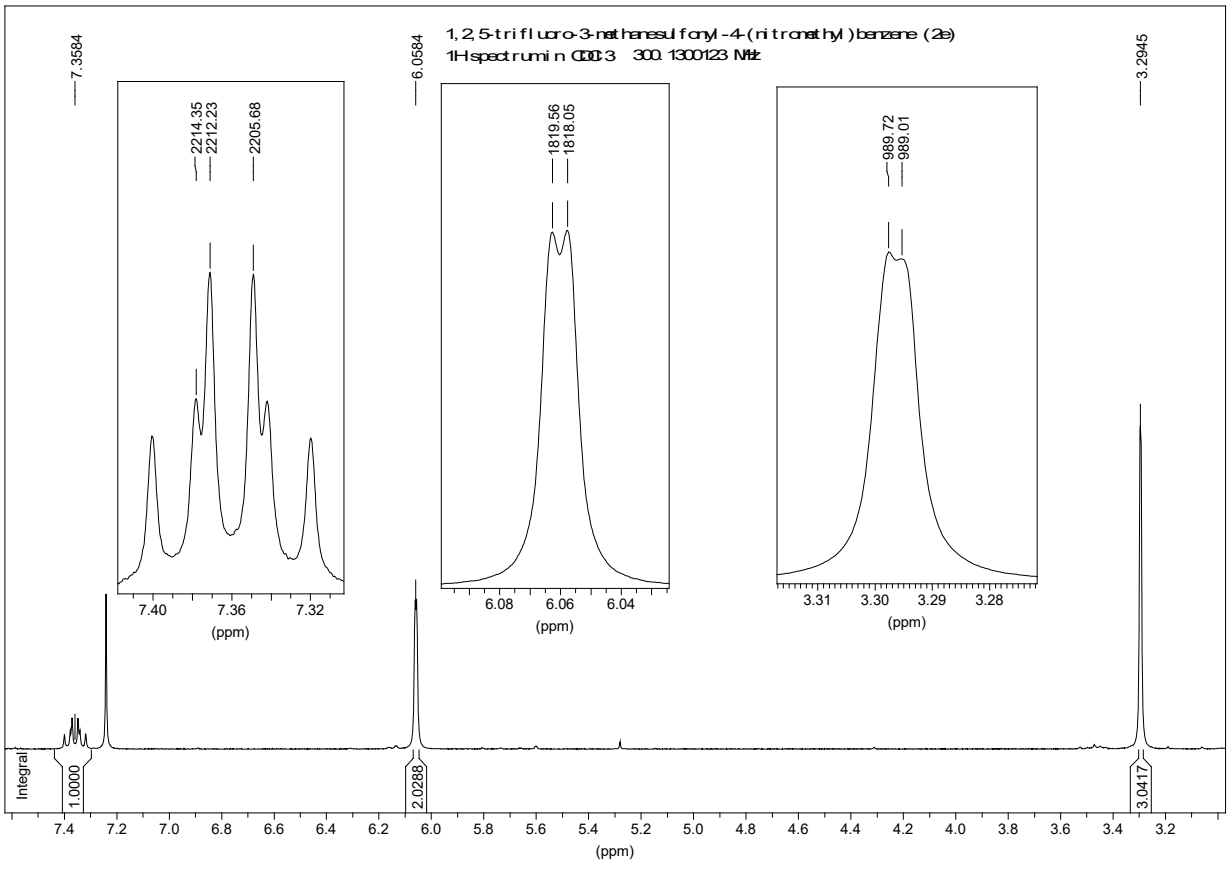


UV spectrum of **5a**.

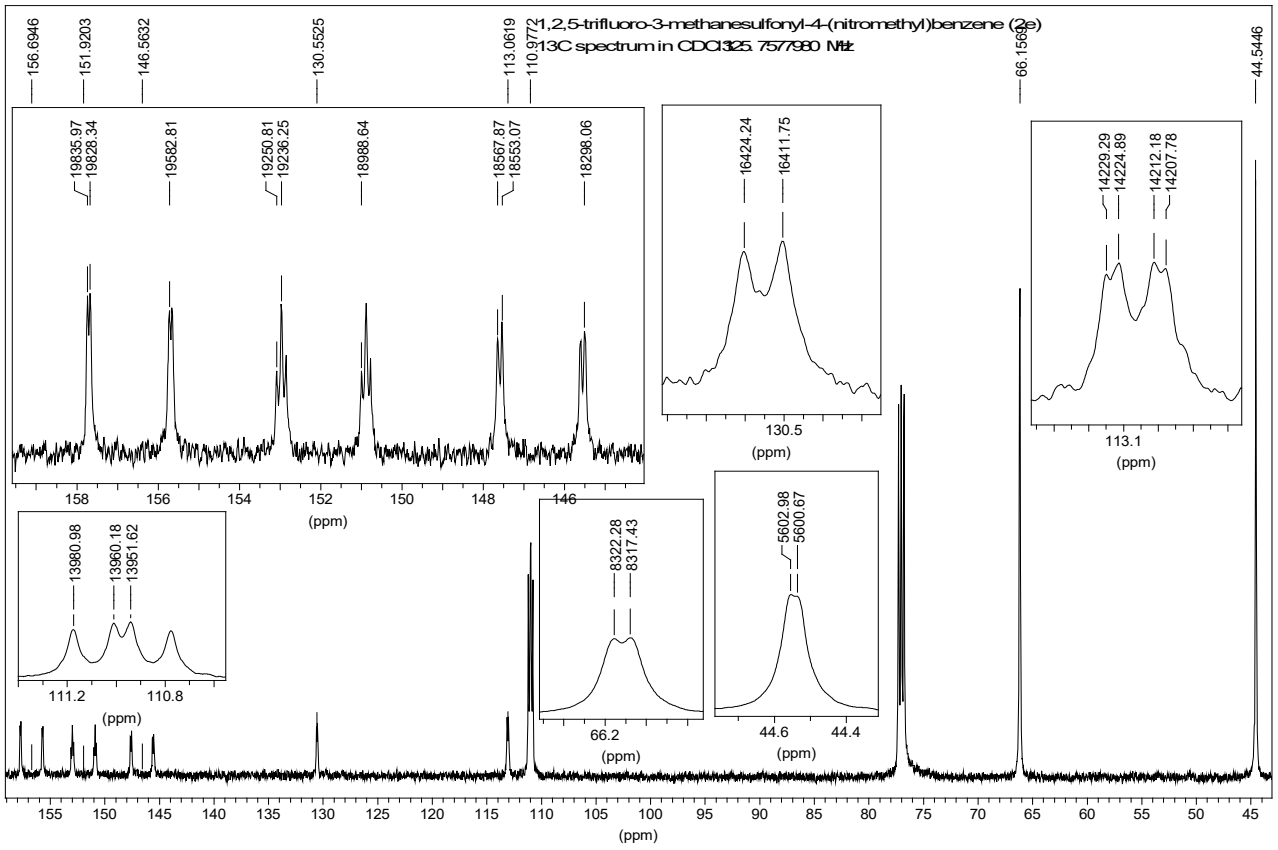


No	nm	A	FWHH	Asym	Intensity
1	281.00	0.206	26.12	-0.31	W
2	315.00	0.011	-	-	VW
3	330.00	0.010	-	-	VW

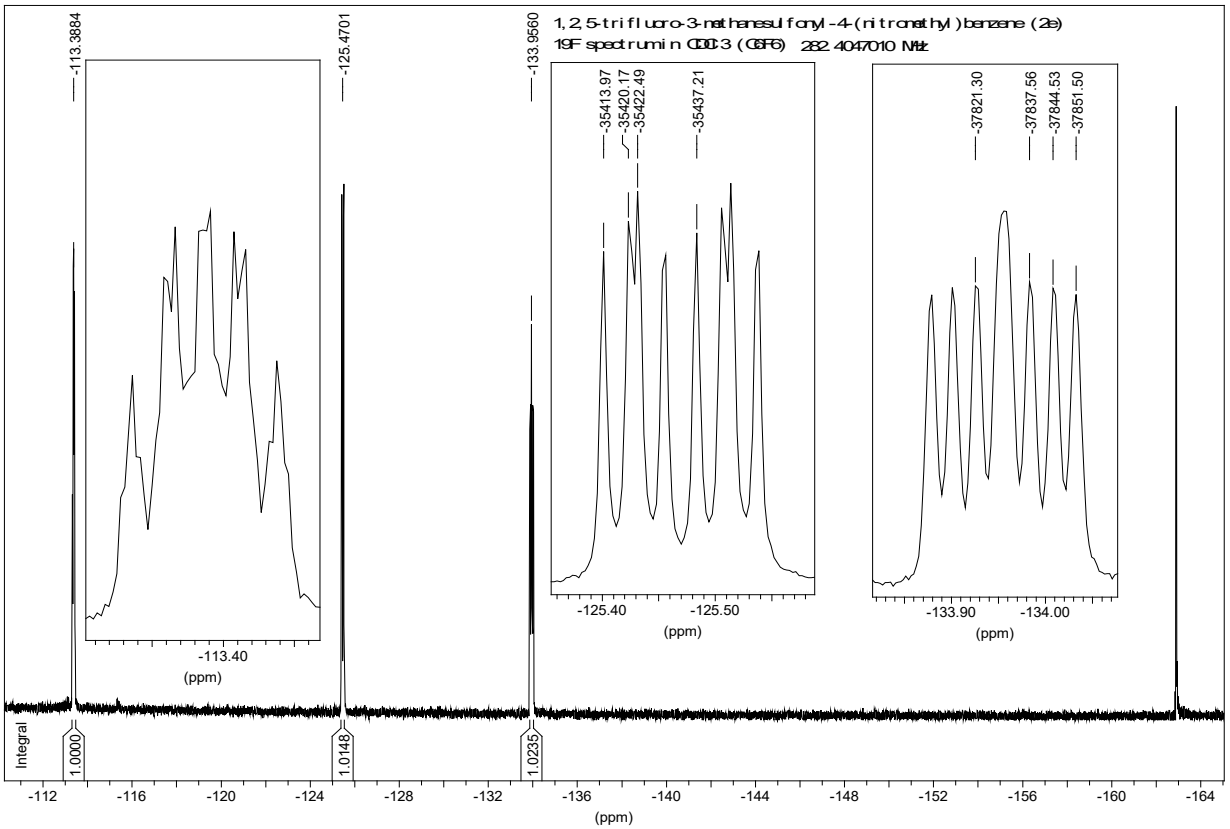
^{1}H NMR spectrum of **5a**.



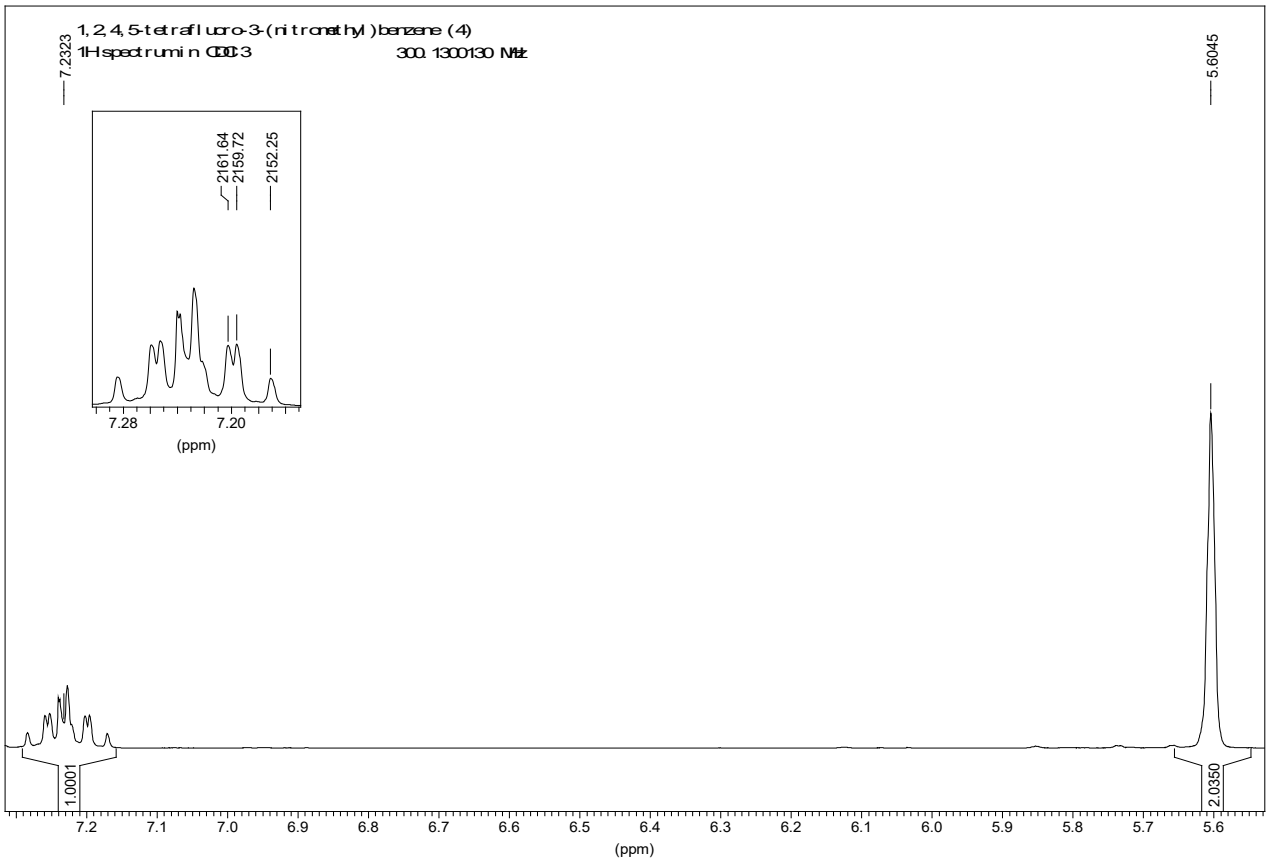
^{13}C NMR spectrum of **5a**.



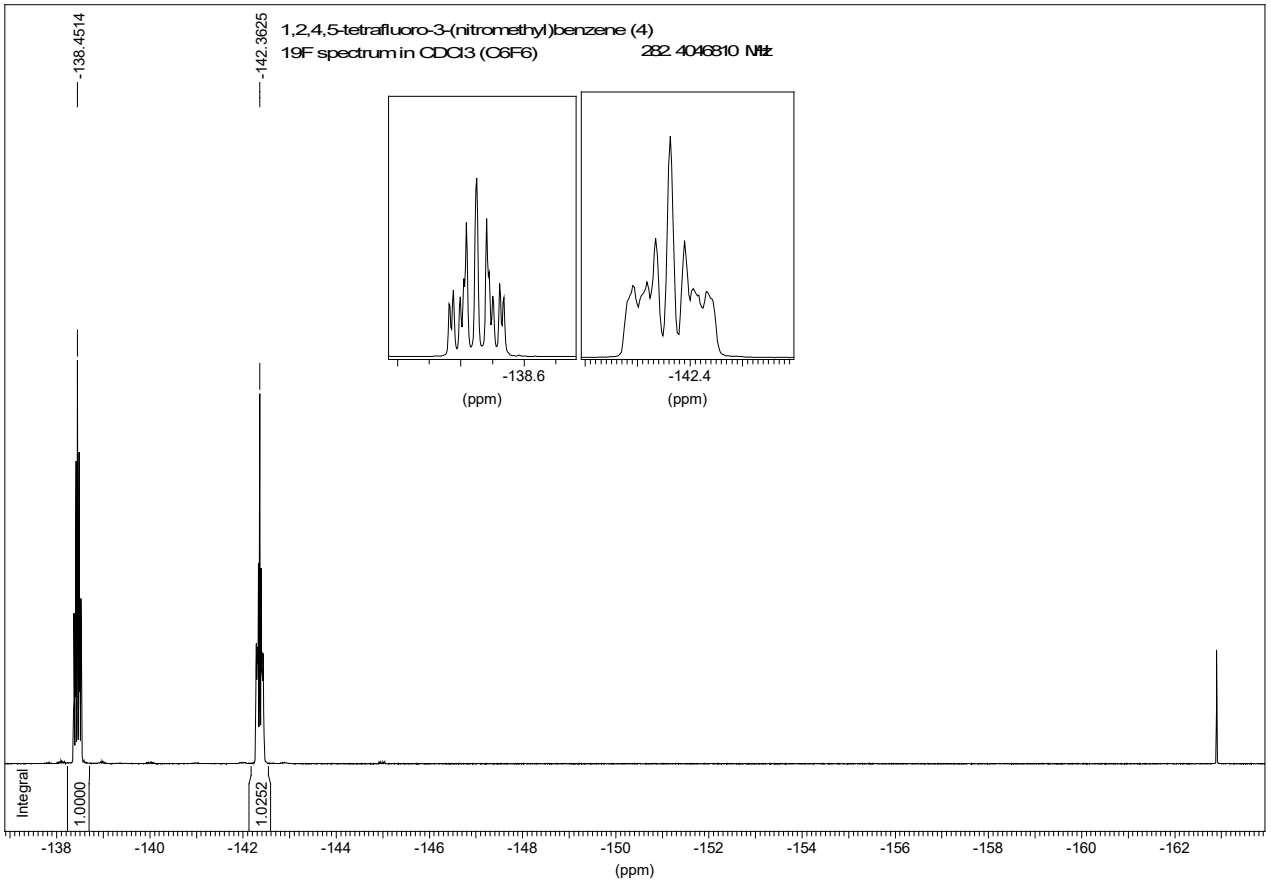
^{19}F NMR spectrum of **5a**.



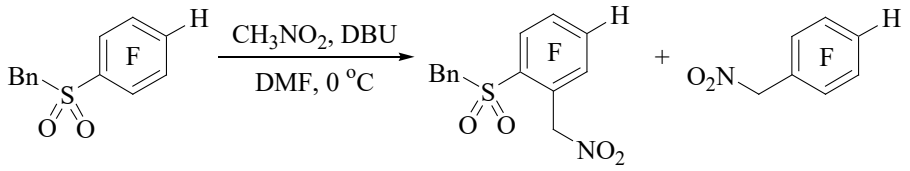
^{1}H NMR spectrum of **6**.



^{19}F NMR spectrum of **6**.



1,2,5-Trifluoro-4-(nitromethyl)-3-phenylmethanesulfonylbenzene (5b).

