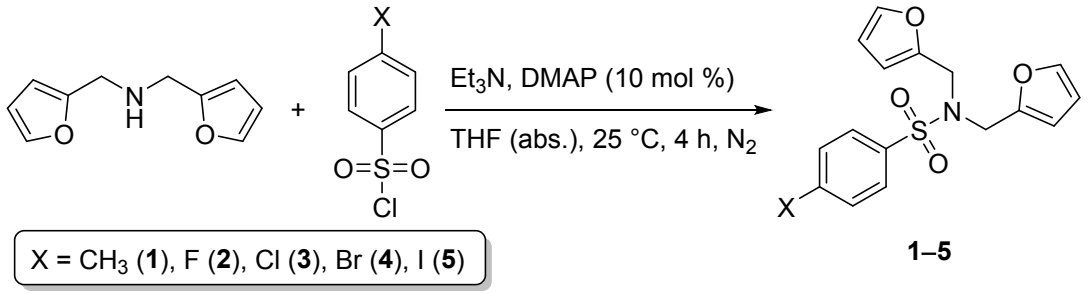
Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2020

Experimental part for the paper

"Synthesis, X-ray characterization and theoretical study of 3a,6:7,9a-diepoxybenzo[*de*]isoquinoline derivatives: on the importance of F···O interactions"

General Procedure for synthesis of *bis*-(*N*,*N*)-furfurylsulfonylamides (1−5).



Bis-(*N,N)*-furfurylamine (1.00 g, 0.910 mL, 5.6 mmol) and triethylamine (0.567 g, 0.781 mL, 5.6 mmol) were dissolved in abs. THF (25 mL) and catalytic amount of DMAP (10 mol %, 0.068 g, 0.56 mmol) was added. Then, a solution of the corresponding sulfochloride (5.6 mmol) in THF (30 mL) was added dropwise under continuous stirring. The reaction mixture was stirred at r.t. for 4 h under the atmosphere of dry nitrogen, then poured into excess of 5% aqueous solution of HCl (*ca*. 200 mL) and vigorously stirred until the precipitate was formed. The precipitate was filtered off, washed with water, dried under vacuum and recrystallized from hexane or ethanol to give the desired products (**1**−**5**) in 81−99% yields.

4-Methyl-N,N-bis(furan-2-ylmethyl)benzenesulfonamide **(1)**

Yield 85 % (1.58 g), m.p. 73-75 °C, white crystalline powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (2H, m, 2H-2,6-Ph), 7.31 – 7.24 (2H, m, 2H-5-Furyl), 7.25 – 7.21 (2H, m, 2H-3,5-Ph), 6.26 (2H, dd, *J* ~ 3.2, 1.9 Hz, 2H-4-Furyl), 6.17 (2H, d, *J* ~ 3.2 Hz, 2H-3-Furyl), 4.36 (4H, s, CH_2-N-CH_2), 2.40 (3H, s, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.56 (C-2,2'-Furyl), 143.21 (C-4-Ph), 142.68 (C-5,5'-Furyl), 137.22 (C-1-Ph), 129.50 (C-3,5-Ph), 127.42 (C-2,6-Ph), 110.43 (C-4,4'-Furyl), 109.70 (C-3,3'-Furyl), 43.05 (CH_2-N-CH_2), 21.58 (CH_3).

4-Fluoro-N,N-bis(furan-2-ylmethyl)benzenesulfonamide **(2)**

Yield 81% (1.52 g), m.p. 73−74 °C, white needles.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (2H, ddd, *J* ~ 9.8, 5.1, 2.5 Hz, 2H-2,6-Ph), 7.27 (2H, dd, *J* ~ 1.8, 0.8 Hz, 2H-5-Furyl),), 7.13 – 7.08 (2H, m, 2H-3,5-Ph), 6.27 (2H, dd, *J* ~ 3.2, 1.9 Hz, 2H-4-Furyl), 6.20 (2H, d, *J* ~ 3.3 Hz, 2H-3-Furyl), 4.38 (4H, s, CH_2-N-CH_2).
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.98 (d, J~ 254.3 Hz C-4-Ph), 149.30 (C-2,2'-Furyl), 142.86 (C-5,5'-Furyl), 136.42 (C-1-Ph), 130.08 (C-2,6-Ph), 116.03 (C-3,5-Ph), 110.50 (C-4,4'-Furyl), 109.93 (C-3,3'-Furyl), 43.11 (CH_2-N-CH_2).
^{19}F NMR ($CDCl_3$, 565 MHz) δ -105.75 (m, C-4-Ph).
IR ν_{max}/cm^{-1} (KBr): 3155 (ν(=CH)), 3108 (ν(=CH)), 2925 (ν(C-H)alkyl), 1591 (ν(C=C)), 1491 (ν(C=C)), 1332 (ν(SO_2)), 1152 (ν(SO_2)).

4-Chloro-N,N-bis(furan-2-ylmethyl)benzenesulfonamide **(3)**

Yield 88% (1.73 g), m.p. 74−75 °C, white needles.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.66 (2H, m, 2H-2,6-Ph), 7.42 – 7.38 (2H, m, 2H-3,5-Ph), 7.28 – 7.28 (2H, m, 2H-5-Furyl), 6.28 (2H, dd, *J* ~ 3.3, 1.9 Hz, 2H-4-Furyl), 6.21 (2H, d, *J* ~ 3.2 Hz, 2H-3-Furyl), 4.38 (4H, s, CH_2-N-CH_2).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.23 (C-2,2'-Furyl), 142.89 (C-5,5'-Furyl), 138.87 (C-4-Ph), 138.82 (C-1-Ph), 129.12 (C-3,5-Ph), 128.84 (C-2,6-Ph), 110.51 (C-4,4'-Furyl), 110.00 (C-3,3'-Furyl), 43.13 (CH_2-N-CH_2).

IR ν_{max}/cm^{-1} (KBr): 3152 (v(=CH)), 3115 (v(=CH)), 2945 (v(C-H)alkyl), 1585 (v(C=C)), 1503(v(C=C)), 1477 (v(C=C)), 1342 (v(SO_2)), 1159 (v(SO_2)).

4-Bromo-N,N-bis(furan-2-ylmethyl)benzenesulfonamide **(4)**

Yield 99% (2.20 g), m.p. 83−84 °C, coral needles.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.59 (2H, m, 2H-2,6-Ph), 7.58 – 7.55 (2H, m, 2H-3,5-Ph), 7.28 (2H, dd, *J* ~ 1.9, 0.9 Hz, 2H-5-Furyl), 6.28 (2H, dd, *J* ~ 3.2, 1.9 Hz, 2H-4-Furyl), 6.23 – 6.20 (2H, m, 2H-3-Furyl), 4.38 (4H, s, CH_2-N-CH_2).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.21 (C-2,2'-Furyl), 142.91 (C-5,5'-Furyl), 139.35 (C-1-Ph), 132.11 (C-3,5-Ph), 128.93 (C-2,6-Ph), 127.35 (C-4-Ph), 110.52 (C-4,4'-Furyl), 110.02 (C-3,3'-Furyl), 43.13 (CH_2-N-CH_2).

IR ν_{max}/cm^{-1} (KBr): 3152 (v(=CH)), 3115 (v(=CH)), 2944 (v(C-H)alkyl), 1574 (v (C=C)), 1503 (v(C=C)), 1472 (v(C=C)), 1342 (v(SO_2)), 1159 (v(SO_2)).

4-Iodo-N,N-bis(furan-2-ylmethyl)-benzenesulfonamide **(5)**

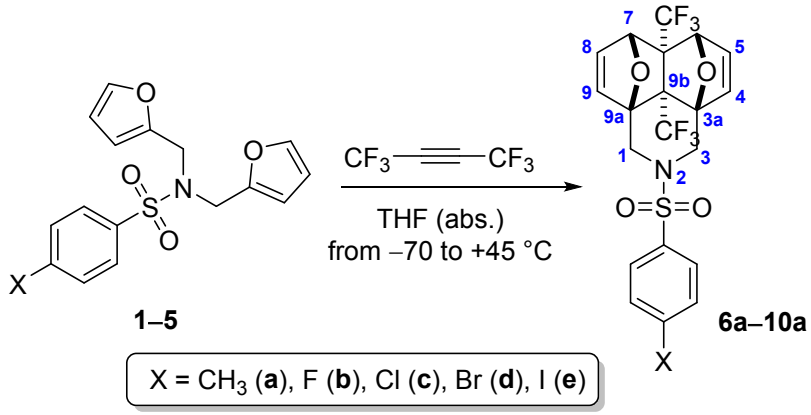
Yield 89% (2.21 g), m.p. 113−114 °C, coral needles.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.74 (2H, m, 2H-2,6-Ph), 7.49 – 7.41 (2H, m, 2H-3,5-Ph), 7.28 (2H, dd, *J* ~ 1.9, 0.9 Hz, 2H-5-Furyl), 6.28 (2H, dd, *J* ~ 3.2, 1.8 Hz, 2H-4-Furyl), 6.21 (2H, d, *J* ~ 3.2 Hz, 2H-3-Furyl), 4.38 (4H, s, CH_2-N-CH_2).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.21 (C-2,2'-Furyl), 142.91 (C-5,5'-Furyl), 140.00 (C-1-Ph), 138.09 (C-3,5-Ph), 128.80 (C-2,6-Ph), 99.73 (C-4-Ph), 110.52 (C-4,4'-Furyl), 110.01 (C-3,3'-Furyl), 43.13 (CH_2-N-CH_2).

IR ν_{max}/cm^{-1} (KBr): 3148 (ν(=CH)), 3119 (ν(=CH)), 3083 (ν(=CH)), 2944 (ν(C-H)alkyl), 1568 (ν(C=C)), 1502 (ν(C=C)), 1472 (ν(C=C)), 1344 (ν(SO_2)), 1161 (ν(SO_2)).

General procedure for synthesis of "pincer"-adducts (6a−10a).



To the solution of corresponding *bis*-furfurylsulfonylamide **1−5** (2 mmol) in abs. THF (15 mL) a slow flow of hexafluorobutyne-2 was bubbled at −70 °C until hexafluoro-2-butyne (2.2 mmol, 0.356 g) was condensed in a reaction vessel (controlled by the weighting of a reaction flask). The flask was sealed and left for 28 d at r.t. with regular shaking. After that, the homogeneous reaction mass was heated at 45 °C for 24 h, cooled down to −70 °C and unsealed. The reaction mixture was transferred in a round bottom flask, the solvent was removed in *vacuo* without overheating of the reaction mixture over 45 °C. The composition of the resulting solids was determined by ^{1}H NMR spectroscopy. It was found out, that the crude reaction mixture contains both "pincer" (**6a−10a**) and "domino" (**6b−10b**) adducts with a slight admixture of the starting sulfonylamides (**1−5**). The title compounds **6a−10a** were isolated by recrystallization from a mixture of CH_2Cl_2/Et_2O or CH_2Cl_2/hexane. Further purification of **6a−10a** by column chromatography on silica gel (using as an eluent a mixture of EtOAc:hexane = 1:4) was performed when necessary. The target "pincer"-adducts **6a−10a** were obtained as white crystal plates.

(3aRS,6SR,7RS,9aSR)-2-[(4-Methylphenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(6a)**

Yield 75 % (0.74 g), m.p. > 220 °C with decomp., white crystals.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.68 (2H, m, 2H-2,6-Ph), 7.35 – 7.29 (2H, m, 2H-3,5-Ph), 6.73 – 6.68 (2H, m, 2H-4,9), 6.49 (2H, dq, J ~ 7.1, 3.6, 2H-5,8), 5.12 (2H, s, H-6 and H-7), 4.34 – 4.29 (2H, m, 2H-1), 3.35 (2H, d, J ~ 13.1 Hz, 2H-3), 2.43 (3H, s, CH_3).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.92 (C-4-Ph), 140.43 (C-4 and C-9), 138.57 (C-5 and C-8), 134.67 (C-1-Ph), 129.85 (C-3,5-Ph), 127.68 (C-2,6-Ph), 125.56 (q, $^{1}J_{C,F}$ ~ 280.3 Hz, CF_3 and CF_3), 87.63 (C-3a and C-9a), 82.88 (d,$^{3}J_{C,F}$ ~ 2.9 Hz, C-6 and C-7), 70.00 (q, $^{2}J_{C,F}$ ~ 26.0 Hz, C-9b) 64.22 (q, $^{2}J_{C,F}$ ~ 26.0 Hz, C-6a), 44.12 (C-1 and C-3), 21.68 (CH_3).

^{19}F NMR (565 MHz, $CDCl_3$) δ −54.50 (s, CF_3), −58.76 (s, CF_3).

IR ν_{max}/cm^{-1} (KBr): 3111 (v (=CH)), 3032 (v(=CH)), 2929 (v(C-H)alkyl), 1599 (v(C=C)), 1346(v(SO_2)), 1183 (v(SO_2)), 1147 (v(C-F)), 750 (v(C-F)).

MS(ESI): m/z = 494.1 $[M+H]^+$.

(3aRS,6SR,7RS,9aSR)-2-[(4-Fluorophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(7a)**

Yield 70 % (0.70 g), m.p. 177−178 °C, white crystals.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.85 (2H, m, 2H-2,6-Ph),), 7.18 – 7.14 (2H, m, 2H-3,5-Ph), 6.73 – 6.68 (2H, m, 2H-4,9), 6.49 (2H, dq, J ~ 7.4, 3.6 Hz, 2H-5,8), 5.05 (2H, s, 2H-6,7), 4.34 – 4.30 (2H, m, H-1A and H-3A), 3.54 – 3.50 (2H, m, H-1B and H-3B).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.33 (d, $^{1}J_{C,F}$ ~ 254.6 Hz, C-4-Ph), 140.49 (C-4 and C-9), 138.51 (C-5 and C-8), 134.48 (C-1), 130.62 (d, $^{3}J_{C,F}$ ~ 10.1 Hz, C-2,6-Ph), 124.59 and 124.55 (q and q, $^{1}J_{C,F}$ ~ 280.3 Hz, CF_3 and CF_3), 116.18 (d, $^{2}J_{C,F}$ ~ 21.7 Hz, C-3,5-Ph), 87.58 (C-3a and C-9b), 82.81 (br. s, C-6 and C-7), 69.79 (br. q, $^{2}J_{C,F}$ ~ 23.1 Hz, C-9b), 64.27 (br. q, $^{2}J_{C,F}$ ~ 23.1 Hz, C-6a) 44.03 (C-1 and C-3).

^{19}F NMR (282 MHz, $CDCl_3$) δ −54.60 (s, CF_3), −58.79 (s, CF_3), −105.01 (s, F-4-C_6H_4).

IR ν_{max}/cm^{-1} (KBr): 3108 (ν(=CH)), 3072 (ν(=CH)), 2930 (ν(C-H)alkyl), 1591 (ν(C=C)), 1332 (ν(SO_2)), 1178 (ν(SO_2)), 1147 (ν(C-F)), 753(C-F).

(3aRS,6SR,7RS,9aSR)-2-[(4-Chlorophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(8a)**

Yield 77 % (0.79 g), m.p. > 220 °C with decomp., white crystals.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.74 (2H, m, 2H-2,6-Ph), 7.48 – 7.44 (2H, m, 2H-3,5-Ph), 6.72 – 6.68 (2H, m, 2H-4,9), 6.50 (2H, dq, *J* ~ 7.4, 3.7 Hz, 2H-5,8), 5.05 (2H, s, 2H-6,7), 4.42 – 4.22 (2H, m, H-1A and H-3A), 3.53 (2H, d, *J* ~ 13.6 Hz, H-1B and H-3B).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.52 (C-4 and C-9), 139.41 (C-4-Ph), 138.49 (C-5 and C-8), 137.04 (C-1-Ph), 129.33 (C-2,6-Ph), 129.25 (C-3,5-Ph), 124.59 and 124.55 (q and q, $^{1}J_{C,F}$ ~ 280.3, CF_3 and CF_3), 87.57 (C-3a and C-9a), 82.85 (q, $^{3}J_{C,F}$ ~ 2.1 Hz, C-6 and C-7), 69.85 (br. q, $^{2}J_{C,F}$ ~ 23.1 Hz, C-9b), 64.20 (br. q, $^{2}J_{C,F}$ ~ 23.1 Hz, C-6a), 44.05 (C-1 and C-3).

^{19}F NMR (282 MHz, $CDCl_3$) δ −54.58 (s, CF_3), −58.76 (s, CF_3).

IR ν_{max}/cm^{-1} (KBr): 3096 (ν(=CH)), 3023 (ν(=CH)), 2924 (ν(C-H)alkyl), 1589 (ν(C=C)), 1350(ν(SO_2)), 1179 (ν(SO_2)), 1148 (ν(C-F)), 750 (C-F).

MS (ESI): m/z = 514.1 [M+H, $^{35}Cl]^+$, 516.1 [M+H, $^{37}Cl]^+$.

(3aRS,6SR,7RS,9aSR)-2-[(4-Bromophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(9a)**

Yield 90 % (1.00 g), m.p. > 220 °C with decomp., white crystals.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.70 (2H, m, 2H-2,6-Ph), 7.64 – 7.61 (2H, m, 2H-3,5-Ph), 6.70 (2H, s, 2H-4,9), 6.49 (2H, dq, *J* ~ 7.4, 3.6 Hz, 2H-5,8), 5.05 (2H, s, 2H-6,7), 4.34 – 4.30 (2H, m, H-1A and H-3A), 3.55 – 3.51 (2H, m, H-1B and H-3B).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.53 (C-4 and C-9), 138.50 (C-5 and C-8), 132.22 (C-2,6-Ph), 129.44 (C-3,5-Ph), 124.59 and 124.55 (q and q, $^1J_{C,F}$ ~ 280.3 Hz, CF_3), 87.59 (C-3a and C-9a), 82.87 (q, $^3J_{C,F}$ ~ 1.9 Hz, C-6 and C-7), 69.83 (br. q, $^2J_{C,F}$ ~ 23.1 Hz, C-9b), 64.40 (br. q, $^2J_{C,F}$ ~ 23.1 Hz, C-6a), 44.06 (C-1 and C-3).

^{19}F NMR (282 MHz, $CDCl_3$) δ −54.57 (s, CF_3), −58.76 (s, CF_3).

IR ν_{max}/cm^{-1} (KBr): 3095 (ν(=CH)), 3021 (ν(=CH)), 2922 (ν(C-H)alkyl), 1577 (ν(C=C)), 1350(ν(SO_2)), 1181 (ν(SO_2)), 1147 (ν(C-F)), 740 (C-F).

MS (ESI): m/z = 557.9 [M+H, $^{79}Br]^+$, 560.0 [M+H, $^{81}Br]^+$.

(3aRS,6SR,7RS,9aSR)-2-[(4-Iodophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(10a)**

Yield 74 % (0.90 g), m.p. > 220 °C with decomp., white crystals.

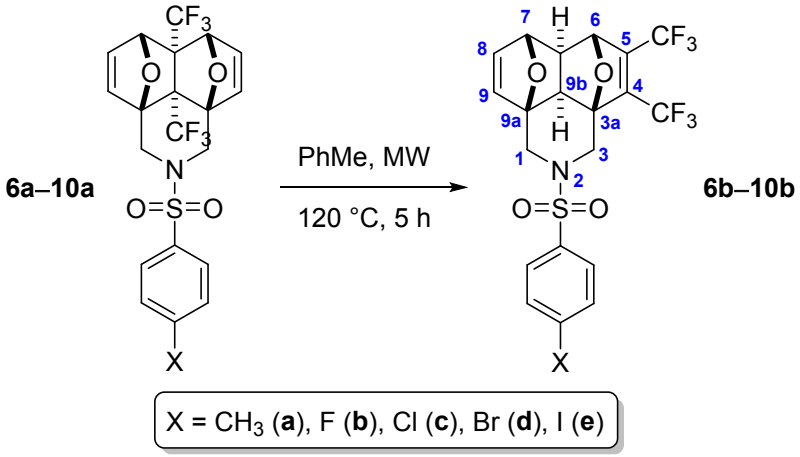
^{1}H NMR (600 MHz, DMSO-d_6) δ 8.08 – 7.99 (2H, m, 2H-3,5-Ph), 7.63 – 7.55 (2H, m, 2H-2,6-Ph) 6.79 (2H, s, 2H-4,9), 6.68 (2H, dq, *J* ~ 6.8, 3.3 Hz, 2H-5,8), 5.33 (2H, s, 2H-7,8), 4.11 (2H, d, *J* ~ 14.0 Hz, H-1A and H-3A), 3.31 (2H, d, *J* ~ 14.1 Hz, H-1B and H-3B).

^{13}C NMR (151 MHz, DMSO-d_6) δ 140.21 (C-4 and C-9), 138.88 (C-5 and C-8), 138.33 (C-3,5-Ph), 136.34 (C-1-Ph), 128.83 (C-2,6-Ph), 125.14 and 124.96 (q and q, $^1J_{C,F}$ ~ 281.8 Hz, CF_3 and CF_3), 101.75 (C-4-Ph), 87.05 (C-3a and C-9a), 81.87 (m, C-6 and C-7), 69.02 (q, $^2J_{C,F}$ ~ 26.0 Hz, C-6a), 63.41 (q, $^2J_{C,F}$ ~ 23.1 Hz, C-9b), 43.89 (C-1 and C-3).

^{19}F NMR (282 MHz, $CDCl_3$) δ −53.80 (s, CF_3), −57.78 (s, CF_3).

MS (ESI): m/z = 605.9 $[M+H]^+$.

General procedure for synthesis of “domino”-adducts 6b−10b



A solution of corresponding “pincer”-adduct **6a−10a** (0.6 mmol) in toluene (4 mL) was heated to 120 °C under MW irradiation for 5 h. During the cooling of reaction mixture to r.t white crystal needles were formed. The precipitate was filtered off, dried under vacuum to give crystals of the “domino” adducts **6b−10b**. Then filtrate was evaporated under reduced pressure. The residue was recrystallized from CH_2Cl_2/hexane or CH_2Cl_2/Et_2O and combined with previously obtained crystalline precipitate to afford adducts **6b−10b** in good yield (see Table 1).

(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Methylphenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(6b)**

Yield 72% (0.21 g), m.p. > 220 °C with decomp., white crystalline powder.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.70 (2H, m, 2H-2,6-Ph), 7.34 (2H, d, *J* ~ 7.9 Hz, 2H-3,5-Ph), 6.55 (1H, dd, *J* ~ 5.7, 1.8 Hz, H-8), 6.33 (1H, d, *J* ~ 5.7 Hz, H-9), 5.19 (1H, d, *J* ~ 1.3 Hz, H-6), 5.03 (1H, d, *J* ~ 1.7 Hz, H-7), 4.47 (1H, d, *J* ~ 13.7 Hz, H-1A),

4.44 – 4.41 (m, H-3A), 3.20 and 3.14 (2H, d, J ~ 13.6 Hz, H-1B and H-3B), 2.44 (3H, s, CH_3), 2.29 and 1.92 (2H, d, J ~ 6.1 Hz, H-9b and H-6a).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.34 (qq, $^2J_{C,F}$ ~ 38.3 Hz, $^3J_{C,F}$ ~ 4.3 Hz, C-4), 142.11 (qq, $^2J_{C,F}$ ~ 38.3 Hz, $^3J_{C,F}$ ~ 4.3 Hz, C-5), 144.00 (C-4-Ph), 139.83 (C-8), 138.11 (C-9), 134.62 (C-1-Ph), 129.92 (C-3,5-Ph), 127.77 (C-2,6-Ph), 120.32 (q, $^1J_{C,F}$ ~ 271.6, CF_3), 120.50 (q, $^1J_{C,F}$ ~ 270.2, CF_3), 85.92 (br.s, C-3a), 83.26 (C-6), 81.44 (q, $^5J_{C,F}$ ~ 2.2 Hz, C-9a), 80.70 (C-7), 50.88 (br. s, C-6a), 48.92 (C-1), 45.77 (C-3), 44.12 (m, C-9b), 21.70 (CH_3).

^{19}F NMR (565 MHz, $CDCl_3$) δ -58.83 (q, $^5J_{F,F}$ ~ 8.8 Hz, CF_3), -60.07 (q, $^5J_{F,F}$ ~ 8.8 Hz, CF_3).

IR ν_{max}/cm^{-1} (KBr): 3097 (ν(=CH)), 2998 (ν(=CH)), 2934 (ν(C-H)alkyl), 1600 (ν(C=C)), 1348 (ν(SO_2)), 1172 (ν(SO_2)), 1135 (ν(C-F)), 758 (C-F).

MS(ESI): m/z = 494.1 $[M+H]^+$.

(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Fluorophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(7b)**

Yield 70 % (0.21 g), m.p. > 220 °C with decomp., white needles.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.91 (2H, dd, J ~ 9.0, 4.9 Hz, 2H-2,6-Ph), 7.50 (2H, t, J ~ 8.6 Hz, 2H-3,5-Ph), 6.55 (1H, d, J ~ 5.6 Hz, H-8), 6.37 (1H, d, J ~ 5.5 Hz, H-9), 5.45 (1H, s, H-6), 4.97 (1H, s, H-7), 4.23 and 4.08 (1H, d, J ~ 13.3 Hz, H-1A and H-3A), 3.41 (1H, d, J ~ 13.2 Hz, H-1B), 3.28 (1H, s, H-3B), 2.28 – 2.20 (1H, m, H-6a), 2.04 (1H, d, J ~ 6.1 Hz, H-9b).

^{13}C NMR (151 MHz, DMSO-d_6) δ 164.65 (d, J ~ 251.4 Hz, C-4-Ph), 145.72 (qq, $^2J_{C,F}$ ~ 36.5 Hz, $^3J_{C,F}$ ~ 4.8 Hz, C-4), 142.51 (qq, $^2J_{C,F}$ ~ 36.5 Hz, $^3J_{C,F}$ ~ 4.8 Hz, C-5), 139.38 (C-8), 138.22 (C-9), 133.46 (d, J ~ 3.4 Hz, C-1-Ph), 130.38 (d, J ~ 9.4 Hz, C-3,5-Ph),

120.86(q, $^{1}J_{C,F}$ ~ 278.1 Hz, CF_3), 120.90 (q, $^{1}J_{C,F}$ ~ 278.1 Hz, CF_3), 116.59 (d, *J* ~ 22.7 Hz, C-2,6-Ph), 85.85 (C-9a), 82.99 (C-7), 80.63 (C-3a), 79.77 (C-6), 49.99 (C-6b), 47.61 (C-3), 45.09 (C-1), 43.38 (C9-b).

^{19}F NMR (565 MHz, DMSO-d_6) δ −58.11 (q, $^{5}J_{F,F}$ ~ 9.7 Hz, CF_3), −58.72 (q, $^{5}J_{F,F}$ ~ 9.5 Hz, CF_3), −105.94 (m, F-4-C_6H_4).

(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Chlorophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(8b)**

Yield 78 % (0.24 g), m.p. > 220 °C with decomp., white needles.

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.85 (2H, d, *J* ~ 8.4 Hz, 2H-2,6-Ph), 7.64 (2H, d, *J* ~ 8.5 Hz, 2H-3,5-Ph), 6.56 (1H, d, *J* ~ 5.5 Hz, H-8), 6.41 (1H , d, *J* ~ 5.5 Hz, H-9), 5.35 (1H, s, H-6), 4.97 (1H, s, H-7), 4.28 and 4.15 (2H, d, *J* ~ 13.7 Hz, H-1A and H-3A), 3.57 and 3.50 (2H, d, *J* ~ 13.6 Hz, H-1B and H-3B), 2.27 and 2.08 (2H, d, *J* ~ 6.1 Hz, H-9b and H-6a).

^{13}C NMR (151 MHz, DMSO-d_6) δ 144.89 (qq, $^{2}J_{C,F}$ ~ 36.1 Hz, $^{3}J_{C,F}$ ~ 4.3 Hz, C-4), 141.69 (qq, $^{2}J_{C,F}$ ~ 36.1 Hz, $^{3}J_{C,F}$ ~ 4.3 Hz, C-5), 139.04 (C-8), 137.84 (C-9), 137.69 (C-1-Ph), 136.34 (C-4-Ph), 129.04 (C-3,5-Ph), 128.84(C-2,6-Ph), 120.11 (q, $^{1}J_{C,F}$ ~ 274.7 Hz, CF_3), 120.05 (q, $^{1}J_{C,F}$ ~ 275.5 Hz, CF_3), 85.62(C-3a), 82.68 (C-6), 80.41(br.s, C-9a), 79.53 (C-7), 49.80 (br.s, C-6a), 47.44 (s, C-1), 44.77 (s, C-3), 43.07 (br.s, C-9b).

^{19}F NMR (565 MHz, DMSO-d_6) δ −58.36 (q, $^{5}J_{F,F}$ ~ 9.01 Hz, CF_3), −58.69 (q, $^{5}J_{F,F}$ ~ 9.1 Hz, CF_3).

IR ν_{max}/cm^{-1} (KBr): 3094 (ν(=CH)), 2996 (ν(=CH)), 2921 (ν(C-H)alkyl), 1586 (ν(C=C)), 1349 (ν(SO_2)), 1174 (ν(SO_2)), 1140 (ν(C-F)), 746 (C-F).

MS (ESI): m/z = 514.1 [M+H, ^{35}Cl]$^{+}$, 516.1 [M+H, ^{37}Cl]$^{+}$.

(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Bromophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(9b)**

Yield 88 % (0.29 g), m.p. > 220 °C with decomp., white needles.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.72 (2H, m, 2H-2,6-Ph), 7.66 – 7.62 (2H, m, 2H-3,5-Ph), 6.57 – 6.54 (1H, m, H-8), 6.35 – 6.33 (1H, m, H-9), 5.13 (1H, s, H-6), 4.96 (1H, s, H-7), 4.46 (2H, dd, *J* ~ 18.7, 14.2 Hz, H-1A and H-3A), 3.38 and 3.32 (2H, dd, *J* ~ 35.2, 14.0 Hz, H-1B and H-3B), 2.28 (1H, dd, *J* ~ 6.1, 1.5 Hz, H-6a), 1.96 (1H, d, *J* ~ 6.1 Hz, H-9b).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.73 (qq, $^{2}J_{C,F}$ ~ 36.1 Hz, $^{3}J_{C,F}$ ~ 4.3 Hz, C-4), 142.42 (qq, $^{2}J_{C,F}$ ~ 36.1 Hz, $^{3}J_{C,F}$ ~ 4.3 Hz, C-5), 139.93 (C-8), 138.72 (C-9), 136.88 (C-1-Ph), 133.03 (C-3,5-Ph), 129.80 (C-2,6-Ph), 127.70 (C-4-Ph), 120.94 (q, $^{1}J_{C,F}$ ~ 270.2 Hz, CF_3), 120.90 (q, $^{1}J_{C,F}$ ~ 273.1 Hz, CF_3), 86.37 (C-3a), 83.51 (C-6), 81.16 (br.s, C-9a), 80.30 (C-7), 50.52 (br.s, C-6a), 48.15 (s, C-1), 45.61 (s, C-3), 43.90 (br.s, C-9b).

^{19}F NMR (565 MHz, $CDCl_3$) δ −58.85 (q, $^{5}J_{F,F}$ ~ 8.8 Hz, CF_3), −60.04 (q, $^{5}J_{F,F}$ ~ 8.8 Hz, CF_3).

IR ν_{max}/cm^{-1} (KBr): 3094 (ν(=CH)), 2991 (ν(=CH)), 2928 (ν(C-H)alkyl), 1574 (ν(C=C)), 1348 (ν(SO_2)), 1174 (ν(SO_2)), 1139 (ν(C-F)), 763 (C-F).

MS (ESI): m/z = 557.9 [M+H, ^{79}Br]$^{+}$, 560.0 [M+H, ^{81}Br]$^{+}$.

(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Iodophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(10b)**

Yield 82 % (0.30 mg), m.p. > 220 °C with decomp., white needles.

^{1}H NMR (300 MH, DMSO-d_6) δ 8.03 (2H, d, J ~ 8.44 Hz, 2H-2,6-Ph), 7.59 (2H, d, J ~ 8.44 Hz, 2H-3,5-Ph) , 6.55 (1H, dd, *J* ~ 5.50, 1.83 Hz, H-8), 6.37 (1H, d, *J* ~ 5.50 Hz, H-9), 5.44 (s, H-7), 4.98 (d, *J* ~ 1.47 Hz, H-6), 4.22 and 4.07 (2H, d, *J* ~ 13.20 Hz, H-1A and H-3A), 3.46 and 3.42 (s, H-1B and H-3B), 2.25 (1H, d, *J* ~ 6.24 Hz, H-6a), 2.04 (1H, d, *J* ~ 6.24 Hz, H-9b).

^{13}C NMR (151 MHz, DMSO-d_6) δ 145.71(qq, $^{2}J_{C,F}$ ~ 36.1 Hz, $^{3}J_{C,F}$ ~ 4.8 Hz, C-4), 142.42 (qq, $^{2}J_{C,F}$ ~ 36.1 Hz, $^{3}J_{C,F}$ ~ 4.8 Hz, C-5), 139.85 (C-8), 138.81 (C-9), 138.68 (C-1-Ph), 137.13 (C-4-Ph), 129.37 (C-3,5-Ph), 120.89 (q, $^{1}J_{C,F}$ ~ 269.8 Hz, CF_3), 120.85 (q, $^{1}J_{C,F}$ ~ 272.2 Hz, CF_3), 102.06 (C-2,6-Ph), 86.34 (br.s, C-3a), 83.47 (C-6) 81.10 (br.s, C-9a), 80.25 (C-7), 50.49 (br.s C-6a), 48.10 (s, C-1), 45.58 (s, C-3), 43.86 (br.s , C-9b).

^{19}F NMR (565 MHz, $CDCl_3$) δ −58.85 (q, $^{5}J_{F,F}$ ~ 8.8 Hz, CF_3), −60.04 (q, $^{5}J_{F,F}$ ~ 8.8 Hz, CF_3).

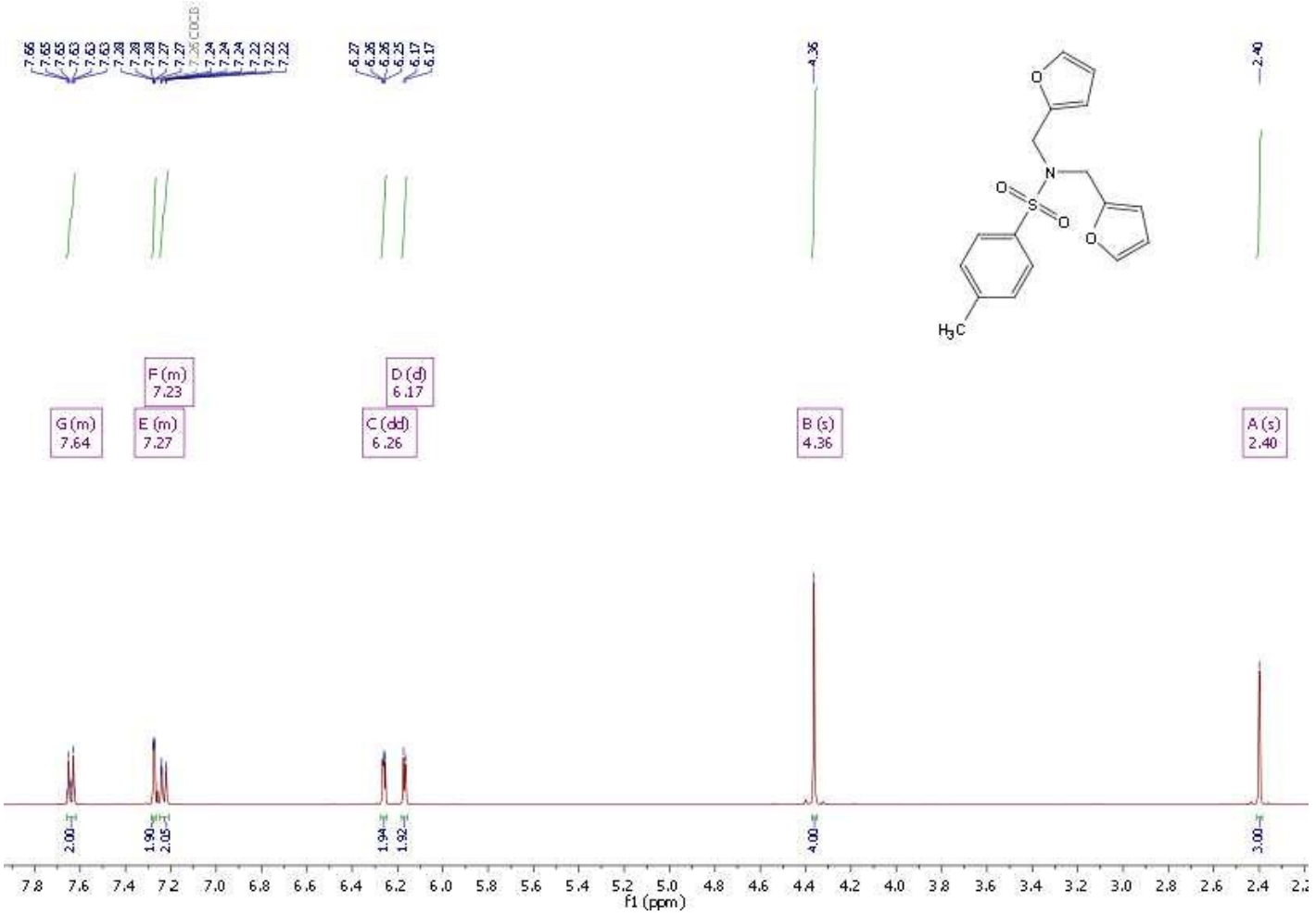
IR ν_{max}/cm^{-1} (KBr): 3122 (ν(=CH)), 3082 (ν(=CH)), 2924 (ν(C-H)alkyl), 1570 (ν(C=C)), 1350 (ν(SO_2)), 1180 (ν(SO_2)), 1148 (ν(C-F)), 750 (C-F).

MS (ESI): m/z = 605.9 $[M+H]^+$.

