# Supporting Information

## Oxidative Addition/Cycloaddition of Triflamide to N-Allyltriflamide and N,N-Diallyltriflamide

(RSC Advances)

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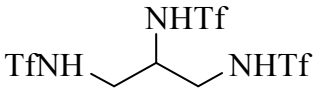
**General methods:**

IR spectra were taken on Varian 3100 FT-IR and Bruker Vertex 70 spectrophotometers in KBr. NMR spectra were registered on a Bruker DPX-400 spectrometer with working frequencies 400 ($^{1}$H), 100 ($^{13}$C) and 376 MHz ($^{19}$F) in $CD_3CN$ or $CDCl_3$, chemical shifts are given with respect to TMS ($^{1}$H, $^{13}$C) and $CCl_3F$ ($^{19}$F). Elemental analysis on was performed on a CHN-analyzer Thermo-Finnigan Flash EA (Milan, Italy). The reactions were monitored by TLC on silica plates 60 F-254, eluents – hexane:ether = 1:1 or hexane:ether:acetone = 2:3:1. The reaction products were separated by column chromatography using coarse (Alfa Aesar 0.060-0.200 mm) or fine silica (Fluka 0.04-0.063 mm). Melting points were determined on a Boetius apparatus (VEB Analytik).

**Synthetic procedures:**

1. Synthesis of compounds **6**

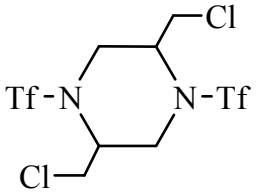
*N*,*N*′,*N*″-Propane-1,2,3-triyltris(triflamide):




To 1.20 g (8 mmol) of trifluoromethanesulfonamide and 3.61 g (24 mmol) of NaI 80 ml of $CH_3CN$ was added. To this solution, 1.10 ml (8 mmol) of N-allyltriflamide was added, the mixture was cooled to –30°C, and 2.75 ml (24 mmol) of *t*-BuOCl was added dropwise. The reaction was carried out during 24 h in argon atmosphere in the dark. After completion, the solvent was removed under reduced pressure, the residue dissolved in 80 ml of diethyl ether, treated with 80 ml of aqueous $Na_2S_2O_3$, the extract dried over $CaCl_2$. The solvent was removed in vacuum, dark-brown residue (~2.0 g) placed in a column with coarse silica and eluted with hexane to separate tarry admixtures, then with hexane–ether =1:1 and pure ether to afford (1.93 g 100%) of product **5**, a white powder, m. p. 186°C. IR (KBr, $\nu$/cm$^{-1}$): br. 3319, 1457, 1382, 1233, 1196, 1145, 1080, 1005, 950, 879, 817, 610, 511, 453. $^1$H NMR ($CD_3CN$) δ: 7.01 br.s. (3H, NH), 3.73 m (CH), 3.46 d.d. (2H, $CH_2$, *J* 14.8, 4.8 Hz), 3.34 d.d. (2H, $CH_2$, *J* 14.6, 7.3 Hz). $^{13}$C NMR ($CD_3CN$) δ: 120.4 (q, $2CF_3$, *J* 320.8 Hz), 120.2 (q, $CF_3$, *J* 320.0 Hz), 56.7 (CH), 45.7 ($2CH_2$). $^{19}$F NMR ($CD_3CN$) $\delta_F$: –77.5 ($2CF_3$), -77.7 ($CF_3$). Found (%): C, 15.11; H, 1.95; N, 8.39; S 19.69; F 35.20. Calc. for $C_6H_8F_9N_3O_6S_3$ (%): C, 14.85; H, 1.66; N, 8.66; S 19.82; F 35.23.

2. Synthesis of compounds **7**

2,5-Bis(chloromethyl)-1,4-bis[(trifluoromethyl)sulfonyl]piperazine **(7)**:

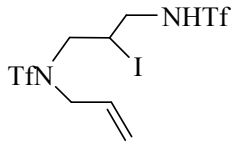



To 8 mmol of arenesulfonamide **3a–d** or trifluoroacetamide **4** and 3.57 g (24 mmol) of NaI 80 ml of $CH_3CN$ was added. To this solution, 1.10 ml (8 mmol) of N-allyltriflamide was added, the mixture was cooled to –30°C, and 2.72 ml (24 mmol) of *t*-BuOCl was added dropwise. The reaction was carried out during 24 h in argon atmosphere in the dark. After completion, the solvent was removed under reduced pressure, the residue dissolved in 80 ml of diethyl ether, treated with 80 ml of aqueous $Na_2S_2O_3$, the extract dried over $CaCl_2$. The solvent was removed in vacuum, dark-brown residue (~2.63 g) placed in a column with coarse silica and eluted with hexane, then with hexane–ether = 1:1 and pure ether. From ethereal extract unreacted

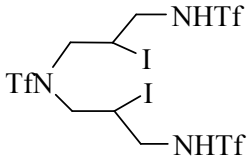
arenesulfonamide or trifluoroacetamide was recovered. From hexane extract product **7** was obtained. White powder, m. p. 188°C. IR (KBr, $\nu$/cm$^{-1}$): 2982, 2262, 1454, 1389, 1333, 1293, 1231, 1193, 1143, 1101, 1054, 1005, 941, 857, 807, 758, 652, 585, 493. $^1$H NMR ($CD_3CN$) δ: 4.31-4.19 m (2CH), 4.02 d (2H, CH$\underline{H}^A$, *J* 14.9 Hz), 3.88 d.d (2H, $CH_2Cl$, *J* 11.4, 9.6 Hz), 3.74 d.d (2H, $CH_2Cl$, *J* 11.7, 5.9 Hz), 3.65 d.d (2H, CH$\underline{H}^B$, *J* 14.9, 3.6 Hz). $^{13}$C NMR ($CD_3CN$) δ: 120.1 (q, $CF_3$, *J* 321.2 Hz), 55.0 (2CH), 43.0 ($2CH_2Cl$), 40.4 ($2CH_2$). $^{19}$F NMR ($CD_3CN$) $\delta_F$: -76.0. Mass spectrum, *m/z* ($I_{rel}$, %): 446 (0.3) $[M]^+$, 397 (100) $[M–CH_2Cl]^+$, 313 (3.9) $[M–CF_3SO_2]^+$, 263 (84.6) $[M–CH_2Cl–CF_3SO_2]^+$, 131 (26.1) $[264–CF_3SO_2]^+$, 95 (36.7) $[131–HCl]^+$, 90 (33.3) $[131–C_3H_5]^+$, 69 (54.5) $[CF_3]$. Found (%): C, 21.43; H, 2.10; N, 6.02; Cl 15.86%. Calc. for $C_8H_{10}Cl_2F_6N_2O_4S_2$ (%): C, 21.49; H, 2.25; N, 6.26; Cl 15.86%.

3. Synthesis of compounds **8–11**

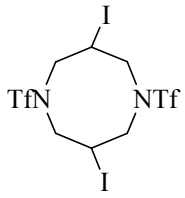
1,1,1-Trifluoro-*N*-(2-iodo-3-{[(trifluoromethyl)sulfonyl]amino}propyl)-*N*-prop-2-en-1-ylmethanesulfonamide **(8)**:



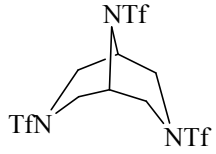

1,1,1-Trifluoro-*N*,*N*-bis(2-iodo-3-{[(trifluoromethyl)sulfonyl]amino}propyl)methanesulfonamide **(9)**:




3,7-Diiodo-1,5-bis[(trifluoromethyl)sulfonyl]-1,5-diazocane **(10)**:




3,7,9-Tris[(trifluoromethyl)sulfonyl]-3,7,9-triazabicyclo[3.3.1]nonane **(11)**:




To 3.87 g (26 mmol) of trifluoromethanesulfonamide and 11.69 g (39 mmol) of NaI 80 ml of $CH_3CN$ was added. To this solution, 2.35 ml (13 mmol) of N,N-diallyltriflamide was added, the mixture cooled to –30°C and 8.86 ml (78 mmol) of *t*-BuOCl was added dropwise. The reaction was carried out during 24 h in argon atmosphere in the dark. Then, the solvent was removed at a

reduced pressure, the residue dissolved in 80 ml of diethyl ether and treated with 80 ml of aqueous $Na_2S_2O_3$. The extract was dried over $CaCl_2$, the solvent removed in vacuum, dark-red residue (~3.5 g) washed with chloroform (3×15 ml) to obtain ~2.0 g of viscous liquid residue and ~1.5 g of crystalline residue, which was crystallized from minimal amount of chloroform. The precipitated crystals were filtered and dried to give 0.40 g (9%) of product **11** as colorless crystals with m.p. 283°C. From the filtrate, the solvent was removed in vacuum, the crystalline residue washed with ether to give 0.85 g (16%) of product **10** as a white powder, m.p. 253°C. The remained viscous liquid (~2.0 g) was dissolved in hot hexane and cooled to give two layers: ~1.1 g of brown viscous layer and 0.9 g of transparent liquid of purple color. Viscous brown fraction was purified on a column with coarse silica with hexane and hexane–methylene chloride = 3:1 as eluents to obtain 0.91 g (21%) of product **8**, light-brown liquid. Similarly, the second purple fraction was purified on a column with coarse silica with the same eluents to obtain 0.59 g (9%) of product **9** as a colorless liquid.

**1,1,1-Trifluoro-*N*-(2-iodo-3-{[(trifluoromethyl)sulfonyl]amino}propyl)-*N*-prop-2-en-1-yl-methanesulfonamide (8).** IR (KBr, $\nu$/cm$^{-1}$): br. 3300, 2936, 1646, 1432, 1391, 1324, 1280, 1224, 1192, 1133, 1051, 990, 937, 914, 862, 787, 745, 708, 649, 594, 499. $^1$H NMR ($CDCl_3$) δ: 5.90–5.77 m (1H, C<u>H</u>=$CH_2$), 5.47–5.38 m (2H, CH=C<u>H</u>$_2$), 4.54–4.45 m (1H, CHI), 4.20 d.d (1H, NC<u>H</u>$^B$CHI, $J$ 15.4, 6.7 Hz), 4.09–3.94 m (2H, NHC<u>H</u>$_2$CHI), 3.90–3.81 m (2H, C<u>H</u>$_2$CH=$CH_2$), 3.70 d.d (1H, NC<u>H</u>$^A$CHI, $J$ 15.4, 7.6 Hz). $^{13}$C NMR ($CDCl_3$) δ: 119.9 (q, $CF_3$, $J$ 323.3 Hz), 130.6 (CH), 122.2 ($CH_2$), 52.7 (<u>C</u>H$_2$CHI), 52.4 (<u>C</u>H$_2$CHCH$_2$), 47.7 ($CH_2$NH), 26.0 (CHI). $^{19}$F NMR ($CDCl_3$) $\delta_F$: –75.2. Found (%): C, 19.57; H, 2.70; N, 5.15; S 12.23; F 22.15; I 24.60. Calc. for $C_8H_{11}F_6IN_2O_4S_2$ (%): C, 19.06; H, 2.20; N, 5.56; S 12.72; F 22.61; I 25.17.

**1,1,1-Trifluoro-*N*,*N*-bis(2-iodo-3-{[(trifluoromethyl)sulfonyl]amino}propyl)methanesulfonamide (9).** IR (KBr, $\nu$/cm$^{-1}$): br. 3301, 2950, 2858, 1435, 1392, 1324, 1264, 1222, 1196, 1131, 1058, 982, 916, 857, 784, 740, 706, 599, 497. $^1$H NMR ($CDCl_3$) δ: 4.63–4.55 m (2H, C<u>H</u>I, first diastereoisomer), 4.54–4.44 m (2H, C<u>H</u>I, second diastereoisomer), 4.18–4.08 m (4H, NHC<u>H</u>$_2$CHI, first diastereomer), 4.05–3.95 (4H, NHC<u>H</u>$_2$CHI, second diastereomer), 3.92–3.73 (8H, NC<u>H</u>$_2$CHI in the two diastereomers). $^{13}$C NMR ($CDCl_3$) δ: 119.6 (q, $CF_3$, $J$ 323.4 Hz), 119.5 (q, $CF_3$, $J$ 323.4 Hz), 56.0 ($CH_2$N), 55.7 ($CH_2$N), 47.8 ($CH_2$NH), 25.7 (CHI), 25.5 (CHI). $^{19}$F NMR ($CDCl_3$) $\delta_F$: –74.1. Found (%): C, 14.28; H, 1.34; N, 4.90; S 11.84; F 21.38; I 33.12. Calc. for $C_9H_{12}F_9I_2N_3O_6S_3$ (%): C, 13.87; H, 1.55; N, 5.39; S 12.35; F 21.94; I 32.57.

**3,7-Diiodo-1,5-bis[(trifluoromethyl)sulfonyl]-1,5-diazocane (10).** IR (KBr, $\nu$/cm$^{-1}$): 1631, 1456, 1395, 1307, 1221, 1197, 1130, 1001, 862, 801, 777, 734, 661, 591, 496, 423. $^1$H NMR ($CD_3CN$) δ: 4.57 m (2H, C<u>H</u>I), 4.27 d (4H, C<u>H</u>$_2$N, $J$ 15.4 Hz), 3.85 d (2H, C<u>H</u>$_2$N, $J$ 15.7 Hz), 3.82 d (2H, C<u>H</u>$_2$N, $J$ 15.7 Hz). $^{13}$C NMR ($CD_3CN$) δ: 117.8 (q, $CF_3$, $J$ 324.0 Hz), 60.7 ($CH_2$N),

25.2 (CHI). $^{19}$F NMR ($CDCl_3$) $\delta_F$: -73.7. Mass spectrum, *m/z* ($I_{rel}$, %): 630 (0.2) $[M]^+$, 503 (50) $[M–I]^+$, 375 (12) $[503–HI]^+$, 243 (42) $[503–HI–CF_3SO_2]^+$, 69 (62) $[CF_3]^+$, 41 (100) $[CH_2CHCH_2]^+$. Found (%): C, 15.70; H, 1.48; N, 4.48; S 10.58; F 18.35; I 40.04. Calc. for $C_8H_{10}F_6I_2N_2O_4S_2$ (%): C, 15.25; H, 1.60; N, 4.45; S 10.18; F 18.09; I 40.28.

