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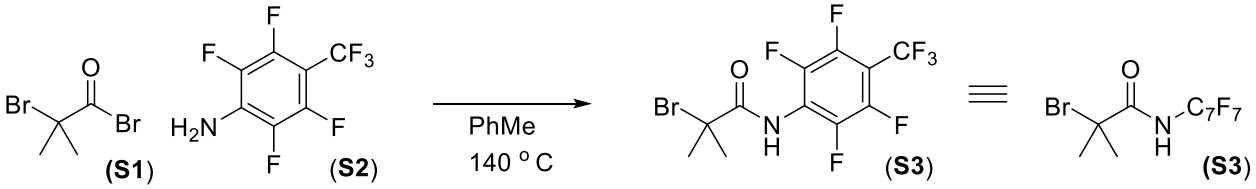
I. General Procedures, Materials, and Methods for Synthesis and C-H Activation

Instrumental Information. NMR spectra were obtained on Varian 400 MHz, Varian 500 MHz, or Varian 700 MHz NMR spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million relative to TMS with the residual solvent peak (most commonly $CDCl_3$) used as an internal reference (δ 7.26 for ^{1}H NMR and δ 77.2 for ^{13}C NMR for $CDCl_3$). ^{19}F NMR spectra were referenced to the solvent lock. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High resolution mass spectra were obtained at the University of Michigan core facility. Elemental analysis was conducted by Midwest Microlab, Indianapolis, IN. Flash chromatography was conducted on a Biotage Isolera One auto chromatography system using preloaded high performance silica gel columns (10 g, 25 g, 50 g, or 100 g as appropriate). GC-FID was conducted on a Shimadzu CG-17A system. Melting points were obtained on a OptiMelt automated melting point system. IR were obtained on an FT Perkin Elmer instrument via thin film deposition.

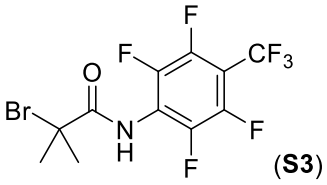
Materials. All reagents were obtained from a commercial vendor (Aldrich, CombiBlocks, Oakwood, AstaTech, Synthonix, Enamine, Manchester Organics, Carbosynth, Pressure Chemicals, Matrix, SantaCruz Biotech, or Ontario Chemicals) and were used without further purification unless otherwise stated. Reagents were stored under ambient conditions unless otherwise stated. The solvent *tert*-amyl alcohol was stored over activated molecular sieves. Solutions of SmI_2 were stored and used inside of a nitrogen filled glove box.

General Methods. The manipulation of solid reagents was conducted on the benchtop unless otherwise stated. Reactions were conducted under an ambient atmosphere unless otherwise stated. Reaction vessels were sealed with either a septum (flask) or a Teflon lined cap (4 mL or 20 mL vial). Reactions conducted at elevated temperatures were heated on a hot plate using an aluminum block. Temperatures were regulated using an external thermocouple. For reactions that were heated in excess of the ambient boiling point of the solvent (i.e. *tert*-amyl alcohol heated to 140 ºC), electrical tape was wrapped around the cap of the sealed vial prior to heating. For TLC analysis, R_f values are reported based on normal phase silica plates with fluorescent indicator, and sample detection was conducted based on quenched fluorescence at 254 nm.

II. Synthesis and Characterization of Amine Derivatives

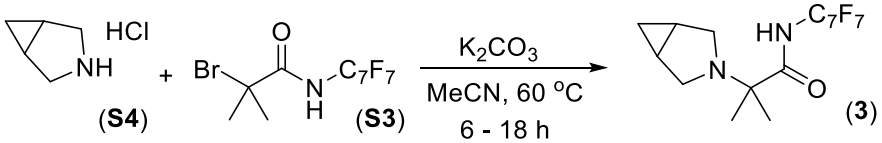


A round bottom flask was charged with 2,3,5,6-tetrafluoro-4-(trifluoromethyl)aniline (7.01 g, 30.1 mmol) and toluene (30 mL). To this solution, 2-bromoisobutyryl bromide (4 mL, 32.3 mmol, 1.1 equiv) was added. The flask was fitted with a reflux condenser topped with a drying tube that was packed with K_2CO_3 (5 g). The reaction was heated to an external temperature of 140 ºC. After 18 h, the reaction mixture was cooled to room temperature and concentrated under vacuum. The solid residue was redissolved in a minimum amount of hexanes and heated to reflux. Upon slow cooling, a crystalline solid precipitated from solution. The solid was collected and rinsed with several small volumes of cold hexanes (3 x 5 mL). The solid was then dried under vacuum to afford product **S3** as white needles (10.9 g, 95% yield).

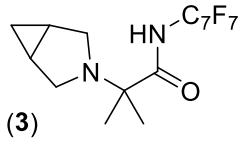


MP 125-126 ºC
IR (thin film): 1685 cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 8.19 (s, 1H), 2.06 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.7 Hz, 3F), –141.2 (m, 2F), -144.2 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 170.2, 60.7, 32.2.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{11}H_8BrF_7NO^+$: 381.9677; Found: 381.9668.
R_f = 0.55 in 20% EtOAc in hexanes

Synthesis of Starting Materials:

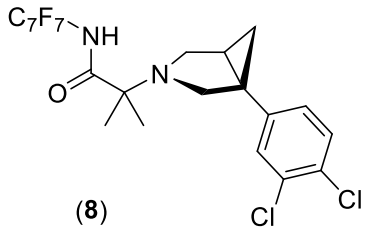


A 20 mL scintillation vial was charged with solid 3-azabicyclo[3.1.0]hexane hydrochloride **S4** (121 mg, 1.01 mmol), α-bromo propanamide **S3** (430 mg, 1.1 mmol, 1.1 equiv), and K_2CO_3 (442 mg, 3.2 mmol, 3.2 equiv). To the solids, anhydrous acetonitrile (5 mL) was added. The vial was sealed, and the reaction was heated to an external temperature of 60 ºC. After 18 h, the reaction was cooled to room temperature, diluted with EtOAc (~5 mL), and filtered through Celite. The filtrate was concentrated under reduced pressure. Final purification via column chromatography (gradient elution from 0% to 20% EtOAc in hexanes) afforded product **3** (315 mg, 81% yield) as a white solid. Other amine derivatives were prepared in an analogous manner by using the appropriate amine starting material. When an amine hydrochloride was used, 3.2 equiv of K_2CO_3 were used. When the amine free base was used, 2 equiv of K_2CO_3 were used. See substrate specific notes below.



(**3**)

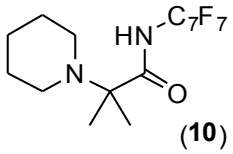
MP 114-116 ºC
IR (thin film): 1700 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.02 (s, 1H), 2.88 (d, *J* = 8.5 Hz, 2H), 2.69 (dt, *J* = 8.5, 1.6 Hz, 2H), 1.43 (m, 2H), 1.31 (s, 6H), 0.63 (q, *J* = 4.2 Hz, 1H), 0.48 (td, *J* = 7.7, 4.3 Hz, 1H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, *J* = 21.7 Hz, 3F), –141.2 (m, 2F), –144.2 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.1, 61.1, 47.6, 21.0, 14.5, 6.5.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{16}H_{16}F_7N_2O^+$: 385.1151; Found: 385.1145.
R_f = 0.60 in 20% EtOAc in hexanes



(**8**)

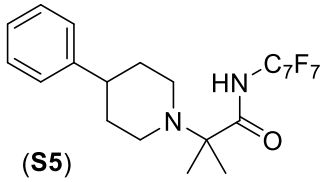
Compound **8** was isolated in 87% yield as a white solid using standard conditions above.
MP 75-77 ºC
IR (thin film): 1716 (br) cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 2.2 Hz, 1H), 6.99 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.22 (d, *J* = 8.5 Hz, 1H), 3.02 (d, *J* = 8.6 Hz, 1H), 2.95-2.88

(multiple peaks, 2H), 1.82 (dt, J = 7.9, 3.9 Hz, 1H), 1.41 – 1.38 (multiple peaks, 4H), 1.37 (s, 3H), 0.93 (dd, J = 8.0, 4.8 Hz, 1H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.7 Hz, 3F), –141.0 (dd, J = 21.7, 11.7 Hz, 2F), –144.1 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.5, 142.3, 132.3, 130.2, 130.0, 128.5, 125.9, 61.3, 51.5, 47.9, 29.3, 23.8, 21.2, 20.7, 16.6.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{22}H_{18}F_7N_2O^+$: 529.0684; Found: 529.0679.
R_f = 0.60 in 20% EtOAc in hexanes



(**10**)

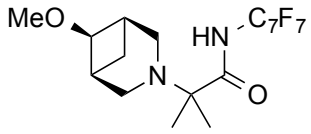
Note: 2 equiv of piperidine and 2 equiv of K_2CO_3 were used. Amide **S3** was the limiting reagent. Isolated in 84% yield as a white solid using standard conditions above.
MP 72-74 ºC
IR (thin film): 1707 (br) cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.50 (br s, 1H), 2.50 (br s, 4H), 1.66 (br s, 4H), 1.51 (br s, 2H), 1.29 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.7 Hz, 3F), –141.2 (m, 2F), –144.2 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.9, 64.9, 48.0, 26.7, 24.5, 20.5.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{16}H_{18}F_7N_2O^+$: 387.1307; Found: 387.1304.
R_f = 0.60 in 20% EtOAc in hexanes



(**S5**)

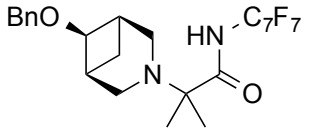
Compound **S5** was isolated in 80% yield as a white solid using the standard conditions.
MP 138-141 ºC
IR (thin film): 1717 (br) cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.25-7.20 (multiple peaks, 3H), 2.99 (d, J = 11.2 Hz, 2H), 2.58 (tt, J = 12.4, 3.9 Hz, 1H), 2.40 (td, J = 11.5, 2.1 Hz, 2H), 1.99 (dt, J = 12.7, 2.9 Hz, 2H), 1.79 (m, 2H), 1.36 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.0 (t, J = 21.7 Hz, 3F), –141.0 (m, 2F), –144.1 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to

the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.7, 145.6, 128.5, 126.7, 126.4, 64.8, 47.8, 42.6, 34.0, 20.5.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{22}H_{22}F_7N_2O^+$: 463.1620; Found: 463.1621.
R_f = 0.60 in 20% EtOAc in hexanes



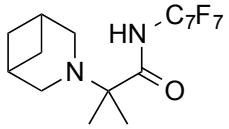
(**S6**)

Note: The trifluoroacetate salt of the amine was used as the precursor. Preparative TLC (10% EtOAc in hexanes) was used for isolation of the substrate.
Compound **S6** was isolated in 33% yield as a white solid using the standard conditions.
MP 89-91 ºC
IR (thin film): 1700 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (s, 1H), 3.57 (t, J = 5 Hz, 1H), 3.29 (s, 3H), 3.14-3.06 (multiple peaks, 4H), 2.65 (br s, 2H), 1.59 (d, J = 10 Hz, 1H), 1.50 (m, 1H), 1.43 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 18.9 Hz, 3F), –141.4 (m, 2F), –143.7 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 75.3, 63.4, 56.5, 44.7, 37.6, 22.8, 22.5.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{18}H_{20}F_7N_2O_2$: 429.1408 ; Found: 429.1411.
R_f = 0.27 in 10% EtOAc in hexanes



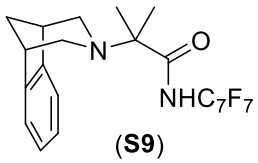
(**S7**)

Note: The hydrochloric salt of the amine was used as the precursor.
Compound **S7** was isolated in 51% yield as a white solid using the standard conditions.
MP 111-113 ºC
IR (thin film): 1693 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.60 (br s, 1H), 7.22 (d, J = 7 Hz, 2H), 7.14 (t, J = 7 Hz, 2H), 7.08 (t, J = 7 Hz, 1H), 4.47 (s, 2H), 3.87 (t, J = 9.1 Hz, 1H), 3.25 (d, J = 14 Hz, 2H), 3.15 (d, J = 9.1 Hz, 2H), 2.73 (t, J = 4.9 Hz, 2 H), 1.57 (m, 1H), 1.46 (app d, J = 9.1 Hz, 1H), 1.42 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.20 (t, J = 21.5 Hz, 3F), –142.31 (m, 2F), –143.57 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.8, 137.2, 128.2, 128.1, 128.0, 74.5, 72.1, 63.1, 45.7, 38.2, 24.2, 23.2.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{24}H_{23}F_7N_2O_2$: 505.1721; Found: 505.1721.
R_f = 0.19 in 10% EtOAc in hexanes



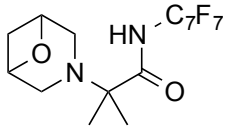
(**S8**)

Compound **S8** was isolated in 56% yield as a white solid using the standard conditions.
MP 91-93 ºC
IR (thin film): 1701 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.22 (br s, 1H), 2.95 (s, 4H), 2.41 (tt, *J* = 5.9, 1.6 Hz, 2H), 2.05 (m, 2H), 1.49 (m, 2H), 1.38 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, *J* = 21.7 Hz, 3F), –141.2 (m, 2F), –144.3 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.5, 63.2, 49.9, 33.2, 32.6, 20.7.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{17}H_{18}F_7N_2O^+$: 399.1307; Found: 399.1300.
R_f = 0.60 in 20% EtOAc in hexanes



(**S9**)

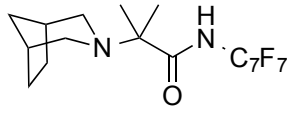
Compound **S9** was isolated in 86% yield as a white solid using the standard conditions.
MP 121-123 ºC
IR (thin film): 1712 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.49 (br s, 1H), 7.16 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.06 (dd, *J* = 5.3, 3.1 Hz, 2H), 3.21 (t, *J* = 4.2 Hz, 2H), 2.70 (m, 2H), 2.69 (d, *J* = 10.4 Hz, 2H), 2.31 (dt, *J* = 10.3, 3.6, Hz, 1H), 1.74 (d, *J* = 10.4 Hz, 1H), 1.20 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, *J* = 21.8 Hz, 3F), –141.5 (m, 2F), –143.0 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.2, 145.5, 126.7, 121.6, 63.7, 50.5, 43.6, 41.0, 21.6.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{22}H_{20}F_7N_2O^+$: 461.1464; Found: 461.1469.
R_f = 0.55 in 20% EtOAc in hexanes



(**S10**)

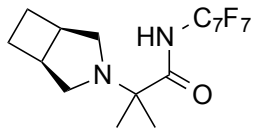
Note: The tosylate salt of the amine was used as the precursor.
Compound **S10** was isolated in 59% yield as an oil using the standard conditions.
IR (thin film): 1702 (br) cm^{-1}

^{1}H NMR (700 MHz, $CDCl_3$) δ) 8.97 (s, 1H), 4.58 (m, 2H), 3.12-3.03 (multiple peaks, 3H), 2.96 (dt, J = 11.5, 2.0 Hz, 2H), 2.26 (d, J = 8.3 Hz, 1H), 1.39 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.3 (t, J = 21.7 Hz, 3F), –141.4 (m, 2F), –144.5 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.6, 79.1, 63.3, 48.8, 30.0, 20.6.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{16}H_{16}F_7N_2O_2^+$: 401.1100; Found: 401.1095.
R_f = 0.30 in 35% EtOAc in hexanes



(**S11**)

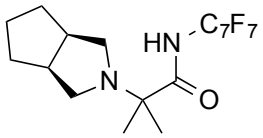
Compound **S11** was isolated in 93% yield as a white solid using standard conditions, except that purification was conducted via column chromatography, followed by recrystallization of the substrate from hot hexanes.
MP 121-123 ºC
IR (thin film): 1699 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1H), 2.61 (dd, J = 4, 11 Hz, 2H), 2.37 (d, J = 11 Hz, 2H), 2.23 (br s, 2H), 1.66 (m, 4 H), 1.50 (m, 1H), 1.39 (d, J = 11 Hz, 1H), 1.26 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$): –56.3 (t, J = 23.6 Hz, 3F), –141.7 (m, 2F), –143.7 (m, 2F)
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.0, 64.2, 53.3, 37.5, 35.2, 28.2, 20.8.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{18}H_{20}F_7N_2O$: 413.1458 ; Found: 413.1460.
R_f = 0.29 in 5% EtOAc in hexanes



(**S12**)

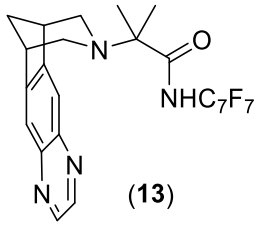
Note: The hydrochloric salt of the amine was used as the precursor.
Compound **S12** was isolated in 40% yield as a white solid using the standard conditions.
MP 84-86 ºC
IR (thin film): 1700 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (br s, 1H), 2.86 (m, 2H), 2.75 (d, J = 9.5 Hz, 2H), 2.46 (dd, J = 9.5, 5 Hz, 2H), 2.25 (s, J = 6.5 Hz, 2H), 1.72 (m, 2H), 1.39 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.0 (t, J = 23.6 Hz, 3F), –141.2 (m, 2F), –143.7 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 61.7, 53.7, 36.5, 24.4, 21.2.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{17}H_{18}F_7N_2O$: 399.1302; Found: 399.1299.
R_f = 0.33 in 10% EtOAc in hexanes



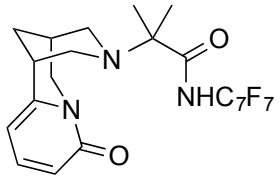
(**S13**)

Note: The hydrochloric salt of the amine was used as the precursor.
Compound **S13** was isolated in 45% yield as a white solid using the standard conditions.
MP 68-70 ºC
IR (thin film): 1698 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.38 (br s, 1H), 2.75 (app t, *J* = 7.7 Hz, 2H), 2.58 (m, 2H), 2.37 (app d, *J* = 7.7 Hz, 2H), 1.81 (app sextet, *J* = 7 Hz, 2H), 1.65 (septet, *J* = 7 Hz, 1H), 1.52 (septet, *J* = 7 Hz, 1H), 1.39 (m, 2H), 1.32 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.04 (t, *J* = 21.9 Hz, 3F), –141.24 (m, 2F), –143.95 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.5, 61.7, 54.0, 41.8, 33.6, 26.8, 20.9.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{18}H_{19}F_7N_2O$: 413.1458; Found: 413.1458.
R_f = 0.23 in 10% EtOAc in hexanes



(**13**)

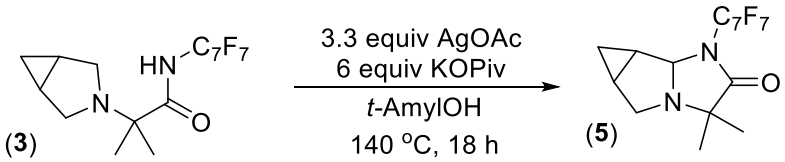
Note: the tartrate salt of the amine was used as the precursor
Compound **13** was isolated in 81% yield as a white solid using standard conditions.
MP 153-155 ºC
IR (thin film): 1718 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.67 (s, 2H), 7.76 (s, 2H), 7.37 (s, 1H), 3.46 (t, *J* = 4.5 Hz, 2H), 2.96 (dd, *J* = 11.0, 4.3, Hz, 2H), 2.83 (d, *J* = 10.8 Hz, 2H), 2.38 (dt, *J* = 11.0, 4.5, Hz, 1H), 1.92 (d, *J* = 10.9 Hz, 1H), 1.16 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, *J* = 21.7 Hz, 3F), –141.4 (m, 2F), –144.3 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.9, 149.6, 143.9, 143.1, 120.9, 63.8, 51.7, 42.8, 40.9, 21.3.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{24}H_{20}F_7N_4O^+$: 513.1525; Found: 513.1519.
R_f = 0.50 in 50% EtOAc in hexanes



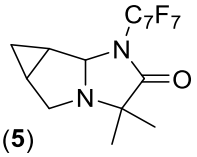
(16)

Note: Sodium iodide (1 equiv) was added to the reaction mixture.
Compound **16** was isolated in 85% yield as light yellow solid using the standard conditions.
MP 65-67 ºC
IR (thin film): 1700, 1653 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.02 (dd, *J* = 6.5, 9 Hz, 1H), 6.28 (app d, *J* = 9 Hz, 1H), 5.94 (app d, *J* = 6.5 Hz, 1H), 4.18 (d, *J* = 15.5 Hz, 1H), 3.87 (dd, *J* = 6 Hz, 15.5 Hz, 1H), 3.10-3.07 (multiple peaks, 2H), 2.87 (m, 1H), 2.66-2.56 (multiple peaks, 3H), 1.98 (m, 1H), 1.86 (m, 1H), 1.29 (s, 3H), 1.19 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, *J* = 22.6 Hz, 3F), –141.0 (m, 2F), –142.8 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 163.0, 150.3, 138.3, 116.9, 104.8, 64.5, 55.7, 53.0, 49.9, 35.5, 28.0, 26.1, 23.5, 17.7.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{22}H_{21}F_7N_3O_2$: 492.1517; Found: 492.1517.
R_f = 0.09 in 60% EtOAc in hexanes

Isolation of Aminal Products



Under ambient conditions, a 4 mL scintillation vial was charged with amine **3** (45 mg, 0.12 mmol), AgOAc (65 mg, 0.39 mmol, 3.3 equiv), and KOPiv (94 mg, 0.67 mmol, 6 equiv). To the solids, *tert*-amyl alcohol (0.8 mL) was added. The vial was sealed with a Teflon-lined cap, wrapped in electrical tape, and heated to an external temperature of 140 ºC. After 18 h, the reaction was removed from the heat source, diluted with EtOAc, and filtered through a plug of Celite. The filtrate was concentrated under reduced pressure. Final purification by column chromatography (10 g cartridge, gradient elution from 0% to 20% EtOAc in hexanes) afforded aminal **5** (26 mg, 58% yield) as a yellow oil.



(**5**)

IR (thin film): 1728 (br) cm^{-1}

^1H NMR (700 MHz, $CDCl_3$) δ 5.29 (s, 1H), 3.10-3.03 (multiple peaks, 2H), 1.60 (m, 1H), 1.43 (ddd, J = 9.2, 6.2, 3.5 Hz, 1H), 1.38 (s, 3H), 1.37 (s, 3H), 0.82 (q, J = 4.3, Hz, 1H), 0.58 (td, J = 8.1, 4.9 Hz, 1H).

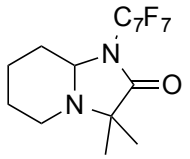
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.2 (t, J = 21.8 Hz, 3F), –139.5 (br s, 1F), –140.2 (br s, 1F), –140.6 (m, 1F), –144.5 (m, 1F).

The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.

^{13}C NMR (176 MHz, $CDCl_3$) δ 177.4, 79.9, 63.7, 49.8, 24.9, 19.4, 17.5, 16.6, 6.0.

HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{16}H_{14}F_7N_2O^+$: 383.0994; Found: 383.0992.

R_f = 0.30 in 20% EtOAc in hexanes



(**S14**)

Note: No KOPiv was used; instead 20 mol% $Pd(OAc)_2$ was added.

Compound **S14** was isolated as faintly yellow solid in 47% yield.

MP 83 ºC

IR (thin film): 1736 cm^{-1}

^1H NMR (700 MHz, $CDCl_3$) δ 4.25 (d, J = 8.3 Hz, 1H), 2.90 (m, 1H), 2.44 (td, J = 11.4, 2.7 Hz, 1H), 1.90 (m, 1H), 1.74-1.69 (m, 2H), 1.63 (m, 1H), 1.40 (t, J = 4.5 Hz, 2H), 1.36 (s, 3H), 1.16 (s, 3H).

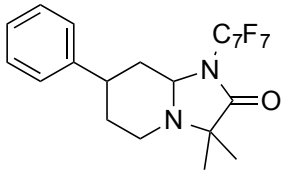
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.2 (t, J = 21.7 Hz, 3F), –139.1 (dd, J = 22.0, 11.1 Hz, 1F), –139.5 (m, 1F), –140.8 (m, 1F), –143.7 (dd, J = 21.9, 10.3 Hz, 1F).

The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.

^{13}C NMR (176 MHz, $CDCl_3$) δ 175.9, 74.7, 61.0, 42.8, 29.4, 25.1, 23.0, 22.6, 14.6.

HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{16}H_{16}F_7N_2O^+$: 385.1151; Found: 385.1145.

R_f = 0.35 in 20% EtOAc in hexanes

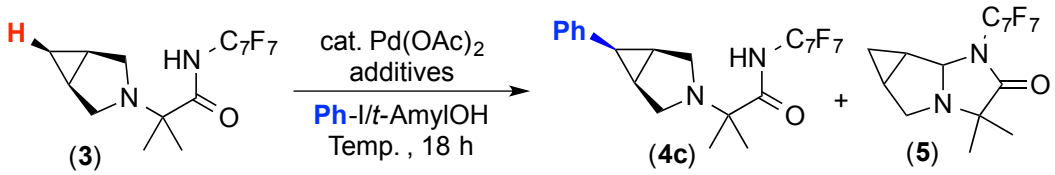


(**S15**)

Compound **S15** was isolated as a yellow oil in 30% yield.

IR (thin film): 1741 (br) cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.7, 6.7 Hz, 2H), 7.27 – 7.19 (multiple peaks, 3H), 4.45 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.07 (dd, *J* = 11.2, 4.6, Hz, 1H), 2.72 (tt, *J* = 12.3, 3.9 Hz, 1H), 2.63 (td, *J* = 11.3, 2.9 Hz, 1H), 1.97 (m, 1H), 1.89 (m, 2H), 1.65 (q, *J* = 11.2 Hz, 1H), 1.43 (s, 3H), 1.23 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.3 (t, *J* = 21.7 Hz, 3F), –139.0 (dd, *J* = 22.1, 10.7 Hz, 1F), –139.3 (m, 1F), –140.6 (m, 1F), –143.8 (dd, *J* = 22.1, 10.6 Hz, 1F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.8, 144.2, 128.6, 126.8, 126.7, 74.30, 60.9, 42.3, 41.4, 36.7, 32.9, 23.1, 14.7.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{22}H_{20}F_7N_2O^+$: 461.1464; Found: 461.1458.
R_f = 0.55 in 20% EtOAc in hexanes

III. Optimization and Scope of C–H Arylation of Azabicyclo[3.1.0]hexane 3

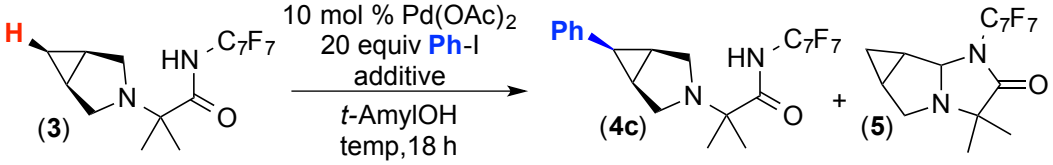


Under ambient conditions, a stock solution of $Pd(OAc)_2$ (21 mg, 0.09 mmol) was prepared in dichloromethane (2 mL). An aliquot of this solution was transferred to a vial (4 mL capacity, 200 µL, 0.009 mmol Pd, 30 mol %). The dichloromethane was removed by heating the open vial to 100 ºC for approximately 20 s. To the concentrated $Pd(OAc)_2$, solid AgX (2 equiv) and/or base (3 equiv) were added.

A separate vial was charged with substrate (120 mg, 0.31 mmol). A mixture of PhI (710 µL, 6.2 mmol, 20 equiv) and *tert*-amyl alcohol (2.8 mL) was gently heated (at ~60 ºC) to form a homogeneous solution. An aliquot (370 µL, 0.031 mmol substrate) of this solution was transferred to the vial containing $Pd(OAc)_2$, AgX, and/or base (prepared as described above). The vial was sealed with a Teflon lined cap, wrapped in electrical tape, and heated to the designated temperature on an aluminum heating block. After 18 h, the reaction was removed from the heat source and hydrazine (28 µL, 35% in H_2O, 0.3 mmol, 10 equiv) was added to the warm solution. The addition of hydrazine resulted in the immediate precipitation of a black solid (presumably Pd^0). A solution of internal standard (1,3,5-trimethoxybenzene, 168 mg in 5 mL of DCM) was prepared, and an aliquot (150 µL) of the stock standard solution was added to the reaction vial. The reaction solution was then diluted with EtOAc to an approximate total volume of 2 mL. The solution was then filtered through a pipette packed with Celite and was analyzed by GC-FID. The average value of duplicate GC injections was used to determine the GC yield based on a linear calibration curve (minimum 5 points) with 1,3,5-trimethoxybenzene.

Variations of this procedure were used in all optimization reactions (Table S1) where the yield was determined by GC-FID. For instance, the impact of the mol % of $Pd(OAc)_2$ was determined by following the same procedure outlined above except that different volumes of the $Pd(OAc)_2$ stock solution were transferred to each vial.

Table S1. Optimization for the C-H arylation of substrate 3 with iodobenzene.



entry	Temp	mol % Pd	AgX	base	conversion	yield **4c**	yield **5**
1	100 °C	20%	Ag_2CO_3	none	75%	36%	11%
2	100 °C	20%	Ag_2O	none	84%	21%	21%
3	100 °C	20%	AgOAc	none	73%	56%	6%
4	100 °C	20%	AgTFA	none	94%	21%	44%
5	100 °C	20%	AgOAc	K_2CO_3	67%	6%	17%
6	100 °C	20%	AgOAc	Cs_2CO_3	78%	6%	29%
7	100 °C	20%	AgOAc	KOAc	86%	78%	3%
8	100 °C	20%	AgOAc	KOPiv	94%	83%	8%
9	100 °C	20%	AgOAc	CsOPiv	93%	56%	13%
10	100 °C	10%	AgOAc	KOPiv	75%	35%	7%
11	110 °C	10%	AgOAc	KOPiv	81%	37%	9%
12	120 °C	10%	AgOAc	KOPiv	89%	68%	6%
13	130 °C	10%	AgOAc	KOPiv	99%	61%	9%
14	130 °C	0%	AgOAc	KOPiv	85%	0%	28%
15	130 °C	10%	none	KOPiv	99%	43%	4%
16[a]	130 °C	10%	none	CsOPiv	69%	61%	8%
17[b]	130 °C	10%	none	CsOPiv	100%	73%	4%
18[c]	130 °C	10%	none	CsOPiv	99%	93%	5%

a) neat conditions, no *t*-AmylOH; b) *t*-AmylOH not dried; c) set up in glove box under N_2

Under the optimal conditions, the crude reaction solution used from GC-FID analysis was concentrated under reduced pressure to remove excess PhI and *tert*-amylOH. The residue was dissolved in $CDCl_3$ to provide the ^1H NMR spectrum below:

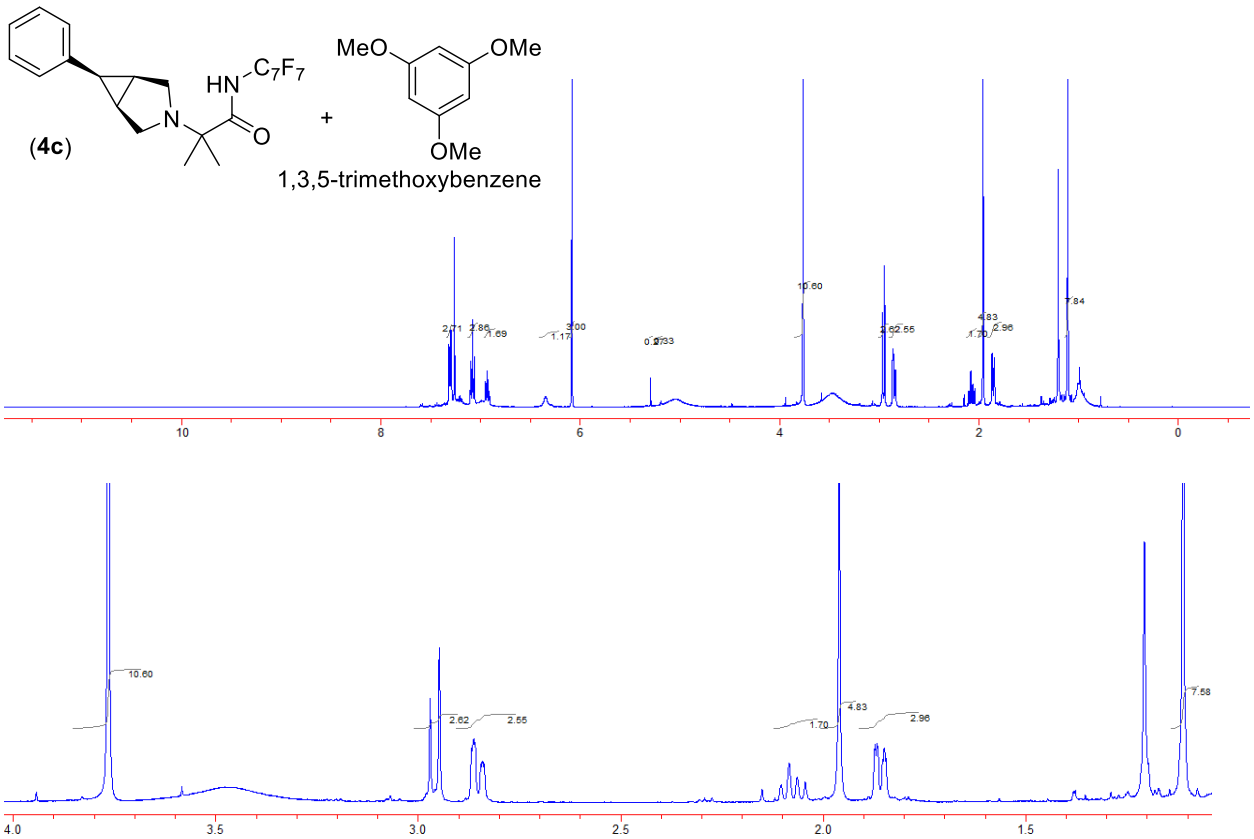
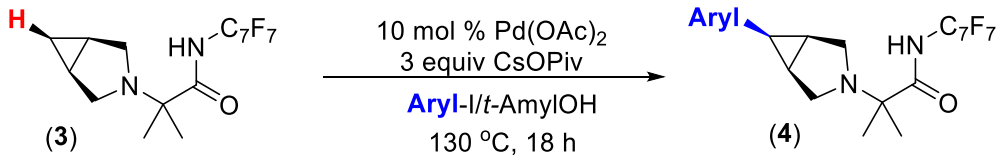


Figure S1. Crude ^1H NMR Spectrum of the C–H arylation of **3** after removal of volatiles.

IV. Scope of Ar-I for C–H Arylation of 3 (Isolated Yields)

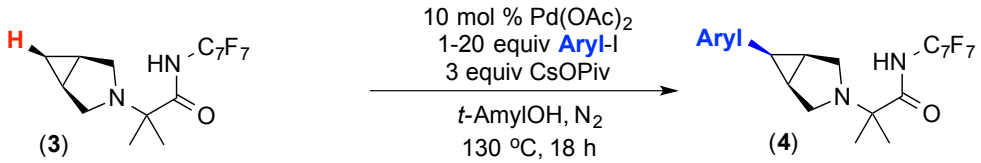
Conditions A (CsOPiv)

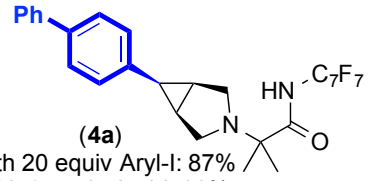


Under ambient conditions, a 20 mL scintillation vial was charged with solid substrate **3** (100 mg, 0.26 mmol, 1 equiv), $Pd(OAc)_2$ (6 mg, 0.03 mmol, 10 mol %) and iododoarene (when solid, 1-20 equiv). The vial was then brought inside of a glove box. To these solids, iodoarene (when liquid, 1-20 equiv), cesium pivalate (182 mg, 0.78 mmol, 3 equiv), and *tert*-amyl alcohol (2.4 mL) were added.[1] The vial was sealed with a Teflon-lined cap, wrapped in electrical tape, removed from the glove box, and heated to an external temperature of 130 ºC. After 18 h, the reaction was removed from the heat source, and hydrazine (250 µL, 35% in H_2O, 2.7 mmol, 10 equiv) was added to the warm solution. The mixture was then allowed to stir for 10 to 30 min at 60 °C to remove ligated Pd from the product. The resulting solution was diluted with EtOAc (~5 mL) and filtered through a layered plug of Celite and basic alumina. The plug was rinsed with additional EtOAc, and the resulting solution was concentrated under reduced pressure. Purification by column chromatography (25 g cartridge, gradient elution from 0% to 20% EtOAc in hexanes) afforded the desired product. Table S2 (below) summarizes the results using these conditions with various Aryl-I.

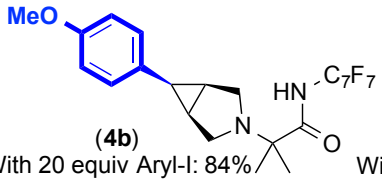
[1] The use of a glove box was not necessary to obtain reliable conversion in the C-H activation reaction. In general, the yield using a glove box was 10-15% higher than when conducted under ambient atmosphere with reagents stored under ambient conditions. This observation was unique to the azabicyclo[3.1.0]hexane system (substrate **3**).

Table S2. C-H arylation of azabicyclo[3.1.0]hexane system under conditions A.

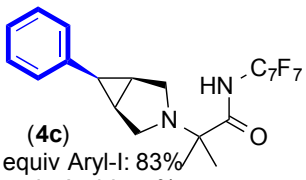




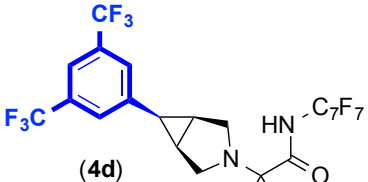
(**4a**)
With 20 equiv Aryl-I: 87%
With 1 equiv Aryl-I: 80%



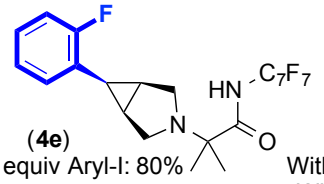
(**4b**)
With 20 equiv Aryl-I: 84%
With 1 equiv Aryl-I: 75%



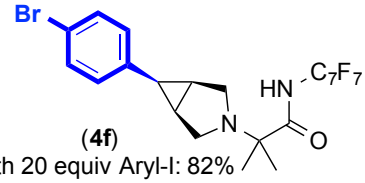
(**4c**)
With 20 equiv Aryl-I: 83%
With 1 equiv Aryl-I: 74%



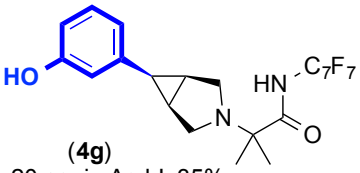
(**4d**)
With 20 equiv Aryl-I: 78%
With 1 equiv Aryl-I: 69%



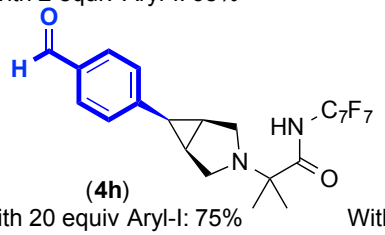
(**4e**)
With 20 equiv Aryl-I: 80%
With 2 equiv Aryl-I: 68%



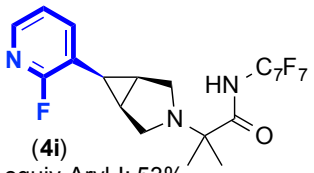
(**4f**)
With 20 equiv Aryl-I: 82%
With 2 equiv Aryl-I:70%



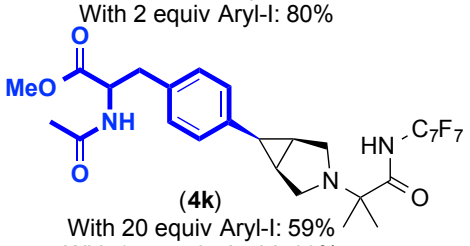
(**4g**)
With 20 equiv Aryl-I: 35%
With 2 equiv Aryl-I: 57%



(**4h**)
With 20 equiv Aryl-I: 75%
With 1 equiv Aryl-I: 88%

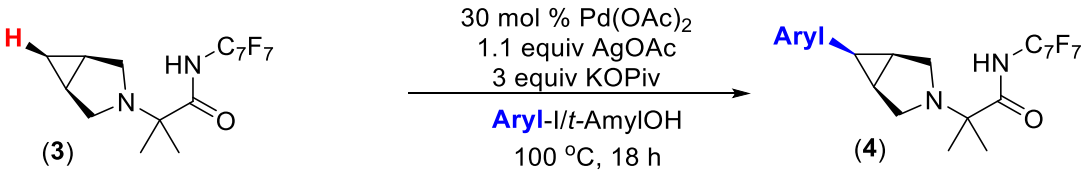


(**4i**)
With 20 equiv Aryl-I: 53%
With 2 equiv Aryl-I: 80%



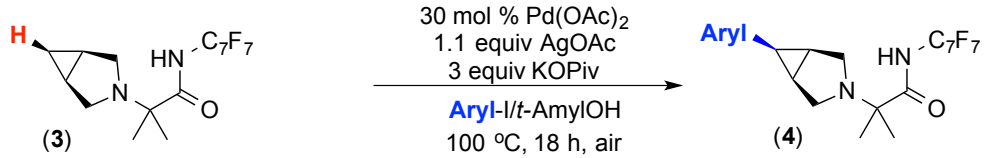
(**4k**)
With 20 equiv Aryl-I: 59%
With 1.5 equiv Aryl-I: 63%
(1:1 er)

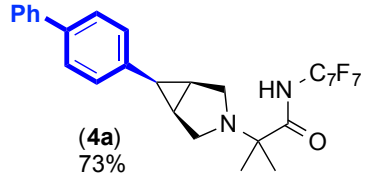
Conditions B (AgOAc and KOPiv)

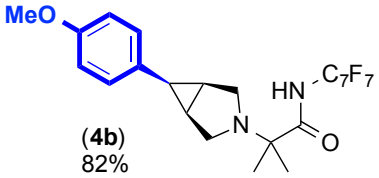


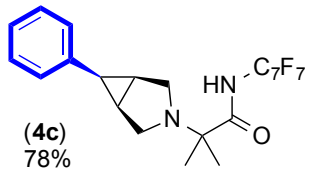
Example given for Aryl-I = PhI: Under ambient conditions, a 20 mL scintillation vial was charged with solid substrate (100 mg, 0.26 mmol, 1 equiv), $Pd(OAc)_2$ (18 mg, 0.08 mmol, 30 mol %), AgOAc (52 mg, 0.31 mmol, 1.2 equiv), and KOPiv (109 mg, 0.78 mmol, 3 equiv). To these solids, PhI (590 µL, 5.2 mmol, 20 equiv) and *tert*-amyl alcohol (2.4 mL) were added. The vial was sealed with a Teflon-lined cap and heated to an external temperature of 100 ºC. After 18 h, the reaction was removed from the heat source, and hydrazine (250 µL, 35% in H_2O, 2.7 mmol, 10 equiv) was added to the warm solution. The addition of hydrazine resulted in the immediate precipitation of a black solid. The reaction mixture was diluted with EtOAc and filtered through a layered plug of Celite and basic alumina. The resulting solution was concentrated under vacuum. Final purification by column chromatography (25 g cartridge, gradient elution from 0% to 20% EtOAc in hexanes) afforded the desired product (95 mg, 79% yield) as a white solid. Table S3 (below) summarizes the results using these conditions with various Aryl-I.

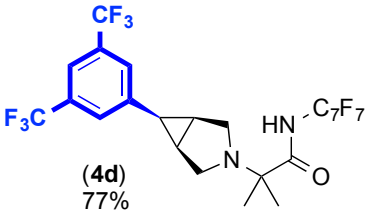
Table S3. C-H arylation of azabicyclo[3.1.0]hexane system under conditions B.

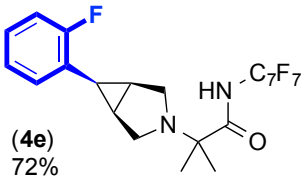


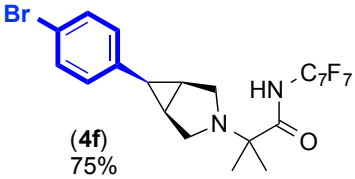


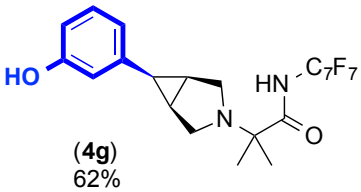


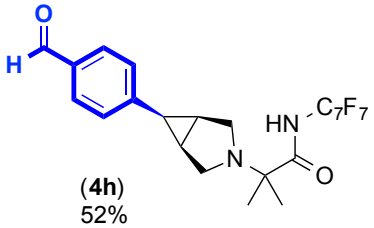


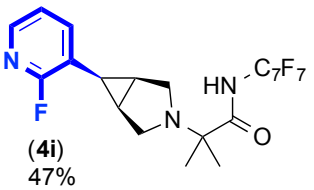


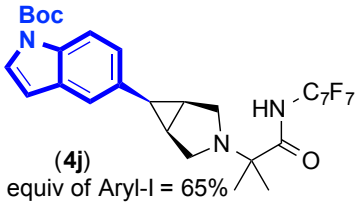


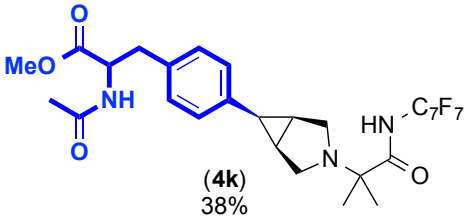


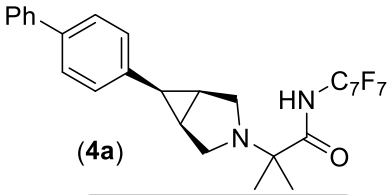




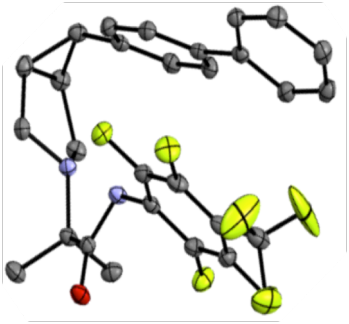




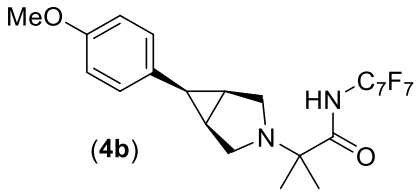




(**4a**)



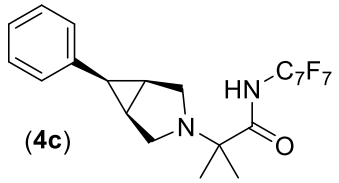
Isolated yield using standard conditions A (using 1 equiv of Aryl-I): 80% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 84%, 89%; 87% average yield
Isolated yield using standard conditions B: 82%, 63%; 73% average yield
MP 116-118 ºC (white solid)
IR (thin film): 1705 (br) cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.43-7.36 (multiple peaks, 4H), 7.34-7.21 (multiple peaks, 5H), 6.37 (s, 1H), 3.01 (d, J = 9.2 Hz, 2H), 2.90 (dt, J = 9.2, 1.7 Hz, 2H), 2.13 (t, J = 8.1 Hz, 1H), 1.89 (dt, J = 8.2, 1.6 Hz, 2H), 1.16 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.2 (t, J = 21.7 Hz, 3F), –141.4 (m, 2F), –143.0 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.4, 138.9, 137.9, 137.1, 128.8, 128.7, 127.5, 126.3, 125.4, 61.04, 45.2, 22.4, 21.1, 20.1.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{28}H_{24}F_7N_2O^+$: 537.1777; Found: 537.1773.
R_f = 0.55 in 20% EtOAc in hexanes



(**4b**)

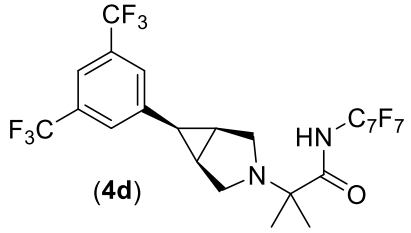
Isolated yield using standard conditions A (using 1 equiv of Aryl-I): 75% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 83%, 84%; 84% average yield
Isolated yield using standard conditions B: 81%, 82%; 82% average yield
MP 75-77 ºC (white solid)
IR (thin film): 1711 cm^{-1}

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.20 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 3.53 (s, 3H), 2.94 (d, J = 9.1 Hz, 2H), 2.87 (ddd, J = 9.1, 2.6, 1.4 Hz, 2H), 1.99 (t, J = 8.0 Hz, 1H), 1.81 (ddd, J = 8.0, 2.6, 1.3 Hz, 2H), 1.14 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.8 Hz, 3F), –141.4 (m, 2F), –143.1 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.1, 157.5, 129.7, 128.9, 113.4, 60.9, 54.6, 45.1, 22.8, 20.9, 20.0.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{23}H_{22}F_7N_2O_2^+$: 491.1570; Found: 491.1560.
R_f = 0.50 in 20% EtOAc in hexanes



(**4c**)

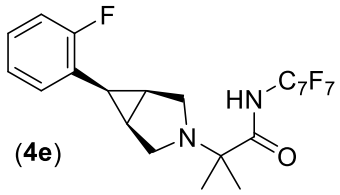
Isolated yield using standard conditions A (using 1 equiv of Aryl-I): 74% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 75%, 90%, 84%; 83% average yield
Isolated yield using standard conditions B: 74%, 80%, 79%; 78% average yield
MP 83-85 ºC (white solid)
IR (thin film): 1711 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.30 (d, J = 7.5 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.34 (s, 1H), 2.95 (d, J = 9.1 Hz, 2H), 2.85 (dt, J = 9.1, 2.0 Hz, 2H), 2.08 (t, J = 8.1 Hz, 1H), 1.86 (dt, J = 8.4, 1.8 Hz, 2H), 1.11 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.0 (t, J = 21.7 Hz, 3F), –141.5 (m, 2F), –144.6 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.9, 138.0, 128.1, 128.0, 125.9, 60.9, 45.0, 22.8, 20.8, 19.9.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{22}H_{20}F_7N_2O^+$: 461.1464; Found: 461.1458.
Anal. Calc for $C_{22}H_{19}F_7N_2O$: C, 57.39; H, 4.16. Found C, 57.14; H, 3.99. Found C, 57.12; H, 4.03.
R_f = 0.67 in 20% EtOAc in hexanes



(**4d**)

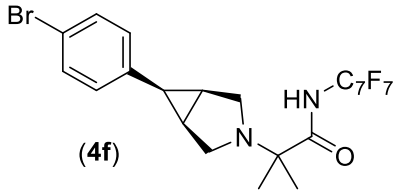
Isolated yield using standard conditions A (using 1 equiv of Aryl-I): 69% yield

Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 77%, 79%; 78% average yield
Isolated yield using standard conditions B: 75%, 79%; 77% average yield
MP 116-118 ºC (white solid)
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.56 (s, 1H), 6.09 (s, 1H), 2.97 (d, J = 9.7 Hz, 2H), 2.93 (ddd, J = 9.7, 2.5, 1.4 Hz, 2H), 2.15 (t, J = 8.0 Hz, 1H), 2.00 (ddd, J = 8.0, 2.5, 1.3 Hz, 2H), 1.14 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.3 (t, J = 21.8 Hz, 3F), –63.5 (s, 6F), –141.3 (m, 2F), –143.7 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.6, 141.0, 131.5 (q, $J_{C\text{-}F}$ = 33.9 Hz), 128.5 (q, $J_{C\text{-}F}$ = 3.1 Hz), 122.9 (q, $J_{C\text{-}F}$ = 271 Hz), 119.7 (q, $J_{C\text{-}F}$ = 3.9 Hz), 61.2, 45.0, 22.5, 20.6, 20.5.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{24}H_{18}F_{13}N_2O^+$: 597.1212; Found: 597.1206.
R_f = 0.67 in 20% EtOAc in hexanes



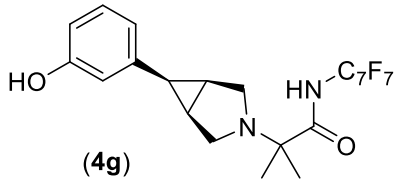
(**4e**)

Isolated yield using standard conditions A (using 2 equiv of Aryl-I): 68% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 80%, 79%; 80% average yield
Isolated yield using standard conditions B: 78%, 65%; 72% average yield
MP 60-65 ºC (white solid)
IR (thin film): 1712 (br) cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.33 (td, J = 7.4, 1.6 Hz, 1H), 6.93 (m, 1H), 6.89-6.81 (multiple peaks, 2H), 6.48 (s, 1H), 3.00 (d, J = 9.3 Hz, 2H), 2.84 (dt, J = 9.3, 1.7 Hz, 2H), 1.94 (multiple peaks, 3H), 1.13 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.1 (t, J = 21.8 Hz, 3F), –116.1 (q, J = 7.4 Hz, 1F), –141.5 (m, 2F), –143.5 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.64, 161.2 (d, $J_{C\text{-}F}$ = 247 Hz), 130.4 (d, $J_{C\text{-}F}$ = 4.5 Hz), 127.5 (d, $J_{C\text{-}F}$ = 7.7 Hz), 125.5 (d, $J_{C\text{-}F}$ = 16.1 Hz), 123.3 (d, $J_{C\text{-}F}$ = 3.1 Hz), 115.2 (d, $J_{C\text{-}F}$ = 22.2 Hz), 61.10, 45.6, 20.7, 19.9, 18.1.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{22}H_{19}F_8N_2O^+$: 479.1370; Found: 479.1364.
R_f = 0.67 in 20% EtOAc in hexanes



(**4f**)

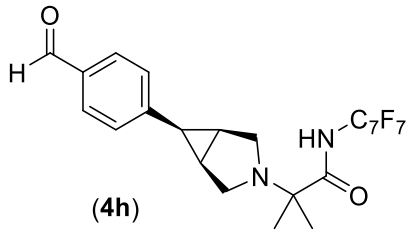
Isolated yield using standard conditions A (using 2 equiv of Aryl-I): 70% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 81%, 83%; 82% average yield
Isolated yield using standard conditions B: 81%, 68%; 75% average yield
MP 105-108 ºC (white solid)
IR (thin film): 1712 cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.22 – 7.15 (multiple peaks, 4H), 6.39 (s, 1H), 2.93 (d, J = 9.3 Hz, 2H), 2.88 (ddd, J = 9.2, 2.6, 1.4 Hz, 2H), 2.00 (t, J = 8.0 Hz, 1H), 1.87 (ddd, J = 8.0, 2.6, 1.3 Hz, 2H), 1.14 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.2 (t, J = 21.7 Hz, 3F), –141.1 (m, 2F), –143.0 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.9, 137.0, 131.3, 129.9, 119.9, 61.0, 45.0, 22.3, 21.0, 20.0.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{22}H_{17}BrF_7N_2O^+$: 539.0569; Found: 539.0561.
Anal. Calc for $C_{22}H_{16}BrF_7N_2O$: C, 49.00; H, 3.36. Found C, 48.93; H, 3.40. Found C, 49.10; H, 3.33.
R_f = 0.50 in 20% EtOAc in hexanes



(**4g**)

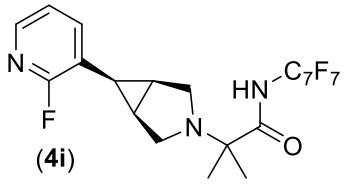
NOTE: chromatography gradient was 0% to 30% EtOAc in hexanes
Isolated yield using standard conditions A (using 2 equiv of Aryl-I): 57% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 35%, 32%; 34% average yield
Isolated yield using standard conditions B: 64%, 59%; 62% average yield
MP 200-203 ºC (white solid)
IR (thin film): 1684 cm^{-1}
^1H NMR (700 MHz, CD_3OD) δ 6.97 (t, J = 7.8 Hz, 1H), 6.82 (dd, J = 7.8, 1.2 Hz, 1H), 6.68 (dd, J = 2.6, 1.4 Hz, 1H), 6.27 (dd, J = 8.0, 2.4 Hz, 1H), 3.00 (d, J = 9.0 Hz, 2H), 2.86 (ddd, J = 9.0, 2.5, 1.4 Hz, 2H), 2.00 (t, J = 8.0 Hz, 1H), 1.83 (ddd, J = 8.0, 2.6, 1.2 Hz, 2H), 1.11 (s, 6H).
^{19}F NMR (377 MHz, CD_3OD) δ –56.9 (t, J = 21.2 Hz, 3F), –144.1 (multiple peaks, 4F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.

^{13}C NMR (176 MHz, CD_3OD) δ 177.3, 157.0, 139.5, 128.9, 118.8, 114.5, 112.4, 60.6, 44.5, 22.4, 19.9, 19.4.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{22}H_{20}F_7N_2O_2^+$: 477.1413; Found: 477.1408.
R_f = 0.40 in 20% EtOAc in hexanes



(**4h**)

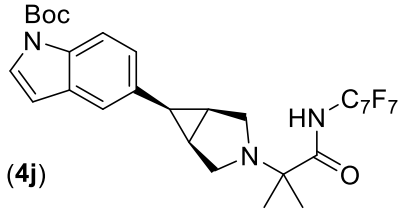
NOTE: Due to the rapid formation of a hydrazone, hydrazine was not used in the isolation of this aldehyde. Instead, the reaction was diluted with MeOH (0.2 mL) and heated at 60 °C for 4 h prior to filtration.
Isolated yield using standard conditions A (using 1 equiv of Aryl-I): 88% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 75%, 76%; 75% average yield
Isolated yield using standard conditions B: 54%, 50%; 52% average yield
MP 116 ºC (white solid)
IR (thin film): 1704, 1700 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.61 (m, 2H), 7.46 (m, 2H), 6.19 (s, 1H), 2.95 (d, J = 9.5 Hz, 2H), 2.88 (ddd, J = 9.4, 2.4, 1.3 Hz, 2H), 2.13 (t, J = 8.0 Hz, 1H), 1.94 (ddd, J = 8.1, 2.6, 1.3 Hz, 2H), 1.11 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.2 (t, J = 21.7 Hz, 3F), –140.9 (m, 2F), –143.0 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 190.6, 175.3, 145.3, 134.5, 129.2, 128.7, 61.0, 45.0, 23.0, 20.8, 20.2.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{23}H_{20}F_7N_2O_2^+$: 489.1413; Found: 489.1407.
R_f = 0.45 in 20% EtOAc in hexanes



(**4i**)

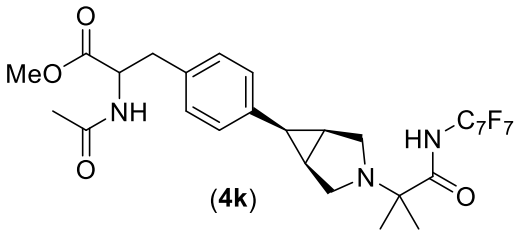
NOTE: chromatography gradient was 0% to 40% EtOAc in hexanes.
Isolated yield using standard conditions A (using 2 equiv of Aryl-I): 80% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 53% yield
Isolated yield using standard conditions B: 45%, 48%; 47% average yield
MP 118-120 ºC (white solid)
IR (thin film): 1710 cm^{-1}

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.90 (d, J = 4.4 Hz, 1H), 7.78 (t, J = 8.4 Hz, 1H), 6.99 (ddd, J = 6.9, 4.8, 1.7 Hz, 1H), 6.46 (s, 1H), 2.98 (d, J = 9.5 Hz, 2H), 2.86 (dt, J = 9.6, 1.7 Hz, 2H), 2.01 – 1.93 (m, 3H), 1.13 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.1 (t, J = 21.8 Hz, 3F), –70.1 (d, J = 9.1 Hz, 1F), –141.1 (m, 2F), –142.8 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.86, 162.6 (d, $J_{C\text{-}F}$ = 241 Hz), 145.2 (d, $J_{C\text{-}F}$ = 13.8 Hz), 140.5 (d, $J_{C\text{-}F}$ = 5.5 Hz), 120.6 (d, $J_{C\text{-}F}$ = 4.3 Hz), 120.5 (d, $J_{C\text{-}F}$ = 30.7 Hz), 61.3, 45.5, 20.6, 20.1, 17.5 (d, $J_{C\text{-}F}$ = 3.2 Hz).
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{21}H_{18}F_8N_3O^+$: 480.1322; Found: 480.1318.
R_f = 0.80 in 50% EtOAc in hexanes



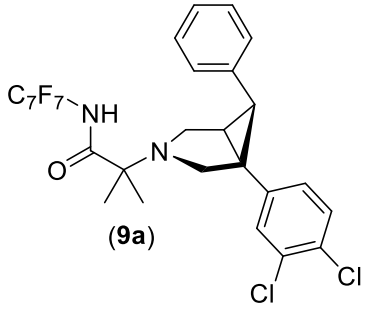
(**4j**)

Isolated yield using standard conditions B (using 2 equiv of Aryl-I): 59% yield
Isolated yield using standard conditions B (using 20 equiv of Aryl-I): 62%, 67%; 65% average yield
MP 158-161 ºC (white solid)
IR (thin film): 1733, 1701 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 1H), 7.40 (s, 1H), 7.30 (m, 1H), 7.17 (d, J = 3.8 Hz, 1H), 6.15 – 6.10 (multiple peaks, 2H), 3.00 (d, J = 9.1 Hz, 2H), 2.88 (dt, J = 9.2, 1.9 Hz, 2H), 2.14 (t, J = 8.1 Hz, 1H), 1.86 (dt, J = 8.1, 1.9 Hz, 2H), 1.64 (s, 9H), 1.11 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.2 (t, J = 21.7 Hz, 3F), –142.0 (m, 7.4 Hz, 2F), –143.9 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.2, 149.0, 132.12, 130.1, 125.6, 124.3, 119.9, 115.0, 112.9, 105.8, 83.9, 60.76, 45.04, 27.89, 22.70, 21.4 (br s), 20.07.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{29}H_{29}F_7N_3O_3^+$: 600.2097; Found: 600.2091.
R_f = 0.60 in 20% EtOAc in hexanes



(**4k**)

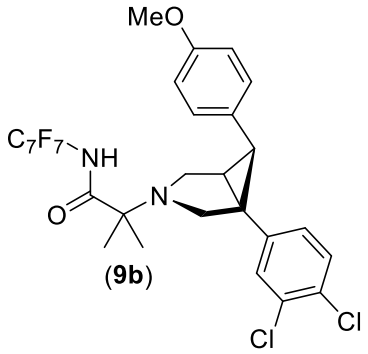
NOTE: Hydrazine was not used in the isolation of this substrate due to the rapid N-deacylation of the product in the presence of hydrazine. Instead, the reaction was diluted with MeOH (0.4 mL) and heated at 60 °C for 4 h prior to filtration. Chromatography gradient was 0% to 60% EtOAc in hexanes.
Isolated yield using standard conditions A (using 1.5 equiv of Aryl-I): 63% yield
Isolated yield using standard conditions A (using 20 equiv of Aryl-I): 59%, 59%; 59% average yield (1:1 er)
Isolated yield using standard conditions B: 43%, 33%; 38% average yield (93:7 er)
MP 112-115 ºC (white solid)
IR (thin film): 1700 (br) cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.22 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 7.9 Hz, 2H), 6.42 (s, 1H), 5.78 (d, J = 7.8 Hz, 1H), 4.65 (dt, J = 7.9, 5.9 Hz, 1H), 3.68 (s, 3H), 2.94 (dd, J = 9.2, 6.7 Hz, 2H), 2.84 (dd, J = 9.3, 2.9 Hz, 2H), 2.74 (dd, J = 13.9, 6.1 Hz, 1H), 2.63 (dd, J = 13.9, 5.8 Hz, 1H), 2.02 (t, J = 8.0 Hz, 1H), 1.93 (s, 3H), 1.88-1.81 (multiple peaks, 2H), 1.11 (s, 3H), 1.10 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.8 Hz, 3F), –141.4 (m, 2F), –142.6 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.8, 171.9, 169.3, 136.8, 133.8, 128.8, 128.3, 61.0, 52.9, 52.2, 45.1, 45.0, 37.2, 22.9, 22.4, 21.0, 20.6, 19.9, 19.8
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{28}H_{29}F_7N_3O_4^+$: 604.2046; Found: 604.2038.
R_f = 0.30 in 50% EtOAc in hexanes



(**9a**)

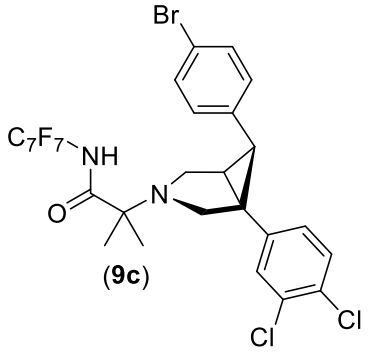
NOTE: The arylation reaction was conducted at 120 ºC under air. $NaBH_4$ reduction was required on this substrate following the **Isolation Procedure B** found in the **Standard Conditions for C-H Arylation of Alicyclic Amines** section.
Isolated as a colorless oil.
Isolated yield using modified standard conditions: 52%, 54%; 53% average yield
Isolated yield when based on recovered starting material: 61%, 59%; 60% average yield
IR (thin film): 1710 (br) cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 2.0 Hz, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.17 – 7.08 (multiple peaks, 3H), 7.00 (t, J = 7.4 Hz, 1H), 6.25 (s, 1H), 3.28 (d, J = 9.2 Hz, 1H), 3.15 (d, J = 9.6 Hz, 1H), 3.10 (dd, J = 9.6, 3.9 Hz, 1H), 3.04 (d, J = 9.2 Hz, 1H), 2.42 (d, J = 8.5 Hz, 1H), 2.21 (dd, J = 8.5, 3.7 Hz, 1H), 1.16 (s, 3H), 1.10 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.8 Hz, 3F), –141.4 (m, 2F), –142.3 (m, 2F).

The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.2, 142.4, 137.0, 132.6, 130.5, 130.5, 129.0, 128.2, 127.6, 126.4, 126.3, 61.2, 49.8, 45.5, 35.0, 32.5, 28.1, 20.8, 20.6.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{28}H_{22}Cl_2F_7N_2O^+$: 605.0997; Found: 605.0996.
R_f = 0.60 in 20% EtOAc in hexanes



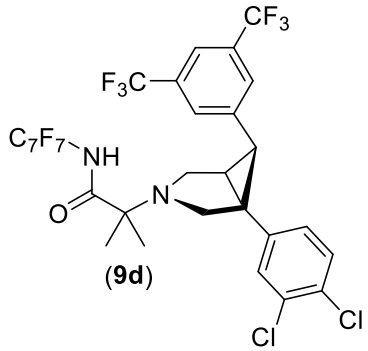
(**9b**)

NOTE: The arylation reaction was conducted at 120 °C under air.
Isolated yield using modified standard conditions (using 1 equiv of Aryl-I): 40% yield
Isolated yield using modified standard conditions (using 20 equiv of Aryl-I): 50%, 51%; 51% average yield
Isolated yield when based on recovered starting material (using 20 equiv of Aryl-I): 77%, 69%; 73% average yield
MP 140-143 ºC (white solid)
IR (thin film): 1707 cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.43 (s, 1H), 3.56 (s, 3H), 3.26 (d, *J* = 9.1 Hz, 1H), 3.16 – 3.09 (multiple peaks, 2H), 3.05 (d, *J* = 9.1 Hz, 1H), 2.36 (d, *J* = 8.4 Hz, 1H), 2.18 (dd, *J* = 8.5, 3.8 Hz, 1H), 1.20 (s, 3H), 1.18 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, *J* = 21 Hz, 3F), –141.4 (m, 2F), –143.0 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.4, 157.8, 142.6, 132.6, 130.5, 130.4, 128.9, 128.6, 128.5, 126.2, 113.6, 61.2, 54.6, 49.8, 45.6, 35.0, 32.0, 28.2, 21.4, 20.4.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{29}H_{24}Cl_2F_7N_2O^+$: 635.1103; Found: 635.1098.
R_f = 0.60 in 20% EtOAc in hexanes



(**9c**)

NOTE: The arylation reaction was conducted at 120 ºC under air.
Isolated yield using modified standard conditions: 44%, 24%; 35% average yield
Isolated yield when based on recovered starting material: 54%, 27%; 41% average yield
MP 162-165 ºC (white solid)
IR (thin film): 1709 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.30 (s, 1H), 3.25 (d, *J* = 9.3 Hz, 1H), 3.12 (m, 2H), 3.06 (d, *J* = 9.3 Hz, 1H), 2.35 (d, *J* = 8.4 Hz, 1H), 2.25 (dd, *J* = 8.5, 3.8 3Hz, 1H), 1.20 (s, 3H), 1.19 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.2 (t, *J* = 21.8, Hz, 3F), –140.8 (m, 2F), –142.9 (dt, *J* = 13.7, 8.8 Hz, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.2, 141.9, 135.9, 132.7, 131.5, 130.7, 130.6, 129.4, 128.9, 126.2, 120.4, 61.2, 49.8, 45.6, 35.1, 32.0, 28.0, 21.4, 20.5.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{28}H_{21}BrCl_2F_7N_2O^+$: 683.0103; Found: 683.0093.
R_f = 0.52 in 20% EtOAc in hexanes



(**9d**)

NOTE: The arylation reaction was conducted at 120 ºC under air. $NaBH_4$ reduction was required on this substrate following the **Isolation Procedure B** found on **Standard Conditions for C-H Arylation of Alicyclic Amines** section. Isolated as colorless oil.
Isolated yield using modified standard conditions: 33%, 34%, 46%, 33%; 37% average yield
Isolated yield when based on recovered starting material: 55%, 46%, 54%, 37%; 49% average yield
IR (thin film): 1717 cm^{-1}

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.63 (s, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.38 (d, J = 2.2 Hz, 1H), 7.15 (dd, J = 8.3, 2.2 Hz, 1H), 6.01 (s, 1H), 3.28 (d, J = 9.7 Hz, 1H), 3.19-3.09 (multiple peaks, 3H), 2.49 (d, J = 8.4 Hz, 1H), 2.35 (dd, J = 8.5, 3.7 Hz, 1H), 1.20 (s, 3H), 1.19 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.2 (t, J = 21 Hz, 3F), –63.5 (s, 6F), –141.2 (m, 2F), –143.5 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.0, 140.9, 140.0, 132.9, 131.9 (q, $J_{C\text{-}F}$ = 33 Hz), 131.2, 130.7, 128.8, 127.9, 126.2, 122.8 (q, $J_{C\text{-}F}$ = 273 Hz), 120.2 (q, $J_{C\text{-}F}$ = 3.9 Hz), 61.4, 49.8, 45.5, 35.5, 31.7, 28.2, 20.8, 20.4.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{30}H_{20}Cl_2F_{13}N_2O^+$: 741.0745; Found: 741.0744.
R_f = 0.60 in 20% EtOAc in hexanes

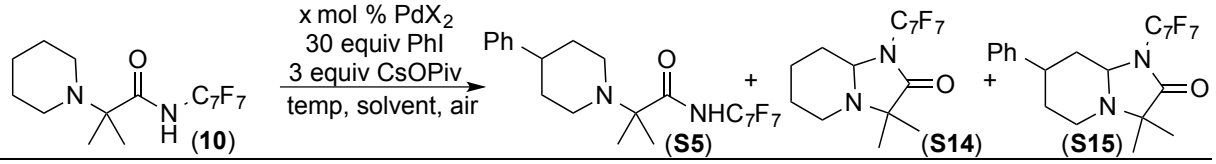
V. Optimization and Scope of Alicyclic Amines for C-H Arylation

The conditions employed for the azabicyclo[3.1.0]hexane system provided a modest yield of 4-phenylpiperidine (**S5**). To increase both the conversion and selectivity, the reaction was re-optimized following the general procedure below.

A stock solution of $Pd(OAc)_2$ was prepared by dissolving 22.5 mg of $Pd(OAc)_2$ in 5 mL of dichloromethane (0.02 M solution of $Pd(OAc)_2$). To a 4-mL vial a 150 μL aliqoute of the Pd stock solution was added (0.7mg, 0.003 mmol, 10 mol%). The solvent was let to evaporate by heating the vial gently to 40 °C. After, substrate **10** (12 mg, 0.03 mmol, 1 equiv), CsOPiv (21 mg, 0.09 mmol, 3 equiv) and iodoarene (30 equiv) were added to the vial containing Pd. Finally, solvent was added if shown in entry of Table S4 (0.12 M). The vial was sealed with a teflon-lined cap and heated to the corresponding temperature for 18 hours. After the reaction mixture was removed from the heat source and hydrazine (50 μL, 65% in H_2O, 0.6 mmol, 20 equiv) was added to the warm solution. The addition of hydrazine resulted in the precipitate of a black solid. A solution of internal standard (1,3,5-trimethoxybenzene, 168 mg in 5 mL of DCM) was prepared, and an aliquot (150 μL, 0.03 mmol) of the stock standard solution was added to the reaction vial. The reaction solution was then diluted with DCM to an approximate total volume of 4 mL. The solution was then filtered through a pipette packed with Celite and was analyzed by GC-FID. The average value of duplicate GC injections was used to determine the GC yield based on a linear calibration curve with 1,3,5-trimethoxybenzene.

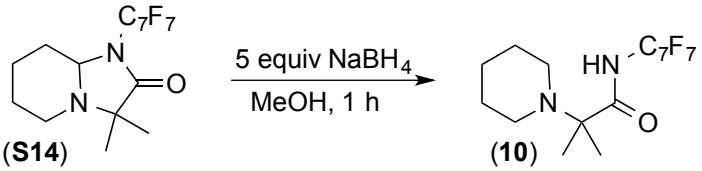
A summary of the re-optimization is as follows:

Table S4. Re-optimization of the C-H arylation on piperidine.



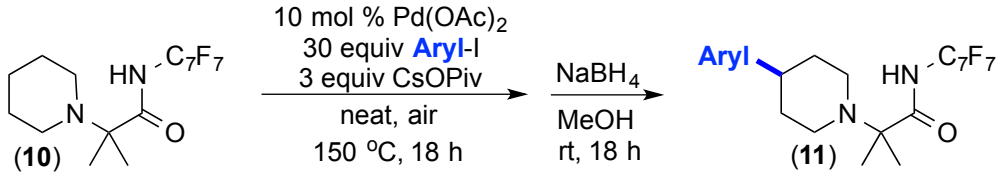
entry	Temp	mol % Pd	PdX_2	solvent	conversion	yield **S5**	yield **S14**	yield **S15**
1	140 °C	10%	$Pd(OAc)_2$	*t*AmylOH	54%	23%	14%	1%
2	140 °C	10%	$Pd(OAc)_2$	HFIPA	86%	22%	18%	6%
3	140 °C	10%	$Pd(OAc)_2$	tBuOH	63%	30%	13%	2%
4	140 °C	10%	$Pd(OAc)_2$	TFE	79%	3%	26%	2%
5	140 °C	10%	$Pd(OAc)_2$	xylene	60%	24%	14%	2%
6	140 °C	10%	$Pd(OAc)_2$	none	77%	44%	16%	6%
7	130 °C	10%	$Pd(OAc)_2$	none	56%	37%	12%	3%
8	**150 °C**	**10%**	**$Pd(OAc)_2$**	**none**	**93%**	**44%**	**28%**	**11%**
9	150 °C	5%	$Pd(OAc)_2$	none	82%	35%	24%	9%
10	150 °C	20%	$Pd(OAc)_2$	none	96%	46%	17%	13%
11	150 °C	30%	$Pd(OAc)_2$	none	89%	36%	13%	21%
12	150 °C	10%	$Pd(OPiv)_2$	none	76%	44%	15%	6%
13	150 °C	10%	$Pd(OTFA)_2$	none	74%	41%	14%	5%
14	150 °C	10%	$PdCl_2$	none	60%	29%	14%	3%
15	150 °C	10%	$Pdpy_2Cl_2$	none	18%	10%	6%	<1%

Work-up to Effect Reduction of Aminal Products



A solution of aminal (15 mg, 0.04 mmol) in MeOH (0.2 mL) was pre-cooled in an ice bath, and solid $NaBH_4$ (7.5 mg, 0.2 mmol, 5 equiv) was added in one portion. The solution was allowed to gradually warm to room temperature. After 1 h, the reaction was poured onto water, the resulting mixture was extracted with CH_2Cl_2 (3 x ~10 mL), and the organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Analysis of the crude oil by ^1H NMR, ^{19}F NMR, and GC-FID indicated full conversion of the aminal **S14** to the piperidine **10**.

Standard Conditions for C-H Arylation of Alicyclic Amines



Under ambient conditions, a 20 mL scintillation vial was charged with solid substrate **10** (96.6 mg, 0.25 mmol, 1 equiv), $Pd(OAc)_2$ (5.6 mg, 0.0325 mmol, 10 mol %), cesium pivalate (176 mg, 0.75 mmol, 3 equiv), and iodoarene (30 equiv). The vial was sealed with a Teflon-lined cap and heated to an external temperature of 150 ºC. After 24 h, the reaction was removed from the heat source and diluted with hexanes (5 mL). Hydrazine (250 µL, 35% in H_2O, 2.6 mmol, 10 equiv) was added to the warm solution. The mixture was allowed to stir for 30 min at 60 ºC to remove Pd from the product.

Isolation Procedure A: If aminal (such as **S14**) is not formed during the reaction.

The mixture was filtered through a small plug of silica gel with 100% EtOAc. The resulting solution was concentrated under vacuum. Purification by column chromatography (25 g cartridge, gradient elution using Hex, EtOAc and/or THF) or preparative TLC afforded the desired product. Modifications to the procedure and chromatography conditions are noted under each substrate.

Isolation Procedure B: If aminal (such as **S14**) is formed during the reaction.

This mixture was loaded onto a small plug of silica gel over which hexanes (150 mL) was passed to remove iodoarene.[2] The plug of silica was then rinsed with EtOAc (150 mL) to elute the products, and this solution was concentrated under reduced pressure. The mixture of products was dissolved in MeOH (2 mL), and cooled in an ice bath to 0 ºC. $NaBH_4$ (total 100 mg, 2.6 mmol, 20 equiv) was added portion-wise over 30 min. [*Caution: gas evolution occurs!*] The solution was allowed to warm to room temperature. After stirring for 12 h, the reaction was diluted with water and the resulting solution was extracted with CH_2Cl_2, dried (Na_2SO_4), and concentrated under reduced pressure. Purification by column chromatography (25 g cartridge, gradient elution using Hex, EtOAc and/or THF) or preparative TLC afforded the desired product. Modifications to the procedure and chromatography conditions are noted under each substrate.

[2] The hexanes solution was checked by TLC and GC to confirm that no product co-eluted with iodoarene.

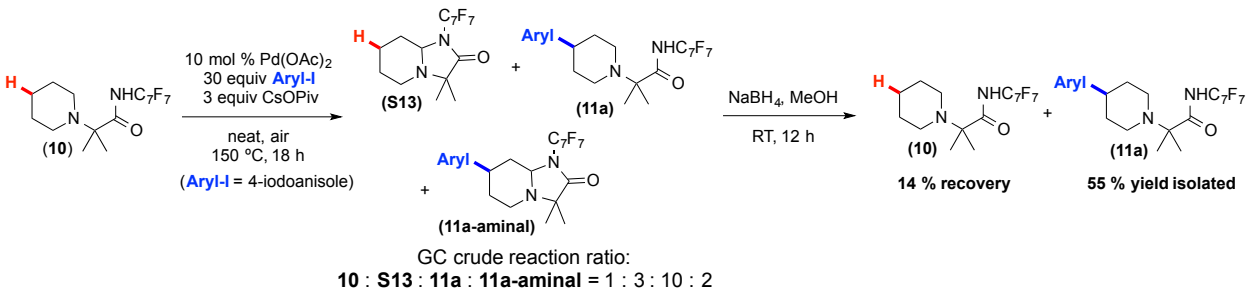
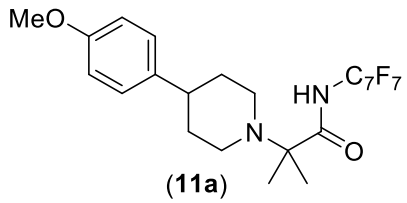


Figure S2. Crude reaction ratios of **10** before the reductive workup. Ratios are determined by gas chromatography (GC).



(**11a**)

NOTE: Aminal formation was observed. $NaBH_4$ reduction was required on this substrate following **Isolation Procedure B**.

Isolated yield using standard conditions: 57%, 52%; 55% average yield

Isolated yield when calculated based on recovered starting material: 67%, 62%; 65% average yield

MP 121 ºC (white solid)

IR (thin film): 1715 (br) cm^{-1}

^1H NMR (700 MHz, $CDCl_3$) δ 9.45 (br s, 1H), 7.15 (m, 2H), 6.87 (m, 2H), 3.79 (s, 3H), 2.97 (dt, J = 11.3, 2.1 Hz, 2H), 2.53 (tt, J = 12.3, 3.8 Hz, 1H), 2.39 (td, J = 11.6, 2.2 Hz, 2H), 1.96 (d, J = 12.5 Hz, 2H), 1.75 (qd, J = 12.5, 3.6 Hz, 2H), 1.35 (s, 6H).

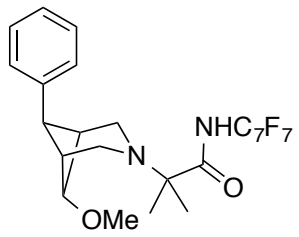
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.8 Hz, 3F), –141.2 (m, 2F), –144.1 (m, 2F).

The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.

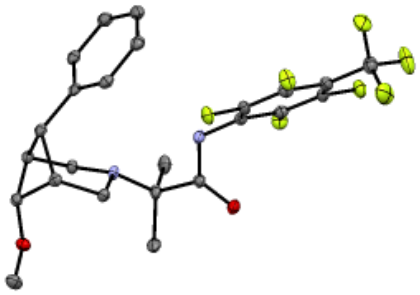
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.6, 158.0, 137.7, 127.5, 113.8, 64.8, 55.2, 47.8, 41.7, 34.3, 20.5.

HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{23}H_{24}F_7N_2O_2^+$: 493.1726; Found: 493.1718.

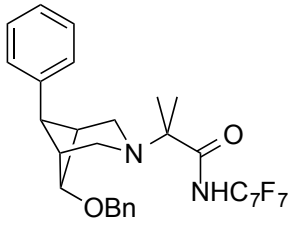
R_f = 0.50 in 20% EtOAc in hexanes



(**11b**)



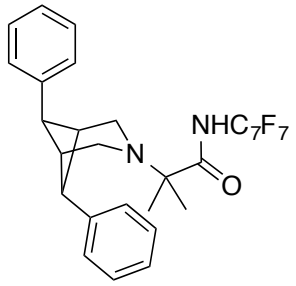
NOTE: The arylation reaction was conducted at 100 °C for 16 h. Aminal was not observed, thus purification was performed following **Isolation Procedure A**.
A mixture of starting material and product were isolated from the initial column chromatography (10% THF in hexanes). Then, the mixture of product and recovered starting material were subjected to a preparative TLC (5% THF in hexanes, plate was run four times).
Isolated yield: 62% yield.
MP 101-103 ºC (white solid)
IR (thin film): 1712 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, J = 7.5 Hz, 2H), 7.12 (t, J = 7.5 Hz, 2H), 6.96 (t, J = 7.5 Hz, 1H), 6.75 (s, 1H), 3.60 (t, J = 5.5 Hz, 1H), 3.38 (s, 3H), 3.08-2.96 (multiple peaks, 7H), 1.19 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.1 (t, J = 23.6 Hz, 3F), –141.8 (m, 2F), –142.3 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 140.9, 128.2, 125.5, 125.1, 72.9, 63.2, 55.8, 39.8, 39.6, 34.7, 21.1.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{24}H_{24}F_7N_2O_2$: 505.1721; Found: 505.1721.
R_f = 0.12 in 5% THF in hexanes



(**11c**)

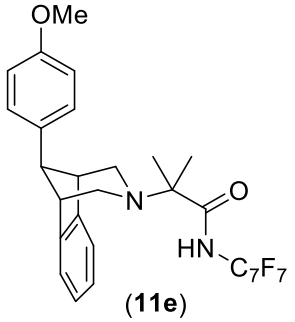
NOTE: The arylation reaction was conducted at 120 °C for 16 h. Aminal formation was observed. $NaBH_4$ reduction was required on this substrate following **Isolation Procedure B**. Purification via column chromatography (10 g cartridge, gradient elution from 0% to 5% THF in hexanes) afforded a colorless oil. This oil was diluted with a small amount of methanol (~0.3 mL). Slow evaporation at RT of the methanol to about 0.15 mL yielded pure product as a white solid. The supernatant was removed by decantation.
Isolated yield: 66% yield.
MP 114-116 ºC (white solid)

IR (thin film): 1690 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 (app d, J = 7.7 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H), 7.22 (app d, J = 7.7 Hz, 2H), 7.14 (t, J = 7.7 Hz, 2H), 6.99 (t, J = 7 Hz, 1H), 6.90 (br s, 1H), 4.57 (s, 2H), 3.83 (t, J = 5.6 Hz, 1H), 3.16 (d, J = 9.8 Hz, 2H), 3.10 (m, 2H), 3.04 (app d, J = 9.1 Hz, 2H), 2.99 (t, J = 5.6 Hz, 1H), 1.16 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.11 (t, J = 21.5 Hz, 3F), –141.87 (m, 2F), –142.38 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.4, 140.6, 137.8, 128.6, 128.2, 128.0, 127.9, 125.6, 125.2, 71.6, 70.8, 63.2, 40.12, 40.11, 34.9, 21.5
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{30}H_{28}F_7N_2O_2$: 581.2034; Found: 581.2034.
R_f = 0.19 in 5% THF in hexanes



(**11d**)

NOTE: The arylation reaction was conducted at 100 °C. Aminal was not observed, thus purification was performed following **Isolation Procedure A**. No starting material was recovered from this reaction.
Isolated yield using standard conditions: 35%, 34%; 35% average yield
MP 152-156 ºC (white solid)
IR (thin film): 1715 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.20 (d, J = 7.4 Hz, 4H), 7.10 (t, J = 7.4 Hz, 2H), 6.48 (s, 1H), 3.48 (m, 2H), 3.40 (m, 2H), 3.11(m, 4H), 0.76 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.8 Hz, 3F), –141.8 (m, 2F), –142.5 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.7, 128.3, 128.3, 126.3, 125.6, 62.9, 40.9, 40.1, 38.0, 20.2.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{29}H_{26}F_7N_2O^+$: 551.1933; Found: 551.1926.
R_f = 0.80 in 20% EtOAc in hexanes



(**11e**)

NOTE: Aminal formation was observed. $NaBH_4$ reduction was required on this substrate following **Isolation Procedure B**.

Isolated yield using standard conditions: 47%, 45%; 46% average yield

Isolated yield when based on recovered starting material: 66%, 75%; 71% average yield

MP 161-164 ºC (white solid)

IR (thin film): 1713 cm^{-1}

^1H NMR (700 MHz, $CDCl_3$) δ 7.47 (br s, 1H), 7.31-7.22 (multiple peaks, 4H), 7.13 (dd, J = 5.3, 3.1 Hz, 2H), 6.96 (m, 2H), 3.84 (s, 3H), 3.69 (t, J = 4.2 Hz, 2H), 3.58 (t, J = 4.4 Hz, 1H), 3.01 (d, J = 10.8 Hz, 2H), 2.56 (dd, J = 11.0, 4.2 Hz, 2H), 1.04 (s, 6H).

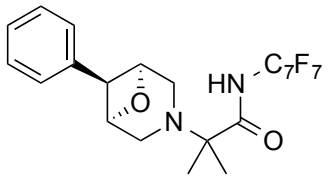
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.8 Hz, 3F), –141.5 (m, 2F), –142.9 (m, 2F).

The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.

^{13}C NMR (176 MHz, $CDCl_3$) δ 176.0, 157.6, 146.2, 130.8, 129.2, 126.7, 121.7, 114.2, 63.5, 55.2, 51.0, 43.6, 42.6, 21.4.

HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{27}H_{26}F_7N_2O_2^+$: 567.1882; Found: 567.1874.

R_f = 0.50 in 20% EtOAc in hexanes



(**11f**)

Note: The arylation reaction was conducted at 95 ºC. Aminal was not observed, thus purification was performed following **Isolation Procedure A**.

Isolated yield using standard conditions: 32%, 34%; 33% average yield

Isolated yield when calculated based on recovered starting material: 69%, 74%; 72% average yield

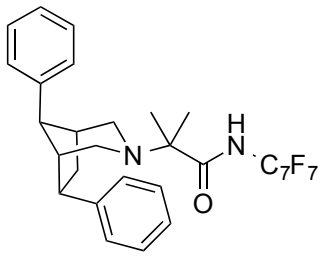
MP 202 ºC (white solid)

IR (thin film): 1713 cm^{-1}

^1H NMR (700 MHz, $CDCl_3$) δ 7.12 (t, J = 7.7 Hz, 2H), 7.05 (d, J = 7.7 Hz, 2H), 7.00 (t, J = 7.7 Hz, 1H), 6.42 (s, 1H), 4.95 (d, J = 6.1 Hz, 2H), 4.60 (t, J = 6.3 Hz, 1H), 3.19 (d, J = 11.6 Hz, 2H), 3.09 (d, 11.4 Hz, 2H), 1.23 (s, 6H).

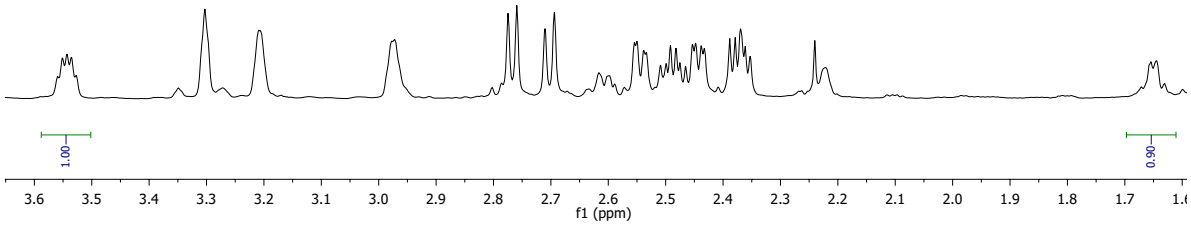
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.8 Hz, 3F), –141.4 (m, 2F), –142.5 (m, 2F).

The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.2, 139.2, 128.3, 126.1, 123.8, 81.4, 63.0, 45.8, 44.7, 20.5.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{22}H_{20}F_7N_2O_2^+$: 477.1413; Found: 477.1505.
R_f = 0.38 in 35% EtOAc in hexanes



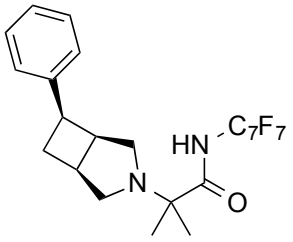
(11g)

NOTE: The reaction was performed at a larger scale (0.4 mmol of substrate), and was conducted at 145 °C in *t*-amylOH (0.13 M in substrate). Aminal formation was observed. $NaBH_4$ reduction was required on this substrate following a modified **Isolation Procedure B** where iodobenzene was removed under vacuum instead of via filtration through silica gel plug.
The yield for compound **11g** was determined by isolating a mixture of recovered starting material **S11** and compound **11g** via column chromatography (2% THF in hexanes). The mixture was analyzed by ^1H NMR spectroscopy to determine the ratio of **S11**:**11g** (ca. 0.23:1). This ratio, in combination with the isolated mass of the mixture and the respective molecular masses, was used to determine a yield of **11g** based on the mixture. Pure **11g** was obtained after repeated chromatography (2% THF in hexanes). An excerpt of the NMR used to determine the ratio is below:

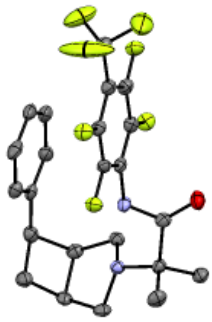


Yield: 34% yield
MP 142-144 ºC (white solid)
IR (thin film): 1716 cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.41-7.38 (multiple peaks, 4H), 7.34 (app d, J = 8.4 Hz, 2H), 7.23 (t, J = 7.7 Hz, 1 H), 7.16 (t, J = 7.7 Hz, 2H), 6.75 (t, J = 7.7 Hz, 1H), 3.58 (quintet, J = 5.6 Hz, 1H), 3.34 (br s, 1H), 3.25 (br s, 1H), 3.01 (m, 1H), 2.80 (d, J = 10.5 Hz, 1H), 2.73 (d, J = 12.6 Hz, 1H), 2.58 (dd, J = 3.5, 11.2 Hz, 1 H), 2.53 (m, 1H), 2.48 (dd, J = 4.2, 11.2 Hz, 1H), 2.41 (dd, J = 7, 5.6 Hz, 1H), 1.01 (s, 3H), 0.77 (s, 3H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 22.6 Hz, 3F), –142.1 (m, 2H), –143.2 (m, 2H).

The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.3, 143.4, 139.6, 128.92, 128.86, 128.6, 127.2, 126.0, 125.1, 63.9, 47.6, 46.9, 44.9, 41.5, 40.0, 36.4, 32.4, 22.5, 18.3.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{30}H_{28}F_7N_2O$: 565.2084; Found: 565.2089.
R_f = 0.10 in 2% THF in hexanes

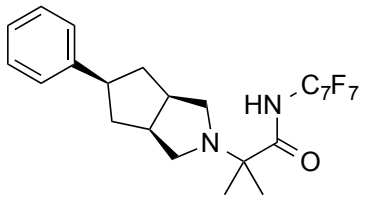


(**11h**)



NOTE: The arylation reaction was conducted at 130 °C in *t*-AmylOH (0.12 M in substrate). Aminal was not observed, thus purification was performed following **Isolation Procedure A**.

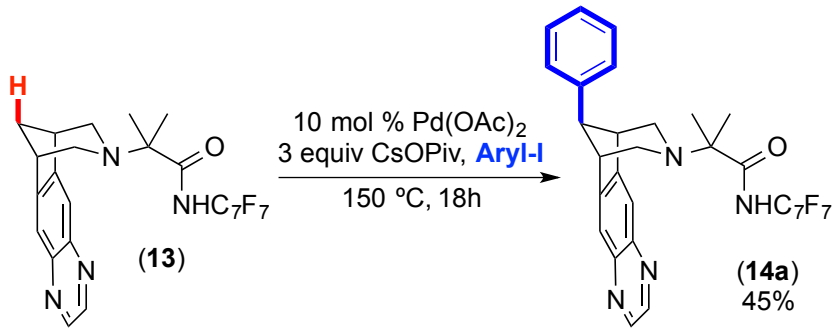
Isolated yield using standard conditions: 54% yield
Isolated yield when calculated based on recovered starting material: 57% yield
MP 138-140 ºC (white solid)
IR (thin film): 1708 cm^{-1}
^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (br s, 1H), 7.08 (multiple peaks, 4H), 6.64 (m, 1H), 3.79 (q, J = 9.5 Hz, 1H), 3.26 (q, J = 8 Hz, 1H), 2.97 (m, 1H), 2.76 (dd, J = 15, 10 Hz, 2H), 2.61 (m, 1H), 2.42 (dd, J = 9, 5.5 Hz, 1H), 2.35 (dd, J = 10, 7 Hz, 1H), 2.25 (m, 1H), 1.31 (s, 3H), 1.14 (s, 3H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.0 (t, J = 22.1 Hz, 3F), –142.1 (m, 2F), –143.5 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 142.3, 128.1, 126.7, 124.8, 61.3, 53.0, 48.0, 41.5, 36.5, 32.9, 28.9, 25.1, 16.8.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{23}H_{22}F_7N_2O$: 475.1615; Found: 475.1612.
R_f = 0.21 in 5% THF in hexanes



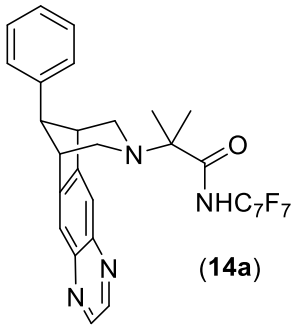
(**11i**)

NOTE: Aminal formation was observed. $NaBH_4$ reduction was required on this substrate following **Isolation Procedure B**. Purification via preparative TLC (5% THF in hexanes).
Isolated yield: 44% yield.
MP 93-95 ºC (white solid)
IR (thin film): 1722 cm^{-1}
^1H NMR (500 MHz, $CDCl_3$) δ 9.36 (br s, 1H), 7.31-7.18 (multiple peaks, 5H), 3.01 (app septet, J = 5.5 Hz, 1 H), 2.71-2.59 (multiple peaks, 6H), 2.42 (m, 2H), 1.49 (m, 2H), 1.37 (s, 6H).
^{19}F NMR (471 MHz, $CDCl_3$) δ –56.02 (t, J = 18.8 Hz, 3F), –141.10 (m, 2F), –143.77 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 143.8, 128.5, 127.0, 126.3, 61.7, 53.2, 46.9, 41.7, 41.5, 21.1.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{24}H_{24}F_7N_2O$: 489.1771; Found: 489.1772.
R_f = 0.13 in 5% THF in hexanes

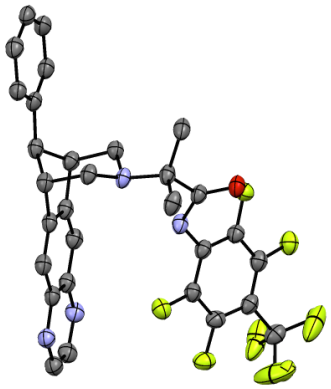
VI. Diversification of varenicline core via transannular C–H arylation



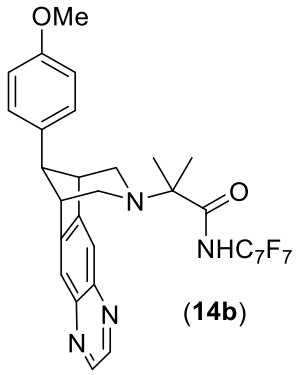
Example given for Aryl-I = PhI: Under ambient conditions, a 20 mL scintillation vial was charged with solid substrate **13** (77 mg, 0.15 mmol, 1 equiv), $Pd(OAc)_2$ (3.5 mg, 0.01 mmol, 10 mol %), cesium pivalate (105 mg, 0.45 mmol, 3 equiv), and iododobenzene (0.55 mL, 5.3 mmol 30 equiv). The vial was sealed with a Teflon-lined cap and heated to an external temperature of 150 ºC. After 24 h, the reaction was removed from the heat source and diluted with hexanes (5 mL). Hydrazine (300 µL, 35% in H_2O, 1.5 mmol, 20 equiv) was added to the warm solution. The mixture was allowed to stir for 60 min at 60 ºC to remove Pd from the product. This solution was loaded onto a small plug of silica gel over which hexanes (150 mL) was passed to remove iodoarene.[3] The plug of silica was then rinsed with EtOAc (150 mL) to elute the product, and this solution was concentrated under reduced pressure. Purification by column chromatography (25 g cartridge, gradient elution from 0% to 40% EtOAc in hexanes) afforded recovered starting material (26 mg) along with the desired product (45 mg, 51%, 77% BRSM).



[3] The hexanes solution was checked by TLC to confirm that no product co-eluted with iodoarene.

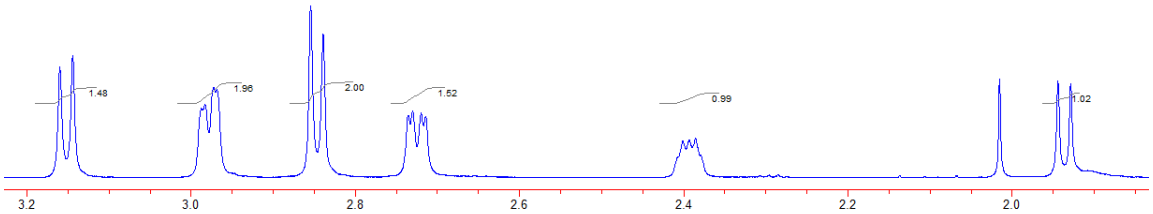


Isolated yield using modified standard conditions: 41%, 55%, 44%; 45% average yield
Isolated yield when calculated based on recovered starting material: 63%, 77%, 61%; 67% average yield
MP 203-205 ºC (white solid)
IR (thin film): 1721 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.76 (s, 2H), 7.93 (s, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.40-7.35 (multiple peaks, 3H), 7.30 (m, 1H), 4.03 (t, J = 4.3 Hz, 2H), 3.77 (m, 1H), 3.17 (d, J = 11.0 Hz, 2H), 2.76 (dd, J = 11.2, 4.2 Hz, 2H), 1.02 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.6 Hz, 3F), –141.4 (m, 2F), –144.4 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.8, 149.9, 144.1, 143.0, 138.0, 129.1, 128.2, 126.5, 121.1, 63.8, 51.4, 44.9, 42.5, 21.2.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{30}H_{24}F_7N_4O^+$: 589.1838; Found: 589.1830.
R_f = 0.60 in 50% EtOAc in hexanes

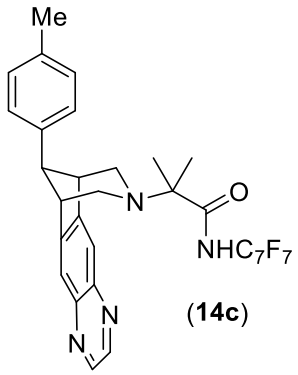


(**14b**)

The yield for compound **14b** was determined by isolating a mixture of recovered starting material **13** and compound **14b** from the column chromatography. The mixture was analyzed by ^{1}H NMR spectroscopy to determine the ratio of **13**:**14b** (ca. 2:1.6 depending on sample). This ratio, in combination with the isolated mass of the mixture and the respective molecular masses, was used to determine a yield of **14b** based on the mixture. Pure **14b** was isolated after repeated chromatography. An excerpt of the NMR spectrum used to determine the ratio is below:



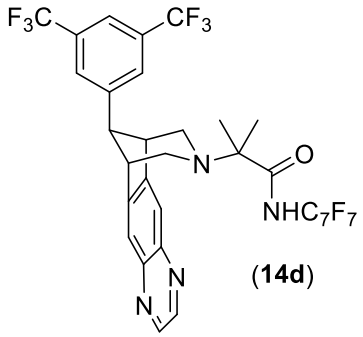
Yield: 41%, 38%; 40% average yield
Yield calculated based on recovered starting material: 80%, 70%; 75% average yield
MP 161-164 ºC (white solid)
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.91 (s, 2H), 7.36 (s, 1H), 7.28 (m, 2H), 6.99 (m, 2H), 3.97 (t, J = 4.2 Hz, 2H), 3.86 (s, 3H), 3.71 (m, 1H), 3.17 (d, J = 11.0 Hz, 2H), 2.74 (dd, J = 11.1, 4.1 Hz, 2H), 1.03 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.7 Hz, 3F), –141.4 (qd, J = 21.7, 12.6 Hz, 2F), –144.3 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.8, 157.9, 150.0, 144.0, 143.1, 129.9, 129.2, 121.1, 114.5, 63.8, 55.2, 50.7, 44.8, 42.7, 21.2.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{31}H_{26}F_7N_4O_2^+$: 619.1944; Found: 619.1936.
R_f = 0.50 in 50% EtOAc in hexanes



(**14c**)

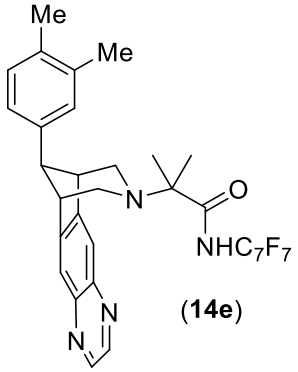
Isolated yield using modified standard conditions: 41%, 43%; 42% average yield
Isolated yield when calculated based on recovered starting material: 55%, 53%; 54% average yield
MP 239-244 ºC (light brown solid)
IR (thin film): 1721 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.91 (s, 2H), 7.37 (s, 1H), 7.26 (s, 4H), 3.99 (t, J = 4.3 Hz, 2H), 3.72 (t, J = 4.3 Hz, 1H), 3.17 (d, J = 11.0 Hz, 2H), 2.75 (dd, J = 11.2, 4.2 Hz, 2H), 2.39 (s, 3H), 1.03 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.6 Hz, 3F), –141.4 (m, 2F), –144.3 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to

the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.9, 150.0, 144.0, 143.0, 136.0, 134.8, 129.7, 128.0, 121.1, 63.8, 51.1, 44.8, 42.6, 21.2, 21.0.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{31}H_{26}F_7N_4O^+$: 603.1995; Found: 603.1989.
R_f = 0.65 in 50% EtOAc in hexanes



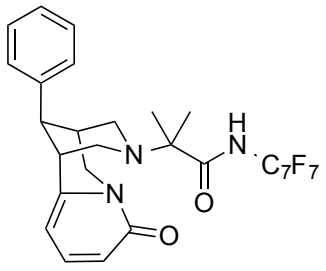
(**14d**)

NOTE: This reaction was conducted at 140 ºC using 20 mol % $Pd(OAc)_2$, 3 equiv AgOAc, and 3 equiv KOPiv per general conditions B for the azabicyclo[3.1.0]hexane system.
Isolated yield using modified standard conditions: 36%, 39%, 34%; 37% average yield
Isolated yield when calculated based on recovered starting material: 51%, 46%, 53%%; 50% average yield
MP >250 ºC (dec.) (white solid)
IR (thin film): 1715 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.77 (s, 2H), 7.96 (s, 2H), 7.86 (s, 1H), 7.84 (s, 2H), 7.18 (s, 1H), 4.13 (t, J = 4.2 Hz, 2H), 3.85 (bs, 1H), 3.02 (d, J = 11.4 Hz, 2H), 2.87 (dd, J = 11.6, 4.2 Hz, 2H), 1.05 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.7 Hz, 3F), –62.8 (s, 6F), –141.2 (m, 2F), –144.4 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.3, 148.5, 144.4, 143.1, 140.9, 132.5 (q, $J_{C\text{-}F}$ = 33 Hz), 128.6 (q, $J_{C\text{-}F}$ = 4.0 Hz), 123.1 (q, $J_{C\text{-}F}$ = 273 Hz), 121.5, 120.7 (q, $J_{C\text{-}F}$ = 4.0 Hz), 63.8, 51.1, 44.8, 42.3, 21.1.
HRMS (ESI$^+$) $[M+H]^+$ Calcd for $C_{32}H_{22}F_{13}N_4O^+$: 725.1586; Found: 725.1575.
R_f = 0.70 in 50% EtOAc in hexanes



(**14e**)

Isolated yield using modified standard conditions: 44%, 42%; 43% average yield
Isolated yield when calculated based on recovered starting material: 78%, 74%; 76% average yield
MP 228-231 ºC (brown solid)
IR (thin film): 1714 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.91 (s, 2H), 7.37 (s, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.13 (s, 1H), 7.09 (d, J = 7.7 Hz, 1H), 4.00 (t, J = 4.3 Hz, 2H), 3.70 (m, 1H), 3.18 (d, J = 10.9 Hz, 2H), 2.75 (dd, J = 11.1, 4.2 Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 1.04 (s, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.7 Hz, 3F), –141.4 (m, 2F), –144.4 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of $^{13}C/^{19}F$ coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.9, 150.1, 144.0, 143.1, 137.2, 135.3, 134.6, 130.2, 129.3, 125.5, 121.0, 63.8, 51.1, 44.9, 42.5, 21.2, 20.0, 19.3.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{32}H_{28}F_7N_4O^+$: 617.2151; Found: 617.2145.
R_f = 0.70 in 50% EtOAc in hexanes



(17)

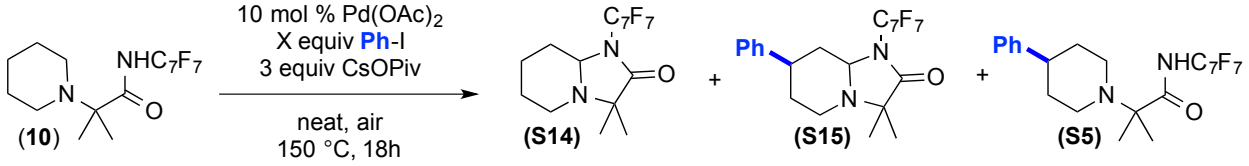
NOTE: The arylation reaction was conducted in *t*AmylOH (0.13 M in substrate). $NaBH_4$ reduction was not required on this substrate.
Isolated yield using standard conditions: 25% yield (yellow oil).
Isolated yield when calculated based on recovered starting material: 32%
IR (thin film): 1717, 1653 cm^{-1}
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.44 (t, J = 14 Hz, 2H), 7.38 (d, J = 14 Hz, 2H), 7.31 (t, J = 14 Hz, 1H), 7.09 (dd, J = 7, 0.7 Hz, 1H), 6.38 (app d, J = 10.5 Hz, 1H), 6.09 (app d, J = 7 Hz, 1H), 4.45 (d, J = 15.4 Hz, 1H), 4.15 (dd, J = 6.3, 15.4 Hz, 1H), 3.65 (br s, 1H), 3.38 (br s, 1H), 3.18 (br s, 1H), 2.95 (m, 1H), 2.89 (m, 1H), 2.82 (d, J = 11.9 Hz, 1H), 2.65 (app d, J = 11.9 Hz, 1H), 1.24 (s, 3H), 1.08 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ –56.1 (t, J = 21.9 Hz, 3F), –140.9 (m, 2F), –142.9 (m, 2F).
The carbon resonances corresponding to the perfluoroarene (C_7F_7) in this compound appear as a complex series of multiplets between 105 ppm to 155 ppm as a result of ^{13}C/^{19}F coupling. Due to the complexities of the system, the peaks are not listed. ^{19}F NMR and HRMS were used to confirm the presence of this ring system.
^{13}C NMR (176 MHz, $CDCl_3$) δ 174.8, 163.1, 150.9, 138.6, 137.7, 129.3, 127.3, 127.1, 117.5, 105.0, 64.6, 52.6, 50.0, 48.0, 39.7, 36.1, 31.1, 23.7, 17.8.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{28}H_{25}F_7N_3O_2$: 568.1830; Found: 568.1829.
R_f = 0.25 in 60% EtOAc in hexanes

VII. Other Experiments

Effect of amount of aryl iodide on yields:

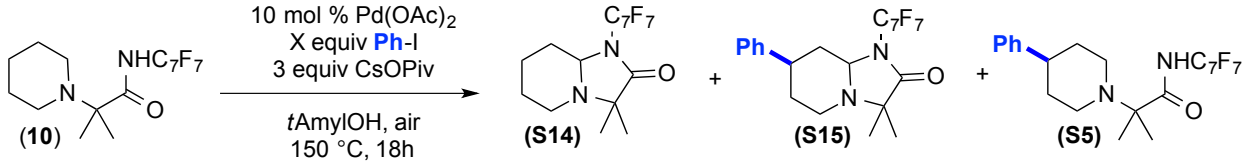
Table S5. Evaluation of equivalents of iodobenzene for substrate **10** under neat conditions.



Entry	Equiv PhI	Conversion	Yield **S14**[a]	Yield **S15**[a]	Yield **S5**[a]
1	1	43%	18%	nd	nd
2	5	82%	9%	nd	5%
3	10	91%	5%	2%	14%
4	15	89%	7%	2%	25%
5	20	86%	11%	4%	32%
6	**30**	**93%**	**28%**	**11%**	**44%**
7	70	84%	14%	8%	40%

[a] All yields determined by gas chromatography (GC). nd, not detected.

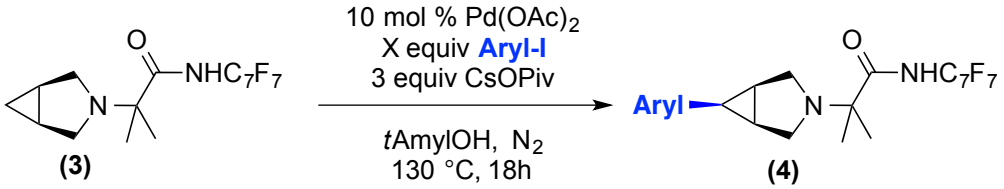
Table S6. Evaluation of equivalents of iodobenzene for substrate **10** in *t*-AmylOH.



Entry	Equiv PhI	Conversion	Yield **S14**[a]	Yield **S15**[a]	Yield **S5**[a]
1	1	59%	26%	nd	5%
2	5	68%	24%	2%	14%
3	10	68%	19%	2%	19%
4	15	71%	20%	2%	24%
5	20	74%	18%	3%	26%
6	30	78%	17%	4%	29%
7	70	78%	14%	4%	39%

[a] All yields determined by gas chromatography (GC). nd, not detected.

Table S7. Evaluation of equivalents of aryl iodide for C-H arylation of substrate **3**.

