Identifying the potential of pulsed irradiation in synthesis: copper-photocatalysed C–F functionalisation

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Supplementary Information

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I. General

NMR experiments were performed either on a Bruker Avance III NMR spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) or 376 MHz (^{19}F) or on a Bruker Avance III NMR spectrometer operating at 600 MHz (^{1}H), 150 MHz (^{13}C) or 564 MHz (^{19}F). The deuterated solvent used was $CDCl_3$. Chemical shifts were recorded in ppm. Spectra were calibrated by assignment of the residual solvent peak to δ_H 7.26 and δ_C 77.16 for $CDCl_3$. Coupling constants (J) were recorded in Hz. Infrared spectrometry was performed on a Shimadzu FTIR 8400s spectrometer, with samples analyzed either as thin films on NaCl plates or using an ATR attachment. ESIMS analyses were conducted on a Thermo-Scientific LTQ-Orbitrap mass spectrometer. EIMS analyses were performed using a Kratos Analytical Concept ISQ hybrid magnetic sector quadrupole tandem or Shimadzu GCMS-QP2010 mass spectrometers.

TLC was performed using Merck silica gel 60-F_{254} plates. Developed TLC plates were visualized by UV absorbance (254 nm) or through application of heat to a plate stained with cerium molybdate {$Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, H_2SO_4, H_2O}. Flash column chromatography was performed with flash grade silica gel (60 μm) and the indicated eluent in accordance with standard techniques.[1] Unless otherwise specified, reactions were conducted with magnetic stirring under N_2. Unless otherwise specified all reagents employed in these studies were used as received from Sigma-Aldrich, AK Scientific, Combi-Blocks, and Oakwood and were used without purification. *i*-Pr_2NEt (Sigma-Aldrich) was distilled prior to use. [Cu(bcp)(XP)]PF_6 (**2**) was prepared according to a literature procedure.[2]

1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
2. Mejia, E.; Luo, S.-P.; Karnahl, M.; Friedrich, A.; Tschierlei, S.; Surkus, A.-E.; Junge, H.; Gladiali, S.; Lochbrunner, S.; Beller, M. *Chem. Eur. J.* **2013**, *19*, 15972.

II. Pulsed LED Photoreactor Experimental Set-Up

Circuit. Our in-house constructed circuit featured a series of integrated circuits (IC) (making up the timing circuit) and voltage regulating components that were used to pulse the blue LED photoreactor:

A Goodwill Instrument Co. GPD-5030 dual tracking power supply was used to provide 12 V DC to a voltage regulator (**L7805CP**), which reduced this output to 5 V DC (Figs. S1A & S1B). This enabled the power supply to drive both the integrated circuits (ICs) and the LED photoreactor. The timing circuit was created by taking the 5 V output of the regulator and connecting the 555-timer chip (**NE555**) in an astable configuration and feedback from the resistors and capacitor (between the voltage regulator output and common ground) causes a voltage instability in the 555-timer chip that allows it to oscillate between on and off.

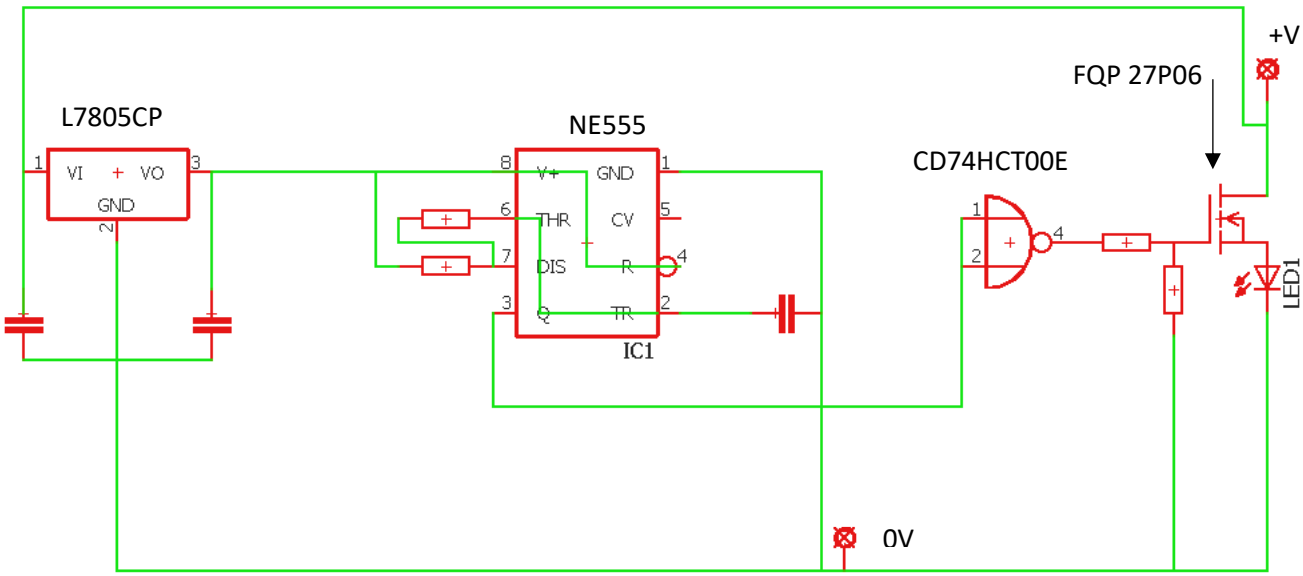


Figure S1A. Schematic representation of the circuit used to pulse the LED photoreactor.

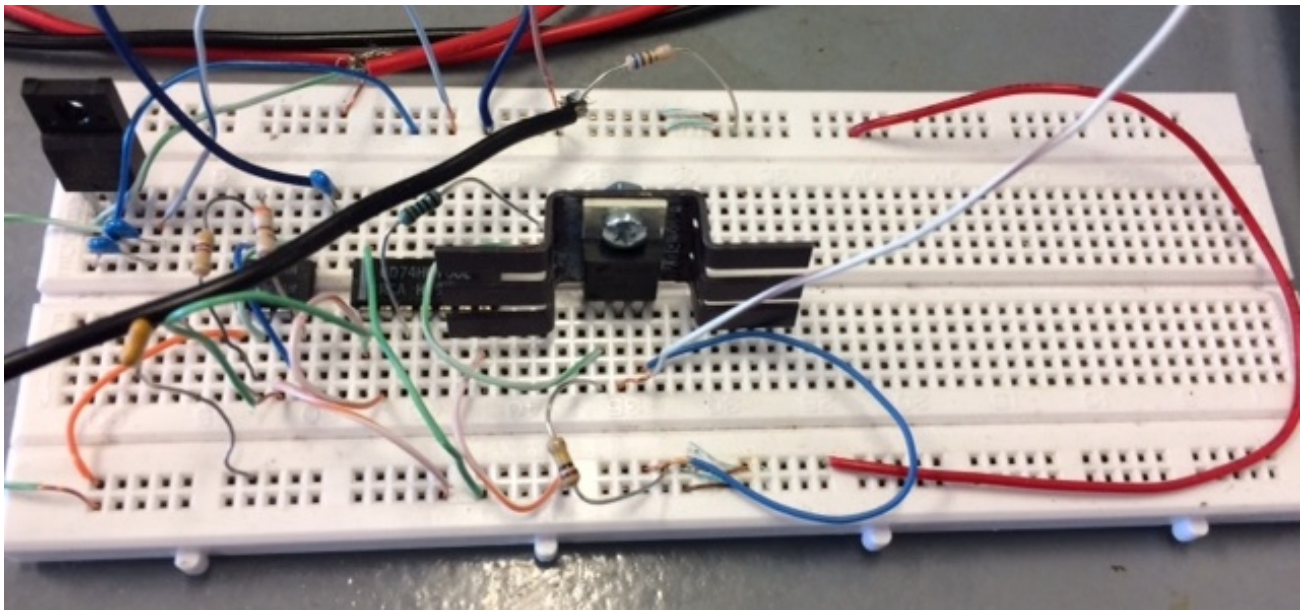


Figure S1B. Photograph of the circuit constructed and employed to pulse the LED photoreactor.

The combination of the resistor and capacitor values in the circuit caused an oscillation of approximately 100 kHz with a 75% duty cycle. However, because LEDs operating at these currents with 75% duty cycle would overheat, the output of the 555-timer chip was inverted by a quad NOR flip-flop IC (**CD74HCT00E**). The NOR flip-flop gate inputs were connected in parallel, meaning that they were either both low or both high. The NOR flip-flop gate inverts the input, so when the input is high, the output was low and vice versa. This created an output that was a square wave voltage operating at 100 kHz and a 25% duty cycle, which was then fed into the base of a MOSFET transistor (**FQP27P06**). This allowed current to flow from the collector to the emitter, this activation completed the circuit and turned the LEDs back on. The transistor was needed as it allowed the controlled timing and pulsing obtained by the timing circuit and enabled the 12 V power supply to drive the LEDs. As a result the LEDs operated at 100 kHz and a 25% duty cycle.

Photoreactor. Our custom photoreactor was constructed using of 2 m of blue LEDs strips (120 LEDs) purchased from Banggood.com (Fig. S2A). Under our above-mentioned pulsed LED conditions this photoreactor operates at 18-W (12 V, 1.5 A) providing 454 nm, ~28,000 lux (measured at the center of the photoreactor using a Trotec BF05 Luxmeter). A photograph of the complete experimental set-up is provided (Fig. S2B). Under conventional (continuous) operation this photoreactor operates at 24-W (12 V, 2 A) providing 453 nm, ~28,000 lux (measured at the center of the photoreactor using a Trotec BF05 Luxmeter).

Figure S2A. Photograph of blue LED photoreactor.

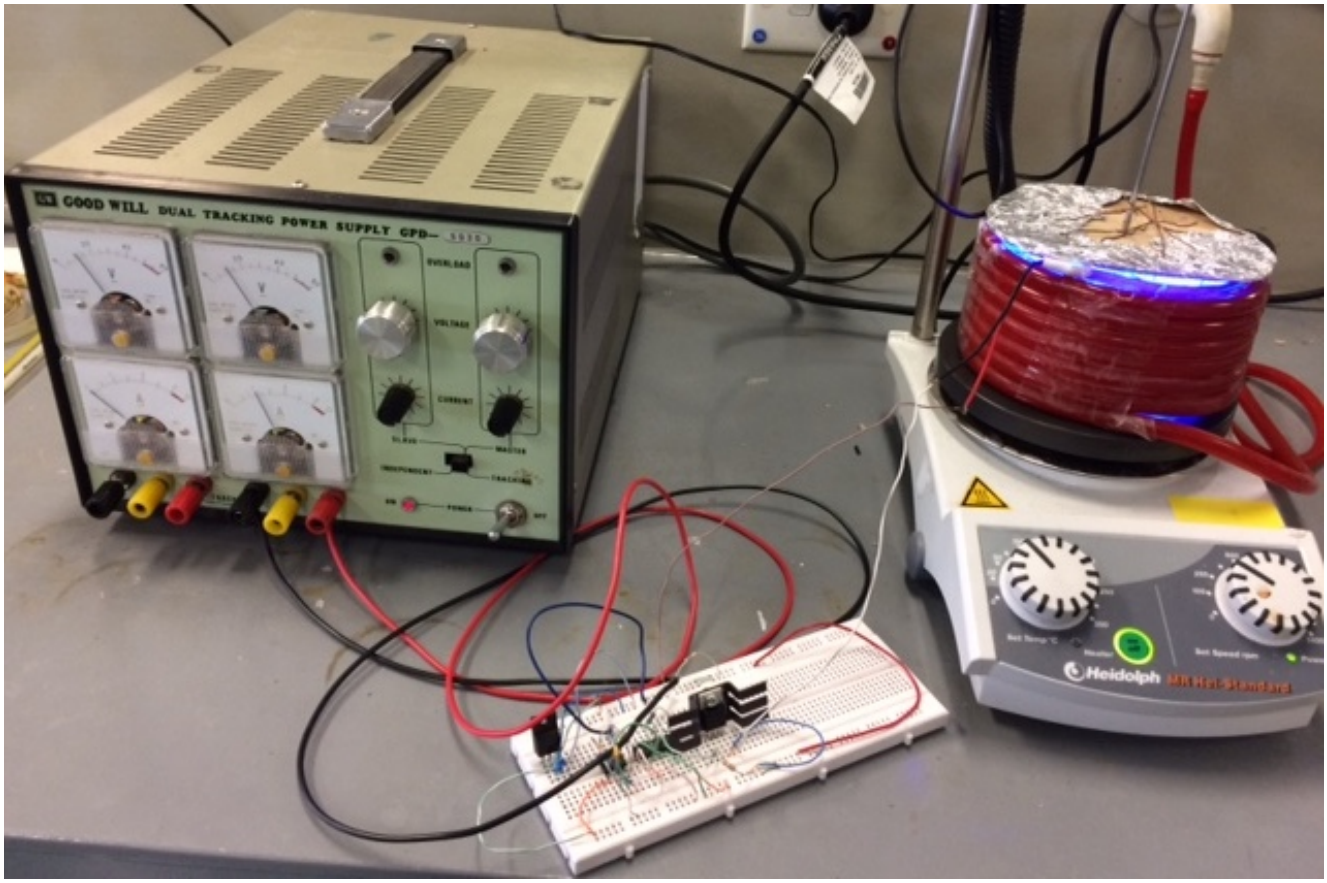
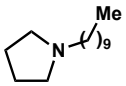


Figure S2B. Photograph of Pulsed LED Photoreactor Experimental Set-Up.

III. Preparation of Materials

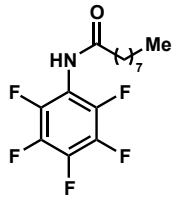
Experimental procedures for the preparation of previously unreported compounds are described below. These procedures were not optimized.

1-Decylpyrrolidine (4h)



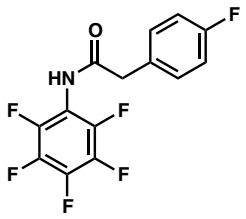
Pyrrolidine (3.5 mL, 42 mmol) was added to a magnetically stirred solution of 1-iododecane (4.3 mL, 20 mmol) in MeCN (10 mL) maintained at r.t. under N_2 and the ensuing mixture heated at reflux. After 16 h, the mixture was concentrated under reduced pressure to provide a yellow oil. The ensuing oil was then added to a magnetically stirred mixture of KOH (3.0 g, 53 mmol) in MeOH (20 mL) and the bright yellow solution maintained at r.t. under N_2. After 4 h, the mixture was concentrated under reduced pressure. The ensuing residue was then subjected to chromatography (silica plug, contained in a sintered glass funnel: Et_2O elution) to provide title compound **4h** (780 mg, 15% yield) as a colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.54–2.48 (m, 4H), 2.43 (t, J = 8 Hz, 2H), 1.82–1.76 (m, 4H), 1.56–1.50 (m, 2H), 1.35–1.25 (m, 14H), 0.89 (t, J = 7 Hz, 3H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 56.7, 54.3, 31.9, 29.62, 29.59, 29.58, 29.3, 29.1, 27.8, 23.4, 22.7, 14.1 ppm.
IR (NaCl) 2925, 2784, 2960, 1460, 1378, 1350, 1292, 1237, 1149 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 211 (M^+, 2), 84 (100).

***N*-(Pentafluorophenyl)nonanamide (6a)**



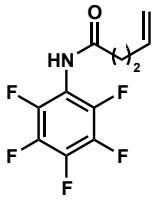
Nonanoic acid (0.92 g, 6.00 mmol) was added to a magnetically stirred solution of pentafluoroaniline (1.10 g, 6.00 mmol), EDCI (1.30 g, 8.50 mmol) and DMAP (100 mg, 0.70 mmol) in CH_2Cl_2 (20 mL) maintained at 0 °C under N_2. After 5 min, NEt_3 (1.50 mL, 12.0 mmol) was added slowly and the reaction mixture warmed to room temperature. After 16 h, $KHSO_4$ (10 mL of a saturated aqueous solution) was added and the phases separated. The organic layer was then washed with $NaHCO_3$ (10 mL of a saturated aqueous solution) and H_2O (10 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc to provide title compound **6a** (310 mg, 15% yield) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (s, 1H), 2.37 (s, 1H), 2.28 (t, J = 6 Hz, 1H), 1.70–1.62 (m, 1H), 1.60–1.53 (m, 1H), 1.31–1.16 (m, 10H), 0.84–0.80 (m, 3H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 171.8, 143.7, 142.1, 138.6, 136.9, 36.2, 31.8 29.3, 29.1, 29.0, 25.5, 22.7, 14.1 ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –144.9 (d, J = 18 Hz, 2F), –156.6 (s, 1F), –162.4 (s, 2F) ppm.
IR (NaCl) 3250, 2924, 2957, 1682, 1652, 1524, 1490, 1458, 1002, 953 cm^{-1}.
EIMS (*m/z*, relative intensity) 323 (M^+, 2), 183 (70), 141 (45), 57 (100).

2-(4-Fluorophenyl)-*N*-(pentafluorophenyl)acetamide (6c)



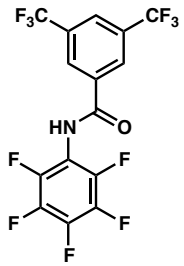
DMAP (67 mg, 546 μmol) was added to a magnetically stirred solution of pentafluoroaniline (1.00 g, 5.46 mmol) and 2-(4-fluorophenyl)acetic acid (926 mg, 6.01 mmol) in DMF (20 mL) maintained at 0 °C under N_2. After 5 min, EDCI (1.47 g, 7.65 mmol) and NEt_3 (1.90 mL, 13.7 mmol) were added and the ensuing mixture was slowly warmed to 25 °C. After 16h, the reaction mixture was diluted with H_2O and EtOAc/hexane (20 mL of a 1:1 v/v solution). The phases were separated and the aqueous layer was further extracted with EtOAc/hexane (2 x 20 mL of a 1:1 v/v solution). The combined organic phase was then washed with $KHSO_4$ (20 mL of a saturated aqueous solution), $NaHCO_3$ (20 mL of a saturated aqueous solution), and H_2O (20 mL), successively. The organic phase was then dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The ensuing residue was then subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt_3 was present in the eluent) to provide title compound **6c** (400 mg, 24% yield) as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 8.0, 5.5 Hz, 2H), 7.13 (t, J = 8.8 Hz, 2H), 6.64 (bs, 1H), 3.81 (s, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) δ –113.9 (s, 1F), –144.8 (d, J = 16 Hz, 2F), –155.9 (t, J = 21 Hz, 1F), –162.1 (t, J = 19 Hz, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 163.3, 161.6, 143.0 (d, J = 143 Hz), 137.8 (d, J = 253 Hz), 131.1 (d, J = 8 Hz), 129.3 (d, J = 3 Hz), 116.3 (d, J = 22 Hz), 111.5 (t, J = 19 Hz), 42.5 ppm.
IR (NaCl) 3153, 2989, 2982, 1671, 1511, 1496, 1227, 1016, 1002, 963, 838 cm^{-1}.
EIMS (*m/z*, relative intensity) 319 (M^+, 1), 136 (55), 109 (100).

***N*-(Pentafluorophenyl)pent-4-enamide (6d)**



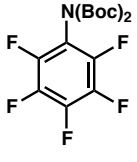
4-Pentenoic acid (0.50 g, 5.00 mmol) was added to a magnetically stirred solution of pentafluoroaniline (1.10 g, 6.00 mmol), EDCI (1.30 g, 8.50 mmol) and DMAP (100 mg, 0.70 mmol) in CH_2Cl_2 (20 mL) maintained at 0 °C under N_2. After 5 min, NEt_3 (1.50 mL, 12.0 mmol) was added slowly and the reaction mixture was warmed to room temperature. After 16 h, $KHSO_4$ (10 mL of a saturated aqueous solution) was added and the phases separated. The organic phase was then washed with $NaHCO_3$ (10 mL of a saturated aqueous solution) and H_2O (10 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc to provide title compound **6d** (220 mg, 20% yield) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.71 (s, 1H), 5.87–5.76 (m, 1H), 5.11–5.00 (m, 2H), 2.51–2.40 (m, 4H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 143.9, 142.3, 138.6, 137.0, 116.5, 111.7, 60.4, 35.5 ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –144.8 (d, J = 12 Hz, 2F), –156.5 (s, 1F), –162.3 (s, 2F) ppm.
IR (NaCl) 3245, 1681, 1648, 1543, 1502, 1490, 1000 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 265 (M^+, 2), 183 (50), 55 (100).

***N*-(Pentafluorophenyl)-3,5-bis(trifluoromethyl)benzamide (6f)**



3,5-Bis(trifluoromethyl)benzoic acid (0.65 g, 2.50 mmol) was added to a magnetically stirred solution of pentafluoroaniline (0.50 g, 2.50 mmol), EDCI (0.60 g, 3.50 mmol) and DMAP (60 mg, 0.40 mmol) in CH_2Cl_2 (20 mL) maintained at 0 °C under N_2. After 5 min, NEt_3 (0.90 mL, 7.50 mmol) was added slowly and the reaction mixture warmed to room temperature. After 16 h, $KHSO_4$ (10 mL of a saturated aqueous solution) was added and the phases separated. The organic phase was then washed with $NaHCO_3$ (10 mL of a saturated aqueous solution) and H_2O (10 mL) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc to provide title compound **6f** (80 mg, 6% yield) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 2 H), 8.05 (s, 1 H), 7.72 (s, 1 H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 143.1 (dm, J = 340 Hz), 141.1 (dm, J =180 Hz), 139.3 (dm, J = 200 Hz), 137.1, 134.5, 132.8 (q, J = 88 Hz), 127.9, 126.3, 122.7 (q, J = 360 Hz) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –62.8 (d, J = 18 Hz), –144.4 (m, 1F), –154.8 (m, 1F), –161.5 (m, 1F) ppm.
IR (NaCl) 1680, 1653, 1500, 1278, 1188, 1135, 1005, 940, 910 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 423 (M^+, 4), 241 (100), 213 (60), 163 (15).

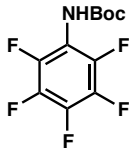
Compound S1



S1

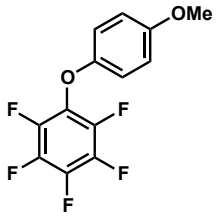
DMAP (13.3 mg, 0.109 mmol) was added to a magnetically stirred mixture of pentafluoroaniline (1.00 g, 5.46 mmol), Boc_2O (1431 mg, 6.55 mmol) and Na_2CO_3 (1158 mg, 10.92 mmol) in THF (10 mL) maintained at r.t. under N_2. The ensuing mixture was then heated at 60 °C. After 16h, the mixture was cooled to r.t. and H_2O (5 mL) and EtOAc (20 mL) were added and the phases were separated. The ensuing aqueous phase was then extracted with EtOAc (2x 20 mL) and the combined organic fractions were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The ensuing residue was then subjected to chromatography (silica plug, contained in a sintered glass funnel: ~3 cm height, 5 cm diameter; CH_2Cl_2 elution) to provide title compound **S1** (1.15 g, 55% yield) as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 18H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) δ –145.9 (d, J = 17 Hz, 2F), –154.7 (t, J = 21 Hz, 1F), –163.0 (t, J = 19 Hz, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 143.6 (d, J = 251 Hz), 141.1 (d, J = 256 Hz), 137.5 (d, J = 252 Hz), 115.0 (td, J = 15, 5 Hz), 84.6, 27.7 ppm.
IR (NaCl) 1810, 1777, 1734, 1519, 1372, 1271, 12448, 1149, 1119, 1099, 1066, 994, 852 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 227 {[M–(Boc, *t*-Bu)]$^+$, 7}, 57 (100).

***tert*-Butyl (pentafluorophenyl)carbamate (6g)**



TFA (260 µL, 3.39 mmol) was added to a CH_2Cl_2 solution (10 mL) containing compound **S1** (1.30 g, 3.39 mmol) maintained at 0 °C under N_2. After 3 h, the solution was concentrated under reduced pressure. The resulting residue was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution; 1% NEt_3 was present in the eluent) to provide title compound **6g** (490 mg, 51% yield) as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (bs, 1H), 1.53 (s, 9H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) δ –146.3 (d, J = 16 Hz, 2F), –157.8 (t, J = 21 Hz, 1F), –162.8 (m, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 152.2, 142.9 (d, J = 254 Hz), 149.7 (d, J = 256 Hz), 137.8 (d, J = 252 Hz), 112.7, 82.4, 28.0 ppm.
IR (NaCl) 3318, 1710, 1525, 1487, 1451, 1326, 1278, 1251, 1162, 1012, 974 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 183 {[M–Boc]$^+$, 6}, 41 (30), 57 (100).

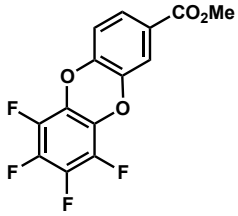
1,2,3,4,5-pentafluoro-6-(4-methoxyphenoxy)benzene (6i)



4-Methoxyphenol (1.00 g, 8.05 mmol) was added to a magnetically stirred solution of hexafluorobenzene (1.10 g, 6.00 mmol) and K_2CO_3 in MeCN (20 mL) maintained at r.t. under N_2. The ensuing mixture was then heated at reflux. After 16 h, the reaction mixture was cooled, NaCl (30 mL of a saturated aqueous solution) was added and the phases separated. The aqueous phase was then further extracted with EtOAc (3x 20 mL) and organic fractions were combined, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The ensuing residue was subjected to flash column chromatography (silica gel, 10→30% EtOAc/hexane elution) to provide title compound **6i** (800 mg, 46% yield) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.88–6.82 (m, 2H), 6.79–6.75 (m, 2H), 3.71 (s, 3H) ppm.

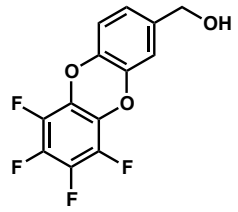
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.1, 151.3, 142.2 (dm, J = 320 Hz), 139.2 (dm, J = 160 Hz), 137.5 (dm, J = 140 Hz), 130.7, 116.8, 114.8, 55.7 ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –154.4 (t, J = 18 Hz, 2F), –160.6 (t, J = 24 Hz, 1F), –162.3 (td, J = 3, 21 Hz, 2F) ppm.
IR (NaCl) 2964, 2458, 1596, 1506, 1299, 1251, 1180, 1103, 1021 cm^{-1}.
EIMS (*m/z*, relative intensity) 290 (M^+, 100), 275 (70), 247 (20), 169 (25), 123 (30).

Methyl 6,7,8,9-tetrafluorodibenzo[*b*,*e*][1,4]dioxine-2-carboxylate (6k)



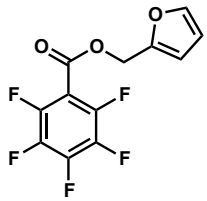
H_2SO_4 (one drop) was added to a mixture of 3,4-dihydroxybenzoic acid (0.92 g, 6.00 mmol) in MeOH (20 mL) maintained under N_2. The ensuing mixture was then heated at reflux. After 16 h, the mixture was concentrated under reduced pressure and MeCN (20 mL) added. Hexafluorobenzene (1.10 g, 6.00 mmol) and K_2CO_3 were then added to the ensuing mixture and the magnetically stirred mixture was then heated at reflux. After 16 h, the reaction mixture was quenched with NaCl (30 mL of a saturated aqueous solution) and phases separated. The aqueous phase was then further extracted with EtOAc (3x 20 mL) and organic fractions were combined, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc and triturated (Et_2O) to provide title compound **6k** (300 mg, 12% yield) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (dd, J = 8, 2 Hz, 1H), 7.68 (d, J = 2 Hz, 1H), 7.03 (d, J = 9 Hz, 1H), 3.93 (s, 3H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.2, 143.8, 139.8, 137.7, 136.7, 136.0, 128.7, 128.5, 127.6, 127.2, 118.4, 116.9, 52.4, 30.9 ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –161.8 (m, 2F), –164.0 (m, 1F), –164.5 (m, 1F) ppm.
IR (NaCl) 1722, 1700, 1521, 1506, 1443, 1305, 1020 cm^{-1}.
EIMS (*m/z*, relative intensity) 314 (M^+, 75), 283 (100), 255 (44).

(6,7,8,9-Tetrafluorodibenzo[*b*,*e*][1,4]dioxin-2-yl)methanol (6l)



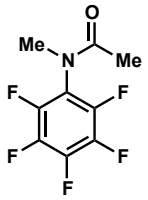
$LiAlH_4$ (96 mg, 2.53 mmol) was added to a magnetically stirred solution of ester **6k** (276 mg, 0.88 mmol) in Et_2O (20 mL) maintained at r.t. under N_2. After 14 h, the reaction mixture was cooled to 0 °C, and H_2O (100 μL), NaOH (100 μL of a 1 M aqueous solution), and H_2O (300 μL), were added successively. The mixture was warmed to r.t. After 0.25 h, $MgSO_4$ was added. After 0.25 h, the mixture was filtered through Celite® to provide title compound **6l** (230 mg, 91% yield) as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06–6.95 (m, 3H), 4.64 (s, 2H), 1.72 (bs, 1H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 140.0, 139.3, 138.4, 137.5, 138.1, 137.6, 135.9, 123.4, 128.9, 116.9, 115.4, 64.2 ppm; 12 signals observed.
^{19}F NMR (376 MHz, $CDCl_3$) δ –162.4 (m, 2F), –165.2 (m, 2F) ppm.
IR (NaCl) 3384, 1509, 1505, 1269, 1017 cm^{-1}.
EIMS (*m/z*, relative intensity) 286 (M^+, 80), 257 (28), 151 (24), 77 (100).

Furan-2-ylmethyl 2,3,4,5,6-pentafluorobenzoate (8i)



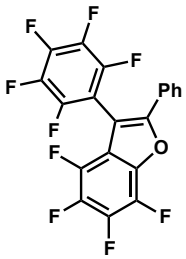
DMAP (52 mg, 429 μmol) was added to a magnetically stirred solution of pentafluorobenzoic acid (1.00 g, 4.72 mmol) and furfuryl alcohol (371 μL, 4.29 mmol) in CH_2Cl_2 (20 mL) at 0 °C under N_2. After 5 min, EDCI (1.15 g, 6.00 mmol) and NEt_3 (1.19 mL, 10.7 mmol) were added and the ensuing mixture was warmed to r.t. After 16h, the reaction mixture was washed with $KHSO_4$ (20 mL of a saturated aqueous solution), $NaHCO_3$ (20 mL of a saturated aqueous solution), and H_2O (20 mL) successively. The organic phase was then dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The ensuing residue was then subjected to chromatography (silica plug contained in a sintered glass funnel: ~3 cm height, 5 cm diameter; 10% EtOAc/hexane elution) to provide title compound **8i** as a colorless oil (521 mg, 38% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 1.8, 0.6 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 6.42 (dd, J = 3.3, 1.8 Hz, 1H), 5.38 (s, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) δ –137.8 (m, 2F), –148.3 (t, J = 21 Hz, 1F), –160.3 (m, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 148.1, 145.5 (d, J = 256 Hz), 143.8, 143.3 (d, J = 262 Hz), 137.7 (d, J = 253 Hz), 111.7, 110.7, 107.9 (td, J = 16, 3.9 Hz), 60.0 ppm.
IR (NaCl) 1739, 1501, 1391, 1298, 1192, 951 cm^{-1}.
EIMS (m/z, relative intensity) 292 (M^+, 15), 195 (15), 81 (100).

***N*-Methyl-*N*-(pentafluorophenyl)acetamide (8j)**



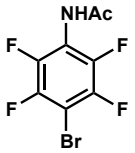
NaH (149 mg of 60% dispersion in mineral oil, 3.73 mmol) was added to a magnetically stirred solution of *N*-(pentafluorophenyl)acetamide (500 mg, 2.22 mmol) in DMF (8 mL) maintained at 0 °C under N_2. After 0.5 h, iodomethane (166 μL, 2.66 mmol) was added dropwise and the ensuing mixture was warmed to room temperature. After 16 h, EtOAc/hexane (20 mL of 1:1 v/v solution) and H_2O (10 mL) were added and the phases separated. The aqueous phase was then further extracted with EtOAc/hexane (2x 20 mL of 1:1 v/v solution) and the combined organic fractions were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The ensuing residue was subjected to flash column chromatography (silica gel, 20% EtOAc/hexane elution) to provide title compound **8j** (358 mg, 67% yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (s, 0.7H), 3.23 (s, 2.3H), 2.33 (s, 0.7H), 1.94 (s, 2.3H) ppm; 4 signals observed (rotamers present).
^{19}F NMR (376 MHz, $CDCl_3$) δ –145.16 (d, J = 15.8 Hz, 0.4F), –145.72 (d, J = 15.8 Hz, 1.6F), –153.0 (t, J = 21.3 Hz, 0.8F), –155.4 (t, J = 21.3 Hz, 0.2F), –160.3 (m, 1.6 F), –162.2 (m, 0.4F) ppm; 6 signals observed (rotamers present).
^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.1, 144.1 (d, J = 250 Hz), 141.4 (d, J = 255 Hz), 140.9 (d, J = 255 Hz), 138.0 (d, J = 257 Hz), 119.0 (td, J = 15Hz, 6 Hz), 117.9 (td, J = 15 Hz, 6 Hz), 38.4, 35.8, 21.4, 21.1 ppm; 12 signals observed (rotamers present).
IR (NaCl) 1685, 1522, 1510, 1374, 1342, 1323, 991 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 240.0442. $C_9H_6F_5NO$ requires $[M + H]^+$, 240.0442.

4,5,6,7-Tetrafluoro-3-(pentafluorophenyl)-2-phenylbenzofuran (8l)



Acetophenone (2.32 mL, 20.0 mmol) was added to a magnetically stirred mixture of hexafluorobenzene (2.30 mL, 20.0 mmol) and NaH (800 mg of 60% dispersion in mineral oil, 20.0 mmol) in DMF (20 mL) maintained under N_2. The ensuing mixture was then heated at 80 °C. After 5 h, the mixture was cooled, and Et_2O (50 mL) and H_2O (50 mL) were added and the phases separated. The aqueous phase was then further extracted with Et_2O (2x 20 mL) and the combined organic fractions were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The ensuing residue was subjected to flash column chromatography (silica gel, 10% CH_2Cl_2/hexane, then EtOAc elution) to provide title compound **8l** (150 mg, 3% yield) as a colorless solid (after recrystallization from hexane).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, J = 7.2 Hz, 2H), 7.52–7.40 (complex m, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –137.5 (d, J = 21 Hz, 2F), –151.7 (t, J = 21 Hz, 1F), –152.4 (m, 1F), –159.5 (t, J = 20 Hz, 1F), –160.5 (td, J = 21, 7 Hz, 2F), –160.9 (t, J = 19 Hz, 2F), –162.4 (t, J = 20 Hz, 1F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 145.0 (d, J = 250 Hz), 142.0 (d, J = 254 Hz), 139.3 (d, J = 250 Hz), 137.9 (d, J = 250 Hz), 134.2 (d, J = 252 Hz), 130.6, 129.2, 128.0, 126.5, 114.9 (d, J = 16 Hz), 106.1 (td, J = 19, 4 Hz), 99.4 ppm.
IR (NaCl) 1538, 1489, 1451, 1440, 1157, 1092, 1047, 1031, 1010, 990, 767, 690 cm^{-1}.
EIMS (m/z, relative intensity) 432 (M^+, 100), 412 (40), 206 (15).

***N*-(4-Bromo-2,3,5,6-tetrafluorophenyl)acetamide (12)**



2,3,5,6-Tetrafluoroaniline (0.50 g, 2.80 mmol) was added to a magnetically stirred mixture of $NaHCO_3$ (0.33g, 3.9 mmol) and Br_2 (0.2 mL, 3.6 mmol) in MeOH (30 mL) maintained under N_2. After 48 h, the solution was quenched with NaS_2O_3 (20 mL of a saturated aqueous solution) and extracted with Et_2O (3x 50 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure, to provide an off-white solid. The ensuing solid was then added to a magnetically stirred mixture of Ac_2O (0.2 mL, 2.3 mmol) and H_2SO_4 (0.05 mL) in PhMe (20 mL), which was then heated at 80 ˚C. After 48 h, the mixture was concentrated under reduced pressure to provide a crude solid, which was recrystallized from hot PhMe to provide title compound **12** (180 mg, 20% yield) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (s, 1H), 2.32 (s, 3H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 146.0, 138.5, 123.6, 98.1, 24.0 ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –145.4 (d, J = 16 Hz, 2F), –161.5 (s, 2F) ppm.
IR (NaCl) 3256, 3224, 3178, 1695, 1524, 1519, 1497 1020, 987 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 285.9487. $C_8H_5BrF_4NO$ requires $[M + H]^+$, 285.9485.

IV. Visible Light-Mediated Copper-Photocatalysed Reactions

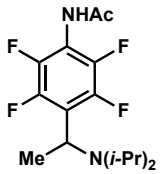
General Procedure 1: Dual α-Amino C–H/ C–F Functionalization Reactions

In a nitrogen-filled glovebox, [Cu(bcp)(XP)]PF_6 (**2**) (8.6 mg, 7.5 μmol) was added to a 20-mL screw-top vial (PTFE tape-lined thread) containing the perfluorinated substrate (500 μmol), tertiary amine (1.00 mmol), $Gd(OTf)_3$ (121 mg, 200 μmol), MeCN (3.85 mL), and a stir bar. The vial was then capped, the joint was wrapped with PARAFILM®, and removed from the glovebox and placed in a water bath (suspended with Cu wire) maintained at 45 °C that was contained within a 18 W blue LED photoreactor (switched off) and magnetically stirred (Figure S2). The vial was then irradiated (25% duty cycle at 100 kHz). After 24 h, the reaction mixture was quenched by exposure to air and analyzed by ^{19}F NMR spectroscopy (after the addition of 1-bromo-4-fluorobenzene as an internal standard) or concentrated under reduced pressure and the ensuing residue was purified by flash column chromatography on silica gel.

General Procedure 2: Hydrodefluorination Reactions

In a nitrogen-filled glovebox, [Cu(bcp)(XP)]PF_6 (**2**) (8.6 mg, 7.5 μmol) was added to a 20-mL screw-top vial (PTFE tape-lined thread) containing the perfluorinated substrate (500 μmol), *i*-Pr_2NEt (**4a**) (129 mg, 1.00 mmol), MeCN (7.70 mL), and a stir bar. The vial was then capped, the joint was wrapped with PARAFILM®, and removed from the glovebox and placed in a water bath (suspended with Cu wire) maintained at 45 °C that was contained within a 18 W blue LED photoreactor (switched off) and magnetically stirred (Figure S2). The vial was then irradiated (25% duty cycle at 100 kHz). After 24 h, the reaction mixture was quenched by exposure to air and analyzed by ^{19}F NMR spectroscopy (after the addition of 1-bromo-4-fluorobenzene as an internal standard) or concentrated under reduced pressure and the ensuing residue was purified by flash column chromatography on silica gel.

***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)acetamide (5a)**



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt_3 was also present in the eluent) and then was recrystallized to provide title compound **5a** as a colorless solid (145 mg, 87% yield).

^1H NMR (600 MHz, $CDCl_3$) δ 7.04 (bs, 1H), 4.66 (q, J = 7.3 Hz, 1H), 3.37 (sept, J = 6.7 Hz, 2H), 2.24 (s, 3H), 1.51 (d, J = 7.2 Hz, 3H), 1.12 (d, J = 6.6 Hz, 6H), 0.94 (d, J = 6.8 Hz, 6H) ppm.

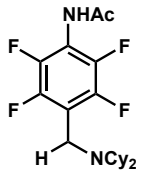
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.2 (s, 2F), –146.6 (s, 2F) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 144.8 (d, J = 242 Hz), 142.3 (d, J = 249 Hz), 124.5, 113.7, 46.0, 45.7, 22.7, 22.4, 19.7 ppm.

IR (ATR) 2965, 1673, 1529, 1501, 1275, 1215, 1148, 1083, 1005, 985, 940, 726 cm^{-1}.

HRESIMS Found: $[M + H]^+$, 335.1738. $C_{16}H_{23}F_4N_2O$ requires $[M + H]^+$, 335.1741.

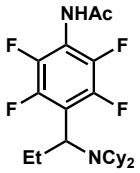
***N*-(4-((dicyclohexylamino)methyl)-2,3,5,6-tetrafluorophenyl)acetamide (5b)**



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and Cy_2NMe (**4b**) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt_3 was also present in the eluent) to provide title compound **5b** as a colorless solid (115 mg, 57% yield).

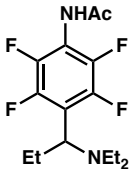
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (bs, 1H), 3.85 (s, 2H), 2.46 (t, J = 11.8 Hz, 2H), 2.25 (s, 3H), 1.76 (complex m, 8H), 1.61 (d, J = 12.9 Hz, 2H), 1.36 (m, 4H), 1.22 (m, 4H), 1.08 (m, 2H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –144.3 (s, 2F), –147.0 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 145.6 (d, J = 249 Hz), 141.9 (d, J = 249 Hz), 118.8, 114.4, 57.7, 37.8, 31.8, 26.6, 26.2 ppm.
IR (NaCl) 2929, 2853, 2362, 2339, 1684, 1499, 1477, 1296, 1272, 1033, 891, 668 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 401.2205. $C_{21}H_{29}F_4N_2O$ requires $[M + H]^+$, 401.2211.

***N*-(4-(1-(Dicyclohexylamino)propyl)-2,3,5,6-tetrafluorophenyl)acetamide (5c)**



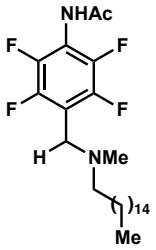
Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (395 μmol) and Cy_2NPr (**4c**) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide title compound **5c** as a colorless solid (32 mg, 19% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (bs, 1H), 4.33 (dd, J = 9.2, 6.2, 1H), 2.86 (t, J = 11.5 Hz, 2H), 2.24 (s, 3H), 2.01 (m, 1H), 1.86 (m, 1H), 1.78 (d, J = 11.1 Hz, 2H), 1.68 (t, J = 14.4 Hz, 4H), 1.59 (d, J = 12.2 Hz, 2H), 1.46 (qd, J = 12.2, 3.1 Hz, 2H), 1.37–1.17 (complex m, 8H), 1.05 (qt, J = 12.8, 3.5 Hz, 2H), 0.81 (t, J = 7.3 Hz, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –140.9 (s, 2F), –146.4 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 145.1 (d, J = 245 Hz), 142.2 (d, J = 249 Hz), 123.3, 113.7, 55.5, 53.7, 34.1, 33.6, 26.9, 26.8, 26.3, 26.0, 11.8 ppm.
IR (NaCl) 3251, 2929, 2853, 1683, 1646, 1520, 1476, 1453, 1371, 1272, 1182, 1134, 1117, 1098, 986, 892, 735 cm^{-1}.
EIMS (*m/z*, relative intensity) 428 (M^+, 1), 181 (8), 138 (100), 56 (50).

***N*-(4-(1-(Diethylamino)propyl)-2,3,5,6-tetrafluorophenyl)acetamide(5d)**



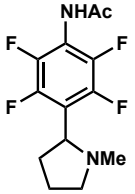
Reaction between *N*-(perfluorophenyl)acetamide (**3a**) (500 μmol) and triethylamine (**4d**) following General Procedure 1 {$Gd(OTf)_3$ not added}. Title compound **5d** was formed in 66% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→50% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **5d** as a colorless solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (bs, 1H), 4.43 (q, J = 7.1 Hz, 1H), 2.72 (sextet, J = 7.2 Hz, 2H), 2.38 (sextet, J = 6.5 Hz, 2H), 2.25 (s, 3H), 1.55 (d, J = 7.3 Hz, 3H), 1.06 (t, J = 6.7 Hz, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) δ –140.3 (s, 2F), –146.0 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.2, 145.4 (d, J = 246 Hz), 142.3 (d, J = 251 Hz), 118.9, 114.9, 51.4, 43.4, 29.7, 23.0, 17.2, 12.5 ppm.
IR (NaCl) 3254, 2975, 2938, 1684, 1646, 1496, 1472, 1373, 1275, 1102, 982, 944 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 307.1424. $C_{14}H_{19}F_4N_2O$ requires $[M + H]^+$, 307.1428.

***N*-(2,3,5,6-tetrafluoro-4-((hexadecyl(methyl)amino)methyl)phenyl)acetamide (5e)**



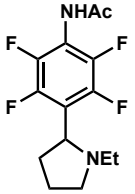
Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *N*,*N*-dimethylhexadecan-1-amine (**4e**) following General Procedure 1. Title compound **5e** was formed in 21% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **5e** (+ co-eluting starting material **3a**) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (bs, 1H), 3.72 (s, 2H), 2.42 (t, J = 7.5 Hz, 2H), 2.25 (s, 6H), 1.53 (t, J = 6.6 Hz, 2H), 1.28 (s, 24H), 0.90 (t, J = 7.1 Hz, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –139.5, (s, 0.35F), –142.3 (s, 1.65F), –145.7 (s, 0.3F), –146.1 (s, 1.7F) ppm; 4 signals observed (rotamers present).
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 145.5 (d, J = 247 Hz), 142.1 (d, J = 250 Hz), 115.4, 111.8, 61.0, 57.2, 48.1, 41.8, 41.5, 31.9, 29.69, 29.67, 29.66, 29.63, 29.61, 29.56, 29.47, 29.44, 29.36, 27.3, 22.7, 14.1 ppm.

***N*-(2,3,5,6-Tetrafluoro-4-(1-methylpyrrolidin-2-yl)phenyl)acetamide (5f)**



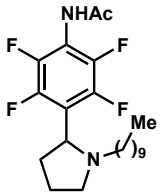
Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *N*-methylpyrrolidine (**4f**) following General Procedure 1. Title compound **5f** was formed in 26% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→60% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **5f** as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (bs, 1H), 3.66 (t, J = 8.3 Hz, 1H), 3.22 (t, J = 8.3 Hz, 1H), 2.31 (q, J = 8.8 Hz, 1H), 2.27 (s, 3H), 2.24–2.16 (complex m, 4H), 2.14–2.06 (complex m, 2H), 1.88 (m, 1H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –143.5 (s, 2F), –146.4 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 145.5 (d, J = 249 Hz), 142.4 (d, J = 249 Hz), 119.3, 115.5 (t, J = 14 Hz), 60.4, 57.3, 40.8, 30.7, 23.6 ppm.
IR (NaCl) 3257, 2975, 2792, 1684, 1525, 1501, 1478, 1373, 1277, 1034, 1002, 985, 937 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 290 (M^+, 25), 84 (100).

***N*-(4-(1-Ethylpyrrolidin-2-yl)-2,3,5,6-tetrafluorophenyl)acetamide (5g)**



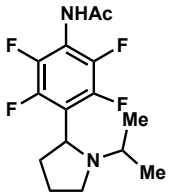
Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *N*-ethylpyrrolidine (**4g**) following General Procedure 1. Title compound **5g** was formed in 34% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→60% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **5g** (+ co-eluting starting material **3a**) as a colorless solid.
^1H NMR (600 MHz, $CDCl_3$) δ 7.67 (bs, 1H), 3.81 (t, J = 7.6 Hz, 1H), 3.29 (t, J = 7.6 Hz, 1H), 2.60 (m, 1H), 2.31-2.13 (complex m, 6H), 2.07 (m, 2H), 1.87 (m, 1H), 1.02 (t, J = 7.3 Hz, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –143.3 (s, 2F), –146.7 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 145.4 (d, J = 247 Hz), 142.2 (d, J = 250 Hz), 120.3, 114.6 (t, J = 14 Hz), 58.9, 53.5, 48.6, 30.6, 23.4, 13.4 ppm.
IR (NaCl) 3254, 3218, 1684, 1652, 1540, 1506, 1471, 1370, 1276, 1149, 1090, 1000, 984, 923 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 304 (M^+, 15), 289 (100), 218 (55), 178 (35), 98 (60).

_N_-(4-(1-Decylpyrrolidin-2-yl)-2,3,5,6-tetrafluorophenyl)acetamide (5h)



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *N*-decylpyrrolidine (**4h**) following General Procedure 1. Title compound **5h** was formed in 50% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 10→60% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **5h** as a colorless solid.
^1H NMR (600 MHz, $CDCl_3$) δ 7.01 (bs, 1H), 3.70 (t, J = 7.6 Hz, 1H), 3.20 (t, J = 8.2 Hz, 1H), 2.39 (m, 1H), 2.21–2.04 (complex m, 6H), 1.97 (m, 2H), 1.77 (d, J = 9.1 Hz, 1H), 1.31 (quin, J = 6.7 Hz, 2H), 1.23–1.07 (complex m, 14H), 0.80 (t, J = 7.5 Hz, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –143.2 (s, 2F), –146.8 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.3, 145.5 (d, J = 249 Hz), 142.2 (d, J = 250 Hz), 120.6, 114.5, 59.2, 54.9, 53.9, 31.9, 30.7, 29.57, 29.56, 29.4, 29.3, 28.6, 27.4, 23.5, 22.7, 14.1 ppm.
IR (NaCl) 3225, 2927, 2855, 2793, 1683, 1652, 1531, 1501, 1475, 1456, 1277, 1147, 1093, 997, 983 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 416 (M^+, 2), 289 (100), 218 (24), 178 (14).

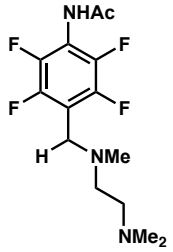
_N_-(2,3,5,6-Tetrafluoro-4-(1-isopropylpyrrolidin-2-yl)phenyl)acetamide (5i)



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (400 μmol) and *N*-isopropylpyrrolidine (**4i**) following General Procedure 1. Title compound **5i** was formed in 17% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 30→60% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **5i** (+ co-eluting starting material **3a**) as a colorless solid.

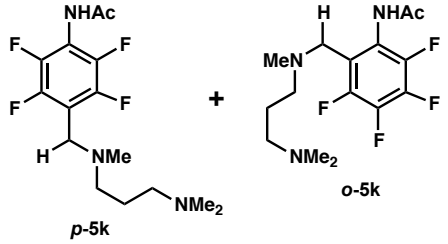
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (bs, 1H), 4.20 (t, J = 6.9 Hz, 1H), 3.10 (t, J = 8.3 Hz, 1H), 2.79 (quin, J = 6.5 Hz, 1H), 2.60 (q, J = 7.9 Hz, 1H), 2.25-2.13 (complex m, 4H), 2.02 (m, 2H), 1.82 (m, 1H), 1.02 (d, J = 6.6 Hz, 3H), 0.96 (d, J = 6.3 Hz, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –143.6 (s, 2F), –146.8 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 145.3 (d, J = 247 Hz), 142.3 (d, J = 250 Hz), 121.6, 114.5 (t, J = 14 Hz), 54.5, 50.0, 47.4, 31.6, 23.8, 21.5, 16.0 ppm.
IR (NaCl) 3242, 2970, 2937, 1684, 1521, 1501, 1476, 1456, 1277, 992,cm^{-1}.
EIMS (*m/z*, relative intensity) 318 (M^+, 10), 303 (100), 218 (70), 178 (20).

***N*-(4-(((2-(Dimethylamino)ethyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenyl)acetamide (5j)**



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and TMEDA (**4j**) following General Procedure 1 {Gd(OTf)$_3$ not added}. Title compound **5j** was formed in 67% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was dissolved in CH_2Cl_2 (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH_2Cl_2 (3x 10 mL) then treated with K_2CO_3 (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH_2Cl_2 (3x 10 mL) to provide a sample of product **5j** as a pale yellow solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (bs, 1H), 3.65 (s, 2H), 2.49 (t, J = 7.0 Hz, 2H), 2.42 (t, J = 6.3 Hz, 2H), 2.21 (s, 6H), 2.16 (s, 3H), 2.12 (s, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.7 (s, 2F), –145.9 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 145.4 (d, J = 245 Hz), 142.2 (d, J = 250 Hz), 115.9 (t, J = 14 Hz), 113.8 (t, J = 18 Hz), 57.0, 54.5, 48.4, 45.5, 41.5, 22.7 ppm.
IR (NaCl) 3200, 2951, 2826, 1700, 1481, 1371, 1295, 1276, 1136, 1124, 1026, 910 cm^{-1}.
EIMS (*m/z*, relative intensity) 321 (M^+, 1), 263 (11), 178 (20), 58 (100).

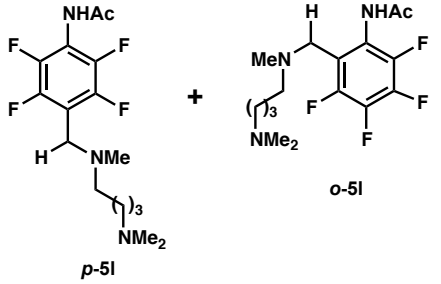
***N*-(4-(((3-(Dimethylamino)propyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenyl)acetamide (*p*-5k)**



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *N*,*N*,*N*',*N*'-tetramethylpropane-1,3-diamine (**4k**) following General Procedure 1 {Gd(OTf)$_3$ not added}. Compound ***p*-5k** was formed in 60% yield (average of two experiments) and compound ***o*-5k** was formed in 6% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was dissolved in CH_2Cl_2 (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH_2Cl_2 (3x 10 mL) then treated with K_2CO_3 (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH_2Cl_2 (3x 10 mL) to provide a sample of product ***p*-5k** (which contained traces of compound ***o*-5k**) as a pale yellow solid.

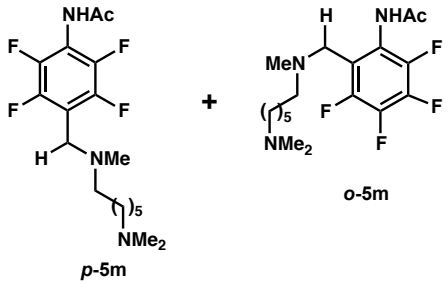
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (bs, 1H), 3.66 (s, 1.5H), 3.60 (s, 0.5H) 2.41 (t, J = 7.3 Hz, 2H), 2.31 (t, J = 7.7 Hz, 2H), 2.22 (s, 6H), 2.19 (s, 6H), 1.67 (t, J = 7.4 Hz, 2H) ppm; 8 signals observed (rotamers present).
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.9 (s, 1.5F), –143.3 (s, 0.5F) –146.1 (s, 1.5F), –146.3 (s, 0.5F) ppm; 4 signals observed (rotamers present).
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 145.4 (d, J = 246 Hz), 142.2 (d, J = 251 Hz), 115.8 (t, J = 14 Hz), 114.3 (t, J = 17 Hz), 57.6, 55.1, 48.0, 45.3, 41.5, 25.4, 22.7 ppm.
IR (NaCl) 3205, 2450, 2793, 1688, 1527, 1483, 1371, 1295, 1277, 1124, 1029, 910 cm^{-1}.
EIMS (*m/z*, relative intensity) 335 (M$^+$, 1), 263 (5), 178 (25), 115 (30), 58 (100).