**3,7,9-Tris[(trifluoromethyl)sulfonyl]-3,7,9-triazabicyclo[3.3.1]nonane (11).** IR (KBr, *v*/cm$^{-1}$): 1641, 1401, 1336, 1235, 1189, 1119, 1099, 1054, 990, 947, 909, 770, 734, 666, 590, 462. $^1$H NMR ($CD_3CN$) δ: 4.32 m (2H, C<u>H</u>I), 4.13 d (4H, C<u>H$_2$</u>N, *J* 13.2 Hz), 3.61 d (4H, C<u>H$_2$</u>N, *J* 13.0 Hz). $^{13}$C NMR ($CD_3CN$) δ: 119.0 (q, $CF_3$, *J* 323.2 Hz), 118.4 (q, $CF_3$, *J* 320.2 Hz), 49.8 (CHN), 49.3 (CHN), 30.6 ($CH_2N$). $^{19}$F NMR ($CDCl_3$) $\delta_F$: -75.3 ($CF_3NCH$), -78.3 ($CF_3NCH_2$). Mass spectrum, *m/z* ($I_{rel}$, %): 523 (2) $[M]^+$, 390 (64) $[M–CF_3SO_2]^+$, 257 (55) $[390–CF_3SO_2]^+$, 124 (95) $[257–CF_3SO_2]^+$, 95 (92) $[124–CH_2N]^+$, 69 (100) $[CF_3]^+$, 42 (86) $[C_3H_6]^+$. Found (%): C, 20.98; H, 1.80; N, 7.81; S 17.95; F 32.19. Calc. for $C_9H_{10}F_9N_3O_6S_3$ (%): C, 20.65; H, 1.93; N, 8.03; S 18.38; F 32.67.

**Reactions of N,N-diallyltriflamide 1 with arenesulfonamides 3a-d and trifluoroacetamide 4.** To the solution of 7 mmol of arenesulfonamide **3** or trifluoroacetamide **4** and 20 mmol of NaI 50 ml of MeCN was added. To this solution, 7 mmol of compound **1** was added, the mixture was cooled to –30°C and 2.24 ml (20 mmol) of *t*-BuOCl was added dropwise. The mixture was stirred for 24 h in argon atmosphere in the dark. After completion, the solvent was removed at a reduced pressure, the residue dissolved in 50 ml of ethyl acetate, treated with 50 ml of aqueous $Na_2S_2O_3$, the extract dried over $CaCl_2$. The solvent was removed, the residue separated by column chromatography on silica by successive elution with hexane, hexane–ether 1:1, ether. From ethereal fraction the unreacted sulfonamide 3 or amide 4 was isolated, the product was further purified by column chromatography on fine silica with hexane and ether as eluents.

**N-(2-iodo-3-{prop-2-en-1-yl[(triflamido)propyl]}tosylamide 12a.** IR (KBr, *v*/cm$^{-1}$): 3281, 2928, 1650, 1599, 1438, 1389, 1331, 1224, 1192, 1161, 1137, 1092, 1045, 937, 815, 785, 749, 708, 665, 592, 553, 498. $^1$H NMR ($CDCl_3$) δ: 2.48 s (3H, $CH_3$), 3.76-3.65 m (2H, $CH_2CH=CH_2$), 3.89-3.82 m (2H, NHCH$^A$HCHI), 4.20 dd (2H, NCHH$^B$CHI, *J* 15.8, 6.4 Hz), 4.55–4.44 m (1H, CHI), 4.95 s (1H, NH), 5.47–5.37 m (2H, $CH=CH_2$), 5.92-5.71 m (1H, $CH=CH_2$), 7.39-7.34 m (2H, CH$^{3,5}$, *J* 17.0, 8.5, 0.42 Hz), 7.75 dd (2H, C*H*$^{2,6}$, *J* 6.7, 1.5 Hz), 7.83 dd (2H, CH$^{2,6}$, *J* 8.3, 3.0 Hz). $^{13}$C NMR ($CDCl_3$), $\delta_C$: 21.6 (CHI), 21.6 ($CH_3$), 47.9 ($CH_2N$), 52.1 (*C*$H_2CHCH_2$), 52.5 (*C*$H_2$CHI), 122.6 ($=CH_2$), 126.5 q ($CF_3$, *J* 328.1 Hz), 127.1 (C$^o$), 130.1 (C$^m$), 130.6 (*C*H=), 136.5 (C$^i$),144.2 (C$^p$). $^{19}$F NMR ($CDCl_3$) $\delta_F$: –75.0. Found (%): C, 31.70; H, 3.38; N, 4.92; S 11.63; F 10.48; I 23.49. Calc. for $C_{14}H_{18}F_3IN_2O_4S_2$ (%): C, 31.95; H, 3.45; N, 5.32; S 12.18; F 10.83; I 24.11.

**N-[3-(N-allyltriflamido)-2-iodopropyl]benzenesulfonamide 12b**. IR (KBr, $\nu$/cm$^{-1}$): 3330, 3081, 2930, 2858, 2611, 1972, 1894, 1730, 1646, 1443, 1391, 1331, 1290, 1224, 1190, 1135, 1050, 991, 937, 915, 862, 788, 740, 695, 594, 500. $^1$H NMR, δ: 3.70 dd (1H, NCH$^A$CHI, $J$ 14.6, 7.5 Hz), 3.85 dd (2H, C$H_2$CH=CH$_2$, $J$ 11.0, 7.3 Hz), 4.11-3.92 m (2H, NHC$H_2$CHI), 4.19 dd (1H, NC$H^B$CHI, $J$ 15.4, 6.0 Hz), 4.56–4.38 m (1H, CHI), 5.47–5.38 m (2H, =CH$_2$), 5.90–5.70 m (1H, CH=), 7.66-7.43 m (2H, CH$^{3,5}$), 7.77-7.66 m (1H, CH$^4$), 8.01-7.81 m (2H, CH$^{2,6}$). $^{13}$C NMR, $\delta_C$: 26.0 (*C*HI), 47.6 (*C*H$_2$NH), 52.3 (*C*H$_2$CHCH$_2$), 52.6 (*C*H$_2$CHI), 119.7 q (CF$_3$, $J$ 323.0 Hz), 122.3 (=*C*H$_2$), 127.6 (C$^o$), 129.2 (C$^m$), 129.4 (C$^p$), 130.6 (*C*H=), 133.2 (C$^i$). $^{19}$F NMR, $\delta_F$: –75.1. Found (%): C, 29.96; H, 3.02; N, 5.43; S 12.46; F 11.10; I 24.30. Calc. for $C_{13}H_{16}F_3IN_2O_4S_2$ (%): C, 30.48; H, 3.15; N, 5.47; S 12.52; F 11.13; I 24.77.

**N-Allyl-*N*-(3-chloro-2-iodopropyl)triflamide 13.** IR (KBr, $\nu$/cm$^{-1}$): 3086, 2987, 2943, 2881, 1646, 1431, 1390, 1280, 1222, 1190, 1134, 1050, 990, 936, 915, 862, 787, 746, 708, 594, 499. $^1$H NMR, δ: 3.69 dd (1H, NC$H^A$CHI, $J$ 15.1, 8.0 Hz), 3.83 dd (2H, C$H_2$CH=CH$_2$, $J$ 12.0, 7.0 Hz), 4.07-3.90 m (2H, ClC$H_2$CHI), 4.17 dd (1H, NC$H^B$CHI, $J$ 15.7, 6.5 Hz), 4.52-4.41 m (1H, CHI), 5.45-5.35 m (2H, =CH$_2$), 5.88-5.73 m (1H, CH=). $^{13}$C NMR, $\delta_C$: 26.3 (*C*HI), 48.0 (*C*H$_2$Cl), 52.6 (*C*H$_2$CHCH$_2$), 53.0 (*C*H$_2$CHI), 120.0 q (CF$_3$, $J$ 323.4 Hz), 122.4 (=CH$_2$), 130.9 (CH=). $^{19}$F NMR, $\delta_F$: –75.2. Found (%): C, 21.46; H, 2.57; N, 3.58; S 8.20; F 13.93; I 32.11; Cl 8.93. Calc. for $C_7H_{10}ClF_3INO_2S$ (%): C, 21.47; H, 2.57; N, 3.58; S 8.19; F 14.56; I 32.41; Cl 9.05.

**N-[3-(N-Allyltriflamido)-2-iodopropyl]trifluoroacetamide 12e.** IR (KBr, $\nu$/cm$^{-1}$): 3384, 3325, 3094, 2937, 1718, 1648, 1552, 1439, 1389, 1220, 1189, 1138, 1034, 995, 939, 909, 788, 729, 592, 503. $^1$H NMR, $\delta_H$: 3.76-3.50 m (2H, C$H_2$CH=CH$_2$), 4.01-3.76 m (2H, NC$H^A$HCHI), 4.19-4.01 m (2H, NHCH$H^B$CHI), 4.45-4.30 m (1H, CHI), 5.48–5.31 m (2H, =CH$_2$), 5.92-5.67 m (1H, CH=), 7.20 t (1H, NH, $J$ 5.7 Hz). $^{13}$C NMR, $\delta_C$: 23.8 (*C*HI), 44.1 (*C*H$_2$NH), 52.4 (*C*H$_2$CHCH$_2$), 53.0 (*C*H$_2$CHI), 115.8 q (CF$_3$, $J$ 287.3 Гц), 119.8 q (CF$_3$, $J$ 322.1 Hz), 122.1 (=CH$_2$), 130.8 (CH=), 157.8 q (C=O, $J$ 37.6 Hz). $^{19}$F NMR, $\delta_F$: –75.8. Found (%): C, 22.99; H, 2.30; N, 5.58; S 6.47; F 24.20; I 26.74. Calc. for $C_9H_{11}F_6IN_2O_3S$ (%): C, 23.09; H, 2.37; N, 5.98; S 6.85; F 24.35; I 27.11.

**Single crystal X-ray structure determinations:**

The single crystals of **7** were obtained by slow vaporization from acetonitrile, **10** from chloroform, **11** from diethyl ether. Crystal data were collected on a Bruker D8 Venture diffractometer with MoKα radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set [1]. Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set [1]. **CCDC 1545539 (7)** , **CCDC 1520698 (10)** and **CCDC 1520697 (11)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

**References:**

[1] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.

**Figure 1. Moleculare structure of compound 7**

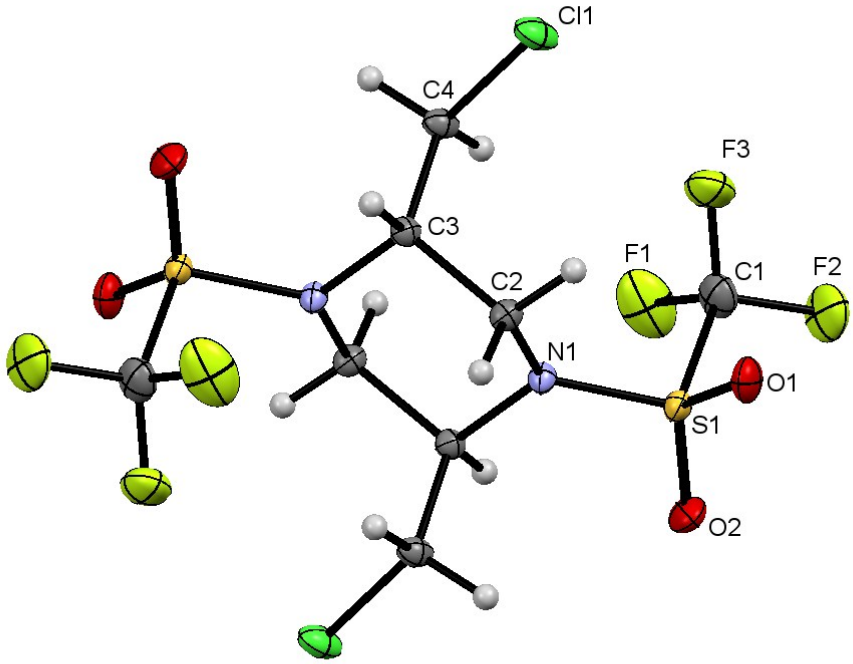


**Table 1.** Crystal Data, Details of Intensity Measurements, and Structure Refinement for compound **7**

| | |
|---|---|
| Empirical formula | $C_4H_5ClF_3NO_2S$ |
| Formula weight / g·mol$^{-1}$ | 223.60 |
| Crystal system | Monoclinic |
| Space group | P 21/c |
| *a* / Å | 8.8090(4) |
| *b* / Å | 12.7998(6) |
| *c* / Å | 7.2200(3) |
| *β* / ° | 91.795(2) |
| Volume / Å$^3$ | 813.68(6) |
| *Z* | 4 |
| Density (calculated) / g·cm$^{-3}$ | 1.825 |
| Absorptions coefficient / mm$^{-1}$ | 0.737 |
| Radiation ($\lambda$ / Å) | MoKα (0.71073) |
| Temperature / K | 100(2) |
| 2$\Theta$ range / ° | 5.62 – 60.10 |
| Crystal size / mm | 0.180 × 0.350 × 0.450 |
| Crystal habit | colorless prizm |
| F(000) | 448 |
| Index ranges | $-12 \le h \le 12$, $-18 \le k \le 18$, $-8 \le l \le 10$ |
| Reflections collected | 21282 |
| Independent reflections | 2381 |
| Max. and min. transmission | 0.6398 / 0.7460 |
| Number of ref. parameters | 109 |
| $R_1$ / $wR_2$ [$I > 2\sigma(I)$] | 0.0257 / 0.0640 |
| $R_1$ / $wR_2$ (all data) | 0.0314 / 0.0671 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Largest diff. peak and hole / e·Å$^{-3}$ | 0.433 / -0.322 |
| Weight scheme | $w=1/[\sigma^2(F_o^2)+(0.0307P)^2+0.4853P]$ where $P=(F_o^2+2F_c^2)/3$ |

**Table 2**. Selected bond lengths, bond and torsion angles in compound **7**

| Bond | *l*, Å | Angle | φ, ° | Torsion angle | θ, ° |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| Cl1-C4 | 1.7851(12) | O1-S1-O2 | 122.03(6) | O1-S1-N1-C2 | -9.39(11) |
| S1-O1 | 1.4226(10) | O1-S1-N1 | 110.36(6) | O2-S1-N1-C2 | -146.55(9) |
| S1-O2 | 1.4255(10) | O2-S1-N1 | 109.67(6) | C1-S1-N1-C2 | 102.80(10) |
| S1-N1 | 1.6063(10) | O1-S1-C1 | 105.31(6) | O1-S1-N1-C3 | 152.48(8) |
| S1-C1 | 1.8362(14) | O2-S1-C1 | 104.20(7) | O2-S1-N1-C3 | 15.32(10) |
| F1-C1 | 1.3248(18) | N1-S1-C1 | 103.36(6) | C1-S1-N1-C3 | -95.33(9) |
| F2-C1 | 1.3194(16) | C2-N1-C3 | 117.08(9) | O1-S1-C1-F2 | -67.78(12) |
| F3-C1 | 1.3230(18) | C3-C4-Cl1 | 109.67(8) | N1-S1-C1-F2 | 176.39(10) |
| N1-C2 | 1.4800(14) | C3-N1-S1 | 119.44(8) | C3-N1-C2-C3 | 55.64(13) |
| N1-C3 | 1.4819(14) | F2-C1-F3 | 108.65(12) | S1-N1-C2-C3 | -142.08(8) |
| C2-C3 | 1.5266(16) | F2-C1-S1 | 109.81(10) | N1-C2-C3-C4 | 72.09(12) |
| C3-N1 | 1.4819(14) | C2-C3-C4 | 114.50(10) | N1-C3-C4-Cl1 | -171.93(8) |
| C3-C4 | 1.5277(16) | N1-C2-C3 | 109.95(9) | C2-C3-C4-Cl1 | 65.83(11) |