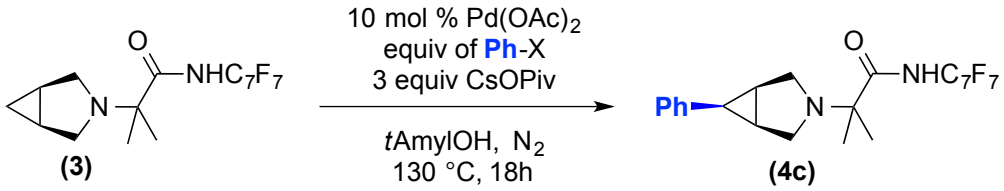


Entry	Aryl Iodide	Yield **4** (20 equiv of Aryl-I)[a]	Yield **4** (5 equiv of Aryl-I)[a]	Yield **4** (2 equiv of Aryl-I)[a]	Yield **4** (1 equiv of Aryl-I)[a]
1	4-iodoanisole	93%	91%	86%	83%
2	iodobenzene	89%	86%	90%	87%
3	1-iodo-3,5-bis(trifluoromethyl)benzene	88%	89%	88%	85%
4	2-fluoroidobenzene	77%	80%	75%	65%
5	1-bromo-4-iodobenzene	76%	72%	81%	72%
6	3-iodophenol	53%	62%	66%	57%
7	4-iodobenzaldehyde	61%	63%	67%	61%
8	2-fluoro-3-iodopyridine	42%	70%	69%	53%
9	1-BOC-5-iodoindole	55%	55%	51%	39%

[a] Uncalibrated yields determined by gas chromatography (GC) using trimethoxybenzene as internal standard.

Use of other aryl halides and triflates in the C-H arylation reaction of **3**:

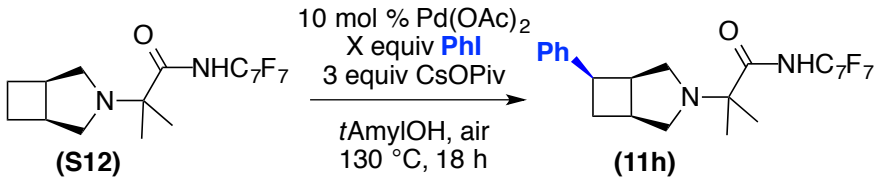
Table S8. Evaluation of Ph-Cl, -OTf, -Br for C-H arylation of substrate **3**.



Entry	Ph-X (equiv)	Conversion	Yield **5**[a]	Yield **4c**[a]
1	Chlorobenzene (20)	26%	14%	nd
2	Phenyl triflate (20)	17%	8%	nd
3	**Bromobenzene (20)**	**43%**	**17%**	**14%**
4	Bromobenzene (2)	43%	13%	<2%
5	Bromobenzene (1)	47%	13%	<2%

[a] All yields determined by gas chromatography (GC).

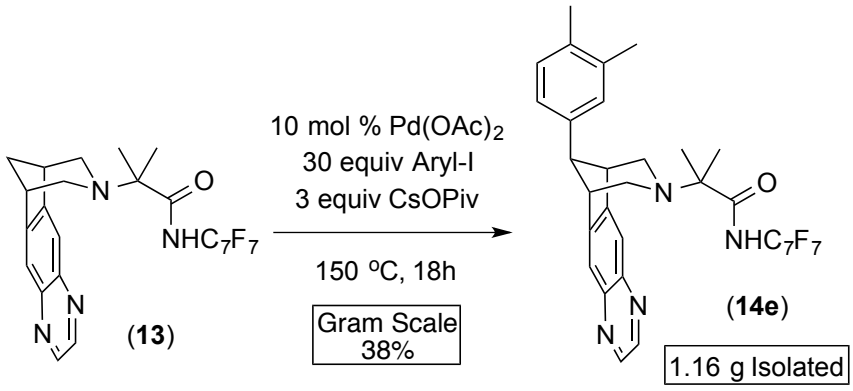
Table S9. Evaluation of equivalents of iodidobenzene for C-H arylation of substrate **S12**.



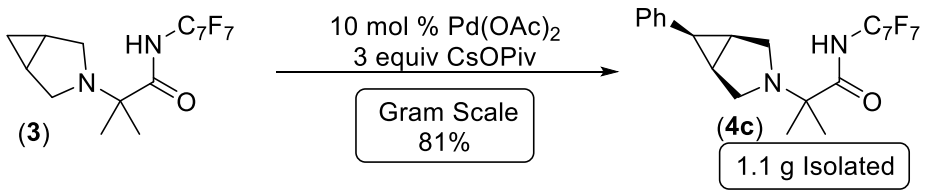
Entry	Equiv PhI	Yield **11h**[a]
1	30	59%
2	10	53%
3	2	35%
4	1	24%

[a] Uncalibrated yields determined by gas chromatography (GC) using trimethoxybenzene as internal standard.

Gram scale C–H arylation reactions:

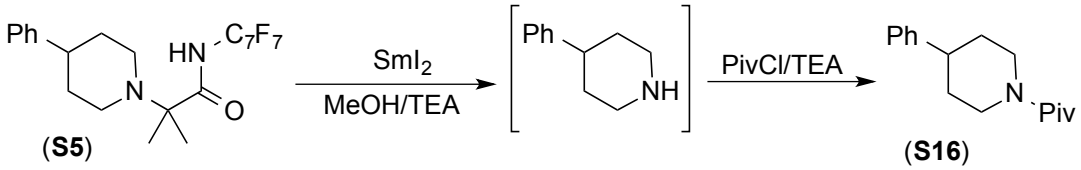


Under ambient conditions, a 50 mL round bottom flask was charge with substrate **13** (2.51 g, 4.0 mmol, 1 equiv), $Pd(OAc)_2$ (110 mg, 0.49 mmol, 10 mol%), cesium pivalate (3.45 g, 14.7 mmol, 3 equiv) and 4-iodo-*o*-xylene (20.9 mL, 147 mmol, 30 equiv). The flask was sealed with a glass stopper, and heated to an external temperature of 150 ºC. After reaching the appropriate temperature, excess pressure was vented from the flask, and it was resealed. After 24 h, the reaction was removed from the heat source, hydrazine (3 mL, 65% in H_2O, 40 mmol, 8 equiv) and hexanes (5 mL) were added to the warm solution. The mixture was then allowed to stir for 1 h at 60 ºC to remove Pd from the product. This solution was loaded onto a large plug of silica gel over which hexanes (1.5 L) was passed to remove iodobenzene. The plug of silica was then rinsed with EtOAc (1 L) to elute the product, and this solution was concentrated under reduced pressure. Purification by column chromatography (100 g cartridge, gradient elution from 0% to 40% EtOAc in hexanes) afforded the desired product **14e** as a brown solid (1.16 g, 38% yield).



Under ambient conditions, a 50 mL round bottom flask was charged with substrate **3** (1.17 g, 3.04 mmol, 1 equiv), $Pd(OAc)_2$ (74 mg, 0.33 mmol, 10 mol %), cesium pivalate (2.38 g, 10 mmol, 3 equiv), iodobenzene (7 mL, 62 mmol, 20 equiv), and *t*-amyl alcohol (21 mL). The flask was sealed with a septum, and heated to an external temperature of 130 ºC. After reaching the appropriate temperature, excess pressure was vented from the flask, and it was resealed. After 23 h, the reaction was removed from the heat source, and hydrazine (1 mL, 35% in H_2O, 10 mmol, 3 equiv) was added to the warm solution. The mixture was then allowed to stir for 30 min at 60 ºC to remove Pd from the product. The resulting solution was diluted with EtOAc and filtered through a layered plug of celite and basic alumina. The pad was rinsed with additional EtOAc, and the resulting solution was concentrated under reduced pressure. Purification by column chromatography (50 g cartridge, gradient elution from 0% to 20% EtOAc in hexanes) afforded the desired product as an oil. The oil was triturated with hexanes, and the volatiles were removed under reduced pressure to afford the desired product **4c** as a white solid (1.14 g, 81% yield).

Optimization of C-N bond cleavage mediated by SmI_2

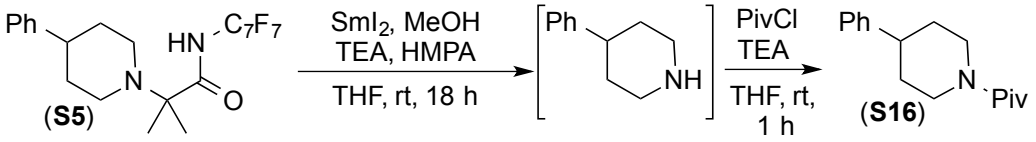


Inside of a glove box at room temperature, a stock solution of amine **S5** (121 mg, 0.26 mmol) was prepared in THF (3 mL). An aliquot of this solution was transferred to a vial (4 mL capacity, 200 µL, 0.018 mmol amine **S5**, 1 equiv), and SmI_2 (2 mL, 0.1 M in THF, 0.2 mmol, 10 equiv), MeOH, (varied from 3.5 µL to 28 µL) and TEA (varied from 12 µL to 100 µL) were added. The vial was sealed with a Teflon-lined cap and removed from the glove box. The solutions maintained a deep blue color for varying amounts of time depending on the equiv of various reagents added. After 18 h, pivaloyl chloride (100 µL, 0.8 mmol) and additional TEA (200 µL,

1.4 mmol) were added, which immediately quenched the blue color (if any remained) and resulted in a clear solution with white precipitate. A solution of internal standard (1,3,5-trimethoxybenzene, 59 mg in 4 mL DCM) was prepared, and an aliquot (200 μL) of the stock standard solution was added to the reaction vial. The reaction solution was then diluted with EtOAc and HCl (2M, aqueous), which produced a yellow solution free of precipitates. The phases were separated, and the organic layer was filtered through a pipette packed with Na_2SO_4 and was analyzed by GC-FID. The average value of duplicate GC injections was used to determine the GC yield based on a linear 5-point calibration curve with 1,3,5-trimethoxybenzene.

Variations of this procedure were used in all optimization reactions (Table S10) where the yield was determined by GC-FID. For instance, the impact of equiv SmI_2 could be determined by following the same procedure outlined above except that different volumes of SmI_2 in THF solution were transferred to each vial.

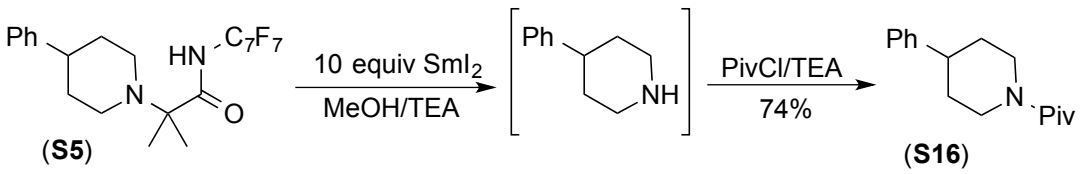
Table S10. Optimization for the directing group removal.



entry	equiv SmI_2	equiv MeOH	equiv TEA	conversion	yield **S16**
1	3	0	0	<10%	<10%
2	5	0	0	<10%	<10%
3	10	0	0	<10%	<10%
4	5	5	5	<10%	<10%
5	10	10	10	21%	13%
6	10	5	10	74%	42%
7	10	10	10	81%	56%
8	10	20	10	91%	52%
9	10	40	10	98%	57%
10	10	10	5	44%	22%
11	10	10	10	54%	23%
12	10	10	20	55%	25%
13	10	10	40	78%	35%
14	10	15	15	74%	39%
15	10	20	20	73%	47%
16	10	30	30	88%	53%
17	10	50	50	94%	62%
18[a]	**10**	**50**	**50**	**100%**	**95%**

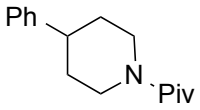
[a] additional 8 equiv HMPA were added

Isolation of C-N bond cleavage product



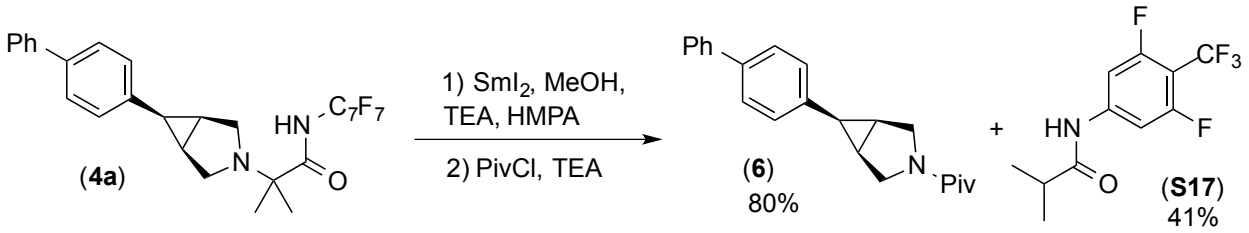
In a glove box, a vial was charged with solid amine **S5** (66 mg, 0.14 mmol) to which a solution of SmI_2 (15 mL, 0.1M in THF, 1.5 mmol) was added. To this solution, MeOH (0.3 mL, 7.5 mmol) and TEA (1.0 mL, 14 mmol) were added. The vial was then sealed with a Teflon-lined

cap and removed from the glove box. The solution was allowed to stand at room temperature for 18 h, after which the reaction was quenched by dropwise addition of pivaloyl chloride (1.0 mL, 8.1 mmol) followed by the addition of additional TEA (1.0 mL, 14 mmol). The resulting solution was allowed to remain at room temperature for 90 min, after which it was poured onto 2M HCl. The mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by column chromatography (25 g cartridge, gradient elution from 0% to 40% EtOAc in hexanes) afforded amide **S15** (29 mg, 78% yield). In a replicate experiment, amide **S16** was isolated in 70% yield for an average of 74% yield.



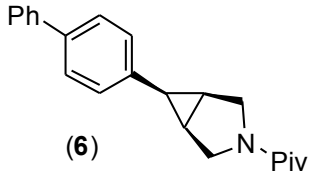
(**S16**)

Isolated yield: 78%, 70%; 74% average yield
MP 87 ºC (off white solid)
IR (thin film): 1617 cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.23-7.19 (multiple peaks, 3H), 4.58 (d, J = 12.2 Hz, 2H), 2.87 (t, J = 12.9 Hz, 2H), 2.76 (tt, J = 12.2, 4.1 Hz, 1H), 1.90 (d, J = 13.1 Hz, 2H), 1.63 (qd, J = 12.6, 4.1 Hz, 2H), 1.31 (s, 9H).
^{13}C NMR (176 MHz, $CDCl_3$) δ 176.1, 145.3, 128.5, 126.7, 126.4, 45.8, 42.8, 38.7, 33.5, 28.4.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{16}H_{24}NO^+$: 246.1858; Found: 246.1852.
R_f = 0.40 in 20% EtOAc in hexanes



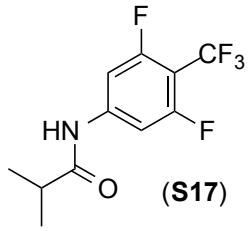
In a glove box, a vial was charged with solid amine **4a** (53 mg, 0.10 mmol) to which a solution of SmI_2 (12 mL, 0.1M in THF, 1.2 mmol) was added. To this solution, MeOH (160 µL, 4.0 mmol), TEA (550 µL, 8 mmol), and HMPA (100 µL, 0.55 mmol) were added. The vial was then sealed with a Teflon-lined cap and removed from the glove box. The solution was allowed to stand at room temperature for 18 h, after which the reaction was quenched by dropwise addition of pivaloyl chloride (1.0 mL, 8.1 mmol) followed by the addition of additional TEA (1.0 mL, 14 mmol). The resulting solution was allowed to remain at room temperature for 90 min, after which it was poured onto 2M HCl. The mixture was extracted with EtOAc. The combined

organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. Purification by column chromatography (25 g cartridge, gradient elution from 0% to 40% EtOAc in hexanes) afforded amide **6** (26 mg, 82% yield) and the isopropyl amide **S17** (11 mg, 41% yield). In a replicate experiment, the amide product **6** was isolated in 78% yield for an average of 80%.



(**6**)

Isolated yield: 82%, 78%; 80% average yield
MP 162 ºC (white solid)
IR (thin film): 1616 cm^{-1}
^1H NMR (700 MHz, $CDCl_3$, at 52 °C) δ 7.52-7.48 (multiple peaks, 4H), 7.40 (t, J = 7.5 Hz, 2H), 7.32-7.29 (multiple peaks, 3H), 3.90 (br s, 2H), 3.62 (d, J = 11.6 Hz, 2H), 2.21 (t, J = 7.9 Hz, 1H), 1.98 (d, J = 7.2 Hz, 2H), 0.83 (s, 9H).
^{13}C NMR (176 MHz, $CDCl_3$, at 52 °C) δ 175.6, 141.1, 139.6, 133.7, 129.6, 128.6, 127.2, 127.0, 126.9, 47.0, 38.6, 26.9, 22.6, 20.6.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{22}H_{26}NO^+$: 320.2014; Found: 320.2004.
R_f = 0.11 in 20% EtOAc in hexanes



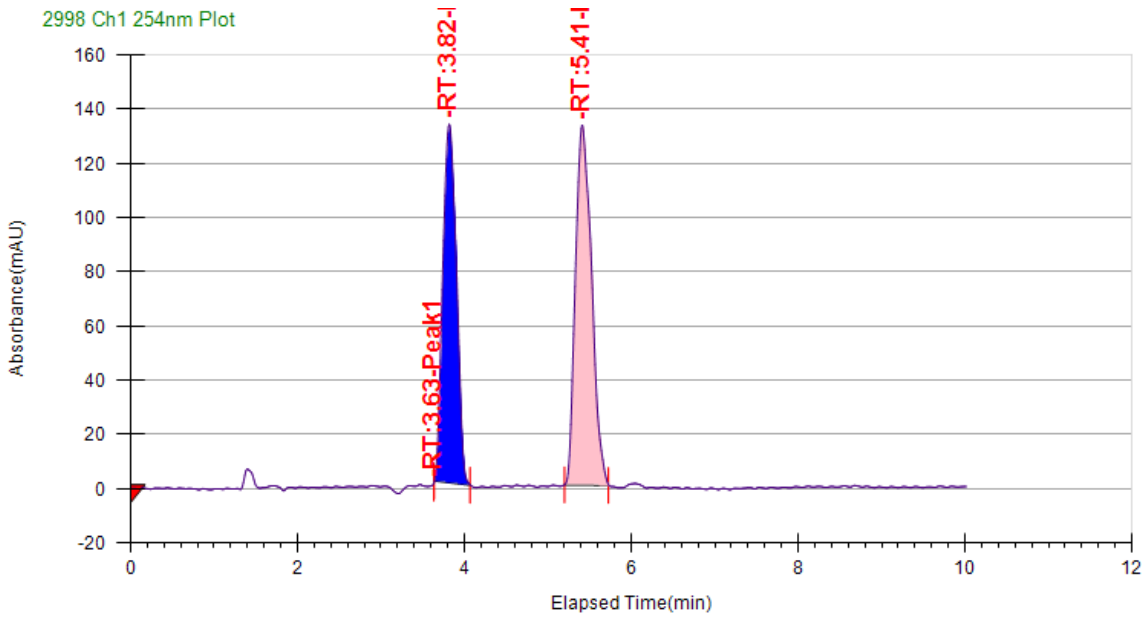
(**S17**)

Isolated yield: 41%, 40%; 41% average yield
MP 140 ºC (white solid)
IR (thin film): 1683 cm^{-1}
^1H NMR (700 MHz, $CDCl_3$) δ 7.41 (br s, 1H), 7.29 (d, J = 11.5 Hz, 2H), 2.52 (septet, J = 7.0 Hz, 1H), 1.25 (d, J = 7.0 Hz, 6H).
^{19}F NMR (377 MHz, $CDCl_3$) δ –56.0 (t, J = 21.3 Hz, 3F), –108.8 (qd, J = 21.3, 11.2 Hz, 2F).
^{13}C NMR (176 MHz, $CDCl_3$) δ 175.7, 160 (m), 142.9 (t, $J_{C\text{-}F}$ = 13.4 Hz) 121.6 (q, $J_{C\text{-}F}$ = 272 Hz), 103.1 (dd, $J_{C\text{-}F}$ = 26.6, 3.7 Hz), 102.7 (m), 36.8, 19.3.
HRMS (ESI^+) $[M+H]^+$ Calcd for $C_{11}H_{11}F_5NO^+$: 268.0761; Found: 268.0751.
R_f = 0.38 in 20% EtOAc in hexanes

Determination of the er for Phenylalanine derived product 4k

A racemic sample of **4k** was prepared as follows: Product **4k** (18 mg, 0.03 mmol) was dissolved in dioxane (0.5 mL) and solid NaOMe (7 mg, 0.13 mmol) was added at room temperature. After 15 min, the reaction was quenched by addition of AcOH (20 µL, 0.3 mmol) and the solution was passed through a plug of layered Celite, basic alumina, and silica gel. The plug was rinsed with EtOAc and the eluent was concentrated under reduced pressure.

Analysis was conducted on a Waters SFC system with an analytical AD-H chiral column (4.6 mm x 250 mm). The run program was conducted with the following parameters: isocratic 10% IPA co-solvent, flow rate of 3.2 mL/min, temperature of column oven at 40 °C, 120 bar backpressure. Below is a representative chromatogram:



Peak Information

Peak No	% Area	Area	Ret. Time	Height	Cap. Factor
1	0	0	3.63 min	0	3632.3333
2	45.4422	1465.6752	3.82 min	132.2653	3815.6667
3	54.5578	1759.6885	5.41 min	132.8034	5407.3333

VIII. X-Ray Crystallographic analysis of 4a, 14a, analog of 11g, 11b, 11h.

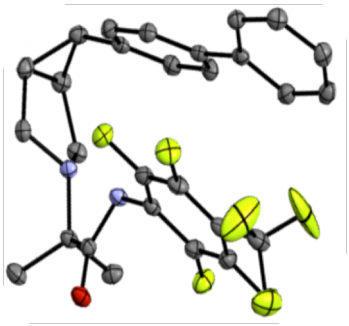


Figure S3. Structure determination of compound **4a.**

White block-like crystals of **4a** were grown from a dichlorlmethane/butyl ether solution of the compound at 22 deg. C. A crystal of dimensions 0.20 x 0.14 x 0.14 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 4151 images were collected with an oscillation width of 1.0° in ω. The exposure time was 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 66373 reflections to a maximum 2θ value of 136.48° of which 4320 were independent and 3972 were greater than $2\sigma(I)$. The final cell constants (Table S11) were based on the xyz centroids 29330 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/n with Z = 4 for the formula $C_{28}H_{23}N_2OF_7$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized or refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0459 and wR2 = 0.1150 [based on I > 2sigma(I)], R1 = 0.0487 and wR2 = 0.01170 for all data. Additional details are presented below. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

CrystalClear Expert 2.0 r12, Rigaku Americas and Rigaku Corporation (2011), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table S11. Crystal data and structure refinement for **4a**.

Empirical formula	C_{28} H_{23} F_7 N_2 O
Formula weight	536.48
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 6.421(2) A α = 90 °.
	b = 18.0944(3) A β = 98.590(11) °.
	c = 20.5377(14) A γ = 90 °.
Volume	2359.2(8) A^3
Z, Calculated density	4, 1.513 Mg/m^3
Absorption coefficient	1.131 mm^{-1}
F(000)	1104
Crystal size	0.20 x 0.14 x 0.14 mm
Theta range for data collection	3.27 to 68.24 deg.
Limiting indices	-7<=h<=7, -21<=k<=21, -24<=l<=24
Reflections collected / unique	66373 / 4320 [R(int) = 0.0583]
Completeness to theta	= 68.24 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8578 and 0.8055
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4320 / 0 / 349
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1150
R indices (all data)	R1 = 0.0487, wR2 = 0.1170
Largest diff. peak and hole	0.968 and -0.490 $e.A^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic 4a
displacement parameters (A^2 x 10^3)
U(eq) is defined as one third of the trace of the orthogonalized
Uij tensor.

	x	y	z	U(eq)
O(1)	8292(2)	2225(1)	12984(1)	22(1)
N(1)	8249(2)	1501(1)	12082(1)	18(1)
N(2)	8365(2)	254(1)	12769(1)	17(1)
F(1)	7306(3)	4229(1)	10067(1)	78(1)
F(2)	10265(4)	3795(1)	9929(1)	95(1)
F(3)	10011(3)	4528(1)	10714(1)	46(1)
F(4)	12347(2)	3429(1)	11338(1)	33(1)

F(5)	11943(2)	2295(1)	12131(1)	29(1)
F(6)	4866(2)	2002(1)	11160(1)	26(1)
F(7)	5251(2)	3106(1)	10344(1)	32(1)
C(1)	9111(4)	3962(1)	10376(1)	30(1)
C(2)	8808(3)	3316(1)	10814(1)	23(1)
C(3)	10485(3)	3080(1)	11281(1)	24(1)
C(4)	10289(3)	2491(1)	11690(1)	21(1)
C(5)	8410(3)	2102(1)	11658(1)	19(1)
C(6)	6736(3)	2341(1)	11201(1)	20(1)
C(7)	6938(3)	2925(1)	10782(1)	23(1)
C(8)	8426(3)	1612(1)	12748(1)	17(1)
C(9)	8999(3)	917(1)	13167(1)	18(1)
C(10)	11419(3)	956(1)	13322(1)	23(1)
C(11)	8063(3)	974(1)	13809(1)	24(1)
C(12)	6123(3)	44(1)	12690(1)	20(1)
C(13)	6067(3)	-740(1)	12432(1)	21(1)
C(14)	8312(3)	-1024(1)	12575(1)	21(1)
C(15)	9606(3)	-420(1)	12938(1)	20(1)
C(16)	7285(3)	-902(1)	11874(1)	20(1)
C(17)	7778(3)	-310(1)	11414(1)	18(1)
C(18)	9799(3)	-152(1)	11287(1)	20(1)
C(19)	10132(3)	375(1)	10822(1)	20(1)
C(20)	8454(3)	766(1)	10460(1)	17(1)
C(21)	6431(3)	600(1)	10588(1)	18(1)
C(22)	6107(3)	78(1)	11056(1)	20(1)
C(23)	8820(3)	1313(1)	9949(1)	17(1)
C(24)	10797(3)	1638(1)	9948(1)	21(1)
C(25)	11182(3)	2104(1)	9444(1)	24(1)
C(26)	9584(3)	2270(1)	8930(1)	24(1)
C(27)	7591(3)	1978(1)	8937(1)	23(1)
C(28)	7209(3)	1506(1)	9438(1)	19(1)

Bond lengths [A] and angles [°] for 4a.

O(1)-C(8)	1.218(2)
N(1)-C(8)	1.370(2)
N(1)-C(5)	1.406(2)
N(1)-H(1)	0.85(3)
N(2)-C(15)	1.470(2)
N(2)-C(9)	1.474(2)
N(2)-C(12)	1.474(2)
F(1)-C(1)	1.326(3)
F(2)-C(1)	1.298(3)
F(3)-C(1)	1.321(2)
F(4)-C(3)	1.342(2)

F(5)-C(4)	1.337(2)
F(6)-C(6)	1.340(2)
F(7)-C(7)	1.341(2)
C(1)-C(2)	1.506(3)
C(2)-C(7)	1.386(3)
C(2)-C(3)	1.397(3)
C(3)-C(4)	1.374(3)
C(4)-C(5)	1.390(3)
C(5)-C(6)	1.387(3)
C(6)-C(7)	1.381(3)
C(8)-C(9)	1.538(2)
C(9)-C(11)	1.532(2)
C(9)-C(10)	1.540(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.512(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(16)	1.509(3)
C(13)-C(14)	1.517(3)
C(13)-H(13)	1.0000
C(14)-C(15)	1.502(3)
C(14)-C(16)	1.507(2)
C(14)-H(14)	1.0000
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.494(2)
C(16)-H(16)	1.0000
C(17)-C(18)	1.391(3)
C(17)-C(22)	1.396(3)
C(18)-C(19)	1.387(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.406(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.395(3)
C(20)-C(23)	1.486(2)
C(21)-C(22)	1.385(3)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.400(3)
C(23)-C(28)	1.403(2)
C(24)-C(25)	1.386(3)

C(24)-H(24)	0.9500
C(25)-C(26)	1.390(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.386(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.388(3)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
C(8)-N(1)-C(5)	120.03(15)
C(8)-N(1)-H(1)	117.5(16)
C(5)-N(1)-H(1)	120.1(16)
C(15)-N(2)-C(9)	116.69(13)
C(15)-N(2)-C(12)	107.33(14)
C(9)-N(2)-C(12)	117.04(14)
F(2)-C(1)-F(3)	107.5(2)
F(2)-C(1)-F(1)	107.3(2)
F(3)-C(1)-F(1)	104.55(18)
F(2)-C(1)-C(2)	112.34(17)
F(3)-C(1)-C(2)	111.92(16)
F(1)-C(1)-C(2)	112.75(19)
C(7)-C(2)-C(3)	116.76(17)
C(7)-C(2)-C(1)	123.78(18)
C(3)-C(2)-C(1)	119.46(18)
F(4)-C(3)-C(4)	118.29(17)
F(4)-C(3)-C(2)	120.07(17)
C(4)-C(3)-C(2)	121.63(18)
F(5)-C(4)-C(3)	118.97(17)
F(5)-C(4)-C(5)	119.53(16)
C(3)-C(4)-C(5)	121.50(17)
C(6)-C(5)-C(4)	116.94(17)
C(6)-C(5)-N(1)	122.64(17)
C(4)-C(5)-N(1)	120.42(16)
F(6)-C(6)-C(7)	118.57(16)
F(6)-C(6)-C(5)	119.74(16)
C(7)-C(6)-C(5)	121.69(17)
F(7)-C(7)-C(6)	117.61(17)
F(7)-C(7)-C(2)	120.93(17)
C(6)-C(7)-C(2)	121.46(17)
O(1)-C(8)-N(1)	122.17(16)
O(1)-C(8)-C(9)	123.05(16)
N(1)-C(8)-C(9)	114.56(15)
N(2)-C(9)-C(11)	114.85(15)
N(2)-C(9)-C(8)	109.38(14)
C(11)-C(9)-C(8)	109.64(14)
N(2)-C(9)-C(10)	109.75(14)
C(11)-C(9)-C(10)	109.40(15)

C(8)-C(9)-C(10)	103.18(14)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(2)-C(12)-C(13)	104.57(14)
N(2)-C(12)-H(12A)	110.8
C(13)-C(12)-H(12A)	110.8
N(2)-C(12)-H(12B)	110.8
C(13)-C(12)-H(12B)	110.8
H(12A)-C(12)-H(12B)	108.9
C(16)-C(13)-C(12)	117.47(15)
C(16)-C(13)-C(14)	59.74(12)
C(12)-C(13)-C(14)	106.13(15)
C(16)-C(13)-H(13)	119.3
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-H(13)	119.3
C(15)-C(14)-C(16)	119.93(15)
C(15)-C(14)-C(13)	106.78(15)
C(16)-C(14)-C(13)	59.87(12)
C(15)-C(14)-H(14)	118.4
C(16)-C(14)-H(14)	118.4
C(13)-C(14)-H(14)	118.4
N(2)-C(15)-C(14)	104.24(14)
N(2)-C(15)-H(15A)	110.9
C(14)-C(15)-H(15A)	110.9
N(2)-C(15)-H(15B)	110.9
C(14)-C(15)-H(15B)	110.9
H(15A)-C(15)-H(15B)	108.9
C(17)-C(16)-C(14)	127.25(16)
C(17)-C(16)-C(13)	121.58(15)
C(14)-C(16)-C(13)	60.39(12)
C(17)-C(16)-H(16)	112.6
C(14)-C(16)-H(16)	112.6
C(13)-C(16)-H(16)	112.6
C(18)-C(17)-C(22)	117.58(17)
C(18)-C(17)-C(16)	123.93(16)
C(22)-C(17)-C(16)	118.35(16)

C(19)-C(18)-C(17)	120.93(16)
C(19)-C(18)-H(18)	119.5
C(17)-C(18)-H(18)	119.5
C(18)-C(19)-C(20)	121.69(17)
C(18)-C(19)-H(19)	119.2
C(20)-C(19)-H(19)	119.2
C(21)-C(20)-C(19)	116.94(16)
C(21)-C(20)-C(23)	121.74(16)
C(19)-C(20)-C(23)	121.29(16)
C(22)-C(21)-C(20)	121.20(16)
C(22)-C(21)-H(21)	119.4
C(20)-C(21)-H(21)	119.4
C(21)-C(22)-C(17)	121.65(17)
C(21)-C(22)-H(22)	119.2
C(17)-C(22)-H(22)	119.2
C(24)-C(23)-C(28)	117.49(17)
C(24)-C(23)-C(20)	121.36(16)
C(28)-C(23)-C(20)	121.12(16)
C(25)-C(24)-C(23)	121.34(17)
C(25)-C(24)-H(24)	119.3
C(23)-C(24)-H(24)	119.3
C(24)-C(25)-C(26)	120.34(17)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(27)-C(26)-C(25)	119.12(17)
C(27)-C(26)-H(26)	120.4
C(25)-C(26)-H(26)	120.4
C(26)-C(27)-C(28)	120.56(18)
C(26)-C(27)-H(27)	119.7
C(28)-C(27)-H(27)	119.7
C(27)-C(28)-C(23)	121.05(17)
C(27)-C(28)-H(28)	119.5
C(23)-C(28)-H(28)	119.5

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (A^2 x 10^3) for 4a.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
O(1)	30(1)	16(1)	21(1)	-2(1)	5(1)	3(1)
N(1)	26(1)	12(1)	17(1)	0(1)	4(1)	0(1)
N(2)	18(1)	12(1)	19(1)	-1(1)	2(1)	2(1)

F(1)	76(1)	56(1)	88(1)	51(1)	-30(1)	-21(1)
F(2)	213(3)	26(1)	72(1)	9(1)	107(2)	13(1)
F(3)	78(1)	22(1)	37(1)	4(1)	3(1)	-14(1)
F(4)	34(1)	29(1)	35(1)	2(1)	6(1)	-13(1)
F(5)	25(1)	32(1)	27(1)	6(1)	-3(1)	-4(1)
F(6)	24(1)	24(1)	29(1)	1(1)	0(1)	-3(1)
F(7)	37(1)	30(1)	26(1)	7(1)	-6(1)	4(1)
C(1)	53(1)	19(1)	19(1)	-2(1)	8(1)	-3(1)
C(2)	39(1)	16(1)	16(1)	-2(1)	5(1)	-1(1)
C(3)	30(1)	20(1)	22(1)	-3(1)	5(1)	-8(1)
C(4)	26(1)	20(1)	17(1)	-1(1)	0(1)	0(1)
C(5)	27(1)	13(1)	16(1)	-2(1)	5(1)	0(1)
C(6)	23(1)	17(1)	20(1)	-3(1)	2(1)	-1(1)
C(7)	31(1)	19(1)	16(1)	0(1)	-1(1)	2(1)
C(8)	18(1)	16(1)	18(1)	0(1)	4(1)	0(1)
C(9)	23(1)	15(1)	16(1)	-1(1)	2(1)	1(1)
C(10)	22(1)	19(1)	26(1)	-2(1)	-2(1)	1(1)
C(11)	36(1)	21(1)	18(1)	-1(1)	6(1)	2(1)
C(12)	19(1)	20(1)	20(1)	2(1)	5(1)	1(1)
C(13)	24(1)	19(1)	21(1)	3(1)	4(1)	-3(1)
C(14)	28(1)	15(1)	21(1)	2(1)	2(1)	1(1)
C(15)	24(1)	16(1)	19(1)	1(1)	1(1)	4(1)
C(16)	25(1)	15(1)	20(1)	-1(1)	1(1)	-1(1)
C(17)	24(1)	14(1)	16(1)	-3(1)	1(1)	1(1)
C(18)	21(1)	19(1)	19(1)	-1(1)	2(1)	4(1)
C(19)	18(1)	21(1)	21(1)	-1(1)	3(1)	2(1)
C(20)	20(1)	15(1)	16(1)	-4(1)	1(1)	1(1)
C(21)	18(1)	18(1)	19(1)	-1(1)	0(1)	2(1)
C(22)	19(1)	20(1)	21(1)	-1(1)	2(1)	-1(1)
C(23)	19(1)	14(1)	19(1)	-4(1)	3(1)	2(1)
C(24)	19(1)	19(1)	24(1)	-2(1)	2(1)	2(1)
C(25)	22(1)	19(1)	33(1)	-1(1)	8(1)	-2(1)
C(26)	30(1)	16(1)	27(1)	3(1)	9(1)	1(1)
C(27)	28(1)	18(1)	22(1)	1(1)	1(1)	2(1)
C(28)	21(1)	17(1)	20(1)	-1(1)	2(1)	-1(1)

Hydrogen coordinates (x 10^4) and isotropic for 4a

displacement parameters (A^2 x 10^3)

	x	y	z	U(eq)
H(1)	8400(40)	1063(14)	11950(11)	25(6)
H(10A)	12021	903	12913	34
H(10B)	11936	556	13625	34
H(10C)	11839	1433	13526	34

H(11A)	8406	525	14072	36
H(11B)	6530	1026	13708	36
H(11C)	8655	1405	14060	36
H(12A)	5262	375	12374	23
H(12B)	5587	66	13118	23
H(13)	4880	-1072	12505	25
H(14)	8548	-1543	12735	26
H(15A)	9807	-509	13419	24
H(15B)	11004	-384	12792	24
H(16)	6837	-1374	11642	24
H(18)	10968	-408	11521	24
H(19)	11529	474	10747	24
H(21)	5256	850	10350	22
H(22)	4712	-18	11135	24
H(24)	11897	1538	10300	25
H(25)	12544	2311	9450	29
H(26)	9855	2579	8578	29
H(27)	6478	2103	8597	28
H(28)	5835	1310	9435	23

Torsion angles [°] for 4a.

F(2)-C(1)-C(2)-C(7)	-106.5(3)
F(3)-C(1)-C(2)-C(7)	132.4(2)
F(1)-C(1)-C(2)-C(7)	14.9(3)
F(2)-C(1)-C(2)-C(3)	73.1(3)
F(3)-C(1)-C(2)-C(3)	-48.0(3)
F(1)-C(1)-C(2)-C(3)	-165.56(19)
C(7)-C(2)-C(3)-F(4)	179.64(16)
C(1)-C(2)-C(3)-F(4)	0.0(3)
C(7)-C(2)-C(3)-C(4)	-0.1(3)
C(1)-C(2)-C(3)-C(4)	-179.69(17)
F(4)-C(3)-C(4)-F(5)	0.7(3)
C(2)-C(3)-C(4)-F(5)	-179.54(17)
F(4)-C(3)-C(4)-C(5)	-179.80(16)
C(2)-C(3)-C(4)-C(5)	-0.1(3)
F(5)-C(4)-C(5)-C(6)	178.71(16)
C(3)-C(4)-C(5)-C(6)	-0.7(3)
F(5)-C(4)-C(5)-N(1)	-0.6(3)
C(3)-C(4)-C(5)-N(1)	179.95(17)
C(8)-N(1)-C(5)-C(6)	-114.4(2)
C(8)-N(1)-C(5)-C(4)	64.9(2)
C(4)-C(5)-C(6)-F(6)	-177.97(15)
N(1)-C(5)-C(6)-F(6)	1.3(3)
C(4)-C(5)-C(6)-C(7)	1.8(3)
N(1)-C(5)-C(6)-C(7)	-178.94(17)

F(6)-C(6)-C(7)-F(7)	-1.9(3)
C(5)-C(6)-C(7)-F(7)	178.32(16)
F(6)-C(6)-C(7)-C(2)	177.73(16)
C(5)-C(6)-C(7)-C(2)	-2.0(3)
C(3)-C(2)-C(7)-F(7)	-179.25(16)
C(1)-C(2)-C(7)-F(7)	0.3(3)
C(3)-C(2)-C(7)-C(6)	1.1(3)
C(1)-C(2)-C(7)-C(6)	-179.31(18)
C(5)-N(1)-C(8)-O(1)	15.3(3)
C(5)-N(1)-C(8)-C(9)	-159.54(16)
C(15)-N(2)-C(9)-C(11)	-85.14(19)
C(12)-N(2)-C(9)-C(11)	44.0(2)
C(15)-N(2)-C(9)-C(8)	151.12(15)
C(12)-N(2)-C(9)-C(8)	-79.77(18)
C(15)-N(2)-C(9)-C(10)	38.6(2)
C(12)-N(2)-C(9)-C(10)	167.71(14)
O(1)-C(8)-C(9)-N(2)	161.64(16)
N(1)-C(8)-C(9)-N(2)	-23.6(2)
O(1)-C(8)-C(9)-C(11)	34.9(2)
N(1)-C(8)-C(9)-C(11)	-150.38(16)
O(1)-C(8)-C(9)-C(10)	-81.6(2)
N(1)-C(8)-C(9)-C(10)	93.15(17)
C(15)-N(2)-C(12)-C(13)	-31.68(17)
C(9)-N(2)-C(12)-C(13)	-165.11(14)
N(2)-C(12)-C(13)-C(16)	-46.5(2)
N(2)-C(12)-C(13)-C(14)	17.31(18)
C(16)-C(13)-C(14)-C(15)	115.31(16)
C(12)-C(13)-C(14)-C(15)	2.53(19)
C(12)-C(13)-C(14)-C(16)	-112.78(16)
C(9)-N(2)-C(15)-C(14)	166.86(15)
C(12)-N(2)-C(15)-C(14)	33.24(18)
C(16)-C(14)-C(15)-N(2)	43.0(2)
C(13)-C(14)-C(15)-N(2)	-21.44(18)
C(15)-C(14)-C(16)-C(17)	16.0(3)
C(13)-C(14)-C(16)-C(17)	108.9(2)
C(15)-C(14)-C(16)-C(13)	-92.93(18)
C(12)-C(13)-C(16)-C(17)	-24.5(2)
C(14)-C(13)-C(16)-C(17)	-117.89(19)
C(12)-C(13)-C(16)-C(14)	93.40(17)
C(14)-C(16)-C(17)-C(18)	50.9(3)
C(13)-C(16)-C(17)-C(18)	125.79(19)
C(14)-C(16)-C(17)-C(22)	-133.38(19)
C(13)-C(16)-C(17)-C(22)	-58.5(2)
C(22)-C(17)-C(18)-C(19)	0.2(3)
C(16)-C(17)-C(18)-C(19)	175.92(16)
C(17)-C(18)-C(19)-C(20)	-0.4(3)

C(18)-C(19)-C(20)-C(21)	0.0(3)
C(18)-C(19)-C(20)-C(23)	-178.14(16)
C(19)-C(20)-C(21)-C(22)	0.6(3)
C(23)-C(20)-C(21)-C(22)	178.68(16)
C(20)-C(21)-C(22)-C(17)	-0.7(3)
C(18)-C(17)-C(22)-C(21)	0.3(3)
C(16)-C(17)-C(22)-C(21)	-175.62(16)
C(21)-C(20)-C(23)-C(24)	160.98(17)
C(19)-C(20)-C(23)-C(24)	-21.0(3)
C(21)-C(20)-C(23)-C(28)	-20.9(3)
C(19)-C(20)-C(23)-C(28)	157.15(17)
C(28)-C(23)-C(24)-C(25)	-3.2(3)
C(20)-C(23)-C(24)-C(25)	174.95(17)
C(23)-C(24)-C(25)-C(26)	1.2(3)
C(24)-C(25)-C(26)-C(27)	1.6(3)
C(25)-C(26)-C(27)-C(28)	-2.3(3)
C(26)-C(27)-C(28)-C(23)	0.2(3)
C(24)-C(23)-C(28)-C(27)	2.6(3)
C(20)-C(23)-C(28)-C(27)	-175.63(16)

Symmetry transformations used to generate equivalent atoms:

Hydrogen bonds for 4a [A and °.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(2)	0.85(3)	2.23(2)	2.656(2)	110.8(19)

Symmetry transformations used to generate equivalent atoms:

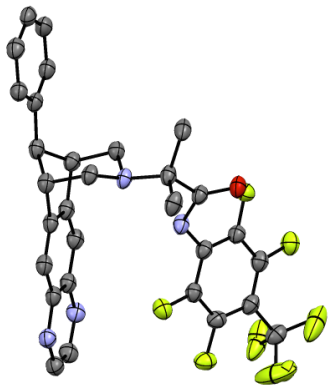


Figure S4. Structure determination of compound **14a.**

White plates of **14a** were grown by vapor diffusion of pentane to a solution of the compound in dichloromethane at 25 °C. A crystal of dimensions 0.24 x 0.19 x 0.10 mm was mounted on a

Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 4 sec. for the low angle images, 20 sec. for high angle. The integration of the data yielded a total of 39629 reflections to a maximum 2θ value of 136.44° of which 4617 were independent and 3752 were greater than $2\sigma(I)$. The final cell constants (Table S12) were based on the xyz centroids 14067 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{30}H_{23}N_4OF_7$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a mixture of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0746 and wR2 = 0.2080 [based on I > 2sigma(I)], R1 = 0.0824 and wR2 = 0.2228 for all data. Additional details are presented below. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S12. Crystal data and structure refinement for **14a**.

Empirical formula	$C_{30}H_{23}F_7N_4O$
Formula weight	588.52
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.9681(9) A α = 90 °.
	b = 16.7751(3) A β = 91.492(6) °.
	c = 11.7778(2) A γ = 90 °.
Volume	2561.29(19) A^3
Z, Calculated density	4, 1.526 Mg/m^3
Absorption coefficient	1.124 mm^{-1}
F(000)	1208
Crystal size	0.24 x 0.19 x 0.10 mm
Theta range for data collection	3.41 to 68.22 °.
Limiting indices	-15<=h<=15, -20<=k<=20, -13<=l<=11
Reflections collected / unique	39629 / 4617 [R(int) = 0.1037]

Completeness to theta = 68.22	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8959 and 0.7743
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4617 / 33 / 413
Goodness-of-fit on F^2	1.117
Final R indices [I>2sigma(I)]	R1 = 0.0746, wR2 = 0.2080
R indices (all data)	R1 = 0.0824, wR2 = 0.2228
Extinction coefficient	0.0053(6)
Largest diff. peak and hole	0.643 and -0.359 e.A^-3

Atomic coordinates (x 10^4) and equivalent isotropic for 14a

displacement parameters (A^2 x 10^3) for **14a**.
U(eq) is defined as one third of the trace of the orthogonalized
Uij tensor.

	x	y	z	U(eq)
O(1)	2829(1)	6427(1)	816(2)	40(1)
F(1)	7847(2)	6340(2)	638(2)	37(1)
F(2)	8262(3)	5163(2)	1185(5)	69(2)
F(3)	8247(3)	5904(4)	2409(4)	112(2)
F(1A)	7874(4)	6397(3)	837(6)	103(2)
F(2A)	8127(3)	5168(2)	971(5)	63(1)
F(3A)	8202(3)	6133(2)	2371(3)	39(1)
F(4)	6033(1)	6112(1)	-108(1)	46(1)
F(5)	4096(1)	5812(1)	305(1)	41(1)
F(6)	5048(1)	4825(1)	3928(1)	42(1)
F(7)	7028(1)	5059(1)	3480(1)	45(1)
N(1)	3474(1)	5244(1)	2475(2)	35(1)
N(2)	1632(1)	4699(1)	2986(2)	32(1)
N(3)	5270(1)	2884(1)	3694(2)	39(1)
N(4)	4464(1)	3121(1)	5881(2)	37(1)
C(1)	7721(2)	5792(1)	1464(2)	42(1)
C(2)	6600(2)	5628(1)	1689(2)	37(1)
C(3)	5821(2)	5817(1)	921(2)	37(1)
C(4)	4794(2)	5677(1)	1141(2)	34(1)
C(5)	4502(2)	5362(1)	2177(2)	33(1)
C(6)	5286(2)	5141(1)	2929(2)	34(1)
C(7)	6314(2)	5272(1)	2692(2)	37(1)
C(8)	2698(2)	5797(1)	2294(2)	34(1)
C(9)	1672(2)	5573(1)	2839(2)	36(1)
C(10)	778(2)	5919(1)	2123(2)	44(1)
C(11)	1719(2)	5991(1)	3999(2)	44(1)
C(12)	1548(2)	4258(1)	1908(2)	33(1)

C(13)	1682(2)	3357(1)	2136(2)	34(1)
C(14)	2555(2)	3239(1)	2996(2)	34(1)
C(15)	3588(2)	3100(1)	2851(2)	36(1)
C(16)	4245(2)	3041(1)	3828(2)	34(1)
C(17)	5840(2)	2839(1)	4633(2)	41(1)
C(18)	5445(2)	2963(1)	5717(2)	39(1)
C(19)	3845(2)	3148(1)	4923(2)	34(1)
C(20)	2768(2)	3286(1)	5052(2)	35(1)
C(21)	2153(2)	3323(1)	4099(2)	33(1)
C(22)	1009(2)	3499(1)	3957(2)	34(1)
C(23)	884(2)	4410(1)	3815(2)	34(1)
C(24)	756(2)	3061(1)	2826(2)	35(1)
C(25)	-316(2)	3172(1)	2297(2)	35(1)
C(26)	-487(2)	3145(1)	1126(2)	38(1)
C(27)	-1476(2)	3217(1)	658(2)	40(1)
C(28)	-2311(2)	3313(1)	1351(2)	41(1)
C(29)	-2158(2)	3327(1)	2506(2)	43(1)
C(30)	-1168(2)	3258(1)	2987(2)	38(1)

Bond lengths [A] and angles [°] for 14a.

O(1)-C(8)	1.212(2)
F(1)-C(1)	1.351(4)
F(2)-C(1)	1.314(4)
F(3)-C(1)	1.303(5)
F(1A)-C(1)	1.273(6)
F(2A)-C(1)	1.315(5)
F(3A)-C(1)	1.350(4)
F(4)-C(3)	1.345(3)
F(5)-C(4)	1.340(3)
F(6)-C(6)	1.334(3)
F(7)-C(7)	1.342(3)
N(1)-C(8)	1.380(3)
N(1)-C(5)	1.402(3)
N(1)-H(1)	0.88(3)
N(2)-C(12)	1.471(3)
N(2)-C(23)	1.476(3)
N(2)-C(9)	1.478(2)
N(3)-C(17)	1.317(3)
N(3)-C(16)	1.368(3)
N(4)-C(18)	1.319(3)
N(4)-C(19)	1.368(3)
C(1)-C(2)	1.511(3)
C(2)-C(3)	1.375(3)
C(2)-C(7)	1.382(3)

C(3)-C(4)	1.383(3)
C(4)-C(5)	1.392(3)
C(5)-C(6)	1.382(3)
C(6)-C(7)	1.388(3)
C(8)-C(9)	1.539(3)
C(9)-C(10)	1.529(3)
C(9)-C(11)	1.536(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.544(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.513(3)
C(13)-C(24)	1.549(3)
C(13)-H(13)	1.0000
C(14)-C(15)	1.375(3)
C(14)-C(21)	1.420(3)
C(15)-C(16)	1.418(3)
C(15)-H(15)	0.9500
C(16)-C(19)	1.414(3)
C(17)-C(18)	1.404(4)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.427(3)
C(20)-C(21)	1.361(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.518(3)
C(22)-C(23)	1.544(3)
C(22)-C(24)	1.549(3)
C(22)-H(22)	1.0000
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.519(3)
C(24)-H(24)	1.0000
C(25)-C(26)	1.392(3)
C(25)-C(30)	1.396(3)
C(26)-C(27)	1.388(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.382(3)
C(27)-H(27)	0.9500
C(28)-C(29)	1.370(4)
C(28)-H(28)	0.9500

C(29)-C(30)	1.394(3)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500
C(8)-N(1)-C(5)	124.14(17)
C(8)-N(1)-H(1)	115.9(17)
C(5)-N(1)-H(1)	119.0(17)
C(12)-N(2)-C(23)	111.71(16)
C(12)-N(2)-C(9)	113.51(17)
C(23)-N(2)-C(9)	115.42(16)
C(17)-N(3)-C(16)	116.1(2)
C(18)-N(4)-C(19)	115.7(2)
F(1A)-C(1)-F(3)	107.2(4)
F(1A)-C(1)-F(2)	113.8(4)
F(3)-C(1)-F(2)	93.3(4)
F(1A)-C(1)-F(2A)	108.0(4)
F(3)-C(1)-F(2A)	106.6(4)
F(2)-C(1)-F(2A)	13.3(4)
F(1A)-C(1)-F(3A)	92.6(4)
F(3)-C(1)-F(3A)	16.9(4)
F(2)-C(1)-F(3A)	107.4(3)
F(2A)-C(1)-F(3A)	120.4(3)
F(1A)-C(1)-F(1)	10.6(4)
F(3)-C(1)-F(1)	116.6(4)
F(2)-C(1)-F(1)	106.9(3)
F(2A)-C(1)-F(1)	99.6(3)
F(3A)-C(1)-F(1)	102.7(2)
F(1A)-C(1)-C(2)	114.4(3)
F(3)-C(1)-C(2)	111.1(3)
F(2)-C(1)-C(2)	114.8(2)
F(2A)-C(1)-C(2)	109.2(2)
F(3A)-C(1)-C(2)	111.4(2)
F(1)-C(1)-C(2)	112.7(2)
C(3)-C(2)-C(7)	116.98(19)
C(3)-C(2)-C(1)	122.4(2)
C(7)-C(2)-C(1)	120.6(2)
F(4)-C(3)-C(2)	120.99(19)
F(4)-C(3)-C(4)	116.8(2)
C(2)-C(3)-C(4)	122.1(2)
F(5)-C(4)-C(3)	118.0(2)
F(5)-C(4)-C(5)	120.96(18)
C(3)-C(4)-C(5)	120.9(2)
C(6)-C(5)-C(4)	116.89(18)
C(6)-C(5)-N(1)	119.3(2)
C(4)-C(5)-N(1)	123.7(2)
F(6)-C(6)-C(5)	119.29(18)
F(6)-C(6)-C(7)	119.1(2)

C(5)-C(6)-C(7)	121.5(2)
F(7)-C(7)-C(2)	120.77(19)
F(7)-C(7)-C(6)	117.8(2)
C(2)-C(7)-C(6)	121.4(2)
O(1)-C(8)-N(1)	123.12(19)
O(1)-C(8)-C(9)	122.69(17)
N(1)-C(8)-C(9)	114.01(17)
N(2)-C(9)-C(10)	114.46(17)
N(2)-C(9)-C(11)	110.44(19)
C(10)-C(9)-C(11)	109.20(18)
N(2)-C(9)-C(8)	108.89(15)
C(10)-C(9)-C(8)	109.18(18)
C(11)-C(9)-C(8)	104.14(17)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(2)-C(12)-C(13)	109.67(17)
N(2)-C(12)-H(12A)	109.7
C(13)-C(12)-H(12A)	109.7
N(2)-C(12)-H(12B)	109.7
C(13)-C(12)-H(12B)	109.7
H(12A)-C(12)-H(12B)	108.2
C(14)-C(13)-C(12)	108.82(16)
C(14)-C(13)-C(24)	100.59(18)
C(12)-C(13)-C(24)	108.61(16)
C(14)-C(13)-H(13)	112.7
C(12)-C(13)-H(13)	112.7
C(24)-C(13)-H(13)	112.7
C(15)-C(14)-C(21)	120.9(2)
C(15)-C(14)-C(13)	130.8(2)
C(21)-C(14)-C(13)	108.26(18)
C(14)-C(15)-C(16)	118.5(2)
C(14)-C(15)-H(15)	120.7
C(16)-C(15)-H(15)	120.7
N(3)-C(16)-C(19)	120.7(2)
N(3)-C(16)-C(15)	119.0(2)
C(19)-C(16)-C(15)	120.32(19)

N(3)-C(17)-C(18)	123.0(2)
N(3)-C(17)-H(17)	118.5
C(18)-C(17)-H(17)	118.5
N(4)-C(18)-C(17)	122.7(2)
N(4)-C(18)-H(18)	118.7
C(17)-C(18)-H(18)	118.7
N(4)-C(19)-C(16)	121.75(19)
N(4)-C(19)-C(20)	118.2(2)
C(16)-C(19)-C(20)	120.0(2)
C(21)-C(20)-C(19)	118.3(2)
C(21)-C(20)-H(20)	120.9
C(19)-C(20)-H(20)	120.9
C(20)-C(21)-C(14)	121.92(19)
C(20)-C(21)-C(22)	130.5(2)
C(14)-C(21)-C(22)	107.46(19)
C(21)-C(22)-C(23)	107.64(16)
C(21)-C(22)-C(24)	100.77(17)
C(23)-C(22)-C(24)	110.88(18)
C(21)-C(22)-H(22)	112.3
C(23)-C(22)-H(22)	112.3
C(24)-C(22)-H(22)	112.3
N(2)-C(23)-C(22)	109.16(16)
N(2)-C(23)-H(23A)	109.8
C(22)-C(23)-H(23A)	109.8
N(2)-C(23)-H(23B)	109.8
C(22)-C(23)-H(23B)	109.8
H(23A)-C(23)-H(23B)	108.3
C(25)-C(24)-C(13)	117.31(19)
C(25)-C(24)-C(22)	117.74(17)
C(13)-C(24)-C(22)	98.64(16)
C(25)-C(24)-H(24)	107.5
C(13)-C(24)-H(24)	107.5
C(22)-C(24)-H(24)	107.5
C(26)-C(25)-C(30)	118.1(2)
C(26)-C(25)-C(24)	121.5(2)
C(30)-C(25)-C(24)	120.2(2)
C(27)-C(26)-C(25)	120.8(2)
C(27)-C(26)-H(26)	119.6
C(25)-C(26)-H(26)	119.6
C(28)-C(27)-C(26)	120.4(2)
C(28)-C(27)-H(27)	119.8
C(26)-C(27)-H(27)	119.8
C(29)-C(28)-C(27)	119.5(2)
C(29)-C(28)-H(28)	120.2
C(27)-C(28)-H(28)	120.2
C(28)-C(29)-C(30)	120.7(2)

C(28)-C(29)-H(29)	119.7
C(30)-C(29)-H(29)	119.7
C(29)-C(30)-C(25)	120.4(2)
C(29)-C(30)-H(30)	119.8
C(25)-C(30)-H(30)	119.8

Symmetry transformations used to generate equivalent atoms for 14a:

Anisotropic displacement parameters (A^2 x 10^3) for 14a.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

	U11	U22	U33	U23	U13	U12
O(1)	38(1)	27(1)	56(1)	4(1)	9(1)	-1(1)
F(1)	37(1)	45(2)	29(1)	11(1)	7(1)	-15(1)
F(2)	38(2)	30(2)	141(4)	-10(2)	17(2)	-1(1)
F(3)	37(2)	225(5)	73(3)	-18(3)	1(2)	-33(3)
F(1A)	51(2)	41(2)	219(7)	-3(3)	26(3)	-9(2)
F(2A)	48(2)	39(2)	104(3)	-4(2)	49(2)	4(2)
F(3A)	33(2)	37(1)	47(2)	-4(1)	7(1)	-9(1)
F(4)	46(1)	45(1)	47(1)	5(1)	13(1)	-5(1)
F(5)	38(1)	40(1)	44(1)	3(1)	-4(1)	3(1)
F(6)	44(1)	41(1)	43(1)	5(1)	5(1)	2(1)
F(7)	36(1)	47(1)	52(1)	-3(1)	-8(1)	7(1)
N(1)	28(1)	27(1)	51(1)	4(1)	8(1)	0(1)
N(2)	31(1)	23(1)	42(1)	-2(1)	9(1)	-1(1)
N(3)	35(1)	35(1)	48(1)	1(1)	5(1)	4(1)
N(4)	35(1)	30(1)	44(1)	3(1)	2(1)	0(1)
C(1)	33(1)	44(1)	50(1)	-7(1)	6(1)	0(1)
C(2)	31(1)	32(1)	47(1)	-5(1)	6(1)	-2(1)
C(3)	37(1)	32(1)	43(1)	-1(1)	9(1)	-1(1)
C(4)	31(1)	30(1)	42(1)	0(1)	3(1)	0(1)
C(5)	28(1)	29(1)	43(1)	-2(1)	5(1)	-1(1)
C(6)	34(1)	29(1)	40(1)	0(1)	5(1)	1(1)
C(7)	31(1)	33(1)	47(1)	-5(1)	-3(1)	5(1)
C(8)	30(1)	25(1)	45(1)	-1(1)	4(1)	-1(1)
C(9)	32(1)	24(1)	52(1)	1(1)	6(1)	1(1)
C(10)	32(1)	30(1)	69(2)	8(1)	8(1)	0(1)
C(11)	45(1)	31(1)	56(2)	-8(1)	15(1)	-4(1)
C(12)	31(1)	29(1)	38(1)	2(1)	6(1)	-1(1)
C(13)	34(1)	28(1)	41(1)	-3(1)	4(1)	0(1)
C(14)	33(1)	24(1)	45(1)	-2(1)	8(1)	2(1)

C(15)	36(1)	29(1)	44(1)	-2(1)	6(1)	2(1)
C(16)	33(1)	25(1)	43(1)	-1(1)	6(1)	2(1)
C(17)	36(1)	36(1)	51(1)	3(1)	3(1)	4(1)
C(18)	38(1)	33(1)	45(1)	4(1)	1(1)	1(1)
C(19)	36(1)	24(1)	44(1)	2(1)	6(1)	0(1)
C(20)	34(1)	28(1)	44(1)	1(1)	10(1)	0(1)
C(21)	32(1)	24(1)	43(1)	2(1)	8(1)	1(1)
C(22)	33(1)	29(1)	41(1)	1(1)	8(1)	-1(1)
C(23)	30(1)	30(1)	42(1)	-2(1)	10(1)	-1(1)
C(24)	37(1)	24(1)	44(1)	0(1)	6(1)	1(1)
C(25)	36(1)	24(1)	44(1)	-1(1)	3(1)	-4(1)
C(26)	38(1)	28(1)	49(1)	2(1)	6(1)	-3(1)
C(27)	46(1)	30(1)	44(1)	1(1)	-2(1)	-5(1)
C(28)	39(1)	25(1)	58(2)	3(1)	-4(1)	-4(1)
C(29)	37(1)	33(1)	59(2)	4(1)	6(1)	1(1)
C(30)	37(1)	32(1)	44(1)	4(1)	3(1)	-2(1)

Hydrogen coordinates (x 10^4) and isotropic for 14a

displacement parameters (A^2 x 10^3) for 14a.

	x	y	z	U(eq)
H(1)	3320(20)	4839(16)	2910(20)	41(7)
H(10A)	800	5706	1350	65
H(10B)	839	6501	2099	65
H(10C)	122	5773	2462	65
H(11A)	1043	5958	4350	65
H(11B)	1906	6552	3897	65
H(11C)	2238	5731	4491	65
H(12A)	2085	4444	1388	39
H(12B)	864	4358	1541	39
H(13)	1777	3043	1424	41
H(15)	3856	3045	2112	43
H(17)	6552	2716	4575	49
H(18)	5902	2933	6359	47
H(20)	2488	3351	5784	42
H(22)	603	3286	4601	41
H(23A)	174	4535	3545	41
H(23B)	1007	4677	4555	41
H(24)	856	2478	2965	42
H(26)	81	3077	641	46
H(27)	-1579	3201	-143	48
H(28)	-2986	3368	1029	49
H(29)	-2731	3386	2984	51
H(30)	-1073	3269	3789	45

Torsion angles [°] for 14a.

F(1A)-C(1)-C(2)-C(3)	30.3(4)
F(3)-C(1)-C(2)-C(3)	151.8(4)
F(2)-C(1)-C(2)-C(3)	-103.9(4)
F(2A)-C(1)-C(2)-C(3)	-90.9(4)
F(3A)-C(1)-C(2)-C(3)	133.7(3)
F(1)-C(1)-C(2)-C(3)	18.8(3)
F(1A)-C(1)-C(2)-C(7)	-149.9(4)
F(3)-C(1)-C(2)-C(7)	-28.4(4)
F(2)-C(1)-C(2)-C(7)	75.9(4)
F(2A)-C(1)-C(2)-C(7)	88.9(4)
F(3A)-C(1)-C(2)-C(7)	-46.5(3)
F(1)-C(1)-C(2)-C(7)	-161.4(2)
C(7)-C(2)-C(3)-F(4)	-175.20(18)
C(1)-C(2)-C(3)-F(4)	4.6(3)
C(7)-C(2)-C(3)-C(4)	1.3(3)
C(1)-C(2)-C(3)-C(4)	-178.87(19)
F(4)-C(3)-C(4)-F(5)	2.7(3)
C(2)-C(3)-C(4)-F(5)	-173.94(19)
F(4)-C(3)-C(4)-C(5)	179.06(18)
C(2)-C(3)-C(4)-C(5)	2.4(3)
F(5)-C(4)-C(5)-C(6)	171.32(18)
C(3)-C(4)-C(5)-C(6)	-4.9(3)
F(5)-C(4)-C(5)-N(1)	-7.1(3)
C(3)-C(4)-C(5)-N(1)	176.60(19)
C(8)-N(1)-C(5)-C(6)	136.8(2)
C(8)-N(1)-C(5)-C(4)	-44.8(3)
C(4)-C(5)-C(6)-F(6)	-179.05(18)
N(1)-C(5)-C(6)-F(6)	-0.5(3)
C(4)-C(5)-C(6)-C(7)	3.9(3)
N(1)-C(5)-C(6)-C(7)	-177.55(18)
C(3)-C(2)-C(7)-F(7)	179.13(19)
C(1)-C(2)-C(7)-F(7)	-0.7(3)
C(3)-C(2)-C(7)-C(6)	-2.3(3)
C(1)-C(2)-C(7)-C(6)	177.83(19)
F(6)-C(6)-C(7)-F(7)	1.2(3)
C(5)-C(6)-C(7)-F(7)	178.26(18)
F(6)-C(6)-C(7)-C(2)	-177.35(19)
C(5)-C(6)-C(7)-C(2)	-0.3(3)
C(5)-N(1)-C(8)-O(1)	3.0(4)
C(5)-N(1)-C(8)-C(9)	-172.2(2)
C(12)-N(2)-C(9)-C(10)	54.2(2)
C(23)-N(2)-C(9)-C(10)	-76.6(2)

C(12)-N(2)-C(9)-C(11)	177.89(17)
C(23)-N(2)-C(9)-C(11)	47.1(2)
C(12)-N(2)-C(9)-C(8)	-68.3(2)
C(23)-N(2)-C(9)-C(8)	160.87(18)
O(1)-C(8)-C(9)-N(2)	160.6(2)
N(1)-C(8)-C(9)-N(2)	-24.1(3)
O(1)-C(8)-C(9)-C(10)	35.0(3)
N(1)-C(8)-C(9)-C(10)	-149.75(19)
O(1)-C(8)-C(9)-C(11)	-81.5(3)
N(1)-C(8)-C(9)-C(11)	93.7(2)
C(23)-N(2)-C(12)-C(13)	-56.1(2)
C(9)-N(2)-C(12)-C(13)	171.29(16)
N(2)-C(12)-C(13)-C(14)	-42.3(2)
N(2)-C(12)-C(13)-C(24)	66.3(2)
C(12)-C(13)-C(14)-C(15)	-93.2(3)
C(24)-C(13)-C(14)-C(15)	152.8(2)
C(12)-C(13)-C(14)-C(21)	84.8(2)
C(24)-C(13)-C(14)-C(21)	-29.22(19)
C(21)-C(14)-C(15)-C(16)	0.1(3)
C(13)-C(14)-C(15)-C(16)	177.79(19)
C(17)-N(3)-C(16)-C(19)	0.2(3)
C(17)-N(3)-C(16)-C(15)	179.82(19)
C(14)-C(15)-C(16)-N(3)	178.51(18)
C(14)-C(15)-C(16)-C(19)	-1.9(3)
C(16)-N(3)-C(17)-C(18)	-1.8(3)
C(19)-N(4)-C(18)-C(17)	0.6(3)
N(3)-C(17)-C(18)-N(4)	1.4(3)
C(18)-N(4)-C(19)-C(16)	-2.2(3)
C(18)-N(4)-C(19)-C(20)	177.71(18)
N(3)-C(16)-C(19)-N(4)	1.8(3)
C(15)-C(16)-C(19)-N(4)	-177.79(18)
N(3)-C(16)-C(19)-C(20)	-178.05(18)
C(15)-C(16)-C(19)-C(20)	2.3(3)
N(4)-C(19)-C(20)-C(21)	179.18(17)
C(16)-C(19)-C(20)-C(21)	-0.9(3)
C(19)-C(20)-C(21)-C(14)	-0.9(3)
C(19)-C(20)-C(21)-C(22)	-176.71(18)
C(15)-C(14)-C(21)-C(20)	1.3(3)
C(13)-C(14)-C(21)-C(20)	-176.83(17)
C(15)-C(14)-C(21)-C(22)	178.02(18)
C(13)-C(14)-C(21)-C(22)	-0.2(2)
C(20)-C(21)-C(22)-C(23)	89.6(3)
C(14)-C(21)-C(22)-C(23)	-86.7(2)
C(20)-C(21)-C(22)-C(24)	-154.2(2)
C(14)-C(21)-C(22)-C(24)	29.49(19)
C(12)-N(2)-C(23)-C(22)	53.7(2)

C(9)-N(2)-C(23)-C(22)	-174.64(18)
C(21)-C(22)-C(23)-N(2)	46.4(2)
C(24)-C(22)-C(23)-N(2)	-62.9(2)
C(14)-C(13)-C(24)-C(25)	173.08(17)
C(12)-C(13)-C(24)-C(25)	58.9(2)
C(14)-C(13)-C(24)-C(22)	45.61(17)
C(12)-C(13)-C(24)-C(22)	-68.6(2)
C(21)-C(22)-C(24)-C(25)	-172.99(17)
C(23)-C(22)-C(24)-C(25)	-59.2(2)
C(21)-C(22)-C(24)-C(13)	-45.82(18)
C(23)-C(22)-C(24)-C(13)	67.93(19)
C(13)-C(24)-C(25)-C(26)	31.8(3)
C(22)-C(24)-C(25)-C(26)	149.32(19)
C(13)-C(24)-C(25)-C(30)	-151.96(19)
C(22)-C(24)-C(25)-C(30)	-34.4(3)
C(30)-C(25)-C(26)-C(27)	1.2(3)
C(24)-C(25)-C(26)-C(27)	177.54(18)
C(25)-C(26)-C(27)-C(28)	-0.3(3)
C(26)-C(27)-C(28)-C(29)	-0.7(3)
C(27)-C(28)-C(29)-C(30)	0.9(3)
C(28)-C(29)-C(30)-C(25)	0.0(3)
C(26)-C(25)-C(30)-C(29)	-1.0(3)
C(24)-C(25)-C(30)-C(29)	-177.43(18)

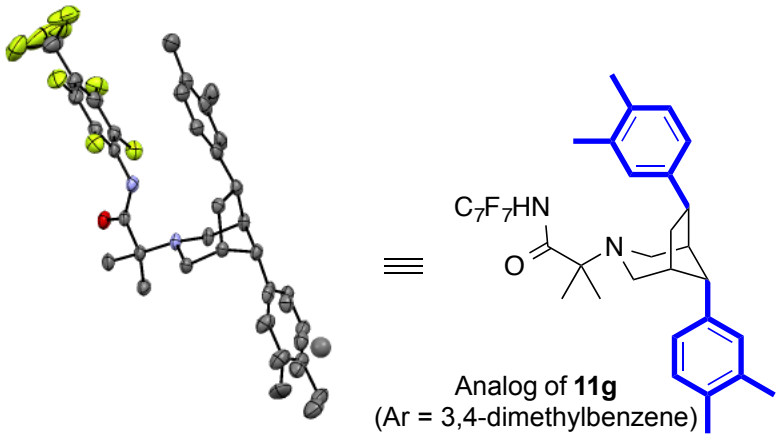


Figure S5. Structure determination of an analogous compound of **11g.**

Colorless plates of **analog of 11g** (Aryl group is 3,4-dimethylbenzene instead of phenyl) were grown from a hexane solution of the compound at 25 °C. A crystal of dimensions 0.18 x 0.12 x 0.06 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray

intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 23406 reflections to a maximum 2θ value of 136.48° of which 5416 were independent and 4654 were greater than 2σ(I). The final cell constants (Table S13) were based on the xyz centroids 12821 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P1bar with Z = 2 for the formula $C_{34}H_{35}N_2OF_7$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0730 and wR2 = 0.1995 [based on I > 2sigma(I)], R1 = 0.0792 and wR2 = 0.2074 for all data. Additional details are presented below. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S13. Crystal data and structure refinement for analog of **11g**.

Empirical formula	$C_{34}H_{35}F_7N_2O$
Formula weight	620.64
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.1197(2) A α = 69.520(5) °. b = 12.3985(2) A β = 85.664(6) °. c = 14.3863(10) A γ = 86.069(6) °.
Volume	1517.95(12) A^3
Z, Calculated density	2, 1.358 Mg/m^3
Absorption coefficient	0.951 mm^{-1}
F(000)	648
Crystal size	0.180 x 0.120 x 0.060 mm
Theta range for data collection	3.284 to 68.240 °.
Limiting indices	-10<=h<=10, -14<=k<=14, -15<=l<=16
Reflections collected / unique	23406 / 5416 [R(int) = 0.0602]
Completeness to theta =	67.679 98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.944 and 0.729
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5416 / 492 / 501

Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0730, wR2 = 0.1995
R indices (all data)	R1 = 0.0792, wR2 = 0.2074
Extinction coefficient	0.0123(9)
Largest diff. peak and hole	0.865 and -0.491 $e.A^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for analog of 11g. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	4234(1)	2157(1)	4480(1)	33(1)
N(1)	6027(2)	1797(1)	5577(1)	30(1)
N(2)	8151(2)	2209(1)	4159(1)	27(1)
C(2)	3214(2)	1112(2)	8167(2)	44(1)
C(3)	4367(2)	359(2)	8085(2)	42(1)
C(4)	5287(2)	600(2)	7243(2)	34(1)
C(5)	5101(2)	1604(2)	6432(1)	29(1)
C(6)	3973(2)	2377(2)	6518(2)	32(1)
C(7)	3041(2)	2133(2)	7372(2)	40(1)
C(8)	5530(2)	1997(1)	4653(1)	27(1)
C(9)	6756(2)	1859(2)	3904(1)	28(1)
C(10)	6309(2)	2509(2)	2844(2)	35(1)
C(11)	6828(2)	561(2)	4084(2)	33(1)
C(12)	8205(2)	3464(2)	3904(2)	31(1)
C(13)	9614(2)	3791(2)	4244(2)	31(1)
C(14)	9957(2)	3083(2)	5330(1)	28(1)
C(15)	10628(2)	1920(2)	5273(1)	28(1)
C(16)	10846(2)	2110(2)	4155(1)	29(1)
C(17)	9505(2)	1730(2)	3794(1)	30(1)
C(18)	8781(2)	3003(2)	6157(2)	33(1)
C(19)	7738(2)	3888(2)	6106(2)	39(1)
C(20)	6743(2)	3852(2)	6925(2)	42(1)
C(21)	6831(2)	2913(2)	7808(2)	44(1)
C(22)	7836(2)	2034(2)	7858(2)	45(1)
C(23)	8801(2)	2064(2)	7053(2)	39(1)
C(24)	5674(2)	4843(2)	6836(2)	49(1)
C(25)	5838(3)	2886(2)	8712(2)	54(1)
C(26)	10972(2)	3419(2)	3698(1)	31(1)
C(27)	11049(4)	4050(3)	2592(3)	28(1)
C(28)	11866(4)	3507(3)	1995(3)	35(1)
C(29)	12177(4)	4057(4)	981(3)	41(1)
C(30)	11683(4)	5192(4)	536(3)	42(1)
C(31)	10853(4)	5725(3)	1115(3)	39(1)

C(32) 10548(4) 5173(3) 2120(3) 31(1)
C(33) 13082(5) 3419(5) 405(3) 67(1)
C(34) 12009(5) 5843(5) -548(3) 62(1)
C(26A) 10972(2) 3419(2) 3698(1) 31(1)
C(27A) 11346(5) 3799(4) 2556(4) 28(1)
C(28A) 12180(6) 3123(5) 2093(4) 36(1)
C(29A) 12577(6) 3586(5) 1092(5) 43(1)
C(30A) 12133(6) 4705(5) 501(4) 40(1)
C(31A) 11299(6) 5373(5) 939(5) 40(1)
C(33A) 10773(8) 6595(6) 380(5) 56(2)
C(32A) 10908(6) 4899(4) 1979(4) 34(1)
C(34A) 12609(8) 5200(7) -596(5) 59(2)
C(1) 2232(3) 797(3) 9105(2) 64(1)
F(1) 1837(5) -346(4) 9332(4) 101(2)
F(2) 977(4) 1270(6) 9079(3) 114(2)
F(3) 2910(5) 796(5) 9866(3) 104(1)
C(1A) 2232(3) 797(3) 9105(2) 64(1)
F(1A) 1359(4) -7(4) 9179(3) 91(1)
F(2A) 1281(4) 1729(4) 9073(3) 77(1)
F(3A) 2979(4) 510(4) 9900(2) 75(1)
F(4) 2006(1) 2935(1) 7402(1) 56(1)
F(5) 3782(1) 3394(1) 5794(1) 39(1)
F(6) 6369(1) -170(1) 7194(1) 43(1)
F(7) 4594(2) -649(1) 8828(1) 57(1)

Bond lengths [A] and angles [°] for analog 11g.

O(1)-C(8) 1.215(2)
N(1)-C(8) 1.371(2)
N(1)-C(5) 1.395(2)
N(1)-H(1A) 0.8800
N(2)-C(12) 1.472(2)
N(2)-C(17) 1.474(2)
N(2)-C(9) 1.483(2)
C(2)-C(3) 1.384(3)
C(2)-C(7) 1.386(3)
C(2)-C(1A) 1.508(3)
C(2)-C(1) 1.508(3)
C(3)-F(7) 1.345(2)
C(3)-C(4) 1.374(3)
C(4)-F(6) 1.341(2)
C(4)-C(5) 1.388(3)
C(5)-C(6) 1.386(3)
C(6)-F(5) 1.335(2)
C(6)-C(7) 1.393(3)

C(7)-F(4) 1.333(3)
C(8)-C(9) 1.537(3)
C(9)-C(10) 1.526(3)
C(9)-C(11) 1.536(3)
C(10)-H(10A) 0.9800
C(10)-H(10B) 0.9800
C(10)-H(10C) 0.9800
C(11)-H(11A) 0.9800
C(11)-H(11B) 0.9800
C(11)-H(11C) 0.9800
C(12)-C(13) 1.536(3)
C(12)-H(12A) 0.9900
C(12)-H(12B) 0.9900
C(13)-C(14) 1.544(3)
C(13)-C(26A) 1.547(3)
C(13)-C(26) 1.547(3)
C(13)-H(13) 1.0000
C(14)-C(18) 1.522(3)
C(14)-C(15) 1.555(3)
C(14)-H(14) 1.0000
C(15)-C(16) 1.540(3)
C(15)-H(15A) 0.9900
C(15)-H(15B) 0.9900
C(16)-C(17) 1.527(3)
C(16)-C(26A) 1.531(3)
C(16)-C(26) 1.531(3)
C(16)-H(16) 1.0000
C(17)-H(17A) 0.9900
C(17)-H(17B) 0.9900
C(18)-C(19) 1.387(3)
C(18)-C(23) 1.402(3)
C(19)-C(20) 1.422(3)
C(19)-H(19) 0.9500
C(20)-C(21) 1.393(3)
C(20)-C(24) 1.491(3)
C(21)-C(22) 1.361(3)
C(21)-C(25) 1.520(3)
C(22)-C(23) 1.392(3)
C(22)-H(22) 0.9500
C(23)-H(23) 0.9500
C(24)-H(24A) 0.9800
C(24)-H(24B) 0.9800
C(24)-H(24C) 0.9800
C(25)-H(25A) 0.9800
C(25)-H(25B) 0.9800
C(25)-H(25C) 0.9800

C(26)-C(27) 1.507(4)
C(26)-H(26) 1.0000
C(27)-C(32) 1.381(5)
C(27)-C(28) 1.408(5)
C(28)-C(29) 1.393(5)
C(28)-H(28) 0.9500
C(29)-C(30) 1.385(6)
C(29)-C(33) 1.504(6)
C(30)-C(31) 1.388(6)
C(30)-C(34) 1.501(5)
C(31)-C(32) 1.383(5)
C(31)-H(31) 0.9500
C(32)-H(32) 0.9500
C(33)-H(33D) 0.9800
C(33)-H(33E) 0.9800
C(33)-H(33F) 0.9800
C(34)-H(34A) 0.9800
C(34)-H(34B) 0.9800
C(34)-H(34C) 0.9800
C(26A)-C(27A) 1.560(6)
C(26A)-H(26A) 1.0000
C(27A)-C(32A) 1.375(7)
C(27A)-C(28A) 1.397(8)
C(28A)-C(29A) 1.380(8)
C(28A)-H(28A) 0.9500
C(29A)-C(30A) 1.400(8)
C(29A)-H(29A) 0.9500
C(30A)-C(31A) 1.367(9)
C(30A)-C(34A) 1.521(9)
C(31A)-C(32A) 1.429(9)
C(31A)-C(33A) 1.510(8)
C(33A)-H(33A) 0.9800
C(33A)-H(33B) 0.9800
C(33A)-H(33C) 0.9800
C(32A)-H(32A) 0.9500
C(34A)-H(34D) 0.9800
C(34A)-H(34E) 0.9800
C(34A)-H(34F) 0.9800
C(1)-F(2) 1.247(5)
C(1)-F(3) 1.297(5)
C(1)-F(1) 1.404(6)
C(1A)-F(1A) 1.288(5)
C(1A)-F(3A) 1.303(4)
C(1A)-F(2A) 1.386(5)
C(8)-N(1)-C(5) 123.55(15)
C(8)-N(1)-H(1A) 118.2

C(5)-N(1)-H(1A) 118.2
C(12)-N(2)-C(17) 111.21(13)
C(12)-N(2)-C(9) 112.94(13)
C(17)-N(2)-C(9) 115.30(15)
C(3)-C(2)-C(7) 117.33(19)
C(3)-C(2)-C(1A) 119.1(2)
C(7)-C(2)-C(1A) 123.5(2)
C(3)-C(2)-C(1) 119.1(2)
C(7)-C(2)-C(1) 123.5(2)
F(7)-C(3)-C(4) 118.1(2)
F(7)-C(3)-C(2) 120.38(19)
C(4)-C(3)-C(2) 121.47(19)
F(6)-C(4)-C(3) 119.09(17)
F(6)-C(4)-C(5) 119.11(17)
C(3)-C(4)-C(5) 121.77(19)
C(6)-C(5)-C(4) 117.07(17)
C(6)-C(5)-N(1) 122.97(16)
C(4)-C(5)-N(1) 119.96(17)
F(5)-C(6)-C(5) 120.57(17)
F(5)-C(6)-C(7) 118.29(17)
C(5)-C(6)-C(7) 121.11(17)
F(4)-C(7)-C(2) 121.63(19)
F(4)-C(7)-C(6) 117.14(18)
C(2)-C(7)-C(6) 121.20(19)
O(1)-C(8)-N(1) 122.87(17)
O(1)-C(8)-C(9) 123.90(17)
N(1)-C(8)-C(9) 112.88(15)
N(2)-C(9)-C(10) 114.97(14)
N(2)-C(9)-C(11) 110.53(14)
C(10)-C(9)-C(11) 108.76(16)
N(2)-C(9)-C(8) 108.20(15)
C(10)-C(9)-C(8) 110.17(15)
C(11)-C(9)-C(8) 103.60(14)
C(9)-C(10)-H(10A) 109.5
C(9)-C(10)-H(10B) 109.5
H(10A)-C(10)-H(10B) 109.5
C(9)-C(10)-H(10C) 109.5
H(10A)-C(10)-H(10C) 109.5
H(10B)-C(10)-H(10C) 109.5
C(9)-C(11)-H(11A) 109.5
C(9)-C(11)-H(11B) 109.5
H(11A)-C(11)-H(11B) 109.5
C(9)-C(11)-H(11C) 109.5
H(11A)-C(11)-H(11C) 109.5
H(11B)-C(11)-H(11C) 109.5
N(2)-C(12)-C(13) 111.62(14)

N(2)-C(12)-H(12A) 109.3
C(13)-C(12)-H(12A) 109.3
N(2)-C(12)-H(12B) 109.3
C(13)-C(12)-H(12B) 109.3
H(12A)-C(12)-H(12B) 108.0
C(12)-C(13)-C(14) 114.35(14)
C(12)-C(13)-C(26A) 109.49(16)
C(14)-C(13)-C(26A) 99.70(14)
C(12)-C(13)-C(26) 109.49(16)
C(14)-C(13)-C(26) 99.70(14)
C(12)-C(13)-H(13) 110.9
C(14)-C(13)-H(13) 110.9
C(26)-C(13)-H(13) 110.9
C(18)-C(14)-C(13) 119.42(15)
C(18)-C(14)-C(15) 116.22(14)
C(13)-C(14)-C(15) 103.70(15)
C(18)-C(14)-H(14) 105.4
C(13)-C(14)-H(14) 105.4
C(15)-C(14)-H(14) 105.4
C(16)-C(15)-C(14) 105.29(14)
C(16)-C(15)-H(15A) 110.7
C(14)-C(15)-H(15A) 110.7
C(16)-C(15)-H(15B) 110.7
C(14)-C(15)-H(15B) 110.7
H(15A)-C(15)-H(15B) 108.8
C(17)-C(16)-C(26A) 110.88(15)
C(17)-C(16)-C(26) 110.88(15)
C(17)-C(16)-C(15) 110.31(14)
C(26A)-C(16)-C(15) 102.15(15)
C(26)-C(16)-C(15) 102.15(15)
C(17)-C(16)-H(16) 111.1
C(26)-C(16)-H(16) 111.1
C(15)-C(16)-H(16) 111.1
N(2)-C(17)-C(16) 109.58(15)
N(2)-C(17)-H(17A) 109.8
C(16)-C(17)-H(17A) 109.8
N(2)-C(17)-H(17B) 109.8
C(16)-C(17)-H(17B) 109.8
H(17A)-C(17)-H(17B) 108.2
C(19)-C(18)-C(23) 116.92(18)
C(19)-C(18)-C(14) 122.30(17)
C(23)-C(18)-C(14) 120.50(17)
C(18)-C(19)-C(20) 121.64(19)
C(18)-C(19)-H(19) 119.2
C(20)-C(19)-H(19) 119.2
C(21)-C(20)-C(19) 119.27(19)

C(21)-C(20)-C(24) 121.4(2)
C(19)-C(20)-C(24) 119.3(2)
C(22)-C(21)-C(20) 119.4(2)
C(22)-C(21)-C(25) 120.3(2)
C(20)-C(21)-C(25) 120.3(2)
C(21)-C(22)-C(23) 121.3(2)
C(21)-C(22)-H(22) 119.3
C(23)-C(22)-H(22) 119.3
C(22)-C(23)-C(18) 121.4(2)
C(22)-C(23)-H(23) 119.3
C(18)-C(23)-H(23) 119.3
C(20)-C(24)-H(24A) 109.5
C(20)-C(24)-H(24B) 109.5
H(24A)-C(24)-H(24B) 109.5
C(20)-C(24)-H(24C) 109.5
H(24A)-C(24)-H(24C) 109.5
H(24B)-C(24)-H(24C) 109.5
C(21)-C(25)-H(25A) 109.5
C(21)-C(25)-H(25B) 109.5
H(25A)-C(25)-H(25B) 109.5
C(21)-C(25)-H(25C) 109.5
H(25A)-C(25)-H(25C) 109.5
H(25B)-C(25)-H(25C) 109.5
C(27)-C(26)-C(16) 122.4(2)
C(27)-C(26)-C(13) 113.52(19)
C(16)-C(26)-C(13) 98.80(14)
C(27)-C(26)-H(26) 107.0
C(16)-C(26)-H(26) 107.0
C(13)-C(26)-H(26) 107.0
C(32)-C(27)-C(28) 116.6(3)
C(32)-C(27)-C(26) 125.5(3)
C(28)-C(27)-C(26) 117.3(3)
C(29)-C(28)-C(27) 122.8(3)
C(29)-C(28)-H(28) 118.6
C(27)-C(28)-H(28) 118.6
C(30)-C(29)-C(28) 119.1(4)
C(30)-C(29)-C(33) 121.6(4)
C(28)-C(29)-C(33) 119.2(4)
C(29)-C(30)-C(31) 118.4(3)
C(29)-C(30)-C(34) 121.8(4)
C(31)-C(30)-C(34) 119.8(4)
C(32)-C(31)-C(30) 122.1(4)
C(32)-C(31)-H(31) 118.9
C(30)-C(31)-H(31) 118.9
C(27)-C(32)-C(31) 120.9(4)
C(27)-C(32)-H(32) 119.5

C(31)-C(32)-H(32) 119.5
C(29)-C(33)-H(33D) 109.5
C(29)-C(33)-H(33E) 109.5
H(33D)-C(33)-H(33E) 109.5
C(29)-C(33)-H(33F) 109.5
H(33D)-C(33)-H(33F) 109.5
H(33E)-C(33)-H(33F) 109.5
C(30)-C(34)-H(34A) 109.5
C(30)-C(34)-H(34B) 109.5
H(34A)-C(34)-H(34B) 109.5
C(30)-C(34)-H(34C) 109.5
H(34A)-C(34)-H(34C) 109.5
H(34B)-C(34)-H(34C) 109.5
C(16)-C(26A)-C(13) 98.80(14)
C(16)-C(26A)-C(27A) 110.9(3)
C(13)-C(26A)-C(27A) 128.0(2)
C(16)-C(26A)-H(26A) 105.7
C(13)-C(26A)-H(26A) 105.7
C(27A)-C(26A)-H(26A) 105.7
C(32A)-C(27A)-C(28A) 118.0(5)
C(32A)-C(27A)-C(26A) 117.7(5)
C(28A)-C(27A)-C(26A) 124.2(4)
C(29A)-C(28A)-C(27A) 119.6(5)
C(29A)-C(28A)-H(28A) 120.2
C(27A)-C(28A)-H(28A) 120.2
C(28A)-C(29A)-C(30A) 122.6(6)
C(28A)-C(29A)-H(29A) 118.7
C(30A)-C(29A)-H(29A) 118.7
C(31A)-C(30A)-C(29A) 118.6(5)
C(31A)-C(30A)-C(34A) 119.9(6)
C(29A)-C(30A)-C(34A) 121.5(6)
C(30A)-C(31A)-C(32A) 118.7(5)
C(30A)-C(31A)-C(33A) 123.2(6)
C(32A)-C(31A)-C(33A) 118.1(6)
C(31A)-C(33A)-H(33A) 109.5
C(31A)-C(33A)-H(33B) 109.5
H(33A)-C(33A)-H(33B) 109.5
C(31A)-C(33A)-H(33C) 109.5
H(33A)-C(33A)-H(33C) 109.5
H(33B)-C(33A)-H(33C) 109.5
C(27A)-C(32A)-C(31A) 122.5(6)
C(27A)-C(32A)-H(32A) 118.8
C(31A)-C(32A)-H(32A) 118.8
C(30A)-C(34A)-H(34D) 109.5
C(30A)-C(34A)-H(34E) 109.5
H(34D)-C(34A)-H(34E) 109.5

C(30A)-C(34A)-H(34F) 109.5
H(34D)-C(34A)-H(34F) 109.5
H(34E)-C(34A)-H(34F) 109.5
F(2)-C(1)-F(3) 111.7(4)
F(2)-C(1)-F(1) 99.0(4)
F(3)-C(1)-F(1) 105.3(4)
F(2)-C(1)-C(2) 118.9(3)
F(3)-C(1)-C(2) 112.4(3)
F(1)-C(1)-C(2) 107.7(3)
F(1A)-C(1A)-F(3A) 109.8(3)
F(1A)-C(1A)-F(2A) 103.4(3)
F(3A)-C(1A)-F(2A) 109.0(3)
F(1A)-C(1A)-C(2) 112.9(3)
F(3A)-C(1A)-C(2) 112.3(3)
F(2A)-C(1A)-C(2) 109.0(3)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (A^2 x 103) for analog of 11g.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [\ h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12\ ]$

U11 U22 U33 U23 U13 U12

O(1) 21(1) 38(1) 38(1) -7(1) -5(1) -8(1)
N(1) 19(1) 35(1) 34(1) -9(1) -3(1) -8(1)
N(2) 20(1) 26(1) 34(1) -7(1) -3(1) -8(1)
C(2) 33(1) 65(1) 36(1) -17(1) 1(1) -17(1)
C(3) 42(1) 47(1) 32(1) -6(1) -5(1) -17(1)
C(4) 32(1) 34(1) 35(1) -9(1) -7(1) -7(1)
C(5) 22(1) 32(1) 33(1) -10(1) -4(1) -9(1)
C(6) 25(1) 35(1) 36(1) -10(1) -5(1) -6(1)
C(7) 23(1) 62(1) 42(1) -25(1) -2(1) -5(1)
C(8) 23(1) 25(1) 30(1) -5(1) -3(1) -9(1)
C(9) 22(1) 29(1) 32(1) -7(1) -3(1) -9(1)
C(10) 29(1) 41(1) 32(1) -8(1) -4(1) -12(1)
C(11) 29(1) 31(1) 38(1) -11(1) -2(1) -11(1)
C(12) 22(1) 27(1) 40(1) -7(1) -5(1) -7(1)
C(13) 22(1) 27(1) 40(1) -8(1) -4(1) -7(1)
C(14) 20(1) 31(1) 36(1) -13(1) -2(1) -6(1)
C(15) 21(1) 31(1) 32(1) -9(1) -3(1) -2(1)
C(16) 21(1) 36(1) 33(1) -13(1) 0(1) -6(1)
C(17) 23(1) 34(1) 33(1) -13(1) 1(1) -7(1)
C(18) 21(1) 44(1) 42(1) -24(1) 0(1) -10(1)
C(19) 24(1) 44(1) 57(1) -26(1) 1(1) -9(1)
C(20) 22(1) 51(1) 68(1) -38(1) -2(1) -8(1)

C(21) 35(1) 56(1) 46(1) -22(1) 1(1) -19(1)
C(22) 35(1) 63(1) 41(1) -19(1) 0(1) -16(1)
C(23) 30(1) 53(1) 37(1) -17(1) -1(1) -14(1)
C(24) 34(1) 46(1) 69(1) -22(1) 5(1) -6(1)
C(25) 41(1) 72(1) 55(1) -30(1) 7(1) -16(1)
C(26) 22(1) 36(1) 34(1) -8(1) -1(1) -11(1)
C(27) 15(1) 36(2) 32(1) -11(1) 4(1) -9(1)
C(28) 29(2) 40(2) 35(2) -14(1) 5(1) -7(1)
C(29) 32(2) 60(2) 35(2) -19(1) 7(1) -17(2)
C(30) 35(2) 62(2) 32(2) -17(1) 4(1) -23(1)
C(31) 37(2) 49(2) 27(2) -5(1) -4(1) -18(1)
C(32) 25(2) 35(1) 32(2) -10(1) 0(1) -10(1)
C(33) 61(2) 100(3) 52(2) -43(2) 27(2) -20(2)
C(34) 50(2) 98(3) 35(2) -14(2) 6(2) -37(2)
C(26A) 22(1) 36(1) 34(1) -8(1) -1(1) -11(1)
C(27A) 11(2) 33(2) 35(2) -6(2) -5(2) -3(2)
C(28A) 29(2) 31(2) 39(2) -1(2) 2(2) 1(2)
C(29A) 33(3) 43(3) 42(3) -3(2) 2(2) 0(2)
C(30A) 38(3) 43(2) 36(2) -8(2) -7(2) -8(2)
C(31A) 30(3) 40(2) 45(3) -8(2) -6(2) -9(2)
C(32A) 24(2) 33(2) 42(2) -10(2) -7(2) -1(2)
C(34A) 52(3) 69(4) 41(3) -3(3) 2(2) -9(3)
C(1) 42(1) 107(2) 39(1) -21(1) 5(1) -21(1)
F(1) 81(2) 129(3) 84(3) -24(2) 32(2) -56(2)
F(2) 46(2) 189(5) 63(2) 4(3) 21(2) 5(2)
F(3) 85(2) 191(3) 52(2) -54(2) 20(2) -78(2)
C(1A) 42(1) 107(2) 39(1) -21(1) 5(1) -21(1)
F(1A) 60(2) 169(3) 56(2) -47(2) 22(1) -63(2)
F(2A) 45(2) 136(3) 54(2) -40(2) 23(1) -18(2)
F(3A) 64(2) 121(3) 28(1) -15(2) -4(1) 18(2)
F(4) 30(1) 84(1) 62(1) -39(1) -4(1) 10(1)
F(5) 34(1) 36(1) 45(1) -10(1) -8(1) 1(1)
F(6) 48(1) 35(1) 44(1) -10(1) -10(1) 4(1)
F(7) 74(1) 53(1) 33(1) 4(1) -5(1) -19(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for analog of 11g.

	x	y	z	U(eq)
H(1A)	6982	1790	5635	36
H(10A)	6117	3326	2752	52
H(10B)	5417	2189	2727	52
H(10C)	7107	2429	2374	52
H(11A)	7461	407	3559	49

H(11B) 5836 308 4076 49
H(11C) 7233 140 4731 49
H(12A) 7336 3746 4223 37
H(12B) 8162 3845 3175 37
H(13) 9597 4636 4124 37
H(14) 10792 3468 5480 34
H(15A) 11581 1720 5593 34
H(15B) 9951 1290 5606 34
H(16) 11767 1698 4010 35
H(17A) 9555 2005 3059 36
H(17B) 9496 879 4043 36
H(19) 7688 4535 5508 47
H(22) 7879 1386 8455 54
H(23) 9488 1435 7111 47
H(24A) 4674 4565 6995 74
H(24B) 5743 5397 6156 74
H(24C) 5903 5220 7301 74
H(25A) 6006 2151 9252 80
H(25B) 4806 2969 8541 80
H(25C) 6061 3522 8927 80
H(26) 11864 3612 3962 38
H(28) 12221 2732 2297 42
H(31) 10483 6495 810 47
H(32) 9986 5572 2492 37
H(33D) 12511 3373 -129 101
H(33E) 13344 2639 850 101
H(33F) 13981 3829 118 101
H(34A) 11676 5413 -943 93
H(34B) 13071 5941 -675 93
H(34C) 11492 6602 -733 93
H(26A) 11849 3596 3987 38
H(28A) 12472 2351 2464 43
H(29A) 13176 3127 791 52
H(33A) 11623 7064 80 83
H(33B) 10212 6915 839 83
H(33C) 10142 6600 -144 83
H(32A) 10324 5362 2284 40
H(34D) 11754 5564 -980 88
H(34E) 13035 4578 -820 88
H(34F) 13347 5775 -696 88

Torsion angles [°] for analog of 11g.

C(7)-C(2)-C(3)-F(7) -179.7(2)
C(1A)-C(2)-C(3)-F(7) 1.0(3)

C(1)-C(2)-C(3)-F(7) 1.0(3)
C(7)-C(2)-C(3)-C(4) -1.3(3)
C(1A)-C(2)-C(3)-C(4) 179.4(2)
C(1)-C(2)-C(3)-C(4) 179.4(2)
F(7)-C(3)-C(4)-F(6) -0.1(3)
C(2)-C(3)-C(4)-F(6) -178.6(2)
F(7)-C(3)-C(4)-C(5) 177.96(18)
C(2)-C(3)-C(4)-C(5) -0.5(3)
F(6)-C(4)-C(5)-C(6) -179.77(17)
C(3)-C(4)-C(5)-C(6) 2.1(3)
F(6)-C(4)-C(5)-N(1) 0.4(3)
C(3)-C(4)-C(5)-N(1) -177.69(19)
C(8)-N(1)-C(5)-C(6) -56.8(3)
C(8)-N(1)-C(5)-C(4) 123.0(2)
C(4)-C(5)-C(6)-F(5) 175.81(17)
N(1)-C(5)-C(6)-F(5) -4.4(3)
C(4)-C(5)-C(6)-C(7) -2.1(3)
N(1)-C(5)-C(6)-C(7) 177.75(18)
C(3)-C(2)-C(7)-F(4) -176.7(2)
C(1A)-C(2)-C(7)-F(4) 2.5(4)
C(1)-C(2)-C(7)-F(4) 2.5(4)
C(3)-C(2)-C(7)-C(6) 1.3(3)
C(1A)-C(2)-C(7)-C(6) -179.4(2)
C(1)-C(2)-C(7)-C(6) -179.4(2)
F(5)-C(6)-C(7)-F(4) 0.6(3)
C(5)-C(6)-C(7)-F(4) 178.52(18)
F(5)-C(6)-C(7)-C(2) -177.55(19)
C(5)-C(6)-C(7)-C(2) 0.4(3)
C(5)-N(1)-C(8)-O(1) 8.9(3)
C(5)-N(1)-C(8)-C(9) -164.53(16)
C(12)-N(2)-C(9)-C(10) 50.4(2)
C(17)-N(2)-C(9)-C(10) -78.99(19)
C(12)-N(2)-C(9)-C(11) 174.00(15)
C(17)-N(2)-C(9)-C(11) 44.60(19)
C(12)-N(2)-C(9)-C(8) -73.20(18)
C(17)-N(2)-C(9)-C(8) 157.40(14)
O(1)-C(8)-C(9)-N(2) 154.52(16)
N(1)-C(8)-C(9)-N(2) -32.17(18)
O(1)-C(8)-C(9)-C(10) 28.1(2)
N(1)-C(8)-C(9)-C(10) -158.63(15)
O(1)-C(8)-C(9)-C(11) -88.1(2)
N(1)-C(8)-C(9)-C(11) 85.18(17)
C(17)-N(2)-C(12)-C(13) -52.6(2)
C(9)-N(2)-C(12)-C(13) 175.95(15)
N(2)-C(12)-C(13)-C(14) -48.4(2)
N(2)-C(12)-C(13)-C(26A) 62.48(19)

N(2)-C(12)-C(13)-C(26) 62.48(19)
C(12)-C(13)-C(14)-C(18) -52.9(2)
C(26A)-C(13)-C(14)-C(18) -169.56(16)
C(26)-C(13)-C(14)-C(18) -169.56(16)
C(12)-C(13)-C(14)-C(15) 78.37(18)
C(26A)-C(13)-C(14)-C(15) -38.30(16)
C(26)-C(13)-C(14)-C(15) -38.30(16)
C(18)-C(14)-C(15)-C(16) 141.77(16)
C(13)-C(14)-C(15)-C(16) 8.64(17)
C(14)-C(15)-C(16)-C(17) -93.12(17)
C(14)-C(15)-C(16)-C(26A) 24.82(17)
C(14)-C(15)-C(16)-C(26) 24.82(17)
C(12)-N(2)-C(17)-C(16) 52.66(19)
C(9)-N(2)-C(17)-C(16) -177.10(13)
C(26A)-C(16)-C(17)-N(2) -65.01(19)
C(26)-C(16)-C(17)-N(2) -65.01(19)
C(15)-C(16)-C(17)-N(2) 47.42(19)
C(13)-C(14)-C(18)-C(19) -31.1(3)
C(15)-C(14)-C(18)-C(19) -156.62(18)
C(13)-C(14)-C(18)-C(23) 155.10(18)
C(15)-C(14)-C(18)-C(23) 29.6(3)
C(23)-C(18)-C(19)-C(20) 0.6(3)
C(14)-C(18)-C(19)-C(20) -173.42(18)
C(18)-C(19)-C(20)-C(21) 1.0(3)
C(18)-C(19)-C(20)-C(24) 178.3(2)
C(19)-C(20)-C(21)-C(22) -2.0(3)
C(24)-C(20)-C(21)-C(22) -179.2(2)
C(19)-C(20)-C(21)-C(25) 176.5(2)
C(24)-C(20)-C(21)-C(25) -0.7(3)
C(20)-C(21)-C(22)-C(23) 1.5(3)
C(25)-C(21)-C(22)-C(23) -177.1(2)
C(21)-C(22)-C(23)-C(18) 0.2(3)
C(19)-C(18)-C(23)-C(22) -1.2(3)
C(14)-C(18)-C(23)-C(22) 172.93(19)
C(17)-C(16)-C(26)-C(27) -56.2(3)
C(15)-C(16)-C(26)-C(27) -173.8(2)
C(17)-C(16)-C(26)-C(13) 68.96(18)
C(15)-C(16)-C(26)-C(13) -48.57(16)
C(12)-C(13)-C(26)-C(27) 64.7(2)
C(14)-C(13)-C(26)-C(27) -175.0(2)
C(12)-C(13)-C(26)-C(16) -66.48(17)
C(14)-C(13)-C(26)-C(16) 53.80(16)
C(16)-C(26)-C(27)-C(32) 150.6(3)
C(13)-C(26)-C(27)-C(32) 32.3(4)
C(16)-C(26)-C(27)-C(28) -38.2(4)
C(13)-C(26)-C(27)-C(28) -156.5(3)

C(32)-C(27)-C(28)-C(29) 0.4(6)
C(26)-C(27)-C(28)-C(29) -171.7(3)
C(27)-C(28)-C(29)-C(30) 0.9(6)
C(27)-C(28)-C(29)-C(33) 178.9(4)
C(28)-C(29)-C(30)-C(31) -2.1(6)
C(33)-C(29)-C(30)-C(31) 180.0(4)
C(28)-C(29)-C(30)-C(34) 178.6(4)
C(33)-C(29)-C(30)-C(34) 0.7(6)
C(29)-C(30)-C(31)-C(32) 2.1(6)
C(34)-C(30)-C(31)-C(32) -178.6(4)
C(28)-C(27)-C(32)-C(31) -0.4(5)
C(26)-C(27)-C(32)-C(31) 170.9(3)
C(30)-C(31)-C(32)-C(27) -0.8(6)
C(17)-C(16)-C(26A)-C(13) 68.96(18)
C(15)-C(16)-C(26A)-C(13) -48.57(16)
C(17)-C(16)-C(26A)-C(27A) -67.6(3)
C(15)-C(16)-C(26A)-C(27A) 174.8(2)
C(12)-C(13)-C(26A)-C(16) -66.48(17)
C(14)-C(13)-C(26A)-C(16) 53.80(16)
C(12)-C(13)-C(26A)-C(27A) 59.0(3)
C(14)-C(13)-C(26A)-C(27A) 179.2(3)
C(16)-C(26A)-C(27A)-C(32A) 153.4(4)
C(13)-C(26A)-C(27A)-C(32A) 32.9(6)
C(16)-C(26A)-C(27A)-C(28A) -31.2(6)
C(13)-C(26A)-C(27A)-C(28A) -151.7(4)
C(32A)-C(27A)-C(28A)-C(29A) 2.2(9)
C(26A)-C(27A)-C(28A)-C(29A) -173.3(5)
C(27A)-C(28A)-C(29A)-C(30A) -2.3(10)
C(28A)-C(29A)-C(30A)-C(31A) 1.4(10)
C(28A)-C(29A)-C(30A)-C(34A) 178.9(6)
C(29A)-C(30A)-C(31A)-C(32A) -0.4(9)
C(34A)-C(30A)-C(31A)-C(32A) -177.9(6)
C(29A)-C(30A)-C(31A)-C(33A) 179.3(6)
C(34A)-C(30A)-C(31A)-C(33A) 1.8(9)
C(28A)-C(27A)-C(32A)-C(31A) -1.2(8)
C(26A)-C(27A)-C(32A)-C(31A) 174.5(5)
C(30A)-C(31A)-C(32A)-C(27A) 0.3(9)
C(33A)-C(31A)-C(32A)-C(27A) -179.4(6)
C(3)-C(2)-C(1)-F(2) -158.8(5)
C(7)-C(2)-C(1)-F(2) 22.0(6)
C(3)-C(2)-C(1)-F(3) 68.1(4)
C(7)-C(2)-C(1)-F(3) -111.2(4)
C(3)-C(2)-C(1)-F(1) -47.5(4)
C(7)-C(2)-C(1)-F(1) 133.3(3)
C(3)-C(2)-C(1A)-F(1A) -73.0(4)
C(7)-C(2)-C(1A)-F(1A) 107.7(4)

C(3)-C(2)-C(1A)-F(3A) 51.7(4)
C(7)-C(2)-C(1A)-F(3A) -127.5(4)
C(3)-C(2)-C(1A)-F(2A) 172.6(3)
C(7)-C(2)-C(1A)-F(2A) -6.6(4)

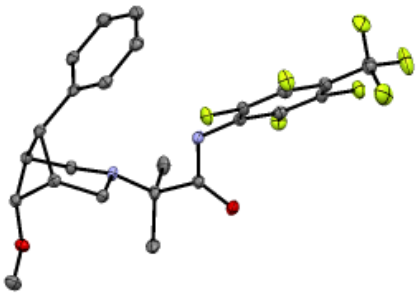


Figure S6. Structure determination of compound **11b.**

Structure Determination.

Colorless plates of **11b** were grown from a chloroform solution of the compound at 22 °C. A crystal of dimensions 0.26 x 0.19 x 0.16 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 0.6 kW power (40 kV, 15 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 8 sec. for high angle. The integration of the data yielded a total of 35070 reflections to a maximum 2Θ value of 136.48° of which 7988 were independent and 7301 were greater than 2σ(I). The final cell constants (Table S14) were based on the xyz centroids 21875 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P1bar with Z = 4 for the formula $C_{24}H_{23}N_2O_2F_7$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0361 and wR2 = 0.0933 [based on I > 2sigma(I)], R1 = 0.0385 and wR2 = 0.0951 for all data. Additional details are presented below. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S14. Crystal data and structure refinement for **11b**.

Empirical formula	$C_{24}H_{23}F_7N_2O_2$
Formula weight	504.44
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions a =	13.1300(2) A α = 77.984(6) °.
b =	13.3882(2) A β= 75.211(5) °.
c =	15.0424(11) A γ= 61.339(4) °.
Volume	2231.9(2) A^3
Z, Calculated density	4, 1.501 Mg/m^3
Absorption coefficient	1.185 mm^{-1}
F(000)	1040
Crystal size	0.260 x 0.190 x 0.160 mm
Theta range for data collection	3.054 to 68.243 °.
Limiting indices	-15<=h<=15, -16<=k<=16, -18<=l<=18
Reflections collected / unique	35070 / 7988 [R(int) = 0.0461]
Completeness to theta =	67.679 98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.814 and 0.669
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7988 / 36 / 674
Goodness-of-fit on	F^2 1.066
Final R indices [I>2sigma(I)] R1 =	0.0361, wR2 = 0.0933
R indices (all data) R1 =	0.0385, wR2 = 0.0951
Extinction coefficient	0.00140(13)
Largest diff. peak and hole	0.448 and -0.261 $e.A^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **11b**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	12273(1)	5846(1)	6220(1)	19(1)
F(2)	12021(1)	5079(1)	4847(1)	21(1)
F(3)	8501(1)	8496(1)	4530(1)	20(1)
F(4)	8746(1)	9228(1)	5944(1)	19(1)
F(5)	11018(1)	5446(1)	3523(1)	41(1)
F(6)	9878(1)	7160(1)	3114(1)	31(1)
F(7)	9167(1)	6151(1)	4090(1)	41(1)
F(5A)	10904(10)	6143(10)	3141(7)	48(2)
F(6A)	9130(11)	7077(9)	3429(8)	54(3)
F(7A)	10014(9)	5370(8)	4135(6)	42(2)
F(8)	3706(1)	4953(1)	7715(1)	21(1)
F(9)	3220(1)	5986(1)	9207(1)	25(1)
F(10)	4001(1)	2472(1)	11074(1)	22(1)
F(11)	4568(1)	1443(1)	9583(1)	20(1)
F(12)	3929(1)	5448(1)	10916(1)	33(1)
F(13)	3287(1)	4315(1)	11806(1)	41(1)
F(14)	2130(1)	5794(1)	11058(1)	38(1)
O(1)	8133(1)	10499(1)	10012(1)	17(1)
O(2)	10711(1)	9595(1)	6149(1)	18(1)
O(3)	4264(1)	1761(1)	4212(1)	17(1)
O(4)	2915(1)	2149(1)	8319(1)	20(1)
N(1)	9950(1)	8767(1)	8484(1)	14(1)
N(2)	10664(1)	7936(1)	6859(1)	15(1)
N(3)	4895(1)	1750(1)	6184(1)	13(1)
N(4)	4451(1)	2582(1)	7823(1)	16(1)
C(1)	7076(1)	11517(1)	9910(1)	24(1)

C(2) 7981(1) 9511(1) 10063(1) 17(1)
C(3) 7882(1) 9190(1) 9168(1) 16(1)
C(4) 8715(1) 9471(1) 8367(1) 15(1)
C(5) 10147(1) 8495(1) 9446(1) 15(1)
C(6) 9101(1) 8370(1) 10093(1) 16(1)
C(7) 8510(1) 7929(1) 9591(1) 17(1)
C(8) 9208(1) 6965(1) 8988(1) 17(1)
C(9) 10230(1) 6016(1) 9212(1) 20(1)
C(10) 10819(1) 5095(1) 8683(1) 25(1)
C(11) 10399(1) 5107(1) 7921(1) 26(1)
C(12) 9382(1) 6044(1) 7690(1) 25(1)
C(13) 8792(1) 6964(1) 8222(1) 20(1)
C(14) 10778(1) 9118(1) 7803(1) 14(1)
C(15) 10566(1) 10342(1) 7829(1) 17(1)
C(16) 12059(1) 8298(1) 7926(1) 18(1)
C(17) 10693(1) 8948(1) 6846(1) 14(1)
C(18) 10543(1) 7576(1) 6097(1) 14(1)
C(19) 11344(1) 6516(1) 5799(1) 14(1)
C(20) 11207(1) 6120(1) 5082(1) 15(1)
C(21) 10269(1) 6780(1) 4619(1) 15(1)
C(22) 9460(1) 7844(1) 4918(1) 15(1)
C(23) 9590(1) 8232(1) 5642(1) 15(1)
C(24) 10087(1) 6376(1) 3836(1) 19(1)
C(25) 3249(1) 2498(1) 3811(1) 21(1)
C(26) 4989(1) 2288(1) 4162(1) 15(1)
C(27) 4614(1) 3192(1) 4830(1) 14(1)
C(28) 4033(1) 2820(1) 5766(1) 14(1)
C(29) 5776(1) 934(1) 5522(1) 14(1)
C(30) 6086(1) 1570(1) 4611(1) 15(1)
C(31) 5965(1) 2736(1) 4780(1) 15(1)
C(32) 6446(1) 2816(1) 5554(1) 14(1)

C(33) 7513(1) 1935(1) 5767(1) 17(1)
C(34) 7969(1) 1983(1) 6484(1) 20(1)
C(35) 7380(1) 2924(1) 6990(1) 21(1)
C(36) 6338(1) 3824(1) 6765(1) 20(1)
C(37) 5866(1) 3769(1) 6054(1) 16(1)
C(38) 4366(1) 1225(1) 7007(1) 15(1)
C(39) 5339(1) 145(1) 7419(1) 21(1)
C(40) 3441(1) 929(1) 6839(1) 21(1)
C(41) 3809(1) 2039(1) 7764(1) 15(1)
C(42) 4169(1) 3158(1) 8597(1) 15(1)
C(43) 3817(1) 4322(1) 8535(1) 16(1)
C(44) 3540(1) 4863(1) 9311(1) 17(1)
C(45) 3571(1) 4280(1) 10193(1) 18(1)
C(46) 3912(1) 3120(1) 10257(1) 17(1)
C(47) 4210(1) 2572(1) 9478(1) 16(1)
C(48) 3235(1) 4944(1) 11003(1) 23(1)

Bond lengths [A] and angles [°] for 11b.