***N*-(4-(((2-(Dimethylamino)butyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenyl)acetamide (5l)**



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *N*,*N*,*N*',*N*'-tetramethylbutane-1,4-diamine (**4l**) following General Procedure 1 {$Gd(OTf)_3$ not added}. Compound ***p*-5l** was formed in 45% yield (average of two experiments) and compound ***o*-5l** was formed in 3% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was dissolved in CH_2Cl_2 (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH_2Cl_2 (3x 10 mL) then treated with K_2CO_3 (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH_2Cl_2 (3x 10 mL) to provide a sample of product ***p*-5l** (which contained traces of compound ***o*-5l**) as a pale yellow solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (bs, 1H), 3.67 (s, 2H), 2.40 (t, J = 6.5 Hz, 2H), 2.31 (m, 2H), 2.24 (s, 3H), 2.21 (s, 6H), 2.19 (s, 3H), 1.50 (m, 4H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –139.8 (s, 0.7H), –142.8 (s, 1.3F), –145.6 (s, 0.7F), –146.1 (s, 1.4F) ppm; 4 signals observed (rotamers present).
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 145.5 (d, J = 247 Hz), 142.2 (d, J = 250 Hz), 115.6, 114.5, 60.8, 59.5, 59.4, 56.8, 48.1, 45.3, 45.1, 41.8, 41.5, 28.8, 25.2, 25.0, 22.8 ppm.
IR (NaCl) 3199, 2947, 2865, 1680, 1516, 1501, 1371, 1275, 1126, 1029, 909 cm^{-1}.
EIMS (*m/z*, relative intensity) 349 (M$^+$, 1), 284 (6), 221 (10), 71 (100).

***N*-(4-(((2-(Dimethylamino)hexyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenyl)acetamide (5m)**



Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (500 μmol) and *N*,*N*,*N*',*N*'-tetramethylhexane-1,6-diamine (**4m**) following General Procedure 1 {$Gd(OTf)_3$ not added}. Compound ***p*-5m** was formed in 65% yield (average of two experiments) and compound ***o*-5m** was formed in 7% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The

ensuing residue obtained from the reaction mixture was dissolved in CH_2Cl_2 (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH_2Cl_2 (3x 10 mL) then treated with K_2CO_3 (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH_2Cl_2 (3x 10 mL) to provide a sample of product ***p*-5m** (which contained traces of compound ***o*-5m**) as a pale yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (bs, 1H), 3.68 (s, 2H), 2.39 (t, J = 7.4 Hz, 2H), 2.29 (m, 2H), 2.27 (s, 6H), 2.24 (s, 3H), 2.23 (s, 3H), 1.46 (m, 4H), 1.29 (m, 4H) ppm.

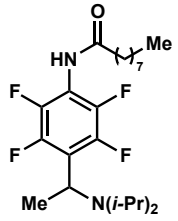
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.8 (s, 2F), –146.2 (s, 2F) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 145.5 (d, J = 247 Hz), 142.3 (d, J = 250 Hz), 115.7 (t, J = 16 Hz), 114.8 (t, J = 17 Hz), 59.6, 56.7, 48.3, 45.1, 41.9, 27.33, 27.29, 27.2, 27.1 ppm.

IR (NaCl) 3209, 2939, 2859, 1679, 1525, 1476, 1448, 1274, 1030 cm^{-1}.

EIMS (*m*/*z*, relative intensity) 377 (M^+, 1), 178 (26), 157 (12), 126 (19), 112 (38) 58 (100).

***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)nonanamide (7a)**



7a

Reaction between *N*-(pentafluorophenyl)nonanamide (**6a**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Title compound **7a** was formed in 63% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **7a** (+ co-eluting starting material **6a**) as a colorless solid.

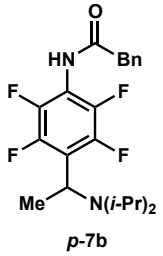
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (bs, 1H), 4.65 (q, J = 7.2 Hz, 1H), 3.36 (sept, J = 6.7 Hz, 2H), 2.43 (t, J = 7.2 Hz, 2H), 1.73 (quin, J = 7.4 Hz, 3H), 1.51 (d, J = 7.1 Hz, 3H), 1.30 (complex m, 15 H), 1.12 (d, J = 6.6 Hz, 6H), 0.94 (d, J = 6.6 Hz, 6H), 0.90 (t, J = 6.6 Hz, 5H) ppm; 44 protons observed (starting material present).

^{19}F NMR (376 MHz, $CDCl_3$) δ –142.3 (d, J = 12 Hz, 2F), –146.6 (d, J = 22 Hz, 2F) ppm.

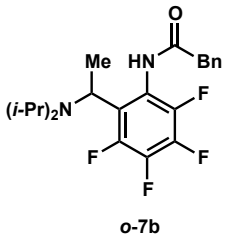
^{13}C NMR (150 MHz, $CDCl_3$) δ 171.9, 145.0 (d, J = 241 Hz), 142.3 (d, J = 253 Hz), 124.5, 113.8 (t, J = 14 Hz), 46.1, 45.8, 31.9, 29.4, 29.3, 29.2, 25.6, 22.81, 22.76, 22.6, 19.8, 14.2 ppm.

HRESIMS Found: $[M + H]^+$, 433.2840. $C_{23}H_{37}F_4N_2O$ requires $[M + H]^+$, 433.2837.

***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-2-phenylacetamide (*p*-7b) & *N*-(2-(1-(Diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenyl)-2-phenylacetamide (*o*-7b)**



***p*-7b**

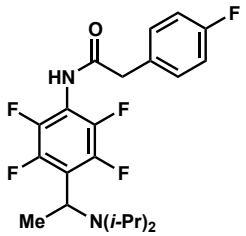


***o*-7b**

Reaction between *N*-(pentafluorophenyl)-2-phenylacetamide (**6b**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Compound ***p*-7b** was formed in 80% yield (average of two experiments) and compound ***o*-7b** was formed in 5% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1%

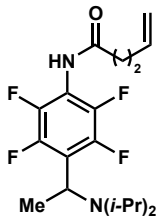
NEt_3 was present in the eluent) to provide compound ***p*-7b** as a colorless solid (which contained traces of compound ***o*-7b**).
^1H NMR (600 MHz, $CDCl_3$) δ 7.31–7.21 (complex m, 5H), 6.94 (bs, 1H), 4.54 (q, J = 7.1 Hz, 1H), 3.69 (s, 2H), 3.25 (sept, J = 6.7 Hz, 2H), 1.39 (d, J = 7.5 Hz, 3H), 1.01 (d, J = 7.0 Hz, 6H), 0.82 (d, J = 7.0 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –124.8 (s, 0.13F), –135.9 (d, J = 22Hz, 0.13F), –141.0 (d, J = 20 Hz, 0.13F), –142.2 (d, J = 13 Hz, 2F), –146.5 (d, J = 24 Hz, 2F), –164.3 (td, J = 21, 8.4 Hz, 0.12F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 144.8 (d, J = 243 Hz), 142.2 (d, J = 250 Hz), 134.0, 129.4, 129.2, 127.8, 124.6 (t, J = 17 Hz), 113.6 (t, J = 15 Hz), 45.9, 45.6, 43.4, 22.7, 22.4, 19.6 ppm.
IR (NaCl) 2927, 2854, 1733, 1514, 1450, 1357, 1287, 1163, 1092, 996 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 411.2045. $C_{22}H_{27}F_4N_2O$ requires $[M + H]^+$, 411.2060.

***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-2-(4-fluorophenyl)acetamide (7c)**



Reaction between 2-(4-fluorophenyl)-*N*-(pentafluorophenyl)acetamide (**6c**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Title compound **7c** was formed in 86% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→20% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **7c** as a colorless solid.
^1H NMR (600 MHz, $CDCl_3$) δ 7.34 (t, J = 5.7 Hz, 2H), 7.09 (t, J = 8.8 Hz, 2H), 6.92 (bs, 1H), 4.65 (q, J = 8.0 Hz, 1H), 3.78 (s, 2H), 3.35 (sept, J = 7.0 Hz. 2H), 1.50 (d, J = 6.8 Hz, 3H), 1.11 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.8 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –114.4 (s, 1F), –142.1 (s, 2F), –146.5 (d, J = 13 Hz, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 163.2, 161.5, 144.8 (d, J = 245 Hz), 142.3 (d, J = 250 Hz), 131.1 (d, J = 8 Hz), 129.7 (d, J = 3 Hz), 124.8 (t, J = 16 Hz), 116.1 (d, J = 21 Hz), 113.4 (t, J = 15 Hz), 46.0, 45.7, 42.5, 22.7, 22.4, 19.6 ppm.
IR (NaCl) 3245, 2971, 2936, 1675, 1648, 1511, 1476, 1197, 1228, 1158, 1005, 948, 839 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 428 (M^+, 3), 413 (20), 192 (83), 109 (50), 86 (100).

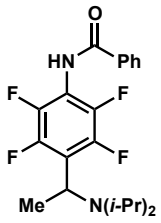
***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)pent-4-enamide (7d)**



Reaction between *N*-(pentafluorophenyl)pent-4-enamide (**6d**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Title compound **7d** was formed in 64% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **7d** as a colorless solid.

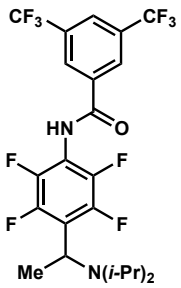
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (bs, 1H), 5.82 (m, 1H), 5.07 (d, J = 17 Hz, 1H), 5.01 (d, J = 9.8 Hz, 1H), 4.56 (q, J = 7.3 Hz, 1H), 3.28 (sept, J = 6.7 Hz, 2H), 2.51–2.40 (complex m, 4H), 1.42 (d, J = 7.4 Hz, 3H), 1.03 (d, J = 6.8 Hz, 6H), 0.86 (d, J = 6.8 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.2 (bs, 2F), –146.5 (d, J = 24Hz, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 144.8 (d, J = 245 Hz), 142.1 (d, J = 250 Hz), 136.4, 124.5 (t, J = 16 Hz), 116.3, 113.6 (t, J = 14 Hz), 46.0, 45.7, 35.5, 29.3, 22.7, 22.4, 19.7 ppm.
IR (ATR) 2971, 1671, 1524, 1476, 1399, 1363, 1290, 1212, 1152, 1084, 1004, 944, 914 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 375.2055. $C_{19}H_{27}F_4N_2O$ requires $[M + H]^+$, 375.2054.

***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)benzamide (7e)**



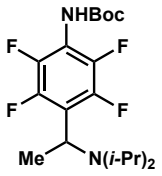
Reaction between *N*-(pentafluorophenyl)benzamide (**6e**) (557 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution; 1% NEt_3 was also present in the eluent) to provide title compound **7e** as a colorless solid (102 mg, 46% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.7 Hz, 2H), 7.62 (bs, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 4.78 (q, J = 6.4 Hz, 1H), 3.28 (sept, J = 6.7 Hz, 2H), 1.43 (d, J = 7.3 Hz, 3H), 1.03 (d, J = 6.6 Hz, 6H), 0.86 (d, J = 6.6 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.1 (d, J = 21 Hz, 2F), –146.3 (d, J = 21 Hz, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 144.9 (d, J = 245 Hz), 142.3 (d, J = 251 Hz), 132.8, 132.6, 128.8, 127.7, 124.4 (t, J = 17 Hz), 114.0 (t, J = 15 Hz), 16.0, 45.7, 22.7, 19.7 ppm.
IR (ATR) 3299, 2968, 1672, 1466, 972 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 397.1900. $C_{21}H_{25}F_4N_2O$ requires $[M + H]^+$, 397.1898.

***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-3,5-bis(trifluoromethyl)benzamide (7f)**



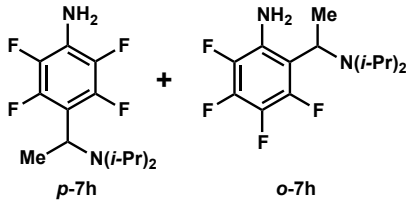
Reaction with *N*-(Pentafluorophenyl)-3,5-bis(trifluoromethyl)benzamide (**6f**) (40 μmol), following the General Procedure 1. Title compound **7f** was formed in 25% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.
^{19}F NMR (564 MHz, $CDCl_3$) δ –63.5 (s, 6F), –140.1 (quin, J = 11 Hz, 2F), –145.8 (m, 2F) ppm.
EIMS (*m/z,* relative intensity) 532 (M^+, 3), 517 (27), 432 (19), 241 (68), 213 (14), 86 (100).
HREIMS Found: M^+, 532.1580. $C_{23}H_{22}F_{10}N_2O$ requires M^+, 532.1572.

***tert*-Butyl (4-(1-(diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)carbamate (7g)**



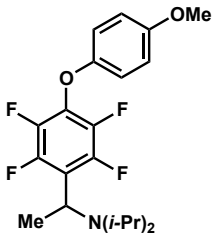
Reaction between *tert*-butyl (pentafluorophenyl)carbamate (**6g**) (326 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→15% EtOAc/hexane elution; 1% NEt_3 was present in the eluent) to provide title compound **7g** as a colorless solid (110 mg, 86% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.00 (bs, 1H), 4.65 (q, J = 7.2 Hz, 1H), 3.37 (sept, J = 6.6 Hz, 2H), 1.53 (s, 9H), 1.51 (d, J = 7.3 Hz, 3H), 1.12 (d, J = 6.5 Hz, 6H), 0.95 (d, J = 6.9 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.5 (dd, J = 22.4, 9.1 Hz, 2F), –148.1 (dd, J = 22.4, 9.6 Hz, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 152.3, 144.8 (d, J = 244 Hz), 142.2 (d, J = 249 Hz), 123.6 (t, J = 18Hz), 114.5 (t, J = 16 Hz), 81.9, 45.9, 45.6, 28.1, 22.6, 22.5, 19.7 ppm.
IR (ATR) 3272, 2972, 1711, 1524, 1475, 1298, 1154, 960, 951, 858 cm^{-1}.
HRESIMS Found: $[M + H]^+$, 393.2157. $C_{19}H_{29}F_4N_2O_2$ requires $[M + H]^+$, 393.2160.

4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenylamine (*p*-7h)
& 2-(1-(Diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenylamine (*o*-7h)



Reaction between pentafluoroaniline (**6h**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→15% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide title compounds **7h** as a colorless oil (90 mg, 1.4:1 mixture of ***p*-7h** : ***o*-7h**, 62% yield).
4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenylamine (*p*-7h)
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.46 (q, J = 7.3 Hz, 1H), 3.75 (bs, 2H), 3.25 (sept, J = 6.6 Hz, 2H), 1.39 (d, J = 7.2 Hz, 3H), 1.02 (d, J = 6.7 Hz, 6H), 0.85 (d, J = 6.8 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –144.1 (d, J = 22 Hz, 2F), –162.4 (d, J = 23 Hz, 2F) ppm.
HRESIMS Found: $[M + H]^+$, 293.1634. $C_{14}H_{21}F_4N_2$ requires $[M + H]^+$, 293.1635.

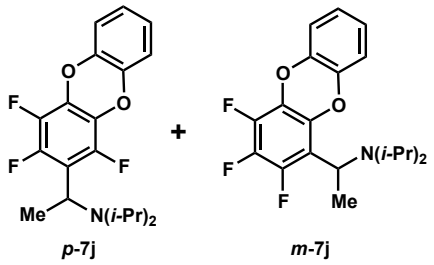
***N*-Isopropyl-N-(1-(2,3,5,6-tetrafluoro-4-(4-methoxyphenoxy)phenyl)ethyl)propan-2-amine (7i)**



Reaction between 1,2,3,4,5-pentafluoro-6-(4-methoxyphenoxy)benzene (**6i**) (400 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Title compound **7i** was formed in 28% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of product **7i** (+ co-eluting starting material **6i**) as a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (m, 2H), 6.77 (m, 2H), 4.57 (q, J = 7.4 Hz, 1H), 3.70 (s, 3H), 3.28 (sept, J = 6.8 Hz, 2H), 2.45 (d, J = 7.4 Hz, 3H), 1.04 (d, J = 6.8 Hz, 6H), 0.87 (d, J = 6.8 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –142.6 (d, J = 22 Hz, 2F), –156.5 (d, J = 24 Hz, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 151.4, 145.2 (d, J = 246 Hz), 141.5 (d, J = 253 Hz), 132.2 (t, J = 13 Hz), 121.9 (t, J = 17 Hz), 55.7, 45.9, 45.7, 22.7, 22.4, 19.8 ppm.
HRESIMS Found: $[M + H]^+$, 400.1890. $C_{21}H_{25}F_4NO_2$ requires $[M + H]^+$, 400.1894.

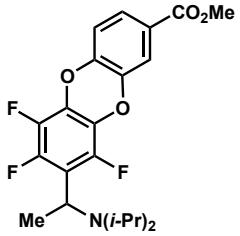
_N_-Isopropyl-_N_-(1-(1,3,4-trifluorodibenzo[_b,e_][1,4]dioxin-2-yl)ethyl)propan-2-amine (_p_-7j) & _N_-Isopropyl-_N_-(1-(2,3,4-trifluorodibenzo[_b,e_][1,4]dioxin-1-yl)ethyl)propan-2-amine (_m_-7j)



p-7j *m*-7j

Reaction between 1,2,3,4-tetrafluorodibenzo[*b*,*e*][1,4]dioxine (**6j**) (400 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Compound ***p*-7j** was formed in 48% yield (average of two experiments) and compound ***m*-7j** was formed in 9% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→15% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of compound ***p*-7j** (which contained traces of compound ***m*-7j**) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90–6.81 (m, 4H), 4.58 (q, J = 7.3 Hz, 1H), 3.37 (sept, J = 6.8 Hz, 2H), 1.50 (d, J = 7.0 Hz, 3H), 1.12 (d, J = 6.7 Hz, 6H), 0.97 (d, J = 6.6 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –141.2 (d, J = 9.5 Hz, 1F), –144.2 (d, J = 23 Hz, 1F),–163.9 (dd, J = 23, 9.8 Hz, 1F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 145.5 (d, J = 237 Hz), 144.7 (d, J = 242 Hz), 141.0 (d, J = 62 Hz), 138.7 (d, J = 250 Hz), 136.9 (J = 250 Hz), 131.0 (t, J = 4.9 Hz), 124.8 (d, J = 34 Hz), 119.3 (td, J = 17, 2.6 Hz), 116.8 (d, J = 11 Hz), 45.7, 45.6, 22.9, 22.5, 20.0 ppm; 14 signals observed.
HRESIMS Found: $[M + H]^+$, 366.1670. $C_{20}H_{23}F_3NO_2$ requires $[M + H]^+$, 366.1675.

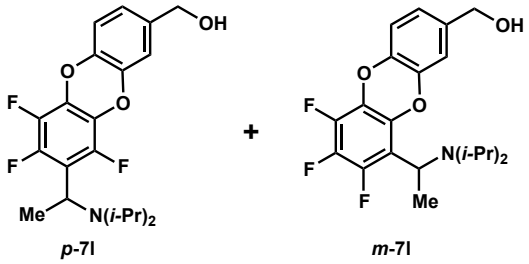
Methyl 8-(1-(diisopropylamino)ethyl)-6,7,9-trifluorodibenzo[_b,e_][1,4]dioxine-2-carboxylate (7k)



Reaction between methyl 6,7,8,9-tetrafluorodibenzo[*b*,*e*][1,4]dioxine-2-carboxylate (**6k**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Title compound **7k** was formed in 71% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of title compound **7k** as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70–7.67 (m, 1H), 7.65–7.63 (m, 1H), 7.02–6.97 (m, 1H), 4.58 (qd, J = 7.20, 2.00 Hz, 1H), 3.91 (s, 3H), 3.36 (sept, J = 6.69 Hz, 2H), 1.50 (d, J = 7.2 Hz, 3H), 1.12 (d, J = 6.7 Hz, 6H), 0.97 (d, J = 6.8 Hz, 6H) ppm.

^{19}F NMR (564 MHz, $CDCl_3$) δ –141.3 (d, J = 29 Hz, 1F), –144.3 (dd, J = 223, 22 Hz, 1F), –164.4 (t, J = 26 Hz, 1F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 145.0 (d, J = 244 Hz), 144.4, 143.9 (d, J = 244 Hz), 140.5, 136.3 (d, J = 249 Hz), 130.3 (dt, J = 12.7, 4.8 Hz), 127.1, 126.8, 119.8 (td, J = 17, 2.5 Hz), 118.3, 117.1 (dd, J = 233, 16 Hz), 116.7, 52.3, 45.7, 45.6, 22.7, 22.5, 19.9 ppm.
HRESIMS Found: $[M + H]^+$, 424.1729. $C_{22}H_{25}F_3NO_4$ requires $[M + H]^+$, 424.1730.

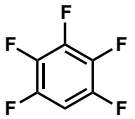
(8-(1-(Diisopropylamino)ethyl)-6,7,9-trifluorodibenzo[*b*,*e*][1,4]dioxin-2-yl)methanol (*p*-7l)
(9-(1-(Diisopropylamino)ethyl)-6,7,8-trifluorodibenzo[*b*,*e*][1,4]dioxin-2-yl)methanol (*m*-7l)



p-7l *m*-7l

Reaction between (6,7,8,9-tetrafluorodibenzo[*b*,*e*][1,4]dioxin-2-yl)methanol (**6l**) (500 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Compound ***p*-7l** was formed in 53% yield (average of two experiments) and compound ***m*-7l** was formed in 9% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of compound ***p*-7l** (which contained traces of compound ***m*-7l**) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01–6.86 (complex m, 3H), 4.62–4.55 (complex m, 3H), 3.36 (sept, J = 6.4 Hz, 2H), 2.15 (bs, 1H), 1.50 (d, J = 7.0 Hz, 3H), 1.12 (d, J = 6.7 Hz, 6H), 0.97 (d, J = 6.7 Hz, 6H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –141.1 (dd, J = 31, 9 Hz, 1F), –144.1 (dd, J = 23, 11 Hz, 1F), –163.8 (qd, J = 21, 9 Hz, 1F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7 (d, J = 242 Hz), 144.0 (d, J = 243 Hz), 140.7, 140.2, 140.0, 139.6, 138.1, 137.9, 136.3, (d, J = 247 Hz), 130.8 (m), 128.1 (dt, J = 18, 4 Hz), 123.0 (d, J = 36 Hz), 119.3 (t, J = 17 Hz), 116.1 (dd, J = 209, 10 Hz), 64.2, 45.63, 45.61, 22.7, 22.5, 20.0 ppm.
IR (NaCl) 3326, 2970, 2873, 1700, 1654, 1596, 1481, 1279, 1214, 1150, 1114, 1005, 988 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 395 (M^+, 6), 380 (28), 295 (65), 86 (100).

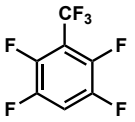
1,2,3,4,5-Pentafluorobenzene (9a)



Reaction with 1,2,3,4,5,6-hexafluorobenzene (**8a**) (500 μmol) following General Procedure 2. Title compound **9a** was formed in 85% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.[3]
^{19}F NMR (564 MHz, $CDCl_3$) δ –139.6 (quin, J = 11 Hz, 2F), –155.1 (t, J = 20 Hz, 1F), –163.2 (m, 2H) ppm.
EIMS (*m*/*z*, relative intensity) 168 (M^+, 13), 154 (14), 114 (63), 86 (100).
HREIMS Found: M^+, 168.0002. C_6HF_5 requires M^+, 167.9998.

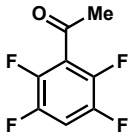
1,2,4,5-Tetrafluoro-3-(trifluoromethyl)benzene (9b)

3. Senaweera, S. M.; Singh, A.; Weaver, J. D. *J. Am. Chem. Soc.* **2014**, *136*, 3002.



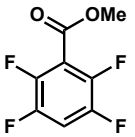
Reaction with 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (**8b**) (500 μmol) following General Procedure 2. Title compound **9b** was formed in 65% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.[3]
^{19}F NMR (564 MHz, $CDCl_3$) δ –57.0 (t, J = 23 Hz, 3F), –137.5 (m, 2H), –141.8 (m, 2H) ppm.
EIMS (*m/z*, relative intensity) 218 (M^+, 14), 189 (14), 114 (54), 86 (100).
HREIMS Found: M^+, 217.9969. C_7HF_7 requires M^+, 217.9966.

1-(2,3,5,6-Tetrafluorophenyl)ethenone (**9c**)



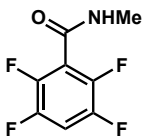
Reaction with 1-(pentafluorophenyl)ethanone (**8c**) (500 μmol) following General Procedure 2. Title compound **9c** was formed in 60% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.[3]
^{19}F NMR (564 MHz, $CDCl_3$) δ –138.8 (quin, J = 10 Hz, 2F), –143.2 (m, 2F) ppm.
EIMS (*m/z*, relative intensity) 192 (M^+, 41), 177 (100), 149 (59), 99 (43), 43 (86).
HREIMS Found: M^+, 192.0194. $C_8H_4F_4O$ requires M^+, 192.0198.

Methyl 2,3,5,6-tetrafluorobenzoate (**9d**)



Reaction with methyl 2,3,4,5,6-pentafluorobenzoate (**8d**) (500 μmol) following General Procedure 2. Title compound **9d** was formed in 83% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.[3]
^{19}F NMR (564 MHz, $CDCl_3$) δ –138.7 (m, 2F), –140.9 (m, 2F) ppm.
EIMS (*m/z*, relative intensity) 208 (M^+, 24), 177 (100), 149 (54), 99 (32).
HREIMS Found: M^+, 208.0142. $C_8H_4F_4O_2$ requires M^+, 208.0147.

2,3,5,6-Tetrafluoro-*N*-methylbenzamide (**9e**)

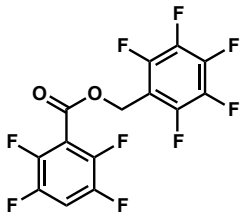


Reaction with 2,3,4,5,6-pentafluoro-*N*-methoxy-*N*-methylbenzamide (**8e**) (500 μmol) following General Procedure 2. Title compound **9e** was formed in 27% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.
^{19}F NMR (564 MHz, $CDCl_3$) δ –139.2 (quin, J = 10 Hz, 2F), –143.2 (m, 2F) ppm.
EIMS (*m/z*, relative intensity) 207 (M^+, 32), 188 (46), 177 (100), 149 (65), 99 (46), 58 (35).
HREIMS Found: M^+, 207.0301. $C_8H_5F_4N_1O_1$ requires M^+, 207.0307.

Phenyl 2,3,5,6-tetrafluorobenzoate (9f)

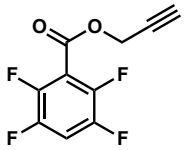
Reaction with phenyl 2,3,4,5,6-pentafluorobenzoate (**8f**) (500 μmol) following General Procedure 2. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution) to provide title compound **9f** (70 mg, 49% yield) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.44–7.37 (complex m, 3H), 7.22 (quin, J = 8.3 Hz, 1H), 5.45 (s, 2H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –137.4 (m, 2F), –139.2 (m, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 145.8 (d, J = 250 Hz), 144.6 (d, J = 257 Hz), 134.6, 128.72, 128.70, 128.4, 113.6 (t, J = 16 Hz), 108.8 (t, J = 22 Hz), 68.4 ppm.
IR (NaCl) 1739, 1501, 1456, 1391, 1297, 1192, 951 cm^{-1}.
EIMS (*m/z*, relative intensity) 284 (M^+, 30), 177 (40), 149 (13), 91 (100).

(Pentafluorophenyl)methyl 2,3,5,6-tetrafluorobenzoate (9g)



Reaction with (pentafluorophenyl)methyl 2,3,4,5,6-pentafluorobenzoate (**8g**) (500 μmol) following General Procedure 2. Title compound **9g** was formed in 35% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/ hexane elution) to provide a sample of title compound **9g** as a colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (quin, J = 8.0 Hz, 1H), 5.43 (s, 2H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –137.0 (m, 2F), –138.8 (m, 2F), –141.4 (dd, J = 21, 7 Hz, 2F), –151.3 (t, J = 20 Hz, 1F), –161.1 (m, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 145.9 (d, J = 250 Hz), 145.8 (d, J = 252 Hz), 144.5 (dt, J = 258, 4 Hz), 142.3 (d, J = 257 Hz), 137.5 (d, J = 253 Hz), 112.5 (t, J = 16 Hz), 109.3 (t, J = 23 Hz), 108.3 (td, J = 17, 4 Hz), 55.0 ppm.
IR (NaCl) 1748, 1525, 1506, 1313, 1295, 1190, 1133, 1059, 969, 939, 712 cm^{-1}.
EIMS (*m/z*, relative intensity) 374 (M^+, 22), 181 (100), 149 (22), 99 (27).
HREIMS Found: M^+, 374.0000. $C_{14}H_3F_9O_2$ requires M^+, 373.9989.

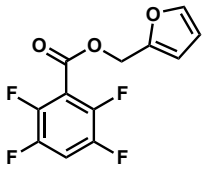
Prop-2-yn-1-yl 2,3,5,6-tetrafluorobenzoate (9h)



Reaction with prop-2-yn-1-yl 2,3,4,5,6-pentafluorobenzoate (**8h**) (500 μmol) following General Procedure 2. Title compound **9h** was formed in 43% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/

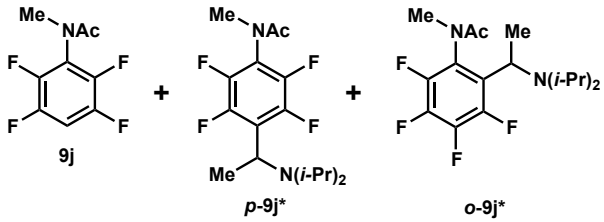
hexane elution) to provide a sample of title compound **9h** (+ co-eluting starting material **8h**) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (quin, J = 8.0 Hz, 1H), 4.98 (d, J = 2.74, 2H), 2.59 (t, J = 2.5 Hz, 1H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –137.3 (m, 2F), –138.9 (m, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.9, 145.9 (d, J = 251 Hz), 144.7 (d, J = 259 Hz), 112.7 (t, J = 16 Hz), 109.2 (t, J = 22 Hz), 76.1, 76.0, 53.8 ppm.
EIMS (*m/z*, relative intensity) 232 (M^+, 10), 177 (100), 149 (30), 99 (25).

Furan-2-ylmethyl 2,3,5,6-tetrafluorobenzoate (**9i**)



Reaction with furan-2-ylmethyl 2,3,4,5,6-pentafluorobenzoate (**8i**) (500 μmol) following General Procedure 2. Title compound **9i** was formed in 48% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/ hexane elution) to provide a sample of title compound **9i** (+ co-eluting starting material **8i**) as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, J = 1.8 Hz, 1H), 7.21 (quin, J = 8.1 Hz, 1H), 6.54 (t, J = 2.2 Hz, 1H), 6.42 (dd, J = 3.2, 1.9 Hz, 1H), 5.38 (s, 2H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –137.4 (m, 2F), –139.2 (m, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 148.2, 145.9 (d, J = 250 Hz), 144.5 (d, J = 260 Hz), 143.8, 113.3 (t, J = 16 Hz), 111.6, 110.7, 108.8 (t, J = 22 Hz), 59.9 ppm.
EIMS (*m/z*, relative intensity) 274 (M^+, 20), 177 (15), 81 (100).

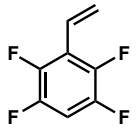
***N*-Methyl-*N*-(2,3,5,6-tetrafluorophenyl)acetamide** (**9j**)
& *N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-*N*-methylacetamide (***p*-9j***) **& *N*-(2-(1-(diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenyl)-*N*-methylacetamide** (***o*-9j***)



Reaction with *N*-methyl-*N*-(pentafluorophenyl)acetamide (**8j**) (500 μmol) following General Procedure 2. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→20% EtOAc/hexane elution; 1% NEt_3 was present in the eluent) to provide hydrodefluorination product **9j** as a colorless solid (49 mg, 44% yield) and a colorless solid (17 mg, 10% yield; 3.7:1 mixture of ***p*-9j*** and ***o*-9j***).
***N*-Methyl-*N*-(2,3,5,6-tetrafluorophenyl)acetamide** (**9j**)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07(quin, J = 8.8 Hz, 0.8H), 6.98 (quin, J = 8.8 Hz, 0.2H), 3.29 (s, 0.5H), 3.16 (s, 2.5H), 2.25 (s, 0.5H), 1.86 (s, 2.5H) ppm; 6 signals observed (rotamers present).
^{19}F NMR (564 MHz, $CDCl_3$) δ –137.3 (quin, J = 10 Hz, 1.7F), –139.0 (quin, J = 10 Hz, 0.3F), –145.5 (m, 0.3F), –146.2 (m, 1.7F) ppm; 4 signals observed (rotamers present).
^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 170.1, 146.1 (d, J = 248 Hz), 143.3 (d, J = 250 Hz), 124.0 (t, J = 15 Hz), 106.0 (t, J = 22 Hz), 105.0 (t, J = 22 Hz), 38.4, 35.7, 21.5, 21.1 ppm; 11 signals observed (rotamers present).
HRESIMS Found: $[M + H]^+$, 222.0539. $C_9H_8F_4NO$ requires $[M + H]^+$, 222.0537.

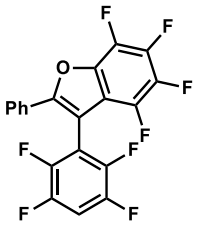
***N*-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-*N*-methylacetamide (*p*-9j*) & *N*-(2-(1-(diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenyl)-*N*-methylacetamide (*o*-9j*)**
HRESIMS Found: $[M + H]^+$, 349.1898. $C_{17}H_{25}F_4N_2O$ requires $[M + H]^+$, 349.1898.

1,2,4,5-Tetrafluoro-3-vinylbenzene (9k)



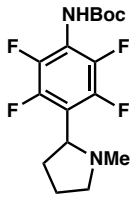
Reaction with 1,2,3,4,5-pentafluoro-6-vinylbenzene (**8k**) (500 μmol) following General Procedure 2. Title compound **9k** was formed in 14% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.
^{19}F NMR (564 MHz, $CDCl_3$) δ –141.4 (quin, J = 11 Hz, 2F), –146.2 (m, 2F) ppm.
EIMS (*m*/*z*, relative intensity) 176 (M^+, 3), 132 (14), 90 (100), 43 (19).
HREIMS Found: M^+, 176.0244. $C_8H_4F_4$ requires M^+, 176.0249.

4,5,7-Trifluoro-3-(pentafluorophenyl)-2-phenylbenzofuran (9l)



Reaction with 4,5,6,7-tetrafluoro-3-(pentafluorophenyl)-2-phenylbenzofuran (**8l**) (100 μmol) following General Procedure 2 (this reaction was performed in a 2:1 MeCN/ DMF solution). Title compound **9l** was formed in 24% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.
^{19}F NMR (564 MHz, $CDCl_3$) δ –137.7 (m, 2F), –138.3 (m, 2F), –152.1 (m, 1F), –159.8 (t, J = 20 Hz, 1F), –161.2 (t, J = 19 Hz, 1F), –162.7 (t, J = 20 Hz, 1F) ppm.
EIMS (*m*/*z*, relative intensity) 414 (M^+, 100), 394 (50), 197 (20).

Figure 3B: *tert*-Butyl (2,3,5,6-tetrafluoro-4-(1-methylpyrrolidin-2-yl)phenyl)carbamate (10)

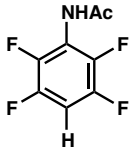


Reaction between *tert*-butyl (pentafluorophenyl)carbamate (**6g**) (1 mmol) and *N*-methylpyrrolidine (**4i**) following General Procedure 1. Title compound **10** was formed in 31% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of compound **10** as a colorless solid.
^1H NMR (600 MHz, $CDCl_3$) δ 6.42 (bs, 1H), 3.66 (dd, J = 9.0, 7.3 Hz, 1H), 3.26 (t, J = 7.6 Hz, 1H), 2.32–2.26 (complex m, 4H), 2.19 (m, 1H), 2.12 (m, 2H), 1.88 (dd, J = 15.7, 9.8 Hz, 1H), 1.52 (s, 9H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –144.0 (dd, J = 21, 9 Hz, 2F), –147.9 (dd, J = 22, 11 Hz, 2F) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.3, 145.5 (d, J = 247 Hz), 142.2 (d, J = 249 Hz), 118.5 (t, J = 14 Hz), 115.8 (t, J = 14 Hz), 82.0, 60.3, 57.3, 40.9, 30.7, 28.1, 23.7 ppm.
IR (NaCl) 3279, 2979, 2734, 1713, 1653, 1520, 1501, 1481, 1368, 1303, 1248, 1159, 974 cm^{-1}.
EIMS (*m*/*z*, relative intensity) 348 (M^+, 15), 291 (8), 247 (7), 57 (100).

Figure 3C
In a nitrogen-filled glovebox, MeCN (150 μL) was added to $[Cu(MeCN)_4]PF_6$ (2.8 mg, 7.5 μmol) and Xantphos (4.3 mg, 7.5 μmol) and the ensuing solution was magnetically stirred. After 2 h, a MeCN solution (40 μL) of bathocuproine (2.7 mg, 7.5 μmol) was added. After 1 h, this solution was added to a 20-mL screw-top vial (PTFE tape-lined thread) containing *N*-(pentafluorophenyl)acetamide (**3a**) (113 mg, 500 μmol), *i*-Pr_2NEt (**4a**) (129 mg, 1.00 mmol), and $Gd(OTf)_3$ (121 mg, 200 μmol) in MeCN (3.66 mL), and a stir bar. The vial was then capped, the joint was wrapped with PARAFILM®, and removed from the glovebox and placed in a water bath (suspended with Cu wire) maintained at 45 °C that was contained within a 18 W blue LED photoreactor (switched off) and magnetically stirred (Figure S2). The vial was then irradiated (25% duty cycle at 100 kHz). After 24 h, the reaction mixture was quenched by exposure to air. Compound **5a** was formed in 39% yield (average of two experiments) as determined via ^{19}F NMR with the aid of a calibrated internal standard.

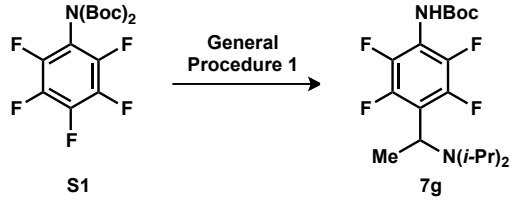
Figure 3D: *N*-(2,3,5,6-Tetrafluorophenyl)acetamide (13)



Reaction between *N*-(4-bromo-2,3,5,6-tetrafluorophenyl)acetamide (**12**) (472 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. Compound **13**) was formed in 54% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.[4] The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_3 was present in the eluent) to provide a sample of compound **13** and starting material as a colorless solid.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (bs, 1H), 7.00 (quin, J = 8.3 Hz, 1H), 2.23 (s, 3H) ppm.
^{19}F NMR (564 MHz, $CDCl_3$) δ –139.2 (s, 2F), –145.5 (s, 2F) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 145.9 (d, J = 247 Hz), 142.2 (d, J = 248 Hz), 116.8 (t, J = 13 Hz), 103.9 (t, J = 23 Hz), 22.8 ppm.
EIMS (*m*/*z*, relative intensity) 207 (M^+, 2), 165 (100), 137 (12).

V. Additional Experiments & Tables

Alternative Synthesis of Compound 7g from Substrate S1



S1 7g

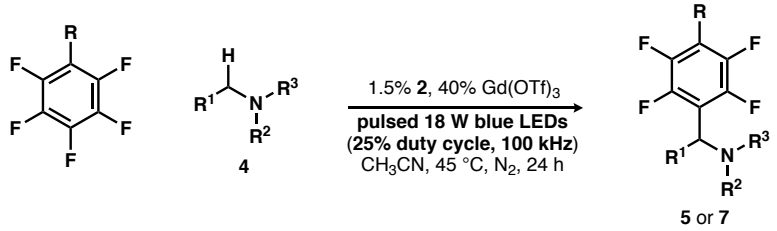
Reaction between compound **S1** (400 μmol) and *i*-Pr_2NEt (**4a**) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica

4. Van Zandt, M. C.; Jones, M. L.; Gunn, D. E.; Geraci, L. S.; Jones, J. H.; Sawicki, D. R.; Sredy, J.; Jacot, J. L.; DiCioccio, A. T.; Petrova, T.; Mitschler, A.; Podjarn, A. D. *J. Med. Chem.* **2005**, *48*, 3141.

gel, 0→10% EtOAc/hexane elution; 1% NEt_3 was present in the eluent) to provide title compound **7g** as a colorless solid (102 mg, 61% yield).

TEMPO Experiment (50% TEMPO)
Reaction between *N*-(pentafluorophenyl)acetamide (**3a**) (400 μmol), *i*-Pr_2NEt (**4a**), and TEMPO (200 μmol) following General Procedure 1. Compound **5a** was formed in 8% yield and substrate **3a** was present in 85% yield (average of two experiments) as determined via ^{19}F NMR spectroscopy with the aid of a calibrated internal standard.

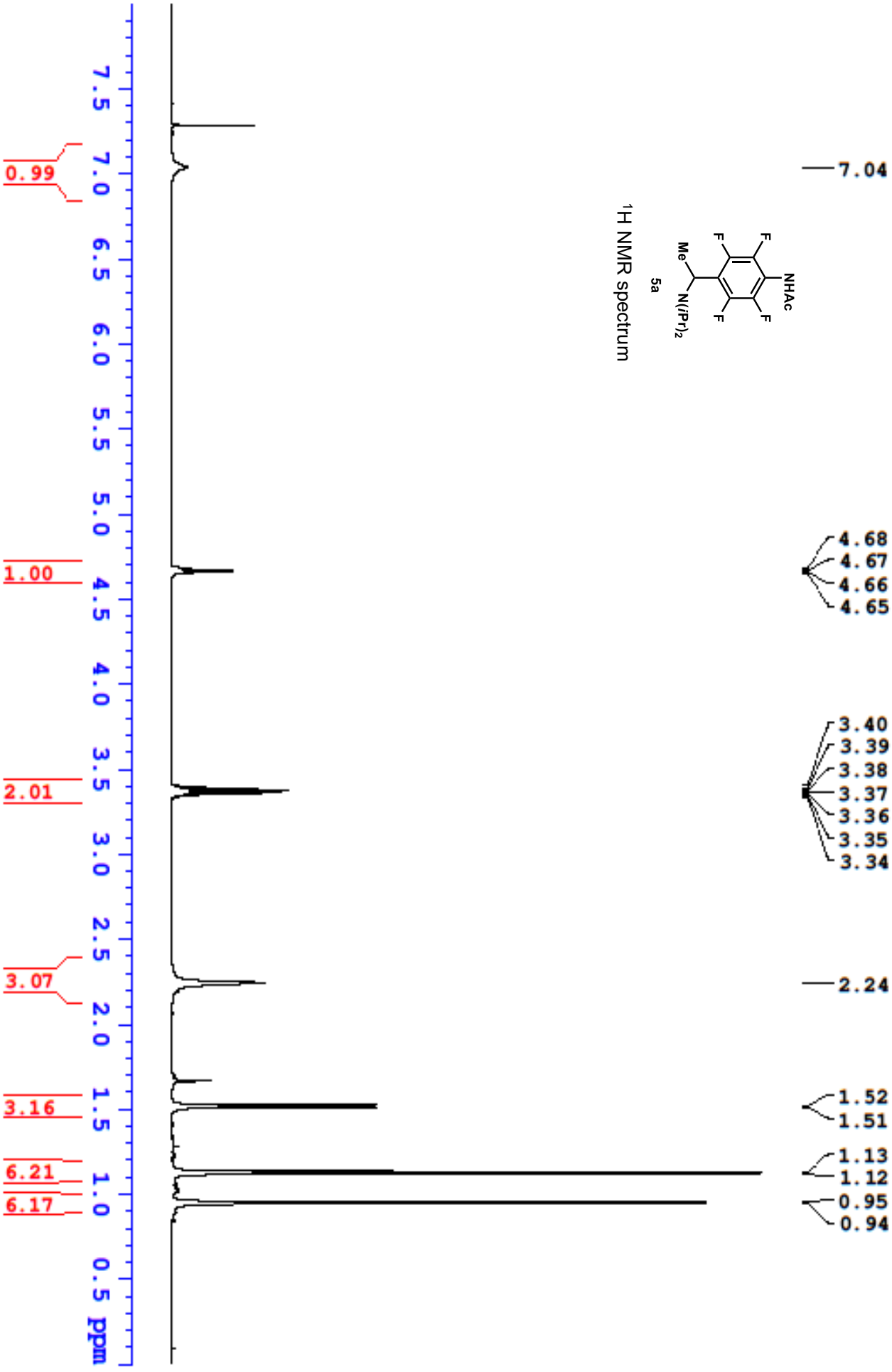
Table S1. Summary of product yields in reactions shown in Figure 3: comparison of product yields employing pulsed irradiation and conventional irradiation.

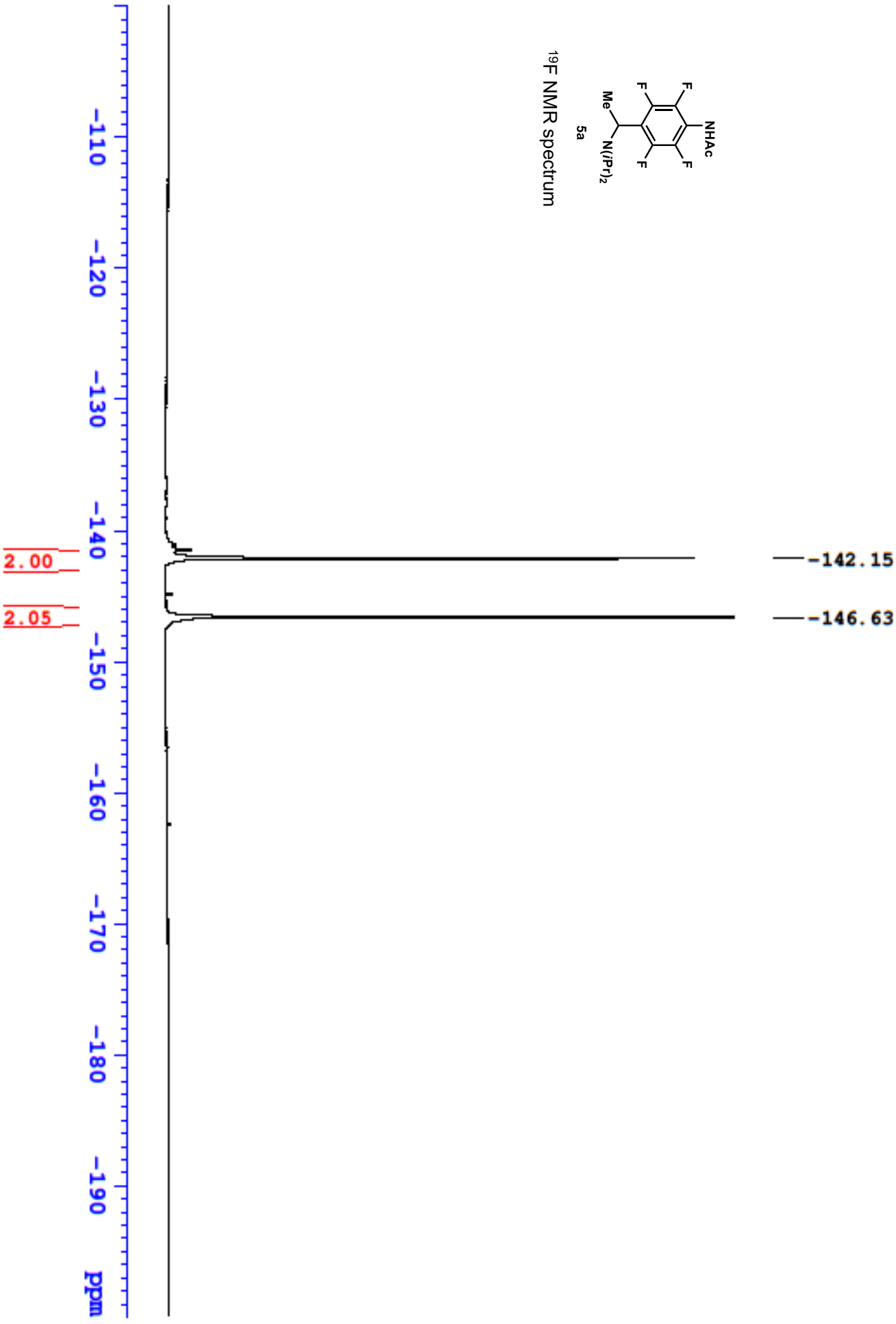


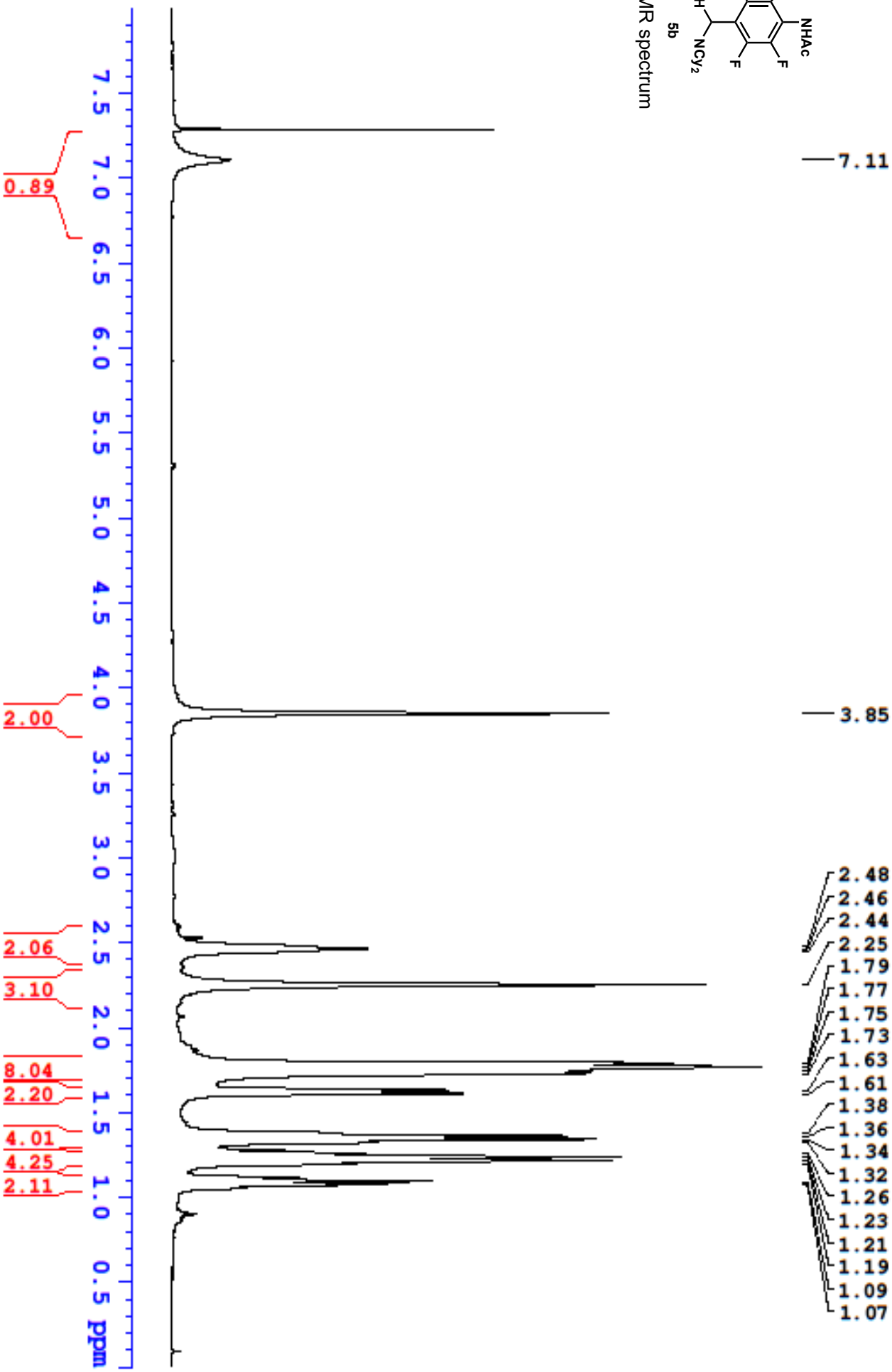
Product	Yield Employing Pulsed Blue LED Irradiation (%)	Yield Employing Conventional Blue LED Irradiation (%)
5a	87	54[a]
5b	57	34[a]
5d	66[a,b]	70[a,b]
5e	21[a]	16[a]
5f	26[a]	13[a]
5g	34[a]	15[a]
5h	50[a]	32[a]
5j	67[a,b]	30[a,b]
5k	60[a,b] (***p*-5k**); 6[a,b] (***o*-5k**)	31[a,b] (***p*-5k**); 2[a,b] (***o*-5k**)
5l	45[a,b] (***p*-5l**); 3[a,b] (***o*-5l**)	43[a,b] (***p*-5l**); 4[a,b] (***o*-5l**)
5m	65[a,b] (***p*-5m**); 7[a,b] (***o*-5m**)	63[a,b] (***p*-5m**); 6[a,b] (***o*-5m**)
7a	63[a]	35[a]
7b	80[a] (***p*-7b**); 5[a] (***o*-7b**)	43[a] (***p*-7b**); <2[a] (***o*-7b**)
7c	86[a]	44[a]
7d	64[a]	41[a]
7g	86[a]	50[a]
7h	62 (1.4:1 ***p*-7h**:***o*-7h**)	6[a] (***p*-7h**); 4[a] (***o*-7h**)
7i	28[a]	24[a]
7j	48[a] (***p*-7j**); 9[a] (***m*-7j**)	39[a] (***p*-7j**); 2[a] (***m*-7j**)
7k	71[a]	36[a]
7l	53[a] (***p*-7l**); 9[a] (***m*-7l**)	31[a] (***p*-7l**); 4[a] (***m*-7l**)

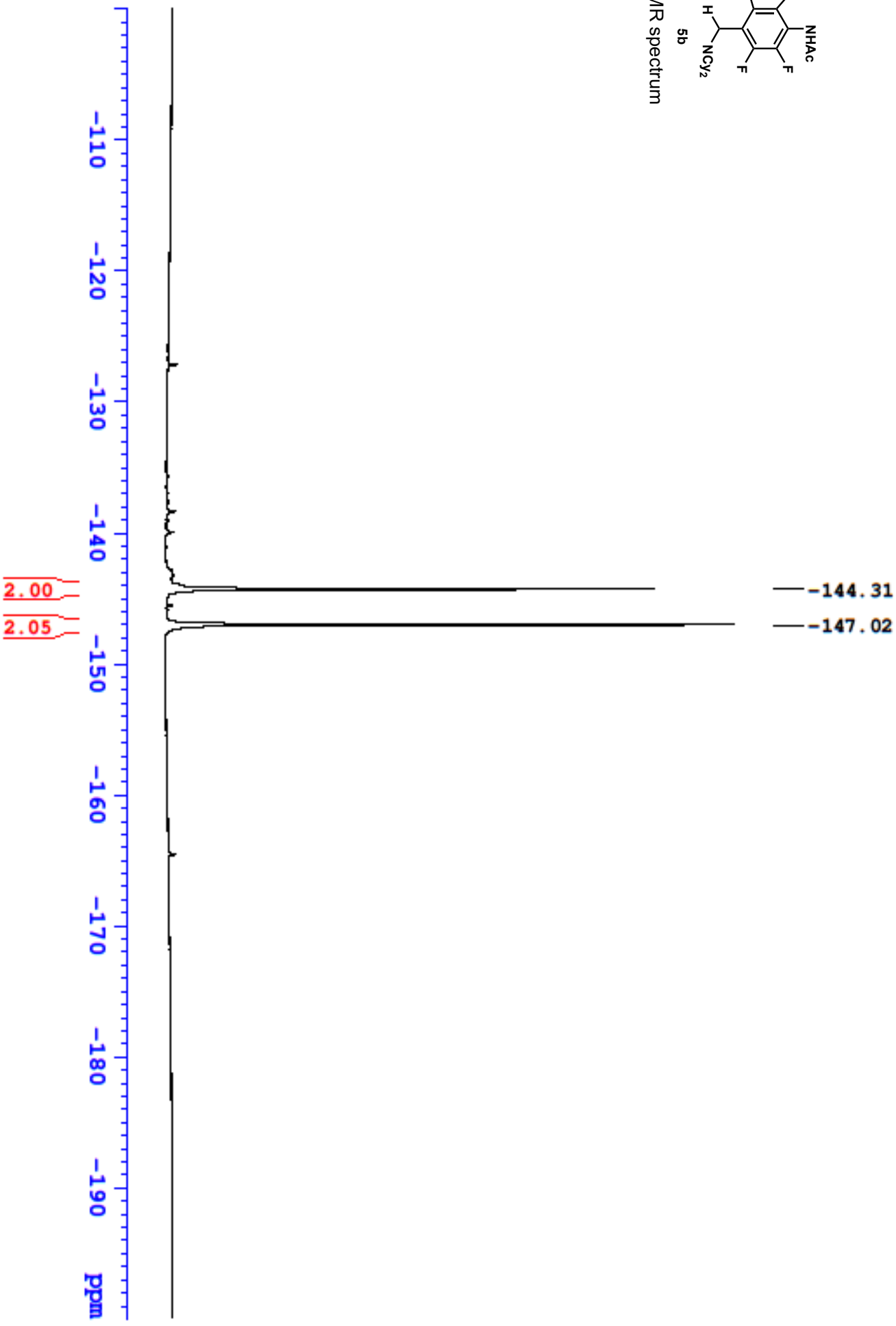
[a]Determined by ^{19}F NMR spectroscopy with the aid of a calibrated internal standard (average of 2 experiments). [b]Reaction performed in the absence of $Gd(OTf)_3$.

