Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic supplementary information

A general photoinduced electron-transfer-directed chemoselective perfluoroalkylation of *N*,*N*-dialkylhydrazones

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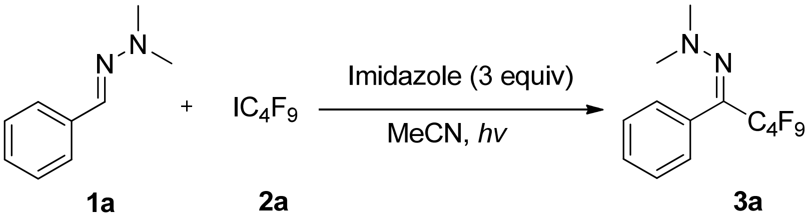
Content

General Information

All the reactions were performed under nitrogen atmosphere. Chemicals (Aldrich, Fluka, Alfa, ABCR, TCI and Merck) were directly used without further purification. Dichloromethane, MeOH, Toluene, THF and MeCN were dispensed from the solvent purification system MB SPS-800. NMR spectra were recorded on Bruker, Avance 300 (300 MHz), Avance 400 (400 MHz), Avance 500 (500 MHz) and Avance 600 (600 MHz) spectrometers. Chemical shifts were referenced to residual solvent protons or TMS as internal standard and reported in ppm. The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet); brs (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet) and m (multiplet) as well as combinations of them. All ^{13}C NMR spectra were measured with ^{1}H-decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH_2-group), q (quartet, CH_3-group)] were determined by DEPT-135 and HSQC spectra. For phosphorous and fluorine containing compounds, the second multiplicity refers to the ^{31}P- or ^{19}F-coupling. The method is denoted in brackets. For the most significant bands the wave number $\tilde{\nu}$ (cm^{-1}) is given. GC-MS spectra were recorded using a Agilent 5890 Series II Plus model, coupled with a HP 5972 Mass Selective Detector. As column, a HP-1 column was used and helium was carrier gas. Unless stated otherwise, the following temperature program was used: injection temperature 60 °C, heating rate: 10 °C/min, 5 min solvent delay. Thin-layer chromatography (TLC) was performed on precoated polyester sheets (POLYGRAM SIL /GUV254), and components were visualized by observation under UV light or by treating the plates with $KMnO_4$ (in 1.5 M Na_2CO_3 (aq)) followed by heating. The hydrazones were synthesized from the corresponding aldehydes with the reported methods.[1] Melting points (°C) are reported without correction.

Optimization of reaction conditions

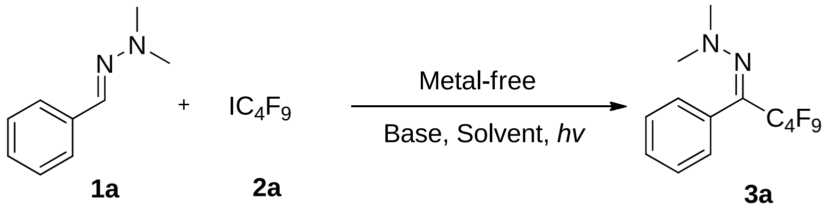
Table 1**:** Screening of suitable light source.



Entry	Light source	Temperature	Time/h	Yield[a]
1	Sunlight (**A**)	rt	8	75%
2	20 W CFL (**B1**)	rt	24	16%
3	70 W CFL (**B2**)	rt	24	16%
4	24 W lamp (**C**) λ = 400-500 nm	rt	24	14%
5	12 W blue leds (**D**)	rt	24	5%
6	24 W lamp (**E**) λ =315-400 nm	rt	12	94% (83%)
7	6 W UV lamp (**F**) λ = 254 nm	rt	12	trace
8	-	60 °C	24	0%
9	**E** with bandpass filter (375 nm)	rt	24	38%

Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv), imidazole (3 equiv), MeCN (0.6 mL), *hv* for indicated time. [a] The yields were determined by ^{19}F NMR with 1,3,5-trifluorobenzene as reference standard; the yield in brackets was the isolated yield.

Table 2: Optimization of base and solvent.



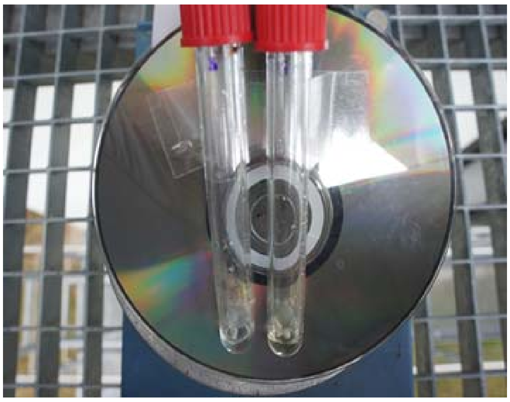
Entry	Base	Solvent	Time/h	Yield
1	Imidazole	MeCN	12	94% (83%)
2	K_2HPO_4	MeCN	12	87%
3	Cs_2CO_3	MeCN	12	70%
4	Na_2CO_3	MeCN	12	68%
5	CsOAc	MeCN	12	90%
6	2,6-lutidine	MeCN	12	88%
7	TMG	MeCN	12	54%
8	Imidazole	MeOH	12	86%

9	Imidazole	CH_2Cl_2	12	90%
10	Imidazole	THF	12	85%
11 [b]	Imidazole	MeCN	12	70%

Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv), base (3 equiv), MeCN (0.6 mL), *hv* for indicated time. [a] The yields were determined by ^{19}F NMR with 1,3,5-trifluorobenzene as reference standard; the yield in brackets was the isolated yield. [b] 1.3 equiv **2a** was used.

General procedures for the perfluoroalkylation of hydrazones

Reaction equipment for sunlight



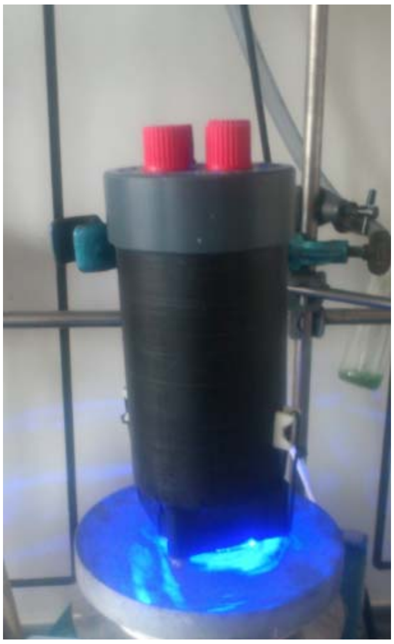
The reaction tubes are fastened to a CD light disk, and then placed under sunlight irradiation at room temperature. (The light disk is for maximizing the amount of sunlight available to the reactions.)

Reaction equipment for UVA light

The photoreactor is equipped with a fan and one magnetic stirring machine at the bottom to keep the reactor at ambient temperature during the reaction processes. In general, 4-5 reaction tubes were fastened to a CD disk, and then they are exposed to light irradiation at room temperature (4*24 W lamps on one side towards CD disk).

The CD disk was about 15 cm far way from the lamps. The lamps (315-400 nm), rayonet PRP-3500 Å were purchased from Southern New England Ultraviolet Company.

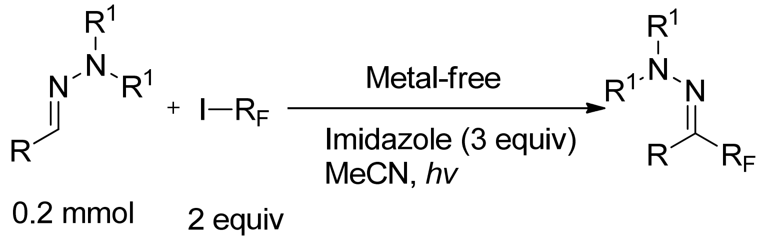
Reaction equipment for LED light



The photoreactor is equipped with a fan at the bottom to keep the reactor at ambient temperature during the reaction processes, and use LED strip (λmax = 465 nm).

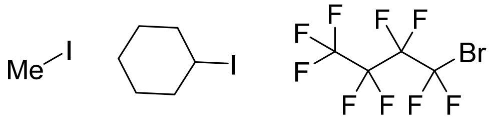
Reaction equipment for CFL light

20/70 W CFL bulb was used.



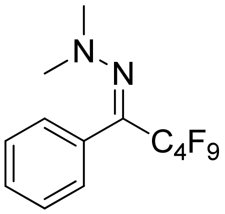
A 10 mL dried pyrex screw-top reaction tube was charged with hydrazones (200 μmol), perfluoroalkyl iodide (2 equiv, 400 μmol), imidazole (3 equiv, 600 μmol) and MeCN (600 μL). The solution was degassed under nitrogen by sparging for 5-10 min at 0 °C (the bp of R_F-I is low). Then, the reaction mixture was placed under light (315-400 nm) for the indicated time in main text. In general, after several hours of irradiation, the color of the reaction mixture becomes light yellow or deep yellow/orange. When it was finished, removing of the solvent by rotavap and the resulting crude product was purified with flash column chromatography on silica gel that was dealt with Et_3N/PE (1:10) over 24 hours (avoiding the decomposition of products in acidic column; 100% PE-1:50 (v/v) PE/EA). The products were characterized with IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS.

unapplicable R-X



Characterization data of products

(*E*)-1,1-dimethyl-2-(nonafluoro-1-phenylpentylidene)hydrazine **3aa** (known compound)[1d]

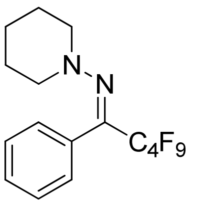


Yellow oil; 83% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40-7.30 (m, 5 H), 2.74 (s, 6 H);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -105.3 (t, J = 13.3 Hz, 2F), -120.0 (m, 2F), -124.3 (m, 2F);

(*E*)-*N*-(nonafluoro-1-phenylpentylidene)piperidin-1-amine **3ab**



Pale-yellow oil; 69% yield.

IR (Reflection): $\tilde{\nu}$ = 3063, 2942, 2860, 2831, 1589, 1493, 1446, 1353, 1241, 1133, 1081, 1030, 1019, 995, 976, 942, 910, 886, 858, 809, 777, 742, 722, 698, 642;

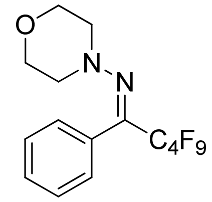
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.43-7.29 (m, 5 H), 3.01-2.90 (m, 4 H), 1.52-1.38 (m, 6 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.7 (s), 131.1 (s; t, J = 27.9 Hz), 129.3 (d), 129.1 (d, 2C), 128.5 (d, 2C), 54.8 (t, 2C), 24.8 (t, 2C), 23.9 (t);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -105.5 (m, 2F), -119.9 (m, 2F), -124.3 (m, 2F);

HRMS (ESI) Calcd for $C_{16}H_{16}F_9N_2$ [M+H]$^+$: 407.11643, found: 407.11710.

(*E*)-*N*-(nonafluoro-1-phenylpentylidene)morpholin-4-amine **3ac**
Yellow oil; 70% yield.



IR (Reflection): $\tilde{\nu}$ = 2970, 2921, 2898, 2856, 1607, 1595, 1493, 1447, 1352, 1230, 1208, 1117, 1091, 1047, 1001, 950, 911, 867, 853, 743, 722, 698;

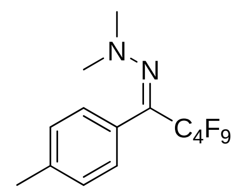
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38-7.22 (m, 5 H), 3.59-3.45 (m, 4 H), 2.98-2.84 (m, 4 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.2 (s; t, *J* = 27.8 Hz), 131.8 (s), 129.8 (d), 129.0 (d, 2C), 128.7 (d, 2C), 60.0 (t), 54.2 (t);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -106.6 (t, *J* = 13.9 Hz, 2F), -120.0 (m, 2F), -124.4 (m, 2F);

HRMS (ESI) Calcd for $C_{15}H_{14}F_9N_2O$ [M+H]$^+$: 409.09569, found: 409.09567.

(*E*)-1,1-dimethyl-2-(nonafluoro-1-(*p*-tolyl)pentylidene)hydrazine **3ad**



Colorless oil; 75% yield

IR (Reflection): $\tilde{\nu}$ = 2965, 2928, 2876, 2841, 2797, 1591, 1510, 1464, 1353, 1283, 1232, 1132, 1045, 1020, 965, 929, 862, 785, 742, 648, 633;

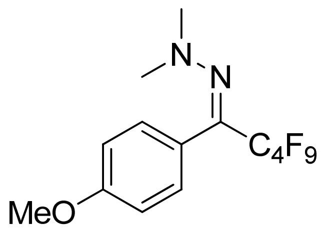
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.16-7.05 (m, 4 H), 2.66 (s, 6 H), 2.29 (s, 3 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 139.0 (s), 130.1 (d, 2C), 129.2 (s), 128.8 (s; t, *J* = 27.8 Hz), 128.6 (d, 2C), 46.4 (q, 2C), 21.3 (q);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.2 (t, *J* = 9.9 Hz, 3F), -105.4 (t, *J* = 12.4 Hz, 2F), -120.0 (m, 2F), -124.4 (m, 2F);

HRMS (ESI) Calcd for $C_{14}H_{14}F_9N_2$ [M+H]$^+$: 381.10078, found: 381.10108.

(*E*)-1,1-dimethyl-2-(nonafluoro-1-(4-methoxyphenyl)pentylidene)hydrazine **3ae**



Yellow oil; 80% yield.

IR (Reflection): $\tilde{\nu}$ = 3008, 2963, 2905, 2842, 2796, 1608, 1510, 1465, 1352, 1290, 1231, 1206, 1130, 1031, 964, 926, 861, 839, 790, 743, 644;

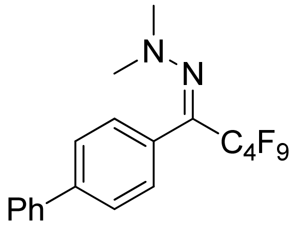
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.20-7.11 (m, 2 H), 6.86-6.76 (m, 2 H), 3.74 (s, 3 H), 2.66 (s, 6 H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.0 (s), 131.5 (d, 2C), 128.9 (s; t, *J* = 27.6 Hz), 124.2 (s), 113.4 (d, 2C), 55.2 (q), 46.4 (q, 2C);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.2 (m, 3F), -105.6 (m, 2F), -120.0 (m, 2F), -124.4 (m, 2F);

HRMS (ESI) Calcd for $C_{14}H_{14}F_9N_2O$ [M+H]$^+$: 397.09569, found: 397.09554.

(*E*)-2-(1-([1,1'-biphenyl]-4-yl)- nonafluoropentylidene)-1,1-dimethylhydrazine **3af**

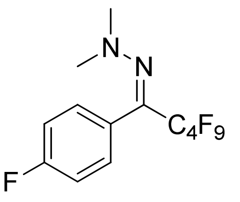


White solid, mp. 61 °C; 71% yield.

IR (ATR): $\tilde{\nu}$ = 1606, 1488, 1354, 1234, 1209, 1156, 1131, 1111, 1055, 1019, 1007, 932, 865, 813, 797, 759, 746, 724, 693, 621;

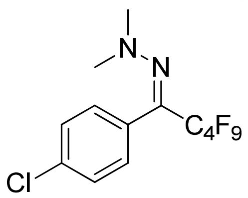
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.56-7.48 (m, 4 H), 7.43-7.24 (m, 5 H), 2.70 (s, 6 H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.7 (s), 140.1 (s), 131.1 (s), 130.6 (d, 2C), 128.8 (d, 2C), 127.9 (s; t, *J* = 28.0 Hz), 127.7 (d), 127.0 (d, 2C), 126.5 (d, 2C), 46.5 (q, 2C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -105.1 (m, 2F), -119.9 (m, 2F), -124.3 (m, 2F);
HRMS (ESI) Calcd for $C_{19}H_{16}F_9N_2$ $[M+H]^+$: 443.11643, found: 443.11805

(*E*)-1,1-dimethyl-2-(nonafluoro-1-(4-fluorophenyl)pentylidene)hydrazine **3ag**



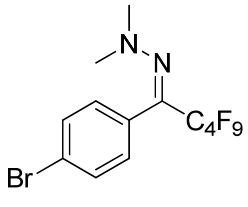
Colorless oil, 97% yield.
IR (Reflection): $\tilde{\nu}$ = 2880, 2799, 1603, 1508, 1467, 1353, 1297, 1229, 1205, 1161, 1130, 1045, 1016, 966, 928, 864, 845, 790, 743;
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28-7.13 (m, 2 H), 7.03-6.93 (m, 2 H), 2.67 (s, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 163.0 (s; d, *J*= 248.0 Hz), 132.2 (d; d, *J* = 7.9 Hz, 2C), 128.2 (s; d, *J*= 4.1 Hz), 126.9 (s; t, *J*= 28.5 Hz), 115.1 (d; d, *J* = 20.9 Hz, 2C), 46.5 (q, 2C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.2 (m, 3F), -105.4 (m, 2F), -111.3 (s, 1F), -120.1 (m, 2F), -124.5 (m, 2F);
HRMS (ESI) Calcd for $C_{13}H_{11}F_{10}N_2$ $[M+H]^+$: 385.07571 found: 385.07676.

(*E*)-2-(1-(4-chlorophenyl)-nonafluoropentylidene)-1,1-dimethylhydrazine **3ah**



Colorless oil; 90% yield.
IR (Reflection): $\tilde{\nu}$ = 2964, 2929, 2880, 2842, 2798, 1590, 1490, 1466, 1448, 1428, 1400, 1353, 1295, 1231, 1131, 1092, 1047, 1016, 965, 929, 862, 838, 788, 744, 734, 628;
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.27 (d, *J* = 8.5 Hz, 2 H), 7.17 (d, *J* = 8.5 Hz, 2 H), 2.60 (s, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.2 (s), 131.7 (d, 2C), 130.8 (s), 128.2 (d, 2C), 126.3 (s; t, *J* = 28.0 Hz), 46.6 (q, 2C);
^{19}F NMR ($CDCl_3$, 470 MHz): δ = -81.2 (t, *J* = 9.9 Hz, 3F), -105.3 (t, *J* = 11.8 Hz, 2F), -120.1 (m, 2F), -124.5 (m, 2F);
HRMS (ESI) Calcd for $C_{13}H_{11}F_9N_2Cl$ $[M+H]^+$: 401.04616, found: 401.04757.

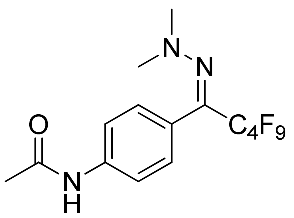
(*E*)-2-(1-(4-bromophenyl)-nonafluoropentylidene)-1,1-dimethylhydrazine **3ai**



Colorless oil; 81% yield.
IR (Reflection): $\tilde{\nu}$ = 2968, 2926, 2879, 2799, 1585, 1487, 1467, 1393, 1353, 1295, 1232, 1131, 1071, 1048, 1012, 965, 948, 929, 862, 837, 788, 744, 733, 683, 652;
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.53 (d, *J* = 8.5 Hz, 2 H), 7.21 (d, *J* = 8.5 Hz, 2 H), 2.80 (s, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 131.9 (d, 2C), 131.3 (s), 131.2 (d, 2C), 126.2 (s; t, *J* = 27.4 Hz), 123.5 (s), 46.6 (q, 2C);
^{19}F NMR ($CDCl_3$, 470 MHz): δ = -81.2 (t, *J* = 10.8 Hz, 3F), -105.8 (t, *J* = 11.3 Hz,

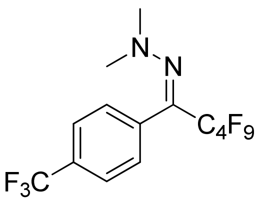
2F), -120.1 (m, 2F), -124.5 (m, 2F);
HRMS (ESI) Calcd for $C_{13}H_{11}F_9N_2Br$ [M+H]$^+$: 444.99564, found: 444.99579.

(*E*)-*N*-(4-(1-(2,2-dimethylhydrazono)-nonafluoropentyl)phenyl)acetamide **3aj**



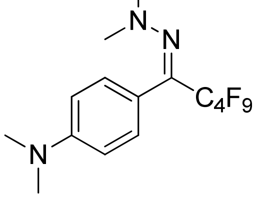
White solid, mp. 109 °C; 80% yield. The titled product was obtained according to the general procedure with eluent: PE/EA = 1:5
IR (ATR): $\tilde{\nu}$ = 3300, 3253, 1668, 1598, 1533, 1511, 1406, 1373, 1351, 1321, 1300, 1229, 1198, 1162, 1131, 1112, 1049, 1019, 966, 932, 867, 852, 835, 811, 789, 743, 733, 720, 675, 643;
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45 (d, J = 8.4 Hz, 2 H), 7.44 (s, 1 H), 7.24-7.14 (m, 2 H), 2.67 (s, 6 H), 2.11 (s, 3 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 168.6 (s), 138.6(s), 131.0 (d, 2C), 127.9(s), 127.6 (s; t, *J* = 27.1 Hz), 118.9(d, 2C), 46.5(q, 2C), 24.6(q, C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -105.3 (t, *J* = 11.9 Hz, 2F), -120.1 (m, 2F), -124.4 (m, 2F);
HRMS (ESI) Calcd for $C_{15}H_{15}F_9N_3O$ [M+H]$^+$: 424.10659, found: 424.10804.

(*E*)-1,1-dimethyl-2-(nonafluoro-1-(4-(trifluoromethyl)phenyl)pentylidene)hydrazine **3ak**



Colorless oil; 85% yield.
IR (Reflection): $\tilde{\nu}$ = 2967, 2934, 2905, 2882, 2844, 2800, 1618, 1590, 1514, 1467, 1448, 1429, 1409, 1353, 1327, 1233, 1172, 1134, 1069, 1020, 957, 933, 864, 847, 794, 740, 651;
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 2.70 (s, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 136.2 (s), 131.2 (s; q, *J* = 32.6 Hz), 130.8 (d, 2C), 125.3 (s; t, *J* = 28.1 Hz), 124.8 (d; q, *J* = 3.6 Hz, 2C), 124.2 (s; q, *J* = 218.6 Hz), 46.7 (q, 2C);
^{19}F NMR ($CDCl_3$, 470 MHz): δ = -63.0 (s, 3F), -81.2 (t, *J* = 10.3 Hz, 3F), -105.0 (t, *J* = 13.2 Hz, 2F), -120.1 (t, *J* = 6.6 Hz, 2F), -124.5 (t, *J* = 9.4 Hz, 2F);
HRMS (ESI) Calcd for $C_{14}H_{11}F_{12}N_2$ [M+H]$^+$: 435.07251, found: 435.07476.

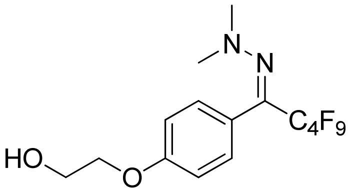
(*E*)-4-(1-(2,2-dimethylhydrazono)-nonafluoropentyl)-N,N-dimethylaniline **3al**



Colorless oil; 63% yield.
IR (Reflection): $\tilde{\nu}$ = 2893, 2837, 2803, 1611, 1523, 1448, 1354, 1281, 1229, 1163, 1130, 1043, 1006, 946, 860, 790, 743;
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.19 (d, *J* = 9.0 Hz, 2 H), 6.69 (d, *J* = 9.0 Hz, 2 H), 3.01 (s, 6 H), 2.76 (s, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 150.5 (s), 131.1 (s; t, *J* = 26.8 Hz), 130.8 (d, 2C), 118.9 (s), 111.1 (d, 2C), 46.4 (q, 2C), 40.1 (q, 2C);
^{19}F NMR ($CDCl_3$, 470 MHz): δ = -81.1 (t, *J* = 8.5 Hz, 3F), -105.8 (t, *J* = 12.2 Hz, 2F), -120.0 (m, 2F), -124.4 (m, 2F);

HRMS (ESI) Calcd for $C_{15}H_{17}F_9N_2$ [M+H]$^+$: 410.12733, found: 410.12835.

(*E*)-2-(4-(1-(2,2-dimethylhydrazono)-nonafluoropentyl)phenoxy)ethanol **3am**



Colorless oil; 91% yields. The titled product was obtained in general procedure with eluent: PE/EA= 1:5.

IR (Reflection): ṽ = 3370, 2935, 2878, 2842, 2797, 1607, 1509, 1459, 1353, 1285, 1228, 1129, 1039, 1011, 965, 919, 861, 839, 789, 743, 710, 634;

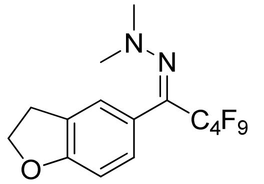
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.25 (d, *J* = 7.5 Hz, 2 H), 6.92 (d, *J* = 7.5 Hz, 2 H), 4.16-4.08 (m, 2 H), 4.02-3.96 (m, 2 H), 2.76 (s, 6 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 159.1 (s), 131.6 (d, 2C), 128.5 (s; t, *J* = 27.5 Hz), 124.7 (s), 114.0 (d, 2C), 69.2 (t), 61.4 (t), 46.4 (q, 2C)

^{19}F NMR ($CDCl_3$, 470 MHz): δ = -81.2 (t, *J* = 9.4 Hz, 3F), -105.6 (t, *J* = 11.3 Hz, 2F), -120.1 (m, 2F), -124.4 (t, *J* =9.9 Hz, 2F);

HRMS (ESI) Calcd for $C_{15}H_{15}F_9N_2NaO_2$ [M+Na]$^+$: 449.08820, found: 449.08849.

(*E*)-2-(1-(2,3-dihydrobenzofuran-5-yl)-2,2,3,3,4,4,5,5,5-nonafluoropentylidene)-1,1-dimethylhydrazine **3an**



Colorless oil; 76% yield.

IR (Reflection): ṽ = 2971, 2901, 2840, 2796, 1610, 1492, 1446, 1353, 1298, 1280, 1230, 1131, 1106, 1043, 983, 945, 889, 852, 790, 743;

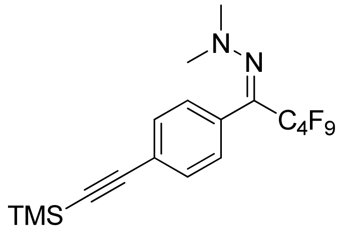
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.05 (s, 1 H), 6.97 (d, *J* = 8.5 Hz, 1 H), 6.68 (d, *J* = 8.5 Hz, 1 H), 4.52 (t, *J* = 8.5 Hz, 2 H), 3.14 (t, *J* = 8.5 Hz, 2 H), 2.66 (s, 6 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 160.7 (s), 130.3 (d), 129.5 (s; t, *J* = 27.6 Hz), 127.0 (s), 126.6 (d), 123.8 (s), 108.8 (d), 71.5 (t), 46.4 (q, 2C), 29.4 (t);

^{19}F NMR ($CDCl_3$, 470 MHz): δ = -81.2 (t, *J* = 9.9 Hz, 3F), -105.5 (t, *J* = 11.8 Hz, 2F), -119.9 (m, 2F), -124.3 (m, 2F);

HRMS (ESI) Calcd for $C_{15}H_{14}F_9N_2ONa$ [M+Na]$^+$: 431.07764, found: 431.07948.

(*E*)-1,1-dimethyl-2-(2,2,3,3,4,4,5,5,5-nonafluoro-1-(4-((trimethylsilyl)ethynyl)phenyl)pentylidene)hydrazine **3ao**



Yellow solid, mp. 63 °C; 50% yield.

IR (Reflection): ṽ = 2966, 2903, 2848, 2803, 2163, 1604, 1498, 1466, 1444, 1430, 1408, 1351, 1312, 1248, 1219, 1158, 1126, 1111, 1070, 1020, 963, 954, 927, 862, 840, 808, 758, 718, 699, 637;

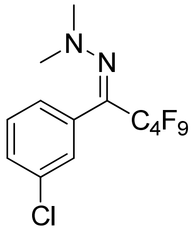
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.25 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 2.55 (s, 6 H), 0.05 (s, 9 H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 132.4 (s), 131.4 (d, 2C), 130.2 (d, 2C), 126.8 (s; t, *J* = 28.5 Hz), 123.9 (s), 104.2 (s), 46.6 (q, 2C), -0.1 (q, 3C);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -105.3 (t, *J* = 13.1 Hz, 2F), -120.1 (m, 2F), -124.5 (m, 2F);

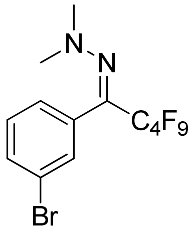
HRMS (ESI) Calcd for $C_{18}H_{20}F_9N_2Si$ $[M+H]^+$: 463.12466, found: 463.12689.

(E)-2-(1-(3-chlorophenyl)-nonafluoropentylidene)-1,1-dimethylhydrazine **3ap**



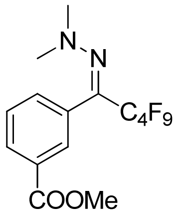
Colorless oil, 90% yield.
IR (Reflection): $\tilde{\nu}$ = 2880, 2843, 2799, 1594, 1567, 1473, 1428, 1408, 1354, 1285, 1245, 1133, 1052, 1000, 969, 944, 889, 864, 806, 777, 744, 733, 712, 693, 644;
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.44-7.20 (m, 4 H), 2.81 (t, J = 0.9 Hz, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 134.1 (s), 134.0 (s), 130.3 (d), 129.3 (d), 129.1 (d), 128.6 (d), 125.5 (s; t, J = 28.1 Hz), 46.6 (q, 2C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.2 (m, 3F), -105.0 (m, 2F), -120.0 (m, 2F), -124.4 (m, 2F);
HRMS (ESI) Calcd for $C_{13}H_{11}F_9N_2Cl$ $[M+H]^+$: 401.04616, found: 401.04797.

(E)-2-(1-(3-bromophenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentylidene)-1,1-dimethylhydrazine **3aq**



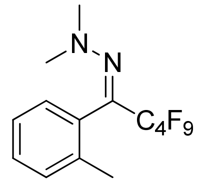
Colorless oil; 79% yield.
IR (Reflection): $\tilde{\nu}$ = 2879, 2799, 1590, 1563, 1470, 1405, 1353, 1287, 1230, 1206, 1130, 1048, 998, 968, 942, 889, 860, 793, 772, 744, 732, 693;
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.50-7.38 (m, 2 H), 7.21-7.15 (m, 2 H), 2.71 (t, J = 1.2 Hz, 6 H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.3 (s), 133.2 (d), 132.2 (d), 129.4 (d), 129.1 (d), 125.5 (s; t, J = 28.5 Hz), 122.0 (s), 46.6 (q, 2C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -104.9 (t, J = 12.5 Hz, 2F), -120.0 9m, 2F), -124.4 (m, 2F);
HRMS (ESI) Calcd for $C_{13}H_{11}F_9N_2Br$ $[M+H]^+$: 444.99564, found: 444.99604.

(E)-methyl 3-(1-(2,2-dimethylhydrazono)-2,2,3,3,4,4,5,5,5-nonafluoropentyl)benzoate **3ar**



Yellow oil; 76% yield. The titled product was obtained in general procedure with eluent PE/EA= 1:15.
IR (Reflection): $\tilde{\nu}$ = 2957, 2905, 2882, 2800, 1729, 1587, 1441, 1352, 1287, 1231, 1131, 1051, 988, 946, 916, 868, 841, 794, 769, 742, 697, 643;
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.02-7.89 (m, 2 H), 7.47-7.33 (m, 2 H), 3.86 (s, 3 H), 2.68 (s, 3 H);
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.4 (s), 134.6 (d), 132.7 (s), 131.4 (d), 130.1 (d), 130.0 (s), 128.1 (d), 126.0 (s; t, J = 22.6 Hz), 52.3 (q), 46.7 (q, 2C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -105.0 (t, J = 13.9 Hz, 2F), -120.0 (m, 2F), -124.4 (m, 2F);
HRMS (ESI) Calcd for $C_{15}H_{14}F_9N_2O_2$ $[M+H]^+$: 425.09061, found: 425.09047.

(*E*)-1,1-dimethyl-2-(nonafluoro-1-(o-tolyl)pentylidene)hydrazine **3as**



Colorless oil; 77% yield.

IR (Reflection): $\tilde{\nu}$ = 3068, 3022, 2969, 2929, 2879, 2842, 2799, 1601, 1464, 1353, 1232, 1208, 1131, 1042, 965, 928, 857, 805, 740, 712;

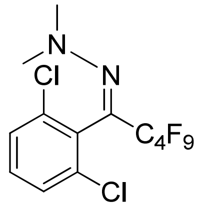
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36-7.08 (m, 4 H), 2.75 (t, *J* = 0.9 Hz, 6 H), 2.27 (s, 3 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 139.0 (s), 131.9 (s), 130.5 (d), 129.6 (d), 129.3 (d), 127.8 (s; t, *J* = 30.3 Hz), 125.1 (d), 45.7 (q, 2C), 19.8 (q);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.2 (m, 3F), -104.1 (m, 2F), -119.7 (m, 2F), -123.9 (m, 2F);

HRMS (ESI) Calcd for $C_{14}H_{14}F_9N_2$ [M+H]$^+$: 381.10078, found: 381.10031.