F(1)-C(19) 1.3421(13)
F(2)-C(20) 1.3392(13)
F(3)-C(22) 1.3413(14)
F(4)-C(23) 1.3374(13)
F(5)-C(24) 1.3256(15)
F(6)-C(24) 1.3258(15)
F(7)-C(24) 1.3259(16)
F(5A)-C(24) 1.259(10)
F(6A)-C(24) 1.363(10)
F(7A)-C(24) 1.368(9)
F(8)-C(43) 1.3409(14)

F(9)-C(44) 1.3392(14)
F(10)-C(46) 1.3440(14)
F(11)-C(47) 1.3380(14)
F(12)-C(48) 1.3399(17)
F(13)-C(48) 1.3174(16)
F(14)-C(48) 1.3419(16)
O(1)-C(2) 1.4146(15)
O(1)-C(1) 1.4195(15)
O(2)-C(17) 1.2152(15)
O(3)-C(26) 1.4123(15)
O(3)-C(25) 1.4202(15)
O(4)-C(41) 1.2170(14)
N(1)-C(4) 1.4699(15)
N(1)-C(5) 1.4740(15)
N(1)-C(14) 1.4753(14)
N(2)-C(17) 1.3686(16)
N(2)-C(18) 1.4030(16)
N(2)-H(2N) 0.808(16)
N(3)-C(28) 1.4709(15)
N(3)-C(38) 1.4749(15)
N(3)-C(29) 1.4758(14)
N(4)-C(41) 1.3780(16)
N(4)-C(42) 1.4033(16)
N(4)-H(4N) 0.859(16)
C(1)-H(1A) 0.9800
C(1)-H(1B) 0.9800
C(1)-H(1C) 0.9800
C(2)-C(6) 1.5324(17)
C(2)-C(3) 1.5475(17)
C(2)-H(2) 1.0000
C(3)-C(4) 1.5241(16)

C(3)-C(7) 1.5557(17)
C(3)-H(3) 1.0000
C(4)-H(4A) 0.9900
C(4)-H(4B) 0.9900
C(5)-C(6) 1.5259(16)
C(5)-H(5A) 0.9900
C(5)-H(5B) 0.9900
C(6)-C(7) 1.5633(17)
C(6)-H(6) 1.0000
C(7)-C(8) 1.5034(17)
C(7)-H(7) 1.0000
C(8)-C(9) 1.3951(18)
C(8)-C(13) 1.3958(19)
C(9)-C(10) 1.3904(19)
C(9)-H(9) 0.9500
C(10)-C(11) 1.388(2)
C(10)-H(10) 0.9500
C(11)-C(12) 1.388(2)
C(11)-H(11) 0.9500
C(12)-C(13) 1.3912(18)
C(12)-H(12) 0.9500
C(13)-H(13) 0.9500
C(14)-C(15) 1.5310(17)
C(14)-C(16) 1.5400(16)
C(14)-C(17) 1.5438(16)
C(15)-H(15A) 0.9800
C(15)-H(15B) 0.9800
C(15)-H(15C) 0.9800
C(16)-H(16A) 0.9800
C(16)-H(16B) 0.9800
C(16)-H(16C) 0.9800

C(18)-C(19) 1.3837(17)
C(18)-C(23) 1.3920(17)
C(19)-C(20) 1.3793(18)
C(20)-C(21) 1.3865(17)
C(21)-C(22) 1.3890(17)
C(21)-C(24) 1.5075(17)
C(22)-C(23) 1.3787(18)
C(25)-H(25A) 0.9800
C(25)-H(25B) 0.9800
C(25)-H(25C) 0.9800
C(26)-C(30) 1.5344(16)
C(26)-C(27) 1.5491(17)
C(26)-H(26) 1.0000
C(27)-C(28) 1.5276(16)
C(27)-C(31) 1.5610(16)
C(27)-H(27) 1.0000
C(28)-H(28A) 0.9900
C(28)-H(28B) 0.9900
C(29)-C(30) 1.5270(16)
C(29)-H(29A) 0.9900
C(29)-H(29B) 0.9900
C(30)-C(31) 1.5587(17)
C(30)-H(30) 1.0000
C(31)-C(32) 1.5028(17)
C(31)-H(31) 1.0000
C(32)-C(33) 1.3937(17)
C(32)-C(37) 1.3959(17)
C(33)-C(34) 1.3861(19)
C(33)-H(33) 0.9500
C(34)-C(35) 1.3898(19)
C(34)-H(34) 0.9500

C(35)-C(36) 1.3870(18)
C(35)-H(35) 0.9500
C(36)-C(37) 1.3958(19)
C(36)-H(36) 0.9500
C(37)-H(37) 0.9500
C(38)-C(41) 1.5319(16)
C(38)-C(40) 1.5354(17)
C(38)-C(39) 1.5374(17)
C(39)-H(39A) 0.9800
C(39)-H(39B) 0.9800
C(39)-H(39C) 0.9800
C(40)-H(40A) 0.9800
C(40)-H(40B) 0.9800
C(40)-H(40C) 0.9800
C(42)-C(43) 1.3859(17)
C(42)-C(47) 1.3916(17)
C(43)-C(44) 1.3786(18)
C(44)-C(45) 1.3926(18)
C(45)-C(46) 1.3835(18)
C(45)-C(48) 1.5063(18)
C(46)-C(47) 1.3824(18)
C(2)-O(1)-C(1) 111.70(10)
C(26)-O(3)-C(25) 112.02(9)
C(4)-N(1)-C(5) 115.50(9)
C(4)-N(1)-C(14) 113.26(9)
C(5)-N(1)-C(14) 115.93(9)
C(17)-N(2)-C(18) 124.18(10)
C(17)-N(2)-H(2N) 115.9(12)
C(18)-N(2)-H(2N) 118.7(12)
C(28)-N(3)-C(38) 113.96(9)
C(28)-N(3)-C(29) 114.82(9)

C(38)-N(3)-C(29) 114.10(9)
C(41)-N(4)-C(42) 120.03(10)
C(41)-N(4)-H(4N) 118.1(11)
C(42)-N(4)-H(4N) 121.6(11)
O(1)-C(1)-H(1A) 109.5
O(1)-C(1)-H(1B) 109.5
H(1A)-C(1)-H(1B) 109.5
O(1)-C(1)-H(1C) 109.5
H(1A)-C(1)-H(1C) 109.5
H(1B)-C(1)-H(1C) 109.5
O(1)-C(2)-C(6) 115.49(10)
O(1)-C(2)-C(3) 118.51(10)
C(6)-C(2)-C(3) 87.27(9)
O(1)-C(2)-H(2) 111.2
C(6)-C(2)-H(2) 111.2
C(3)-C(2)-H(2) 111.2
C(4)-C(3)-C(2) 108.24(10)
C(4)-C(3)-C(7) 110.72(9)
C(2)-C(3)-C(7) 85.43(9)
C(4)-C(3)-H(3) 116.1
C(2)-C(3)-H(3) 116.1
C(7)-C(3)-H(3) 116.1
N(1)-C(4)-C(3) 111.03(9)
N(1)-C(4)-H(4A) 109.4
C(3)-C(4)-H(4A) 109.4
N(1)-C(4)-H(4B) 109.4
C(3)-C(4)-H(4B) 109.4
H(4A)-C(4)-H(4B) 108.0
N(1)-C(5)-C(6) 109.87(10)
N(1)-C(5)-H(5A) 109.7
C(6)-C(5)-H(5A) 109.7

N(1)-C(5)-H(5B) 109.7
C(6)-C(5)-H(5B) 109.7
H(5A)-C(5)-H(5B) 108.2
C(5)-C(6)-C(2) 109.87(10)
C(5)-C(6)-C(7) 111.13(9)
C(2)-C(6)-C(7) 85.68(9)
C(5)-C(6)-H(6) 115.5
C(2)-C(6)-H(6) 115.5
C(7)-C(6)-H(6) 115.5
C(8)-C(7)-C(3) 121.18(10)
C(8)-C(7)-C(6) 122.84(10)
C(3)-C(7)-C(6) 85.91(9)
C(8)-C(7)-H(7) 108.3
C(3)-C(7)-H(7) 108.3
C(6)-C(7)-H(7) 108.3
C(9)-C(8)-C(13) 118.39(11)
C(9)-C(8)-C(7) 121.36(11)
C(13)-C(8)-C(7) 120.09(11)
C(10)-C(9)-C(8) 120.64(13)
C(10)-C(9)-H(9) 119.7
C(8)-C(9)-H(9) 119.7
C(11)-C(10)-C(9) 120.41(13)
C(11)-C(10)-H(10) 119.8
C(9)-C(10)-H(10) 119.8
C(12)-C(11)-C(10) 119.57(12)
C(12)-C(11)-H(11) 120.2
C(10)-C(11)-H(11) 120.2
C(11)-C(12)-C(13) 119.98(13)
C(11)-C(12)-H(12) 120.0
C(13)-C(12)-H(12) 120.0
C(12)-C(13)-C(8) 121.01(12)

C(12)-C(13)-H(13) 119.5
C(8)-C(13)-H(13) 119.5
N(1)-C(14)-C(15) 115.07(9)
N(1)-C(14)-C(16) 110.44(9)
C(15)-C(14)-C(16) 108.16(10)
N(1)-C(14)-C(17) 106.31(9)
C(15)-C(14)-C(17) 111.01(9)
C(16)-C(14)-C(17) 105.44(9)
C(14)-C(15)-H(15A) 109.5
C(14)-C(15)-H(15B) 109.5
H(15A)-C(15)-H(15B) 109.5
C(14)-C(15)-H(15C) 109.5
H(15A)-C(15)-H(15C) 109.5
H(15B)-C(15)-H(15C) 109.5
C(14)-C(16)-H(16A) 109.5
C(14)-C(16)-H(16B) 109.5
H(16A)-C(16)-H(16B) 109.5
C(14)-C(16)-H(16C) 109.5
H(16A)-C(16)-H(16C) 109.5
H(16B)-C(16)-H(16C) 109.5
O(2)-C(17)-N(2) 123.47(11)
O(2)-C(17)-C(14) 124.78(11)
N(2)-C(17)-C(14) 111.64(10)
C(19)-C(18)-C(23) 117.23(11)
C(19)-C(18)-N(2) 120.68(11)
C(23)-C(18)-N(2) 122.01(10)
F(1)-C(19)-C(20) 118.83(10)
F(1)-C(19)-C(18) 119.55(11)
C(20)-C(19)-C(18) 121.62(11)
F(2)-C(20)-C(19) 117.43(10)
F(2)-C(20)-C(21) 121.36(11)

C(19)-C(20)-C(21) 121.21(11)
C(20)-C(21)-C(22) 117.33(11)
C(20)-C(21)-C(24) 122.75(11)
C(22)-C(21)-C(24) 119.90(11)
F(3)-C(22)-C(23) 118.44(10)
F(3)-C(22)-C(21) 120.10(11)
C(23)-C(22)-C(21) 121.40(11)
F(4)-C(23)-C(22) 119.00(10)
F(4)-C(23)-C(18) 119.67(11)
C(22)-C(23)-C(18) 121.20(11)
F(5)-C(24)-F(6) 105.81(11)
F(5)-C(24)-F(7) 107.99(11)
F(6)-C(24)-F(7) 106.84(11)
F(5A)-C(24)-F(6A) 101.0(8)
F(5A)-C(24)-F(7A) 104.1(7)
F(6A)-C(24)-F(7A) 106.2(7)
F(5A)-C(24)-C(21) 116.2(5)
F(5)-C(24)-C(21) 113.02(10)
F(6)-C(24)-C(21) 111.73(10)
F(7)-C(24)-C(21) 111.10(10)
F(6A)-C(24)-C(21) 118.6(4)
F(7A)-C(24)-C(21) 109.3(4)
O(3)-C(25)-H(25A) 109.5
O(3)-C(25)-H(25B) 109.5
H(25A)-C(25)-H(25B) 109.5
O(3)-C(25)-H(25C) 109.5
H(25A)-C(25)-H(25C) 109.5
H(25B)-C(25)-H(25C) 109.5
O(3)-C(26)-C(30) 115.76(9)
O(3)-C(26)-C(27) 119.47(9)
C(30)-C(26)-C(27) 87.00(9)

O(3)-C(26)-H(26) 110.9
C(30)-C(26)-H(26) 110.9
C(27)-C(26)-H(26) 110.9
C(28)-C(27)-C(26) 108.28(9)
C(28)-C(27)-C(31) 111.53(9)
C(26)-C(27)-C(31) 85.32(8)
C(28)-C(27)-H(27) 115.9
C(26)-C(27)-H(27) 115.9
C(31)-C(27)-H(27) 115.9
N(3)-C(28)-C(27) 110.54(9)
N(3)-C(28)-H(28A) 109.5
C(27)-C(28)-H(28A) 109.5
N(3)-C(28)-H(28B) 109.5
C(27)-C(28)-H(28B) 109.5
H(28A)-C(28)-H(28B) 108.1
N(3)-C(29)-C(30) 110.57(9)
N(3)-C(29)-H(29A) 109.5
C(30)-C(29)-H(29A) 109.5
N(3)-C(29)-H(29B) 109.5
C(30)-C(29)-H(29B) 109.5
H(29A)-C(29)-H(29B) 108.1
C(29)-C(30)-C(26) 109.83(9)
C(29)-C(30)-C(31) 110.66(9)
C(26)-C(30)-C(31) 85.90(9)
C(29)-C(30)-H(30) 115.6
C(26)-C(30)-H(30) 115.6
C(31)-C(30)-H(30) 115.6
C(32)-C(31)-C(30) 120.90(10)
C(32)-C(31)-C(27) 121.83(10)
C(30)-C(31)-C(27) 85.74(9)
C(32)-C(31)-H(31) 108.7

C(30)-C(31)-H(31) 108.7
C(27)-C(31)-H(31) 108.7
C(33)-C(32)-C(37) 118.70(11)
C(33)-C(32)-C(31) 119.64(10)
C(37)-C(32)-C(31) 121.63(10)
C(34)-C(33)-C(32) 120.77(11)
C(34)-C(33)-H(33) 119.6
C(32)-C(33)-H(33) 119.6
C(33)-C(34)-C(35) 120.36(11)
C(33)-C(34)-H(34) 119.8
C(35)-C(34)-H(34) 119.8
C(36)-C(35)-C(34) 119.44(12)
C(36)-C(35)-H(35) 120.3
C(34)-C(35)-H(35) 120.3
C(35)-C(36)-C(37) 120.27(12)
C(35)-C(36)-H(36) 119.9
C(37)-C(36)-H(36) 119.9
C(36)-C(37)-C(32) 120.41(11)
C(36)-C(37)-H(37) 119.8
C(32)-C(37)-H(37) 119.8
N(3)-C(38)-C(41) 108.44(9)
N(3)-C(38)-C(40) 114.73(10)
C(41)-C(38)-C(40) 109.48(9)
N(3)-C(38)-C(39) 110.06(9)
C(41)-C(38)-C(39) 104.20(10)
C(40)-C(38)-C(39) 109.40(10)
C(38)-C(39)-H(39A) 109.5
C(38)-C(39)-H(39B) 109.5
H(39A)-C(39)-H(39B) 109.5
C(38)-C(39)-H(39C) 109.5
H(39A)-C(39)-H(39C) 109.5

H(39B)-C(39)-H(39C) 109.5
C(38)-C(40)-H(40A) 109.5
C(38)-C(40)-H(40B) 109.5
H(40A)-C(40)-H(40B) 109.5
C(38)-C(40)-H(40C) 109.5
H(40A)-C(40)-H(40C) 109.5
H(40B)-C(40)-H(40C) 109.5
O(4)-C(41)-N(4) 121.46(11)
O(4)-C(41)-C(38) 123.58(11)
N(4)-C(41)-C(38) 114.76(10)
C(43)-C(42)-C(47) 116.79(11)
C(43)-C(42)-N(4) 122.69(11)
C(47)-C(42)-N(4) 120.50(11)
F(8)-C(43)-C(44) 118.54(11)
F(8)-C(43)-C(42) 120.22(11)
C(44)-C(43)-C(42) 121.22(11)
F(9)-C(44)-C(43) 118.56(11)
F(9)-C(44)-C(45) 119.40(11)
C(43)-C(44)-C(45) 122.03(11)
C(46)-C(45)-C(44) 116.78(11)
C(46)-C(45)-C(48) 124.82(11)
C(44)-C(45)-C(48) 118.41(11)
F(10)-C(46)-C(47) 117.21(11)
F(10)-C(46)-C(45) 121.53(11)
C(47)-C(46)-C(45) 121.24(11)
F(11)-C(47)-C(46) 118.38(11)
F(11)-C(47)-C(42) 119.68(11)
C(46)-C(47)-C(42) 121.93(11)
F(13)-C(48)-F(12) 107.77(11)
F(13)-C(48)-F(14) 106.73(11)
F(12)-C(48)-F(14) 105.79(11)

F(13)-C(48)-C(45) 113.59(11)

F(12)-C(48)-C(45) 111.17(10)

F(14)-C(48)-C(45) 111.38(11)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (A^2 x 10^3) for **11b**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
F(1)	15(1)	17(1)	23(1)	-1(1)	-7(1)	-4(1)
F(2)	18(1)	13(1)	27(1)	-8(1)	-1(1)	-4(1)
F(3)	17(1)	19(1)	23(1)	-1(1)	-9(1)	-6(1)
F(4)	16(1)	15(1)	22(1)	-7(1)	-2(1)	-2(1)
F(5)	38(1)	31(1)	47(1)	-27(1)	-20(1)	4(1)
F(6)	54(1)	30(1)	18(1)	1(1)	-13(1)	-24(1)
F(7)	52(1)	75(1)	28(1)	-11(1)	-1(1)	-55(1)
F(5A)	55(4)	56(5)	41(4)	-28(4)	13(3)	-33(3)
F(6A)	59(4)	37(4)	67(5)	-20(4)	-40(4)	-4(3)
F(7A)	81(5)	35(3)	39(4)	1(3)	-27(4)	-42(3)
F(8)	28(1)	19(1)	14(1)	1(1)	-5(1)	-10(1)
F(9)	37(1)	13(1)	22(1)	-2(1)	-6(1)	-9(1)
F(10)	30(1)	24(1)	14(1)	2(1)	-4(1)	-13(1)
F(11)	25(1)	14(1)	21(1)	-1(1)	-4(1)	-9(1)
F(12)	42(1)	41(1)	30(1)	-14(1)	-2(1)	-27(1)
F(13)	75(1)	36(1)	16(1)	-3(1)	-6(1)	-29(1)
F(14)	30(1)	40(1)	36(1)	-23(1)	0(1)	-6(1)
O(1)	17(1)	15(1)	21(1)	-5(1)	-4(1)	-7(1)
O(2)	21(1)	19(1)	13(1)	0(1)	-2(1)	-11(1)

O(3) 18(1) 17(1) 18(1) -2(1) -4(1) -9(1)
O(4) 20(1) 28(1) 16(1) -5(1) 3(1) -14(1)
N(1) 13(1) 18(1) 11(1) -1(1) -1(1) -9(1)
N(2) 20(1) 17(1) 11(1) -1(1) -2(1) -10(1)
N(3) 14(1) 12(1) 12(1) -1(1) 1(1) -6(1)
N(4) 18(1) 20(1) 14(1) -6(1) 3(1) -12(1)
C(1) 21(1) 22(1) 27(1) -7(1) -7(1) -6(1)
C(2) 17(1) 21(1) 15(1) -4(1) 1(1) -12(1)
C(3) 14(1) 20(1) 16(1) -5(1) 0(1) -9(1)
C(4) 14(1) 18(1) 14(1) -2(1) -3(1) -7(1)
C(5) 16(1) 18(1) 12(1) 0(1) -3(1) -9(1)
C(6) 19(1) 18(1) 12(1) -2(1) -1(1) -10(1)
C(7) 18(1) 21(1) 14(1) -4(1) 2(1) -13(1)
C(8) 21(1) 20(1) 16(1) -4(1) 3(1) -16(1)
C(9) 22(1) 21(1) 20(1) -3(1) -1(1) -13(1)
C(10) 22(1) 22(1) 30(1) -6(1) 3(1) -12(1)
C(11) 30(1) 27(1) 28(1) -13(1) 6(1) -20(1)
C(12) 32(1) 30(1) 22(1) -7(1) -1(1) -22(1)
C(13) 23(1) 22(1) 21(1) -4(1) -1(1) -14(1)
C(14) 15(1) 16(1) 12(1) -1(1) -1(1) -8(1)
C(15) 21(1) 19(1) 16(1) -2(1) -4(1) -12(1)
C(16) 15(1) 23(1) 16(1) -1(1) -2(1) -9(1)
C(17) 10(1) 16(1) 15(1) -4(1) 0(1) -6(1)
C(18) 16(1) 15(1) 13(1) -1(1) -1(1) -9(1)
C(19) 12(1) 15(1) 16(1) 1(1) -3(1) -6(1)
C(20) 14(1) 11(1) 18(1) -4(1) 2(1) -6(1)
C(21) 17(1) 17(1) 16(1) -3(1) -1(1) -11(1)
C(22) 13(1) 15(1) 18(1) 0(1) -3(1) -7(1)
C(23) 14(1) 13(1) 17(1) -4(1) 1(1) -6(1)
C(24) 21(1) 18(1) 21(1) -3(1) -4(1) -11(1)
C(25) 20(1) 20(1) 24(1) -4(1) -8(1) -7(1)

C(26) 17(1) 17(1) 13(1) -1(1) -1(1) -10(1)
C(27) 15(1) 13(1) 15(1) 0(1) -3(1) -7(1)
C(28) 13(1) 13(1) 15(1) -2(1) -1(1) -5(1)
C(29) 15(1) 13(1) 13(1) -3(1) -1(1) -6(1)
C(30) 15(1) 16(1) 13(1) -3(1) 0(1) -7(1)
C(31) 16(1) 15(1) 13(1) -1(1) 0(1) -9(1)
C(32) 15(1) 15(1) 15(1) 0(1) 0(1) -11(1)
C(33) 17(1) 16(1) 16(1) -1(1) 0(1) -10(1)
C(34) 18(1) 22(1) 20(1) 2(1) -4(1) -11(1)
C(35) 23(1) 28(1) 17(1) -1(1) -3(1) -17(1)
C(36) 21(1) 21(1) 21(1) -6(1) 2(1) -13(1)
C(37) 15(1) 15(1) 19(1) -1(1) -1(1) -8(1)
C(38) 20(1) 16(1) 12(1) -2(1) 0(1) -11(1)
C(39) 28(1) 18(1) 16(1) 0(1) -1(1) -10(1)
C(40) 27(1) 28(1) 17(1) -5(1) 2(1) -21(1)
C(41) 17(1) 16(1) 12(1) 0(1) -2(1) -9(1)
C(42) 14(1) 19(1) 15(1) -4(1) -1(1) -9(1)
C(43) 16(1) 18(1) 13(1) 1(1) -3(1) -8(1)
C(44) 18(1) 14(1) 20(1) -2(1) -4(1) -7(1)
C(45) 18(1) 20(1) 16(1) -4(1) -3(1) -9(1)
C(46) 17(1) 20(1) 13(1) 2(1) -3(1) -10(1)
C(47) 15(1) 14(1) 20(1) -2(1) -3(1) -7(1)
C(48) 29(1) 23(1) 19(1) -4(1) -3(1) -13(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 11b.

	x	y	z	U(eq)
H(2N)	10579(13)	7602(13)	7364(11)	21(4)

H(4N) 4973(14) 2613(13) 7354(11) 21(4)
H(1A) 6829 11540 9340 36
H(1B) 7213 12183 9878 36
H(1C) 6455 11531 10440 36
H(2) 7331 9505 10581 20
H(3) 7063 9459 9065 19
H(4A) 8615 9332 7780 18
H(4B) 8512 10290 8330 18
H(5A) 10243 9112 9624 18
H(5B) 10879 7773 9499 18
H(6) 9244 7982 10724 19
H(7) 7911 7752 10062 20
H(9) 10527 6000 9731 24
H(10) 11514 4454 8844 30
H(11) 10805 4477 7559 32
H(12) 9089 6057 7170 30
H(13) 8095 7602 8061 24
H(15A) 9761 10880 7732 26
H(15B) 11133 10511 7339 26
H(15C) 10667 10417 8431 26
H(16A) 12192 8417 8499 27
H(16B) 12603 8450 7401 27
H(16C) 12197 7506 7957 27
H(25A) 2777 3183 4142 31
H(25B) 2775 2099 3855 31
H(25C) 3493 2721 3160 31
H(26) 5208 2578 3510 18
H(27) 4179 4008 4584 17
H(28A) 3708 3428 6183 17
H(28B) 3372 2707 5684 17
H(29A) 5456 446 5406 17

H(29B) 6498 431 5787 17
H(30) 6823 1101 4191 18
H(31) 6288 3076 4190 18
H(33) 7932 1295 5417 20
H(34) 8689 1369 6629 24
H(35) 7688 2951 7487 25
H(36) 5943 4480 7096 24
H(37) 5146 4383 5909 20
H(39A) 5635 -479 7033 32
H(39B) 5014 -79 8046 32
H(39C) 5987 303 7440 32
H(40A) 2746 1636 6698 32
H(40B) 3210 498 7395 32
H(40C) 3776 464 6318 32

Torsion angles [deg] for 11b.

C(1)-O(1)-C(2)-C(6) 175.10(10)
C(1)-O(1)-C(2)-C(3) 73.62(13)
O(1)-C(2)-C(3)-C(4) 36.95(13)
C(6)-C(2)-C(3)-C(4) -80.72(10)
O(1)-C(2)-C(3)-C(7) 147.28(10)
C(6)-C(2)-C(3)-C(7) 29.60(8)
C(5)-N(1)-C(4)-C(3) -34.43(14)
C(14)-N(1)-C(4)-C(3) -171.51(9)
C(2)-C(3)-C(4)-N(1) 63.78(12)
C(7)-C(3)-C(4)-N(1) -28.22(14)
C(4)-N(1)-C(5)-C(6) 33.34(13)
C(14)-N(1)-C(5)-C(6) 169.26(9)
N(1)-C(5)-C(6)-C(2) -63.24(12)

N(1)-C(5)-C(6)-C(7) 29.84(13)
O(1)-C(2)-C(6)-C(5) -38.96(14)
C(3)-C(2)-C(6)-C(5) 81.49(10)
O(1)-C(2)-C(6)-C(7) -149.88(10)
C(3)-C(2)-C(6)-C(7) -29.43(8)
C(4)-C(3)-C(7)-C(8) -47.53(15)
C(2)-C(3)-C(7)-C(8) -155.32(11)
C(4)-C(3)-C(7)-C(6) 78.78(10)
C(2)-C(3)-C(7)-C(6) -29.01(8)
C(5)-C(6)-C(7)-C(8) 44.52(15)
C(2)-C(6)-C(7)-C(8) 154.18(11)
C(5)-C(6)-C(7)-C(3) -80.34(10)
C(2)-C(6)-C(7)-C(3) 29.31(8)
C(3)-C(7)-C(8)-C(9) 144.67(12)
C(6)-C(7)-C(8)-C(9) 37.74(17)
C(3)-C(7)-C(8)-C(13) -40.09(16)
C(6)-C(7)-C(8)-C(13) -147.03(12)
C(13)-C(8)-C(9)-C(10) 0.10(18)
C(7)-C(8)-C(9)-C(10) 175.41(11)
C(8)-C(9)-C(10)-C(11) 0.15(19)
C(9)-C(10)-C(11)-C(12) -0.2(2)
C(10)-C(11)-C(12)-C(13) 0.1(2)
C(11)-C(12)-C(13)-C(8) 0.18(19)
C(9)-C(8)-C(13)-C(12) -0.26(18)
C(7)-C(8)-C(13)-C(12) -175.64(11)
C(4)-N(1)-C(14)-C(15) 60.96(13)
C(5)-N(1)-C(14)-C(15) -75.94(12)
C(4)-N(1)-C(14)-C(16) -176.26(10)
C(5)-N(1)-C(14)-C(16) 46.85(13)
C(4)-N(1)-C(14)-C(17) -62.37(12)
C(5)-N(1)-C(14)-C(17) 160.74(9)

C(18)-N(2)-C(17)-O(2) -6.13(18)
C(18)-N(2)-C(17)-C(14) 177.45(10)
N(1)-C(14)-C(17)-O(2) 140.62(11)
C(15)-C(14)-C(17)-O(2) 14.80(15)
C(16)-C(14)-C(17)-O(2) -102.10(13)
N(1)-C(14)-C(17)-N(2) -43.02(12)
C(15)-C(14)-C(17)-N(2) -168.85(9)
C(16)-C(14)-C(17)-N(2) 74.26(12)
C(17)-N(2)-C(18)-C(19) 126.60(12)
C(17)-N(2)-C(18)-C(23) -56.83(16)
C(23)-C(18)-C(19)-F(1) -179.48(10)
N(2)-C(18)-C(19)-F(1) -2.75(17)
C(23)-C(18)-C(19)-C(20) -0.20(17)
N(2)-C(18)-C(19)-C(20) 176.52(11)
F(1)-C(19)-C(20)-F(2) -0.08(16)
C(18)-C(19)-C(20)-F(2) -179.36(10)
F(1)-C(19)-C(20)-C(21) -179.50(10)
C(18)-C(19)-C(20)-C(21) 1.22(18)
F(2)-C(20)-C(21)-C(22) 179.23(10)
C(19)-C(20)-C(21)-C(22) -1.38(17)
F(2)-C(20)-C(21)-C(24) 0.88(17)
C(19)-C(20)-C(21)-C(24) -179.73(11)
C(20)-C(21)-C(22)-F(3) -176.45(10)
C(24)-C(21)-C(22)-F(3) 1.95(17)
C(20)-C(21)-C(22)-C(23) 0.58(17)
C(24)-C(21)-C(22)-C(23) 178.98(11)
F(3)-C(22)-C(23)-F(4) 1.59(16)
C(21)-C(22)-C(23)-F(4) -175.49(10)
F(3)-C(22)-C(23)-C(18) 177.49(10)
C(21)-C(22)-C(23)-C(18) 0.41(18)
C(19)-C(18)-C(23)-F(4) 175.27(10)

N(2)-C(18)-C(23)-F(4) -1.40(17)
C(19)-C(18)-C(23)-C(22) -0.60(17)
N(2)-C(18)-C(23)-C(22) -177.28(11)
C(20)-C(21)-C(24)-F(5A) -60.2(6)
C(22)-C(21)-C(24)-F(5A) 121.5(6)
C(20)-C(21)-C(24)-F(5) -12.51(17)
C(22)-C(21)-C(24)-F(5) 169.18(11)
C(20)-C(21)-C(24)-F(6) -131.72(12)
C(22)-C(21)-C(24)-F(6) 49.96(15)
C(20)-C(21)-C(24)-F(7) 109.07(13)
C(22)-C(21)-C(24)-F(7) -69.24(15)
C(20)-C(21)-C(24)-F(6A) 179.1(7)
C(22)-C(21)-C(24)-F(6A) 0.8(7)
C(20)-C(21)-C(24)-F(7A) 57.2(5)
C(22)-C(21)-C(24)-F(7A) -121.1(5)
C(25)-O(3)-C(26)-C(30) 177.81(10)
C(25)-O(3)-C(26)-C(27) 75.92(13)
O(3)-C(26)-C(27)-C(28) 36.69(14)
C(30)-C(26)-C(27)-C(28) -81.37(10)
O(3)-C(26)-C(27)-C(31) 147.84(10)
C(30)-C(26)-C(27)-C(31) 29.78(8)
C(38)-N(3)-C(28)-C(27) -169.86(10)
C(29)-N(3)-C(28)-C(27) -35.61(13)
C(26)-C(27)-C(28)-N(3) 65.37(12)
C(31)-C(27)-C(28)-N(3) -26.81(13)
C(28)-N(3)-C(29)-C(30) 34.07(13)
C(38)-N(3)-C(29)-C(30) 168.25(10)
N(3)-C(29)-C(30)-C(26) -63.10(12)
N(3)-C(29)-C(30)-C(31) 30.04(13)
O(3)-C(26)-C(30)-C(29) -40.76(13)
C(27)-C(26)-C(30)-C(29) 80.69(10)

O(3)-C(26)-C(30)-C(31) -151.25(10)
C(27)-C(26)-C(30)-C(31) -29.81(8)
C(29)-C(30)-C(31)-C(32) 44.81(14)
C(26)-C(30)-C(31)-C(32) 154.47(10)
C(29)-C(30)-C(31)-C(27) -80.06(10)
C(26)-C(30)-C(31)-C(27) 29.60(8)
C(28)-C(27)-C(31)-C(32) -45.54(14)
C(26)-C(27)-C(31)-C(32) -153.37(11)
C(28)-C(27)-C(31)-C(30) 78.51(10)
C(26)-C(27)-C(31)-C(30) -29.32(8)
C(30)-C(31)-C(32)-C(33) 38.10(15)
C(27)-C(31)-C(32)-C(33) 143.74(11)
C(30)-C(31)-C(32)-C(37) -143.74(11)
C(27)-C(31)-C(32)-C(37) -38.10(16)
C(37)-C(32)-C(33)-C(34) 2.41(17)
C(31)-C(32)-C(33)-C(34) -179.37(11)
C(32)-C(33)-C(34)-C(35) -1.34(18)
C(33)-C(34)-C(35)-C(36) -0.88(18)
C(34)-C(35)-C(36)-C(37) 1.98(18)
C(35)-C(36)-C(37)-C(32) -0.88(18)
C(33)-C(32)-C(37)-C(36) -1.30(17)
C(31)-C(32)-C(37)-C(36) -179.48(11)
C(28)-N(3)-C(38)-C(41) -64.04(12)
C(29)-N(3)-C(38)-C(41) 161.37(10)
C(28)-N(3)-C(38)-C(40) 58.68(13)
C(29)-N(3)-C(38)-C(40) -75.90(12)
C(28)-N(3)-C(38)-C(39) -177.44(10)
C(29)-N(3)-C(38)-C(39) 47.98(13)
C(42)-N(4)-C(41)-O(4) 8.25(17)
C(42)-N(4)-C(41)-C(38) -166.80(10)
N(3)-C(38)-C(41)-O(4) 145.86(11)

C(40)-C(38)-C(41)-O(4) 20.01(16)
C(39)-C(38)-C(41)-O(4) -96.92(13)
N(3)-C(38)-C(41)-N(4) -39.21(13)
C(40)-C(38)-C(41)-N(4) -165.06(10)
C(39)-C(38)-C(41)-N(4) 78.00(12)
C(41)-N(4)-C(42)-C(43) -118.79(13)
C(41)-N(4)-C(42)-C(47) 59.78(15)
C(47)-C(42)-C(43)-F(8) -177.10(10)
N(4)-C(42)-C(43)-F(8) 1.53(18)
C(47)-C(42)-C(43)-C(44) 1.01(18)
N(4)-C(42)-C(43)-C(44) 179.63(11)
F(8)-C(43)-C(44)-F(9) -2.79(17)
C(42)-C(43)-C(44)-F(9) 179.07(11)
F(8)-C(43)-C(44)-C(45) 176.54(11)
C(42)-C(43)-C(44)-C(45) -1.59(19)
F(9)-C(44)-C(45)-C(46) -179.72(11)
C(43)-C(44)-C(45)-C(46) 0.96(18)
F(9)-C(44)-C(45)-C(48) 0.32(17)
C(43)-C(44)-C(45)-C(48) -179.01(12)
C(44)-C(45)-C(46)-F(10) 178.31(11)
C(48)-C(45)-C(46)-F(10) -1.73(19)
C(44)-C(45)-C(46)-C(47) 0.18(18)
C(48)-C(45)-C(46)-C(47) -179.86(12)
F(10)-C(46)-C(47)-F(11) -0.19(16)
C(45)-C(46)-C(47)-F(11) 178.01(10)
F(10)-C(46)-C(47)-C(42) -178.93(10)
C(45)-C(46)-C(47)-C(42) -0.73(19)
C(43)-C(42)-C(47)-F(11) -178.60(10)
N(4)-C(42)-C(47)-F(11) 2.74(17)
C(43)-C(42)-C(47)-C(46) 0.13(18)
N(4)-C(42)-C(47)-C(46) -178.53(11)

C(46)-C(45)-C(48)-F(13) -0.33(19)

C(44)-C(45)-C(48)-F(13) 179.63(12)

C(46)-C(45)-C(48)-F(12) 121.43(13)

C(44)-C(45)-C(48)-F(12) -58.61(15)

C(46)-C(45)-C(48)-F(14) -120.87(13)

C(44)-C(45)-C(48)-F(14) 59.09(15)

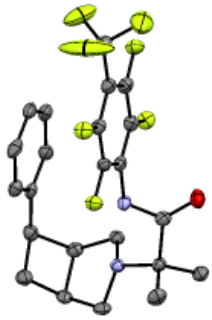


Figure S7. Structure determination of compound **11h.**

Structure Determination

Colorless needles of **11h** were grown from a hexanes solution of the compound at 150 °C. A crystal of dimensions 0.18 x 0.06 x 0.02 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0°in ω . The exposure times were 5 sec. for the low angle images, 25 sec. for high angle. The integration of the data yielded a total of 31795 reflections to a maximum 2Θ value of 136.48°of which 3805 were independent and 3330 were greater than 2 σ (I). The final cell constants (Table S15) were based on the xyz centroids 21356 reflections above 10 σ (I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{23}H_{21}N_2OF_7$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in both idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0550 and wR2 = 0.1561 [based on I > 2sigma(I)], R1 = 0.0602 and wR2 =

0.1621 for all data. Additional details are presented below. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Table S15. Crystal data and structure refinement for **11h**.

Empirical formula	$C_{23}H_{21}F_7N_2O$
Formula weight	474.42
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions a =	6.22970(10) A α = 90 °.
b =	24.9877(5) A β = 100.085(7) °.
c =	13.5847(10) A γ = 90 °.
Volume	2082.00(17) A^3
Z, Calculated density	4, 1.514 Mg/m^3
Absorption coefficient	1.195 mm^{-1}
F(000)	976
Crystal size	0.180 x 0.060 x 0.020 mm
Theta range for data collection	3.537 to 68.245 °.
Limiting indices	-7<=h<=7, -30<=k<=30, -15<=l<=16
Reflections collected / unique	31795 / 3805 [R(int) = 0.0794]
Completeness to theta =	67.679 99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.976 and 0.682
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	3805 / 51 / 333
Goodness-of-fit on	F^2 1.132
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1561
R indices (all data)	R1 = 0.0602, wR2 = 0.1621
Extinction coefficient	0.0034(4)
Largest diff. peak and hole	0.302 and -0.349 $e.A^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **11h**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5110(2)	3502(1)	9092(1)	32(1)
N(1)	7384(2)	3311(1)	8003(1)	23(1)
N(2)	8168(2)	4354(1)	7811(1)	20(1)
F(1)	3319(3)	979(1)	7717(1)	43(1)
F(2)	6494(3)	770(1)	7461(2)	59(1)
F(3)	4087(3)	1059(1)	6266(1)	44(1)
F(1A)	5221(12)	828(2)	8006(3)	56(2)
F(2A)	6648(9)	900(2)	6719(4)	49(1)

F(3A)	3266(10)	1033(2)	6595(5)	63(2)
F(4)	9305(2)	1472(1)	8122(1)	28(1)
F(5)	10335(2)	2495(1)	8460(1)	27(1)
F(6)	3116(2)	3006(1)	7177(1)	28(1)
F(7)	2044(2)	1984(1)	6804(1)	30(1)
C(1)	4970(3)	1121(1)	7218(1)	31(1)
C(2)	5631(3)	1693(1)	7444(1)	23(1)
C(3)	7737(3)	1839(1)	7865(1)	22(1)
C(4)	8283(3)	2371(1)	8050(1)	21(1)
C(5)	6761(3)	2776(1)	7832(1)	21(1)
C(6)	4646(3)	2628(1)	7427(1)	22(1)
C(7)	4101(3)	2101(1)	7234(1)	24(1)
C(8)	6555(3)	3640(1)	8647(1)	24(1)
C(9)	7720(3)	4185(1)	8794(1)	23(1)
C(10)	9879(3)	4087(1)	9511(1)	30(1)
C(11)	6302(3)	4571(1)	9279(1)	28(1)
C(12)	9627(3)	4813(1)	7787(1)	26(1)
C(13)	9421(3)	4921(1)	6675(1)	26(1)
C(14)	10411(3)	4479(1)	6092(1)	29(1)
C(15)	8112(3)	4344(1)	5507(1)	24(1)
C(16)	7077(3)	4731(1)	6196(1)	24(1)
C(17)	6196(3)	4486(1)	7072(1)	23(1)
C(18)	7331(3)	3772(1)	5397(1)	22(1)
C(19)	5124(3)	3669(1)	5053(1)	27(1)
C(20)	4353(3)	3150(1)	4914(1)	31(1)

C(21)	5774(3)	2719(1)	5118(1)	32(1)
C(22)	7965(3)	2817(1)	5458(1)	30(1)
C(23)	8739(3)	3340(1)	5601(1)	25(1)

Bond lengths [A] and angles [°] for 11h.

O(1)-C(8)	1.219(2)
N(1)-C(8)	1.365(2)
N(1)-C(5)	1.401(2)
N(1)-H(1N)	0.87(2)
N(2)-C(12)	1.469(2)
N(2)-C(9)	1.472(2)
N(2)-C(17)	1.482(2)
F(1)-C(1)	1.374(3)
F(2)-C(1)	1.292(2)
F(3)-C(1)	1.323(3)
F(1A)-C(1)	1.285(5)
F(2A)-C(1)	1.451(5)
F(3A)-C(1)	1.255(6)
F(4)-C(3)	1.3399(19)
F(5)-C(4)	1.3380(19)
F(6)-C(6)	1.3407(19)
F(7)-C(7)	1.343(2)
C(1)-C(2)	1.505(2)
C(2)-C(3)	1.384(2)
C(2)-C(7)	1.391(2)
C(3)-C(4)	1.385(2)

C(4)-C(5)	1.383(2)
C(5)-C(6)	1.386(2)
C(6)-C(7)	1.375(2)
C(8)-C(9)	1.540(2)
C(9)-C(11)	1.532(2)
C(9)-C(10)	1.536(2)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.517(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.550(3)
C(13)-C(16)	1.565(2)
C(13)-H(13)	1.0000
C(14)-C(15)	1.548(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(18)	1.509(2)
C(15)-C(16)	1.561(2)
C(15)-H(15)	1.0000
C(16)-C(17)	1.524(2)

C(16)-H(16)	1.0000
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(23)	1.388(2)
C(18)-C(19)	1.397(2)
C(19)-C(20)	1.384(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.390(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.384(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.396(3)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500

C(8)-N(1)-C(5)	123.72(14)
C(8)-N(1)-H(1N)	117.8(16)
C(5)-N(1)-H(1N)	118.5(15)
C(12)-N(2)-C(9)	117.44(13)
C(12)-N(2)-C(17)	104.66(13)
C(9)-N(2)-C(17)	114.36(13)
F(3A)-C(1)-F(1A)	115.3(5)
F(2)-C(1)-F(3)	109.37(19)
F(2)-C(1)-F(1)	106.15(18)
F(3)-C(1)-F(1)	103.49(17)

F(3A)-C(1)-F(2A)	102.3(4)
F(1A)-C(1)-F(2A)	100.4(4)
F(3A)-C(1)-C(2)	118.2(3)
F(1A)-C(1)-C(2)	112.5(3)
F(2)-C(1)-C(2)	115.42(16)
F(3)-C(1)-C(2)	111.33(16)
F(1)-C(1)-C(2)	110.29(15)
F(2A)-C(1)-C(2)	105.2(2)
C(3)-C(2)-C(7)	117.28(15)
C(3)-C(2)-C(1)	122.67(15)
C(7)-C(2)-C(1)	120.05(15)
F(4)-C(3)-C(2)	121.51(15)
F(4)-C(3)-C(4)	117.67(15)
C(2)-C(3)-C(4)	120.81(15)
F(5)-C(4)-C(5)	119.28(14)
F(5)-C(4)-C(3)	118.97(14)
C(5)-C(4)-C(3)	121.76(15)
C(4)-C(5)-C(6)	117.32(15)
C(4)-C(5)-N(1)	120.21(15)
C(6)-C(5)-N(1)	122.46(15)
F(6)-C(6)-C(7)	118.98(15)
F(6)-C(6)-C(5)	119.85(14)
C(7)-C(6)-C(5)	121.10(15)
F(7)-C(7)-C(6)	118.39(15)
F(7)-C(7)-C(2)	119.86(15)

C(6)-C(7)-C(2)	121.72(16)
O(1)-C(8)-N(1)	122.90(16)
O(1)-C(8)-C(9)	123.92(15)
N(1)-C(8)-C(9)	113.10(14)
N(2)-C(9)-C(11)	115.13(14)
N(2)-C(9)-C(10)	109.67(14)
C(11)-C(9)-C(10)	109.53(14)
N(2)-C(9)-C(8)	107.17(13)
C(11)-C(9)-C(8)	108.57(14)
C(10)-C(9)-C(8)	106.38(14)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(2)-C(12)-C(13)	102.53(13)
N(2)-C(12)-H(12A)	111.3
C(13)-C(12)-H(12A)	111.3

N(2)-C(12)-H(12B)	111.3
C(13)-C(12)-H(12B)	111.3
H(12A)-C(12)-H(12B)	109.2
C(12)-C(13)-C(14)	114.21(15)
C(12)-C(13)-C(16)	105.69(14)
C(14)-C(13)-C(16)	89.81(13)
C(12)-C(13)-H(13)	114.8
C(14)-C(13)-H(13)	114.8
C(16)-C(13)-H(13)	114.8
C(15)-C(14)-C(13)	90.11(13)
C(15)-C(14)-H(14A)	113.6
C(13)-C(14)-H(14A)	113.6
C(15)-C(14)-H(14B)	113.6
C(13)-C(14)-H(14B)	113.6
H(14A)-C(14)-H(14B)	110.9
C(18)-C(15)-C(14)	120.64(14)
C(18)-C(15)-C(16)	119.12(14)
C(14)-C(15)-C(16)	90.02(13)
C(18)-C(15)-H(15)	108.5
C(14)-C(15)-H(15)	108.5
C(16)-C(15)-H(15)	108.5
C(17)-C(16)-C(15)	117.46(14)
C(17)-C(16)-C(13)	103.59(13)
C(15)-C(16)-C(13)	89.08(13)
C(17)-C(16)-H(16)	114.5

C(15)-C(16)-H(16)	114.5
C(13)-C(16)-H(16)	114.5
N(2)-C(17)-C(16)	104.48(13)
N(2)-C(17)-H(17A)	110.9
C(16)-C(17)-H(17A)	110.9
N(2)-C(17)-H(17B)	110.9
C(16)-C(17)-H(17B)	110.9
H(17A)-C(17)-H(17B)	108.9
C(23)-C(18)-C(19)	118.27(16)
C(23)-C(18)-C(15)	122.38(15)
C(19)-C(18)-C(15)	119.33(15)
C(20)-C(19)-C(18)	121.10(17)
C(20)-C(19)-H(19)	119.5
C(18)-C(19)-H(19)	119.5
C(19)-C(20)-C(21)	120.30(17)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(22)-C(21)-C(20)	119.16(17)
C(22)-C(21)-H(21)	120.4
C(20)-C(21)-H(21)	120.4
C(21)-C(22)-C(23)	120.47(17)
C(21)-C(22)-H(22)	119.8
C(23)-C(22)-H(22)	119.8
C(18)-C(23)-C(22)	120.69(17)
C(18)-C(23)-H(23)	119.7

C(22)-C(23)-H(23) 119.7

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($A^2 \times 10^3$) for **11h**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	40(1)	24(1)	34(1)	0(1)	17(1)	-2(1)
N(1)	30(1)	17(1)	23(1)	-1(1)	10(1)	-2(1)
N(2)	21(1)	18(1)	20(1)	0(1)	2(1)	-3(1)
F(1)	56(1)	31(1)	49(1)	-9(1)	27(1)	-20(1)
F(2)	38(1)	19(1)	111(2)	-6(1)	-15(1)	2(1)
F(3)	70(1)	33(1)	29(1)	-10(1)	6(1)	-15(1)
F(1A)	118(4)	22(2)	31(2)	-1(2)	20(2)	-9(2)
F(2A)	70(3)	26(2)	52(3)	-10(2)	19(2)	-1(2)
F(3A)	61(3)	37(3)	76(4)	-5(3)	-24(3)	-11(2)
F(4)	27(1)	21(1)	36(1)	0(1)	2(1)	7(1)
F(5)	22(1)	26(1)	31(1)	-2(1)	1(1)	-1(1)

F(6)	29(1)	23(1)	30(1)	4(1)	2(1)	8(1)
F(7)	24(1)	31(1)	34(1)	-3(1)	-1(1)	-3(1)
C(1)	39(1)	23(1)	29(1)	-3(1)	3(1)	-1(1)
C(2)	26(1)	22(1)	22(1)	0(1)	5(1)	-1(1)
C(3)	27(1)	20(1)	22(1)	1(1)	5(1)	3(1)
C(4)	22(1)	22(1)	19(1)	-1(1)	3(1)	-2(1)
C(5)	27(1)	18(1)	19(1)	1(1)	7(1)	-1(1)
C(6)	26(1)	21(1)	19(1)	3(1)	4(1)	4(1)
C(7)	24(1)	25(1)	20(1)	-1(1)	2(1)	-2(1)
C(8)	31(1)	21(1)	20(1)	4(1)	6(1)	0(1)
C(9)	29(1)	19(1)	21(1)	-1(1)	6(1)	0(1)
C(10)	32(1)	31(1)	25(1)	1(1)	0(1)	3(1)
C(11)	32(1)	26(1)	25(1)	-4(1)	7(1)	-1(1)
C(12)	29(1)	21(1)	28(1)	-2(1)	3(1)	-6(1)
C(13)	30(1)	19(1)	30(1)	2(1)	6(1)	-6(1)
C(14)	26(1)	28(1)	33(1)	0(1)	8(1)	-3(1)
C(15)	28(1)	24(1)	22(1)	3(1)	6(1)	-2(1)
C(16)	26(1)	21(1)	26(1)	2(1)	3(1)	2(1)
C(17)	22(1)	21(1)	26(1)	-1(1)	3(1)	1(1)
C(18)	26(1)	25(1)	15(1)	-1(1)	6(1)	0(1)
C(19)	25(1)	33(1)	24(1)	-4(1)	5(1)	1(1)
C(20)	32(1)	36(1)	25(1)	-9(1)	8(1)	-7(1)
C(21)	48(1)	28(1)	22(1)	-6(1)	13(1)	-8(1)
C(22)	44(1)	26(1)	21(1)	-2(1)	10(1)	4(1)
C(23)	29(1)	27(1)	21(1)	0(1)	6(1)	1(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 11h.

	x	y	z	U(eq)
H(1N)	8400(40)	3440(9)	7701(17)	38(6)
H(10A)	10840	3868	9177	45
H(10B)	9590	3901	10109	45
H(10C)	10585	4431	9705	45
H(11A)	6928	4931	9298	41
H(11B)	6248	4451	9961	41
H(11C)	4823	4576	8887	41
H(12A)	11147	4723	8090	32
H(12B)	9143	5125	8140	32
H(13)	9785	5295	6501	32
H(14A)	11421	4617	5665	34
H(14B)	11090	4182	6520	34
H(15)	7956	4508	4827	29
H(16)	6133	5017	5831	29
H(17A)	5262	4744	7354	28
H(17B)	5335	4159	6860	28

H(19)	4135	3960	4912	33
H(20)	2847	3088	4677	37
H(21)	5247	2363	5025	38
H(22)	8950	2525	5596	36
H(23)	10245	3401	5841	30

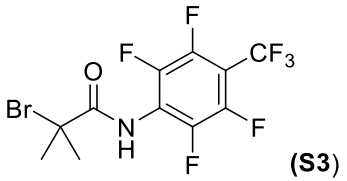
Torsion angles [°] for 11h.

F(3A)-C(1)-C(2)-C(3)	-160.0(4)
F(1A)-C(1)-C(2)-C(3)	61.7(4)
F(2)-C(1)-C(2)-C(3)	1.3(3)
F(3)-C(1)-C(2)-C(3)	-124.1(2)
F(1)-C(1)-C(2)-C(3)	121.62(19)
F(2A)-C(1)-C(2)-C(3)	-46.7(3)
F(3A)-C(1)-C(2)-C(7)	20.2(5)
F(1A)-C(1)-C(2)-C(7)	-118.1(4)
F(2)-C(1)-C(2)-C(7)	-178.5(2)
F(3)-C(1)-C(2)-C(7)	56.1(2)
F(1)-C(1)-C(2)-C(7)	-58.2(2)
F(2A)-C(1)-C(2)-C(7)	133.5(3)
C(7)-C(2)-C(3)-F(4)	177.89(15)
C(1)-C(2)-C(3)-F(4)	-1.9(3)
C(7)-C(2)-C(3)-C(4)	-1.0(3)
C(1)-C(2)-C(3)-C(4)	179.22(16)
F(4)-C(3)-C(4)-F(5)	0.9(2)
C(2)-C(3)-C(4)-F(5)	179.76(15)
F(4)-C(3)-C(4)-C(5)	-178.44(15)
C(2)-C(3)-C(4)-C(5)	0.4(3)
F(5)-C(4)-C(5)-C(6)	-178.63(14)

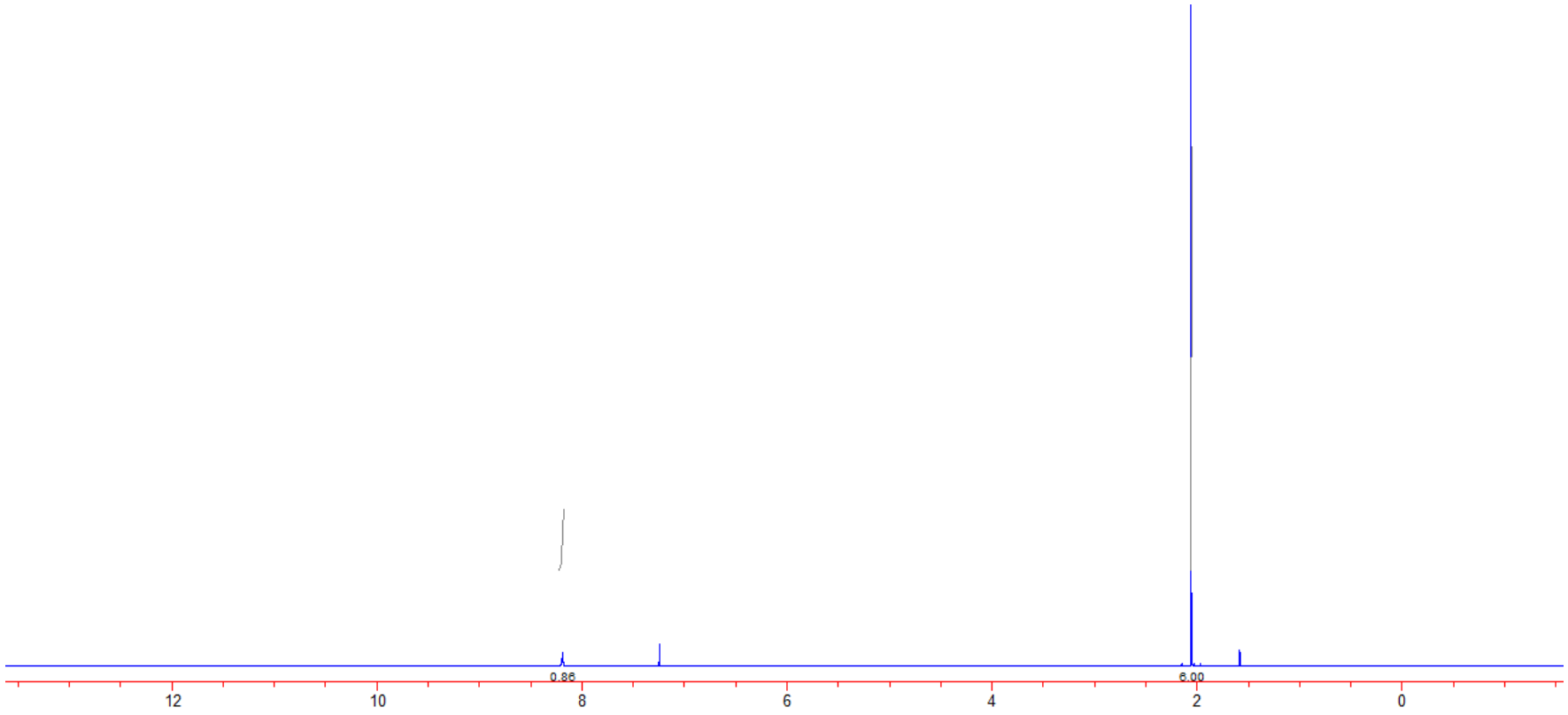
C(3)-C(4)-C(5)-C(6)	0.7(2)
F(5)-C(4)-C(5)-N(1)	2.5(2)
C(3)-C(4)-C(5)-N(1)	-178.20(15)
C(8)-N(1)-C(5)-C(4)	-118.70(19)
C(8)-N(1)-C(5)-C(6)	62.5(2)
C(4)-C(5)-C(6)-F(6)	-178.26(14)
N(1)-C(5)-C(6)-F(6)	0.6(2)
C(4)-C(5)-C(6)-C(7)	-1.3(2)
N(1)-C(5)-C(6)-C(7)	177.56(16)
F(6)-C(6)-C(7)-F(7)	-0.4(2)
C(5)-C(6)-C(7)-F(7)	-177.37(15)
F(6)-C(6)-C(7)-C(2)	177.79(15)
C(5)-C(6)-C(7)-C(2)	0.8(3)
C(3)-C(2)-C(7)-F(7)	178.49(15)
C(1)-C(2)-C(7)-F(7)	-1.7(3)
C(3)-C(2)-C(7)-C(6)	0.3(3)
C(1)-C(2)-C(7)-C(6)	-179.83(16)
C(5)-N(1)-C(8)-O(1)	-3.9(3)
C(5)-N(1)-C(8)-C(9)	172.84(14)
C(12)-N(2)-C(9)-C(11)	70.19(19)
C(17)-N(2)-C(9)-C(11)	-53.04(18)
C(12)-N(2)-C(9)-C(10)	-53.86(18)
C(17)-N(2)-C(9)-C(10)	-177.09(13)
C(12)-N(2)-C(9)-C(8)	-168.94(14)
C(17)-N(2)-C(9)-C(8)	67.83(16)

O(1)-C(8)-C(9)-N(2)	-143.79(16)
N(1)-C(8)-C(9)-N(2)	39.51(18)
O(1)-C(8)-C(9)-C(11)	-18.8(2)
N(1)-C(8)-C(9)-C(11)	164.45(14)
O(1)-C(8)-C(9)-C(10)	98.95(19)
N(1)-C(8)-C(9)-C(10)	-77.75(17)
C(9)-N(2)-C(12)-C(13)	-171.52(13)
C(17)-N(2)-C(12)-C(13)	-43.48(16)
N(2)-C(12)-C(13)-C(14)	-68.10(17)
N(2)-C(12)-C(13)-C(16)	28.94(17)
C(12)-C(13)-C(14)-C(15)	114.68(15)
C(16)-C(13)-C(14)-C(15)	7.52(13)
C(13)-C(14)-C(15)-C(18)	-132.01(16)
C(13)-C(14)-C(15)-C(16)	-7.55(13)
C(18)-C(15)-C(16)-C(17)	28.3(2)
C(14)-C(15)-C(16)-C(17)	-97.39(16)
C(18)-C(15)-C(16)-C(13)	133.18(15)
C(14)-C(15)-C(16)-C(13)	7.47(13)
C(12)-C(13)-C(16)-C(17)	-4.54(17)
C(14)-C(13)-C(16)-C(17)	110.61(14)
C(12)-C(13)-C(16)-C(15)	-122.61(14)
C(14)-C(13)-C(16)-C(15)	-7.46(13)
C(12)-N(2)-C(17)-C(16)	41.16(16)
C(9)-N(2)-C(17)-C(16)	171.04(13)
C(15)-C(16)-C(17)-N(2)	74.66(17)

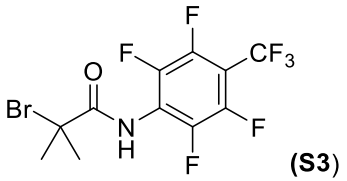
C(13)-C(16)-C(17)-N(2)	-21.48(16)
C(14)-C(15)-C(18)-C(23)	-14.8(2)
C(16)-C(15)-C(18)-C(23)	-124.14(18)
C(14)-C(15)-C(18)-C(19)	166.79(16)
C(16)-C(15)-C(18)-C(19)	57.5(2)
C(23)-C(18)-C(19)-C(20)	-0.3(3)
C(15)-C(18)-C(19)-C(20)	178.11(16)
C(18)-C(19)-C(20)-C(21)	0.2(3)
C(19)-C(20)-C(21)-C(22)	-0.2(3)
C(20)-C(21)-C(22)-C(23)	0.4(3)
C(19)-C(18)-C(23)-C(22)	0.5(3)
C(15)-C(18)-C(23)-C(22)	-177.90(16)
C(21)-C(22)-C(23)-C(18)	-0.5(3)



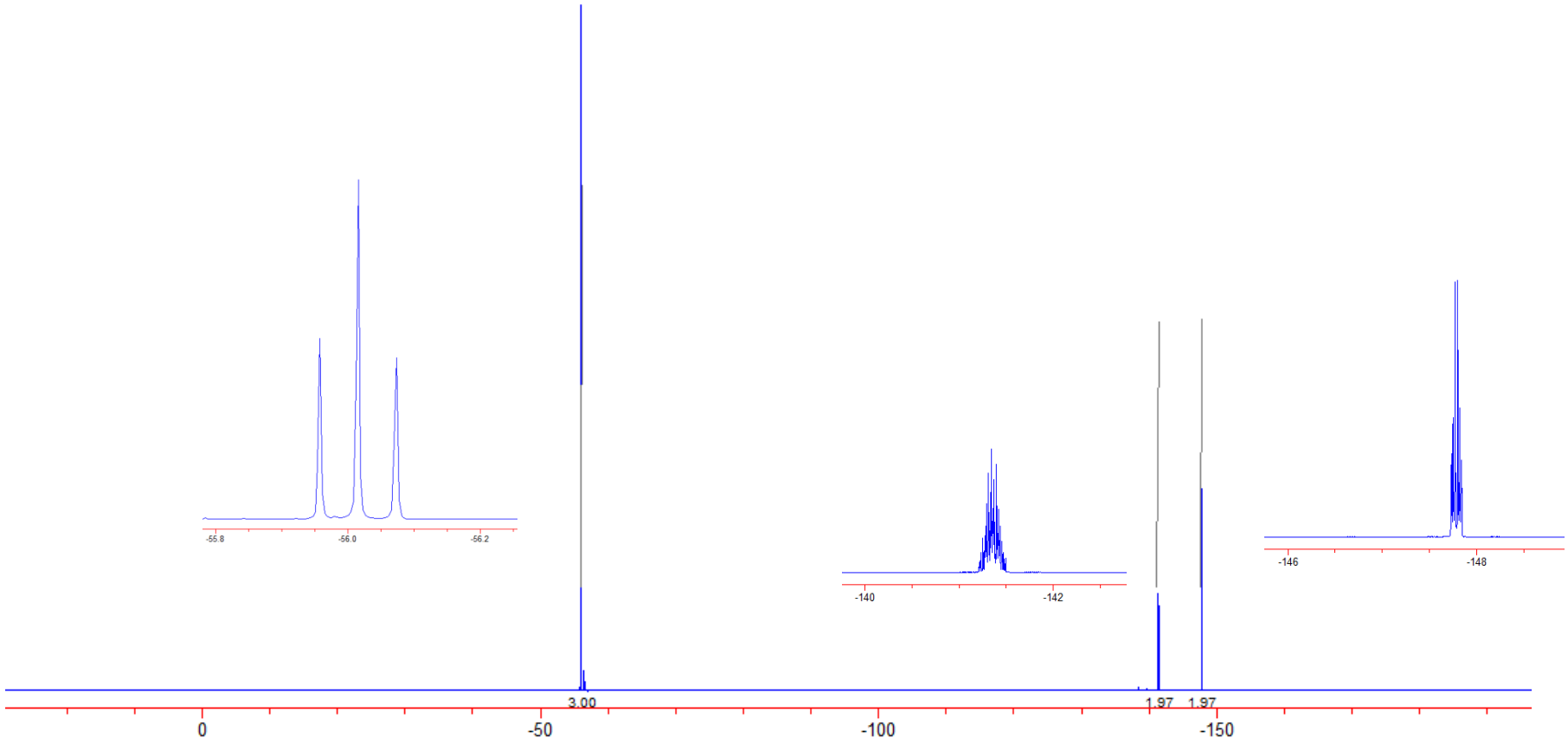
(S3)



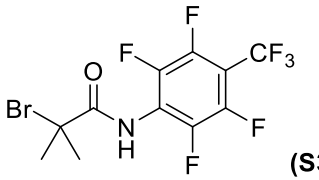
^{1}H NMR Spectrum in $CDCl_3$



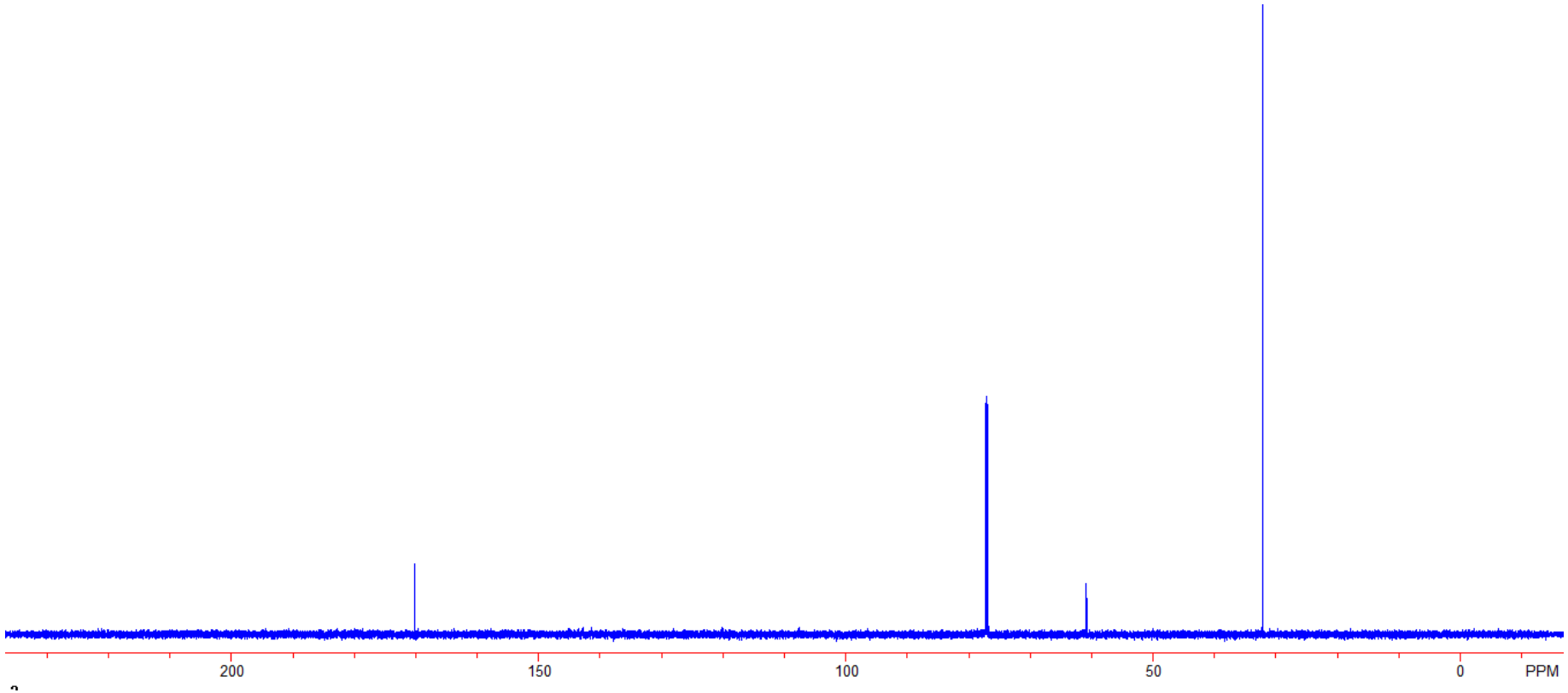
(S3)



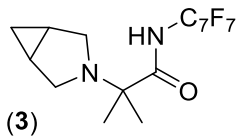
^{19}F NMR Spectrum in $CDCl_3$



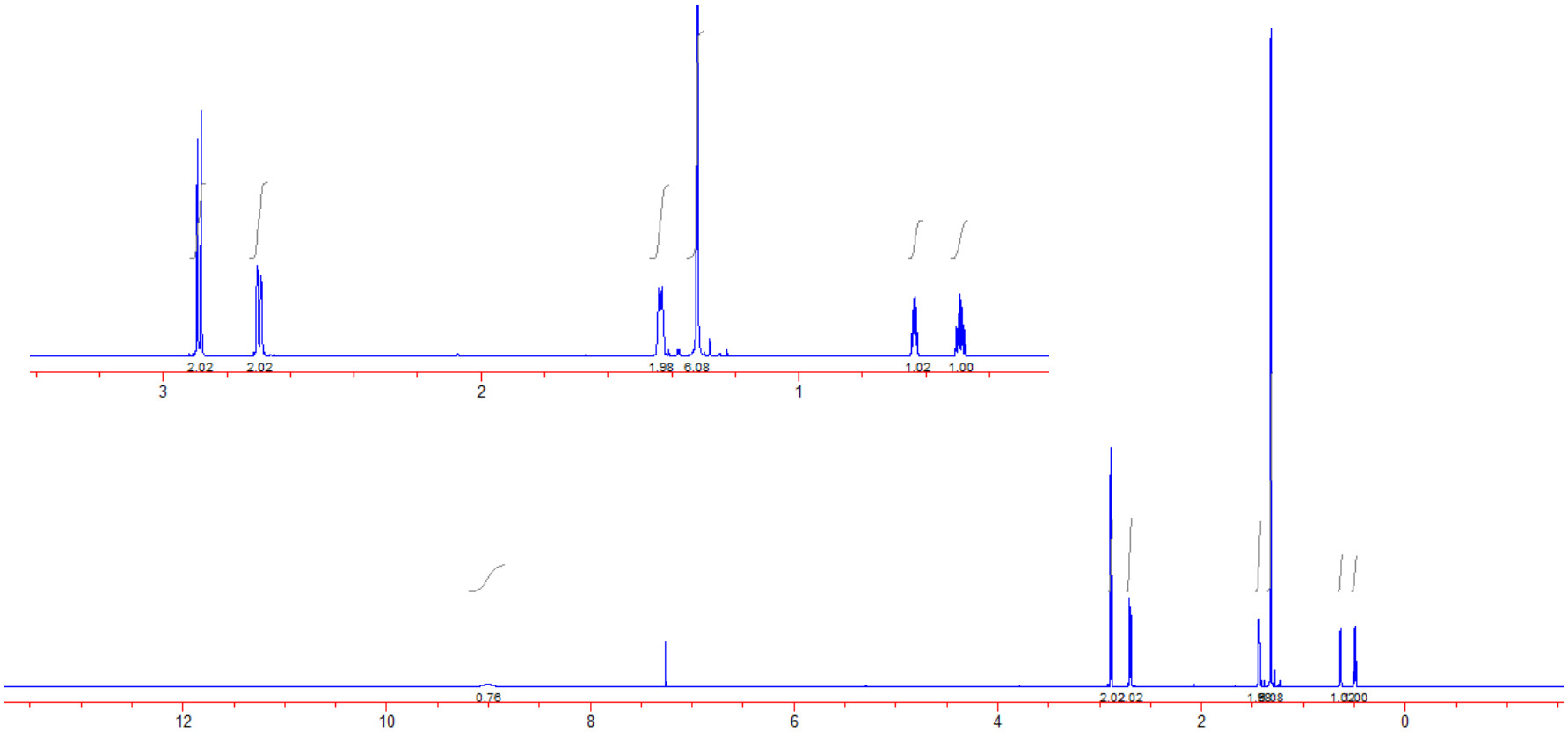
(S3)



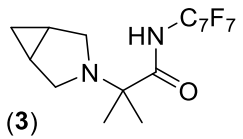
^{13}C NMR Spectrum in $CDCl_3$



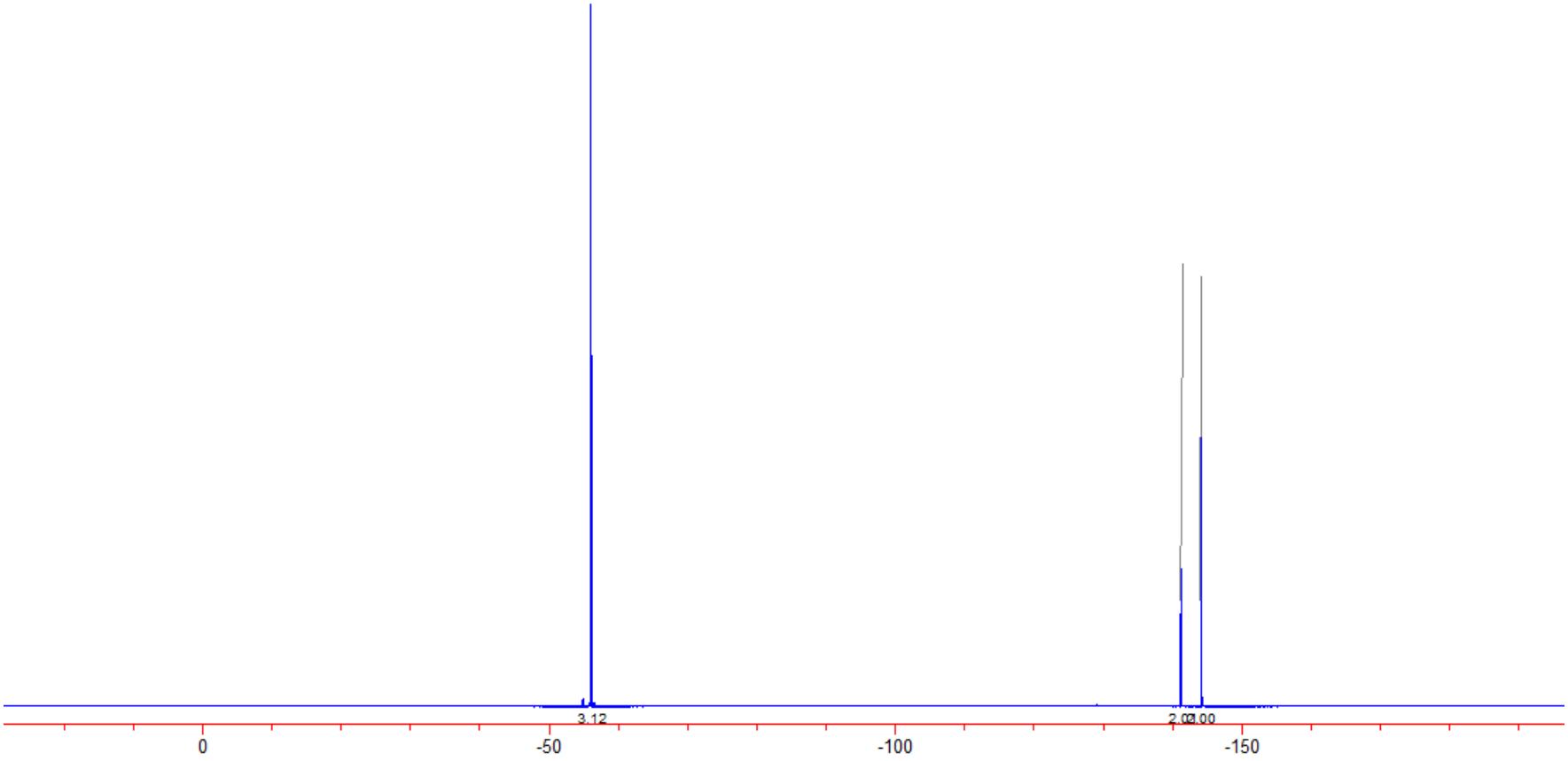
(**3**)



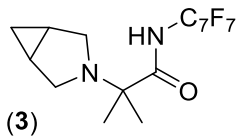
^{1}H NMR Spectrum in $CDCl_3$



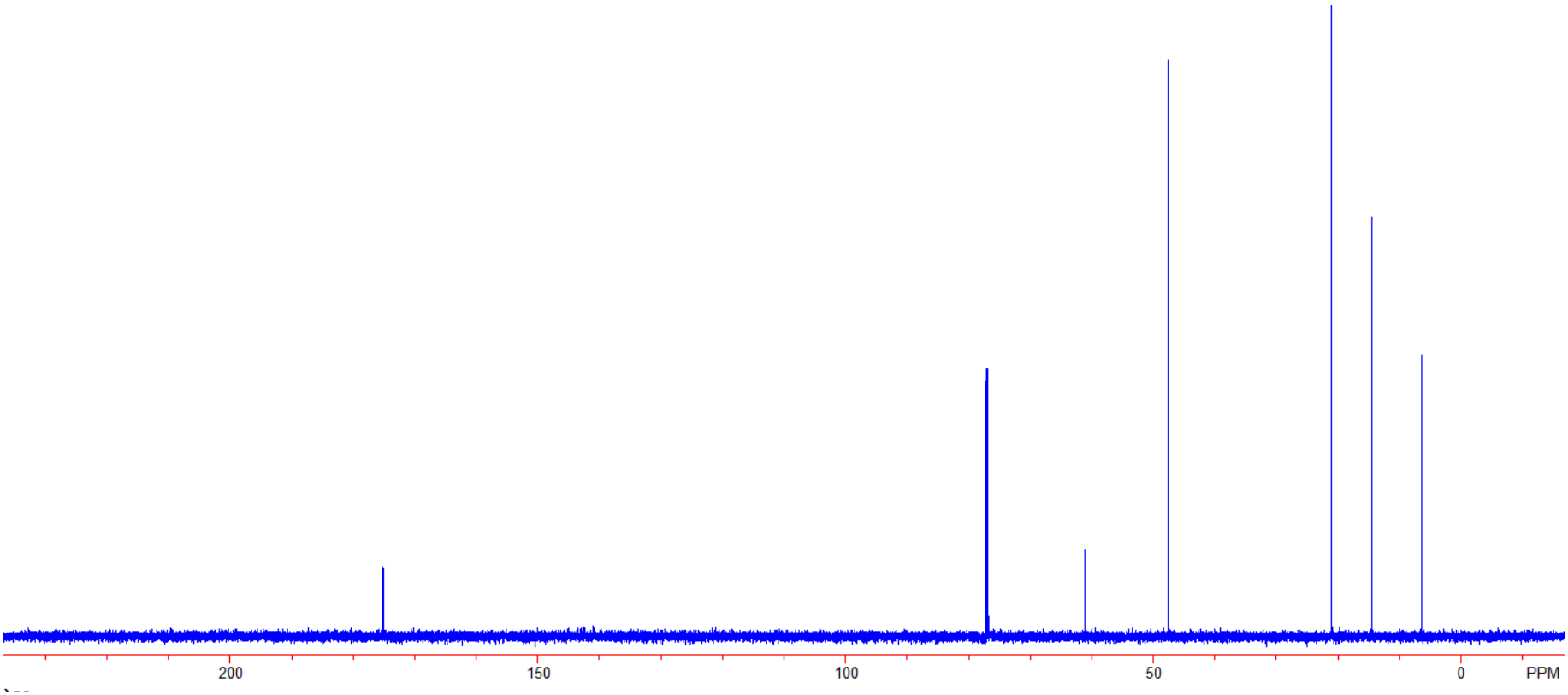
(**3**)



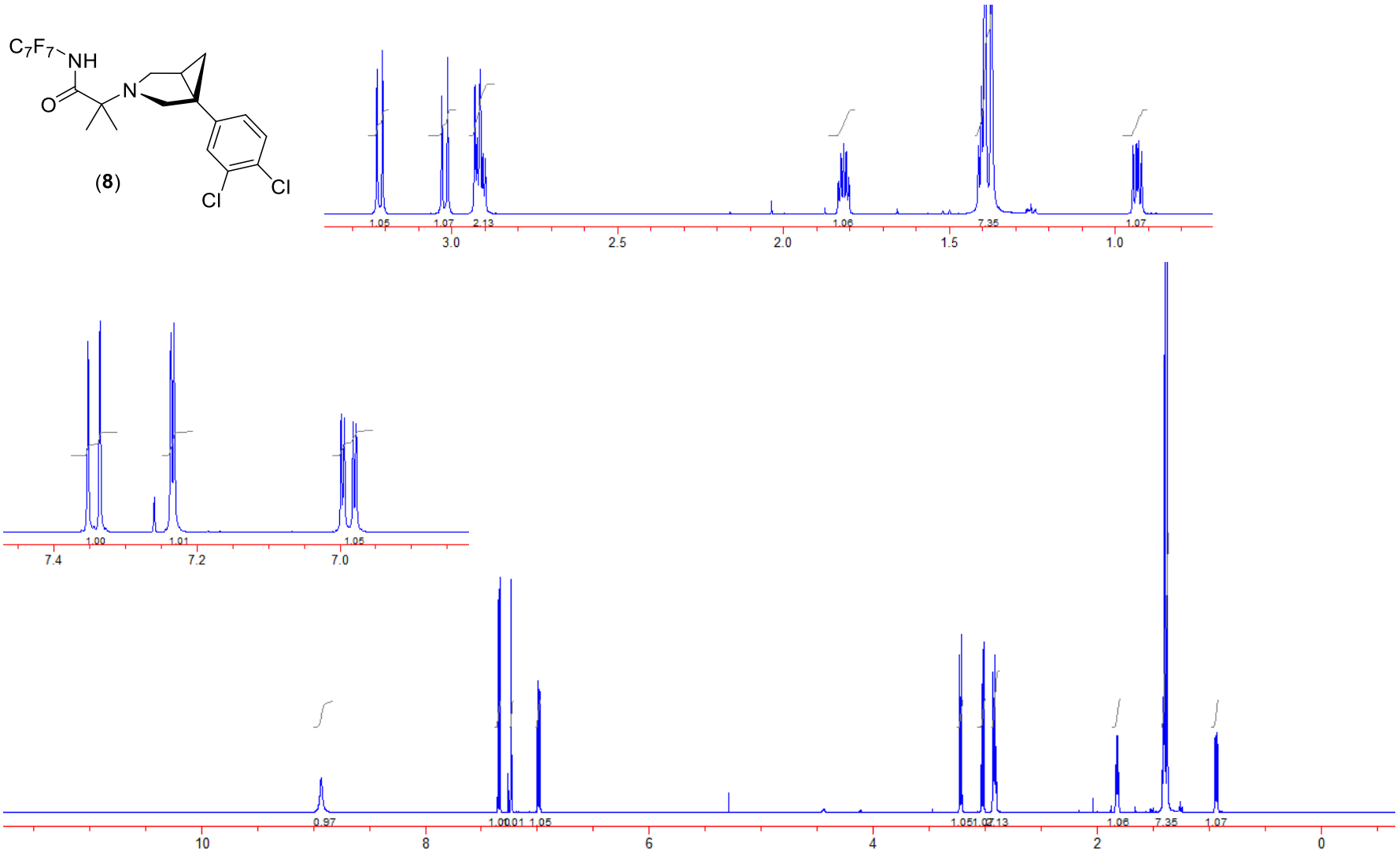
^{19}F NMR Spectrum in $CDCl_3$



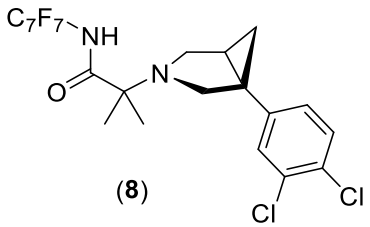
(**3**)



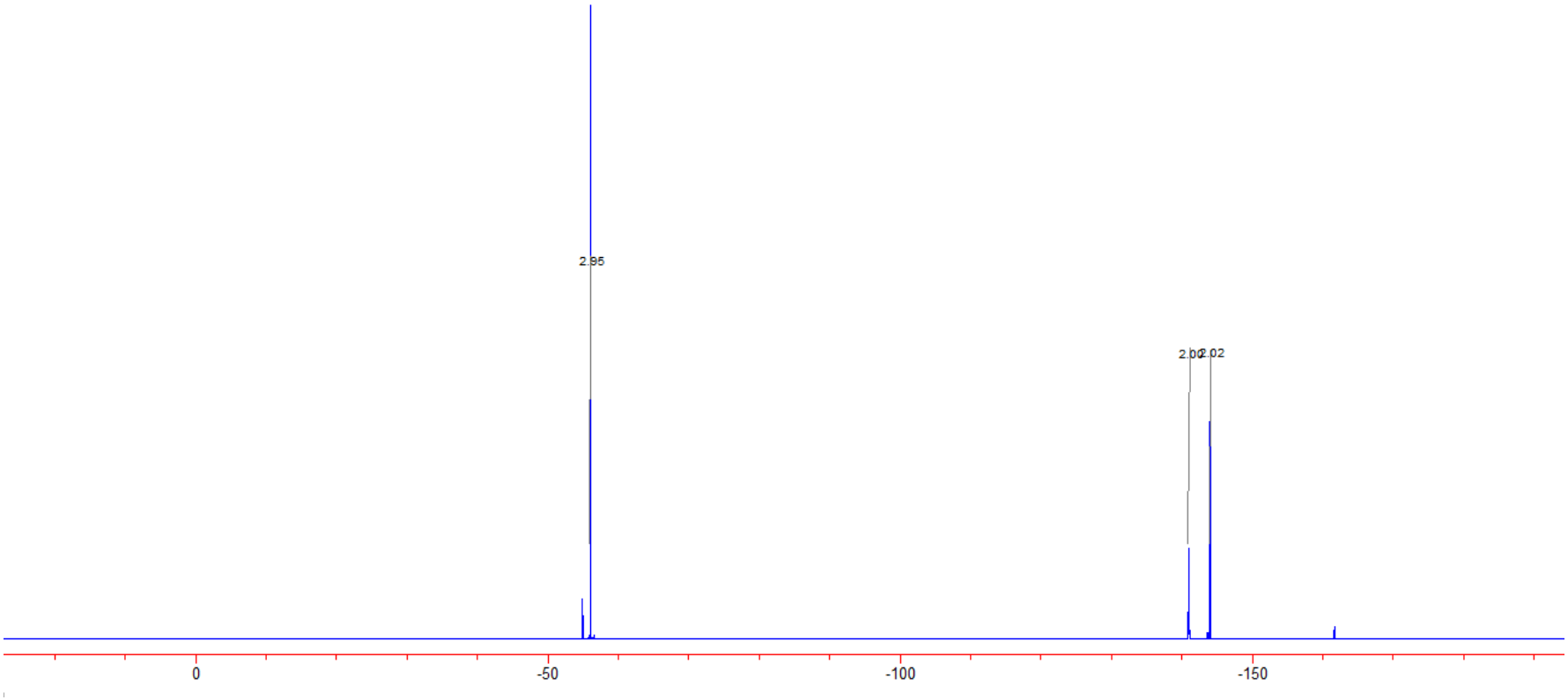
^{13}C NMR Spectrum in $CDCl_3$



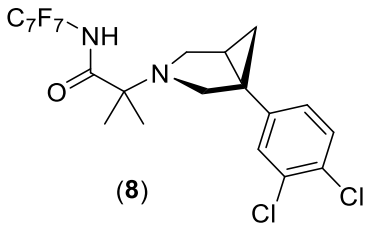
^{1}H NMR Spectrum in $CDCl_3$



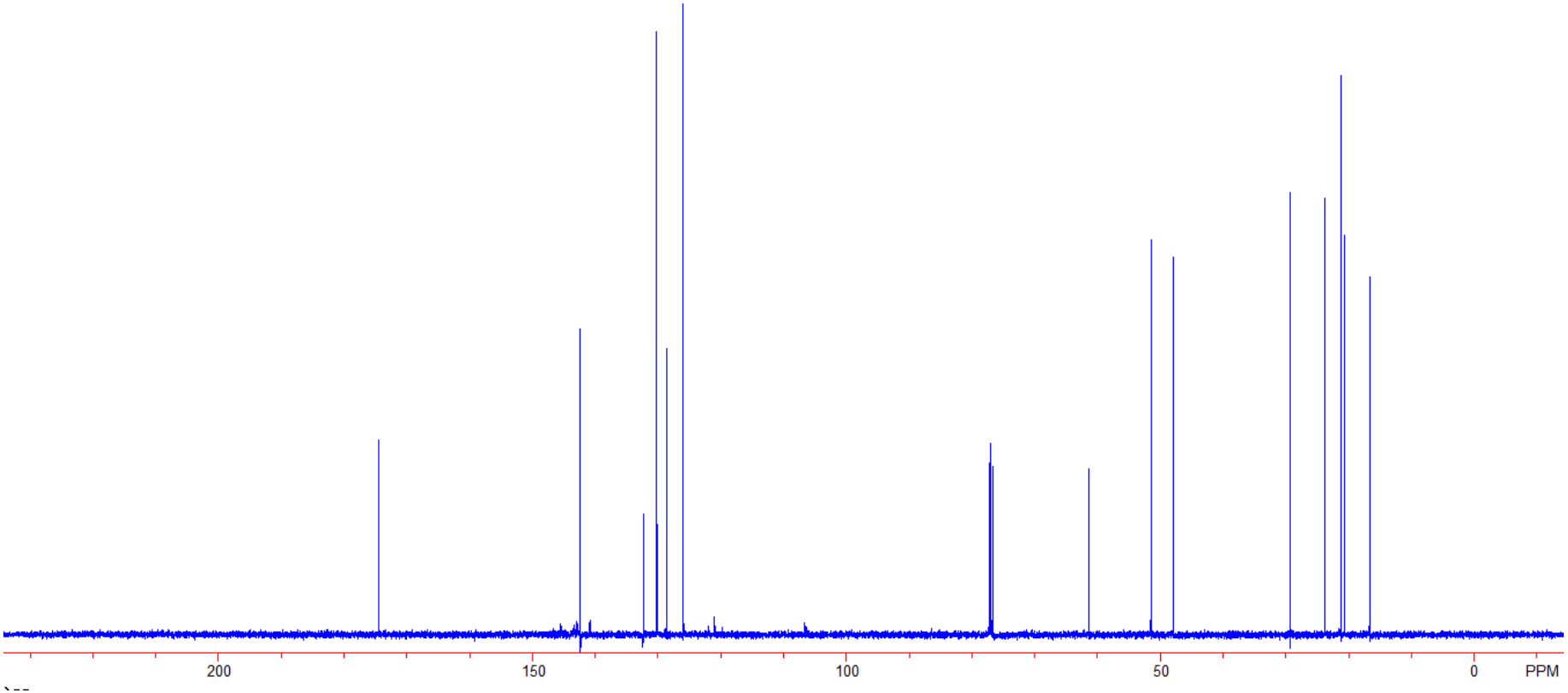
(**8**)



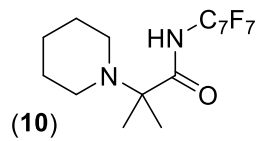
^{19}F NMR Spectrum in $CDCl_3$



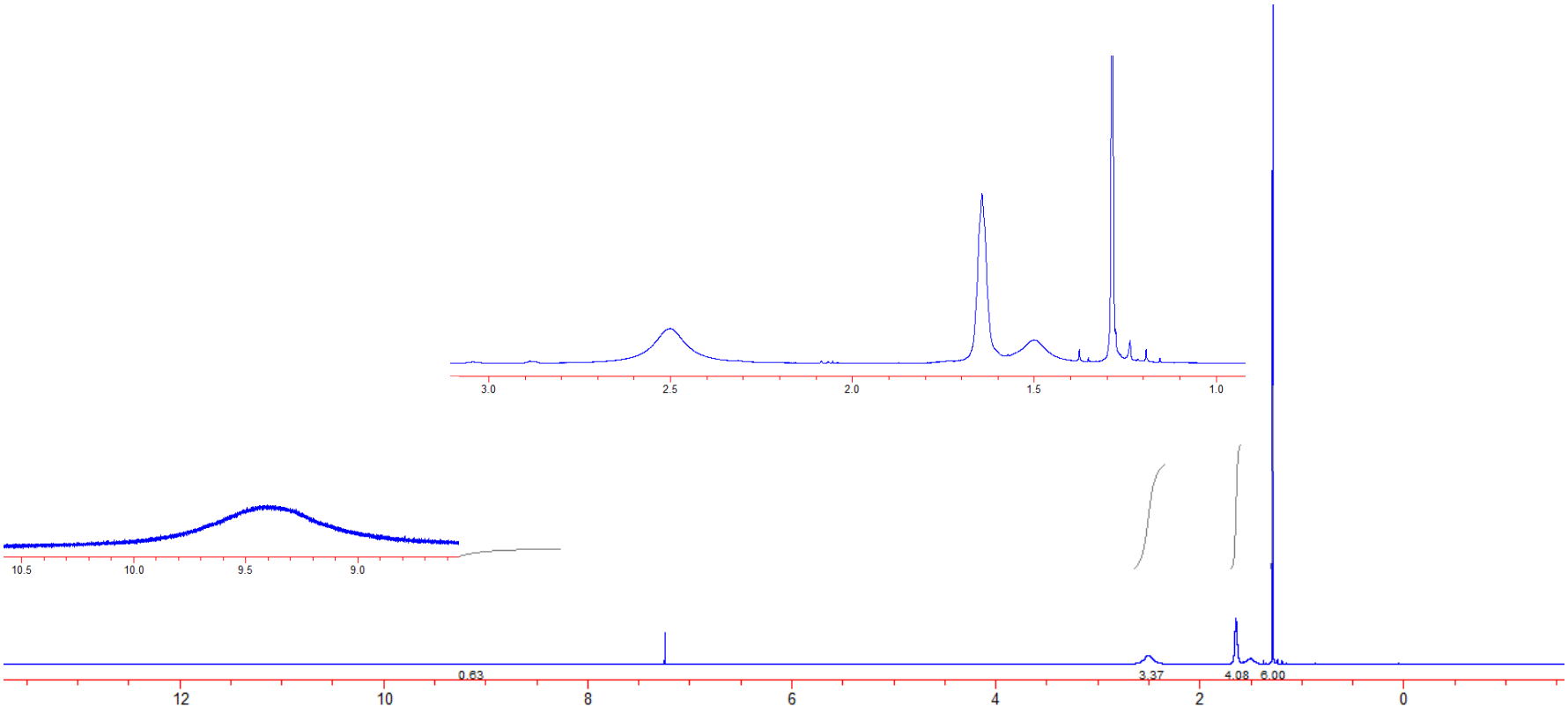
(**8**)



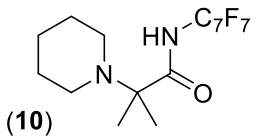
^{13}C NMR Spectrum in $CDCl_3$



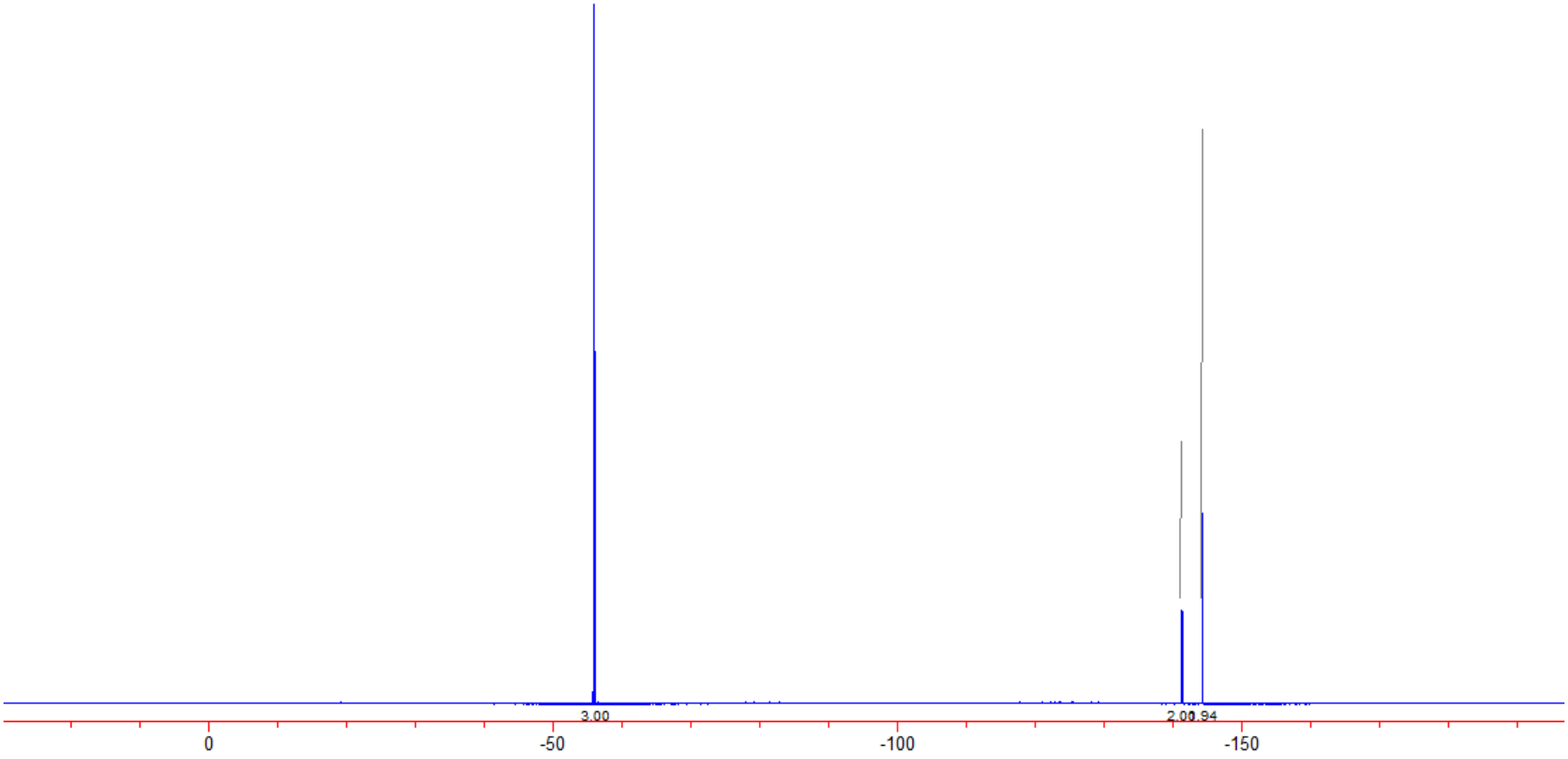
(**10**)



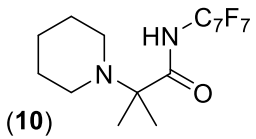
^{1}H NMR Spectrum in $CDCl_3$



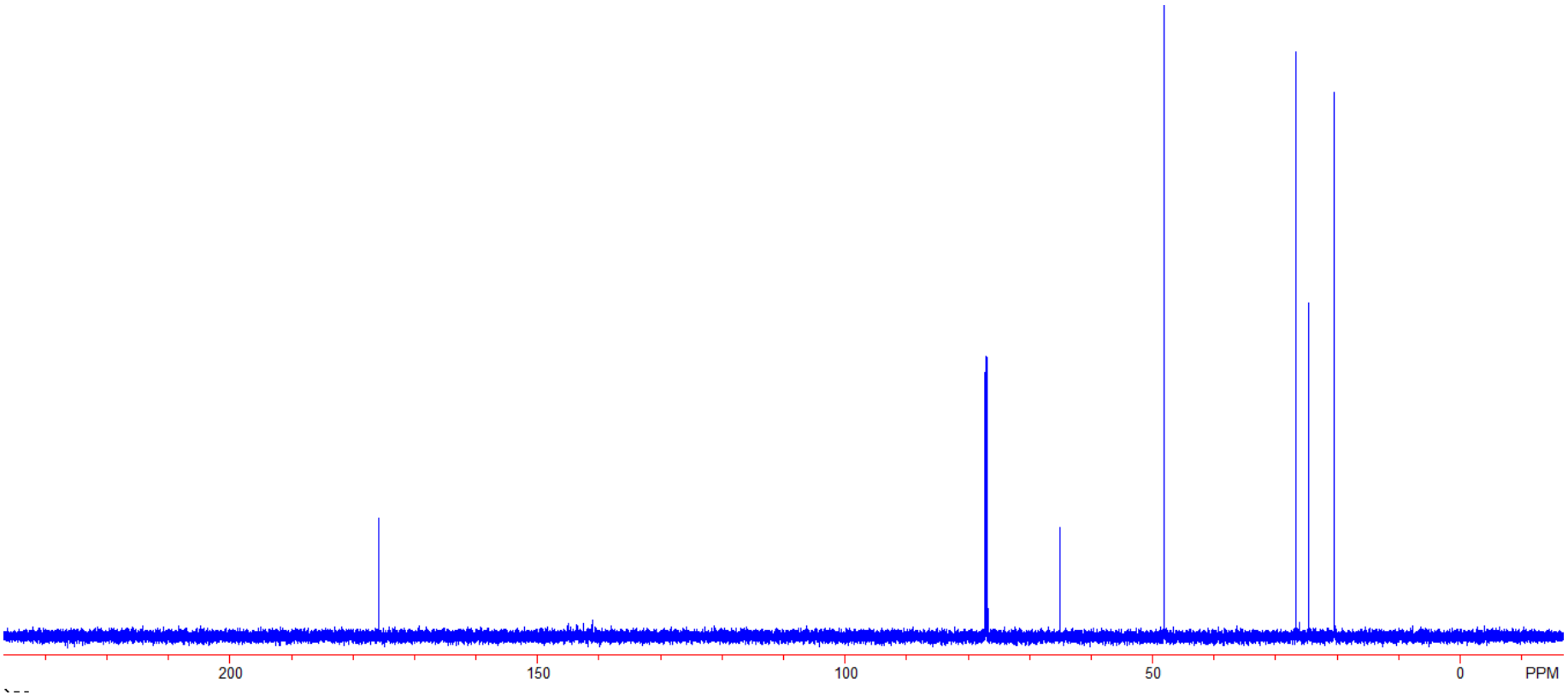
(**10**)



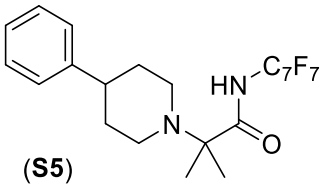
^{19}F NMR Spectrum in $CDCl_3$



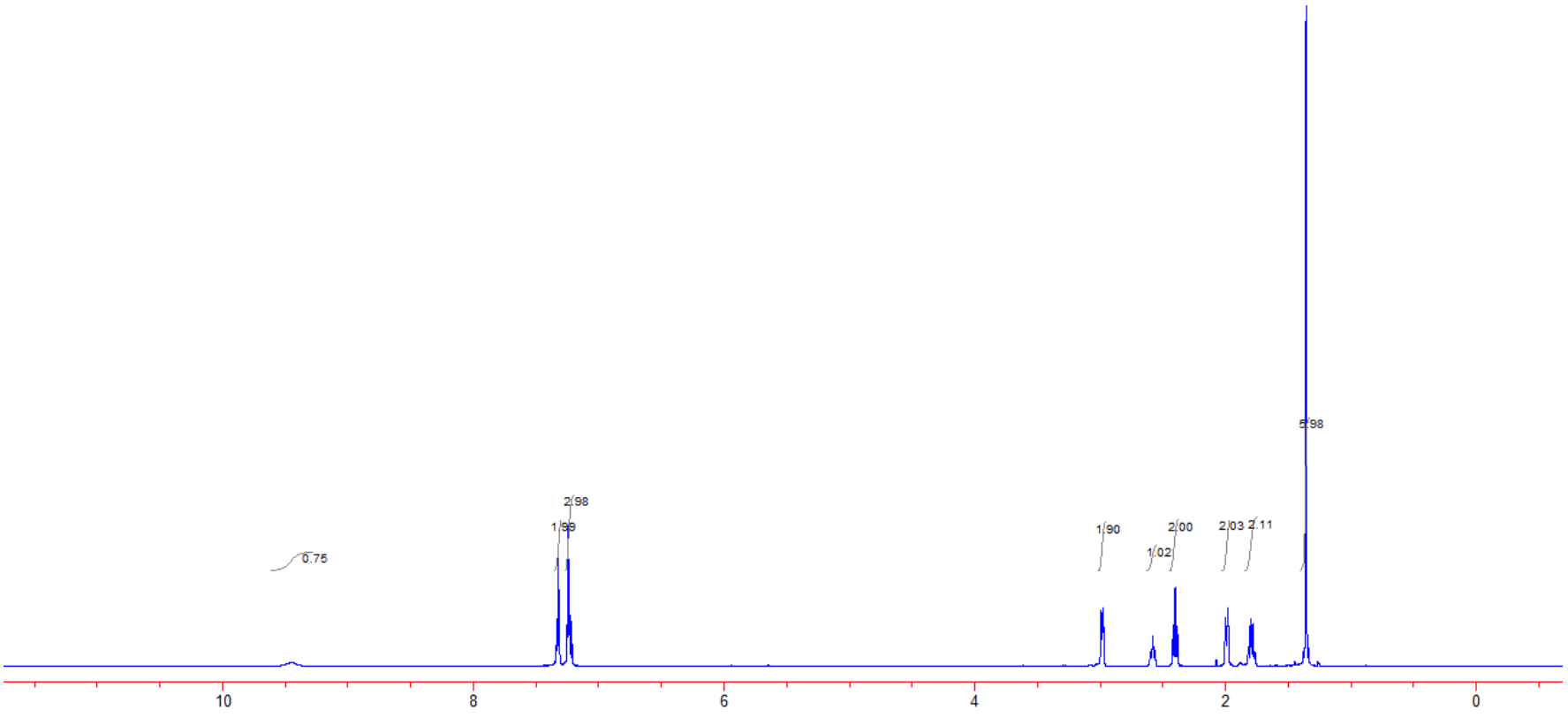
(**10**)



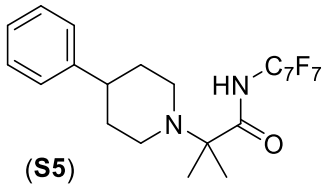
^{13}C NMR Spectrum in $CDCl_3$



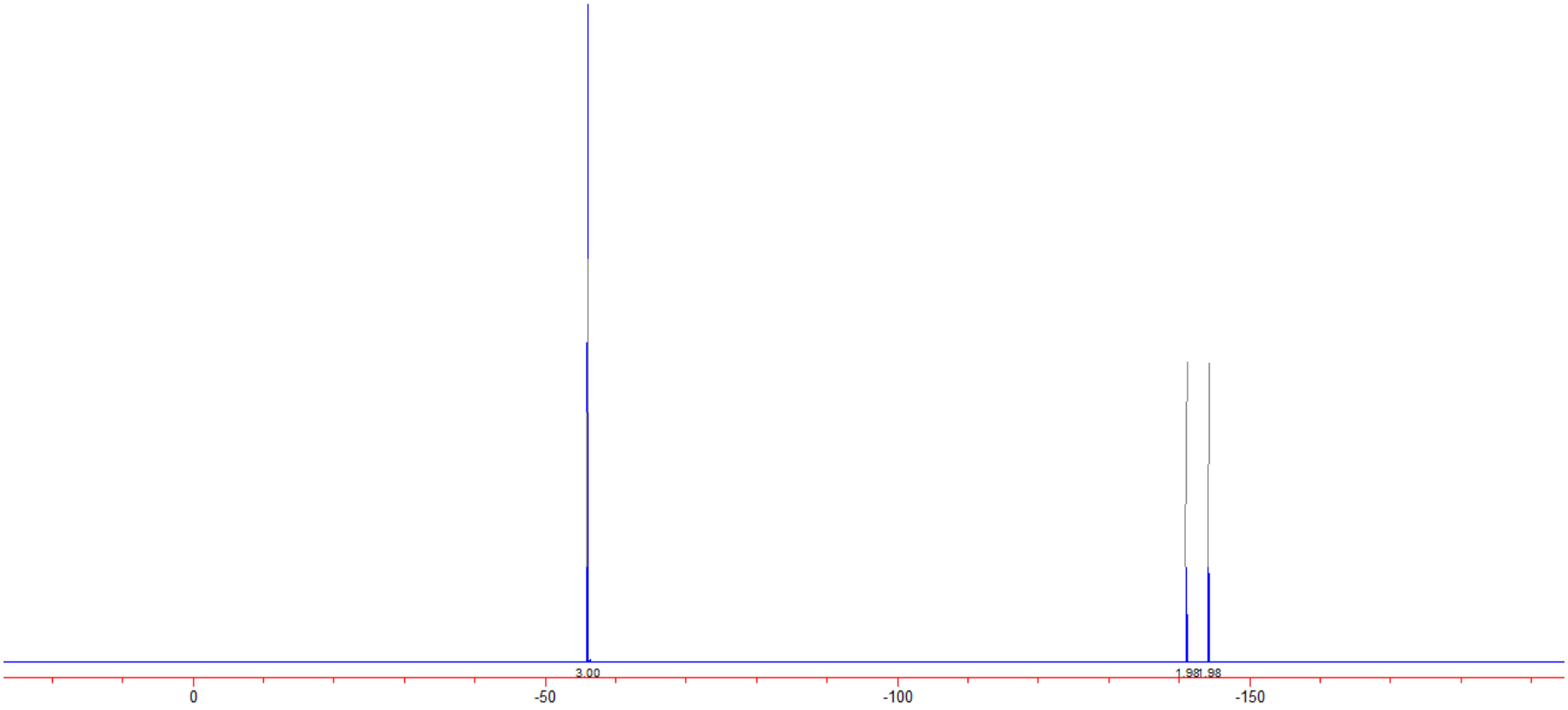
(**S5**)