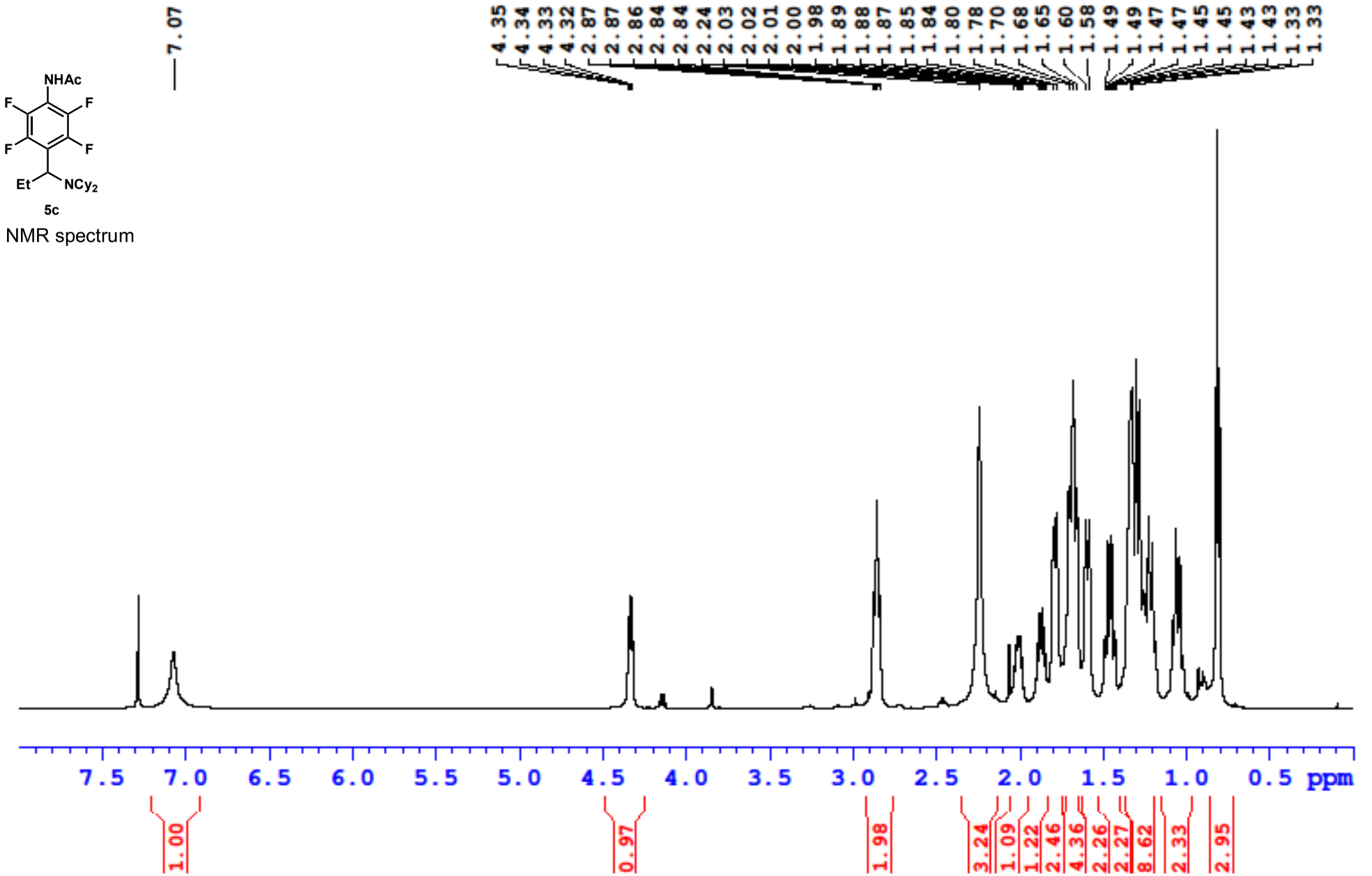
VI. ^{1}H & ^{19}F NMR Spectra



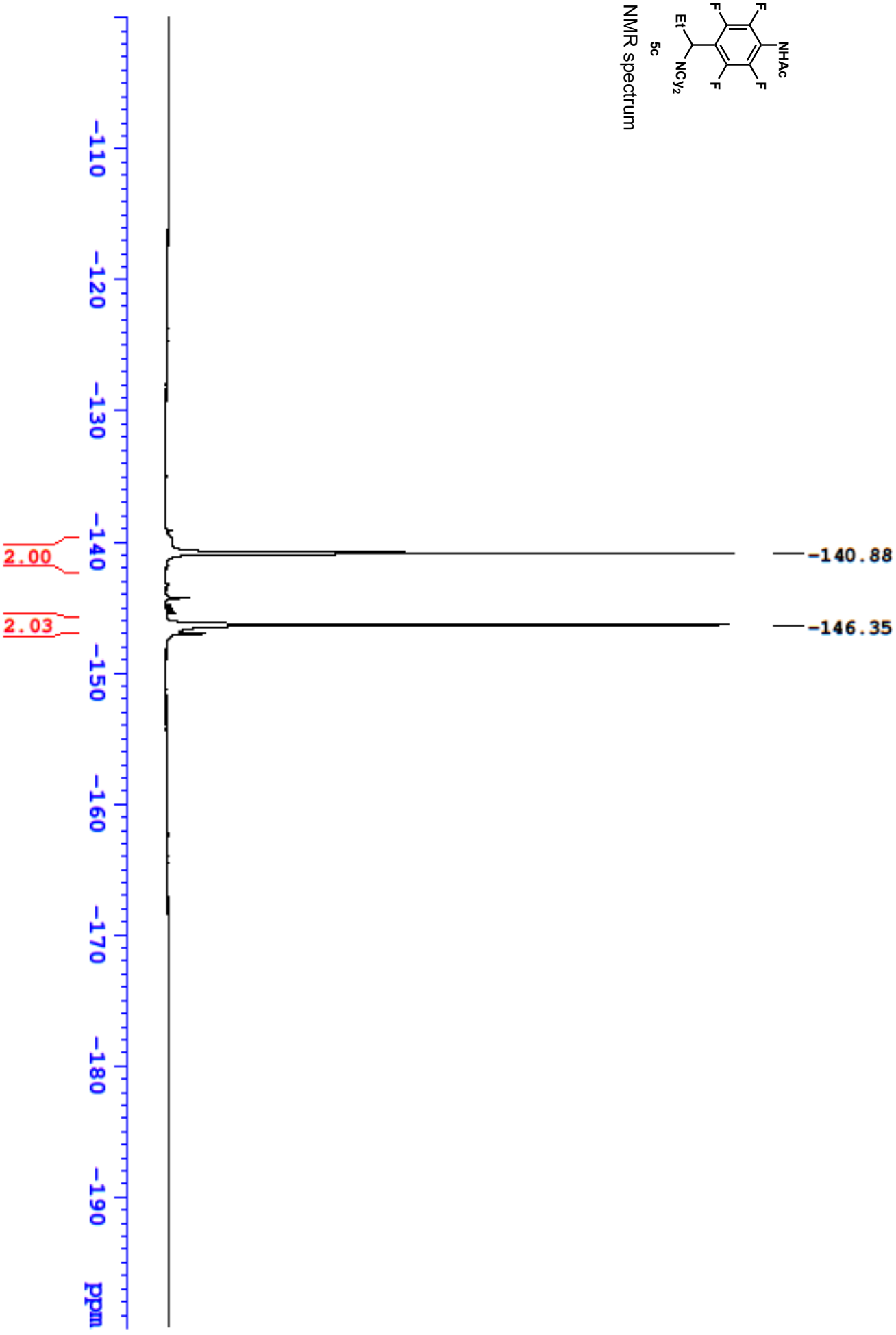

19F NMR spectrum
5a
Me
N(iPr)2
F
F
F
F
NHAc
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.00
2.05
-142.15
-146.63

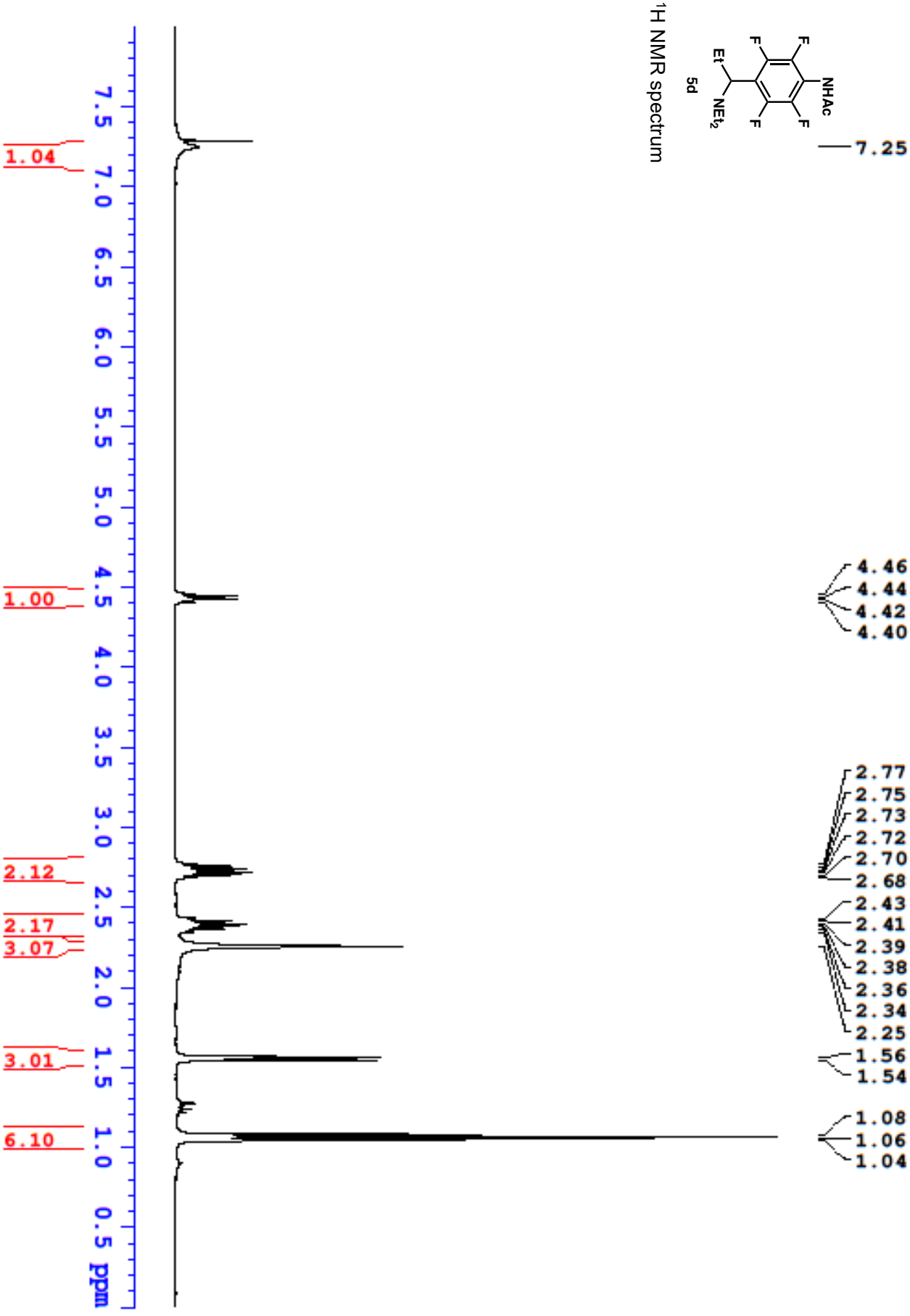

^{1}H NMR spectrum
5b
NHAc
NCy$_2$
F
H
7.11
3.85
2.48
2.46
2.44
2.25
1.79
1.77
1.75
1.73
1.63
1.61
1.38
1.36
1.34
1.32
1.26
1.23
1.21
1.19
1.09
1.07
0.89
2.00
2.06
3.10
8.04
2.20
4.01
4.25
2.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

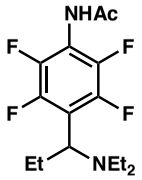

19F NMR spectrum
5b
F
F
NHAc
H
NCy2
F
F
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.00
2.05
-144.31
-147.02



^{1}H NMR spectrum

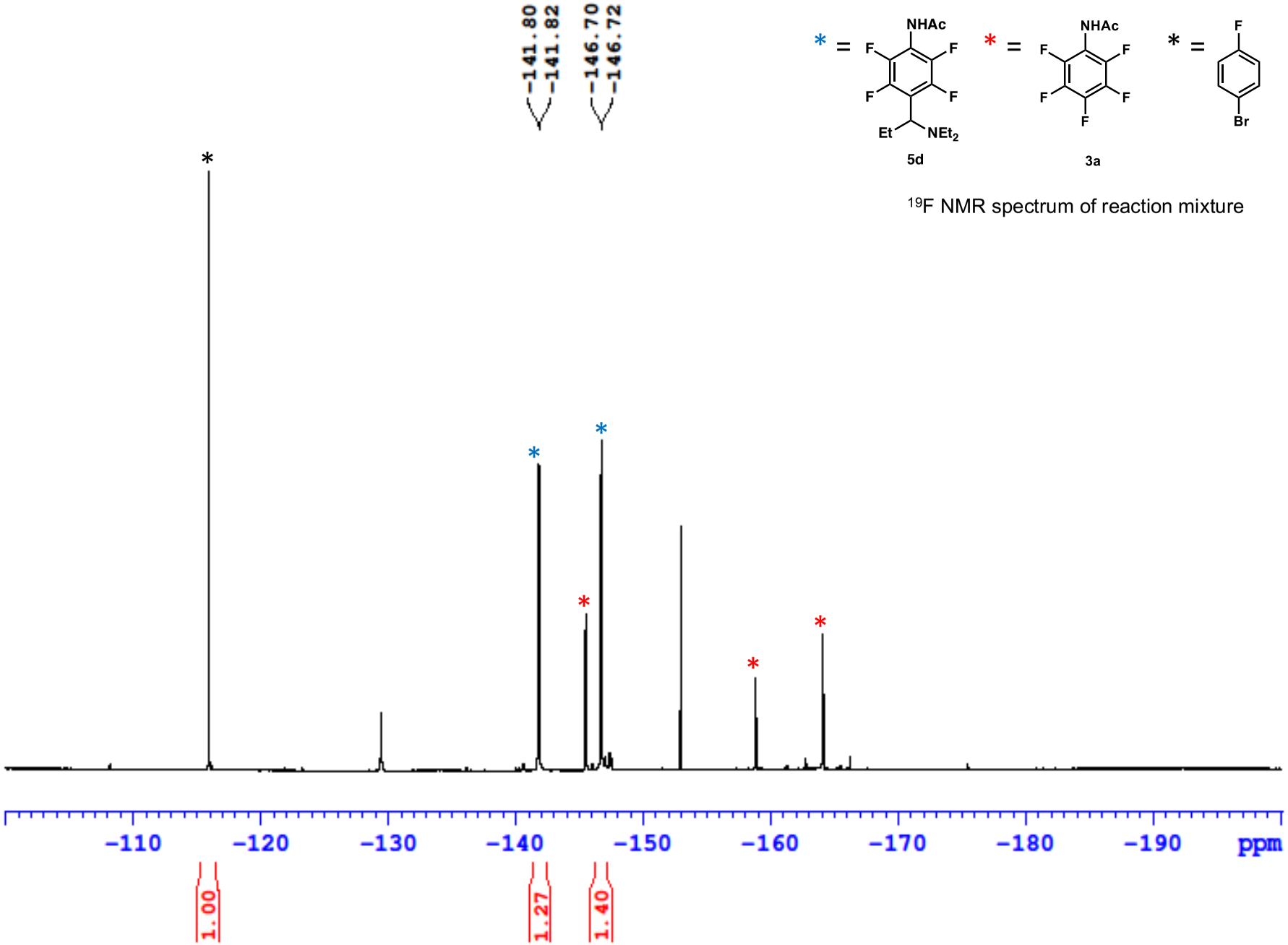

19F NMR spectrum
5c
F
F
Et
NHAc
NCy2
F
F
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.00
2.03
-140.88
-146.35


1H NMR spectrum
5d
Et
NEt2
F
F
F
F
NHAc
7.25
4.46
4.44
4.42
4.40
2.77
2.75
2.73
2.72
2.70
2.68
2.43
2.41
2.39
2.38
2.36
2.34
2.25
1.56
1.54
1.08
1.06
1.04
1.04
1.00
2.12
2.17
3.07
3.01
6.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

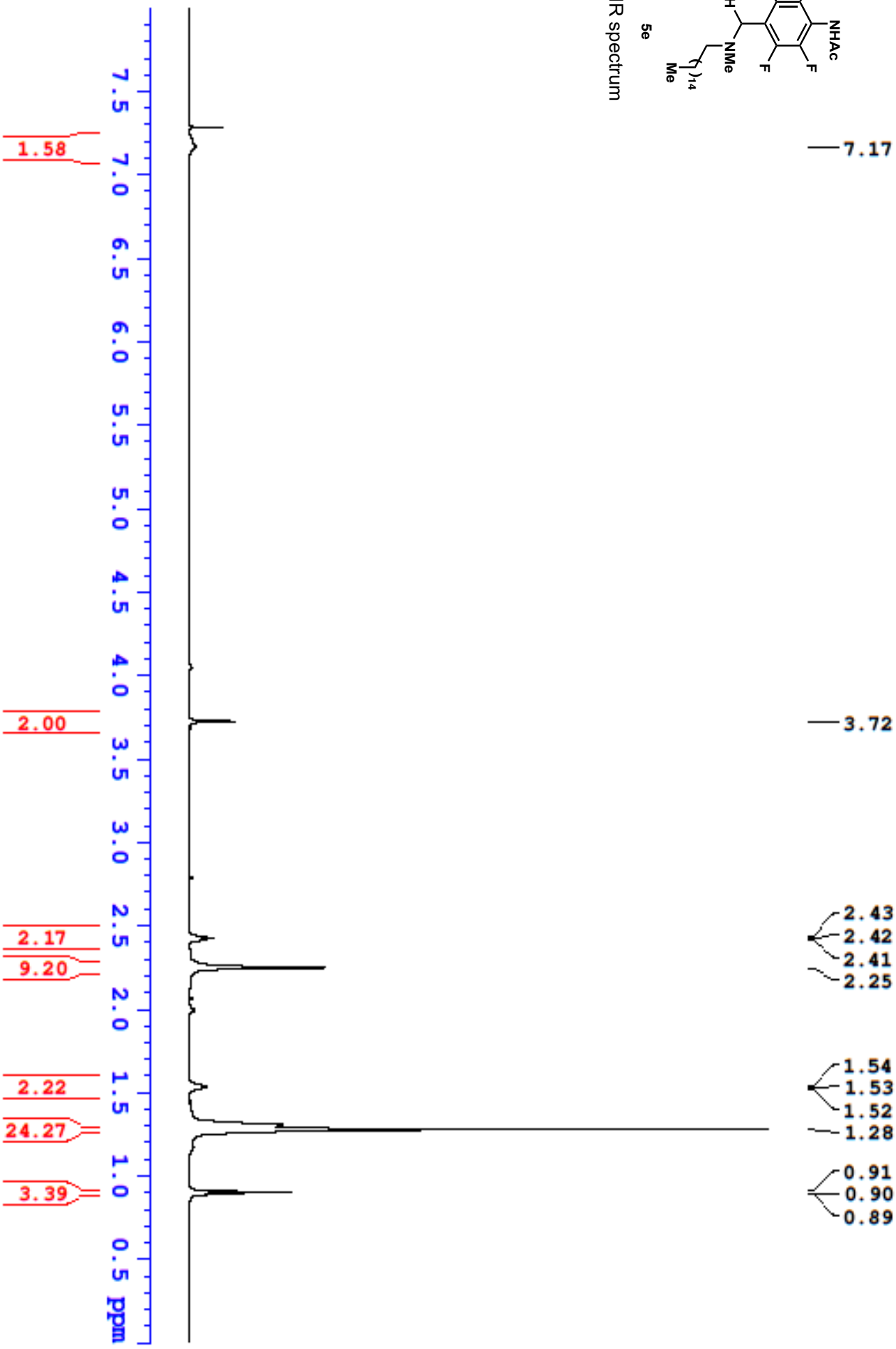


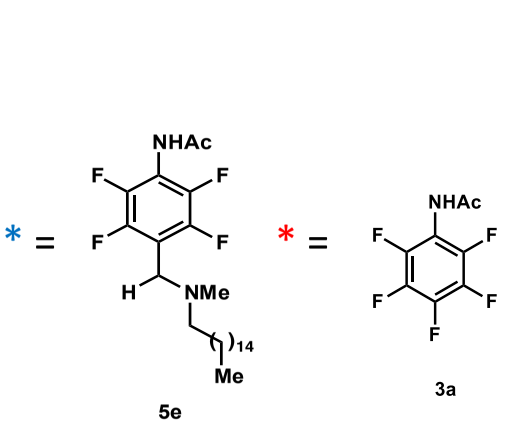
5d

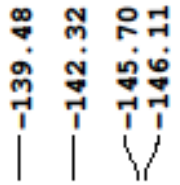
^{19}F NMR spectrum



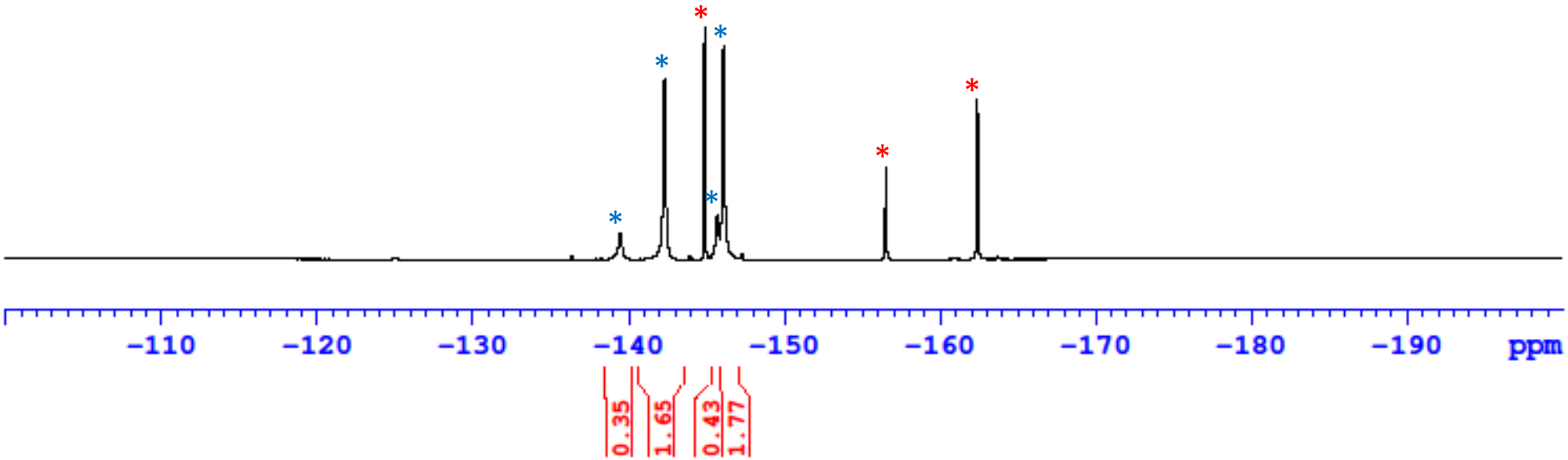
^{19}F NMR spectrum of reaction mixture

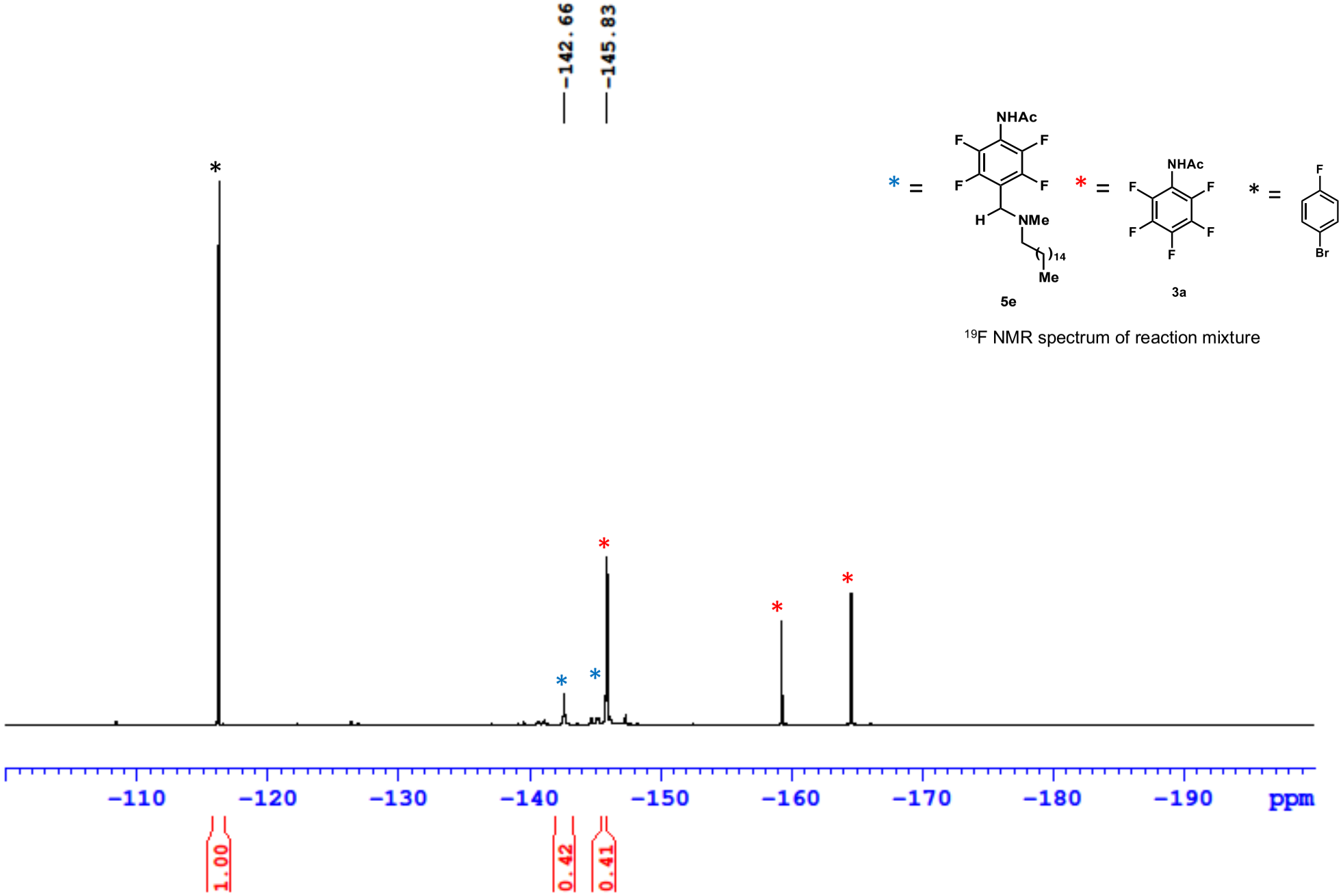

5e
^{1}H NMR spectrum
7.17
3.72
2.43
2.42
2.41
2.25
1.54
1.53
1.52
1.28
0.91
0.90
0.89
1.58
2.00
2.17
9.20
2.22
24.27
3.39
ppm



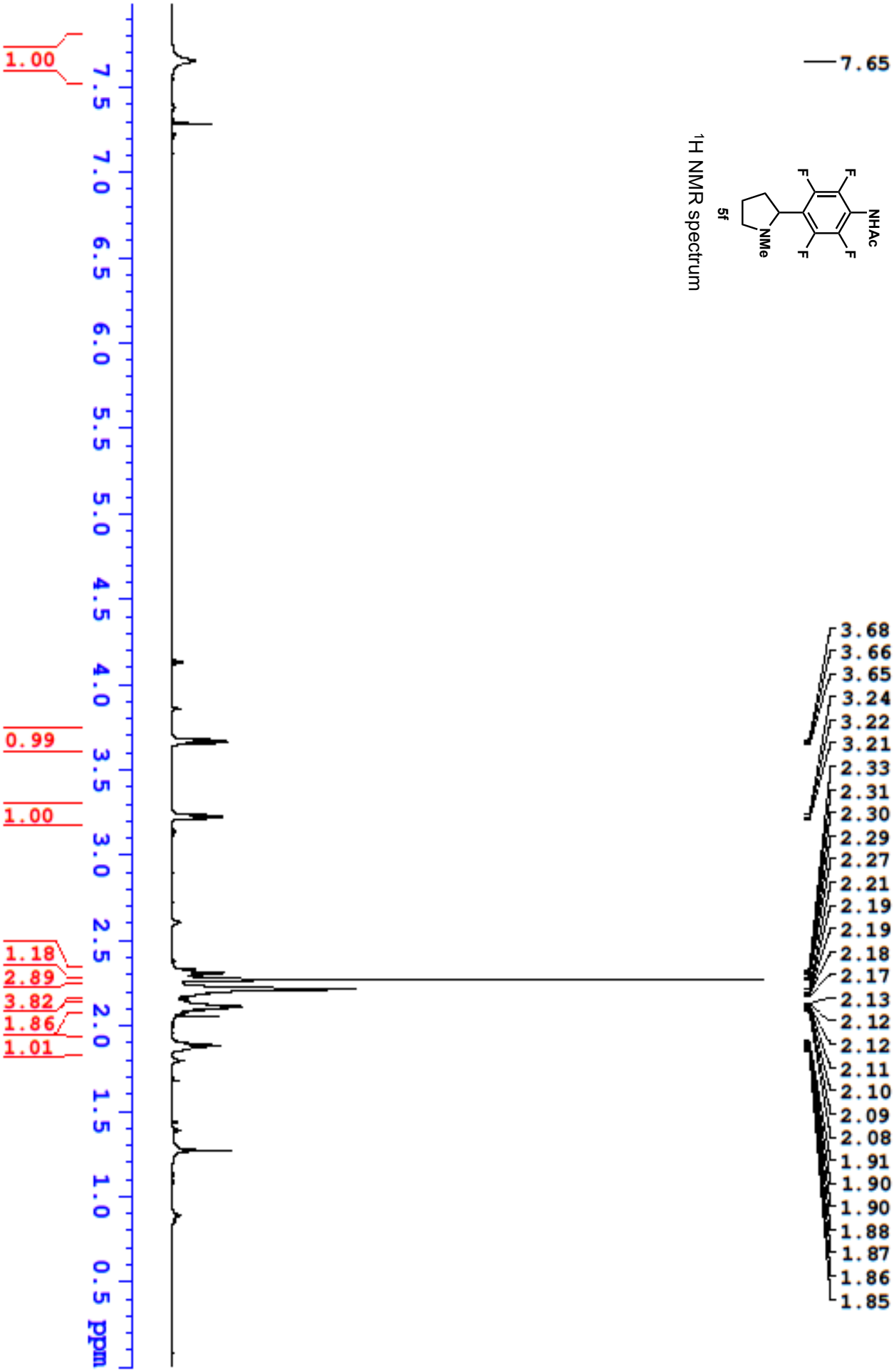


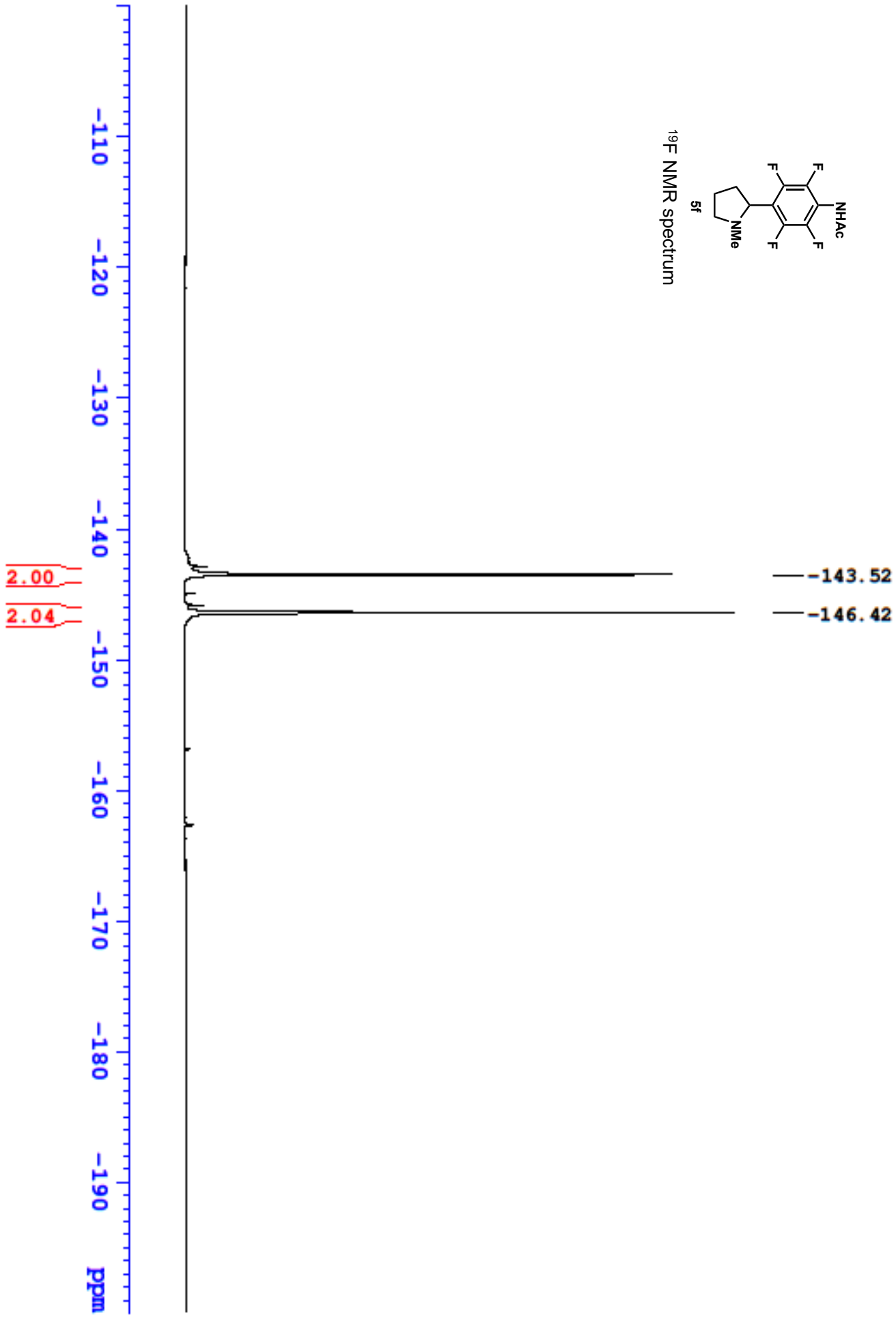
^{19}F NMR spectrum

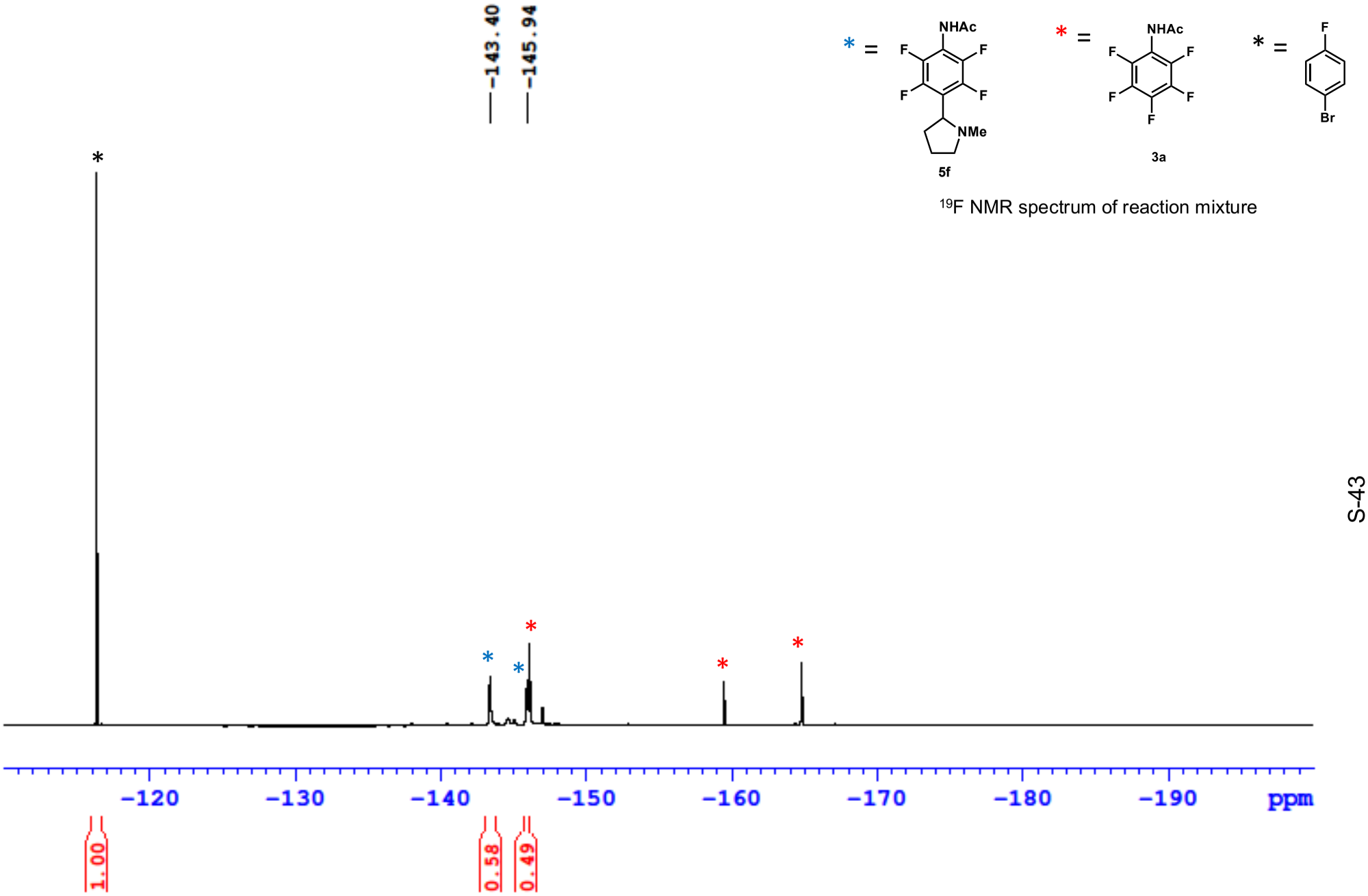




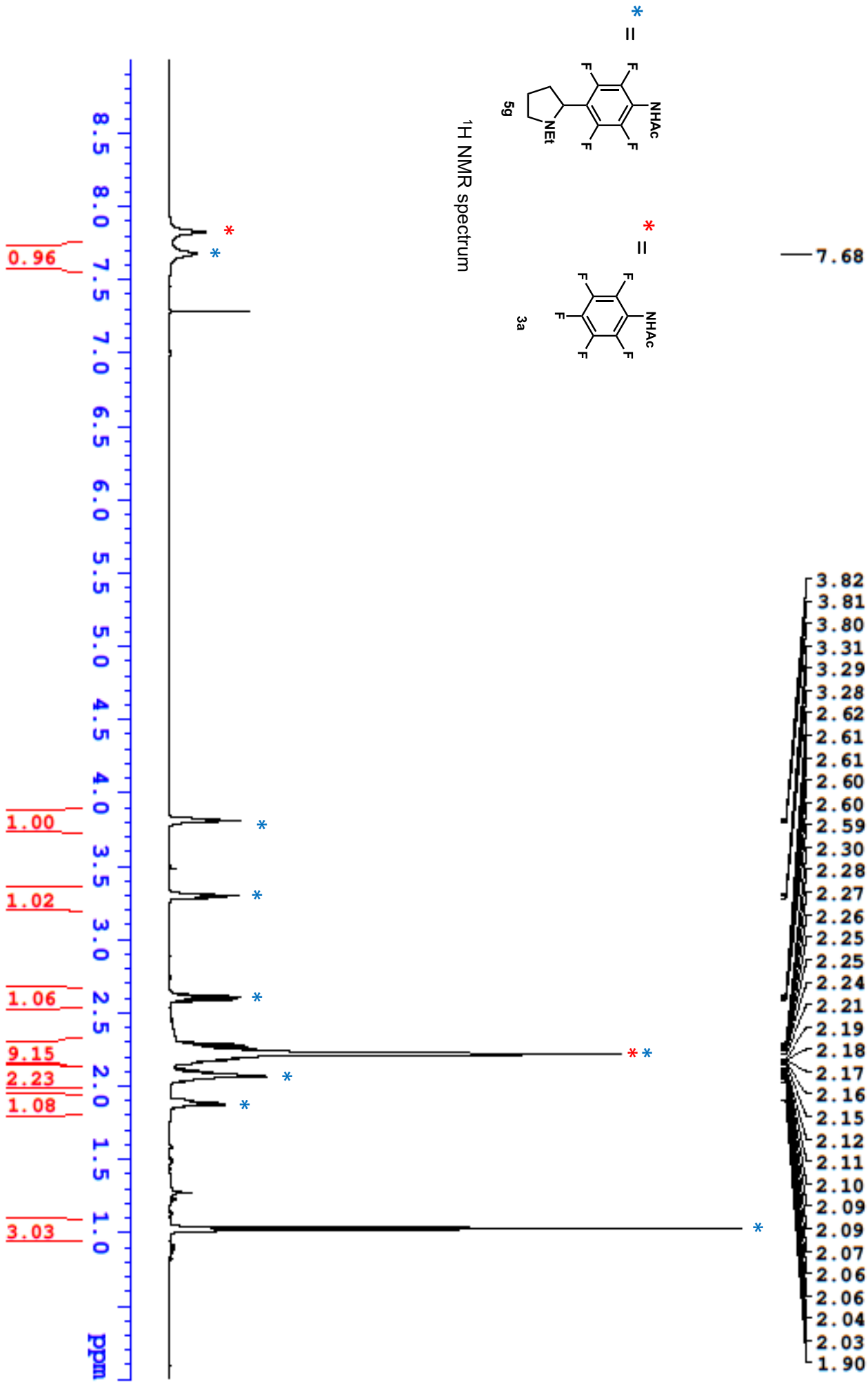
^{19}F NMR spectrum of reaction mixture

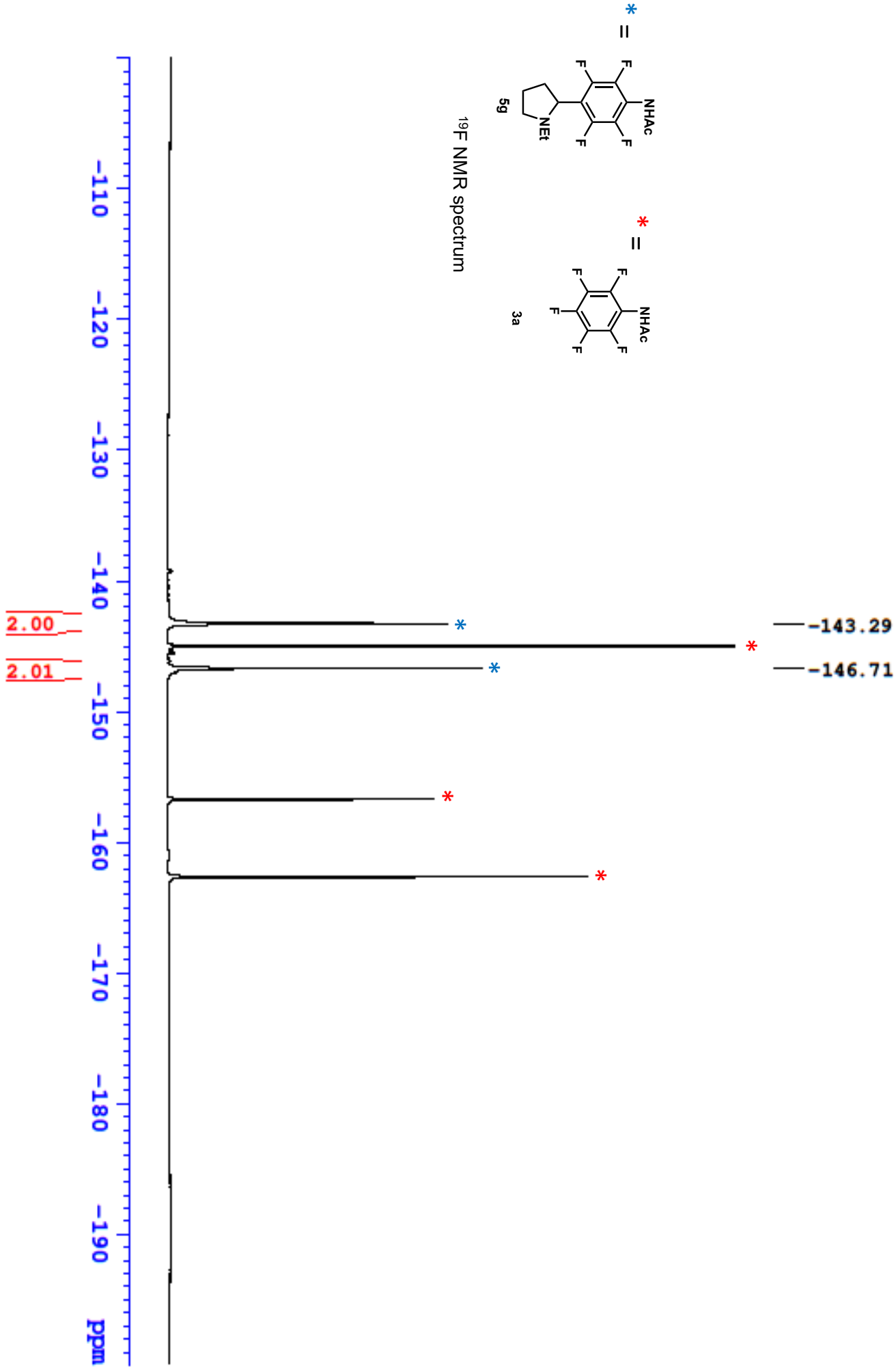

1H NMR spectrum
5f
7.65
3.68
3.66
3.65
3.24
3.22
3.21
2.33
2.31
2.30
2.29
2.27
2.21
2.19
2.19
2.18
2.17
2.13
2.12
2.12
2.11
2.10
2.09
2.08
1.91
1.90
1.90
1.88
1.87
1.86
1.85
1.00
0.99
1.00
1.18
2.89
3.82
1.86
1.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

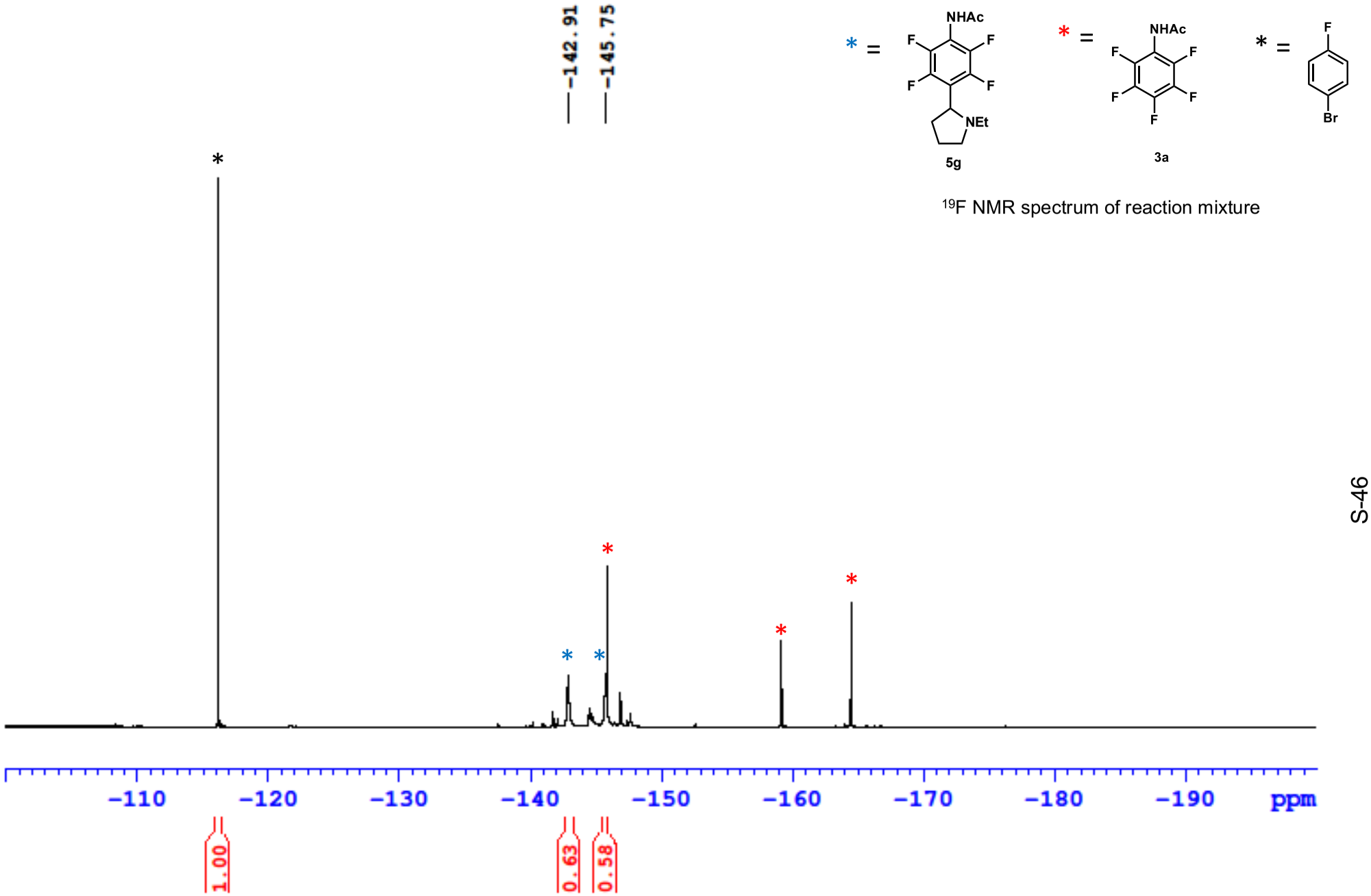

19F NMR spectrum
5f
F
F
NHAc
NMe
F
F
-143.52
-146.42
2.00
2.04
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm



