Supporting Information

for

Differential Formation of Nitrogen-Centered Radicals leading to Unprecedented, Regioselective Bromination of *N*,*N*'-(1,2-phenylene)bisamides and 2-Amidophenols

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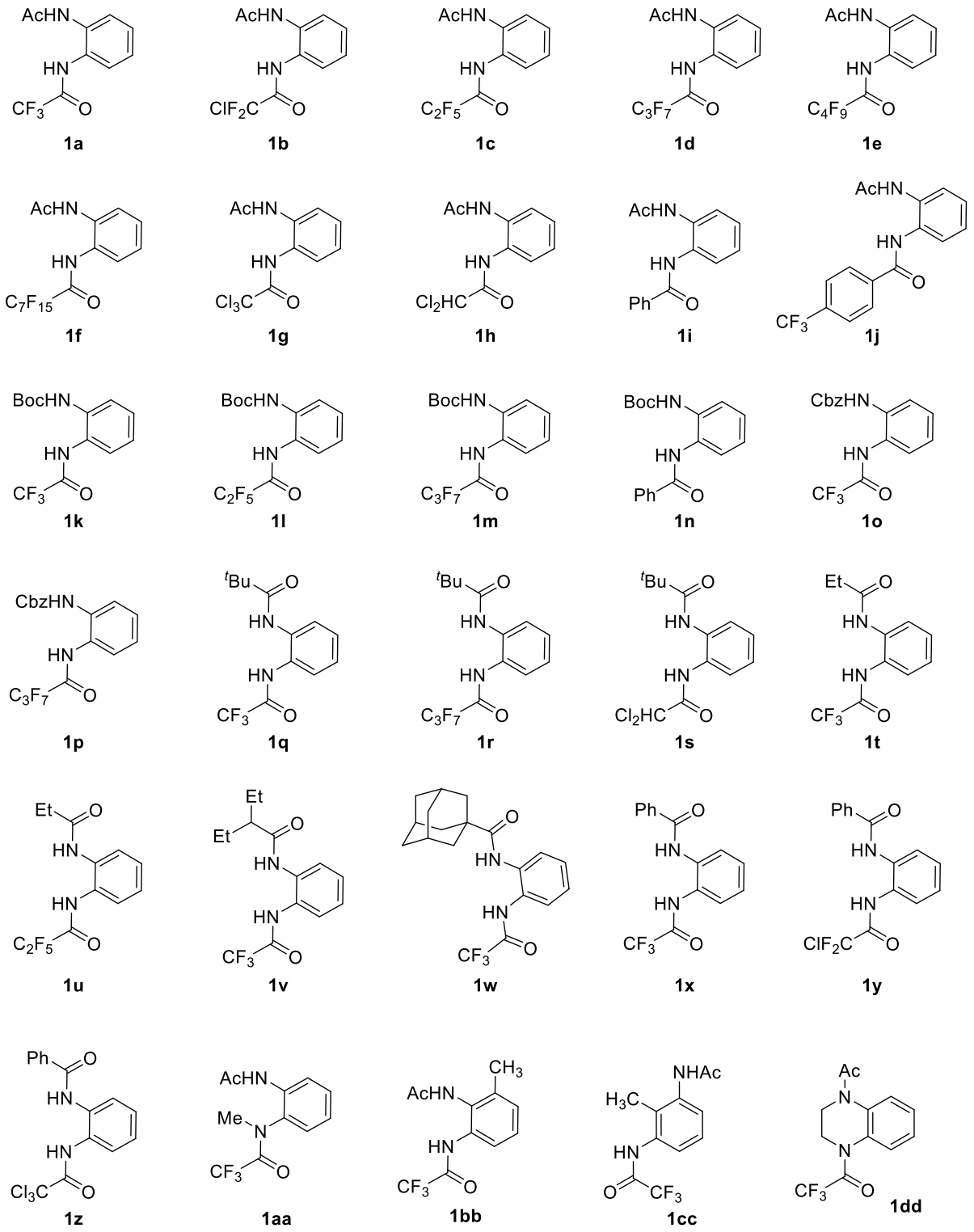
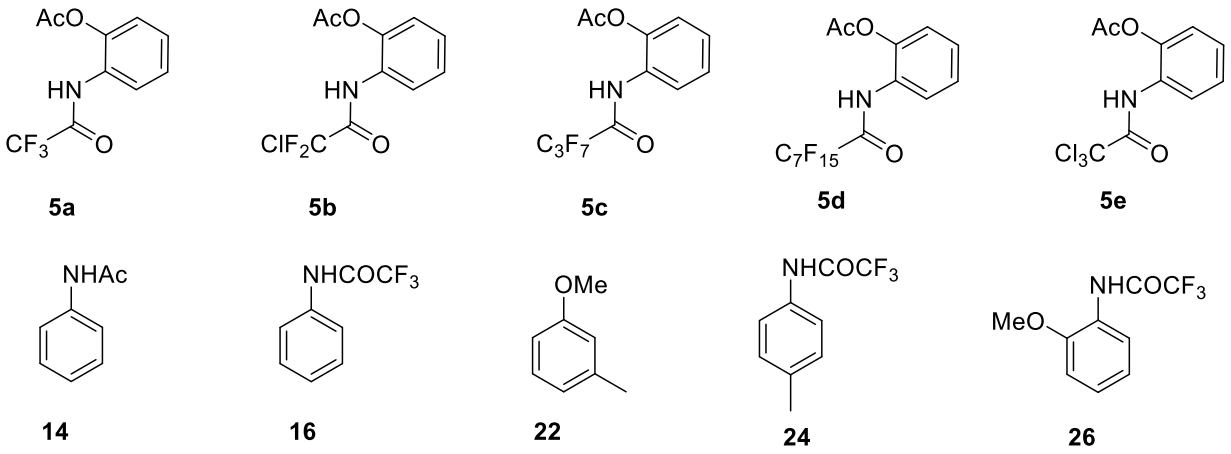
EXPERIMENTAL SECTION

General Experimental Procedures. Glassware was dried in an oven (120 °C), heated under reduced pressure, and cooled under argon before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Reactions were monitored by thin-layer chromatography on Analtech silica gel plates using UV-light and ceric sulfate or *β*-naphthol for visualization. Column chromatography was performed on silica gel (230–400 mesh) using hexanes and ethyl acetate as eluent. Evaporation of solvents was conducted under reduced pressure at 50 °C. FTIR spectra were recorded neat on a Perkin-Elmer Spectrum 65. Microwave reactions were conducted in a Biotage Initiator Classic. NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C), respectively. Deuterated chloroform was used as the solvent, unless otherwise noted, and spectra were calibrated against the residual solvent peak (7.24 ppm for ^{1}H and 77.0 ppm for ^{13}C) or TMS. Chemical shifts (δ) and coupling constants (J) are given in ppm (parts per million) and Hz (Hertz), respectively. The following abbreviations are used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet. Low resolution ESI mass spectra were obtained on a Waters Acquity UPLC H-Class with PDA and SQ mass detectors using a Waters BEH C_{18} 1.7 μm column (2.1x50mm). High resolution mass spectra were obtained on a VG 70–70H or LC/MSD trapSL spectrometer operating at 70 eV using a direct inlet system.

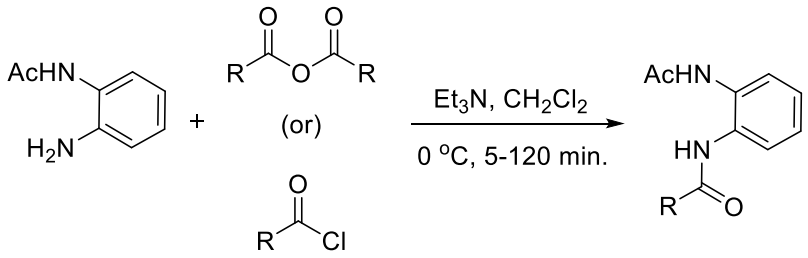
Figure S1: Structures of unsymmetrical amides, 2-amidophenols and other aromatic compounds





3-Methylanisole (**22**; CAS Number: 100-84-5) is commercially available and was used without further purification. All the other starting materials were synthesized as described below.

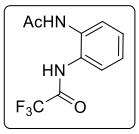
General procedure for the synthesis of diamides 1a-1j:[1]



N-(2-Aminophenyl)acetamide (600 mg, 4.0 mmol) and triethylamine (606 mg, 816 μL, 6.0 mmol, 1.5 equiv.) were dissolved in anhydrous dichloromethane (20 mL), and the mixture was cooled to 0 °C. The corresponding halogenated acid chloride/anhydride (4.2 mmol, 1.05 equiv. in 2 mL of dichloromethane) was added. The reaction mixture was stirred at the same temperature for 5-120 min. After completion of the reaction monitored by TLC, dichloromethane (20 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (30 mL) and brine (30 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexanes, 10:90 to 50:50) to give the corresponding diamide (**1a-j**).

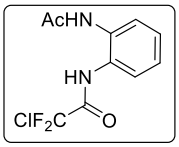
Note: Maintain the reaction at temperature at 0 °C (using ice bath) and start monitoring reaction after 5 min. and quench the reaction mixture immediately once starting material is consumed. New impurity spots may appear in the TLC at longer reaction times, higher temperatures and if you use excess acylating agent. Compounds **1i** and **1j** were reported previously.[1]

***N*-(2-Acetamidophenyl)-2,2,2-trifluoroacetamide (1a):**



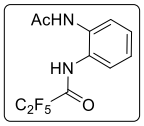
From trifluoroacetic anhydride (882 mg, 588 μL, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 889 mg (90%), R_f = 0.25 (EtOAc/hexanes 30:70), mp = 141-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.78 (s, 1H), 7.68 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.31 (td, *J* = 7.8, 1.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.5 Hz, 1H), 7.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 156.0 (q, *J* = 37.6 Hz), 129.8, 128.6, 127.4, 127.1, 125.9, 124.6, 115.9 (q, *J* = 288.1 Hz), 23.5; FTIR (neat): 3163, 3019, 1756, 1632, 1496, 1331, 1259, 1103, 977, 775 cm^{-1}; MS (ESI): *m/z* 247 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}F_3N_2O_2$($M+H)^+$: 247.0689, found: 247.0693.

***N*-(2-Acetamidophenyl)-2-chloro-2,2-difluoroacetamide (1b):**



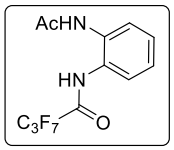
From chlorodifluoroacetic anhydride (1.02 g, 729 μL, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 873 mg (83%), R_f = 0.25 (EtOAc/hexanes 30:70), mp = 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.88 (s, 1H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.32 (td, *J* = 7.8, 1.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.5 Hz, 1H), 7.07 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 158.2 (t, *J* = 30.5 Hz), 130.0, 128.8, 127.4, 127.1, 126.0, 124.7, 119.1 (t, *J* = 302.9 Hz), 23.5; FTIR (neat): 3125, 3013, 1719, 1653, 1501, 1378, 1233, 1097, 932, 841, 698 cm^{-1}; MS (ESI): *m/z* 263 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}ClF_2N_2O_2$ $(M+H)^+$: 263.0393, found: 263.0397.

***N*-(2-Acetamidophenyl)-2,2,3,3,3-pentafluoropropanamide (1c):**



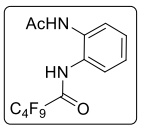
From pentafluoropropionic anhydride (1.32 g, 829 μL, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 1.081 g (91%), R_f = 0.30 (EtOAc/hexanes 30:70), mp = 114-116 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.78 (s, 1H), 7.66 (dd, J = 8.0, 1.1 Hz, 1H), 7.30 (td, J = 7.8, 1.4 Hz, 1H), 7.22 (td, J = 7.7, 1.4 Hz, 1H), 7.04 (dd, J = 7.9, 1.3 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 156.5 (t, J = 25.8 Hz), 129.9, 128.7, 127.5, 127.2, 126.1, 124.6, 117.9 (dt, J = 286.9, 34.8 Hz), 108.3 (dd, J = 266.5, 38.9 Hz), 23.4; FTIR (neat): 3307, 3055, 1733, 1650, 1527, 1322, 1194, 1025, 750, 644 cm^{-1}; MS (ESI): *m/z* 297 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{11}H_{10}F_5N_2O_2$ $(M+H)^+$: 297.0657, found: 297.0661.

***N*-(2-Acetamidophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (1d):**



From perfluorobutyryl chloride (974 mg, 620 μL, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 1.193 g (86%), R_f = 0.31 (EtOAc/hexanes 30:70), mp = 94-96 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.83 (s, 1H), 7.56 (dd, J = 8.0, 1.0 Hz, 1H), 7.26 – 7.18 (m, 1H), 7.13 (td, J = 7.7, 1.4 Hz, 1H), 6.96 (dd, J = 7.9, 1.3 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 156.3 (t, J = 26.3 Hz), 129.9, 128.7, 127.5, 127.1, 126.0, 124.6, 118.8 (t, J = 33.4 Hz), 116.0 (t, J = 33.5 Hz), 108.5 (q, J = 59.9 Hz), 23.3; FTIR (neat): 3315, 3027, 1715, 1638, 1517, 1429, 1259, 1132, 1048, 921, 796 cm^{-1}; MS (ESI): *m/z* 347 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{12}H_{10}F_7N_2O_2$ $(M+H)^+$: 347.0625, found: 347.0626.

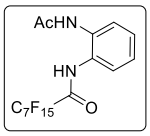
***N*-(2-Acetamidophenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentanamide (1e):**



From nonafluoropentanoyl chloride (1.18 g, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 1.41 g (89%), R_f = 0.35 (EtOAc/hexanes 30:70), mp = 98-100 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.83 (s, 1H), 7.64 (dd, J = 8.1, 1.3 Hz, 1H), 7.29 (td, J = 7.8, 1.4 Hz, 1H),

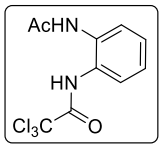
7.21 (td, *J* = 7.7, 1.5 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 156.3 (t, *J* = 26.1 Hz), 129.9, 128.8, 127.5, 127.1, 126.1, 124.6, 118.6 (t, *J* = 31.3 Hz), 115.8 (t, *J* = 32.7 Hz), 111.7 (t, *J* = 33.4 Hz), 109.5 (q, *J* = 31.5 Hz), 23.3; FTIR (neat): 3306, 3078, 1708, 1667, 1540, 1481, 1192, 1135, 918, 836, 750, 647 cm^{-1}; MS (ESI): *m/z* 397 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{10}F_9N_2O_2$ $(M+H)^+$:397.0593, found: 397.0598.

***N*-(2-Acetamidophenyl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide (1f):**



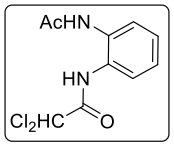
From pentadecafluorooctanoyl chloride (1.81 g, 1.04 mL, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 1.77 g (81%), R_f = 0.35 (EtOAc/hexanes 30:70), mp = 94-96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.72 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.31 (td, *J* = 7.9, 1.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.4 Hz, 1H), 7.07 (dd, *J* = 7.9, 1.2 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 156.3 (t, *J* = 26.0 Hz), 129.9, 128.9, 127.5, 127.2, 126.1, 124.6, 120.0, 118.5, 116.0, 115.7, 113.3, 110.8, 108.8, 23.3; FTIR (neat): 3342, 3149, 3005, 1709, 1670, 1531, 1348, 1197, 1142, 1017, 923, 753 cm^{-1}; MS (ESI): *m/z* 547 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_{10}F_{15}N_2O_2$ $(M+H)^+$: 547.0497, found: 547.0499.

***N*-(2-Acetamidophenyl)-2,2,2-trichloroacetamide (1g):**



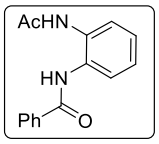
From trichloroacetyl chloride (764 mg, 0.469 μL, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 846 mg (72%), R_f = 0.35 (EtOAc/hexanes 30:70), mp = 138-140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (s, 1H), 7.87 (s, 1H), 7.53 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.22 (td, *J* = 7.9, 1.4 Hz, 1H), 7.12 (td, *J* = 7.7, 1.4 Hz, 1H), 6.96 (dd, *J* = 8.0, 1.3 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 161.2, 130.3, 129.9, 127.4, 127.1, 126.2, 124.8, 92.8, 23.4; FTIR (neat): 3335, 3021, 1707, 1650, 1519, 1409, 1296, 1164, 976, 853, 712 cm^{-1}; MS (ESI): *m/z* 295 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}Cl_3N_2O_2$ $(M+H)^+$: 294.9802, found: 294.9803.

***N*-(2-Acetamidophenyl)-2,2-dichloroacetamide (1h)**:



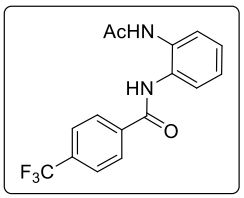
From dichloroacetyl chloride (617 mg, 403 μL, 4.2 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 783 mg (75%), R_f = 0.35 (EtOAc/hexanes 30:70), mp = 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 7.85 (s, 1H), 7.56 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.29 (td, *J* = 7.7, 1.5 Hz, 1H), 7.23 (td, *J* = 7.7, 1.4 Hz, 1H), 7.16 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.06 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 163.4, 130.2, 129.7, 127.2, 127.0, 126.1, 125.1, 66.8, 23.5; FTIR (neat): 3342, 3015, 1736, 1625, 1542, 1396, 1231, 1117, 973, 886, 734 cm^{-1}; MS (ESI): *m/z* 261 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{11}Cl_2N_2O_2$ $(M+H)^+$: 261.0192, found: 261.0195.

***N*-(2-Acetamidophenyl)benzamide (1i)**:[1]



From benzoyl chloride (515 mg, 425 μL, 3.66 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography (hexanes/EtOAc = 80/20; R_f = 0.40 in hexanes/EtOAc = 3/1). The product was obtained as a brown solid, 0.753 g (89%); ^{1}H NMR (400 MHz, 8:2 $CDCl_3$/DMSO-d_6): δ 9.49 (s, 1H), 8.71 (s, 1H), 7.98 − 7.93 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.55 − 7.48 (m, 3H), 7.08 − 7.02 (m, 2H), 6.92 (t, *J* = 7.1 Hz, 1H), 2.04 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, 8:2 $CDCl_3$/DMSO-d_6): δ 170.3, 166.6, 133.5, 132.2, 130.8, 130.4, 128.8, 127.5, 126.3, 126.2, 126.0, 125.0, 23.6; FTIR (neat): 3231, 3091, 1646, 1512, 1431, 1329, 1292, 1155, 1090, 821 cm^{-1}; MS (ESI) m/z 255 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}O_2N_2$ $(M+H)^+$: 255.1128; found 255.1134.

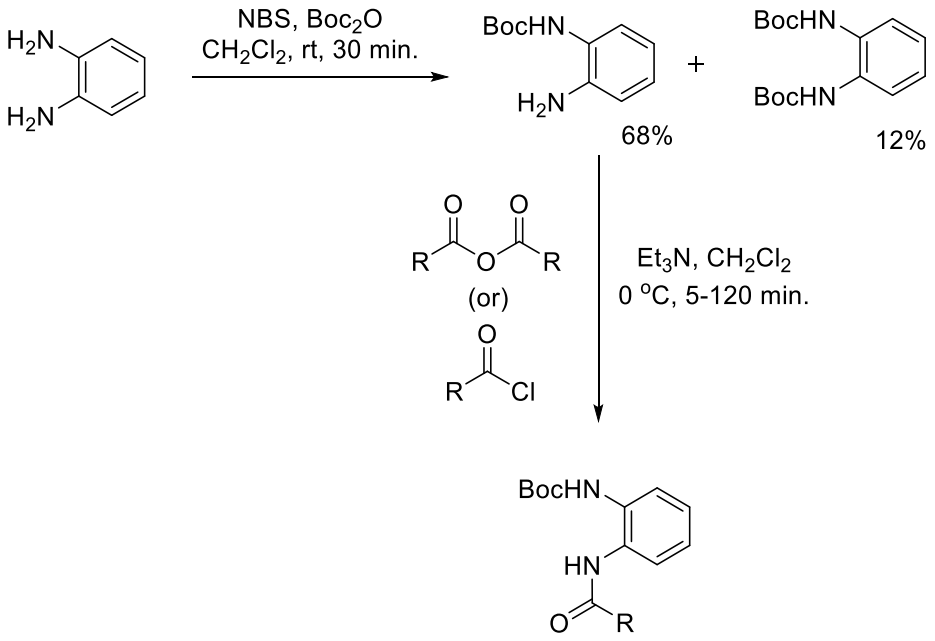
***N*-(2-Acetamidophenyl)-4-(trifluoromethyl)benzamide (1j):[1]**



From 4-(trifluoromethyl)benzoyl chloride (764 mg, 3.66 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography (hexanes/EtOAc = 70/30; R_f = 0.25 in hexanes/EtOAc = 3/1). The product was obtained as a brown solid, 0.792 g (74%); mp = 182−183 °C; ^{1}H NMR (400 MHz, 8:2 $CDCl_3$/DMSO-d_6): δ 10.11 (s, 1H), 9.77 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.76 (d,

J = 8.2 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.19 (s, 3H); ^{13}C{1H}NMR (100 MHz, 8:2 $CDCl_3$/DMSO-d_6): δ 170.3, 164.0, 138.0, 132.7, 130.7, 130.11, 128.1, 125.9, 125.7, 125.5, 125.5, 125.1, 122.5, 23.7; FTIR (neat): 3245, 3056, 2994, 1665, 1602, 1502, 1436, 1367, 1252, 1179, 1025, 822 cm^{-1}; MS (ESI) m/z 323 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_{13}F_3O_2N_2Na$ $(M+H)^+$ 345.0821; found 345.0827.

General procedure for the synthesis of Boc-protected amides (1k-n):[2]

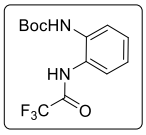


To a stirred solution of benzene-1,2-diamine (1 g, 0.925 mmol) and $(Boc)_2O$ (2.01 g, 0.925 mmol) in dichloromethane (20 mL) was added *N*-bromosuccinimide (177 mg, 0.1 mmol) at room temperature and the reaction mixture turned to a dark brown color. The mixture was stirred for 30 min. and the progress was monitored using TLC. After completion, the reaction mixture was diluted with 20 mL of dichloromethane, washed with 1 molar solution of sodium thiosulphate (40 mL), brine (30 mL) and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 50:50) to afford the *tert*-butyl (2-aminophenyl) carbamate as a brown solid (mono-Boc compound 1.30 g, 68%). ^{1}H and ^{13}C NMR were found to be identical with those reported in the literature. The symmetrical di-Boc compound formed as a minor product in the

reaction (341 mg, 12%). Mono-Boc and di-Boc derivatives were reported in the literature, and their spectral data were in good agreement with reported compounds.[2-3]

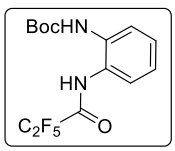
To the mono-Boc compound (312 mg, 1.5 mmol), in dichloromethane (15 mL), was added triethylamine (227 mg, 306 μL, 2.25 mmol), and the mixture was cooled to 0 °C. The corresponding acid chloride/acid anhydride (1.57 mmol), dissolved in 2 mL of dichloromethane, was added. The reaction mixture was stirred at the same temperature for 10-60 min. Dichloromethane (20 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (30 mL) and brine (30 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to give the corresponding Boc-protected diamide (**1k-n**).

(3r,5r,7r)-*N*-(2-*tert*-Butyl (2-(2,2,2-trifluoroacetamido)phenyl)carbamate (1k):



From trifluoroacetic anhydride (325 mg, 220 μL, 1.57 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 430 mg (94%), R_f = 0.25 (EtOAc/hexanes 20:80), mp = 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.79 (dd, J = 8.0, 1.3 Hz, 1H), 7.29 (td, J = 7.8, 1.5 Hz, 1H), 7.23 (td, J = 7.7, 1.6 Hz, 1H), 7.07 (dd, J = 7.9, 1.5 Hz, 1H), 6.61 (s, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 154.8, 129.4, 128.7, 127.2, 126.6, 125.8, 124.3, 117.5, 82.6, 28.0; FTIR (neat): 3356, 3253, 1736, 1676, 1512, 1307, 1147, 900, 743 cm^{-1}; MS (ESI): *m/z* 305 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}F_3N_2O_3$ $(M+H)^+$: 305.1108, found: 305.1111.

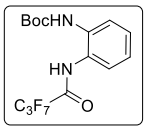
***tert*-Butyl (2-(2,2,3,3-tetrafluoropropanamido)phenyl)carbamate (1l):**



From pentafluoropropionic anhydride (490 mg, 310 μL, 1.57 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 485 mg (91%), R_f = 0.25 (EtOAc/hexanes 20:80), mp = 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.79 (dd, J = 8.0, 1.4 Hz, 1H), 7.37 – 7.19 (m, 2H), 7.09 (dd, J = 7.8, 1.5 Hz, 1H), 6.64 (s, 1H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (t, J = 25.6 Hz), 154.8, 129.5, 128.7, 127.3, 126.6, 125.9, 124.3, 117.9 (dt, J = 286.6, 34.8 Hz), 107.0

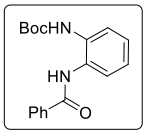
(td, J = 247.2, 38.8 Hz), 82.5, 28.0; FTIR (neat): 3327, 3059, 1709, 1653, 1476, 1308, 1187, 1057, 962, 796, 713 cm^{-1}; MS (ESI): *m/z* 355 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}F_5N_2O_3$ $(M+H)^+$: 355.1076, found: 355.1077.

***tert*-Butyl (2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl)carbamate (1m):**



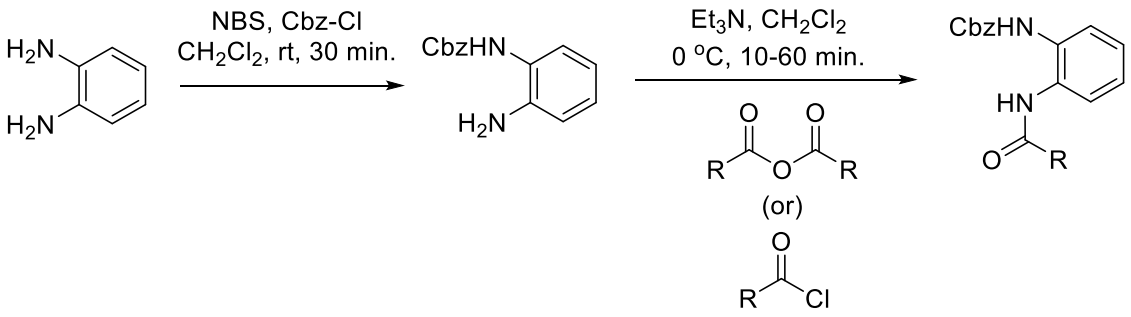
From perfluorobutyryl chloride (364 mg, 232 μL, 1.57 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 550 mg (86%), R_f = 0.25 (EtOAc/hexanes 20:80), mp = 95-97 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.77 (dd, J = 8.0, 1.4 Hz, 1H), 7.34 – 7.16 (m, 2H), 7.07 (dd, J = 7.9, 1.5 Hz, 1H), 6.59 (s, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8 (t, J = 25.6 Hz), 154.8, 129.5, 128.8, 127.3, 126.6, 125.9, 124.2, 116.1, 111.4, 108.7, 82.5, 28.0; FTIR (neat): 3364, 3264, 2987, 1735, 1671, 1519, 1196, 1058, 876, 750 cm^{-1}; MS (ESI): *m/z* 405 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}F_7NaN_2O_3$ $(M+Na)^+$: 427.0863, found: 427.0865.

***tert*-Butyl (2-benzamidophenyl)carbamate (1n):**



From benzoyl chloride (221 mg, 182 μL, 1.57 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography (hexanes/EtOAc = 80/20; R_f = 0.40 in hexanes/EtOAc = 3/1). The product was obtained as a brown solid 380 mg (81%), R_f = 0.25 (EtOAc/hexanes 20:80), mp = 102-104 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.37 (s, 1H), 7.98 – 7.92 (m, 2H), 7.61 – 7.54 (m, 1H), 7.53 – 7.45 (m, 3H), 7.30 – 7.21 (m, 1H), 7.10 – 6.98 (m, 2H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 166.0, 133.6, 132.0, 131.1, 130.8, 128.6, 127.4, 126.2, 126.0, 125.9, 125.9, 39.4, 27.5; FTIR (neat): 3279, 2967, 1654, 1519, 1489, 1310, 1055, 915, 751, 712 cm^{-1}; MS (ESI): *m/z* 313 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{21}N_2O_3$ $(M+H)^+$: 313.1547, found: 313.1551.

General procedure for the synthesis of Cbz-protected amides (1o and 1p):[2, 4]

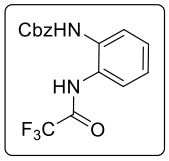


To a stirred solution of benzene-1,2-diamine (1 g, 0.925 mmol) and benzyl chloroformate (1.57 g, 0.925 mmol) in dichloromethane (30 mL) was added *N*-bromosuccinimide (177 mg, 0.1 mmol) at room temperature, and the reaction mixture turned a dark brown color. The mixture was stirred for 30 min. and the progress was monitored using TLC. After completion, the reaction mixture was diluted with 20 mL of dichloromethane, washed with 1 molar solution of sodium thiosulphate (40 mL), brine (30 mL) and dried with $MgSO_4$. The solvent was removed under reduced pressure, and the product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 50:50) to afford benzyl (2-aminophenyl) carbamate as a brown solid (1.61 g, 72%). ^{1}H and ^{13}C NMR of mono-Cbz and di-Cbz derivatives were identical with those reported in the literature.[3b, 4-5]

To the mono-Cbz compound (242 mg, 1 mmol), in dichloromethane (10 mL), triethylamine (152 mg, 204 μL, 1.5 mmol) was added, and the mixture was cooled to 0 °C. The corresponding acid chloride/acid anhydride (1.05 mmol), dissolved in 2 mL of dichloromethane, was added. The reaction mixture was stirred at the same temperature for 10-60 min. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (20 mL) and brine (20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to give the corresponding diamide product (**1o** and **p**).

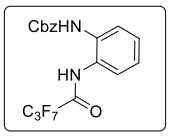
Benzyl (2-(2,2,2-trifluoroacetamido)phenyl)carbamate (1o):

From trifluoroacetic anhydride (217 mg, 147 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 307



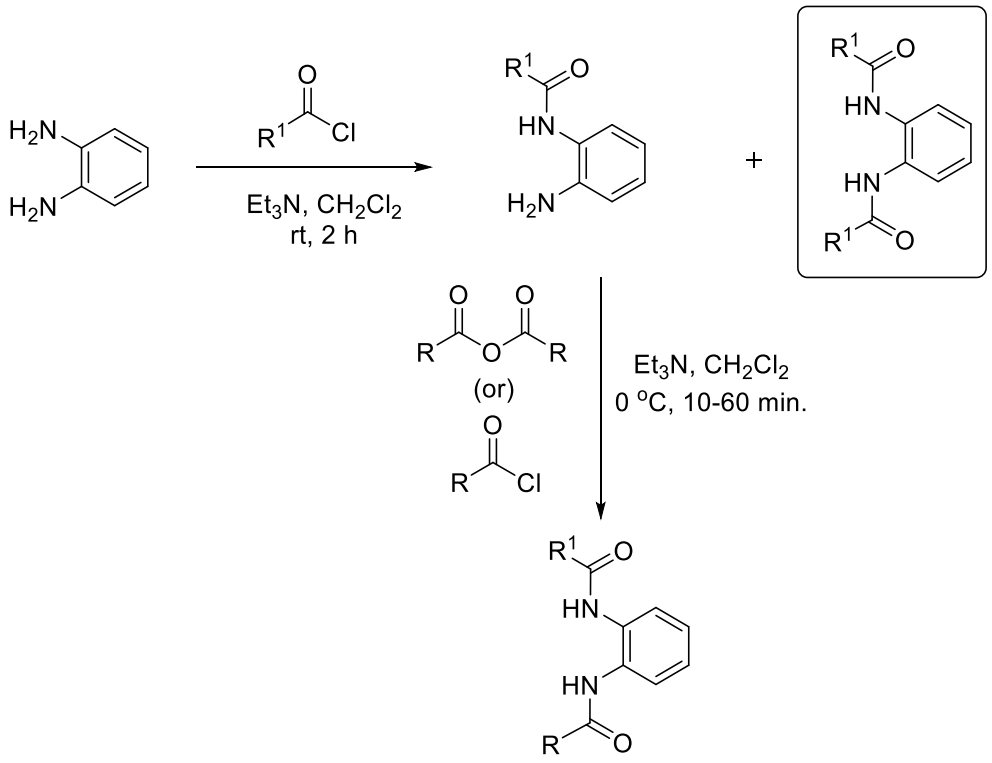
mg (91%), R_f = 0.25 (EtOAc/hexanes 30:70), mp = 94-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 7.61 (dd, J = 7.9, 1.4 Hz, 1H), 7.38 – 7.21 (m, 5H), 7.22 – 7.07 (m, 2H), 7.03 (dd, J = 7.8, 1.6 Hz, 1H), 6.87 (d, J = 37.2 Hz, 1H), 5.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6 (q, J = 37.4 Hz), 155.3, 135.2, 129.7, 128.7, 128.7, 128.4, 128.3, 127.4, 126.7, 125.8, 124.5, 115.9 (q, J = 288.3 Hz), 68.2; FTIR (neat): 3341, 3125, 2976, 1723, 1651, 1534, 1316, 1241, 1097, 1003, 914, 836, 705 cm^{-1}; MS (ESI): *m/z* 339 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_{14}F_3N_2O_3$ $(M+H)^+$: 339.0951, found: 339.0954.

Benzyl (2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl)carbamate (1p):



From perfluorobutyryl chloride (243 mg, 155 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 377 mg (86%), R_f = 0.25 (EtOAc/hexanes 20:80), mp = 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.63 (dd, J = 7.9, 1.4 Hz, 1H), 7.39 – 7.26 (m, 5H), 7.25 – 7.10 (m, 2H), 7.05 (dd, J = 7.8, 1.5 Hz, 1H), 6.74 (s, 1H), 5.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (t, J = 26.2 Hz), 155.3, 135.2, 129.4, 128.7, 128.7, 128.6, 128.5, 127.6, 126.8, 126.0, 124.5, 116.0, 111.3, 108.6, 68.3; FTIR (neat): 3309, 3059, 1732, 1615, 1546, 1401, 1285, 1137, 1029, 913, 786 cm^{-1}; MS (ESI): *m/z* 439 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{14}F_7N_2O_3$ $(M+H)^+$: 439.0887, found: 439.0891.

General procedure for the synthesis of diamides (1q-w):



To a stirred solution of benzene-1,2-diamine (1 g, 9.25 mmol) in dichloromethane (40 mL) Et_3N (642 μL, 4.62 mmol) was added dropwise at RT. The solution was stirred for 10 min. at room temperature and acyl chloride (4.62 mmol) dissolved in dichloromethane (10 mL) was added in one portion. The solution was stirred for 2 h and washed with saturated sodium bicarbonate solution (60 mL) and brine (50 mL), and the layers were separated. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (EtOAc/hexanes, 10:90 to 40:60) to give the corresponding mono-amide (55-69 %) as a major product. The symmetric di-amide was also isolated as a minor product (8-15% yield).

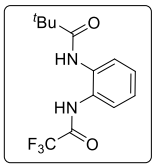
Mono-amide intermediates and symmetric di-amide by-products were reported in the literature and their spectral data were in good agreement with reported compounds. Mono-amide intermediates: *N*- *N*-(2-aminophenyl)pivalamide,[6] *N*-(2-aminophenyl)propionamide,[7] *N*-(2-aminophenyl)-2-ethyl butanamide (commercially available, CAS Number: 946736-41-0) *N*-(2-aminophenyl)adamantane-1-carboxamide,[8] *N*-

(2-amino-6-methylphenyl)acetamide),[9] *N*-(3-amino-2-methylphenyl)acetamide (commercially available, CAS Number 65999-76-0), and 1-(3,4-Dihydroquinoxalin-1(2*H*)-yl)ethan-1-one.[10]

Symmetric di-amide by-product derivatives: *N*,*N*'-(1,2-phenylene)bis(2,2-dimethylpropanamide),[11] *N*,*N*'-(1,2-phenylene)dipropionamide,[12] *N*,*N*'-(1,2-phenylene)bis(2-ethylbutanamide) (commercially available, CAS Number: 548437-71-4) and *N*,*N*'-(1,2-phenylene)bis(adamantane-1-carboxamide).[8]

To the stirred solution of mono-amide (1.0 mmol), in dichloromethane (10 mL), triethylamine (1.5 mmol) was added, and the mixture was cooled to 0 °C. The corresponding acid chloride/acid anhydride (1.05 mmol), dissolved in 2 mL of dichloromethane, was added. The reaction mixture was stirred at the same temperature for 10-60 min. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (20 mL) and brine (25 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to give the corresponding asymmetric diamide (**1q-w**).

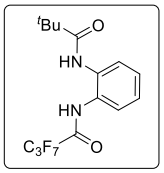
***N*-(2-(2,2,2-Trifluoroacetamido)phenyl)pivalamide (1q):**



From trifluoroacetic anhydride (217 mg, 147 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 262 mg (91%), R_f = 0.30 (EtOAc/hexanes 20:80), mp = 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.81 (s, 1H), 7.65 (dd, J = 8.0, 1.4 Hz, 1H), 7.35 – 7.19 (m, 2H), 7.10 (dd, J = 7.9, 1.5 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 155.8 (q, J = 37.4 Hz), 130.0, 129.0, 127.3, 127.1, 125.9, 125.1, 116.0 (q, J = 288.2 Hz), 39.4, 27.4; FTIR (neat): 3297, 3237, 2968, 1707, 1546, 1451, 1152, 904, 753 cm^{-1}; MS (ESI): *m/z* 289 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}F_3N_2O_2$ $(M+H)^+$: 289.1158, found: 289.1160.

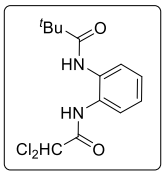
2,2,3,3,4,4,4-Heptafluoro-*N*-(2-pivalamidophenyl)butanamide (**1r**):

From perfluorobutyryl chloride (243 mg, 155 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 345



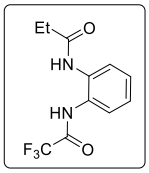
mg (89%), R_f = 0.30 (EtOAc/hexanes 20:80), mp = 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.74 (dd, J = 8.1, 1.4 Hz, 1H), 7.66 (s, 1H), 7.33 (td, J = 7.8, 1.5 Hz, 1H), 7.25 (td, J = 7.7, 1.5 Hz, 1H), 7.10 (dd, J = 7.9, 1.5 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.0, 156.0 (t, J = 26.0 Hz), 129.6, 129.3, 127.3, 127.3, 126.0, 124.7, 118. 9, 116.0, 108.7, 39.5, 27.5; FTIR (neat): 3288, 2972, 1709, 1500, 1354, 1186, 1120, 928, 750 cm^{-1}; MS (ESI): *m/z* 389 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}F_7N_2O_2$ $(M+H)^+$: 389.1095, found: 389.1100.

***N*-(2-(2,2-Dichloroacetamido)phenyl)pivalamide (1s):**



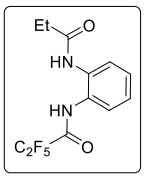
From dichloroacetyl chloride (155 mg, 101 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 217 mg (76%), R_f = 0.30 (EtOAc/hexanes 20:80), mp = 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 7.78 (s, 1H), 7.55 (dd, J = 13.5, 6.1 Hz, 1H), 7.31 – 7.18 (m, 3H), 6.03 (s, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 163.1, 130.3, 130.0, 127.0, 126.9, 125.8, 125.4, 66.8, 39.4, 27.6; FTIR (neat): 3317, 3209, 2971, 1693, 1639, 1510, 1443, 1225, 1175, 929, 809 cm^{-1}; MS (ESI): *m/z* 303 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{17}Cl_2N_2O_2$ $(M+H)^+$: 303.0662, found: 303.0664.

***N*-(2-(2,2,2-Trifluoroacetamido)phenyl)propionamide (1t):**



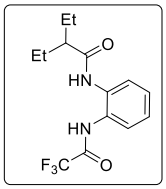
From trifluoroacetic anhydride (217 mg, 147 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 223 mg (86%), R_f = 0.25 (EtOAc/hexanes 30:70), mp = 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.76 (s, 1H), 7.66 (dd, J = 8.0, 1.2 Hz, 1H), 7.30 (td, J = 7.8, 1.5 Hz, 1H), 7.22 (td, J = 7.7, 1.5 Hz, 1H), 7.06 (dd, J = 7.9, 1.4 Hz, 1H), 2.40 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 156.0 (q, J = 37.4 Hz), 129.9, 128.6, 127.4, 127.0, 125.9, 124.6, 116.0 (q, J = 288.2 Hz), 30.0, 9.8; FTIR (neat): 3271, 2985, 2882, 1731, 1601, 1523, 1283, 1135, 906, 759 cm^{-1}; MS (ESI): *m/z* 261 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{11}H_{12}F_3N_2O_2$ $(M+H)^+$: 261.0845, found: 261.0849.

2,2,3,3,3-Pentafluoro-*N*-(2-propionamidophenyl)propanamide (1u):



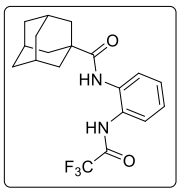
From pentafluoropropionic anhydride (327 mg, 207 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 254 mg (82%), R_f = 0.30 (EtOAc/hexanes 30:70), mp = 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.63 (s, 1H), 7.31 (td, *J* = 7.8, 1.4 Hz, 1H), 7.23 (td, *J* = 7.7, 1.5 Hz, 1H), 7.07 (dd, *J* = 7.9, 1.4 Hz, 1H), 2.43 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 156.4 (t, *J* = 25.8 Hz), 129.8, 128.9, 127.4, 127.1, 126.1, 124.5, 116.5, 107.2, 30.0, 9.7; FTIR (neat): 3315, 2991, 1732, 1644, 1525, 1457, 1175, 1075, 894, 752 cm^{-1}; MS (ESI): *m/z* 311 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{12}H_{12}F_5N_2O_2$ $(M+H)^+$: 311.0813, found: 311.0817.

2-Ethyl-*N*-(2-(2,2,2-trifluoroacetamido)phenyl)butanamide (1v):



From trifluoroacetic anhydride (217 mg, 147 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 265 mg (88%), R_f = 0.25 (EtOAc/hexanes 30:70), mp = 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.75 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.70 (s, 1H), 7.31 (td, *J* = 7.9, 1.4 Hz, 1H), 7.21 (td, *J* = 7.7, 1.5 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.4 Hz, 1H), 2.21 – 2.09 (m, 1H), 1.77 – 1.50 (m, 4H), 0.94 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 155.7 (q, *J* = 37.4 Hz), 129.7, 129.1, 127.2, 127.2, 125.9, 124.5, 116.0 (q, *J* = 288.2 Hz), 51.6, 25.8, 11.9; FTIR (neat): 3277, 2961, 2933, 1741, 1643, 1520, 1448, 1282, 1142, 901, 757 cm^{-1}; MS (ESI): *m/z* 303 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{18}F_3N_2O_2$ $(M+H)^+$: 303.1315, found: 303.1316.

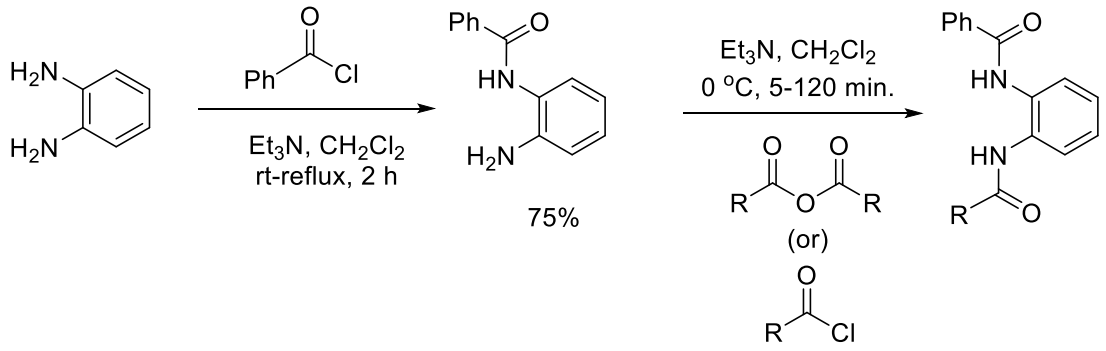
(3r,5r,7r)-*N*-(2-(2,2,2-Trifluoroacetamido)phenyl)adamantane-1-carboxamide (1w):



From trifluoroacetic anhydride (217 mg, 147 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 256 mg (70%), R_f = 0.20 (EtOAc/hexanes 40:60), mp = 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 7.75 (s, 1H), 7.71 (dd, *J* = 8.0, 1.3 Hz, 1H),

7.33 (td, *J* = 7.8, 1.5 Hz, 1H), 7.25 (td, *J* = 7.7, 1.5 Hz, 1H), 7.10 (dd, *J* = 7.9, 1.4 Hz, 1H), 2.14 (s, 3H), 1.96 (d, *J* = 2.7 Hz, 6H), 1.79 (q, *J* = 12.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 155.7 (q, *J* = 37.3 Hz), 129.8, 129.1, 127.2, 127.1, 125.9, 125.0, 116.0 (q, *J* = 288.3 Hz), 41.3, 39.0, 36.2, 27.9; FTIR (neat): 3272, 2901, 2849, 1709, 1553, 1537, 1308, 1169, 925, 749 cm^{-1}; MS (ESI): *m/z* 367 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{19}H_{22}F_3N_2O_2$ $(M+H)^+$: 367.1628, found: 367.1632.

Synthesis of diamides 1x-z:[1]

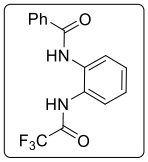


To a stirred solution of benzene-1,2-diamine (4.00 g, 37 mmol, 2 equiv.) in dichloromethane (100 mL) Et_3N (2.6 mL, 18 mmol, 1 equiv) was added dropwise at room temperature. The solution was heated to reflux, and benzoyl chloride (2.15 mL, 18 mmol, 1 equiv) dissolved in dichloromethane (80 mL) was added dropwise via dropping funnel over 90 min. The solution was refluxed for 2 h and concentrated *in vacuo*. The residue was purified by flash chromatography (hexanes: EtOAc 70:30) to afford the *N*-(2-aminophenyl)benzamide (2.86 g, 75%) as a brown solid and the spectral data was in good agreement with reported compound.[1]

To the stirred solution of *N*-(2-aminophenyl) benzamide (212 mg, 1.0 mmol), in dichloromethane (10 mL), triethylamine (205 μL, 1.5 mmol) was added, and the mixture was cooled to 0 °C. The corresponding acid chloride/acid anhydride (1.05 mmol), dissolved in 2 mL of dichloromethane, was added. The reaction mixture was stirred at the same temperature for 5-120 min. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (20 mL) and brine (20 mL), dried over

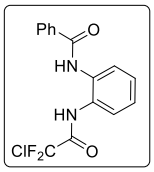
$MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to give the corresponding asymmetric-diamide (**1x-z**).

***N*-(2-(2,2,2-Trifluoroacetamido)phenyl)benzamide (1x)**:[1]



From trifluoroacetic anhydride (217 mg, 147 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 252 mg (82%). R_f = 0.25 (EtOAc/hexanes 30:70), mp = 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 8.60 (s, 1H), 7.87 – 7.80 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.41 (m, 3H), 7.17 – 7.10 (m, 1H), 7.07 – 6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 156.3 (q, J = 37.5 Hz), 132.7, 132.6, 130.1, 128.9, 128.3, 127.6, 127.5, 127.0, 125.8, 125.4, 115.9 (q, J = 288.0 Hz); FTIR (neat): 3239, 3056, 1709, 1646, 1529, 1147, 915, 754 cm^{-1}; MS (ESI): *m/z* 309 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{12}F_3N_2O_2$ $(M+H)^+$: 309.0845, found: 309.0850.

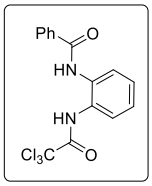
***N*-(2-(2-Chloro-2,2-difluoroacetamido)phenyl)benzamide (1y)**:



From chlorodifluoroacetic anhydride (255 mg, 182 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 223 mg (69%). R_f = 0.25 (EtOAc/hexanes 30:70), mp = 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 8.55 (s, 1H), 7.84 (dd, J = 5.2, 3.3 Hz, 2H), 7.59 – 7.49 (m, 1H), 7.51 – 7.41 (m, 3H), 7.23 – 7.09 (m, 1H), 7.10 – 6.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 151.5 (t, J = 30.7 Hz), 125.7, 125.6, 123.3, 121.8, 121.6, 120.6, 120.5, 120.0, 118.9, 118.4, 112.0 (t, J = 302.8 Hz); FTIR (neat): 3251, 3058, 1709, 1648, 1499, 1309, 1132, 979, 754 cm^{-1}; MS (ESI): *m/z* 325 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{12}ClF_2N_2O_2$ $(M+H)^+$: 325.0550, found: 325.0554.

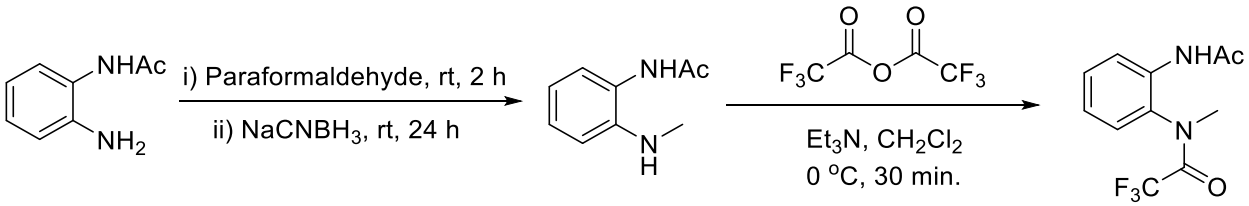
***N*-(2-(2,2,2-Trichloroacetamido)phenyl)benzamide (1z):**

From trichloroacetyl chloride (191 mg, 117 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 234



mg (66%). R_f = 0.25 (EtOAc/hexanes 30:70), mp = 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.50 (s, 1H), 7.97 – 7.87 (m, 2H), 7.60 (dd, J = 8.2, 6.0 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.24 (dt, J = 8.0, 3.8 Hz, 1H), 7.21 – 7.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 161.3, 132.8, 132.5, 130.4, 129.9, 128.8, 127.5, 127.5, 127.1, 126.2, 125.3, 92.8; FTIR (neat): 3301, 3026, 1715, 1637, 1529, 1419, 1293, 1174, 1062, 995, 831, 776 cm^{-1}; MS (ESI): *m/z* 357 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{12}Cl_3N_2O_2$ $(M+H)^+$: 356.9959, found: 356.9963.

***N*-(2-Acetamidophenyl)-2,2,2-trifluoro-*N*-methylacetamide (1aa)**:

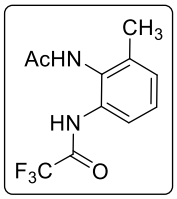


To a solution of *N*-(2-aminophenyl) acetamide (1 g, 6.66 mmol) in 30 mL of dry ethanol, paraformaldehyde (240 mg, 8.00 mmol) and a drop of acetic acid were added. After 2 h at room temperature, sodium cyanoborohydride (8 mL, 8.00 mmol, 1.0 M in THF) was added, and the reaction was stirred for 24 h. The solvent was removed under vacuum, and 50 mL of dichloromethane was added. The resulting mixture was washed with saturated sodium carbonate (50 mL) and water (50 mL) sequentially, dried over $MgSO_4$, concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to afford *N*-(2-(methylamino)phenyl)acetamide as a pale, yellow solid (611 mg, 56% yield; CAS NO: 22902-30-3) and the spectral data was in good agreement with reported literature.[13]

To the stirred solution of *N*-(2-(methylamino)phenyl)acetamide (164 mg, 1.0 mmol), in dichloromethane (10 mL), triethylamine (204 μL, 1.5 mmol) was added, and the mixture was cooled to 0 °C. Trifluoroacetic anhydride (148 uL, 1.05 mmol), dissolved in 1 mL of dichloromethane, was added. The reaction mixture was stirred at the same temperature for 30 min. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica

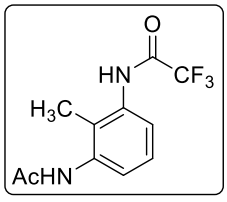
gel (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to give *N*-(2-acetamidophenyl)-2,2,2-trifluoro-*N*-methylacetamide (**1aa**, 234 mg, 90%) as a pale, yellow solid. mp = 121-123 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J = 8.0 Hz, 1H), 7.67 (s, 1H), 7.48 – 7.39 (m, 1H), 7.21 – 7.12 (m, 2H), 3.29 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 158.0 (q, J = 35.6 Hz), 134.7, 130.5, 129.7, 128.3, 124.7, 123.2, 116.1 (q, J = 288.0 Hz), 38.1, 24.4; FTIR (neat): 3341, 3125, 2976, 1723, 1651, 1534, 1316, 1241, 1097, 1003, 914, 836, 705 cm^{-1}; MS (ESI): *m/z* 261 $(M+H)^+$. HRMS (ESI): *m/z* calcd for $C_{11}H_{12}F_3N_2O_2$ $(M+H)^+$: 261.0845, found: 261.0847.

***N*-(2-Acetamido-3-methylphenyl)-2,2,2-trifluoroacetamide (1bb):**



N-(2-Amino-6-methylphenyl)acetamide (100 mg, 0.61 mmol) and triethylamine (92 mg, 124 µL, 0.91 mmol, 1.5 equiv.) were dissolved in anhydrous dichloromethane (10 mL), and the mixture was cooled to 0 ˚C. Trifluoroacetic anhydride (134 mg, 0.64 mmol, 1.05 equiv. in 1 mL of dichloromethane) was added. The reaction mixture was stirred at the same temperature for 1 hour. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (20 mL) and brine (20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexanes, 10:90 to 40:60) to give the *N*-(2-acetamido-3-methylphenyl)-2,2,2-trifluoroacetamide (**1bb**) as a white solid 144 mg, (91%); mp = 175-177 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.59 (s, 1H), 9.40 (s, 1H), 7.36 – 7.13 (m, 3H), 2.21 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.0, 155.2 (q, J = 36.4 Hz), 136.2, 131.8, 131.6, 129.2, 126.8, 124.1, 116.5 (q, J = 288.7 Hz), 23.2, 18.6; FTIR (neat): 3300, 1710, 1661, 1558, 1468, 1283, 1157, 926, 779, 634 cm^{-1}; MS (ESI): *m/z* 261 $(M+H)^+$.

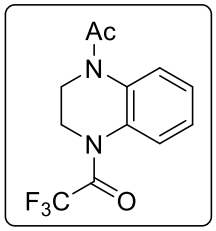
***N*-(3-Acetamido-2-methylphenyl)-2,2,2-trifluoroacetamide (1cc):**



N-(3-Amino-2-methylphenyl)acetamide (100 mg, 0.61 mmol) and triethylamine (92 mg, 124 µL, 0.91 mmol, 1.5 equiv.) were dissolved in anhydrous dichloromethane (10 mL), and the mixture was cooled to 0 ˚C. Trifluoroacetic anhydride (134 mg, 0.64 mmol, 1.05 equiv. in 1 mL of dichloromethane) was added. The reaction mixture was

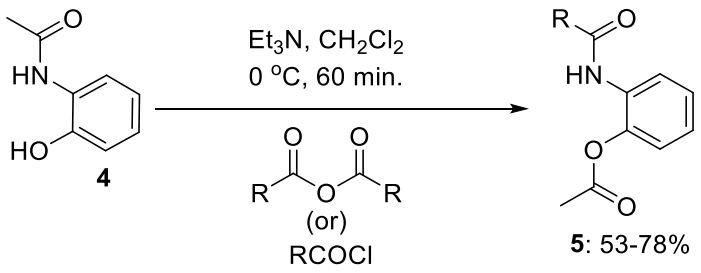
stirred at the same temperature for 1 hour. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (20 mL) and brine (20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexanes, 10:90 to 40:60) to give the *N*-(3-acetamido-2-methylphenyl)-2,2,2-trifluoroacetamide (**1cc**) as a white solid, 128 mg, (81%); mp = 141-143 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.03 (s, 1H), 9.46 (s, 1H), 7.36 (d, J = 7.9 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.8, 155.7 (q, J = 36.5 Hz), 137.9, 134.2, 129.5, 126.2, 125.4, 124.2, 116.6 (q, J = 288.6 Hz), 23.6, 13.2; FTIR (neat): 3326, 2992, 2877, 1703, 1663, 1537, 1460, 1219, 1149, 923, 892, 660 cm^{-1}; MS (ESI): *m/z* 283 $(M+Na)^+$.

1-(4-Acetyl-3,4-dihydroquinoxalin-1(2*H*)-yl)-2,2,2-trifluoroethan-1-one (1dd):



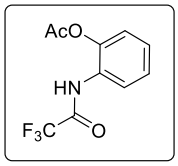
1-(3,4-Dihydroquinoxalin-1(2*H*)-yl)ethan-1-one (108 mg, 0.61 mmol) and triethylamine (92 mg, 124 µL, 0.91 mmol, 1.5 equiv.) were dissolved in anhydrous dichloromethane (10 mL), and the mixture was cooled to 0 °C. Trifluoroacetic anhydride (134 mg, 0.64 mmol, 1.05 equiv. in 1 mL of dichloromethane) was added. The reaction mixture was stirred at the same temperature for 1 hour. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (20 mL) and brine (20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexanes, 10:90 to 40:60) to give the 1-(4-acetyl-3,4-dihydroquinoxalin-1(2*H*)-yl)-2,2,2-trifluoroethan-1-one (**1dd**) as a pale yellow liquid, 138 mg, (83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.09 (m, 4H), 4.04 (d, J = 3.1 Hz, 4H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 137.9, 126.4, 124.8, 124.6, 116.2 (q, J = 288.1 Hz), 114.4, 42.6, 38.6, 22.7; FTIR (neat): 2951, 1663, 1599, 1498, 1327, 1288, 1139, 1080, 756, 669 cm^{-1}; MS (ESI): *m/z* 273 $(M+H)^+$.

Synthesis of 2-amido arylesters with acetyl migration reaction (5a-e):



To the stirred solution of 2-acetamidophenol (151 mg, 1.0 mmol), in dichloromethane (10 mL), triethylamine (204 μL, 1.5 mmol) was added, and the mixture was cooled to 0 °C. The corresponding acid chloride/acid anhydride (1.05 mmol), dissolved in 2 mL of dichloromethane, was added. The reaction mixture was stirred at the same temperature for 60 min. Dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (20 mL) and brine (20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc in EtOH (3:1)/hexanes, 5:95 to 30:70) to give the corresponding acetyl migration product (**5a-e**).

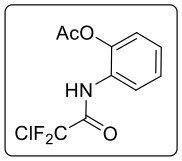
2-(2,2,2-Trifluoroacetamido)phenyl acetate (5a):



From trifluoroacetic anhydride (217 mg, 147 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 193 mg (78%), R_f = 0.51 (EtOAc/hexanes 20:80), mp = 47-48 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.05 (m, 1H), 8.03 (s, 1H), 7.34 – 7.18 (m, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 154.7 (q, J = 37.4 Hz), 141.4, 126.9, 126.8, 126.7, 123.0, 122.4, 115.6 (q, J = 288.7 Hz), 20.8; FTIR (neat): 3301, 1756, 1659, 1532, 1476, 1311, 1153, 913, 776 cm^{-1}; MS (ESI): *m/z* 248 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9F_3NO_3$ $(M+H)^+$: 248.0529, found: 248.0531.

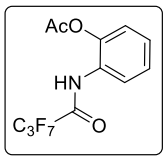
2-(2-Chloro-2,2-difluoroacetamido)phenyl acetate (5b):

From chlorodifluoroacetic anhydride (255 mg, 182 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid,



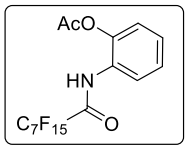
192 mg (73%) of a white solid, R_f = 0.35 (EtOAc/hexanes 20:80), mp = 47-49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.04 (m, 1H), 8.01 (s, 1H), 7.34 – 7.22 (m, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 156.7 (t, J = 30.5 Hz), 141.5, 127.0, 126.9, 126.7, 123.0, 122.4, 118.9 (t, J = 303.1 Hz), 20.9; FTIR (neat): 3278, 1789, 1705, 1532, 1417, 1311, 1128, 1054, 936, 751 cm^{-1}; MS (ESI): *m/z* 264 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9ClF_2NO_3$ $(M+H)^+$:264.0234, found: 264.0236.

2-(2,2,3,3,4,4,4-Heptafluorobutanamido)phenyl acetate (5c):



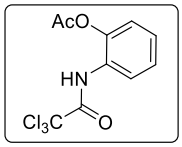
From perfluorobutyryl chloride (243 mg, 155 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a brown solid, 240 mg (69%) of a white solid, R_f = 0.39 (EtOAc/hexanes 20:80), mp = 67-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 8.04 – 7.97 (m, 1H), 7.34 – 7.21 (m, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 155.1 (t, J = 25.7 Hz), 141.7, 127.2, 126.8, 126.7, 123.5, 122.5, 121.4, 118.8, 108.4, 20.7; FTIR (neat): 3289, 1771, 1707, 1529, 1476, 1358, 1236, 1081, 954, 776 cm^{-1}; MS (ESI): *m/z* 348 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{12}H_9F_7NO_3$ $(M+H)^+$: 348.0465, found: 348.0468.

2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctanamido)phenyl acetate (5d):



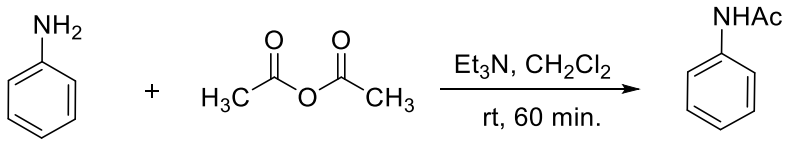
From pentadecafluorooctanoyl chloride (452 mg, 251 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 356 mg (65%) of a white solid, R_f = 0.40 (EtOAc/hexanes 20:80), mp = 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 8.04 – 8.00 (m, 1H), 7.35 – 7.21 (m, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 155.1, 141.6, 127.2, 127.2, 126.8, 126.7, 126.7, 123.4, 123.3, 122.5, 121.4, 118.5, 115.7, 108.9, 20.7; FTIR (neat): 3307, 1773, 1712, 1531, 1421, 1289, 1134, 1020, 913, 770 cm^{-1}; MS (ESI): *m/z* 548 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_9F_{15}NO_3$ $(M+H)^+$: 548.0337, found: 548.0334.

2-(2,2,2-Trichloroacetamido)phenyl acetate (5e):



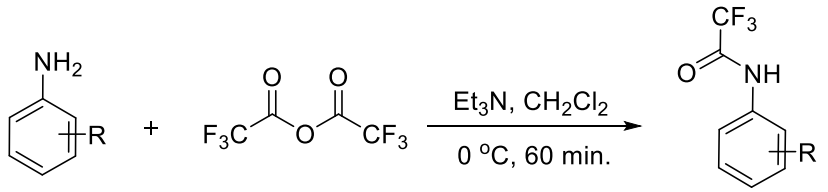
From trichloroacetyl chloride (191 mg, 117 μL, 1.05 mmol) using the above general procedure. The crude residue was purified by silica gel column chromatography. The product was obtained as a white solid, 157 mg (53%) of a white solid, R_f = 0.51 (EtOAc/hexanes 20:80), mp = 113-115 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.13 – 8.01 (m, 1H), 7.39 – 7.18 (m, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 159.2, 141.6, 127.8, 126.7, 126.6, 122.7, 122.3, 92.7, 20.9; FTIR (neat): 3308, 1764, 1709, 1511, 1404, 1279, 1178, 1034, 715 cm^{-1}; MS (ESI): *m/z* 296 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9Cl_3NO_3$ $(M+H)^+$: 295.9643, found: 295.9641.

Synthesis of acetanilide (14):[14]



A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with aniline (1 g, 0.98 mL, 10.7 mmol, 1 equiv.) and anhydrous dichloromethane (20 mL) under an argon atmosphere. Acetic anhydride (1.30 mL, 12.8 mmol, 1.2 equiv.) was added, and the reaction was stirred at room temperature for 60 minutes. After completion of the reaction, the mixture was diluted with 15 mL of dichloromethane and washed with a saturated solution of sodium carbonate. The organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude residue was purified by flash chromatography (EtOAc/hexanes, 5:95 to 60:40) to yield acetanilide (**14**, 1.42 g, 98%) as a brown solid. ^1H and ^{13}C NMR were found to be identical with those reported in the literature.[14]

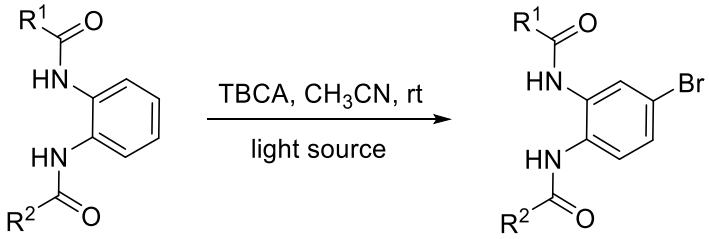
General procedure for the synthesis of trifluoro acetanilide derivatives (16, 24, 26):



16; R = H, 87%
24; R = 4-Me, 93%
26; R = 2-OMe, 87%

Substituted aniline (4.0 mmol) and triethylamine (606 mg, 816 μL, 6.0 mmol, 1.5 equiv.) were dissolved in anhydrous dichloromethane (12 mL), the mixture was cooled to 0 °C and added trifluoroacetic anhydride (217 mg, 147 μL, 4.2 mmol, 1.05 equiv. in 2 mL of dichloromethane). The reaction mixture was stirred at the same temperature for 60 min. After completion of the reaction monitored by TLC, dichloromethane (10 mL) was added, and the mixture was washed with saturated aqueous sodium bicarbonate (30 mL) and brine (30 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexanes, 05:95 to 50:50) to give the corresponding trifluoro acetanilide derivative in 87-93% yield (**16,**[15] **24**[15c] and **26**[15b, 16]). ^{1}H and ^{13}C NMR were found to be identical with those reported in the literature.

General procedure for the regioselective, remote bromination of diamides with tribromoisocyanuric acid under visible-light:



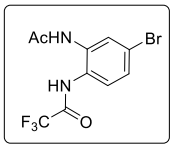
A 10 mL round-bottom flask equipped with a magnetic stir bar was charged with the unsymmetrical diamide (**1**, 0.40 mmol) and acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added

tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 30 min. to 8 hours (24 h reaction time in case of **3e**). After completion of the reaction, acetonitrile was then evaporated, and the crude residue was purified by flash chromatography (EtOAc/hexanes, 5:95 to 60:40) to yield the corresponding halogenated diamide derivatives (**2a-z, 3e, 6a-6e, 23 and 25**).

a)  b)  c) 

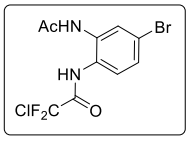
Pictures of the reaction: a) **1a** in acetonitrile; b) Reaction mixture after addition of TBCA; c) Reaction mixture after 30 min. with the white precipitation (cyanuric acid) on the walls of the RB.

***N*-(2-Acetamido-4-bromophenyl)-2,2,2-trifluoroacetamide (2a):**



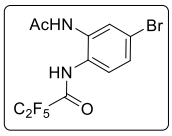
N-(2-Acetamidophenyl)-2,2,2-trifluoroacetamide (**1a**, 99 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 0.5 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 126 mg (97%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.96 (s, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.40 (dd, J = 8.7, 2.1 Hz, 1H), 7.26 (d, J = 2.1 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 156.0 (q, J = 37.7 Hz), 131.1, 130.1, 127.6, 127.6, 127.0, 120.1, 115.8 (q, J = 288.0 Hz), 23.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7; FTIR (neat): 3380, 3255, 1734, 1698, 1516, 1214, 1147, 1032, 867, 705 cm^{-1}; MS (ESI): *m/z* 325 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9BrF_3N_2O_2$ $(M+H)^+$: 324.9794, found: 324.9797.

***N*-(2-Acetamido-4-bromophenyl)-2-chloro-2,2-difluoroacetamide (2b):**



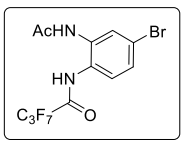
N-(2-Acetamido-4-bromophenyl)-2-chloro-2,2-difluoroacetamide (**1b**, 106 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 125 mg (92%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.91 (s, 1H), 7.48 (d, J = 8.7 Hz, 1H), 7.40 (dd, J = 8.7, 2.1 Hz, 1H), 7.27 (d, J = 2.6 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 158.2 (t, J = 30.8 Hz), 131.3, 130.2, 127.8, 127.7, 127.1, 120.1, 118.9 (t, J = 302.8 Hz), 23.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.2; FTIR (neat): 3242, 2981, 1733, 1654, 1506, 1404, 1284, 1104, 974, 874, 710 cm^{-1}; MS (ESI): *m/z* 341 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9BrClF_2N_2O_2$ $(M+H)^+$: 340.9499, found: 340.9503.

_N_-(2-Acetamido-4-bromophenyl)-2,2,3,3,3-pentafluoropropanamide (2c):



N-(2-Acetamidophenyl)-2,2,3,3,3-pentafluoropropanamide (**1c**, 118 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 144 mg (96%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 160-161 °C; ^{1}H NMR (400 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 10.48 (s, 1H), 9.97 (s, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.50 (d, J = 2.1 Hz, 1H), 7.38 (dd, J = 8.7, 2.1 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 170.3,155.4 (t, J = 25.8 Hz), 131.8, 128.4, 127.0, 126.9, 126.4, 118.9, 117.3 (dt, J = 286.6, 34.8 Hz),106.7 (td, J = 266.5, 38.7 Hz), 22.8; ^{19}F NMR (376 MHz, $CDCl_3$ + DMSO-d_6): δ -82.99 (t, J = 1.8 Hz), -122.94 (d, J = 1.8 Hz); FTIR (neat): 3315, 3025, 1719, 1661, 1536, 1409, 1274, 1095, 937, 817, 776 cm^{-1}; MS (ESI): *m/z* 375 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{11}H_9BrF_5N_2O_2$ $(M+H)^+$: 374.9762, found: 374.9763.

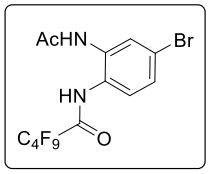
_N_-(2-Acetamido-4-bromophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (2d):



N-(2-Acetamidophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (**1d**, 138 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50)

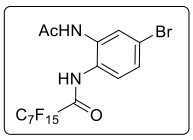
165 mg (96%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 154-156 °C; ^{1}H NMR (400 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 10.45 (s, 1H), 9.94 (s, 1H), 7.63 – 7.54 (m, 1H), 7.47 (dd, J = 10.7, 8.1 Hz, 1H), 7.41 – 7.34 (m, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 170.4, 155.4 (t, J = 26.2 Hz), 131.9, 128.5, 127.2, 127.0, 126.5, 119.0, 118.7 (q, J = 95.2 Hz), 115.6 (t, J = 32.2 Hz), 108.2 (t, J = 30.2 Hz), 22.9; ^{19}F NMR (376 MHz, $CDCl_3$ + DMSO-$d6$): δ -80.54 (t, J = 9.1 Hz), -120.67 (q, J = 9.1 Hz), -127.05; FTIR (neat): 3336, 3023, 1707, 1666, 1502, 1211, 1180, 947, 871, 815 cm^{-1}; MS (ESI): *m/z* 425 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{12}H_9BrF_7N_2O_2$ $(M+H)^+$: 424.9730, found: 424.9735.

***N*-(2-Acetamido-4-bromophenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentanamide (2e):**



N-(2-Acetamidophenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentanamide (**1e**, 159 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 186 mg (98%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.66 (s, 1H), 7.55 (d, J = 8.7 Hz, 1H), 7.43 (dd, J = 8.7, 2.1 Hz, 1H), 7.28 (d, J = 2.1 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 156.2, 131.0, 130.3, 128.0, 127.5, 127.3, 120.1, 118.6, 110.0, 109.0, 107.8, 23.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.81 (ddd, J = 12.5, 10.0, 2.3 Hz), -119.86 (td, J = 12.1, 2.4 Hz), -123.36 – -123.86 (m), -125.71 – -126.09 (m); FTIR (neat): 3337, 3031, 1706, 1667, 1501, 1402, 1196, 1130, 900, 814, 717, 654 cm^{-1}; MS (ESI): *m/z* 475 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_9BrF_9N_2O_2$ $(M+H)^+$: 474.9698, found: 474.9702.

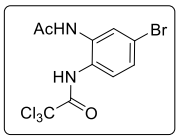
***N*-(2-Acetamido-4-bromophenyl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide (2f):**



N-(2-Acetamidophenyl)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamide (**1f**, 162 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 0.5 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 242 mg (97%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 68-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.69 (s, 1H), 7.55 (d, J = 8.7 Hz, 1H), 7.43 (dd, J = 8.7, 2.1 Hz, 1H), 7.28 (d, J = 2.1 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5,

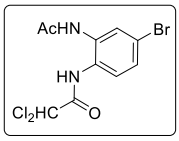
156.2 (t, J = 26.1 Hz), 131.1, 130.3, 128.0, 127.5, 127.4, 120.13, 118.5, 118.2, 117.8, 115.7, 110.9, 110.5, 109.1, 23.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.73 (t, J = 10.5 Hz), -119.59 (t, J = 13.4 Hz), -121.50, -121.94, -122.38 – -122.68 (m), -122.73, -125.91 – -126.27 (m); FTIR (neat): 3310, 3150, 3008, 1703, 1667, 1199, 1017, 819, 662 cm^{-1}; MS (ESI): *m/z* 625 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_9BrF_{15}N_2O_2$ $(M+H)^+$: 624.9602, found: 624.9609.

***N*-(2-Acetamido-4-bromophenyl)-2,2,2-trichloroacetamide (2g):**



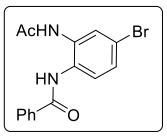
N-(2-Acetamidophenyl)-2,2,2-trichloroacetamide (**1g**, 117 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1.5 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 132 mg (89%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 201-202 ^{o}C; ^{1}H NMR (400 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 10.14 (s, 1H), 10.09 (s, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.46 – 7.36 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 170.0, 159.6, 131.7, 128.4, 128.3, 126.7, 126.4, 118.3, 92.4, 22.6; FTIR (neat): 3384, 2253, 1710, 1650, 1242, 994, 823, 761 cm^{-1}; MS (ESI): *m/z* 373 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9BrCl_3N_2O_2$ $(M+H)^+$: 372.8907, found: 372.8918.

***N*-(2-Acetamido-4-bromophenyl)-2,2-dichloroacetamide (2h):**



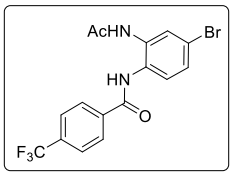
N-(2-Acetamidophenyl)-2,2-dichloroacetamide (**1h**, 104 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 110 mg (81%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 204-206 ^{o}C; ^{1}H NMR (400 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 9.89 (s, 1H), 9.57 (s, 1H), 7.71 – 7.45 (m, 2H), 7.33 (d, J = 8.2 Hz, 1H), 6.35 – 6.16 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 169.3, 162.1, 131.5, 127.9, 127.8, 127.0, 125.8, 118.0, 66.2, 22.8; FTIR (neat): 3212, 3043, 1680, 1589, 1524, 1491, 1369, 1221, 978, 805, 649 cm^{-1}; MS (ESI): *m/z* 339 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}BrCl_2N_2O_2$ $(M+H)^+$: 338.9297, found: 338.9300.

***N*-(2-Acetamido-4-bromophenyl)benzamide (2i):**



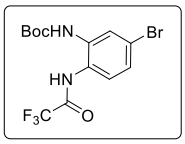
N-(2-Acetamidophenyl)benzamide (**1i**, 102 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 5 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 60 mg (45%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 186-187 ^oC; ^1H NMR (400 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 9.67 (s, 1H), 9.47 (s, 1H), 7.83 (s, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.45 – 7.22 (m, 3H), 7.06 (s, 2H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 169.8, 165.0, 133.5, 132.0, 131.4, 128.9, 128.1, 127.5, 127.5, 127.0, 125.6, 117.9, 23.1; FTIR (neat): 3292, 3254, 3040, 1675, 1632, 1474, 1401, 1285, 1023, 812, 686 cm^{-1}; MS (ESI): *m/z* 333 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{14}BrN_2O_2$ $(M+H)^+$: 333.0233, found: 333.0235.

***N*-(2-Acetamido-4-bromophenyl)-4-(trifluoromethyl)benzamide (2j):**



N-(2-Acetamidophenyl)-4-(trifluoromethyl)benzamide (**1j**, 129 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 8 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 78 mg (49%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 215-217 ^oC; ^1H NMR (400 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 9.97 (s, 1H), 9.55 (s, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.85 (s, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.08 (q, J = 8.5 Hz, 2H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$:DMSO-d_6): δ 169.9, 163.6, 136.9, 132.8, 132.5, 131.6, 129.1, 127.9, 127.6, 125.0 (q, J = 3.6 Hz), 125.0, 123.1 (q, J = 272.5 Hz), 117.9, 23.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.9; FTIR (neat): 3219, 3018, 1653, 1488, 1327, 1106, 924, 853, 770 cm^{-1}; MS (ESI): *m/z* 401 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_{13}BrF_3N_2O_2$ $(M+H)^+$: 401.0107, found: 401.0110.

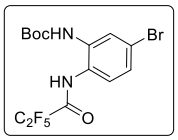
***tert*-Butyl (5-bromo-2-(2,2,2-trifluoroacetamido)phenyl)carbamate (2k):**



tert-Butyl (2-(2,2,2-trifluoroacetamido)phenyl)carbamate (**1k**, 122 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50)

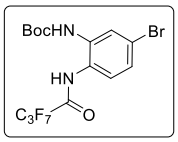
141 mg (92%) of a white solid was obtained. R_f = 0.40 (EtOAc/hexanes 30:70), mp = 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (bs, 1H), 7.95 (d, *J* = 2.1 Hz, 1H), 7.32 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.65 (s, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5 (q, *J* = 37.7 Hz), 154.6, 130.2, 129.7, 128.6, 128.4, 125.5, 119.2, 115.8 (q, *J* = 288.3 Hz), 82.9, 28.0; FTIR (neat): 3355, 2986, 1735, 1682, 1504, 1303, 1245, 1146, 1058, 912, 803 cm^{-1}; MS (ESI): *m/z* 383 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{15}BrF_3N_2O_3$ $(M+H)^+$: 383.0213, found: 383.0217.

***tert*-Butyl (5-bromo-2-(2,2,3,3,3-pentafluoropropanamido)phenyl)carbamate (2l):**



tert-Butyl (2-(2,2,3,3,3-pentafluoropropanamido)phenyl)carbamate (**1l**, 142 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50) 162 mg (94%) of a white solid was obtained. R_f = 0.40 (EtOAc/hexanes 30:70), mp = 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.31 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.23 – 7.09 (m, 1H), 6.59 (d, *J* = 16.3 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (t, *J* = 25.8 Hz), 154.5, 130.9, 129.5, 127.6, 127.1, 127.1, 119.9, 117.8 (dt, *J* = 286.6, 34.6 Hz), 107.0 (td, *J* = 266.6, 38.9 Hz), 83.0, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -82.8 (d, *J* = 1.7 Hz), -123.1; FTIR (neat): 3376, 3275,2984, 2936, 1733, 1698, 1516, 1147, 1030, 818, 704 cm^{-1}; MS (ESI): *m/z* 433 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}BrF_5N_2O_3$ $(M+H)^+$: 433.0181, found: 433.0182.

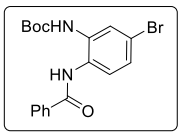
***tert*-Butyl (5-bromo-2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl)carbamate (2m):**



tert-Butyl (2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl)carbamate (**1m**, 162 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1.5 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50) 177 mg (92%) of a white solid was obtained. R_f = 0.40 (EtOAc/hexanes 30:70), mp = 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 6.59 (s, 1H), 1.52 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 154.5, 130.9, 129.7, 129.5, 127.7, 127.1, 127.1, 119.9, 113.3, 110.2, 83.1, 27.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.6 (t, *J* = 9.1 Hz), -

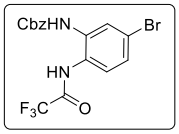
120.8 (q, J = 9.3 Hz), -126.9; FTIR (neat): 3347, 2982, 1702, 1511, 1226, 1116, 853, 752 cm^{-1}; MS (ESI): *m/z* 483 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}BrF_7N_2O_3$ $(M+H)^+$: 483.0149, found: 483.0153.

***tert*-Butyl (2-benzamido-5-bromophenyl)carbamate (2n):**



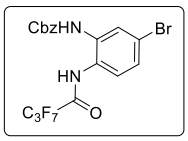
tert-Butyl (2-benzamidophenyl)carbamate (**1n**, 125 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 6 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 84 mg (54%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 171-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 7.99 – 7.92 (m, 3H), 7.59 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 7.21 (dd, J = 8.6, 2.3 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H), 6.88 (s, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 154.5, 133.7, 132.2, 132.1, 128.9, 128.7, 128.7, 128.4, 127.4, 125.8, 118.6, 81.7, 28.2; FTIR (neat): 3251, 2981, 1694, 1647, 1496, 1348, 1308, 1156, 1028, 913, 689 cm^{-1}; MS (ESI): *m/z* 391 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{20}BrN_2O_3$ $(M+H)^+$: 391.0652, found: 391.0653.

Benzyl (5-bromo-2-(2,2,2-trifluoroacetamido)phenyl)carbamate (2o):



Benzyl (2-(2,2,2-trifluoroacetamido)phenyl)carbamate (**1o**, 135 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 143 mg (86%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.56 (d, J = 8.6 Hz, 1H), 7.41 – 7.29 (m, 7H), 6.91 (s, 1H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6 (q, J = 39.3 Hz), 155.0, 135.0, 130.7, 129.7, 128.8, 128.7, 128.5, 127.3, 127.2, 127.0, 120.1, 115.8 (q, J = 288.4 Hz), 68.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7; FTIR (neat): 3331, 3162, 2769, 1737, 1691, 1533, 1415, 1194, 1015, 899, 743 cm^{-1}; MS (ESI): *m/z* 417 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_{13}BrF_3N_2O_3$ $(M+H)^+$: 417.0056, found: 417.0057.

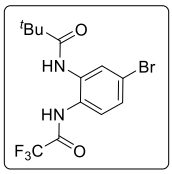
Benzyl (5-bromo-2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl)carbamate (2p):



Benzyl (2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl)carbamate (**1p**, 175 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at

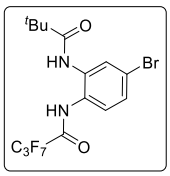
room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 186 mg (90%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 7.46 (d, J = 8.7 Hz, 1H), 7.33 – 7.27 (m, 6H), 7.24 (d, J = 2.2 Hz, 1H), 6.80 (s, 1H), 5.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (t, J = 26.2 Hz), 155.1, 134.9, 130.8, 129.7, 128.8, 128.7, 128.7, 128.5, 127.3, 127.2, 120.3, 118.8 (t, J = 33.6 Hz), 115.9 (t, J = 33.4 Hz), 108.4 (q, J = 26.8 Hz), 68.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.5 (t, J = 9.0 Hz), -120.7 (q, J = 9.1 Hz), -127.0; FTIR (neat): 3366, 3120, 2986, 1715, 1632, 1499, 1315, 1276, 1097, 925, 838, 714 cm^{-1}; MS (ESI): *m/z* 517 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{18}H_{13}BrF_7N_2O_3$ $(M+H)^+$: 516.9992, found: 516.9995.

***N*-(5-Bromo-2-(2,2,2-trifluoroacetamido)phenyl)pivalamide (2q):**



N-(2-(2,2,2-Trifluoroacetamido)phenyl)pivalamide (**1q**, 115 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50) 135 mg (92%) of a white solid was obtained. R_f = 0.40 (EtOAc/hexanes 30:70), mp = 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.74 (s, 1H), 7.55 (d, J = 8.7 Hz, 1H), 7.43 (dd, J = 8.7, 2.2 Hz, 1H), 7.31 (d, J = 2.2 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 155.7 (q, J = 37.6 Hz), 131.2, 130.2, 128.2, 128.0, 127.2, 120.0, 115.8 (q, J = 288.2 Hz), 39.6, 27.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7; FTIR (neat): 3284, 2967, 1711, 1662, 1509, 1406, 1156, 892, 807, 738 cm^{-1}; MS (ESI): *m/z* 367 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{15}BrF_3N_2O_2$ $(M+H)^+$: 367.0264, found: 367.0268.

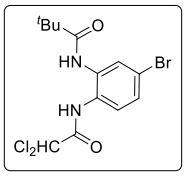
***N*-(4-Bromo-2-pivalamidophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (2r):**



N-(2-Pivalamidophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (**1r**, 155 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 1 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50) 166 mg (89%) of a white solid was obtained. R_f = 0.40 (EtOAc/hexanes 30:70), mp = 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 1H), 7.66 (s, 1H), 7.61 (dd, J = 8.7, 2.8 Hz, 1H), 7.45 (dt, J = 8.7, 2.4 Hz, 1H), 7.30 (t, J = 2.4 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.2, 156.0 (t, J = 26.0 Hz),

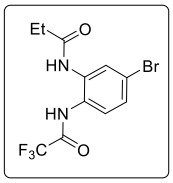
131.0, 130.2, 128.4, 127.7, 127.2, 119.9, 119.0 (q, J = 86.5 Hz), 116.0 (t, J = 28.8 Hz), 108.6 (t, J = 29.2 Hz), 39.6, 27.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.5 (t, J = 9.3 Hz), -120.5 (q, J = 9.3 Hz), -126.8; FTIR (neat): 3341, 3223, 2981, 1710, 1672, 1488, 1228, 1117, 842, 809, 727 cm^{-1}; MS (ESI): *m/z* 467 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}BrF_7N_2O_2$ $(M+H)^+$: 467.0200, found: 467.0204.

***N*-(5-Bromo-2-(2,2-dichloroacetamido)phenyl)pivalamide (2s):**



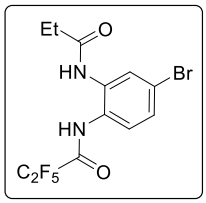
N-(2-(2,2-Dichloroacetamido)phenyl)pivalamide (**1s**, 121 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 4 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50) 114 mg (75%) of a white solid was obtained. R_f = 0.40 (EtOAc/hexanes 30:70), mp = 178-180 ^{o}C; ^{1}H NMR (400 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 10.03 (s, 1H), 8.79 (s, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.46 (d, J = 1.7 Hz, 1H), 7.24 (t, J = 1.5 Hz, 1H), 6.19 (d, J = 2.1 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 177.1, 162.4, 132.2, 127.7, 127.5, 127.5, 125.8, 118.4, 65.9, 38.6, 26.6; FTIR (neat): 3317, 3166, 2959, 1698, 1639, 1478, 1216, 1165, 879, 799 cm^{-1}; MS (ESI): *m/z* 381 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}BrCl_2N_2O_2$ $(M+H)^+$: 380.9767, found: 380.9769.

***N*-(5-Bromo-2-(2,2,2-trifluoroacetamido)phenyl)propionamide (2t):**



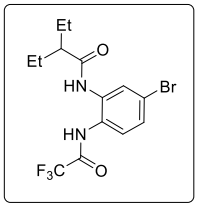
N-(2-(2,2,2-Trifluoroacetamido)phenyl)propionamide (**1t**, 104 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50) 116 mg (86%) of a white solid was obtained. R_f = 0.30 (EtOAc/hexanes 30:70), mp = 141-143 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.86 (s, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.40 (dd, J = 8.7, 2.1 Hz, 1H), 7.30 – 7.22 (m, 1H), 2.43 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 156.0 (q, J = 37.7 Hz), 131.2, 130.0, 127.7, 127.6, 127.1, 120.1, 115.8 (q, J = 288.0 Hz), 30.0, 9.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7; FTIR (neat): 3235, 2923, 1702, 1656, 1512, 1479, 1274, 1148, 1072, 889, 803, 747 cm^{-1}; MS (ESI): *m/z* 339 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{11}H_{11}BrF_3N_2O_2$ $(M+H)^+$: 338.9951, found: 338.9955.

***N*-(4-Bromo-2-propionamidophenyl)-2,2,3,3,3-pentafluoropropanamide (2u):**



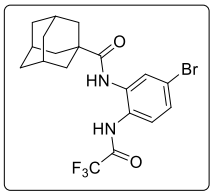
N-(2-Propionamidophenyl)-2,2,3,3,3-pentafluoropropanamide (**1u**, 124 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 143 mg (91%) of a white solid was obtained. R_f = 0.3 (EtOAc/hexanes 30:70), mp = 145-147 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H), 7.72 (s, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 2.44 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 156.4 (t, *J* = 26.0 Hz), 131.1, 130.1, 127.9, 127.6, 127.3, 120.1, 117.8 (dt, *J* = 287.0, 34.8 Hz), 106.9 (td, *J* = 266.7, 39.2 Hz), 29.9, 9.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -82.8 (t, *J* = 1.8 Hz), -122.9 (d, *J* = 1.8 Hz); FTIR (neat): 3276, 2981, 1732, 1645, 1519, 1408, 1311, 1200, 1025, 887, 809, 713 cm^{-1}; MS (ESI): *m/z* 389 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{12}H_{11}BrF_5N_2O_2$ $(M+H)^+$: 388.9919, found: 388.9923.

***N*-(5-Bromo-2-(2,2,2-trifluoroacetamido)phenyl)-2-ethylbutanamide (2v):**



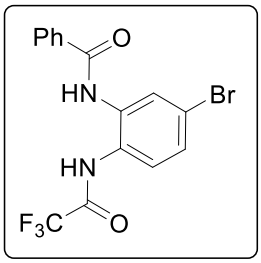
2-Ethyl-*N*-(2-(2,2,2-trifluoroacetamido)phenyl)butanamide (**1v**, 121 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 20:80 to 50:50) 144 mg (95%) of a white solid was obtained. R_f = 0.30 (EtOAc/hexanes 30:70), mp = 166-168 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.89 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.20 (d, *J* = 2.1 Hz, 1H), 2.20 – 2.09 (m, 1H), 1.76 – 1.49 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 155.8 (q, *J* = 37.6 Hz), 131.0, 130.2, 128.0, 127.5, 127.1, 119.9, 115.9 (q, *J* = 288.2 Hz), 51.5, 25.7, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7; FTIR (neat): 3271, 3119, 2964, 2859, 1746, 1641, 1515, 1281, 1138, 812, 708 cm^{-1}; MS (ESI): *m/z* 381 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{14}H_{17}BrF_3N_2O_2$ $(M+H)^+$: 381.0420, found: 381.0423.

(3r,5r,7r)-*N*-(5-Bromo-2-(2,2,2-trifluoroacetamido)phenyl)adamantane-1-carboxamide (2w):



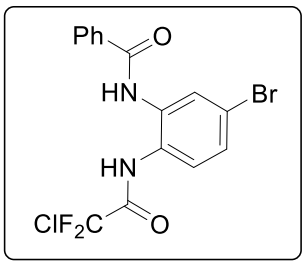
(3r,5r,7r)-*N*-(2-(2,2,2-Trifluoroacetamido)phenyl)adamantane-1-carboxamide (**1w**, 146 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 162 mg (91%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 223-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.70 (s, *J* = 9.5 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.45 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.30 (d, *J* = 2.2 Hz, 1H), 2.15 (s, 3H), 1.96 (d, *J* = 2.6 Hz, 6H), 1.80 (q, *J* = 12.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 155.7 (q, *J* = 37.5 Hz), 131.2, 130.1, 128.3, 127.8, 127.2, 119.9, 115.9 (d, *J* = 288.4 Hz), 41.5, 39.0, 38.9, 36.2, 27.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7; FTIR (neat): 3226, 2903, 1712, 1661, 1485, 1159, 1033, 900, 828, 734 cm^{-1}; MS (ESI): *m/z* 445 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{19}H_{21}BrF_3N_2O_2$ $(M+H)^+$: 445.0733, found: 445.0737.

***N*-(5-Bromo-2-(2,2,2-trifluoroacetamido)phenyl)benzamide (2x):**



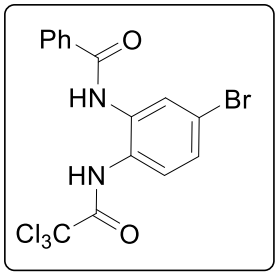
N-(2-(2,2,2-Trifluoroacetamido)phenyl)benzamide (**1x**, 123 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 3 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 108 mg (70%) of a white solid was obtained. R_f = 0.25 (EtOAc/hexanes 30:70), mp = 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.80 (s, 1H), 8.54 (s, 1H), 7.97 – 7.85 (m, 2H), 7.68 – 7.60 (m, 1H), 7.59 – 7.50 (m, 2H), 7.46 (t, *J* = 5.7 Hz, 2H), 7.33 (dd, *J* = 8.7, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 156.2 (q, *J* = 37.9 Hz), 133.0, 132.2, 131.4, 130.2, 129.1, 128.3, 127.6, 127.5, 127.1, 120.5, 115.8 (q, *J* = 288.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.7; FTIR (neat): 3264, 2981, 1712, 1647, 1519, 1484, 1222, 1121, 860, 816, 709 cm^{-1}; MS (ESI): *m/z* 387 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{11}BrF_3N_2O_2$ $(M+H)^+$: 386.9951, found: 386.9954.

***N*-(5-Bromo-2-(2-chloro-2,2-difluoroacetamido)phenyl)benzamide (2y):**



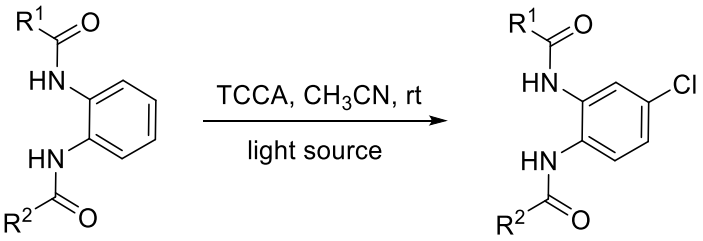
N-(2-(2-Chloro-2,2-difluoroacetamido)phenyl)benzamide (**1y**, 130 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 4 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 121 mg (75%) of a white solid was obtained. R_f = 0.25 (EtOAc/hexanes 30:70), mp = 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 8.74 (s, *J* = 5.0 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.65 – 7.57 (m, 1H), 7.55 – 7.48 (m, 2H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.27 – 7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 158.6 (t, *J* = 31.0 Hz), 132.9, 132.1, 131.7, 130.1, 129.0, 128.5, 127.5, 127.5, 127.1, 121.8, 118.8 (t, *J* = 302.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.2; FTIR (neat): 3249, 3038, 1730, 1634, 1510, 1440, 1322, 1104, 971, 875, 802 cm^{-1}; MS (ESI): *m/z* 403 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{11}BrClF_2N_2O_2$ $(M+H)^+$: 402.9655, found: 402.9658.

***N*-(5-Bromo-2-(2,2,2-trichloroacetamido)phenyl)benzamide (2z):**



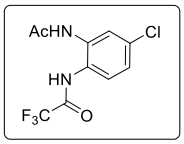
N-(2-(2,2,2-Trichloroacetamido)phenyl)benzamide (**1z**, 142 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 6 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 109 mg (63%) of a white solid was obtained. R_f = 0.25 (EtOAc/hexanes 30:70), mp = 217-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 8.59 (s, 1H), 7.92 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.66 – 7.57 (m, 1H), 7.56 – 7.46 (m, 3H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 161.3, 132.9, 132.4, 131.8, 130.2, 129.0, 128.9, 128.2, 127.6, 127.5, 120.4, 92.4; FTIR (neat): 3330, 3211, 2298, 1702, 1663, 1506, 1482, 1282, 857, 821, 705 cm^{-1}; MS (ESI): *m/z* 435 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{11}BrCl_3N_2O_2$ $(M+H)^+$: 435.9039, found: 435.9042.

General procedure for the synthesis of mono-chloro diamide derivatives (3a-c):



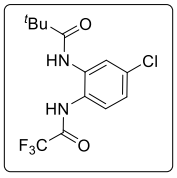
A 10 mL round bottom flask equipped with a magnetic stir bar was charged with unsymmetrical diamide (**1**, 0.40 mmol) and acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added trichloroisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 2-3 hours. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc in EtOH (3:1)/hexanes, 5:95 to 70:30) to yield the corresponding chlorinated diamide derivatives **3a-c**.

***N*-(2-Acetamido-4-chlorophenyl)-2,2,2-trifluoroacetamide (3a):**



N-(2-Acetamidophenyl)-2,2,2-trifluoroacetamide (**1a**, 99 mg, 0.40 mmol) and trichloroisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 40 mg (36%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 161-163 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.72 (s, 1H), 7.63 (d, J = 8.7 Hz, 1H), 7.28 (dd, J = 8.7, 2.3 Hz, 1H), 7.12 (d, J = 2.3 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 155.9 (q, J = 37.8 Hz), 132.6, 130.9, 127.3, 127.3, 127.0, 124.6, 115.9 (q, J = 316.6 Hz), 23.6; FTIR (neat): 3286, 2923, 1726, 1656, 1514, 1412, 1275, 1147, 916, 816 cm^{-1}; MS (ESI): *m/z* 281 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9ClF_3N_2O_2$ $(M+H)^+$: 281.0299, found: 281.0302.

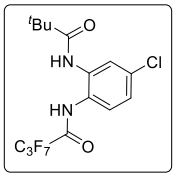
***N*-(5-Chloro-2-(2,2,2-trifluoroacetamido)phenyl)pivalamide (3b):**



tert-Butyl (2-(2,2,2-trifluoroacetamido)phenyl)carbamate (**1q**, 121 mg, 0.40 mmol) and trichloroisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 3 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 70

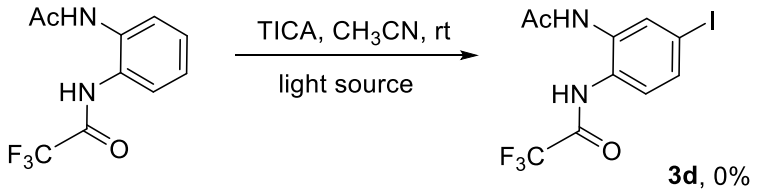
mg (54%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.72 (d, J = 2.3 Hz, 2H), 7.22 (dd, J = 8.6, 2.3 Hz, 1H), 7.01 (t, J = 11.9 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 155.7 (q, J = 37.8 Hz), 132.6, 130.1, 128.4, 127.4, 126.0, 125.8, 115.8 (q, J = 288.3 Hz), 39.5, 27.4; FTIR (neat): 3375, 3213, 2913, 1769, 1653, 1515, 1401, 1347, 1094, 945, 818, 781, 699 cm^{-1}; MS (ESI): *m/z* 323 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{13}H_{15}ClF_3N_2O_2$ $(M+H)^+$: 323.0769, found: 323.0773.

***N*-(4-Chloro-2-pivalamidophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (3c):**



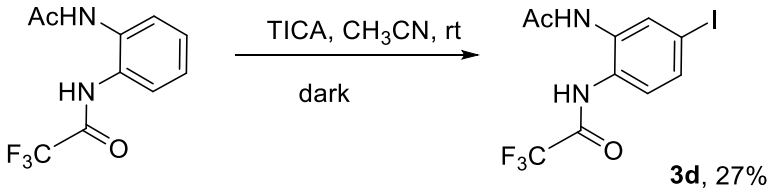
N-(2-Pivalamidophenyl)-2,2,3,3,4,4,4-heptafluorobutanamide (**1r**, 162 mg, 0.40 mmol) and trichloroisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 3 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 83 mg (49%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.78 (d, J = 2.3 Hz, 1H), 7.62 (s, 1H), 7.22 (dd, J = 8.6, 2.3 Hz, 1H), 7.03 (d, J = 8.6 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 155.9, 132.7, 130.3, 128.2, 127.3, 125.8, 125.7, 118.6, 114.8, 111.2, 39.5, 27.4; FTIR (neat): 3331, 3013, 2923, 1752, 1615, 1494, 1401, 1375, 1096, 728 cm^{-1}; MS (ESI): *m/z* 423 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}ClF_7N_2O_2$ $(M+H)^+$: 423.0705, found: 423.0708.

***N*-(2-Acetamido-4-iodophenyl)-2,2,2-trifluoroacetamide (3d):**



A 10 mL round bottom flask equipped with a magnetic stir bar was charged with *N*-(2-acetamidophenyl)-2,2,2-trifluoroacetamide (**1a**, 99 mg, 0.40 mmol) and acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added triiodoisocyanuric acid (73 mg, 0.145 mmol) in one portion, and the resulting

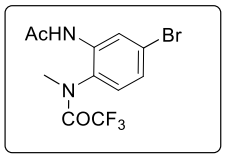
solution was stirred at room temperature for 24 hours. TLC indicated decomposition of **1a** and multiple new spots were observed in the reaction mixture.



3d, 27%

A 10 mL round-bottom flask equipped with a magnetic stir bar was charged with *N*-(2-acetamidophenyl)-2,2,2-trifluoroacetamide (**1a**, 99 mg, 0.40 mmol) and acetonitrile (3 mL) under open air conditions at room temperature, and the reaction vial was covered with aluminum foil to protect from light. To the stirred solution in the dark, was added triiodoisocyanuric acid (73 mg, 0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 24 hours. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc in EtOH (3:1)/hexanes, 5:95 to 70:30) to yield the *N*-(2-acetamido-4-iodophenyl)-2,2,2-trifluoroacetamide (**3d**). 40 mg (27%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 187-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.99 (s, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.25 (dd, J = 8.8, 2.4 Hz, 1H), 7.10 (d, J = 2.3 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 156.1 (q, J = 37.8 Hz), 132.6, 131.0, 127.2, 127.0, 126.8, 124.7, 115.8 (q, J = 288.0 Hz), 23.5; FTIR (neat): 3315, 3031, 2912, 1713, 1667, 1577, 1468, 1319, 1271, 996, 791, 689 cm^{-1}; MS (ESI): *m/z* 373 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_9F_3IN_2O_2$ $(M+H)^+$: 372.9655, found: 372.9659.

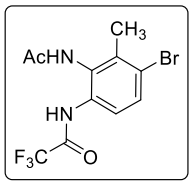
***N*-(2-Acetamido-4-bromophenyl)-2,2,2-trifluoro-*N*-methylacetamide (3e):**



Following the general bromination procedure; *N*-(2-acetamidophenyl)-2,2,2-trifluoro-*N*-methylacetamide (**1aa**, 104 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 24 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 15:85 to 50:50) 32 mg (23%) of a pale, yellow solid was obtained. R_f = 0.25 (EtOAc/hexanes 30:70), mp = 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 1.8 Hz, 1H), 7.37 (dd, J = 8.3, 1.9 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 3.38 (s, 3H), 2.75 (s, 3H); ^{13}C NMR

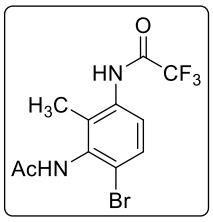
(100 MHz, $CDCl_3$): δ 170.3, 152.1, 129.3, 127.4, 126.9, 119.3 (d, J = 704.7 Hz), 118.9, 115.4, 108.4, 27.2, 25.5; FTIR (neat): 3065, 2922, 1703, 1612, 1428, 1372, 1354, 1162, 1094, 927, 818, 707 cm^{-1}; MS (ESI): *m/z* 339 $(M+H)^+$. HRMS (ESI): *m/z* calcd for $C_{11}H_{11}BrF_3N_2O_2$ $(M+H)^+$: 338.9951, found: 338.9955.

***N*-(2-Acetamido-4-bromo-3-methylphenyl)-2,2,2-trifluoroacetamide (3f):**



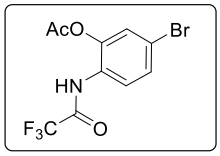
N-(2-Acetamido-3-methylphenyl)-2,2,2-trifluoroacetamide (**1bb**, 104 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) were added to acetonitrile (3 mL), and the reaction mixture was stirred for 0.5 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) **3f** as a white solid was obtained. 122 mg (87%), R_f = 0.20 (EtOAc/hexanes 30:70), mp = 162-163 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 10.74 (s, 1H), 9.55 (s, 1H), 7.59 (d, J = 8.6 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 2.25 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.9, 155.36 (d, J = 37.1 Hz), 136.3, 133.3, 131.6, 130.8, 125.5, 123.0, 23.1, 19.4; FTIR (neat): 3272, 1711, 1656, 1551, 1455, 1285, 1165, 922, 819, 665 cm^{-1}; MS (ESI): *m/z* 339 $(M+H)^+$.

***N*-(3-Acetamido-4-bromo-2-methylphenyl)-2,2,2-trifluoroacetamide (3g):**



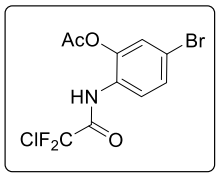
N-(3-Acetamido-2-methylphenyl)-2,2,2-trifluoroacetamide (**1cc**, 50 mg, 0.19 mmol) and tribromoisocyanuric acid (25 mg, 0.067 mmol) were added to acetonitrile (3 mL) and the reaction mixture was stirred for 0.5 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) of **3g** as a white solid was obtained, 54 mg (83%) R_f = 0.20 (EtOAc/hexanes 30:70), mp = 162-163 ^oC; ^1H NMR (400 MHz, DMSO-d_6): δ 11.09 (s, 1H), 9.66 (s, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.1, 155.3 (d, J = 43.0 Hz), 136.4, 135.2, 133.3, 129.7, 126.9, 122.1, 116.0 (d, J = 286.2 Hz), 22.5, 13.9; FTIR (neat): 3285, 3024, 1712, 1669, 1525, 1370, 1173, 1024, 906, 809, 742 cm^{-1}; MS (ESI): *m/z* 339 (M+H).

5-Bromo-2-(2,2,2-trifluoroacetamido)phenyl acetate (6a):



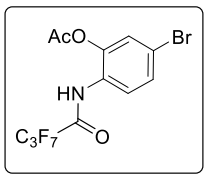
Following the general bromination procedure; 2-(2,2,2-trifluoroacetamido)phenyl acetate (**5a**, 99 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 81 mg (63%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 2.1 Hz, 1H), 7.40 (dd, J = 8.6, 2.1 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 154.6 (q, J = 37.8 Hz), 141.7, 129.7, 126.0, 125.8, 124.0, 119.20, 115.5 (q, J = 288.5 Hz), 20.7; FTIR (neat): 3272, 1760, 1709, 1529, 1404, 1283, 1117, 924, 807, 745 cm^{-1}; MS (ESI): *m/z* 326 $(M+H)^+$. HRMS (ESI): *m/z* calcd for $C_{10}H_8BrF_3NO_3$ $(M+H)^+$: 325.9634, found: 325.9637.

5-Bromo-2-(2-chloro-2,2-difluoroacetamido)phenyl acetate (6b):



Following the general bromination procedure; 2-(2-chloro-2,2-difluoroacetamido)phenyl acetate (**5b**, 105 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 3 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 83 mg (61%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.43 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 156.7 (t, J = 30.8 Hz), 141.8, 129.8, 126.3, 125.8, 123.9, 121.79, 118.8 (t, J = 302.9 Hz), 20.8; FTIR (neat): 3289, 1766, 1717, 1518, 1483, 1373, 1175, 1110, 974, 920, 806 cm^{-1}; MS (ESI): *m/z* 342 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_8BrClF_2NO_3$ $(M+H)^+$: 341.9339, found: 341.9340.

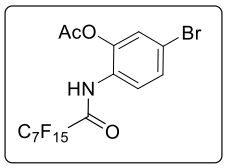
5-Bromo-2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl acetate (6c):



Following the general bromination procedure; 2-(2,2,3,3,4,4,4-heptafluorobutanamido)phenyl acetate (**5c**, 139 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 3 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 136 mg (80%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$):

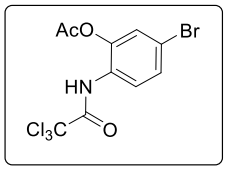
δ 8.02 (s, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.43 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 155.1 (t, J = 26.1 Hz), 141.9, 129.8, 126.0, 125.8, 124.3, 119.5, 116.2, 111.0, 108.4, 20.6; FTIR (neat): 3223, 1773, 1712, 1531, 1491, 1366, 1212, 1116, 945, 873, 814 cm^{-1}; MS (ESI): *m/z* 426 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{12}H_8BrF_7NO_3$ $(M+H)^+$: 425.9404, found: 425.9402.

5-Bromo-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamido)phenyl acetate (6d):



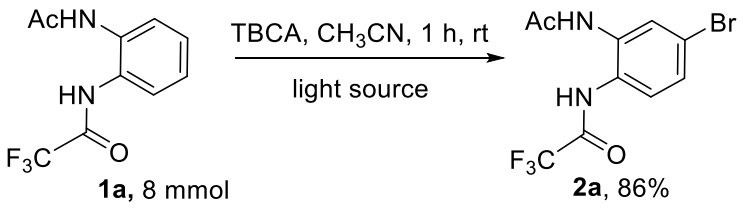
Following the general bromination procedure; 2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanamido)phenyl acetate (**5d**, 219 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 4 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 15:85 to 50:50) 187 mg (75%) of a pale, yellow solid was obtained. R_f = 0.25 (EtOAc/hexanes 30:70), mp = 70-72 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.85 (d, J = 8.6 Hz, 1H), 7.45 – 7.39 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 155.2 (t, J = 26.2 Hz), 142.1, 129.8, 126.0, 125.9, 124.5, 119.6, 118.0, 115.4, 113.2, 110.1, 110.0, 108.1, 107.8, 20.5; FTIR (neat): 3291, 1759, 1713, 1527, 1380, 1232, 1141, 1016, 929, 802 cm^{-1}; MS (ESI): *m/z* 626 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_8BrF_{15}NO_3$ $(M+H)^+$: 625.9443, found: 625.9449.

5-Bromo-2-(2,2,2-trichloroacetamido)phenyl acetate (6e):



Following the general bromination procedure; 2-(2,2,2-trichloroacetamido)phenyl acetate (**5e**, 118 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 30:70 to 50:50) 77 mg (52%) of a white solid was obtained. R_f = 0.20 (EtOAc/hexanes 30:70), mp = 98-100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 7.98 (d, J = 9.3 Hz, 1H), 7.47 – 7.41 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 159.1, 141.8, 129.7, 127.0, 125.6, 123.6, 118.7, 92.5, 20.8; FTIR (neat): 3304, 1763, 1703, 1478, 1369, 1208, 1115, 1013, 894, 816, 756 cm^{-1}; MS (ESI): *m/z* 374 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{10}H_8BrCl_3NO_3$ $(M+H)^+$: 373.8748, found: 373.8751.

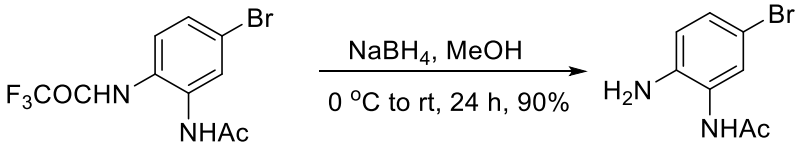
Gram-scale synthesis of 2a:



1a, 8 mmol **2a**, 86%

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with diamide (**1a**, 1.968 g, 8.00 mmol), and acetonitrile (50 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added tribromoisocyanuric acid (1.17 g, 3.2 mmol) in one portion, and the resulting solution was stirred at room temperature for 1 hour. The reaction mixture was filtered through a small pad of Celite, washed with acetonitrile (20 mL) and then evaporated, and the crude residue was purified by flash chromatography (EtOAc in EtOH (3:1)/hexanes, 5:95 to 70:30) to yield **2a** (2.26 grams, 86%) as a pale, yellow solid.

***N*-(2-Amino-5-bromophenyl)acetamide (7):**[17]

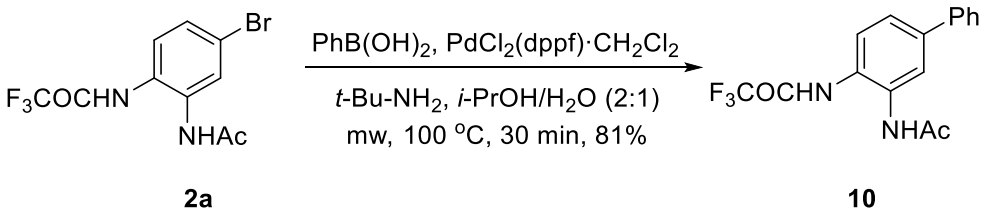


2a **7**

N-(2-Acetamido-4-bromophenyl)-2,2,2-trifluoroacetamide (**2a**,100 mg, 0.29 mmol, 1 equiv) was suspended in MeOH (10 mL) and cooled to 0 °C, sodium borohydride (22 mg, 0.58 mmol) was added and the mixture stirred for 24 h. The reaction was quenched by the addition of water, and the volatile solvent removed *in vacuo*. The remaining aqueous solution was extracted with ethyl acetate (2 x 10 mL), and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography to afford *N*-(2-amino-5-bromophenyl)acetamide (**7**) as a white solid (60 mg, 90% yield), mp = 151-153 °C. ^{1}H NMR (400 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 9.02 (s, 1H), 7.43 (d, J = 2.3 Hz, 1H), 7.06 (dd, J = 8.5, 2.3 Hz, 1H), 6.66 (d, J = 8.5 Hz, 1H), 4.28 (s, 2H),

2.15 (s, 3H); ^{13}C NMR (100 MHz, 8:2, $CDCl_3$ + DMSO-d_6): δ 168.7, 139.6, 128.3, 127.2, 125.0, 117.8, 108.4, 23.0; FTIR (neat): 3325, 3037, 2973, 1713, 1536, 1429, 1298, 1169, 1015, 948, 852, 726 cm^{-1}; MS (ESI): *m/z* 229 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_8H_{10}BrN_2O$ $(M+H)^+$: 228.9971, found: 228.9973.

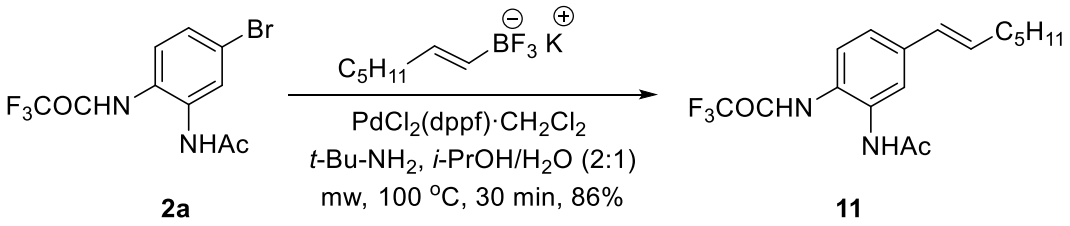
_N_-(3-Acetamido-[1,1'-biphenyl]-4-yl)-2,2,2-trifluoroacetamide (10):[18]



2a **10**

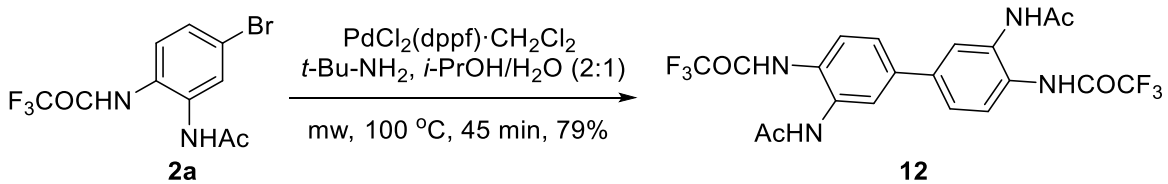
A solution of phenylboronic acid (43 mg, 0.35 mmol, 1.2 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (4.7 mg, 0.0058 mmol, 0.02 equiv), *N*-(2-acetamido-4-bromophenyl)-2,2,2-trifluoroacetamide (**2a**, 100 mg, 0.29 mmol, 1 equiv) and *t*-$BuNH_2$ (63.5 mg, 92 uL, 0.87 mmol, 3 equiv) in *i*-PrOH/H_2O (2:1, 3 mL) was heated at 100 °C under an argon atmosphere for 30 min under microwave conditions, then cooled to room temperature and diluted with water (5 mL), followed by extraction with ethyl acetate (5 mL x 2). The organic layers were combined and washed with 0.1 N HCl (10 mL) and brine (10 mL), dried over $MgSO_4$, and then filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to afford the (*E*)-*N*-(2-acetamido-4-(hept-1-en-1-yl)phenyl)-2,2,2-trifluoroacetamide (**10**) in 81% yield (76 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.85 (s, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.46 – 7.41 (m, 2H), 7.40 – 7.35 (m, 1H), 7.29 (d, J = 2.0 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 155.8 (q, J = 37.4 Hz), 140.5, 139.1, 130.0, 128.9, 128.0, 127.7, 126.9, 126.1, 125.8, 123.0, 116.0 (q, J = 288.1 Hz), 23.6; FTIR (neat): 3325, 3021, 1736, 1653, 1529, 1403, 1263, 1158, 1034, 936, 871, 731 cm^{-1}; MS (ESI): *m/z* 323 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{16}H_{14}F_3N_2O_2$ $(M+H)^+$: 323.1002, found: 323.1006.

Synthesis of (*E*)-*N*-(2-acetamido-4-(hept-1-en-1-yl)phenyl)-2,2,2-trifluoroacetamide (11):[18]



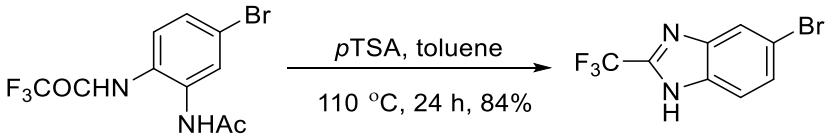
A solution of potassium (*E*)-trifluoro(hept-1-en-1-yl)borate (71.5 mg, 0.35 mmol, 1.2 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (4.7 mg, 0.0058 mmol, 0.02 equiv), *N*-(2-acetamido-4-bromophenyl)-2,2,2-trifluoroacetamide (**2a**, 100 mg, 0.29 mmol, 1 equiv) and *t*-$BuNH_2$ (63.5 mg, 92 uL, 0.87 mmol, 3 equiv) in *i*-PrOH/H_2O (2:1, 3 mL) was heated at 100 °C under an argon atmosphere for 30 min under microwave conditions, then cooled to room temperature and diluted with water (5 mL), followed by extraction with ethyl acetate (5 mL x 2). The organic layers were combined and washed with 0.1 N HCl (10 mL) and brine (10 mL), dried over $MgSO_4$, and then filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (EtOAc in EtOH (3:1)/hexanes, 10:90 to 40:60) to afford the (*E*)-*N*-(2-acetamido-4-(hept-1-en-1-yl)phenyl)-2,2,2-trifluoroacetamide (**11**) in 86% yield (86 mg). mp = 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.90 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.23 (dd, J = 8.4, 1.9 Hz, 1H), 7.00 (d, J = 1.8 Hz, 1H), 6.34 – 6.11 (m, 2H), 2.19 (dt, J = 8.8, 6.4 Hz, 2H), 2.14 (s, 3H), 1.52 – 1.40 (m, 2H), 1.39 – 1.26 (m, 4H), 0.90 (dt, J = 5.9, 3.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 156.0 (q, J = 37.4 Hz), 137.6, 133.3, 130.0, 127.8, 126.6, 125.7, 124.3, 121.8, 115.9 (q, J = 288.0 Hz), 32.9, 31.4, 28.8, 23.4, 22.5, 14.0; FTIR (neat): 3231, 2924, 1722, 1644, 1498, 1284, 1142, 972, 896, 725 cm^{-1}; MS (ESI): *m/z* 343 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}F_3N_2O_2$ $(M+H)^+$: 343.1628, found: 343.1631.

Synthesis of *N,N'*-(3,3'-diacetamido-[1,1'-biphenyl]-4,4'-diyl)bis(2,2,2-trifluoroacetamide) (12):



A solution of $PdCl_2(dppf)\cdot CH_2Cl_2$ (4.7 mg, 0.0058 mmol, 0.02 equiv), *N*-(2-acetamido-4-bromophenyl)-2,2,2-trifluoroacetamide (**2a**, 100 mg, 0.29 mmol, 1 equiv) and *t*-$BuNH_2$ (63.5 mg, 92 uL, 0.87 mmol, 3 equiv) in *i*-PrOH/H_2O (2:1, 3 mL) was heated to 100 °C under an argon atmosphere for 45 min under microwave conditions, then cooled to room temperature and diluted with water (5 mL), followed by extraction with ethyl acetate (5 mL x 2). The organic layers were combined and washed with 0.1 N HCl (10 mL) and brine (10 mL), dried over $MgSO_4$, and then filtered. The solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (EtOAc in EtOH (3:1)/hexanes, 20:80 to 50:50) to afford the *N*,*N*'-(3,3'-diacetamido-[1,1'-biphenyl]-4,4'-diyl)bis(2,2,2-trifluoroacetamide) (**12**) in 79% yield (56 mg), mp = 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 2H), 7.86 (s, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.34 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.20 (d, *J* = 2.2 Hz, 2H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 155.9 (q, *J* = 37.9 Hz), 131.1, 130.1, 127.6, 127.6, 127.1, 120.0, 115.8 (q, *J* = 288.0 Hz), 23.5; FTIR (neat): 3238, 2981, 1703, 1662, 1480, 1279, 1146, 873, 806, 717 cm^{-1}; MS (ESI): *m/z* 491 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_{20}H_{17}F_6N_4O_4$ $(M+H)^+$: 491.1149, found: 491.1153.

5-Bromo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (13):[19]

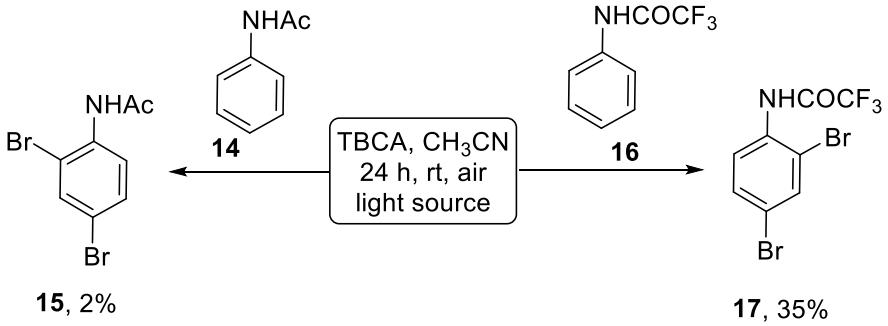


2a **13**

N-(2-Acetamido-4-bromophenyl)-2,2,2-trifluoroacetamide (**2a**, 100 mg, 0.3 mmol) was taken up in toluene (5 mL), and *p*-TsOH·H_2O (5.3 mg, 0.03 mmol) was added. The mixture was allowed to stir under reflux for 24 h. After cooling to room temperature, saturated aqueous sodium bicarbonate solution (10 mL) was added, and the organics were extracted into EtOAc (2 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under vacuum. The product was purified by flash column chromatography on silica gel (EtOAc/hexanes, 10:90 to 40:60) to afford the 5-bromo-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**13**) as a brown solid (67 mg, 84%) and spectral data was found

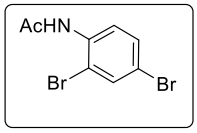
to be identical with those reported in the literature; mp: 188-190 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, J = 1.6 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.53 (dd, J = 8.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.59 (q, J = 39.3 Hz), 139.9, 137.3, 127.6, 123.3, 118.4 (d, J = 81.9 Hz), 116.0 (d, J = 144.3 Hz).

Bromination reaction of mono amide derivatives:



A 10 mL round bottom flask equipped with a magnetic stir bar was charged with amide (**14** or **16**, 0.40 mmol) in acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 24 hours. The progress of the reaction was monitored by TLC. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc/hexanes, 1:99 to 10:90) to yield the dibromo amide derivatives **15** or **17**.

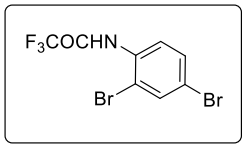
***N*-(2,4-Dibromophenyl)acetamide (15):**[20]



N-Phenylacetamide (**14**, 54 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 24 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 1:99 to 5:95) 2.3 mg (2%) of a white solid (**15**) was obtained (81% recovered **14**) and spectral data was found to be identical with those reported in the literature. R_f = 0.20 (EtOAc/hexanes 05:95); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 2.2 Hz, 1H), 7.55 (s, 1H), 7.43 (dd, J = 8.9, 2.2 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 134.9,

134.3, 131.4, 122.7, 115.2, 112.4, 24.9; FTIR (neat): 3275, 2923, 1659, 1572, 1464, 1365, 1251, 1076, 1039, 825, 732 cm^{-1}; MS (ESI): *m/z* 292 $(M+H)^+$.

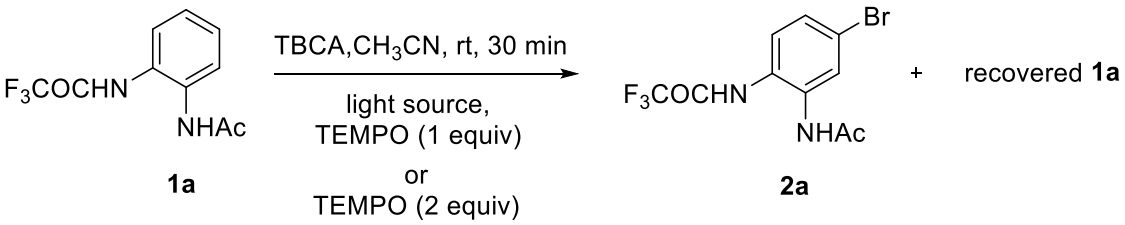
***N*-(2,4-Dibromophenyl)-2,2,2-trifluoroacetamide (17; CAS Number: 340034-26-6):**



2,2,2-Trifluoro-*N*-phenylacetamide (**16**, 76 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 24 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 01:99 to 05:95) 48 mg (35%) of a pale, yellow solid (**17**) was obtained (54% recovered **16**). R_f = 0.25 (EtOAc/hexanes 05:95), mp = 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 2.2 Hz, 1H), 7.45 (dd, J = 8.8, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6 (q, J = 38.1 Hz), 134.9, 132.4, 131.8, 122.9, 119.3, 115.4 (q, J = 288.7 Hz), 114.6; FTIR (neat): 3281, 1707, 1532, 1467, 1277, 1159, 1040, 911, 815, 744 cm^{-1}; MS (ESI): *m/z* 348 $(M+H)^+$; HRMS (ESI): *m/z* calcd for $C_8H_5Br_2F_3NO$ $(M+H)^+$: 347.8685, found: 347.8664.

Mechanistic studies:

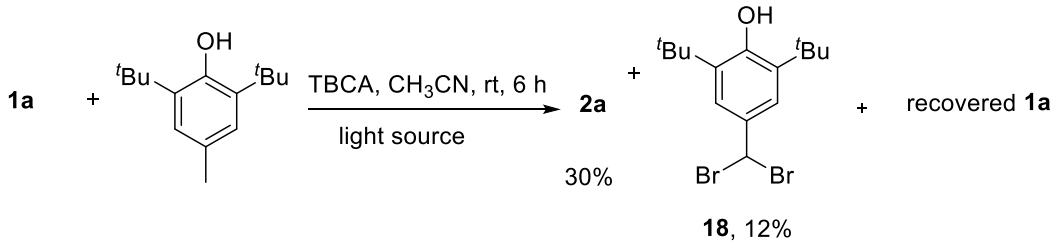
Standard reaction with TEMPO:



A 10 mL round-bottom flask equipped with a magnetic stir bar was charged with diamide (**1a**, 0.40 mmol), TEMPO (two separate reactions with: 65 mg, 1 equivalent and 130 mg, 2 equivalents) and acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 30 min. The progress of the reaction was monitored by TLC. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc in EtOH (3:1)/hexanes, 5:95 to 70:30) to yield the diamide

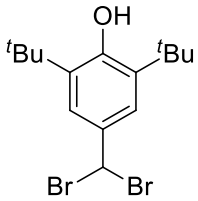
derivative **2a** in 45% yield when 1 equiv. of TEMPO was used (38% recovered **1a**) and 28% yield with 2 equiv. of TEMPO (63% recovered **1a**).

Standard reaction with BHT:



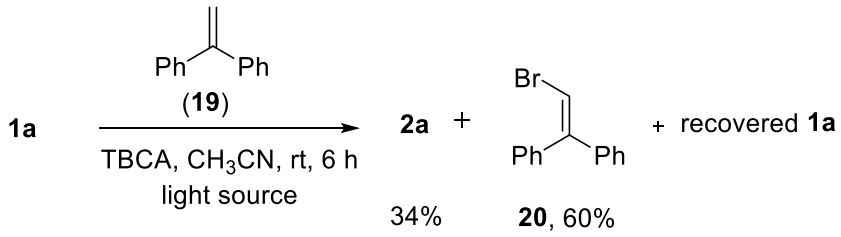
A 10 mL round bottom flask equipped with a magnetic stir bar was charged with diamide (**1a**, 0.40 mmol), BHT (88 mg, 1 equivalent, 0.40 mmol) and acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 6 hours. The progress of the reaction was monitored by TLC. The solvent was then evaporated, and the crude residue was purified by flash chromatography (EtOAc in EtOH (3:1)/hexanes, 5:95 to 70:30) to yield the diamide derivative **2a** in 30% yield and dibromo-BHT **18** in 12% yield with 55% recovered **1a**. The spectral data of compound **18** was found to be identical with those reported in the literature.

2,6-Di-*tert*-butyl-4-(dibromomethyl)phenol (18):[21]



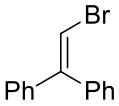
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1H), 7.66 (s, 2H), 5.78 (s, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 159.7, 136.5, 128.7, 127.7, 34.3, 30.1; FTIR (neat): 3321, 2922, 1771, 1643, 1498, 1291, 1142, 971, 899, 723 cm^{-1}; MS (ESI): *m/z* 377 $(M+H)^+$.

Standard reaction with ethene-1,1-diyldibenzene (19):



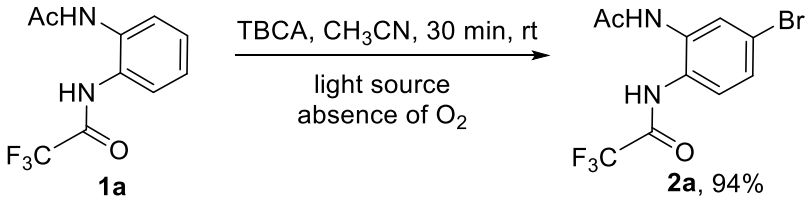
A 10 mL round bottom flask equipped with a magnetic stir bar was charged with diamide (**1a**, 0.40 mmol), ethene-1,1-diyldibenzene (**19**, 72 mg, 1 equivalent, 0.40 mmol) and acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added the tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 6 hours. The progress of the reaction was monitored by TLC. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc in EtOH (3:1)/hexanes, 5:95 to 70:30) to yield the diamide derivative **2a** in 34% yield and (2-bromoethene-1,1-diyl)dibenzene (**20**) in 60% yield with 45% recovered **1a**. The spectral data of compound **20** was found to be identical with those reported in the literature.

(2-Bromoethene-1,1-diyl)dibenzene (20):[22]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 3H), 7.25 – 7.18 (m, 5H), 7.17 – 7.09 (m, 2H), 6.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 140.7, 139.0, 129.6, 128.4, 128.2, 128.1, 128.0, 127.6, 105.2.

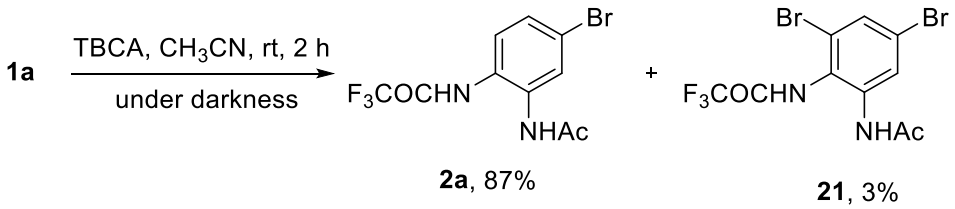
Bromination reaction in the absence of O_2:



A 10 mL round bottom flask equipped with a magnetic stir bar was charged with the unsymmetrical diamide (**1a**, 0.40 mmol) and acetonitrile (3 mL) at room temperature. Argon gas was passed through the solution for 10 min. Two 100-watt household lights were arranged approximately 20 cm from the reaction. In a

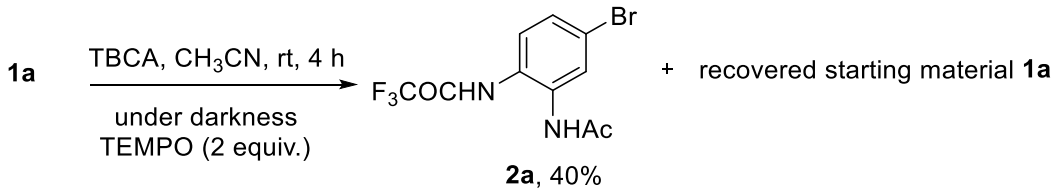
second round-bottom flask, tribromoisocyanuric acid (0.145 mmol) and acetonitrile (2 mL) was degassed for 10 min. The degassed and stirred solution of diamide was added to the tribromoisocyanuric acid solution in one portion through cannula under argon, and the resulting solution was stirred at room temperature for 30 min. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc in EtOH (3:1)/hexanes, 5:95 to 70:30) to yield the corresponding halogenated diamide **2a** in 94% yield.

Bromination reaction of 1a under complete darkness:



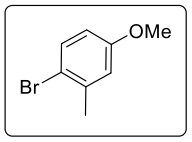
A 10 mL round bottom flask equipped with a magnetic stir bar was charged with diamide (**1a**, 0.40 mmol), and acetonitrile (3 mL) under open air conditions at room temperature, and the flask was covered with aluminum foil. Lights in the fume hood were turned off to create a complete dark atmosphere for the reaction. To the stirred solution was added the tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 2 hours under darkness. The progress of the reaction was monitored by TLC. The solvent was removed under vacuum, and the crude residue was purified by flash chromatography (EtOAc/hexanes, 5:95 to 70:30) to yield the diamide derivative **2a** in 87% yield and dibromo-compound **21** in 3% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.90 (s, 1H), 9.80 (s, 1H), 8.11 (s, 1H), 7.82 (s, 1H), 2.08 (s, 3H).; ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.6, 156.0 (q, J = 37.1 Hz), 134.1, 131.6, 128.8, 127.6, 122.2, 118.5, 116.2 (q, J = 288.3 Hz), 24.1; FTIR (neat): 3231, 2924, 1722, 1644, 1498, 1284, 1142, 972, 896, 725 cm^{-1}; MS (ESI): *m/z* 402 $(M+H)^+$.

Bromination reaction under complete darkness with TEMPO:



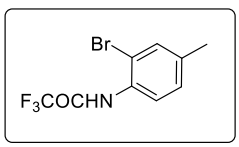
A 10 mL round-bottom flask equipped with a magnetic stir bar was charged with diamide (**1a**, 0.40 mmol), TEMPO (125 mg, 0.8 mmol) and acetonitrile (5 mL) under open air conditions at room temperature, and the flask was covered with aluminum foil and the lights in the fume hood were turned off to create a complete dark atmosphere for the reaction. To the stirred solution was added tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 4 hours under the darkness. The progress of the reaction was monitored by TLC. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc/hexanes, 5:95 to 70:30) to yield the bromo-compound **2a** in 40% yield along with 45% of recovered **1a**.

1-Bromo-4-methoxy-2-methylbenzene (23; CAS Number: 27060-75-9):[23]



Following the general bromination procedure; 1-methoxy-3-methylbenzene (**22**, 49 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 2 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 1:99 to 5:95) 14 mg (18%) of a white solid was obtained and the spectral data was found to be identical with those reported in the literature. R_f = 0.20 (EtOAc/hexanes 5:95); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.7 Hz, 1H), 6.78 (d, J = 2.7 Hz, 1H), 6.61 (dd, J = 8.7, 2.8 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 138.8, 132.8, 116.5, 115.4, 112.9, 55.4, 23.1; FTIR (neat): 2954, 1595, 1475, 1308, 1240, 1161, 1022, 915, 843, 797, 693 cm^{-1}; MS (ESI): *m/z* 201 $(M+H)^+$.

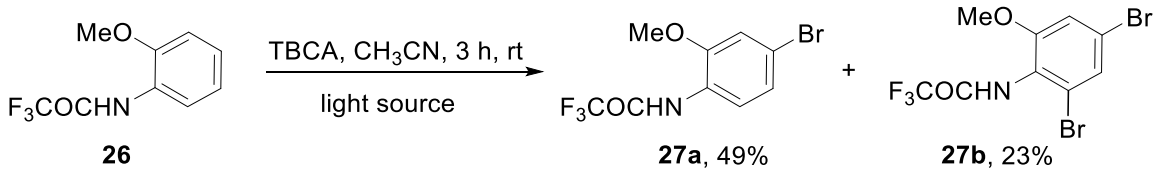
***N*-(2-Bromo-4-methylphenyl)-2,2,2-trifluoroacetamide (25):**



Following the general bromination procedure; 2,2,2-trifluoro-*N*-(*p*-tolyl)acetamide (**24**, 81 mg, 0.40 mmol) and tribromoisocyanuric acid (53 mg, 0.145 mmol) in acetonitrile (3 mL), 3 h at room temperature. After column chromatography (gradient: EtOAc/hexanes 1:99 to 10:90) 100 mg (89%) of a white solid was obtained. R_f = 0.40

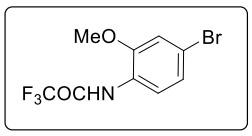
(EtOAc/hexanes 10:90); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 1.2 Hz, 1H), 7.18 (ddd, J = 8.4, 1.3, 0.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5 (q, J = 37.5 Hz), 137.6, 132.8, 130.5, 129.3, 121.8, 115.6 (q, J = 288.7 Hz), 114.0, 20.6; FTIR (neat): 3283, 1709, 1537, 1486, 1277, 1155, 1041, 912, 820, 724 cm^{-1}; MS (ESI): *m/z* 281 $(M+H)^+$. HRMS (ESI): *m/z* calcd for $C_9H_8BrF_3NO$ $(M+H)^+$: 281.9736, found: 281.9739.

Bromination of 2-methoxy amide (26):



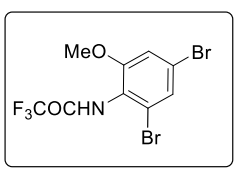
A 10 mL round bottom flask equipped with a magnetic stir bar was charged with 2-methoxyamide (**26**, 0.40 mmol) in acetonitrile (3 mL) under open air conditions at room temperature, and two 100-watt household lights were arranged approximately 20 cm from the reaction. To the stirred solution was added the tribromoisocyanuric acid (0.145 mmol) in one portion, and the resulting solution was stirred at room temperature for 3 hours. The progress of the reaction was monitored by TLC. The reaction mixture was then evaporated, and the crude residue was purified by flash chromatography (EtOAc/hexanes, 1:99 to 10:90) to yield the bromo derivatives **27a** in 49% yield and dibromo-compound **27b** in 23% yield.

***N*-(4-Bromo-2-methoxyphenyl)-2,2,2-trifluoroacetamide (27a; CAS Number: 870838-52-1):**



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 24.7 Hz, 1H), 8.21 (d, J = 8.7 Hz, 1H), 7.15 (dd, J = 8.6, 2.0 Hz, 1H), 7.07 (d, J = 2.0 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3 (q, J = 37.5 Hz), 148.8, 128.8, 124.2, 121.2, 118.6, 115.6 (q, J = 288.5 Hz), 113.9, 56.3; FTIR (neat): 3402, 1720, 1600, 1489, 1398, 1145, 1118, 1022, 901, 819, 730 cm^{-1}.

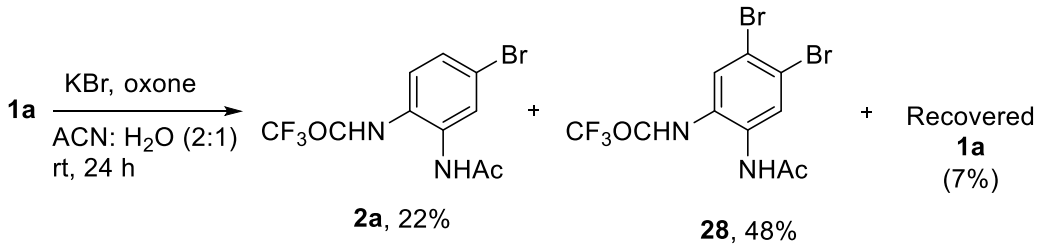
***N*-(2,4-Dibromo-6-methoxyphenyl)-2,2,2-trifluoroacetamide (27b):**



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.41 (d, J = 1.9 Hz, 1H), 7.07 (d, J = 1.9 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 155.0 (q, J = 37.7 Hz),

127.2, 123.1, 123.0, 121.0, 115.8 (q, J = 288.5 Hz), 114.6, 56.6; FTIR (neat): 3218, 1713, 1543, 1444, 1397, 1144, 1031, 927, 840, 705 cm^{-1}.

Bromination reaction of 1a with KBr:[24]



A 10 mL round bottom flask equipped with a magnetic stir bar was charged with diamide (**1a**, 0.40 mmol), and acetonitrile:H_2O (2:1, 3 mL) under open air conditions at room temperature. To the stirred solution were added the potassium bromide (0.40 mmol) and Oxone (0.40 mmol), and the resulting solution was stirred at room temperature for 24 hours. The progress of the reaction was monitored by TLC. Water (10 mL) was added, and the organics were extracted into EtOAc (2 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$. The solvent was removed under vacuum, and the crude residue was purified by flash chromatography (EtOAc/hexanes, 5:95 to 70:30) to yield the monobrominated derivative **2a** in 22% yield and dibrominated derivative **28** in 48% yield and recovered **1a** in 7%.

***N*-(2-acetamido-4,5-dibromophenyl)-2,2,2-trifluoroacetamide** (**28**):

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 8.03 (s, 1H), 7.70 (s, 1H), 7.40 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 155.6 (q, J = 38.2 Hz), 130.1, 129.6, 128.9, 128.8, 122.9, 122.5, 115.7 (q, J = 282.6 Hz), 23.7.

Calculations

The calculations were carried out in Spartan '16 or Spartan '18 (Wavefunction, Inc.) in the ground state either *in vacuo* or in acetonitrile. The starting and intermediate structures were energy minimized using the Equilibrium Geometry option in Spartan with DFT, Hartree-Fock, or Møller-Plesset perturbation levels of theory with the 6-31+G(d,p) basis set. Frequency calculation was used to verify that an energy minimum structure was located successfully. Any imaginary low frequency modes were ignored or subjected to more intense optimization criteria. For neutral radicals or charged intermediates, the total charge and unpaired are selected.

Information reported in the text regarding relative energies are shown below in tabular form based on the total energy and Gibbs energy. Also, the optimized geometry or penultimate optimized geometry are presented.

Table S1. Ground State Minimizations for 1a.