**Figure 2. Moleculare structure of compound 10**

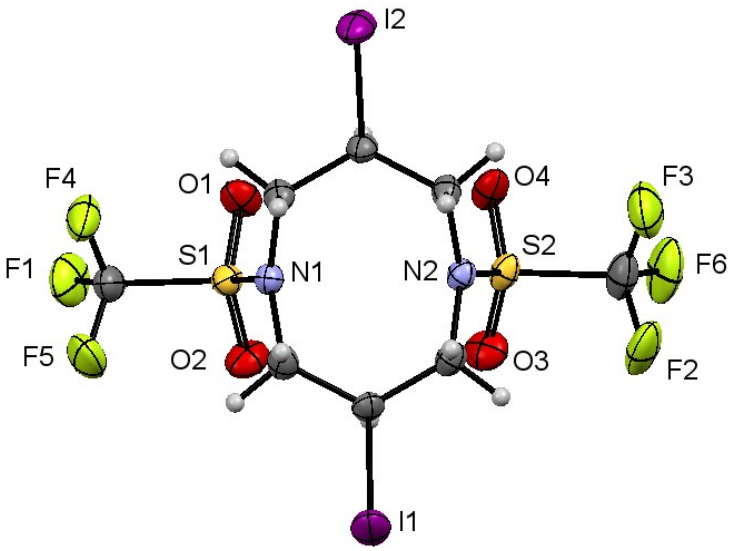


**Table 3.** Crystal Data, Details of Intensity Measurements, and Structure Refinement for compound **10**

| | |
|---|---|
| Empirical formula | $C_8H_{10}F_6I_2N_2O_4S_2$ |
| Formula weight / g·mol$^{-1}$ | 630.10 |
| Crystal system | monoclinic |
| Space group | P 21/c |
| *a* / Å | 11.305(2) |
| *b* / Å | 17.982(3) |
| *c* / Å | 18.058(3) |
| $\alpha$ / ° | 90 |
| $\beta$ / ° | 100.155(5) |
| $\gamma$ / ° | 90 |
| Volume / Å$^3$ | 3613.5(9) |
| *Z* | 8 |
| Density (calculated) / g·cm$^{-3}$ | 2.316 |
| Absorptions coefficient / mm$^{-1}$ | 3.786 |
| Radiation ($\lambda$ / Å) | MoKα (0.71073) |
| Temperature / K | 100(2) |
| 2$\Theta$ range / ° | 4.30 – 60.30 |
| Crystal size / mm | 0.310 × 0.410 × 0.500 |
| Crystal habit | colorless plate |
| F(000) | 2368 |
| Index ranges | -15 ≤ h ≤ 15, -25 ≤ k ≤ 25, -25 ≤ l ≤ 25 |
| Reflections collected | 147899 |
| Independent reflections | 10609 |
| Max. and min. transmission | 0.362 / 0.746 |
| Number of ref. parameters | 434 |
| $R_1$ / $wR_2$ [$I > 2\sigma(I)$] | 0.0431 / 0.0891 |
| $R_1$ / $wR_2$ (all data) | 0.0786 / 0.1031 |
| Goodness-of-fit on $F^2$ | 1.056 |
| Largest diff. peak and hole / e·Å$^{-3}$ | 2.096 / -2.015 |

$w=1/[\sigma^2(F_o^2)+(0.0361P)^2+ 11.1751P]$, where $P=(F_o^2+2F_c^2)/3$

**Table 4**. Selected bond lengths, bond and torsion angles in compound **10**

| Bond | *l*, Å | Angle | φ, ˚ | Torsion angle | θ, ˚ |
|---|---|---|---|---|---|
| I1-C4 | 2.159(4) | O2-S1-O1 | 122.1(2) | C4-C2-N2-C8 | 104.7(4) |
| I2-C7 | 2.165(4) | O2-S1-N1 | 109.8(2) | C4-C2-N2-S2 | -86.1(4) |
| S1-O2 | 1.415(3) | O2-S1-C1 | 105.0(2) | O3-S2-N2-C2 | 30.4(4) |
| S1-O1 | 1.424(3) | N1-S1-C1 | 105.8(2) | C5-S2-N2-C2 | -81.5(4) |
| S1-N1 | 1.596(4) | F1-C1-S1 | 109.1(4) | O2-S1-C1-F1 | -67.5(4) |
| S1-C1 | 1.840(5) | C2-C4-I1 | 106.3(3) | N1-S1-C1-F1 | 176.5(3) |
| F1-C1 | 1.329(6) | C8-C7-C6 | 116.8(4) | O2-S1-N1-C6 | 162.7(3) |
| C2-N2 | 1.482(5) | F2-C5-F3 | 108.7(5) | S1-N1-C6-C7 | -86.2(4) |
| C2-C4 | 1.512(6) | N1-C6-C7 | 113.5(3) | C3-N1-C6-C7 | 105.1(4) |
| N2-C8 | 1.490(5) | C2-C4-C3 | 117.2(4) | N1-C6-C7-C8 | -64.4(5) |

**Figure 3. Moleculare structure of compound 11**

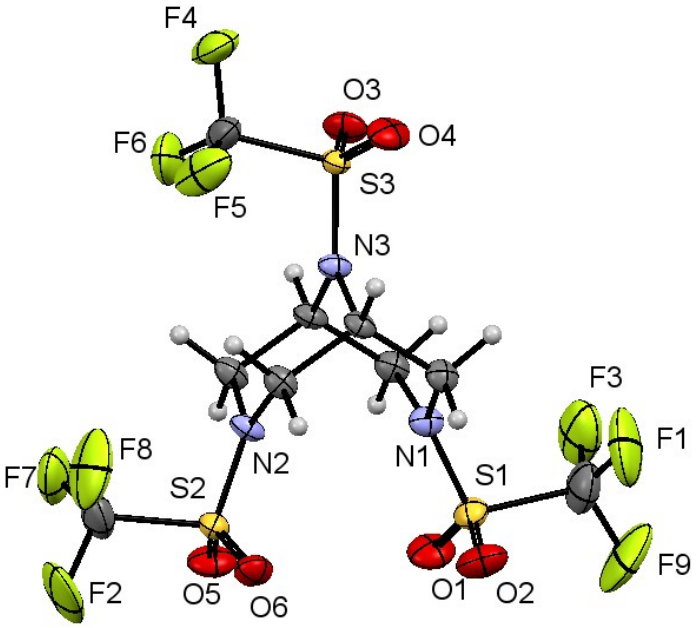


**Table 5.** Crystal Data, Details of Intensity Measurements, and Structure Refinement for compound **11**

| | |
|---|---|
| Empirical formula | $C_9H_{10}F_9N_3O_6S_3$ |
| Formula weight / g·mol$^{-1}$ | 523.38 |
| Crystal system | triclinic |
| Space group | P-1 |
| *a* / Å | 11.214(4) |
| *b* / Å | 11.857(5) |
| *c* / Å | 14.834(7) |
| $\alpha$ / ° | 73.267(1) |
| $\beta$ / ° | 78.954(1) |
| $\gamma$ / ° | 80.979(1) |
| Volume / Å$^3$ | 1848.0(1) |
| *Z* | 4 |
| Density (calculated) / g·cm$^{-3}$ | 1.883 |
| Absorptions coefficient / mm$^{-1}$ | 0.525 |
| Radiation ($\lambda$ / Å) | $Mo_{K\alpha}$ (0.71073) |
| Temperature / K | 100(2) |
| 2$\Theta$ range / ° | 4.92 – 60.24 |
| Crystal size / mm | 0.370 × 0.430 × 0.500 |
| Crystal habit | colorless prizm |
| F(000) | 1050 |
| Index ranges | $-15 \le h \le 15$, $-16 \le k \le 16$, $-21 \le l \le 21$ |
| Reflections collected | 40457 |
| Independent reflections | 9983 |
| Max. and min. transmission | 0.780 / 0.830 |
| Number of ref. parameters | 541 |
| $R_1$ / $wR_2$ [$I > 2\sigma(I)$] | 0.0792 / 0.2262 |
| $R_1$ / $wR_2$ (all data) | 0.1164 / 0.2648 |
| Goodness-of-fit on $F^2$ | 1.051 |
| Largest diff. peak and hole / e·Å$^{-3}$ | 1.486 / -1.469 |

$w=1/[\sigma^2(F_o^2)+(0.1227P)^2+ 9.1291P]$, where $P=(F_o^2+2F_c^2)/3$

**Table 6**. Selected bond lengths, bond and torsion angles in compound **11**

| Bond | *l*, Å | Angle | φ, ˚ | Torsion angle | θ, ˚ |
|---|---|---|---|---|---|
| S1-O1 | 1.416(4) | O1-S1-O2 | 121.7(3) | O1-S1-N1-C9 | -32.1(4) |
| S1-O2 | 1.422(4) | O1-S1-N1 | 109.8(2) | O2-S1-N1-C9 | -168.1(4) |
| S1-N1 | 1.587(4) | O1-S1-C1 | 104.5(3) | C1-S1-N1-C9 | 80.0(4) |
| S1-C1 | 1.834(6) | N1-S1-C1 | 105.6(3) | O1-S1-N1-C2 | 167.4(4) |
| F1-C1 | 1.322(9) | C9-N1-C2 | 115.9(3) | C5-S2-N2-C4 | 87.3(4) |
| F2-C5 | 1.298(8) | F9-C1-F1 | 109.3(6) | S4-N4-C16-C10 | 147.4(3) |
| F3-C1 | 1.330(8) | F1-C1-S1 | 109.6(5) | N1-S1-C1-F9 | -177.7(5) |
| N1-C9 | 1.466(5) | N1-C2-C3 | 110.5(3) | O1-S1-C1-F1 | 176.9(5) |
| N1-C2 | 1.477(5) | N3-C3-C2 | 107.6(3) | O2-S1-C1-F1 | -54.2(6) |
| C2-C3 | 1.534(6) | C2-C3-C4 | 114.9(4) | N1-S1-C1-F1 | 61.1(6) |
| S1-O1 | 1.416(4) | O1-S1-O2 | 121.7(3) | O1-S1-N1-C9 | -32.1(4) |
| S1-O2 | 1.422(4) | O1-S1-N1 | 109.8(2) | O2-S1-N1-C9 | -168.1(4) |
| S1-N1 | 1.587(4) | O1-S1-C1 | 104.5(3) | C1-S1-N1-C9 | 80.0(4) |
| S1-C1 | 1.834(6) | N1-S1-C1 | 105.6(3) | O1-S1-N1-C2 | 167.4(4) |
| F1-C1 | 1.322(9) | C9-N1-C2 | 115.9(3) | C5-S2-N2-C4 | 87.3(4) |