(*E*)-2-(1-(2,6-dichlorophenyl)-nonafluoropentylidene)-1,1-dimethylhydrazine **3at**



Colorless oil, 92% yield.

IR (Reflection): $\tilde{\nu}$ = 2939, 2904, 2882, 2800, 1588, 1559, 1431, 1352, 1298, 1232, 1208, 1131, 1065, 1045, 974, 930, 858, 805, 784, 739, 708, 684, 652;

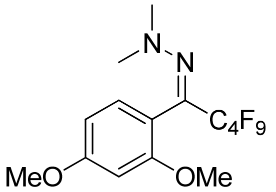
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.29-7.16 (m, 3 H), 2.82 (t, *J* = 0.9 Hz, 6 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.5 (s), 131.6 (s, 2C), 131.1 (d), 127.6 (d, 2C), 118.4 (s; t, *J* = 31.9 Hz), 44.8 (q, 2C);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -103.5 (m, 2F), -119.7 (m, 2F), -124.3 (m, 2F);

HRMS (ESI) Calcd for $C_{13}H_{10}F_9N_2Cl_2$ [M+H]$^+$: 435.00718, found: 435.00805.

(*E*)-2-(1-(2,4-dimethoxyphenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentylidene)-1,1-dimethylhydrazine **3au**



Yellow oil; 75% yield.

IR (Reflection): $\tilde{\nu}$ = 3008, 2963, 2945, 2842, 2795, 1609, 1579, 1505, 1466, 1441, 1417, 1352, 1305, 1208, 1161, 1129, 1033, 975, 964, 932, 858, 838, 789, 744, 734, 704, 641;

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.09 (d, *J* = 8.5 Hz, 1 H), 6.51-6.46 (m, 2 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 2.80 (s, 6 H);

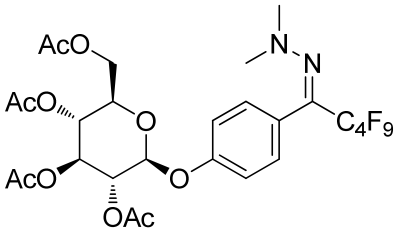
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 162.0 (s), 159.6 (s), 132.3 (d), 124.4 (s; t, *J* = 28.9 Hz), 114.1 (s), 104.0 (d), 98.3 (d), 55.5 (q), 55.3 (q), 45.3 (q, 2C);

^{19}F NMR ($CDCl_3$, 470 MHz): δ = -81.2 (t, *J* = 9.9 Hz, 3F), -106.1 (m, 2F), -120.4 (m, 2F), -124.5 (m, 2F);

HRMS (ESI) Calcd for $C_{15}H_6F_9N_2O_2$ [M+H]$^+$: 427.10626, found: 427.10763.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(4-((*E*)-1-(2,2-dimethylhydrazono)-2,2,3,3,4,4,5,5,5-nonafluoropentyl)phenoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate **3av**(known compound)[1d]

Colorless oil; 80% yield. The titled product was obtained in general procedure with

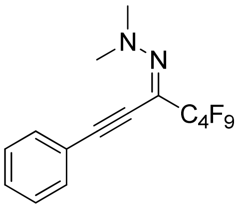


eluent PE/EA = 1:3.

^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.18 (d, *J* = 8.7 Hz, 2 H), 6.95 (d, *J* = 8.7 Hz, 2 H), 5.68 (t, *J* = 3.0 Hz, 1 H), 5.33 (d, *J* = 9 Hz, 1 H), 5.14-4.94 (m, 2 H), 4.25-4.13 (m, 3 H), 2.69 (s, 6 H), 2.10 (s, 3 H), 2.01 (s, 3 H), 1.98 (s, 3 H), 1.96 (s, 3 H);

^{19}F NMR (CDCl$_3$, 283 MHz): δ = -81.1 (t, *J* = 11.0 Hz, 3F), -105.4 (t, *J* = 11.9 Hz, 2F), -120.0 (m, 2F), -124.4 (m, 2F);

(*E*)-1,1-dimethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-1-yn-3-ylidene)hydrazine **4a**



Colorless oil; 60% yield. The titled product was obtained according to the general procedure with 0.2 mmol (*E*)-1,1-dimethyl-2-(3-phenylprop-2-yn-1-ylidene)hydrazine and 3 equiv C_4F_9I.

IR (Reflection): $\tilde{\nu}$ = 3084, 3063, 3025, 2931, 2902, 2880, 2798, 1557, 1490, 1460, 1444, 1424, 1352, 1316, 1248, 1136, 1102, 1074, 1002, 977, 915, 878, 841, 795, 756, 732, 690, 639, 610;

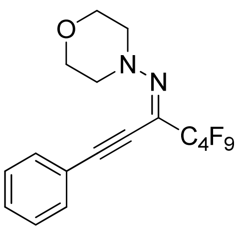
^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.35-7.22 (m, 5 H), 3.35 (s, 6 H);

^{13}C NMR (CDCl$_3$, 125 MHz): δ = 130.9 (d, 2C), 128.9 (d), 128.5 (d, 2C), 122.4 (s), 107.2 (s; t, *J* = 30.0 Hz), 96.9 (s), 80.5 (s), 45.5 (q, 2C);

^{19}F NMR (CDCl$_3$, 470 MHz): δ = -81.0 (t, *J* = 10.3 Hz, 3F), -108.6 (t, *J* = 11.3 Hz, 2F), -122.0 (m, 2F), -125.3 (m, 2F);

HRMS (ESI) Calcd for $C_{15}H_{12}F_9N_2$ [M+H]$^+$: 391.08513, found: 391.08655.

(*E*)-*N*-(4,4,5,5,6,6,7,7,7-nonafluoro-1-phenylhept-1-yn-3-ylidene)morpholin-4-amine **4b**



Colorless oil; 51% yield. The titled product was obtained according to the general procedure with 0.2 mmol (*E*)-N-(3-phenylprop-2-yn-1-ylidene)morpholin-4-amine and 3 equiv C_4F_9I.

IR (Reflection): $\tilde{\nu}$ = 3063, 2971, 2926, 2902, 2859, 2198, 1557, 1489, 1447, 1351, 1310, 1276, 1233, 1134, 1087, 1023, 999, 972, 914, 876, 825, 804, 756, 743, 730, 689, 645;

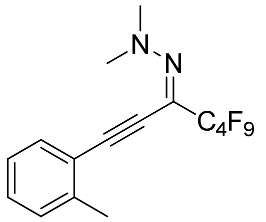
^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.42-7.23 (m, 5 H), 3.82-3.71 (m, 8 H);

^{13}C NMR (CDCl$_3$, 75 MHz): δ = 131.3 (d, 2C), 130.8 (s; t, *J* = 23.4 Hz), 129.6 (s), 128.6 (d, 2C), 121.5 (s), 100.7 (s), 79.4 (s), 66.3 (t), 53.7 (t);

^{19}F NMR (CDCl$_3$, 283 MHz): δ = -81.0 (m, 3F), -109.4 (m, 2F), -121.9 (m, 2F), -125.3 (m, 2F);

HRMS (ESI) Calcd for $C_{17}H_{14}F_9N_2O$ [M+H]$^+$: 433.09569, found: 433.09660.

(*E*)-1,1-dimethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1-(o-tolyl)hept-1-yn-3-ylidene)hydrazine **4c**



Yellow solid, mp. 35 °C; 56% yield. The titled product was obtained according to the general procedure with 0.2 mmol (*E*)-1,1-dimethyl-2-(3-(o-tolyl)prop-2-yn-1-ylidene)hydrazine and 3 equiv C_4F_9I.

IR (ATR): $\tilde{\nu}$ = 2931, 1687, 1555, 1486, 1460, 1423, 1351, 1315, 1236, 1133, 1096, 1076, 976, 880, 847, 788, 759, 745, 732, 715, 688, 652;

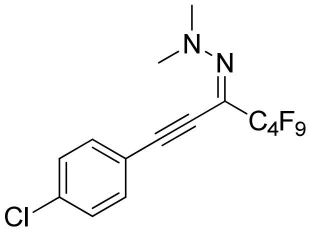
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31-7.03 (m, 4 H), 3.36 (s, 6 H), 2.33 (s, 3 H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 140.3 (s), 131.3 (d), 129.7 (d), 128.9 (d), 125.6 (d), 122.2 (s), 107.4 (s; t, *J* = 29.1 Hz), 96.2 (s), 84.2 (s), 45.5 (q, 2C), 20.5 (q);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.0 (m, 3F), -108.6 (m, 2F), -121.9 (m, 2F), -125.3 (m, 2F);

HRMS (EI) Calcd for $C_{16}H_{13}F_9N_2$ $[M]^+$: 404.0935, found: 404.0943.

(*E*)-2-(1-(4-chlorophenyl)-4,4,5,5,6,6,7,7,7-nonafluorohept-1-yn-3-ylidene)-1,1-dimethylhydrazine **4d**



Yellow oil; 48% yield. The titled product was obtained according to the general procedure with 0.2 mmol (*E*)-2-(3-(4-chlorophenyl)prop-2-yn-1-ylidene)-1,1-dimethyl hydrazine and 3 equiv C_4F_9I.

IR (Reflection): $\tilde{\nu}$ = 2933, 2903, 2879, 2798, 1901, 1594, 1556, 1489, 1461, 1424, 1399, 1351, 1315, 1235, 1133, 1090, 1075, 1014, 1002, 977, 915, 878, 828, 795, 743, 729, 643;

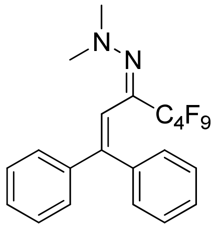
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33-7.21 (m, 4 H), 3.35 (s, 6 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.0 (s), 132.1 (d, 2C), 128.9 (d, 2C), 102.8 (s), 106.6 (s; t, *J* = 29.1 Hz), 95.6 (s), 81.4 (s), 45.5 (q, 2C);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.0 (m, 3F), -108.6 (m, 2F), -122.0 (m, 2F), -125.3 (m, 2F);

HRMS (ESI) Calcd for $C_{15}H_{11}ClF_9N_2$ $[M+H]^+$: 425.04616, found: 425.04622.

(*E*)-1,1-dimethyl-2-(4,4,5,5,6,6,7,7,7-nonafluoro-1,1-diphenylhept-1-en-3-ylidene)hydrazine **4e**



Yellow oil; 47% yield. The titled product was obtained according to the general procedure with 0.2 mmol (*E*)-2-(3,3-diphenylallylidene)-1,1-dimethylhydrazine and 3 equiv C_4F_9I.

IR (Reflection): $\tilde{\nu}$ = 3060, 3026, 2966, 2876, 2836, 2794, 1953, 1887, 1810, 1573, 1493, 1445, 1351, 1240, 1132, 1056, 1001, 874, 849, 793, 774, 760, 743, 699, 637;

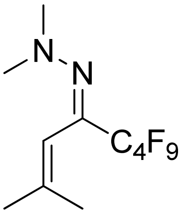
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.41-7.18 (m, 10 H), 6.39 (s, 1 H), 2.84 (s, 6 H);

^{13}C NMR ($CDCl_3$, 150 MHz): δ = 149.0 (s), 141.9 (s), 139.1 (s), 129.3 (d, 2C), 128.5 (d, 3C), 128.3 (d, 3C), 128.1 (s; t, *J* = 25.5 Hz), 128.0 (d, 2C), 117.9 (d), 46.5 (q, 2C);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -107.0 (t, *J* = 11.3 Hz, 2F), -121.2 (m, 2F), -124.5 (m, 2F);

HRMS (ESI) Calcd for $C_{21}H_{18}F_9N_2$ [M+H]$^+$: 469.13208, found: 469.13383.

(*E*)-1,1-dimethyl-2-(5,5,6,6,7,7,8,8,8-nonafluoro-2-methyloct-2-en-4-ylidene)hydrazine **4f**



Yellow oil; 42% yield. The titled product was obtained according to the general procedure with 0.2 mmol (*E*)-1,1-dimethyl-2-(3-methylbut-2-en-1-ylidene)hydrazine and 3 equiv C_4F_9I.

IR (Reflection): $\tilde{\nu}$ = 2974, 2918, 2874, 2796, 1649, 1587, 1449, 1406, 1381, 1352, 1247, 1135, 1050, 978, 891, 856, 827, 778, 743, 729, 645;

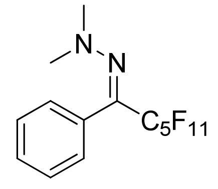
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.65 (s, 1 H), 2.82 (s, 6 H), 1.78 (d, *J* = 1.5 Hz, 3 H), 1.45 (s, 3 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 144.1 (s), 129.8 (s; t, *J* = 26.9 Hz), 116.4 (d), 46.1 (q, 2C), 25.2 (q), 20.8 (q);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -81.1 (m, 3F), -108.9 (m, 2F), -121.4 (m, 2F), -124.8 (m, 2F);

HRMS (EI) Calcd for $C_{11}H_{13}F_9N_2$ [M]$^+$: 344.0935, found: 344.0953.

(*E*)-1,1-dimethyl-2-(2,2,3,3,4,4,5,5,6,6,6-undecafluoro-1-phenylhexylidene)hydrazine **3ba**



Colorless oil; 85% yield.

IR (Reflection): $\tilde{\nu}$ = 3064, 2965, 2928, 2878, 2842, 2798, 1605, 1589, 1493, 1467, 1447, 1429, 1357, 1289, 1225, 1193, 1135, 1101, 1050, 1015, 931, 896, 848, 827, 808, 784, 731, 718, 701, 656;

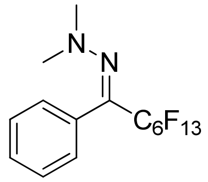
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32-7.19 (m, 5 H), 2.66 (s, 6 H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.4 (s), 130.3 (d, 2C), 129.0 (d), 128.4 (s; t, *J* = 27.7 Hz), 127.9 (d, 2C), 46.5 (q, 2C);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -80.8 (m, 3F), -105.2 (m, 2F), -119.4 (m, 2F), -121.3 (m, 2F), -126.3 (m, 2F);

HRMS (ESI) Calcd for $C_{14}H_{12}F_{11}N_2$ [M+H]$^+$: 417.08194, found: 417.08307.

(*E*)-1,1-dimethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-phenylheptylidene)hydrazine **3ca** (known compound)[1d]

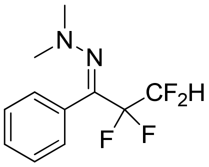


Colorless oil; 88% yield.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.41-7.27 (m, 5 H), 2.74 (s, 6 H);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -80.9 (m, 3F), -105.2 (m, 2F), -119.2 (m, 2F), -120.5 (m, 2F), -122.8 (m, 2F), -126.0 (m, 2F);

(*E*)-1,1-dimethyl-2-(2,2,3,3-tetrafluoro-1-phenylpropylidene)hydrazine **3da**

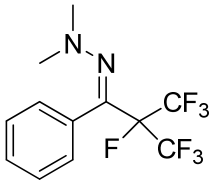


Colorless oil; 68% yield.

IR (Reflection): $\tilde{\nu}$ = 3061, 3022, 2967, 2876, 2841, 2796, 1591, 1494, 1466, 1446, 1396, 1343, 1296, 1223, 1165, 1095, 1055, 1026, 935, 905, 834, 799, 762, 732, 699, 671;

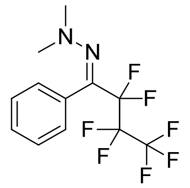
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.41-7.29 (m, 5 H), 6.35 (tt, J = 53.1, 5.7 Hz, 1 H), 2.71 (t, J = 1.2 Hz, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.8 (s; t, J = 32.6 Hz), 132.1 (s), 129.7 (d, 2C), 129.0 (d), 128.0 (d, 2C), 46.6 (q, 2C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -112.1 (t, J = 11.6 Hz, 2F), -138.5 (t, J = 9.3 Hz, 2F);
HRMS (EI) Calcd for $C_{11}H_{12}F_4N_2$ $[M]^+$: 248.0939, found: 248.0928.

(*E*)-1,1-dimethyl-2-(2,3,3,3-tetrafluoro-1-phenyl-2-(trifluoromethyl)propylidene)hydrazine **3ea**



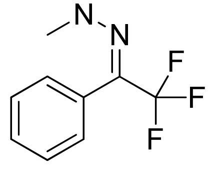
Colorless oil; 74% yield.
IR (Reflection): $\tilde{\nu}$ = 3063, 2968, 2875, 2839, 2796, 1604, 1493, 1467, 1446, 1429, 1303, 1278, 1222, 1153, 1096, 1074, 1048, 1026, 970, 927, 887, 819, 770, 748, 725, 698, 641;
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.44-7.25 (m, 5 H), 2.70 (s, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.4 (s), 130.0 (d, 2C), 129.0 (d), 128.8 (s; d, J = 33.9 Hz), 128.0 (d, 2C), 120.6 (s; qd, J = 300.1, 27.9 Hz), -91.8-89.3 (m), 46.6 (q, 2C);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -74.4 (s, 6F), -176.1 (m, 1F);
HRMS (ESI) Calcd for $C_{12}H_{12}F_7N_2$ $[M+H]^+$: 317.08832, found: 317.08953.

(*E*)-2-(2,2,3,3,4,4,4-heptafluoro-1-phenylbutylidene)-1,1-dimethylhydrazine **3fa**



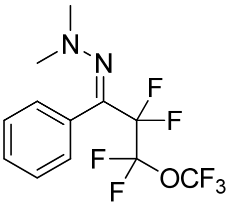
Colorless oil; 70% yield.
IR (Reflection): $\tilde{\nu}$ = 3085, 3063, 3023, 2967, 2878, 2841, 2797, 1958, 1892, 1816, 1604, 1590, 1493, 1467, 1446, 1429, 1407, 1345, 1240, 1110, 1052, 1030, 995, 925, 881, 848, 816, 768, 729, 700, 676, 633;
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.41-7.31 (m, 5 H), 2.77 (t, J = 0.9 Hz, 6 H);
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.3 (s), 130.3 (d, 2C), 129.0 (d), 128.1 (s; t, J = 27.0 Hz), 127.9 (d, 2C), 46.5 (q, 2C)
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -79.6 (t, J = 9.9 Hz, 3F), -106.1 (d, J = 4.2 Hz, 2F), -123.8 (d, J = 4.2 Hz, 2F);
HRMS (EI) Calcd for $C_{12}H_{11}F_7N_2$ $[M]^+$: 316.0810, found: 316.0823.

(*E*)-1,1-dimethyl-2-(2,2,2-trifluoro-1-phenylethylidene)hydrazine **3ga** (known compound)[1d]



Colorless oil; 73% yield. The titled product was obtained according to the general procedure by using 5 equiv CF_3I.
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.58-7.33 (m, 5 H), 2.76 (s, 6 H);
^{19}F NMR ($CDCl_3$, 283 MHz): δ = -65.7 (s, 3F);

(*E*)-1,1-dimethyl-2-(2,2,3,3-tetrafluoro-1-phenyl-3-(trifluoromethoxy)propylidene)hydrazine **3ha**



Yellow oil; 82% yield.

IR (Reflection): $\tilde{\nu}$ = 3065, 3024, 2967, 2878, 2842, 2797, 1605, 1466, 1446, 1362, 1337, 1215, 1135, 1047, 1026, 935, 910, 873, 816, 762, 733, 699;

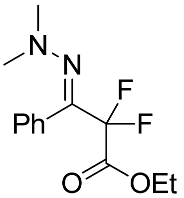
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.50-7.31 (m, 5 H), 2.76 (s, 6 H);

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 132.2 (s), 130.3 (d, 2C), 129.0 (d,), 127.9 (d, 2C), 127.8 (s; t, J = 29.0 Hz), 119.4 (s; q, J = 266.3 Hz), 46.4 (q, 2C);

^{19}F NMR ($CDCl_3$, 283 MHz): δ = -55.0 (t, J = 5.9 Hz, 3F), -85.3 (t, J = 2.3 Hz, 2F), -108.3 (s, 2F);

HRMS (ESI) Calcd for $C_{12}H_{11}F_7N_2O$ $[M]^+$: 332.0760, found: 332.0772.

(*E*)-ethyl 3-(2,2-dimethylhydrazono)-2,2-difluoro-3-phenylpropanoate **3ia** (known compound)[1d]

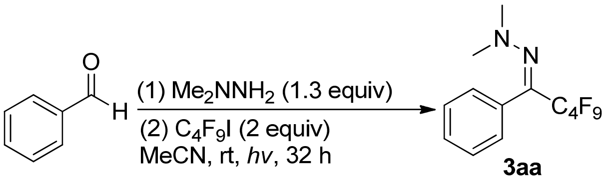


Yellow oil; 80% yield.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.46-7.32 (m, 5 H), 4.40 (q, J = 9.0 Hz, 2 H), 2.70 (s, 6 H), 1.41 (t, J = 9.0 Hz, 3 H);

^{19}F NMR ($CDCl_3$, 470 MHz): δ = -100.1 (s, 2F);

The general procedure for the gram-scale experiment



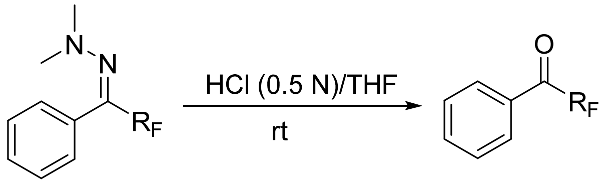
20 mmol

3aa
5.5 g (75%)

Firstly, a 100 mL round bottom flask was charged with benzaldehyde (20 mmol), 1,1-dimethylhydrazine (1.3 equiv), $MgSO_4$ (8 g), CH_2Cl_2 (50 mL), and the resulting mixture was stirred at room temperature overnight to make sure the full conversion of benzaldehyde. Then, filter and the $MgSO_4$ was washed several times with ethyl acetate. The organic solvent was removed under reduced pressure to directly afford the hydrazones in quantitative yield.

Secondly, to a 100 mL borosilicate flask, charged with stirring bar, the obtained hydrazones, C_4F_9I (40 mmol), imidazole (60 mmol) and MeCN (50 mL). The solution was degassed under nitrogen by sparging for 5-10 min at 0 ^{o}C. Then, the reaction mixture was placed under 315-400 nm light for about 32 hours (monitor by TLC). In general, after several hours of irradiation, the color of the reaction mixture becomes light yellow. When the reaction was finished, 50 mL saturated $NaHCO_3$ was added and extracted with ethyl acetate four times (4*50 mL), and the combined organic phase was dried over $MgSO_4$. The solvent was removed by rotavap and the resulting residue was subjected to flash column chromatography on silica gel that was dealt with Et_3N/PE (1:10) over 24 hours (avoiding the decomposition of products in acidic column; 100% PE-1:50 (v/v) PE/EA) to give 5.5 g **3aa**.

The hydrolysis of hydrazones



R_F = CF_3, 83% (**3ga**)
R_F = CF_2COOEt, 87% (**3ia**)
R_F = C_6F_{13}, No Reaction (**3ca**)

In general, the hydrazones can be hydrolyzed to the corresponding ketones by simple acid treatment. However, according to the literature procedure (*Angew. Chem. Int. Ed.* **2016**, *55*, 2934-2938; *Angew. Chem. Int. Ed.* **2013**, *52*, 5346-5349), only the difluoromethylated and trifluoromethylated hydrazones (**3ga** and **3ia**) can ultimately furnish corresponding ketones, and the long-chain perfluoroalkylated hydrazones (**3ca**) seem stable under the identical conditions.

Mechanistic studies

A. UV-vis absorption spectra

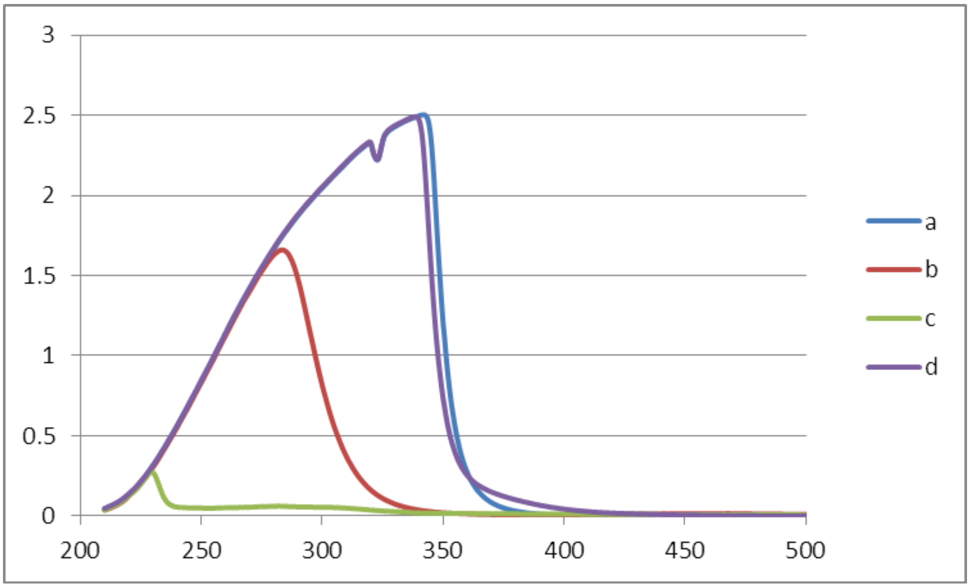


Figure 1. Optical absorption spectra recorded in MeCN in quartz cuvettes (1 cm path). [a] hydrazone **1a**: 0.01 M; [b] C_4F_9I **2a**: 0.02 M; [c] imidazole: 0.03 M; [d] 1 equiv **1a** + 2 equiv **2a**.

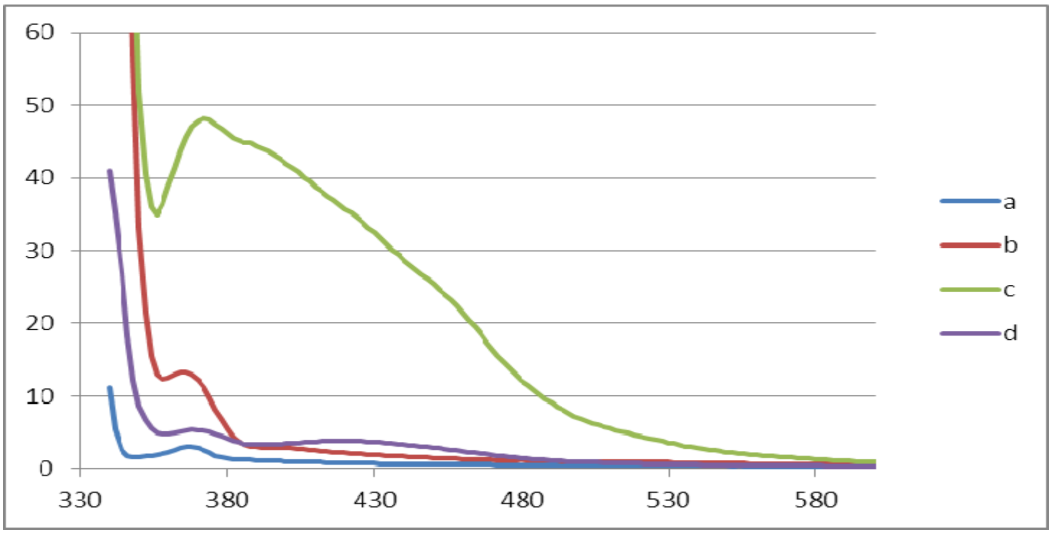
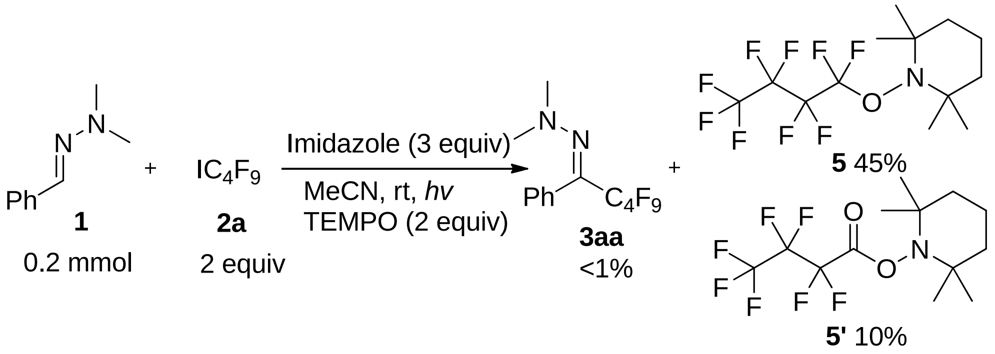


Figure 2. Fluorescence excitation spectra recorded in MeCN. [a] hydrazone **1a**: 0.01 M; [b] C_4F_9I **2a**: 0.02 M; [c] imidazole: 0.03 M; [d] 1 equiv **1a** + 2 equiv **2a**.

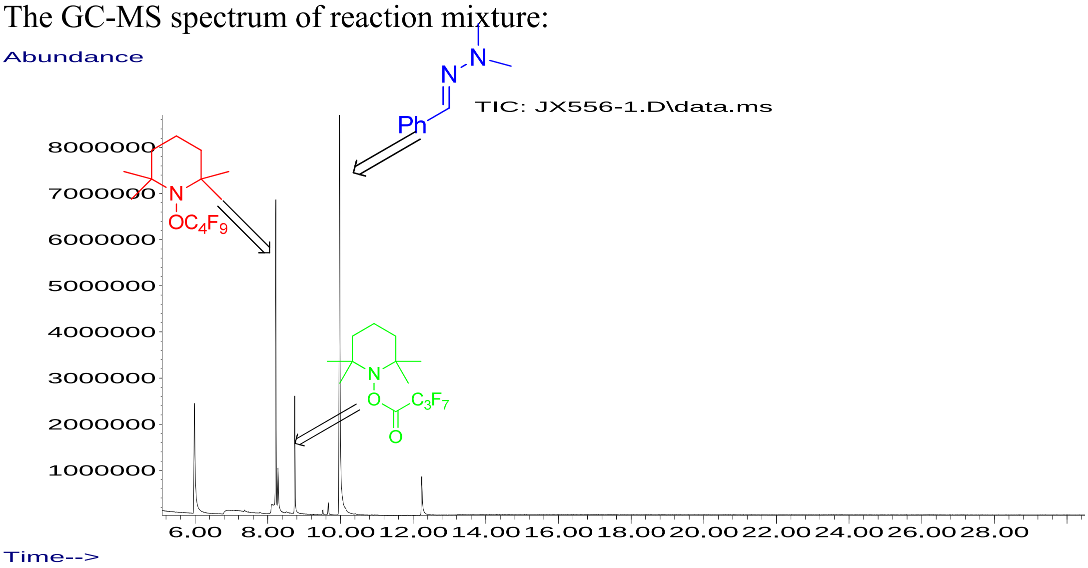
About the EDA pathway, first, we performed the Job's plot experiment, and we can not determine the stoichiometry relationship of **1a** and **2a**. Second, we try to get single crystal of the so-called EDA-complex. However, after several times X-ray analysis of the generated crystals by mixing hydrazones **1h** (and **1i**, **1j**) with C_4F_9-I together under argon, it is surprising to find that no EDA-complex is formed. Third, mixing of hydrazones with Rf-I don't result in color change (one important evidence for EDA, J. Am. Chem. Soc. 2015, 137, 5678−5681). However, at present, we still can not definitively exclude this mechanism. Maybe the slight changes of UV-vis absorption is indicative of the formation of EDA-complex. Therefore, the EDA pathway was proposed as an alternative pathway with the excited-state of hydrazone pathway.