Density Functional Theory (DFT) Calculations of 1a
Gas Phase
B3LYP/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 of 1a	-946.055251	0.99	-945.915501	1.00
Con 2 of 1a	-946.056829	0.00	-945.917102	0.00

Con 1 of 1a

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-0.5362699863	-2.1331621787	2.2929731211
2	C	-0.3654133080	-1.0692704743	2.2062316801
3	C	0.0915257248	1.6523873280	1.9728420551
4	C	-0.3846502881	-0.2584216134	3.3369626847
5	C	-0.1167131623	-0.5447799053	0.9214044856
6	C	0.1086122252	0.8578642334	0.8163861184
7	C	-0.1519436321	1.1130141767	3.2291044756
8	H	-0.1606402186	1.7566253680	4.1022222030
9	H	0.2649574553	2.7221835070	1.8761591705
10	N	-0.0685639505	-1.3514227610	-0.2267308424
11	H	0.1013343331	-0.8118655746	-1.0826273235
12	C	-0.4013727942	-2.6841991814	-0.3796238034
13	O	-0.7300888791	-3.4234998391	0.5417879180
14	C	-0.3419416812	-3.1573079842	-1.8207249710
15	H	-0.1831521106	-4.2362465438	-1.8242893976

16	H	0.4436180997	-2.6573237009	-2.3934653294
17	H	-1.2985286563	-2.9443589261	-2.3111706054
18	N	0.3903702891	1.6229400985	-0.3717891096
19	H	0.6705630512	2.5677652827	-0.1391412920
20	C	0.2937078809	1.4229141772	-1.7030758993
21	O	-0.0469189131	0.4199920877	-2.3161932138
22	C	0.6635252845	2.6711425767	-2.5560221374
23	F	-0.3495313720	2.9774550867	-3.3788062739
24	F	0.9292107919	3.7754999194	-1.8018522307
25	F	1.7545409734	2.4189912223	-3.2971846211
26	H	-0.5762371568	-0.7069163816	4.3066231381

Con 2 of 1a

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-0.6277950521	-1.9040065262	-2.6696661983
2	C	-0.4379272319	-1.9839079233	-1.6014585675
3	C	0.0670477336	-2.1783694757	1.1089974166
4	C	-0.3756719344	-3.2413929434	-1.0136226426
5	C	-0.2566553471	-0.8022252670	-0.8639873572
6	C	-0.0120050864	-0.8958651991	0.5319006272
7	C	-0.1143590576	-3.3329866800	0.3524489015
8	H	-0.0554066965	-4.3009771194	0.8398213159
9	H	0.2651548055	-2.2508217947	2.1685974246
10	N	-0.4102455630	0.3878535859	-1.6461603252
11	H	-0.8531522664	0.1891325392	-2.5325507979
12	C	0.0734895544	1.6691682281	-1.5585174856
13	O	0.6870150242	2.1184262520	-0.5889215025
14	C	-0.1654108553	2.5123311358	-2.7998726548
15	H	-0.2309593839	3.5603682139	-2.5057524958
16	H	-1.0677562224	2.2310513849	-3.3509372423
17	H	0.6960807942	2.4016756182	-3.4685579620
18	N	0.1105454412	0.2806913842	1.3056163284
19	H	0.1731593482	1.1402191974	0.7325075222
20	C	0.4073268328	0.3715344203	2.6287399818
21	O	0.5718481966	-0.5295872116	3.4362781641
22	C	0.4994403133	1.8336221390	3.1465926895
23	F	1.7332848735	2.0865646962	3.6247003772
24	F	0.2286575025	2.7530493324	2.1910191754
25	F	-0.3810957678	2.0140055255	4.1516611884
26	H	-0.5246099551	-4.1295535128	-1.6188758811

Hartree-Fock (HF) Calculations of 1a

Gas Phase

HF/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 of 1a	-940.934972	1.18	-940.781127	1.44
Con 2 of 1a	-940.936855	0.00	-940.783421	0.00

Con 1 of 1a

Coordinates (Angstroms)

ATOM		X	Y	Z

1	H	-0.4780684616	-2.1154092443	2.2696653746
2	C	-0.3283445002	-1.0618643889	2.1782440937
3	C	0.0581078001	1.6404504597	1.9564574981
4	C	-0.3713789246	-0.2645888932	3.3048148591
5	C	-0.0873994164	-0.5320618831	0.9044411918
6	C	0.0990096531	0.8554124022	0.8046214256
7	C	-0.1726764320	1.1018903943	3.2024014008
8	H	-0.1974146454	1.7371347935	4.0682325868
9	H	0.2049783804	2.7032613583	1.8657530810
10	N	0.0087046854	-1.3590979537	-0.2236229895
11	H	0.2046665684	-0.8849517405	-1.0798289811
12	C	-0.4121142010	-2.6522239612	-0.3700236853
13	O	-0.8255225657	-3.3438941859	0.5191820206
14	C	-0.3257352996	-3.1527013179	-1.7948671223
15	H	-0.2797907029	-4.2318912761	-1.7811565177
16	H	0.5323073326	-2.7509959085	-2.3195087551
17	H	-1.2191705684	-2.8479363356	-2.3306190660
18	N	0.3883160120	1.6295958288	-0.3725895118
19	H	0.7081748676	2.5405143742	-0.1320069336
20	C	0.2477388995	1.4455607918	-1.6858257020
21	O	-0.1456775606	0.4820113165	-2.2778233794
22	C	0.6468268443	2.6696206668	-2.5430264488
23	F	-0.3617280502	3.0215044418	-3.3029345687
24	F	0.9898068351	3.7236381806	-1.8128704852
25	F	1.6697273381	2.3660864626	-3.3087217813
26	H	-0.5533438881	-0.7190643821	4.2616123954

Con 2 of 1a

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-0.5862243577	-1.8918577786	-2.6556936593
2	C	-0.4107404123	-1.9682787490	-1.5963249727
3	C	0.0641439276	-2.1545840575	1.0958149550
4	C	-0.3418391233	-3.2156740922	-1.0133455581
5	C	-0.2537220318	-0.7938336050	-0.8616894997
6	C	-0.0207301707	-0.8839588892	0.5178817337
7	C	-0.0964170023	-3.3036648542	0.3464720637
8	H	-0.0346466664	-4.2604393991	0.8321334692
9	H	0.2491999232	-2.2333093829	2.1445239697
10	N	-0.4425327153	0.3954086799	-1.6271987653
11	H	-0.9843416723	0.2316920900	-2.4454655134
12	C	0.1480501195	1.6173768815	-1.5846798934
13	O	0.8781436336	1.9766198900	-0.6956586168
14	C	-0.1510201484	2.4999491157	-2.7771139482
15	H	-0.0252783619	3.5337679291	-2.4908273337
16	H	-1.1488849630	2.3507317725	-3.1735037793
17	H	0.5662513379	2.2717577217	-3.5599874219
18	N	0.0701155473	0.2841722235	1.3064936749
19	H	0.1125396958	1.1382836856	0.7922249209
20	C	0.3896423897	0.3773655670	2.6097726278
21	O	0.5913630423	-0.4952021359	3.3994740985
22	C	0.4600292266	1.8272388503	3.1331819098
23	F	1.6657238866	2.0862060312	3.5904004793
24	F	0.1739134038	2.7279658258	2.2070760539
25	F	-0.3993861812	1.9796943618	4.1196001444
26	H	-0.4733523273	-4.0974276820	-1.6135611392

Table S2. Ground State Minimizations for 2x

Density Functional Theory (DFT) Calculations for 2x

Gas Phase

B3LYP/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 for 2x	-840.078810	0.05	-839.864516	0.05
Con 2 for 2x	-840.078889	0.00	-839.864595	0.00

Con 1 for 2x

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-0.7756694825	2.4010506786	-3.6036872412
2	C	-0.5925969286	1.3642550122	-3.3589484107
3	C	-0.0733074718	-1.2739716012	-2.7082777892
4	C	-0.4284851681	1.0298700536	-1.9996052144
5	C	-0.4944792591	0.4082885938	-4.3647007426
6	C	-0.2321636273	-0.9252147263	-4.0447662535
7	C	-0.1625505913	-0.3250610257	-1.6752548082
8	H	-0.6202877511	0.7105679455	-5.3998891534
9	H	-0.1536591210	-1.6817625392	-4.8189972807
10	H	0.1259681666	-2.3115380190	-2.4495494212
11	N	-0.5034872855	2.0023840762	-0.9929814374
12	H	-0.7364798365	1.6397948077	-0.0622352779
13	N	0.1191042522	-0.8431045871	-0.3734655508
14	H	0.6378559708	-1.7084312286	-0.4149941747
15	C	-0.4857041741	3.3744465205	-1.1197841192
16	C	-0.2986983908	-0.5180024402	0.8847141063
17	C	-0.6952507996	4.1034204730	0.2005479405
18	H	0.0778374755	3.8310397732	0.9277520398
19	H	-1.6651339302	3.8448510155	0.6392559999
20	H	-0.6552971492	5.1762160643	0.0150822635
21	O	-0.3085851273	3.9761219051	-2.1753568198
22	O	-1.1079560197	0.3888348187	1.1344940904
23	C	0.2664187921	-1.3612664404	1.9923812795
24	C	1.2048458788	-2.8943502377	4.1474119138
25	C	-0.4939772475	-1.4752719794	3.1664275712
26	C	1.5128954226	-2.0047051814	1.9184124982
27	C	1.9795363045	-2.7660633146	2.9924219498
28	C	-0.0317813283	-2.2460490771	4.2321210751
29	H	-1.4433861521	-0.9543990260	3.2221922737
30	H	2.1505979996	-1.8858999109	1.0466481844
31	H	2.9510913365	-3.2472146186	2.9305466710
32	H	-0.6336441944	-2.3394075758	5.1311261938
33	H	1.5664294371	-3.4894282083	4.9809576440

Con 2 for 2x

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-1.5306799217	2.7336294442	-3.3817975636
2	C	-1.1493446969	1.7251251150	-3.2401128139
3	C	-0.1490958414	-0.8372373277	-2.8560987098

4	C	-0.7919078881	1.3126904106	-1.9473097291
5	C	-1.0205729953	0.8691697364	-4.3292633933
6	C	-0.5188853878	-0.4201440951	-4.1315314136
7	C	-0.2790898110	0.0141508720	-1.7470590475
8	H	-1.3051092483	1.2084362867	-5.3202097242
9	H	-0.4115475040	-1.1006788069	-4.9706047297
10	H	0.2259860446	-1.8389916963	-2.6967313754
11	N	-1.0681520676	2.2253864247	-0.8814187328
12	H	-1.9321379642	2.7383298158	-0.9931498136
13	N	0.1145121614	-0.4038563878	-0.4592432464
14	H	0.5755021988	0.3197201855	0.0836959282
15	C	-0.2546877301	2.6379700006	0.1369490765
16	C	-0.0391942025	-1.6636252507	0.0686222726
17	C	-0.8189609693	3.7290363727	1.0273870009
18	H	-1.8461855910	4.0148305849	0.7858353057
19	H	-0.1743931631	4.6097111704	0.9483911503
20	H	-0.7796492079	3.3860171825	2.0644579818
21	O	0.8657985098	2.1647912915	0.3432282813
22	O	-0.6395447177	-2.5632304319	-0.5183102740
23	C	0.5634037726	-1.8940004320	1.4352207207
24	C	1.6094742146	-2.5287253768	3.9681581193
25	C	0.3068072687	-3.1416684173	2.0251540978
26	C	1.3537902725	-0.9637677383	2.1327217166
27	C	1.8712471068	-1.2839726093	3.3902038589
28	C	0.8235319445	-3.4579296357	3.2809086085
29	H	-0.3050983928	-3.8478886783	1.4746304561
30	H	1.5905085590	0.0141617956	1.7240513737
31	H	2.4834985947	-0.5568224988	3.9158255803
32	H	0.6143844105	-4.4284407676	3.7216925402
33	H	2.0157922419	-2.7721765386	4.9457064976

2x in Acetonitrile
B3LYP/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 for 2x	-840.103225	0.16	-839.885331	1.40
Con 2 for 2x	-840.103476	0.00	-839.887568	0.00

Con 1 for 2x

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-0.9579607840	2.3521659378	-3.5975734693
2	C	-0.6955334190	1.3398298521	-3.3383949838
3	C	-0.0029524439	-1.2526900739	-2.6644751851
4	C	-0.4589345805	1.0403414944	-1.9856223848
5	C	-0.5713631846	0.3760781448	-4.3325767241
6	C	-0.2140634370	-0.9327894626	-3.9965330537
7	C	-0.1242034513	-0.2934143353	-1.6433261057
8	H	-0.7521547795	0.6516193218	-5.3652594693
9	H	-0.1077575073	-1.6967049144	-4.7577050579
10	H	0.2628574903	-2.2673428276	-2.3894164348
11	N	-0.5545101539	2.0336840279	-0.9887063223
12	H	-0.8220720976	1.6809589110	-0.0699234197

13	N	0.1934217013	-0.7799953987	-0.3427654444
14	H	0.7756088640	-1.5991660234	-0.3896543646
15	C	-0.4102844325	3.3932051168	-1.1279971291
16	C	-0.3222180190	-0.5377317851	0.9020249571
17	C	-0.6596818172	4.1779156306	0.1464131175
18	H	0.0791247680	3.9123631844	0.9037937869
19	H	-1.6509342707	3.9622606620	0.5542082510
20	H	-0.5857988158	5.2412530610	-0.0725221439
21	O	-0.0908680522	3.9461546379	-2.1842144629
22	O	-1.2178048320	0.2908470663	1.1162383966
23	C	0.2521807729	-1.3719511389	2.0055925918
24	C	1.1973312232	-2.9408619905	4.1192517145
25	C	-0.5116985706	-1.5225069547	3.1667543165
26	C	1.5016763449	-1.9980914155	1.9164376579
27	C	1.9720490988	-2.7770257505	2.9694133490
28	C	-0.0451254983	-2.3087532407	4.2145561225
29	H	-1.4693473779	-1.0289229535	3.2342622490
30	H	2.1361993054	-1.8643906467	1.0543713278
31	H	2.9432288008	-3.2479745418	2.8970227874
32	H	-0.6486104091	-2.4283939196	5.1078971416
33	H	1.5601995644	-3.5499696757	4.9384283886

Con 2 for 2x

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-1.6832539007	2.7704139877	-3.2126693552
2	C	-1.2464106170	1.7781894201	-3.1239278686
3	C	-0.1061867875	-0.7303117502	-2.8769258762
4	C	-0.8298786183	1.3423199074	-1.8535326780
5	C	-1.1141690399	0.9746203608	-4.2544835336
6	C	-0.5319410159	-0.2878377314	-4.1283535670
7	C	-0.2634517525	0.0558214193	-1.7234936482
8	H	-1.4531036773	1.3397752420	-5.2192150561
9	H	-0.4042401034	-0.9288878669	-4.9956888300
10	H	0.3440852002	-1.7084070036	-2.7740486491
11	N	-1.1004654928	2.2572834210	-0.7846565129
12	H	-1.8868931940	2.8653556746	-0.9851465696
13	N	0.1683175020	-0.4319793896	-0.4636972173
14	H	0.5198546832	0.2895402027	0.1674203654
15	C	-0.3739575017	2.6308196522	0.3046541565
16	C	0.0765305558	-1.7192307721	-0.0200059673
17	C	-0.9942854693	3.7479041928	1.1190191918
18	H	-1.1251555388	4.6424088040	0.5031751341
19	H	-0.3456874534	3.9778896785	1.9630309488
20	H	-1.9810946522	3.4537833358	1.4948471556
21	O	0.7097878319	2.1122027269	0.6217972627
22	O	-0.4511091896	-2.6366792262	-0.6683028008
23	C	0.6611612669	-1.9823642674	1.3422169338
24	C	1.7147046324	-2.5996779961	3.8703280869
25	C	0.1374490220	-3.0483839794	2.0903281118
26	C	1.7261192170	-1.2347264026	1.8686786660
27	C	2.2522827662	-1.5471397147	3.1242854780
28	C	0.6542826876	-3.3495434676	3.3504219293
29	H	-0.6820461752	-3.6300697180	1.6792581403
30	H	2.1692247045	-0.4270063441	1.2962622275
31	H	3.0849550336	-0.9703275115	3.5147274073

32	H	0.2317729651	-4.1678085918	3.9258958170
33	H	2.1228021115	-2.8379462930	4.8478011173

Table S3. Energy Calculations for Neutral Carbon Radicals of 1a

Density Functional Theory (DFT) Calculations of the 1a carbon radicals

Gas Phase

B3LYP/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 (*para*)	-945.365525	0.82	-945.239575	0.61
Con 1 (*meta*)	-945.364769	1.30	-945.238851	1.07
Con 2 (*para*)	-945.366835	0.00	-945.240549	0.00
Con 2 (*meta*)	-945.366821	0.01	-945.240519	0.02

Con 1 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.5558770691	2.6788989171	-1.8131474667
2	C	0.4853176746	2.4514366065	-0.7571298502
3	C	0.2693966195	1.8863042883	1.9795333863
4	C	0.2160363443	1.1243358523	-0.3498101371
5	C	0.6148039981	3.4043098369	0.2203175100
6	C	0.5216519832	3.2027896345	1.5811760115
7	C	0.1084730039	0.8609084661	1.0363734421
8	H	0.6344163768	3.9981041344	2.3104022734
9	H	0.1894893054	1.6461432761	3.0371976736
10	N	0.0719043786	0.0829808111	-1.2822289965
11	H	0.4560645230	-0.8132689541	-0.9917780460
12	N	-0.2586684086	-0.4217927617	1.5629851832
13	H	-0.9085511728	-0.3995381217	2.3391225446
14	C	-0.3813307810	0.1975586557	-2.5836075741
15	C	0.2712697654	-1.6291479082	1.2710178197
16	C	-0.3594384320	-1.0993321420	-3.3730636028
17	H	0.0393260919	-1.9499127483	-2.8143068607
18	H	0.2409019525	-0.9485761933	-4.2747807203
19	H	-1.3801035200	-1.3263849706	-3.6943829157
20	C	-0.2942184963	-2.8021827877	2.1176367865
21	O	-0.7855268568	1.2455348124	-3.0711248993
22	O	1.1083023703	-1.8840196926	0.4131904210
23	F	-0.9861594447	-3.6484034920	1.3344616095
24	F	-1.1350944414	-2.3781873220	3.1024045692
25	F	0.7058600968	-3.4785581973	2.6995418390

Con 1 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.5974836210	2.6253882312	-1.7089458412
2	C	0.5107292891	2.4220000357	-0.6495172896
3	C	0.2347827958	1.8691684552	2.0841479113
4	C	0.2309929477	1.1048894032	-0.2397753304

5	C	0.6344879112	3.4624070519	0.2772096902
6	C	0.4918063744	3.1296874732	1.6073452284
7	C	0.0909593192	0.8330923792	1.1395550528
8	H	0.8349835743	4.4755464608	-0.0563564148
9	H	0.1471322762	1.6546473783	3.1461008628
10	N	0.0932975657	0.0642766857	-1.1810688435
11	H	0.4915321329	-0.8288168591	-0.9031052104
12	N	-0.2751022765	-0.4493777445	1.6596047753
13	H	-0.9262774519	-0.4300556537	2.4349937483
14	C	-0.4076525849	0.1796347449	-2.4622664378
15	C	0.2678692668	-1.6541812255	1.3727831524
16	C	-0.3817186881	-1.1083932099	-3.2667318844
17	H	0.0196786561	-1.9641866338	-2.7177360005
18	H	0.2196730124	-0.9463206471	-4.1660905451
19	H	-1.4011934512	-1.3339728548	-3.5919888340
20	C	-0.3012735882	-2.8314402174	2.2115668124
21	O	-0.8506154051	1.2232125372	-2.9271417591
22	O	1.1185272544	-1.9016443813	0.5276513994
23	F	-0.9879098987	-3.6748165726	1.4206562963
24	F	-1.1481129854	-2.4116498164	3.1928033205
25	F	0.6959203328	-3.5090950204	2.7963061406

Con 2 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.3572700699	2.6039889143	-2.4060922921
2	C	0.2576954855	2.4633727201	-1.3330159725
3	C	0.0666132073	2.1106978483	1.4391655023
4	C	0.1207296619	1.1633180261	-0.8049987841
5	C	0.2709661547	3.5137631017	-0.4492786481
6	C	0.1794770613	3.4061387118	0.9213834551
7	C	0.0253026608	0.9904855882	0.5930596522
8	H	0.1924051314	4.2664397116	1.5826476965
9	H	-0.0212206351	1.9608645694	2.5080951628
10	N	0.0181874593	0.0931879743	-1.7418527410
11	H	-0.4927349222	0.3184536521	-2.5845491218
12	N	-0.1033843169	-0.3152787623	1.1282372099
13	H	0.4724677017	-1.0287999132	0.6704988077
14	C	0.7227598413	-1.0848379359	-1.7557415329
15	C	-0.8535256948	-0.6381860763	2.2124522120
16	C	0.5358392395	-1.9505535141	-2.9849811753
17	H	-0.1485760816	-1.5286952314	-3.7256309266
18	H	0.1618837281	-2.9282764060	-2.6688209072
19	H	1.5141770986	-2.1085967238	-3.4475702307
20	C	-0.8014132823	-2.1428905101	2.5992137054
21	O	1.4529629853	-1.4337974931	-0.8275033045
22	O	-1.5468292382	0.1051052273	2.8864909275
23	F	-0.3229344403	-2.2839946327	3.8498774755
24	F	-0.0176733869	-2.8828188855	1.7759646094
25	F	-2.0404454887	-2.6690899605	2.5629492206

Con 2 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.3701645752	2.5675966004	-2.2999165347
2	C	0.2669581911	2.4497124699	-1.2238048292

3	C	0.0342519840	2.0993659527	1.5458930993
4	C	0.1190551212	1.1580490896	-0.6972400853
5	C	0.2798534092	3.5779184555	-0.3955357073
6	C	0.1637570204	3.3312119029	0.9552020002
7	C	0.0005361564	0.9713055114	0.6985980448
8	H	0.3814676633	4.5756797836	-0.8098502575
9	H	-0.0636511661	1.9710215425	2.6168083389
10	N	0.0159575784	0.0884144585	-1.6398765374
11	H	-0.5019668729	0.3121379255	-2.4784160619
12	N	-0.1302849635	-0.3338452850	1.2243342140
13	H	0.4389787190	-1.0460352044	0.7536179656
14	C	0.7124647140	-1.0915683898	-1.6529112173
15	C	-0.8475056184	-0.6580029436	2.3321738344
16	C	0.5283141168	-1.9552338765	-2.8840658447
17	H	-0.1481925019	-1.5282071333	-3.6290473378
18	H	0.1465086995	-2.9311940774	-2.5718910913
19	H	1.5088385014	-2.1185531719	-3.3401852444
20	C	-0.8029116195	-2.1671991390	2.7025356499
21	O	1.4352331952	-1.4477256939	-0.7201000645
22	O	-1.5120790497	0.0867428971	3.0319236929
23	F	-0.3268557773	-2.3246468341	3.9513494995
24	F	-0.0232669653	-2.9016178155	1.8711618495
25	F	-2.0456251104	-2.6853270251	2.6592426249

1a Neutral Carbon Radicals in Acetonitrile
B3LYP/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 (*para*)	-945.386880	1.69	-945.258313	2.70
Con 1 (*meta*)	-945.386310	2.05	-945.258016	2.88
Con 2 (*para*)	-945.389581	0.00	-945.262611	0.00
Con 2 (*meta*)	-945.389484	0.06	-945.262418	0.12

Con 1 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.8449423522	2.6083677113	-1.8077605430
2	C	0.6567988881	2.4115130978	-0.7584944250
3	C	0.2130336339	1.9109301062	1.9684551886
4	C	0.2991756590	1.1104885694	-0.3435360969
5	C	0.7457974421	3.3822531142	0.2085105396
6	C	0.5362525212	3.2110788498	1.5614881078
7	C	0.0922531788	0.8735775296	1.0325556767
8	H	0.6167201554	4.0169164878	2.2841208723
9	H	0.0418599232	1.6947279008	3.0195479359
10	N	0.1639614932	0.0666639924	-1.2850287269
11	H	0.6002230439	-0.8178517959	-1.0387598459
12	N	-0.3110278951	-0.4044690245	1.5335690867
13	H	-1.0525315644	-0.3964062453	2.2270002747
14	C	-0.4944621707	0.1529989953	-2.4842351633
15	C	0.3137527883	-1.5717159947	1.3099009825
16	C	-0.4528489107	-1.0989644151	-3.3337300608

17	H	0.0209225533	-1.9456015009	-2.8321989993
18	H	0.0971020057	-0.8769090170	-4.2540729908
19	H	-1.4754035211	-1.3673938933	-3.6134325947
20	C	-0.2821047457	-2.7957891020	2.0539713655
21	O	-1.0845653687	1.1730419791	-2.8560034605
22	O	1.2802950637	-1.7648034854	0.5724393329
23	F	-0.7190650509	-3.7080255656	1.1618591720
24	F	-1.3189356772	-2.4834945069	2.8639970619
25	F	0.6678542027	-3.3811337874	2.8098373102

Con 1 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.8598499768	2.5699421664	-1.7000608821
2	C	0.6586352145	2.3937860660	-0.6491980642
3	C	0.1512609482	1.8990127079	2.0684267408
4	C	0.3015549966	1.1001241770	-0.2358194464
5	C	0.7434517866	3.4509883567	0.2654319848
6	C	0.4791828636	3.1415808947	1.5837840453
7	C	0.0577172812	0.8513558636	1.1306188739
8	H	1.0093748623	4.4501646078	-0.0656776810
9	H	-0.0311191186	1.7025616710	3.1213762378
10	N	0.1868306434	0.0557830573	-1.1870881095
11	H	0.6639432420	-0.8127291152	-0.9627048787
12	N	-0.3381390597	-0.4298227706	1.6205705766
13	H	-1.0864880558	-0.4318352964	2.3069265898
14	C	-0.5356352811	0.1208130605	-2.3473179918
15	C	0.3089196247	-1.5888123590	1.4060968666
16	C	-0.4724856013	-1.1154224115	-3.2188430251
17	H	0.0476081340	-1.9513076813	-2.7458059099
18	H	0.0424954534	-0.8580015971	-4.1502576817
19	H	-1.4916715499	-1.4180026225	-3.4743587132
20	C	-0.2834332015	-2.8217653928	2.1390869081
21	O	-1.1946612927	1.1145312057	-2.6757215197
22	O	1.2925097897	-1.7660334526	0.6894009238
23	F	-0.6893552614	-3.7403788988	1.2391563318
24	F	-1.3403735684	-2.5240370009	2.9281646571
25	F	0.6600271730	-3.3924952362	2.9138131667

Con 2 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.2664271747	2.6098632493	-2.4103488073
2	C	0.2137794291	2.4691882046	-1.3341938611
3	C	0.1221159183	2.1076534613	1.4472672325
4	C	0.1048383168	1.1654637058	-0.8056992278
5	C	0.2539517683	3.5128039758	-0.4425432090
6	C	0.2178695210	3.4063860472	0.9322395708
7	C	0.0455328464	0.9958984643	0.5945163328
8	H	0.2629514374	4.2640750321	1.5960067843
9	H	0.0948216659	1.9530786923	2.5199493690
10	N	0.0027109589	0.0937477770	-1.7341578526
11	H	-0.5109335665	0.3118335615	-2.5801973590
12	N	-0.0753576348	-0.3123973980	1.1365770845
13	H	0.5184729741	-1.0187826075	0.6869796525
14	C	0.7242994721	-1.0642250256	-1.7483180592

15	C	-0.9025094821	-0.6573972513	2.1391211644
16	C	0.5347205673	-1.9532063356	-2.9534071723
17	H	-0.1633940443	-1.5448797585	-3.6867485296
18	H	0.1727784706	-2.9283143371	-2.6137105268
19	H	1.5092749096	-2.1066267194	-3.4265630384
20	C	-0.8082201407	-2.1457289131	2.5733196669
21	O	1.4874211815	-1.3821146942	-0.8197532244
22	O	-1.6985100880	0.0565922924	2.7426236051
23	F	-0.3386345602	-2.2263396364	3.8386623126
24	F	-0.0008667180	-2.8973428102	1.7917085195
25	F	-2.0335403775	-2.7092289766	2.5566695727

Con 2 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.2943005804	2.5775271606	-2.3016558066
2	C	0.2368779268	2.4551931240	-1.2233959508
3	C	0.1048072713	2.0921657181	1.5559034905
4	C	0.1127809713	1.1595854912	-0.6966667491
5	C	0.2773528547	3.5788000195	-0.3887417602
6	C	0.2146512486	3.3273249659	0.9659819943
7	C	0.0307101180	0.9736433849	0.7005866150
8	H	0.3607968652	4.5777112344	-0.8053021373
9	H	0.0709325330	1.9566508562	2.6309656095
10	N	0.0053278069	0.0898387886	-1.6324423332
11	H	-0.5113080524	0.3121439207	-2.4752959212
12	N	-0.0966404707	-0.3340274623	1.2330749398
13	H	0.4880927224	-1.0412509173	0.7700482852
14	C	0.7132311018	-1.0734749053	-1.6477894398
15	C	-0.8969039651	-0.6753706189	2.2600441842
16	C	0.5218201402	-1.9571895209	-2.8565648347
17	H	-0.1658848906	-1.5384076745	-3.5938507702
18	H	0.1458337808	-2.9289883484	-2.5226599397
19	H	1.4978588691	-2.1208770879	-3.3231696605
20	C	-0.8118884766	-2.1681955337	2.6805904697
21	O	1.4678030956	-1.4044672221	-0.7149462717
22	O	-1.6660778842	0.0447397248	2.8893372452
23	F	-0.3391262608	-2.2630582573	3.9432671846
24	F	-0.0132242049	-2.9186917235	1.8896522557
25	F	-2.0421236806	-2.7213251164	2.6630293017

Neutral Carbon Radical of **1a**
Gas Phase
UHF/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 (*para*)	-940.313425	1.19	-940.176459	0.37
Con 1 (*meta*)	-940.313196	1.33	-940.173849	2.01
Con 2 (*para*)	-940.315318	0.00	-940.177051	0.00
Con 2 (*meta*)	-940.315091	0.14	-940.176397	0.40

Con 1 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	3.7180537908	0.1604152663	0.6237972099
2	C	2.9150084330	0.8405167641	0.4186774296
3	C	0.8306756631	2.6403826383	-0.1385032581
4	C	1.6162552808	0.3471366171	0.1995867888
5	C	3.1140547189	2.2059795078	0.3236006257
6	C	2.1228472735	3.1378296743	0.0557723333
7	C	0.5823050924	1.2602364690	-0.0810725788
8	H	2.3247587267	4.1915051920	0.0039878052
9	H	0.0132400401	3.3107081040	-0.3373366448
10	N	1.3409517638	-1.0327026108	0.2916143395
11	H	0.6076235091	-1.2969026943	0.9111262490
12	N	-0.7419774865	0.8245563580	-0.3861792924
13	H	-1.1395018799	1.1628944429	-1.2333059158
14	C	2.0494735383	-2.0046768554	-0.3480268306
15	C	-1.5224006325	0.1043484894	0.4249163959
16	C	1.6176552161	-3.4217256442	-0.0454036894
17	H	0.6660288245	-3.4836523068	0.4677448470
18	H	2.3801558610	-3.8853727722	0.5712052456
19	H	1.5676062583	-3.9702297850	-0.9767295688
20	C	-2.9468046294	-0.1589089376	-0.1018394490
21	O	2.9611702519	-1.7701614851	-1.0922414300
22	O	-1.2204800270	-0.3618774705	1.4840716180
23	F	-3.1126230595	-1.4454949678	-0.3146661977
24	F	-3.1886211172	0.4737931147	-1.2421344900
25	F	-3.8348180242	0.2411308296	0.7764276896

Con 1 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	3.6866647012	0.1277766494	0.6440595031
2	C	2.9126288136	0.8351415749	0.4179291360
3	C	0.8524481191	2.6441440931	-0.1983105657
4	C	1.6078370339	0.3590598519	0.2007467339
5	C	3.2092593944	2.1970536521	0.3050496204
6	C	2.1594234613	3.0520240450	0.0016241017
7	C	0.5801064343	1.2688675185	-0.1098786911
8	H	4.2103975769	2.5568161382	0.4536084955
9	H	0.0632185432	3.3418750635	-0.4129139886
10	N	1.3229975460	-1.0188185477	0.3212628118
11	H	0.6099909214	-1.2705982372	0.9689067663
12	N	-0.7464803239	0.8383377332	-0.4039647567
13	H	-1.1426867284	1.1609258570	-1.2579451447
14	C	1.9811378524	-1.9990415885	-0.3566845957
15	C	-1.5301181612	0.1415393640	0.4257372871
16	C	1.5465433992	-3.4107147159	-0.0334081038
17	H	0.6310955482	-3.4596285249	0.5431072634
18	H	2.3409608240	-3.8918737160	0.5266784953
19	H	1.4226296956	-3.9517760223	-0.9622695455
20	C	-2.9530771806	-0.1353933818	-0.0971859609
21	O	2.8550940057	-1.7753103419	-1.1486495024
22	O	-1.2302732360	-0.2970716725	1.4968892573
23	F	-3.1024322639	-1.4240530231	-0.3183560546
24	F	-3.2073515802	0.5004948236	-1.2331268708

25	F	-3.8415733544	0.2477527417	0.7867313318

Con 2 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	4.1230936665	0.1091155213	-0.6105991052
2	C	3.2751013774	0.7015328513	-0.3172374822
3	C	1.0860280650	2.2518361775	0.5134026155
4	C	2.0024611954	0.1136695192	-0.2209697504
5	C	3.3918578957	2.0481702991	-0.0199071461
6	C	2.3427348242	2.8547102332	0.3944691128
7	C	0.9075192014	0.8966740278	0.1931974148
8	H	2.4782772240	3.8958857390	0.6207969706
9	H	0.2355609950	2.8267818593	0.8257124953
10	N	1.8636089694	-1.2471182480	-0.6003862364
11	H	2.2930881325	-1.5062679695	-1.4585394335
12	N	-0.3738030528	0.3039031046	0.3122864057
13	H	-0.4282232097	-0.5309936167	0.8592876329
14	C	1.3915321849	-2.2418504347	0.1928444758
15	C	-1.4696150678	0.7843658524	-0.2917623460
16	C	1.4910594380	-3.6413788813	-0.3647304728
17	H	1.9485150753	-3.6869714019	-1.3451636792
18	H	0.4934312562	-4.0600986899	-0.4161329009
19	H	2.0664526283	-4.2419656954	0.3292282795
20	C	-2.7444071416	-0.0571967942	-0.0814333050
21	O	0.9040772908	-2.0318962680	1.2744808135
22	O	-1.5515982360	1.7610913977	-0.9715630499
23	F	-3.7219675241	0.6959097154	0.3654330127
24	F	-2.5690151742	-1.0476648653	0.7793706282
25	F	-3.1162178173	-0.5898390059	-1.2289157407

Con 2 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	4.1045336260	0.0000685997	-0.5232575096
2	C	3.2787641931	0.6359423329	-0.2574421314
3	C	1.0957101275	2.2392464182	0.4817781626
4	C	1.9893973625	0.0830850074	-0.1967161616
5	C	3.4937677870	1.9896095500	0.0198593512
6	C	2.3829971721	2.7364595748	0.3793251325
7	C	0.8916272945	0.8849097449	0.1703320589
8	H	4.4774293152	2.4172096045	-0.0365627611
9	H	0.2694031395	2.8602437106	0.7654119172
10	N	1.8384186068	-1.2766815215	-0.5832233305
11	H	2.3031651878	-1.5431975730	-1.4201788863
12	N	-0.3989669215	0.3113716817	0.2560558905
13	H	-0.4647341769	-0.5468635739	0.7633670756
14	C	1.3271990404	-2.2659091021	0.1904958631
15	C	-1.5015628252	0.8708215237	-0.2630784244
16	C	1.4379969887	-3.6666398686	-0.3613988379
17	H	1.9620952564	-3.7197410214	-1.3073036338
18	H	0.4388353961	-4.0665779861	-0.4832233813
19	H	1.9520160356	-4.2778176725	0.3699709775
20	C	-2.7911586909	0.0502784011	-0.0668955029
21	O	0.7944652154	-2.0499736204	1.2499114269
22	O	-1.5788515962	1.8990462982	-0.8619474818

23	F	-3.7324000948	0.7963660274	0.4639493457
24	F	-2.6155502496	-1.0013998413	0.7183280896
25	F	-3.2152891412	-0.3902510195	-1.2340238823

Neutral Carbon Radical of **1a**
Acetonitrile
UHF/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 (*para*)	-940.339328	0.97	-940.201278	1.42
Con 1 (*meta*)	-940.339177	1.07	-940.197520	3.78
Con 2 (*para*)	-940.340880	0.00	-940.203547	0.00
Con 2 (*meta*)	-940.340740	0.09	-940.203431	0.07

Con 1 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	1.0238818278	2.5822788759	-1.7858892397
2	C	0.7809823932	2.3884205158	-0.7581053170
3	C	0.1887268064	1.8933053982	1.9519335276
4	C	0.3548812401	1.1079821859	-0.3628236969
5	C	0.8579840277	3.3712845953	0.2164836567
6	C	0.5764330619	3.1814016375	1.5630297654
7	C	0.0740449923	0.8700566521	0.9965730419
8	H	0.6571132569	3.9744668242	2.2827234687
9	H	-0.0318218450	1.6746643771	2.9806870058
10	N	0.2430396801	0.0646482943	-1.3119829923
11	H	0.7953271507	-0.7511642557	-1.1594357841
12	N	-0.3802287083	-0.4045309495	1.4426107050
13	H	-1.2260830159	-0.4228748236	1.9724284148
14	C	-0.6001695312	0.0866215287	-2.3656135747
15	C	0.3446280900	-1.5126417786	1.3636047484
16	C	-0.5323750415	-1.1016717364	-3.2894531506
17	H	0.0189999392	-1.9320831971	-2.8696668547
18	H	-0.0469976471	-0.7813906320	-4.2053605997
19	H	-1.5393095295	-1.4149686090	-3.5318974681
20	C	-0.2732188429	-2.7676426670	2.0102525512
21	O	-1.3608763108	1.0077269736	-2.5771408874
22	O	1.4160457270	-1.6372113653	0.8305383188
23	F	-0.4511234035	-3.6977130563	1.0948382523
24	F	-1.4362902673	-2.5357700850	2.5872224808
25	F	0.5464059500	-3.2431947037	2.9244436280

Con 1 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	1.0012834328	2.5515451117	-1.6846089037
2	C	0.7562364269	2.3835794447	-0.6524097858
3	C	0.1262377568	1.8822627446	2.0473623490
4	C	0.3391587436	1.1025022756	-0.2548681114
5	C	0.8361298747	3.4301607749	0.2747227774
6	C	0.5111395841	3.1326148826	1.5913263810

7	C	0.0357431123	0.8523996344	1.0966454302
8	H	1.1433306145	4.4137940752	-0.0286365941
9	H	-0.1001507438	1.6891219333	3.0794882495
10	N	0.2488419950	0.0600949159	-1.2106108497
11	H	0.8500526592	-0.7253651548	-1.0896201878
12	N	-0.4055600274	-0.4285173645	1.5325650639
13	H	-1.2580394759	-0.4621047963	2.0504890599
14	C	-0.6372515774	0.0458086402	-2.2271254752
15	C	0.3395350718	-1.5247240087	1.4586216736
16	C	-0.5484098393	-1.1303614510	-3.1654457061
17	H	0.0725312241	-1.9292873519	-2.7833330564
18	H	-0.1320974271	-0.7763141755	-4.1026437503
19	H	-1.5462334248	-1.5017146621	-3.3582781218
20	C	-0.2716619201	-2.7945983823	2.0804208965
21	O	-1.4538955061	0.9279174064	-2.3971486879
22	O	1.4242927180	-1.6259780959	0.9490383905
23	F	-0.4227909339	-3.7158538730	1.1507448196
24	F	-1.4473996546	-2.5852307978	2.6408045618
25	F	0.5389773163	-3.2717517261	3.0024995771

Con 2 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.1267284999	2.5773525111	-2.3932450227
2	C	0.1502515425	2.4430102719	-1.3270613982
3	C	0.2572950056	2.1035976870	1.4646382412
4	C	0.0654519854	1.1513409230	-0.7780062127
5	C	0.2608677621	3.5086911698	-0.4493711507
6	C	0.3240206451	3.3966195340	0.9320675890
7	C	0.1037284966	0.9933734158	0.6207256362
8	H	0.4267693551	4.2527966152	1.5730876856
9	H	0.3104053351	1.9496904068	2.5264477885
10	N	-0.0976108280	0.0525927334	-1.6570626229
11	H	-0.7674067226	0.1705189100	-2.3861423532
12	N	0.0207680201	-0.3084453184	1.1849294341
13	H	0.6884826658	-0.9785860797	0.8628765409
14	C	0.7618011916	-0.9810848749	-1.7619561459
15	C	-0.9438170586	-0.6860724481	2.0157768630
16	C	0.5104903044	-1.9523617008	-2.8849681473
17	H	-0.3542600794	-1.6959281631	-3.4817781553
18	H	0.3770244971	-2.9393863048	-2.4578927002
19	H	1.3907052684	-1.9744576576	-3.5167365895
20	C	-0.8654547326	-2.1473385873	2.4997835510
21	O	1.6861422600	-1.1349552109	-0.9860530757
22	O	-1.8572408447	-0.0226756429	2.4279052445
23	F	-0.7864215389	-2.1791587066	3.8144369978
24	F	0.1696501974	-2.8066425622	2.0156131657
25	F	-1.9583712275	-2.7924909208	2.1419848371

Con 2 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.1583041064	2.5447505690	-2.2893620961
2	C	0.1818461210	2.4346800931	-1.2200855021
3	C	0.2715500074	2.0840604013	1.5718070490
4	C	0.0801434044	1.1459832770	-0.6685604935

5	C	0.3047340340	3.5593985376	-0.3946320151
6	C	0.3480038962	3.3313438514	0.9737360131
7	C	0.1080716219	0.9722549028	0.7288617010
8	H	0.3725755629	4.5465727043	-0.8135779872
9	H	0.3240374306	1.9549594163	2.6371360944
10	N	-0.0933492768	0.0514431775	-1.5535210831
11	H	-0.7712154238	0.1723315160	-2.2745390723
12	N	0.0124534354	-0.3318252810	1.2814914310
13	H	0.6655859206	-1.0090102984	0.9403923806
14	C	0.7561867084	-0.9882336428	-1.6652616264
15	C	-0.9351346956	-0.6997659451	2.1369875981
16	C	0.4916344463	-1.9554474632	-2.7883251396
17	H	-0.3352838408	-1.6570150124	-3.4184726012
18	H	0.2841900265	-2.9282235324	-2.3568526325
19	H	1.3916113949	-2.0366312442	-3.3860333623
20	C	-0.8709322841	-2.1682738570	2.6025023275
21	O	1.6810106710	-1.1547760031	-0.8910102701
22	O	-1.8232634978	-0.0230754927	2.5819187633
23	F	-0.7566009863	-2.2162649643	3.9147481705
24	F	0.1386962318	-2.8401440625	2.0830274028
25	F	-1.9848550143	-2.7890916467	2.2676249506

Møller-Plesset Perturbation (MP2) Calculations

Neutral Carbon Radical of **1a**
Gas Phase
MP2/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 (*para*)	-942.776458	0.83	-942.643910	1.05
Con 1 (*meta*)	-942.775286	1.56	-942.642132	2.17
Con 2 (*para*)	-942.777775	0.00	-942.645594	0.00
Con 2 (*meta*)	-942.777430	0.22	-942.641318	0.27

Con 1 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.5775344772	2.6363851911	-1.7934046765
2	C	0.4959283274	2.4137869183	-0.7413321096
3	C	0.2763040499	1.8898500440	1.9519685676
4	C	0.2084345529	1.1271000736	-0.3218821690
5	C	0.6407303082	3.3523740323	0.2147415039
6	C	0.5489511776	3.1696429501	1.5589121400
7	C	0.0951999804	0.8832899204	1.0337261003
8	H	0.6844735833	3.9684138675	2.2730606181
9	H	0.1945614296	1.6528065922	3.0070612467
10	N	0.0480290628	0.0736220350	-1.2286797873
11	H	0.4562654186	-0.8108873097	-0.9415563147
12	N	-0.2945720883	-0.3978565978	1.5409363288
13	H	-1.0302553544	-0.4052746496	2.2353963810
14	C	-0.3997870406	0.1872915270	-2.5357787981
15	C	0.3125897128	-1.5760682723	1.2840093140

16	C	-0.3891107001	-1.1125180328	-3.3074602371
17	H	0.0207629293	-1.9457006638	-2.7396400584
18	H	0.1958543430	-0.9681441820	-4.2139830104
19	H	-1.4113549045	-1.3440415944	-3.6023258562
20	C	-0.2778572998	-2.7795596052	2.0409750923
21	O	-0.7976005841	1.2430698328	-3.0281624380
22	O	1.2384145791	-1.7775271436	0.4908610278
23	F	-0.8606730246	-3.6300931640	1.1709202994
24	F	-1.2238603982	-2.4119719687	2.9522397243
25	F	0.6910374626	-3.4379898007	2.6993971109

Con 1 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.7008266451	2.5460282325	-1.6902912628
2	C	0.5675957277	2.3705556372	-0.6327277666
3	C	0.1973669777	1.8843567759	2.0520580791
4	C	0.2601607062	1.0918194151	-0.2101556908
5	C	0.6697758622	3.4066759190	0.2519780762
6	C	0.4792291643	3.1104385569	1.5668362227
7	C	0.0764080168	0.8607985222	1.1334217128
8	H	0.8991346170	4.4061889241	-0.0891748621
9	H	0.0748383906	1.6909672511	3.1100205177
10	N	0.1326832627	0.0376733127	-1.1346922719
11	H	0.6070674291	-0.8269069319	-0.8960858608
12	N	-0.3094430871	-0.4201037212	1.6308453200
13	H	-1.0340768479	-0.4307698284	2.3370237580
14	C	-0.4821987031	0.1485716915	-2.3665736469
15	C	0.3255937474	-1.5906226265	1.3879967167
16	C	-0.4388726943	-1.1114731810	-3.2006941060
17	H	-0.0856734992	-1.9790277158	-2.6460231426
18	H	0.2178301991	-0.9400271513	-4.0530337383
19	H	-1.4395811922	-1.3030809784	-3.5818489693
20	C	-0.2768332670	-2.8030618635	2.1220693113
21	O	-1.0198201319	1.1847552382	-2.7632945656
22	O	1.2816951595	-1.7772466596	0.6312980853
23	F	-0.8591372350	-3.6341925280	1.2329450165
24	F	-1.2268159880	-2.4434792762	3.0322696638
25	F	0.6822467403	-3.4788370149	2.7758334037

Con 2 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.1938404706	2.5976789509	-2.3810646275
2	C	0.1659196460	2.4493514940	-1.3091740224
3	C	0.1648802811	2.0937614757	1.4177442469
4	C	0.0928576805	1.1762771035	-0.7808907311
5	C	0.2141436503	3.4783480528	-0.4361054707
6	C	0.2169637936	3.3666791275	0.9182423643
7	C	0.0874223097	1.0007003342	0.5841014866
8	H	0.2629092405	4.2235205774	1.5748574598
9	H	0.1561868487	1.9315845839	2.4868820714
10	N	-0.0359225200	0.0892265786	-1.6853529571
11	H	-0.5892343929	0.2786292066	-2.5091647537
12	N	-0.0043100000	-0.3042693636	1.1238398359
13	H	0.6141542034	-1.0063196804	0.7168838715

14	C	0.7490987657	-1.0401271160	-1.7181071347
15	C	-0.8575312925	-0.6321814032	2.1281975904
16	C	0.5150616553	-1.9614303277	-2.8900524750
17	H	-0.1940282360	-1.5672993879	-3.6155469949
18	H	0.1465101457	-2.9131150170	-2.5100420278
19	H	1.4714372796	-2.1428539585	-3.3767053906
20	C	-0.8296319992	-2.1273220546	2.5010781783
21	O	1.5776247914	-1.3054263439	-0.8371730807
22	O	-1.6274258549	0.1110912625	2.7320814886
23	F	-0.5548129812	-2.2793029368	3.8118523458
24	F	0.0987360793	-2.8324382124	1.7997935305
25	F	-2.0348495648	-2.6847629452	2.2538251961

Con 2 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	0.3014389147	2.5565032301	-2.2737458552
2	C	0.2315785990	2.4378044169	-1.1983217756
3	C	0.0959984800	2.0778262883	1.5256210276
4	C	0.1041806288	1.1704670201	-0.6803349523
5	C	0.2705131417	3.5400005775	-0.3871637149
6	C	0.1997177194	3.2934882791	0.9464721502
7	C	0.0348775009	0.9869608791	0.6849744048
8	H	0.3608789252	4.5369264387	-0.7938002692
9	H	0.0397154430	1.9469414020	2.5956727292
10	N	-0.0228342992	0.0868279495	-1.5975181968
11	H	-0.6069640876	0.2629100614	-2.4023452460
12	N	-0.0823197005	-0.3205533534	1.1992659053
13	H	0.5067679258	-1.0257393168	0.7515327812
14	C	0.7433720051	-1.0494907060	-1.6239791623
15	C	-0.8496794506	-0.6480207252	2.2742364323
16	C	0.5200627979	-1.9657581511	-2.8016586740
17	H	-0.1720868739	-1.5619777394	-3.5380949571
18	H	0.1374374497	-2.9158365254	-2.4320696916
19	H	1.4830233429	-2.1532483974	-3.2727114804
20	C	-0.8251521528	-2.1518874503	2.6136229230
21	O	1.5509022774	-1.3304455588	-0.7251514617
22	O	-1.5441850783	0.0982074072	2.9579797799
23	F	-0.4056057584	-2.3364003484	3.8812822528
24	F	-0.0048498733	-2.8666691501	1.7979440374
25	F	-2.0667878769	-2.6688365269	2.4982910137

Table S4. Energy Calculations for Brominated Cation of 1a

Density Functional Theory (DFT) Calculations

Bromine Cation of **1a**

Gas Phase

B3LYP/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 (*para*)	-3519.62621	9.99	-3519.49110	9.47
Con 1 (*meta*)	-3519.64213	0.00	-3519.50619	0.00

Con 2 (*para*)	-3519.63771	2.77	-3519.50344	1.73
Con 2 (*meta*)	-3519.63365	5.32	-3519.49812	5.06

Con 1 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-2.2113176268	0.1390863266	-1.9301928220
2	C	-1.8087670054	-0.4949881238	-1.1523705221
3	C	-0.2695697551	-0.8956860206	0.6542607418
4	C	-2.4536018782	-1.8014755875	-0.9477062647
5	C	-0.7263202248	-0.0552550100	-0.4163924916
6	N	0.7610931626	-0.5958948298	1.5121560425
7	H	1.1031962618	-1.3846684892	2.0566712281
8	N	-0.0495653900	1.0958984279	-0.8280774418
9	H	0.3024415314	1.7322130832	-0.1215713642
10	C	0.1808568838	1.3584029472	-2.1827561846
11	O	-0.2444114353	0.6093655981	-3.0503288368
12	C	0.9877821450	2.5970595957	-2.4780981985
13	H	0.4186679885	3.2273593326	-3.1667953732
14	H	1.9055413285	2.2991490257	-2.9937482911
15	H	1.2442830949	3.1736516757	-1.5863773670
16	C	1.2836737026	0.6286512331	1.9498968741
17	O	0.8701909874	1.7257494346	1.6676498610
18	C	2.5145655369	0.4628031586	2.8937739933
19	F	2.5435893904	-0.7843150136	3.4321179599
20	F	2.4647477839	1.3555843949	3.8713250584
21	F	3.6316419822	0.6355646682	2.1744242033
22	H	-2.5725843927	-2.3409722224	-1.8942969954
23	C	-0.8593725529	-2.1923844209	0.8752839907
24	H	-0.4664004432	-2.8055604807	1.6809411454
25	C	-1.8815858589	-2.6484593312	0.1137751803
26	H	-2.3108889878	-3.6306637989	0.2815916319
27	Br	-4.3578862289	-1.4102155735	-0.4151557579

Con 1 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	C	-0.6519377296	0.7609861685	0.4788030748
2	C	-1.3516668865	0.9771511052	2.8678022954
3	C	-1.2907758253	1.4388661679	1.4683508001
4	C	0.0778377509	-0.4734972584	0.8147636647
5	H	-1.8243537865	2.3557712617	1.2339048384
6	N	-0.8509851422	1.2507985951	-0.8480982166
7	H	-1.7016842027	1.7941825696	-0.9560407361
8	N	0.7847340884	-1.1021652686	-0.1218283325
9	H	0.9497674924	-0.5646172189	-0.9956262612
10	C	-0.0351660471	1.2773454475	-1.9369710827
11	O	1.0387649163	0.7043621391	-2.0625523220
12	C	-0.5829319002	2.1124685017	-3.1314852152
13	C	1.4950992804	-2.3791651300	-0.0435759877
14	O	1.3788624512	-3.1036743716	0.9113764561
15	C	2.3256295801	-2.6454793238	-1.2653781713
16	H	3.0910486405	-1.8699502276	-1.3848624794
17	H	1.7044216129	-2.6374097431	-2.1682171994
18	H	2.8025545265	-3.6188290067	-1.1576534837

19	F	-0.7953375713	1.3092885322	-4.1776006685
20	F	-1.7560351747	2.7189814602	-2.8128199914
21	F	0.3037462211	3.0518625110	-3.4607748103
22	H	-1.0692015436	1.7686691474	3.5695318602
23	Br	-3.2959740261	0.6754546925	3.3091713610
24	C	0.0148896065	-0.9655213010	2.1732908738
25	H	0.5258519796	-1.8911858957	2.3942981361
26	C	-0.6393102127	-0.2849041600	3.1417733973
27	H	-0.6478480983	-0.6597893943	4.1604182001

Con 2 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-1.8405065935	-0.2006092594	-2.6586398548
2	C	-1.6313251862	-0.6539432197	-1.6941277715
3	C	-0.4253159581	-0.7403148441	0.4169104182
4	C	-2.4260224169	-1.8434031858	-1.3395691450
5	C	-0.7059695778	-0.0877709443	-0.8710882947
6	N	0.5629311670	-0.2633598250	1.1831880833
7	H	1.2284446863	0.4040559329	0.6765738649
8	N	-0.1706278356	1.1676362868	-1.2755747179
9	H	-0.7770846958	1.6654633221	-1.9152952277
10	C	1.0889500387	1.7166958629	-1.1377826917
11	O	1.9405566361	1.2278501142	-0.3898602057
12	C	1.3670389219	2.9535067693	-1.9478381734
13	H	1.7878894415	3.7158961738	-1.2876158637
14	H	0.4902210678	3.3551925215	-2.4594826611
15	H	2.1336205181	2.7090559285	-2.6908254657
16	C	0.9090925144	-0.6588170364	2.5030528487
17	O	0.2897934144	-1.4172313583	3.1985201747
18	C	2.2172027944	0.0358697513	2.9827821307
19	F	2.4975695226	-0.3115151813	4.2284094117
20	F	2.0675189381	1.3753721046	2.9091238174
21	F	3.2313511854	-0.3236574063	2.1714349470
22	H	-2.3893316296	-2.6057607766	-2.1252293176
23	Br	-4.3680071920	-1.3023229323	-1.3537714029
24	C	-1.2104502715	-1.8848542825	0.8125577066
25	H	-1.0166040171	-2.3221653986	1.7811443834
26	C	-2.1454976406	-2.4160177853	-0.0104210586
27	H	-2.7054378323	-3.2948513321	0.2934240655

Con 2 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	C	0.6752122474	0.4067606797	0.3362227965
2	C	1.6082374502	1.2979729757	0.8019313082
3	C	-0.1027976866	0.7848056344	-0.8262861451
4	H	2.2178593599	1.0276475127	1.6547136669
5	N	0.4161686072	-0.7727205630	1.0510734676
6	H	0.2287808130	-1.6239905348	0.5220549374
7	N	-1.0052983244	0.0023686647	-1.4696526973
8	H	-1.5763577736	0.5075900152	-2.1418934782
9	C	0.4076211670	-0.8079548937	2.4279229748
10	O	0.6631210077	0.1233839593	3.1620172722
11	C	-0.0196137853	-2.1811787455	3.0191140922
12	C	-1.1584139733	-1.4300449224	-1.5942932590

13	O	-0.3696989892	-2.1951243148	-1.0913500931
14	C	-2.3343926874	-1.8249407654	-2.4420774389
15	H	-2.4222595017	-2.9106562437	-2.4272460125
16	H	-2.1896581606	-1.4963327610	-3.4785323083
17	H	-3.2599004636	-1.3744442275	-2.0670200082
18	F	-1.2693631032	-2.0872662604	3.5037011563
19	F	-0.0100773681	-3.1508525553	2.0716337912
20	F	0.8069469022	-2.5387136092	4.0007991932
21	C	1.8165721500	2.6392349228	0.2297395747
22	H	1.8389502182	3.4041406000	1.0139914255
23	C	0.0234087805	2.1200511552	-1.3659489267
24	H	-0.6078101218	2.3906677191	-2.2079094231
25	C	0.9195850102	3.0083170492	-0.8806969774
26	H	1.0124718332	3.9992253641	-1.3133147675
27	Br	3.6907063920	2.6820541443	-0.4886941213

Bromine Cation Intermediate of **1a**
Acetonitrile
B3LYP/6-31+G**

Conformation	Total Energy (au)	Relative Energy (kcal/mol)	Gibbs Energy (au)	Relative Energy (kcal/mol)
Con 1 (*para*)	-3519.72291	10.97	-3519.58314	11.23
Con 1 (*meta*)	-3519.72291	0.00	-3519.60103	0.00
Con 2 (*para*)	-3519.73055	6.17	-3519.59370	4.60
Con 2 (*meta*)	-3519.73433	3.80	-3519.59613	3.07

Con 1 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-2.2071745104	0.0958068266	-1.9674003168
2	C	-1.8251669197	-0.5188943159	-1.1626631571
3	C	-0.2810368588	-0.9209760263	0.6421925357
4	C	-2.4918493702	-1.8085524820	-0.9208440233
5	C	-0.7375296184	-0.0906139006	-0.4463387171
6	N	0.7547276171	-0.6129594581	1.4844589438
7	H	1.1183543195	-1.4090848234	2.0077586951
8	N	-0.0440746829	1.0586966271	-0.8551214556
9	H	0.2533491606	1.7138688029	-0.1402458909
10	C	0.2824716529	1.3223149667	-2.1708523375
11	O	-0.0269655896	0.5637058555	-3.0905598777
12	C	1.0345645184	2.6109400861	-2.3989137349
13	H	0.3587998584	3.3225529986	-2.8855937913
14	H	1.8647504211	2.4157513327	-3.0819133964
15	H	1.4121190176	3.0561863303	-1.4761297960
16	C	1.2410135827	0.6112922641	1.9189642142
17	O	0.7821496130	1.7051865830	1.6788198162
18	C	2.5066016546	0.4991121889	2.8217621065
19	F	2.6273400681	-0.7164763991	3.3946050799
20	F	2.4570049994	1.4222105704	3.7873168261
21	F	3.6029698048	0.7199927815	2.0718999111
22	H	-2.5928836611	-2.3777382716	-1.8532734256
23	C	-0.8775208862	-2.2046869389	0.8865063947
24	H	-0.4770851403	-2.8125342357	1.6914176682

25	C	-1.9341007322	-2.6397245481	0.1594030297
26	H	-2.3907898774	-3.6032271792	0.3585834818
27	Br	-4.4100384412	-1.4021496351	-0.4538387834

Con 1 (*meta*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	C	0.5671799861	-0.3975453995	-0.8819130369
2	C	1.4046539156	-2.7065546222	-1.2807617669
3	C	1.3088579106	-1.2724301469	-1.6071887644
4	C	-0.1649960158	-0.8787973895	0.2936078397
5	H	1.8332202698	-0.9296538351	-2.4942292731
6	N	0.4391481196	0.9206881793	-1.4183517067
7	H	0.4820751981	0.9504728553	-2.4337137064
8	N	-0.8149837852	-0.0095947985	1.0701679185
9	H	-0.5657869070	0.9817061436	0.9415238118
10	C	0.4726292383	2.1136566234	-0.7928488502
11	O	0.4637467830	2.3172971462	0.4185971611
12	C	0.4628200139	3.3480406634	-1.7371436757
13	C	-1.7174197456	-0.2609474771	2.1671592875
14	O	-2.1886052910	-1.3602685901	2.3658897053
15	C	-2.0004307849	0.9679094857	2.9774320722
16	H	-2.3543079501	1.7801588322	2.3339094084
17	H	-1.0771201663	1.3073891027	3.4608467149
18	H	-2.7504442271	0.7333847782	3.7318396721
19	F	1.3762039485	4.2409059713	-1.3260884970
20	F	0.7292460494	3.0348794315	-3.0232402945
21	F	-0.7501361441	3.9356616953	-1.6960553103
22	H	1.2185590063	-3.3232757833	-2.1664218821
23	Br	3.3428652140	-3.1150528127	-0.8792857076
24	C	-0.1451954318	-2.2901363875	0.5970252701
25	H	-0.7232960629	-2.6379263969	1.4390972391
26	C	0.6062833275	-3.1519099531	-0.1242185613
27	H	0.6413520456	-4.2033568684	0.1416975513

Con 2 (*para*)

Coordinates (Angstroms)

ATOM		X	Y	Z
1	H	-1.9172931945	-0.1273924550	-2.6101779921
2	C	-1.6735992132	-0.6125967630	-1.6700989036
3	C	-0.4133745206	-0.7522347736	0.3967234962
4	C	-2.4396466097	-1.8188389173	-1.3225362300
5	C	-0.7055437056	-0.0840303781	-0.8689970765
6	N	0.5811153671	-0.2680469626	1.1686426681
7	H	1.2626948252	0.3638027724	0.6439193063
8	N	-0.1540911082	1.1599524560	-1.2795351178
9	H	-0.7685374334	1.6734589196	-1.9023367767
10	C	1.1064839863	1.6731483845	-1.1750656681
11	O	1.9873664857	1.1506852412	-0.4668798721
12	C	1.3837883294	2.9227924339	-1.9640540480
13	H	1.8251428250	3.6666361421	-1.2956677586
14	H	0.4959299823	3.3367756396	-2.4437505720
15	H	2.1265680067	2.6800340279	-2.7312715752
16	C	0.8653960223	-0.5975646909	2.4931661517
17	O	0.1935665448	-1.2690562257	3.2389046580
18	C	2.1831256225	0.0611149161	3.0038789802

19	F	2.5399569453	-0.4720155134	4.1754224590
20	F	2.0044390015	1.3887923519	3.1738212448
21	F	3.1910460168	-0.1148479221	2.1254891467
22	H	-2.3931577241	-2.5608249970	-2.1288018906
23	Br	-4.4013422702	-1.3325254208	-1.3128038612
24	C	-1.1646699742	-1.9157847668	0.7836530341
25	H	-0.9290527774	-2.3914742879	1.7236075638
26	C	-2.1251303105	-2.4306513150	-0.0208633939
27	H	-2.6611811195	-3.3293078961	0.2656120274

Con 2 (*meta*)

Coordinates (Angstroms)

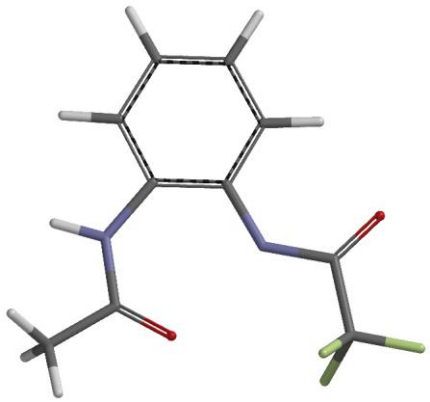
ATOM		X	Y	Z
1	H	-1.9172931945	-0.1273924550	-2.6101779921
2	C	-1.6735992132	-0.6125967630	-1.6700989036
3	C	-0.4133745206	-0.7522347736	0.3967234962
4	C	-2.4396466097	-1.8188389173	-1.3225362300
5	C	-0.7055437056	-0.0840303781	-0.8689970765
6	N	0.5811153671	-0.2680469626	1.1686426681
7	H	1.2626948252	0.3638027724	0.6439193063
8	N	-0.1540911082	1.1599524560	-1.2795351178
9	H	-0.7685374334	1.6734589196	-1.9023367767
10	C	1.1064839863	1.6731483845	-1.1750656681
11	O	1.9873664857	1.1506852412	-0.4668798721
12	C	1.3837883294	2.9227924339	-1.9640540480
13	H	1.8251428250	3.6666361421	-1.2956677586
14	H	0.4959299823	3.3367756396	-2.4437505720
15	H	2.1265680067	2.6800340279	-2.7312715752
16	C	0.8653960223	-0.5975646909	2.4931661517
17	O	0.1935665448	-1.2690562257	3.2389046580
18	C	2.1831256225	0.0611149161	3.0038789802
19	F	2.5399569453	-0.4720155134	4.1754224590
20	F	2.0044390015	1.3887923519	3.1738212448
21	F	3.1910460168	-0.1148479221	2.1254891467
22	H	-2.3931577241	-2.5608249970	-2.1288018906
23	Br	-4.4013422702	-1.3325254208	-1.3128038612
24	C	-1.1646699742	-1.9157847668	0.7836530341
25	H	-0.9290527774	-2.3914742879	1.7236075638
26	C	-2.1251303105	-2.4306513150	-0.0208633939
27	H	-2.6611811195	-3.3293078961	0.2656120274

Conformers and Boltzmann Analysis of Amidyl Radicals (1a) in the Gas Phase and in Acetonitrile

For isomers 1 and 2, we systematically constructed six different conformations based on potential hydrogen bonding interactions in the following way. Isomer 1 refers to the nitrogen-centered radical of the more electron-deficient amide; while isomer 2 refers to the nitrogen-centered radical of the more electron-rich amide. Using **1a**, the following conformations were used as a template:

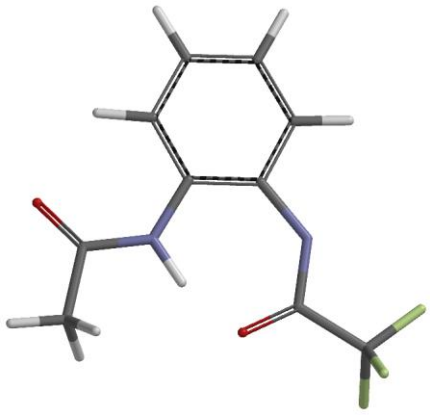
Con 1

The carbonyl group (C=O) of the EDG is pointed down and directed toward the nitrogen radical, and the carbonyl group (C=O) of the EWG is pointed up.



Con 2

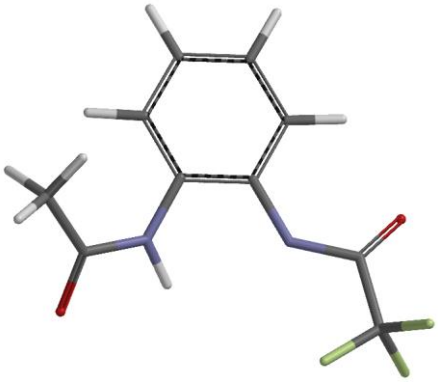
The carbonyl group (C=O) of the EDG is pointed up and, and the carbonyl group (C=O) of the EWG is pointed down to form a classical N-H hydrogen bond with the ortho amide.



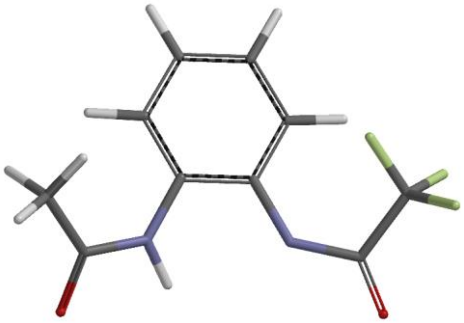
Con 3 (CH_3 down and CF_3 down)

Both carbonyl groups (C=O) of the EDG and EWG are pointed up and, such that N-H hydrogen bond of the EWG can form a hydrogen bond with the nitrogen radical of the ortho amide.

Con 4 (CH_3 up and CF_3 down)
The carbonyl group (C=O) of the EDG is pointed down and eclipsing the N-H bond, and the carbonyl group (C=O) of the EWG is pointed up to allow formation of an N-H hydrogen bond with the ortho amide.



Con 5 ((CH_3 up and CF_3 up)
The carbonyl group (C=O) of the EDG is pointed down and eclipsing the N-H bond, and the carbonyl group (C=O) of the EWG is pointed down to allow formation of an N-H hydrogen bond with the ortho amide.



Con 6 (CH_3 down and CF_3 up)
The carbonyl group (C=O) of the EDG is pointed up and eclipsing the N-H bond, and the carbonyl group (C=O) of the EWG is pointed up to allow formation of an N-H hydrogen bond with the ortho amide.

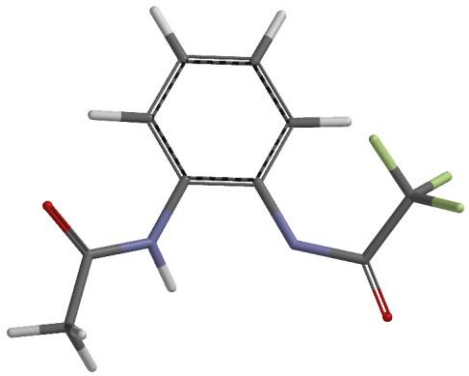
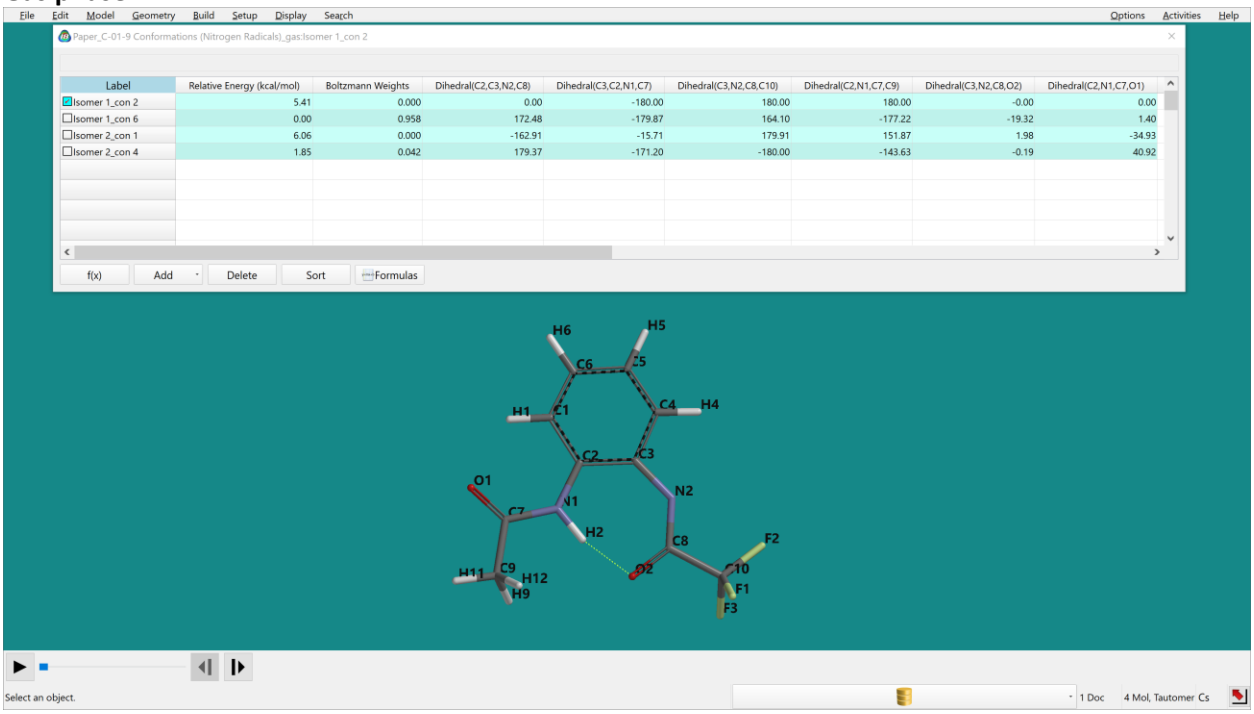


Table S5. Dihedral Angles and Atom Coordinates for the amidyl radical conformers of 1a.

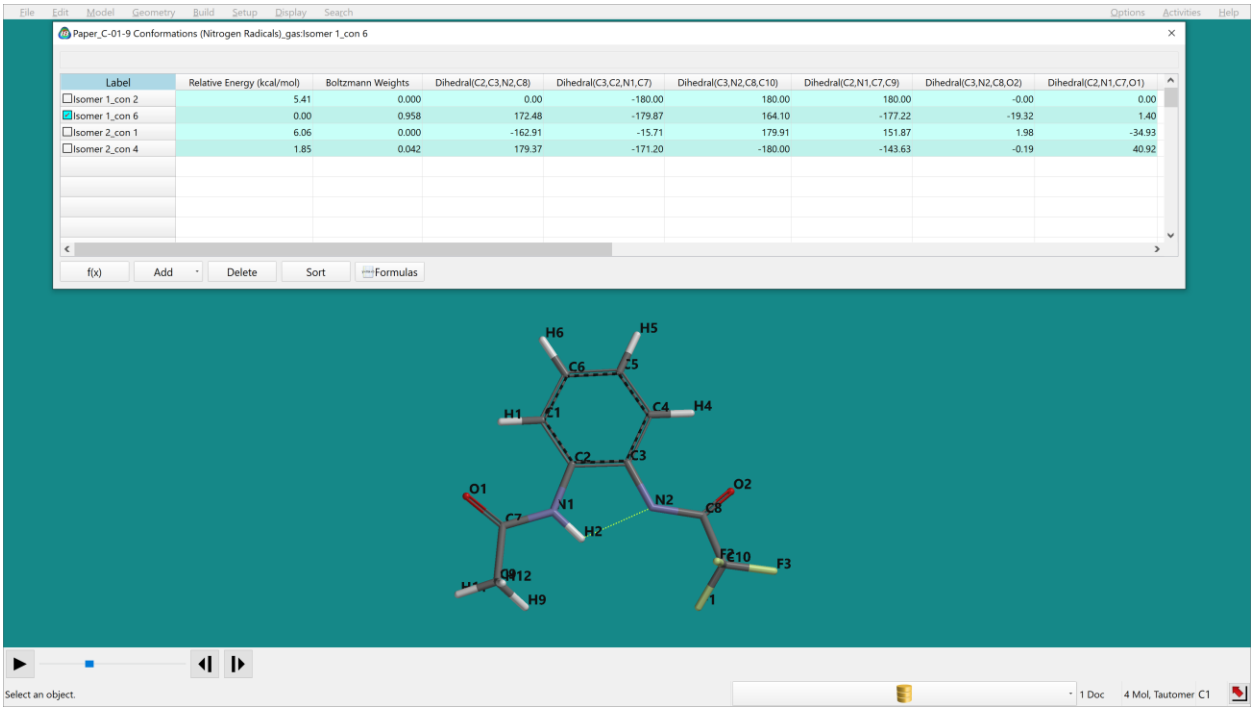
Gas phase




```
Cartesian Coordinates (Angstroms)
      Atom            X             Y             Z
    ---------    ------------ ------------ ------------

  1 H   H1          -0.2689088    0.0000000    3.0651690
  2 C   C1          -0.9345393    0.0000000    2.2146247
  3 C   C4          -2.6679038    0.0000000    0.0115816
  4 C   C2          -0.3616497    0.0000000    0.9196690
  5 C   C6          -2.3051329    0.0000000    2.3892001
  6 C   C5          -3.1872764    0.0000000    1.2796824
  7 C   C3          -1.2549292    0.0000000   -0.2515504
  8 H   H6          -2.7065252    0.0000000    3.3982465
  9 H   H5          -4.2613559    0.0000000    1.4344954
```

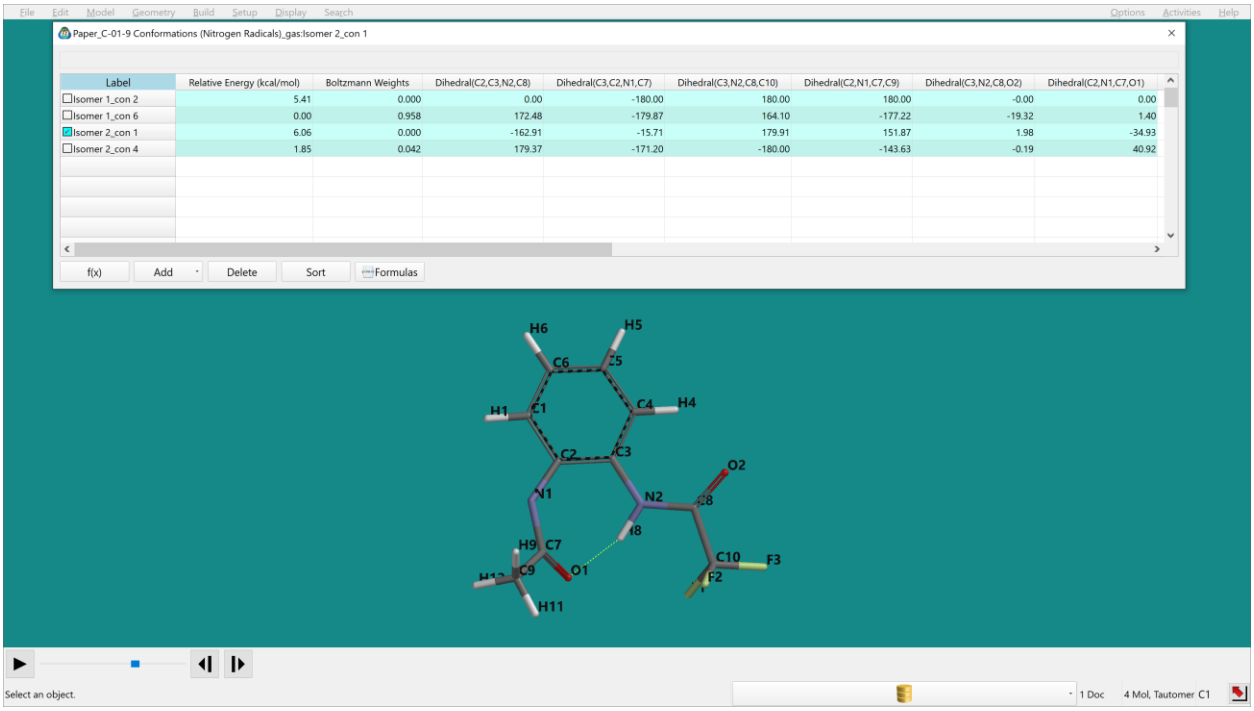
10	H	H4	-3.3043971	0.0000000	-0.8659566
11	N	N1	0.9956710	0.0000000	0.7284340
12	H	H2	1.3011973	-0.0000001	-0.2647919
13	N	N2	-0.9814203	0.0000000	-1.5751469
14	C	C7	2.0280434	0.0000000	1.6789751
15	C	C8	0.1735455	0.0000000	-2.2533705
16	C	C9	3.4068871	0.0000000	1.0524086
17	H	H9	3.5464943	-0.8819551	0.4181177
18	H	H11	4.1504027	0.0000000	1.8487711
19	H	H12	3.5464944	0.8819551	0.4181177
20	C	C10	-0.0094668	0.0000000	-3.7969394
21	O	O1	1.8423659	-0.0000001	2.8854119
22	O	O2	1.3618368	0.0000000	-1.8780388
23	F	F1	0.5894593	1.0921942	-4.3262211
24	F	F2	-1.2883518	0.0000000	-4.2046683
25	F	F3	0.5894593	-1.0921942	-4.3262211



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	0.5169761	-0.6629491	3.0538915
2	C	C1	-0.2859932	-0.5552817	2.3388181
3	C	C4	-2.4070748	-0.2712871	0.4626786
4	C	C2	0.0203237	-0.2650085	1.0008227
5	C	C6	-1.6159219	-0.6931173	2.7163354
6	C	C5	-2.6735085	-0.5475376	1.7827877
7	C	C3	-1.0528743	-0.1240320	0.0137021
8	H	H6	-1.8472262	-0.9144622	3.7539313
9	H	H5	-3.7008444	-0.6588434	2.1151243
10	H	H4	-3.2028413	-0.1736272	-0.2632556
11	N	N1	1.2943741	-0.0932985	0.5071310

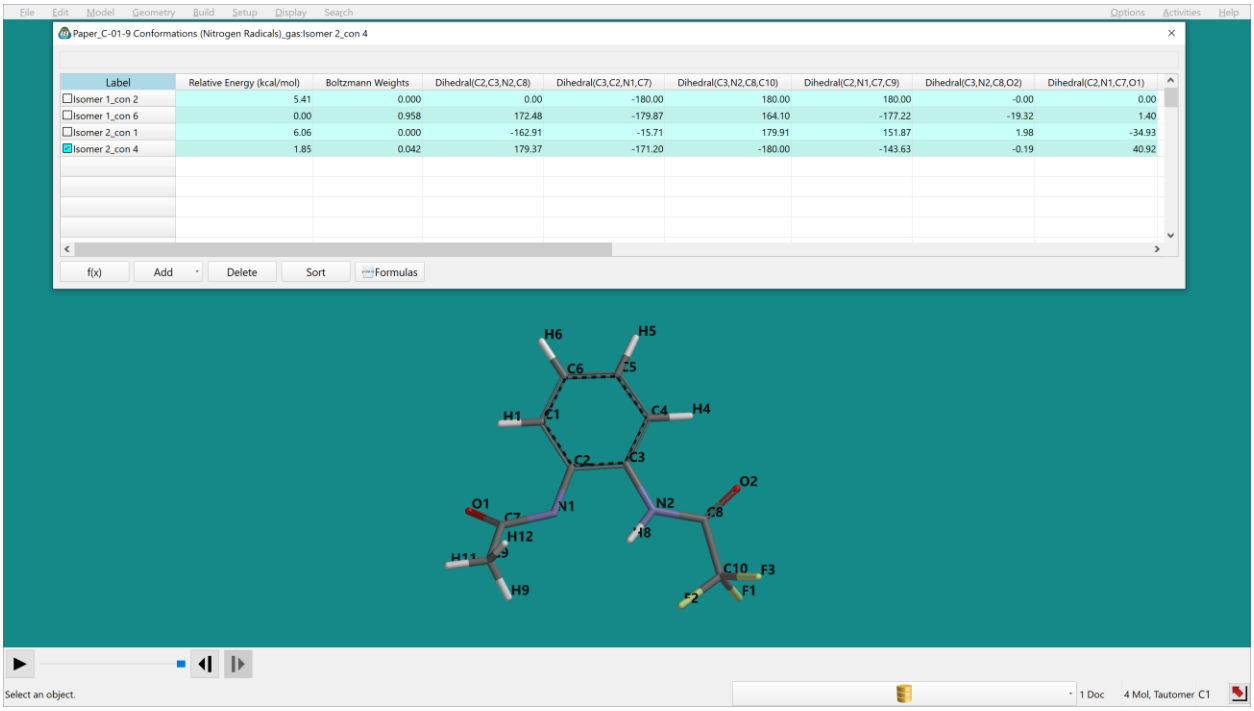
12	H	H2	1.2943070	0.1296550	-0.4873517
13	N	N2	-0.6447586	0.1703099	-1.2268762
14	C	C7	2.5155438	-0.1632046	1.1732618
15	C	C8	-1.4723850	0.1972847	-2.3157354
16	C	C9	3.7139417	0.1509275	0.3004611
17	H	H9	3.5737147	-0.1539794	-0.7405390
18	H	H11	4.5886667	-0.3495464	0.7175077
19	H	H12	3.8977117	1.2313680	0.3188980
20	C	C10	-0.8020923	0.9451948	-3.5038728
21	O	O1	2.6100713	-0.4281787	2.3619187
22	O	O2	-2.5725119	-0.3122114	-2.4717404
23	F	F1	0.3167334	0.2980674	-3.9148858
24	F	F2	-0.4356313	2.1986859	-3.1408353
25	F	F3	-1.6287003	1.0450716	-4.5521779



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	1.0361999	2.3931600	-2.3515070
2	C	C1	0.6587750	2.3078254	-1.3384035
3	C	C4	-0.3385472	1.9735904	1.2580417
4	C	C2	0.4457337	0.9701858	-0.8543830
5	C	C6	0.3705391	3.4173645	-0.5785555
6	C	C5	-0.1437299	3.2461045	0.7226361
7	C	C3	-0.0336303	0.8265124	0.5143396
8	H	H6	0.5315957	4.4135501	-0.9776987
9	H	H5	-0.3801463	4.1131582	1.3317837
10	H	H4	-0.7219304	1.8600980	2.2621126
11	N	N1	0.6431048	0.0142150	-1.7705487
12	N	N2	-0.1426967	-0.4576503	1.0536424
13	H	H8	0.4414938	-1.1725450	0.5876836

14	C	C7	0.7424146	-1.3473217	-1.6784226
15	C	C8	-0.8573280	-0.8208732	2.1612432
16	C	C9	0.3091786	-2.0902146	-2.9182222
17	H	H9	-0.5843550	-1.6366606	-3.3569408
18	H	H11	0.1292050	-3.1381394	-2.6741262
19	H	H12	1.1072624	-2.0309093	-3.6669761
20	C	C10	-0.7519341	-2.3439471	2.4691145
21	O	O1	1.2641774	-1.9388876	-0.7179743
22	O	O2	-1.5540841	-0.1104211	2.8622324
23	F	F1	0.5205148	-2.7888286	2.3540844
24	F	F2	-1.5136025	-3.0523382	1.6000251
25	F	F3	-1.1782103	-2.6070278	3.7068189

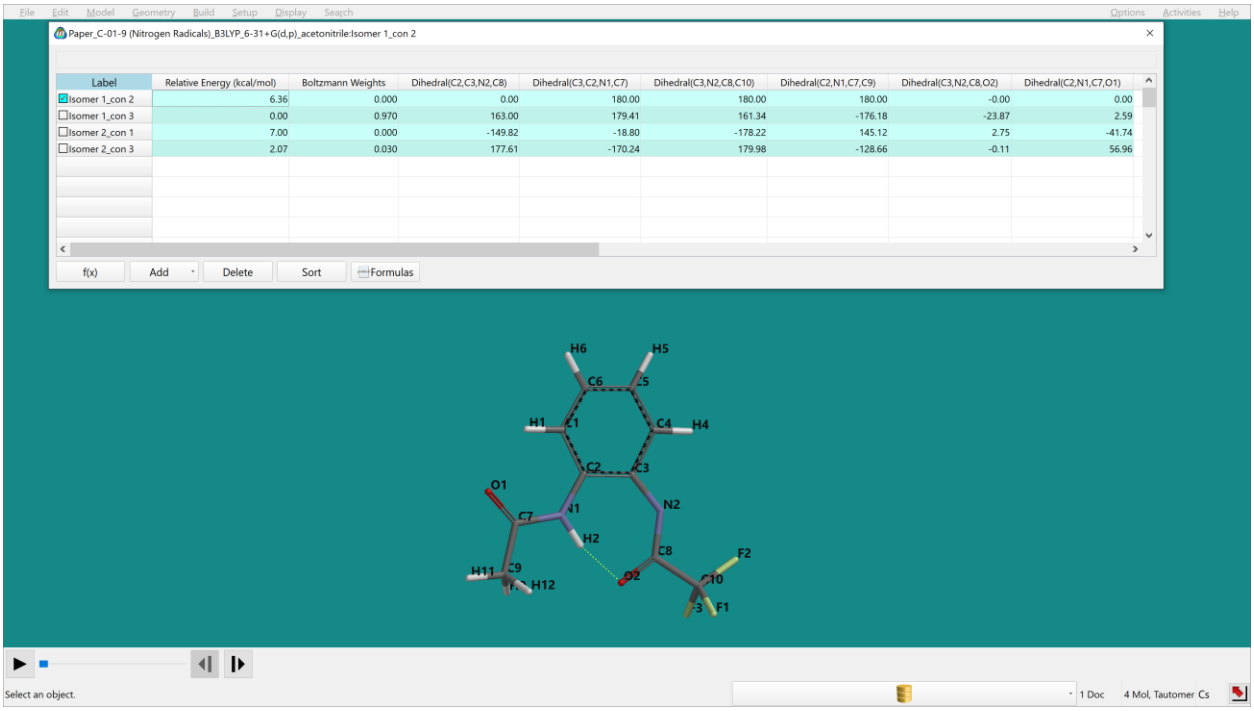


Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.3719755	1.1392468	-1.7348931
2	C	C1	-2.1313862	0.8093866	-0.7321179
3	C	C4	-1.4498186	-0.0168198	1.8944296
4	C	C2	-0.7821769	0.4123394	-0.4511424
5	C	C6	-3.0874433	0.7905926	0.2607545
6	C	C5	-2.7493657	0.3819244	1.5682532
7	C	C3	-0.4668653	-0.0106381	0.9054619
8	H	H6	-4.1054331	1.0941391	0.0375543
9	H	H5	-3.5106209	0.3729240	2.3422916
10	H	H4	-1.2006716	-0.3301182	2.8988190
11	N	N1	0.2187478	0.3526464	-1.3325817
12	N	N2	0.8586317	-0.3914434	1.1042895
13	H	H8	1.4174476	-0.3339745	0.2529113
14	C	C7	0.1384136	0.8848713	-2.6235709
15	C	C8	1.4480382	-0.8180369	2.2555764
16	C	C9	0.8594170	0.0583454	-3.6646855

17	H	H9	1.9303733	0.0323153	-3.4363031
18	H	H11	0.7054487	0.4966376	-4.6515737
19	H	H12	0.5012435	-0.9766471	-3.6509831
20	C	C10	2.9572041	-1.1596612	2.1024721
21	O	O1	-0.3893405	1.9617335	-2.8733544
22	O	O2	0.9267793	-0.9483526	3.3482934
23	F	F1	3.6989652	-0.3392259	2.8665804
24	F	F2	3.3961032	-1.0383416	0.8208283
25	F	F3	3.1882845	-2.4238430	2.4926903

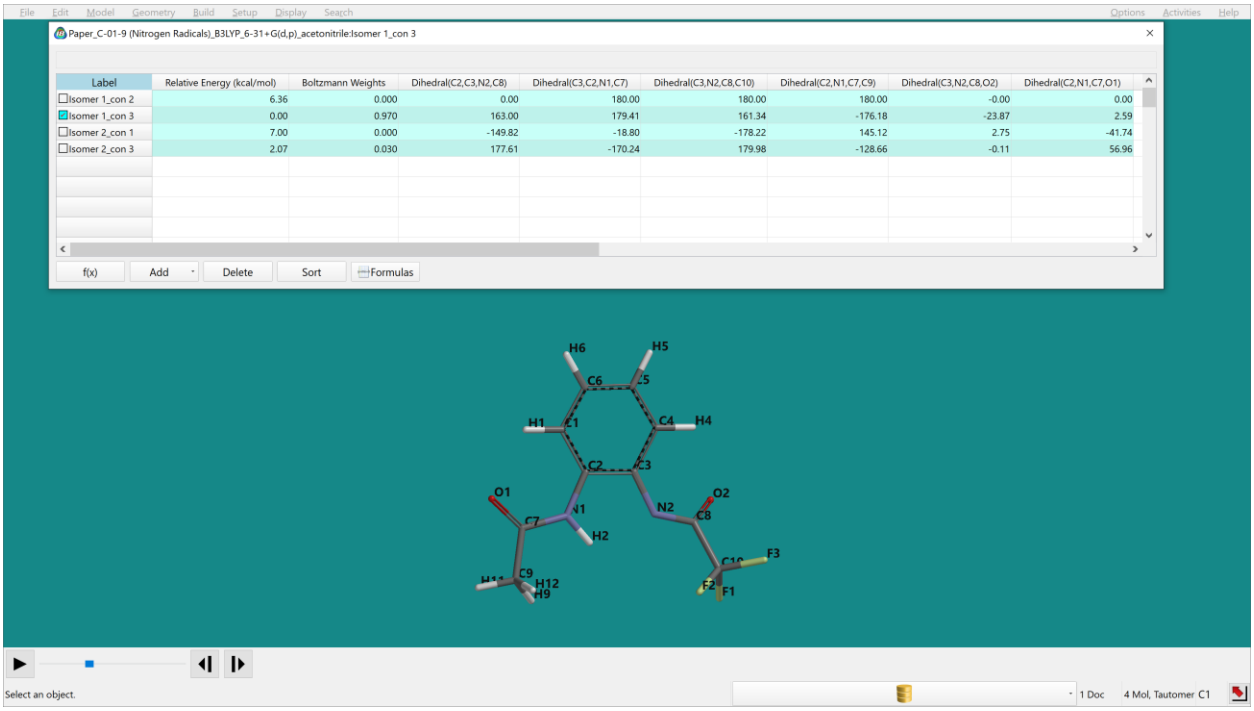
Acetonitrile



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.2785417	0.0000000	3.0728087
2	C	C1	-0.9367708	0.0000000	2.2176376
3	C	C4	-2.6654366	0.0000000	0.0104460
4	C	C2	-0.3596870	0.0000000	0.9240125
5	C	C6	-2.3063943	0.0000000	2.3914578
6	C	C5	-3.1868182	0.0000000	1.2779787
7	C	C3	-1.2540034	0.0000000	-0.2500507
8	H	H6	-2.7112261	0.0000000	3.3988401
9	H	H5	-4.2609112	0.0000000	1.4316598
10	H	H4	-3.3098360	0.0000000	-0.8615468
11	N	N1	0.9961434	0.0000000	0.7362045
12	H	H2	1.3074909	0.0000000	-0.2522738
13	N	N2	-0.9743162	0.0000000	-1.5763049
14	C	C7	2.0323046	0.0000000	1.6782156

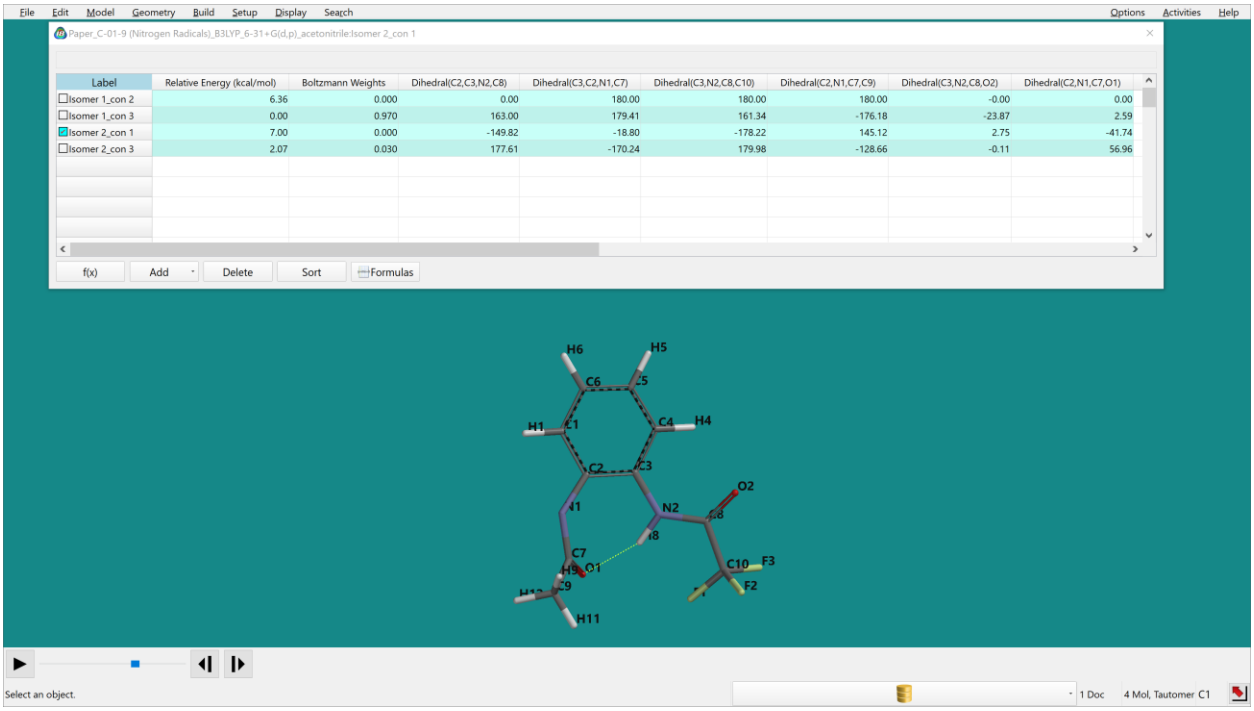
15	C	C8	0.1748751	0.0000000	-2.2500499
16	C	C9	3.4056176	0.0000000	1.0505473
17	H	H9	3.5364097	-0.8841002	0.4172430
18	H	H11	4.1574400	0.0000000	1.8392719
19	H	H12	3.5364097	0.8841002	0.4172430
20	C	C10	-0.0111294	0.0000000	-3.7929564
21	O	O1	1.8475864	0.0000000	2.8903622
22	O	O2	1.3714253	0.0000000	-1.8918868
23	F	F1	0.5892527	1.0909082	-4.3330057
24	F	F2	-1.2891372	0.0000000	-4.2128479
25	F	F3	0.5892527	-1.0909082	-4.3330058



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	0.0499943	0.0271263	3.1864285
2	C	C1	-0.6229640	0.0489224	2.3421897
3	C	C4	-2.4247581	0.1184330	0.1456420
4	C	C2	-0.1047458	-0.0055227	1.0380567
5	C	C6	-1.9955824	0.1405808	2.5300836
6	C	C5	-2.8975117	0.1833575	1.4333661
7	C	C3	-1.0194980	0.0053833	-0.1052926
8	H	H6	-2.3863480	0.1888649	3.5418963
9	H	H5	-3.9633432	0.2699766	1.6185713
10	H	H4	-3.1015663	0.1529080	-0.6983102
11	N	N1	1.2329404	-0.0746273	0.7267691
12	H	H2	1.4139239	-0.0879412	-0.2754988
13	N	N2	-0.4438358	-0.0269036	-1.3164424
14	C	C7	2.3404528	-0.0913872	1.5668765
15	C	C8	-1.0869053	-0.3492802	-2.4582817
16	C	C9	3.6638212	-0.0830587	0.8394201

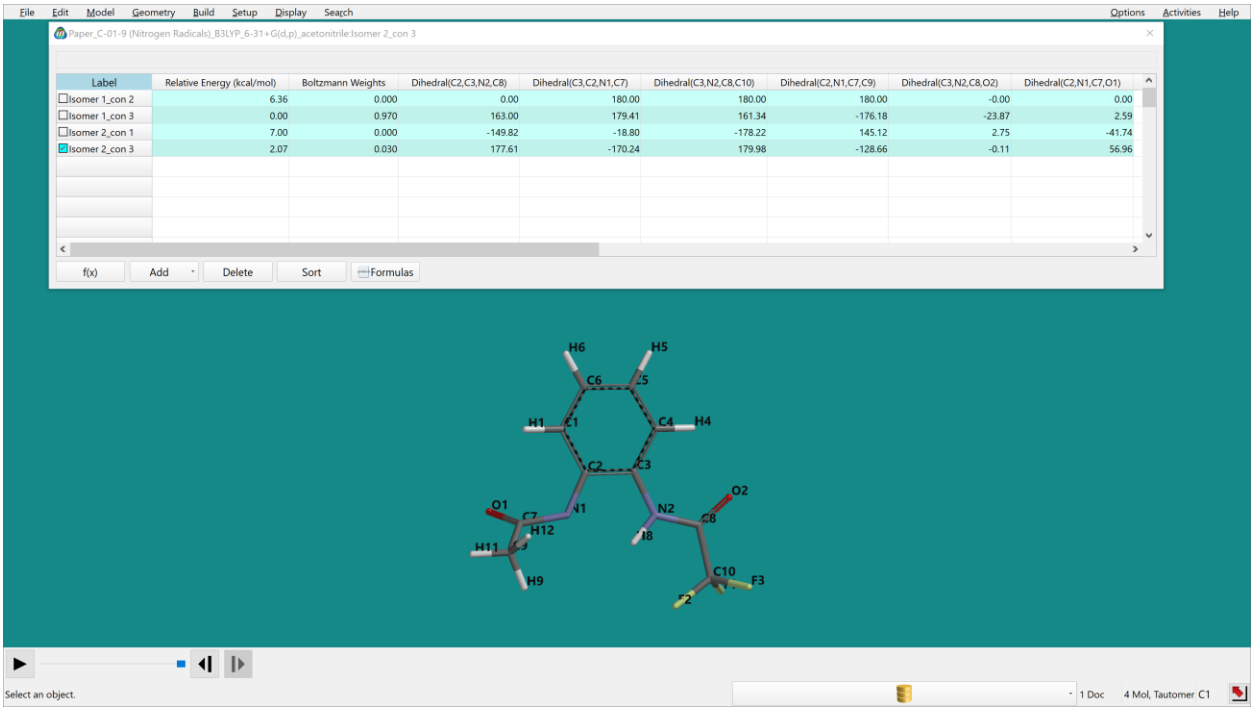
17	H	H9	3.6527217	-0.7466465	-0.0299013
18	H	H11	4.4519278	-0.3856997	1.5292227
19	H	H12	3.8724932	0.9336349	0.4858045
20	C	C10	-0.3525744	0.1196919	-3.7466248
21	O	O1	2.2435869	-0.0889075	2.7911999
22	O	O2	-2.1051825	-1.0228326	-2.6250179
23	F	F1	0.0094505	-0.9496074	-4.4979328
24	F	F2	0.7577888	0.8478182	-3.5200806
25	F	F3	-1.1842860	0.8757167	-4.5021438



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	0.9668739	2.4781809	-2.3698683
2	C	C1	0.6215448	2.3590361	-1.3483457
3	C	C4	-0.2698580	1.9538780	1.2772178
4	C	C2	0.4655065	1.0105148	-0.8732904
5	C	C6	0.3333108	3.4487378	-0.5568437
6	C	C5	-0.1185314	3.2459241	0.7615499
7	C	C3	0.0148821	0.8348969	0.4976187
8	H	H6	0.4558299	4.4549229	-0.9441168
9	H	H5	-0.3391836	4.0965361	1.3986398
10	H	H4	-0.5954541	1.8210326	2.3003139
11	N	N1	0.6850970	0.0550195	-1.7809339
12	N	N2	-0.0939669	-0.4680457	1.0183333
13	H	H8	0.5668706	-1.1536439	0.6398526
14	C	C7	0.8925712	-1.2887969	-1.6687096
15	C	C8	-0.9728673	-0.8746158	1.9651461
16	C	C9	0.3164910	-2.1229141	-2.7830769

17	H	H9	-0.6076030	-1.6865227	-3.1710154
18	H	H11	0.1381145	-3.1387044	-2.4250291
19	H	H12	1.0416661	-2.1640009	-3.6046806
20	C	C10	-0.8352714	-2.3660828	2.3792703
21	O	O1	1.6182300	-1.7825385	-0.7831046
22	O	O2	-1.8527576	-0.2171720	2.5050830
23	F	F1	0.2045063	-3.0002428	1.7955639
24	F	F2	-1.9608112	-3.0374258	2.0554185
25	F	F3	-0.6751904	-2.4579732	3.7150072



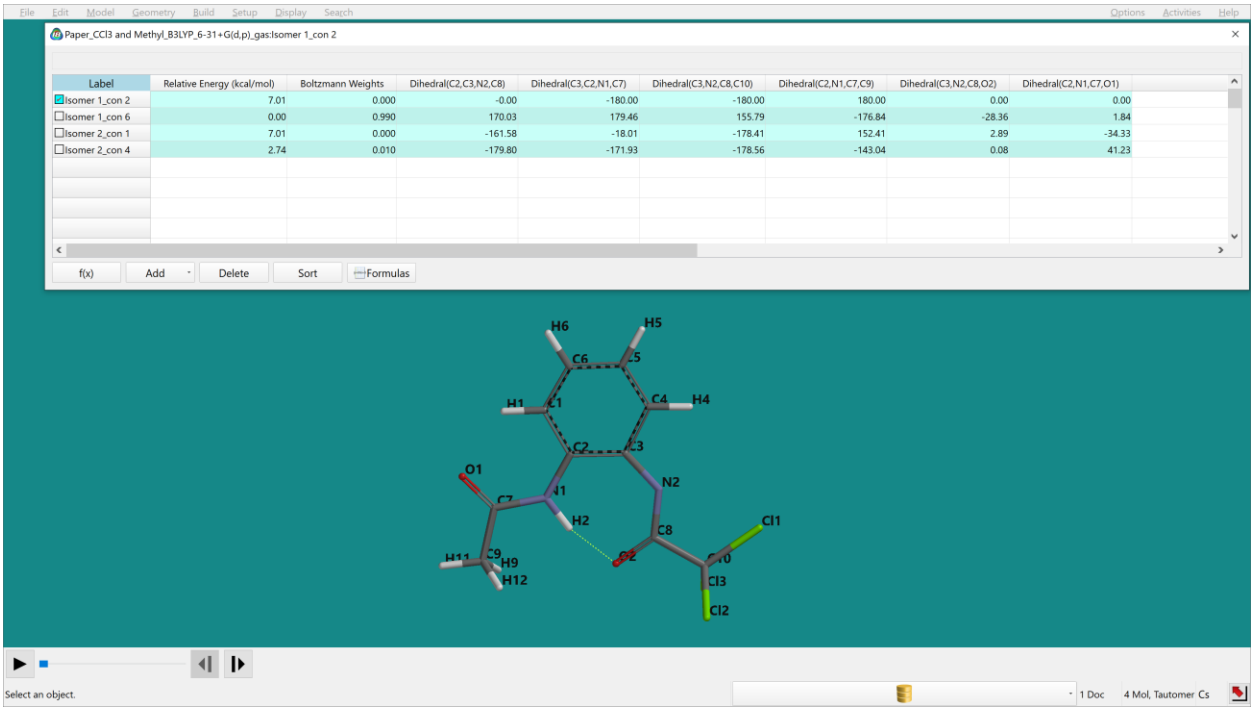
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.0828523	0.6587262	-2.2271468
2	C	C1	-1.9987303	0.3546103	-1.1900231
3	C	C4	-1.7500081	-0.4519374	1.5132146
4	C	C2	-0.6929675	0.2683672	-0.6021091
5	C	C6	-3.1235062	0.0535419	-0.4511753
6	C	C5	-3.0020829	-0.3457486	0.8968015
7	C	C3	-0.5989568	-0.1558929	0.7861976
8	H	H6	-4.1059790	0.1211929	-0.9075222
9	H	H5	-3.8925462	-0.5811898	1.4710205
10	H	H4	-1.6731996	-0.7627808	2.5453601
11	N	N1	0.4527113	0.5091965	-1.2369386
12	N	N2	0.7007104	-0.2318525	1.2919307
13	H	H8	1.4159522	-0.0059591	0.6006046
14	C	C7	0.5530680	1.1018074	-2.4887173
15	C	C8	1.0965156	-0.5492314	2.5452297
16	C	C9	1.3990093	0.3403103	-3.4777080

17	H	H9	2.4392822	0.3331047	-3.1332277
18	H	H11	1.3434619	0.8152992	-4.4583799
19	H	H12	1.0689484	-0.7017428	-3.5410614
20	C	C10	2.6357717	-0.5359557	2.7565765
21	O	O1	0.0748665	2.2132420	-2.7232923
22	O	O2	0.3913370	-0.8361962	3.5041905
23	F	F1	2.9638140	0.3718323	3.6987072
24	F	F2	3.3359931	-0.2385187	1.6380110
25	F	F3	3.0493874	-1.7442249	3.1894572

Table S6. Dihedral Angles and Atom Coordinates for the amidyl radical conformers of 1g.

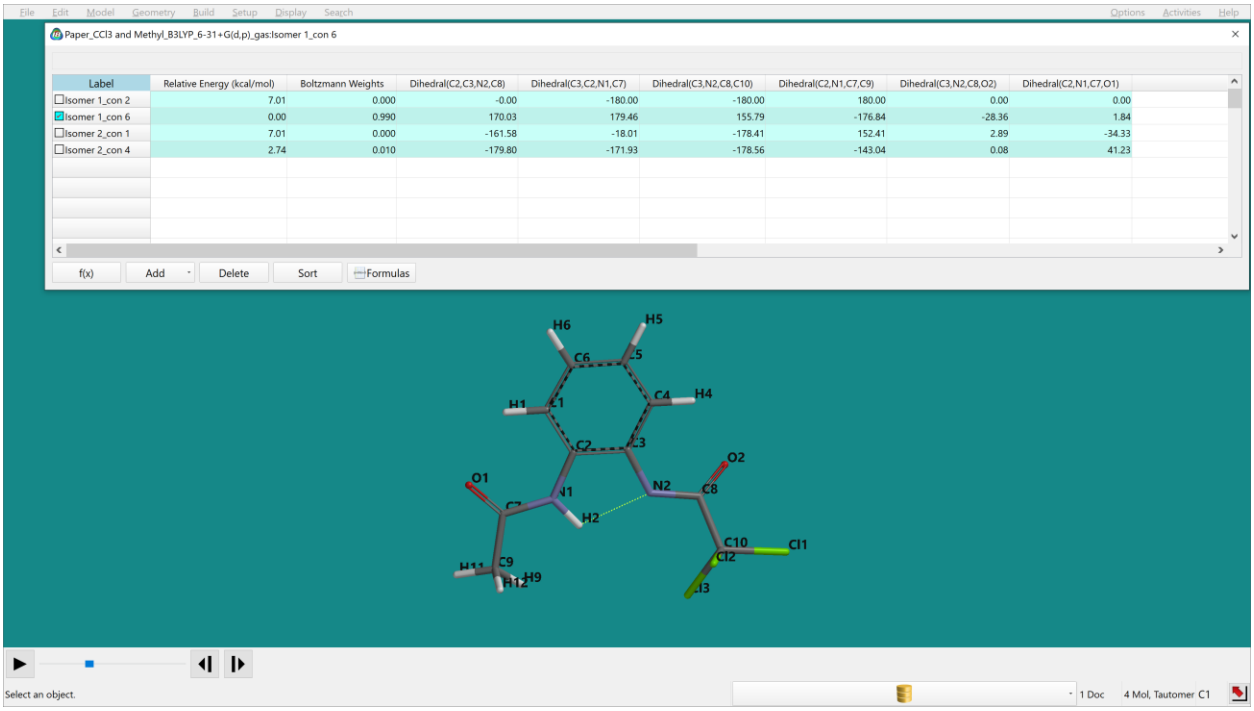
Gas Phase



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.2608227	0.0000000	3.0840110
2	C	C1	-0.9292632	0.0000000	2.2356171
3	C	C4	-2.6681484	0.0000000	0.0381352
4	C	C2	-0.3596257	0.0000000	0.9393638
5	C	C6	-2.2994390	0.0000000	2.4144527
6	C	C5	-3.1843412	0.0000000	1.3074211
7	C	C3	-1.2555826	0.0000000	-0.2301045
8	H	H6	-2.6979345	0.0000000	3.4246572
9	H	H5	-4.2580309	0.0000000	1.4649763
10	H	H4	-3.3070339	0.0000000	-0.8376118
11	N	N1	0.9973029	0.0000000	0.7453545
12	H	H2	1.2973742	-0.0000001	-0.2495999

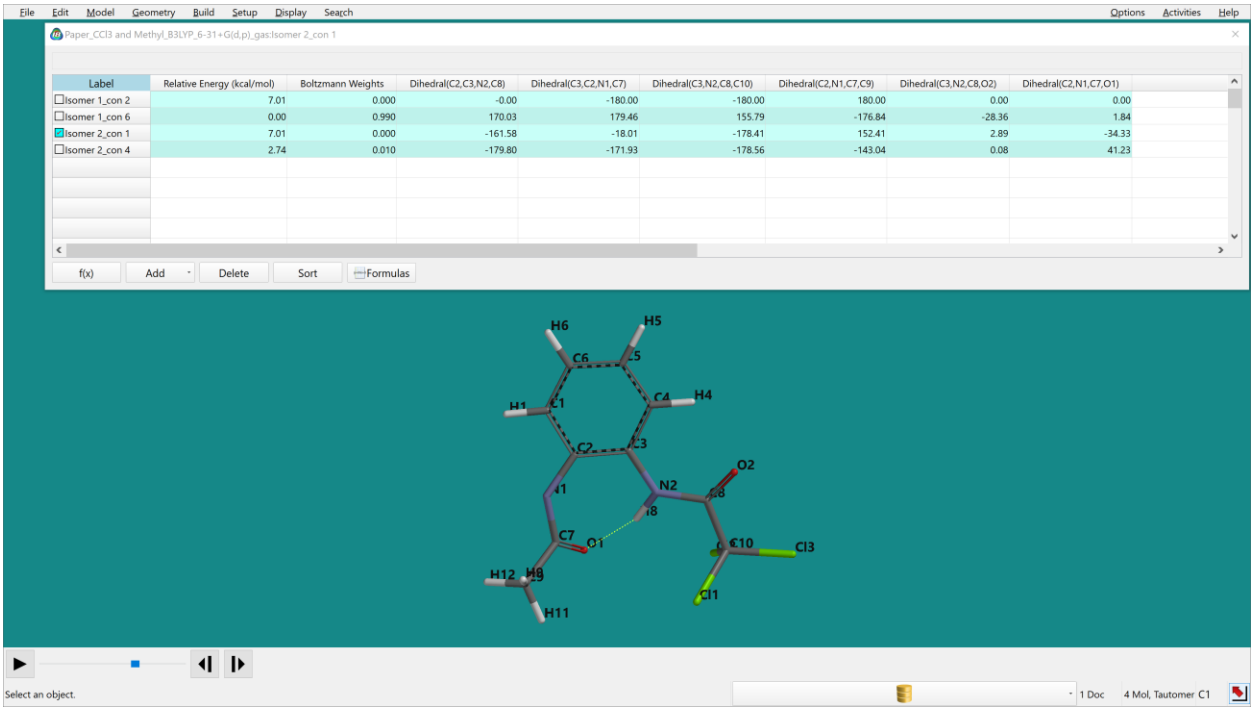
13	N	N2	-0.9888844	0.0000000	-1.5543015
14	C	C7	2.0320731	0.0000000	1.6922055
15	C	C8	0.1597481	0.0000000	-2.2400483
16	C	C9	3.4089125	0.0000000	1.0608950
17	H	H9	3.5461751	-0.8819346	0.4260580
18	H	H11	4.1553379	0.0000000	1.8545481
19	H	H12	3.5461752	0.8819346	0.4260580
20	C	C10	-0.0179129	0.0000000	-3.8024380
21	O	O1	1.8508534	-0.0000001	2.8995433
22	O	O2	1.3427397	0.0000000	-1.8558683
23	Cl	Cl1	-1.7185202	0.0000000	-4.3560385
24	Cl	Cl2	0.8044236	1.4739605	-4.4436430
25	Cl	Cl3	0.8044236	-1.4739605	-4.4436429



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	0.5698379	-0.7642347	3.0310245
2	C	C1	-0.2390594	-0.6426415	2.3249308
3	C	C4	-2.3741162	-0.3192933	0.4799561
4	C	C2	0.0567307	-0.3249477	0.9917918
5	C	C6	-1.5670148	-0.7865500	2.7138252
6	C	C5	-2.6334328	-0.6189423	1.7958699
7	C	C3	-1.0240439	-0.1657556	0.0211248
8	H	H6	-1.7870697	-1.0276851	3.7494057
9	H	H5	-3.6584202	-0.7309562	2.1349062
10	H	H4	-3.1766933	-0.1956074	-0.2353710
11	N	N1	1.3285211	-0.1394679	0.4894921
12	H	H2	1.3232124	0.1085929	-0.4984031
13	N	N2	-0.6418253	0.1678701	-1.2159377
14	C	C7	2.5524321	-0.2092238	1.1473631
15	C	C8	-1.4833091	0.1677809	-2.2944863

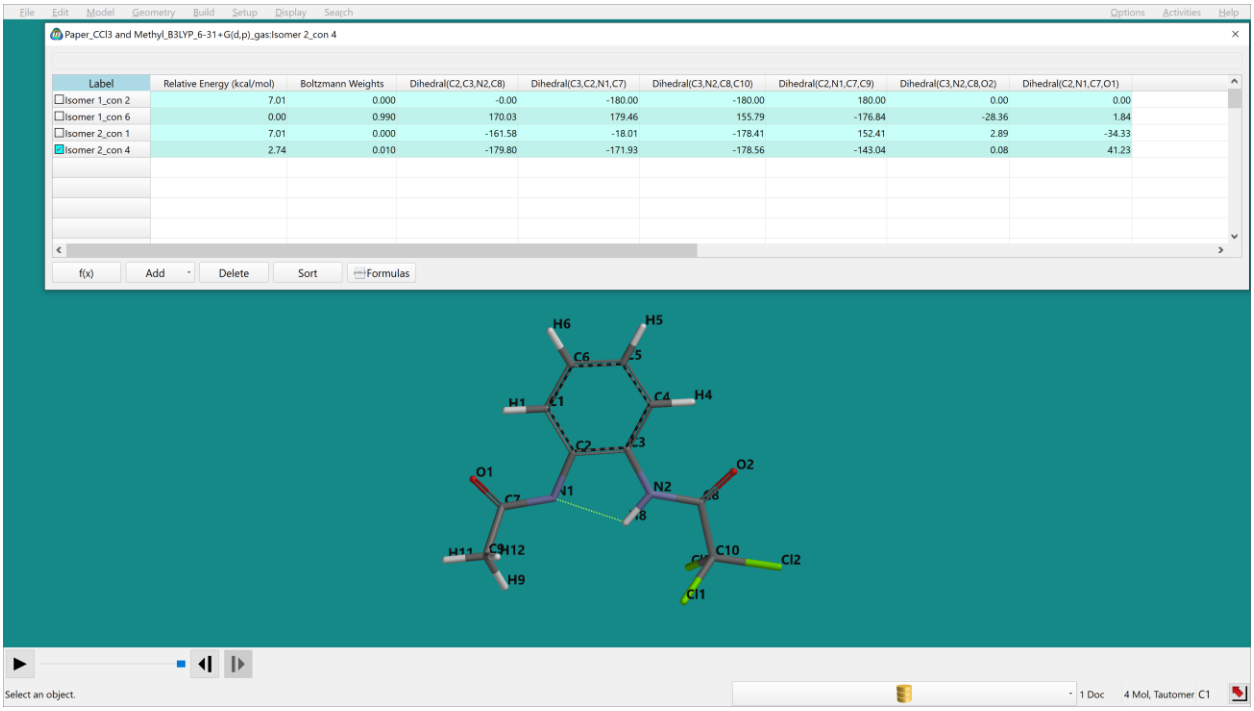
16	C	C9	3.7427779	0.1308905	0.2721524
17	H	H9	3.6117206	-0.1948095	-0.7638553
18	H	H11	4.6315144	-0.3364118	0.6972638
19	H	H12	3.8917340	1.2170762	0.2705133
20	C	C10	-0.9827479	1.1387480	-3.4276765
21	O	O1	2.6577073	-0.4941576	2.3309564
22	O	O2	-2.4725502	-0.5201028	-2.4748594
23	Cl	Cl1	-2.1386380	1.1755413	-4.7800713
24	Cl	Cl2	-0.8123234	2.7973908	-2.7331688
25	Cl	Cl3	0.6250557	0.5668964	-4.0267468



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.4171762	0.9795399	-2.3749980
2	C	C1	-2.3273200	0.6336983	-1.3510515
3	C	C4	-1.9789865	-0.2796133	1.2723905
4	C	C2	-0.9874664	0.4253829	-0.8714965
5	C	C6	-3.4328853	0.3844395	-0.5726421
6	C	C5	-3.2540675	-0.0846847	0.7444251
7	C	C3	-0.8336106	-0.0175191	0.5092297
8	H	H6	-4.4309567	0.5433917	-0.9680195
9	H	H5	-4.1174557	-0.2870501	1.3708908
10	H	H4	-1.8628121	-0.6318743	2.2870469
11	N	N1	-0.0379534	0.5943482	-1.7987815
12	N	N2	0.4562519	-0.1396253	1.0341151
13	H	H8	1.1675307	0.4341035	0.5566993
14	C	C7	1.3195518	0.7314354	-1.7147750
15	C	C8	0.8117961	-0.8553361	2.1463268

16	C	C9	2.0728120	0.2600417	-2.9347006
17	H	H9	1.6688998	-0.6880859	-3.3022072
18	H	H11	3.1324939	0.1595671	-2.6960810
19	H	H12	1.9552162	0.9978292	-3.7362560
20	C	C10	2.3452876	-0.7587422	2.4977209
21	O	O1	1.8942748	1.3115748	-0.7784003
22	O	O2	0.0724413	-1.5380475	2.8262862
23	Cl	Cl1	3.2967892	-1.5028435	1.1511105
24	Cl	Cl2	2.8163946	0.9690813	2.6954852
25	Cl	Cl3	2.6709500	-1.6410116	4.0076821

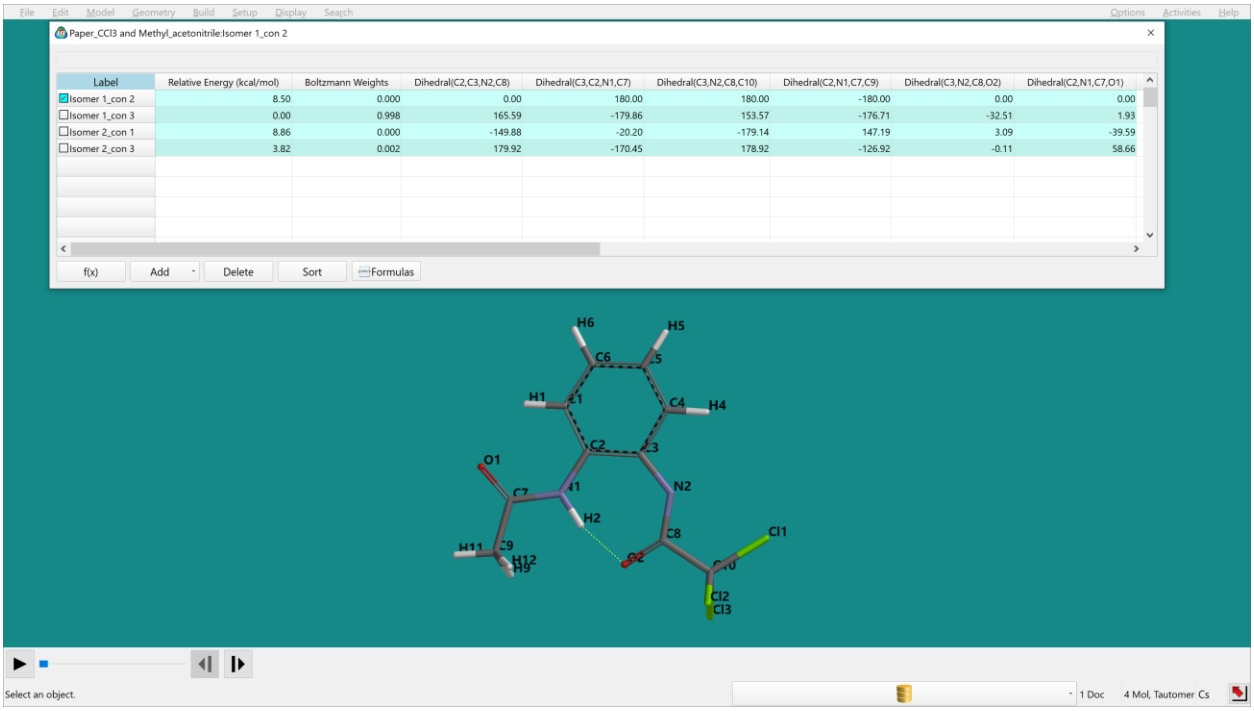


Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.3645129	1.2376872	-1.6942616
2	C	C1	-2.1375181	0.8511296	-0.7089208
3	C	C4	-1.4946716	-0.1186580	1.8777627
4	C	C2	-0.7924249	0.4369356	-0.4319487
5	C	C6	-3.1079569	0.7775881	0.2666656
6	C	C5	-2.7888697	0.2963544	1.5545883
7	C	C3	-0.4946608	-0.0564434	0.9066679
8	H	H6	-4.1223591	1.0944060	0.0454793
9	H	H5	-3.5617582	0.2433459	2.3152922
10	H	H4	-1.2620377	-0.4880377	2.8666166
11	N	N1	0.2209808	0.4195048	-1.3004405
12	N	N2	0.8284158	-0.4411835	1.1004958
13	H	H8	1.3877687	-0.3278229	0.2546433
14	C	C7	0.1580439	1.0034496	-2.5701768
15	C	C8	1.4037620	-0.9413162	2.2314654
16	C	C9	0.8884537	0.2154146	-3.6343770
17	H	H9	1.9484100	0.1327687	-3.3719924

18	H	H11	0.7828228	0.7131376	-4.5990871
19	H	H12	0.4920837	-0.8045087	-3.6925922
20	C	C10	2.9455314	-1.2290172	2.0750858
21	O	O1	-0.3669175	2.0893735	-2.7839523
22	O	O2	0.8430865	-1.1423521	3.2897929
23	Cl	Cl1	3.2424546	-2.2477047	0.6083808
24	Cl	Cl2	3.5527810	-2.0687863	3.5142962
25	Cl	Cl3	3.7990924	0.3547350	1.8805163

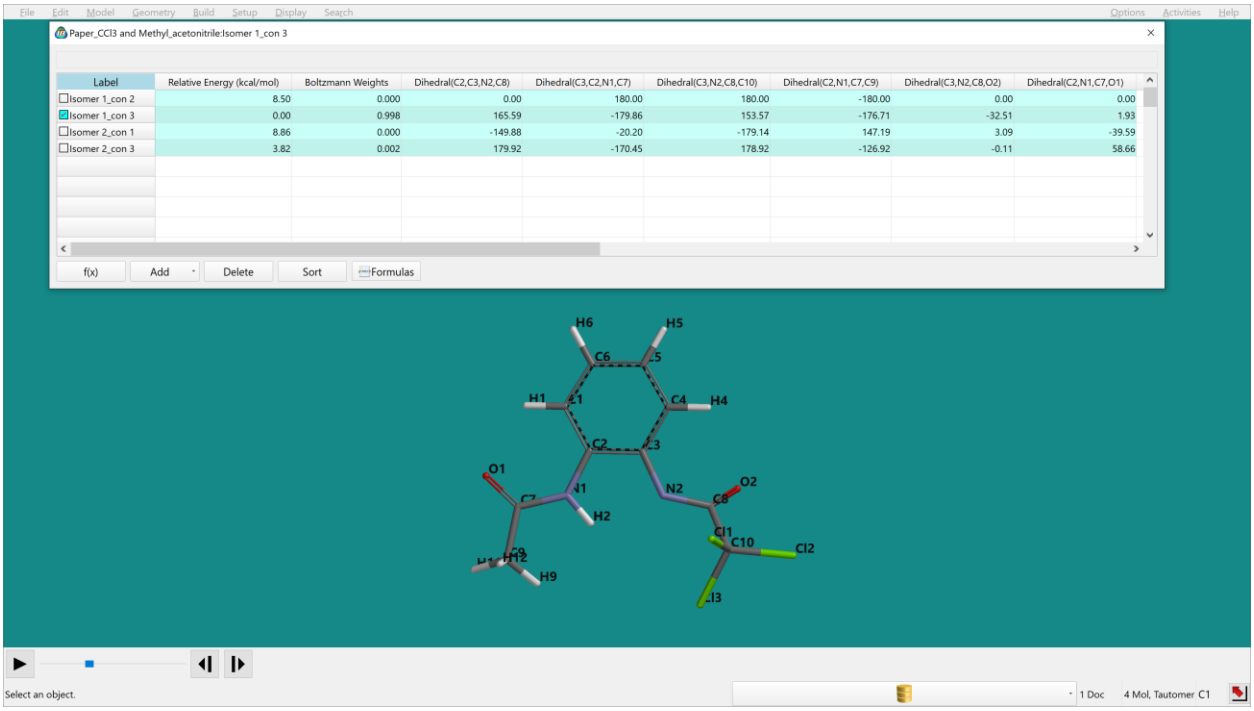
Acetonitrile



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.2705030	0.0000000	3.0920645
2	C	C1	-0.9313747	0.0000000	2.2388670
3	C	C4	-2.6654489	0.0000000	0.0373517
4	C	C2	-0.3573942	0.0000000	0.9442020
5	C	C6	-2.3007951	0.0000000	2.4168403
6	C	C5	-3.1839091	0.0000000	1.3059303
7	C	C3	-1.2541166	0.0000000	-0.2282966
8	H	H6	-2.7026914	0.0000000	3.4254233
9	H	H5	-4.2576298	0.0000000	1.4622233
10	H	H4	-3.3120117	0.0000000	-0.8329858
11	N	N1	0.9983779	0.0000000	0.7537078
12	H	H2	1.3040200	0.0000000	-0.2367186
13	N	N2	-0.9817875	0.0000000	-1.5551468
14	C	C7	2.0365257	0.0000000	1.6921489
15	C	C8	0.1609958	0.0000000	-2.2370256
16	C	C9	3.4082174	0.0000000	1.0604697
17	H	H9	3.5372012	-0.8840835	0.4267760
18	H	H11	4.1625196	0.0000000	1.8468425

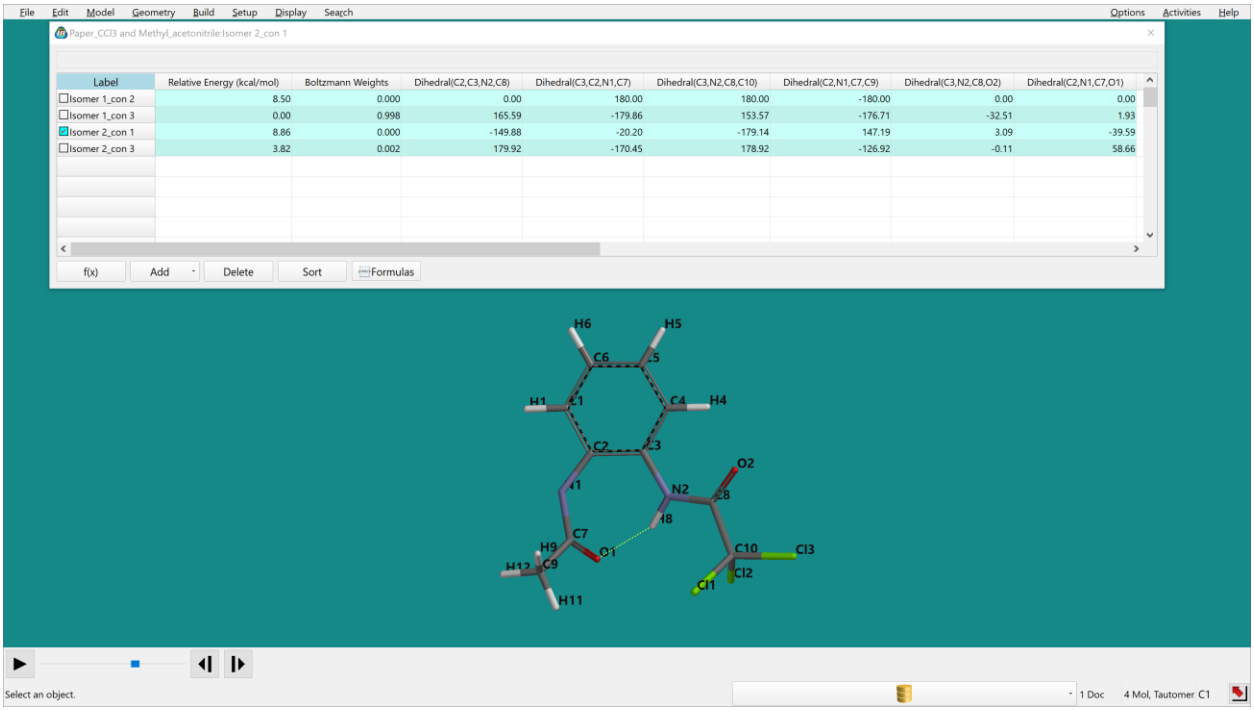
19	H	H12	3.5372012	0.8840835	0.4267759
20	C	C10	-0.0204022	0.0000000	-3.8019530
21	O	O1	1.8559360	0.0000000	2.9052296
22	O	O2	1.3516195	0.0000000	-1.8681702
23	Cl	Cl1	-1.7202042	0.0000000	-4.3656829
24	Cl	Cl2	0.8028270	1.4733584	-4.4544366
25	Cl	Cl3	0.8028270	-1.4733584	-4.4544366



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	0.0744508	0.0932799	3.1816072
2	C	C1	-0.6060013	0.1132130	2.3431795
3	C	C4	-2.4234488	0.1776891	0.1627645
4	C	C2	-0.1026920	-0.0121321	1.0397527
5	C	C6	-1.9741388	0.2679632	2.5402877
6	C	C5	-2.8829728	0.3058467	1.4515178
7	C	C3	-1.0246546	0.0039429	-0.0955419
8	H	H6	-2.3520093	0.3673709	3.5531958
9	H	H5	-3.9432687	0.4388824	1.6409533
10	H	H4	-3.1061962	0.2073532	-0.6772624
11	N	N1	1.2304573	-0.1591943	0.7184556
12	H	H2	1.3982262	-0.2148638	-0.2836322
13	N	N2	-0.4675946	-0.0879454	-1.3080870
14	C	C7	2.3412014	-0.2152488	1.5457378
15	C	C8	-1.1423562	-0.3673591	-2.4484767
16	C	C9	3.6616022	-0.3063485	0.8165146
17	H	H9	3.5643621	-0.7324828	-0.1847546
18	H	H11	4.3537664	-0.9054437	1.4108957
19	H	H12	4.0771696	0.7039344	0.7224835
20	C	C10	-0.4208479	0.2251200	-3.7172192

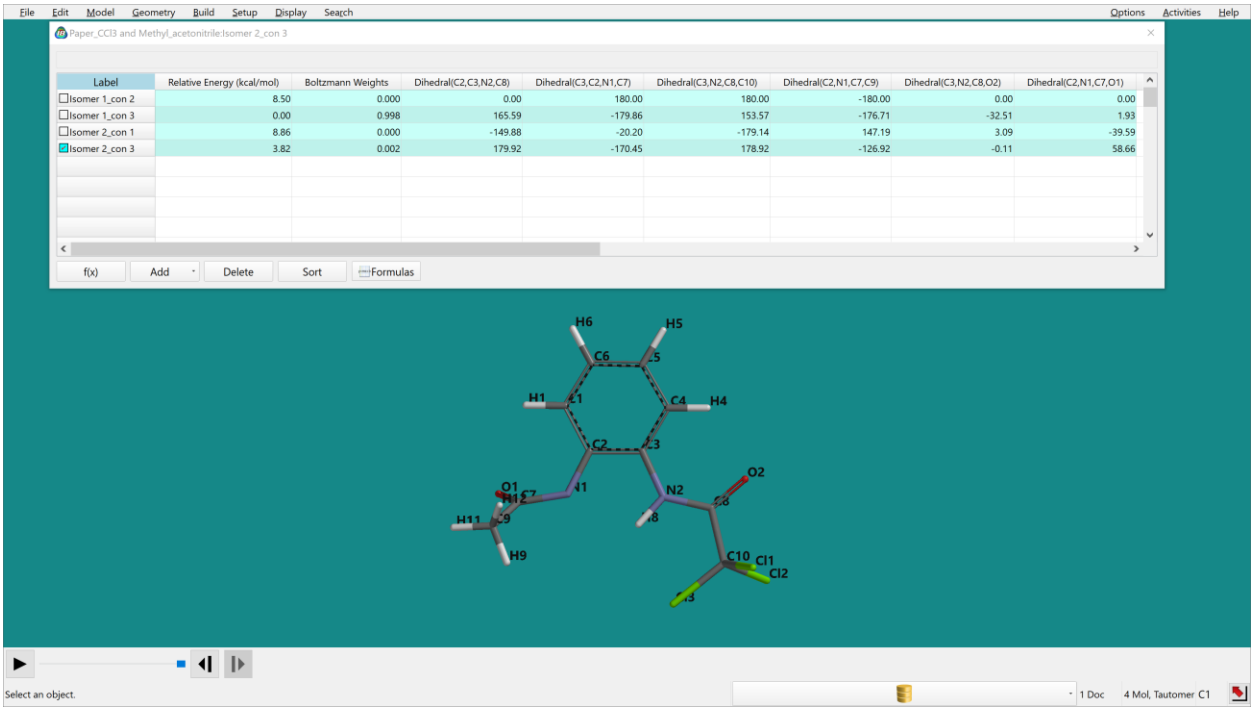
21	O	O1	2.2607288	-0.1682327	2.7720443
22	O	O2	-2.1307005	-1.0765691	-2.5932895
23	Cl	Cl1	-0.0180608	1.9592337	-3.4337774
24	Cl	Cl2	-1.4685313	0.0922201	-5.1588284
25	Cl	Cl3	1.1015088	-0.7102292	-3.9985207



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.4746685	0.8778384	-2.4099648
2	C	C1	-2.3626690	0.5817433	-1.3723114
3	C	C4	-1.9739897	-0.1811129	1.2953640
4	C	C2	-1.0165552	0.4277714	-0.8880655
5	C	C6	-3.4574041	0.3551186	-0.5691138
6	C	C5	-3.2621094	-0.0303574	0.7720300
7	C	C3	-0.8474733	0.0405099	0.5038861
8	H	H6	-4.4612085	0.4763377	-0.9629457
9	H	H5	-4.1167115	-0.1990978	1.4196446
10	H	H4	-1.8488106	-0.4572786	2.3336583
11	N	N1	-0.0590041	0.5918066	-1.8059938
12	N	N2	0.4535105	-0.0709099	1.0267202
13	H	H8	1.1409937	0.5661855	0.6144270
14	C	C7	1.2832768	0.8114986	-1.7025722
15	C	C8	0.8367416	-0.9167979	2.0198461
16	C	C9	2.1144280	0.2063359	-2.8038944
17	H	H9	1.7594161	-0.7968835	-3.0564416
18	H	H11	3.1626913	0.1754744	-2.5027241
19	H	H12	2.0210888	0.8276173	-3.7023784
20	C	C10	2.3609898	-0.8015885	2.4104404
21	O	O1	1.7752004	1.5650898	-0.8388175
22	O	O2	0.1309616	-1.7427435	2.5728925

23	Cl	Cl1	3.3442427	-1.4788938	1.0545296
24	Cl	Cl2	2.8220648	0.9169721	2.6978940
25	Cl	Cl3	2.6749978	-1.7446356	3.8938904



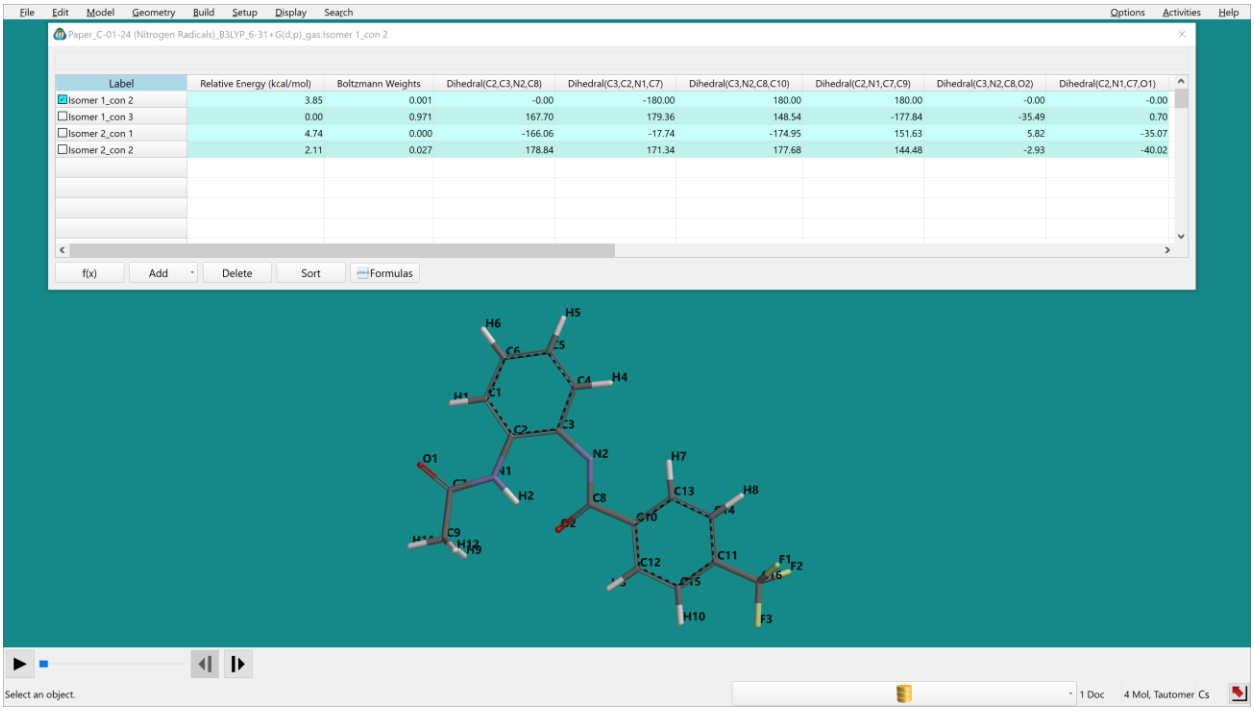
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.1002781	0.6371217	-2.2372727
2	C	C1	-2.0116881	0.3427348	-1.1976594
3	C	C4	-1.7478349	-0.4379098	1.5110334
4	C	C2	-0.7035203	0.2755447	-0.6115398
5	C	C6	-3.1317082	0.0359043	-0.4549435
6	C	C5	-3.0020887	-0.3508971	0.8958345
7	C	C3	-0.6001755	-0.1346110	0.7813522
8	H	H6	-4.1158413	0.0893831	-0.9095015
9	H	H5	-3.8884194	-0.5907830	1.4747178
10	H	H4	-1.6669539	-0.7387212	2.5453175
11	N	N1	0.4368471	0.5211925	-1.2542863
12	N	N2	0.7033087	-0.1851841	1.2820798
13	H	H8	1.4070155	0.0678025	0.5892174
14	C	C7	0.5228431	1.0989428	-2.5143682
15	C	C8	1.0999629	-0.5275160	2.5289324
16	C	C9	1.3383458	0.3145547	-3.5111343
17	H	H9	2.3830504	0.2869045	-3.1821249
18	H	H11	1.2761634	0.7825414	-4.4947204
19	H	H12	0.9858513	-0.7211008	-3.5611719
20	C	C10	2.6511673	-0.5171851	2.7954406
21	O	O1	0.0563813	2.2147592	-2.7512710
22	O	O2	0.3720052	-0.8572381	3.4542377
23	Cl	Cl1	3.1370015	-2.2188516	3.1367046
24	Cl	Cl2	2.9479003	0.5013485	4.2484771

25	Cl	Cl3	3.6506648	0.1112632	1.4366490

Table S7. Dihedral Angles and Atom Coordinates for the amidyl radical conformers of 1j.

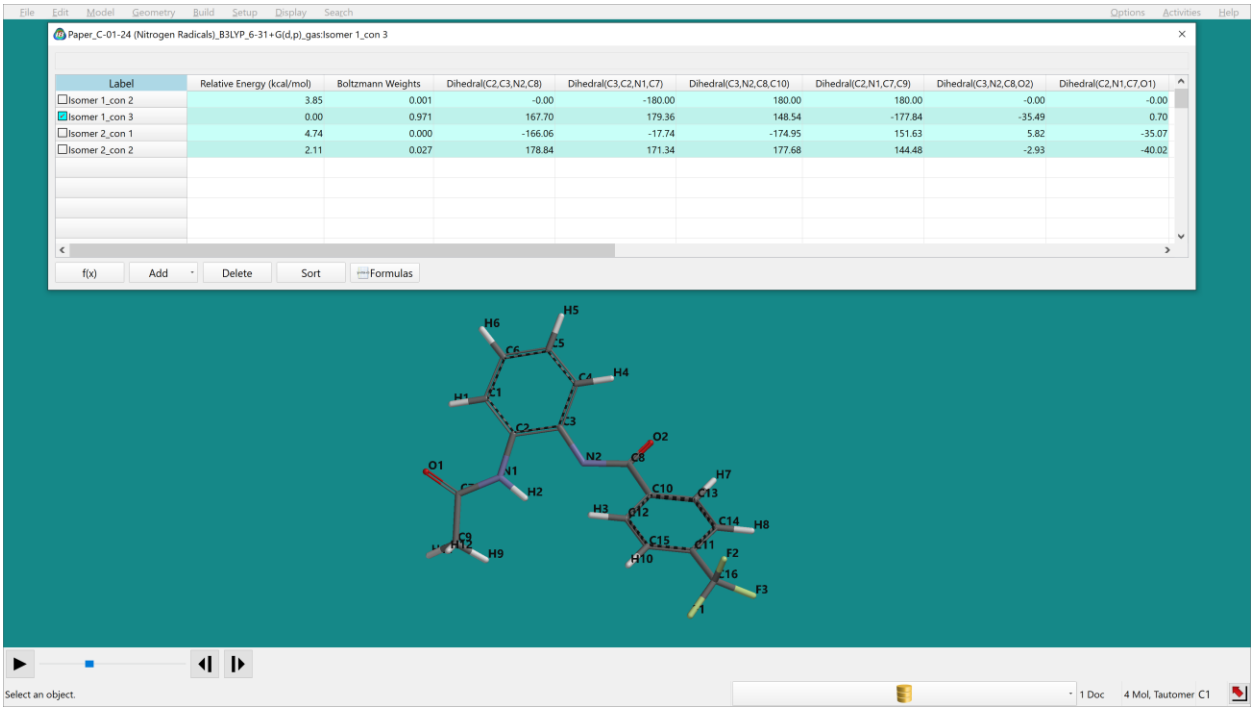
Gas Phase



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.1536735	0.0000000	5.0262040
2	C	C1	-0.8231778	0.0000000	4.1784102
3	C	C4	-2.5581710	0.0000000	1.9862154
4	C	C2	-0.2519383	0.0000000	2.8842971
5	C	C6	-2.1942957	0.0000000	4.3607801
6	C	C5	-3.0774253	0.0000000	3.2545187
7	C	C3	-1.1434116	0.0000000	1.7112157
8	H	H6	-2.5912704	0.0000000	5.3716149
9	H	H5	-4.1516226	0.0000000	3.4094249
10	H	H4	-3.2014865	0.0000001	1.1136397
11	N	N1	1.1079574	0.0000000	2.6953146
12	H	H2	1.4036766	0.0000000	1.6946199
13	N	N2	-0.8842221	0.0000000	0.3877856
14	C	C7	2.1344344	-0.0000001	3.6424022
15	C	C8	0.2796106	0.0000001	-0.3238044
16	C	C9	3.5158467	-0.0000001	3.0170086
17	H	H9	3.6561565	-0.8821153	2.3831223
18	H	H11	4.2585402	-0.0000001	3.8142596
19	H	H12	3.6561565	0.8821152	2.3831223
20	O	O1	1.9556768	-0.0000001	4.8520969
21	O	O2	1.4545421	0.0000001	0.1142625
22	C	C10	0.0816269	0.0000001	-1.8115303

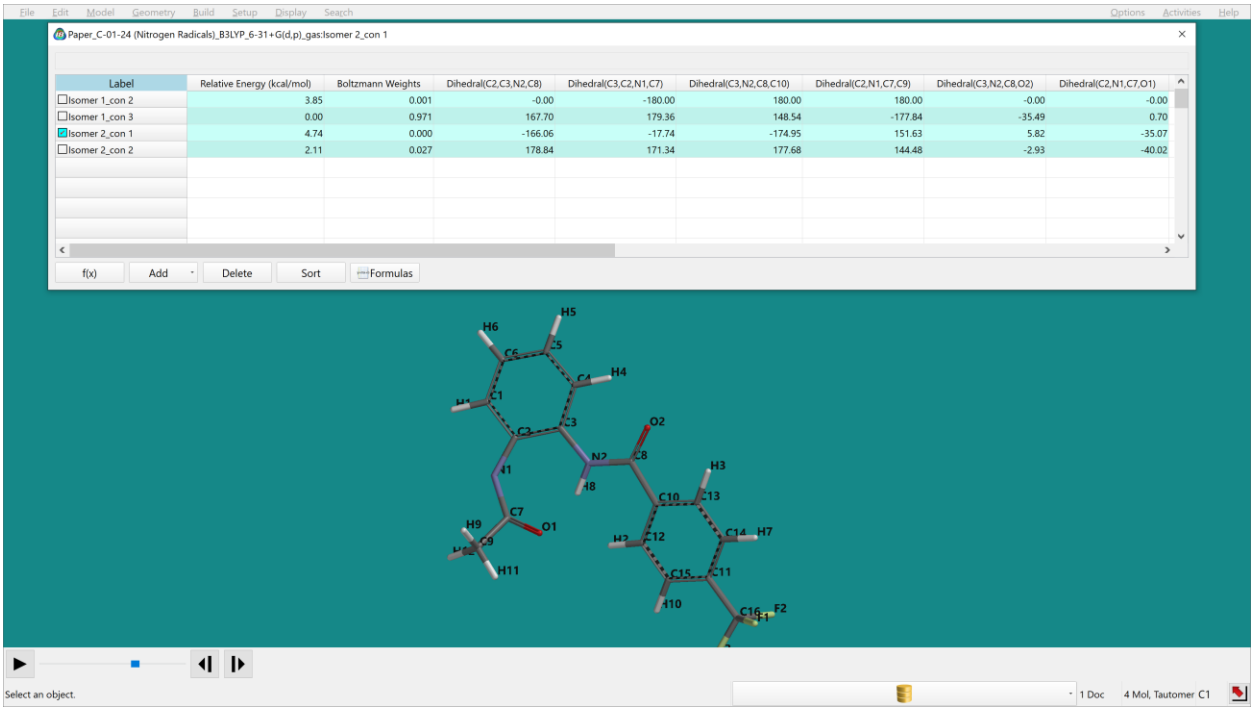
23	C	C11	-0.2035782	0.0000000	-4.5964294
24	C	C12	1.2123764	0.0000001	-2.6418733
25	C	C13	-1.1968526	0.0000000	-2.3936715
26	C	C14	-1.3397976	-0.0000001	-3.7782248
27	C	C15	1.0739261	0.0000001	-4.0284039
28	H	H3	2.1960374	0.0000001	-2.1864777
29	H	H7	-2.0658029	-0.0000001	-1.7478342
30	H	H8	-2.3299925	-0.0000001	-4.2225441
31	H	H10	1.9512825	0.0000001	-4.6650671
32	C	C16	-0.3874143	-0.0000001	-6.0919805
33	F	F1	-1.0855556	1.0881638	-6.5141537
34	F	F2	-1.0855555	-1.0881640	-6.5141536
35	F	F3	0.7873971	0.0000000	-6.7641667



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.4224029	0.1880104	4.9662230
2	C	C1	-1.0399407	0.1377747	4.0806922
3	C	C4	-2.6731447	-0.0013041	1.7639302
4	C	C2	-0.4468568	-0.1591331	2.8481388
5	C	C6	-2.4138941	0.3608055	4.1429128
6	C	C5	-3.2280096	0.2924253	2.9881339
7	C	C3	-1.2624799	-0.2345629	1.6395328
8	H	H6	-2.8653530	0.5920553	5.1030377
9	H	H5	-4.2957611	0.4699114	3.0708631
10	H	H4	-3.2855117	-0.0743392	0.8746075
11	N	N1	0.9022172	-0.4085974	2.6647995
12	H	H2	1.1276533	-0.6098365	1.6936512
13	N	N2	-0.6051457	-0.4658455	0.4995325
14	C	C7	1.9308001	-0.4028120	3.5957881

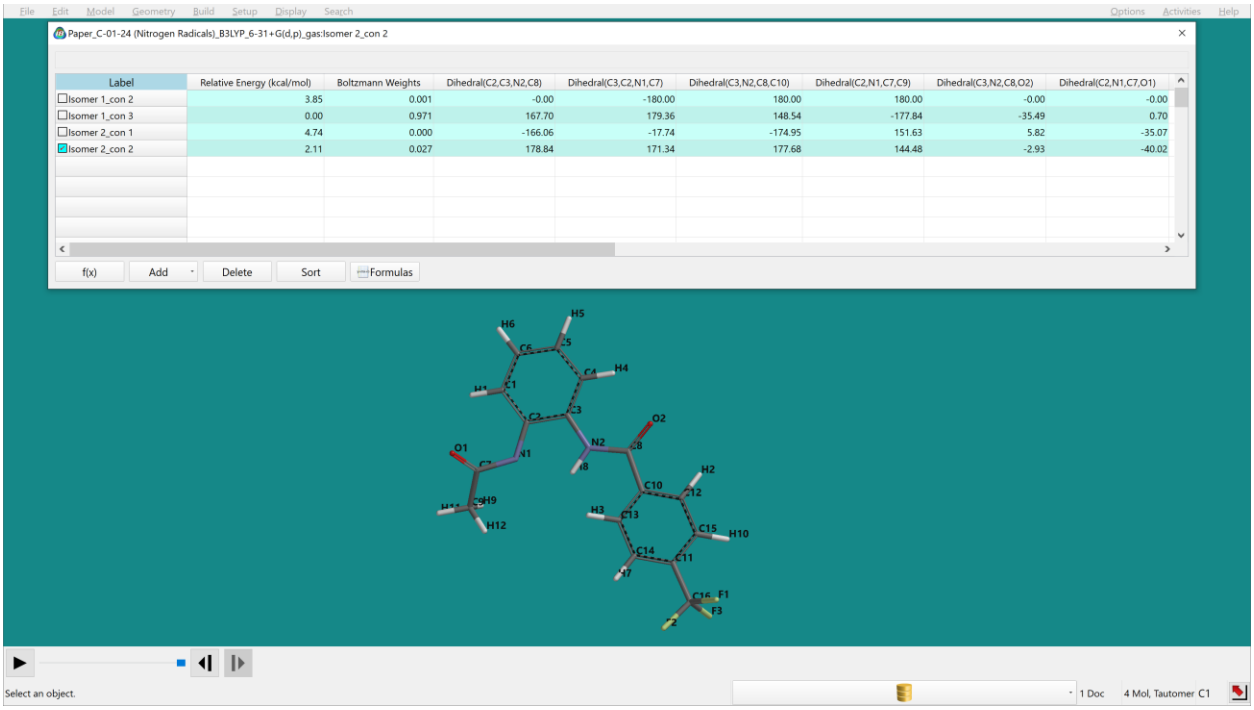
15	C	C8	-1.2411594	-0.8101661	-0.6864423
16	C	C9	3.3040769	-0.6761095	3.0109875
17	H	H9	3.2733356	-1.2772816	2.0979148
18	H	H11	3.9065532	-1.1852112	3.7647541
19	H	H12	3.7896178	0.2789400	2.7802617
20	O	O1	1.7580408	-0.1705177	4.7839347
21	O	O2	-2.2472612	-1.5170829	-0.7433065
22	C	C10	-0.5576529	-0.3325132	-1.9356793
23	C	C11	0.6336176	0.5292104	-4.3154612
24	C	C12	0.5776195	0.4902123	-1.9009996
25	C	C13	-1.0939006	-0.7130873	-3.1744321
26	C	C14	-0.5027720	-0.2868852	-4.3609258
27	C	C15	1.1712367	0.9225643	-3.0855432
28	H	H3	0.9933680	0.7864924	-0.9448699
29	H	H7	-1.9737218	-1.3470981	-3.1875809
30	H	H8	-0.9163615	-0.5908250	-5.3163140
31	H	H10	2.0533850	1.5530554	-3.0557326
32	C	C16	1.2561656	1.0316350	-5.5924961
33	F	F1	2.5998563	1.1838916	-5.4800998
34	F	F2	0.7592314	2.2474108	-5.9521021
35	F	F3	1.0345545	0.1988137	-6.6377108



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-4.0457833	1.3753492	-3.1436475
2	C	C1	-3.9064025	1.0145418	-2.1304240
3	C	C4	-3.4330810	0.0429790	0.4554140
4	C	C2	-2.5518988	0.7121519	-1.7496410
5	C	C6	-4.9664774	0.8232618	-1.2789335
6	C	C5	-4.7241245	0.3207714	0.0181198

7	C	C3	-2.3237034	0.2525308	-0.3813812
8	H	H6	-5.9785160	1.0478628	-1.6000829
9	H	H5	-5.5539447	0.1575698	0.6991804
10	H	H4	-3.2642898	-0.3317024	1.4539687
11	N	N1	-1.6649401	0.8115009	-2.7449004
12	N	N2	-1.0145719	0.0721143	0.0513462
13	H	H8	-0.3155925	0.5662293	-0.5103745
14	C	C7	-0.3060737	0.8423474	-2.7924096
15	C	C8	-0.5924459	-0.5979538	1.1912041
16	C	C9	0.2891029	0.3038114	-4.0723322
17	H	H9	-0.2771147	-0.5564552	-4.4389807
18	H	H11	1.3348219	0.0375626	-3.9095348
19	H	H12	0.2419356	1.0830481	-4.8418232
20	O	O1	0.4090615	1.3812240	-1.9255935
21	O	O2	-1.3603846	-1.2170715	1.9217333
22	C	C10	0.8831227	-0.5490633	1.4944387
23	C	C11	3.5862898	-0.5916661	2.2308610
24	C	C12	1.8217762	0.2171698	0.7874431
25	C	C13	1.3159605	-1.3314956	2.5786028
26	C	C14	2.6560064	-1.3558399	2.9463613
27	C	C15	3.1682786	0.1951661	1.1563653
28	H	H2	1.5383878	0.8369261	-0.0560285
29	H	H3	0.5808008	-1.9161336	3.1196665
30	H	H7	2.9806318	-1.9676487	3.7815620
31	H	H10	3.8869444	0.7881784	0.6024143
32	C	C16	5.0316958	-0.6100142	2.6566104
33	F	F1	5.4715202	-1.8731990	2.8931566
34	F	F2	5.2275947	0.0854295	3.8093679
35	F	F3	5.8554130	-0.0694831	1.7282708

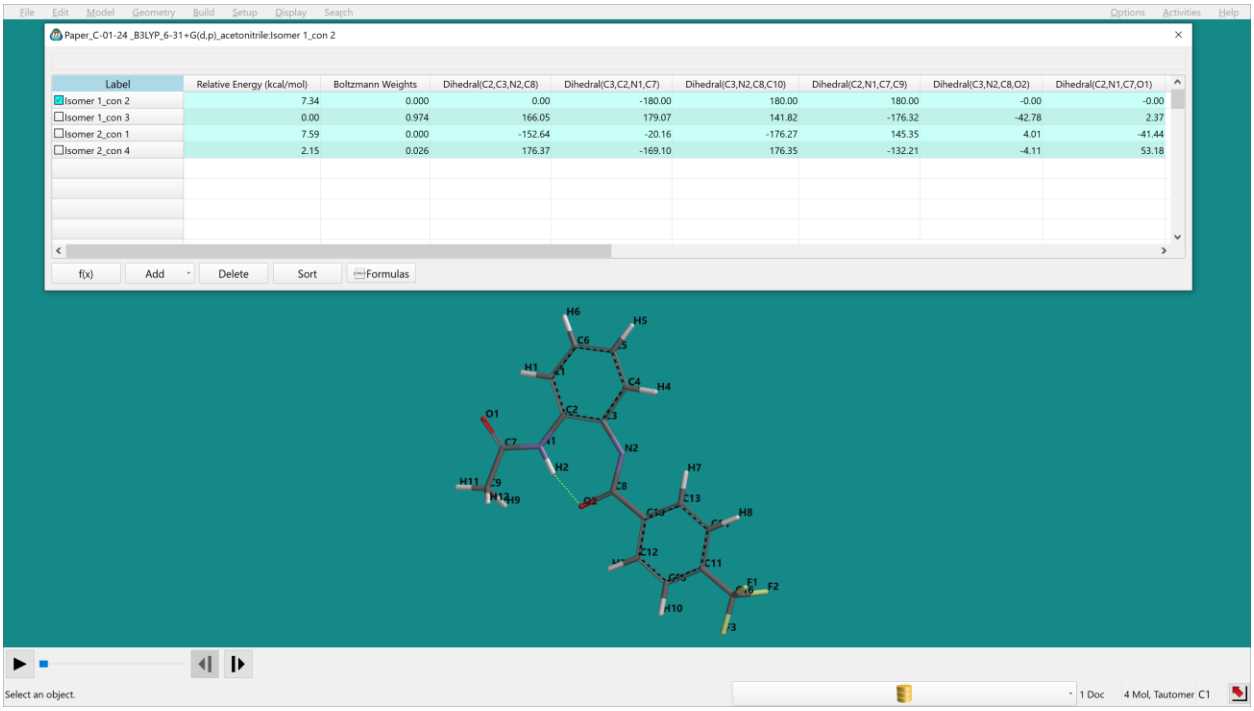


Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1	H	H1	3.6565753	-0.3126337	-3.3715221
2	C	C1	3.5001868	-0.6742608	-2.3634306
3	C	C4	3.0727518	-1.5607459	0.2985798
4	C	C2	2.2644468	-0.3526746	-1.7090700
5	C	C6	4.4683320	-1.4033803	-1.7098934
6	C	C5	4.2565733	-1.8427362	-0.3834867
7	C	C3	2.0714694	-0.8236272	-0.3411163
8	H	H6	5.4006487	-1.6397551	-2.2131783
9	H	H5	5.0287719	-2.4157521	0.1209483
10	H	H4	2.9127798	-1.9059394	1.3099818
11	N	N1	1.2400614	0.3120916	-2.2508150
12	N	N2	0.8579440	-0.4701845	0.2266115
13	H	H8	0.2716911	0.0394848	-0.4301907
14	C	C7	1.3192105	0.9787880	-3.4756427
15	C	C8	0.3638543	-0.7734580	1.4789868
16	C	C9	0.0408316	0.9152074	-4.2839519
17	H	H9	-0.2872934	-0.1223764	-4.4077534
18	H	H11	0.1989723	1.3792042	-5.2582470
19	H	H12	-0.7577769	1.4438693	-3.7521150
20	O	O1	2.2958625	1.6288030	-3.8316327
21	O	O2	0.9593892	-1.4838841	2.2828547
22	C	C10	-0.9815559	-0.1818685	1.8029111
23	C	C11	-3.4940148	0.8124014	2.5389051
24	C	C12	-1.7008834	-0.7749026	2.8524403
25	C	C13	-1.5283811	0.9257615	1.1397649
26	C	C14	-2.7801354	1.4230587	1.5063054
27	C	C15	-2.9510704	-0.2870357	3.2161646
28	H	H2	-1.2605501	-1.6187276	3.3720103
29	H	H3	-0.9822552	1.4359314	0.3522055
30	H	H7	-3.1934660	2.2829491	0.9919963
31	H	H10	-3.5049740	-0.7569155	4.0225277
32	C	C16	-4.8472459	1.3298656	2.9556842
33	F	F1	-4.8291718	1.8255733	4.2211493
34	F	F2	-5.2959889	2.3198381	2.1492887
35	F	F3	-5.7855896	0.3480309	2.9427297

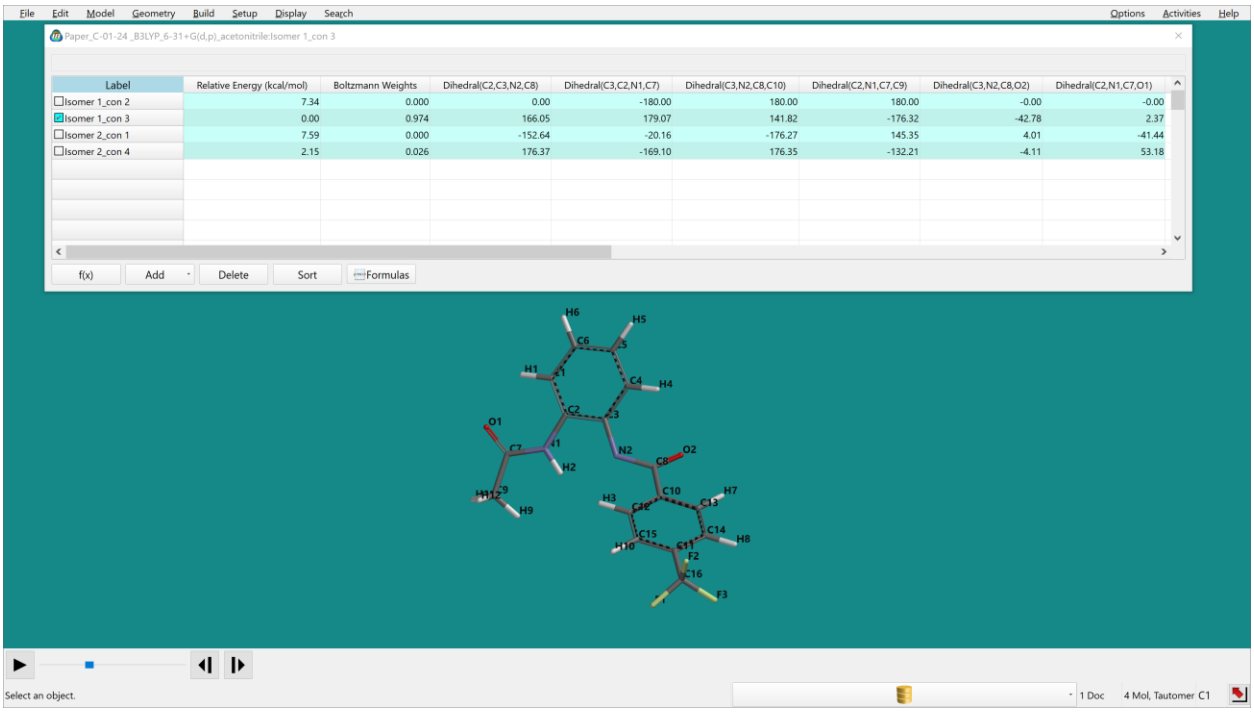
Acetonitrile



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.1728410	0.0000026	5.0358050
2	C	C1	-0.8298416	0.0000015	4.1792551
3	C	C4	-2.5520934	-0.0000017	1.9776687
4	C	C2	-0.2489113	0.0000020	2.8916201
5	C	C6	-2.2033934	-0.0000004	4.3546739
6	C	C5	-3.0800387	-0.0000021	3.2425152
7	C	C3	-1.1345589	0.0000009	1.7126045
8	H	H6	-2.6067424	-0.0000004	5.3628348
9	H	H5	-4.1549576	-0.0000031	3.3913836
10	H	H4	-3.1937972	-0.0000026	1.1036930
11	N	N1	1.1137398	0.0000028	2.7088844
12	H	H2	1.4138329	0.0000025	1.7119917
13	N	N2	-0.8679481	0.0000030	0.3895401
14	C	C7	2.1389852	0.0000023	3.6467800
15	C	C8	0.2924862	-0.0000017	-0.3235216
16	C	C9	3.5181901	-0.0000001	3.0257390
17	H	H9	3.6542319	-0.8839155	2.3933849
18	H	H11	4.2662287	-0.0000022	3.8182347
19	H	H12	3.6542355	0.8839156	2.3933860
20	O	O1	1.9590243	0.0000035	4.8638800
21	O	O2	1.4696309	-0.0000057	0.1127984
22	C	C10	0.0899054	-0.0000016	-1.8126293
23	C	C11	-0.2082258	0.0000003	-4.5966053
24	C	C12	1.2168760	-0.0000023	-2.6497686
25	C	C13	-1.1917888	-0.0000005	-2.3898623
26	C	C14	-1.3424697	0.0000007	-3.7742414
27	C	C15	1.0732007	-0.0000015	-4.0363375

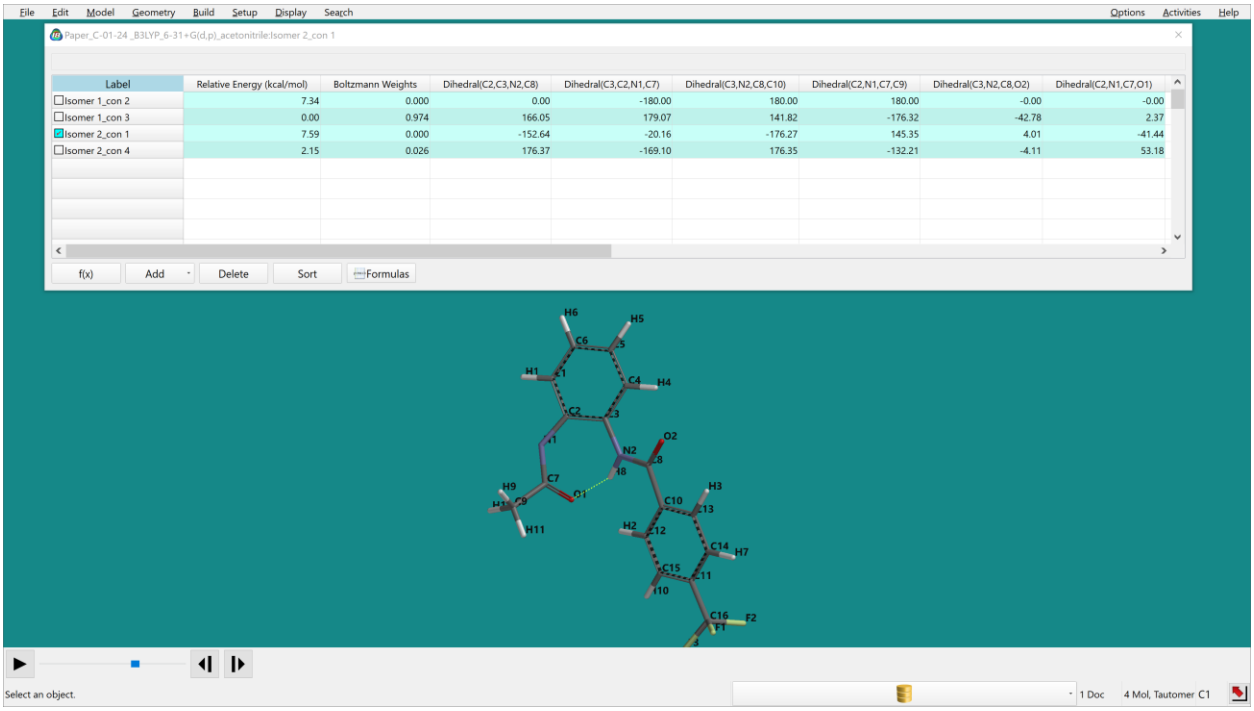
28	H	H3	2.2071886	-0.0000033	-2.2091501
29	H	H7	-2.0634536	-0.0000006	-1.7476122
30	H	H8	-2.3371309	0.0000021	-4.2089951
31	H	H10	1.9513167	-0.0000020	-4.6721022
32	C	C16	-0.3984011	0.0000016	-6.0887512
33	F	F1	-1.1008319	1.0881354	-6.5160623
34	F	F2	-1.1008321	-1.0881315	-6.5160640
35	F	F3	0.7691844	0.0000020	-6.7749701



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.4638881	0.2577764	4.9466010
2	C	C1	-1.0495335	0.1928796	4.0414713
3	C	C4	-2.6193406	0.0346573	1.6884307
4	C	C2	-0.4256446	-0.1595840	2.8384359
5	C	C6	-2.4179921	0.4596387	4.0606888
6	C	C5	-3.2016152	0.3855798	2.8847065
7	C	C3	-1.2161037	-0.2583036	1.6144428
8	H	H6	-2.8869145	0.7356072	5.0002111
9	H	H5	-4.2629309	0.6088807	2.9286106
10	H	H4	-3.2082856	-0.0224853	0.7809011
11	N	N1	0.9232432	-0.4406103	2.6984267
12	H	H2	1.1862935	-0.6650082	1.7413933
13	N	N2	-0.5539776	-0.5620902	0.4969629
14	C	C7	1.9311381	-0.4212507	3.6424004
15	C	C8	-1.1520577	-0.9635247	-0.6781702
16	C	C9	3.3123258	-0.7053156	3.0968592
17	H	H9	3.2933226	-1.2968540	2.1786157
18	H	H11	3.8939511	-1.2250682	3.8604558
19	H	H12	3.8062612	0.2496031	2.8825536

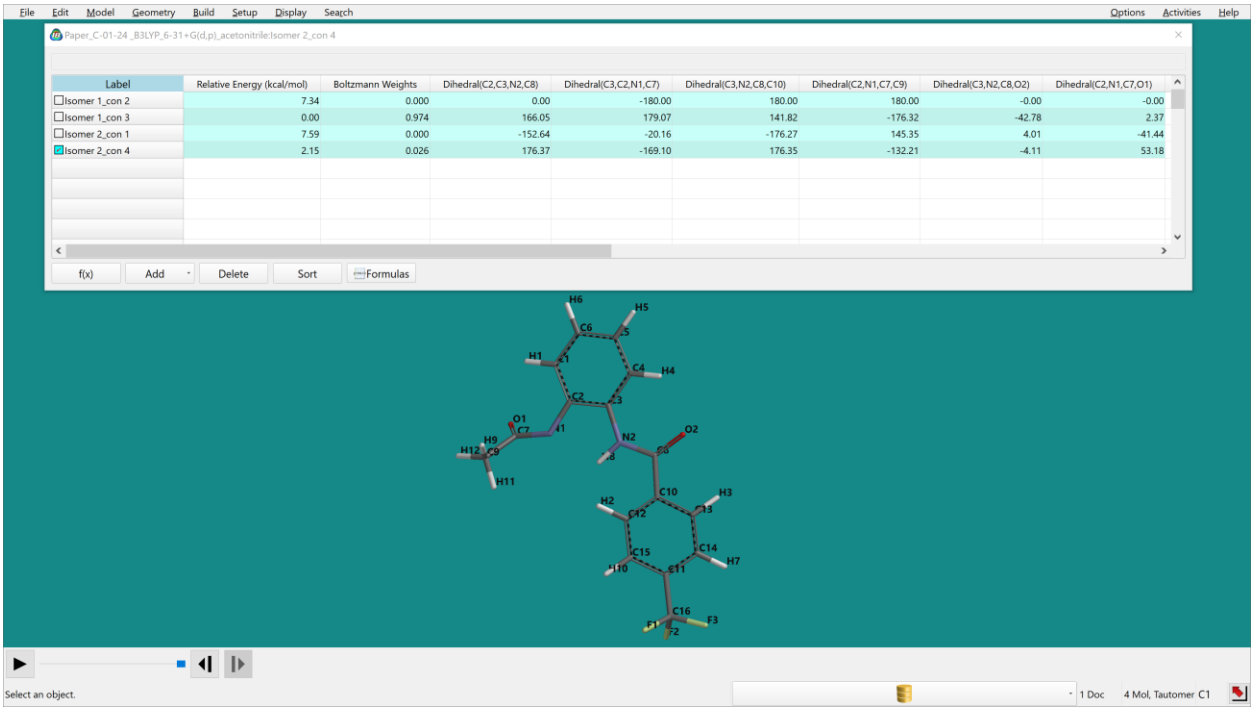
20	O	O1	1.7306540	-0.1685186	4.8314186
21	O	O2	-2.0873849	-1.7736043	-0.7221677
22	C	C10	-0.5221027	-0.4321174	-1.9315768
23	C	C11	0.5809730	0.5497260	-4.3043173
24	C	C12	0.6101365	0.3966747	-1.8945902
25	C	C13	-1.0974295	-0.7608633	-3.1683355
26	C	C14	-0.5522498	-0.2718891	-4.3531962
27	C	C15	1.1618138	0.8877720	-3.0769139
28	H	H3	1.0626995	0.6499909	-0.9427555
29	H	H7	-1.9736796	-1.3990308	-3.1945625
30	H	H8	-1.0034711	-0.5312634	-5.3048678
31	H	H10	2.0402049	1.5231424	-3.0410062
32	C	C16	1.1478159	1.1247691	-5.5738173
33	F	F1	2.4912001	1.3111858	-5.5070321
34	F	F2	0.6086288	2.3467053	-5.8628357
35	F	F3	0.9139400	0.3427930	-6.6574412



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-4.1171562	1.2579680	-3.1743710
2	C	C1	-3.9534627	0.9470244	-2.1479133
3	C	C4	-3.4311514	0.1322106	0.4832346
4	C	C2	-2.5879251	0.7222101	-1.7528796
5	C	C6	-5.0027194	0.7598841	-1.2790508
6	C	C5	-4.7383002	0.3460325	0.0441329
7	C	C3	-2.3411892	0.3178196	-0.3740454
8	H	H6	-6.0236653	0.9306682	-1.6048155
9	H	H5	-5.5575458	0.2060330	0.7425815
10	H	H4	-3.2518835	-0.1644174	1.5070192
11	N	N1	-1.6858323	0.8294488	-2.7321600

12	N	N2	-1.0211816	0.1603723	0.0583811
13	H	H8	-0.3443381	0.7538880	-0.4191317
14	C	C7	-0.3323412	0.9633581	-2.7348845
15	C	C8	-0.5778001	-0.6698149	1.0646813
16	C	C9	0.3793155	0.2752001	-3.8722565
17	H	H9	-0.1458658	-0.6322173	-4.1801759
18	H	H11	1.4040530	0.0425995	-3.5757369
19	H	H12	0.4128659	0.9562684	-4.7312028
20	O	O1	0.2758922	1.7072589	-1.9366483
21	O	O2	-1.3267465	-1.4434585	1.6659941
22	C	C10	0.8883576	-0.5995576	1.4052393
23	C	C11	3.5794947	-0.5991826	2.1824325
24	C	C12	1.8401263	0.1196818	0.6667961
25	C	C13	1.3047515	-1.3195484	2.5377634
26	C	C14	2.6390608	-1.3191767	2.9303279
27	C	C15	3.1817395	0.1196385	1.0531307
28	H	H2	1.5715084	0.6813387	-0.2212664
29	H	H3	0.5705152	-1.8782254	3.1063160
30	H	H7	2.9445260	-1.8768458	3.8098663
31	H	H10	3.9070306	0.6754380	0.4699533
32	C	C16	5.0164087	-0.5980011	2.6283034
33	F	F1	5.4781667	-1.8554862	2.8722125
34	F	F2	5.1915824	0.0966101	3.7895029
35	F	F3	5.8537099	-0.0450198	1.7186697



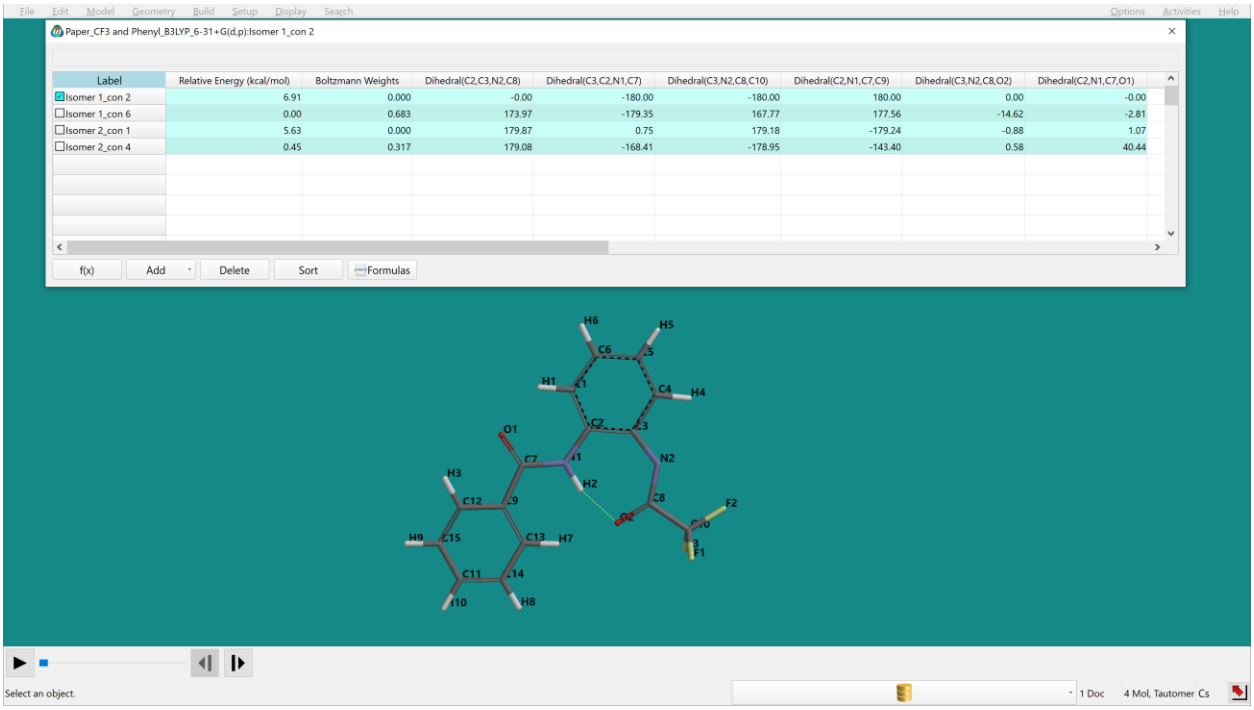
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-4.0652944	1.3730751	-2.4795640
2	C	C1	-3.8445709	1.0351709	-1.4736021
3	C	C4	-3.2334649	0.1346288	1.1403034

4	C	C2	-2.4747523	0.7975035	-1.1172980
5	C	C6	-4.8547173	0.8341019	-0.5594551
6	C	C5	-4.5489579	0.3876176	0.7463061
7	C	C3	-2.1871901	0.3241000	0.2319707
8	H	H6	-5.8873820	1.0152218	-0.8404412
9	H	H5	-5.3507352	0.2311091	1.4613879
10	H	H4	-3.0161088	-0.2072833	2.1416014
11	N	N1	-1.4377594	0.9338230	-1.9433250
12	N	N2	-0.8465864	0.0887796	0.5020623
13	H	H8	-0.2470896	0.2678336	-0.3000614
14	C	C7	-1.4920627	1.5678244	-3.1738987
15	C	C8	-0.2511343	-0.2913553	1.6816948
16	C	C9	-0.8582896	0.7947873	-4.3044917
17	H	H9	-1.2780578	-0.2152413	-4.3578429
18	H	H11	0.2165241	0.6924973	-4.1184587
19	H	H12	-1.0173955	1.3170368	-5.2493406
20	O	O1	-1.9295265	2.7142512	-3.3088860
21	O	O2	-0.8685277	-0.4143718	2.7425838
22	C	C10	1.2280239	-0.5436714	1.6060289
23	C	C11	3.9776451	-1.0499860	1.6150277
24	C	C12	1.8702871	-0.9798448	0.4370458
25	C	C13	1.9759659	-0.3721891	2.7811516
26	C	C14	3.3466425	-0.6147271	2.7871085
27	C	C15	3.2419205	-1.2341845	0.4402281
28	H	H2	1.3120817	-1.1576866	-0.4767155
29	H	H3	1.4777701	-0.0453051	3.6870343
30	H	H7	3.9172667	-0.4713043	3.6984161
31	H	H10	3.7253993	-1.5829802	-0.4655984
32	C	C16	5.4647461	-1.2804869	1.6163525
33	F	F1	5.8567590	-2.1770149	0.6775600
34	F	F2	6.1611574	-0.1330501	1.3633155
35	F	F3	5.9174137	-1.7386791	2.8117996

Table S8. Dihedral Angles and Atom Coordinates for the amidyl radical conformers of 1x.