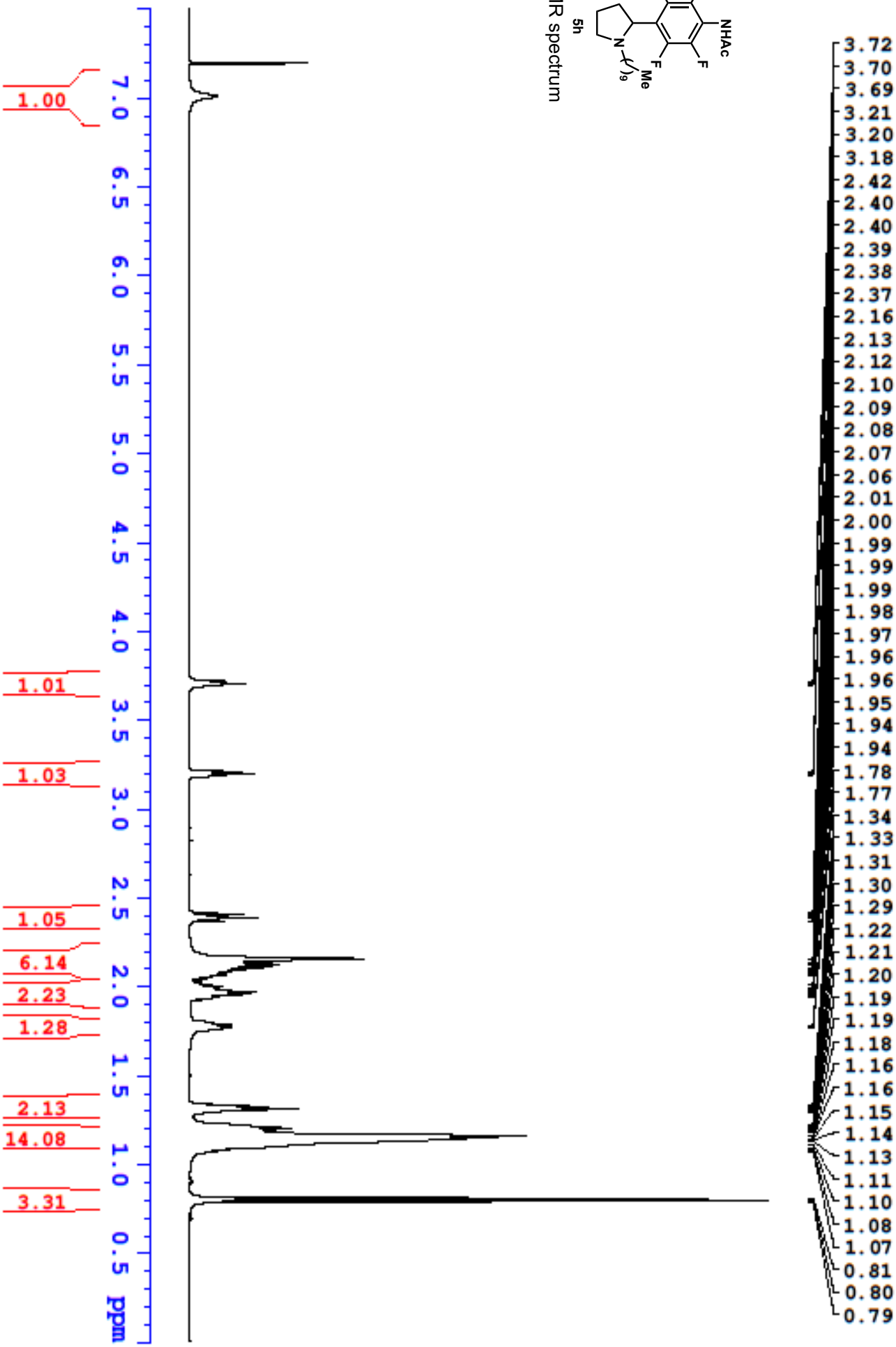
^{19}F NMR spectrum of reaction mixture

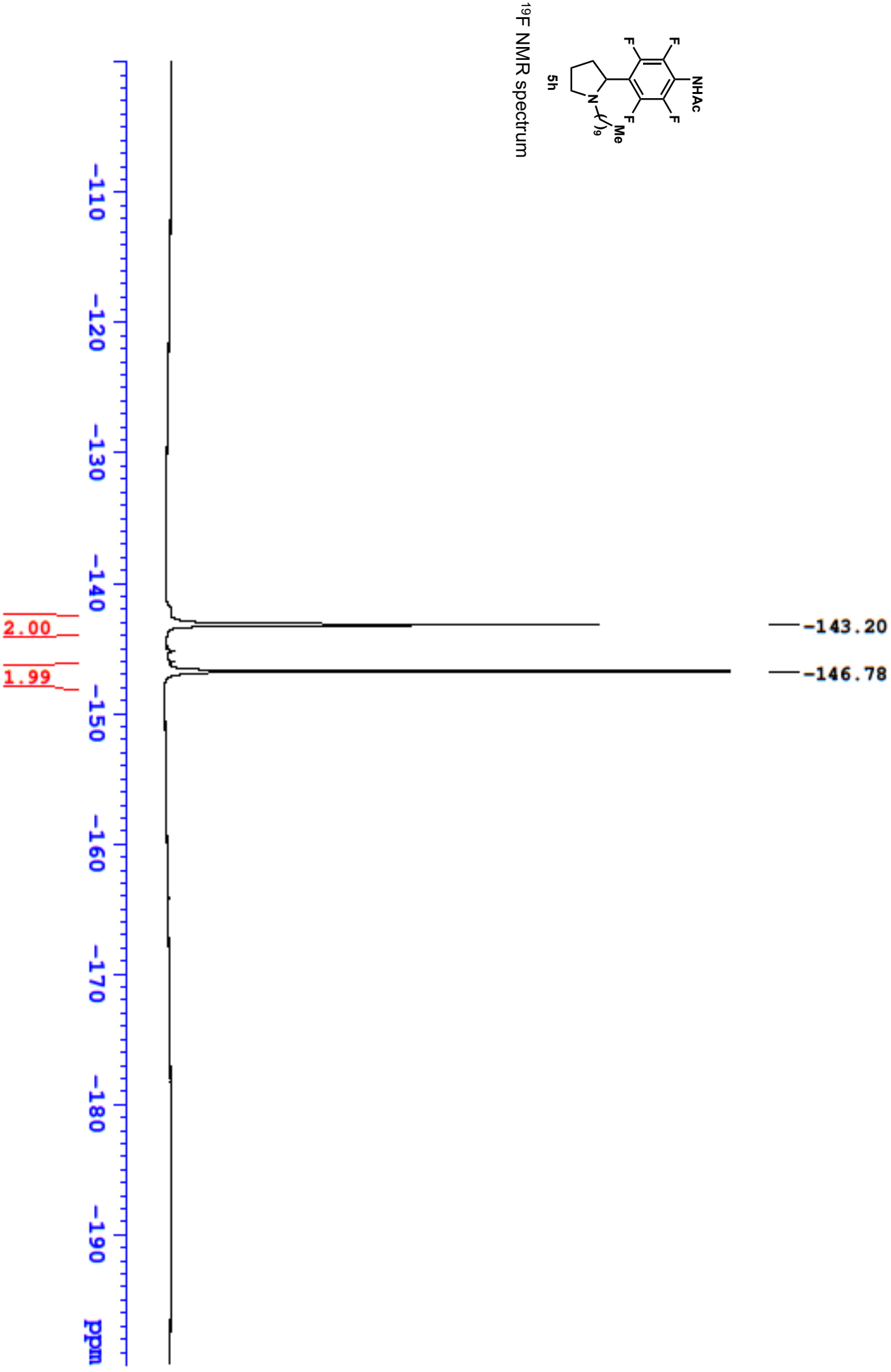

1H NMR spectrum
5g
3a
NHAc
NEt
F
0.96
1.00
1.02
1.06
9.15
2.23
1.08
3.03
7.68
3.82
3.81
3.80
3.31
3.29
3.28
2.62
2.61
2.61
2.60
2.60
2.59
2.30
2.28
2.27
2.26
2.25
2.25
2.24
2.21
2.19
2.18
2.17
2.16
2.15
2.12
2.11
2.10
2.09
2.09
2.07
2.06
2.06
2.04
2.03
1.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

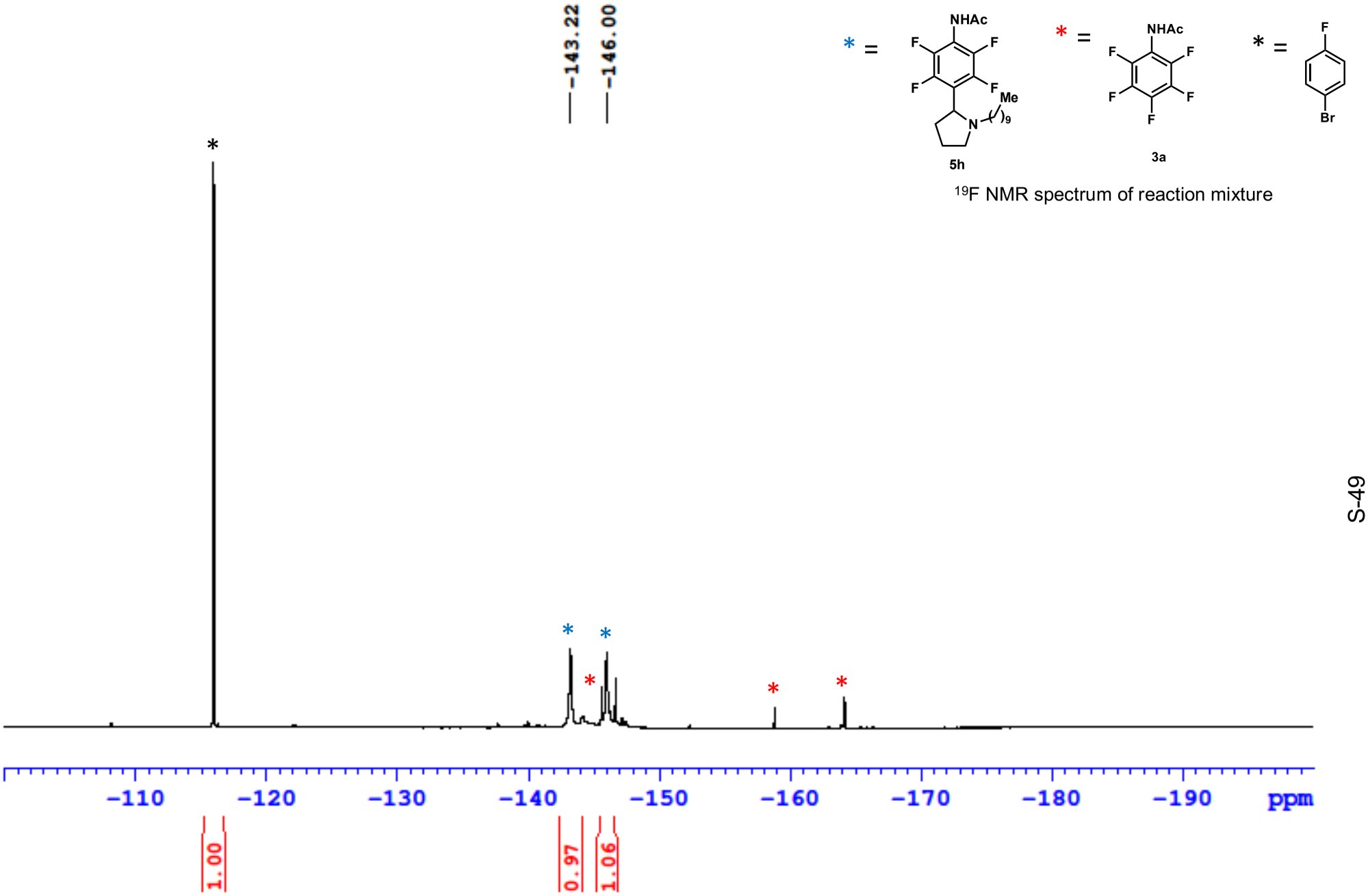

* =
F
F
NHAc
F
F
NEt
5g
* =
F
F
F
NHAc
F
F
3a
19F NMR spectrum
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.00
2.01
-143.29
-146.71



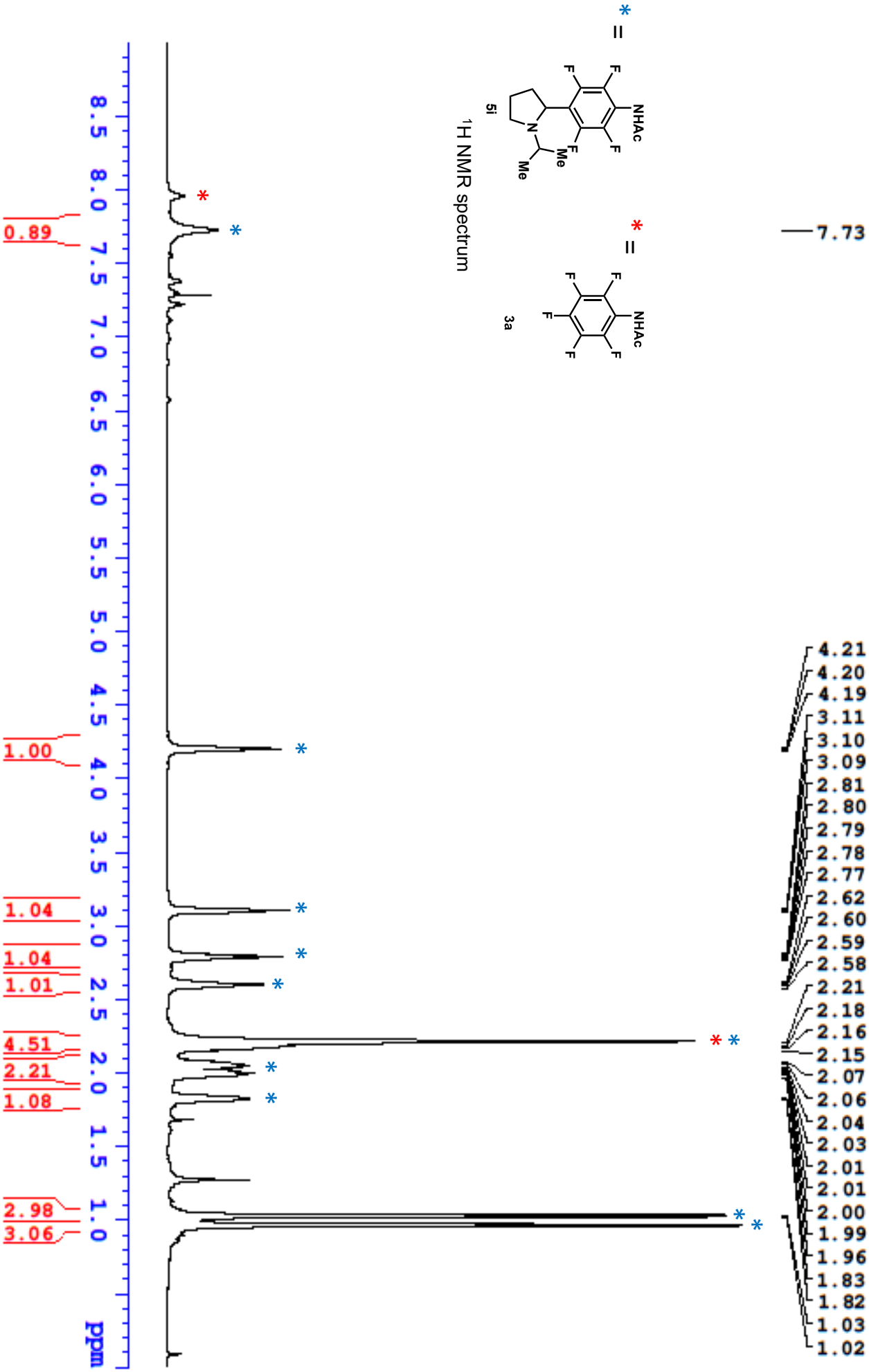
^{19}F NMR spectrum of reaction mixture

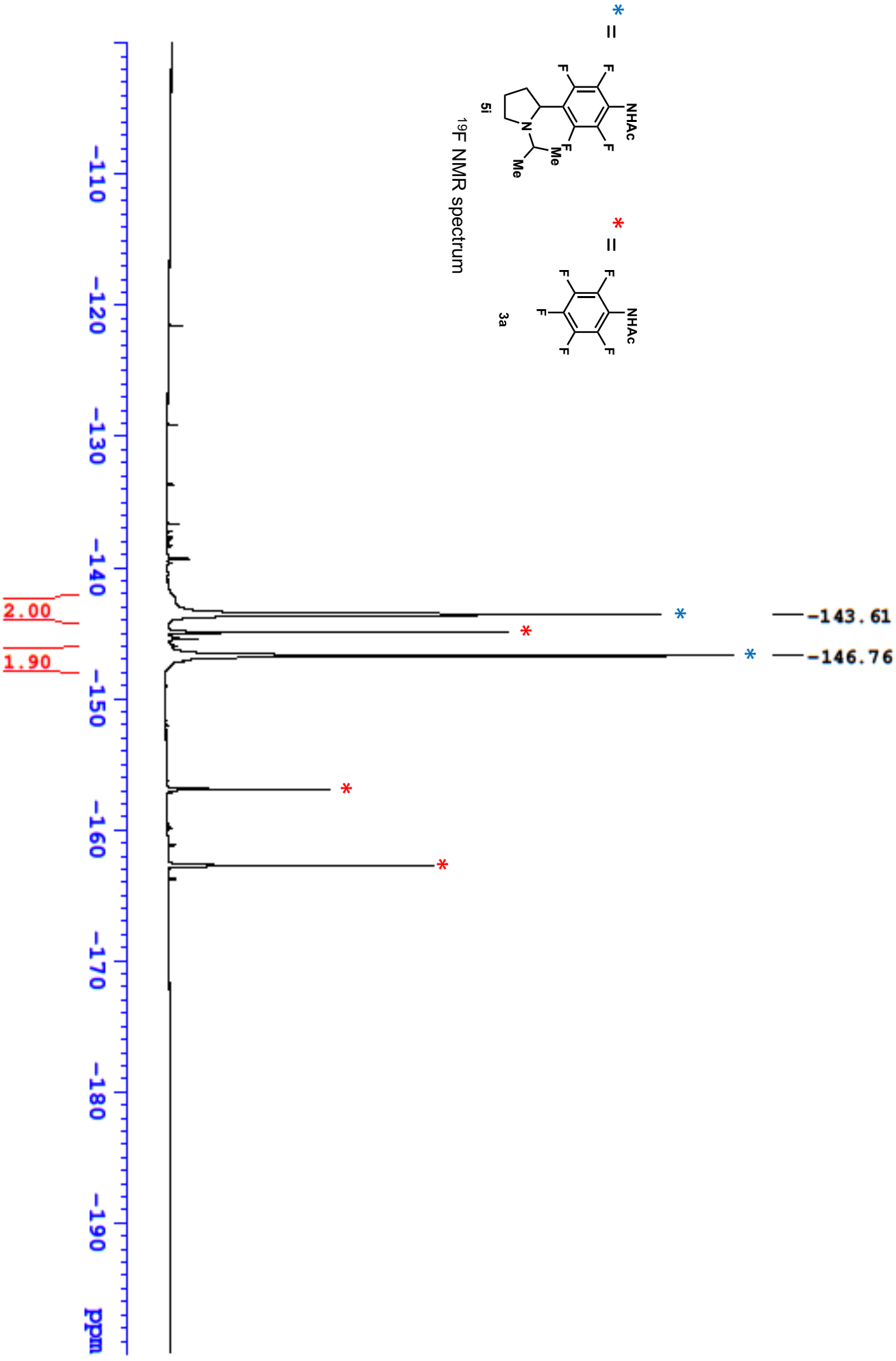

1H NMR spectrum
5h
NHAc
F
F
F
F
Me
N
9
1.00
1.01
1.03
1.05
6.14
2.23
1.28
2.13
14.08
3.31
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.72
3.70
3.69
3.21
3.20
3.18
2.42
2.40
2.40
2.39
2.38
2.37
2.16
2.13
2.12
2.10
2.09
2.08
2.07
2.06
2.01
2.00
1.99
1.99
1.99
1.98
1.97
1.96
1.96
1.95
1.94
1.94
1.78
1.77
1.34
1.33
1.31
1.30
1.29
1.22
1.21
1.20
1.19
1.19
1.18
1.16
1.16
1.15
1.14
1.13
1.11
1.10
1.08
1.07
0.81
0.80
0.79

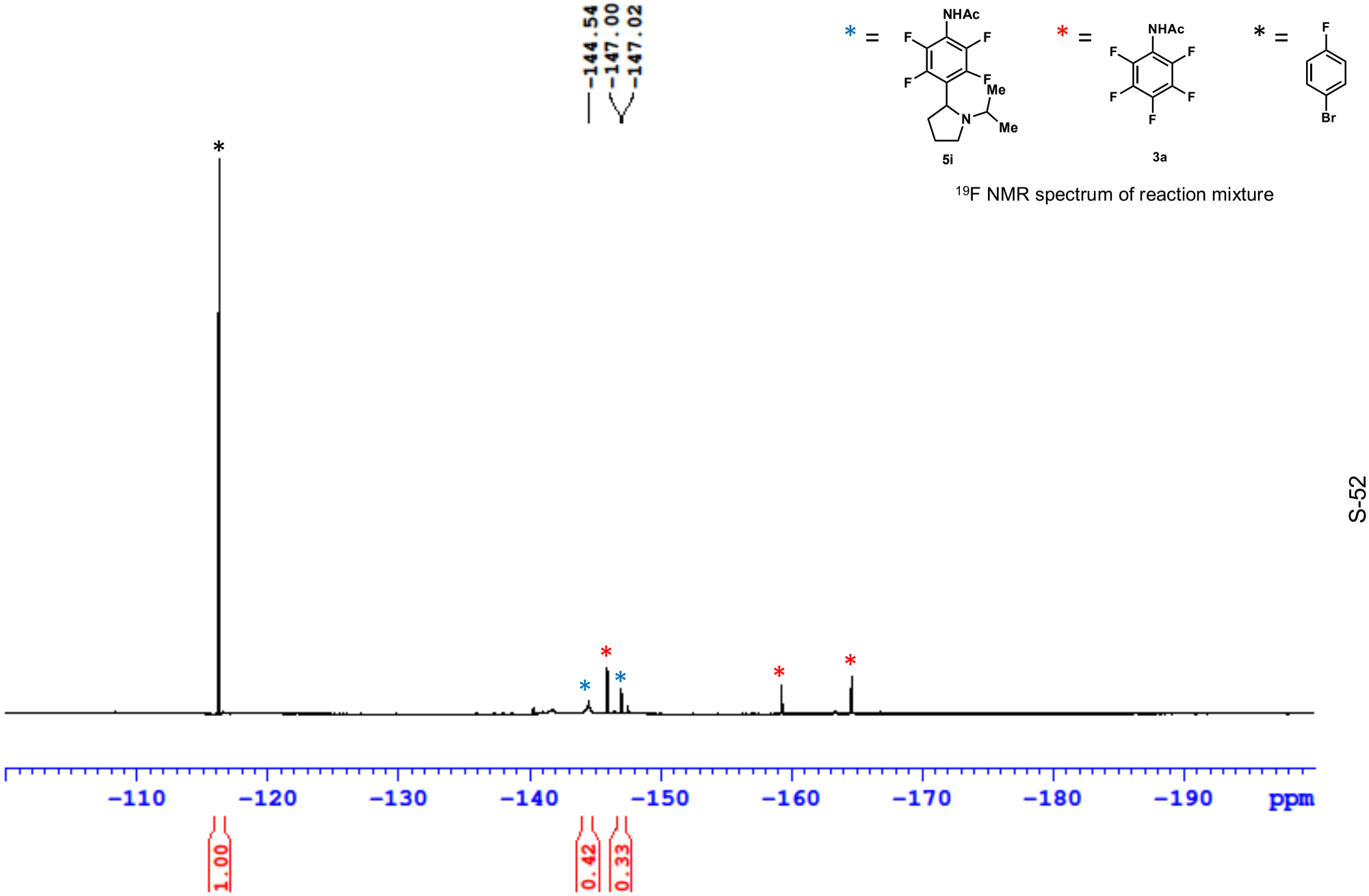

19F NMR spectrum
5h
NHAc
F
F
F
F
Me
N
9
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.00
1.99
-143.20
-146.78



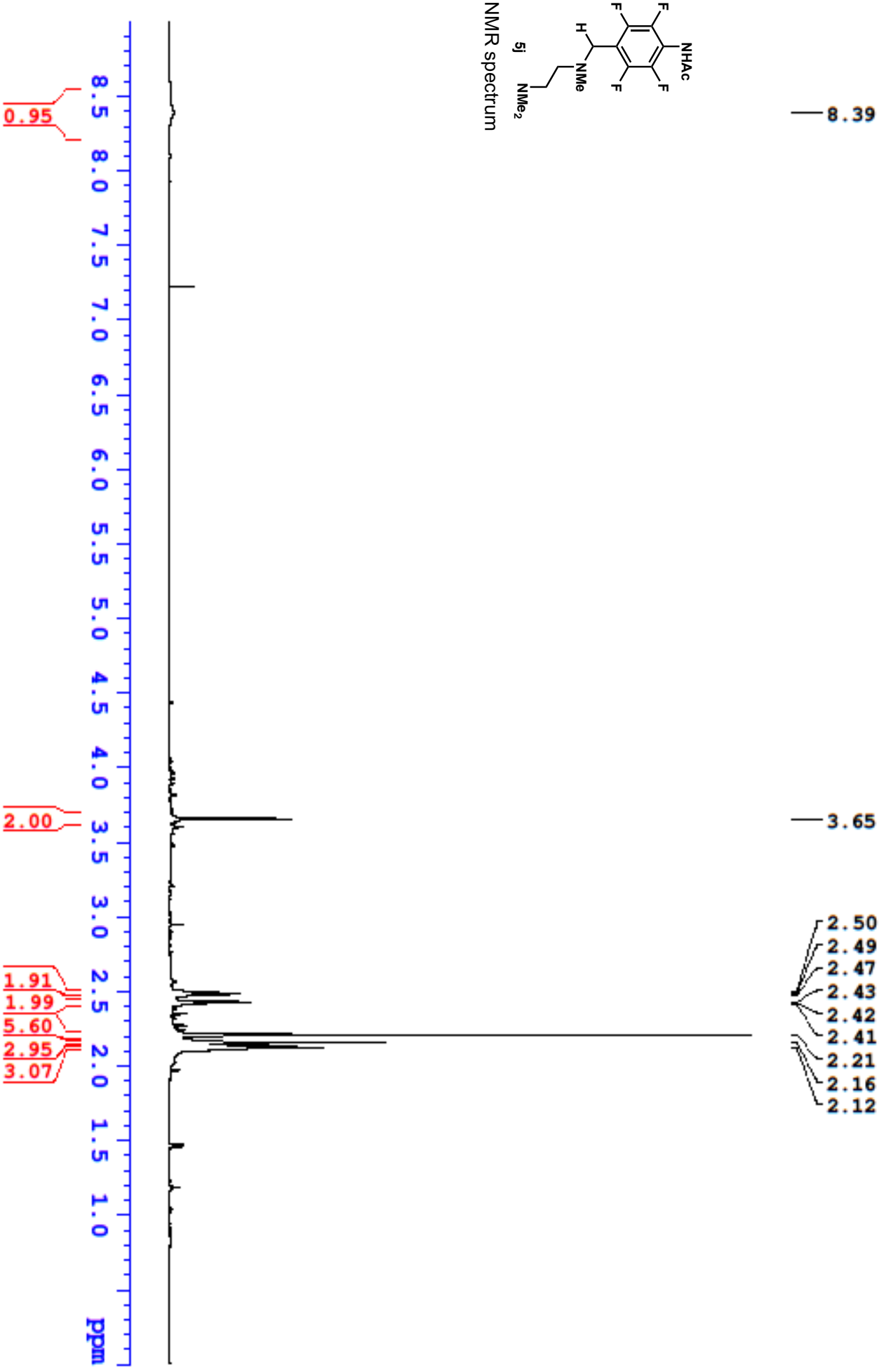
^{19}F NMR spectrum of reaction mixture

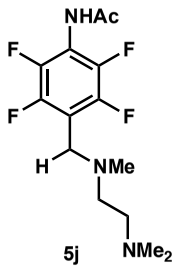

1H NMR spectrum
5i
3a
NHAc
Me
F
7.73
4.21
4.20
4.19
3.11
3.10
3.09
2.81
2.80
2.79
2.78
2.77
2.62
2.60
2.59
2.58
2.21
2.18
2.16
2.15
2.07
2.06
2.04
2.03
2.01
2.01
2.00
1.99
1.96
1.83
1.82
1.03
1.02
0.89
1.00
1.04
1.04
1.01
4.51
2.21
1.08
2.98
3.06
ppm


19F NMR spectrum
5i
3a
NHAc
Me
Me
F
-143.61
-146.76
2.00
1.90
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm



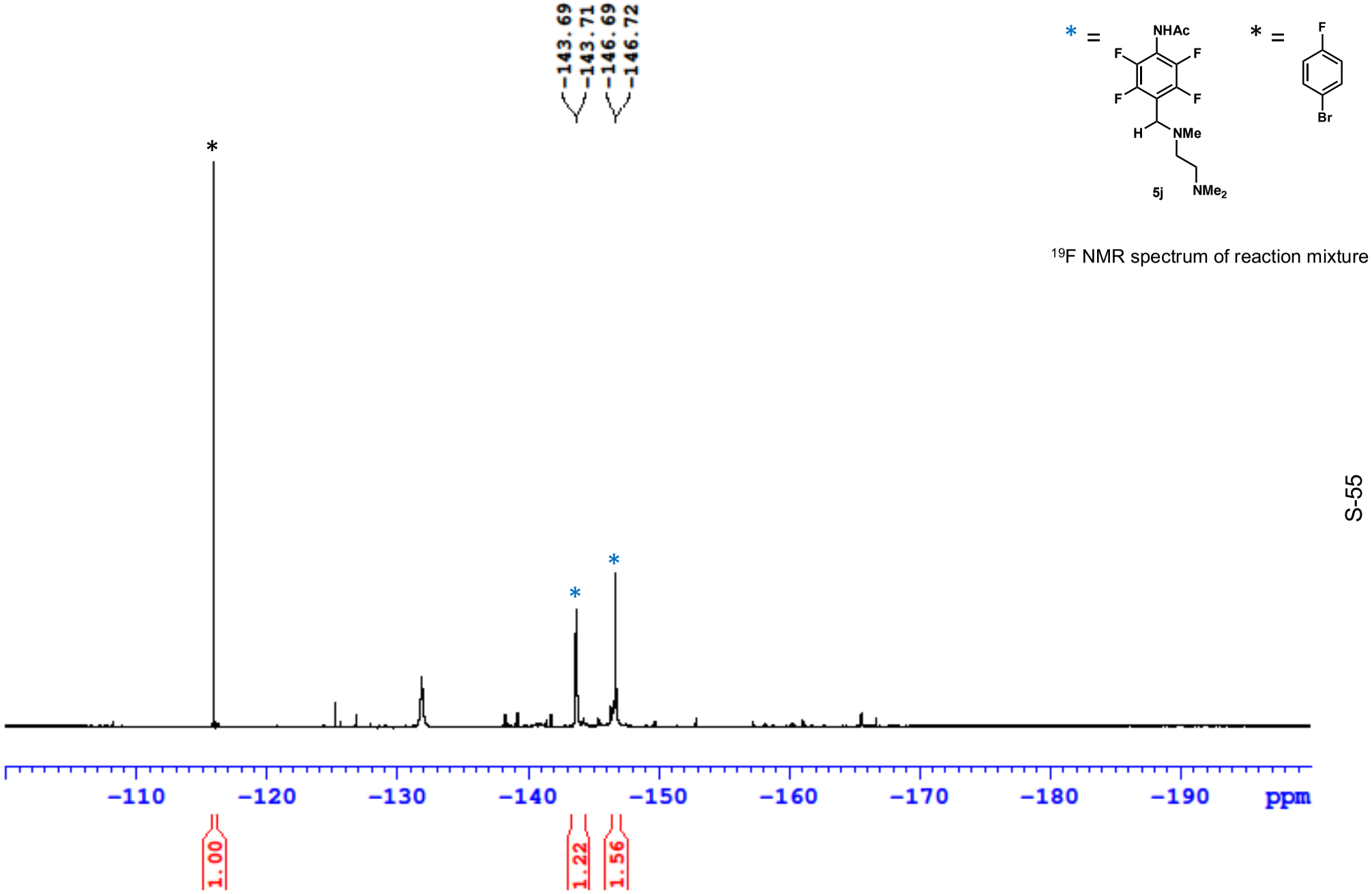
^{19}F NMR spectrum of reaction mixture


^{1}H NMR spectrum
5j
NHAc
NMe
NMe$_2$
F
H
8.39
3.65
2.50
2.49
2.47
2.43
2.42
2.41
2.21
2.16
2.12
0.95
2.00
1.91
1.99
5.60
2.95
3.07
ppm

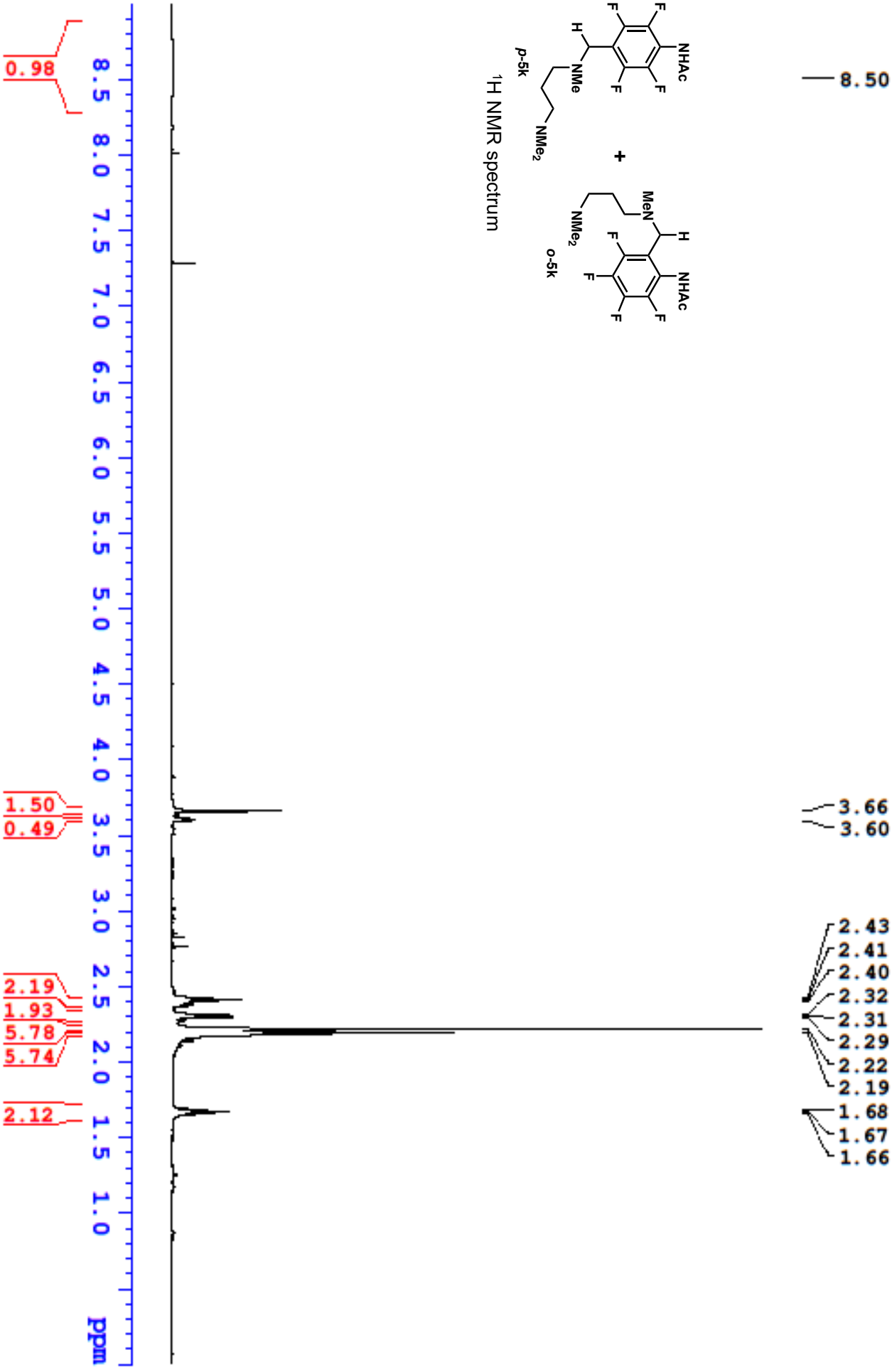


5j

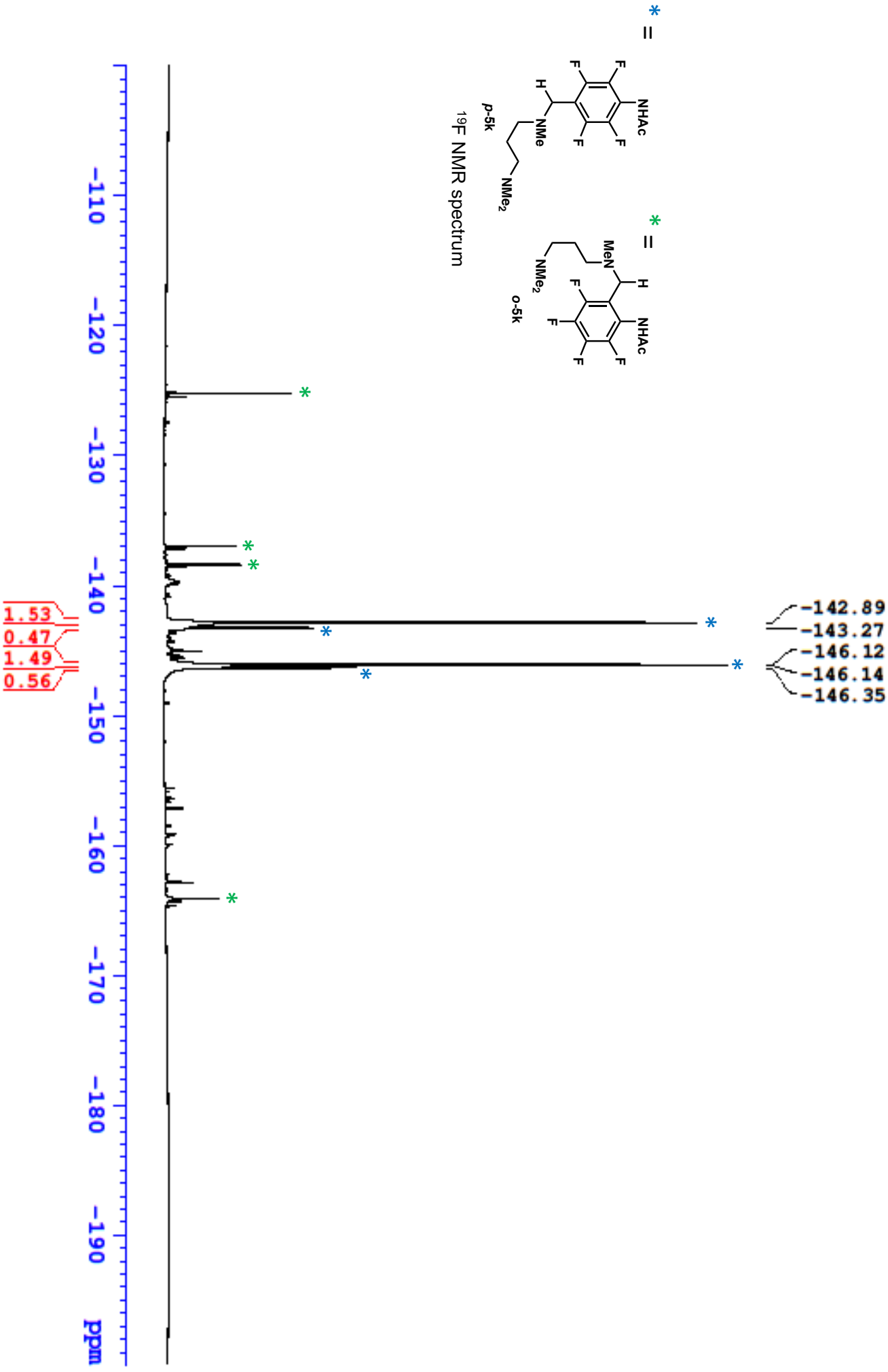
^{19}F NMR spectrum

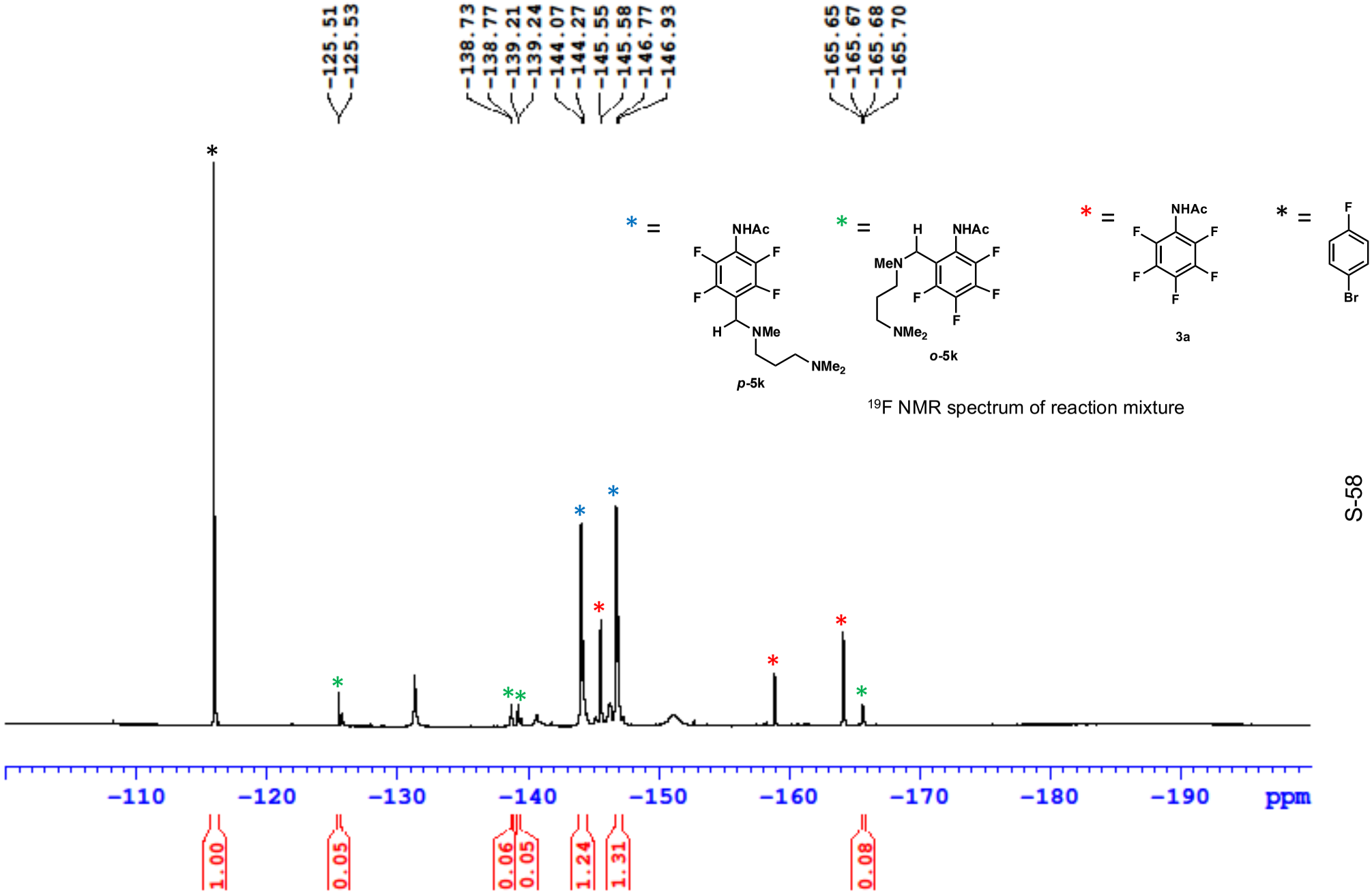


^{19}F NMR spectrum of reaction mixture

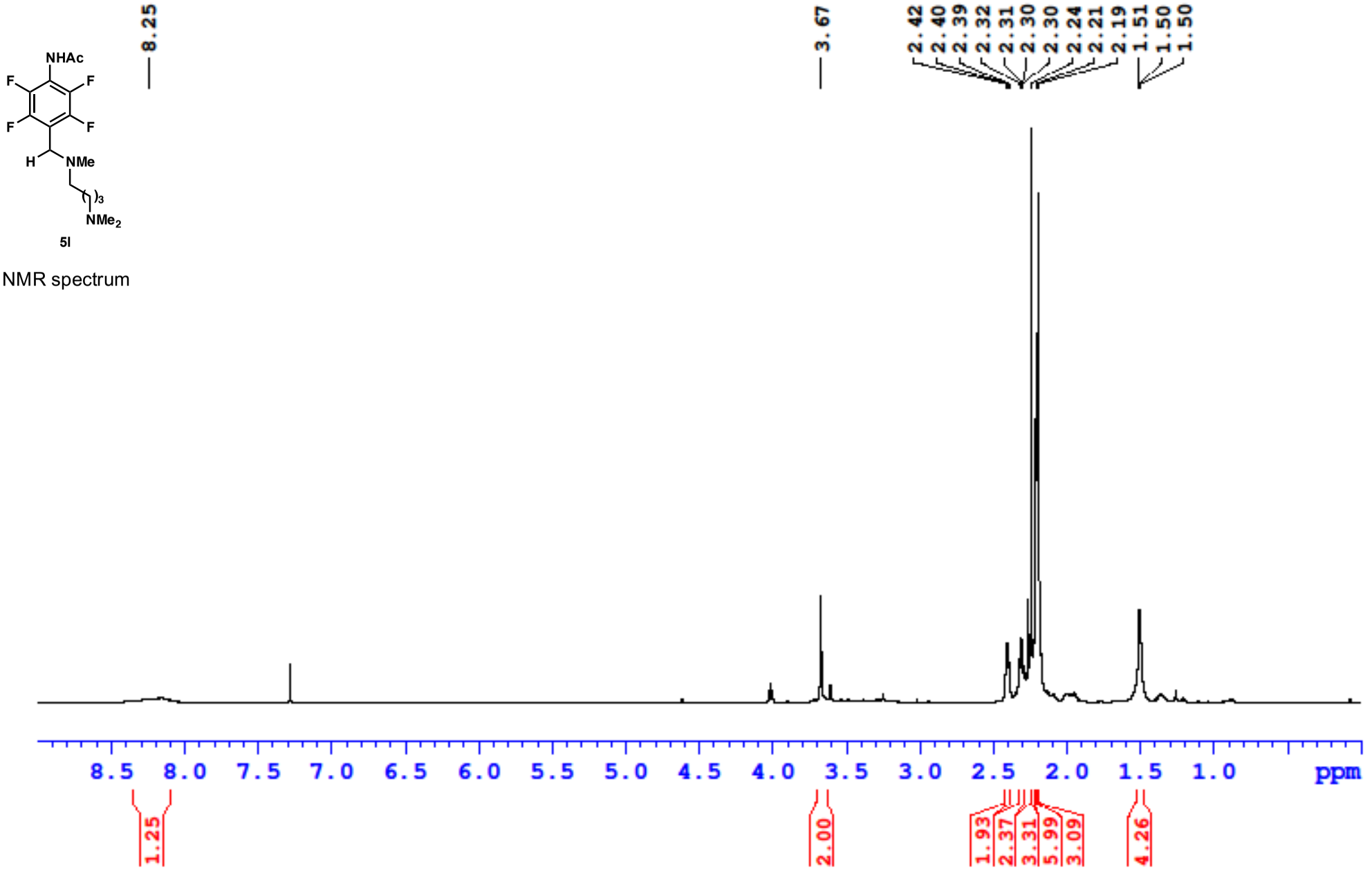


^{1}H NMR spectrum

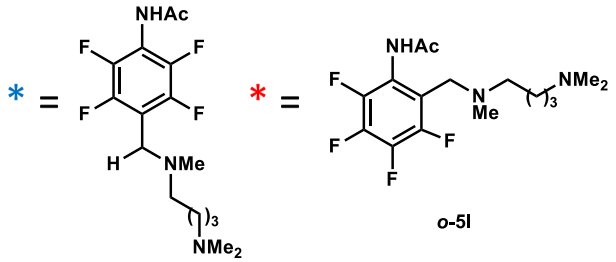

* = p-5k
* = o-5k
19F NMR spectrum
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
1.53
0.47
1.49
0.56
-142.89
-143.27
-146.12
-146.14
-146.35