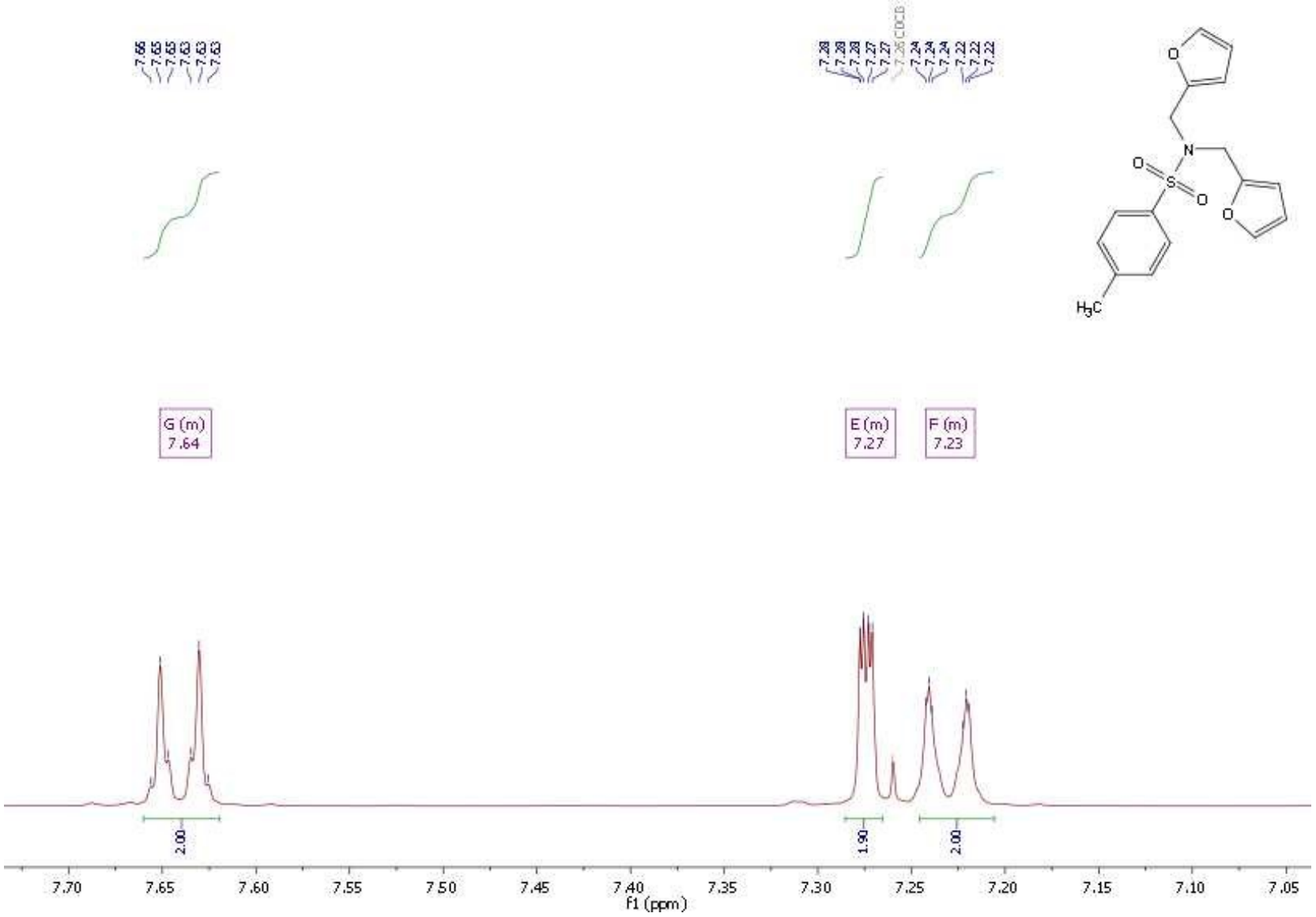
NMR SPECTRA

4-Methyl-N,N-bis(furan-2-ylmethyl)benzenesulfonamide (1)

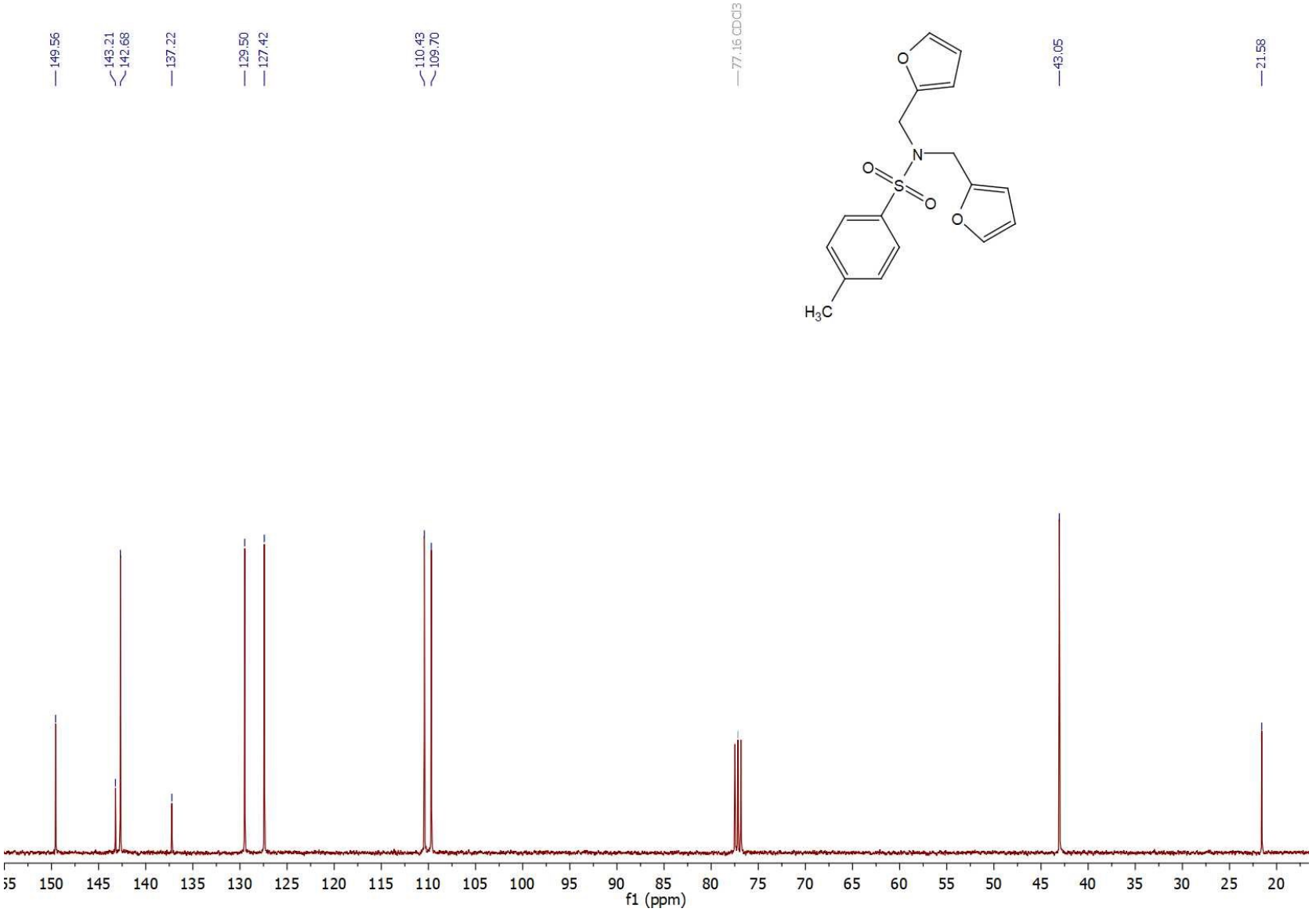
^{1}H NMR spectrum of compound (1)



^{1}H NMR spectrum of compound (1)

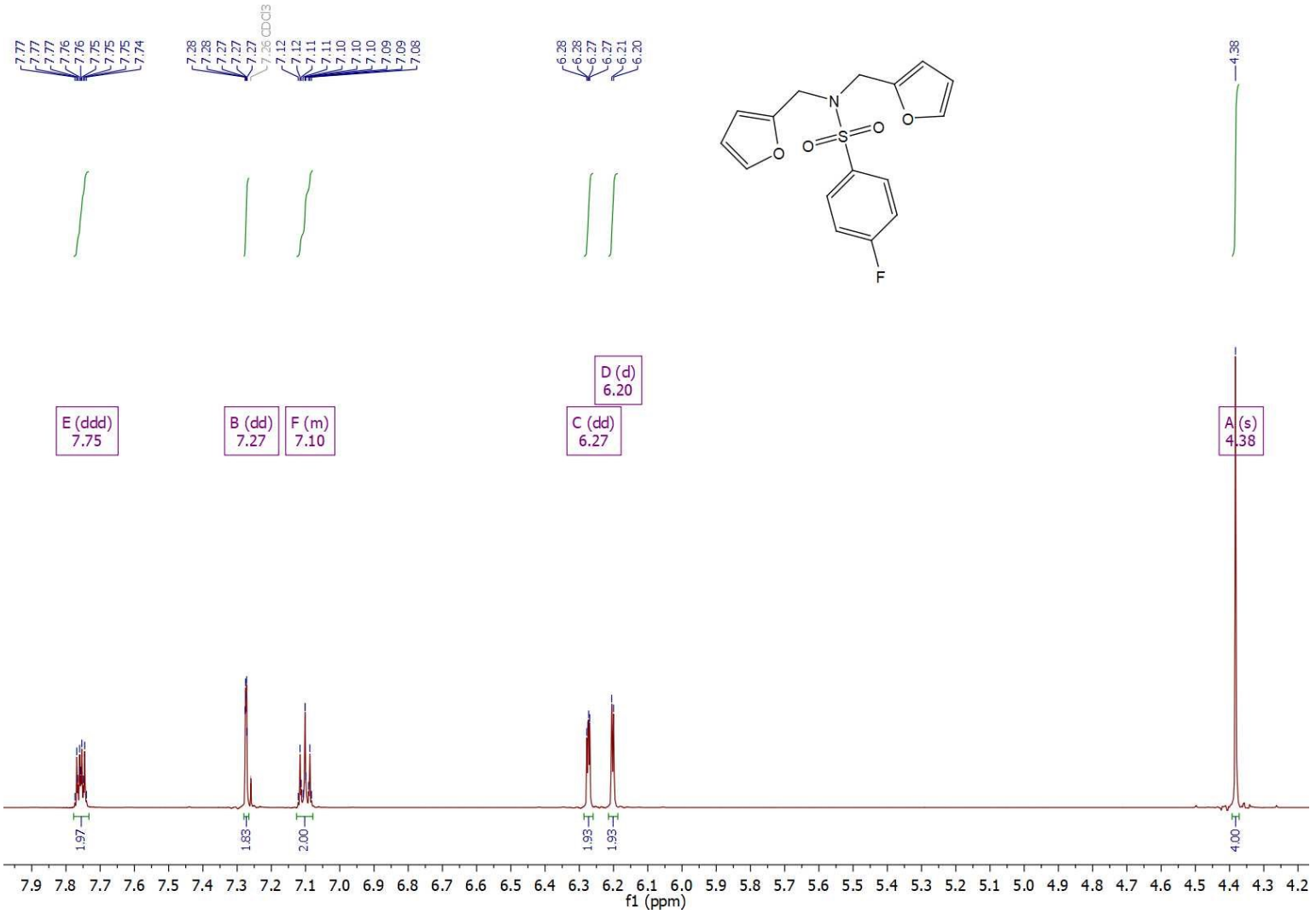


^{13}C NMR spectrum of compound (1)

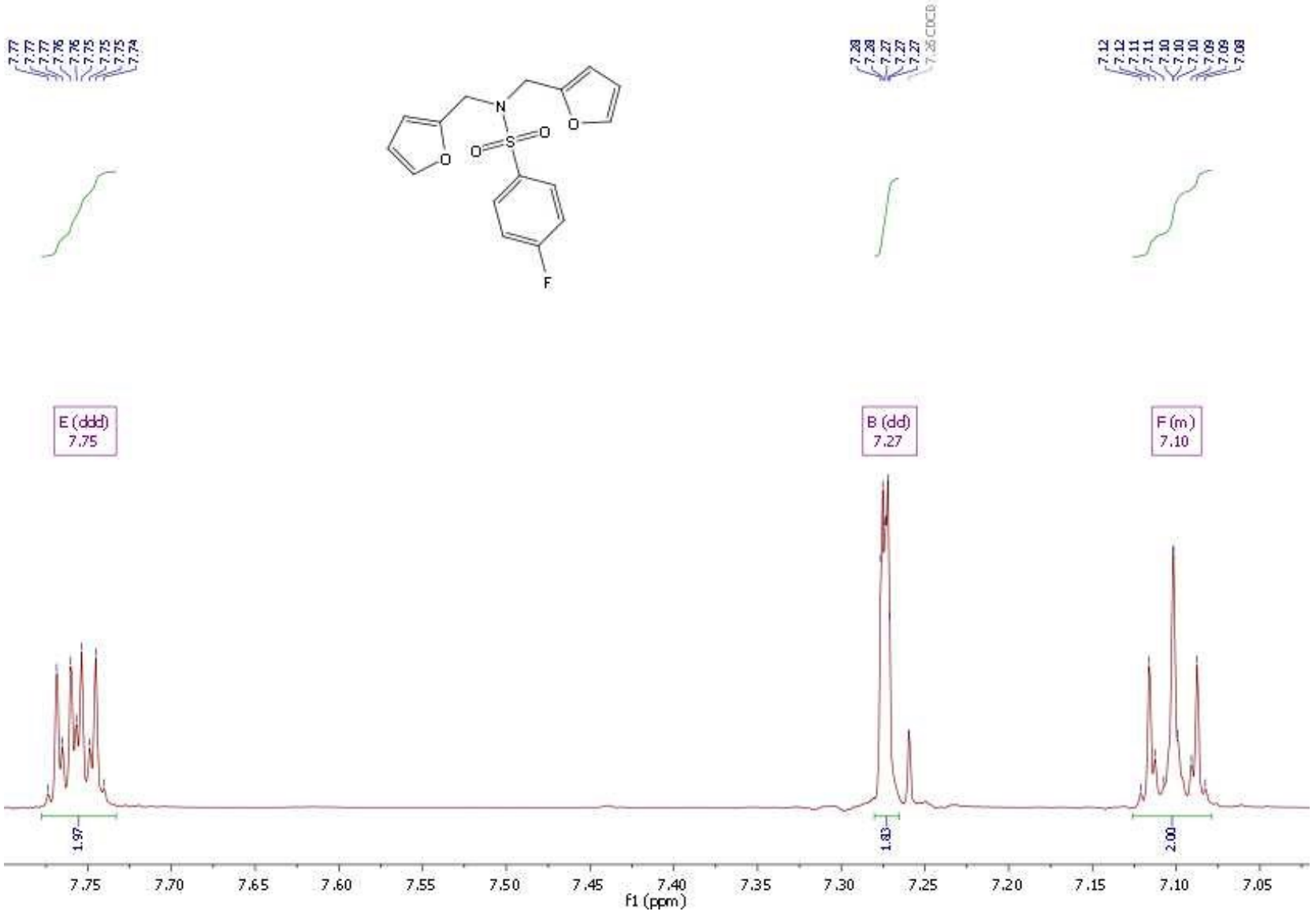


***4-Fluoro-N,N-bis(furan-2-ylmethyl)benzenesulfonamide* (2)**

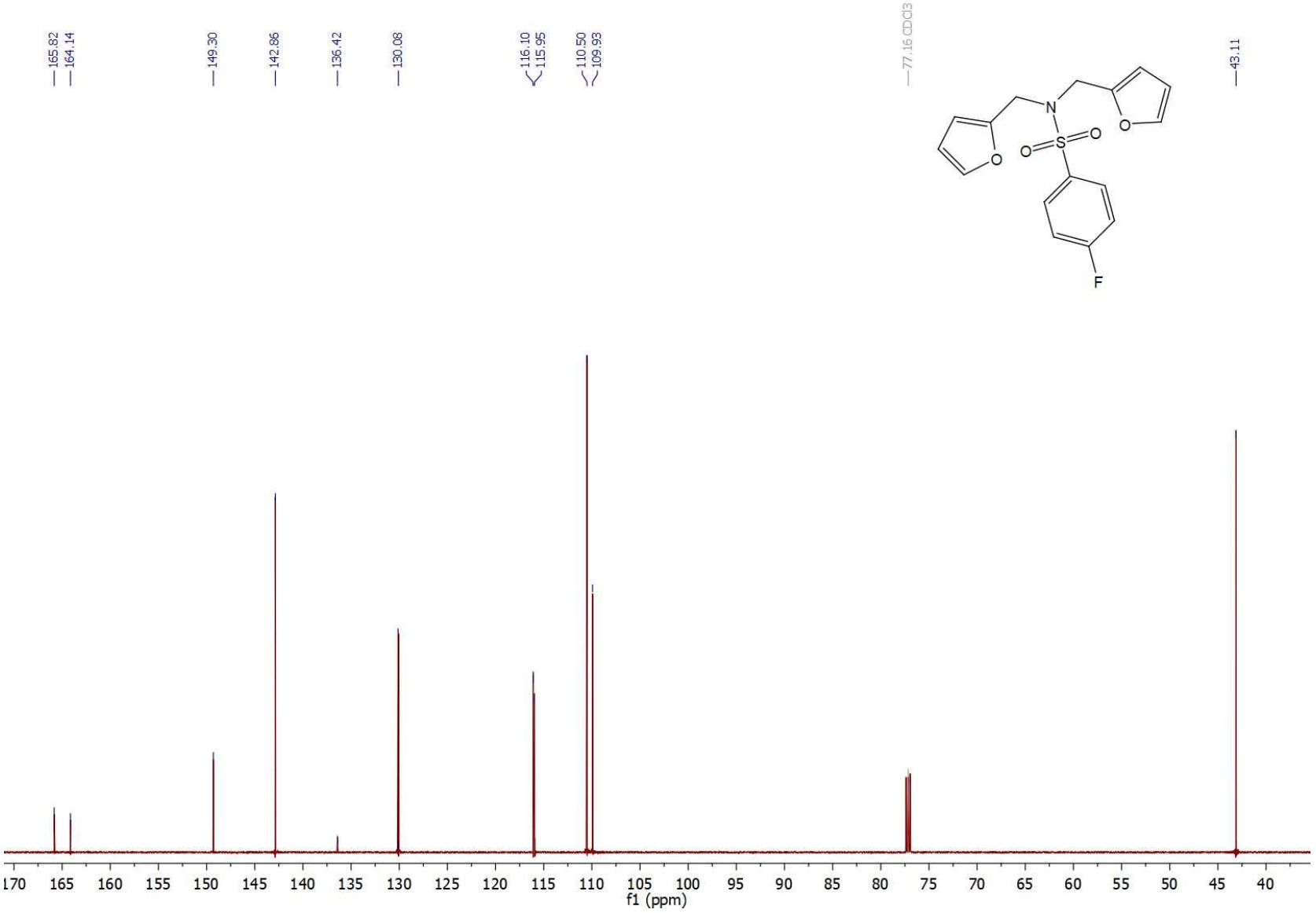
^{1}H NMR spectrum of compound (2)



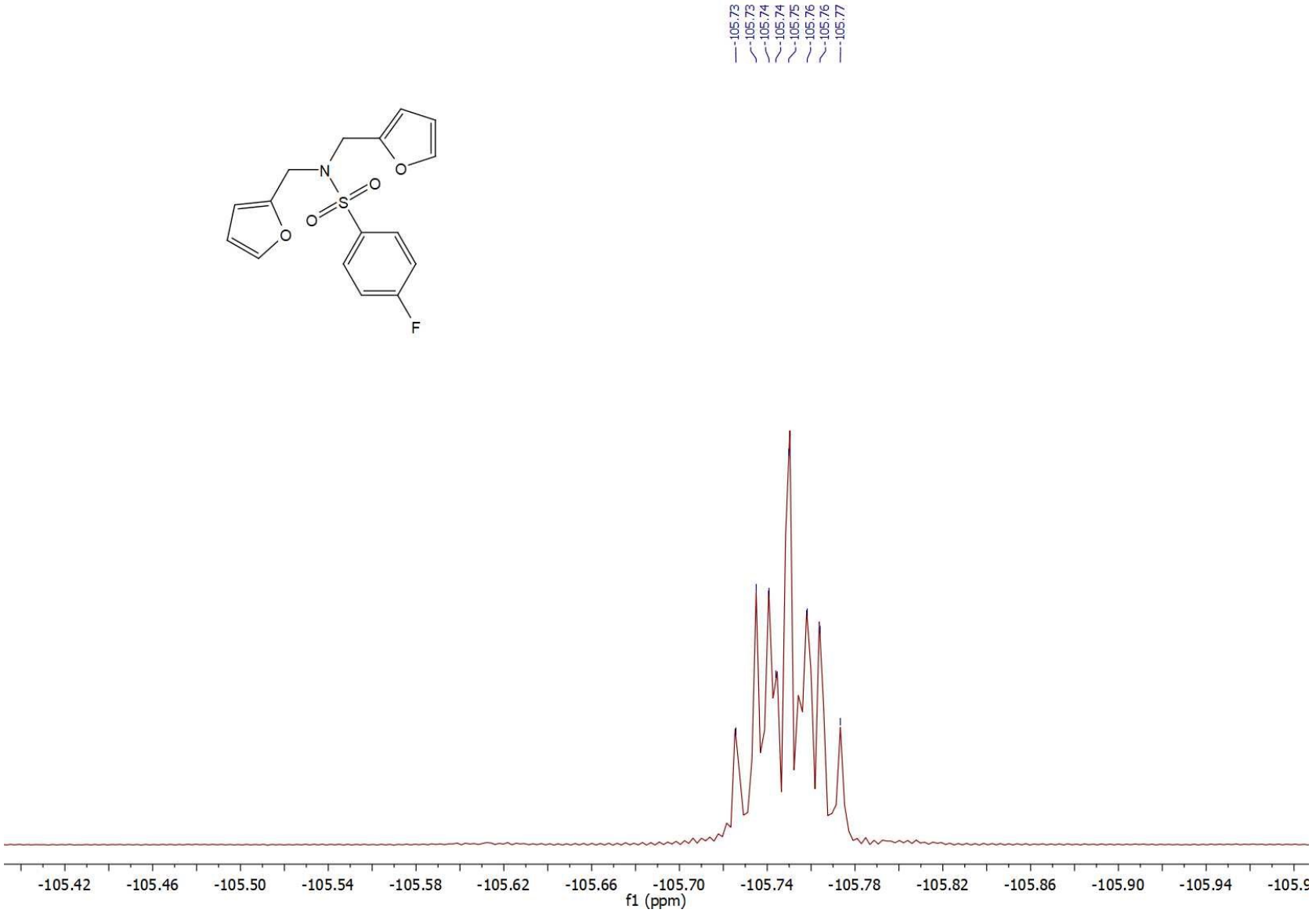
^{1}H NMR spectrum of compound (2)



^{13}C NMR spectrum of compound (2)

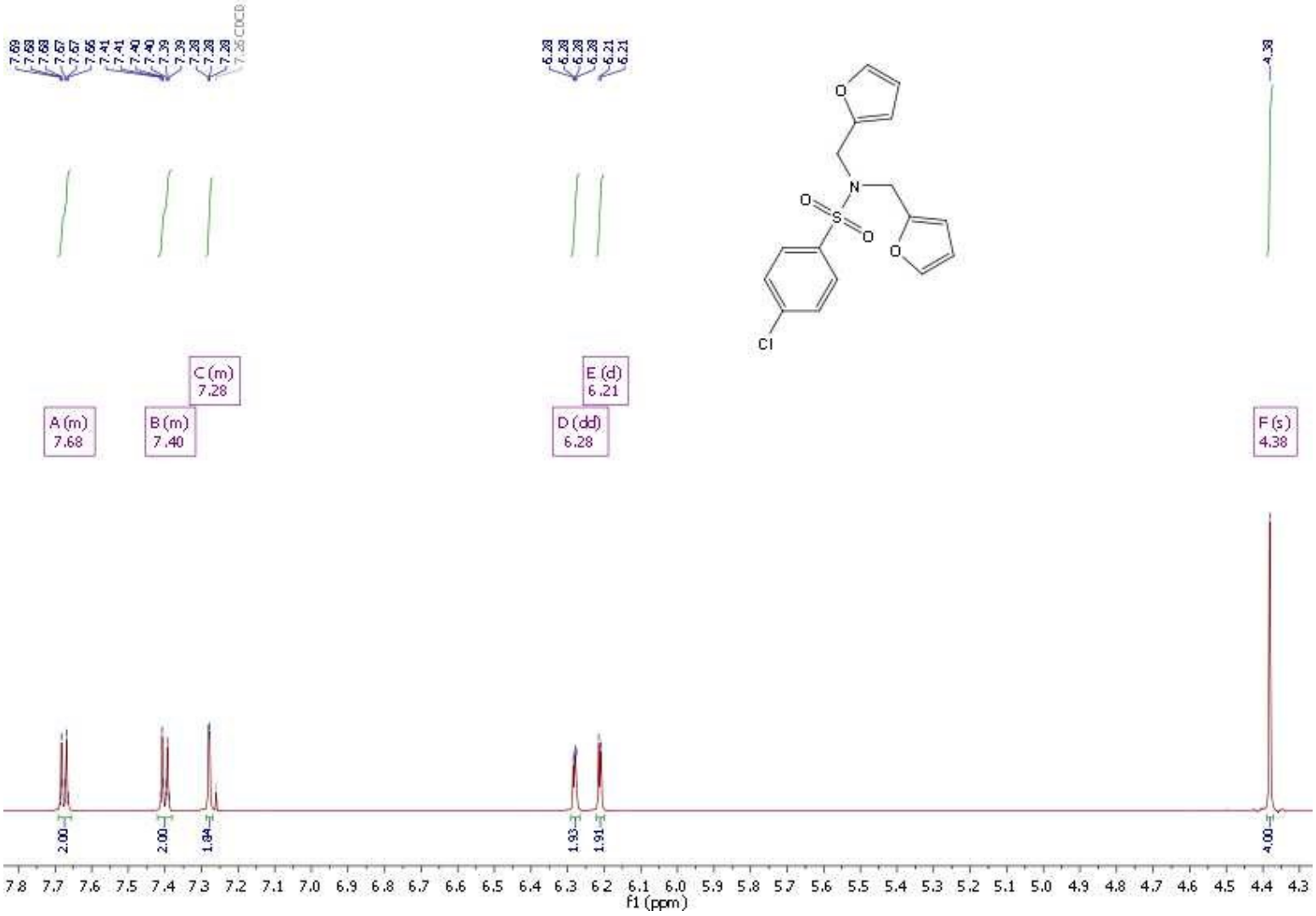


^{19}F NMR spectrum of compound (2)

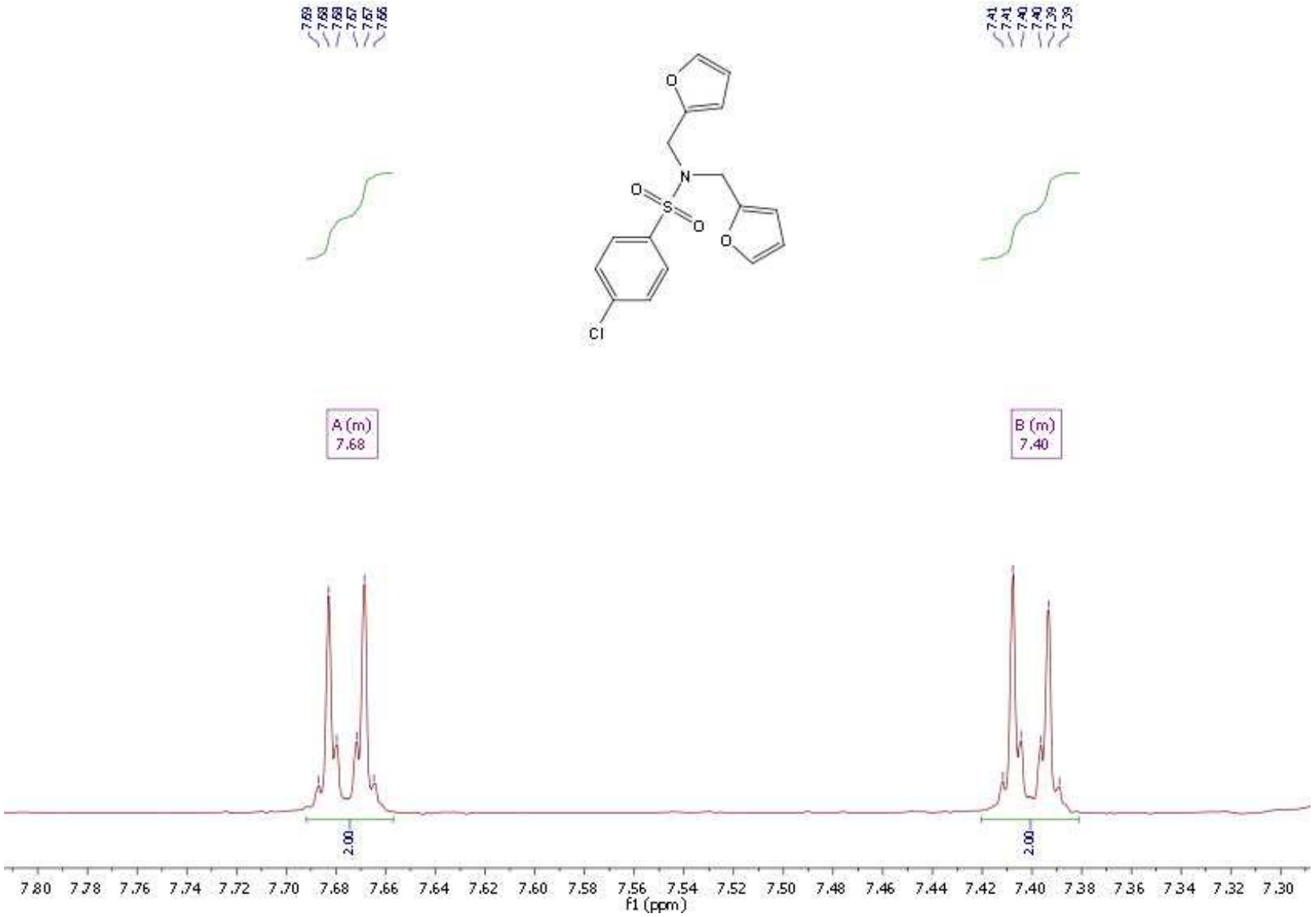


***4-Chloro-N,N-bis(furan-2-ylmethyl)benzenesulfonamide* (3)**

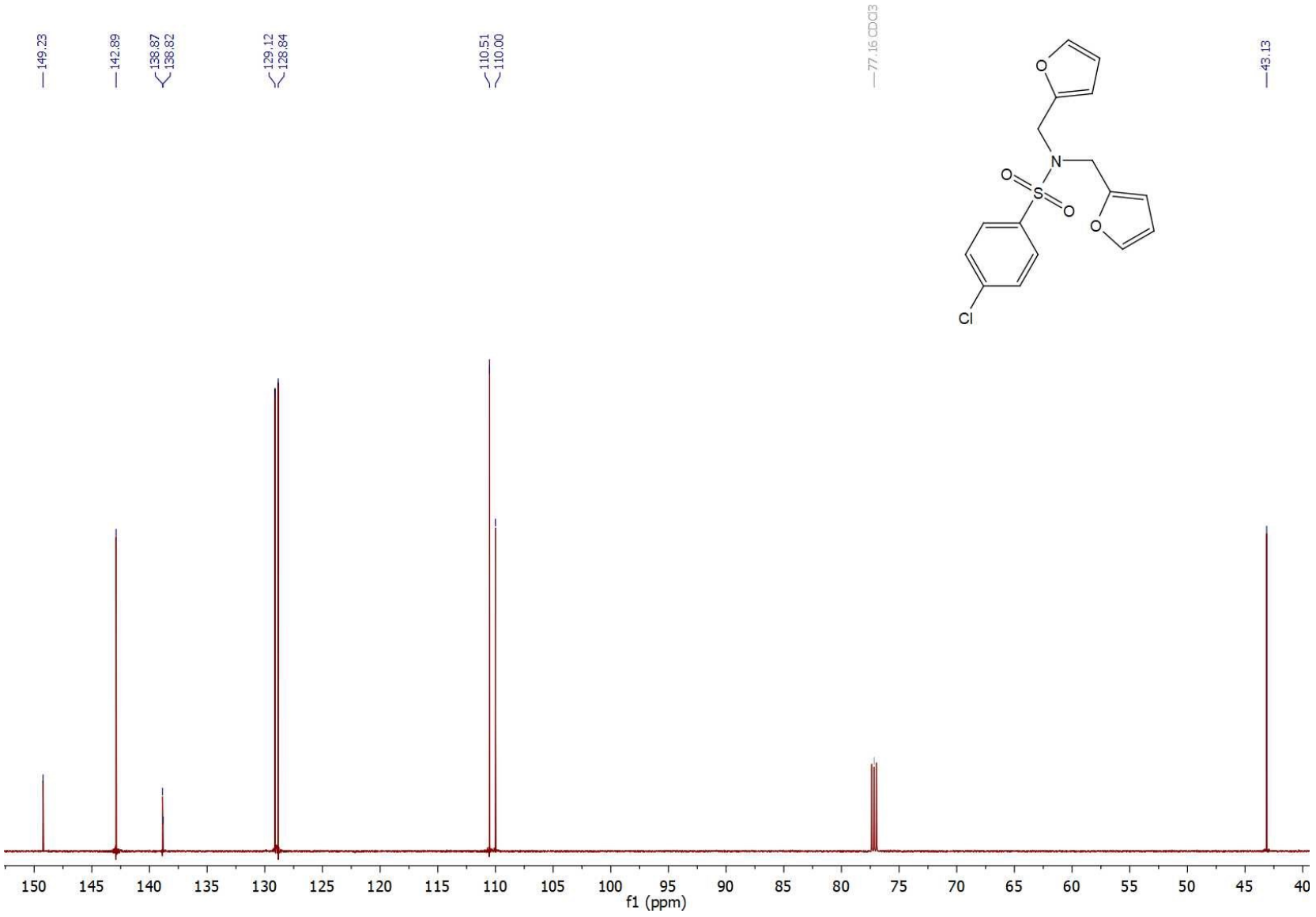
^{1}H NMR spectrum of compound (3)



^{1}H NMR spectrum of compound (3)

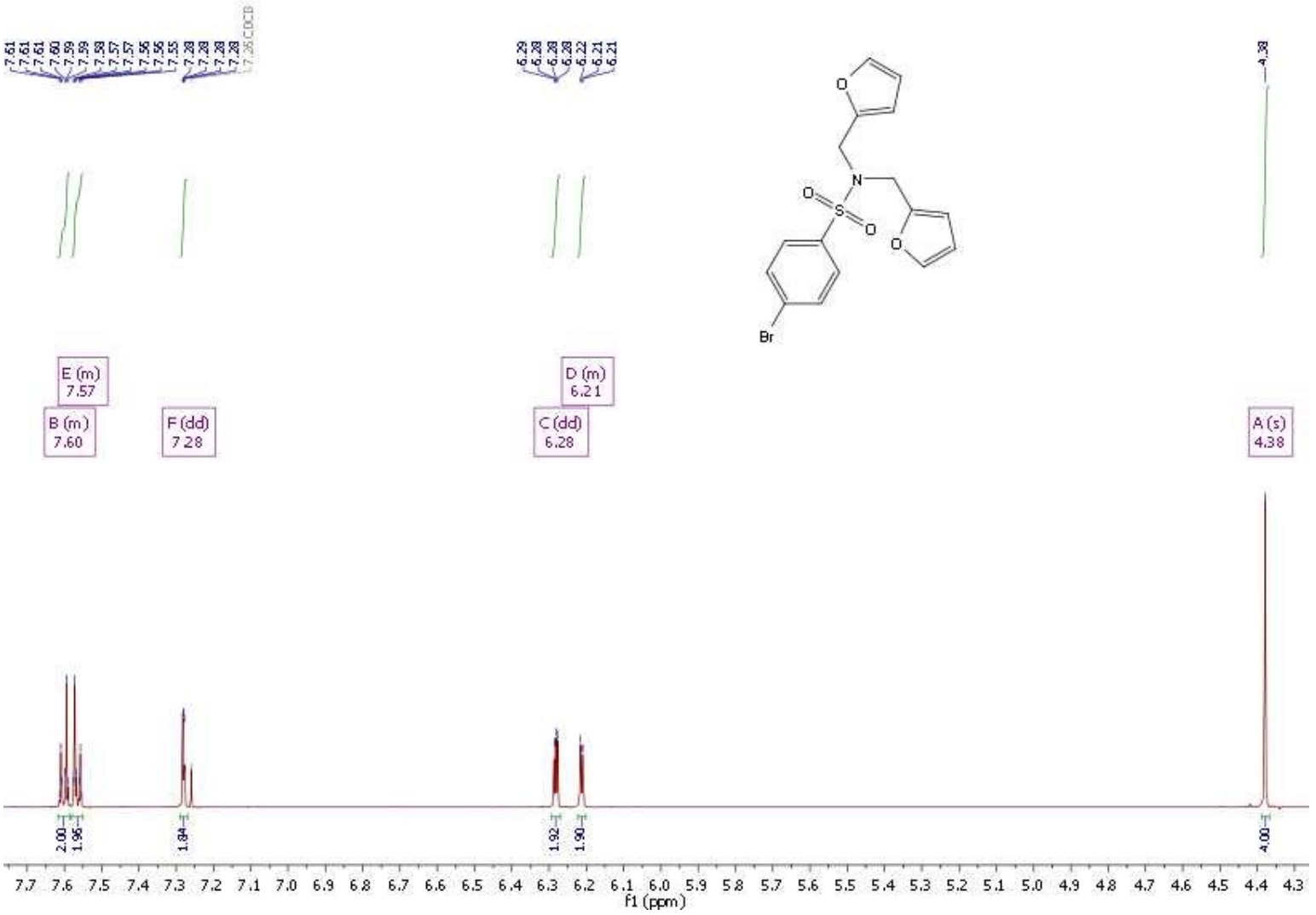


^{13}C NMR spectrum of compound (3)

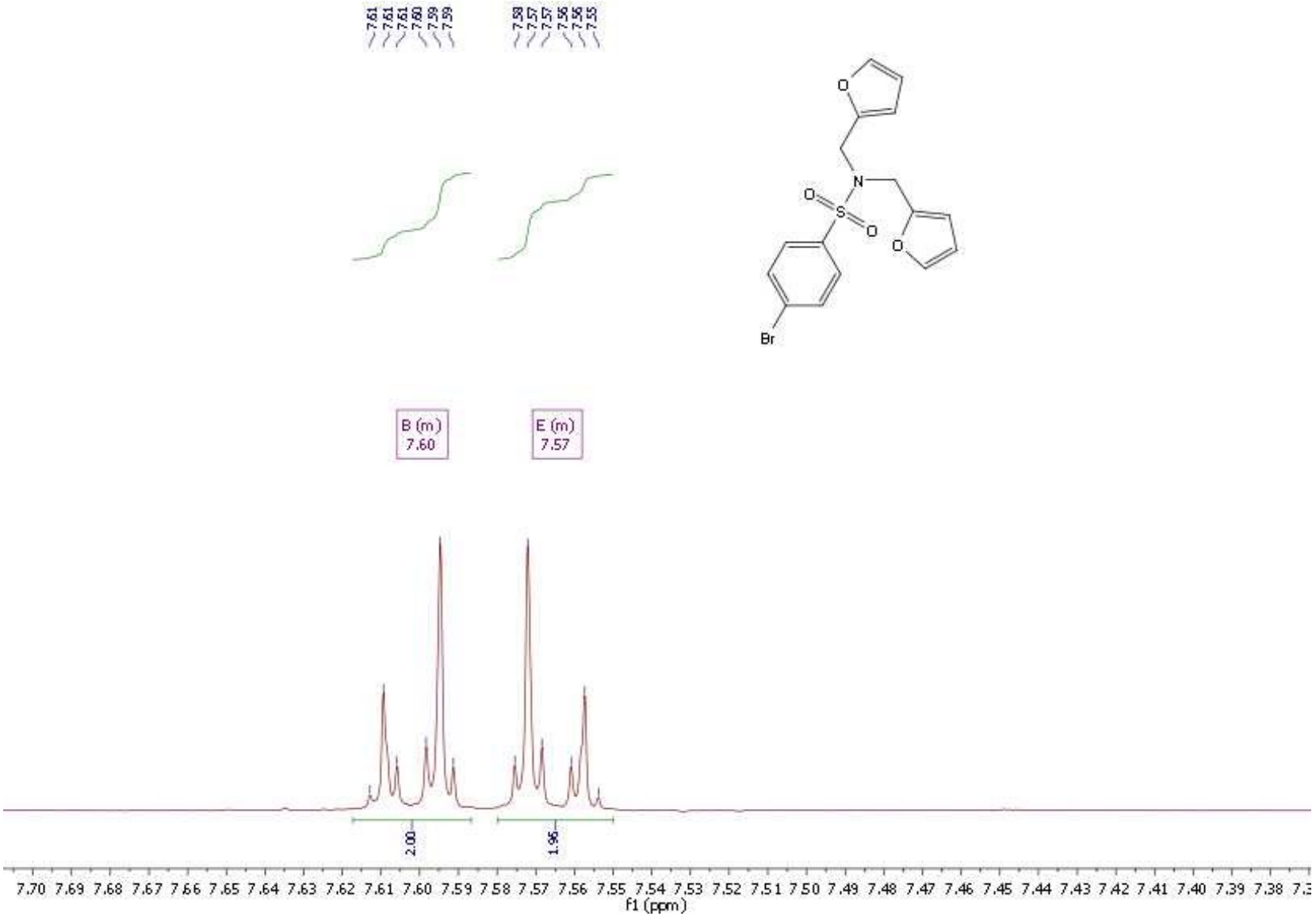


***4-Bromo-N,N-bis(furan-2-ylmethyl)benzenesulfonamide* (4)**

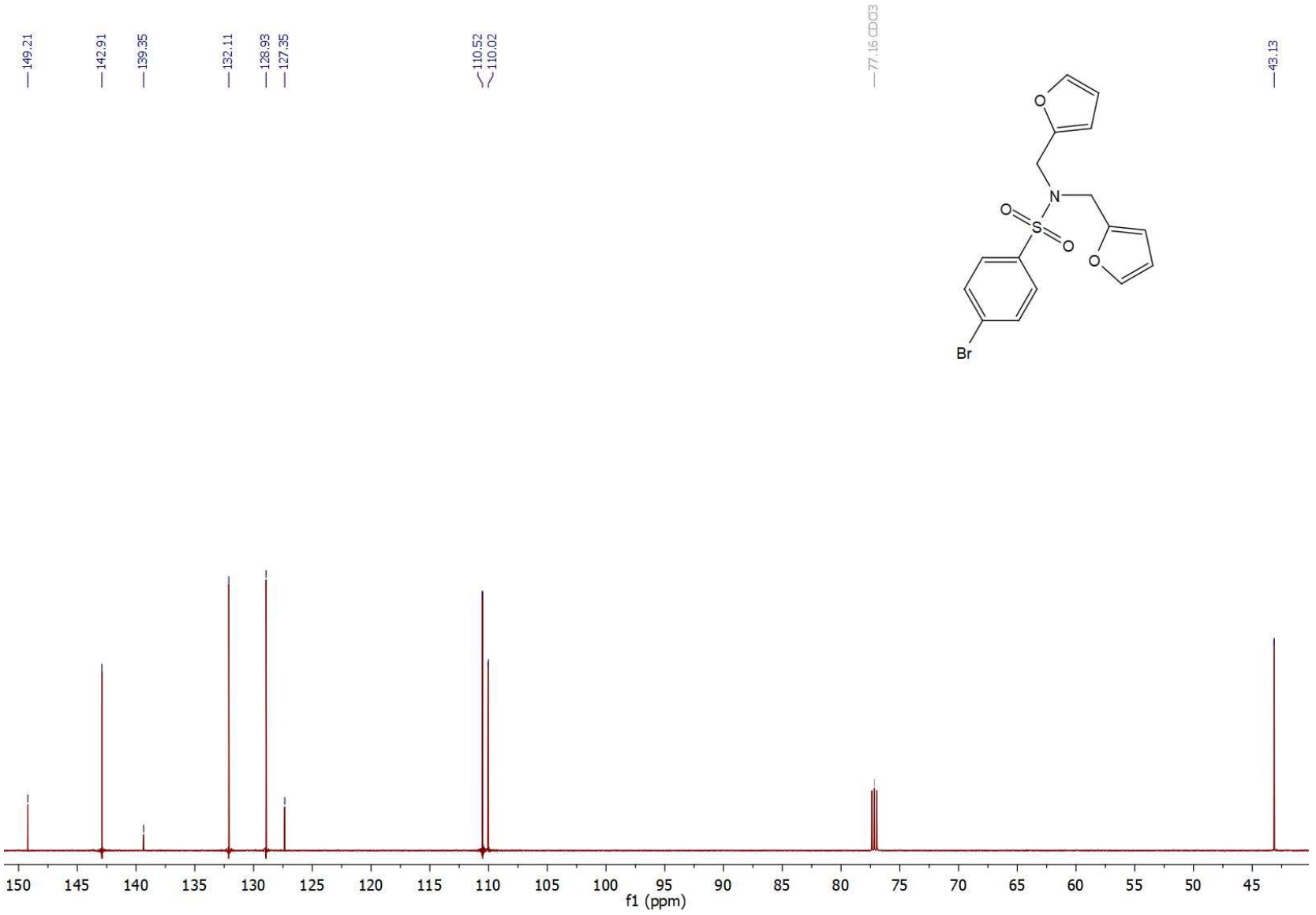
^{1}H NMR spectrum of compound (4)