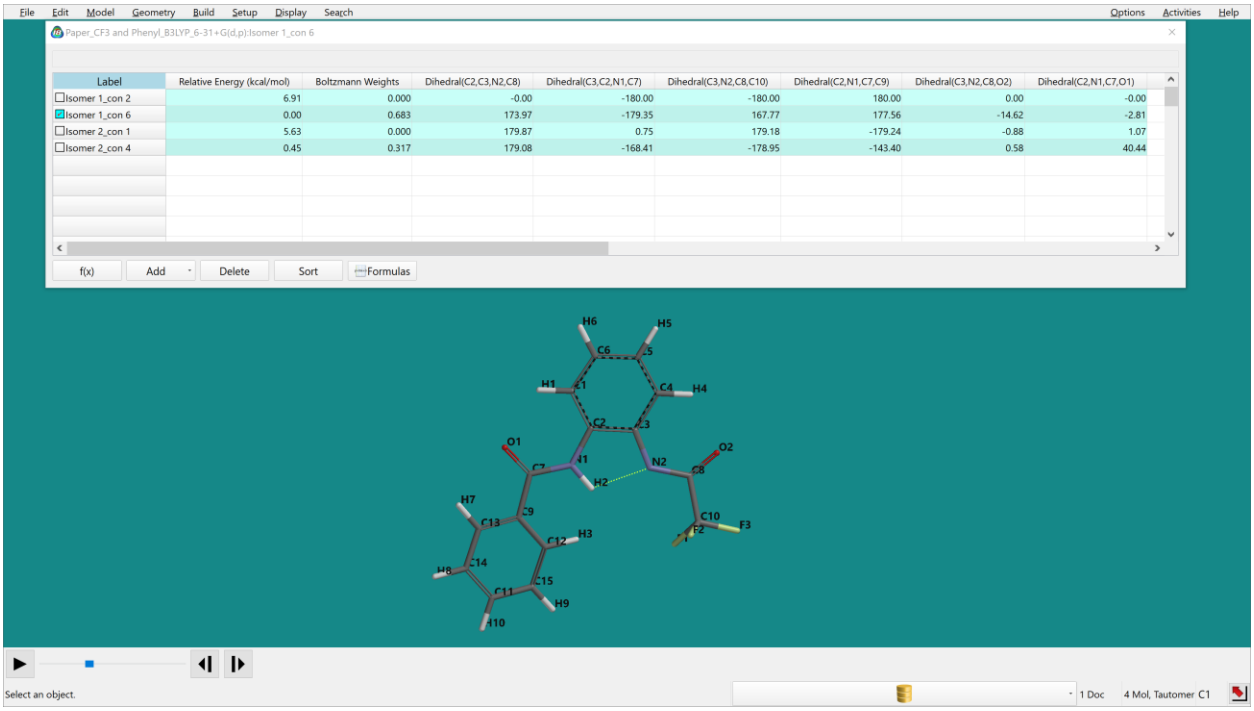
Gas Phase



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-1.3390156	-0.0000002	2.9607736
2	C	C1	-2.0535883	-0.0000002	2.1538285
3	C	C4	-3.9324864	-0.0000001	0.0849231
4	C	C2	-1.5584104	-0.0000001	0.8248002
5	C	C6	-3.4077988	0.0000001	2.4246003
6	C	C5	-4.3669382	0.0000001	1.3830754
7	C	C3	-2.5404167	-0.0000002	-0.2791981
8	H	H6	-3.7336756	0.0000002	3.4605595
9	H	H5	-5.4279386	0.0000003	1.6111945
10	H	H4	-4.6257262	-0.0000002	-0.7482378
11	N	N1	-0.2083028	0.0000001	0.5534480
12	H	H2	0.0257968	0.0000003	-0.4530385
13	N	N2	-2.3878065	-0.0000003	-1.6217437
14	C	C7	0.8554191	0.0000001	1.4779810
15	C	C8	-1.2981515	-0.0000001	-2.3952368
16	C	C10	-1.6079042	0.0000000	-3.9178911
17	O	O1	0.6627554	-0.0000001	2.6885591
18	O	O2	-0.0856762	0.0000001	-2.1149247
19	F	F1	-1.0539595	1.0920885	-4.4948685
20	F	F2	-2.9160063	0.0000001	-4.2180499
21	F	F3	-1.0539596	-1.0920885	-4.4948687
22	C	C9	2.2523272	0.0000001	0.9295952
23	C	C11	4.9518547	-0.0000001	0.1488719
24	C	C12	3.2788984	0.0000001	1.8927128

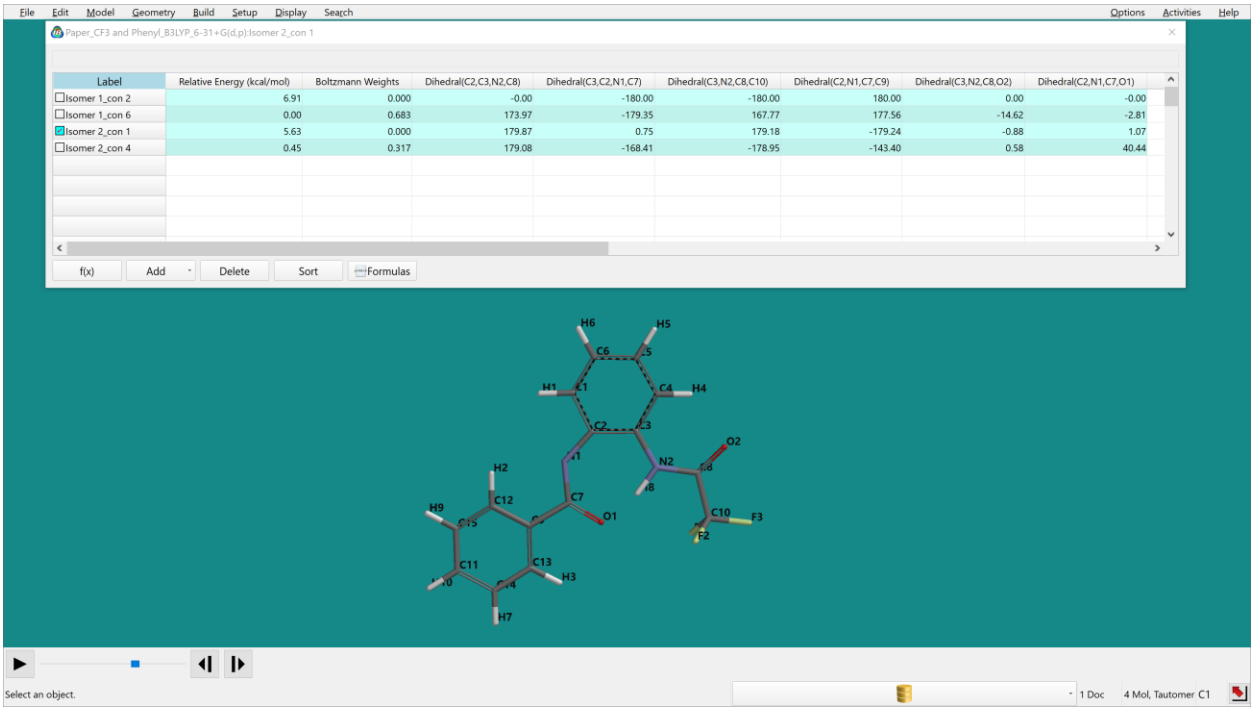
25	C	C13	2.5974731	0.0000001	-0.4328960
26	C	C14	3.9411120	0.0000001	-0.8138521
27	C	C15	4.6157780	0.0000000	1.5067673
28	H	H3	3.0030845	0.0000001	2.9408068
29	H	H7	1.8490880	0.0000001	-1.2136370
30	H	H8	4.1931846	0.0000000	-1.8697980
31	H	H9	5.3952015	-0.0000001	2.2632627
32	H	H10	5.9943727	-0.0000001	-0.1569051



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.9795893	-0.5406608	3.2422011
2	C	C1	-1.7321950	-0.4067601	2.4788146
3	C	C4	-3.7218009	-0.0398561	0.4726309
4	C	C2	-1.3322541	-0.1793229	1.1513445
5	C	C6	-3.0861132	-0.4440226	2.7804677
6	C	C5	-4.0777332	-0.2575031	1.7824879
7	C	C3	-2.3384374	0.0036435	0.0989450
8	H	H6	-3.3912241	-0.6166170	3.8082059
9	H	H5	-5.1270678	-0.2897708	2.0586796
10	H	H4	-4.4672966	0.0907860	-0.2998664
11	N	N1	-0.0306002	-0.1116404	0.7199776
12	H	H2	0.0211865	0.0940198	-0.2764255
13	N	N2	-1.8354049	0.2256547	-1.1220837
14	C	C7	1.1485663	-0.2525756	1.4474021
15	C	C8	-2.5917517	0.3042528	-2.2582196
16	C	C10	-1.7521911	0.8687984	-3.4401484
17	O	O1	1.1494230	-0.4203854	2.6615730
18	O	O2	-3.7517151	-0.0295003	-2.4555475
19	F	F1	-0.6769384	0.0815362	-3.6977569

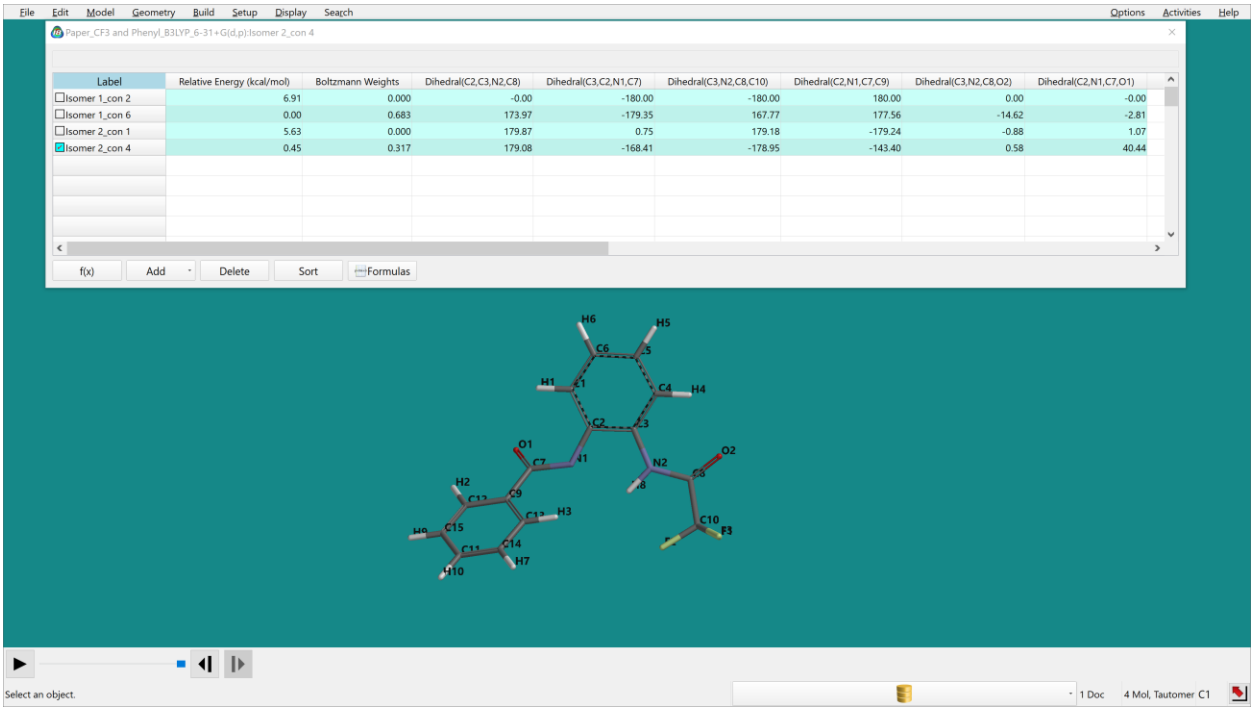
20	F	F2	-1.2832845	2.1070022	-3.1482335
21	F	F3	-2.4746290	0.9568844	-4.5634302
22	C	C9	2.4142517	-0.1766655	0.6489548
23	C	C11	4.8784004	-0.0414116	-0.6859737
24	C	C12	2.4662757	-0.2358304	-0.7543413
25	C	C13	3.6112471	-0.0580015	1.3741476
26	C	C14	4.8342559	0.0132542	0.7109333
27	C	C15	3.6935801	-0.1688996	-1.4153020
28	H	H3	1.5695991	-0.3552719	-1.3551622
29	H	H7	3.5578471	-0.0231932	2.4567373
30	H	H8	5.7526980	0.1103747	1.2820077
31	H	H9	3.7213417	-0.2205721	-2.4992700
32	H	H10	5.8315540	0.0122540	-1.2037499



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-3.0070847	0.3916376	-1.3121339
2	C	C1	-2.9388681	0.1404220	-0.2599147
3	C	C4	-2.6607413	-0.5080081	2.4391551
4	C	C2	-1.5997558	-0.0221492	0.2504046
5	C	C6	-4.0639046	-0.0074137	0.5114231
6	C	C5	-3.9184848	-0.3345317	1.8763142
7	C	C3	-1.4863195	-0.3653580	1.6750211
8	H	H6	-5.0499189	0.1258966	0.0782353
9	H	H5	-4.7963609	-0.4558322	2.5038598
10	H	H4	-2.5635388	-0.7596407	3.4848764
11	N	N1	-0.6751338	0.1824603	-0.7077283
12	N	N2	-0.2325780	-0.5476594	2.2369049
13	H	H8	0.5650956	-0.4258782	1.5547760
14	C	C7	0.6973588	0.1260485	-0.6797645

15	C	C8	0.0626921	-0.8653308	3.5347411
16	C	C10	1.5968785	-1.0038100	3.7728594
17	O	O1	1.4196932	-0.1626272	0.3004295
18	O	O2	-0.7061937	-1.0387377	4.4639246
19	F	F1	2.2301384	0.1708112	3.5444742
20	F	F2	2.1352009	-1.9276552	2.9424763
21	F	F3	1.8469512	-1.3759767	5.0306818
22	C	C9	1.3481756	0.4449289	-1.9836192
23	C	C11	2.6481780	1.0347999	-4.3959162
24	C	C12	0.6025881	0.7717147	-3.1298050
25	C	C13	2.7523724	0.4167665	-2.0592311
26	C	C14	3.3969038	0.7102546	-3.2581685
27	C	C15	1.2521505	1.0647493	-4.3289709
28	H	H2	-0.4780317	0.7919866	-3.0653027
29	H	H3	3.3180170	0.1640468	-1.1692947
30	H	H7	4.4813288	0.6863859	-3.3091047
31	H	H9	0.6703185	1.3150550	-5.2110697
32	H	H10	3.1528735	1.2626447	-5.3305330

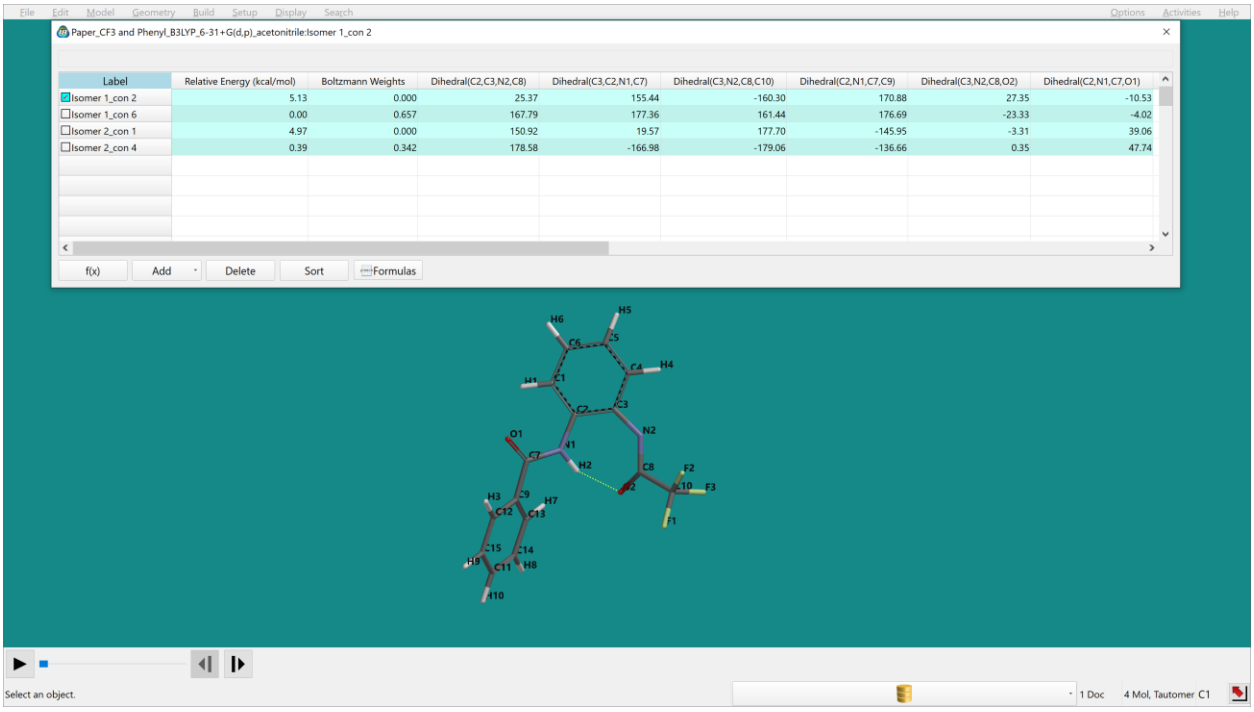


Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.2519940	2.1381174	0.0978963
2	C	C1	-1.8779521	1.7291959	1.0276013
3	C	C4	-0.8431078	0.6738943	3.4469915
4	C	C2	-0.6923028	0.9233950	0.9882903
5	C	C6	-2.5123468	1.9845712	2.2242880
6	C	C5	-1.9977459	1.4616291	3.4293540
7	C	C3	-0.1871957	0.3984310	2.2476821
8	H	H6	-3.4110015	2.5931191	2.2407850
9	H	H5	-2.5042605	1.6713192	4.3664129

10	H	H4	-0.4537354	0.2790045	4.3749983
11	N	N1	-0.0235038	0.5666519	-0.1106611
12	N	N2	0.9735333	-0.3659793	2.1389657
13	H	H8	1.3001554	-0.4559432	1.1771745
14	C	C7	-0.2356257	1.1690508	-1.3548173
15	C	C8	1.6813468	-0.9675463	3.1351959
16	C	C10	2.9477620	-1.7219804	2.6407305
17	O	O1	-0.4087966	2.3808500	-1.4760501
18	O	O2	1.4305445	-0.9631123	4.3268534
19	F	F1	4.0565027	-1.1258926	3.1146850
20	F	F2	3.0447760	-1.7517305	1.2844222
21	F	F3	2.9317880	-2.9918064	3.0760361
22	C	C9	-0.1491191	0.2574537	-2.5346633
23	C	C11	-0.0443653	-1.3781786	-4.8062527
24	C	C12	-0.3469940	0.8067913	-3.8119913
25	C	C13	0.0992724	-1.1180953	-2.4048285
26	C	C14	0.1507103	-1.9318073	-3.5376818
27	C	C15	-0.2937813	-0.0074566	-4.9411820
28	H	H2	-0.5389605	1.8713087	-3.8956907
29	H	H3	0.2558884	-1.5424512	-1.4194291
30	H	H7	0.3465971	-2.9946489	-3.4309854
31	H	H9	-0.4457346	0.4233990	-5.9264573
32	H	H10	-0.0003535	-2.0115532	-5.6876724

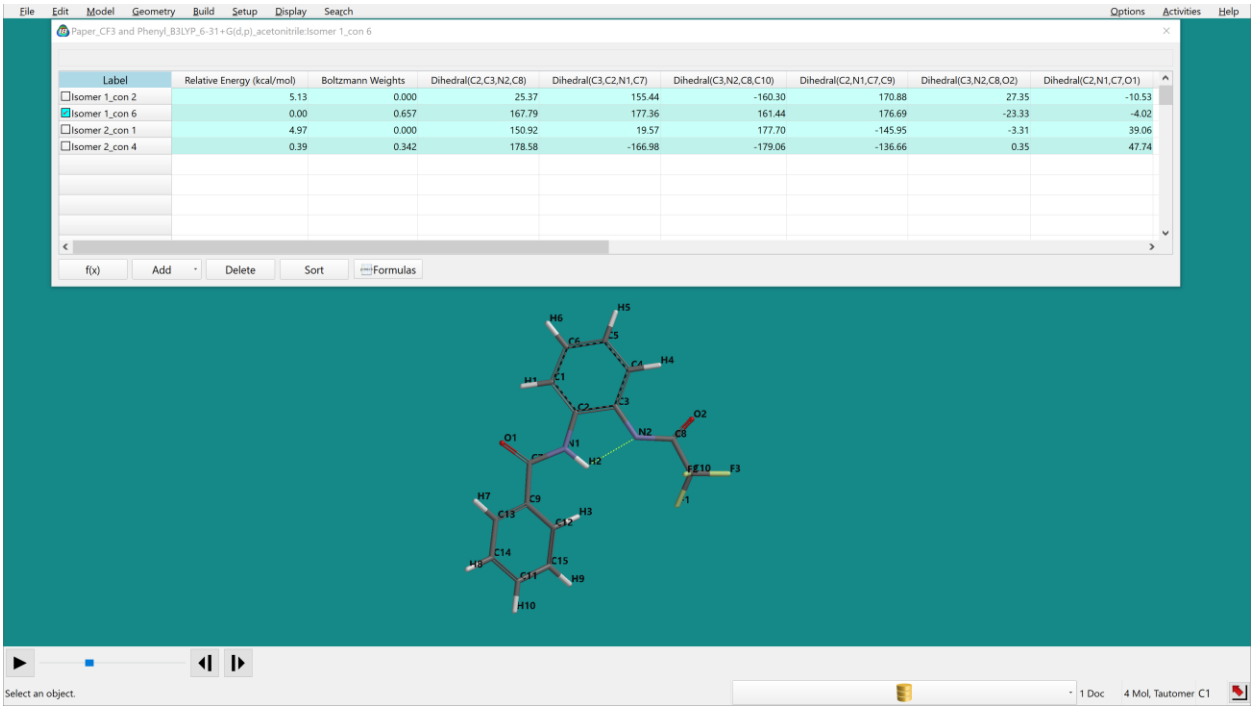
Acetonitrile



Cartesian Coordinates (Angstroms)

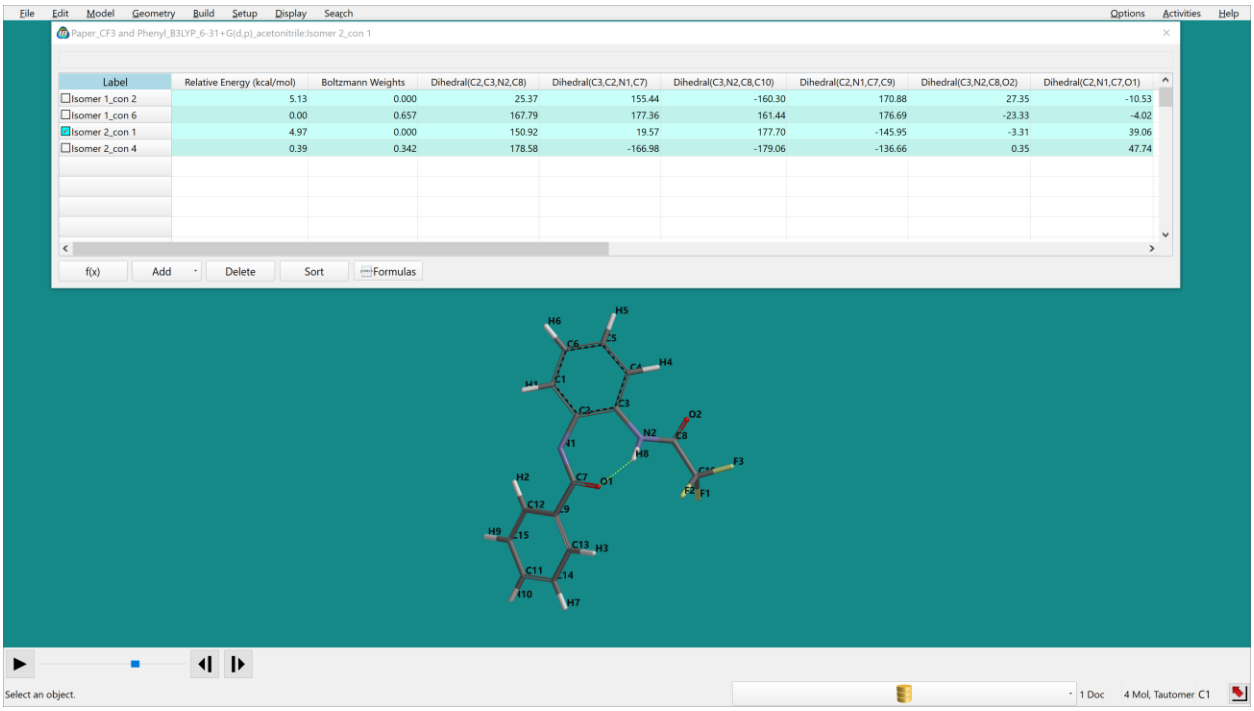
	Atom		X	Y	Z
1	H	H1	-1.3664832	-0.3040474	2.9401756
2	C	C1	-2.0710539	-0.2896630	2.1207387
3	C	C4	-3.9424973	-0.2974313	0.0201186

4	C	C2	-1.5895599	-0.1626030	0.8065339
5	C	C6	-3.4287543	-0.4342210	2.3700668
6	C	C5	-4.3741105	-0.4473189	1.3122407
7	C	C3	-2.5502254	-0.1253165	-0.2960182
8	H	H6	-3.7664293	-0.5575334	3.3943841
9	H	H5	-5.4300358	-0.5703353	1.5291474
10	H	H4	-4.6367807	-0.2835361	-0.8131619
11	N	N1	-0.2367323	-0.1006552	0.5244064
12	H	H2	0.0357569	-0.3966727	-0.4150320
13	N	N2	-2.2908730	0.1632775	-1.5777042
14	C	C7	0.7782207	0.3424694	1.3678076
15	C	C8	-1.1921677	0.0694718	-2.3272023
16	C	C10	-1.2561111	0.9630705	-3.5950926
17	O	O1	0.5482759	0.9179393	2.4311301
18	O	O2	-0.2255324	-0.7015241	-2.2195032
19	F	F1	-0.0177704	1.2893424	-4.0147338
20	F	F2	-1.9333056	2.1120848	-3.3907783
21	F	F3	-1.8691996	0.3041185	-4.6104561
22	C	C9	2.1681793	0.1002194	0.8764968
23	C	C11	4.8209259	-0.2967621	0.0679539
24	C	C12	3.1747598	0.9884856	1.2914124
25	C	C13	2.5013705	-0.9949577	0.0618099
26	C	C14	3.8260293	-1.1932749	-0.3347358
27	C	C15	4.4932035	0.7950547	0.8810437
28	H	H3	2.9121752	1.8289941	1.9253138
29	H	H7	1.7444244	-1.7122365	-0.2396605
30	H	H8	4.0794398	-2.0491121	-0.9530178
31	H	H9	5.2643525	1.4926672	1.1939624
32	H	H10	5.8490931	-0.4499940	-0.2470322



Cartesian Coordinates (Angstroms)

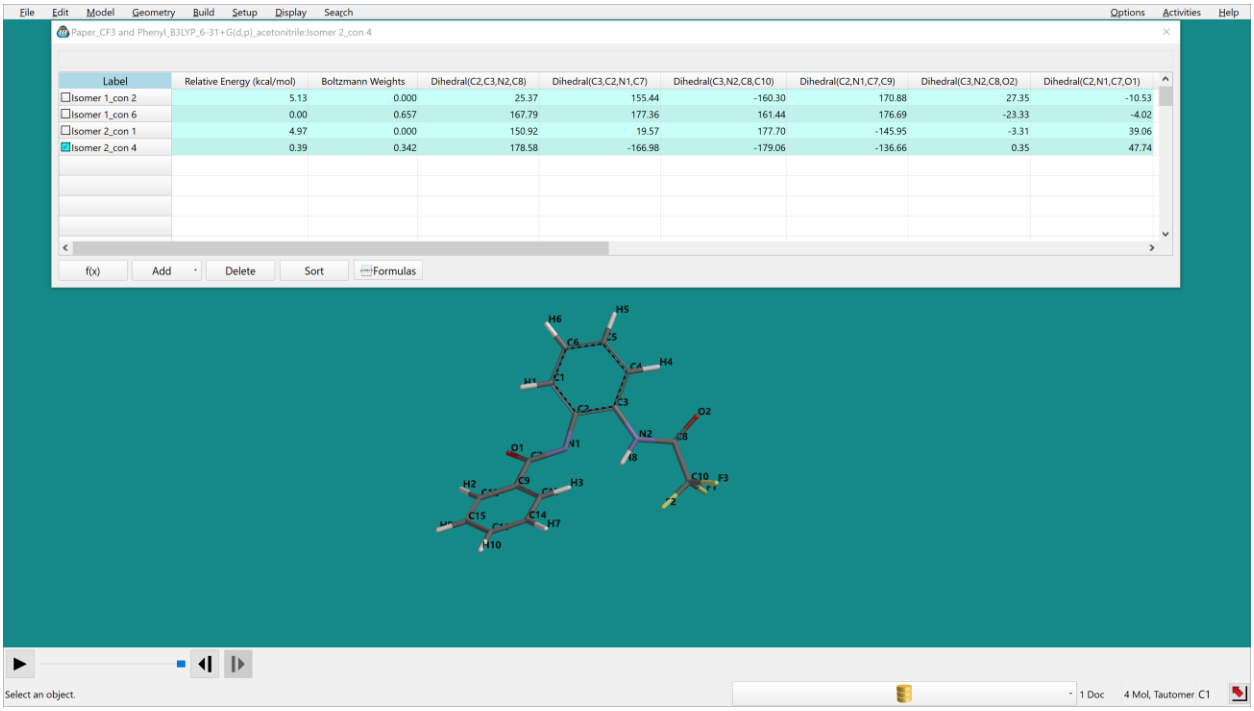
	Atom		X	Y	Z
1	H	H1	-0.9891750	-0.6440003	3.2123433
2	C	C1	-1.7284882	-0.4744268	2.4443946
3	C	C4	-3.7031740	-0.0134705	0.4517685
4	C	C2	-1.3157524	-0.2020245	1.1292364
5	C	C6	-3.0836058	-0.5114434	2.7425040
6	C	C5	-4.0713083	-0.2732206	1.7495803
7	C	C3	-2.3194355	0.0225156	0.0839285
8	H	H6	-3.3934475	-0.7205890	3.7617140
9	H	H5	-5.1213909	-0.2976163	2.0225741
10	H	H4	-4.4489673	0.1652333	-0.3112899
11	N	N1	-0.0081123	-0.1355241	0.7098903
12	H	H2	0.0745291	0.0928405	-0.2790238
13	N	N2	-1.8338351	0.3006606	-1.1342475
14	C	C7	1.1609194	-0.2506111	1.4508493
15	C	C8	-2.5727569	0.3054639	-2.2682980
16	C	C10	-1.8562372	1.0979035	-3.4005305
17	O	O1	1.1520871	-0.3685120	2.6767516
18	O	O2	-3.6292773	-0.2666763	-2.5293898
19	F	F1	-0.7002570	0.4914814	-3.7675417
20	F	F2	-1.5445712	2.3572635	-3.0087125
21	F	F3	-2.6272507	1.1972778	-4.4988362
22	C	C9	2.4328511	-0.2056052	0.6658759
23	C	C11	4.8984160	-0.1310685	-0.6716170
24	C	C12	2.5116227	-0.5465714	-0.6959678
25	C	C13	3.6034468	0.1614481	1.3521640
26	C	C14	4.8271875	0.2061817	0.6853772
27	C	C15	3.7408187	-0.5112449	-1.3576527
28	H	H3	1.6348587	-0.8740466	-1.2457025
29	H	H7	3.5407461	0.4167310	2.4045440
30	H	H8	5.7240185	0.5010962	1.2220687
31	H	H9	3.7933968	-0.7878751	-2.4062677
32	H	H10	5.8521441	-0.1015705	-1.1904871



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-3.4100010	-0.3991137	-1.3954387
2	C	C1	-3.2042738	-0.3776515	-0.3304546
3	C	C4	-2.5768524	-0.3227336	2.4000612
4	C	C2	-1.8224584	-0.4640501	0.0606692
5	C	C6	-4.2181277	-0.2574326	0.5933822
6	C	C5	-3.9028439	-0.2239820	1.9662128
7	C	C3	-1.5323879	-0.4508306	1.4860254
8	H	H6	-5.2509821	-0.1890832	0.2678772
9	H	H5	-4.6937121	-0.1367632	2.7044777
10	H	H4	-2.3586336	-0.3169295	3.4596169
11	N	N1	-0.9453312	-0.4652174	-0.9467208
12	N	N2	-0.2003357	-0.5971059	1.9116433
13	H	H8	0.3994356	-1.1585418	1.2944092
14	C	C7	0.3784091	-0.7973051	-0.9978190
15	C	C8	0.3332047	-0.0862768	3.0467531
16	C	C10	1.8233138	-0.4587674	3.2845236
17	O	O1	0.8516169	-1.7664429	-0.3636945
18	O	O2	-0.2099538	0.6320789	3.8757904
19	F	F1	2.5970344	0.6429217	3.1759634
20	F	F2	2.2975084	-1.3806783	2.4183249
21	F	F3	1.9777553	-0.9484697	4.5309400
22	C	C9	1.2078384	-0.0053360	-1.9470482
23	C	C11	2.8315767	1.4936901	-3.6701645
24	C	C12	0.6401846	0.9743948	-2.7806237
25	C	C13	2.5955444	-0.2273763	-1.9832722
26	C	C14	3.4020290	0.5183153	-2.8425097
27	C	C15	1.4509299	1.7205913	-3.6371348
28	H	H2	-0.4316652	1.1386041	-2.7612971

29	H	H3	3.0298598	-0.9799463	-1.3337459
30	H	H7	4.4735054	0.3429096	-2.8663374
31	H	H9	1.0063831	2.4734212	-4.2811831
32	H	H10	3.4614292	2.0731069	-4.3392260



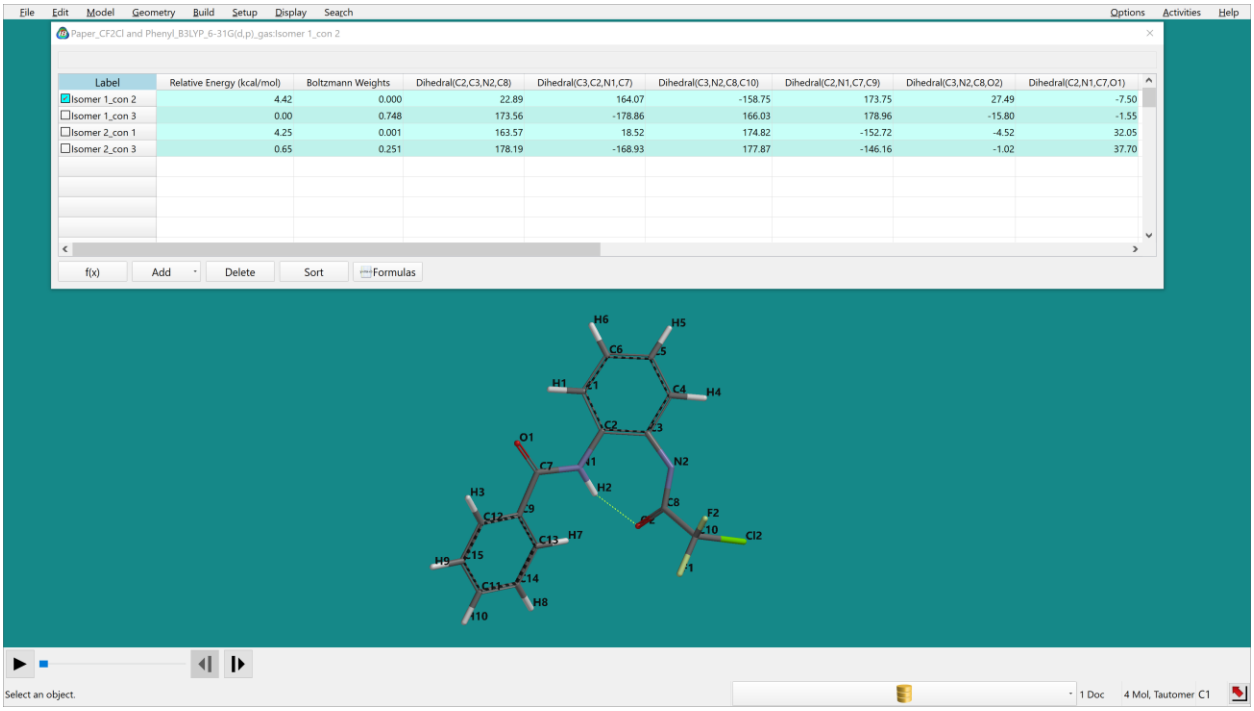
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.2226608	2.0571597	0.0247508
2	C	C1	-1.8535914	1.6702988	0.9668055
3	C	C4	-0.8677433	0.6363706	3.4123089
4	C	C2	-0.6432607	0.9012247	0.9649691
5	C	C6	-2.5332260	1.9083767	2.1419939
6	C	C5	-2.0408259	1.3972543	3.3623574
7	C	C3	-0.1662775	0.3790617	2.2358005
8	H	H6	-3.4504778	2.4884317	2.1310614
9	H	H5	-2.5810896	1.5910073	4.2836807
10	H	H4	-0.5056671	0.2503904	4.3545462
11	N	N1	0.0637540	0.5809052	-0.1192758
12	N	N2	1.0140262	-0.3625396	2.1616355
13	H	H8	1.3746601	-0.4521723	1.2117122
14	C	C7	-0.0974349	1.1986653	-1.3521630
15	C	C8	1.7045328	-0.9446376	3.1691283
16	C	C10	2.9989091	-1.6785083	2.7204199
17	O	O1	-0.1406087	2.4294146	-1.4641626
18	O	O2	1.4309261	-0.9456316	4.3619337
19	F	F1	4.0793788	-1.0689198	3.2509782
20	F	F2	3.1639238	-1.7134801	1.3778548
21	F	F3	2.9847454	-2.9496219	3.1655872
22	C	C9	-0.1118111	0.2899635	-2.5352140
23	C	C11	-0.1867314	-1.3612459	-4.7988723

24	C	C12	-0.3199471	0.8445954	-3.8098971
25	C	C13	0.0555577	-1.0993899	-2.4034613
26	C	C14	0.0190550	-1.9199458	-3.5327023
27	C	C15	-0.3578179	0.0224013	-4.9352683
28	H	H2	-0.4527160	1.9172018	-3.9052466
29	H	H3	0.2210074	-1.5306777	-1.4220309
30	H	H7	0.1539537	-2.9921803	-3.4251526
31	H	H9	-0.5192681	0.4568773	-5.9174363
32	H	H10	-0.2132748	-2.0006494	-5.6766411

Table S9. Dihedral Angles and Atom Coordinates for the amidyl radical conformers of 1y.

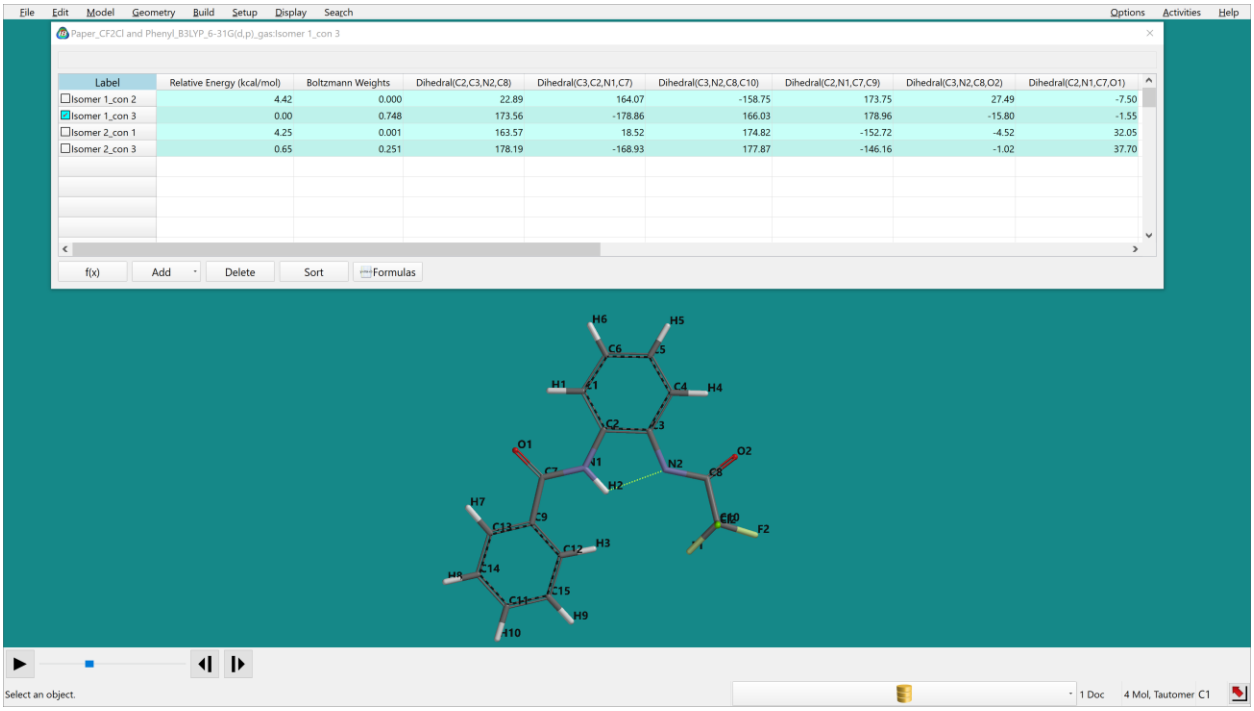
Gas Phase



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-1.3812288	-0.0265381	2.9669381
2	C	C1	-2.0846828	-0.1024700	2.1513365
3	C	C4	-3.9444390	-0.2779755	0.0525198
4	C	C2	-1.5920921	-0.0931775	0.8311466
5	C	C6	-3.4434689	-0.2173494	2.4034456
6	C	C5	-4.3846707	-0.3178237	1.3497332
7	C	C3	-2.5506246	-0.1403608	-0.2744446
8	H	H6	-3.7848368	-0.2402213	3.4339926
9	H	H5	-5.4429197	-0.4145538	1.5695759
10	H	H4	-4.6288061	-0.3238641	-0.7873622
11	N	N1	-0.2407945	-0.0631924	0.5428338
12	H	H2	0.0081079	-0.3746991	-0.3979921
13	N	N2	-2.3015181	0.0263411	-1.5776823

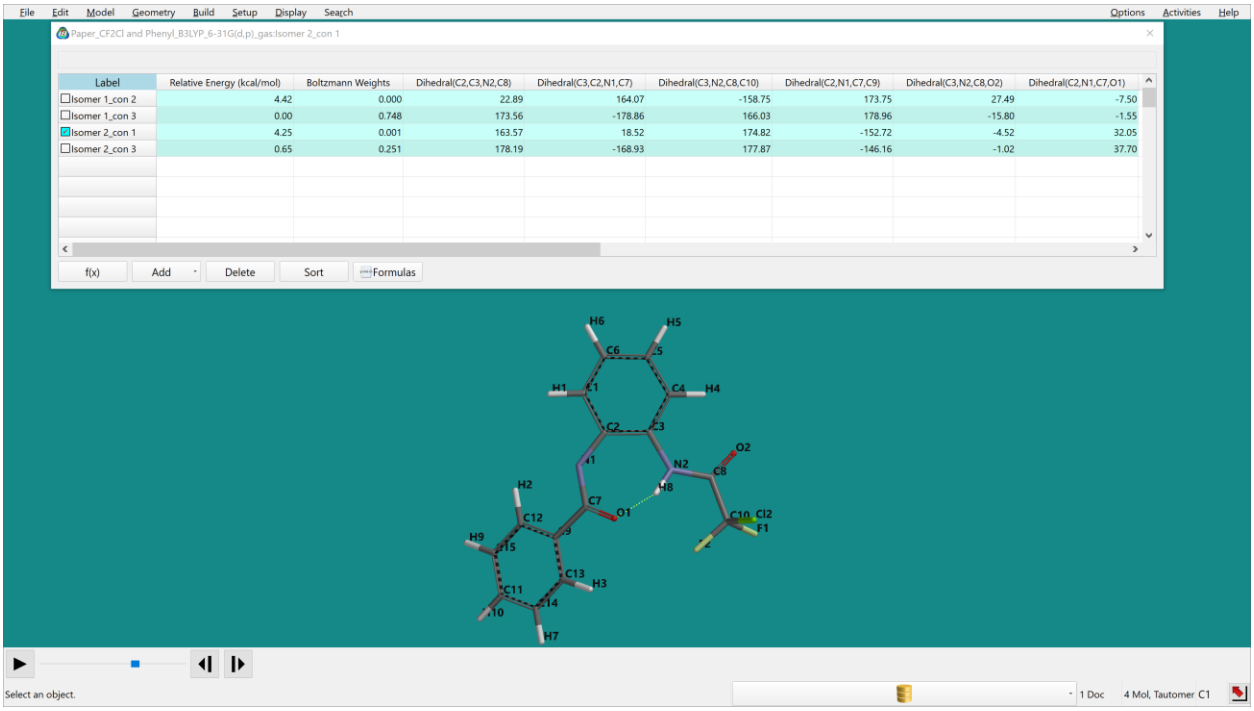
14	C	C7	0.8026115	0.2876891	1.4081440
15	C	C8	-1.1993766	-0.1096336	-2.3238271
16	C	C10	-1.2759391	0.6824896	-3.6576664
17	O	O1	0.5959327	0.7482438	2.5248446
18	O	O2	-0.2205187	-0.8434874	-2.1342772
19	Cl	Cl2	-2.2104921	-0.2142168	-4.8992677
20	F	F1	-0.0332828	0.9018821	-4.1301163
21	F	F2	-1.8557695	1.8906287	-3.4645327
22	C	C9	2.1906816	0.0950701	0.8794668
23	C	C11	4.8572885	-0.1814171	0.0567926
24	C	C12	3.2233434	0.7374217	1.5838141
25	C	C13	2.5081725	-0.6954323	-0.2376717
26	C	C14	3.8375495	-0.8317544	-0.6419647
27	C	C15	4.5468442	0.6042114	1.1719746
28	H	H3	2.9648767	1.3350493	2.4510716
29	H	H7	1.7422007	-1.2177579	-0.8001803
30	H	H8	4.0723446	-1.4470824	-1.5050260
31	H	H9	5.3361038	1.1113031	1.7189338
32	H	H10	5.8894034	-0.2873224	-0.2645529



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-1.2143608	0.2560791	3.1976555
2	C	C1	-1.9074149	0.2365014	2.3691426
3	C	C4	-3.7383820	0.1918772	0.1870091
4	C	C2	-1.4100662	0.1205363	1.0605428
5	C	C6	-3.2780835	0.3305003	2.5661257
6	C	C5	-4.1906282	0.3133106	1.4794620
7	C	C3	-2.3337209	0.0861149	-0.0789548
8	H	H6	-3.6582474	0.4224006	3.5790931

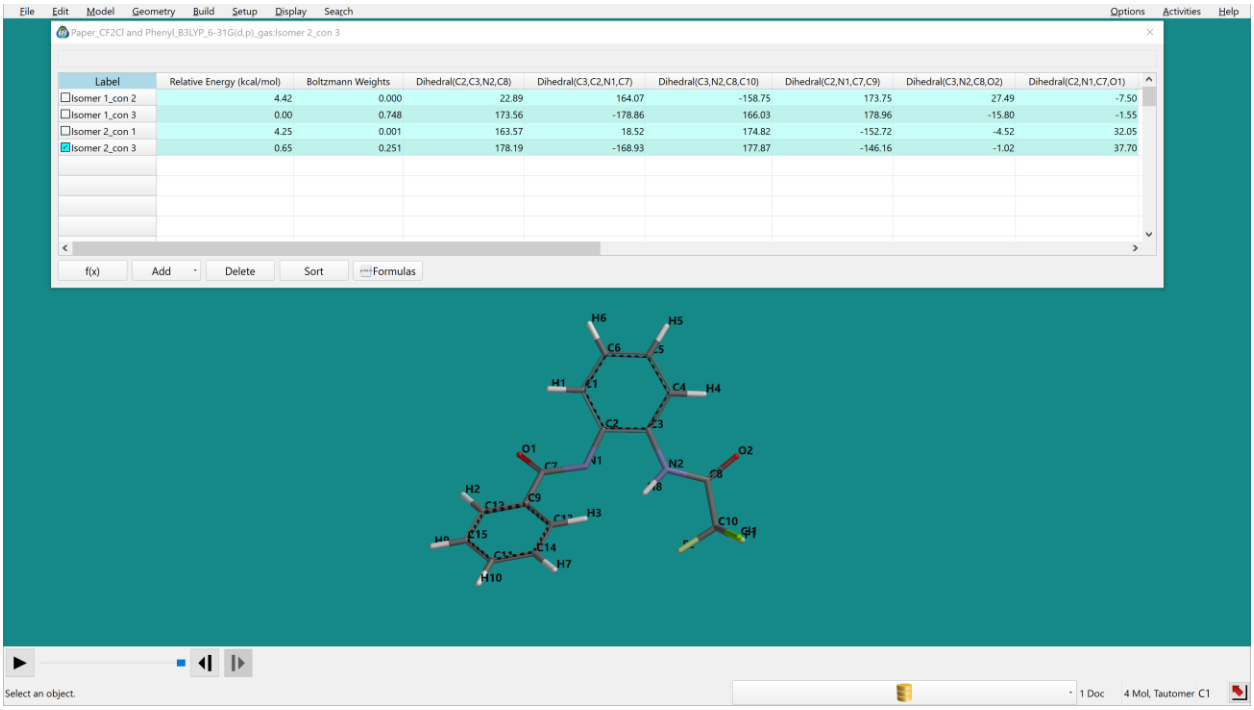
9	H	H5	-5.2556259	0.3940106	1.6736465
10	H	H4	-4.4229953	0.1607740	-0.6495029
11	N	N1	-0.0815203	0.0281160	0.7251635
12	H	H2	0.0437036	-0.0153925	-0.2846616
13	N	N2	-1.7406048	-0.0144470	-1.2755461
14	C	C7	1.0372467	0.0086556	1.5534101
15	C	C8	-2.4186664	-0.1887593	-2.4489425
16	C	C10	-1.5032064	0.0790780	-3.6805440
17	O	O1	0.9473574	0.1058842	2.7722486
18	O	O2	-3.5738528	-0.5374969	-2.6438144
19	Cl	Cl2	-1.2277993	1.8475965	-3.8871505
20	F	F1	-0.2947680	-0.5269515	-3.5390812
21	F	F2	-2.0632280	-0.4020447	-4.8014055
22	C	C9	2.3572199	-0.1267824	0.8568694
23	C	C11	4.9123593	-0.3520441	-0.2792207
24	C	C12	2.5034787	-0.4441281	-0.5046412
25	C	C13	3.5054122	0.0689567	1.6418590
26	C	C14	4.7740627	-0.0395230	1.0769507
27	C	C15	3.7760667	-0.5566254	-1.0661198
28	H	H3	1.6464969	-0.6255008	-1.1459227
29	H	H7	3.3775601	0.3050832	2.6925495
30	H	H8	5.6544442	0.1181813	1.6926179
31	H	H9	3.8769910	-0.8057236	-2.1178639
32	H	H10	5.9007717	-0.4382372	-0.7209742



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-3.2884706	-0.3237110	-1.4067288
2	C	C1	-3.1256999	-0.3195212	-0.3344836
3	C	C4	-2.5903943	-0.2964583	2.4122682

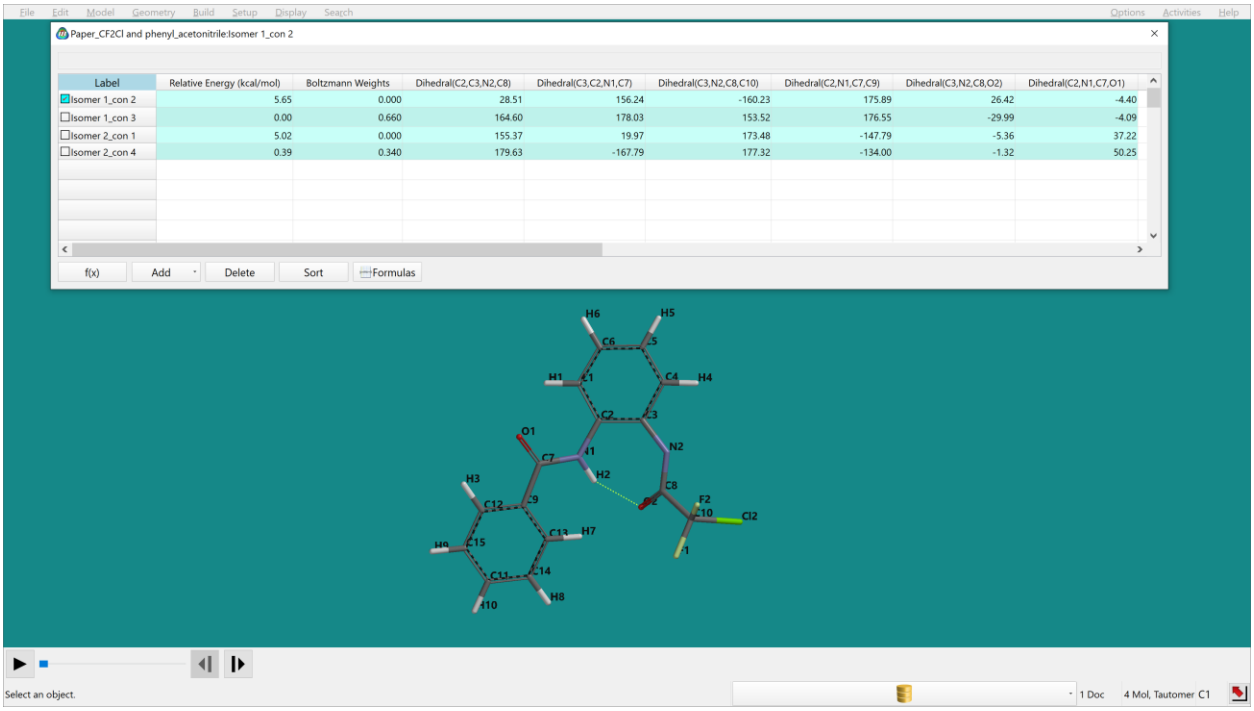
4	C	C2	-1.7533425	-0.3831905	0.0934085
5	C	C6	-4.1713878	-0.2349215	0.5540470
6	C	C5	-3.8976470	-0.2126734	1.9366597
7	C	C3	-1.5065003	-0.4058343	1.5312079
8	H	H6	-5.1943784	-0.1799095	0.1959813
9	H	H5	-4.7121067	-0.1404514	2.6509656
10	H	H4	-2.3993215	-0.2805187	3.4757024
11	N	N1	-0.8655785	-0.3304880	-0.9056826
12	N	N2	-0.1947588	-0.5532522	1.9886000
13	H	H8	0.4553400	-0.9784078	1.3059170
14	C	C7	0.4744866	-0.6073868	-0.9503505
15	C	C8	0.2584381	-0.2865270	3.2508875
16	C	C10	1.7496588	-0.6773397	3.4706241
17	O	O1	1.0176375	-1.4783189	-0.2417229
18	O	O2	-0.3674651	0.1939061	4.1776169
19	Cl	C12	1.8758440	-2.3618344	4.0727174
20	F	F1	2.2988953	0.1517050	4.3721205
21	F	F2	2.4684658	-0.5732385	2.3240998
22	C	C9	1.2457887	0.1282599	-1.9903224
23	C	C11	2.7749132	1.5188904	-3.8782240
24	C	C12	0.6228642	0.9960247	-2.9024843
25	C	C13	2.6398153	-0.0395065	-2.0326728
26	C	C14	3.3994264	0.6525619	-2.9737366
27	C	C15	1.3874250	1.6897741	-3.8404776
28	H	H2	-0.4550553	1.1096409	-2.8751661
29	H	H3	3.1059335	-0.7131340	-1.3216240
30	H	H7	4.4769076	0.5202957	-3.0020535
31	H	H9	0.9019327	2.3580331	-4.5455052
32	H	H10	3.3683341	2.0575315	-4.6115889



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.8247629	0.5654943	-1.3038903
2	C	C1	-2.7779422	0.2490010	-0.2699635
3	C	C4	-2.6191489	-0.5310654	2.4525874
4	C	C2	-1.4961161	0.2167074	0.3737208
5	C	C6	-3.9179656	-0.0997467	0.4219411
6	C	C5	-3.8414497	-0.4862509	1.7770734
7	C	C3	-1.4511204	-0.1891885	1.7714507
8	H	H6	-4.8819203	-0.0723326	-0.0764546
9	H	H5	-4.7472810	-0.7556915	2.3113338
10	H	H4	-2.5664384	-0.8233296	3.4921008
11	N	N1	-0.3187947	0.4810931	-0.1970943
12	N	N2	-0.1773412	-0.2019770	2.3352377
13	H	H8	0.5476810	0.0767649	1.6743661
14	C	C7	-0.2017336	1.0931409	-1.4486519
15	C	C8	0.1708665	-0.5020295	3.6179673
16	C	C10	1.7063505	-0.4600646	3.8694222
17	O	O1	-0.9559516	1.9913952	-1.8204034
18	O	O2	-0.5741094	-0.8033574	4.5316564
19	Cl	Cl1	2.3851215	-2.1143085	3.9307499
20	F	F1	1.9501715	0.1618509	5.0343474
21	F	F2	2.3567113	0.2333153	2.8915969
22	C	C9	0.9612556	0.6427085	-2.2709405
23	C	C11	3.0981186	-0.1548758	-3.8971615
24	C	C12	1.1495581	1.2317157	-3.5319924
25	C	C13	1.8509675	-0.3511438	-1.8326571
26	C	C14	2.9147700	-0.7475808	-2.6445711
27	C	C15	2.2129722	0.8351307	-4.3398012
28	H	H2	0.4533430	1.9977245	-3.8566573
29	H	H3	1.7090057	-0.8028175	-0.8573953
30	H	H7	3.6026297	-1.5131534	-2.2979353
31	H	H9	2.3544758	1.2955564	-5.3131354
32	H	H10	3.9280775	-0.4626858	-4.5268465

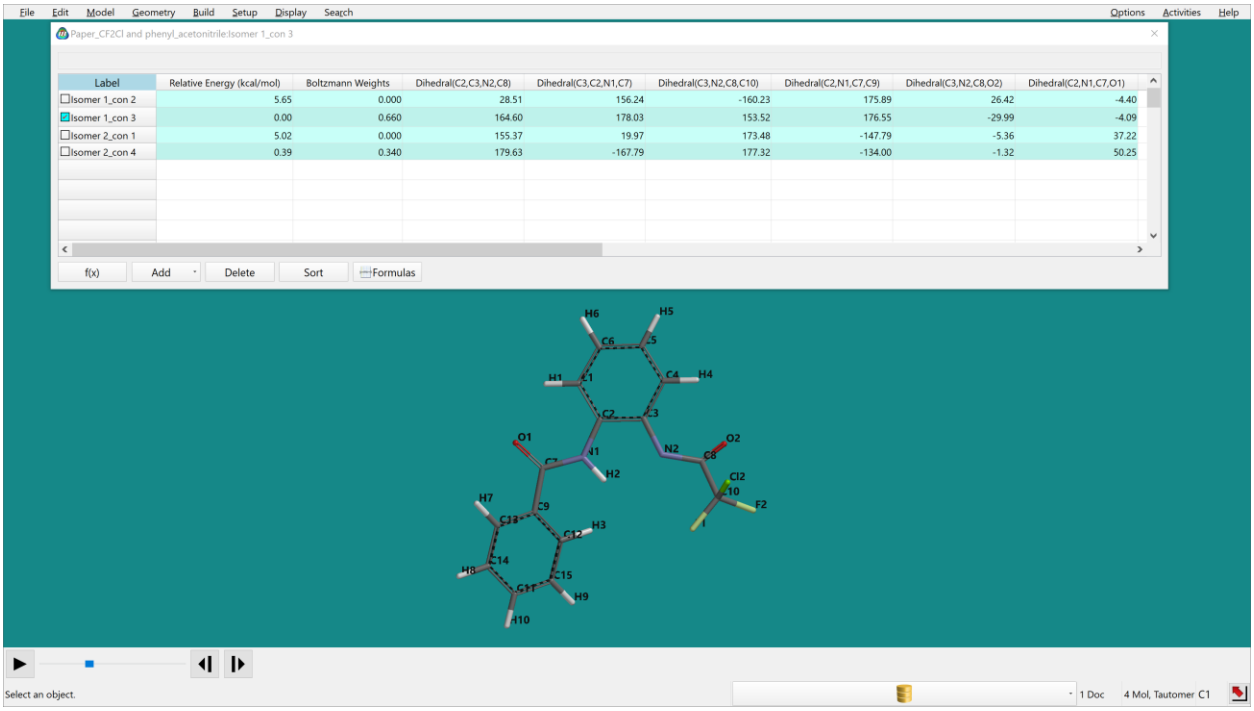
Acetonitrile



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-1.3669290	-0.0481445	2.9789534
2	C	C1	-2.0761903	-0.0807327	2.1654443
3	C	C4	-3.9687593	-0.1942554	0.0898883
4	C	C2	-1.6002533	-0.0959087	0.8447075
5	C	C6	-3.4384716	-0.1352605	2.4359682
6	C	C5	-4.3954550	-0.1941625	1.3923541
7	C	C3	-2.5719110	-0.1396801	-0.2489531
8	H	H6	-3.7688292	-0.1489148	3.4700476
9	H	H5	-5.4540132	-0.2382756	1.6262513
10	H	H4	-4.6687801	-0.2290595	-0.7378767
11	N	N1	-0.2451866	-0.0890377	0.5460433
12	H	H2	0.0086468	-0.5404582	-0.3315363
13	N	N2	-2.3128225	-0.0341040	-1.5582735
14	C	C7	0.7836190	0.3952738	1.3471159
15	C	C8	-1.2439956	-0.3459540	-2.2899062
16	C	C10	-1.2132751	0.3880540	-3.6588623
17	O	O1	0.5641263	0.9600914	2.4191347
18	O	O2	-0.3697588	-1.1985723	-2.0723349
19	Cl	Cl2	-2.1901240	-0.4805911	-4.8909463
20	F	F1	0.0597809	0.4688207	-4.1063244
21	F	F2	-1.6816257	1.6547061	-3.5547741
22	C	C9	2.1795720	0.2019575	0.8377066
23	C	C11	4.8604210	-0.0980102	0.0496231
24	C	C12	3.2233174	0.4301411	1.7522336
25	C	C13	2.4962535	-0.1731794	-0.4795617
26	C	C14	3.8296228	-0.3192215	-0.8685544

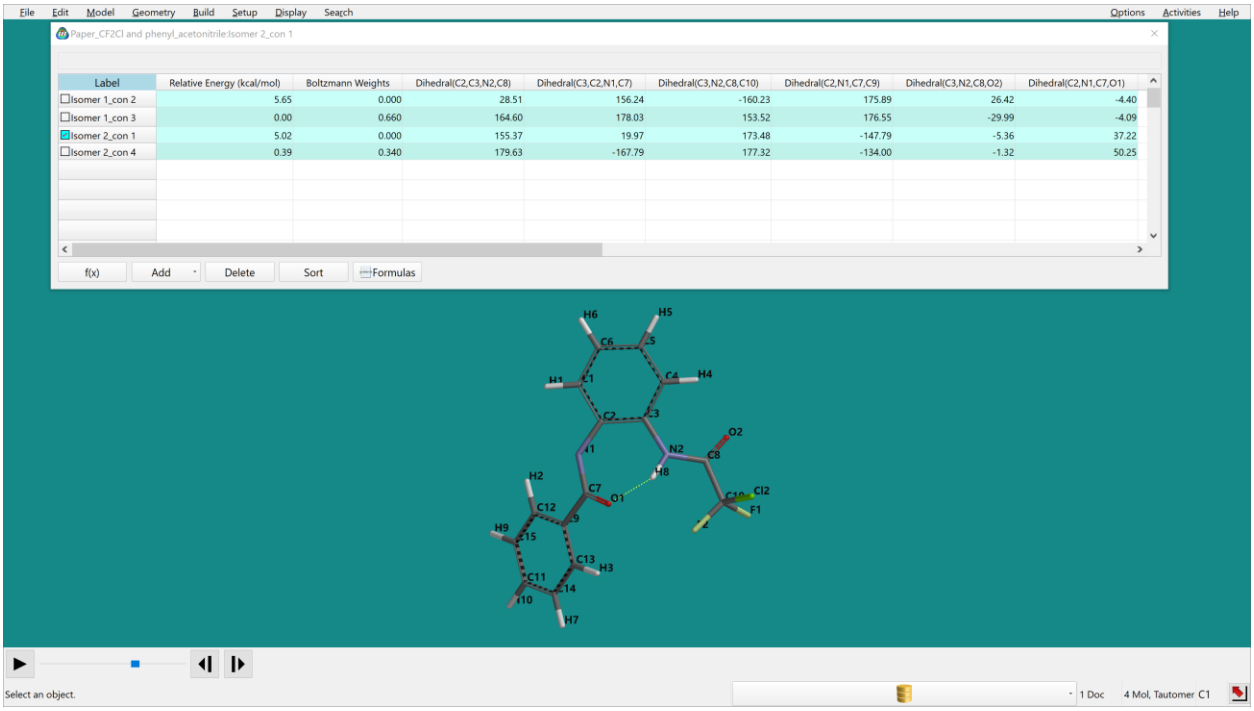
27	C	C15	4.5529882	0.2763465	1.3628243
28	H	H3	2.9784453	0.7208617	2.7678194
29	H	H7	1.7256702	-0.3430150	-1.2232533
30	H	H8	4.0595468	-0.6031745	-1.8910362
31	H	H9	5.3482708	0.4482782	2.0820767
32	H	H10	5.8960991	-0.2148187	-0.2559991



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-1.2280798	0.1744131	3.1777127
2	C	C1	-1.8979491	0.1767883	2.3309909
3	C	C4	-3.6898202	0.1987983	0.1262172
4	C	C2	-1.3730016	0.1062425	1.0309714
5	C	C6	-3.2732824	0.2560699	2.5118368
6	C	C5	-4.1699857	0.2738623	1.4108845
7	C	C3	-2.2810402	0.1063473	-0.1173367
8	H	H6	-3.6688168	0.3113475	3.5213308
9	H	H5	-5.2376965	0.3501616	1.5896202
10	H	H4	-4.3628978	0.2146965	-0.7217948
11	N	N1	-0.0344416	0.0165142	0.7219904
12	H	H2	0.1392203	-0.0150547	-0.2802639
13	N	N2	-1.7032116	0.0846149	-1.3246964
14	C	C7	1.0648833	0.0291060	1.5688744
15	C	C8	-2.3490705	-0.2157775	-2.4749699
16	C	C10	-1.6801853	0.4448718	-3.7177308
17	O	O1	0.9591415	0.2040361	2.7833816
18	O	O2	-3.3121306	-0.9558720	-2.6570284
19	Cl	Cl2	-2.1325714	2.1837975	-3.8174995
20	F	F1	-0.3282682	0.3556987	-3.6752528
21	F	F2	-2.0823629	-0.1641417	-4.8532286

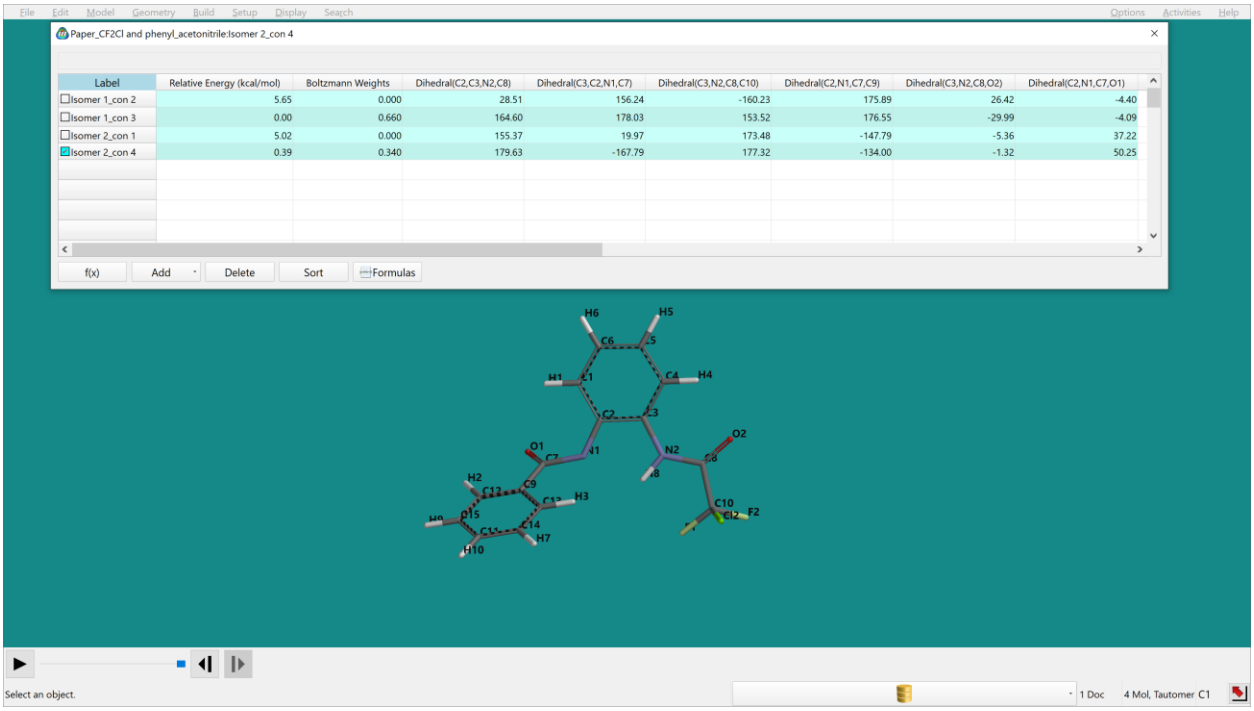
22	C	C9	2.3908858	-0.1692983	0.9060064
23	C	C11	4.9429611	-0.5121614	-0.2066804
24	C	C12	2.5454607	-0.8428461	-0.3182712
25	C	C13	3.5276465	0.3198244	1.5720329
26	C	C14	4.7950438	0.1562548	1.0145478
27	C	C15	3.8178085	-1.0150030	-0.8675205
28	H	H3	1.6908388	-1.2647142	-0.8382232
29	H	H7	3.4057319	0.8337695	2.5196042
30	H	H8	5.6661659	0.5484802	1.5308353
31	H	H9	3.9283217	-1.5470299	-1.8075543
32	H	H10	5.9307025	-0.6437964	-0.6387859



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-3.3737046	-0.3479743	-1.4076051
2	C	C1	-3.1772442	-0.3446574	-0.3407618
3	C	C4	-2.5728775	-0.3304265	2.3948094
4	C	C2	-1.7972290	-0.4239022	0.0593355
5	C	C6	-4.1998480	-0.2515210	0.5755933
6	C	C5	-3.8949093	-0.2386430	1.9516712
7	C	C3	-1.5173099	-0.4341751	1.4878670
8	H	H6	-5.2307008	-0.1874602	0.2429434
9	H	H5	-4.6921949	-0.1718871	2.6851841
10	H	H4	-2.3651795	-0.3371944	3.4560536
11	N	N1	-0.9174716	-0.3960089	-0.9457390
12	N	N2	-0.1887408	-0.5820504	1.9175402
13	H	H8	0.4243336	-1.0934188	1.2690966
14	C	C7	0.4078295	-0.7163908	-1.0082733
15	C	C8	0.3226122	-0.1641790	3.1024215
16	C	C10	1.7912209	-0.6165068	3.3503720

17	O	O1	0.9008465	-1.6762972	-0.3742367
18	O	O2	-0.2375337	0.4894040	3.9709705
19	Cl	Cl2	1.8299664	-2.1242726	4.3180122
20	F	F1	2.4452927	0.3503871	4.0266497
21	F	F2	2.4678868	-0.8275864	2.1943991
22	C	C9	1.2184817	0.0778065	-1.9718114
23	C	C11	2.8093804	1.5748435	-3.7278154
24	C	C12	0.6274433	1.0132918	-2.8396208
25	C	C13	2.6129311	-0.1005299	-1.9907928
26	C	C14	3.4032894	0.6450229	-2.8649968
27	C	C15	1.4219147	1.7575983	-3.7130064
28	H	H2	-0.4491719	1.1430928	-2.8353917
29	H	H3	3.0648896	-0.8186318	-1.3149604
30	H	H7	4.4801509	0.5049584	-2.8730497
31	H	H9	0.9593936	2.4741131	-4.3851757
32	H	H10	3.4262523	2.1531954	-4.4096828



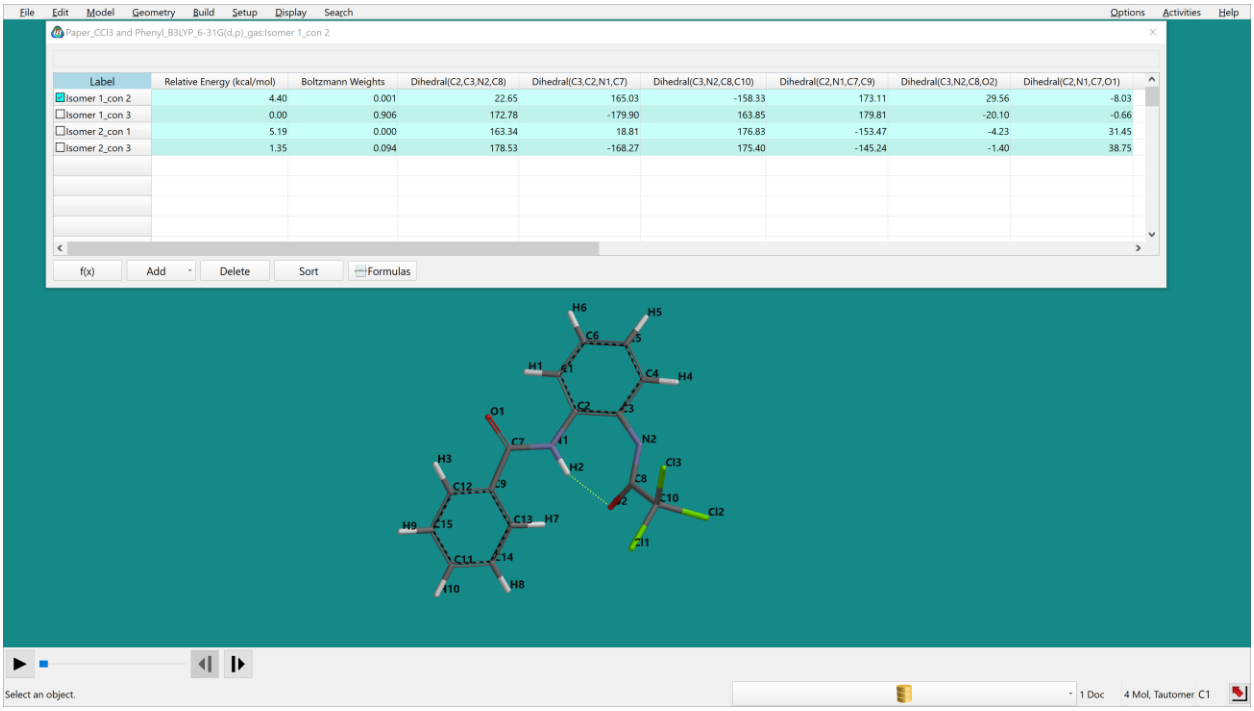
Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	2.2229293	-2.0392392	0.0003006
2	C	C1	1.8535871	-1.6649770	0.9478967
3	C	C4	0.8737224	-0.6468649	3.4021490
4	C	C2	0.6241908	-0.9264995	0.9595560
5	C	C6	2.5531329	-1.8834495	2.1151548
6	C	C5	2.0631963	-1.3807974	3.3399764
7	C	C3	0.1515730	-0.4083987	2.2340135
8	H	H6	3.4843167	-2.4405968	2.0942431
9	H	H5	2.6189167	-1.5587770	4.2553133
10	H	H4	0.5145433	-0.2675019	4.3481264
11	N	N1	-0.1043663	-0.6327934	-0.1172975

12	N	N2	-1.0427401	0.3108436	2.1708169
13	H	H8	-1.4207304	0.3803926	1.2259762
14	C	C7	0.0620565	-1.2389216	-1.3541948
15	C	C8	-1.7227299	0.9004137	3.1826600
16	C	C10	-2.9907997	1.6750191	2.7196002
17	O	O1	0.1023009	-2.4689829	-1.4781005
18	O	O2	-1.4355410	0.9025773	4.3713963
19	Cl	Cl2	-2.6470483	3.4254981	2.5602125
20	F	F1	-3.4642736	1.2179120	1.5311182
21	F	F2	-3.9688025	1.5083068	3.6331649
22	C	C9	0.0894722	-0.3180602	-2.5275542
23	C	C11	0.1968355	1.3602342	-4.7698785
24	C	C12	0.3414062	-0.8544476	-3.8021096
25	C	C13	-0.1056456	1.0665191	-2.3850819
26	C	C14	-0.0536567	1.9003706	-3.5037935
27	C	C15	0.3958612	-0.0185731	-4.9167437
28	H	H2	0.4975859	-1.9231456	-3.9062698
29	H	H3	-0.3084716	1.4838923	-1.4051049
30	H	H7	-0.2111480	2.9686337	-3.3877049
31	H	H9	0.5934123	-0.4388627	-5.8985075
32	H	H10	0.2369145	2.0102762	-5.6393337

Table S10. Dihedral Angles and Atom Coordinates for the Amidyl Radical Conformers of 1z.

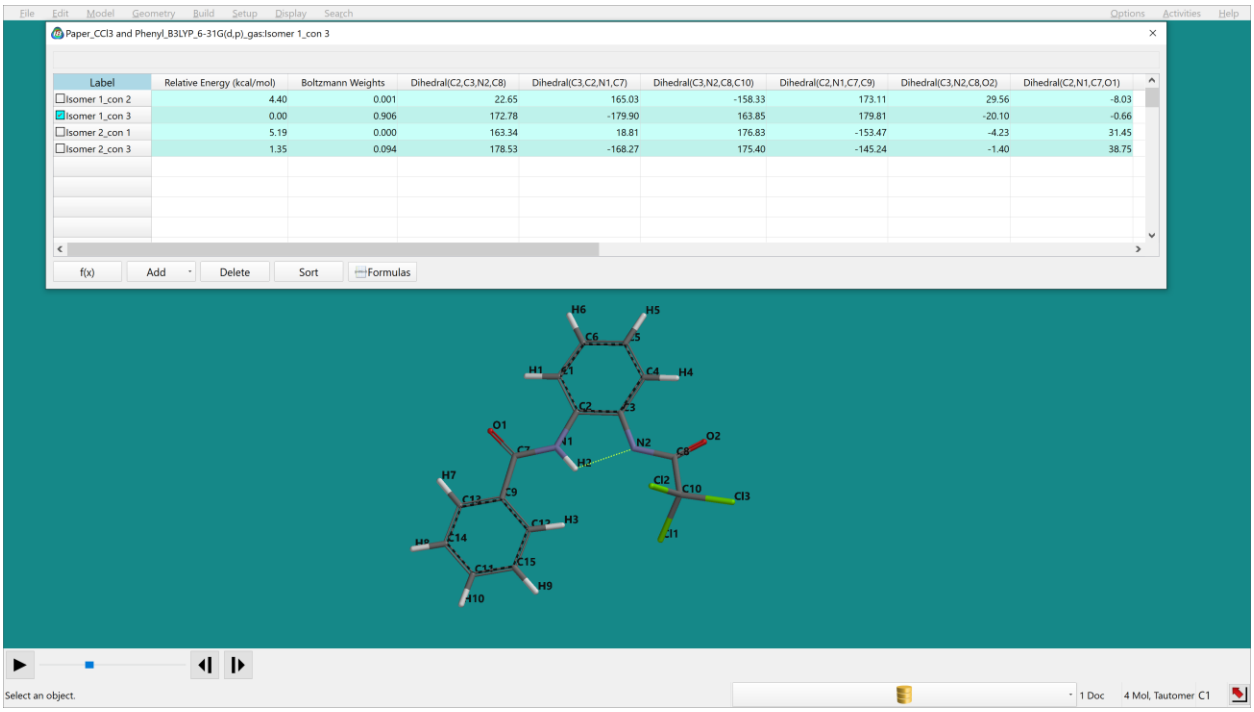
Gas Phase



Cartesian Coordinates (Angstroms)

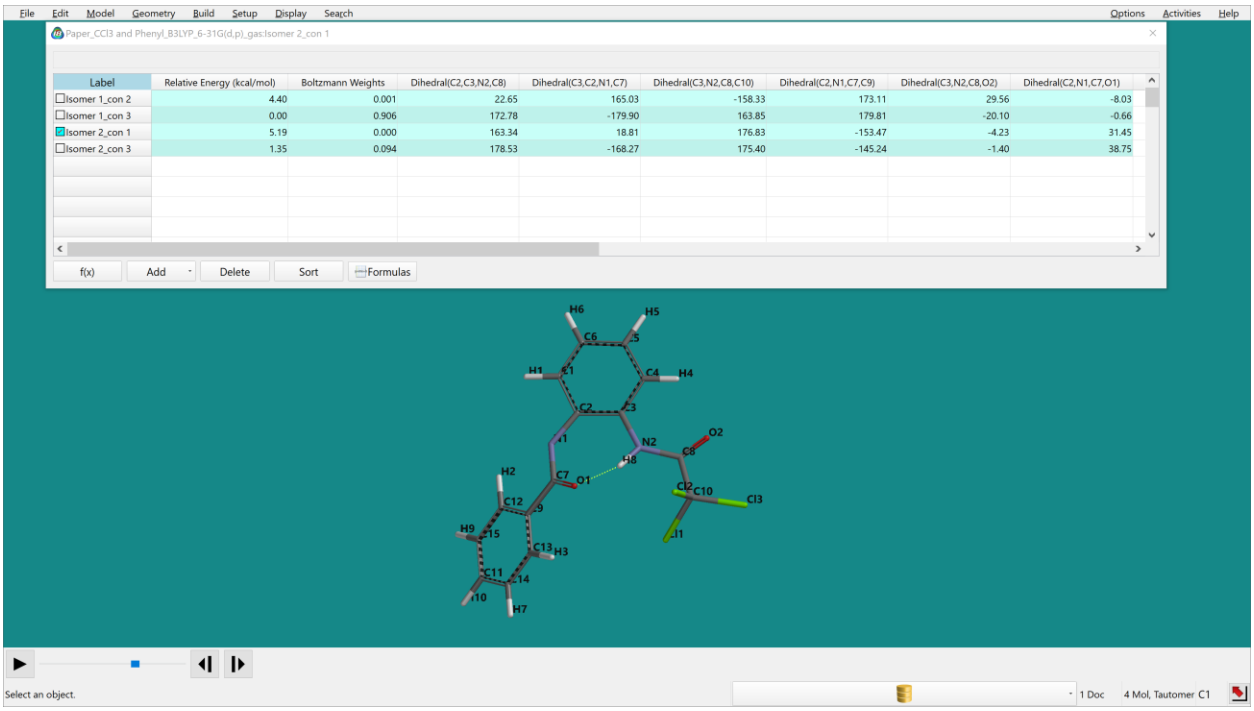
	Atom	X	Y	Z
1	H H1	-1.3905946	-0.0242832	2.9700504
2	C C1	-2.0928109	-0.1055976	2.1537733

3	C	C4	-3.9477086	-0.2995679	0.0532711
4	C	C2	-1.5995541	-0.0924667	0.8350139
5	C	C6	-3.4520662	-0.2304920	2.4046943
6	C	C5	-4.3900243	-0.3404819	1.3505799
7	C	C3	-2.5551105	-0.1479589	-0.2701269
8	H	H6	-3.7944155	-0.2544521	3.4349152
9	H	H5	-5.4477997	-0.4460519	1.5685678
10	H	H4	-4.6307162	-0.3540119	-0.7872630
11	N	N1	-0.2467509	-0.0578242	0.5461216
12	H	H2	0.0028976	-0.3713097	-0.3926566
13	N	N2	-2.3009069	0.0197721	-1.5719389
14	C	C7	0.7971276	0.2821705	1.4122400
15	C	C8	-1.1992030	-0.1023411	-2.3191042
16	C	C10	-1.2720901	0.7004881	-3.6625240
17	O	O1	0.5950498	0.7379172	2.5320678
18	O	O2	-0.2379905	-0.8563043	-2.1312697
19	Cl	Cl2	-2.1490519	-0.3235329	-4.8616022
20	C	C9	2.1843585	0.0817820	0.8820096
21	C	C11	4.8484838	-0.2103900	0.0557633
22	C	C12	3.2216657	0.7174939	1.5851724
23	C	C13	2.4959951	-0.7105241	-0.2355111
24	C	C14	3.8239617	-0.8545100	-0.6417352
25	C	C15	4.5439517	0.5765048	1.1717034
26	H	H3	2.9675371	1.3159366	2.4531435
27	H	H7	1.7263969	-1.2288365	-0.7969456
28	H	H8	4.0538877	-1.4714737	-1.5050061
29	H	H9	5.3369436	1.0783486	1.7181289
30	H	H10	5.8795842	-0.3226019	-0.2667786
31	Cl	Cl1	0.3800757	1.0427054	-4.2530764
32	Cl	Cl3	-2.1511230	2.2518933	-3.4316779



Cartesian Coordinates (Angstroms)

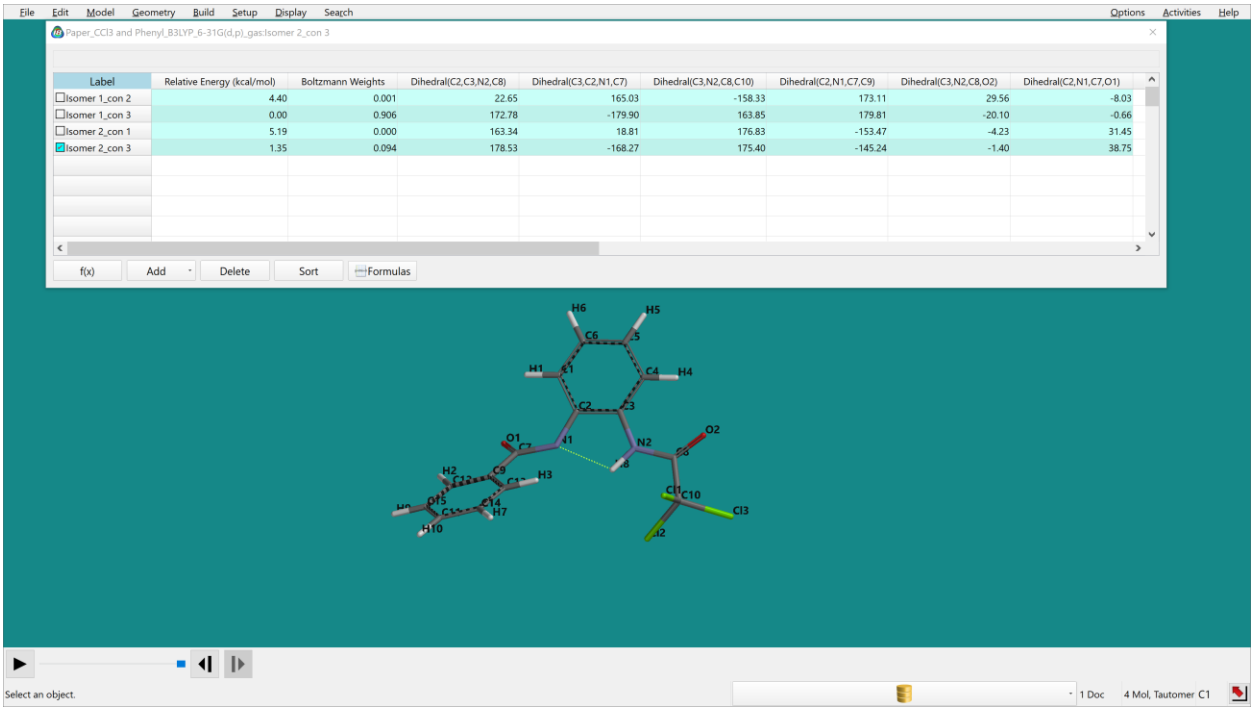
	Atom		X	Y	Z
1	H	H1	-1.2198843	0.2900246	3.1927964
2	C	C1	-1.9133507	0.2600297	2.3649602
3	C	C4	-3.7440168	0.1935028	0.1868755
4	C	C2	-1.4162848	0.1216472	1.0591659
5	C	C6	-3.2842198	0.3641721	2.5622368
6	C	C5	-4.1966345	0.3358244	1.4772886
7	C	C3	-2.3402409	0.0725899	-0.0774645
8	H	H6	-3.6627620	0.4731951	3.5741262
9	H	H5	-5.2613659	0.4236315	1.6697391
10	H	H4	-4.4296213	0.1524860	-0.6485742
11	N	N1	-0.0853851	0.0255674	0.7262760
12	H	H2	0.0437470	-0.0343565	-0.2812718
13	N	N2	-1.7539024	-0.0479534	-1.2744170
14	C	C7	1.0311756	0.0368356	1.5556868
15	C	C8	-2.4380180	-0.2532400	-2.4398393
16	C	C10	-1.5365785	0.0532842	-3.6930187
17	O	O1	0.9381572	0.1544211	2.7727337
18	O	O2	-3.5675962	-0.6836010	-2.6000322
19	Cl	Cl2	-0.8034076	1.6913453	-3.5227332
20	C	C9	2.3569598	-0.0930574	0.8666174
21	C	C11	4.9225232	-0.3024382	-0.2513996
22	C	C12	2.5156216	-0.4016993	-0.4953287
23	C	C13	3.4986606	0.1028026	1.6608408
24	C	C14	4.7722553	0.0012319	1.1054167
25	C	C15	3.7928663	-0.5054202	-1.0479853
26	H	H3	1.6652454	-0.5805022	-1.1458982
27	H	H7	3.3616672	0.3337062	2.7115277
28	H	H8	5.6472250	0.1580829	1.7290869
29	H	H9	3.9023323	-0.7460057	-2.1009355
30	H	H10	5.9146135	-0.3828096	-0.6860357
31	Cl	Cl1	-0.2201279	-1.1921403	-3.7581275
32	Cl	Cl3	-2.4896536	-0.0211567	-5.1923131



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-3.2919113	-0.3543022	-1.3918296
2	C	C1	-3.1332497	-0.3332149	-0.3191890
3	C	C4	-2.6073032	-0.2720512	2.4288082
4	C	C2	-1.7620458	-0.3884228	0.1142295
5	C	C6	-4.1819716	-0.2384855	0.5640110
6	C	C5	-3.9121885	-0.1958659	1.9472958
7	C	C3	-1.5186223	-0.3931491	1.5537232
8	H	H6	-5.2040437	-0.1917639	0.2021034
9	H	H5	-4.7292198	-0.1154698	2.6578374
10	H	H4	-2.4221416	-0.2445428	3.4926648
11	N	N1	-0.8723396	-0.3461165	-0.8837574
12	N	N2	-0.2082837	-0.5417761	2.0117761
13	H	H8	0.4287480	-0.9915465	1.3329453
14	C	C7	0.4664959	-0.6246894	-0.9279518
15	C	C8	0.2474892	-0.2560868	3.2711591
16	C	C10	1.7680270	-0.6103713	3.4879033
17	O	O1	1.0136126	-1.4825351	-0.2063668
18	O	O2	-0.3975182	0.2399756	4.1728175
19	Cl	Cl2	2.0340351	-2.3581684	3.1304933
20	C	C9	1.2337659	0.0891869	-1.9867442
21	C	C11	2.7545444	1.4365051	-3.9131806
22	C	C12	0.6091756	0.9489658	-2.9050402
23	C	C13	2.6253829	-0.0929344	-2.0428035
24	C	C14	3.3807204	0.5770902	-3.0032142
25	C	C15	1.3694252	1.6216855	-3.8617549
26	H	H2	-0.4672587	1.0731551	-2.8671426
27	H	H3	3.0930290	-0.7609512	-1.3276051
28	H	H7	4.4562682	0.4322259	-3.0430747

29	H	H9	0.8821496	2.2848274	-4.5703585
30	H	H10	3.3445823	1.9580913	-4.6614208
31	Cl	Cl1	2.7693206	0.4014412	2.3727454
32	Cl	Cl3	2.2313261	-0.2707063	5.1709207

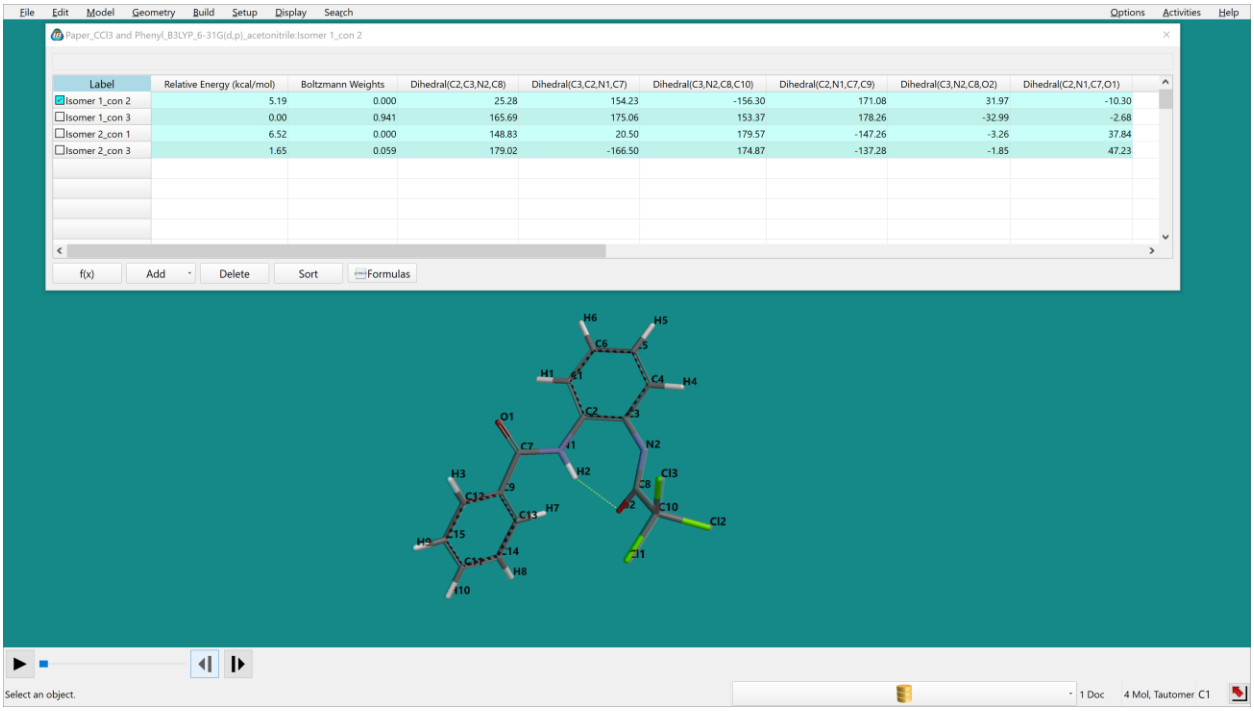


Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.8151786	0.4919590	-1.3226027
2	C	C1	-2.7713948	0.2004619	-0.2811319
3	C	C4	-2.6239496	-0.5132499	2.4584779
4	C	C2	-1.4952014	0.2020859	0.3735202
5	C	C6	-3.9126897	-0.1479739	0.4083197
6	C	C5	-3.8411166	-0.5008481	1.7726783
7	C	C3	-1.4530992	-0.1717229	1.7803944
8	H	H6	-4.8724465	-0.1468196	-0.0987997
9	H	H5	-4.7471838	-0.7694199	2.3070256
10	H	H4	-2.5783059	-0.7821380	3.5041904
11	N	N1	-0.3199384	0.4736524	-0.1980520
12	N	N2	-0.1822845	-0.1479374	2.3497879
13	H	H8	0.5356641	0.1316715	1.6819487
14	C	C7	-0.2058072	1.0709077	-1.4556399
15	C	C8	0.1621161	-0.4194124	3.6405068
16	C	C10	1.7145488	-0.4047530	3.9054331
17	O	O1	-0.9583690	1.9687788	-1.8321560
18	O	O2	-0.6034498	-0.7120655	4.5374791
19	Cl	Cl1	2.3678683	-1.9825597	3.3014677
20	C	C9	0.9523221	0.6101468	-2.2800471
21	C	C11	3.0747637	-0.2118621	-3.9125159
22	C	C12	1.1449815	1.1989463	-3.5402957
23	C	C13	1.8307410	-0.3949785	-1.8449142

24	C	C14	2.8868255	-0.8043105	-2.6605106
25	C	C15	2.2017058	0.7905600	-4.3510706
26	H	H2	0.4579416	1.9745295	-3.8618167
27	H	H3	1.6855207	-0.8470388	-0.8701159
28	H	H7	3.5643463	-1.5808071	-2.3177701
29	H	H9	2.3475192	1.2518499	-5.3234121
30	H	H10	3.8988917	-0.5294156	-4.5450654
31	Cl	Cl2	2.5284200	0.9495104	3.0272466
32	Cl	Cl3	2.0262384	-0.2477470	5.6474399

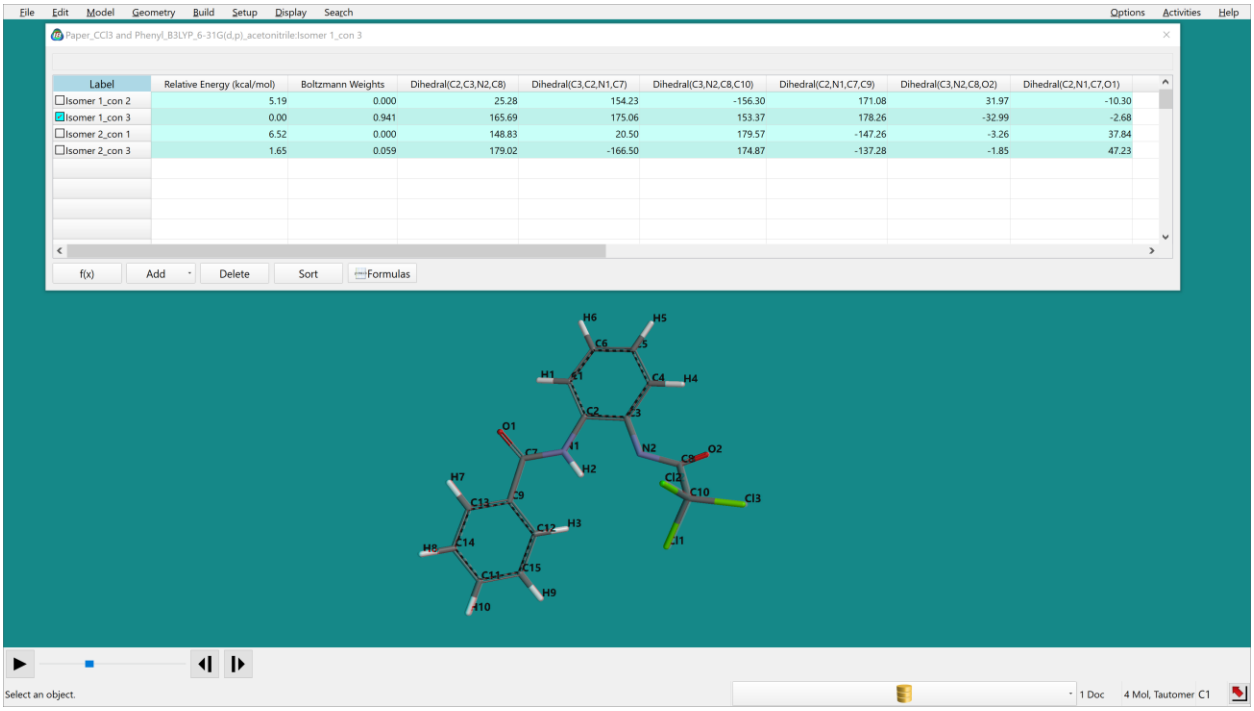
Acetonitrile



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-1.3733814	-0.2944662	2.9489892
2	C	C1	-2.0795086	-0.2821956	2.1305242
3	C	C4	-3.9543340	-0.2990616	0.0343013
4	C	C2	-1.6011356	-0.1692627	0.8165872
5	C	C6	-3.4401305	-0.4128421	2.3847727
6	C	C5	-4.3858217	-0.4301524	1.3299074
7	C	C3	-2.5609528	-0.1395213	-0.2832317
8	H	H6	-3.7763366	-0.5220556	3.4111832
9	H	H5	-5.4424300	-0.5433324	1.5489229
10	H	H4	-4.6496910	-0.2921287	-0.7982193
11	N	N1	-0.2452282	-0.1158095	0.5289389
12	H	H2	0.0259578	-0.4509998	-0.3952295
13	N	N2	-2.2918776	0.1281821	-1.5651613
14	C	C7	0.7689135	0.3523502	1.3540102
15	C	C8	-1.1935047	0.0165761	-2.3129059
16	C	C10	-1.1914487	0.9726375	-3.5578536

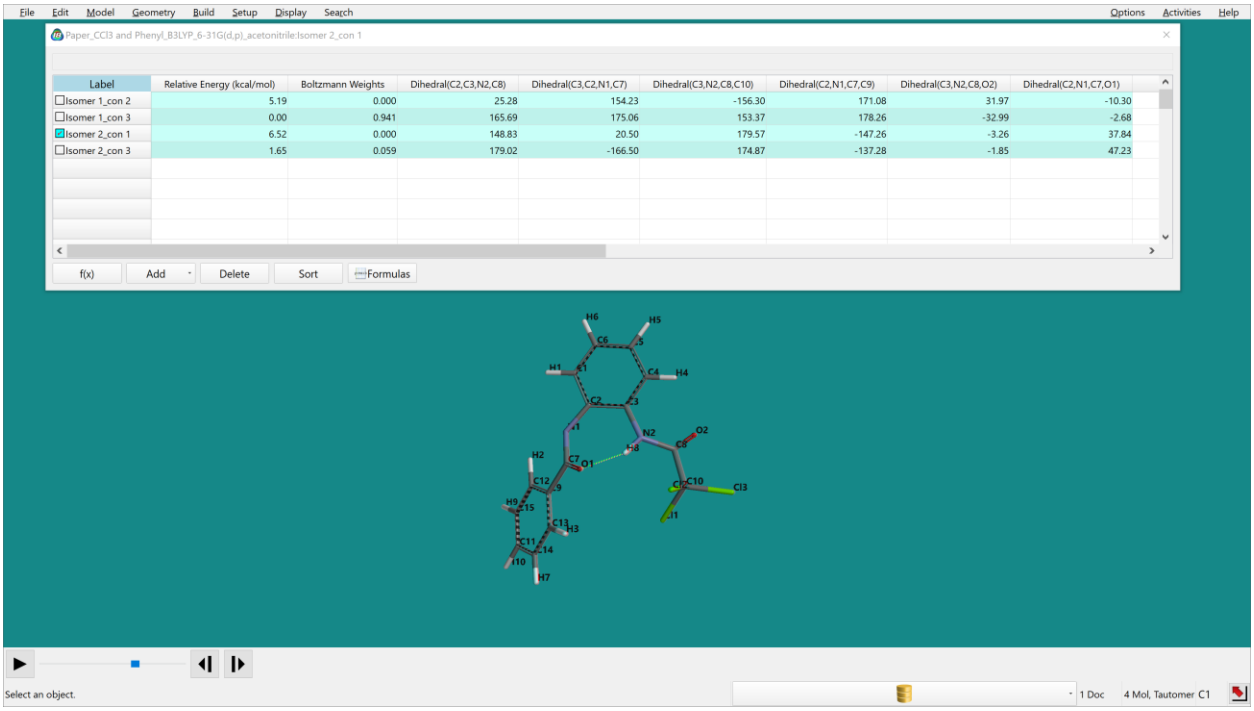
17	O	O1	0.5428362	0.9575707	2.4025586
18	O	O2	-0.2876020	-0.8210423	-2.2168314
19	Cl	Cl2	-2.0474953	0.1159789	-4.9030793
20	C	C9	2.1587608	0.0988455	0.8645491
21	C	C11	4.8095196	-0.3147117	0.0563065
22	C	C12	3.1631295	1.0061426	1.2413371
23	C	C13	2.4932579	-1.0235928	0.0882606
24	C	C14	3.8168544	-1.2298833	-0.3080731
25	C	C15	4.4805094	0.8042697	0.8310198
26	H	H3	2.8998049	1.8673527	1.8464698
27	H	H7	1.7387413	-1.7554164	-0.1834591
28	H	H8	4.0712192	-2.1061874	-0.8966508
29	H	H9	5.2498569	1.5163638	1.1143610
30	H	H10	5.8368310	-0.4744585	-0.2582427
31	Cl	Cl1	0.4948594	1.3205196	-4.0522738
32	Cl	Cl3	-2.0301727	2.5203310	-3.2017880



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-1.2447748	0.1558453	3.1890626
2	C	C1	-1.9145095	0.1619916	2.3421602
3	C	C4	-3.7049578	0.1974277	0.1394321
4	C	C2	-1.3899007	0.0809641	1.0436388
5	C	C6	-3.2900174	0.2570368	2.5238690
6	C	C5	-4.1855794	0.2824516	1.4239575
7	C	C3	-2.2971485	0.0841801	-0.1035236
8	H	H6	-3.6839230	0.3184472	3.5336530
9	H	H5	-5.2525616	0.3711666	1.6014275
10	H	H4	-4.3775335	0.2174462	-0.7090488
11	N	N1	-0.0491228	-0.0174211	0.7364975

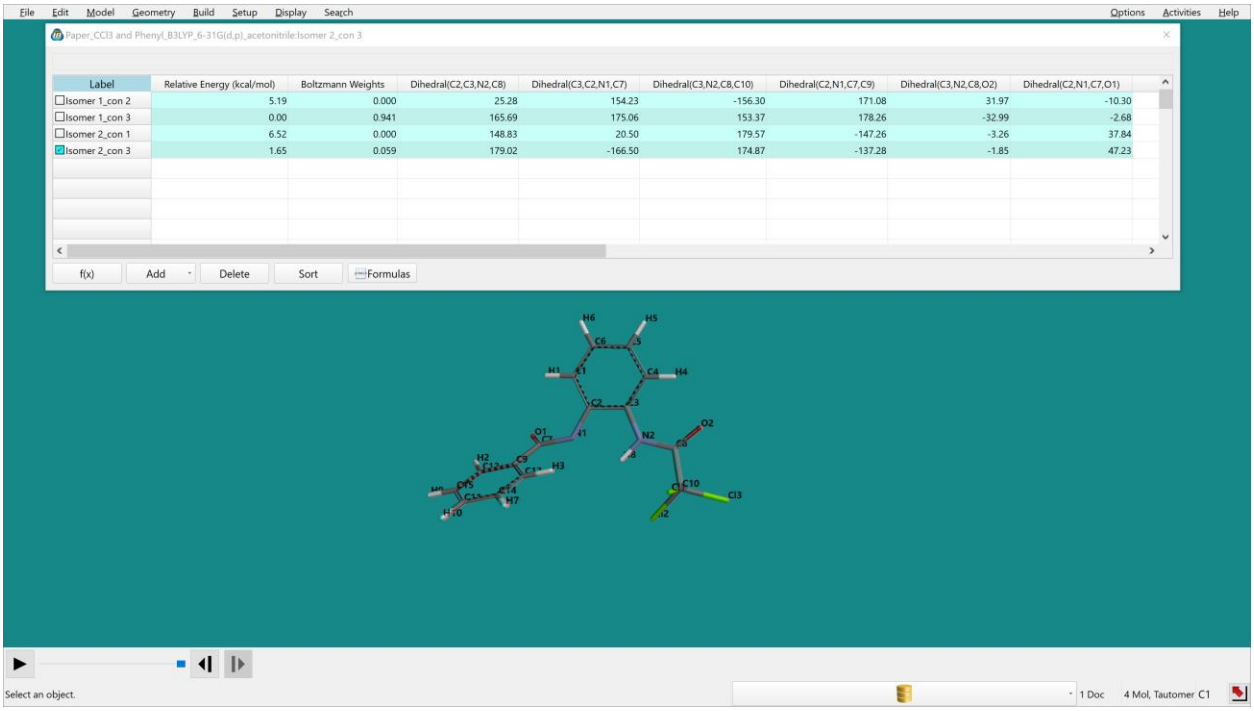
12	H	H2	0.1253482	-0.0709401	-0.2644115
13	N	N2	-1.7220839	0.0427594	-1.3100390
14	C	C7	1.0498373	0.0459453	1.5790495
15	C	C8	-2.3708251	-0.2369755	-2.4656980
16	C	C10	-1.6629008	0.4162235	-3.7120671
17	O	O1	0.9460088	0.2585769	2.7881363
18	O	O2	-3.3226249	-0.9878146	-2.6397661
19	Cl	Cl2	-1.2808861	2.1434040	-3.3726182
20	C	C9	2.3775959	-0.1403199	0.9152095
21	C	C11	4.9256025	-0.4407216	-0.2168682
22	C	C12	2.5452442	-0.8880268	-0.2628493
23	C	C13	3.4992201	0.4427735	1.5285173
24	C	C14	4.7646044	0.3001692	0.9601692
25	C	C15	3.8160002	-1.0386643	-0.8223349
26	H	H3	1.7014928	-1.3828366	-0.7339561
27	H	H7	3.3673135	1.0154328	2.4404899
28	H	H8	5.6242027	0.7658014	1.4330772
29	H	H9	3.9379293	-1.6284228	-1.7258493
30	H	H10	5.9118253	-0.5539995	-0.6575781
31	Cl	Cl1	-0.1295310	-0.4911013	-4.0267745
32	Cl	Cl3	-2.7133443	0.3192009	-5.1549643



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-3.4193384	-0.3496395	-1.3841225
2	C	C1	-3.2159476	-0.3498702	-0.3184612
3	C	C4	-2.5930883	-0.3536575	2.4126240
4	C	C2	-1.8345036	-0.4484586	0.0729024
5	C	C6	-4.2311521	-0.2469129	0.6050735
6	C	C5	-3.9175995	-0.2453042	1.9792561

7	C	C3	-1.5447594	-0.4603724	1.4988866
8	H	H6	-5.2633515	-0.1695553	0.2794928
9	H	H5	-4.7097187	-0.1757210	2.7181437
10	H	H4	-2.3781229	-0.3726886	3.4726319
11	N	N1	-0.9579413	-0.4377090	-0.9350642
12	N	N2	-0.2136802	-0.6113238	1.9243935
13	H	H8	0.3775609	-1.1749327	1.3029673
14	C	C7	0.3588494	-0.7908099	-0.9983865
15	C	C8	0.3161583	-0.0788009	3.0569752
16	C	C10	1.8380400	-0.4224525	3.2869022
17	O	O1	0.8233623	-1.7715671	-0.3754129
18	O	O2	-0.2590827	0.6525819	3.8454371
19	Cl	Cl2	2.1909516	-2.1524248	2.9306617
20	C	C9	1.1925428	-0.0059178	-1.9508890
21	C	C11	2.8231899	1.4747389	-3.6839790
22	C	C12	0.6323526	0.9847335	-2.7764064
23	C	C13	2.5764733	-0.2476454	-1.9998260
24	C	C14	3.3863191	0.4886322	-2.8641126
25	C	C15	1.4464125	1.7218449	-3.6377753
26	H	H2	-0.4367949	1.1643453	-2.7472673
27	H	H3	3.0057245	-1.0071947	-1.3552420
28	H	H7	4.4548950	0.2976351	-2.8976278
29	H	H9	1.0072149	2.4831918	-4.2754662
30	H	H10	3.4556315	2.0467530	-4.3569544
31	Cl	Cl1	2.8084030	0.6369253	2.1879422
32	Cl	Cl3	2.2809993	-0.0784233	4.9827029



Cartesian Coordinates (Angstroms)

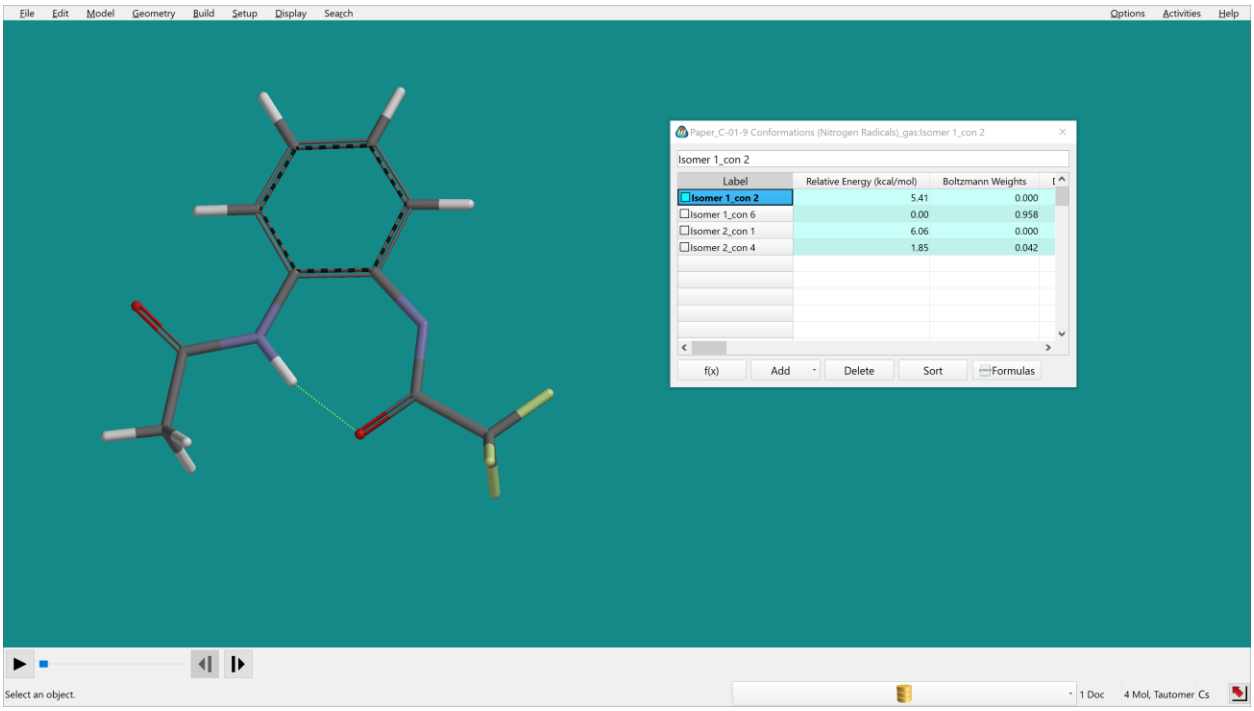
	Atom	X	Y	Z
1	H H1	-2.6979343	0.4500020	-1.3648649

2	C	C1	-2.6805410	0.1727958	-0.3176756
3	C	C4	-2.6029722	-0.5580943	2.4178664
4	C	C2	-1.4317451	0.2227478	0.3856073
5	C	C6	-3.8331735	-0.2245077	0.3245176
6	C	C5	-3.7965068	-0.5847442	1.6894609
7	C	C3	-1.4216197	-0.1677560	1.7881244
8	H	H6	-4.7721944	-0.2626309	-0.2183939
9	H	H5	-4.7094844	-0.8939115	2.1884640
10	H	H4	-2.5923213	-0.8390031	3.4608692
11	N	N1	-0.2564754	0.5486545	-0.1527311
12	N	N2	-0.1695304	-0.1095846	2.4005483
13	H	H8	0.5661519	0.1885760	1.7602152
14	C	C7	-0.1161227	1.1927017	-1.3731788
15	C	C8	0.1461497	-0.3929616	3.6892494
16	C	C10	1.6890328	-0.3411768	4.0068027
17	O	O1	-0.7842573	2.1912836	-1.6663214
18	O	O2	-0.6362056	-0.7262372	4.5638996
19	Cl	Cl1	2.3981034	-1.9081279	3.4466987
20	C	C9	0.9623935	0.6671905	-2.2609015
21	C	C11	2.9426826	-0.2950833	-3.9957723
22	C	C12	1.1541847	1.2651680	-3.5182143
23	C	C13	1.7707452	-0.4178781	-1.8798682
24	C	C14	2.7563134	-0.8958228	-2.7459191
25	C	C15	2.1393228	0.7861229	-4.3806714
26	H	H2	0.5267464	2.1013747	-3.8080031
27	H	H3	1.6308359	-0.8765540	-0.9068432
28	H	H7	3.3797839	-1.7323141	-2.4443769
29	H	H9	2.2827829	1.2527749	-5.3508160
30	H	H10	3.7108736	-0.6668082	-4.6679555
31	Cl	Cl2	2.5138363	1.0235980	3.1638030
32	Cl	Cl3	1.9311450	-0.1697941	5.7663807

Table S11. Boltzmann Analysis of Conformers of 1a in the gas phase and in acetonitrile. Isomer I is the nitrogen radical of the more electron deficient amide, while isomer II is the nitrogen radical of the more electron rich amide.

Gas Phase

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-945.398717	5.41	0.00
Isomer 1_con 6	-945.407336	0.00	0.958
Isomer 2_con 1	-945.397685	6.06	0.000
Isomer 2_con 4	-945.404382	1.85	0.042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Options Activities Help
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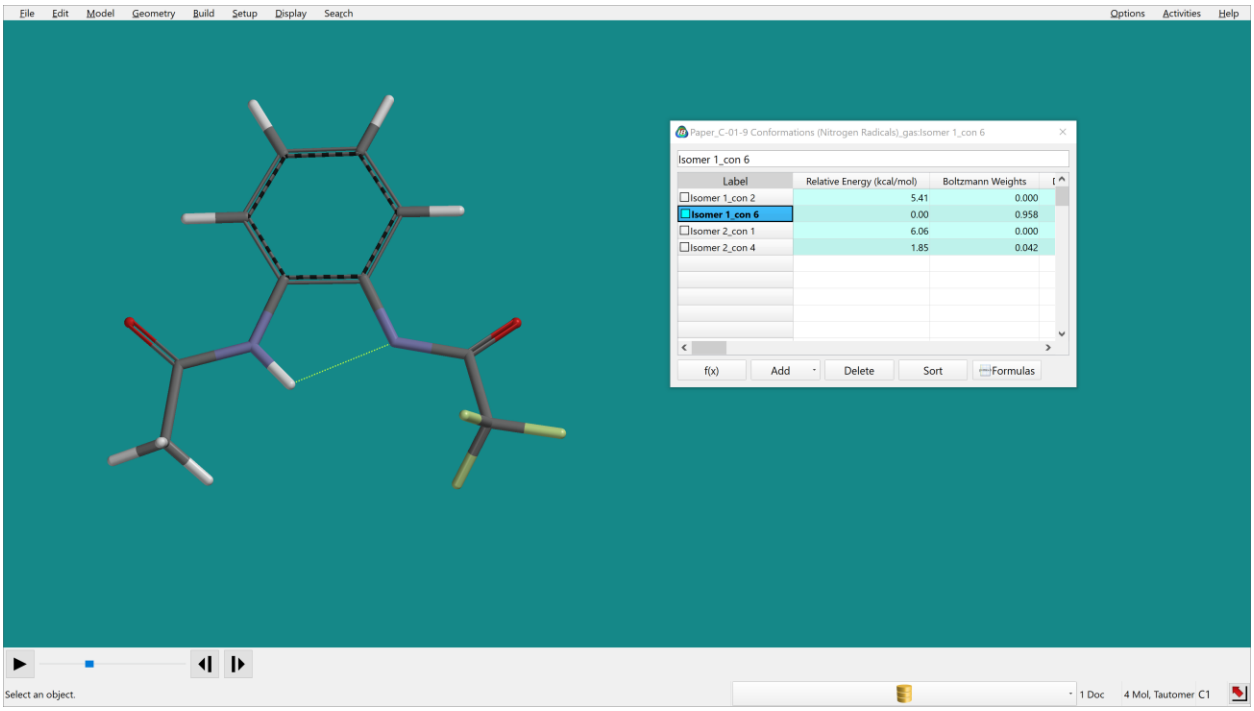
Isomer 1_con 2
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 5.41 0.000
Isomer 1_con 6 0.00 0.958
Isomer 2_con 1 6.06 0.000
Isomer 2_con 4 1.85 0.042
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer Cs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Isomer 1_con 6
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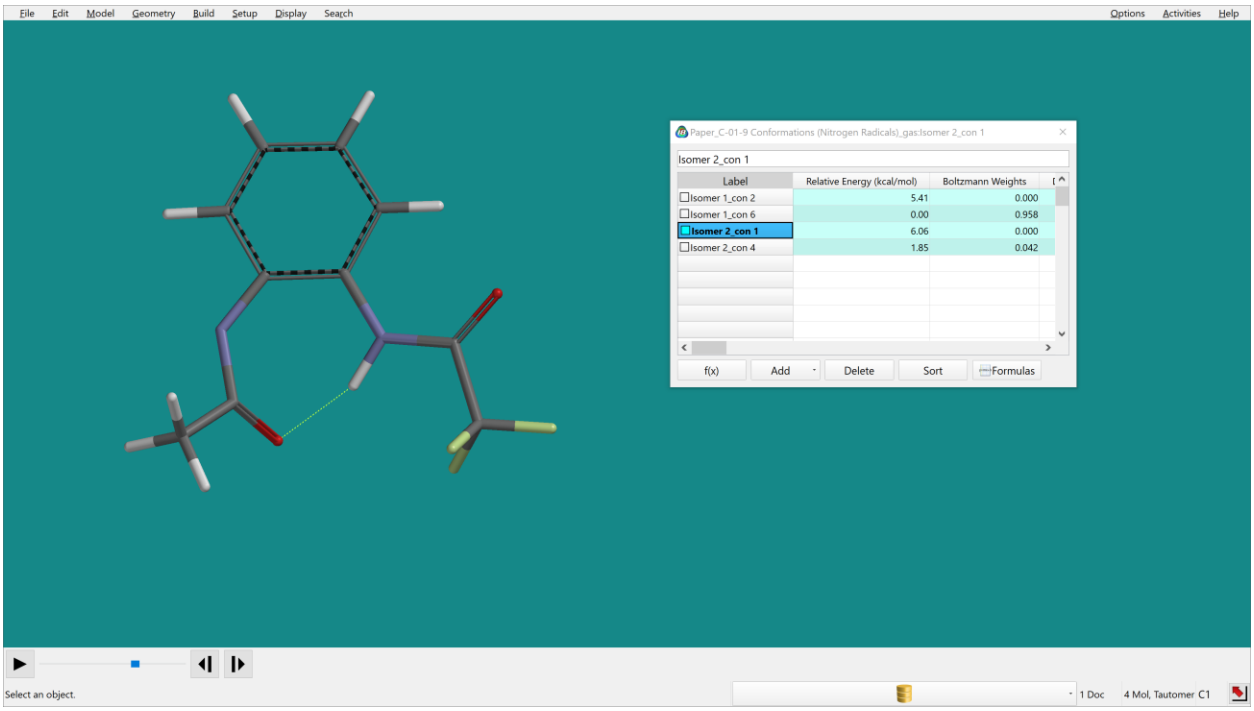
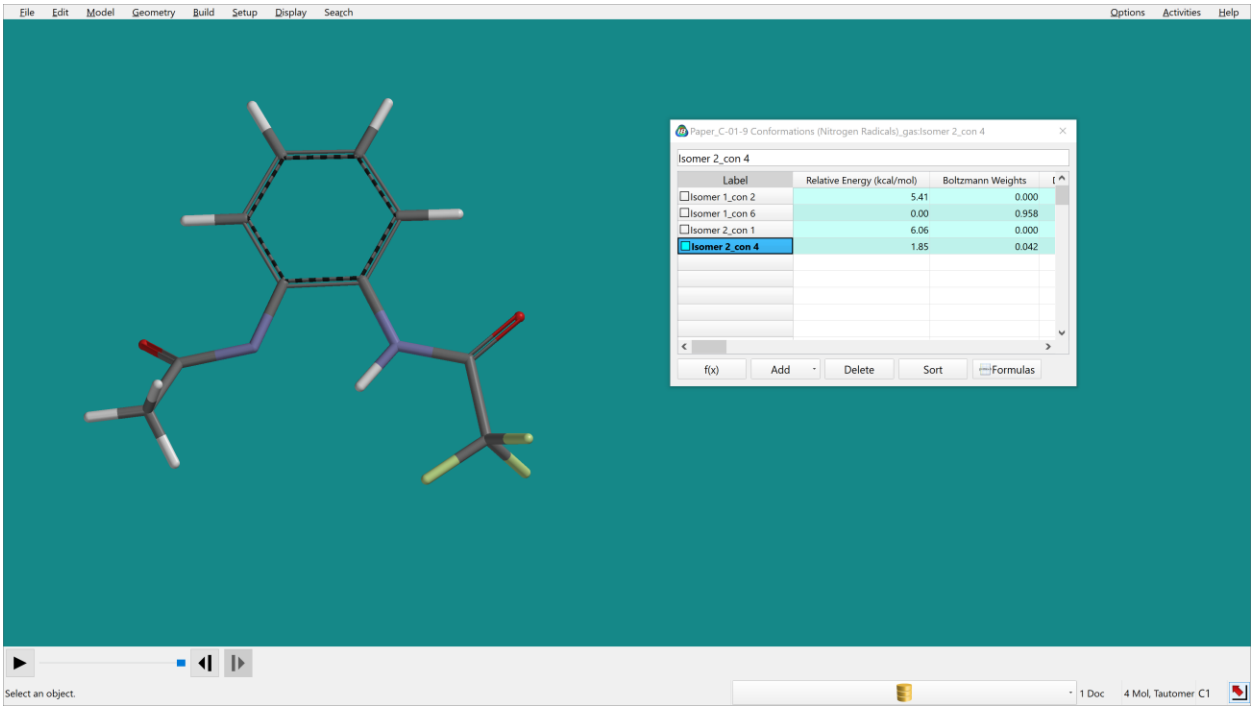
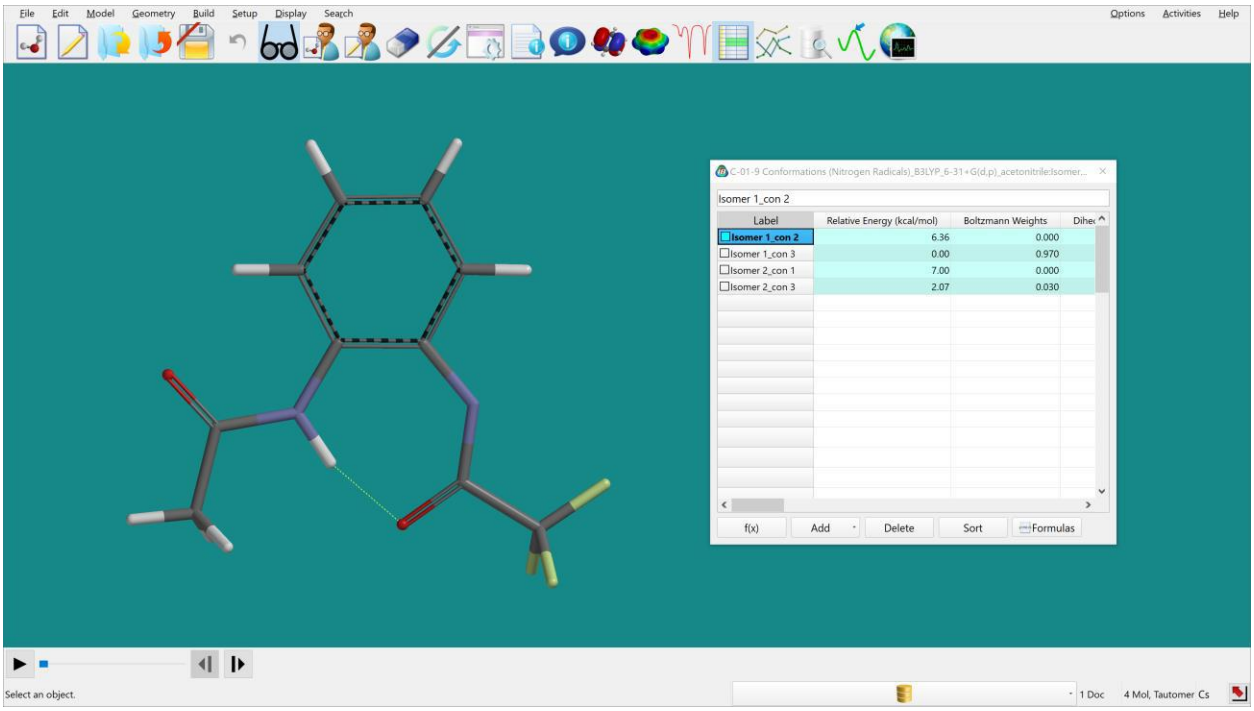
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 5.41 0.000
Isomer 1_con 6 0.00 0.958
Isomer 2_con 1 6.06 0.000
Isomer 2_con 4 1.85 0.042
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

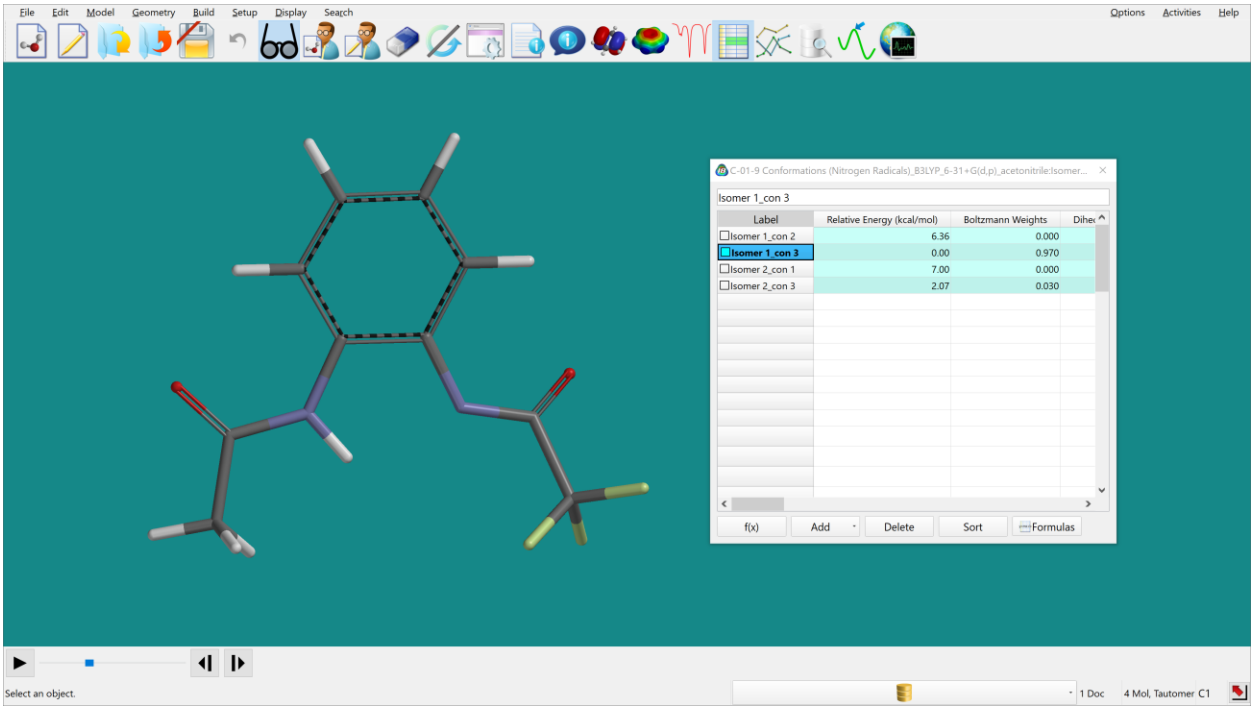


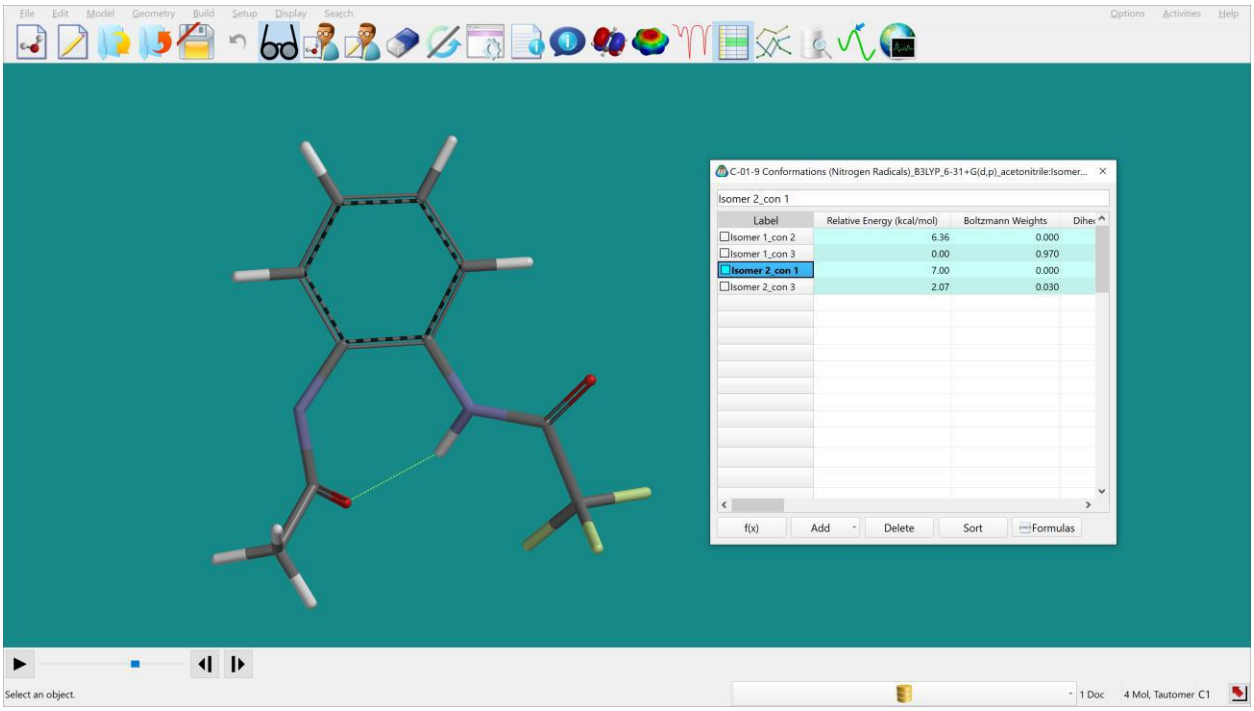


Acetonitrile

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-945.414554	6.36	0.000
Isomer 1_con 3	-945.424695	0.00	0.970
Isomer 2_con 1	-945.413536	7.00	0.000
Isomer 2_con 3	-945.421398	2.07	0.030


File Edit Model Geometry Build Setup Display Search
Options Activities Help
C-01-9 Conformations (Nitrogen Radicals)_B3LYP_6-31+G(d,p)_acetonitrile:Isomer...
Isomer 1_con 2
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 6.36 0.000
Isomer 1_con 3 0.00 0.970
Isomer 2_con 1 7.00 0.000
Isomer 2_con 3 2.07 0.030
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer Cs


File Edit Model Geometry Build Setup Display Search
Options Activities Help
C-01-9 Conformations (Nitrogen Radicals)_B3LYP_6-31+G(d,p)_acetonitrile:Isomer...
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 6.36 0.000
Isomer 1_con 3 0.00 0.970
Isomer 2_con 1 7.00 0.000
Isomer 2_con 3 2.07 0.030
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1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Options Activities Help
C-01-9 Conformations (Nitrogen Radicals)_B3LYP_6-31+G(d,p)_acetonitrile:Isomer...
Isomer 2_con 1
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 6.36 0.000
Isomer 1_con 3 0.00 0.970
Isomer 2_con 1 7.00 0.000
Isomer 2_con 3 2.07 0.030
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

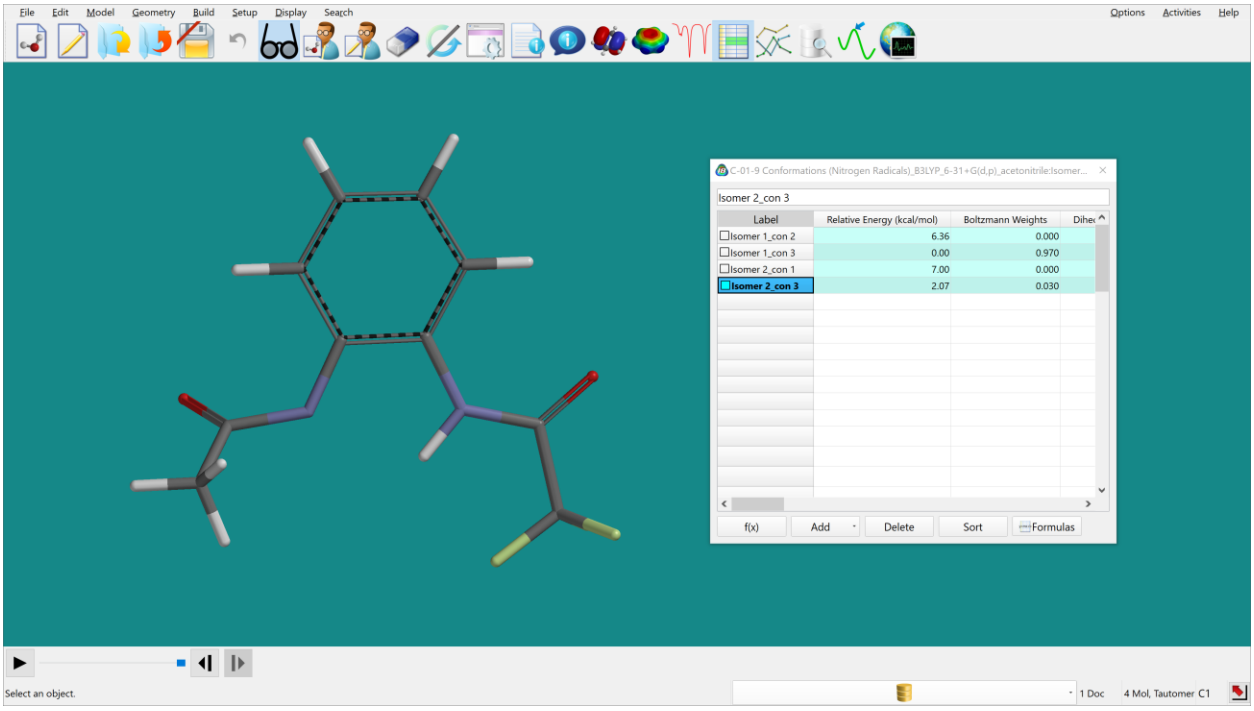
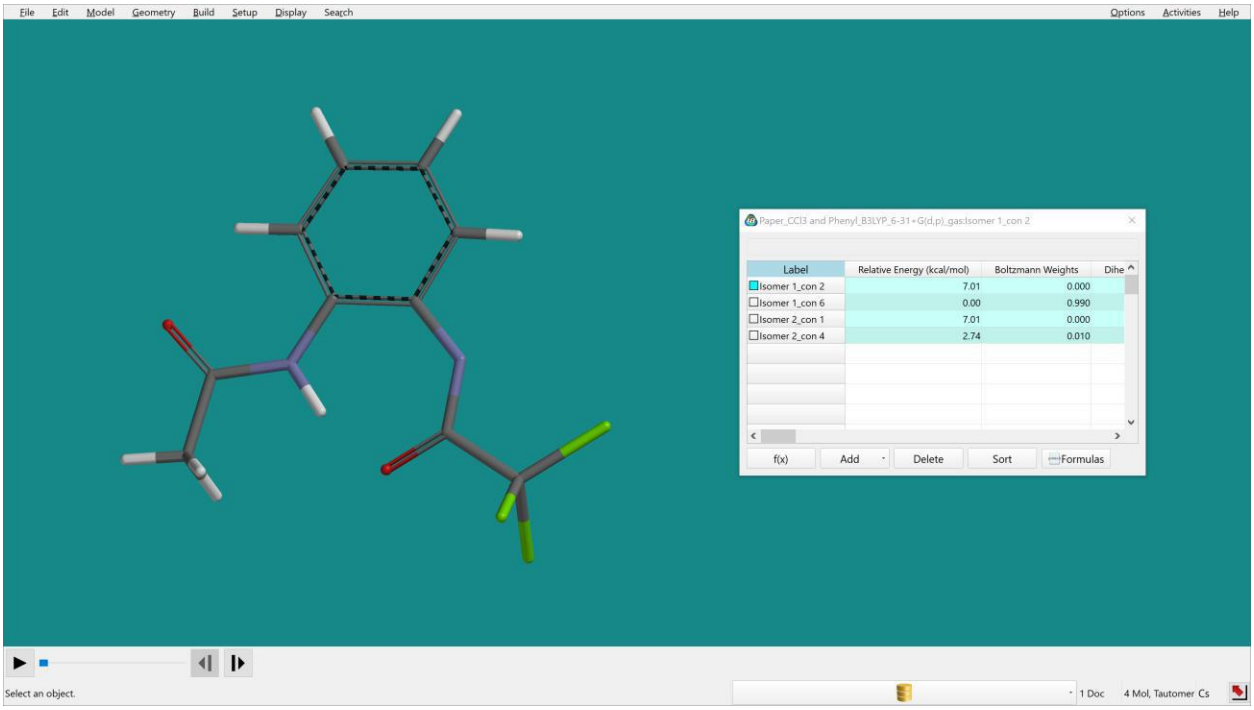
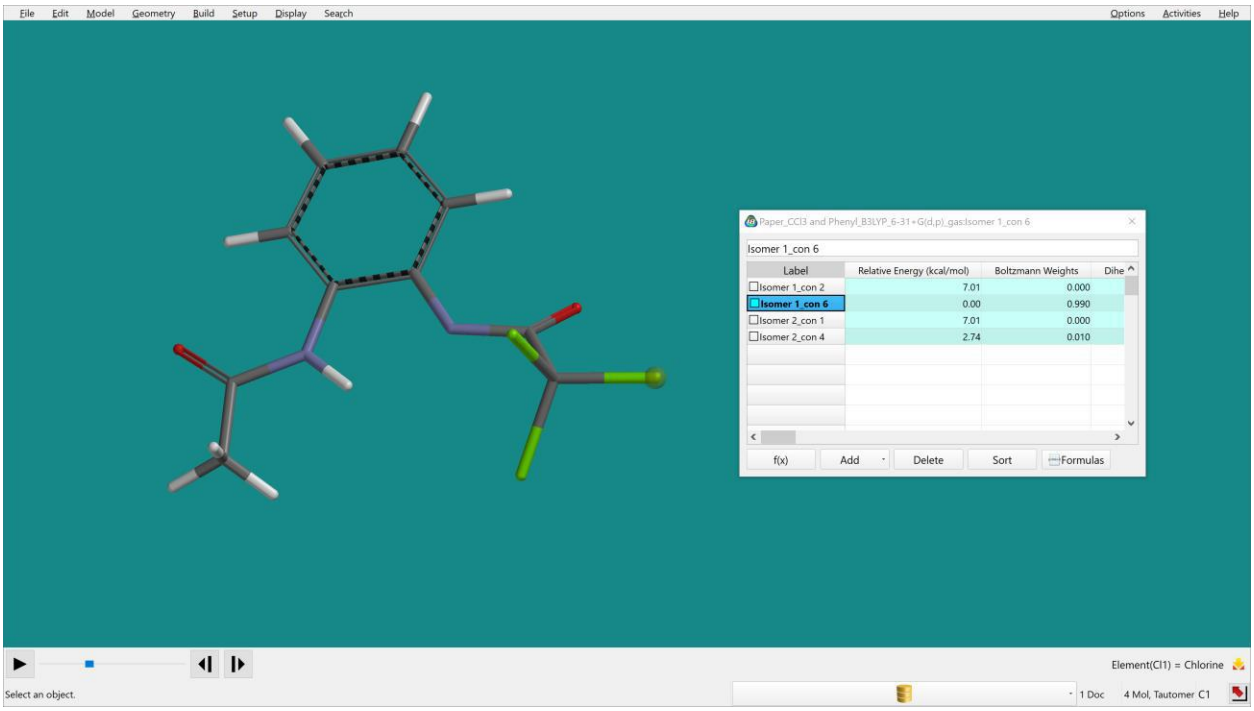

File Edit Model Geometry Build Setup Display Search
Options Activities Help
C-01-9 Conformations (Nitrogen Radicals)_B3LYP_6-31+G(d,p)_acetonitrile:Isomer...
Isomer 2_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 6.36 0.000
Isomer 1_con 3 0.00 0.970
Isomer 2_con 1 7.00 0.000
Isomer 2_con 3 2.07 0.030
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

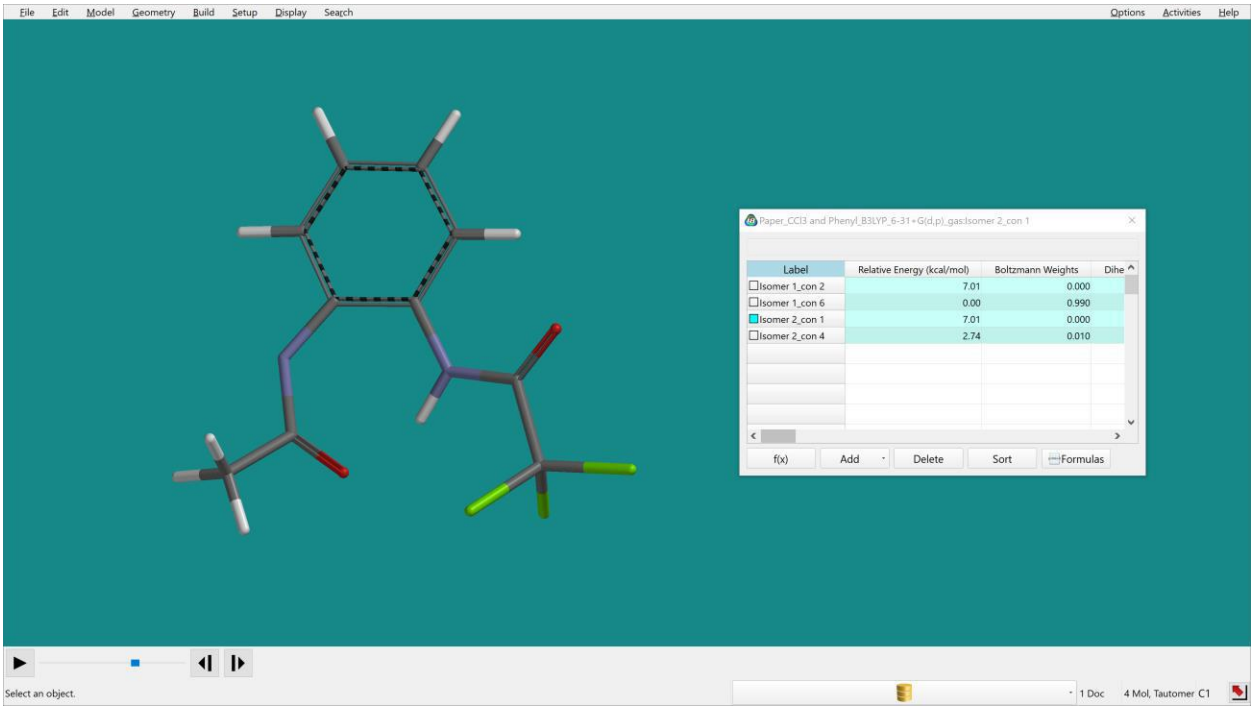
Table S12. Boltzmann Analysis of Conformers of 1g in the gas phase and in acetonitrile. Isomer I is the nitrogen radical of the more electron deficient amide, while isomer II is the nitrogen radical of the more electron rich amide.

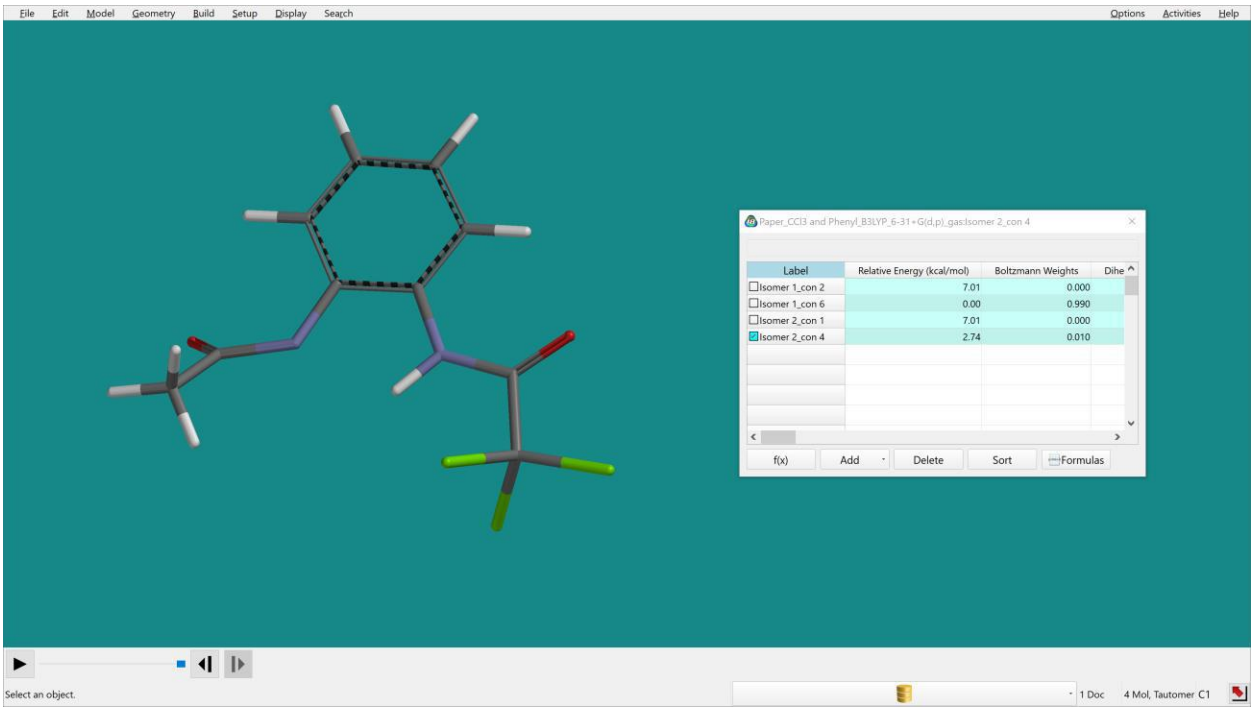
Gas Phase

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-2026.42123	7.01	0.000
Isomer 1_con 6	-2026.43240	0.00	0.990
Isomer 2_con 1	-2026.42123	7.01	0.000
Isomer 2_con 4	-2026.42803	2.74	0.010



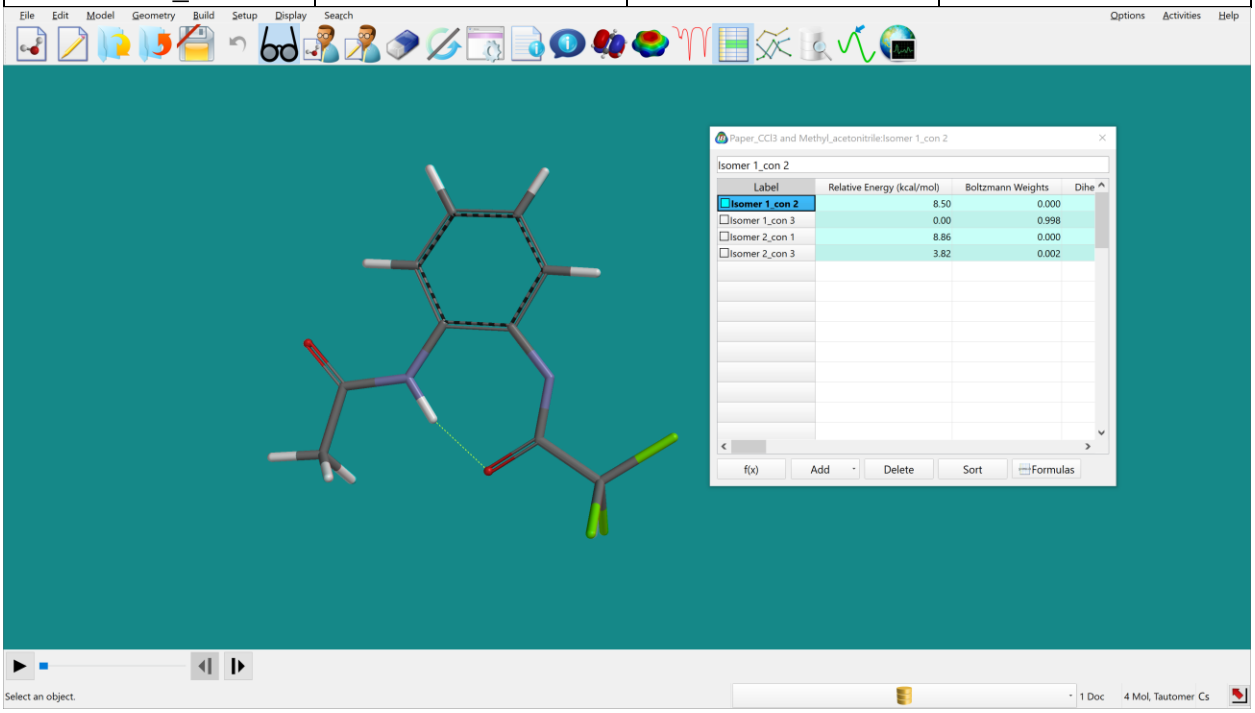

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Phenyl_B3LYP_6-31+G(d,p)_gas:Isomer 1_con 6
Isomer 1_con 6
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 7.01 0.000
Isomer 1_con 6 0.00 0.990
Isomer 2_con 1 7.01 0.000
Isomer 2_con 4 2.74 0.010
f(x)
Add
Delete
Sort
Formulas
Element(Cl1) = Chlorine
Select an object.
1 Doc
4 Mol, Tautomer C1

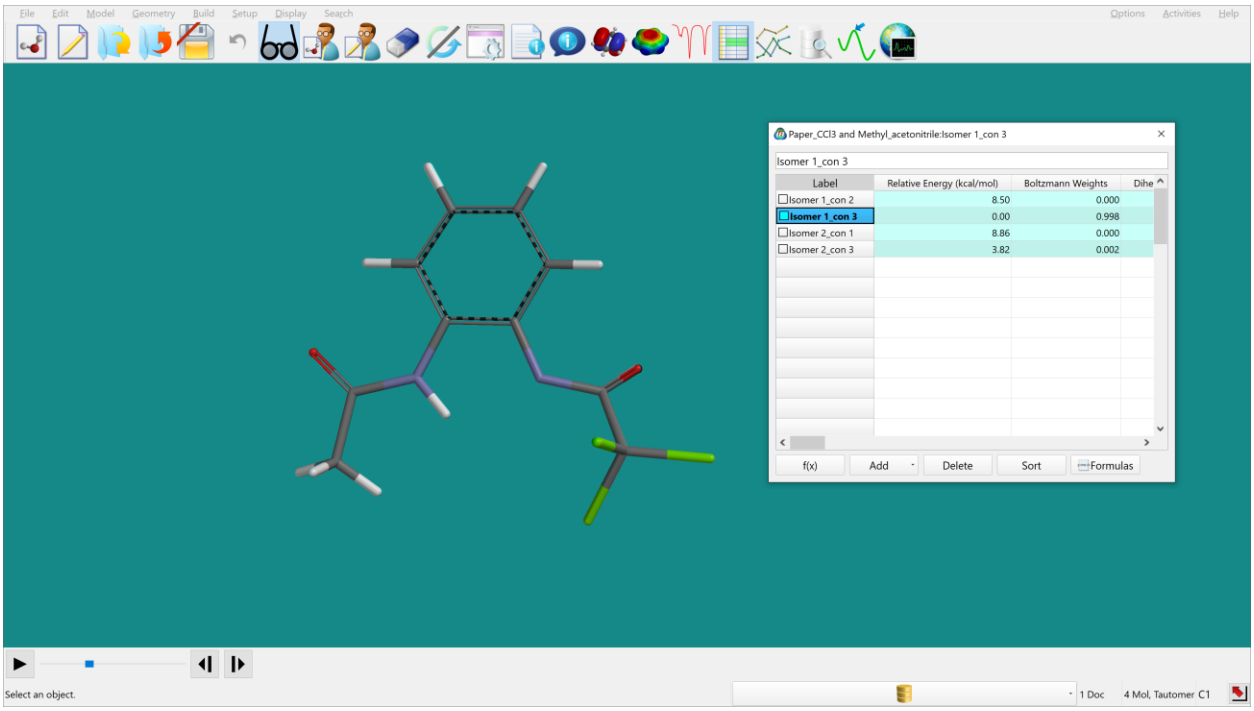

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Phenyl_B3LYP_6-31+G(d,p)_gas:Isomer 2_con 1
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 7.01 0.000
Isomer 1_con 6 0.00 0.990
Isomer 2_con 1 7.01 0.000
Isomer 2_con 4 2.74 0.010
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

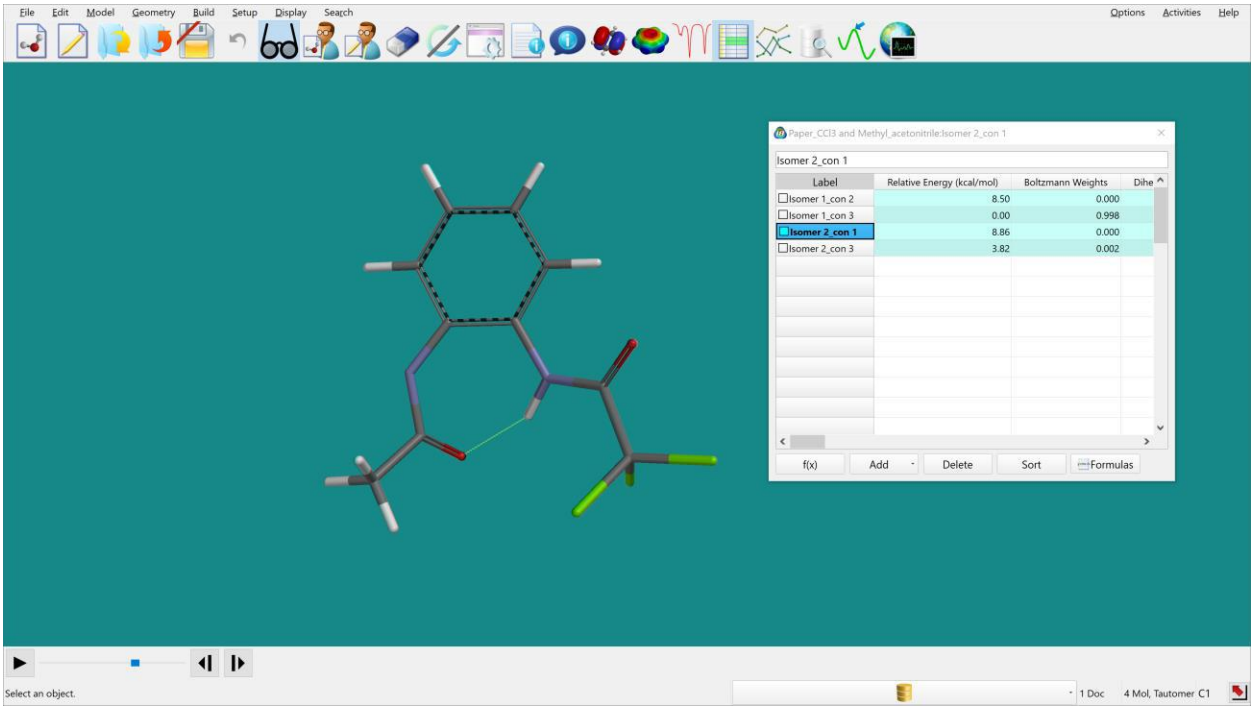


Acetonitrile

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-2026.43650	8.50	0.000
Isomer 1_con 3	-2026.45005	0.00	0.998
Isomer 2_con 1	-2026.43592	8.86	0.000
Isomer 2_con 3	-2026.44397	3.82	0.002




File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Methyl_acetonitrile:Isomer 1_con 3
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 8.50 0.000
Isomer 1_con 3 0.00 0.998
Isomer 2_con 1 8.86 0.000
Isomer 2_con 3 3.82 0.002
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Methyl_acetonitrile:Isomer 2_con 1
Isomer 2_con 1
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 8.50 0.000
Isomer 1_con 3 0.00 0.998
Isomer 2_con 1 8.86 0.000
Isomer 2_con 3 3.82 0.002
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

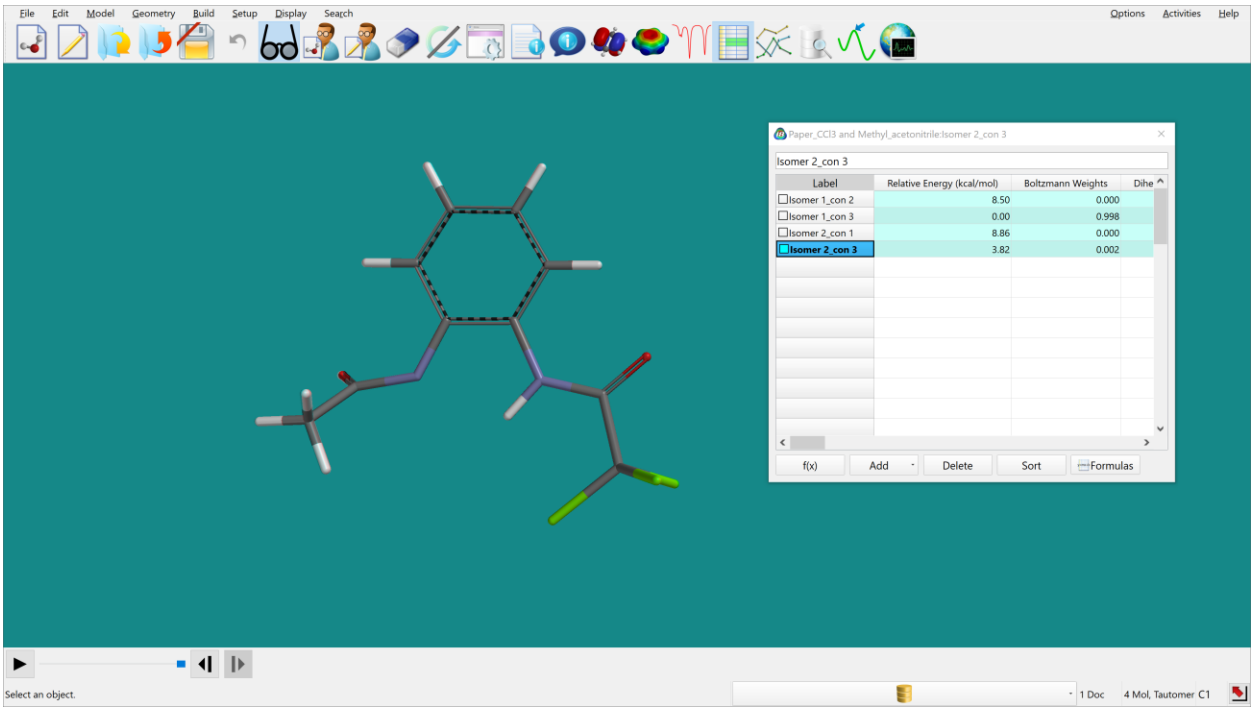
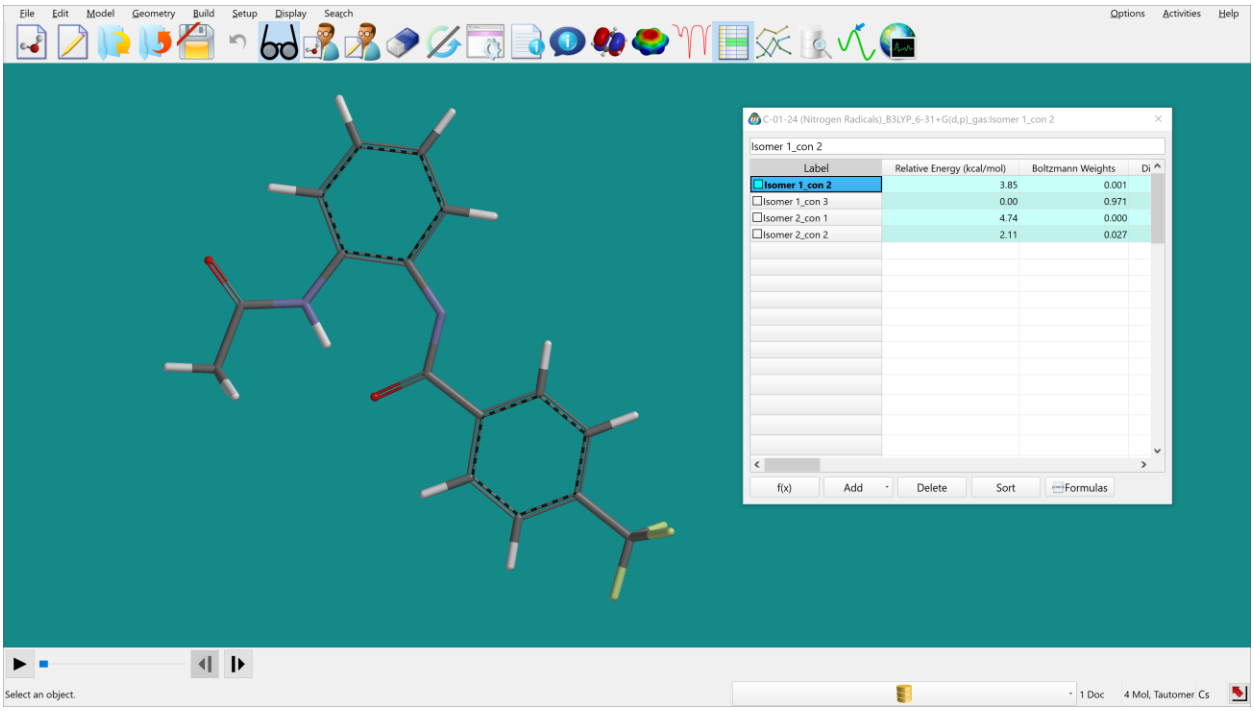
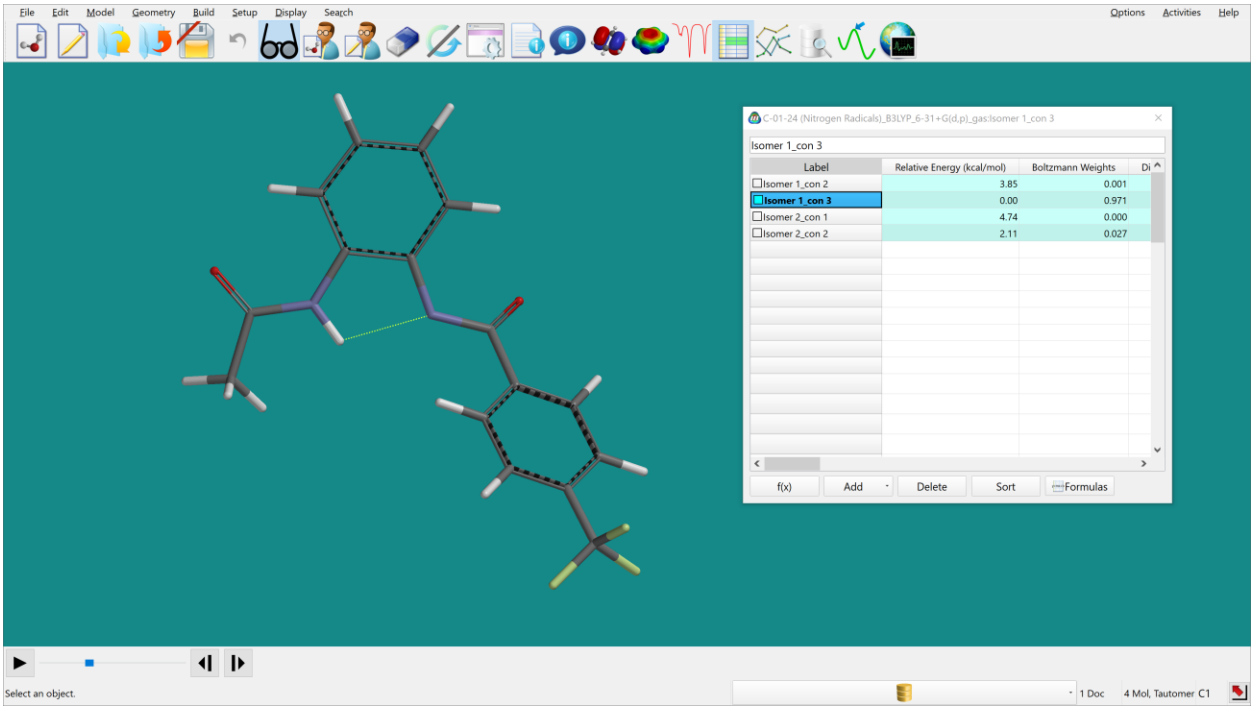


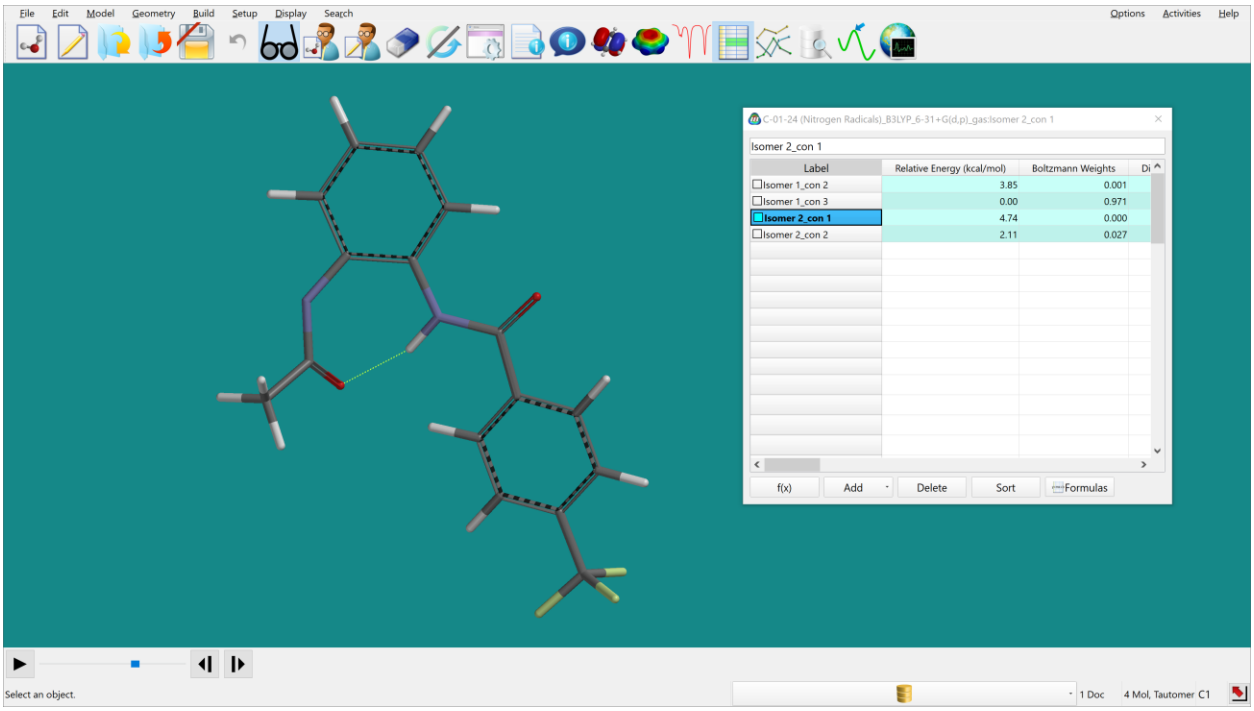
Table S13. Boltzmann Analysis of Conformers of 1j in the gas phase and in acetonitrile. Isomer I is the nitrogen radical of the more electron deficient amide, while isomer II is the nitrogen radical of the more electron rich amide.