^{19}F NMR spectrum of reaction mixture



^{1}H NMR spectrum

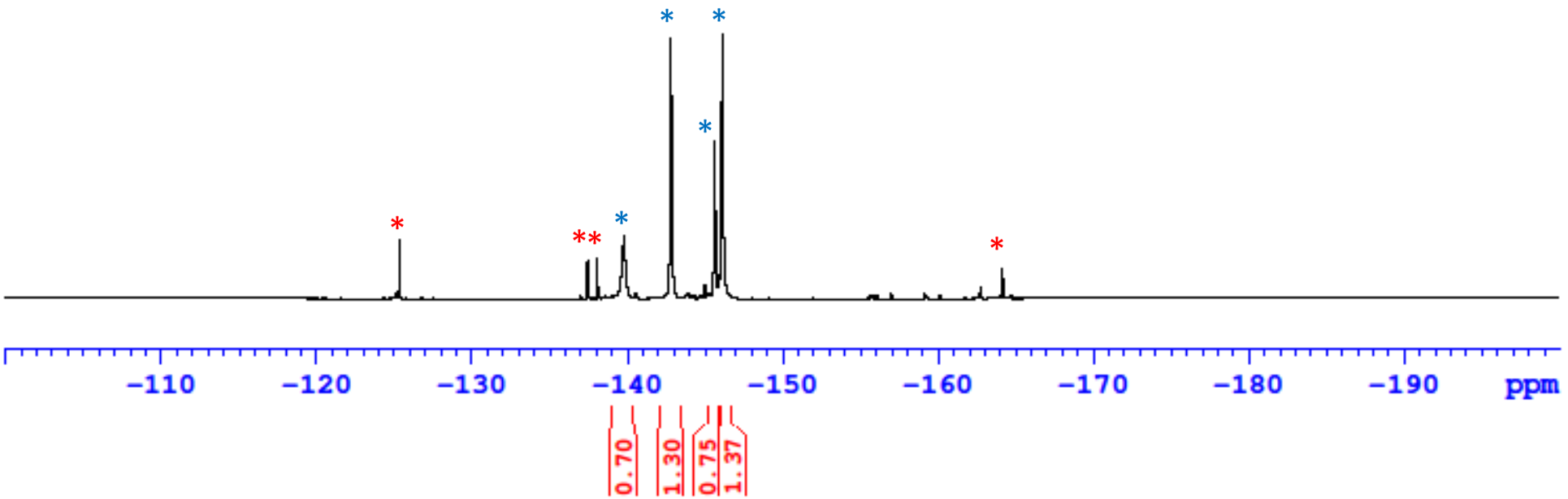


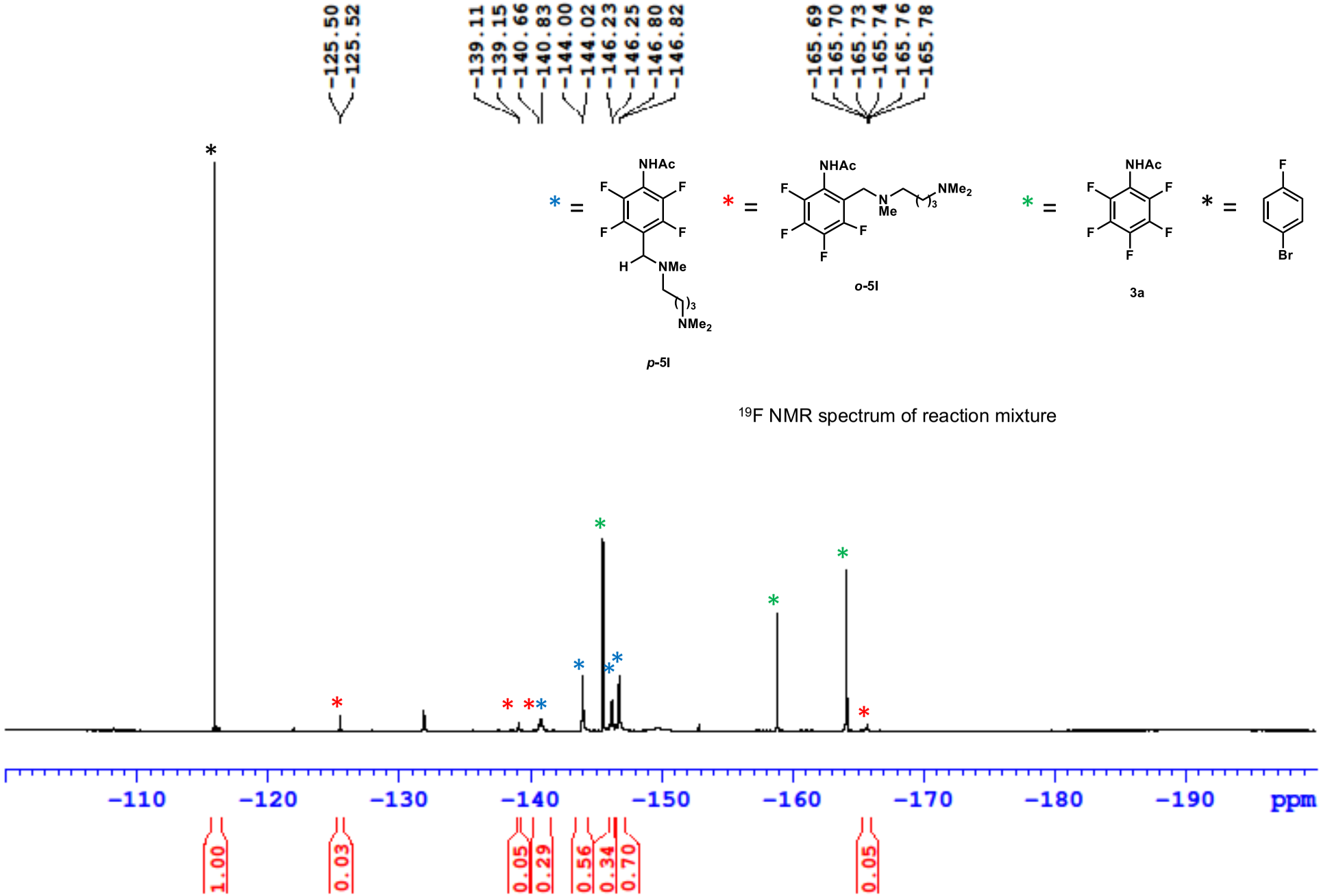
p-5l

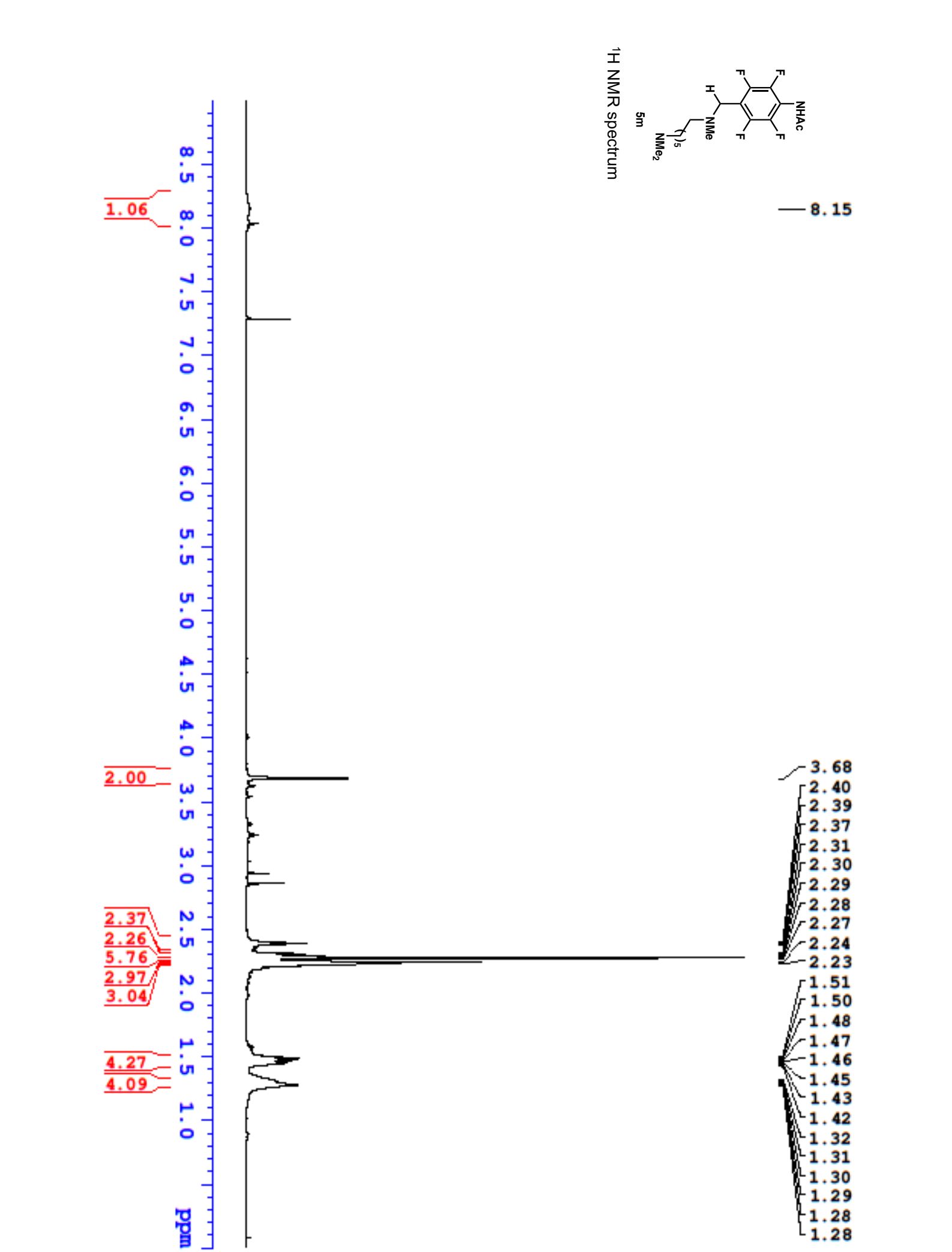
o-5l

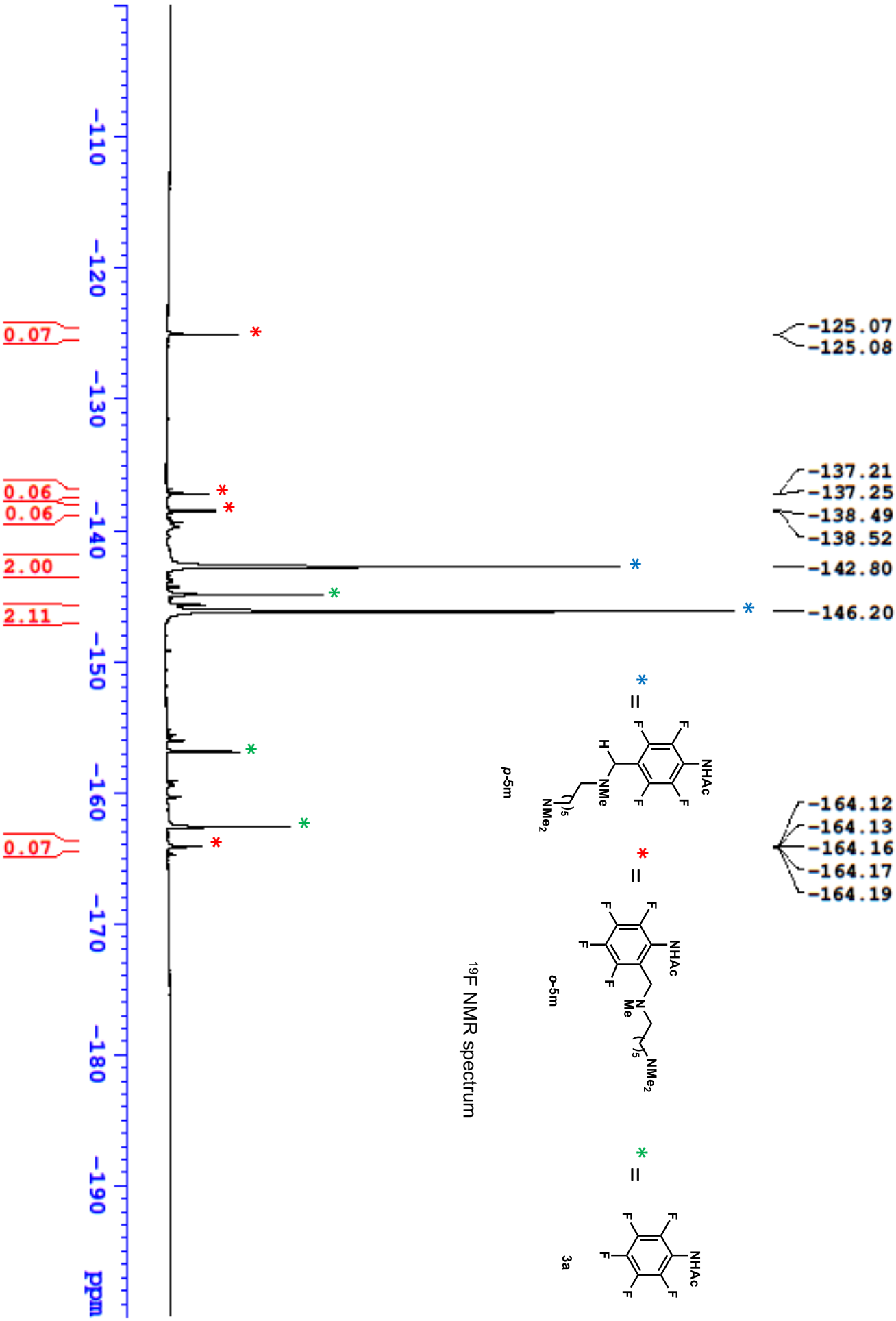
−139.80
−142.83
−145.64
−146.14

^{19}F NMR spectrum

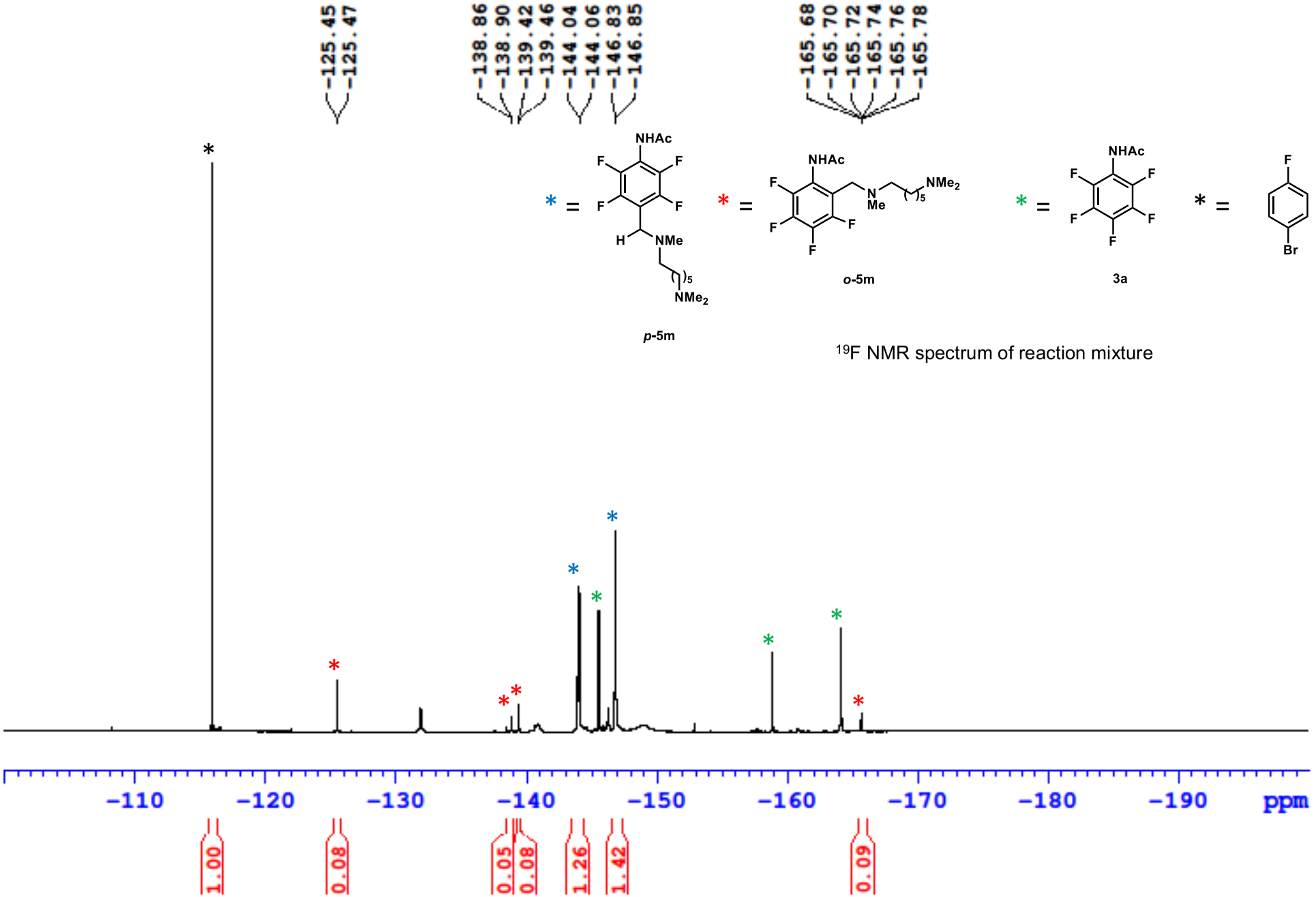



-125.50
-125.52
-139.11
-139.15
-140.66
-140.83
-144.00
-144.02
-146.23
-146.25
-146.80
-146.82
-165.69
-165.70
-165.73
-165.74
-165.76
-165.78
NHAc
NMe
NMe2
p-5l
o-5l
3a
Br
19F NMR spectrum of reaction mixture
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
1.00
0.03
0.05
0.29
0.56
0.34
0.70
0.05

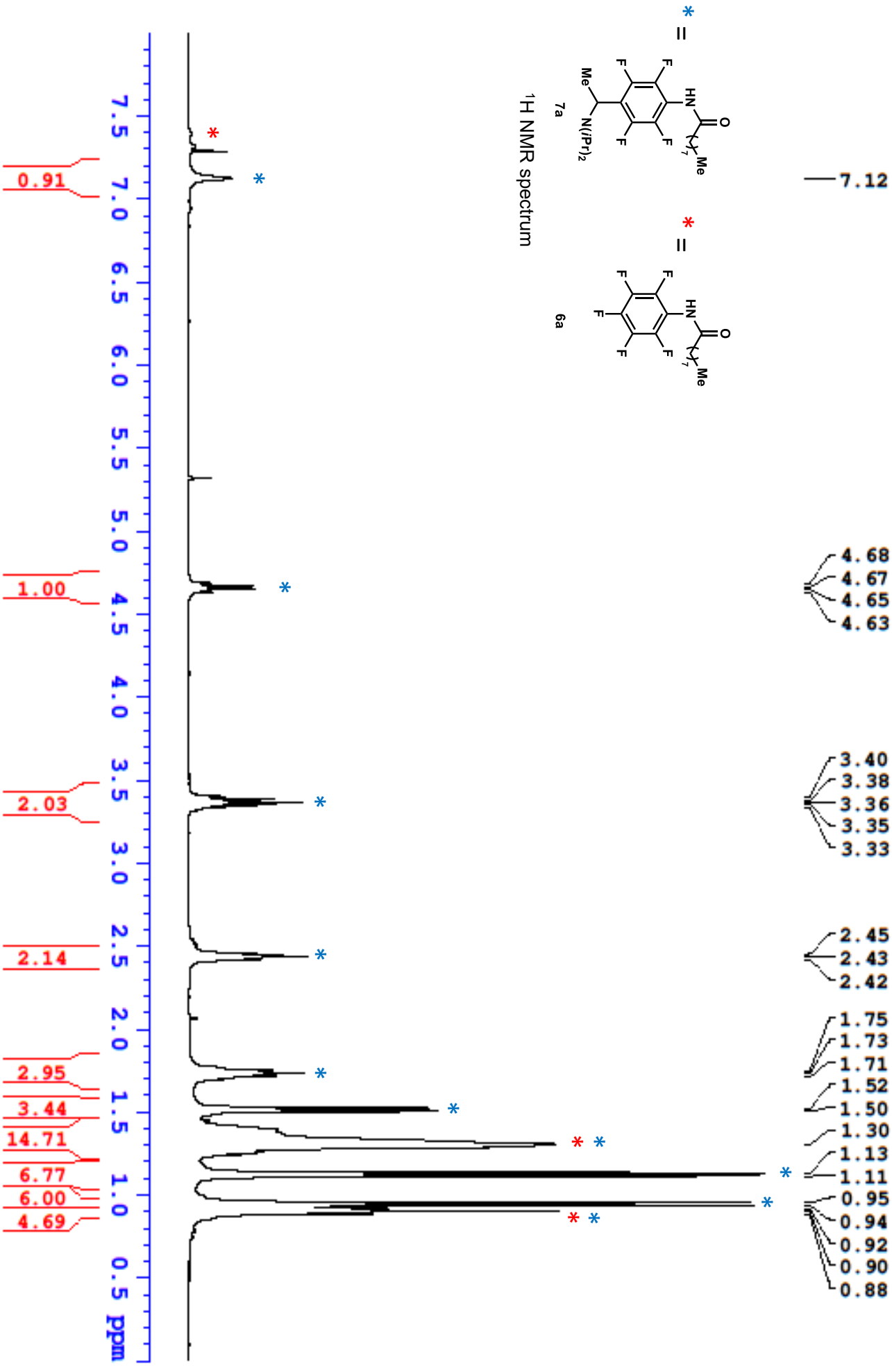

1H NMR spectrum
5m
NHAc
NMe
NMe2
F
H
8.15
3.68
2.40
2.39
2.37
2.31
2.30
2.29
2.28
2.27
2.24
2.23
1.51
1.50
1.48
1.47
1.46
1.45
1.43
1.42
1.32
1.31
1.30
1.29
1.28
1.28
1.06
2.00
2.37
2.26
5.76
2.97
3.04
4.27
4.09
ppm

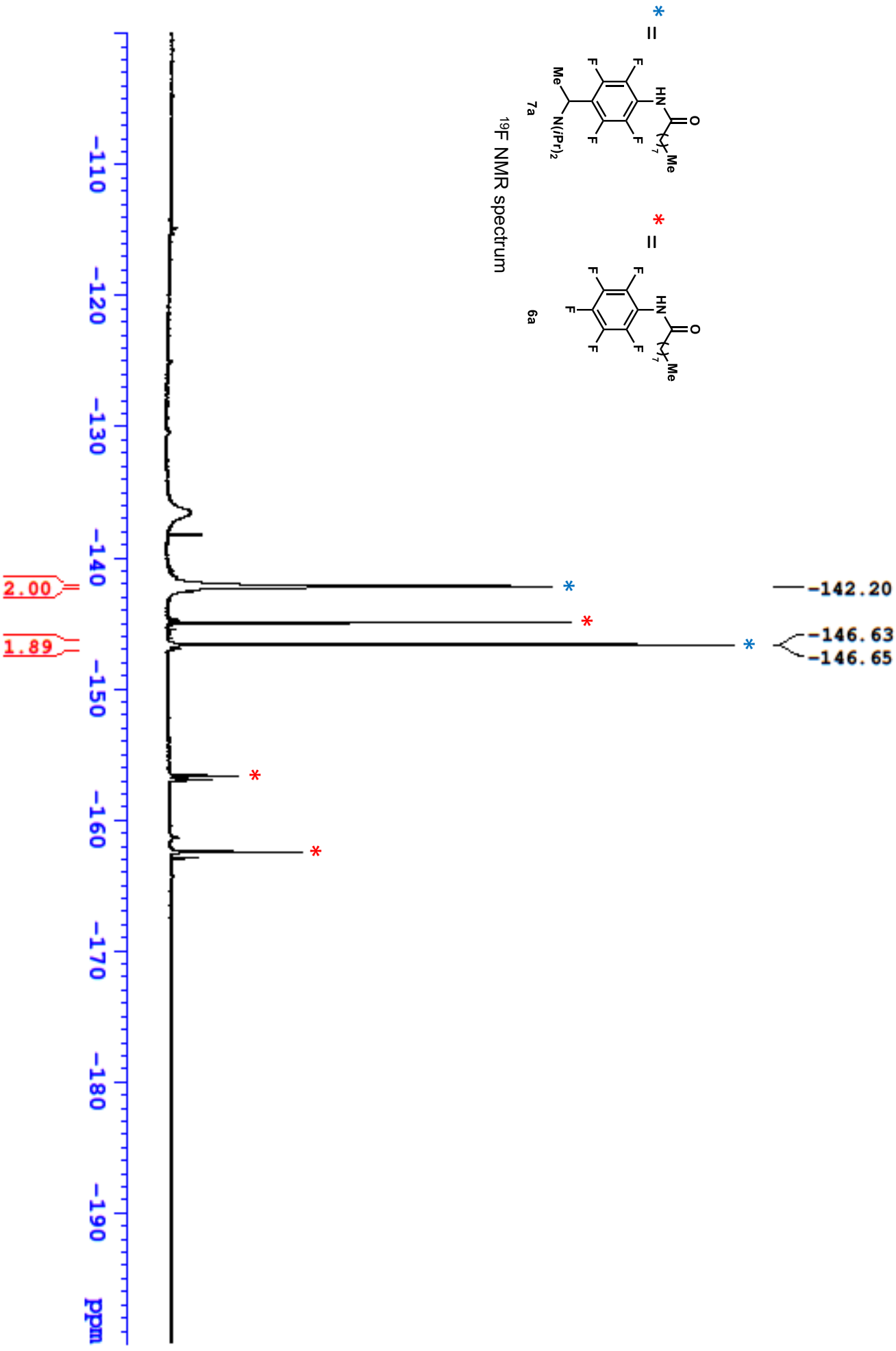


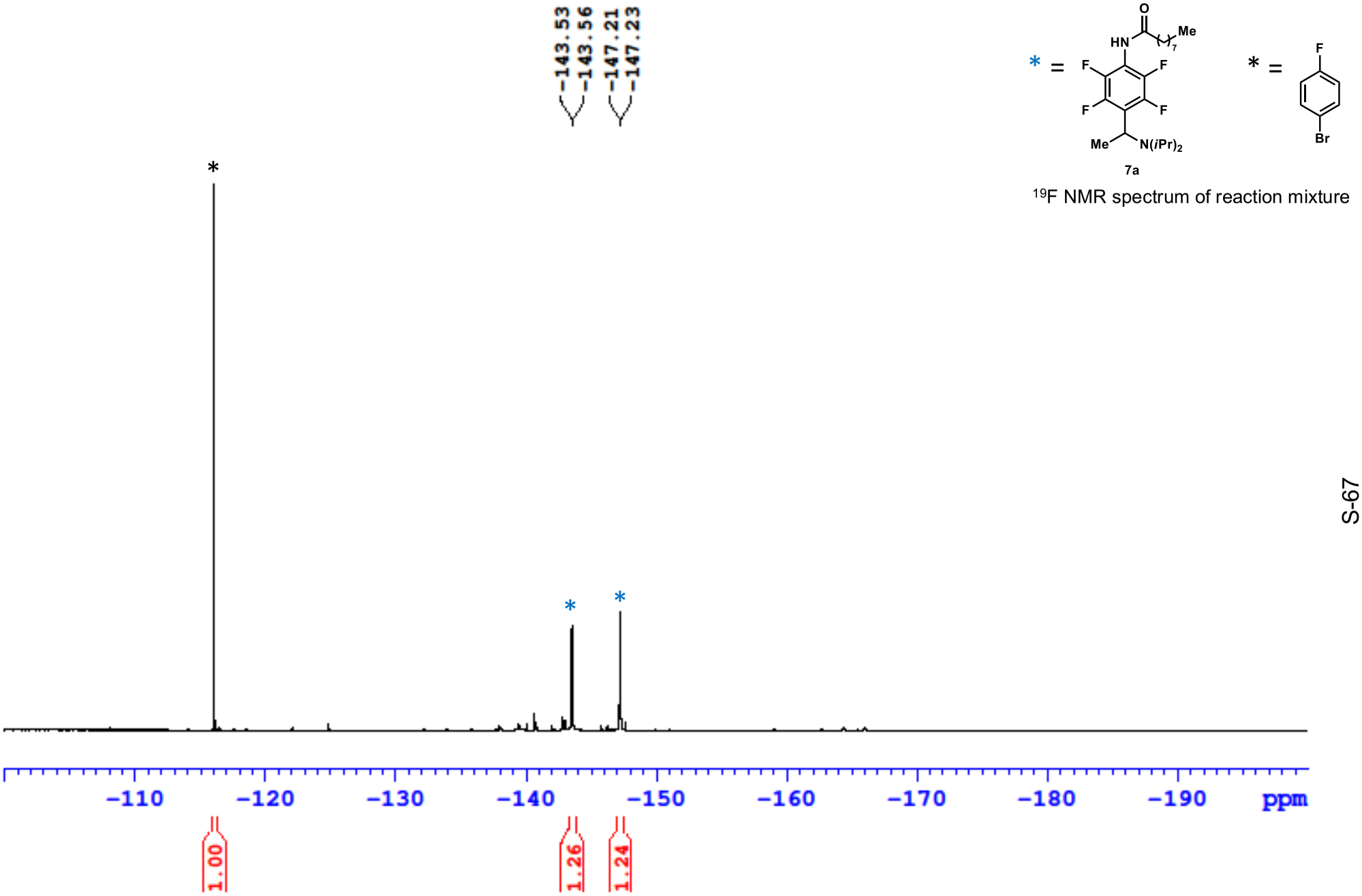
^{19}F NMR spectrum



^{19}F NMR spectrum of reaction mixture

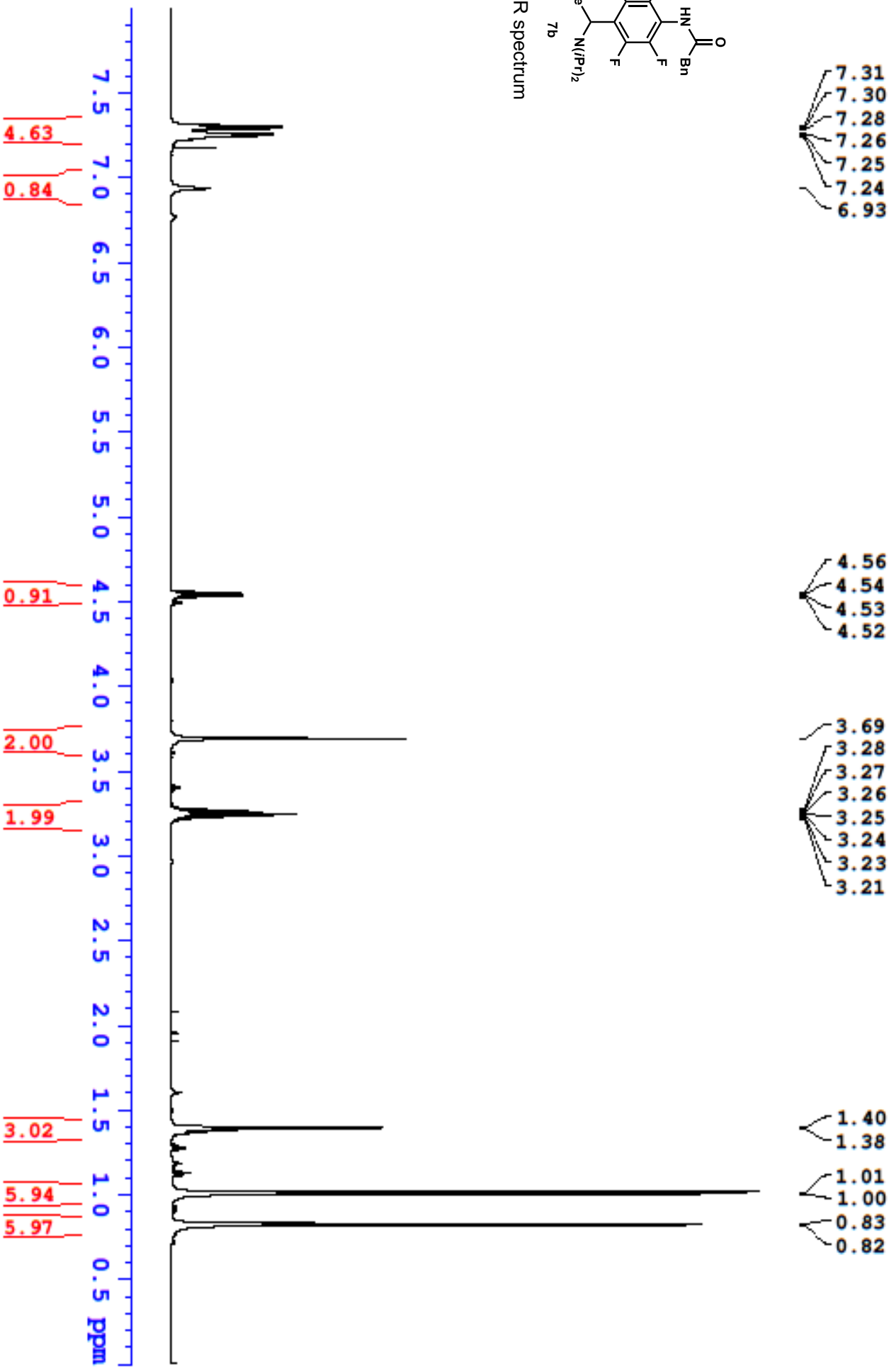

¹H NMR spectrum
7a
6a
7.12
4.68
4.67
4.65
4.63
3.40
3.38
3.36
3.35
3.33
2.45
2.43
2.42
1.75
1.73
1.71
1.52
1.50
1.30
1.13
1.11
0.95
0.94
0.92
0.90
0.88
0.91
1.00
2.03
2.14
2.95
3.44
14.71
6.77
6.00
4.69
ppm

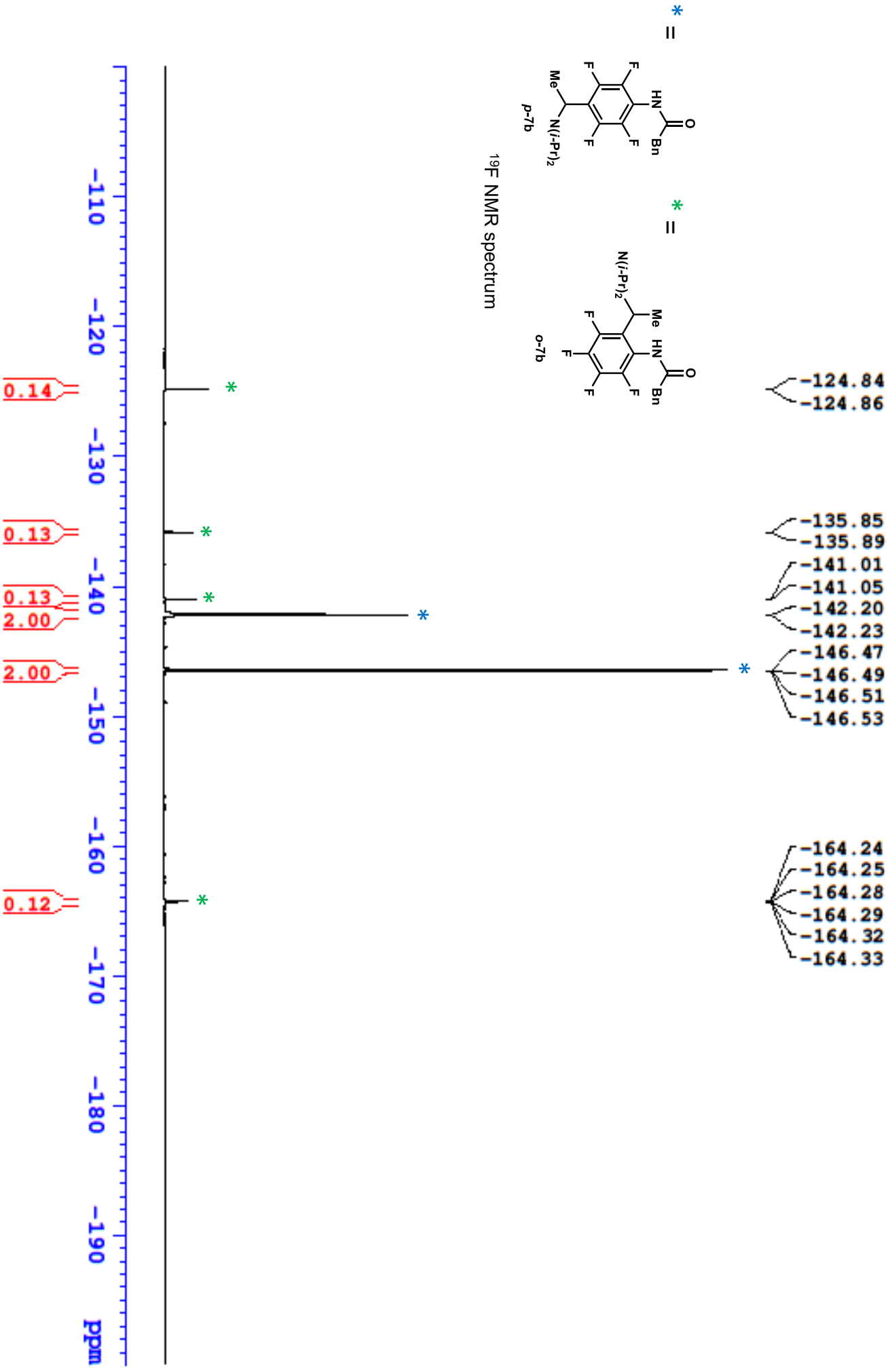

19F NMR spectrum
7a
6a
Me
N(iPr)2
HN
O
Me
F
2.00
1.89
-142.20
-146.63
-146.65
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

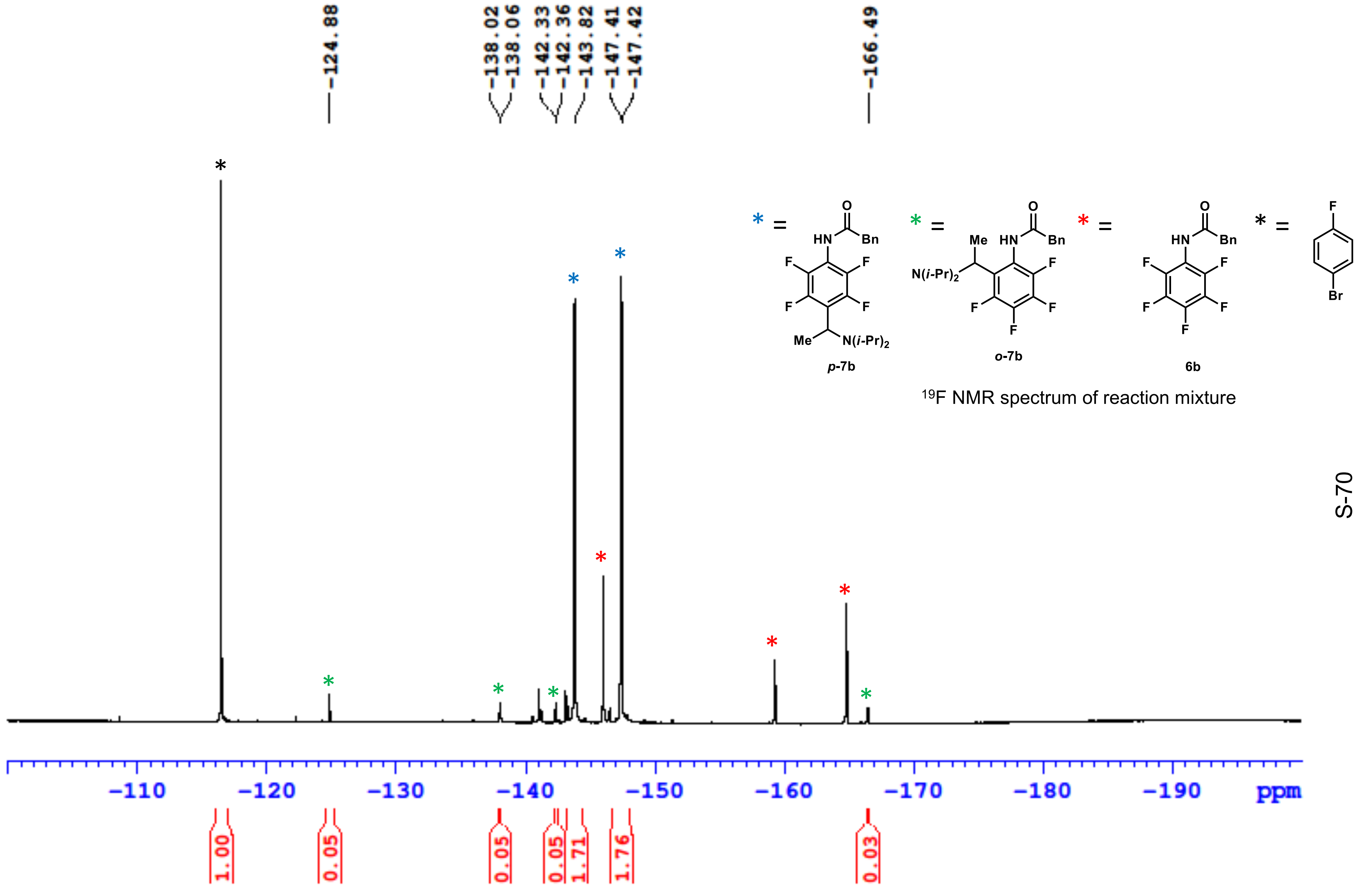


7a

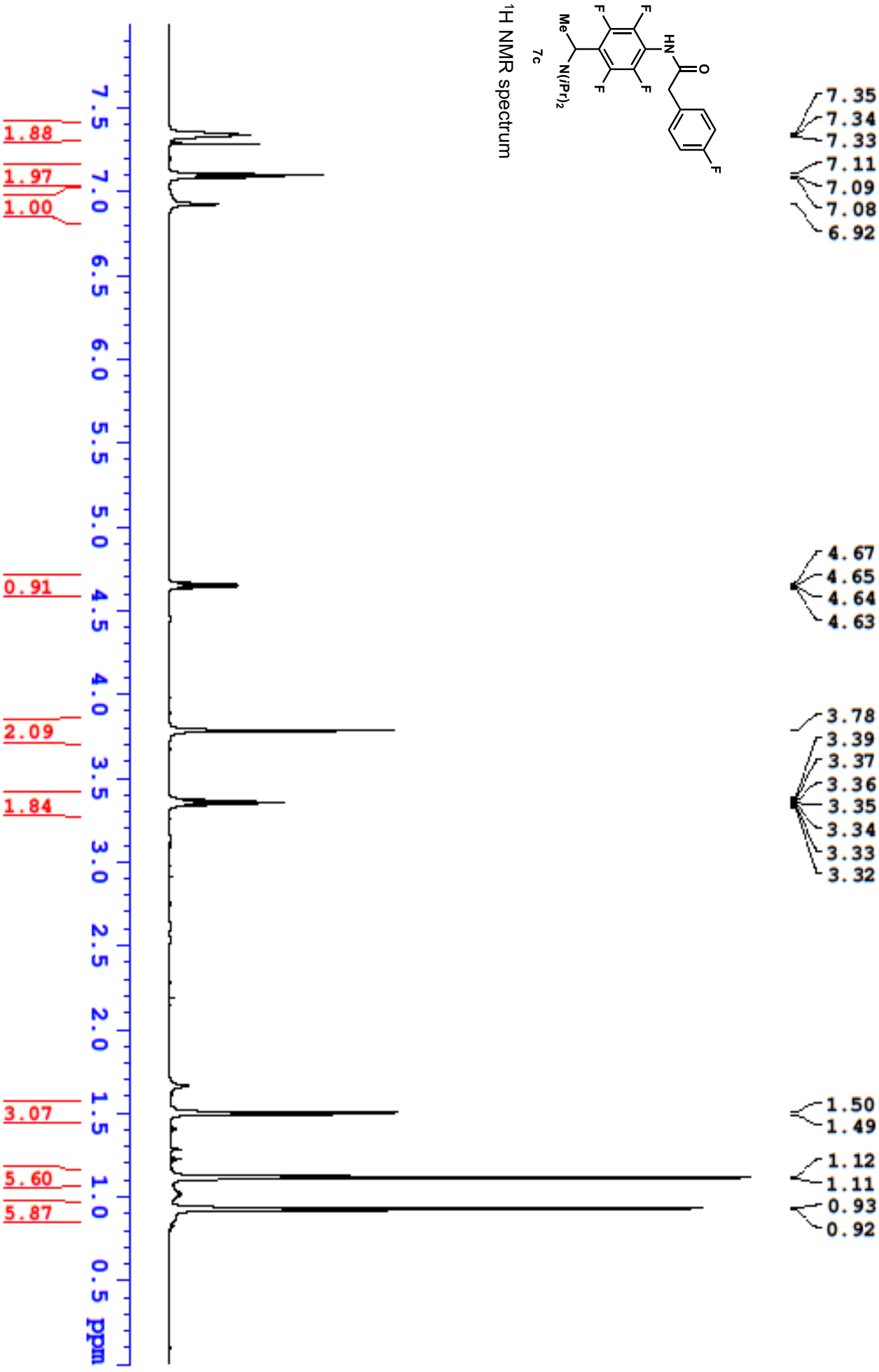
^{19}F NMR spectrum of reaction mixture

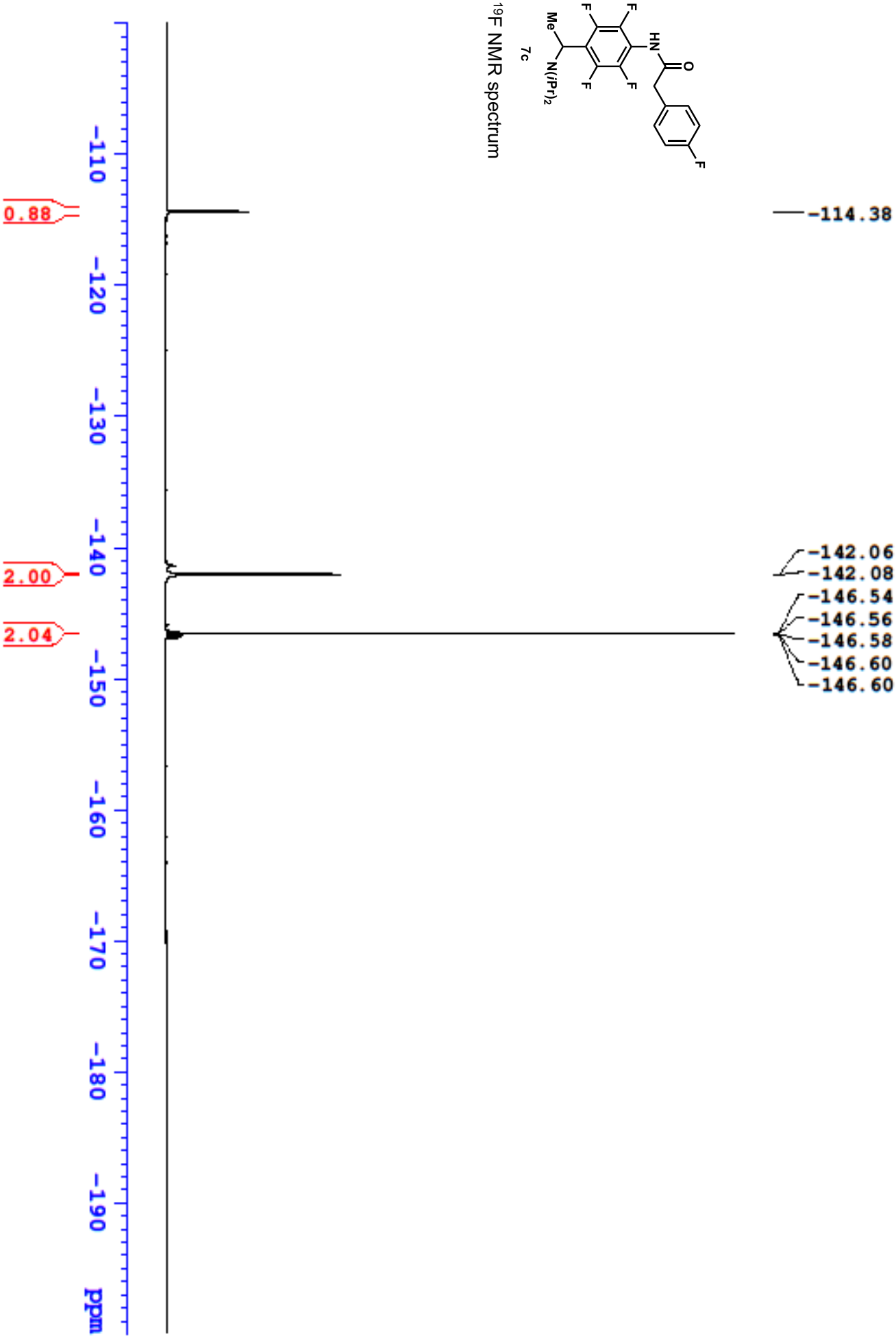

^{1}H NMR spectrum
7b
Me
N(iPr)$_2$
F
F
F
F
HN
O
Bn
7.31
7.30
7.28
7.26
7.25
7.24
6.93
4.56
4.54
4.53
4.52
3.69
3.28
3.27
3.26
3.25
3.24
3.23
3.21
1.40
1.38
1.01
1.00
0.83
0.82
4.63
0.84
0.91
2.00
1.99
3.02
5.94
5.97
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

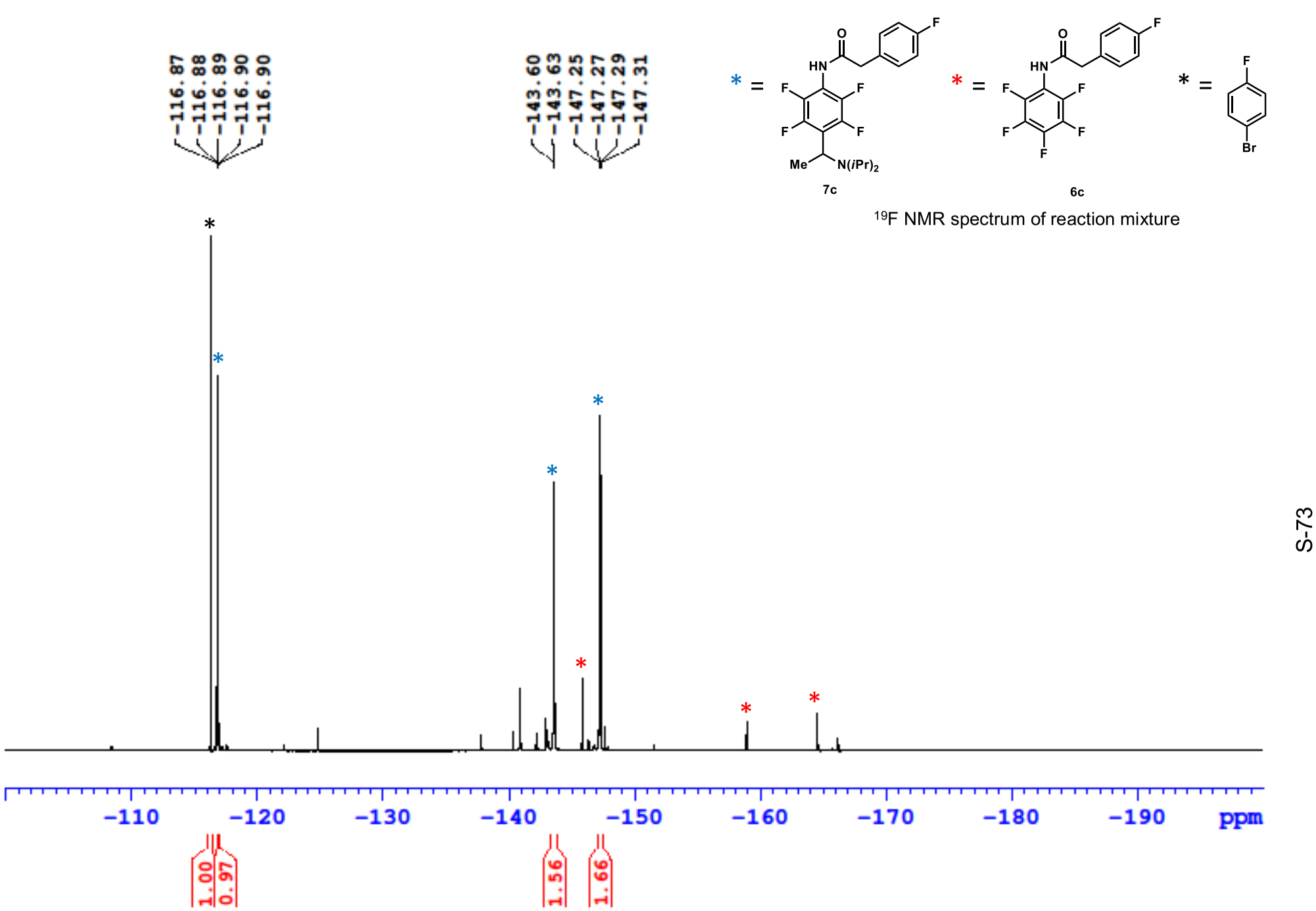

* = p-7b
* = o-7b
19F NMR spectrum
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
0.14
0.13
0.13
2.00
2.00
0.12
-124.84
-124.86
-135.85
-135.89
-141.01
-141.05
-142.20
-142.23
-146.47
-146.49
-146.51
-146.53
-164.24
-164.25
-164.28
-164.29
-164.32
-164.33

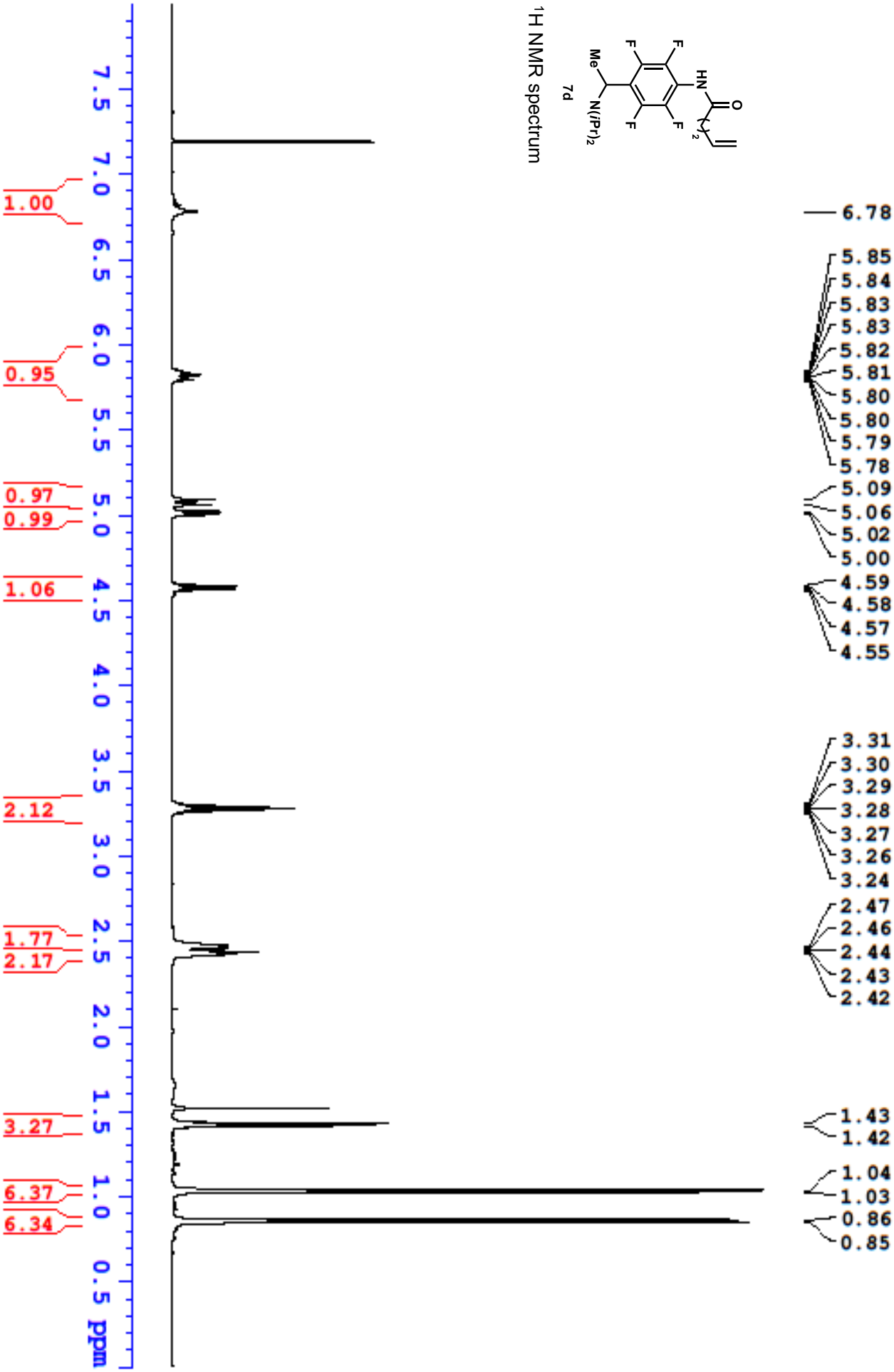


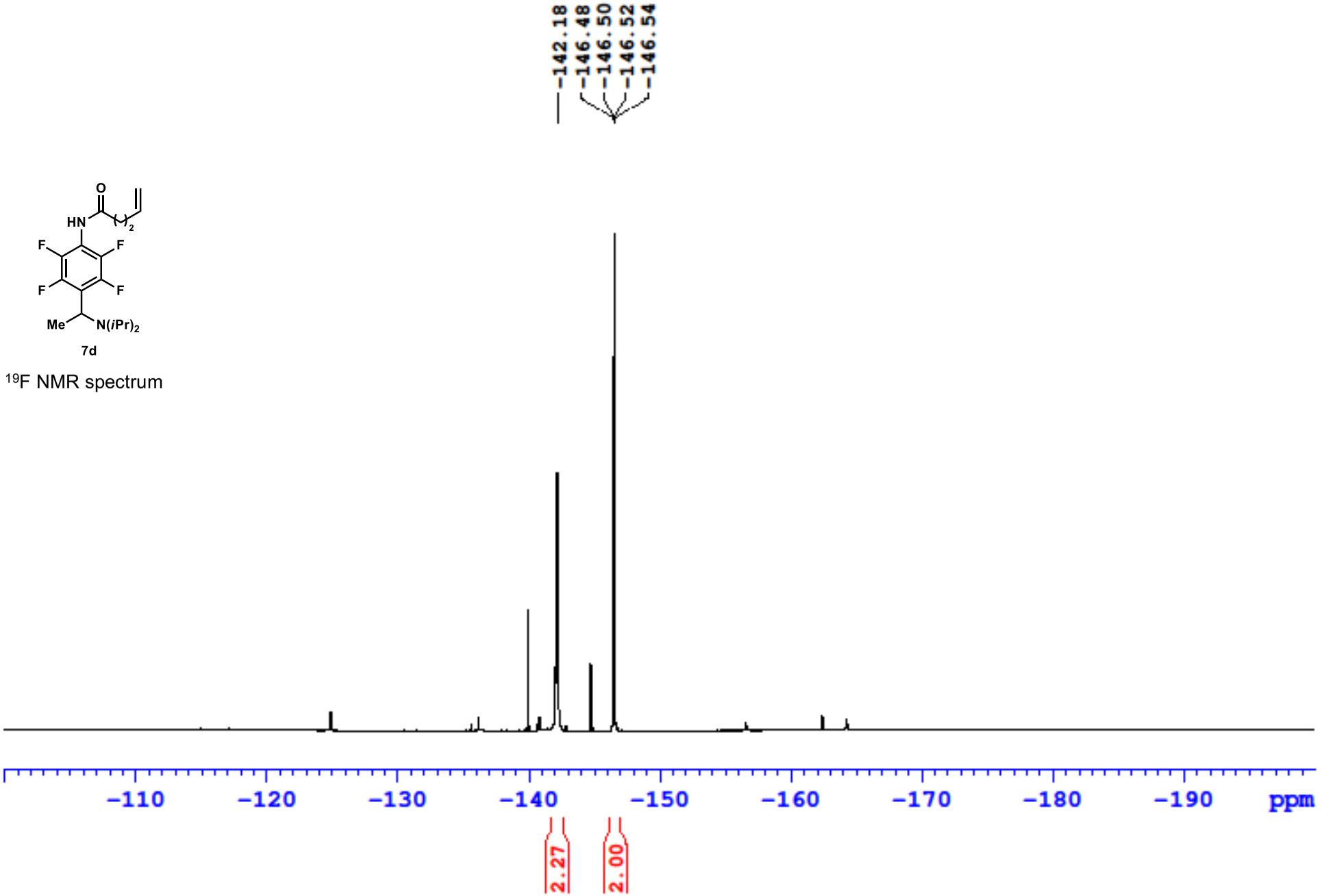
^{19}F NMR spectrum of reaction mixture

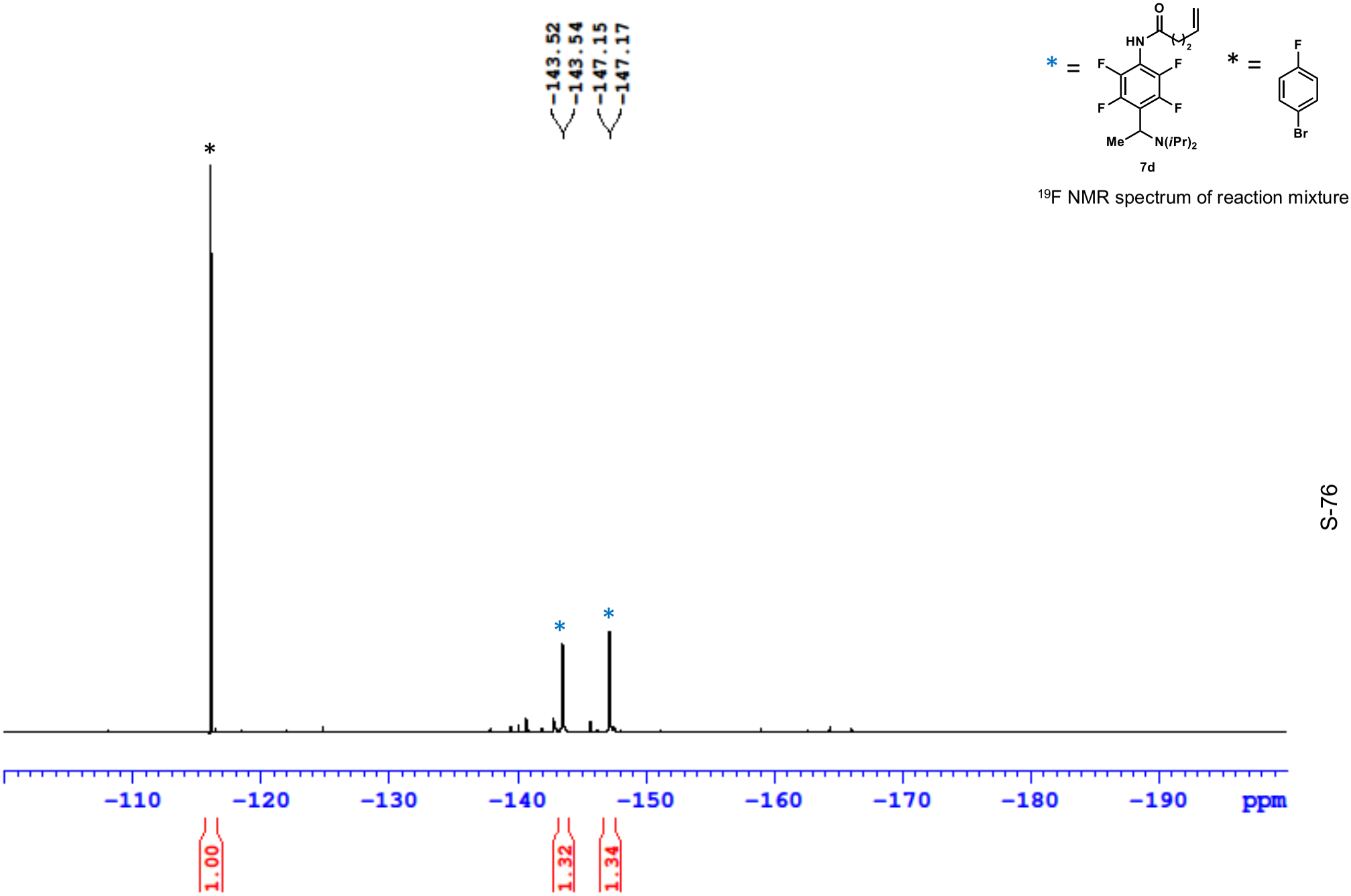

^{1}H NMR spectrum
7c
Me
N(iPr)$_2$
HN
O
F
7.35
7.34
7.33
7.11
7.09
7.08
6.92
4.67
4.65
4.64
4.63
3.78
3.39
3.37
3.36
3.35
3.34
3.33
3.32
1.50
1.49
1.12
1.11
0.93
0.92
1.88
1.97
1.00
0.91
2.09
1.84
3.07
5.60
5.87
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