^{1}H NMR spectrum of compound (4)

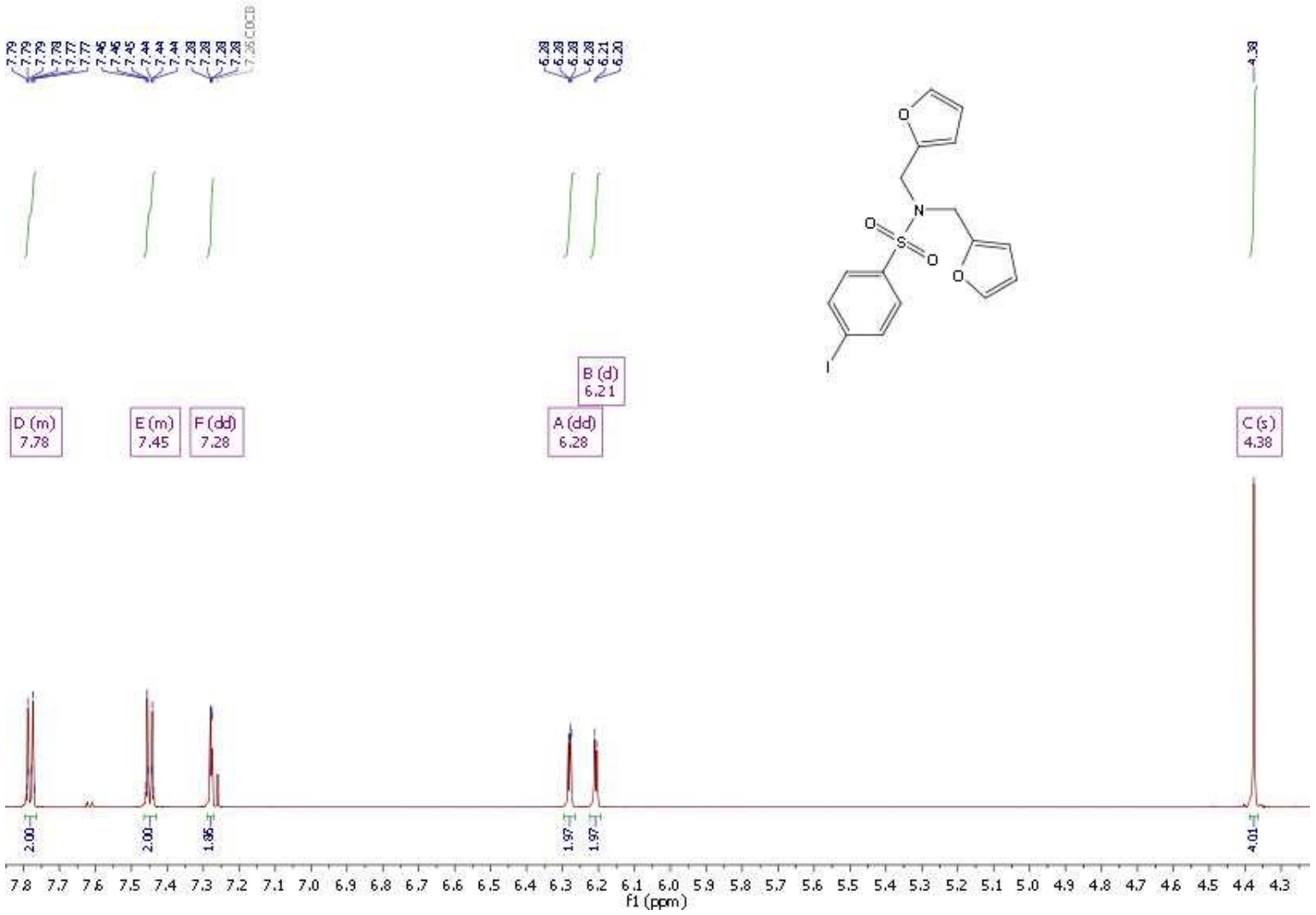


^{13}C NMR spectrum of compound (4)

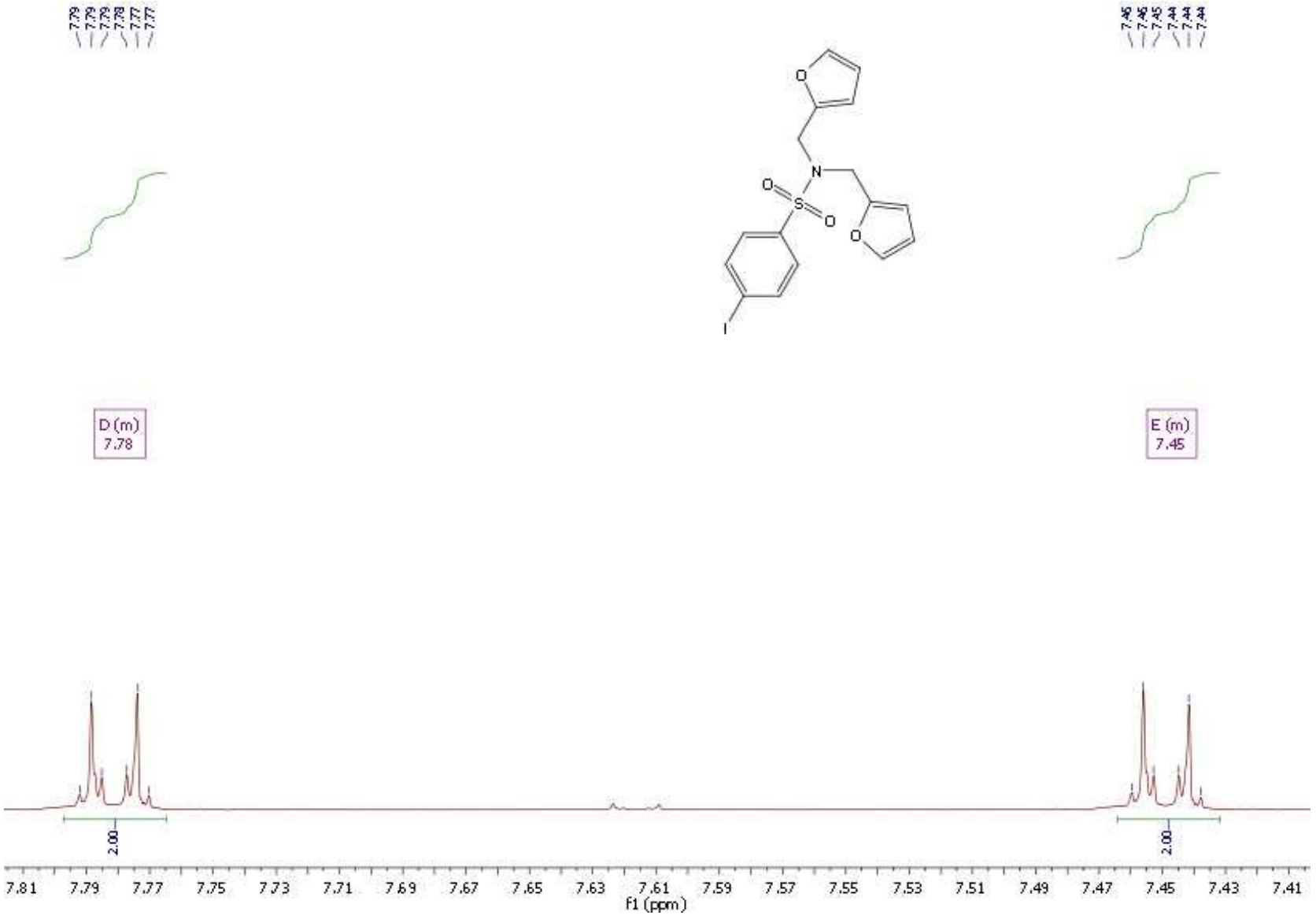


4-Iodo-N,N-bis(furan-2-ylmethyl)-benzenesulfonamide **(5)**

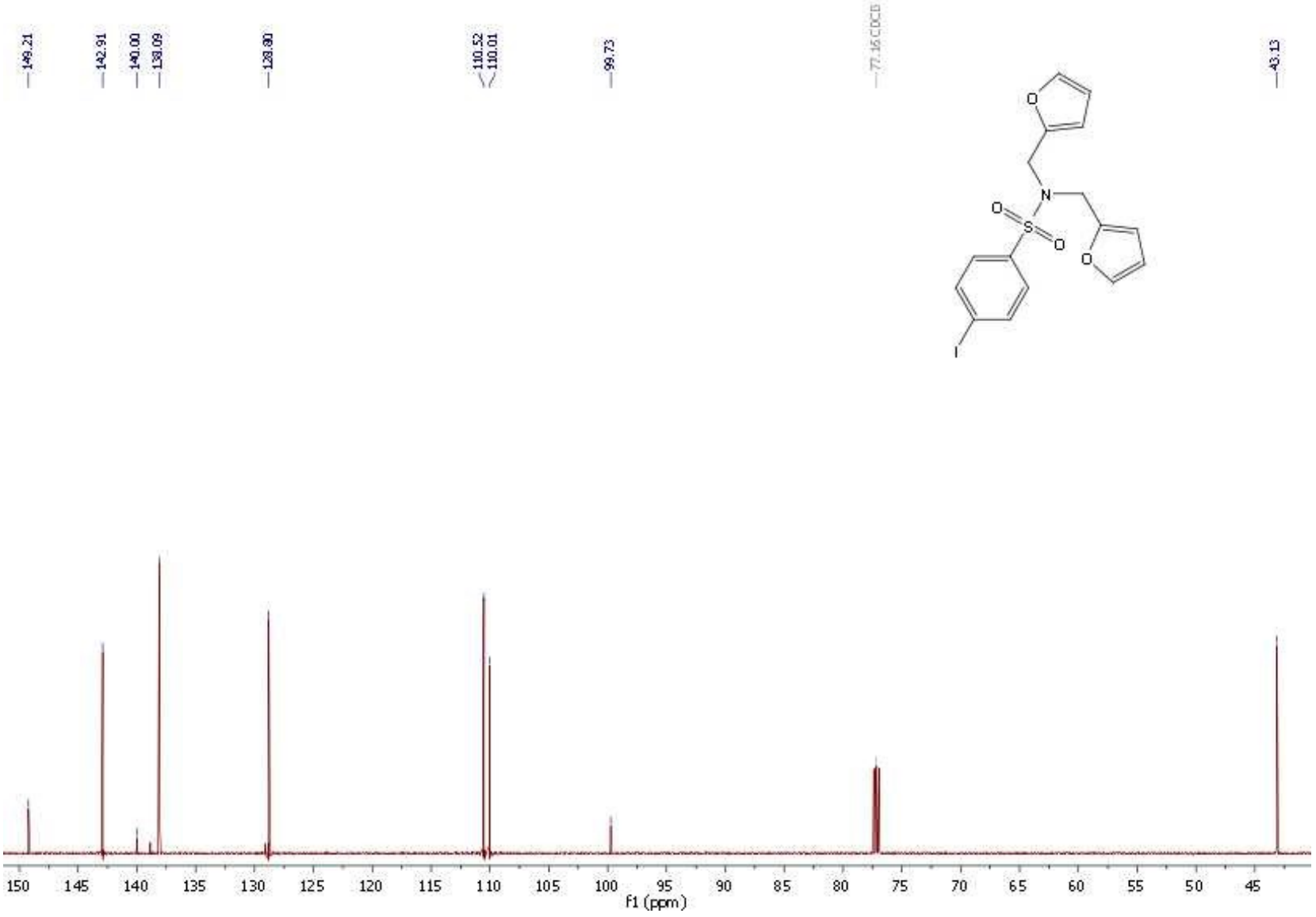
^{1}H NMR spectrum of compound (5)



^{1}H NMR spectrum of compound (5)

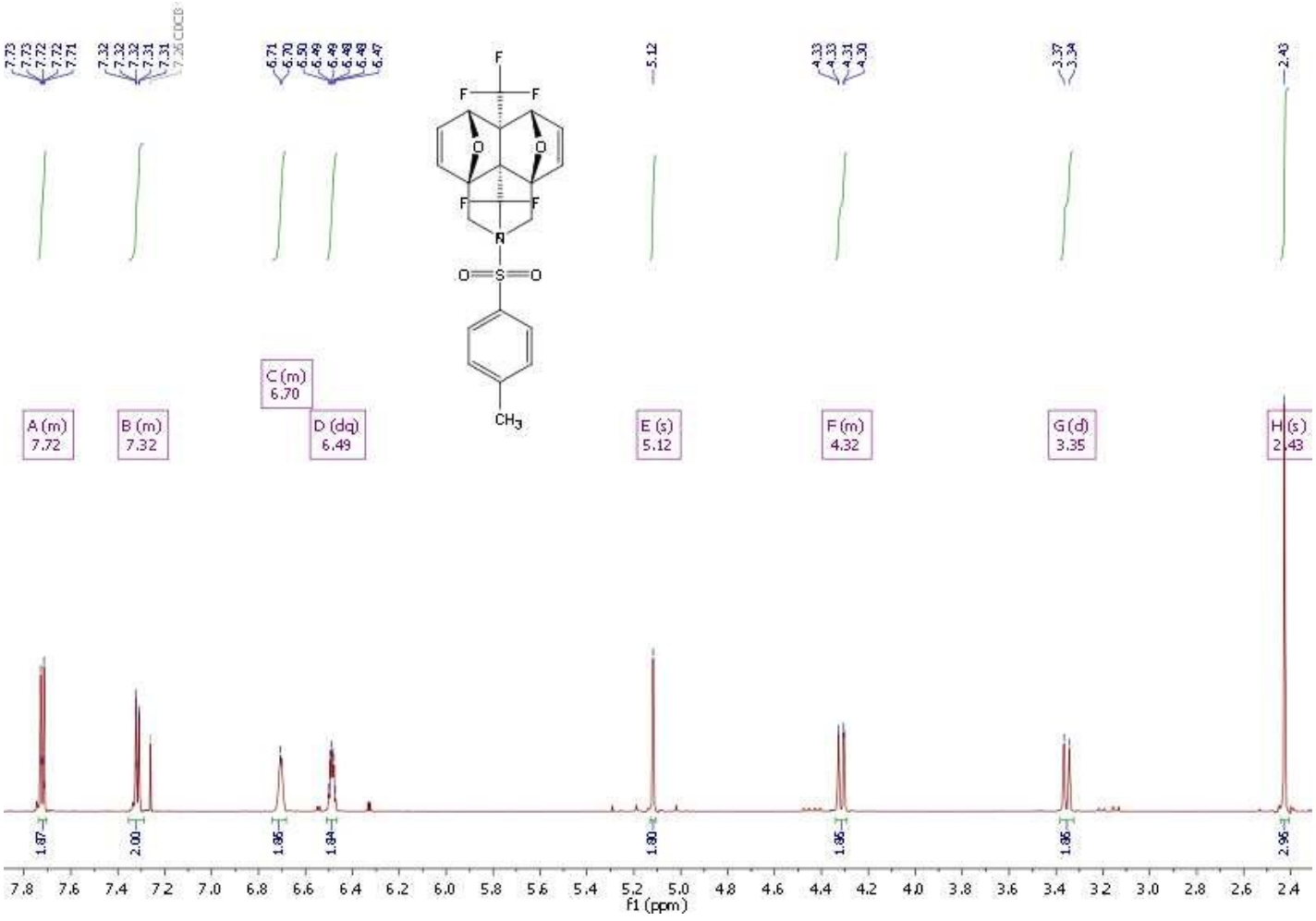


^{13}C NMR spectrum of compound (5)

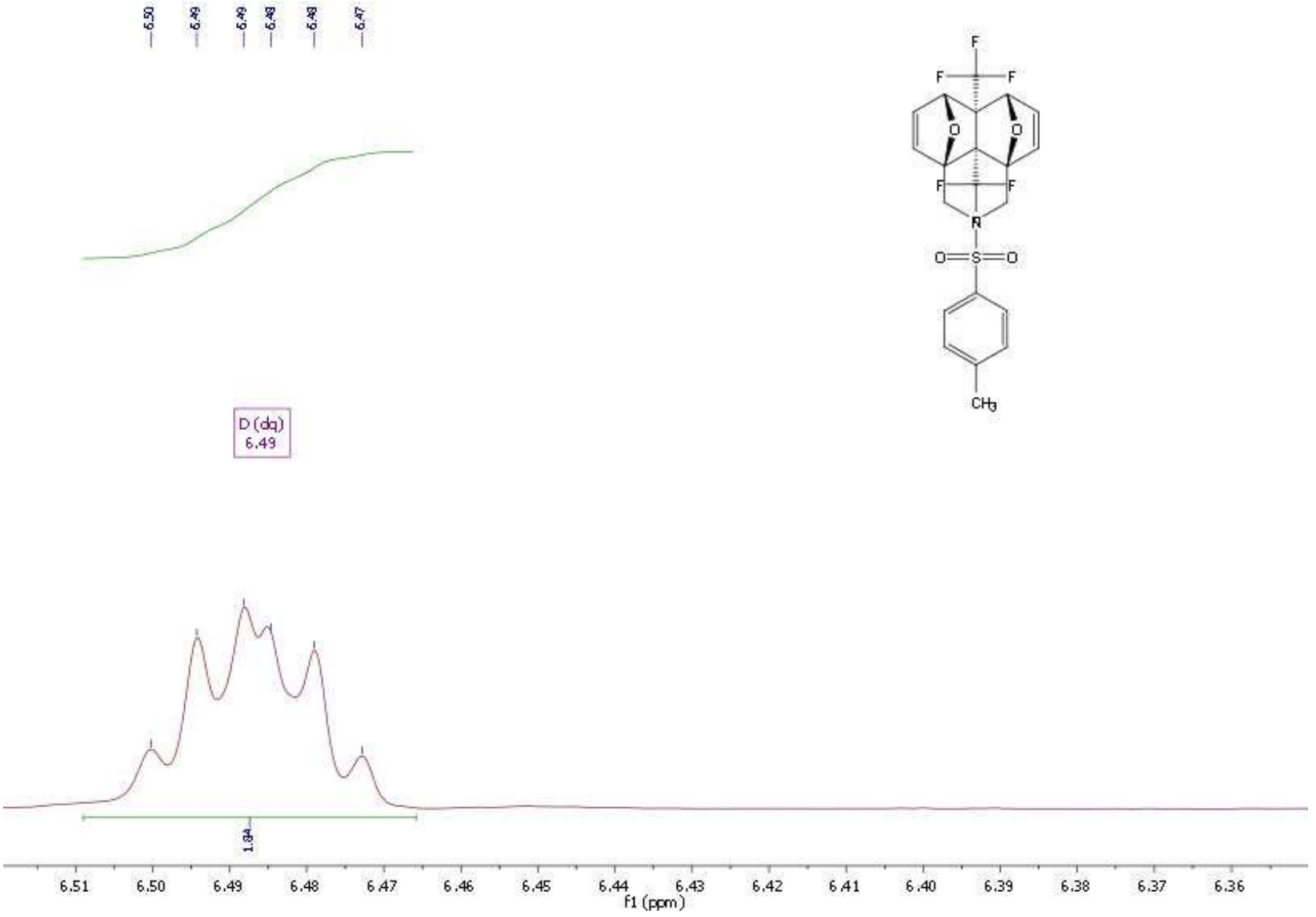


(3aRS,6SR,7RS,9aSR)-2-[(4-Methylphenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(6a)**

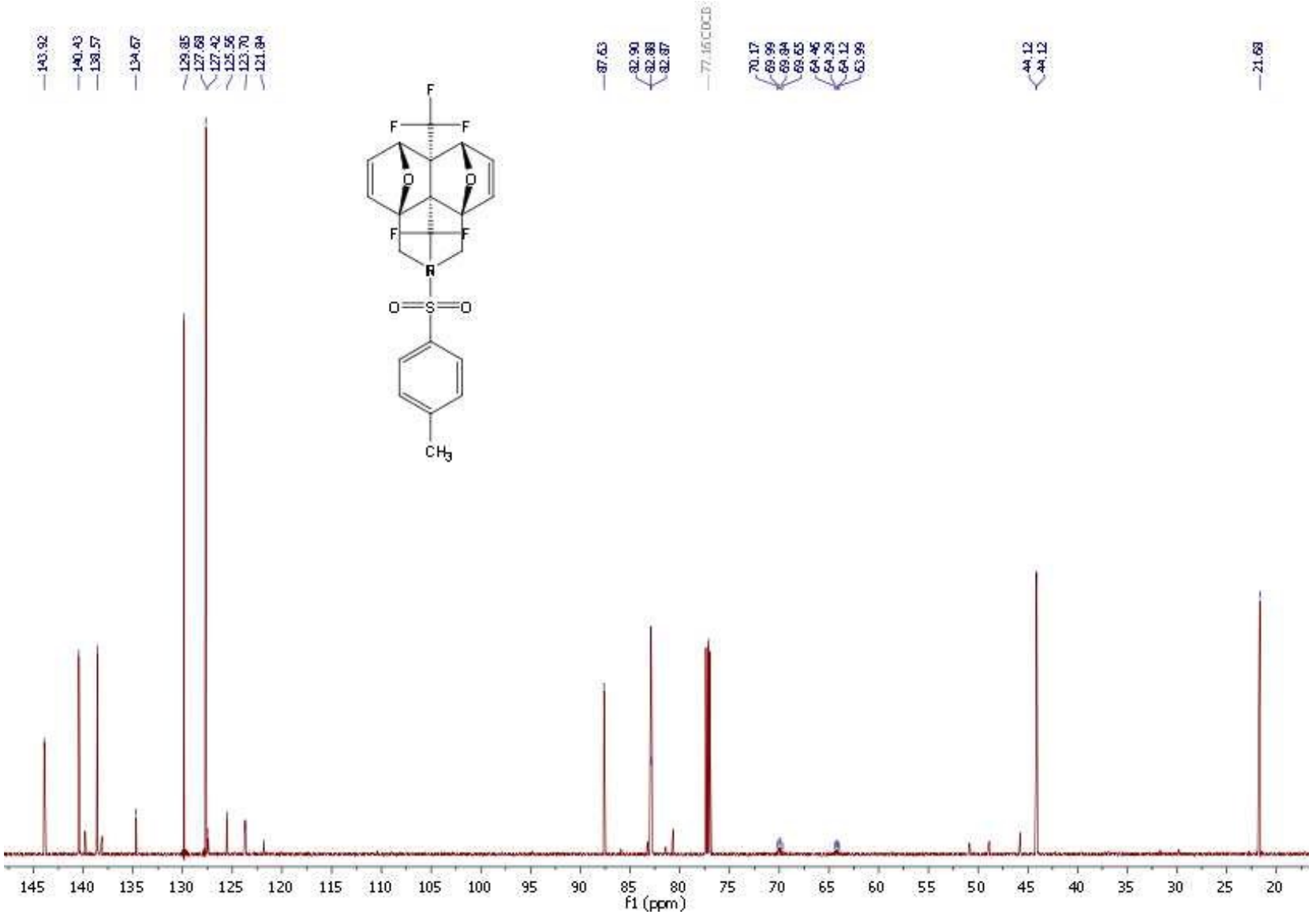
^{1}H NMR spectrum of compound (6a)



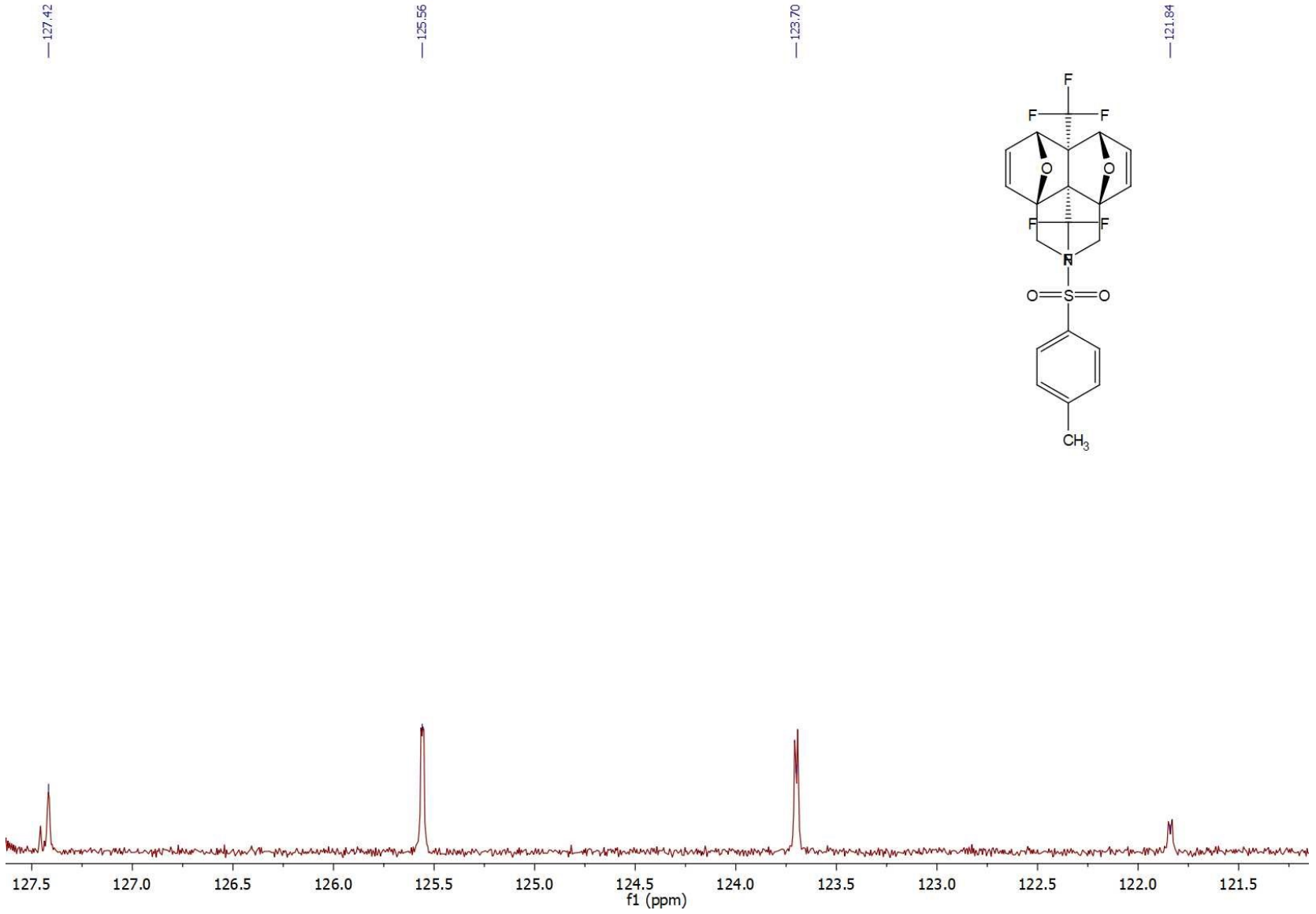
^{1}H NMR spectrum of compound (6a)



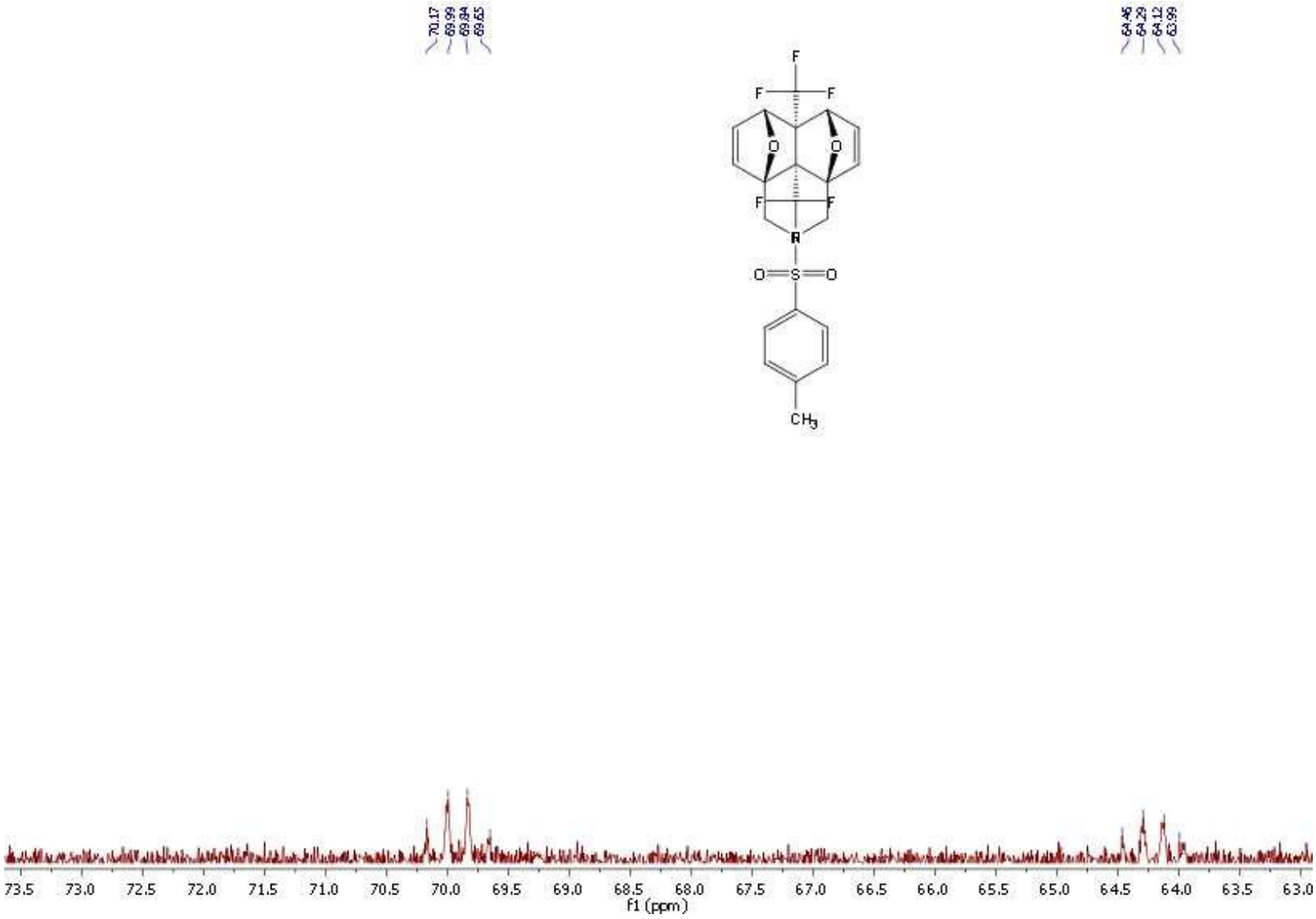
^{13}C NMR spectrum of compound (6a)



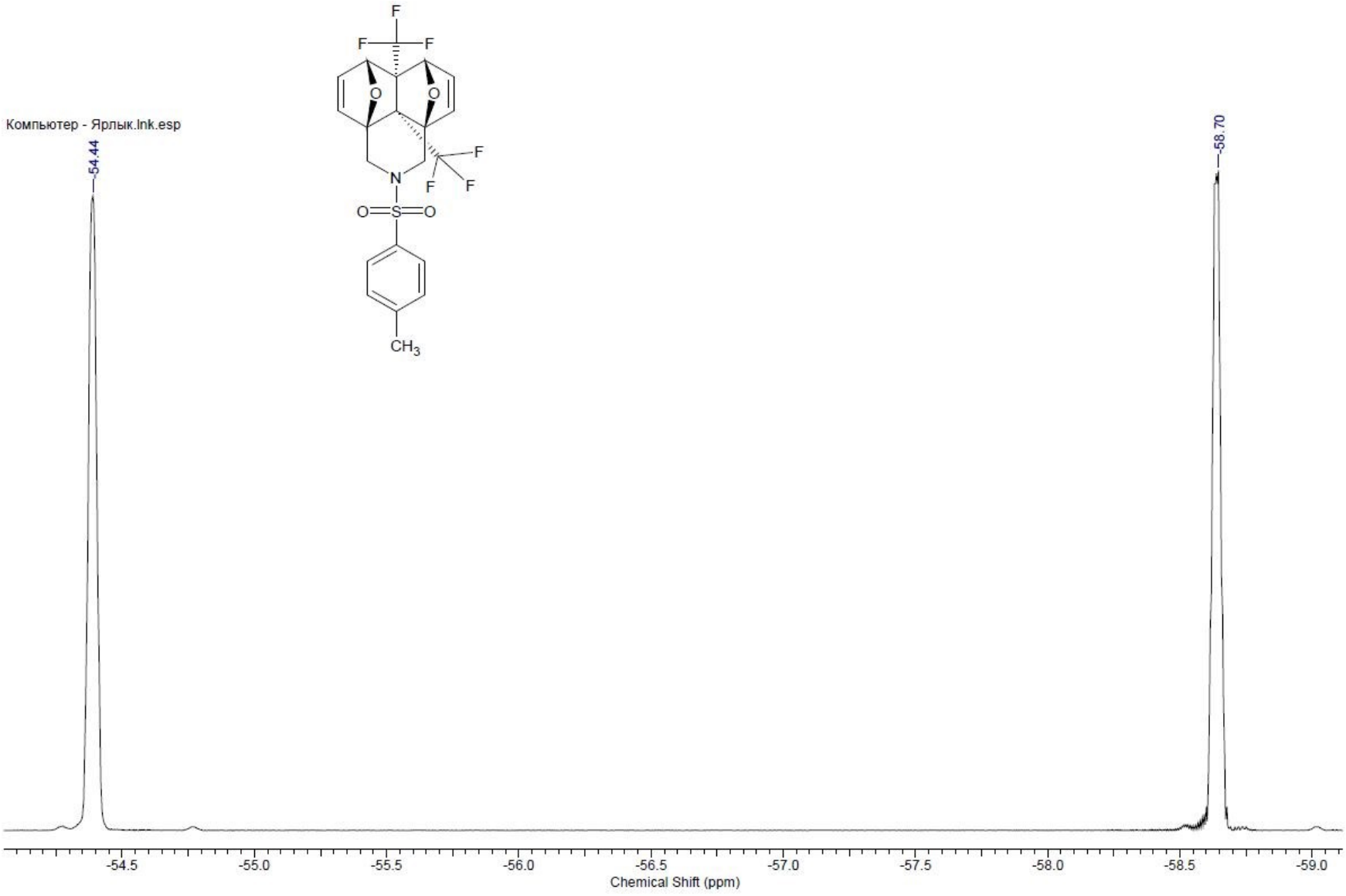
^{13}C NMR spectrum of compound (6a)



^{13}C NMR spectrum of compound (6a)

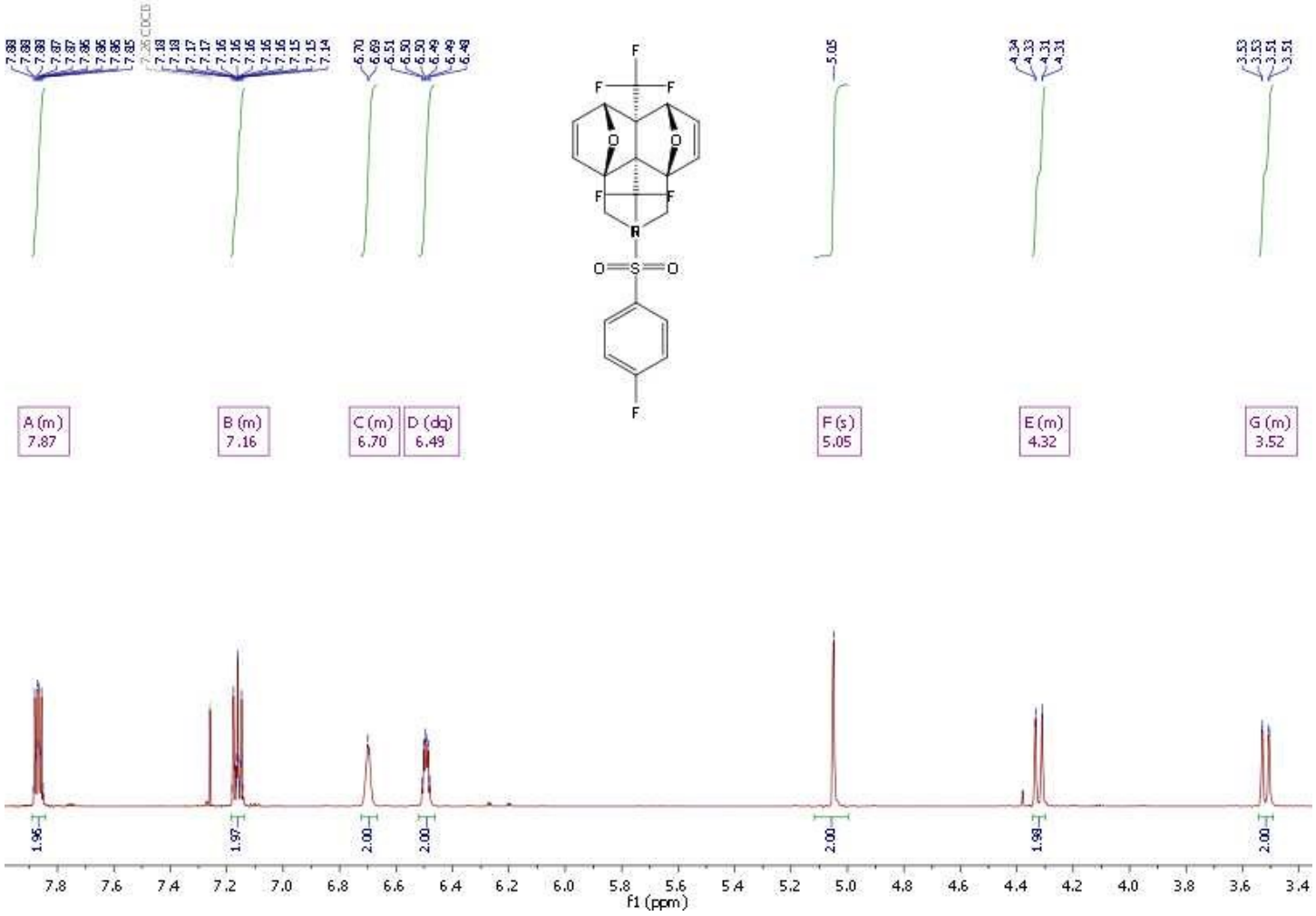


^{19}F NMR spectrum of compound (6a)