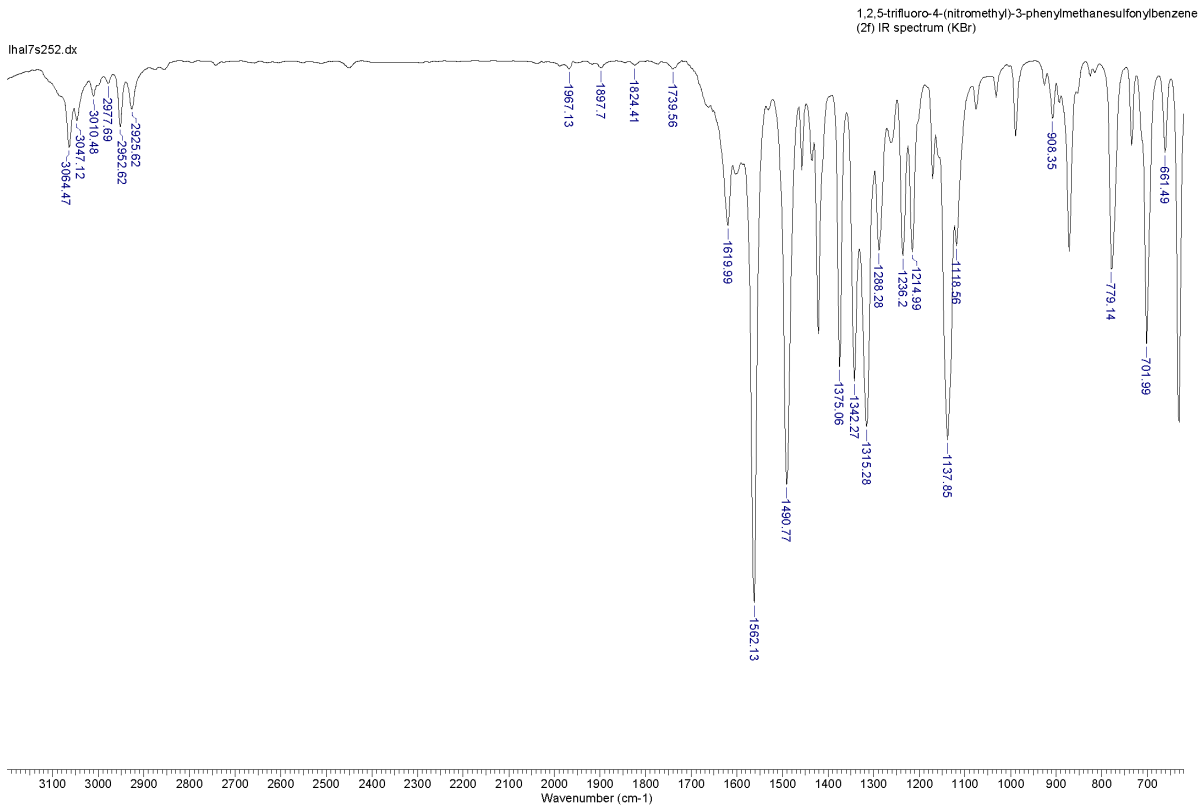


4b **5b** **6**

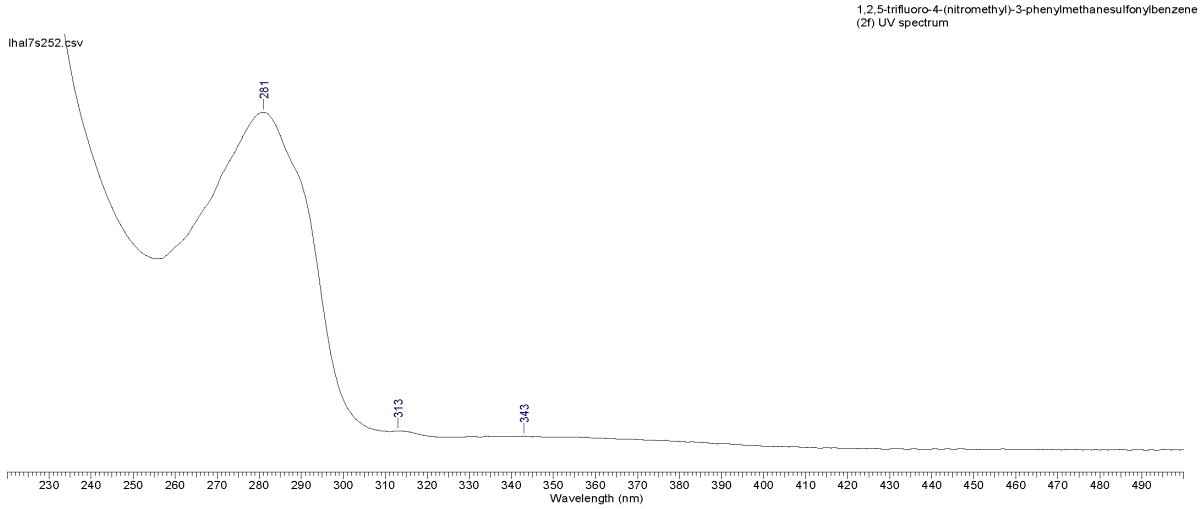
From sulfone **4b** (32.14 g, 105.63 mmol) in DMF (105 ml), nitromethane (86.07 g, 1.41 mol) and DBU (35.55 g, 233.51 mmol) in DMF (105 ml) at 0 °C for 6.5 h, a mixture of **5b** and **6** was obtained with ratio 93 : 7 respectively according to ^{19}F NMR. 32.52 g (yield - 89 %) of nitromethyl derivative **5b** obtained after treatment. White solid. Mp 147-149 °C. IR (KBr, ν_{max}, cm^{-1}): 3064(w) (CH), 3047(w) (CH), 3010(vw) (CH), 2978(vw) (CH), 2953(w) (CH), 2926(vw) (CH), 1967(vw), 1898(vw), 1824(vw), 1740(vw), 1620(m) (ArF), 1562(vs) (NO_2), 1491(s) (ArF), 1375(m) (NO_2), 1342(m) (CF), 1315(s) (SO_2), 1288(m) (CF), 1236(m) (CF), 1215(m) (CF), 1138(vs) (SO_2), 1119(m) (CF), 908(w) (C-NO_2), 779(m) (C-S), 702(m) (C-S), 661(w) (C-NO_2). UV, λ_{max}, nm (log ε): 281 (3.61), 313 (2.45), 343 (2.34). ^{1}H NMR [CD_3CN, 300.13 MHz]: δ_H 4.67 (s, 2H, C$\underline{H}_2$Bn), 5.54 (d, $^4J_{HF}$ 1.7, 2H, C$\underline{H}_2NO_2$), 7.27 (m, 2H, H-(2',6')), 7.33-7.46 (m, 3H, H-(3'-5')), 7.64 (td, $^3J_{HF}$ 9.5, $^4J_{HF}$ 6.7, 1H, H-(6)) ppm; ^{13}C NMR [CD_3CN, 100.61 MHz]: δ_C 63.4 (d, $^4J_{CF}$ 1.8, $\underline{C}H_2$Bn), 67.9 (d, $^3J_{CF}$ 5.3, $\underline{C}H_2NO_2$), 111.0 (dd, $^2J_{CF}$ 30.1, $^2J_{CF}$ 21.3, C-(6)), 112.7 (dd, $^2J_{CF}$ 17.6, $^3J_{CF}$ 4.8, C-(4)), 127.4 (C-(1')), 129.3 (dd, $^2J_{CF}$ 12.1, $^3J_{CF}$ 1.8, C-(3)), 129.9 (C-(2',6') or C-(3',5')), 130.5 (C-(4')), 132.3 (C-(2',6') or C-(3',5')), 147.7 (ddd, $^1J_{CF}$ 254.7, $^2J_{CF}$ 14.7, $^4J_{CF}$ 3.9, C-(2)), 153.1 (ddd, $^1J_{CF}$ 258.2, $^2J_{CF}$ 15.4, $^3J_{CF}$ 13.8, C-(1)), 158.1 (ddd, $^1J_{CF}$ 252.0, $^3J_{CF}$ 10.1, $^4J_{CF}$ 2.8, C-(5)) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -133.0 (ddd, $^3J_{FF}$ 23.2, $^5J_{FF}$ 13.9, $^4J_{HF}$ 6.2, 1F, F-(2)), -125.9 (ddd, $^3J_{FF}$ 23.2, $^3J_{HF}$ 8.5, $^4J_{FF}$ 7.0, 1F, F-(1)), -112.8 (m, 1F, F-(5)) ppm. Anal. calcd for $C_{14}H_{10}F_3NO_4S$, %: C 48.70; H 2.92; F 16.51; N 4.06; S 9.28; M^+ 345.0277. Found, %: C 48.40; H 3.30; F 16.78; N 3.94; S 9.25; M^+ 345.0276.

Residue (1.65 g) from hexane solutions contained 87% of arene **6** (yield - 6 %) according to NMR (PhF).

IR spectrum of **5b**.

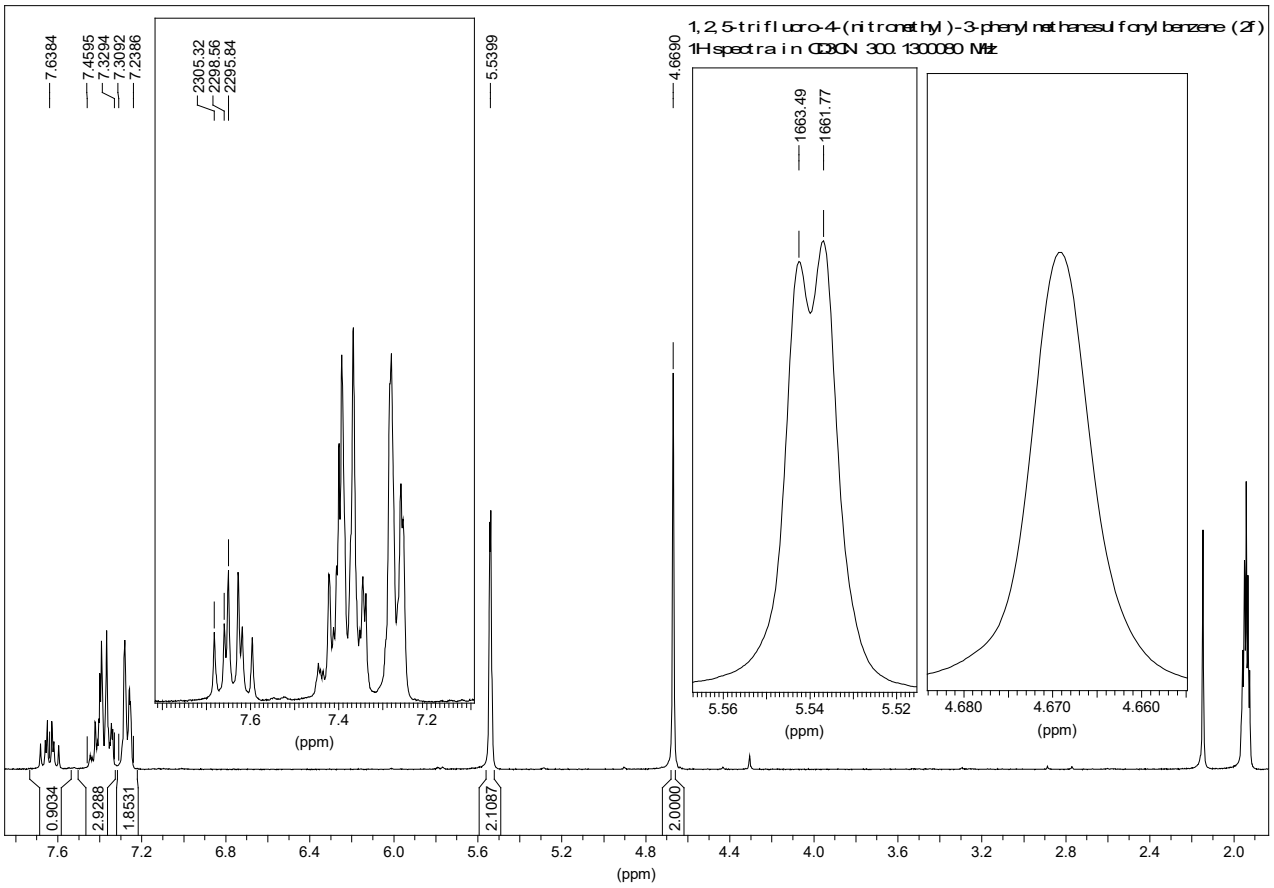


UV spectrum of **5b**.

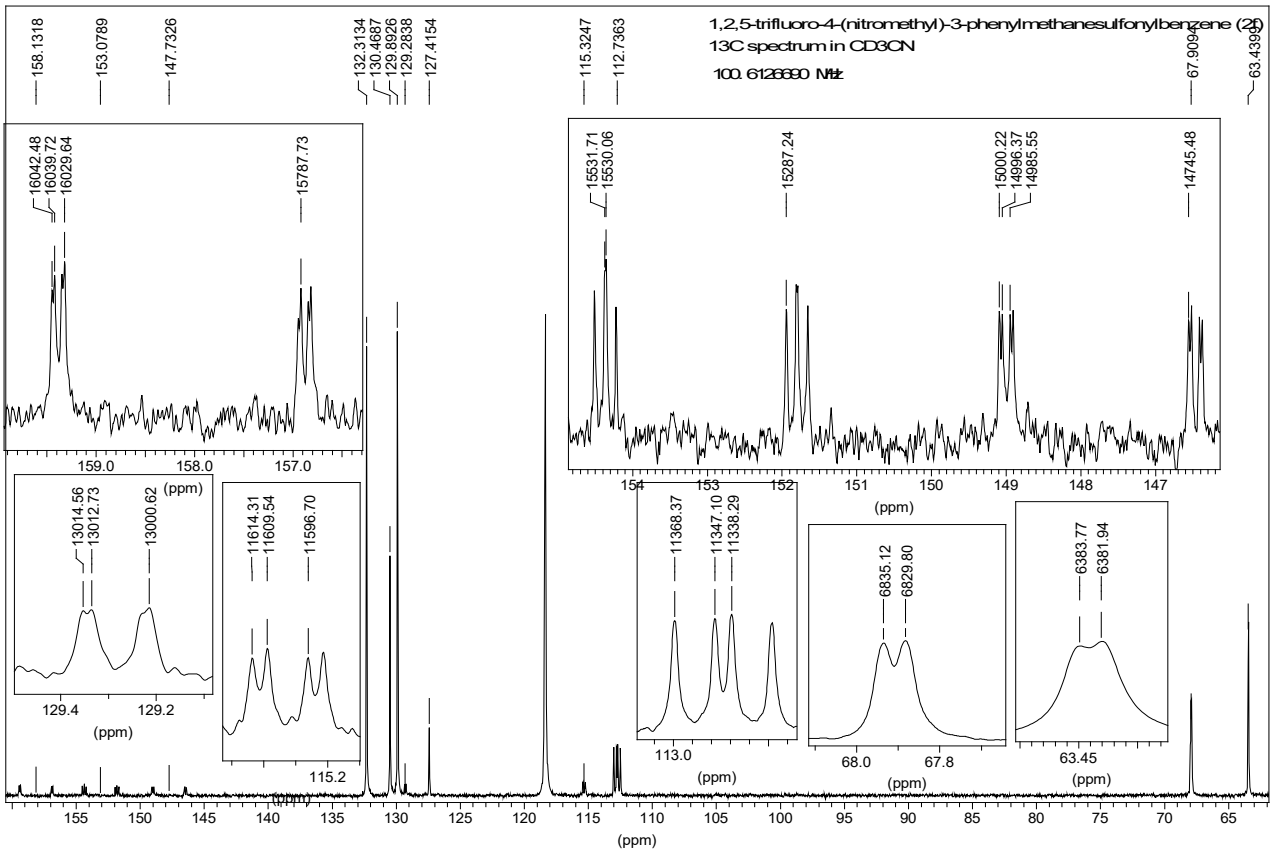


No	nm	A	Intensity
1	281.00	0.203	W
2	313.00	0.014	VW
3	343.00	0.011	VW

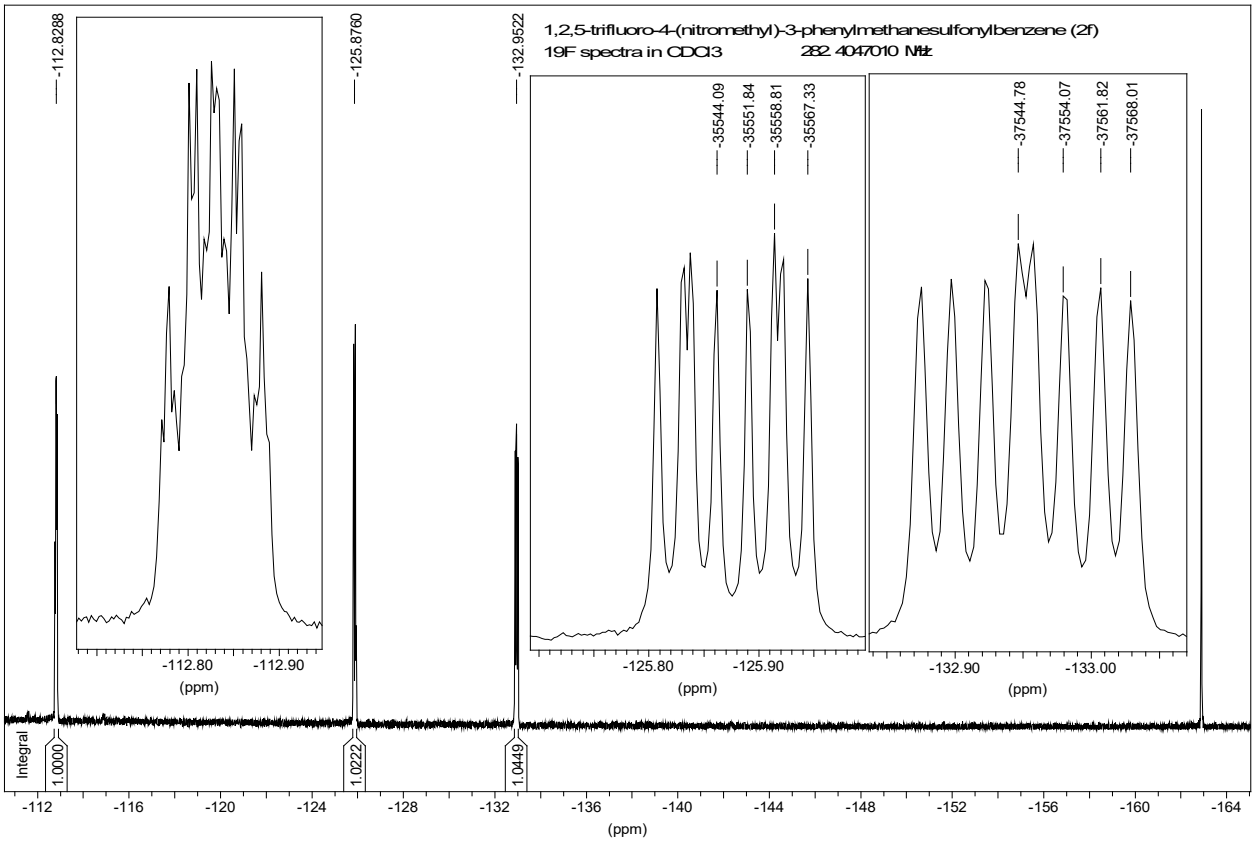
^{1}H NMR spectrum of **5b**.



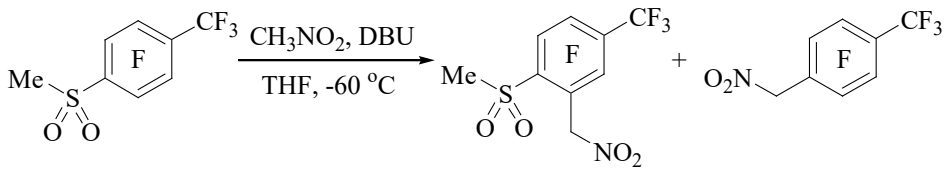
^{13}C NMR spectrum of **5b**.



^{19}F NMR spectrum of **5b**.



1,2,4-Trifluoro-6-methanesulfonyl-5-nitromethyl-3-(trifluoromethyl)benzene (5c).



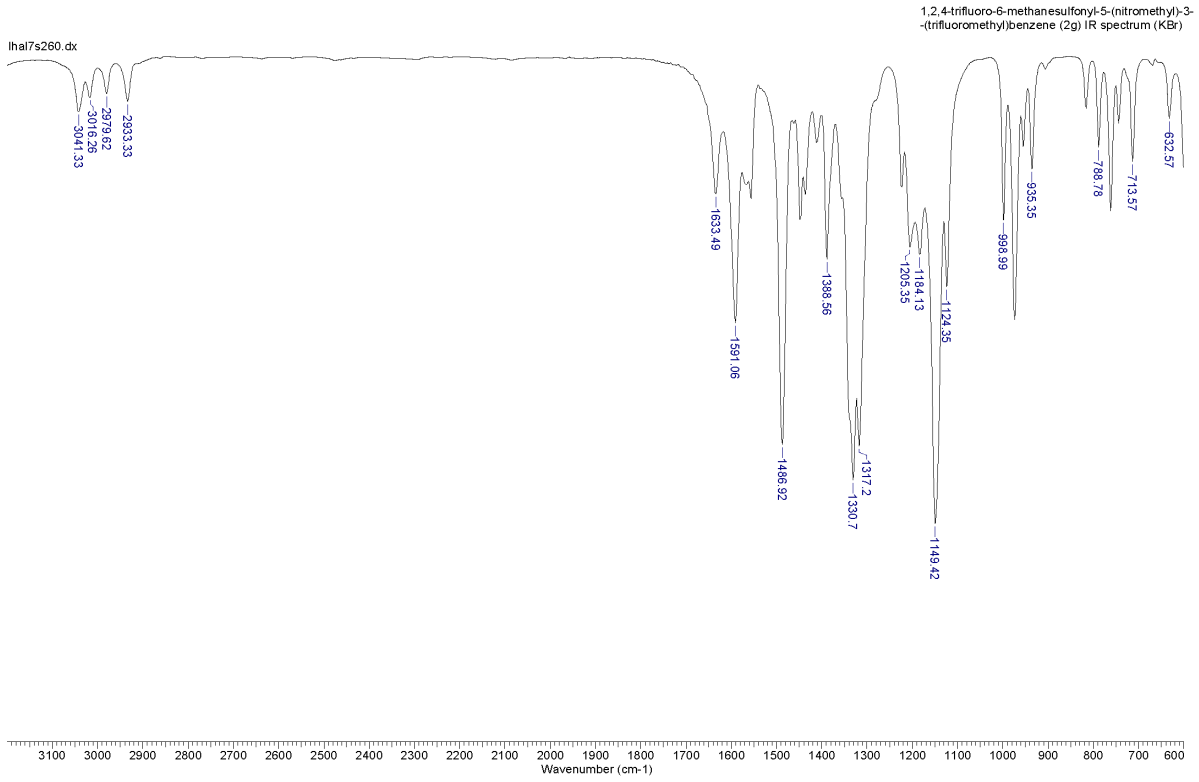
4c **5c** **6'**

From sulfone **4c** (30.04 g, 101.43 mmol) in THF (100 ml), nitromethane (83.71 g, 1.37 mol) and DBU (34.32 g, 225.43 mmol) in THF (100 ml) at -60 °C for 8.5 h, the mixture of **5c** and **6'** with ratio 65 : 35 was obtained according to ^{19}F NMR. 18.52 g (55 %) of sulfone **5c** obtained after recrystallization. White solid. Mp 109-111 °C. IR (KBr, ν_{max}, cm^{-1}): 3041(w) (CH), 3016(vw) (CH), 2980(vw) (CH), 2933(vw) (CH), 1633(w) (ArF), 1591(m) (NO_2), 1487(s) (ArF), 1389(m) (NO_2), 1331(vs) (SO_2), 1317(s) (CF), 1205(m) (CF), 1184(m) (CF), 1149(vs) (SO_2), 1124(m) (CF), 999(vs) (CF), 935(w) (C-NO_2), 789(w) (C-S), 714(w) (C-S), 633(w) (C-NO_2). UV, λ_{max}, nm (log ε): 288 (3.60). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 3.33 (d, $^5J_{HF}$ 1.2, 3H, C$\underline{H}_3SO_2$), 6.10 (d, $^4J_{HF}$ 2.1, C$\underline{H}_2NO_2$) ppm; ^{13}C NMR [CD_3CN, 150.92 MHz]: δ_C 45.5 (d, $^4J_{CF}$ 3.5, $\underline{C}H_3SO_2$), 67.6 (d, $^3J_{CF}$ 6.9, $\underline{C}H_2NO_2$), 114.0 (qdd, $^2J_{CF}$ 34.7, $^2J_{CF}$ 18.5, $^2J_{CF}$ 11.6, C-(3)), 115.8 (dd, $^2J_{CF}$ 17.9, $^3J_{CF}$ 5.2, C-(5)), 121.6 (q, $^1J_{CF}$ 274.0, $\underline{C}F_3$), 134.4 (d, $^2J_{CF}$ 12.7, C-(6)), 148.0 (ddd, $^1J_{CF}$ 254.3, $^2J_{CF}$ 15.0, $^4J_{CF}$ 4.6, C-(1)), 151.2 (ddd, $^1J_{CF}$ 269.3, $^2J_{CF}$ 11.6, $^3J_{CF}$ 2.3, C-(2)), 155.3 (dd, $^1J_{CF}$ 260.1, $^3J_{CF}$ 2.3, C-(4)) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F