19F NMR spectrum
7c
Me
N(iPr)2
HN
O
F
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
0.88
2.00
2.04
-114.38
-142.06
-142.08
-146.54
-146.56
-146.58
-146.60
-146.60

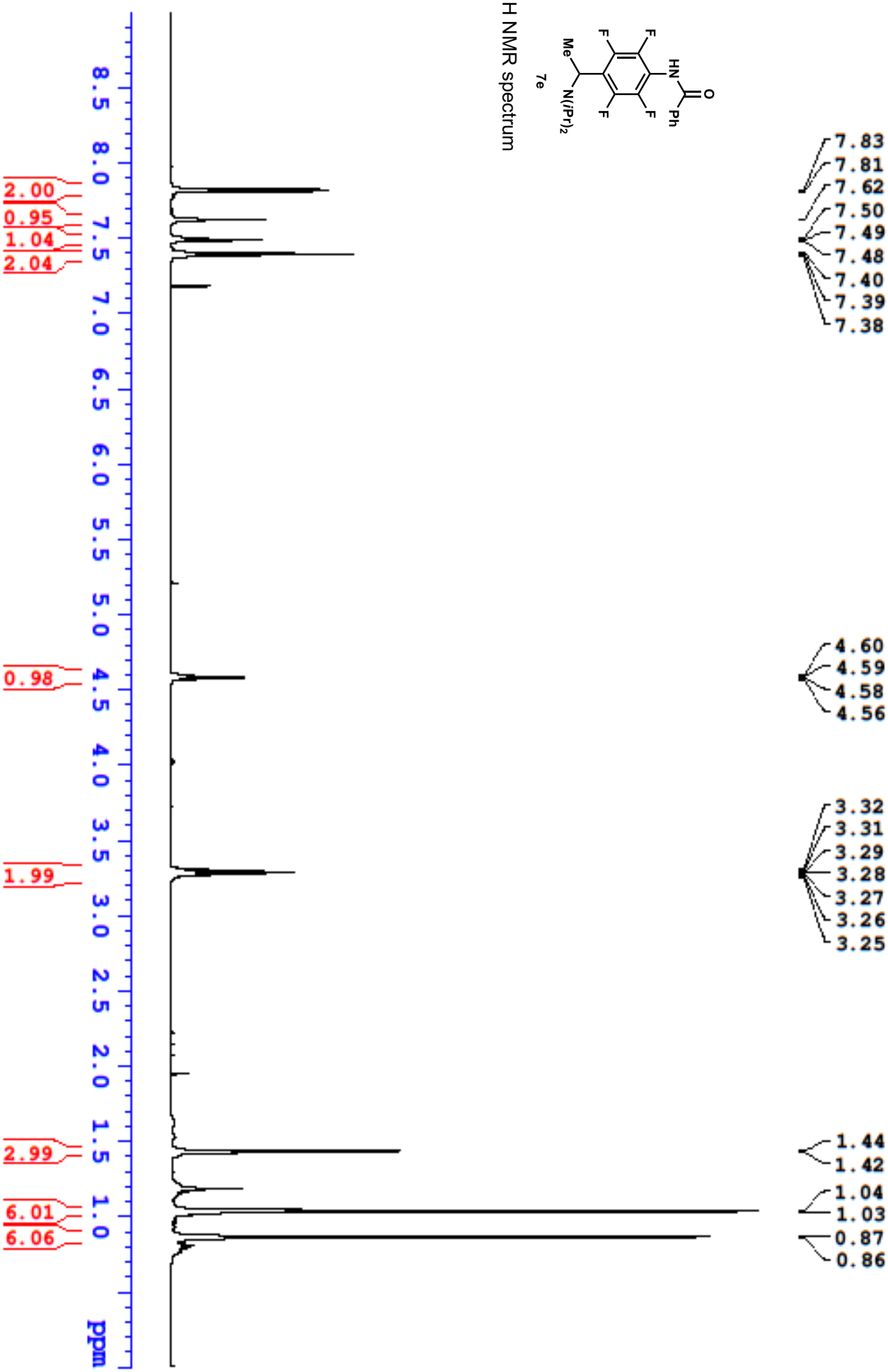

-116.87
-116.88
-116.89
-116.90
-116.90
-143.60
-143.63
-147.25
-147.27
-147.29
-147.31
* =
HN
O
F
F
F
F
Me
N(iPr)2
7c
* =
HN
O
F
F
F
F
F
6c
* =
F
Br
19F NMR spectrum of reaction mixture
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
1.00
0.97
1.56
1.66

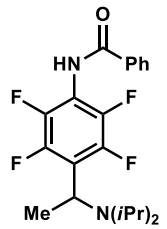

^{1}H NMR spectrum
7d
Me
N(iPr)$_2$
F
F
F
F
HN
O
6.78
5.85
5.84
5.83
5.83
5.82
5.81
5.80
5.80
5.79
5.78
5.09
5.06
5.02
5.00
4.59
4.58
4.57
4.55
3.31
3.30
3.29
3.28
3.27
3.26
3.24
2.47
2.46
2.44
2.43
2.42
1.43
1.42
1.04
1.03
0.86
0.85
1.00
0.95
0.97
0.99
1.06
2.12
1.77
2.17
3.27
6.37
6.34
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


-142.18
-146.48
-146.50
-146.52
-146.54
HN
F
F
F
F
Me
N(iPr)2
7d
19F NMR spectrum
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.27
2.00



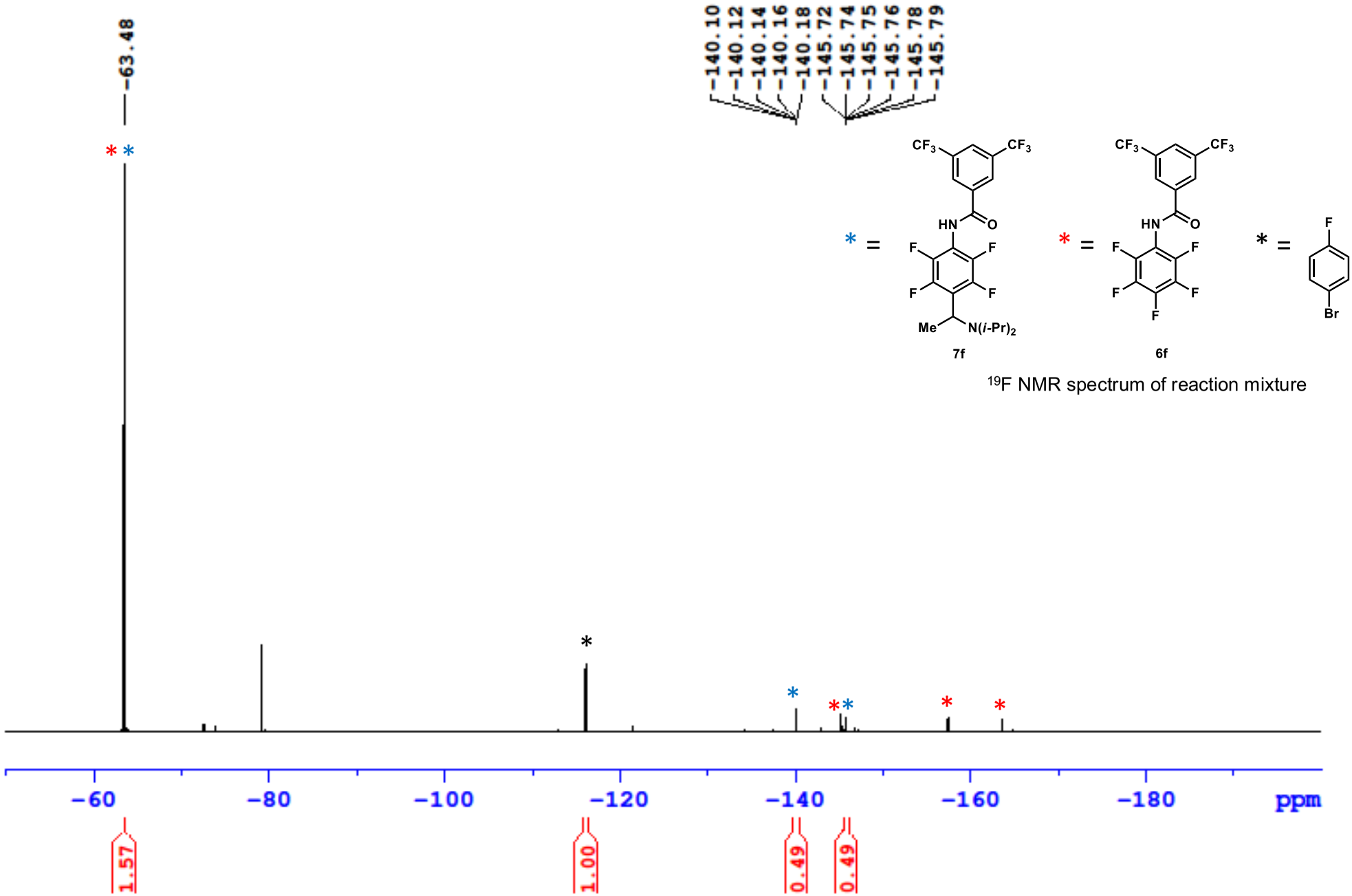
^{19}F NMR spectrum of reaction mixture


^{1}H NMR spectrum
7e
Me
N(iPr)$_2$
F
F
F
F
HN
O
Ph
7.83
7.81
7.62
7.50
7.49
7.48
7.40
7.39
7.38
4.60
4.59
4.58
4.56
3.32
3.31
3.29
3.28
3.27
3.26
3.25
1.44
1.42
1.04
1.03
0.87
0.86
2.00
0.95
1.04
2.04
0.98
1.99
2.99
6.01
6.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

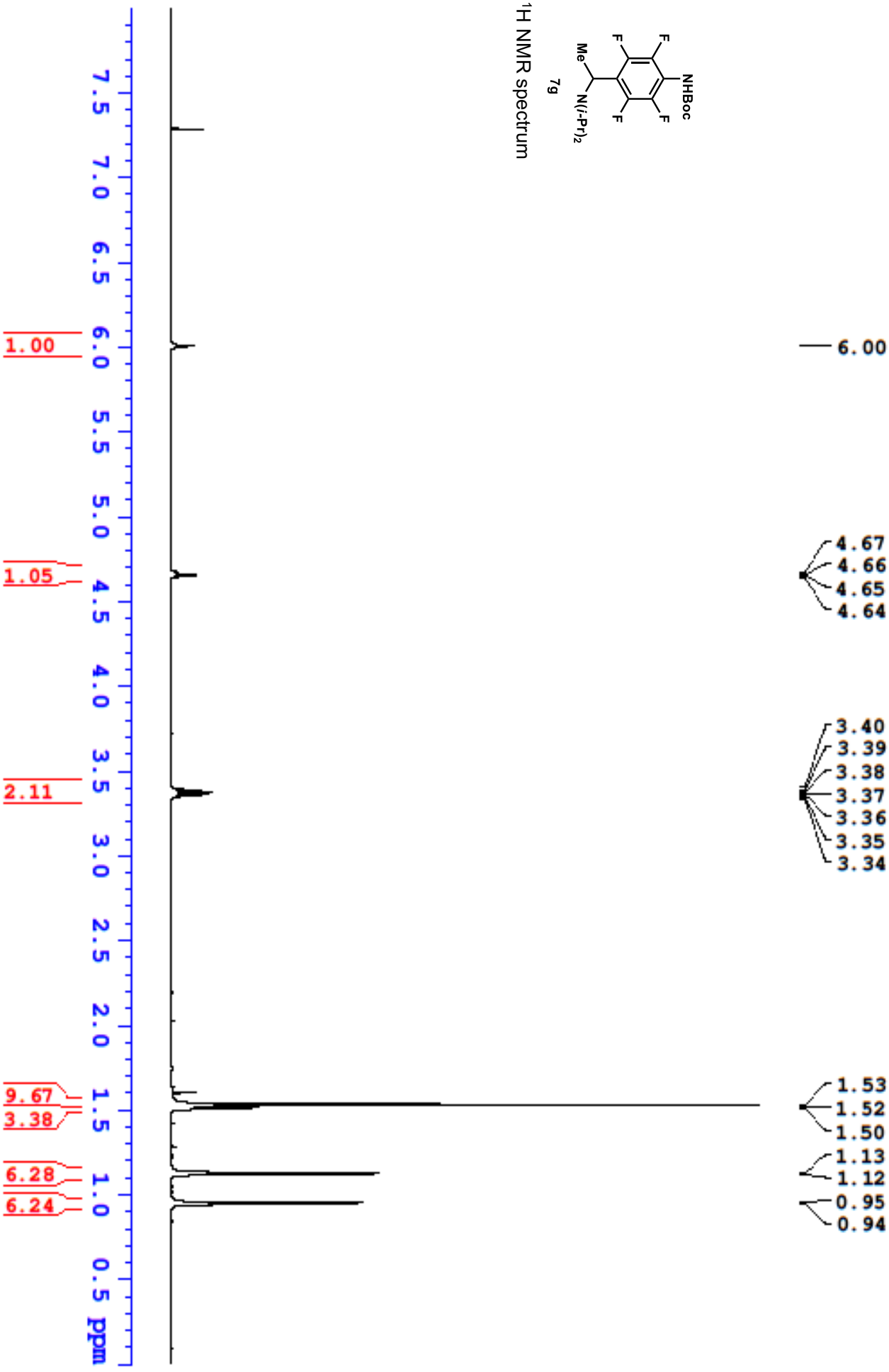


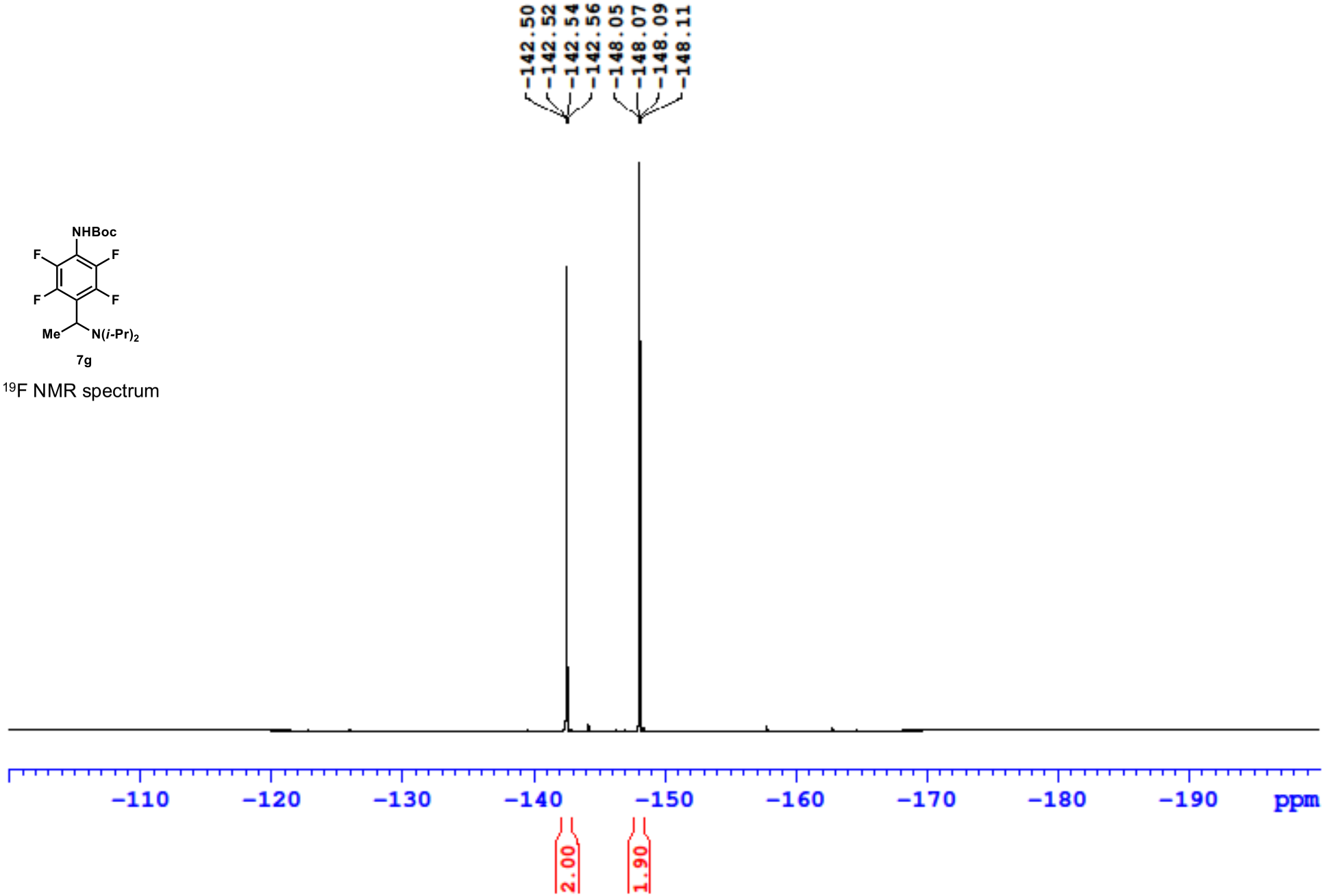
7e

^{19}F NMR spectrum



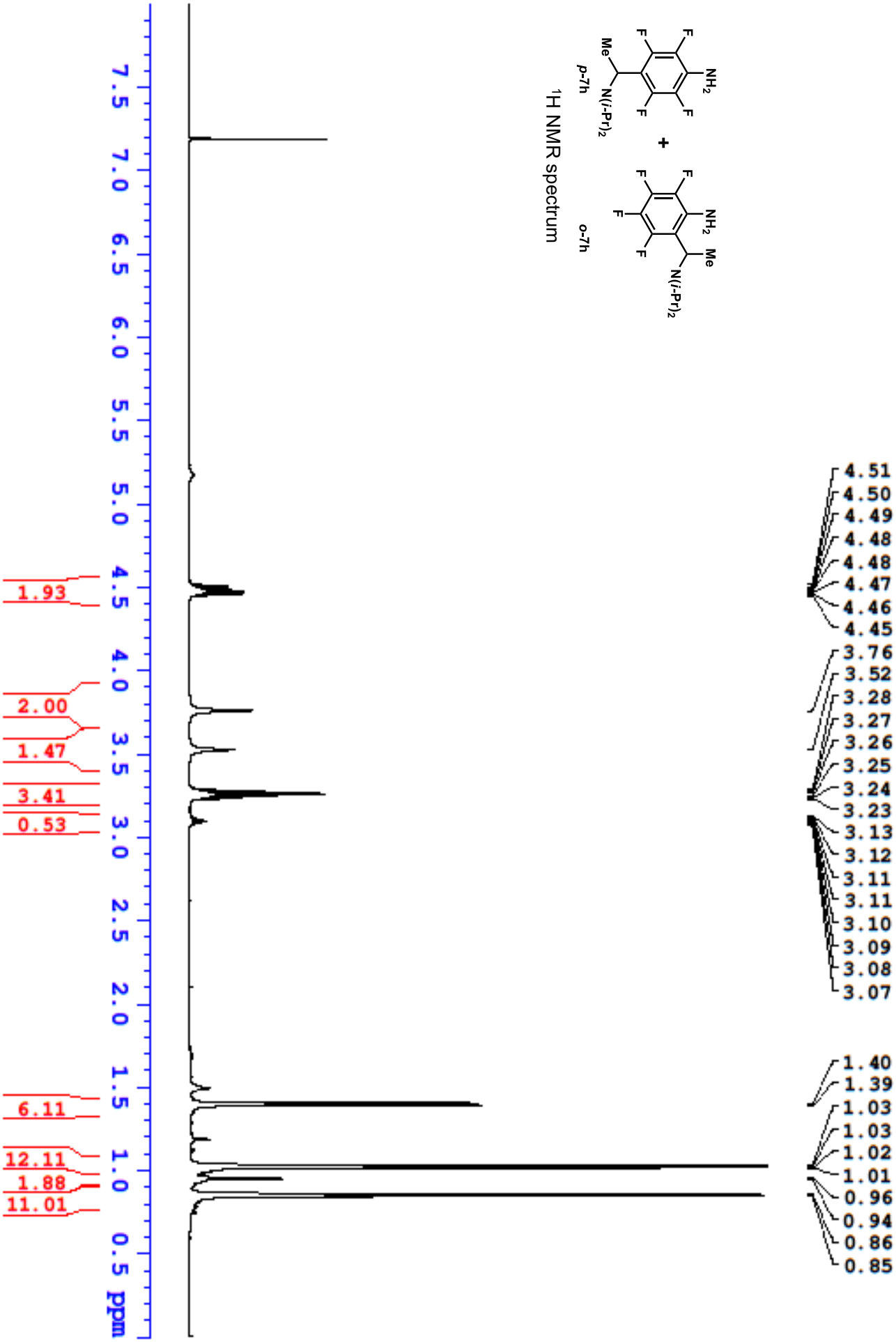
^{19}F NMR spectrum of reaction mixture

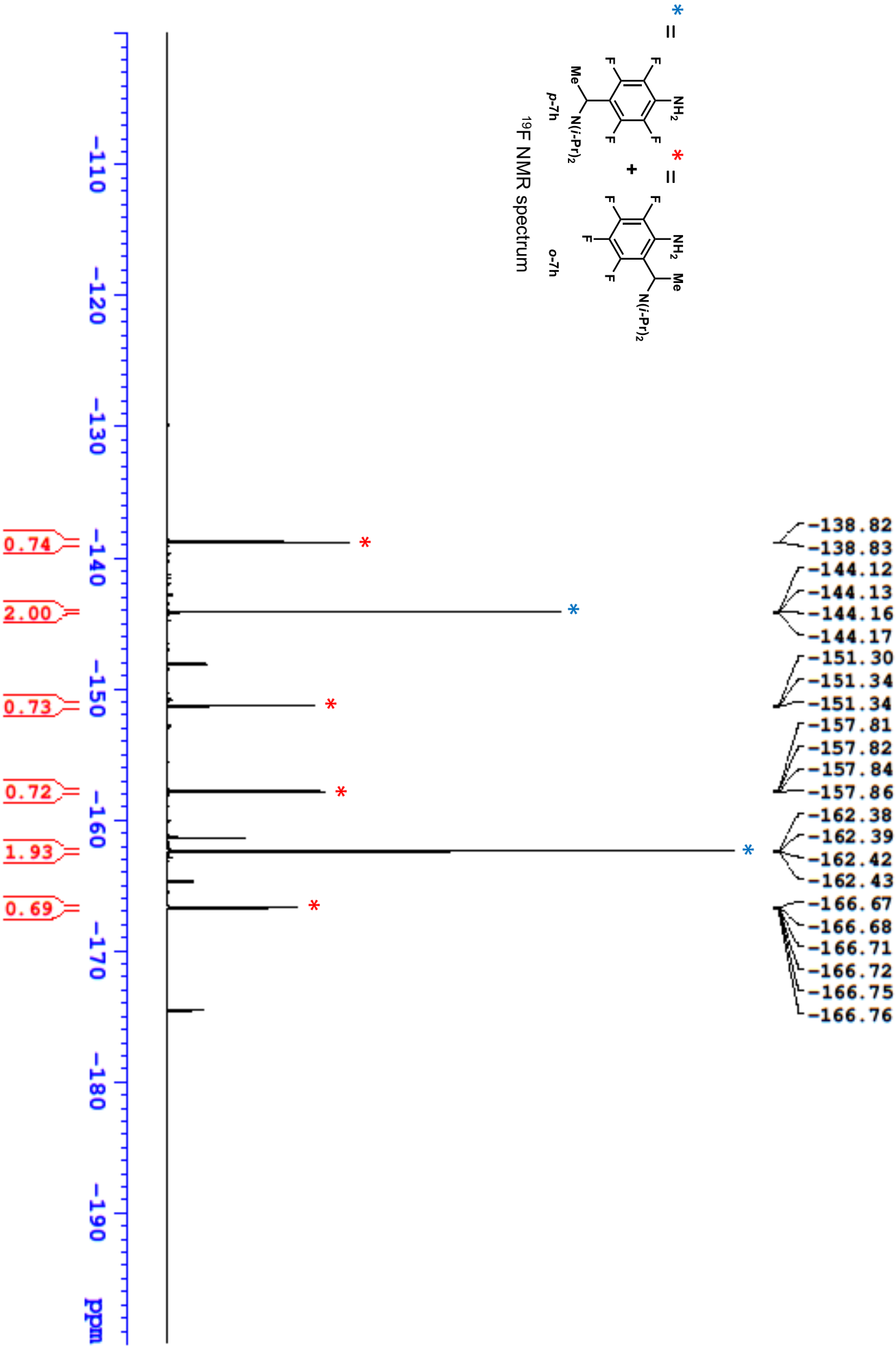

^{1}H NMR spectrum
7g
Me
N(i-Pr)$_2$
F
F
F
F
NHBoc
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.05
2.11
9.67
3.38
6.28
6.24
6.00
4.67
4.66
4.65
4.64
3.40
3.39
3.38
3.37
3.36
3.35
3.34
1.53
1.52
1.50
1.13
1.12
0.95
0.94

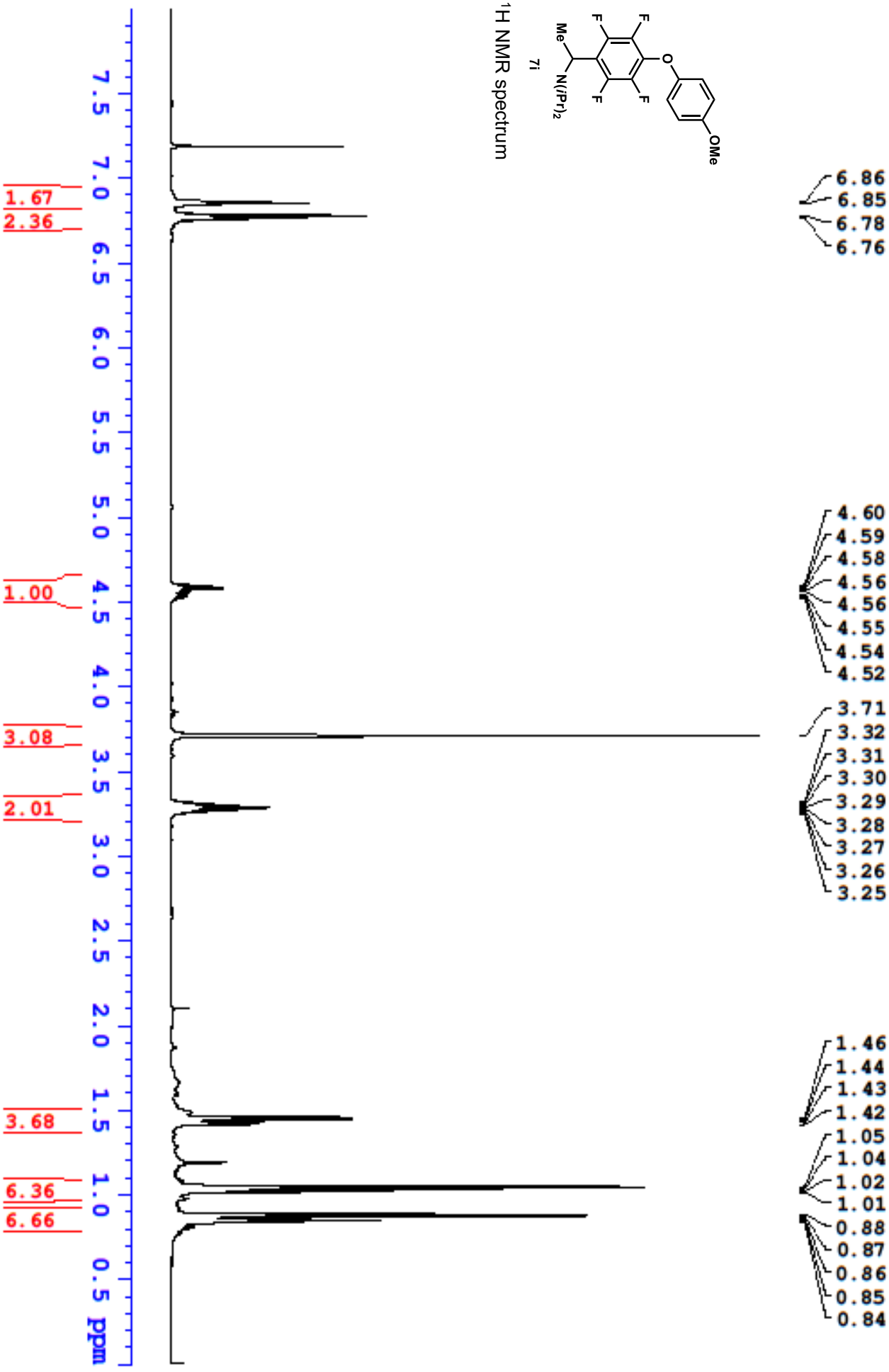


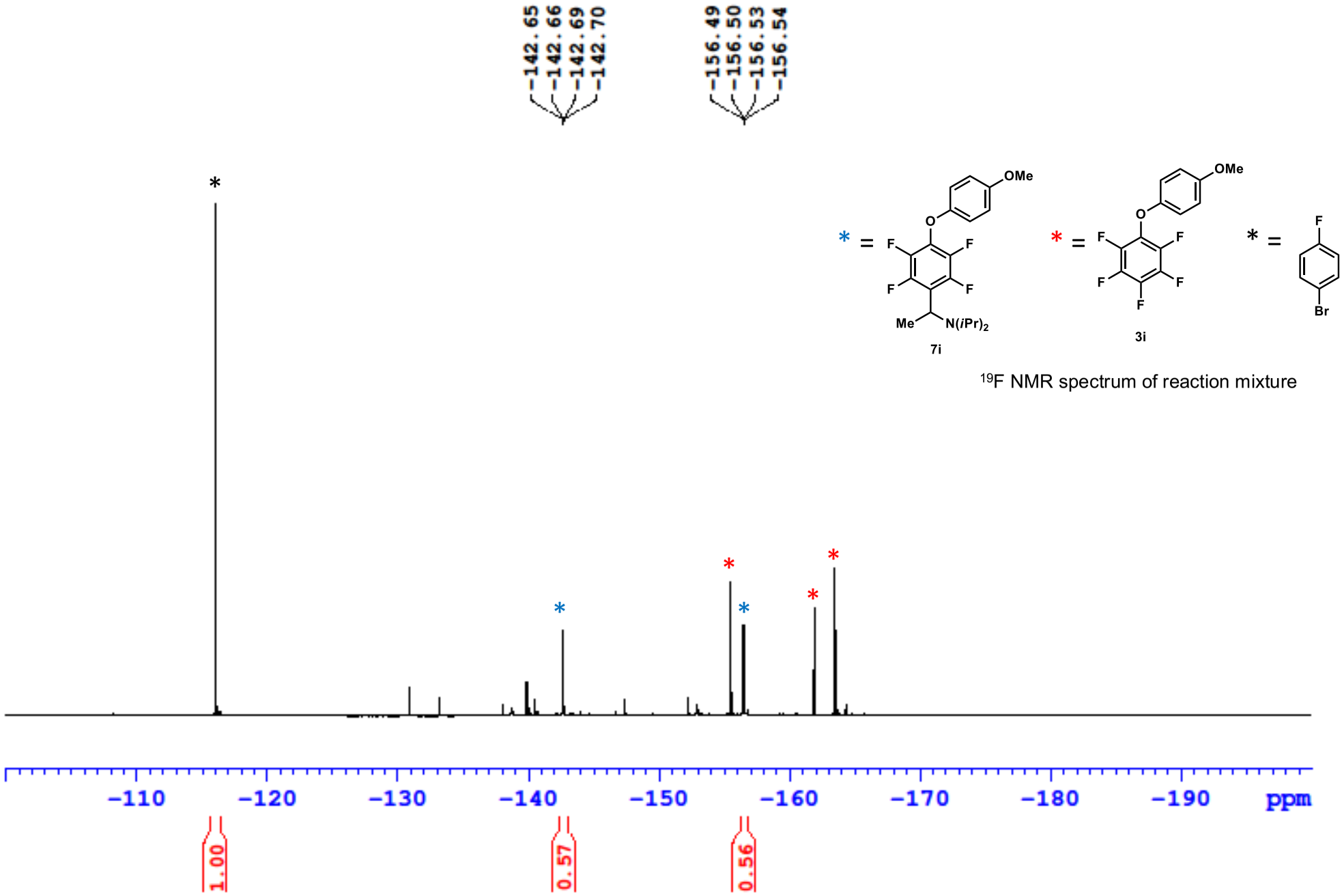
7g

^{19}F NMR spectrum

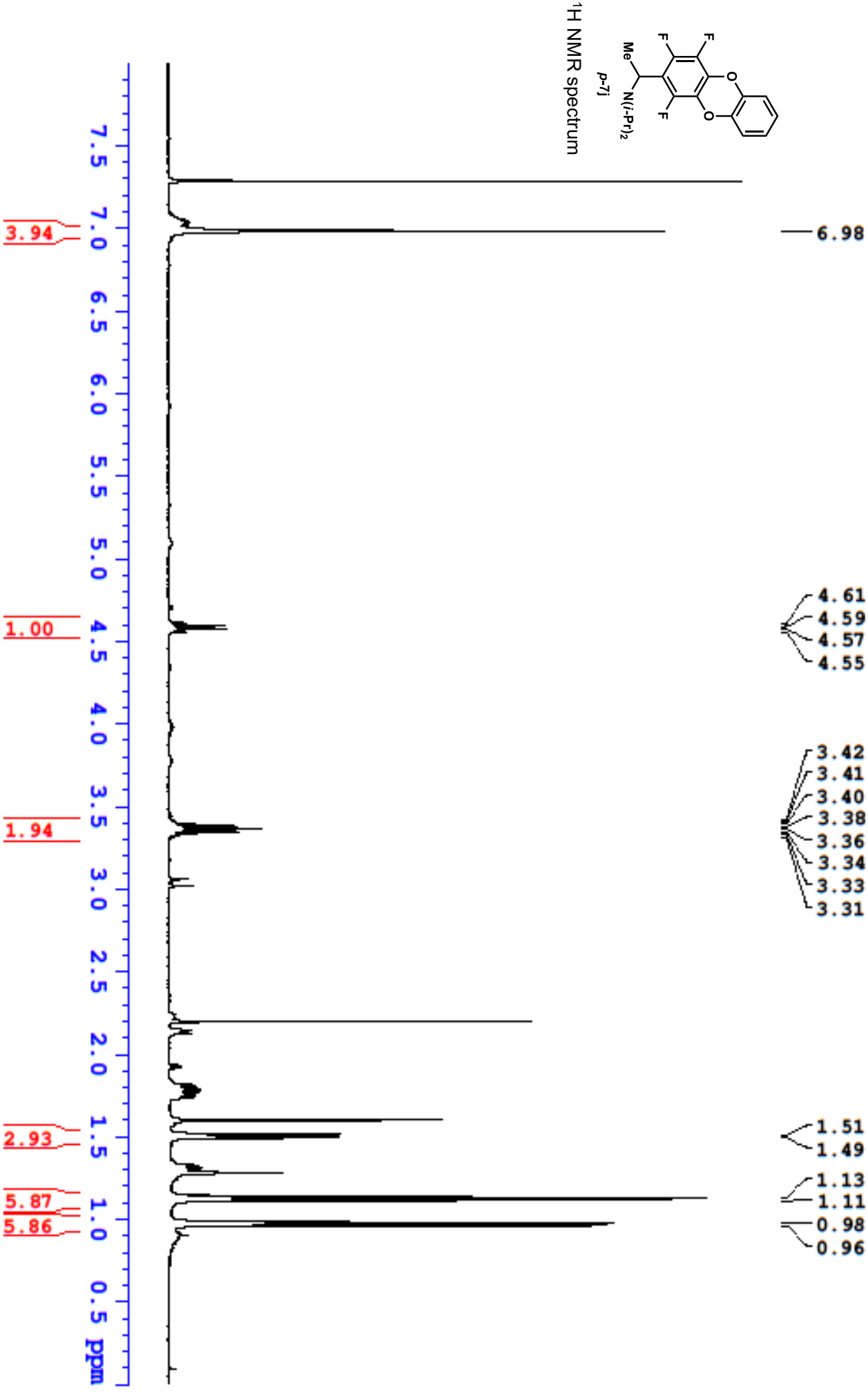

p-7h
o-7h
1H NMR spectrum
1.93
2.00
1.47
3.41
0.53
6.11
12.11
1.88
11.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.51
4.50
4.49
4.48
4.48
4.47
4.46
4.45
3.76
3.52
3.28
3.27
3.26
3.25
3.24
3.23
3.13
3.12
3.11
3.11
3.10
3.09
3.08
3.07
1.40
1.39
1.03
1.03
1.02
1.01
0.96
0.94
0.86
0.85

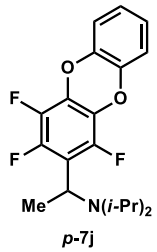

* =
Me
N(i-Pr)2
p-7h
+
* =
NH2
Me
N(i-Pr)2
o-7h
19F NMR spectrum
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
0.74
2.00
0.73
0.72
1.93
0.69
-138.82
-138.83
-144.12
-144.13
-144.16
-144.17
-151.30
-151.34
-151.34
-157.81
-157.82
-157.84
-157.86
-162.38
-162.39
-162.42
-162.43
-166.67
-166.68
-166.71
-166.72
-166.75
-166.76


1H NMR spectrum
7i
Me
N(iPr)2
F
F
F
F
O
OMe
6.86
6.85
6.78
6.76
4.60
4.59
4.58
4.56
4.56
4.55
4.54
4.52
3.71
3.32
3.31
3.30
3.29
3.28
3.27
3.26
3.25
1.46
1.44
1.43
1.42
1.05
1.04
1.02
1.01
0.88
0.87
0.86
0.85
0.84
1.67
2.36
1.00
3.08
2.01
3.68
6.36
6.66
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



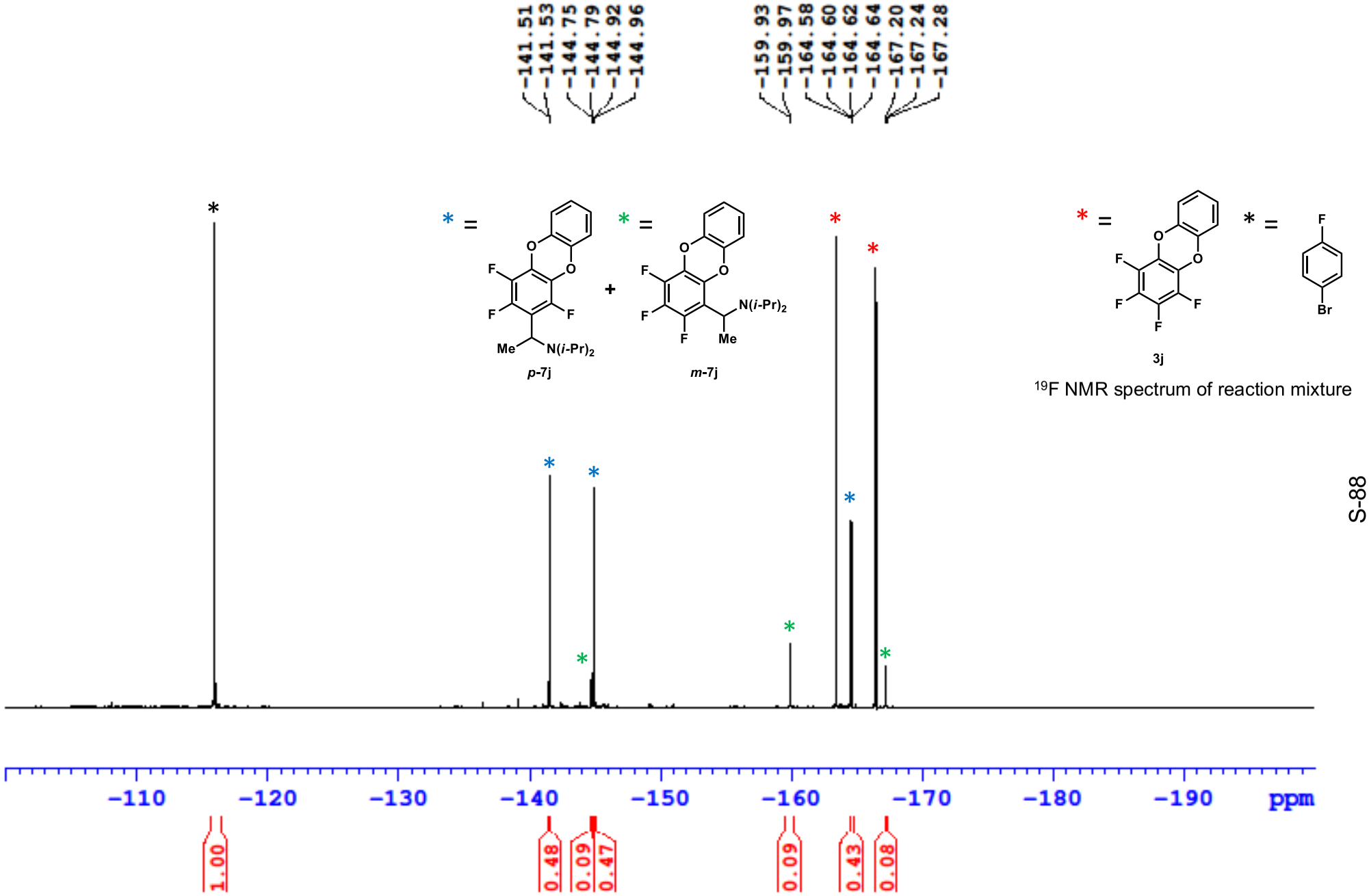
^{19}F NMR spectrum of reaction mixture


¹H NMR spectrum
p-7j
Me
N(i-Pr)2
F
F
F
O
O
3.94
1.00
1.94
2.93
5.87
5.86
6.98
4.61
4.59
4.57
4.55
3.42
3.41
3.40
3.38
3.36
3.34
3.33
3.31
1.51
1.49
1.13
1.11
0.98
0.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

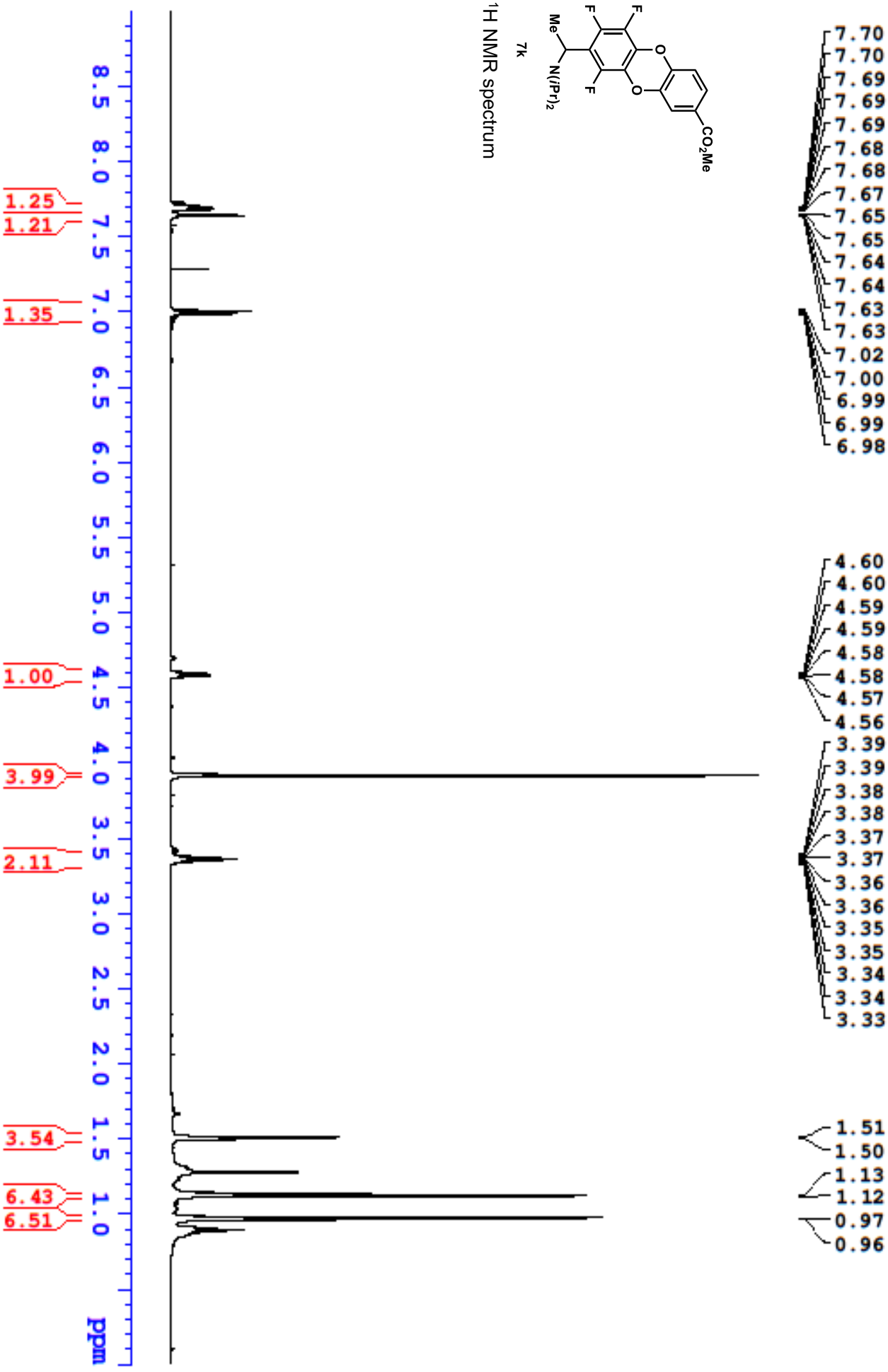


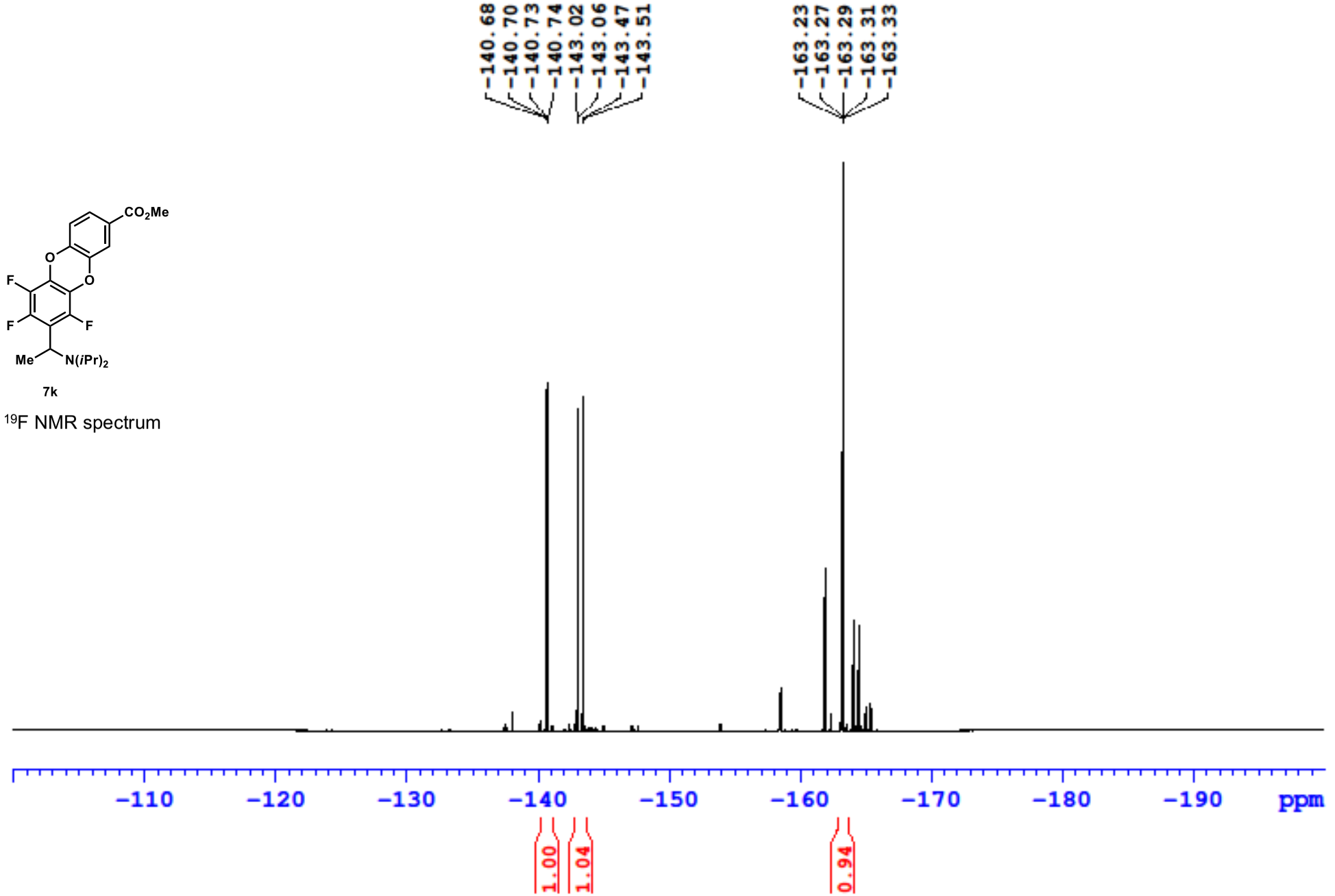
p-7j

^{19}F NMR spectrum



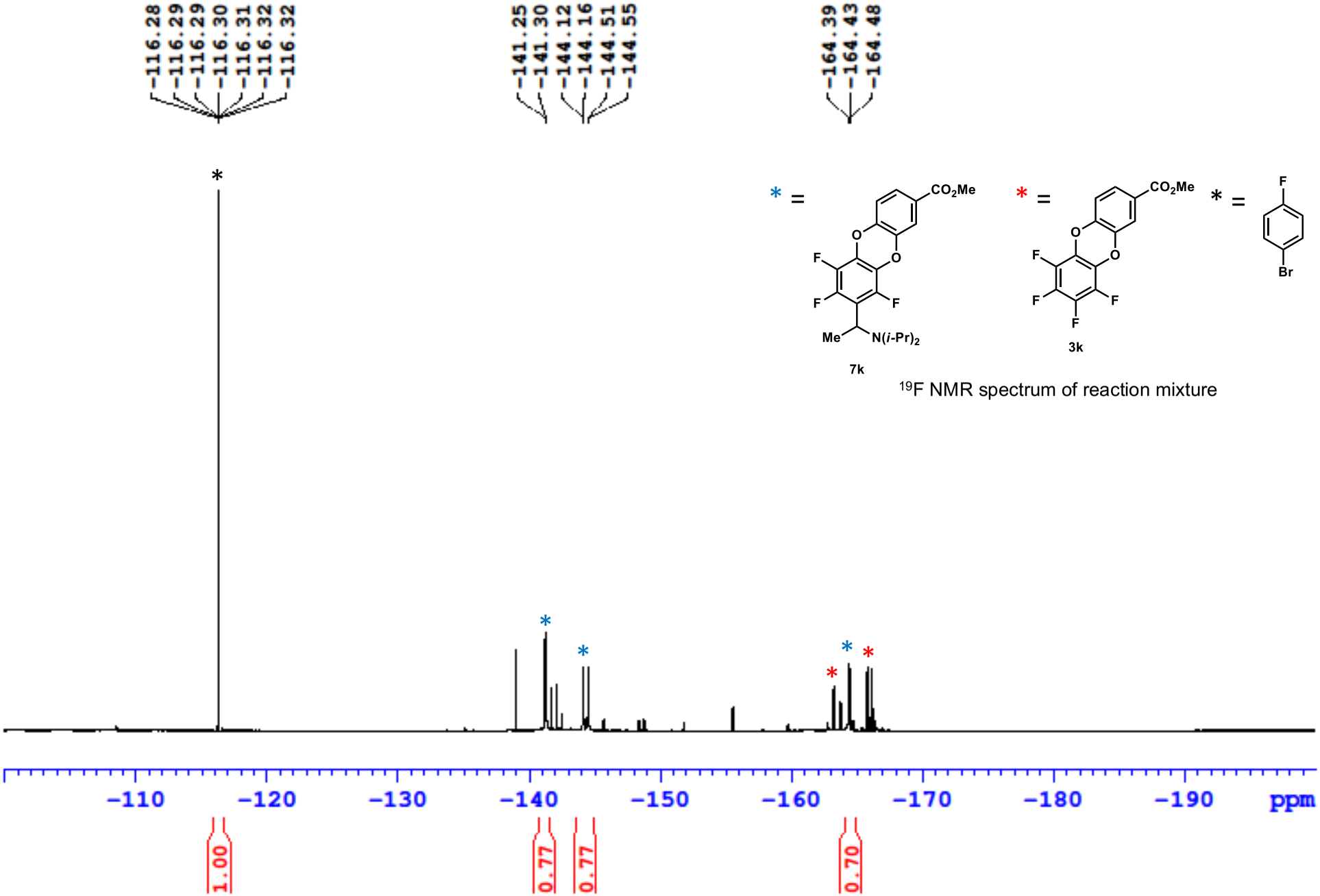
^{19}F NMR spectrum of reaction mixture


7k
1H NMR spectrum
Me
N(iPr)2
F
F
F
O
O
CO2Me
7.70
7.70
7.69
7.69
7.69
7.68
7.68
7.67
7.65
7.65
7.64
7.64
7.63
7.63
7.02
7.00
6.99
6.99
6.98
4.60
4.60
4.59
4.59
4.58
4.58
4.57
4.56
3.39
3.39
3.38
3.38
3.37
3.37
3.36
3.36
3.35
3.35
3.34
3.34
3.33
1.51
1.50
1.13
1.12
0.97
0.96
1.25
1.21
1.35
1.00
3.99
2.11
3.54
6.43
6.51
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