**Figure 4. $^{1}$H NMR spectrum of compound 6 (400 MHz, $CD_3CN$).**

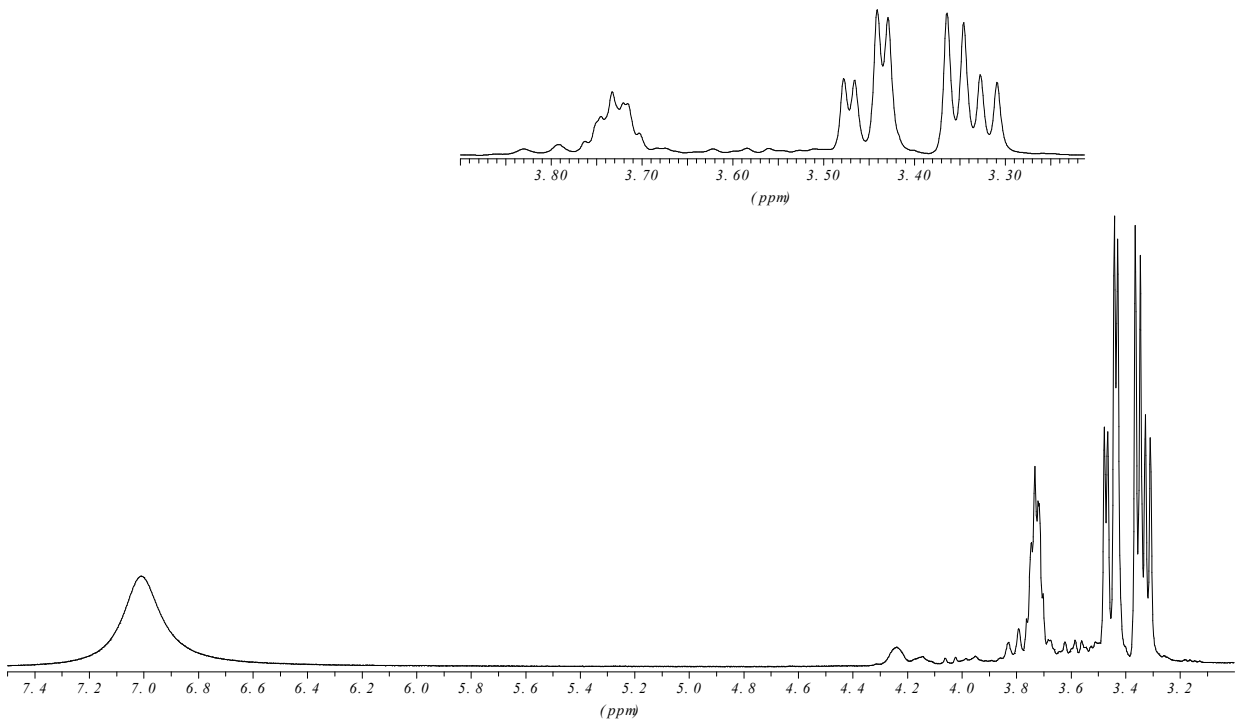


**Figure 5. $^{13}C$ NMR spectrum of compound 6 (400 MHz, $CD_3CN$).**

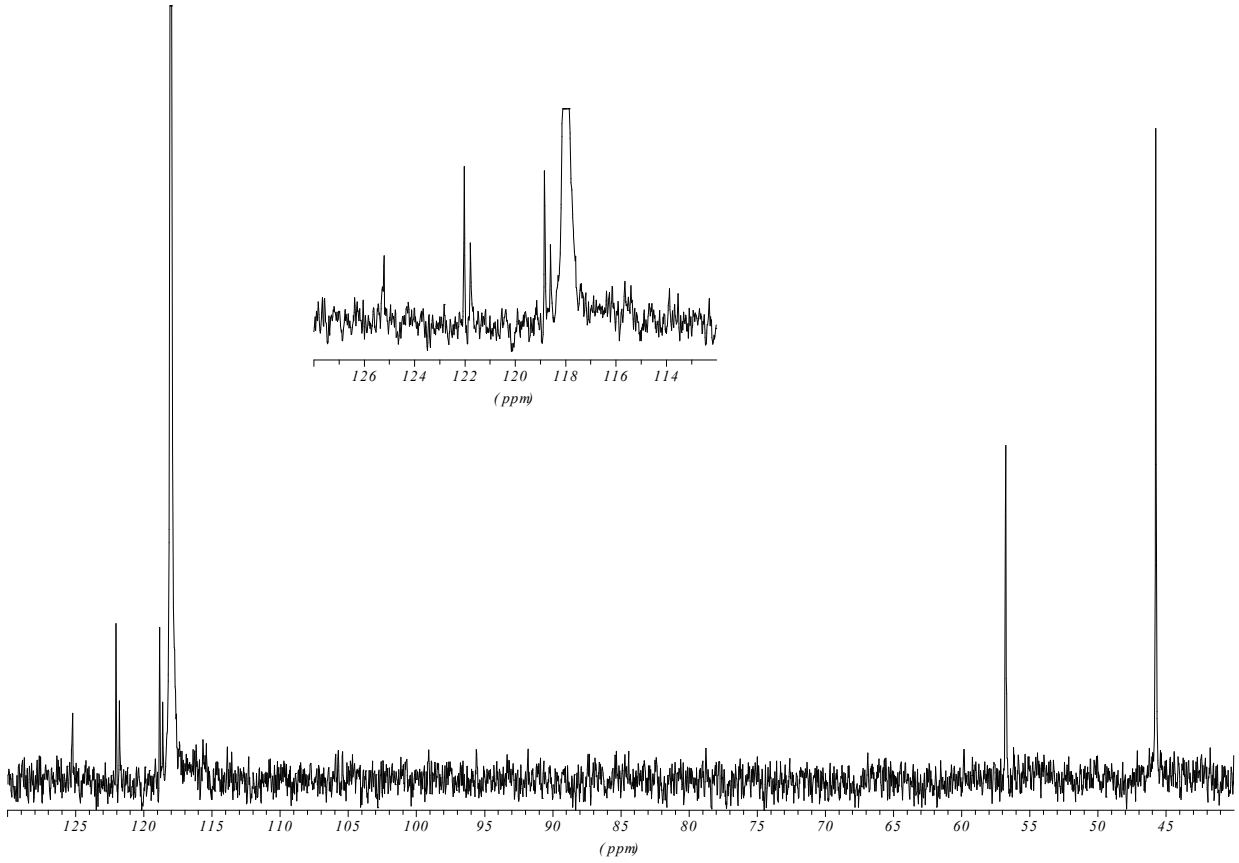


**Figure 6. $^{19}F$ NMR spectrum of compound 6 (400 MHz, $CD_3CN$).**

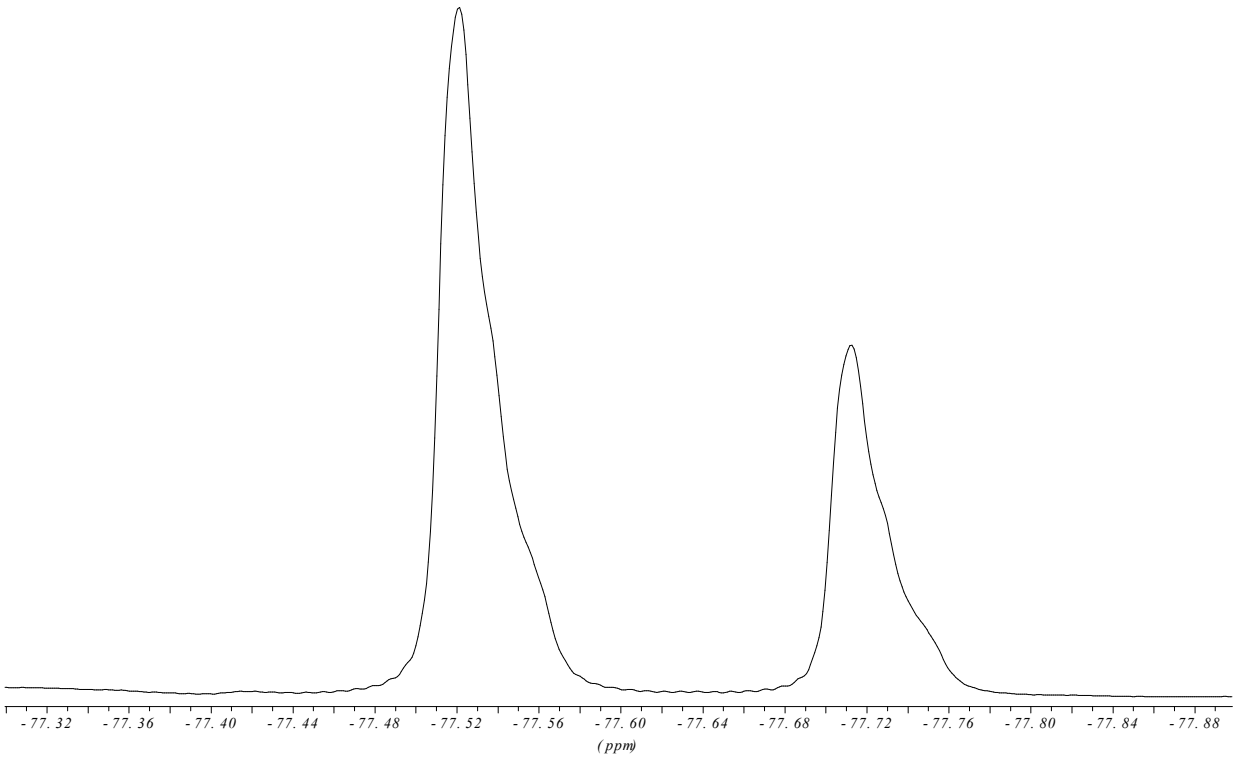


**Figure 7. FT-IR spectrum of compound 6 (KBr)**

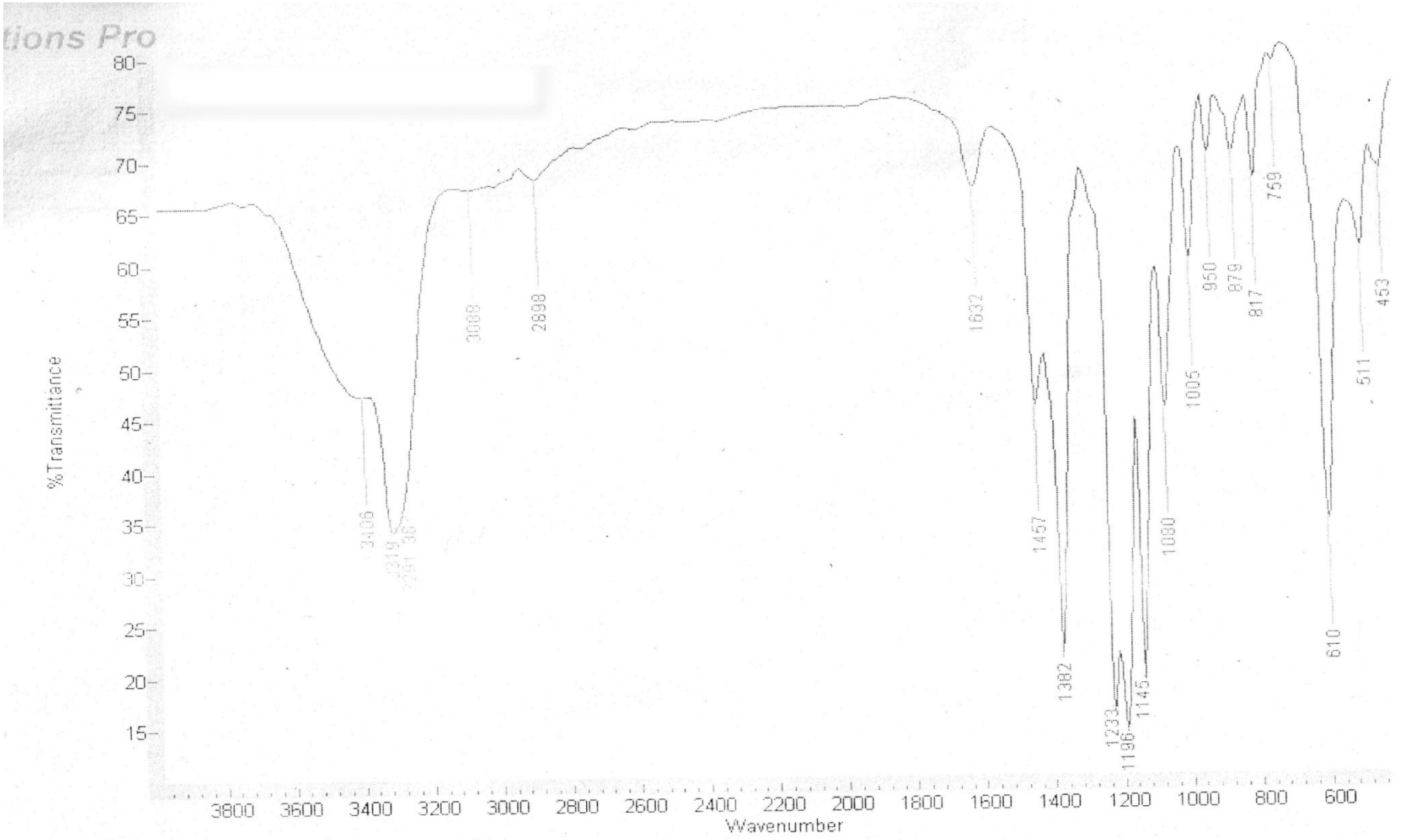


**Figure 8. $^{1}$H NMR spectrum of compound 7 (400 MHz, $CD_3CN$).**

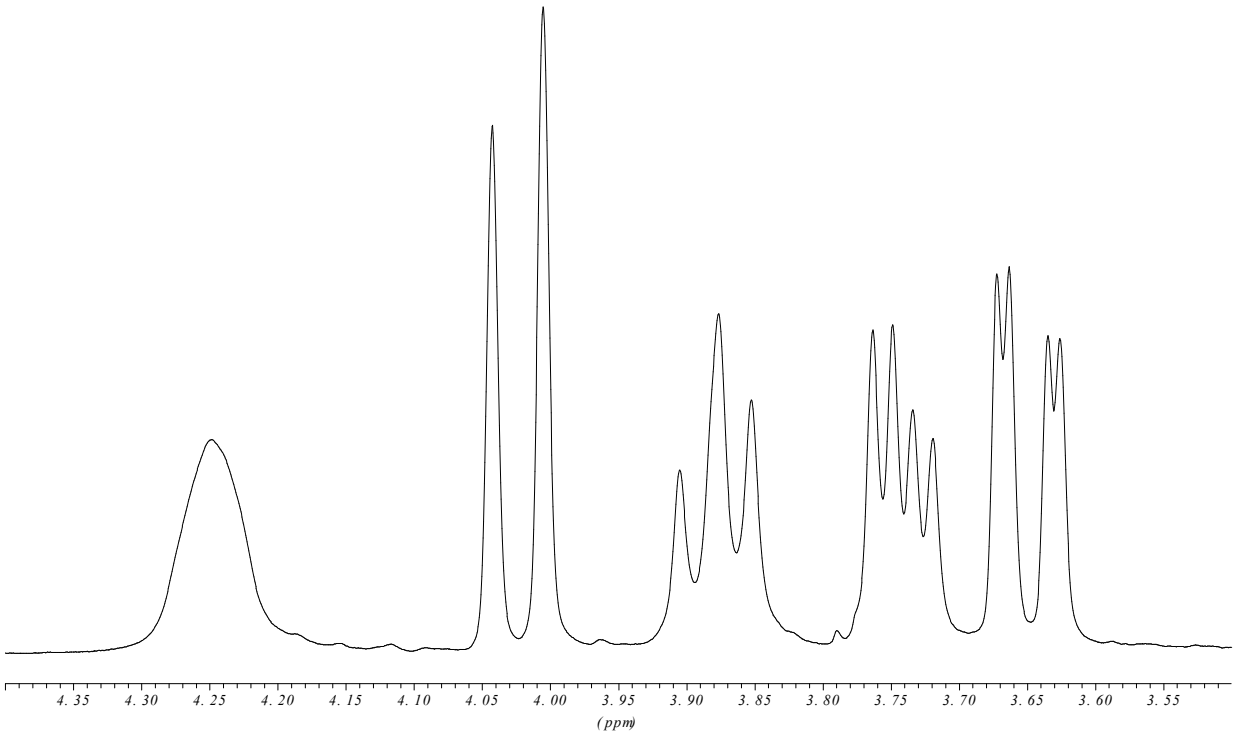