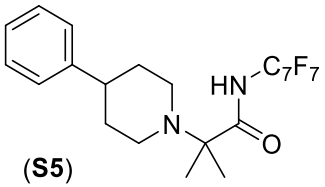
^{1}H NMR Spectrum in $CDCl_3$



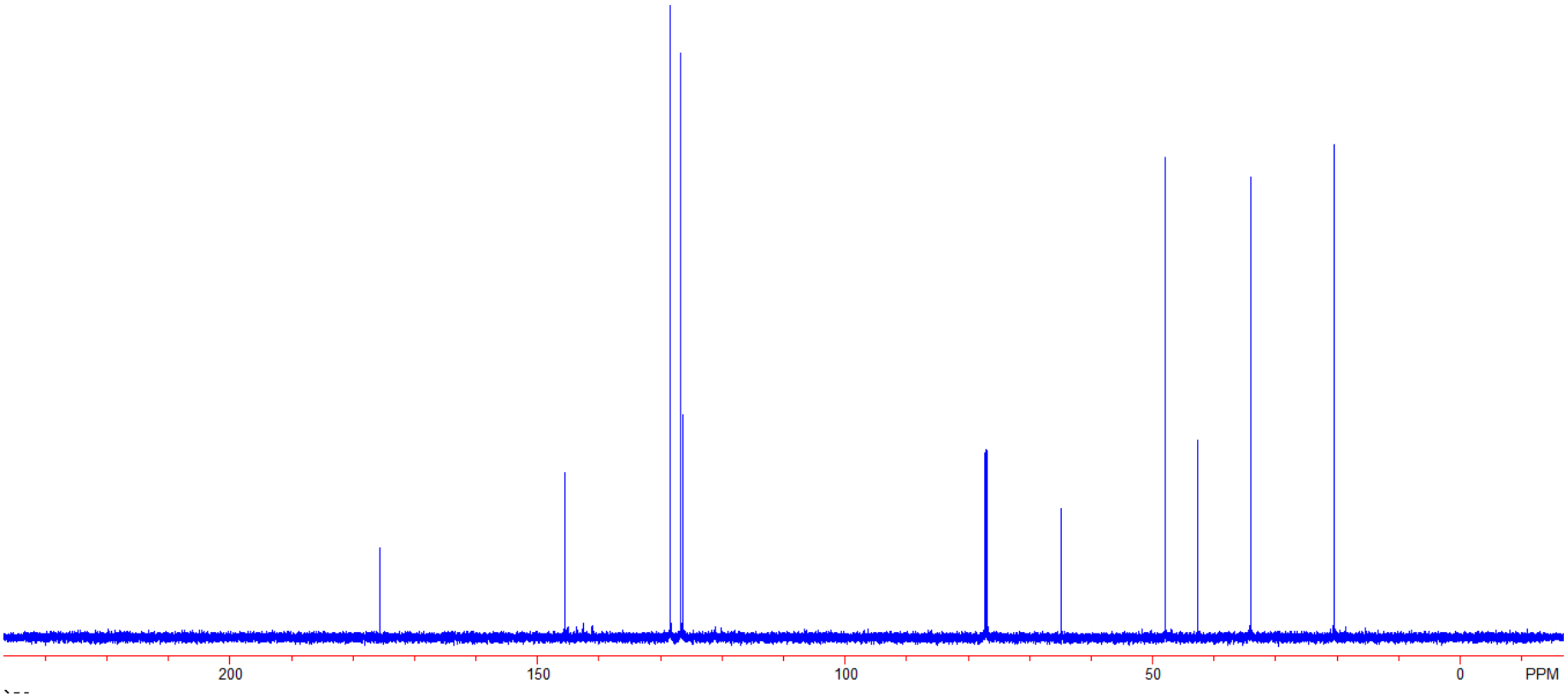
(**S5**)



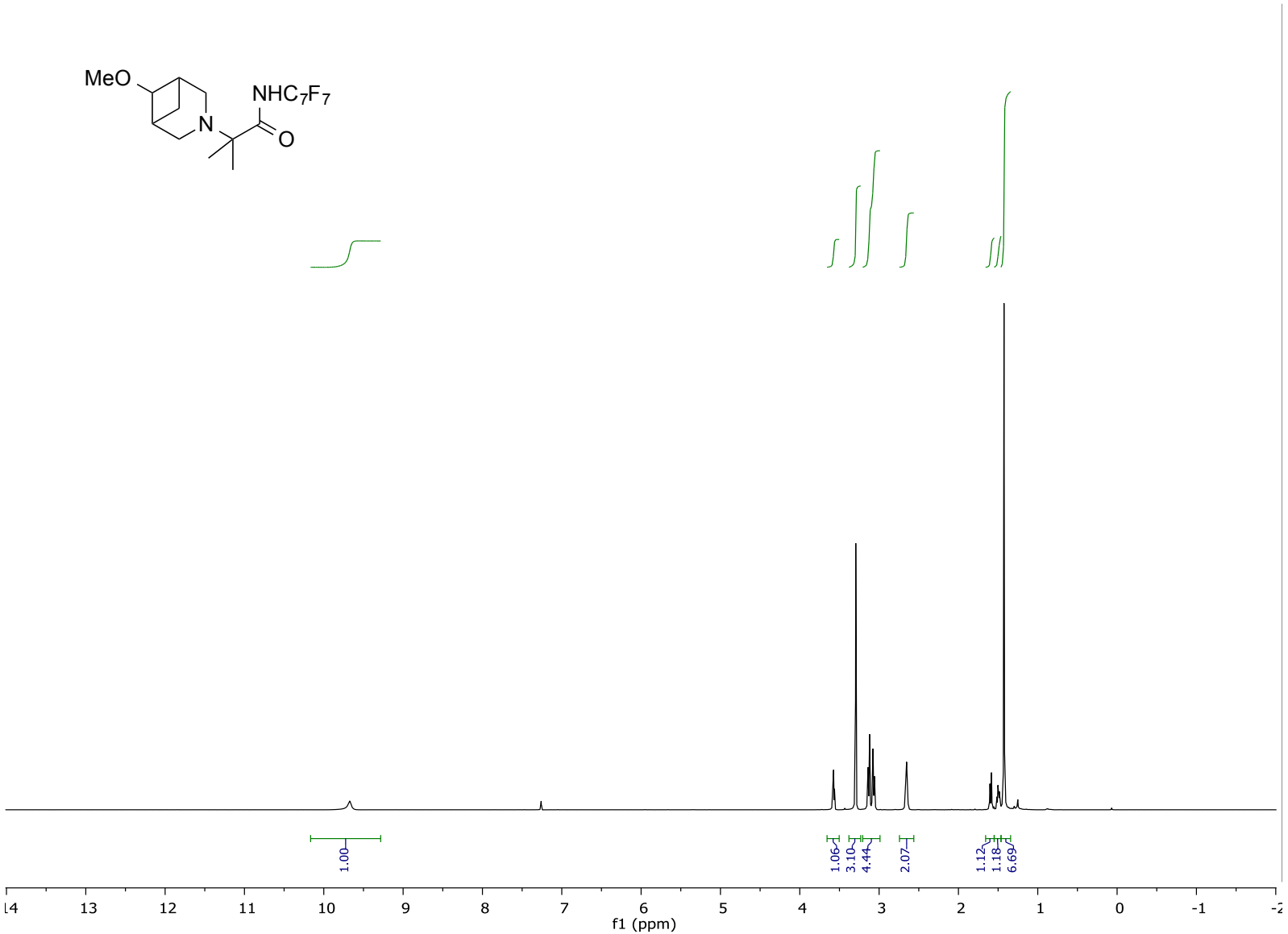
^{19}F NMR Spectrum in $CDCl_3$



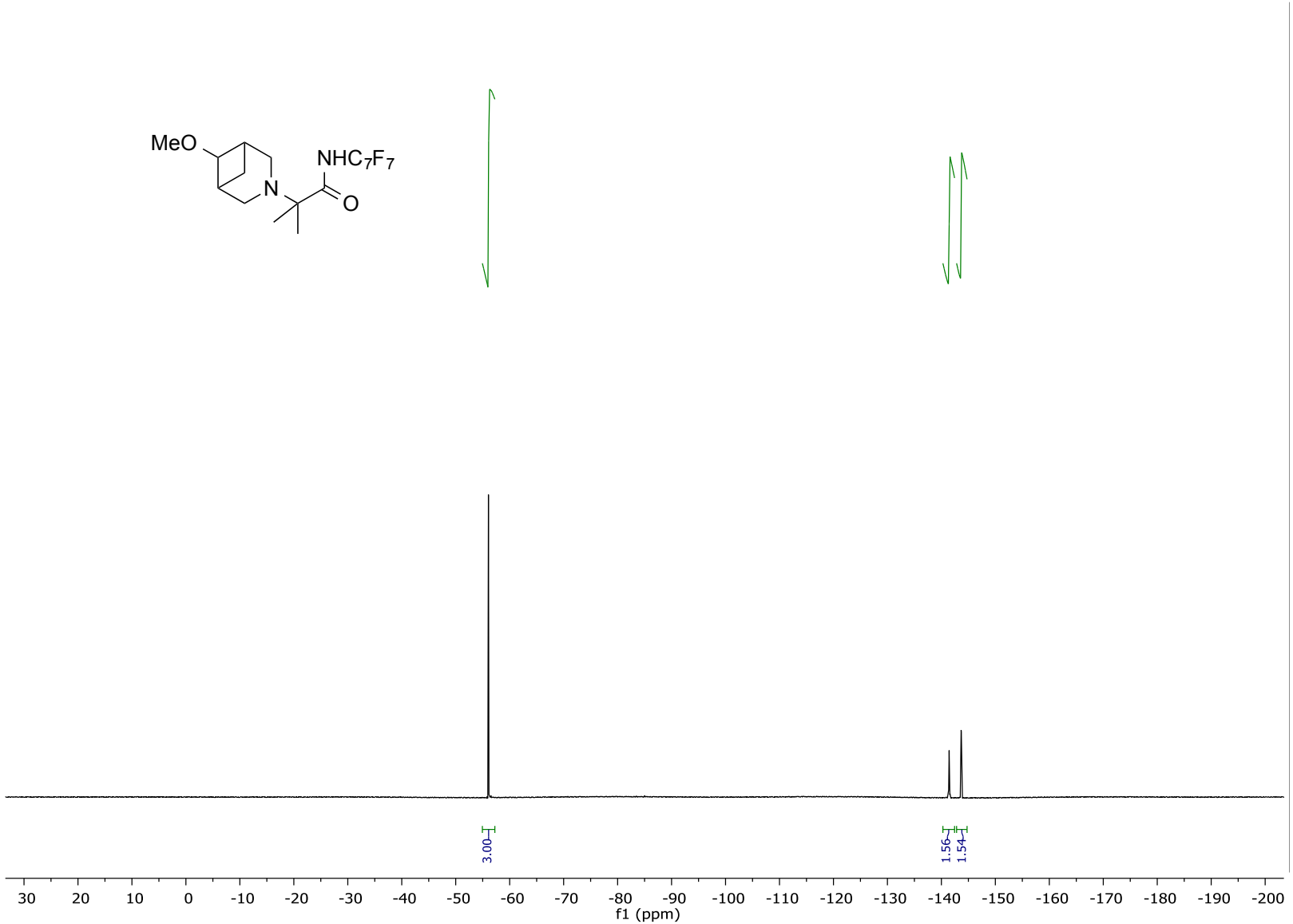
(**S5**)



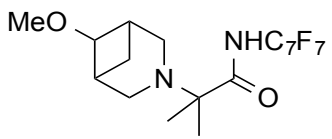
^{13}C NMR Spectrum in $CDCl_3$

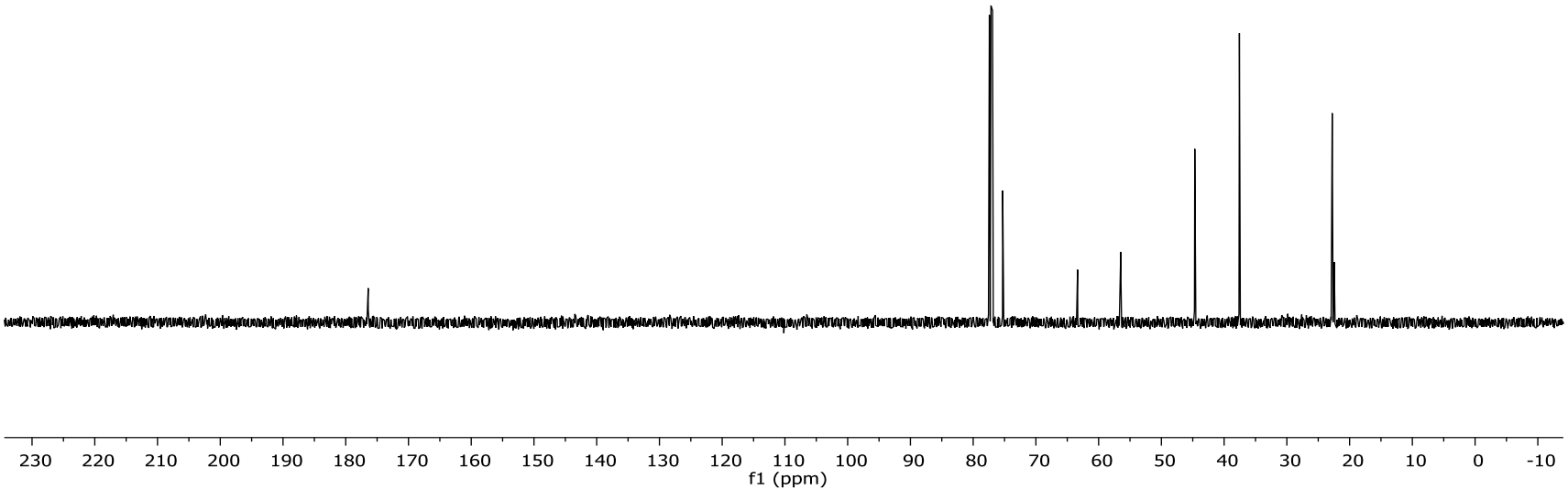


^{1}H NMR Spectrum of **S6** in $CDCl_3$

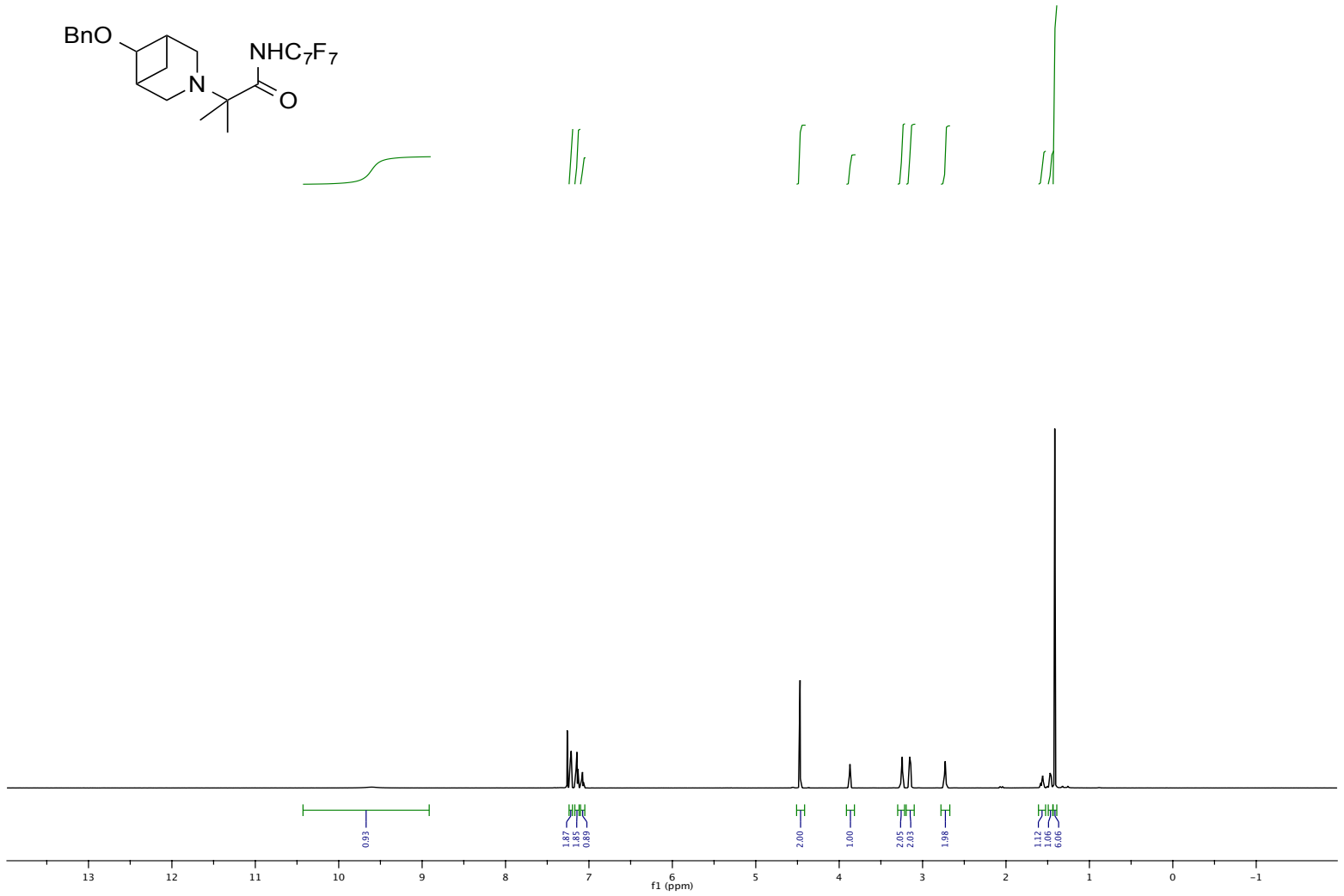


^{19}F NMR Spectrum of **S6** in $CDCl_3$

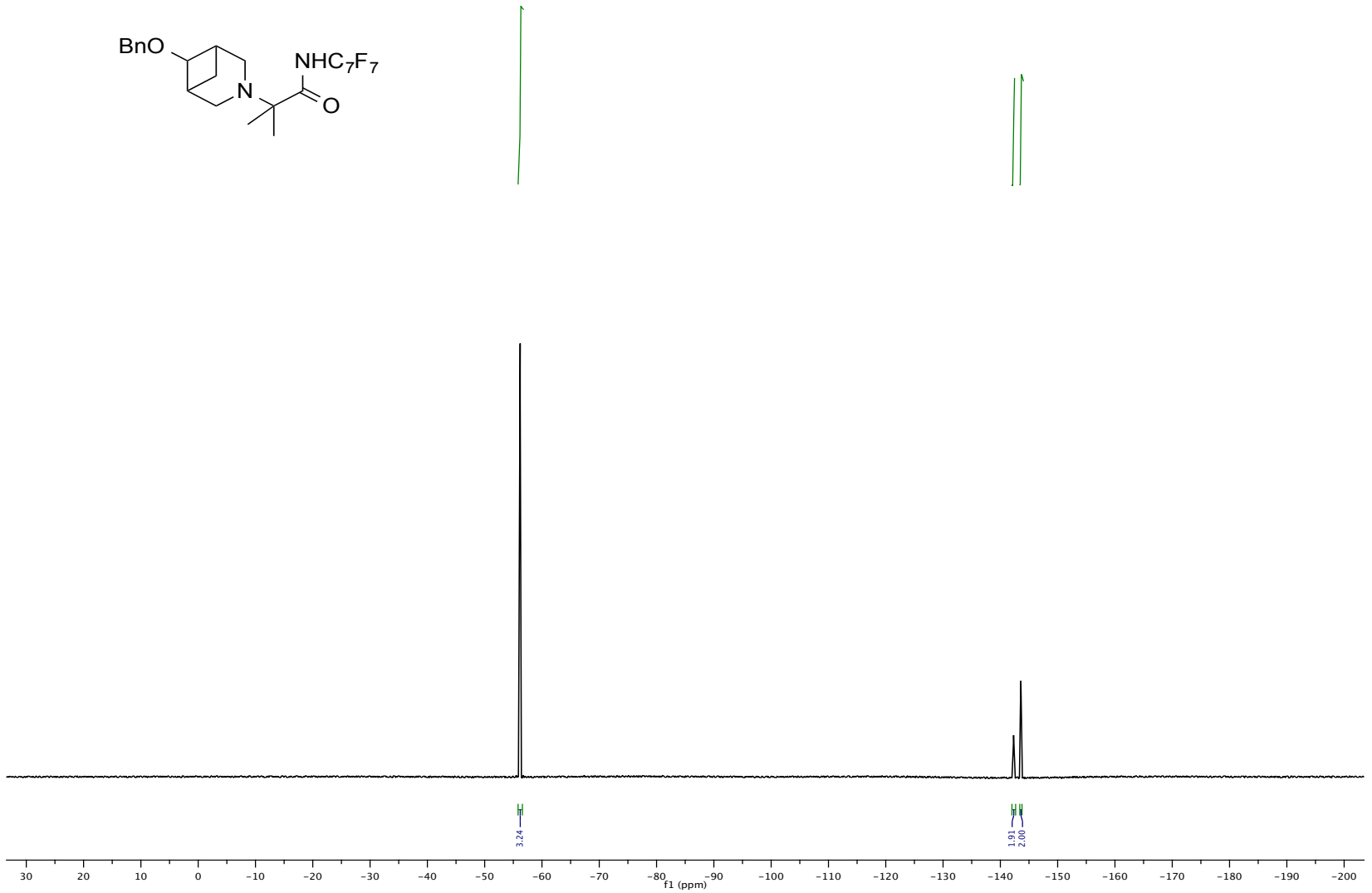




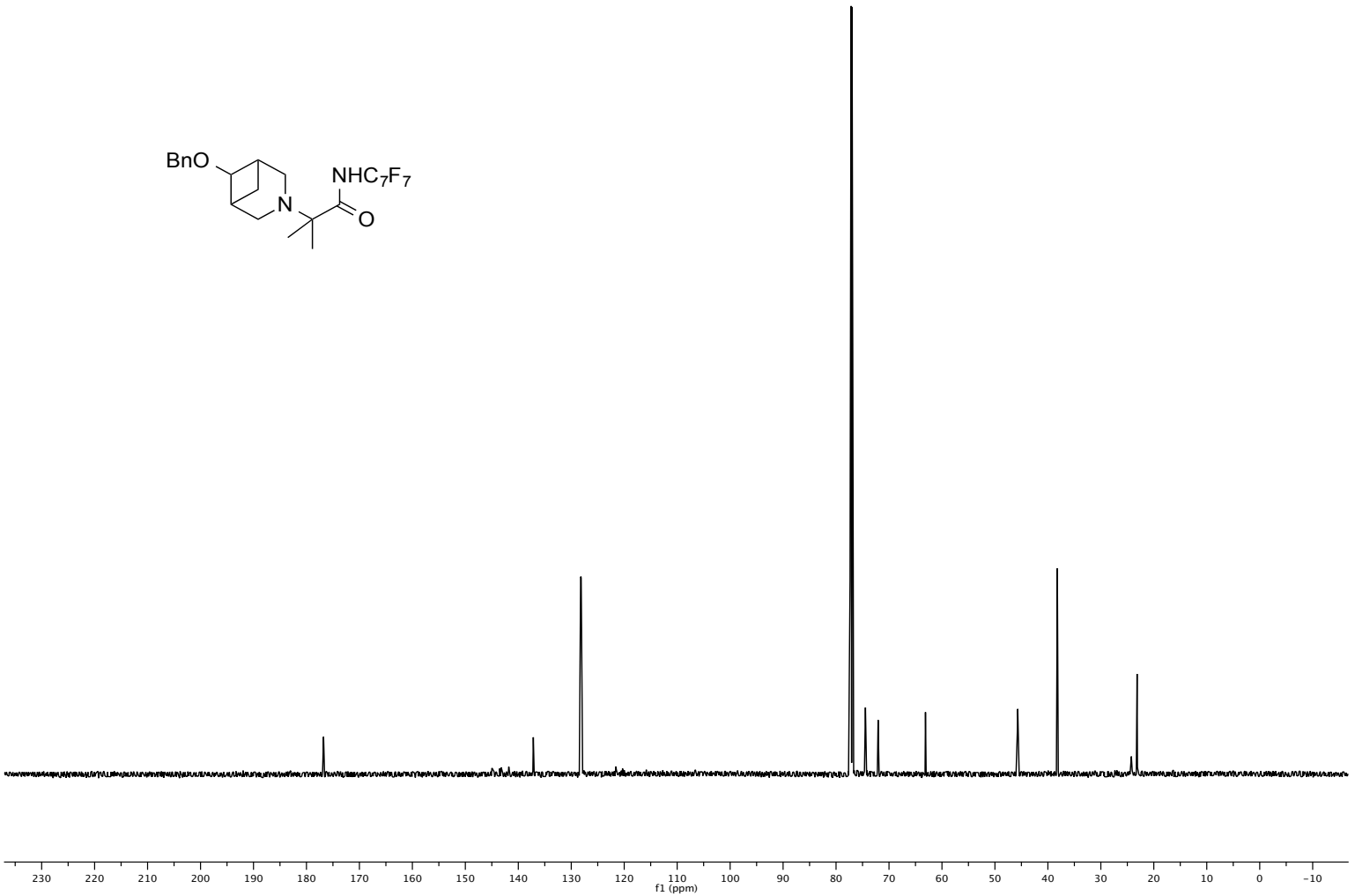
^{13}C NMR Spectrum of **S6** in $CDCl_3$



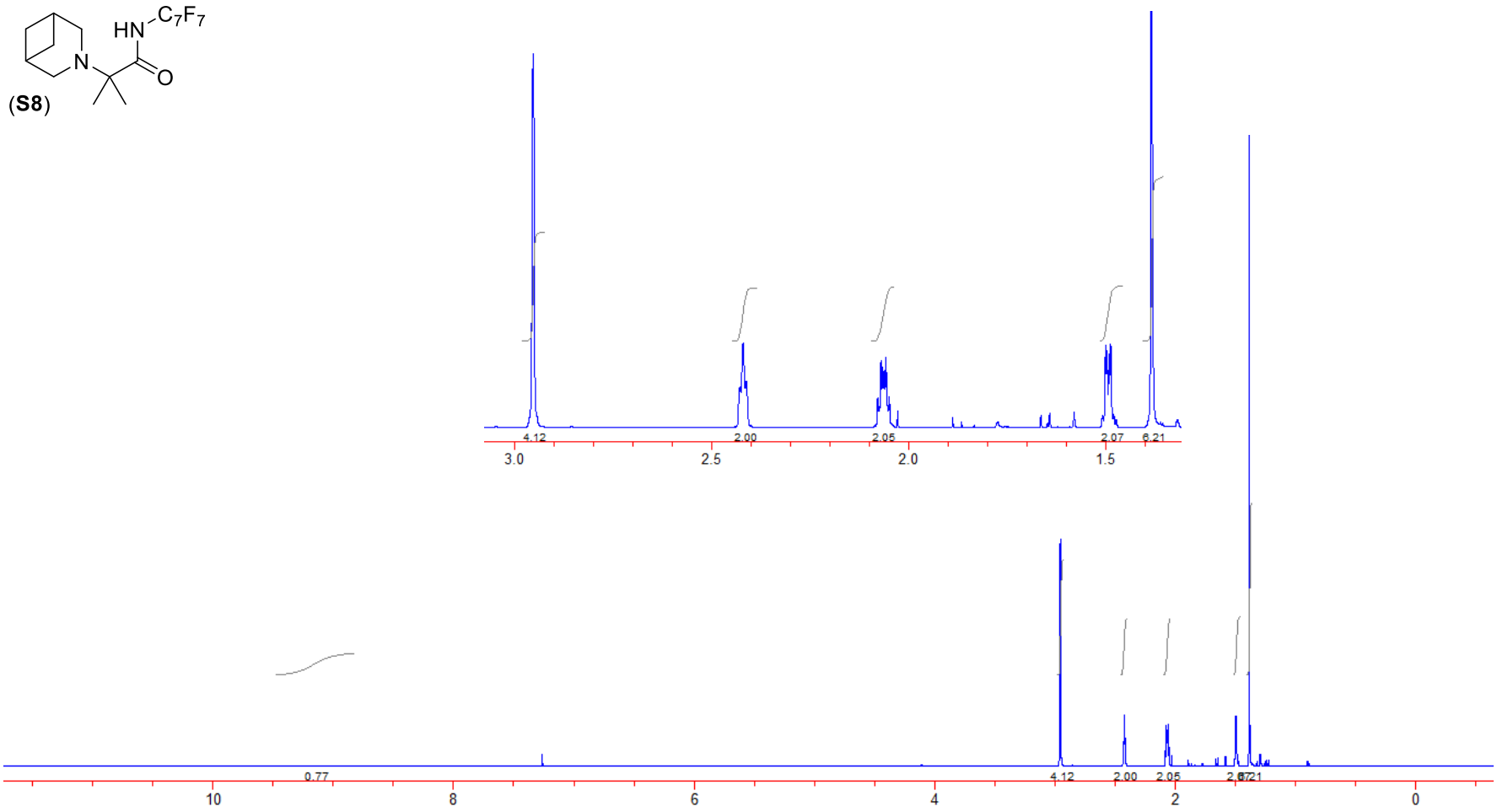
^{1}H NMR Spectrum of **S7** in $CDCl_3$



^{19}F NMR Spectrum of **S7** in $CDCl_3$

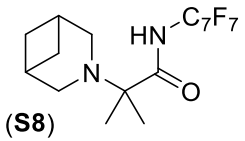


^{13}C NMR Spectrum of **S7** in $CDCl_3$

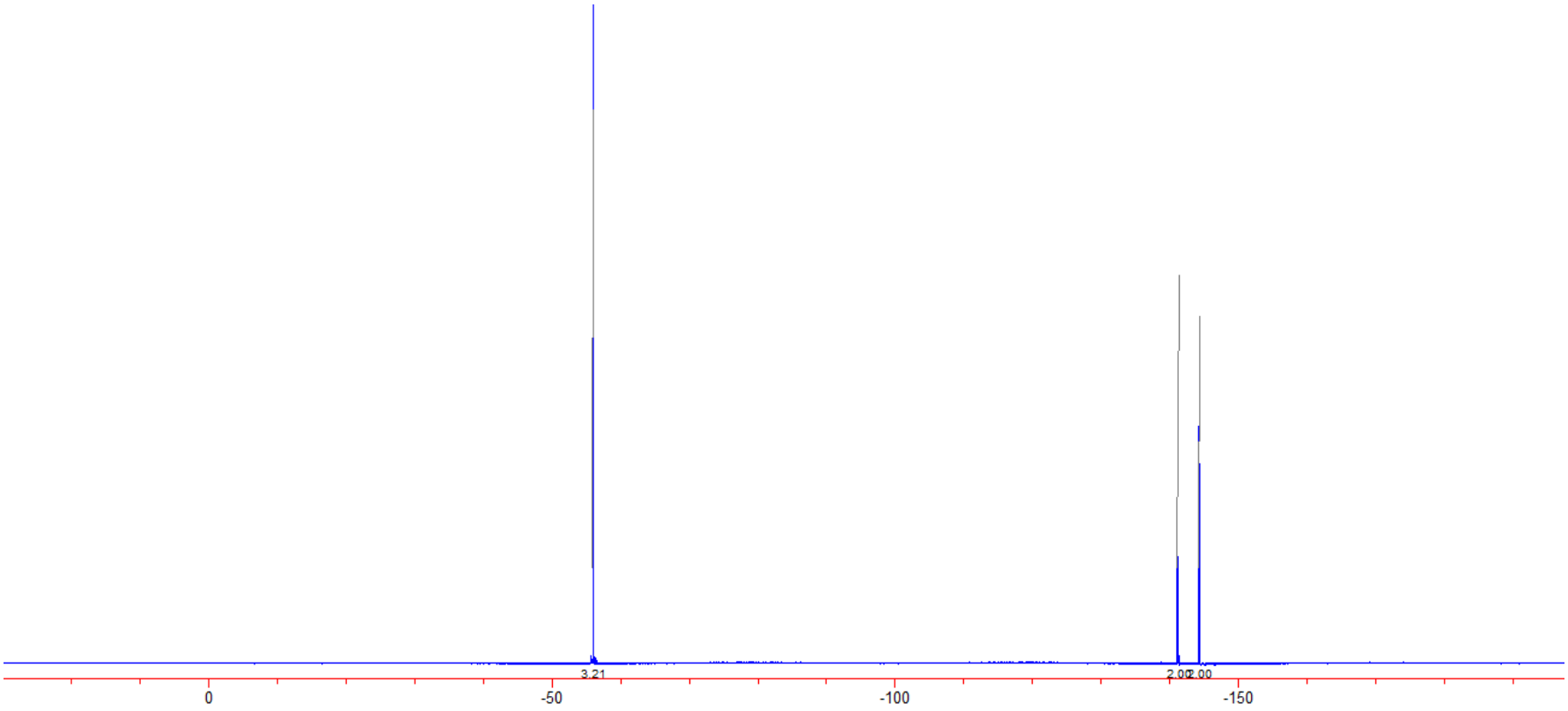


(**S8**)

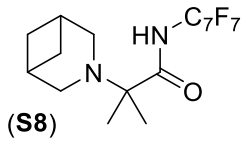
^{1}H NMR Spectrum in $CDCl_3$



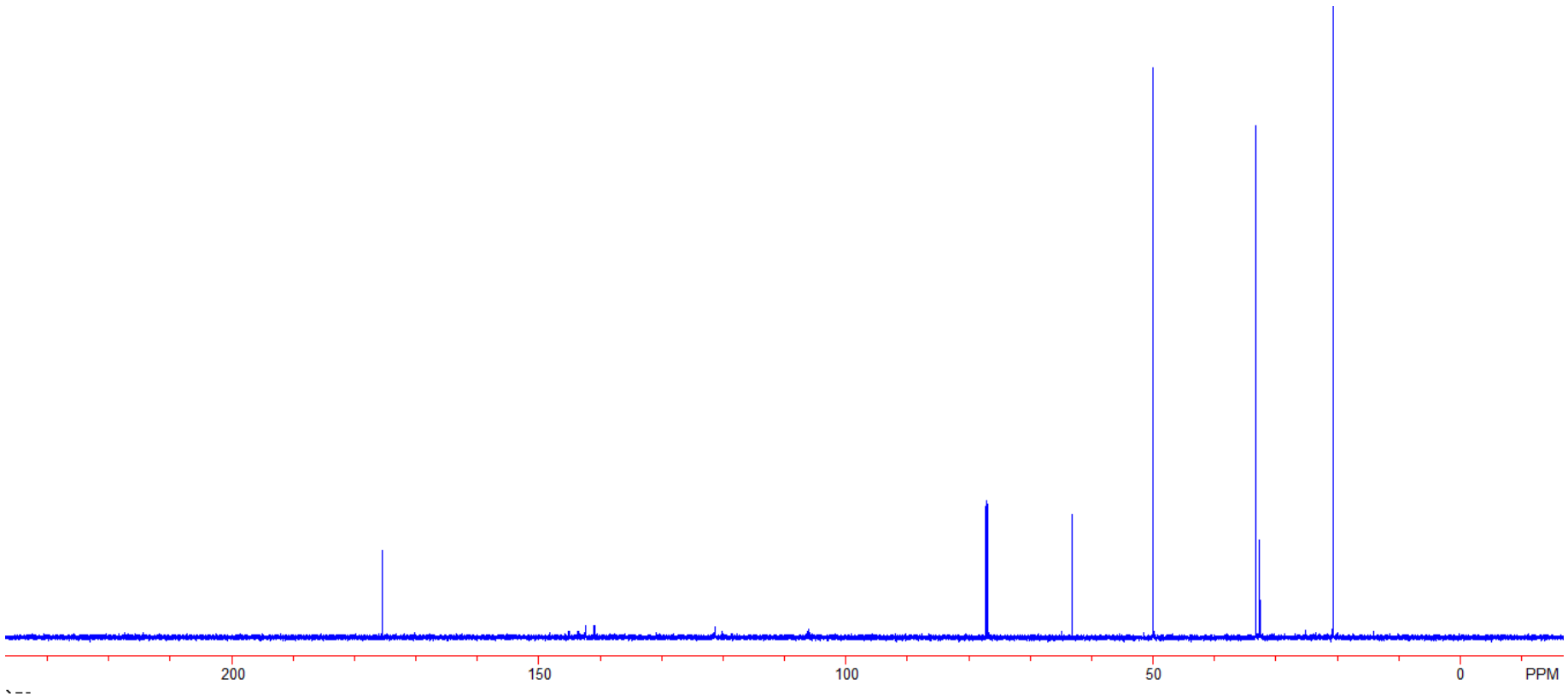
(**S8**)



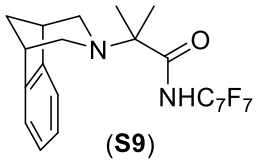
^{19}F NMR Spectrum in $CDCl_3$



(**S8**)



^{13}C NMR Spectrum in $CDCl_3$



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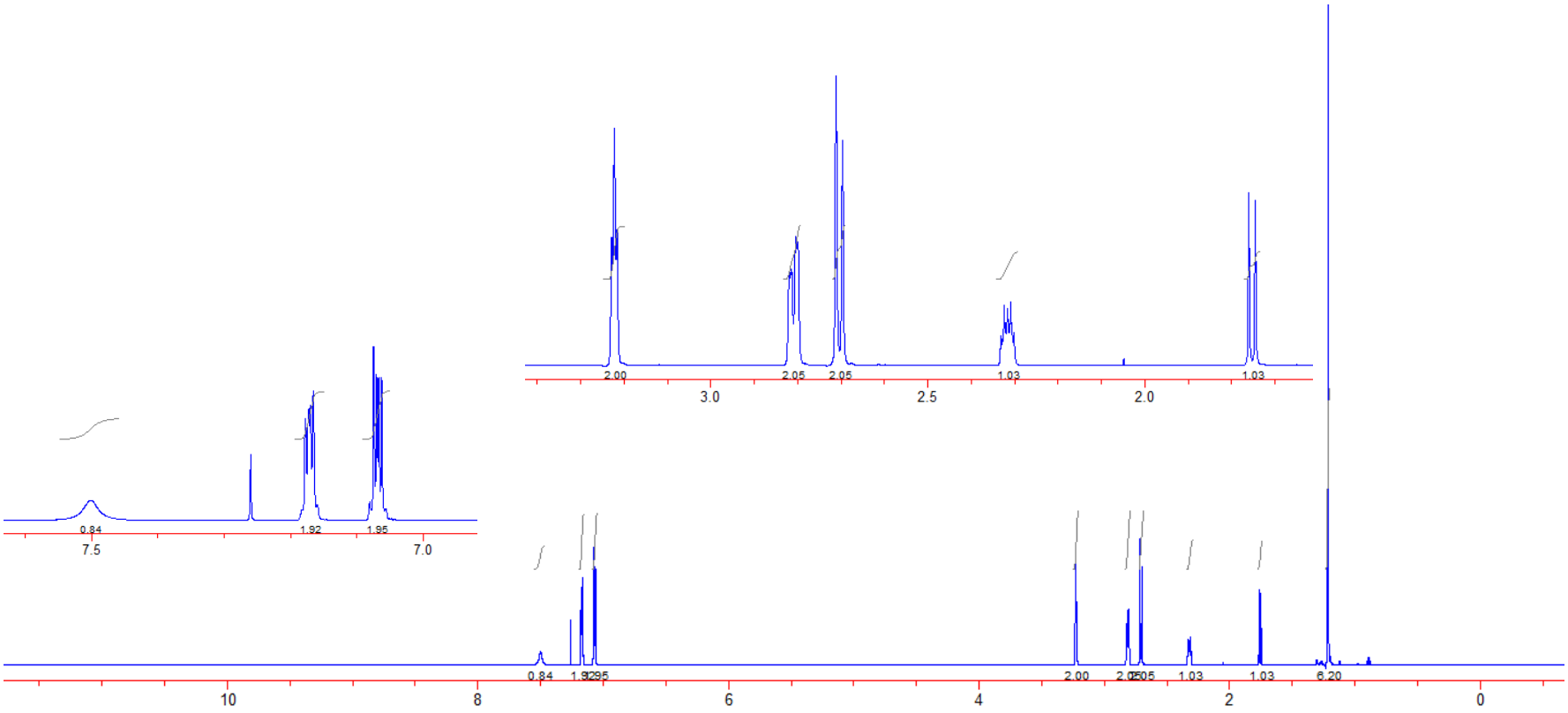
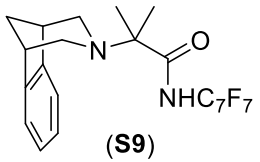


^{1}H NMR Spectrum in $CDCl_3$



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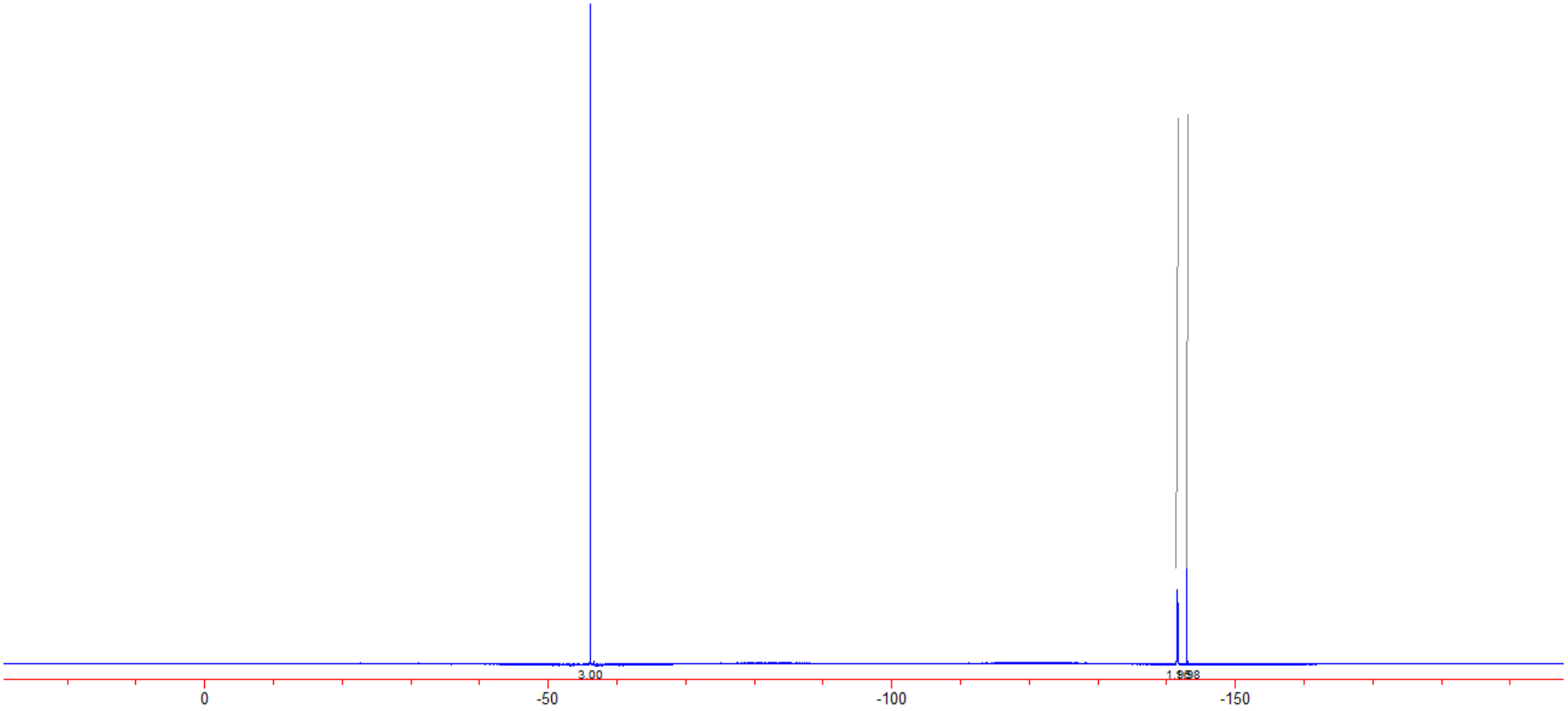
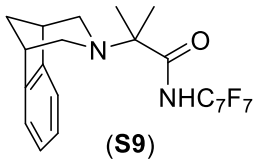
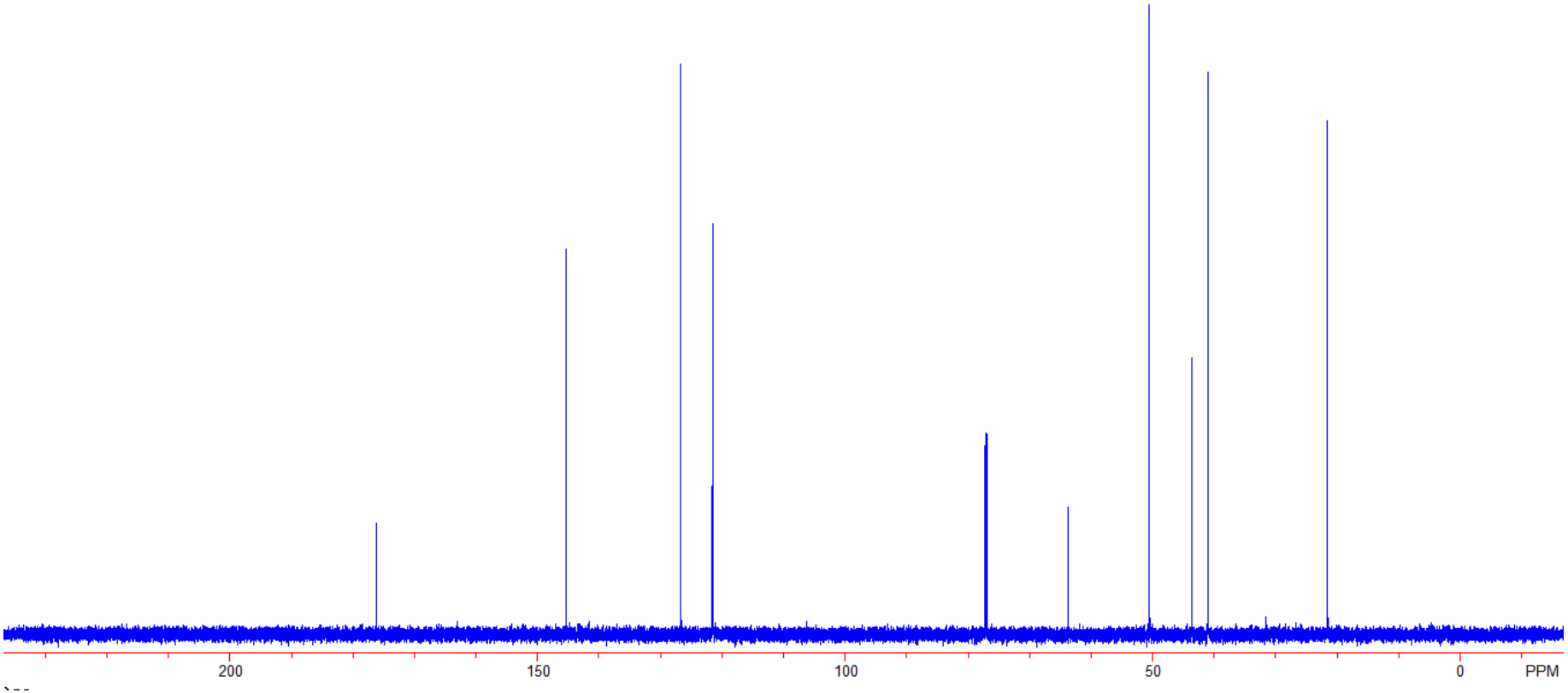


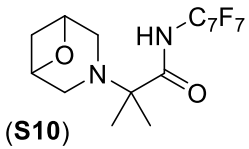
^{19}F NMR Spectrum in $CDCl_3$



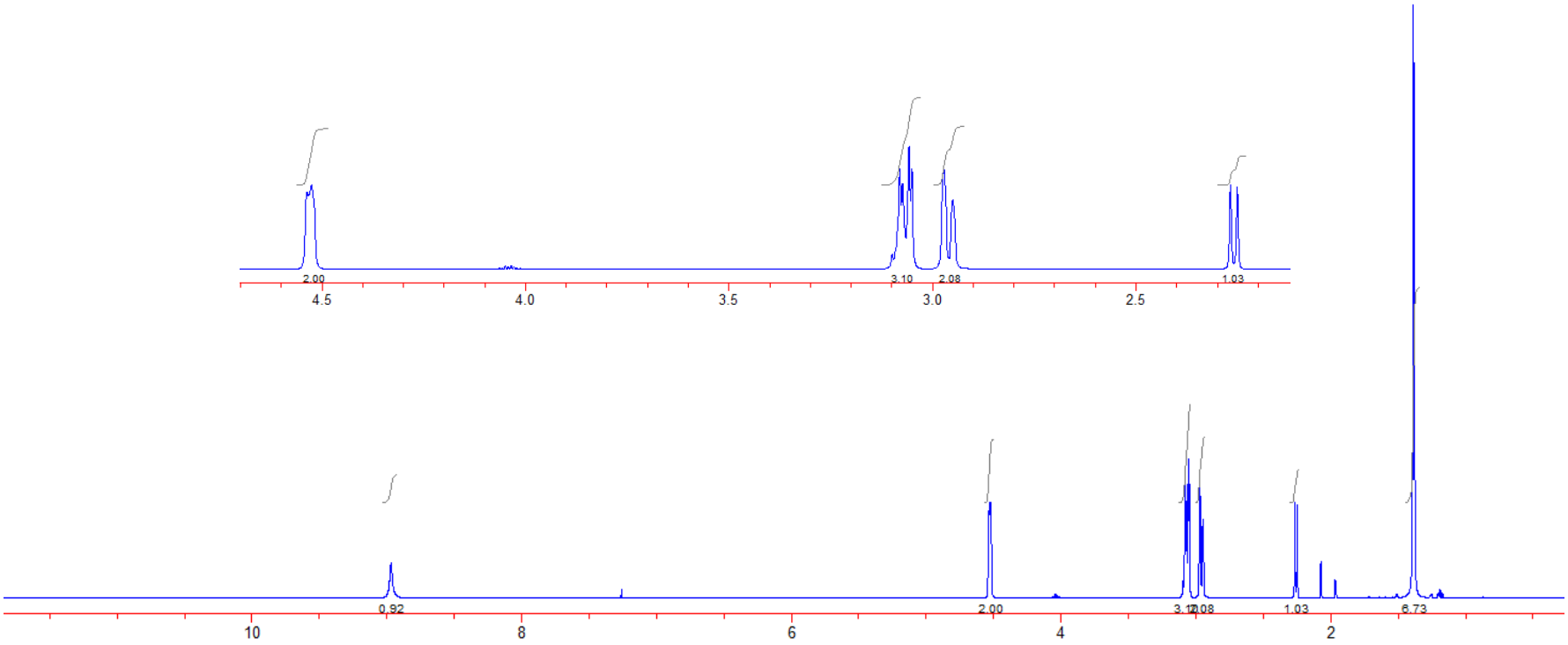
(**S9**)



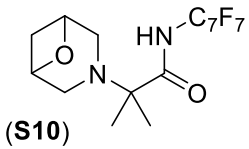
^{13}C NMR Spectrum in $CDCl_3$



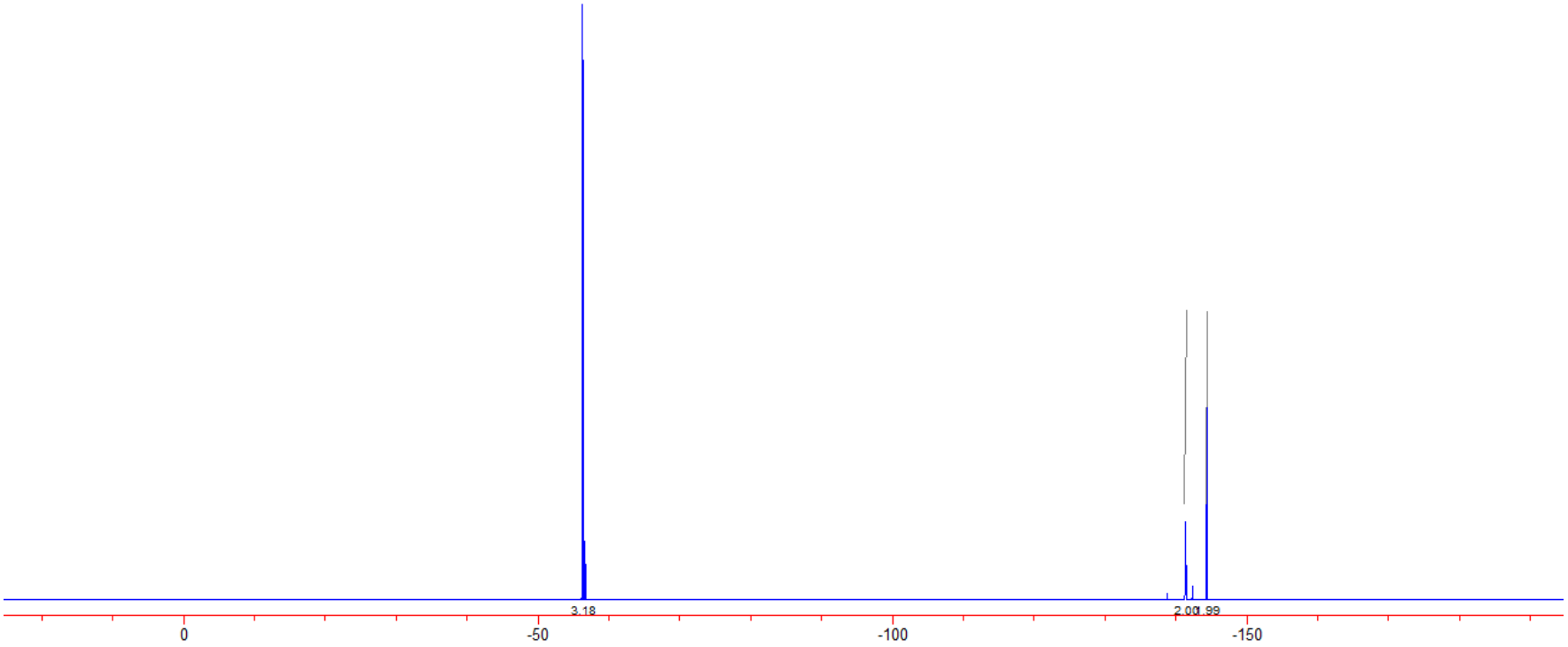
(**S10**)



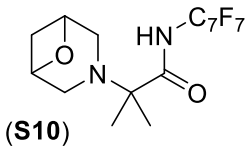
^{1}H NMR Spectrum in $CDCl_3$



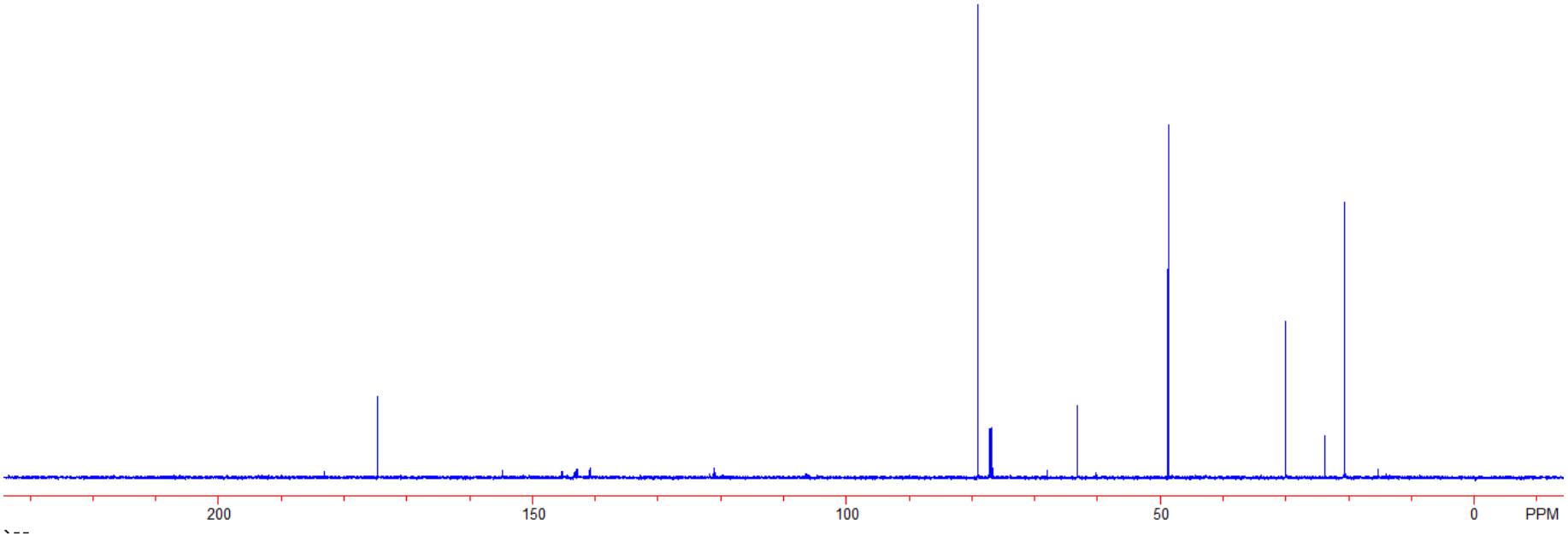
(**S10**)



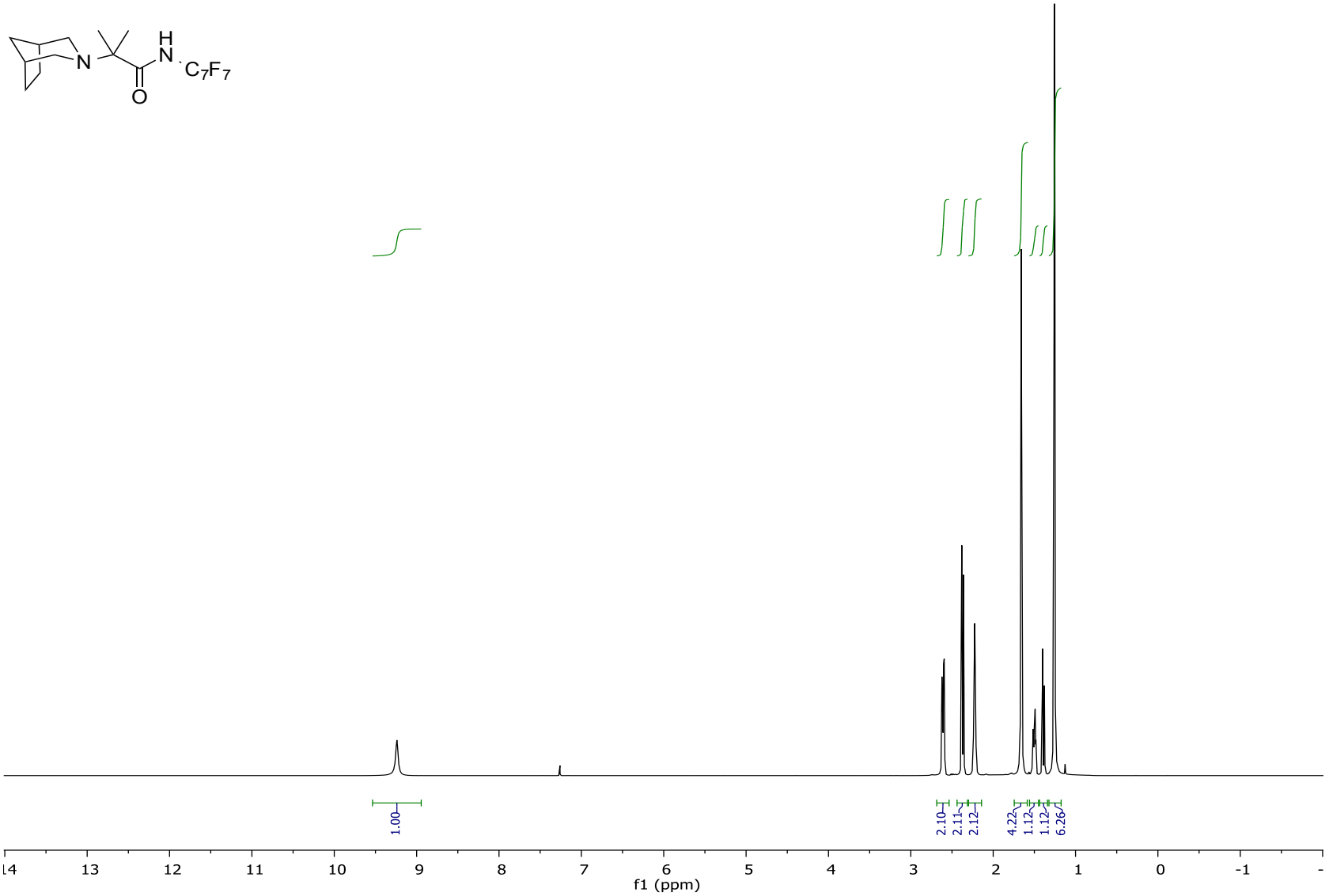
^{19}F NMR Spectrum in $CDCl_3$



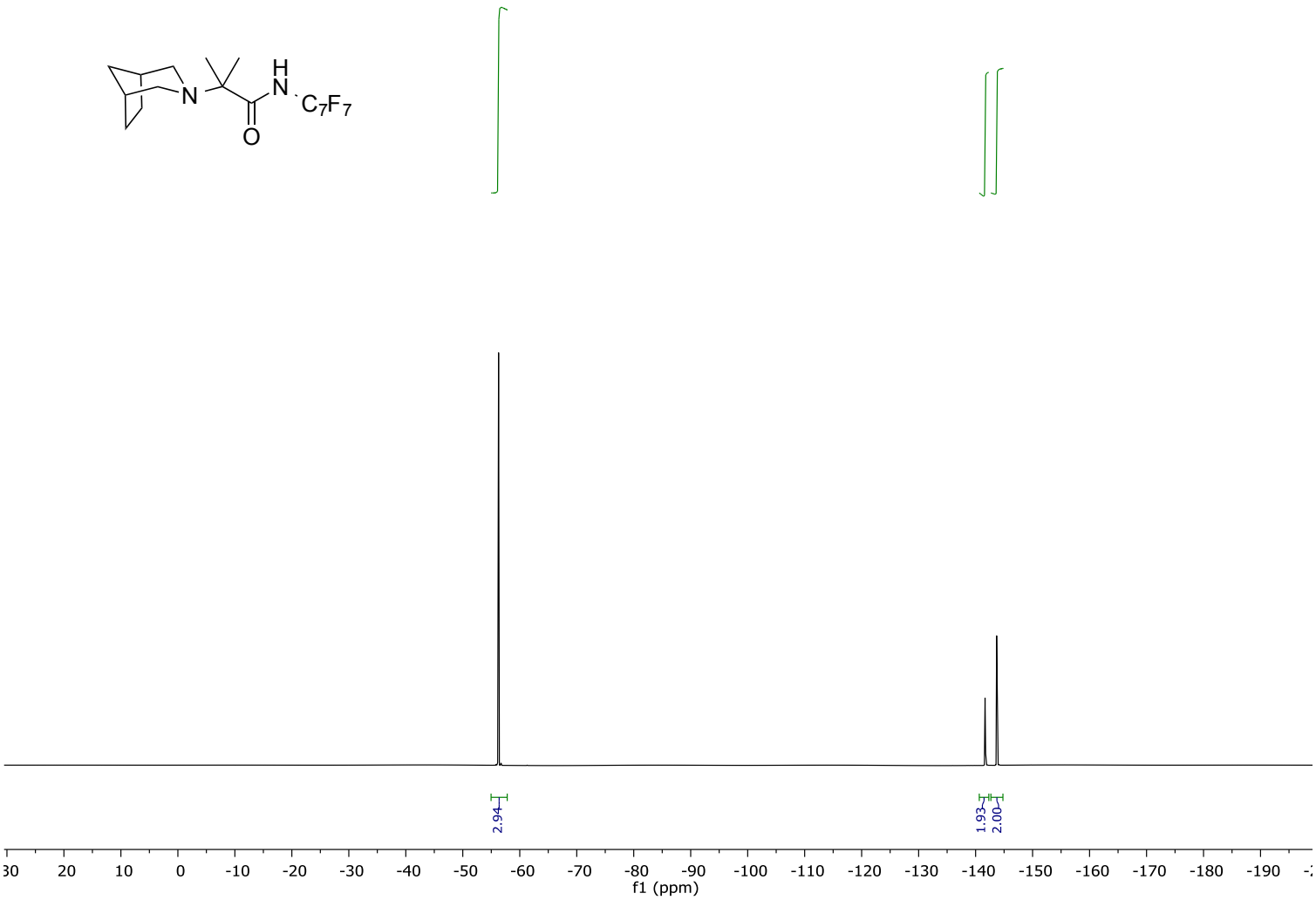
(**S10**)



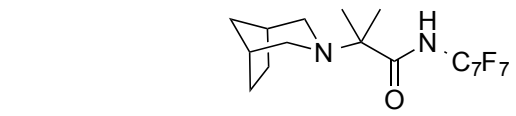
^{13}C NMR Spectrum in $CDCl_3$

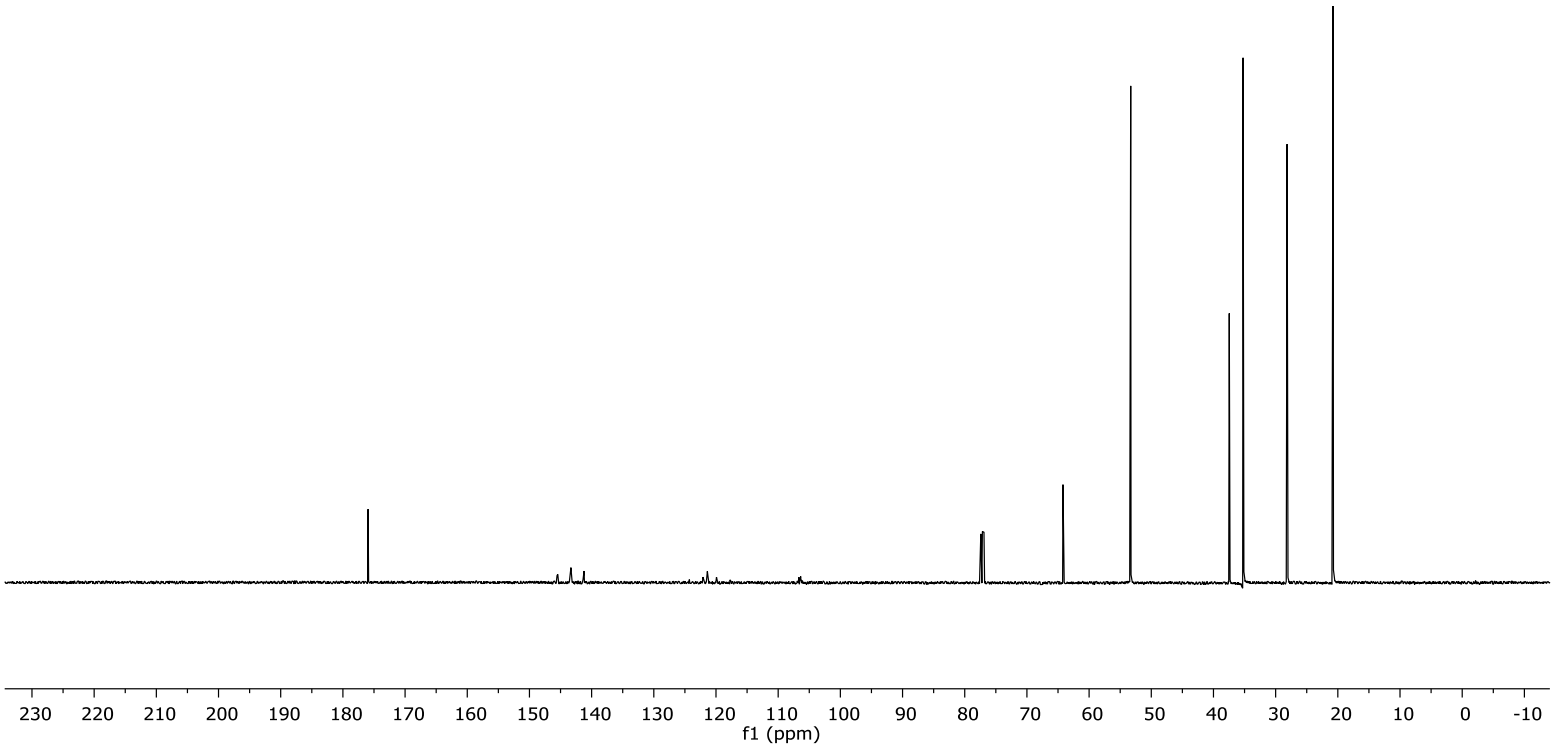


^{1}H NMR Spectrum of **S11** in $CDCl_3$

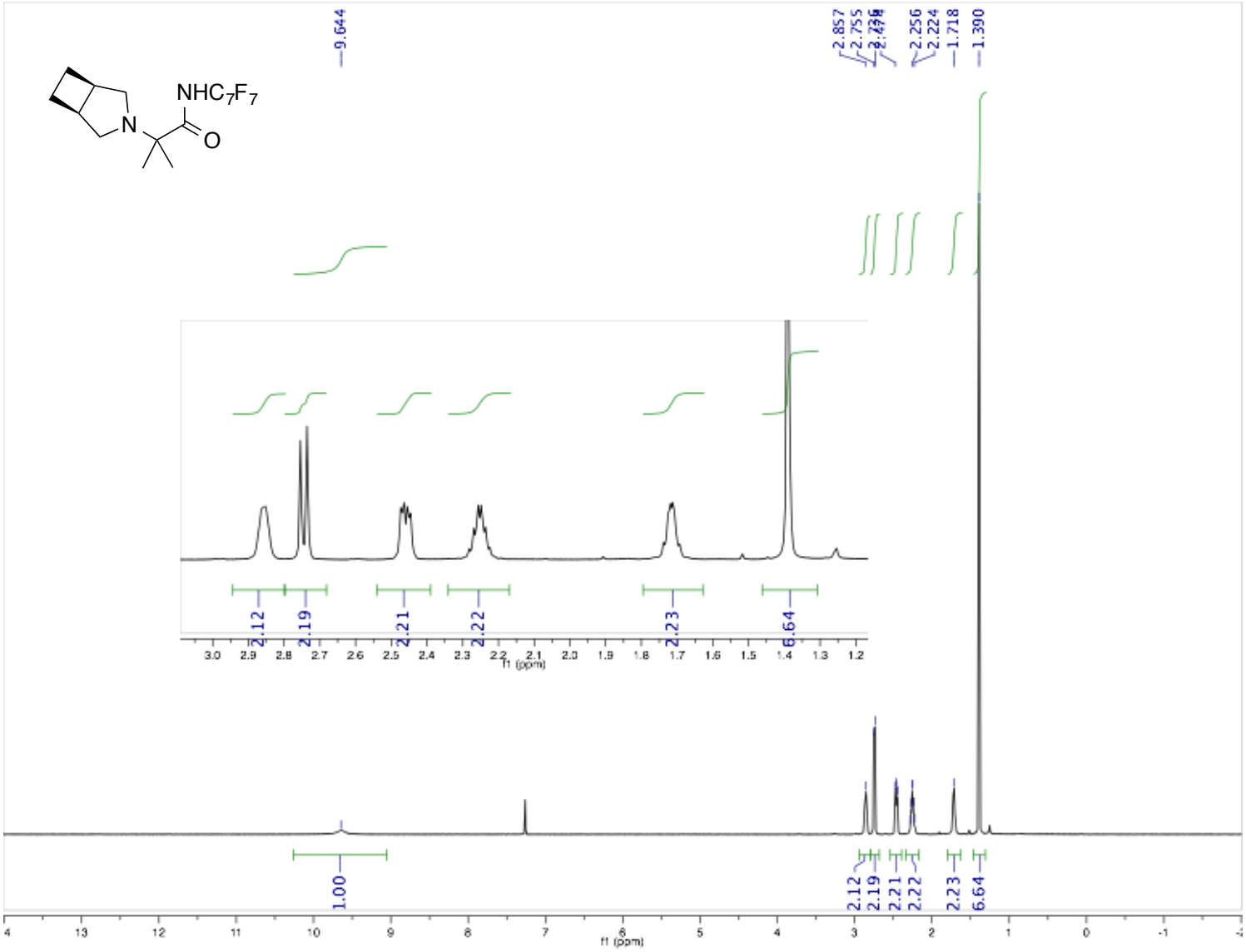


^{19}F NMR Spectrum of **S11** in $CDCl_3$

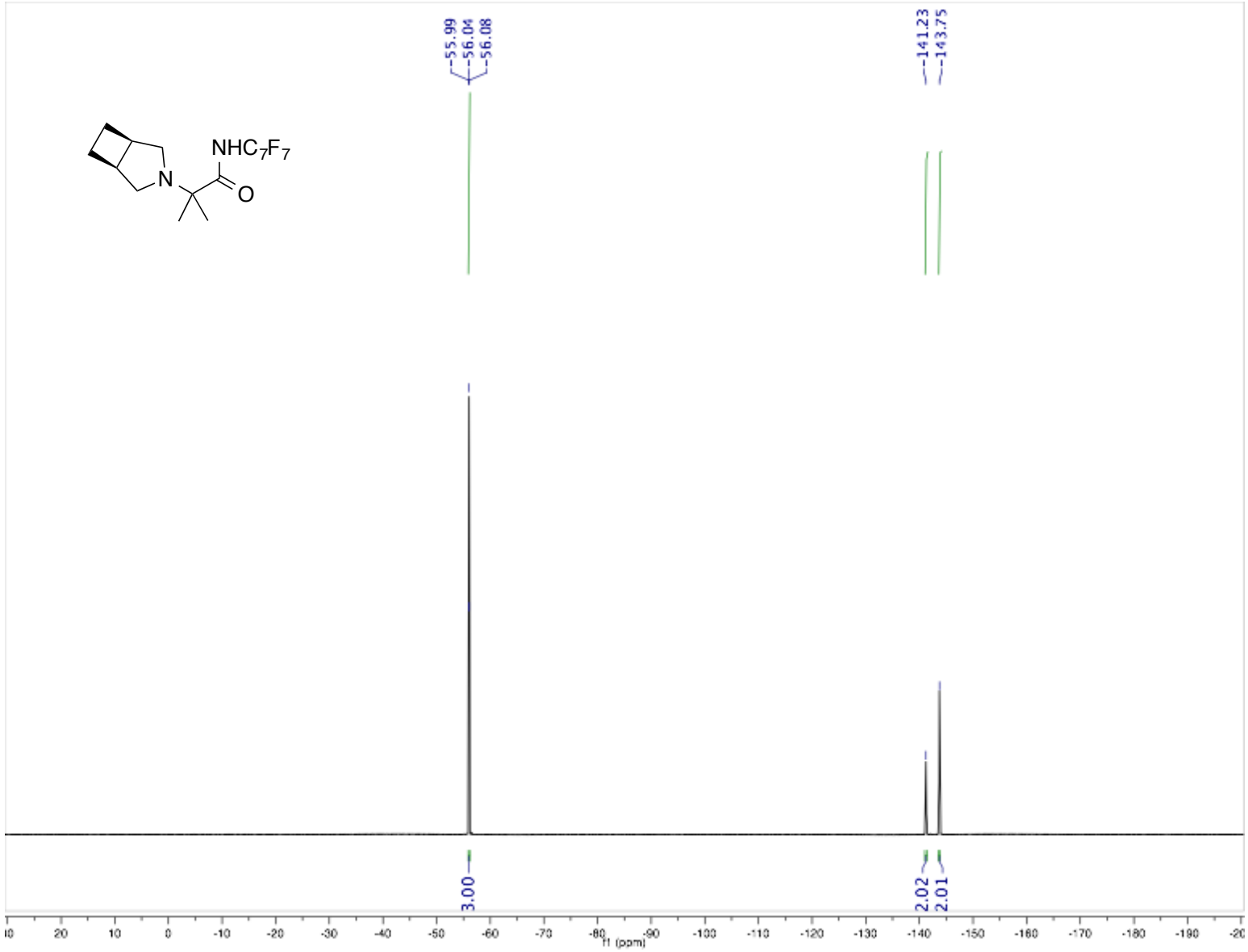




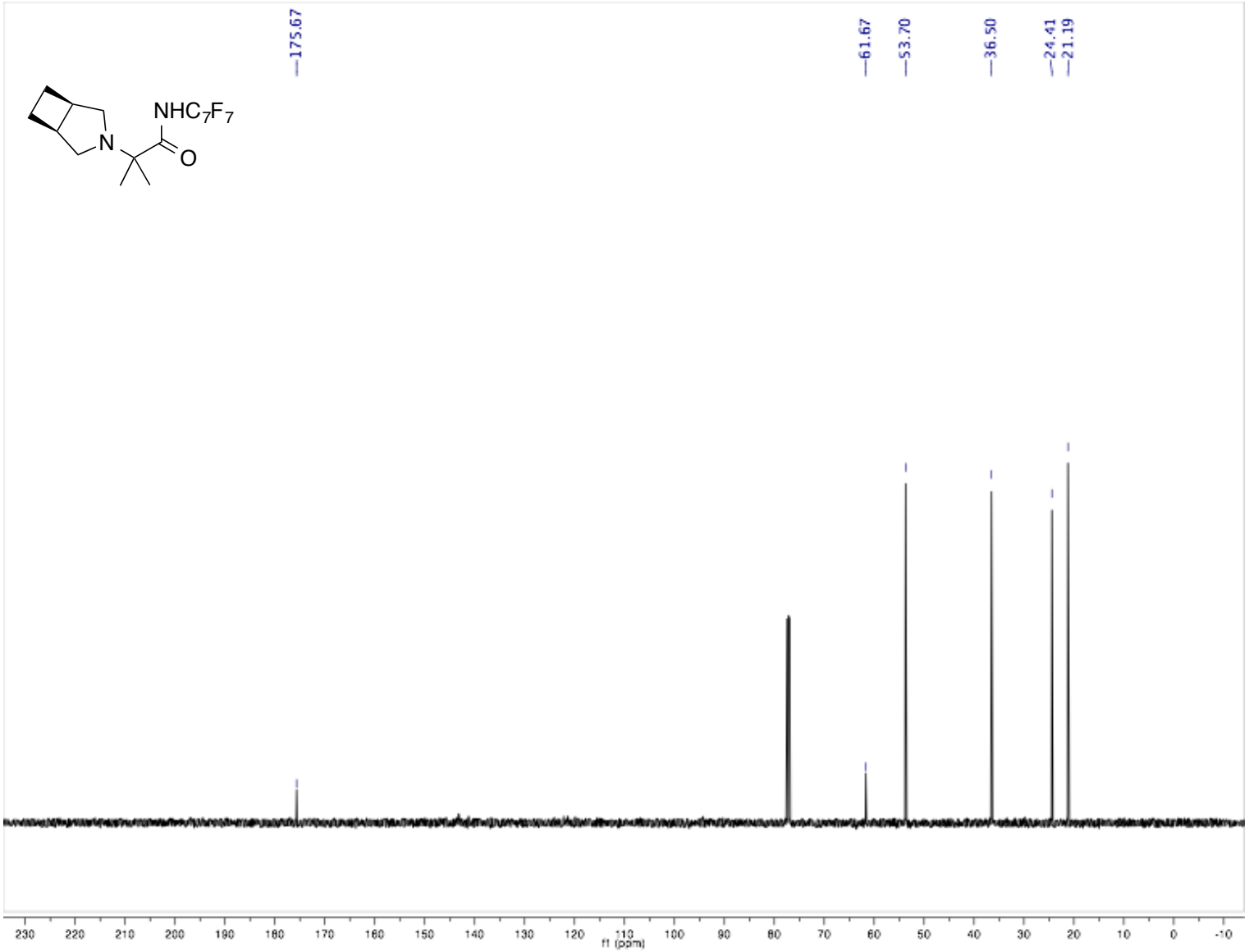
^{13}C NMR Spectrum of **S11** in $CDCl_3$



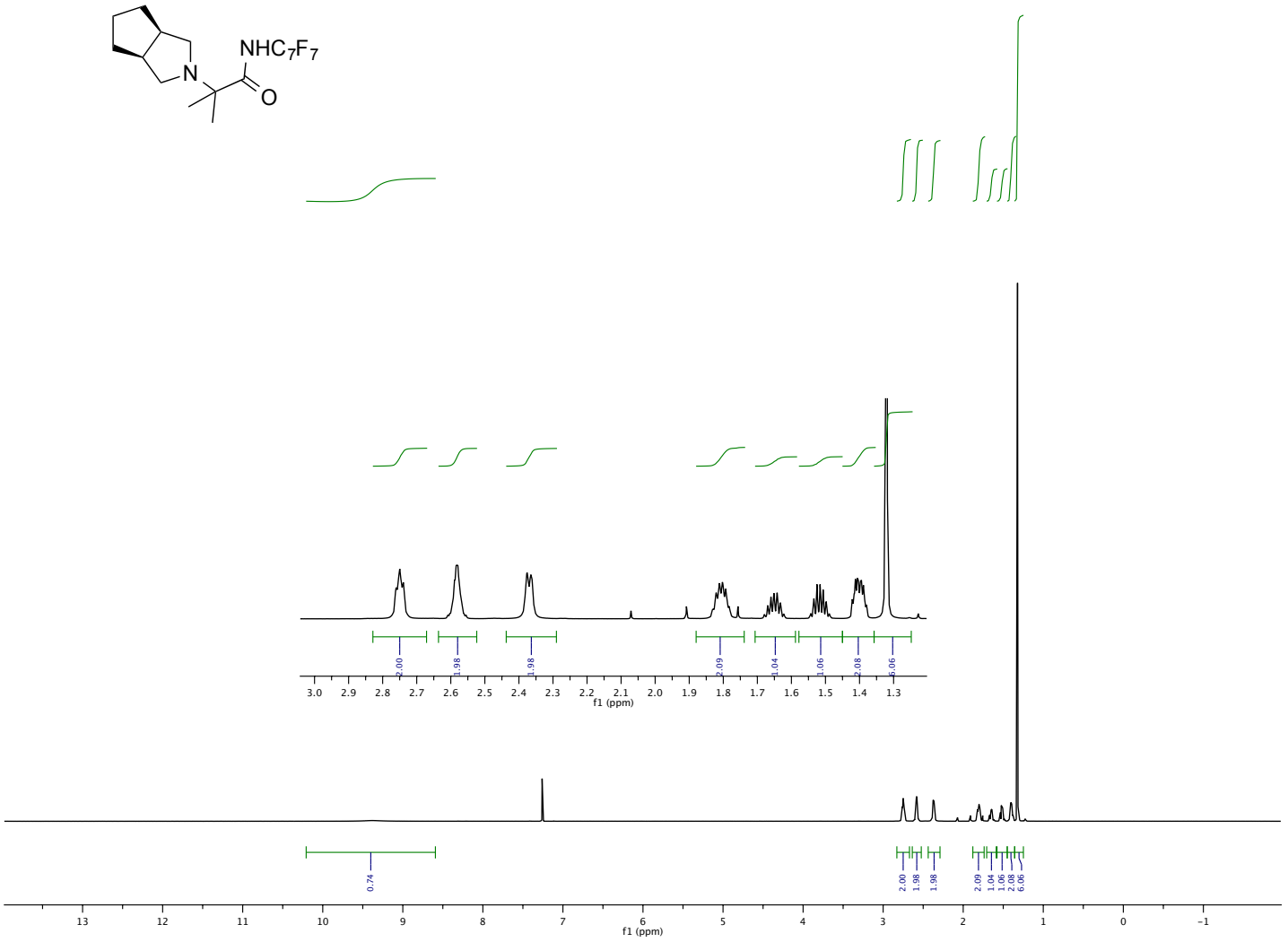
^{1}H NMR Spectrum of **S12** in $CDCl_3$



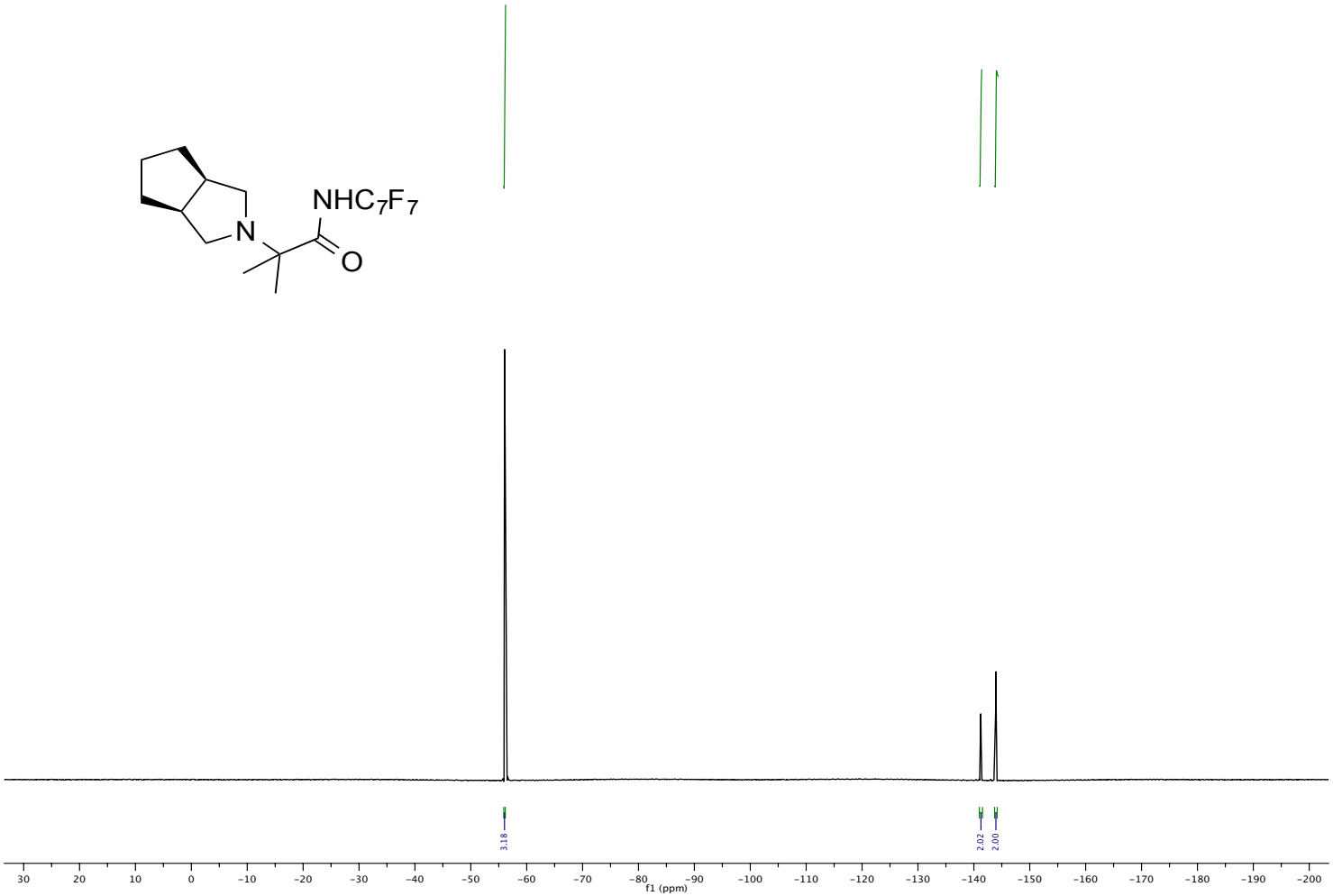
^{19}F NMR Spectrum of **S12** in $CDCl_3$



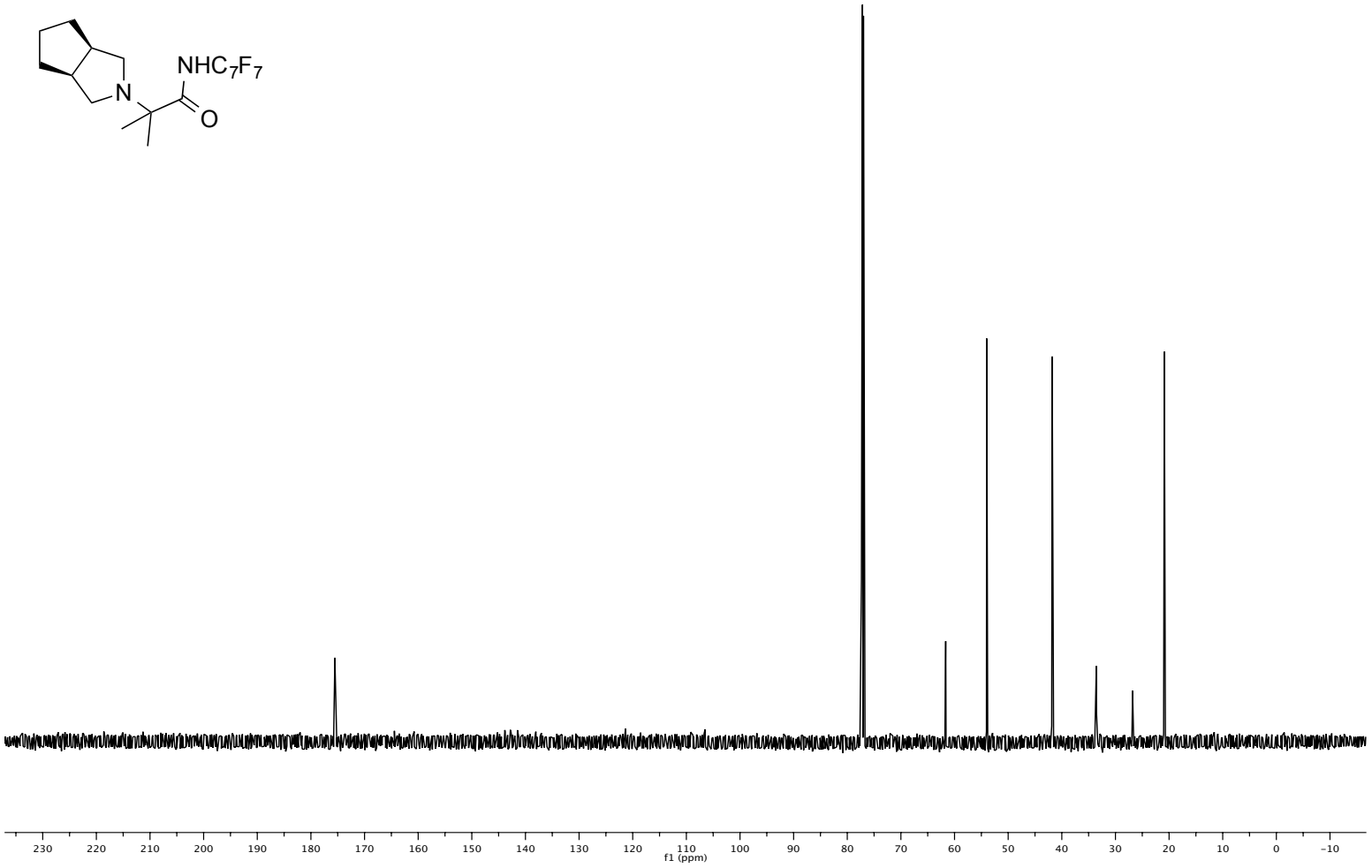
^{13}C NMR Spectrum of **S12** in $CDCl_3$



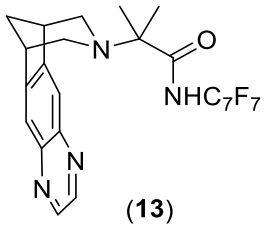
^{1}H NMR Spectrum of **S13** in $CDCl_3$



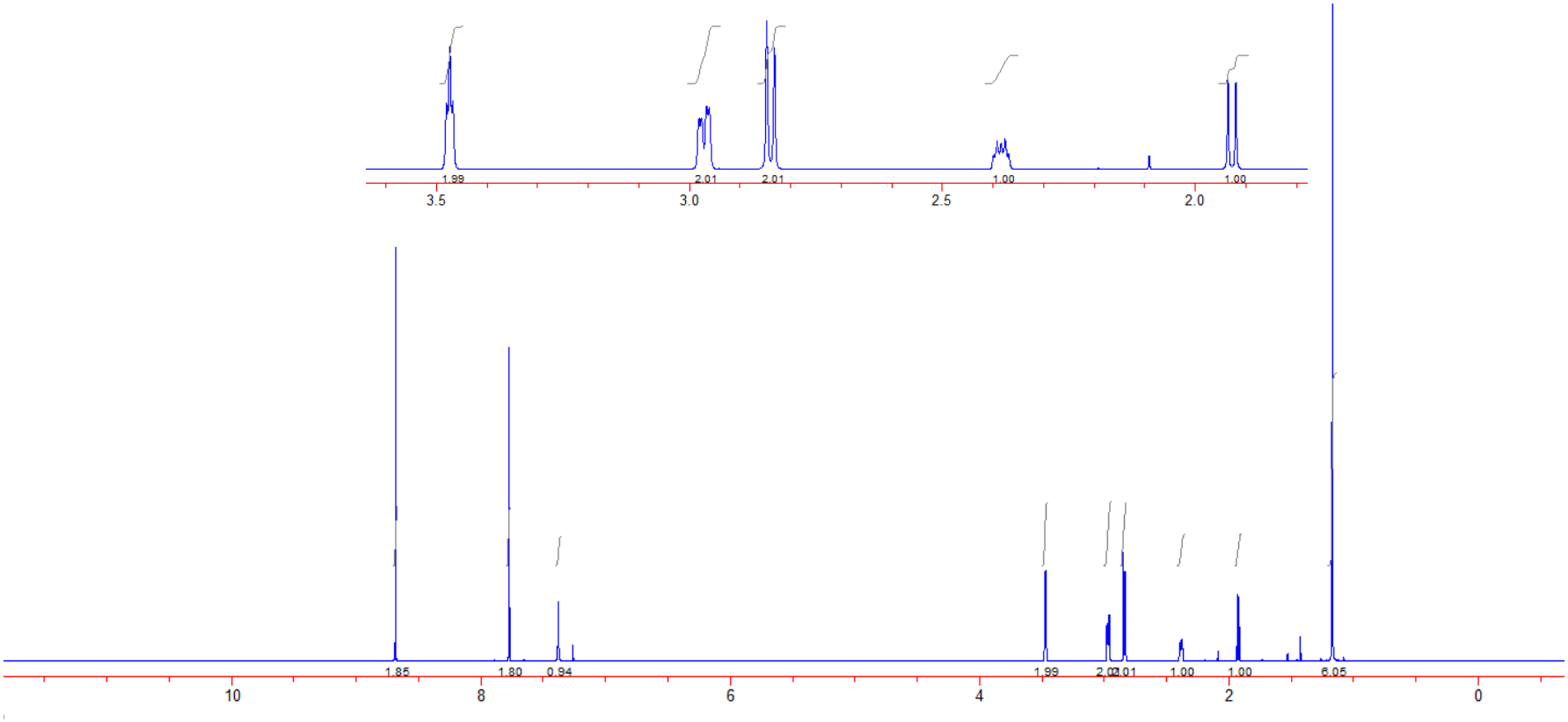
^{19}F NMR Spectrum of **S13** in $CDCl_3$



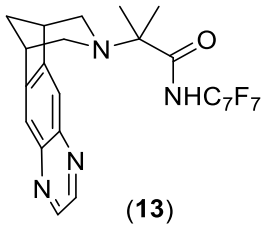
^{13}C NMR Spectrum of **S13** in $CDCl_3$



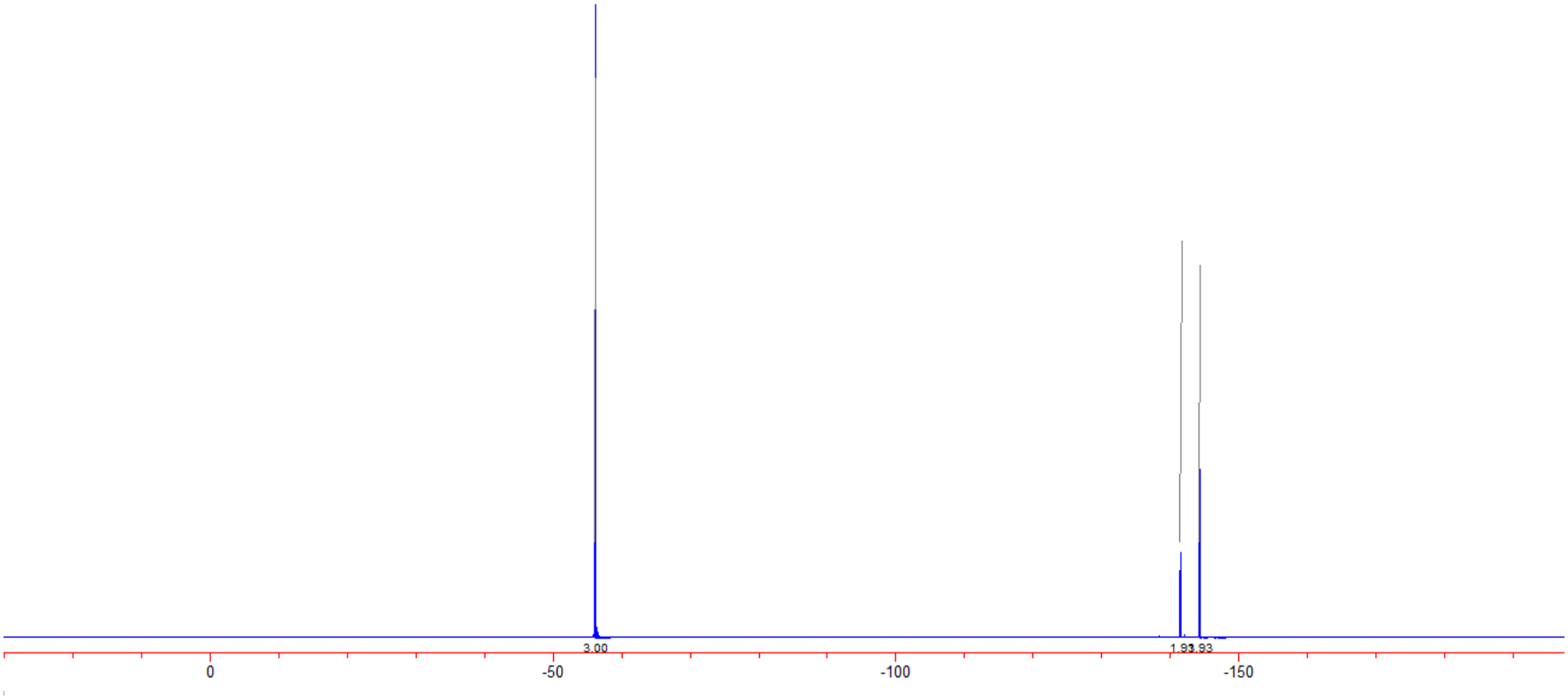
(**13**)



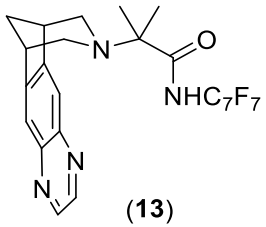
^{1}H NMR Spectrum in $CDCl_3$



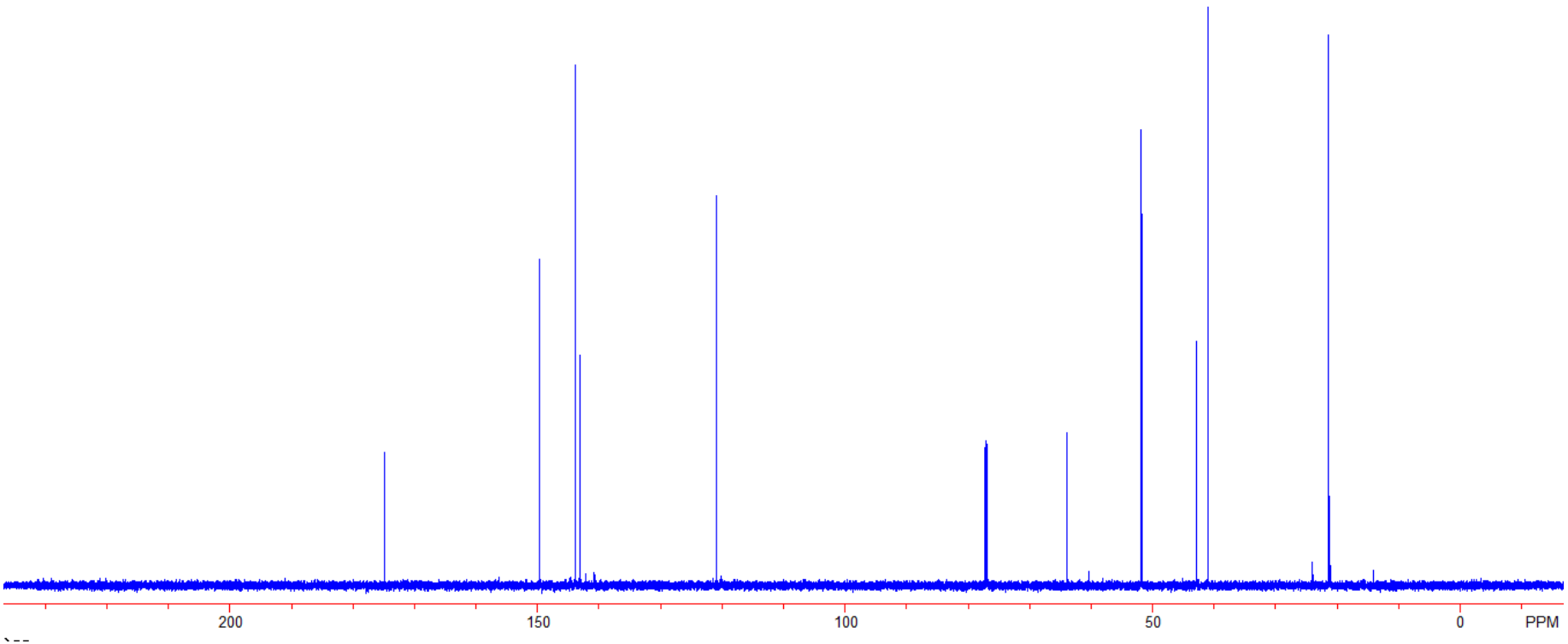
(**13**)



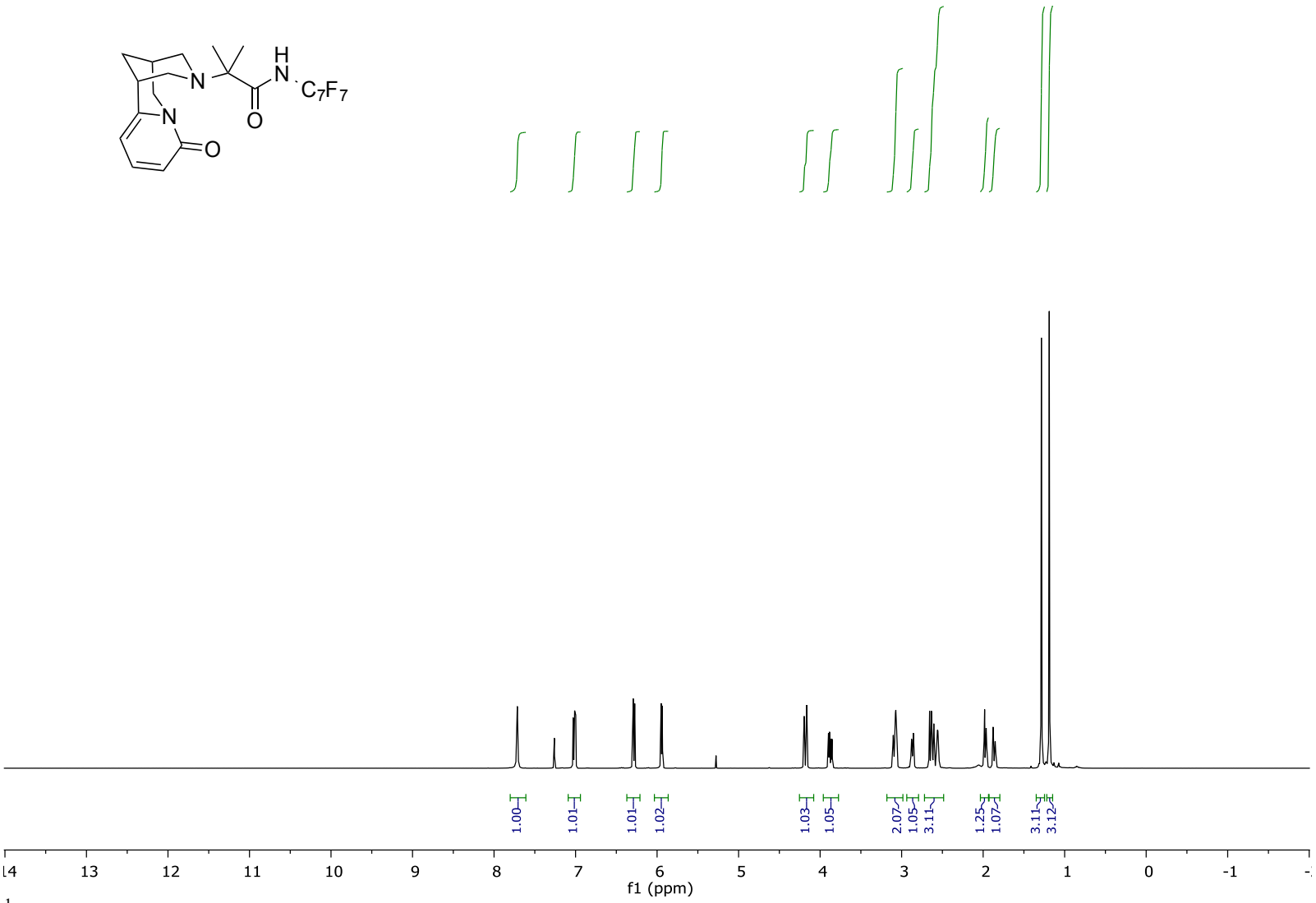
^{19}F NMR Spectrum in $CDCl_3$



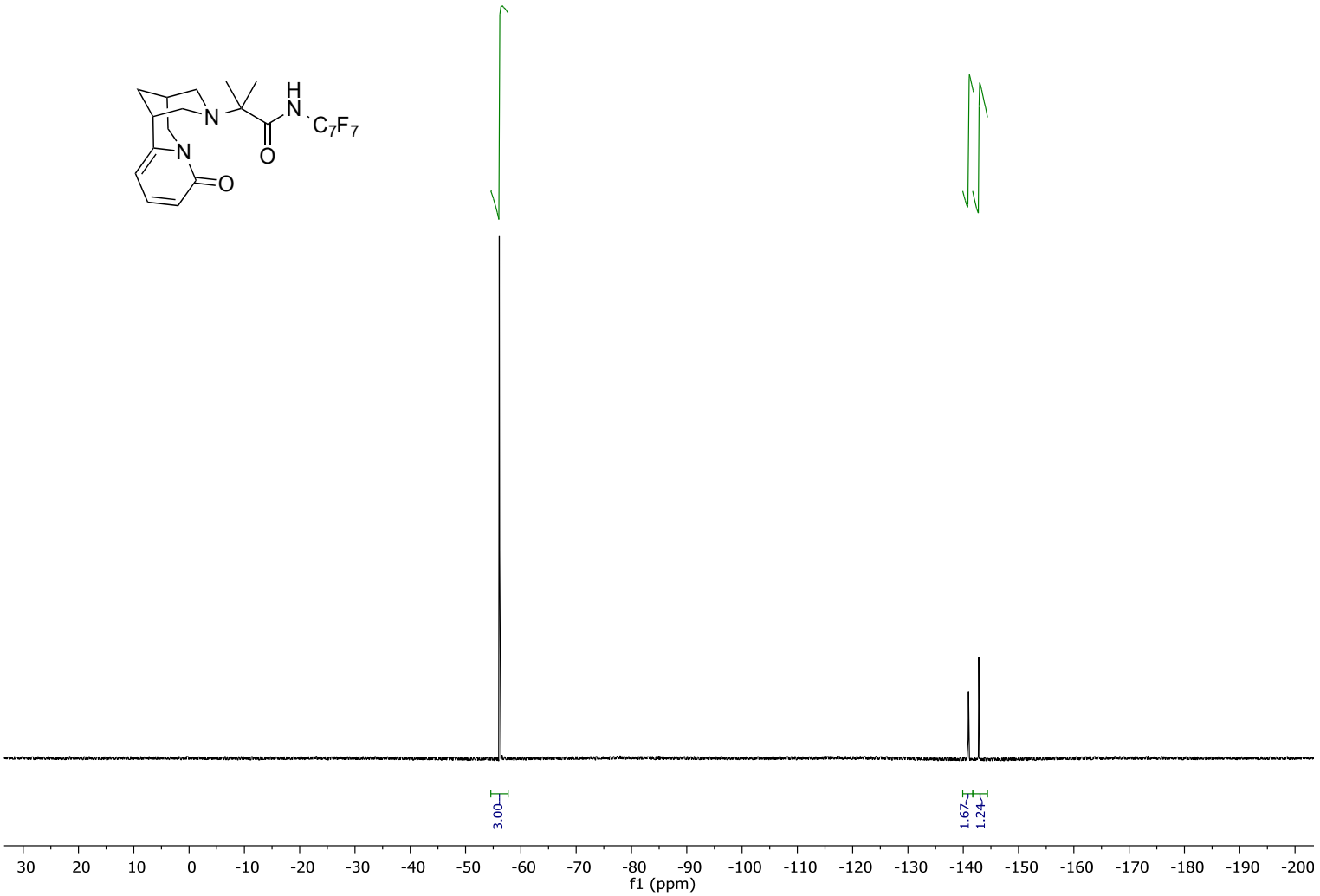
(**13**)



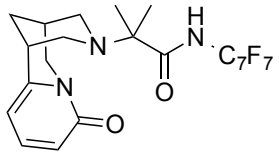
^{13}C NMR Spectrum in $CDCl_3$

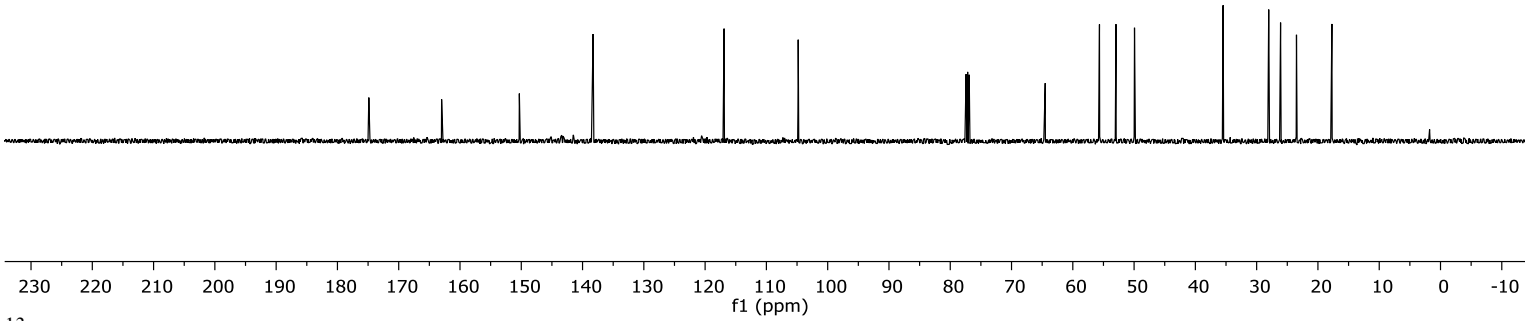


^{1}H NMR Spectrum of **16** in $CDCl_3$

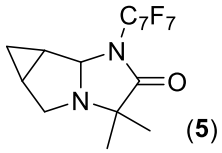


^{19}F NMR Spectrum of **16** in $CDCl_3$

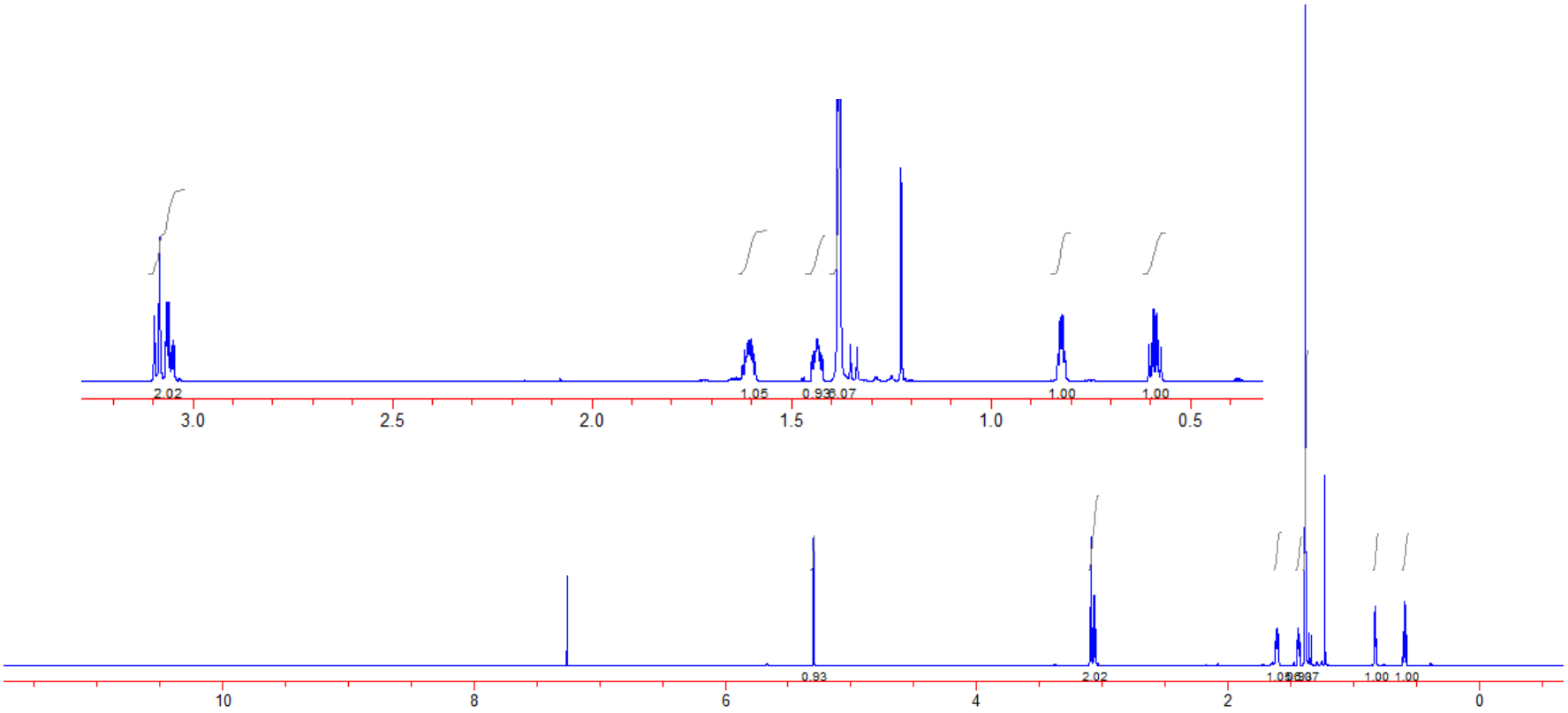




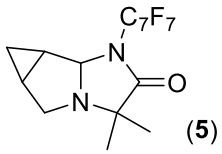
^{13}C NMR Spectrum of **16** in $CDCl_3$