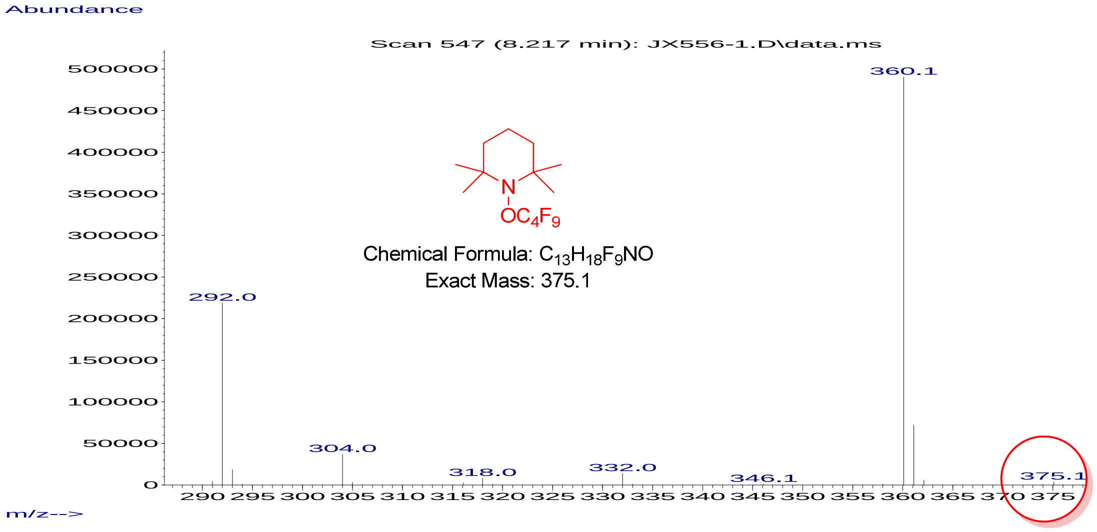
B. Radical trapping experiments

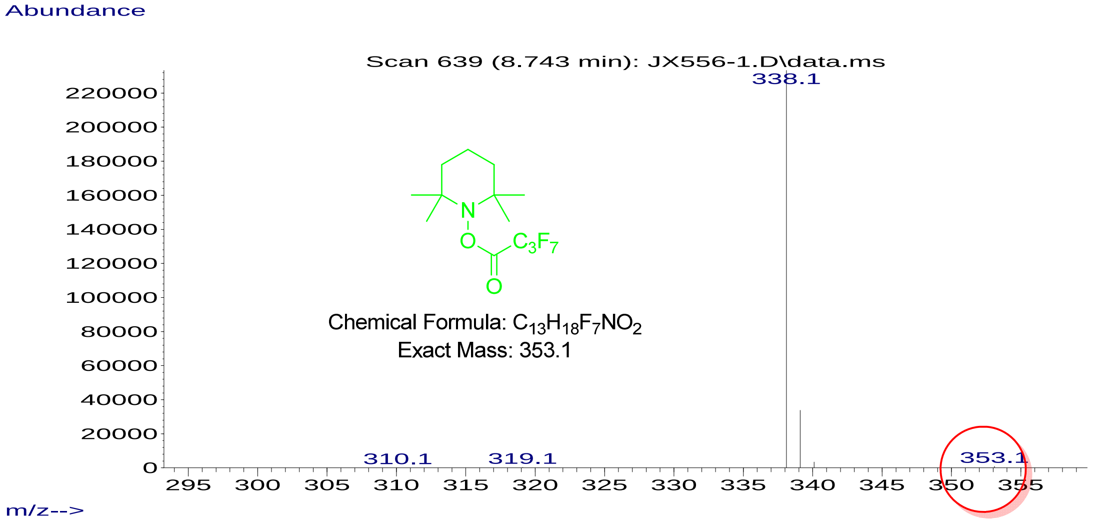


When 2 equiv TEMPO was added into the model reaction of **1a** and **2a** for 12 hours, only trace amount of desired product **3aa** was formed, instead with the formation of by-product TEMPO-C_4F_9 **5** (45%) and TEMPO-COC_3F_7 **5'** (10%). Both byproducts was determined by ^{19}F NMR, GC-MS and HRMS (EI). The successful trapping of C_4F_9 radical with TEMPO strongly suggests a radical mechanism.

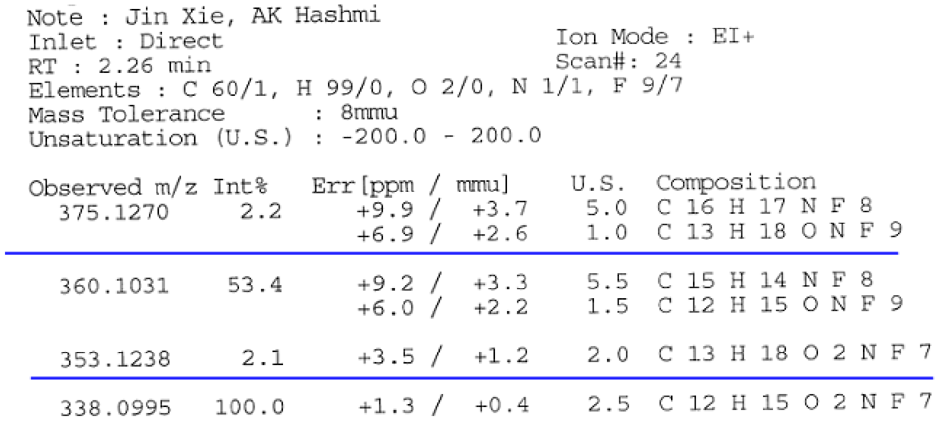
The GC-MS spectrum of reaction mixture:



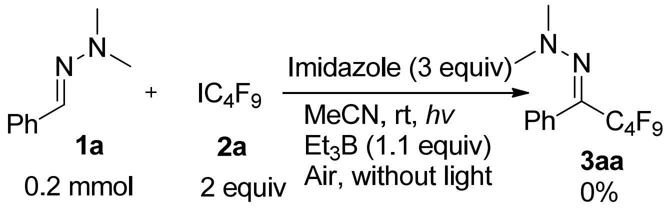




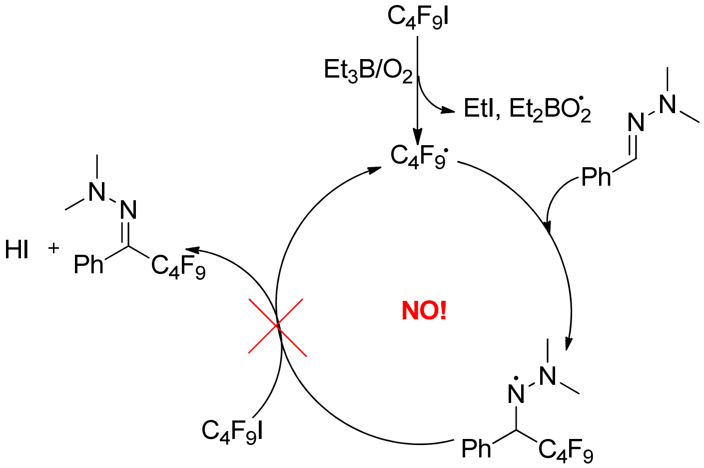
The HRMS (EI) report:


```
Note : Jin Xie, AK Hashmi
Inlet : Direct                                   Ion Mode : EI+
RT : 2.26 min                                    Scan#: 24
Elements : C 60/1, H 99/0, O 2/0, N 1/1, F 9/7
Mass Tolerance        : 8mmu
Unsaturation (U.S.)   : -200.0 - 200.0

Observed m/z  Int%    Err[ppm / mmu]    U.S.  Composition
  375.1270     2.2       +9.9 /  +3.7    5.0  C 16 H 17 N F 8
                         +6.9 /  +2.6    1.0  C 13 H 18 O N F 9

  360.1031    53.4       +9.2 /  +3.3    5.5  C 15 H 14 N F 8
                         +6.0 /  +2.2    1.5  C 12 H 15 O N F 9

  353.1238     2.1       +3.5 /  +1.2    2.0  C 13 H 18 O 2 N F 7

  338.0995   100.0       +1.3 /  +0.4    2.5  C 12 H 15 O 2 N F 7
```

C. Radical chain experiments

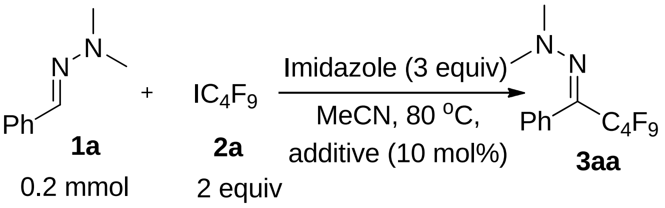


In a 10 mL dried tube was charged with **1a** (0.2 mmol), **2a** (2 equiv), imidazole (3 equiv), Et_3B (1 M in THF, 1.1 equiv) and MeCN (0.6 mL). The reaction mixture was stirred for 12 hours and 1,3,5-trifluorobenzene was added into the reaction mixture as a reference standard. Then, the above mixture was taken out for ^{19}F NMR analysis. It was found that there wasn't any desired product **3aa** was produced. This experiment may indicate that radical chain propagation is less likely because the Et_3B/air radical system was reported as an efficient method for radical trifluoromethylation with CF_3I.[2]



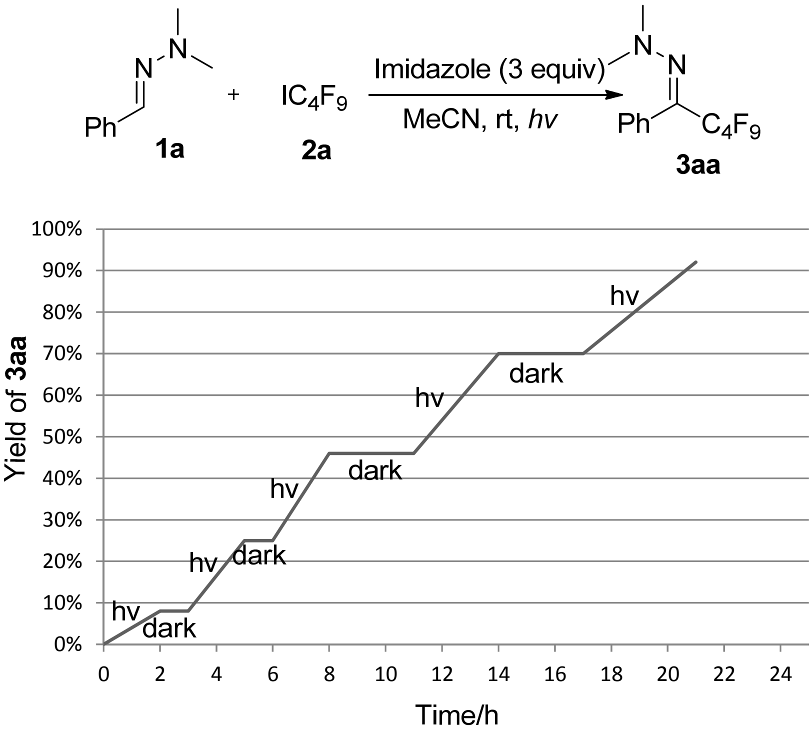
Scheme 1. The unsuccessful radical-chain mechanism.

However, given the presence of oxygen in the air, in its triplet state, oxygen can partially quench the radical chains through the electron or energy transfer. Thus, it's still cautious for us to make this conclusion and other experiments need to be done. Next, we performed several control experiments by adding other radical inhibitors. When AIBN or ^{t}BuOOBu^t was added into the model reaction upon heating at 80 °C, no **3aa** was formed. Thus, a radical chain mechanism of this reaction could be rule.d out



Addtive			**3aa**
AIBN	N_2	12 h	0%
^{t}BuOOBu^{t}	N_2	12 h	0%
Et_3B	air	12 h	0%

D. The time-profile experiment



Scheme 2. The light on/off experiment. Reaction conditions: **1a** (0.4 mmol), **2a** (2 equiv), imidazole (3 equiv), MeCN (1.2 mL), with 315-400 nm light irradiation for the indicated time and then placed under dark for the indicated time. The yields were determined by ^{19}F NMR spectra with 1,3,5-trifluorobenzene as reference standard.

E. Quantum yield measurement

The quantum yield (ϕ) was determined by the known ferrioxalate actinometry method. A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in Handbook of

Photochemistry.[3] 240 W UVA lamps (PRP-3500 Å, purchased from Southern New England Ultraviolet Company) were used. The irradiated light intensity was estimated to 3.54×10^{-7} einstein S^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.

Model reaction solution: (*E*)-2-benzylidene-1,1-dimethylhydrazine (3 mmol), nonafluoro-4-iodobutane **2a** (2 equiv) and imidazole (3 equiv) were added to a 10 mL volumetric flask, and then filled to the mark with anhydrous acetonitrile. [c = 0.30 mmol/mL]

For every tube, 1 mL model reaction solution was taken out into five 10 mL dried pyrex screw-top reaction tube, respectively, and degassed under nitrogen by sparging for 5-10 min. Then, the reaction mixtures were irradiation with 240 W UVA lamps for specified time intervals (5 min, 10 min, 15 min, 20 min and 25 min). The moles of products formed were determined by ^{19}F NMR measurement with 1,3,5-trifluorobenzene as reference standard. The number of moles of products (y axis) per unit time is related to the number of photons (x axis, calculated from the light intensity). The slope gives the quantum yield (Φ) of the photoreaction, 0.023 (2.3%).

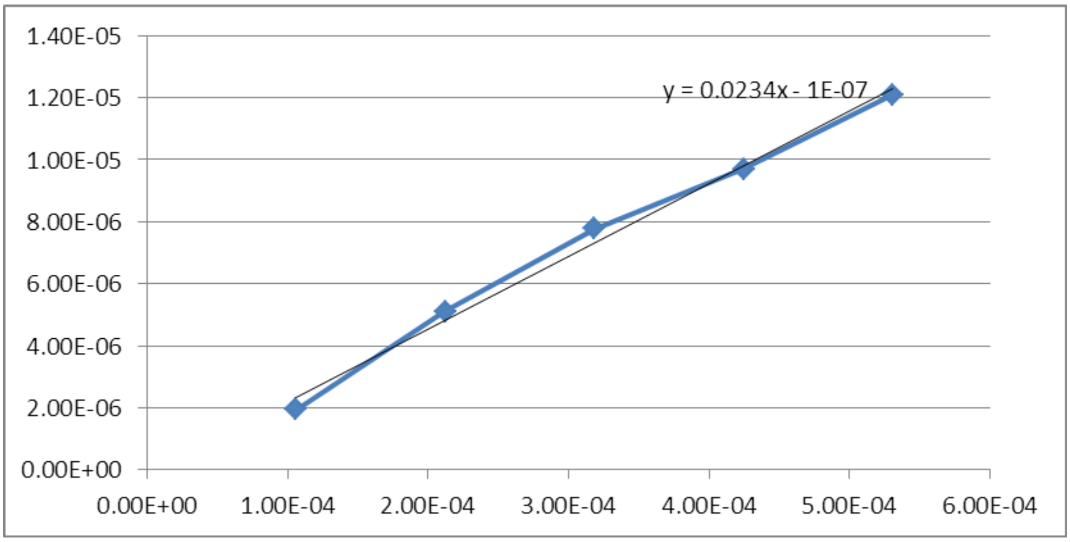


Figure 3. The quantum yield of the model reaction.

F. Cyclic voltammetry experiments

Cyclic voltammetry experiments were carried out in a conventional three-electrode electrochemical cell using VersaSTAT3 Instrument (Princeton Applied research). A gold electrode in PEEK (Serial #: ET076-0240) and Pt/Ti titanium wire anode (Serial #: ET078-0264) were used as the working and counter electrodes, respectively. A silver wire was used as a pseudo-reference electrode at a scan rate of 0.2 V/s. The redox potentials were determined through cyclic voltammetry by employing 2.0 mM (*E*)-2-benzylidene-1,1-dimethylhydrazine **1a**, 5.0 mM C_4F_9I **2a** in a 0.2 M solution of Bu_4NPF_6 in dry MeCN with a gold working electrode at a scan rate of 0.2 V/s. Prior to each measurement, solutions were purged with N_2.

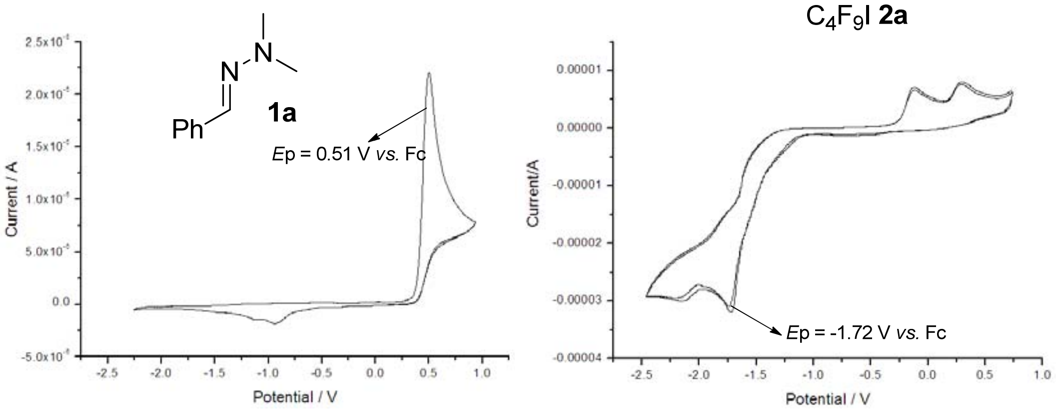
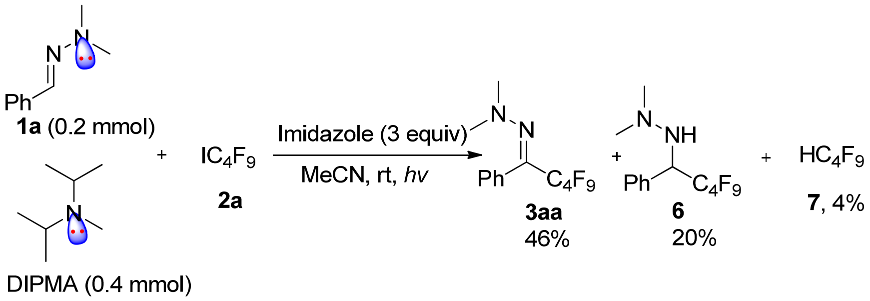


Figure 4. Cyclic voltammogram: The current peak was determined by using the blank measurement and corrected with the redox potential of FeCp2 (Fc/Fc^{+}) as an internal standard.

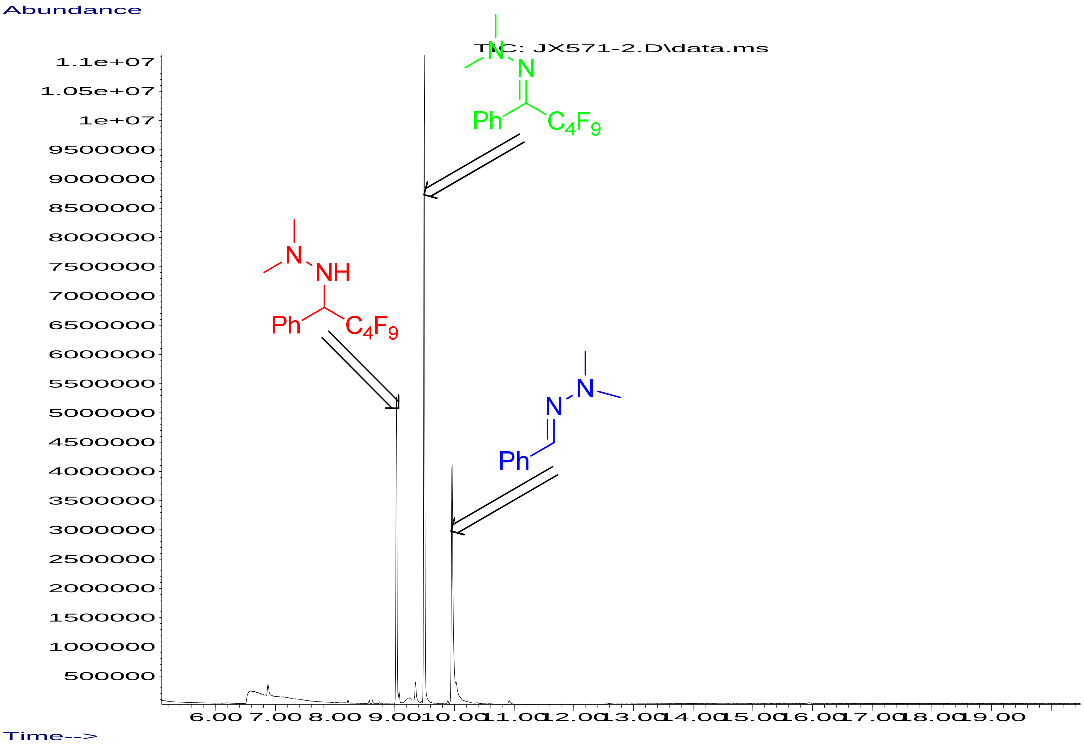
The cyclic voltammetry of **1a** and **2a** exhibited an irreversible oxidation and reduction respectively with a peak potential at 0.51 V vs Fc (0.91 V vs SCE) and -1.72 V vs Fc (-1.32 V vs SCE) in MeCN. This finding further stress the electron-donating ability of **1a** and the electron-accepting ability of **2a**.

G. Competitive Electron-Donors



Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv), DIPMA (2 equiv), imidazole (3 equiv), MeCN (0.6 mL), with 315-400 nm light irradiation for 12 hours. When the reaction was finished, 1,3,5-trifluorobenzene was added. Then, the reaction mixture was taken for NMR analysis. The yields of **3aa** were determined by ^{19}F NMR spectra with 1,3,5-trifluorobenzene as reference standard. The yield of by-product **6** and HC_4F_9 were determined by ^{1}H NMR analysis of the reaction mixture.

The GC-MS spectra of reaction mixture: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11.00
12.00
13.00
14.00
15.00
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NH
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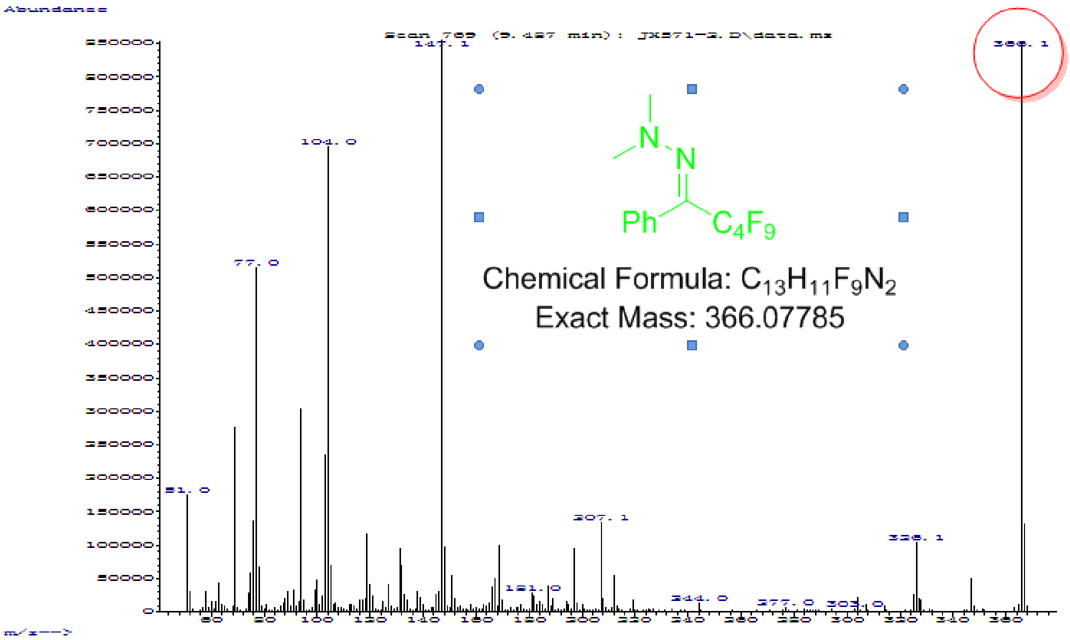
N
N
Ph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50000
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104.0
77.0
51.0
207.1
181.0
244.0
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303.0
328.1
366.1
60
80
100
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m/z-->
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Ph
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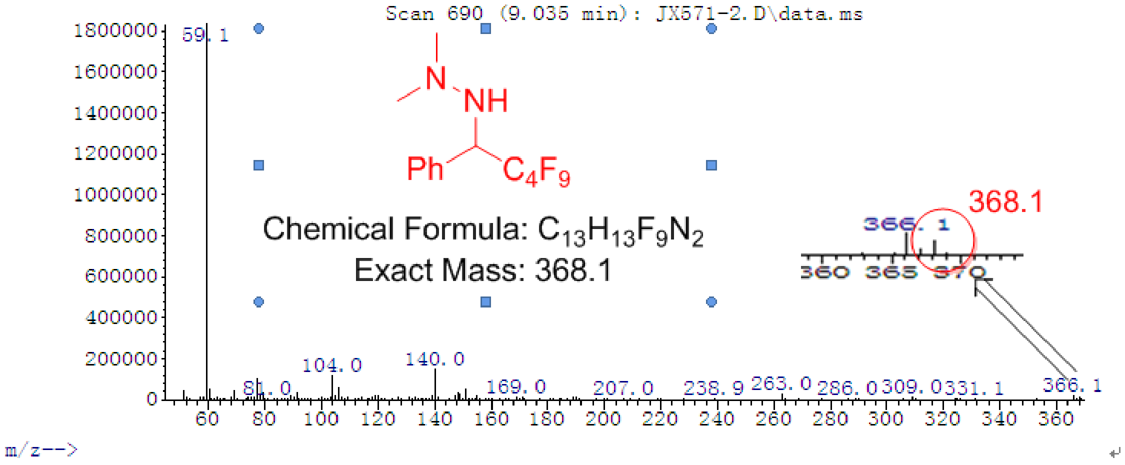
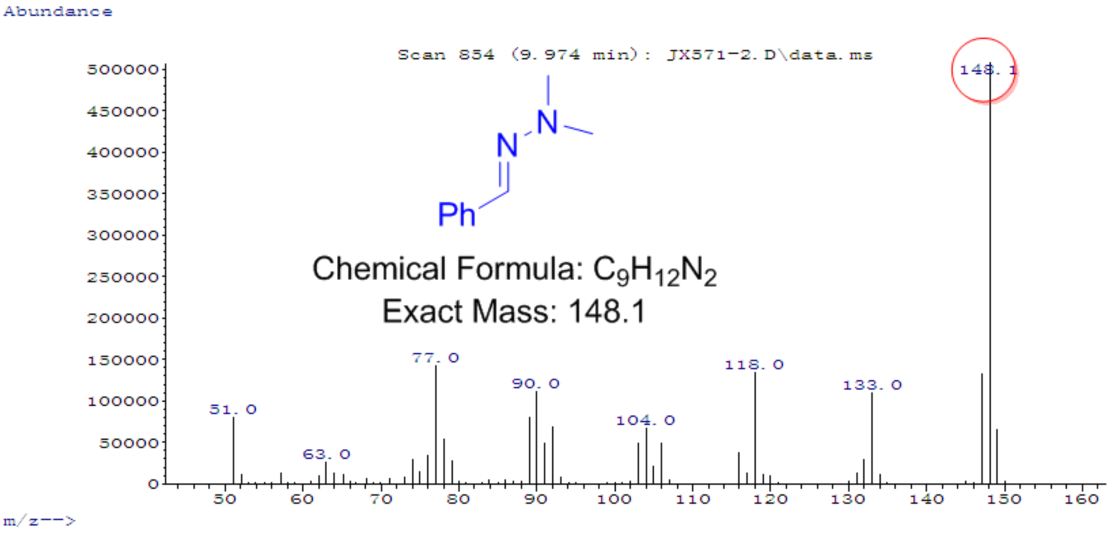
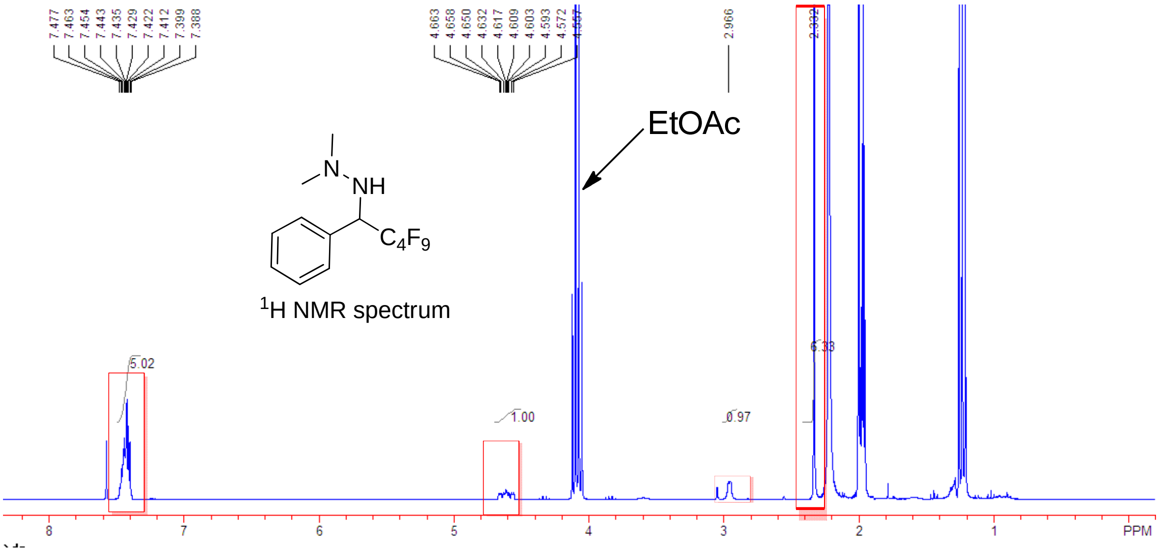
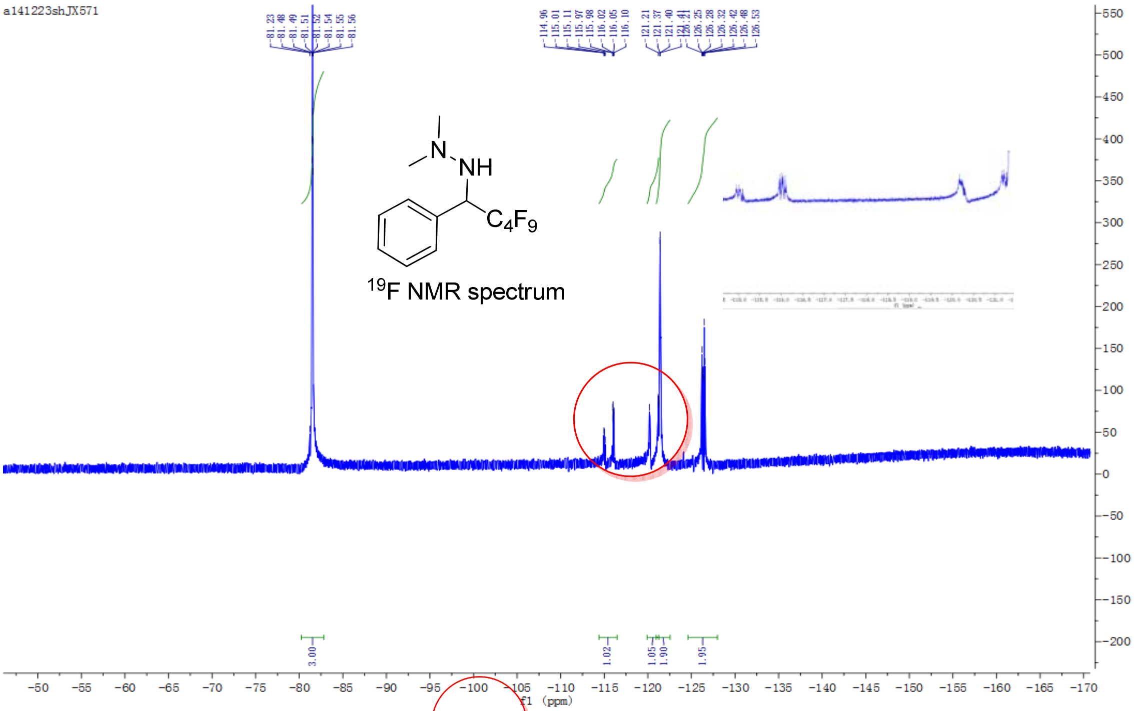
Exact Mass: 366.07785

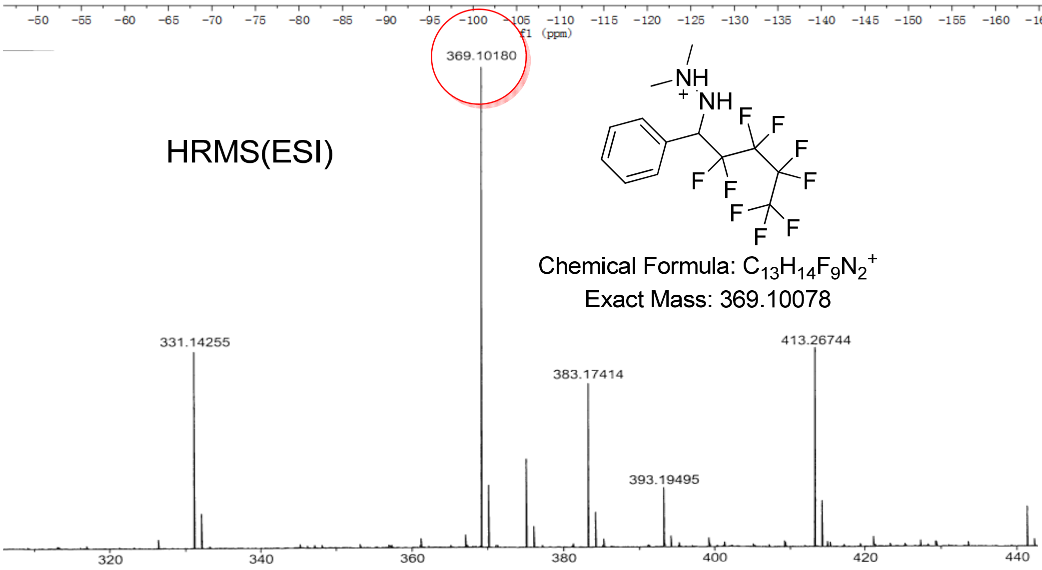




When 2 equiv *N*,*N*-diisopropylmethylamine (DIPMA) was added into the model reaction, the reaction rate was decreased, and 28% starting material **1a** was left. Moreover, some very interesting by-products were detected. The reduction product **6** was formed in 20% NMR yield, and 4% HC_4F_9 was first observed (neither byproduct **6** nor **7** was found in our model reaction). The desired product **3aa** was produced in 46% ^{19}F NMR yield (without DIPMA, 94% yield). We tried to isolate the byproduct **6**, but it's rather difficult to do this by column chromatography mainly because it was volatile. At last, a very small amount of product **6** was obtained by isolating the reaction mixture with preparative thin layer chromatography (PTLC) by using solvent mixture of (PE/EA = 20:1), which was then extracted from silica with $CD_3CN/CDCl_3$ (v/v = 1:3). The obtained deuterated solution was subjected directly to ^{1}H NMR and ^{19}F NMR analysis and HRMS (ESI) analysis.