**Figure 9. $^{13}C$ NMR spectrum of compound 7 (400 MHz, $CD_3CN$).**

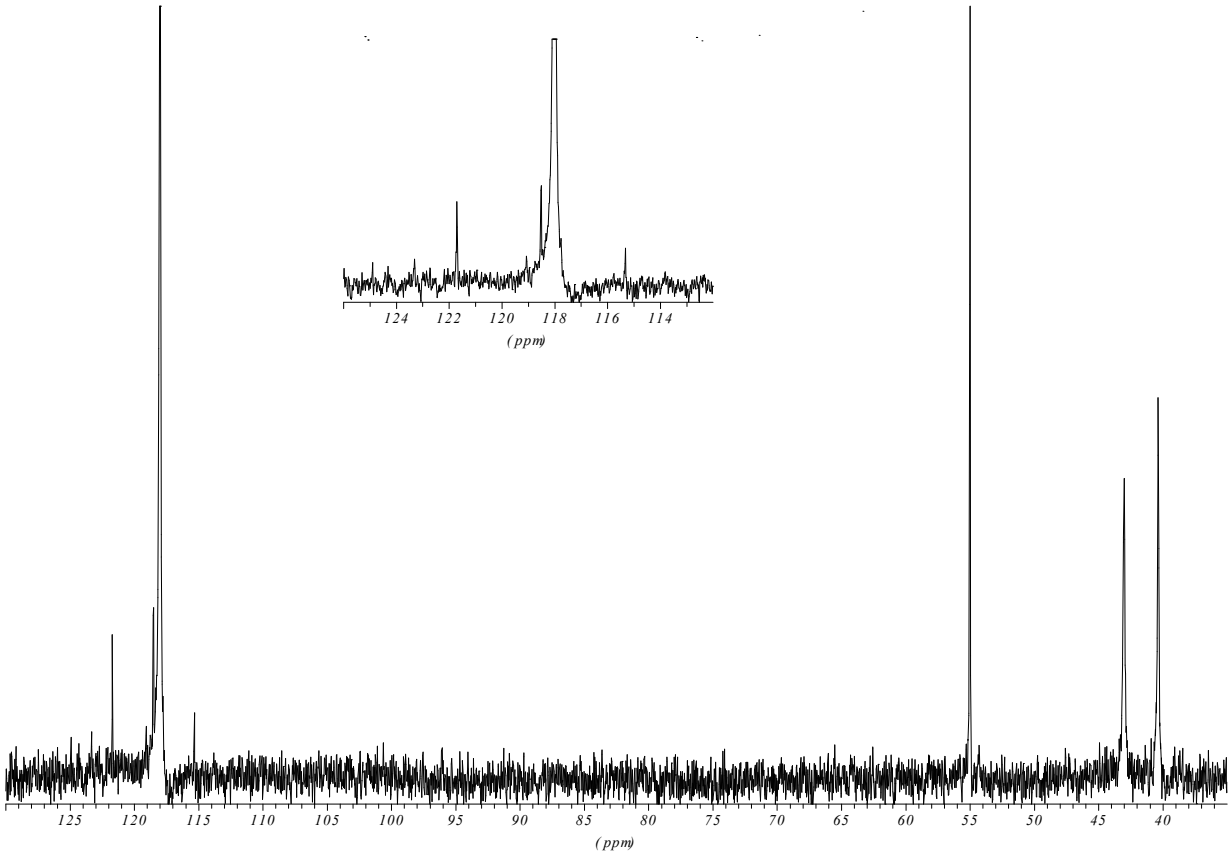


**Figure 10. $^{19}F$ NMR spectrum of compound 7 (400 MHz, $CD_3CN$).**

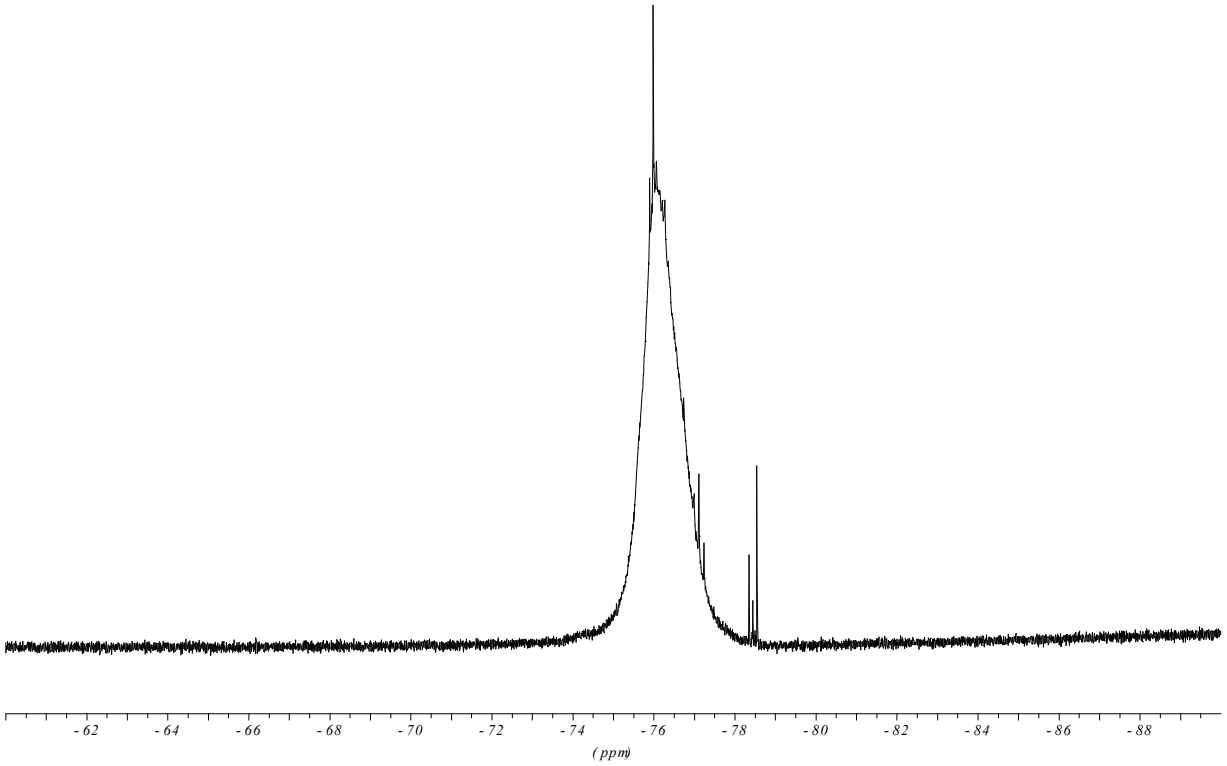


**Figure 11. FT-IR spectrum of compound 7 (film)**

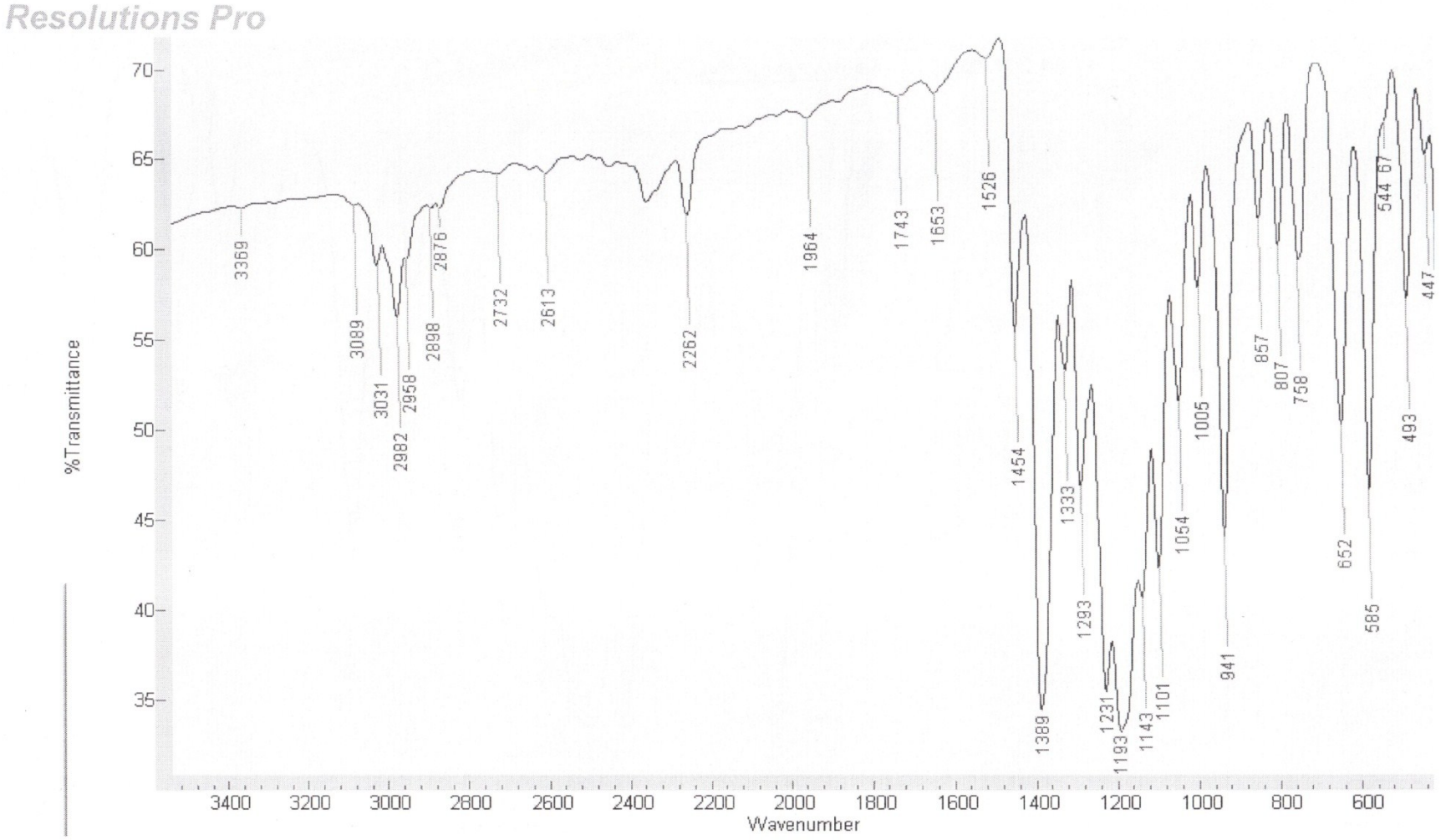


**Figure 12. $^{1}H$ NMR spectrum of compound 8 (400 MHz, $CDCl_3$).**

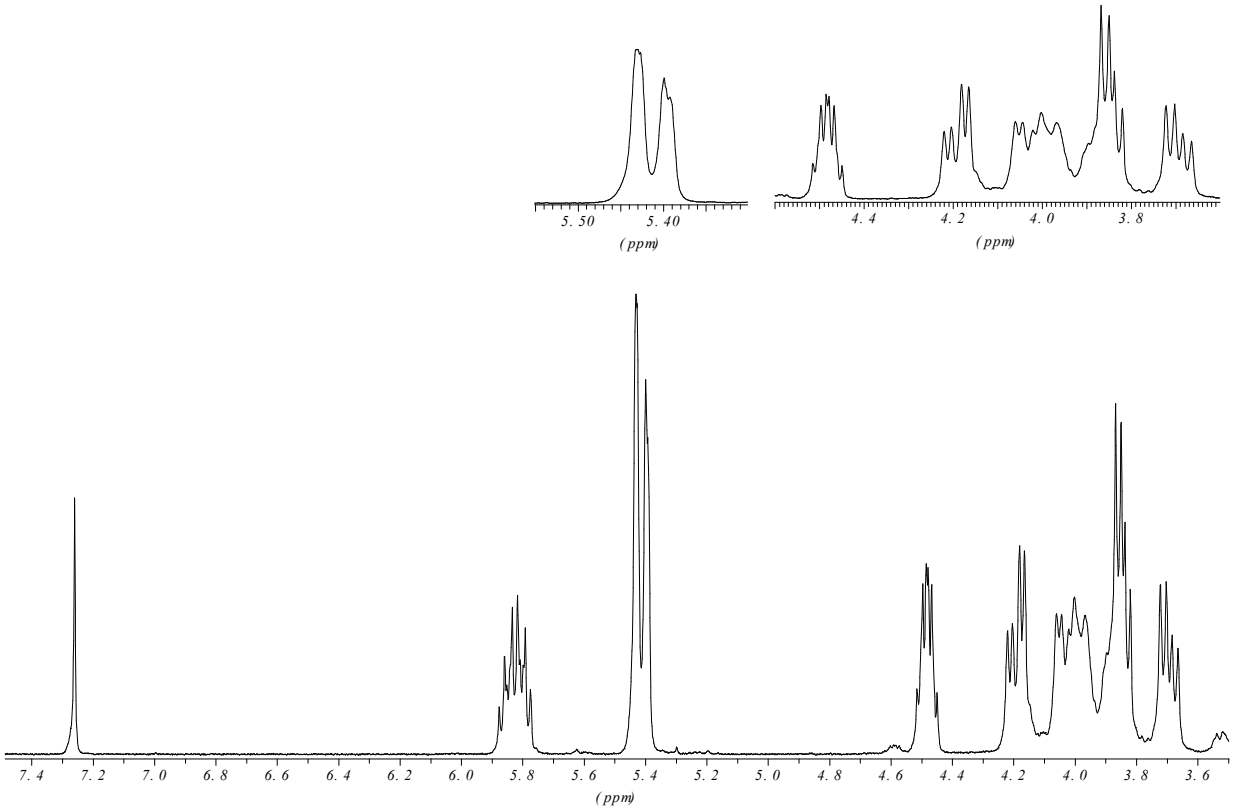


**Figure 13. $^{13}C$ NMR spectrum of compound 8 (400 MHz, $CDCl_3$).**

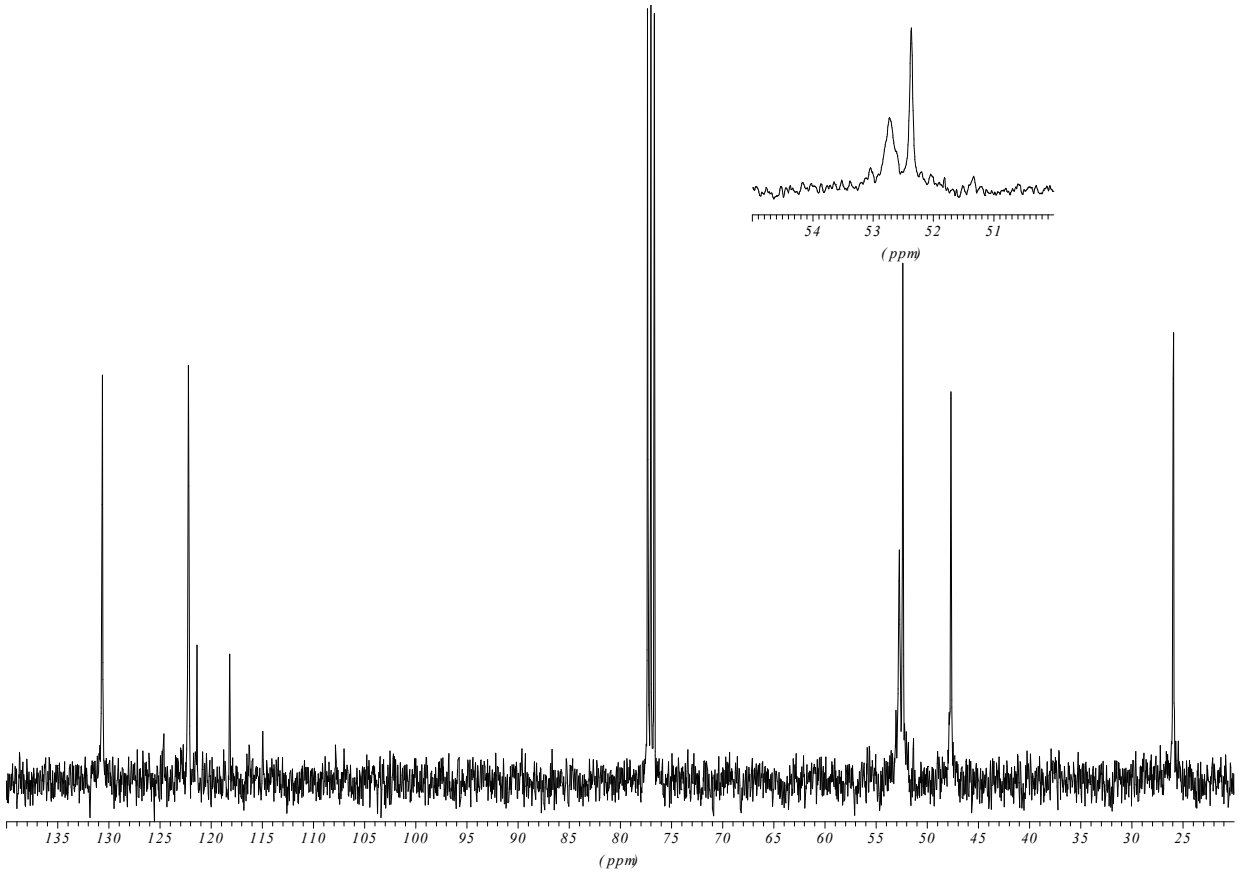