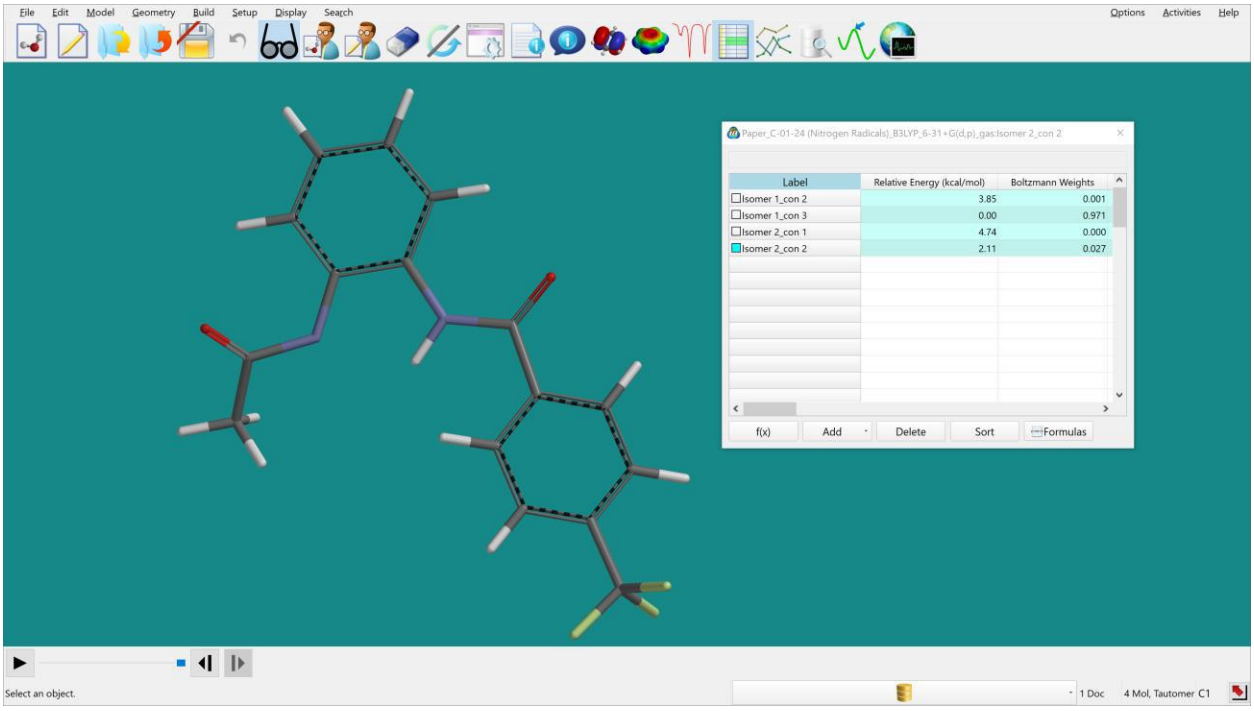
Gas Phase

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-1176.48234	3.85	0.001
Isomer 1_con 3	-1176.48848	0.00	0.971
Isomer 2_con 1	-1176.48093	4.74	0.000
Isomer 2_con 2	-1176.48511	2.11	0.027


File Edit Model Geometry Build Setup Display Search
Options Activities Help
C-01-24 (Nitrogen Radicals)_B3LYP_6-31+G(d,p)_gas:Isomer 1_con 2
Isomer 1_con 2
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 3.85 0.001
Isomer 1_con 3 0.00 0.971
Isomer 2_con 1 4.74 0.000
Isomer 2_con 2 2.11 0.027
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer Cs

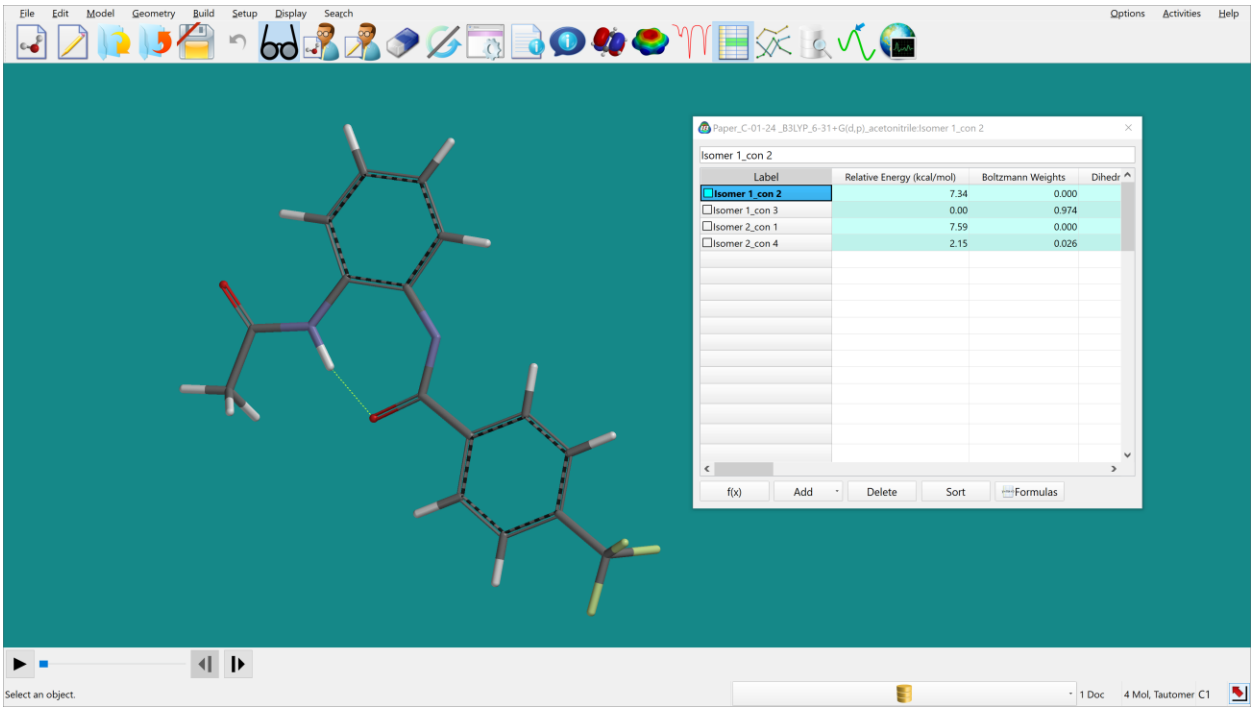

File Edit Model Geometry Build Setup Display Search
Options Activities Help
C-01-24 (Nitrogen Radicals)_B3LYP_6-31+G(d,p)_gas:Isomer 1_con 3
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 3.85 0.001
Isomer 1_con 3 0.00 0.971
Isomer 2_con 1 4.74 0.000
Isomer 2_con 2 2.11 0.027
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

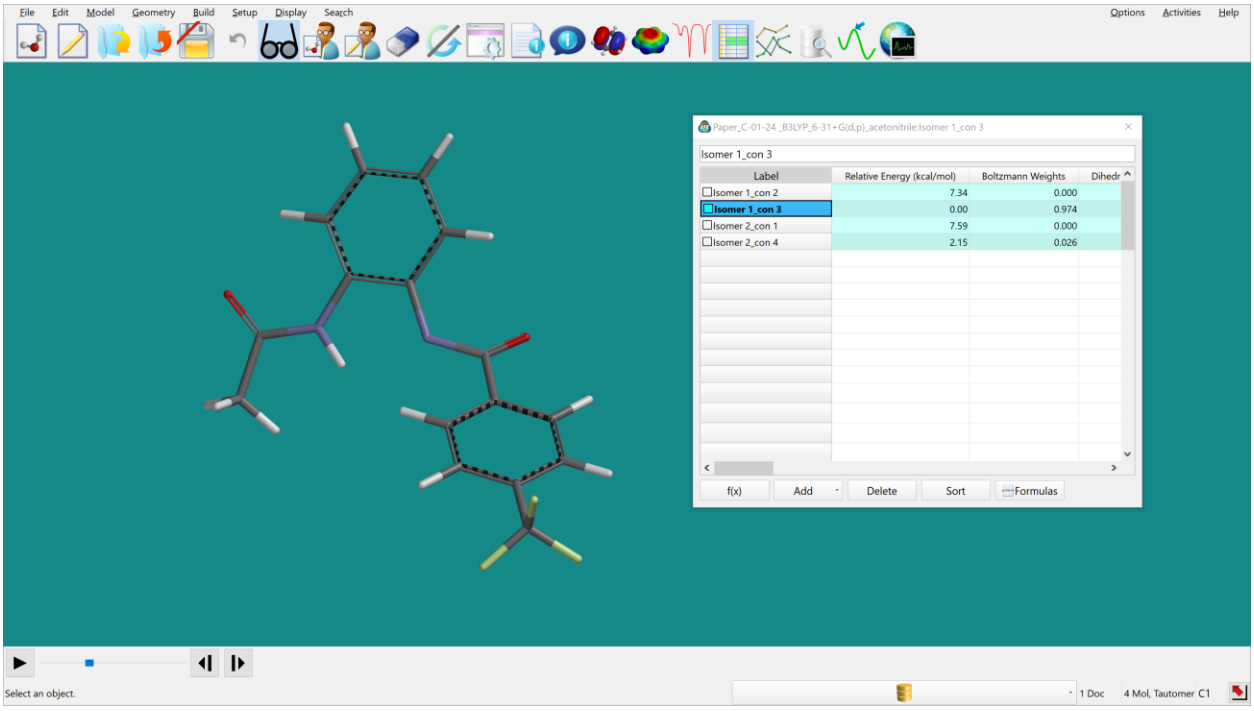


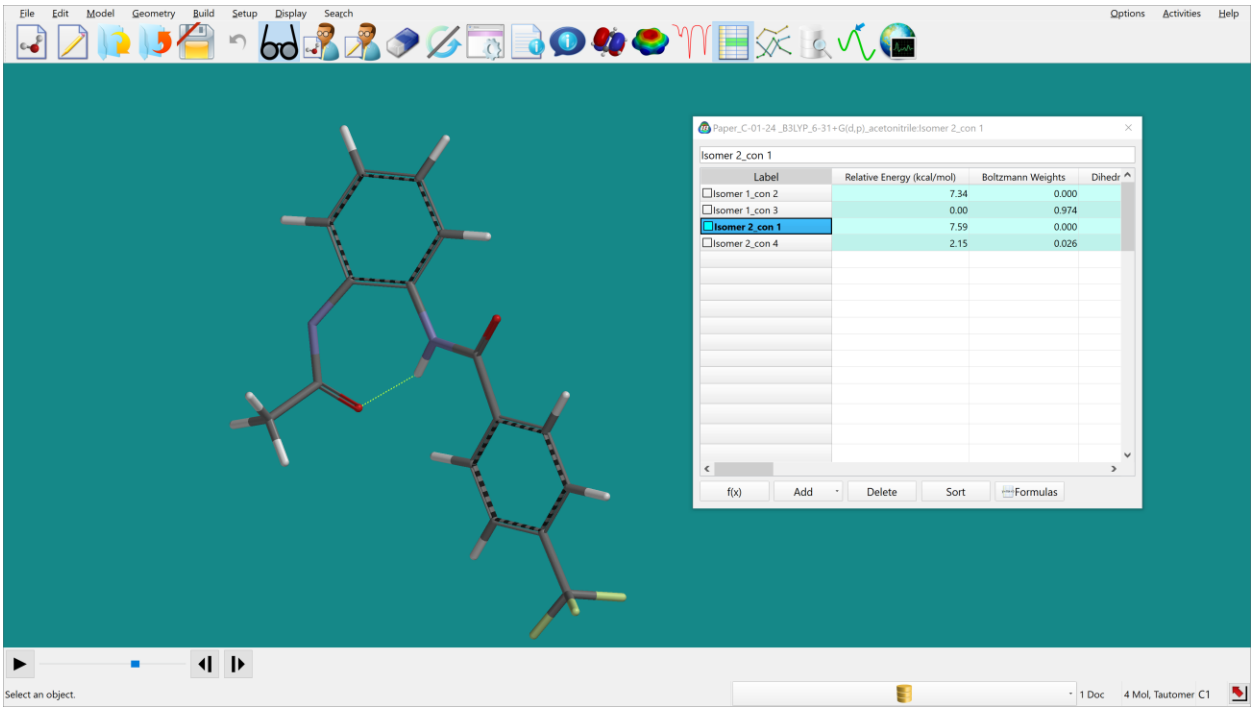


Acetonitrile

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-1176.49766	7.34	0.000
Isomer 1_con 3	-1176.50936	0.00	0.974
Isomer 2_con 1	-1176.49726	7.59	0.000
Isomer 2_con 4	-1176.50594	2.15	0.026


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_C-01-24 _B3LYP_6-31+G(d,p)_acetonitrile:Isomer 1_con 2
Isomer 1_con 2
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihedr
Isomer 1_con 2 7.34 0.000
Isomer 1_con 3 0.00 0.974
Isomer 2_con 1 7.59 0.000
Isomer 2_con 4 2.15 0.026
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_C-01-24 _B3LYP_6-31+G(d,p)_acetonitrile:Isomer 1_con 3
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihedr
Isomer 1_con 2 7.34 0.000
Isomer 1_con 3 0.00 0.974
Isomer 2_con 1 7.59 0.000
Isomer 2_con 4 2.15 0.026
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_C-01-24 _B3LYP_6-31+G(d,p)_acetonitrile:Isomer 2_con 1
Isomer 2_con 1
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihedr
Isomer 1_con 2 7.34 0.000
Isomer 1_con 3 0.00 0.974
Isomer 2_con 1 7.59 0.000
Isomer 2_con 4 2.15 0.026
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

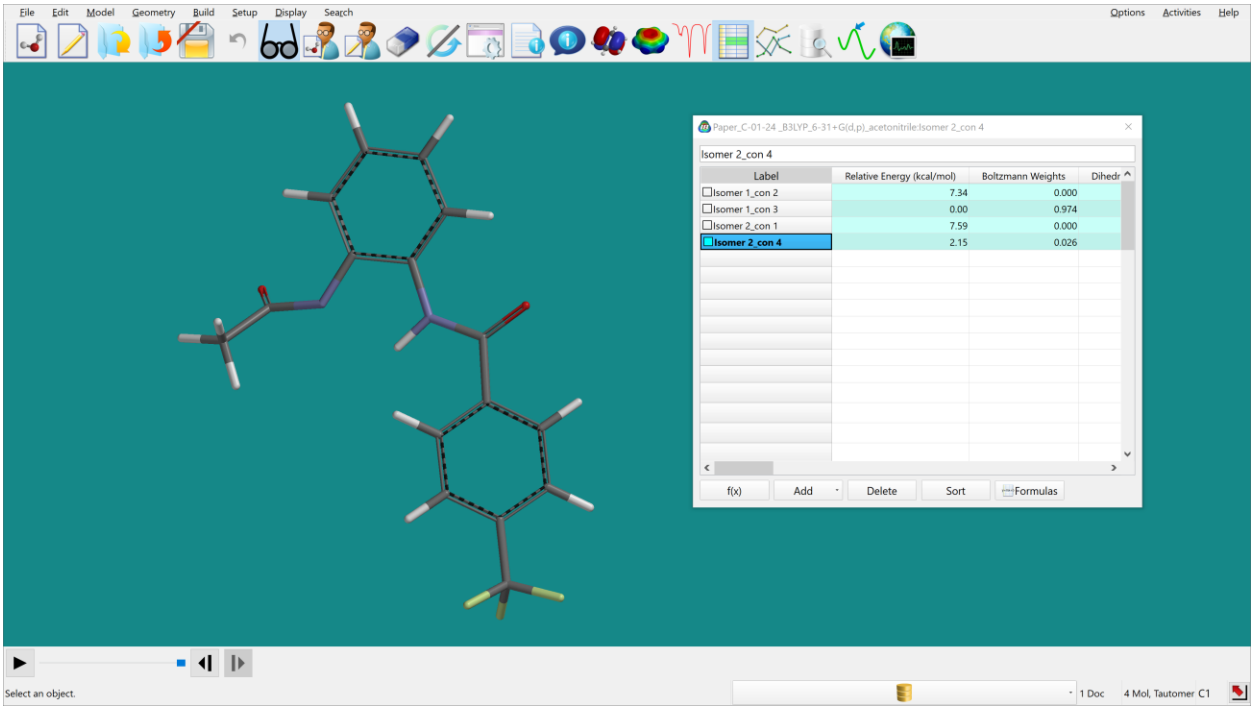
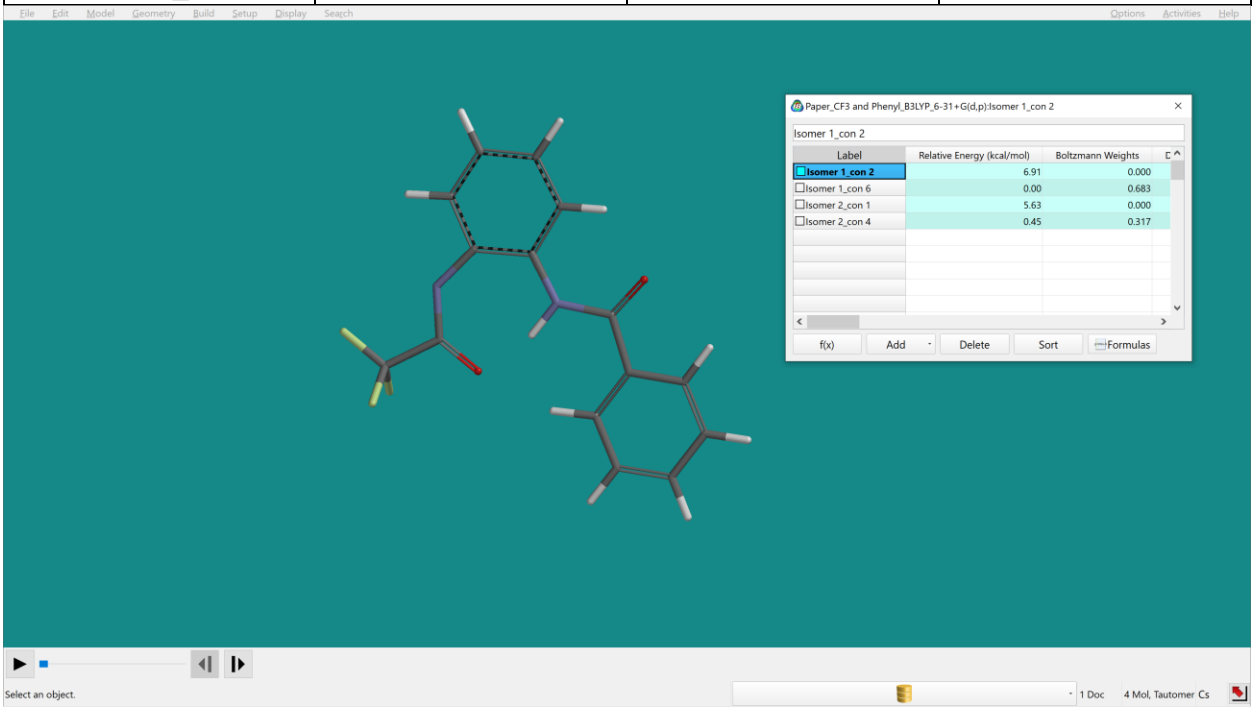
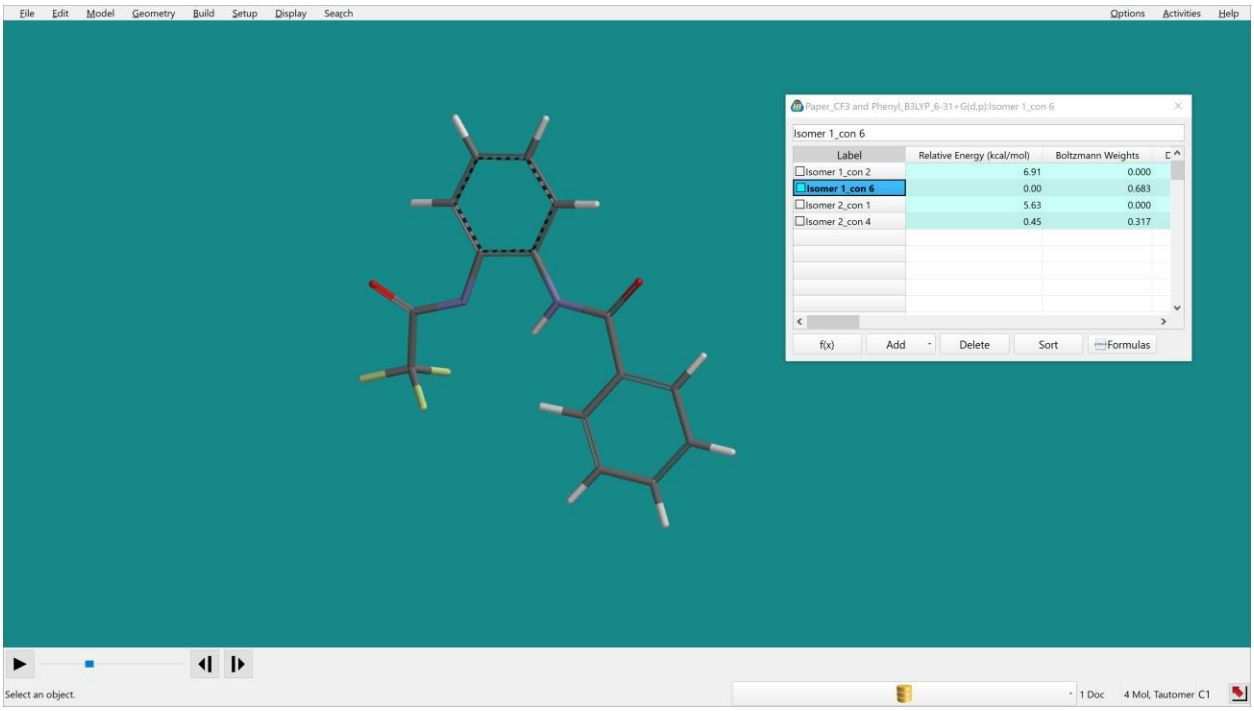

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_C-01-24 _B3LYP_6-31+G(d,p)_acetonitrile:Isomer 2_con 4
Isomer 2_con 4
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihedr
Isomer 1_con 2 7.34 0.000
Isomer 1_con 3 0.00 0.974
Isomer 2_con 1 7.59 0.000
Isomer 2_con 4 2.15 0.026
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

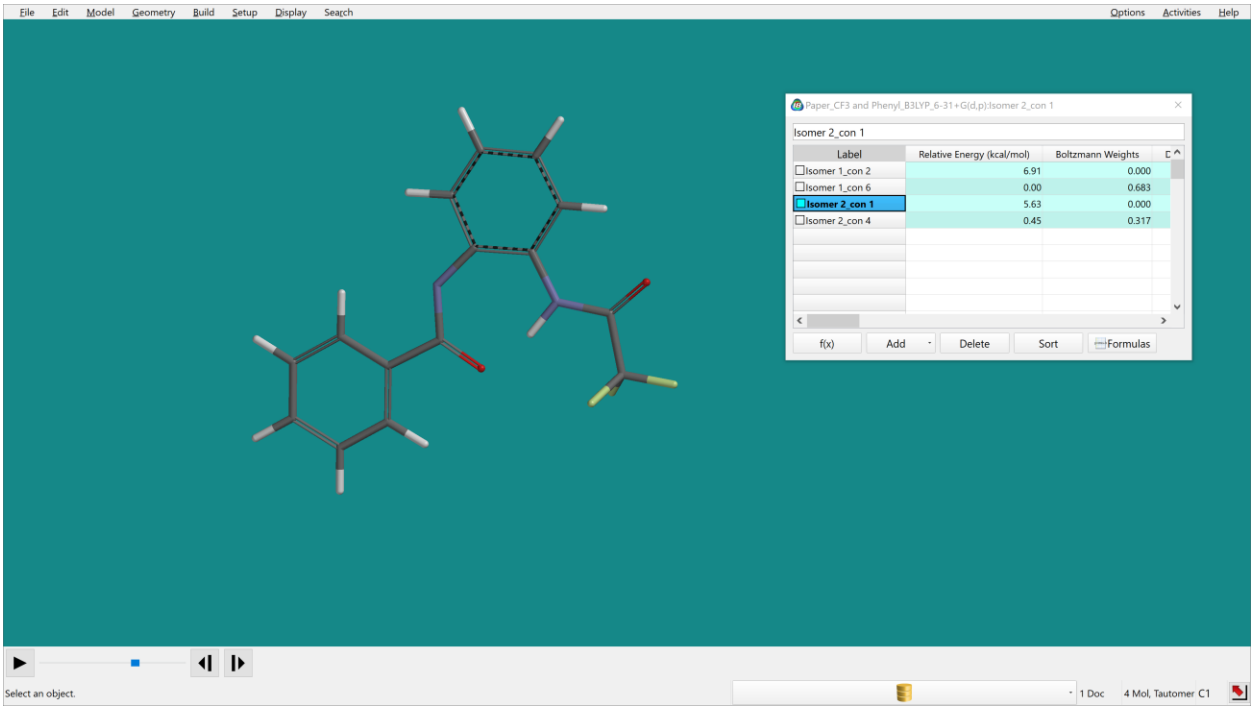
Table S14. Boltzmann Analysis of Conformers of 1x in the gas phase and in acetonitrile. Isomer I is the nitrogen radical of the more electron deficient amide, while isomer II is the nitrogen radical of the more electron rich amide.

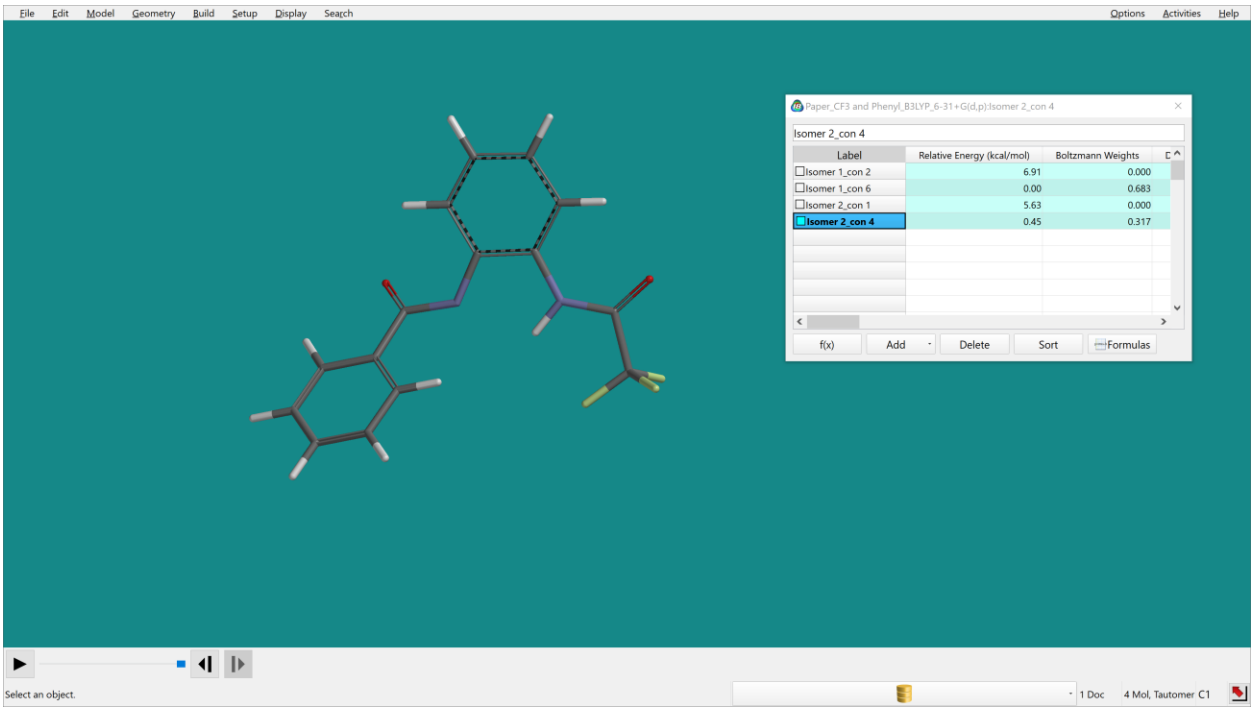
Gas Phase

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-1137.14422	6.91	0.000
Isomer 1_con 6	-1137.15523	0.00	0.683
Isomer 2_con 1	-1137.14626	5.63	0.000
Isomer 2_con 4	-1137.15451	0.45	0.317



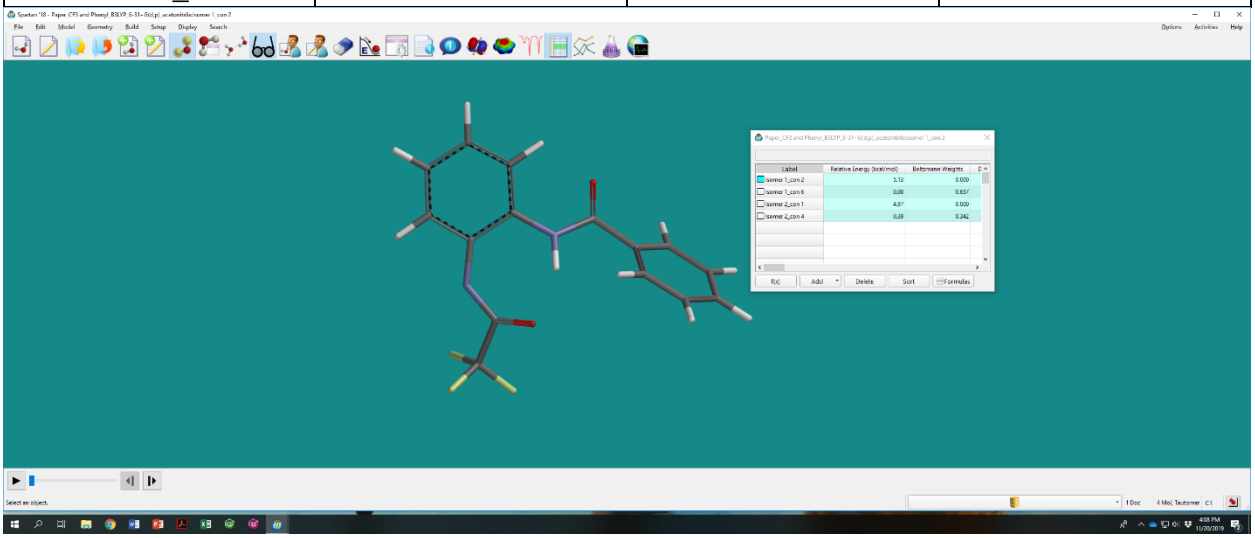

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF3 and Phenyl_B3LYP_6-31+G(d,p):Isomer 1_con 6
Isomer 1_con 6
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 6.91 0.000
Isomer 1_con 6 0.00 0.683
Isomer 2_con 1 5.63 0.000
Isomer 2_con 4 0.45 0.317
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

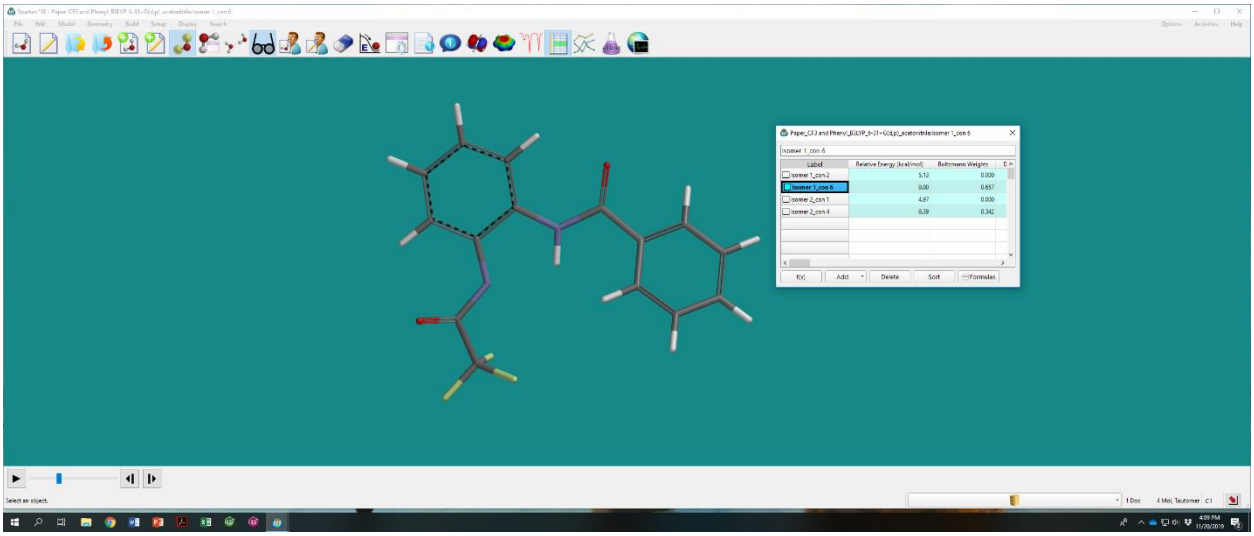

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF3 and Phenyl_B3LYP_6-31+G(d,p):Isomer 2_con 1
Isomer 2_con 1
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Isomer 1_con 2 6.91 0.000
Isomer 1_con 6 0.00 0.683
Isomer 2_con 1 5.63 0.000
Isomer 2_con 4 0.45 0.317
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

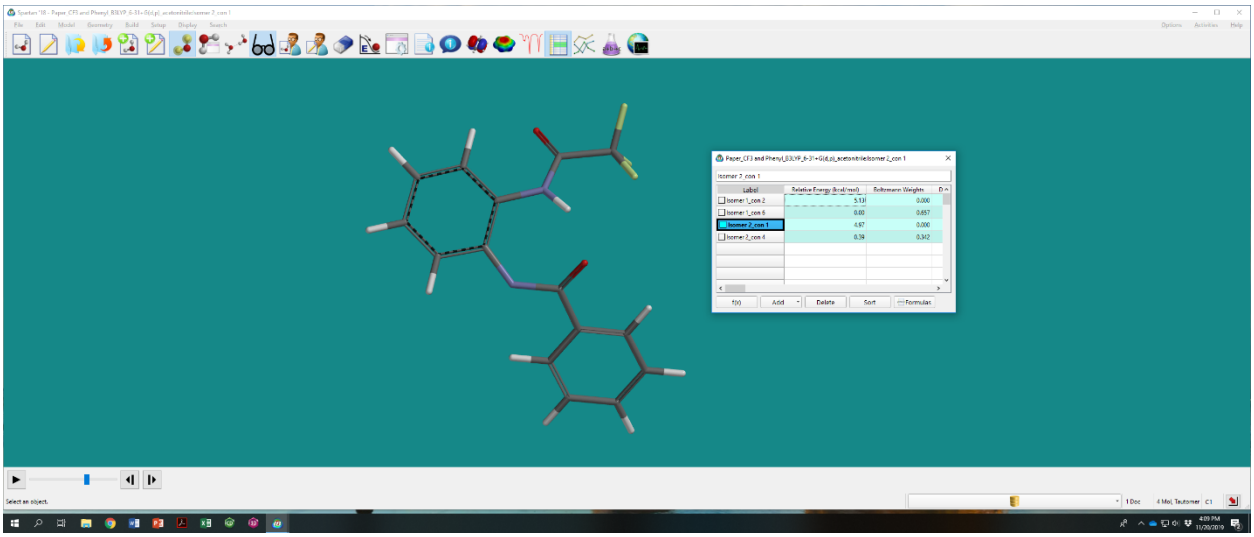


Acetonitrile

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-1137.16485	5.13	0.000
Isomer 1_con 6	-1137.17302	0.00	0.657
Isomer 2_con 1	-1137.16510	4.97	0.000
Isomer 2_con 4	-1137.17240	0.39	0.342







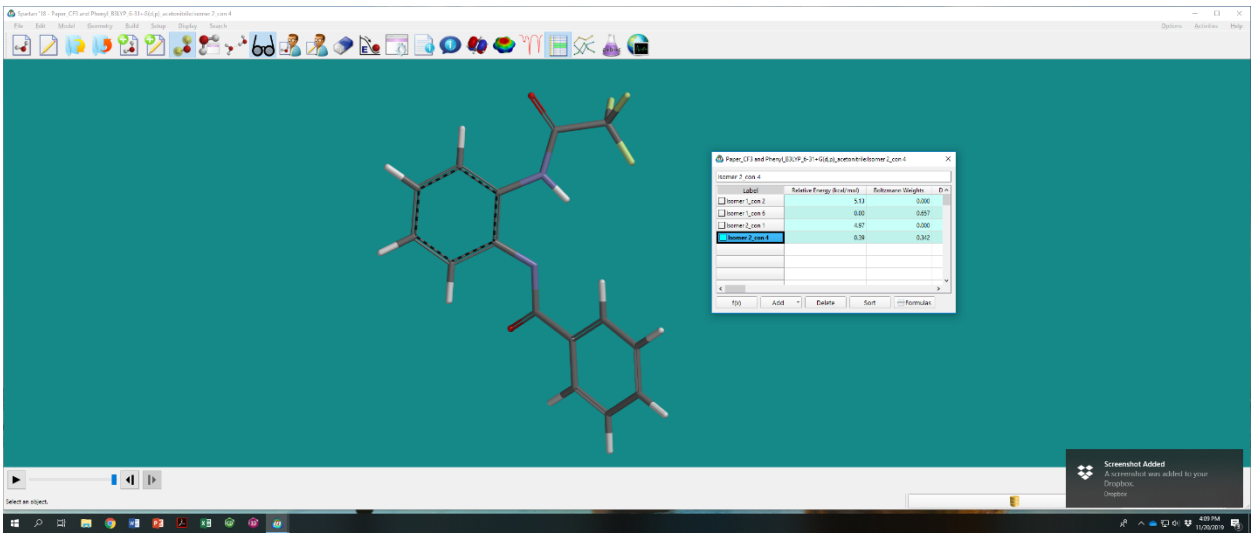
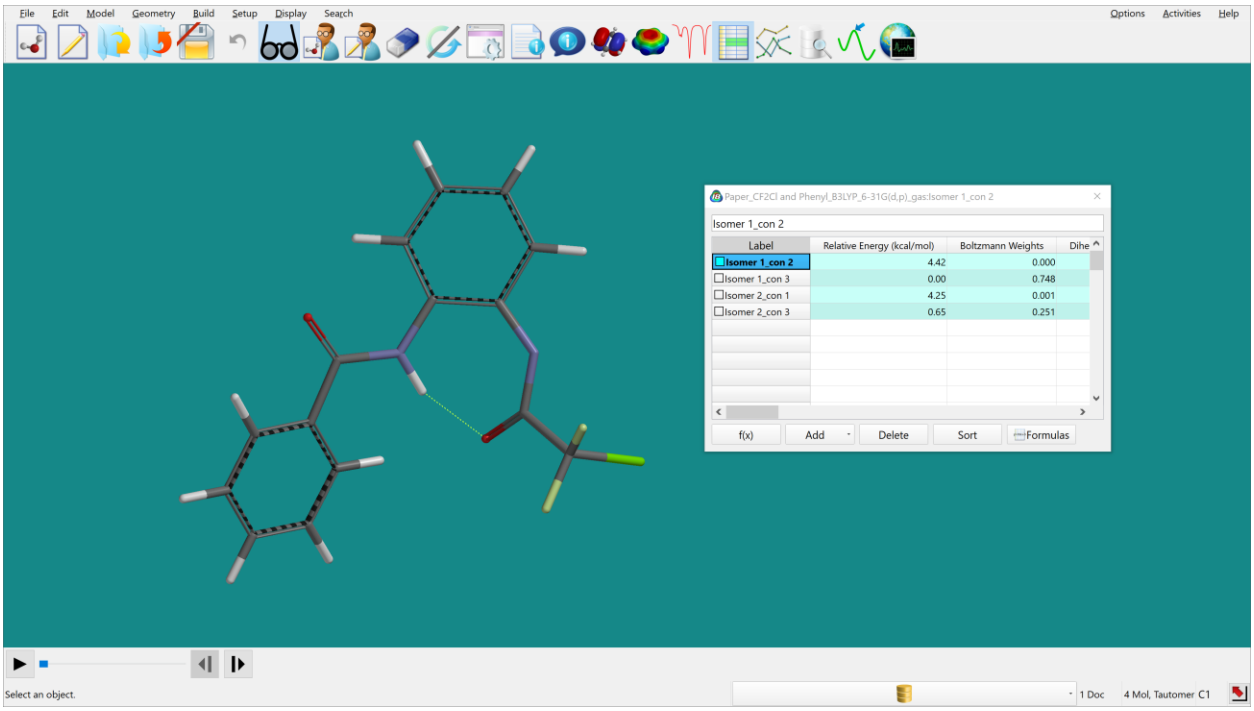
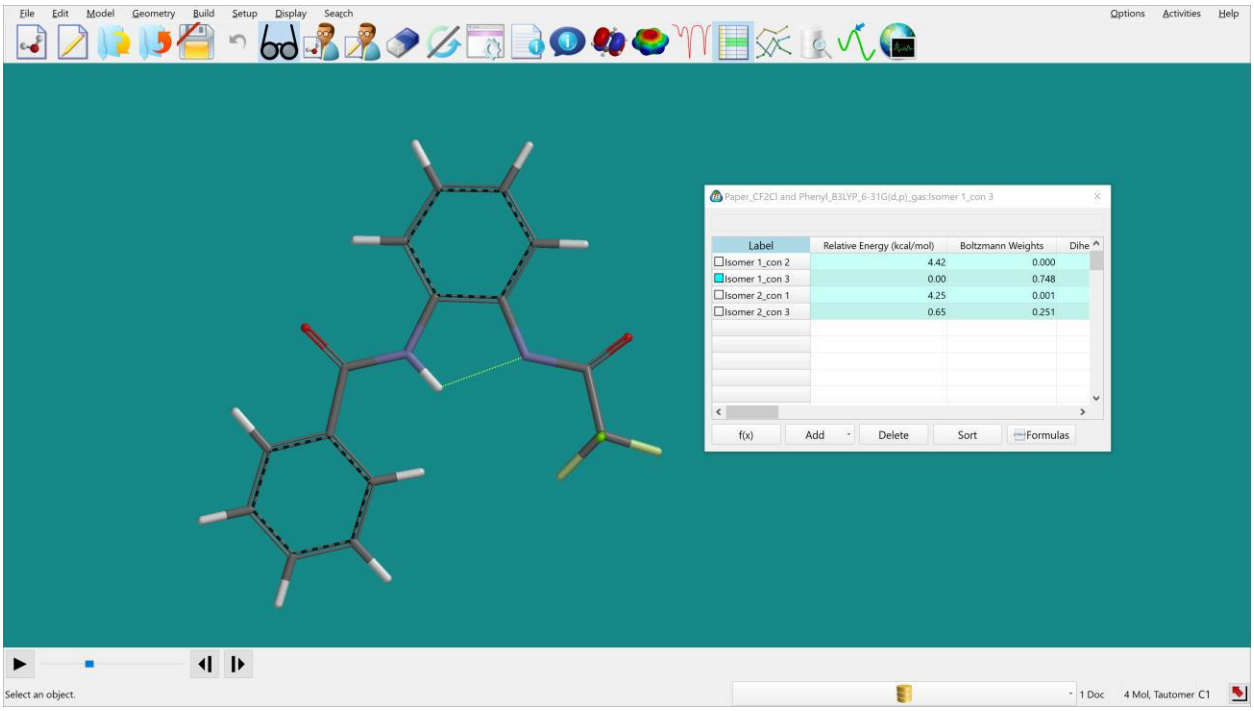


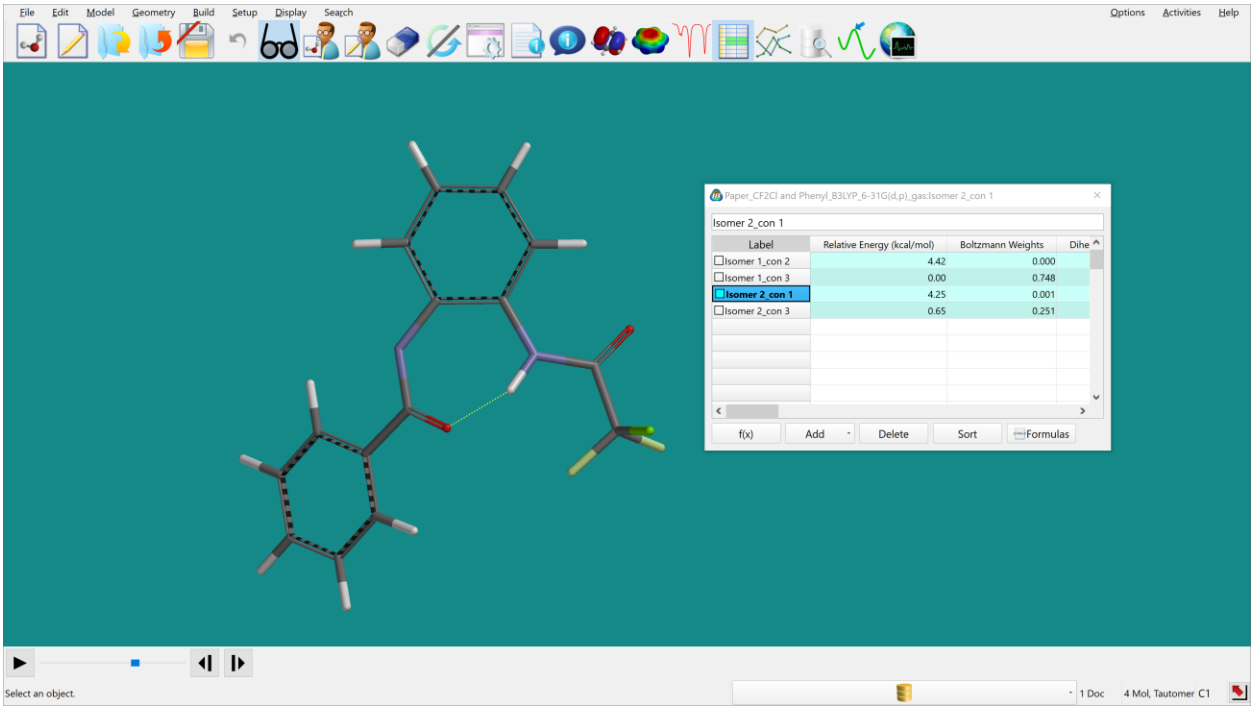
Table S15. Boltzmann Analysis of Conformers of 1y in the gas phase and in acetonitrile. Isomer I is the nitrogen radical of the more electron deficient amide, while isomer II is the nitrogen radical of the more electron rich amide.

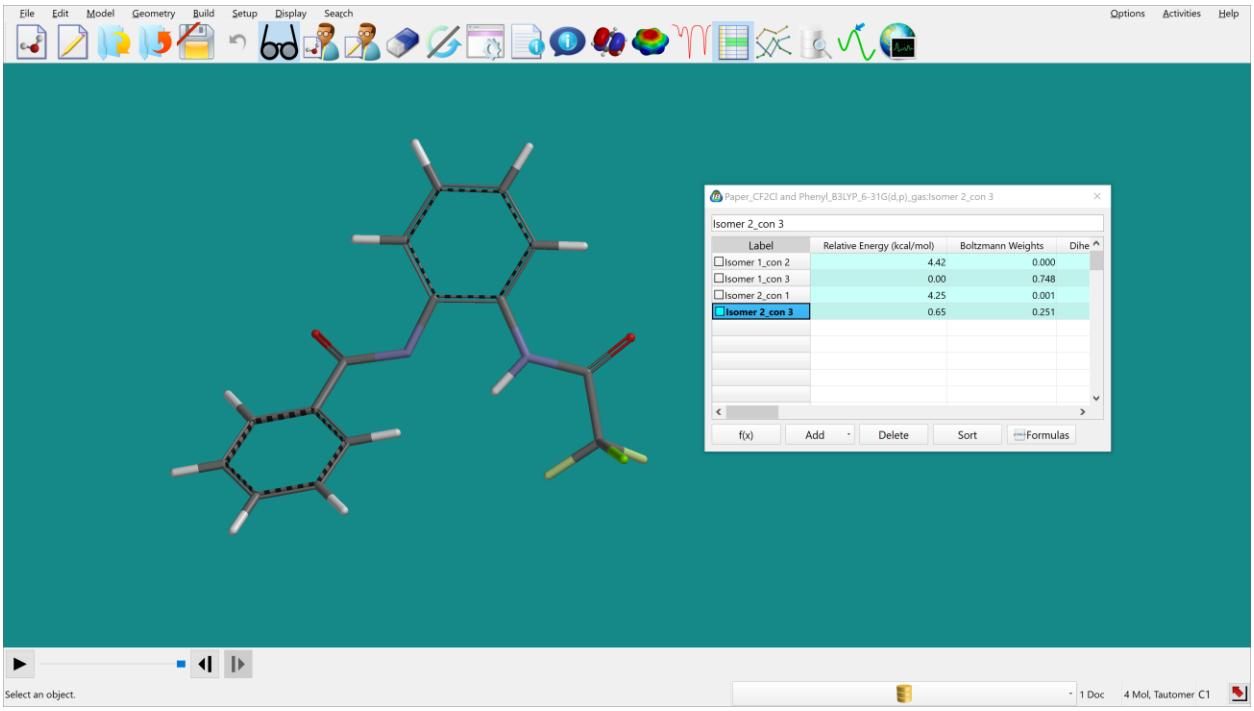
Gas Phase

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-1497.48840	4.42	0.000
Isomer 1_con 3	-1497.49545	0.00	0.748
Isomer 2_con 1	-1497.48868	4.25	0.001
Isomer 2_con 3	-1497.49442	0.65	0.251



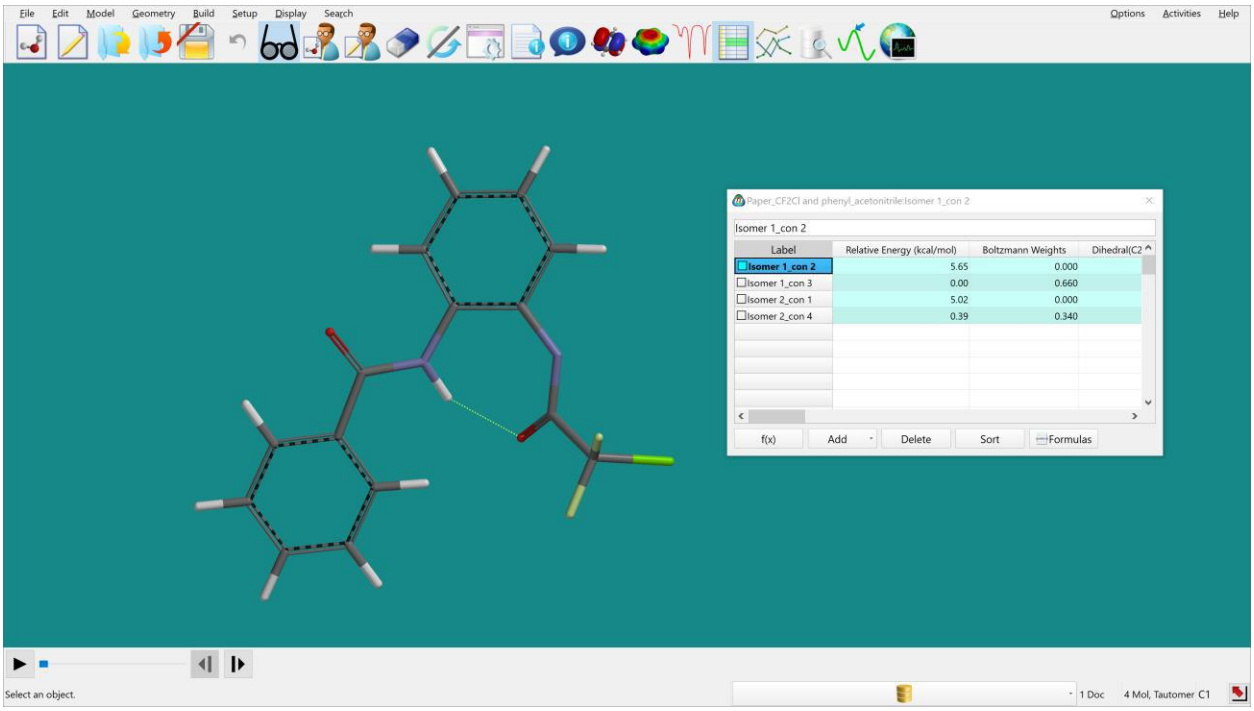

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF2Cl and Phenyl_B3LYP_6-31G(d,p)_gas:Isomer 1_con 3
Label | Relative Energy (kcal/mol) | Boltzmann Weights | Dihe
Isomer 1_con 2 | 4.42 | 0.000
Isomer 1_con 3 | 0.00 | 0.748
Isomer 2_con 1 | 4.25 | 0.001
Isomer 2_con 3 | 0.65 | 0.251
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

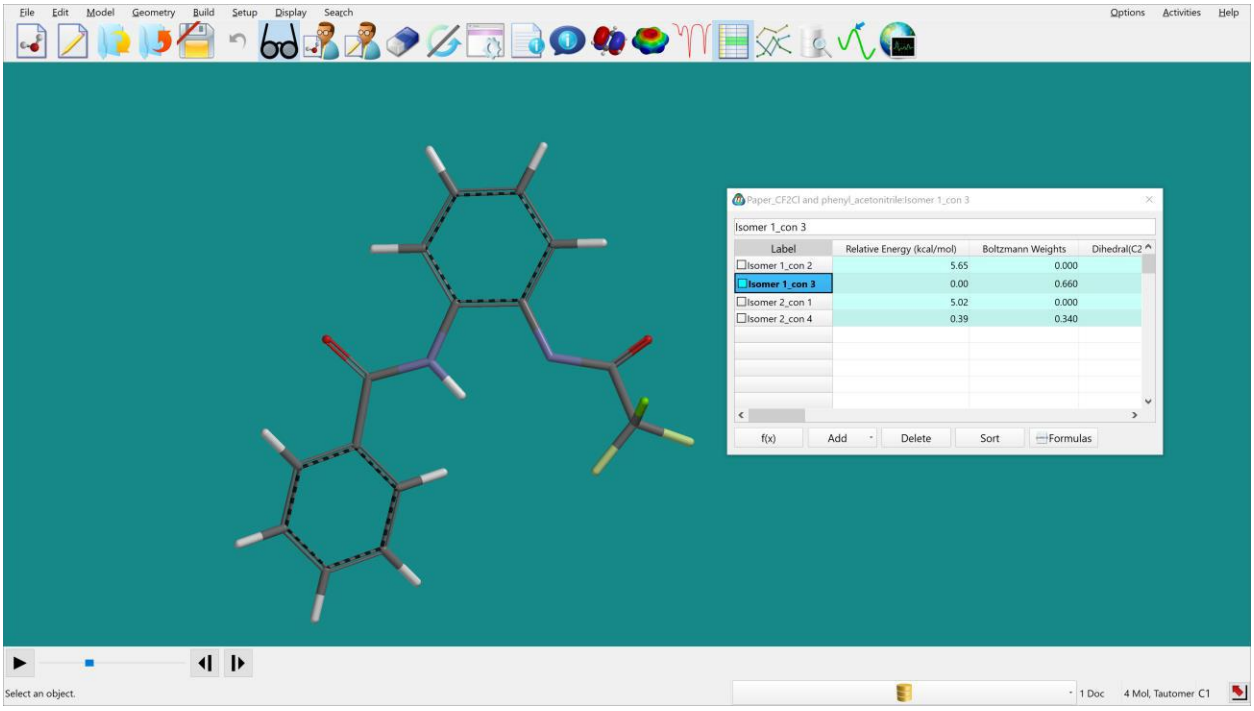

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF2Cl and Phenyl_B3LYP_6-31G(d,p)_gas:Isomer 2_con 1
Isomer 2_con 1
Label | Relative Energy (kcal/mol) | Boltzmann Weights | Dihe
Isomer 1_con 2 | 4.42 | 0.000
Isomer 1_con 3 | 0.00 | 0.748
Isomer 2_con 1 | 4.25 | 0.001
Isomer 2_con 3 | 0.65 | 0.251
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

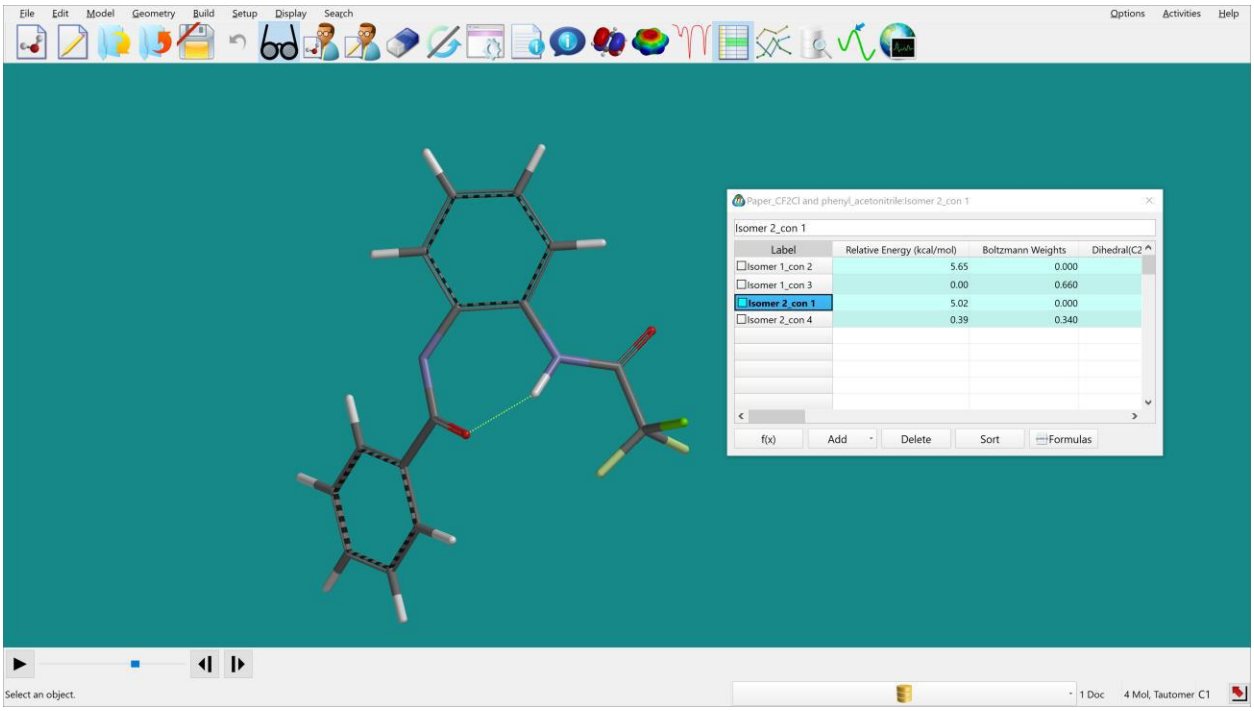


Acetonitrile

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-1497.50383	5.65	0.000
Isomer 1_con 3	-1497.51284	0.00	0.660
Isomer 2_con 1	-1497.50483	5.02	0.000
Isomer 2_con 4	-1497.51221	0.39	0.340


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF2Cl and phenyl_acetonitrile:Isomer 1_con 2
Isomer 1_con 2
Label | Relative Energy (kcal/mol) | Boltzmann Weights | Dihedral(C2
Isomer 1_con 2 | 5.65 | 0.000
Isomer 1_con 3 | 0.00 | 0.660
Isomer 2_con 1 | 5.02 | 0.000
Isomer 2_con 4 | 0.39 | 0.340
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF2Cl and phenyl_acetonitrile:Isomer 1_con 3
Isomer 1_con 3
Label | Relative Energy (kcal/mol) | Boltzmann Weights | Dihedral(C2
Isomer 1_con 2 | 5.65 | 0.000
Isomer 1_con 3 | 0.00 | 0.660
Isomer 2_con 1 | 5.02 | 0.000
Isomer 2_con 4 | 0.39 | 0.340
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF2Cl and phenyl_acetonitrile:Isomer 2_con 1
Isomer 2_con 1
Label | Relative Energy (kcal/mol) | Boltzmann Weights | Dihedral(C2
Isomer 1_con 2 | 5.65 | 0.000
Isomer 1_con 3 | 0.00 | 0.660
Isomer 2_con 1 | 5.02 | 0.000
Isomer 2_con 4 | 0.39 | 0.340
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

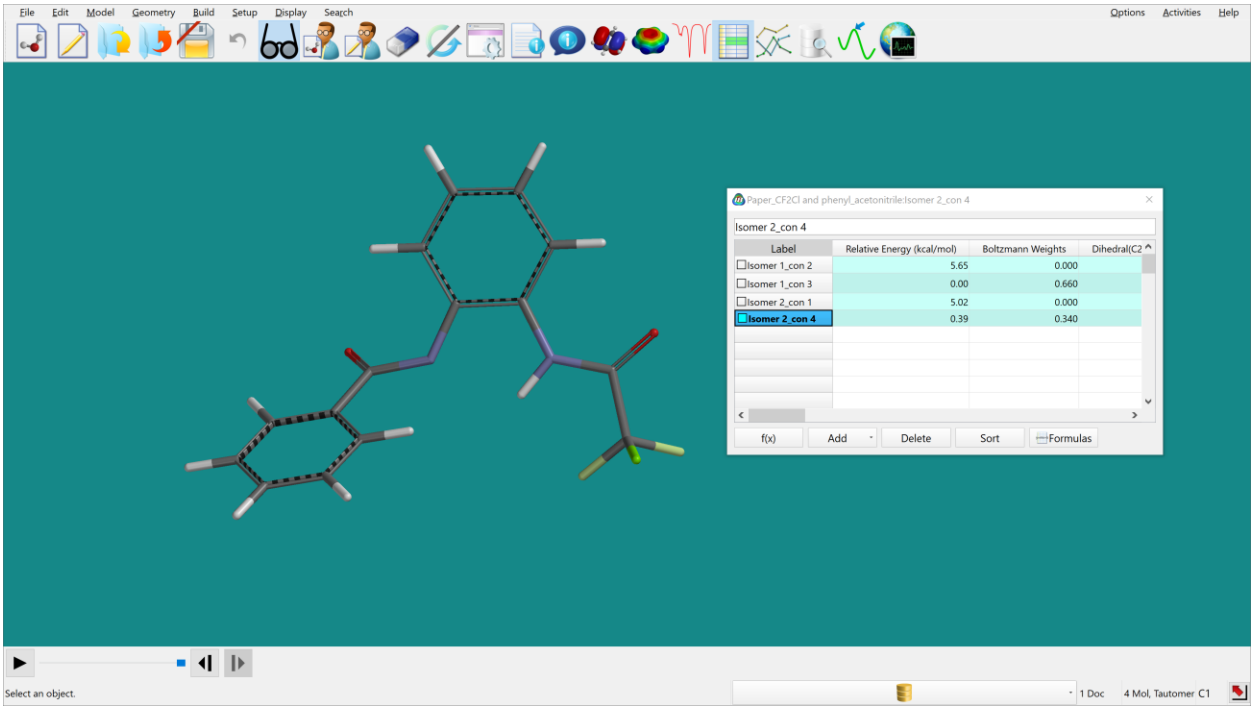
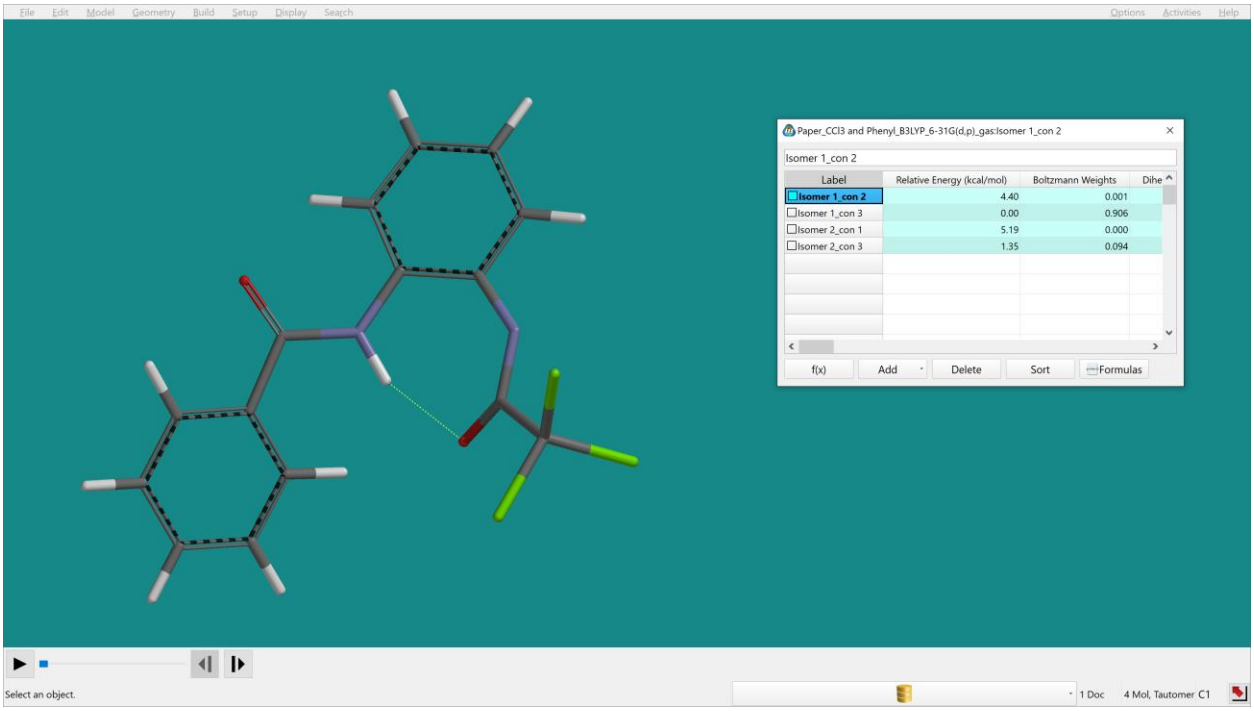
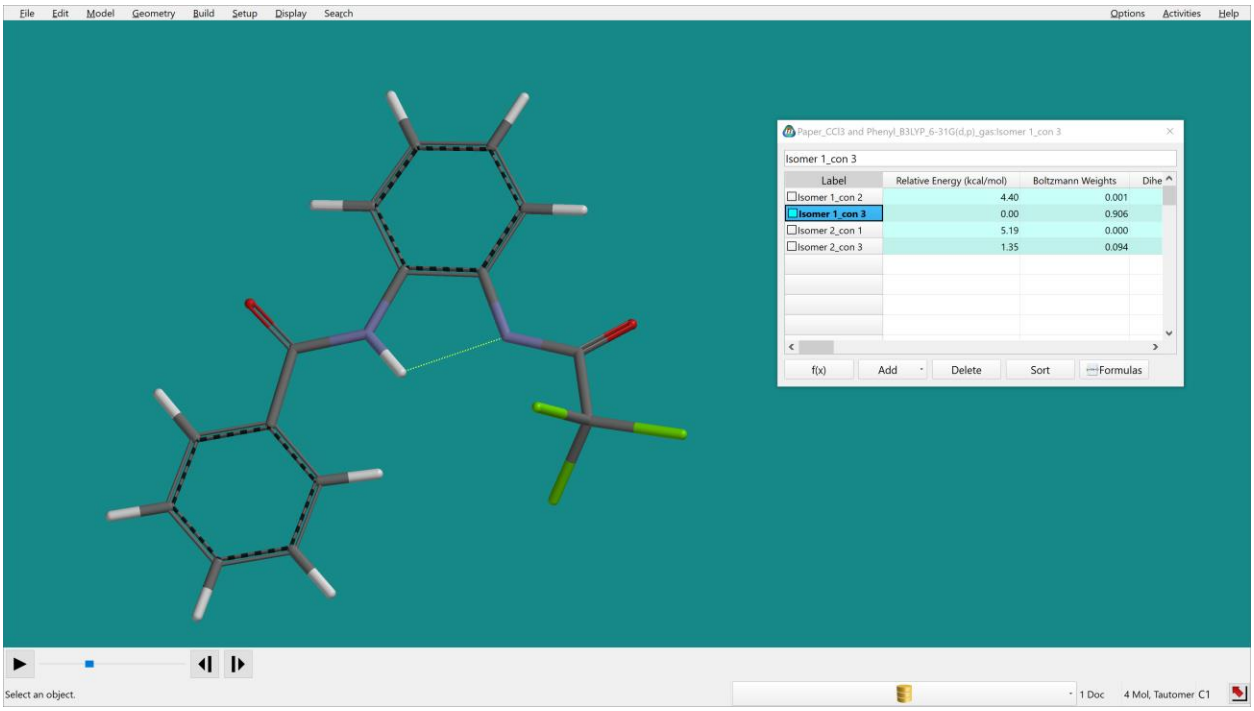

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CF2Cl and phenyl_acetonitrile:Isomer 2_con 4
Isomer 2_con 4
Label | Relative Energy (kcal/mol) | Boltzmann Weights | Dihedral(C2
Isomer 1_con 2 | 5.65 | 0.000
Isomer 1_con 3 | 0.00 | 0.660
Isomer 2_con 1 | 5.02 | 0.000
Isomer 2_con 4 | 0.39 | 0.340
f(x) Add Delete Sort Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

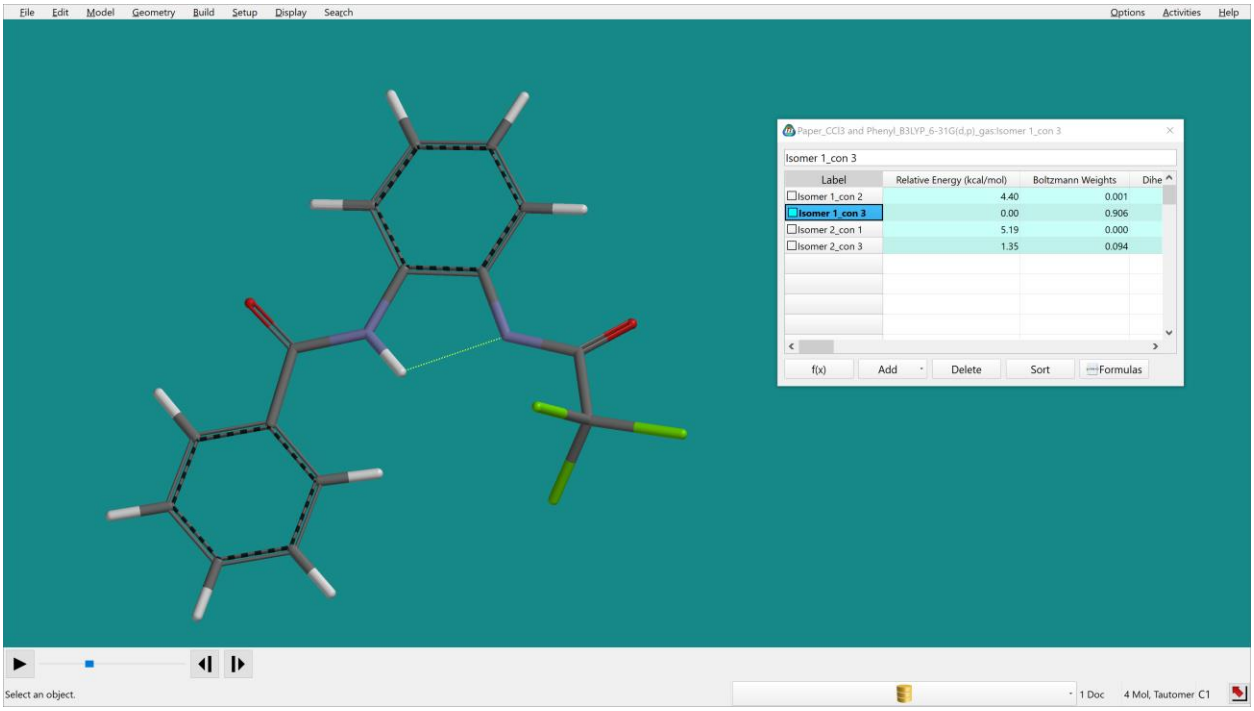
Table S16. Boltzmann Analysis of Conformers of 1z in the gas phase and in acetonitrile. Isomer I is the nitrogen radical of the more electron deficient amide, while isomer II is the nitrogen radical of the more electron rich amide.

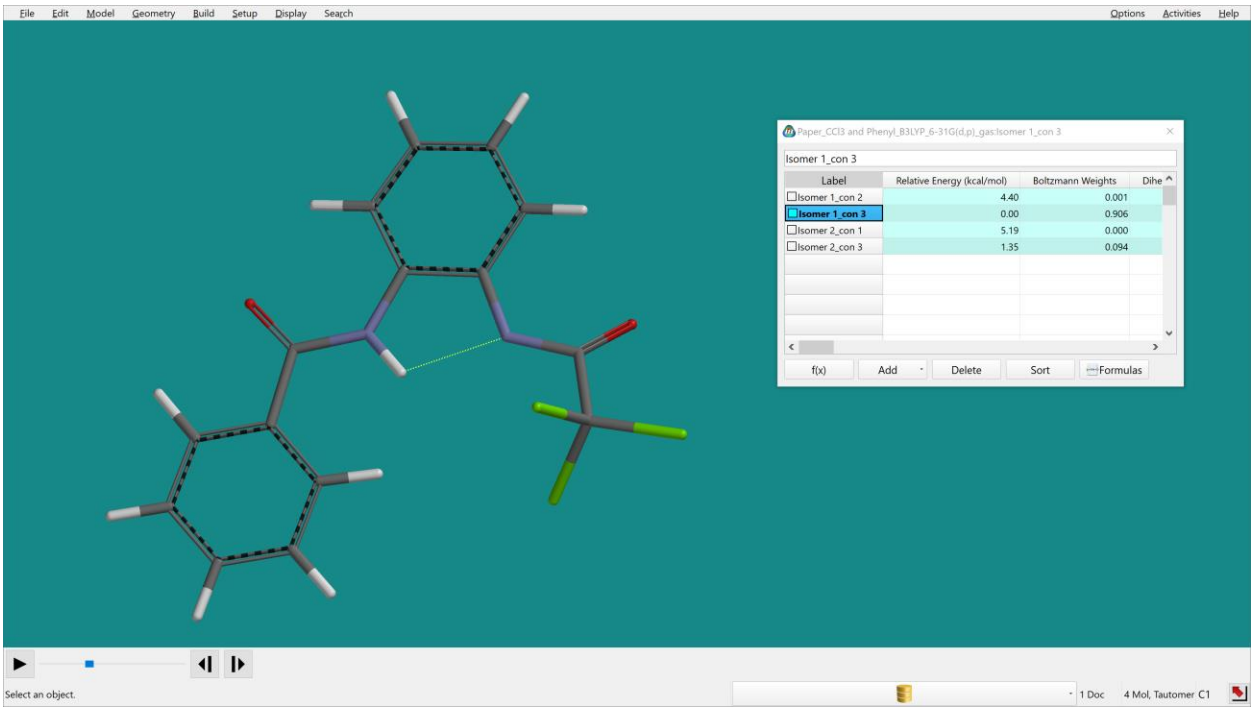
Gas Phase

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-2218.17325	4.40	0.001
Isomer 1_con 3	-2218.18026	0.00	0.906
Isomer 2_con 1	-2218.17200	5.19	0.000
Isomer 2_con 3	-2218.17812	1.35	0.094



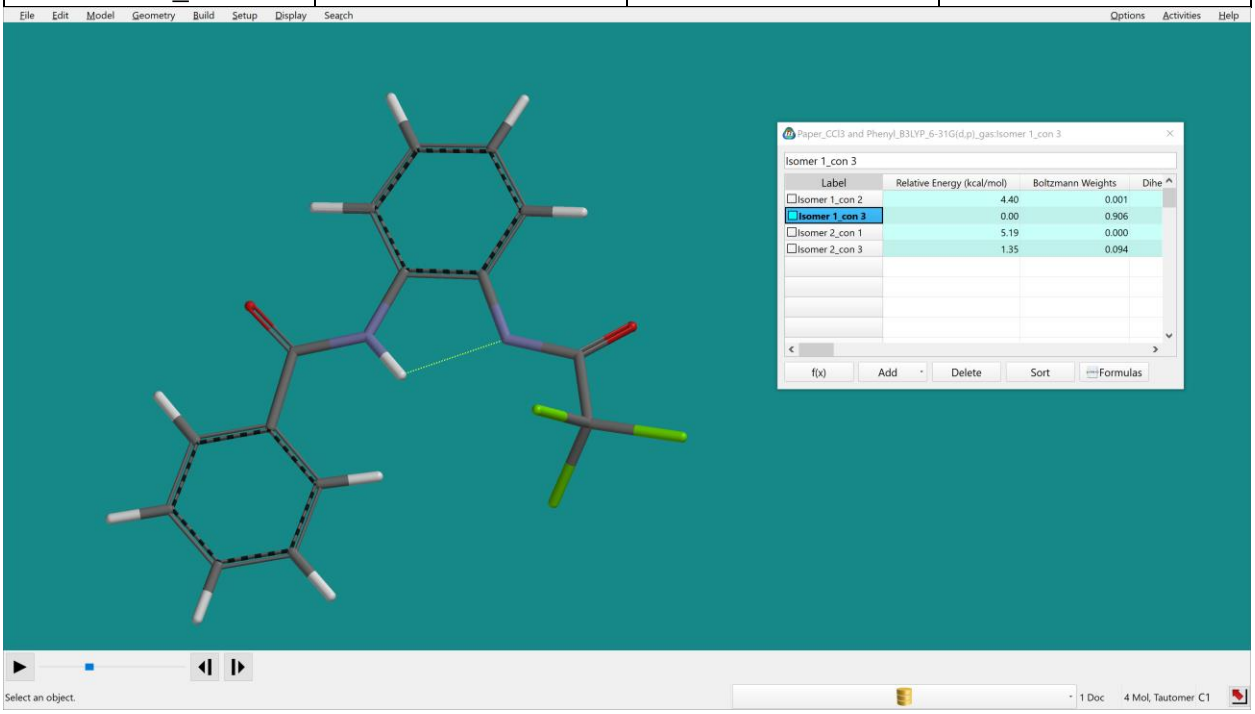

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Phenyl_B3LYP_6-31G(d,p)_gas:Isomer 1_con 3
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 4.40 0.001
Isomer 1_con 3 0.00 0.906
Isomer 2_con 1 5.19 0.000
Isomer 2_con 3 1.35 0.094
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

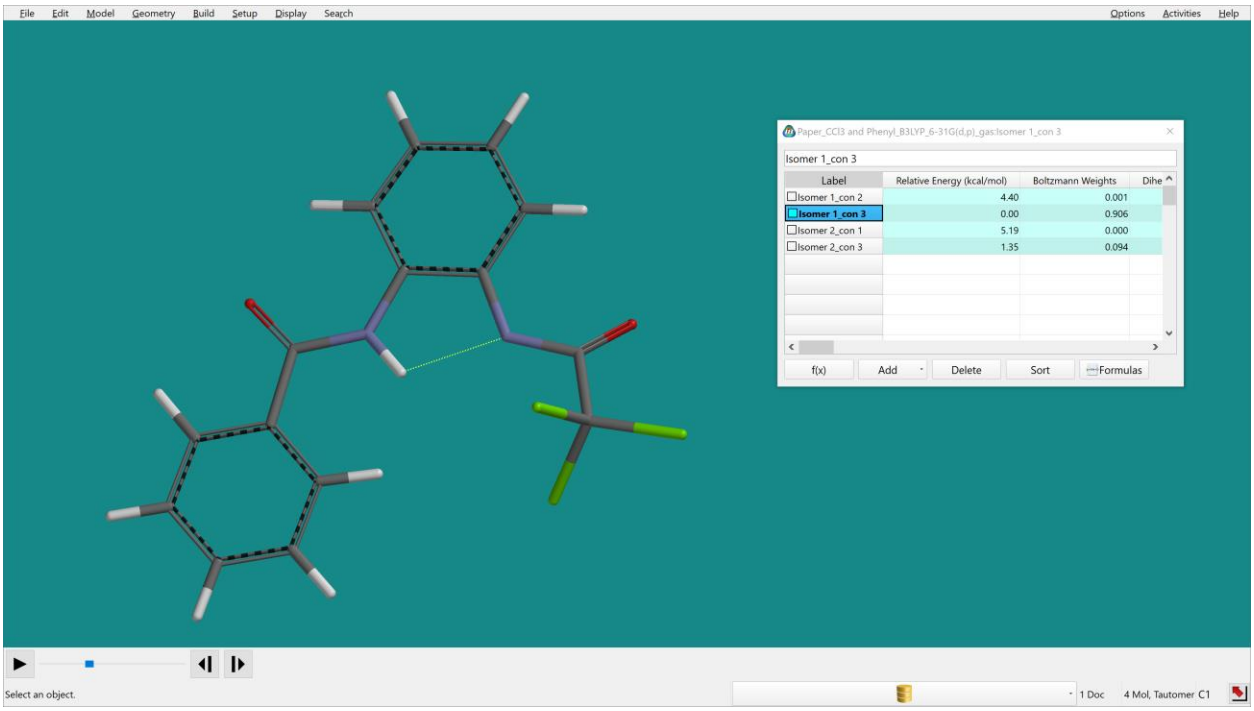

File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Phenyl_B3LYP_6-31G(d,p)_gas:Isomer 1_con 3
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 4.40 0.001
Isomer 1_con 3 0.00 0.906
Isomer 2_con 1 5.19 0.000
Isomer 2_con 3 1.35 0.094
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

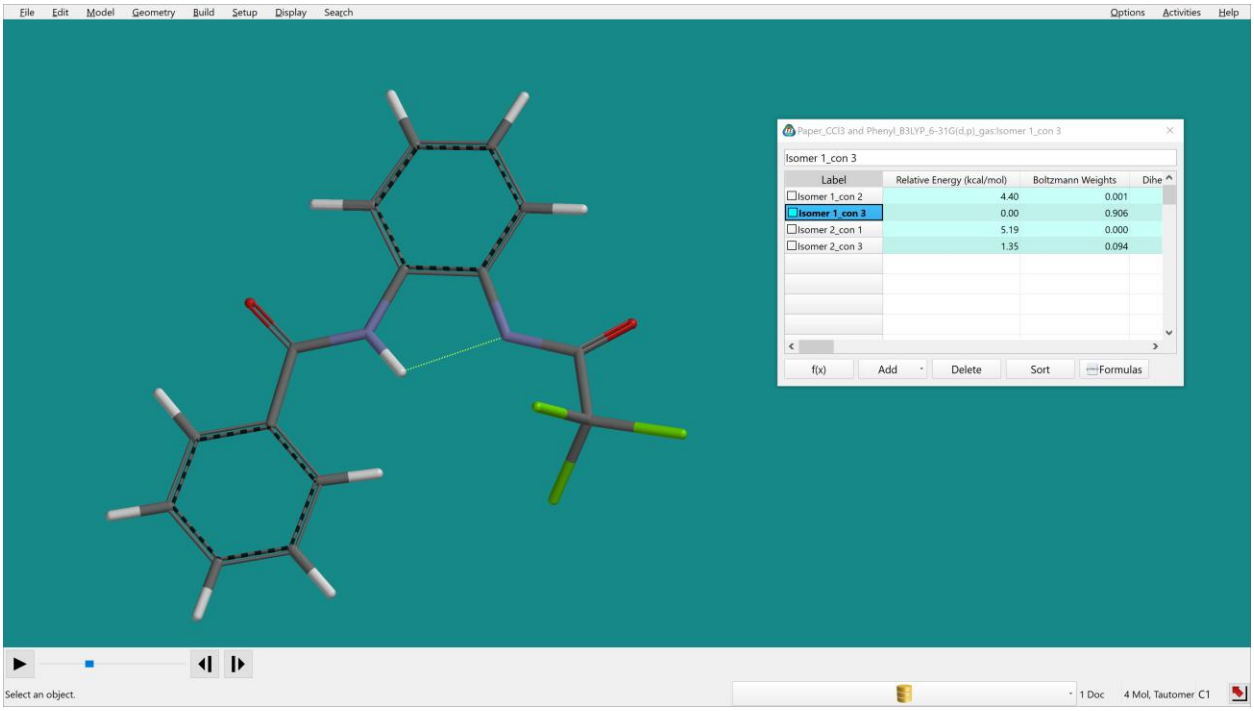


Acetonitrile

Conformer	Energy (au)	Rel. Energy (kcal/mol)	Boltzmann Weights
Isomer 1_con 2	-2218.18940	5.19	0.000
Isomer 1_con 3	-2218.19768	0.00	0.941
Isomer 2_con 1	-2218.18730	6.52	0.000
Isomer 2_con 3	-2218.19506	1.65	0.059




File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Phenyl_B3LYP_6-31G(d,p)_gas:Isomer 1_con 3
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 4.40 0.001
Isomer 1_con 3 0.00 0.906
Isomer 2_con 1 5.19 0.000
Isomer 2_con 3 1.35 0.094
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1


File Edit Model Geometry Build Setup Display Search
Options Activities Help
Paper_CCl3 and Phenyl_B3LYP_6-31G(d,p)_gas:Isomer 1_con 3
Isomer 1_con 3
Label
Relative Energy (kcal/mol)
Boltzmann Weights
Dihe
Isomer 1_con 2 4.40 0.001
Isomer 1_con 3 0.00 0.906
Isomer 2_con 1 5.19 0.000
Isomer 2_con 3 1.35 0.094
f(x)
Add
Delete
Sort
Formulas
Select an object.
1 Doc
4 Mol, Tautomer C1

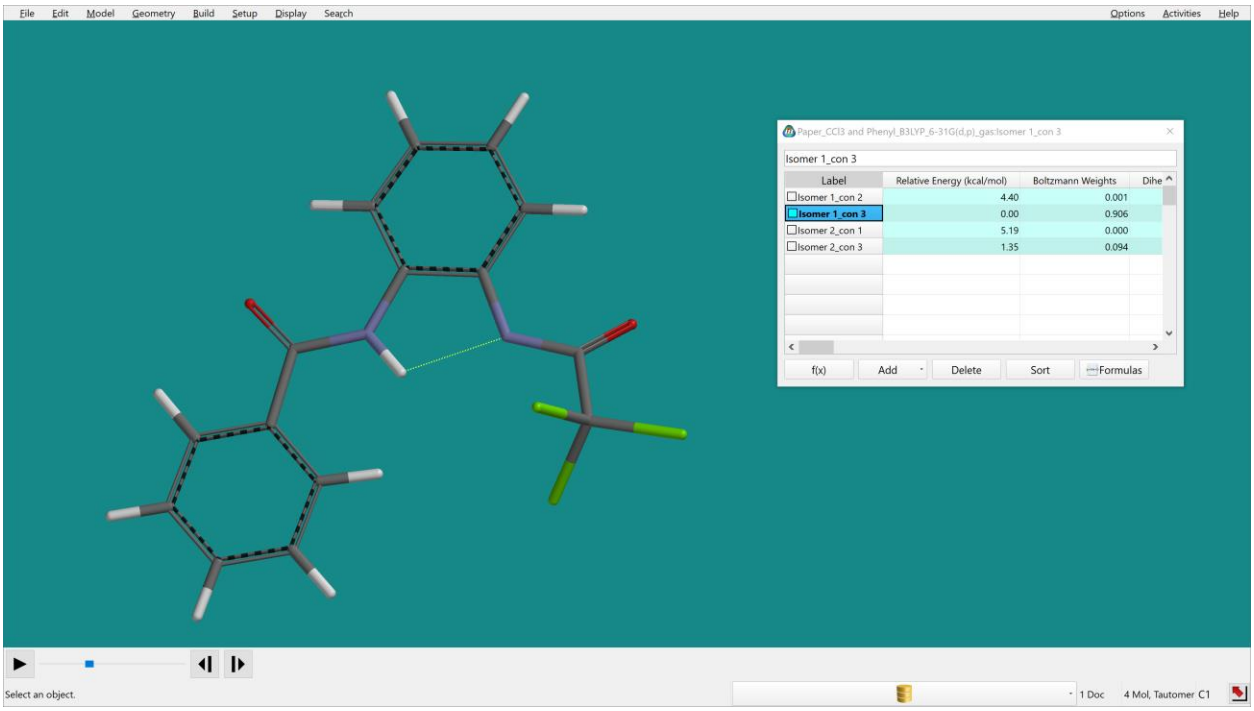
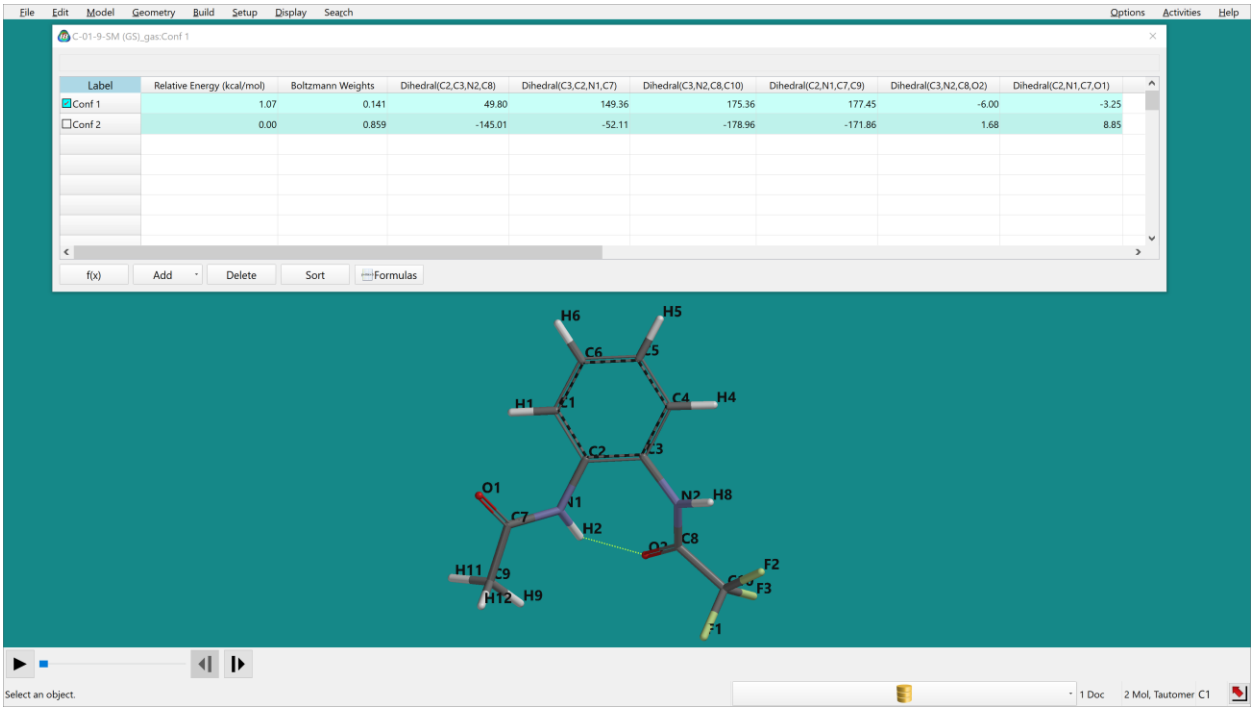
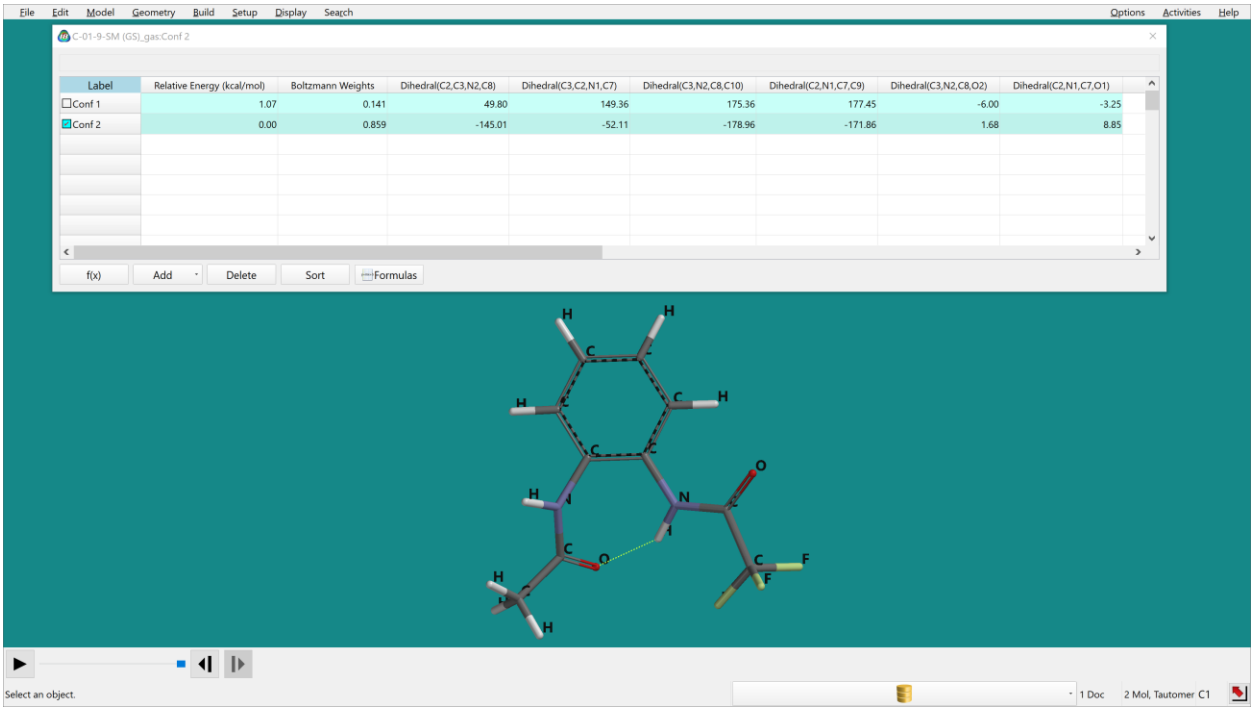


Table S17. Coordinates and dihedral angles of the two lowest energy conformers (con1 and con2) of 1a.



Cartesian Coordinates (Angstroms)

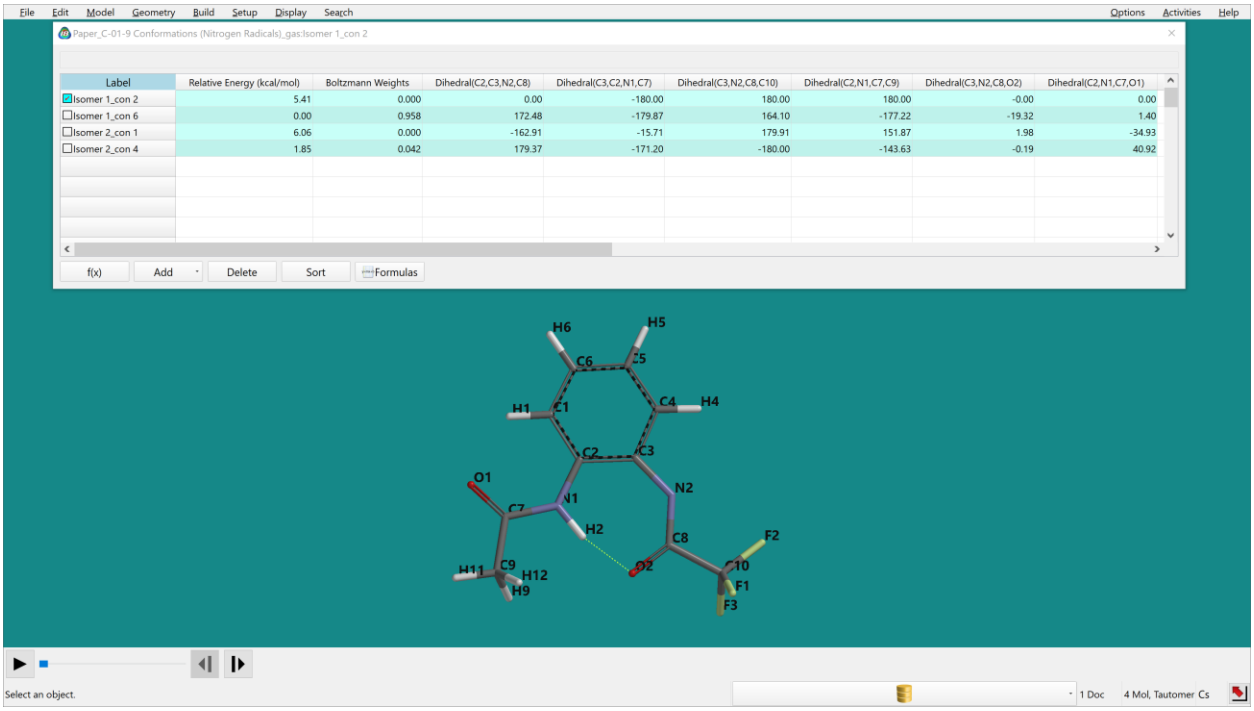
	Atom		X	Y	Z
1	H	H1	0.5541417	2.4841537	-1.7939501
2	C	C1	0.4735330	2.2721043	-0.7366712
3	C	C4	0.2203930	1.7164251	1.9774928
4	C	C2	0.2019319	0.9511914	-0.3384969
5	C	C6	0.6011030	3.2926080	0.2008668
6	C	C5	0.4761166	3.0205391	1.5660385
7	C	C3	0.0758985	0.6833763	1.0418626
8	H	H6	0.8017527	4.3040255	-0.1386254
9	H	H5	0.5811333	3.8106529	2.3024160
10	H	H4	0.1299914	1.4843603	3.0354330
11	N	N1	0.0609887	-0.0872220	-1.2791378
12	H	H2	0.4434083	-0.9852491	-0.9939600
13	N	N2	-0.2872452	-0.5991442	1.5691899
14	H	H8	-0.9258232	-0.5747127	2.3546327
15	C	C7	-0.4214286	0.0275465	-2.5679281
16	C	C8	0.2383065	-1.8080281	1.2748881
17	C	C9	-0.3969696	-1.2652207	-3.3654399
18	H	H9	0.0041204	-2.1184912	-2.8123067
19	H	H11	0.2036701	-1.1081448	-4.2661021
20	H	H12	-1.4169358	-1.4919701	-3.6886823
21	C	C10	-0.3268700	-2.9787992	2.1249760
22	O	O1	-0.8504656	1.0715159	-3.0443099
23	O	O2	1.0723490	-2.0671925	0.4154773
24	F	F1	-1.0255884	-3.8231305	1.3457324
25	F	F2	-1.1612411	-2.5522910	3.1143845
26	F	F3	0.6737290	-3.6589033	2.7022200



Cartesian Coordinates (Angstroms)

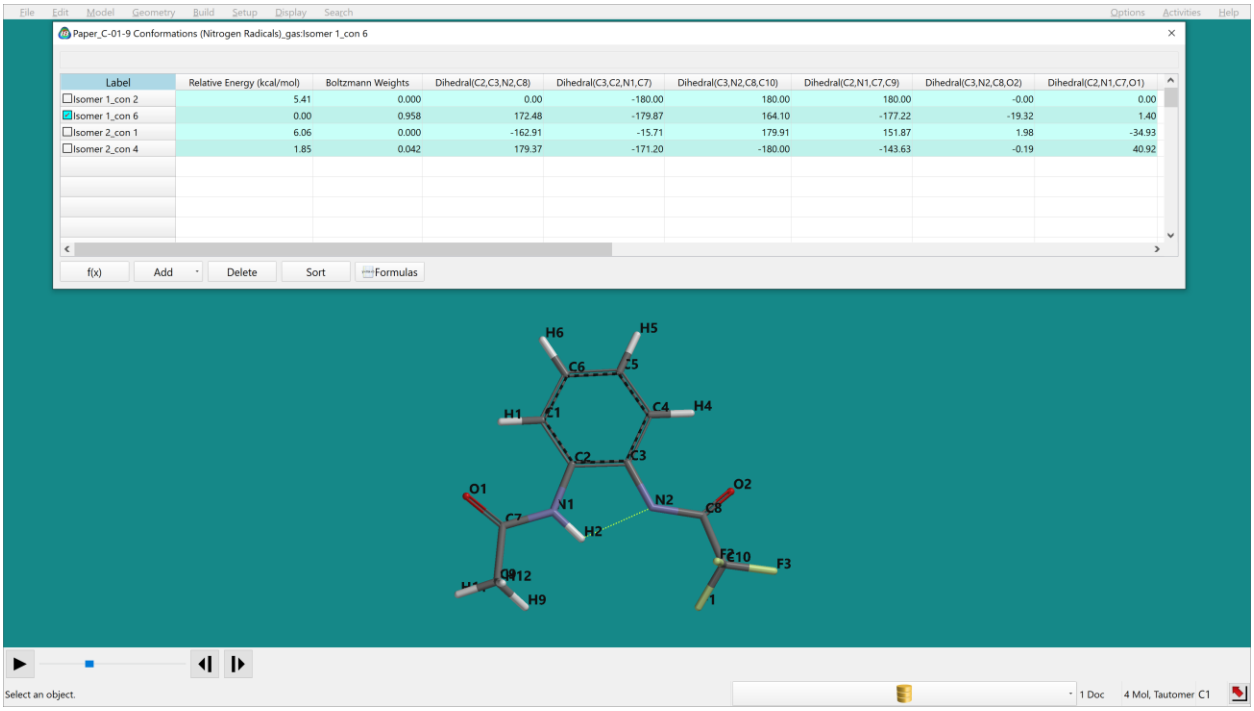
	Atom		X	Y	Z
1	H	H1	0.3440342	2.4087627	-2.3581097
2	C	C1	0.2482290	2.2842276	-1.2827058
3	C	C4	0.0417561	1.9355680	1.4680227
4	C	C2	0.1126846	0.9893204	-0.7637898
5	C	C6	0.2643156	3.3961858	-0.4452871
6	C	C5	0.1612405	3.2167472	0.9361769
7	C	C3	0.0059377	0.8099476	0.6311404
8	H	H6	0.3641925	4.3906657	-0.8684189
9	H	H5	0.1761826	4.0725818	1.6035460
10	H	H4	-0.0508156	1.7924416	2.5365725
11	N	N1	0.0120675	-0.0784113	-1.7069005
12	H	H2	-0.4890035	0.1544061	-2.5532606
13	N	N2	-0.1256315	-0.4945317	1.1655419
14	H	H8	0.4413157	-1.2105510	0.6993843
15	C	C7	0.7031657	-1.2621118	-1.7194849
16	C	C8	-0.8635757	-0.8169044	2.2584253
17	C	C9	0.5209234	-2.1200228	-2.9553188
18	H	H9	-0.1552726	-1.6900202	-3.6988690
19	H	H11	0.1394906	-3.0975971	-2.6478872
20	H	H12	1.5018784	-2.2807309	-3.4115721
21	C	C10	-0.8116113	-2.3227155	2.6418063
22	O	O1	1.4208769	-1.6254722	-0.7859135
23	O	O2	-1.5491377	-0.0748237	2.9416321
24	F	F1	-0.3325047	-2.4662651	3.8921304
25	F	F2	-0.0294335	-3.0624751	1.8171680
26	F	F3	-2.0513050	-2.8482217	2.6059711

Table S18. Relative energies, coordinates and dihedral angles for the two lowest energy conformations (isomer I and isomer II) of the amidyl radicals.



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-0.2689088	0.0000000	3.0651690
2	C	C1	-0.9345393	0.0000000	2.2146247
3	C	C4	-2.6679038	0.0000000	0.0115816
4	C	C2	-0.3616497	0.0000000	0.9196690
5	C	C6	-2.3051329	0.0000000	2.3892001
6	C	C5	-3.1872764	0.0000000	1.2796824
7	C	C3	-1.2549292	0.0000000	-0.2515504
8	H	H6	-2.7065252	0.0000000	3.3982465
9	H	H5	-4.2613559	0.0000000	1.4344954
10	H	H4	-3.3043971	0.0000000	-0.8659566
11	N	N1	0.9956710	0.0000000	0.7284340
12	H	H2	1.3011973	-0.0000001	-0.2647919
13	N	N2	-0.9814203	0.0000000	-1.5751469
14	C	C7	2.0280434	0.0000000	1.6789751
15	C	C8	0.1735455	0.0000000	-2.2533705
16	C	C9	3.4068871	0.0000000	1.0524086
17	H	H9	3.5464943	-0.8819551	0.4181177
18	H	H11	4.1504027	0.0000000	1.8487711
19	H	H12	3.5464944	0.8819551	0.4181177
20	C	C10	-0.0094668	0.0000000	-3.7969394
21	O	O1	1.8423659	-0.0000001	2.8854119
22	O	O2	1.3618368	0.0000000	-1.8780388
23	F	F1	0.5894593	1.0921942	-4.3262211
24	F	F2	-1.2883518	0.0000000	-4.2046683
25	F	F3	0.5894593	-1.0921942	-4.3262211



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
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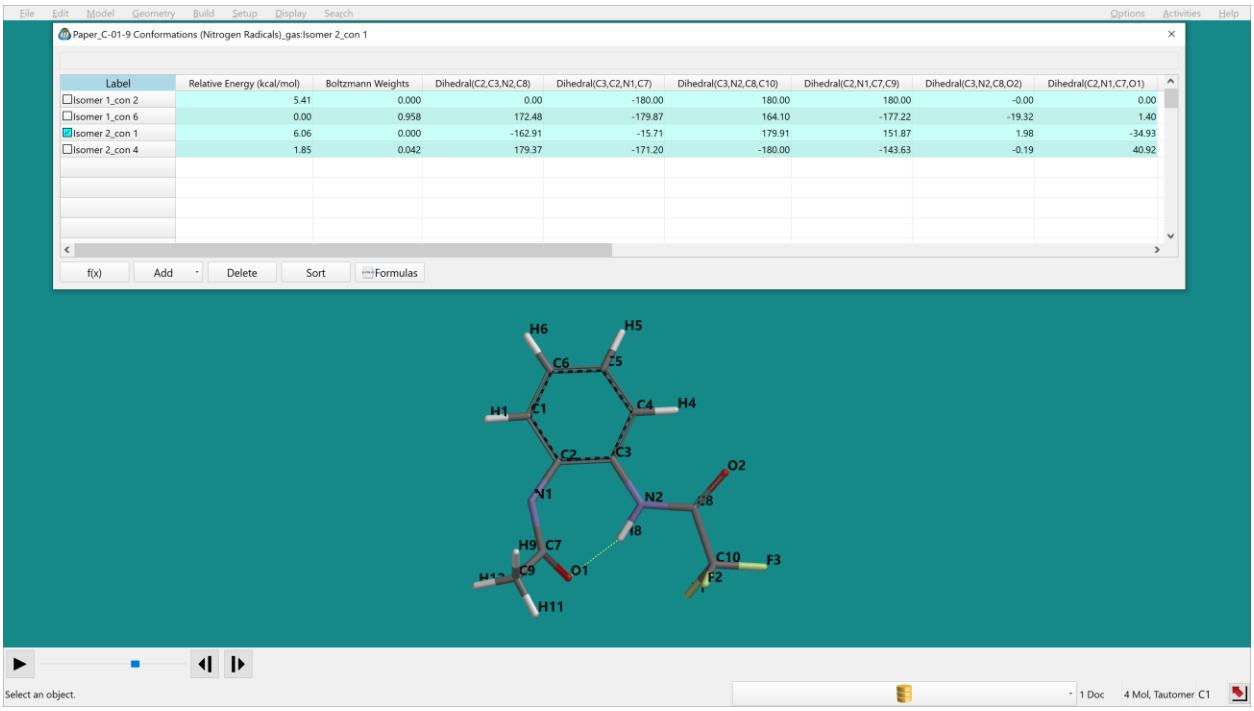
3	C	C4	-2.4070748	-0.2712871	0.4626786
4	C	C2	0.0203237	-0.2650085	1.0008227
5	C	C6	-1.6159219	-0.6931173	2.7163354
6	C	C5	-2.6735085	-0.5475376	1.7827877
7	C	C3	-1.0528743	-0.1240320	0.0137021
8	H	H6	-1.8472262	-0.9144622	3.7539313
9	H	H5	-3.7008444	-0.6588434	2.1151243
10	H	H4	-3.2028413	-0.1736272	-0.2632556
11	N	N1	1.2943741	-0.0932985	0.5071310
12	H	H2	1.2943070	0.1296550	-0.4873517
13	N	N2	-0.6447586	0.1703099	-1.2268762
14	C	C7	2.5155438	-0.1632046	1.1732618
15	C	C8	-1.4723850	0.1972847	-2.3157354
16	C	C9	3.7139417	0.1509275	0.3004611
17	H	H9	3.5737147	-0.1539794	-0.7405390
18	H	H11	4.5886667	-0.3495464	0.7175077
19	H	H12	3.8977117	1.2313680	0.3188980
20	C	C10	-0.8020923	0.9451948	-3.5038728
21	O	O1	2.6100713	-0.4281787	2.3619187
22	O	O2	-2.5725119	-0.3122114	-2.4717404
23	F	F1	0.3167334	0.2980674	-3.9148858
24	F	F2	-0.4356313	2.1986859	-3.1408353
25	F	F3	-1.6287003	1.0450716	-4.5521779



Cartesian Coordinates (Angstroms)

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2	C	C1	0.6587750	2.3078254	-1.3384035
3	C	C4	-0.3385472	1.9735904	1.2580417
4	C	C2	0.4457337	0.9701858	-0.8543830
5	C	C6	0.3705391	3.4173645	-0.5785555
6	C	C5	-0.1437299	3.2461045	0.7226361
7	C	C3	-0.0336303	0.8265124	0.5143396
8	H	H6	0.5315957	4.4135501	-0.9776987
9	H	H5	-0.3801463	4.1131582	1.3317837
10	H	H4	-0.7219304	1.8600980	2.2621126
11	N	N1	0.6431048	0.0142150	-1.7705487
12	N	N2	-0.1426967	-0.4576503	1.0536424
13	H	H8	0.4414938	-1.1725450	0.5876836
14	C	C7	0.7424146	-1.3473217	-1.6784226
15	C	C8	-0.8573280	-0.8208732	2.1612432
16	C	C9	0.3091786	-2.0902146	-2.9182222
17	H	H9	-0.5843550	-1.6366606	-3.3569408
18	H	H11	0.1292050	-3.1381394	-2.6741262
19	H	H12	1.1072624	-2.0309093	-3.6669761
20	C	C10	-0.7519341	-2.3439471	2.4691145
21	O	O1	1.2641774	-1.9388876	-0.7179743
22	O	O2	-1.5540841	-0.1104211	2.8622324
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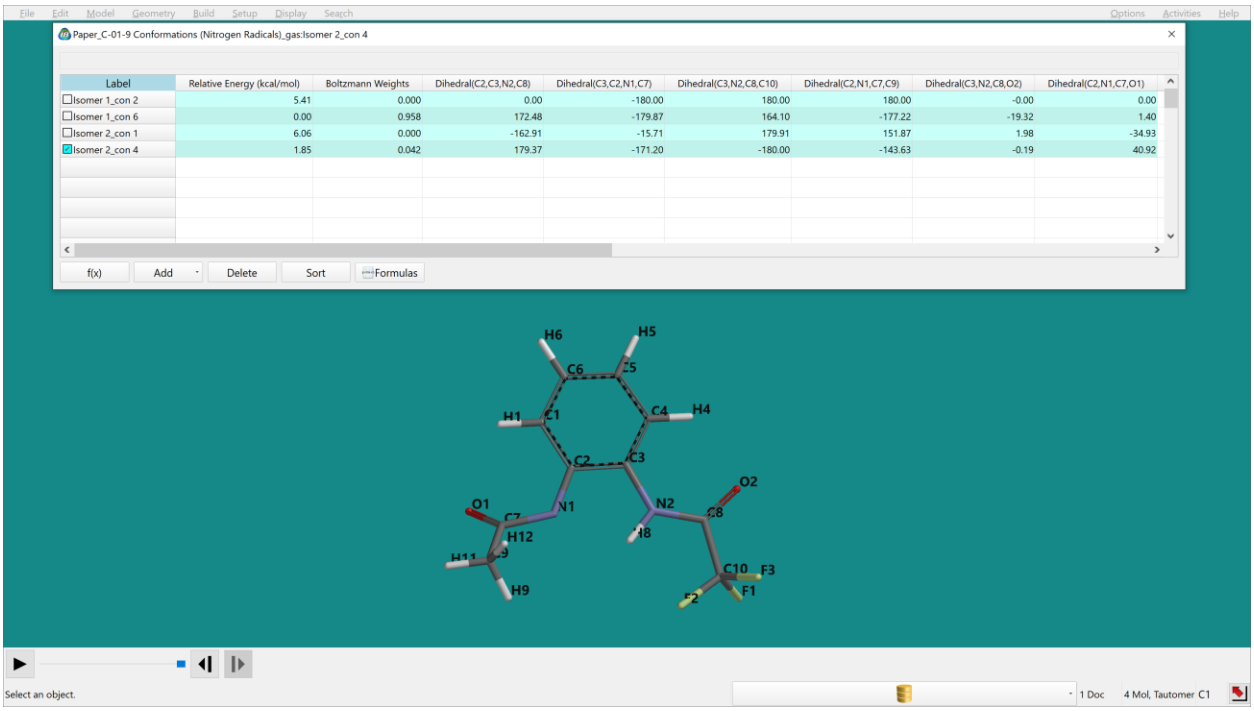

Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	H	H1	-2.3719755	1.1392468	-1.7348931
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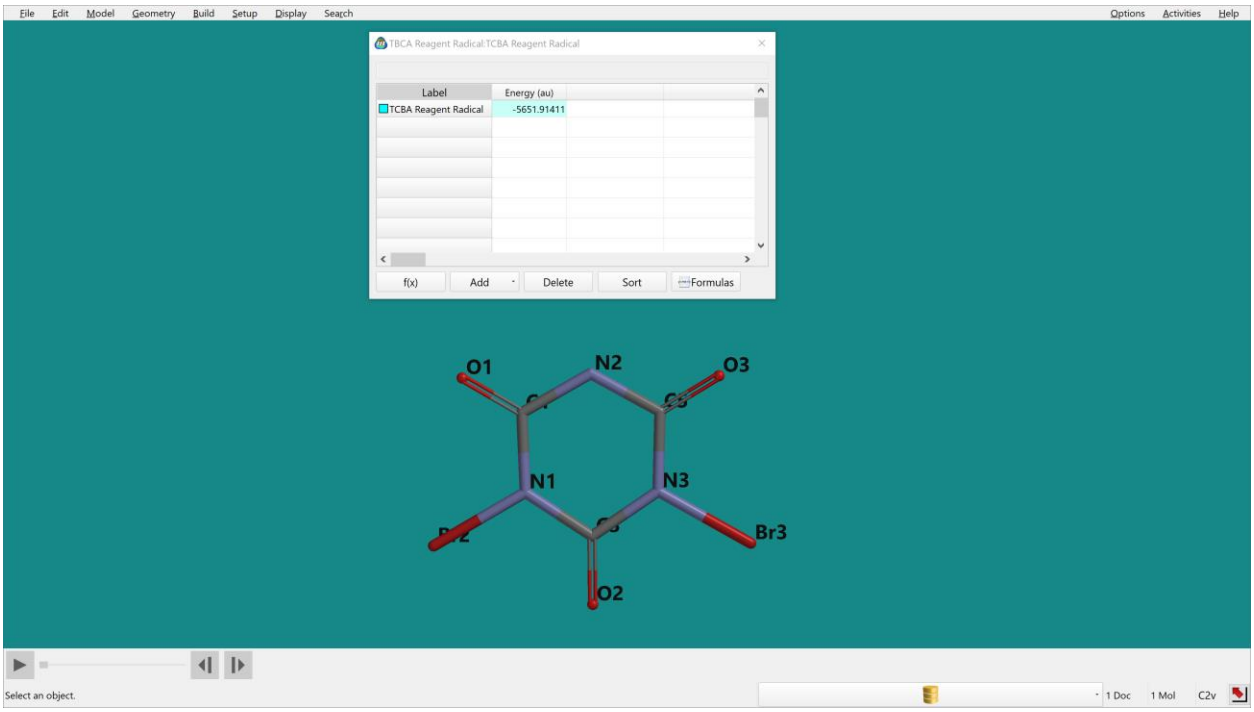
3	C	C4	-1.4498186	-0.0168198	1.8944296
4	C	C2	-0.7821769	0.4123394	-0.4511424
5	C	C6	-3.0874433	0.7905926	0.2607545
6	C	C5	-2.7493657	0.3819244	1.5682532
7	C	C3	-0.4668653	-0.0106381	0.9054619
8	H	H6	-4.1054331	1.0941391	0.0375543
9	H	H5	-3.5106209	0.3729240	2.3422916
10	H	H4	-1.2006716	-0.3301182	2.8988190
11	N	N1	0.2187478	0.3526464	-1.3325817
12	N	N2	0.8586317	-0.3914434	1.1042895
13	H	H8	1.4174476	-0.3339745	0.2529113
14	C	C7	0.1384136	0.8848713	-2.6235709
15	C	C8	1.4480382	-0.8180369	2.2555764
16	C	C9	0.8594170	0.0583454	-3.6646855
17	H	H9	1.9303733	0.0323153	-3.4363031
18	H	H11	0.7054487	0.4966376	-4.6515737
19	H	H12	0.5012435	-0.9766471	-3.6509831
20	C	C10	2.9572041	-1.1596612	2.1024721
21	O	O1	-0.3893405	1.9617335	-2.8733544
22	O	O2	0.9267793	-0.9483526	3.3482934
23	F	F1	3.6989652	-0.3392259	2.8665804
24	F	F2	3.3961032	-1.0383416	0.8208283
25	F	F3	3.1882845	-2.4238430	2.4926903

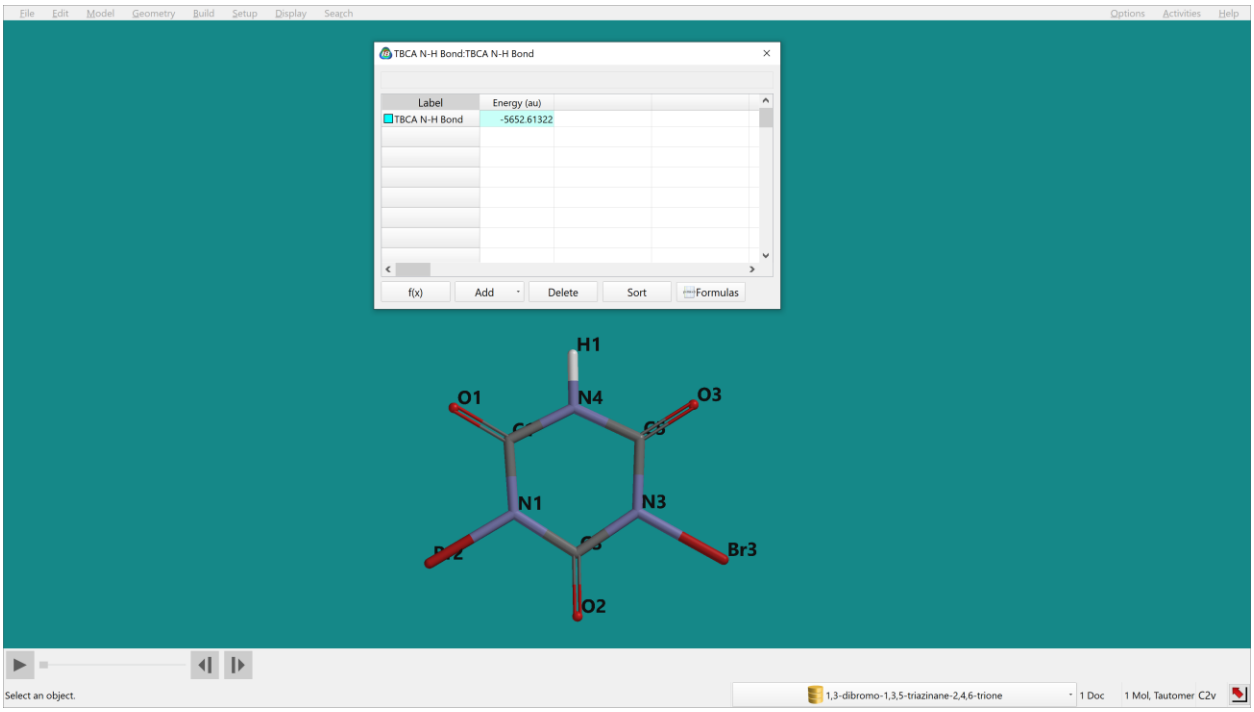
Table S19. Total energy and coordinates for the lowest energy conformation of the nitrogen-centered radical of TBCA.



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.2192040	0.0000000	-1.0118870
2	C	C3	0.0000000	0.0000000	1.1739919
3	C	C5	-1.2192040	0.0000000	-1.0118870
4	N	N3	-1.1728059	0.0000000	0.3925593
5	N	N2	0.0000000	0.0000000	-1.6921301
6	N	N1	1.1728059	0.0000000	0.3925593
7	O	O1	2.2674875	0.0000000	-1.6334417
8	O	O2	0.0000000	0.0000000	2.3783426
9	O	O3	-2.2674875	0.0000000	-1.6334417
10	Br	Br2	2.8006101	0.0000000	1.3226673
11	Br	Br3	-2.8006101	0.0000000	1.3226673

Table S19. Total energy and coordinates for the lowest energy conformation of dibromoisocyanuric acid (DBCA).



Cartesian Coordinates (Angstroms)

	Atom		X	Y	Z
1	C	C1	1.2499055	0.0000000	0.7968929
2	C	C3	0.0000000	0.0000000	-1.3831460
3	C	C5	-1.2499055	0.0000000	0.7968929
4	N	N3	-1.1766644	0.0000000	-0.6066011
5	N	N4	0.0000000	0.0000000	1.4006777
6	N	N1	1.1766644	0.0000000	-0.6066011
7	O	O1	2.2825508	0.0000000	1.4272076
8	O	O2	0.0000000	0.0000000	-2.5883059
9	O	O3	-2.2825508	0.0000000	1.4272076
10	Br	Br2	2.8003009	0.0000000	-1.5391102
11	Br	Br3	-2.8003009	0.0000000	-1.5391102
12	H	H1	0.0000000	0.0000000	2.4139957

Energy Determinations for Neutral, Carbon Radical Intermediates of 1a.

Neutral, Carbon Radical Intermediates

The possible free radical mechanism would likely involve the abstraction of a hydrogen atom either *para* or *meta* to the electron-deficient amide group. As noted above, there are two possible hydrogen bonding interactions between the amide side chains for each neutral radical. For our prototypical compound **1a**, this means four potential neutral radical intermediates—**Con 1/2** for the *para* radical and **Con 1/2** for the *meta* radical (Figure S1).

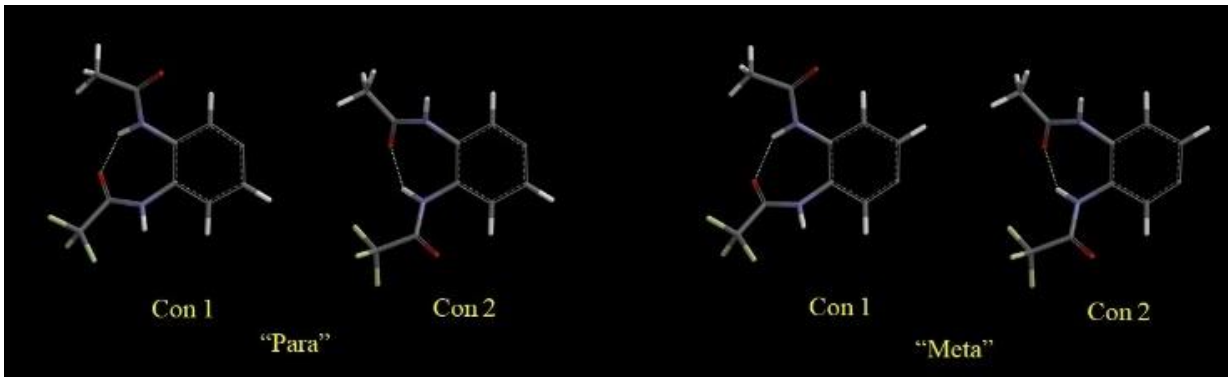


Figure S1 There are two conformations for both the *para* (Con 1/2) and *meta* (Con 1/2) neutral radicals for **1a**. There is a slight energetic preference for the Con 2 (*para*) conformation with full geometry optimizations at the B3LYP level of theory with 6-31+G(d,p) and 6-311+G(d,p) basis sets, as well as with MP2/6-31+G(d,p).

Our initial thought was that the regiospecificity might be reflected in the preferential formation of a lower energy, neutral free radical generated by the removal of a hydrogen atom in the *para* position or an appreciable difference in electron density between the *para* and *meta* isomeric free radicals. Based on B3LYP/6-31+G(d,p) calculations in the gas phase using unrestricted hybrid HF-DFT SCF calculations in Spartan 16 for **1a**, both the *para* (**Con 2**) and *meta* (**Con 1**) neutral free radicals have essentially the same energy. Furthermore, the **Con 2** (*para*) and **Con 2** (*meta*) relative energies are 0.00 and 0.01 kcal/mol, respectively. The **Con 1** (*para*) and **Con 1** (*meta*) relative energies are 0.82 kcal/mol and 1.30 kcal/mol higher in energy, respectively, than the most stable *para* configuration (**Con 2**). Carrying out the same set of calculations on **1a** in acetonitrile showed that the relative energy for **Con 2** (*para*) and **Con 2** (*meta*) are 0.00 and 0.06 kcal/mol, respectively. The **Con 1** (*para*) and **Con 1** (*meta*) are 1.69 kcal/mol and 2.05 kcal/mol higher in energy, respectively, compared to the most stable *para* configuration (**Con 2**).

In many cases, the calculations of the *para* and *meta* neutral free radicals do show a slight energy preference for the observed products but not enough to account for the observed product specificity. This energy trend is not consistent, however. For example, in the case of **1x**, the lowest energy isomer is **Con 2** (*meta*), not the *para* isomer. **Con 1** (*para*) is 0.10 kcal/mol higher in energy. **Con 2** (*para*) and **Con 1** (*meta*) are essentially equivalent in energy with a relative energy difference of 0.36 kcal/mol and 0.35 kcal/mol, respectively, compared to the lowest energy isomer, **Con 2** (*meta*). The trends are similar for the calculations run in acetonitrile. The lowest energy isomer is **Con 2** (*meta*). **Con 1** (*para*) is 0.17 kcal/mol higher in energy. **Con 2** (*para*) and **Con 1** (*meta*) are higher in energy with a relative energy difference of 0.20 kcal/mol and 0.35 kcal/mol, respectively, compared to the lowest energy isomer, **Con 2** (*meta*).

The electrostatic, Mulliken, and natural charges (in electrons) for the neutral radical structures were also examined to determine if there were differences in electron density. There were no definitive trends for the

para or *meta* carbon atoms that would support the regiospecific products that are observed experimentally. For the **1a** neutral free radical in the gas phase, the natural charges for **Con 1** and **Con 2** (*para*) are 0.179 and 0.172 kcals/mol, respectively; while, the natural charges for **Con 1** and **Con 2** (*meta*) are 0.166 and 0.174 kcals/mol, respectively. The natural charges for the **2x** neutral free radical in acetonitrile for the **Con 1** and **Con 2** (*para*) are 0.156 and 0.158 kcals/mol, respectively, and for **Con 1** and **Con 2** (*meta*) are 0.155 and 0.153 kcals/mol, respectively.

The energy preference and charge distribution values may be a consequence of the B3LYP density functional level of theory, the basis set used, the solvation model, and/or some combination thereof. Other levels of theory and basis sets were used to ascertain if there were substantial differences. Using full geometry optimization with the MP2/6-31+G(d,p) level of theory gave similar computational results to the aforementioned DFT calculations. For the **1a** neutral free radical in the gas phase, the natural charges for **Con 1** and **Con 2** (*para*) are 0.278 and 0.254 kcals/mol, respectively, and for **Con 1** and **Con 2** (*meta*) are 0.230 and 0.249 kcals/mol, respectively. The relative energies from the Møller-Plesset method are similar to those of the DFT method discussed above. The MP2/6-31+G(d,p) relative energies are **Con 2** (*para*, 0.00 kcal/mol) < **Con 2** (*meta*, 0.22 kcal/mol) < **Con 1** (*para*, 0.83 kcal/mol) < **Con 1** (*meta*, 1.56 kcal/mol).

Cation Intermediates

A second plausible mechanism involves an ionic addition of a bromonium ion to yield positively charged intermediates (*para*) and (*meta*). The **Con 1** (*meta*) intermediate is calculated at the B3LYP/6-31+G(d,p) level of theory to be 2.77 kcal/mol more stable than the **Con 2** (*para*) intermediate (Figure S2). The stability is increased to 6.17 kcal/mol using acetonitrile. MP2/6-31G(d) calculations show the same order of stability. This order of stability, however, is contrary to the experimentally observed results.

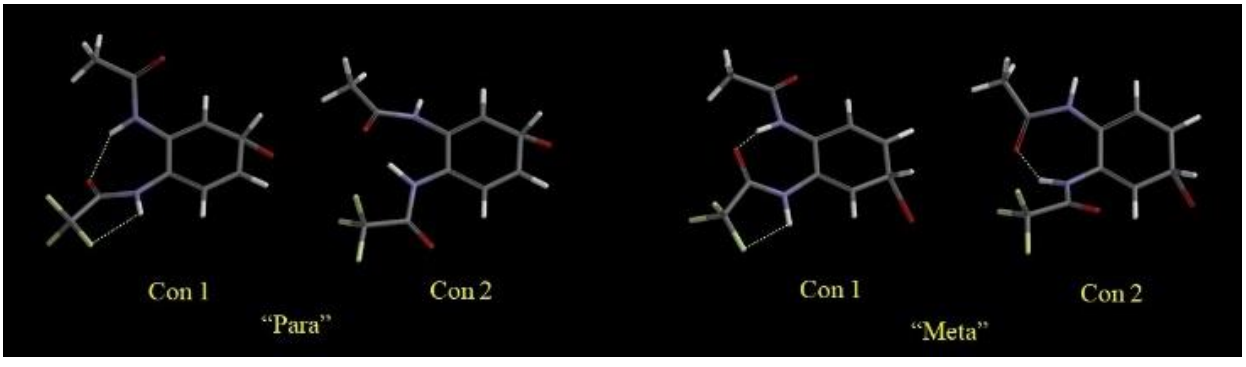


Figure S2 There are two conformations for both the *para* and *meta* cation intermediates of 1a. The Con 1 (*meta*) conformation is lower in energy than the Con 2 (*para*) structure at the B3LYP/6-31+G(d,p) and MP2/6-31G(p) levels of theory.

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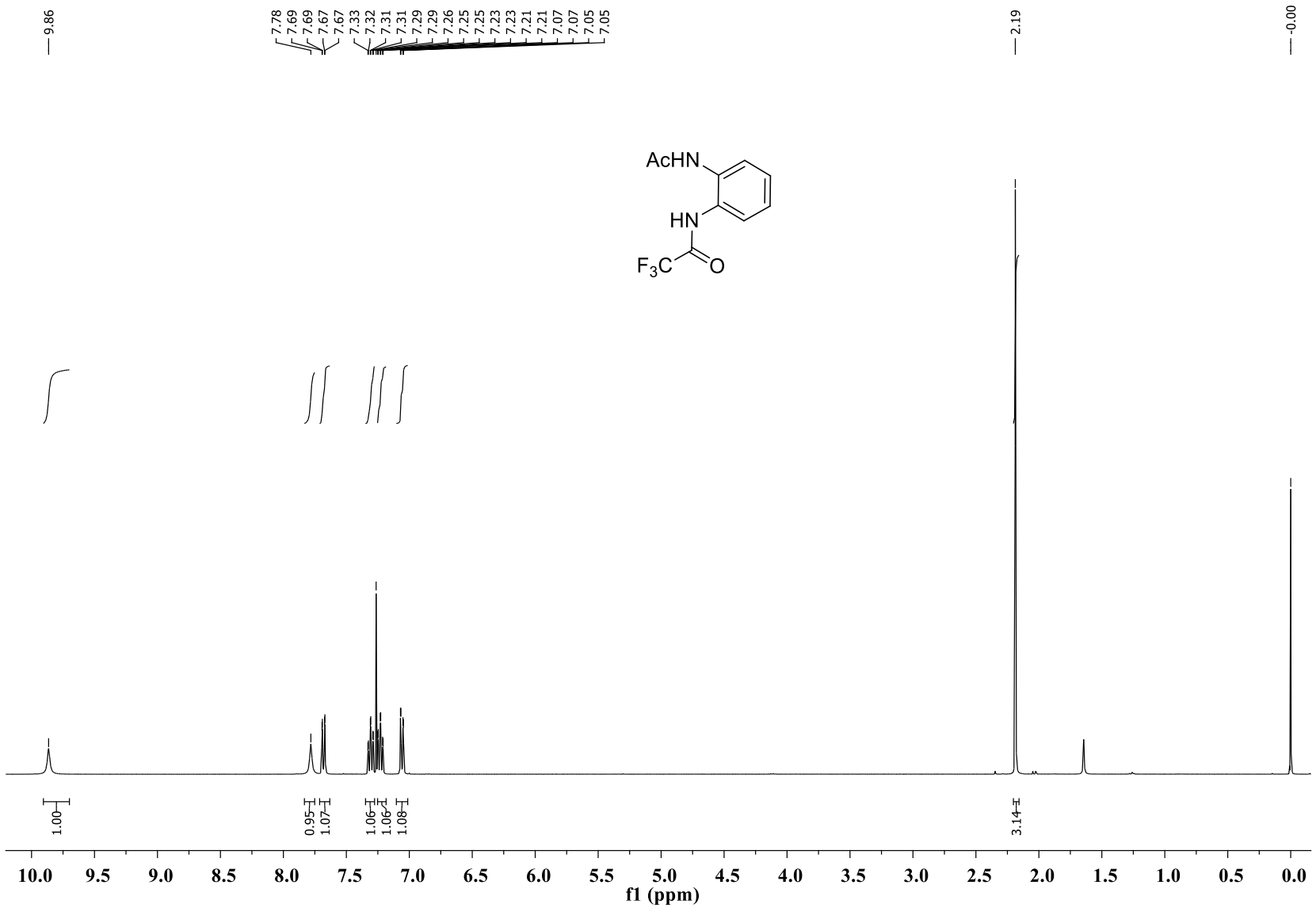
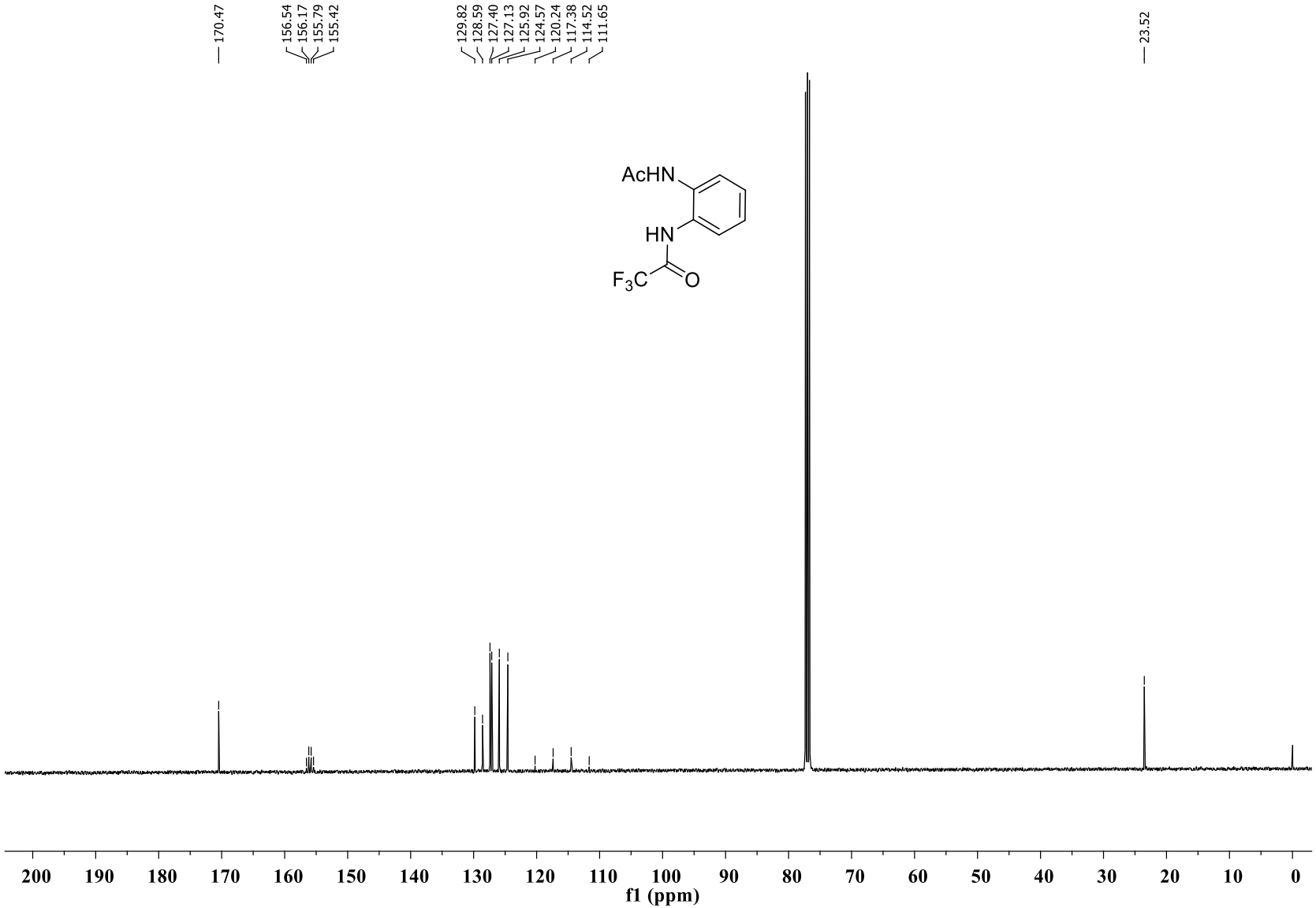
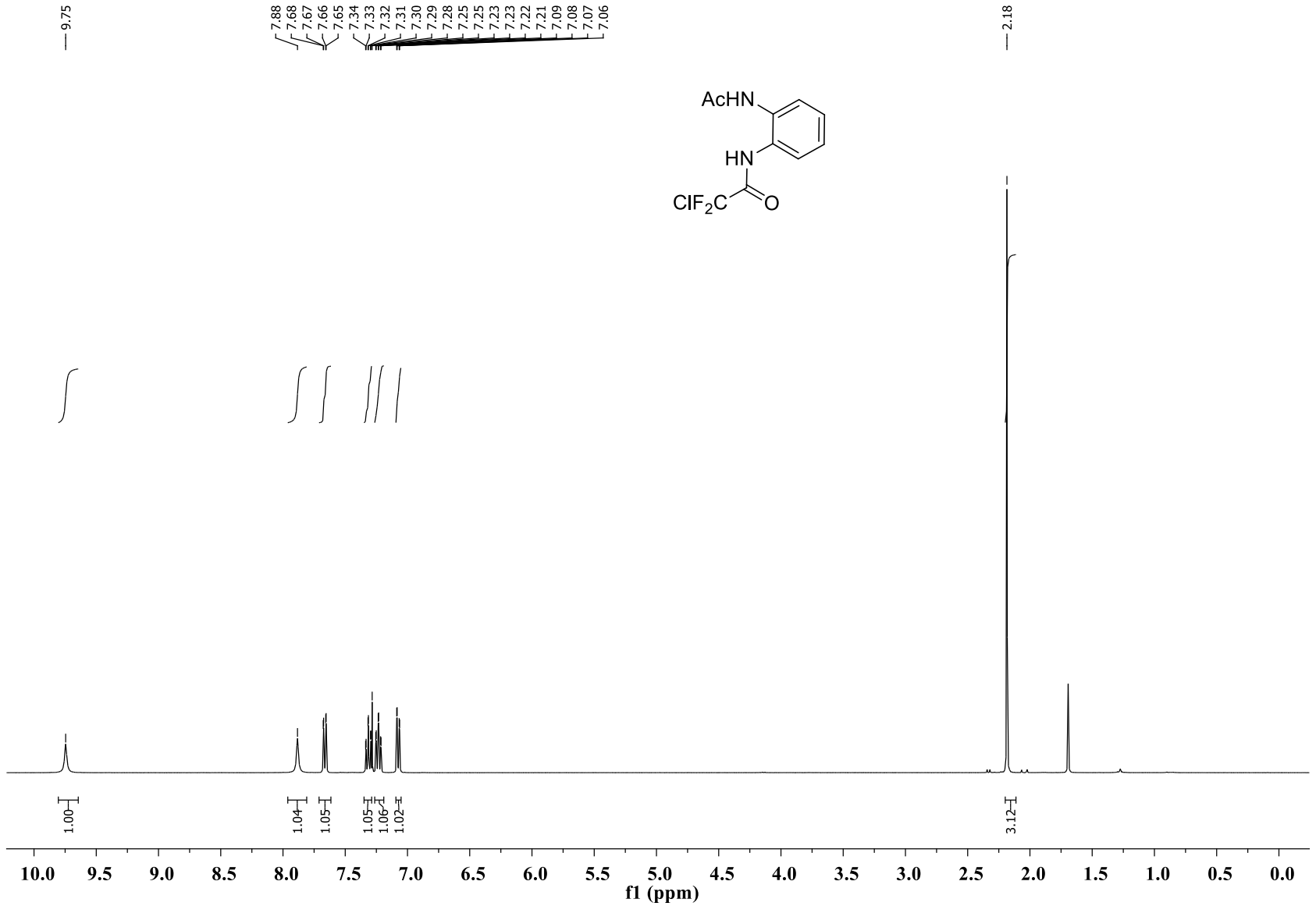
^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 400 MHz)**:**



^{13}C NMR spectrum of compound **1a** ($CDCl_3$, 100 MHz)**:**



^{1}H NMR spectrum of compound **1b** ($CDCl_3$, 400 MHz)**:**



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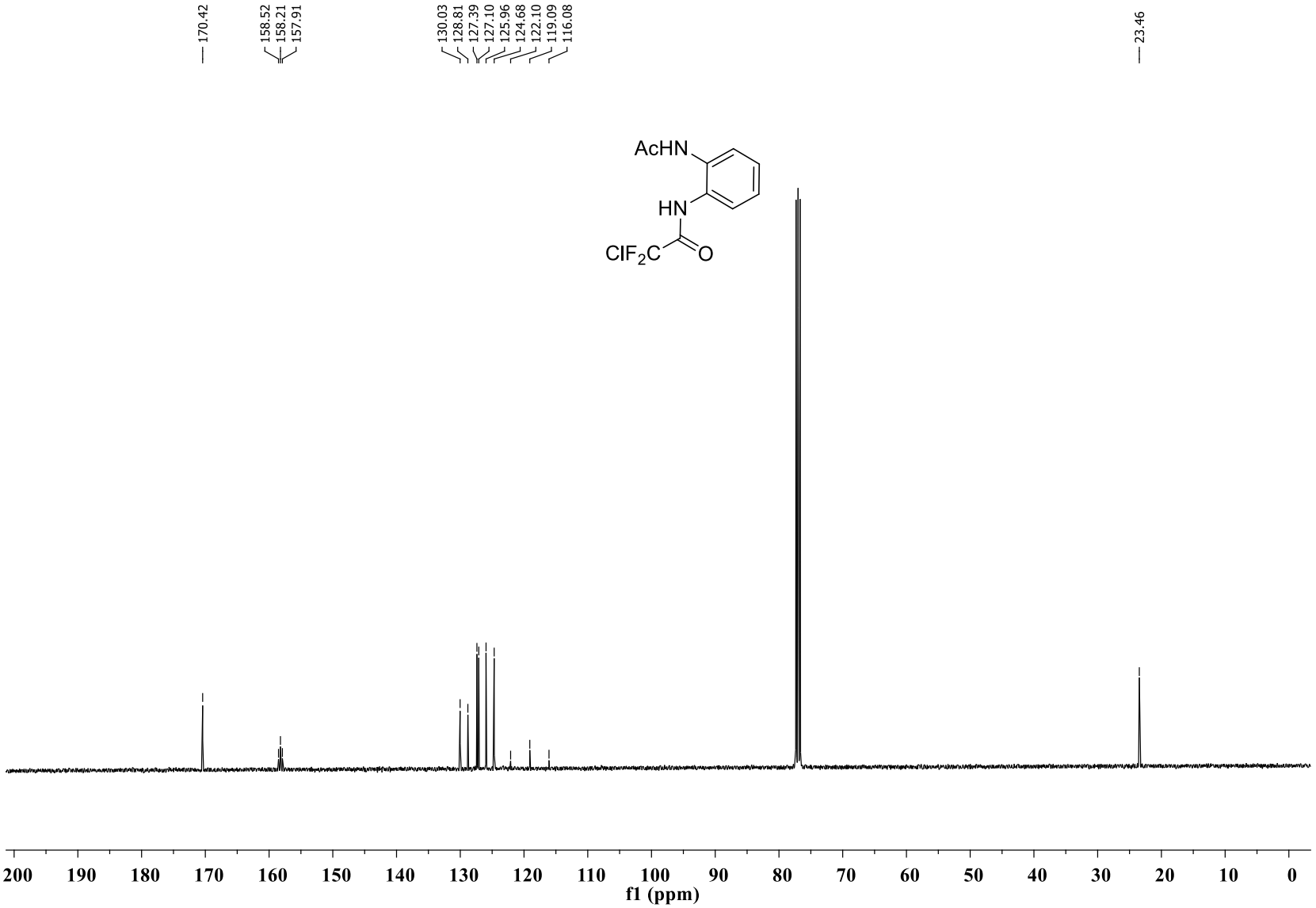
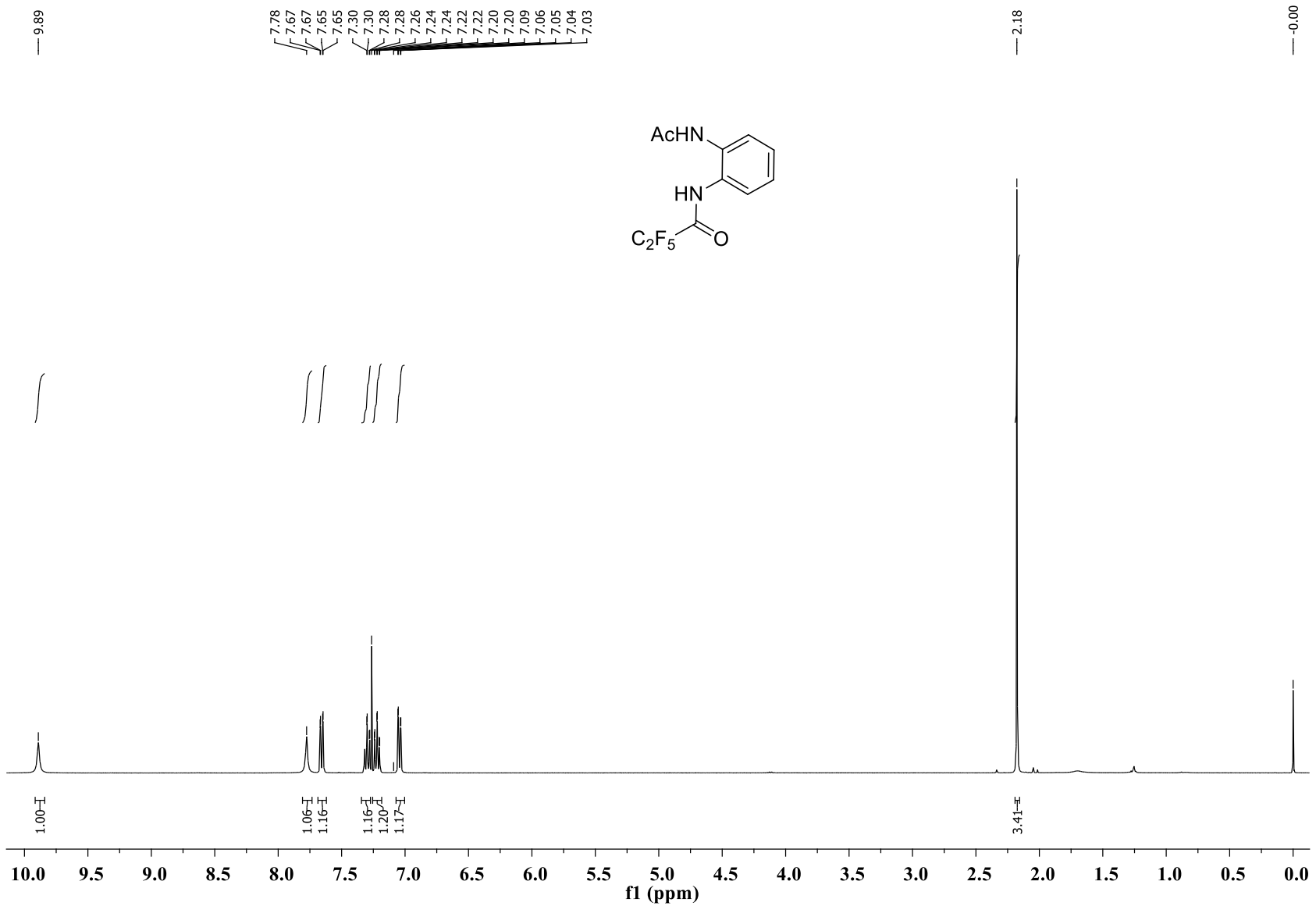
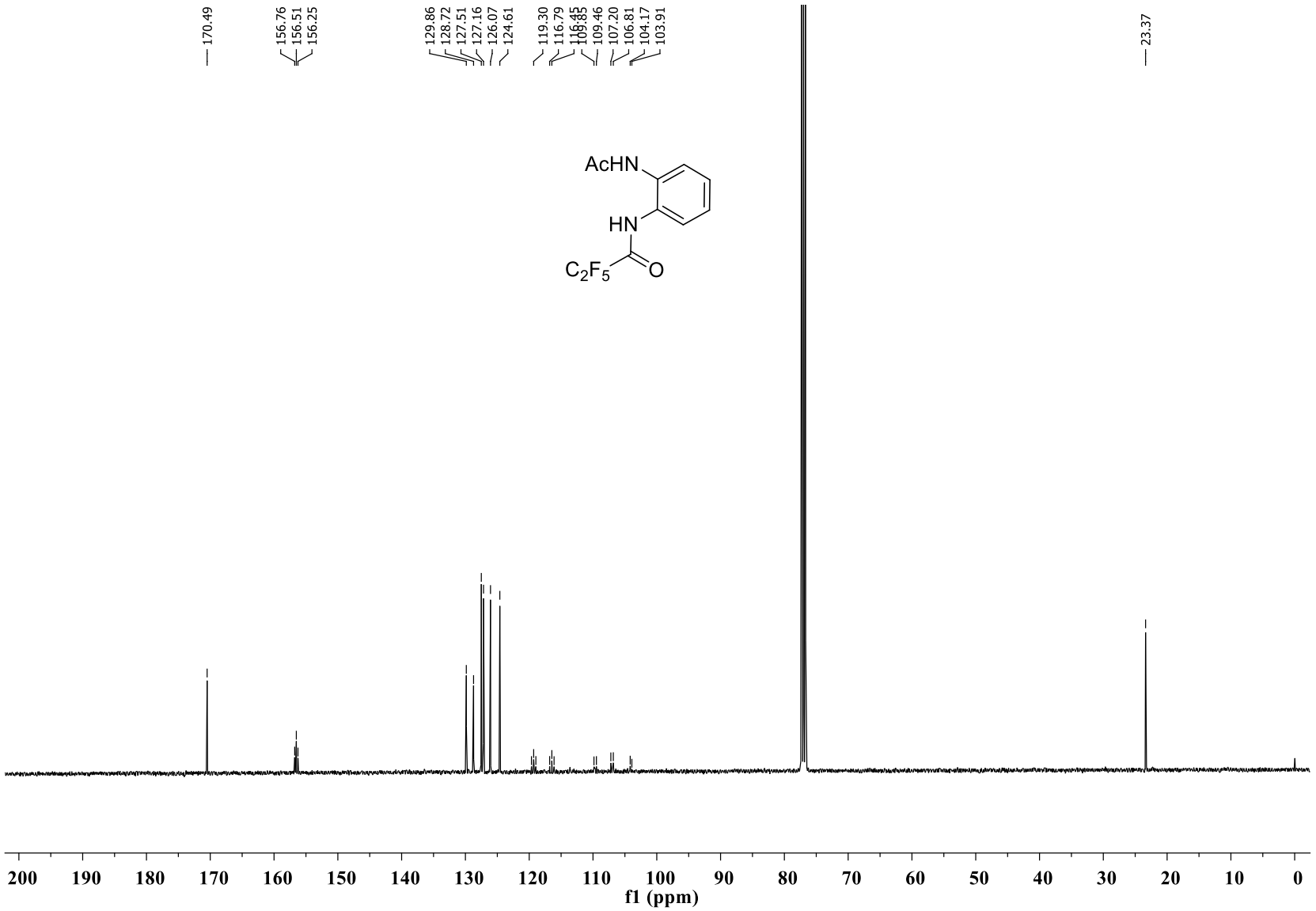


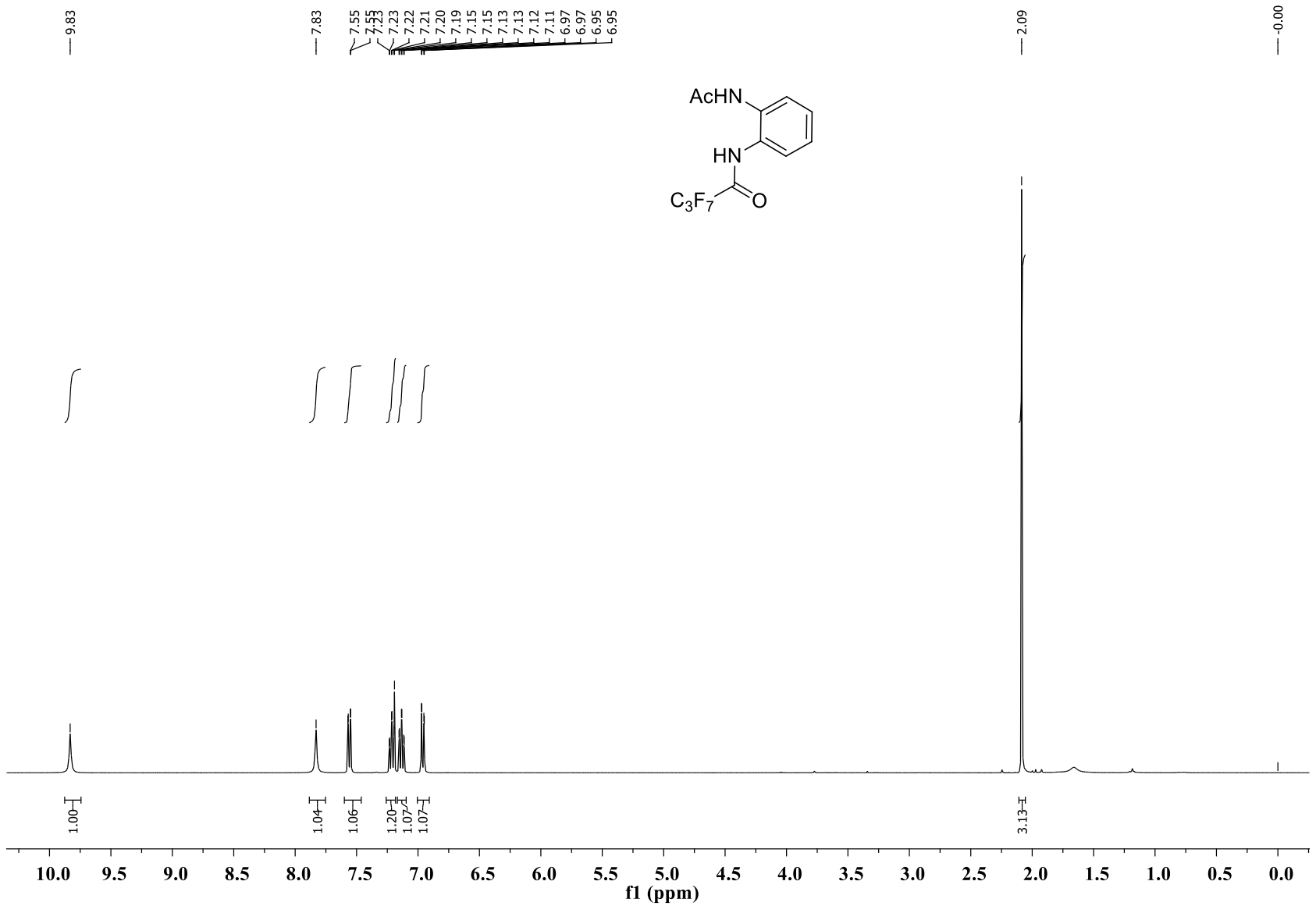
^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 400 MHz)**:**



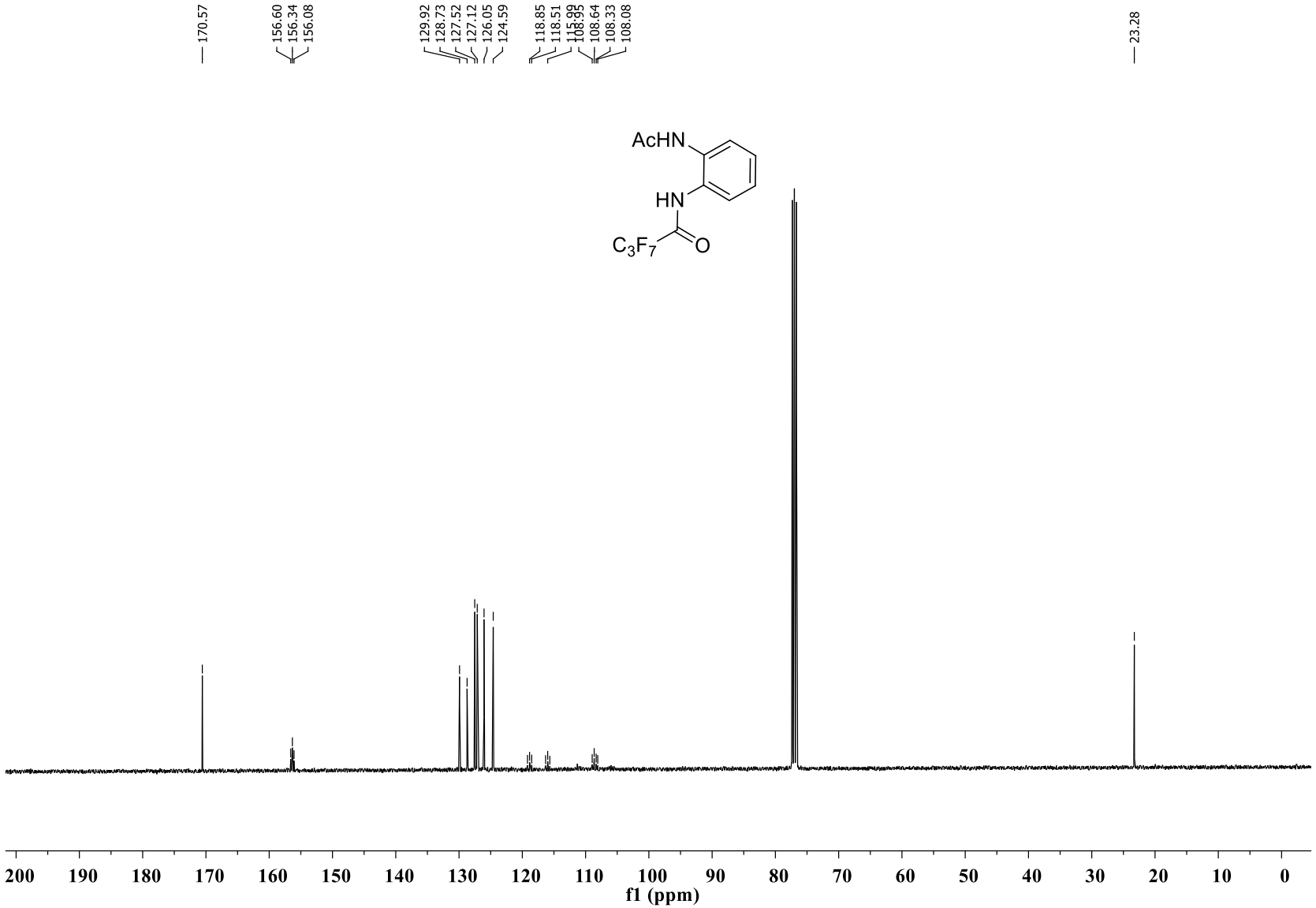
^{13}C NMR spectrum of compound **1c** ($CDCl_3$, 100 MHz)**:**



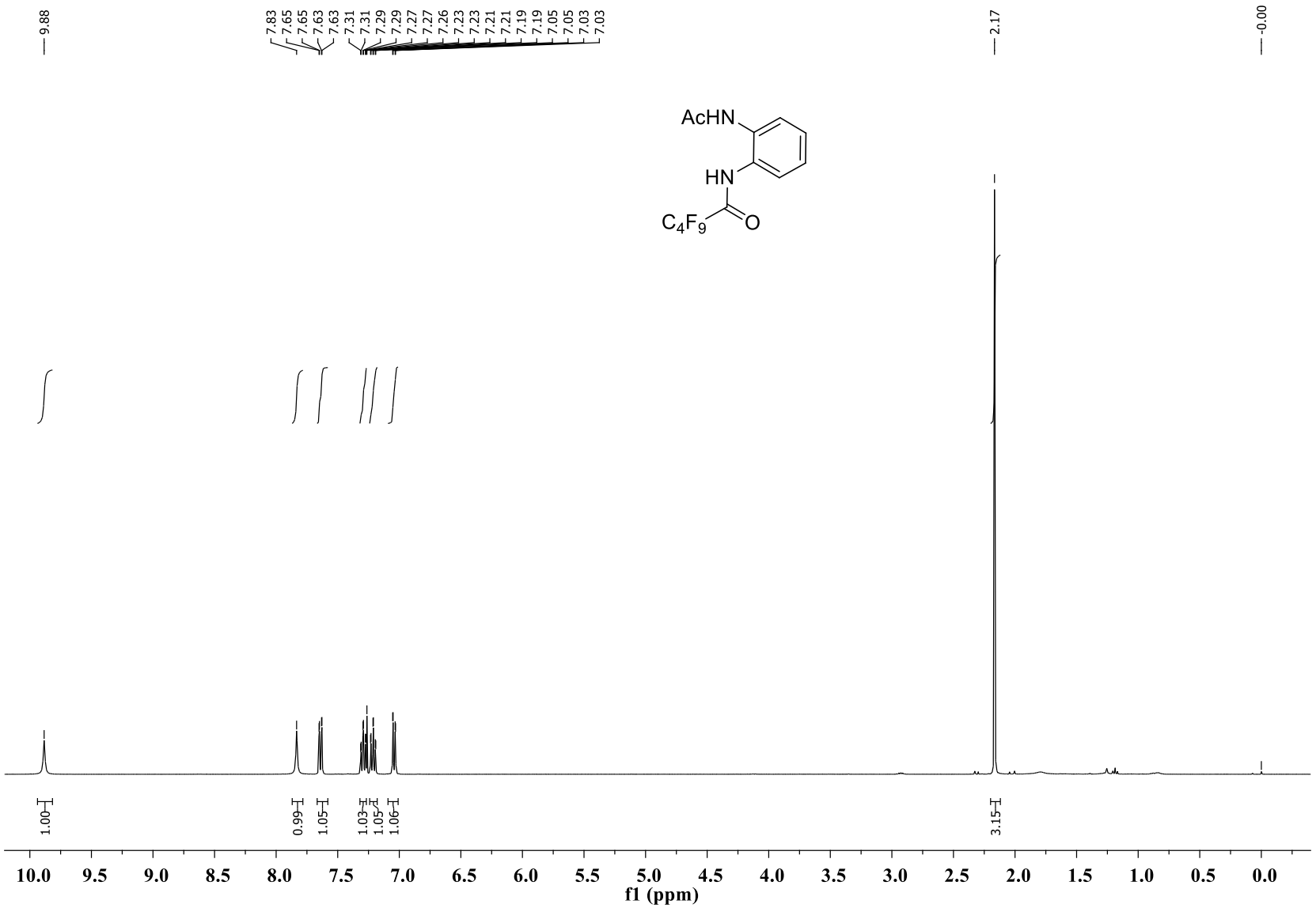
^{1}H NMR spectrum of compound **1d** ($CDCl_3$, 400 MHz)**:**



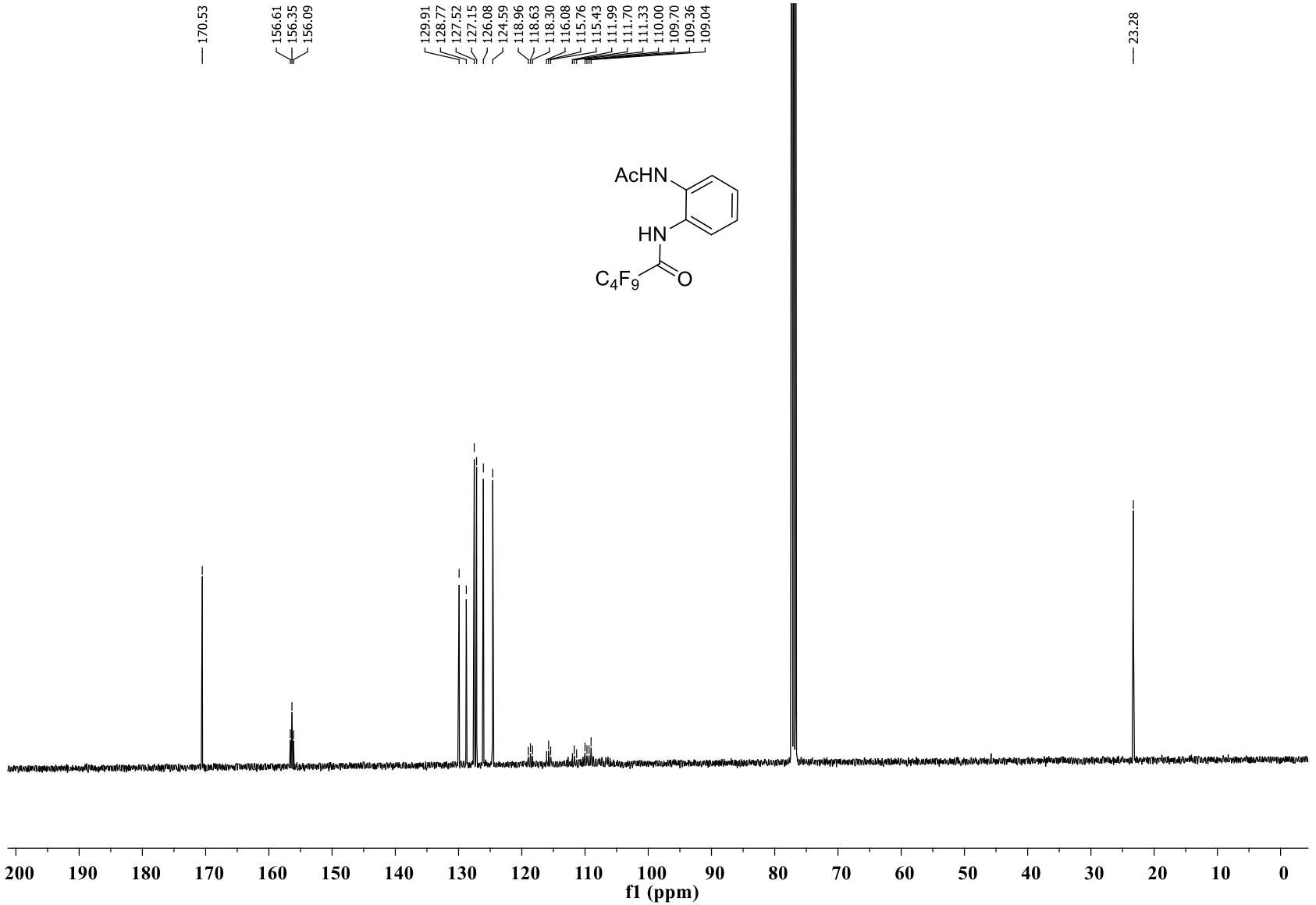
^{13}C NMR spectrum of compound **1d** ($CDCl_3$, 100 MHz)**:**



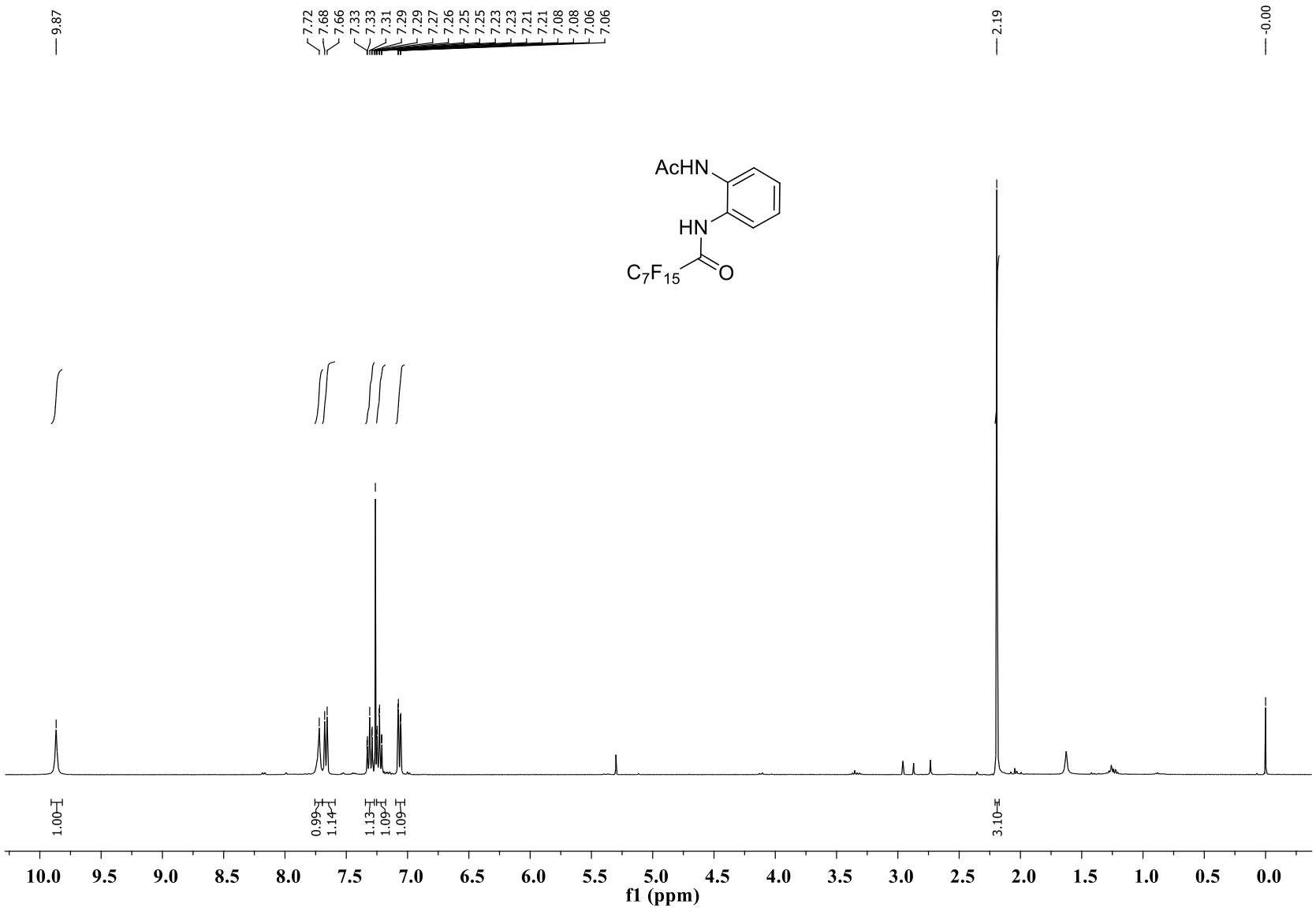
^{1}H NMR spectrum of compound **1e** ($CDCl_3$, 400 MHz)**:**