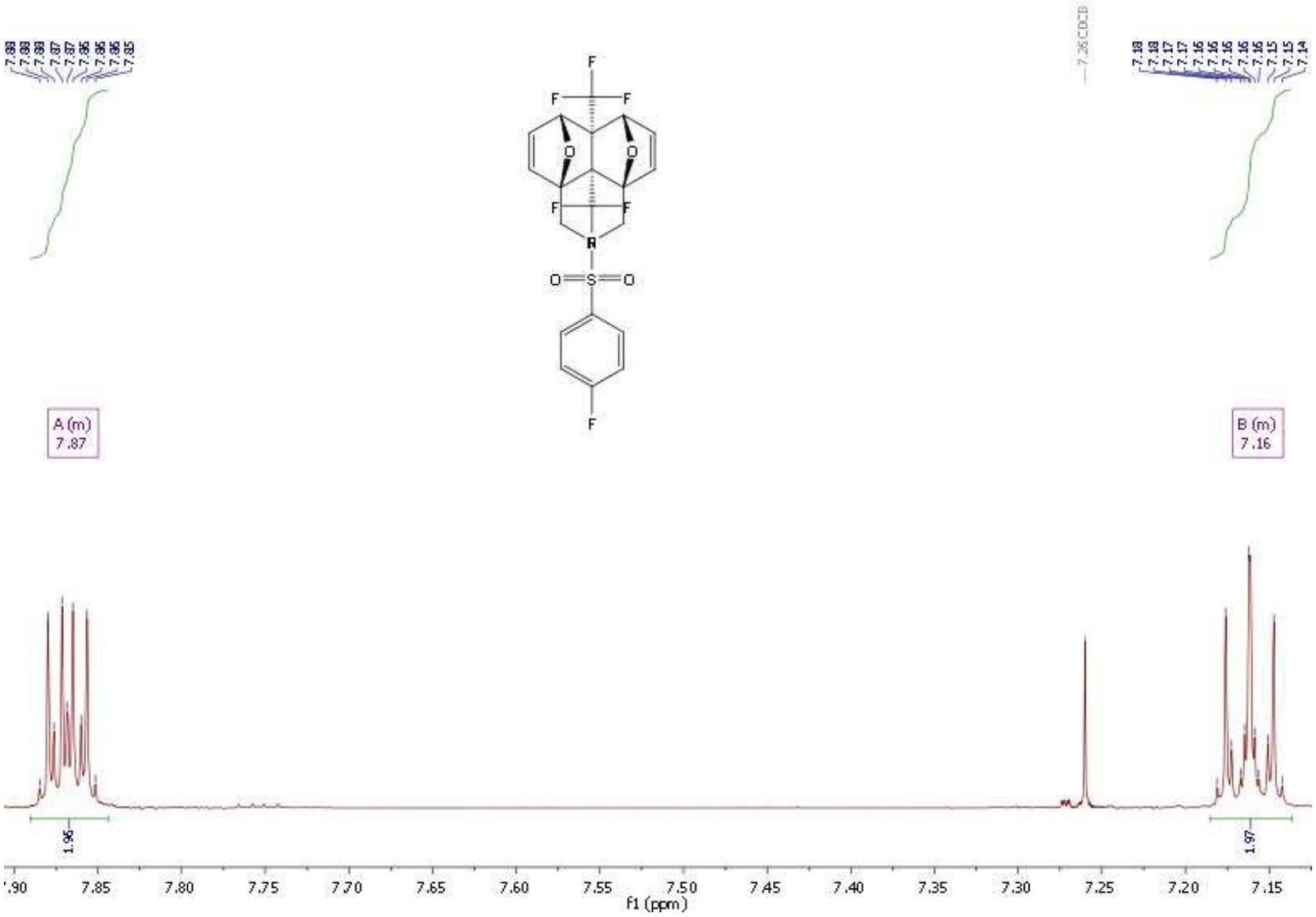


(3aRS,6SR,7RS,9aSR)-2-[(4-Fluorophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(7a)**

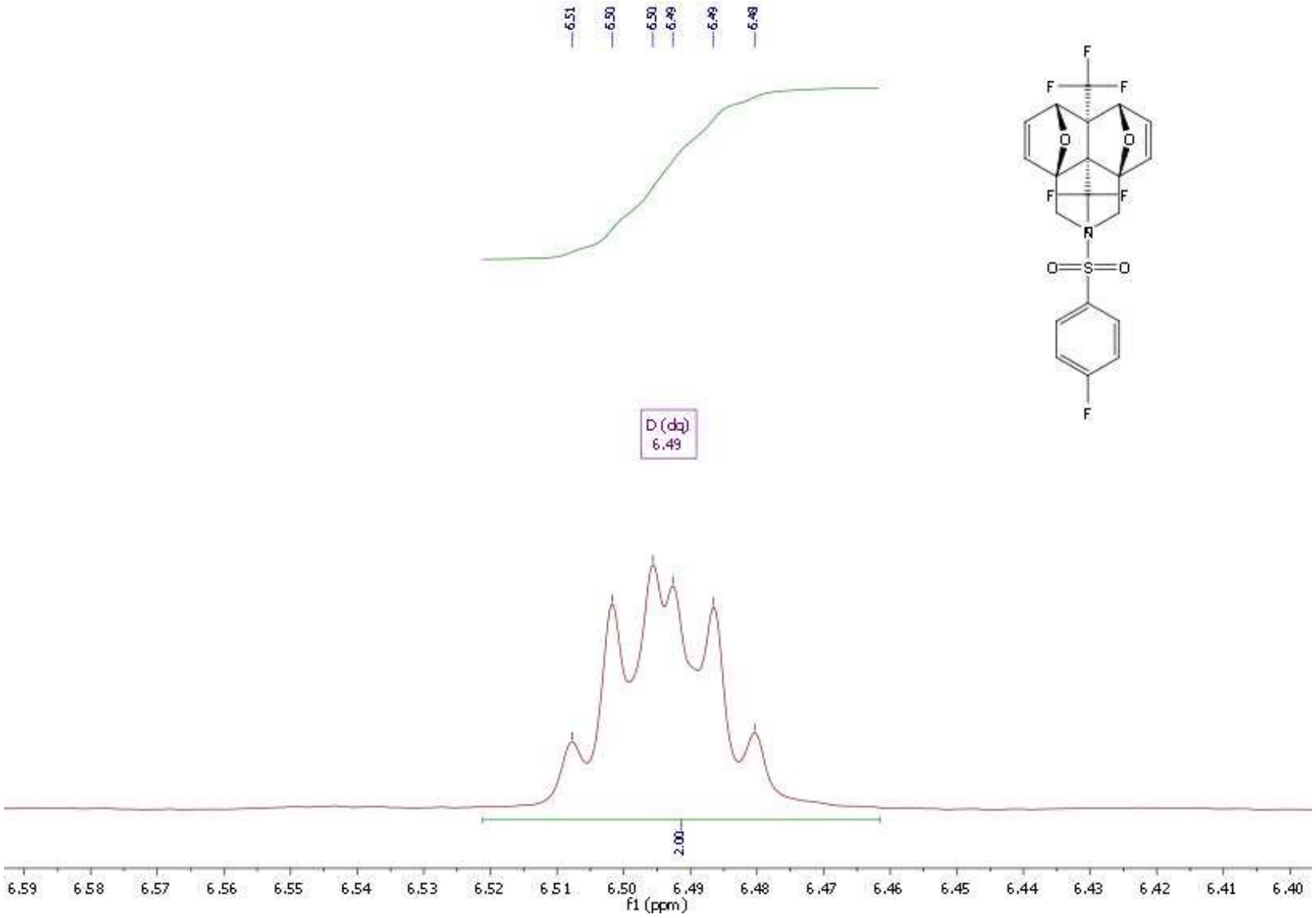
^{1}H NMR spectrum of compound (7a)



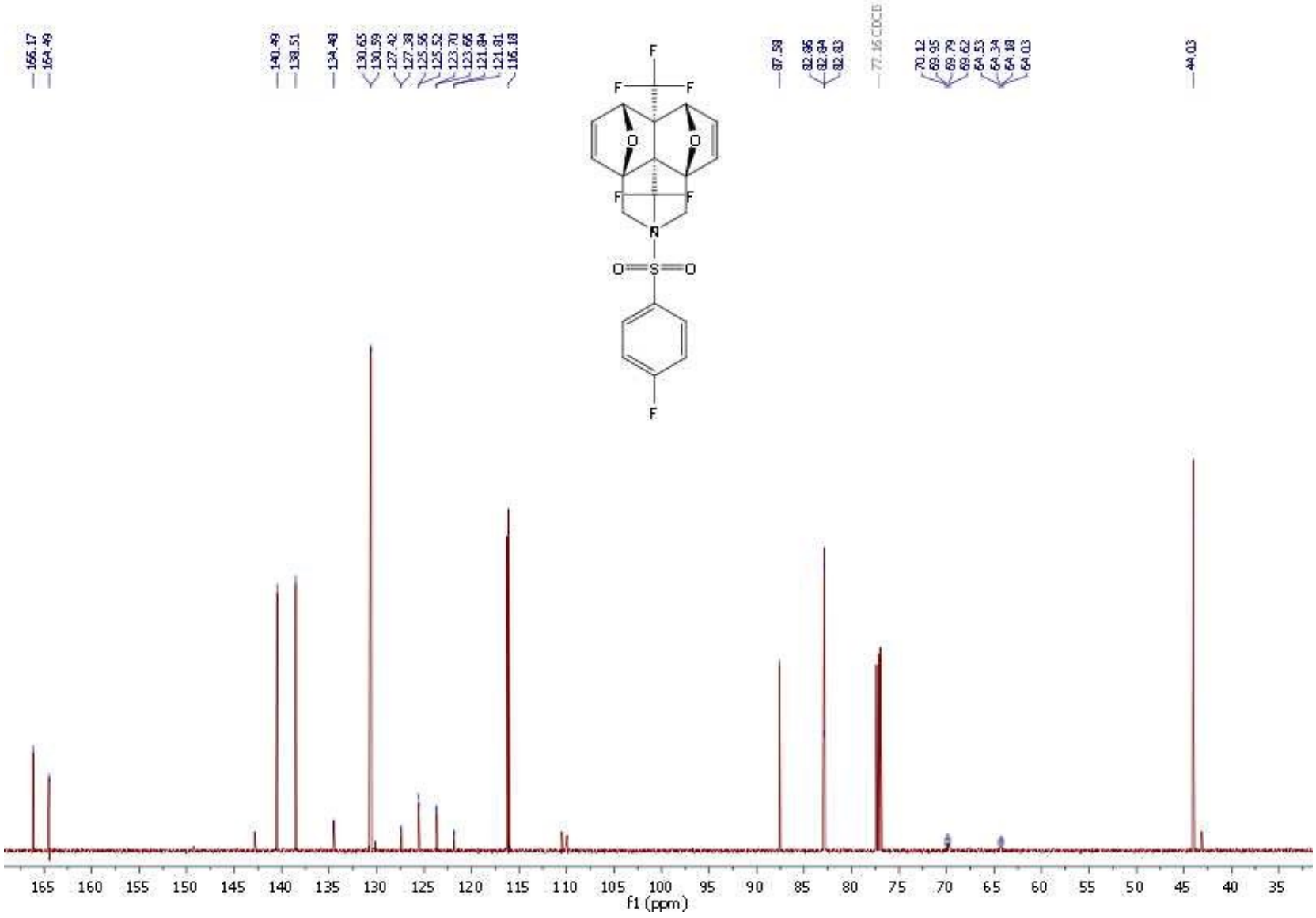
^{1}H NMR spectrum of compound (7a)



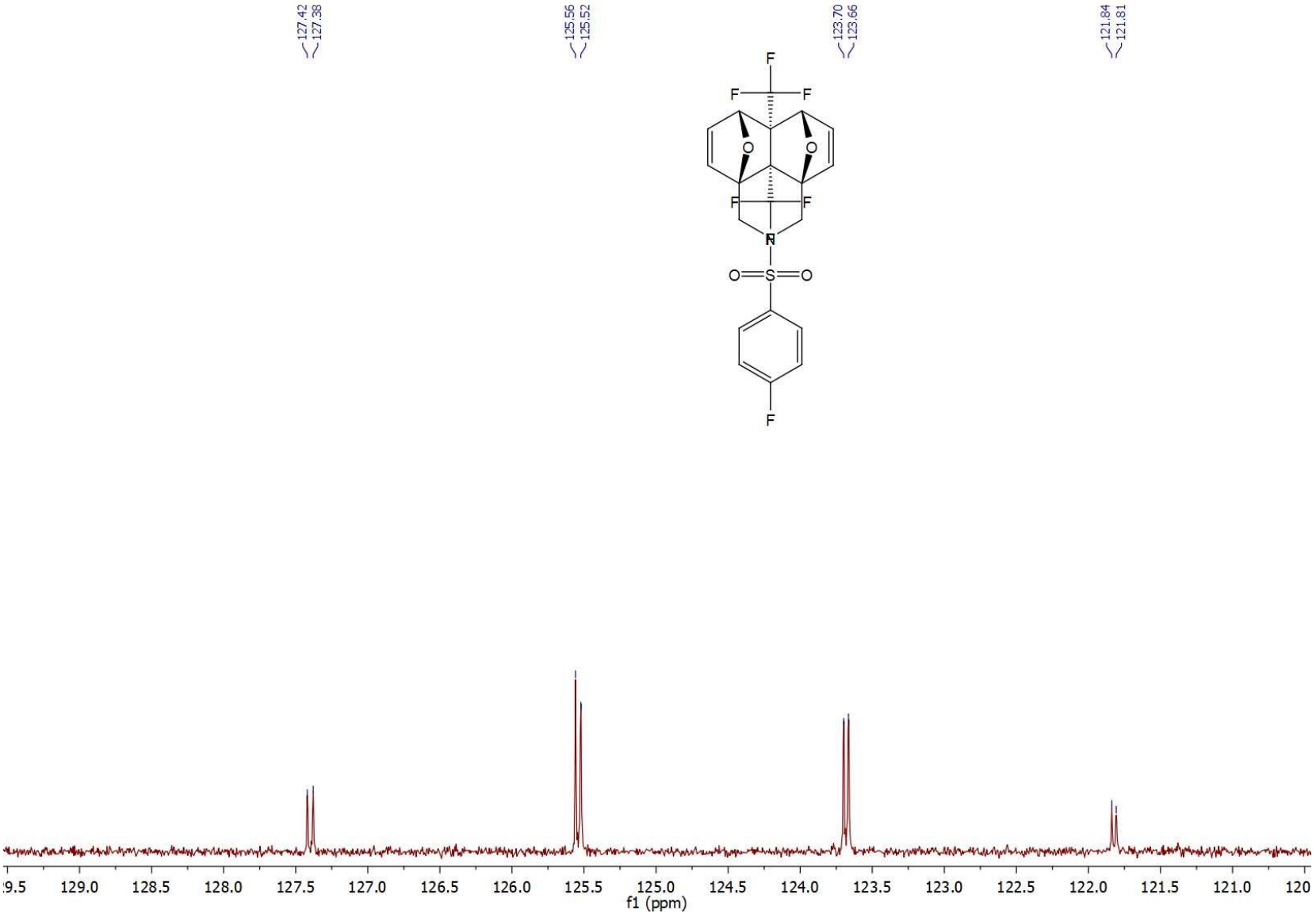
^{1}H NMR spectrum of compound (7a)



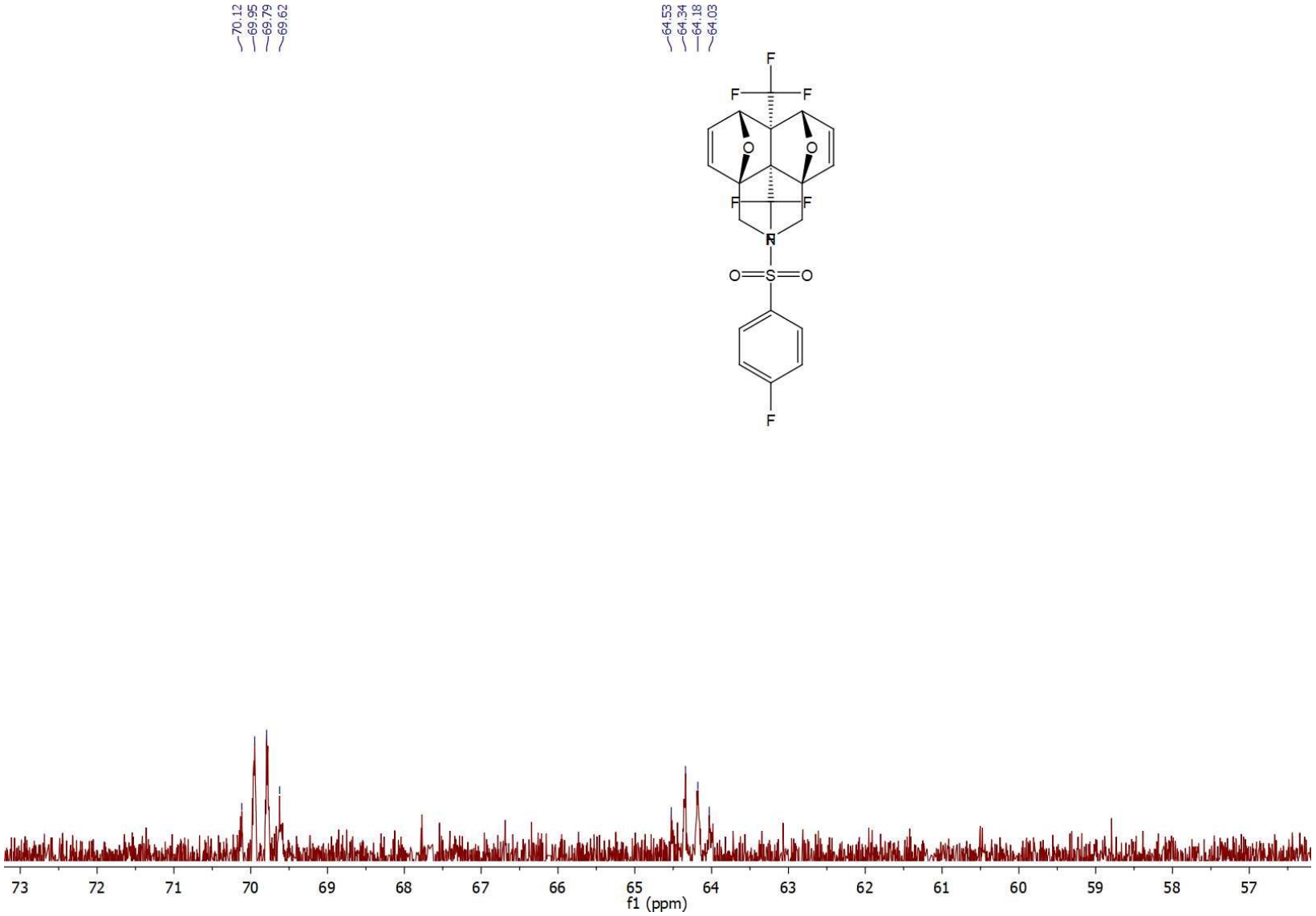
^{13}C NMR spectrum of compound (7a)



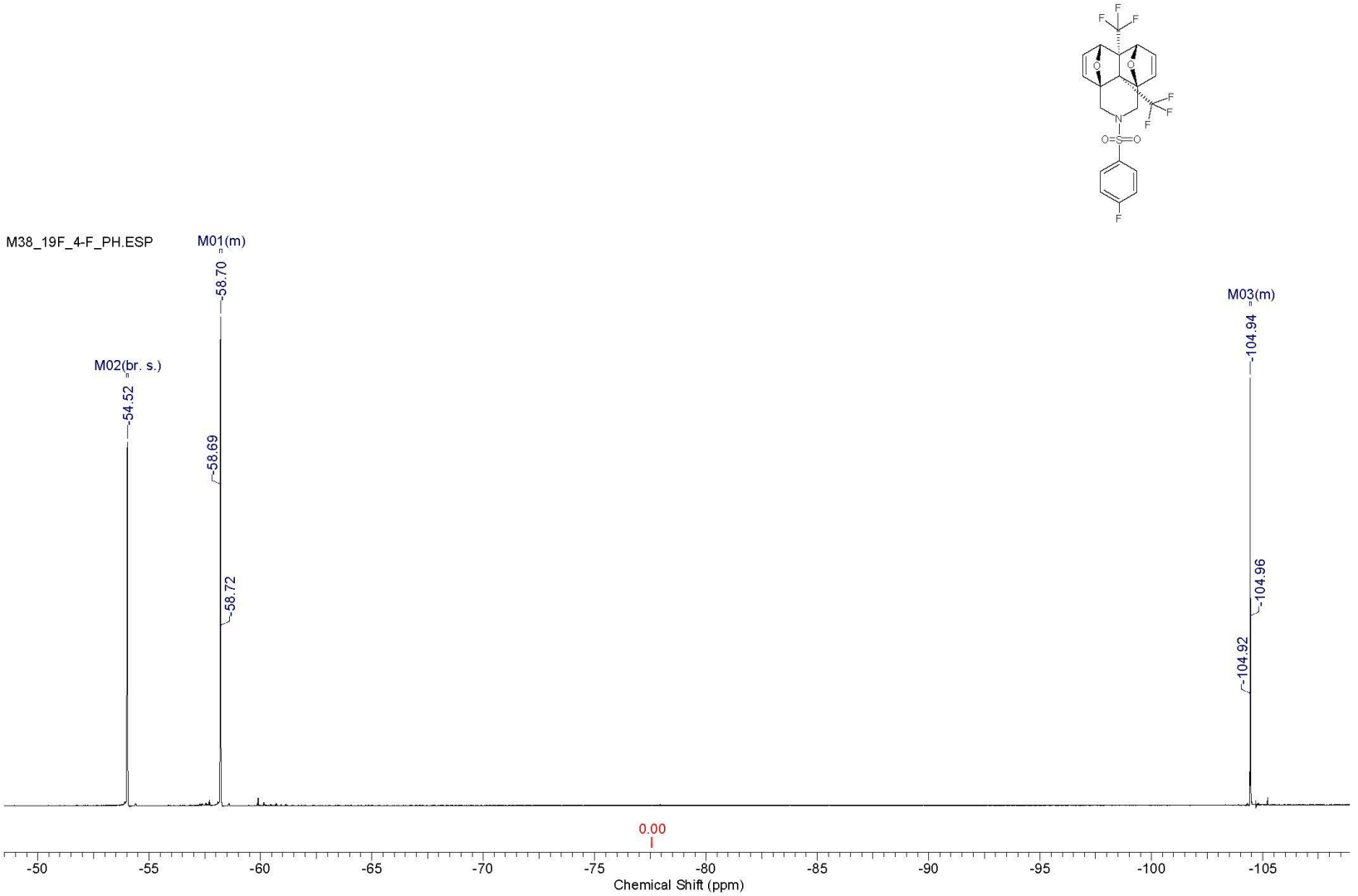
13C NMR spectrum of compound (7a)



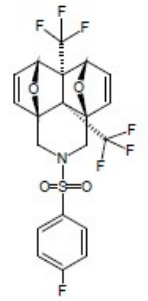
^{13}C NMR spectrum of compound (7a)

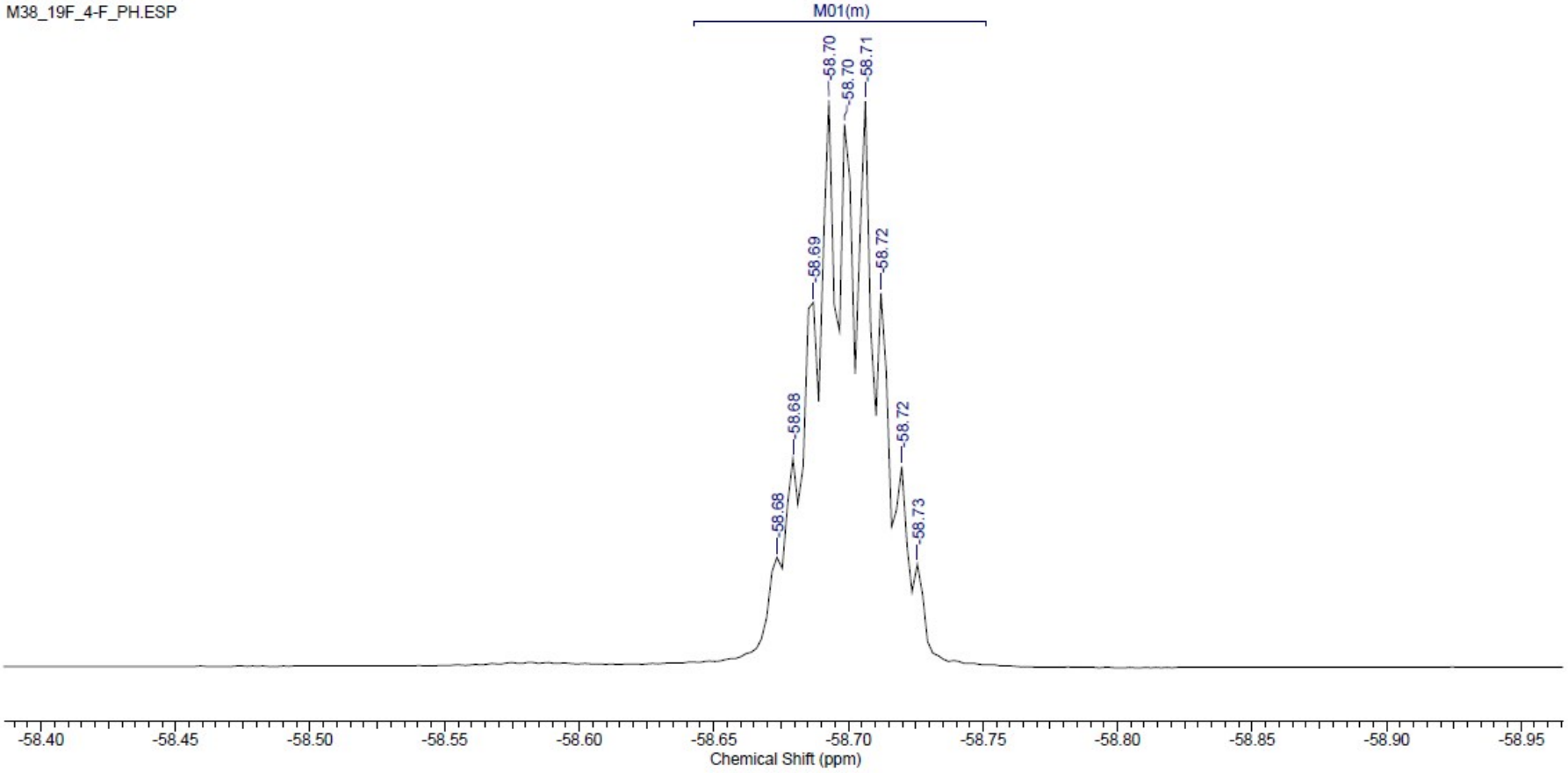


^{19}F NMR spectrum of compound (7a)

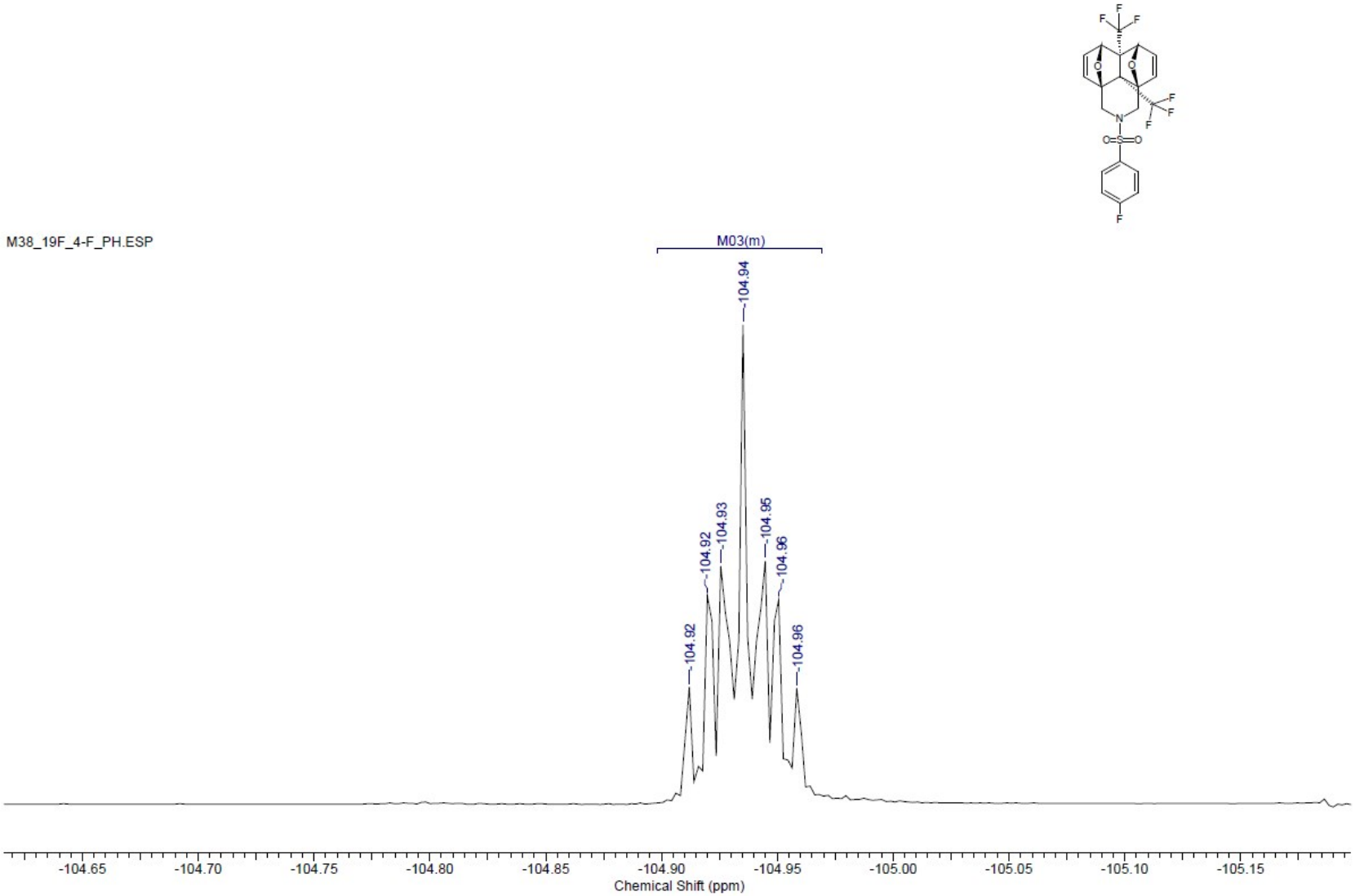


19F NMR spectrum of compound (7a)



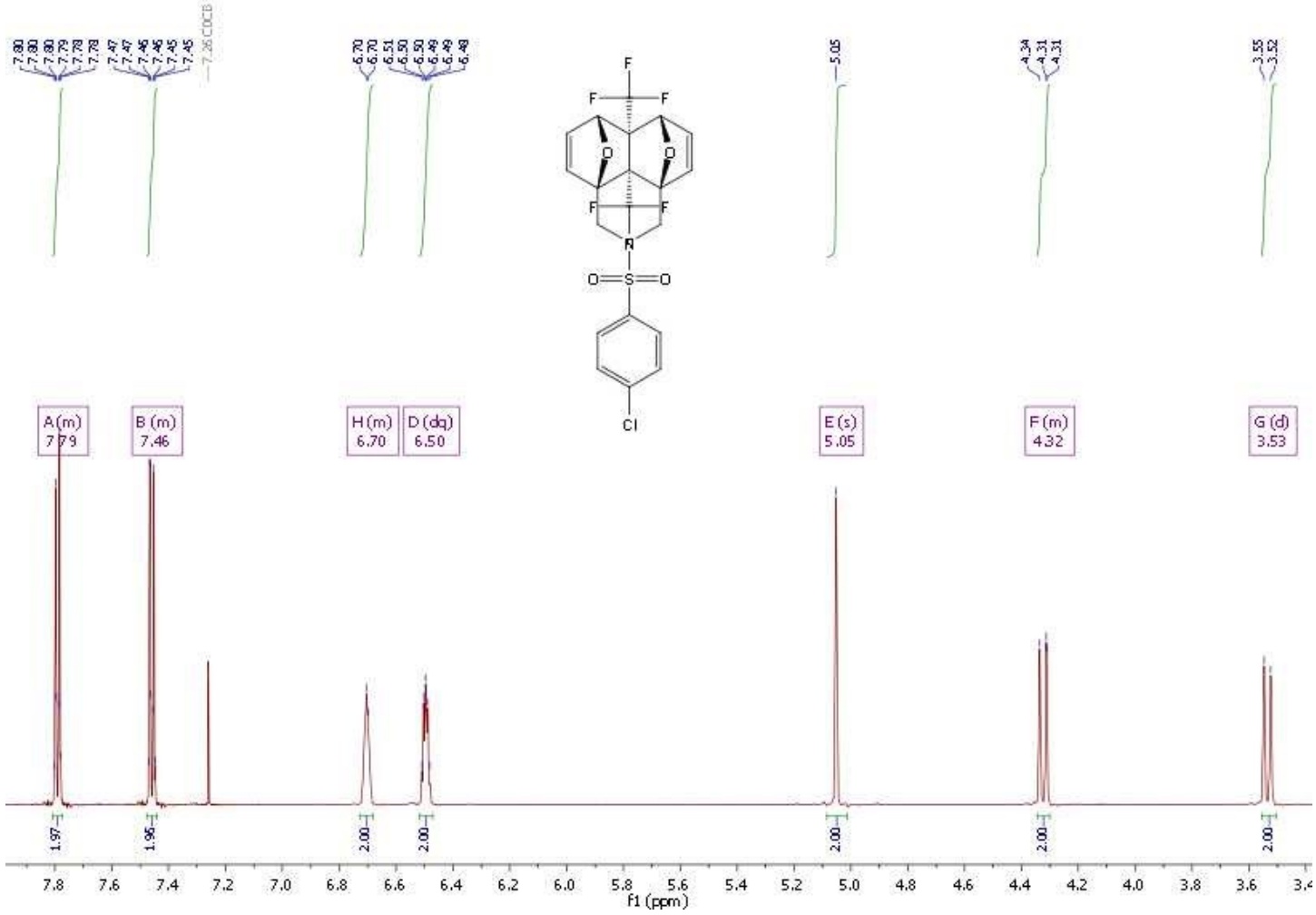


19F NMR spectrum of compound (7a)

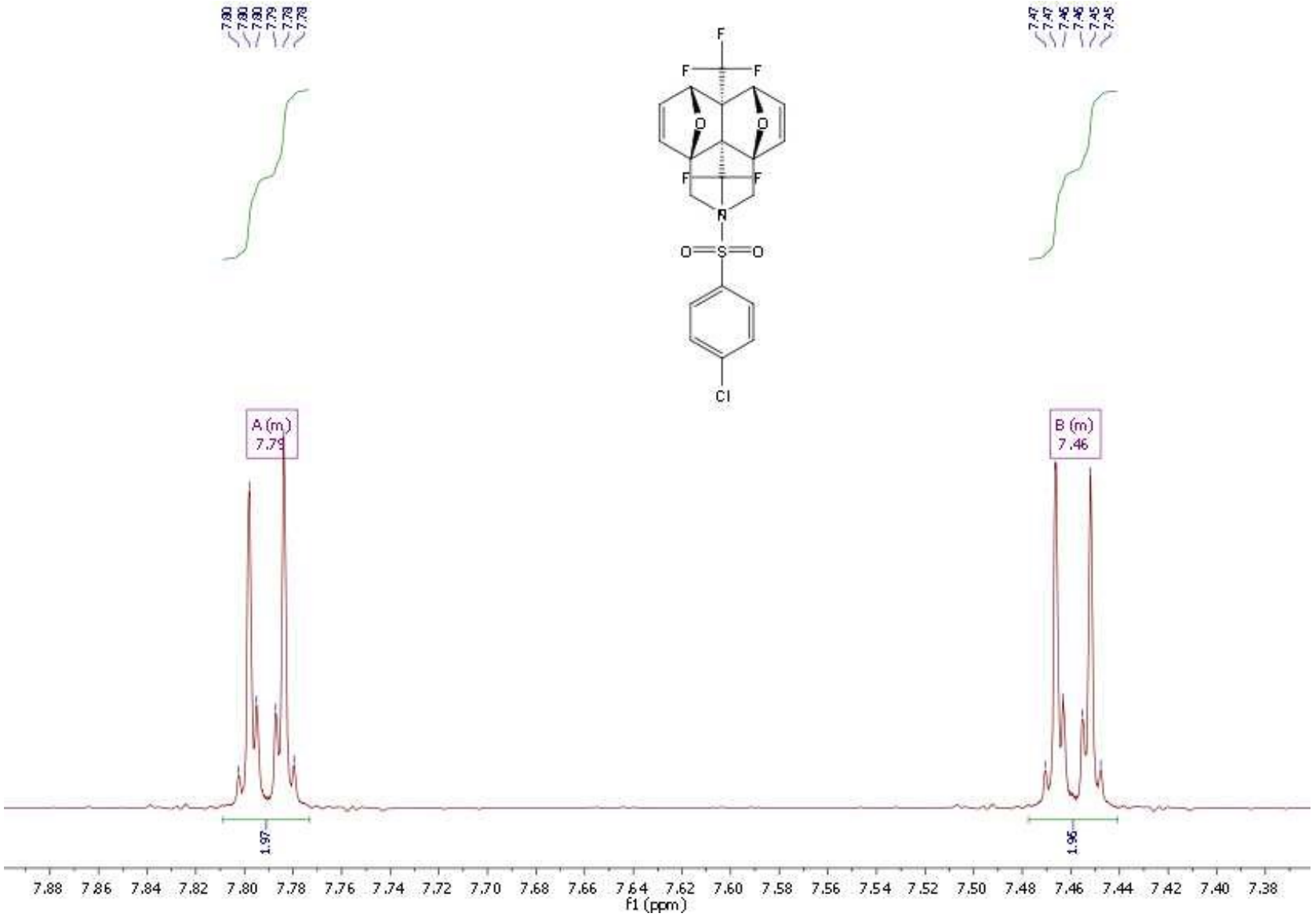


(3aRS,6SR,7RS,9aSR)-2-[(4-Chlorophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(8a)**

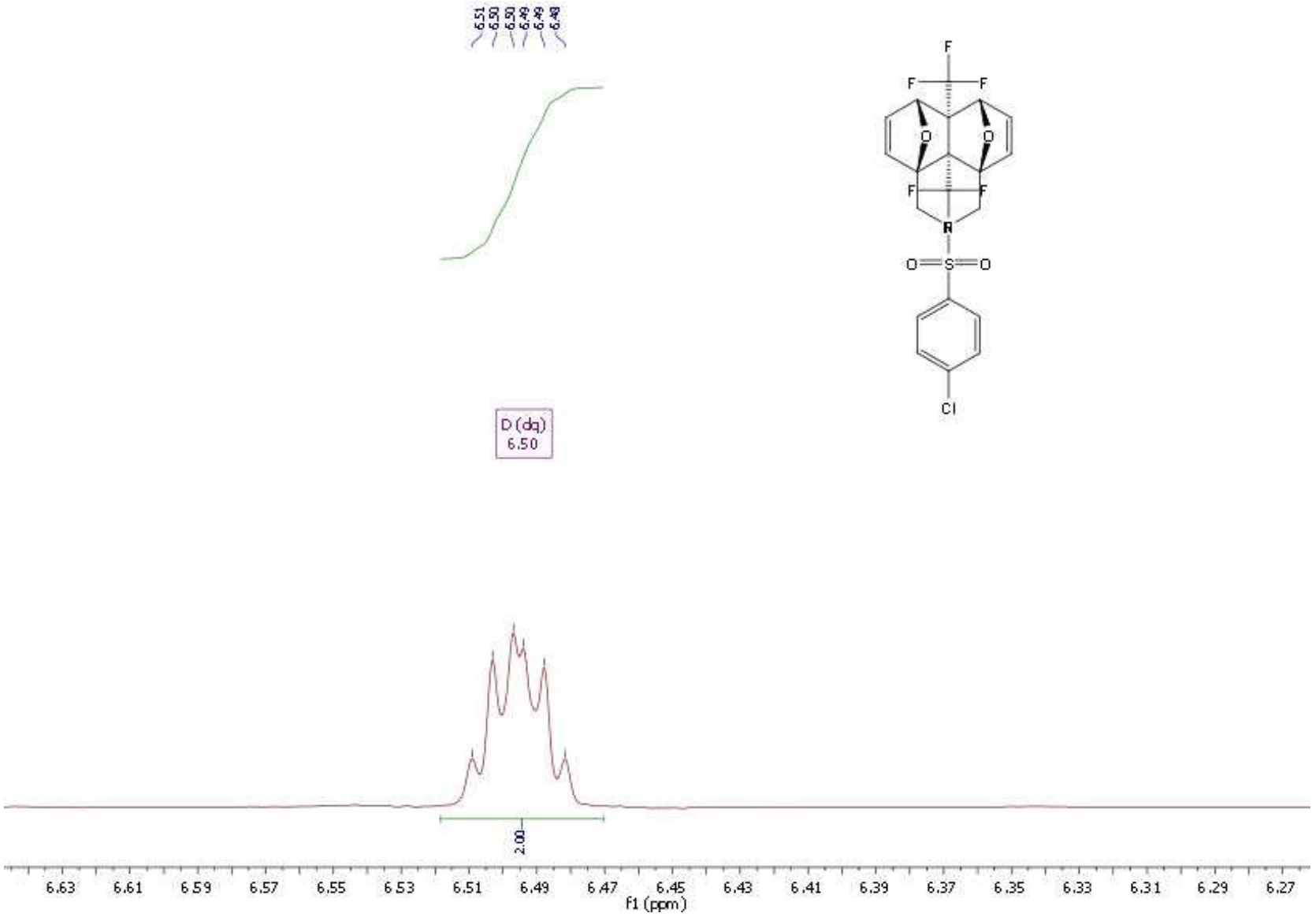
^{1}H NMR spectrum of compound (8a)