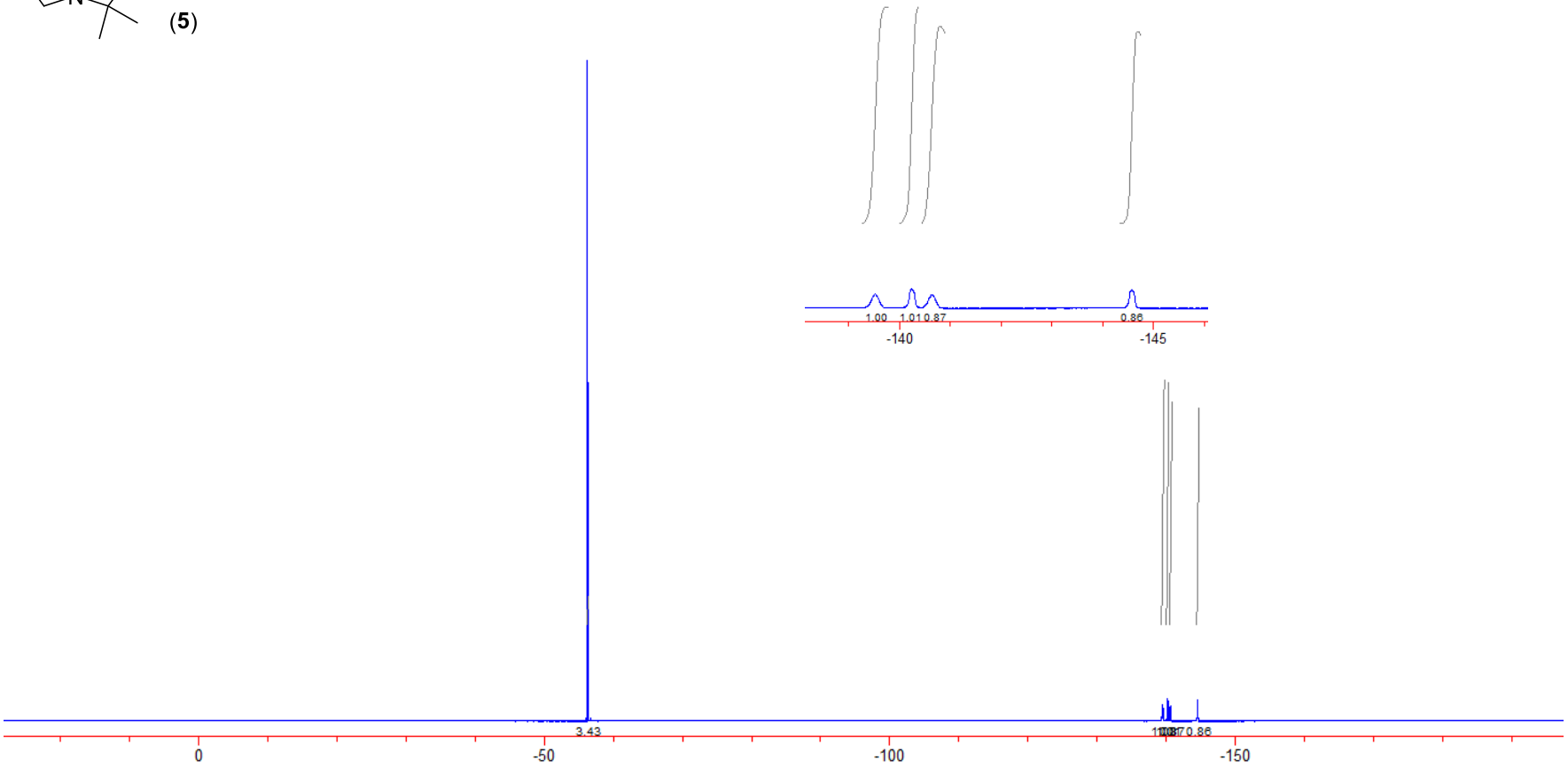
(**5**)



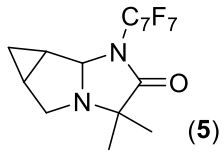
^{1}H NMR Spectrum in $CDCl_3$



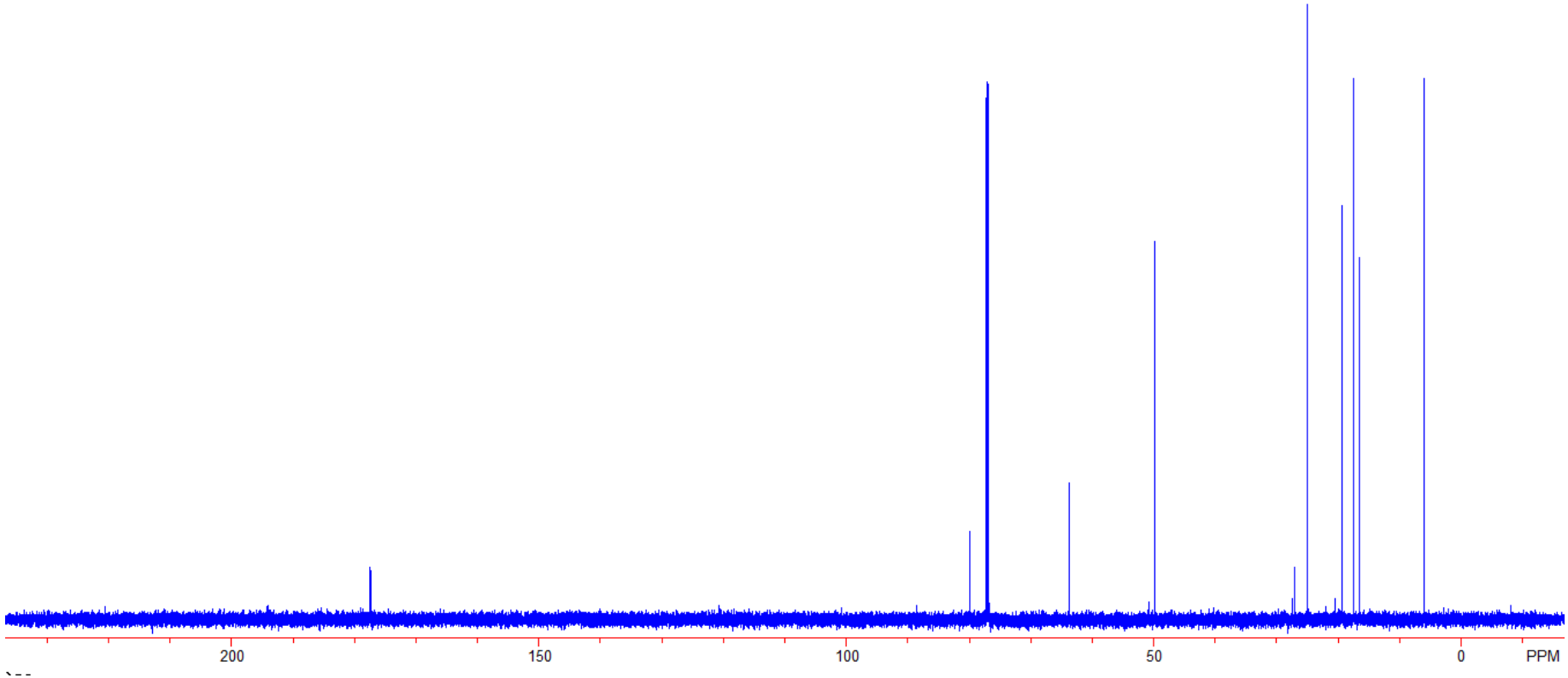
(**5**)



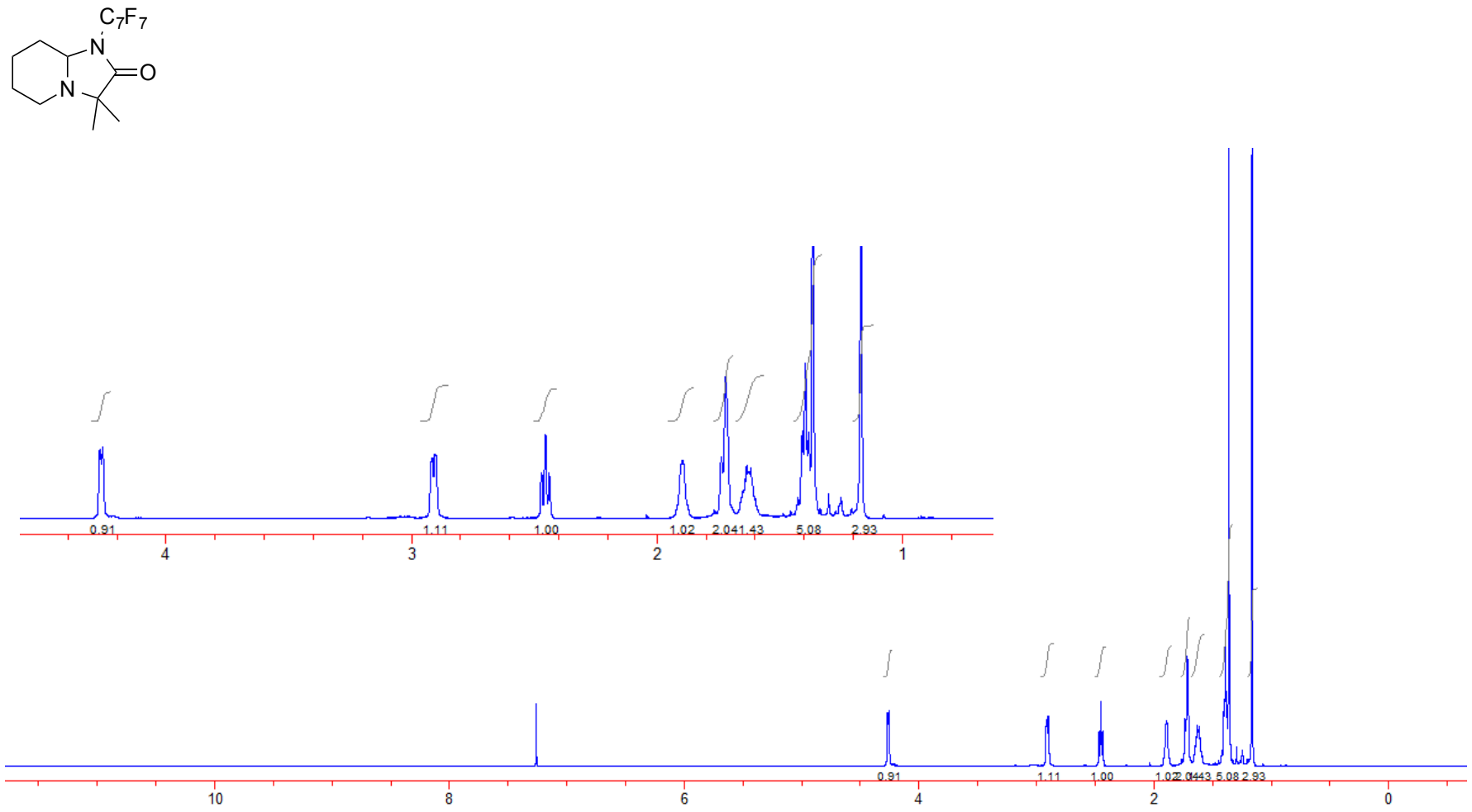
^{19}F NMR Spectrum in $CDCl_3$



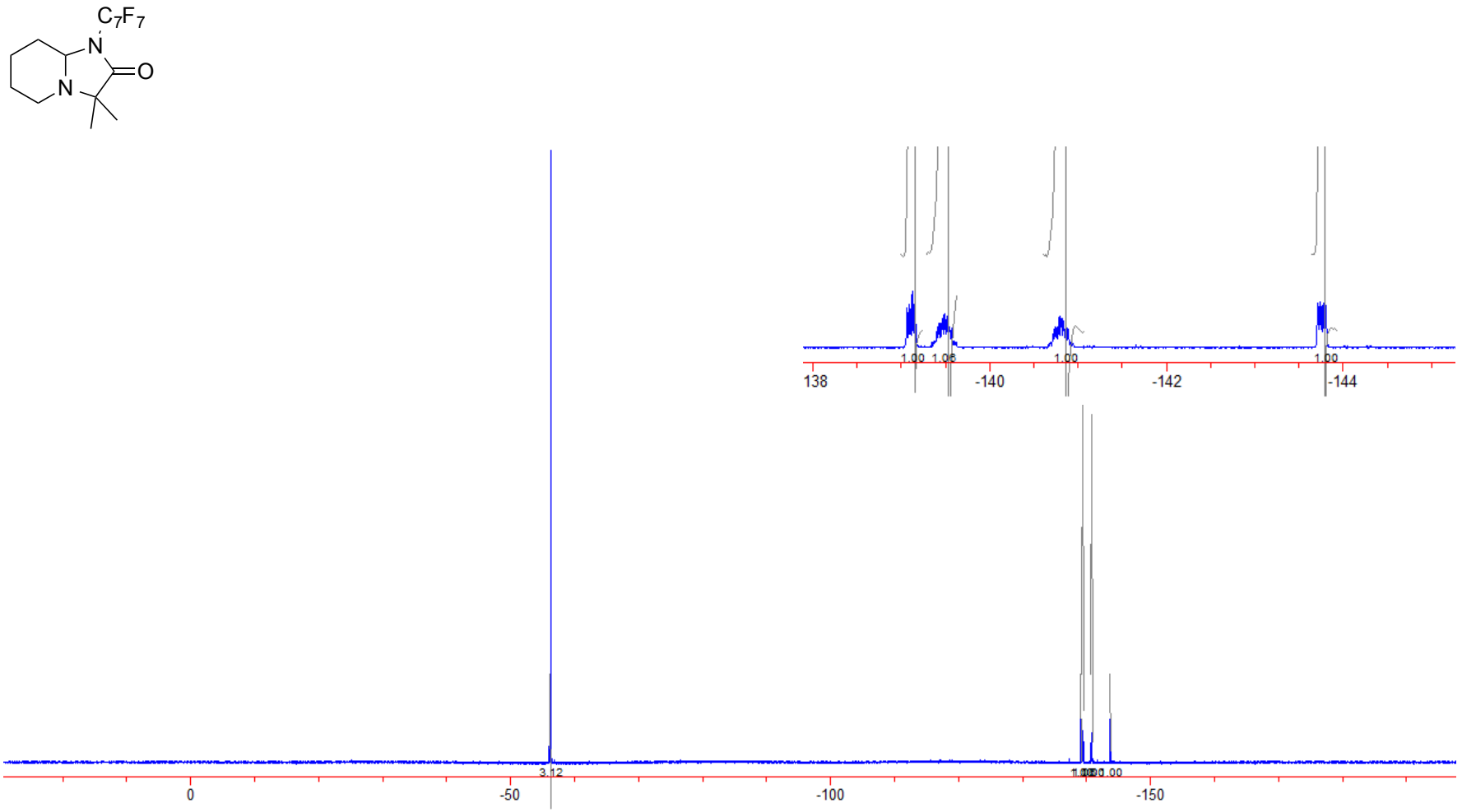
(**5**)



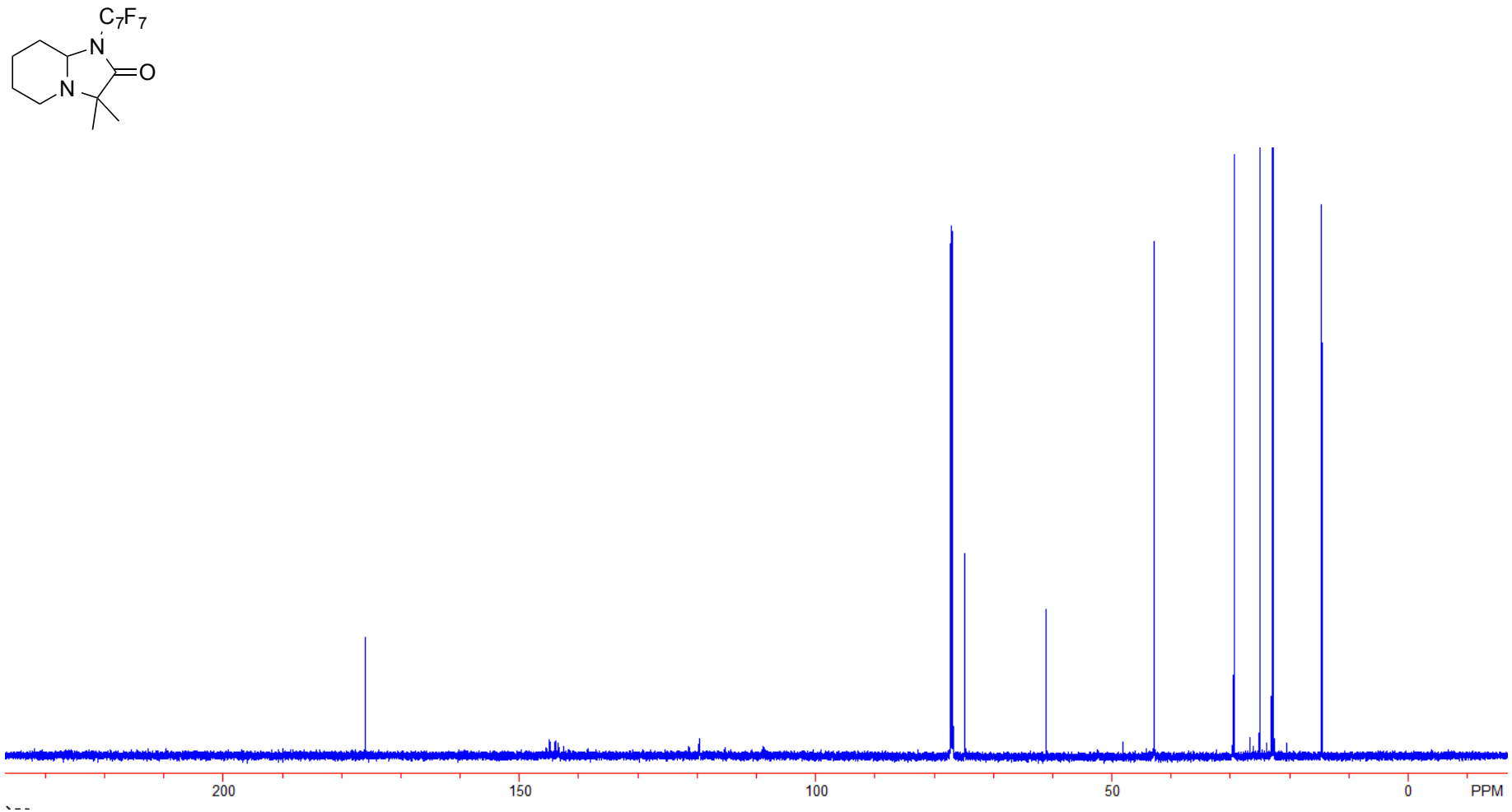
^{13}C NMR Spectrum in $CDCl_3$



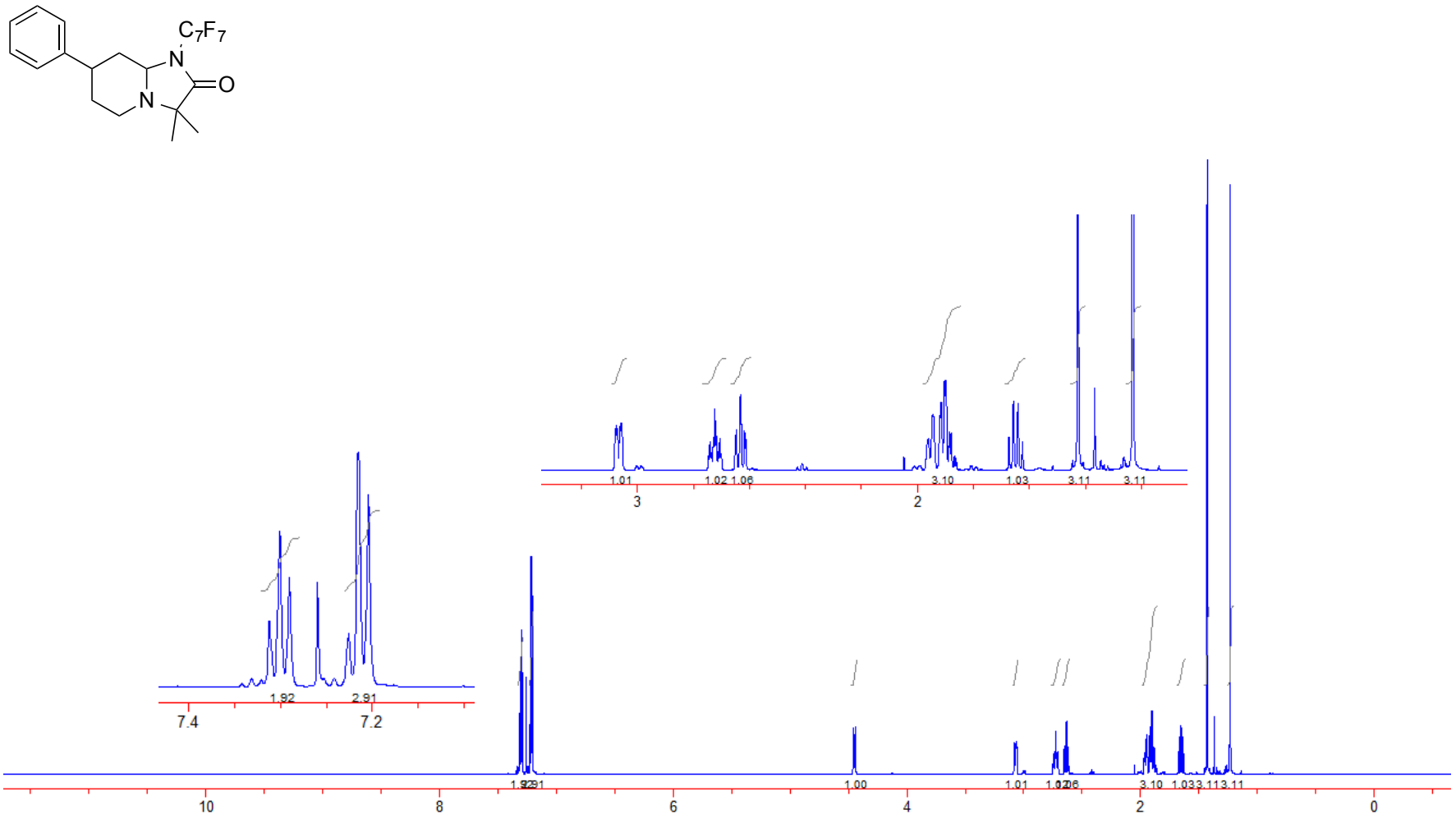
^{1}H NMR Spectrum of **S14** in $CDCl_3$



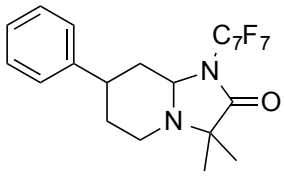
^{19}F NMR Spectrum of **S14** in $CDCl_3$

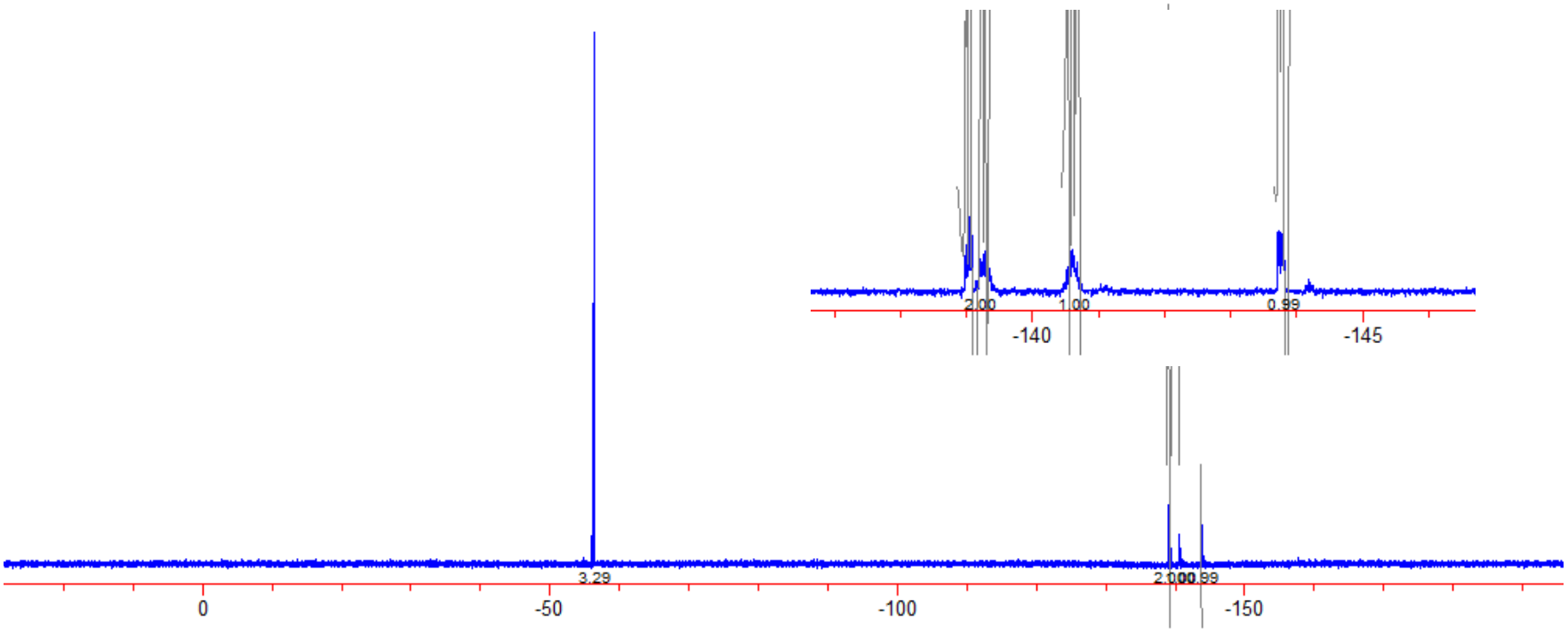


^{13}C NMR Spectrum of **S14** in $CDCl_3$

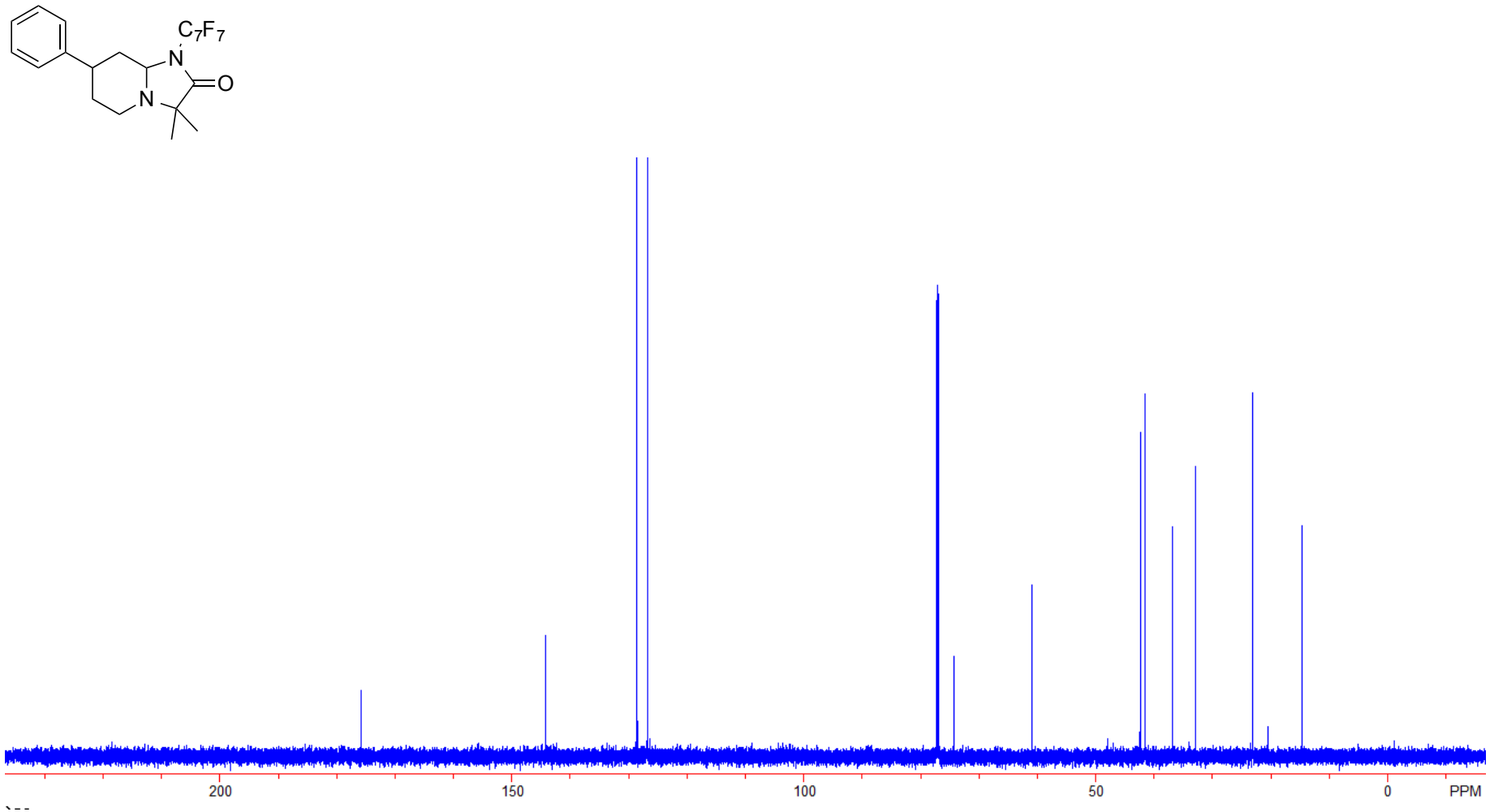


^{1}H NMR Spectrum of **S15** in $CDCl_3$

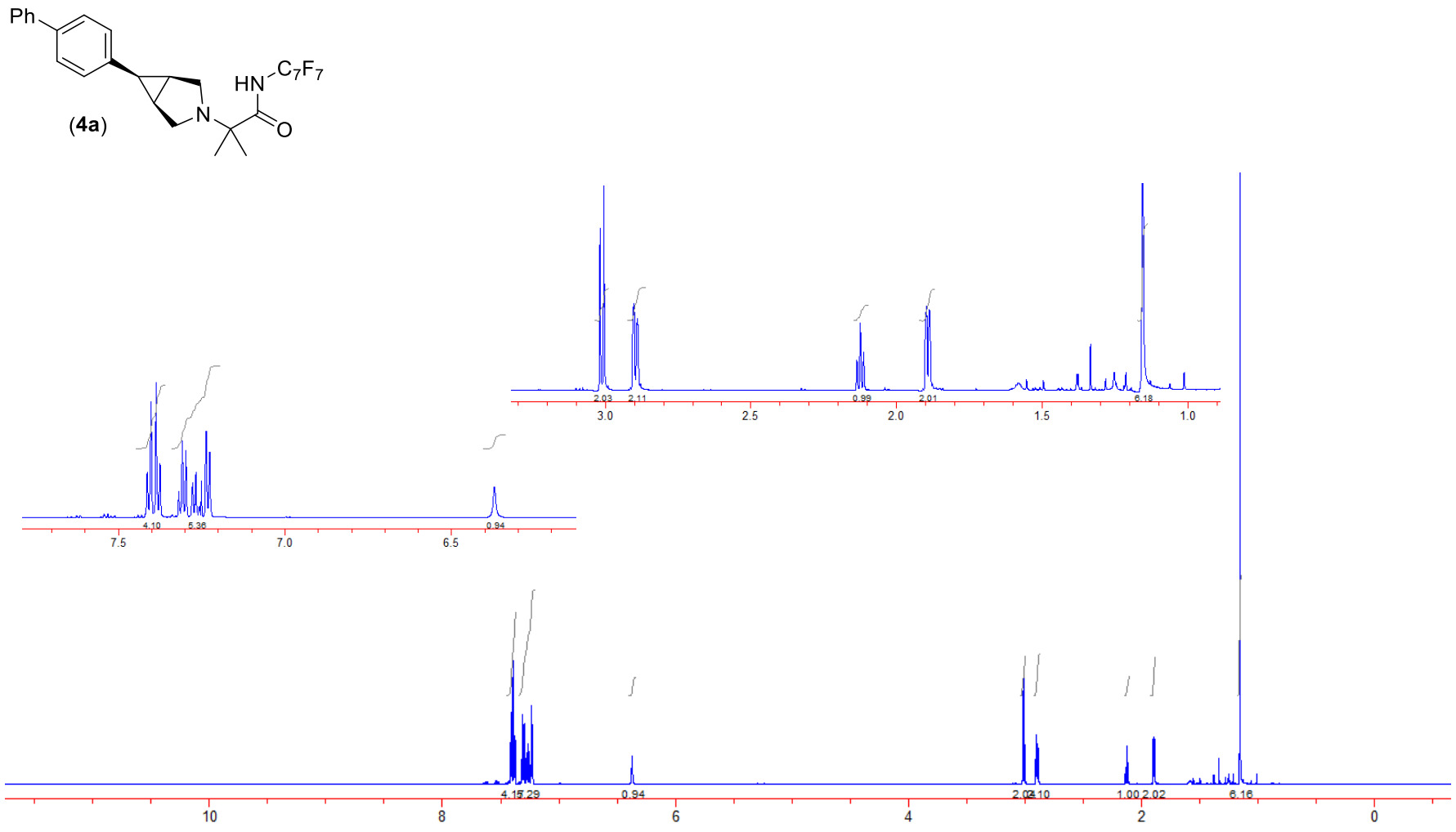




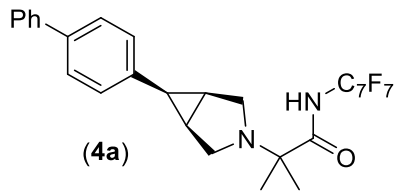
^{19}F NMR Spectrum of **S15** in $CDCl_3$



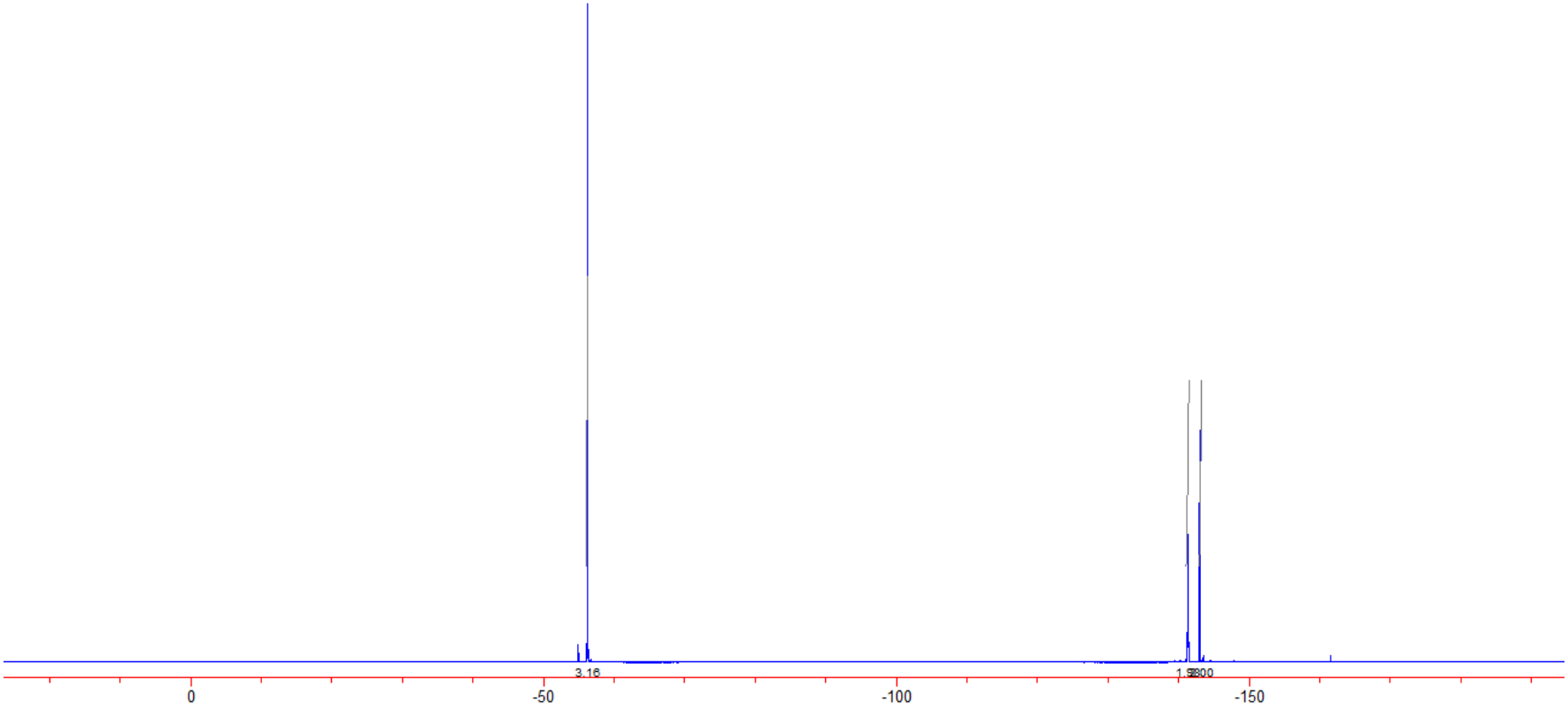
^{13}C NMR Spectrum of **S15** in $CDCl_3$



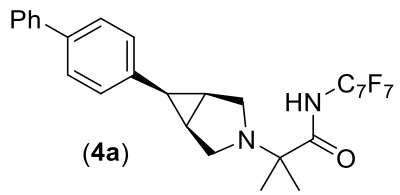
^{1}H NMR Spectrum in $CDCl_3$



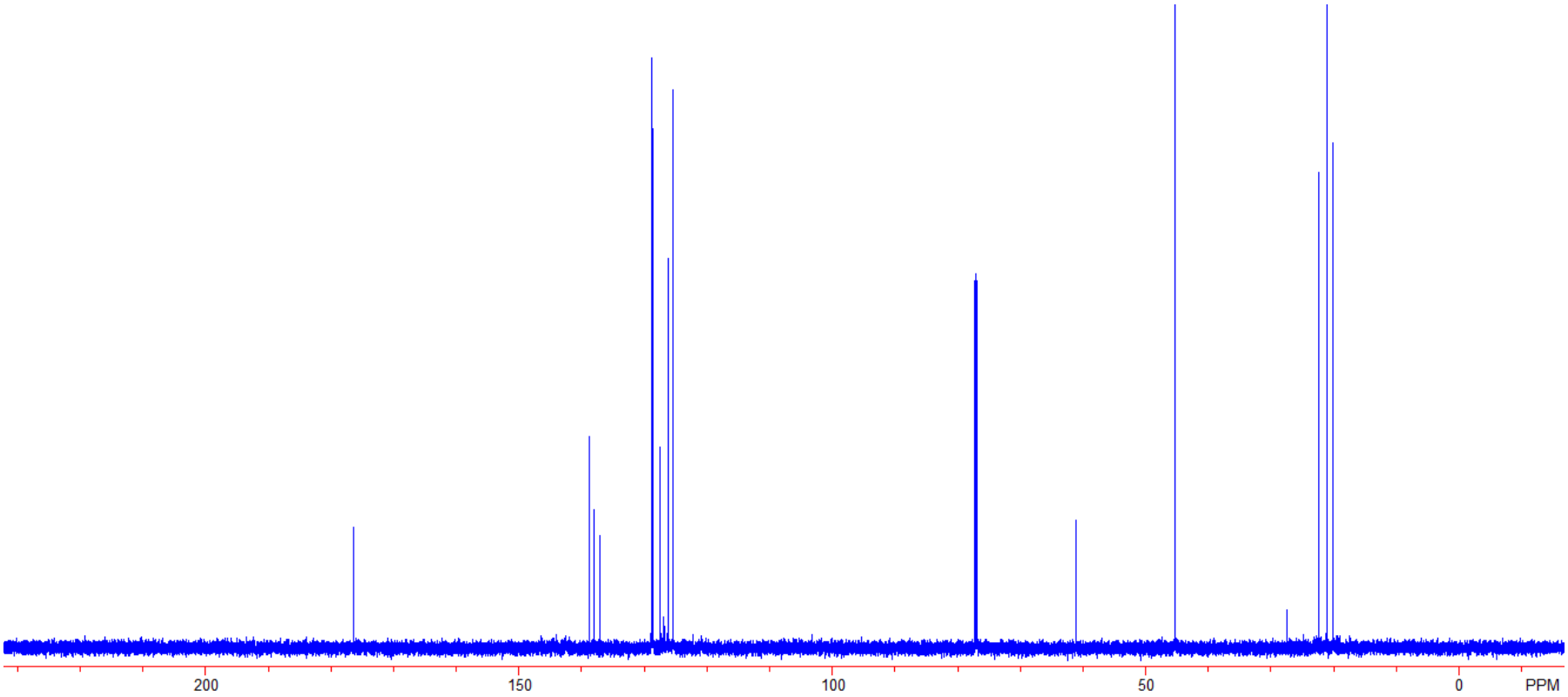
(**4a**)



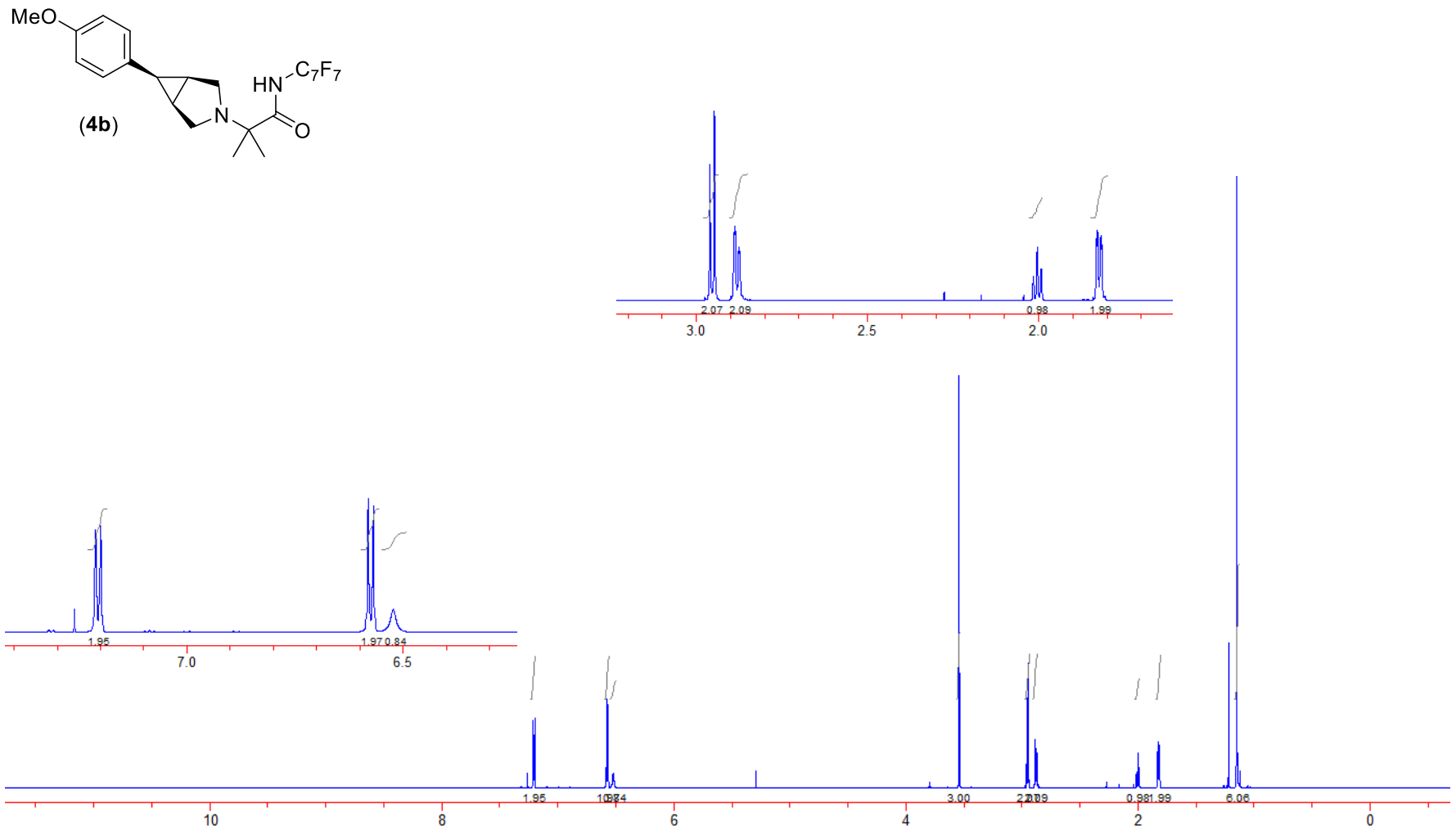
^{19}F NMR Spectrum in $CDCl_3$



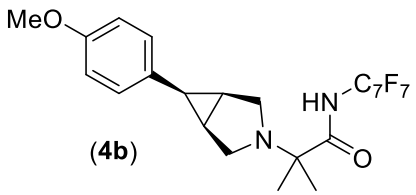
(**4a**)



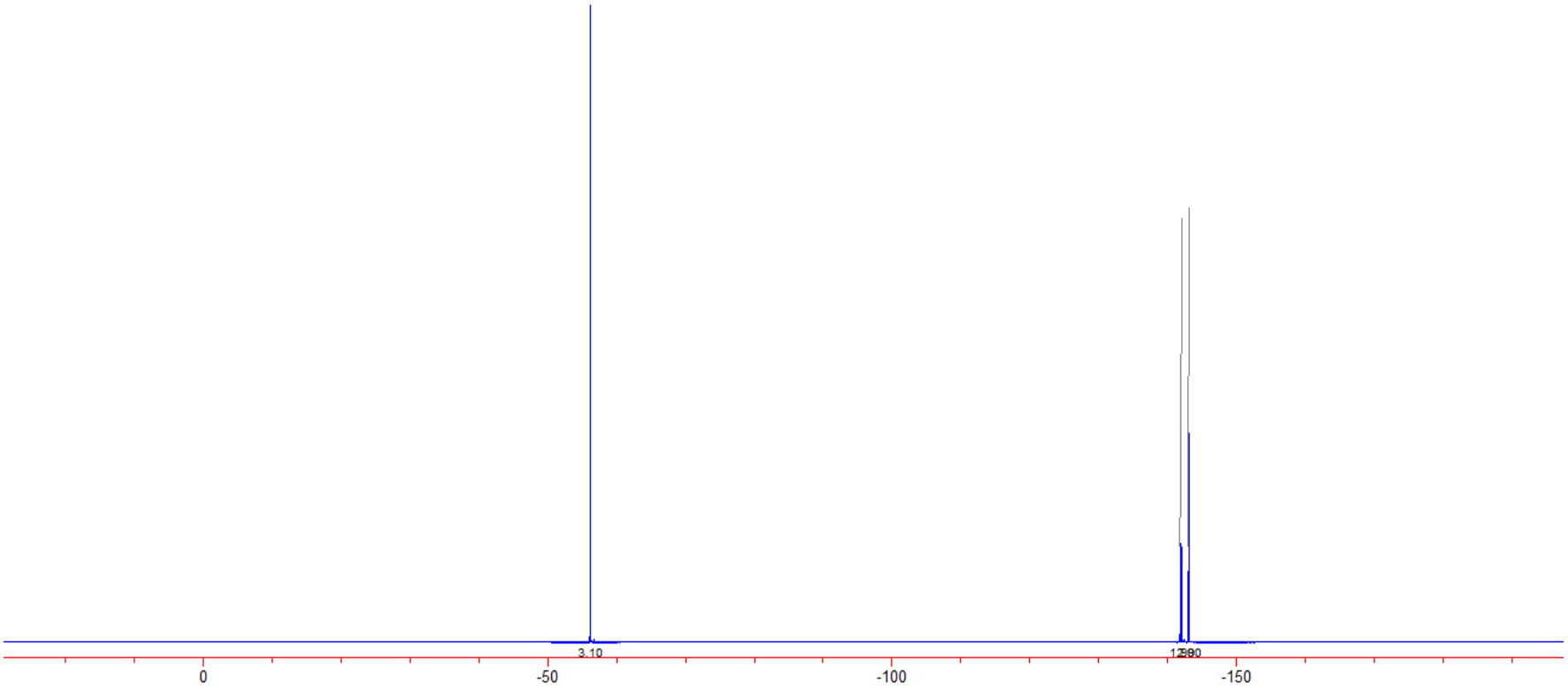
^{13}C NMR Spectrum in $CDCl_3$



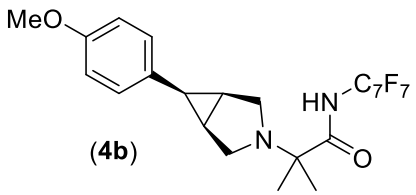
^{1}H NMR Spectrum in $CDCl_3$



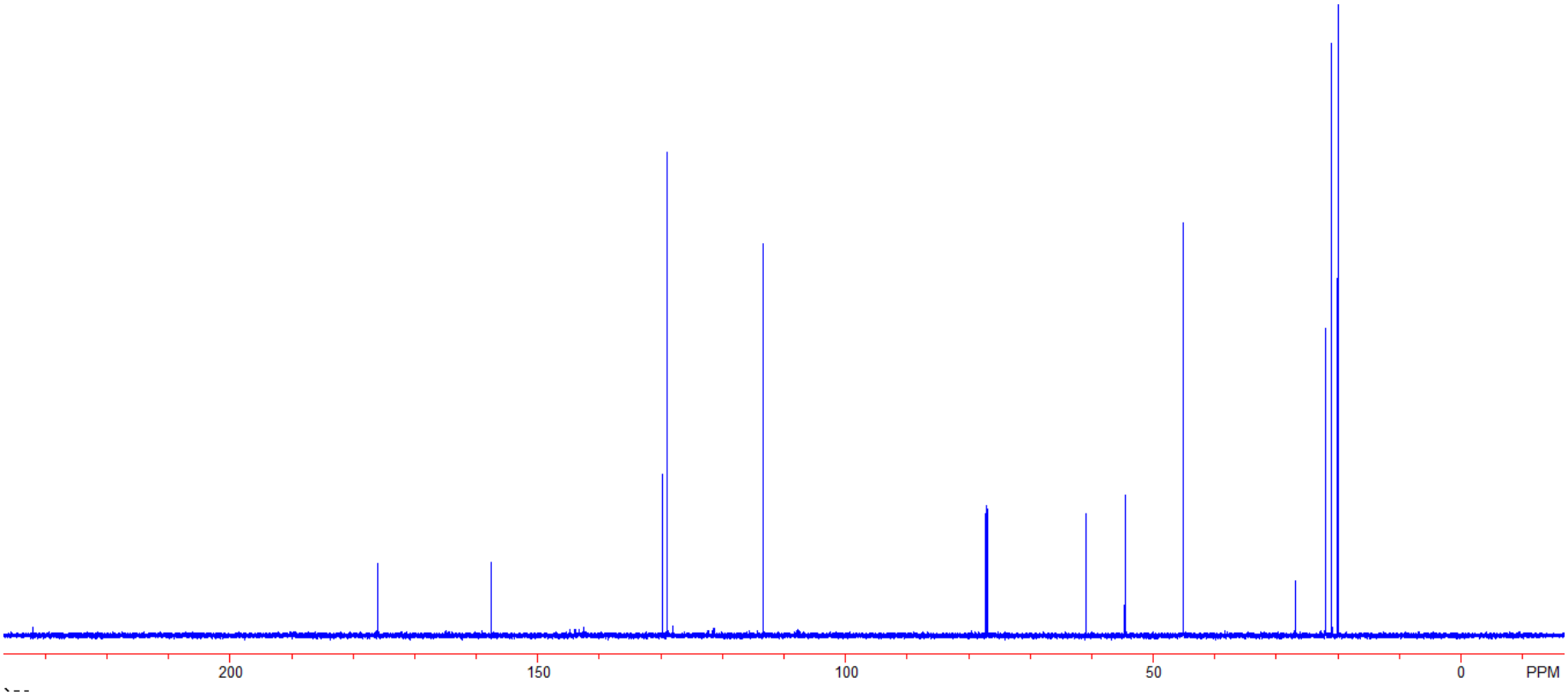
(**4b**)



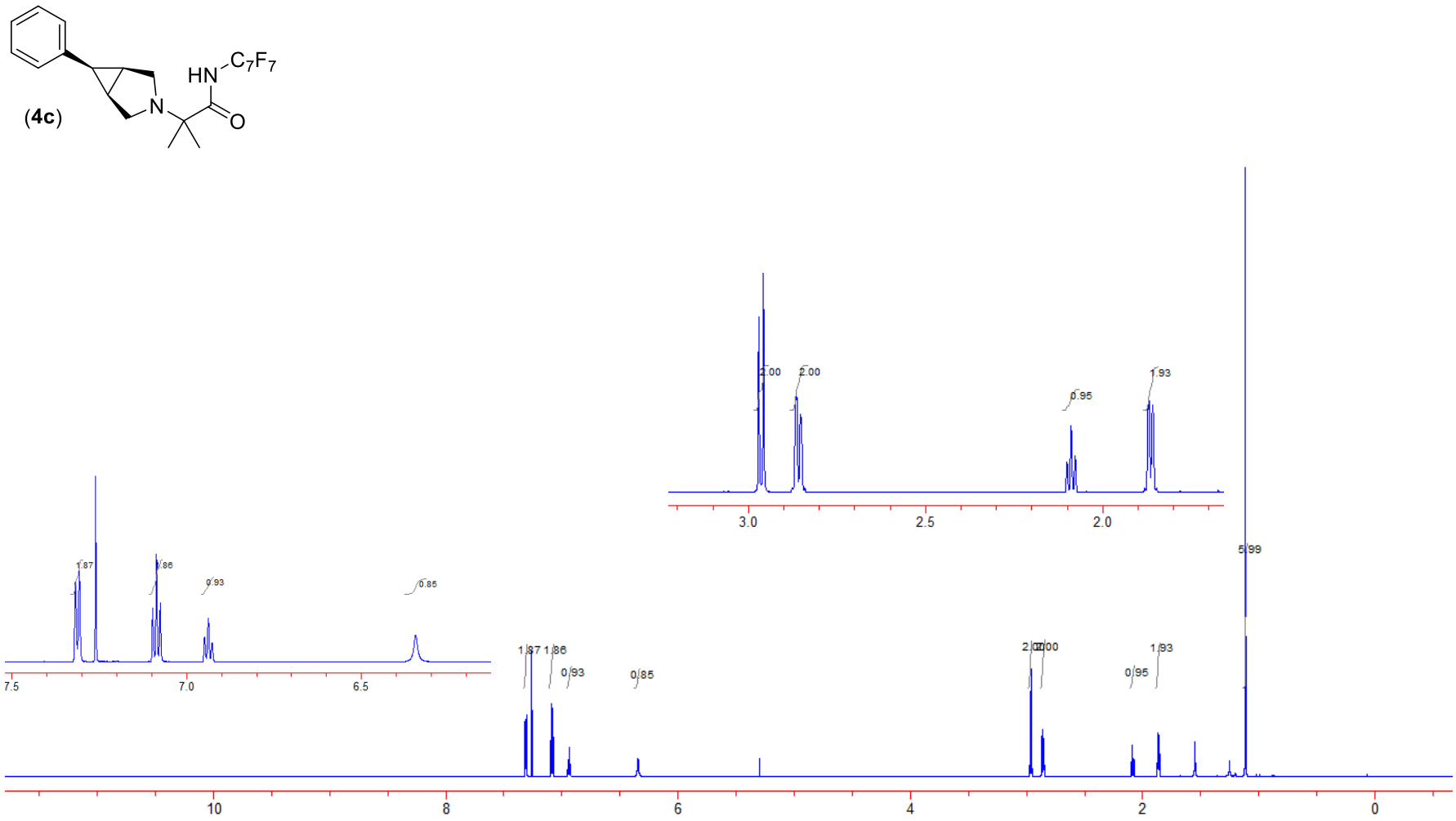
^{19}F NMR Spectrum in $CDCl_3$



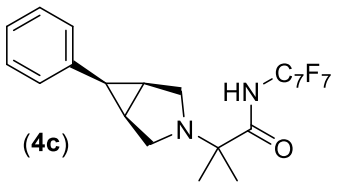
(**4b**)



^{13}C NMR Spectrum in $CDCl_3$



^{1}H NMR Spectrum in $CDCl_3$



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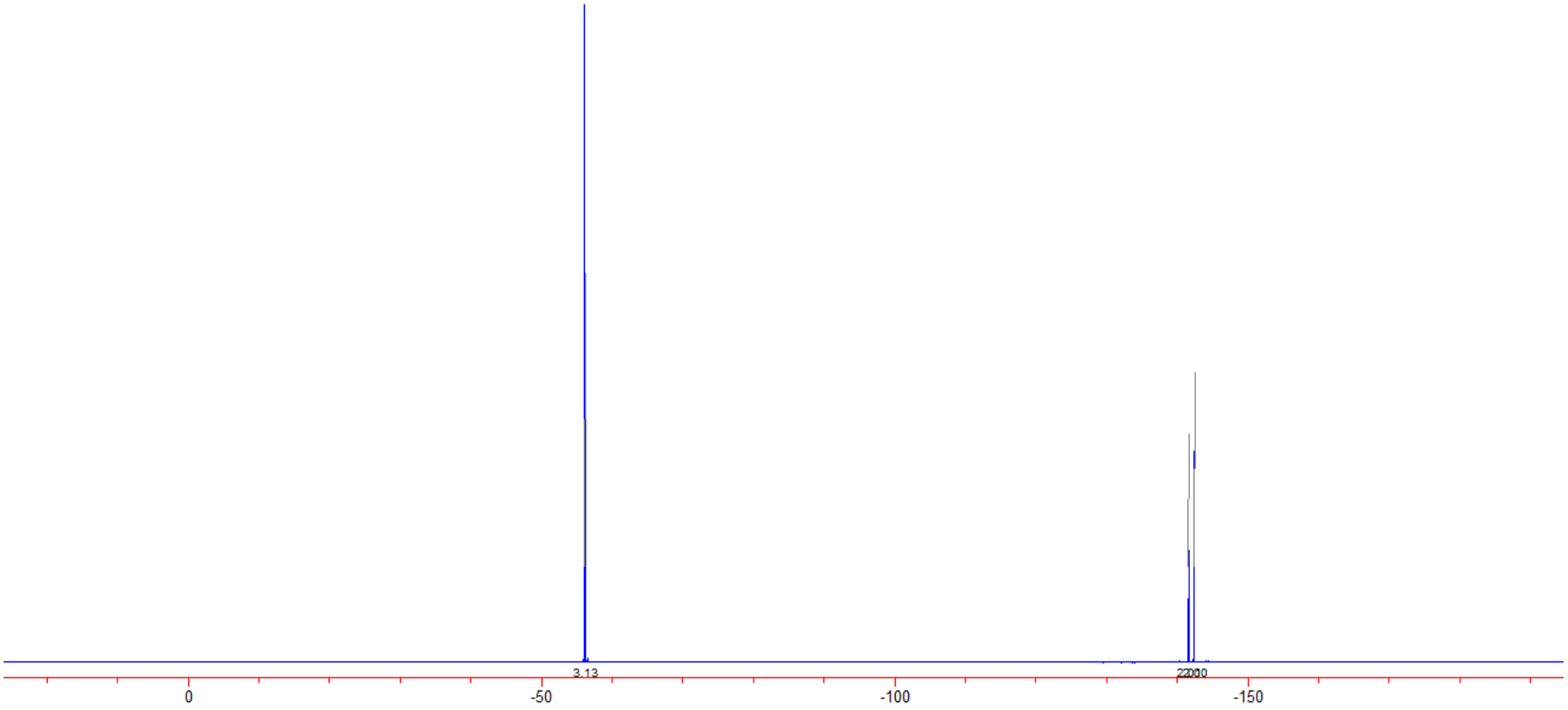
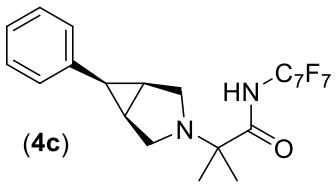
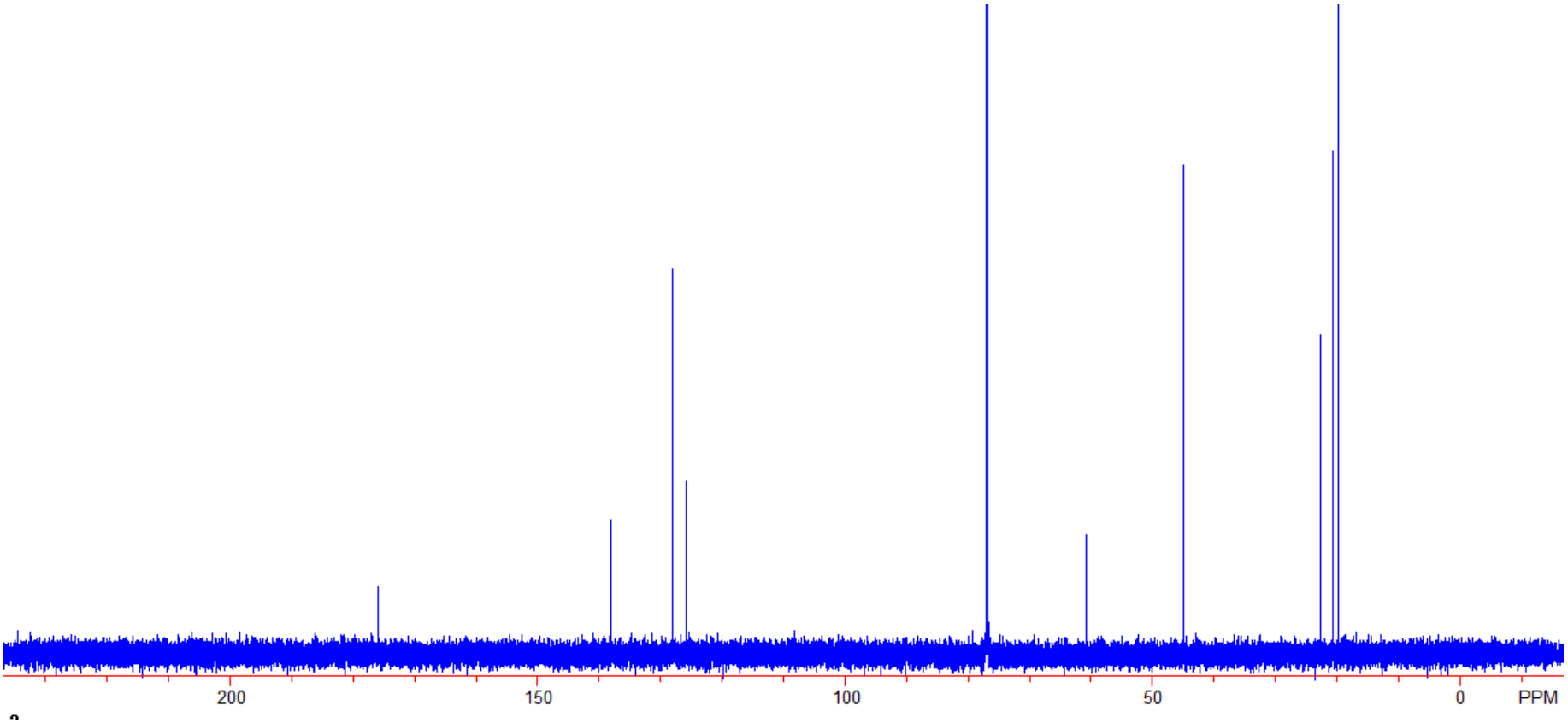


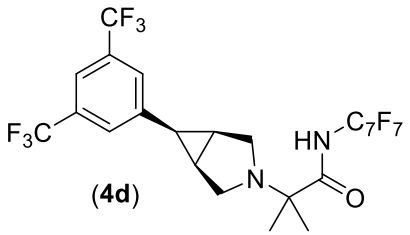
^{19}F NMR Spectrum in $CDCl_3$



(**4c**)



^{13}C NMR Spectrum in $CDCl_3$



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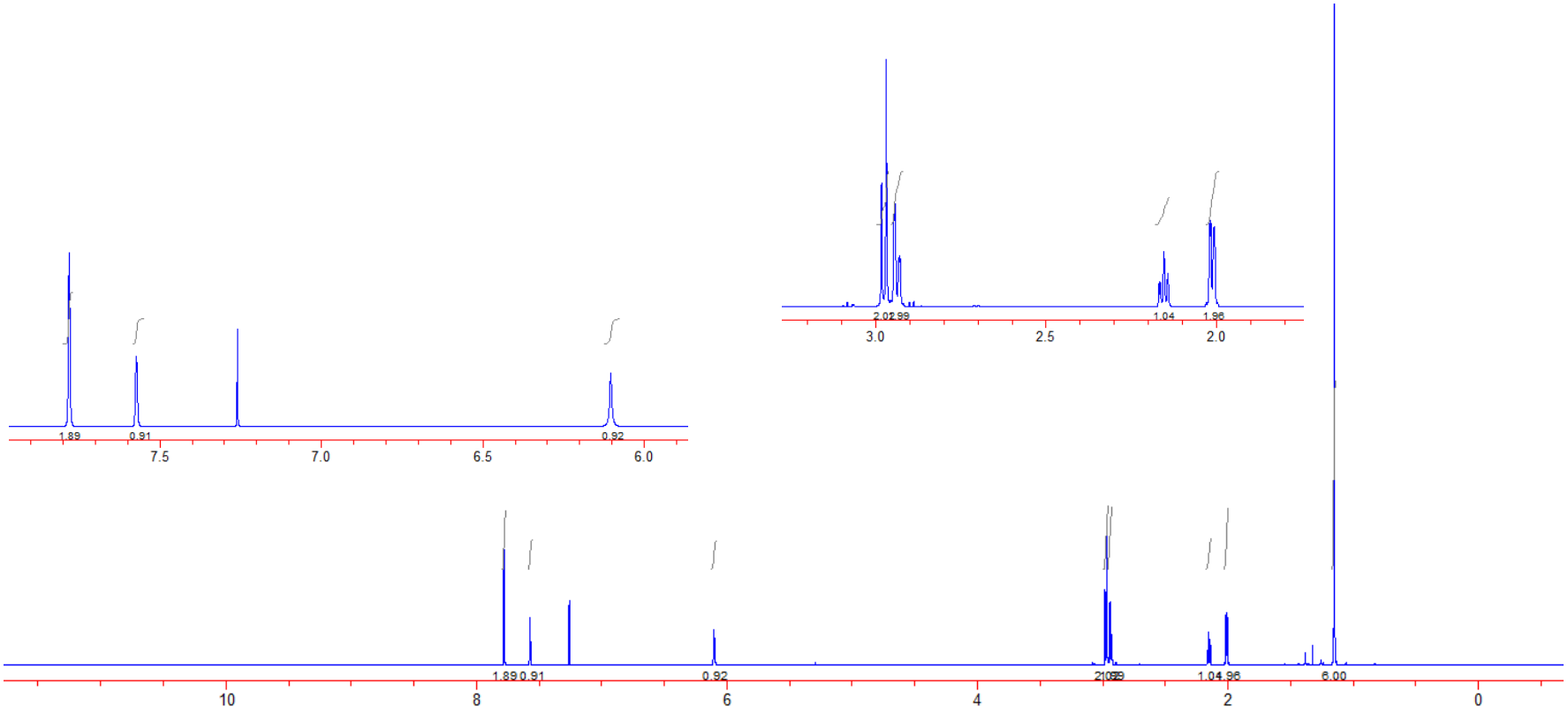
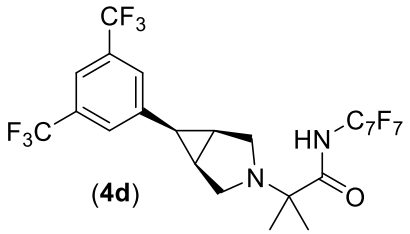


^{1}H NMR Spectrum in $CDCl_3$



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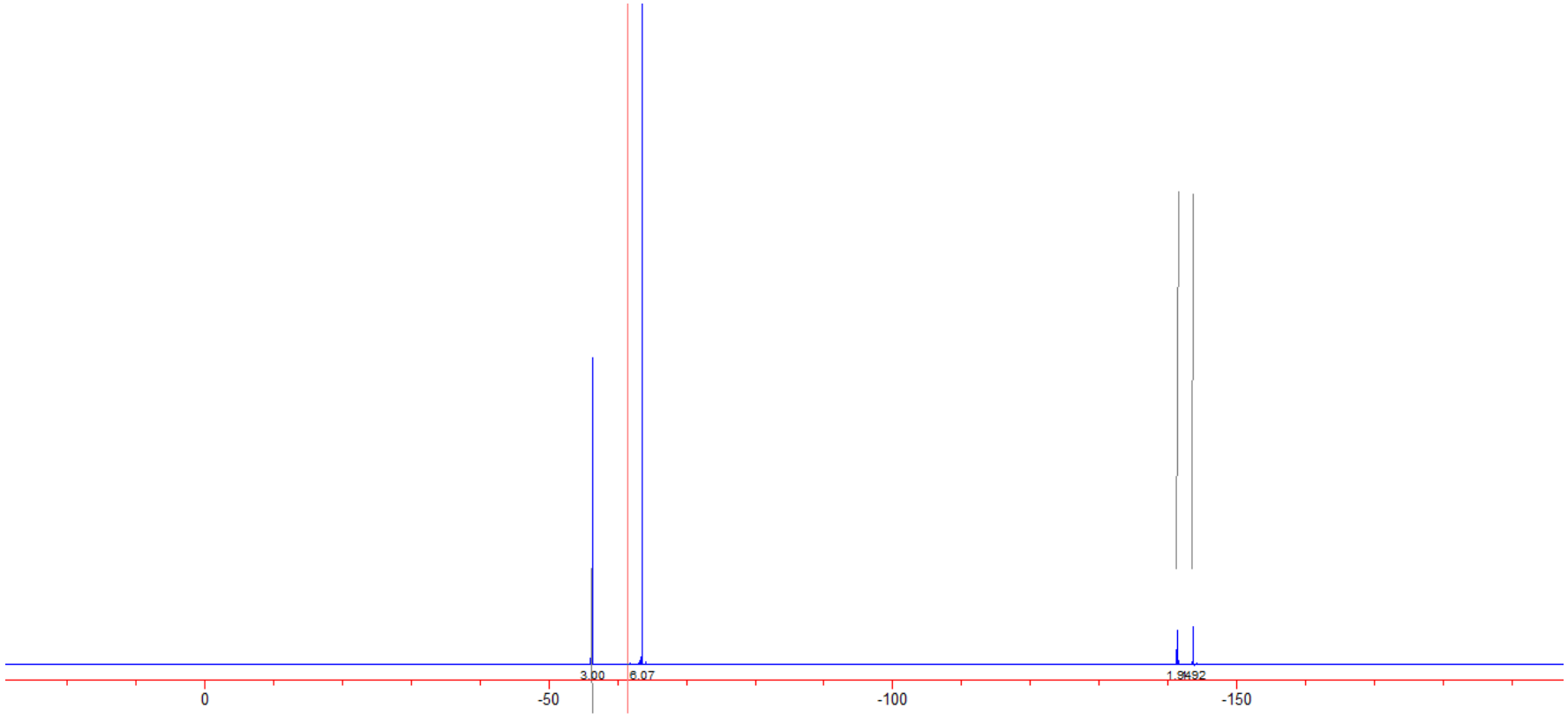
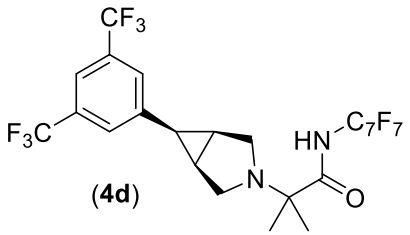
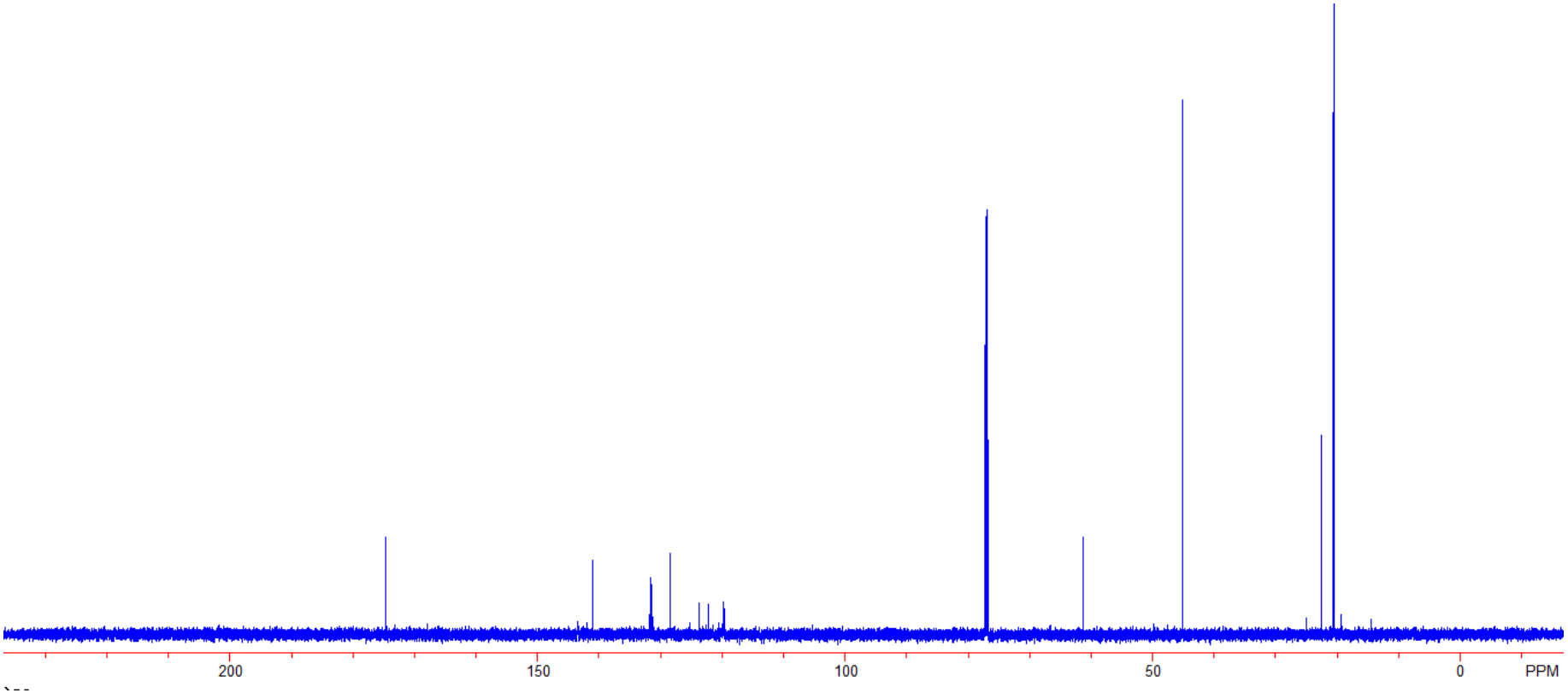


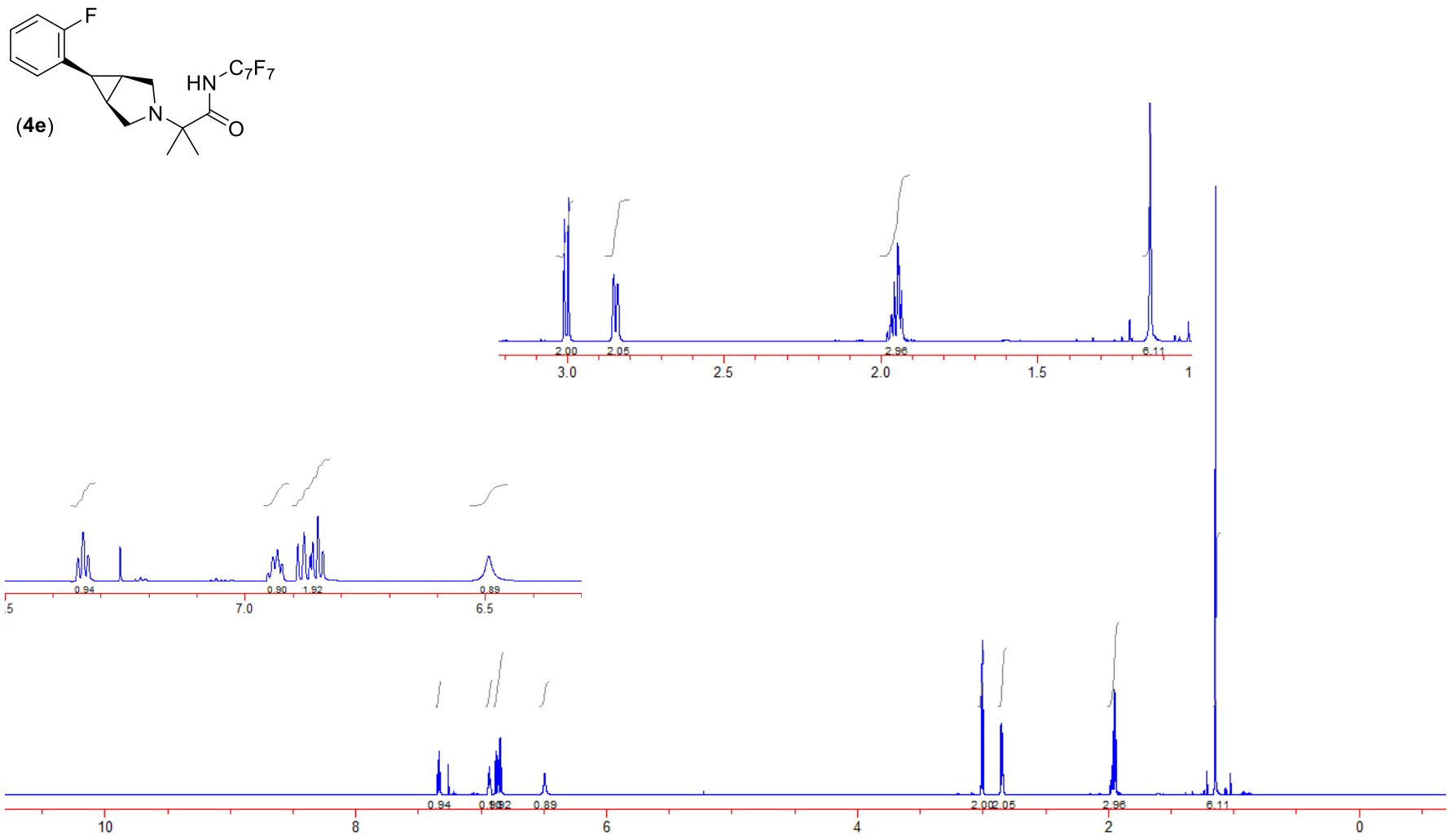
^{19}F NMR Spectrum in $CDCl_3$



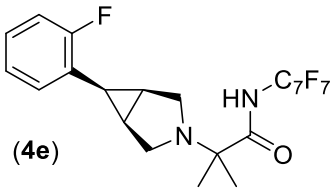
(**4d**)



^{13}C NMR Spectrum in $CDCl_3$



^{1}H NMR Spectrum in $CDCl_3$



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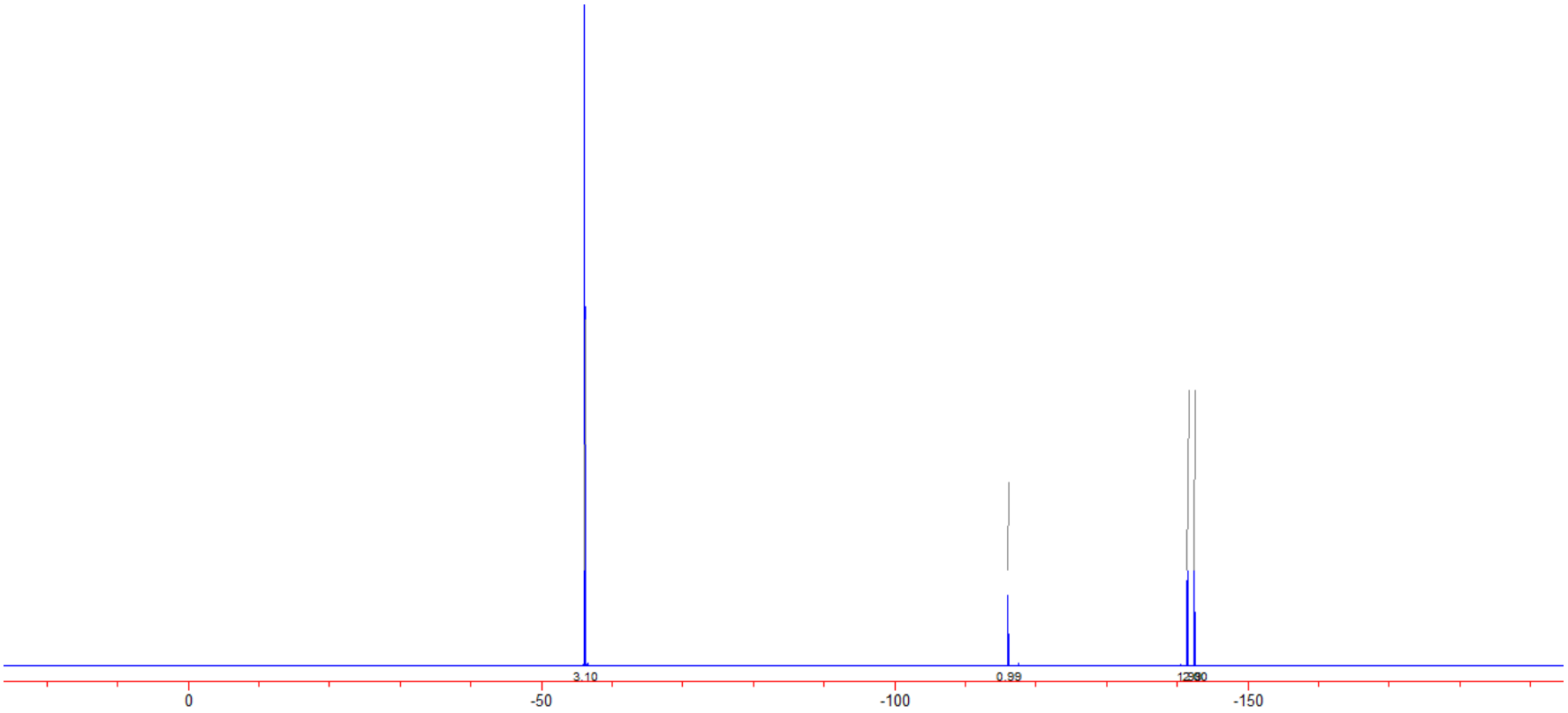
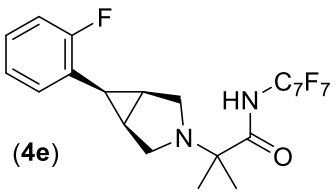


^{19}F NMR Spectrum in $CDCl_3$



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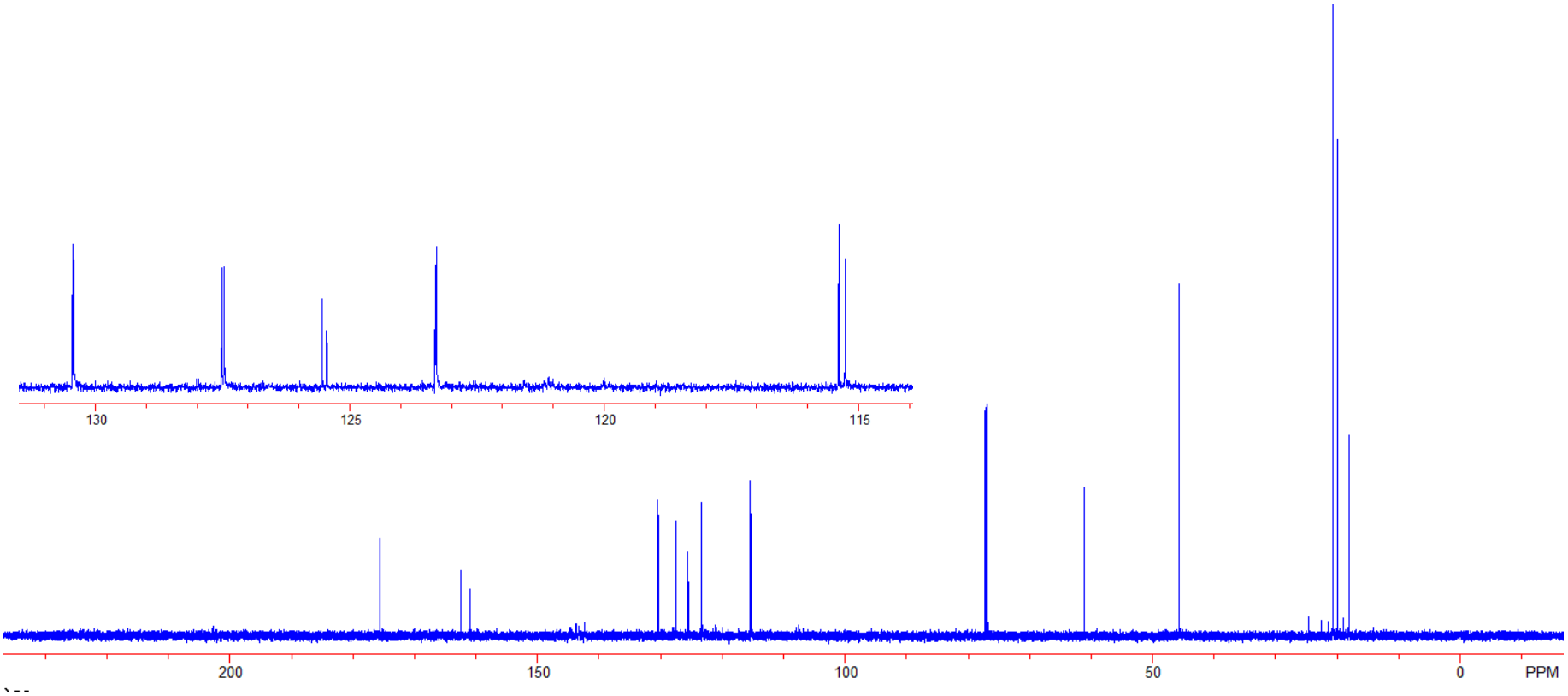
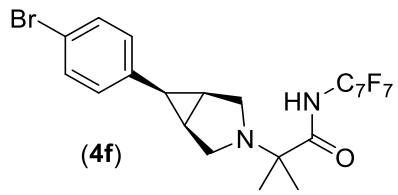


^{13}C NMR Spectrum in $CDCl_3$



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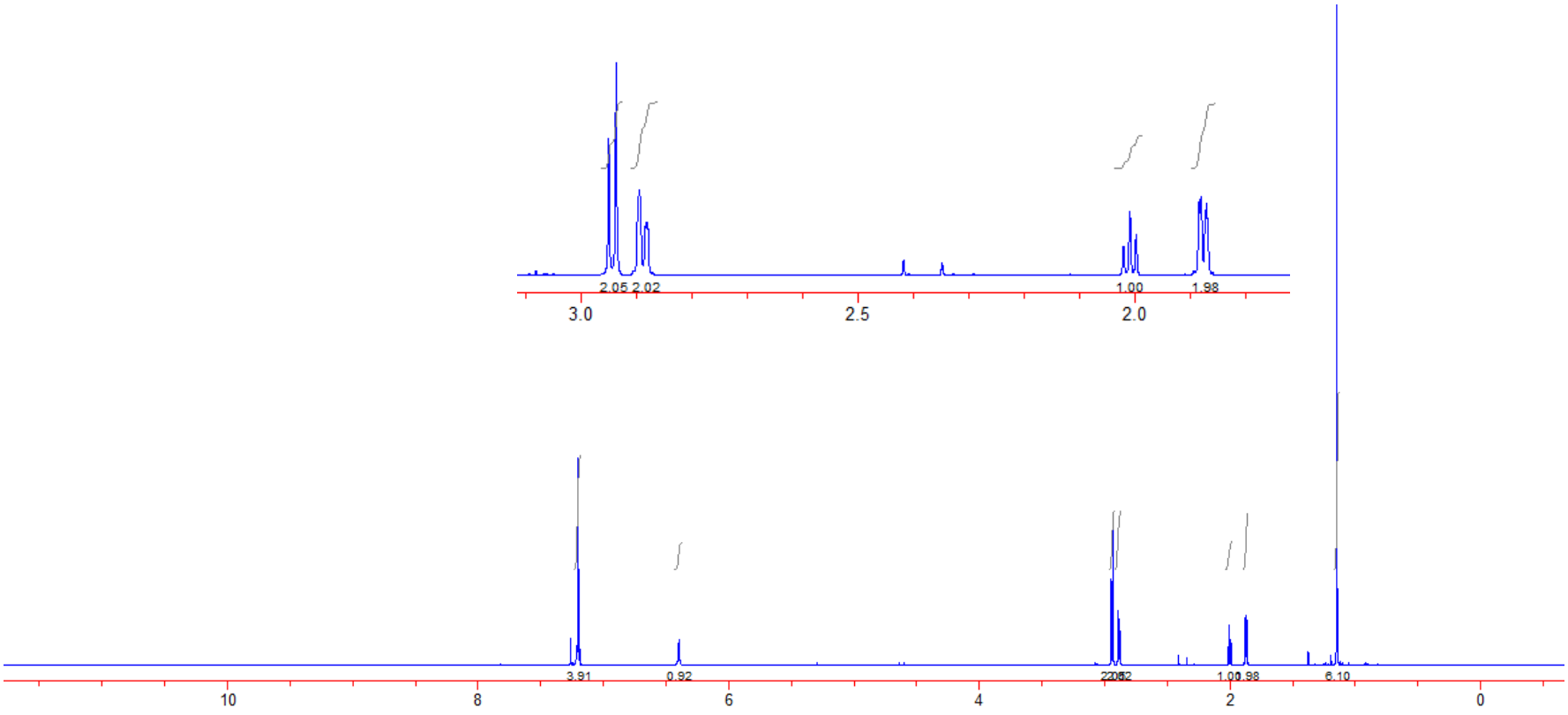
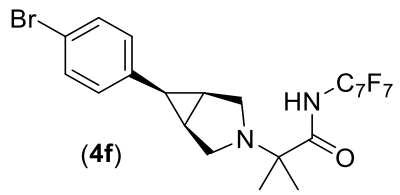


^{1}H NMR Spectrum in $CDCl_3$



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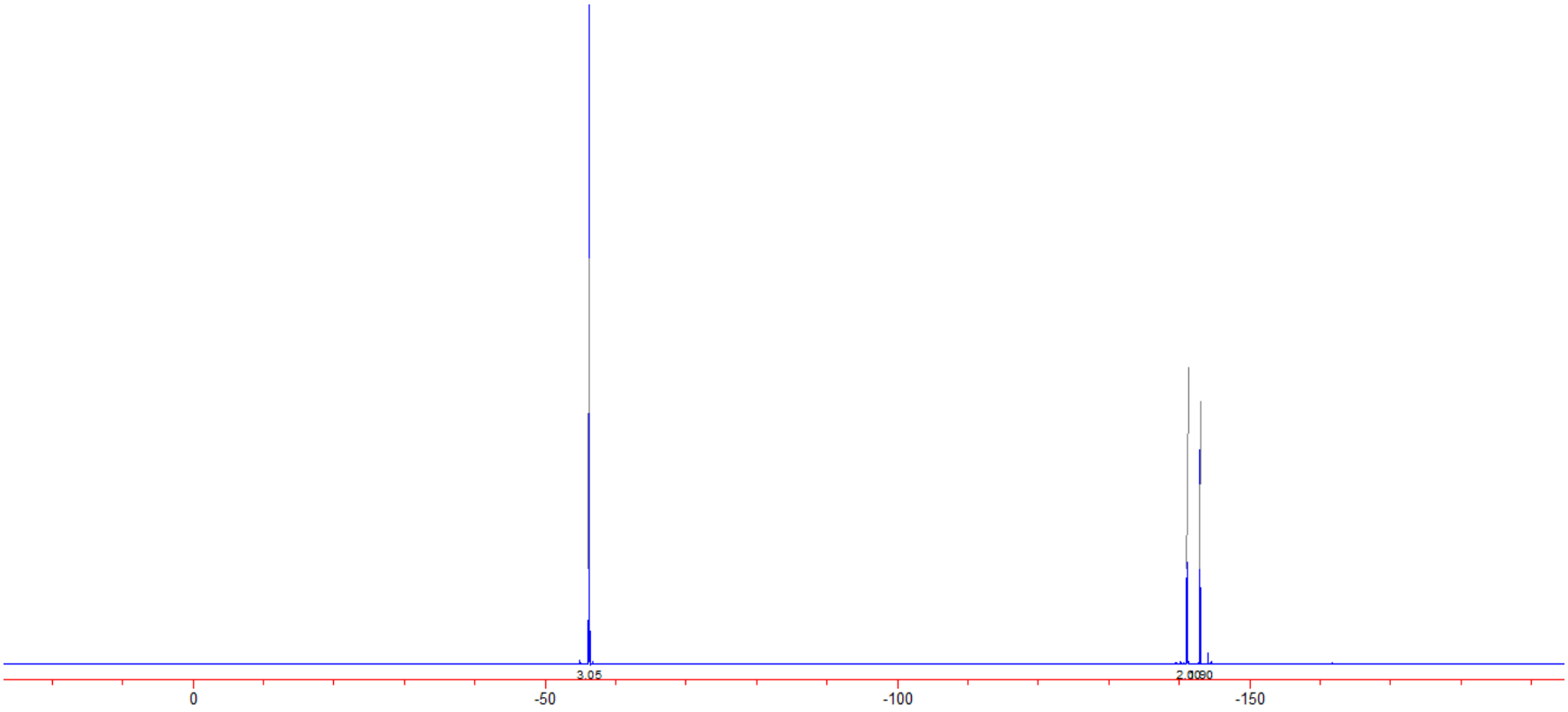
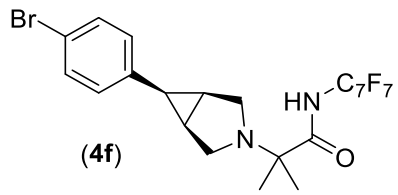


^{19}F NMR Spectrum in $CDCl_3$



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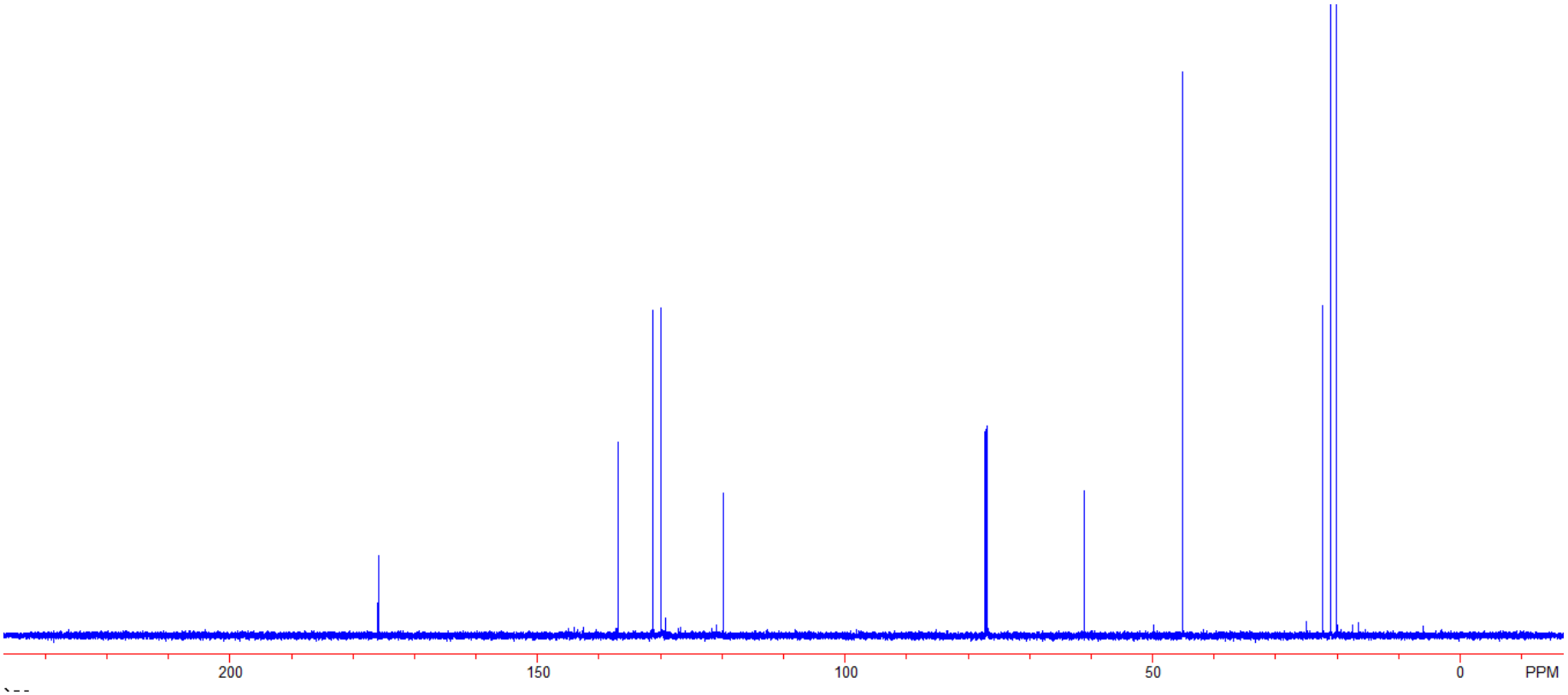
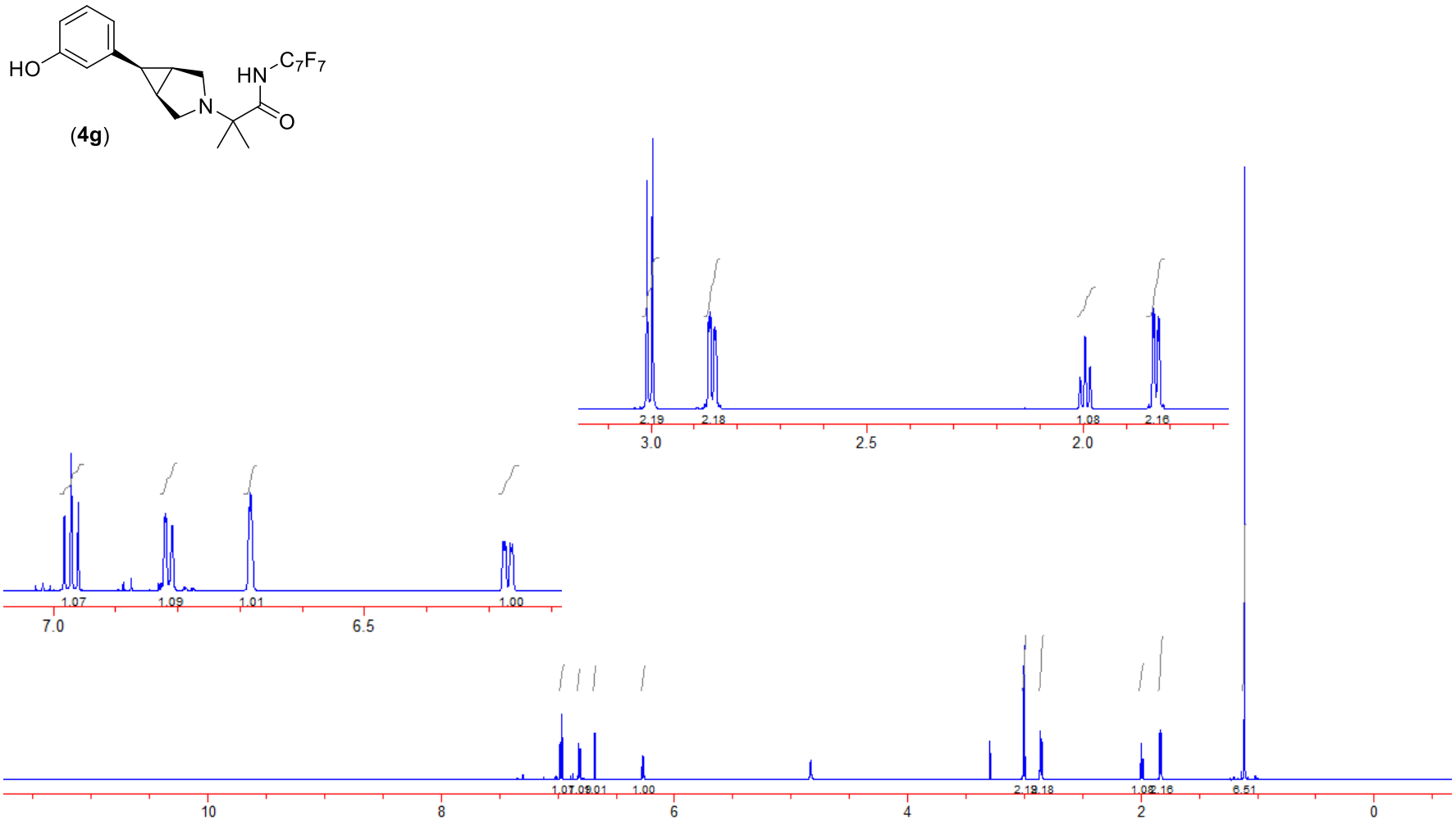
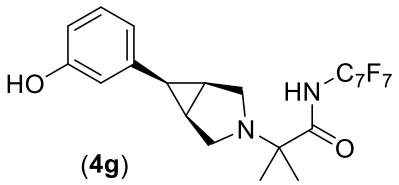


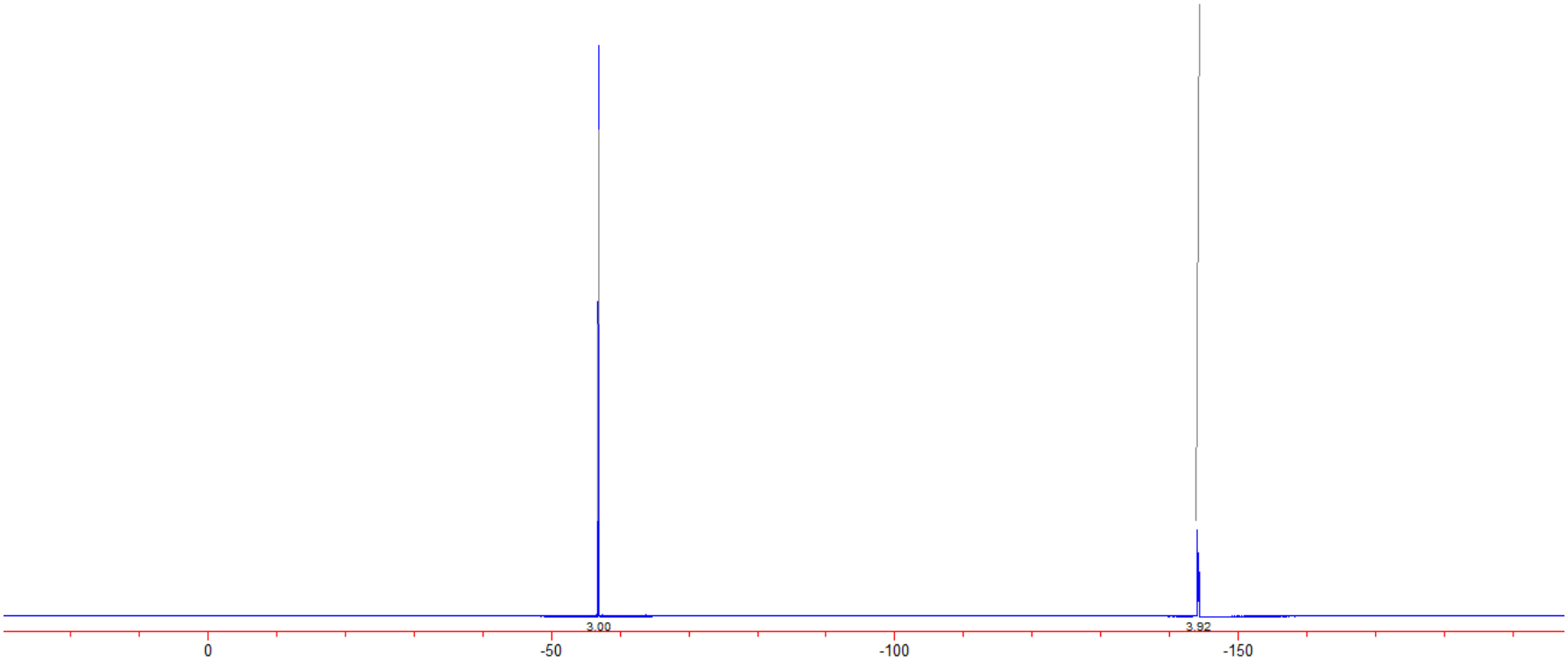
^{13}C NMR Spectrum in $CDCl_3$



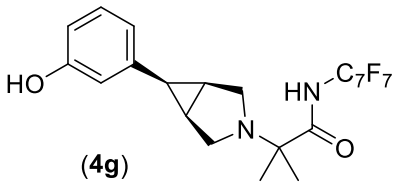
^{1}H NMR Spectrum in MeOD



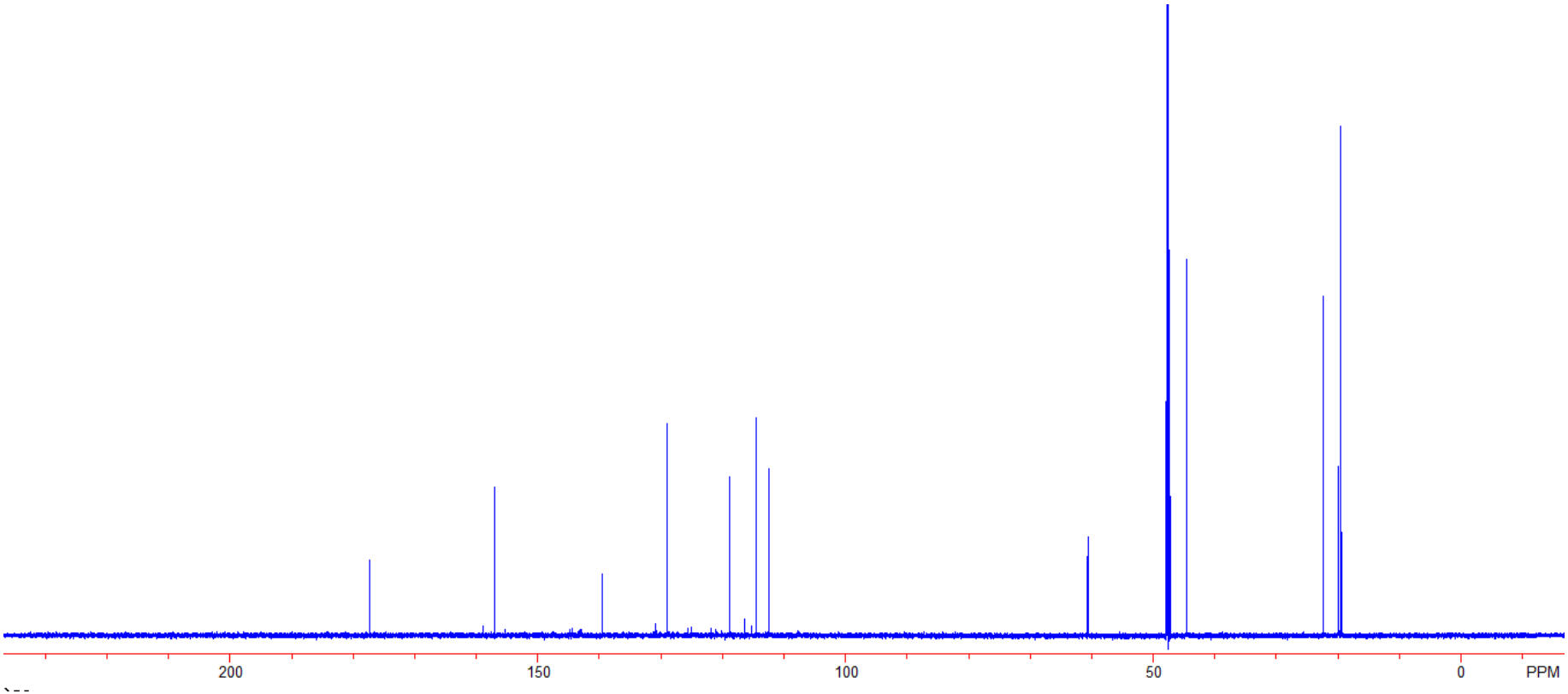
(**4g**)



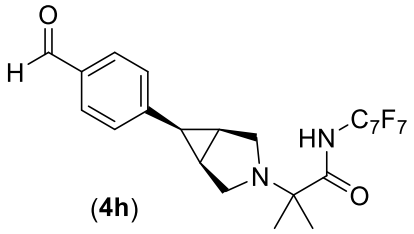
^{19}F NMR Spectrum in MeOD



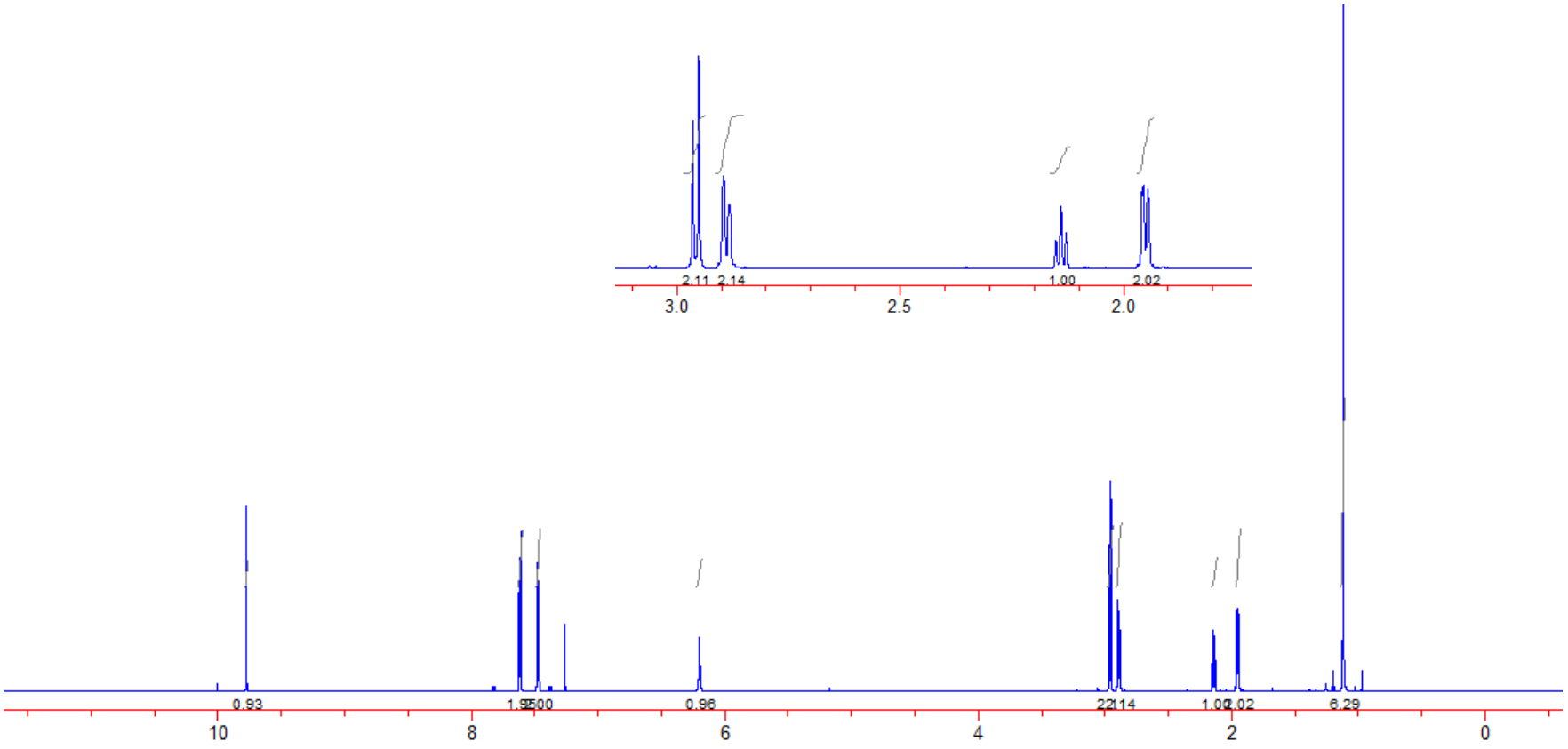
(**4g**)