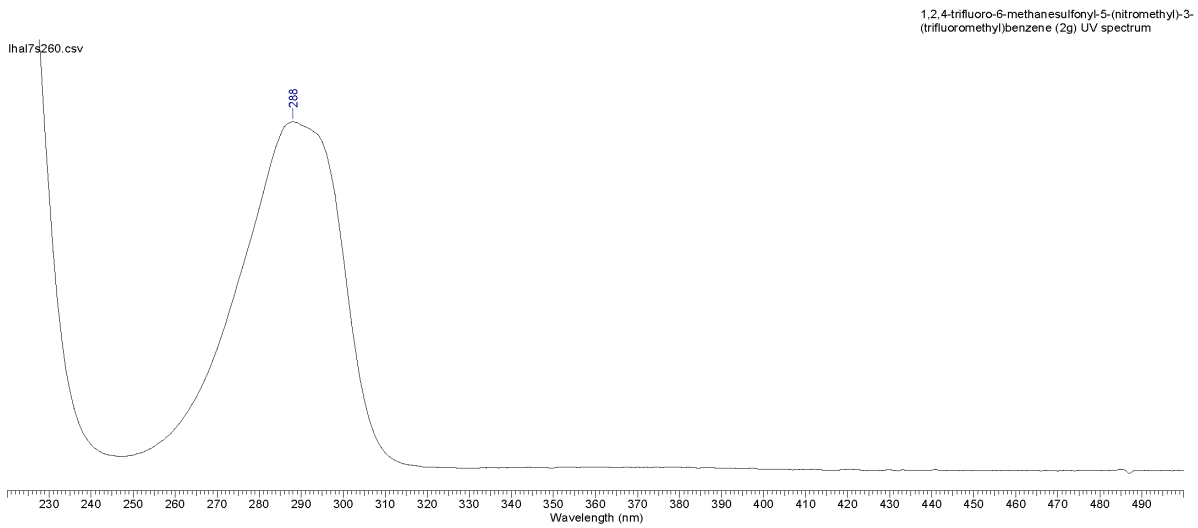
-131.2 (dd, $^{3}J_{FF}$ 22.5, $^{5}J_{FF}$ 14.7, 1F, F-(1)), -125.6 (dq, $^{3}J_{FF}$ ~23, $^{4}J_{FF}$ ~23, 1F, F-(2)), -114.7 (qd, $^{4}J_{FF}$ 21.7, $^{5}J_{FF}$ 14.7, 1F, F-(4)), -58.2 (dd, $^{4}J_{FF}$ 23.2, $^{4}J_{FF}$ 21.7, 3F, C<u>F</u>$_3$) ppm. Anal. calcd for $C_9H_5F_6NO_4S$, %: C 32.06; H 1.49; F 33.81; N 4.15; S 9.51; M^+ 336.9838, $(M\text{-}F)^+$ 317.9854. Found, %: C 32.04; H 1.49; F 33.83; N 4.01; S 9.84; $(M\text{-}F)^+$ 317.9858, M 335 (KNAUER K-7000).

9.09 g (yield - 33 %) of **1,2,4,5-tetrafluoro-3-nitromethyl-6-(trifluoromethyl)benzene** (**6'**) were obtained after steam distillation. ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 5.65 (s, 2H, C<u>H</u>$_2$NO$_2$) ppm;[S9] ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -139.9 (m, 2F, F-(2,4)), -139.7 (m, 2F, F-(1,5)), -57.7 (t, $^{4}J_{FF}$ 22.5, 3F, C<u>F</u>$_3$) ppm. [S9] Anal. calcd for $C_7H_3F_4NO_2$: M^+ 277. Found by GC-MS: M^+ 277.

IR spectrum of **5c**.

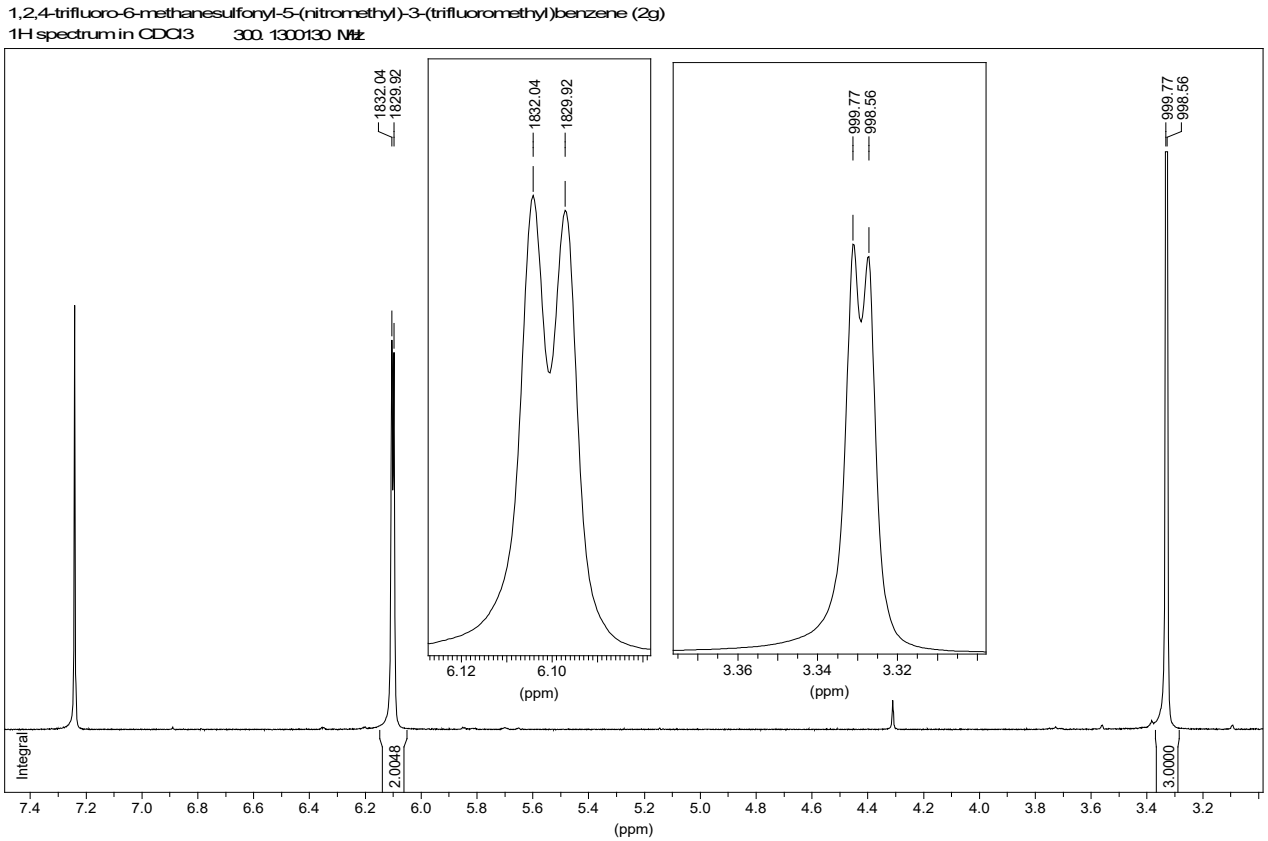


UV spectrum of **5c**.

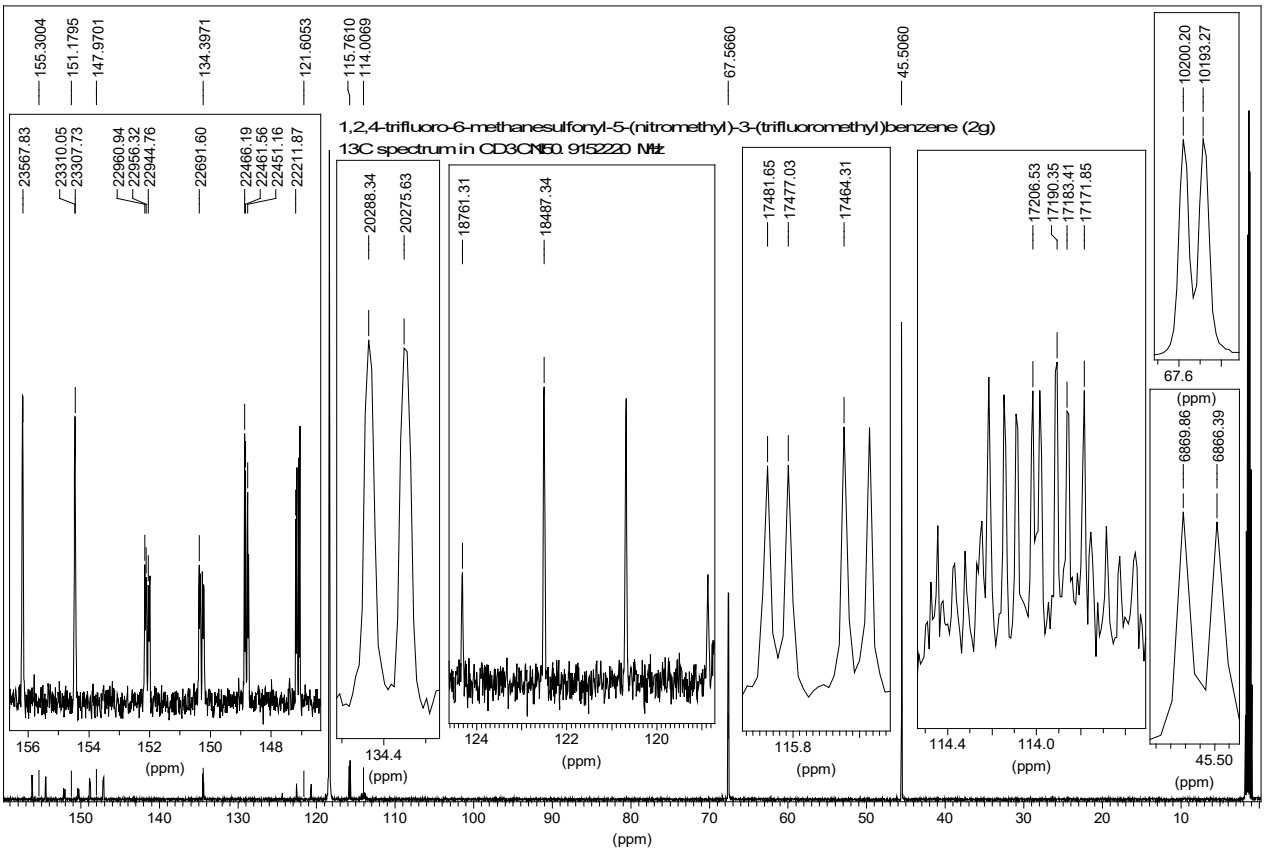


No	nm	A	FWHH	Asym	Intensity
1	288.00	0.203	27.33	-0.07	W

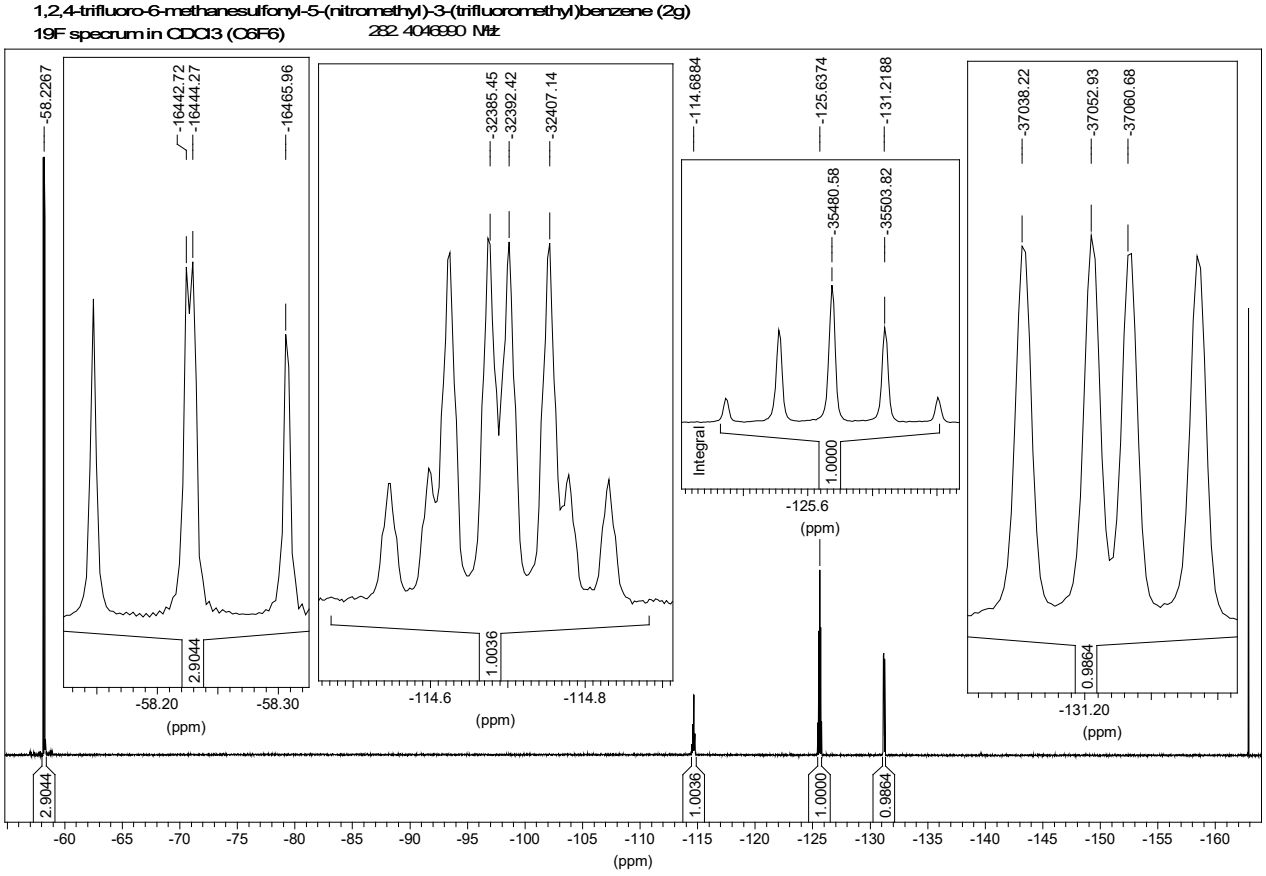
^{1}H NMR spectrum of **5c**.



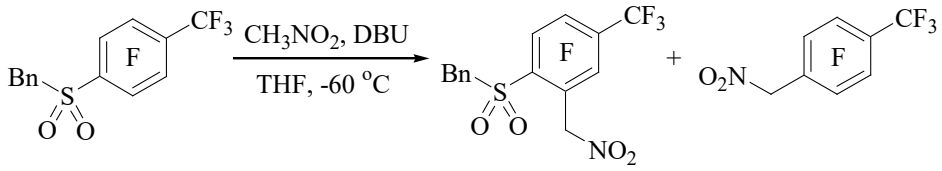
^{13}C NMR spectrum of **5c**.



^{19}F NMR spectrum of **5c**.



1,2,4-Trifluoro-5-nitromethyl-6-phenylmethanesulfonyl-3-(trifluoromethyl)benzene (5d).

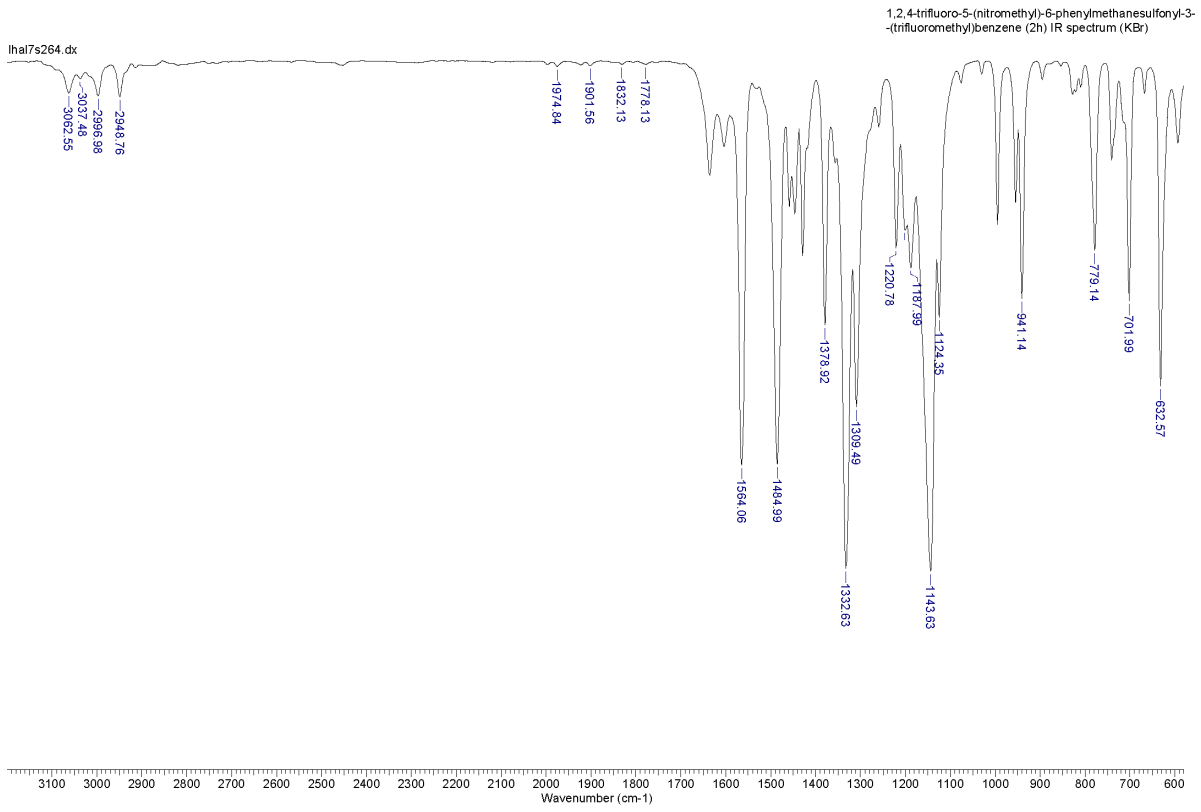


4d **5d** **6'**

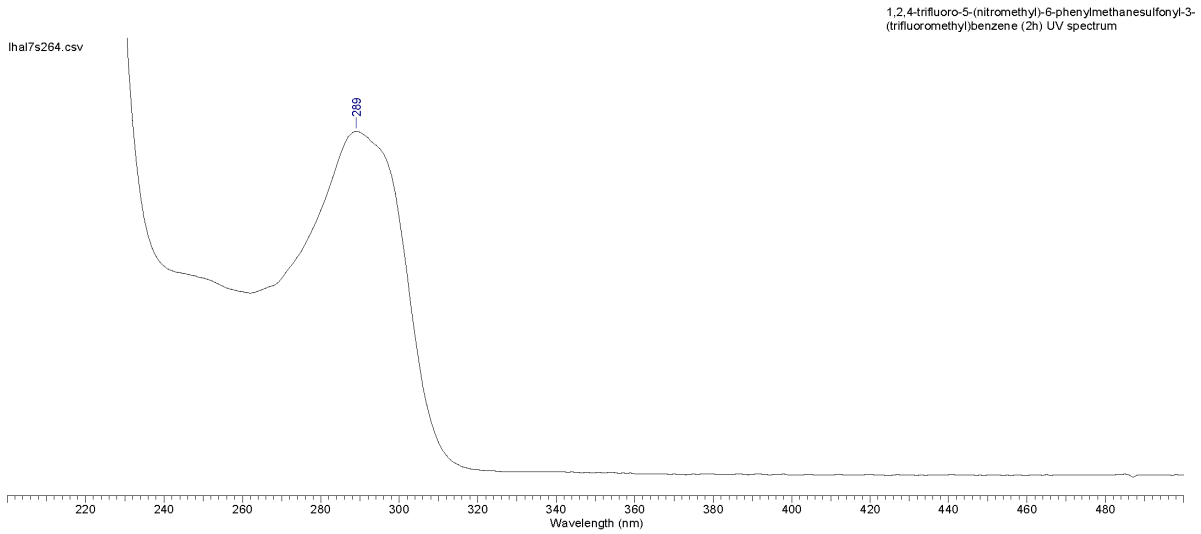
From sulfone **4d** (38.83 g, 101.84 mmol) in THF (100 ml), nitromethane (83.11 g, 1.36 mol) and DBU (33.93 g, 222.87 mmol) in THF (100 ml) at -60 °C for 12 h, a mixture of **4d** and **6'** with ratio 36 : 64 was obtained according to ^{19}F NMR. 11.85 g (yield - 29 %) of sulfone **4d** was obtained after recrystallization. White solid. Mp 154-155 ºC. IR (KBr, ν_{max}, cm^{-1}): 3063(vw) (CH), 3037(vw) (CH), 2997(vw) (CH), 2949(vw) (CH), 1975(vw), 1902(vw), 1832(vw), 1778(vw), 1564(s) (NO_2), 1485(vs) (ArF), 1379(m) (NO_2), 1333(vs) (SO_2), 1309(s) (CF), 1221(m) (CF), 1201(m) (CF), 1188(m) (CF), 1144(vs) (SO_2), 1124(m) (CF), 941(w) (C-NO_2), 779(m) (C-S), 702(m) (C-S), 633(s) (C-NO_2). UV, λ_{max}, nm (log ε): 289 (3.59). ^{1}H NMR [CD_3CN, 300.13 MHz]: δ_H 4.72 (s, PhC$\underline{H}_2SO_2$), 5.60 (d, $^4J_{HF}$ 2.2, 2H, C$\underline{H}_2NO_2$), 7.31 (m, 2H, H-(2',6')), 7.36-7.48 (m, 3H, H-(3'-5')) ppm; ^{13}C NMR [CD_3CN, 100.60 MHz]: δ_C 63.4 (d, $^4J_{CF}$ 2.0, Ph$\underline{C}H_2SO_2$), 67.5 (d, $^3J_{CF}$ 6.4, $\underline{C}H_2NO_2$), 114.4 (qdd, $^2J_{CF}$ 34.8, $^2J_{CF}$ 18.7, $^2J_{CF}$ 11.2, C-(3)), 116.5 (dd, $^2J_{CF}$ 18.0, $^3J_{CF}$ 5.3, C-(5)), 121.5 (q, $^1J_{CF}$ 274.2, $\underline{C}F_3$), 126.8 (C-(1')), 130.0 (C-(3',5')), 130.7 (C-(4')), 132.5 (C-(2',6')), 132.6 (d, $^2J_{CF}$ 13.2, C-(6)), 148.0 (ddd, $^1J_{CF}$ 256.6, $^2J_{CF}$ 14.9, $^4J_{CF}$ 4.4, C-(1)), 151.2 (ddd, $^1J_{CF}$ 267.8, $^2J_{CF}$ 17.8, $^3J_{CF}$ 5.0, C-(2)), 155.3 (d, $^1J_{CF}$ 261.9, C-(4)) ppm; ^{19}F NMR [CD_3CN, 282.4 MHz]: δ_F -129.4 (dd, $^3J_{FF}$ 21.7, $^5J_{FF}$ 13.9, 1F, F-(1)), -125.9 (dq, $^3J_{FF}$ ~23, $^4J_{FF}$ ~23, 1F, F-(2)), -113.3 (qd, $^3J_{FF}$ 21.7, $^5J_{FF}$ 13.9, 1F, F-(4)), -56.6 (d, $^4J_{FF}$ 24.0, $^4J_{FF}$ 21.7, 3F, C$\underline{F}_3$) ppm. Anal. calcd for $C_{15}H_9F_6NO_4S$, %: C 43.59; H 2.20; F 27.58; N 3.39; S 7.76; M^+ 413.0151. Found, %: C 43.89; H 2.45; F 27.84; N 3.12; S 8.08; M^+ 413.0159.