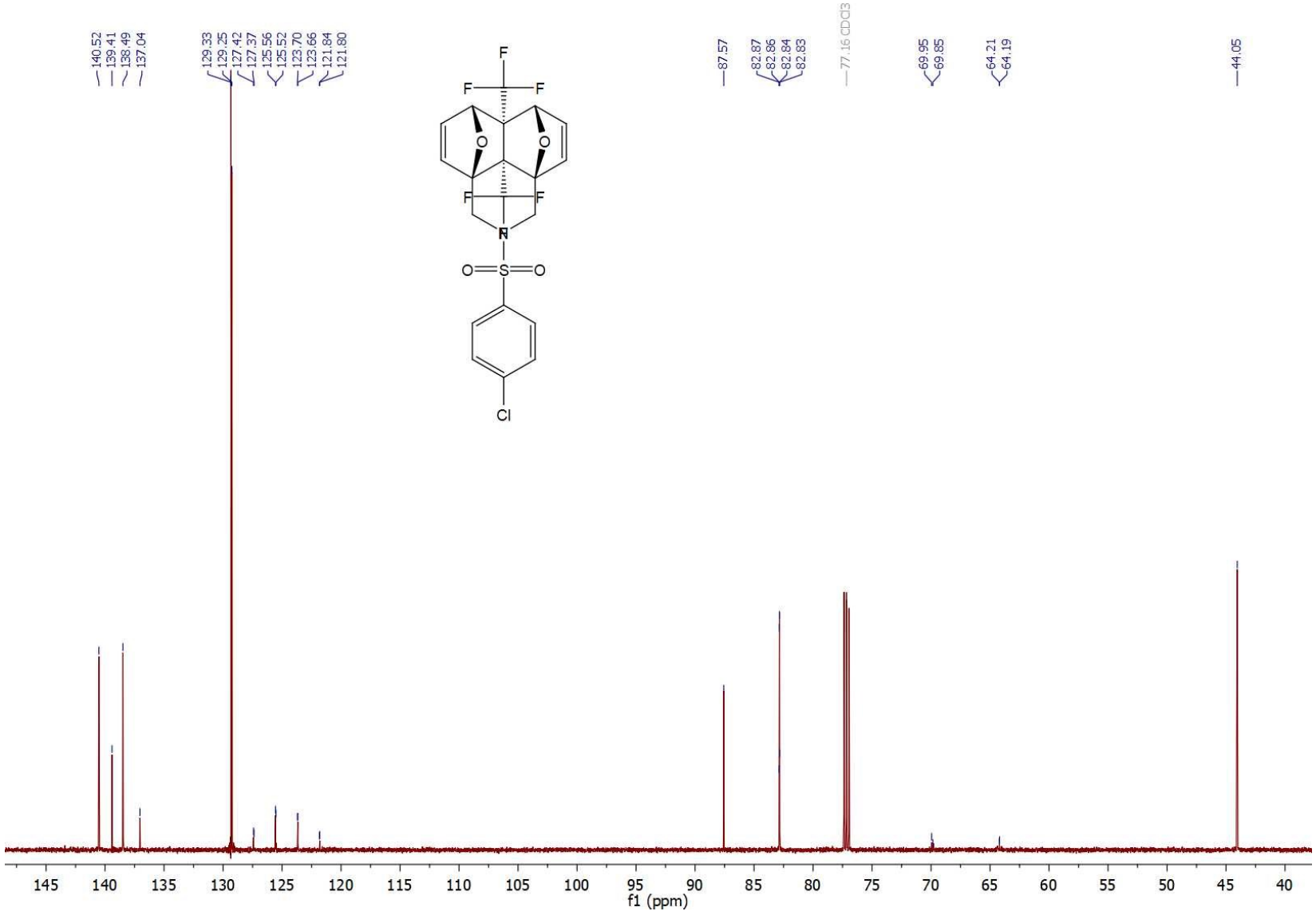
^{1}H NMR spectrum of compound (8a)



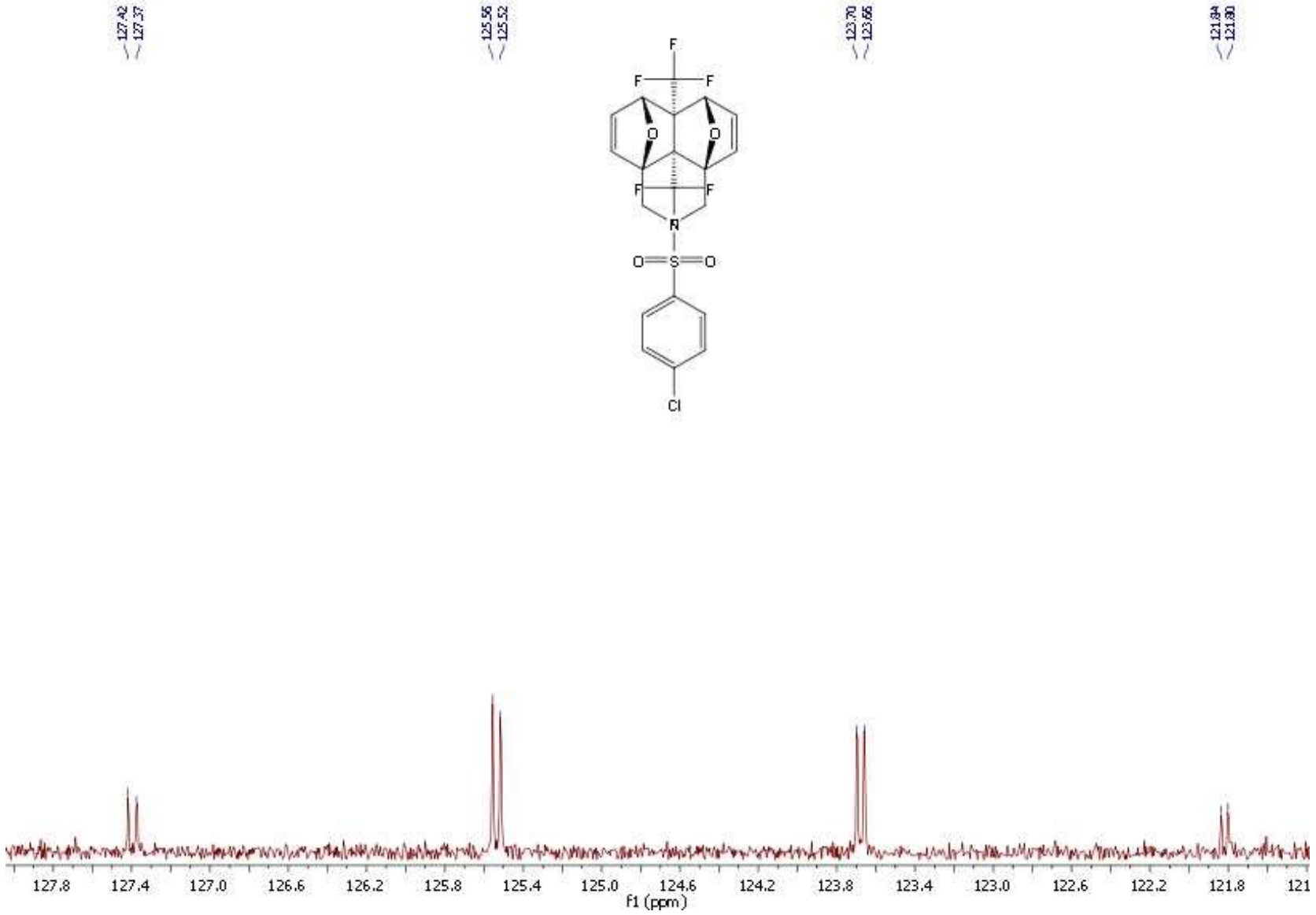
^{1}H NMR spectrum of compound (8a)



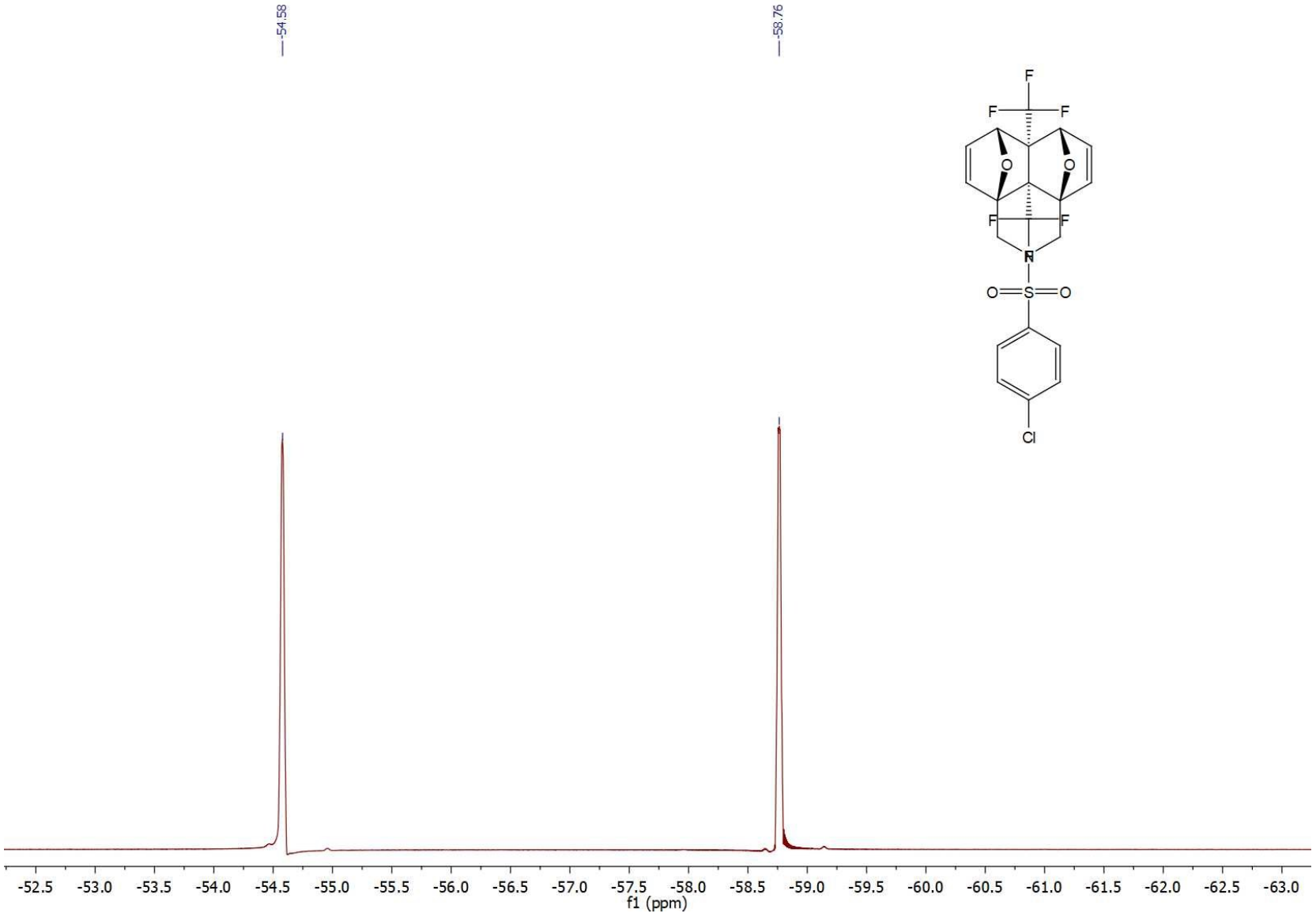
^{13}C NMR spectrum of compound (8a)



^{13}C NMR spectrum of compound (8a)

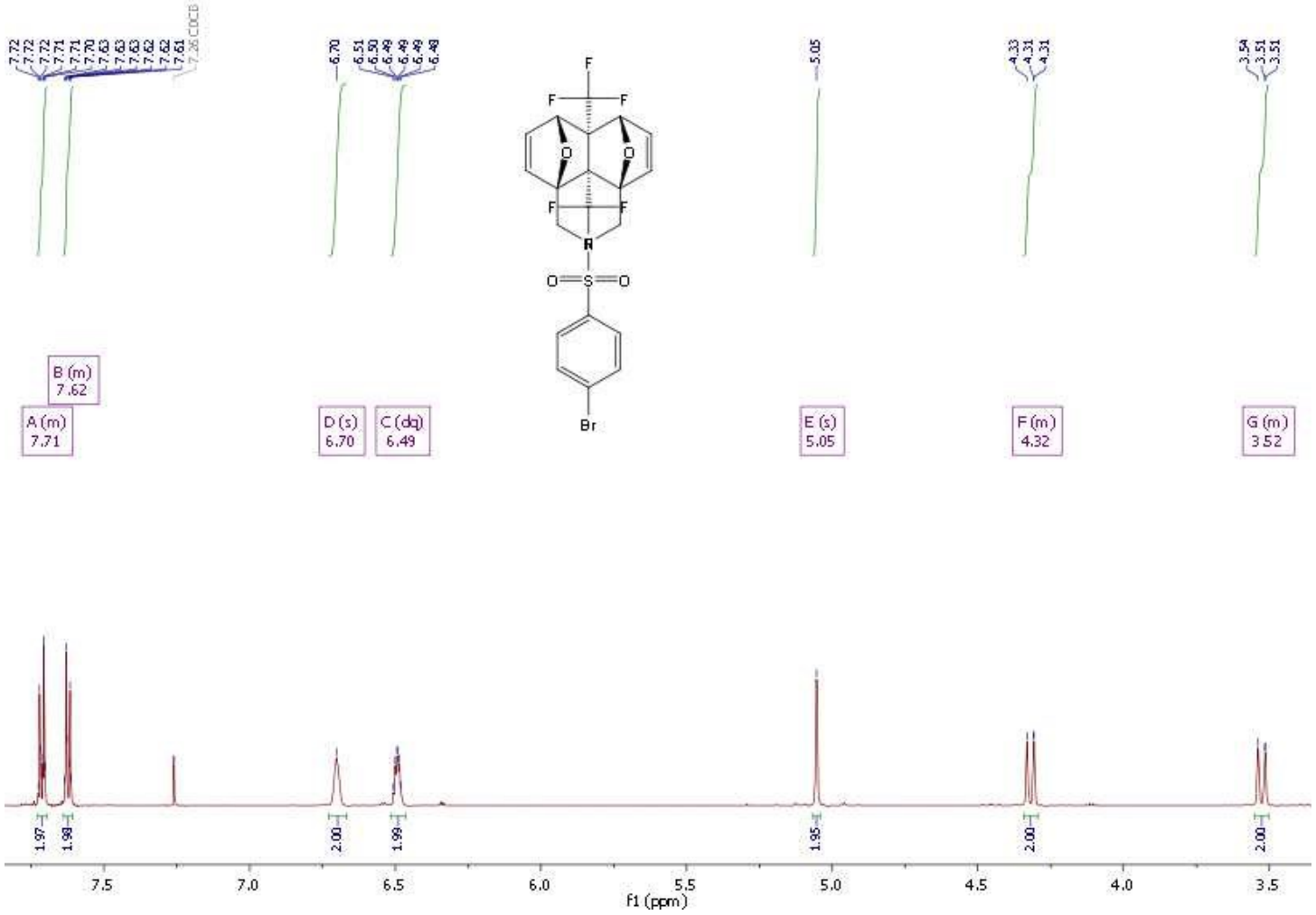


^{19}F NMR spectrum of compound (8a)

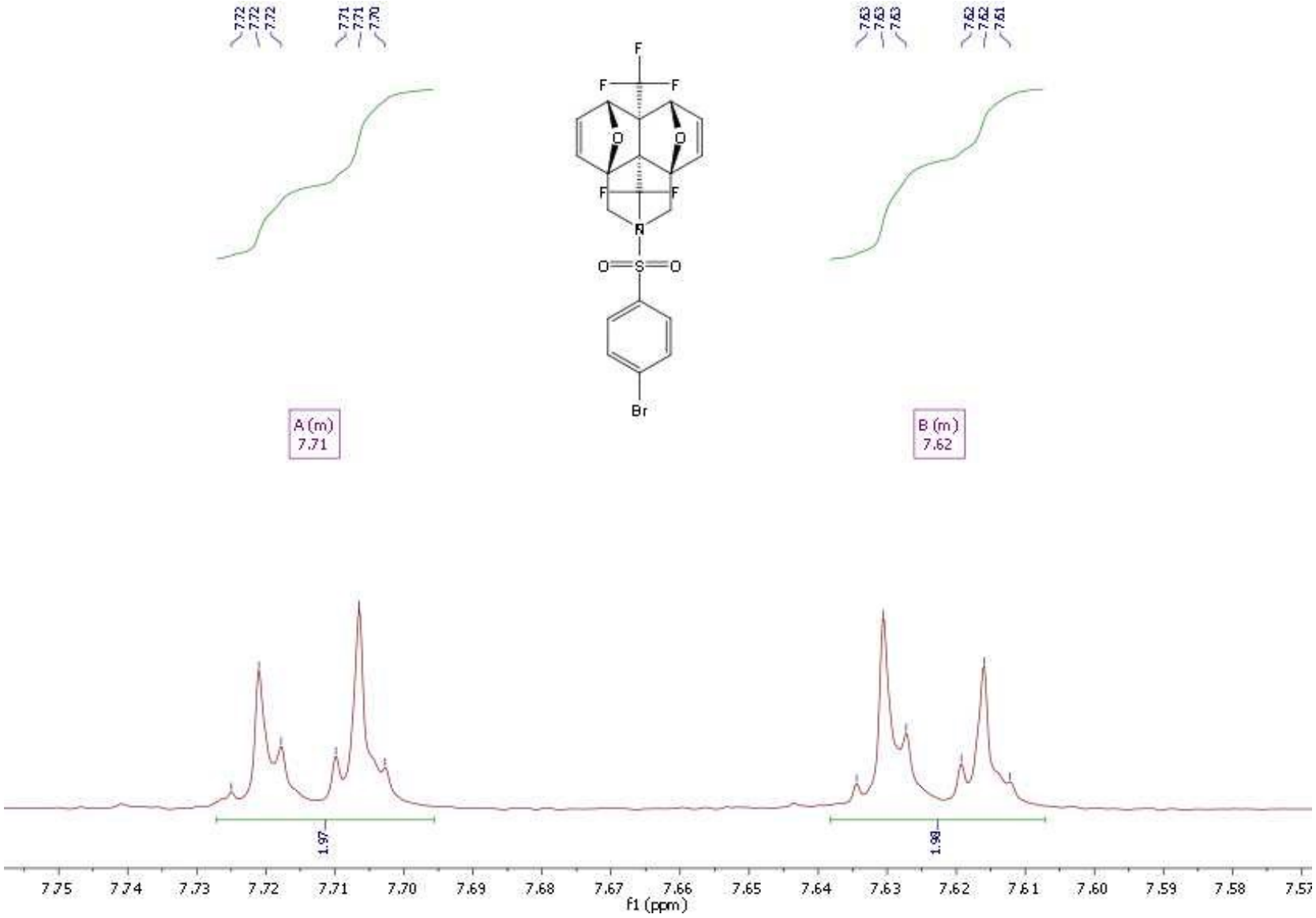


(3aRS,6SR,7RS,9aSR)-2-[(4-Bromophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(9a)**

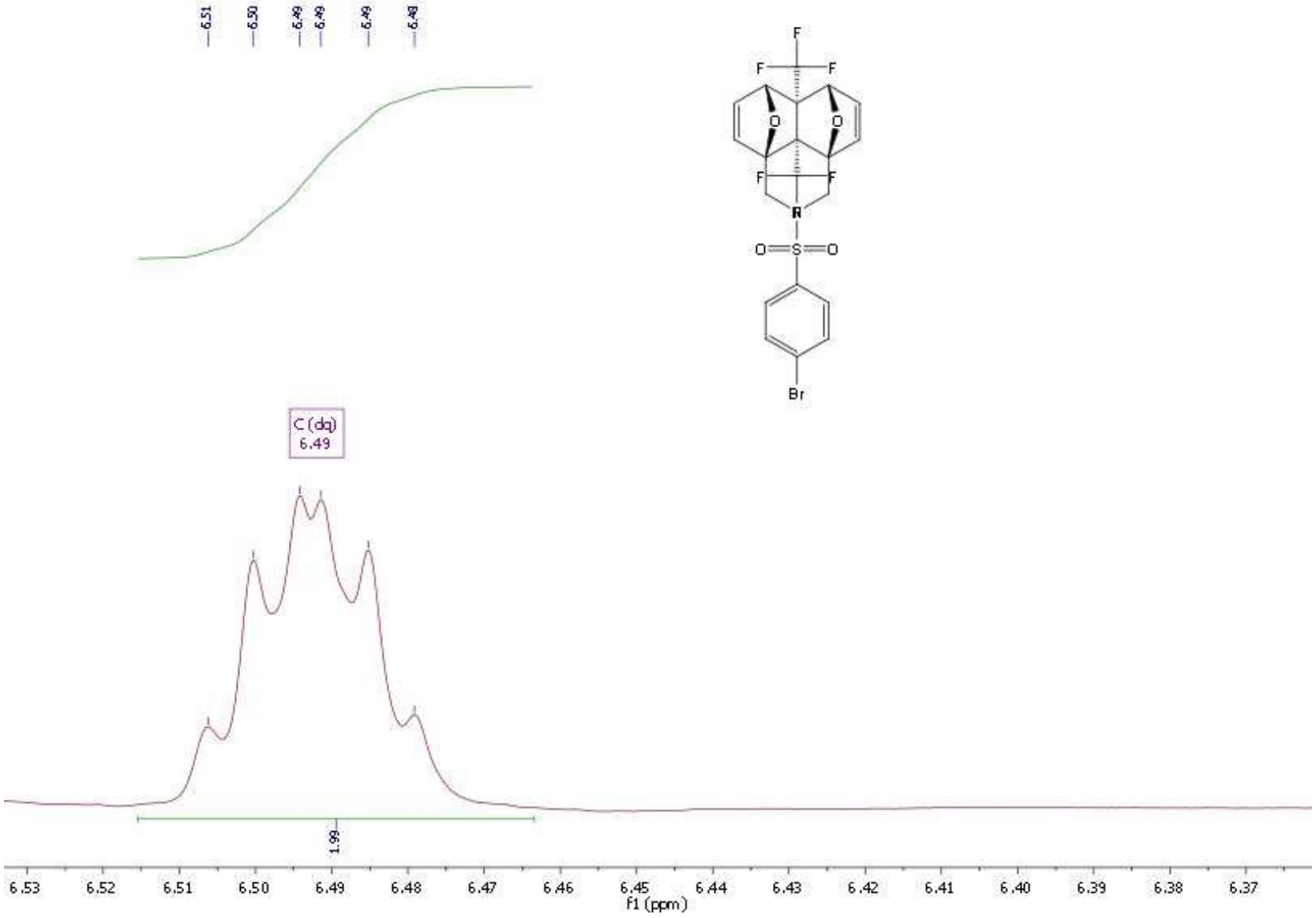
^{1}H NMR spectrum of compound (9a)



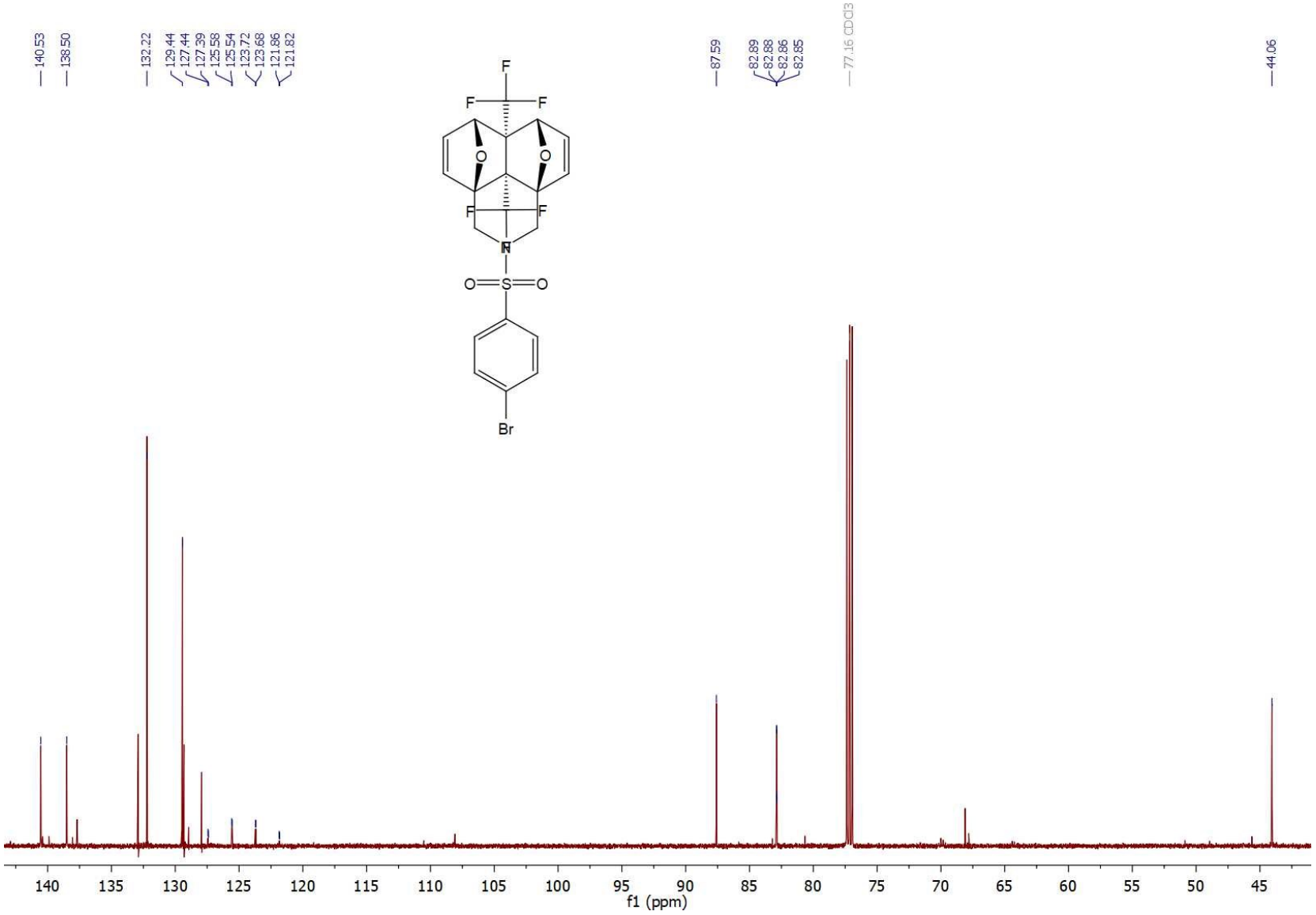
^{1}H NMR spectrum of compound (9a)



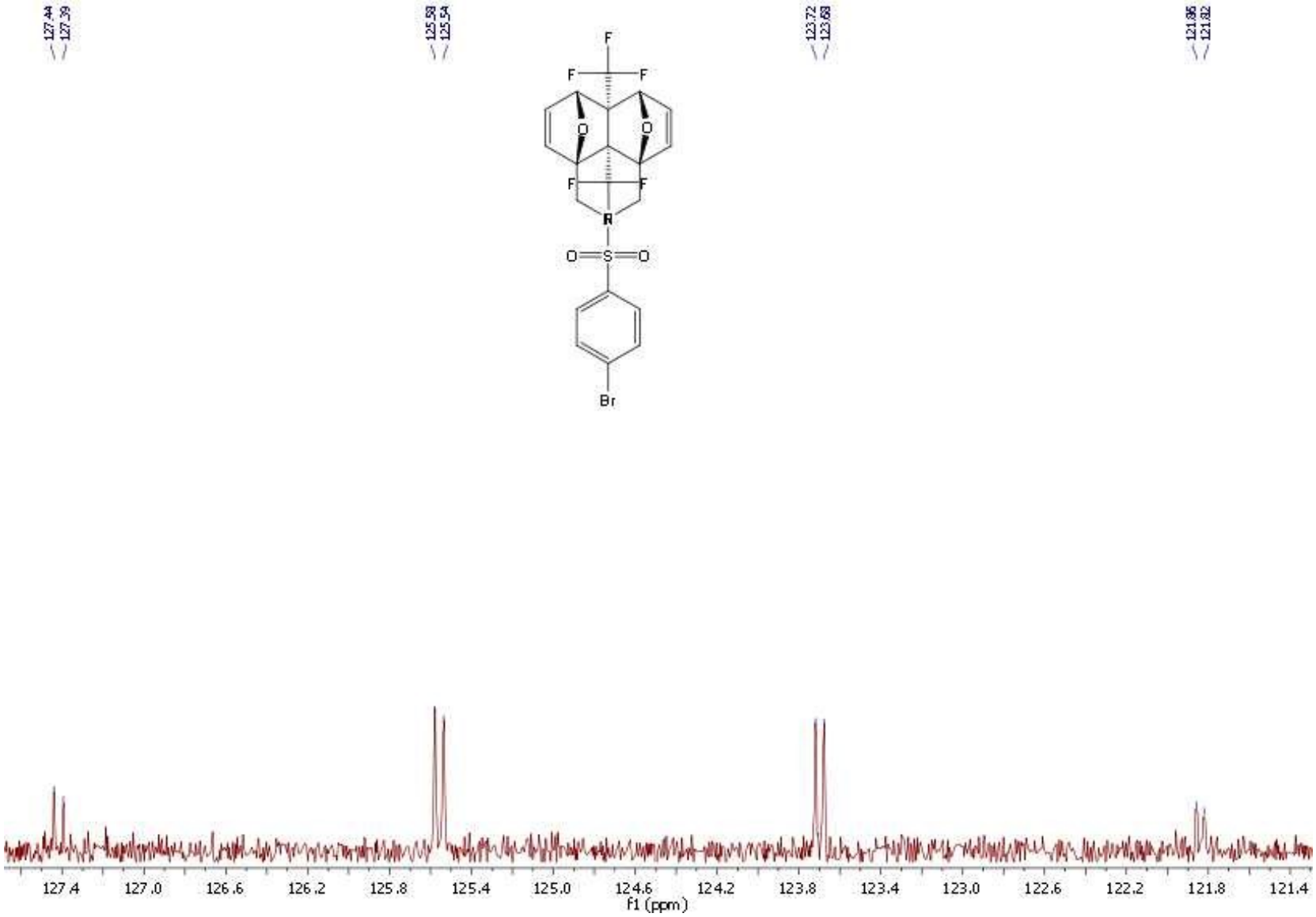
^{1}H NMR spectrum of compound (9a)



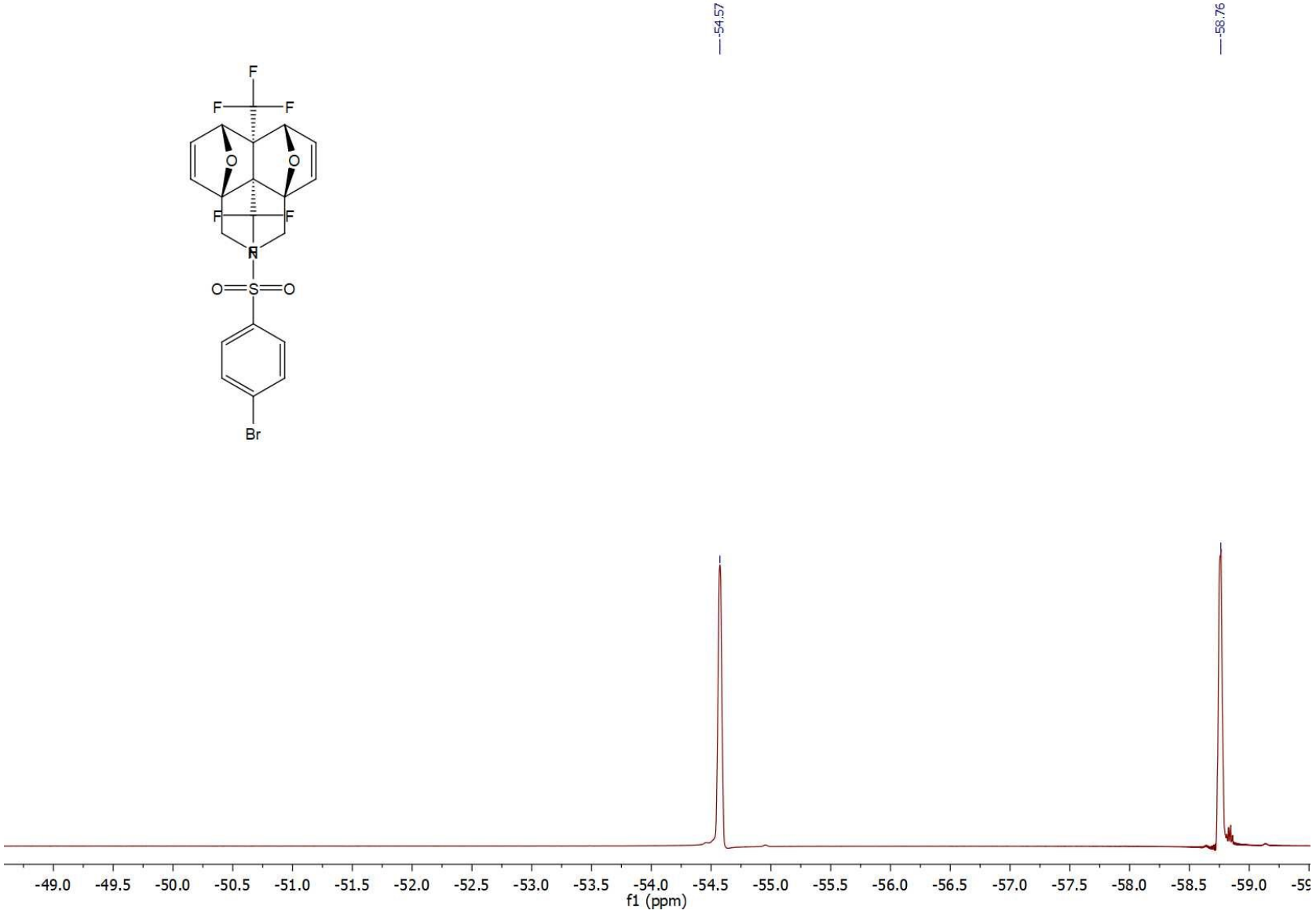
^{13}C NMR spectrum of compound (9a)



^{13}C NMR spectrum of compound (9a)

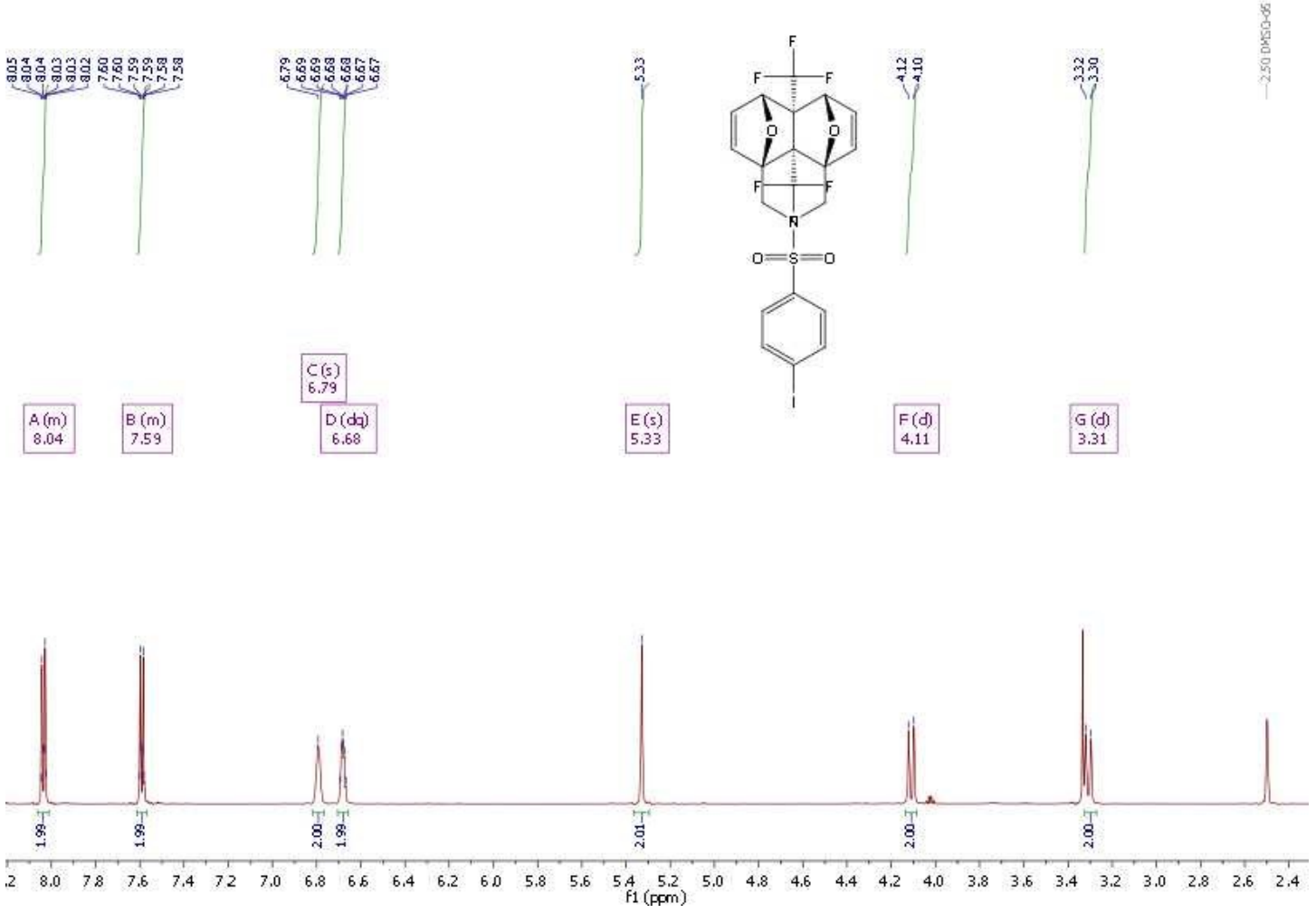


^{19}F NMR spectrum of compound (9a)

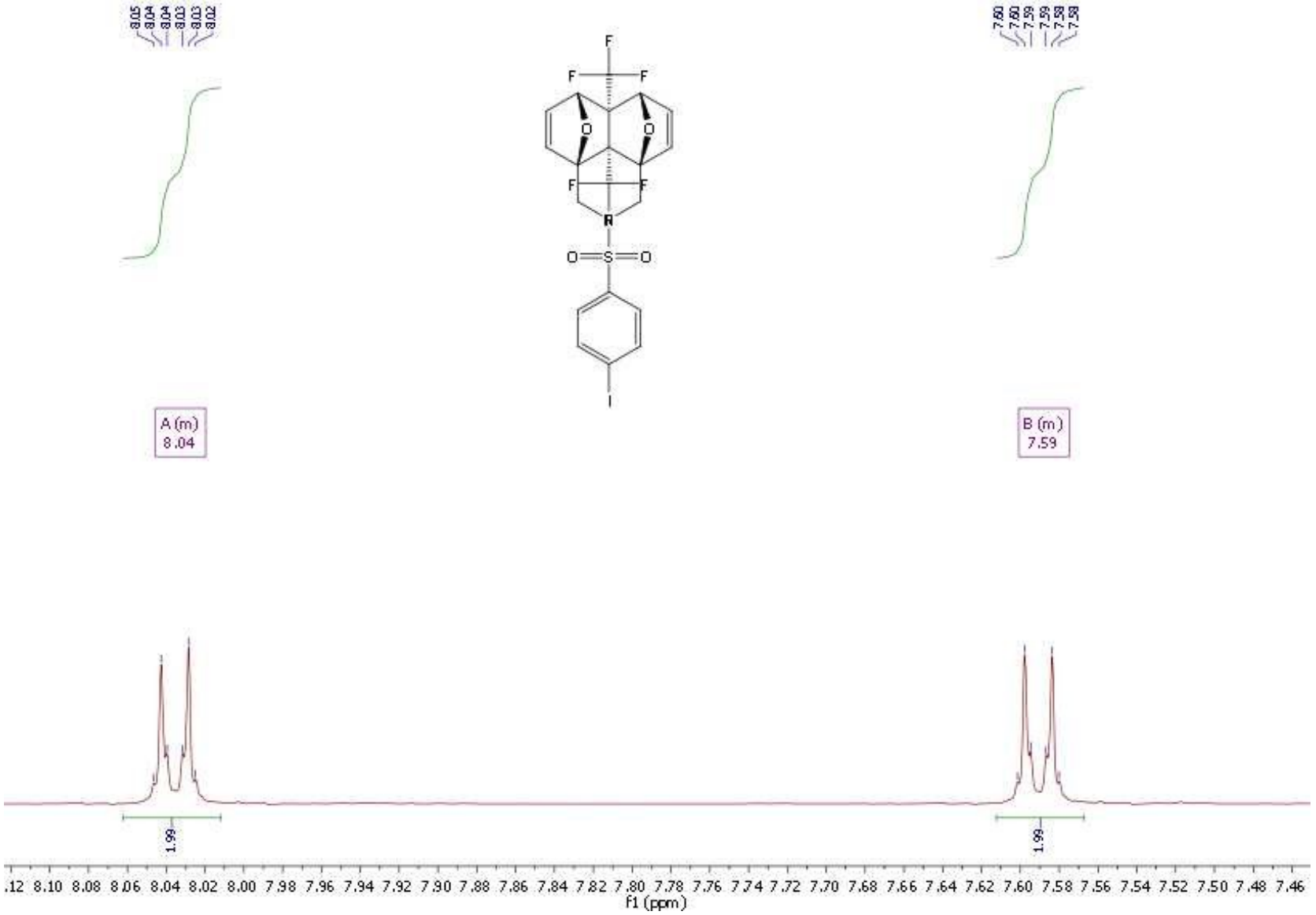


(3aRS,6SR,7RS,9aSR)-2-[(4-Iodophenyl)sulfonyl]-6a,9b-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(10a)**