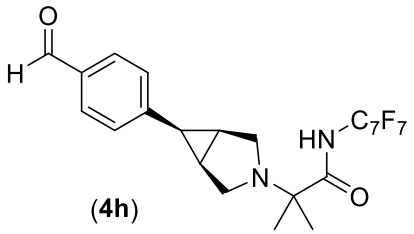
^{13}C NMR Spectrum in MeOD



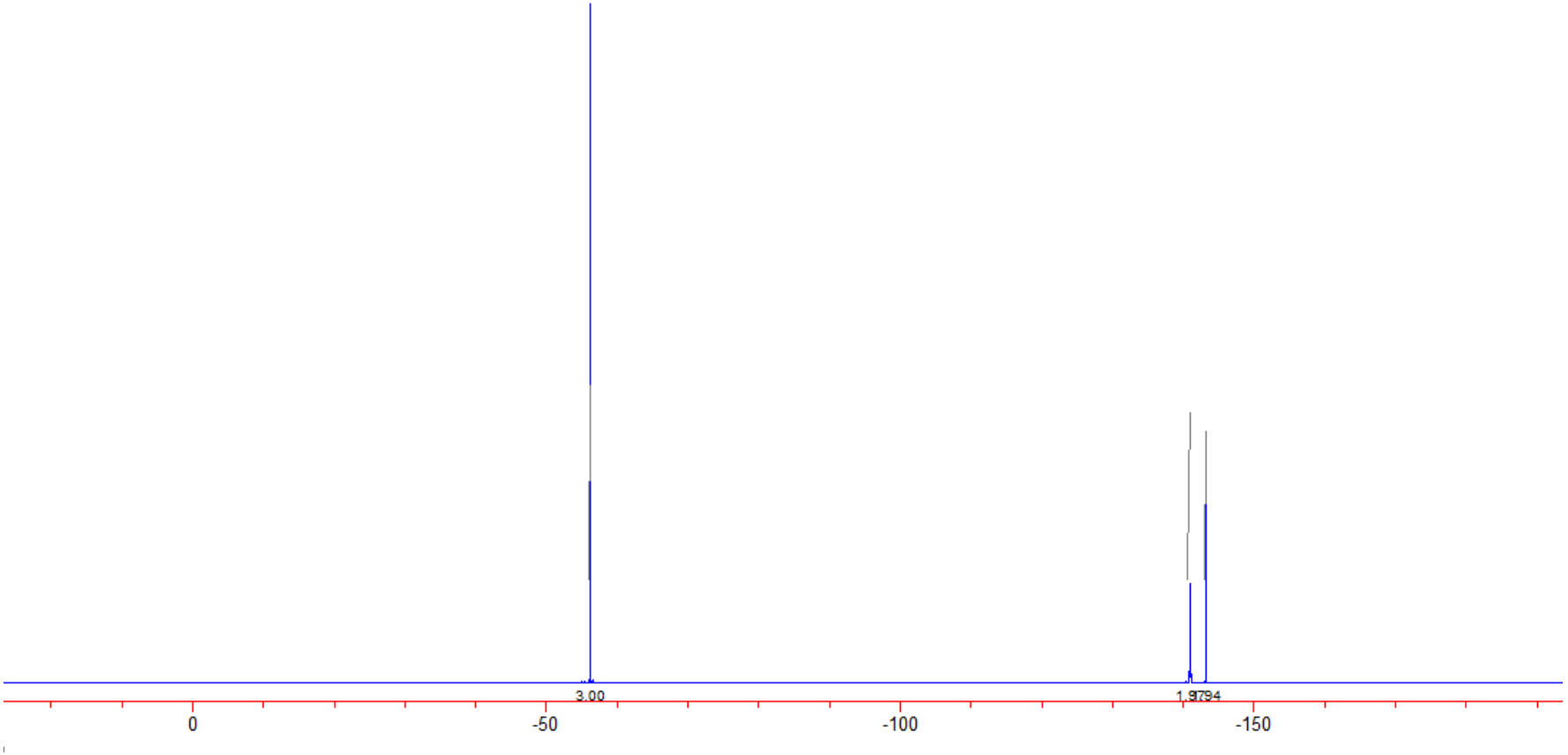
(**4h**)



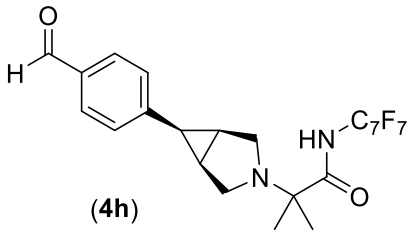
^{1}H NMR Spectrum in $CDCl_3$



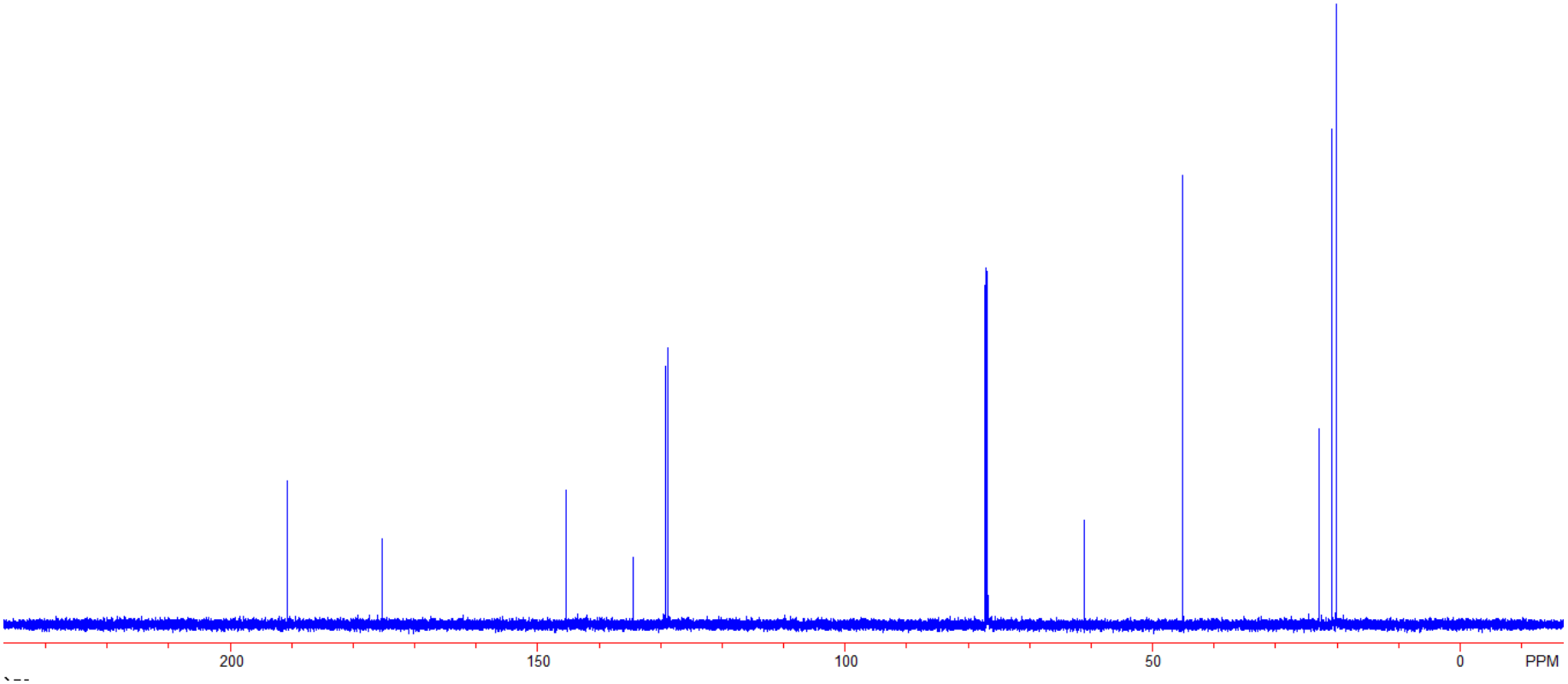
(**4h**)



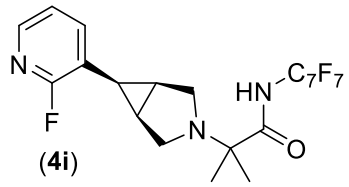
^{19}F NMR Spectrum in $CDCl_3$



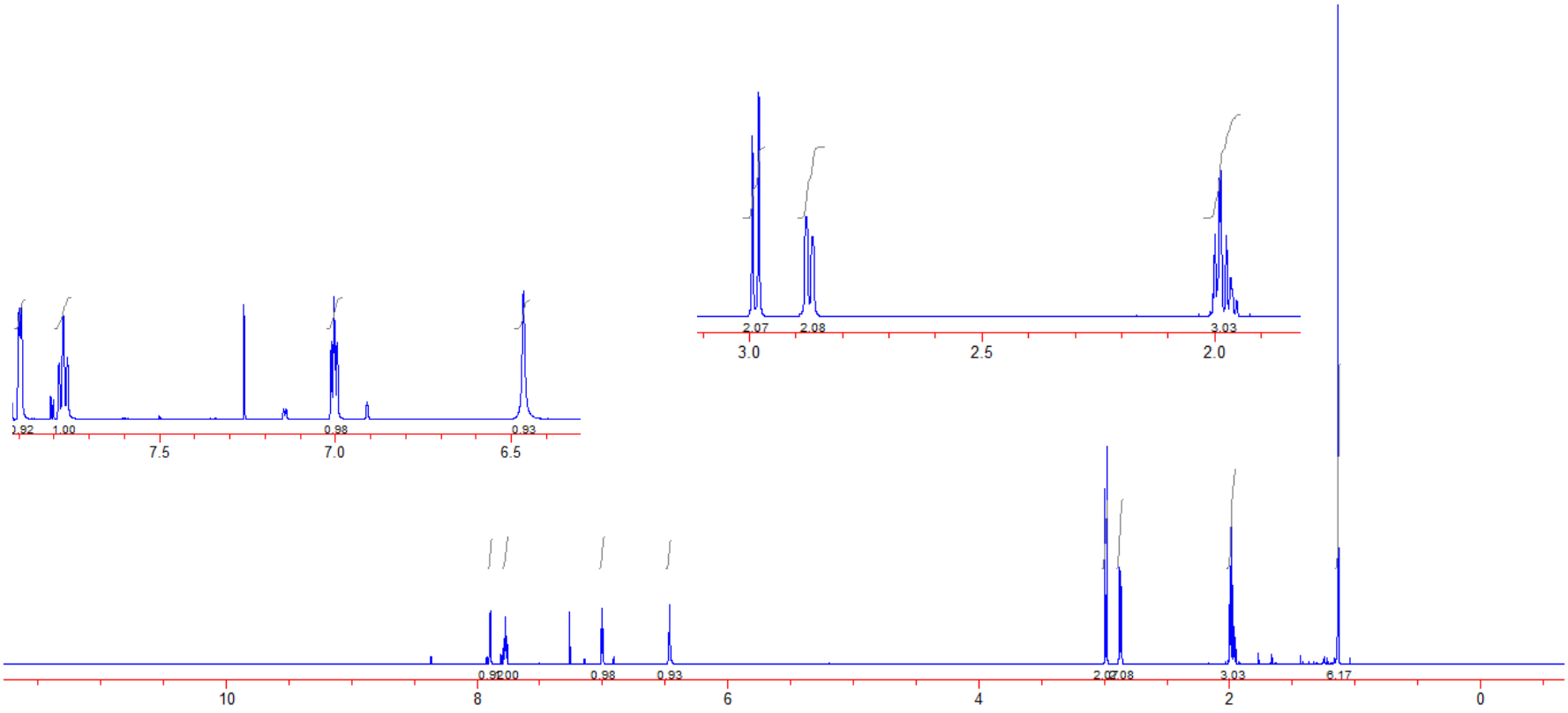
(**4h**)



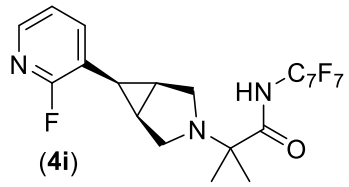
^{13}C NMR Spectrum in $CDCl_3$



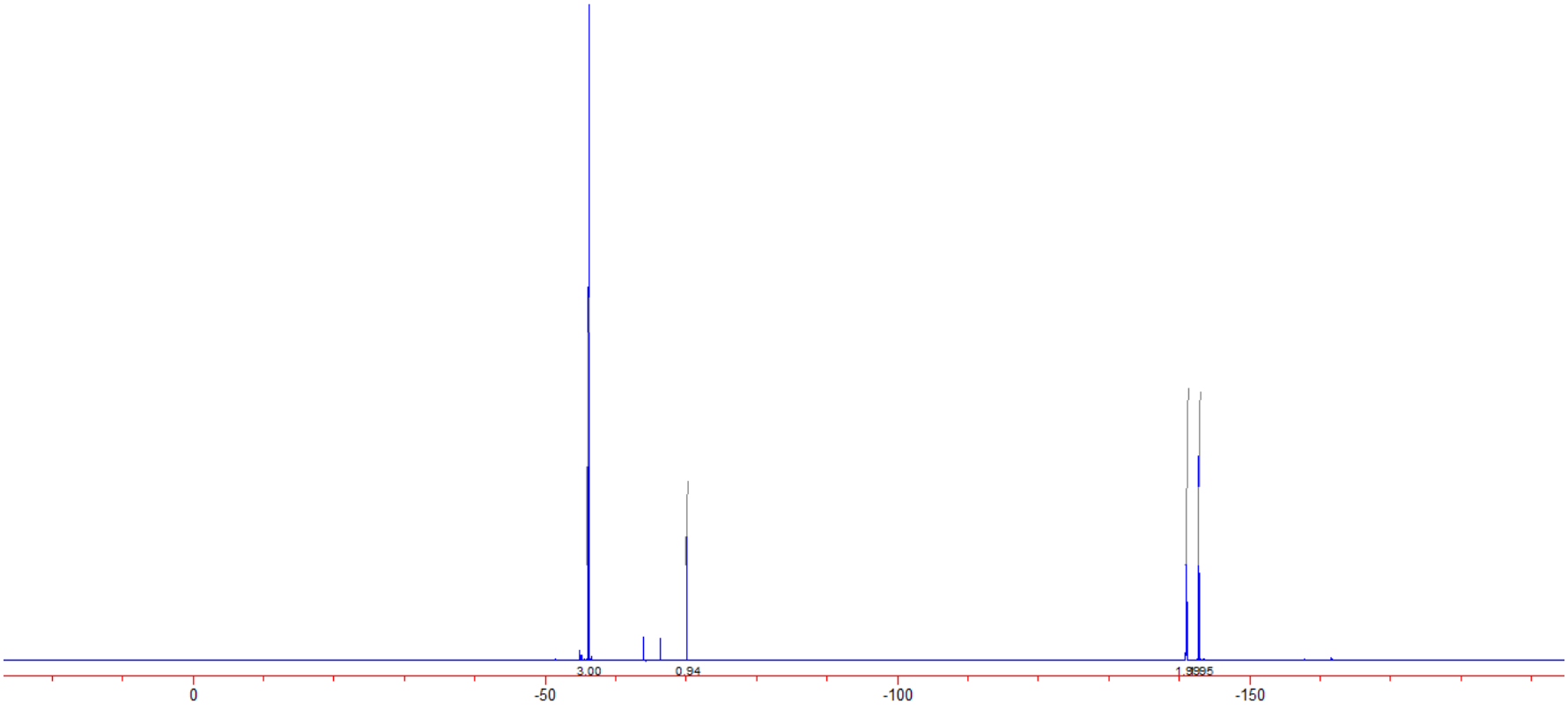
(**4i**)



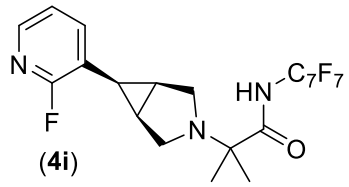
^{1}H NMR Spectrum in $CDCl_3$



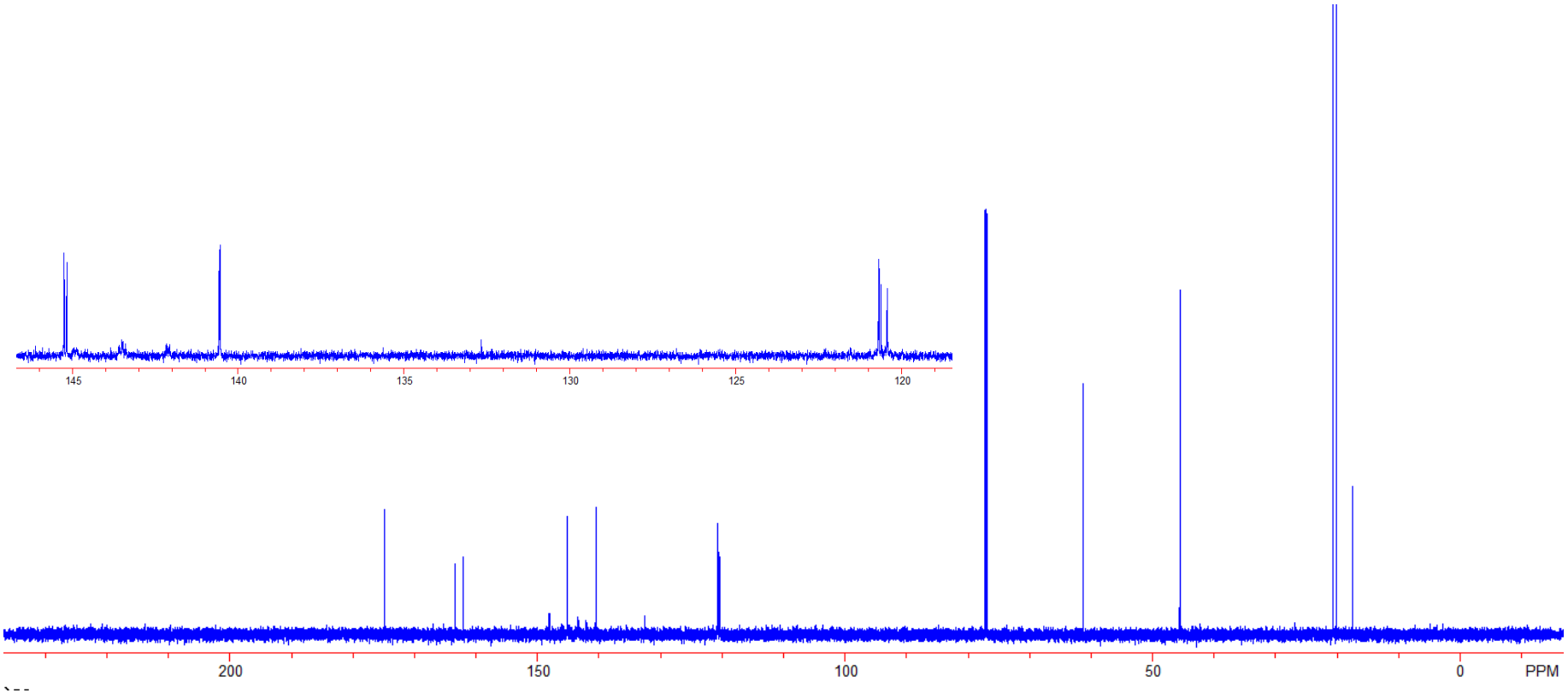
(**4i**)



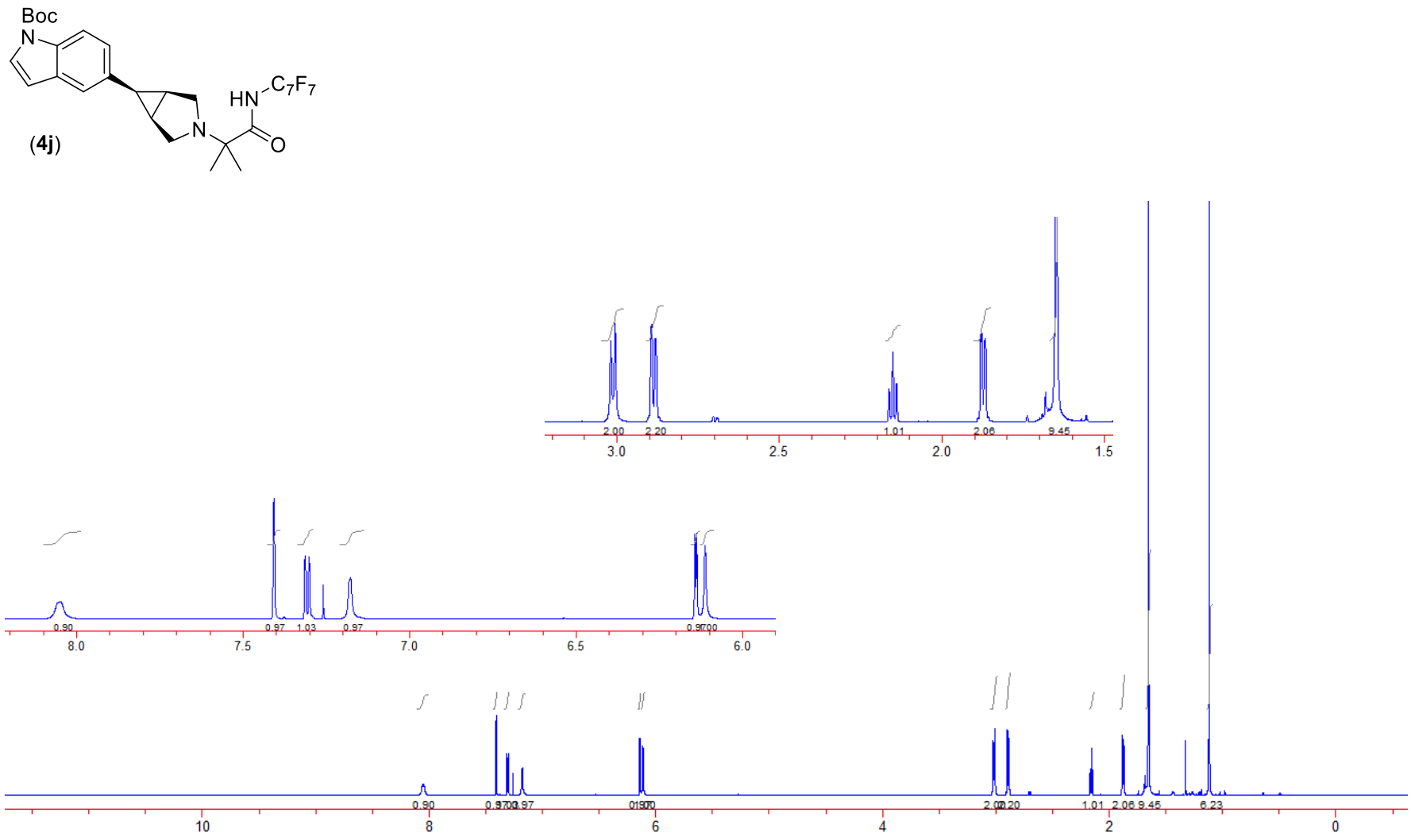
^{19}F NMR Spectrum in $CDCl_3$



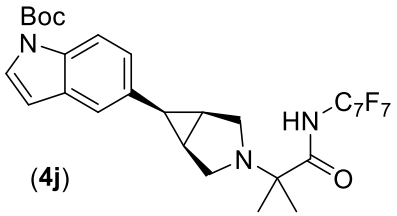
(**4i**)



^{13}C NMR Spectrum in $CDCl_3$



^{1}H NMR Spectrum in $CDCl_3$



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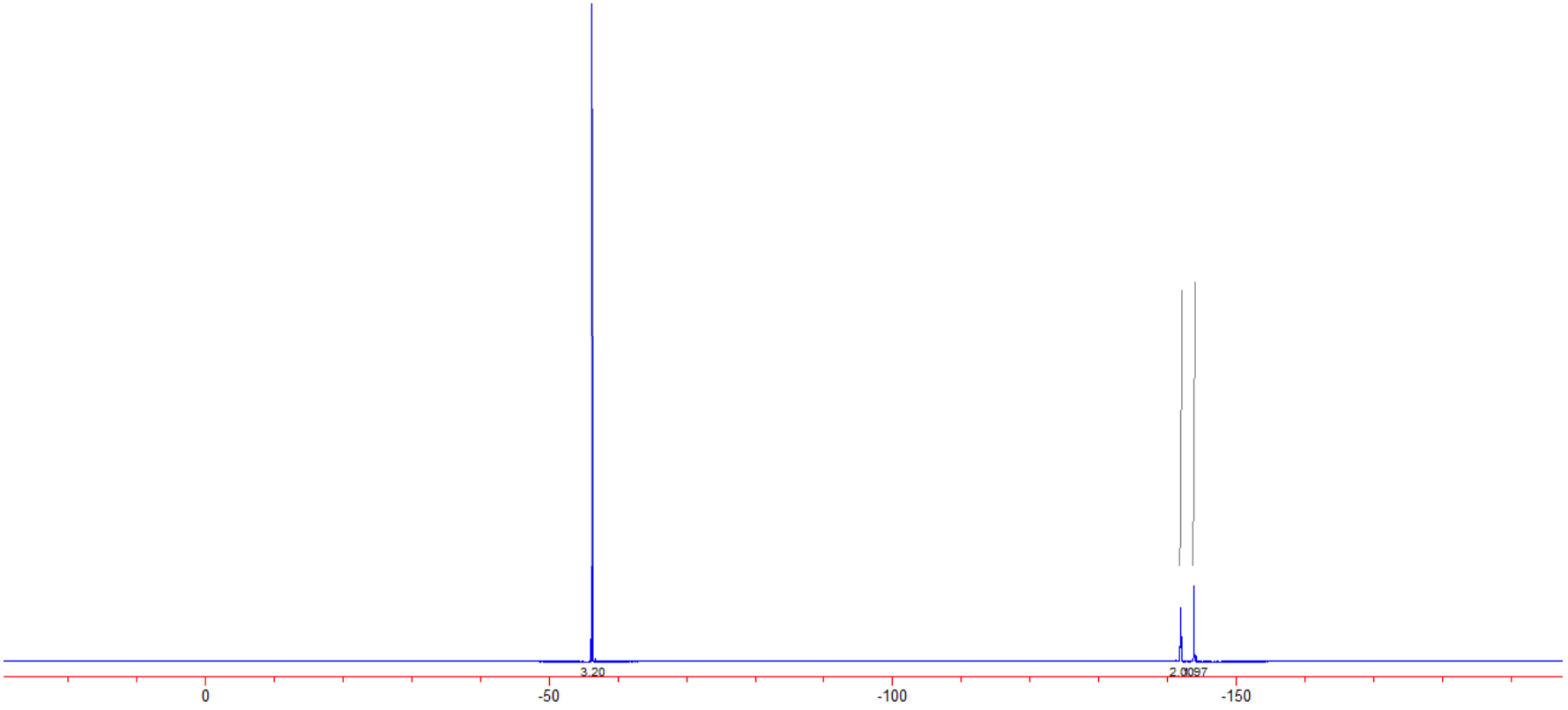
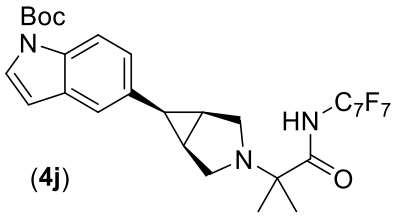
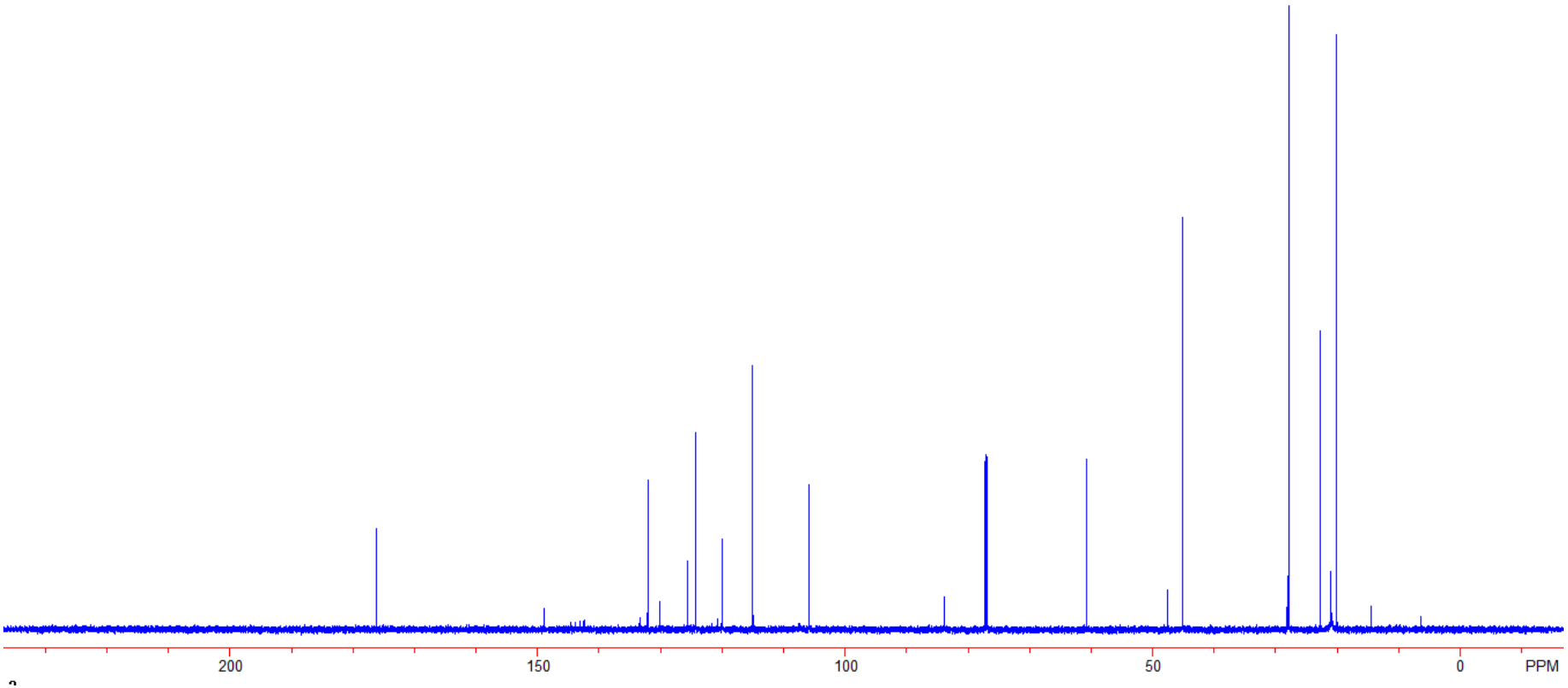


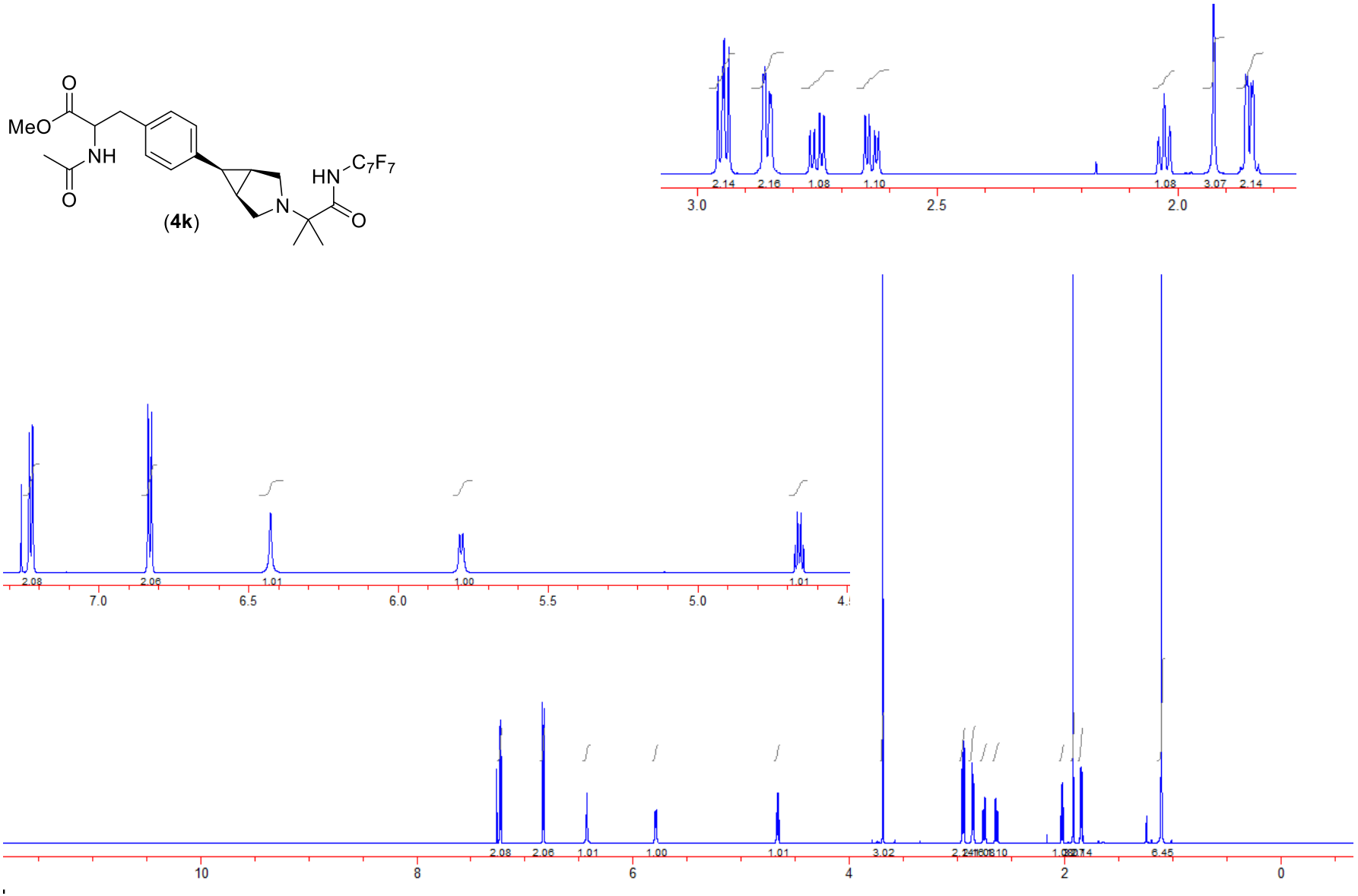
^{19}F NMR Spectrum in $CDCl_3$



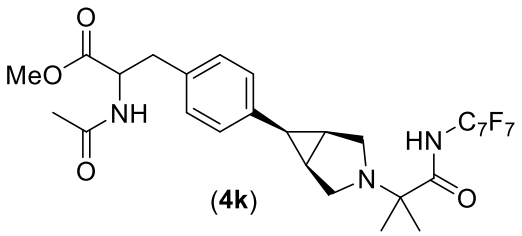
(**4j**)



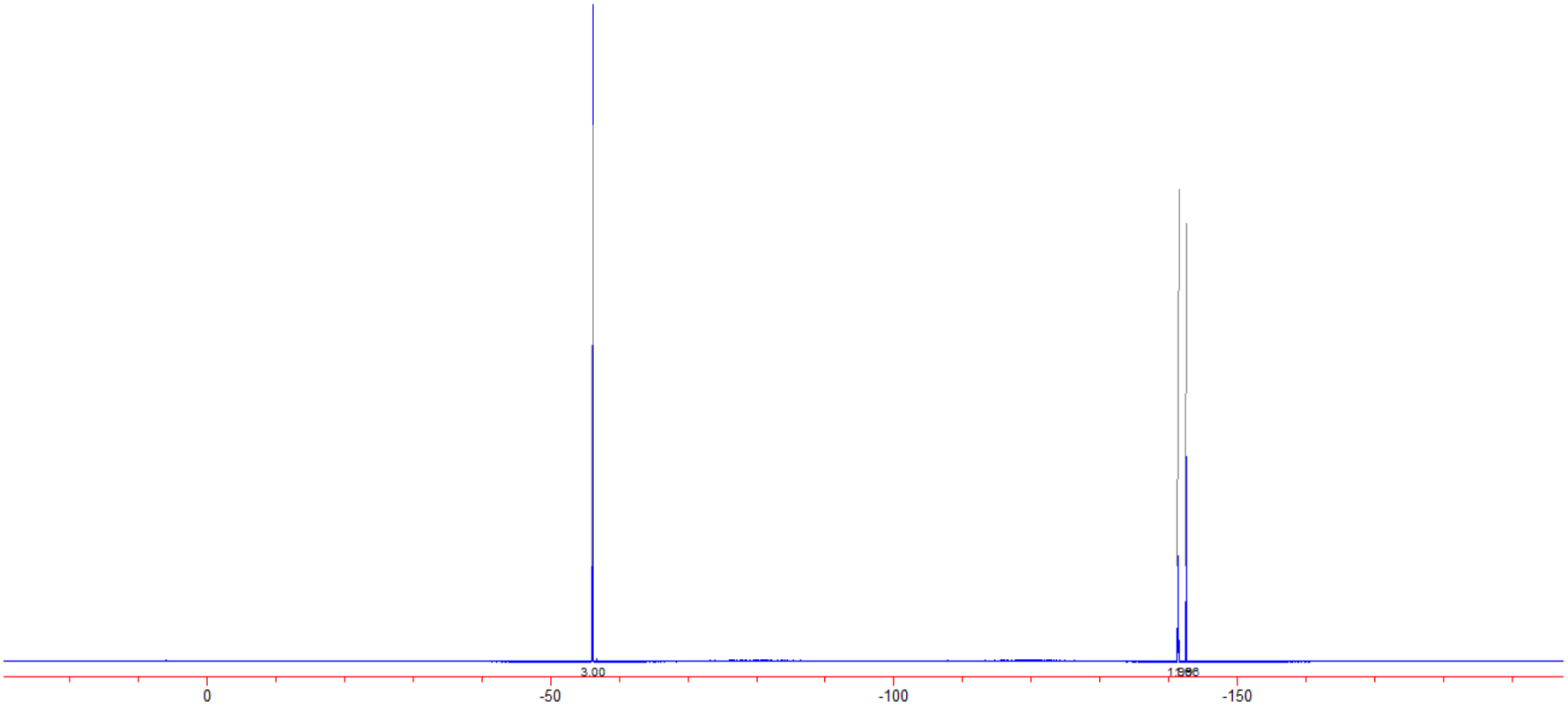
^{13}C NMR Spectrum in $CDCl_3$



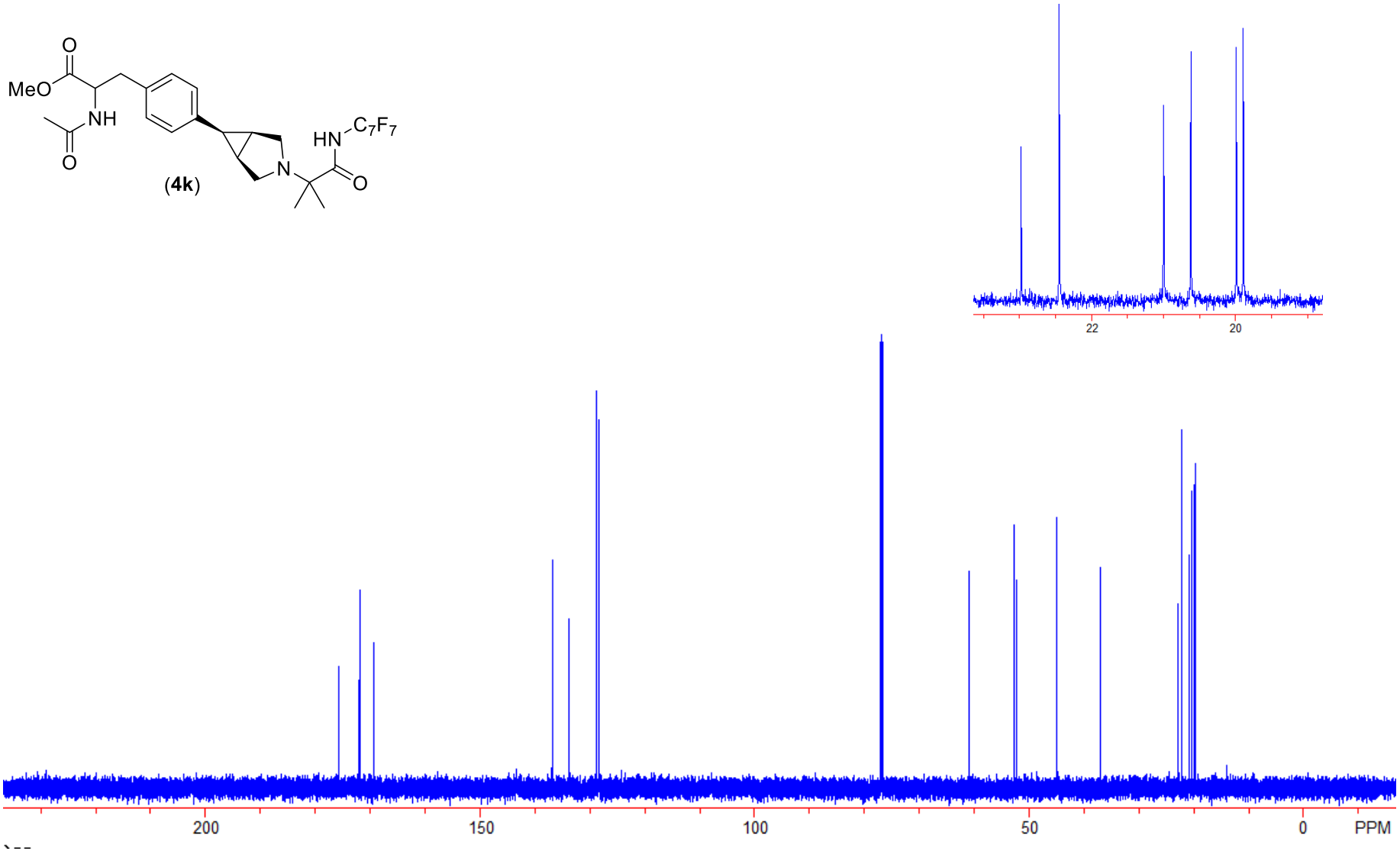
^{1}H NMR Spectrum in $CDCl_3$



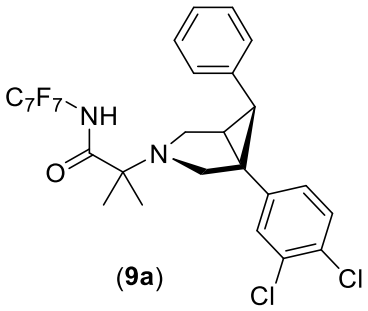
(**4k**)



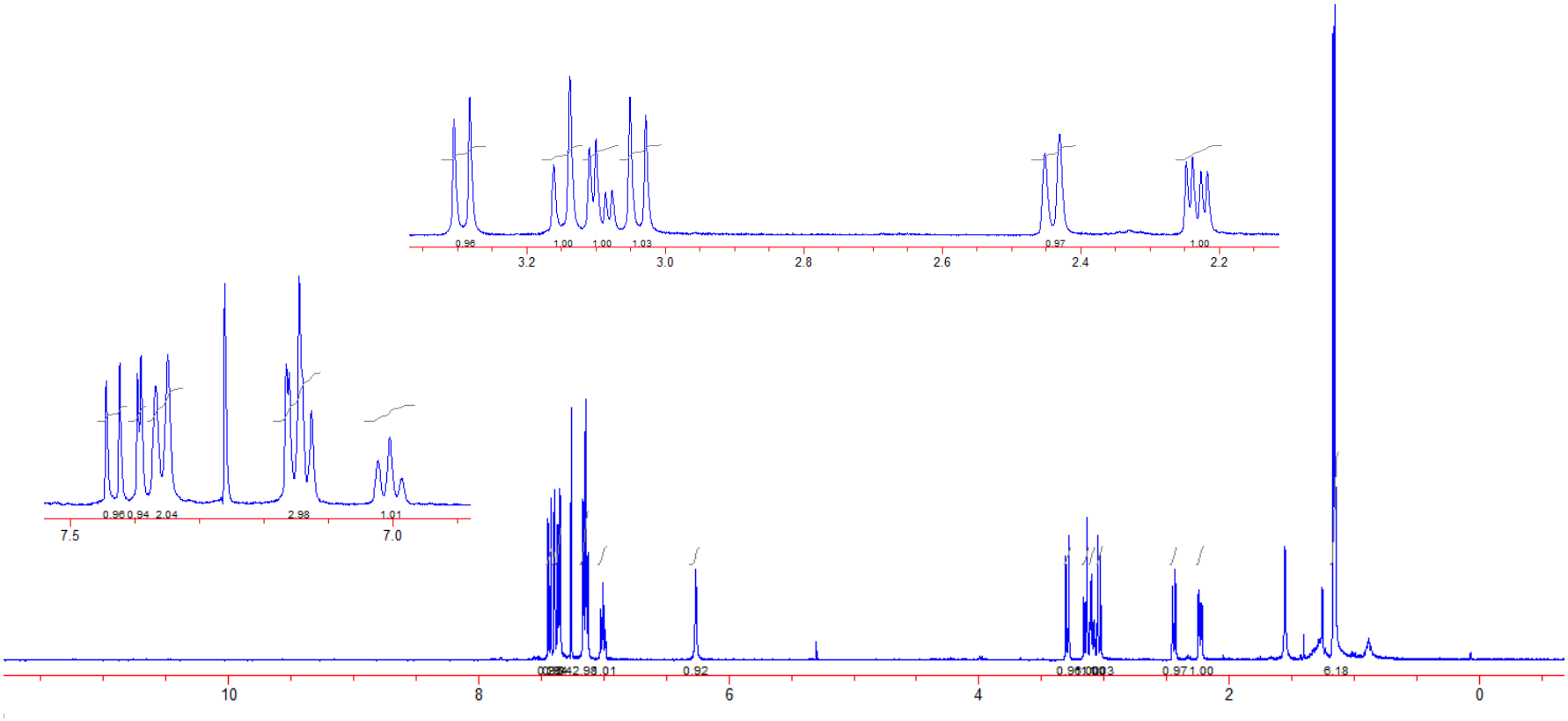
^{19}F NMR Spectrum in $CDCl_3$



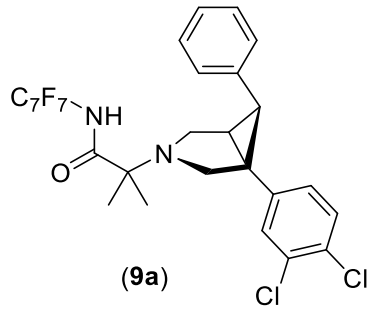
^{13}C NMR Spectrum in $CDCl_3$



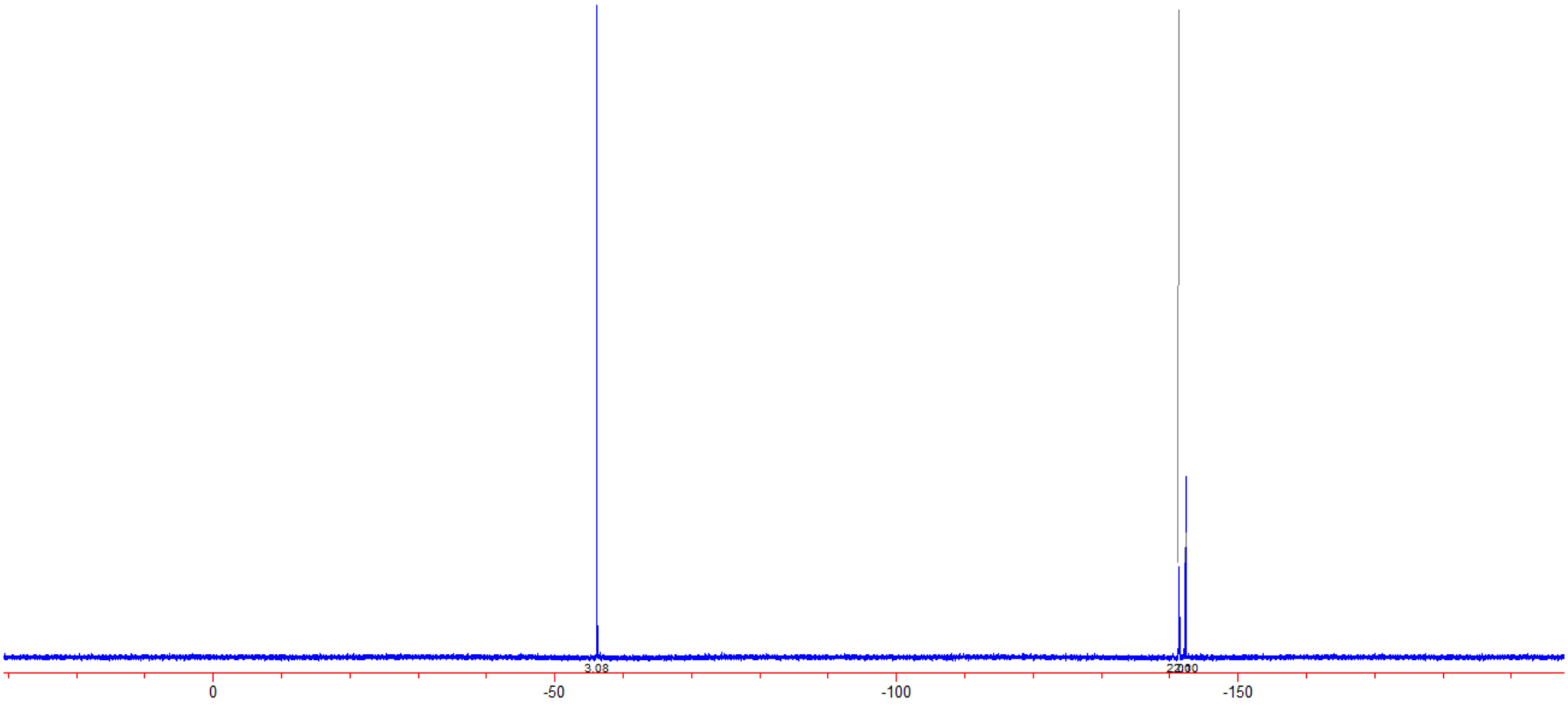
(**9a**)



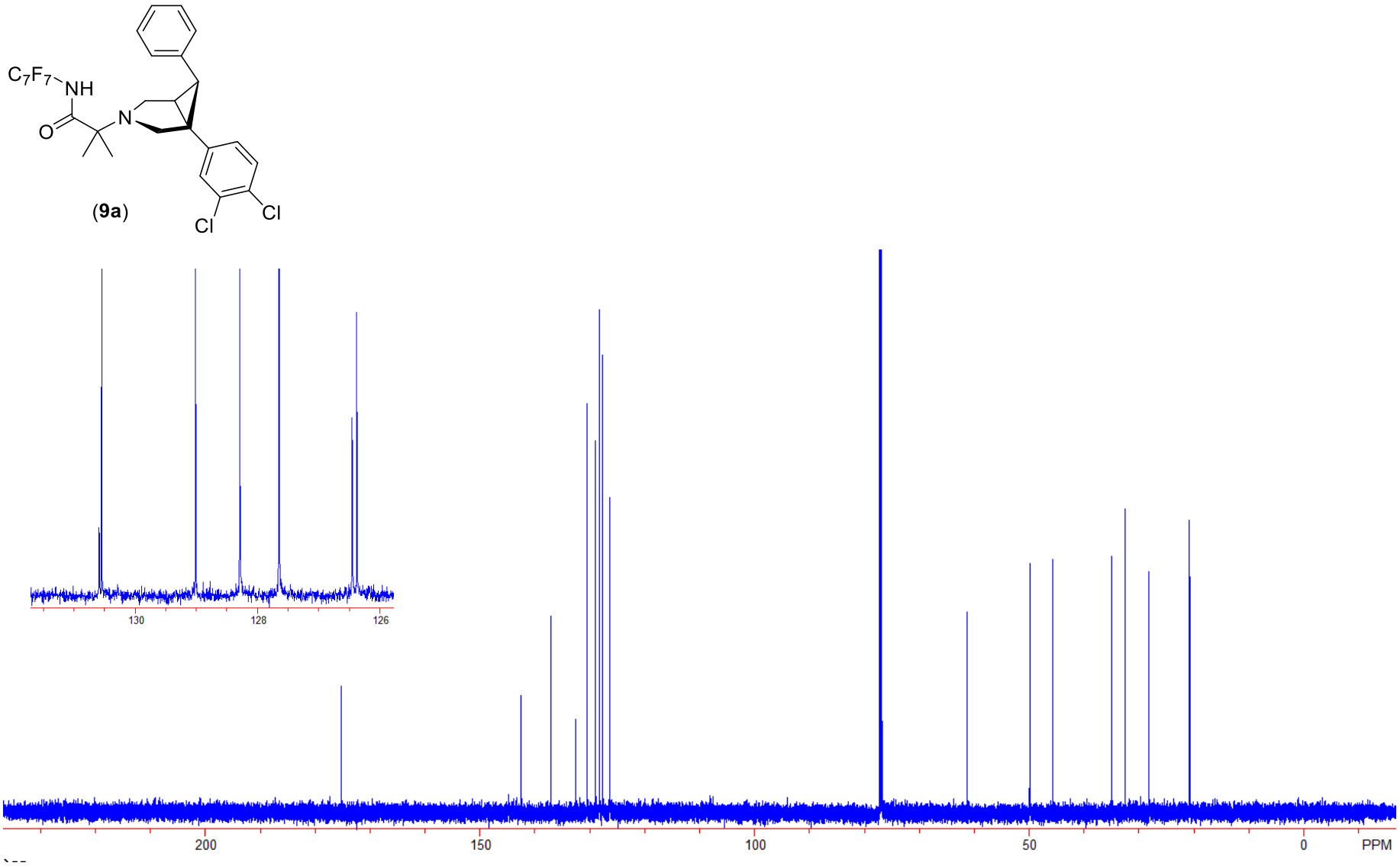
^{1}H NMR Spectrum in $CDCl_3$



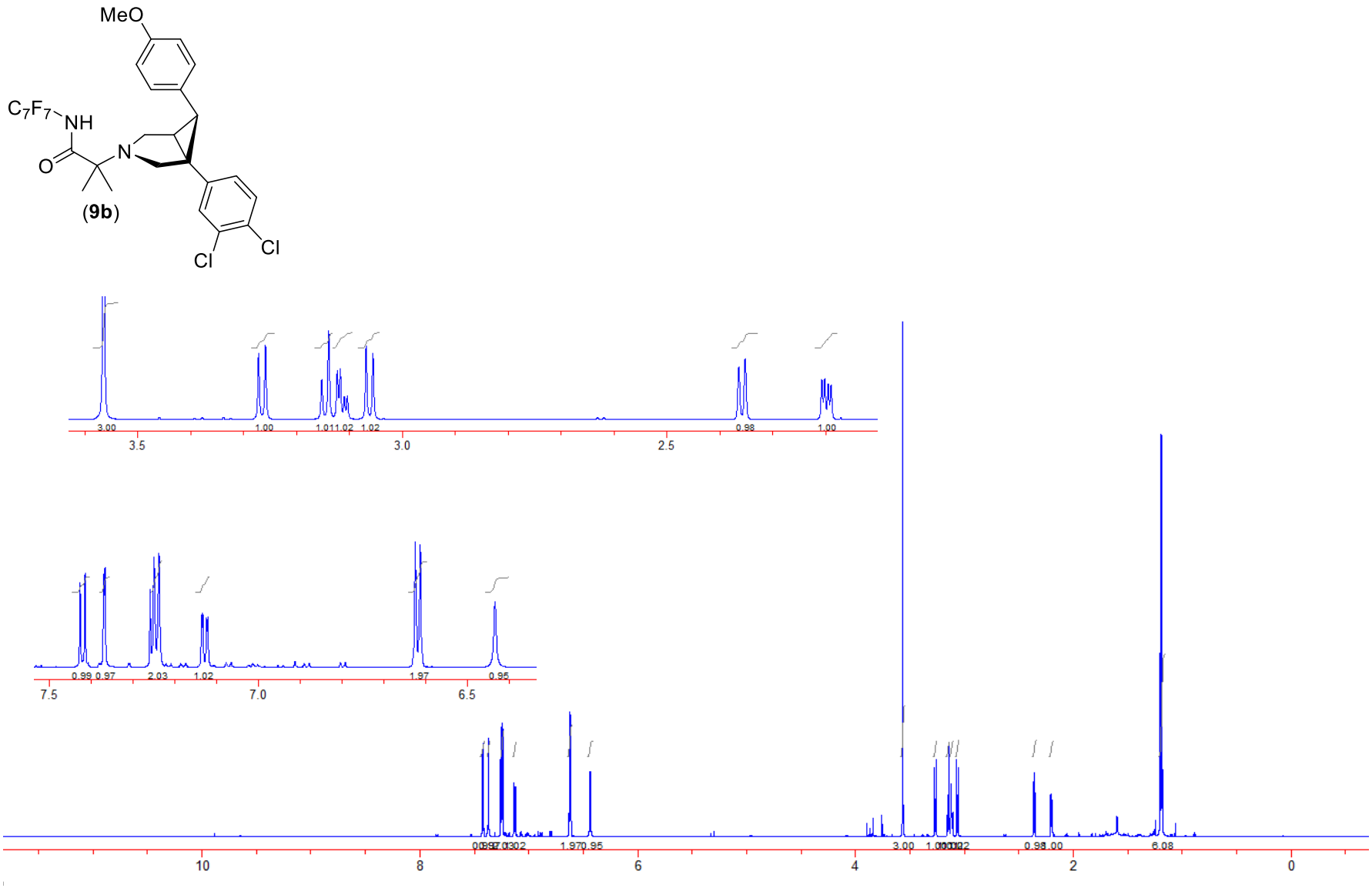
(**9a**)



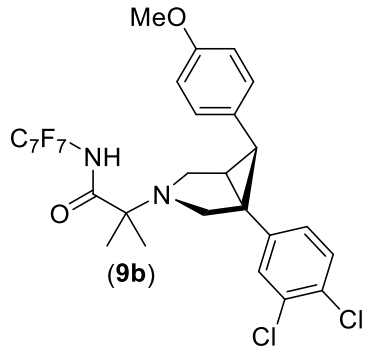
^{19}F NMR Spectrum in $CDCl_3$



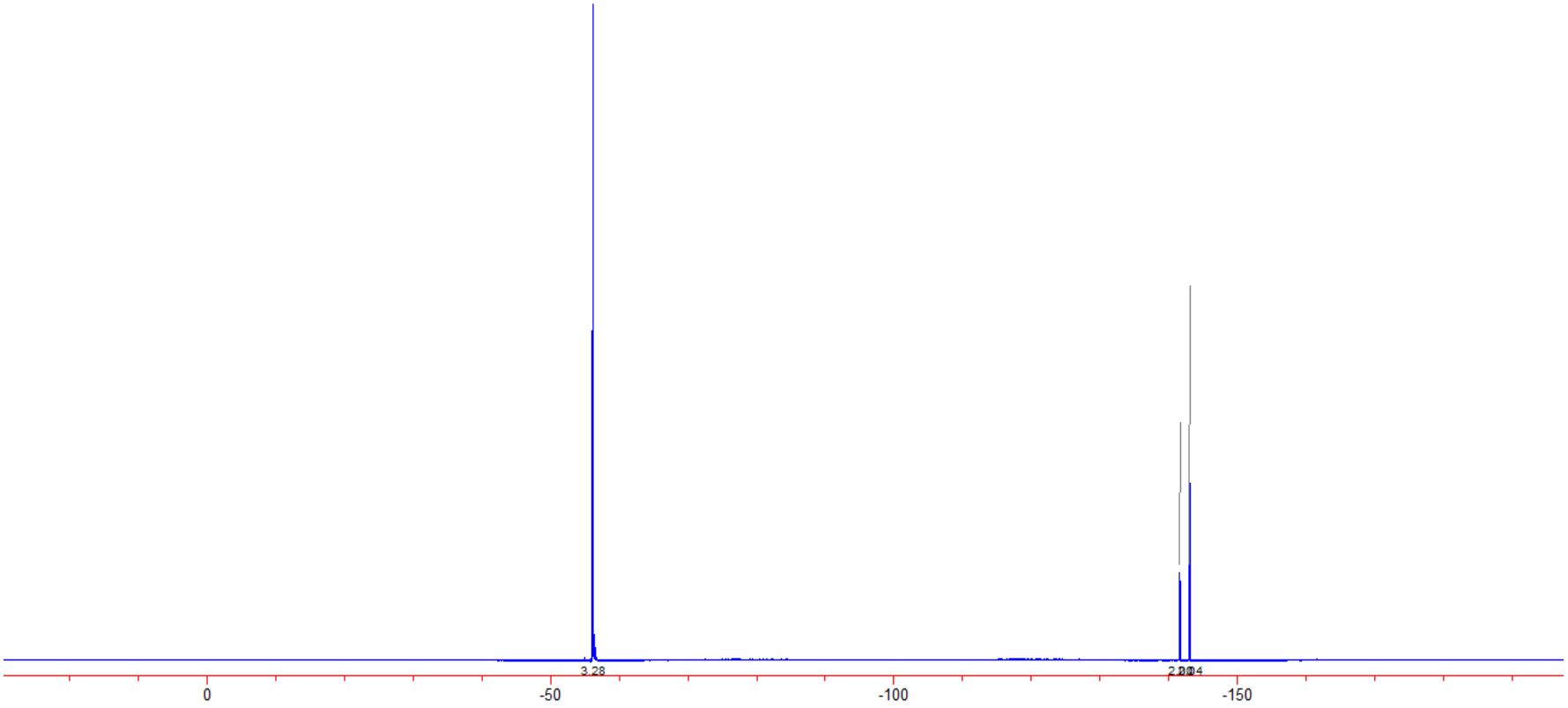
^{13}C NMR Spectrum in $CDCl_3$



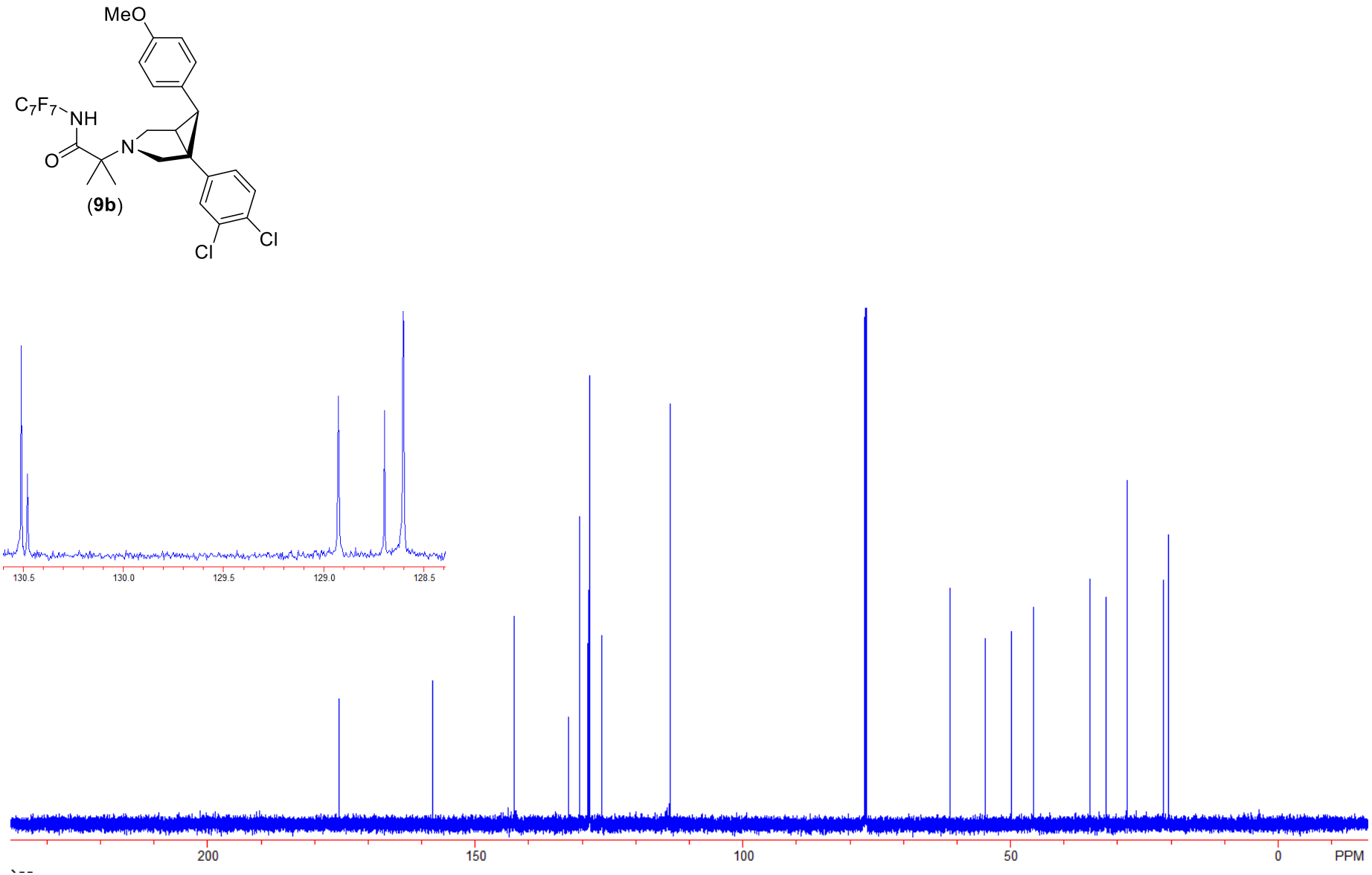
^{1}H NMR Spectrum in $CDCl_3$



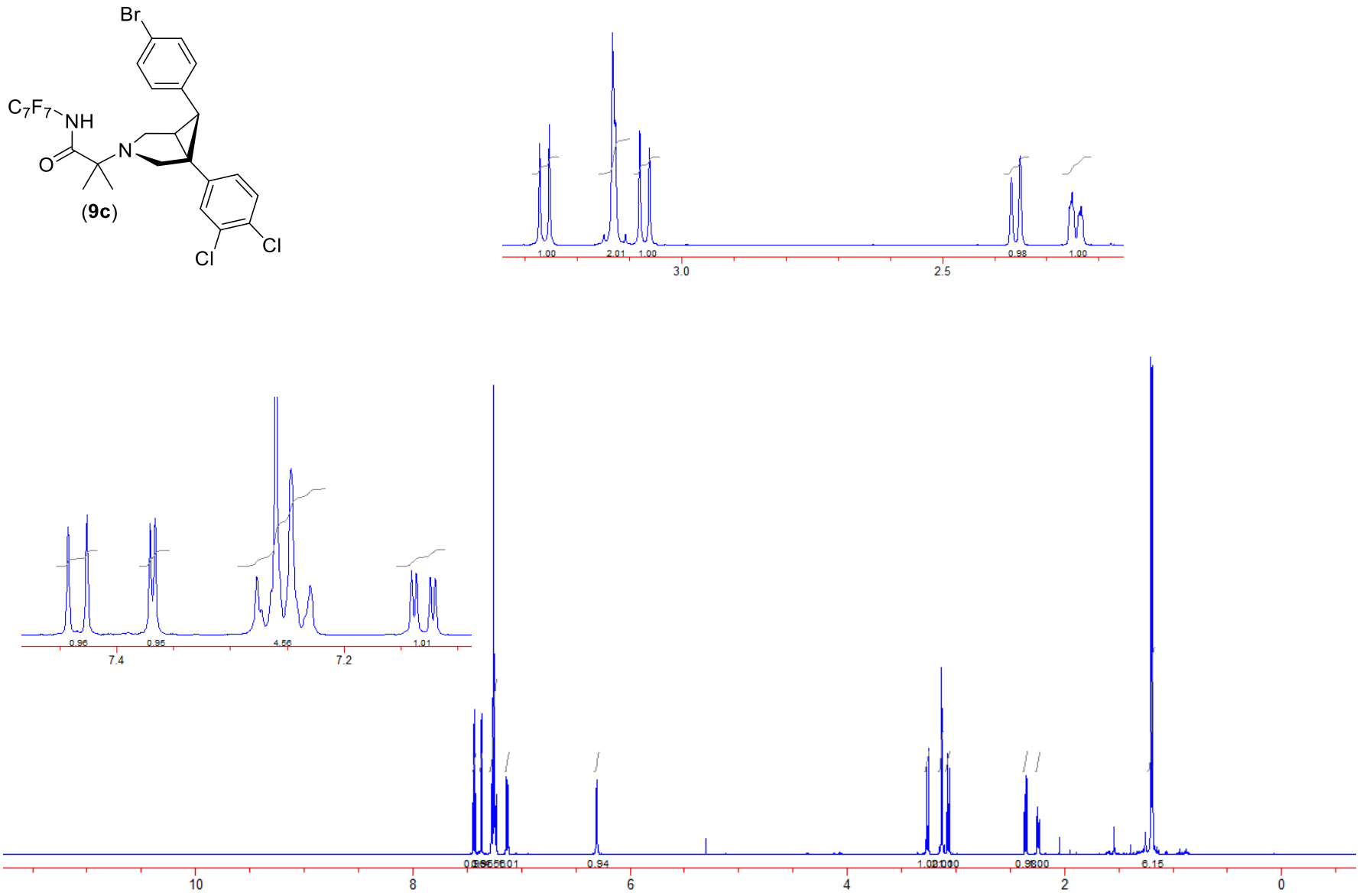
(**9b**)



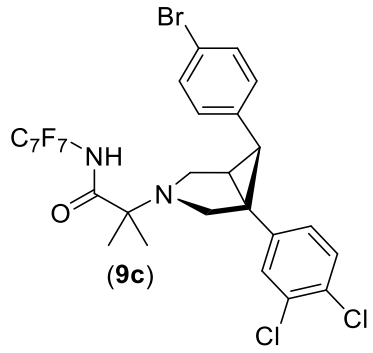
^{19}F NMR Spectrum in $CDCl_3$



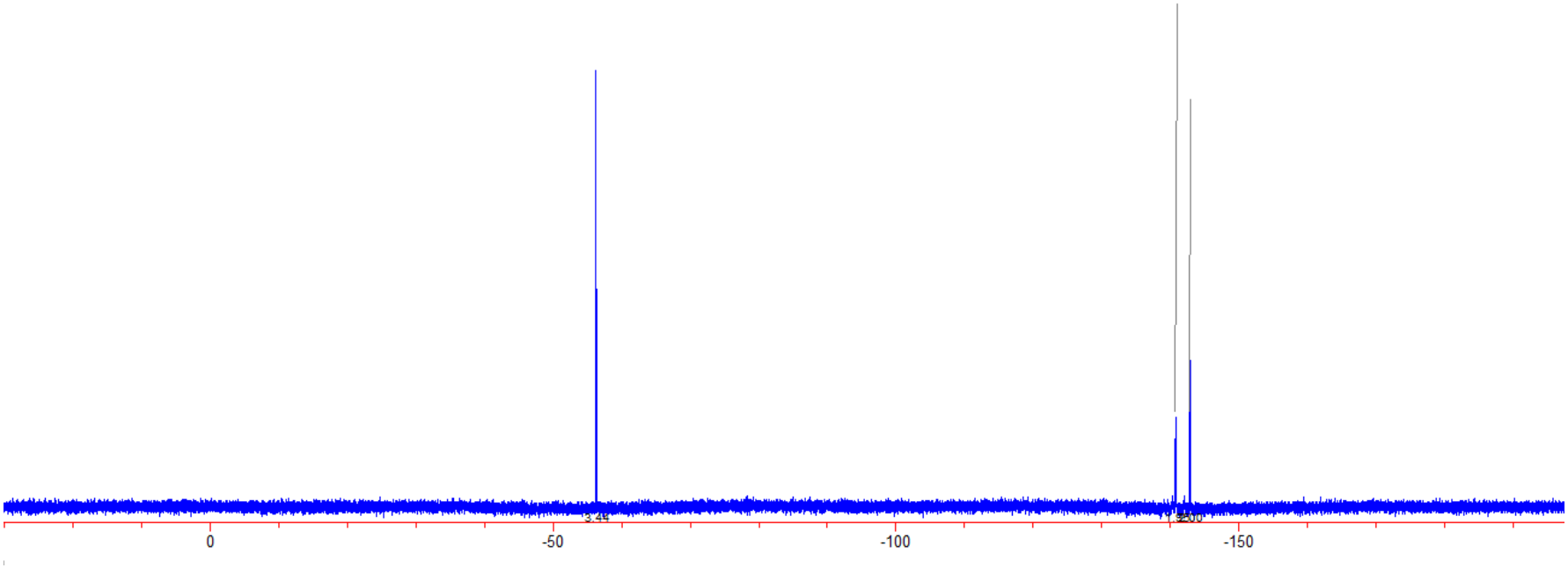
^{13}C NMR Spectrum in $CDCl_3$



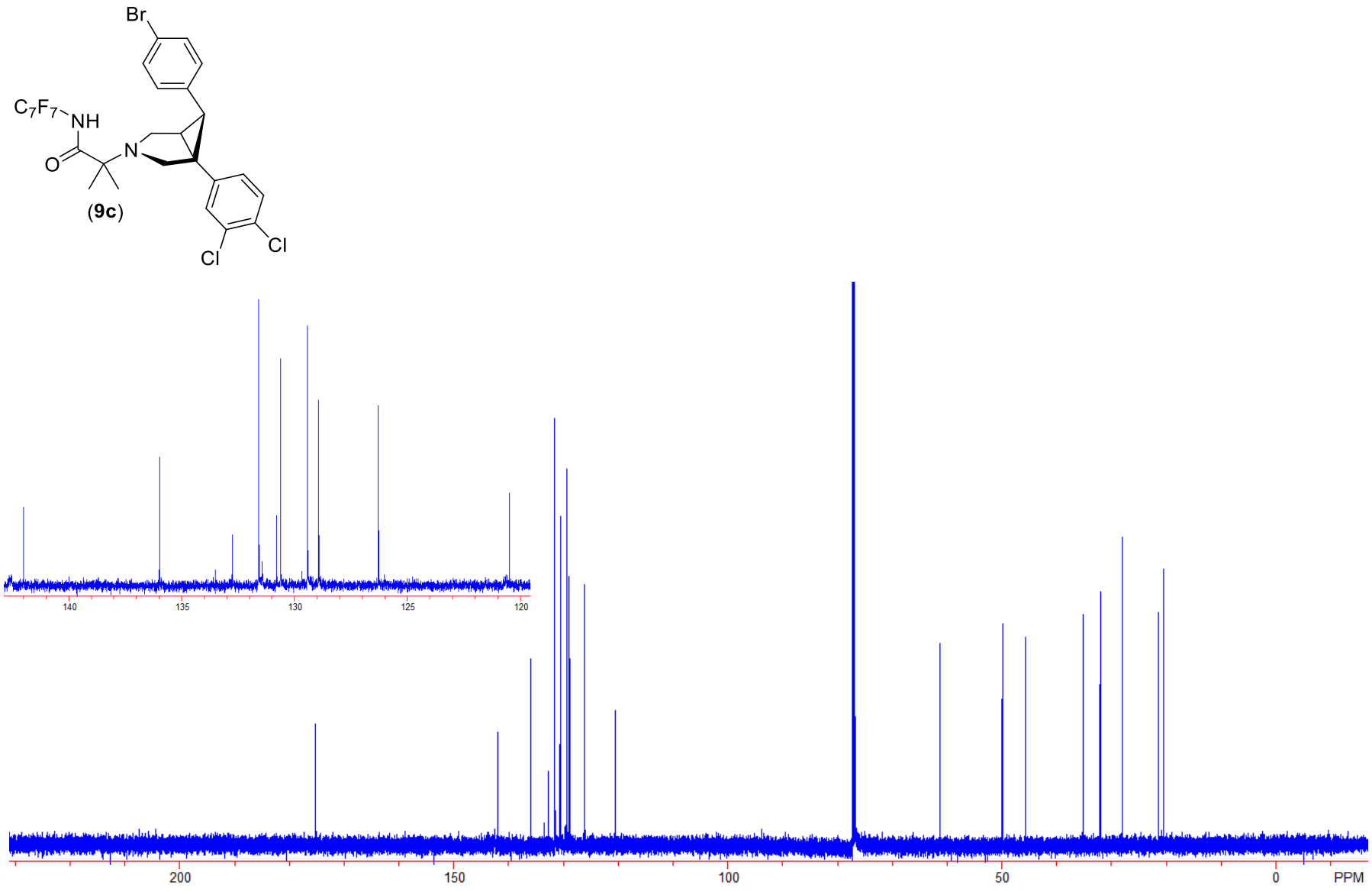
^{1}H NMR Spectrum in $CDCl_3$



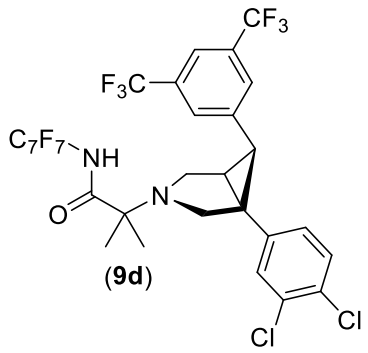
(**9c**)



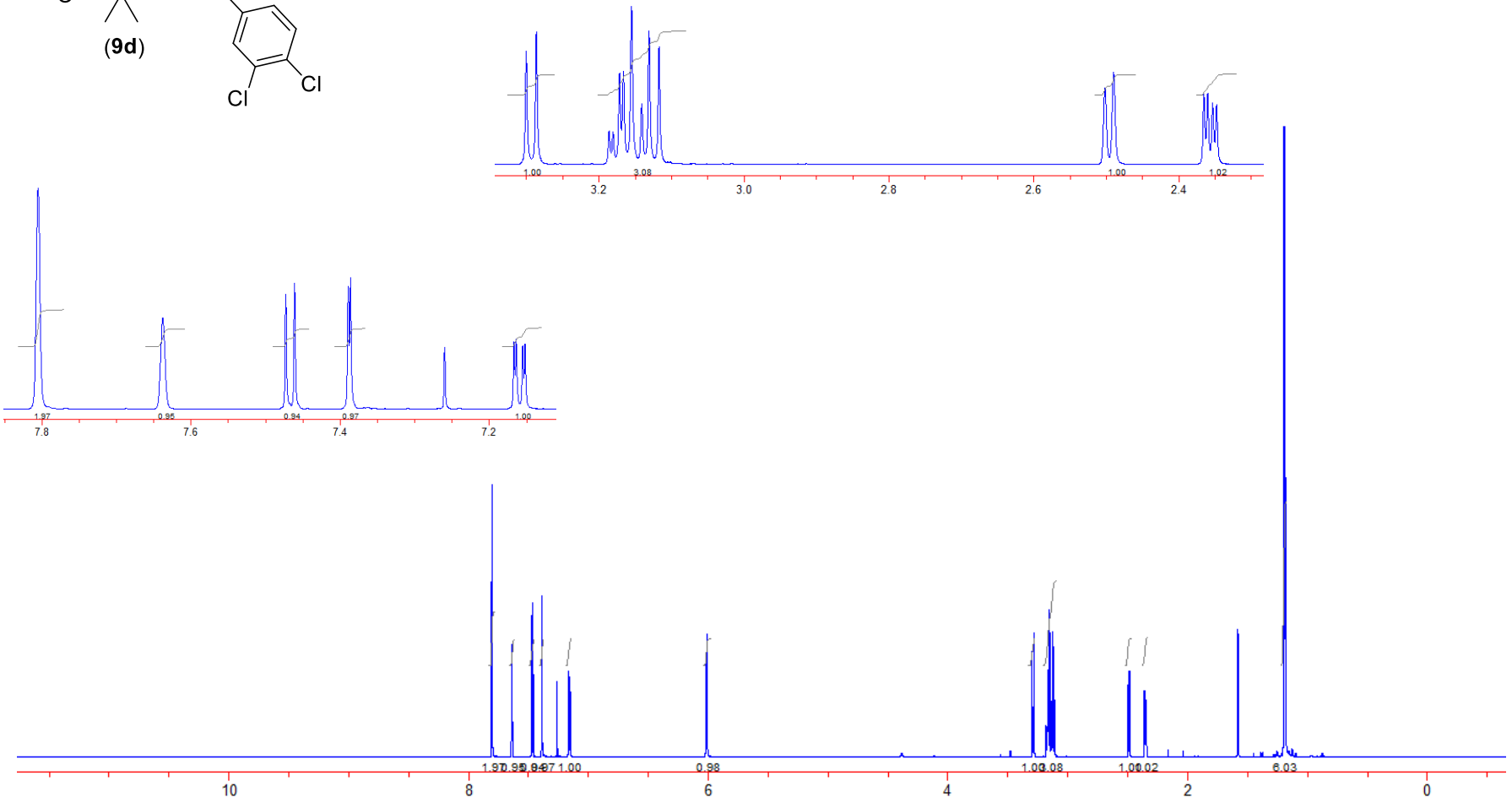
^{19}F NMR Spectrum in $CDCl_3$



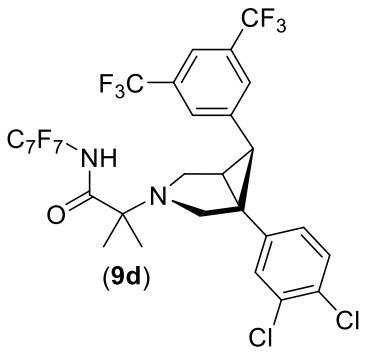
^{13}C NMR Spectrum in $CDCl_3$



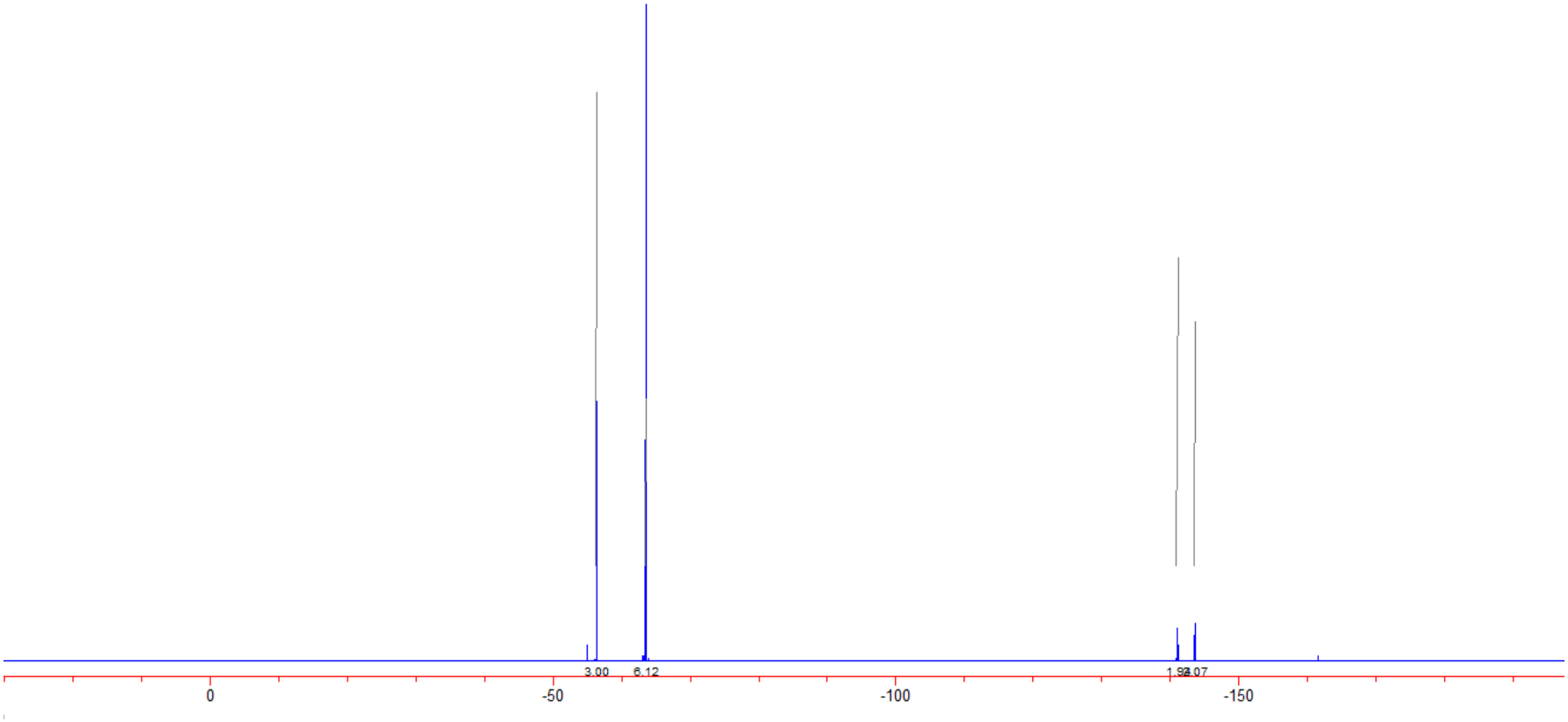
(**9d**)



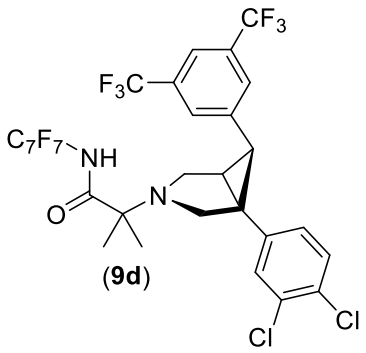
^{1}H NMR Spectrum in $CDCl_3$



(**9d**)



^{19}F NMR Spectrum in $CDCl_3$



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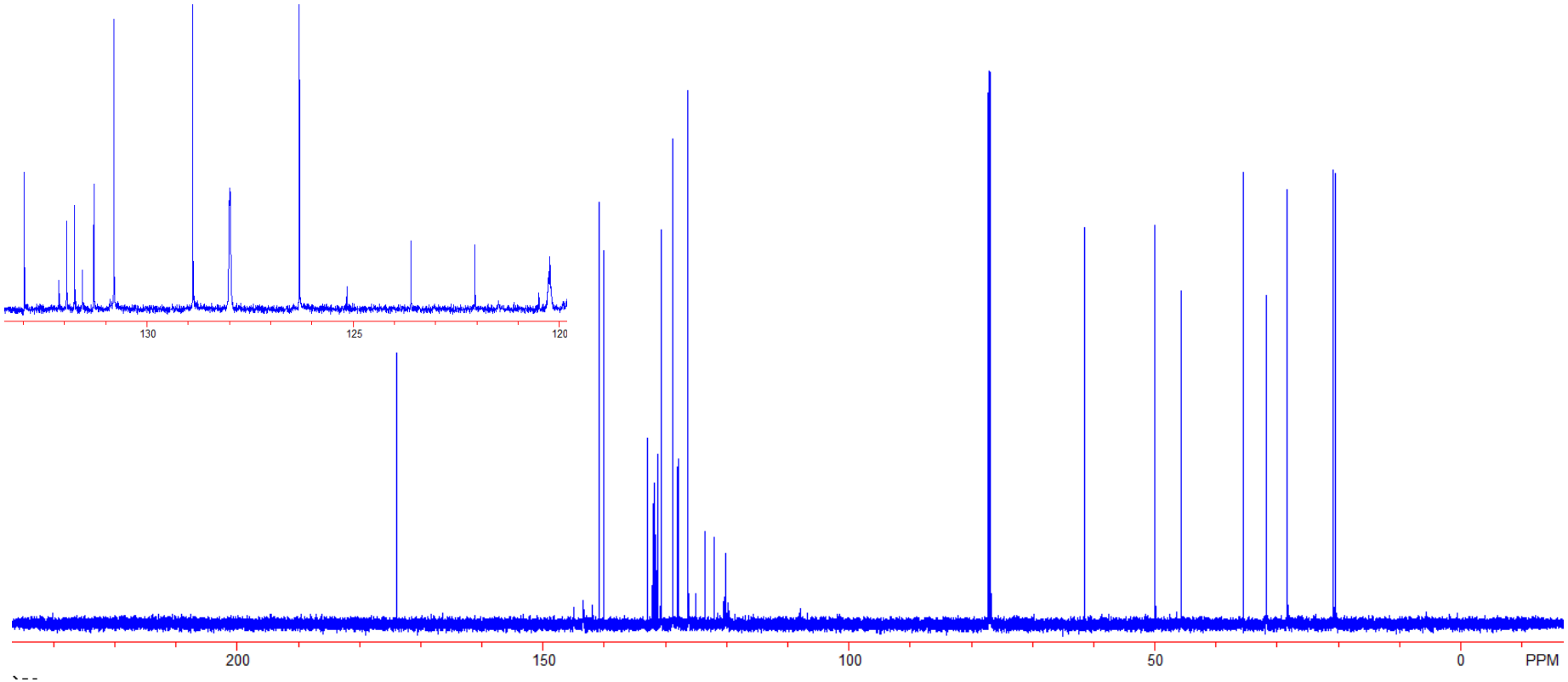
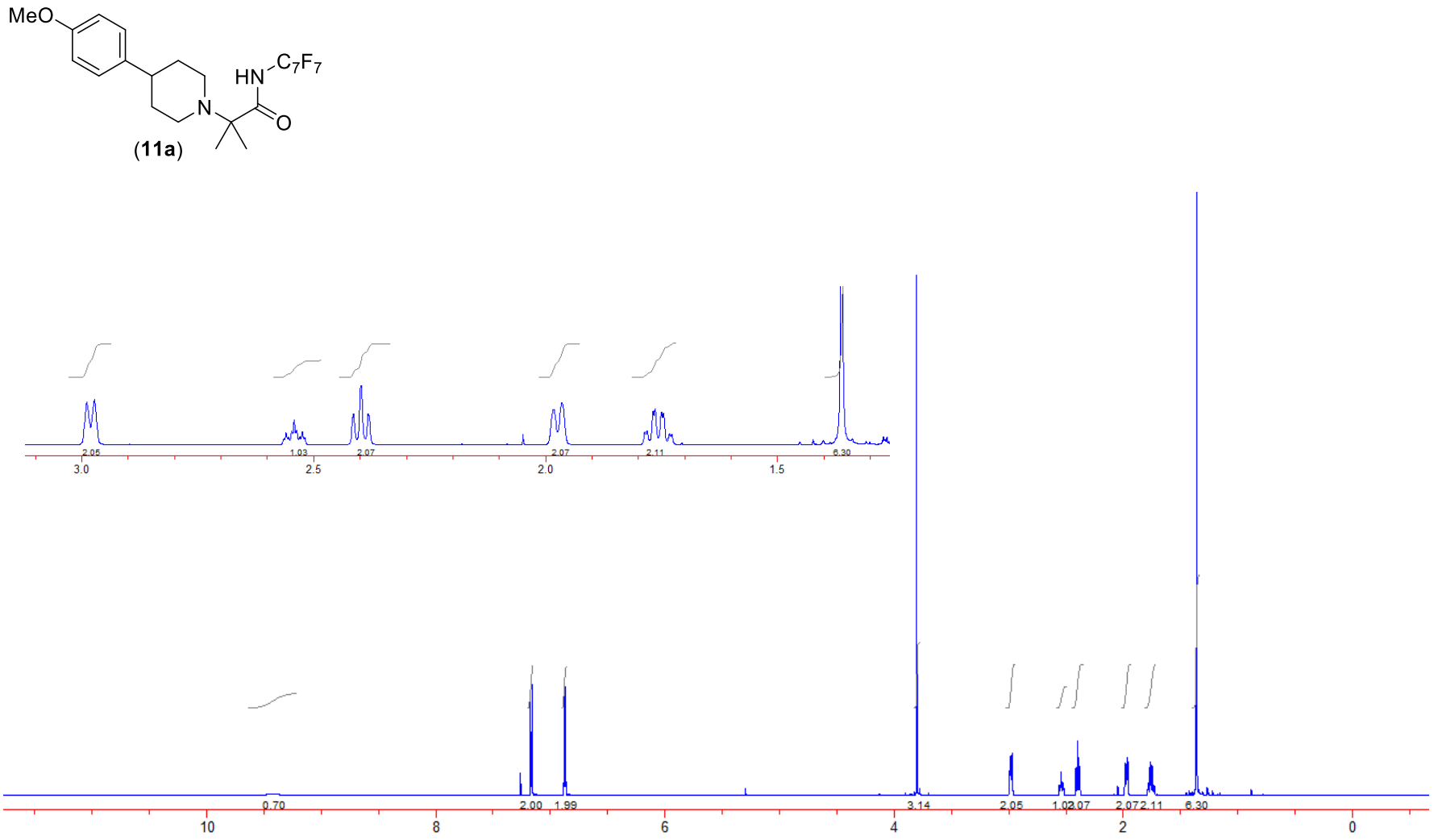
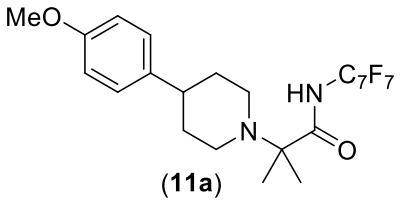


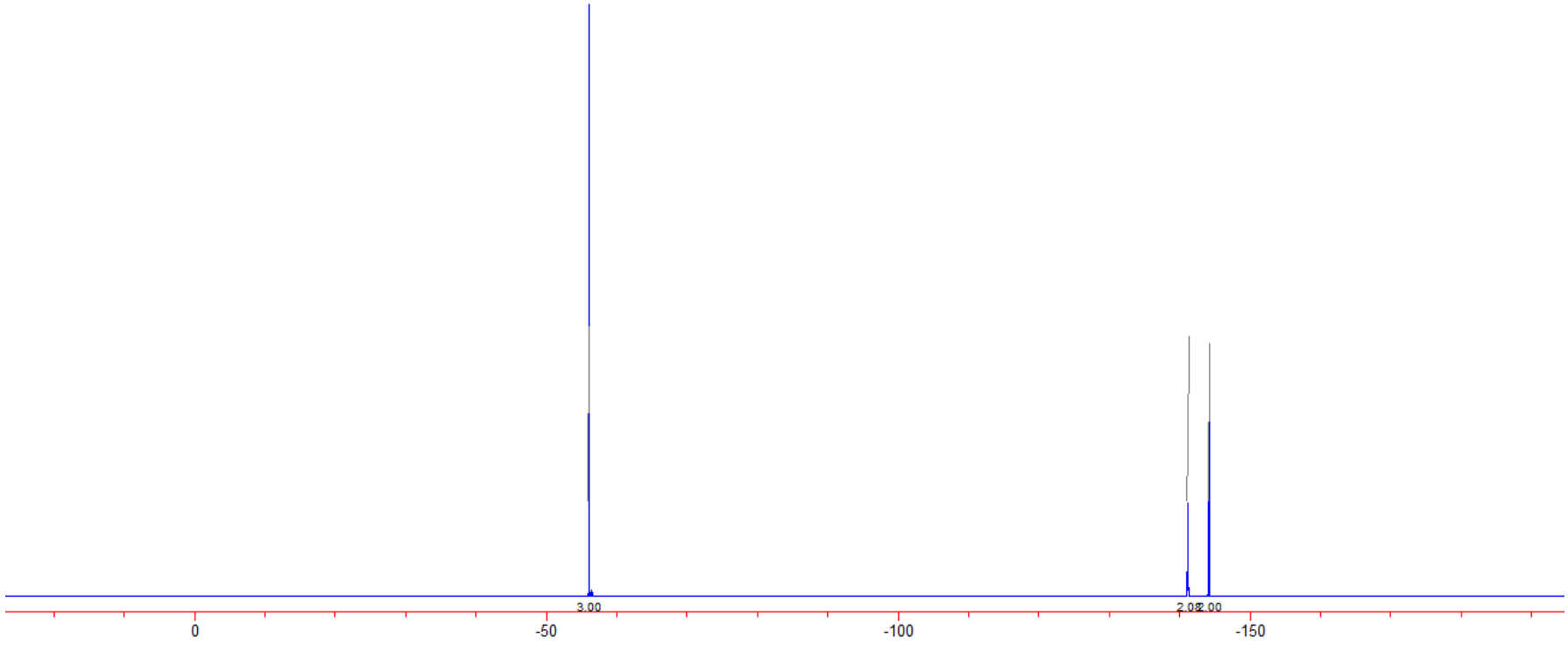
^{13}C NMR Spectrum in $CDCl_3$



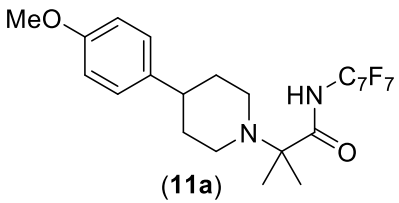
^{1}H NMR Spectrum in $CDCl_3$



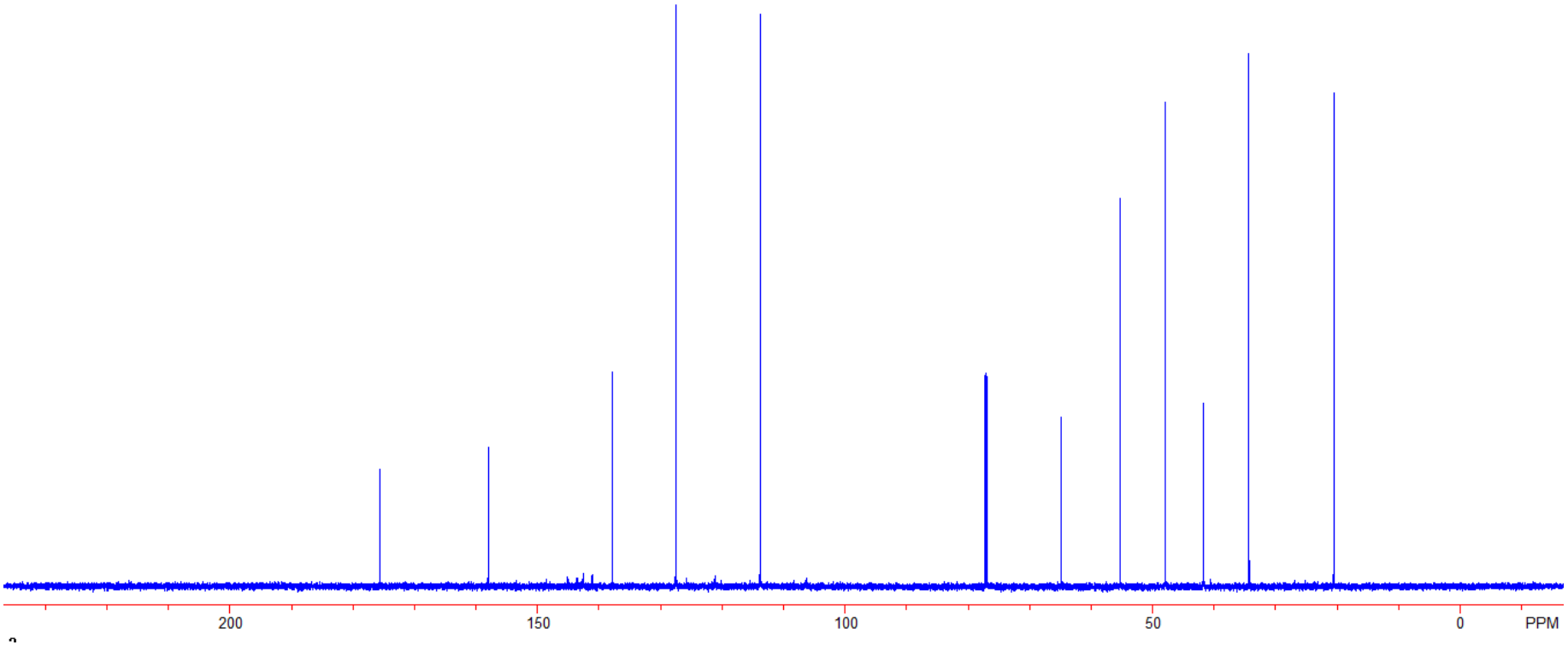
(**11a**)



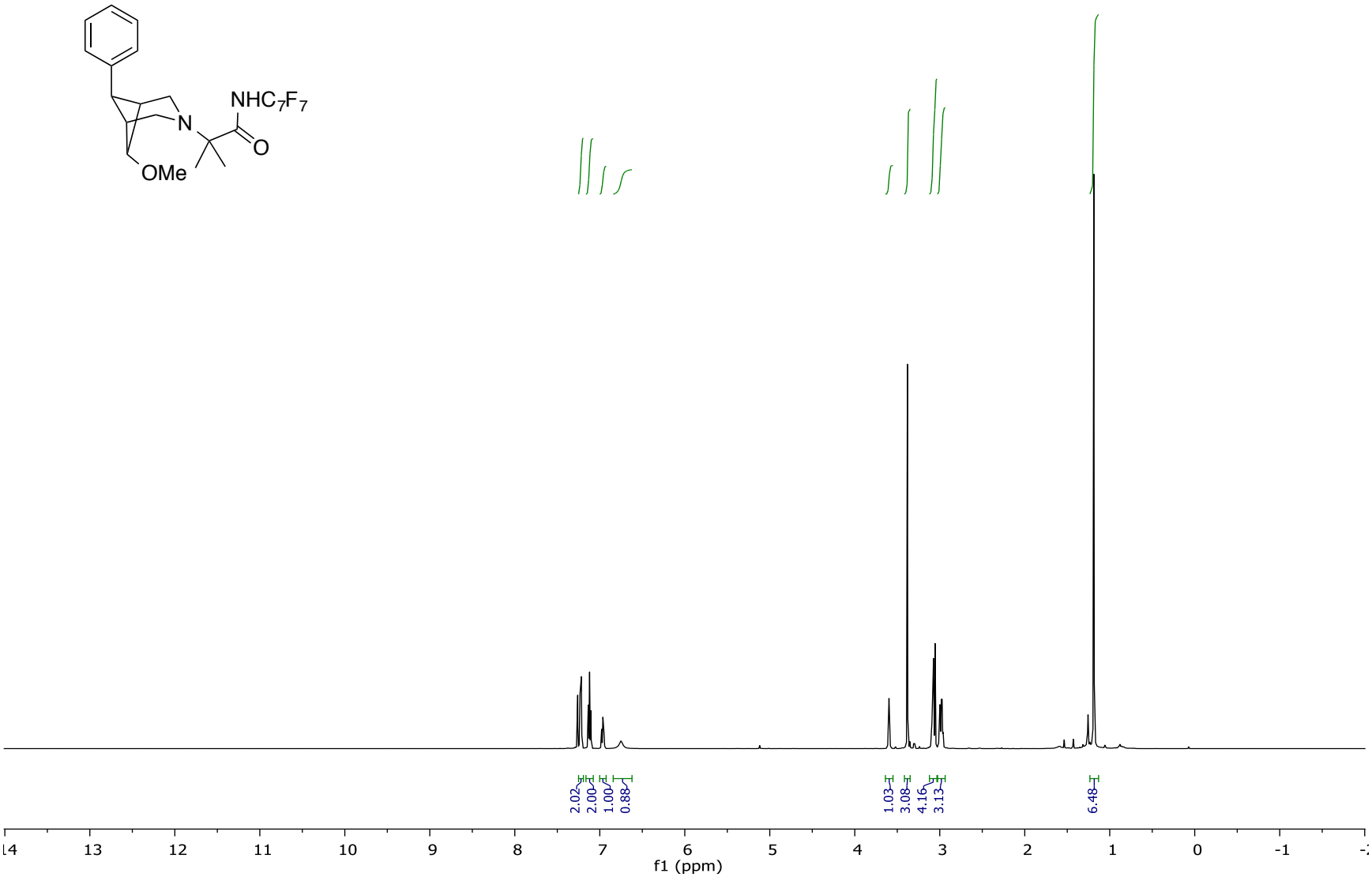
^{19}F NMR Spectrum in $CDCl_3$



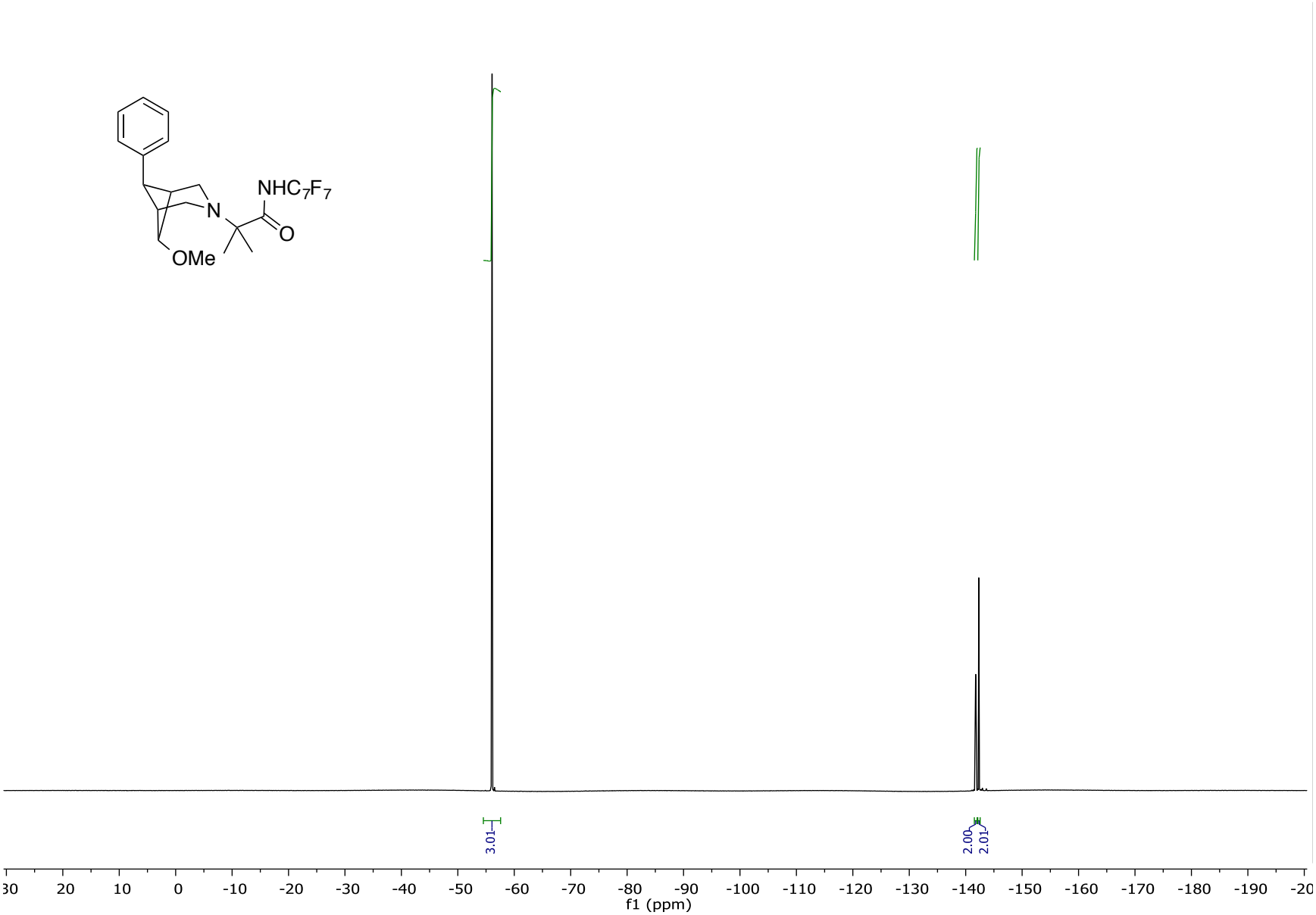
(**11a**)



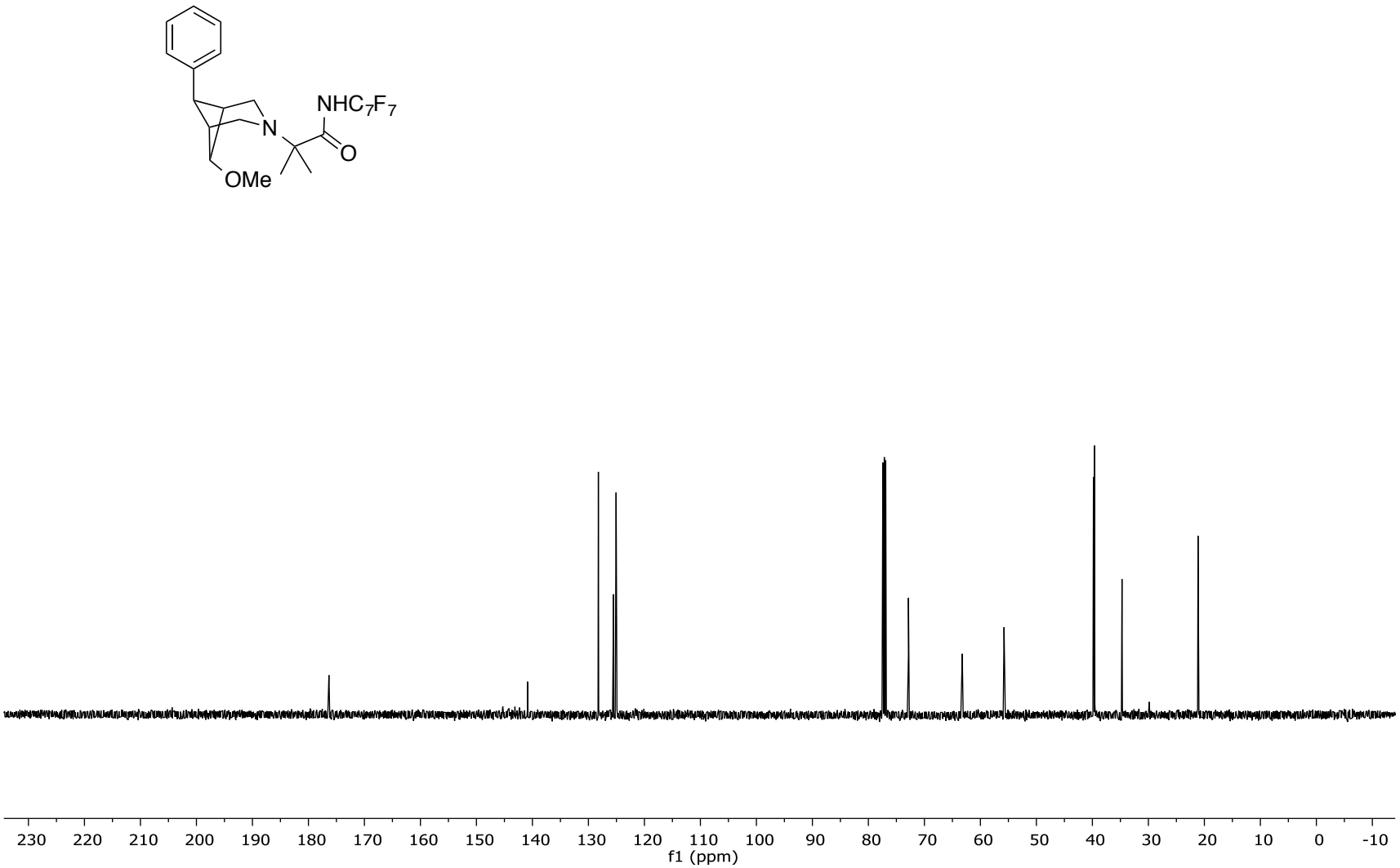
^{13}C NMR Spectrum in $CDCl_3$



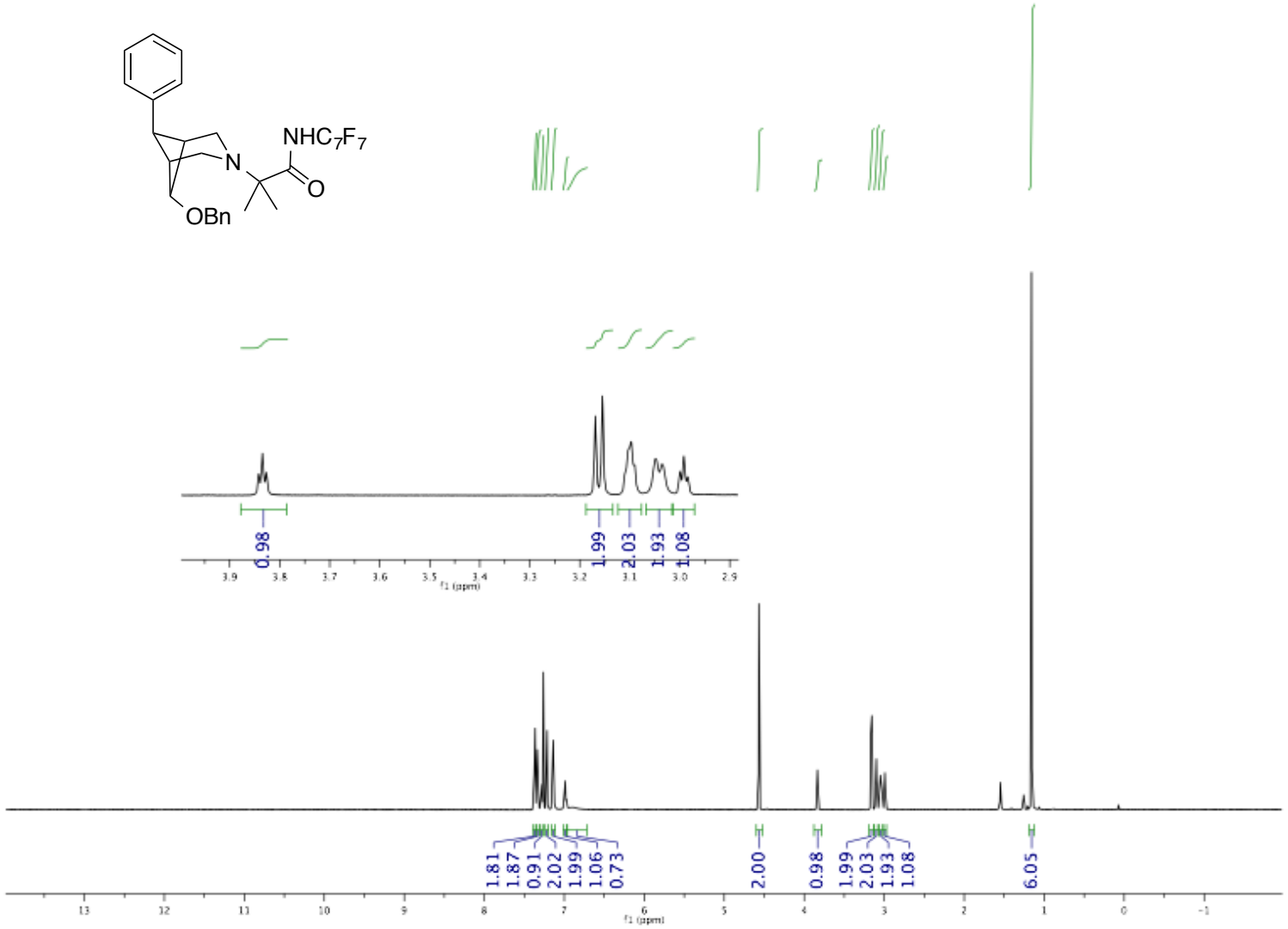
^{1}H NMR Spectrum of **11b** in $CDCl_3$