**Figure 14. $^{19}F$ NMR spectrum of compound 8 (400 MHz, $CDCl_3$).**

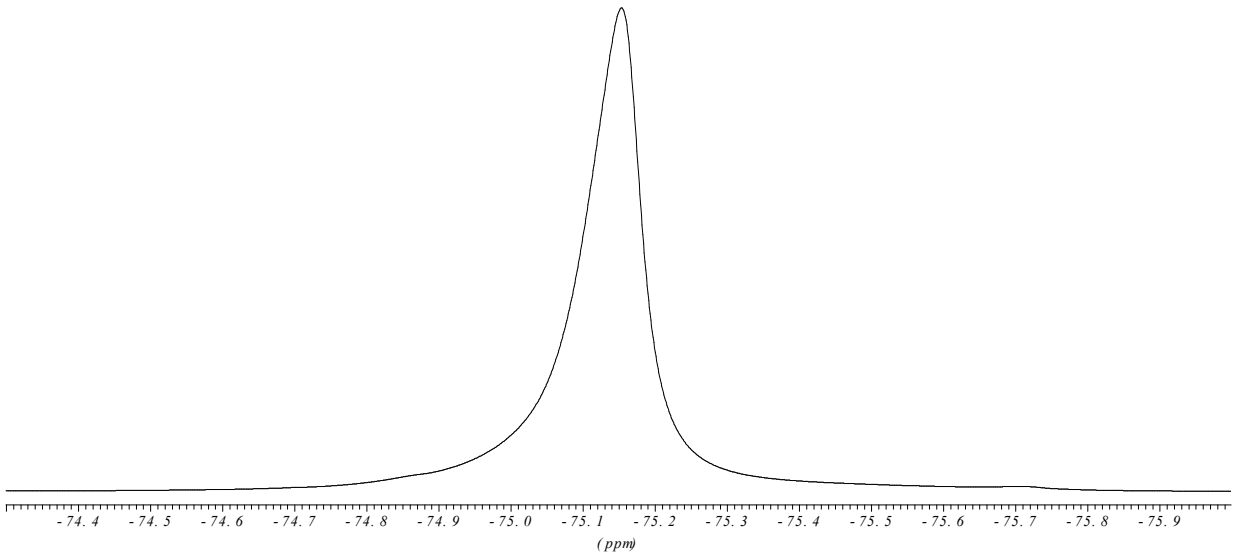


**Figure 15. FT-IR spectrum of compound 8 (film)**

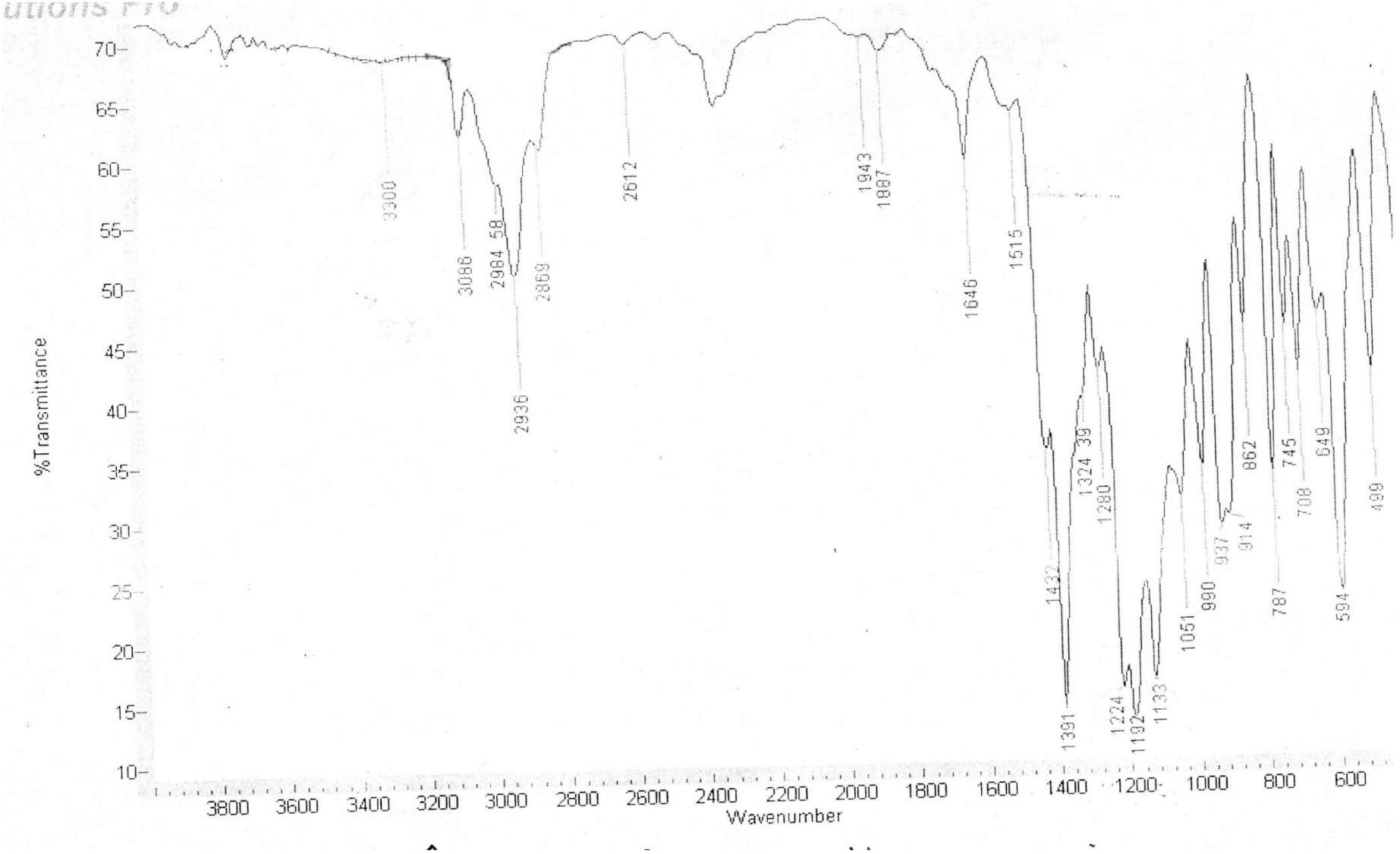


**Figure 16. $^{1}H$ NMR spectrum of compound 9 (400 MHz, $CDCl_3$).**

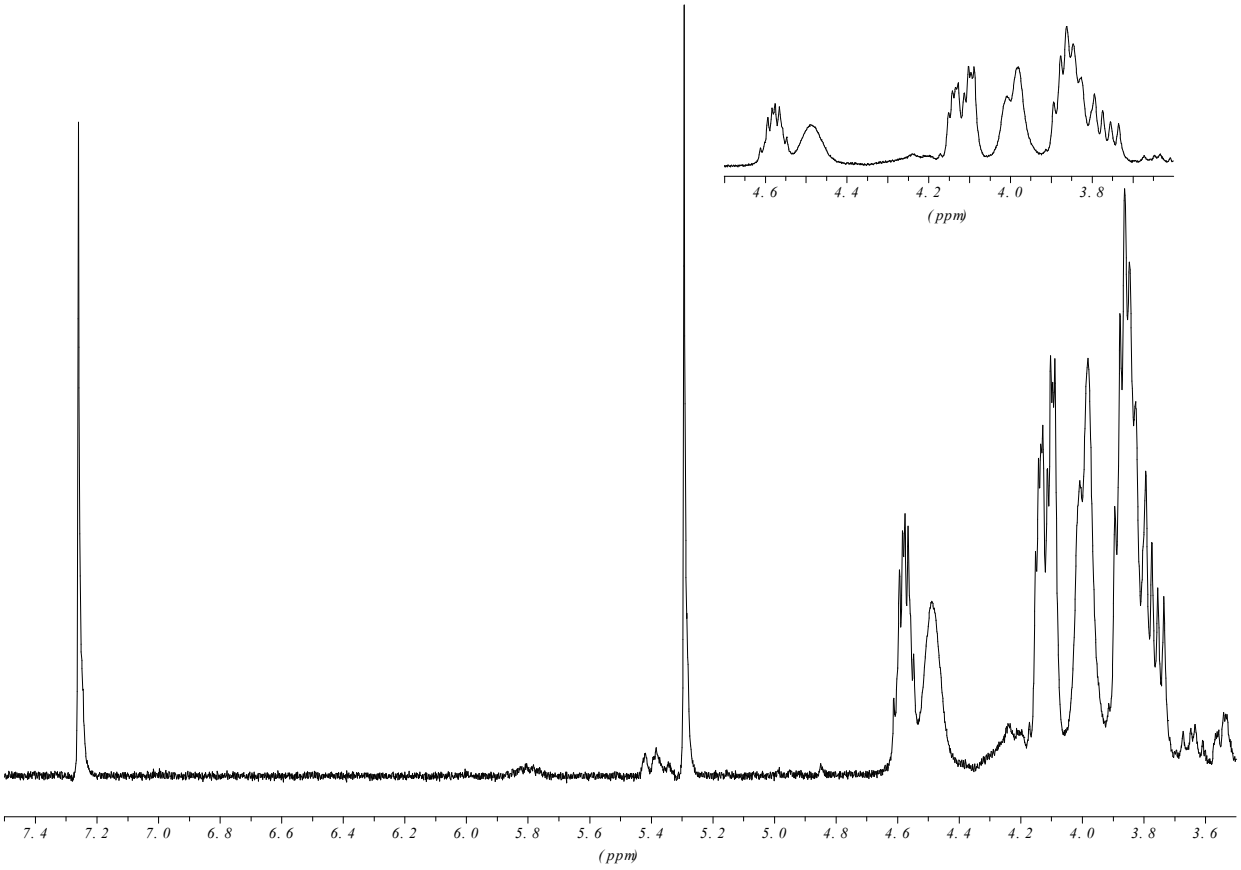


**Figure 17. $^{13}C$ NMR spectrum of compound 9 (400 MHz, $CDCl_3$).**

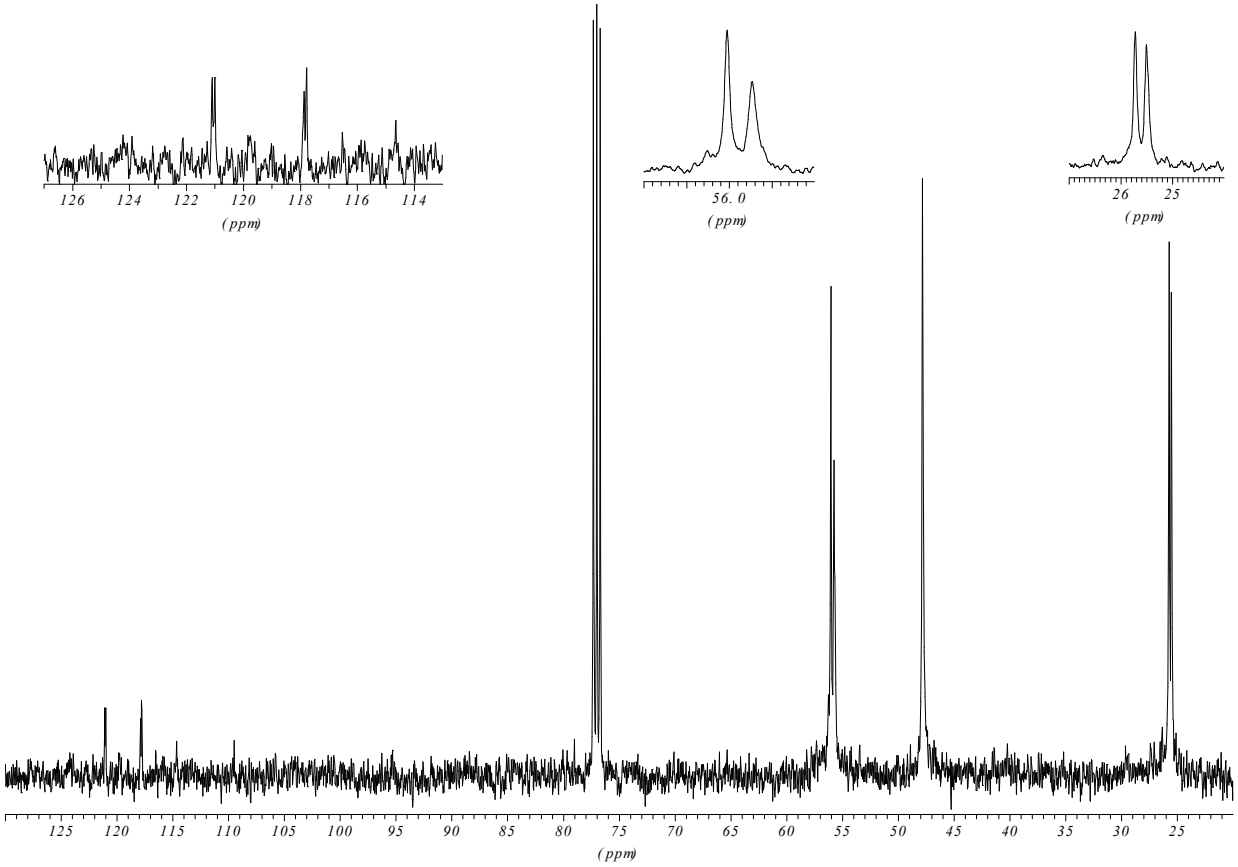


**Figure 18. $^{13}C$ NMR (*J-modulation*) spectrum of compound 9 (400 MHz, $CDCl_3$).**

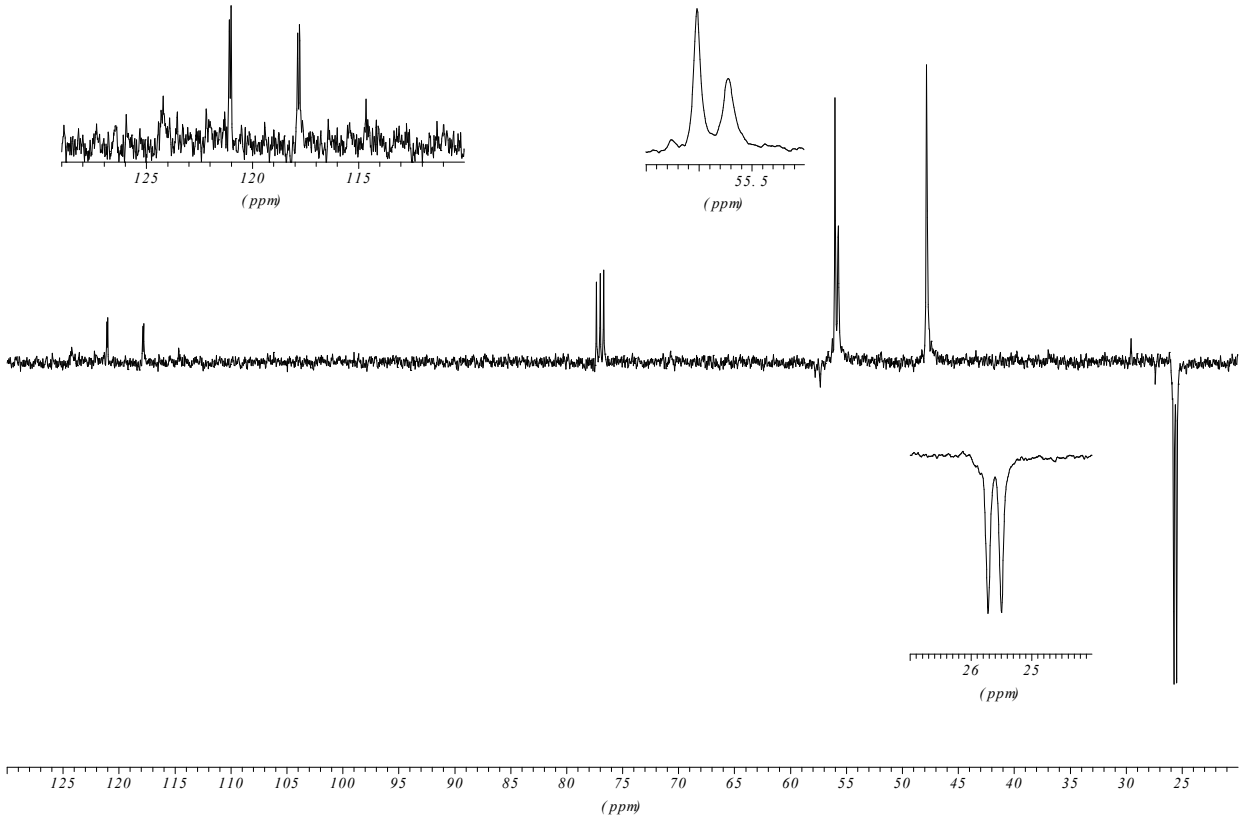