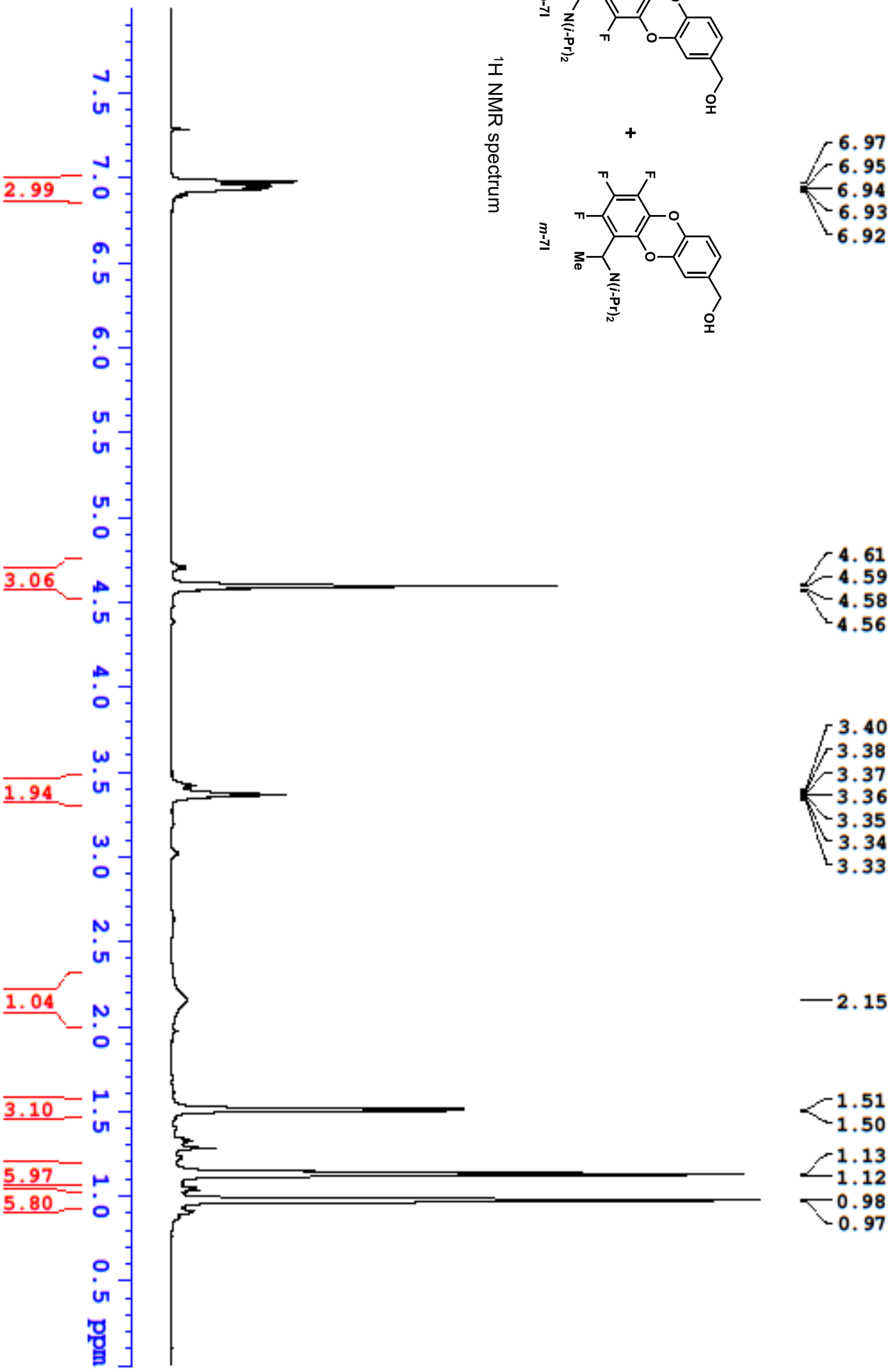


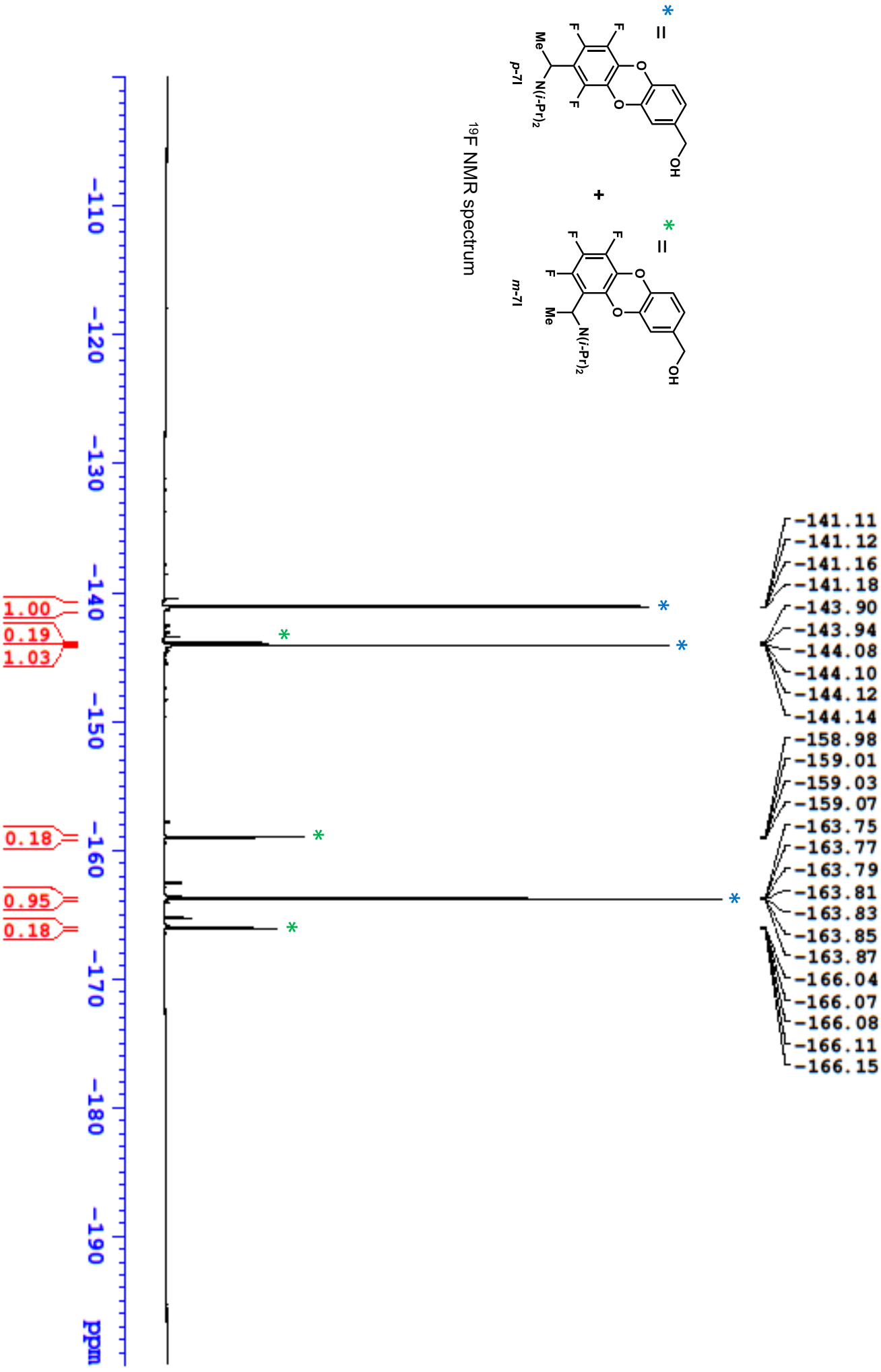
7k

^{19}F NMR spectrum



^{19}F NMR spectrum of reaction mixture


1H NMR spectrum
p-7l
m-7l
Me
N(i-Pr)2
F
O
OH
6.97
6.95
6.94
6.93
6.92
4.61
4.59
4.58
4.56
3.40
3.38
3.37
3.36
3.35
3.34
3.33
2.15
1.51
1.50
1.13
1.12
0.98
0.97
2.99
3.06
1.94
1.04
3.10
5.97
5.80
ppm


19F NMR spectrum
p-7l
m-7l
Me
N(i-Pr)2
OH
F
O
1.00
0.19
1.03
0.18
0.95
0.18
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
-141.11
-141.12
-141.16
-141.18
-143.90
-143.94
-144.08
-144.10
-144.12
-144.14
-158.98
-159.01
-159.03
-159.07
-163.75
-163.77
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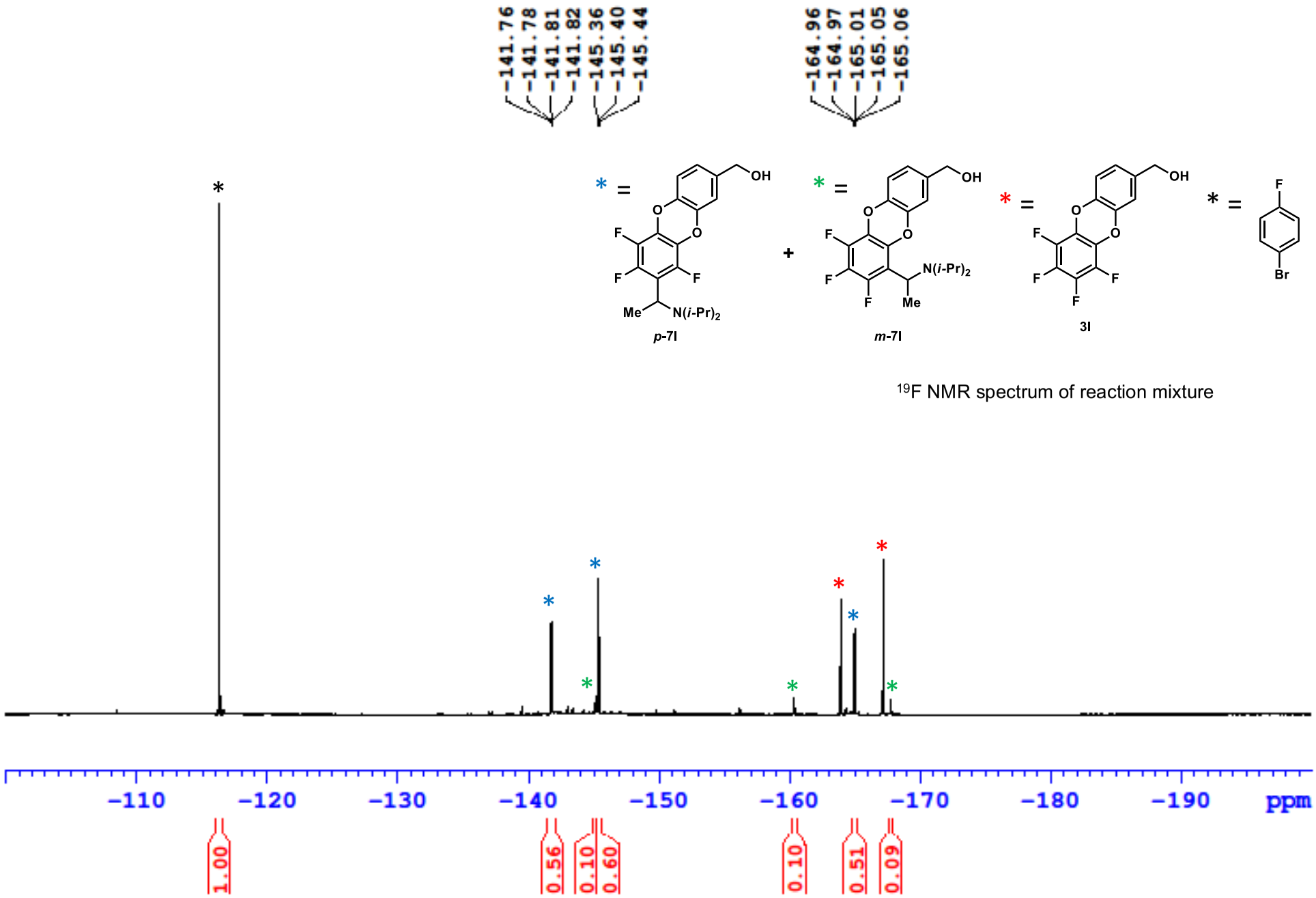
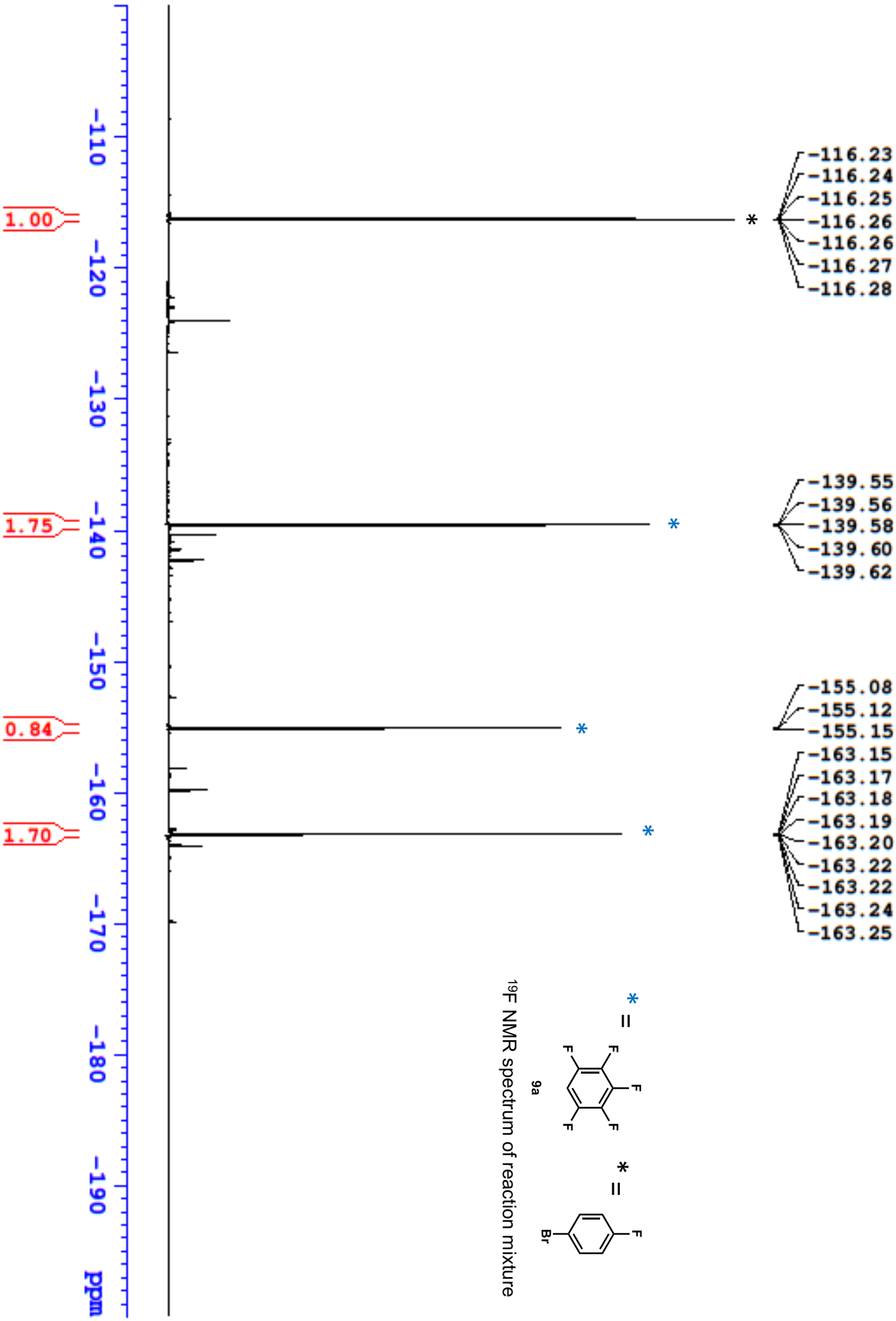
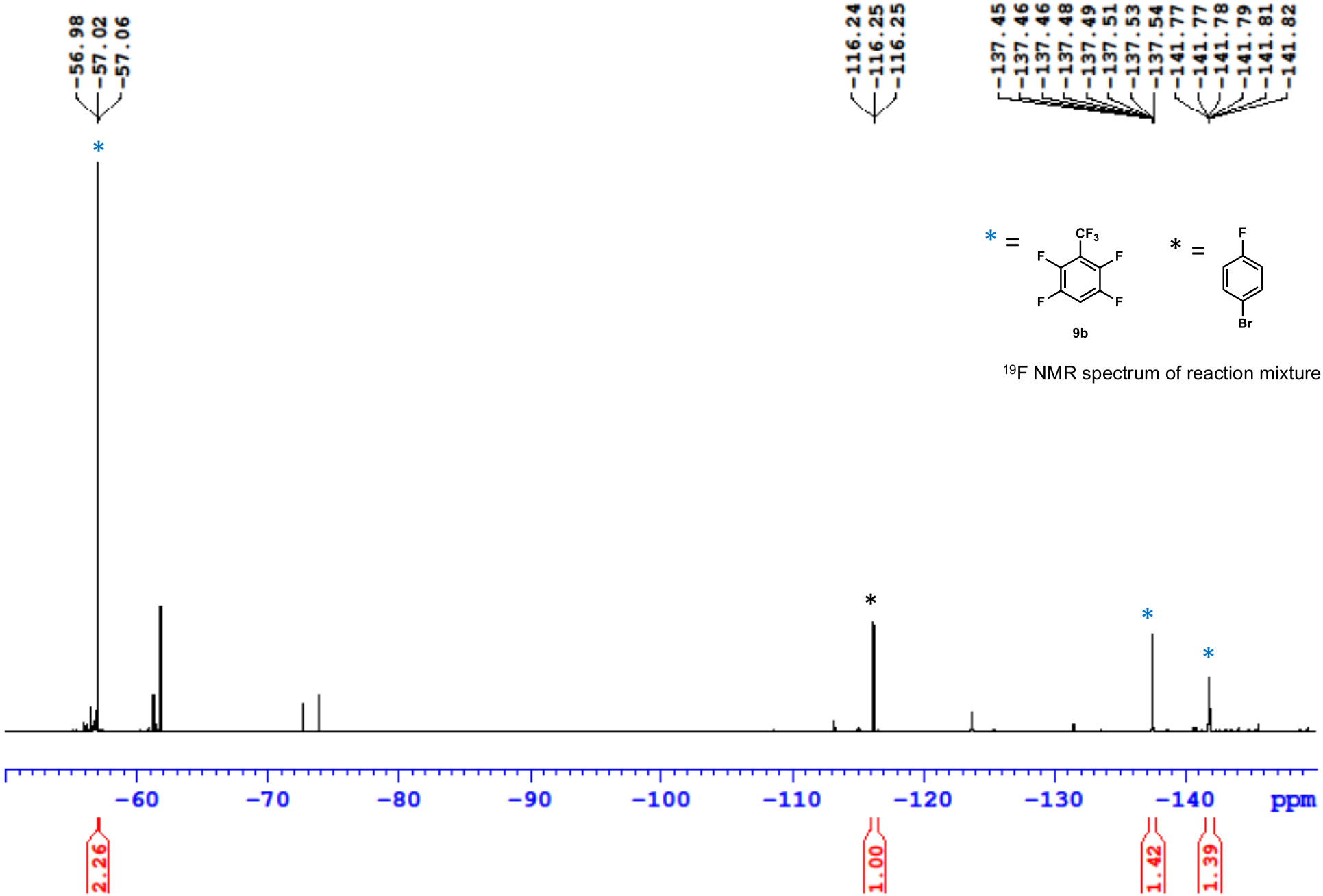
-166.04
-166.07
-166.08
-166.11
-166.15



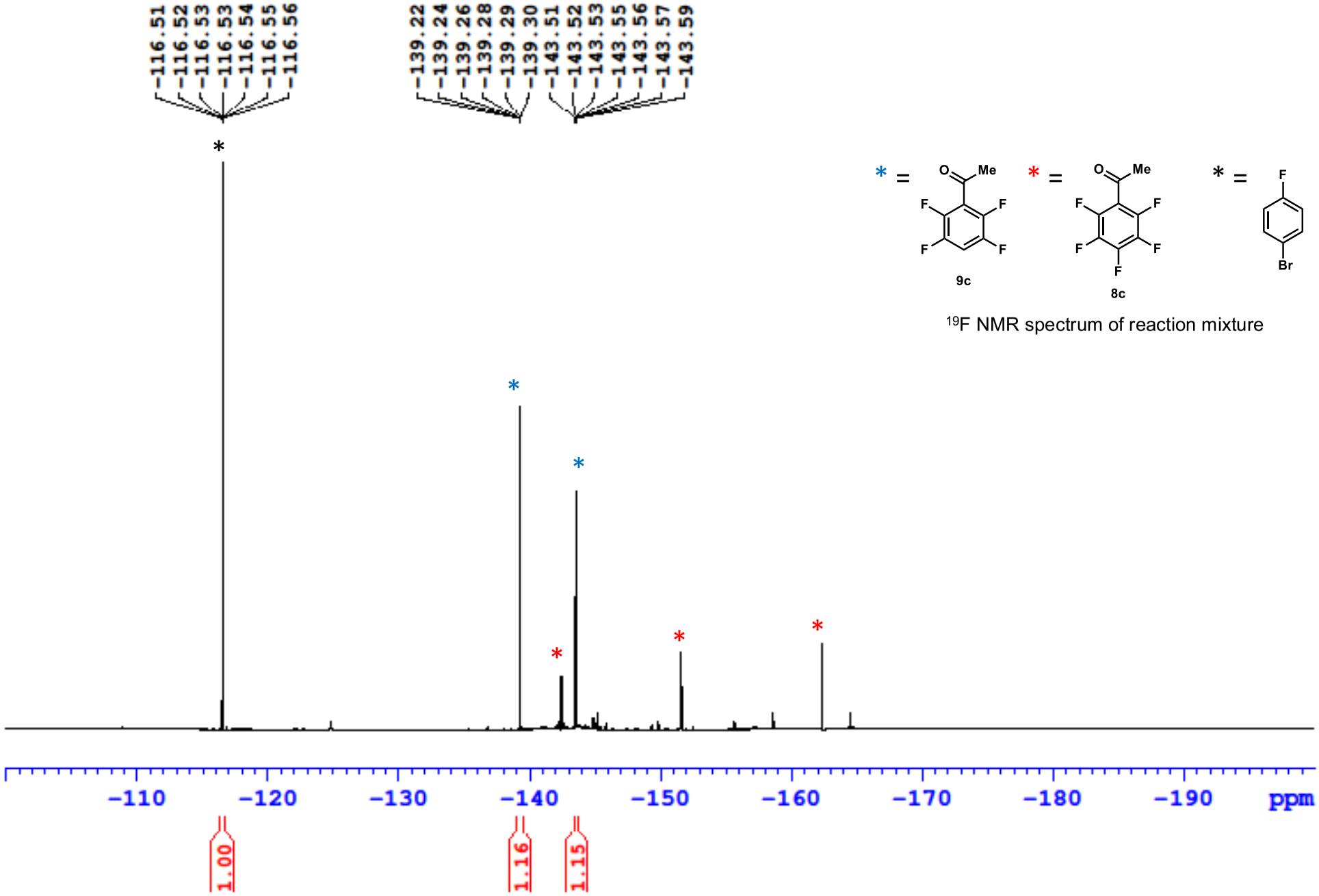
^{19}F NMR spectrum of reaction mixture



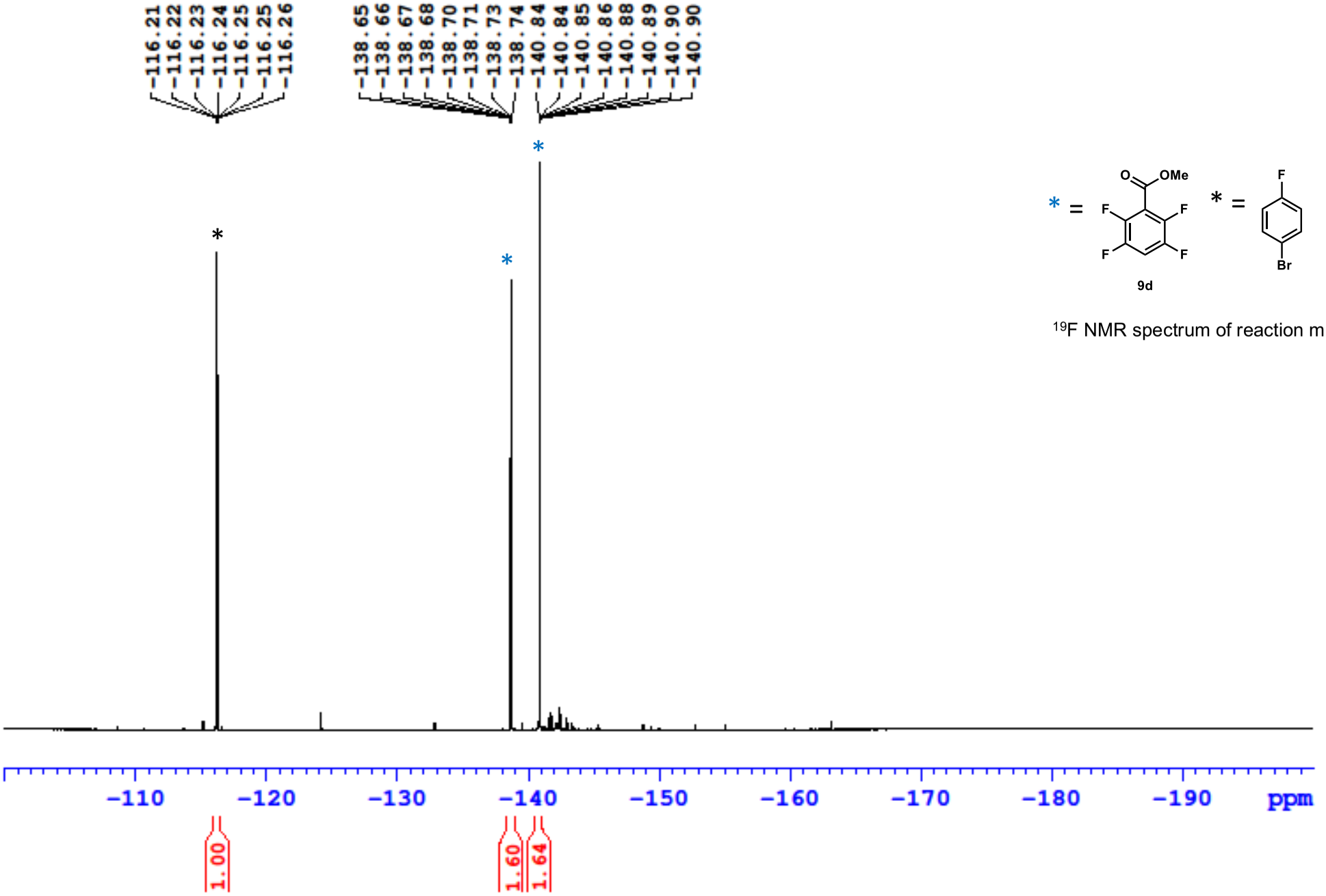
^{19}F NMR spectrum of reaction mixture



^{19}F NMR spectrum of reaction mixture



^{19}F NMR spectrum of reaction mixture

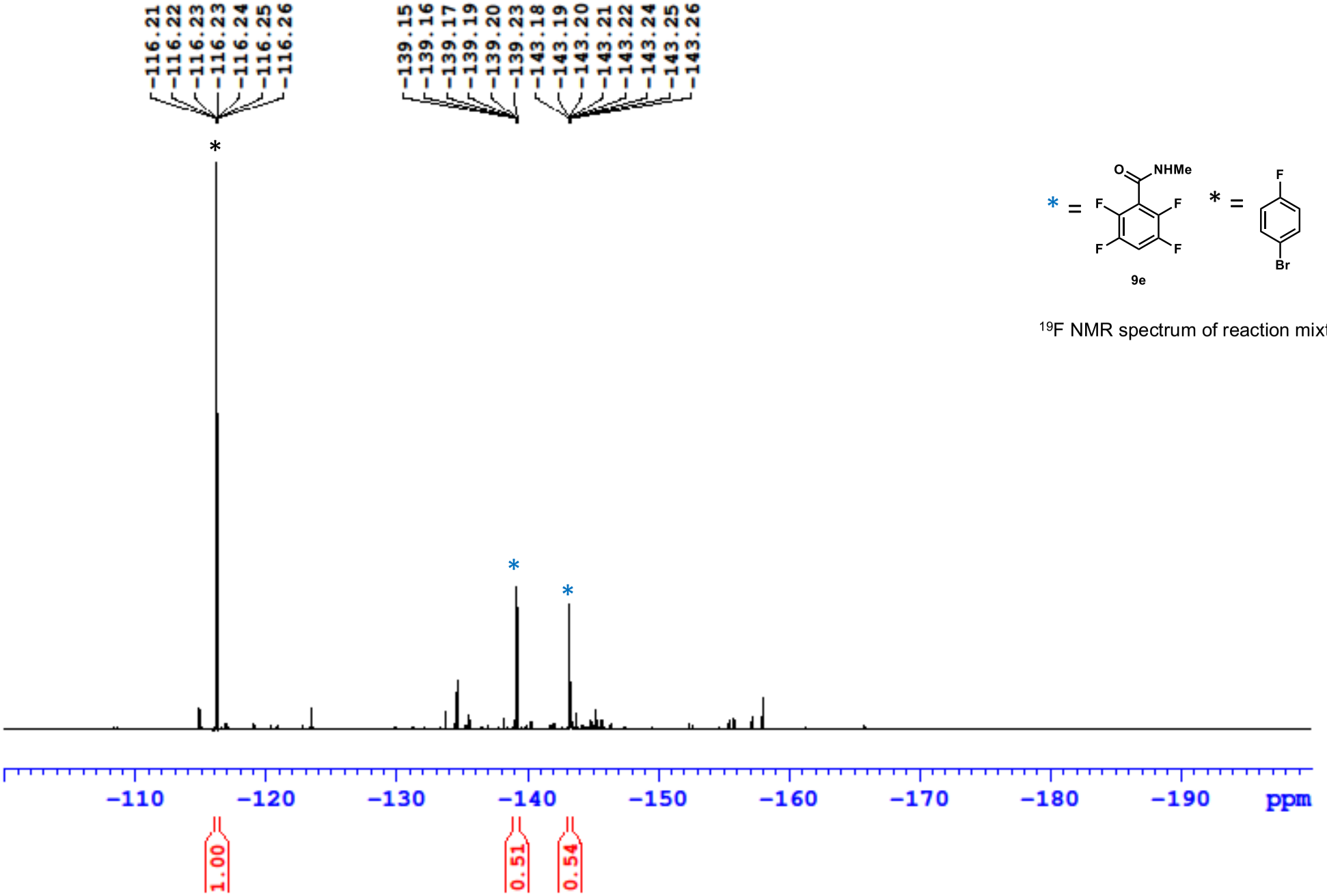


* =

9d

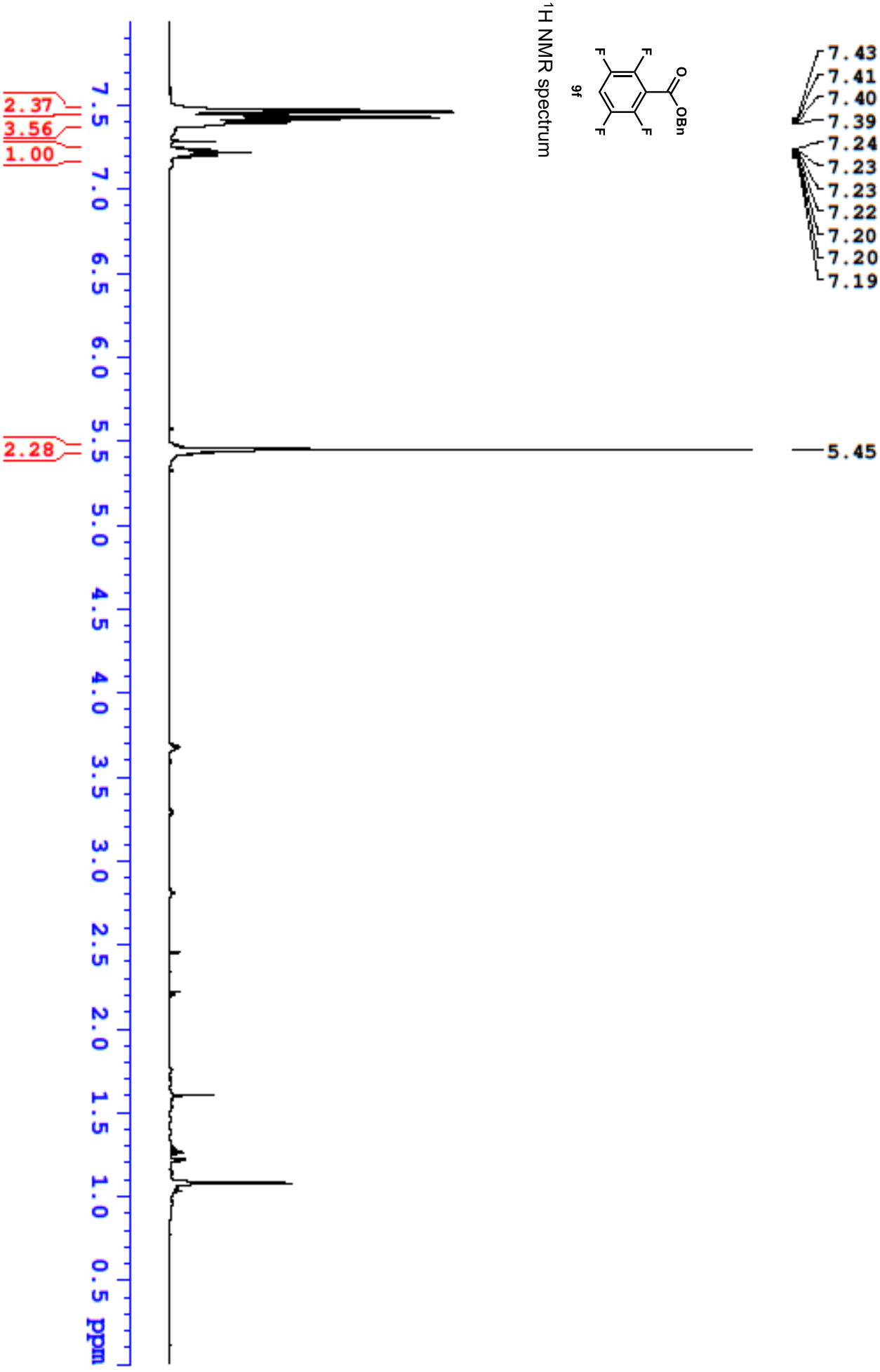
* =

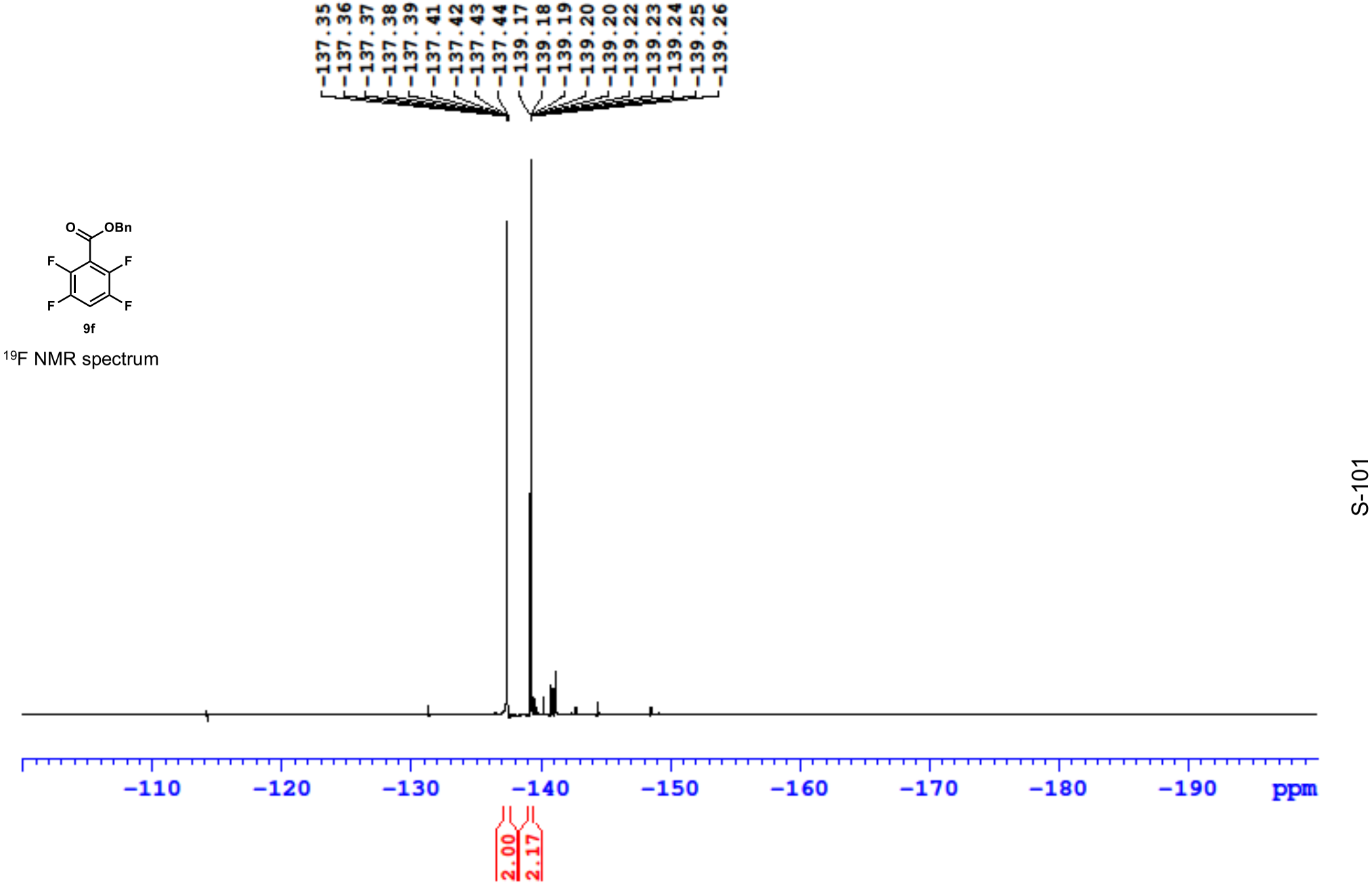
^{19}F NMR spectrum of reaction mixture



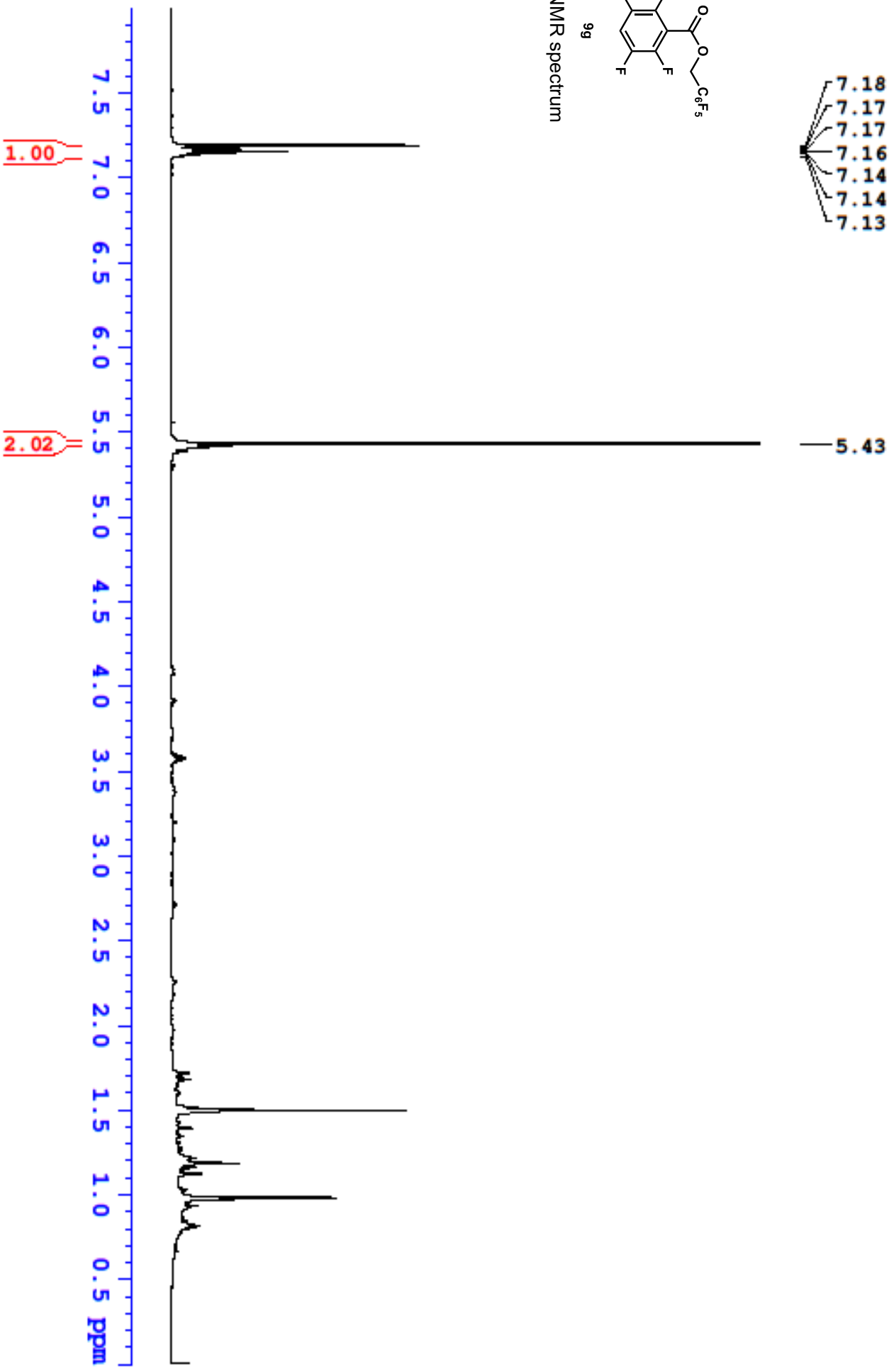
9e

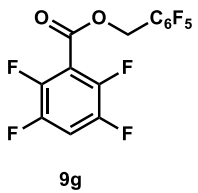
^{19}F NMR spectrum of reaction mixture


^{1}H NMR spectrum
9f
F
F
F
F
O
OBn
7.43
7.41
7.40
7.39
7.24
7.23
7.23
7.22
7.20
7.20
7.19
5.45
2.37
3.56
1.00
2.28
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



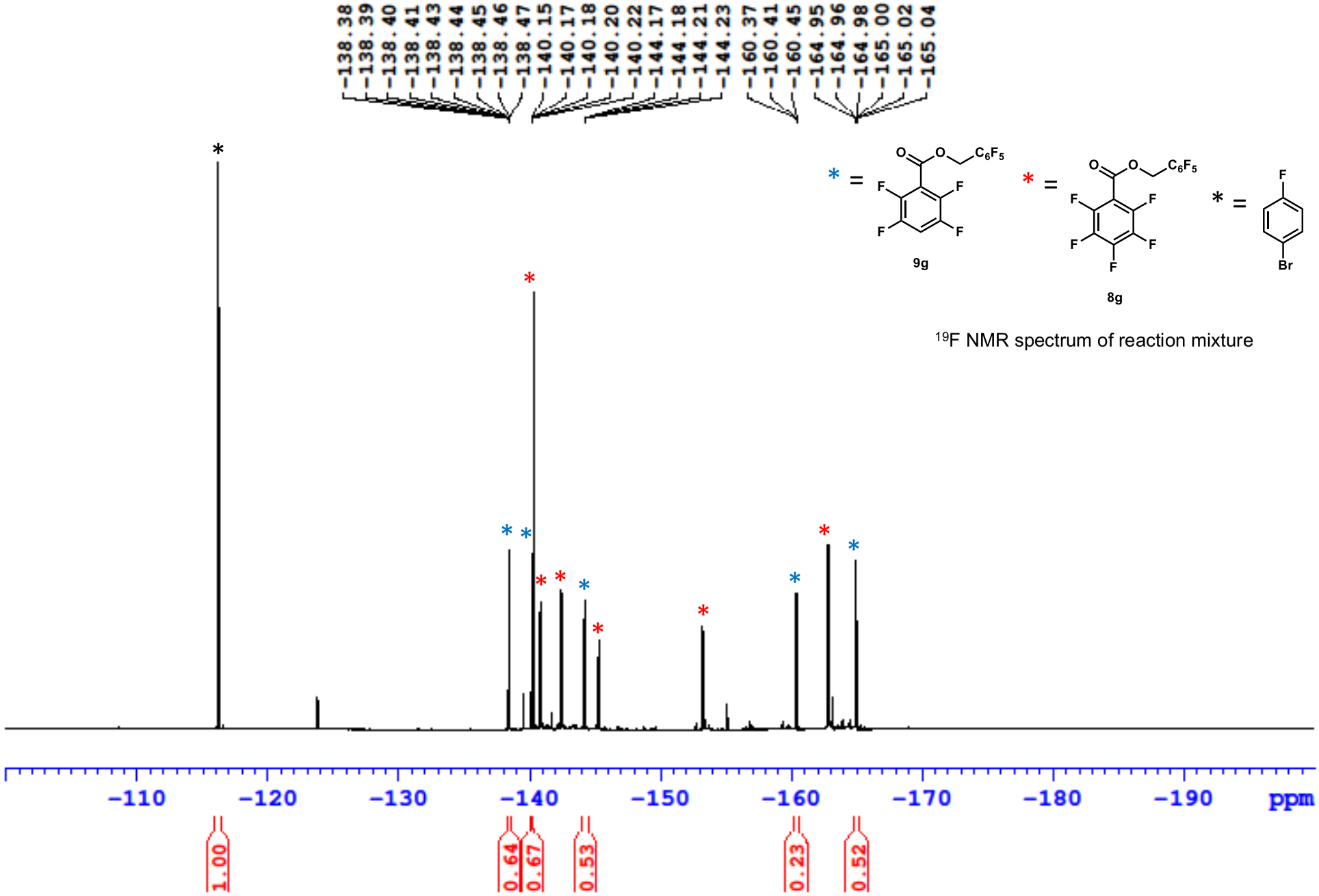
^{19}F NMR spectrum


1H NMR spectrum
9g
F
F
F
F
O
O
C6F5
7.18
7.17
7.17
7.16
7.14
7.14
7.13
5.43
1.00
2.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

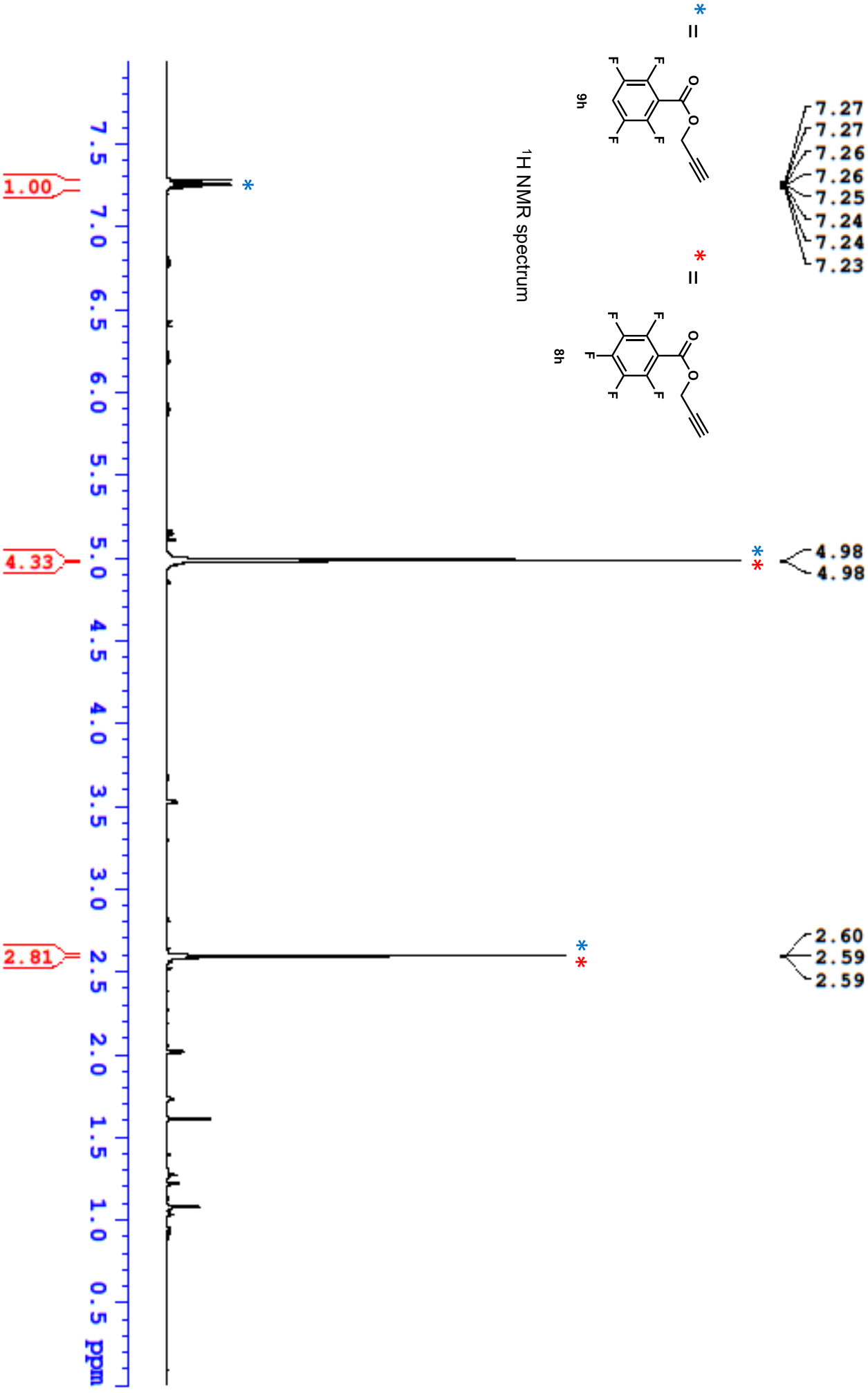


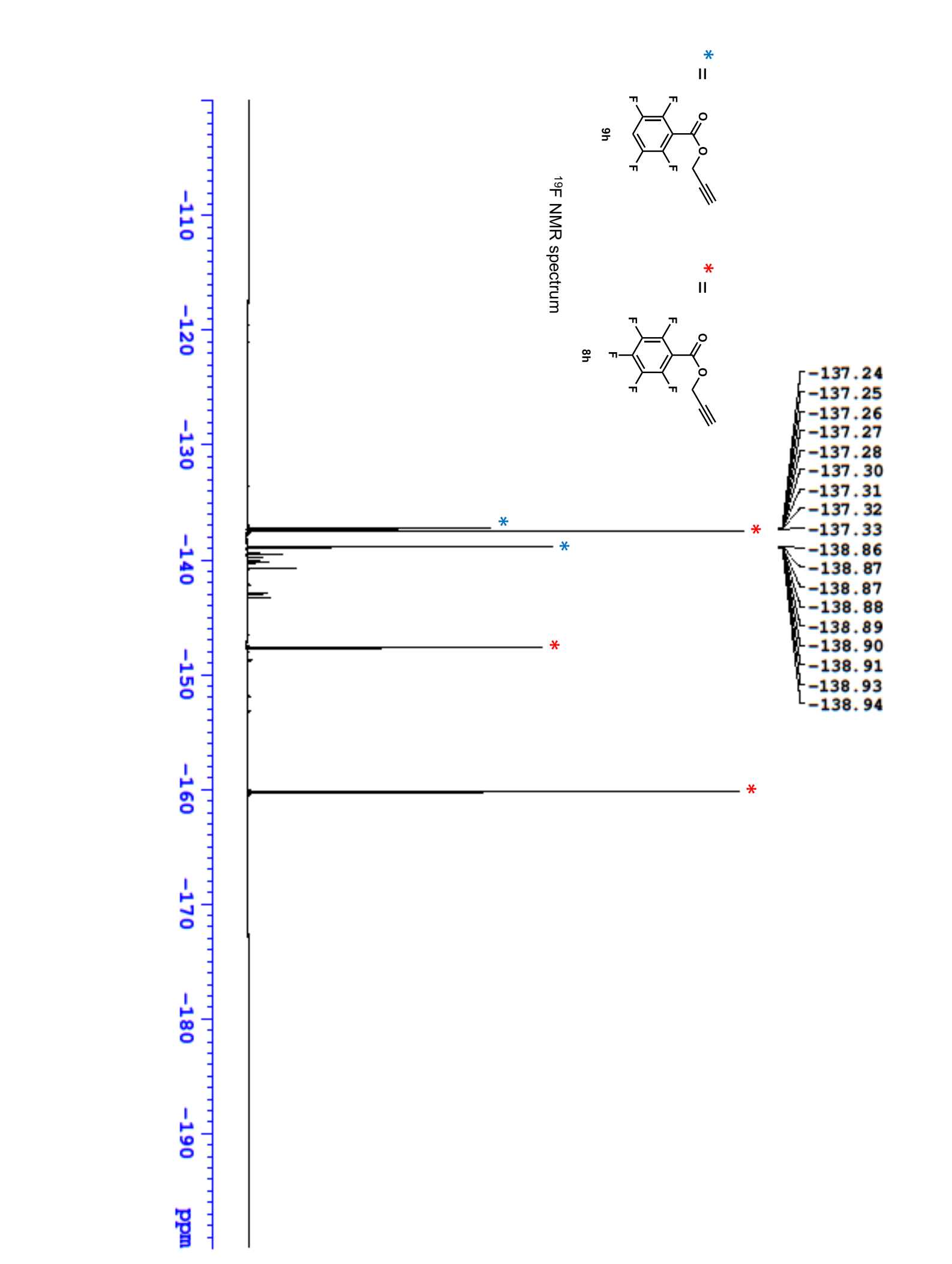
9g

^{19}F NMR spectrum

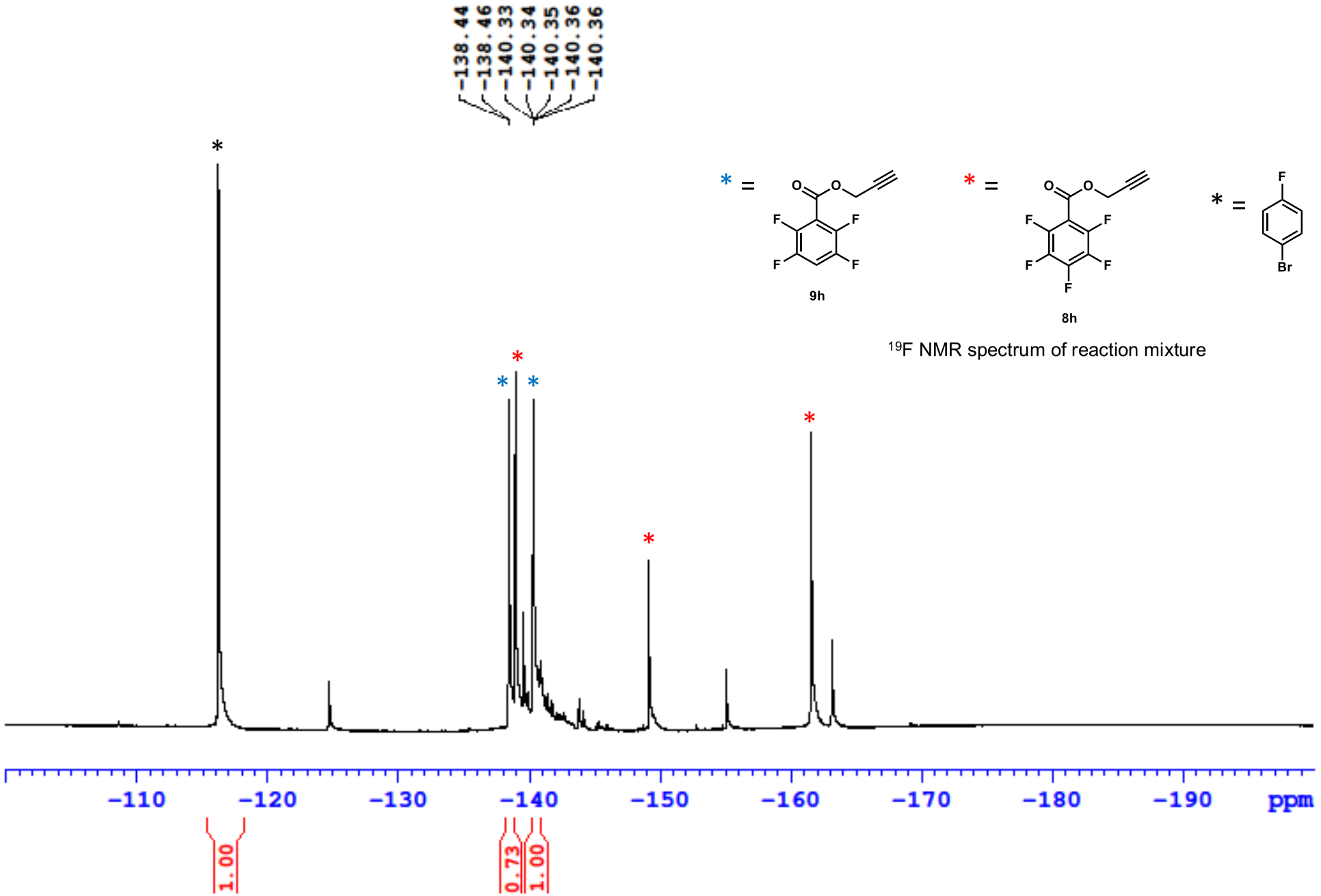


^{19}F NMR spectrum of reaction mixture

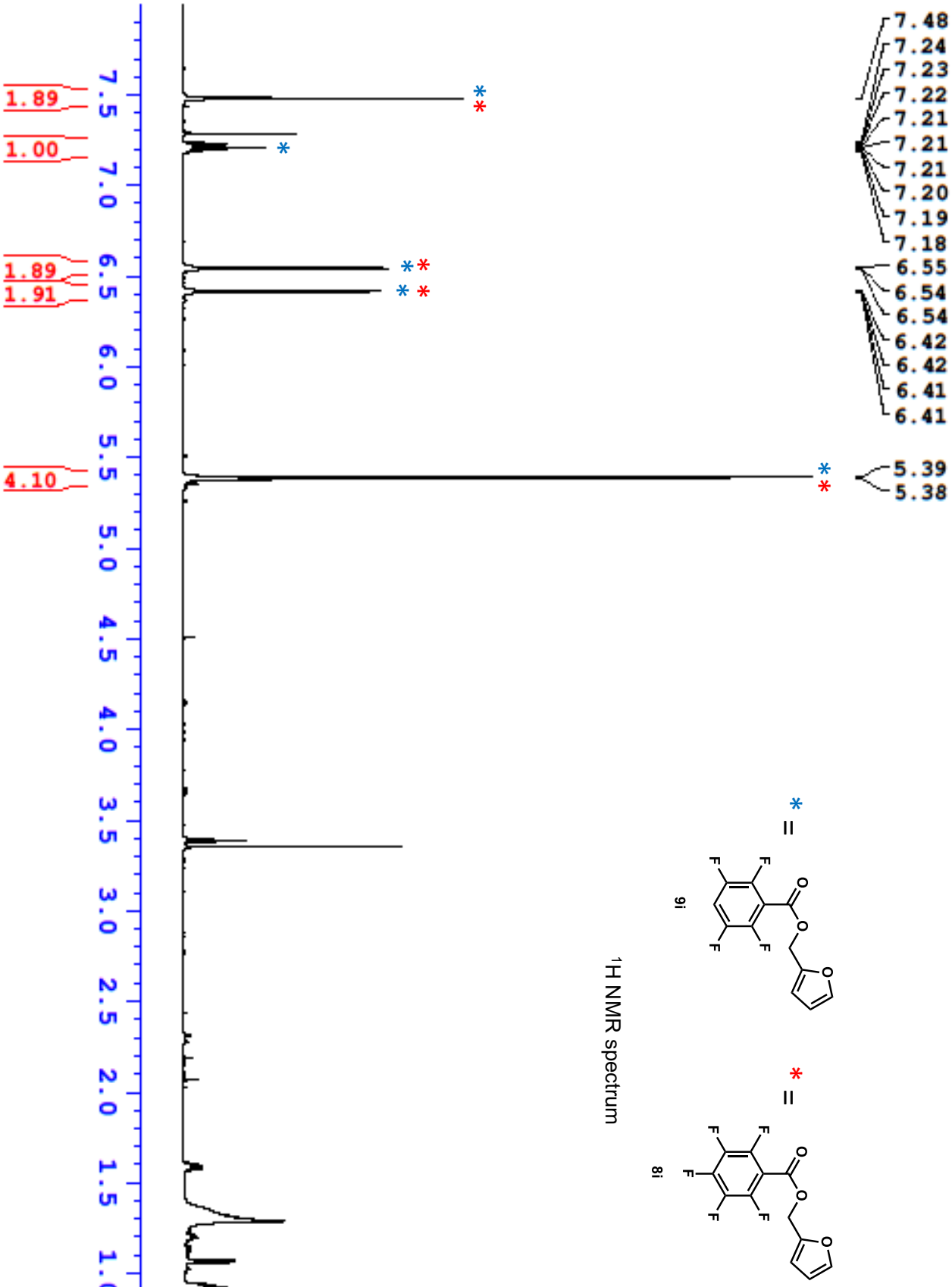

1H NMR spectrum
9h
8h
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.23
4.98
4.98
2.60
2.59
2.59
1.00
4.33
2.81
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