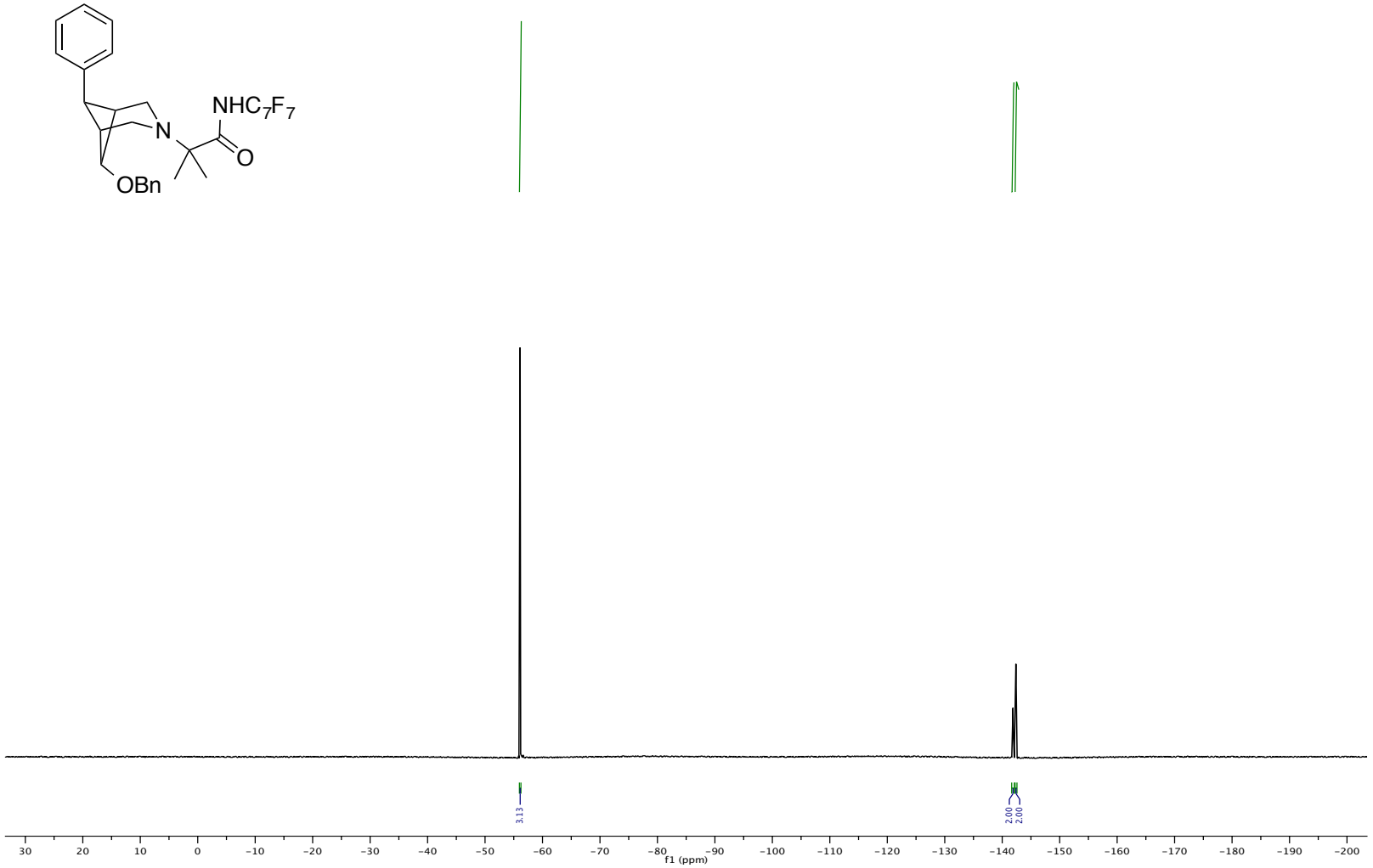
^{19}F NMR Spectrum of **11b** in $CDCl_3$



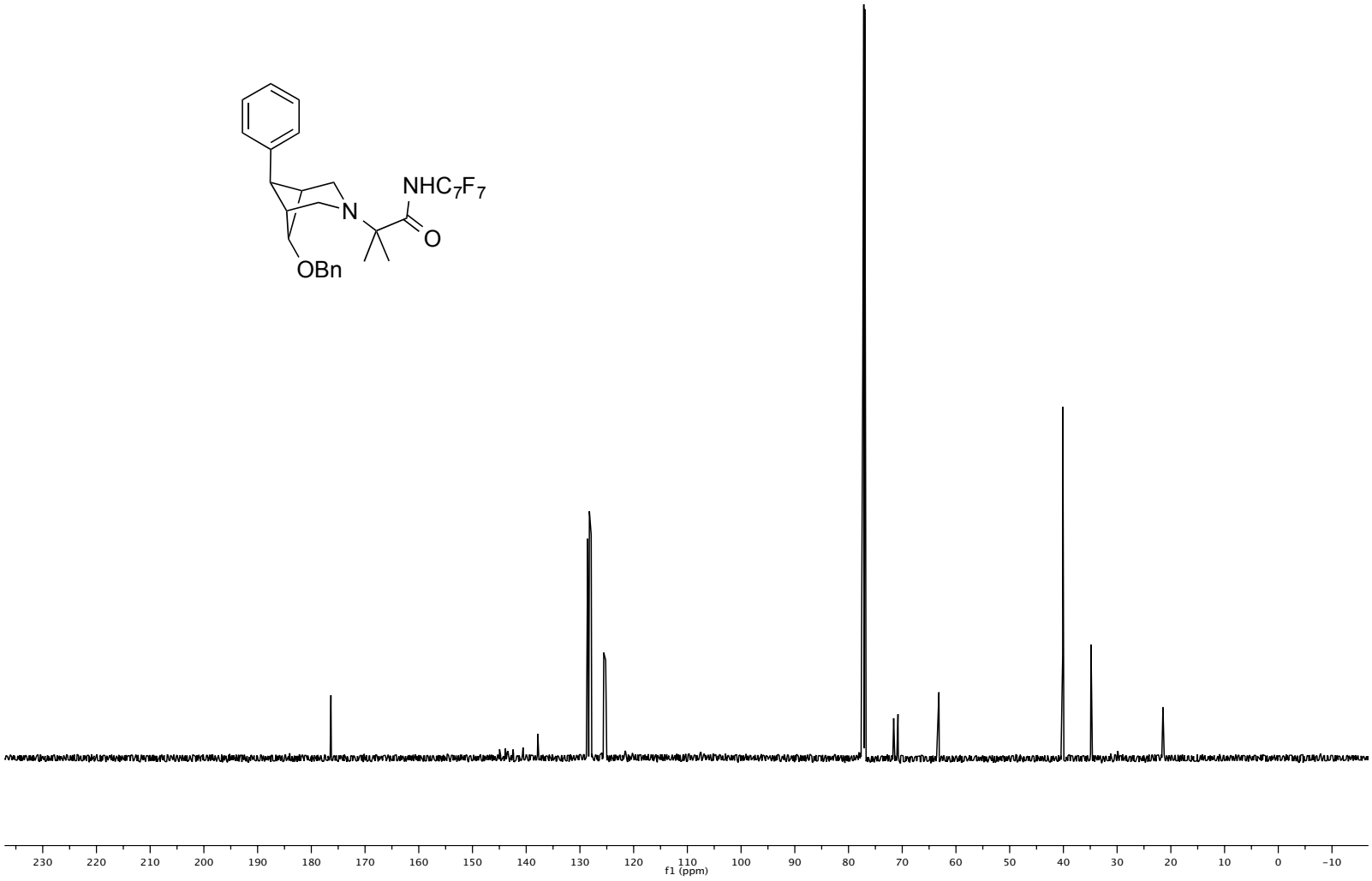
^{13}C NMR Spectrum of **11b** in $CDCl_3$



^{1}H NMR Spectrum of **11c** in $CDCl_3$

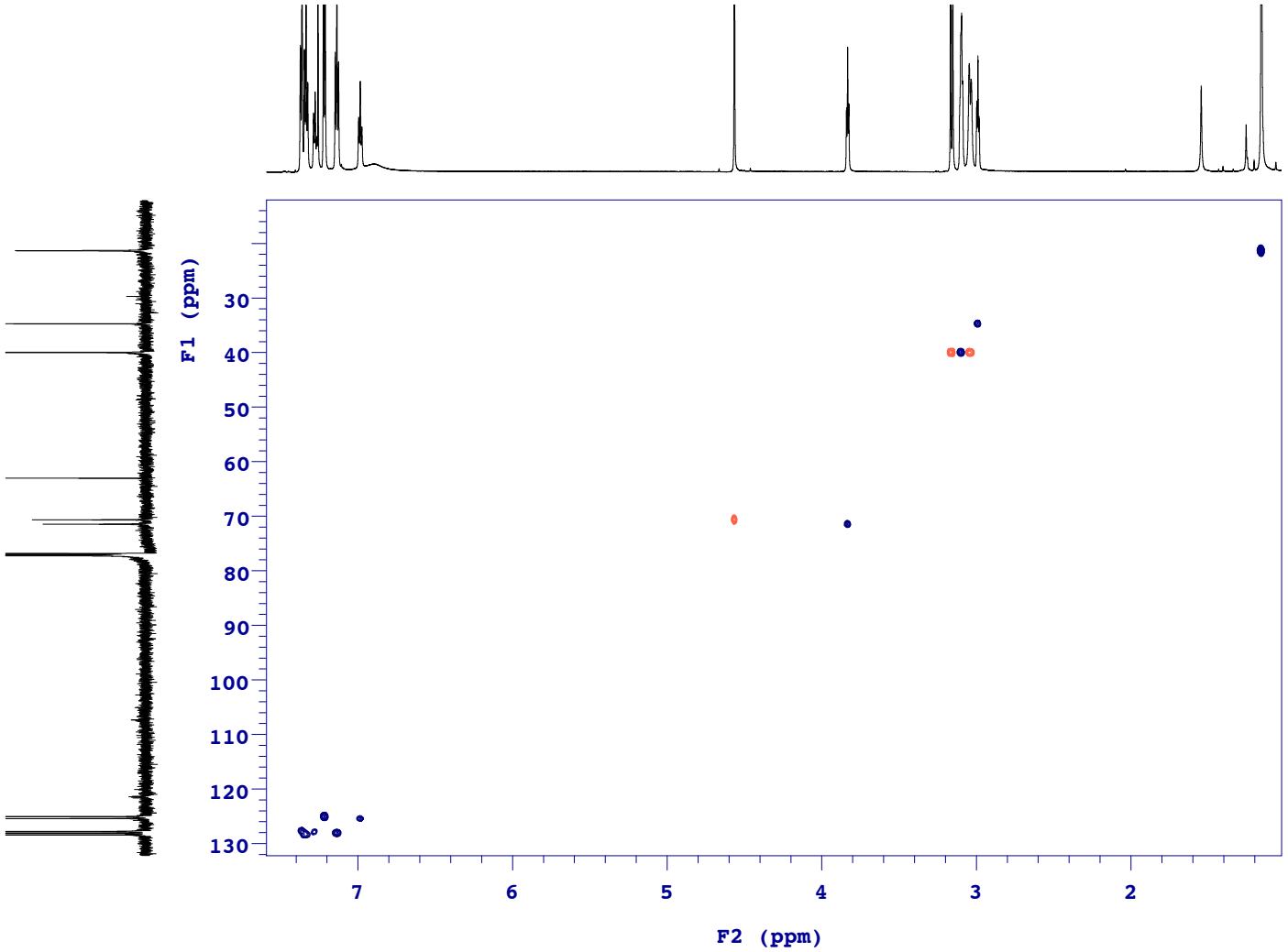


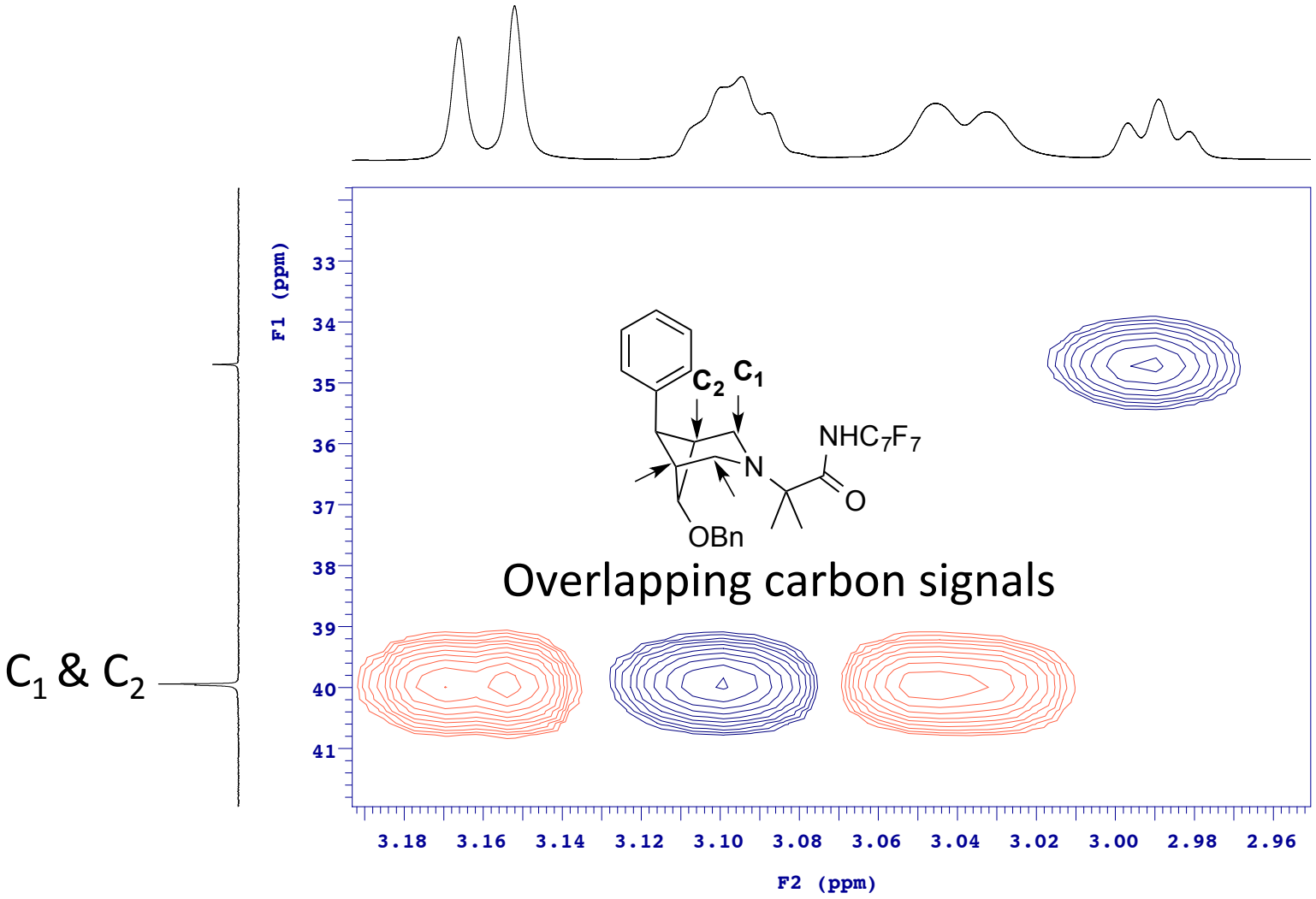
^{19}F NMR Spectrum of **11c** in $CDCl_3$



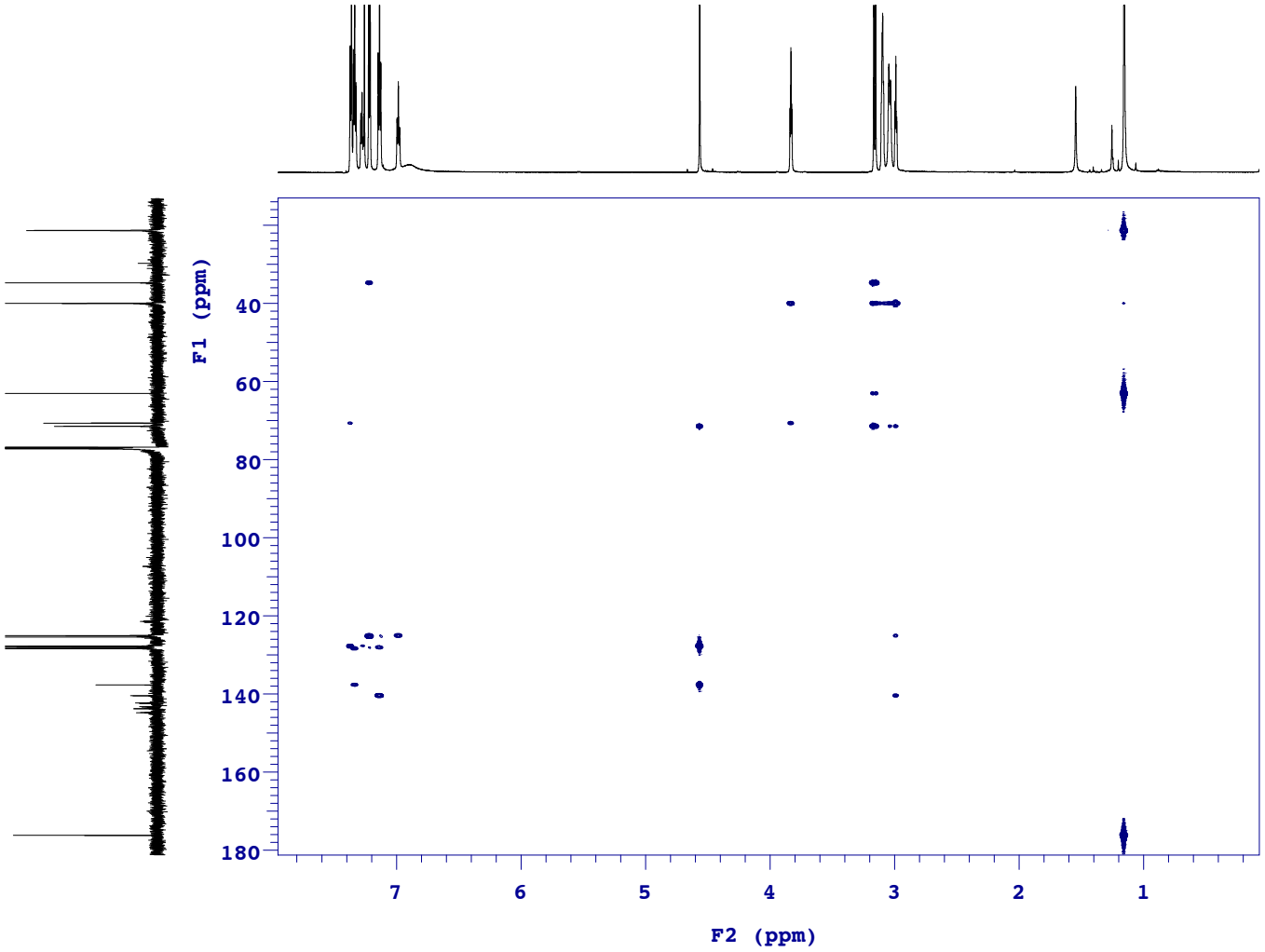
^{13}C NMR Spectrum of **11c** in $CDCl_3$

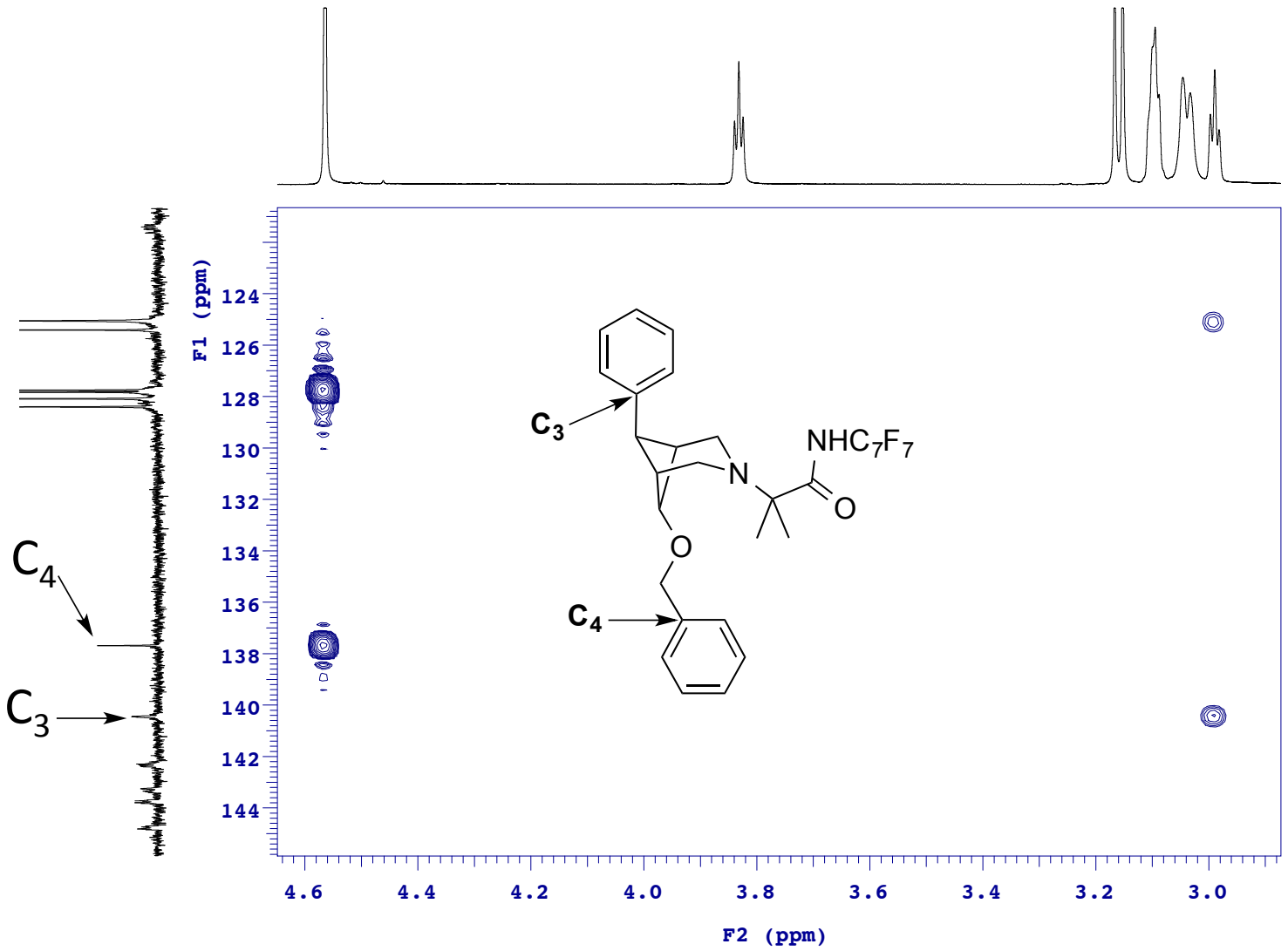
(^{1}H-^{13}C) HSQC of **11c** in $CDCl_3$

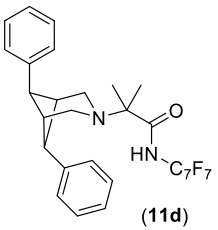



F1 (ppm)
33
34
35
36
37
38
39
40
41
3.18
3.16
3.14
3.12
3.10
3.08
3.06
3.04
3.02
3.00
2.98
2.96
F2 (ppm)
C2
C1
NHC7F7
N
O
OBn
Overlapping carbon signals
C1 & C2

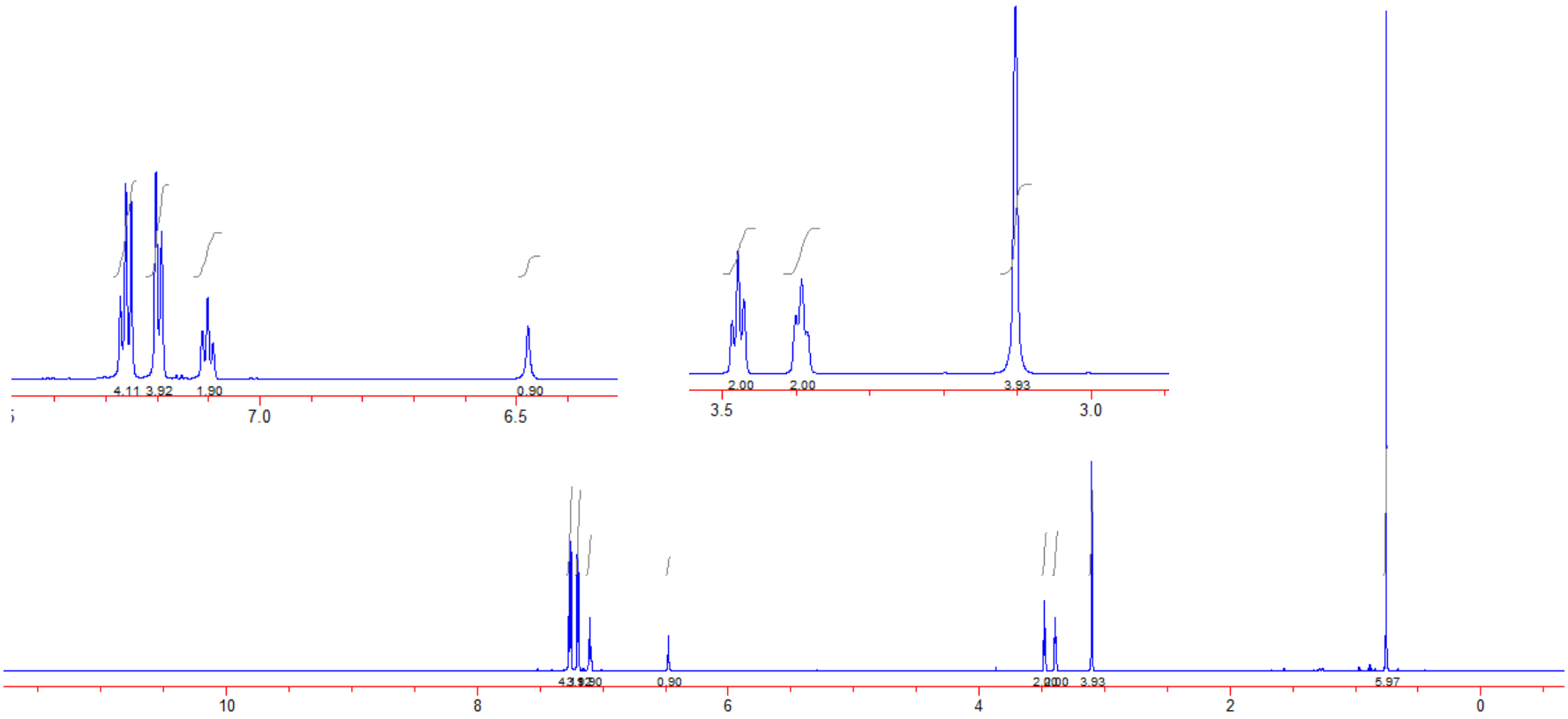
(^{1}H-^{13}C) HMBC of **11c** in $CDCl_3$



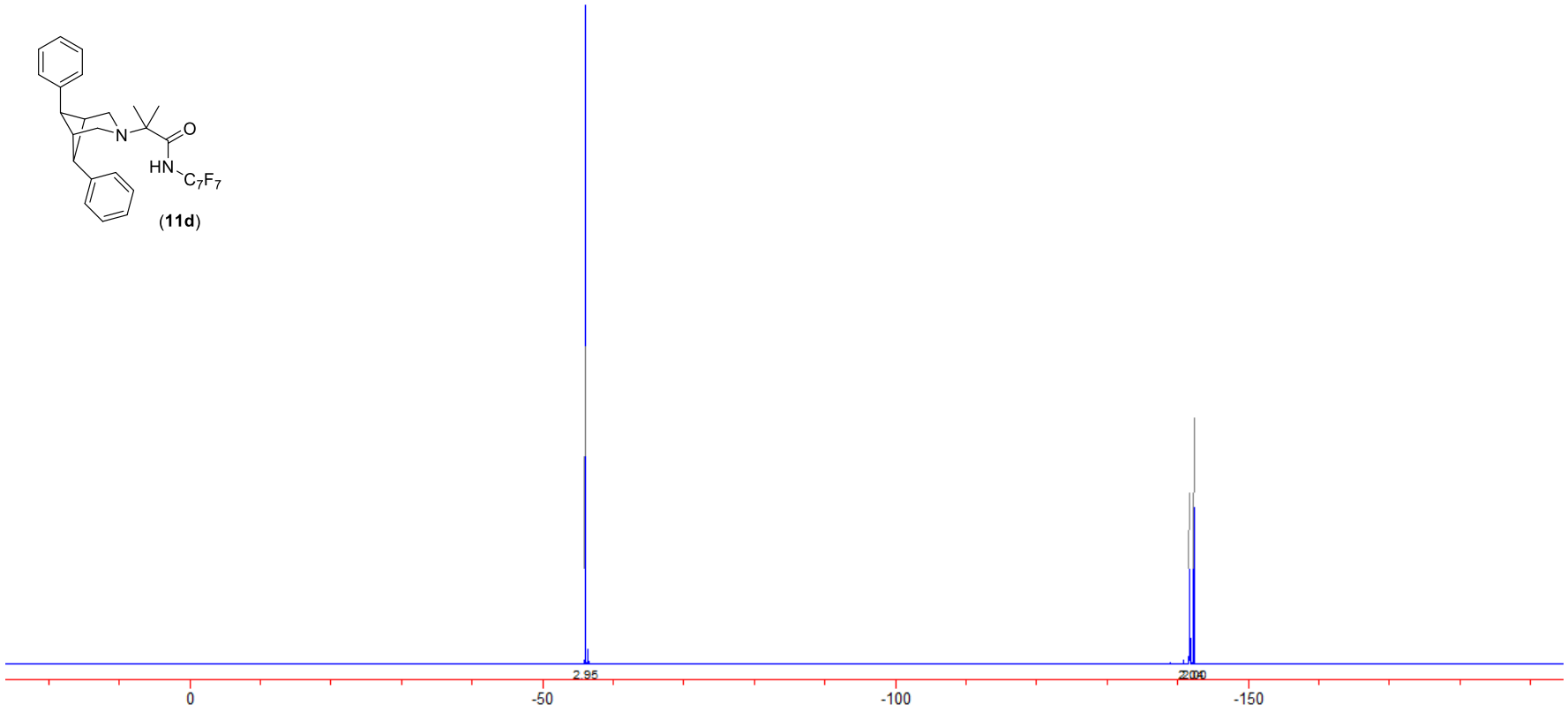

F1 (ppm)
124
126
128
130
132
134
136
138
140
142
144
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
F2 (ppm)
C4
C3
C3
C4
NHC7F7
N
O
O



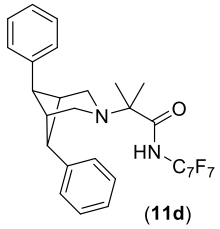
(**11d**)



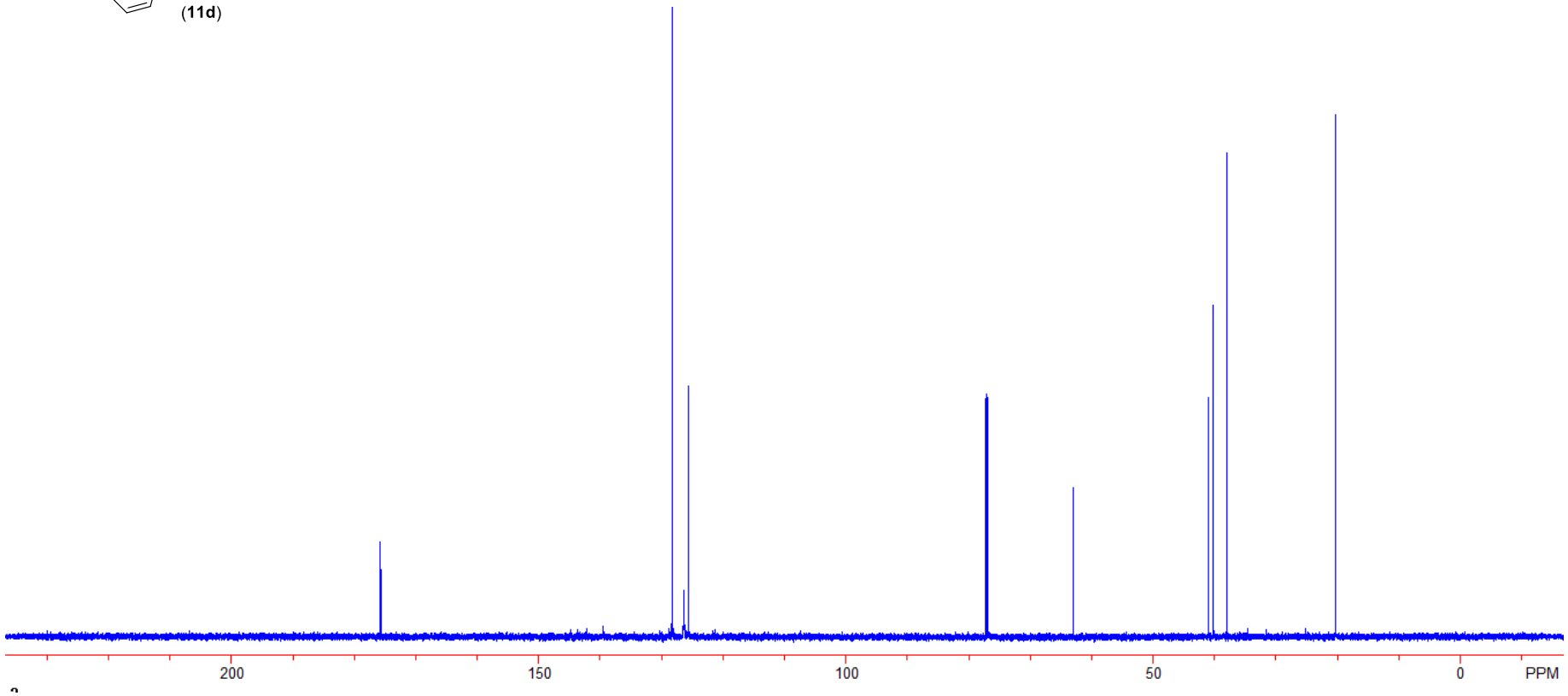
^{1}H NMR Spectrum in $CDCl_3$



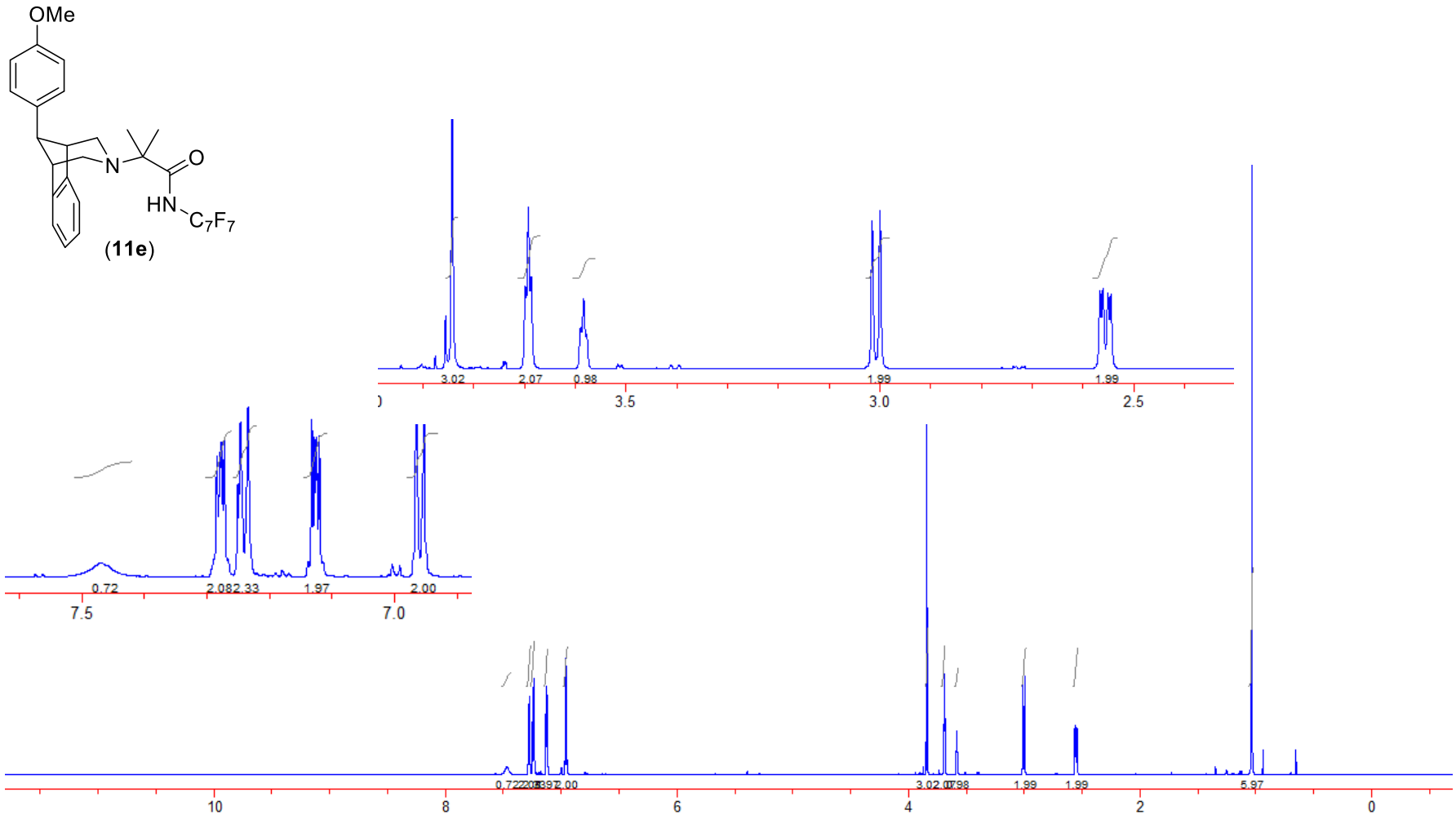
^{19}F NMR Spectrum in $CDCl_3$



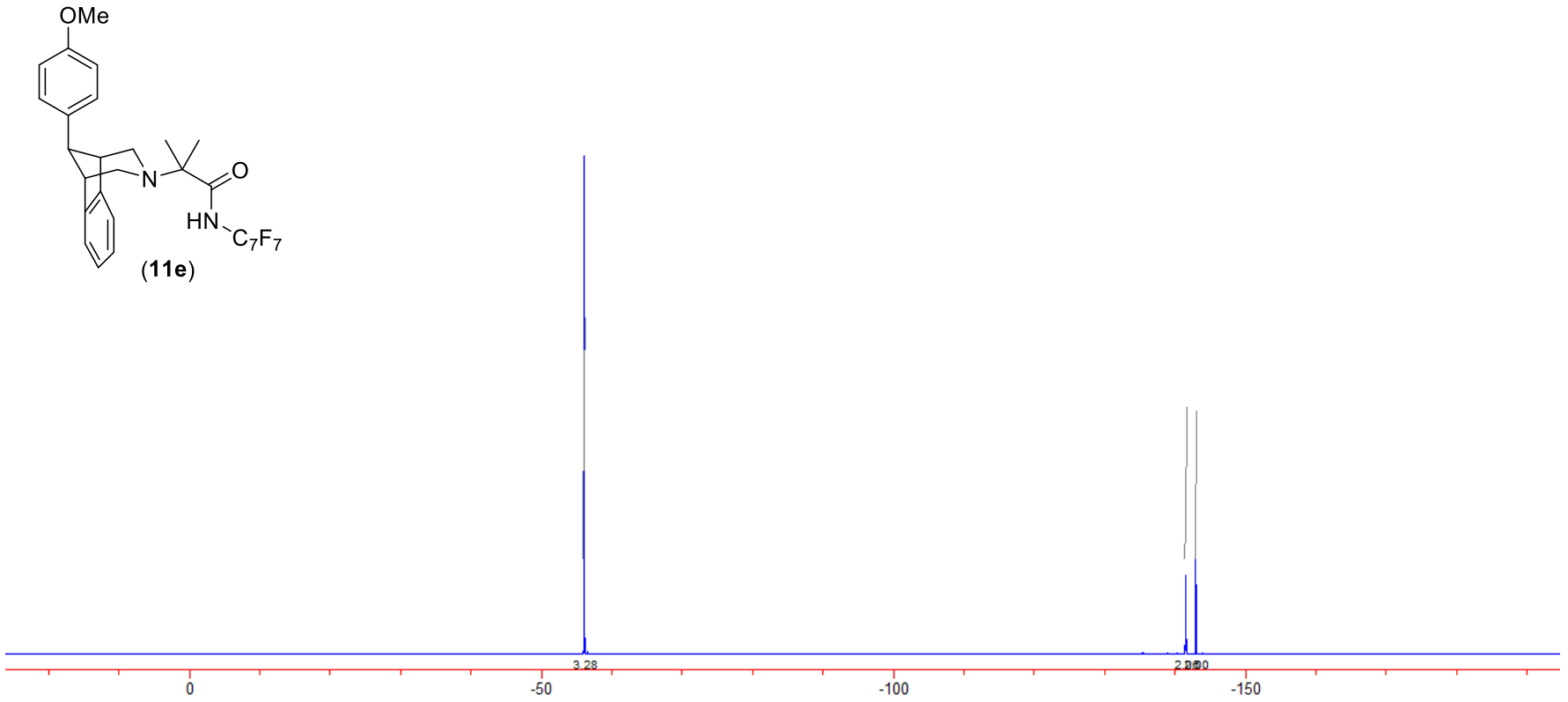
(**11d**)



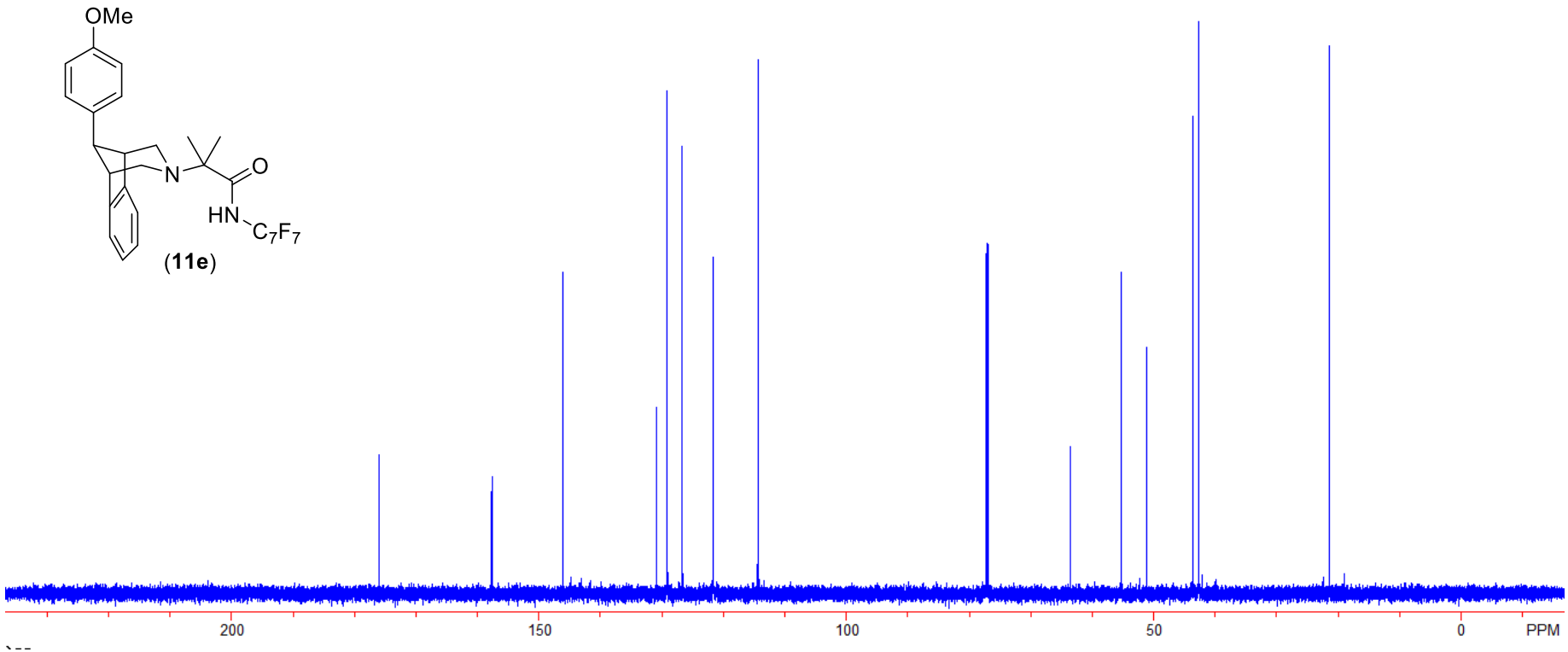
^{13}C NMR Spectrum in $CDCl_3$



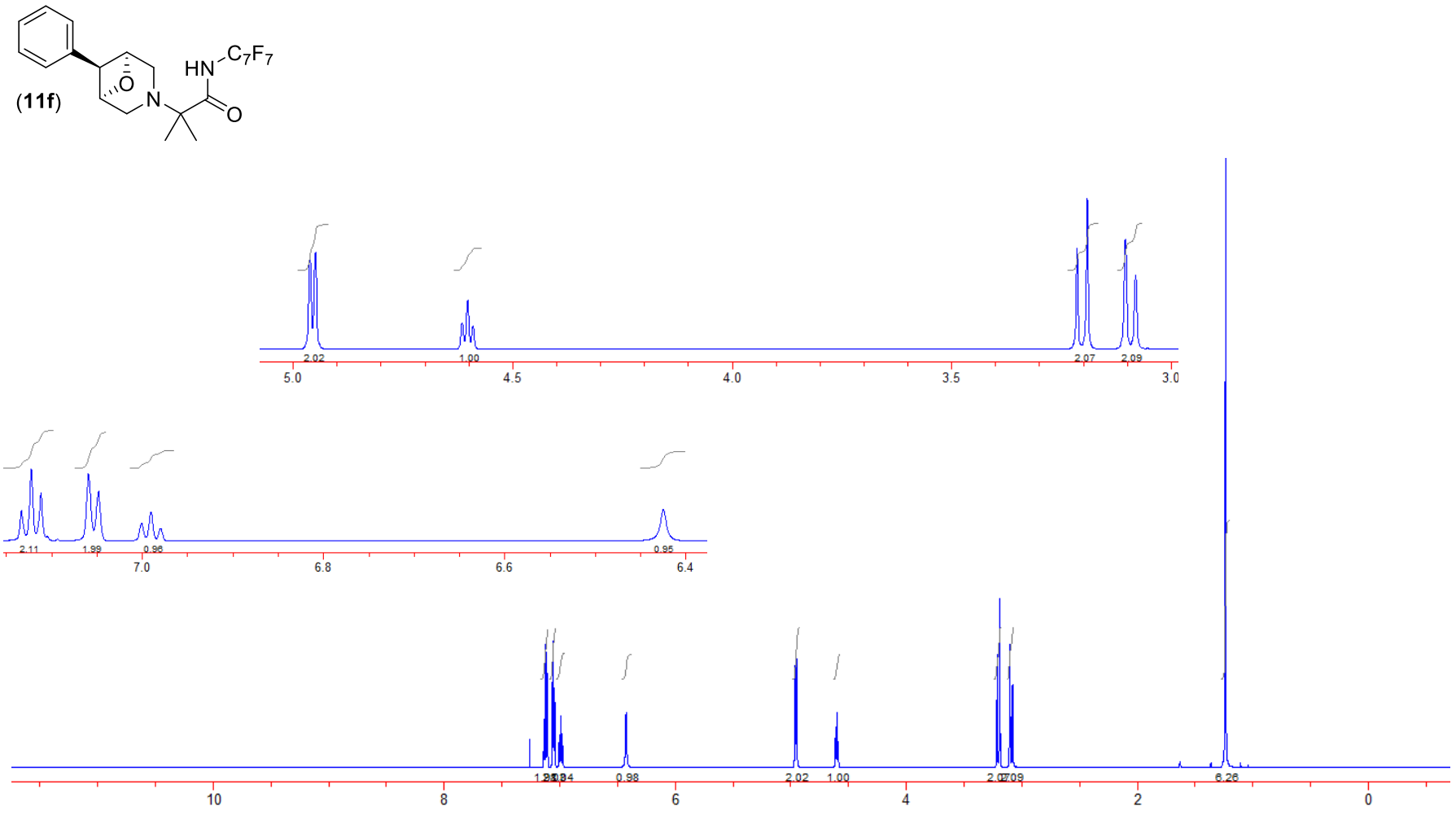
^{1}H NMR Spectrum in $CDCl_3$



^{19}F NMR Spectrum in $CDCl_3$

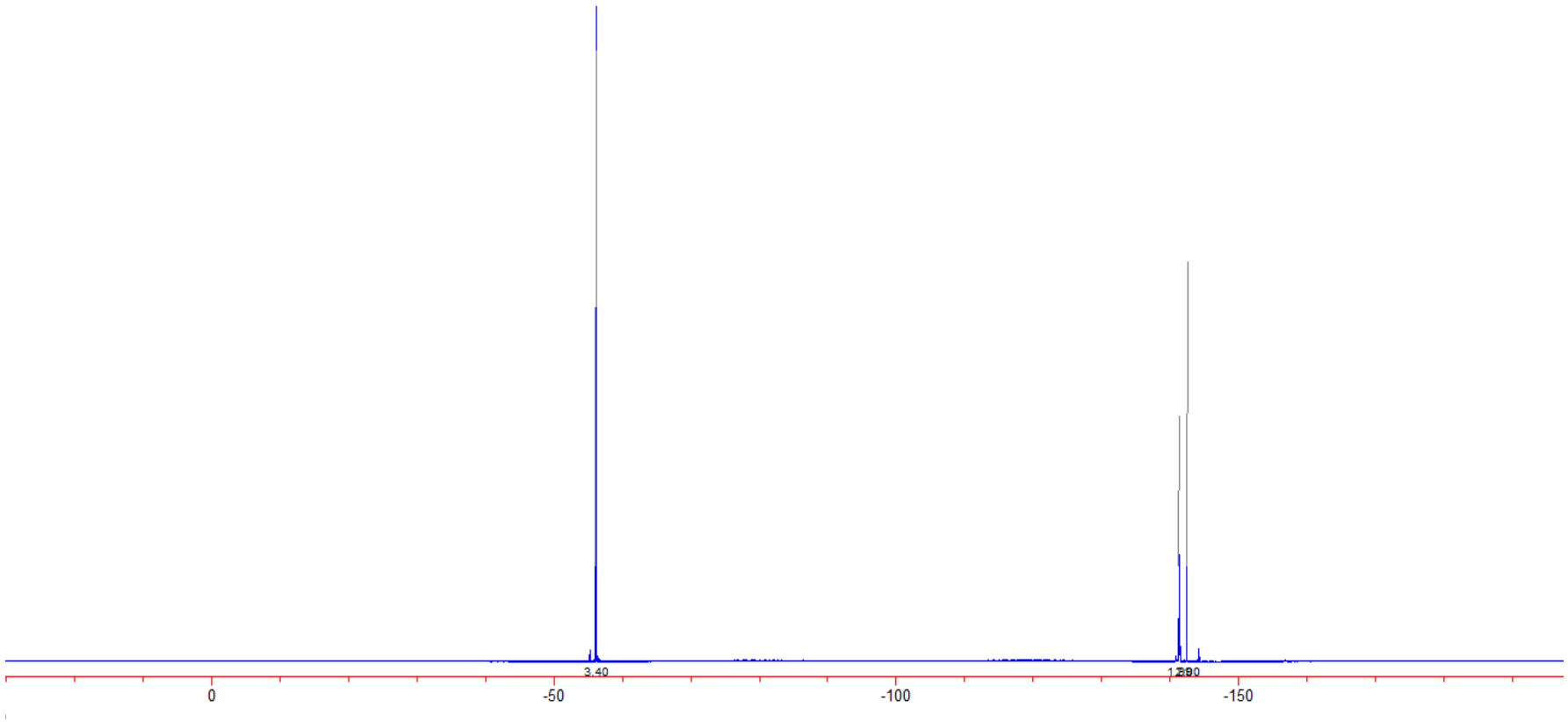


^{13}C NMR Spectrum in $CDCl_3$

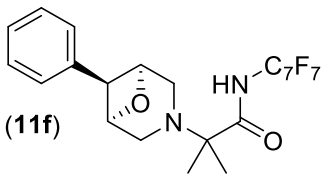


^{1}H NMR Spectrum in $CDCl_3$

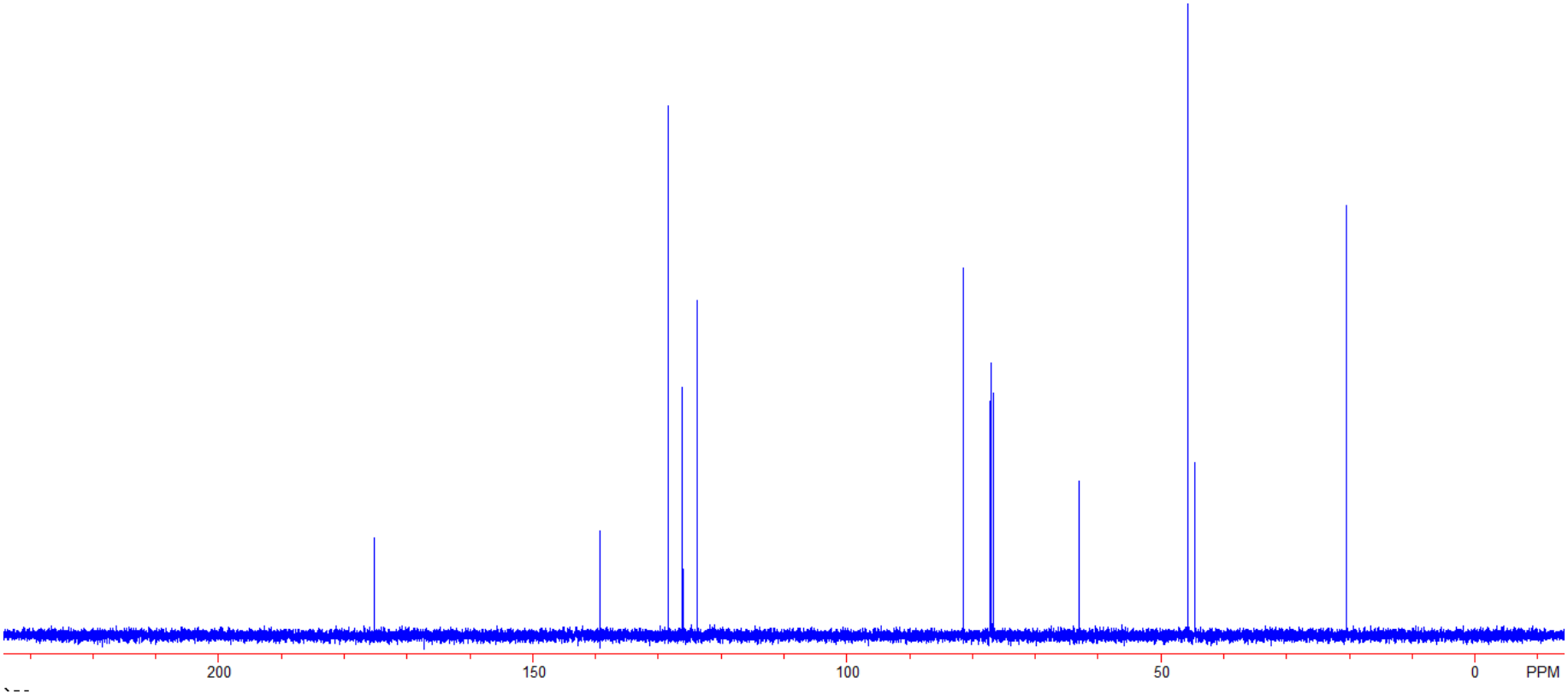
(**11f**)



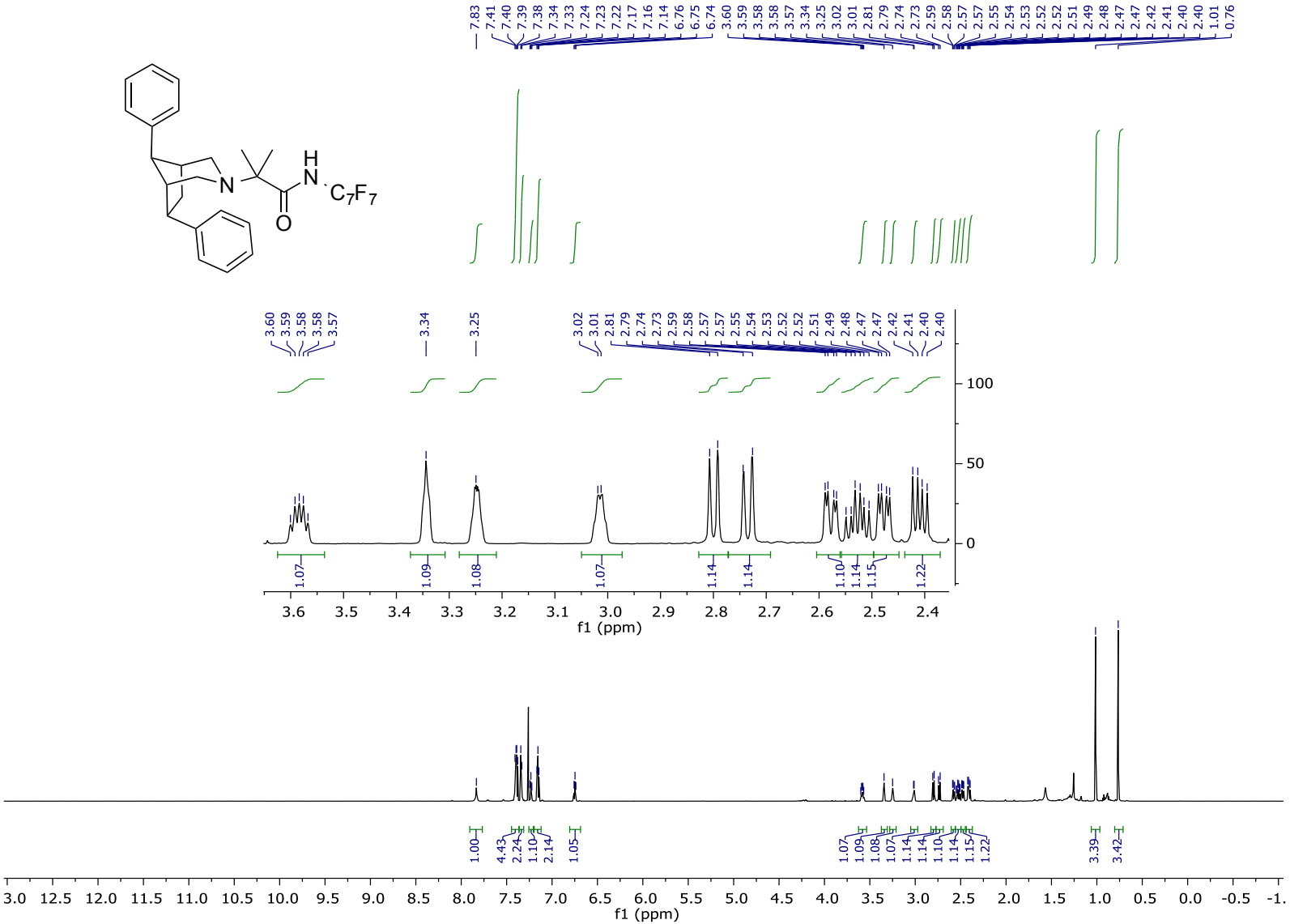
^{19}F NMR Spectrum in $CDCl_3$



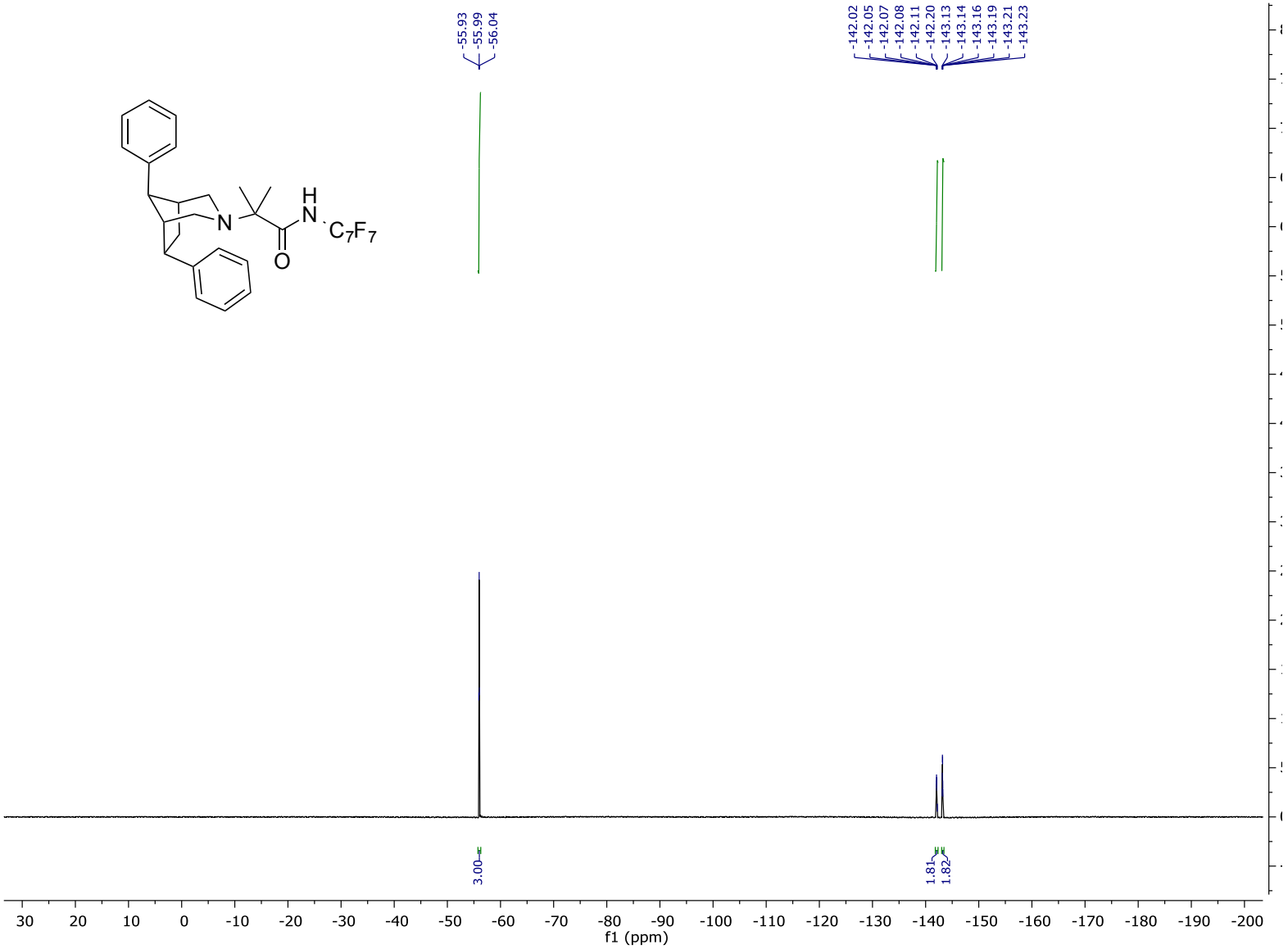
(**11f**)



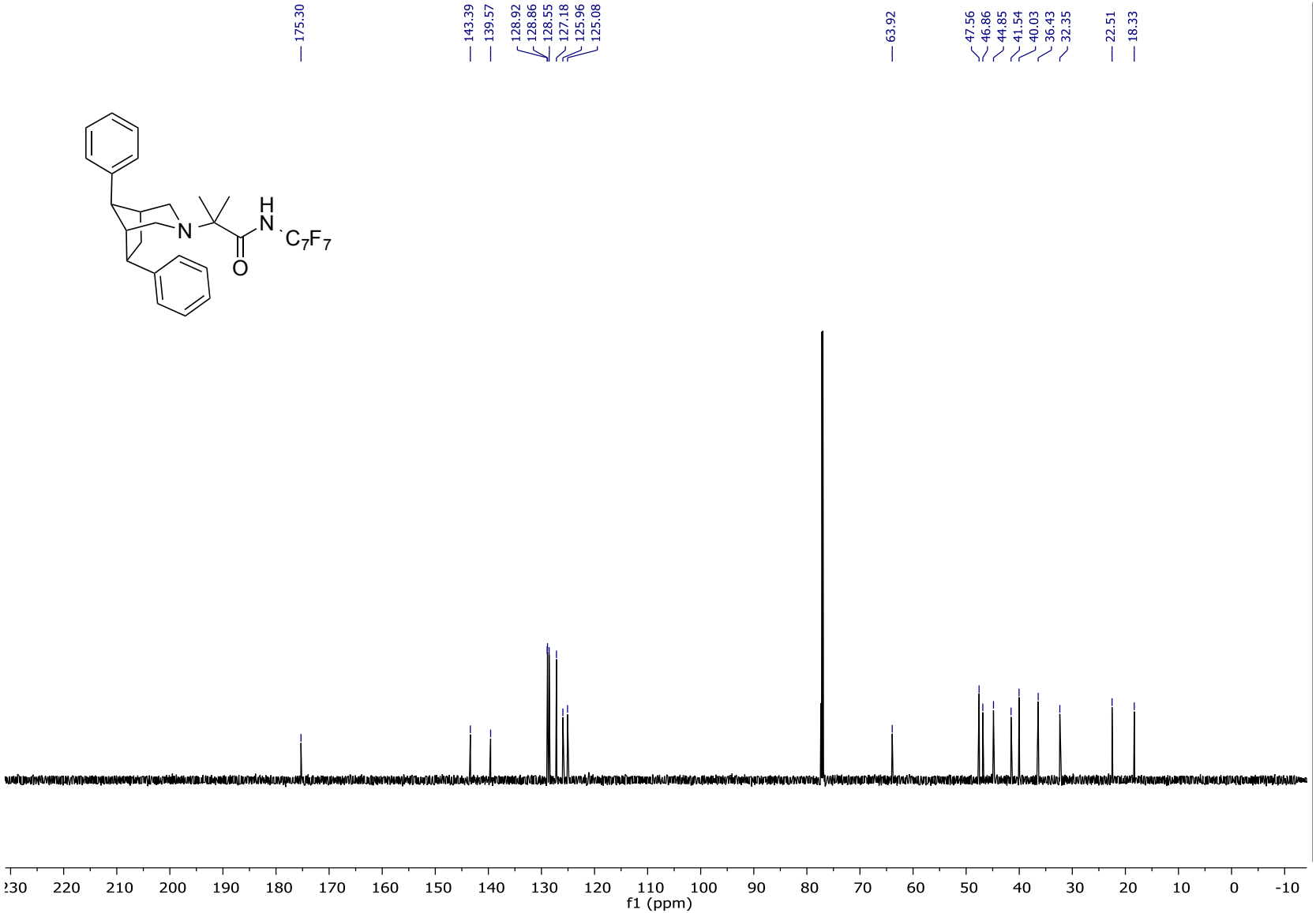
^{13}C NMR Spectrum in $CDCl_3$



^{1}H NMR Spectrum of **11g** in $CDCl_3$

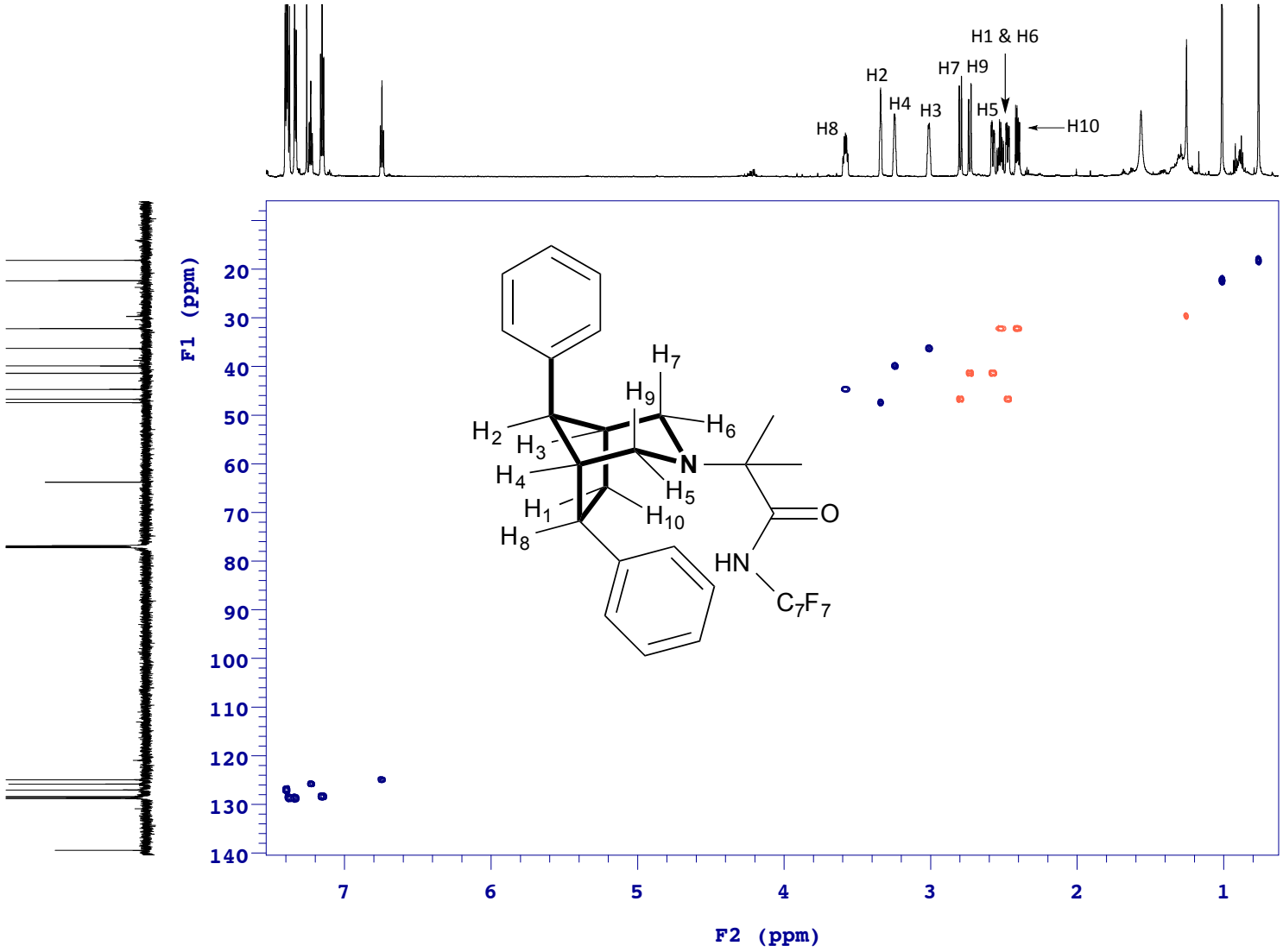


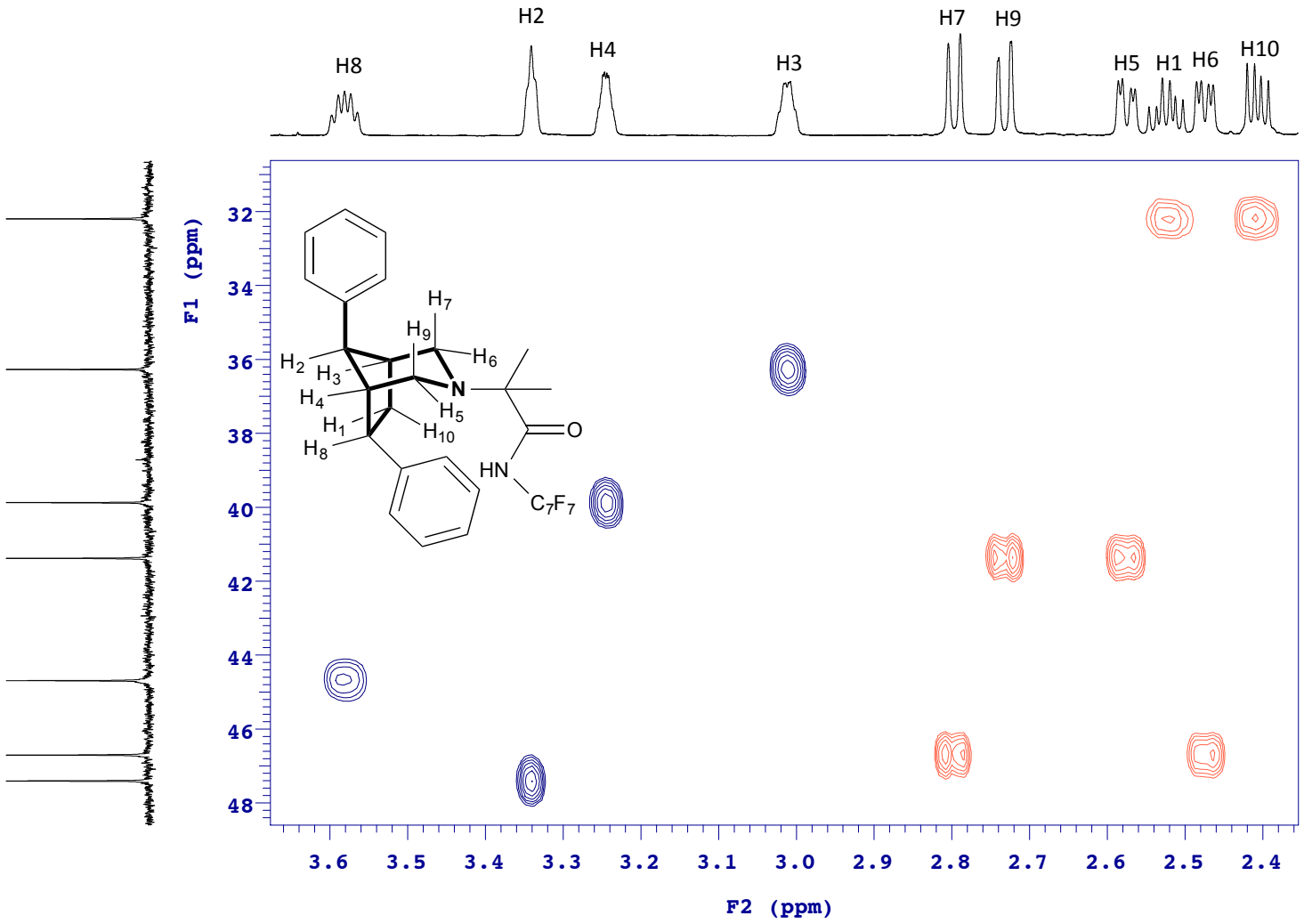
^{19}F NMR Spectrum of **11g** in $CDCl_3$



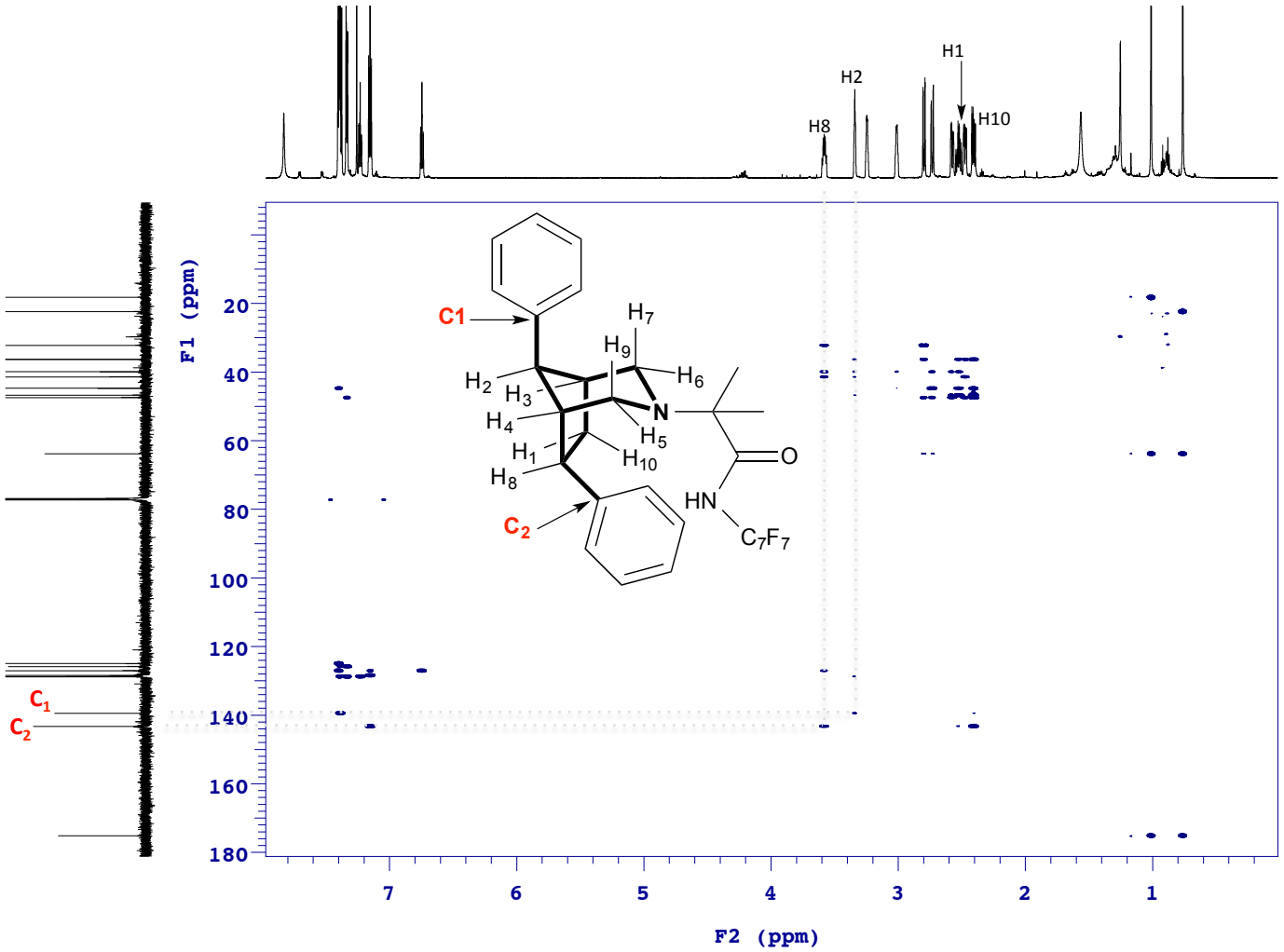
^{13}C NMR Spectrum of **11g** in $CDCl_3$

^{1}H-^{13}C HSQC Spectrum of **11g** in $CDCl_3$

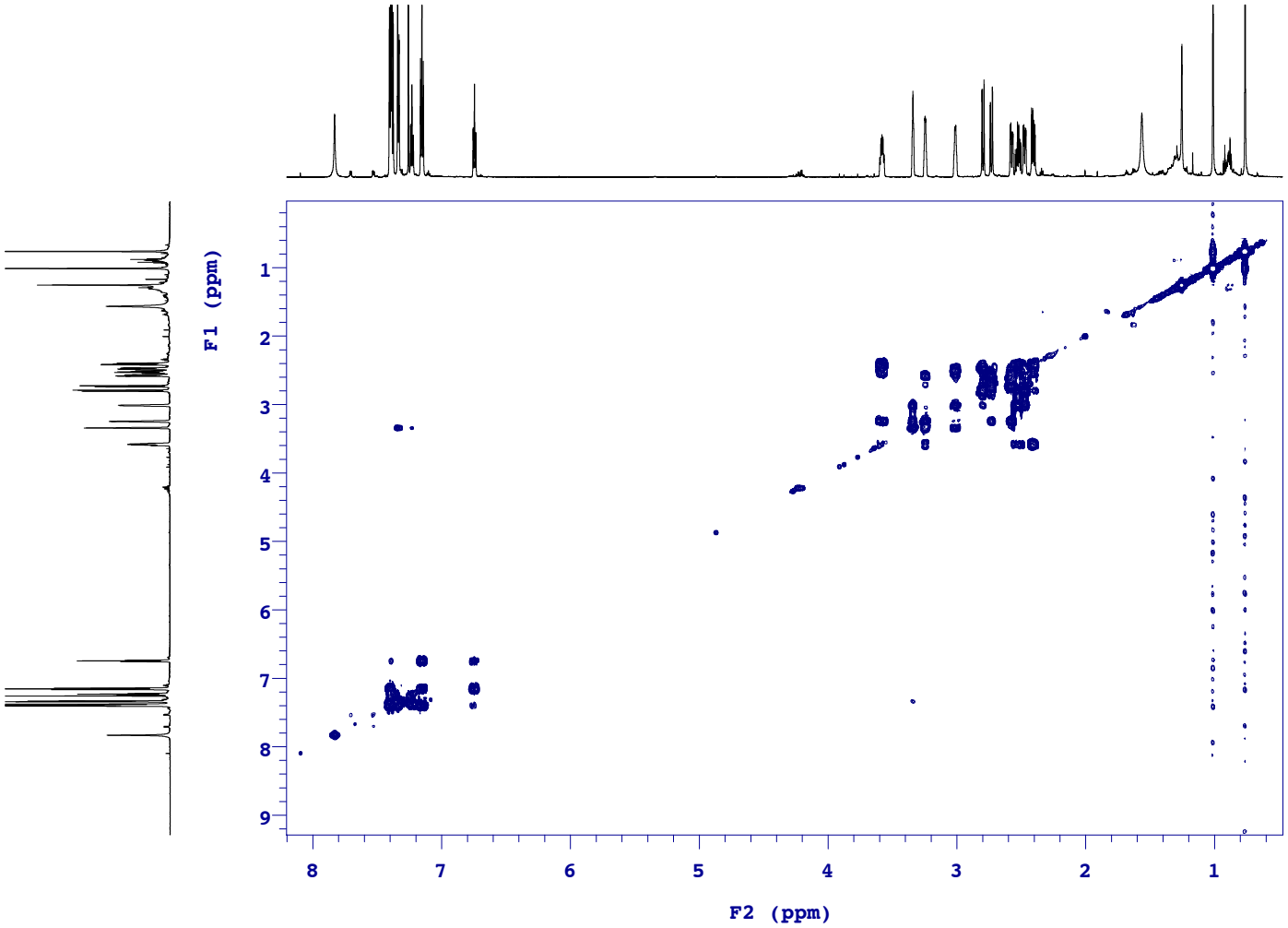


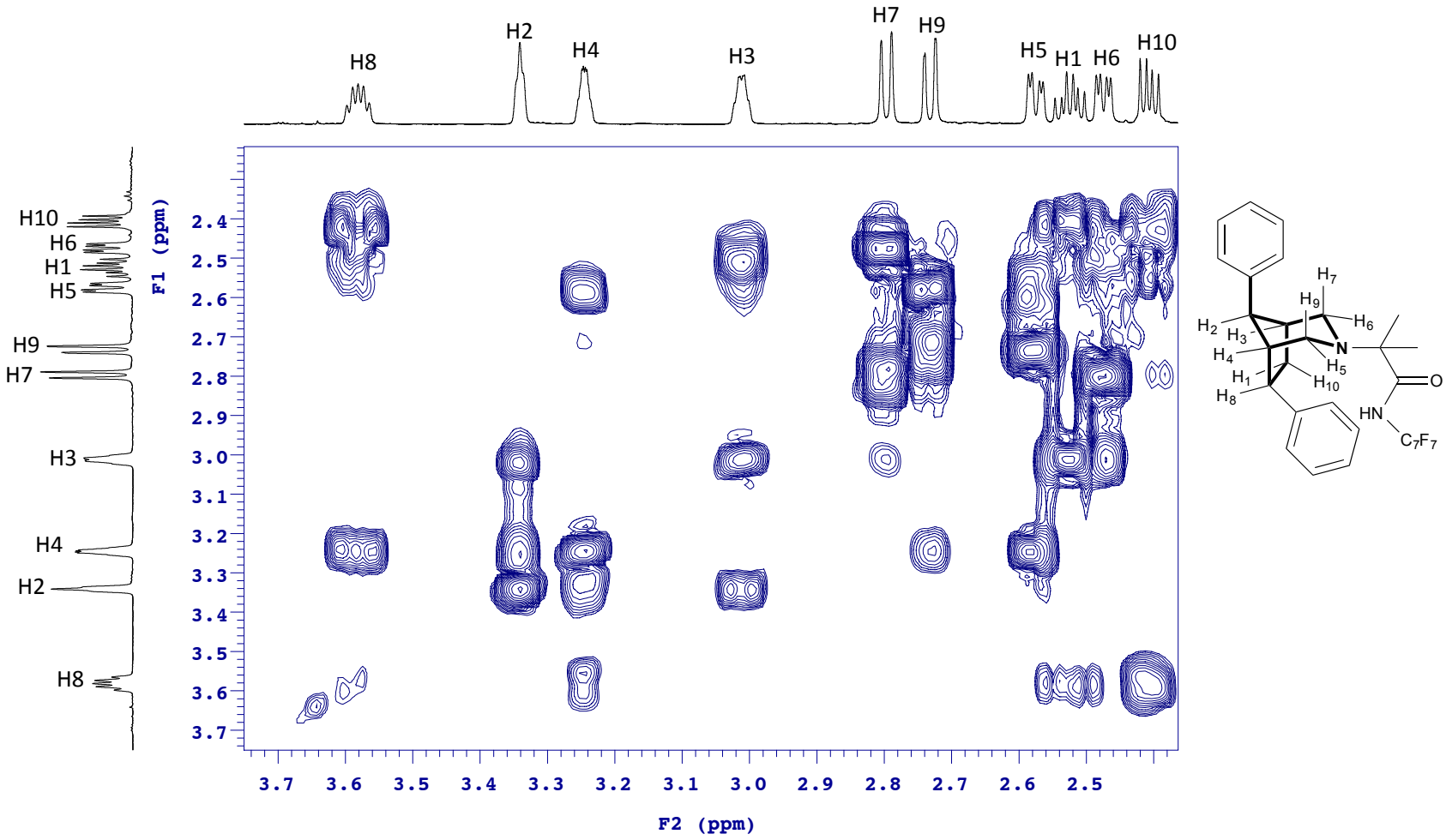

H8
H2
H4
H3
H7
H9
H5
H1
H6
H10
F1 (ppm)
32
34
36
38
40
42
44
46
48
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
F2 (ppm)
H7
H9
H2
H3
H6
N
H4
H5
H1
H10
H8
O
HN
C7F7

^{1}H-^{13}C HMBC Spectrum of **11g** in $CDCl_3$ **(Pale gray lines placed to visualize relevant cross-peaks)**

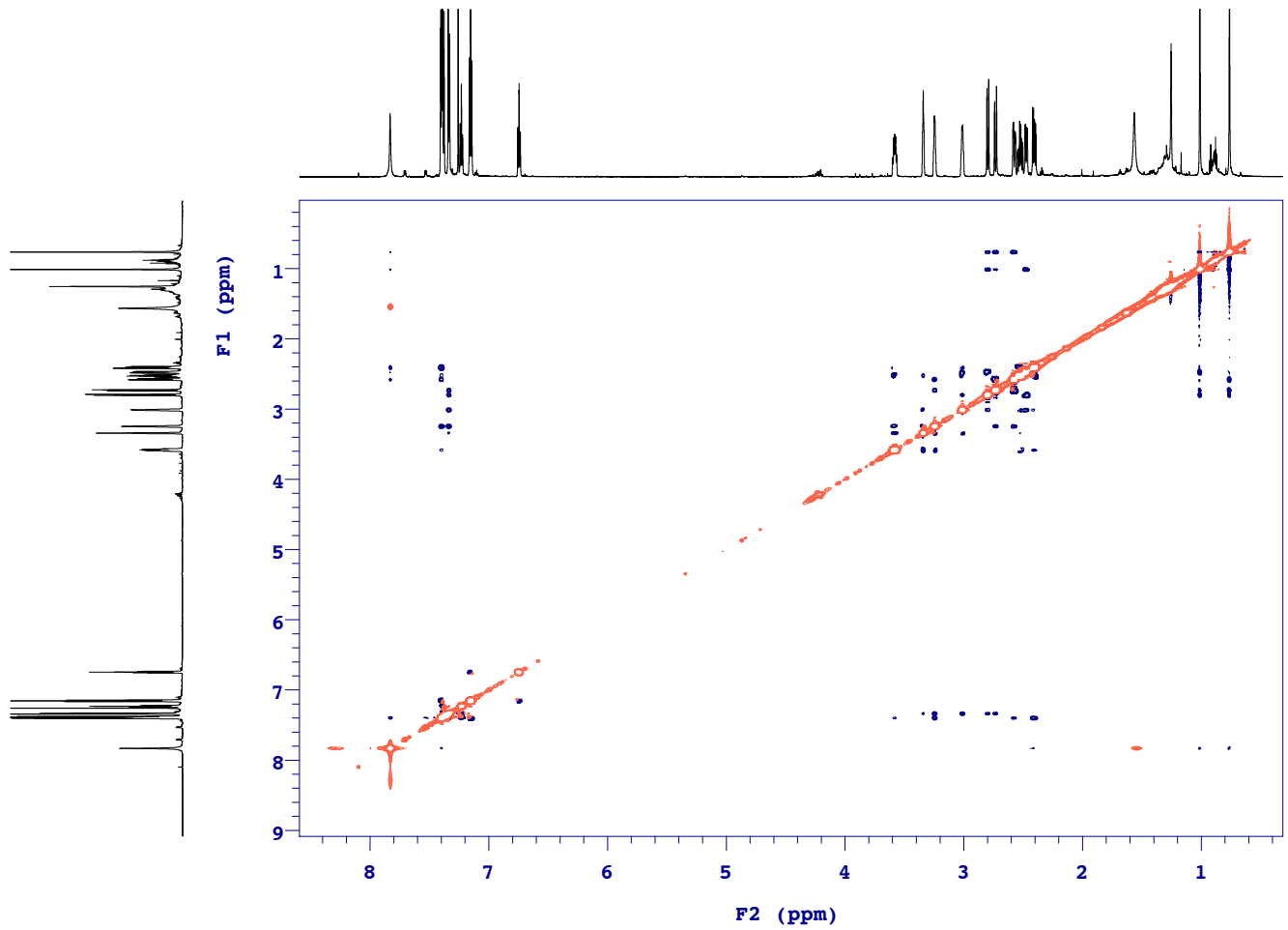


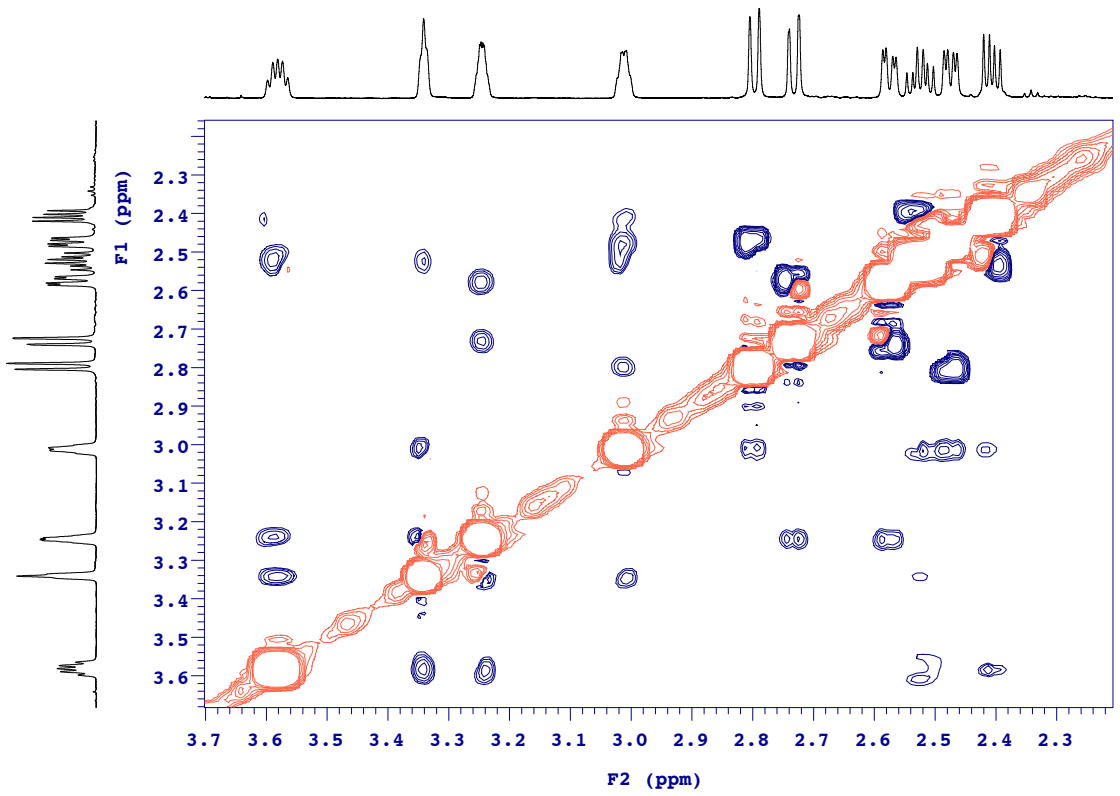
^{1}H-^{1}H COSY Spectrum of **11g** in $CDCl_3$

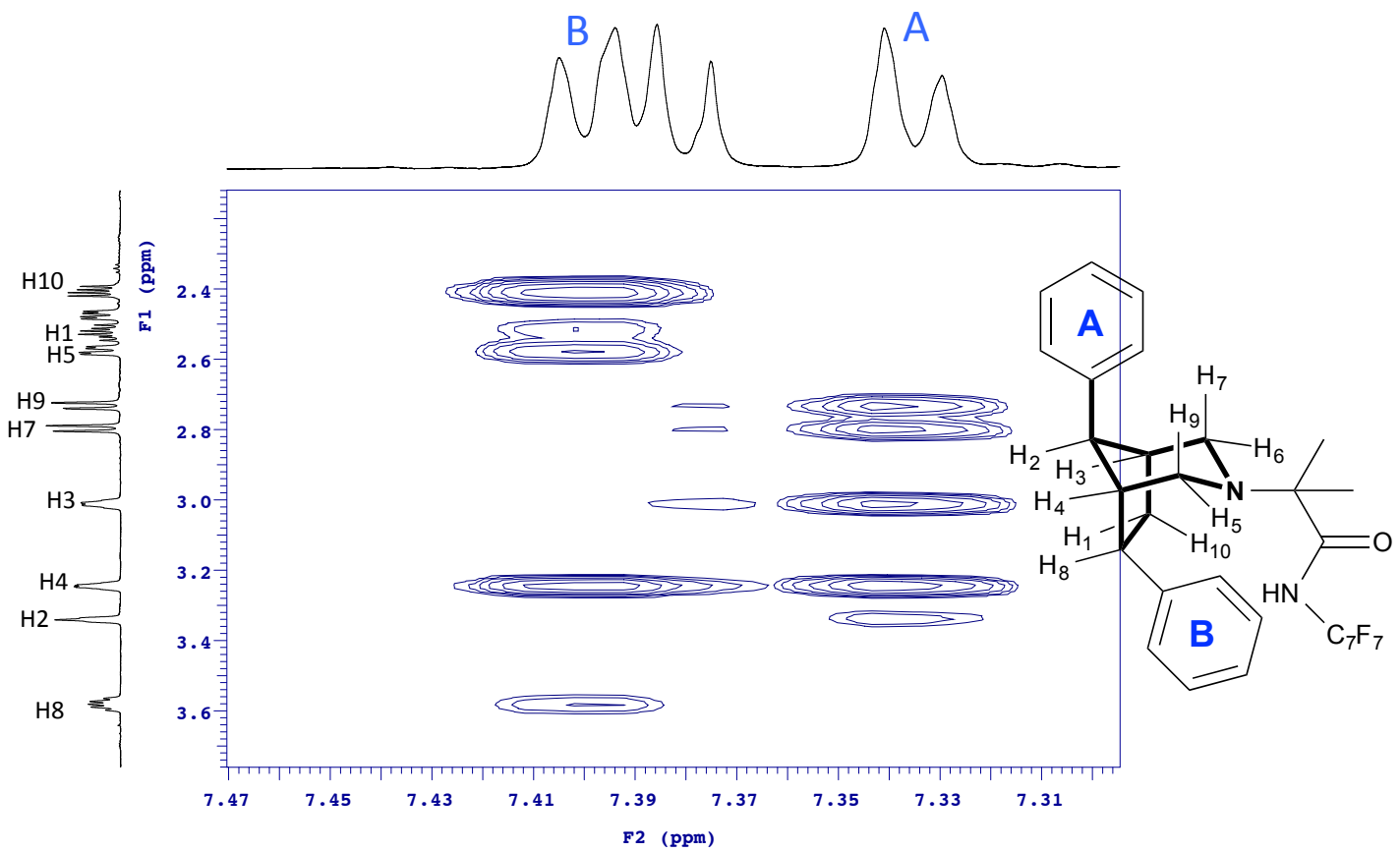


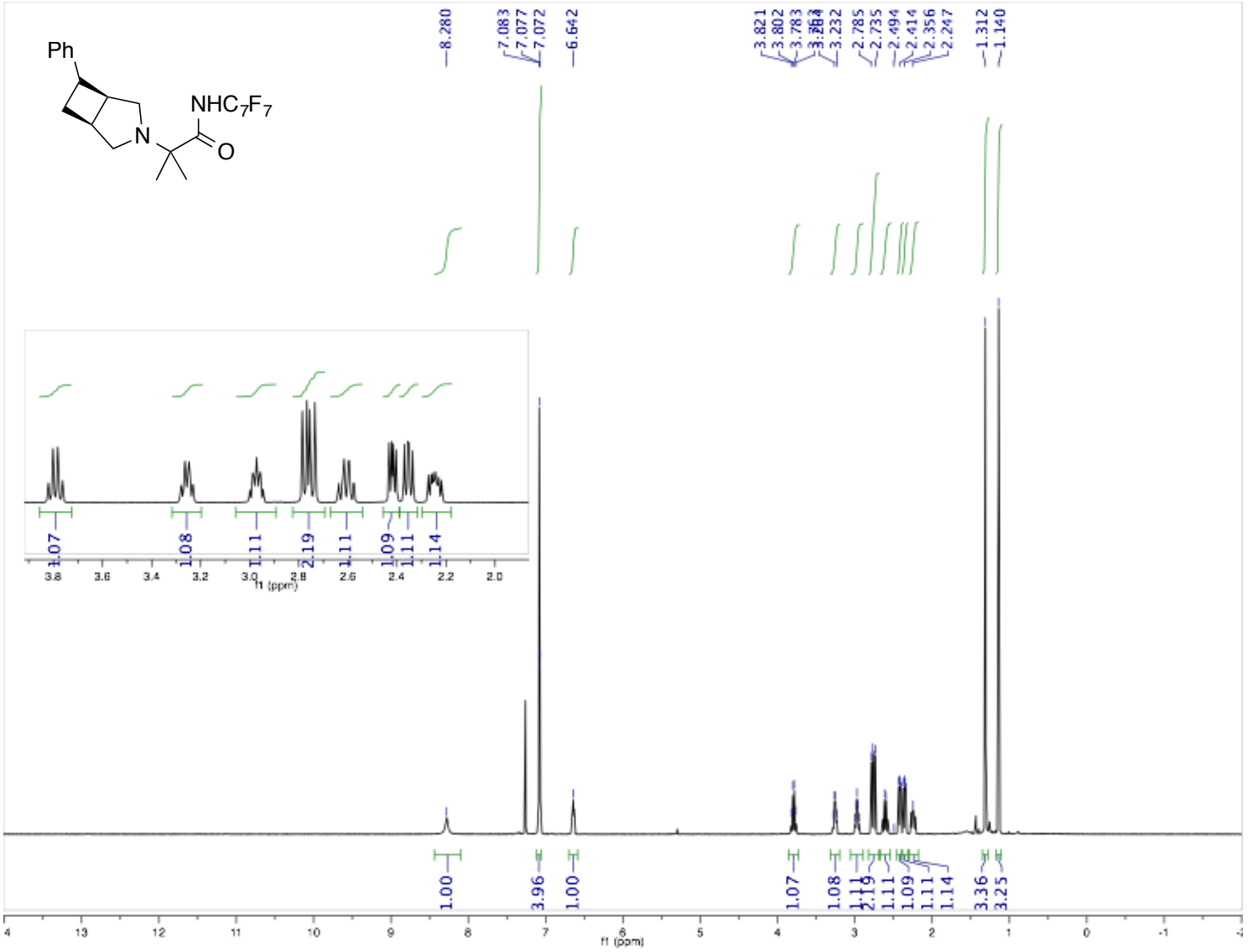

H8
H2
H4
H3
H7
H9
H5
H1
H6
H10
H10
H6
H1
H5
H9
H7
H3
H4
H2
H8
F1 (ppm)
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5
F2 (ppm)
H7
H9
H2
H3
H6
N
H4
H5
H1
H10
H8
O
HN
C7F7

^{1}H-^{1}H NOESY Spectrum of **11g** in $CDCl_3$

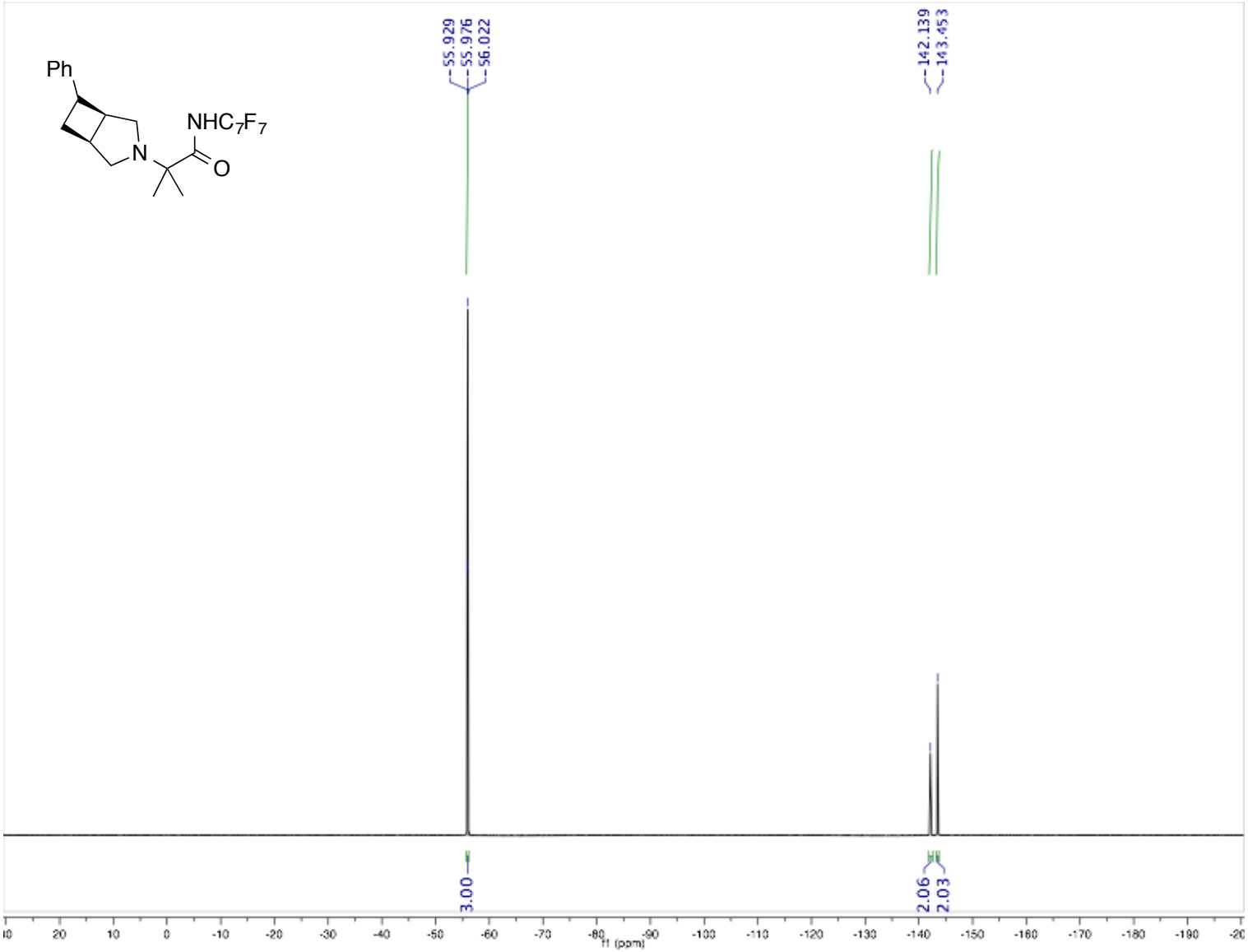



F1 (ppm)
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3
F2 (ppm)

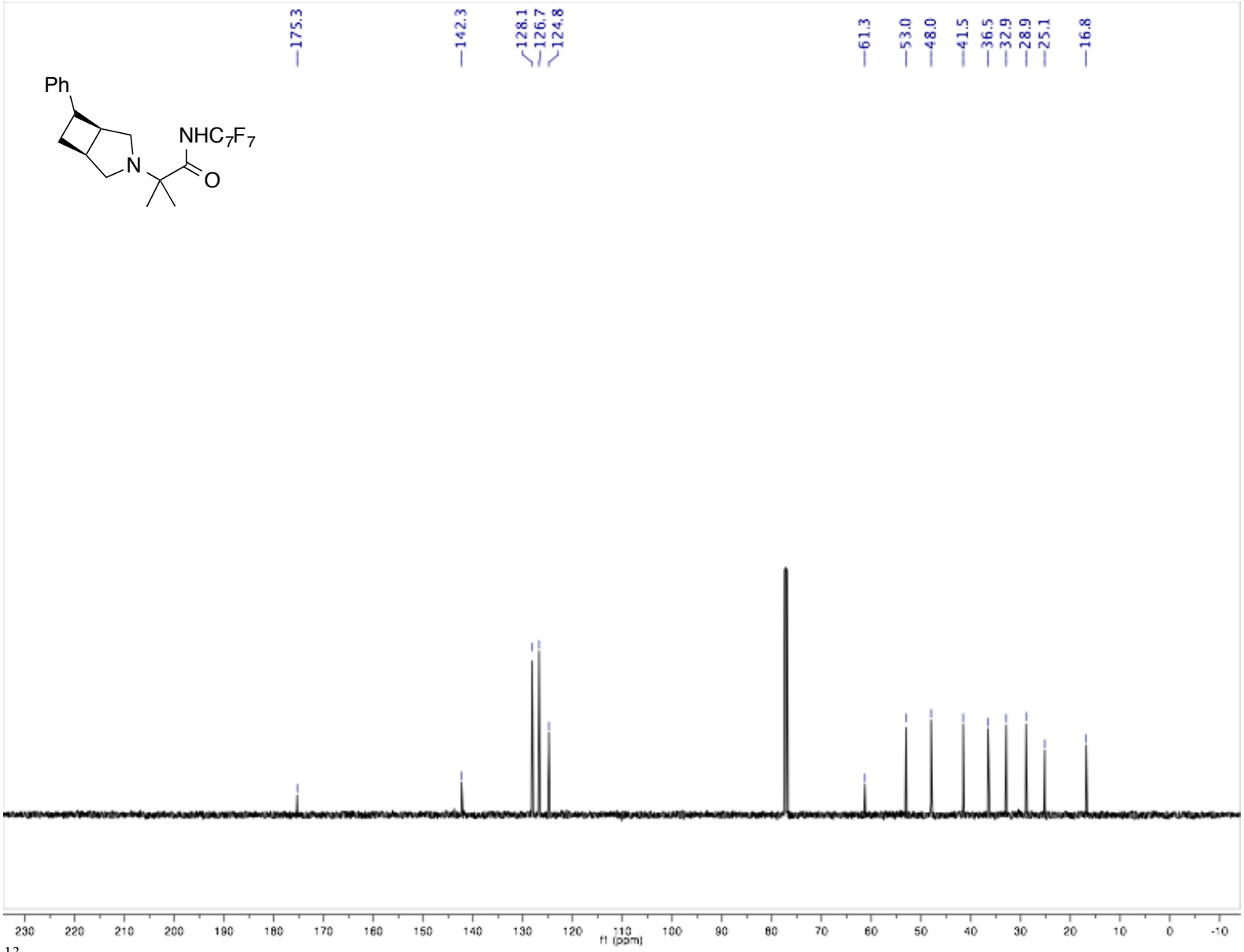

B
A
H10
H1
H5
H9
H7
H3
H4
H2
H8
F1 (ppm)
2.4
2.6
2.8
3.0
3.2
3.4
3.6
7.47
7.45
7.43
7.41
7.39
7.37
7.35
7.33
7.31
F2 (ppm)
A
B
H7
H9
H6
H2
H3
H4
N
H5
H1
H10
H8
HN
O
C7F7