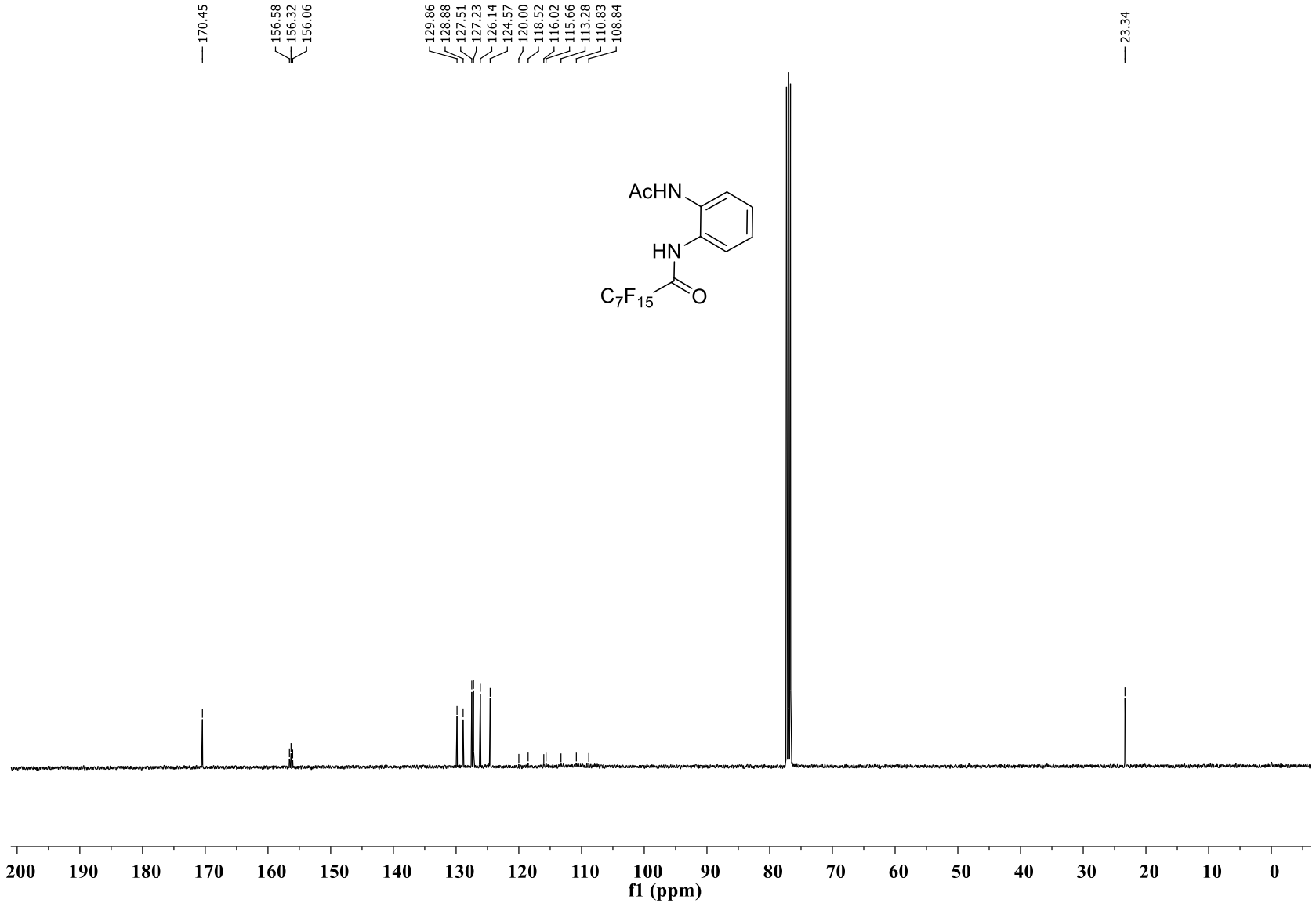
^{13}C NMR spectrum of compound **1e** ($CDCl_3$, 100 MHz)**:**



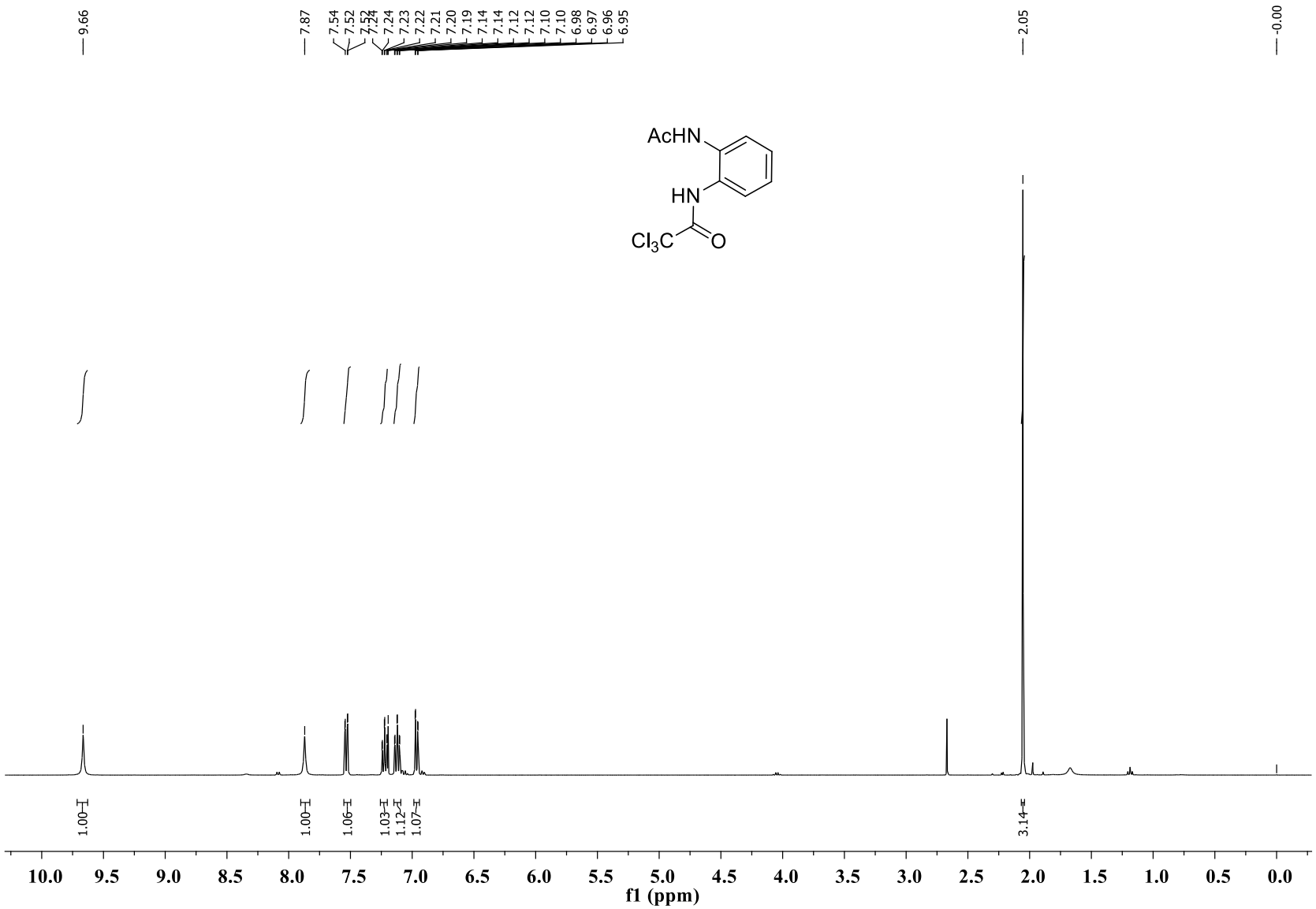
^{1}H NMR spectrum of compound **1f** ($CDCl_3$, 400 MHz)**:**



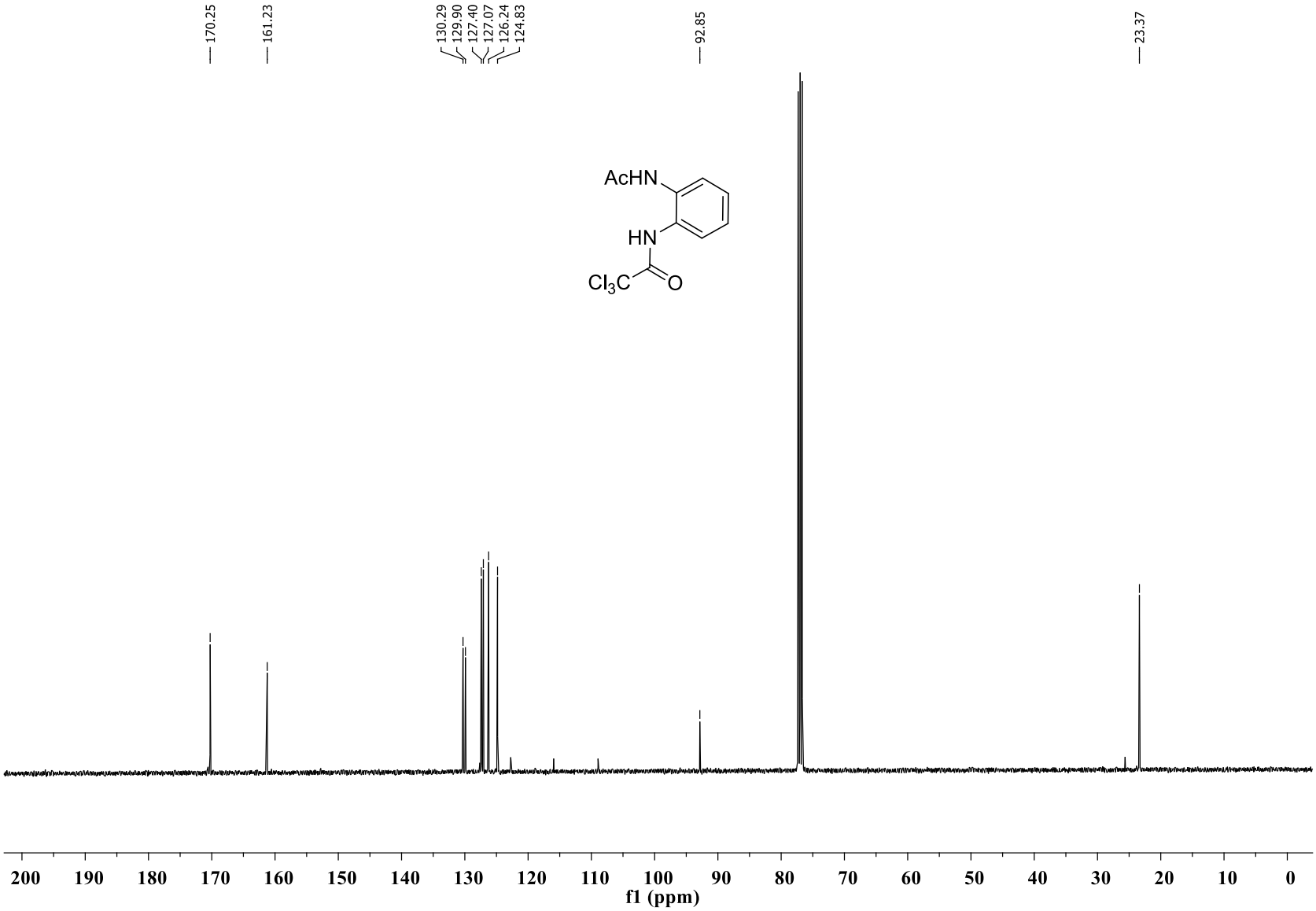
^{13}C NMR spectrum of compound **1f** ($CDCl_3$, 100 MHz)**:**



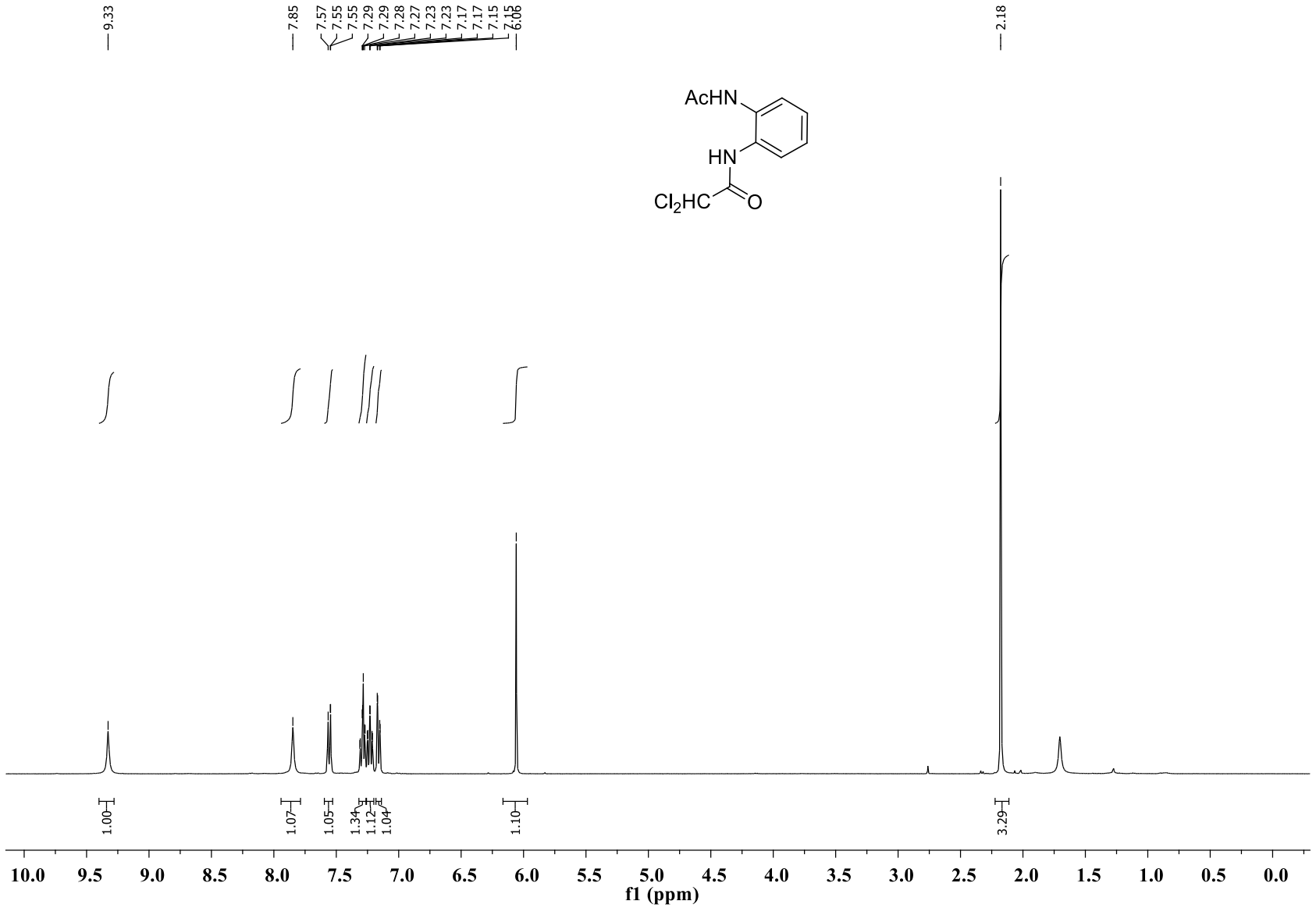
^{1}H NMR spectrum of compound **1g** ($CDCl_3$, 400 MHz)**:**



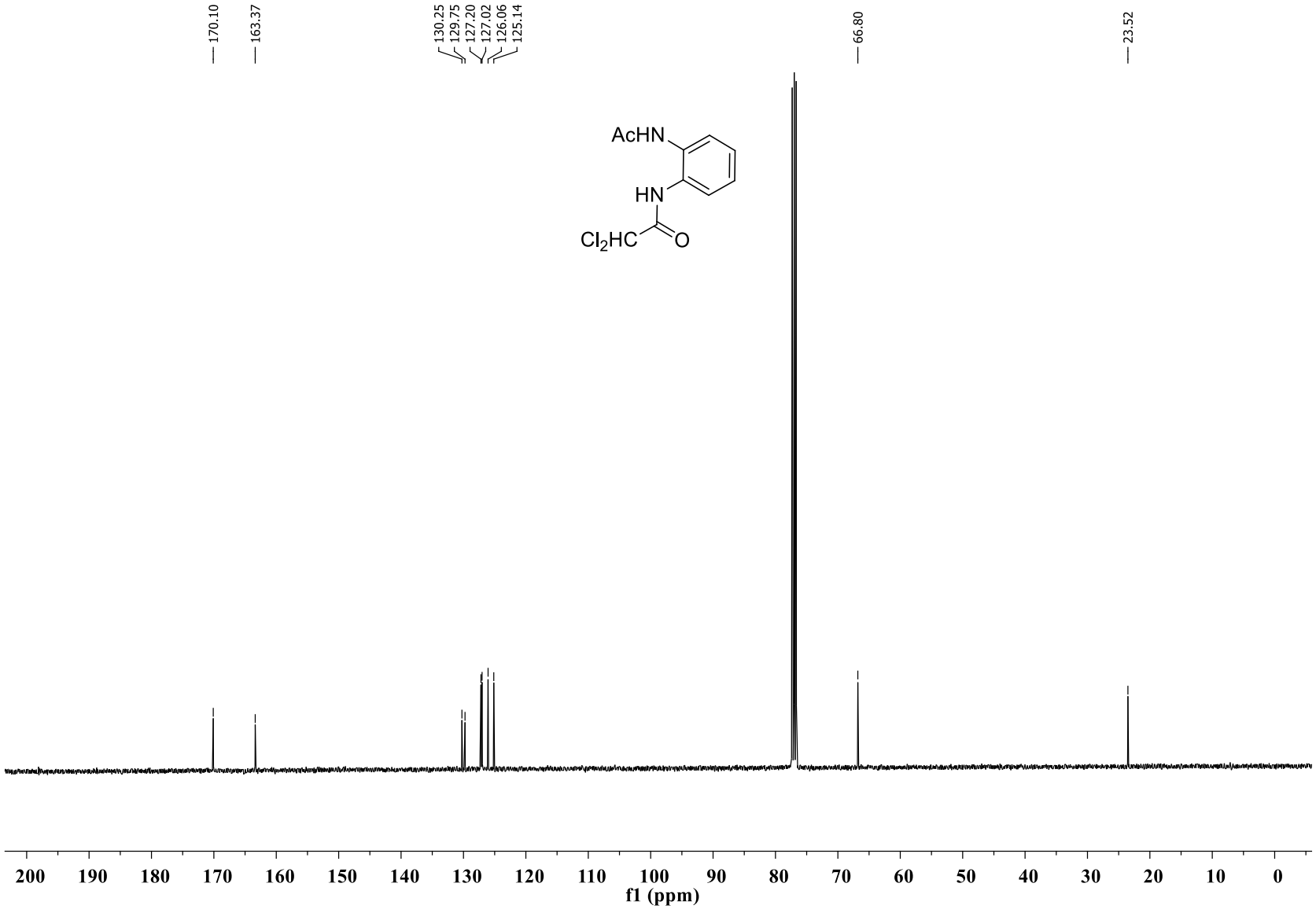
^{13}C NMR spectrum of compound **1g** ($CDCl_3$, 100 MHz)**:**



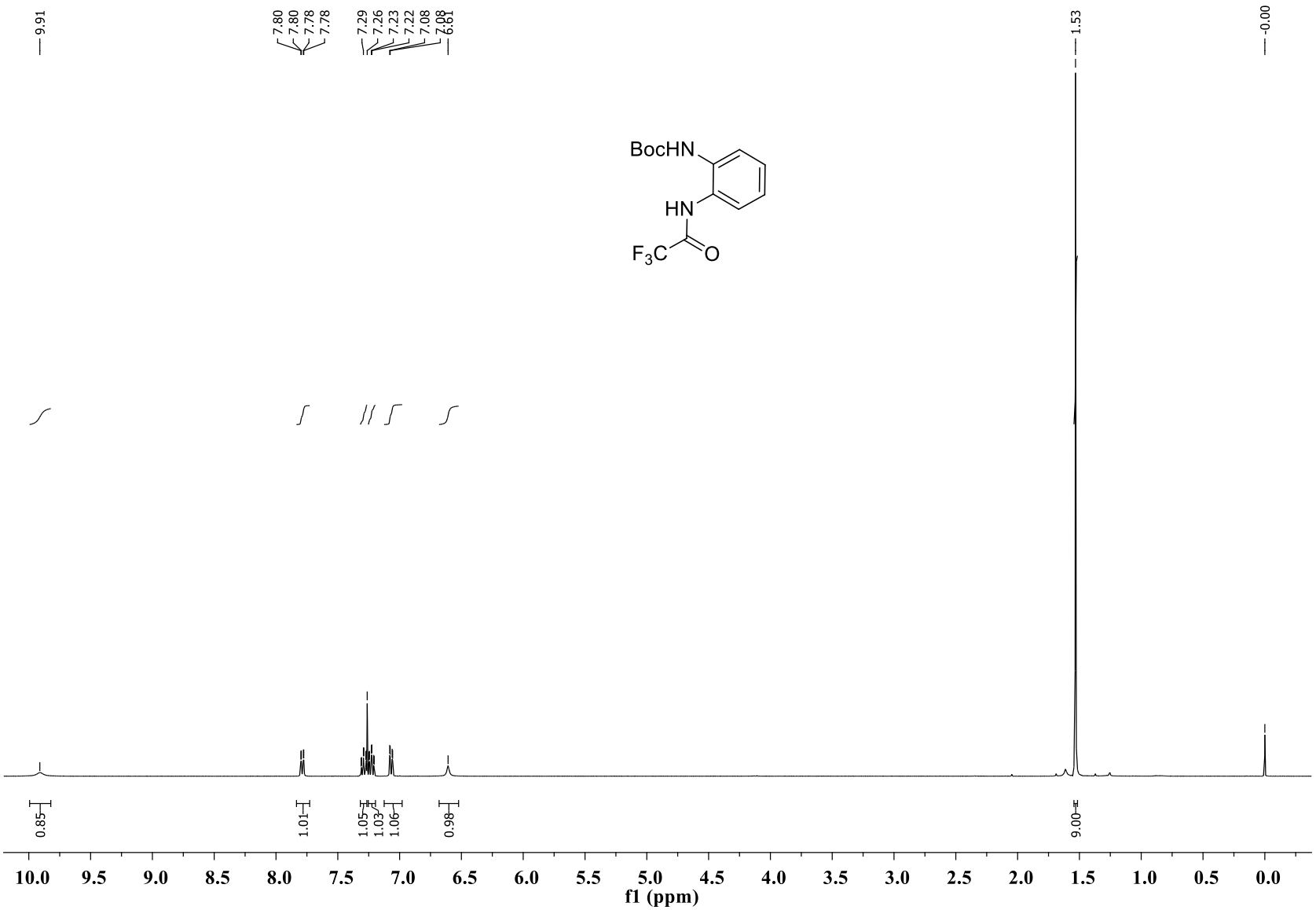
^{1}H NMR spectrum of compound **1h** ($CDCl_3$, 400 MHz)**:**



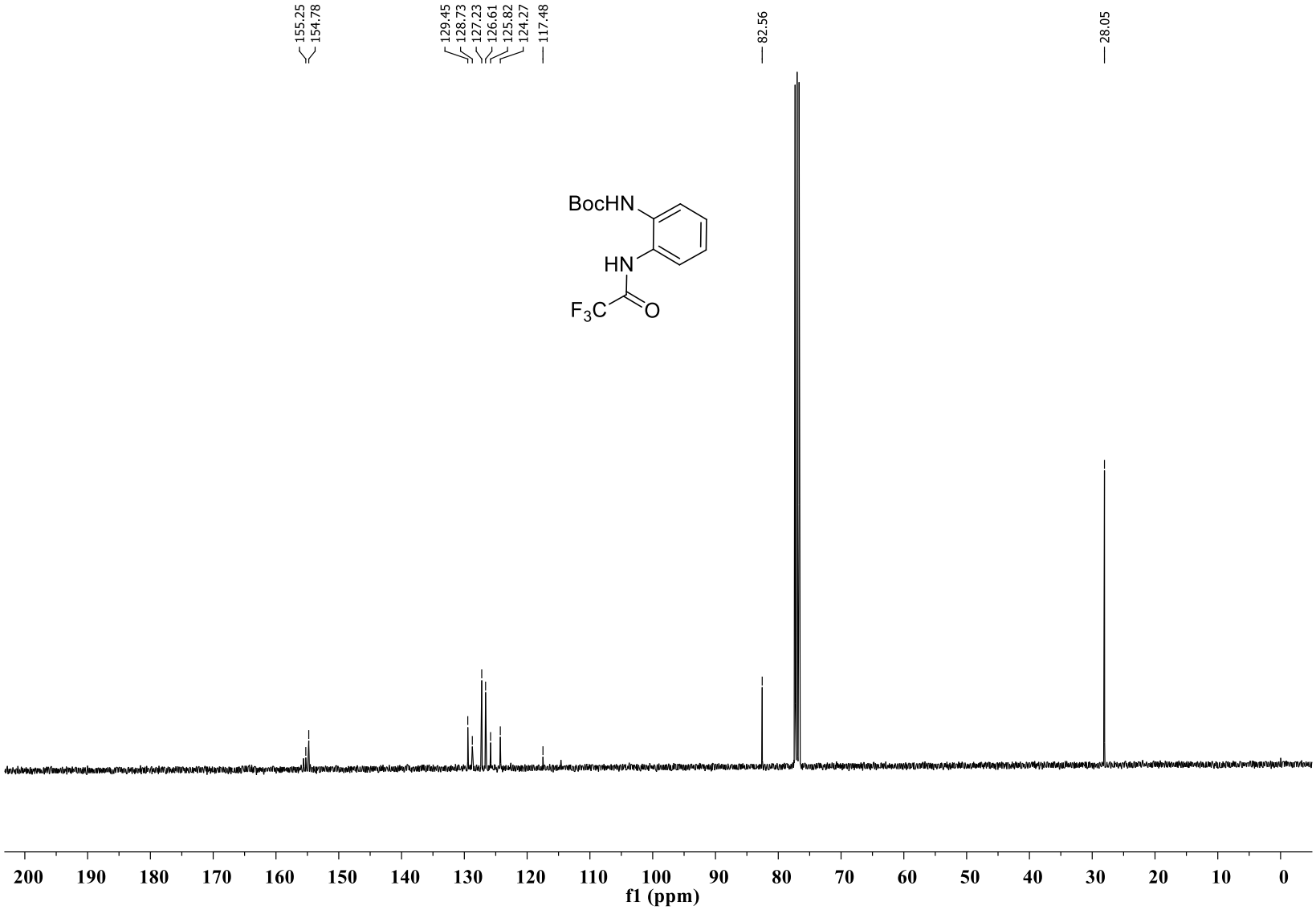
^{13}C NMR spectrum of compound **1h** ($CDCl_3$, 100 MHz)**:**



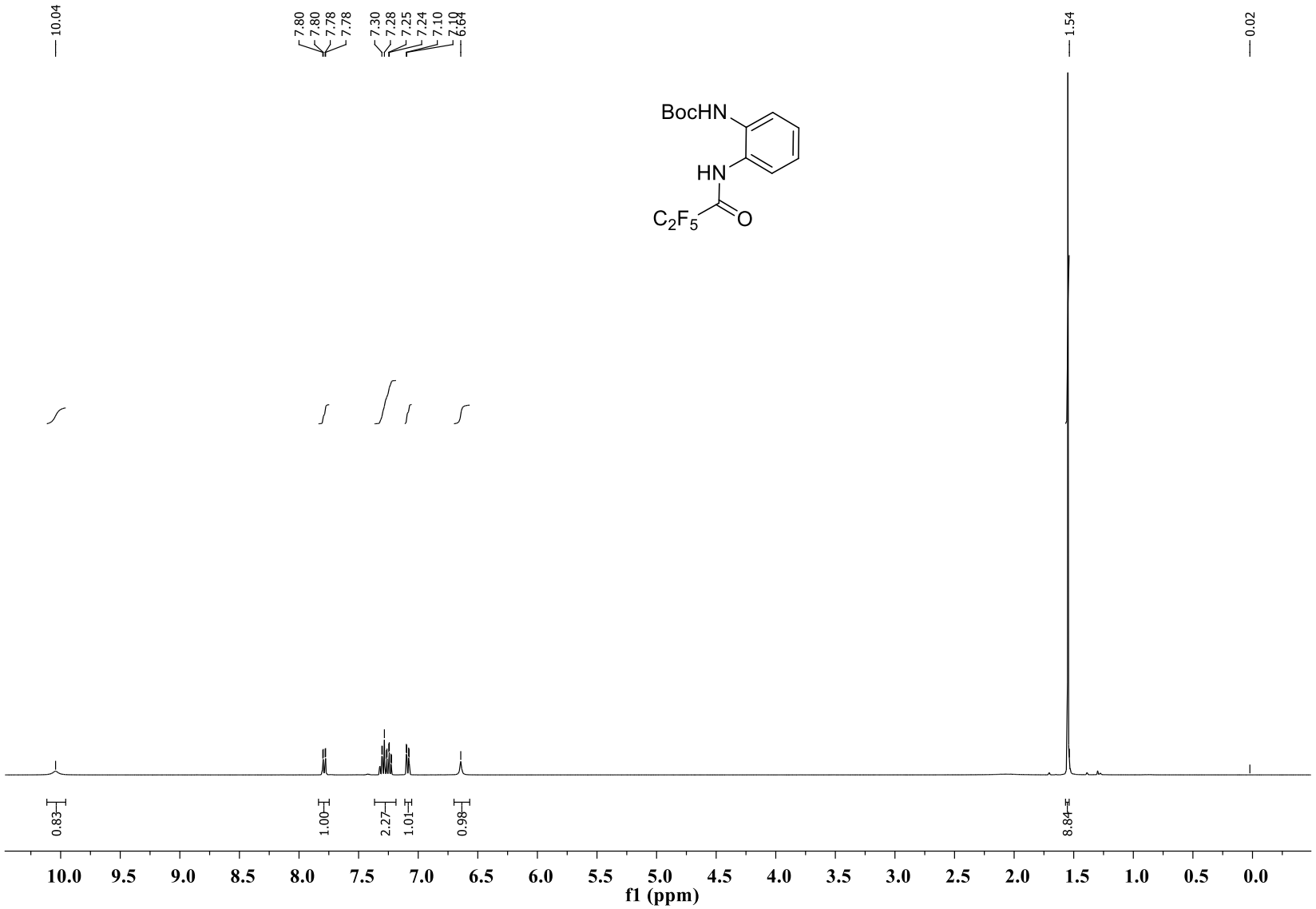
^{1}H NMR spectrum of compound **1k** ($CDCl_3$, 400 MHz)**:**



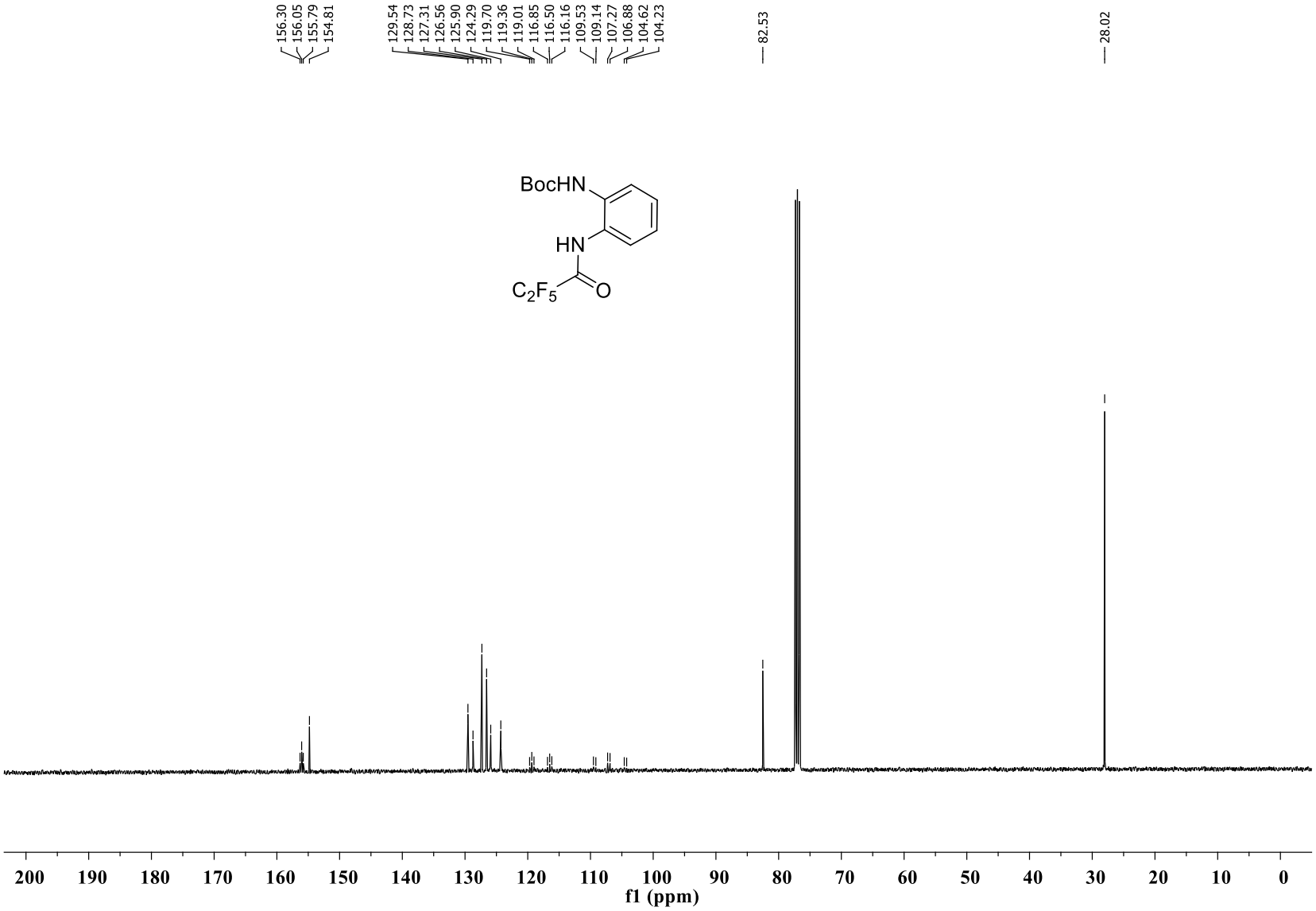
^{13}C NMR spectrum of compound **1k** ($CDCl_3$, 100 MHz)**:**



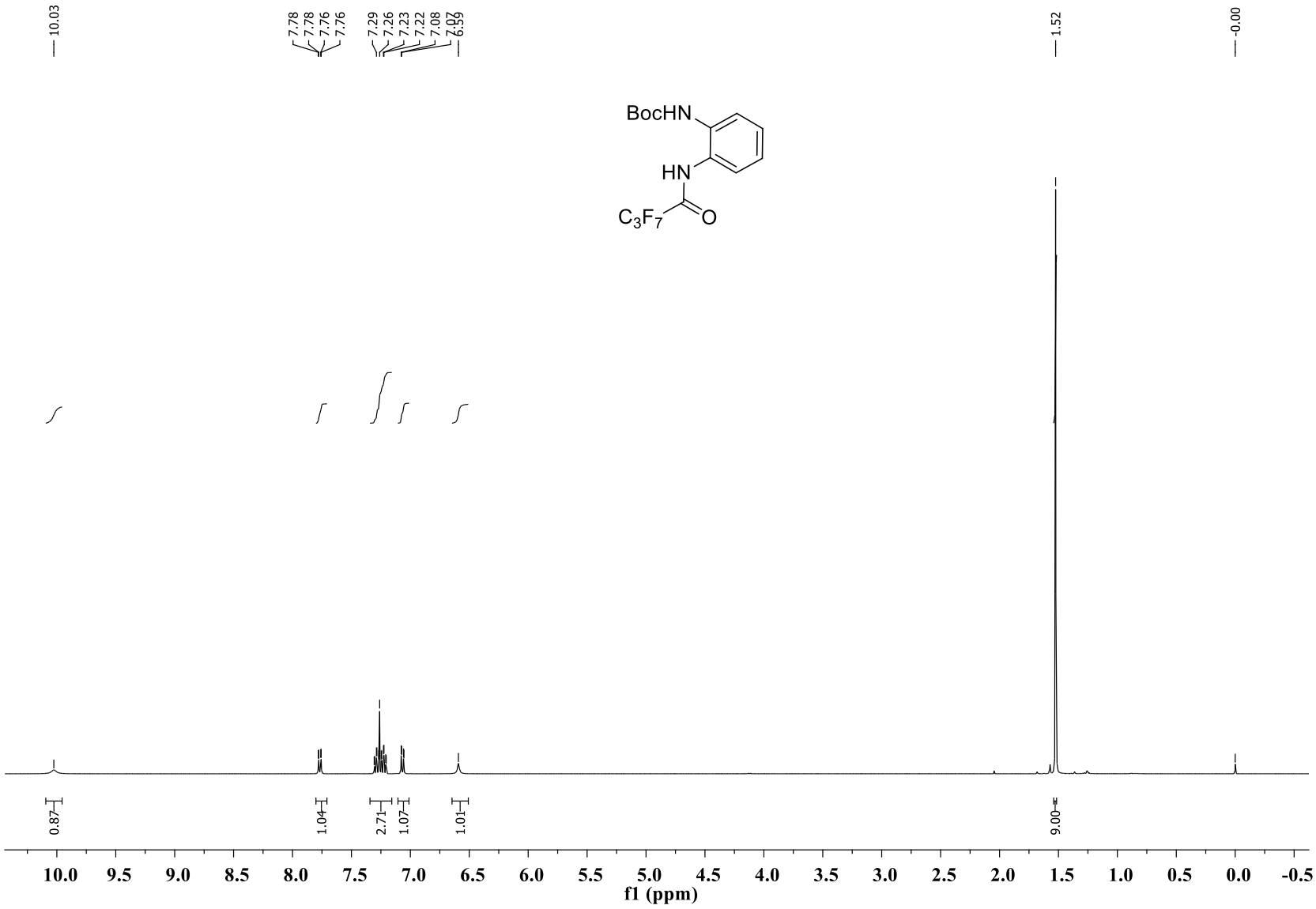
^{1}H NMR spectrum of compound **1l** ($CDCl_3$, 400 MHz)**:**



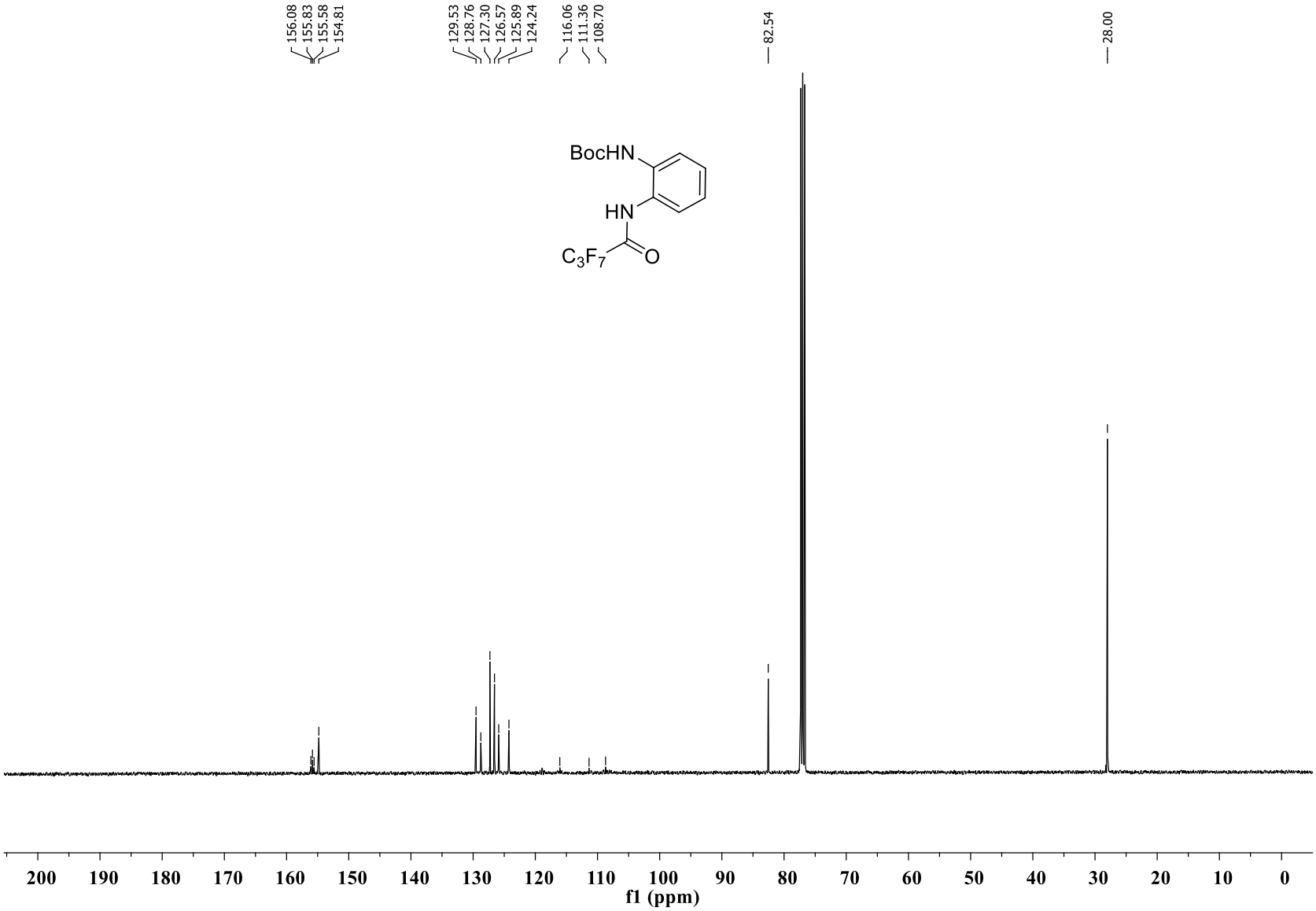
^{13}C NMR spectrum of compound **1l** ($CDCl_3$, 100 MHz)**:**



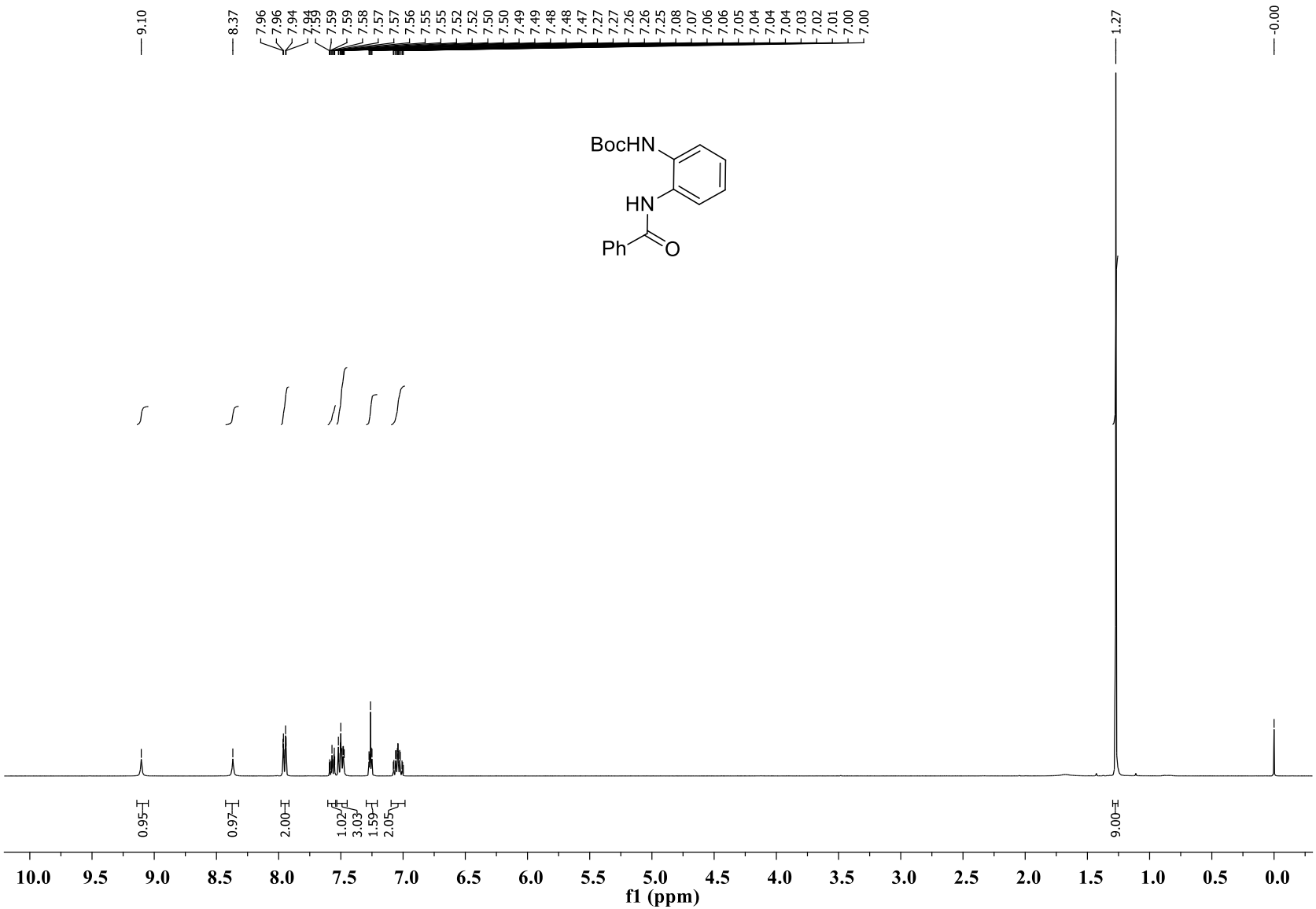
^{1}H NMR spectrum of compound **1m** ($CDCl_3$, 400 MHz)**:**



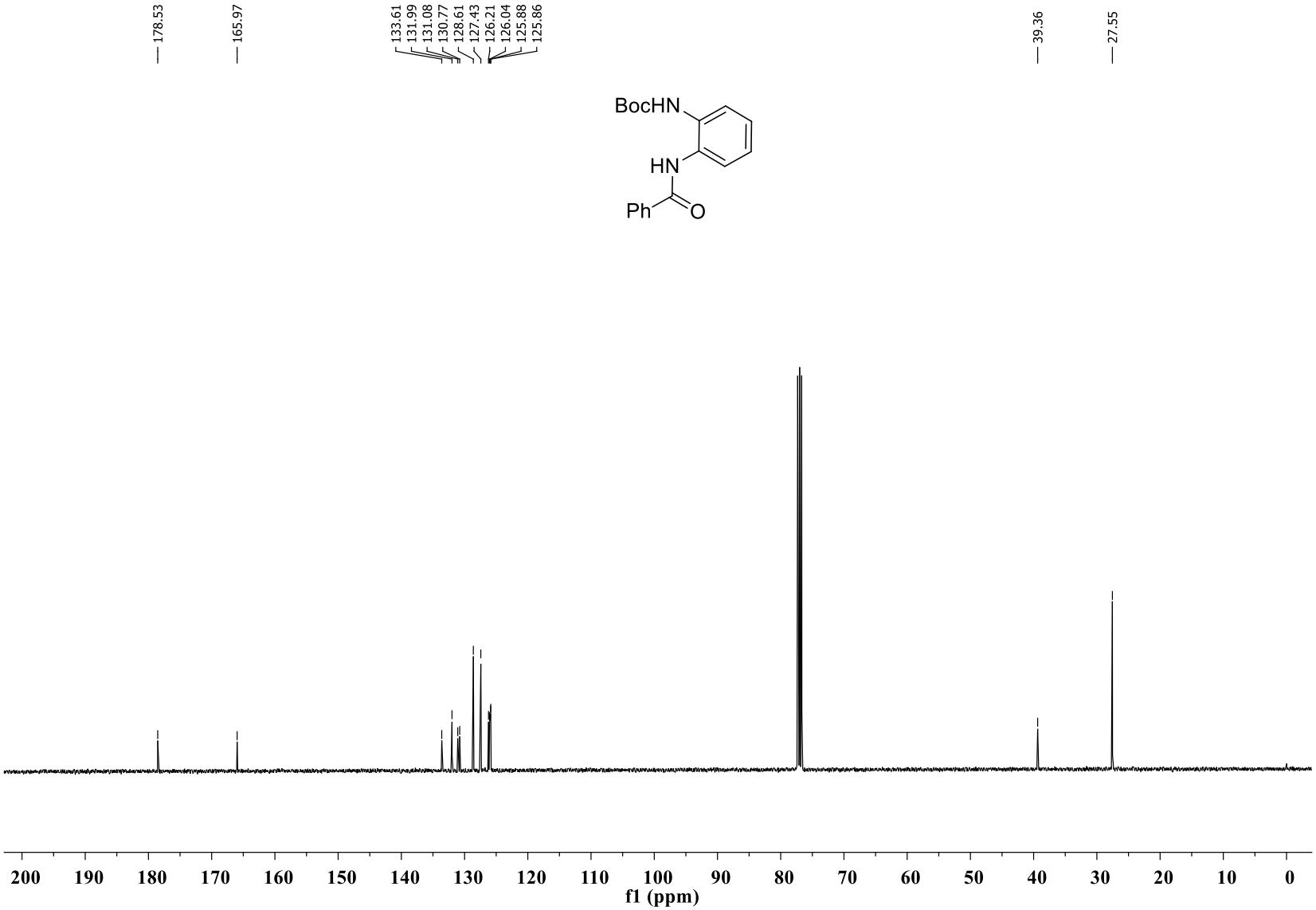
^{13}C NMR spectrum of compound **1m** ($CDCl_3$, 100 MHz)**:**



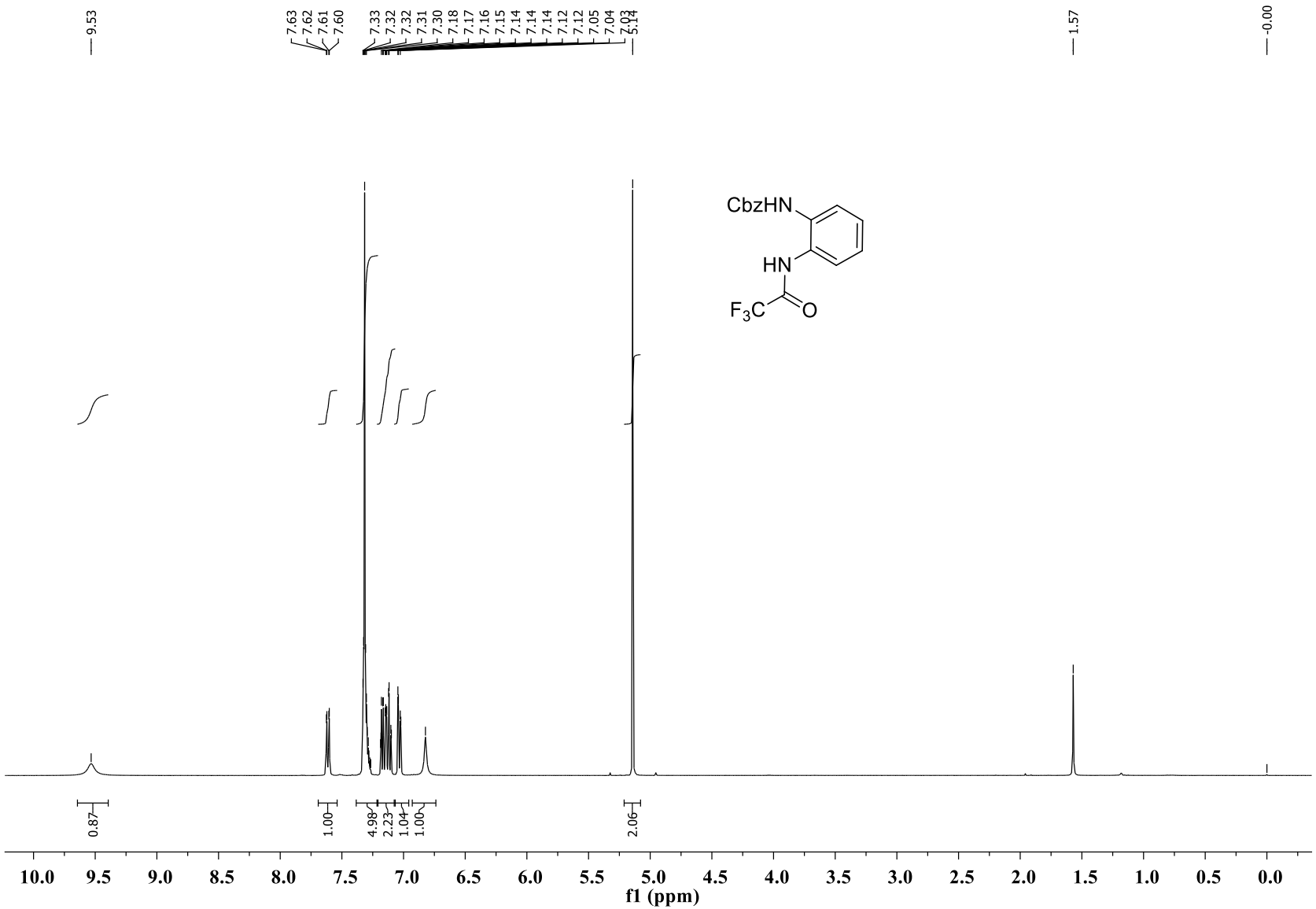
^{1}H NMR spectrum of compound **1n** ($CDCl_3$, 400 MHz)**:**



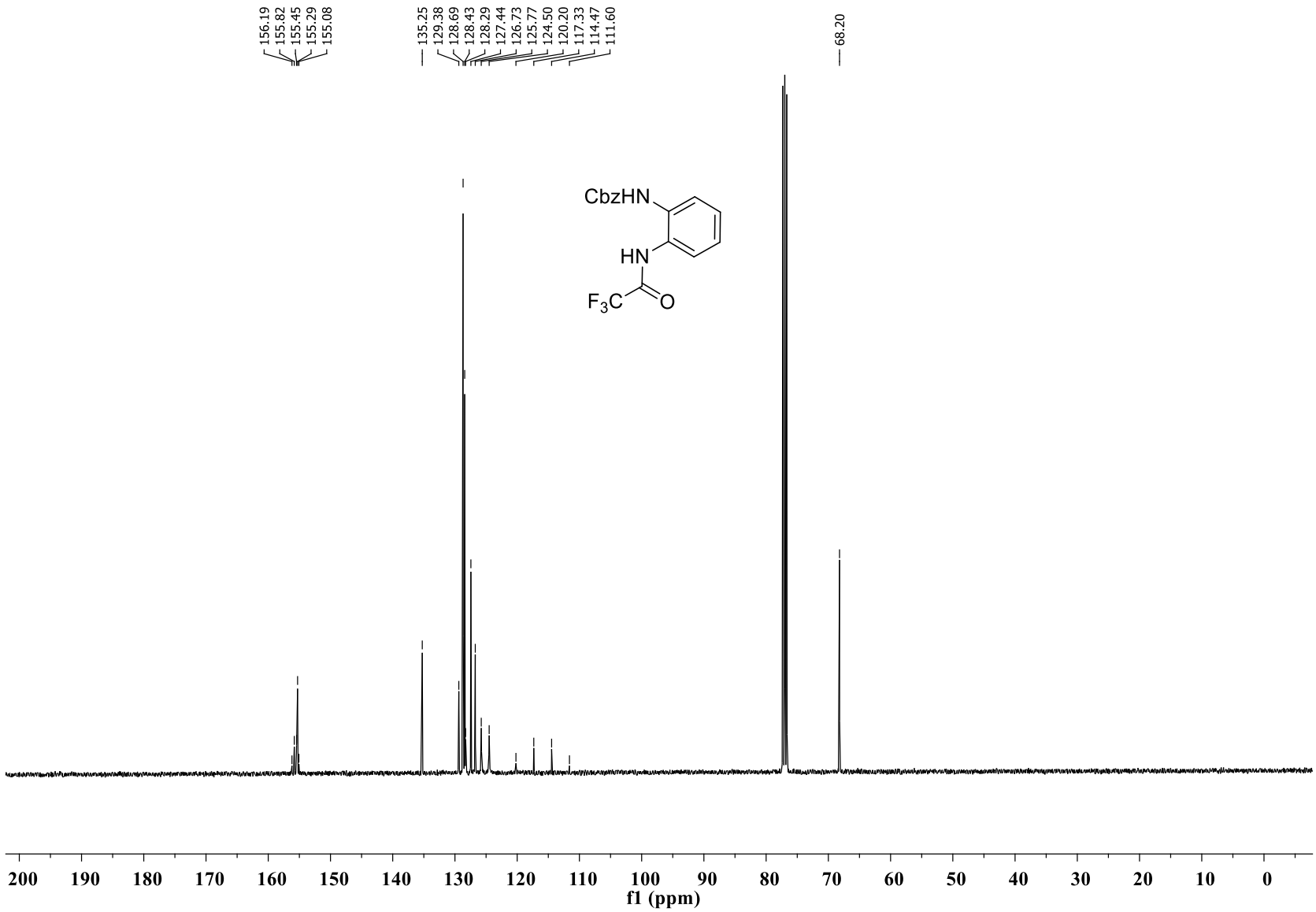
^{13}C NMR spectrum of compound **1n** ($CDCl_3$, 100 MHz)**:**



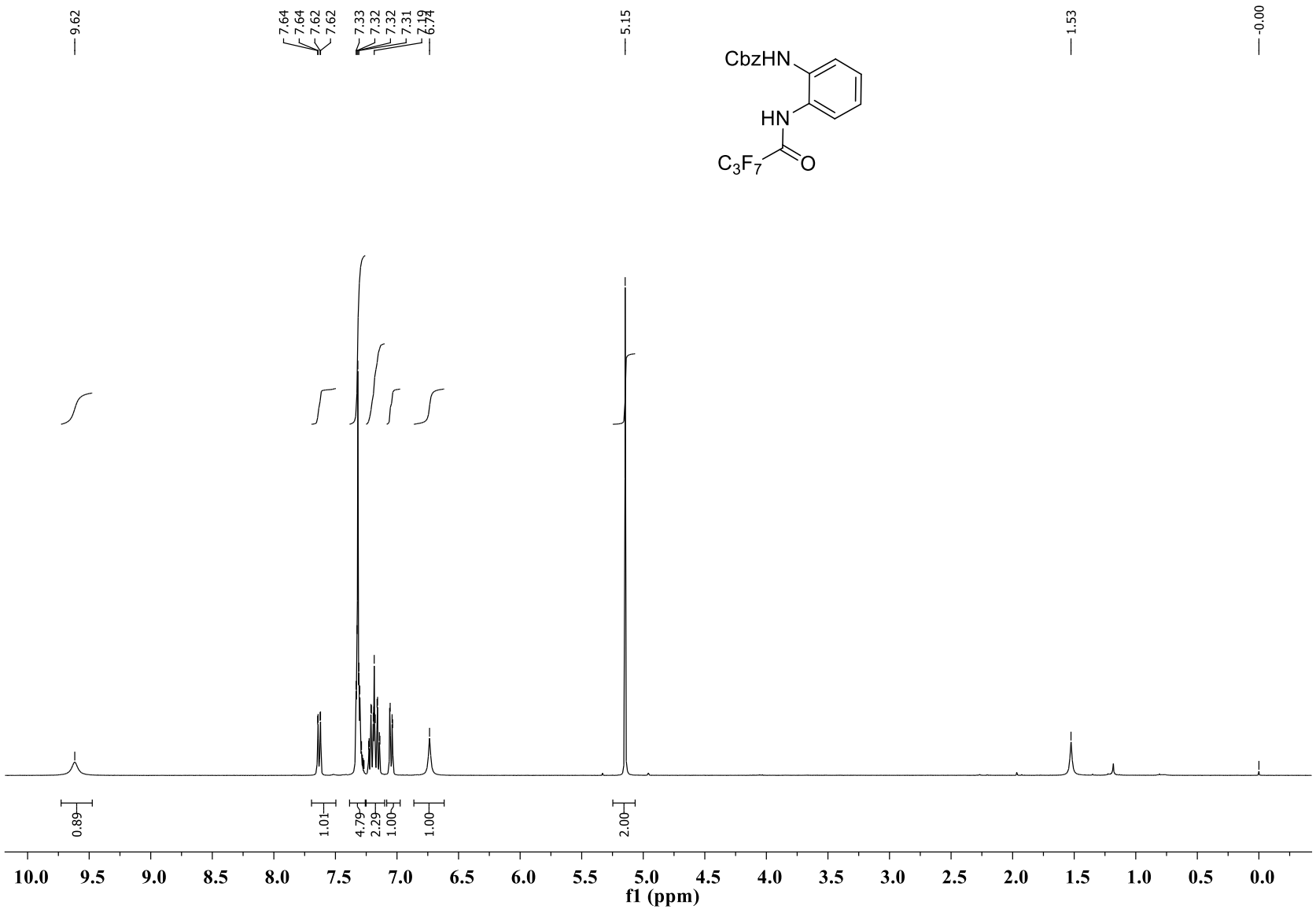
^{1}H NMR spectrum of compound **1o** ($CDCl_3$, 400 MHz)**:**



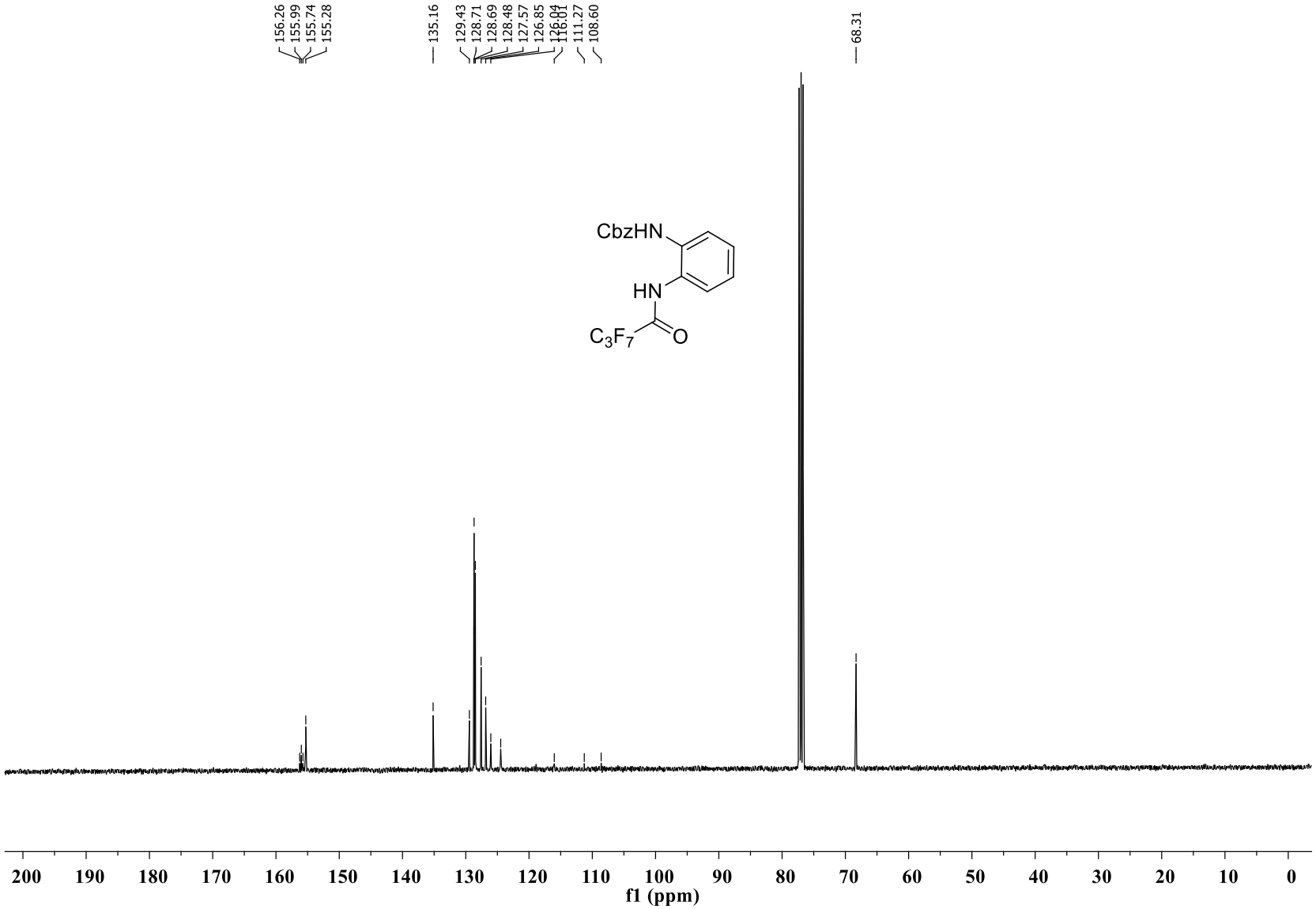
^{13}C NMR spectrum of compound **1o** ($CDCl_3$, 100 MHz)**:**



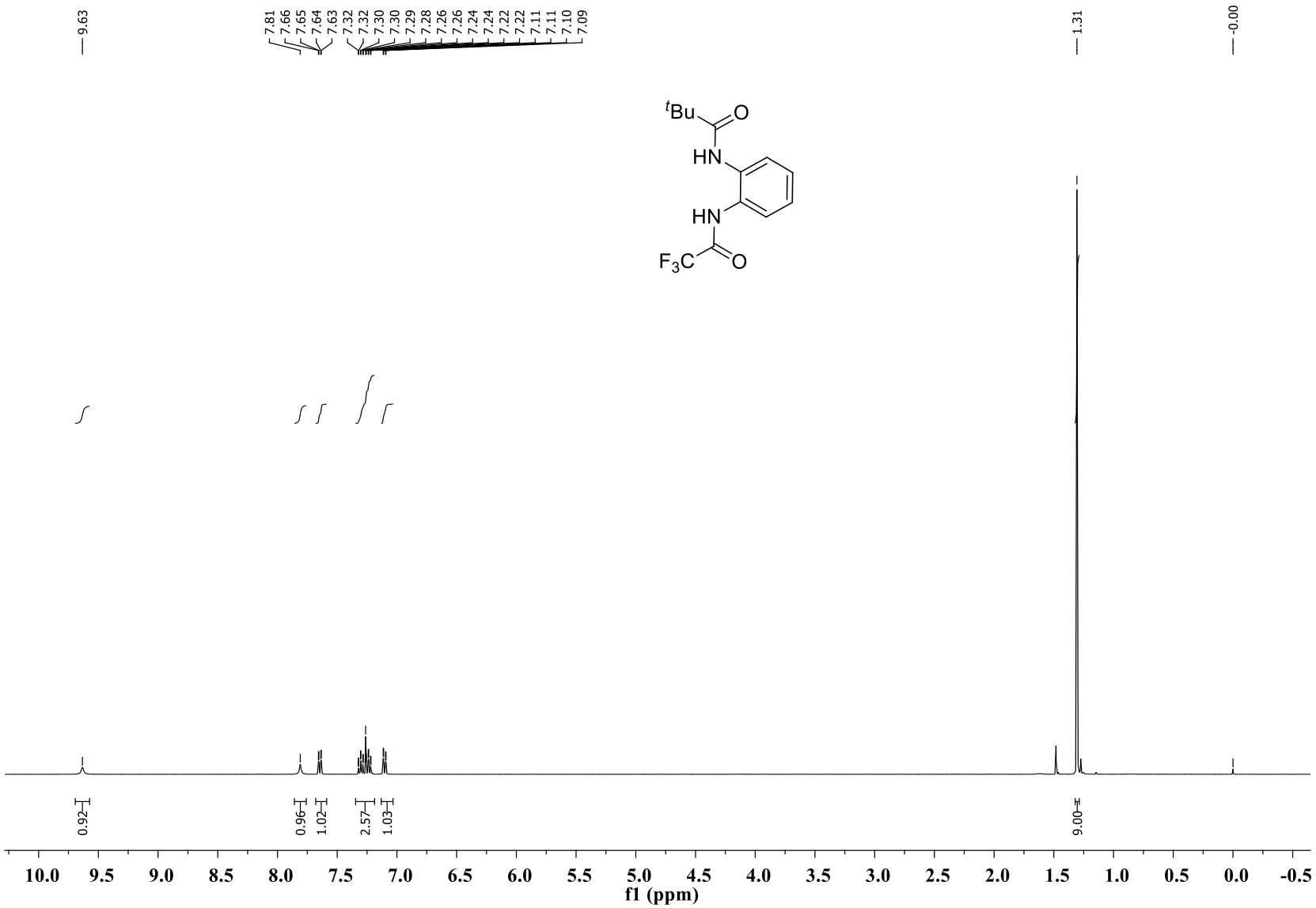
^{1}H NMR spectrum of compound **1p** ($CDCl_3$, 400 MHz)**:**



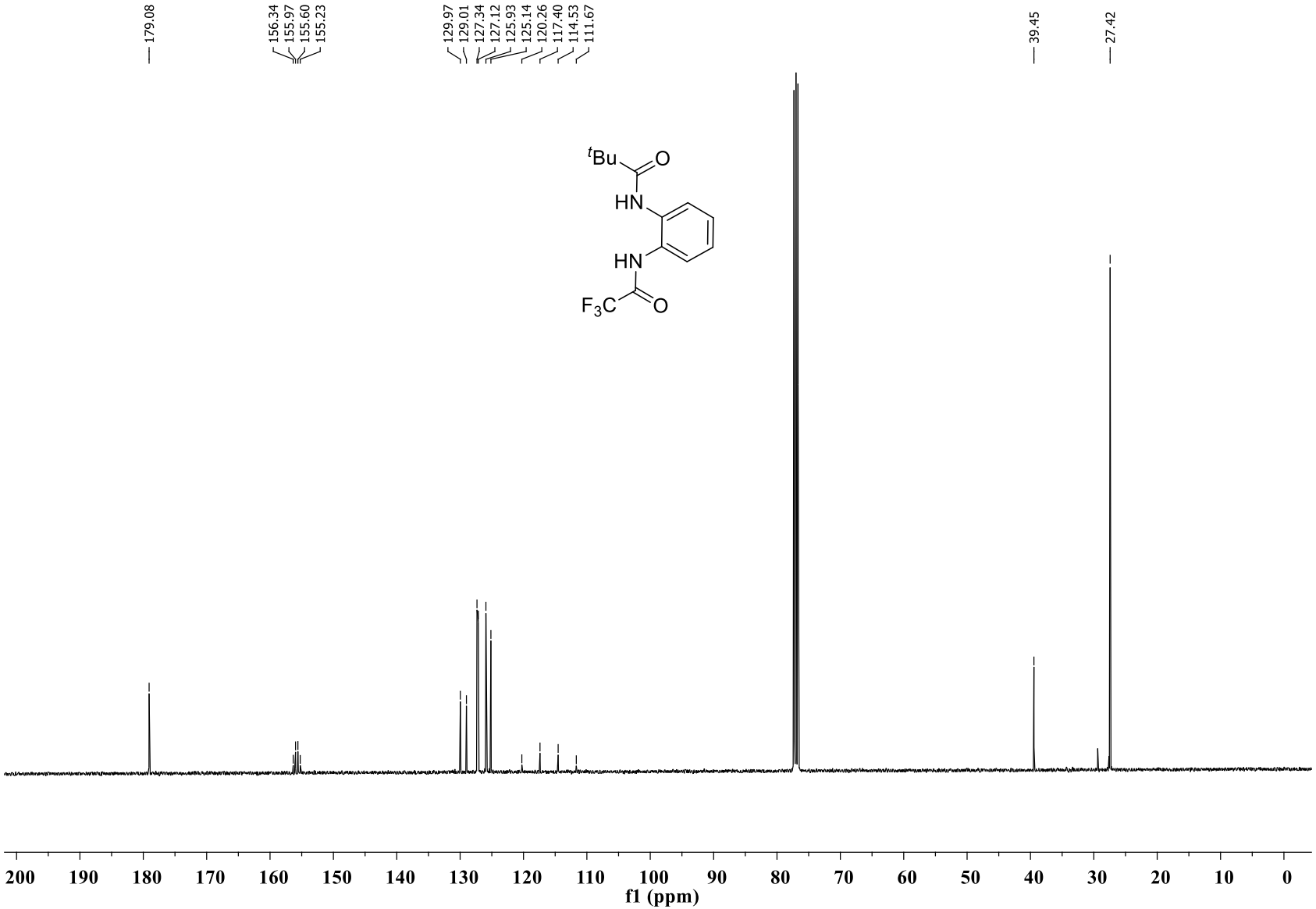
^{13}C NMR spectrum of compound **1p** ($CDCl_3$, 100 MHz)**:**



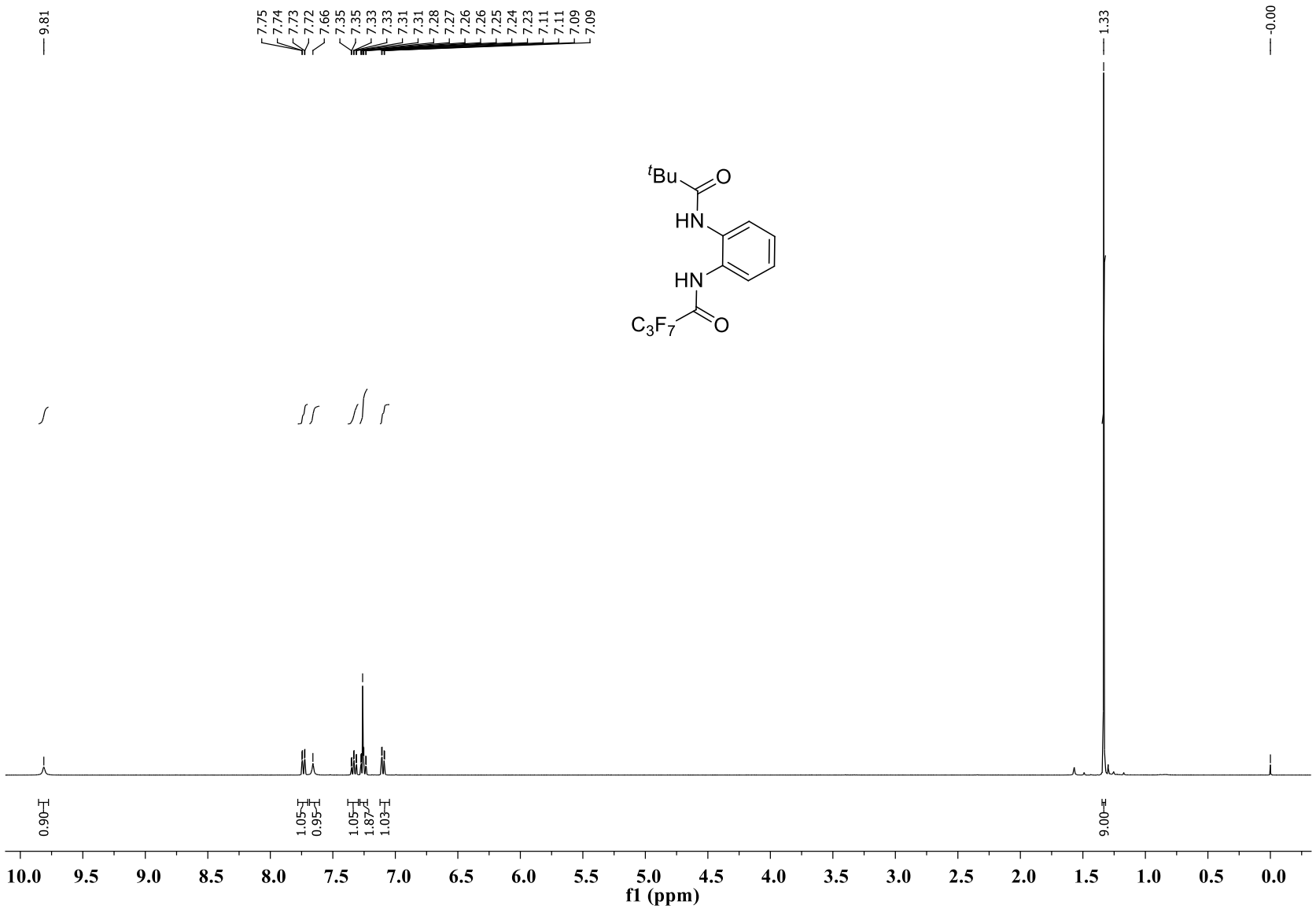
^{1}H NMR spectrum of compound **1q** ($CDCl_3$, 400 MHz)**:**



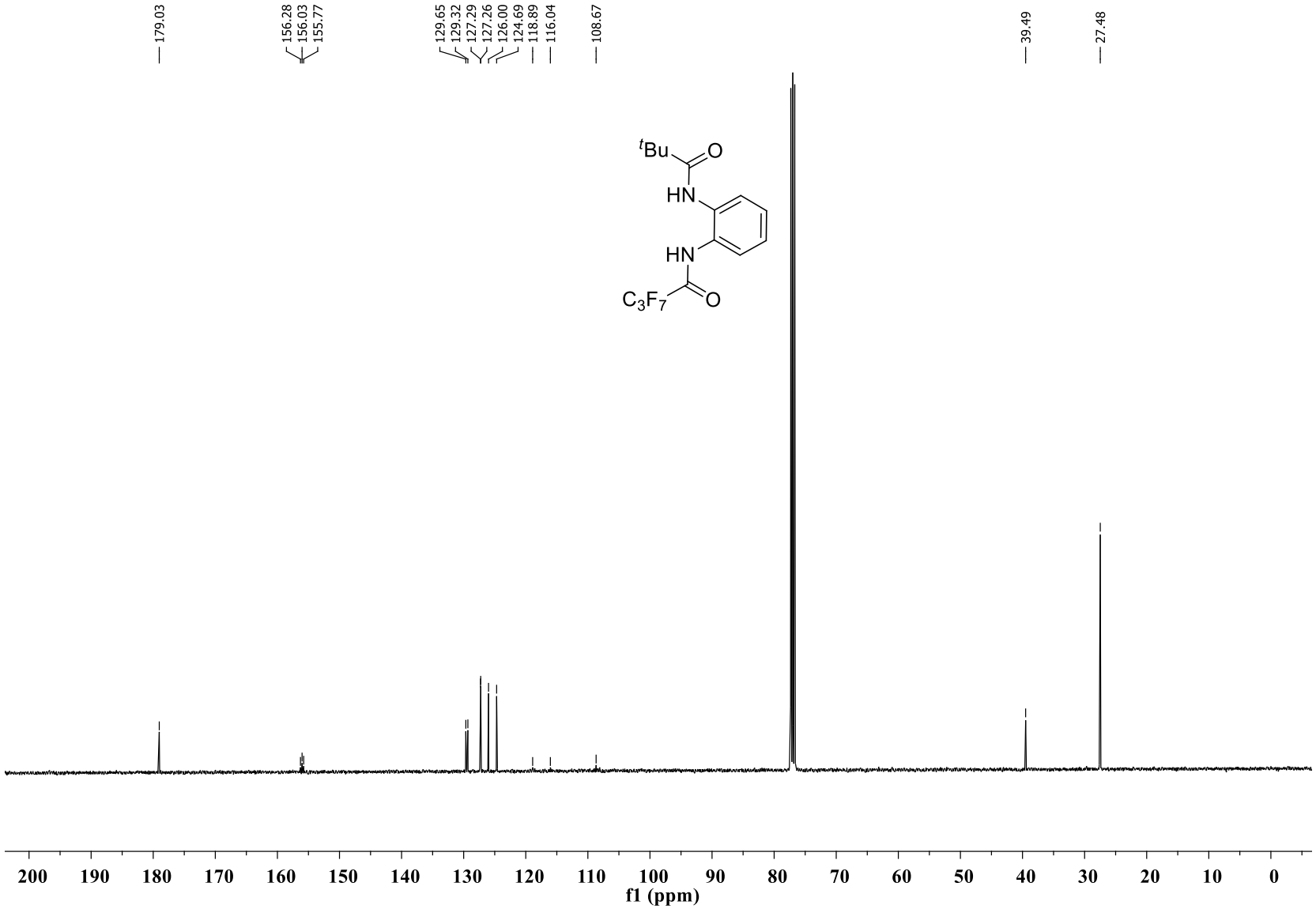
^{13}C NMR spectrum of compound **1q** ($CDCl_3$, 100 MHz)**:**



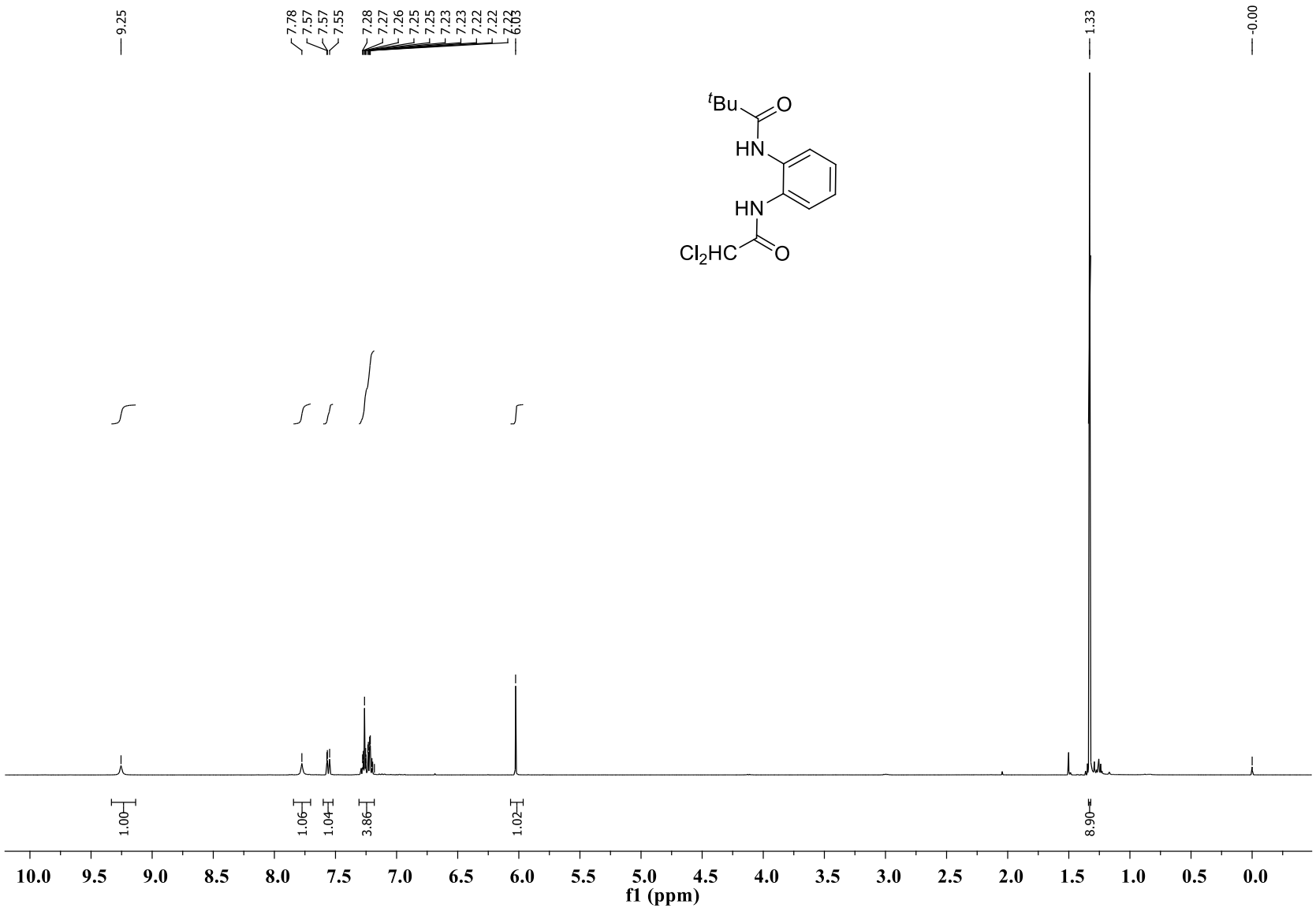
^{1}H NMR spectrum of compound **1r** ($CDCl_3$, 400 MHz)**:**



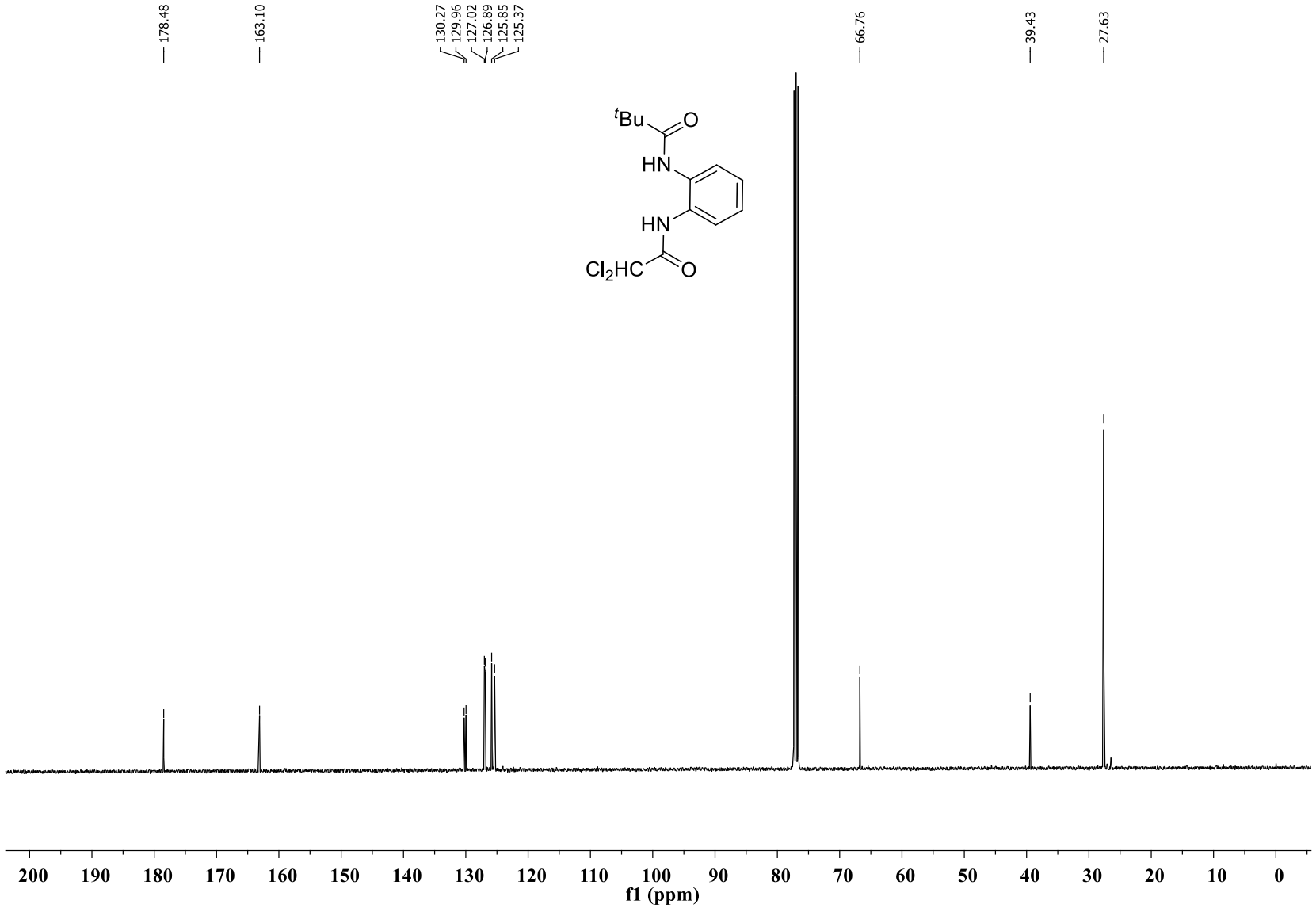
^{13}C NMR spectrum of compound **1r** ($CDCl_3$, 100 MHz)**:**



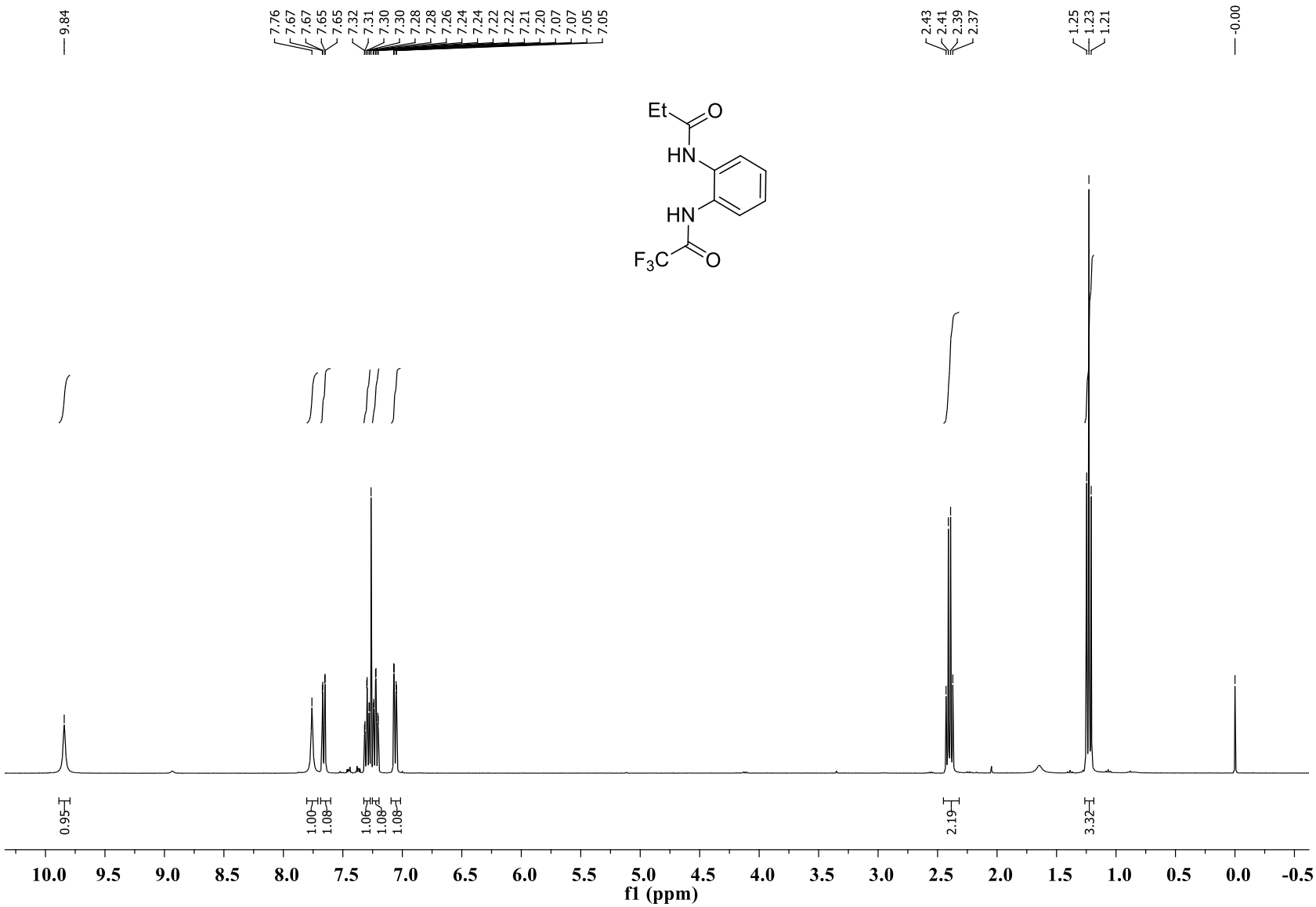
^{1}H NMR spectrum of compound **1s** ($CDCl_3$, 400 MHz)**:**



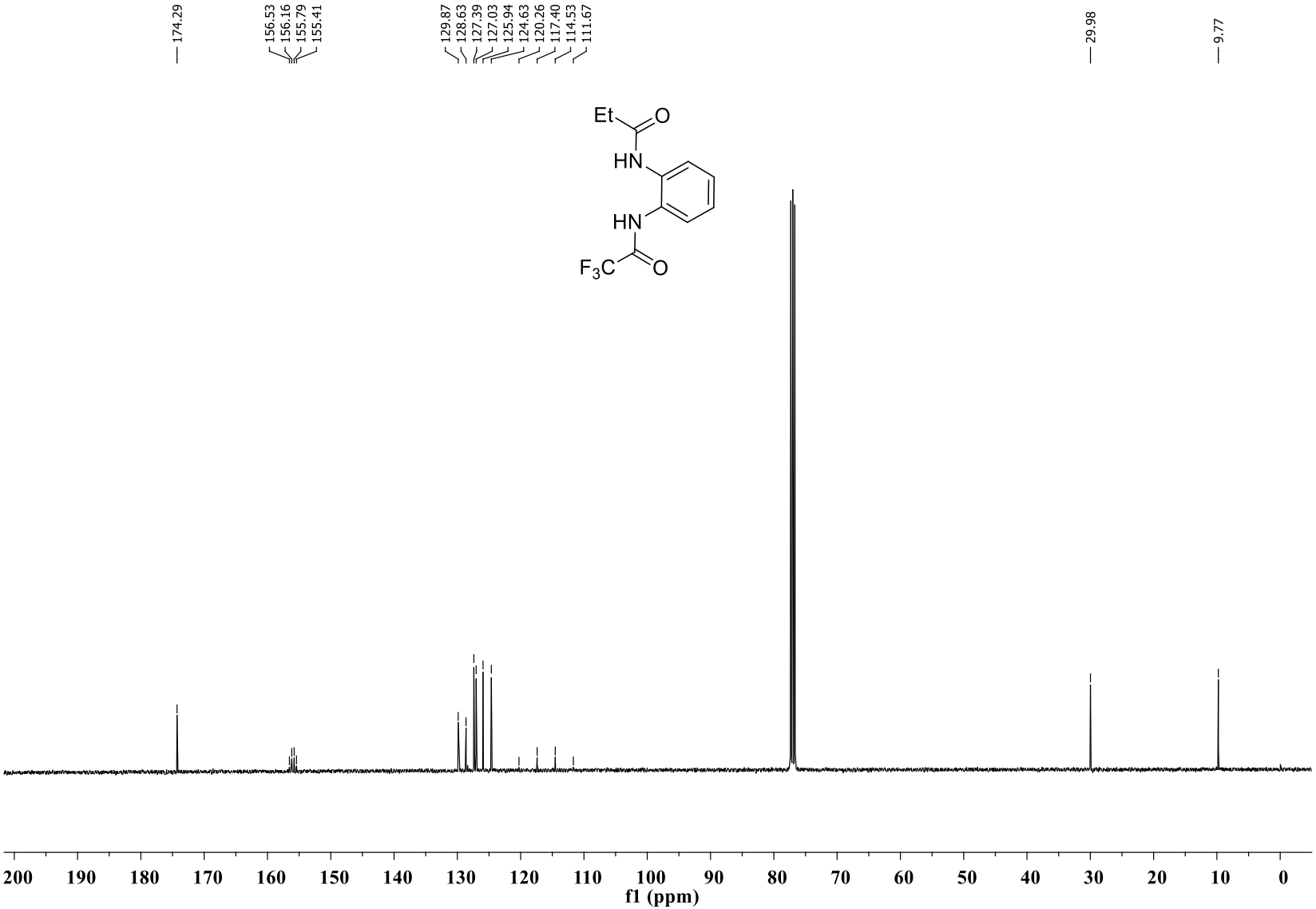
^{13}C NMR spectrum of compound **1s** ($CDCl_3$, 100 MHz)**:**



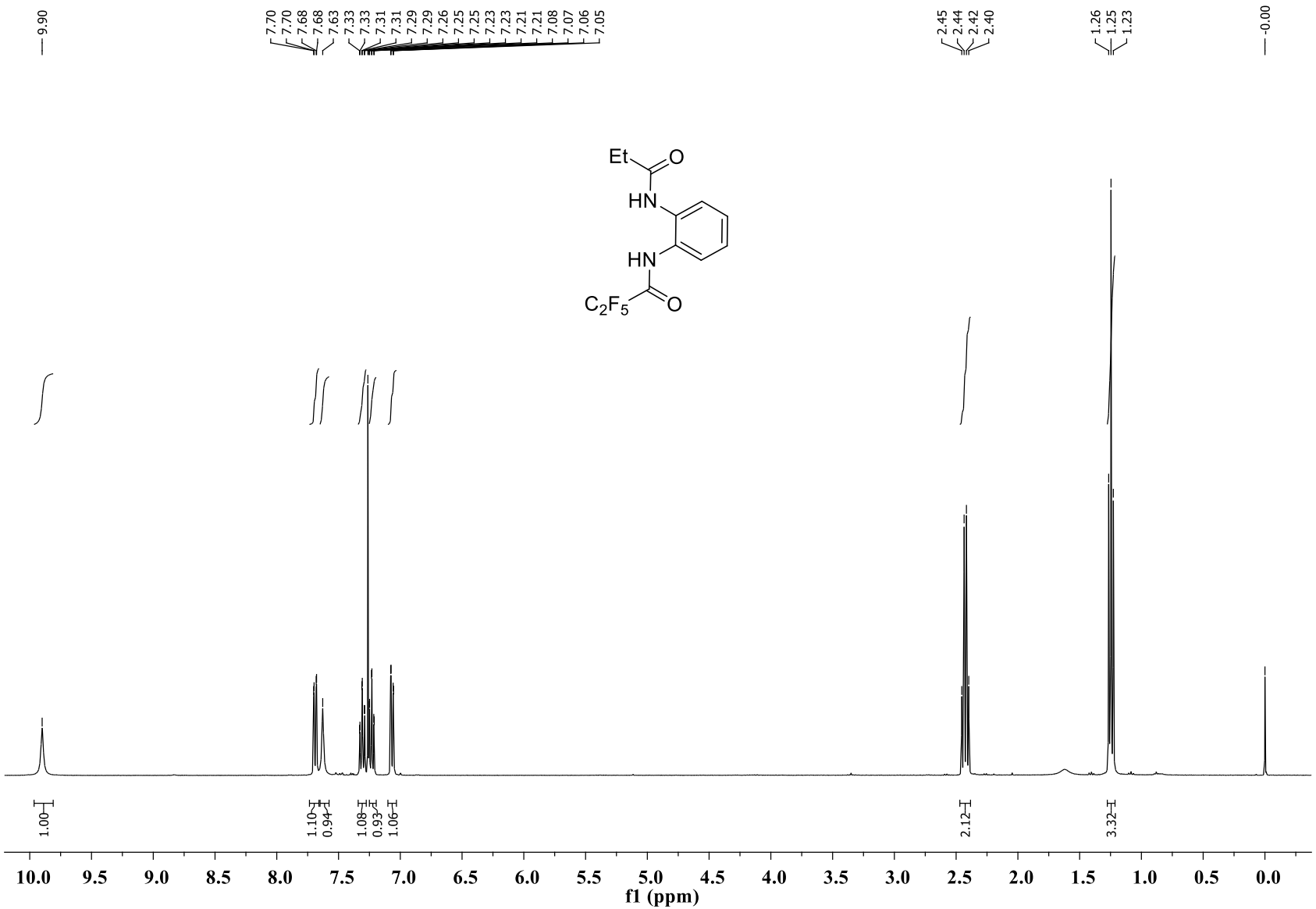
^{1}H NMR spectrum of compound **1t** ($CDCl_3$, 400 MHz)**:**



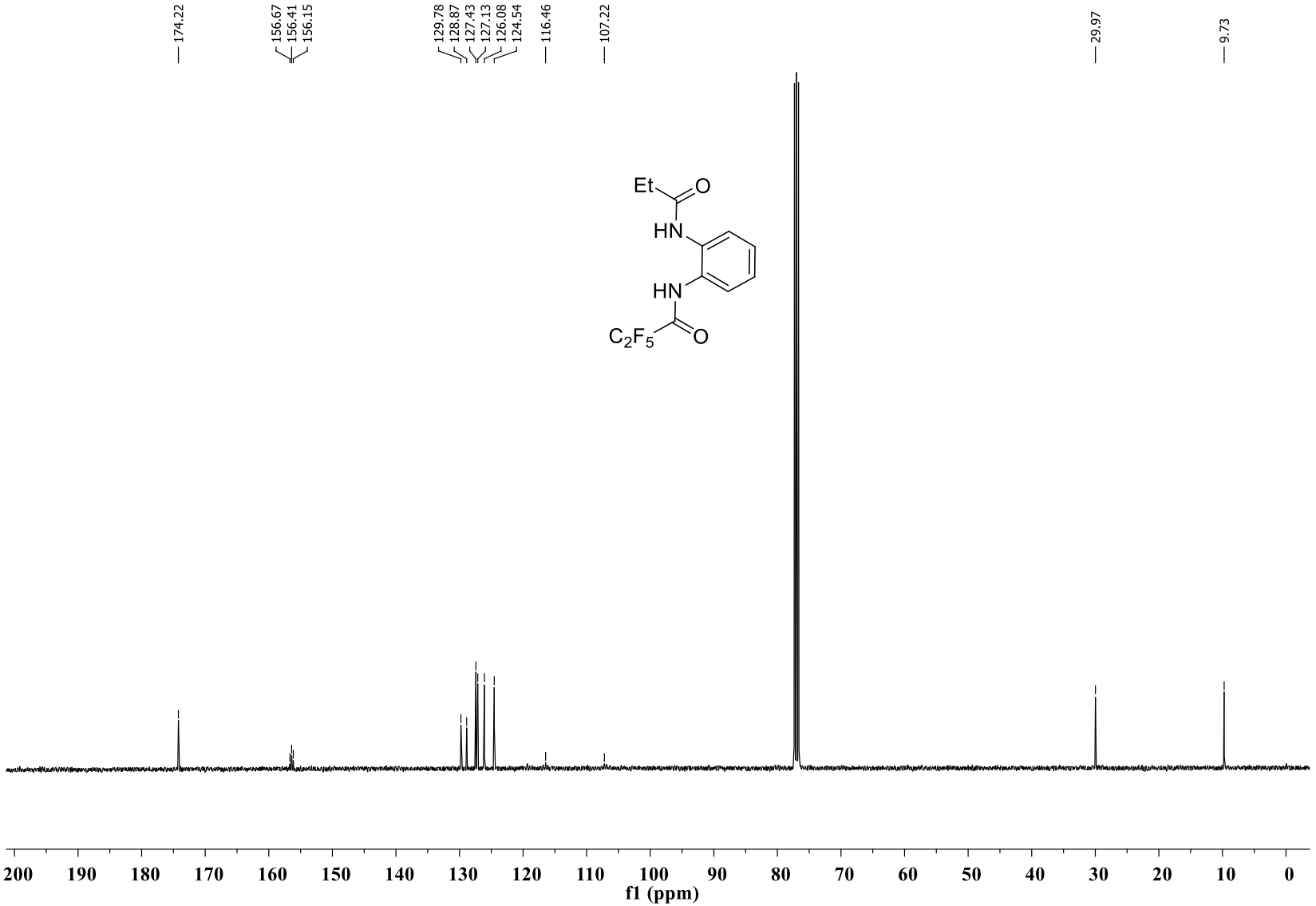
^{13}C NMR spectrum of compound **1t** ($CDCl_3$, 100 MHz)**:**



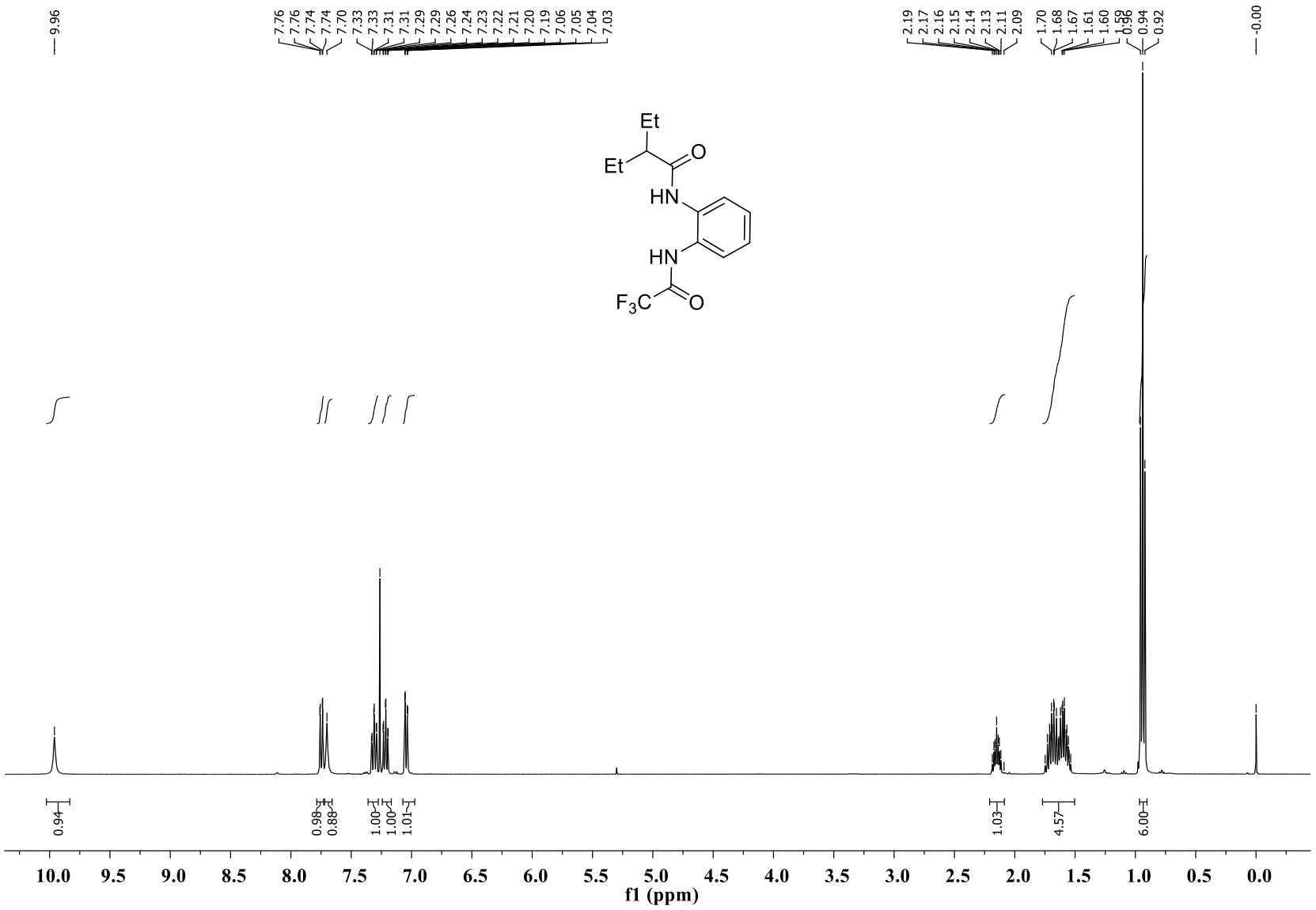
^{1}H NMR spectrum of compound **1u** ($CDCl_3$, 400 MHz)**:**



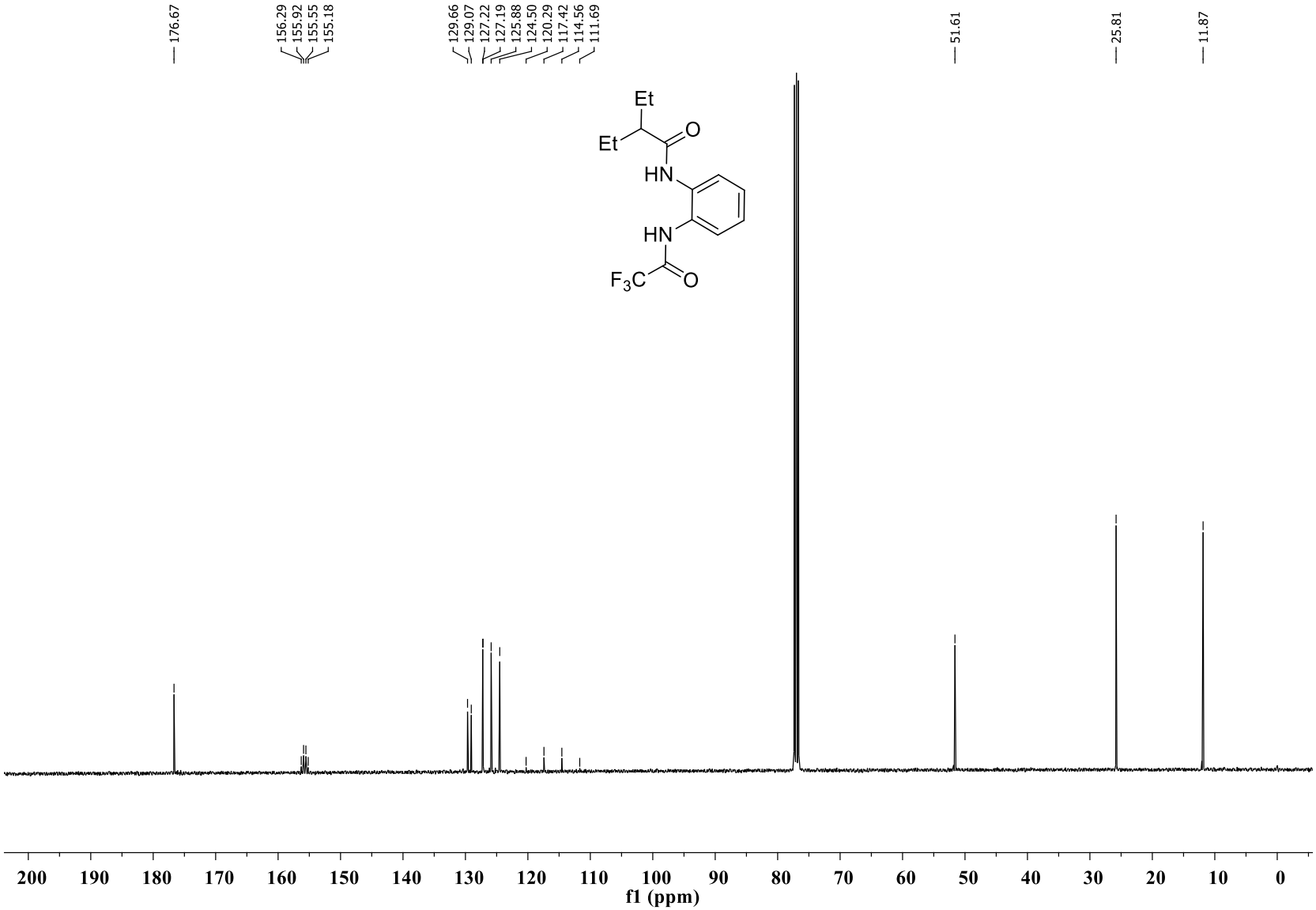
^{13}C NMR spectrum of compound **1u** ($CDCl_3$, 100 MHz)**:**



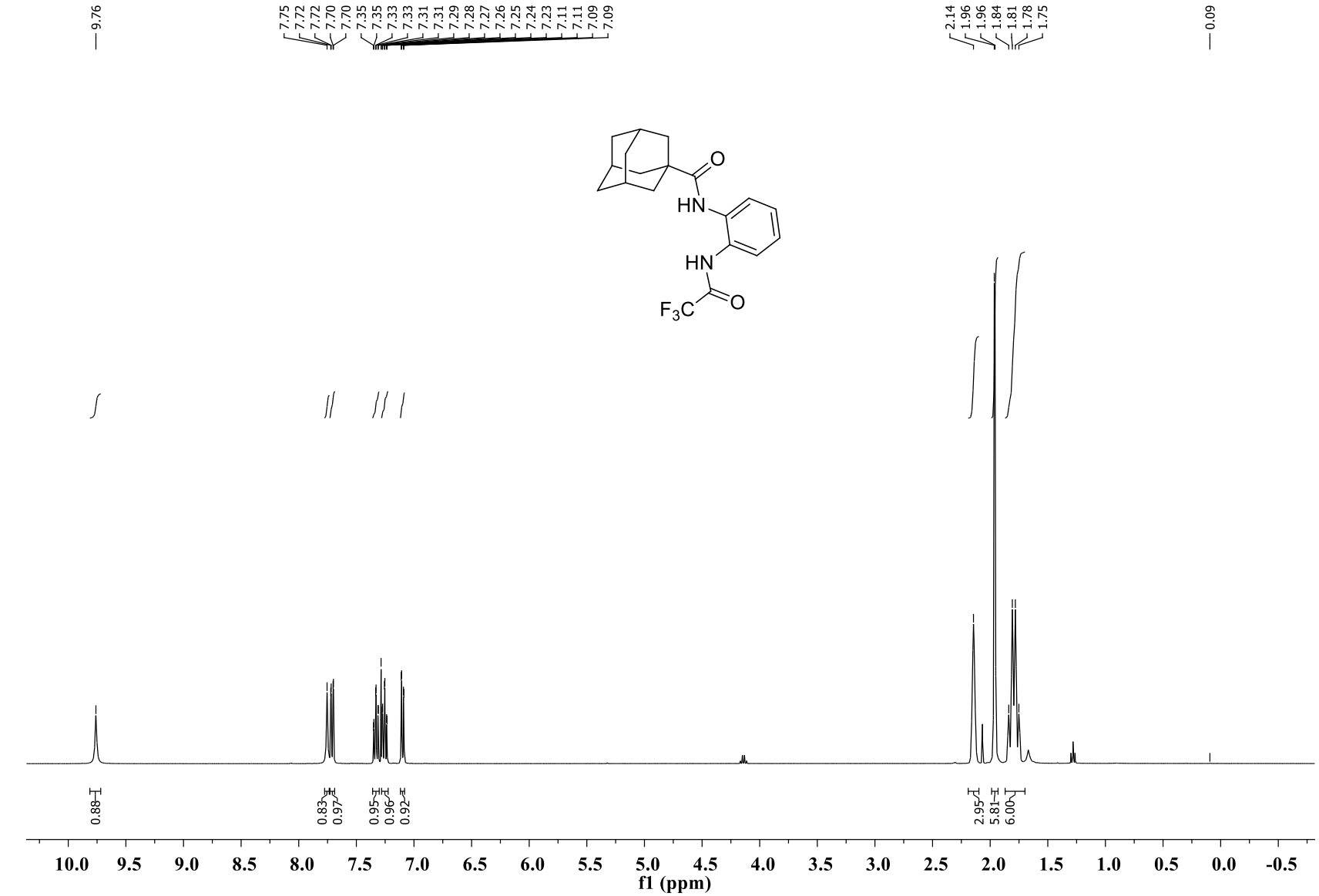
^{1}H NMR spectrum of compound **1v** ($CDCl_3$, 400 MHz)**:**



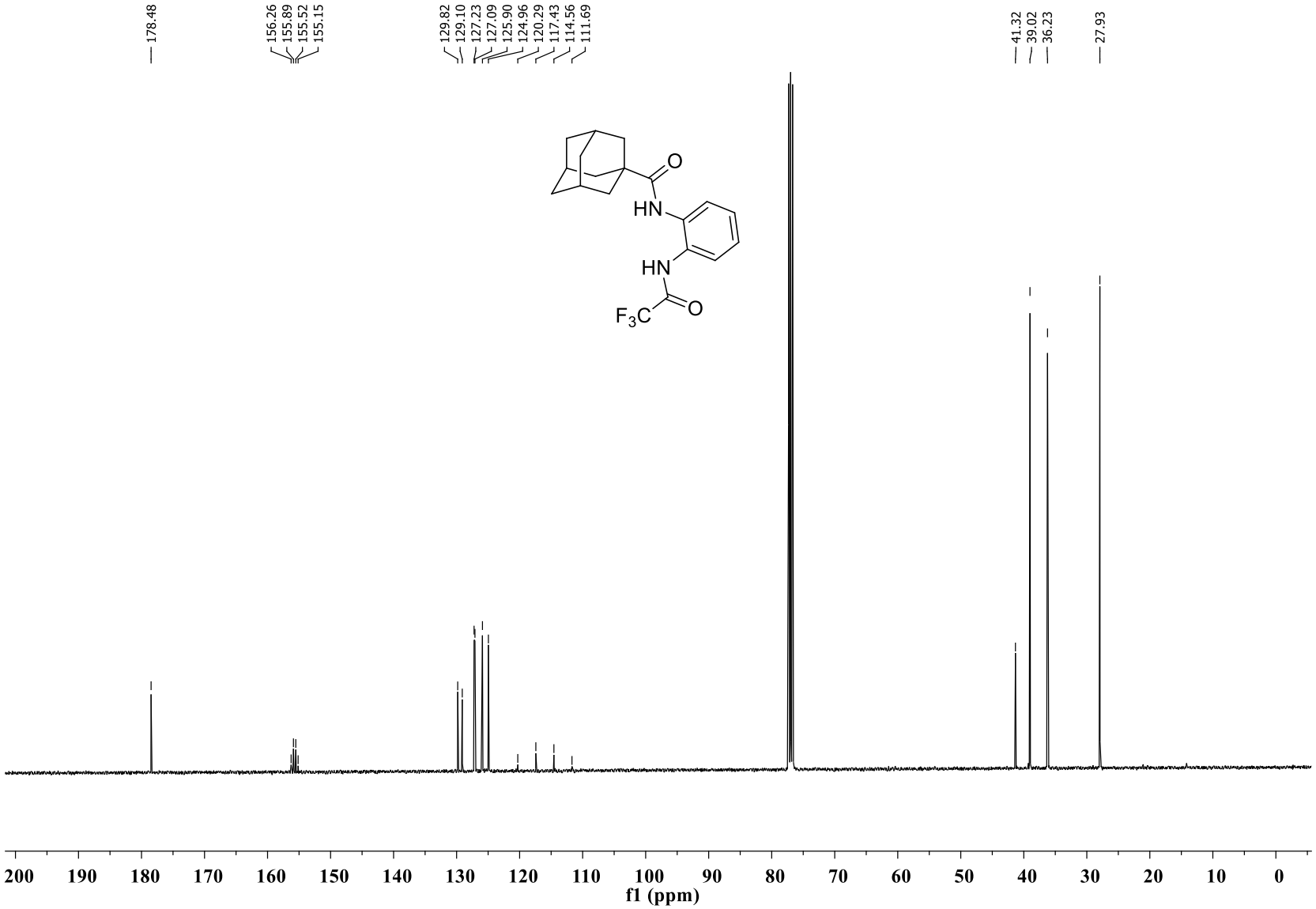
^{13}C NMR spectrum of compound **1v** ($CDCl_3$, 100 MHz)**:**



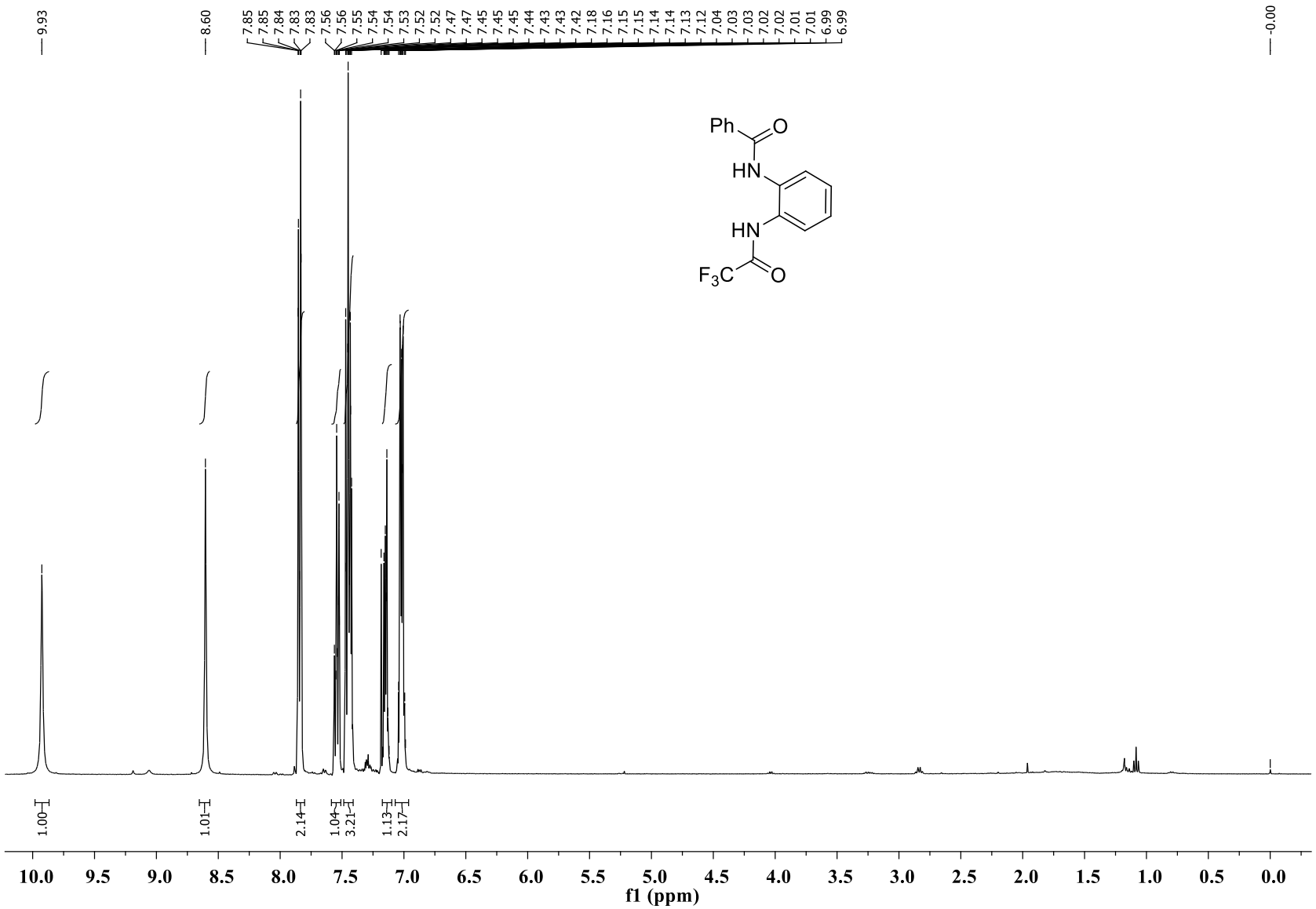
^{1}H NMR spectrum of compound **1w** ($CDCl_3$, 400 MHz)**:**



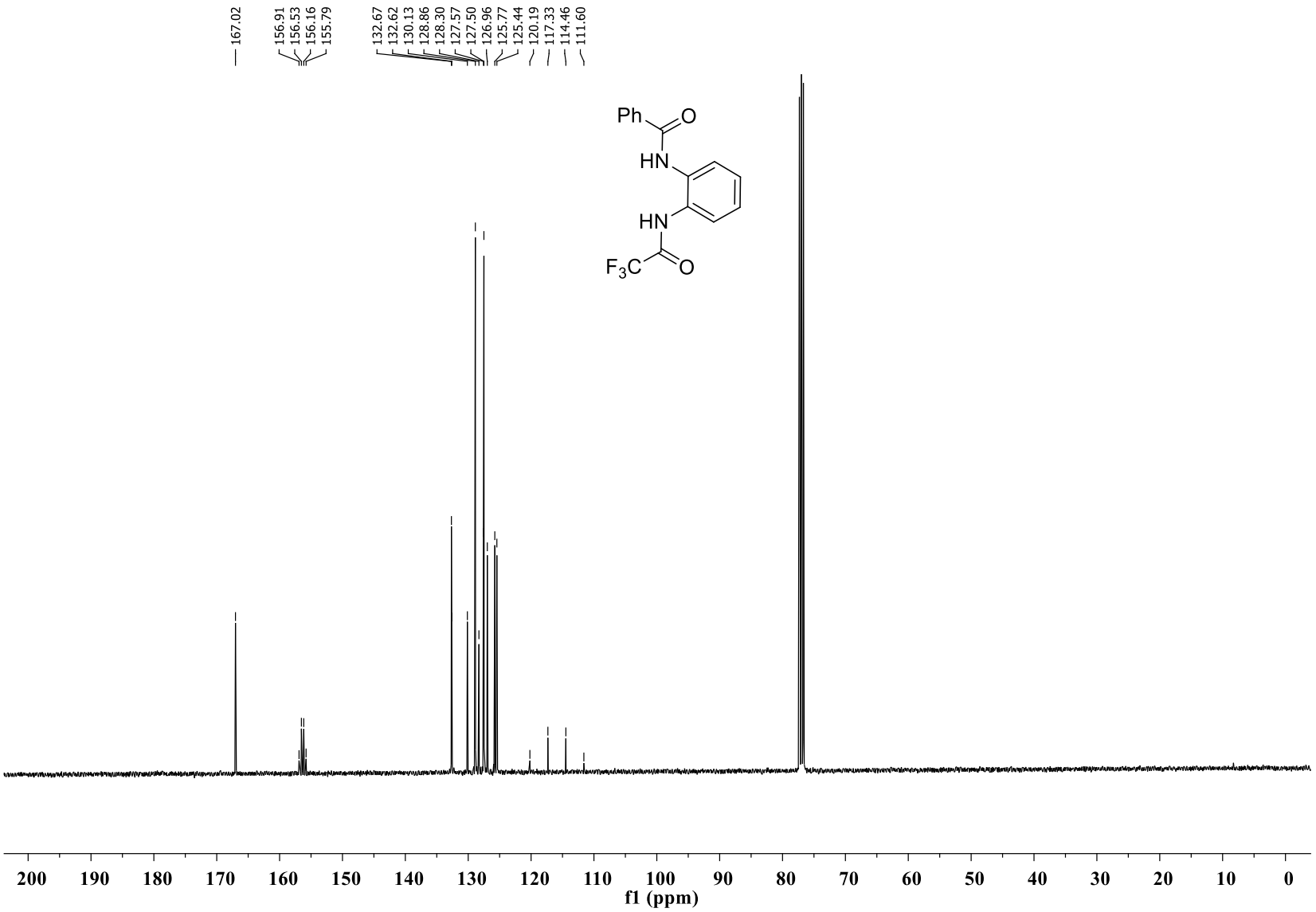
^{13}C NMR spectrum of compound **1w** ($CDCl_3$, 100 MHz)**:**



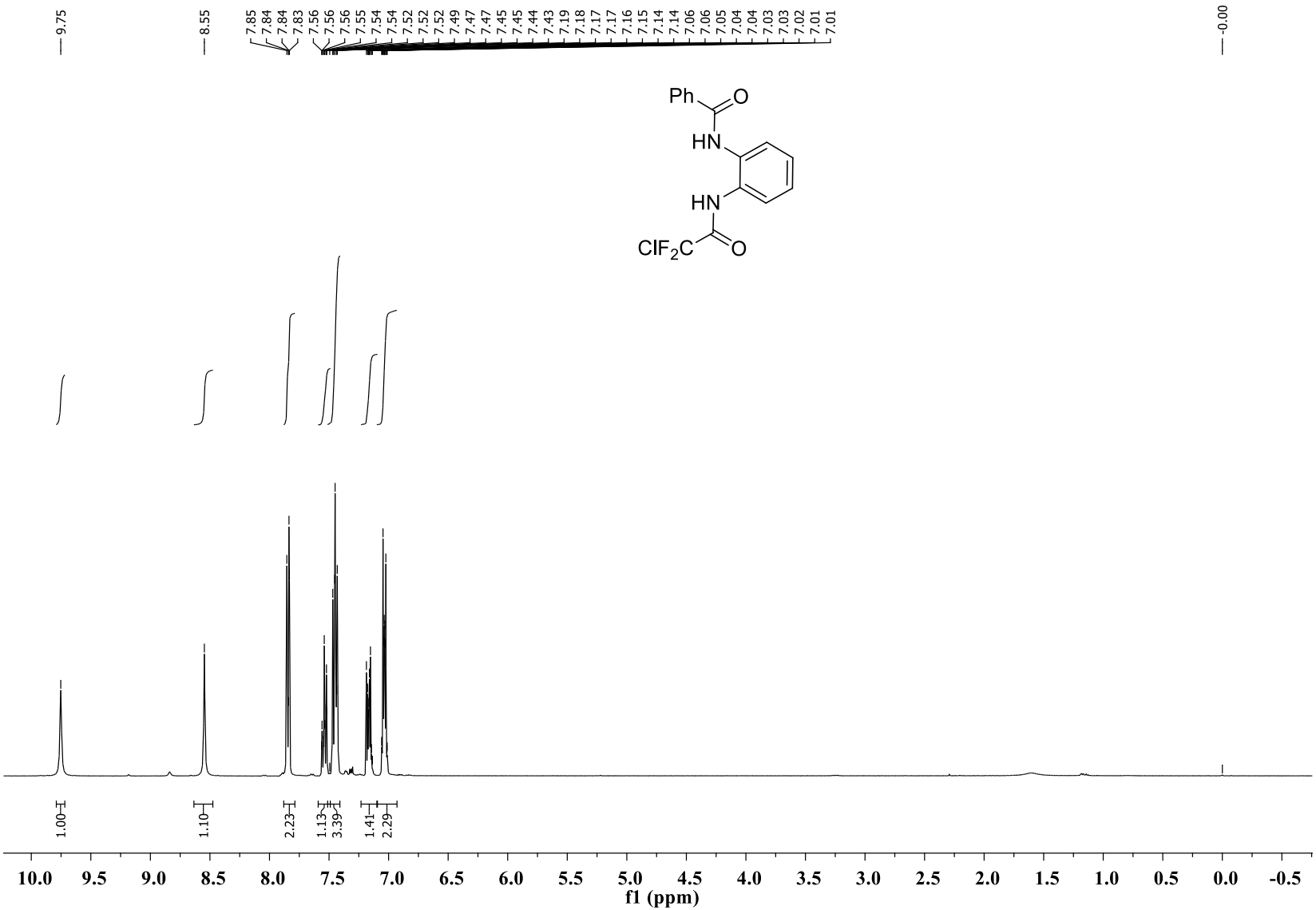
^{1}H NMR spectrum of compound **1x** ($CDCl_3$, 400 MHz)**:**



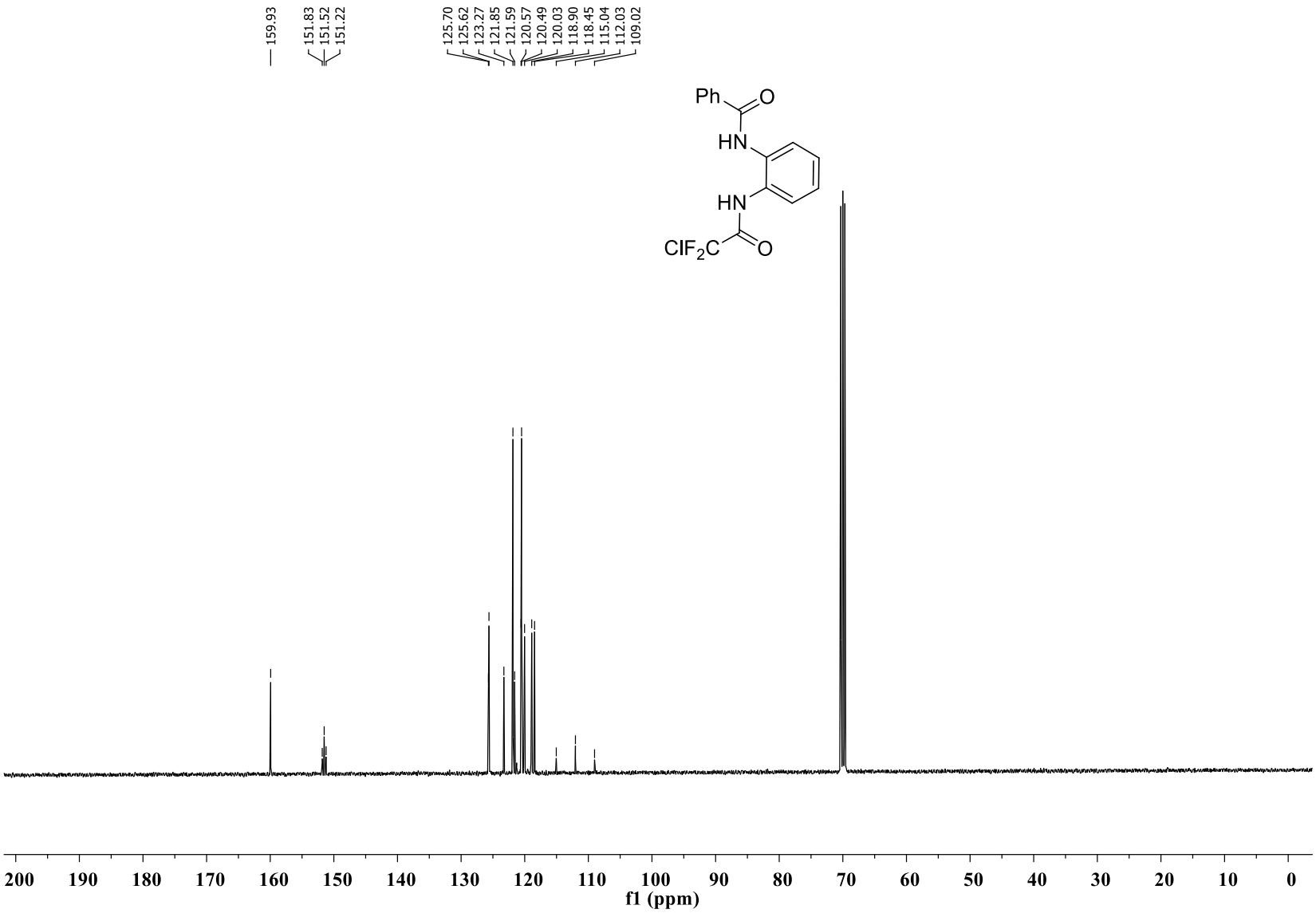
^{13}C NMR spectrum of compound **1x** ($CDCl_3$, 100 MHz)**:**



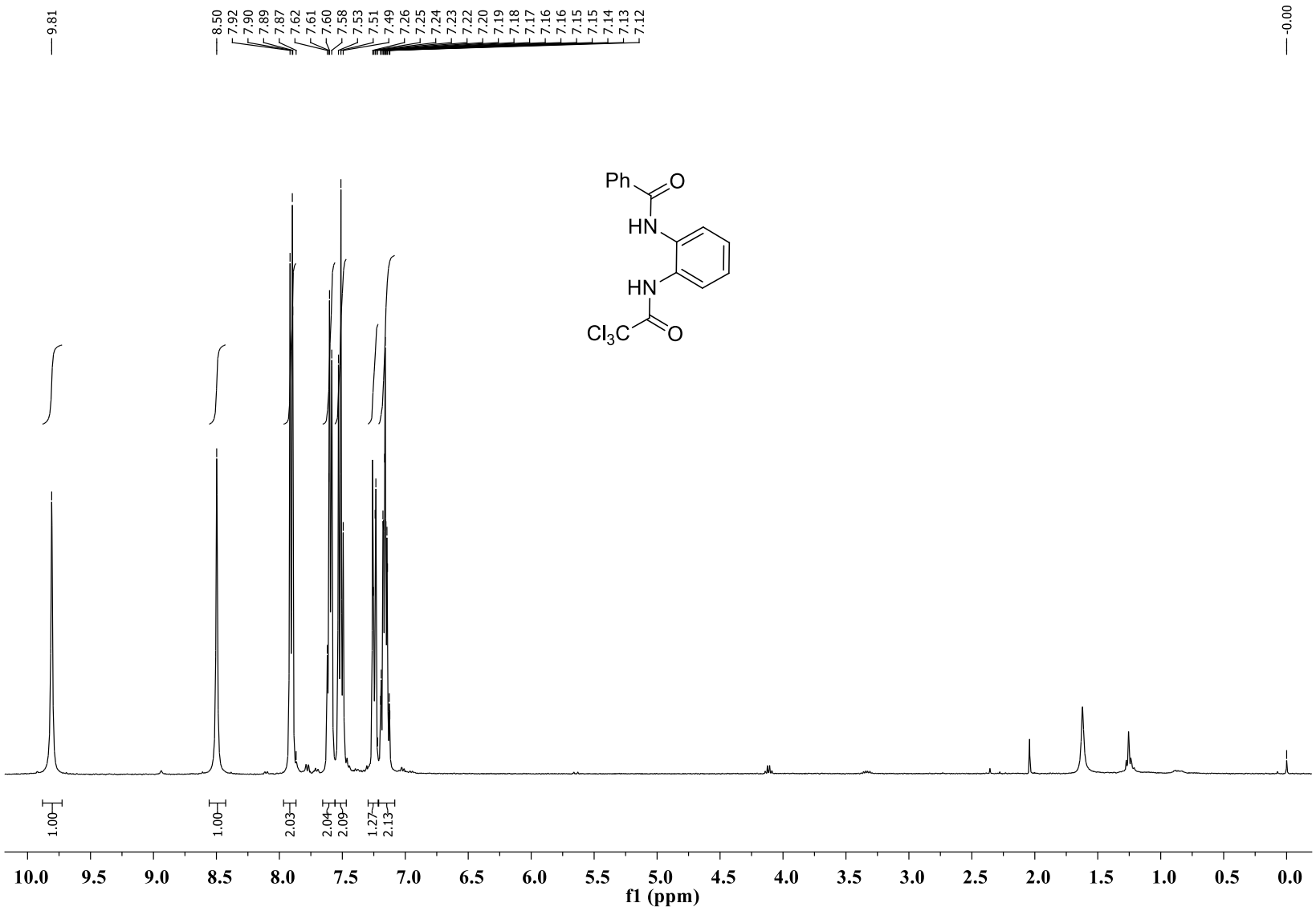
^{1}H NMR spectrum of compound **1y** ($CDCl_3$, 400 MHz)**:**



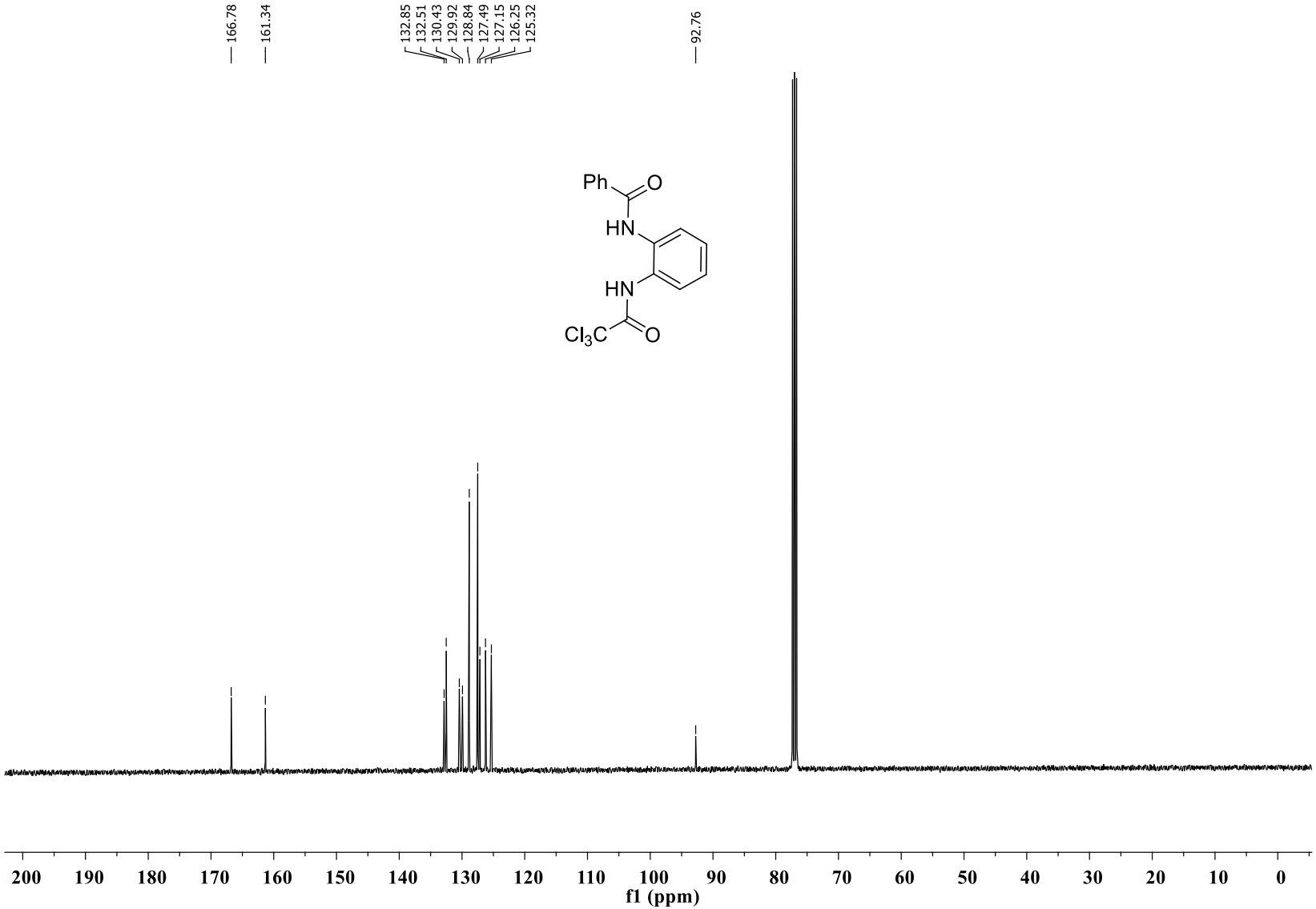
^{13}C NMR spectrum of compound **1y** ($CDCl_3$, 100 MHz)**:**



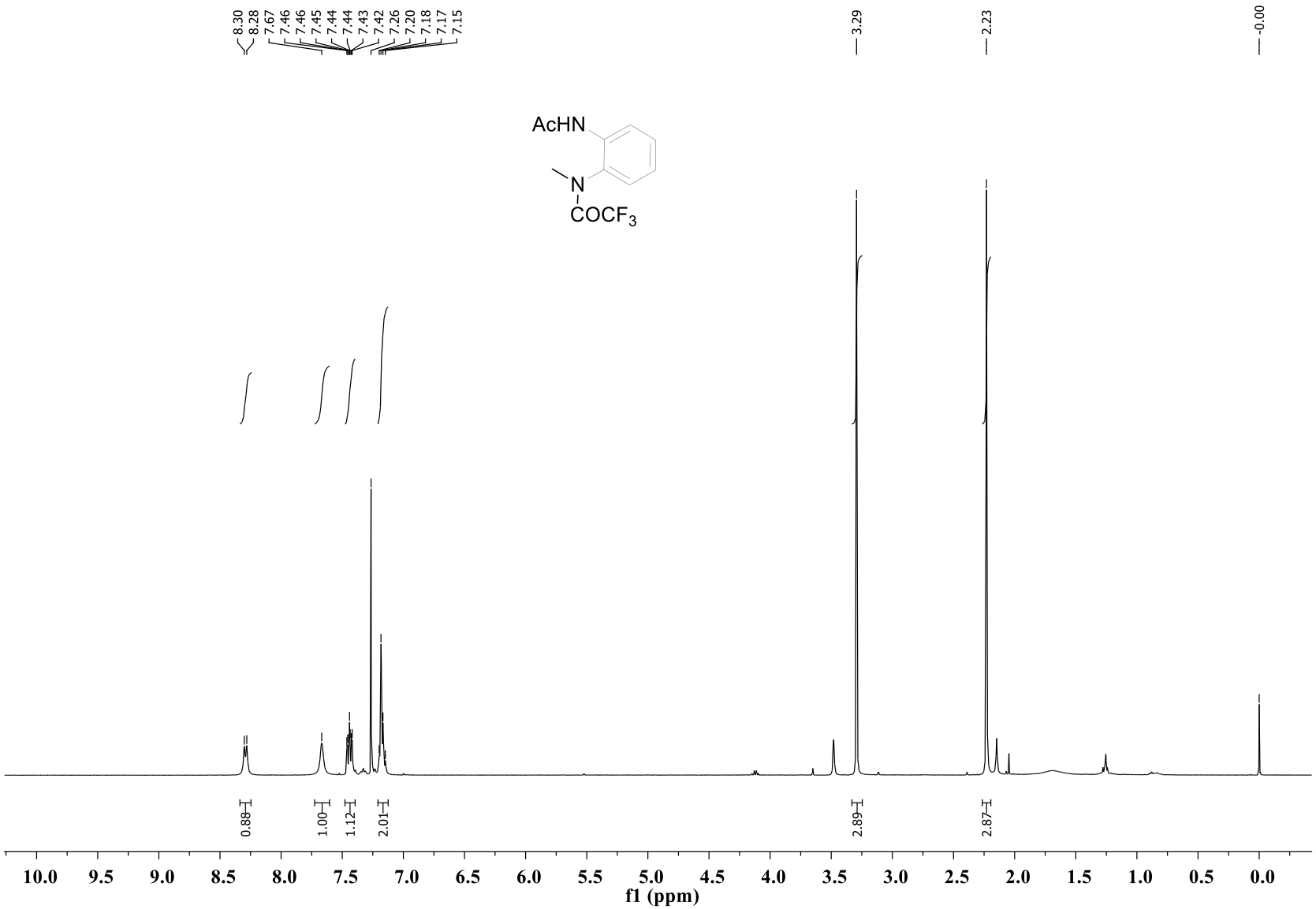
^{1}H NMR spectrum of compound **1z** ($CDCl_3$, 400 MHz)**:**



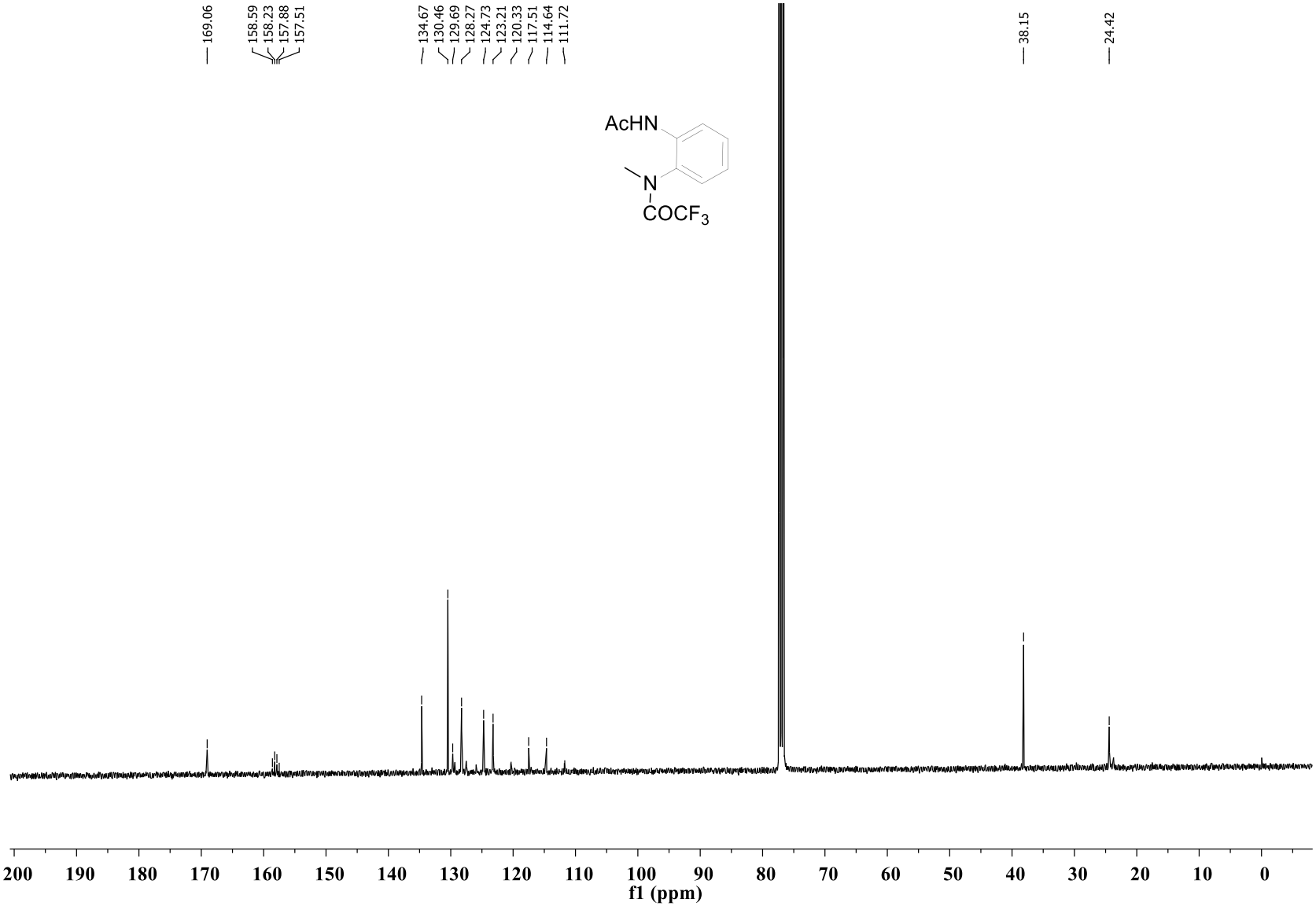
^{13}C NMR spectrum of compound **1z** ($CDCl_3$, 100 MHz)**:**



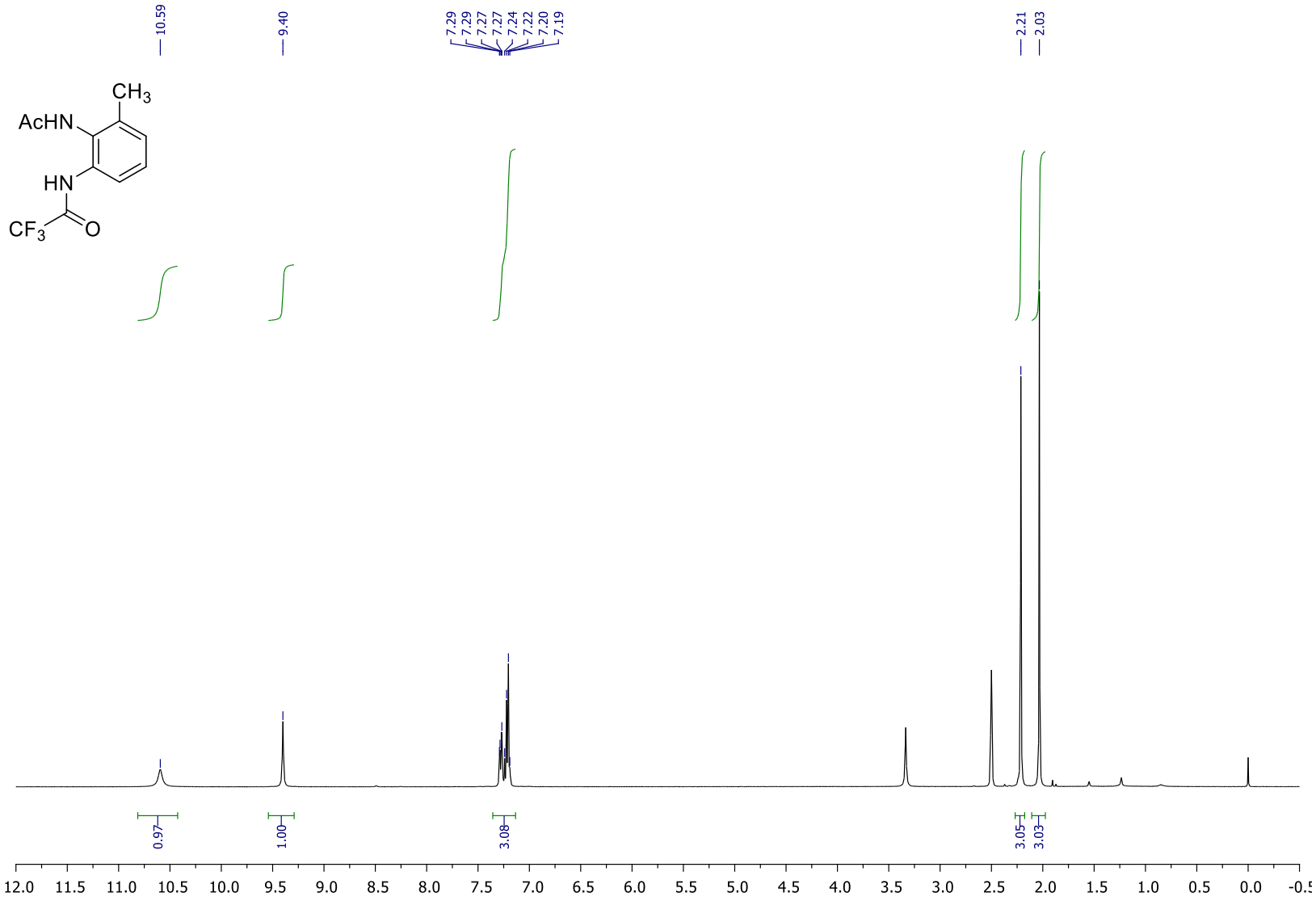
^{1}H NMR spectrum of compound **1aa** ($CDCl_3$, 400 MHz)**:**



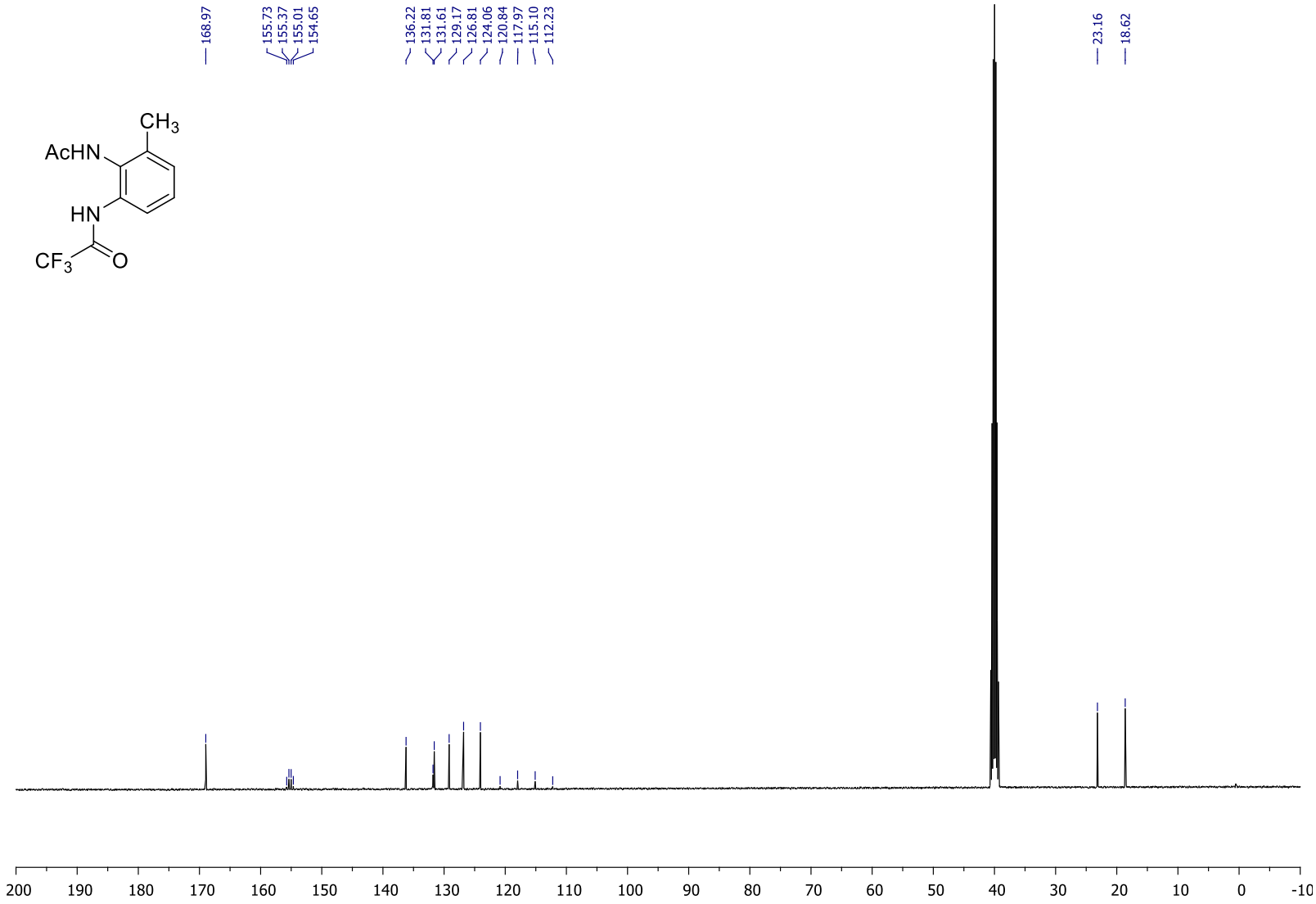
^{13}C NMR spectrum of compound **1aa** ($CDCl_3$, 100 MHz)**:**



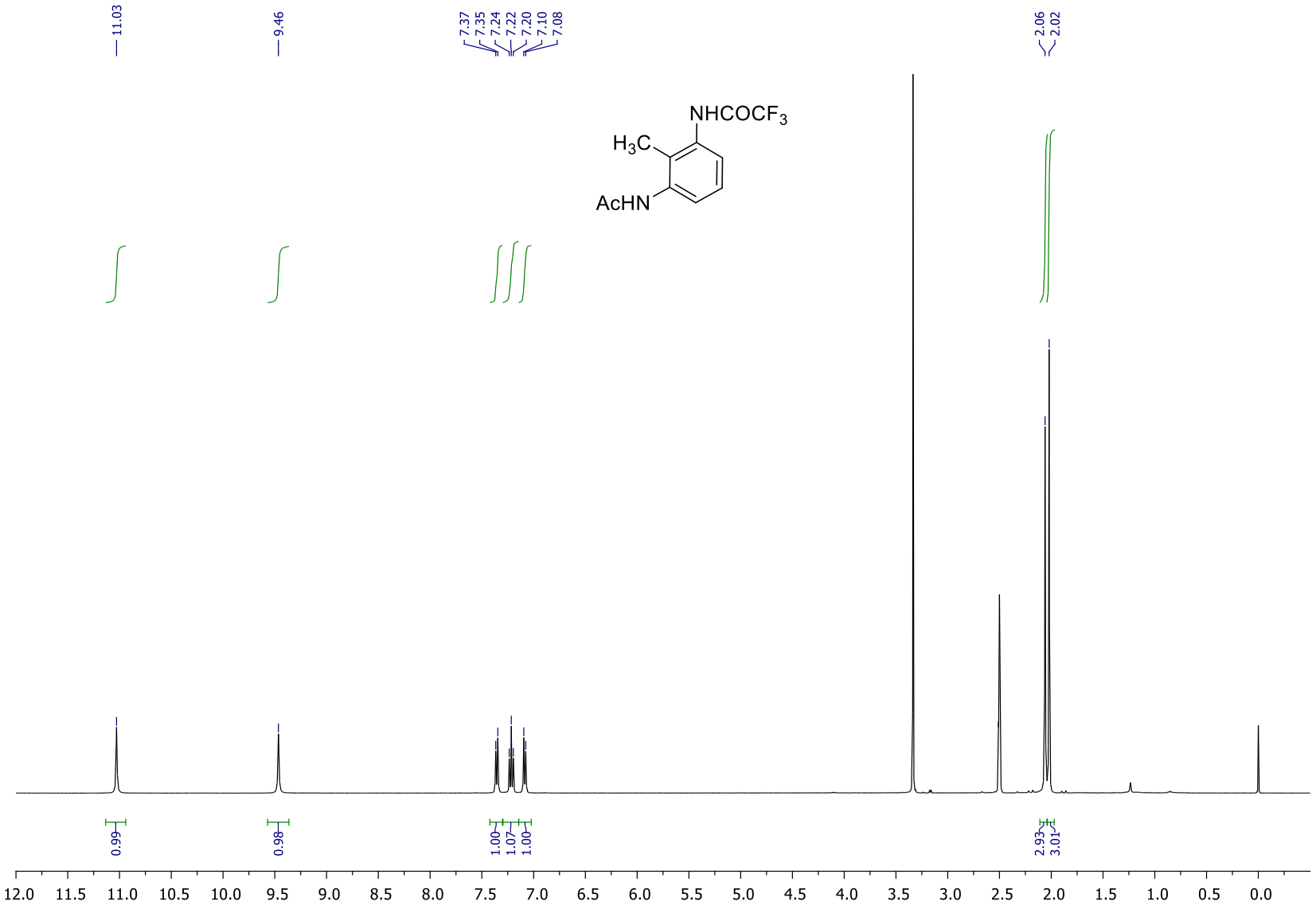
^{1}H NMR spectrum of compound **1bb** ($CDCl_3$, 400 MHz)**:**



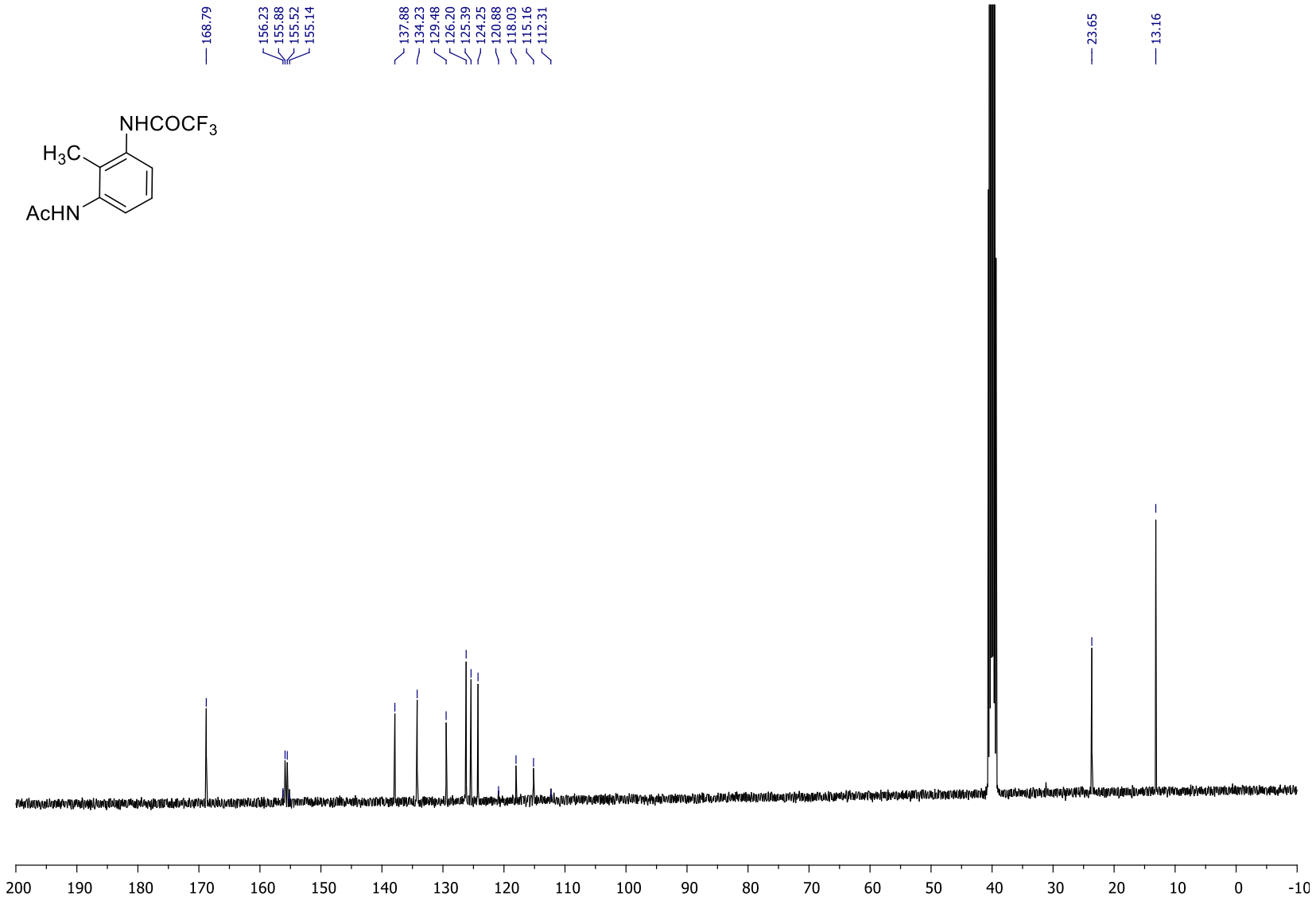
^{13}C NMR spectrum of compound **1bb** ($CDCl_3$, 100 MHz)**:**



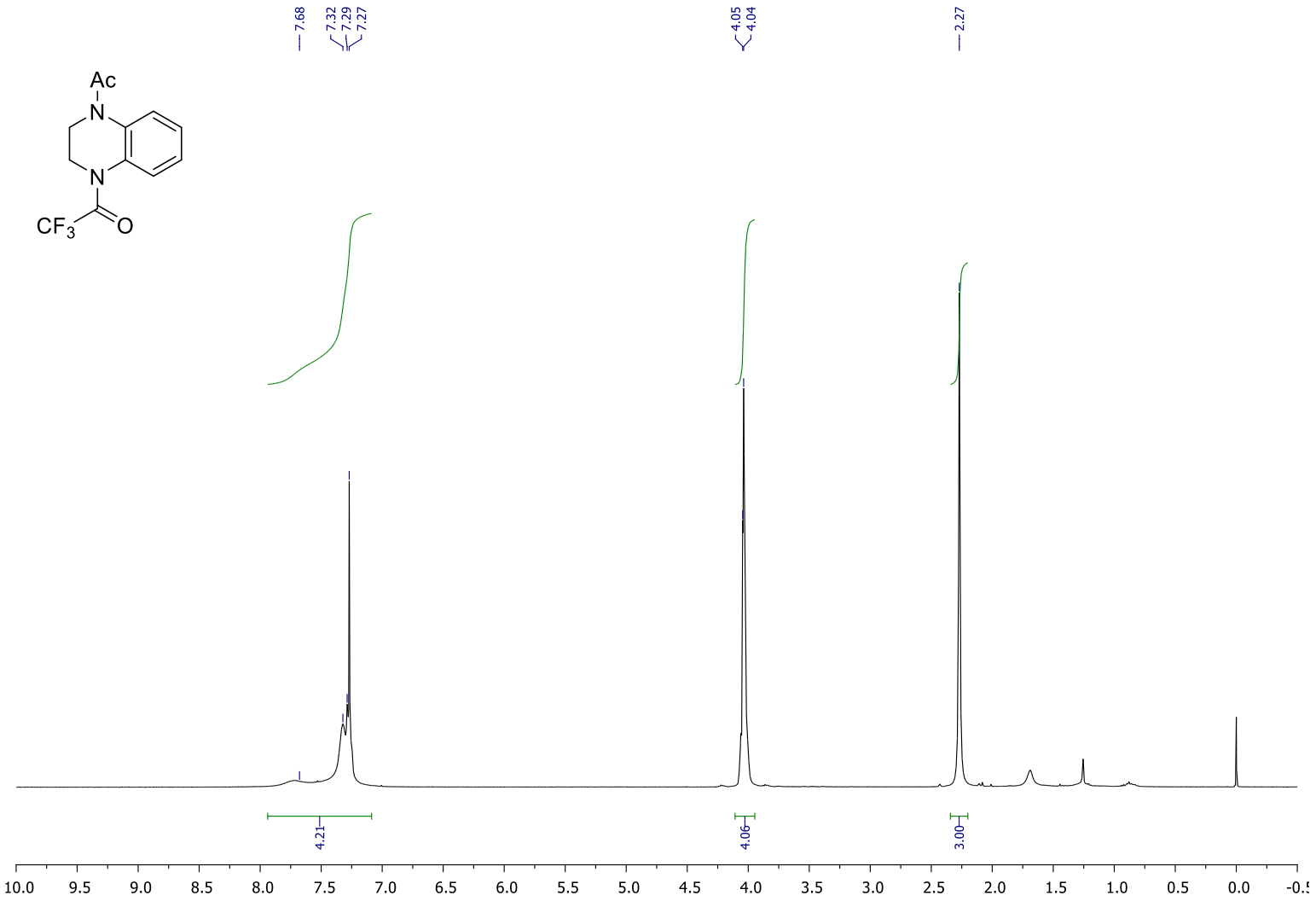
^{1}H NMR spectrum of compound **1cc** (DMSO-d_6, 400 MHz)**:**