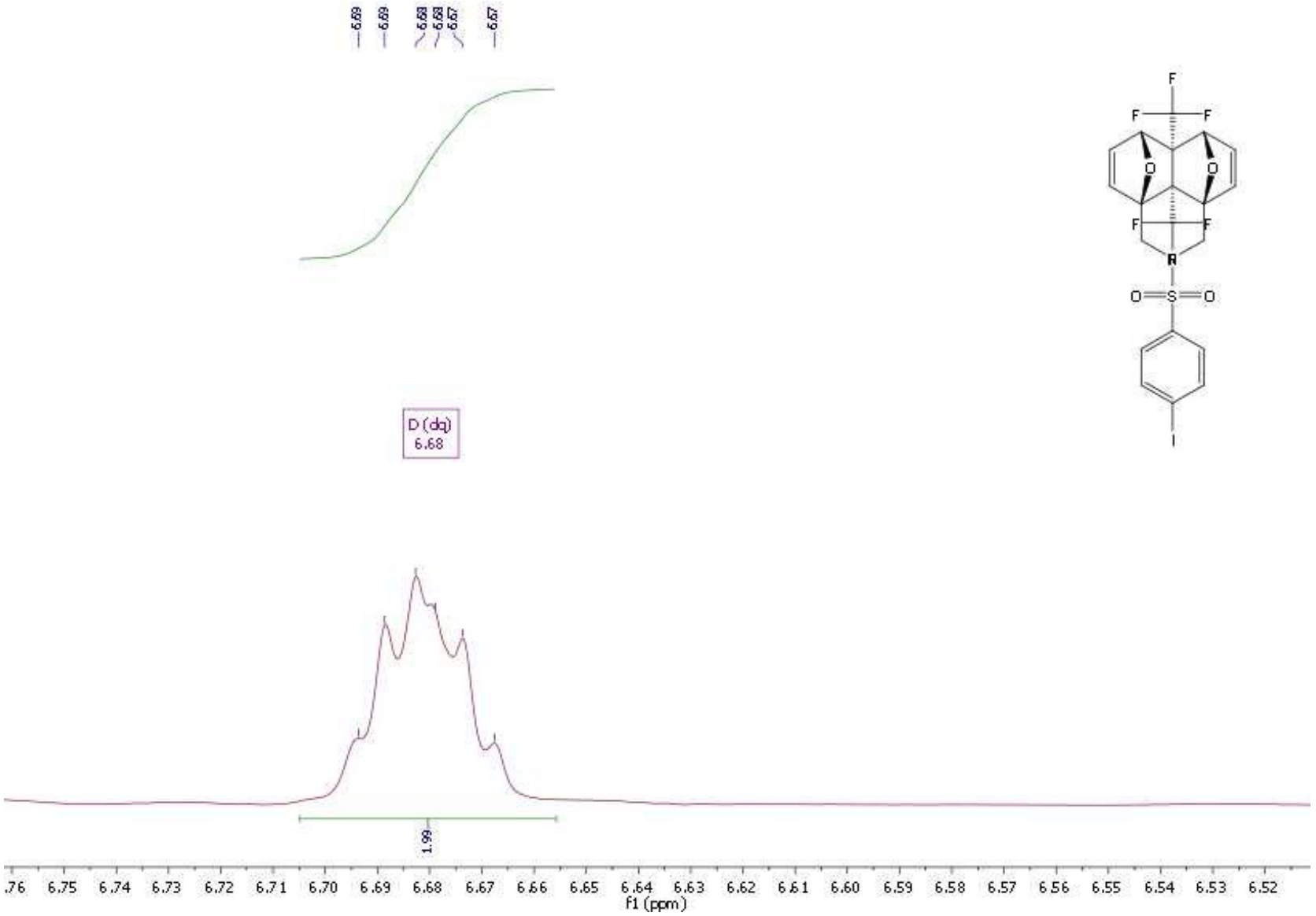
^{1}H NMR spectrum of compound (10a)



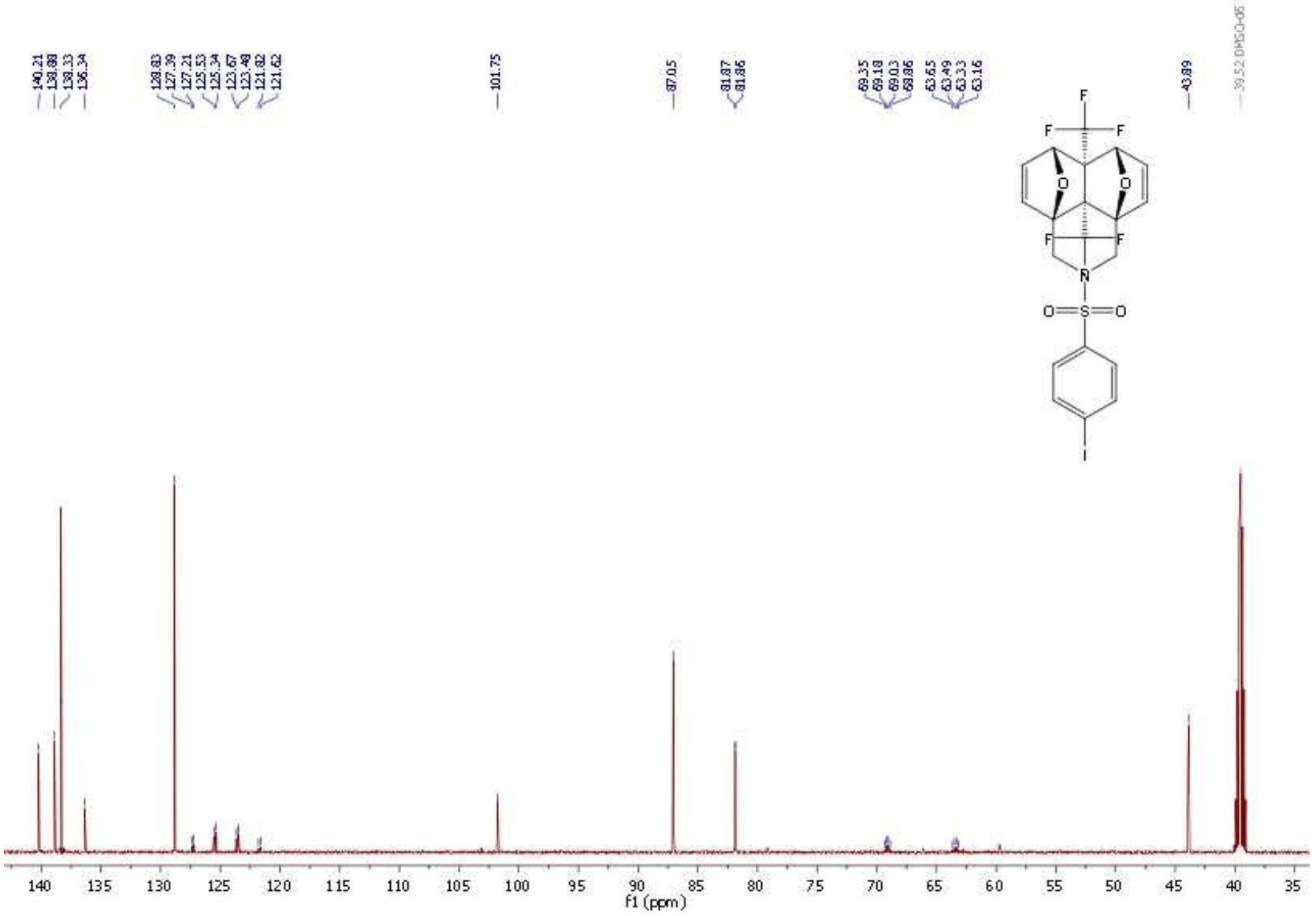
^{1}H NMR spectrum of compound (10a)



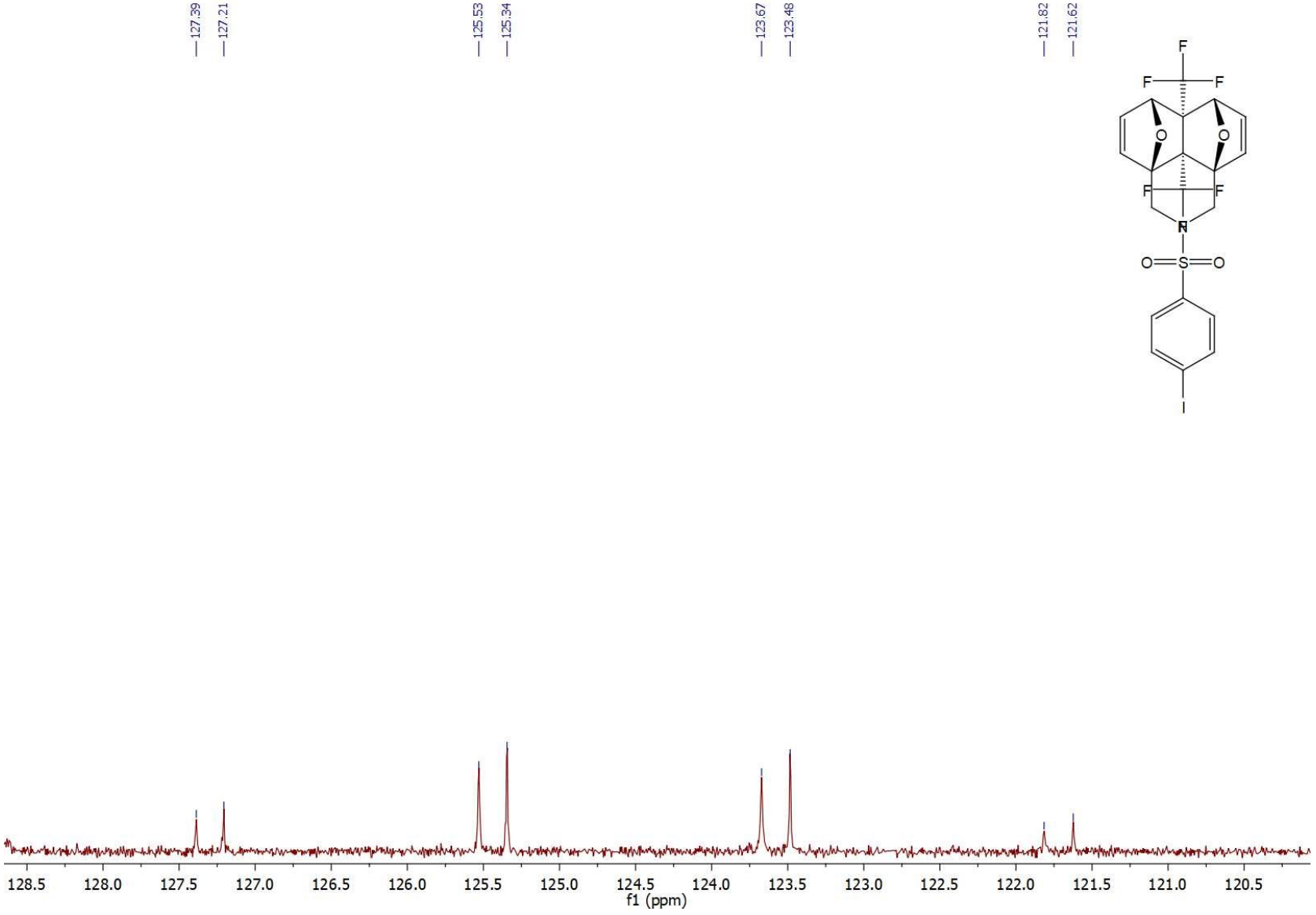
^{1}H NMR spectrum of compound (10a)



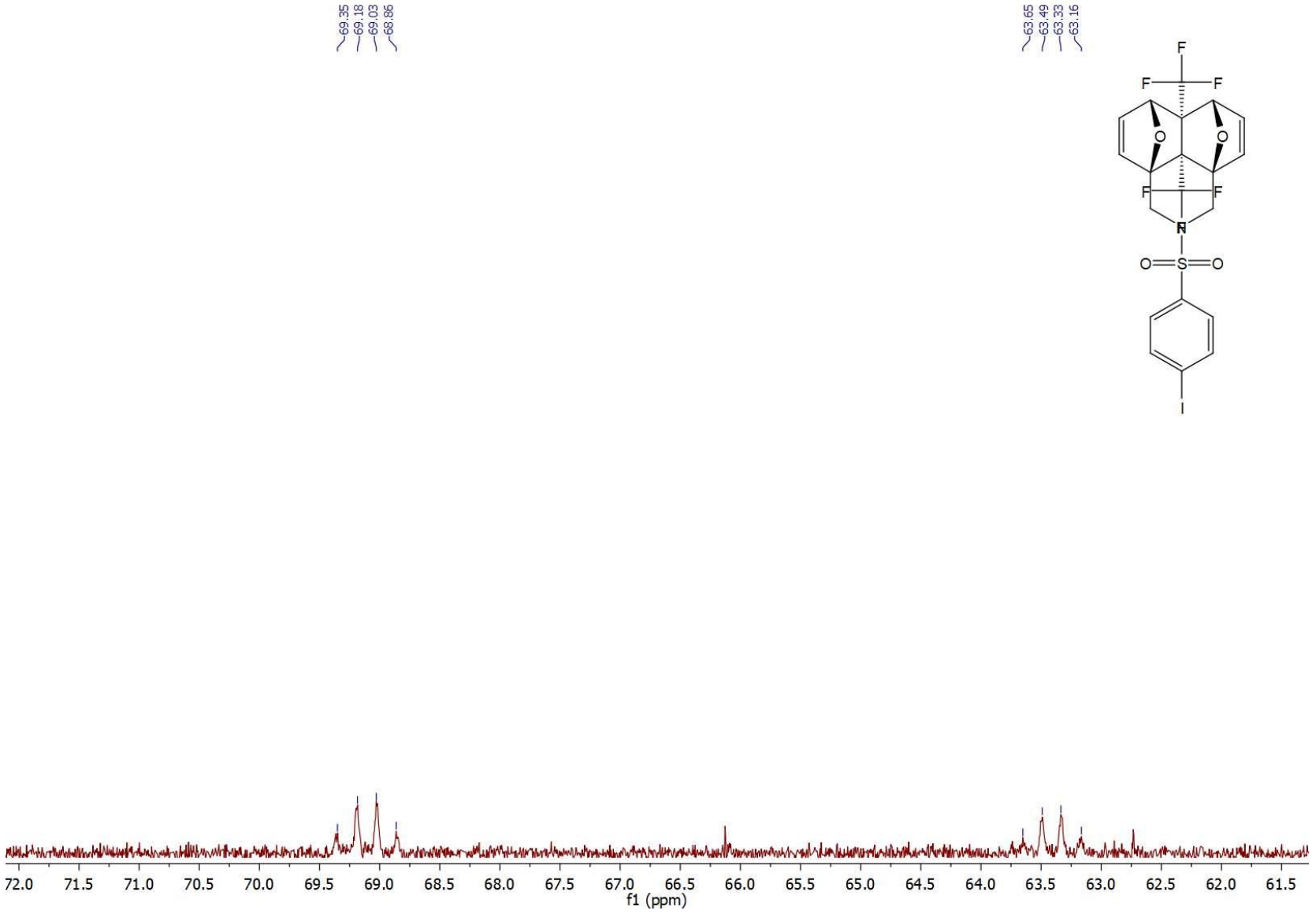
^{13}C NMR spectrum of compound (10a)



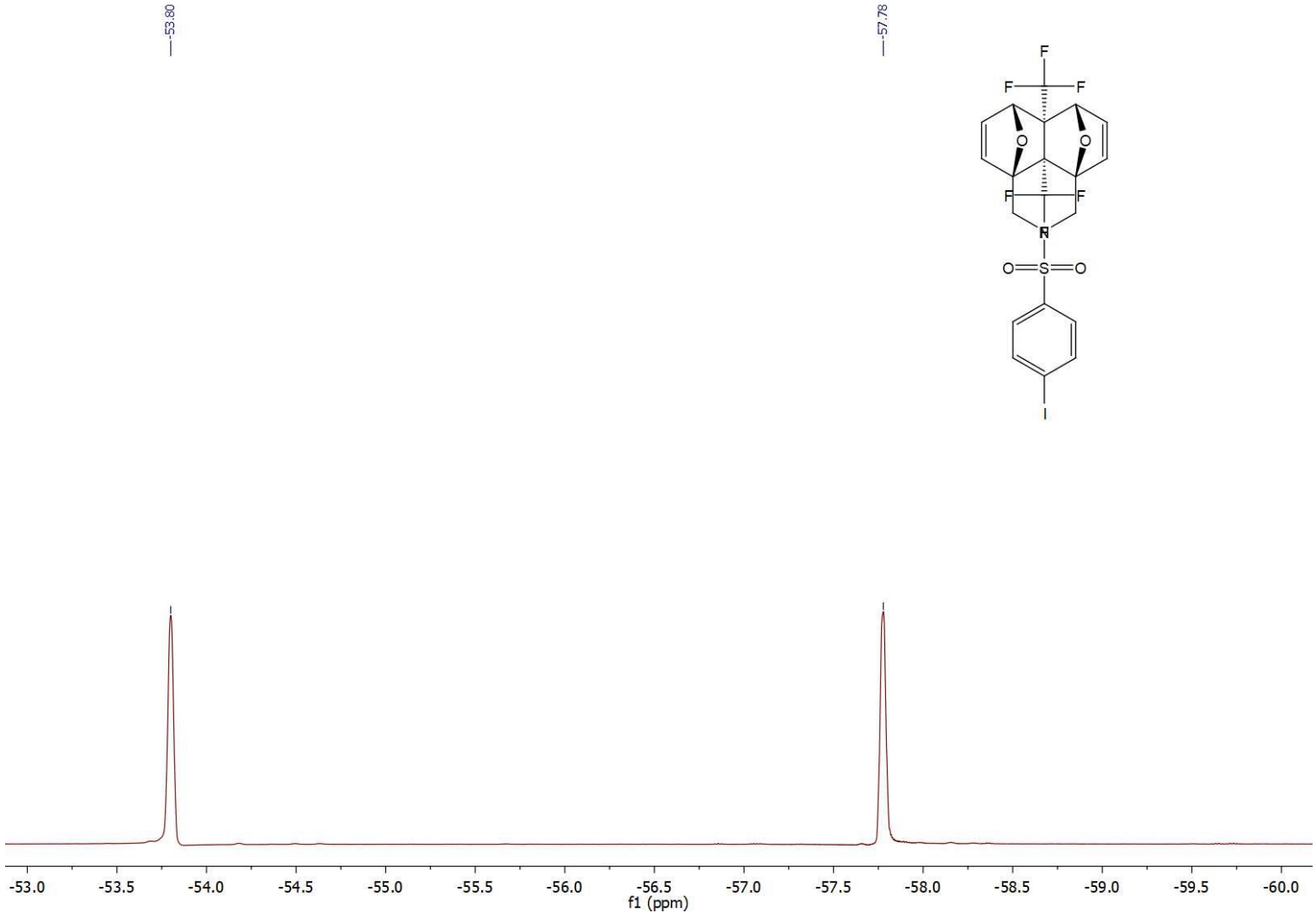
^{13}C NMR spectrum of compound (10a)



^{13}C NMR spectrum of compound (10a)

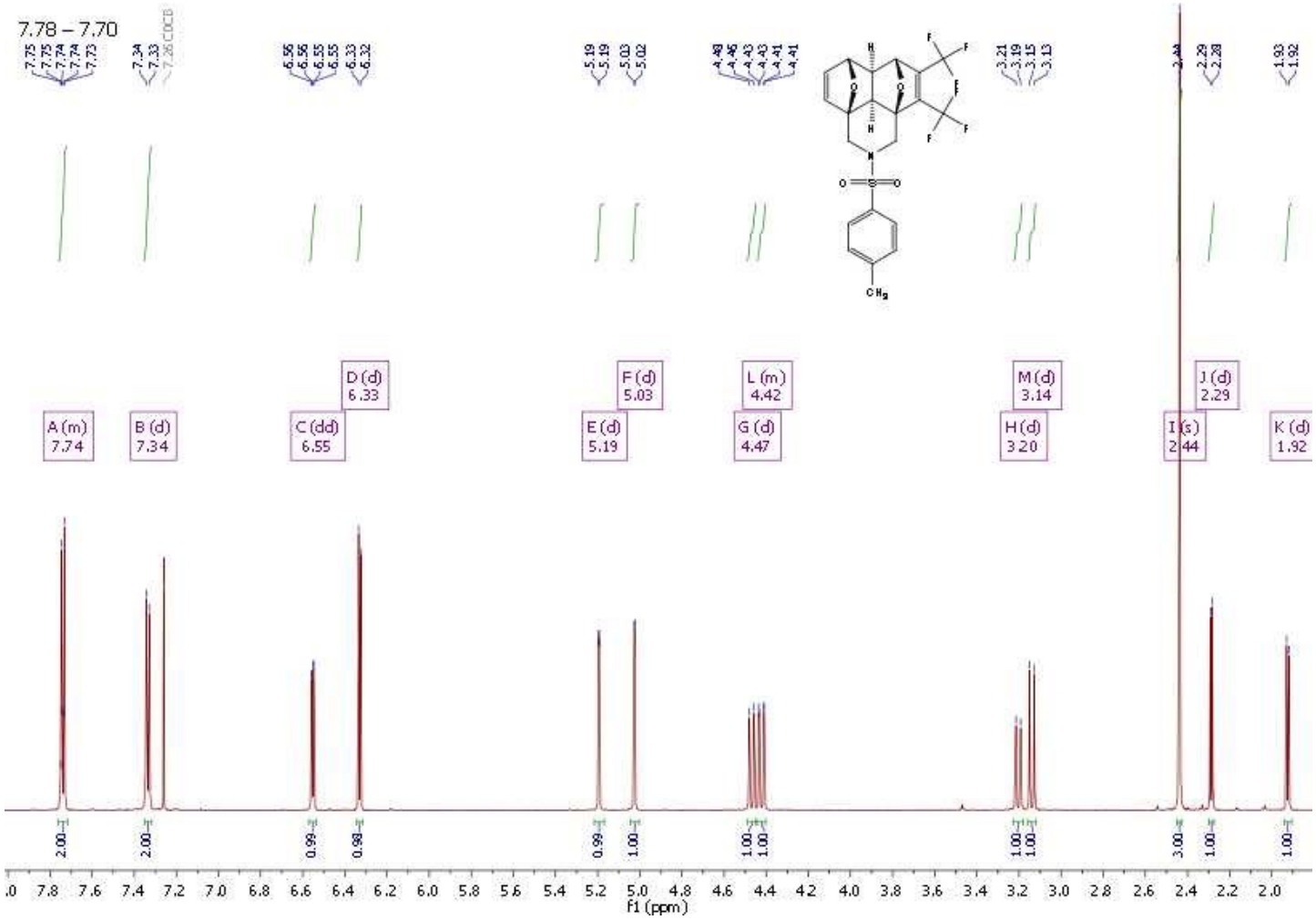


^{19}F NMR spectrum of compound (10a)

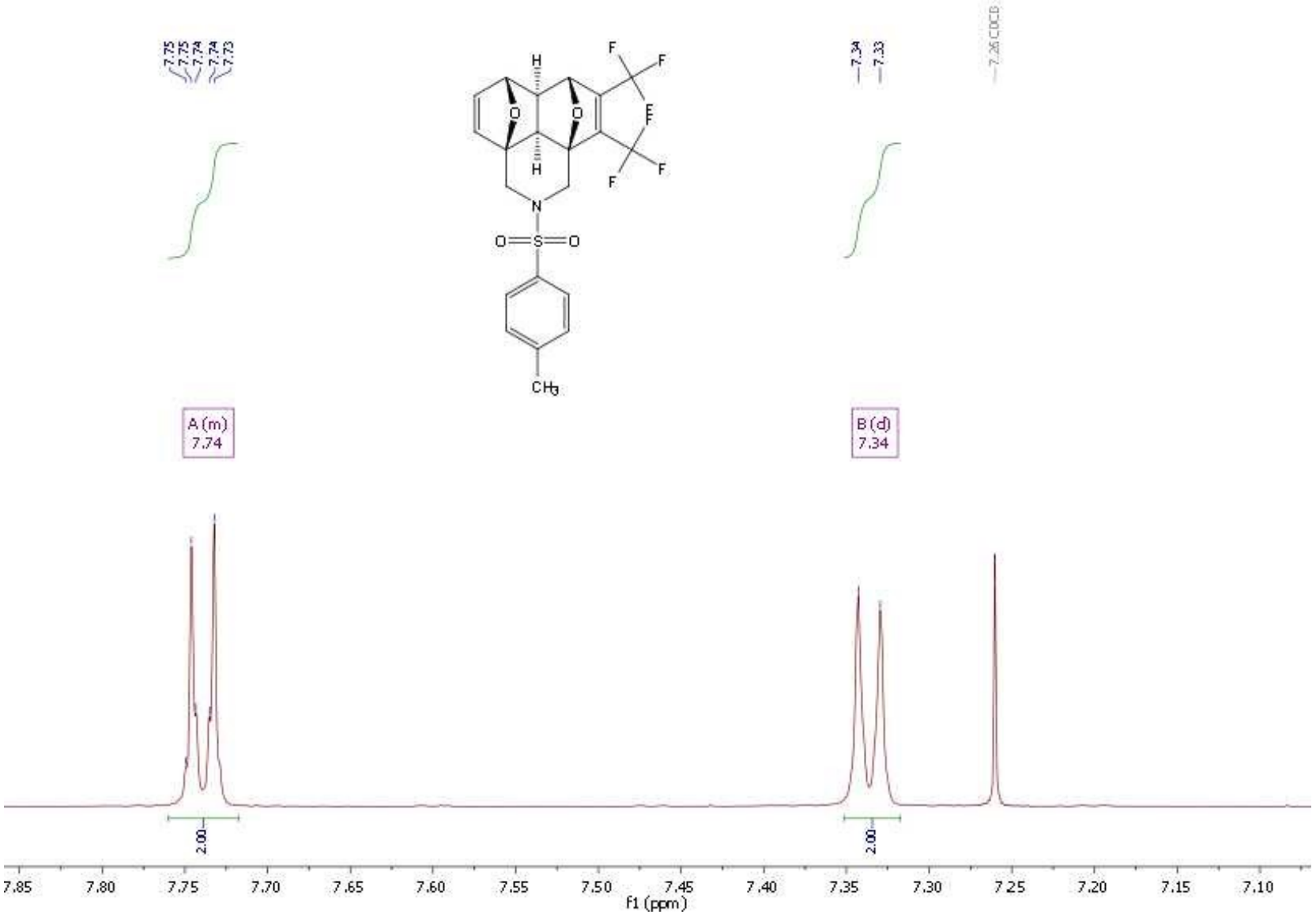


(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Methylphenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(6b)**

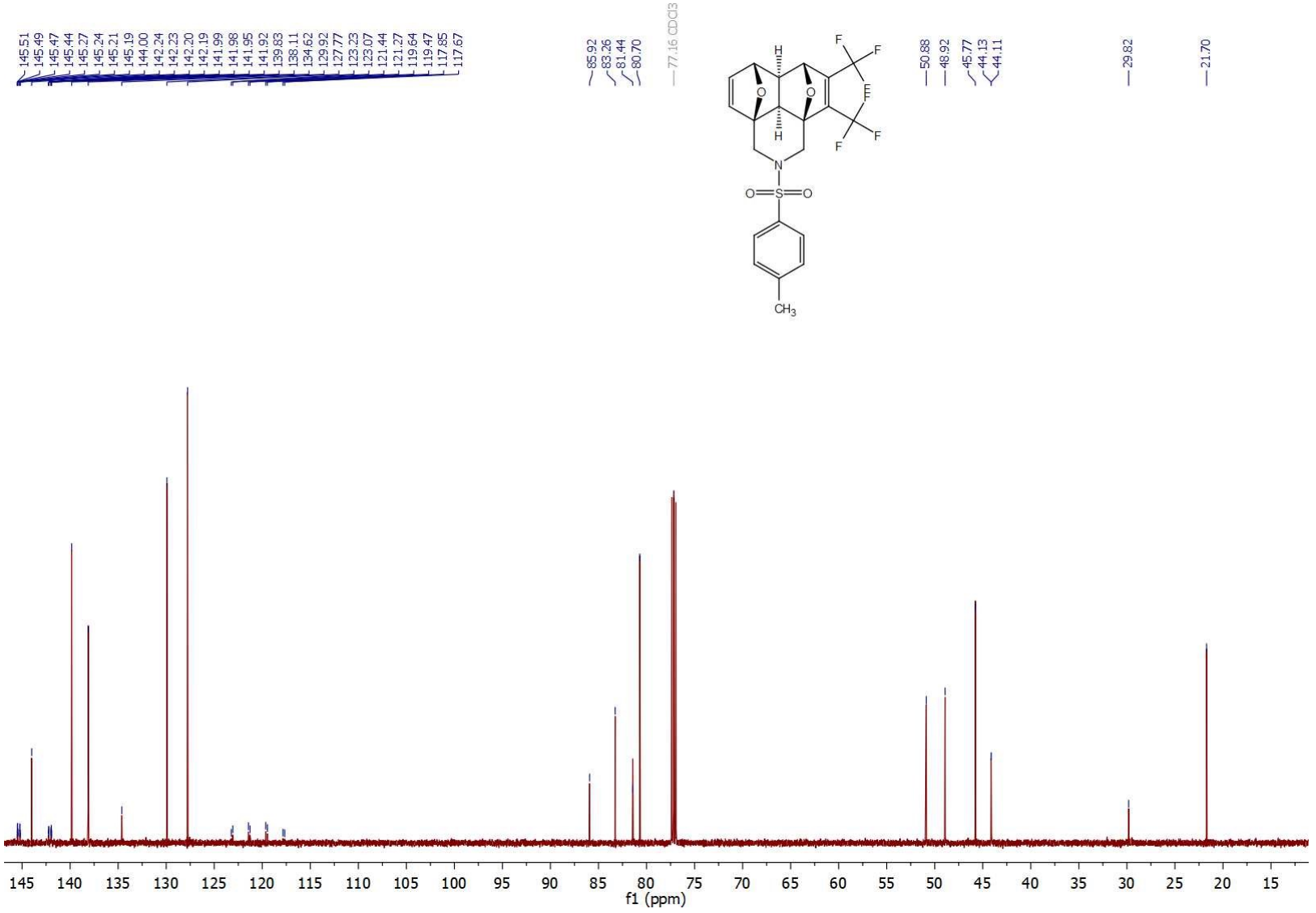
^{1}H NMR spectrum of compound (6b)



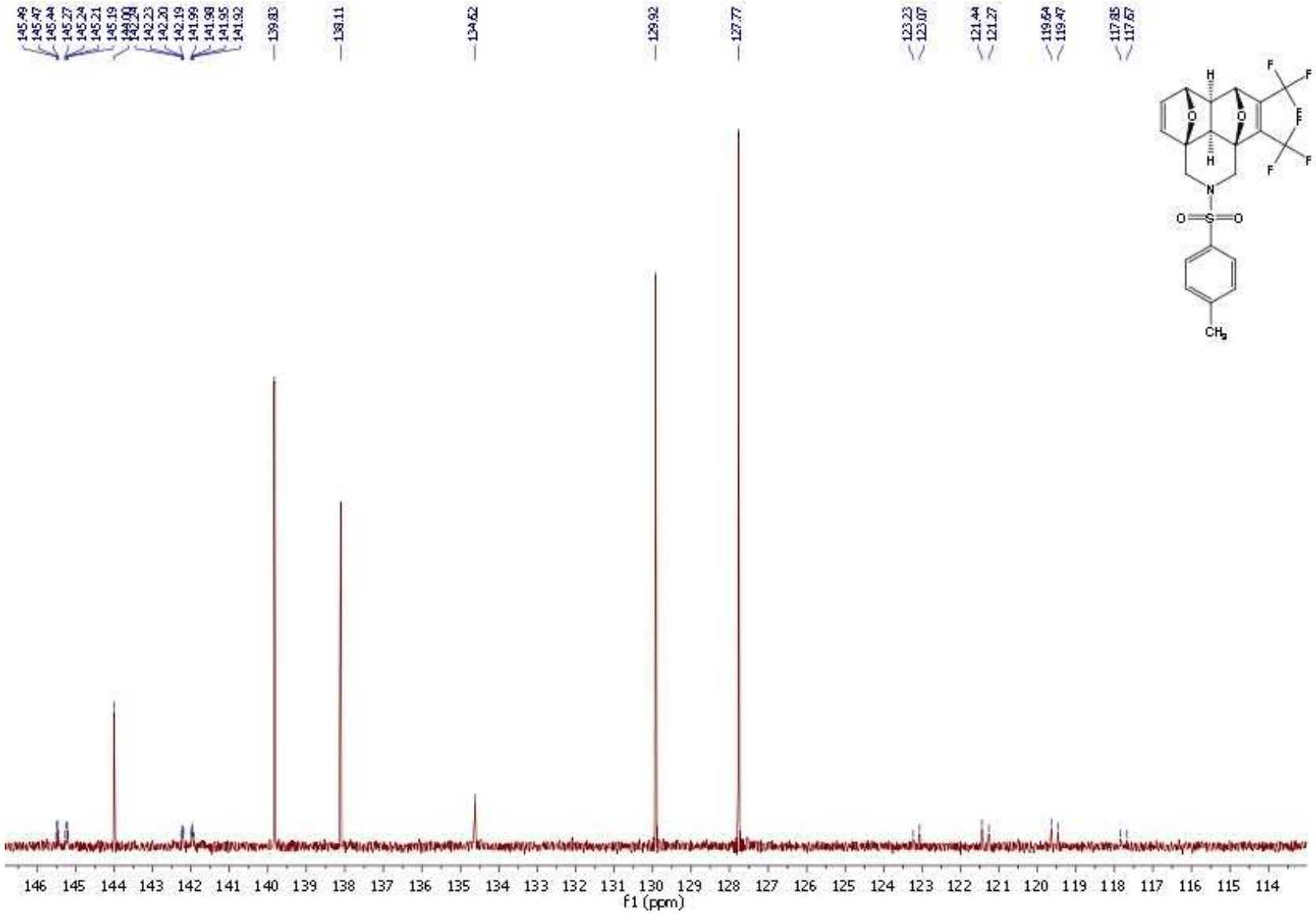
^{1}H NMR spectrum of compound (6b)



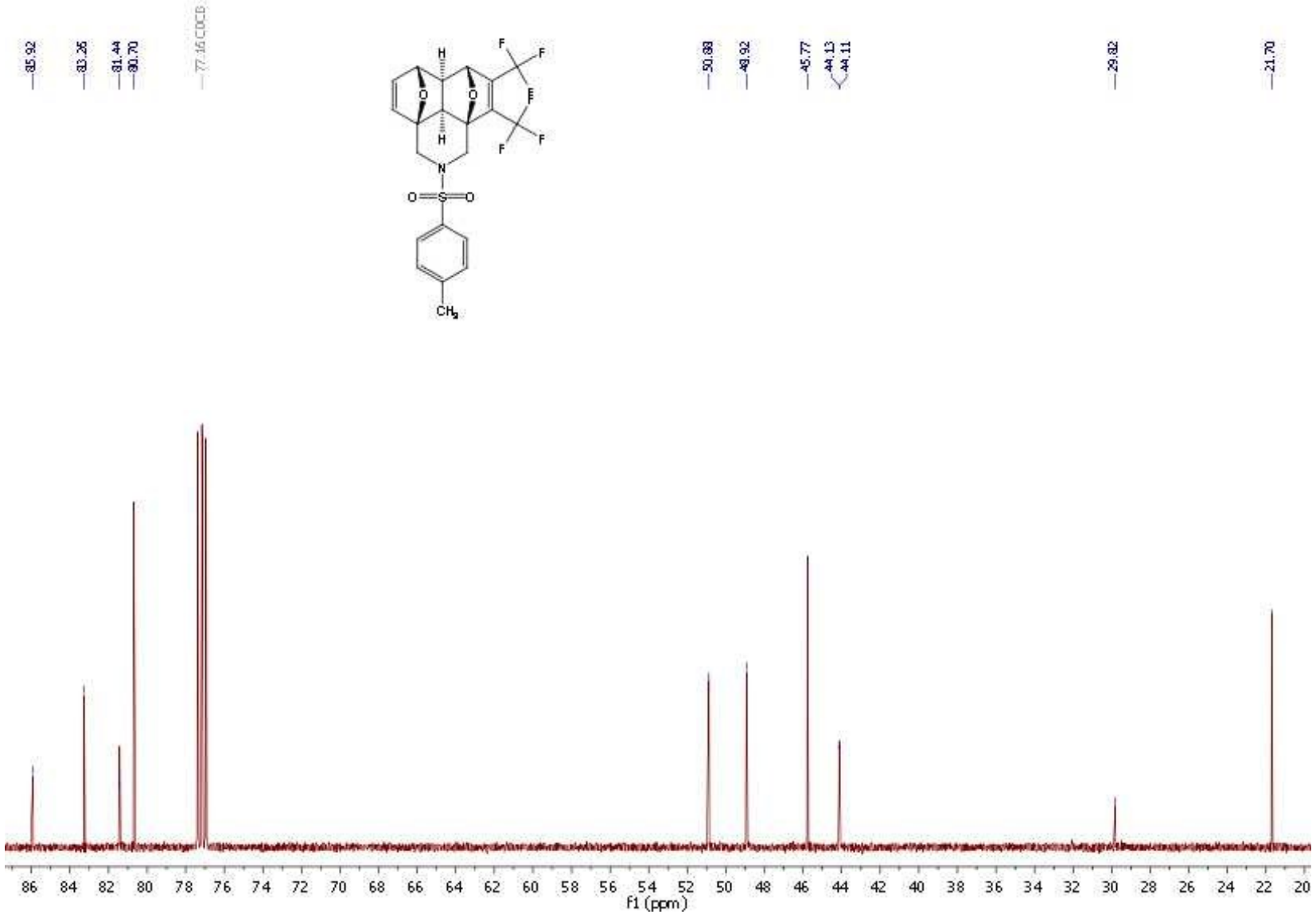
^{13}C NMR spectrum of compound (6b)



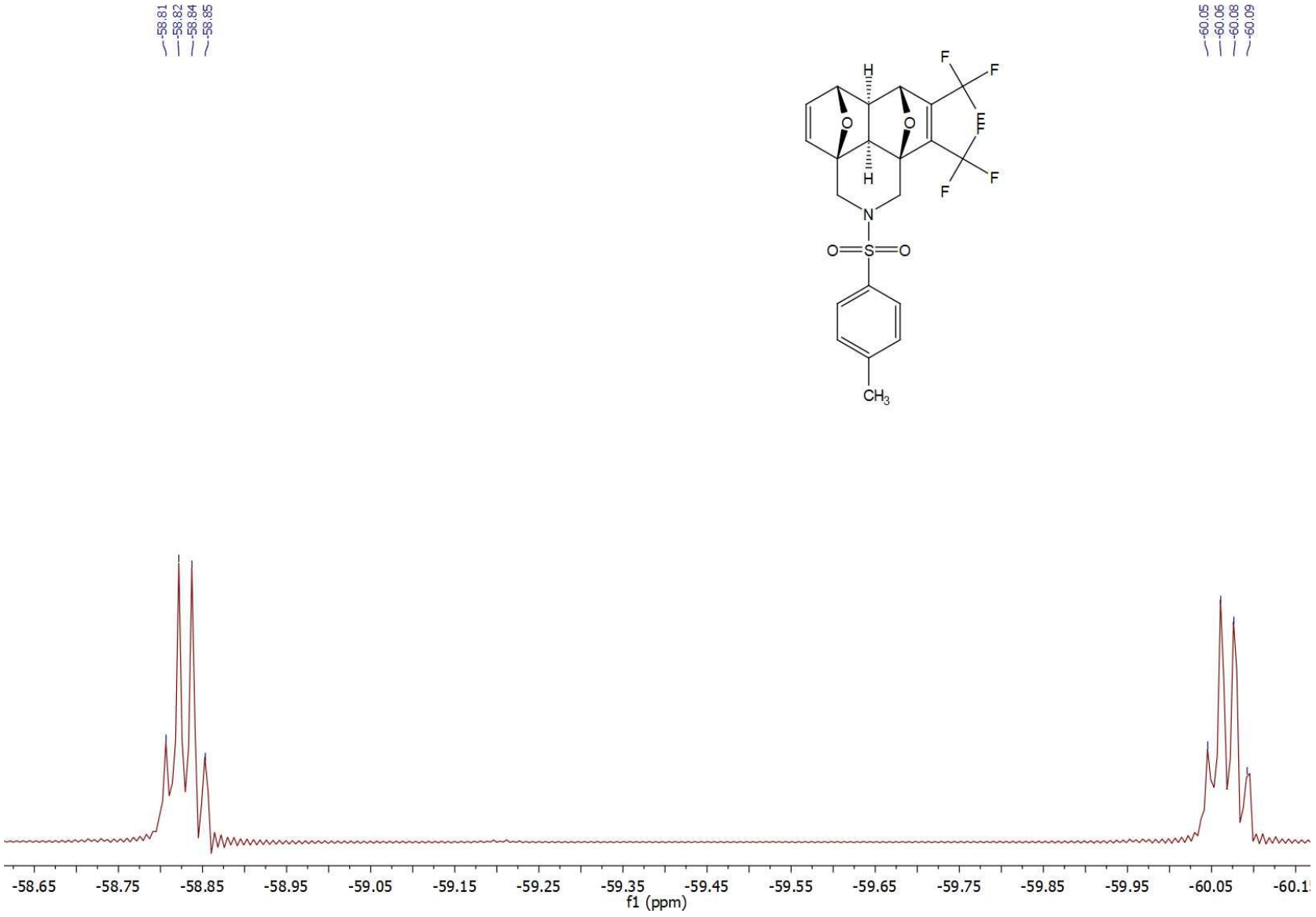
^{13}C NMR spectrum of compound (6b)