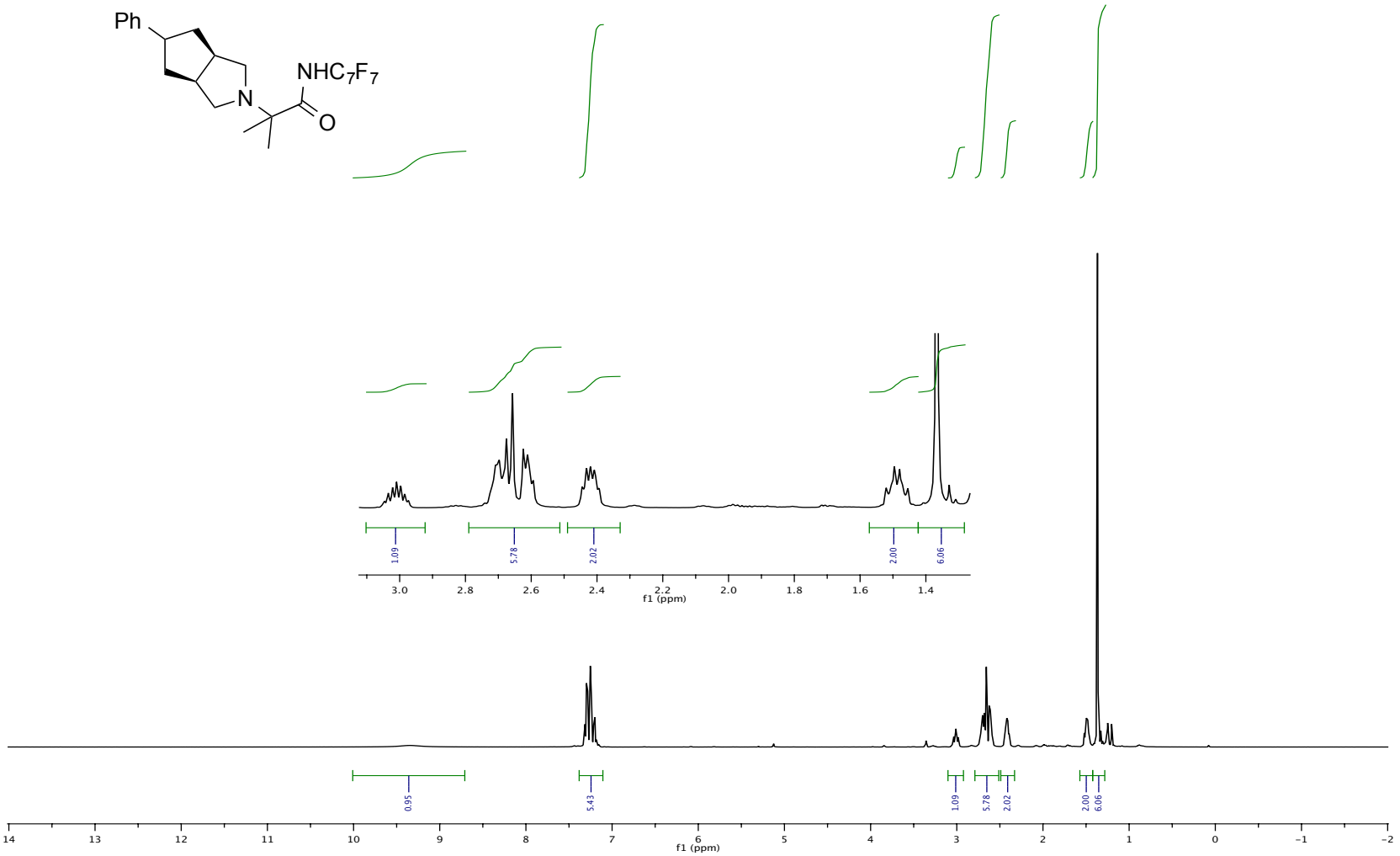
^{1}H NMR Spectrum of **11h** in $CDCl_3$



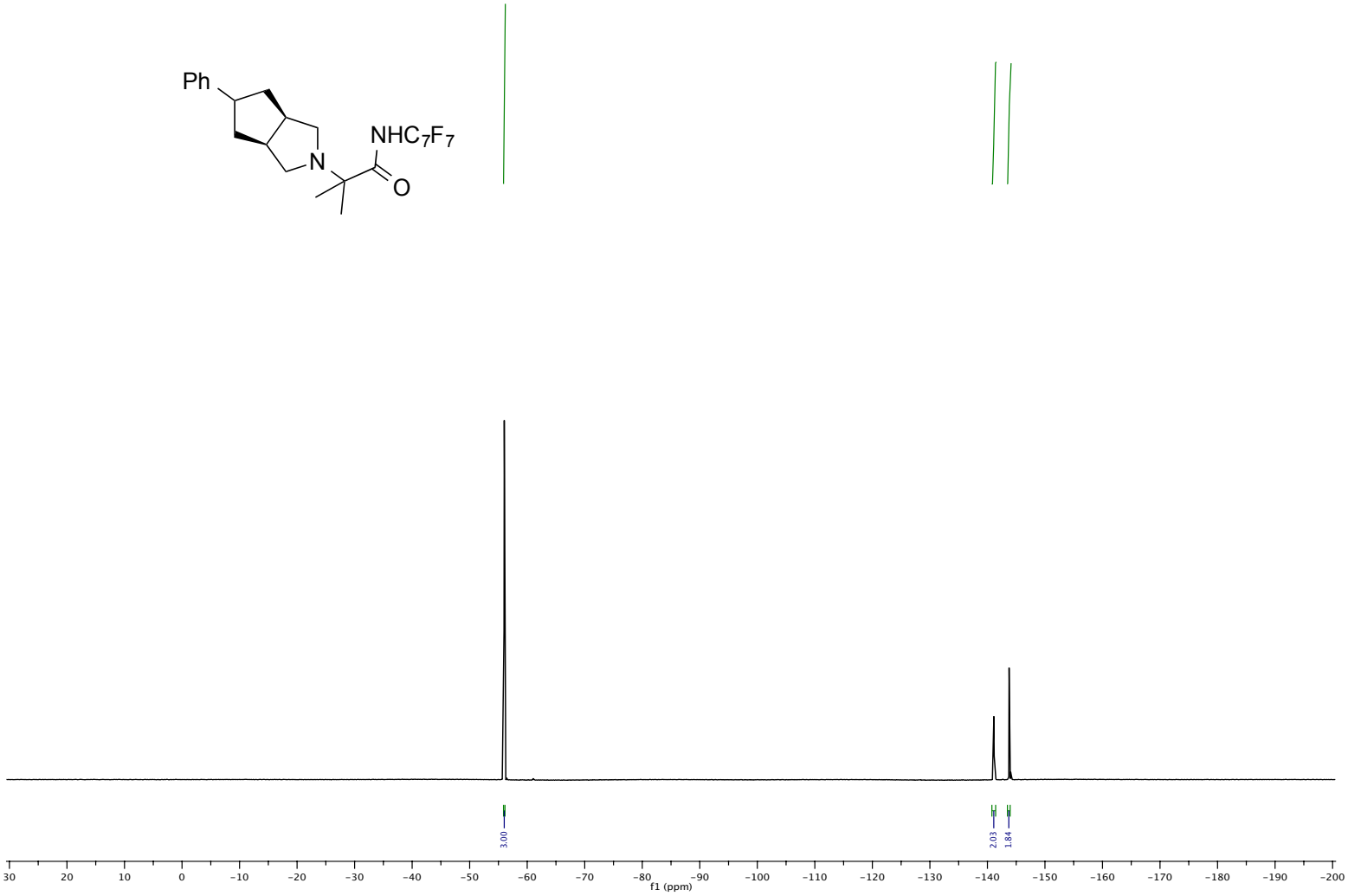
^{19}F NMR Spectrum of **11h** in $CDCl_3$



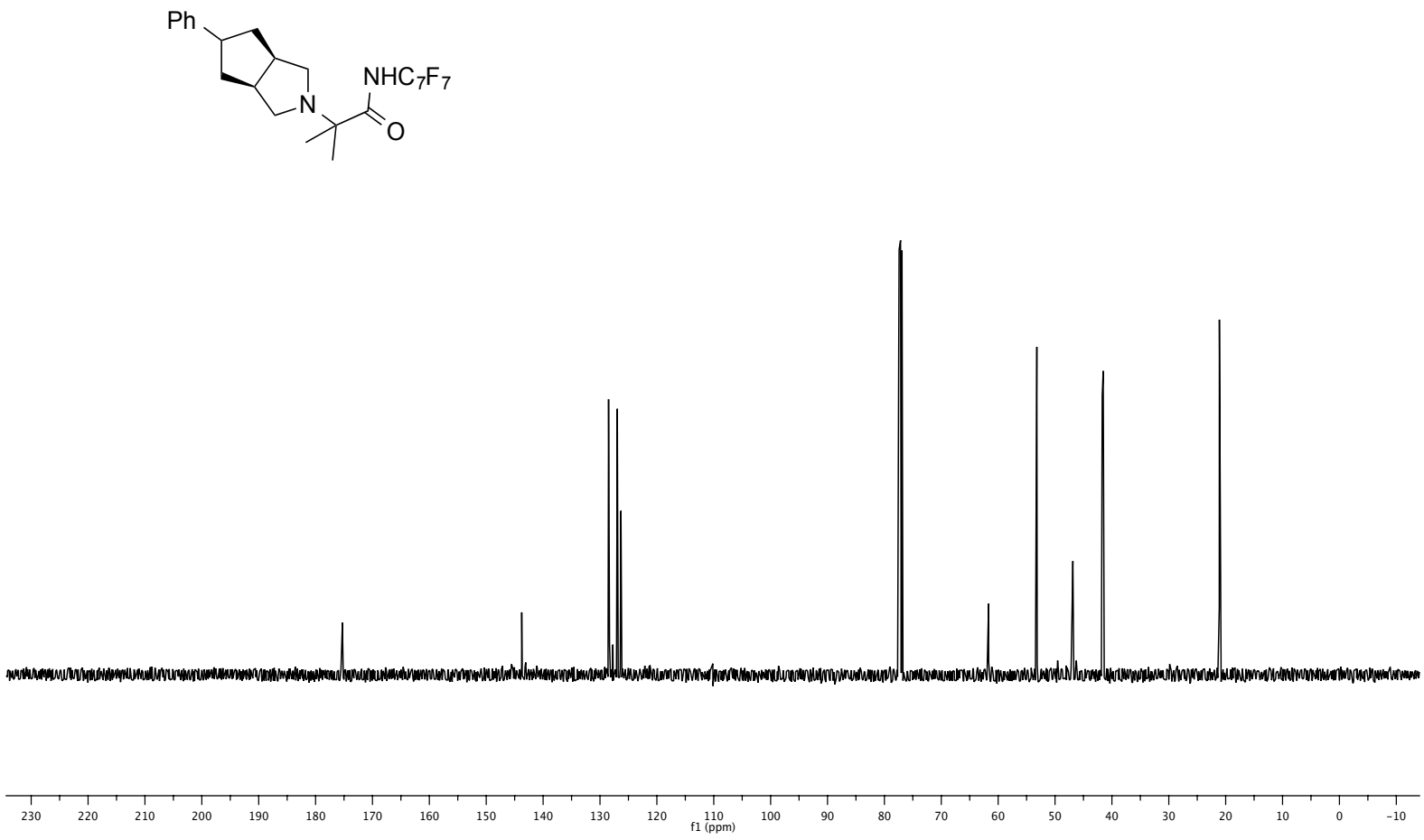
^{13}C NMR Spectrum of **11h** in $CDCl_3$



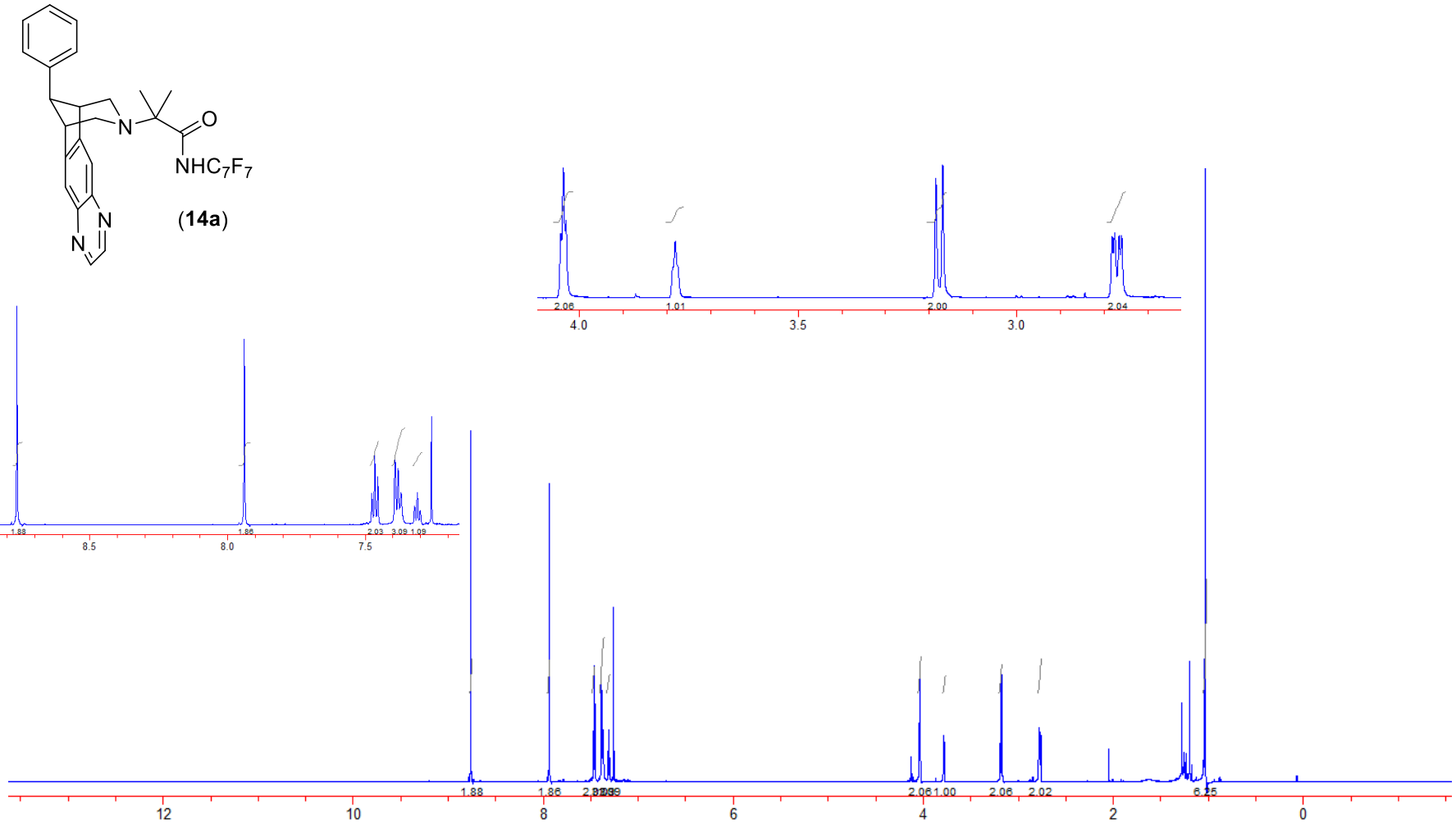
^{1}H NMR Spectrum of **11i** in $CDCl_3$



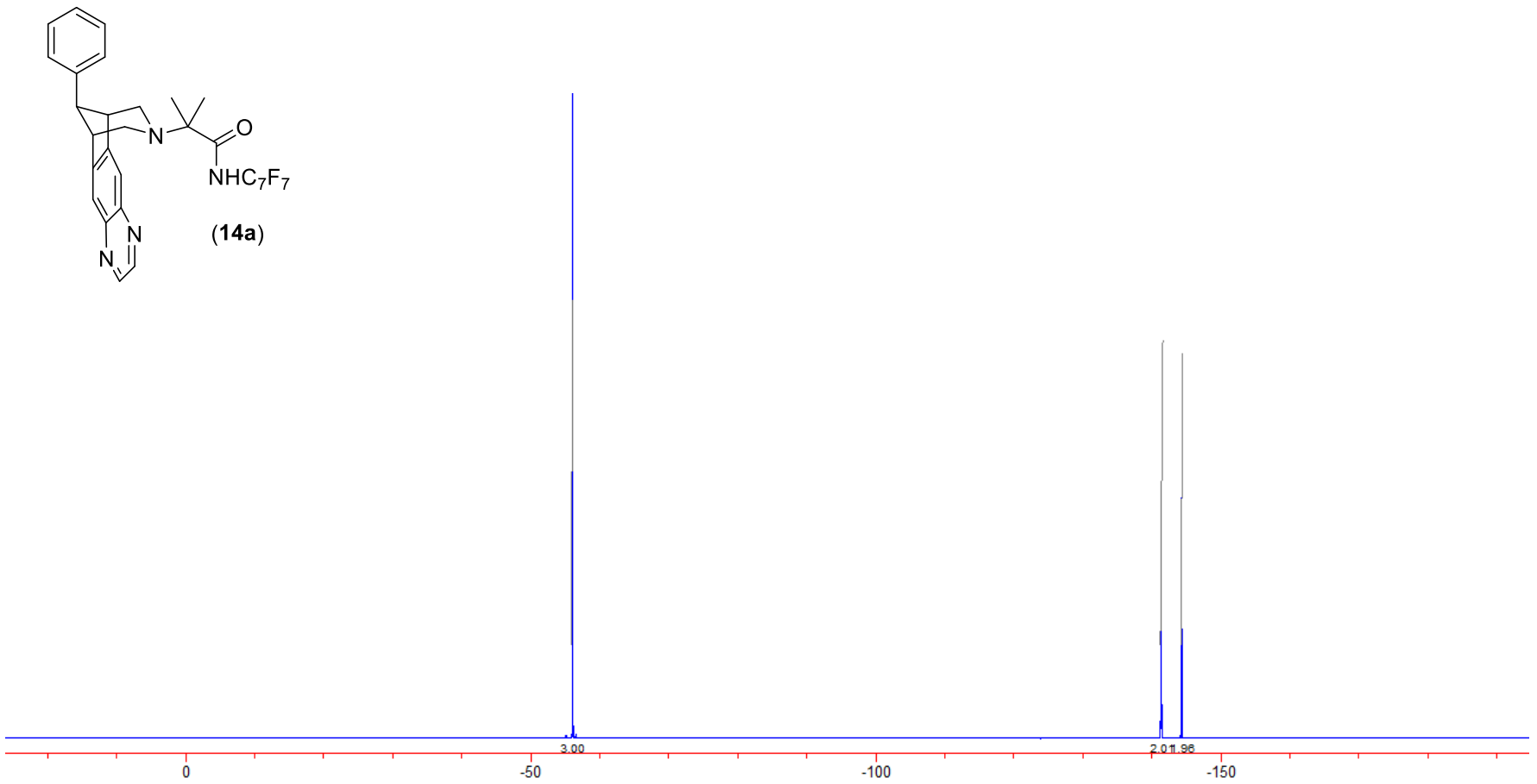
^{19}F NMR Spectrum of **11i** in $CDCl_3$



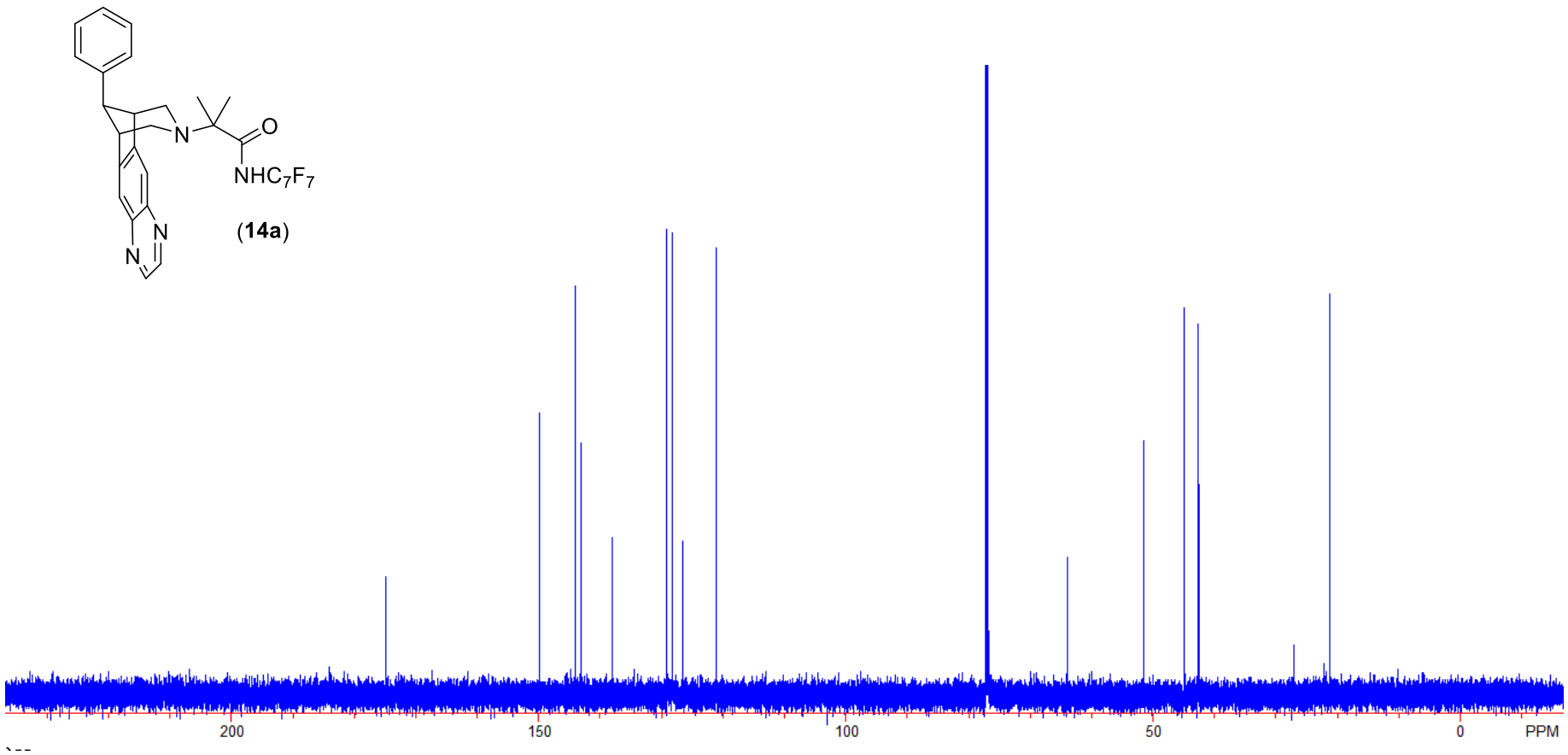
^{13}C NMR Spectrum of **11i** in $CDCl_3$



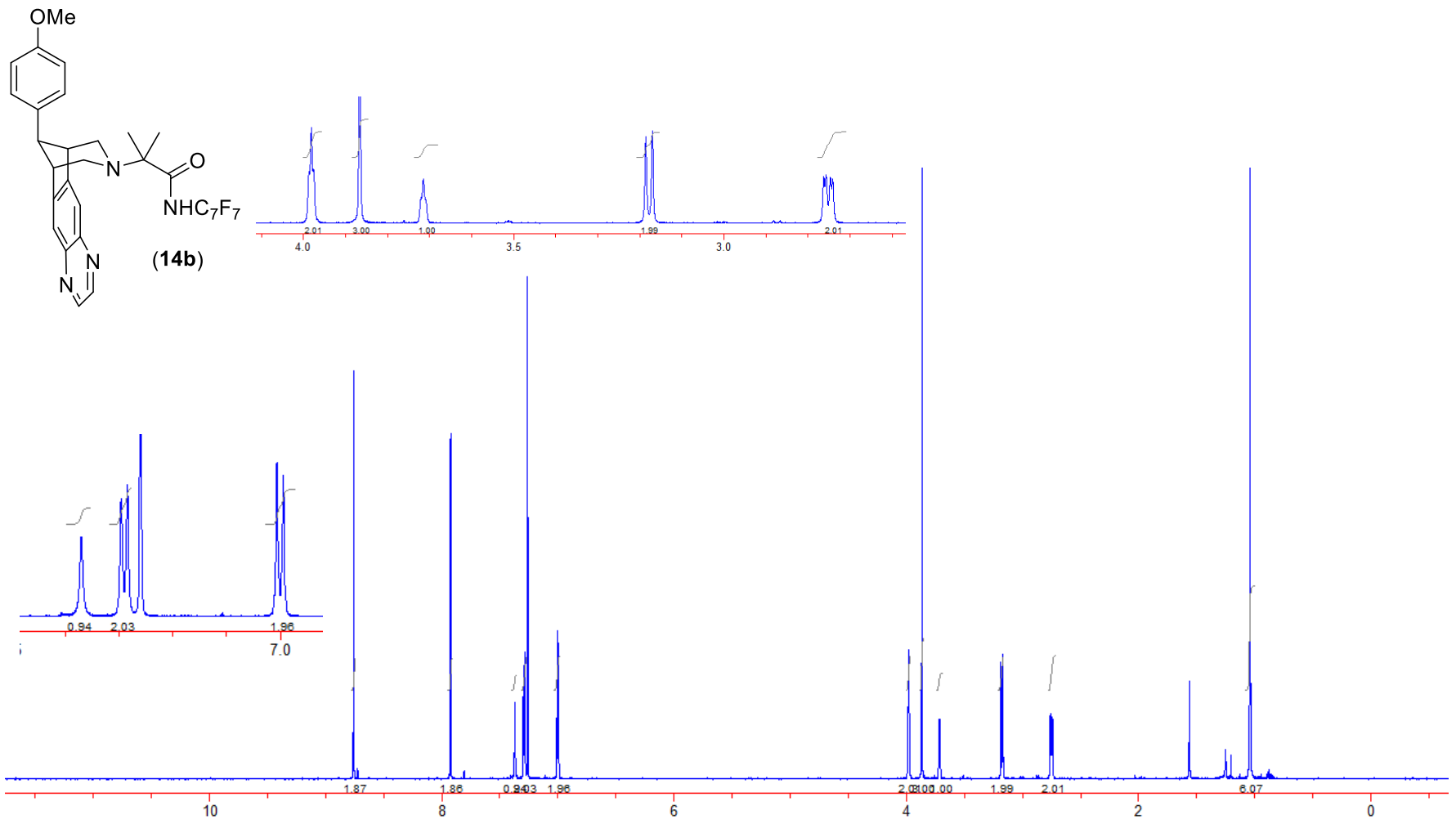
^{1}H NMR Spectrum in $CDCl_3$



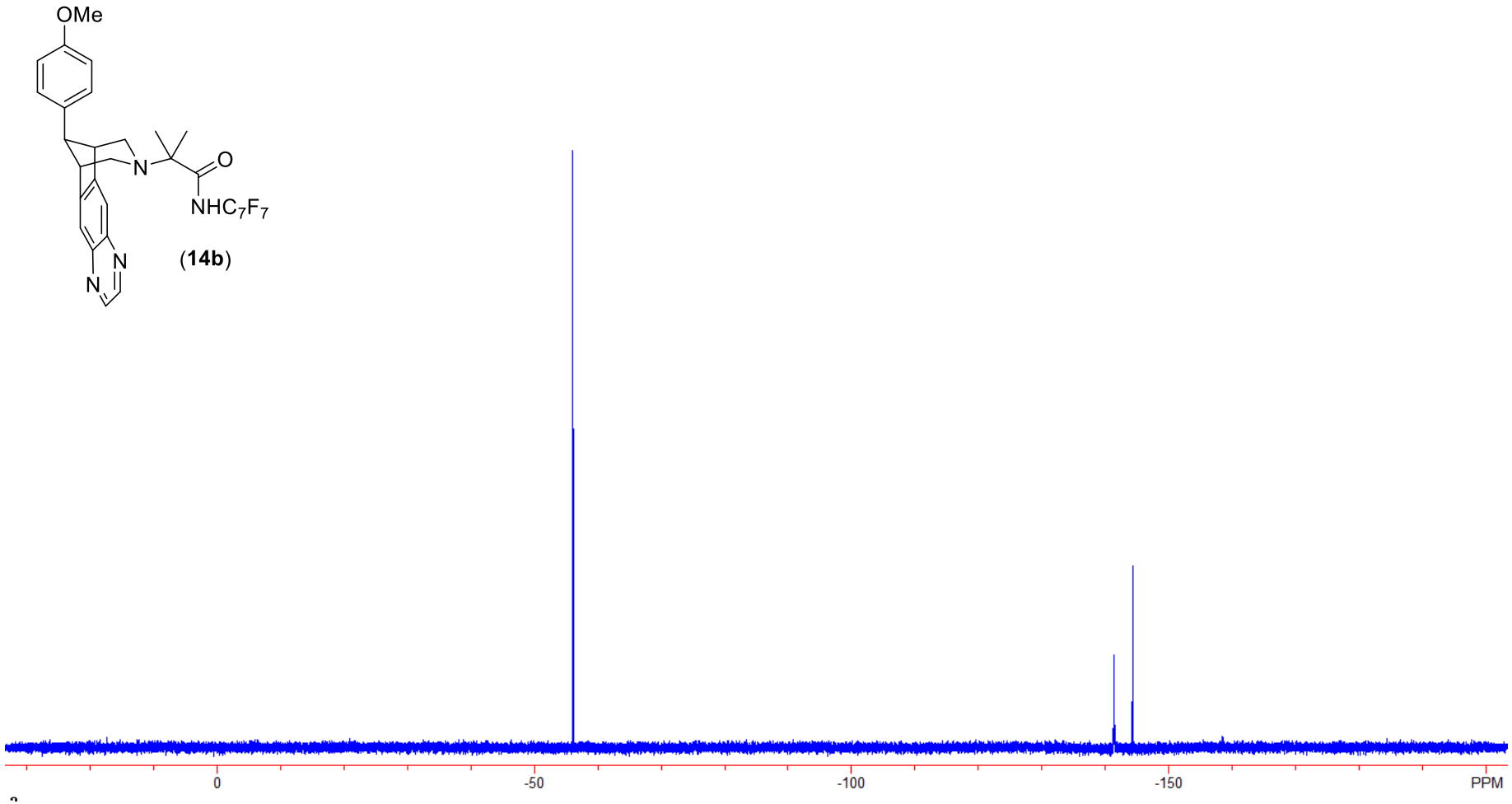
^{19}F NMR Spectrum in $CDCl_3$



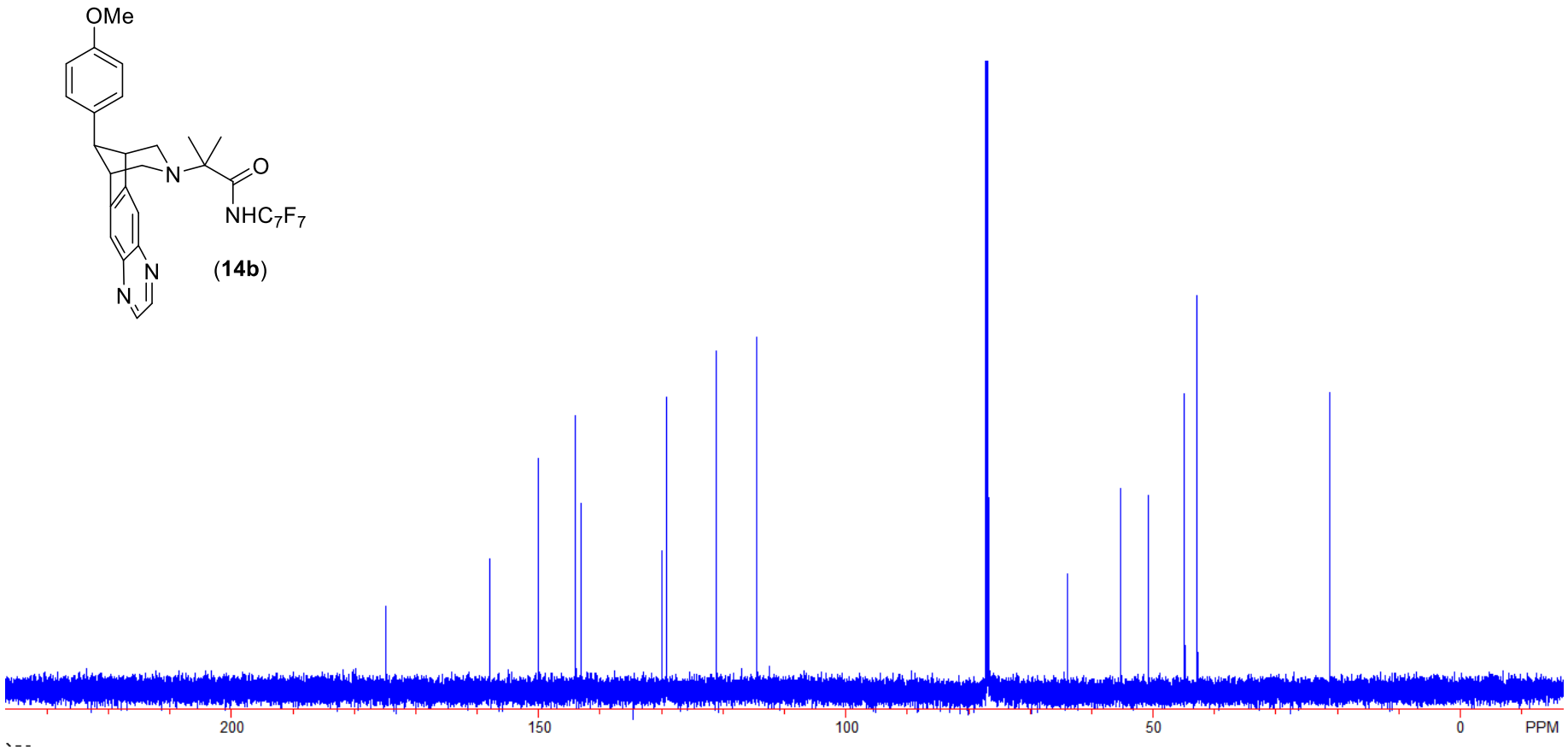
^{13}C NMR Spectrum in $CDCl_3$



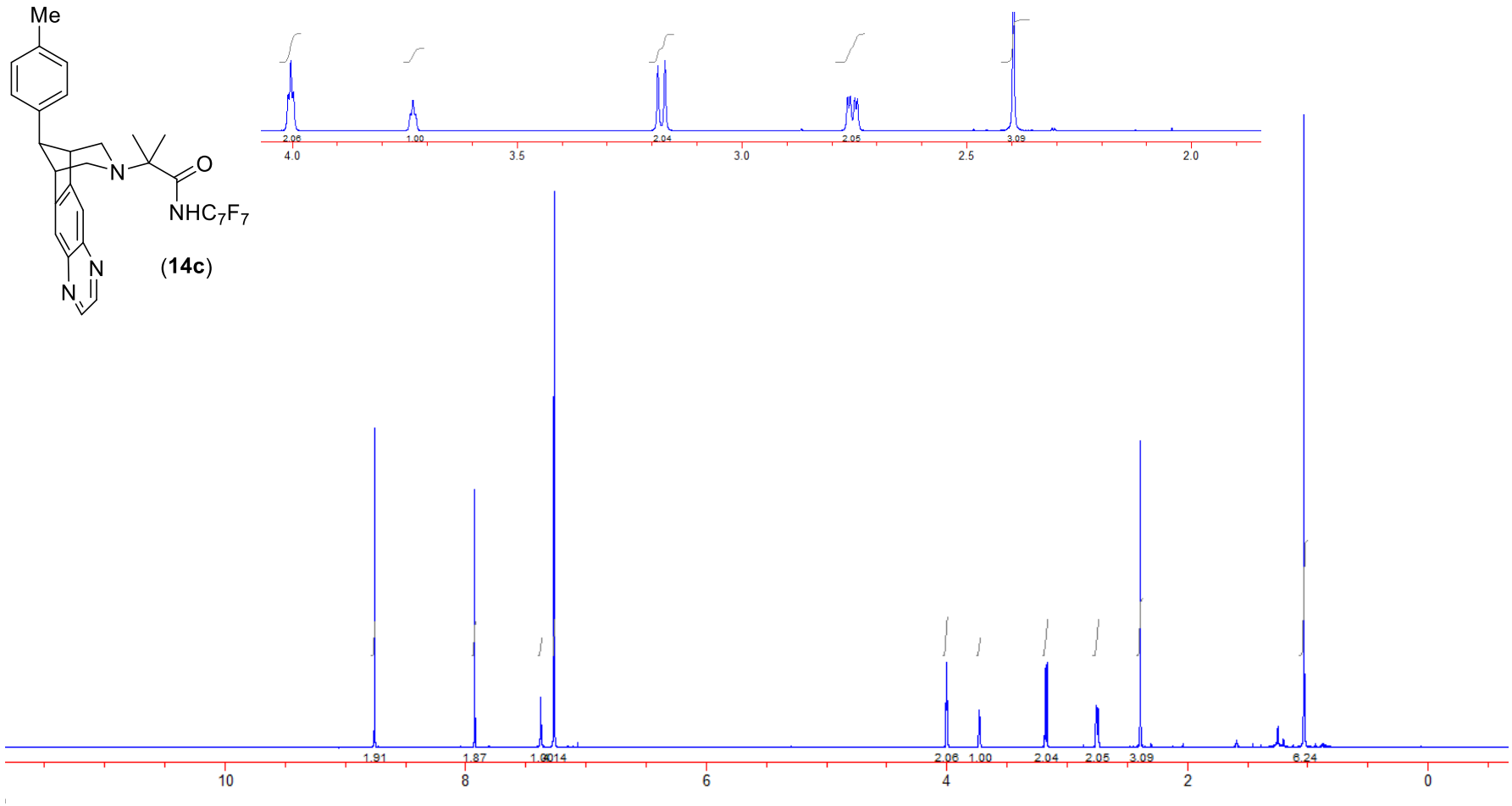
^{1}H NMR Spectrum in $CDCl_3$



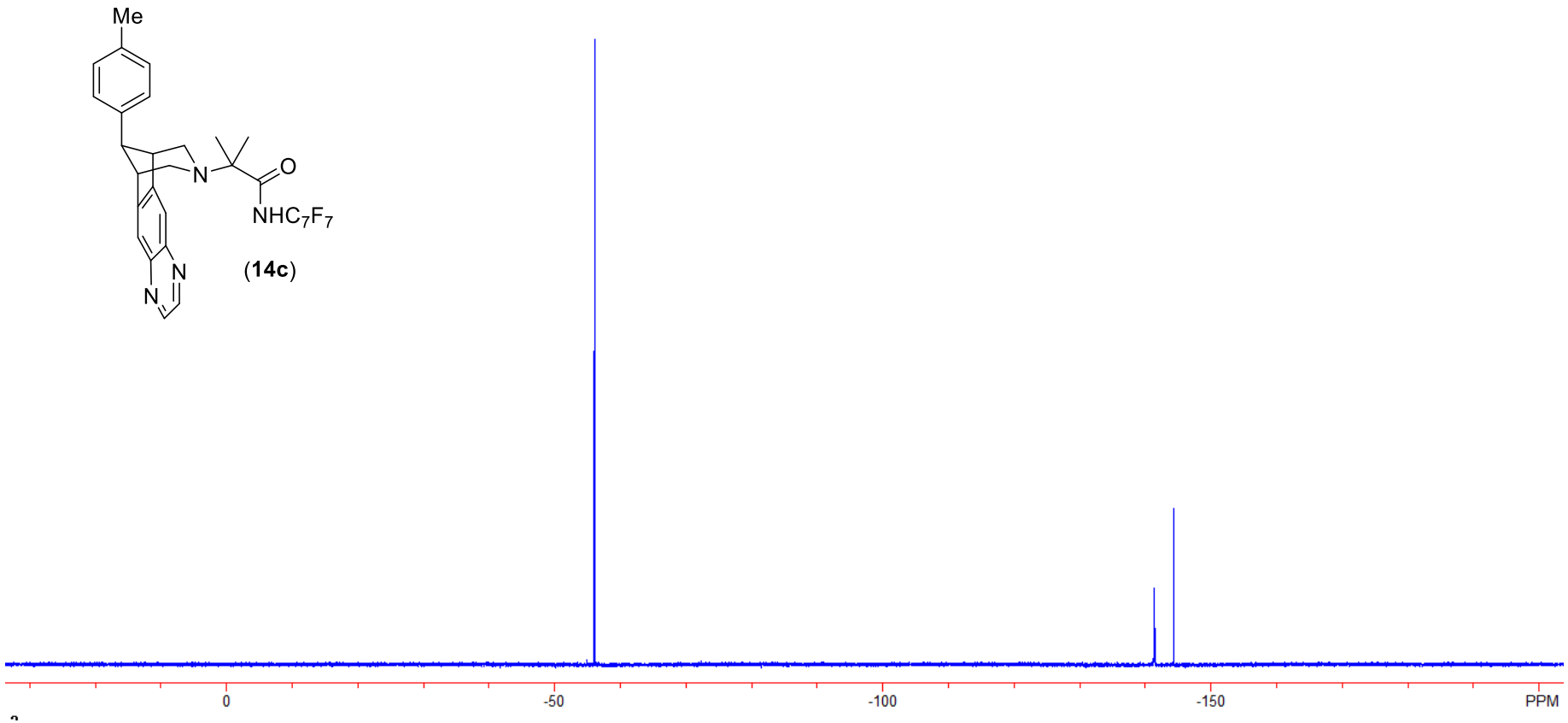
^{19}F NMR Spectrum in $CDCl_3$



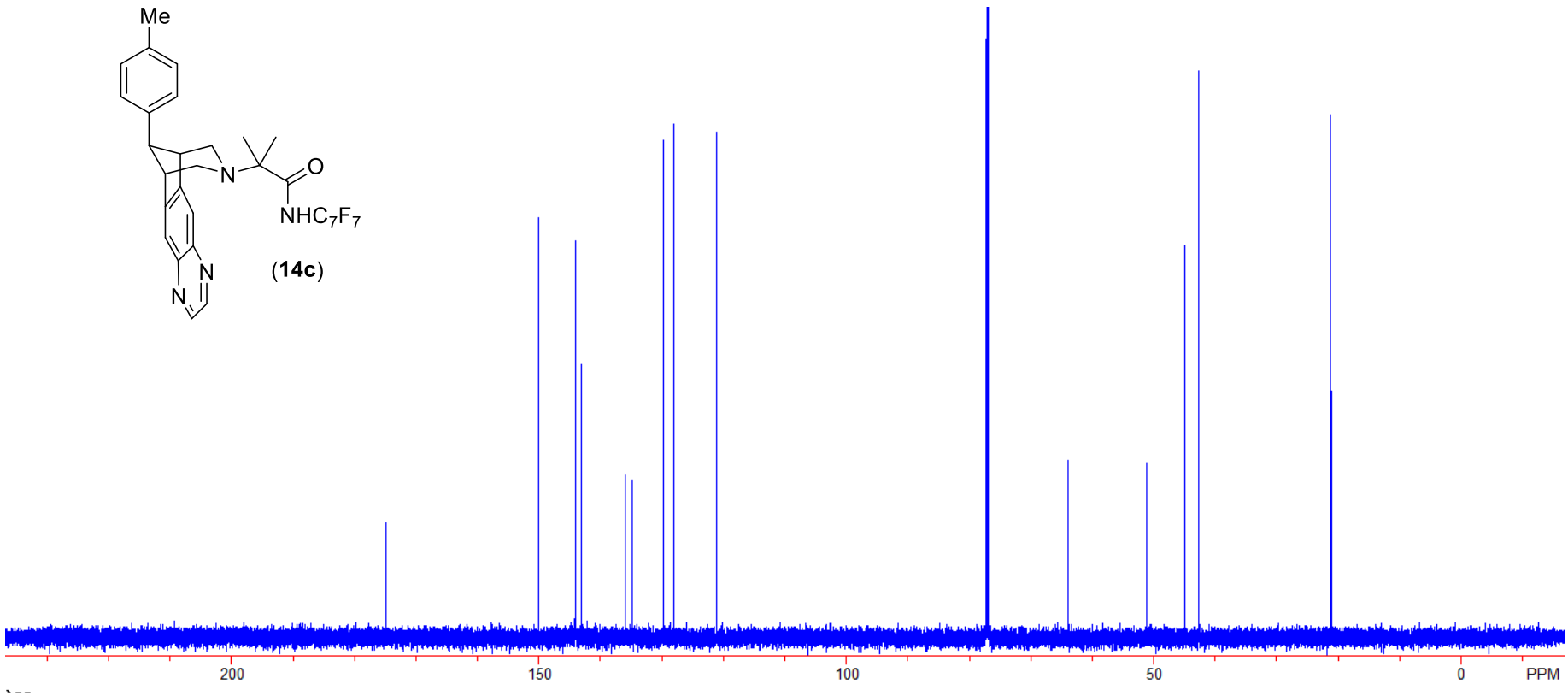
^{13}C NMR Spectrum in $CDCl_3$



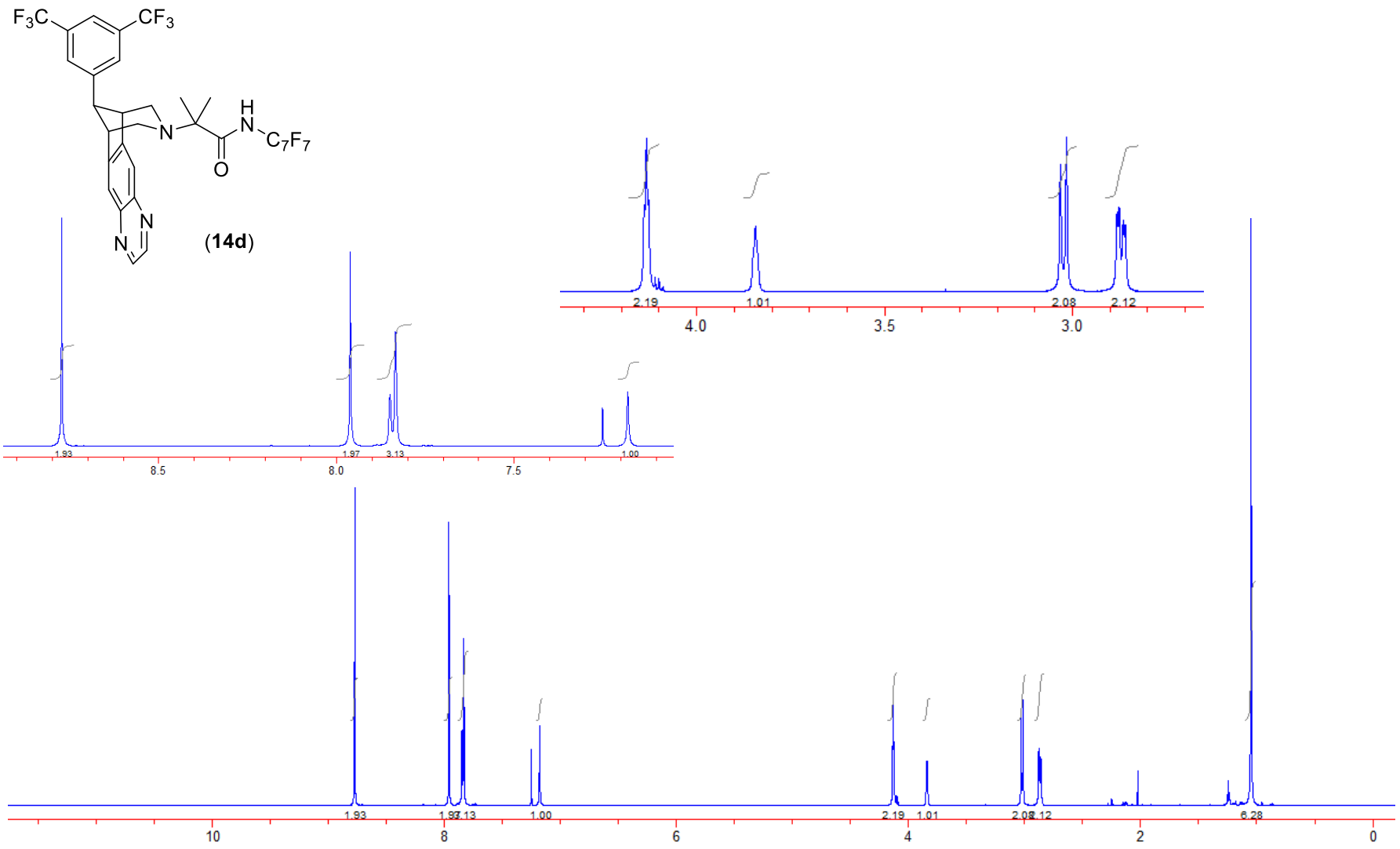
^{1}H NMR Spectrum in $CDCl_3$



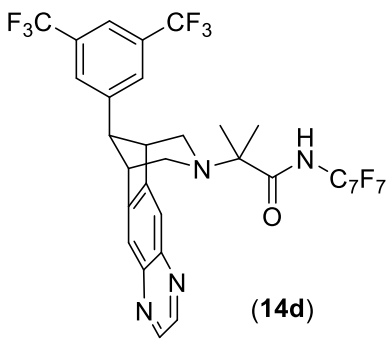
^{19}F NMR Spectrum in $CDCl_3$



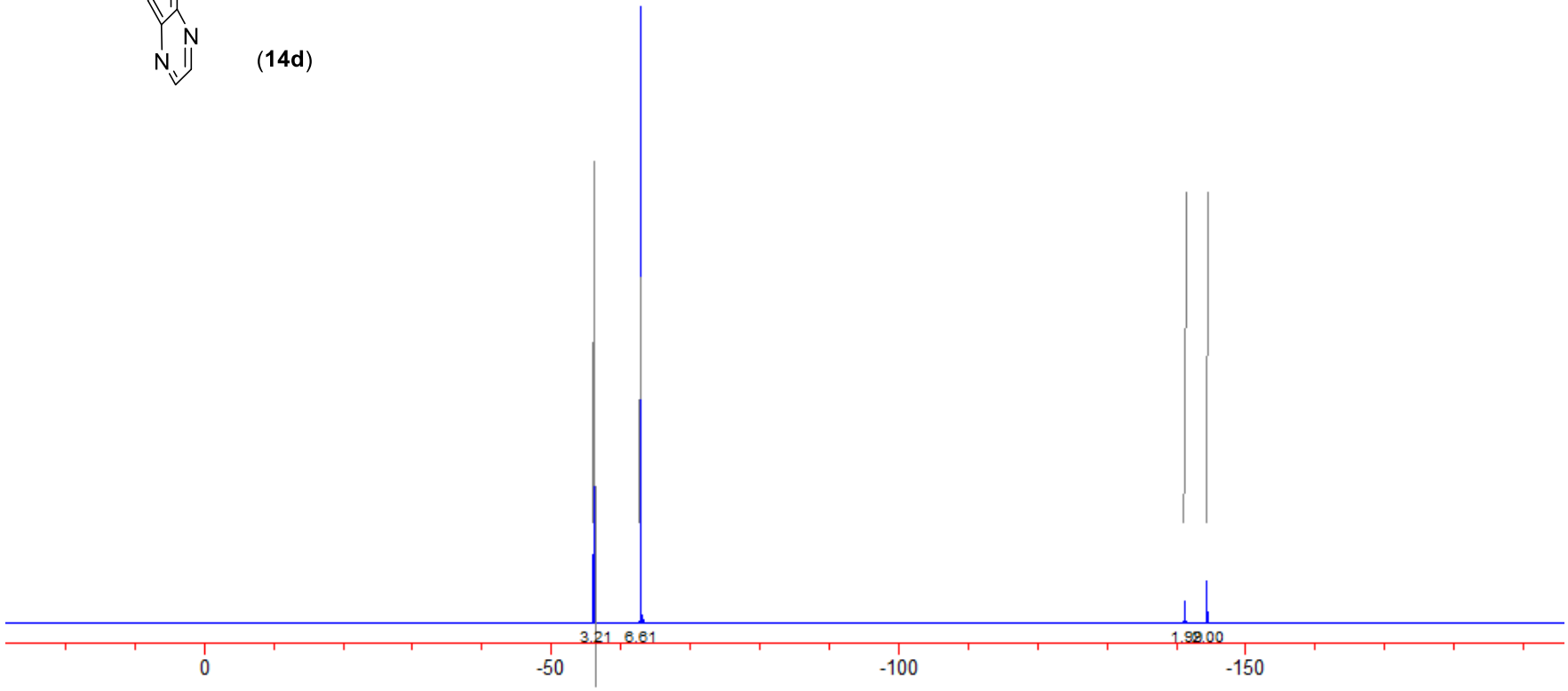
^{13}C NMR Spectrum in $CDCl_3$



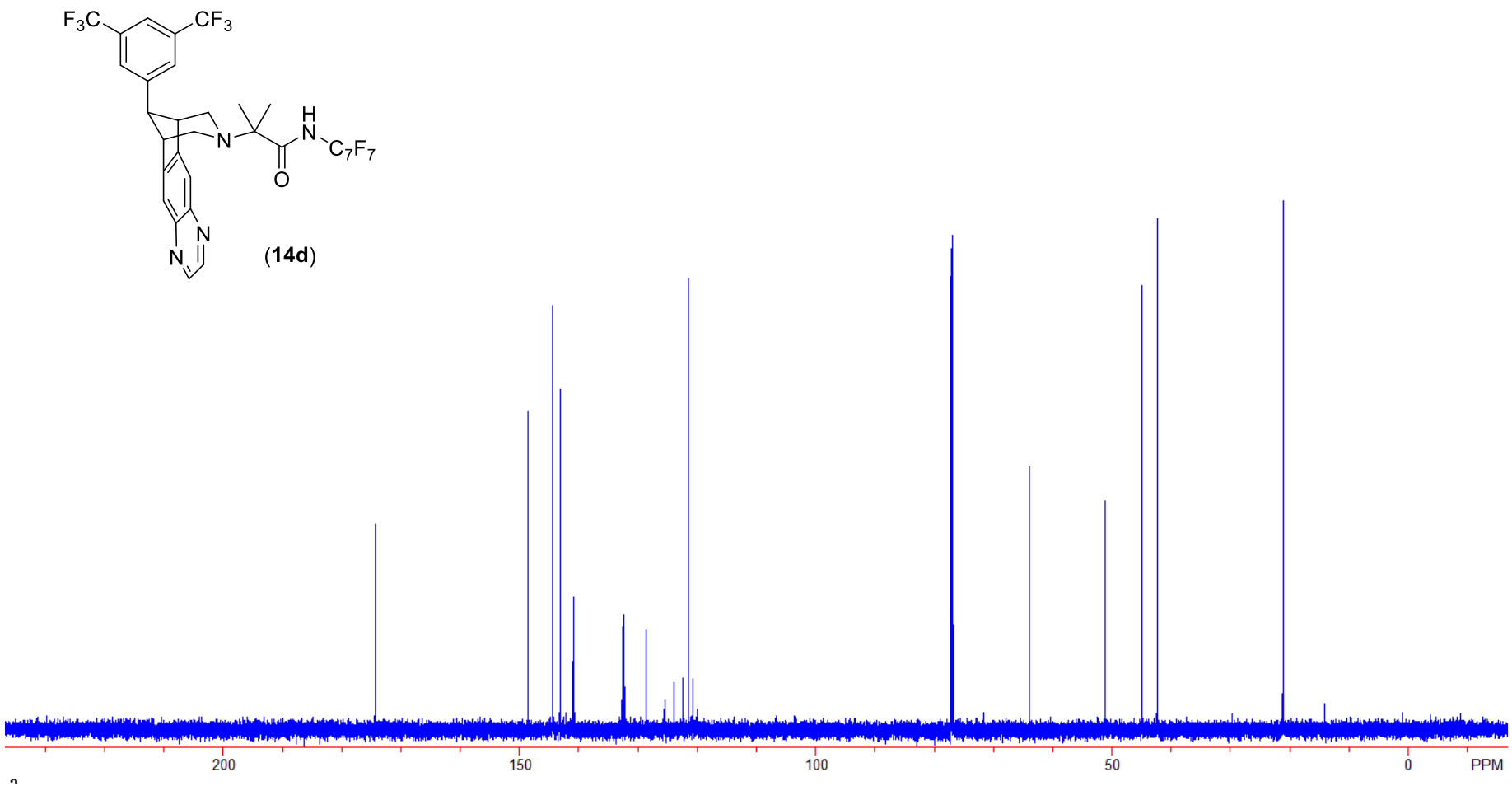
^{1}H NMR Spectrum in $CDCl_3$



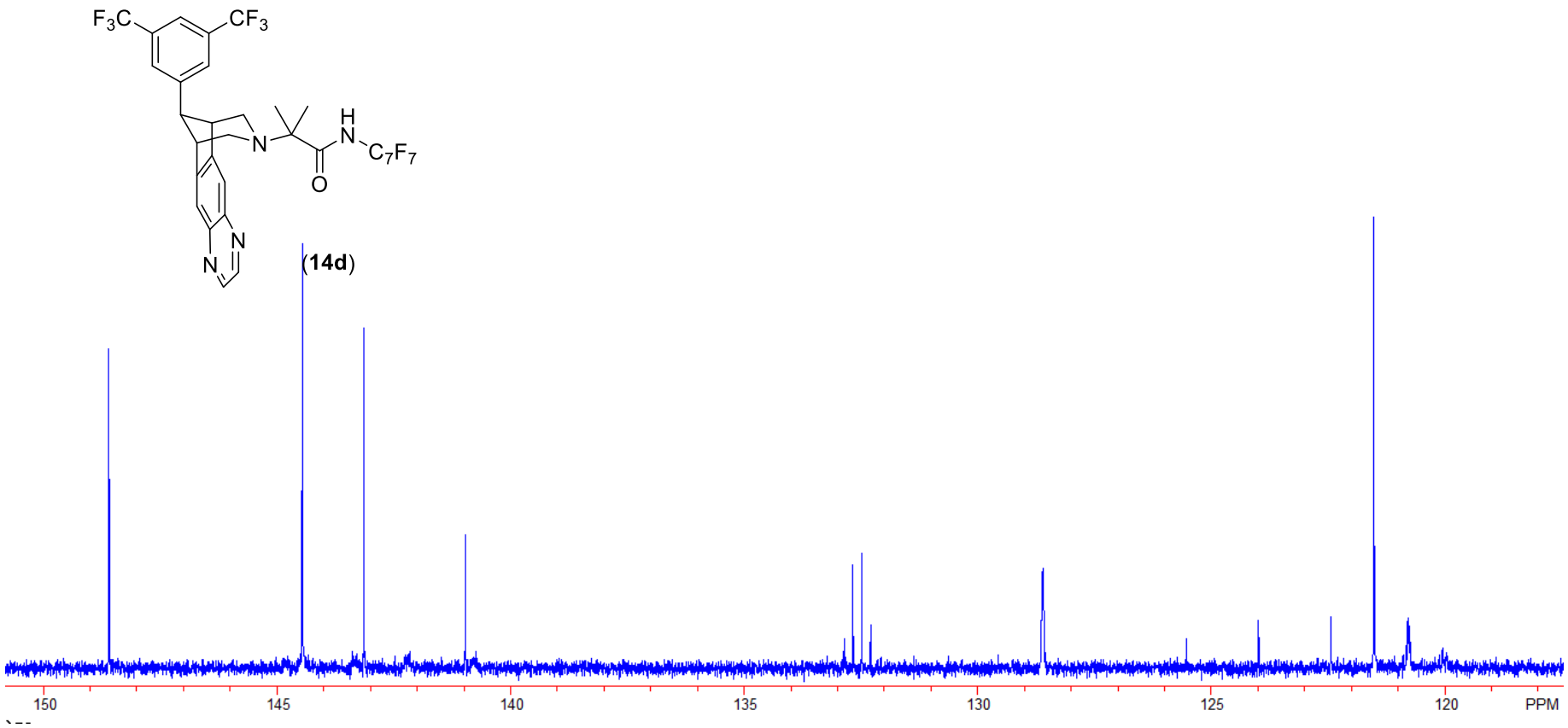
(**14d**)



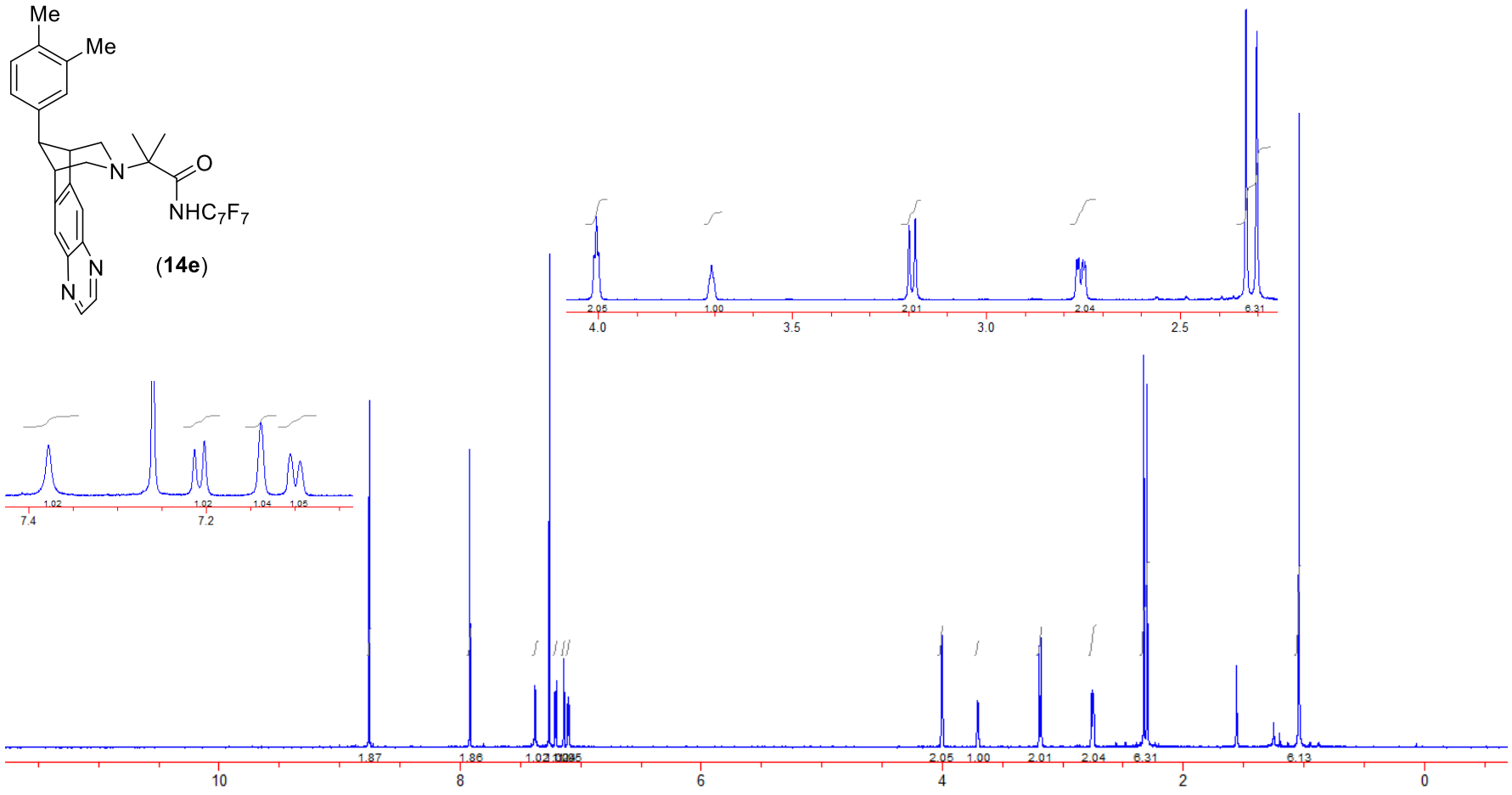
^{19}F NMR Spectrum in $CDCl_3$



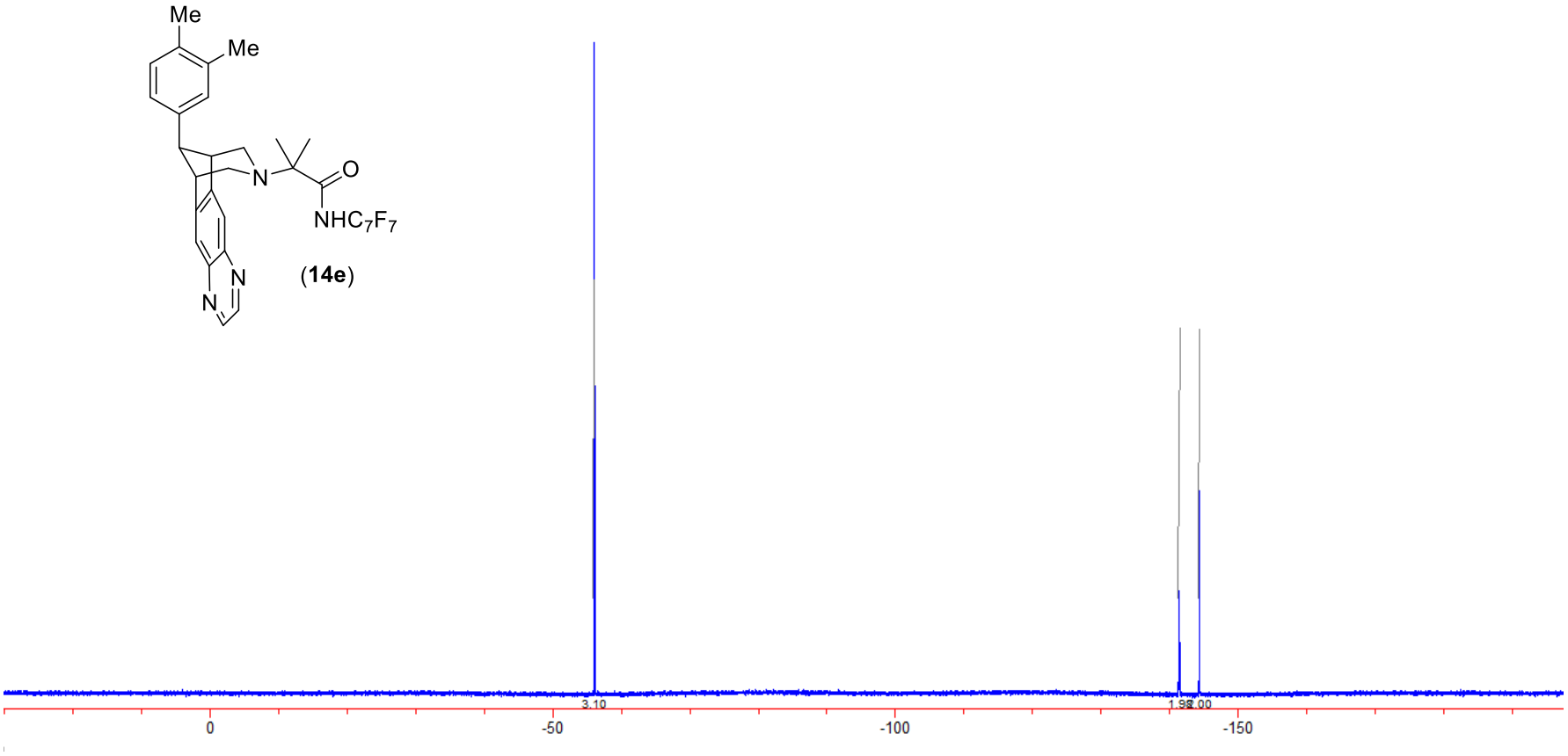
^{13}C NMR Spectrum in $CDCl_3$



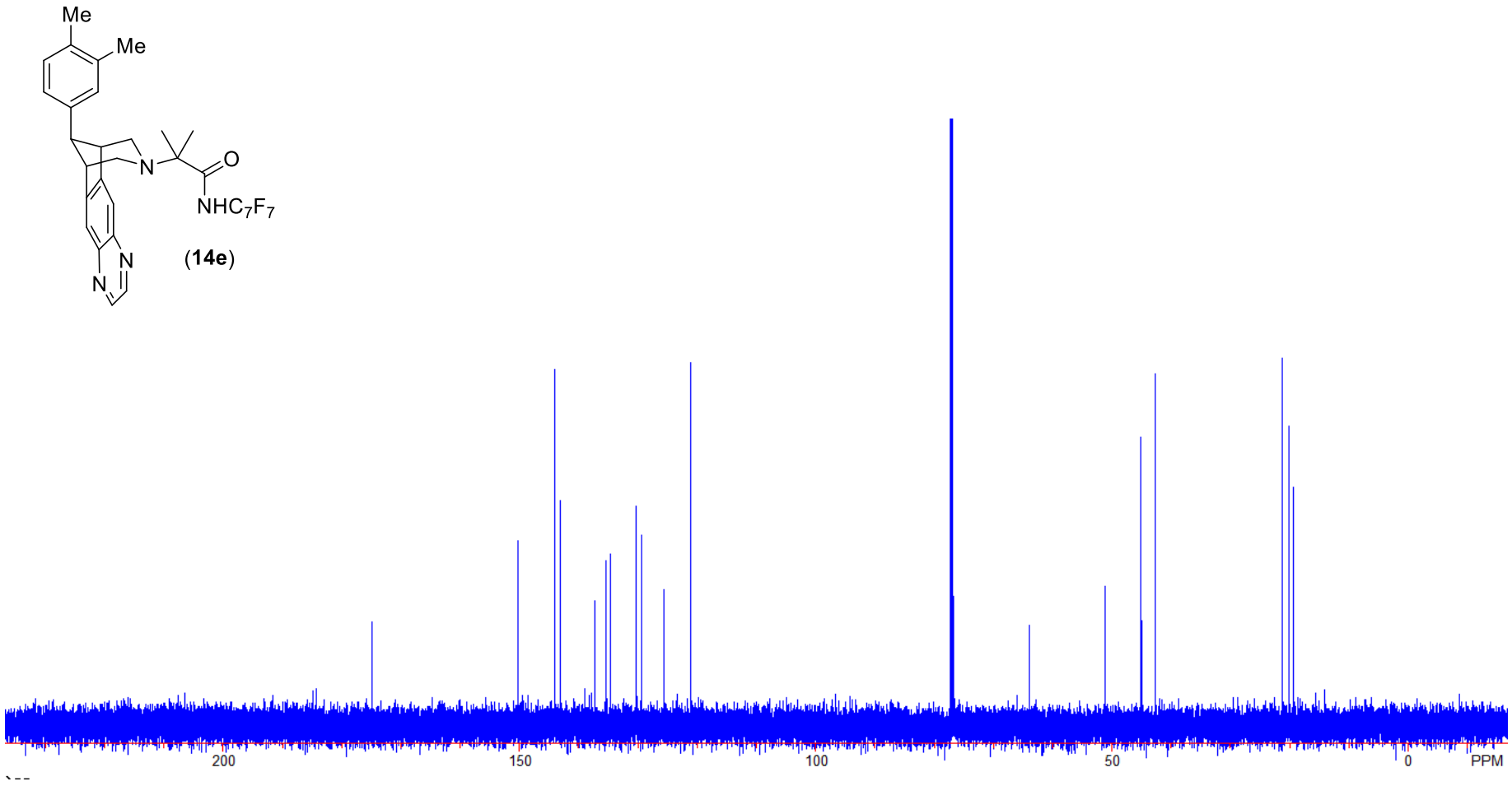
^{13}C NMR Spectrum in $CDCl_3$ (Expansion)



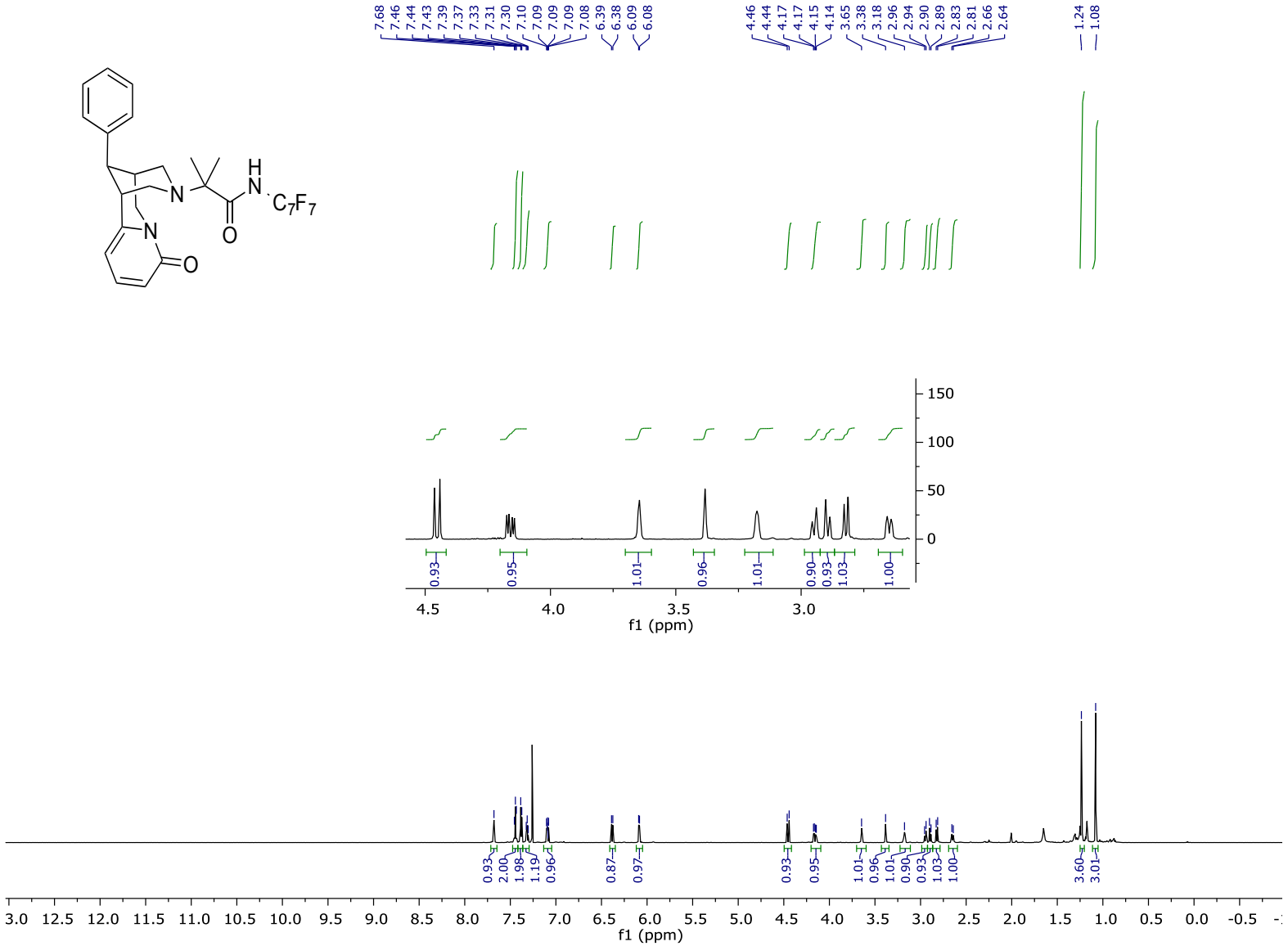
^{1}H NMR Spectrum in $CDCl_3$



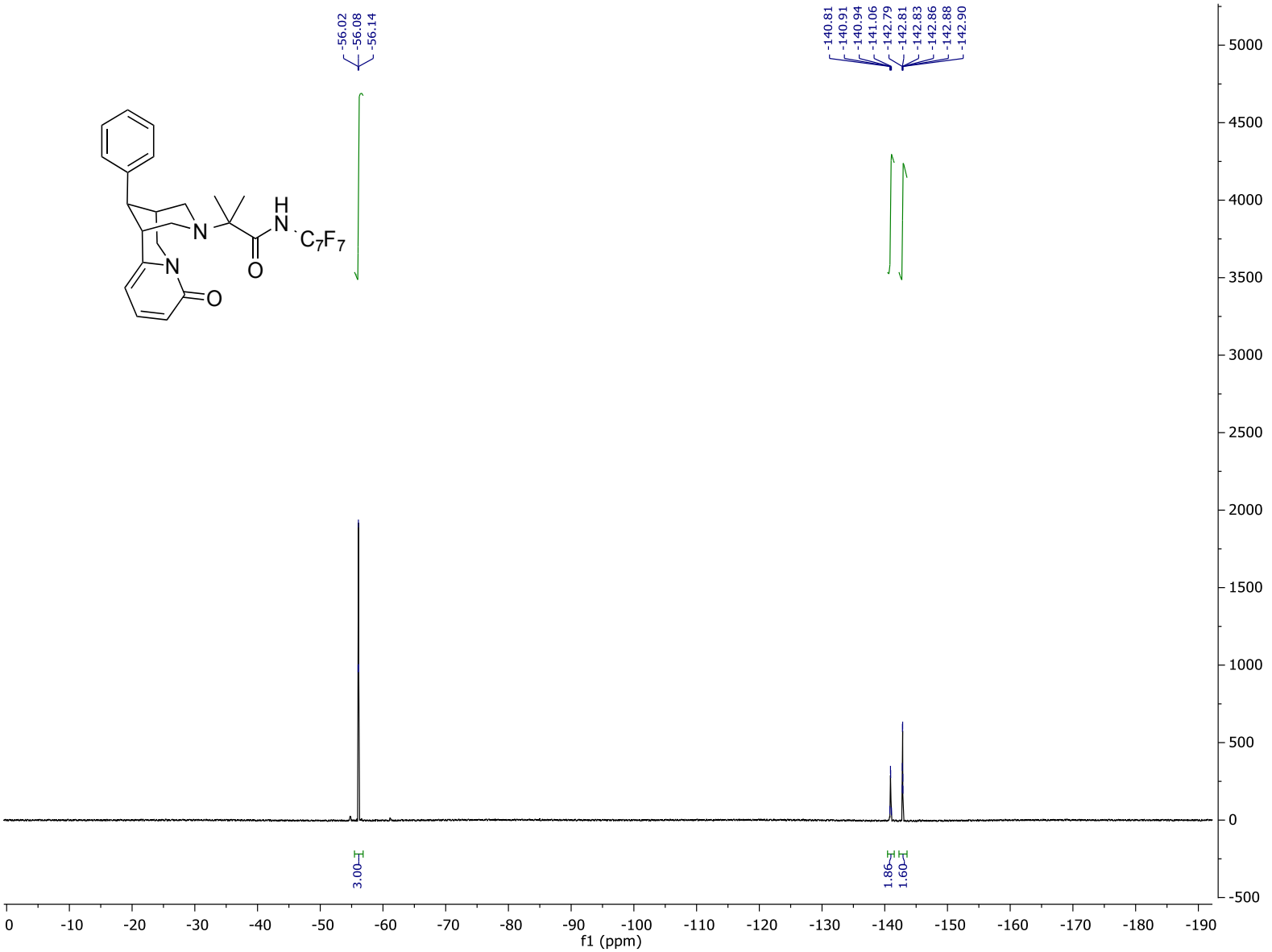
^{19}F NMR Spectrum in $CDCl_3$



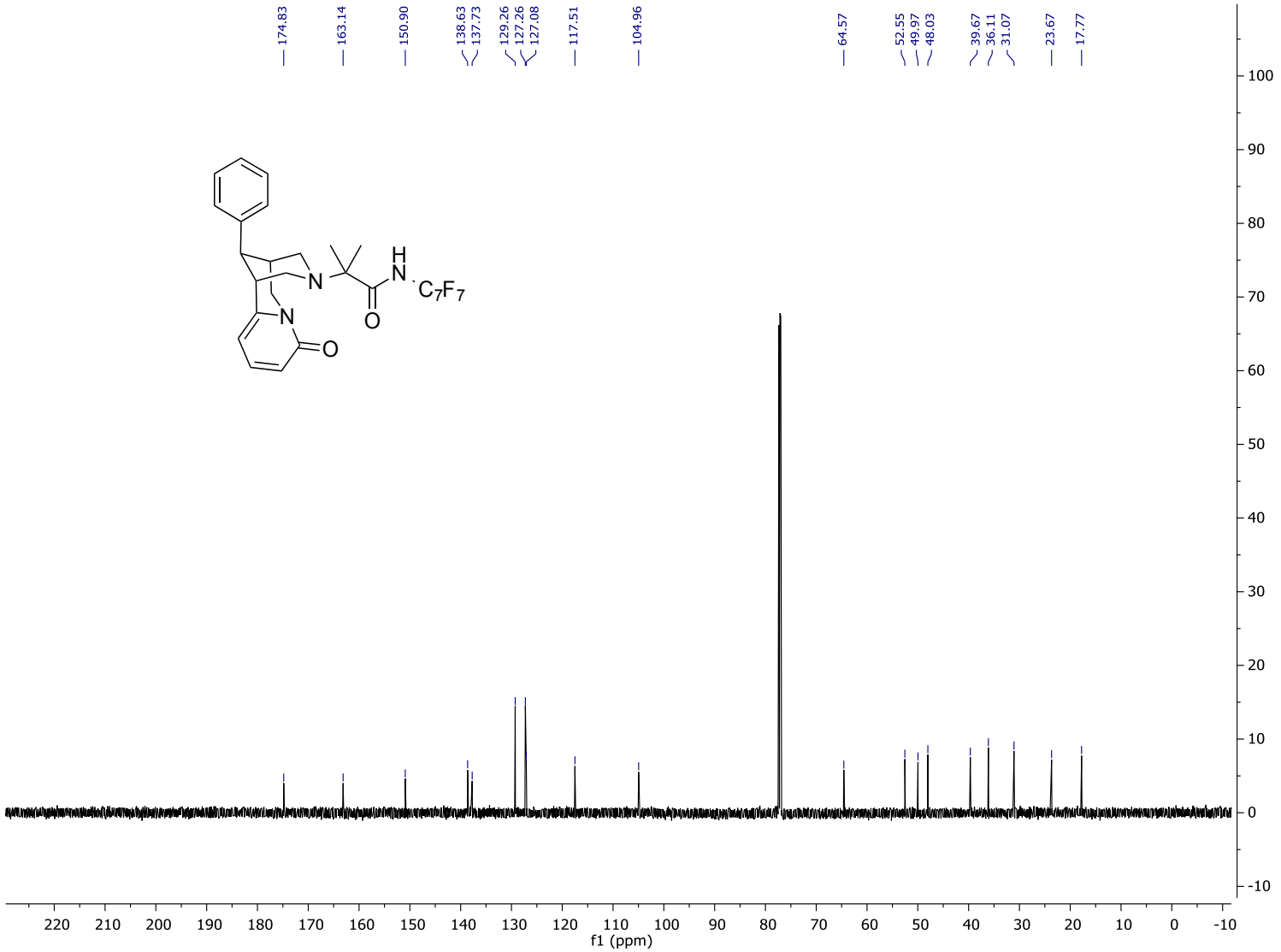
^{13}C NMR Spectrum in $CDCl_3$



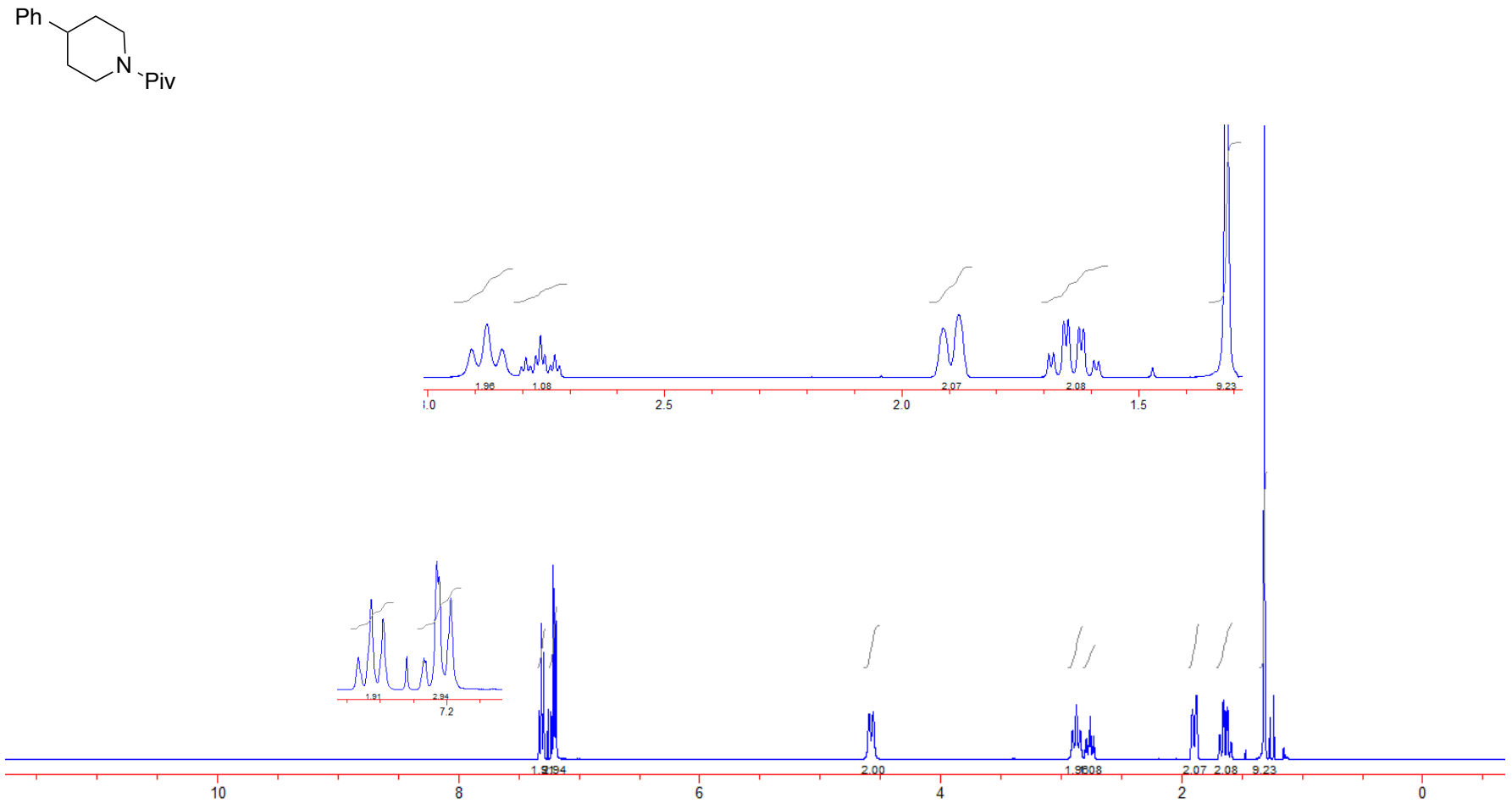
^{1}H NMR Spectrum of **17** in $CDCl_3$



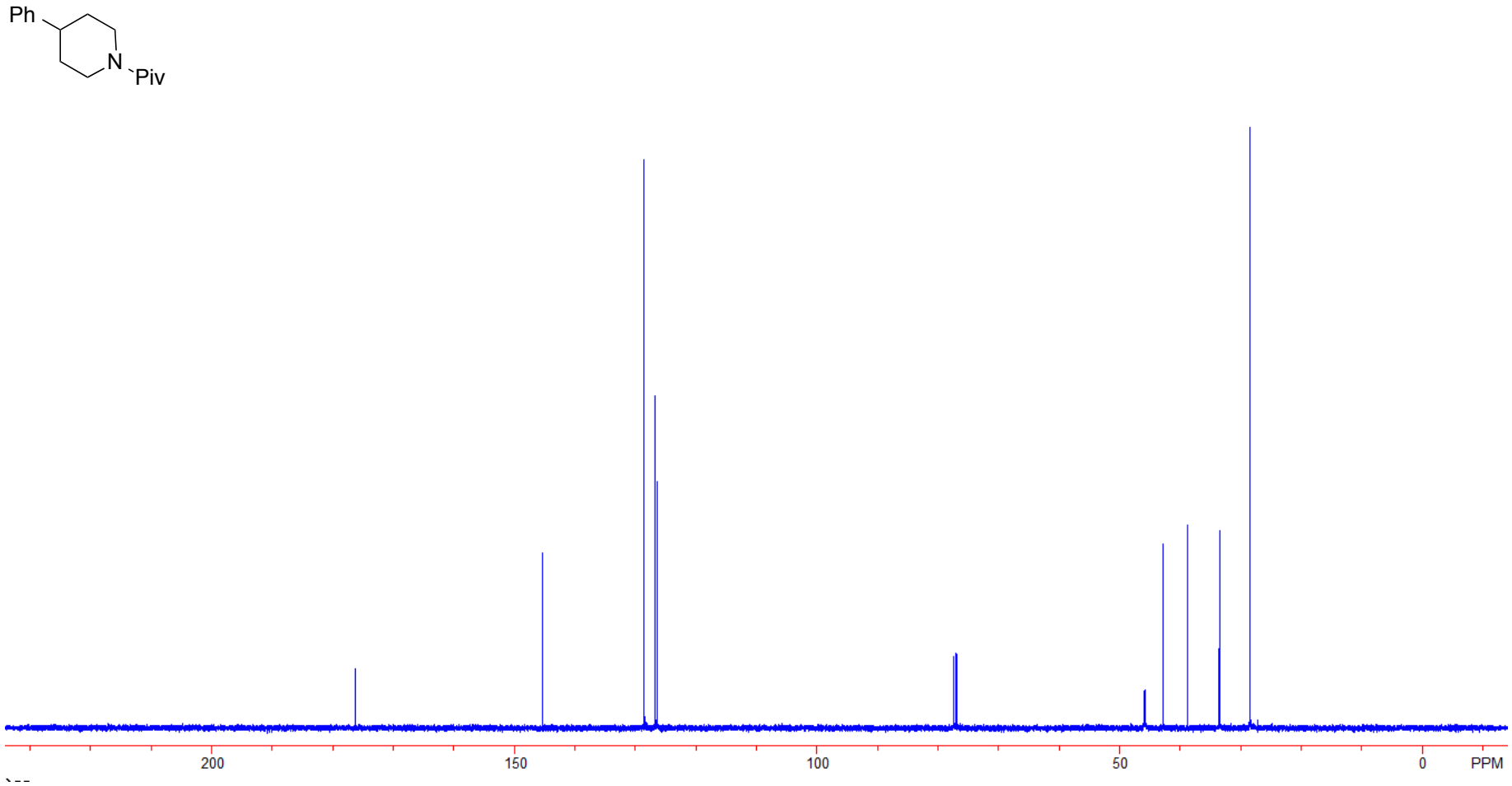
^{19}F NMR Spectrum of **17** in $CDCl_3$



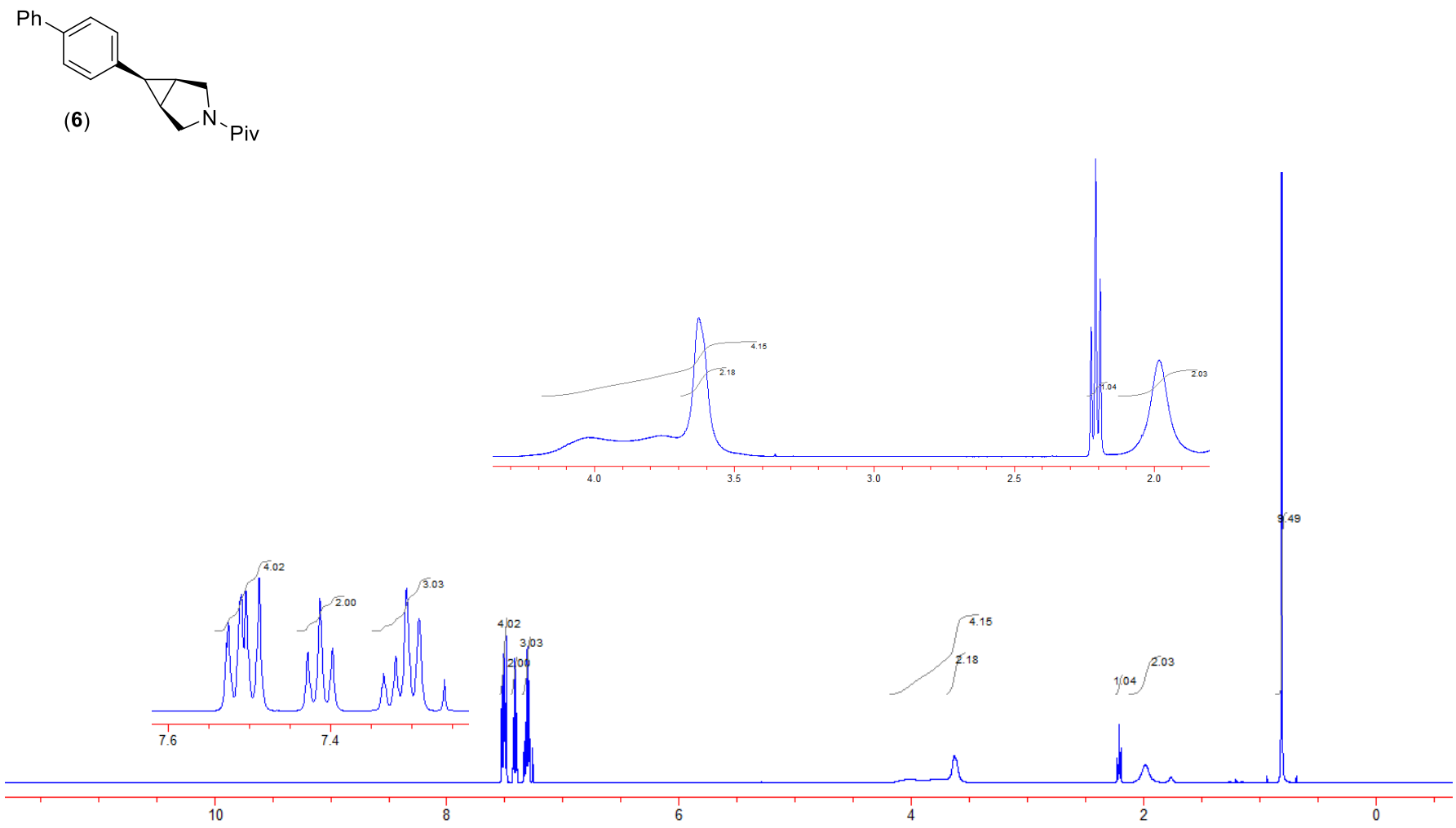
^{13}C NMR Spectrum of **17** in $CDCl_3$



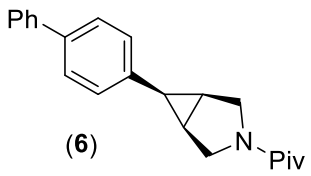
^{1}H NMR Spectrum of **S16** in $CDCl_3$



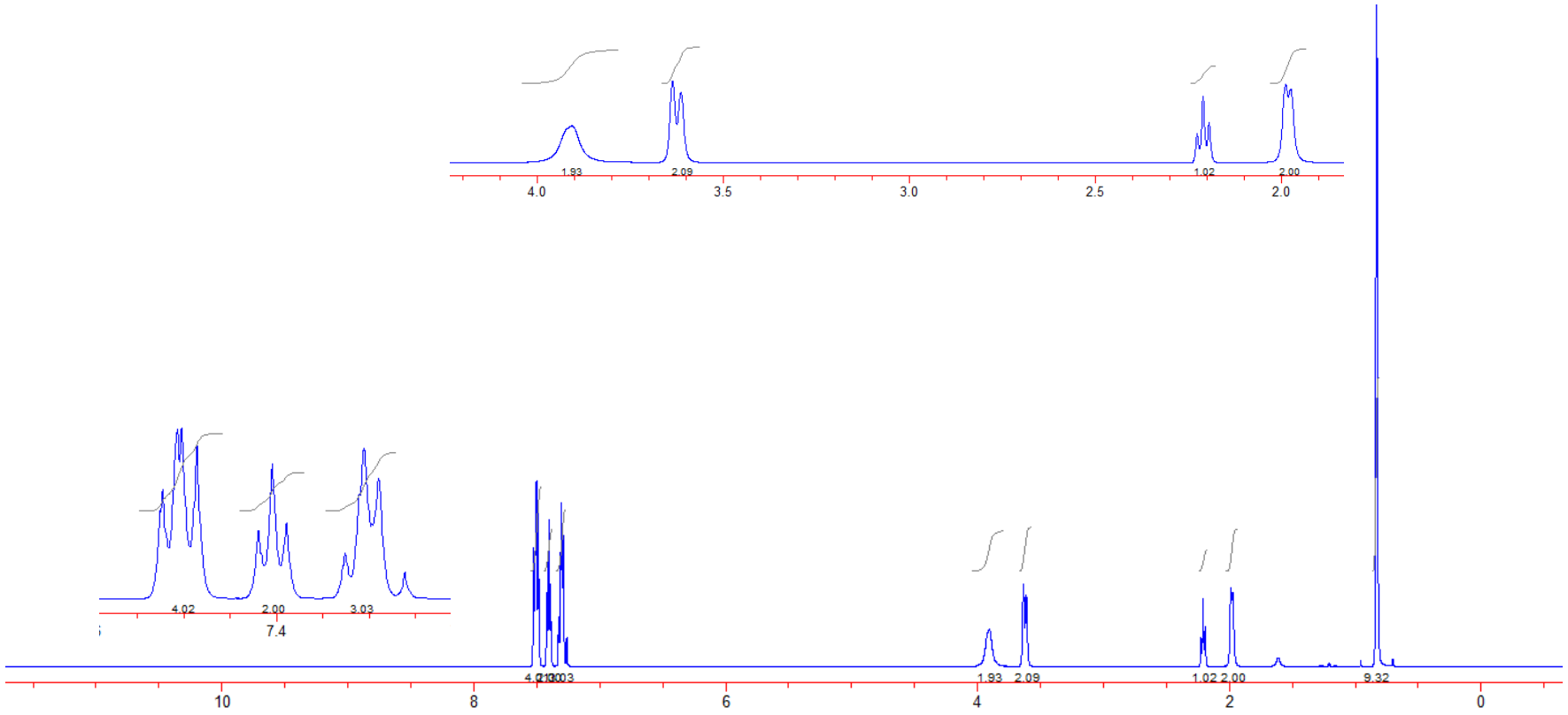
^{13}C NMR Spectrum of **S16** in $CDCl_3$



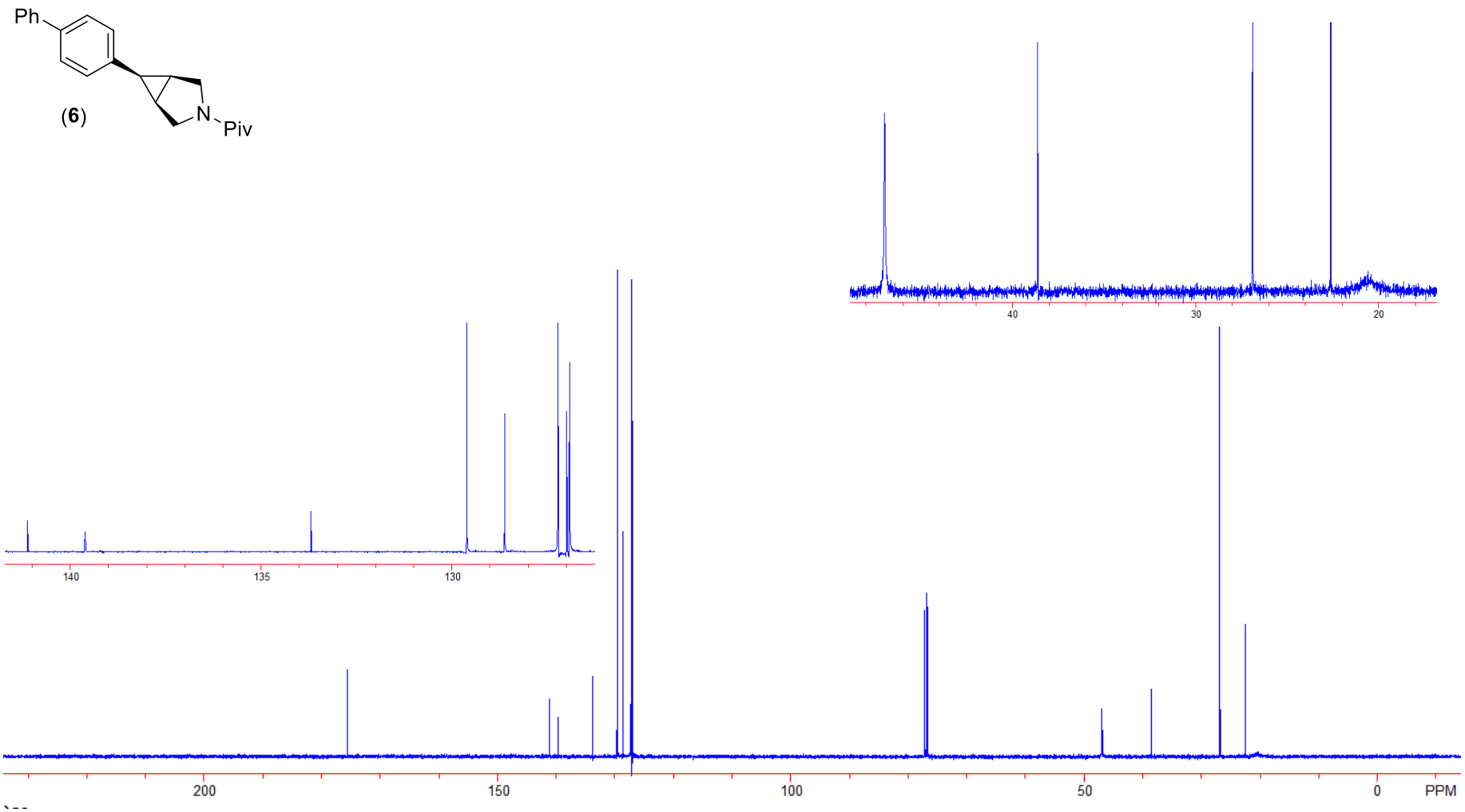
^{1}H NMR Spectrum in $CDCl_3$ at 25 °C



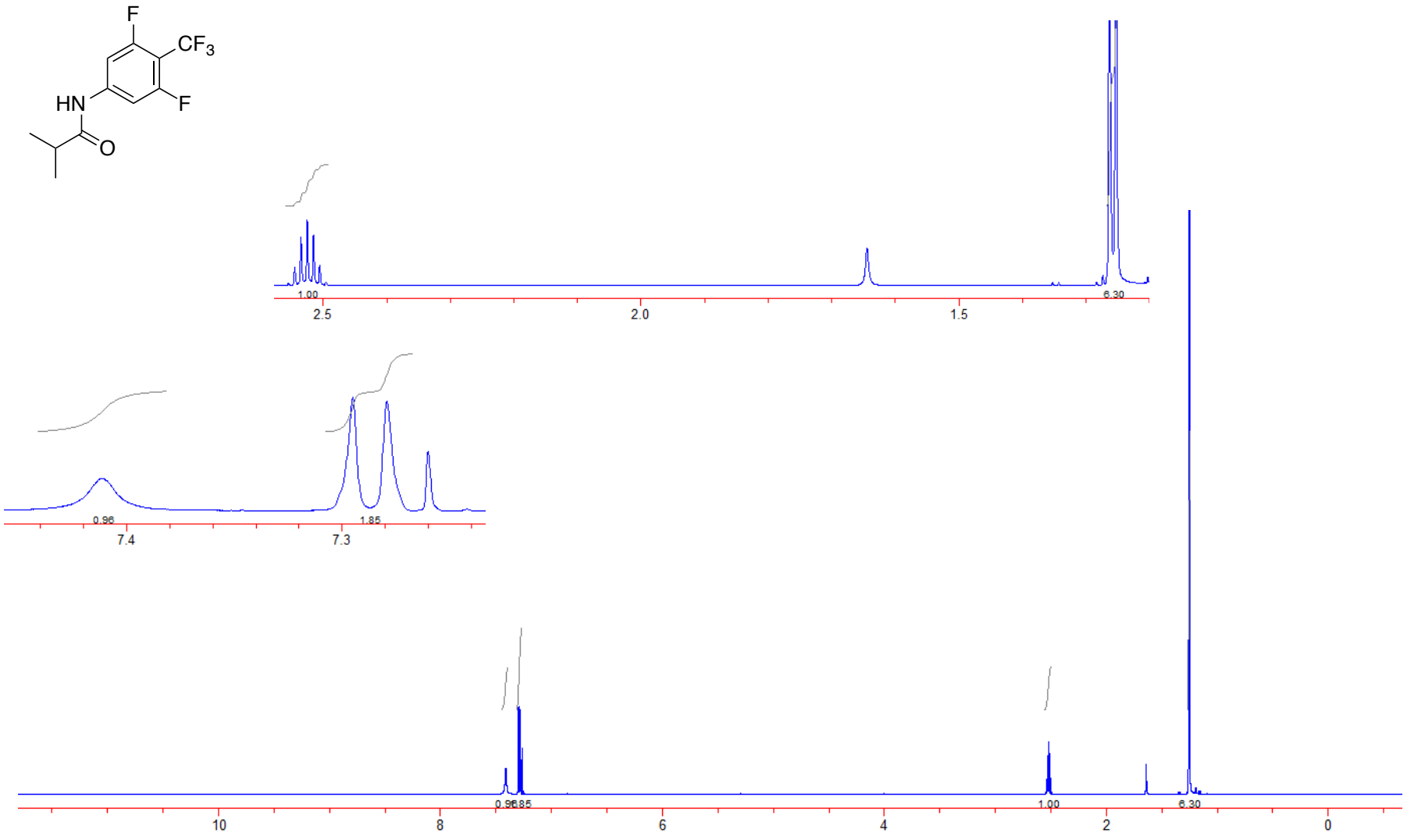
(**6**)



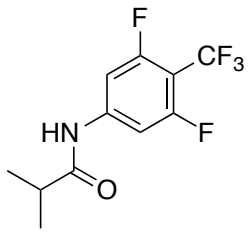
^{1}H NMR Spectrum in $CDCl_3$ at 52 °C

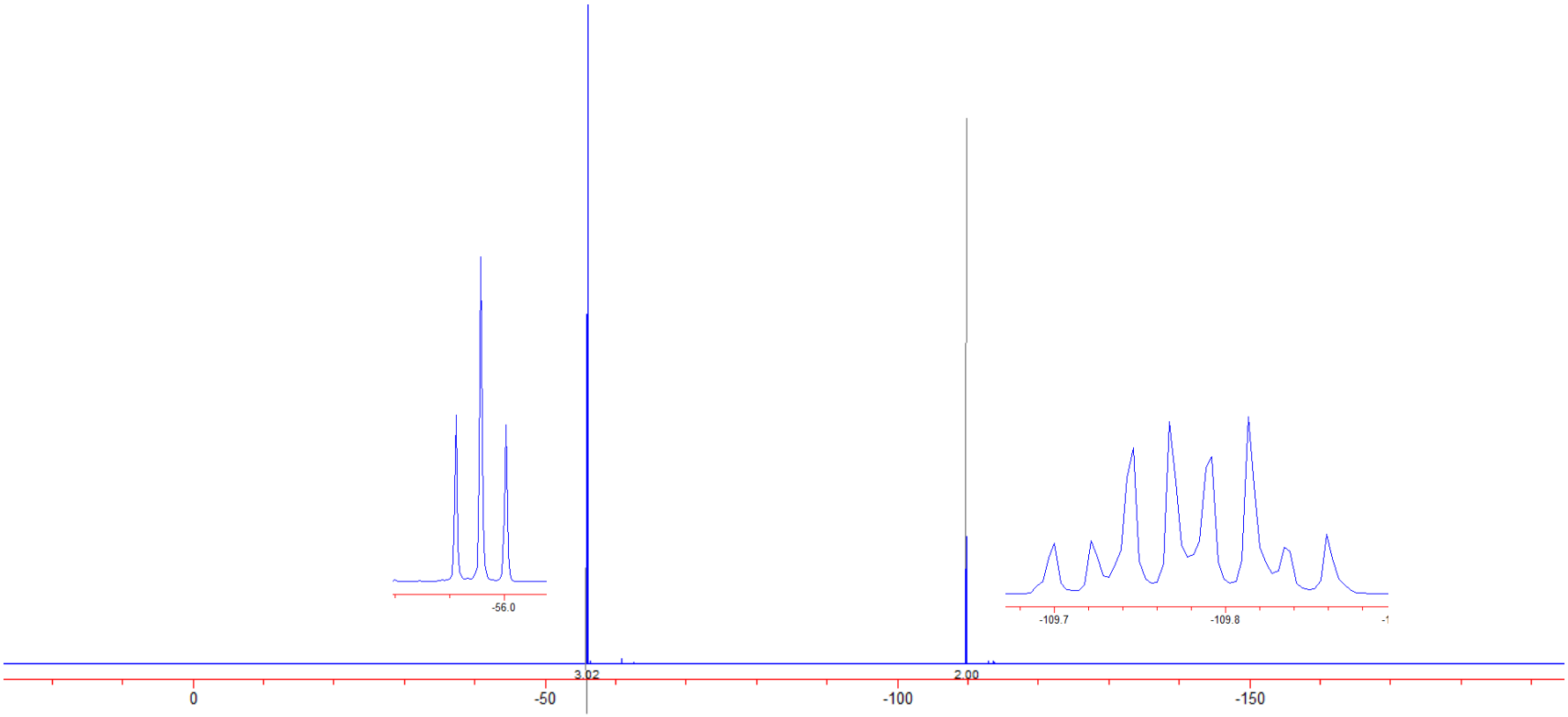


^{13}C NMR Spectrum in $CDCl_3$ at 52 °C

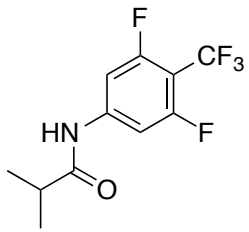


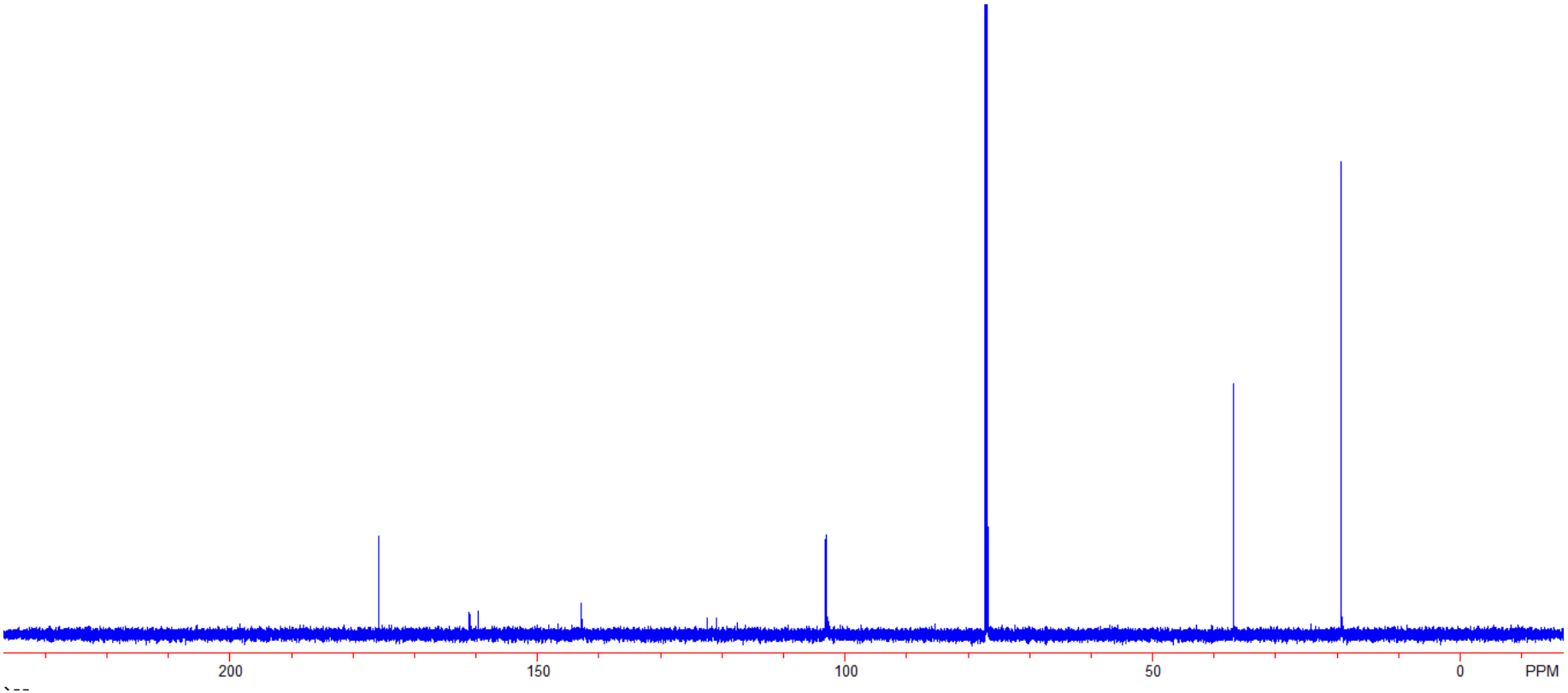
^{1}H NMR Spectrum of **S17** in $CDCl_3$





^{19}F NMR Spectrum of **S17** in $CDCl_3$





^{13}C NMR Spectrum of **S17** in $CDCl_3$