**Figure 19. $^{19}F$ NMR spectrum of compound 9 (400 MHz, $CDCl_3$).**

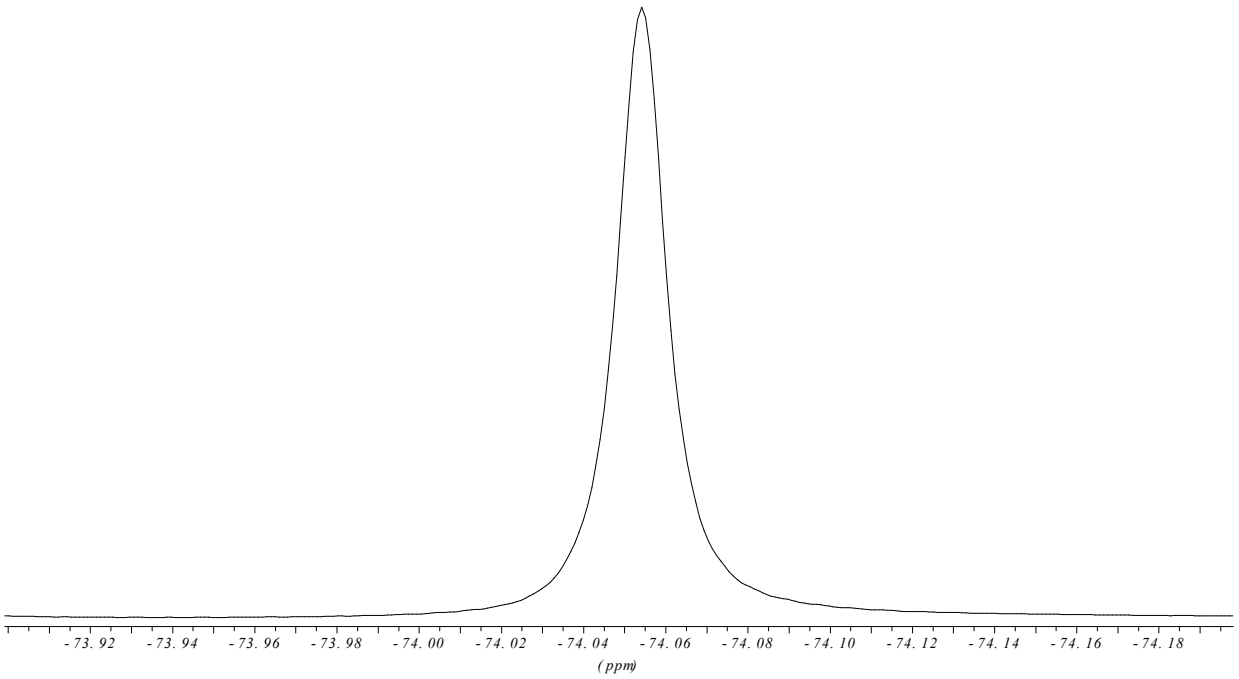


**Figure 20. FT-IR spectrum of compound 9 (film)**

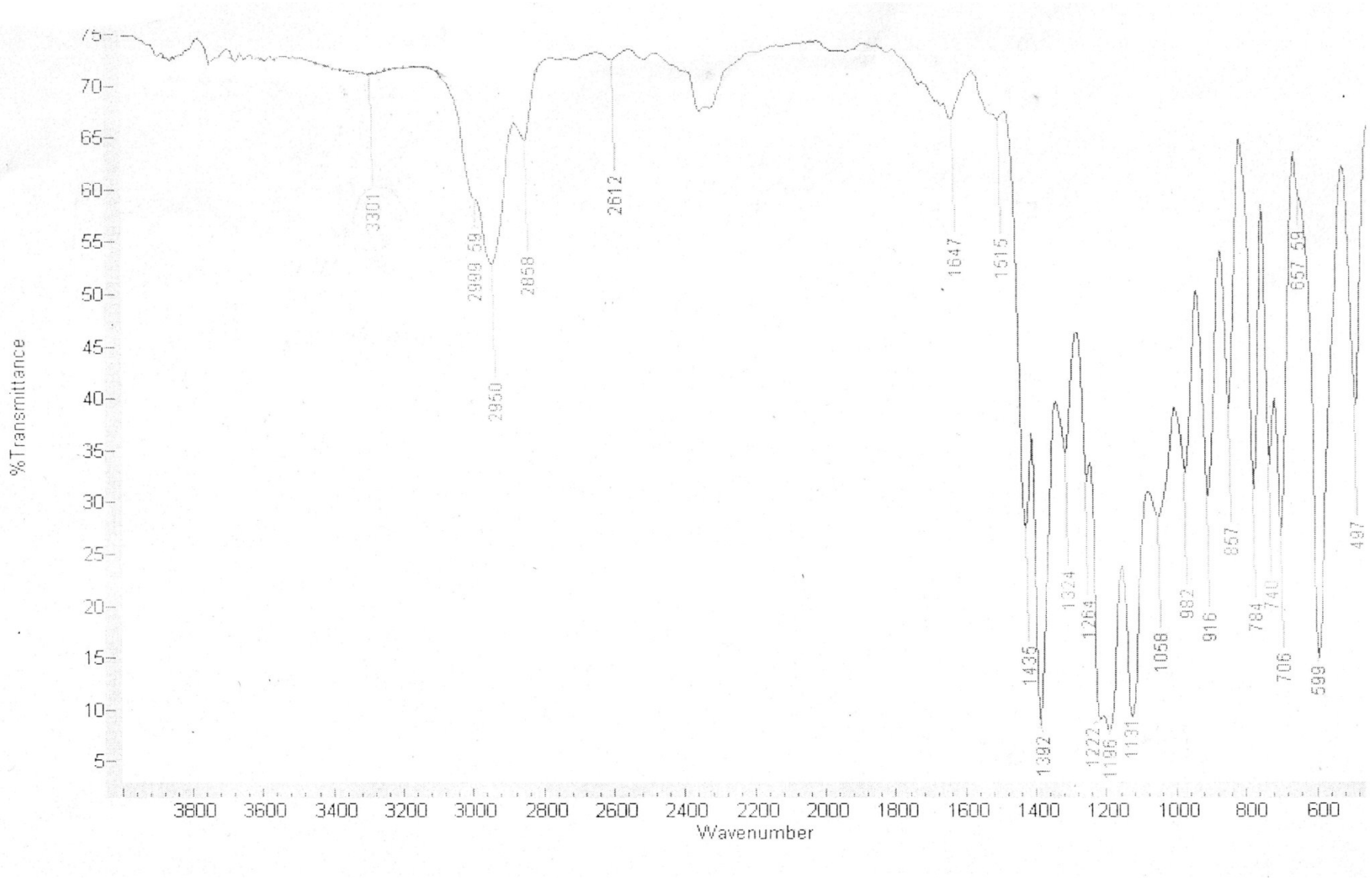


**Figure 21. $^{1}$H NMR spectrum of compound 10 (400 MHz, $CD_3CN$).**

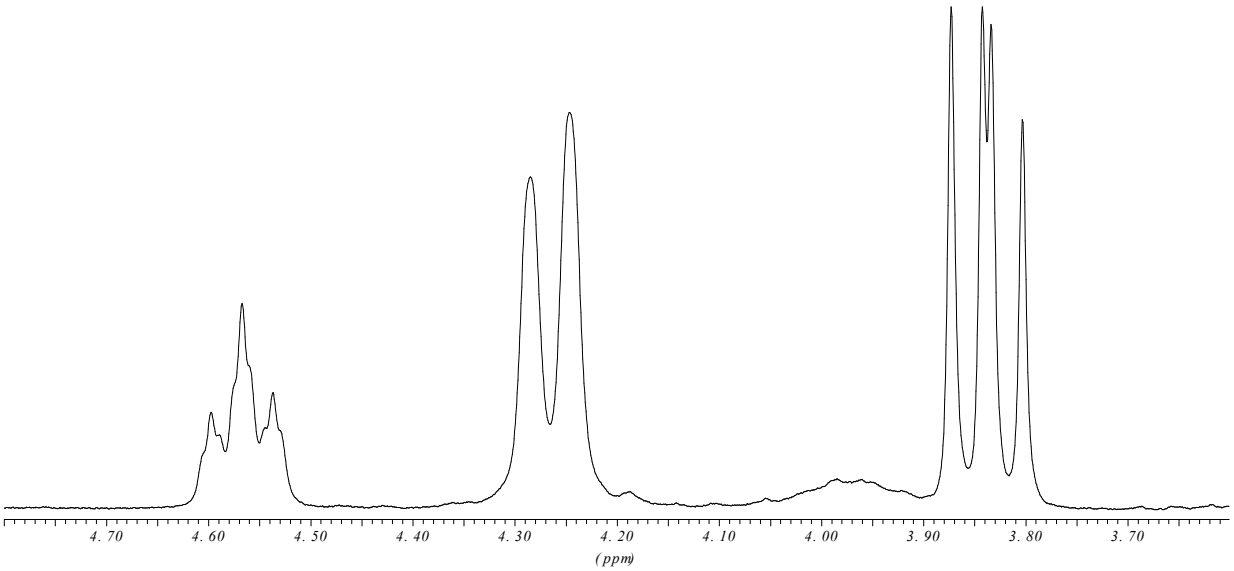


**Figure 22. $^{13}C$ NMR spectrum of compound 10 (400 MHz, $CD_3CN$).**

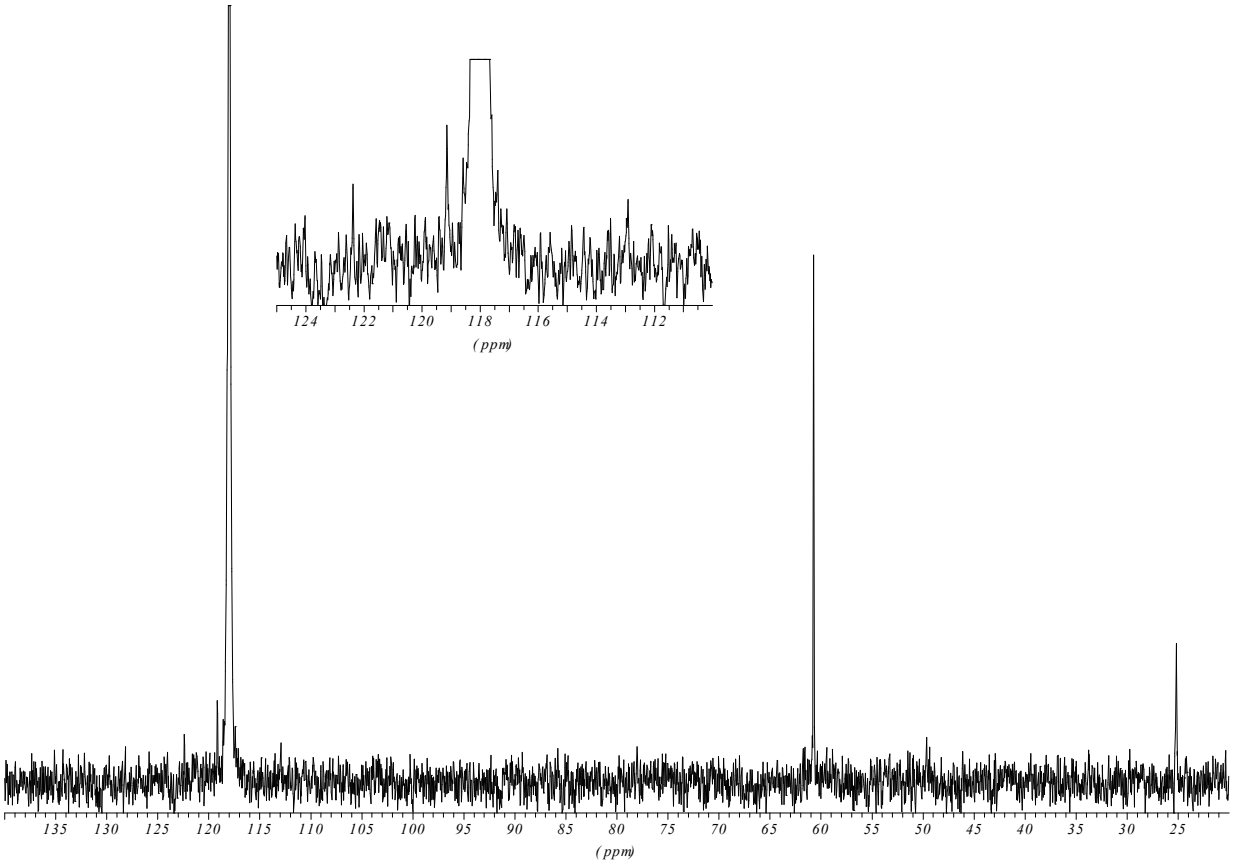


**Figure 23. $^{19}F$ NMR spectrum of compound 10 (400 MHz, $CD_3CN$).**

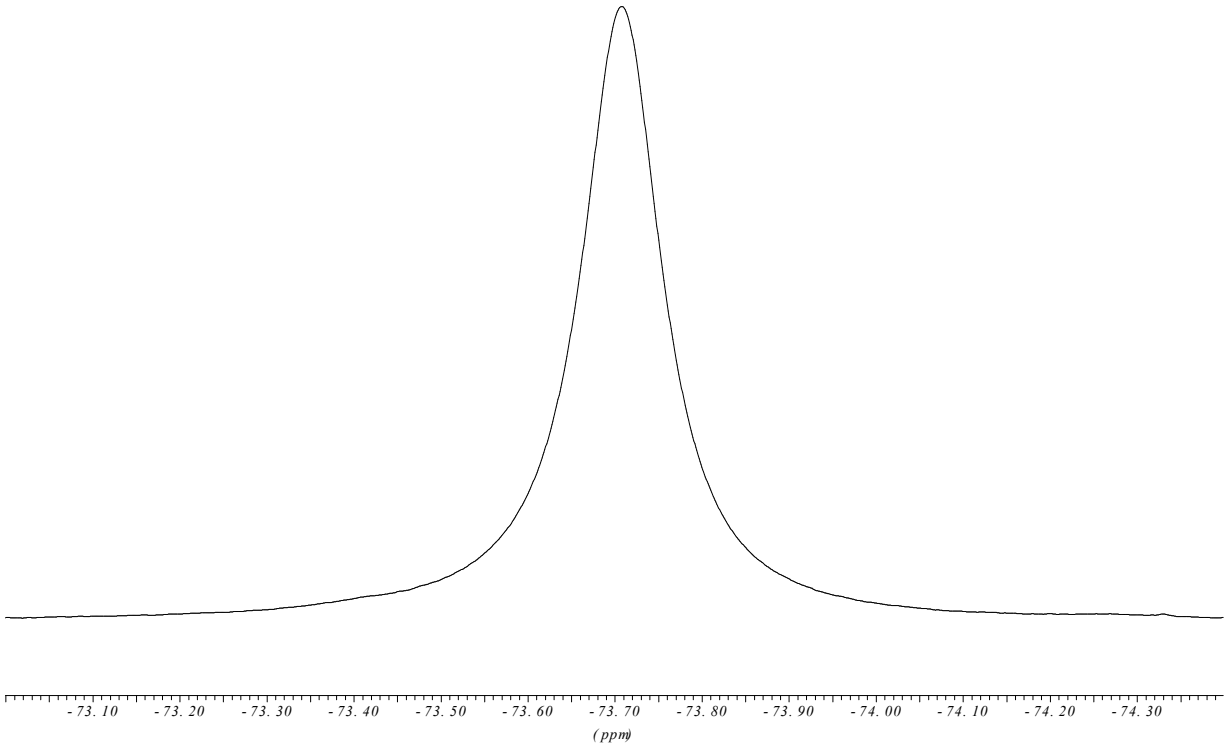