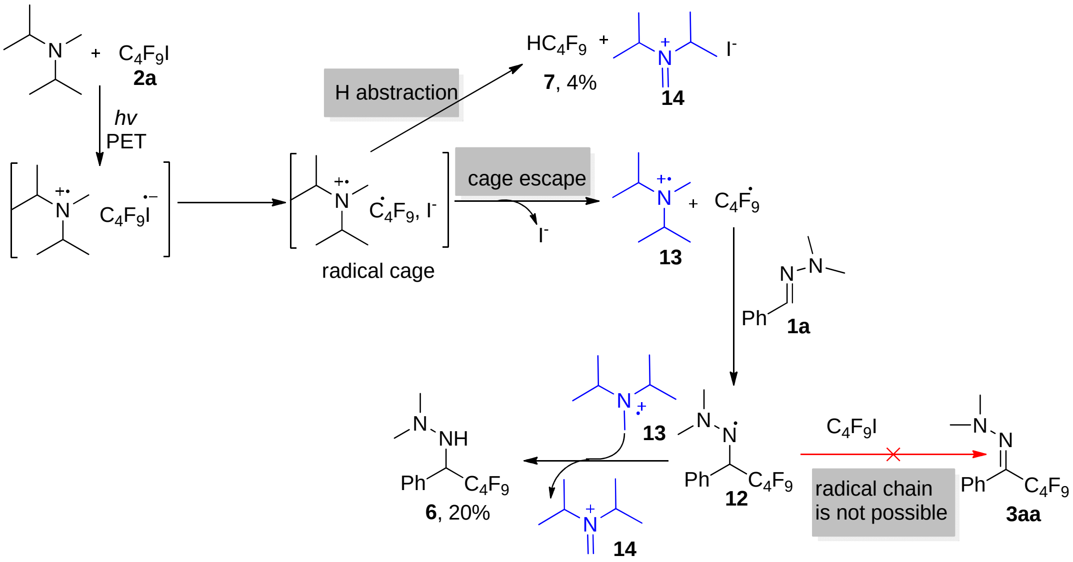






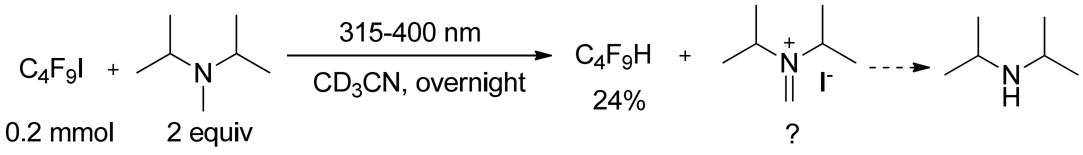
Chemical Formula: $C_{13}H_{14}F_9N_2^+$
Exact Mass: 369.10078

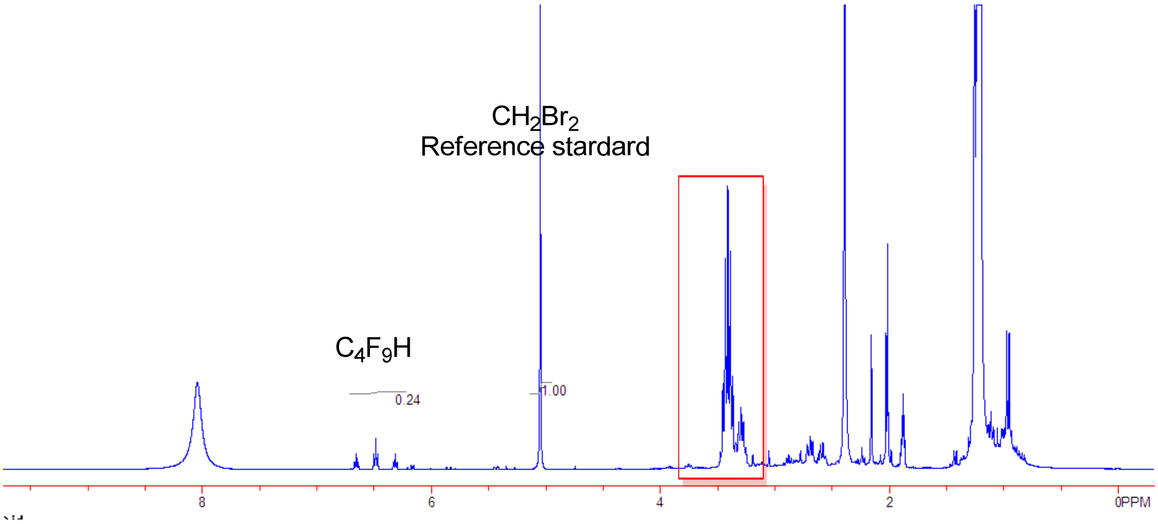
^{1}H NMR ($CDCl_3$/CD_3CN, 300 MHz): δ = 7.50-7.37 (m, 5 H), 4.69-4.54 (m, 1 H), 2.97 (brs, 1 H), 2.33 (s, 6 H);
^{19}F NMR ($CDCl_3$/CD_3CN, 283 MHz): δ = -81.5 (m, 3F), -118.1 (m, 2F); -121.3 (m, 2F), -126.3 (m, 2F);
HRMS (ESI) Calcd for $C_{13}H_{14}F_9N_2$ $[M+H]^+$: 369.10078, found: 369.10180.



Scheme 3. The possible mechanism for the formation of by-product **6**.

The possible mechanism for the generation of by-product **6** is proposed in Scheme 3. The DIPMA can undergo a competing photo-induced electron transfer under light irradiation. Firstly, under the irradiation of light, amine radical cation species **13** and C_4F_9 radical can be generated in situ. Then, the generated C_4F_9 radical can either abstract one hydrogen atom from the amine radical cation **13** to form byproduct **7** or add to the substrate **1a** to produce the aminyl radical intermediate **12** through cage escaping. As the above control experiments show **12** cannot undergo the radical chain propagation process with C_4F_9I to produce **3aa**. Thus, intermediate **12** can directly abstract one hydrogen atom form amine radical cation species **13** to generate by-product **6**. This competitive electron-donor experiment further stresses the possibility of the electron-transfer from substrate **1a** to nonafluoro-4-iodobutane **2a** to produce the desired product **3aa**. Moreover, the HC_4F_9 were not observed in our standard reaction conditions, and thus an in-cage radical combination might be involved for the highly efficient and chemoselective perfluoroalkylation of hydrazones without the formation of the perfluoroalkylation of arenes and other by-products.

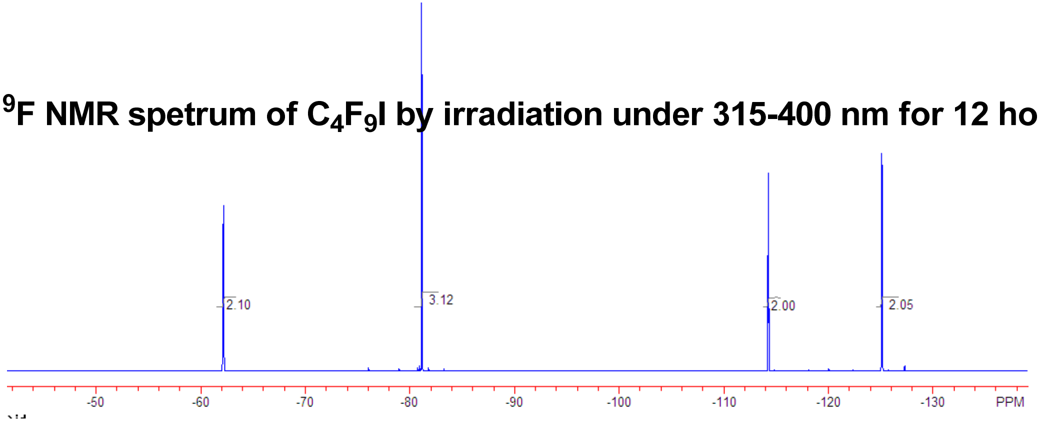


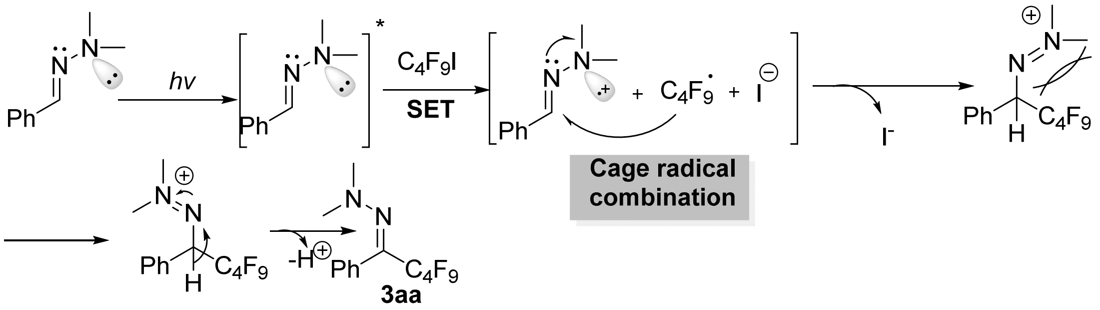


To verify the possibility of a SET between DIPMA and C_4F_9I, we perform a control experiment by mixing 0.2 mmol C_4F_9I and 2 equiv DIMPA together in 0.5 mL CD_3CN for irradiation under 315-400 nm light overnight. Then, CH_2Br_2 was added as a reference standard for ^1H NMR analysis. To our delight, 24% HC_4F_9 was obtained. And from the ^1H NMR spectrum, it also found that DIPMA might form the imiumion ions or hydrolysis to diisopropylamine. At the present step, it is clear conclude that a nitrogen atom could donate one electron to C_4F_9I under the irradiation of light.

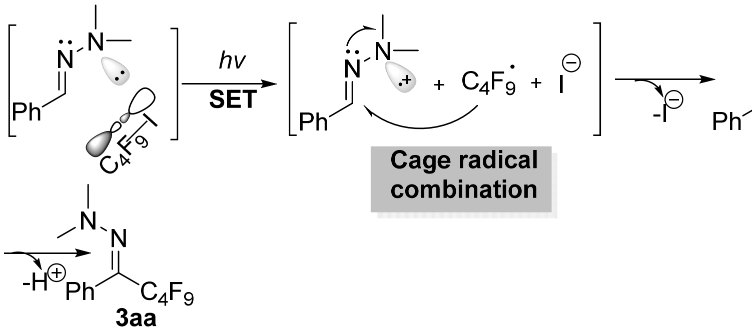
H. Possible Reaction Mechanism

To exclude the possibility of homolytic cleavage of C_4F_9I to C_4F_9 radical and I radical, we perform some control experiment. Irradiation of C_4F_9I in MeCN solution for 12 hours, the mixture was subjected to ^{19}F NMR analysis with $CDCl_3$. As shown in the following ^{19}F NMR spectrum, no decomposition of C_4F_9I was observed. In general, much C_4F_9I was remaining in our perfluoroalkylation reaction solution after it was finished. The radical addition of perfluoroalkyl radical to hydrazone and subsequent SET with C_4F_9I could not give the desired product **3aa** in the radical-chain experiments. Thus, the addition of C_4F_9 radical which was generated by photolysis of C_4F_9I to hydrazones is less likely.


^{19}F NMR spetrum of C_4F_9I by irradiation under 315-400 nm for 12 hours



Scheme 4. Alternative mechanism 1.



Scheme 5. Alternative mechanism 2.

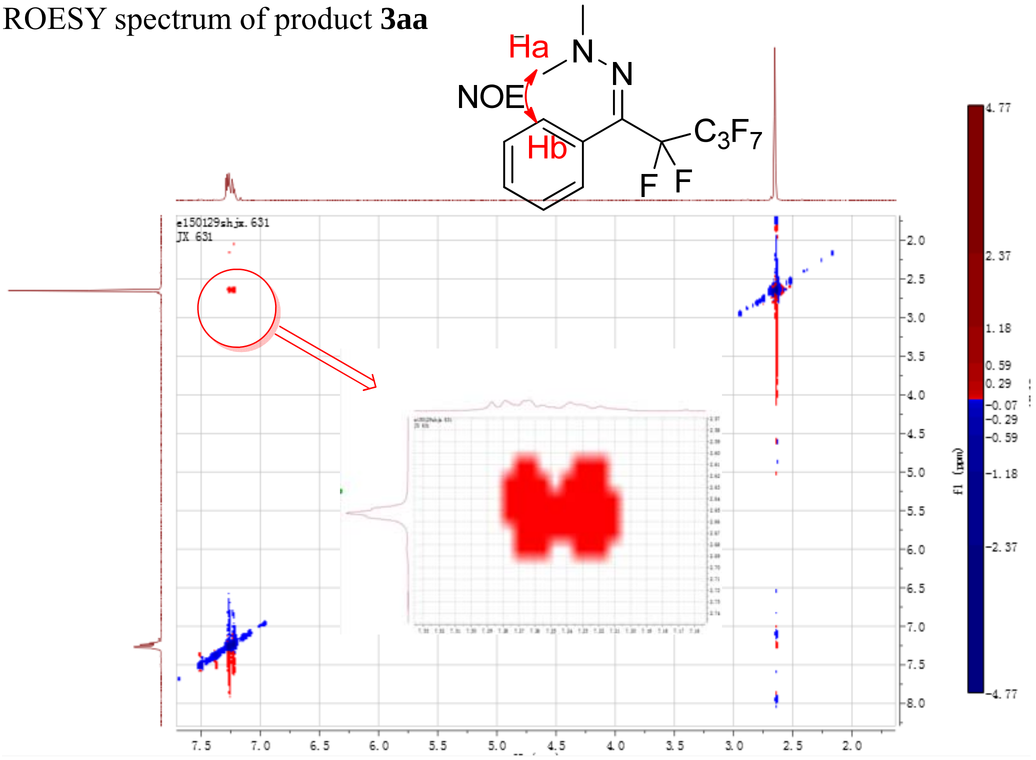
At the present, it's premature to get a clear and accurate mechanism. Two plausible mechanisms for the generation of product **3aa** are proposed.

For the homolytic cleavage pathway, we think it is not likely. Several reasons are list herein: 1) Using 254 nm light irradiation of the model reaction only leads to trace amount of products; 2) Under the optimized conditions with a bandpass filter (375 nm), 38% yield can be obtained (Homolysis of C_4F_9I is not possible for this wavelength light); 3) if the homolytic cleavage pathway work, the Et_3B/Air radical system for the generation of C_4F_9 radical can also deliver the expected products (indeed no desired product was formed under Et_3B/Air radical reaction conditions).

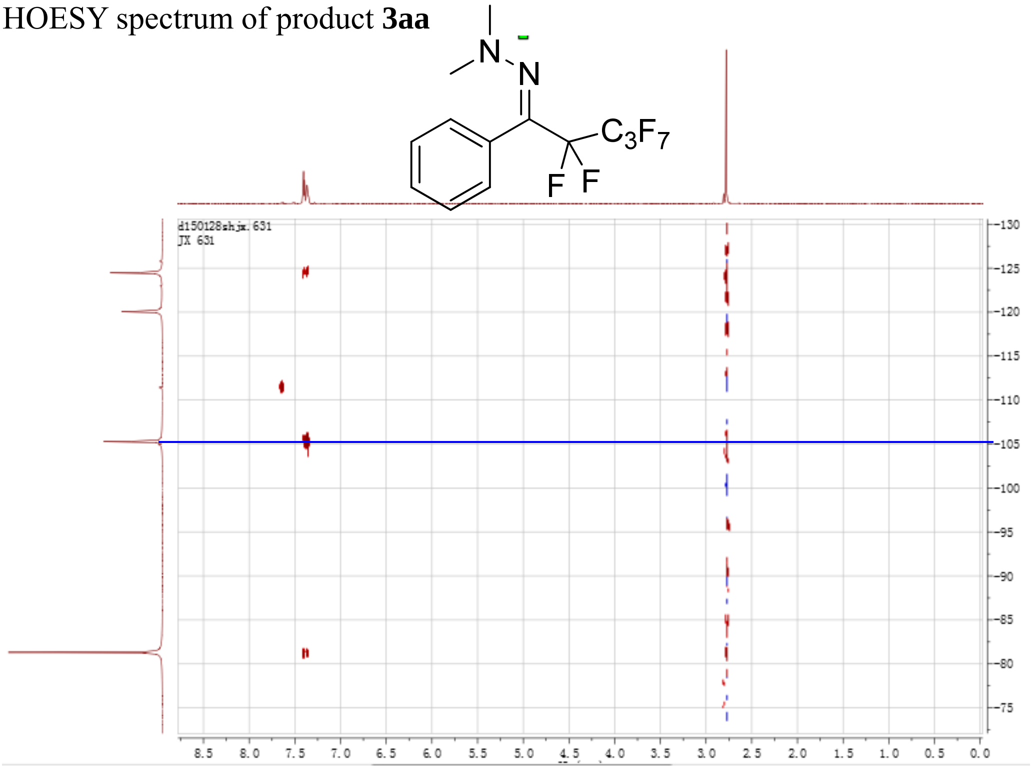
For the second mechanism, although we could not observe very significant changes between **1a** and the mixture of **1a** and **2a** from UV-vis absorption, its possibility can not be ruled out (a slight additional shoulder might be indicative of a equivocal charge transfer complex). Owing to lack of effective fluorescent of hydrazone **1a** the luminescence quenching experiments of excited hydrazones with C_4F_9I can not be measured. Instead, the HOMO-LUMO gap of hydrazone **1a** and C_4F_9I **2a** are calculated as 0.16080 eV and 0.19858 eV respectively, which indicates hydrazone **1a** is more easily excited than **2a**. It was also found that the reaction could efficiently occur with irradiation of 315-400 nm light, and this is in accordance with the UV-vis absorption of hydrazone **1a** or the co-called EDA-complex (range from 340-360 nm). Therefore, the excited state of hydrazone **1a** and EDA pathway are two alternative mechanisms for this transformation.

Determination of the geometry of the C=N double bond of products

ROESY spectrum of product **3aa**

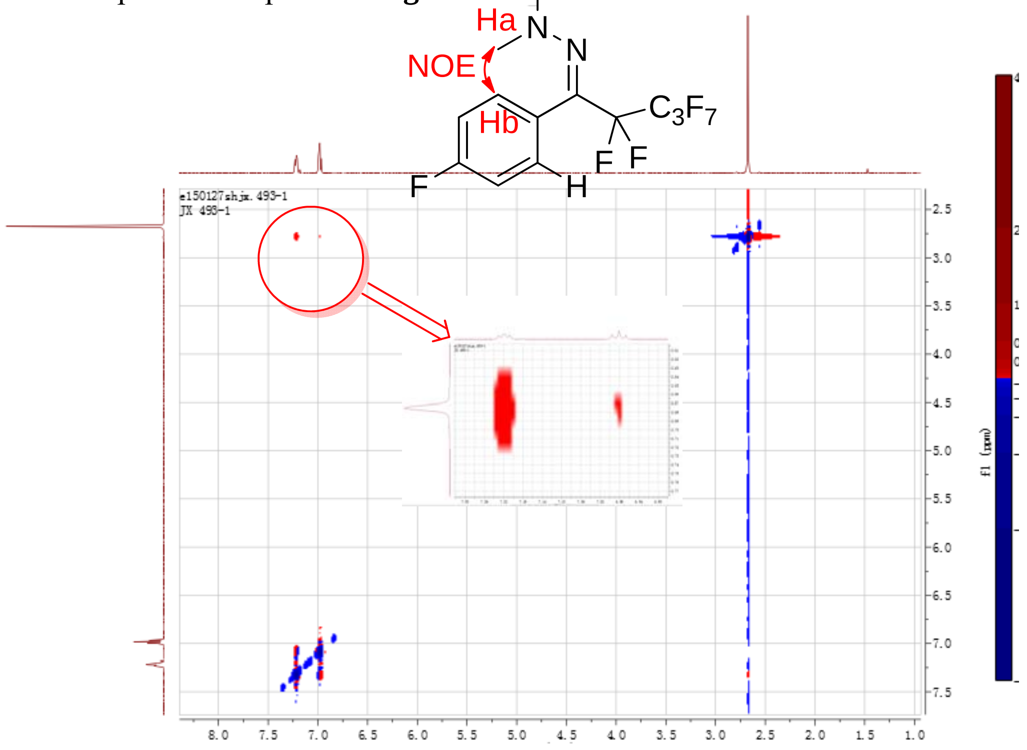


HOESY spectrum of product **3aa**



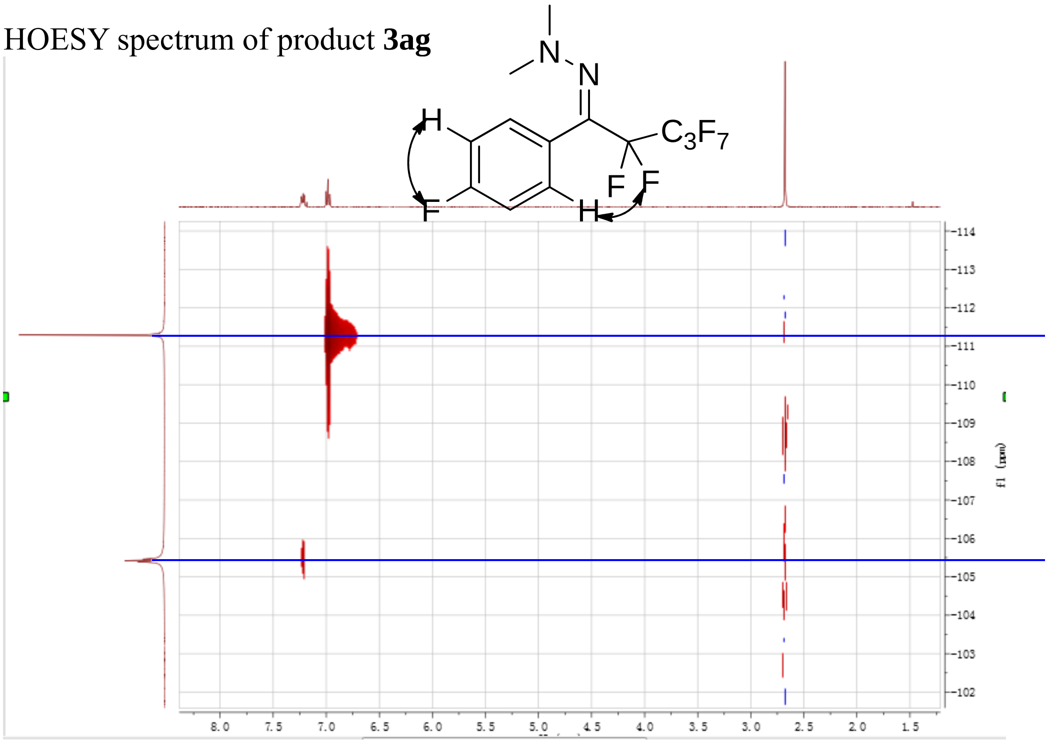
The Ha and Hb have strong NOE effect, but don’t have strong HOESY effect. Its configuration was determined as *E* configuration.

ROESY spectrum of product **3ag**



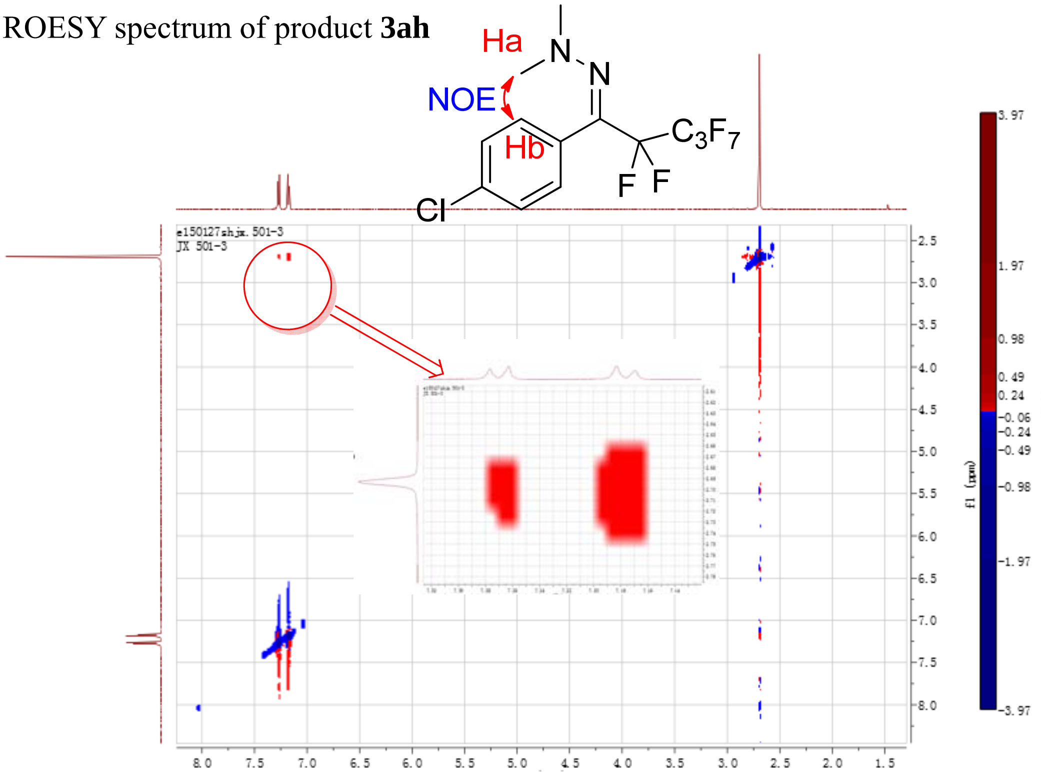
From the roesy spectrum, Ha and Hb have strong NOE effect.

HOESY spectrum of product **3ag**



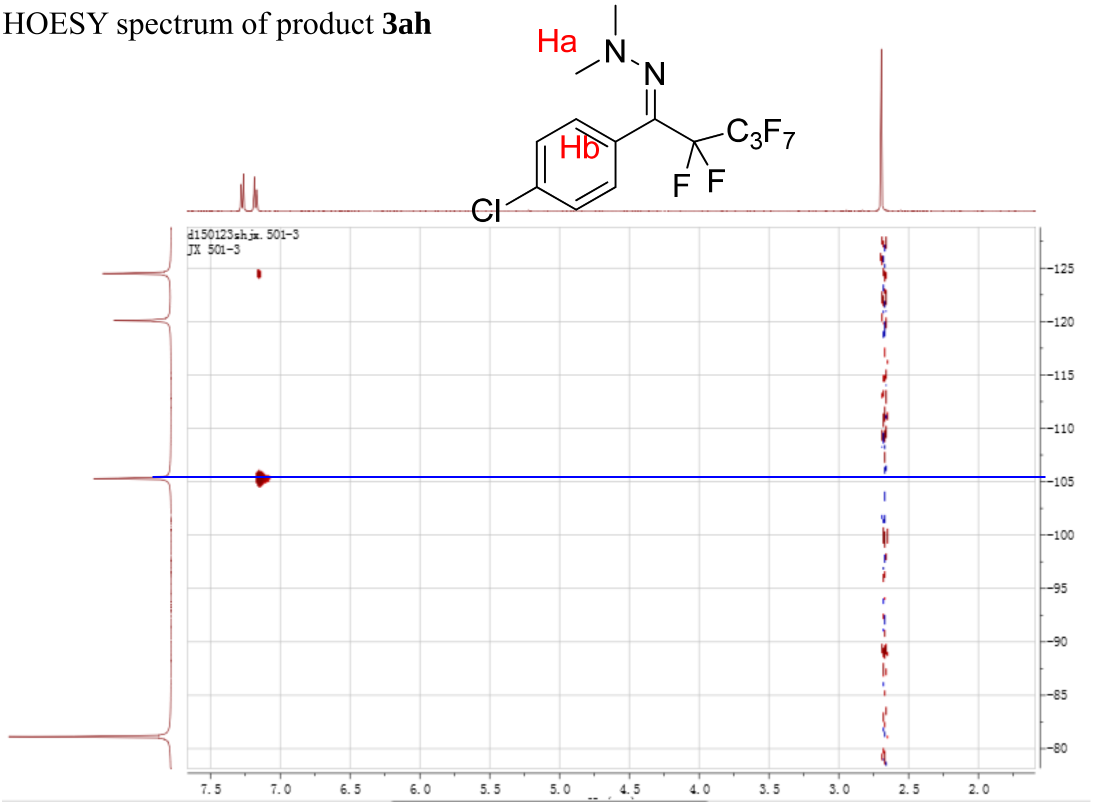
From the Hoesy spectrum, Ha and Hb don’t have strong H-F NOE effect. Thus, its configuration should be in *E*.

ROESY spectrum of product **3ah**



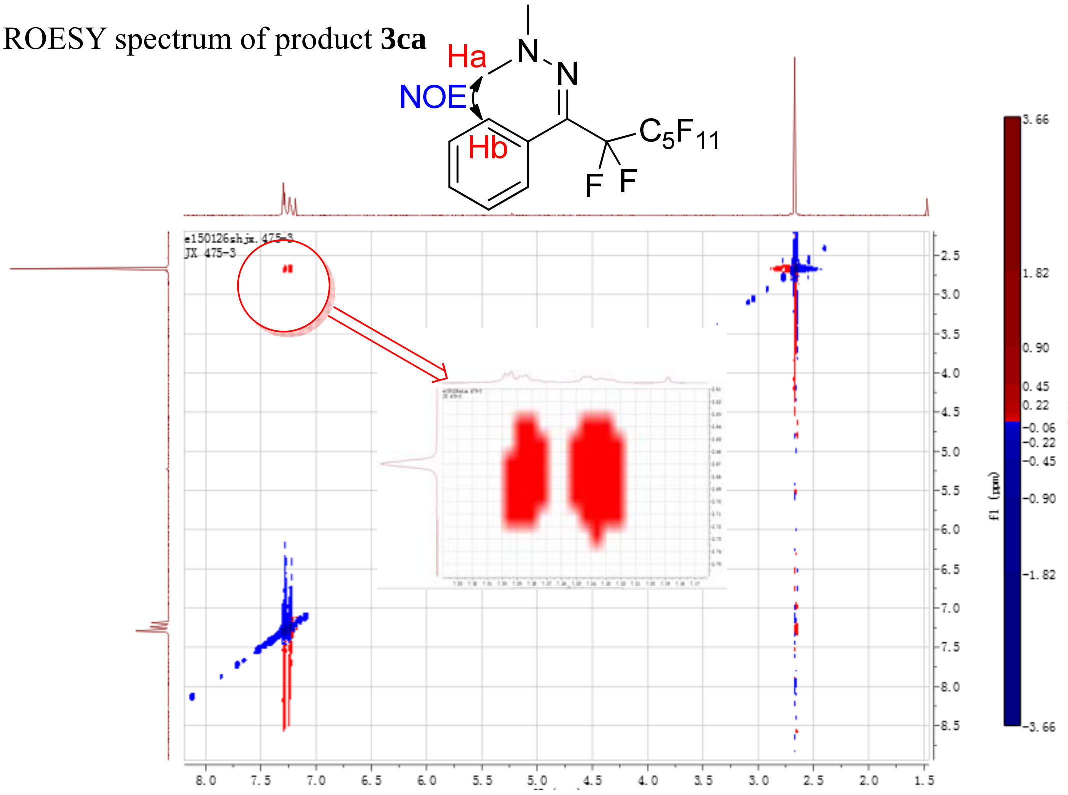
From the roesy spectrum, Ha and Hb have strong NOE effect.