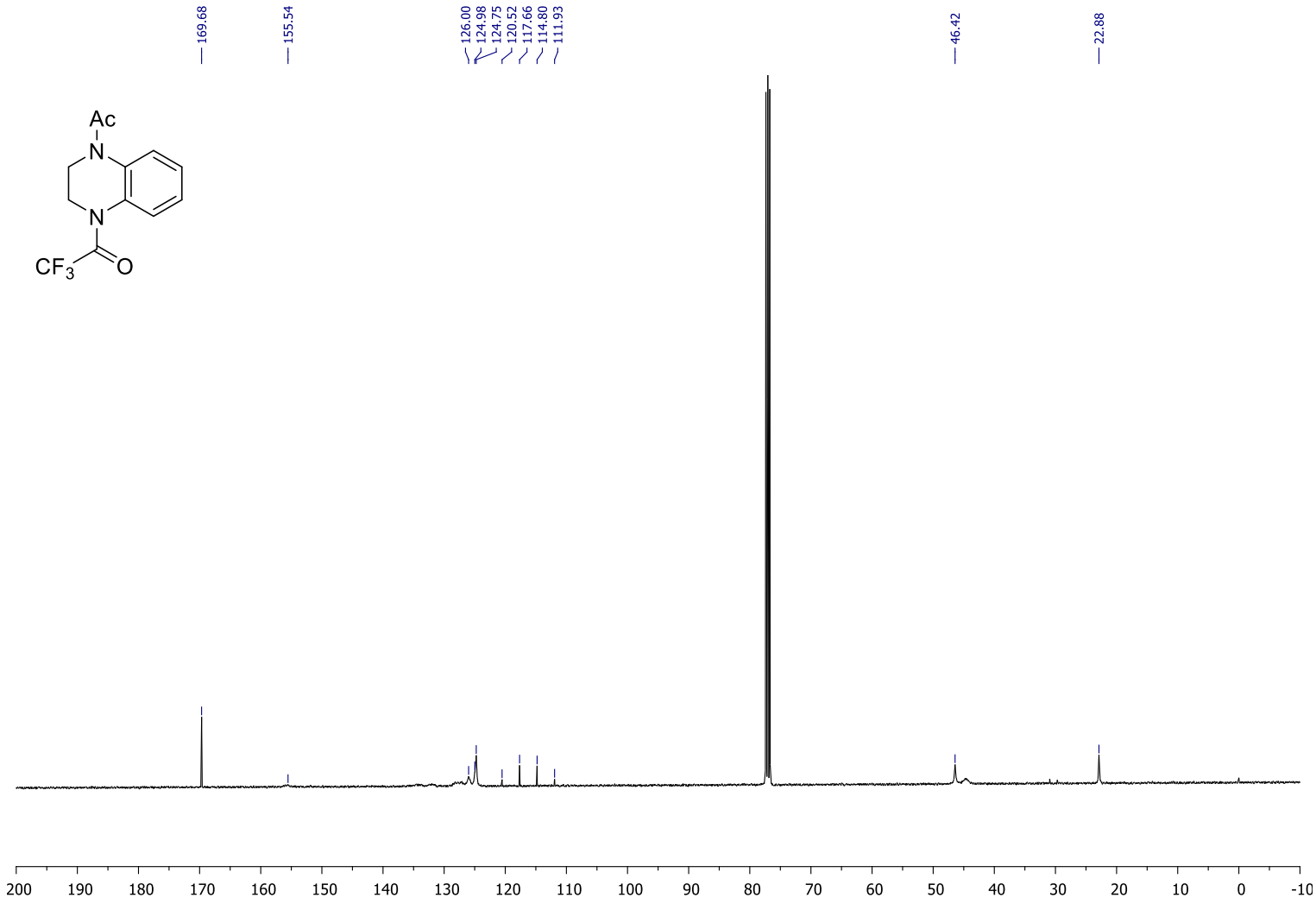
^{13}C NMR spectrum of compound **1cc** (DMSO-d_6, 100 MHz)**:**



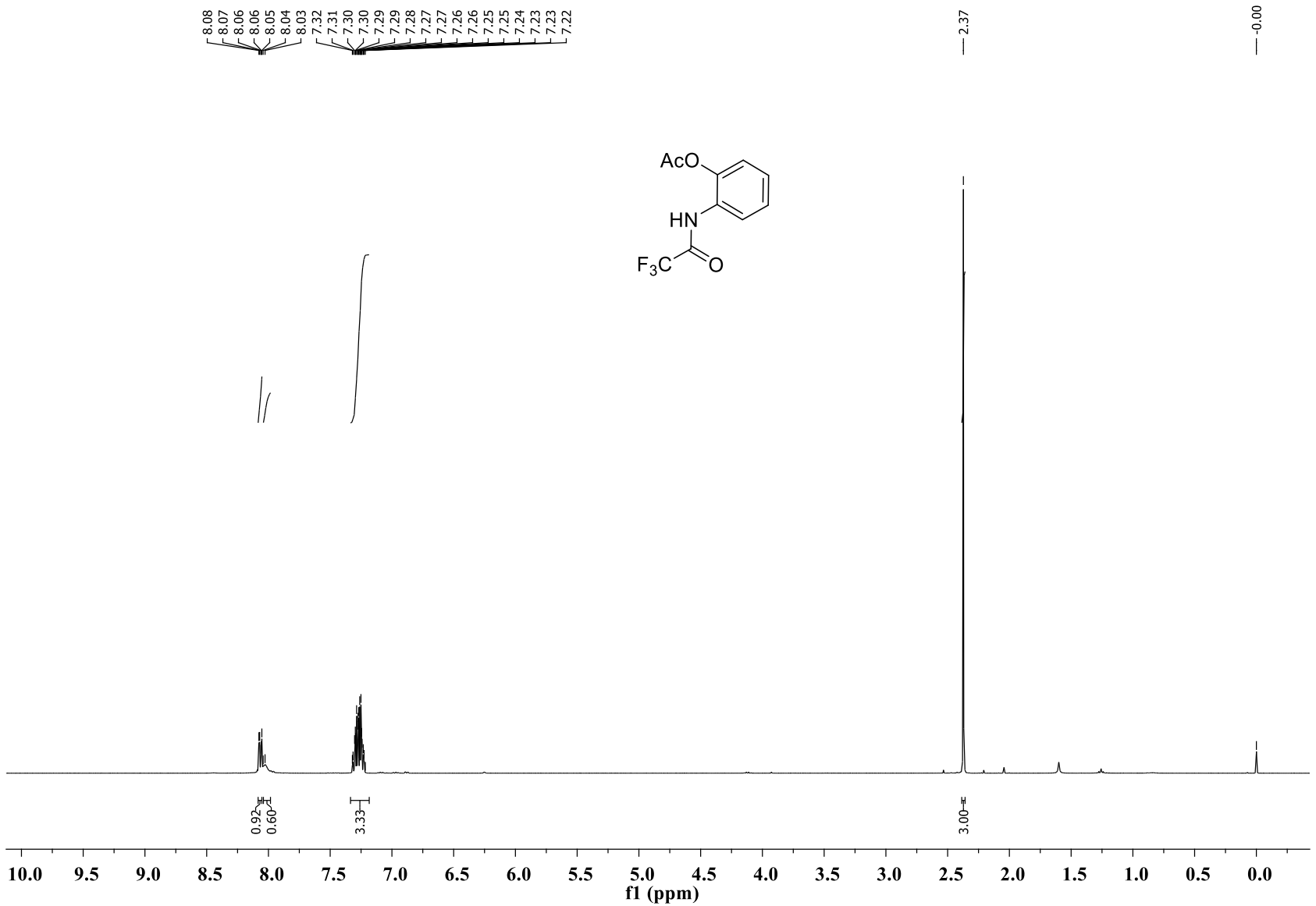
^{1}H NMR spectrum of compound **1dd** (DMSO-d_6, 400 MHz)**:**



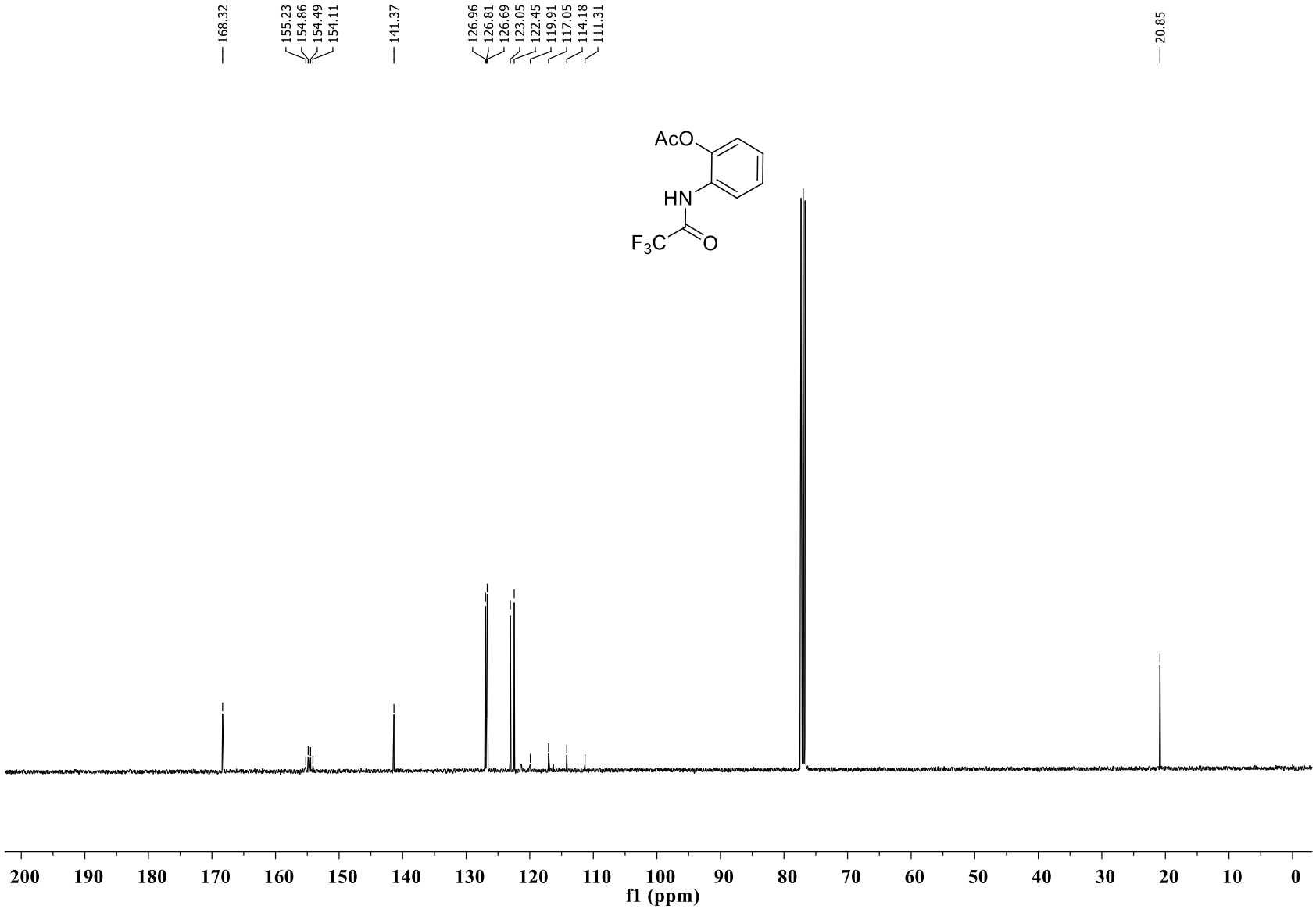
^{13}C NMR spectrum of compound **1dd** (DMSO-d_6, 100 MHz)**:**



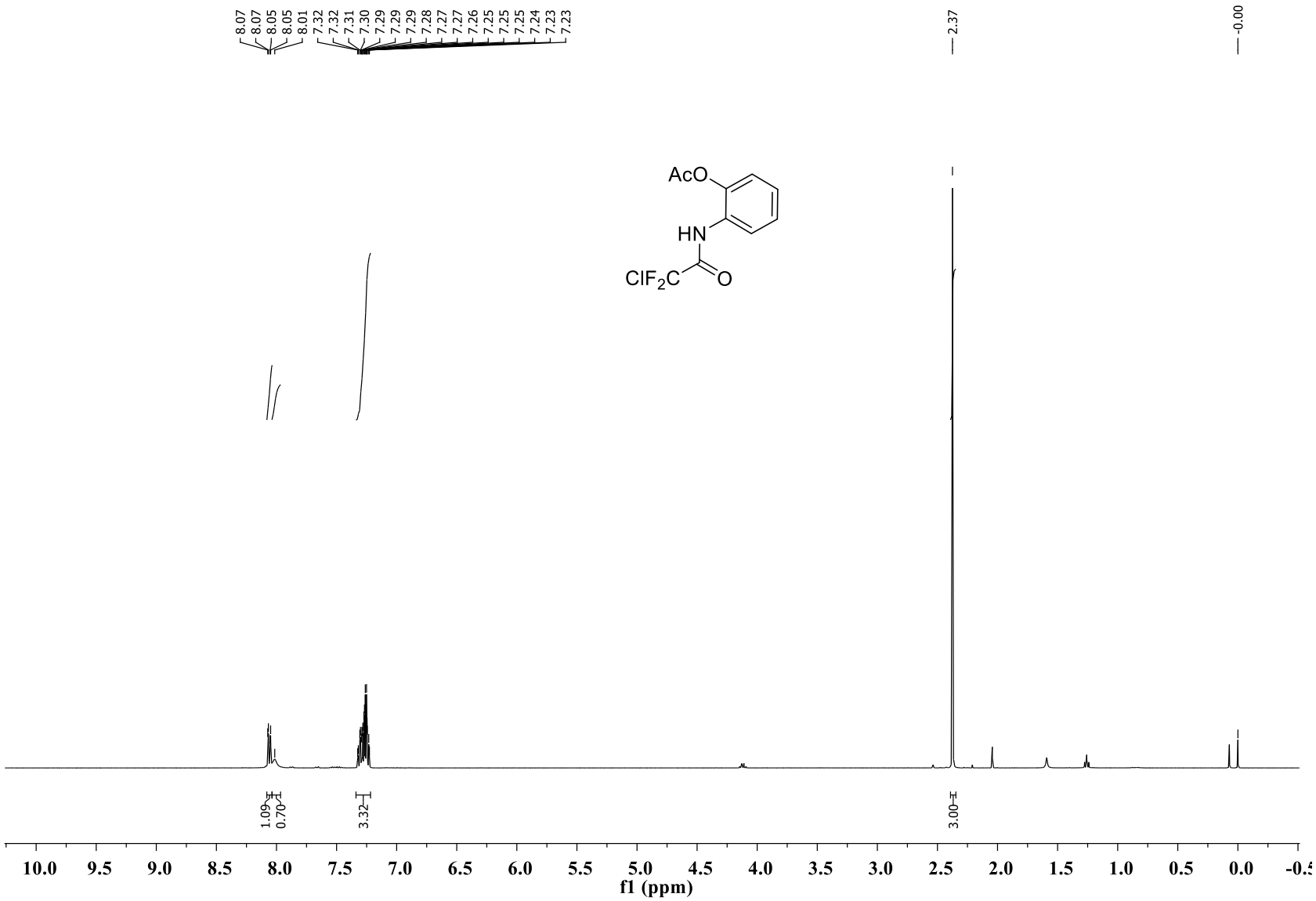
^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 400 MHz)**:**



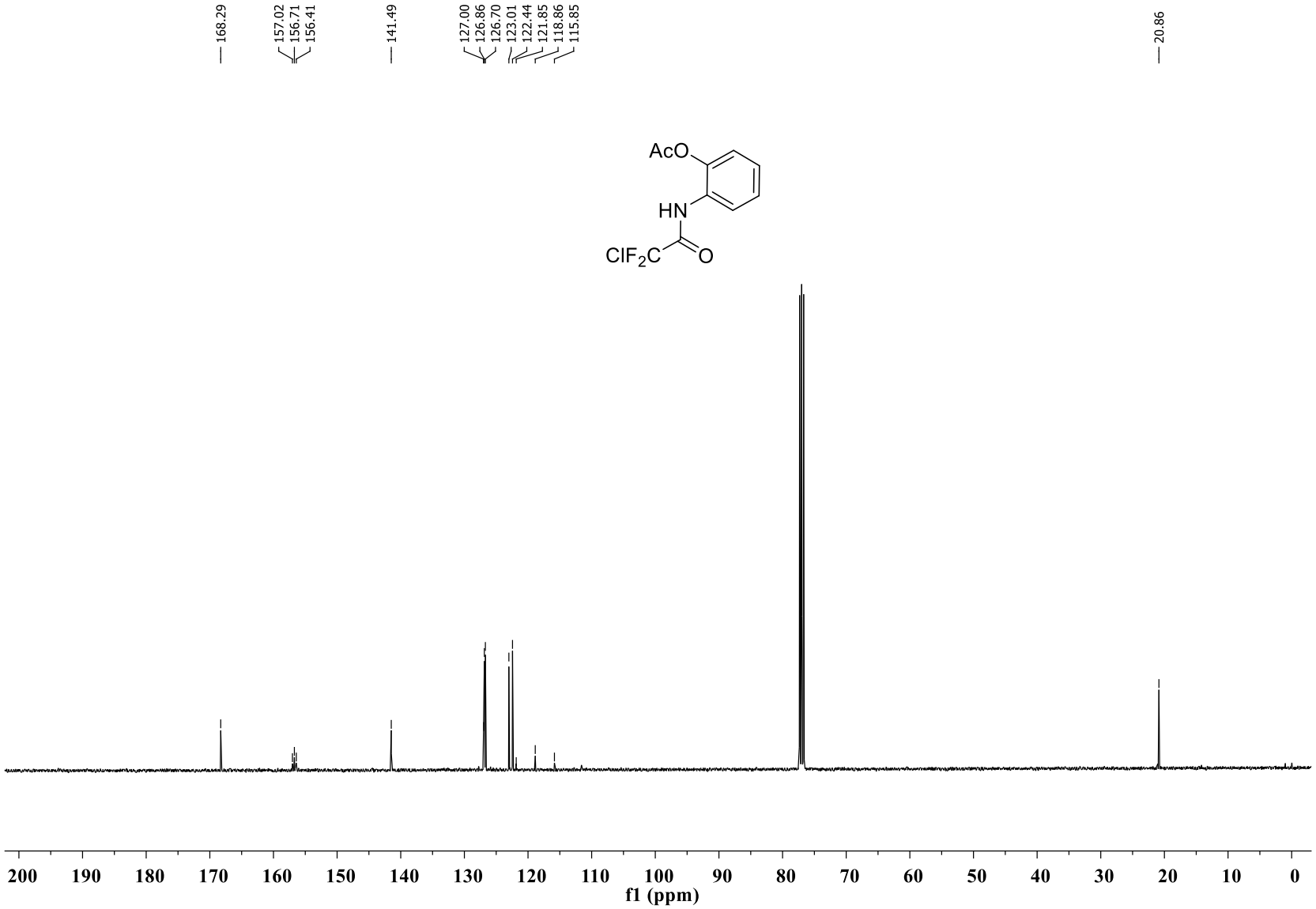
^{13}C NMR spectrum of compound **5a** ($CDCl_3$, 100 MHz)**:**



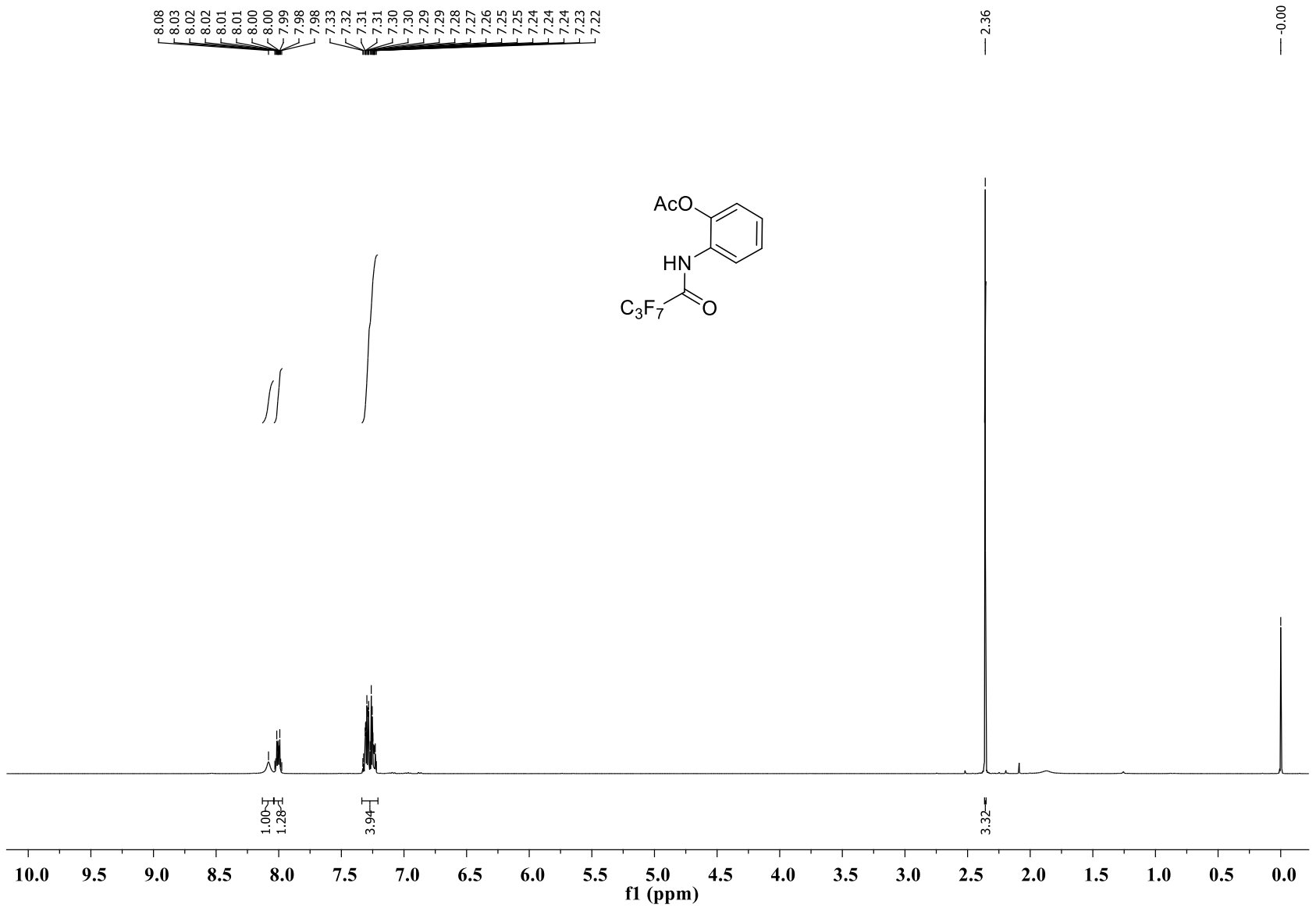
^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 400 MHz)**:**



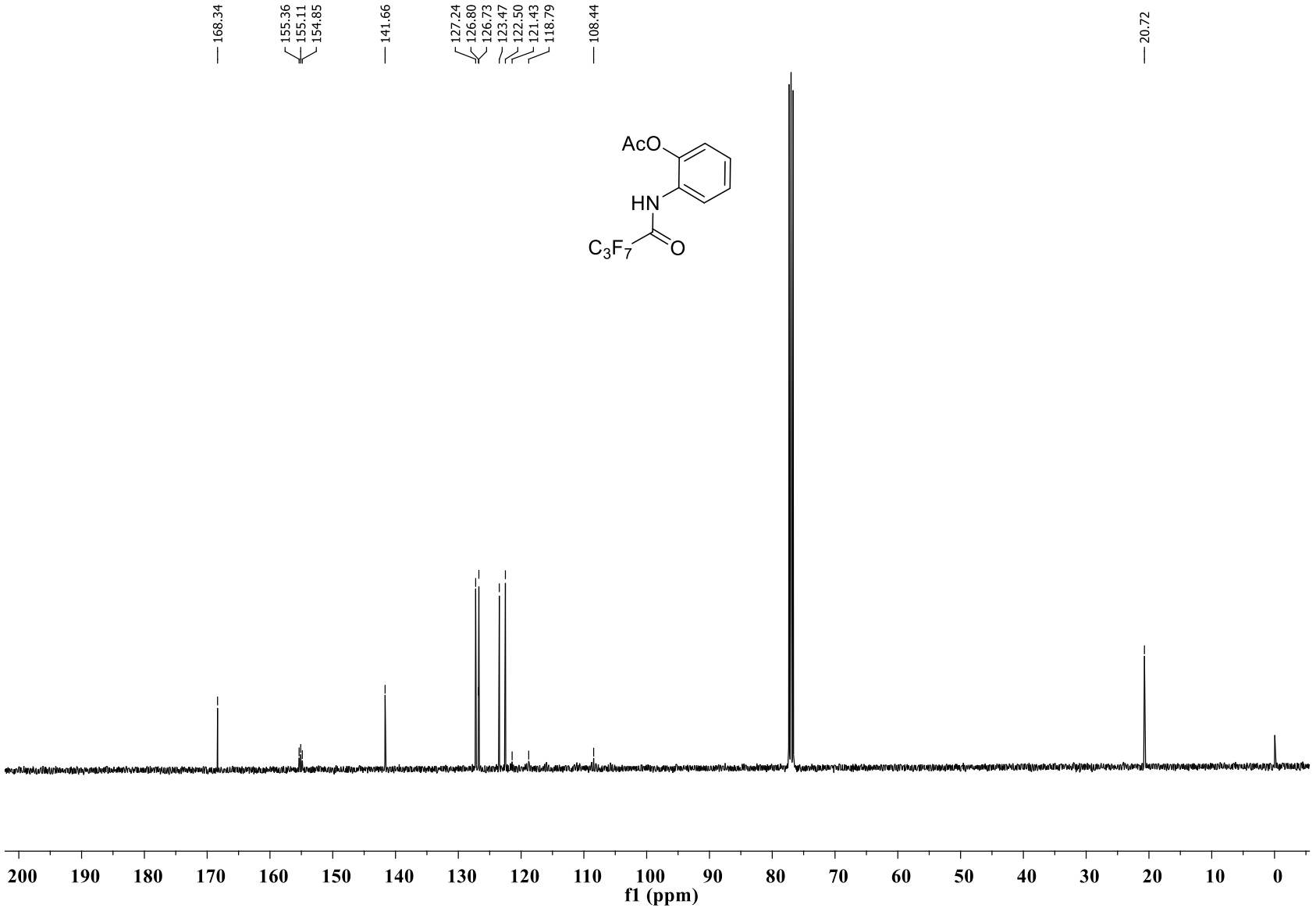
^{13}C NMR spectrum of compound **5b** ($CDCl_3$, 100 MHz)**:**



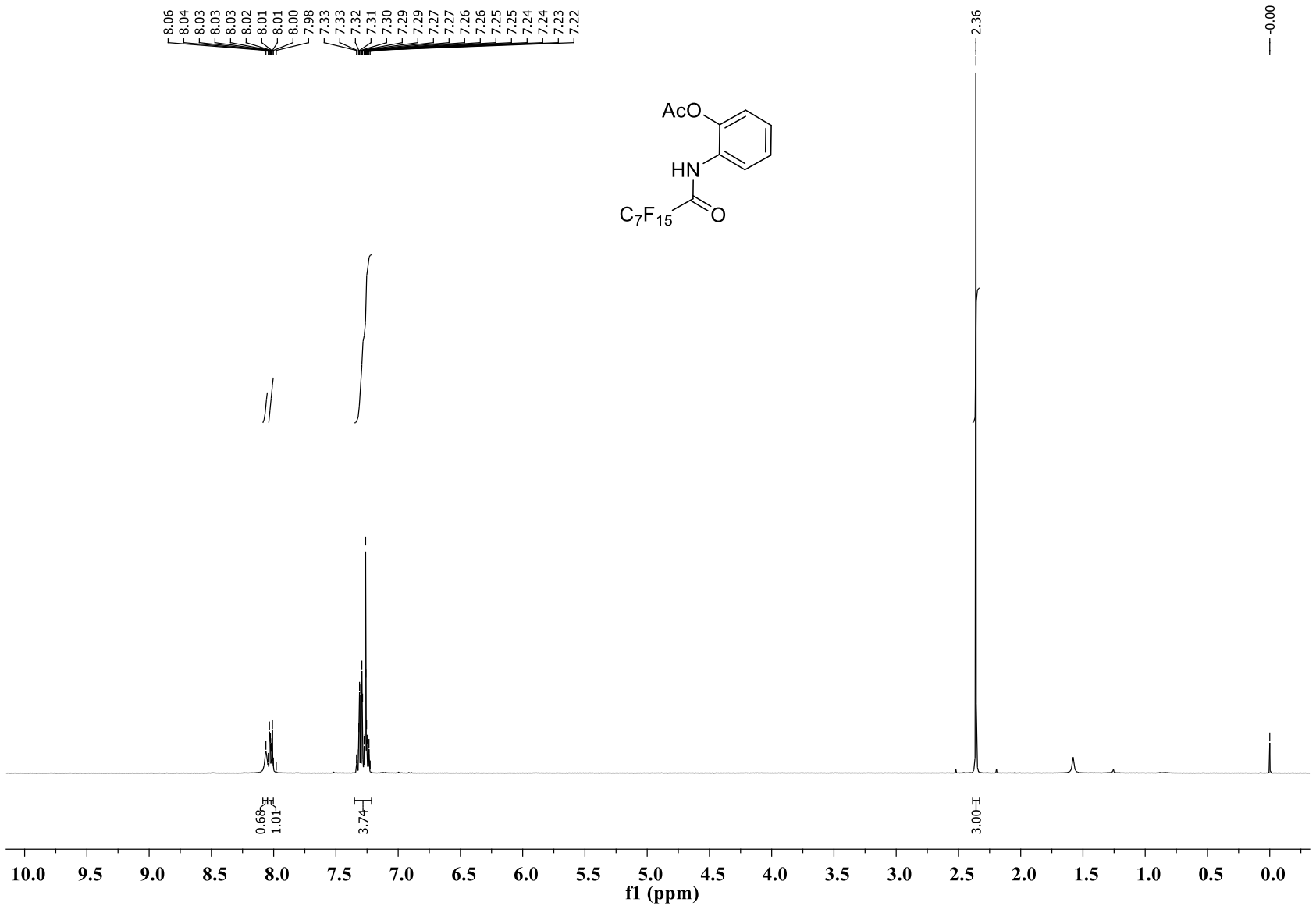
^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 400 MHz)**:**



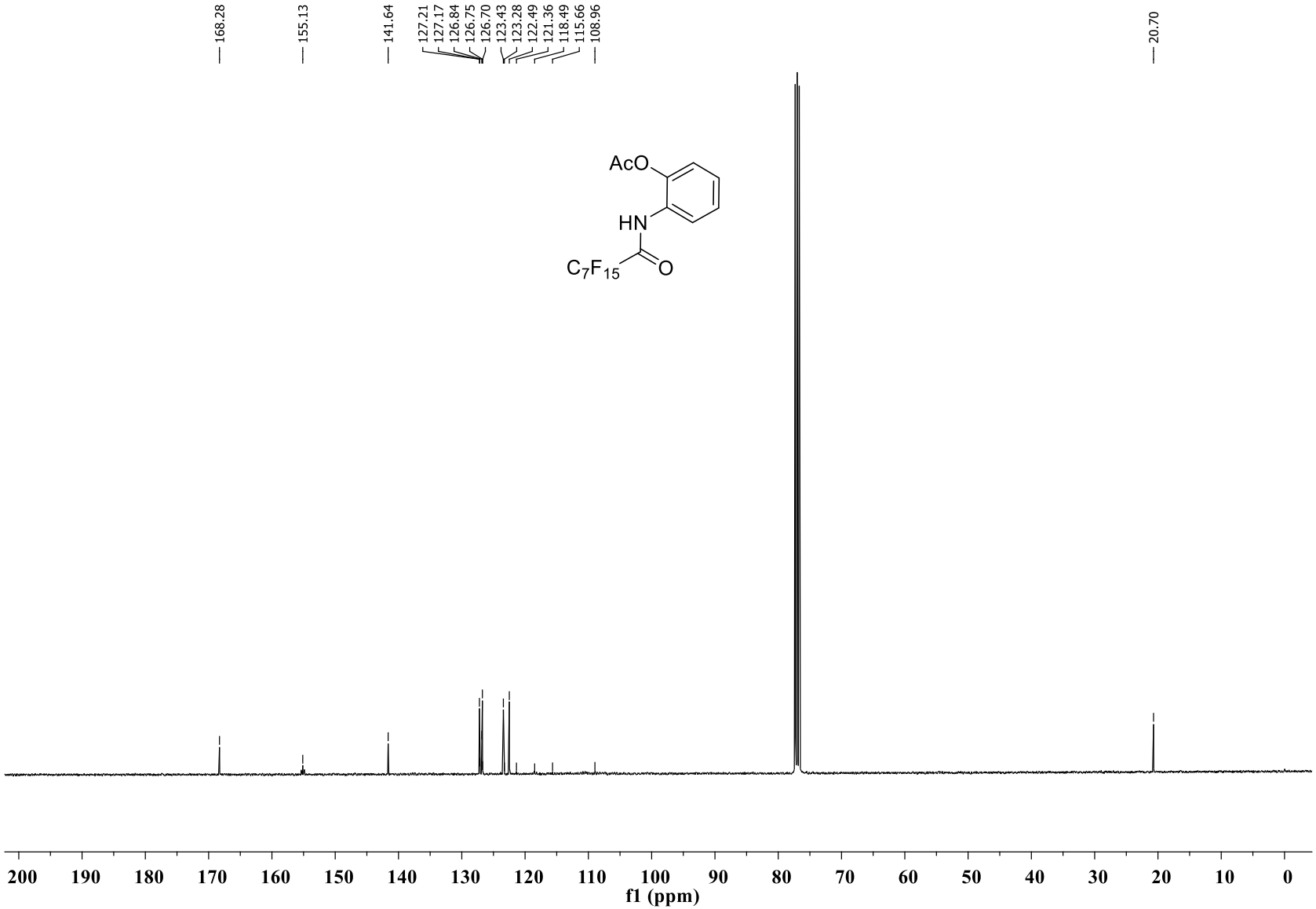
^{13}C NMR spectrum of compound **5c** ($CDCl_3$, 100 MHz)**:**



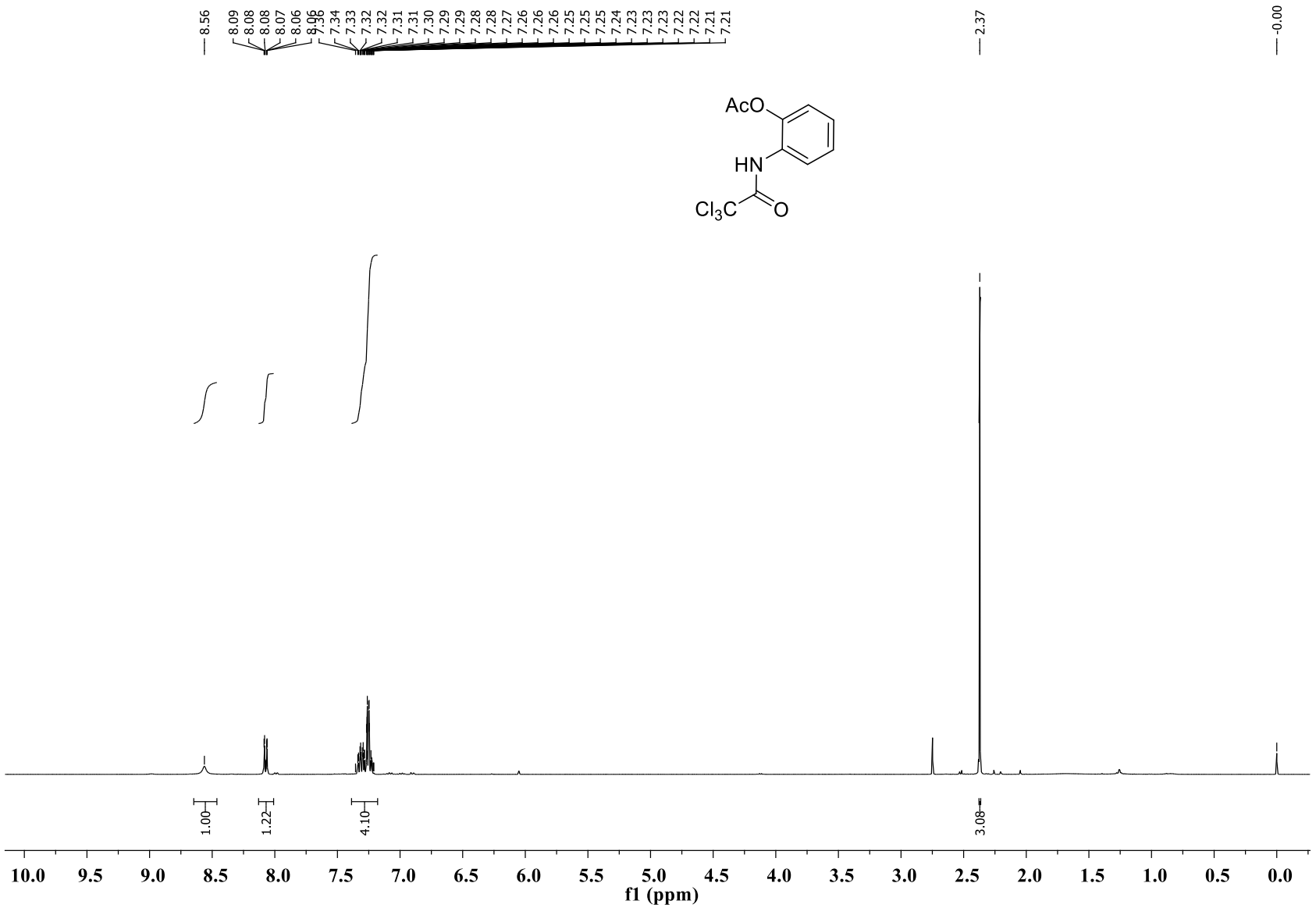
^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 400 MHz)**:**



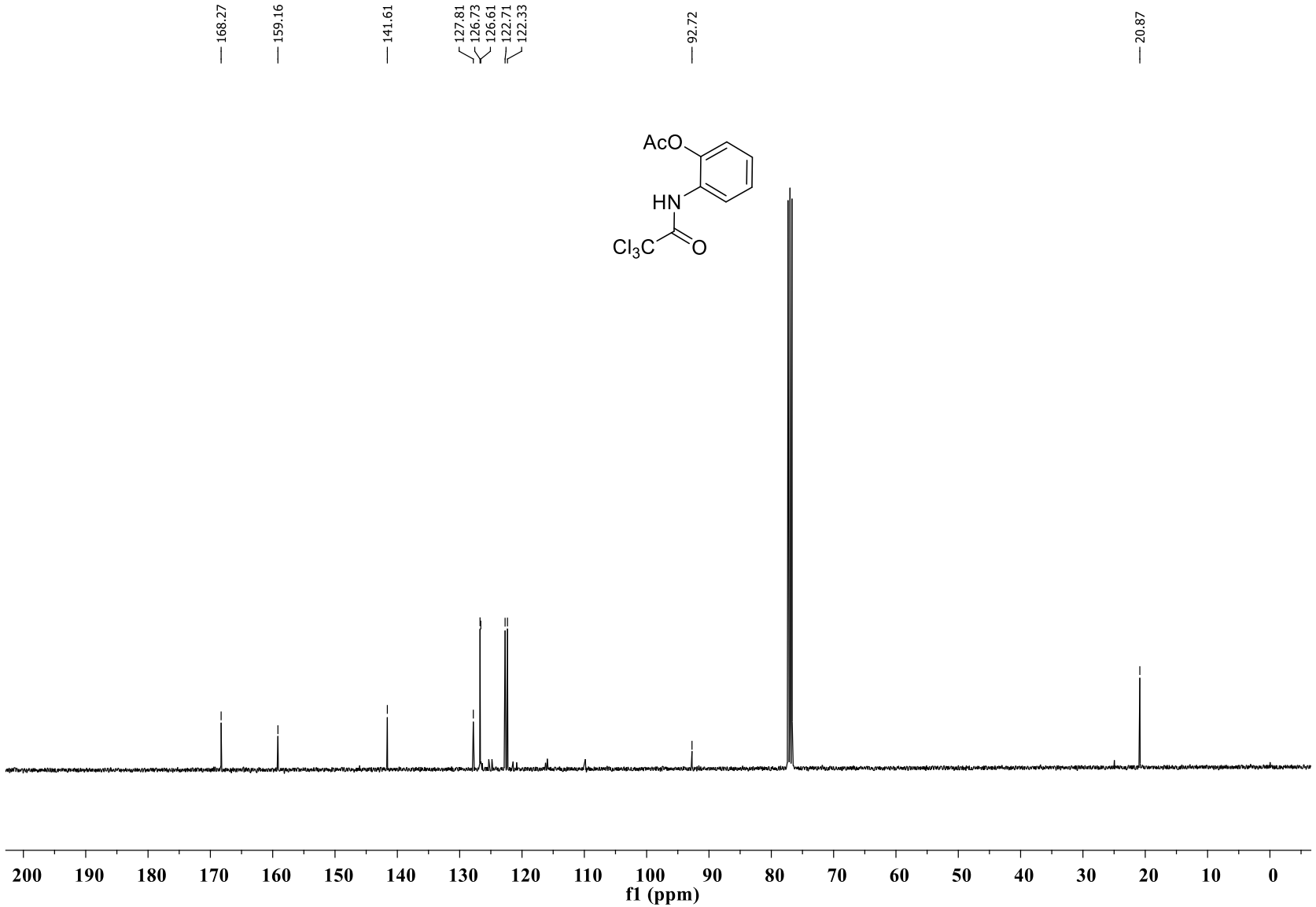
^{13}C NMR spectrum of compound **5d** ($CDCl_3$, 100 MHz)**:**



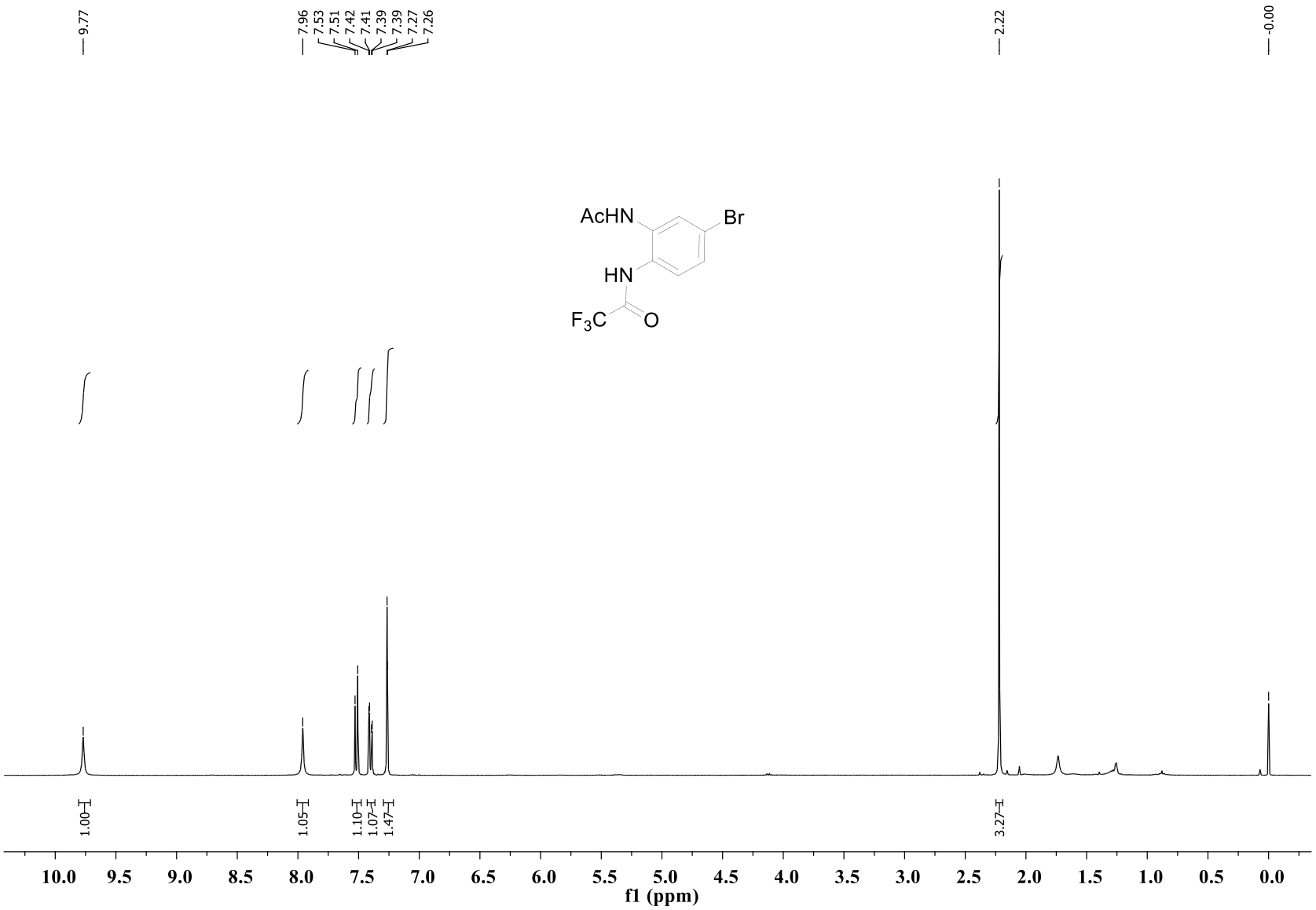
^{1}H NMR spectrum of compound **5e** ($CDCl_3$, 400 MHz)**:**



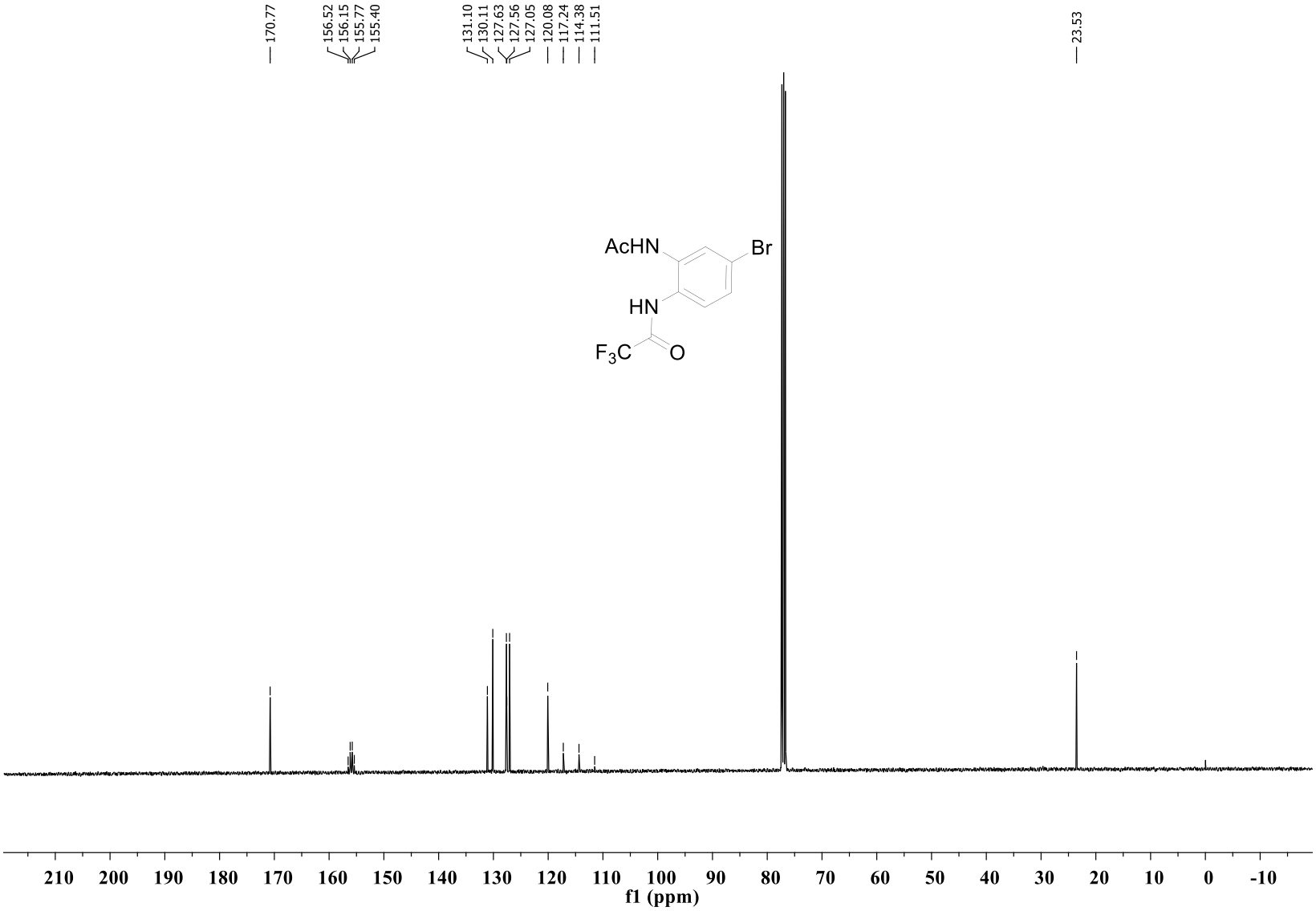
^{13}C NMR spectrum of compound **5e** ($CDCl_3$, 100 MHz)**:**



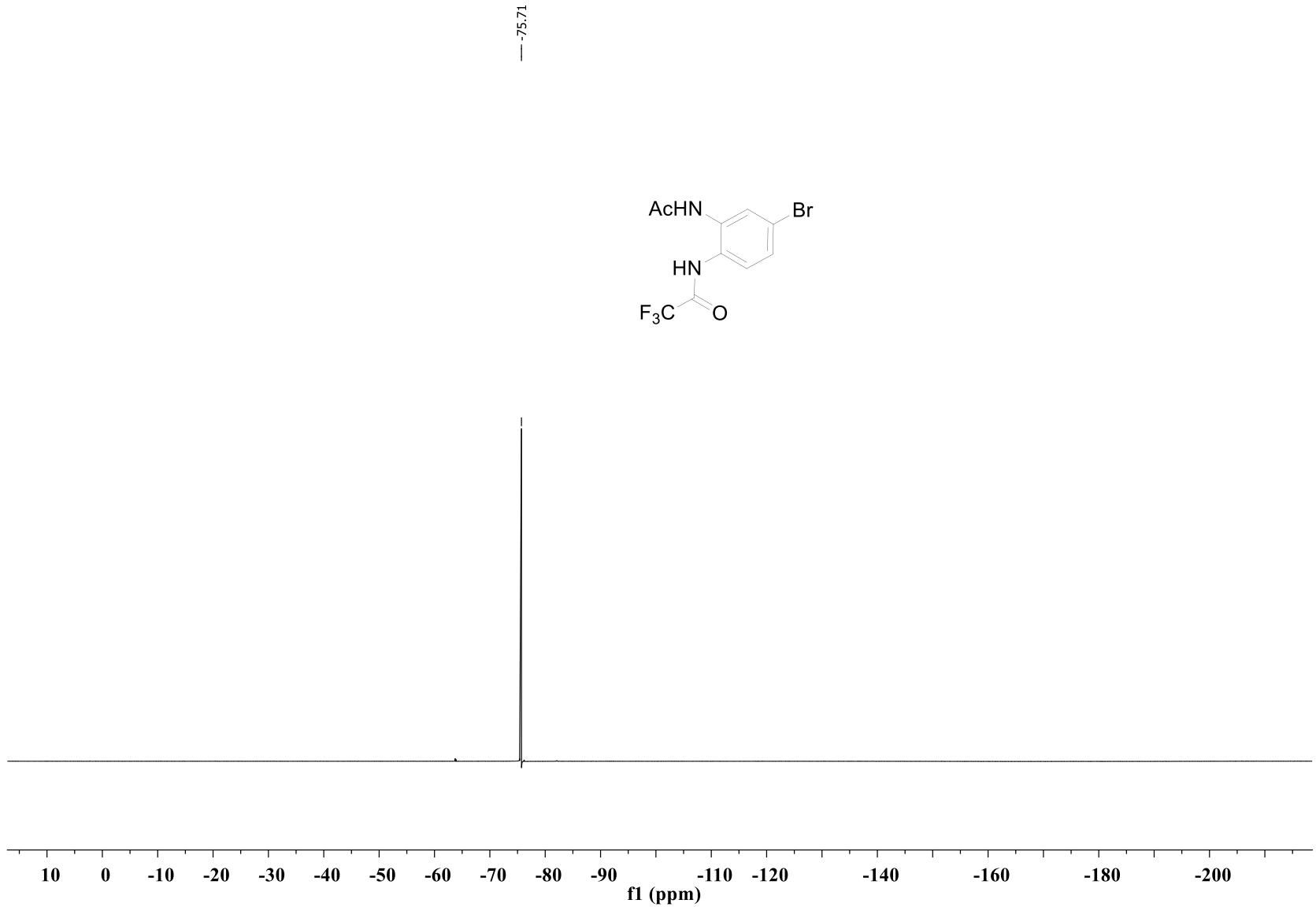
^{1}H NMR spectrum of compound **2a,** ($CDCl_3$, 400 MHz)**:**



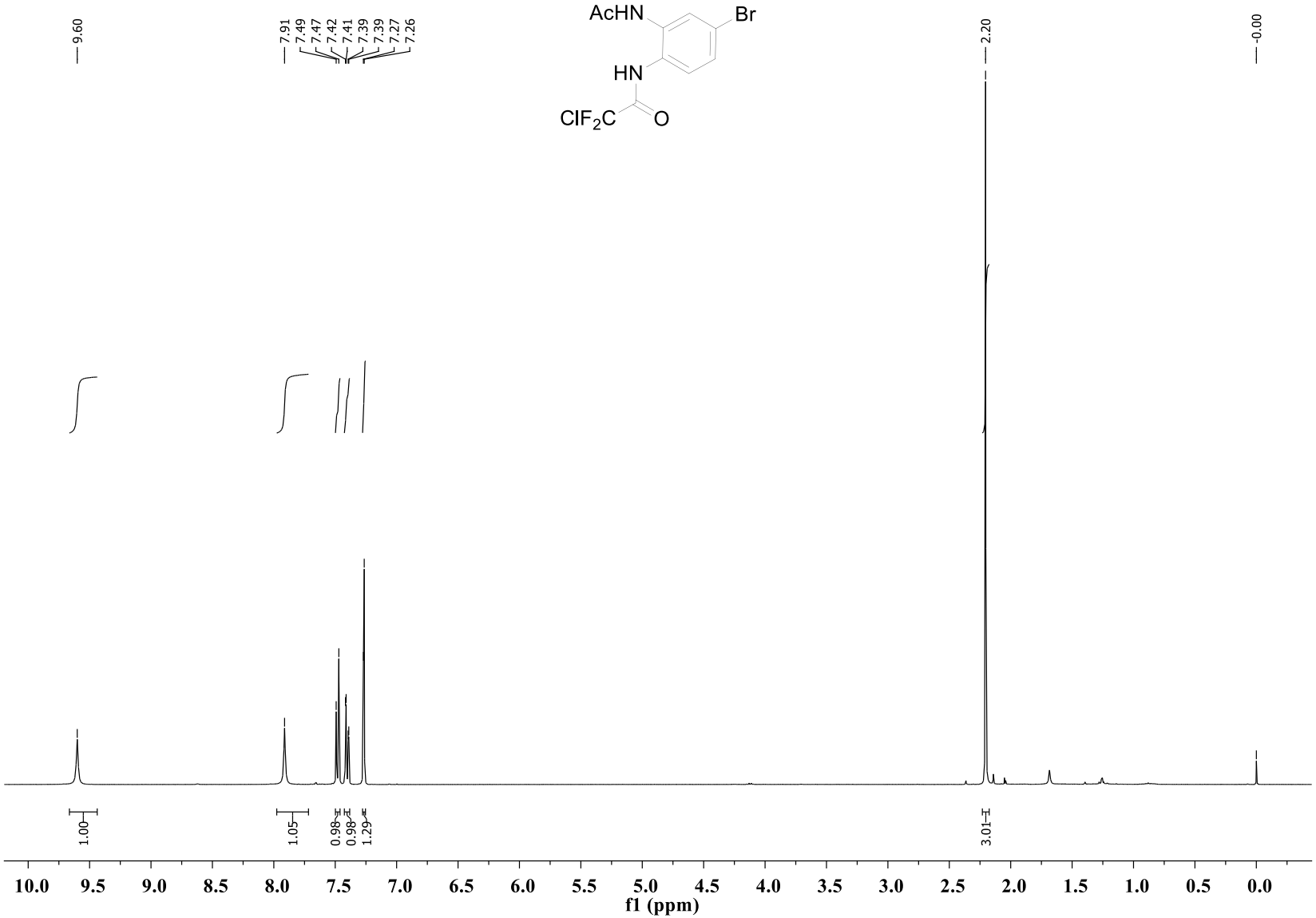
^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 100 MHz)**:**



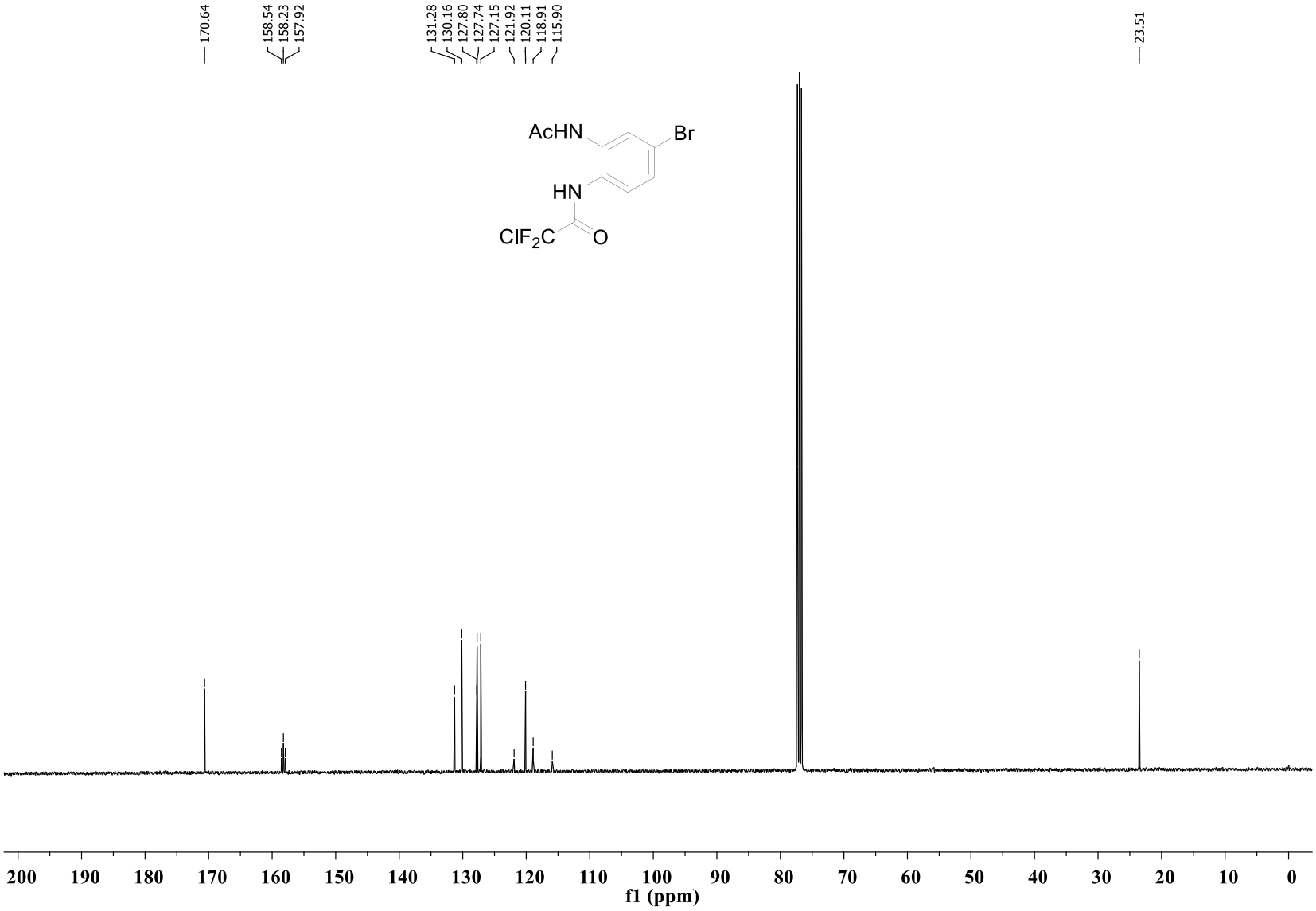
^{19}F NMR spectrum of compound **2a** ($CDCl_3$, 376 MHz)**:**



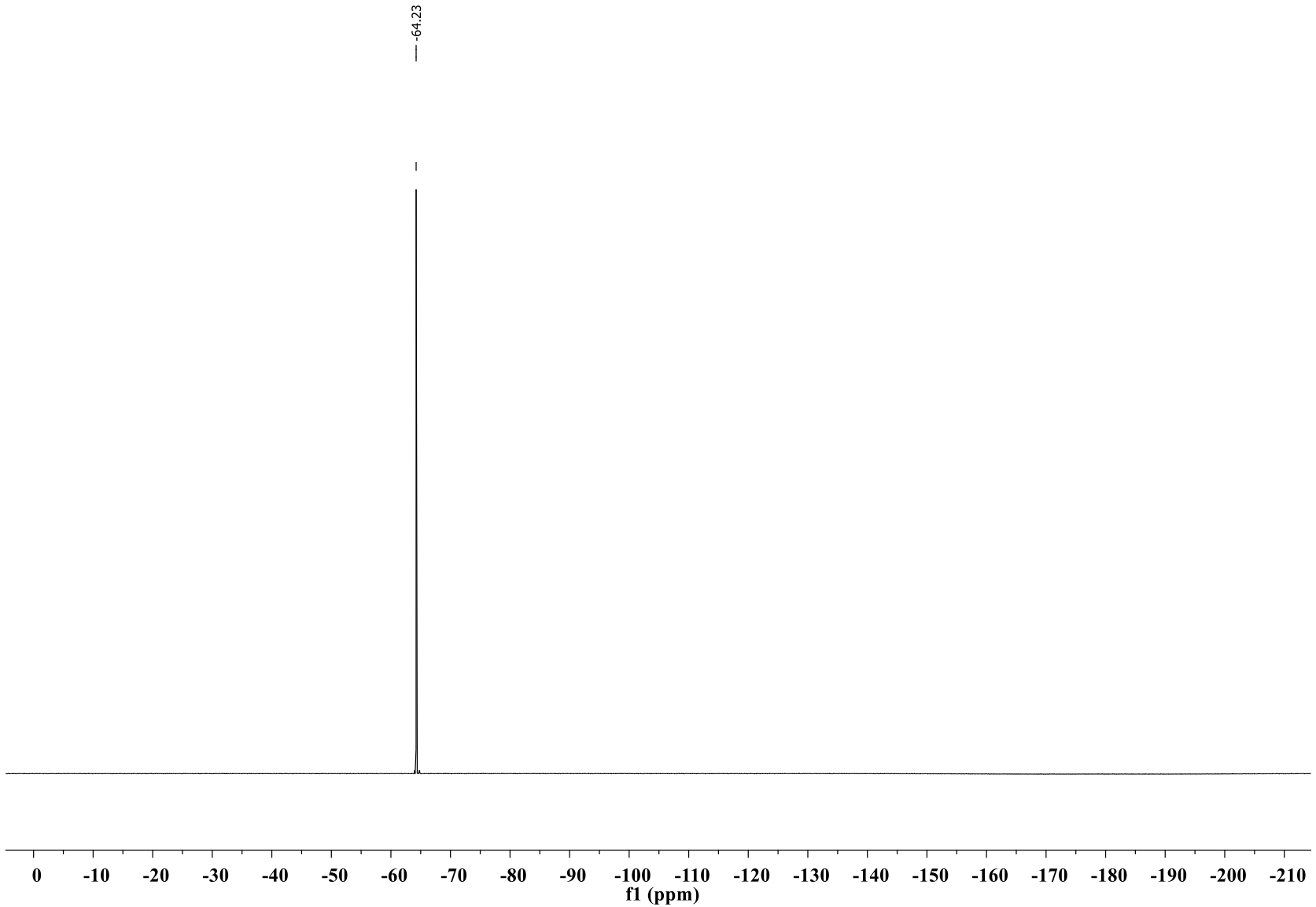
^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400 MHz)**:**



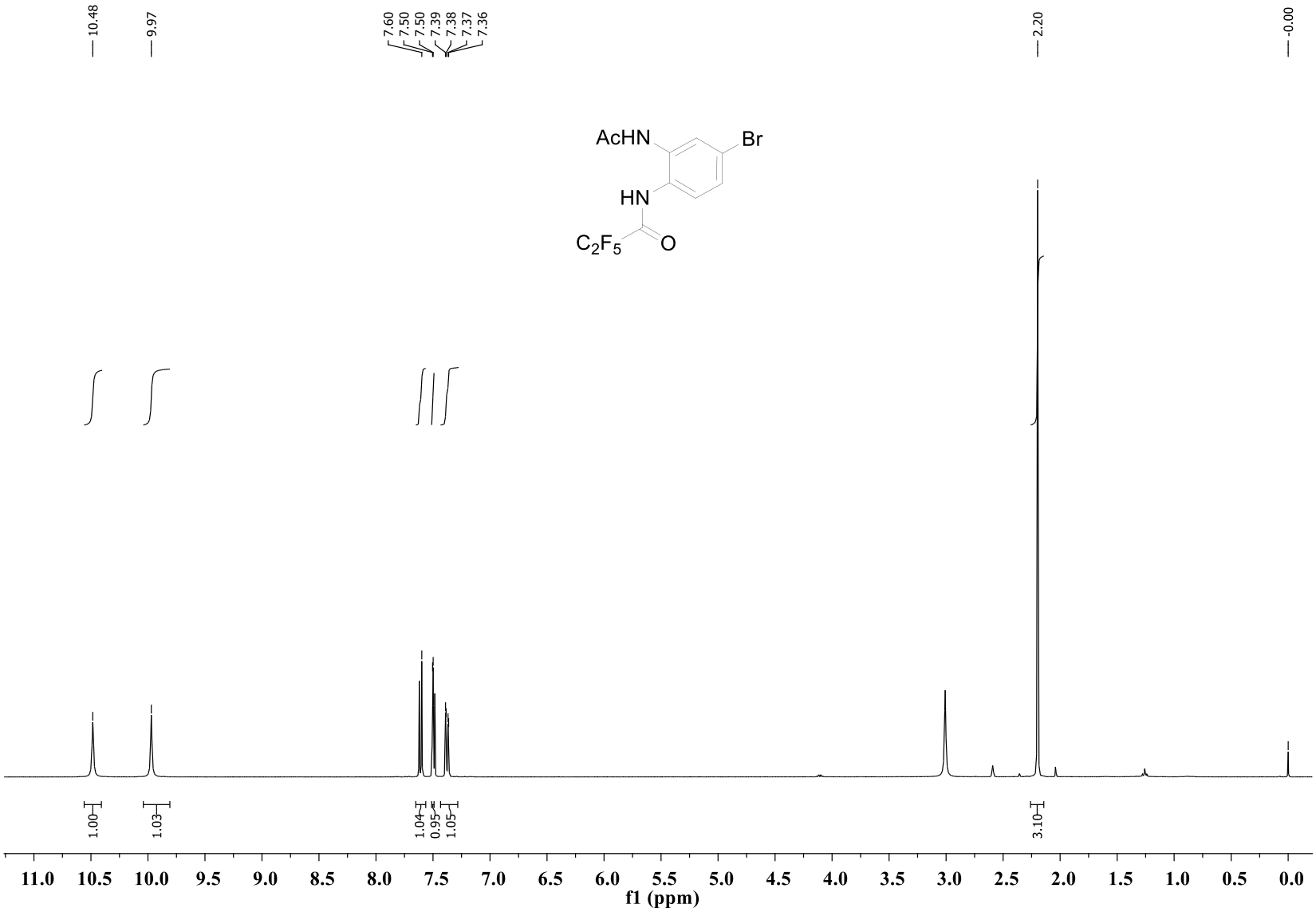
^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 100 MHz)**:**



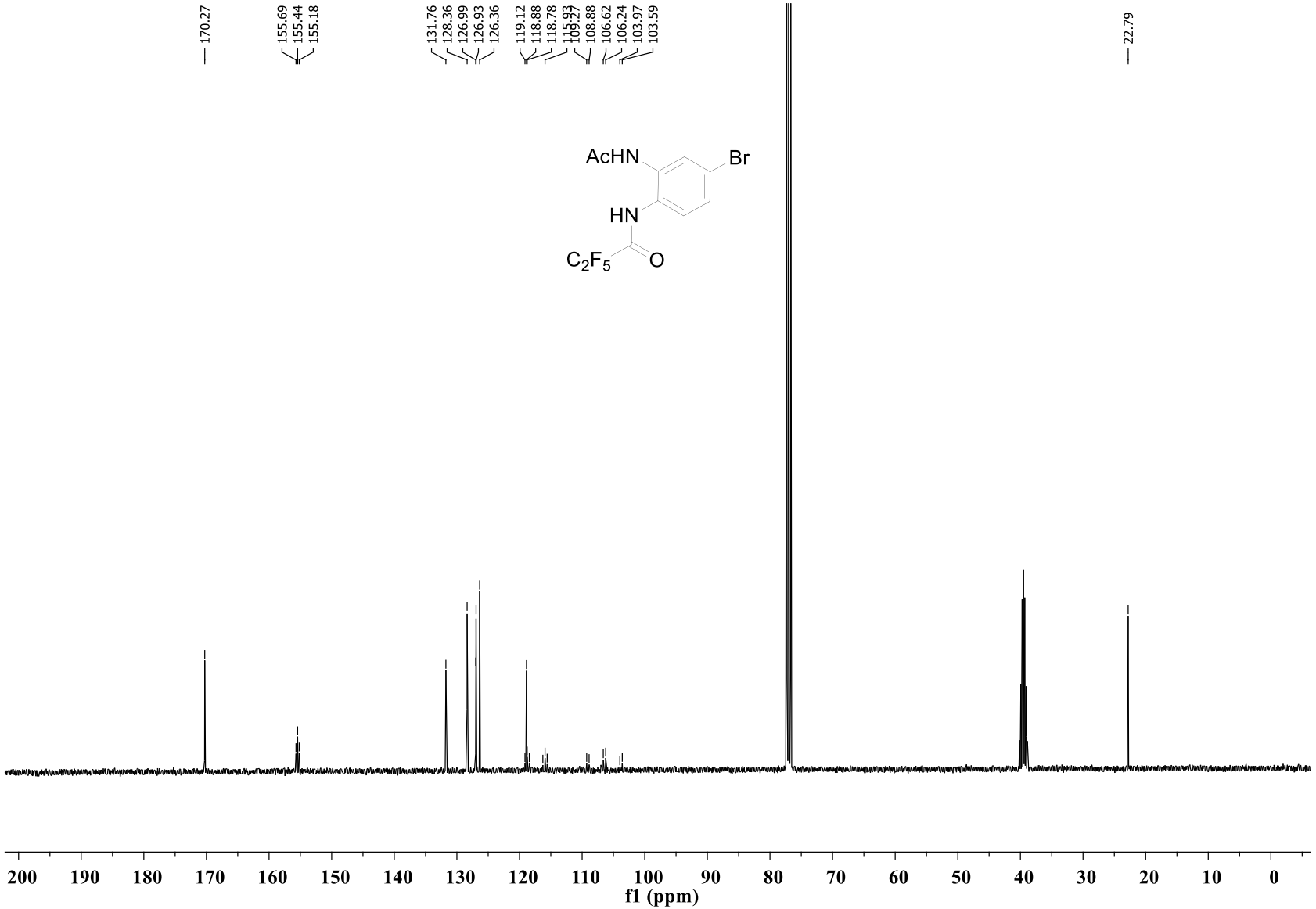
^{19}F NMR spectrum of compound **2b** ($CDCl_3$, 376 MHz)**:**



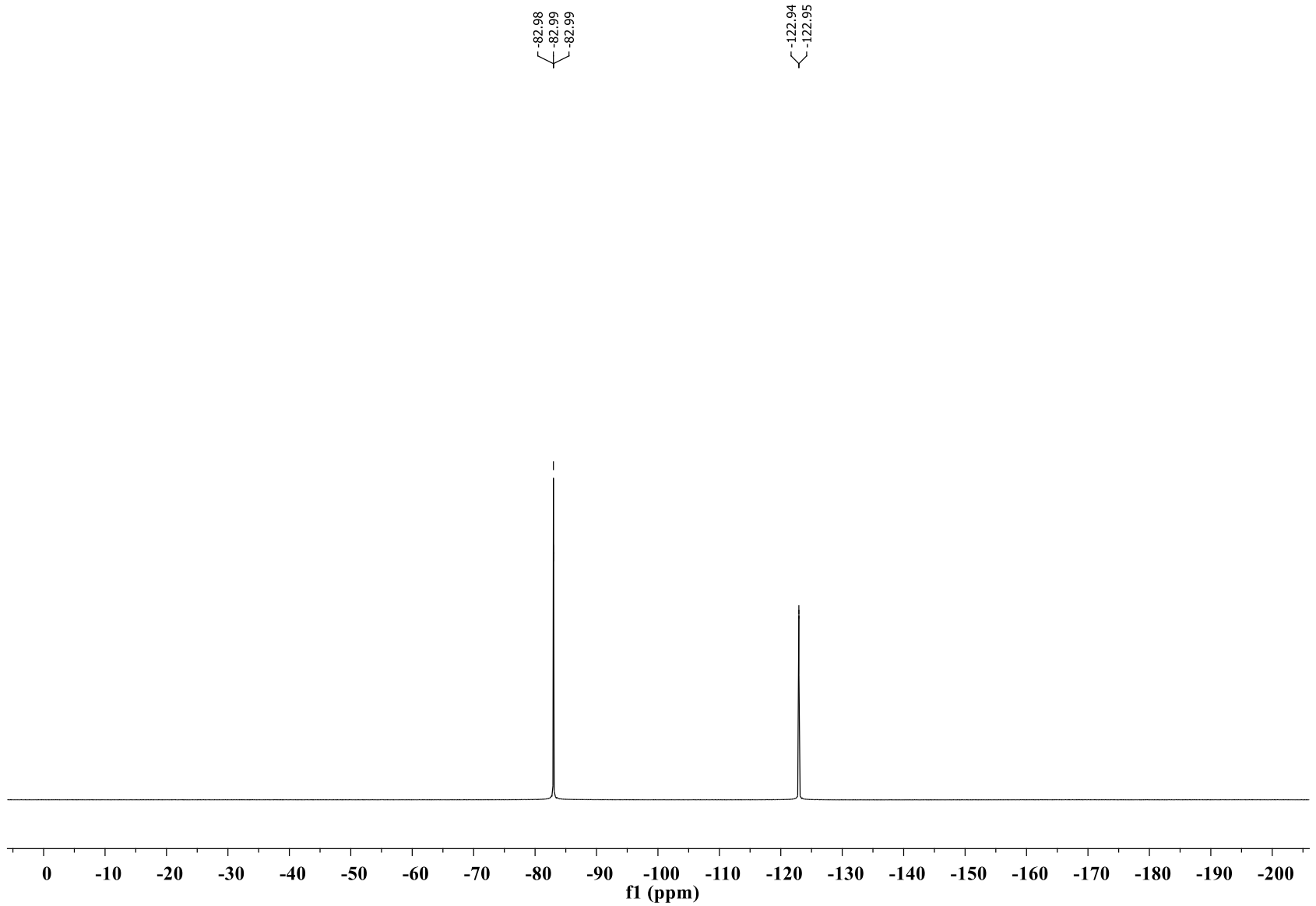
^{1}H NMR spectrum of compound **2c** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



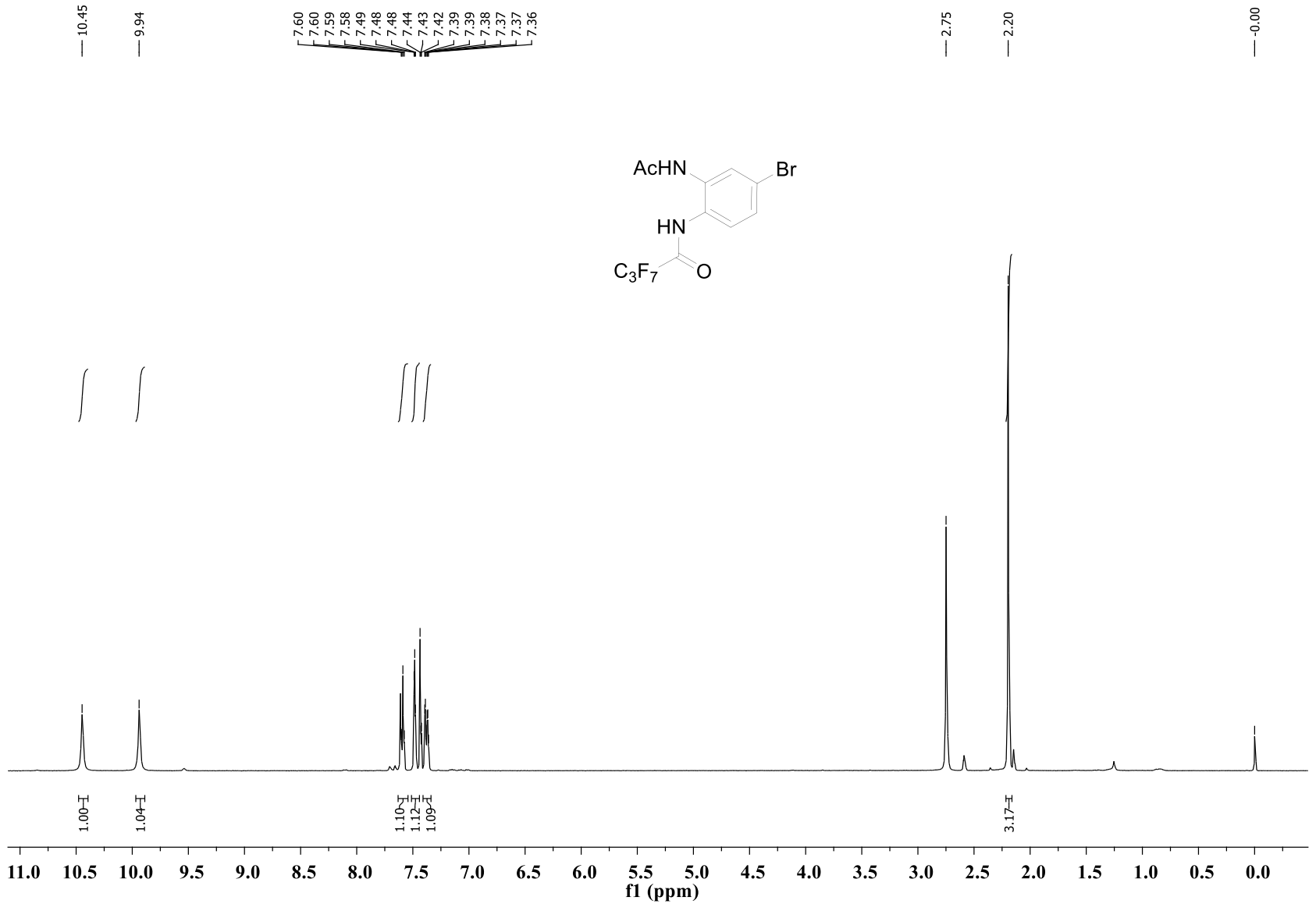
^{13}C NMR spectrum of compound **2c** (8:2, $CDCl_3$ + DMSO-*d6*, 100 MHz)**:**



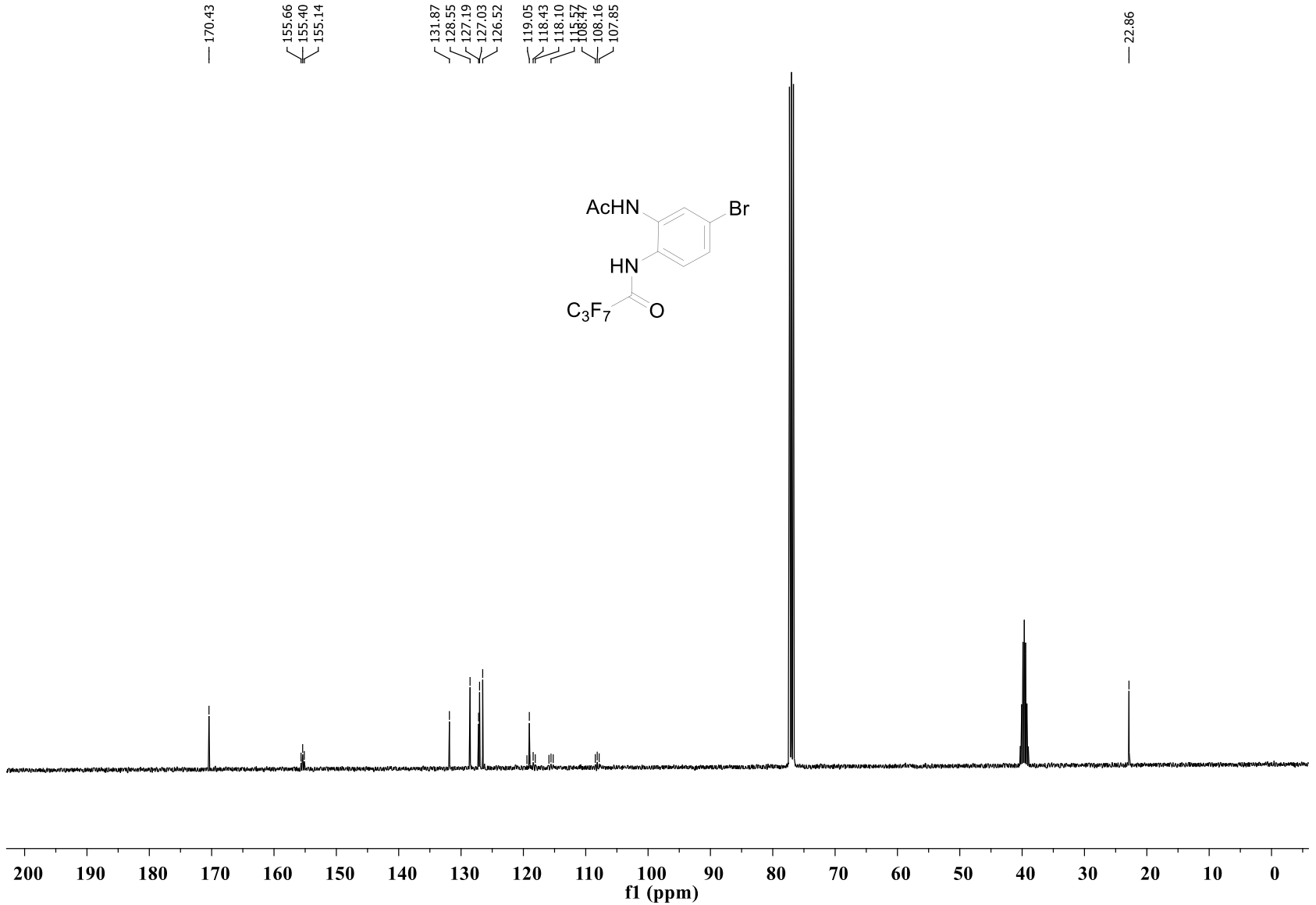
^{19}F NMR spectrum of compound **2c** (8:2, $CDCl_3$ + DMSO-*d6*, 376 MHz)**:**



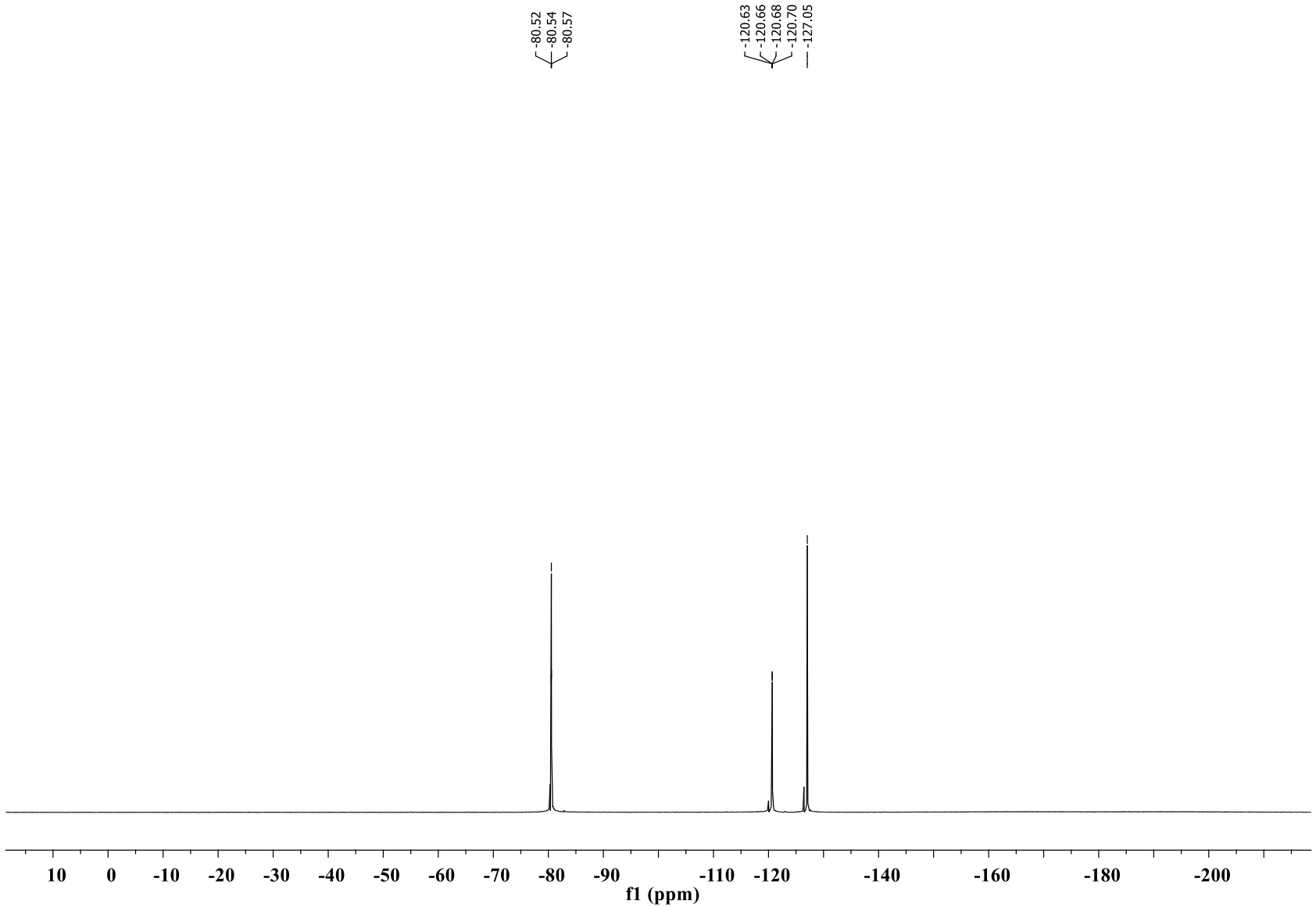
[1]H NMR spectrum of compound **2d** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



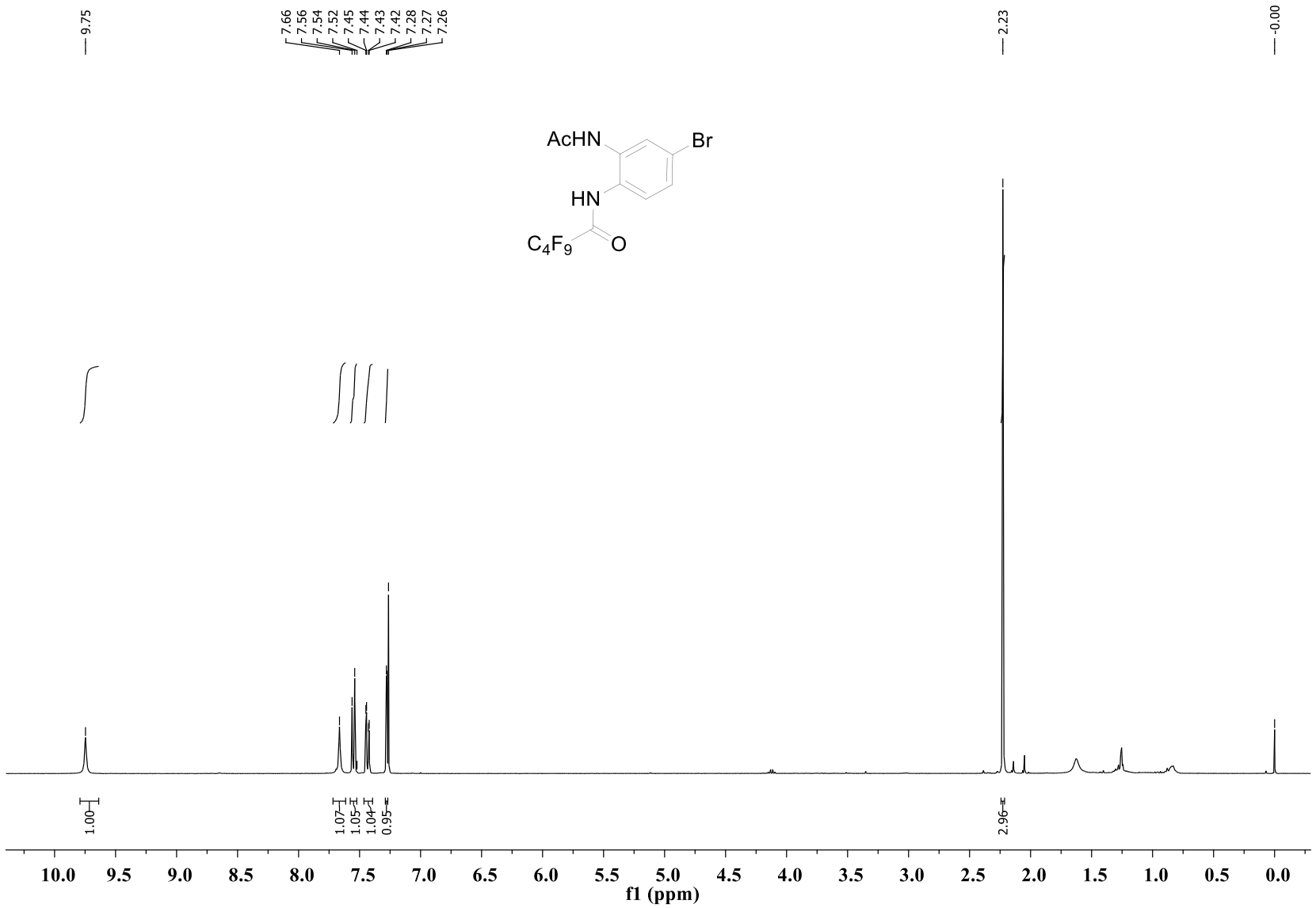
^{13}C NMR spectrum of compound **2d** (8:2, $CDCl_3$ + DMSO-*d6*, 100 MHz)**:**



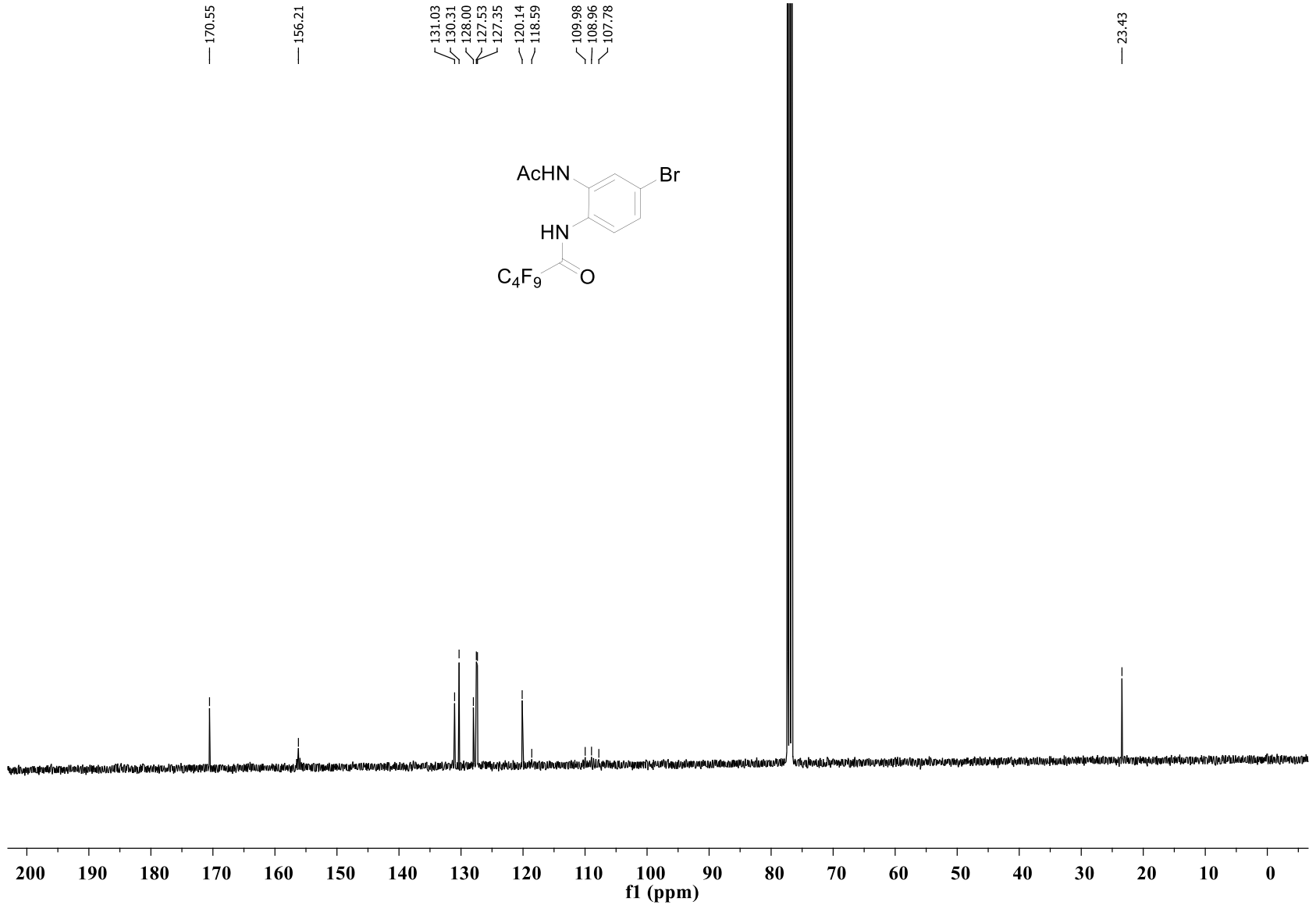
^{19}F NMR spectrum of compound **2d** (8:2, $CDCl_3$ + DMSO-*d6*, 376 MHz)**:**



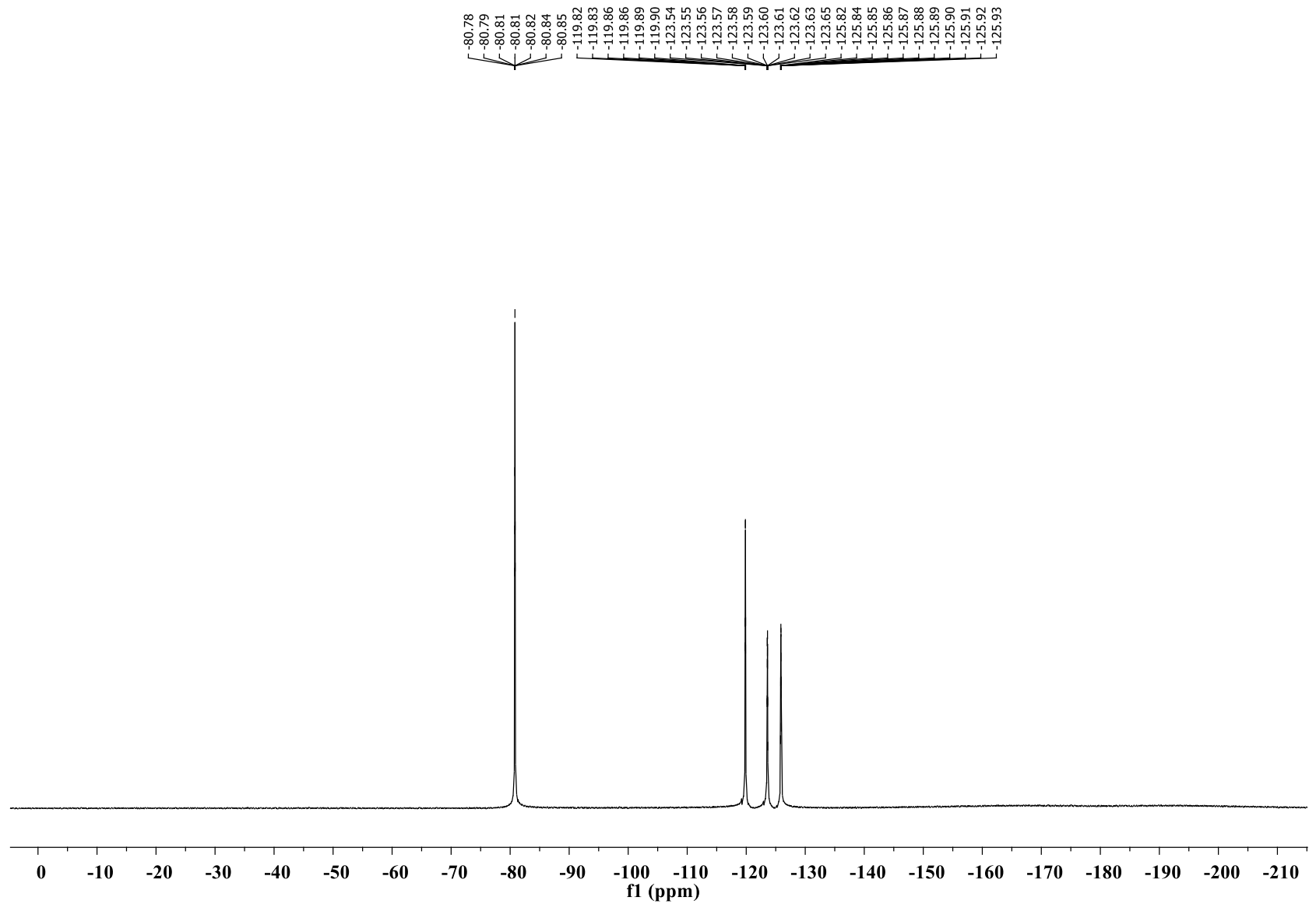
^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz)**:**



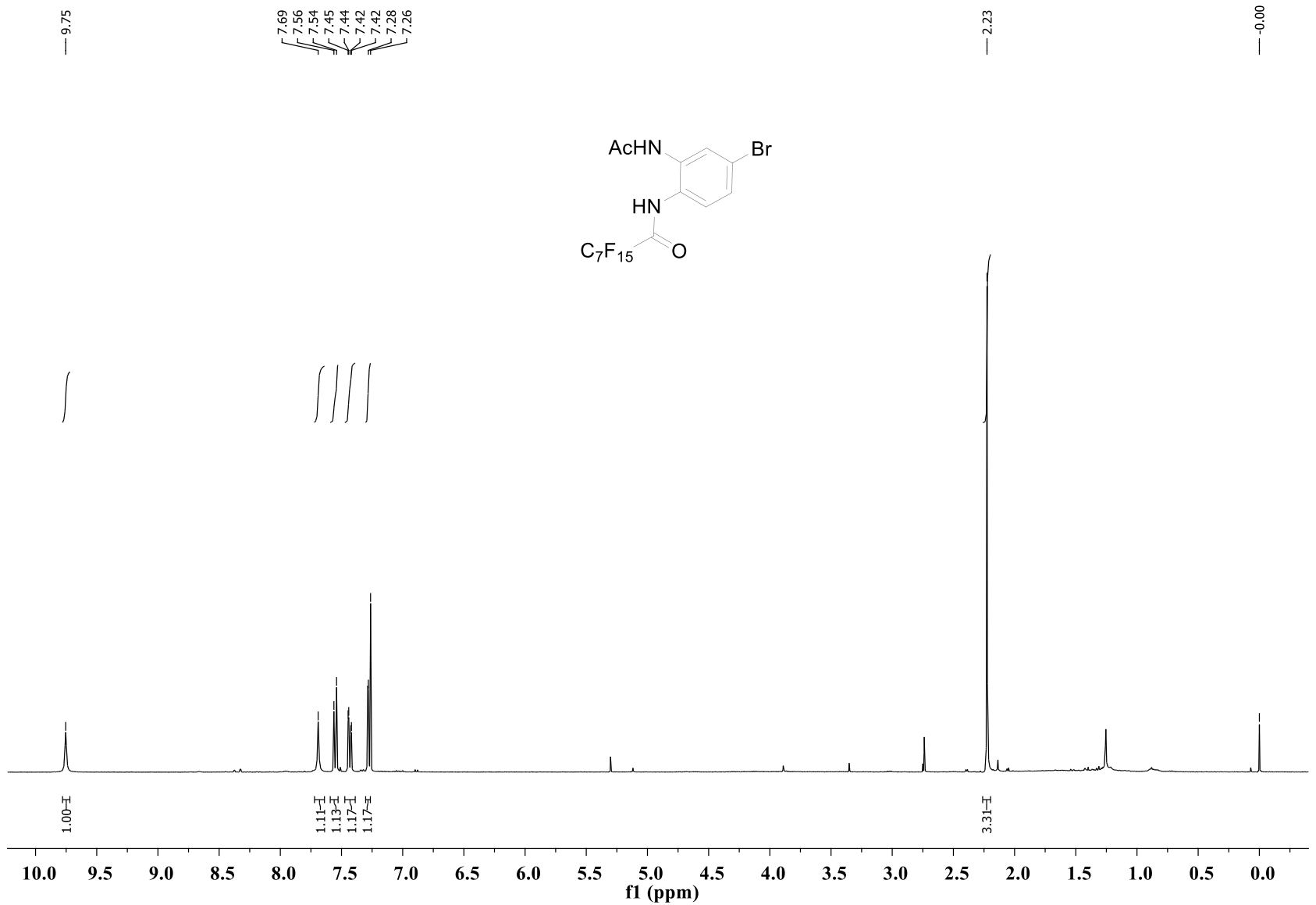
^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 100 MHz)**:**



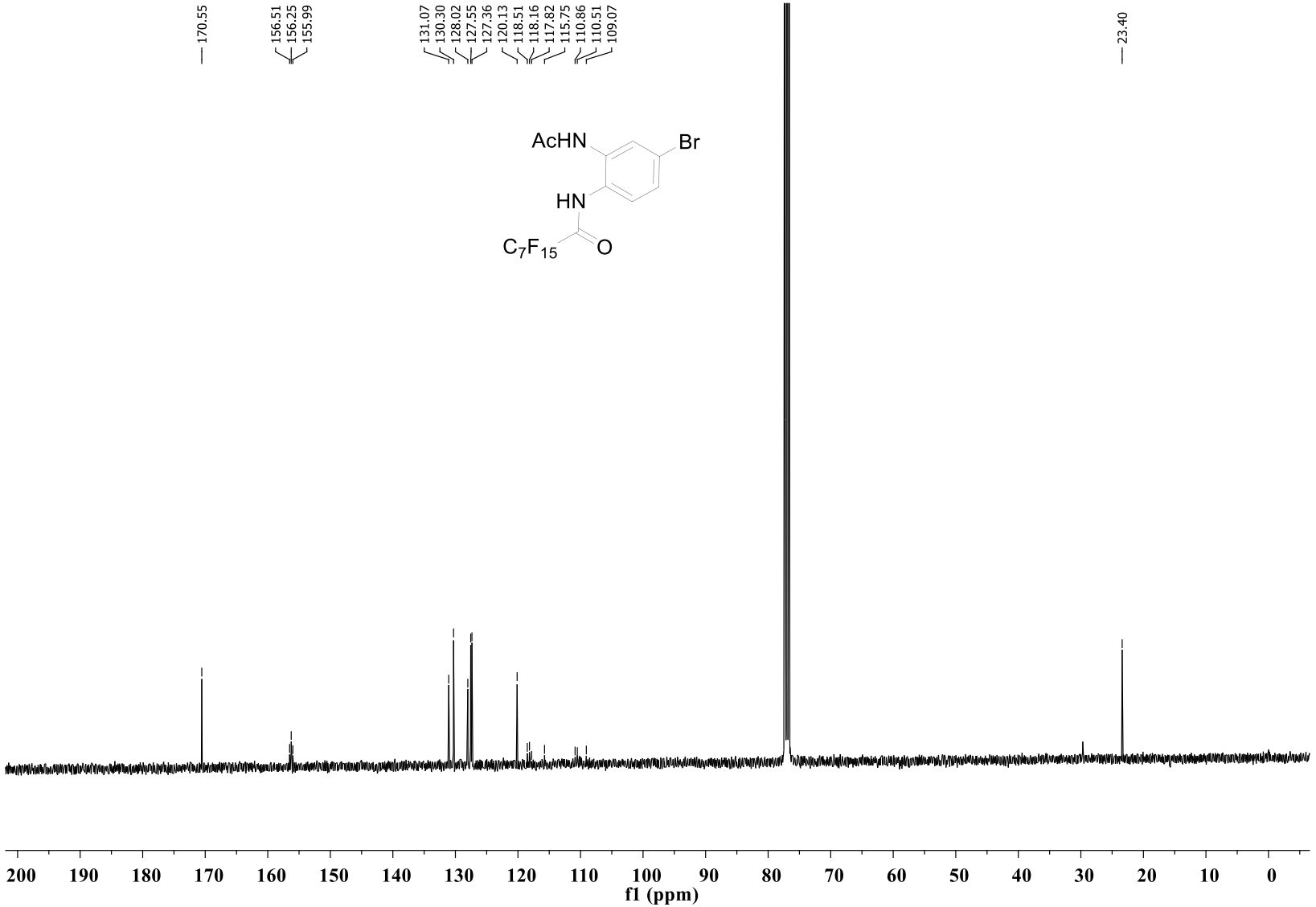
^{19}F NMR spectrum of compound **2e** ($CDCl_3$, 376 MHz)**:**



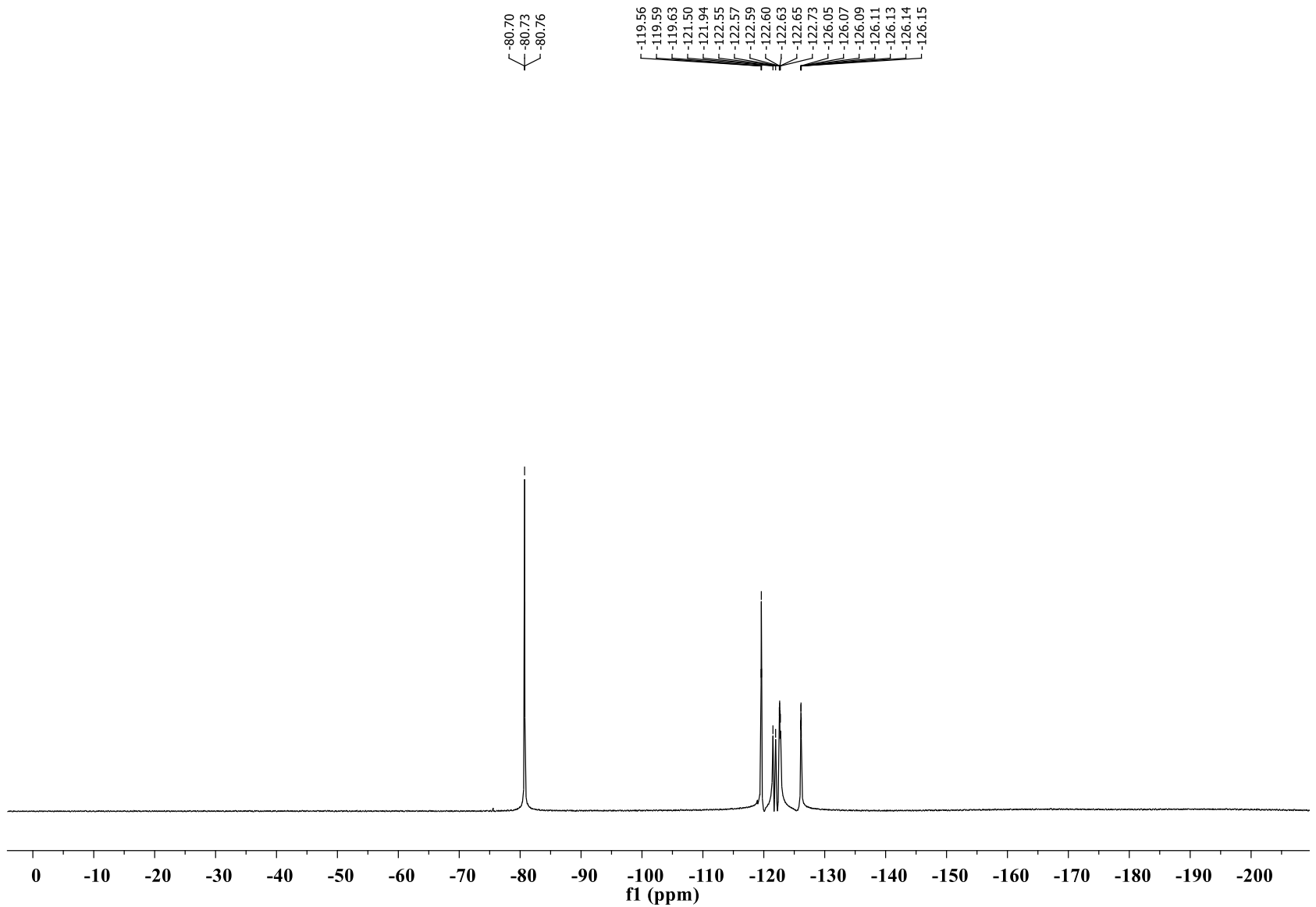
^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz)**:**



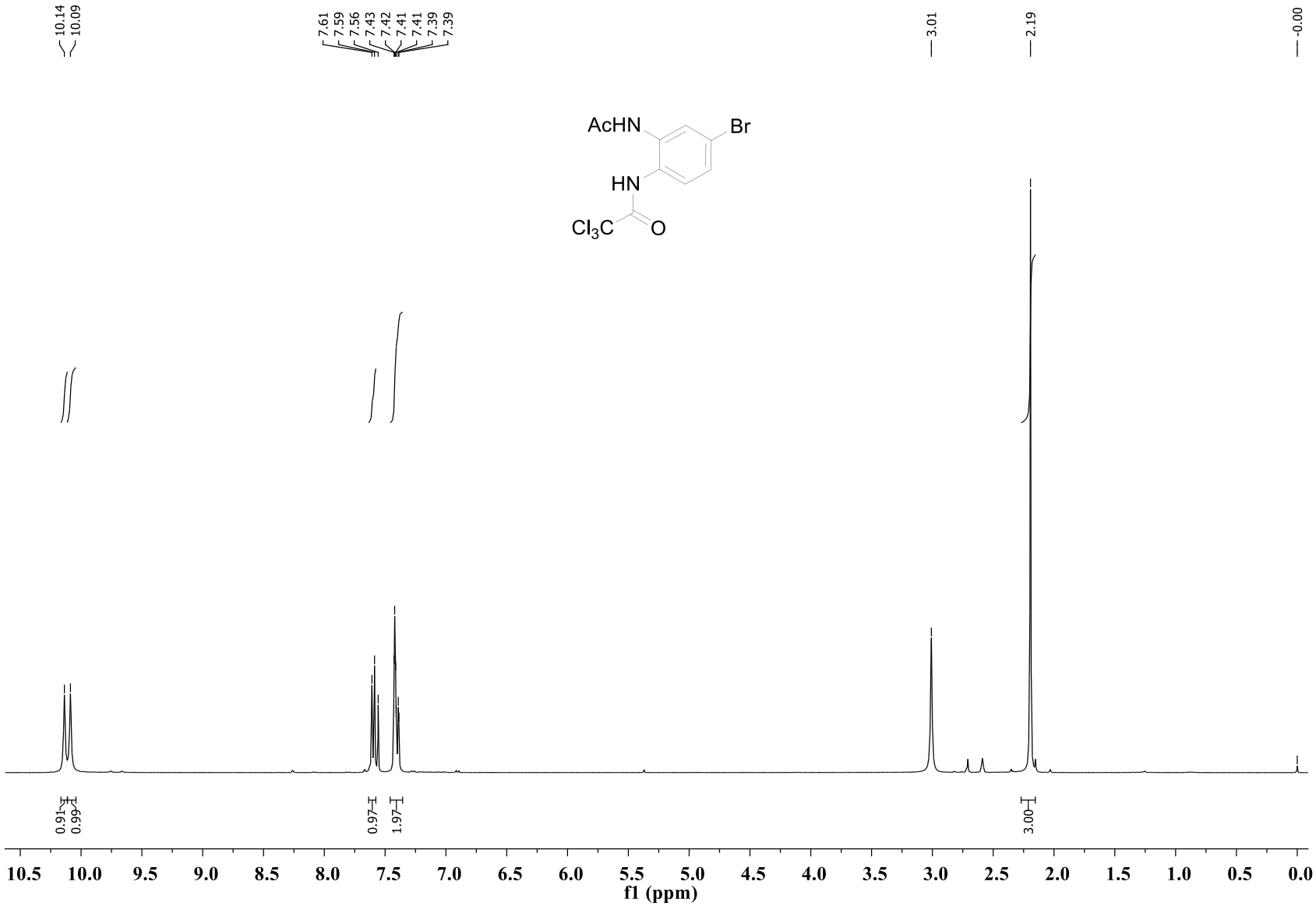
^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 100 MHz)**:**



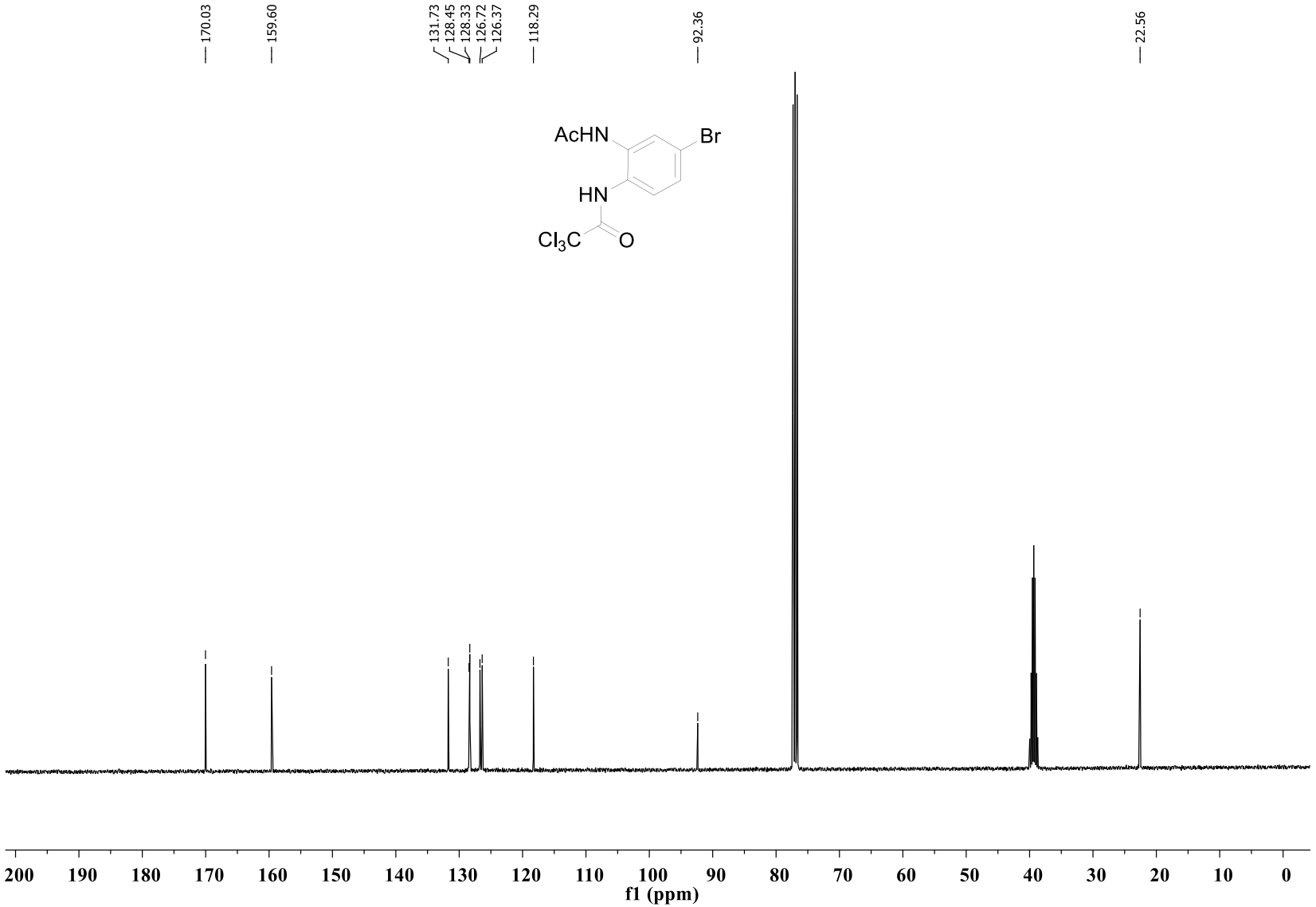
^{19}F NMR spectrum of compound **2f** ($CDCl_3$, 376 MHz)**:**



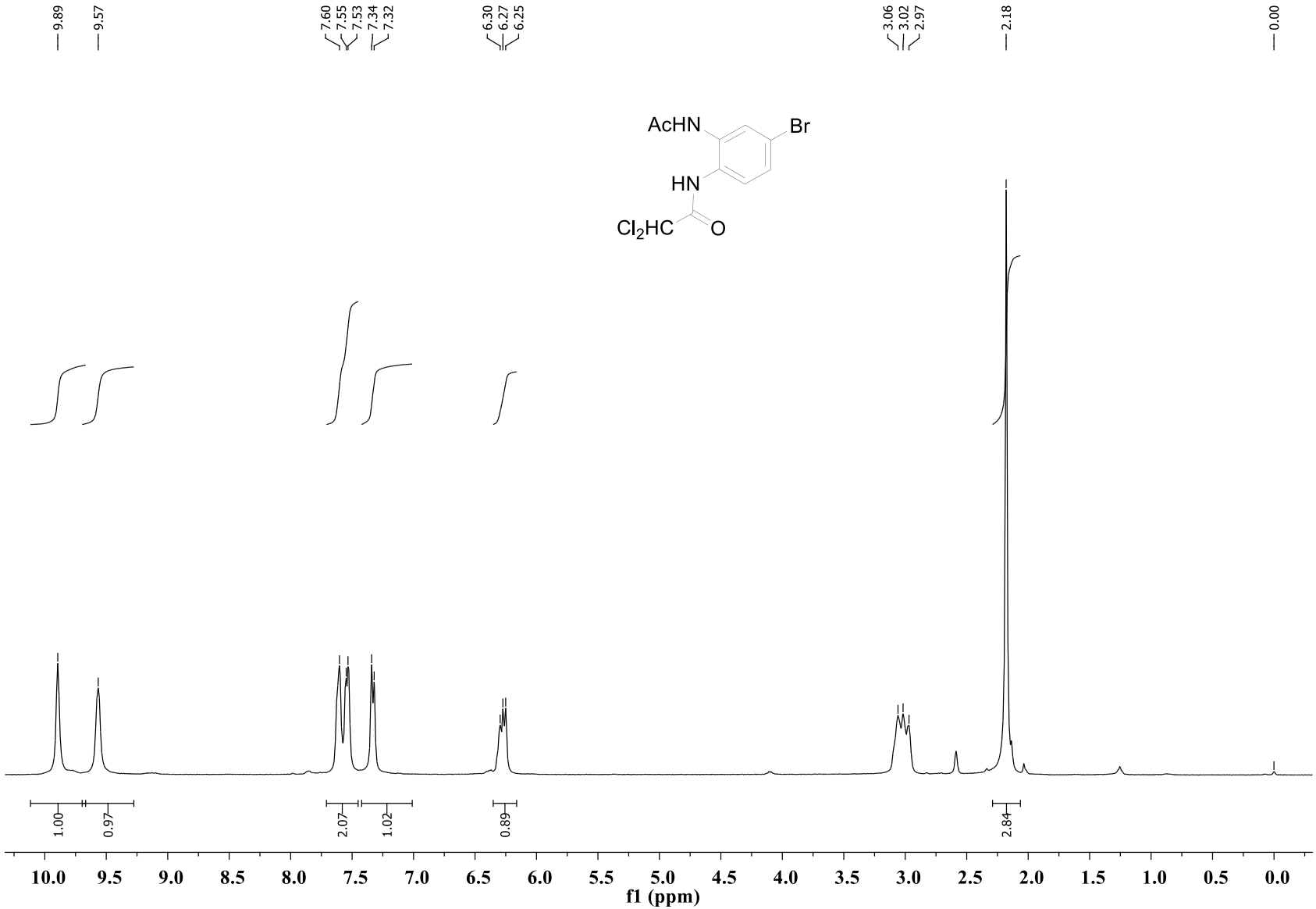
^{1}H NMR spectrum of compound **2g** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



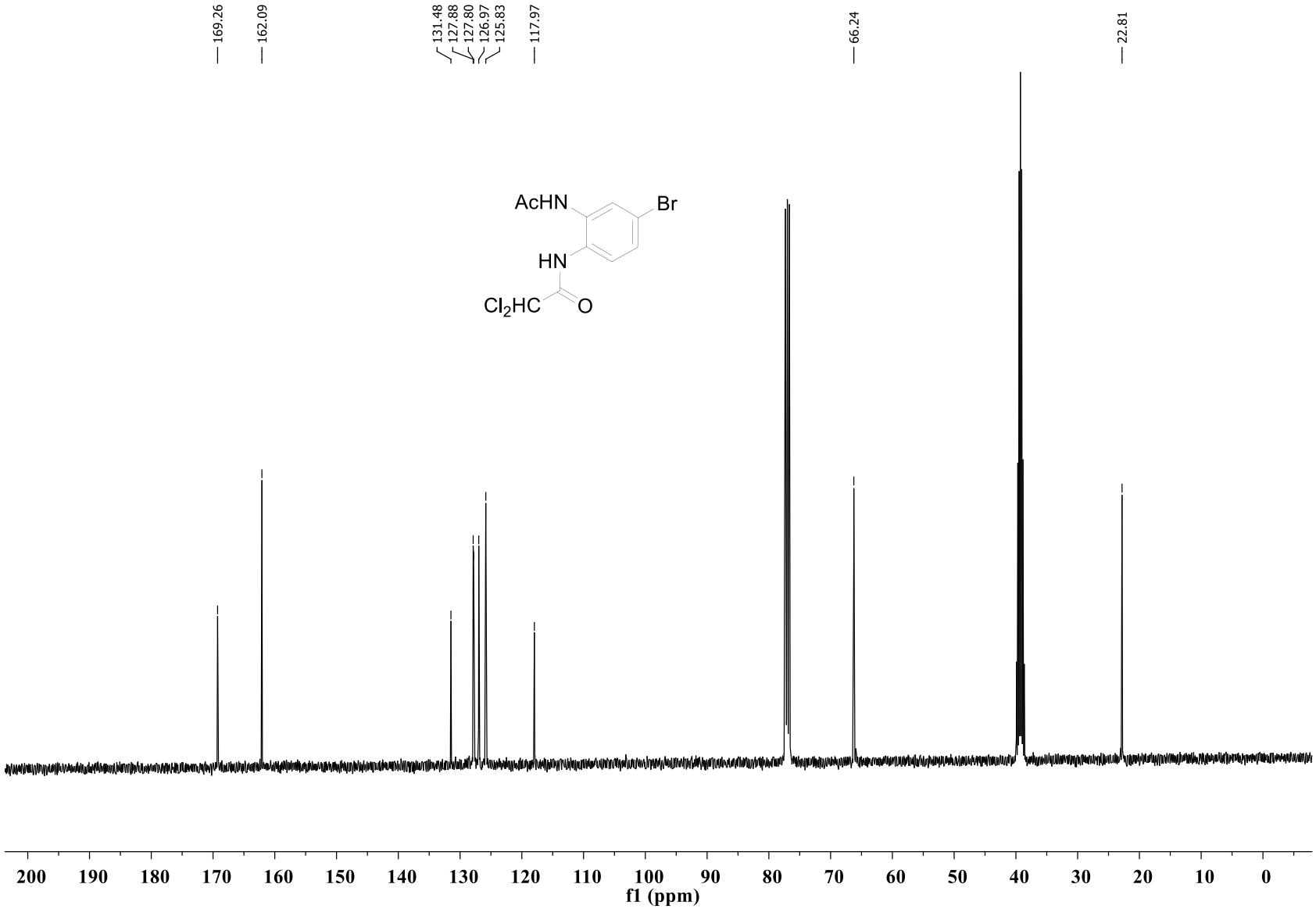
^{13}C NMR spectrum of compound **2g** (8:2, $CDCl_3$ + DMSO-*d6*, 100 MHz)**:**



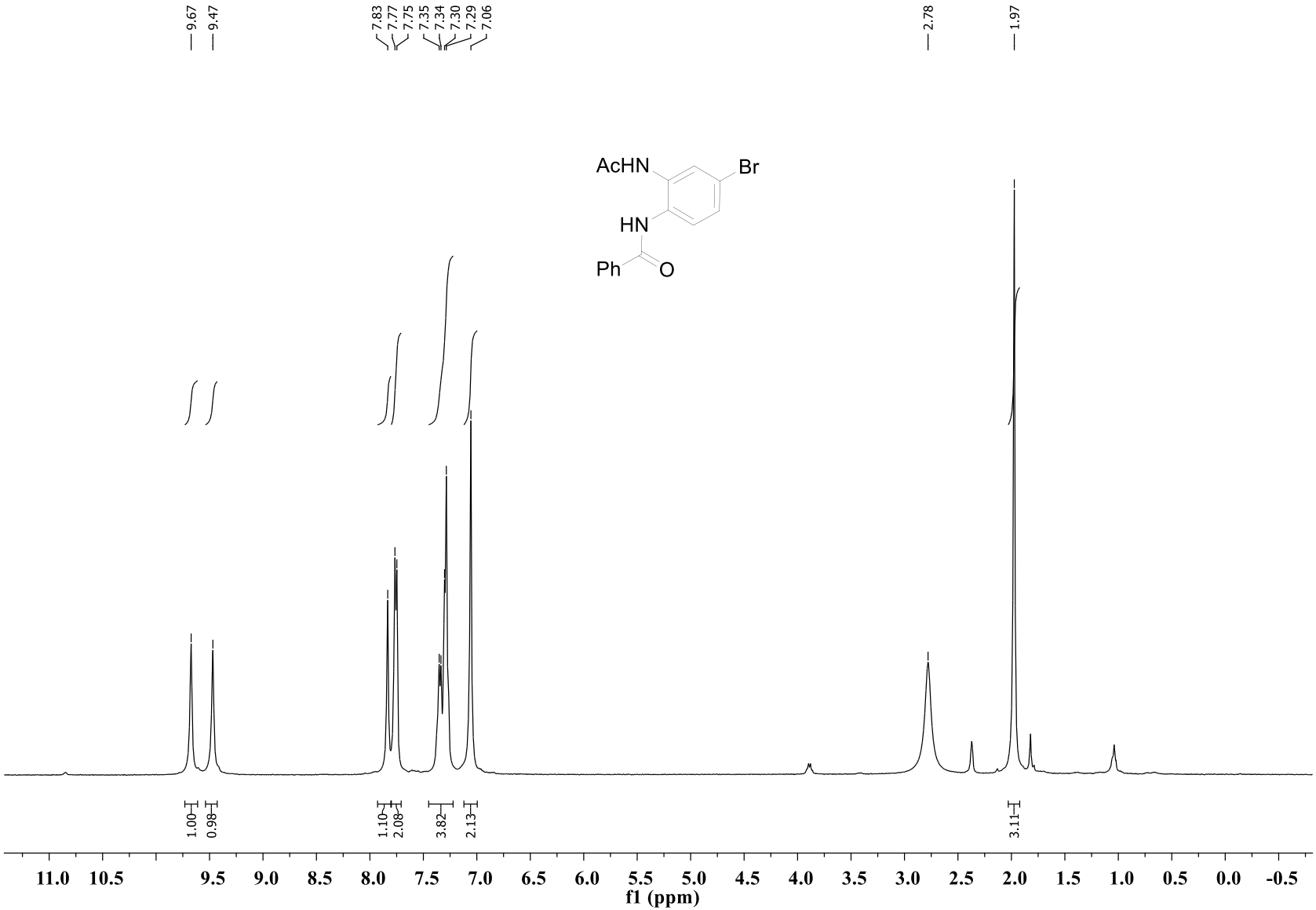
[1]H NMR spectrum of compound **2h** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



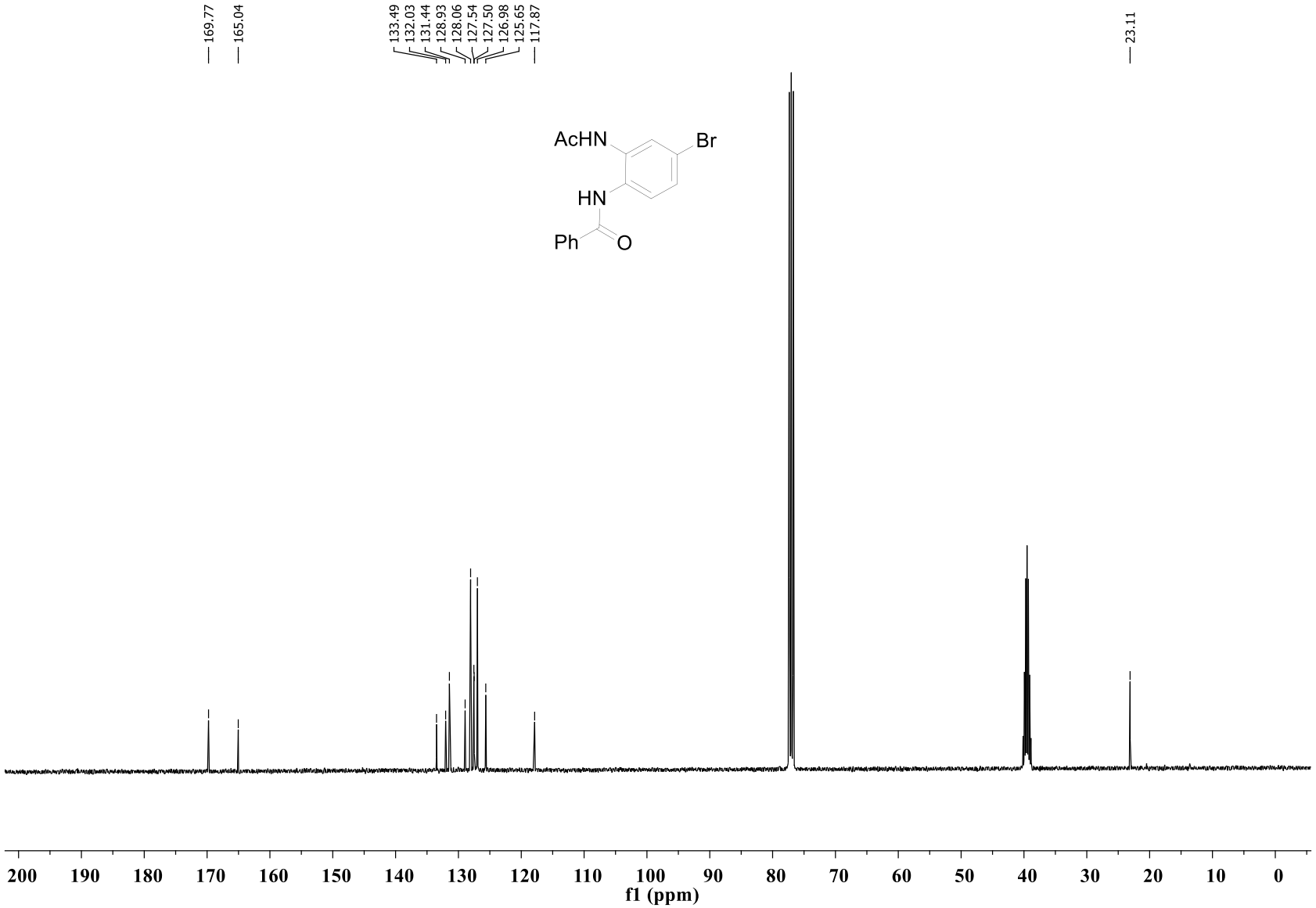
^{13}C NMR spectrum of compound **2h** (8:2, $CDCl_3$ + DMSO-*d6*, 100 MHz)**:**



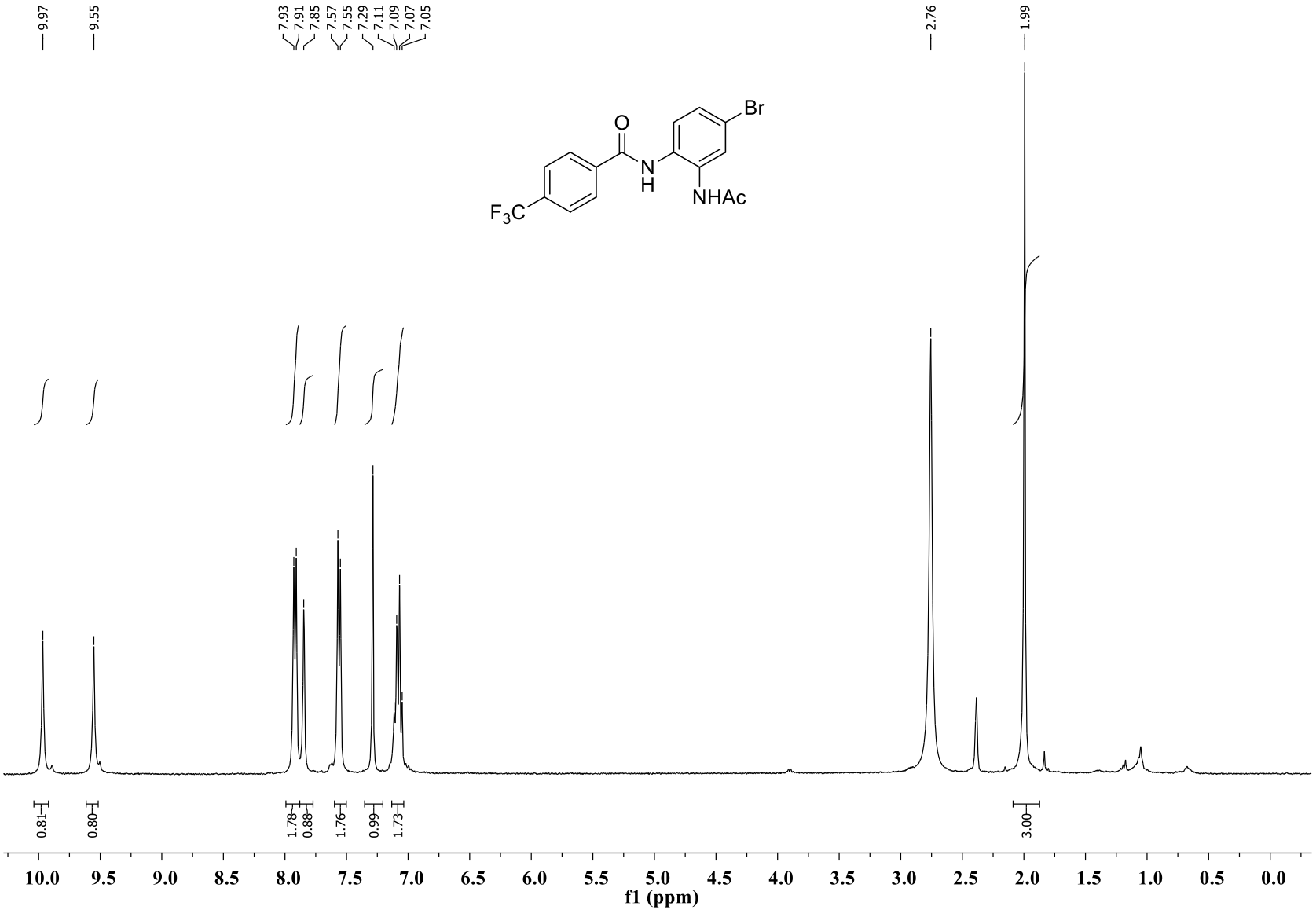
^{1}H NMR spectrum of compound **2i** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



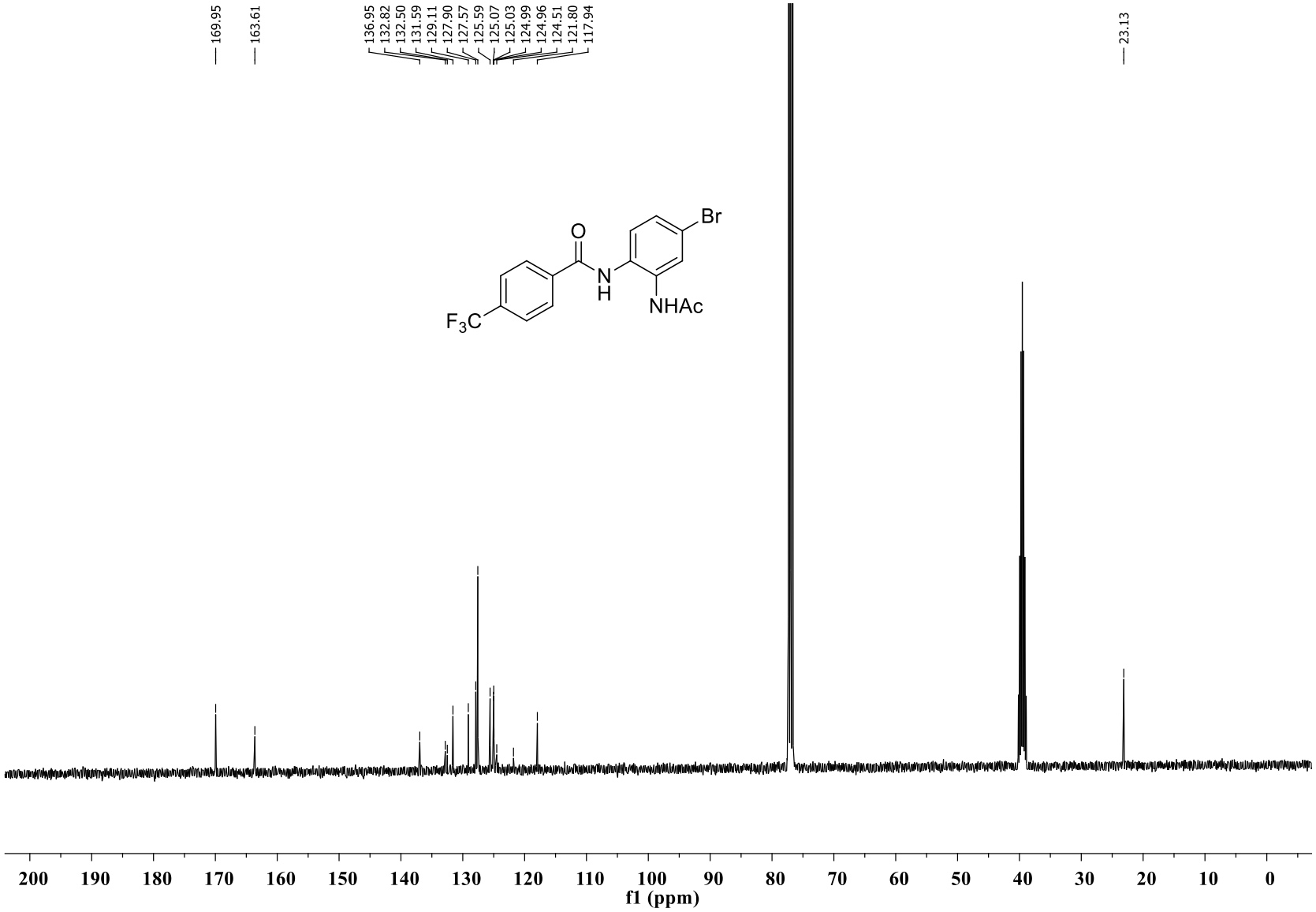
^{13}C NMR spectrum of compound **2i** (8:2, $CDCl_3$ + DMSO-*d6*, 100 MHz)**:**



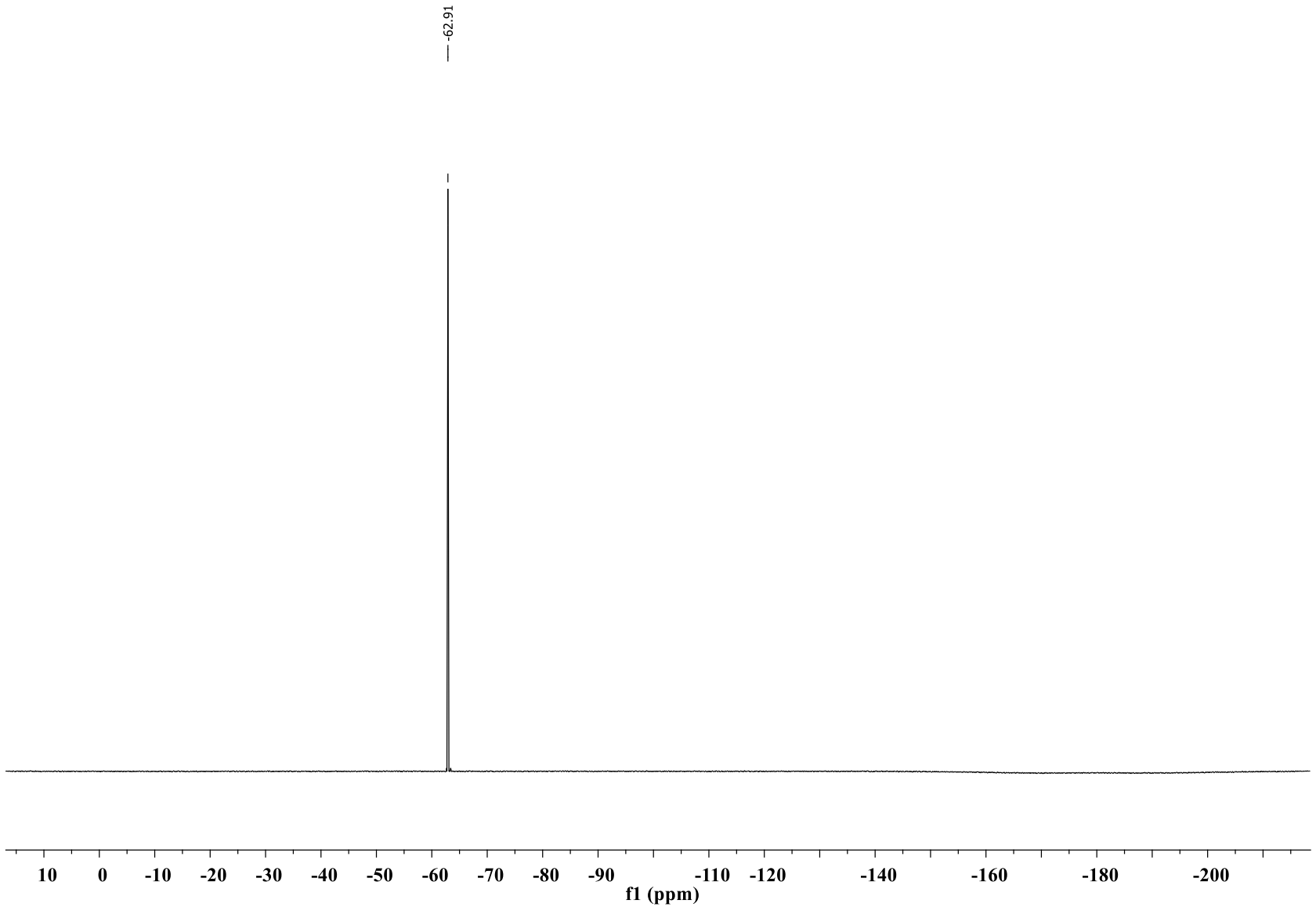
[1]H NMR spectrum of compound **2j** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



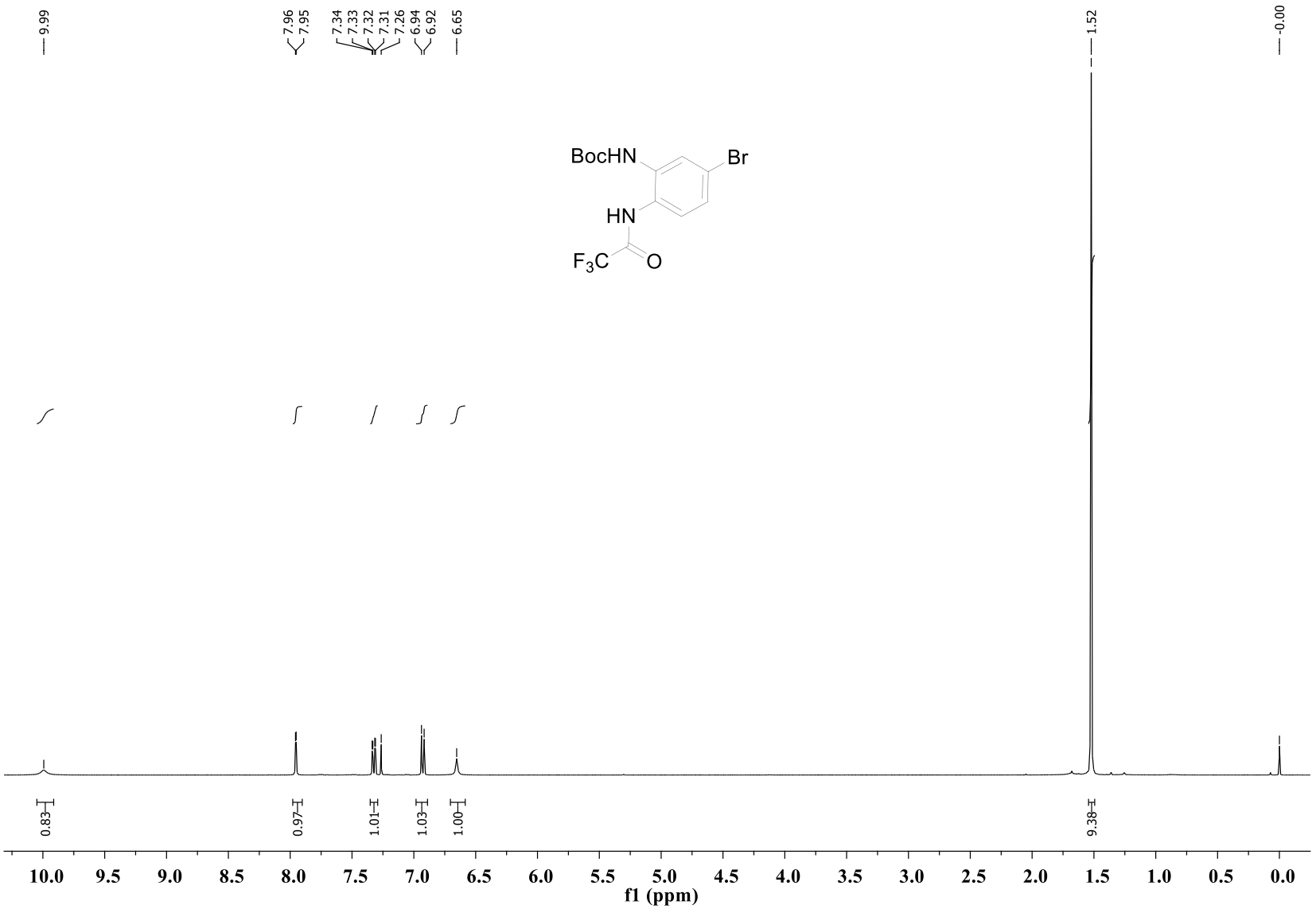
^{13}C NMR spectrum of compound **2j** (8:2, $CDCl_3$ + DMSO-*d6*, 100 MHz)**:**



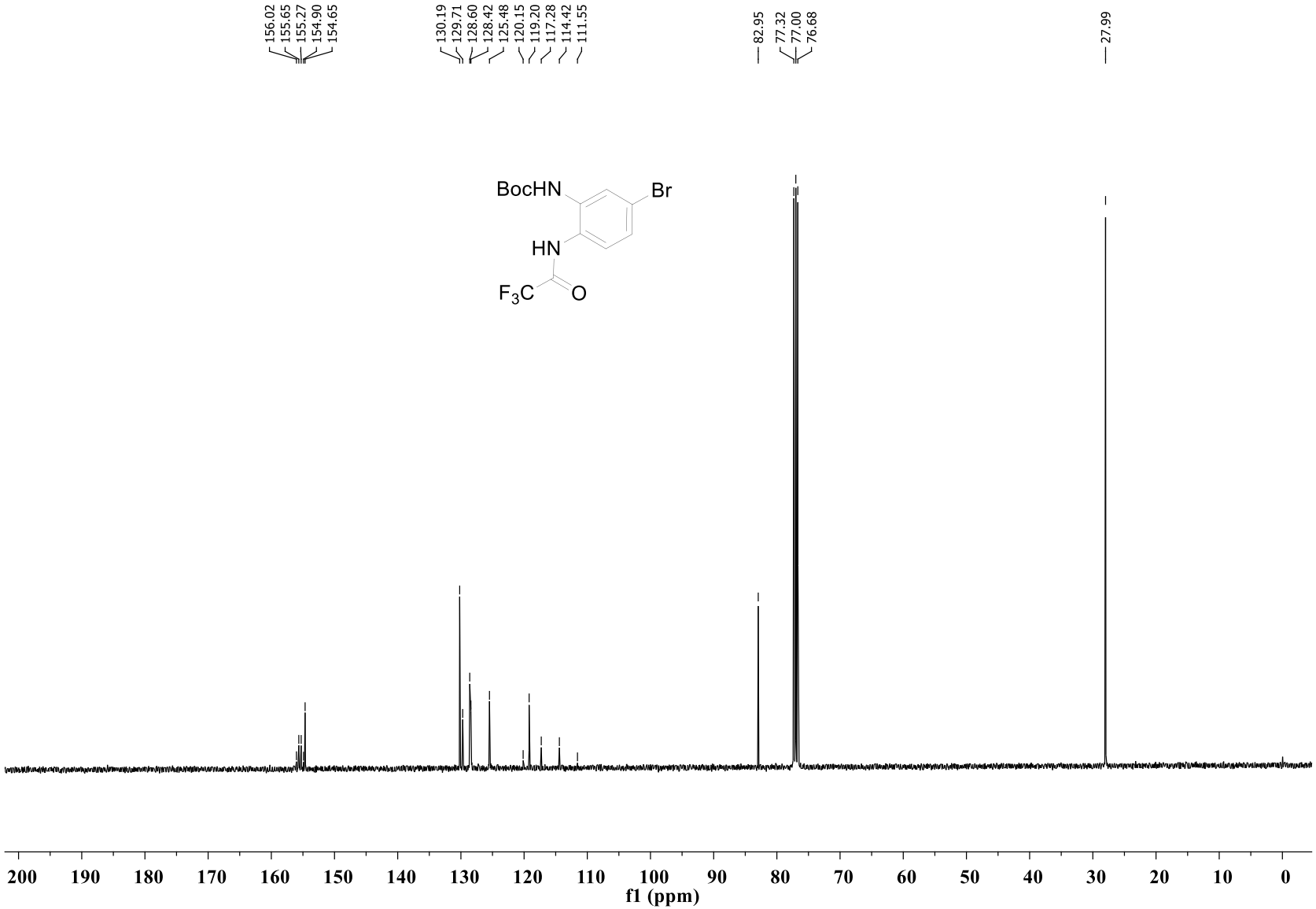
^{19}F NMR spectrum of compound **2j** ($CDCl_3$, 376 MHz)**:**



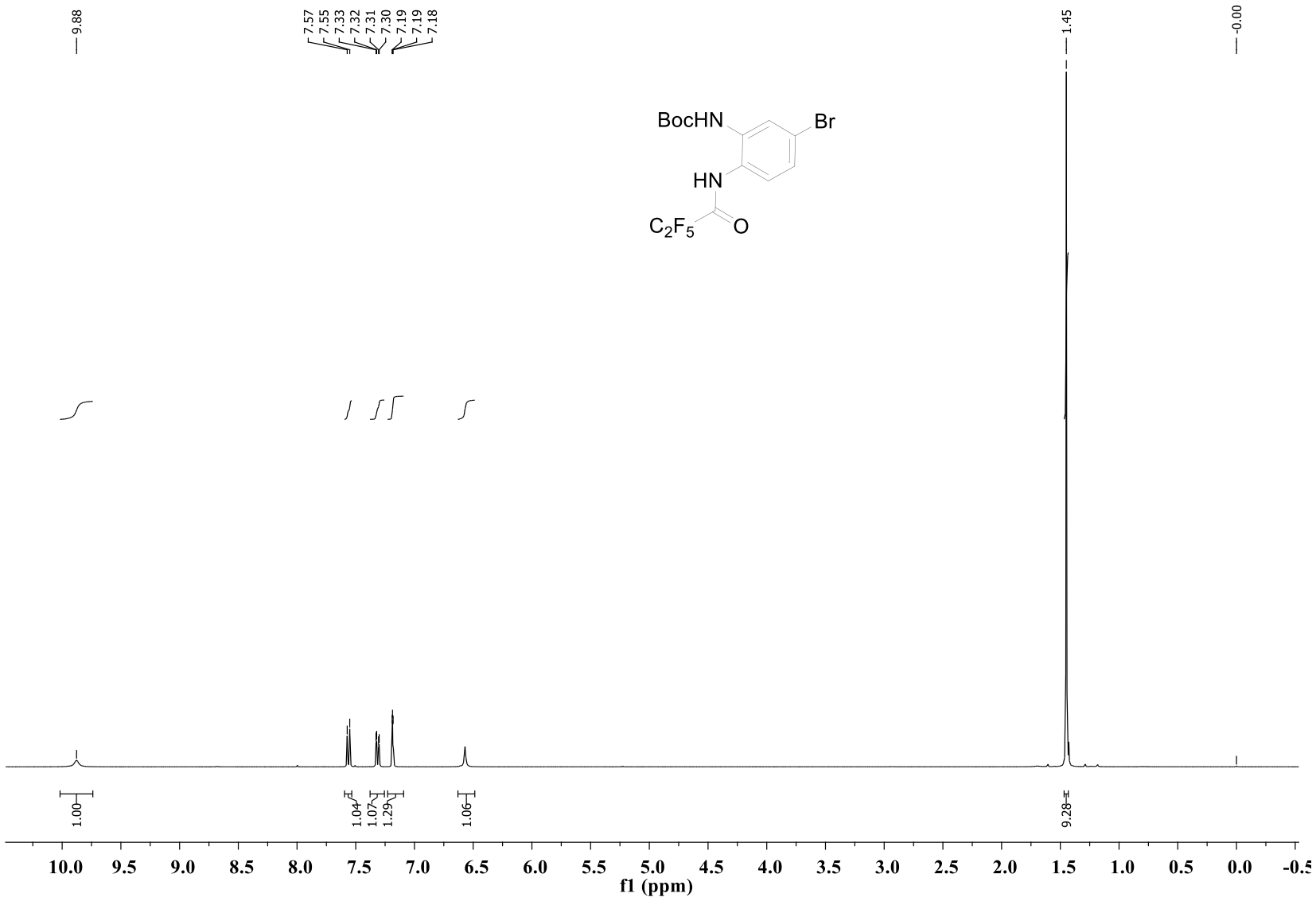
^{1}H NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz)**:**



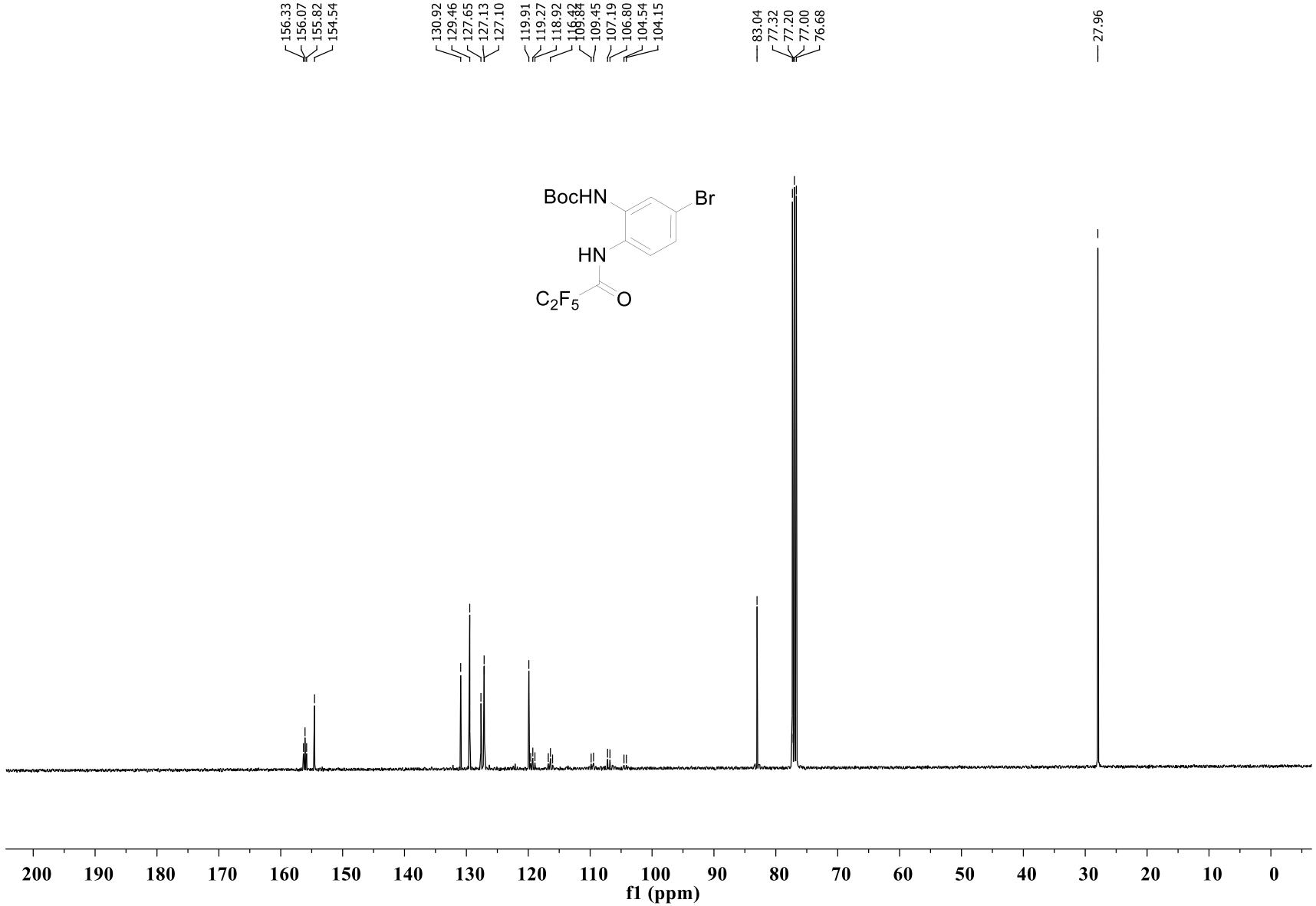
^{13}C NMR spectrum of compound **2k** ($CDCl_3$, 100 MHz)**:**



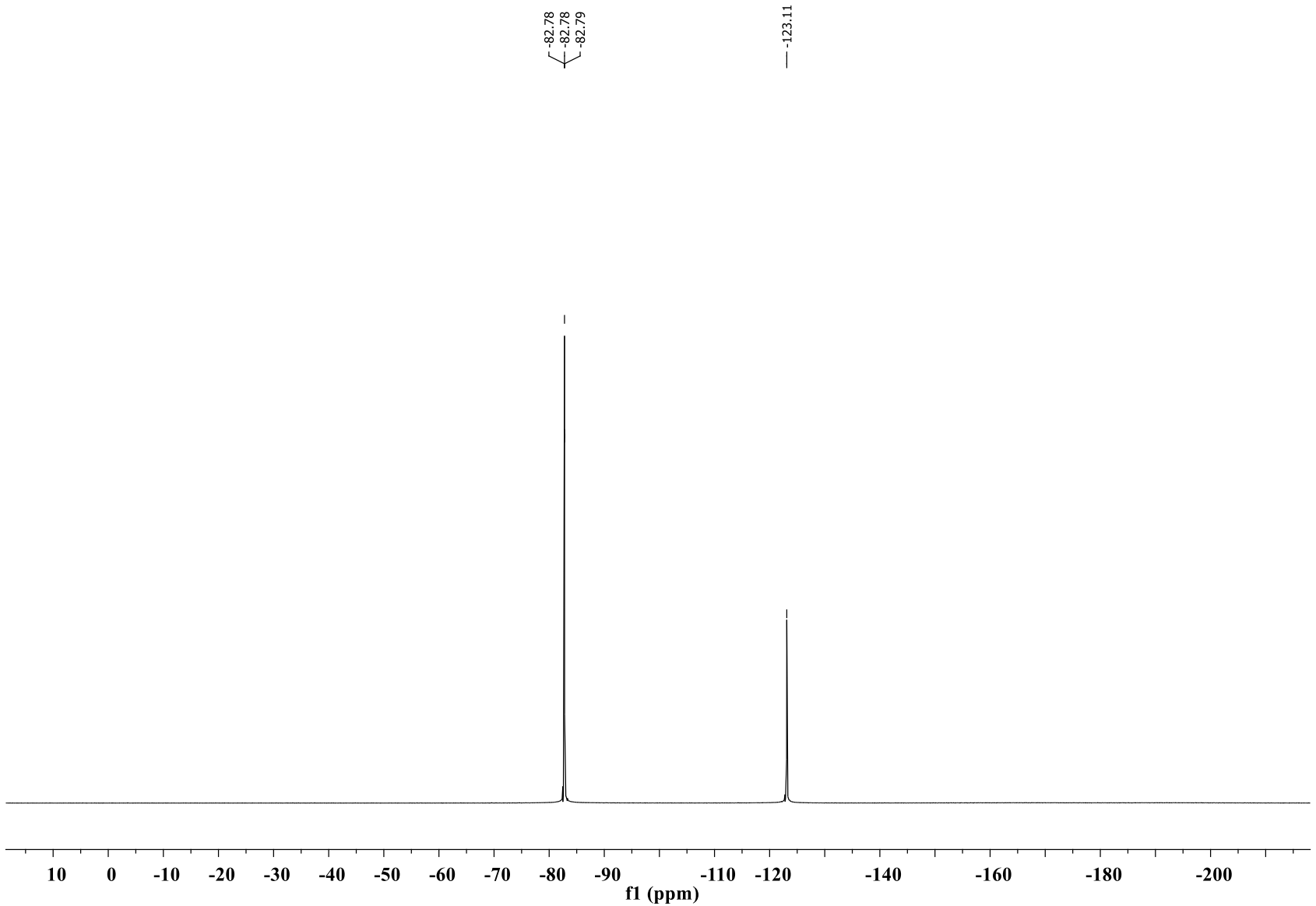
^{1}H NMR spectrum of compound **2l** ($CDCl_3$, 400 MHz)**:**



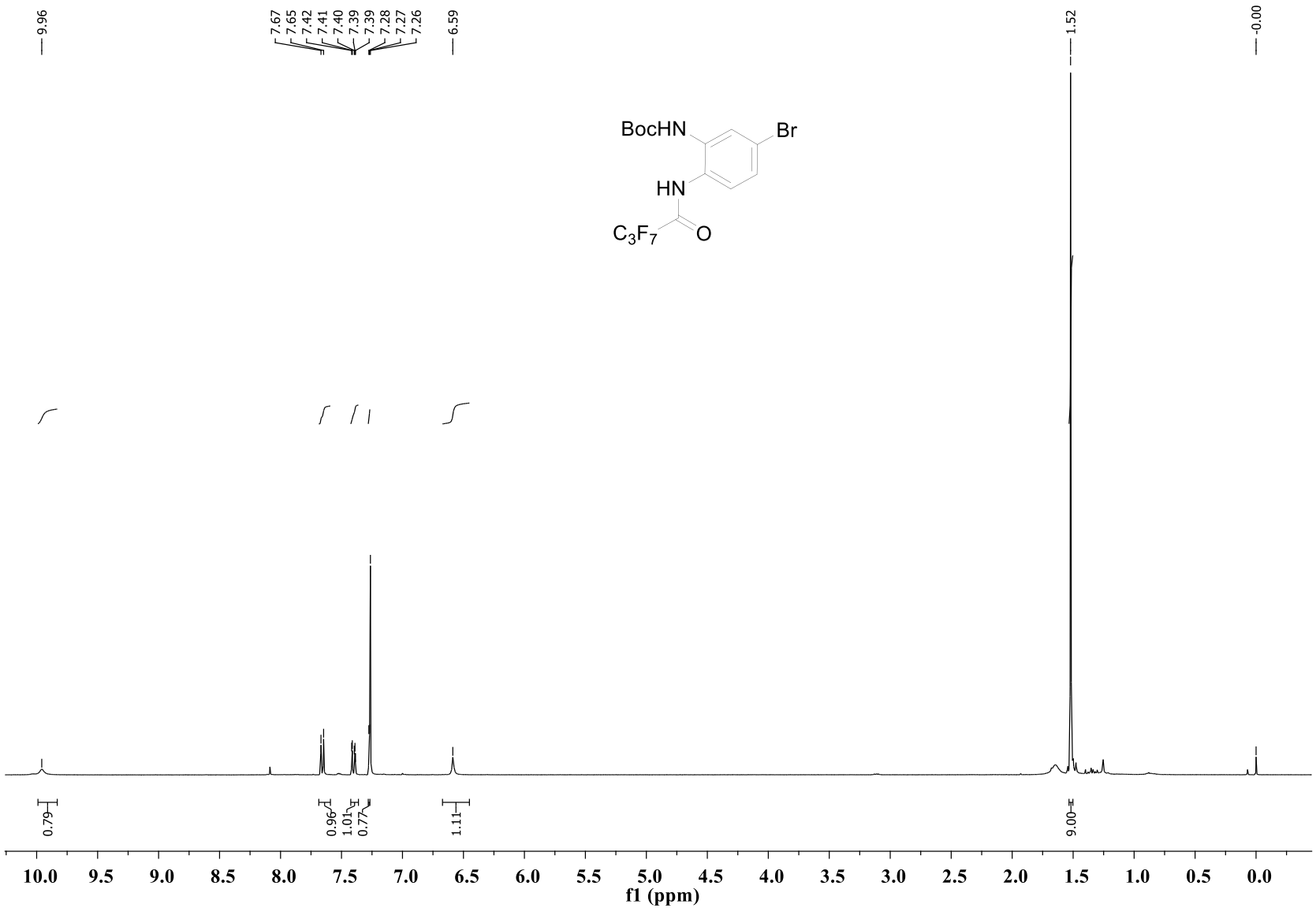
^{13}C NMR spectrum of compound **2l** ($CDCl_3$, 100 MHz)**:**