^{13}C NMR spectrum of compound (6b)

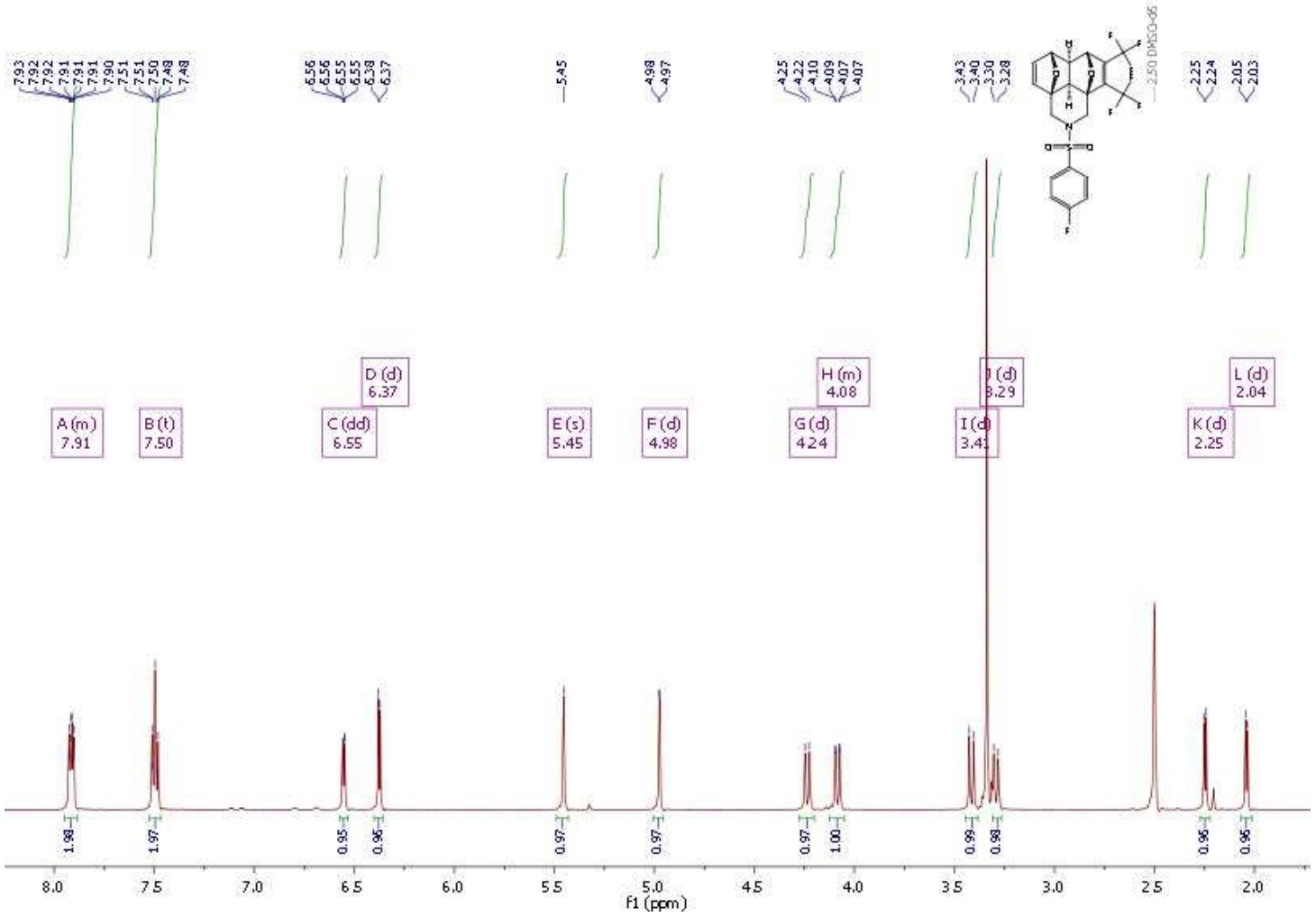


^{19}F NMR spectrum of compound (6b)

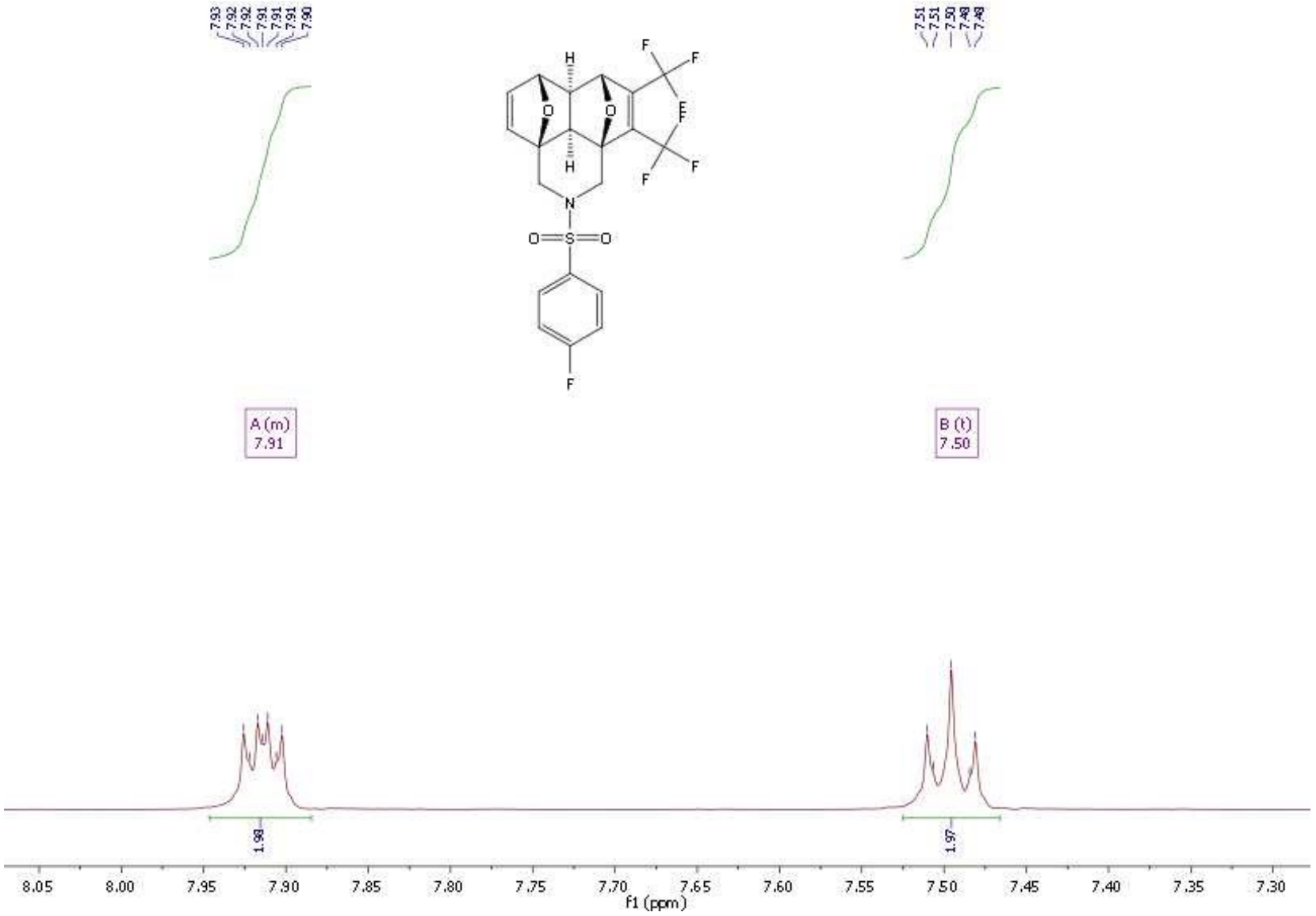


(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Fluorophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(7b)**

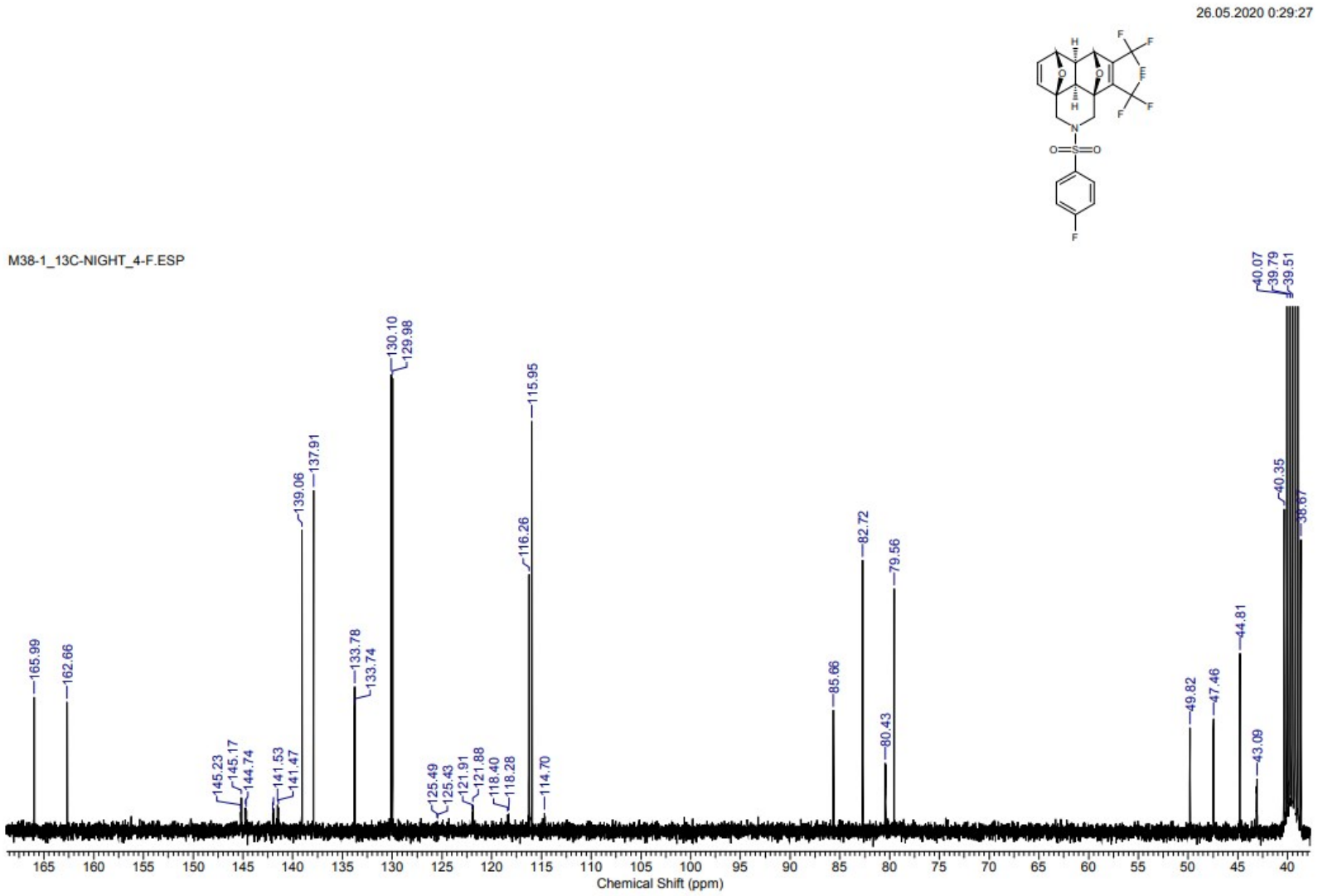
^{1}H NMR spectrum of compound (7b)



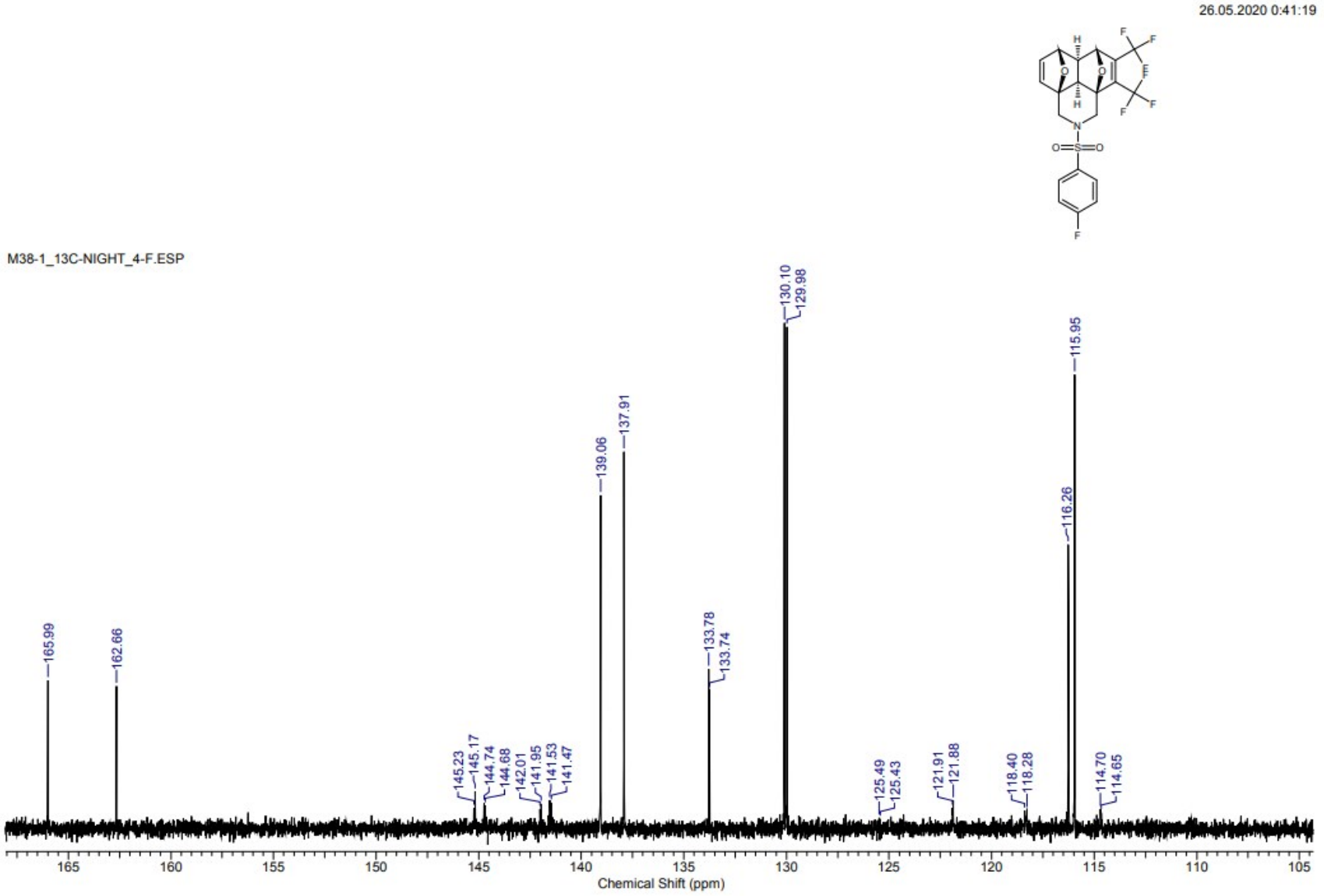
^{1}H NMR spectrum of compound (7b)



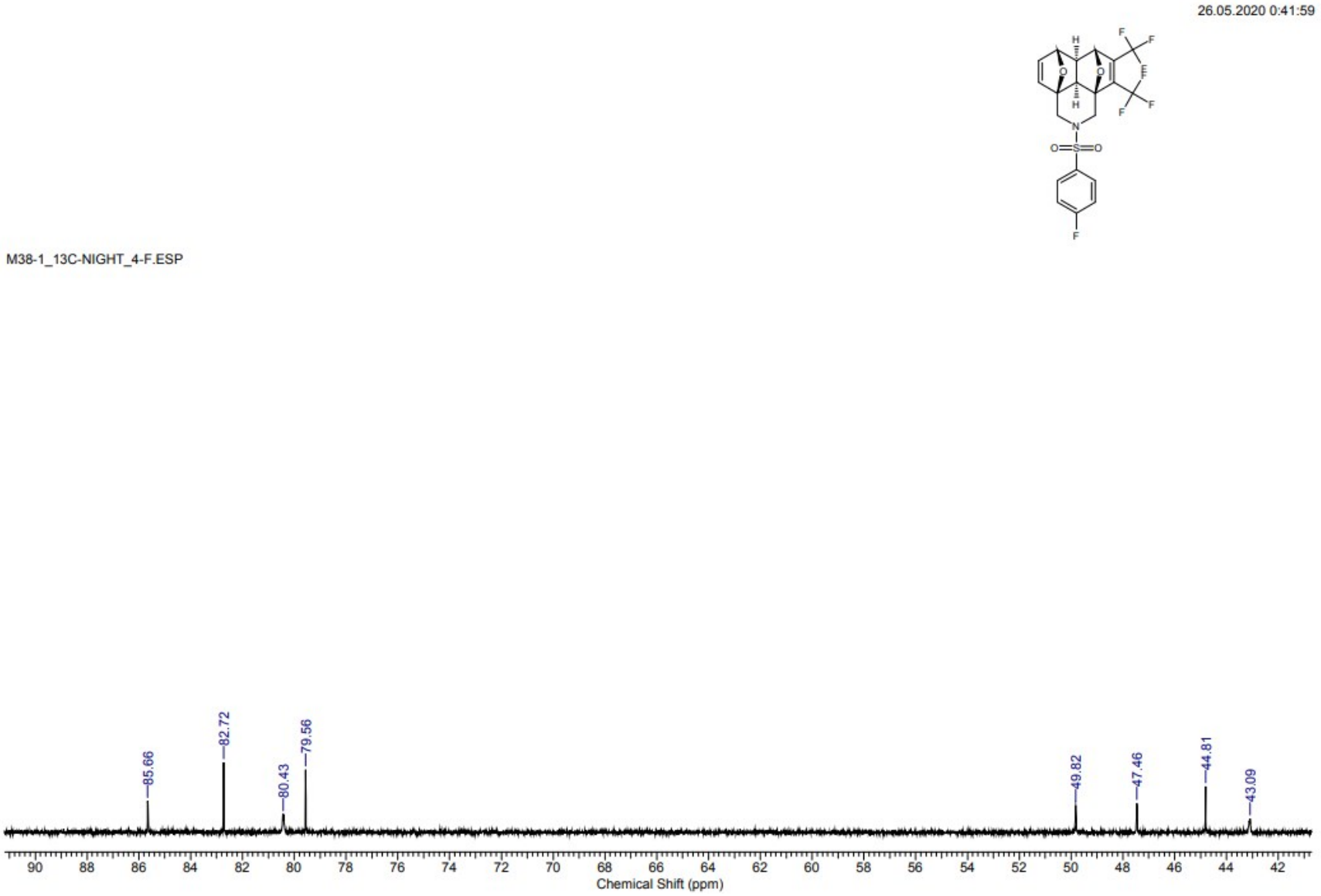
^{13}C NMR spectrum of compound (7b)



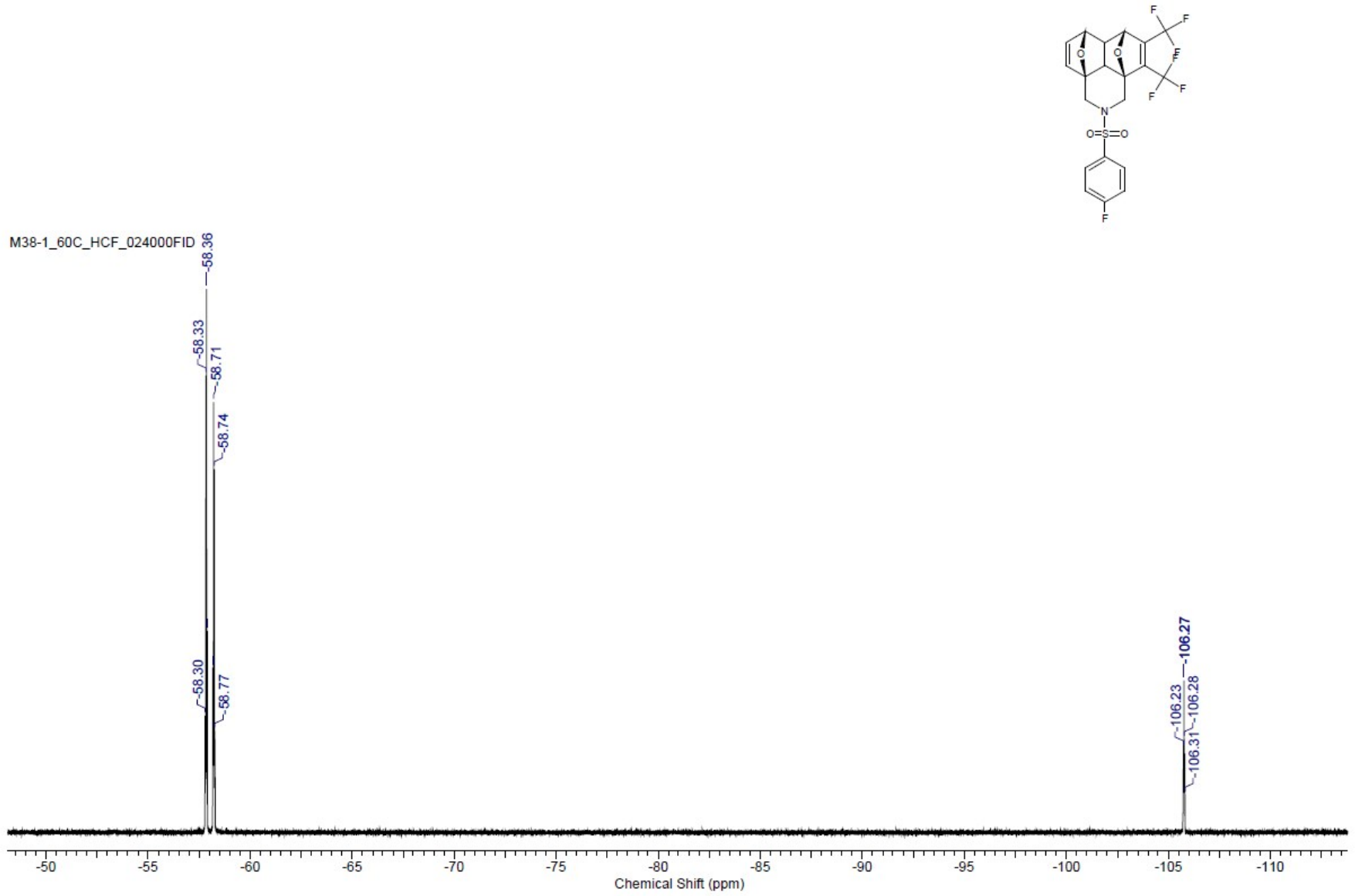
^{13}C NMR spectrum of compound (7b)



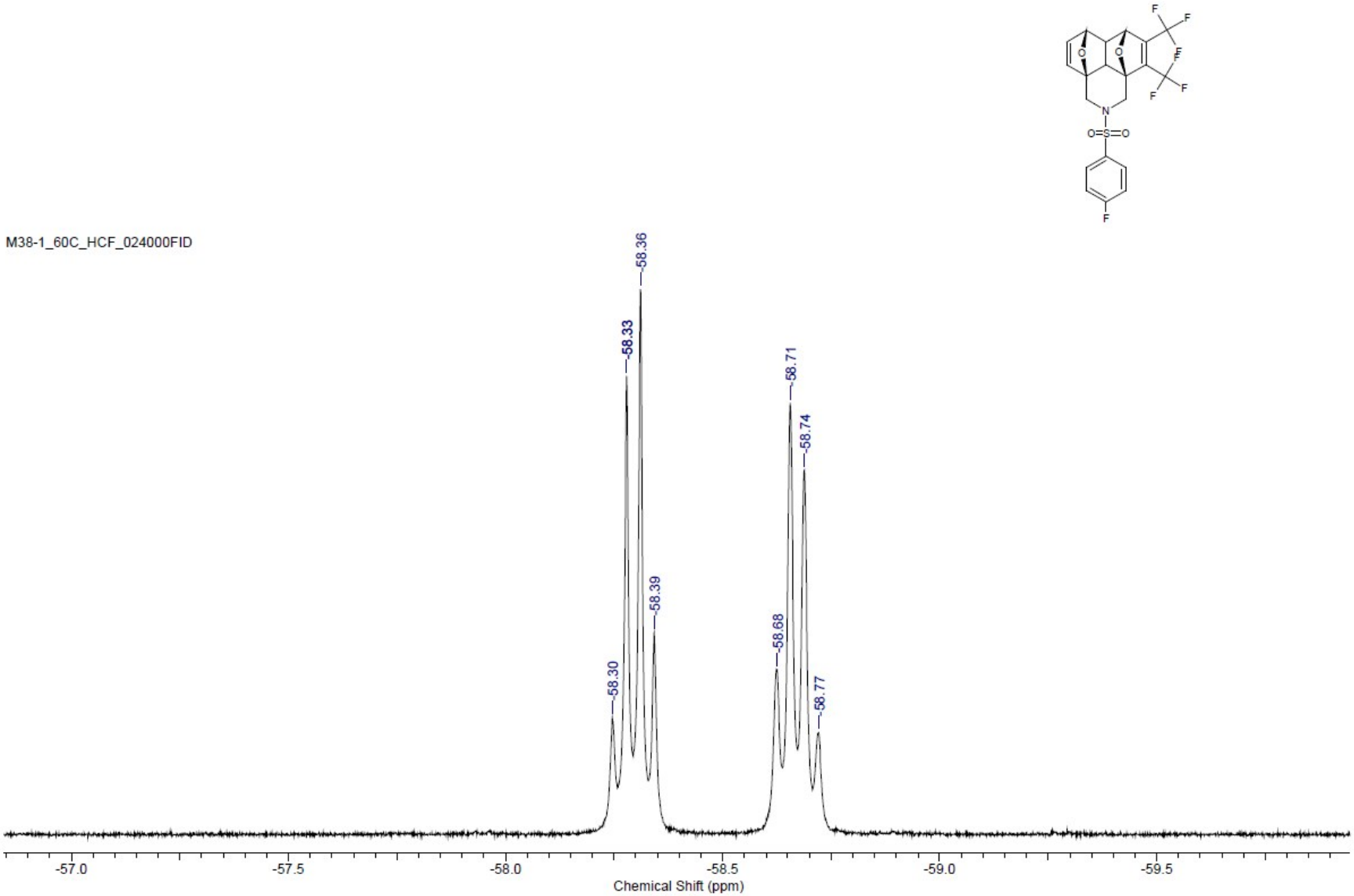
^{13}C NMR spectrum of compound (7b)



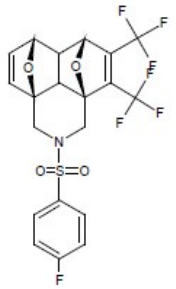
^{19}F NMR spectrum of compound (7b)



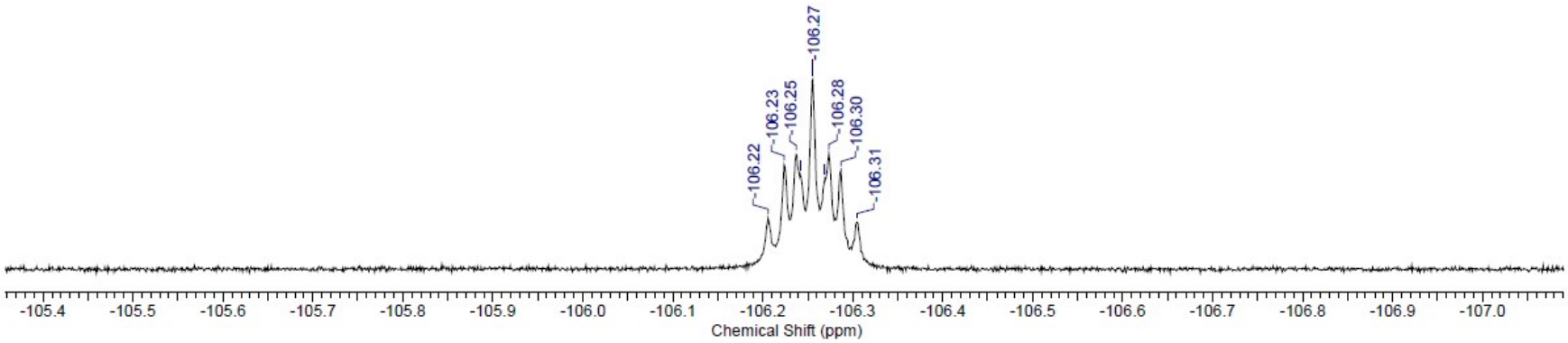
^{19}F NMR spectrum of compound (7b)



^{19}F NMR spectrum of compound (7b)

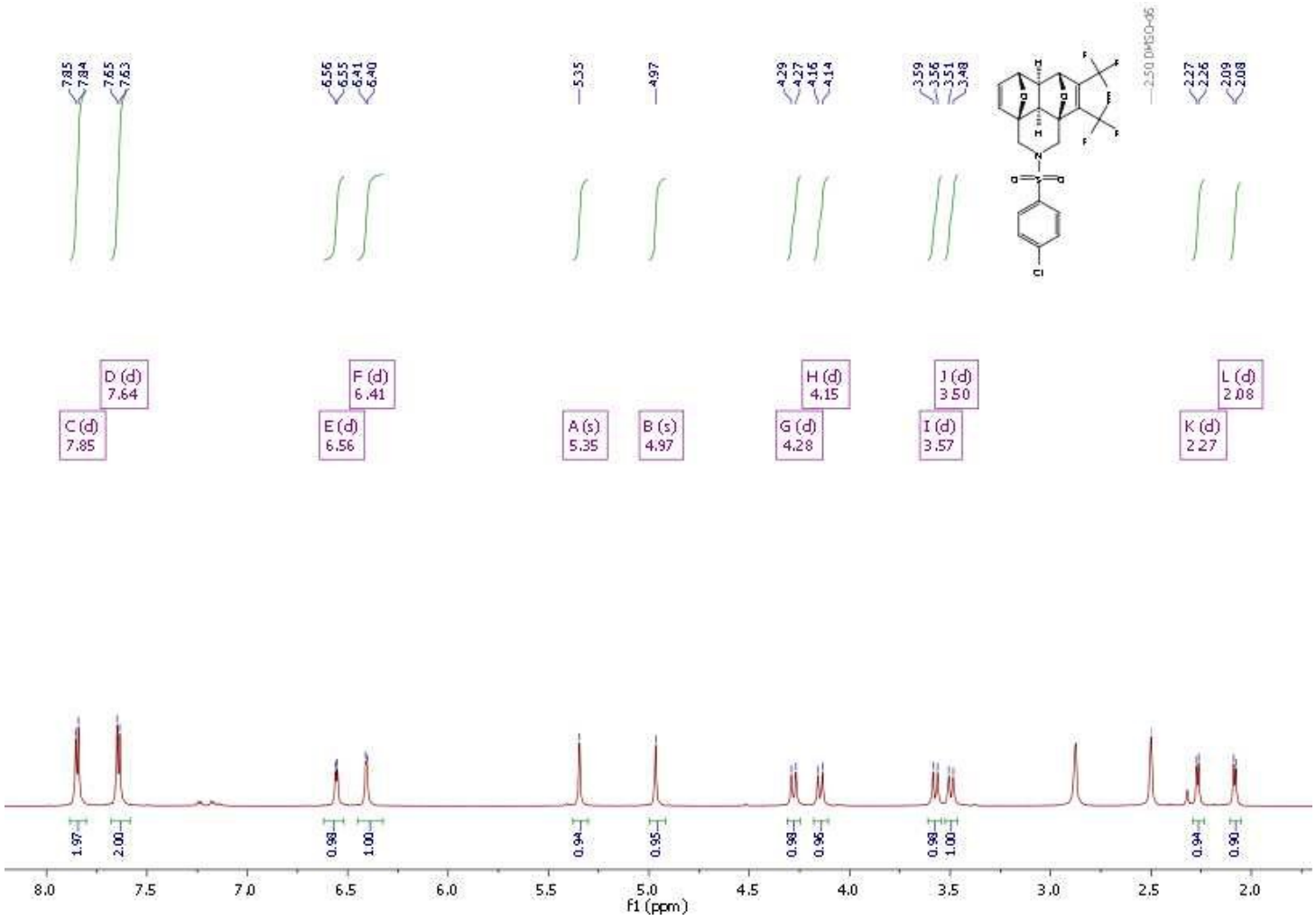


M38-1_60C_HCF_024000FID

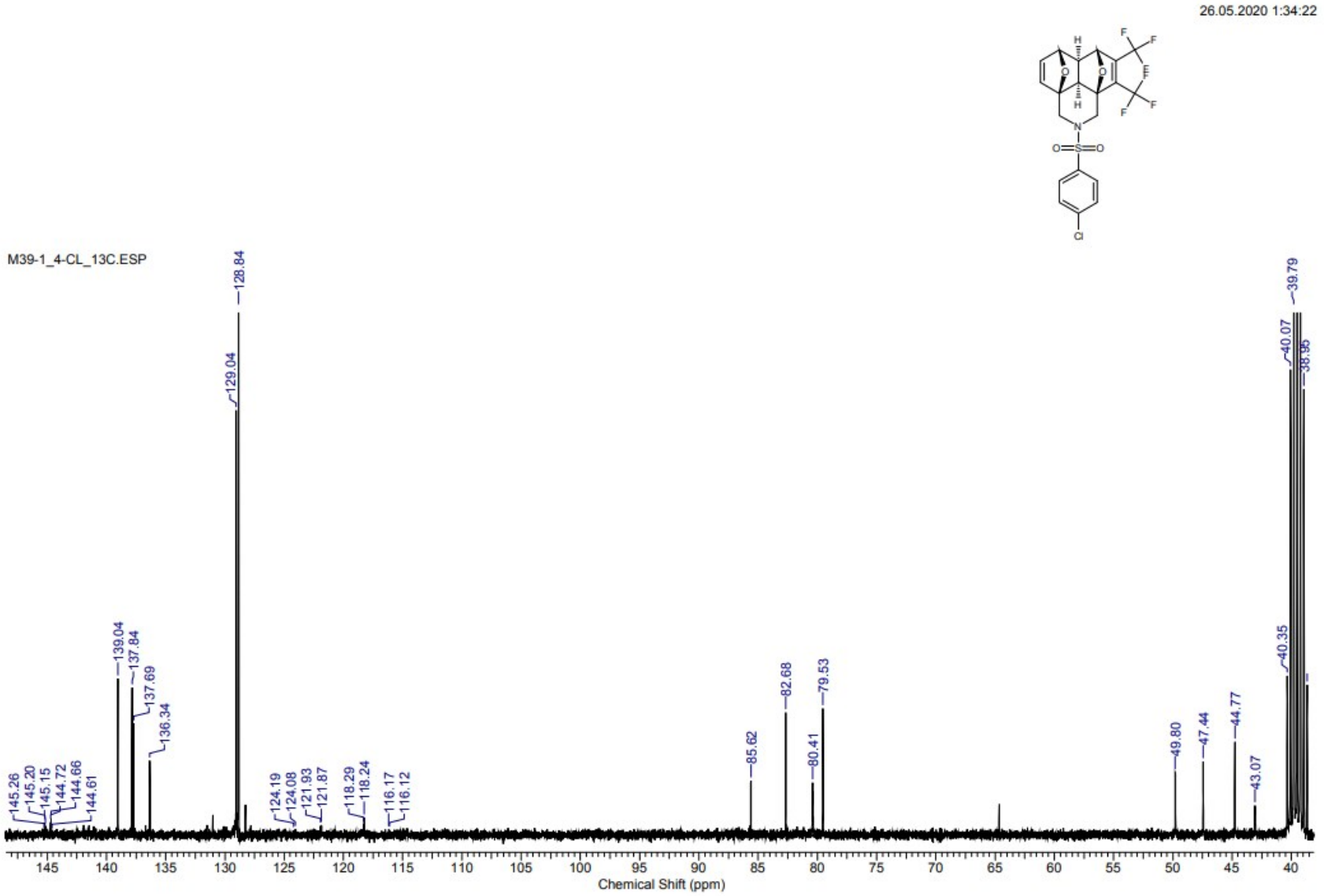


(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Chlorophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(8b)**

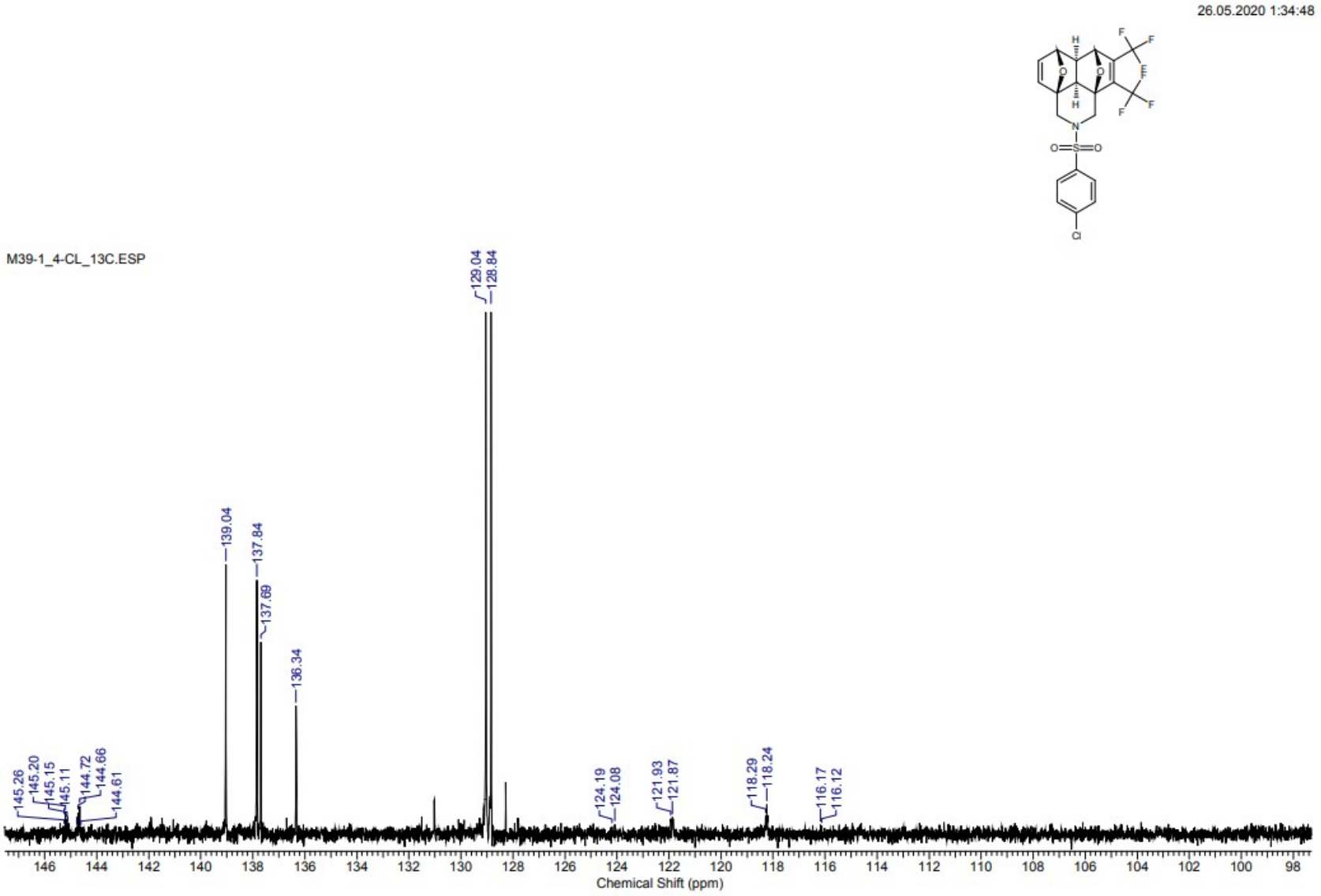
^{1}H NMR spectrum of compound (8b)