HOESY spectrum of product **3ah**



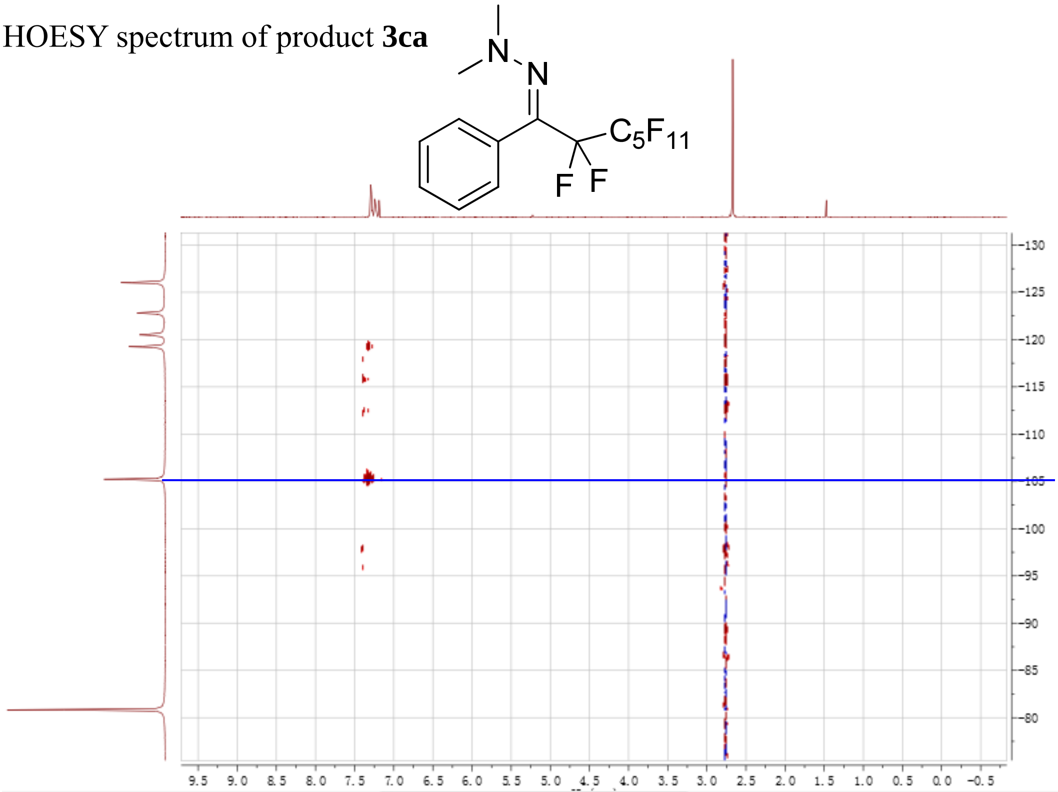
From the Hoesy spetrum, Ha and Hb don’t have strong H-F NOE effect. Thus, its configuration should be in *E*.

ROESY spectrum of product **3ca**



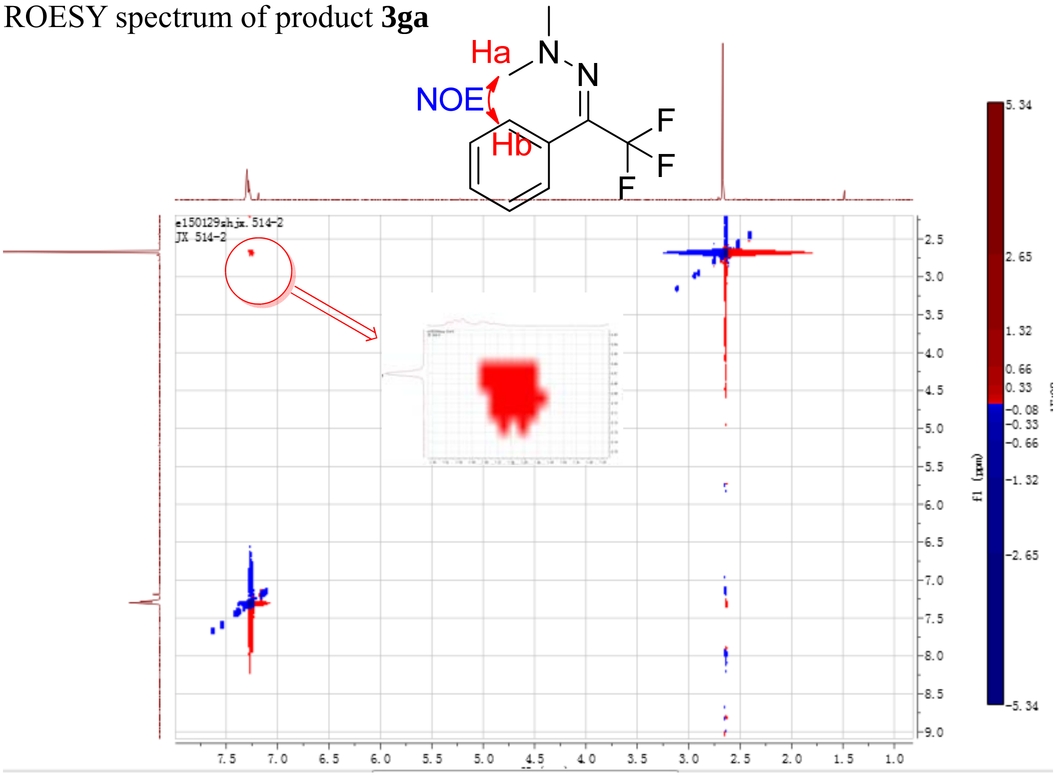
From the roesy spectrum, Ha and Hb have strong NOE effect.

HOESY spectrum of product **3ca**

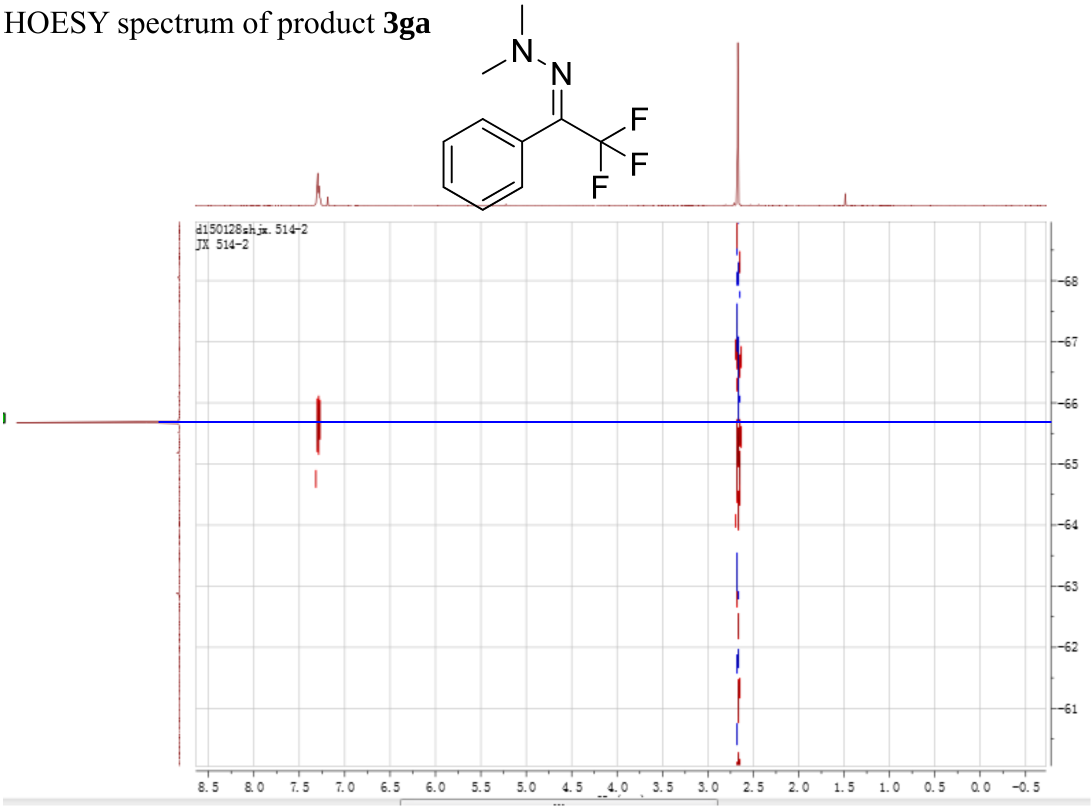


From the Hoesy spetrum, Ha and Hb don’t have strong H-F NOE effect. Thus, its configuration should be in *E* configuration.

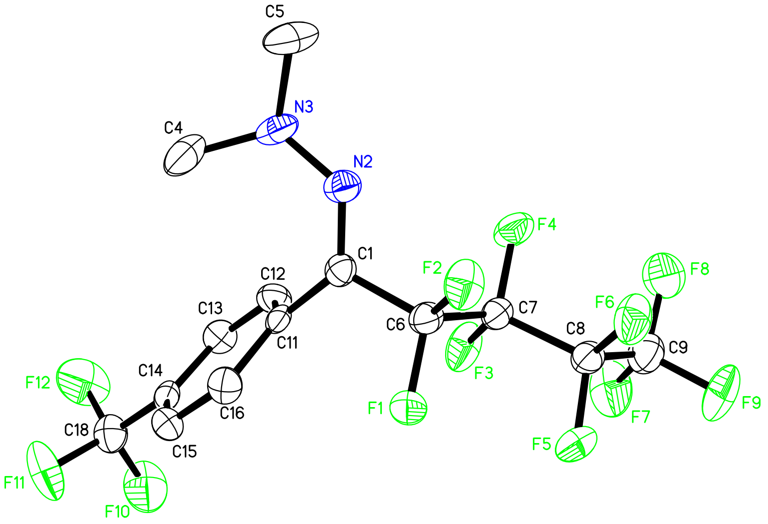
ROESY spectrum of product **3ga**



HOESY spectrum of product **3ga**



The Ha and Hb have strong NOE effect, but don’t have strong HOESY effect. Its configuration was determined as *E* configuration.



CCDC 1053855 (**3ak**, freezer under -20 °C in pentane, melting point is below 20 °C)

Colourless crystal (needle), dimensions 0.410 x 0.180 x 0.150 mm^3, crystal system monoclinic, space group P2$_1$/n, Z=4, a=10.0639(19) Å, b=8.1630(16) Å, c=20.469(4) Å, alpha=90 deg, beta=101.995(3) deg, gamma=90 deg, V=1644.8(5) Å^3, rho=1.754 g/cm^3, T=200(2) K, Theta$_{max}$= 26.758 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.90 and a completeness of 85.8% to a resolution of 0.79 Å, 11766 reflections measured, 3013 unique (R(int)=0.0846), 1716 observed (I > 2□(I)), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS based on the Laue symmetry of the reciprocal space, mu=0.20mm^{-1}, T$_{min}$=0.76, T$_{max}$=0.98, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software, 283 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.05 for observed reflections, final residual values R1(F)=0.063, wR(F^2)=0.135 for observed reflections, residual electron density -0.27 to 0.25 eÅ^{-3}.

Table 3: Crystal data and structure refinement for jx3 (**3ak**).

Identification code	jx3	
Empirical formula	$C_{14}H_{10}F_{12}N_2$	
Formula weight	434.24	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2$_1$/n	
Z	4	
Unit cell dimensions	a = 10.0639(19) Å	α = 90 deg.
	b =8.1630(16) Å	β = 101.995(3) deg.
	c = 20.469(4) Å	γ = 90 deg.
Volume	1644.8(5) Å^3	
Density (calculated)	1.75 g/cm^3	
Absorption coefficient	0.20 mm^{-1}	
Crystal shape	needle	
Crystal size	0.410 x 0.180 x 0.150 mm^3	
Crystal colour	colourless	

Theta range for data collection	2.0 to 26.8 deg.
Reflections collected	11766
Independent reflections	3013 (R(int) = 0.0846)
Observed reflections	1716 (I > 2□(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.98 and 0.76
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3013 / 282 / 283
Goodness-of-fit on F^2	1.05
Final R indices (I>2sigma(I))	R1 = 0.063, wR2 = 0.135
Largest diff. peak and hole	0.25 and -0.27 eÅ^{-3}

Table 4: Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for jx3. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C1	0.5946(3)	0.6663(4)	0.4058(2)	0.0242(8)
N2	0.6122(3)	0.7545(3)	0.4593(1)	0.0297(7)
N3	0.7047(3)	0.7218(4)	0.5150(1)	0.0388(8)
C4	0.8309(4)	0.6359(5)	0.5153(2)	0.0451(11)
H4A	0.8135	0.5178	0.5113	0.068
H4B	0.8955	0.6586	0.5572	0.068
H4C	0.8691	0.6732	0.4776	0.068
C5	0.7142(5)	0.8550(5)	0.5637(2)	0.0535(12)
H5A	0.7845	0.9326	0.5570	0.080
H5B	0.7379	0.8100	0.6090	0.080
H5C	0.6267	0.9116	0.5575	0.080
C6	0.4814(4)	0.7360(4)	0.3517(2)	0.0270(8)
F1	0.5048(2)	0.6960(3)	0.2904(1)	0.0398(6)
F2	0.4757(2)	0.9007(2)	0.3541(1)	0.0393(6)
C7	0.3399(3)	0.6709(4)	0.3544(2)	0.0254(8)
F3	0.3414(2)	0.5071(2)	0.3489(1)	0.0446(6)
F4	0.3149(2)	0.7071(3)	0.4154(1)	0.0423(6)
C8	0.2171(4)	0.7372(4)	0.3028(2)	0.0293(8)
F5	0.2381(2)	0.7101(3)	0.2410(1)	0.0469(6)
F6	0.2064(2)	0.8979(2)	0.3110(1)	0.0450(6)
C9	0.0807(4)	0.6621(5)	0.3058(2)	0.0413(10)
F7	0.0785(2)	0.5021(3)	0.2958(1)	0.0629(7)
F8	0.0464(2)	0.6892(3)	0.3640(1)	0.0586(7)
F9	-0.0159(2)	0.7279(3)	0.2592(1)	0.0662(8)
C11	0.6549(3)	0.5076(4)	0.3927(1)	0.0209(8)
C12	0.6252(4)	0.3677(4)	0.4263(2)	0.0300(9)
H12	0.5634	0.3747	0.4555	0.036
C13	0.6845(4)	0.2206(4)	0.4175(2)	0.0296(8)
H13	0.6638	0.1263	0.4406	0.035
C14	0.7745(3)	0.2086(4)	0.3749(2)	0.0250(8)
C15	0.8008(4)	0.3439(4)	0.3393(2)	0.0295(9)
H15	0.8601	0.3358	0.3089	0.035
C16	0.7398(4)	0.4917(4)	0.3483(2)	0.0301(9)
H16	0.7569	0.5845	0.3232	0.036
C18	0.8404(4)	0.0495(5)	0.3660(2)	0.0379(9)
F10	0.7610(3)	-0.0514(3)	0.3244(1)	0.0687(9)
F11	0.9524(3)	0.0655(3)	0.3423(2)	0.0615(9)
F12	0.8753(3)	-0.0338(3)	0.4228(1)	0.0753(11)
F10B	0.965(3)	0.048(6)	0.402(2)	0.041(7)
F11B	0.780(4)	-0.085(4)	0.380(2)	0.033(7)
F12B	0.849(6)	0.029(6)	0.3027(10)	0.042(7)

Table 5: Hydrogen coordinates and isotropic displacement parameters (Å^2) for jx3.

Atom	x	y	z	U_{eq}
H4A	0.8135	0.5178	0.5113	0.068
H4B	0.8955	0.6586	0.5572	0.068
H4C	0.8691	0.6732	0.4776	0.068
H5A	0.7845	0.9326	0.5570	0.080
H5B	0.7379	0.8100	0.6090	0.080
H5C	0.6267	0.9116	0.5575	0.080
H12	0.5634	0.3747	0.4555	0.036
H13	0.6638	0.1263	0.4406	0.035
H15	0.8601	0.3358	0.3089	0.035
H16	0.7569	0.5845	0.3232	0.036

Table 6: Anisotropic displacement parameters (Å^2) for jx3. The anisotropic displacement factor exponent takes the form: -2 pi^2 (h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12})

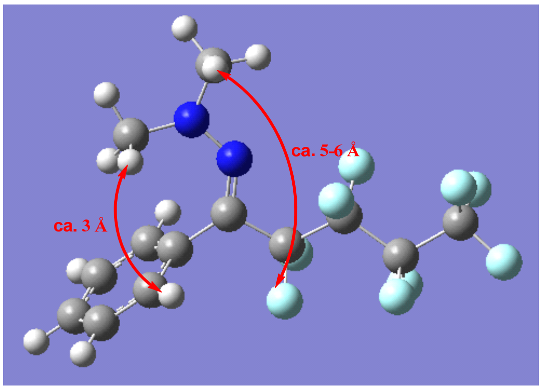
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.021(2)	0.0262(19)	0.0251(17)	0.0005(13)	0.0043(13)	-0.0027(15)
N2	0.0309(18)	0.0317(18)	0.0259(15)	-0.0033(12)	0.0046(12)	-0.0028(14)
N3	0.041(2)	0.046(2)	0.0240(15)	-0.0097(13)	-0.0044(13)	-0.0028(16)
C4	0.042(3)	0.048(3)	0.037(2)	-0.0011(17)	-0.0124(17)	0.000(2)
C5	0.067(3)	0.056(3)	0.033(2)	-0.0186(18)	-0.0010(19)	-0.009(2)
C6	0.030(2)	0.025(2)	0.0241(17)	-0.0016(13)	0.0021(13)	0.0015(16)
F1	0.0362(13)	0.0597(15)	0.0245(10)	0.0034(9)	0.0089(8)	0.0125(11)
F2	0.0367(14)	0.0252(12)	0.0529(12)	0.0056(9)	0.0024(9)	0.0005(10)
C7	0.028(2)	0.0202(19)	0.0254(17)	-0.0004(12)	0.0006(13)	0.0015(15)
F3	0.0397(14)	0.0243(12)	0.0608(13)	0.0056(9)	-0.0101(10)	-0.0002(10)
F4	0.0315(13)	0.0735(16)	0.0215(10)	0.0027(9)	0.0047(8)	-0.0036(12)
C8	0.033(2)	0.025(2)	0.0269(17)	-0.0028(13)	0.0008(14)	0.0042(16)
F5	0.0445(15)	0.0678(16)	0.0243(11)	0.0016(9)	-0.0019(9)	0.0079(12)
F6	0.0401(14)	0.0310(13)	0.0571(13)	0.0006(10)	-0.0054(10)	0.0056(11)
C9	0.035(2)	0.041(2)	0.044(2)	-0.0039(16)	-0.0009(17)	0.0004(18)
F7	0.0393(16)	0.0458(16)	0.0992(19)	-0.0145(13)	0.0045(13)	-0.0110(13)
F8	0.0342(15)	0.0863(19)	0.0576(15)	-0.0069(13)	0.0149(11)	-0.0010(14)
F9	0.0342(15)	0.086(2)	0.0661(16)	0.0091(13)	-0.0179(12)	0.0064(14)
C11	0.0151(19)	0.0264(19)	0.0189(16)	-0.0007(12)	-0.0020(13)	-0.0015(14)
C12	0.034(2)	0.033(2)	0.0241(17)	0.0018(13)	0.0096(15)	0.0015(17)
C13	0.033(2)	0.026(2)	0.0303(18)	0.0050(14)	0.0069(15)	-0.0016(17)
C14	0.0189(19)	0.0271(19)	0.0265(17)	-0.0012(13)	-0.0014(13)	0.0014(15)
C15	0.025(2)	0.036(2)	0.0290(18)	-0.0004(14)	0.0091(15)	0.0018(17)
C16	0.029(2)	0.030(2)	0.0320(18)	0.0041(14)	0.0072(15)	-0.0006(17)
C18	0.034(2)	0.035(2)	0.044(2)	0.0000(16)	0.0072(17)	0.0021(18)
F10	0.057(2)	0.0472(17)	0.099(2)	-0.0347(14)	0.0104(15)	-0.0031(14)
F11	0.0437(18)	0.0438(17)	0.107(2)	0.0054(14)	0.0384(15)	0.0112(14)
F12	0.109(3)	0.0565(18)	0.0631(17)	0.0226(13)	0.0251(16)	0.0475(18)
F10B	0.032(7)	0.029(14)	0.058(13)	-0.003(10)	0.001(7)	0.005(6)
F11B	0.023(13)	0.031(8)	0.041(15)	0.003(8)	0.000(10)	0.008(8)
F12B	0.049(17)	0.033(14)	0.046(7)	-0.003(6)	0.013(7)	0.003(11)

Table 7: Bond lengths (Å) and angles (deg) for jx3.

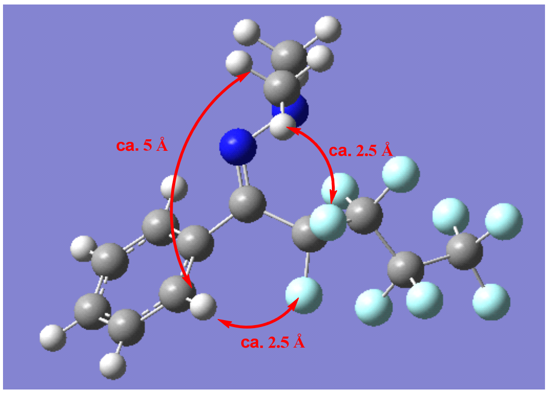
C1-N2	1.291(4)
C1-C11	1.479(4)
C1-C6	1.525(4)
N2-N3	1.341(4)
N3-C4	1.450(5)
N3-C5	1.464(4)
C4-H4A	0.9800
C4-H4B	0.9800
C4-H4C	0.9800
C5-H5A	0.9800
C5-H5B	0.9800
C5-H5C	0.9800
C6-F2	1.347(4)
C6-F1	1.363(4)
C6-C7	1.532(5)
C7-F3	1.342(4)
C7-F4	1.355(4)
C7-C8	1.547(5)
C8-F6	1.330(4)
C8-F5	1.345(4)
C8-C9	1.516(5)
C9-F7	1.322(4)
C9-F9	1.325(4)
C9-F8	1.326(4)
C11-C16	1.377(4)
C11-C12	1.397(4)
C12-C13	1.370(5)
C12-H12	0.9500
C13-C14	1.385(5)
C13-H13	0.9500
C14-C15	1.378(4)
C14-C18	1.487(5)
C15-C16	1.383(5)
C15-H15	0.9500
C16-H16	0.9500
C18-F11B	1.319(15)
C18-F10B	1.322(15)
C18-F11	1.324(4)
C18-F10	1.326(4)
C18-F12B	1.326(15)
C18-F12	1.328(4)
N2-C1-C11	130.8(3)
N2-C1-C6	111.0(3)
C11-C1-C6	117.8(3)
C1-N2-N3	124.0(3)
N2-N3-C4	123.5(3)
N2-N3-C5	111.5(3)
C4-N3-C5	115.0(3)
N3-C4-H4A	109.5
N3-C4-H4B	109.5
H4A-C4-H4B	109.5
N3-C4-H4C	109.5
H4A-C4-H4C	109.5
H4B-C4-H4C	109.5
N3-C5-H5A	109.5
N3-C5-H5B	109.5
H5A-C5-H5B	109.5
N3-C5-H5C	109.5
H5A-C5-H5C	109.5
H5B-C5-H5C	109.5
F2-C6-F1	106.8(3)
F2-C6-C1	112.1(3)
F1-C6-C1	109.5(3)
F2-C6-C7	107.3(3)
F1-C6-C7	106.9(2)
C1-C6-C7	113.8(3)
F3-C7-F4	107.6(3)
F3-C7-C6	108.4(3)
F4-C7-C6	108.1(2)
F3-C7-C8	108.2(3)
F4-C7-C8	106.1(3)
C6-C7-C8	118.0(3)
F6-C8-F5	108.3(3)
F6-C8-C9	107.2(3)
F5-C8-C9	107.0(3)
F6-C8-C7	109.5(3)
F5-C8-C7	109.0(3)
C9-C8-C7	115.6(3)
F7-C9-F9	107.6(3)
F7-C9-F8	107.8(3)
F9-C9-F8	106.8(3)
F7-C9-C8	112.3(3)
F9-C9-C8	110.0(3)
F8-C9-C8	112.1(3)
C16-C11-C12	118.3(3)
C16-C11-C1	122.5(3)
C12-C11-C1	119.3(3)
C13-C12-C11	120.5(3)
C13-C12-H12	119.7
C11-C12-H12	119.7
C12-C13-C14	120.3(3)
C12-C13-H13	119.8
C14-C13-H13	119.8
C15-C14-C13	119.9(3)
C15-C14-C18	119.8(3)
C13-C14-C18	120.3(3)
C14-C15-C16	119.3(3)
C14-C15-H15	120.3
C16-C15-H15	120.3
C11-C16-C15	121.5(3)
C11-C16-H16	119.2
C15-C16-H16	119.2
F11B-C18-F10B	108(2)
F11-C18-F10	105.7(3)
F11B-C18-F12B	103(2)
F10B-C18-F12B	108(2)
F11-C18-F12	106.3(3)
F10-C18-F12	105.0(3)
F11B-C18-C14	118(2)
F10B-C18-C14	110(2)
F11-C18-C14	113.2(3)
F10-C18-C14	113.4(3)
F12B-C18-C14	110(2)
F12-C18-C14	112.6(3)

DFT energy calculation for the optimized conformation

The optimized structures at DFT/B3LYP/6-31+G(d) level.



(*E*)-**3aa**



(*Z*)-**3aa**

Selective distances between selected atoms under the optimized structures. The distance between the NCH_3 and Ar-*H* of (*E*)-**3aa** is about 3 Å, so the strong H-H NOE effect were found in the ROESY spectra. In contrast, the distance between NCH_3 and CF_2, Ar-*H* and CF_2 in (*Z*)-**3aa** are almost the same, should produce the strong H-F NOE effect. In general, the (*E*)-**3aa** should have no or very weak H-F NOE effect and (*Z*)-**3aa** should have no or very weak H-H NOE effect. As the above NMR study and DFT optimized structures calculations, the configuration of product **3aa** and its similar compounds should be in *E* style.

Table 8. The relative energies of the cis vs trans conformations calculated at DFT/B3LYP/6-31+G(d) level.

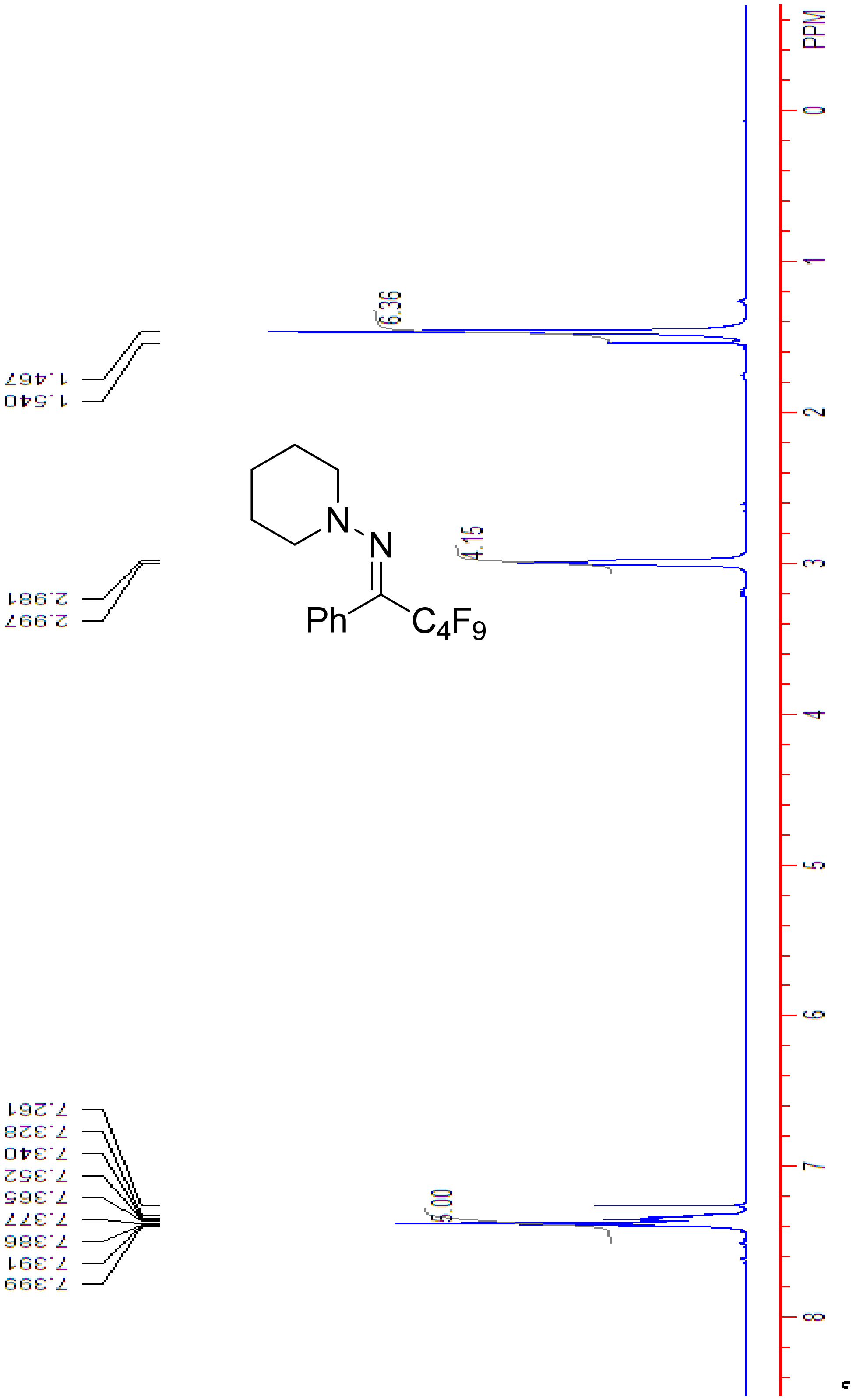
substrate/kcal/mol	**3aa**	**3ca**
ΔE_0 (E_Z-E_E)	8.29	8.59

References:

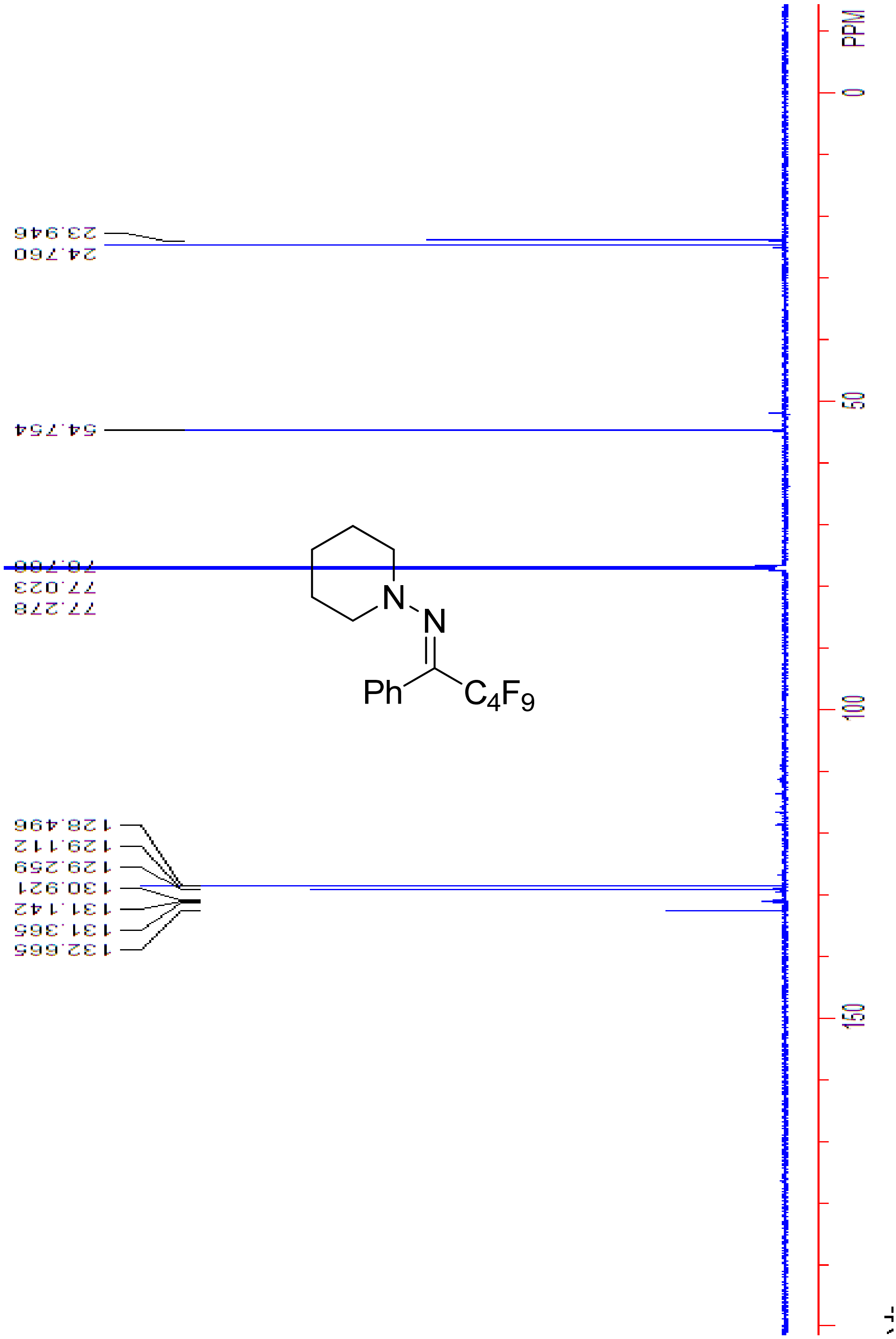
[1]. a) A.V. Dubrovskiy, R. C. Larock, *J. Org. Chem.* **2012**, *77*, 11232; b) E. Pair, N. Monteriro, D. Bouyssi, O. Baudoin, *Angew. Chem. Int. Ed.* **2013**, 52, *5346*; c) A. Ros, B. Estepa, R. L. Rodriguez, E. Alvarez, R. Fernandez, J. Lassaletta, *Angew. Chem. Int. Ed.* **2011**, *50*, 11724; d) J. Xie, T. Zhang, F. Chen, N. Mehrkens, F. Rominger, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* 2016, 55, 2934.
[2]. Y. Itoh, K. Mikami, *Org. Lett.* **2005**, *7*, 4883-4885.
[3]. S. Murov, L., *Handbook of Photochemistry*, Marcel Dekker, New York, **1973**.