16.75 g (yield - 59 %) of arene **6'** were obtained after steam distillation.

IR spectrum of **5d**.

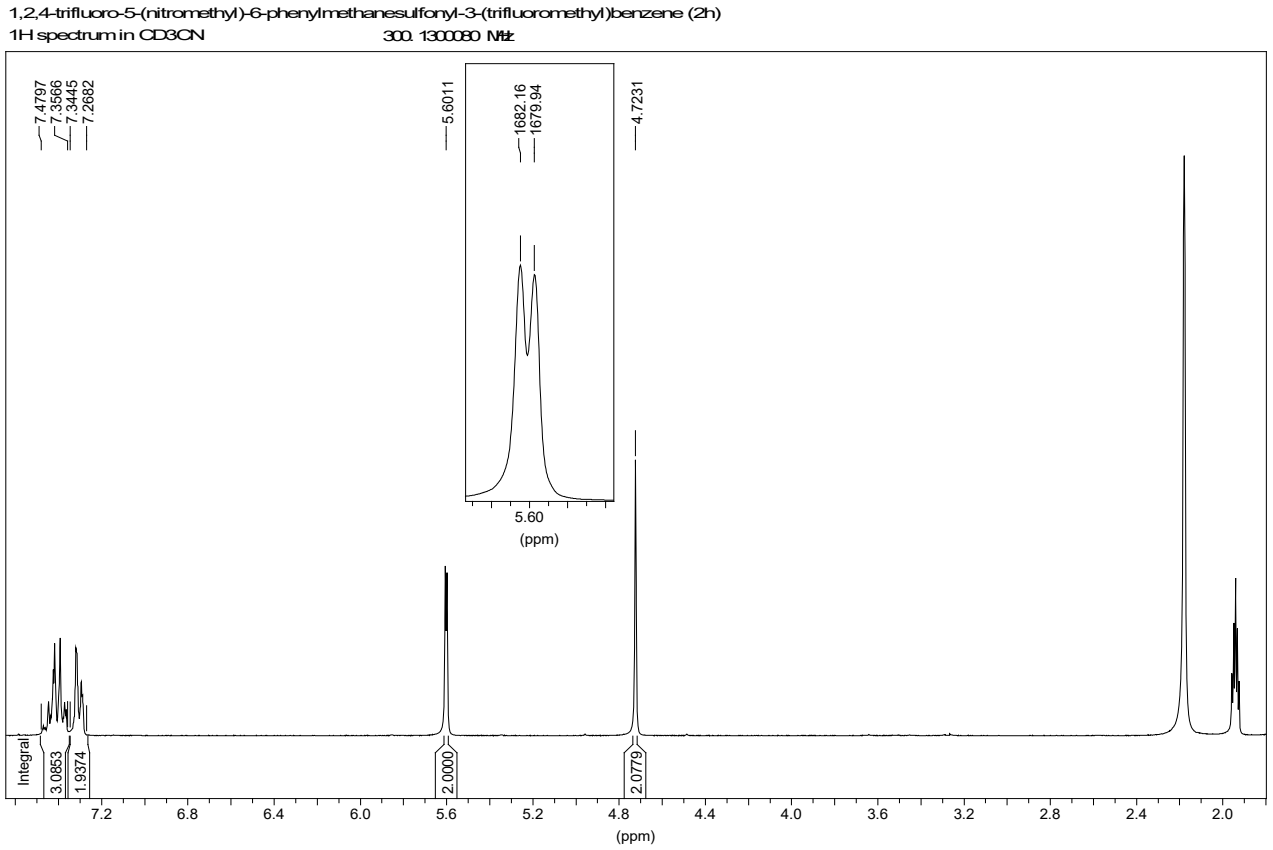


UV spectrum of **5d**.

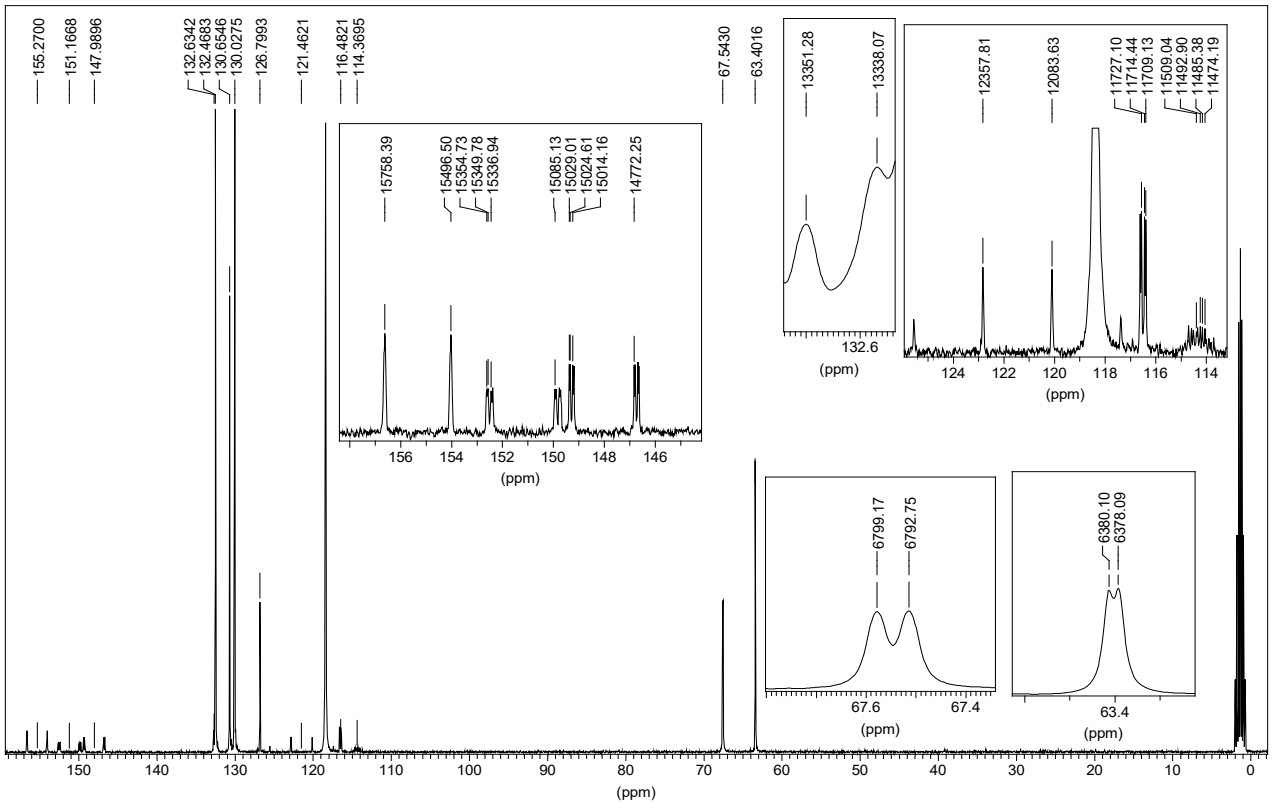


No	nm	A	Intensity
1	289.00	0.197	W

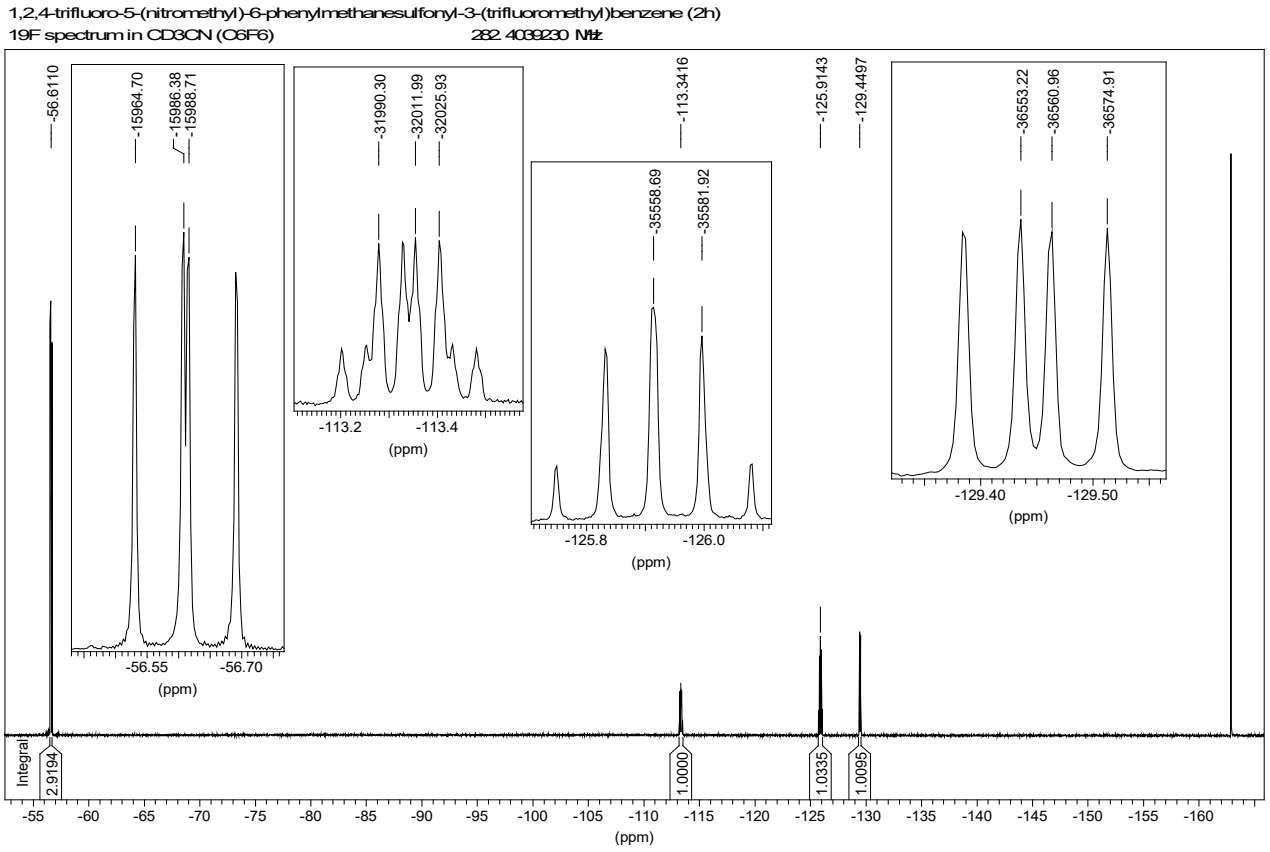
^{1}H NMR spectrum of **5d**.



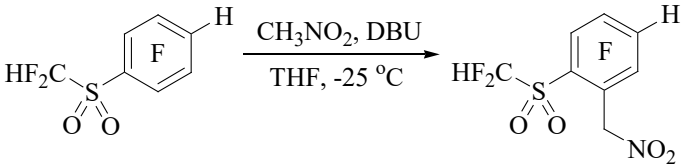
^{13}C NMR spectrum of **5d**.



^{19}F NMR spectrum of **5d**.



3-Difluoromethanesulfonyl-1,2,5-trifluoro-4-(nitromethyl)benzene (5e).

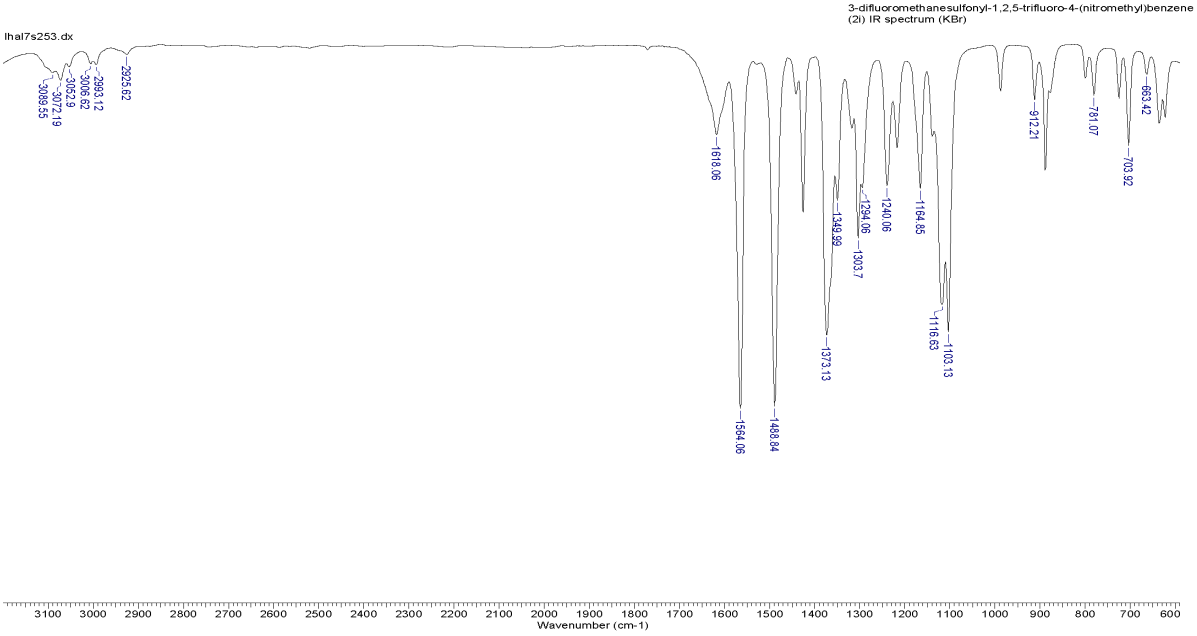


4e **5e**

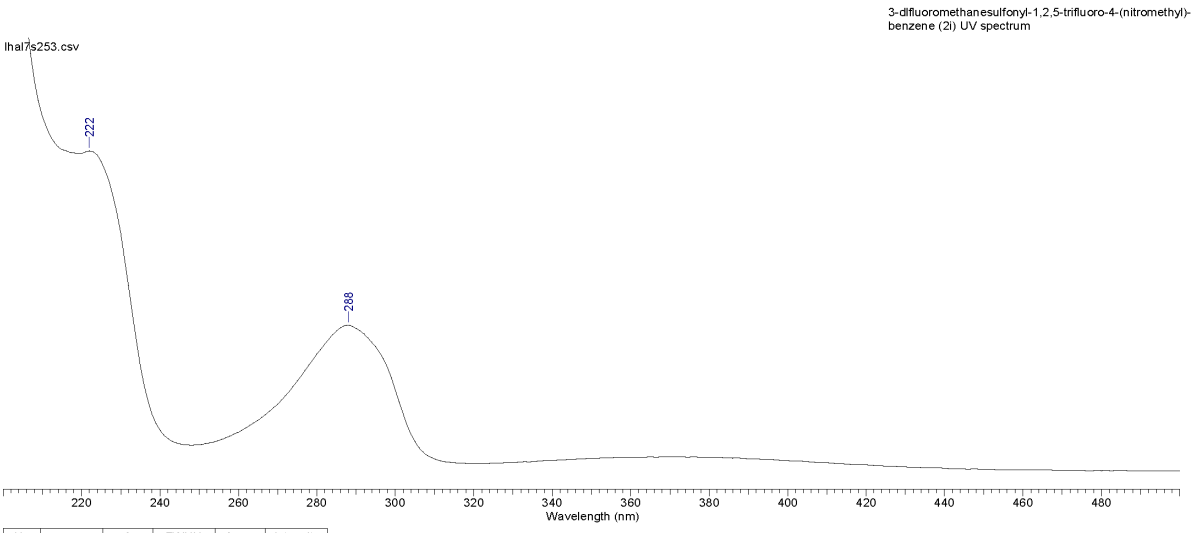
From sulfone **4e** (26.50 g, 100.33 mmol) in THF (100 ml), nitromethane (81.35 g, 1.33 mol) and DBU (33.55 g, 220.38 mmol) in THF (100 ml) at -25 °C for 3 h, a 26.86 g (88 %) of sulfone **5e** was obtained after recrystallization from $CHCl_3$. Pale-yellow solid. Mp 76-78 ºC. IR (KBr, ν_{max}, cm^{-1}): 3090(vw) (CH), 3072(w) (CH), 3053(vw) (CH), 3007(vw) (CH), 2993(w) (CH), 2926(vw) (CH), 1618(w) (ArF), 1564(vs) (NO_2), 1489(vs) (ArF), 1373(s) (NO_2), 1350(m) (CF), 1304(m) (SO_2), 1294(m) (CF), 1240(m) (CF), 1165(m) (SO_2), 1117(s) (CF), 1103(s) (CF), 912(w) (C-NO_2), 781(w) (C-S), 704(w) (C-S), 663(vw) (C-NO_2). UV, λ_{max}, nm (log ε): 222 (3.87), 288 (3.53). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 5.96 (d, $^4J_{HF}$ 2.0, 1H, C$\underline{H}_2NO_2$), 6.39 (dt, $^2J_{HF}$ 53.5, $^5J_{HF}$ 1.2, 1H, C$\underline{H}F_2SO_2$), 7.50 (td, $^3J_{HF}$ 8.7, $^4J_{HF}$ 6.6, 1H, H-(6)) ppm; ^{13}C NMR [CD_3CN, 150.91 MHz]: δ_C 68.3 (d, $^4J_{CF}$ 5.8, $\underline{C}H_2NO_2$), 115.1 (dd, $^2J_{CF}$ 30.1, $^2J_{CF}$ 20.8, C-(6)), 115.9 (t, $^1J_{CF}$ 285.5, $\underline{C}HF_2SO_2$), 116.6 (dd, $^2J_{CF}$ 17.3, $^3J_{CF}$ 4.6, C-(4)), 123.8 (d, $^2J_{CF}$ 11.6, C-(3)), 149.1 (ddd, $^1J_{CF}$ 258.9, $^2J_{CF}$ 15.0, $^4J_{CF}$ 3.5, C-(2)), 153.3 (dt, $^1J_{CF}$ 260.1, $^{2,3}J_{CF}$ 13.9, C-(1)), 158.7 (ddd, $^1J_{CF}$ 253.2, $^3J_{CF}$ 10.4, $^4J_{CF}$ 2.3, C-(5)) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -129.7 (m, 1F, F-(2)), -124.1 (ddd, $^3J_{FF}$ 23.2, $^3J_{HF}$ 8.5, $^4J_{FF}$ 7.0, 1F, F-(1)), -122.4 (dd, $^2J_{FH}$ 53.5,

$^5J_{FF}$ 10.8, 2F, $SO_2C\underline{F}_2H$), -111.0 (m, 1F, F-(5)) ppm. Anal. calcd for $C_8H_4F_5NO_4S$, %: C 31.49; H 1.32; F 31.13; N 4.59; S 10.51; M^+ 304.9776, $(M\text{-}NO_2)^+$ 258.9845. Found, %: C 31.85; H 1.08; F 31.09; N 4.61; S 10.27; m/z 258.9847, M 302 (KNAUER K-7000).