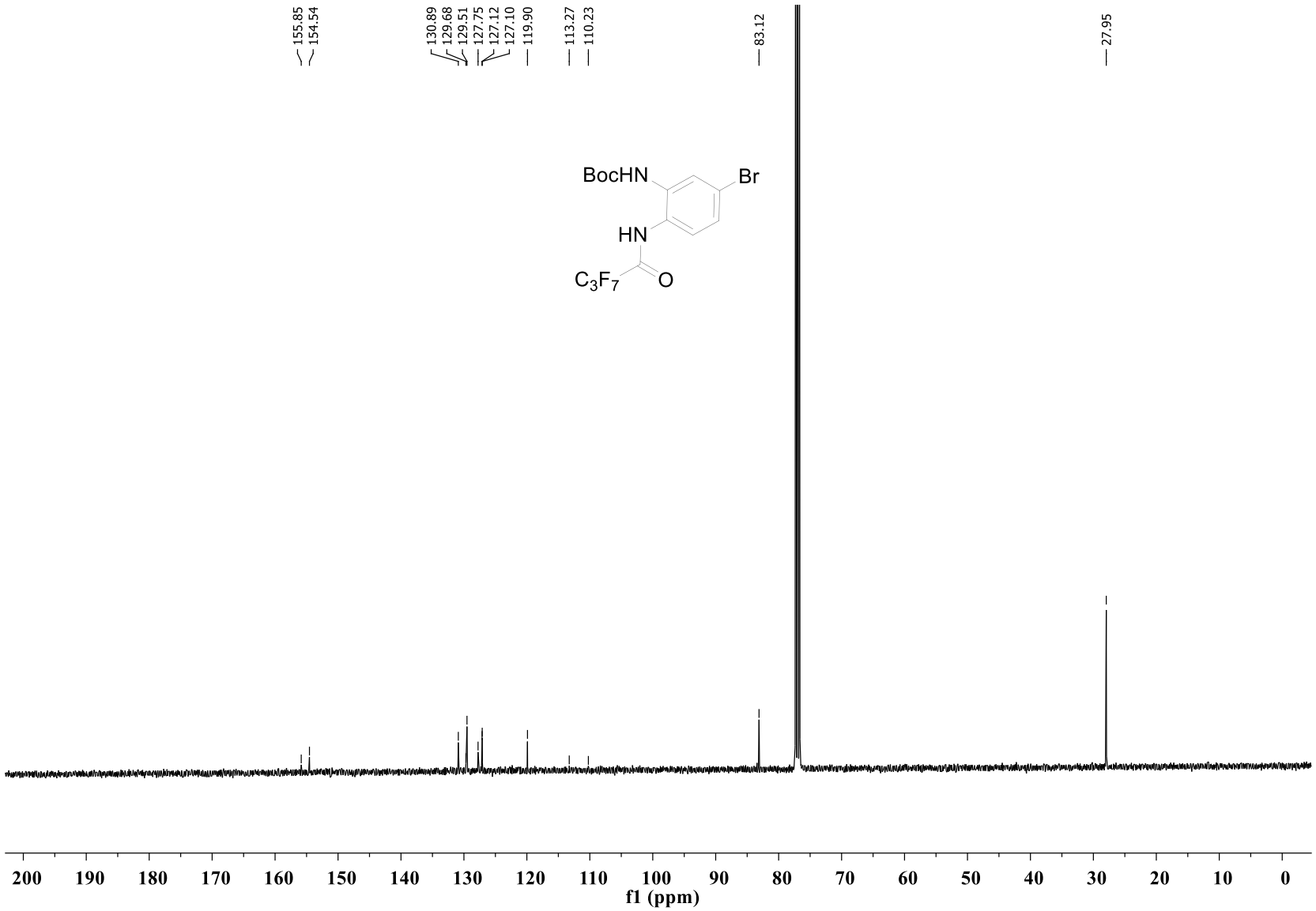
^{19}F NMR spectrum of compound **2l** ($CDCl_3$, 376 MHz)**:**



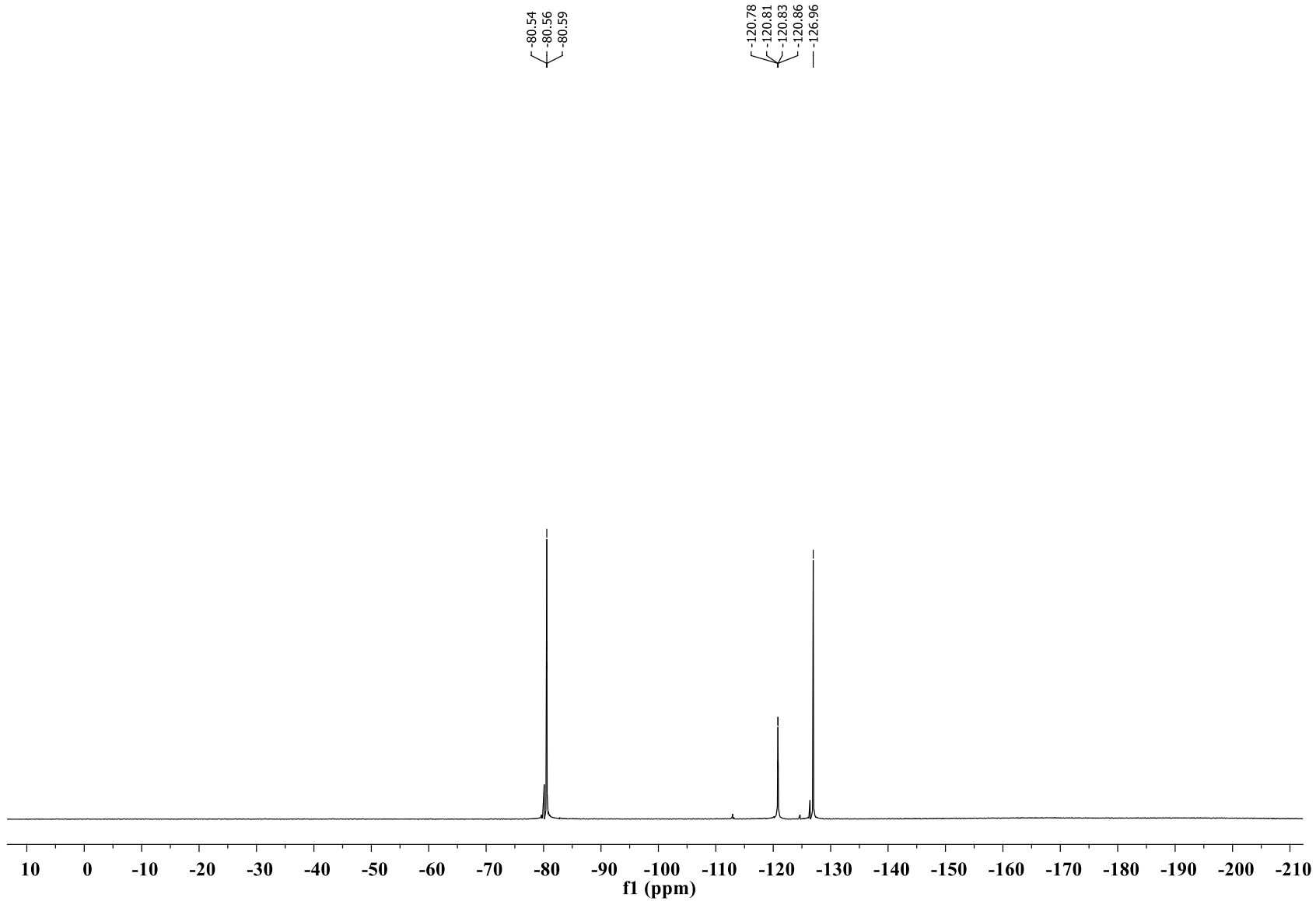
^{1}H NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz)**:**



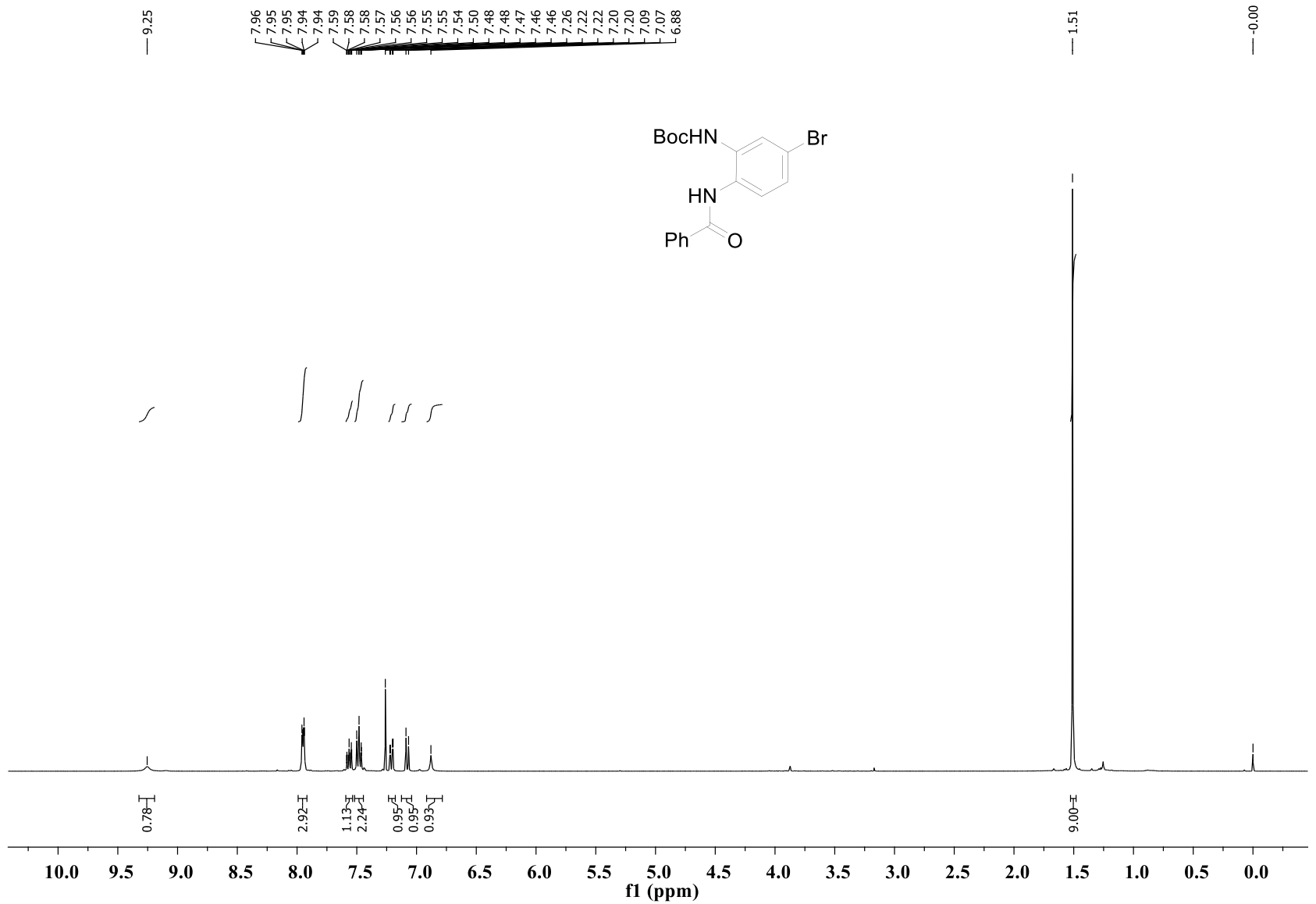
^{13}C NMR spectrum of compound **2m** ($CDCl_3$, 100 MHz)**:**



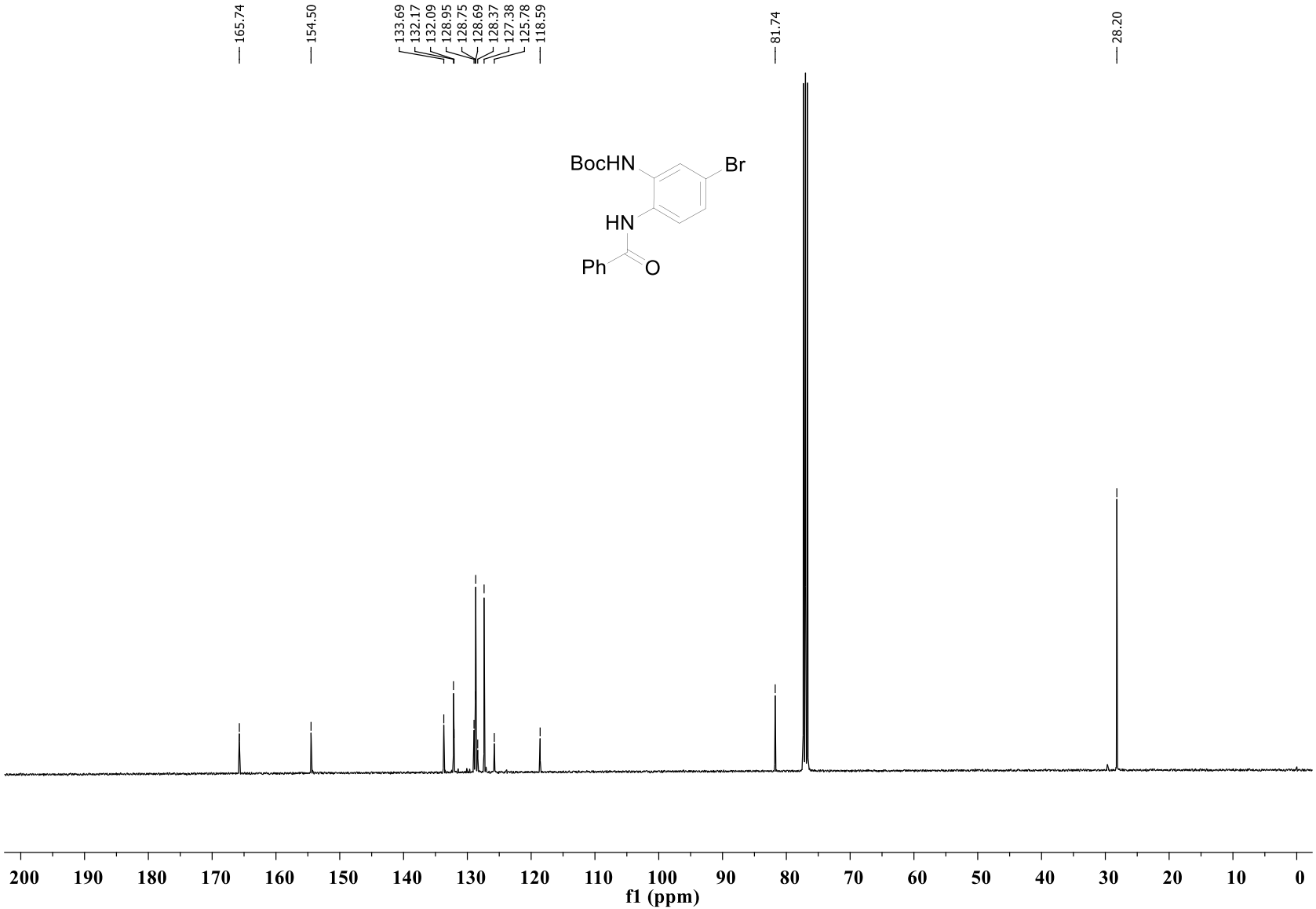
^{19}F NMR spectrum of compound **2m** ($CDCl_3$, 376 MHz)**:**



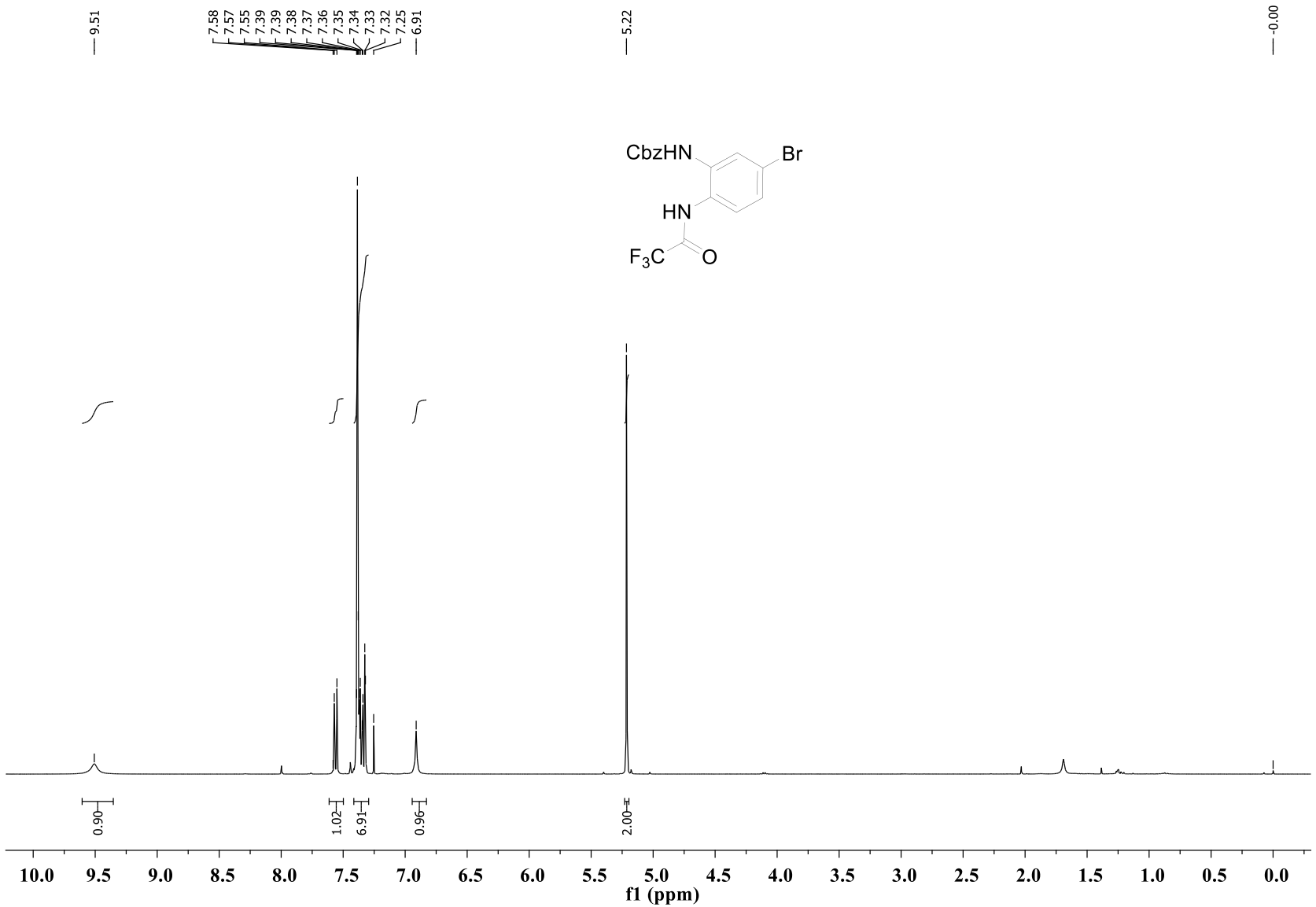
^{1}H NMR spectrum of compound **2n** ($CDCl_3$, 400 MHz)**:**



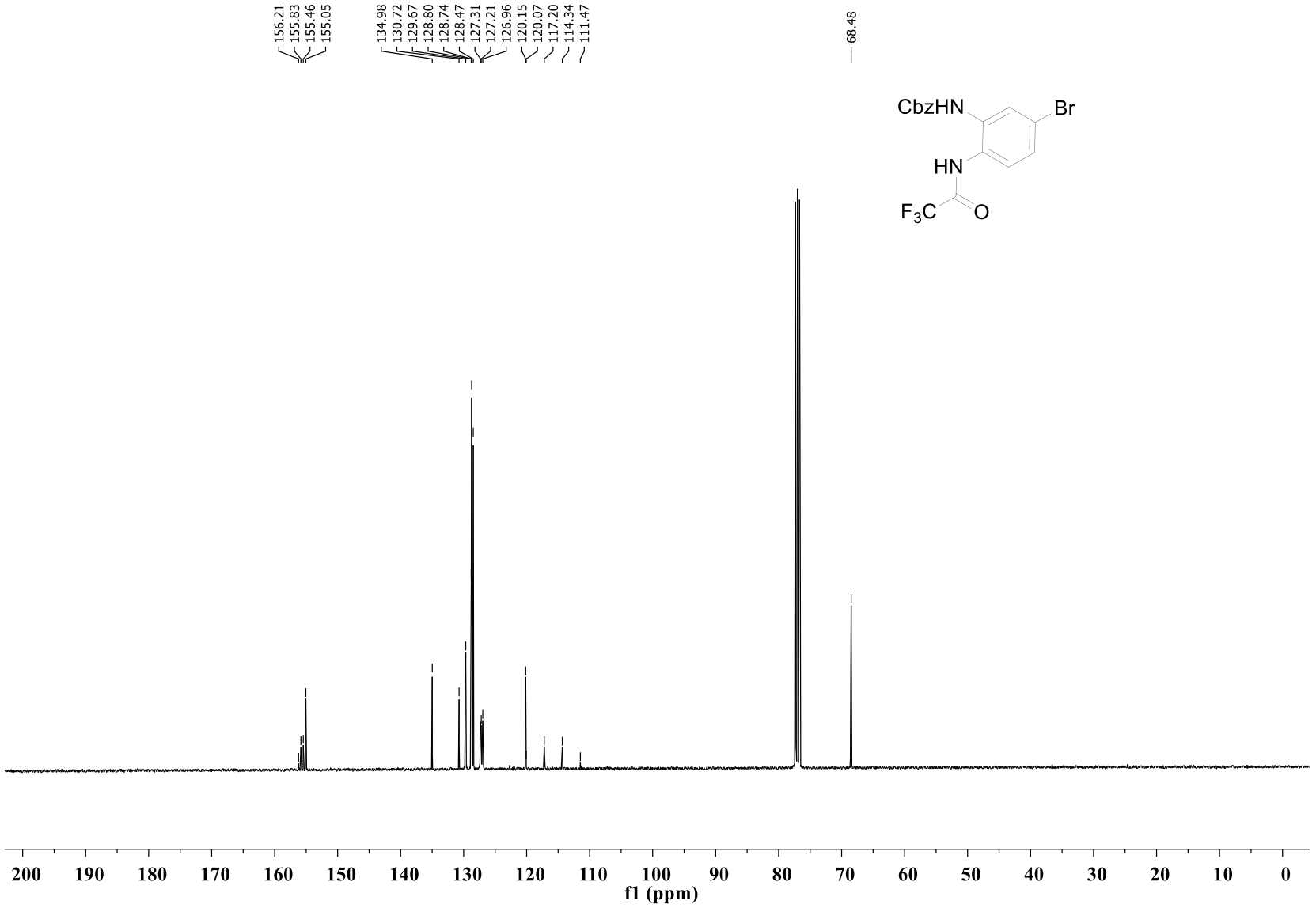
^{13}C NMR spectrum of compound **2n** ($CDCl_3$, 100 MHz)**:**



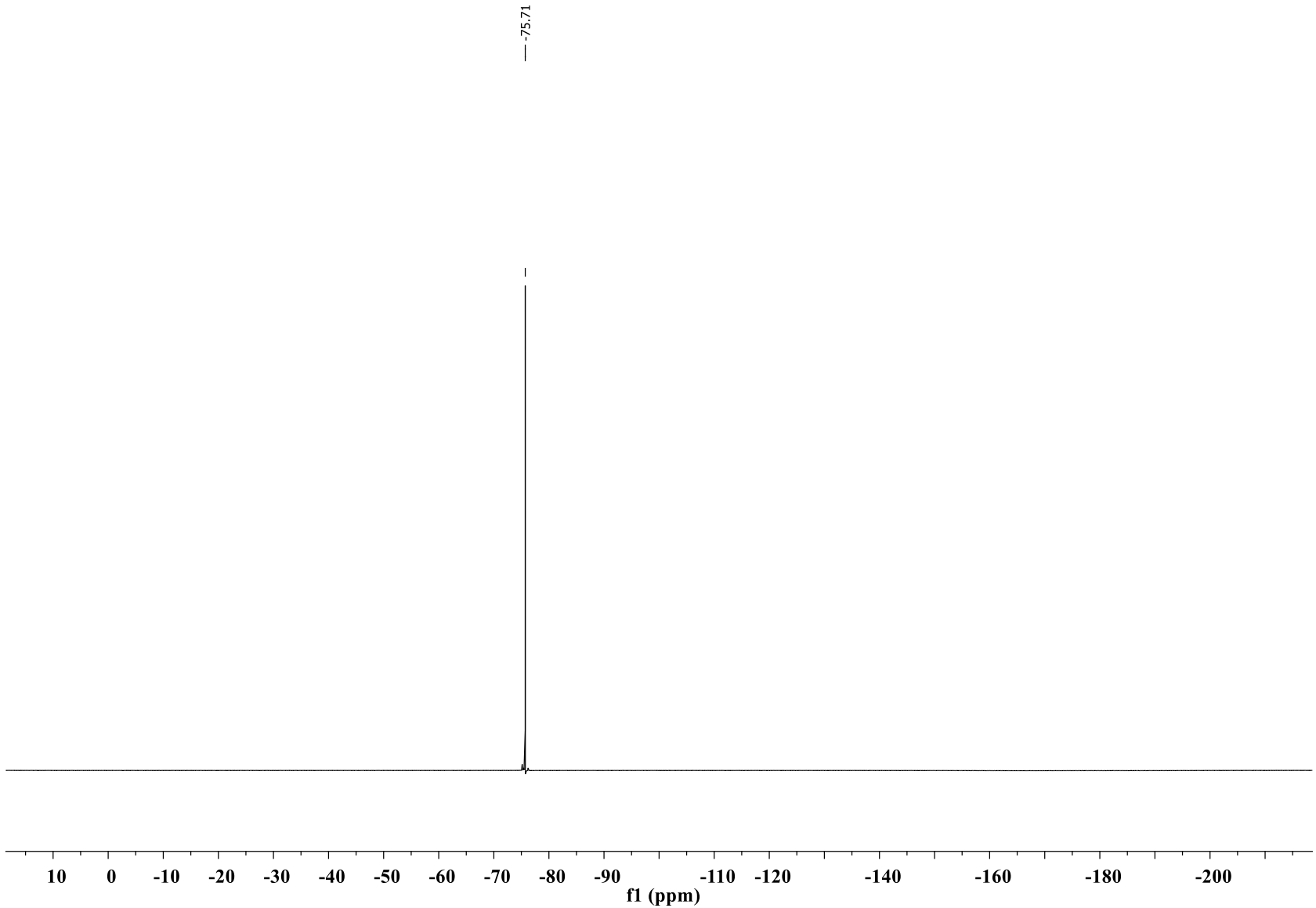
^{1}H NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz)**:**



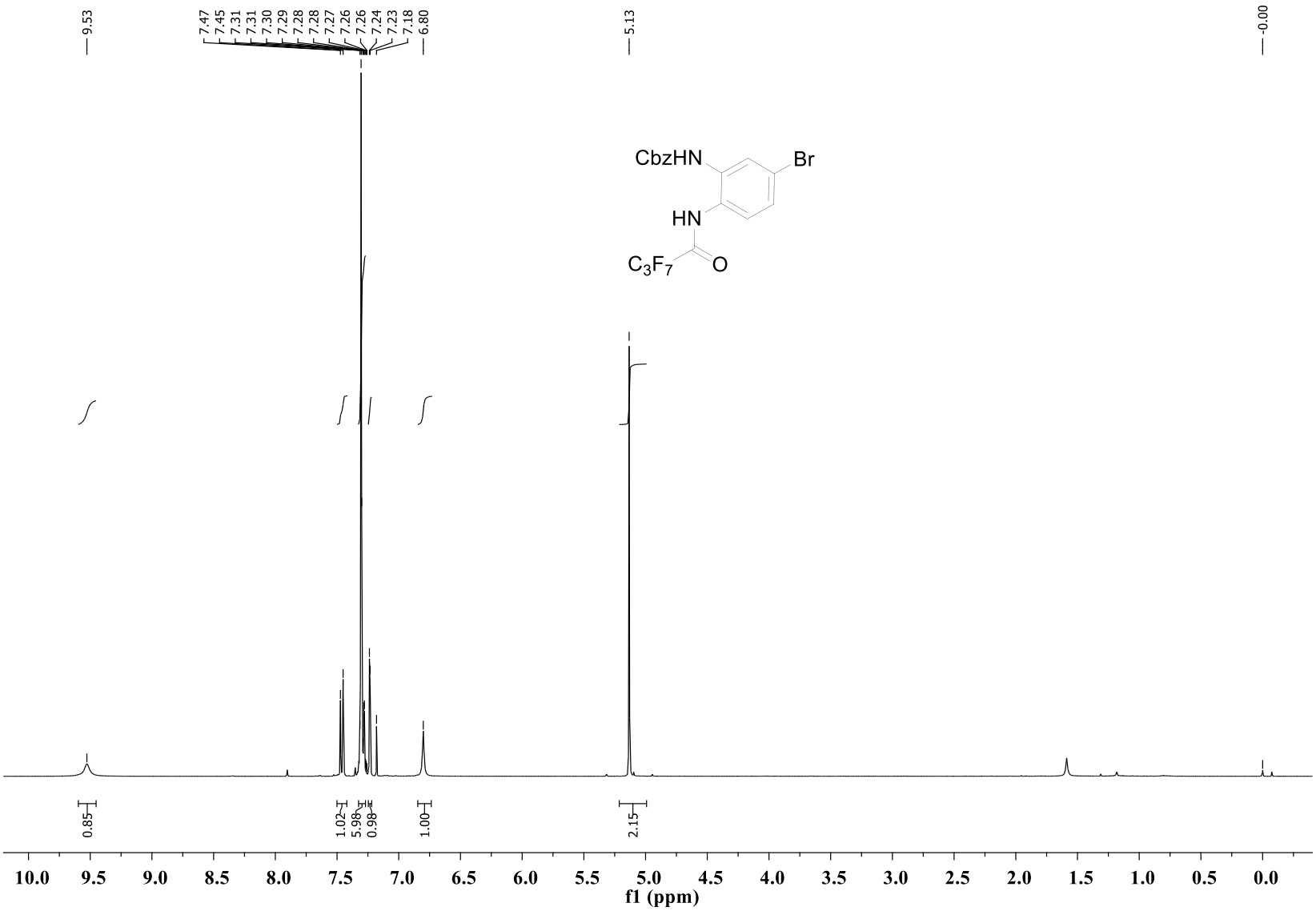
^{13}C NMR spectrum of compound **2o** ($CDCl_3$, 100 MHz)**:**



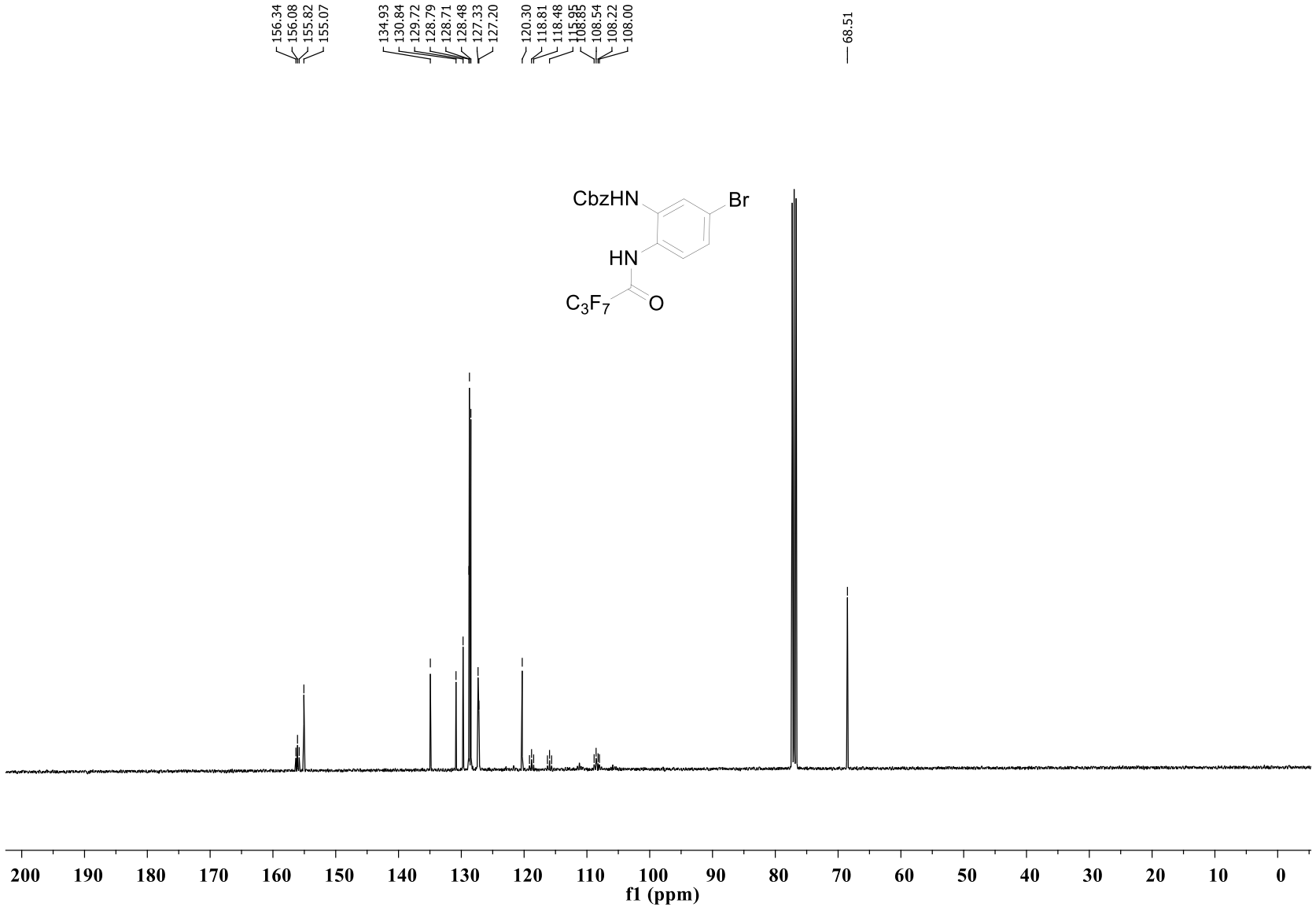
^{19}F NMR spectrum of compound **2o** ($CDCl_3$, 376 MHz)**:**



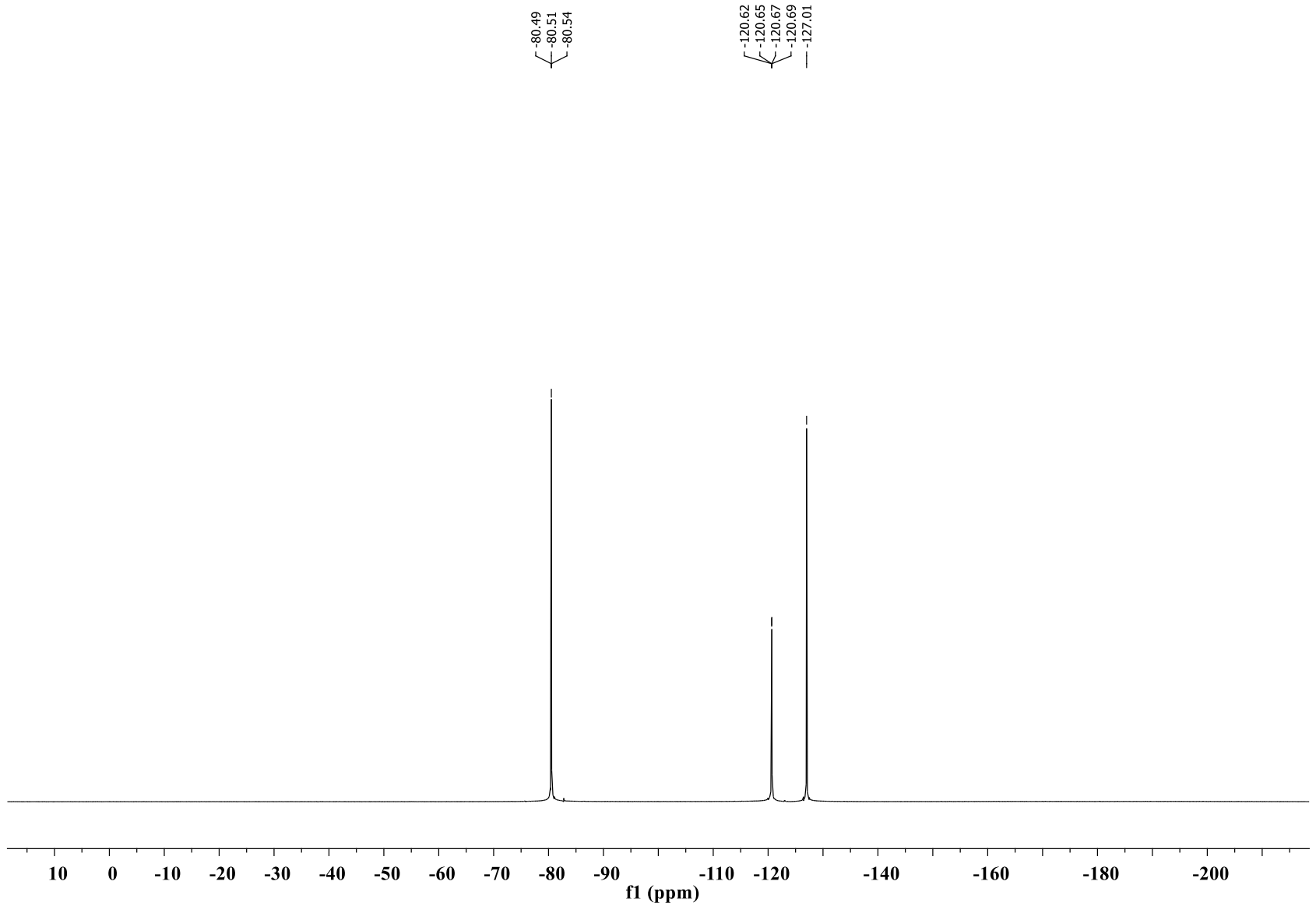
^{1}H NMR spectrum of compound **2p** ($CDCl_3$, 400 MHz)**:**



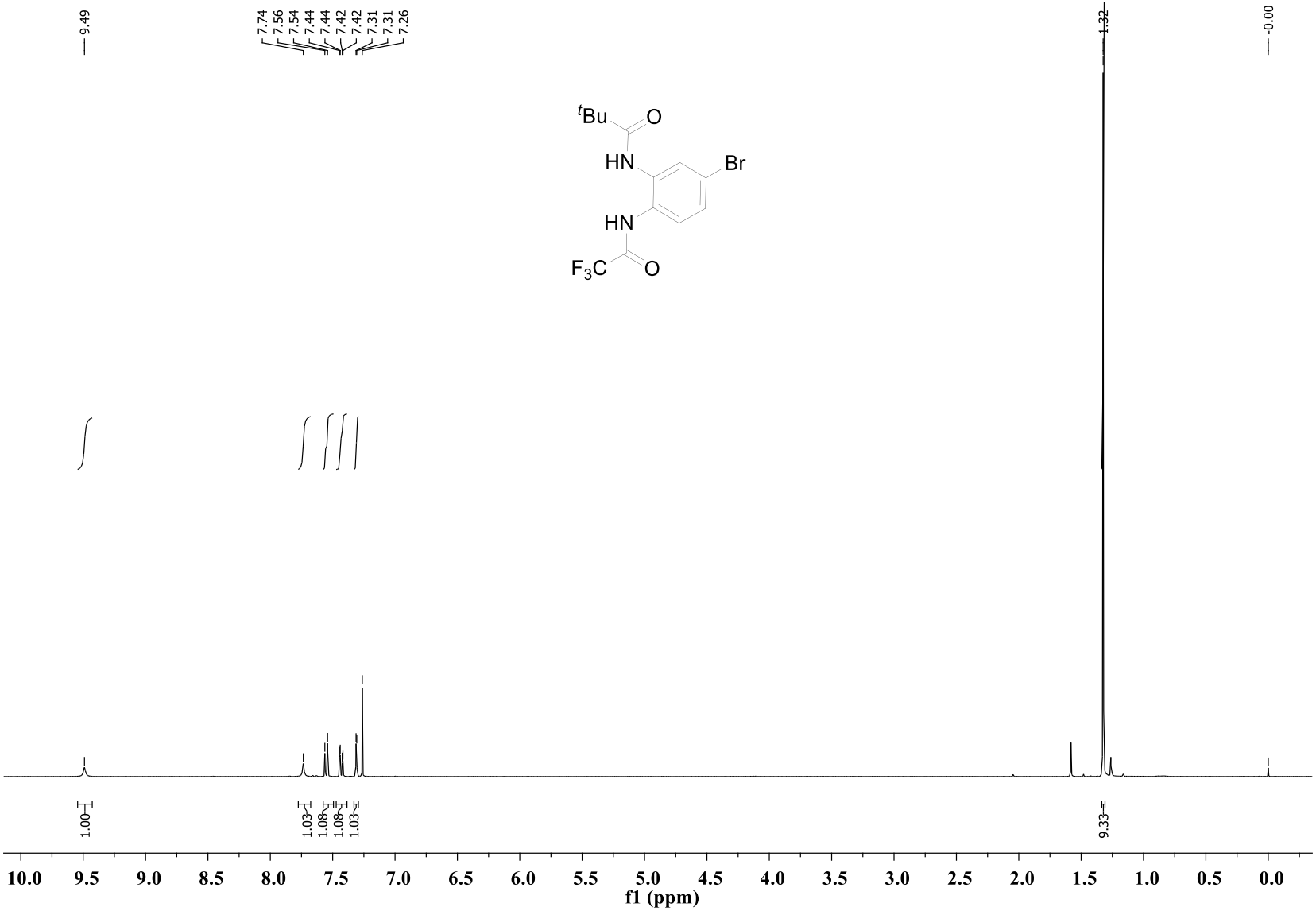
^{13}C NMR spectrum of compound **2p** ($CDCl_3$, 100 MHz)**:**



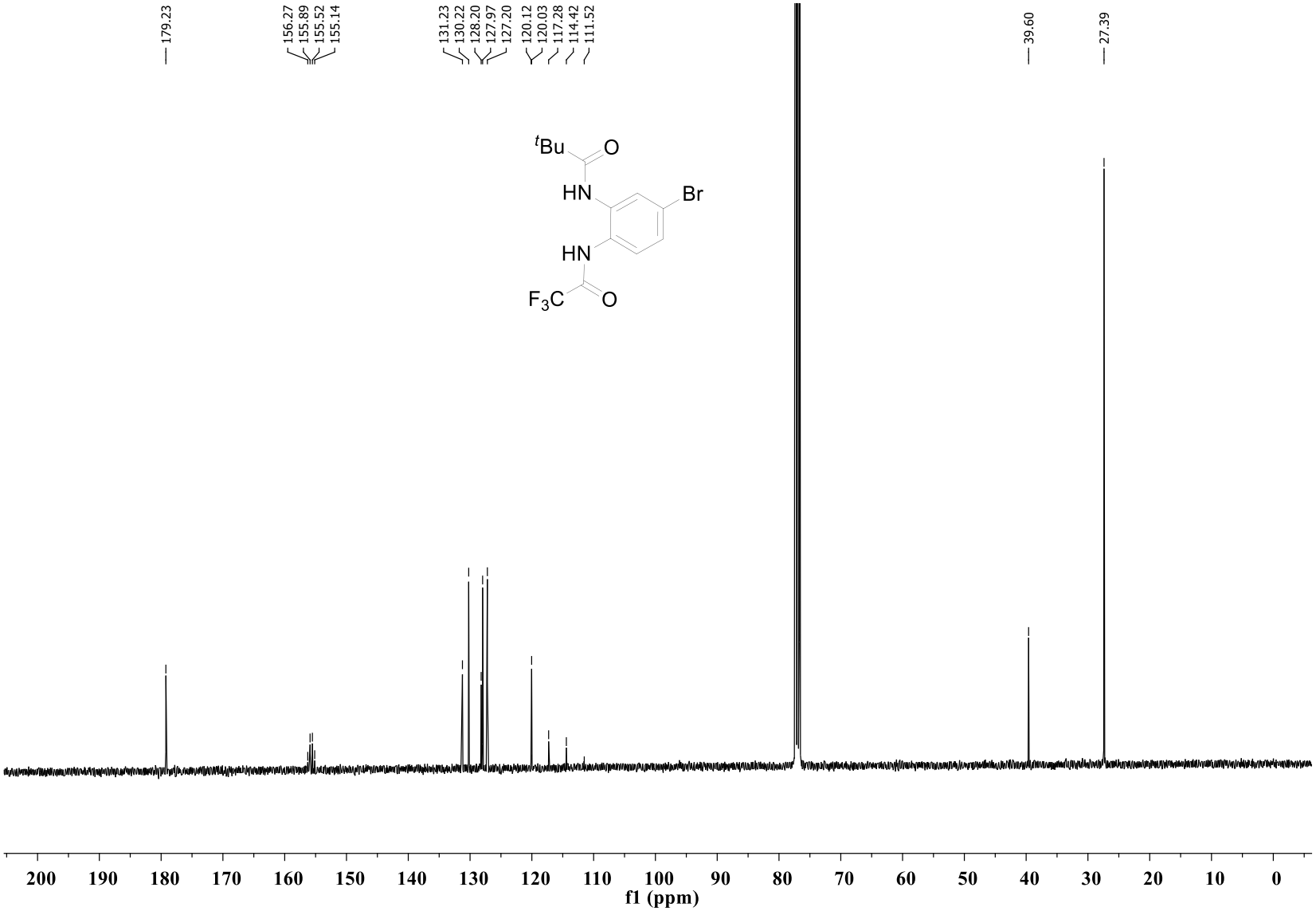
^{19}F NMR spectrum of compound **2p** ($CDCl_3$, 376 MHz)**:**



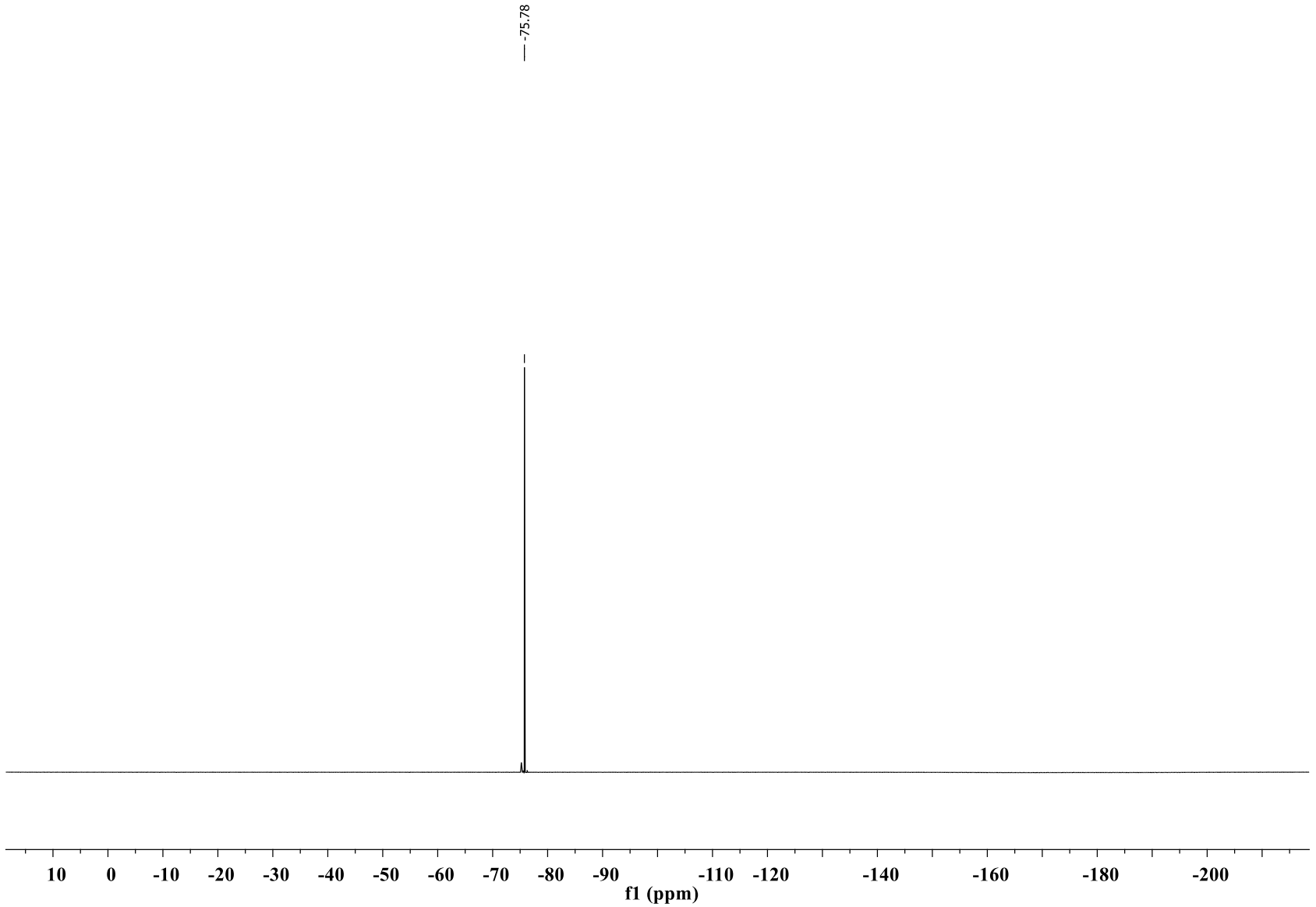
^{1}H NMR spectrum of compound **2q** ($CDCl_3$, 400 MHz)**:**



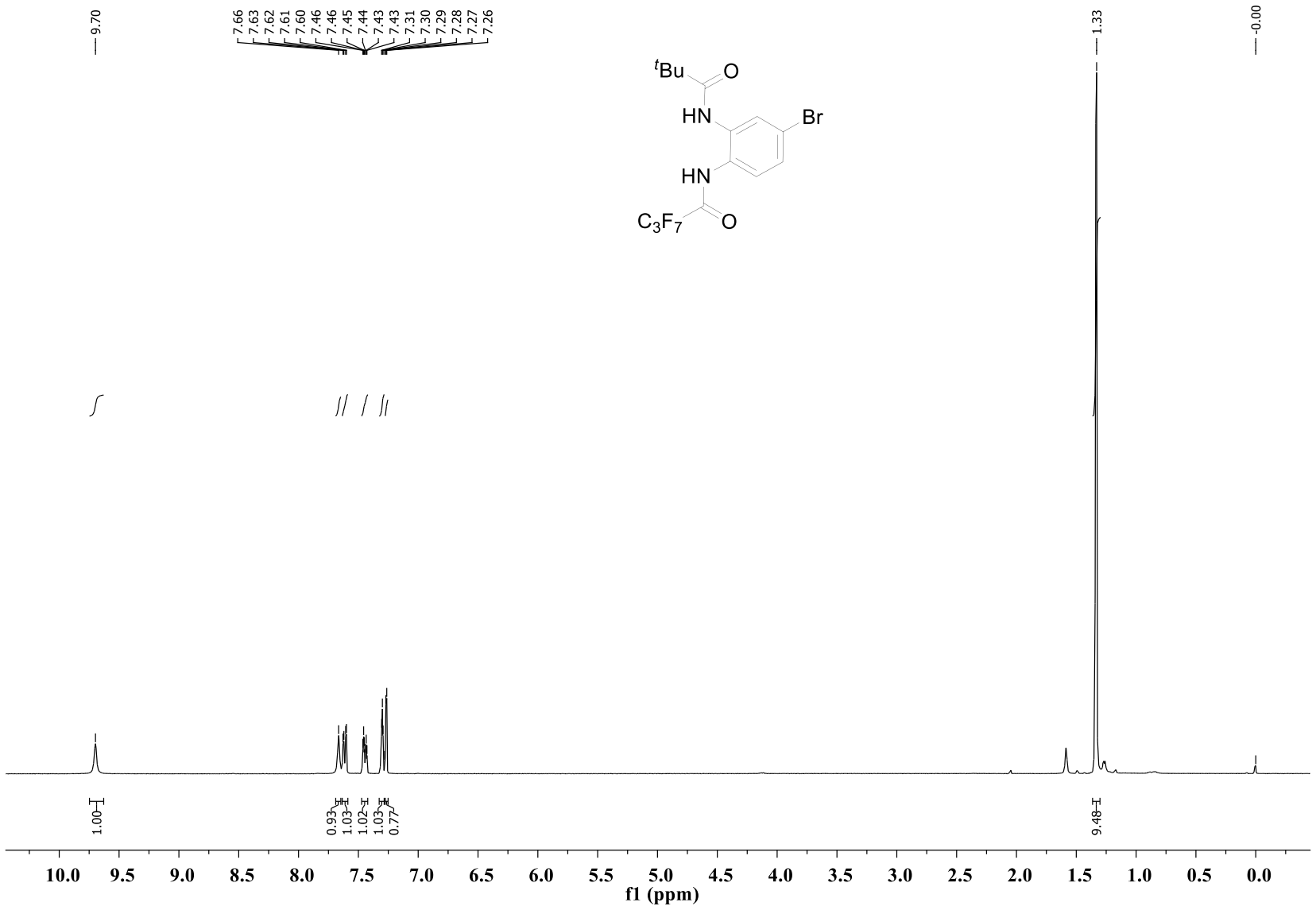
^{13}C NMR spectrum of compound **2q** ($CDCl_3$, 100 MHz)**:**



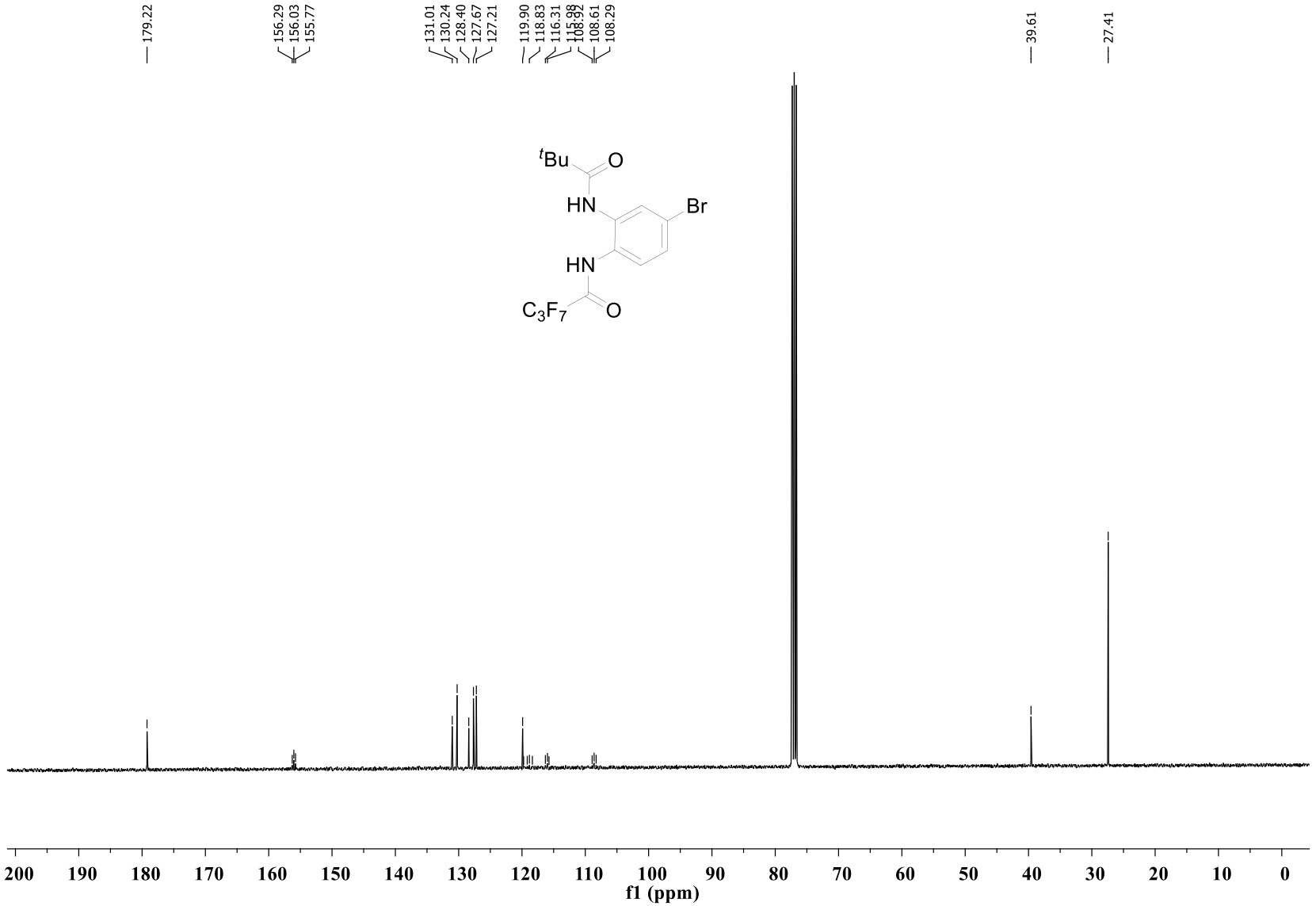
^{19}F NMR spectrum of compound **2q** ($CDCl_3$, 376 MHz):



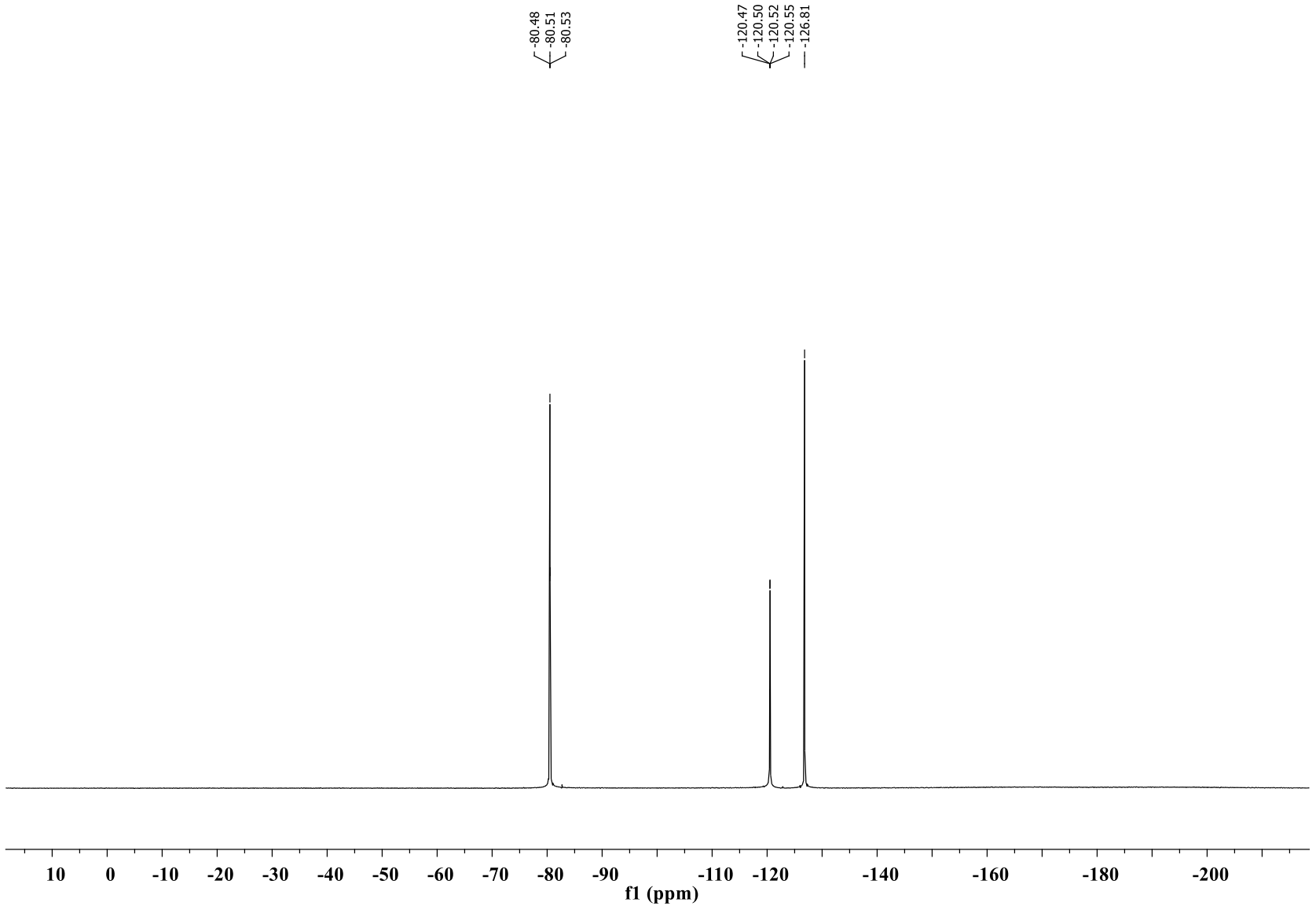
^{1}H NMR spectrum of compound **2r** ($CDCl_3$, 400 MHz)**:**



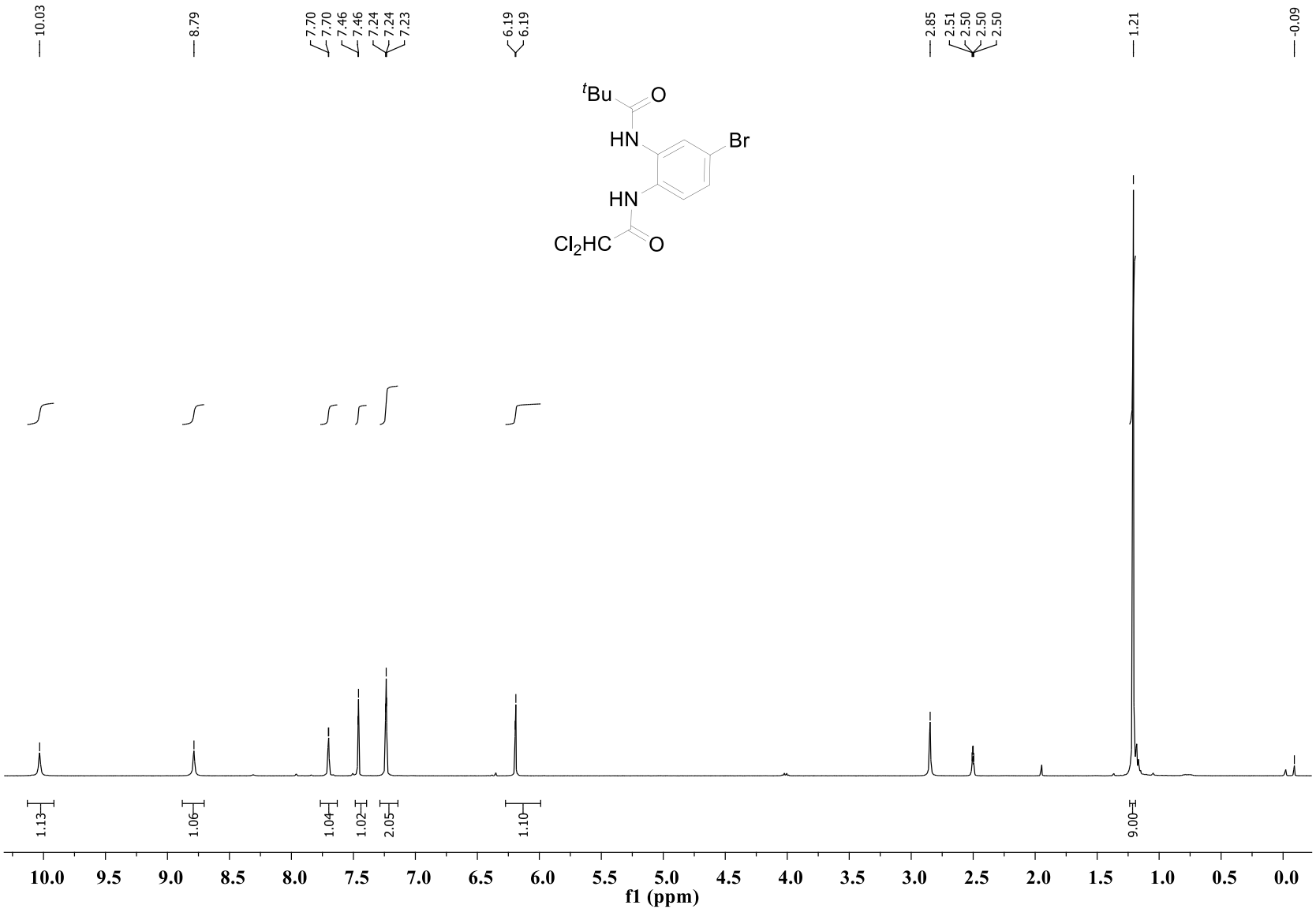
^{13}C NMR spectrum of compound **2r** ($CDCl_3$, 100 MHz)**:**



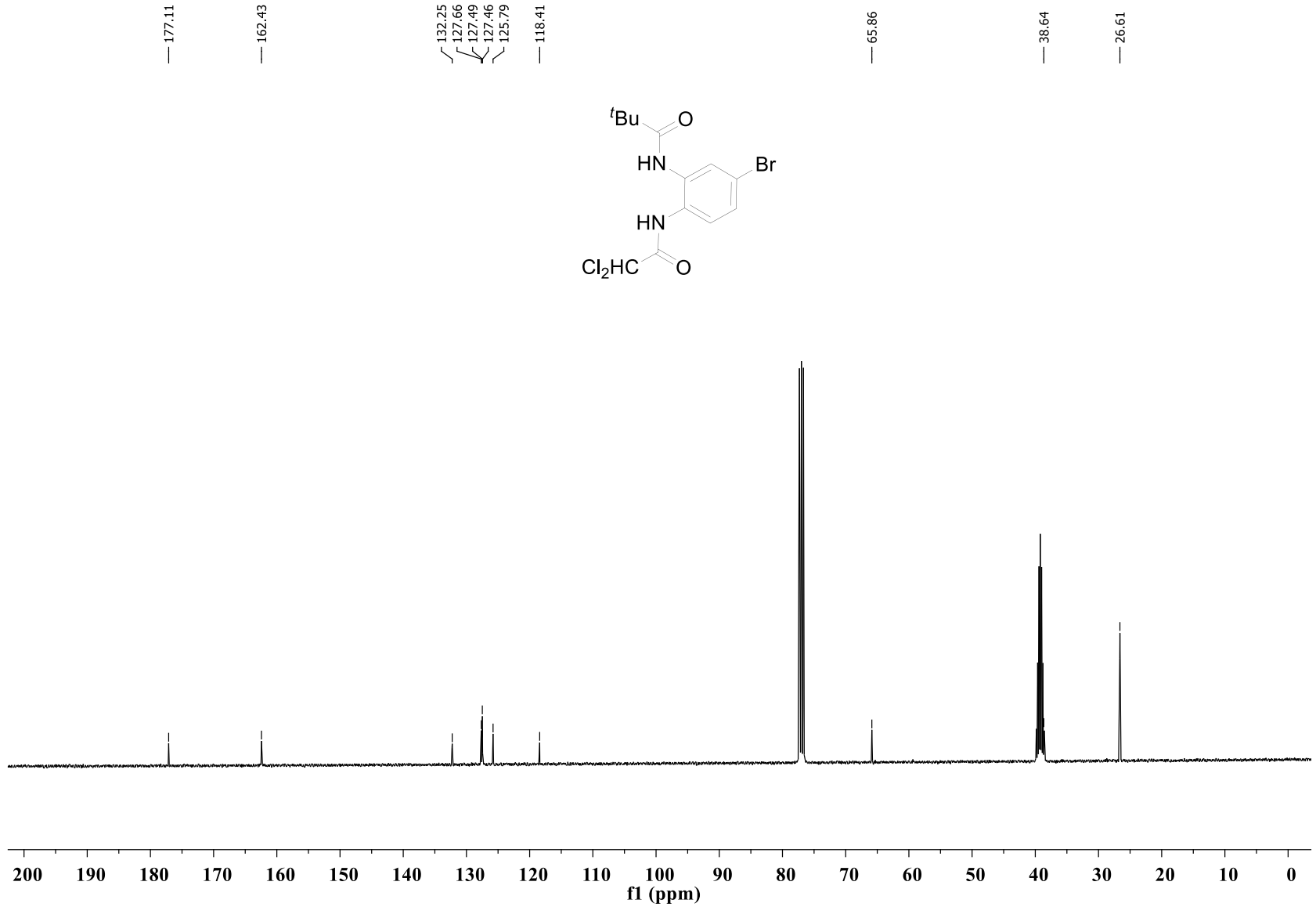
^{19}F NMR spectrum of compound **2r** ($CDCl_3$, 376 MHz):



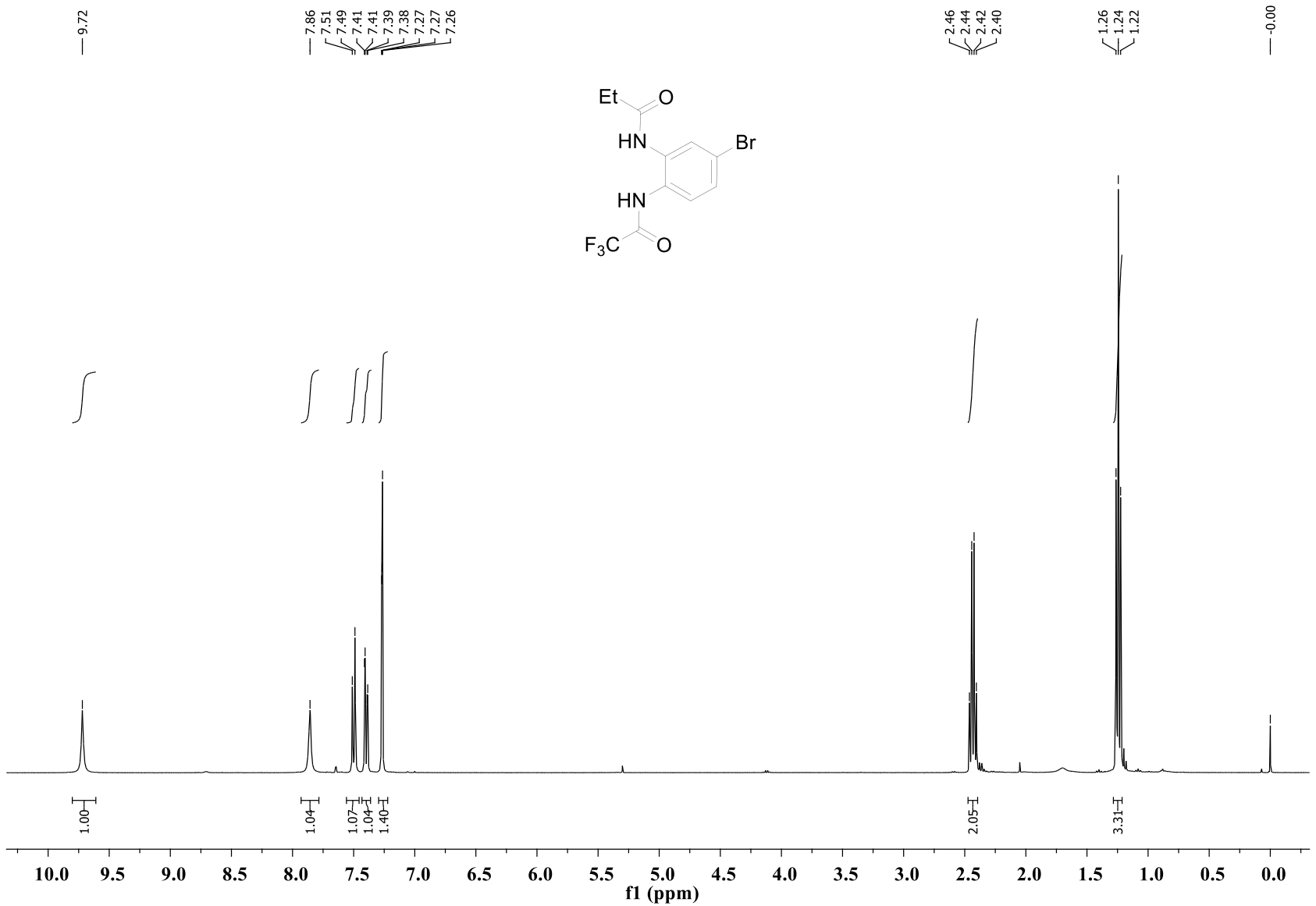
^{1}H NMR spectrum of compound **2s** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



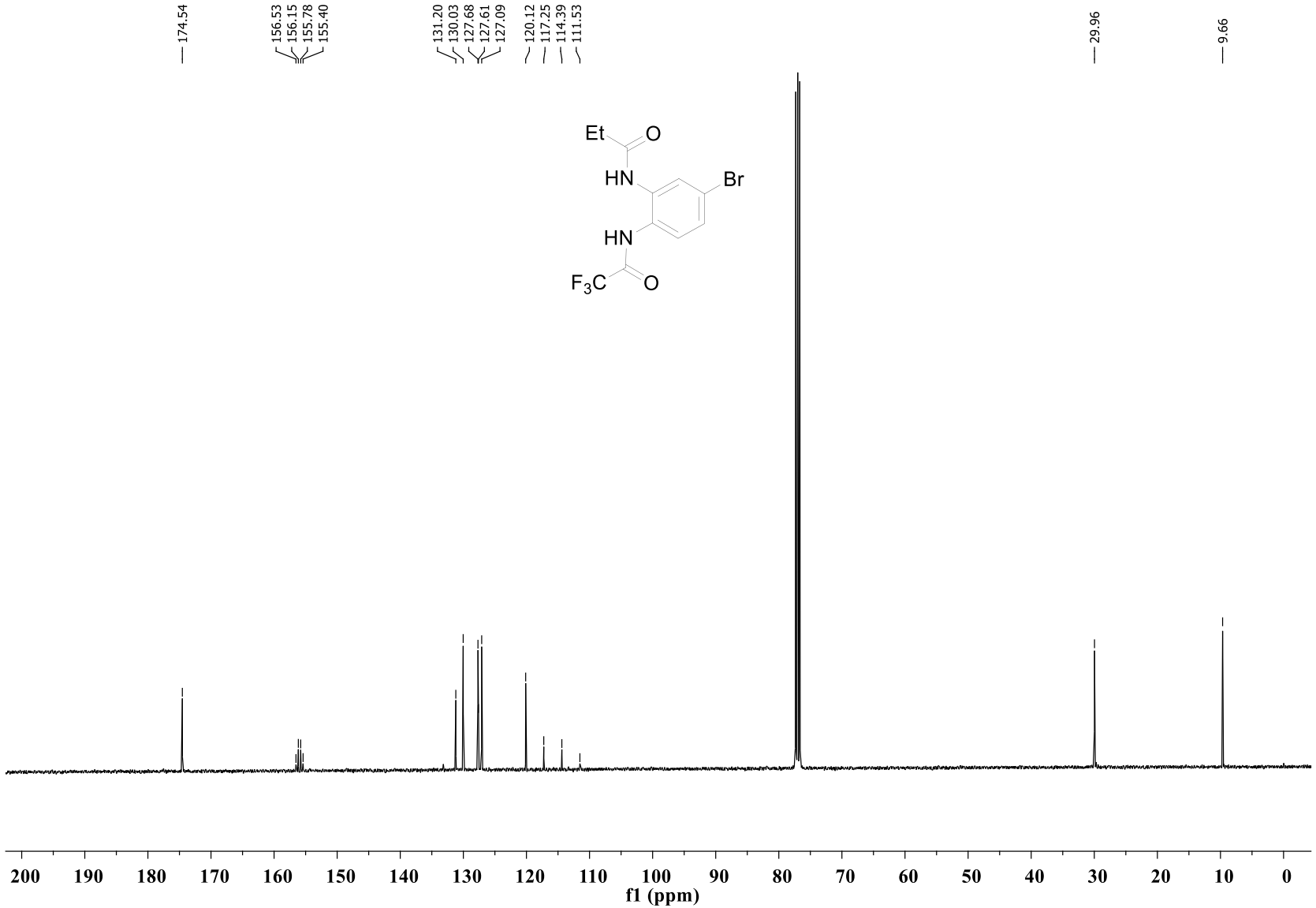
^{13}C NMR spectrum of compound **2s** (8:2, $CDCl_3$ + DMSO-*d6*, 100 MHz)**:**



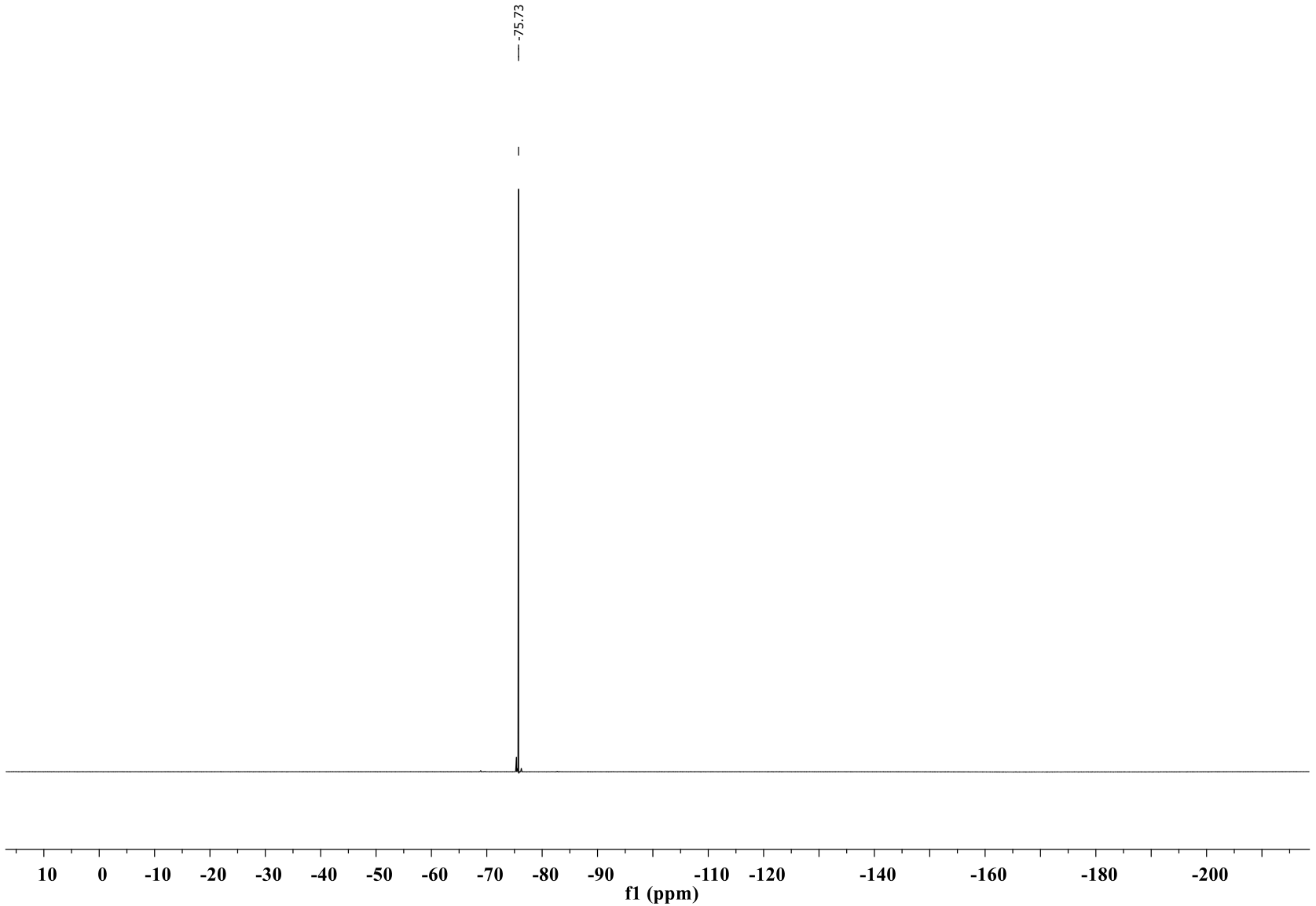
^{1}H NMR spectrum of compound **2t** ($CDCl_3$, 400 MHz)**:**



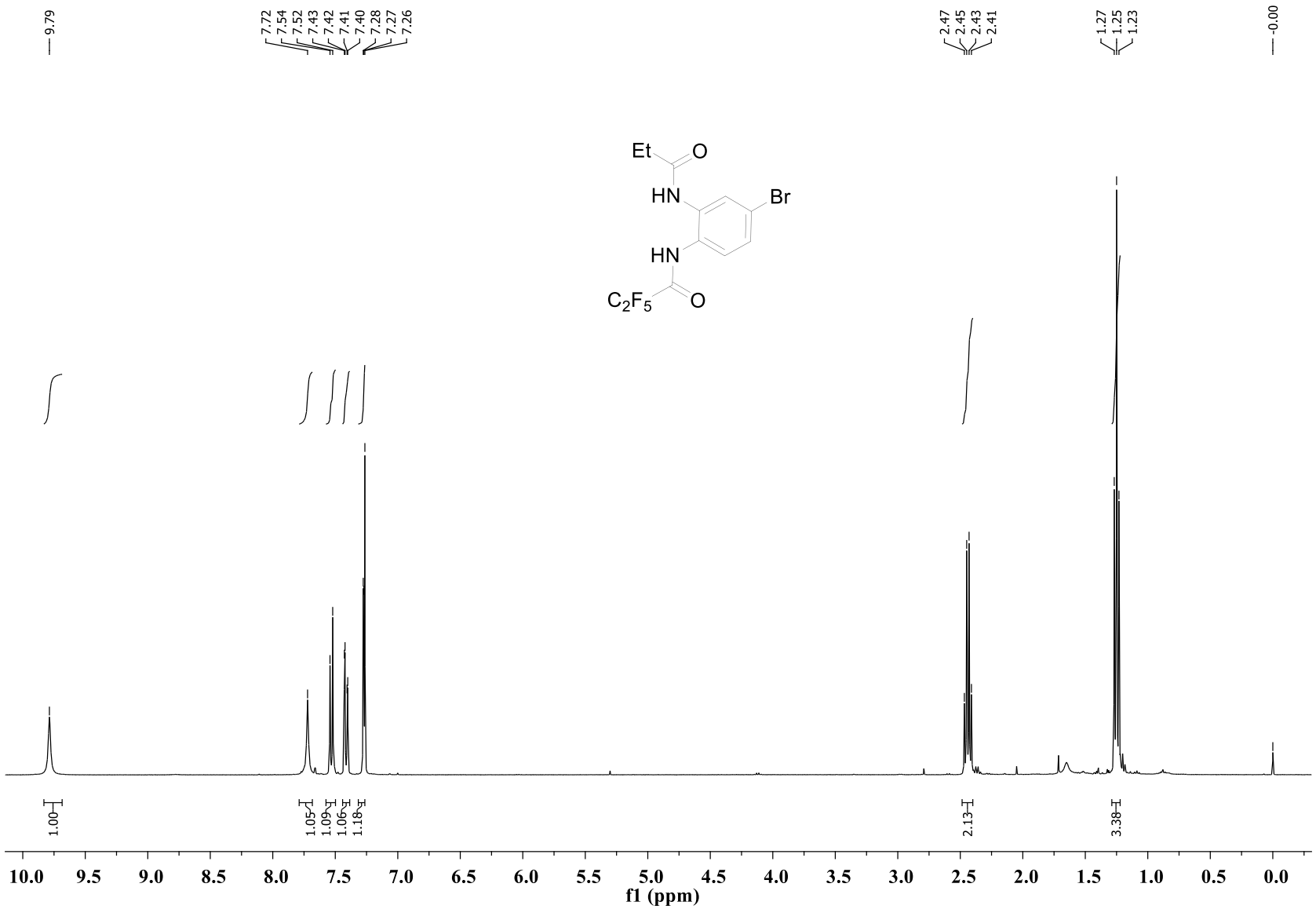
^{13}C NMR spectrum of compound **2t** ($CDCl_3$, 100 MHz)**:**



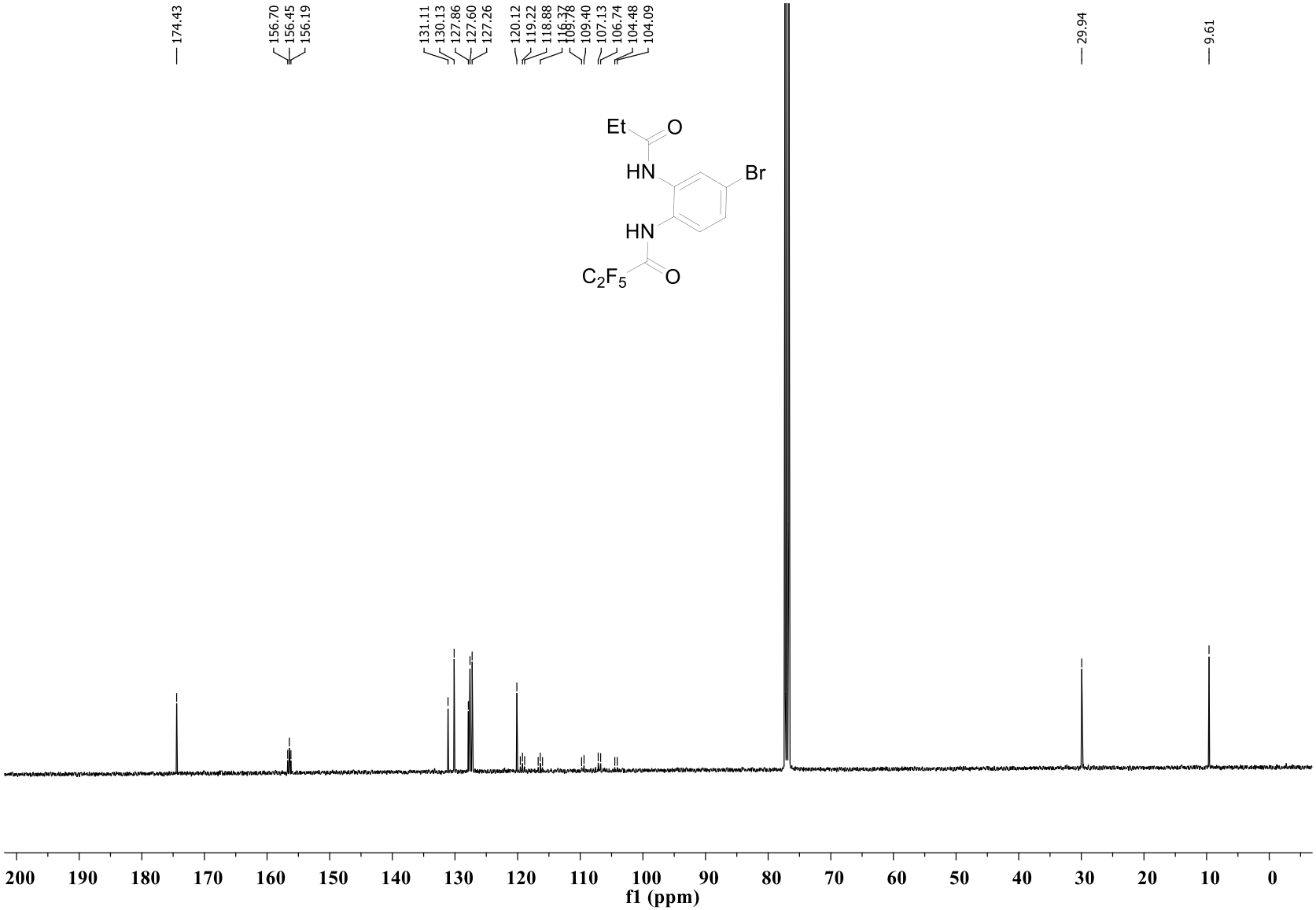
^{19}F NMR spectrum of compound **2t** ($CDCl_3$, 376 MHz):



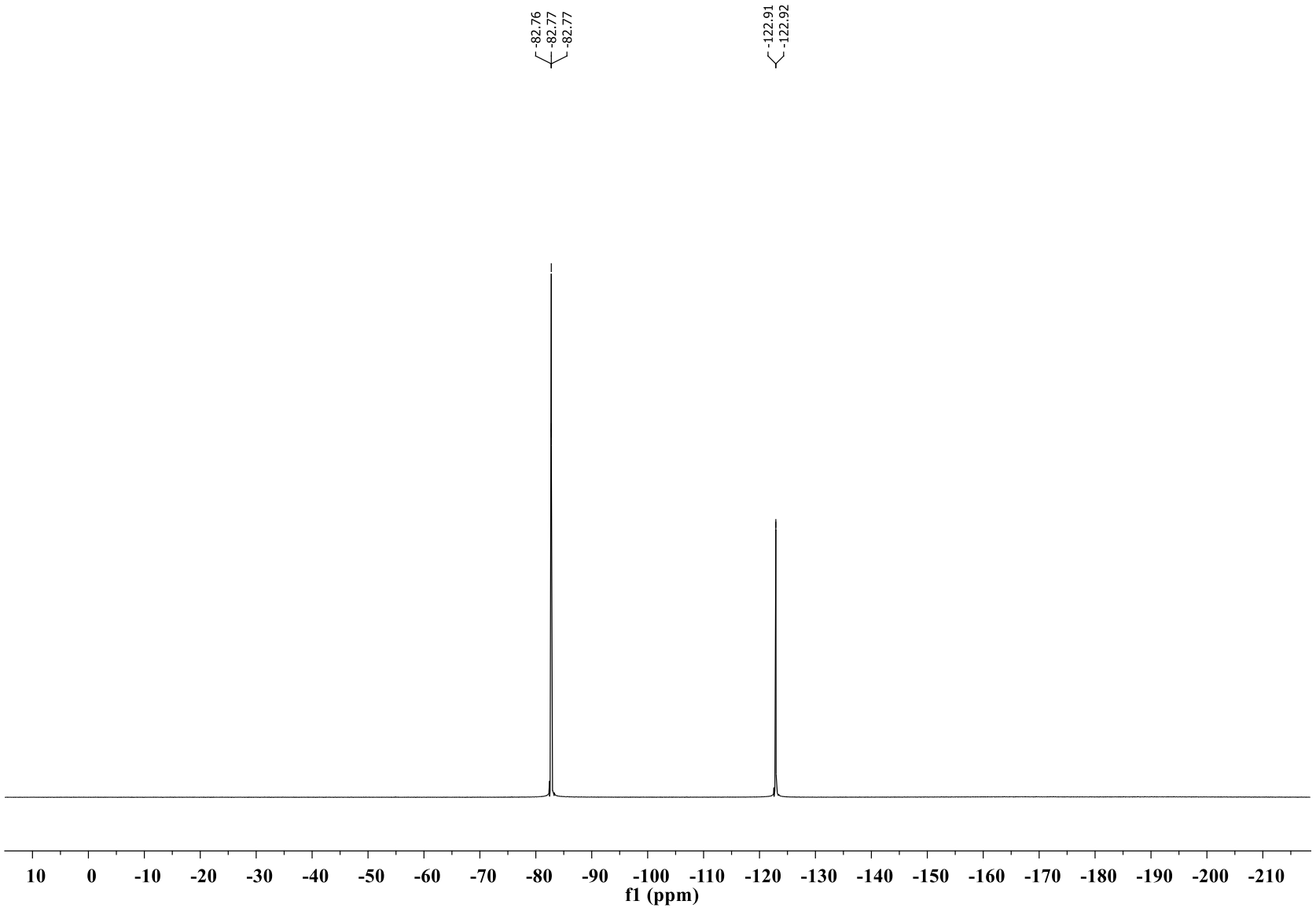
^{1}H NMR spectrum of compound **2u** ($CDCl_3$, 400 MHz)**:**



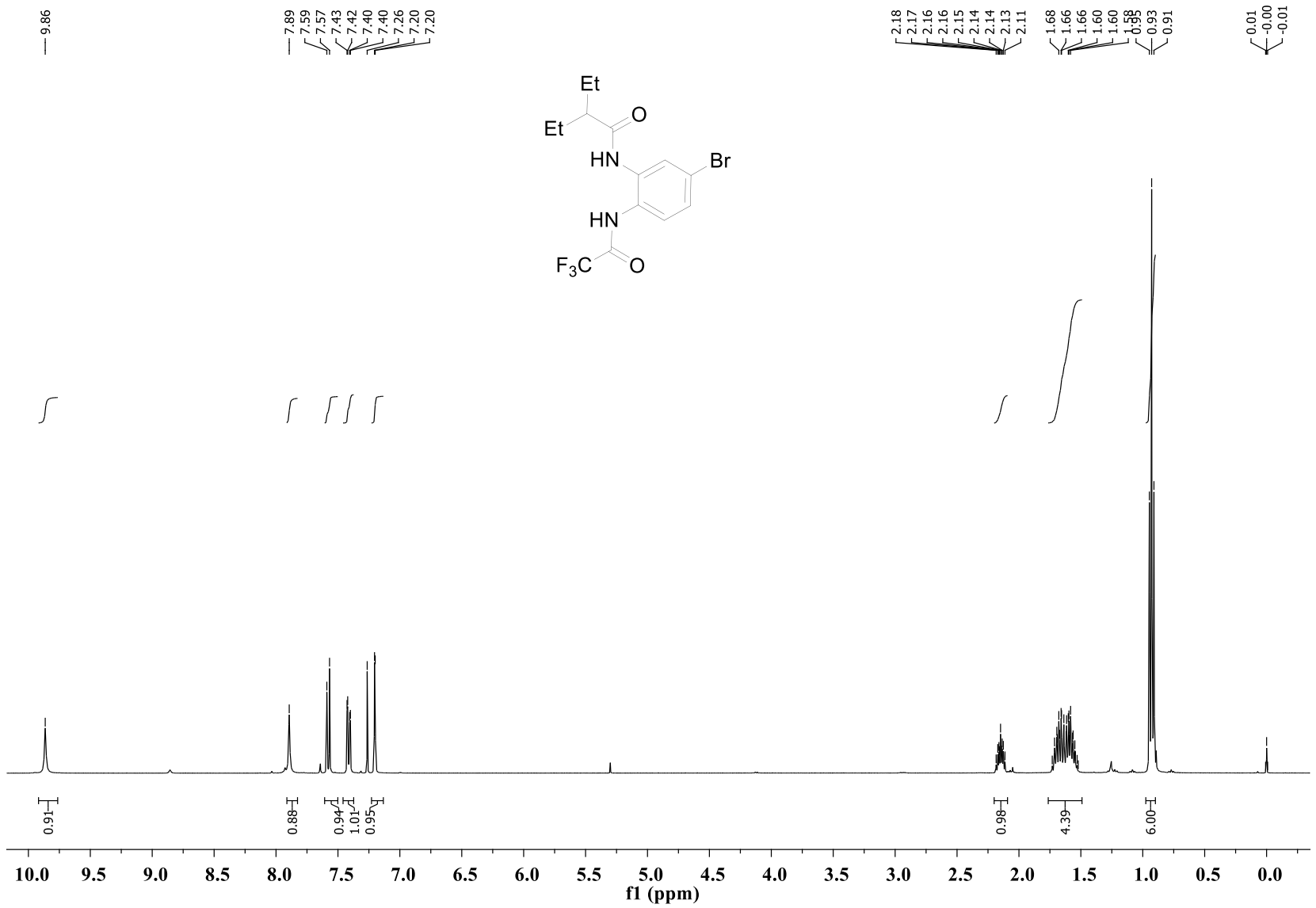
^{13}C NMR spectrum of compound **2u** ($CDCl_3$, 100 MHz)**:**



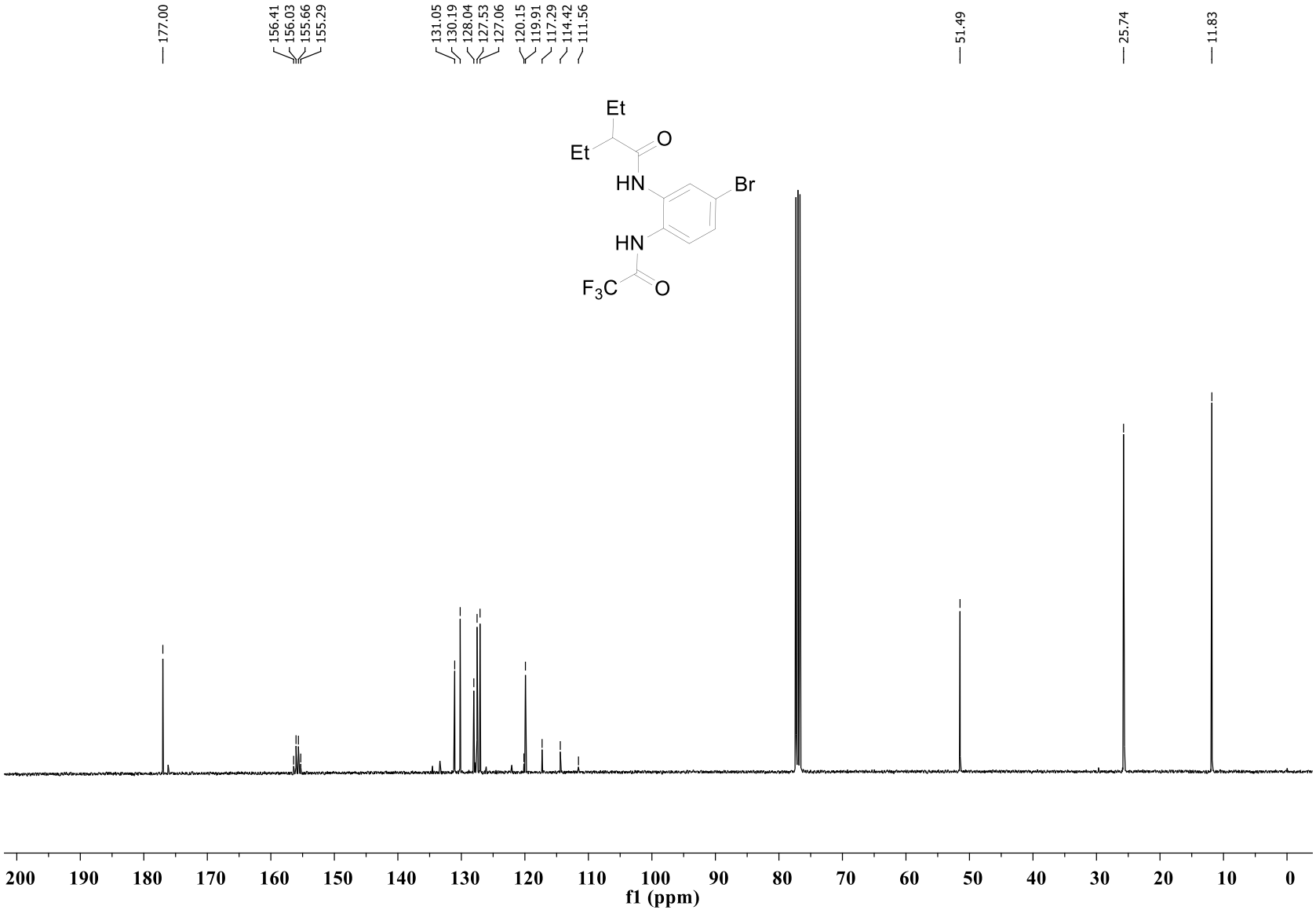
^{19}F NMR spectrum of compound **2u** ($CDCl_3$, 376 MHz):



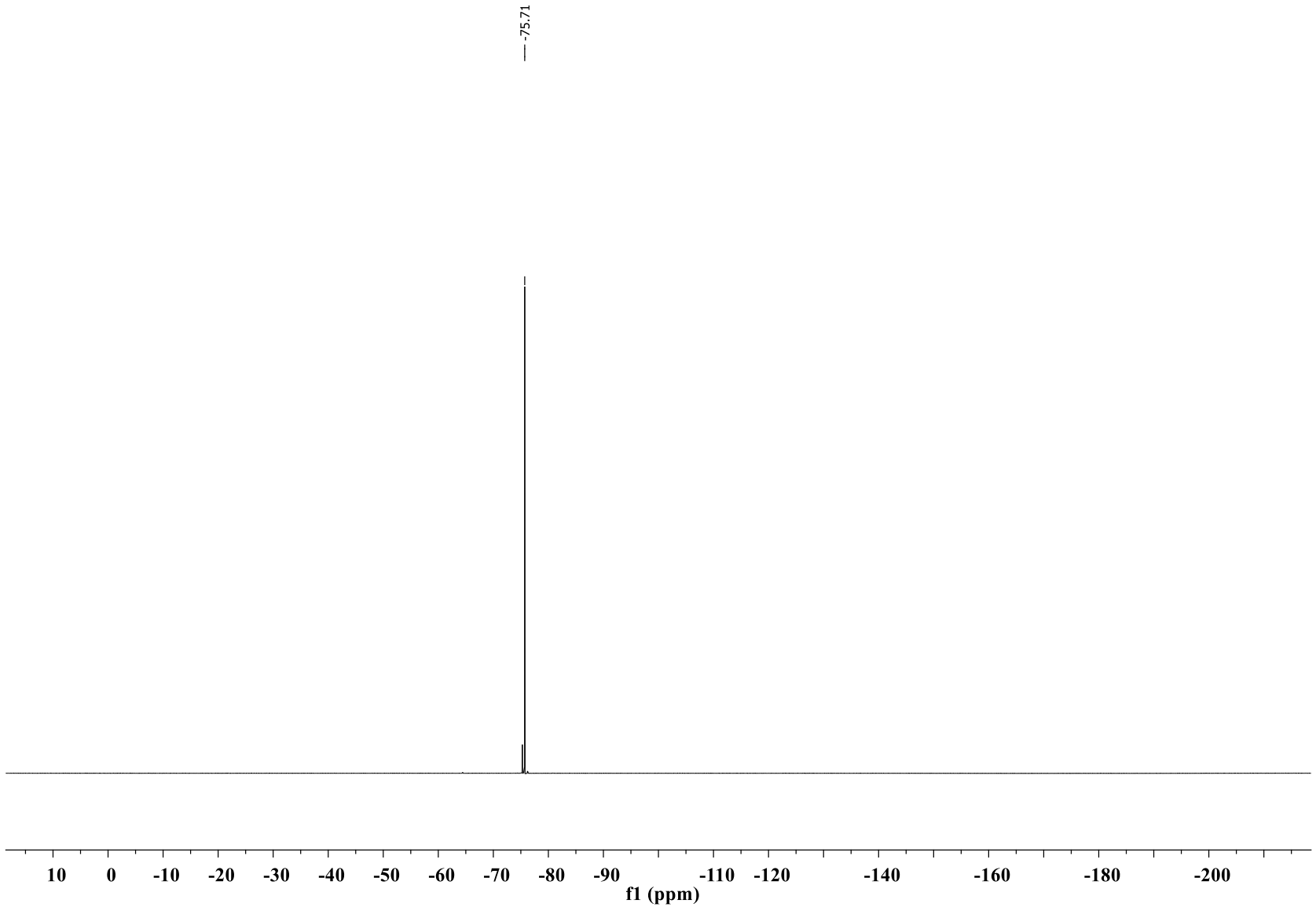
^{1}H NMR spectrum of compound **2v** ($CDCl_3$, 400 MHz):



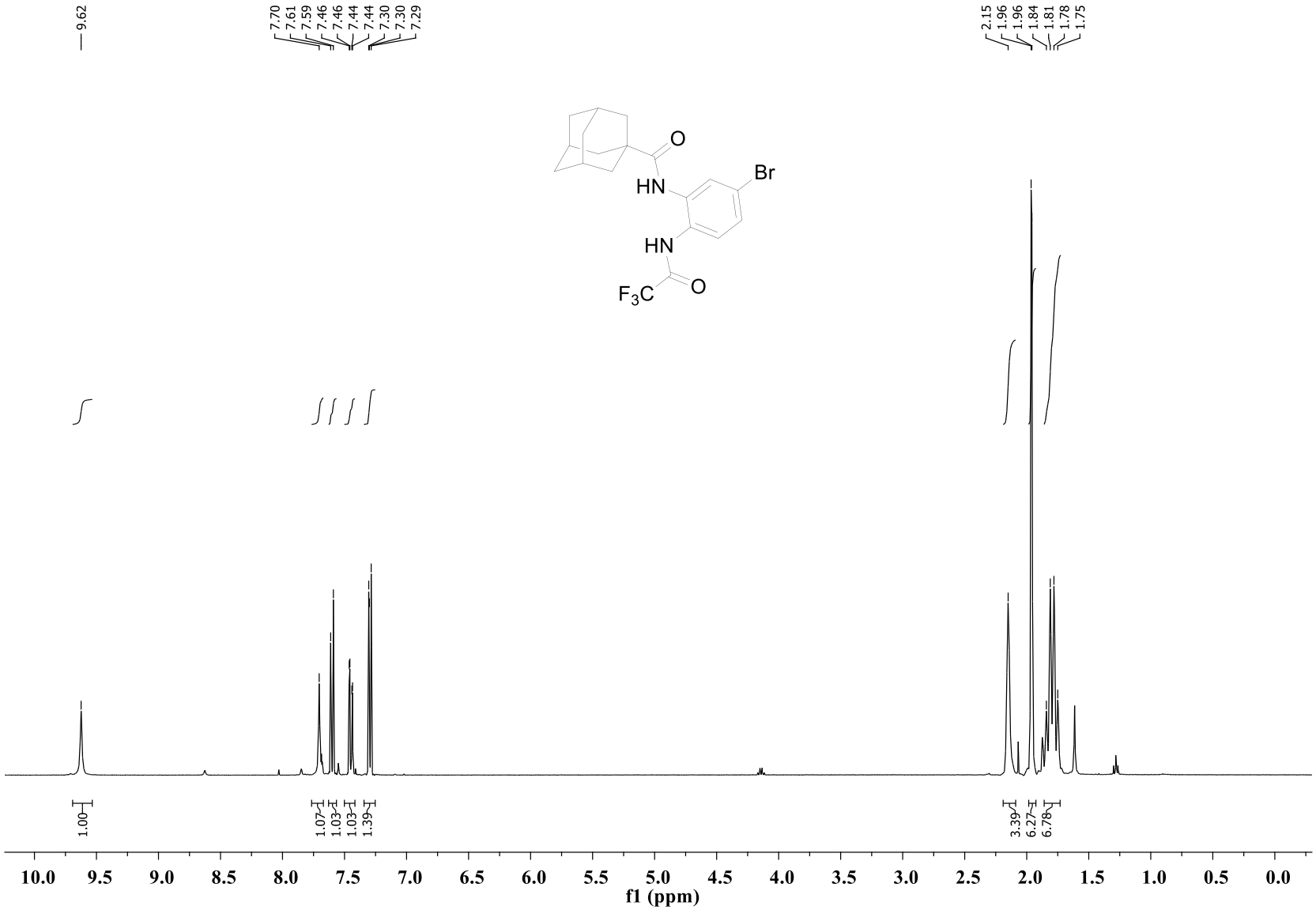
^{13}C NMR spectrum of compound **2v** ($CDCl_3$, 100 MHz)**:**



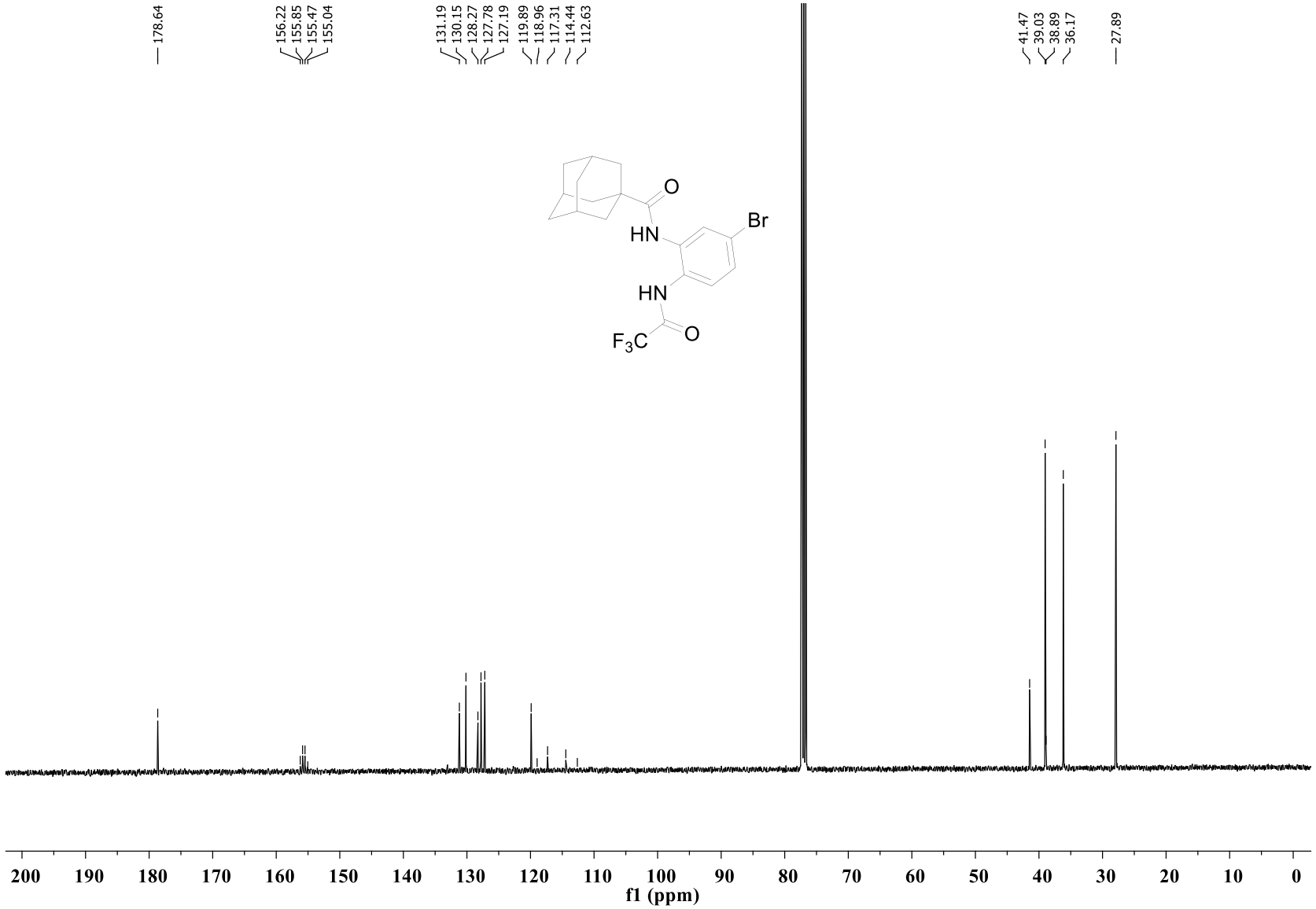
^{19}F NMR spectrum of compound **2v** ($CDCl_3$, 376 MHz):



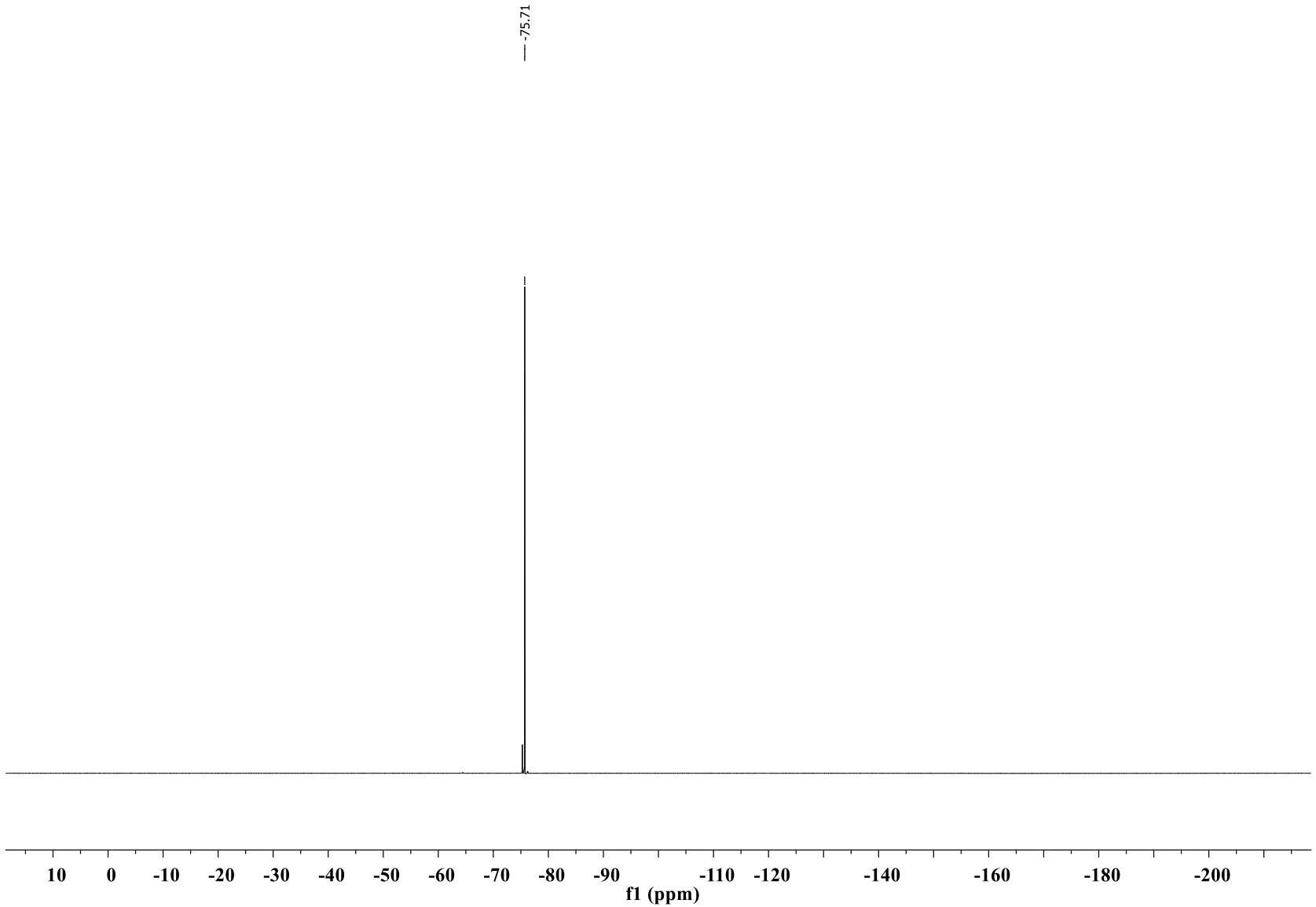
^{1}H NMR spectrum of compound **2w** ($CDCl_3$, 400 MHz)**:**



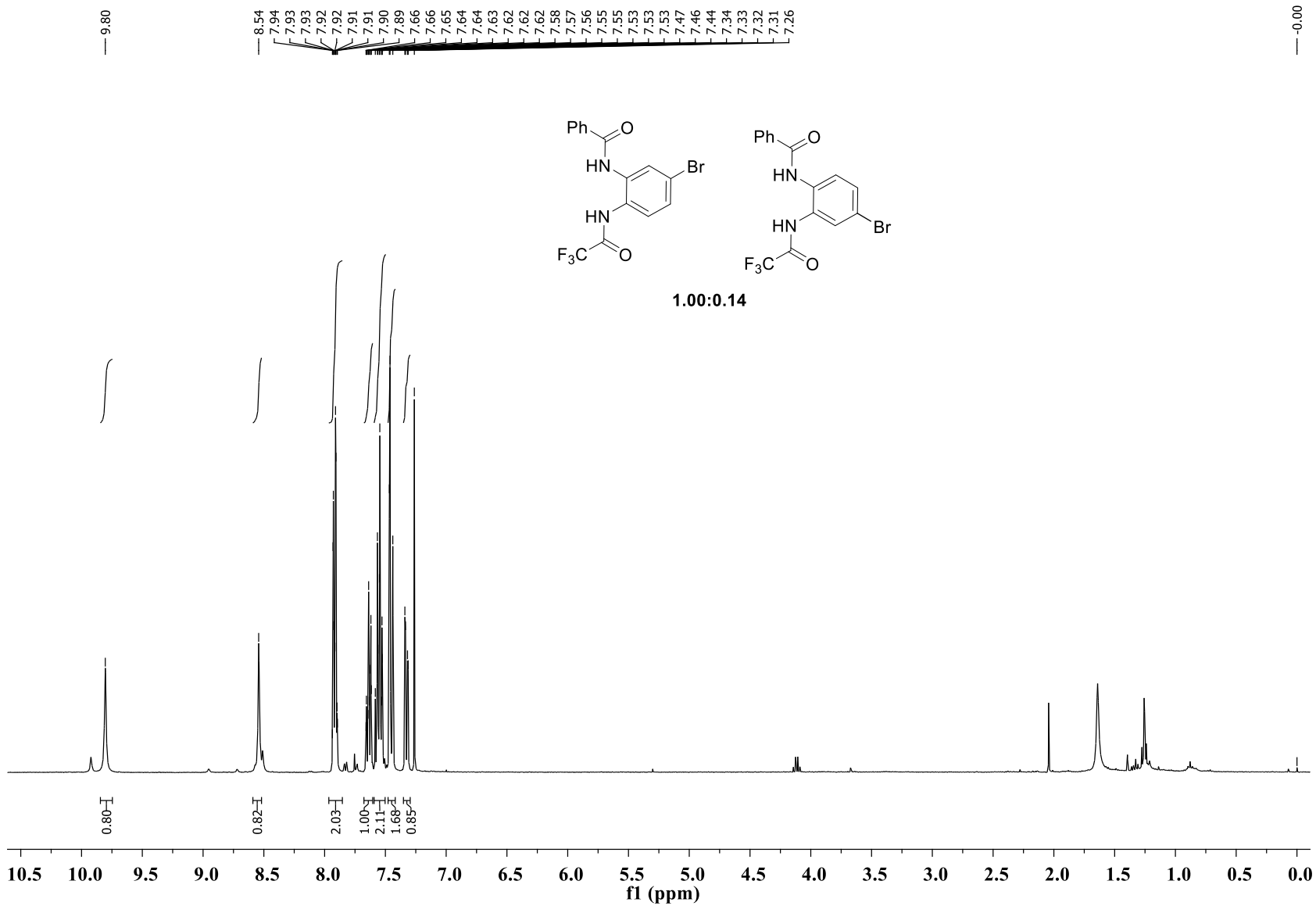
^{13}C NMR spectrum of compound **2w** ($CDCl_3$, 100 MHz)**:**



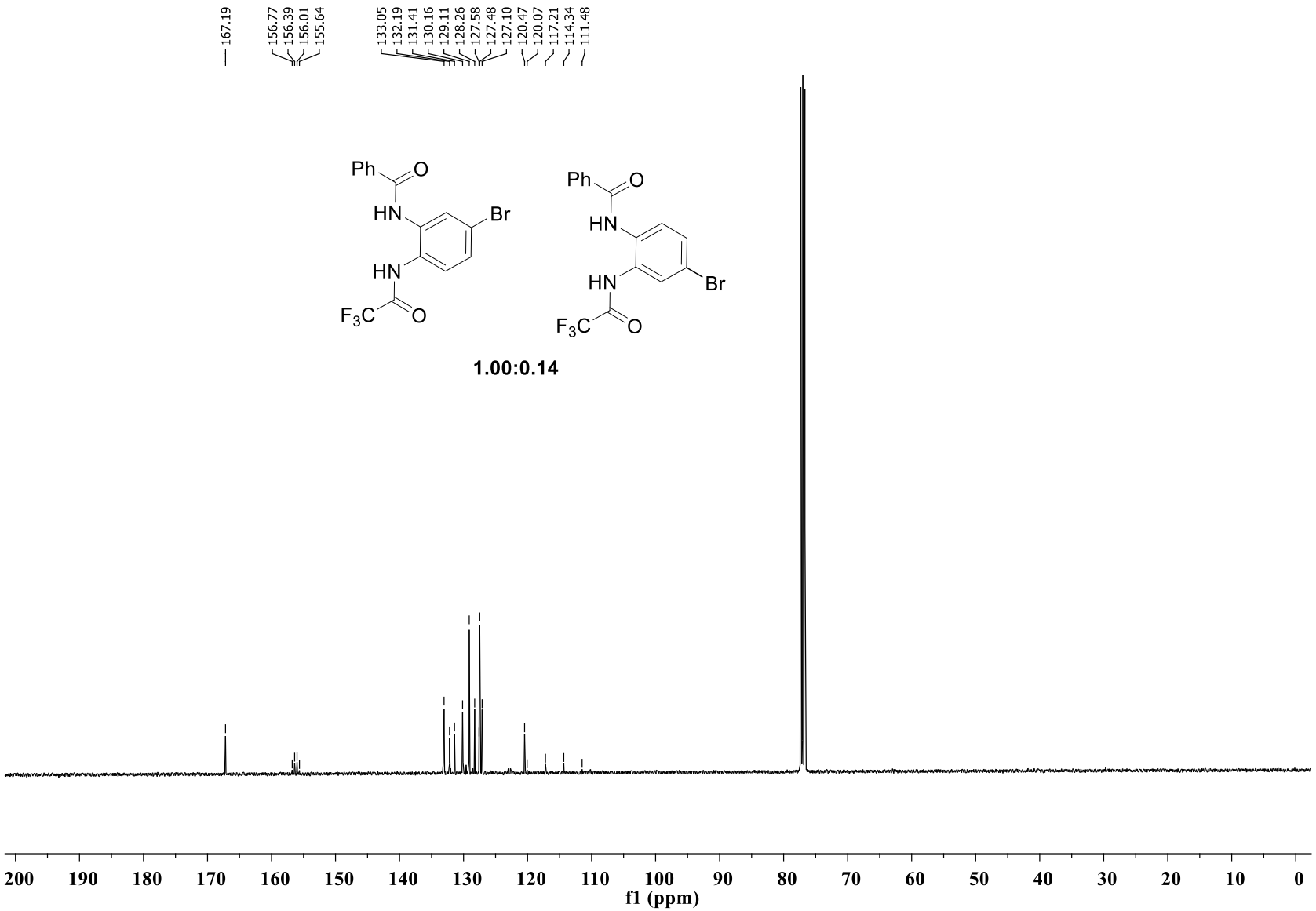
^{19}F NMR spectrum of compound **2w** ($CDCl_3$, 376 MHz):



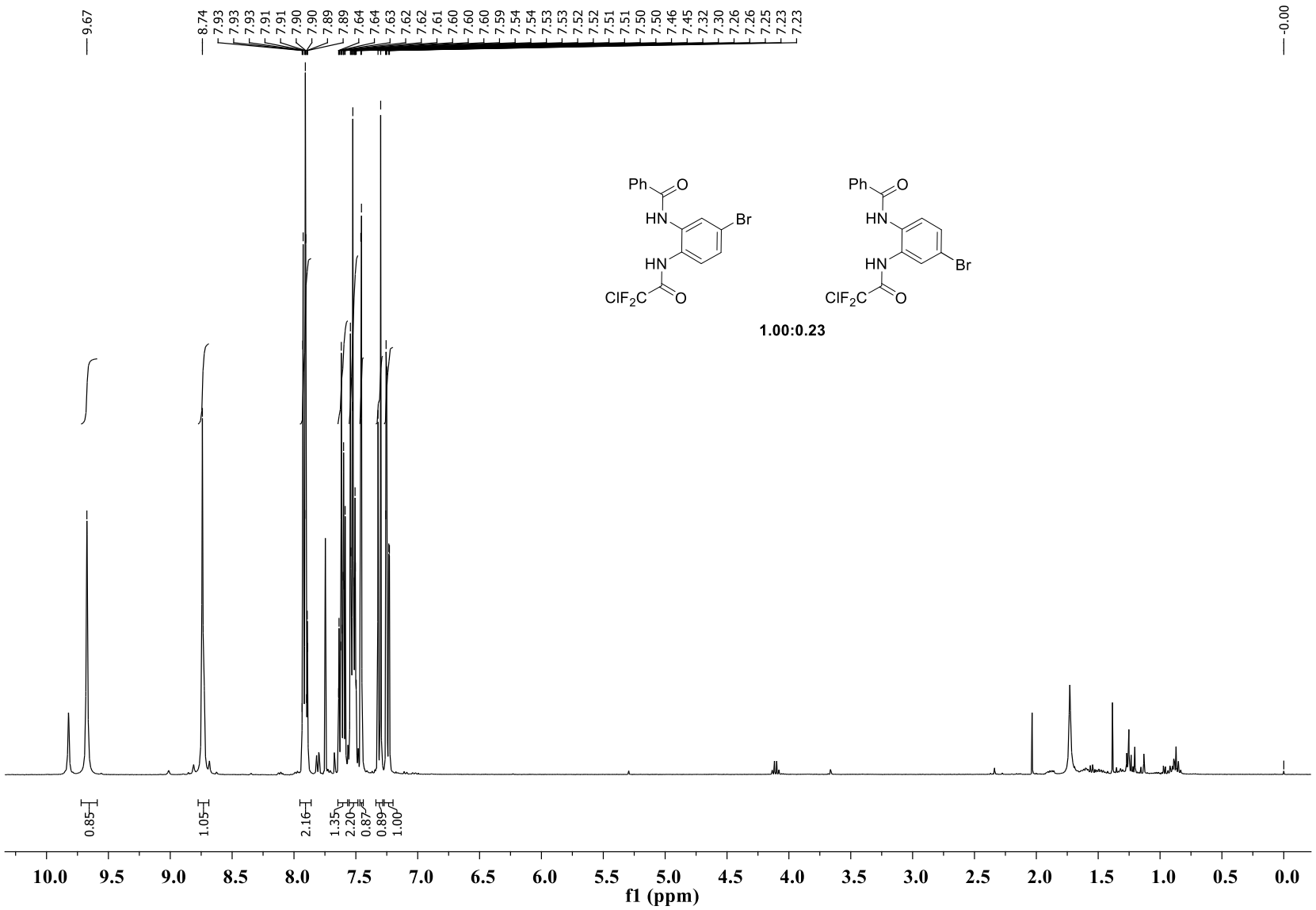
^{1}H NMR spectrum of compound **2x** ($CDCl_3$, 400 MHz):



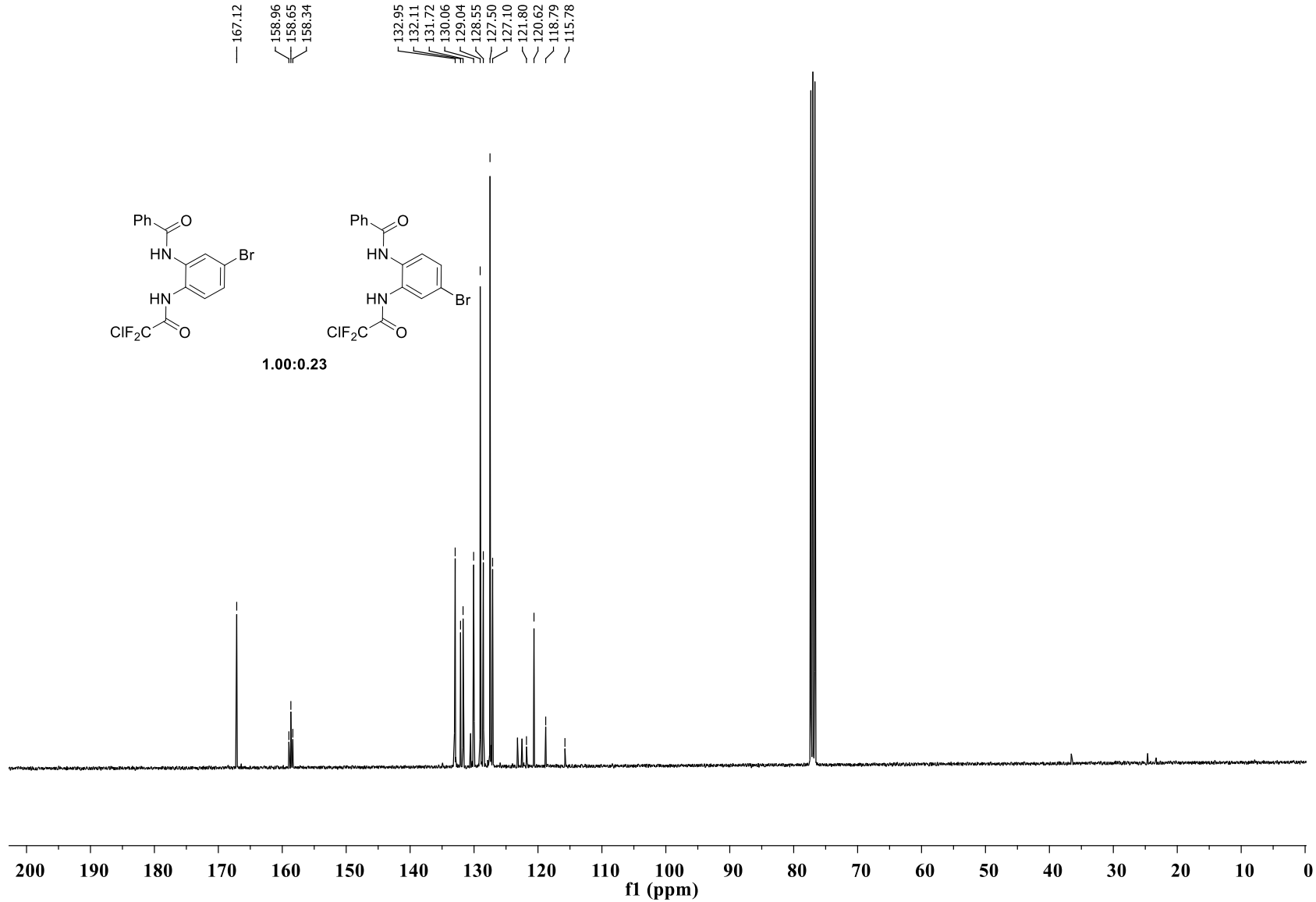
^{13}C NMR spectrum of compound **2x** ($CDCl_3$, 100 MHz)**:**



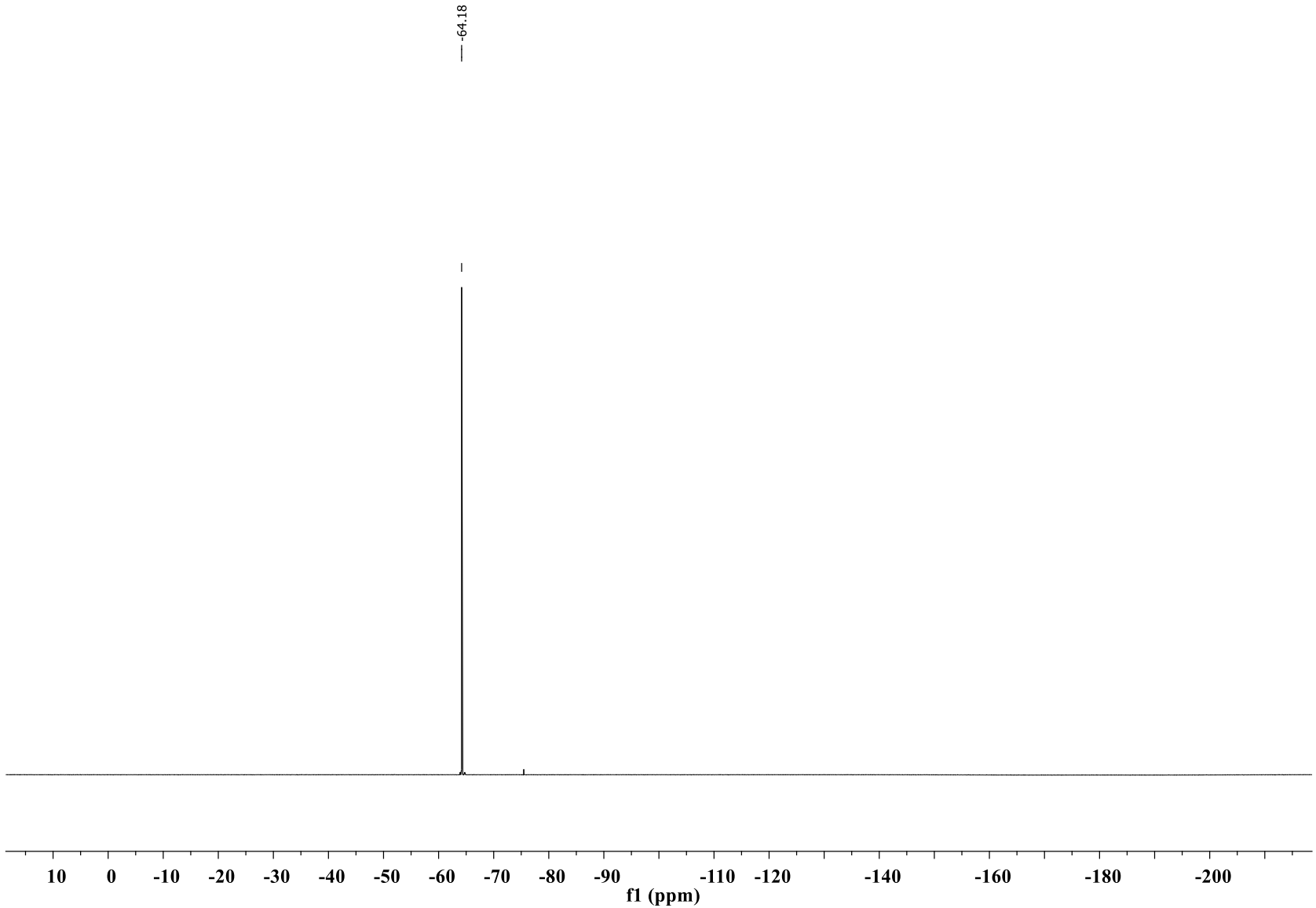
^{1}H NMR spectrum of compound **2y** ($CDCl_3$, 400 MHz)**:**



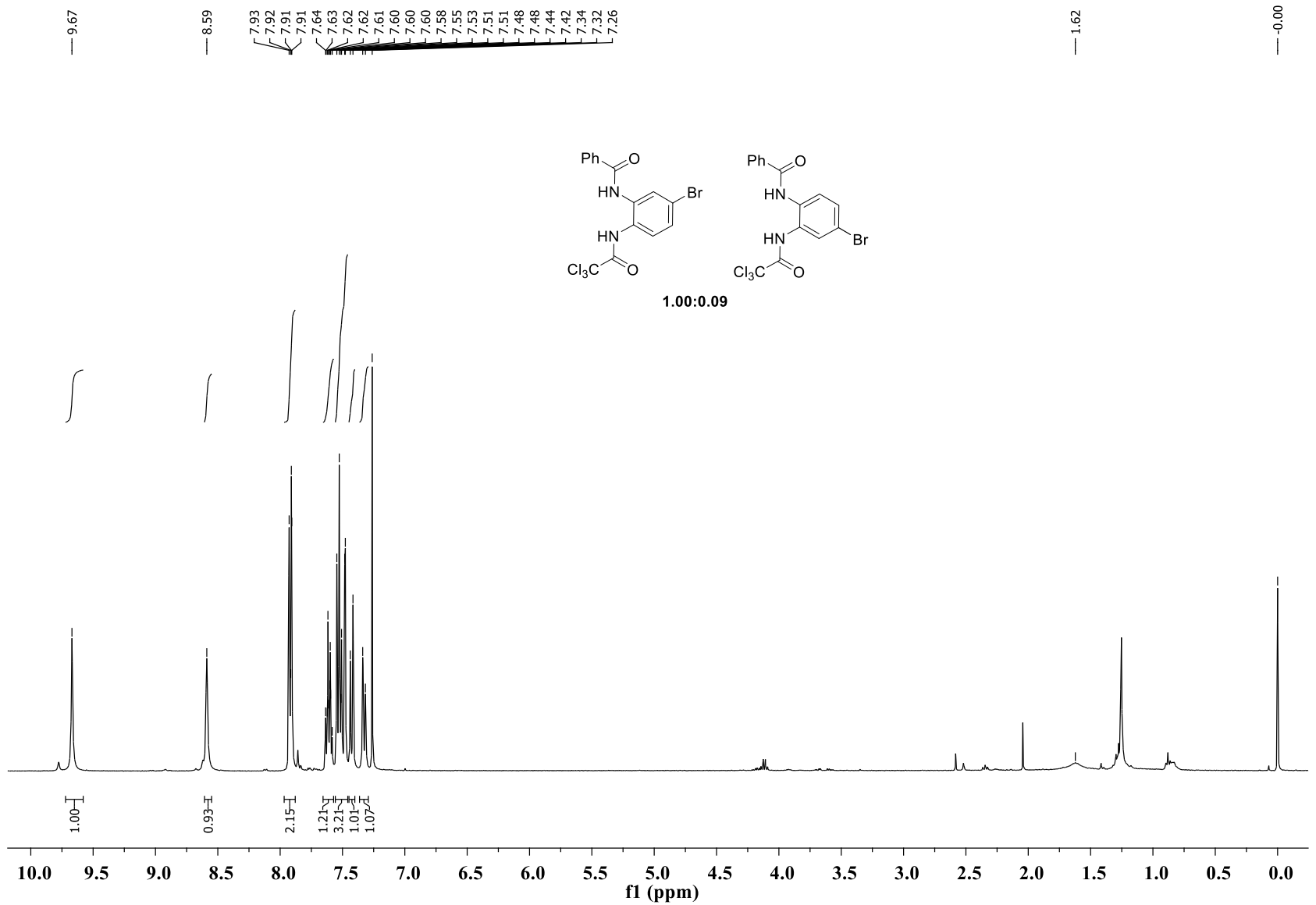
^{13}C NMR spectrum of compound **2y** ($CDCl_3$, 100 MHz)**:**



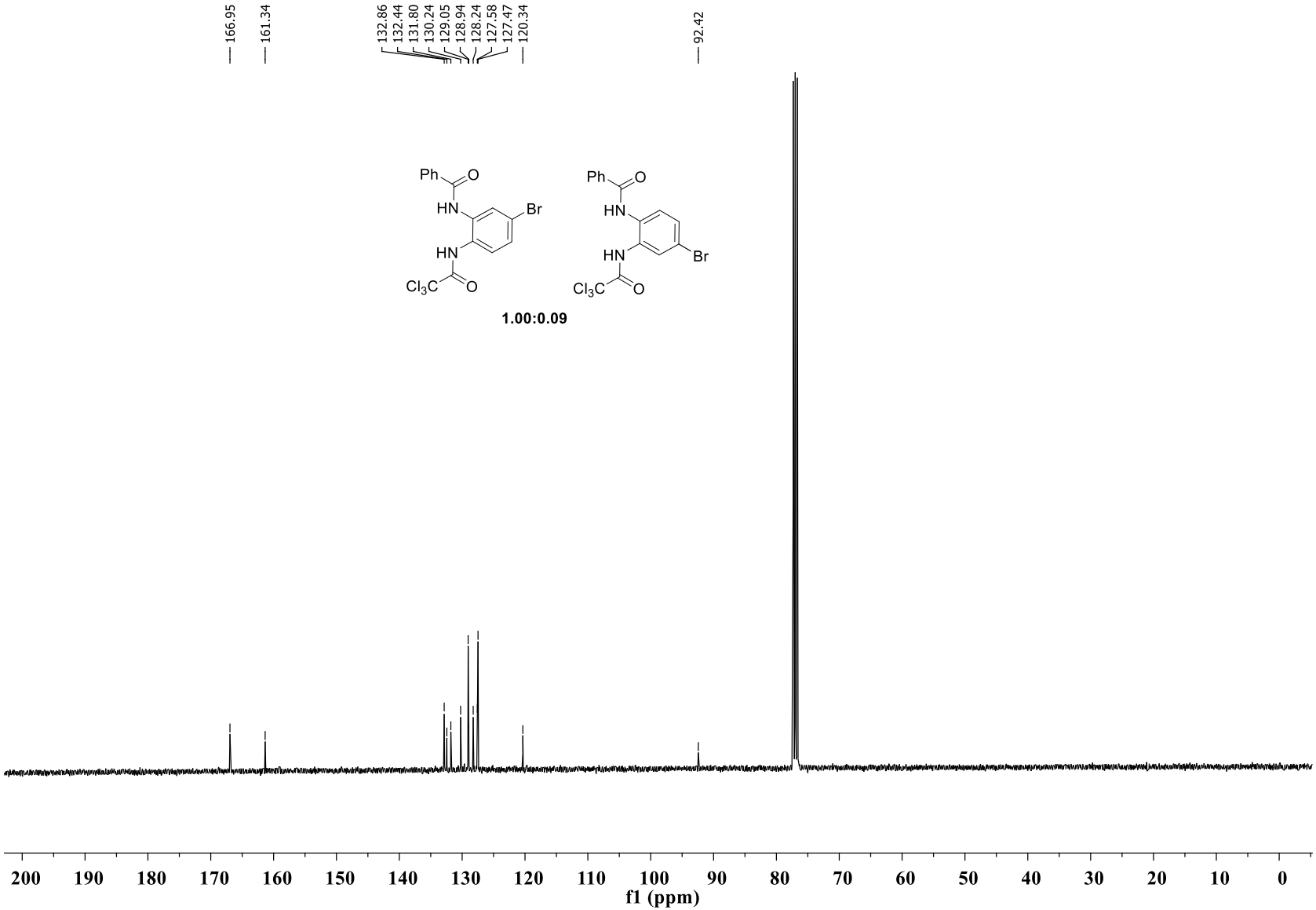
^{19}F NMR spectrum of compound **2y** ($CDCl_3$, 376 MHz):



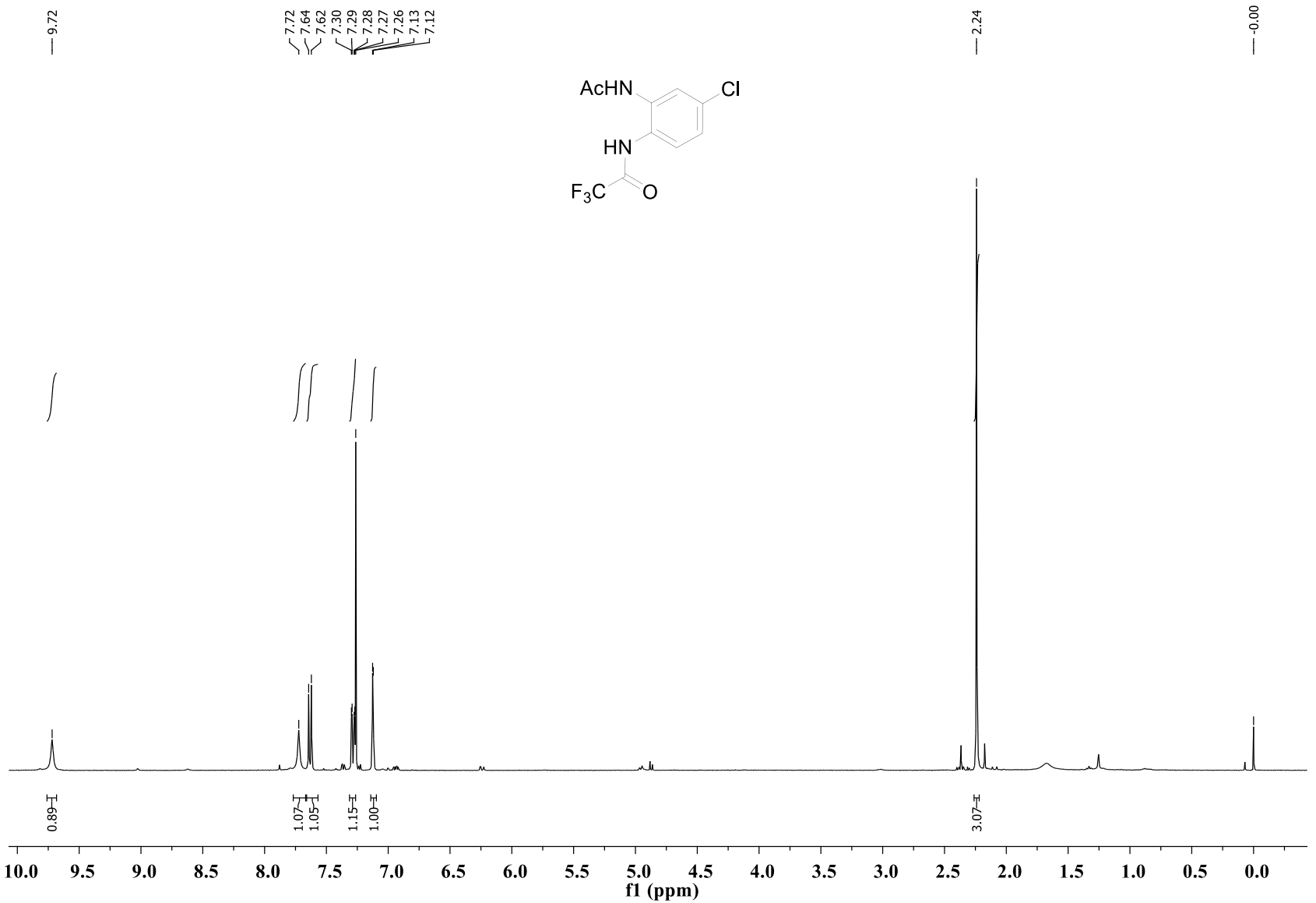
^{1}H NMR spectrum of compound **2z** ($CDCl_3$, 400 MHz)**:**



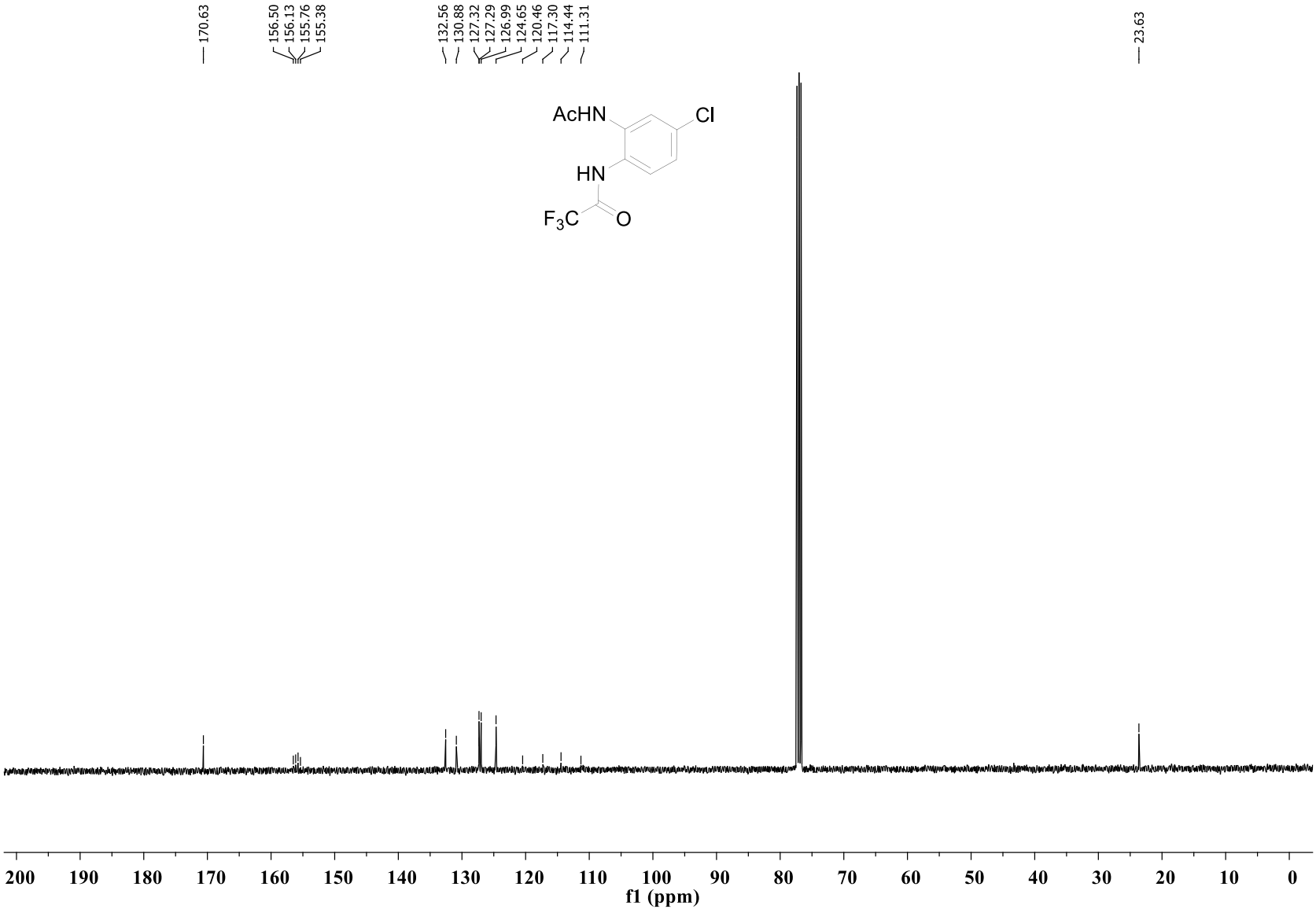
^{13}C NMR spectrum of compound **2z** ($CDCl_3$, 100 MHz)**:**



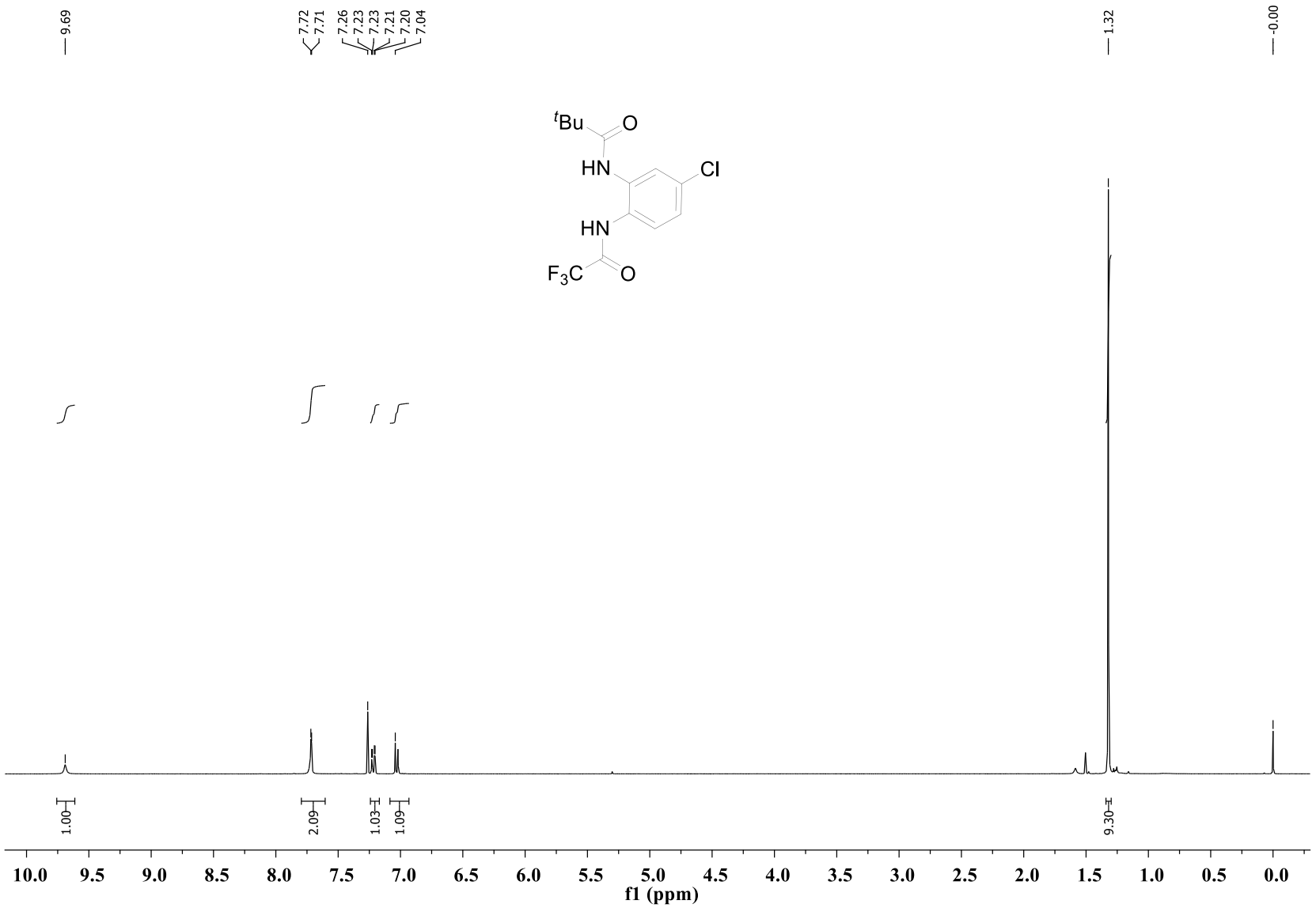
^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz)**:**



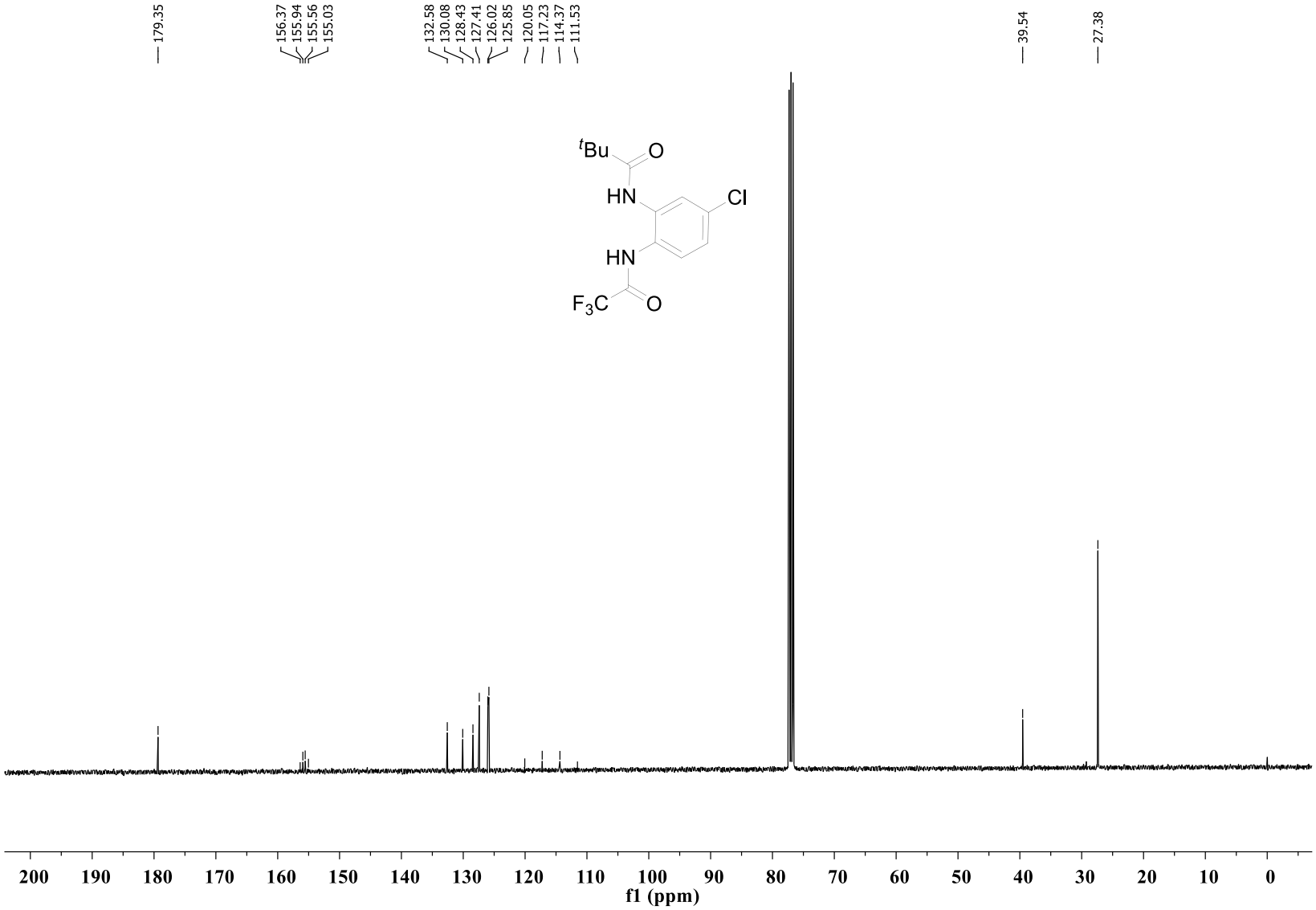
^{13}C NMR spectrum of compound **3a** ($CDCl_3$, 100 MHz)**:**



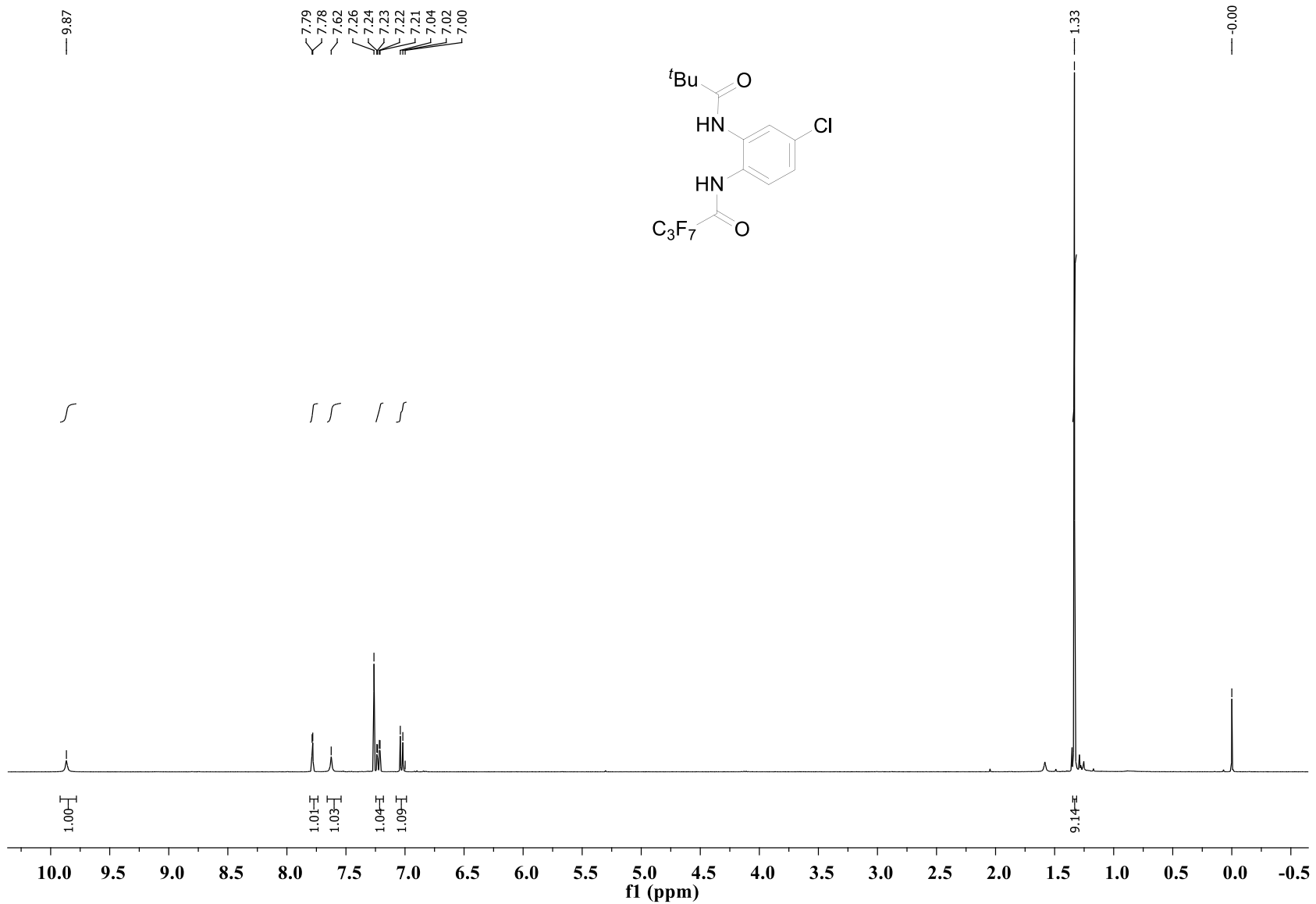
^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz)**:**



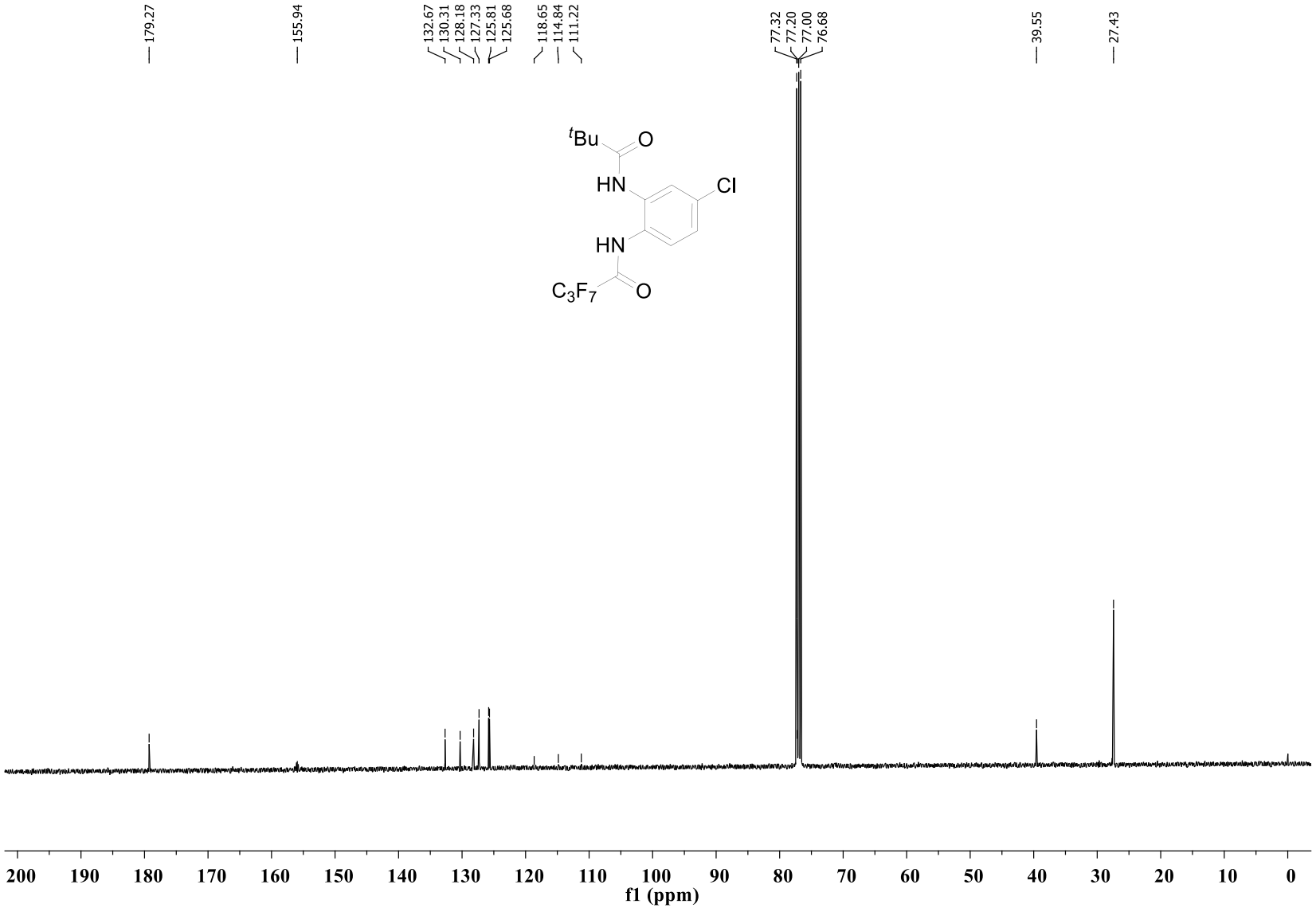
^{13}C NMR spectrum of compound **3b** ($CDCl_3$, 100 MHz)**:**



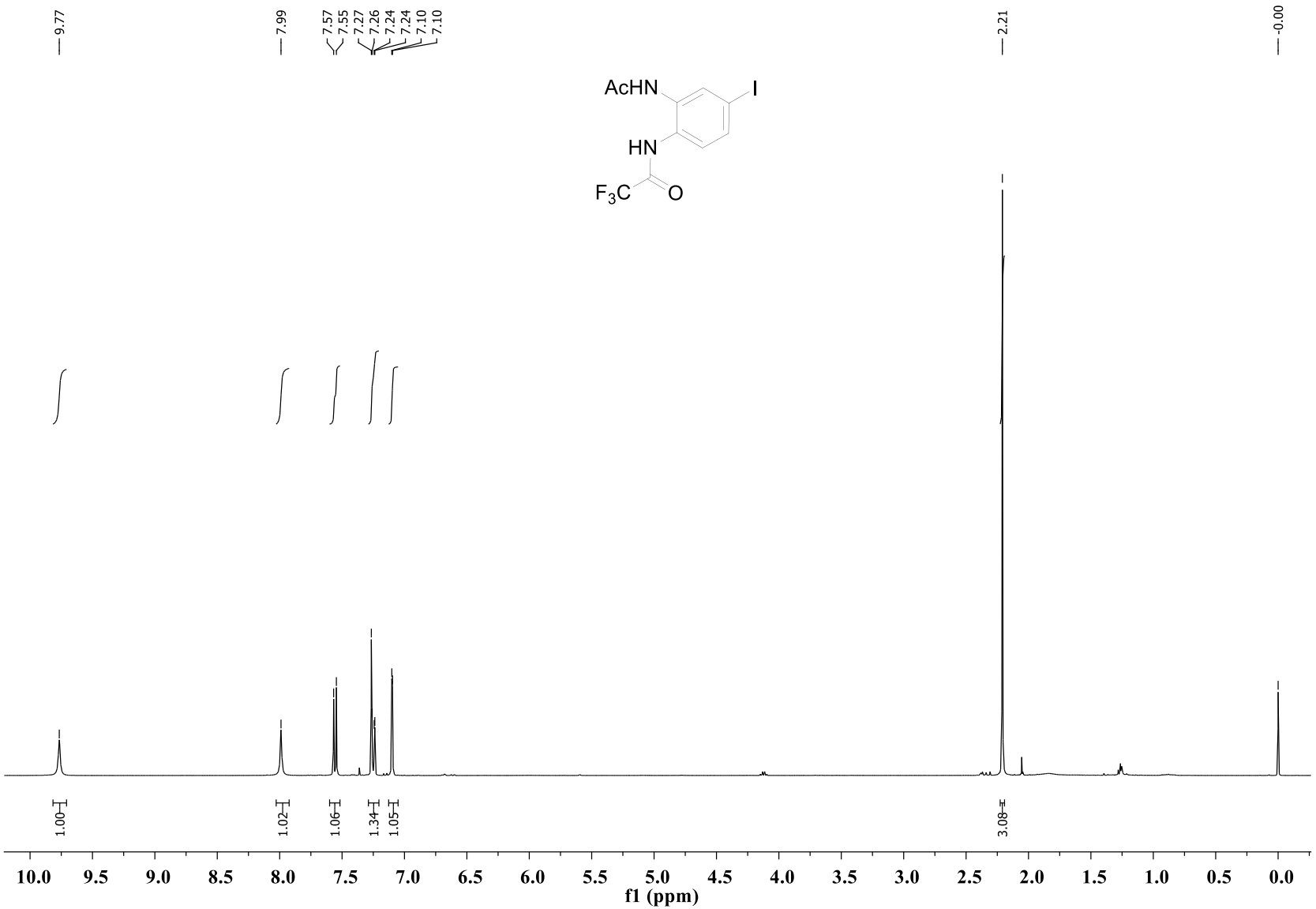
^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 400 MHz)**:**