Copies of NMR spectra

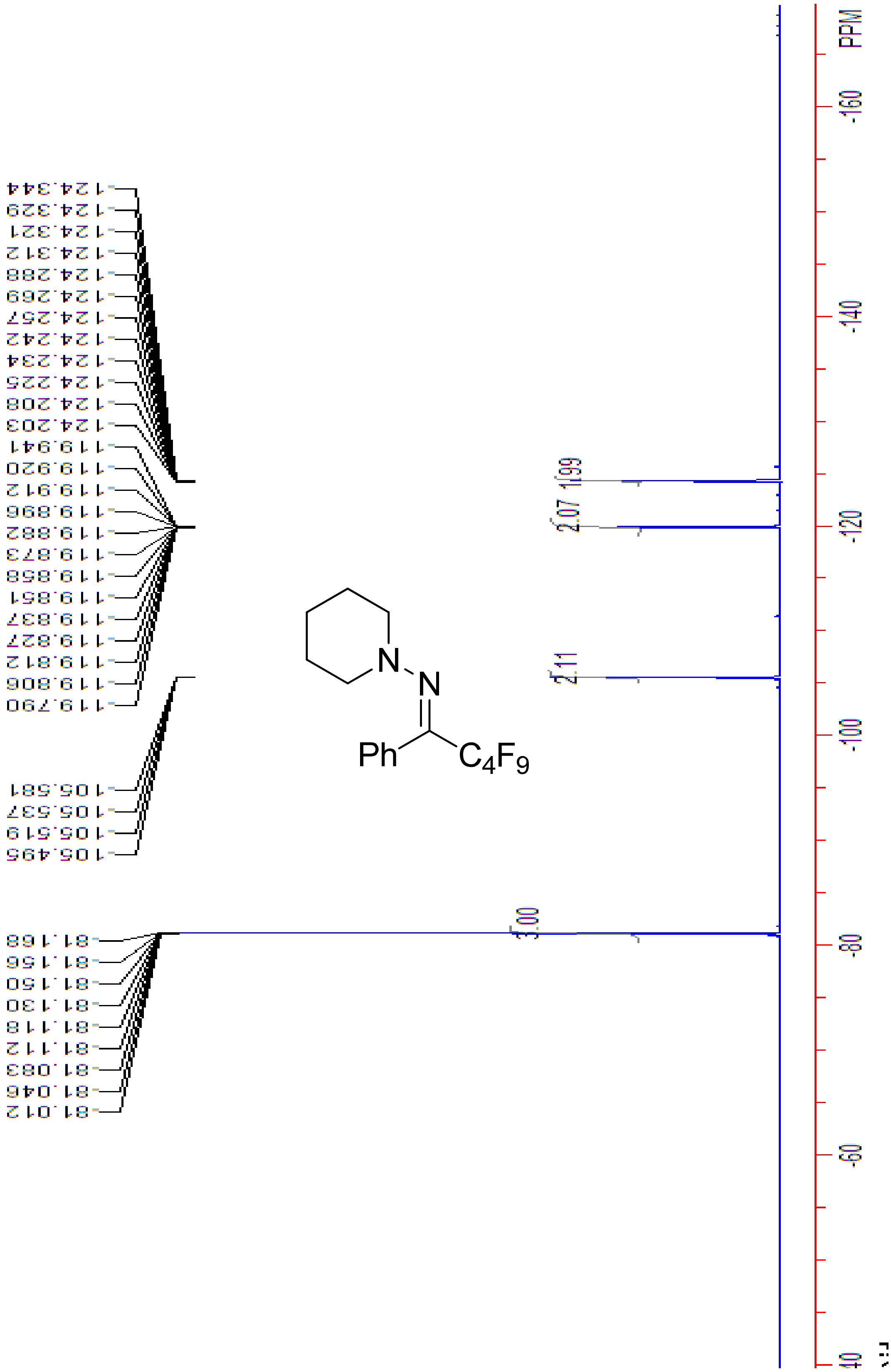
^{1}H NMR spectrum of **3ab**



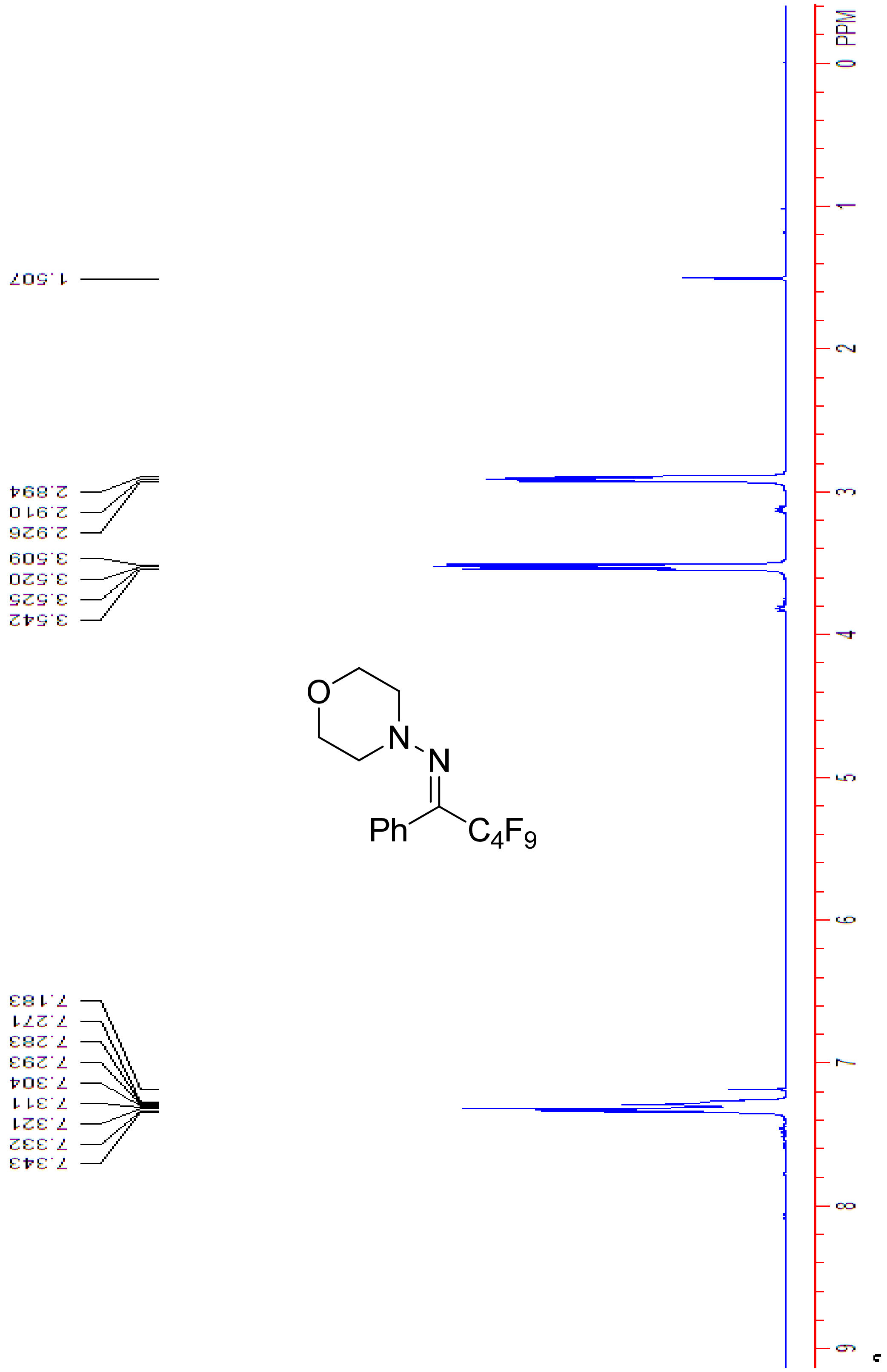
^{13}C NMR spectrum of **3ab**



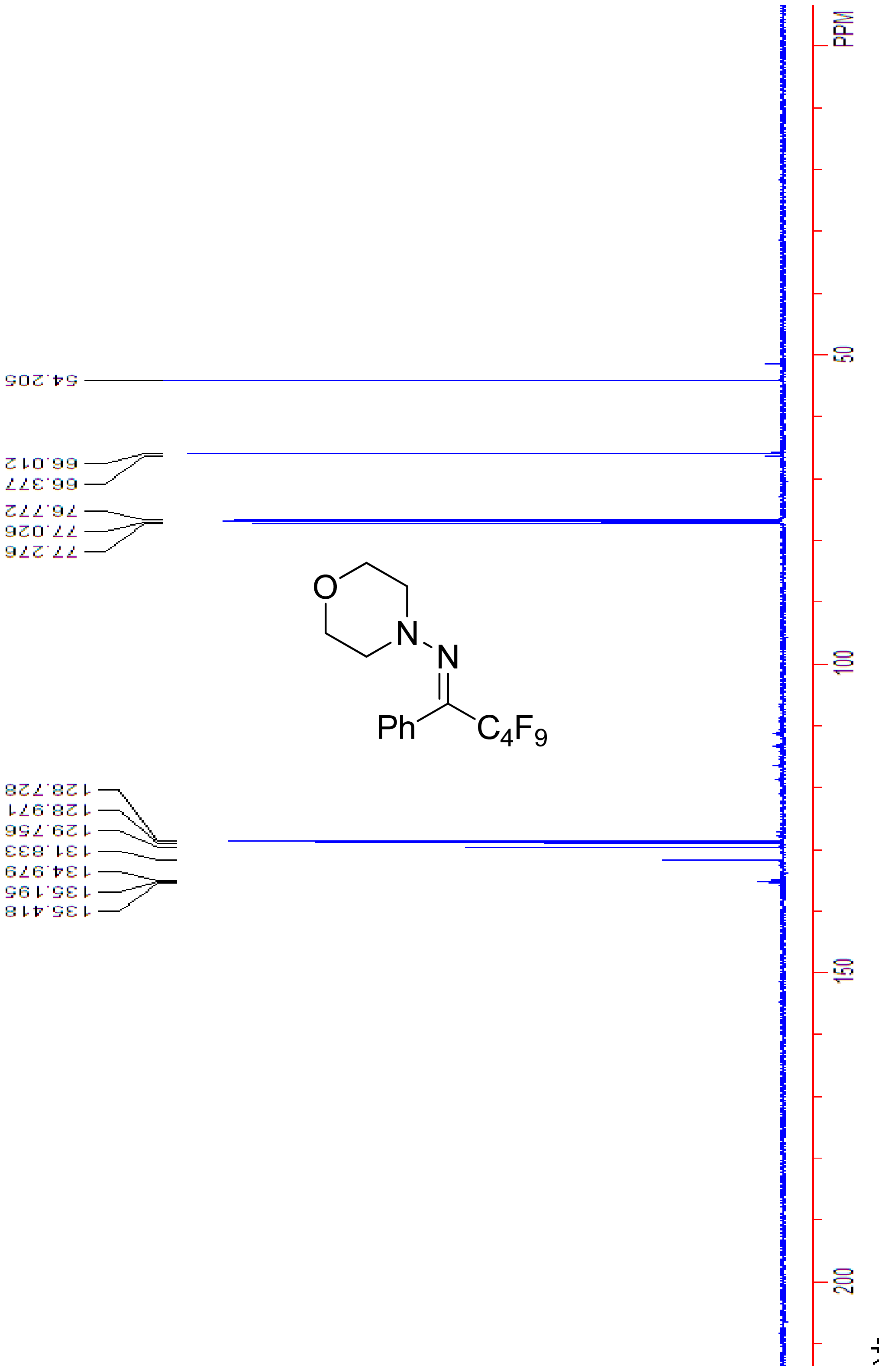
^{19}F NMR spectrum of **3ab**



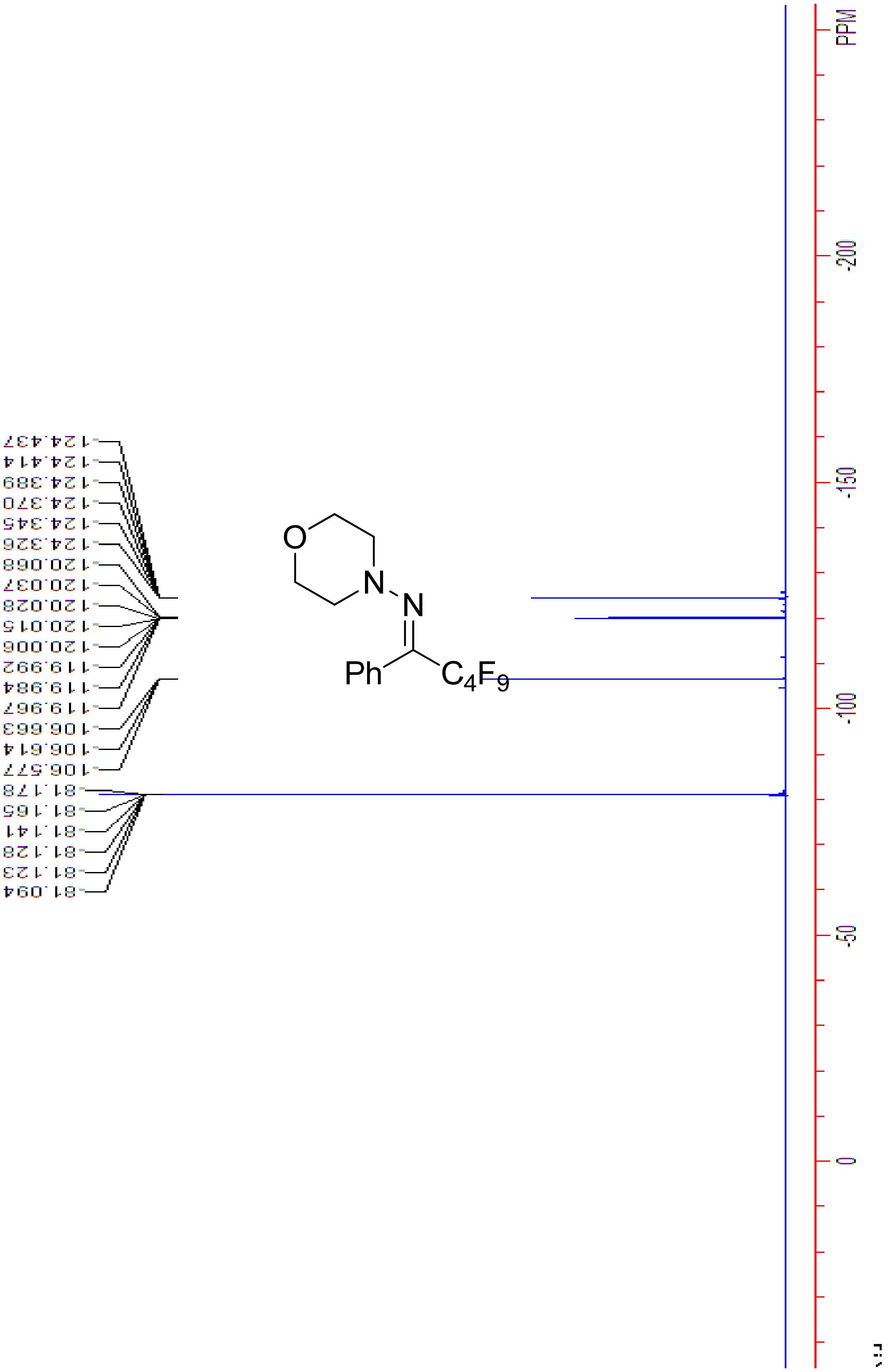
^{1}H NMR spectrum of **3ac**



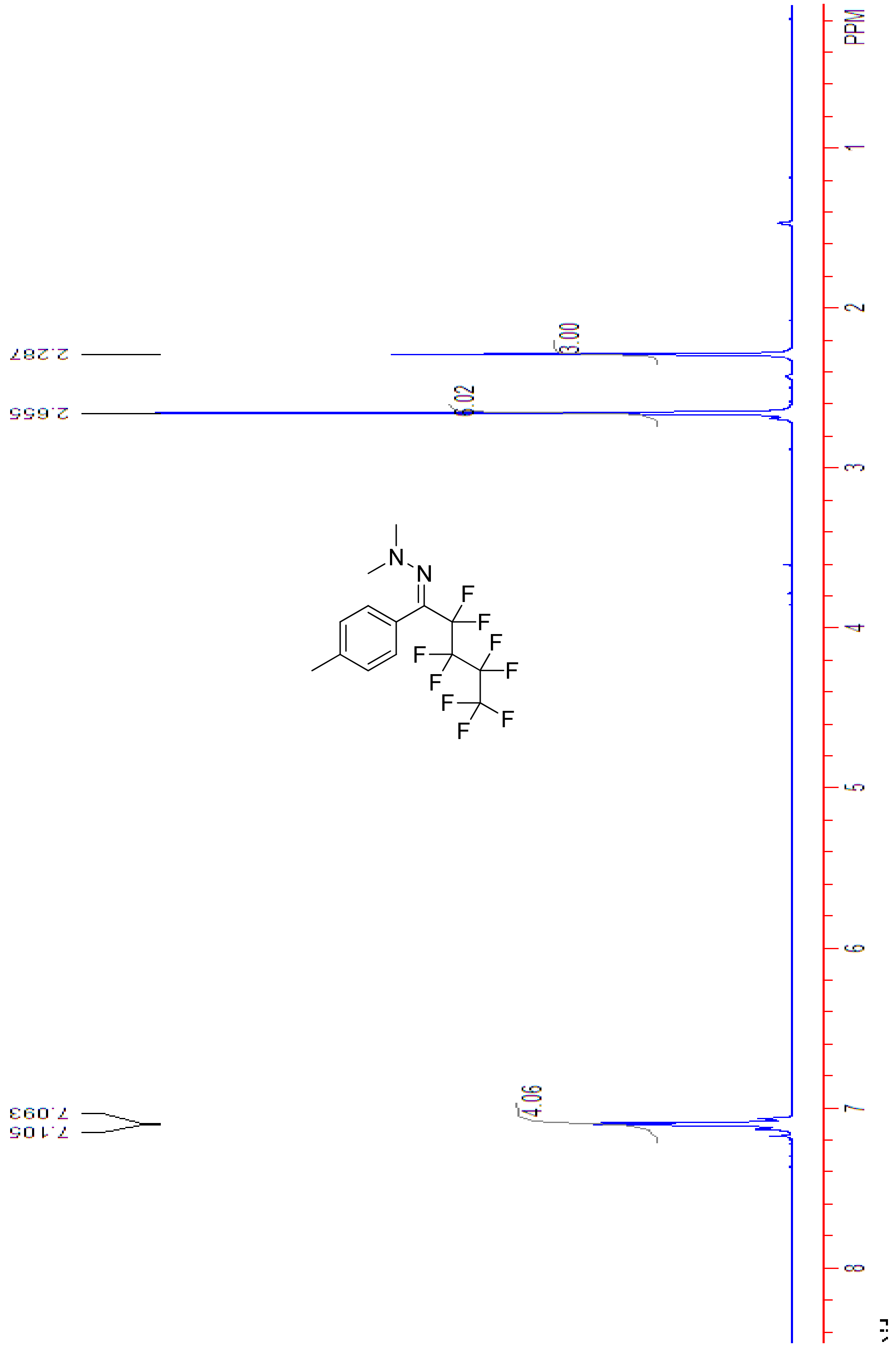
^{13}C NMR spectrum of **3ac**



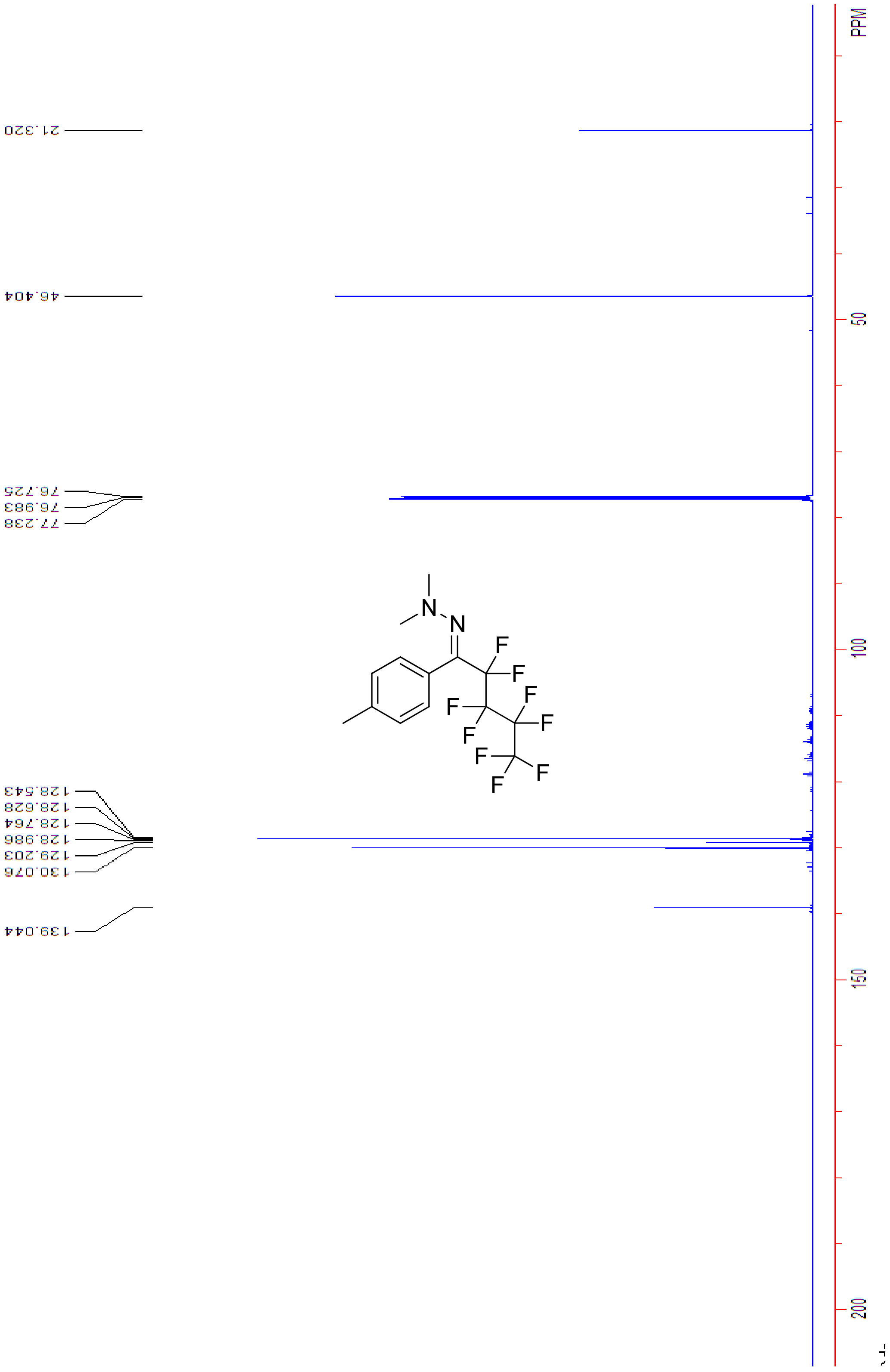
^{19}F NMR spectrum of **3ac**



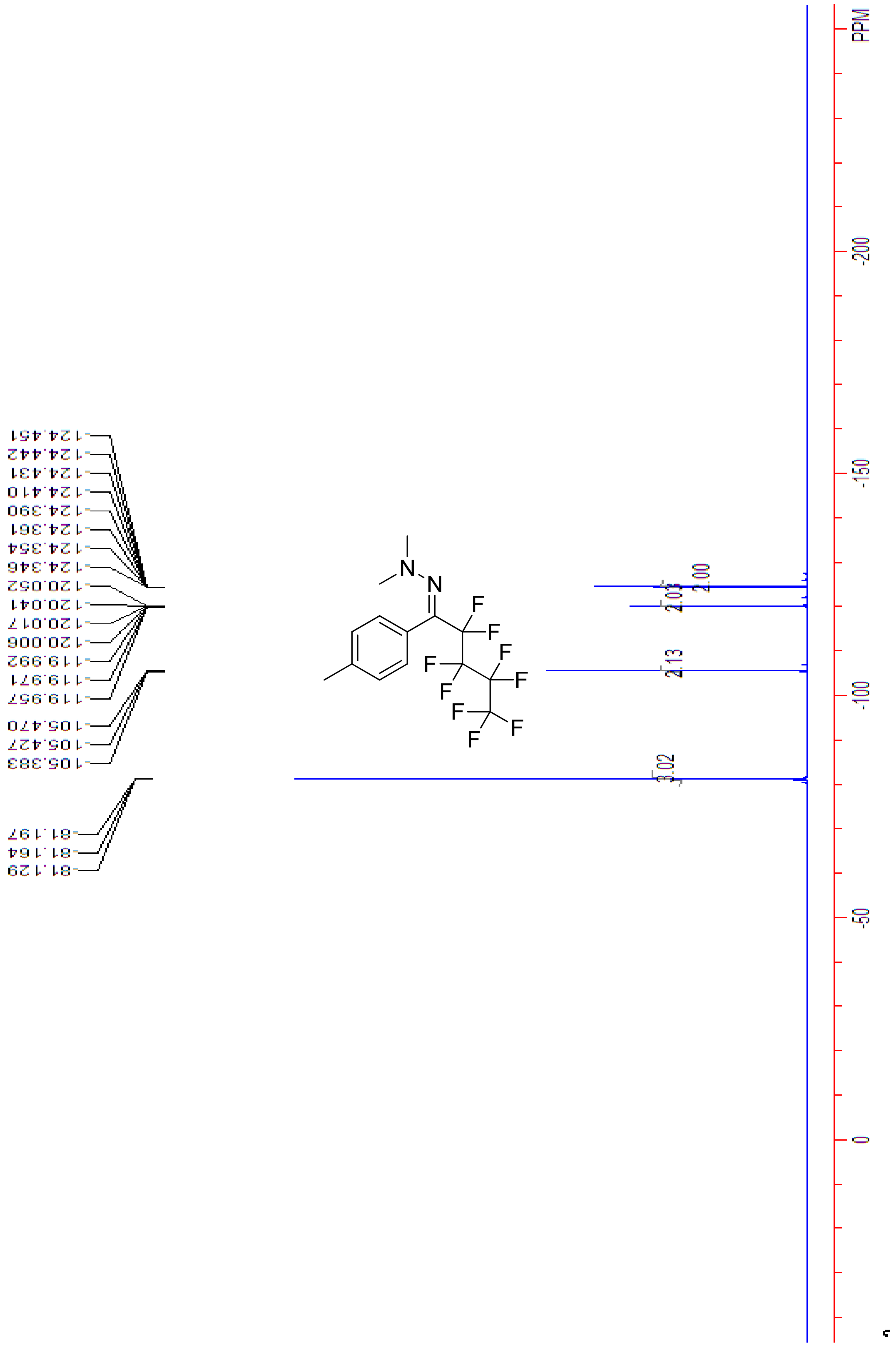
^{1}H NMR spectrum of **3ad**



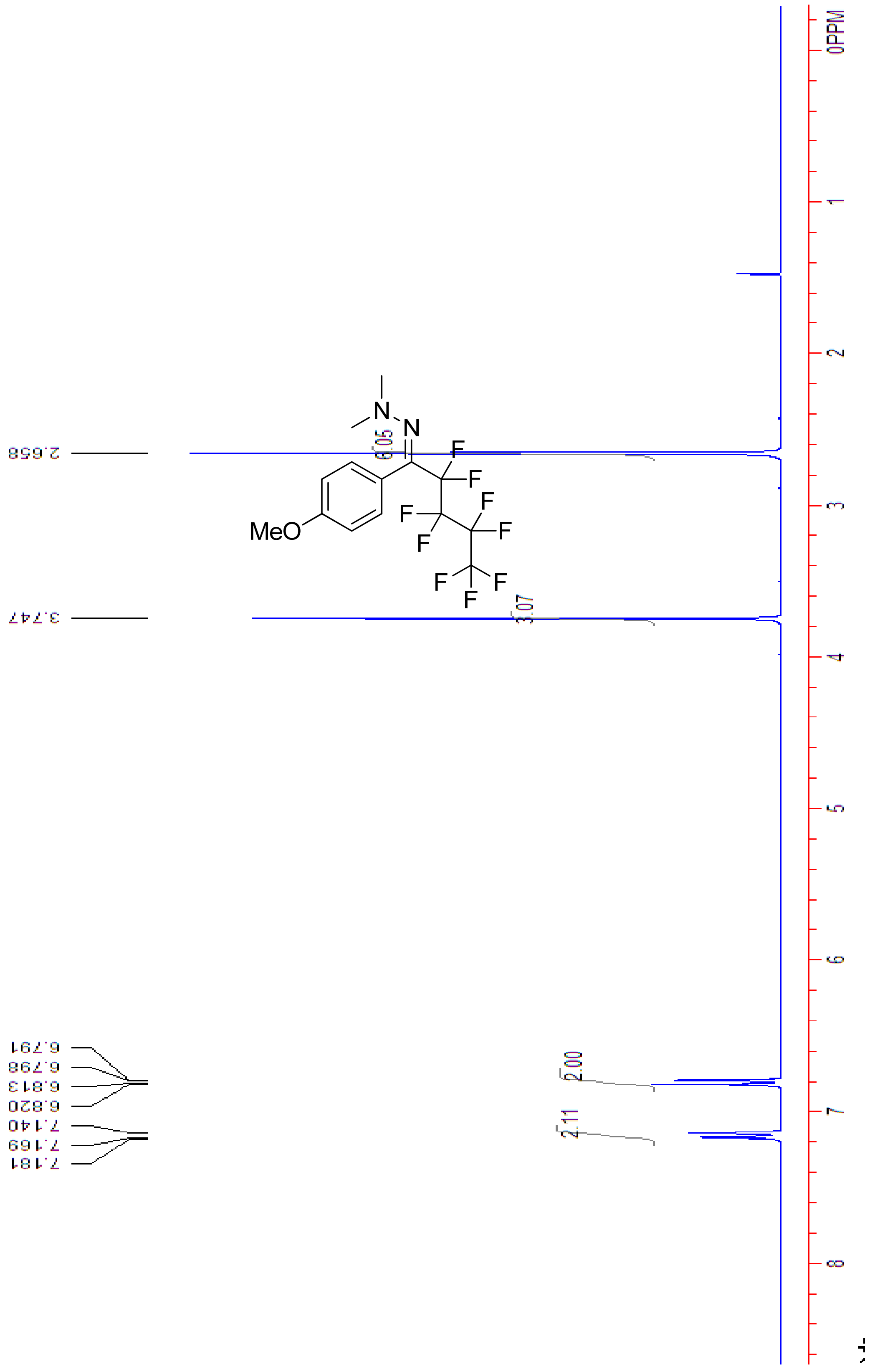
^{13}C NMR spectrum of **3ad**



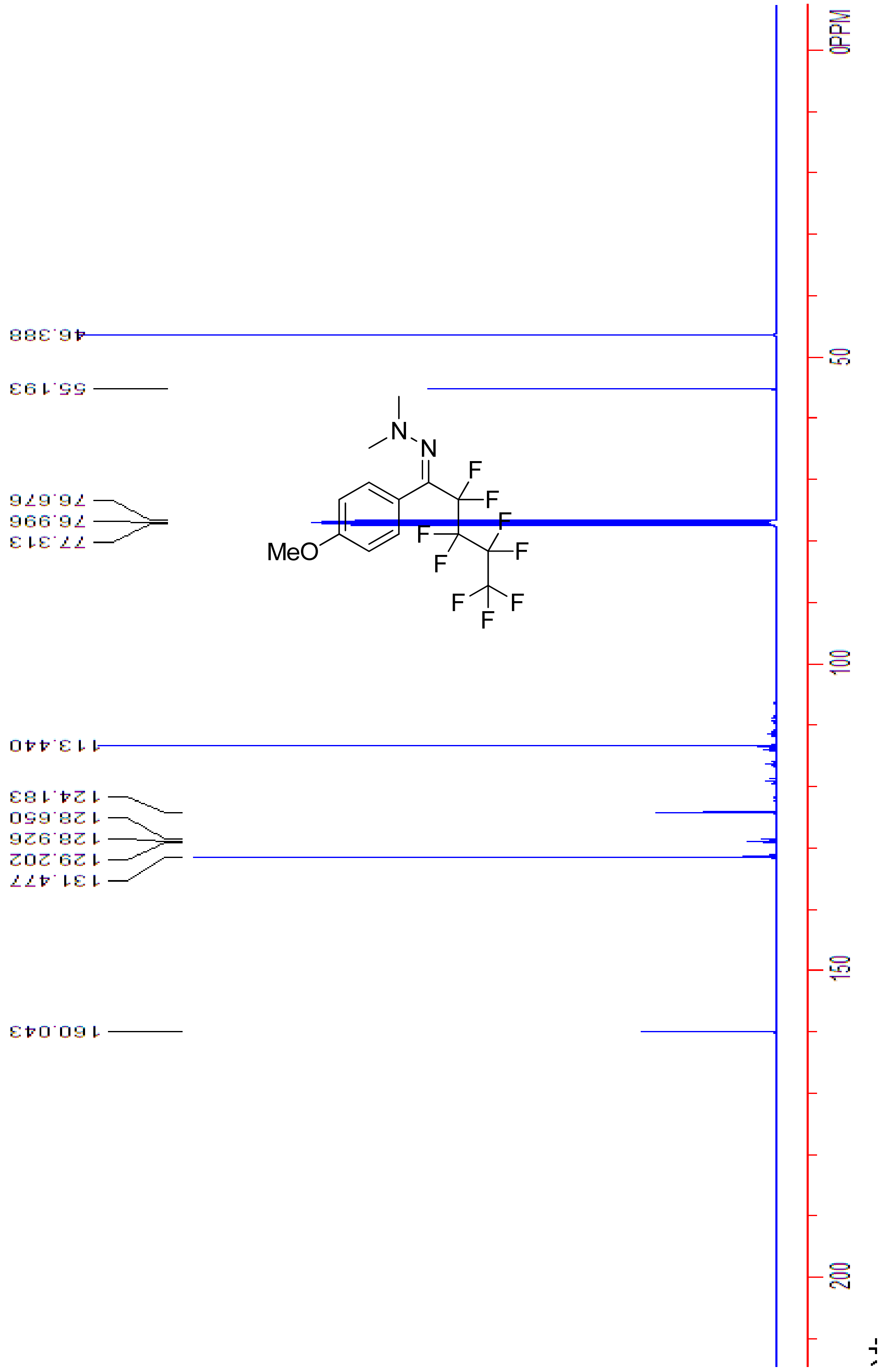
^{19}F NMR spectrum of **3ad**