IR spectrum of **5e**.

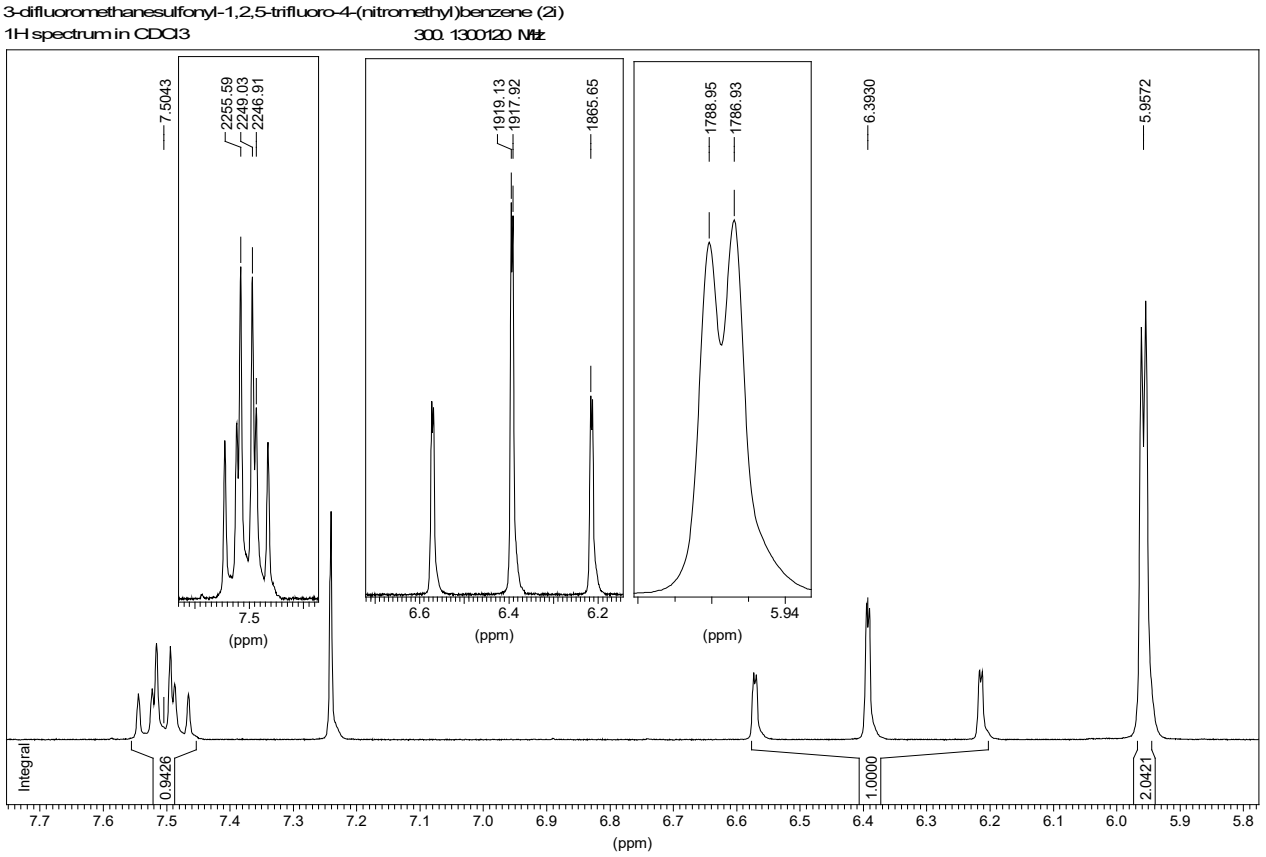


UV spectrum of **5e**.

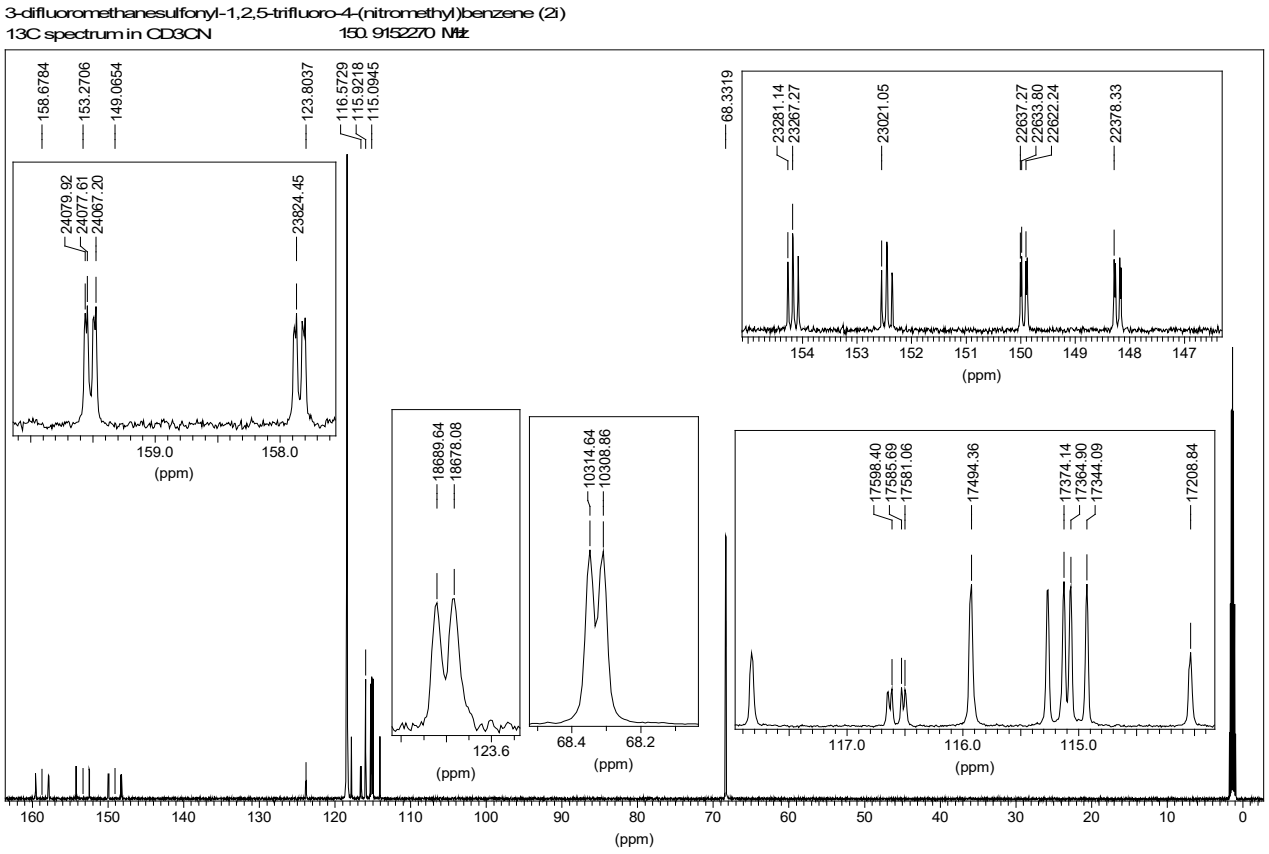


No	nm	A	FWHH	Asym	Intensity
1	222.00	0.370	-	-	M
2	288.00	0.169	29.34	-0.31	W

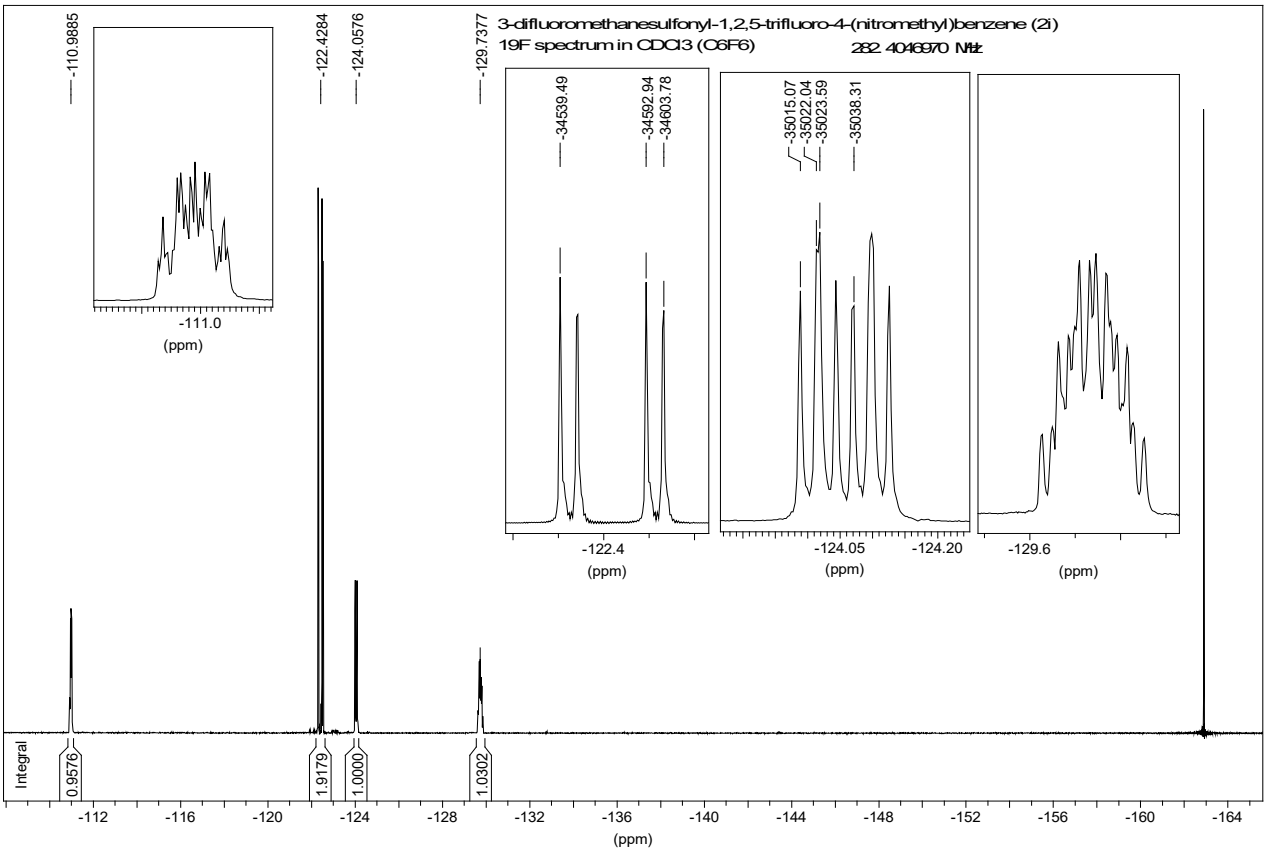
^{1}H NMR spectrum of **5e**.



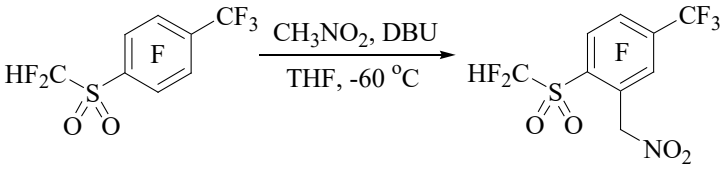
^{13}C NMR spectrum of **5e**.



^{19}F NMR spectrum of **5e**.



1-Difluoromethylsulfonyl-2,3,5-trifluoro-6-nitromethyl-4-(trifluoromethyl)benzene (5f).

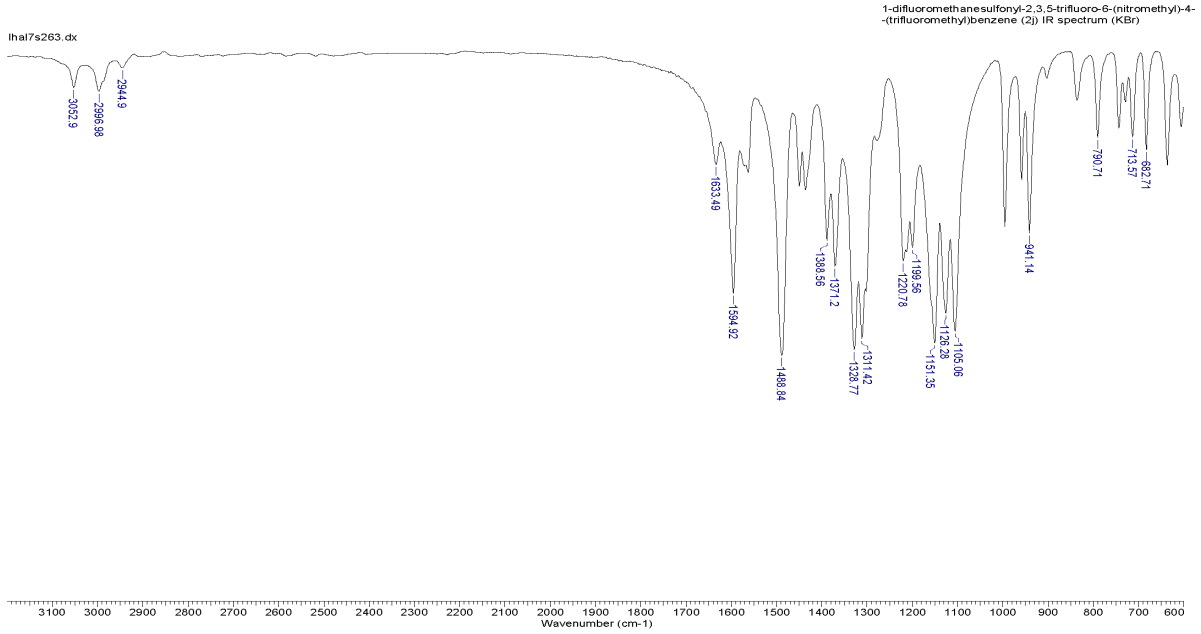


4f **5f**

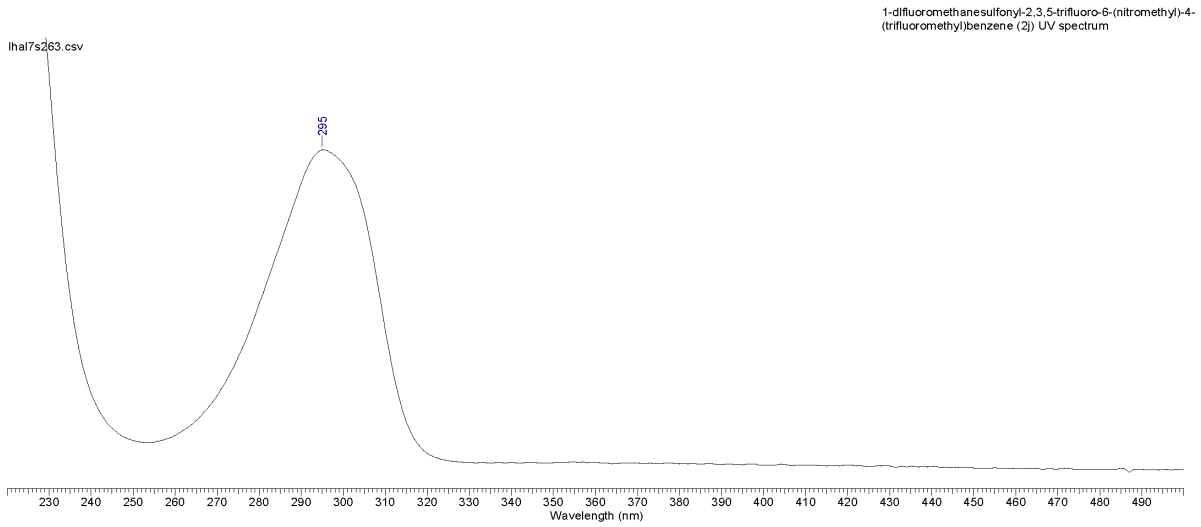
From sulfonylbenzene (**4f**) (33.44 g, 100.68 mmol) in THF (100 ml), nitromethane (81.69 g, 1.34 mol) and DBU (35.55 g, 220.97 mmol) in THF (100 ml) at -60 °C for 0.5 h a 30.17 g (80 %) of sulfone **5f** was obtained after recrystallization from $CHCl_3$. Pale-yellow crystals. Mp 82-84 °C. IR (KBr, ν_{max}, cm^{-1}): 3053(w) (CH), 2997(w) (CH), 2945(vw) (CH), 1634(m) (ArF), 1595(s) (NO_2), 1489(vs) (ArF), 1389(s) (NO_2), 1371(s) (CF), 1329(vs) (SO_2), 1311(vs) (CF), 1302(s) (CF), 1221(s) (CF), 1200(s) (CF), 1151(vs) (SO_2), 1126(s) (CF), 1105(vs) (CF), 941(s), 903(w) (C-NO_2), 790(m) (C-S), 714(m) (C-S), 683(m) (C-NO_2). UV, λ_{max}, nm (log ε): 295 (3.65). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 6.00 (d, $^4J_{HF}$ 2.5, 2H, C<u>H</u>$_2NO_2$), 6.43 (dt, $^2J_{HF}$ 53.4, $^5J_{HF}$ 1.3, 1H, SO_2CF_2<u>H</u>) ppm; ^{13}C NMR [CD_3CN, 100.61 MHz]: δ_C 68.0 (d, $^3J_{CF}$ 6.6, <u>C</u>H_2NO_2), 116.1 (td, $^1J_{CF}$ 286.8, $^4J_{CF}$ 2.4, SO_2<u>C</u>F_2H), 116.2 (qddd, $^2J_{CF}$ 34.9, $^2J_{CF}$ 18.9, $^2J_{CF}$ 10.7, $^3J_{CF}$ 1.2, C-(4)), 117.8 (dd, $^2J_{CF}$ 18.3, $^3J_{CF}$ 5.7, C-(6)), 121.3 (qdt, $^1J_{CF}$ 274.9, $^3J_{CF}$ 2.8, $^{3,4}J_{CF}$ 1.7, C<u>F</u>$_3$), 127.3 (dd, $^2J_{CF}$ 12.3, $^3J_{CF}$ 2.2, C-(1)), 149.3 (ddd, $^1J_{CF}$ 261.0, $^2J_{CF}$ 15.3, $^4J_{CF}$ 4.5, C-(2)), 151.5 (ddq, $^1J_{CF}$ 270.3, $^2J_{CF}$ 17.6, $^3J_{CF}$ 1.7, C-(3)), 155.8 (dm, $^1J_{CF}$ 261.7, C-(5)) ppm; ^{19}F NMR [$CDCl_3$, 282.40 MHz]: δ_F -126.7 (m, 1F, F-(2)), -124.2 (broad dq, $^3J_{FF}$ ~23, $^4J_{FF}$ ~23, 1F, F-

(3)), -121.6 (dd, $^{2}J_{FH}$ 53.4, $^{5}J_{FF}$ 10.8, 2F, C<u>F</u>$_2$H), -112.5 (m, 1F, F-(5)), -58.3 (dd, $^{4}J_{FF}$ 23.2, $^{4}J_{FF}$ 22.5, 3F, C<u>F</u>$_3$) ppm. Anal. calcd for $C_9H_3F_8NO_4S$, %: C 28.97; H 0.81; F 40.73; N 3.75; S 8.59; M^+ 372.9650, $(M\text{-}F)^+$ 353.9666. Found, %: C 28.60; H 0.90; F 40.37; N 3.61; S 8.59; $(M\text{-}F)^+$ 353.9663, M 369 (KNAUER K-7000).

IR spectrum of **5f**.

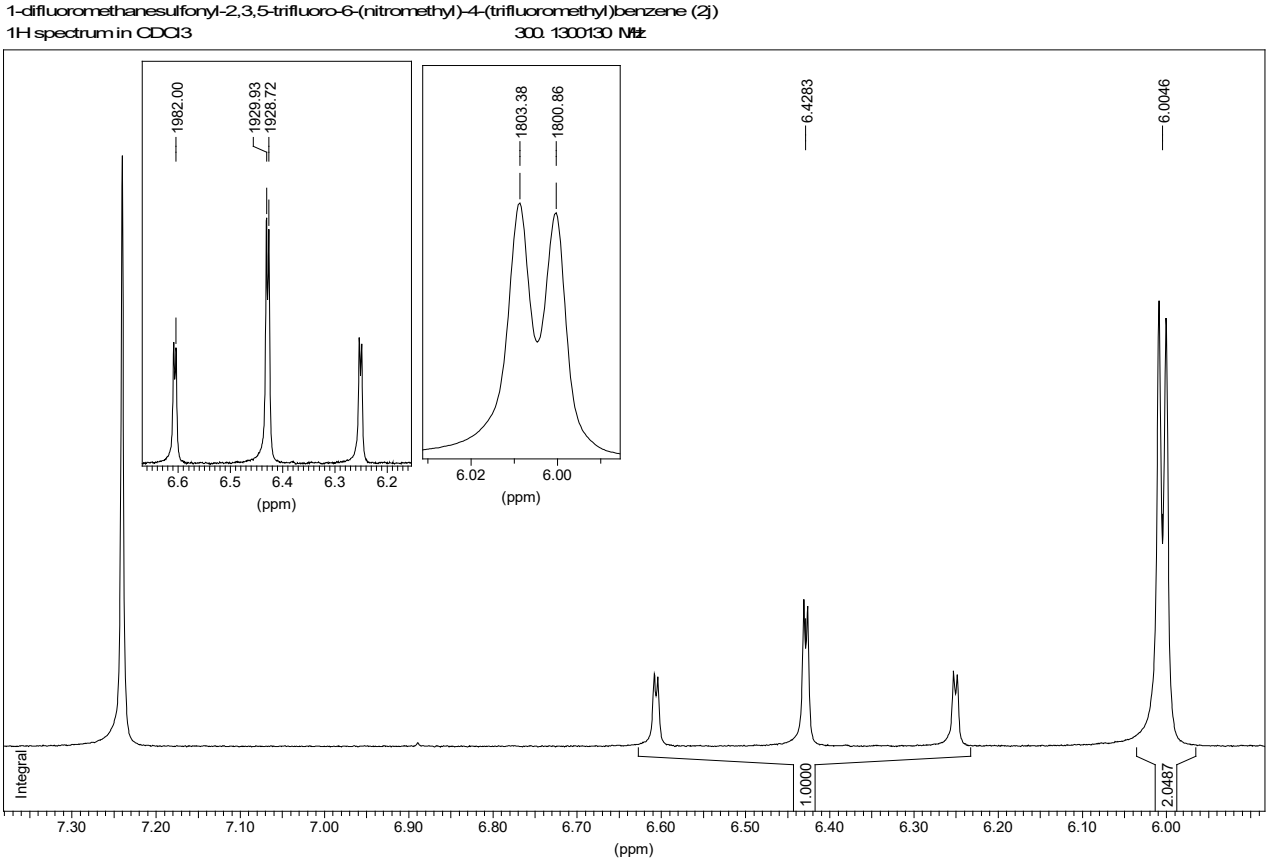


UV spectrum of **5f**.