**Figure 24. FT-IR spectrum of compound 10 (KBr)**

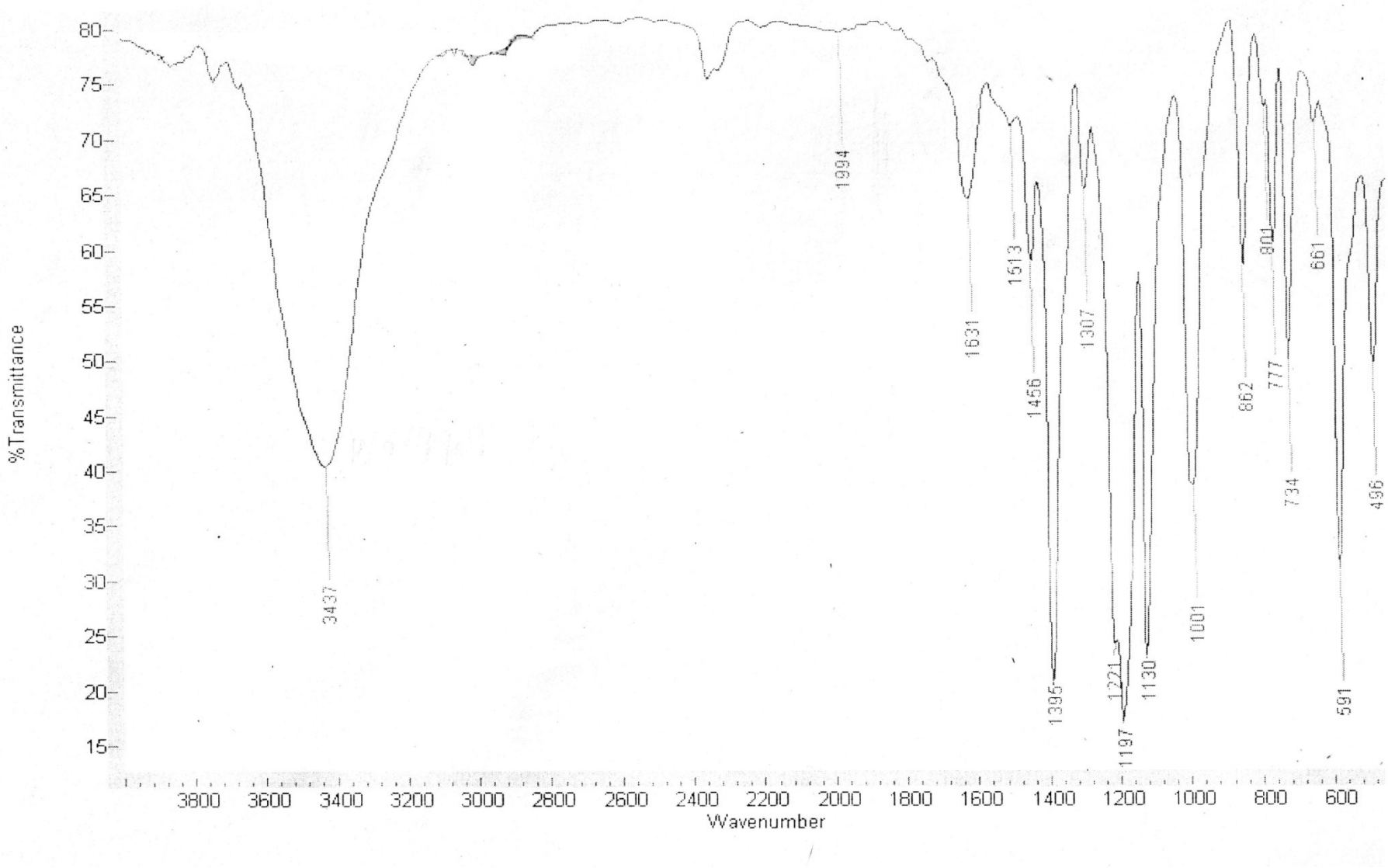


**Figure 25. $^{1}$H NMR spectrum of compound 11 (400 MHz, $CD_3CN$).**

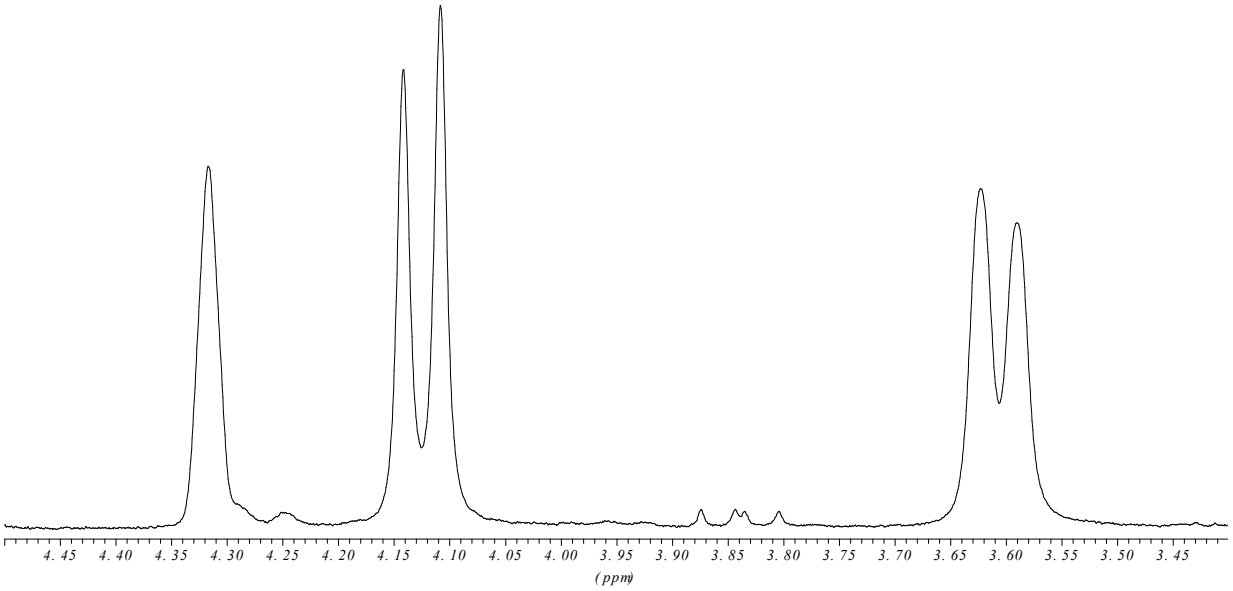


**Figure 26. $^{13}C$ NMR spectrum of compound 11 (400 MHz, $CD_3CN$).**

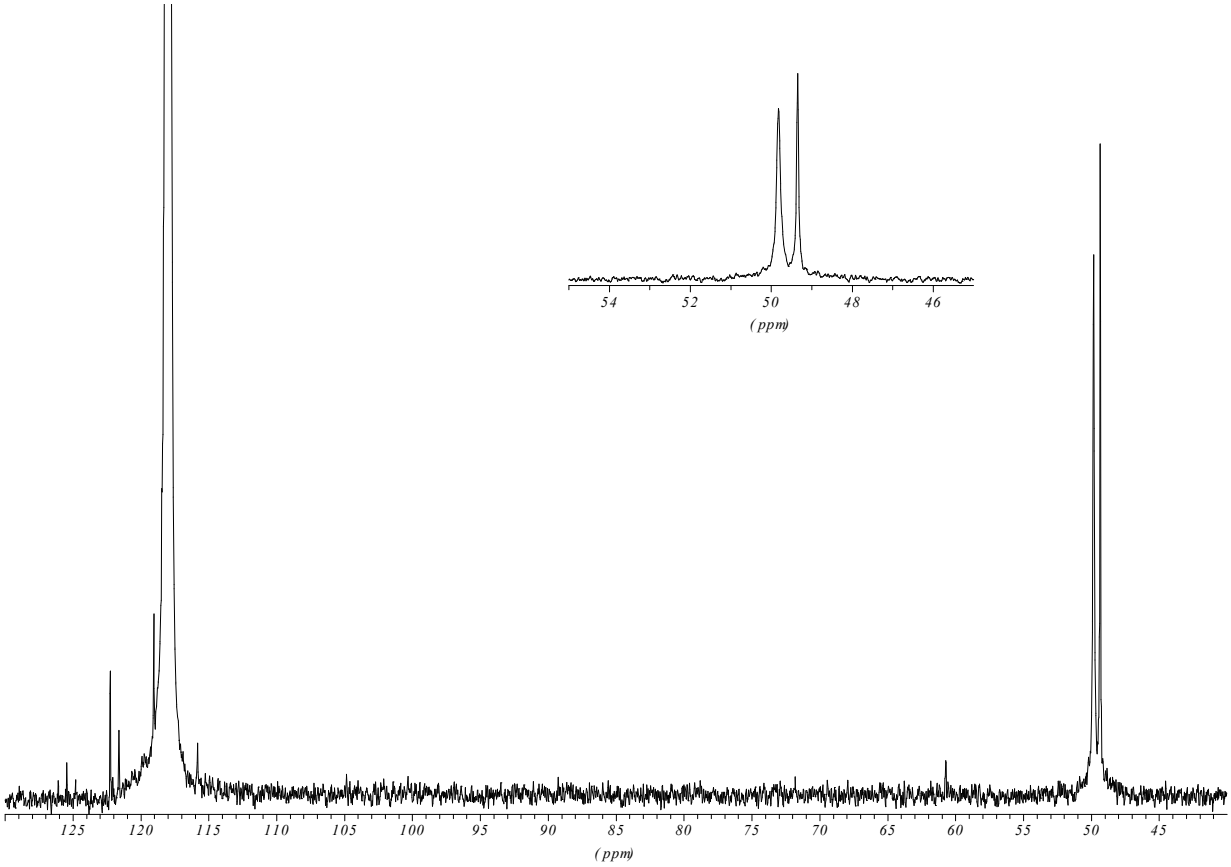


**Figure 27. $^{19}F$ NMR spectrum of compound 11 (400 MHz, $CD_3CN$).**

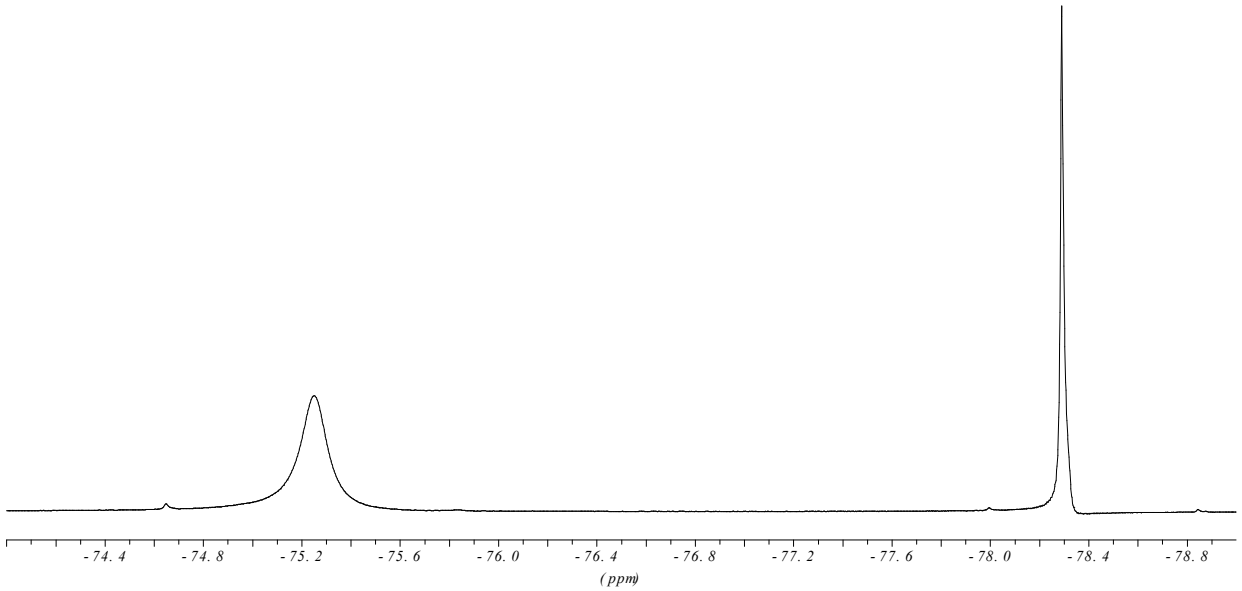


**Figure 28. FT-IR spectrum of compound 11 (KBr)**