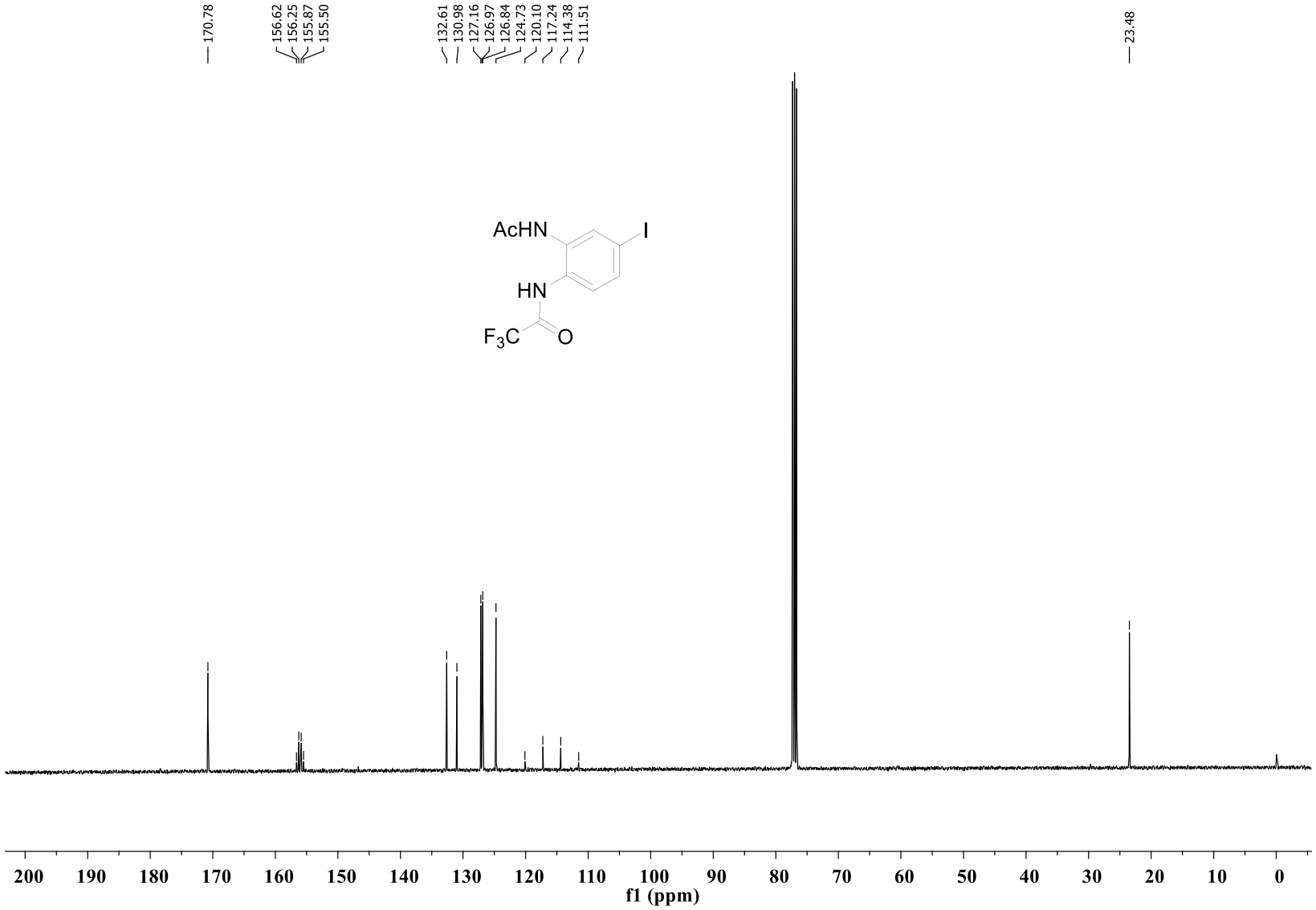
^{13}C NMR spectrum of compound **3c** ($CDCl_3$, 100 MHz)**:**



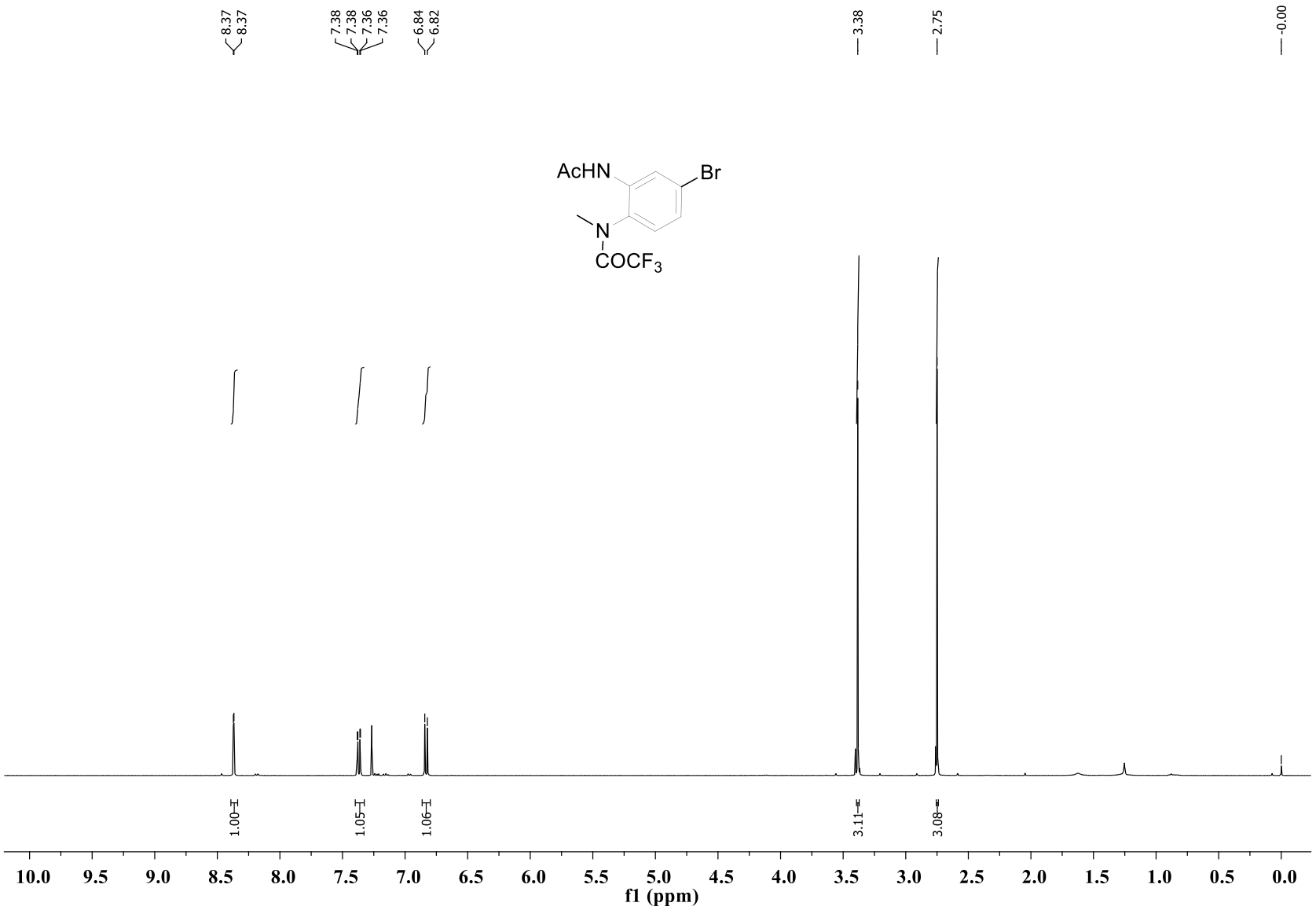
^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 400 MHz)**:**



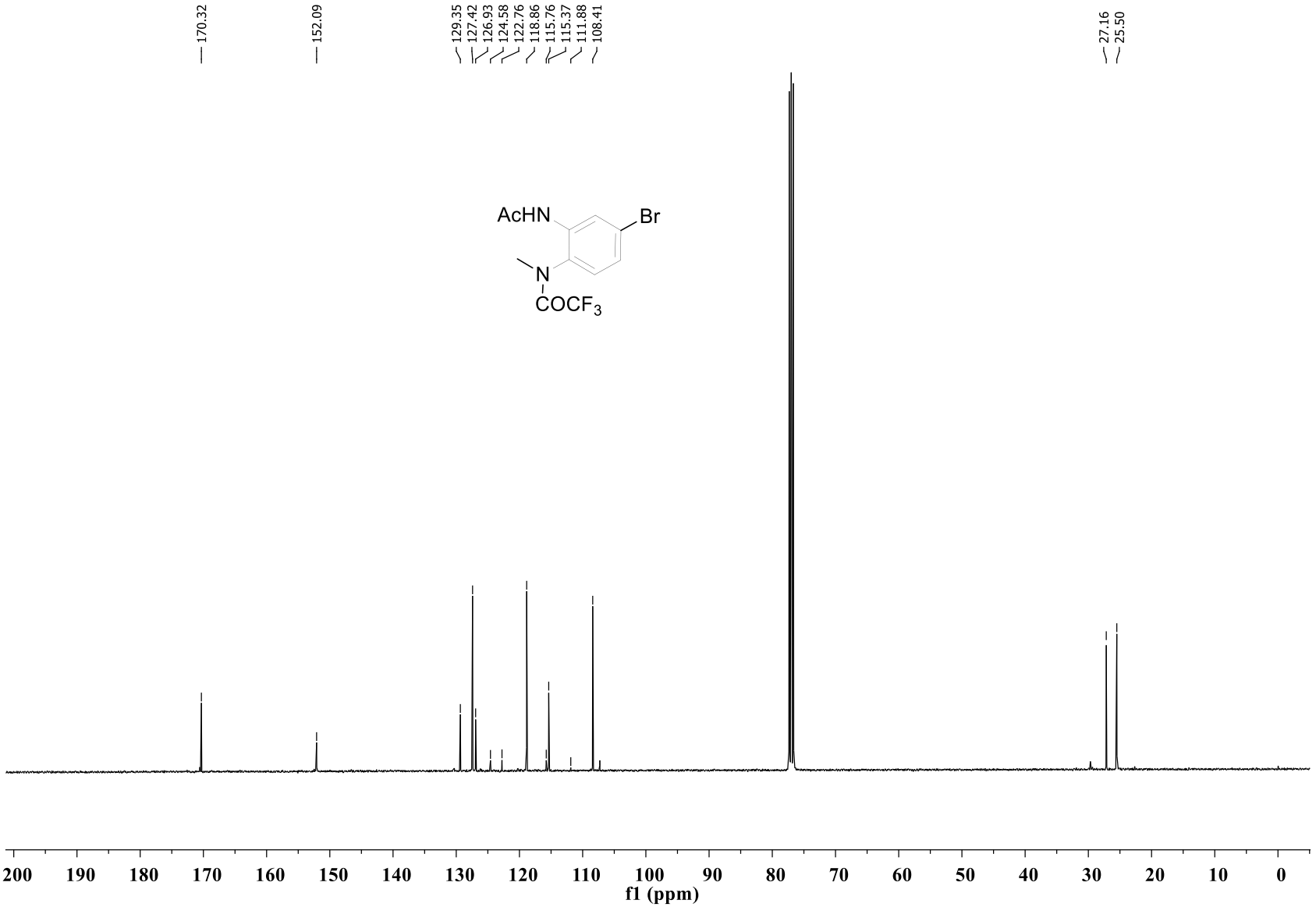
^{13}C NMR spectrum of compound **3d** ($CDCl_3$, 100 MHz)**:**



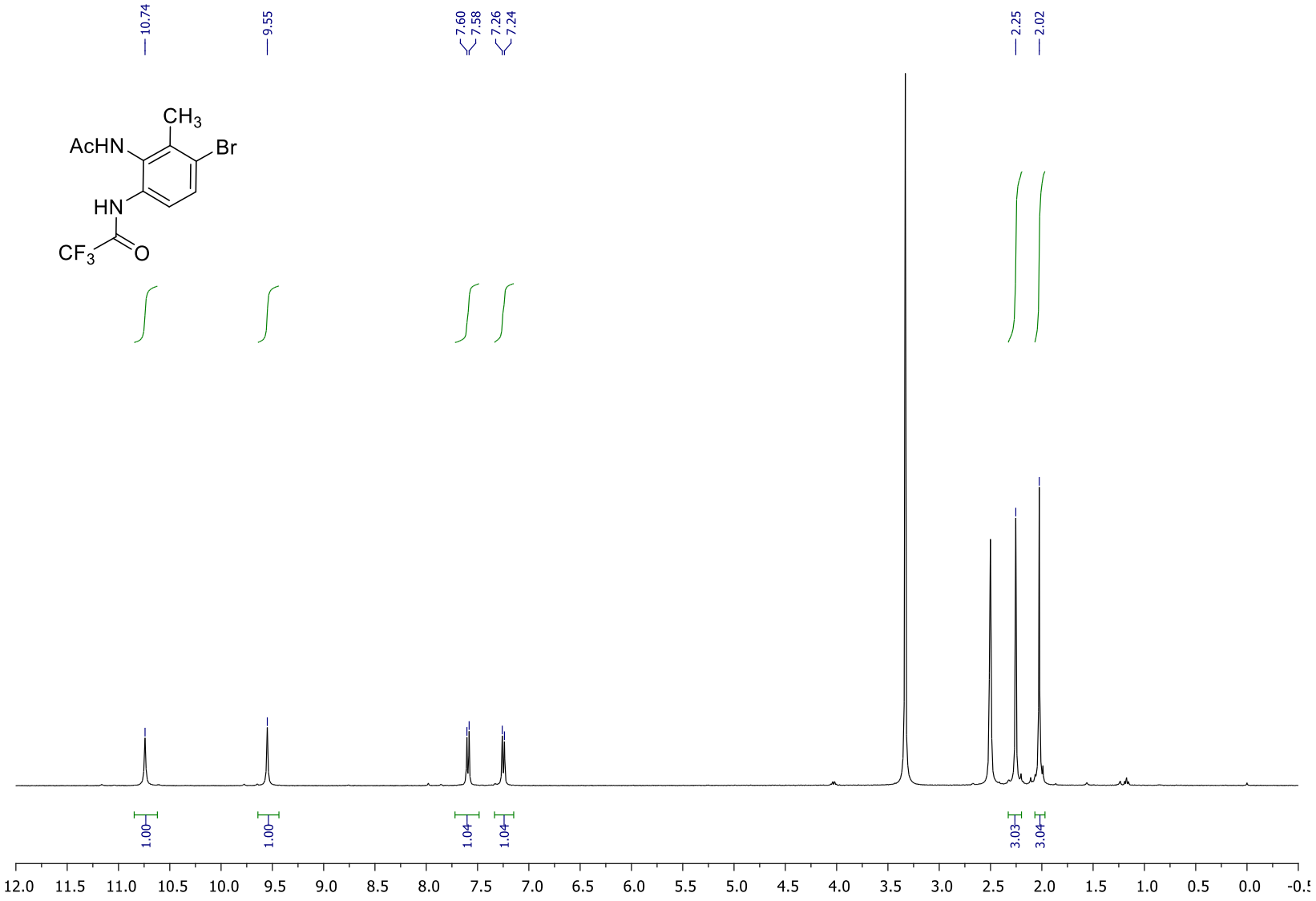
^{1}H NMR spectrum of compound **3e** ($CDCl_3$, 400 MHz)**:**



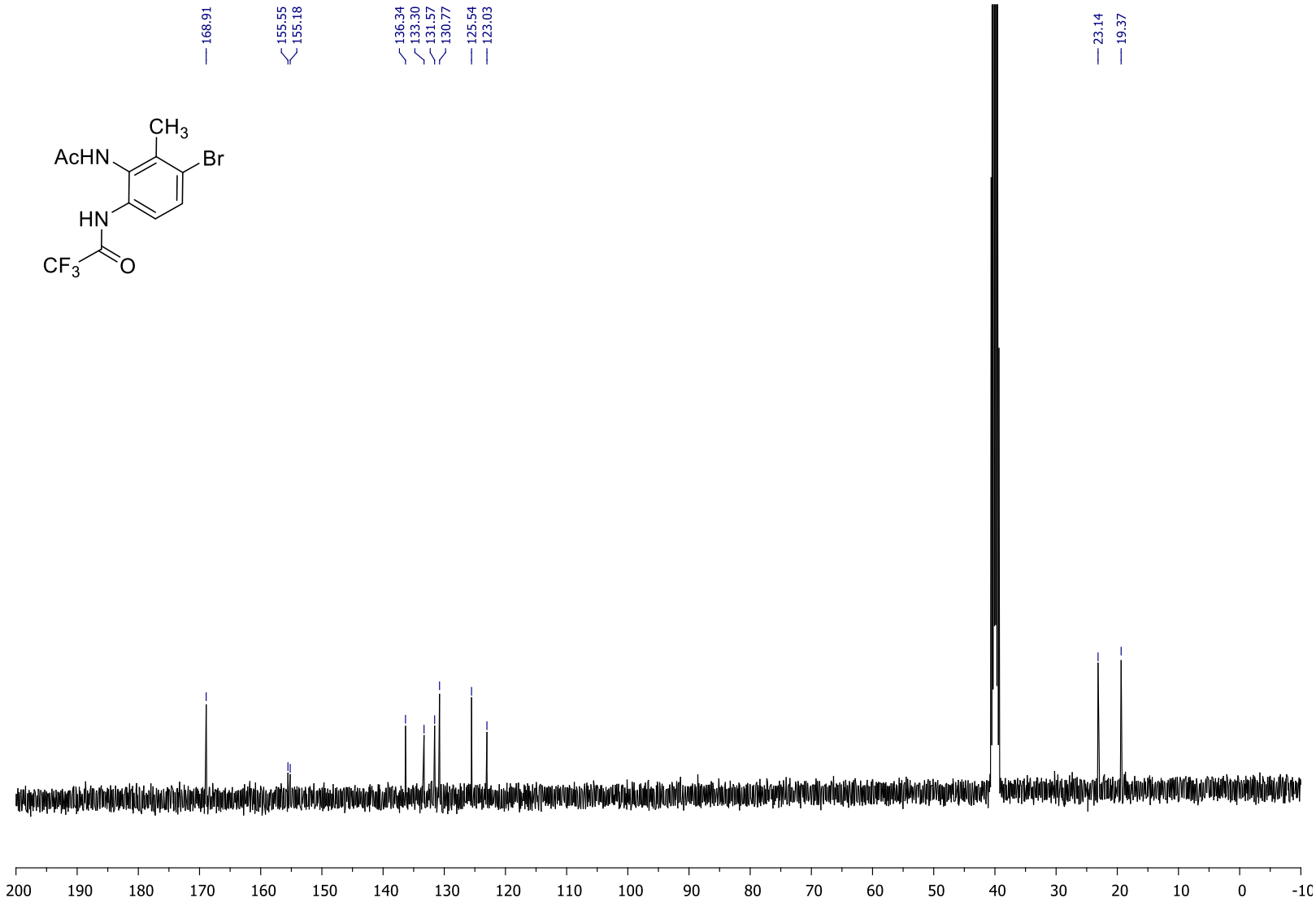
^{13}C NMR spectrum of compound **3e** ($CDCl_3$, 100 MHz)**:**



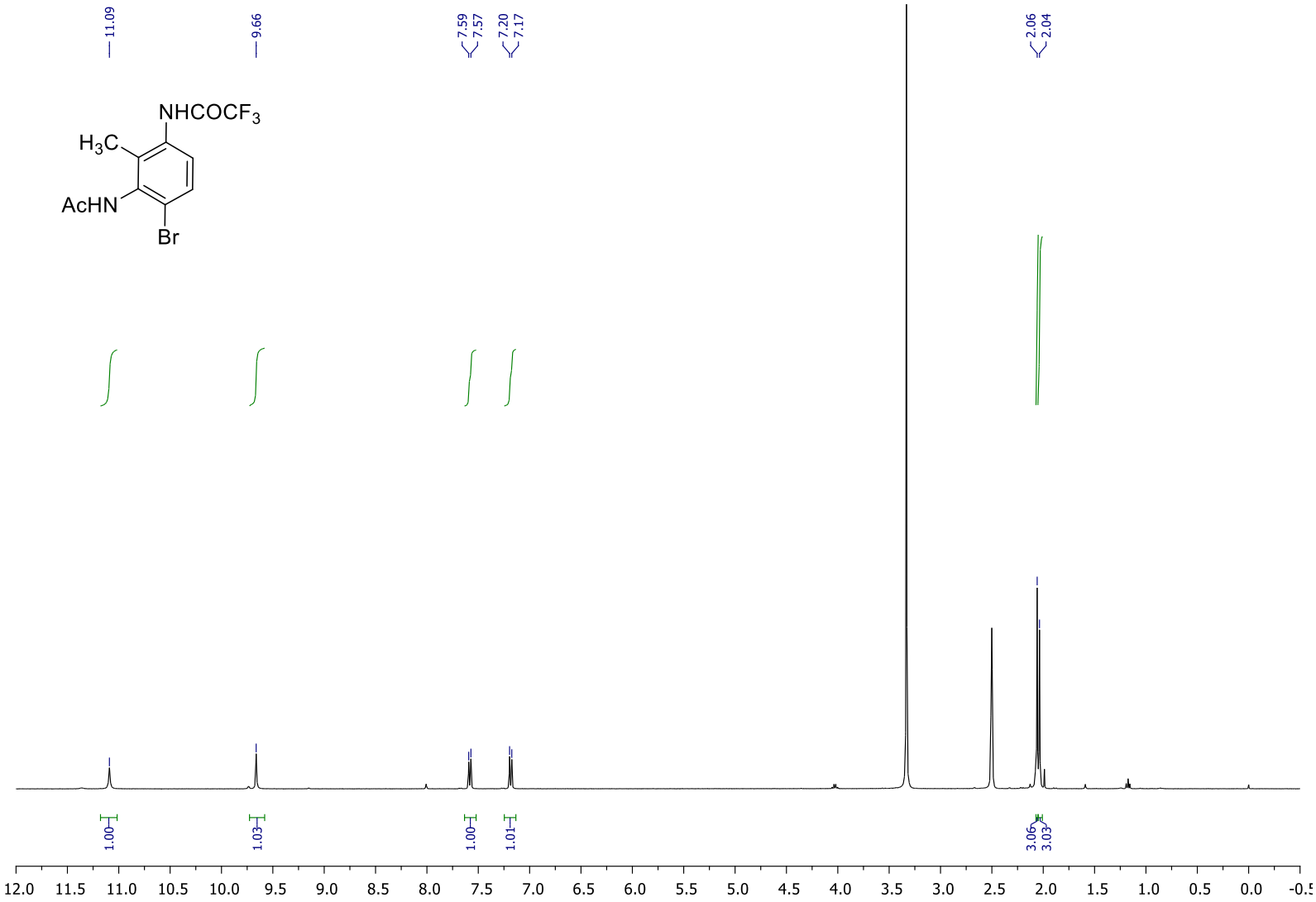
^{1}H NMR spectrum of compound **3f** (DMSO-d_6, 400 MHz)**:**



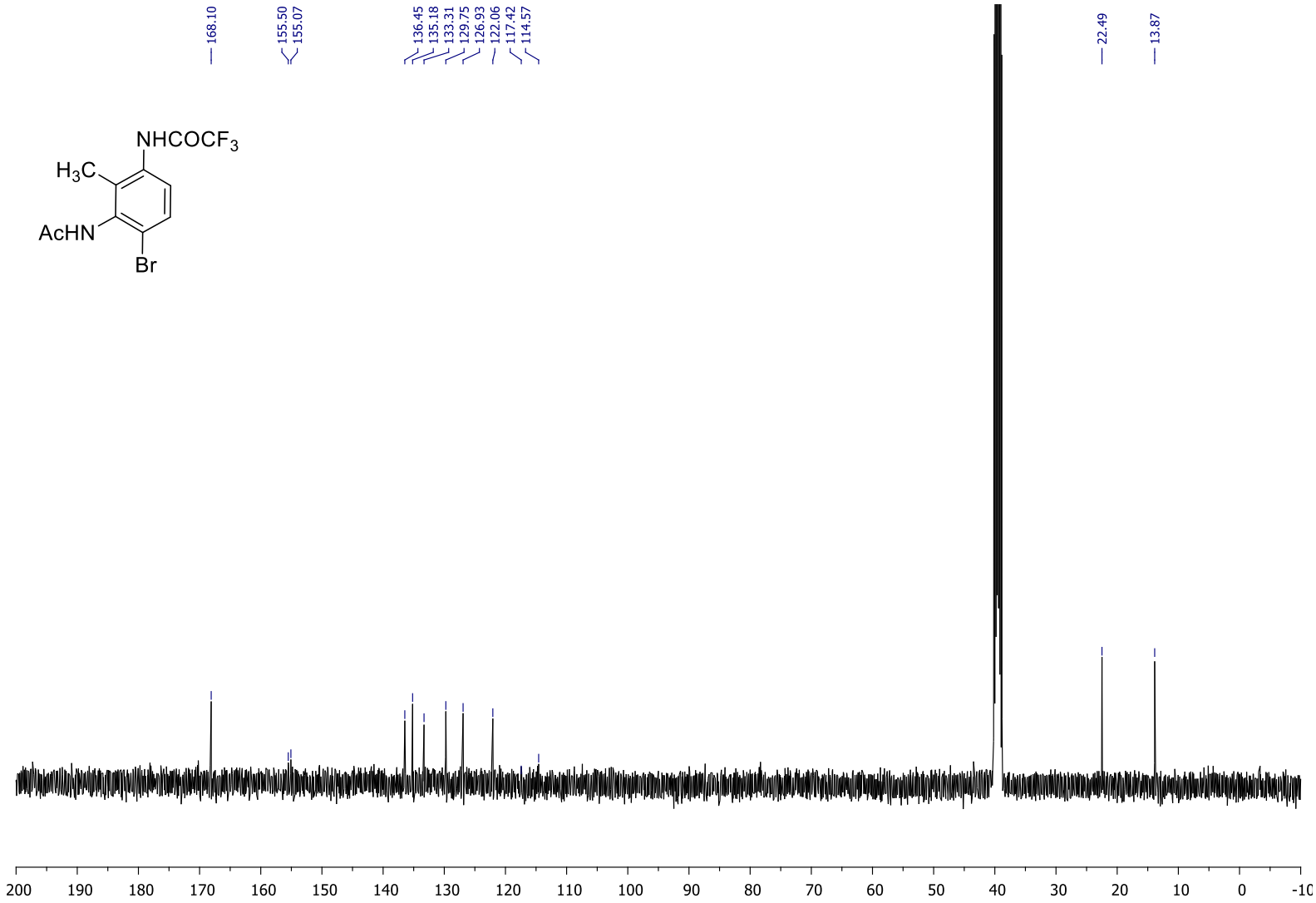
^{13}C NMR spectrum of compound **3f** (DMSO-d_6, 100 MHz)**:**



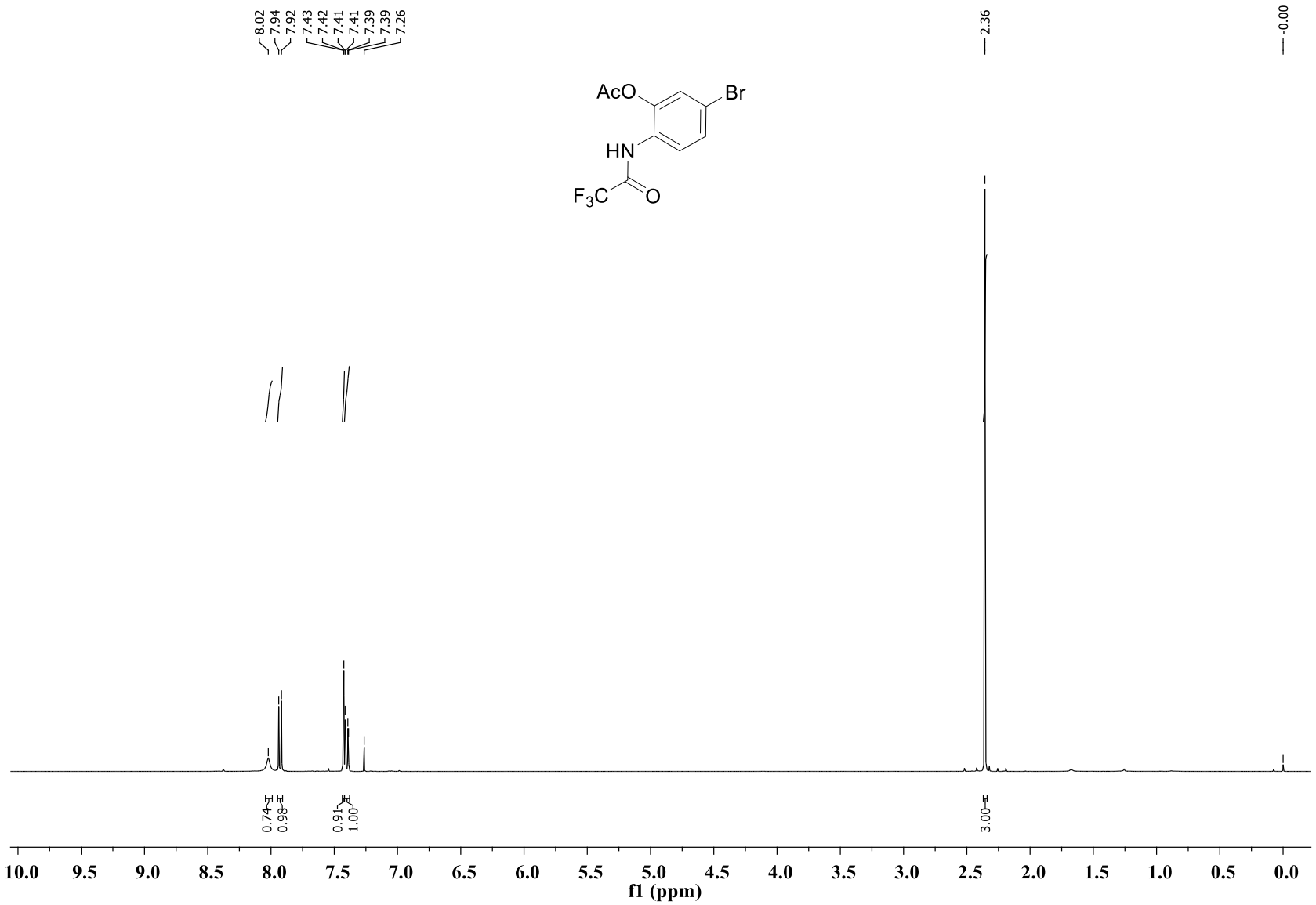
^{1}H NMR spectrum of compound **3g** (DMSO-d_6, 400 MHz)**:**



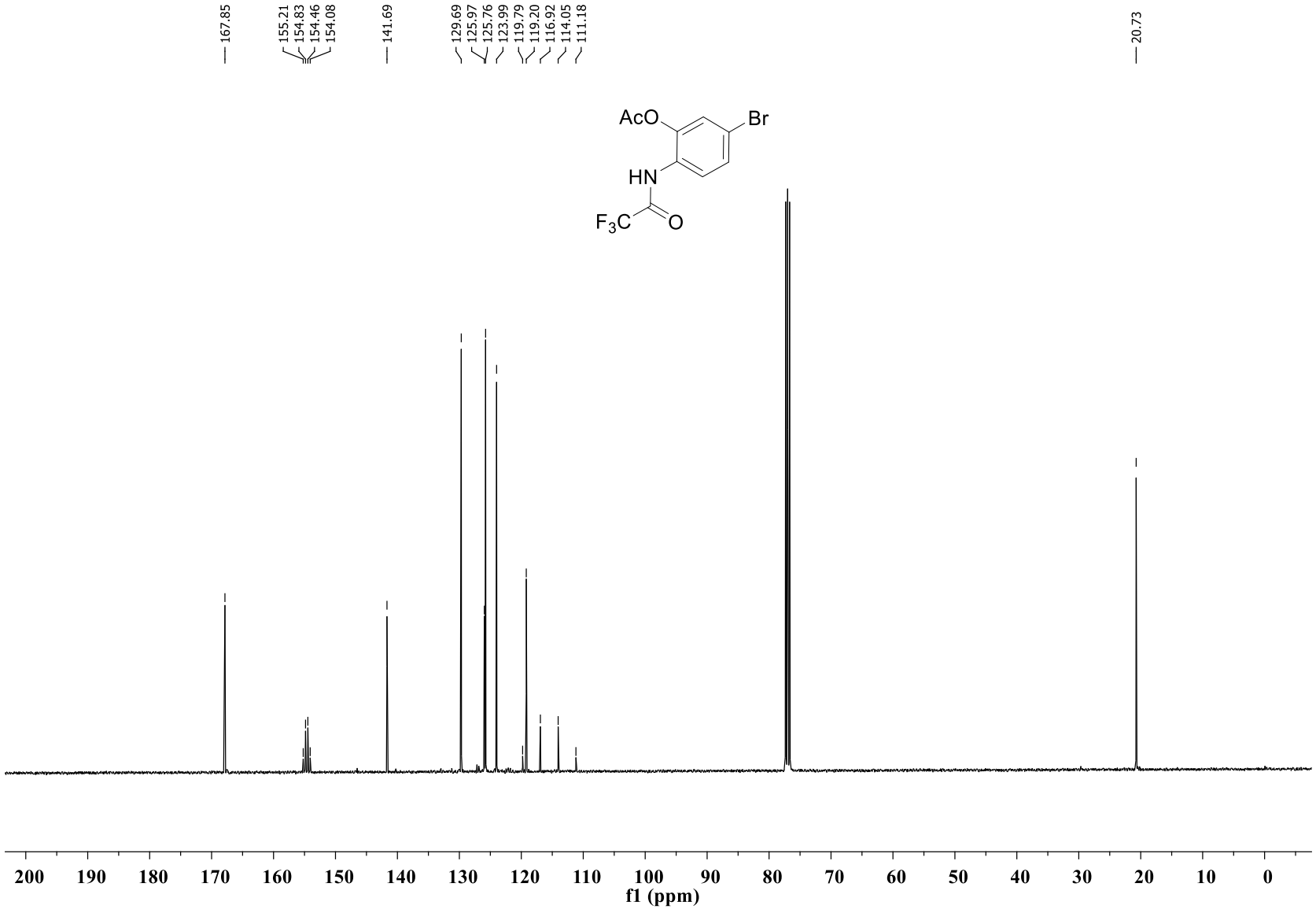
^{13}C NMR spectrum of compound **3g** (DMSO-d_6, 100 MHz)**:**



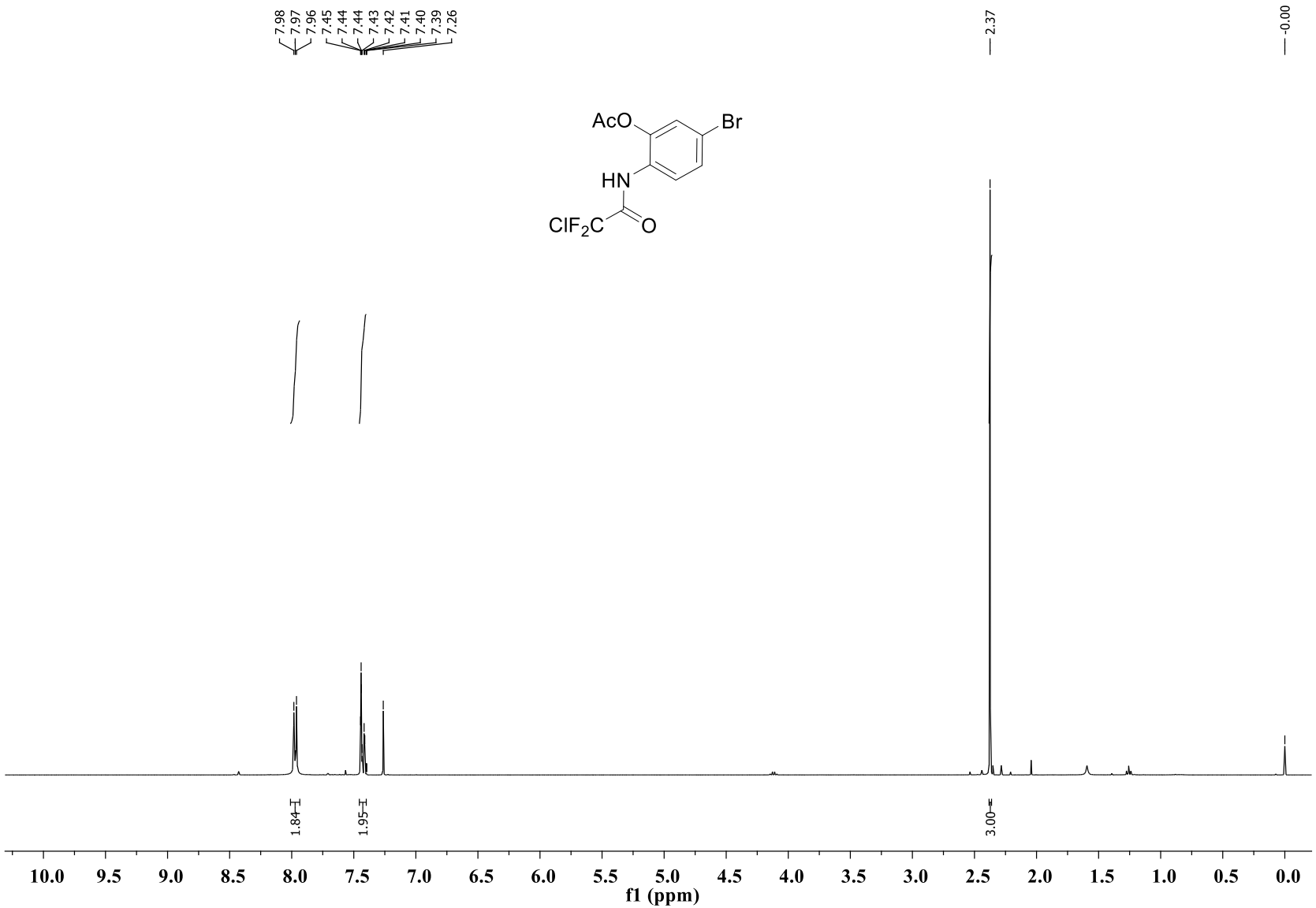
^{1}H NMR spectrum of compound **6a** ($CDCl_3$, 400 MHz)**:**



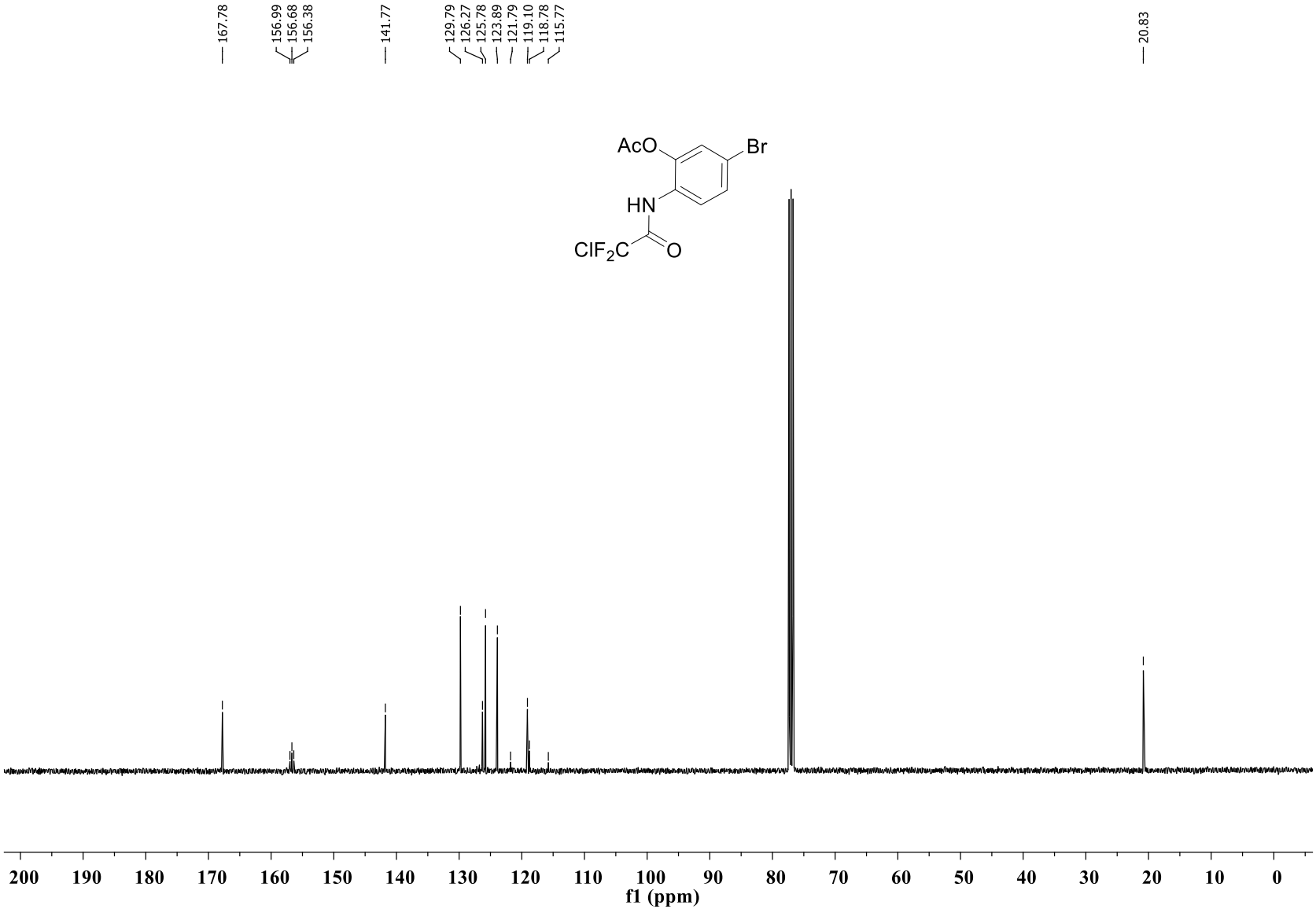
^{13}C NMR spectrum of compound **6a** ($CDCl_3$, 100 MHz)**:**



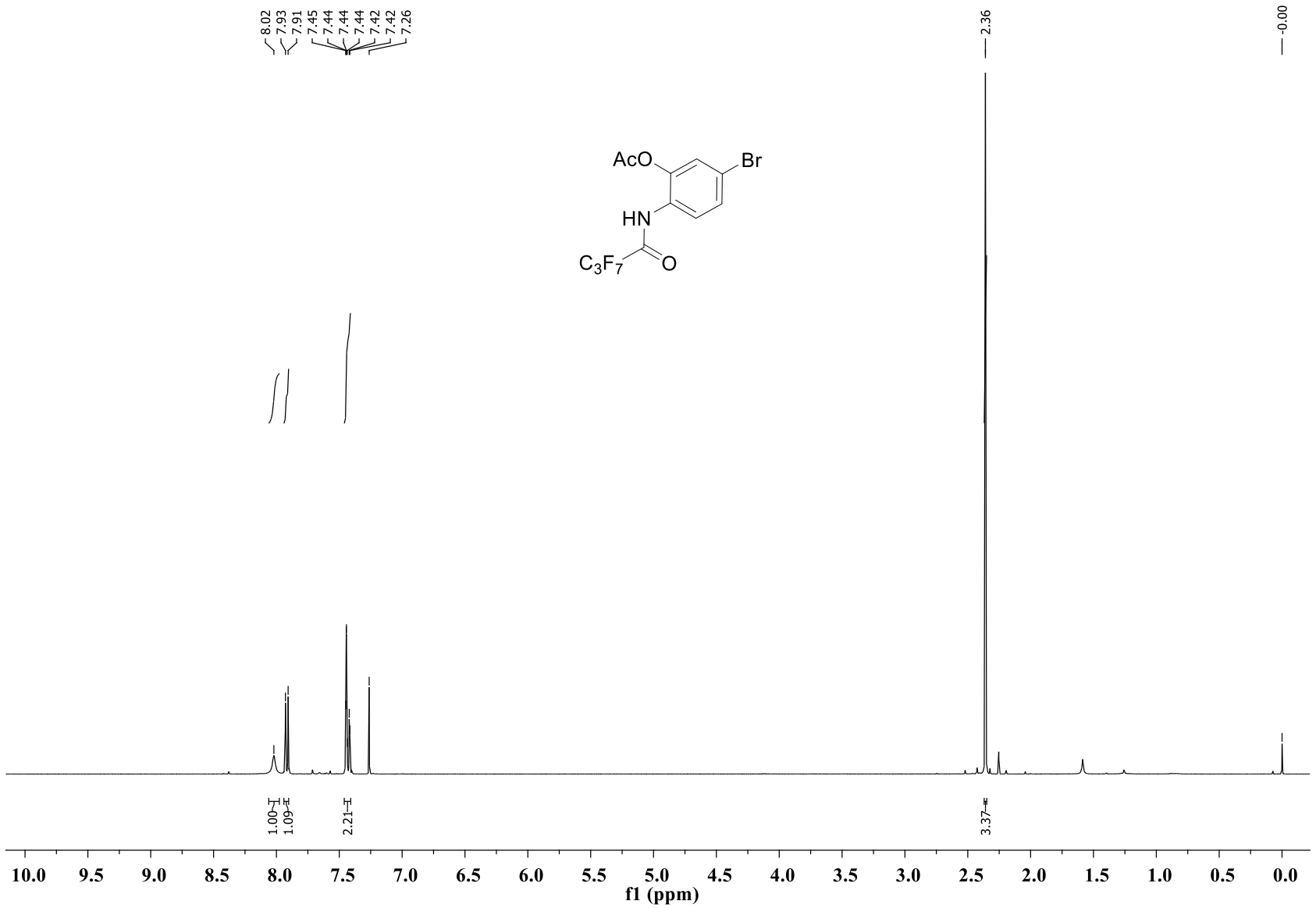
^{1}H NMR spectrum of compound **6b** ($CDCl_3$, 400 MHz)**:**



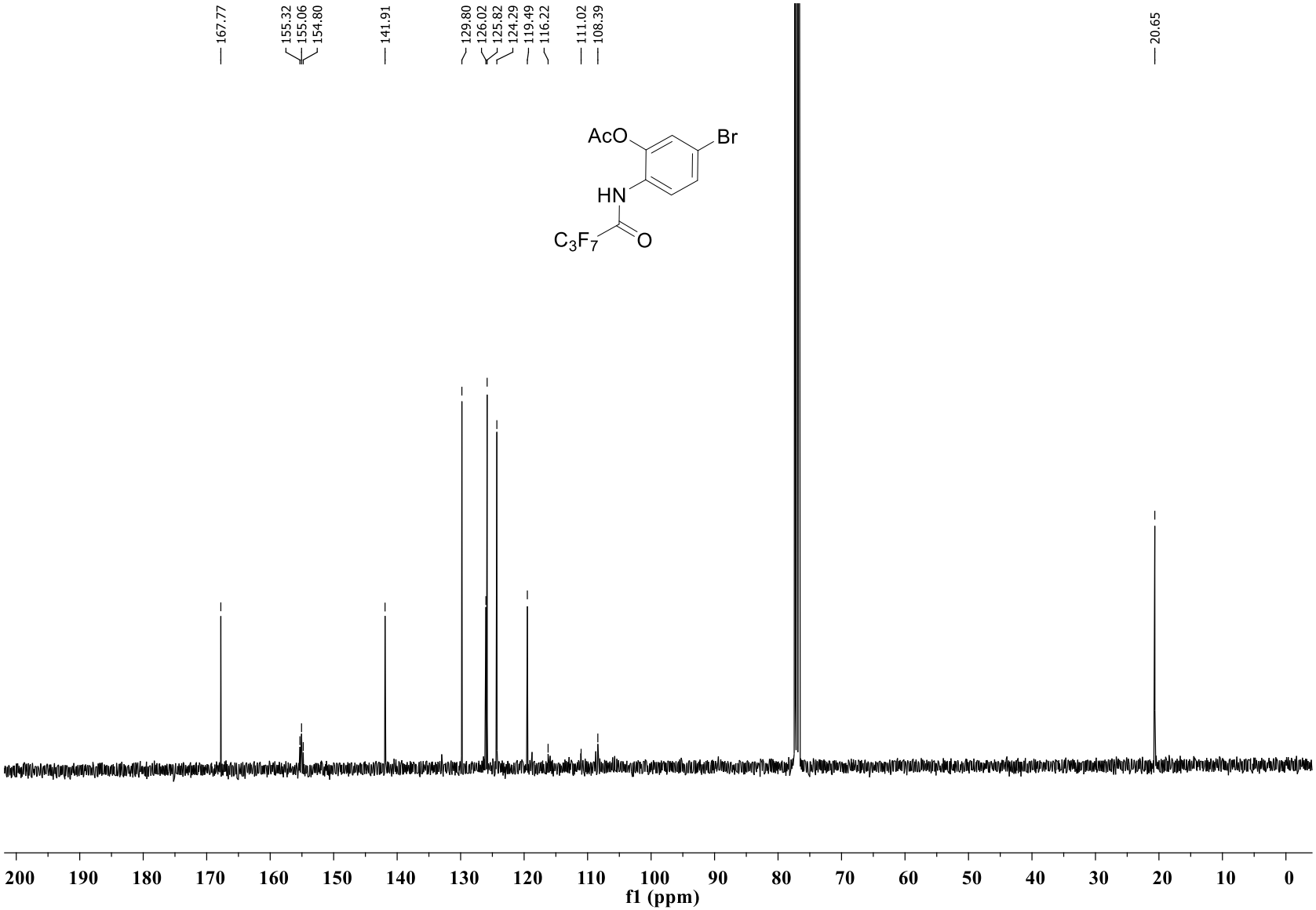
^{13}C NMR spectrum of compound **6b** ($CDCl_3$, 100 MHz)**:**



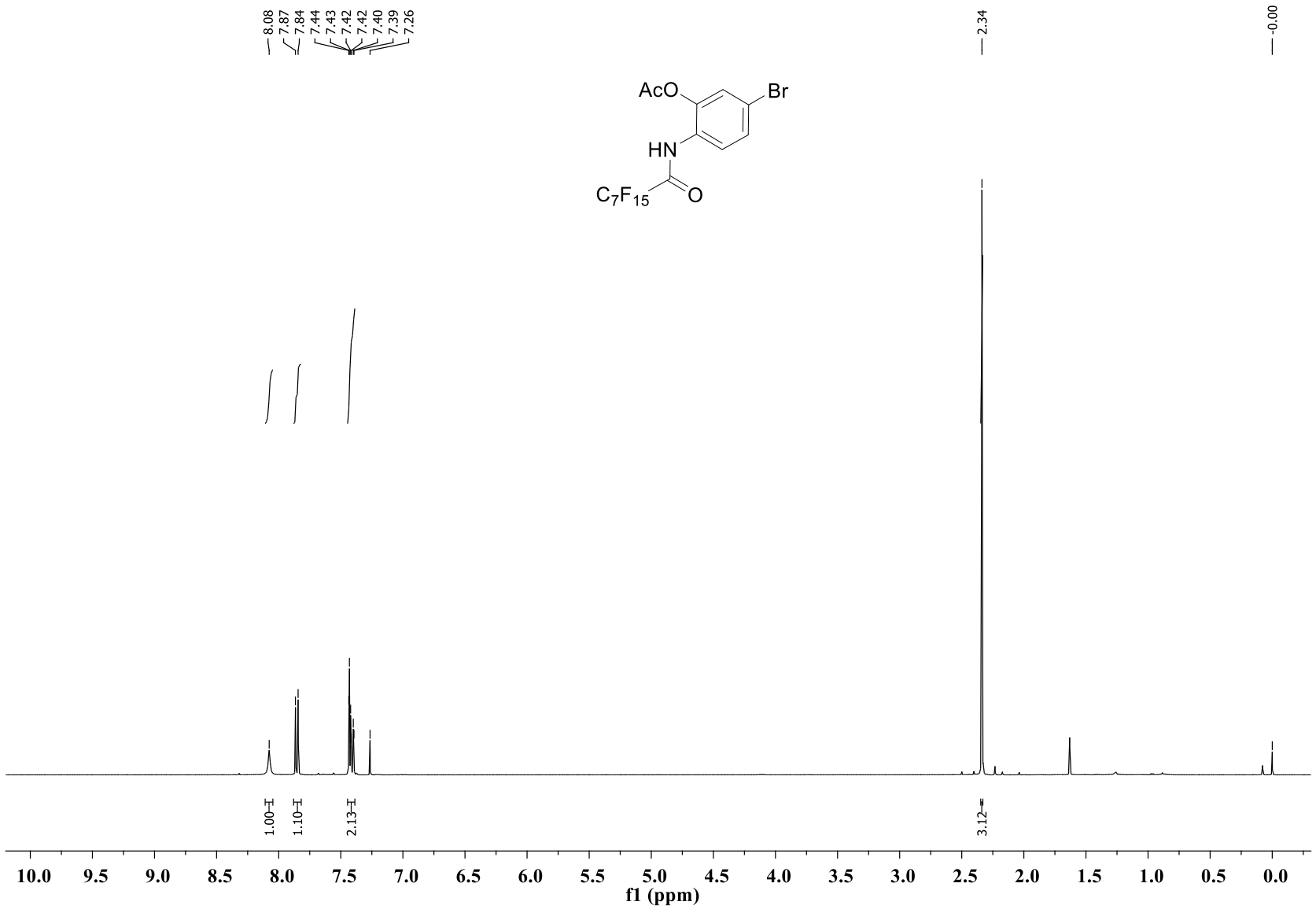
^{1}H NMR spectrum of compound **6c** ($CDCl_3$, 400 MHz)**:**



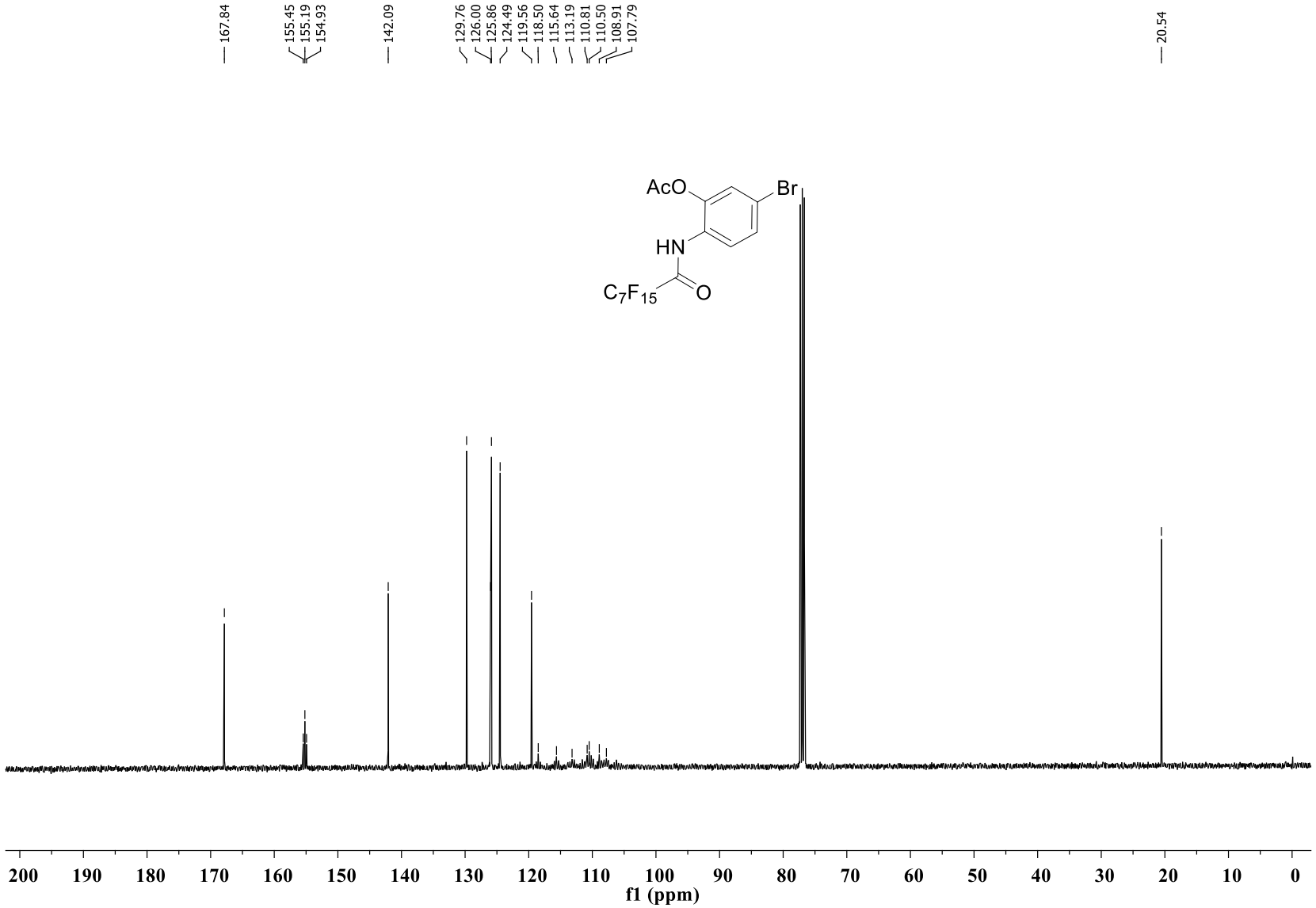
^{13}C NMR spectrum of compound **6c** ($CDCl_3$, 100 MHz)**:**



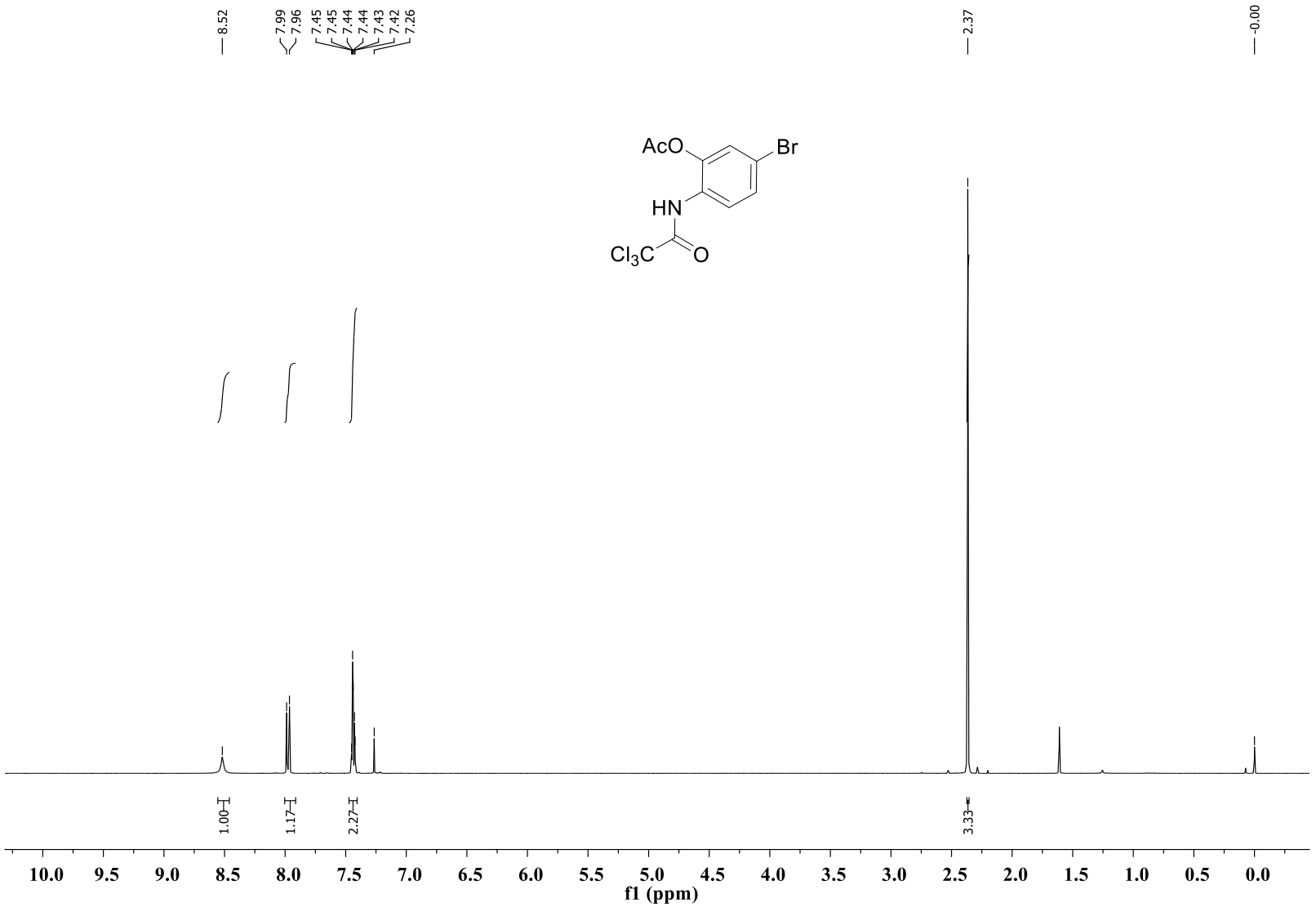
^{1}H NMR spectrum of compound **6d** ($CDCl_3$, 400 MHz)**:**



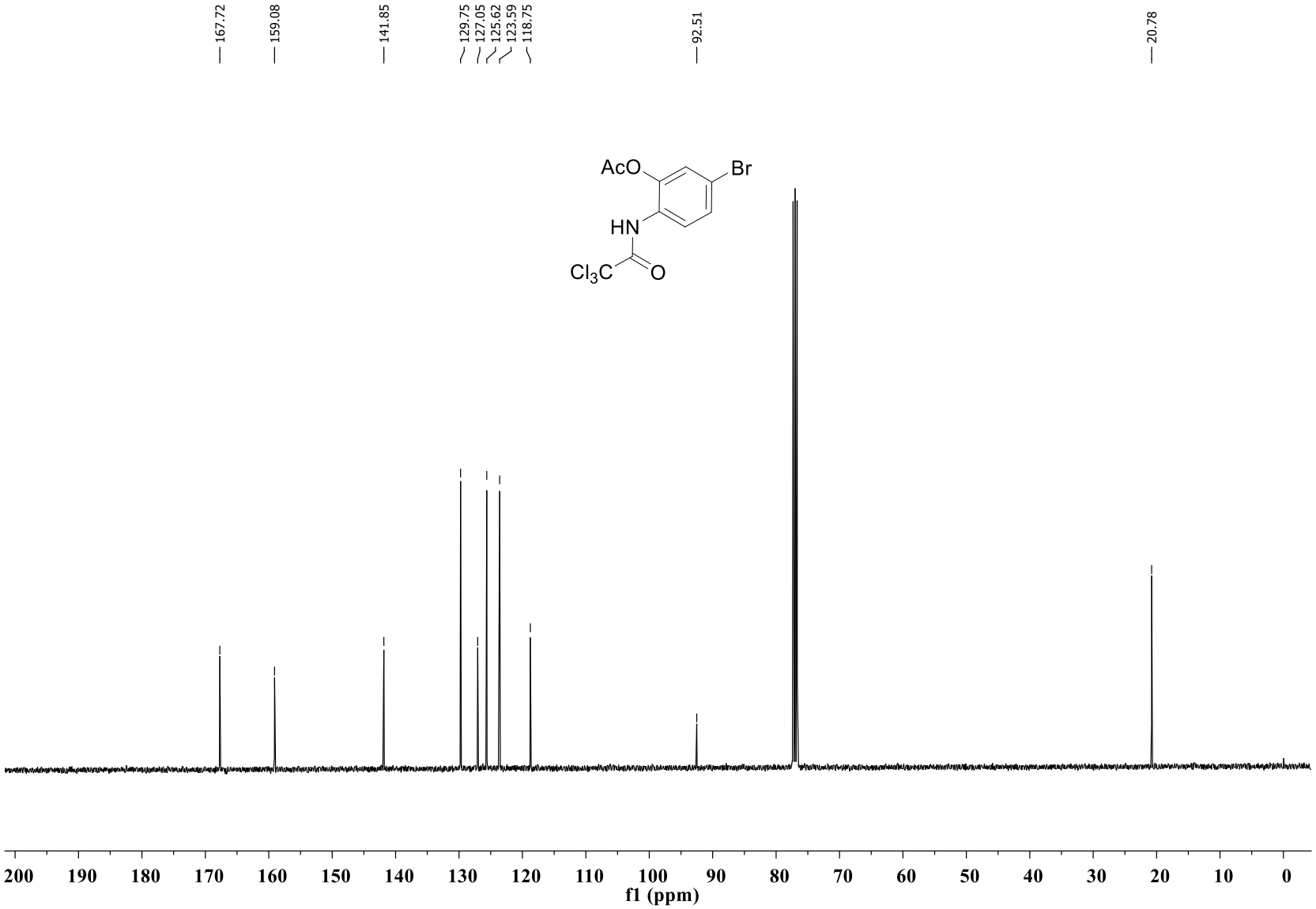
^{13}C NMR spectrum of compound **6d** ($CDCl_3$, 100 MHz)**:**



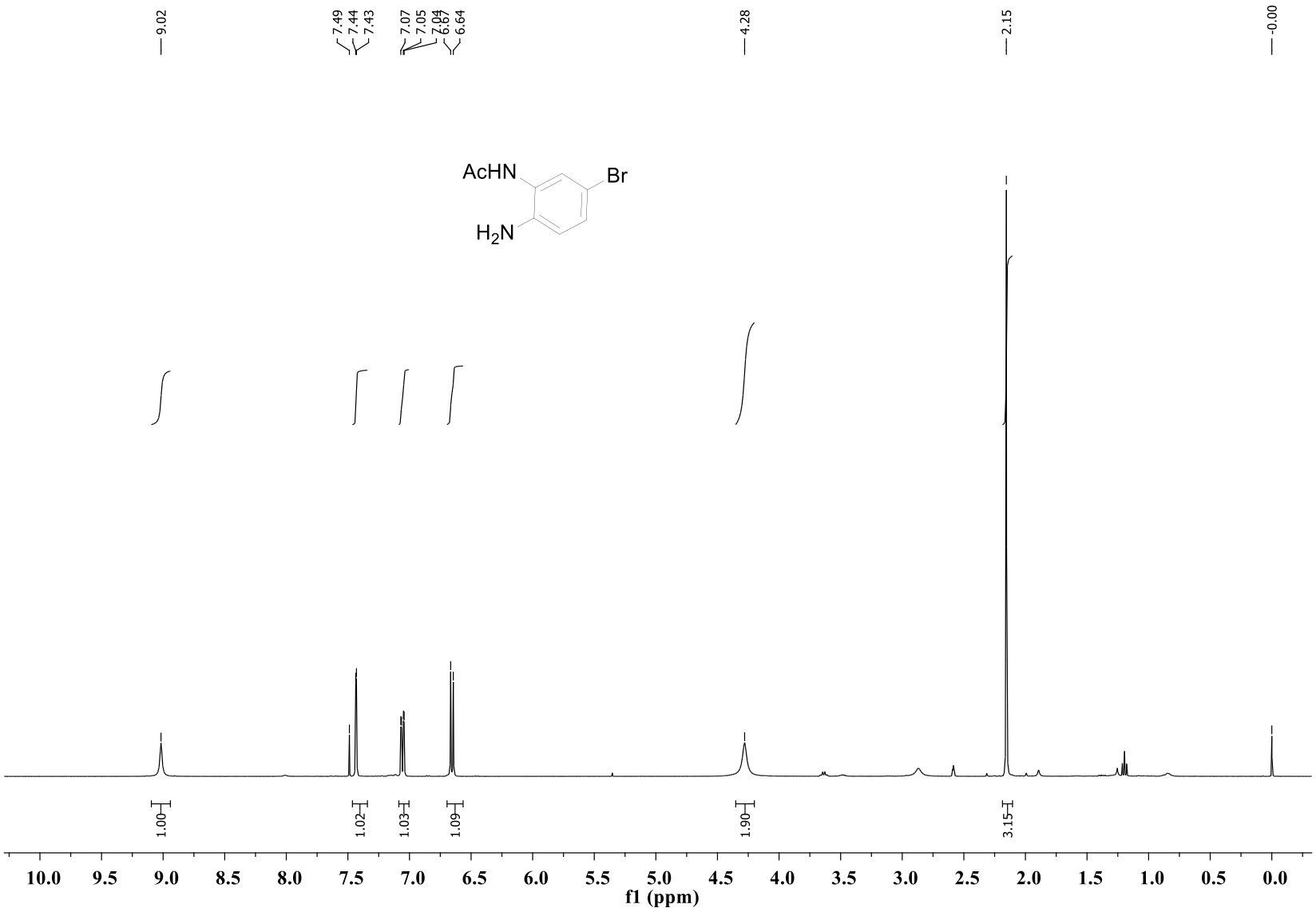
^{1}H NMR spectrum of compound **6e** ($CDCl_3$, 400 MHz)**:**



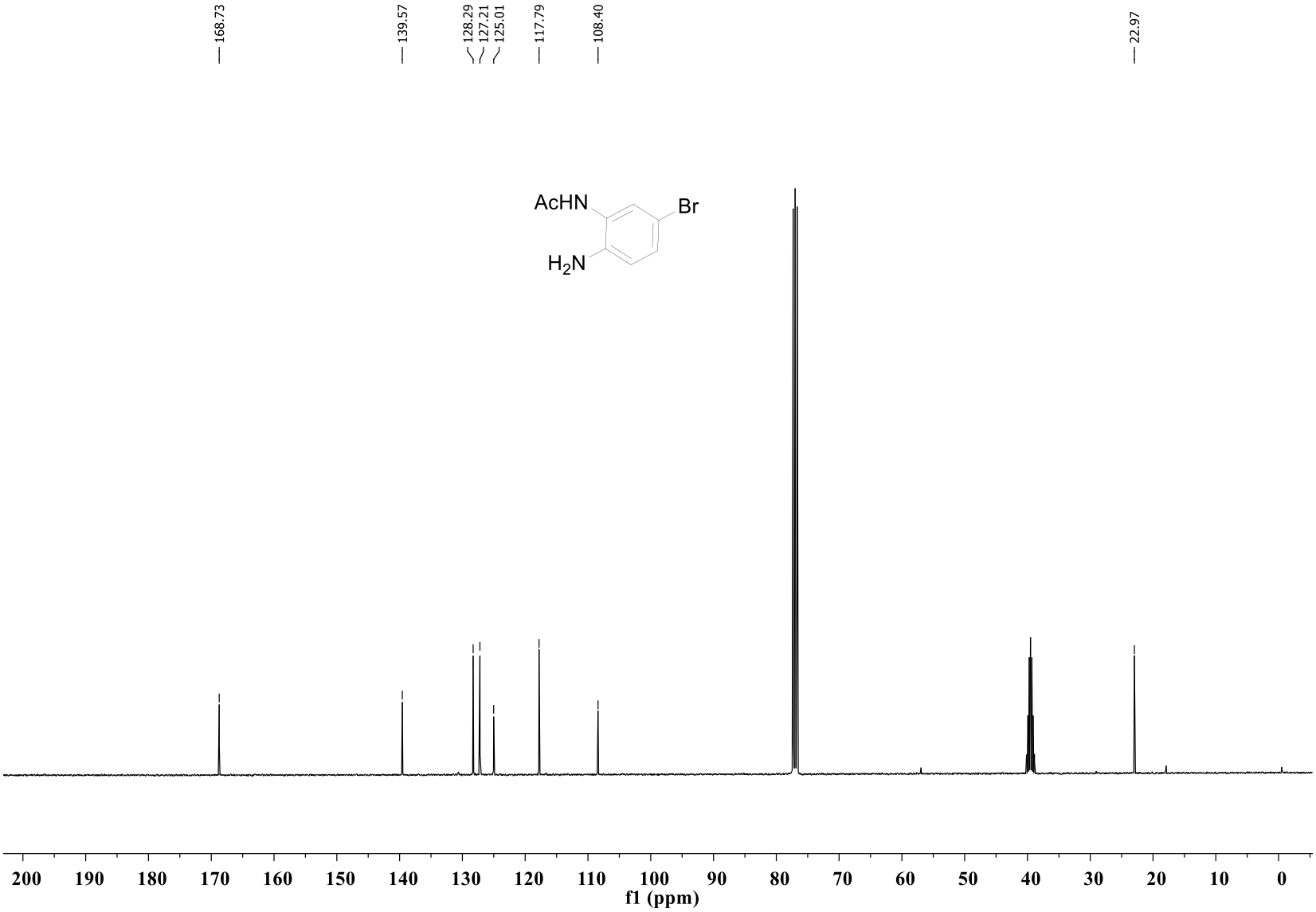
^{13}C NMR spectrum of compound **6e** ($CDCl_3$, 100 MHz)**:**



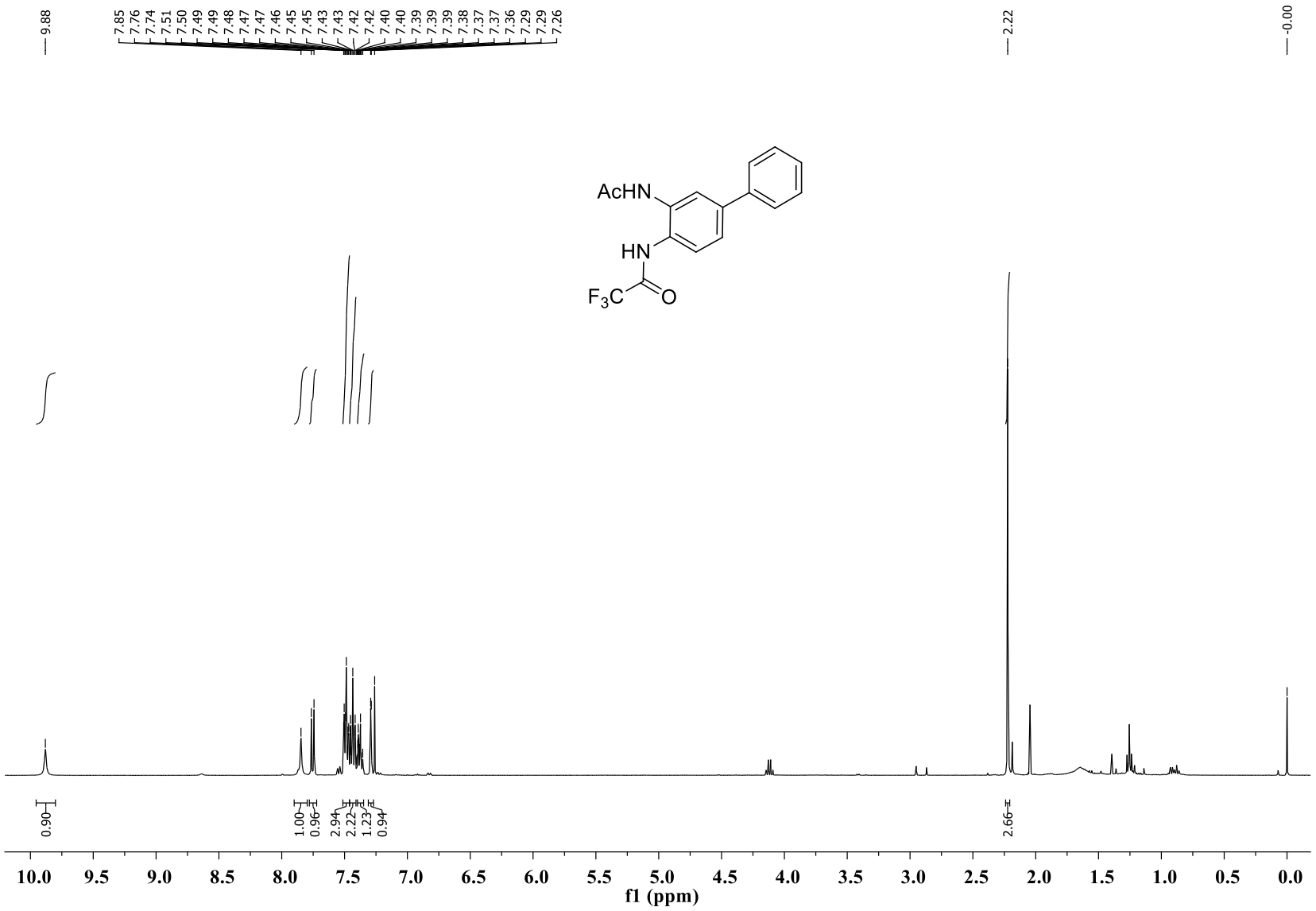
^{1}H NMR spectrum of compound **7** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



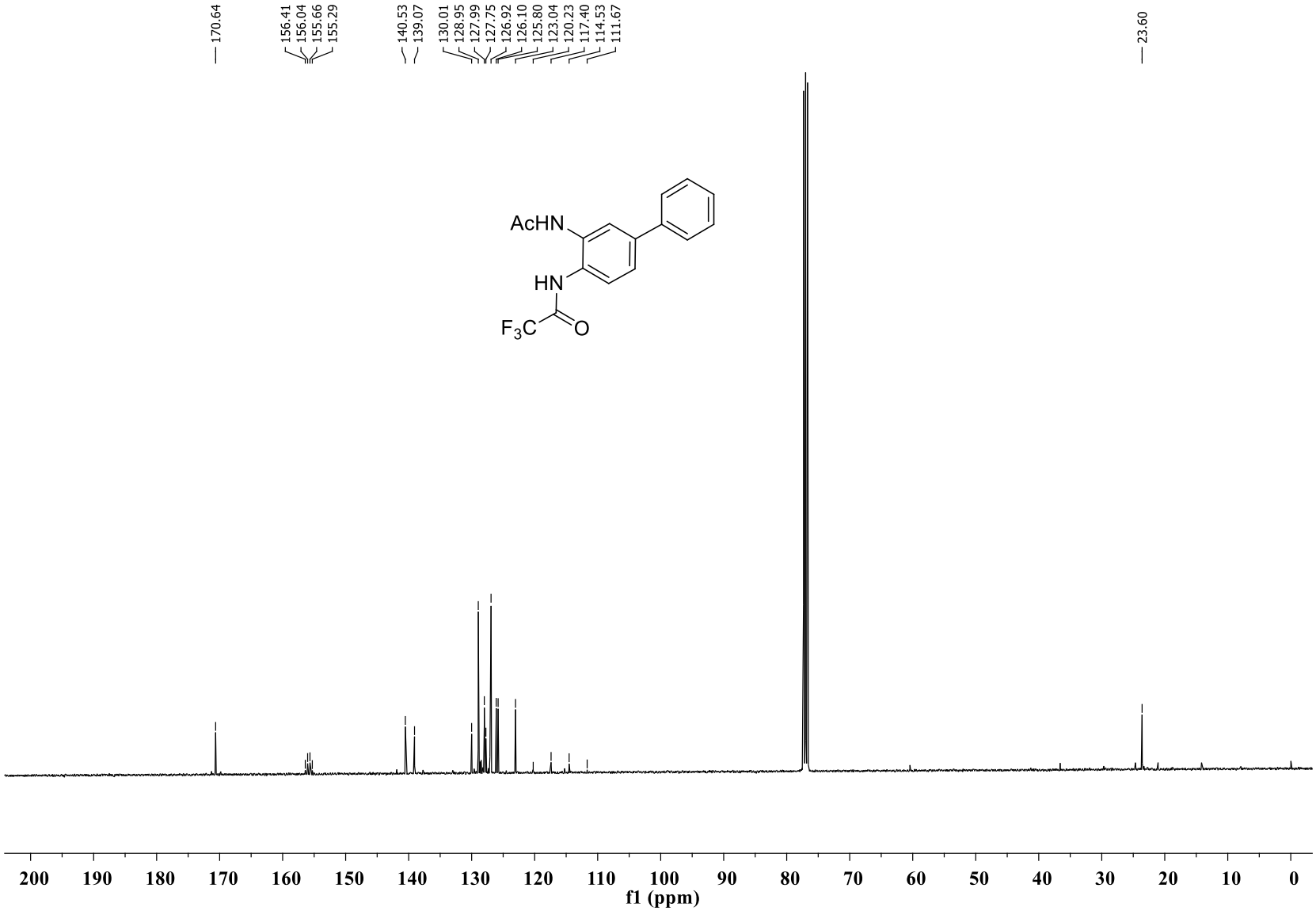
^{13}C NMR spectrum of compound **7** (8:2, $CDCl_3$ + DMSO-*d6*, 400 MHz)**:**



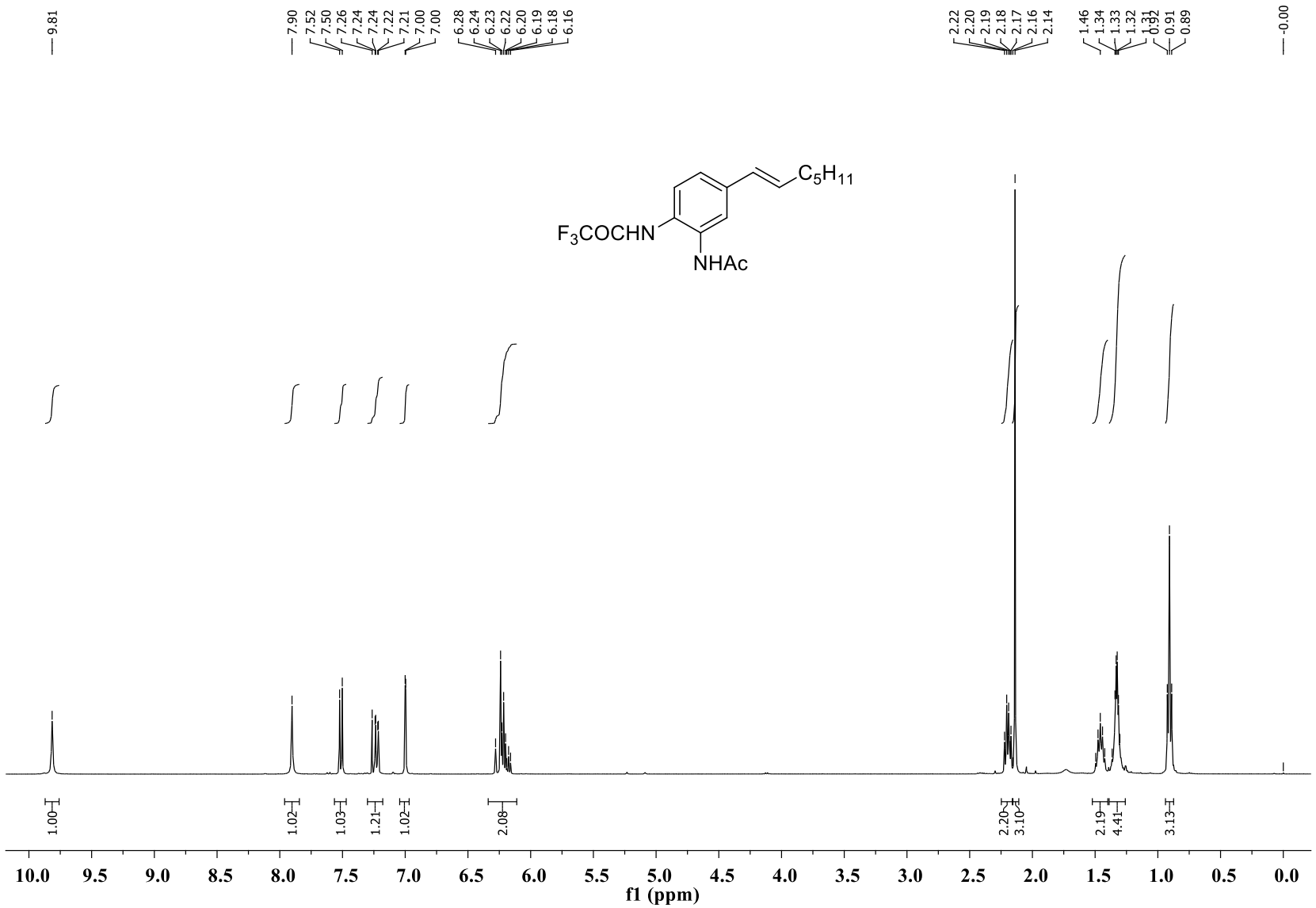
^{1}H NMR spectrum of compound **10** ($CDCl_3$, 400 MHz)**:**



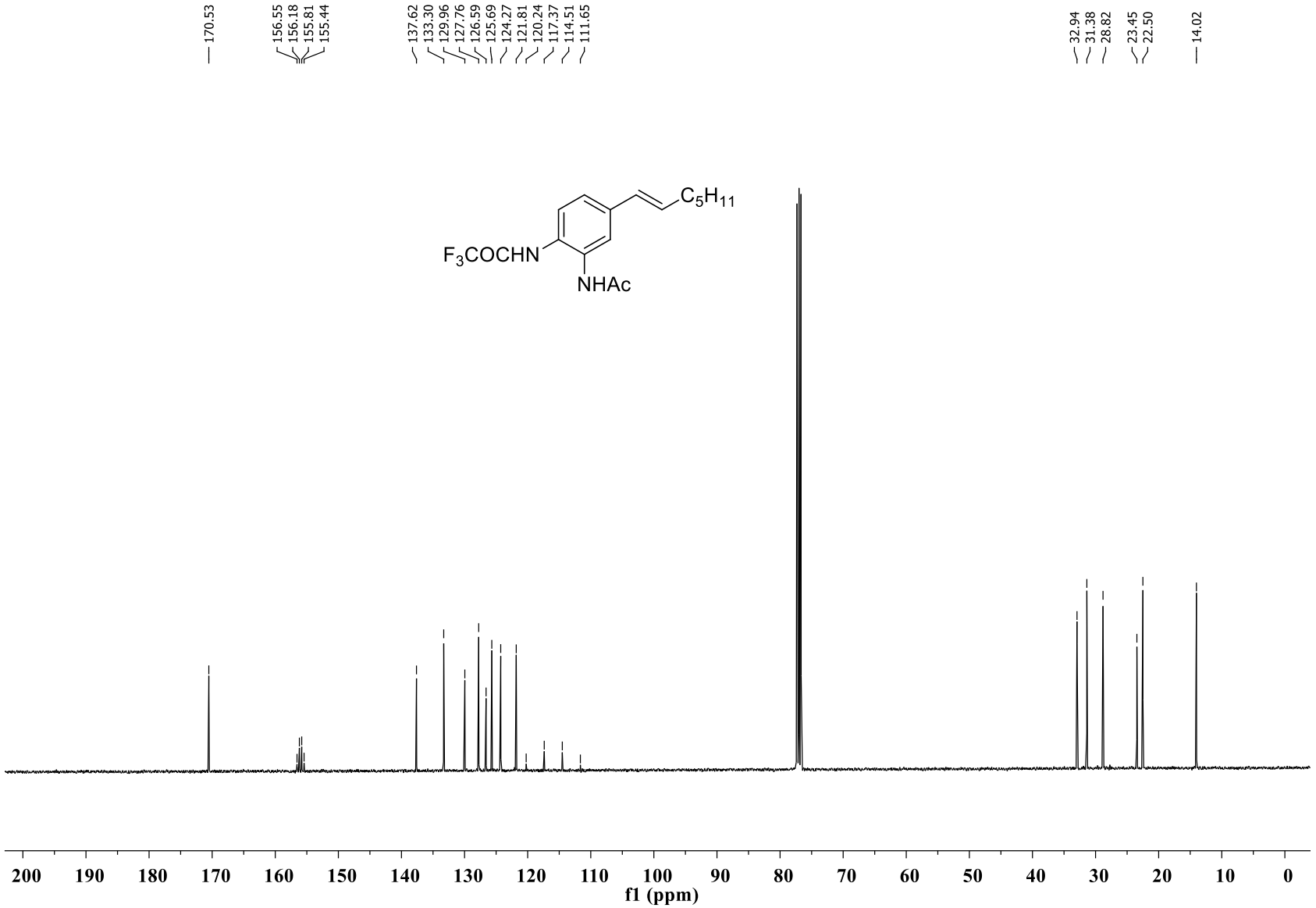
^{13}C NMR spectrum of compound **10** ($CDCl_3$, 100 MHz)**:**



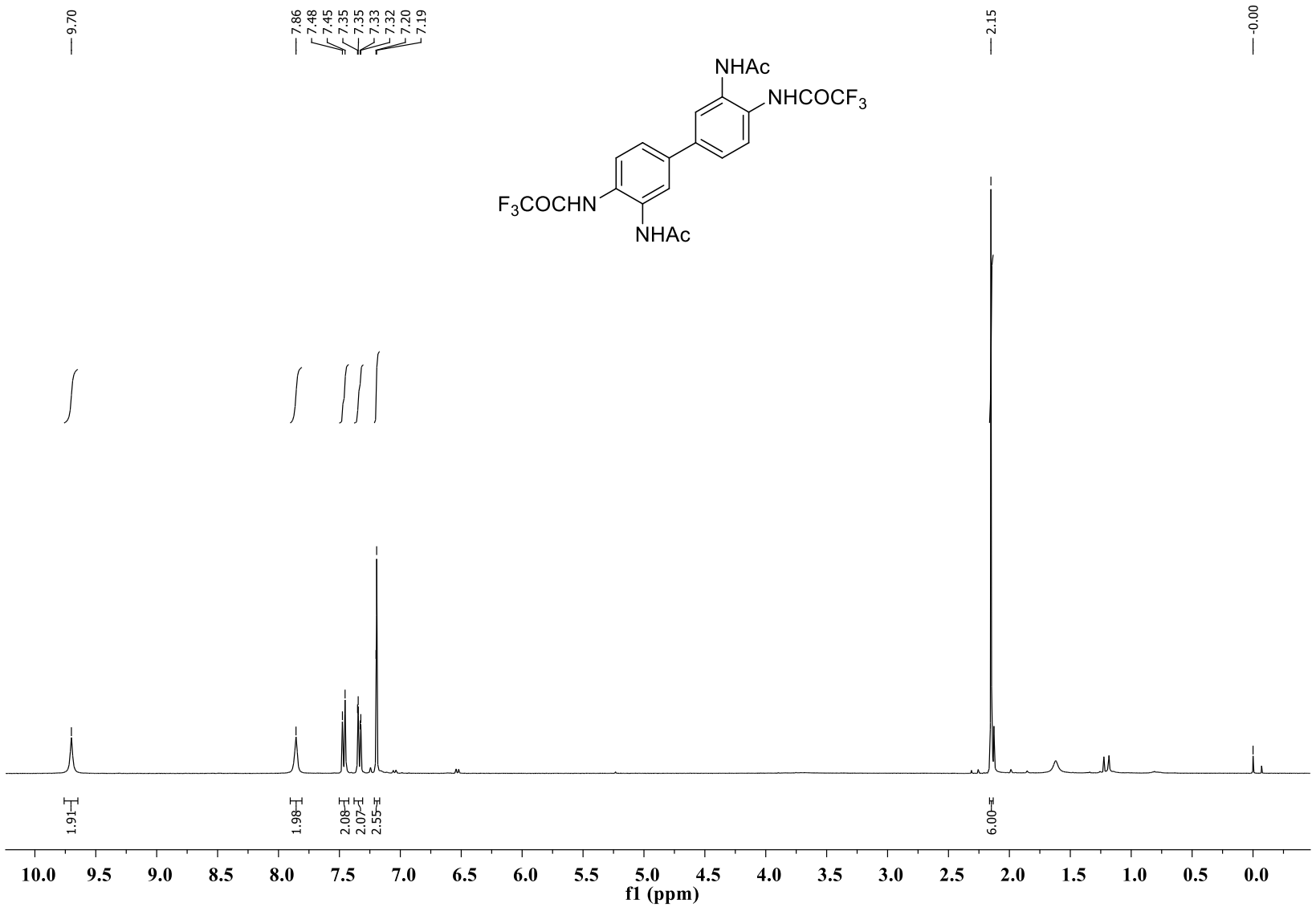
^{1}H NMR spectrum of compound **11** ($CDCl_3$, 400 MHz)**:**



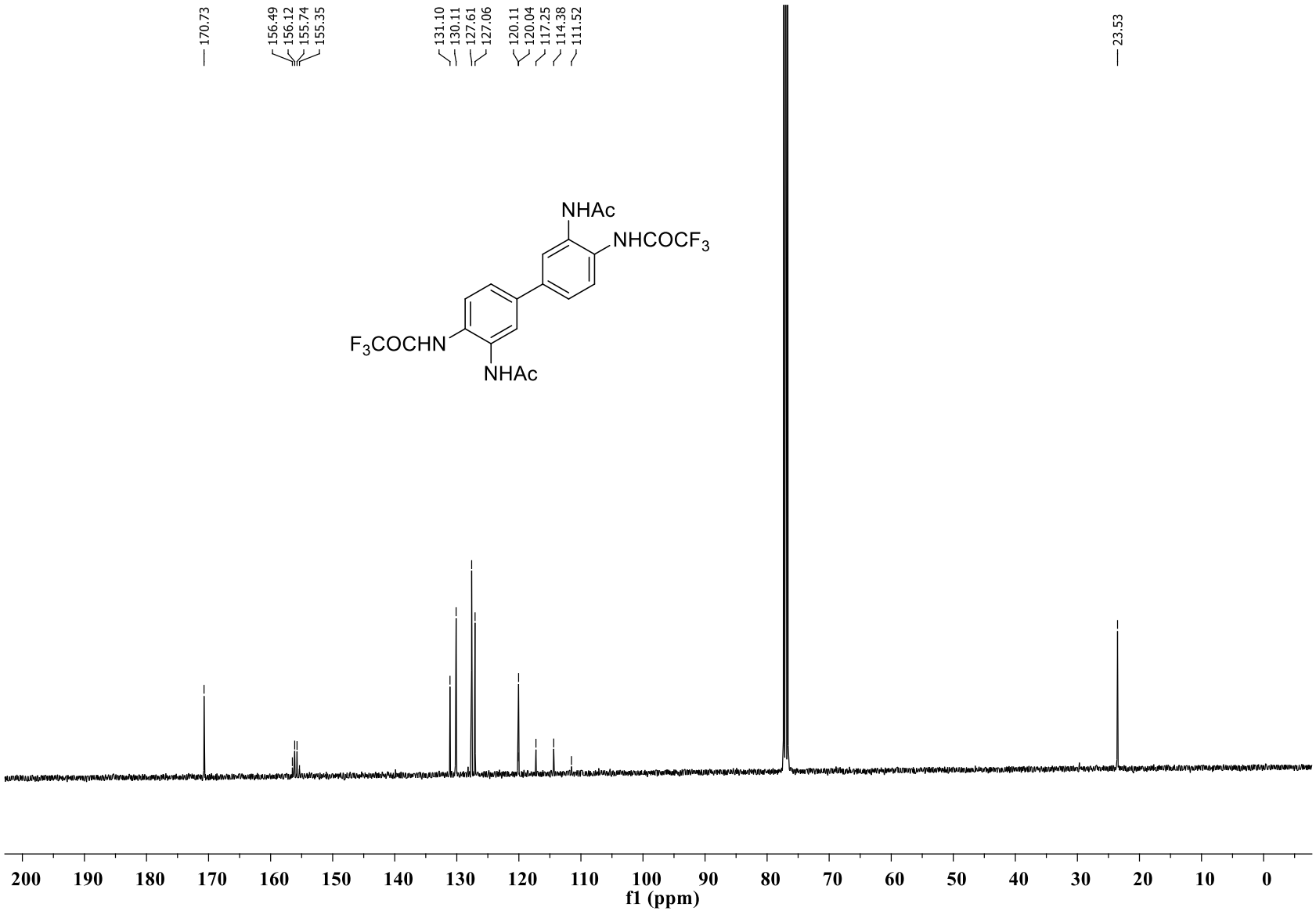
^{13}C NMR spectrum of compound **11** ($CDCl_3$, 100 MHz)**:**



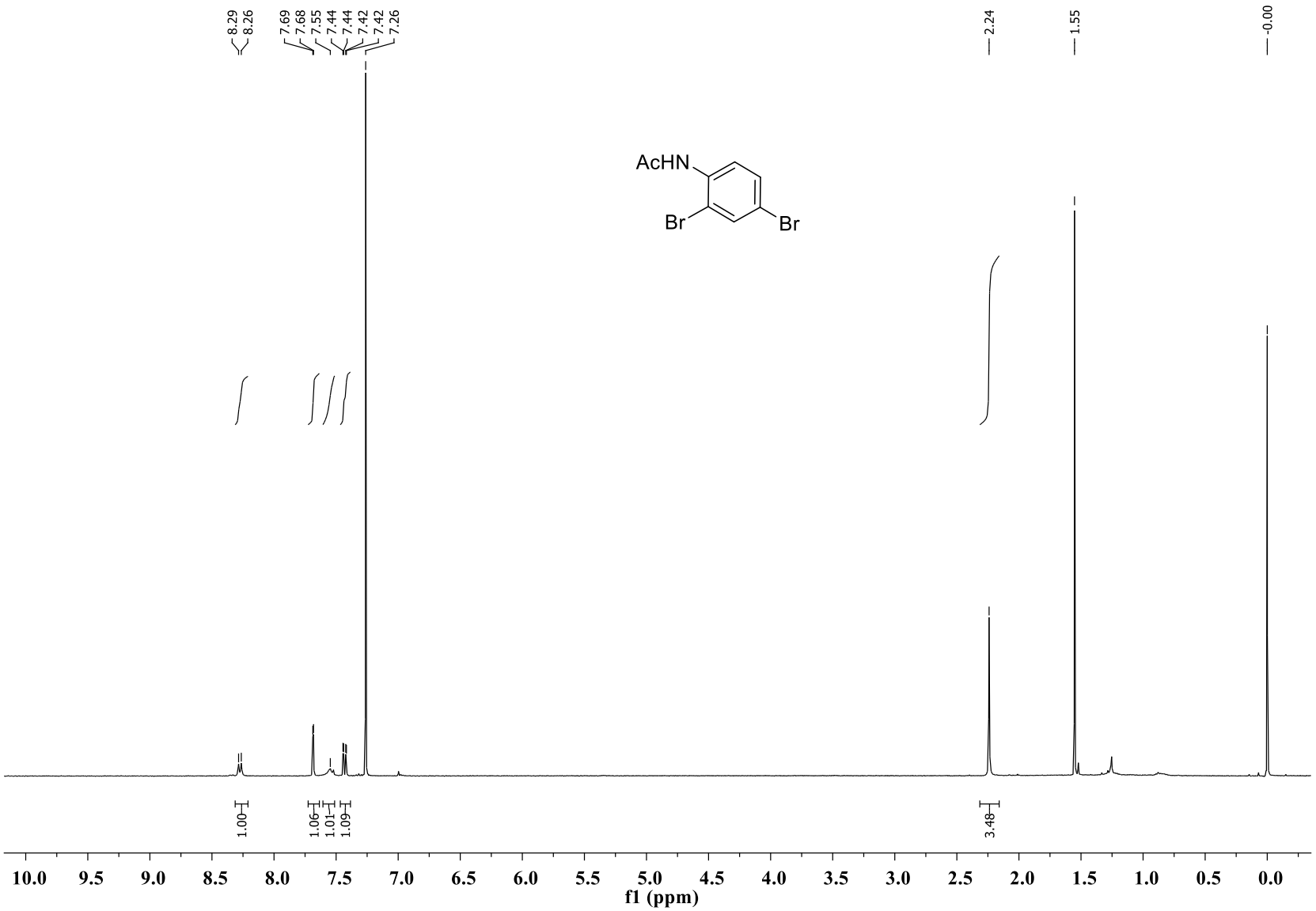
^{1}H NMR spectrum of compound **12** ($CDCl_3$, 400 MHz)**:**



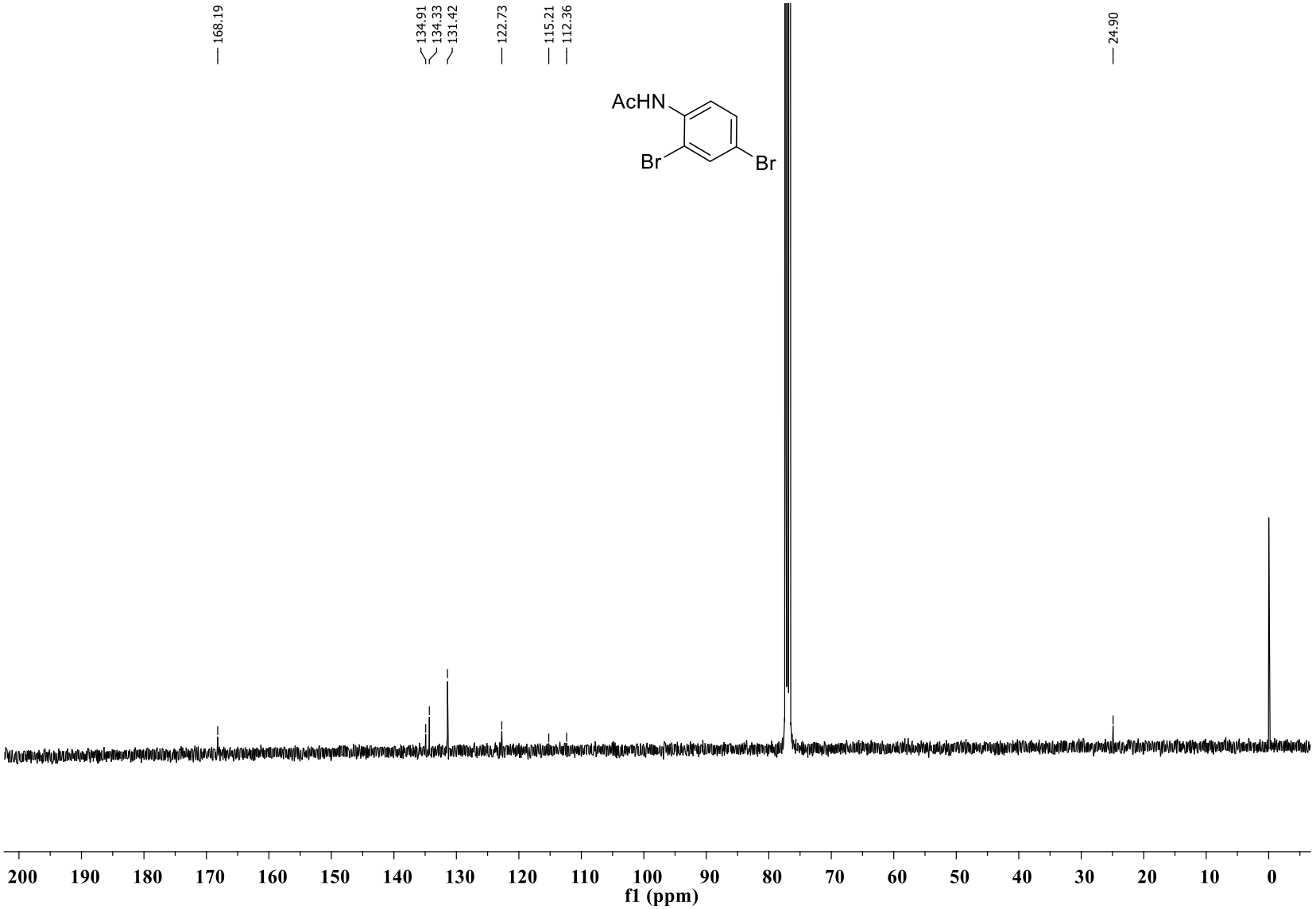
^{13}C NMR spectrum of compound **12** ($CDCl_3$, 100 MHz)**:**



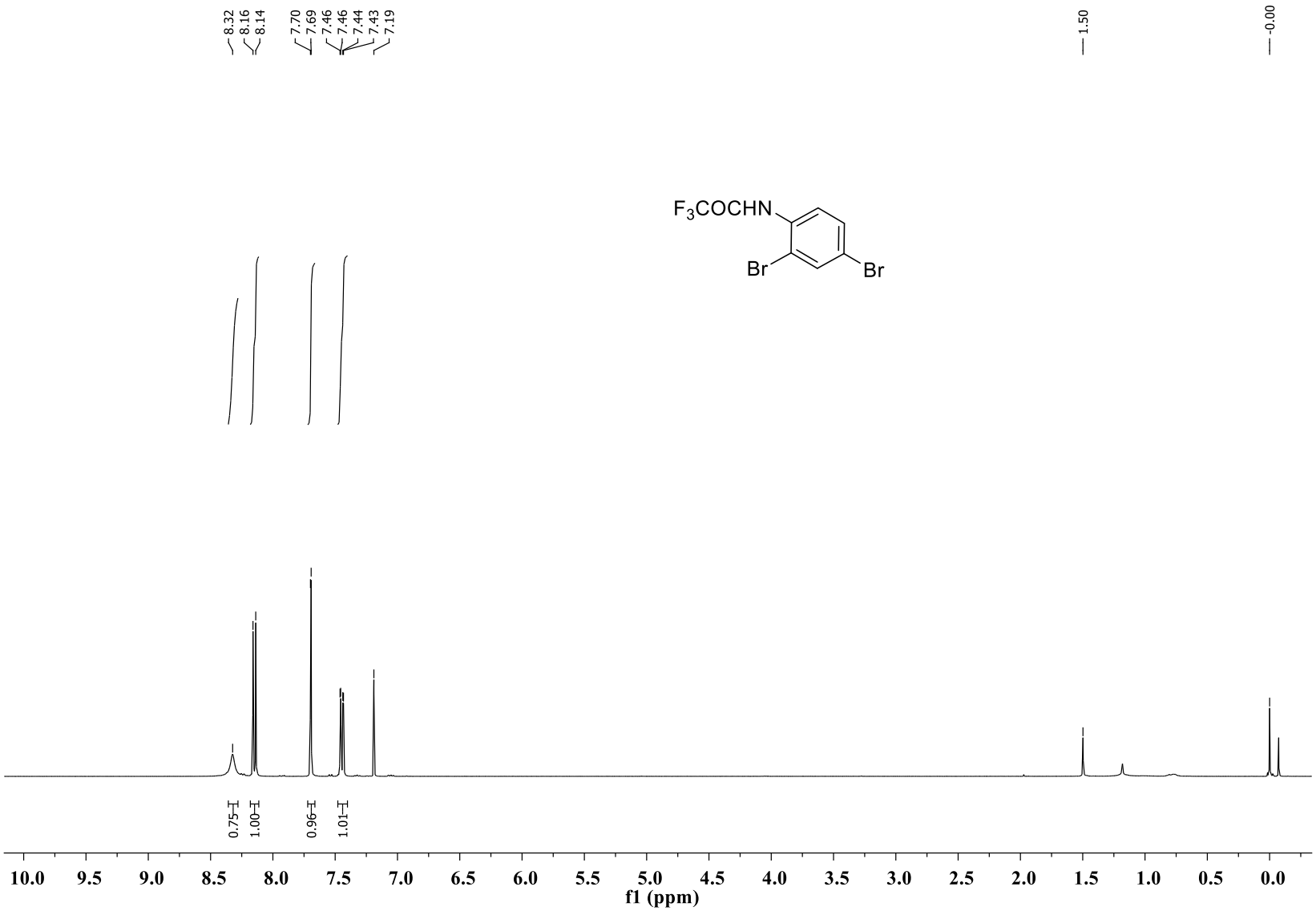
^{1}H NMR spectrum of compound **15** ($CDCl_3$, 400 MHz)**:**



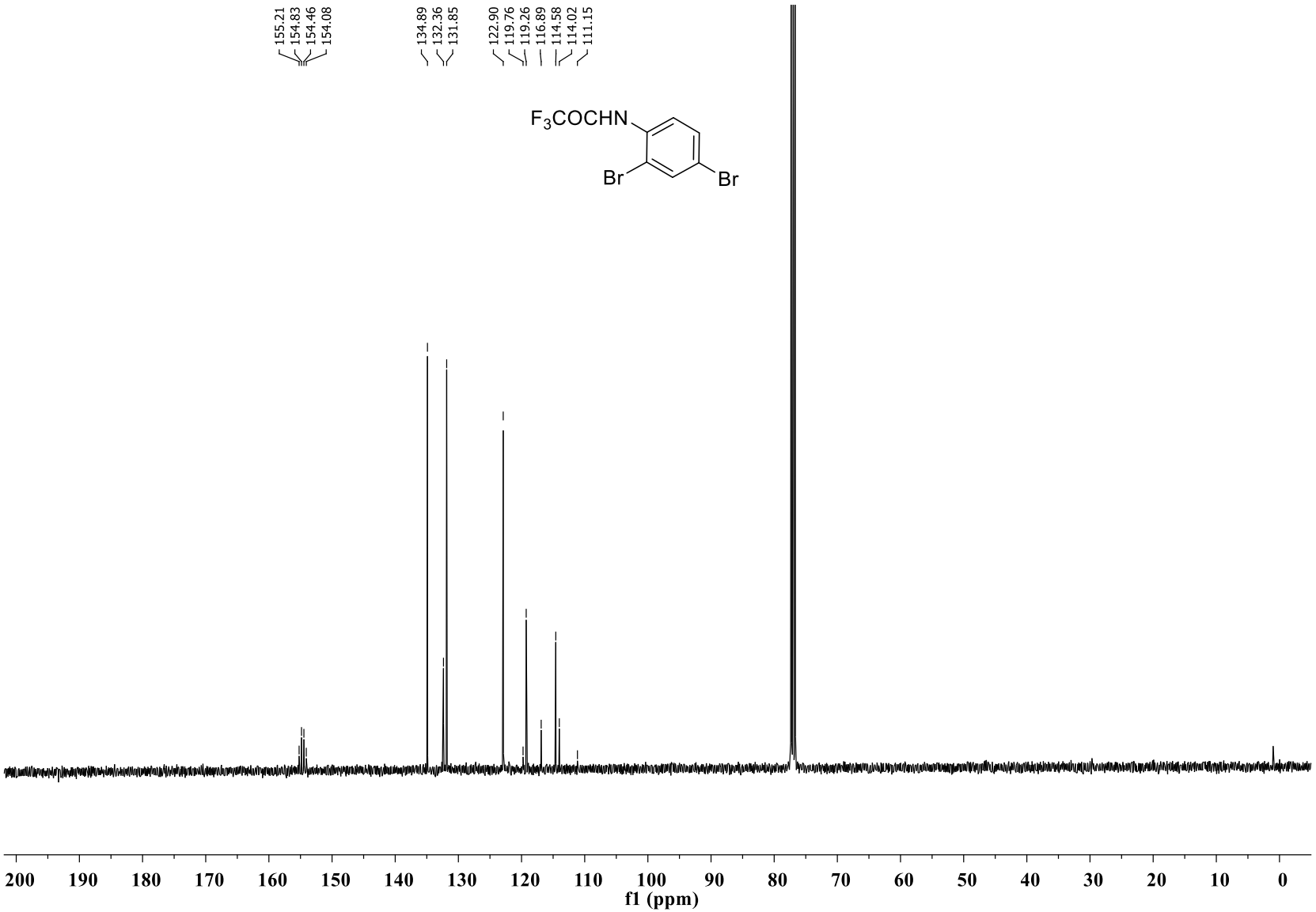
^{13}C NMR spectrum of compound **15** ($CDCl_3$, 100 MHz)**:**



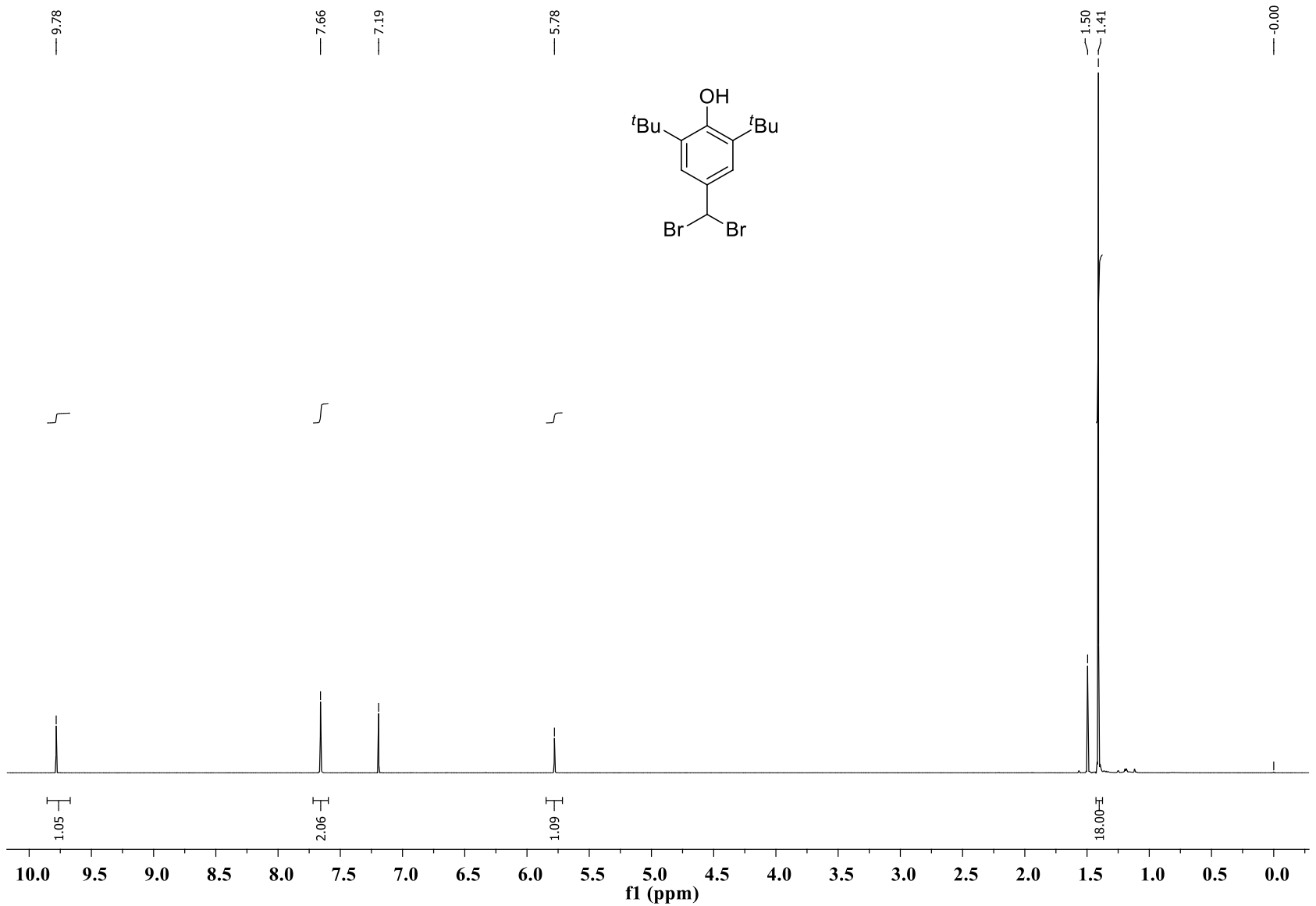
^{1}H NMR spectrum of compound **17** ($CDCl_3$, 400 MHz)**:**



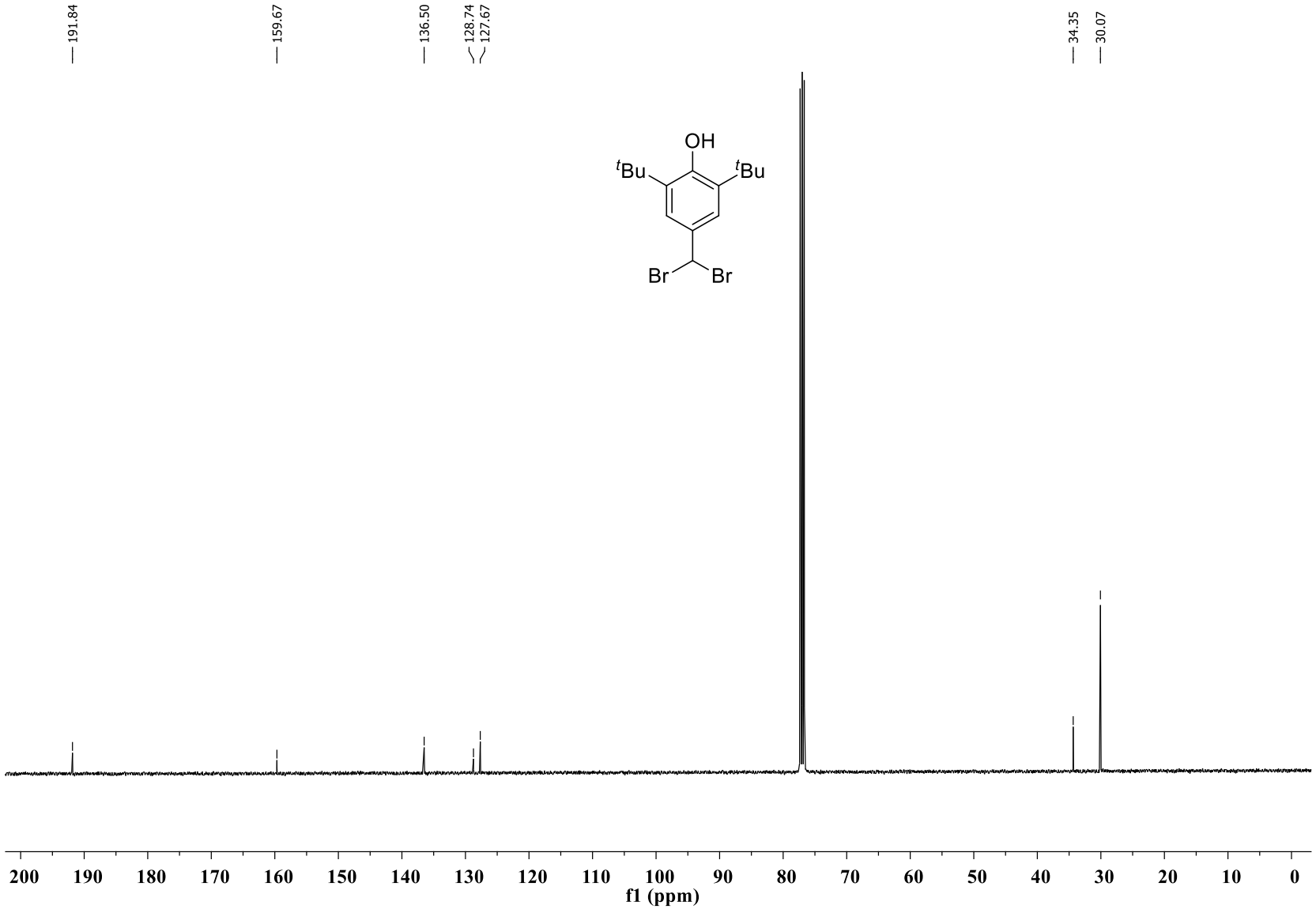
^{13}C NMR spectrum of compound **17** ($CDCl_3$, 100 MHz)**:**



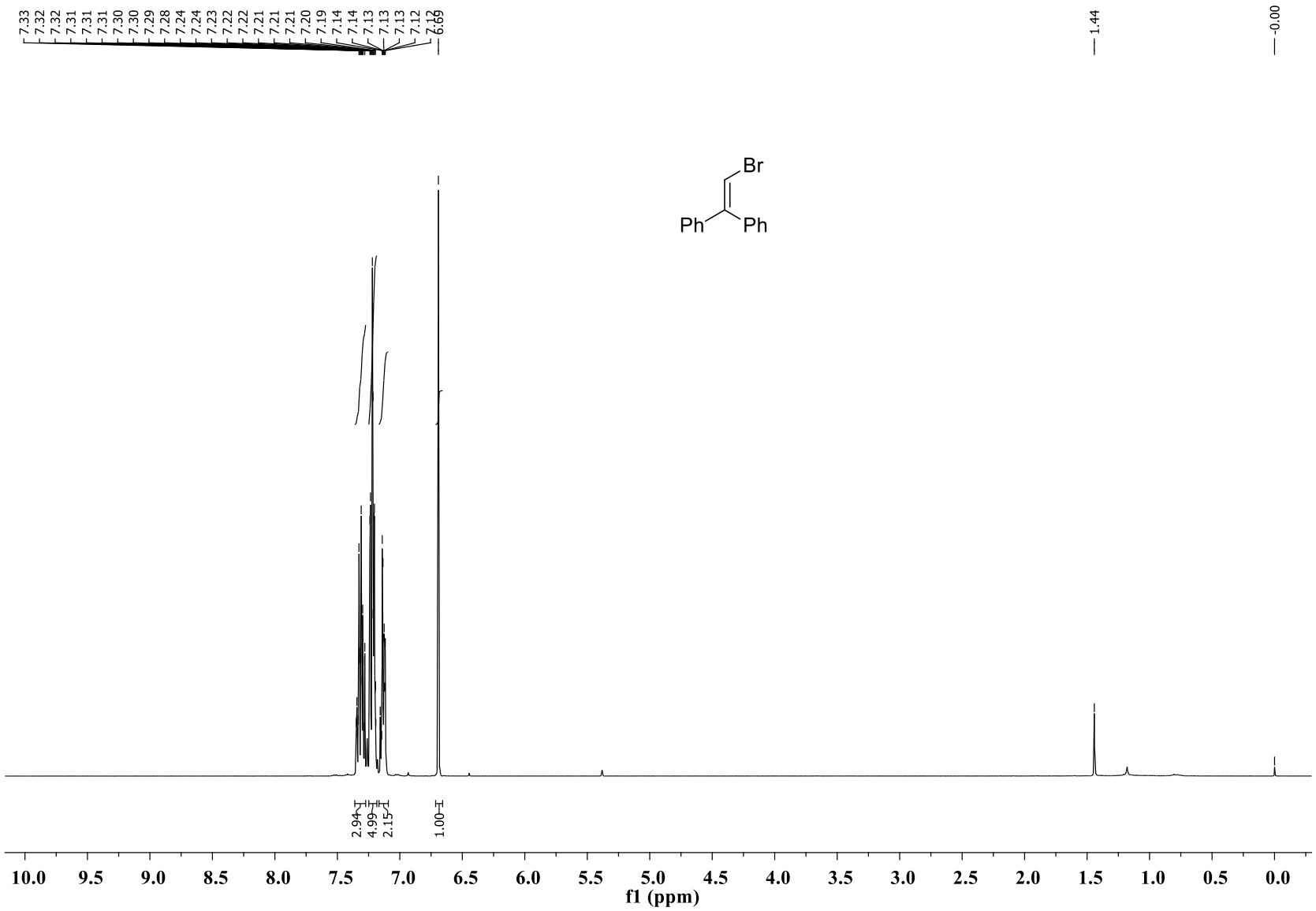
^{1}H NMR spectrum of compound **18** ($CDCl_3$, 400 MHz)**:**



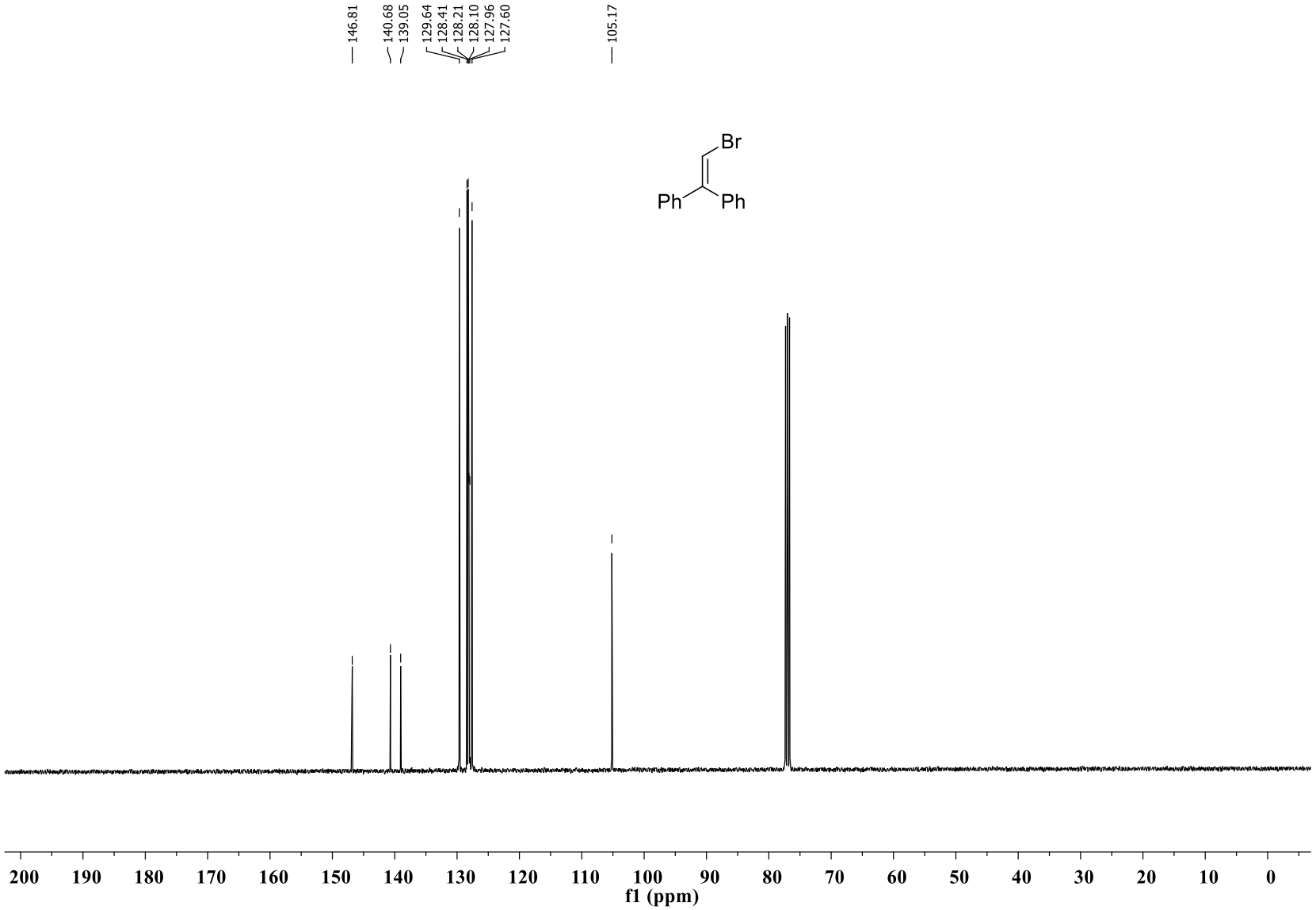
^{13}C NMR spectrum of compound **18** ($CDCl_3$, 100 MHz)**:**



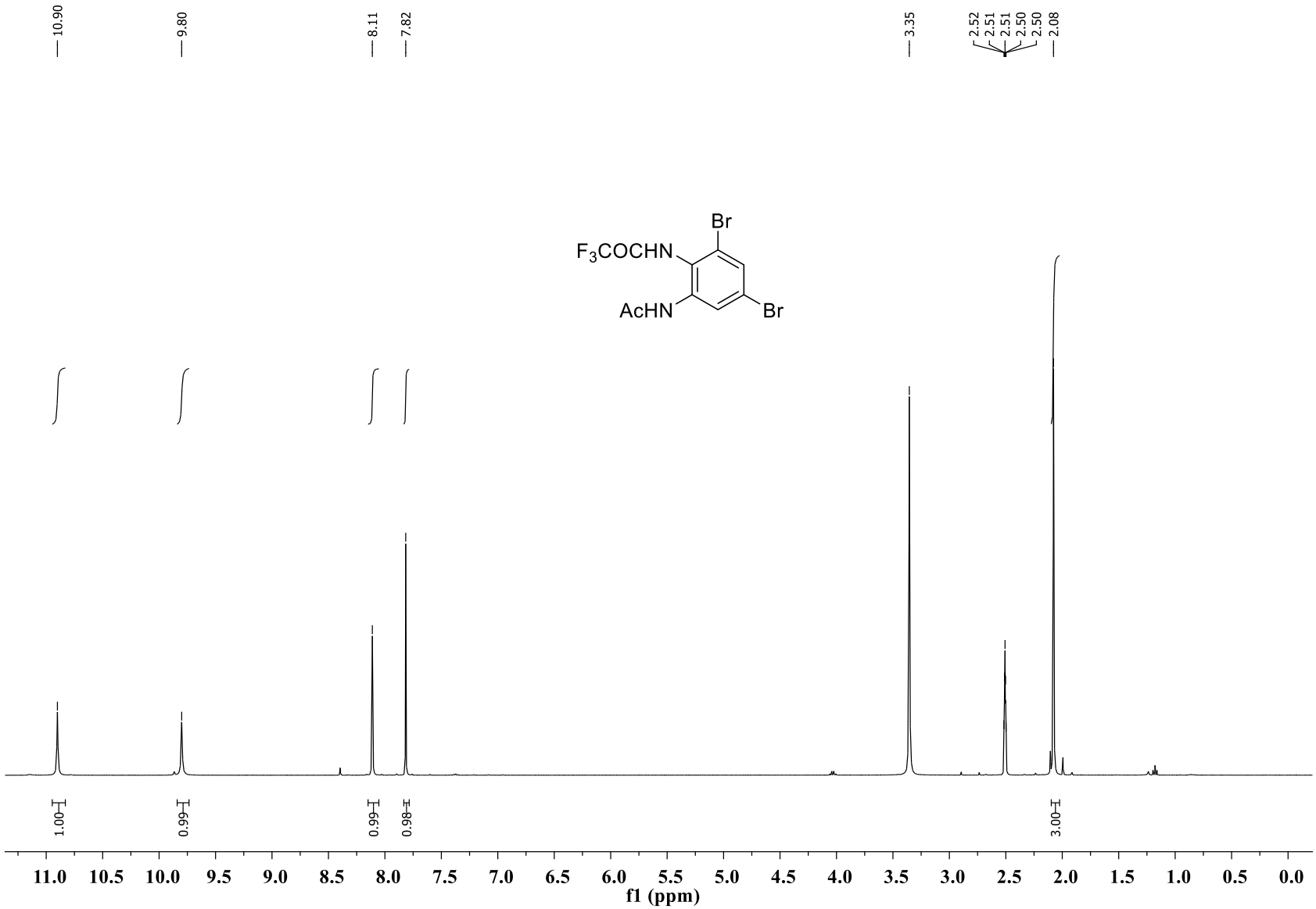
^{1}H NMR spectrum of compound **20** ($CDCl_3$, 400 MHz):



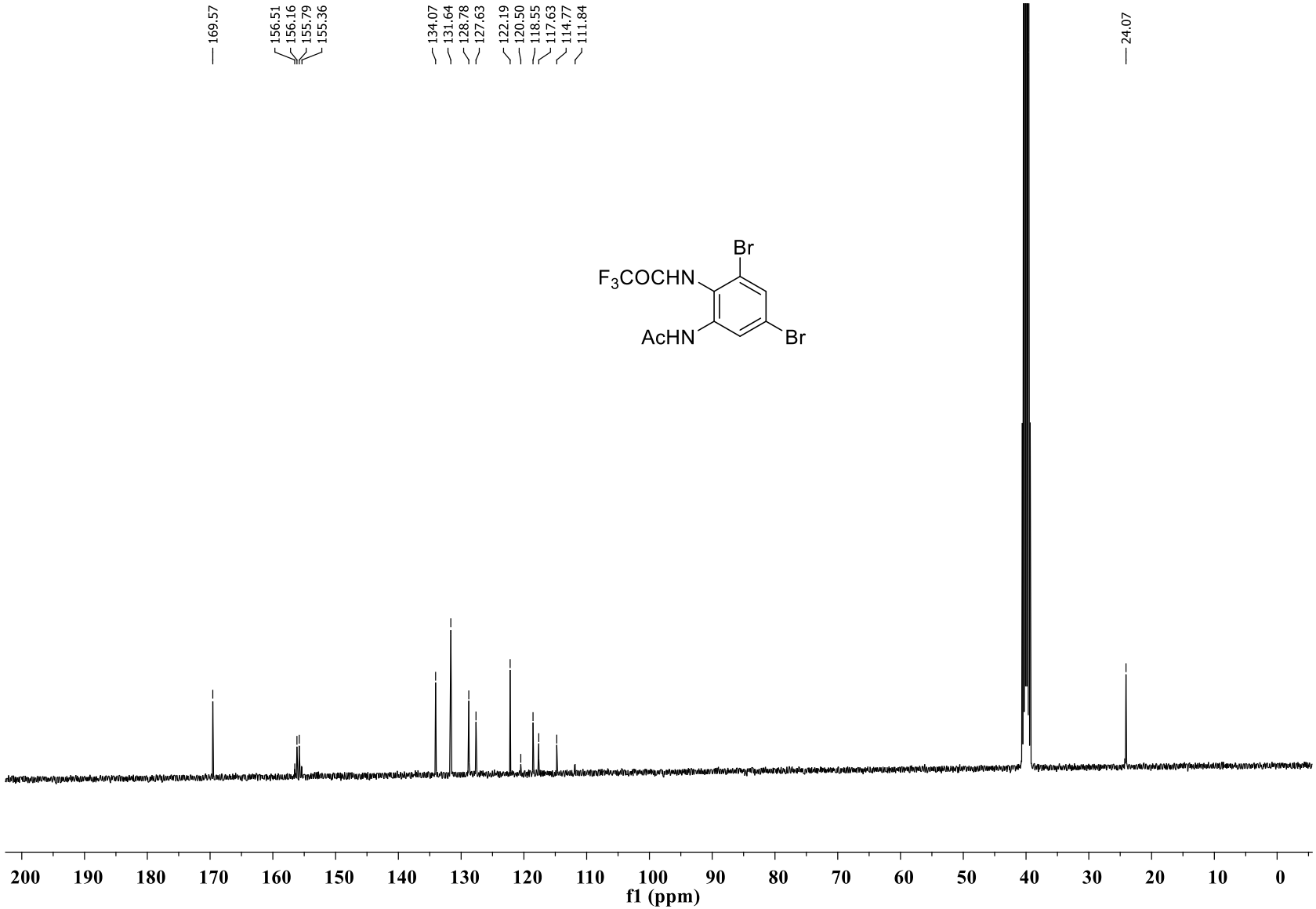
^{13}C NMR spectrum of compound **20** ($CDCl_3$, 100 MHz)**:**



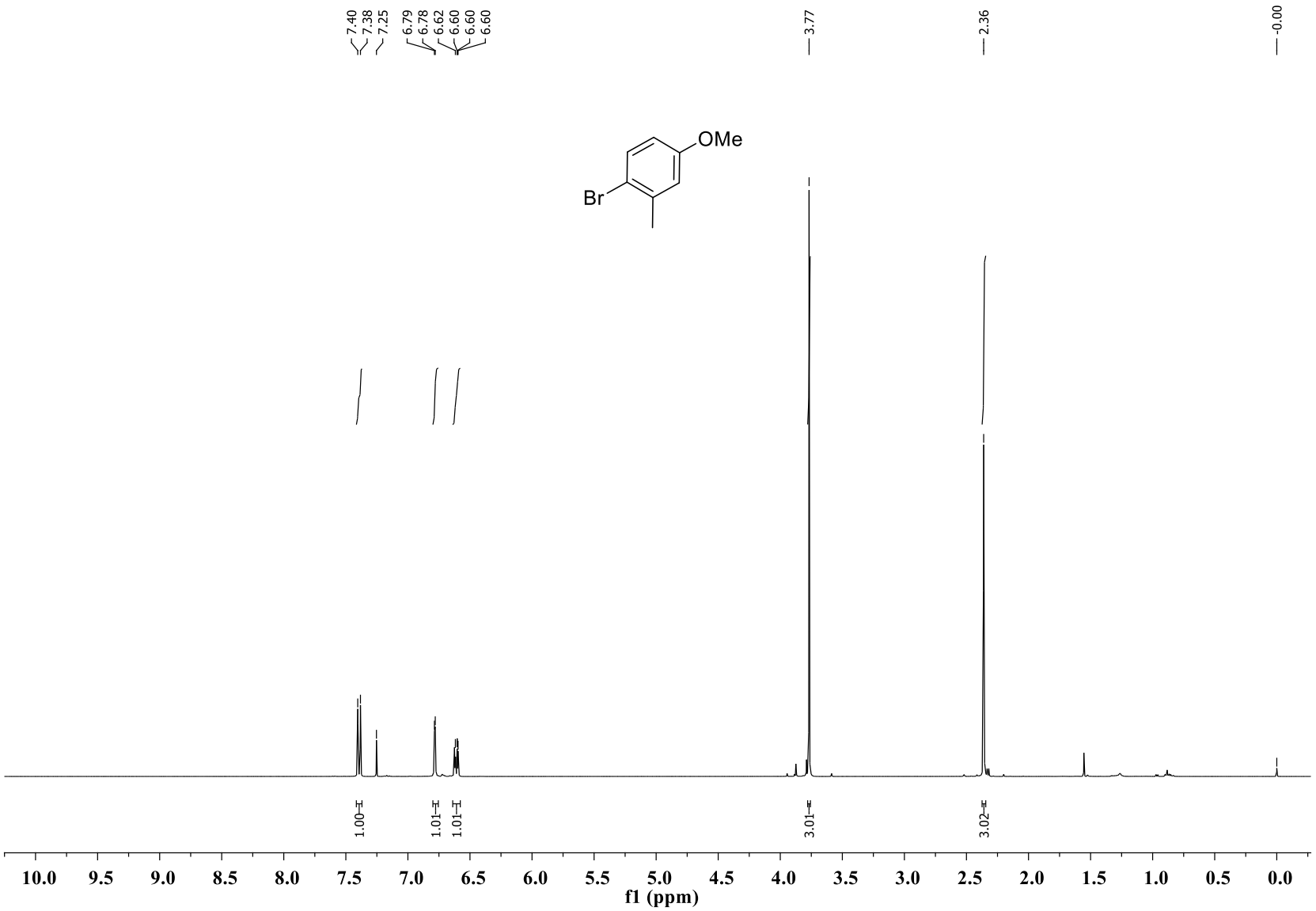
[1]H NMR spectrum of compound **21** (DMSO-*d6*, 400 MHz)**:**



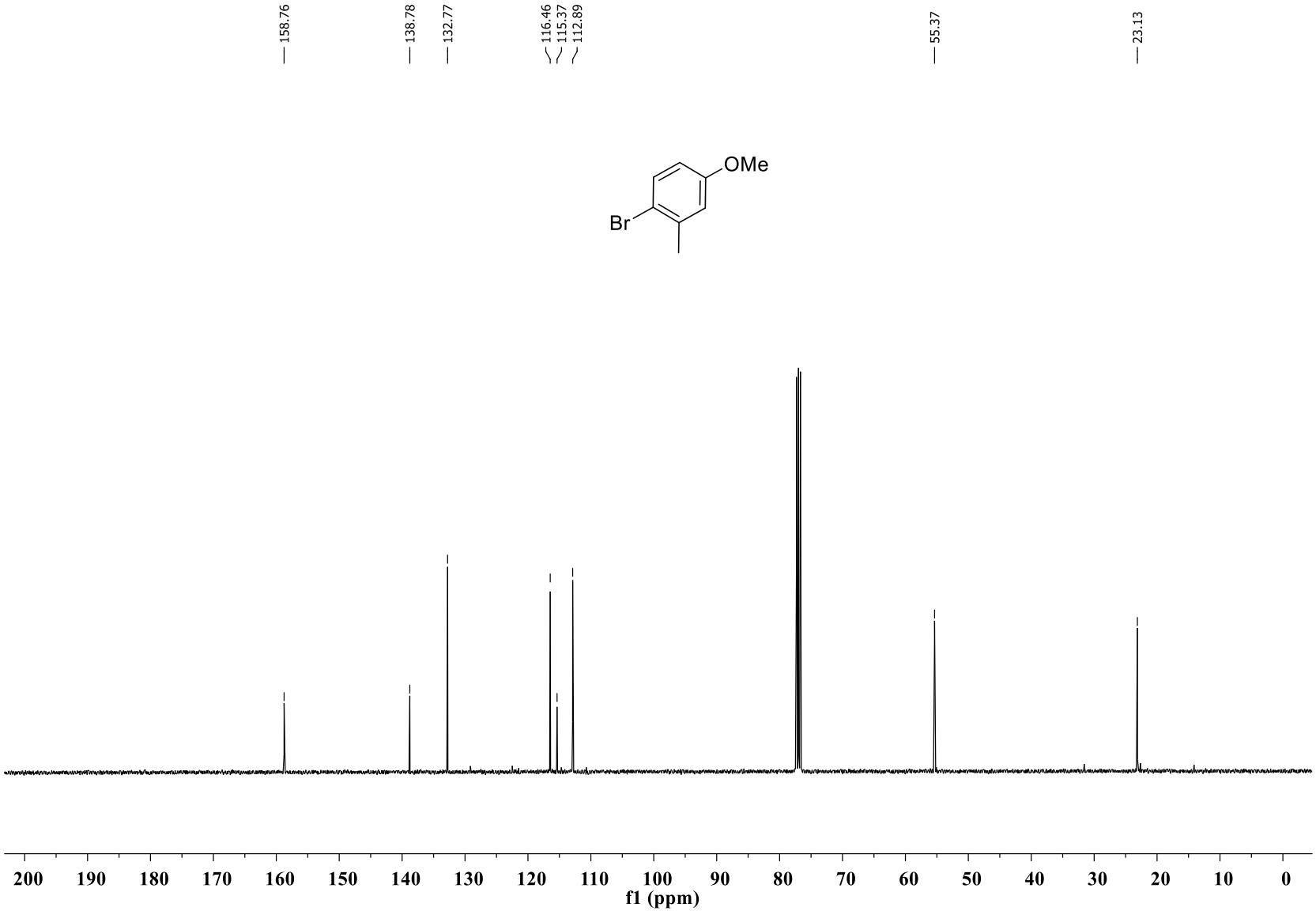
^{13}C NMR spectrum of compound **21** (DMSO-*d6*, 100 MHz)**:**



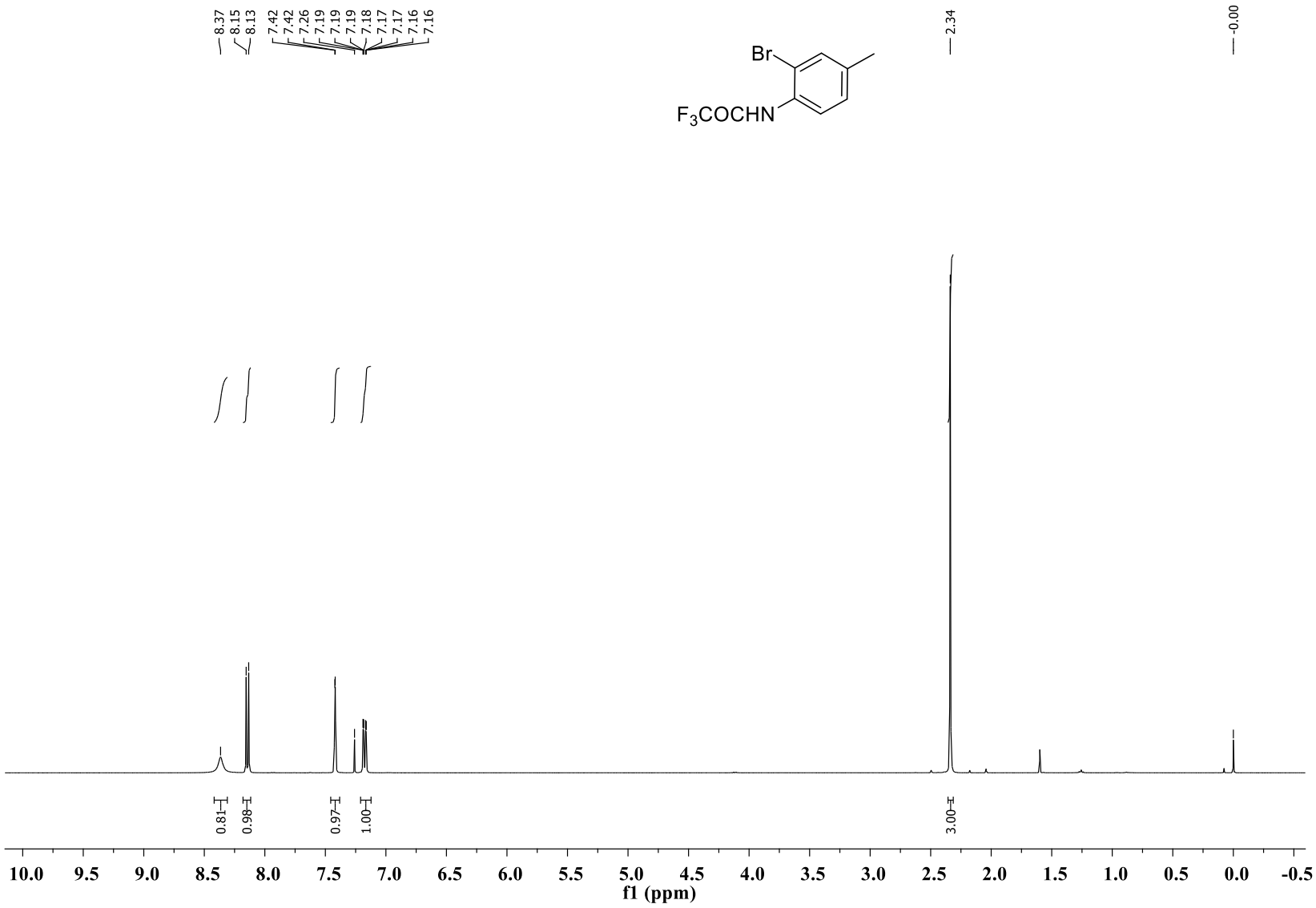
^{1}H NMR spectrum of compound **23** ($CDCl_3$, 400 MHz)**:**



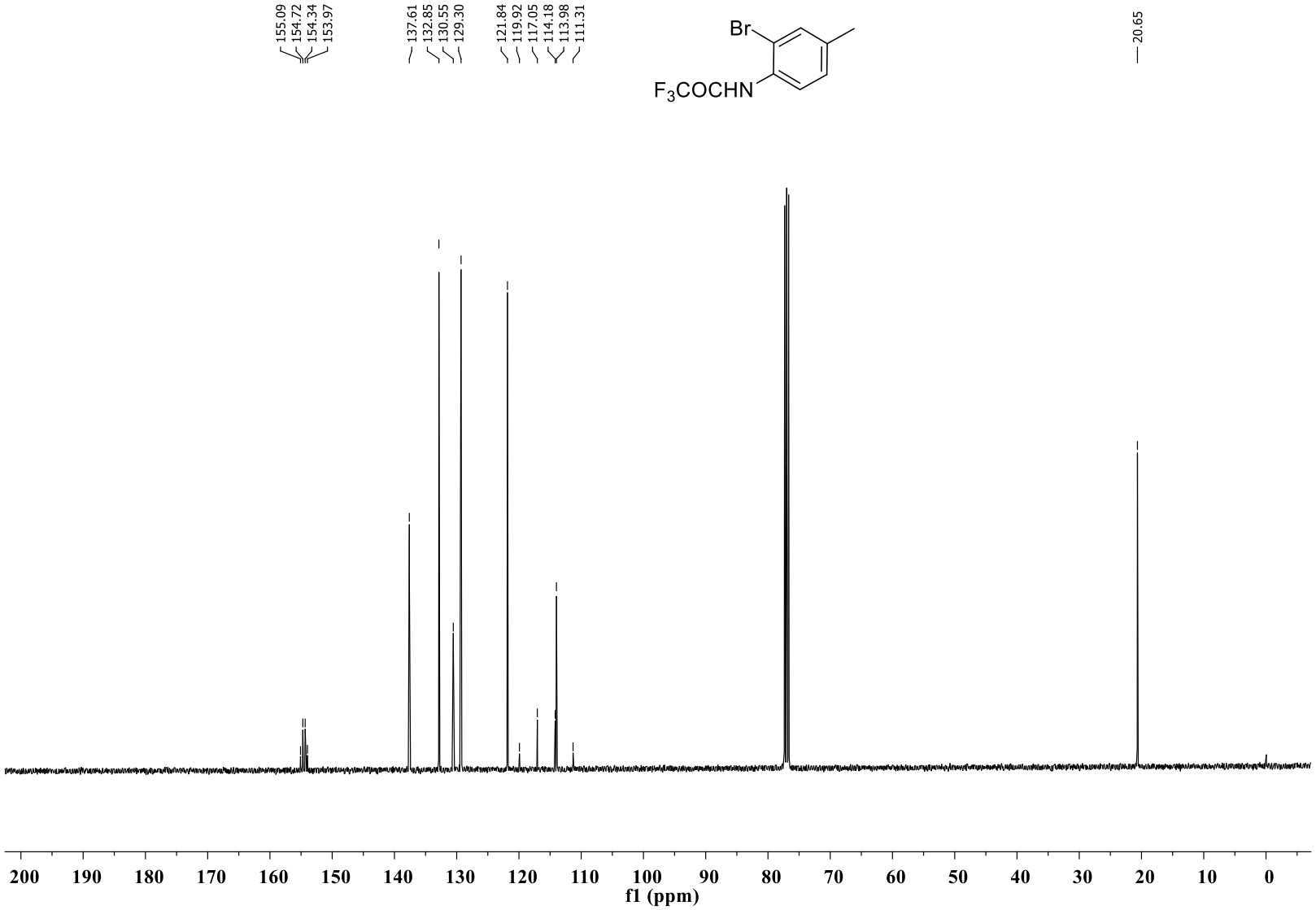
^{13}C NMR spectrum of compound **23** ($CDCl_3$, 100 MHz)**:**



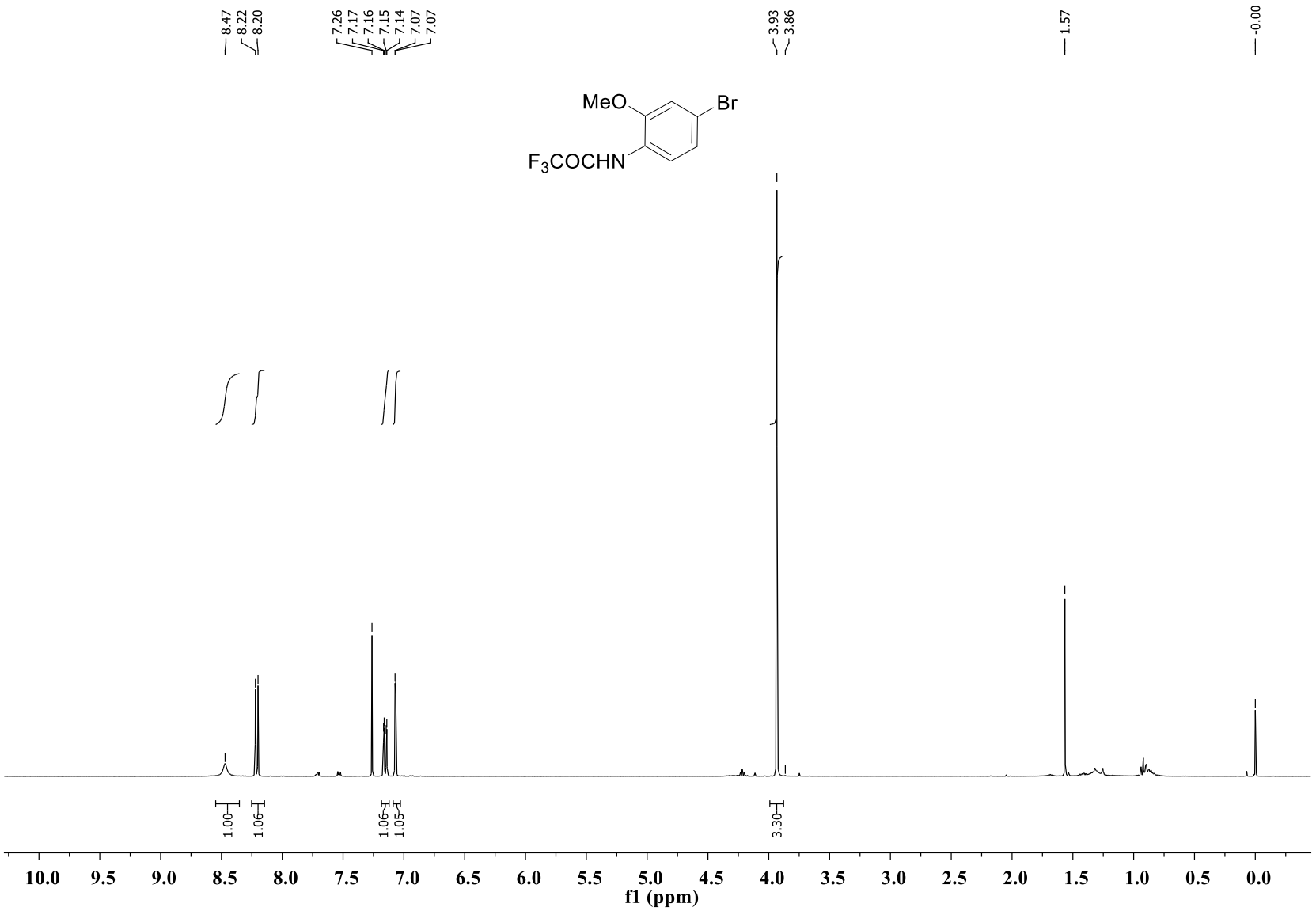
^{1}H NMR spectrum of compound **25**($CDCl_3$, 400 MHz)**:**



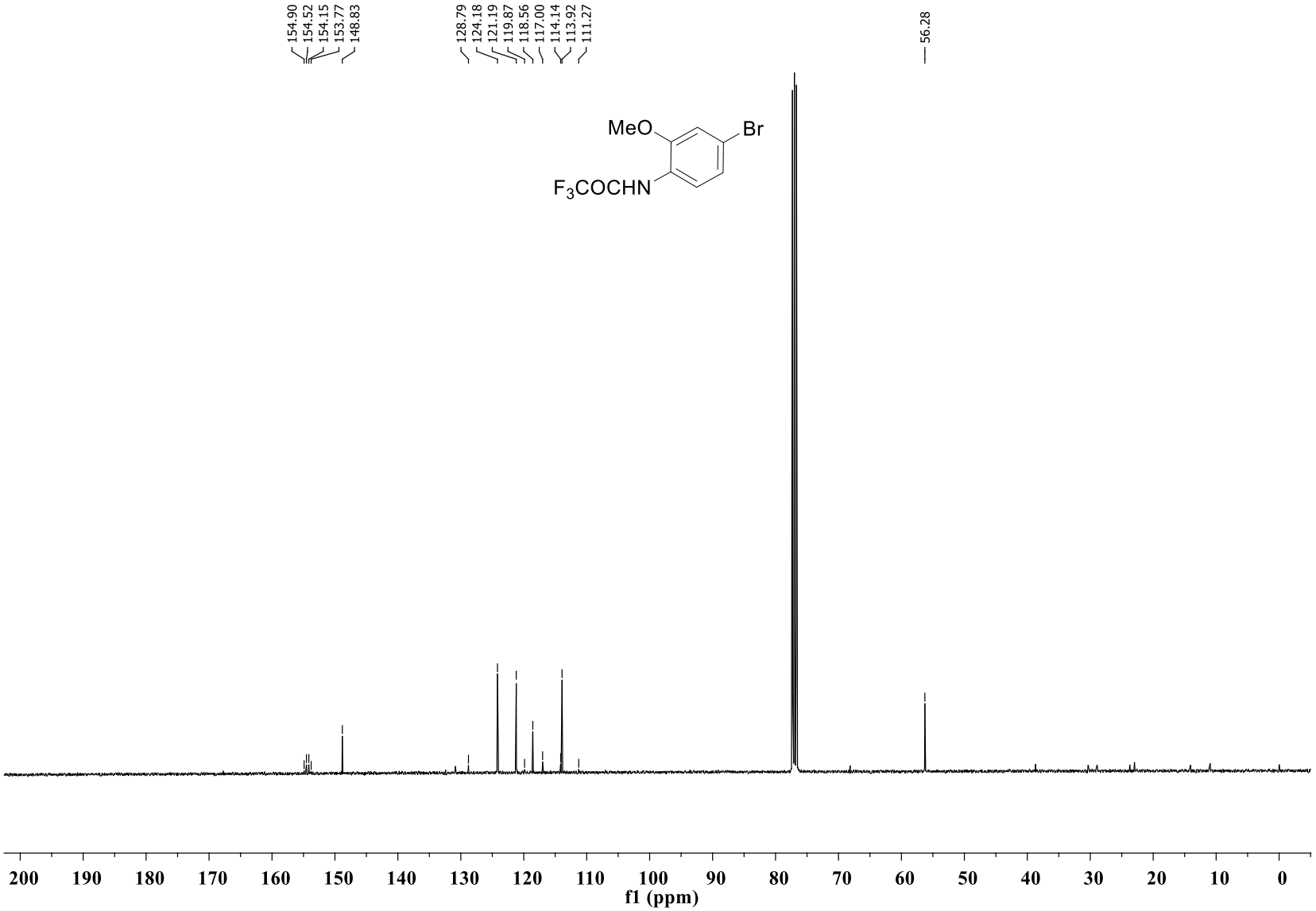
^{13}C NMR spectrum of compound **25** ($CDCl_3$, 100 MHz)**:**



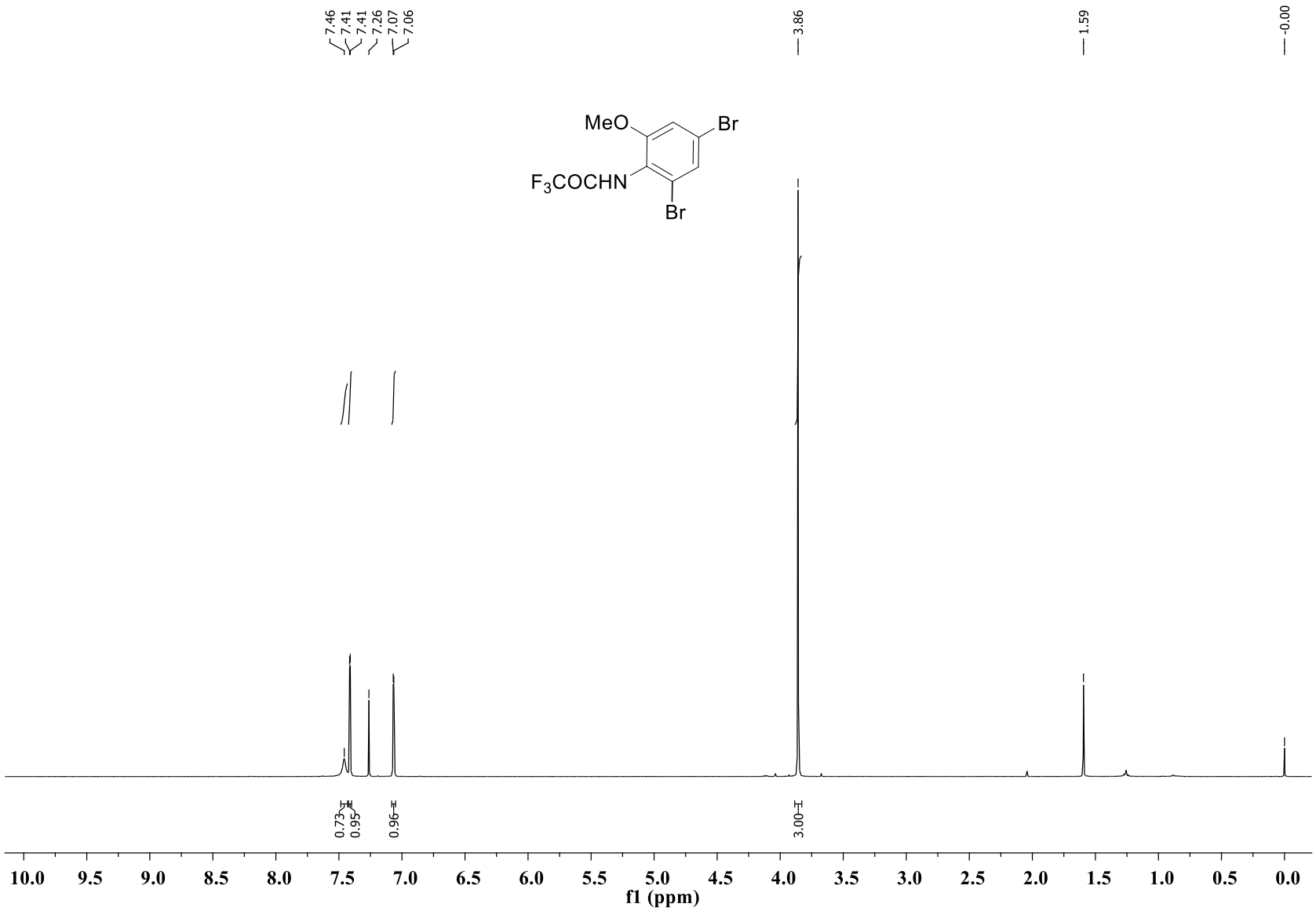
[1]H NMR spectrum of compound **27a** ($CDCl_3$, 400 MHz)**:**



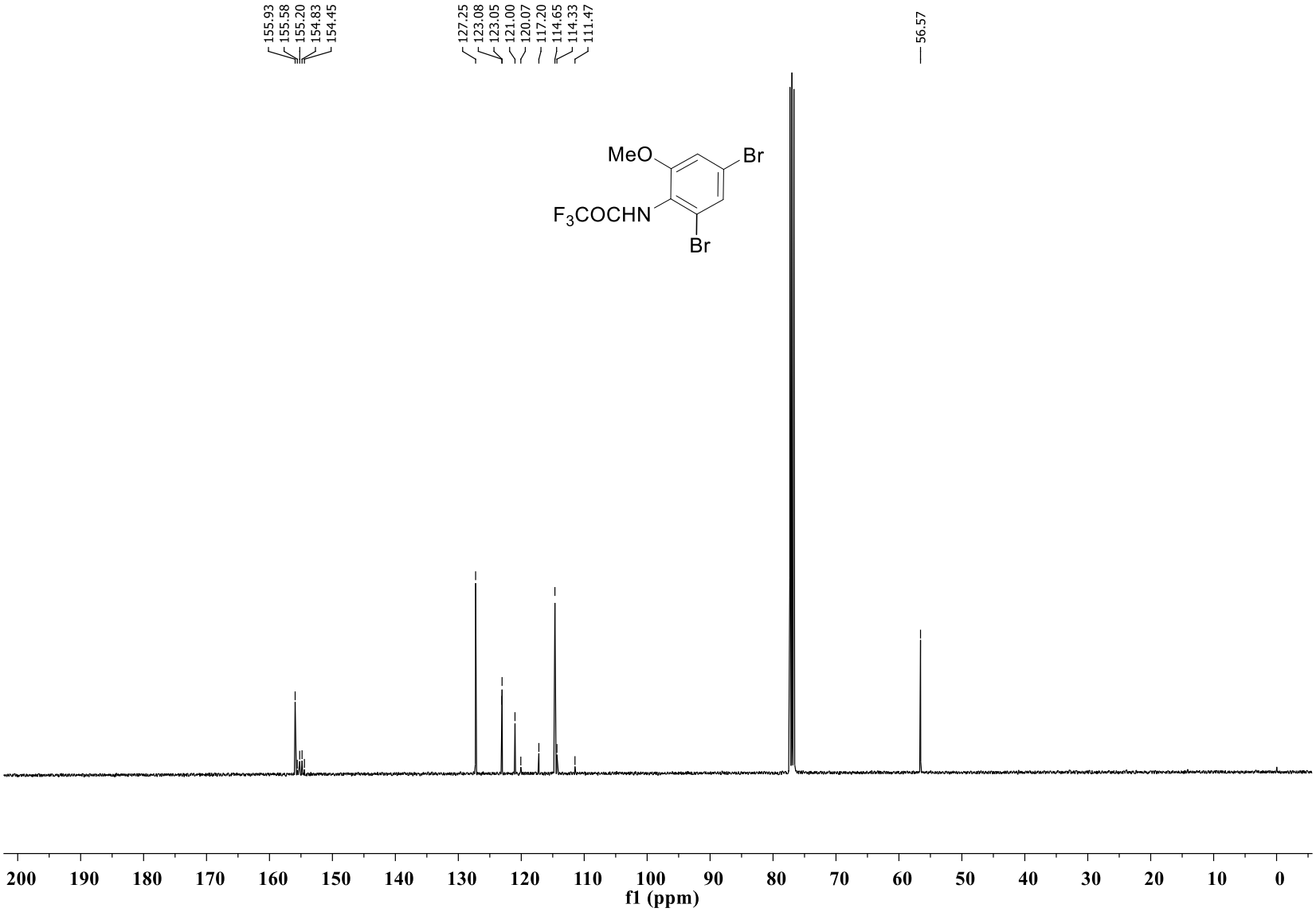
^{13}C NMR spectrum of compound **27a** ($CDCl_3$, 100 MHz)**:**



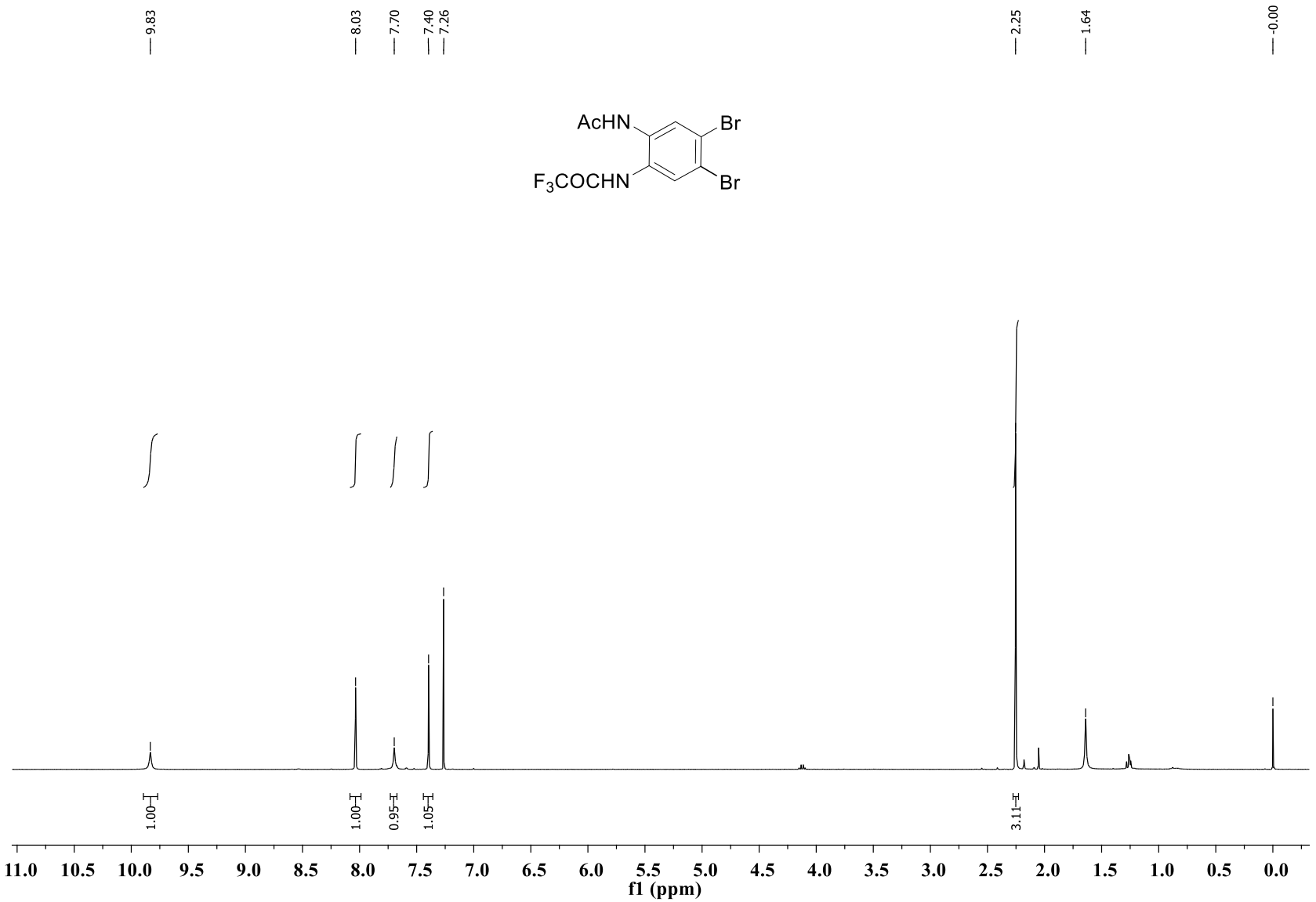
^{1}H NMR spectrum of compound **27b** ($CDCl_3$, 400 MHz)**:**



^{13}C NMR spectrum of compound **27b** ($CDCl_3$, 100 MHz)**:**



^{1}H NMR spectrum of compound **28** ($CDCl_3$, 400 MHz)**:**



^{13}C NMR spectrum of compound **28** ($CDCl_3$, 100 MHz)**:**