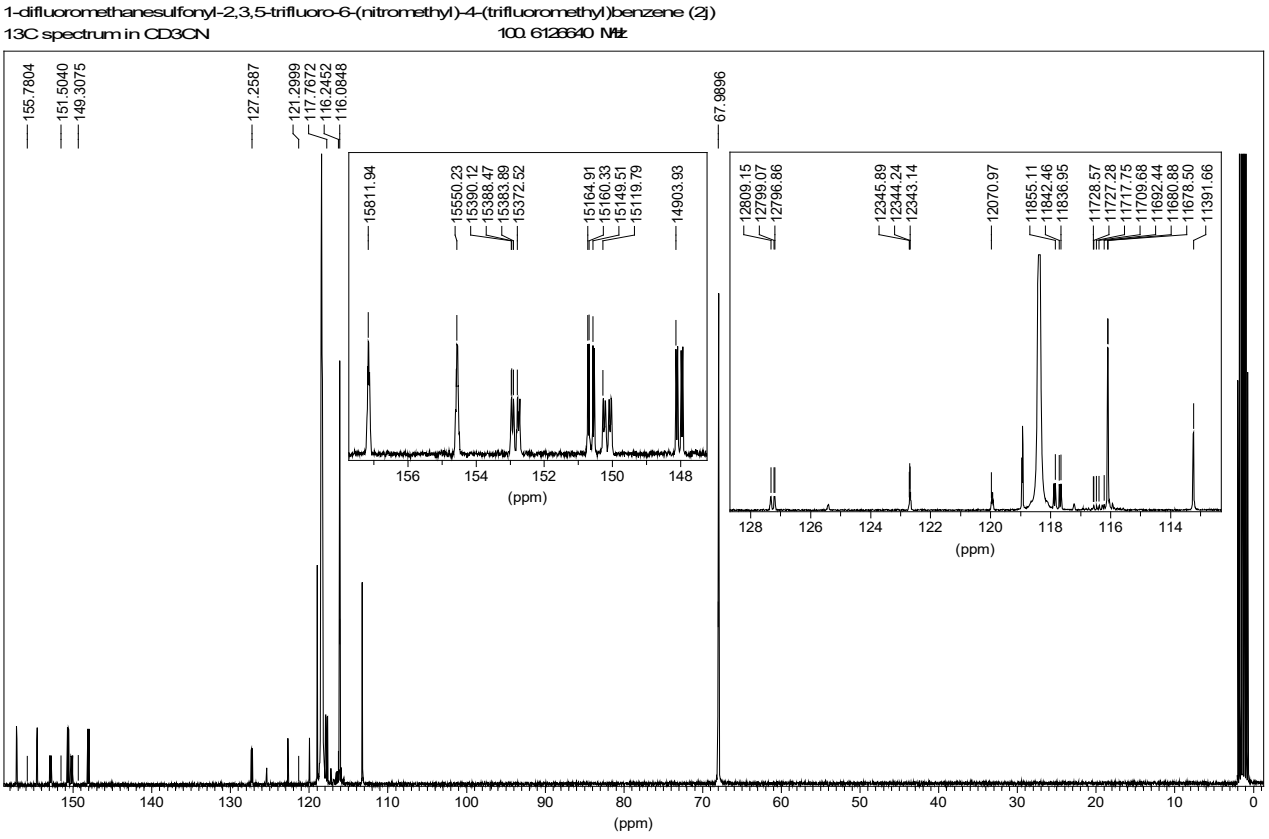


No	nm	A	FWHH	Asym	Intensity
1	295.00	0.223	29.94	-0.10	W

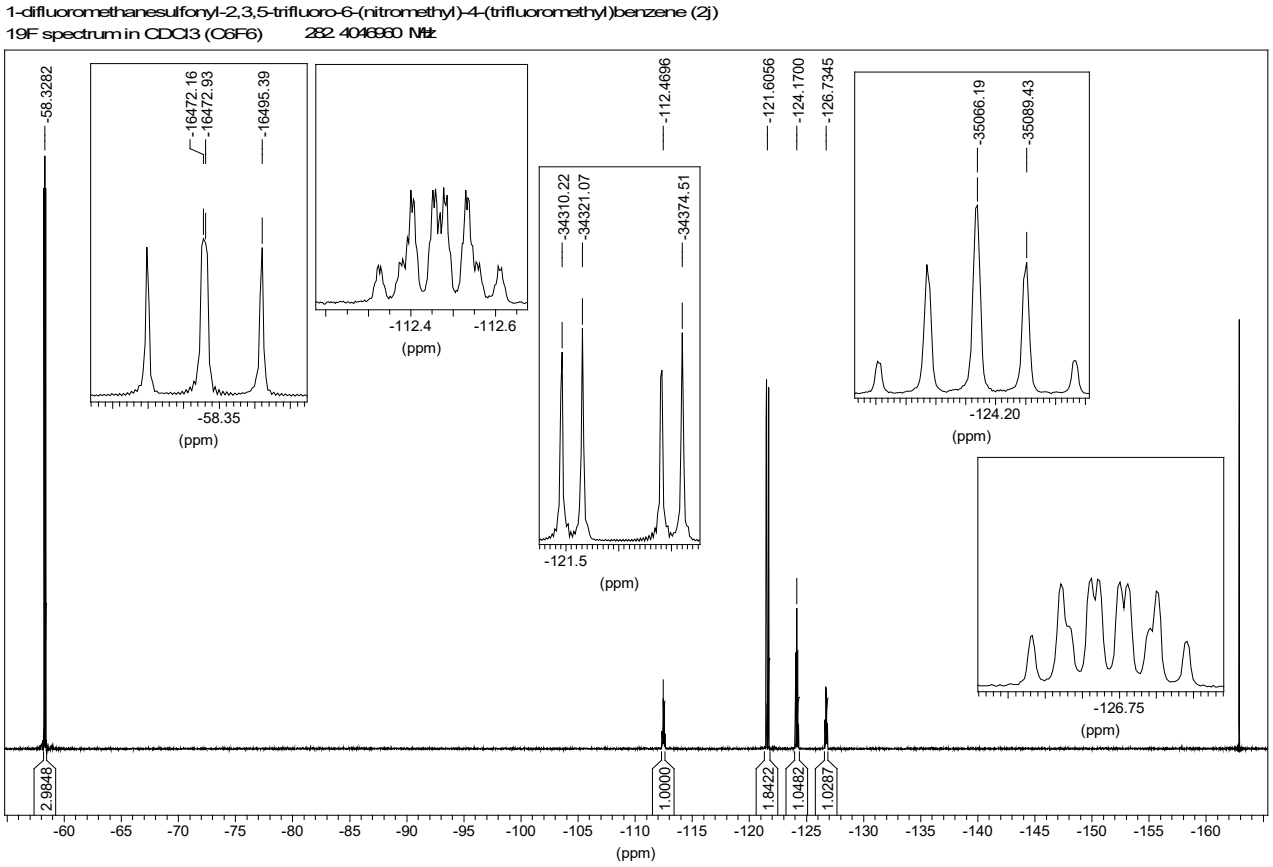
^{1}H NMR spectrum of **5f**.



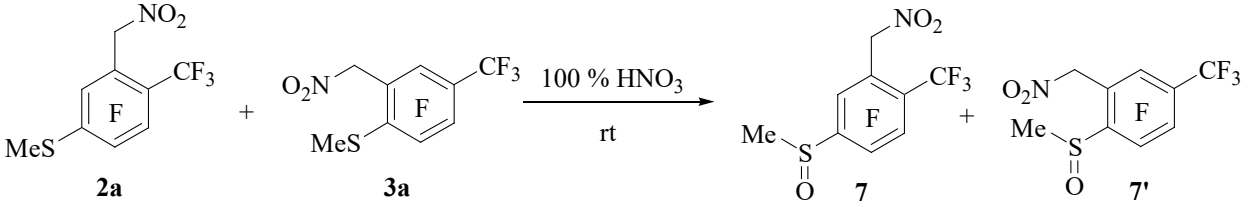
^{13}C NMR spectrum of **5f**.



^{19}F NMR spectrum of **5f**.



Synthesis of 1,2,5-trifluoro-6-methanesulfinyl-4-nitromethyl-3-(trifluoromethyl)benzene (7).

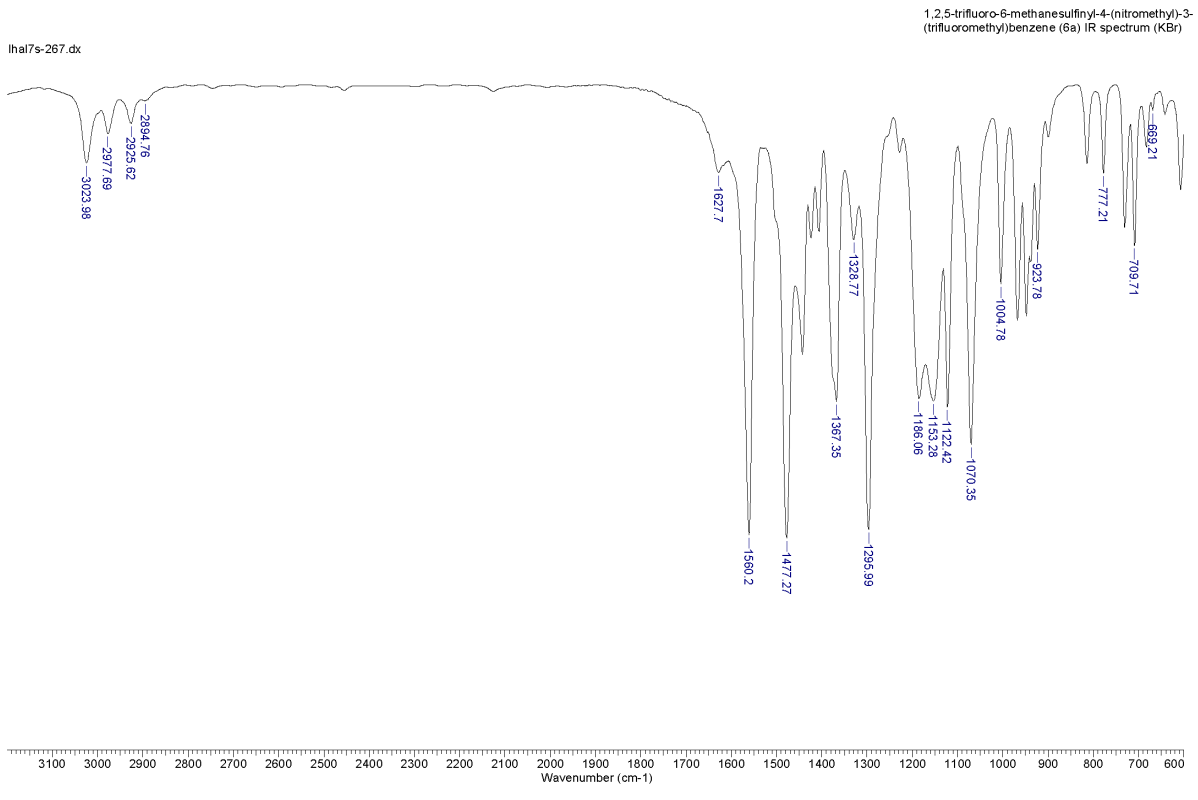


100 % HNO_3 (3.22 g, 51.10 mmol) was added to the mixture of sulfanes **2a** и **3a** (2.77 g, 9.08 mmol) obtained earlier, with such rate that the temperature of the mixture was not risen above 30 °C. Resulting solution was stirred at room temperature for 0.5 h, progress of reaction was monitored by ^{19}F NMR. When reaction was completed, the obtaining solution was poured into mixture of $CHCl_3$ (20 ml) and water (20 ml), then $NaHCO_3$ was added until pH was become 8. Organic layer was separated, water layer was washed with $CHCl_3$ (20 ml), combined organic solutions dried $MgSO_4$, then $CHCl_3$ was evaporated. Obtaining solid (2.60 g) contained according to GC-MS and ^{1}H, ^{19}F NMR 81 % of **7** and 6 % of **7'**. Recrystallization from mixture of PhH - hexane (3 : 1 v/v) gave 2.00 g (yield - 69 %) of individual sulfoxide **7**. Pale-yellow solid. Mp 70-72 ˚C. IR (KBr, ν_{max}, cm^{-1}): 3024(w) (CH), 2978(w) (CH), 2926(w) (CH), 2895(vw) (CH), 1628(w) (ArF), 1560(vs) (NO_2), 1477(vs) (ArF), 1367(s) (NO_2), 1329(m) (CF), 1296(vs) (CF), 1186(s) (CF), 1153(s) (CF), 1122(s) (CF), 1070(s) (SO), 1005(m) (CF), 924(m) (C-NO_2), 777(w) (C-S), 710(m) (C-S), 669(w) (C-NO_2). UV, λ_{max}, nm (log ε): 286 (3.76). ^{1}H NMR [$CDCl_3$, 300.13 MHz]: δ_H 3.18 (s, 3H, C$\underline{H}_3$SO), 5.67 (s, 2H, C$\underline{H}_2$$NO_2$) ppm; ^{13}C

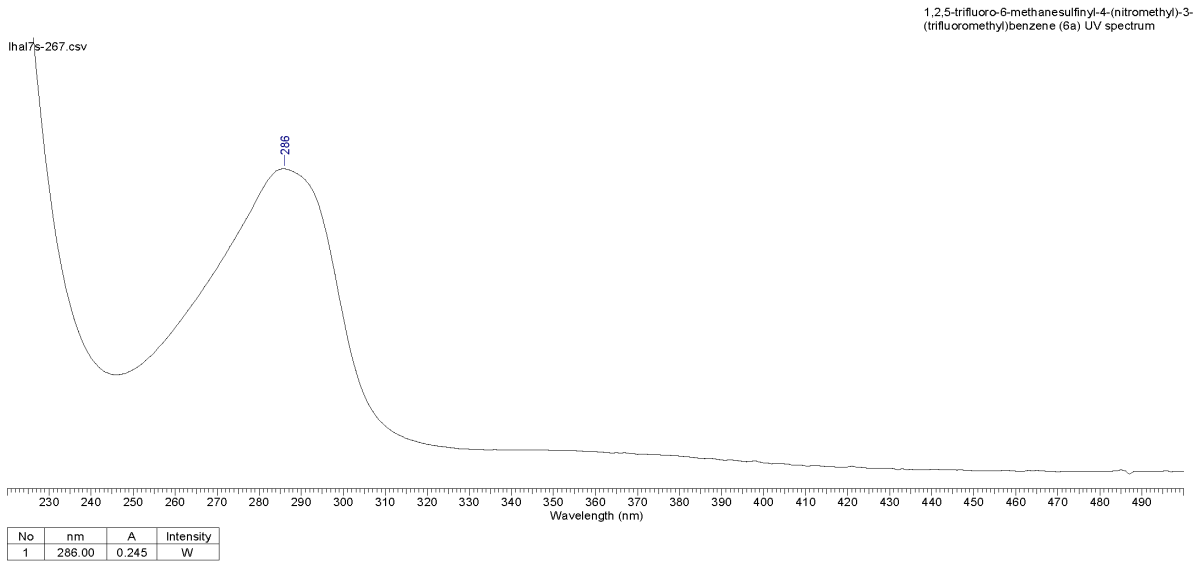
NMR [$CDCl_3$, 100.61 MHz]: δ_C 40.5 ($SO\underline{C}H_3$), 67.3 ($\underline{C}H_2NO_2$), 112.9 (dd, $^2J_{CF}$ 18.7, $^3J_{CF}$ 4.4, C-(4)), 121.3 (q, $^1J_{CF}$ 276.8, $\underline{C}F_3$), 122.6 (qdd, $^2J_{CF}$ ~33, $^2J_{CF}$ ~9, $^3J_{CF}$ ~2, C-(3)), 127.4 (dd, $^2J_{CF}$ 22.4, $^2J_{CF}$ 15.2, C-(6)), 145.9 (ddd, $^1J_{CF}$ 265.7, $^2J_{CF}$ 15.5, $^4J_{CF}$ 1.7, C-(2)), 150.5 (ddd, $^1J_{CF}$ 264.2, $^2J_{CF}$ 15.6, $^3J_{CF}$ 8.2, C-(1)), 154.9 (dd, $^1J_{CF}$ 255.3, $^3J_{CF}$ 4.6, C-(5)) ppm; ^{19}F NMR [$CDCl_3$, 282.4 MHz]: δ_F -136.8 (qdd, $^4J_{FF}$ 26.3, $^3J_{FF}$ 20.9, $^5J_{FF}$ 15.5, 1F, F-(2)), -127.1 (dd, $^3J_{FF}$ 20.9, $^4J_{FF}$ 3.1, 1F, F-(1)), -115.3 (d, $^5J_{FF}$ 15.5, 1F, F-(5)), -56.8 (d, $^4J_{FF}$ 26.3, 3F, $C\underline{F}_3$) ppm. Anal. calcd for $C_9H_5F_6NO_3S$, %: C 33.66; H 1.57; F 35.49; N 4.36; S 9.98; M^+ 320.9889. Found, %: C 33.62; H 1.62; F 35.25; N 4.33; S 10.15; M^+ 320.9887.

1,2,4-Trifluoro-6-methanesulfinyl-5-nitromethyl-3-(trifluoromethyl)benzene (7'). (from mixture of isomers) ^{1}H NMR [$CDCl_3$, 400.13 MHz]: δ_H 3.11 (d, 3H, $^5J_{HF}$ 0.7, $C\underline{H}_3SO_2$), 5.81 (dd, $^2J_{HH}$ 15.5, $^4J_{HF}$ 1.3, $C\underline{H}_2NO_2$), 6.55 (dd, $^2J_{HH}$ 15.5, $^4J_{HF}$ 3.0, 1H, $C\underline{H}_2NO_2$) ppm; ^{19}F NMR [$CDCl_3$, 376.5 MHz]: δ_F -138.6 (dd, $^3J_{FF}$ 22.5, $^5J_{FF}$ 14.8, 1F, F-(1)), -128.8 (dq, $^3J_{FF}$ ~23, $^4J_{FF}$ ~23, 1F, F-(2)), -116.7 (qd, $^4J_{FF}$ 21.7, $^5J_{FF}$ 14.8, 1F, F-(5)), -57.9 (t, $^4J_{FF}$ ~22, 3F, $C\underline{F}_3$) ppm. Anal. calcd for $C_9H_5F_6NO_3S$: M^+ by GL-MS 321. Found: M^+ by GL-MS 321, 1S.

IR spectrum of **7**.