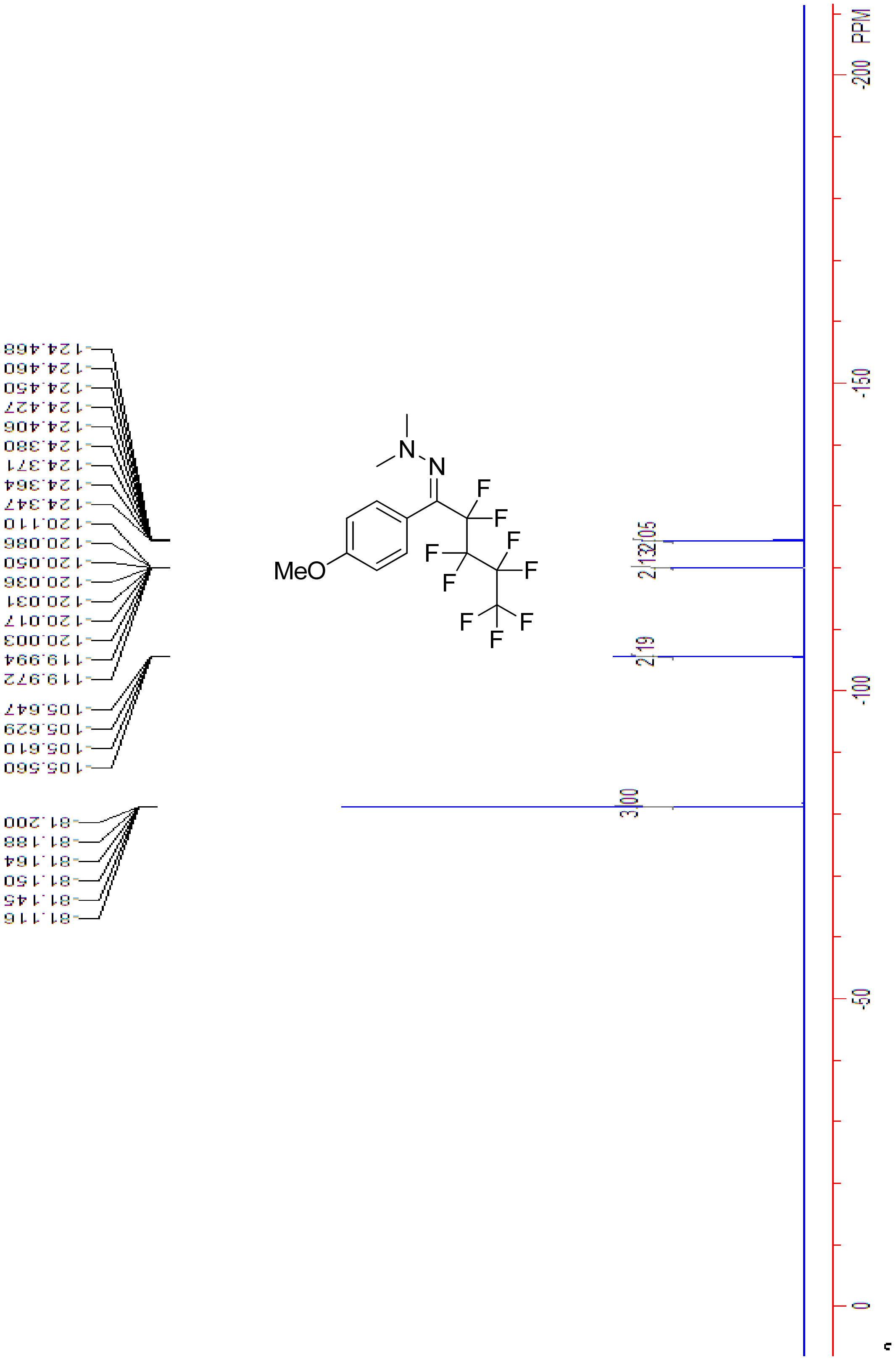
^{1}H NMR spectrum of **3ae**



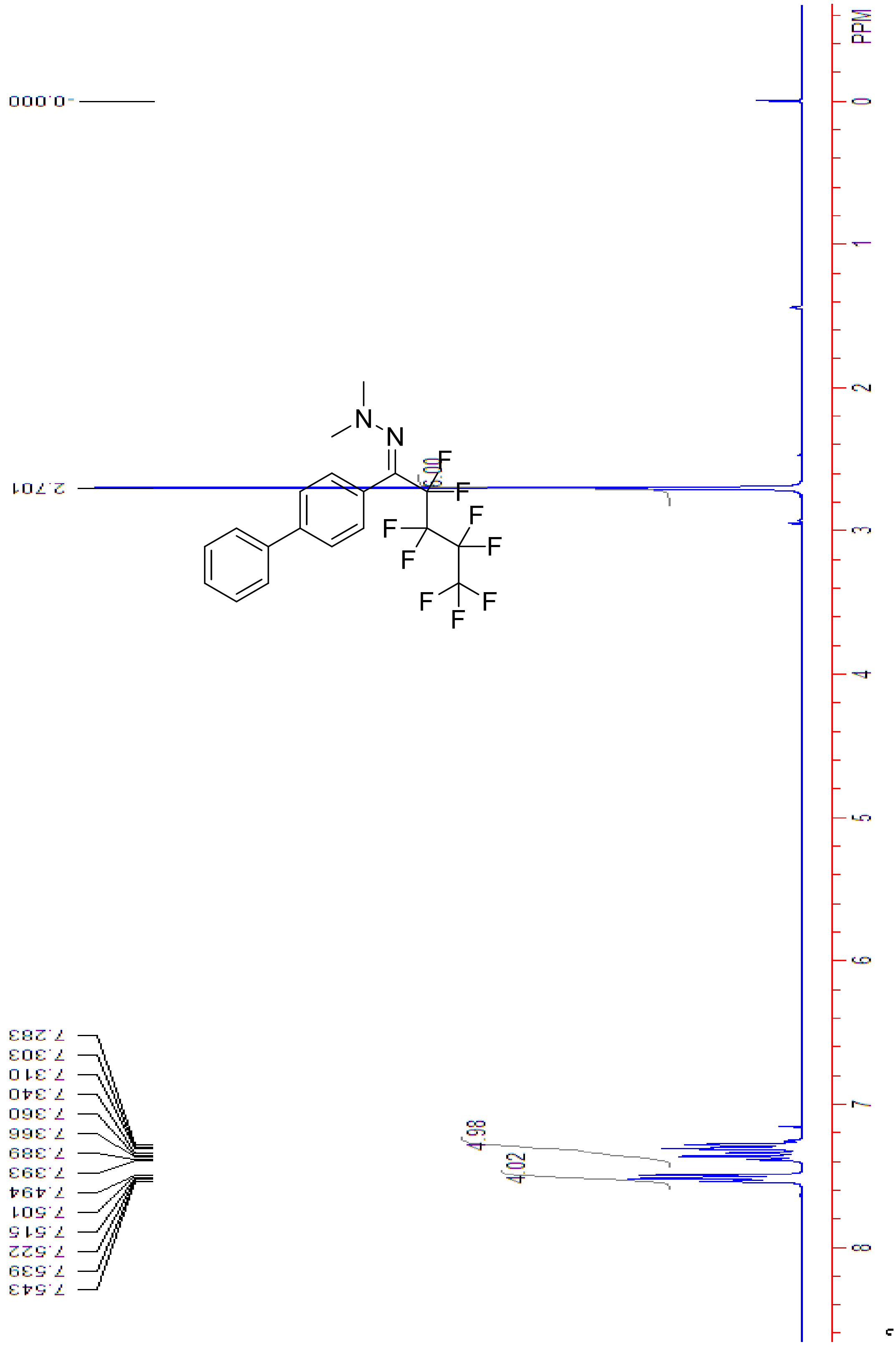
^{13}C NMR spectrum of **3ae**



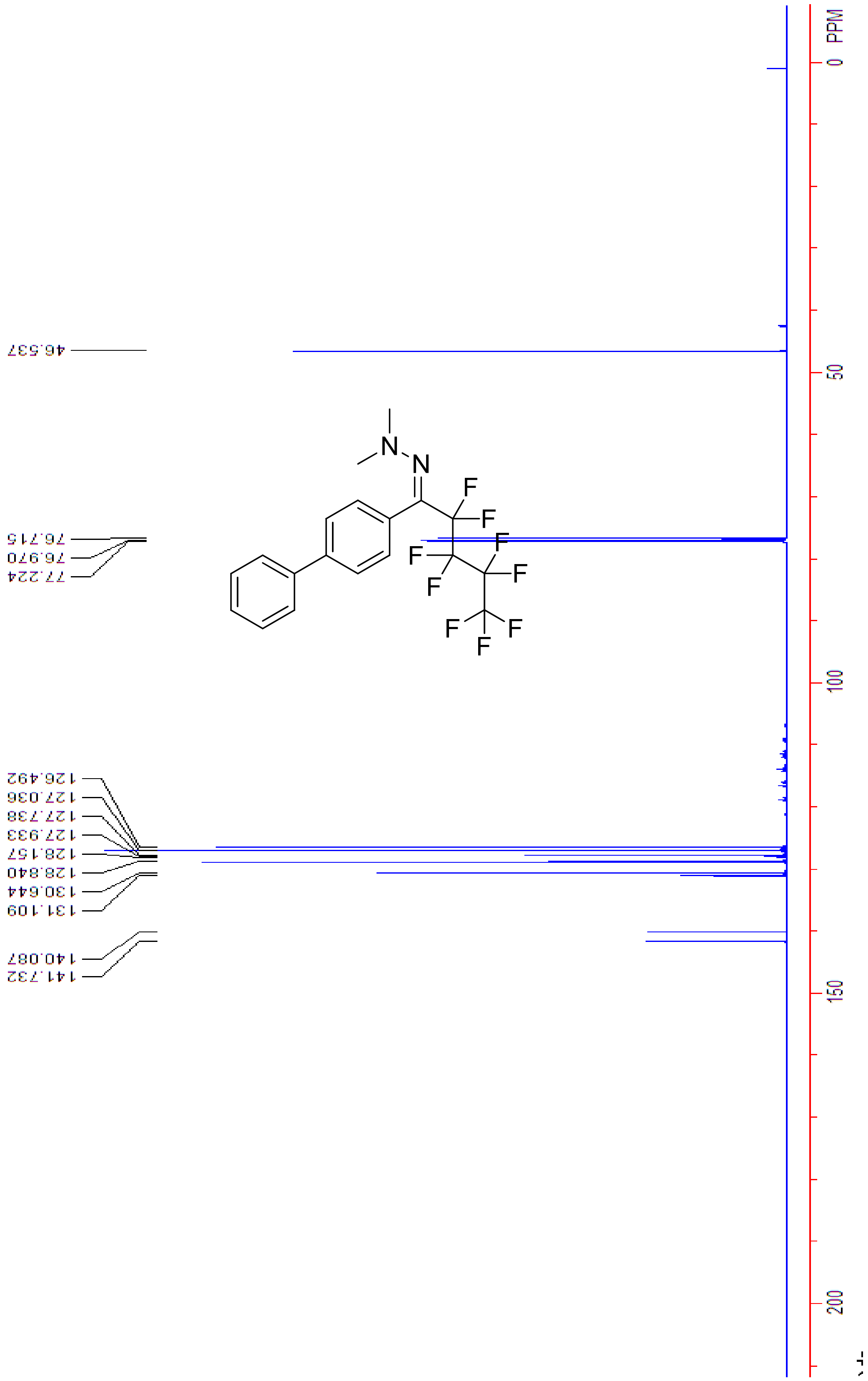
^{19}F NMR spectrum of **3ae**



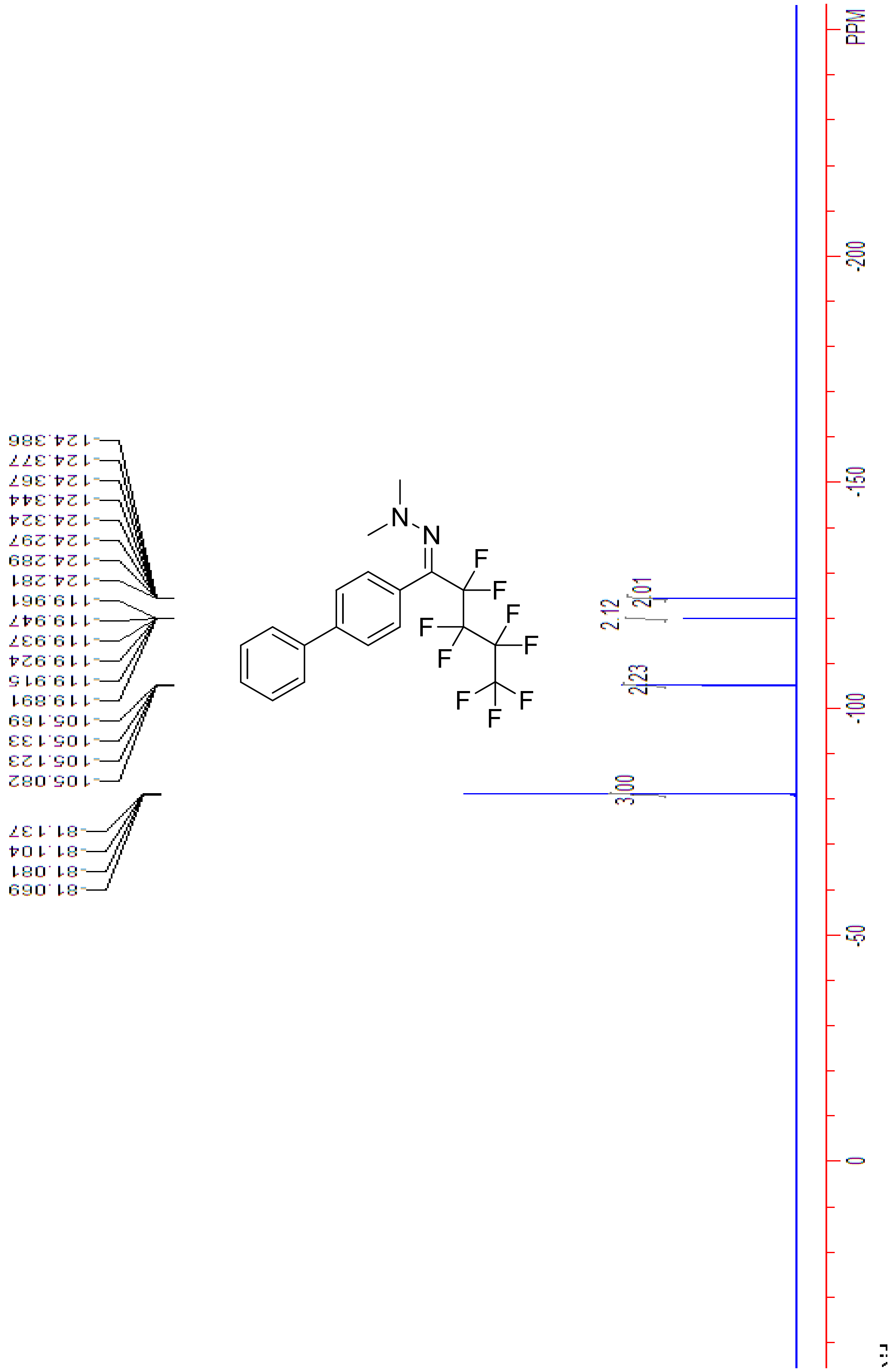
^{1}H NMR spectrum of **3af**



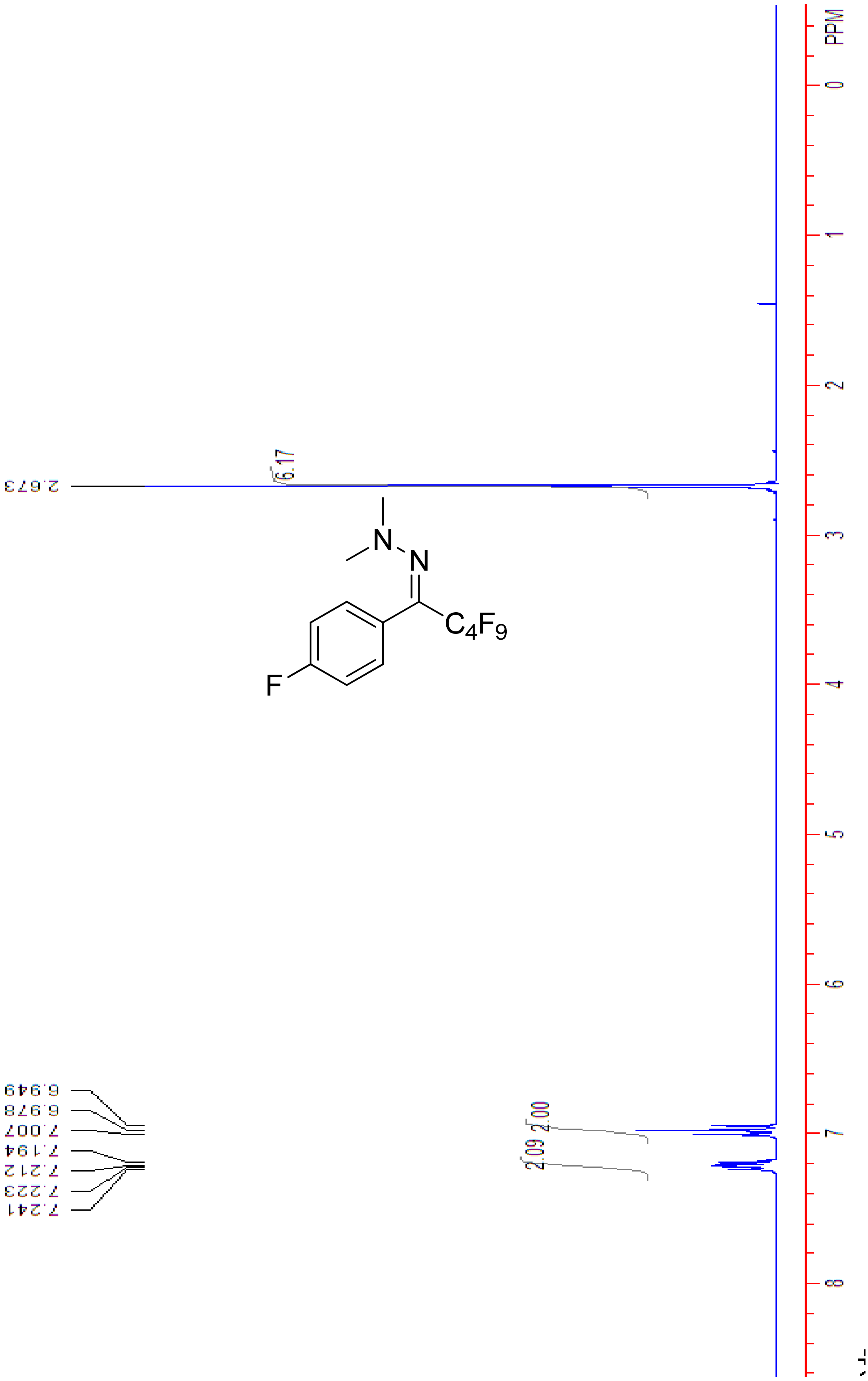
^{13}C NMR spectrum of **3af**



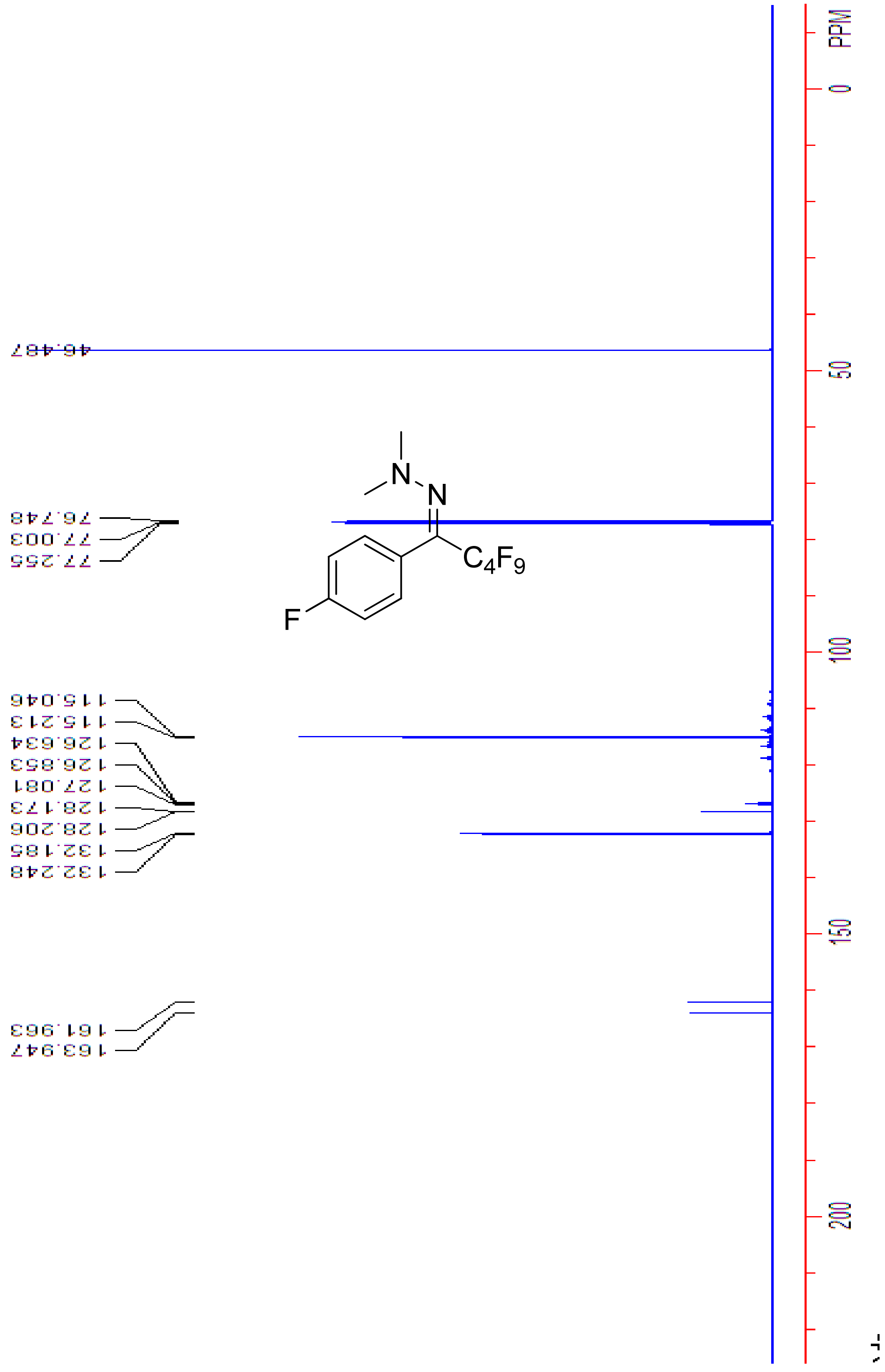
^{19}F NMR spectrum of **3af**



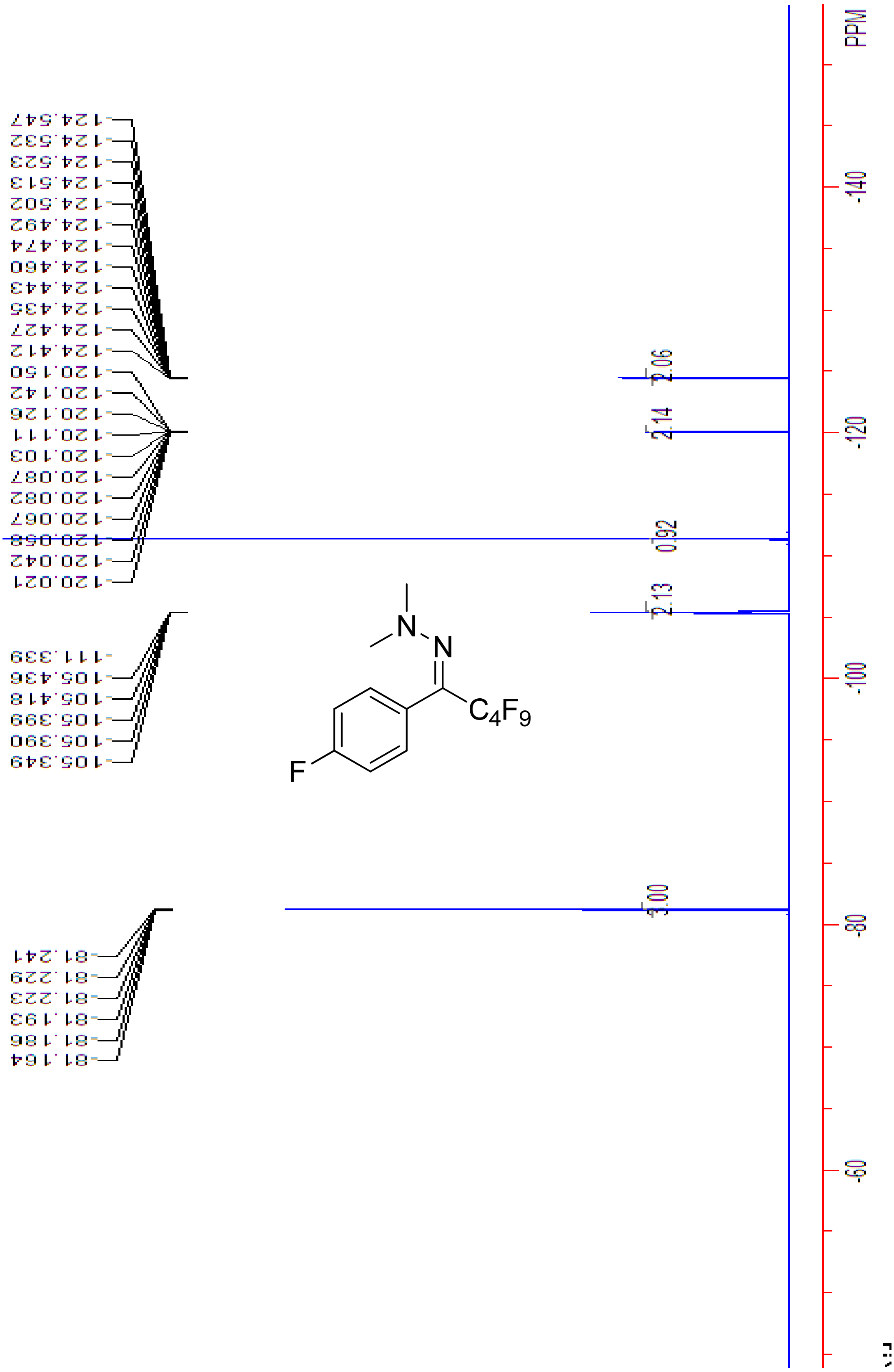
^{1}H NMR spectrum of **3ag**



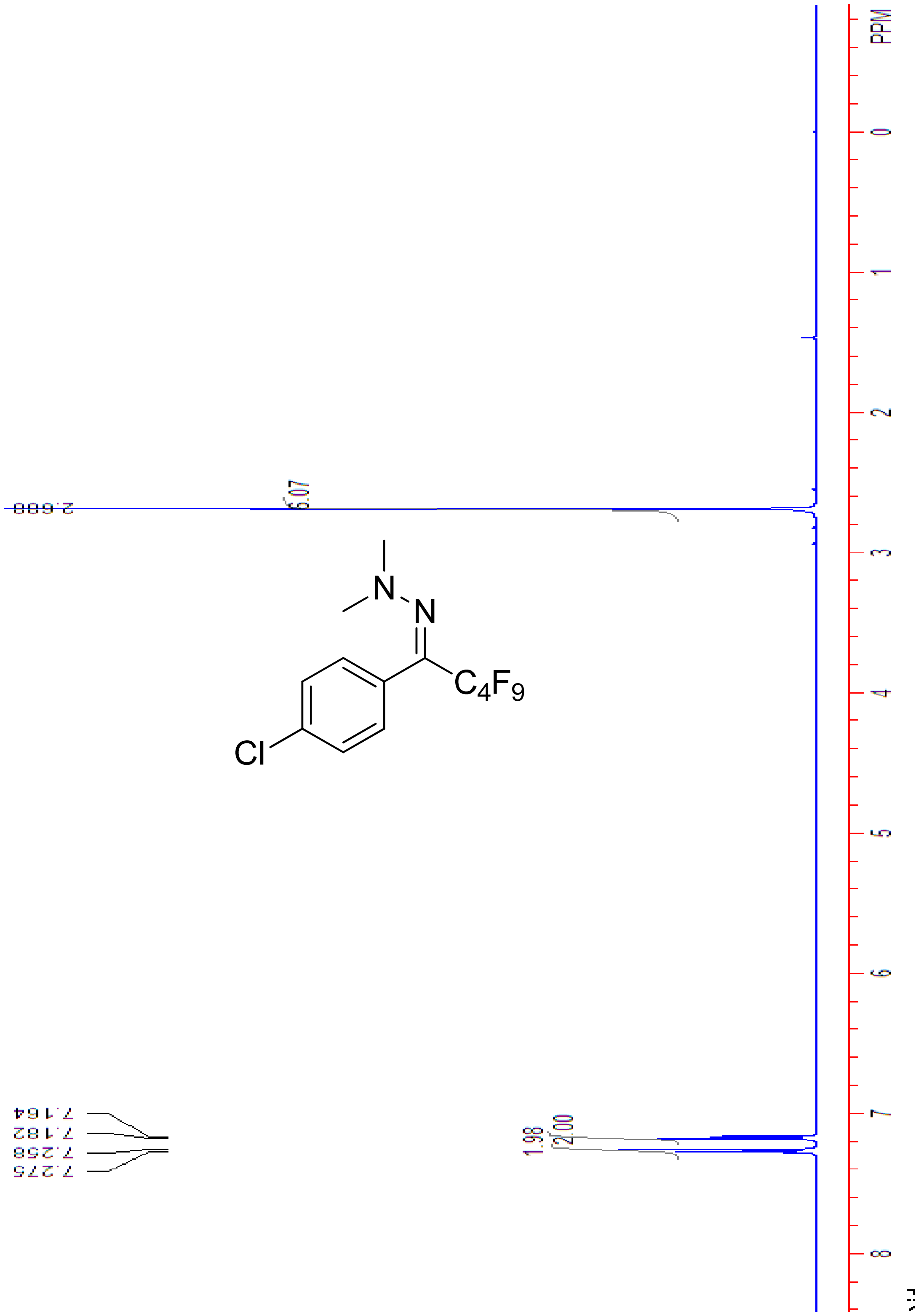
^{13}C NMR spectrum of **3ag**



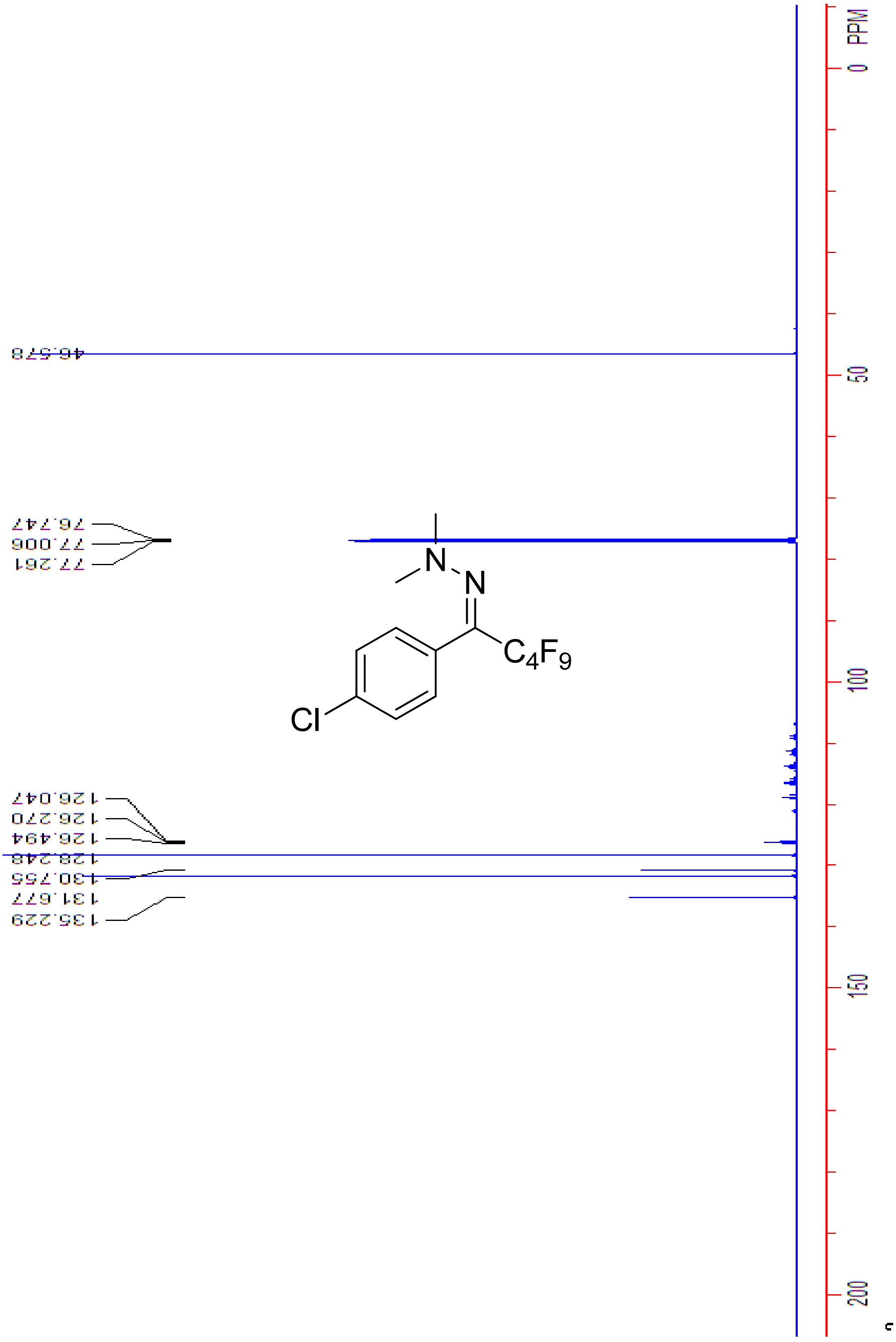
^{19}F NMR spectrum of **3ag**



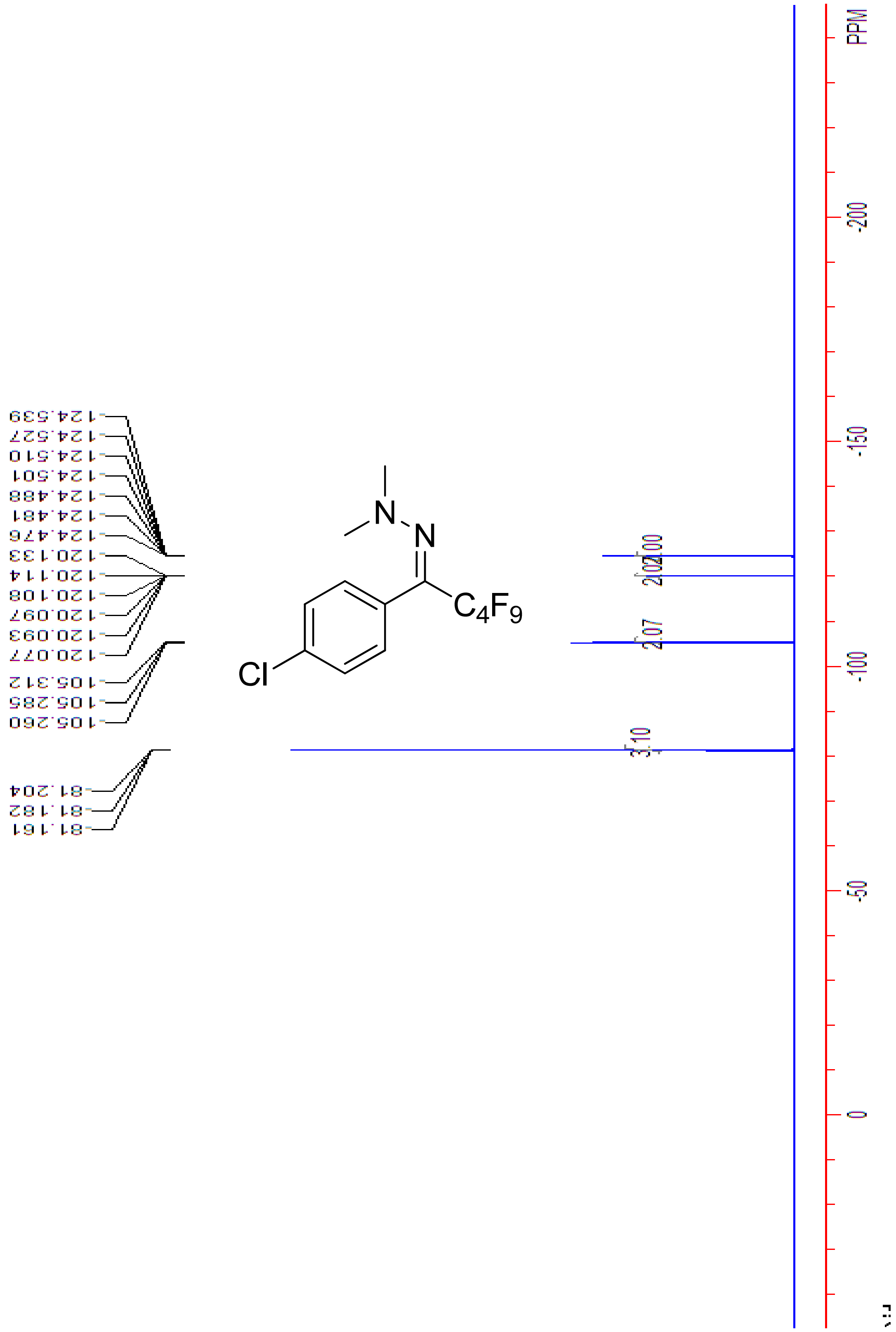