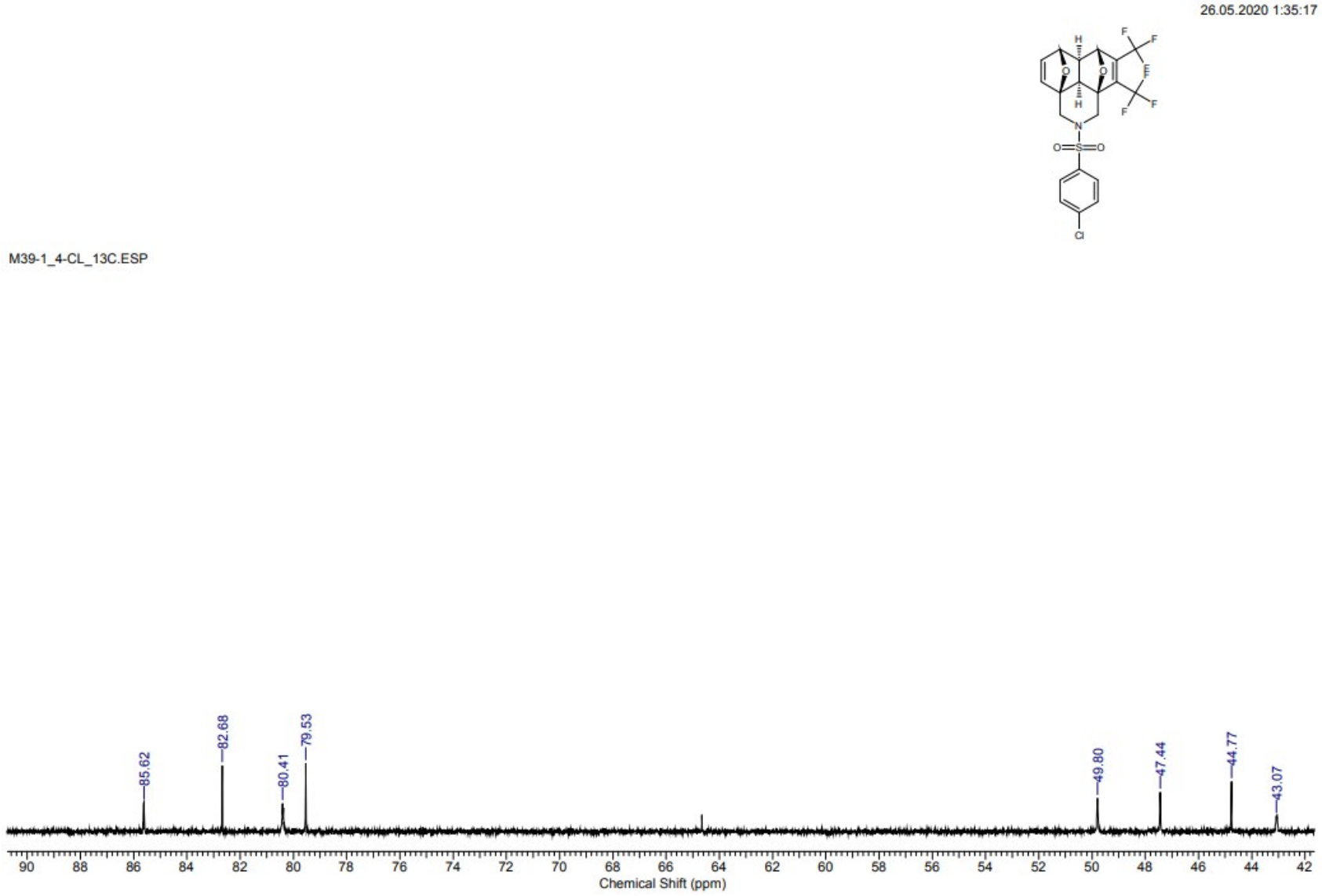
^{13}C NMR spectrum of compound (8b)



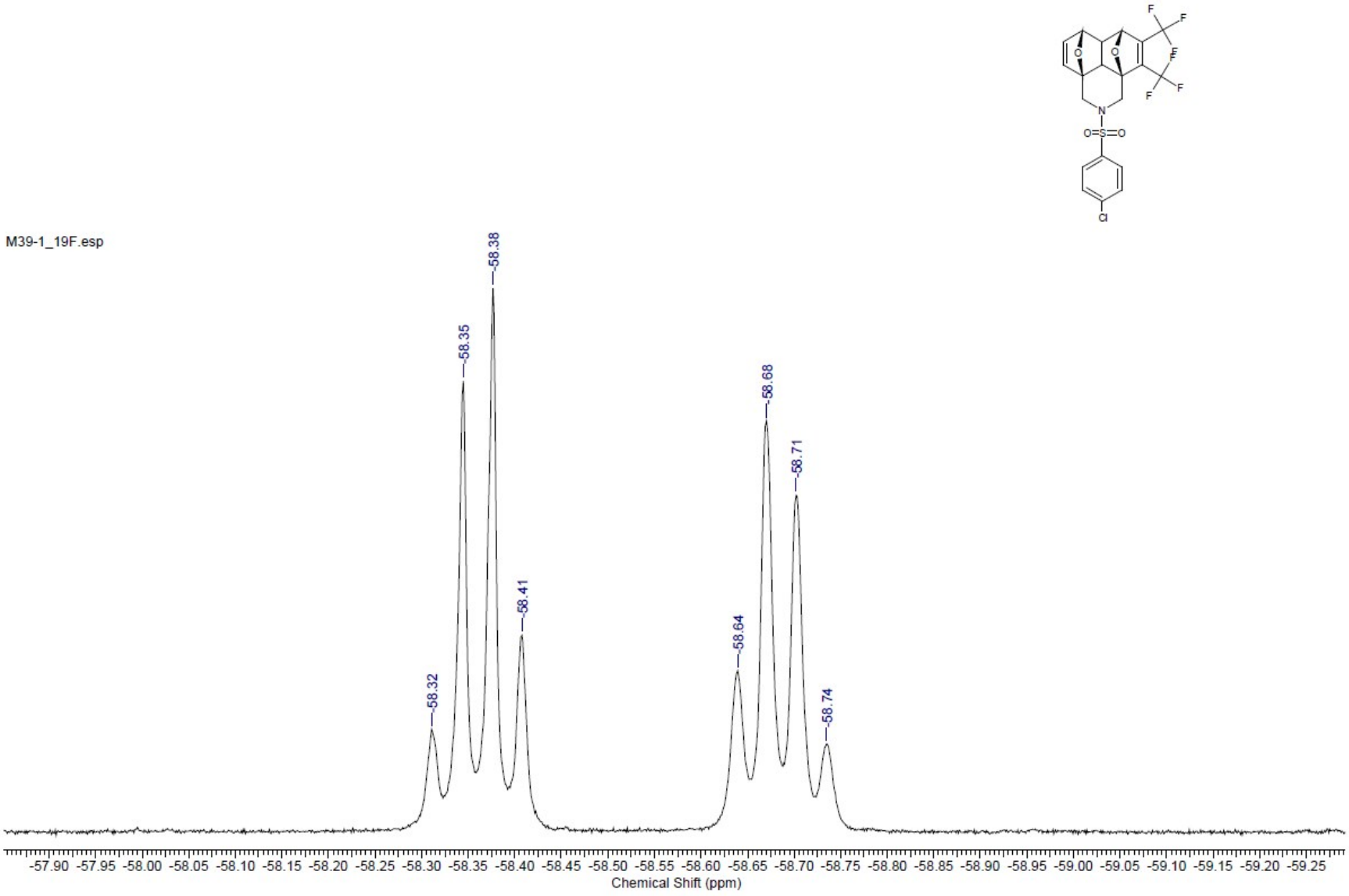
^{13}C NMR spectrum of compound (8b)



^{13}C NMR spectrum of compound (8b)

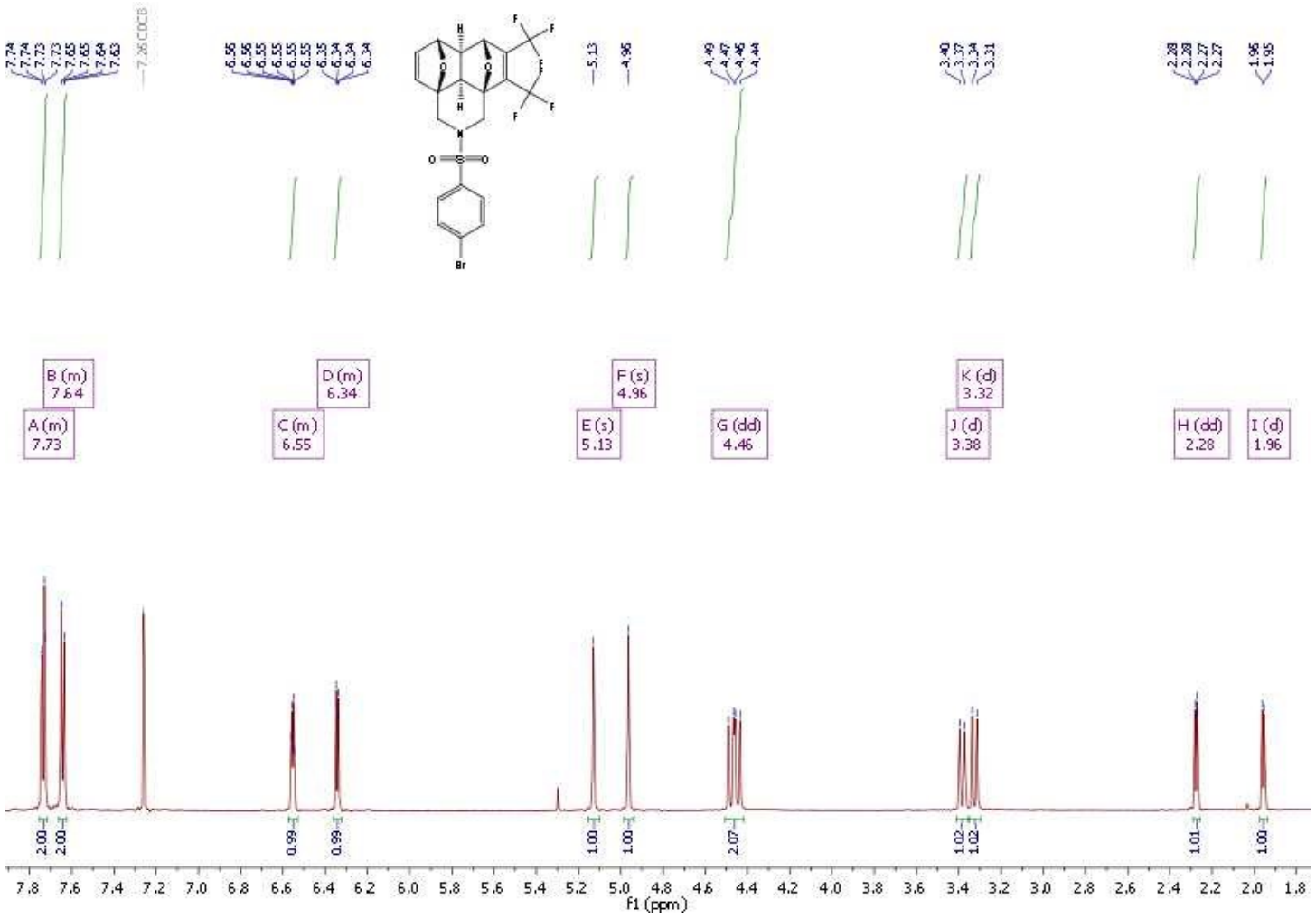


^{19}F NMR spectrum of compound (8b)

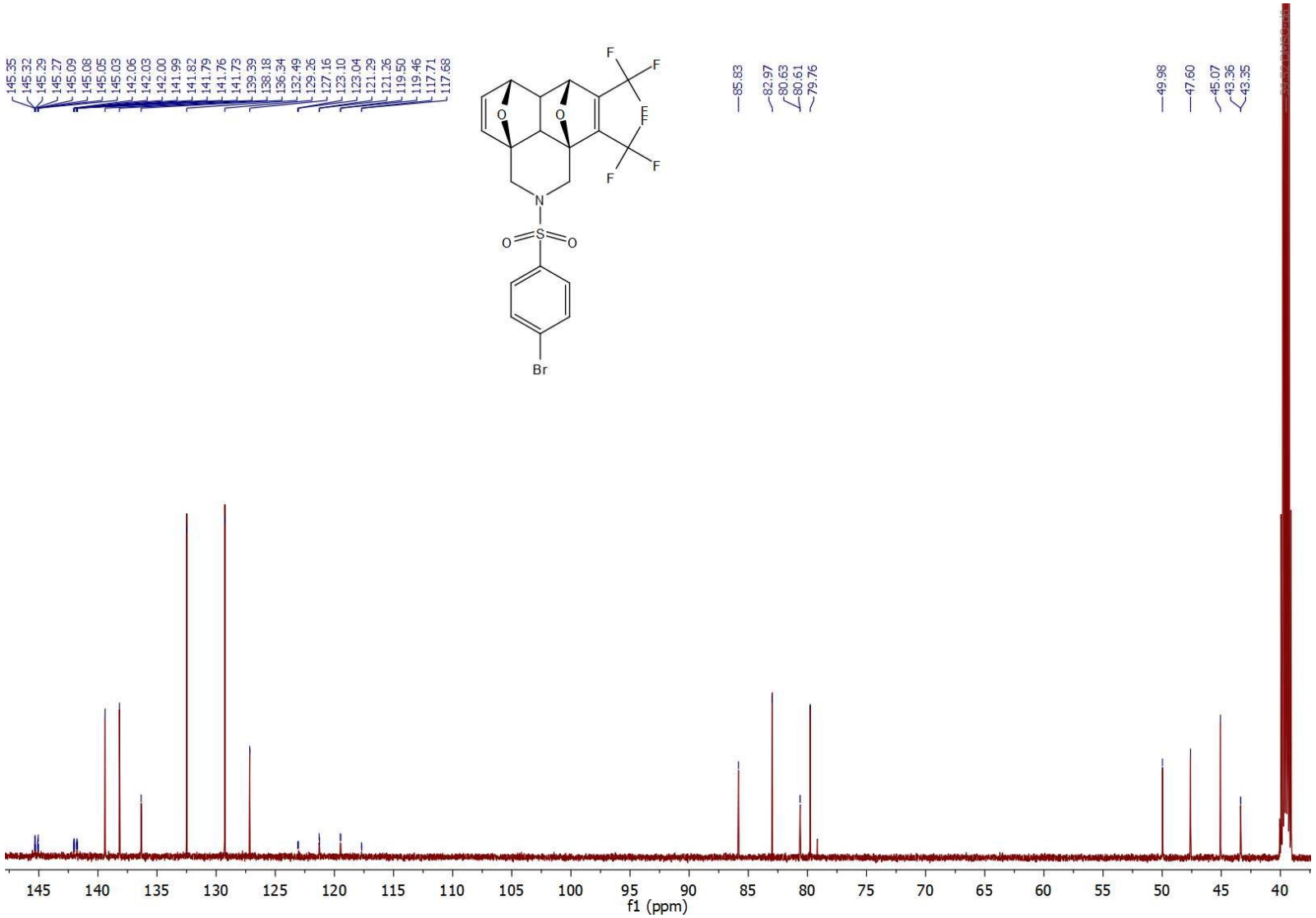


(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Bromophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(9b)**

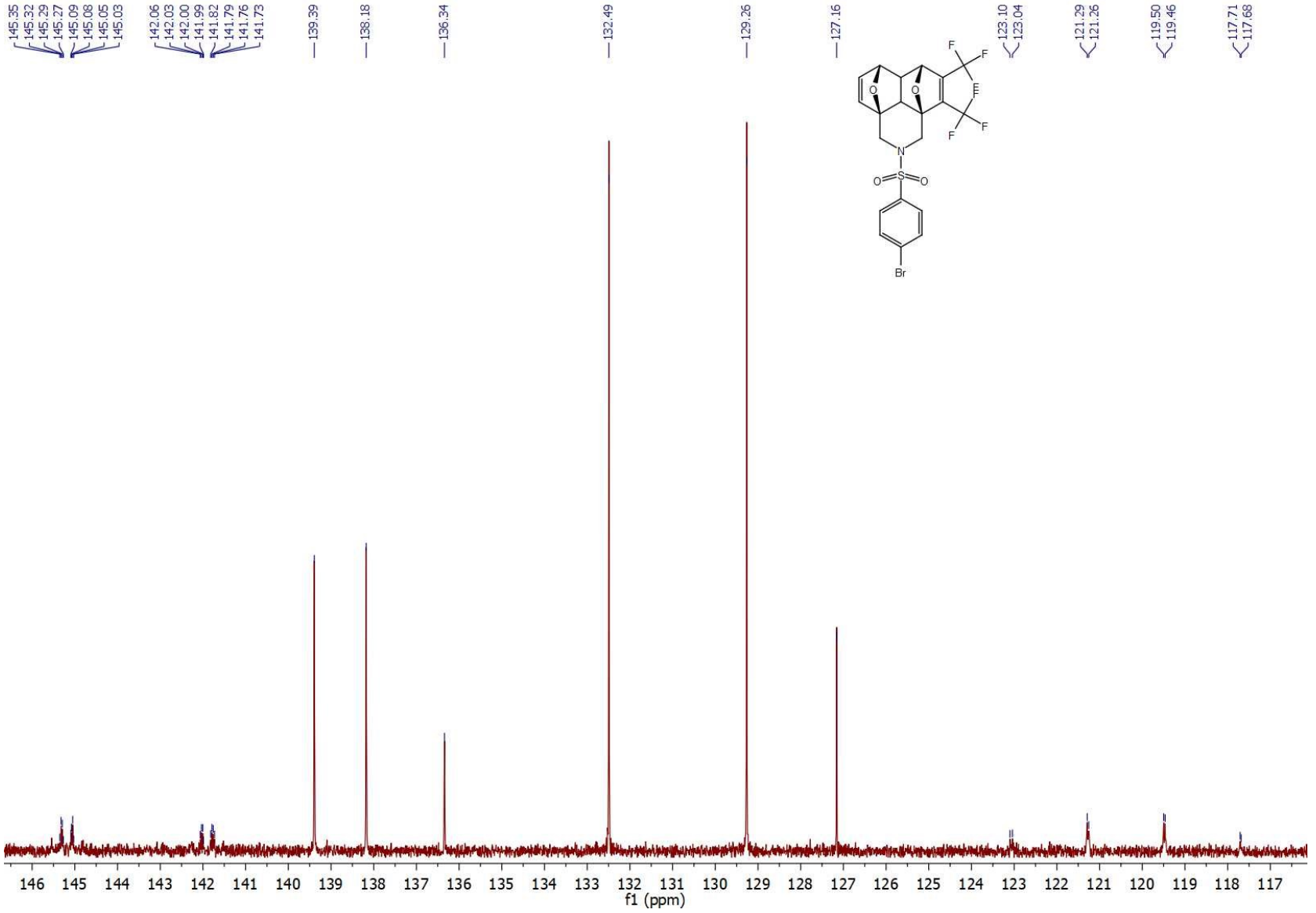
^{1}H NMR spectrum of compound (9b)



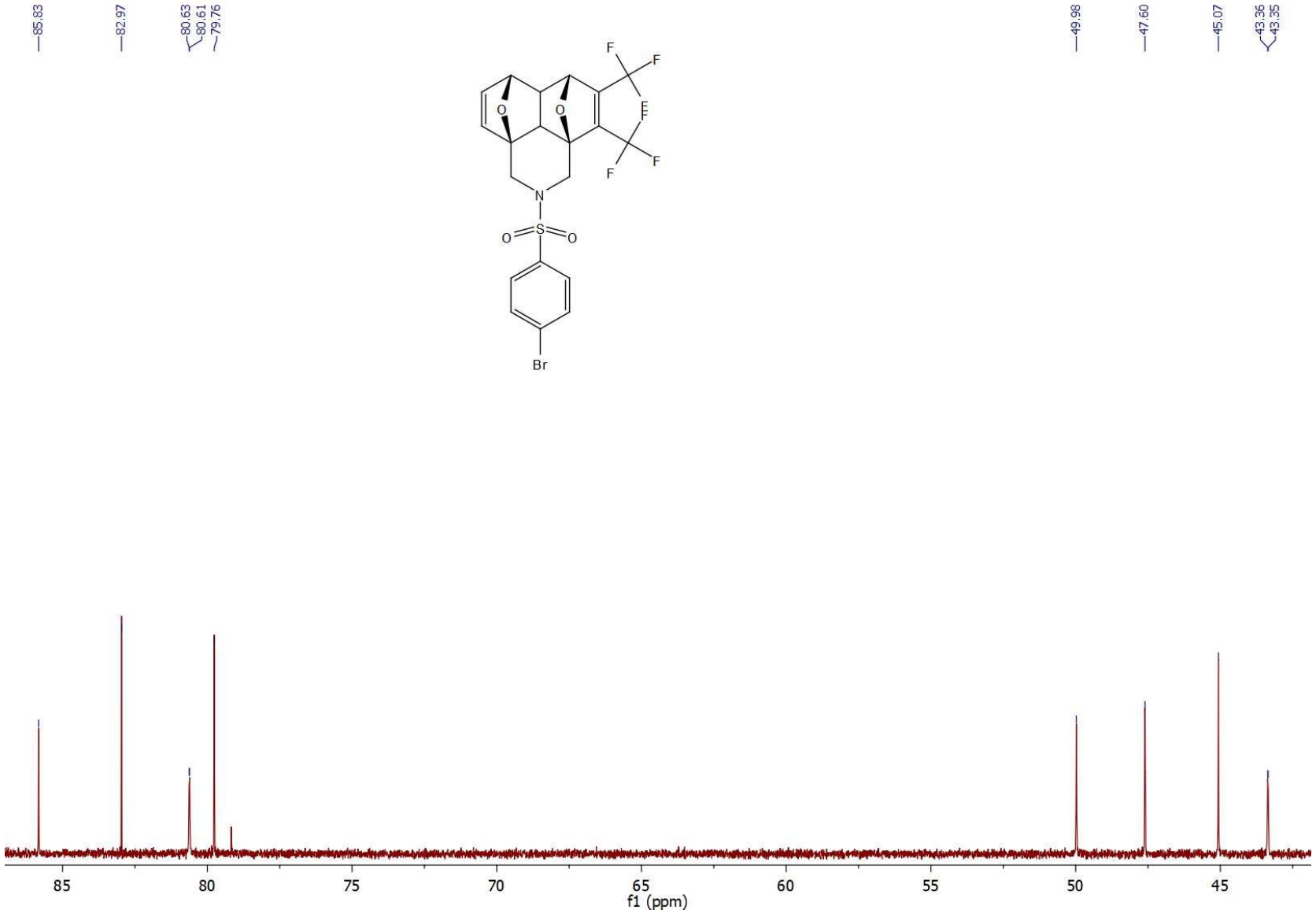
^{13}C NMR spectrum of compound (9b)



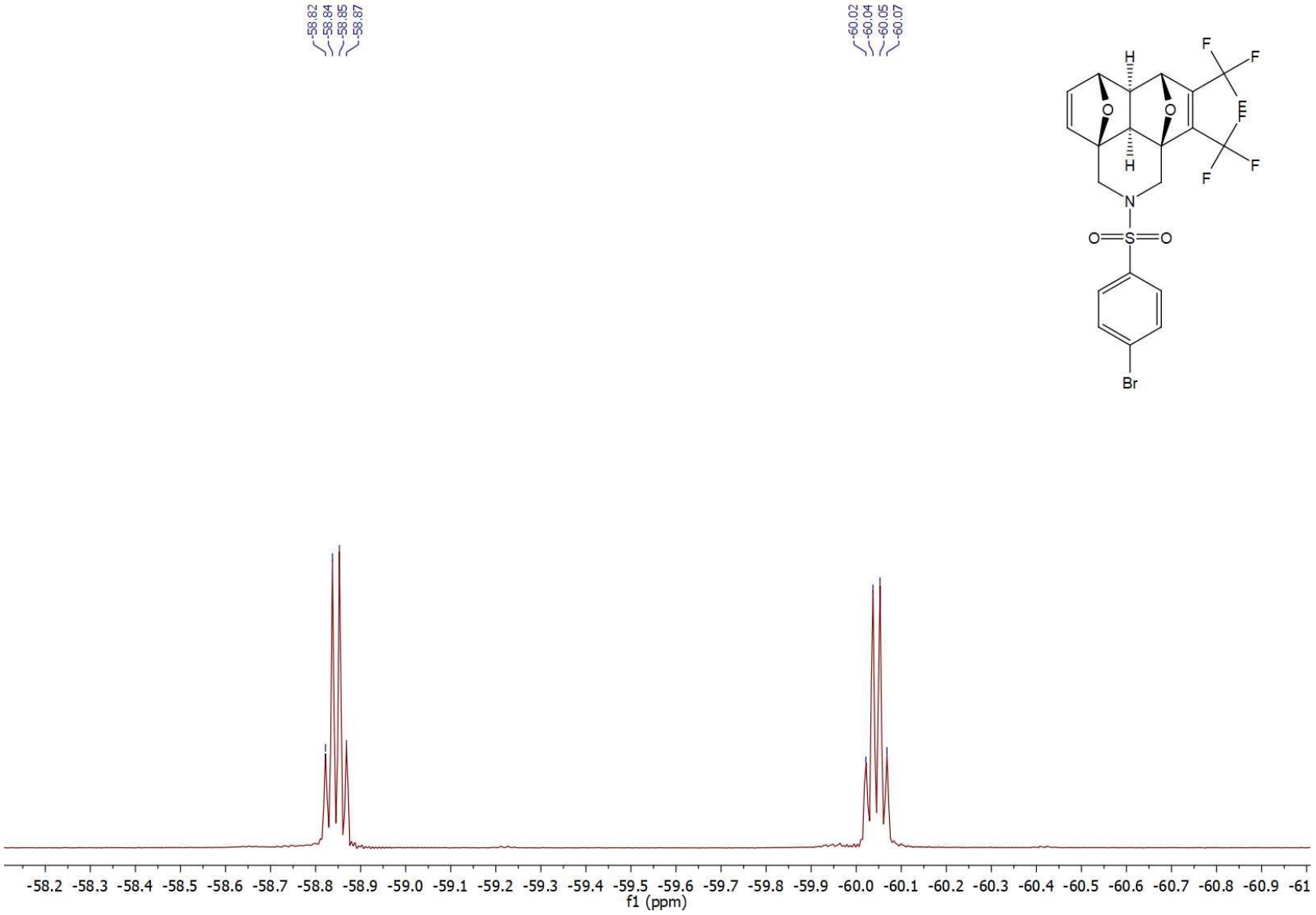
^{13}C NMR spectrum of compound (9b)



^{13}C NMR spectrum of compound (9b)

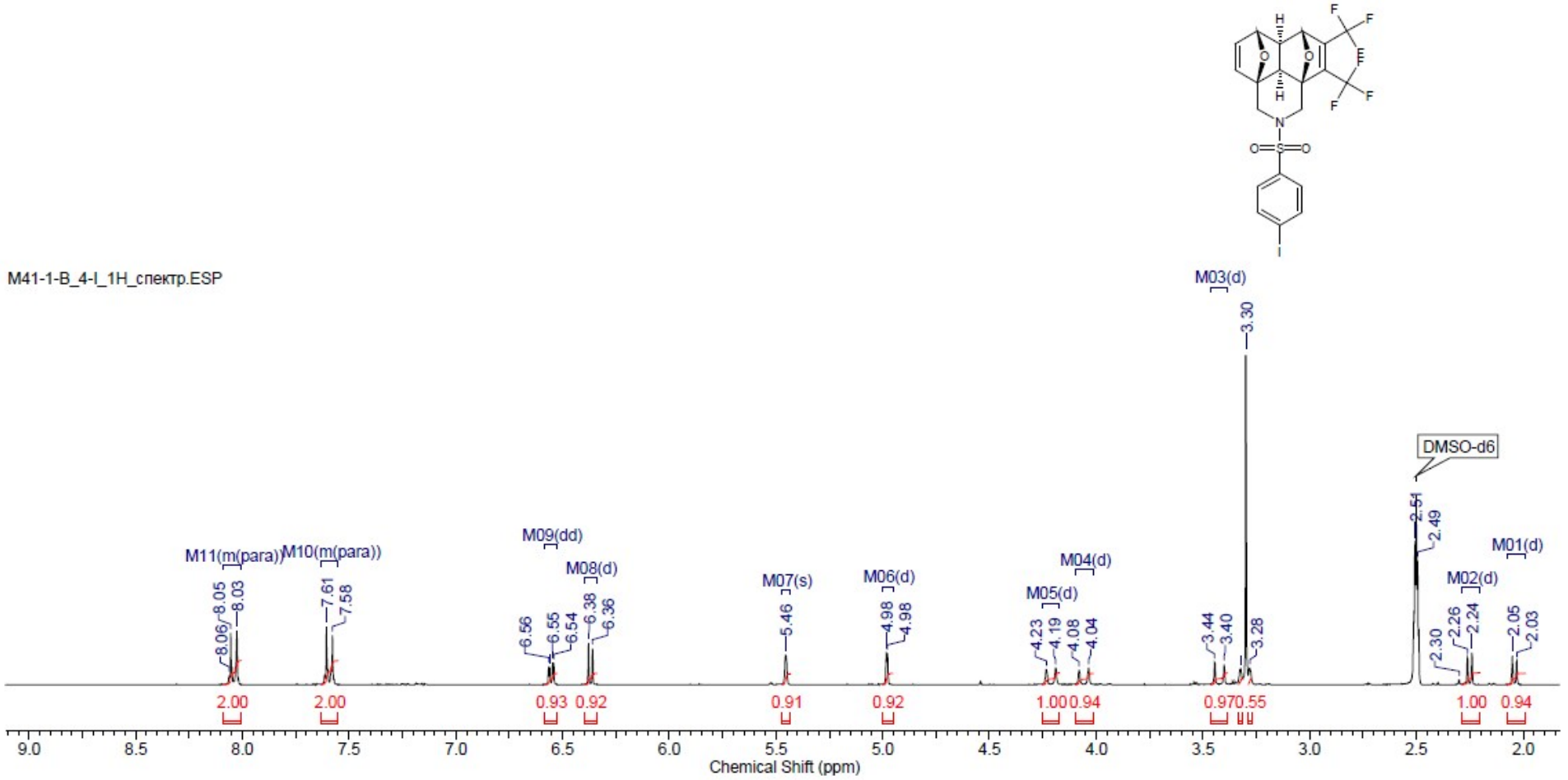


^{19}F NMR spectrum of compound (9b)

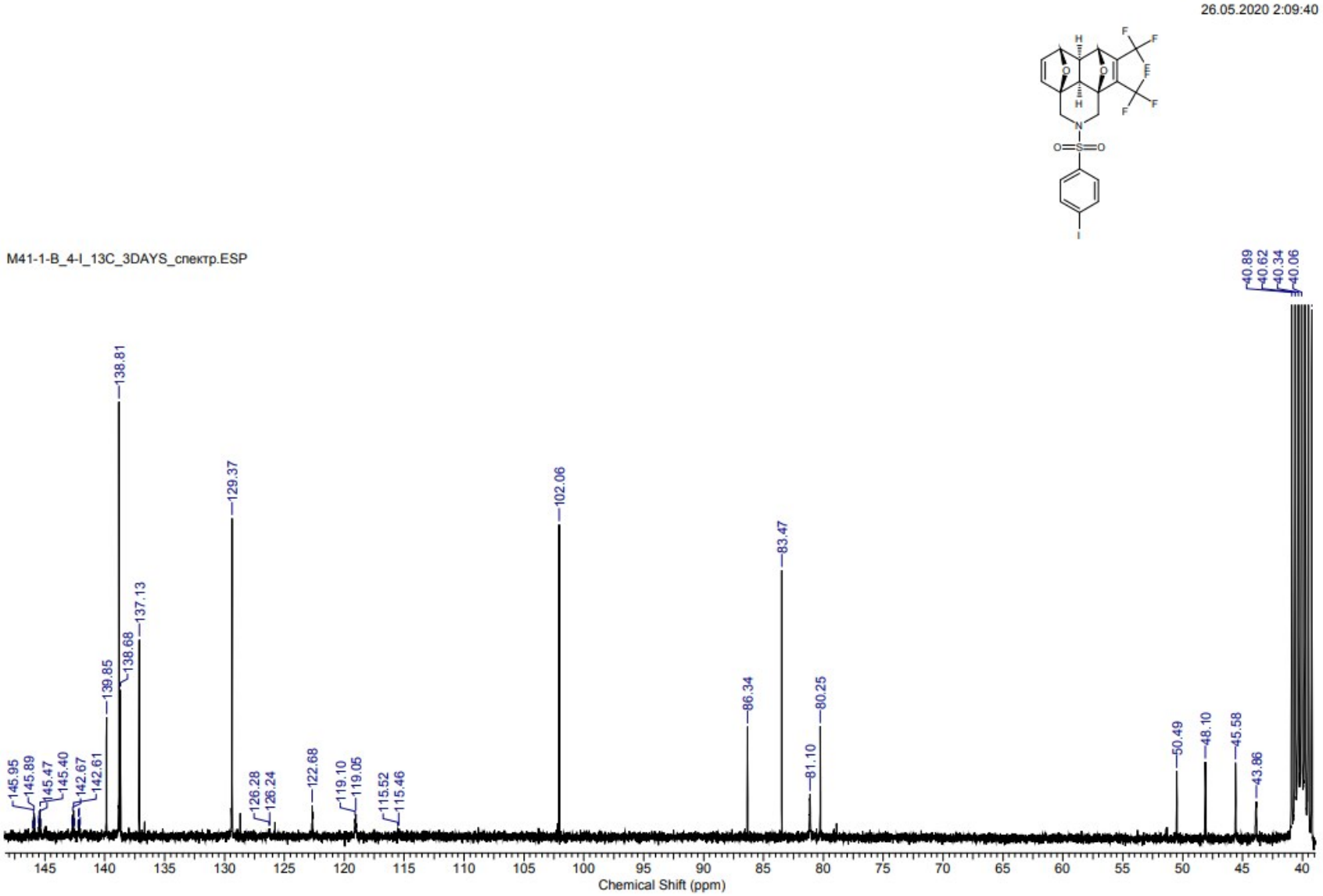


(3aRS,6SR,6aRS,7SR,9aRS,9bSR)-2-[(4-Iodophenyl)sulfonyl]-4,5-bis(trifluoromethyl)-2,3,6a,9b-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline **(10b)**

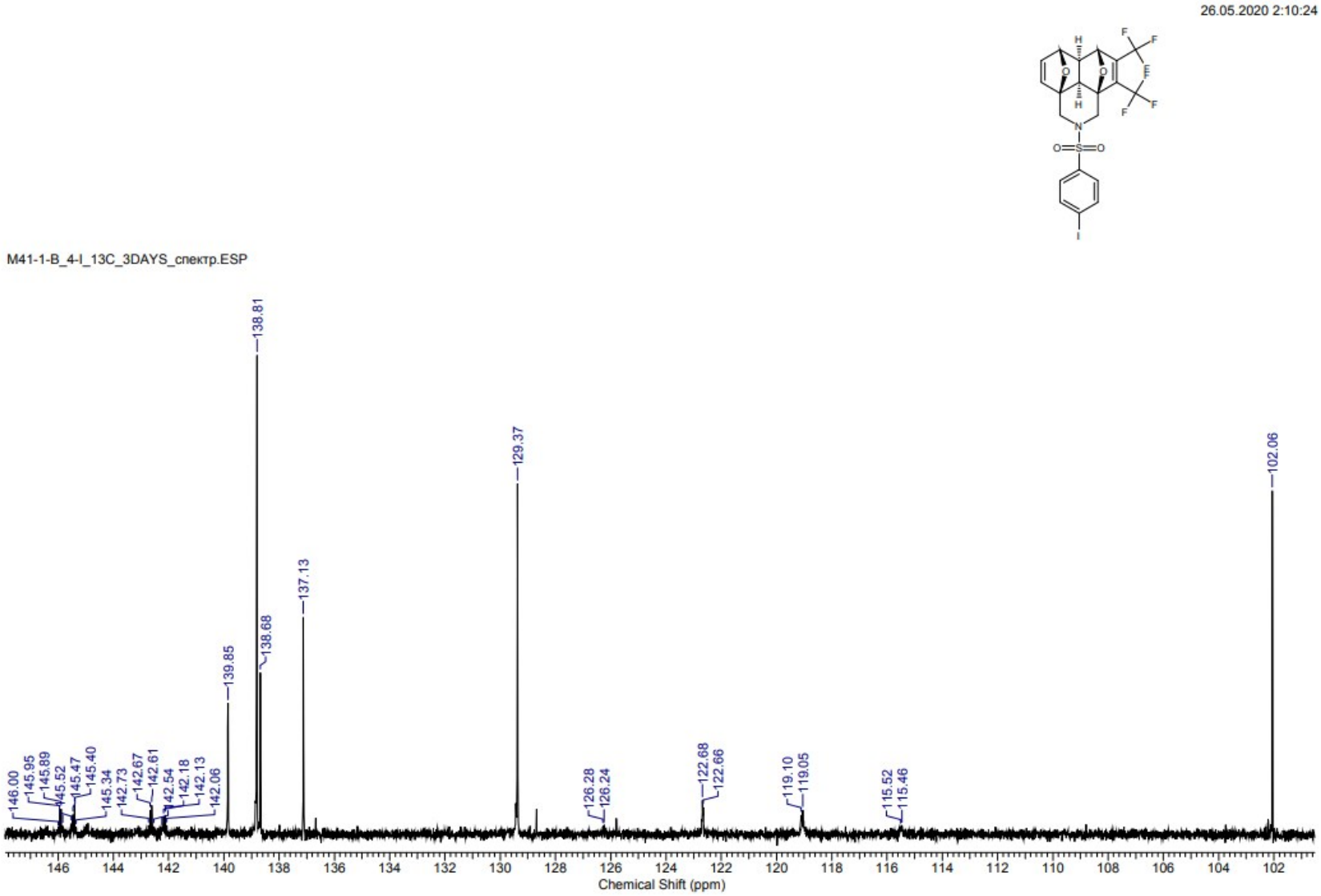
^{1}H NMR spectrum of compound (10b)



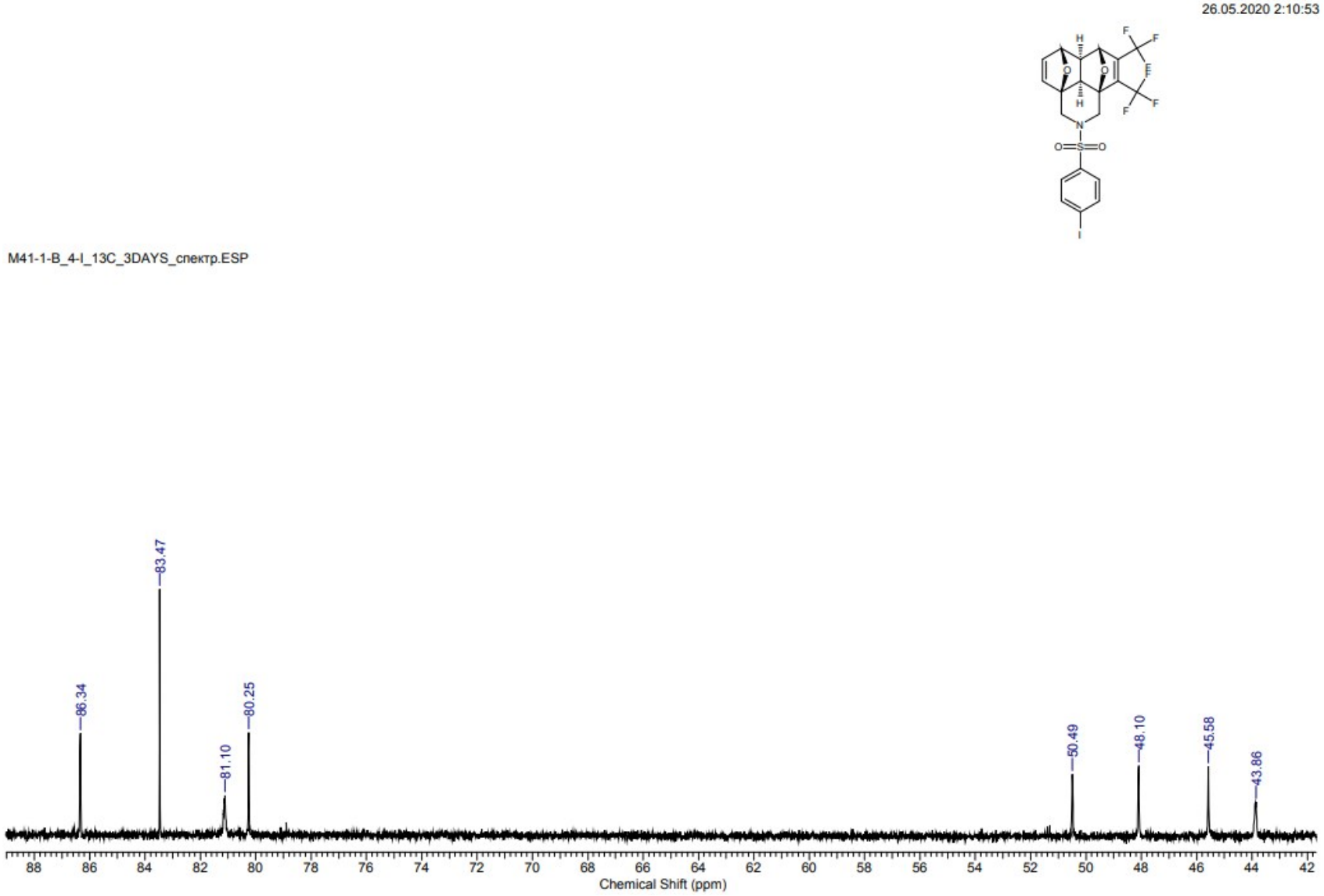
^{13}C NMR spectrum of compound (10b)



^{13}C NMR spectrum of compound (10b)



^{13}C NMR spectrum of compound (10b)



^{19}F NMR spectrum of compound (10b)