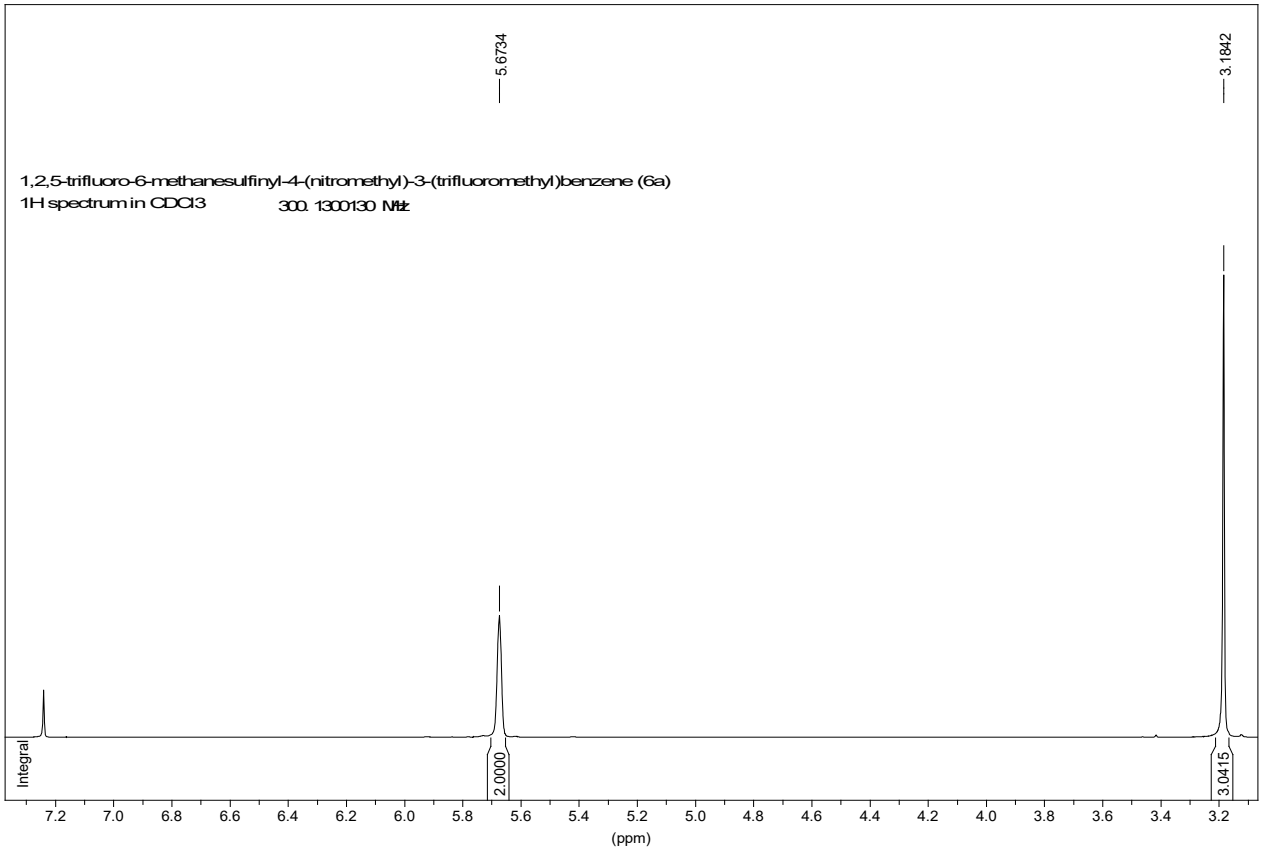


UV spectrum of **7**.

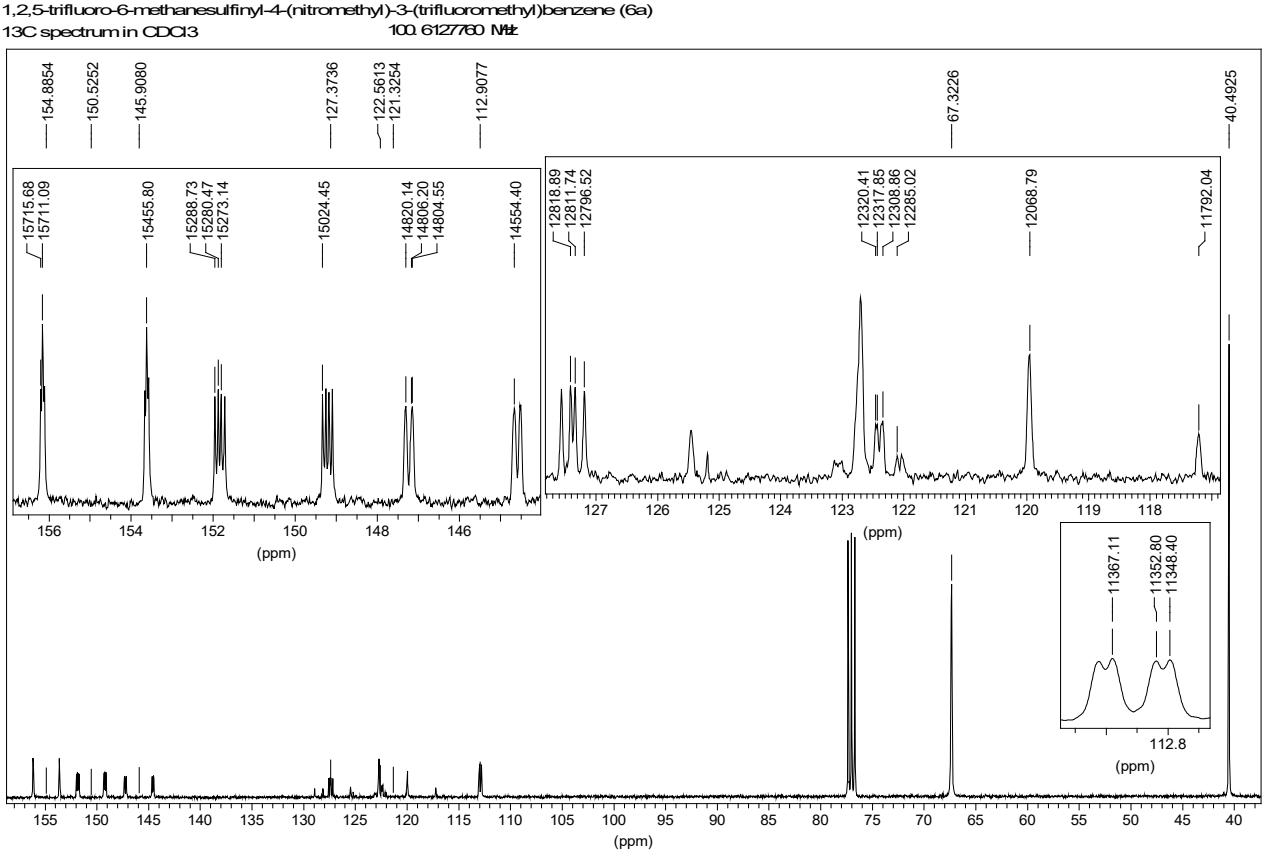


No	nm	A	Intensity
1	286.00	0.245	W

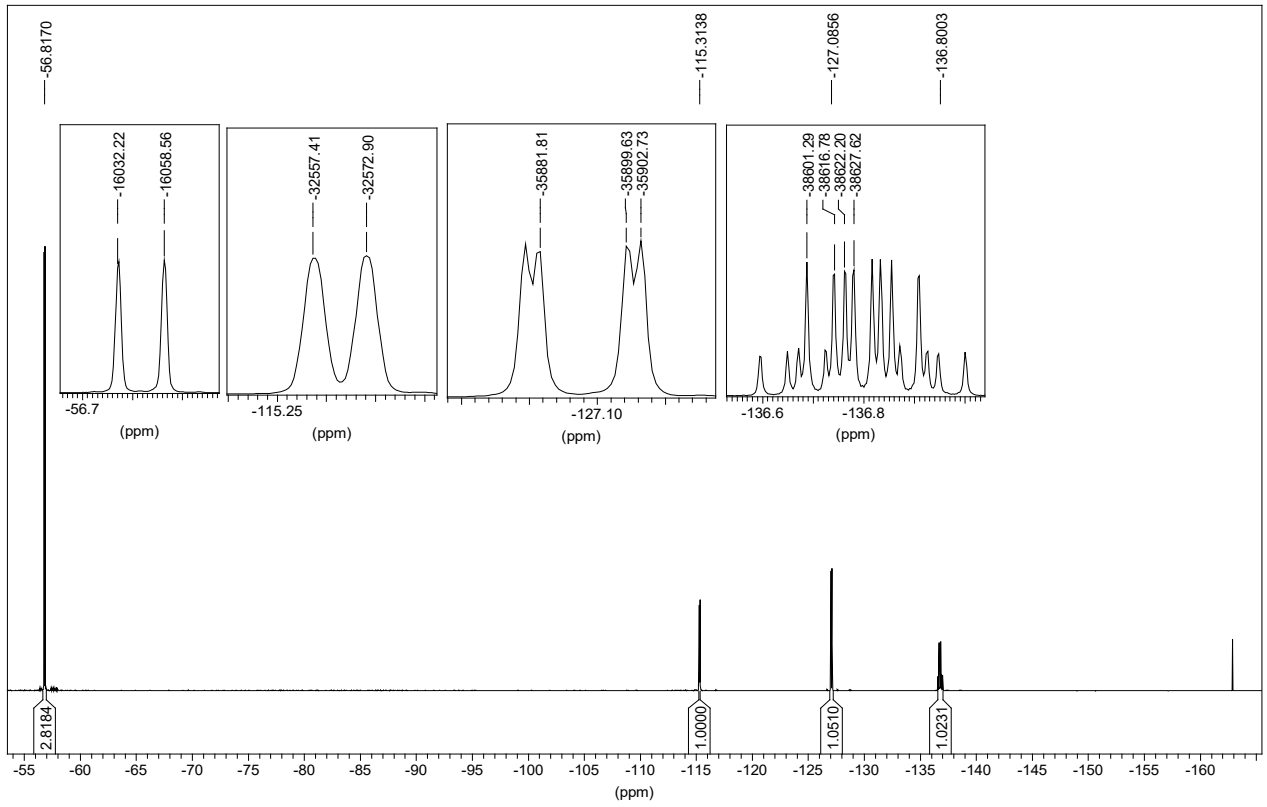
^{1}H NMR spectrum of **7**.



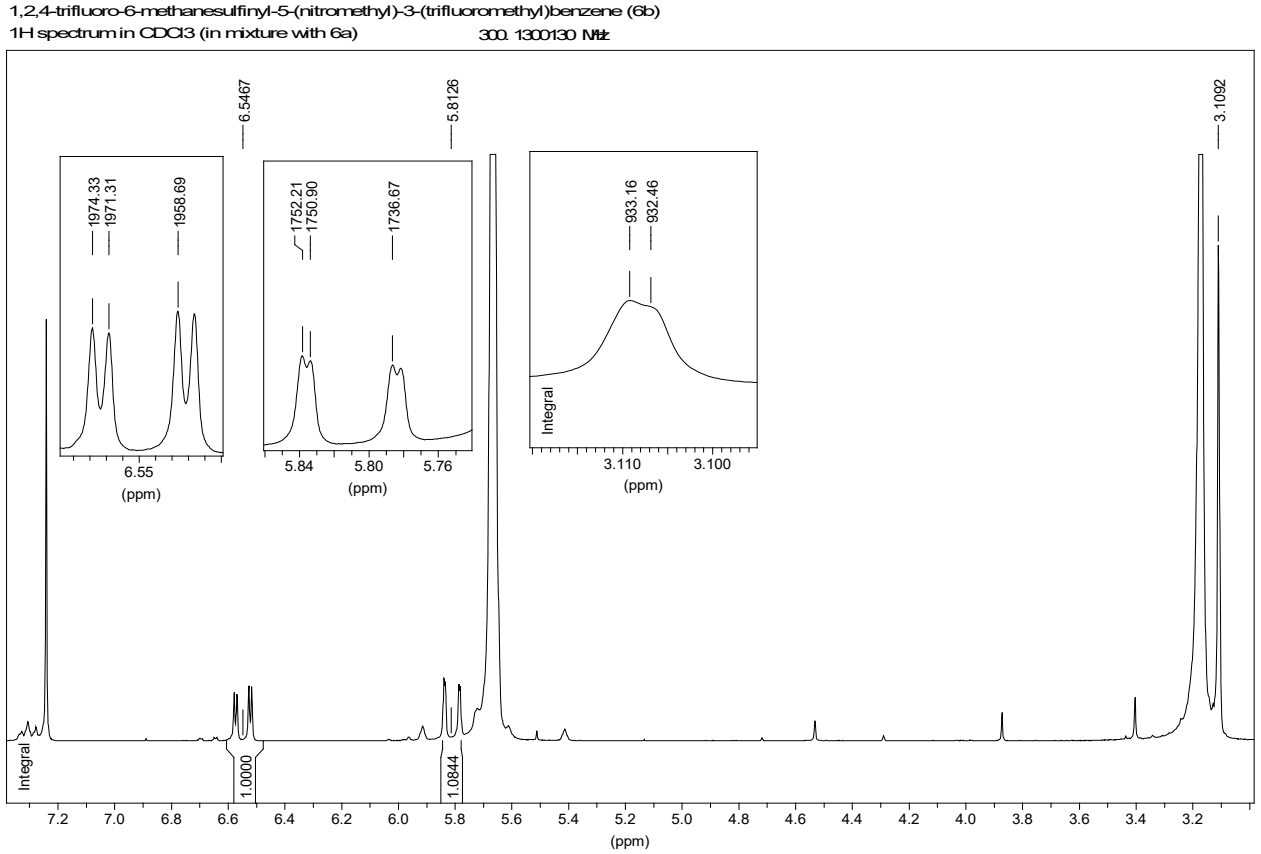
^{13}C NMR spectrum of **7**.



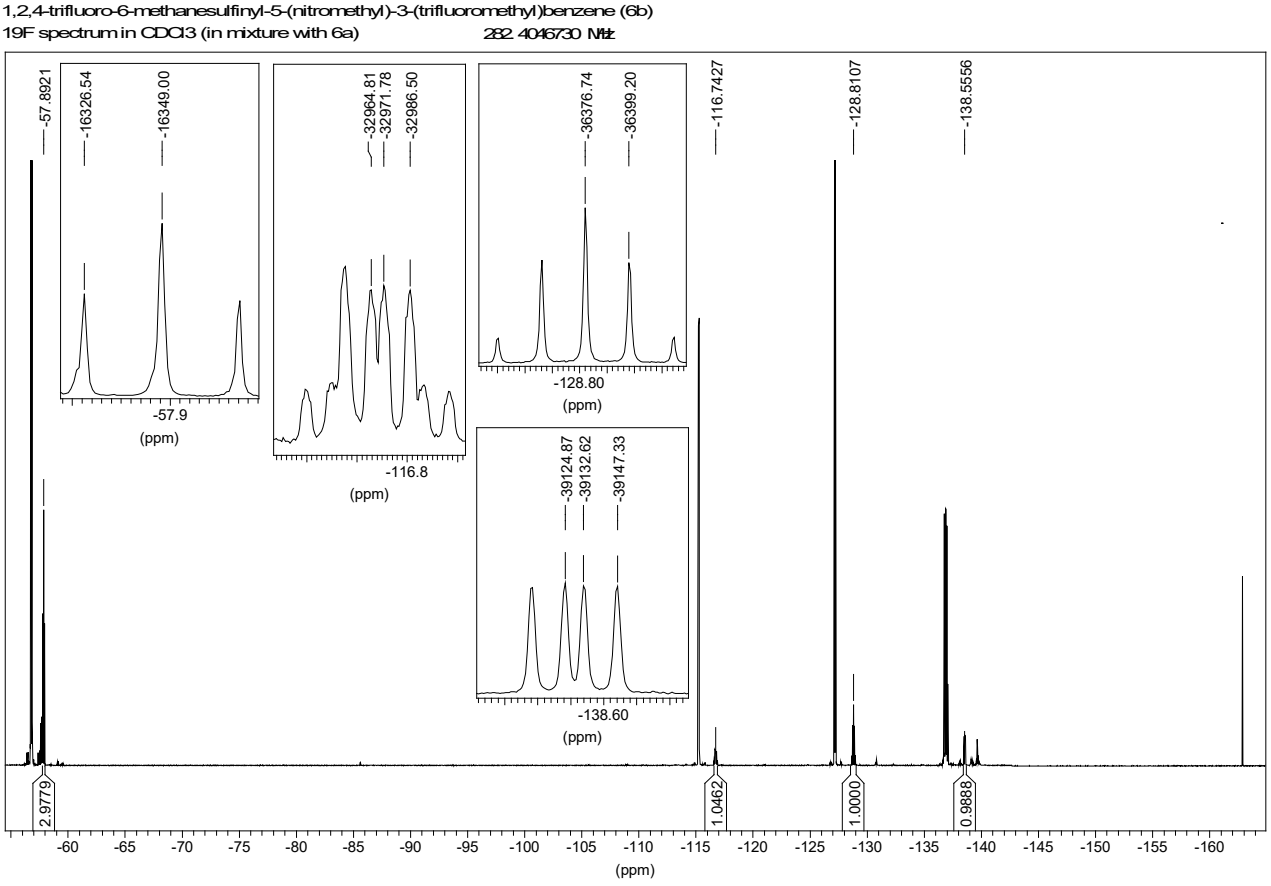
^{19}F NMR spectrum of **7**.



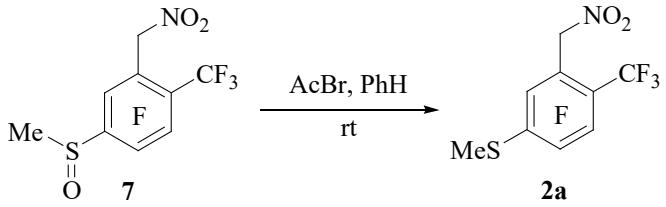
^{1}H NMR spectrum of **7'**.



^{19}F NMR spectrum of **7'**.



Reduction of 7 by using AcBr.



Acetyl bromide (1.418 g, 11.533 mmol) was added to the solution of sulfoxide **7** (1.506 g, 4.689 mmol) in PhH (9 ml). Resulting solution was stirred at room temperature for 0.5 h, progress of reaction was controlled by ^{19}F NMR. After interaction was completed the reaction mass was diluted with water (20 ml) and Et_2O (20 ml), then Na_2SO_3 was added until bromine color disappeared. Organic layer was separated, water layer washed with Et_2O (20 ml). Combined organic layers was washed with 5 % $NaHCO_3$ (40 ml), then 5 % HCl (40 ml), after was dried $MgSO_4$, then solvent was evaporated. Crude product was sublimated (0.64 - 0.69 Torr, 120 - 130 °C), 1.174 g (yield - 82 %) of sulfane **2a** was obtained.

Details of quantum chemical calculations

Calculations of all structures were performed at the DFT level using the functional B3LYP with the basis set 6-31G(d). All calculations were performed with default parameters using the GAMESS program.[S10] The solvent influence was taken into account by the polarizable continuum model (PCM), its reparameterized version SMD.[S11] In each case we use the built-in parameters for DMF, THF. Images of calculated structures were built by the MOLDEN program.[S12] Frequency calculations were carried out for all the TS-species to establish their nature as transition states.

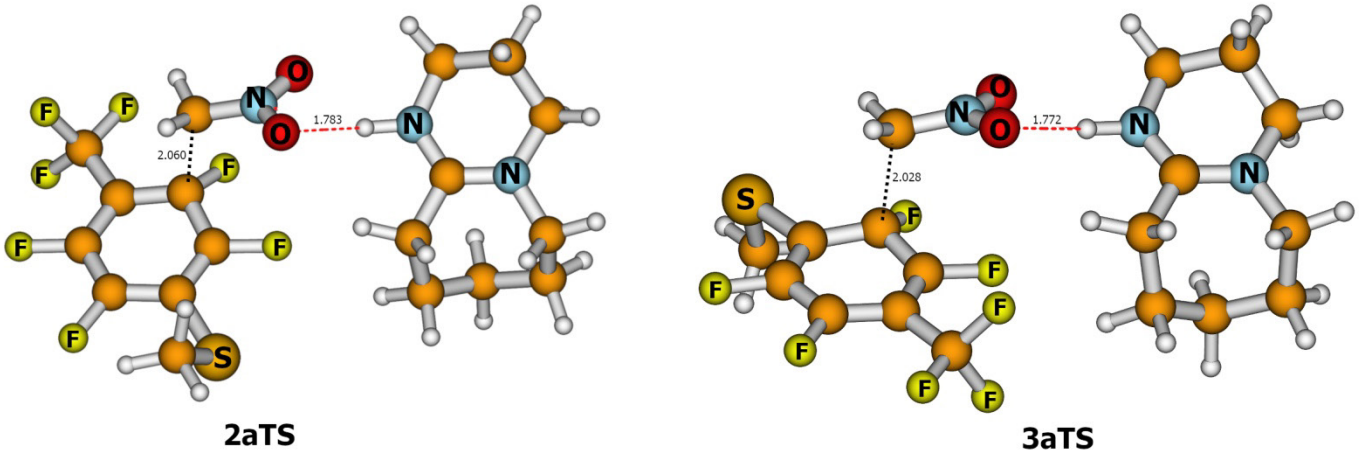


Figure S1. Calculated transition states for the reaction of substrate **1a.**

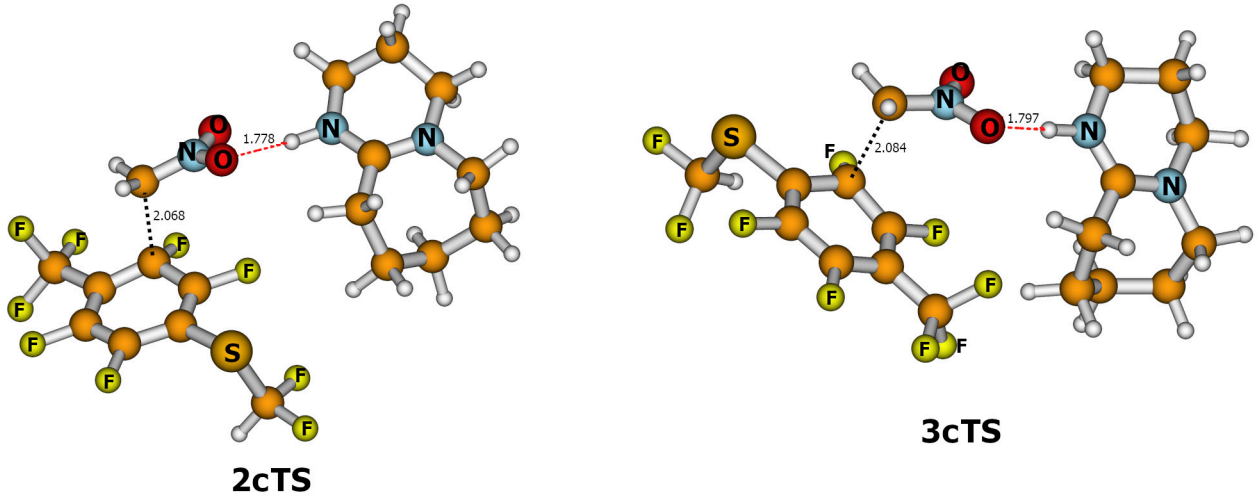


Figure S2. Calculated transition states for substrate **1c**

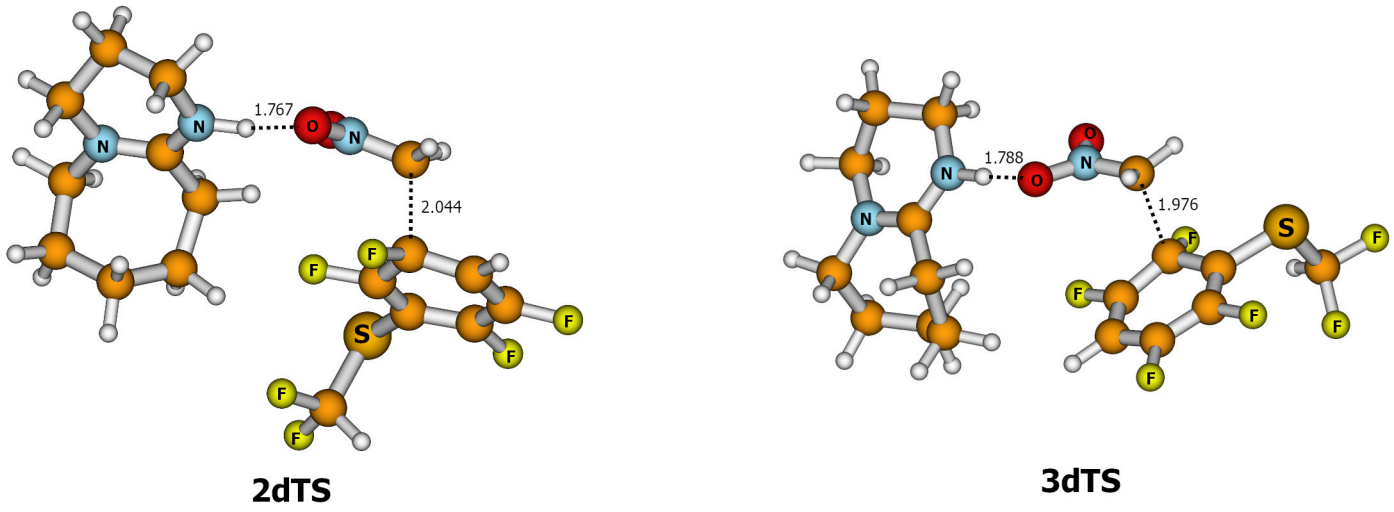


Figure S3. Calculated transition states for substrate **1d**

SI-1. Cartesian coordinates of the stationary structures of transition states by B3LYP/6-31G(d)/PCM-SMD (DMF), GAMESS.