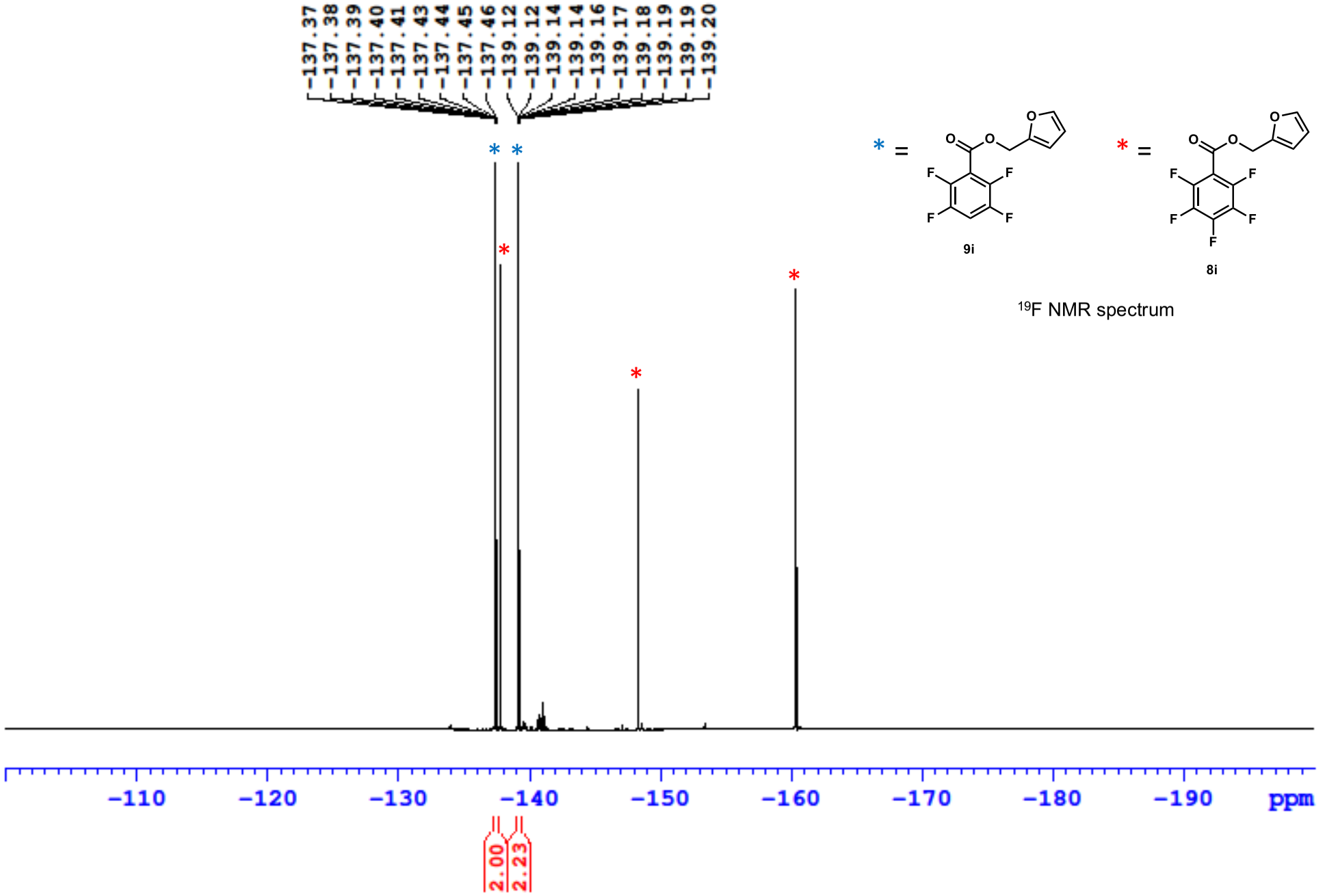
^{19}F NMR spectrum

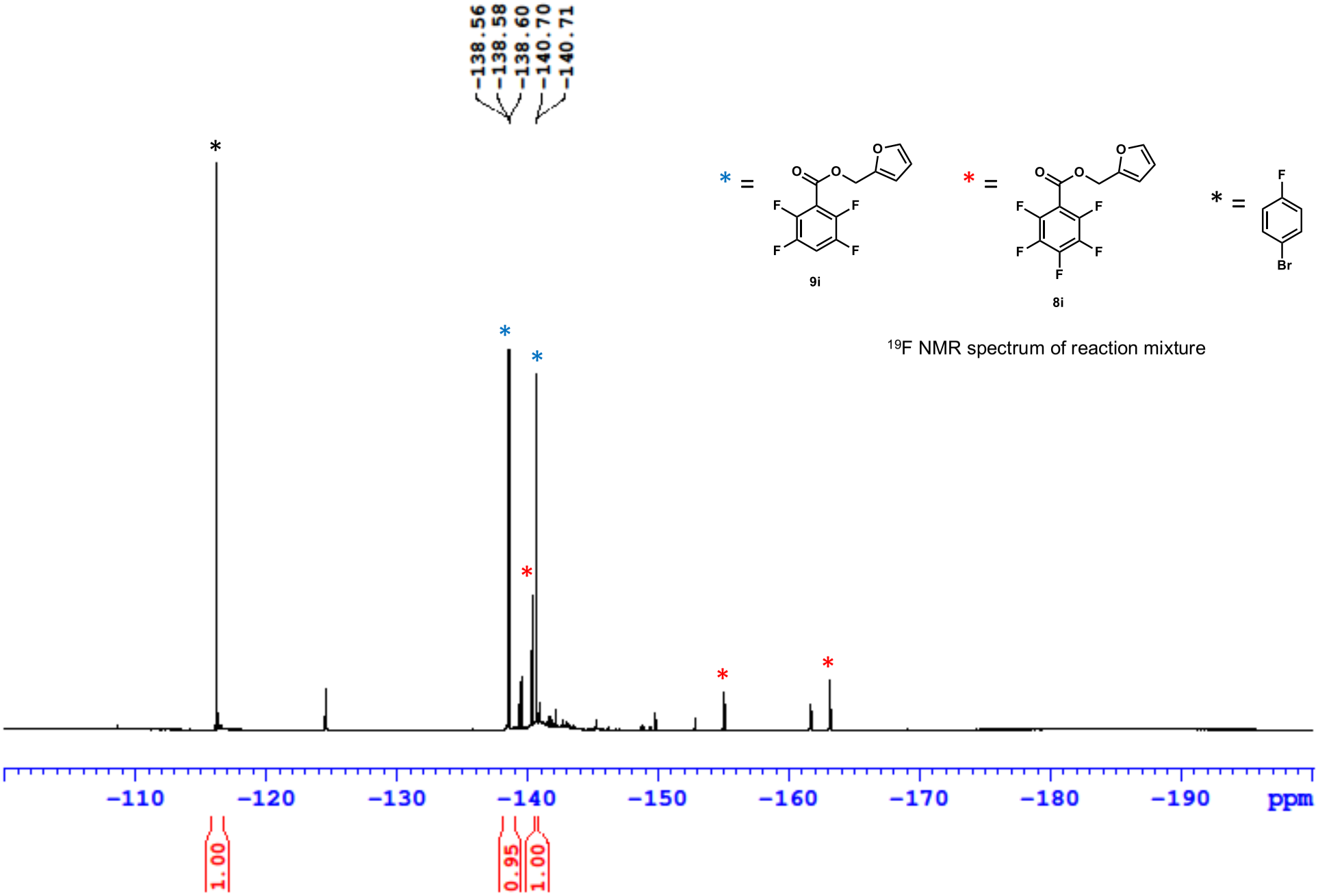


^{19}F NMR spectrum of reaction mixture

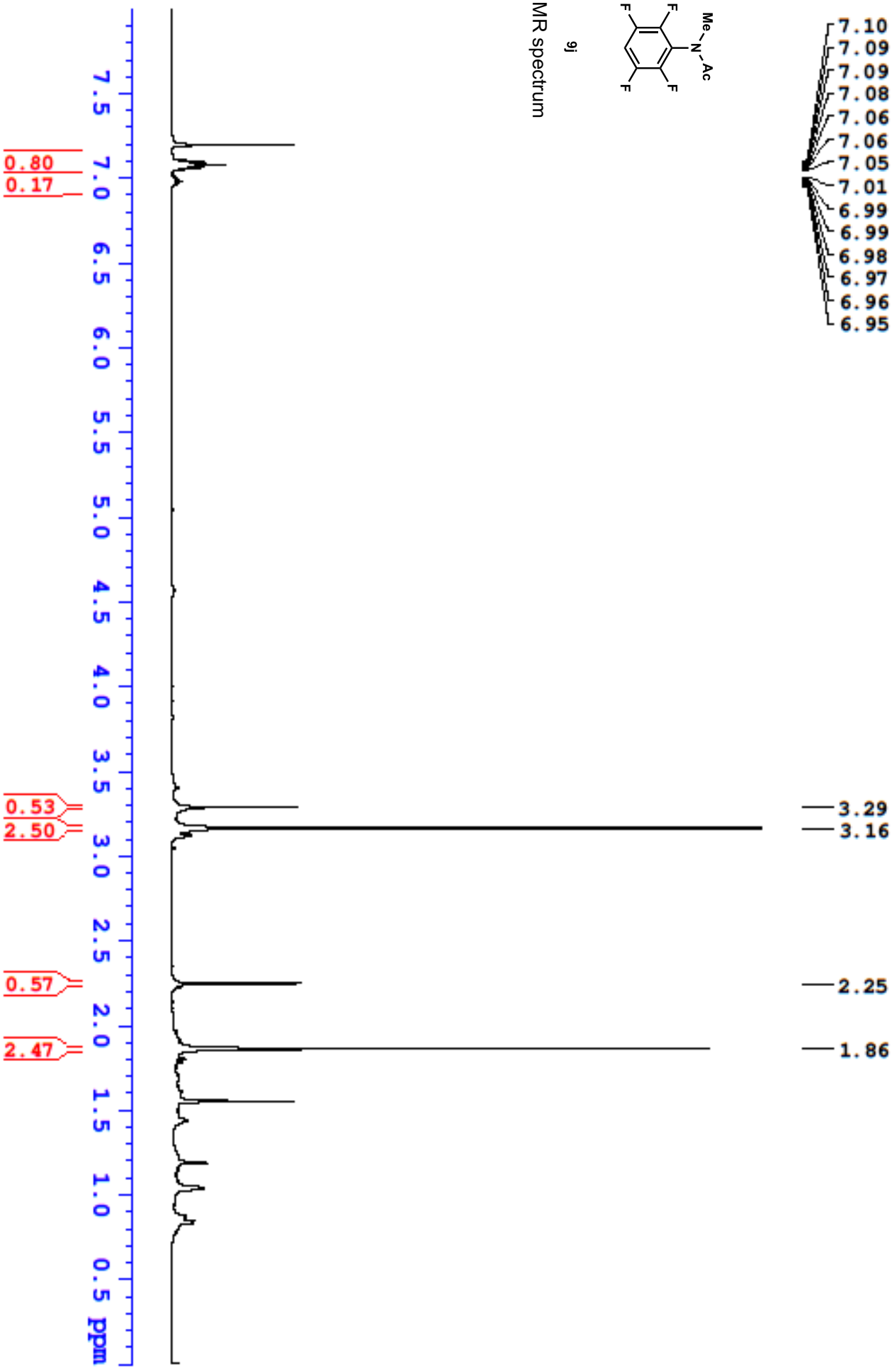


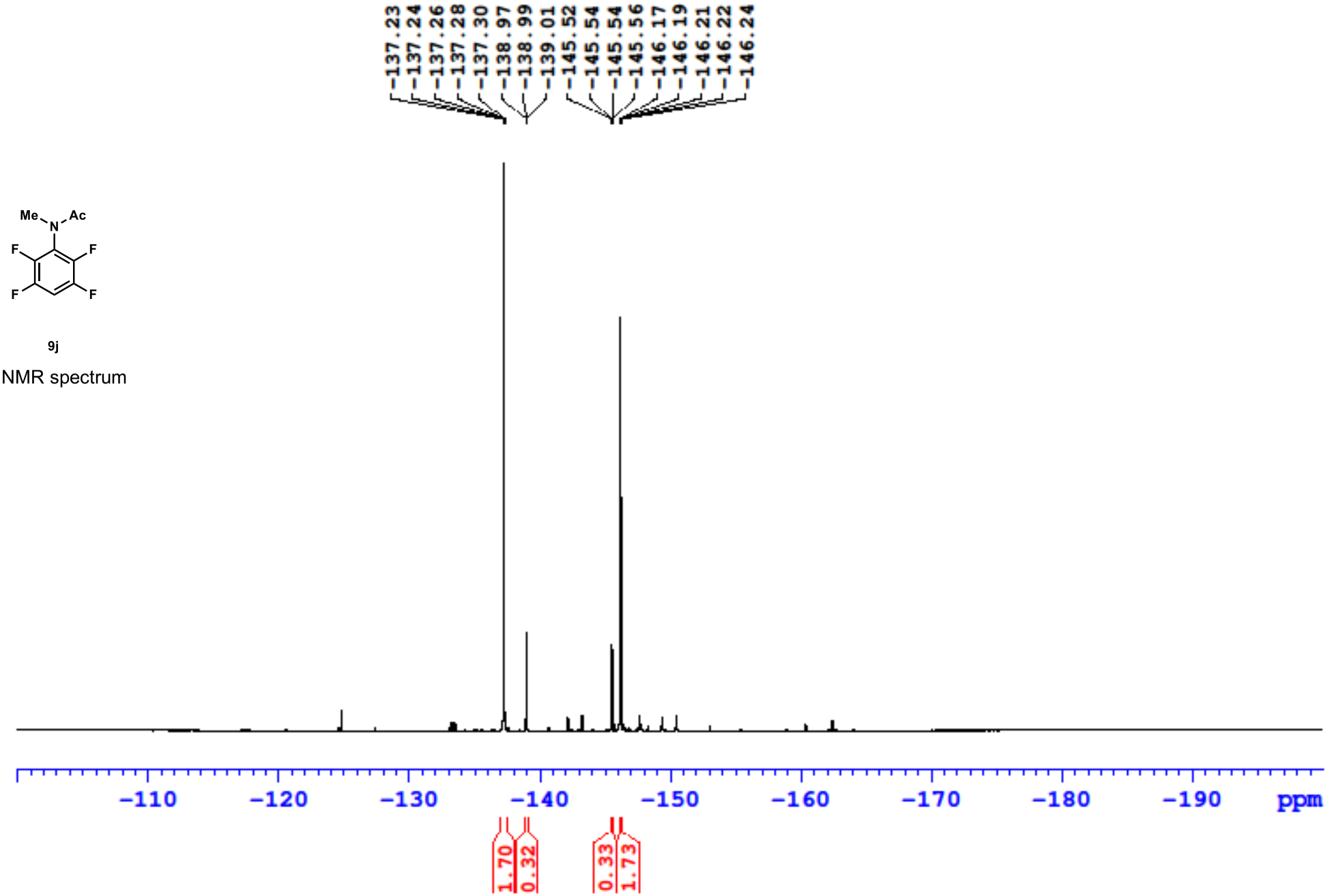
^{1}H NMR spectrum


-137.37
-137.38
-137.39
-137.40
-137.41
-137.43
-137.44
-137.45
-137.46
-139.12
-139.12
-139.14
-139.14
-139.16
-139.17
-139.18
-139.19
-139.19
-139.20
* =
9i
* =
8i
19F NMR spectrum
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.00
2.23



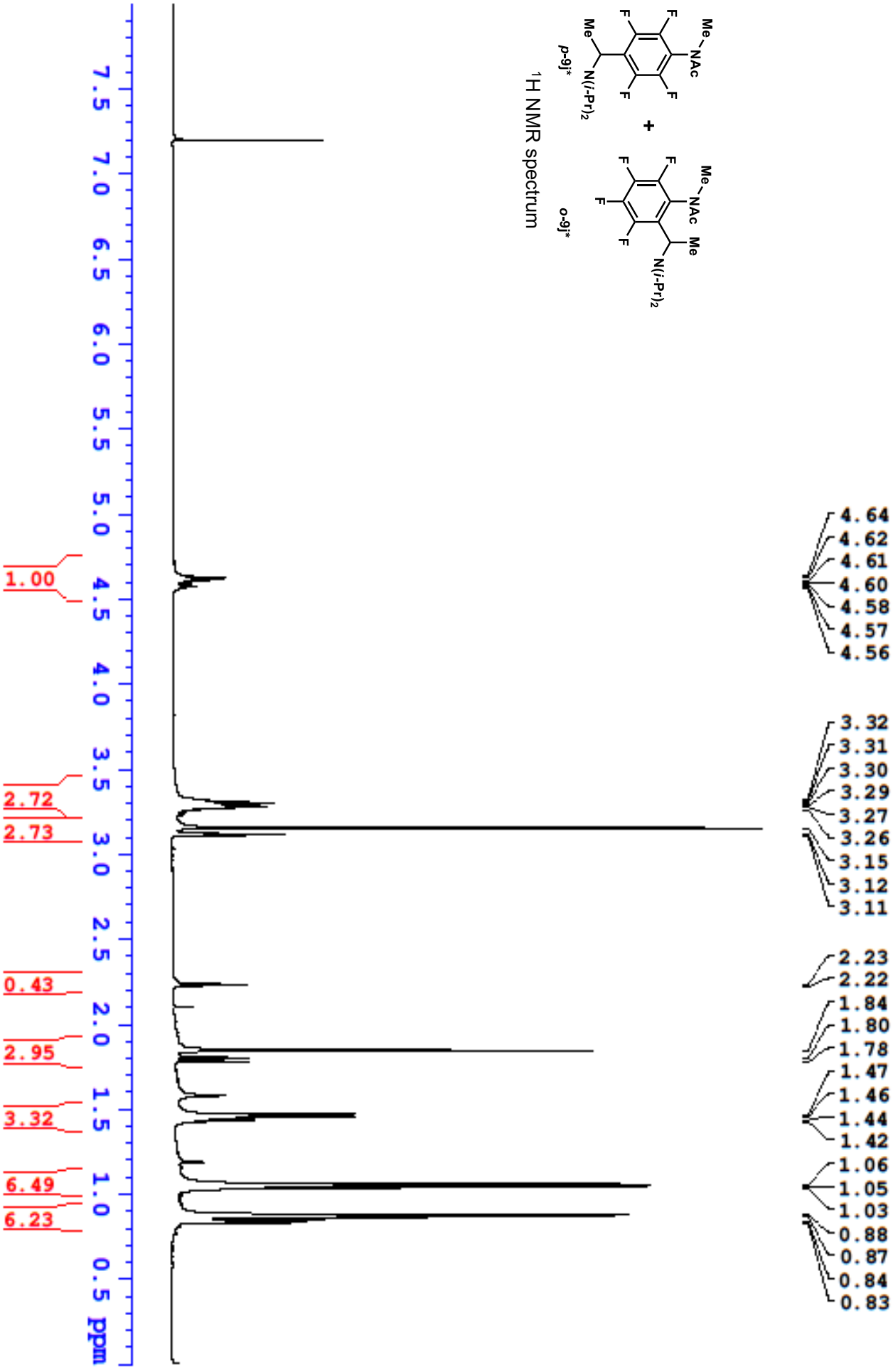
^{19}F NMR spectrum of reaction mixture

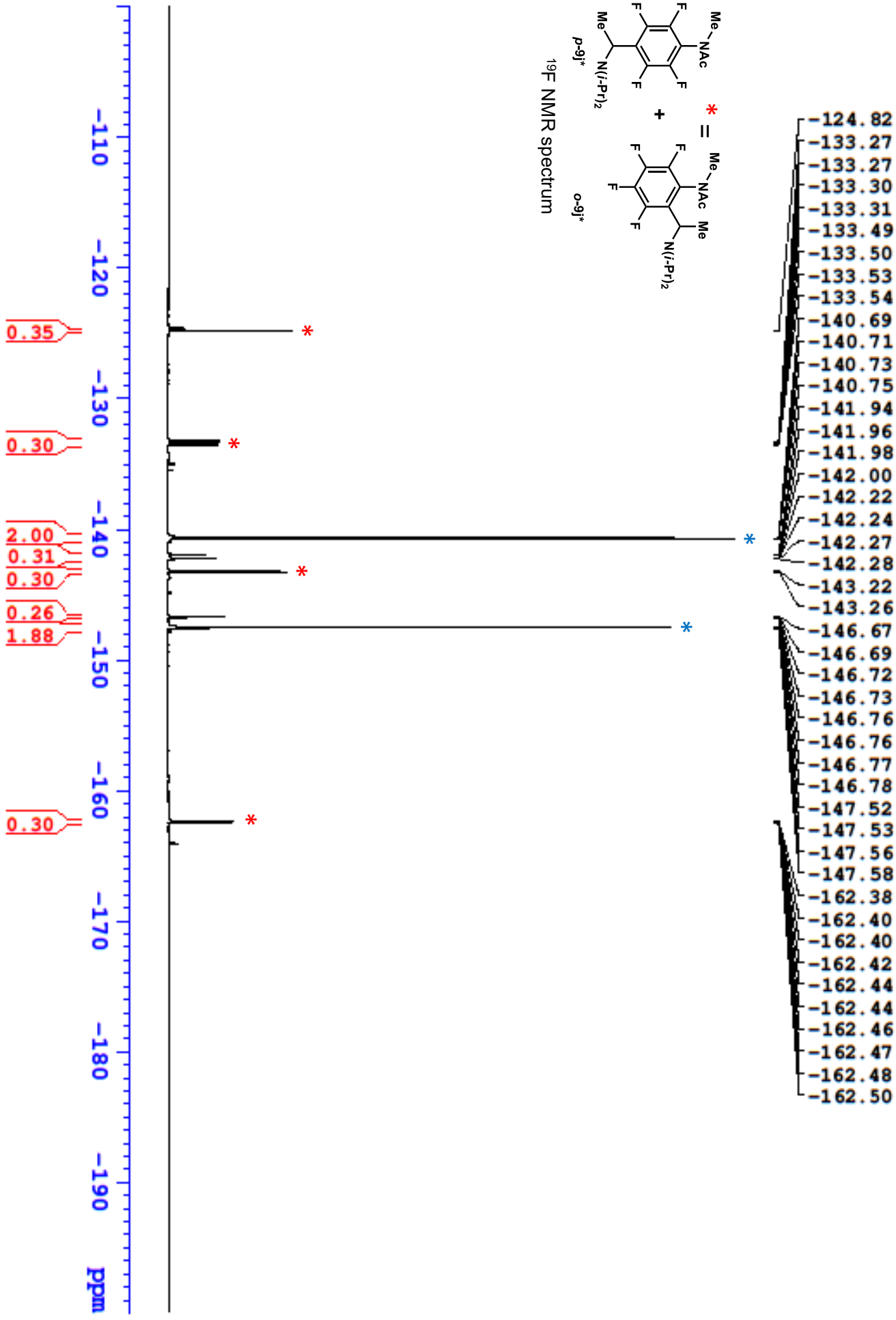

9j
¹H NMR spectrum
Me
N
Ac
F
F
F
F
7.10
7.09
7.09
7.08
7.06
7.06
7.05
7.01
6.99
6.99
6.98
6.97
6.96
6.95
3.29
3.16
2.25
1.86
0.80
0.17
0.53
2.50
0.57
2.47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

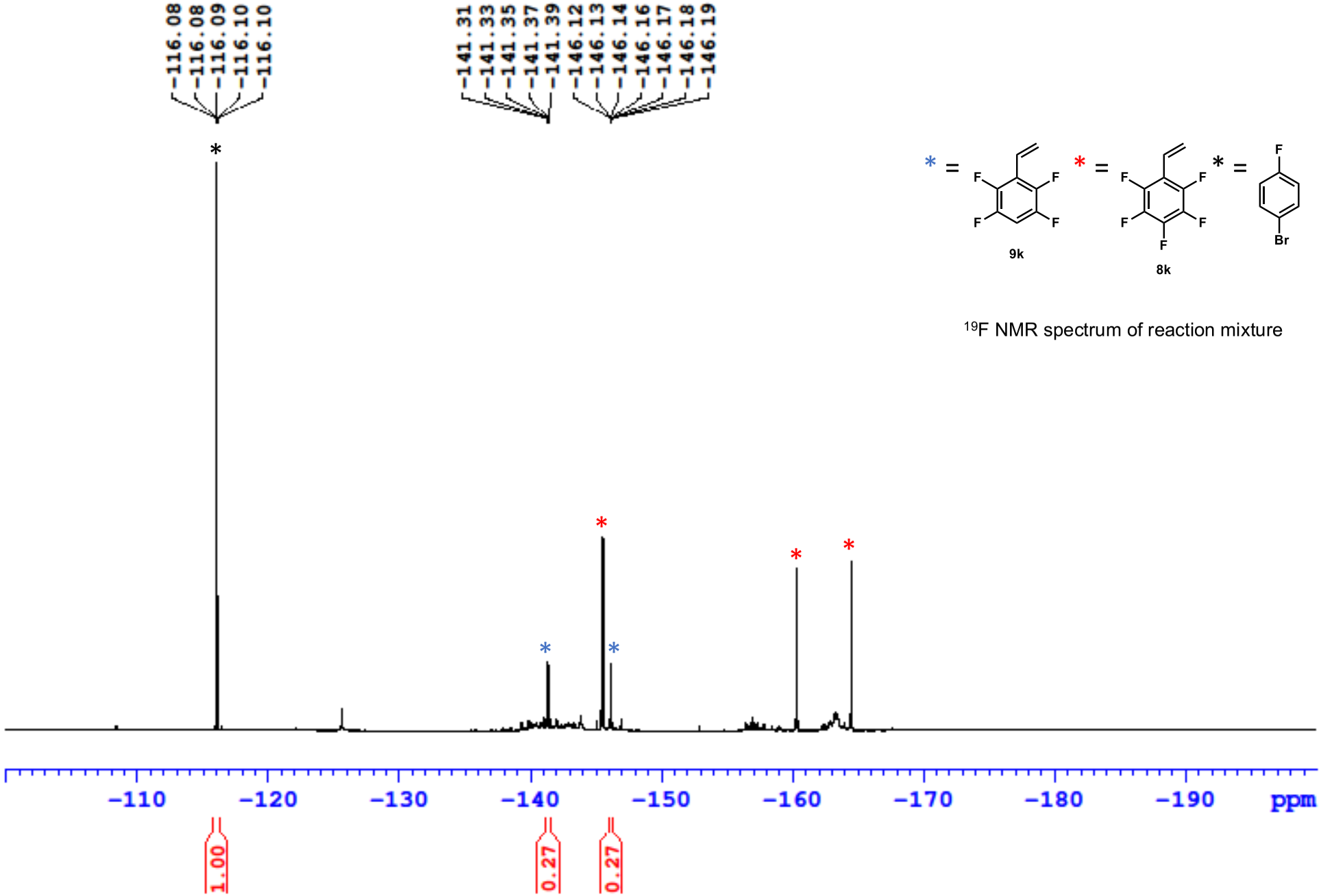


9j

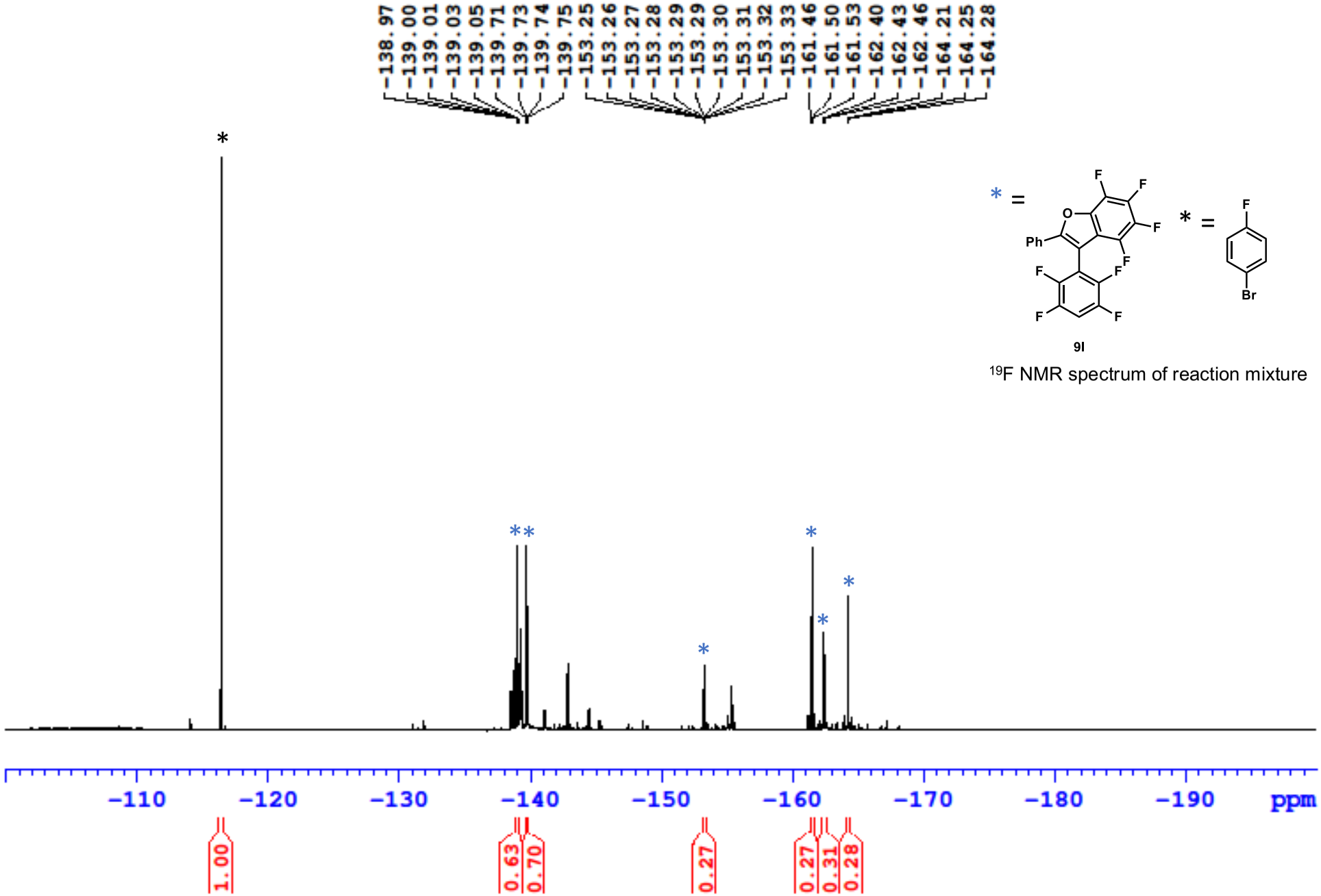
^{19}F NMR spectrum


^{1}H NMR spectrum
p-9j*
o-9j*
Me
NAc
N(*i*-Pr)$_2$
F
+
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.72
2.73
0.43
2.95
3.32
6.49
6.23
4.64
4.62
4.61
4.60
4.58
4.57
4.56
3.32
3.31
3.30
3.29
3.27
3.26
3.15
3.12
3.11
2.23
2.22
1.84
1.80
1.78
1.47
1.46
1.44
1.42
1.06
1.05
1.03
0.88
0.87
0.84
0.83


* =
Me
NAc
N(i-Pr)2
p-9j*
+
* =
Me
NAc
Me
N(i-Pr)2
o-9j*
19F NMR spectrum
-124.82
-133.27
-133.27
-133.30
-133.31
-133.49
-133.50
-133.53
-133.54
-140.69
-140.71
-140.73
-140.75
-141.94
-141.96
-141.98
-142.00
-142.22
-142.24
-142.27
-142.28
-143.22
-143.26
-146.67
-146.69
-146.72
-146.73
-146.76
-146.76
-146.77
-146.78
-147.52
-147.53
-147.56
-147.58
-162.38
-162.40
-162.40
-162.42
-162.44
-162.44
-162.46
-162.47
-162.48
-162.50
0.35
0.30
2.00
0.31
0.30
0.26
1.88
0.30
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

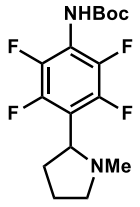


^{19}F NMR spectrum of reaction mixture



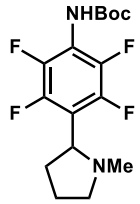
9l

^{19}F NMR spectrum of reaction mixture



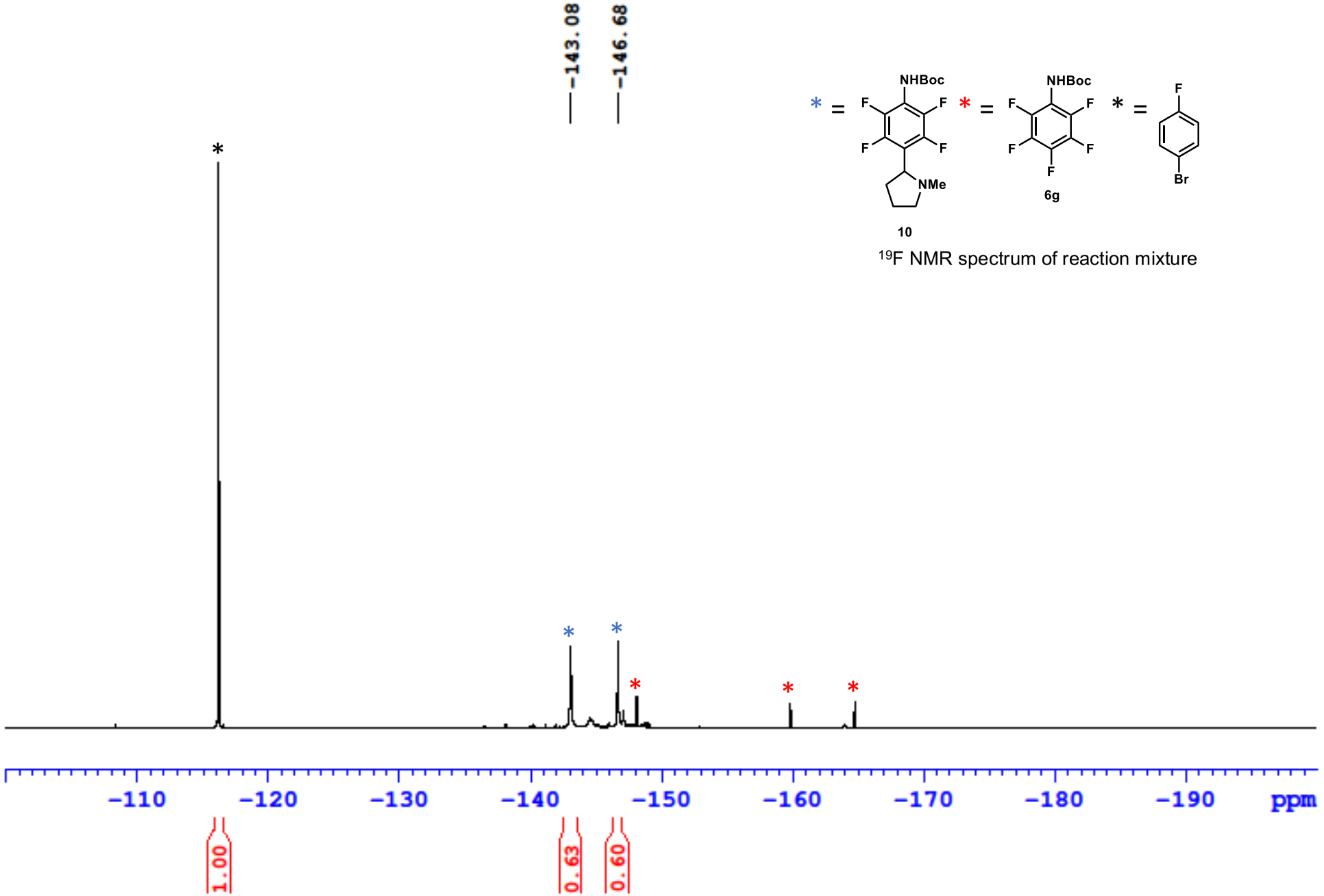
10

^{1}H NMR spectrum

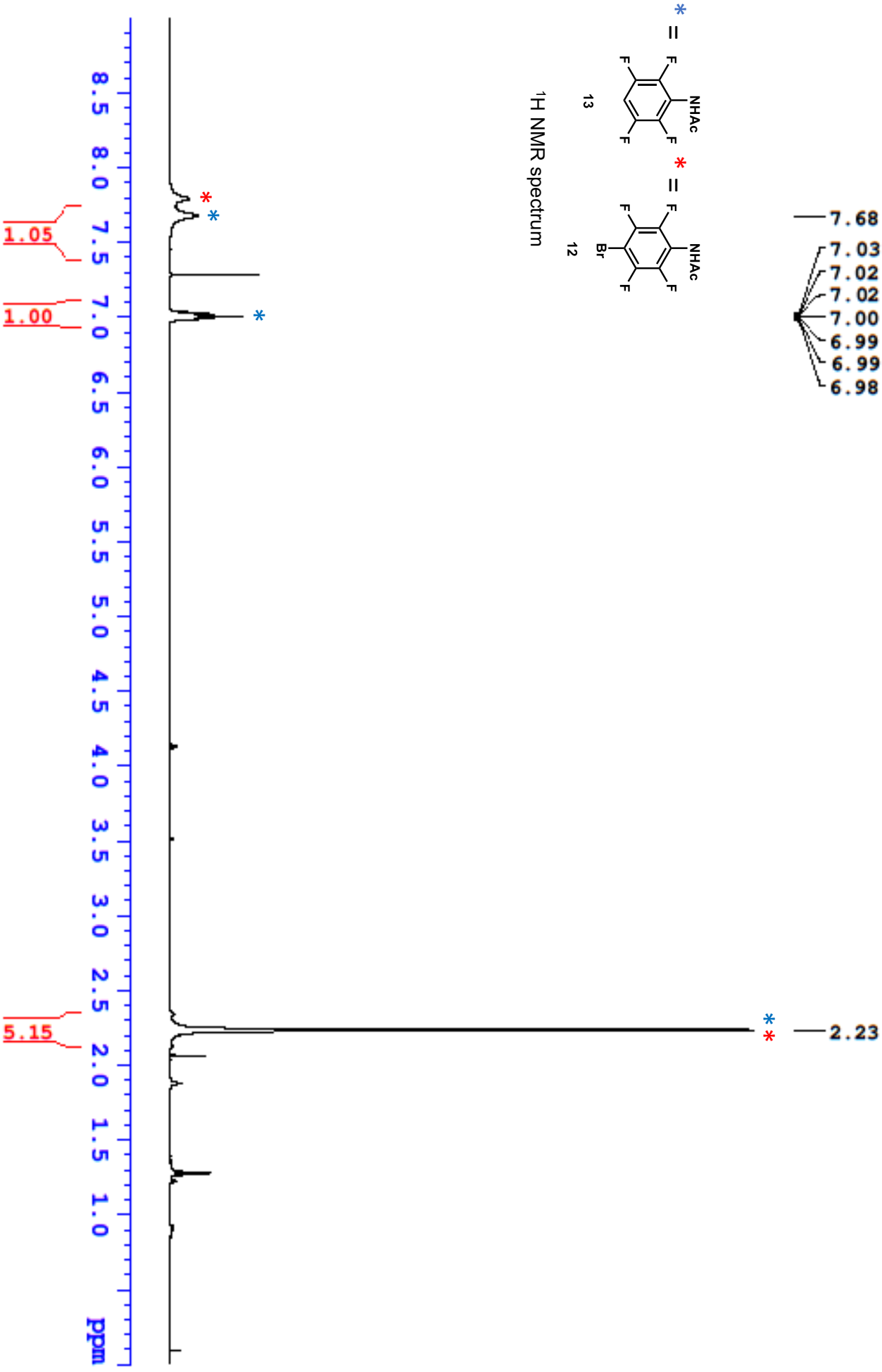


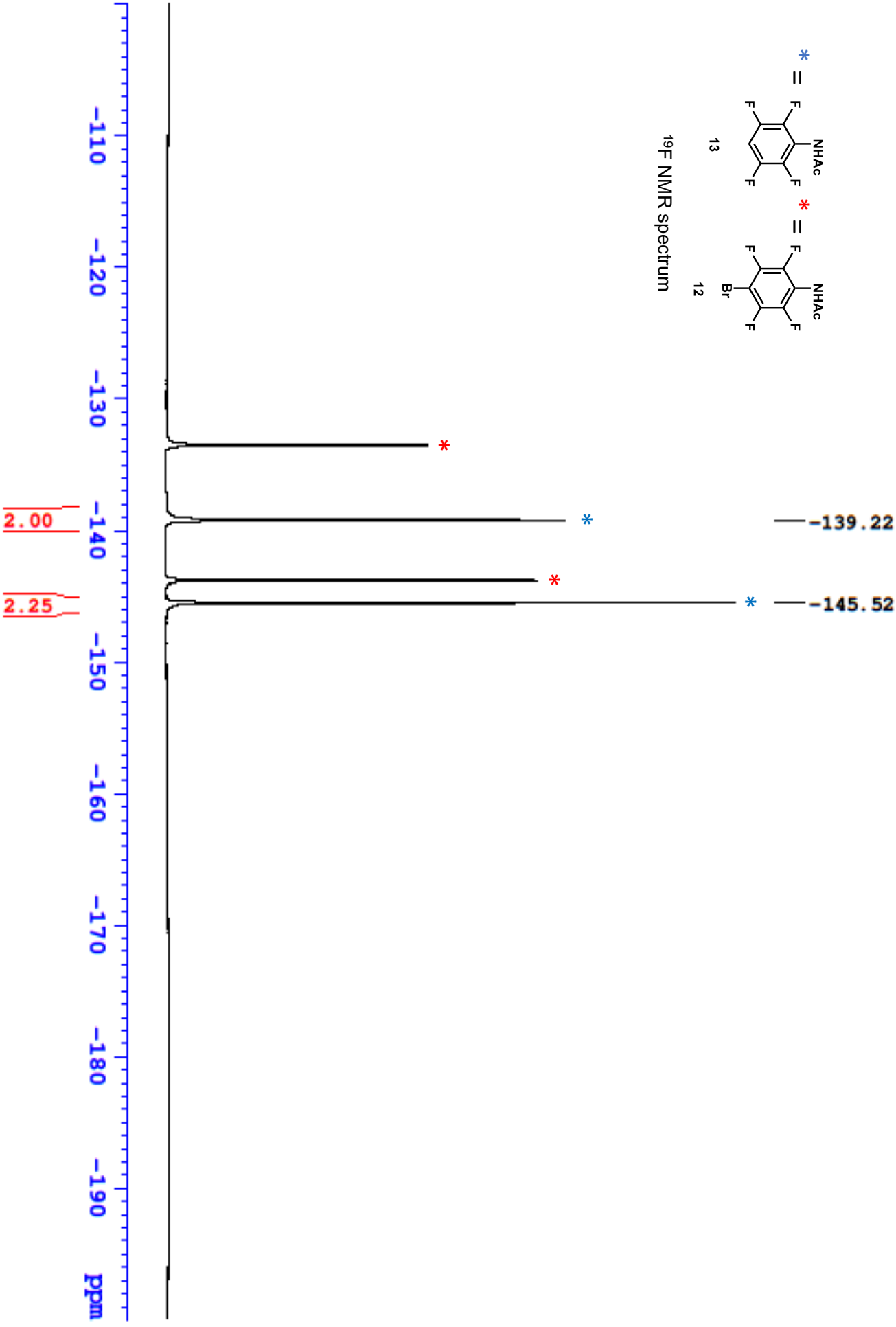
10

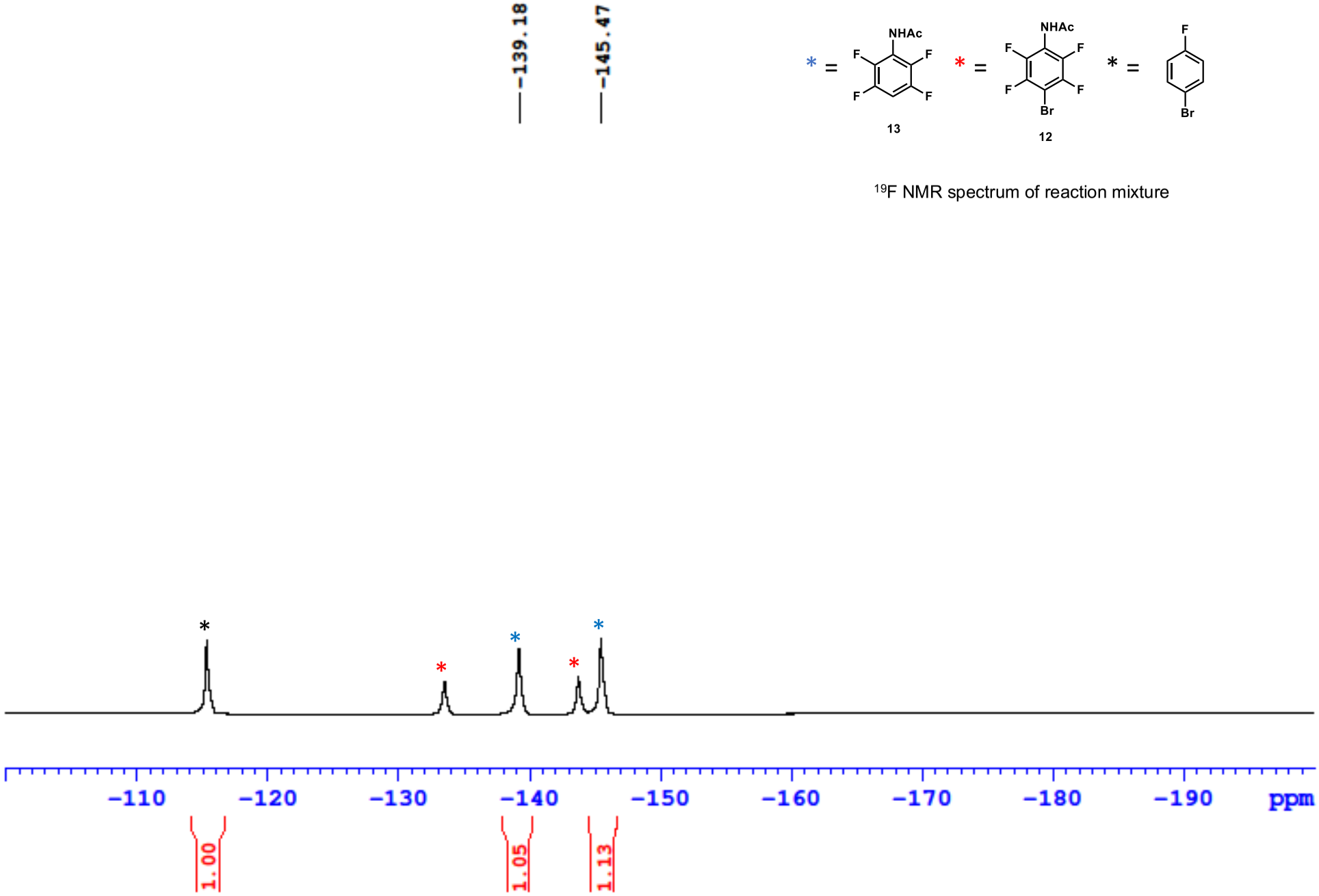
^{19}F NMR spectrum



^{19}F NMR spectrum of reaction mixture


1H NMR spectrum
13
12
NHAc
Br
F
7.68
7.03
7.02
7.02
7.00
6.99
6.99
6.98
2.23
1.05
1.00
5.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


* = F F NHAc F F
13
* = F F NHAc Br F F
12
19F NMR spectrum
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm
2.00
2.25
-139.22
-145.52



^{19}F NMR spectrum of reaction mixture