2aTS **E = -2109.8706003462**

C	-3.8956245900	2.6916594378	-0.4208374571
N	-3.3666297257	1.3361491081	-0.5774212178
C	-4.0681047925	0.2408531845	-0.3484287499
N	-5.3536743907	0.2894637389	0.0174172688
C	-6.0526945956	1.5793459489	0.1957132684
C	-5.4042756037	2.6754679521	-0.6482017038
C	-3.3796006801	-1.0961239473	-0.5000571528
C	-3.2652041533	-1.9281559344	0.8195659507
C	-4.1440733631	-1.4639846400	1.9922815877
C	-5.6590751420	-1.5204765757	1.7393431538
C	-6.0696113789	-0.9522250020	0.3703112697
O	-0.7769826130	1.0417641714	-1.6412855857
N	-0.0468181471	1.8350660248	-0.9510805530
O	-0.5688497279	2.6701737714	-0.1695354851
C	1.3240734770	1.6853059240	-1.0116951093
C	1.9684526745	0.3846804441	0.4505578867
C	3.3944253234	0.3178748218	0.3358989072
C	3.9669399085	-0.8200894763	-0.2469815779
C	3.2348561893	-1.9480458628	-0.5514771308
C	1.8458174266	-1.9851968503	-0.2923616721
C	1.2747205364	-0.8565097795	0.2557882515

C	4.2735383714	1.4949322413	0.6000946096
F	5.2985358337	-0.8405862306	-0.4756242318
F	3.8714941957	-3.0287776254	-1.0620238308
S	0.8779004281	-3.4667238853	-0.5287960546
F	-0.0390007701	-0.8342608481	0.5730713355
F	1.4499394898	1.1426651282	1.4795404738
C	1.1746485347	-3.8321858911	-2.3033266310
H	1.8519280182	2.5759752247	-0.6928925391
H	1.6565186254	1.1913919518	-1.9171910562
H	-7.0944370381	1.4341957833	-0.1064644721
H	-5.8374313576	3.6432920634	-0.3778503930
H	-3.6463868901	3.0589594722	0.5821977648
H	-2.3850503490	1.2399928069	-0.8978815828
H	-7.1387866272	-0.7267790144	0.3483723646
H	-5.8954728715	-1.6886094043	-0.4197432058
H	-6.1755589098	-0.9785233158	2.5413017989
H	-6.0188189937	-2.5569188847	1.7810933200
H	-3.9191618337	-1.6635134715	-1.2672477174
H	-2.3798059713	-0.9099472061	-0.8991593433
H	-3.8602522202	-0.4391871121	2.2669753805
H	-3.9082473908	-2.0785331539	2.8695479252
H	-3.4821136487	-2.9771889293	0.5851144545
H	-2.2207362817	-1.8934238622	1.1428750612
H	-6.0540207987	1.8467512691	1.2597294171
H	-5.6173948699	2.5014414211	-1.7094965789
H	-3.3820336628	3.3338569495	-1.1406565445
H	0.5831473539	-4.7257278313	-2.5257601681
H	0.8288450795	-3.0088273264	-2.9334102658
H	2.2281547770	-4.0420023068	-2.4938982743
F	3.6273193047	2.5026506125	1.2253719064
F	5.3467895309	1.1763632133	1.3669248077
F	4.7840248656	2.0283116693	-0.5487497169

3aTS **E = -2109.8699152185**

C	-3.9423455400	2.6252312452	-0.5734231750
N	-3.2641921289	1.3289673118	-0.6520584207
C	-3.8546480138	0.1666548741	-0.4384897489
N	-5.1494963281	0.0826753089	-0.1130283641
C	-5.9681869995	1.3004672105	0.0592709993
C	-5.4366983224	2.4353377251	-0.8135645317
C	-3.0267460359	-1.0920830255	-0.5611448883
C	-2.8763939261	-1.9129746873	0.7615656001

C	-3.8517003237	-1.5571874405	1.8950537072
C	-5.3378674236	-1.7782676728	1.5735503885
C	-5.7529373148	-1.2279300153	0.1974294749
O	-0.6626464292	1.2662242214	-1.6954649942
N	-0.0169239651	2.1847977450	-1.0769479414
O	-0.6196350216	3.0173826201	-0.3515867369
C	1.3608361309	2.1616063431	-1.1427192564
C	2.0938563974	1.0208939483	0.3654921843
C	3.5197279464	0.9567124632	0.1811455499
C	4.0640345244	-0.2113275956	-0.3533532571
C	3.3199984912	-1.3669122533	-0.5586016241
C	1.9658782882	-1.3953448517	-0.1752619248
C	1.4196346267	-0.2393612342	0.3506726718
S	4.5355164968	2.3958357120	0.4298531204
F	5.3771255440	-0.2698355692	-0.6541916038
F	3.9399636506	-2.4468274536	-1.0864489713
C	1.1020015590	-2.6269722017	-0.2552542497
F	0.0025170621	-2.4234467628	-1.0218705849
F	0.1341417304	-0.2332400763	0.7785013423
F	1.6456380371	1.8732946230	1.3575092558
F	1.7433600371	-3.6932466638	-0.7661990976
F	0.6511705585	-2.9895813072	0.9715655083
C	4.6141895010	2.4917864682	2.2644898141
H	3.6126109369	2.5971894769	2.6849336806
H	5.2053176186	3.3820248266	2.5029406589
H	5.1098974061	1.6102631648	2.6793752373
H	1.8156051721	3.1125332572	-0.8916075985
H	1.7294310909	1.6373508643	-2.0167086317
H	-6.9947861820	1.0505103696	-0.2227403308
H	-5.9773427898	3.3573542711	-0.5793415289
H	-3.7509559740	3.0725869556	0.4095153696
H	-2.2721357964	1.3295701544	-0.9563591418
H	-6.8374258386	-1.1055349637	0.1412958049
H	-5.4811794731	-1.9288778005	-0.5973400929
H	-5.9474133789	-1.3165409832	2.3604943043
H	-5.5756577835	-2.8499831088	1.5806307433
H	-3.4786390501	-1.7105563421	-1.3454563806
H	-2.0385382759	-0.8066866968	-0.9271614030
H	-3.6962857298	-0.5100354964	2.1876539017
H	-3.5901639159	-2.1515570511	2.7788478071
H	-2.9669301429	-2.9780917023	0.5168437785
H	-1.8576802165	-1.7687687772	1.1320819442

H	-5.9741845237	1.5849878050	1.1194014386
H	-5.6174160768	2.2024129713	-1.8695561669
H	-3.4899958696	3.2805804236	-1.3221906999

2cTS E = -2308.2705984640

C	4.0527911623	0.6221083377	0.5100335353
N	3.3246302741	1.7243029616	0.5500486982
C	3.8441240484	3.0624799768	0.2595198773
C	5.3444314366	3.0966786118	0.5319185448
C	6.0283357417	1.9142130702	-0.1518212960
N	5.3507168367	0.6471113794	0.1905996894
C	6.1117570790	-0.6122872079	0.0830440626
C	5.7894509351	-1.4054372531	-1.1949748851
C	4.2868260105	-1.4484348075	-1.5163053698
C	3.3757203389	-1.7485310309	-0.3155079063
C	3.3825937479	-0.6923284869	0.8394955793
O	0.7213727961	1.5607646527	1.6393436867
N	0.0120111351	2.3176329615	0.8896575008
O	0.5540958508	3.0901297603	0.0588349437
C	-1.3600132011	2.1883926318	0.9400503218
C	-1.9434465212	0.7570051970	-0.4367723925
C	-1.1854804754	-0.4292000607	-0.1576933033
C	-1.7046860308	-1.5255193185	0.4978043201
C	-3.0848304745	-1.5265661759	0.7986527828
C	-3.8766039319	-0.4695019766	0.3954737696
C	-3.3655934170	0.6276003341	-0.3109718147
F	0.1145829528	-0.3792375898	-0.5034315441
F	-1.4586699177	1.4641194677	-1.5130862022
C	-4.2779433207	1.7635443246	-0.6463641655
F	-5.4642565149	1.3473337949	-1.1461110735
F	-5.1957701239	-0.5288840075	0.6736341784
F	-3.6487929556	-2.5622335509	1.4538075285
S	-0.6764519865	-2.8999575353	0.9861501288
C	-0.4985642815	-3.7555112753	-0.6266248670
F	0.2386436967	-3.0238178930	-1.5094346793
F	-4.5741623504	2.5216854610	0.4521736778
F	-3.7455878055	2.6127410396	-1.5510367357
F	0.1920230840	-4.8973876197	-0.3601916486
H	-1.8776936511	3.0525665526	0.5408432404
H	-1.7168631513	1.7657169451	1.8718891992
H	7.0674386862	1.8315507288	0.1793163452
H	5.7746887507	4.0304968536	0.1579986414

H	3.6239065521	3.3145237622	-0.7852161074
H	2.3397946768	1.6572135395	0.8644497878
H	7.1728016743	-0.3544843368	0.1220971393
H	5.9070987034	-1.2169491685	0.9713322428
H	6.3296533984	-0.9774866593	-2.0482640600
H	6.1797635476	-2.4217030845	-1.0533022689
H	3.8800532349	-1.0997103973	1.7277444720
H	2.3545622591	-0.4724524265	1.1368223228
H	3.9842981672	-0.4957044250	-1.9722782280
H	4.1106544187	-2.2099658786	-2.2856611037
H	3.6393180000	-2.7239843129	0.1110803747
H	2.3495268776	-1.8432075697	-0.6810344959
H	6.0391846945	2.0382432026	-1.2422495042
H	5.5281139527	3.0539096576	1.6119531675
H	3.2980411241	3.7712834061	0.8860866920
H	-1.4580638585	-3.9983357760	-1.0887341565

3cTS **E = -2308.2708227342**

C	1.0332428830	0.4750464527	-0.2084387643
C	1.8639499054	-0.6770610572	-0.0666203778
C	3.2303984499	-0.4122924721	0.2770439996
C	3.5610802713	0.8460654428	0.7878170662
C	2.6566167189	1.8968161562	0.8240994892
C	1.3674482170	1.7225365499	0.2820752719
F	1.6514218779	-1.6471295855	-1.0229772785
S	4.4412282787	-1.7079772835	0.2379542643
C	4.8042251694	-1.7300746450	-1.5623938254
F	4.8065287656	1.0838788931	1.2373992497
F	3.0578789861	3.0745627934	1.3483276139
C	0.3493444916	2.8303136103	0.1784235941
F	-0.0681388756	2.9926630175	-1.0998312781
F	-0.1761647875	0.2701510008	-0.7756009893
F	-0.7556696659	2.5629349157	0.9156005595
F	0.8179569391	4.0205995518	0.5922823791
C	1.0636221833	-1.8342083520	1.4713938131
N	-0.2995633387	-1.9263712638	1.3025040732
O	-0.8080793304	-2.8285506507	0.5890686151
O	-1.0296730003	-1.0067415057	1.8174237269
N	-3.6224773084	-1.4123693186	0.8109849229
C	-4.2022979080	-2.7473615499	0.9803668496
C	-5.7201881163	-2.6345058226	1.0818711603
C	-6.2522597488	-1.7551132682	-0.0483783032

N	-5.5531848336	-0.4545063636	-0.0566499589
C	-4.2795943724	-0.3666143468	0.3430022542
C	-3.5548505279	0.9575865237	0.2699310676
C	-3.3901375365	1.5478425403	-1.1691294312
C	-4.2328209285	0.8853171447	-2.2712773614
C	-5.7542755062	1.0119401049	-2.0903351951
C	-6.2229501377	0.7157246389	-0.6555225531
H	3.9093191110	-1.8918730019	-2.1670524553
F	5.6908201093	-2.7444846974	-1.7595290483
F	5.4008416783	-0.5727778360	-1.9598690541
H	1.5834883935	-2.7678609952	1.2933104653
H	1.3447233759	-1.2460537404	2.3368035357
H	-7.3198475982	-1.5600842115	0.0829489674
H	-6.1771230461	-3.6266944026	1.0243234735
H	-3.9021441290	-3.3798649778	0.1362017558
H	-2.6374014357	-1.2841542350	1.1103271211
H	-7.2978092360	0.5205041247	-0.6305180874
H	-6.0516924097	1.5810060426	-0.0083648197
H	-6.2595447848	0.3400145263	-2.7950863824
H	-6.0840718787	2.0296560239	-2.3363987240
H	-4.0952171510	1.6630479919	0.9123533581
H	-2.5725818665	0.8204903751	0.7254808833
H	-3.9613157867	-0.1767510696	-2.3431843019
H	-3.9532711014	1.3246675453	-3.2366471904
H	-3.6129079146	2.6208431236	-1.1294265380
H	-2.3360240499	1.4641581584	-1.4473795465
H	-6.1199193781	-2.2444189300	-1.0224721851
H	-5.9986139109	-2.1968349817	2.0477394410
H	-3.7687641771	-3.1815903650	1.8853379568

2dTS **E = -1971.3590880614**

C	3.6323994434	-1.9087582478	-0.6722156885
C	2.2206873111	-1.6927242762	-0.7504621616
C	1.7936007655	-0.3762262054	-0.3756480005
C	2.6039020049	0.5257438522	0.2973325676
C	3.9537600983	0.1877471151	0.5114200231
C	4.4364080522	-1.0168089672	0.0127524721
F	1.6131078458	-2.1689827662	-1.9150821698
F	0.4988869355	-0.0803987229	-0.6360672075
S	1.9635271919	2.0800226801	0.9008516675
C	1.9451347398	3.0318110768	-0.6664297809
F	1.5856706394	4.3020229304	-0.3328248551

F	4.7916023318	1.0261097254	1.1660197792
F	5.7547487315	-1.2887062683	0.1674700304
H	4.0601439010	-2.8232381248	-1.0705357065
F	1.0120216255	2.5542056326	-1.5382957919
C	1.3525890759	-3.0349551659	0.4114273465
N	-0.0238751331	-2.8616875903	0.4275698659
O	-0.7514483039	-3.3726148378	-0.4610199118
O	-0.5190857232	-2.0773087257	1.3091181545
N	-3.0806893234	-1.3834916140	0.3657243635
C	-3.4656589999	-0.1348796878	0.5647597940
N	-4.7300160681	0.2522689739	0.3649213373
C	-5.7584415647	-0.7032521634	-0.0954271958
C	-5.4046983608	-2.1263209622	0.3331015753
C	-3.9743111412	-2.4526239639	-0.0848130273
C	-2.4336040674	0.8686195151	1.0250669228
C	-2.1725740349	2.0532406700	0.0356103092
C	-3.1806769879	2.2114311925	-1.1141915252
C	-4.6173977095	2.5379309384	-0.6771488250
C	-5.0991568888	1.6745719947	0.5009277549
H	1.6460247428	-3.9504066352	-0.0922881676
H	1.8006886111	-2.8405765249	1.3793284881
H	-6.7114680278	-0.3939636177	0.3428264684
H	-6.1034805936	-2.8295161062	-0.1298125226
H	-3.8948640191	-2.5534992764	-1.1747372742
H	-2.1084121314	-1.6449892182	0.6131077722
H	-6.1864631982	1.7190263447	0.5990508448
H	-4.6889763531	2.0491180573	1.4430990017
H	-5.2927534220	2.4180067050	-1.5333425456
H	-4.6933258305	3.5873088091	-0.3631489499
H	-2.7551421703	1.2484387270	2.0020246387
H	-1.5014487650	0.3252143679	1.1956705184
H	-3.1821429647	1.2947665032	-1.7191197486
H	-2.8231583170	3.0039789329	-1.7826885325
H	-2.1290844275	2.9832581346	0.6152632744
H	-1.1797969503	1.9145322624	-0.3997269284
H	-5.8555400088	-0.6328516785	-1.1867833689
H	-5.5066466118	-2.2218145900	1.4204616781
H	-3.6196240271	-3.3874905307	0.3555177097
H	2.9173378853	3.0375796451	-1.1656980376

3dTS **E = -1971.3637321313**

C	-4.2672633695	0.0832204888	0.3364544610

N	-3.6331615039	-0.9796448335	0.7973211714
C	-4.2356543152	-2.3085040757	0.9315806731
C	-5.7529174504	-2.1744735458	1.0156390820
C	-6.2564826991	-1.2671126525	-0.1053209944
N	-5.5361110117	0.0217186637	-0.0830135400
C	-6.1798278219	1.2115187137	-0.6718816331
C	-5.6918413398	1.5170095004	-2.0972685996
C	-4.1670537865	1.3942578251	-2.2521766540
C	-3.3511454866	2.0360922828	-1.1181617732
C	-3.5224584261	1.3986630245	0.3001668139
O	-1.0643431416	-0.6605422260	1.8669931951
N	-0.3127130060	-1.5194373440	1.2805784497
O	-0.8039813977	-2.3916328036	0.5192248626
C	1.0518501001	-1.3880542449	1.4301419675
C	1.8022616443	-0.1586823868	-0.0203362762
C	0.9706813365	1.0057893892	-0.0744214291
C	1.3286560429	2.2129991810	0.4671745477
C	2.6307994215	2.3657958714	0.9622443890
C	3.5369548647	1.3247409034	0.8593734751
C	3.1805185594	0.0877320978	0.3030267850
F	-0.2670167120	0.8294067600	-0.6033004648
F	1.5716054788	-1.0668021911	-1.0417720526
S	4.3810004368	-1.2113236975	0.1886384182
C	4.7057309040	-1.1888290919	-1.6170646878
F	5.2951628801	-0.0222787230	-2.0022809313
F	4.8015394186	1.5363456623	1.2769284241
F	3.0192217755	3.5448173704	1.5091131129
H	0.6291890320	3.0426653398	0.4906304770
F	5.5890560987	-2.1989441498	-1.8584201414
H	3.7984618441	-1.3355762152	-2.2066126703
H	1.5939728838	-2.2987742922	1.2039775298
H	1.3234056770	-0.8444923125	2.3274664634
H	-7.3220996644	-1.0560709868	0.0170911649
H	-6.2248026616	-3.1580330571	0.9344907817
H	-3.9337771273	-2.9281483376	0.0784142197
H	-2.6509821647	-0.8740857153	1.1185992062
H	-7.2581991613	1.0353380169	-0.6583289472
H	-5.9982712367	2.0650712207	-0.0119359416
H	-6.1856999047	0.8493088226	-2.8140514128
H	-6.0187930353	2.5361739695	-2.3412027891
H	-4.0466768805	2.0909238126	0.9701520191
H	-2.5393218873	1.2273858488	0.7440475253

H	-3.8917131382	0.3344797351	-2.3396569625
H	-3.8683125762	1.8541638576	-3.2019860534
H	-3.5923032161	3.1037410992	-1.0504373242
H	-2.2915253135	1.9745160567	-1.3818751647
H	-6.1209942125	-1.7428148175	-1.0857478756
H	-6.0372633011	-1.7498896849	1.9856914900
H	-3.8208413562	-2.7683784187	1.8328418316

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