^{1}H NMR spectrum of **3ah**



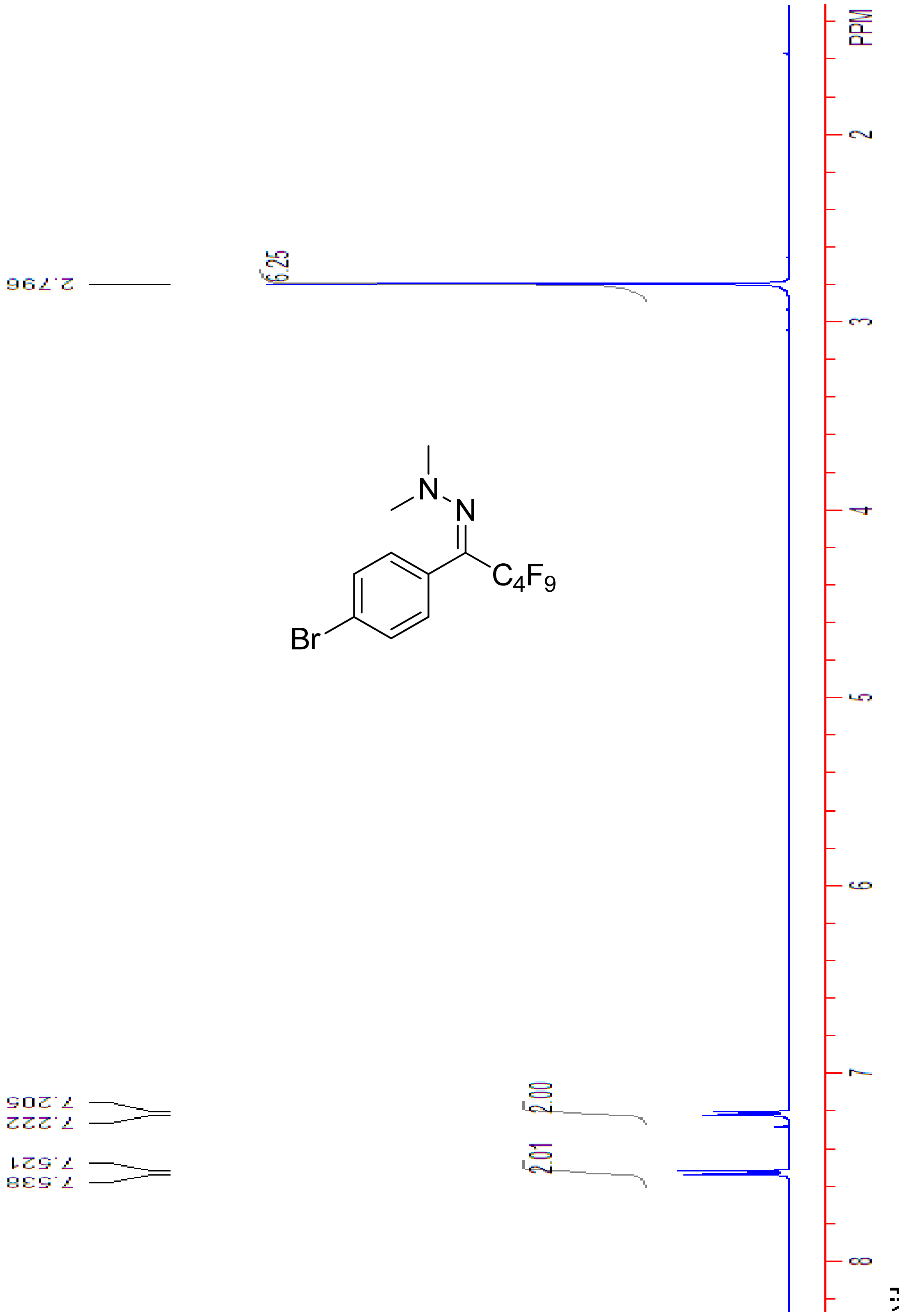
^{13}C NMR spectrum of **3ah**



^{19}F NMR spectrum of **3ah**



^{1}H NMR spectrum of **3ai**



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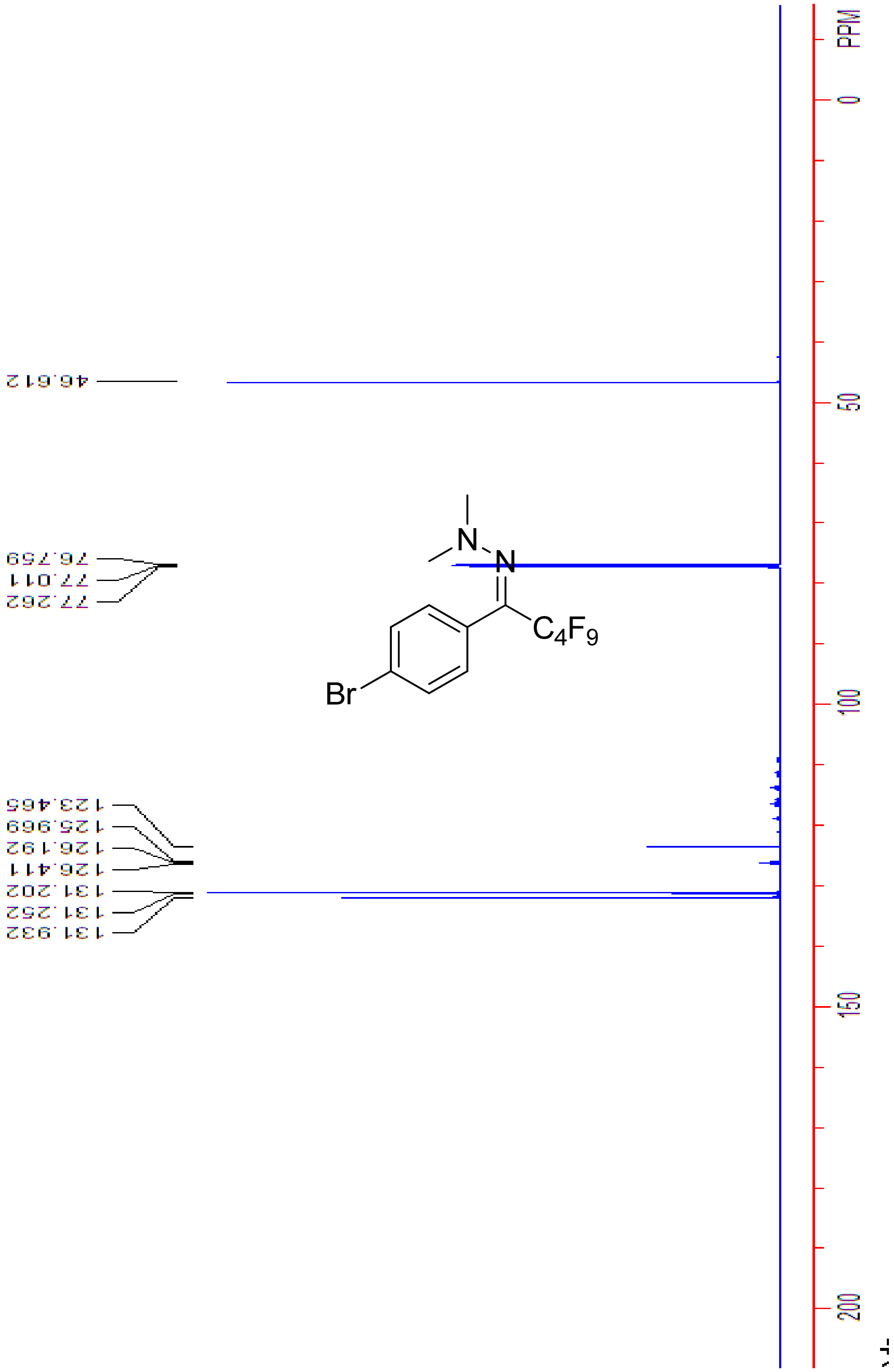

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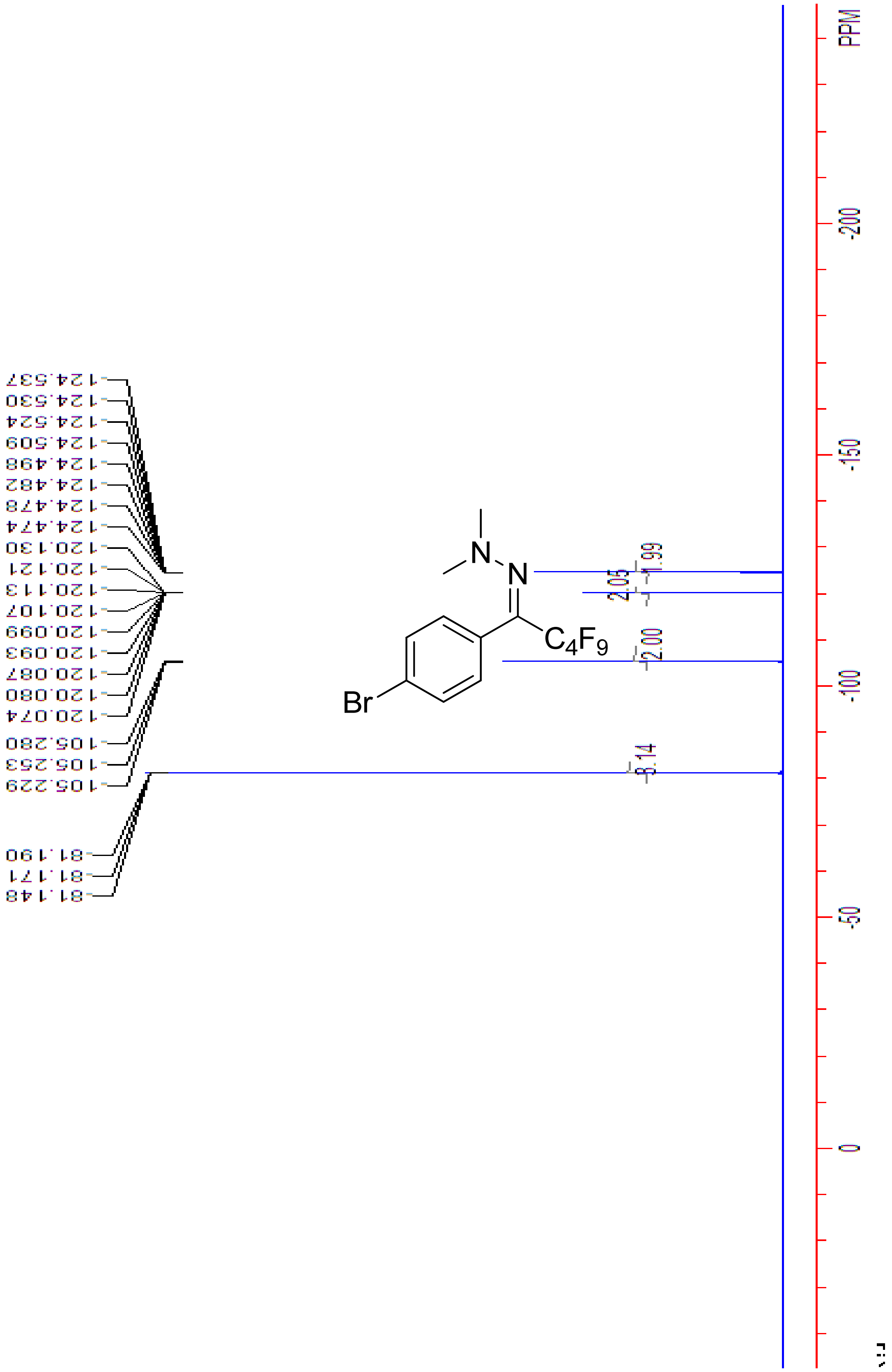

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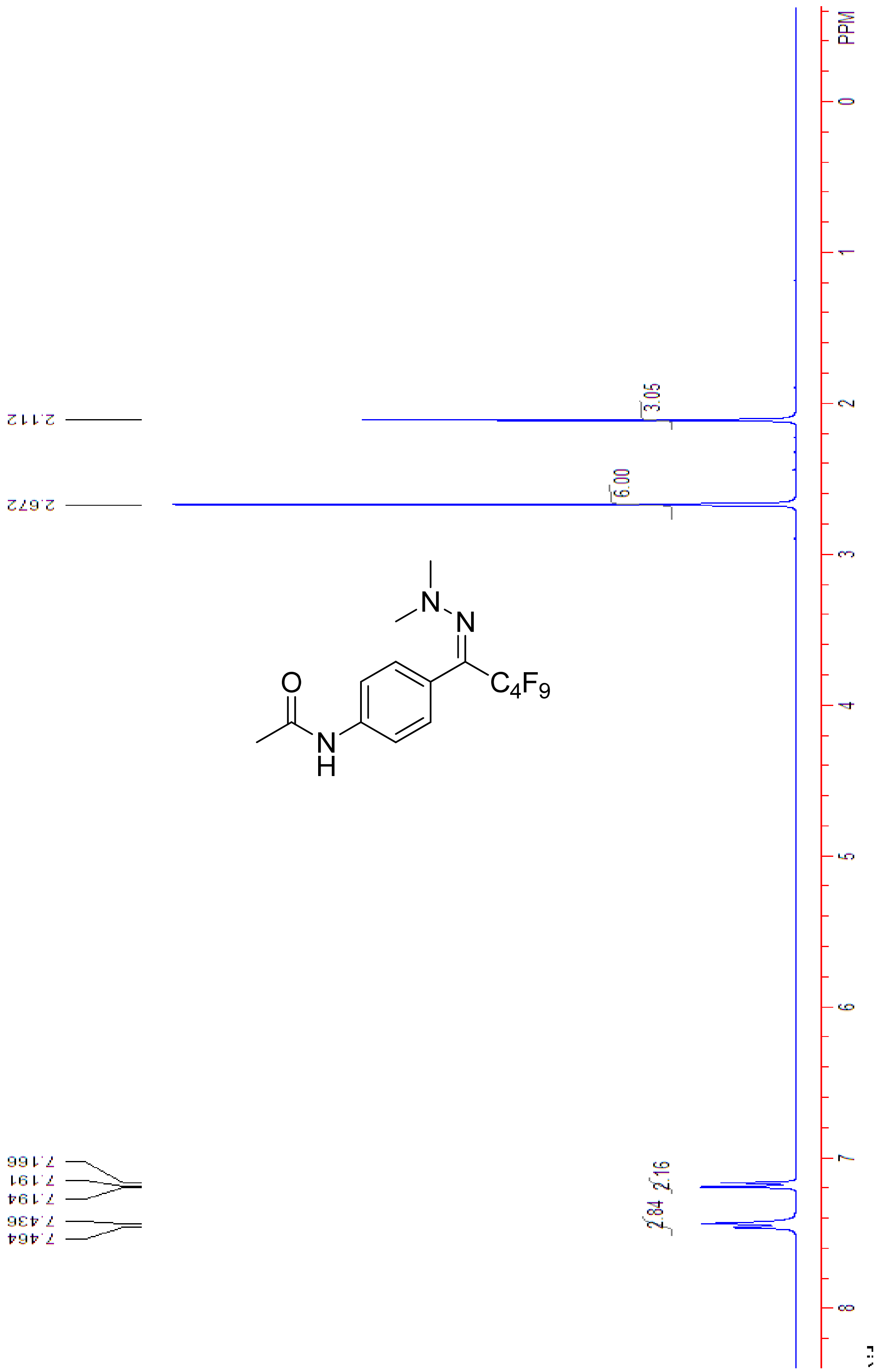

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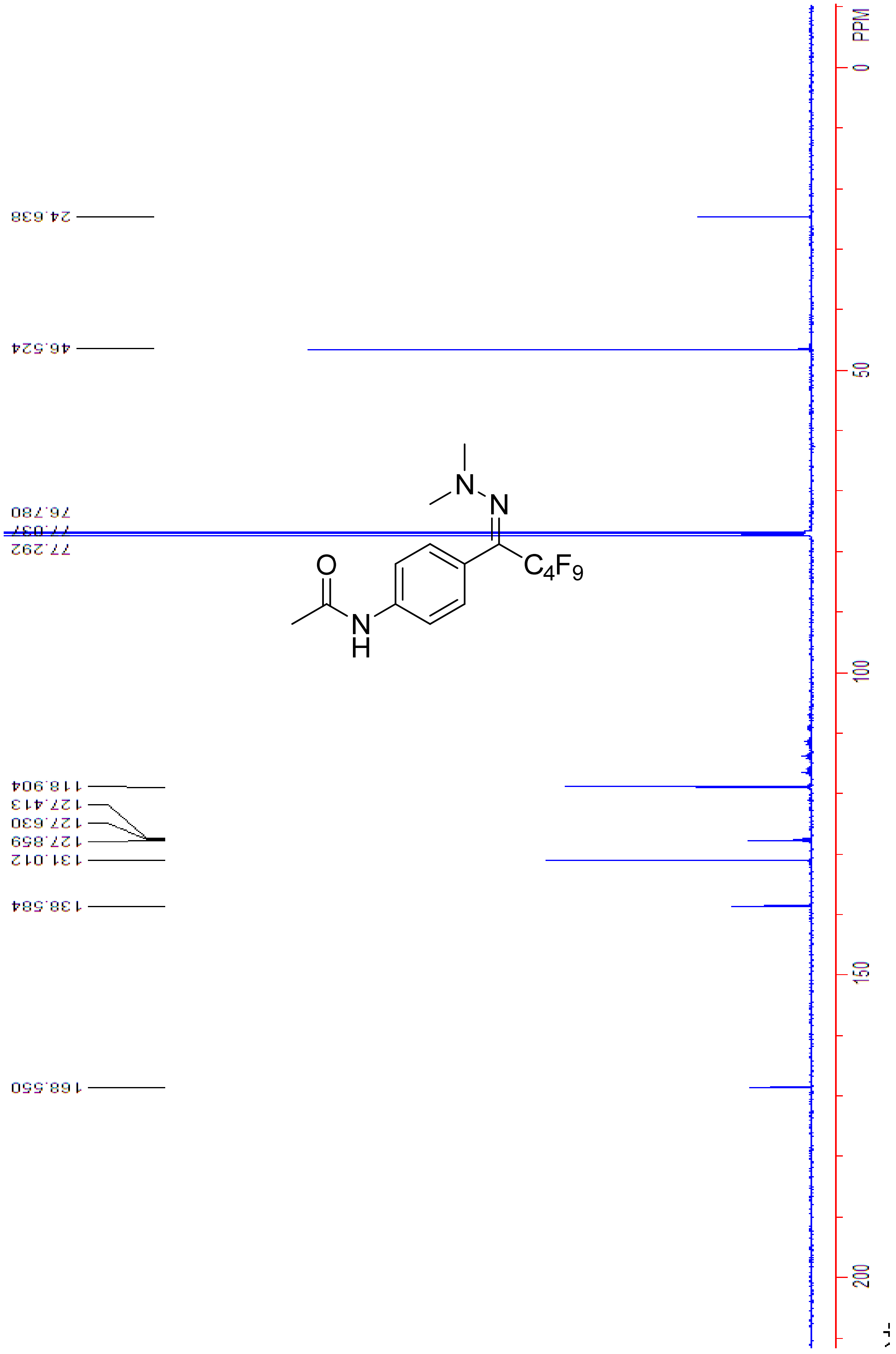

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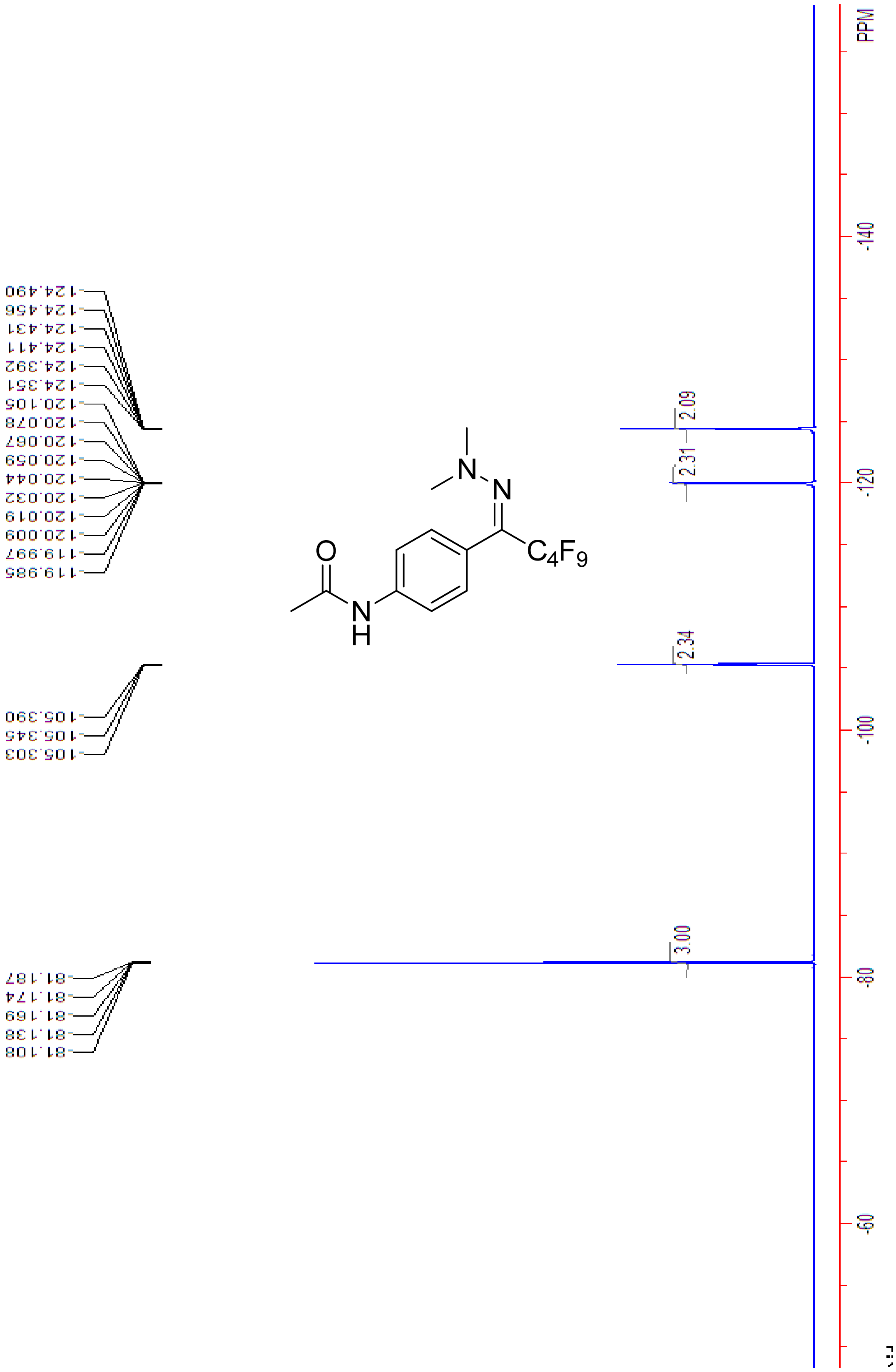
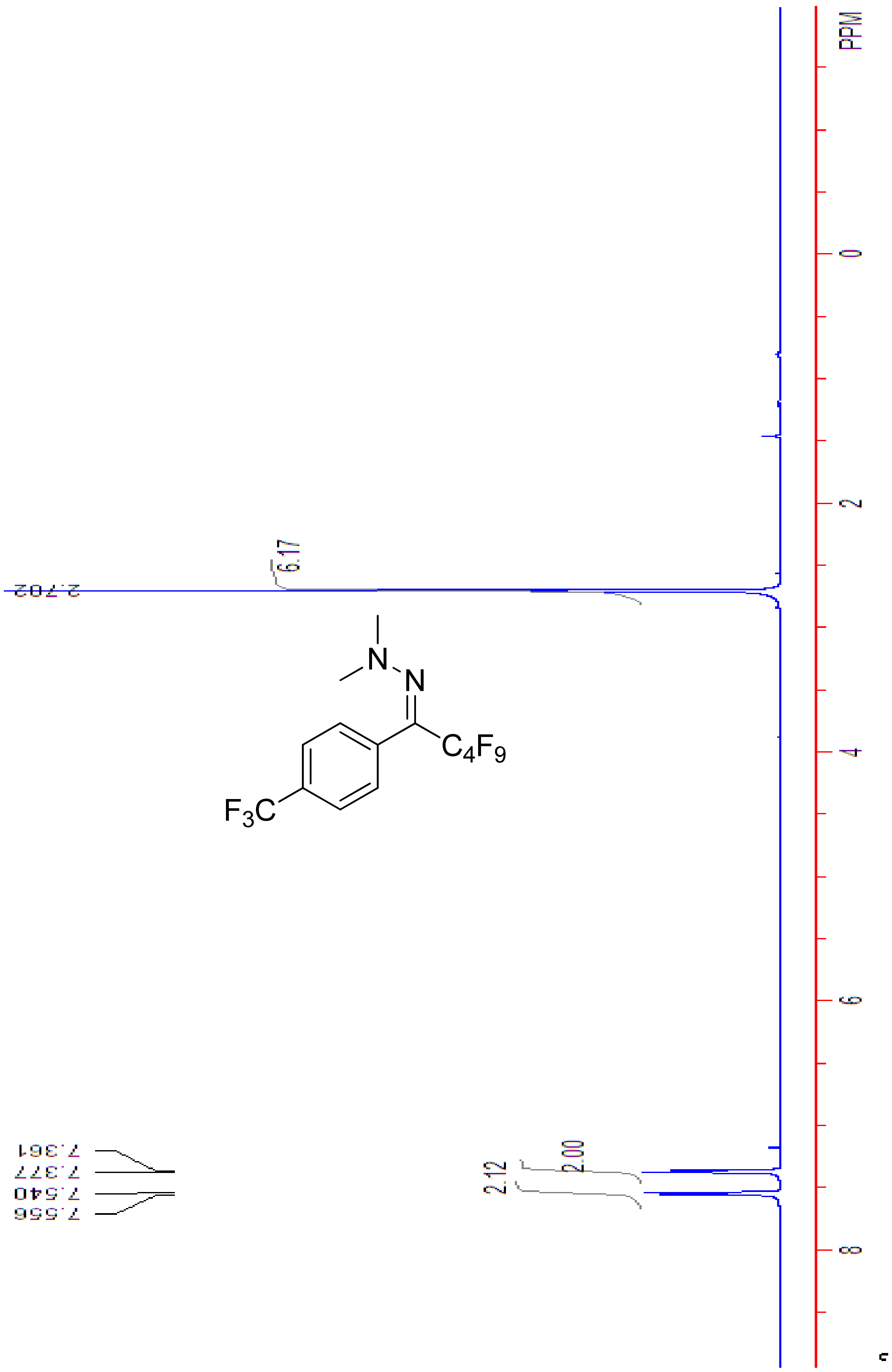
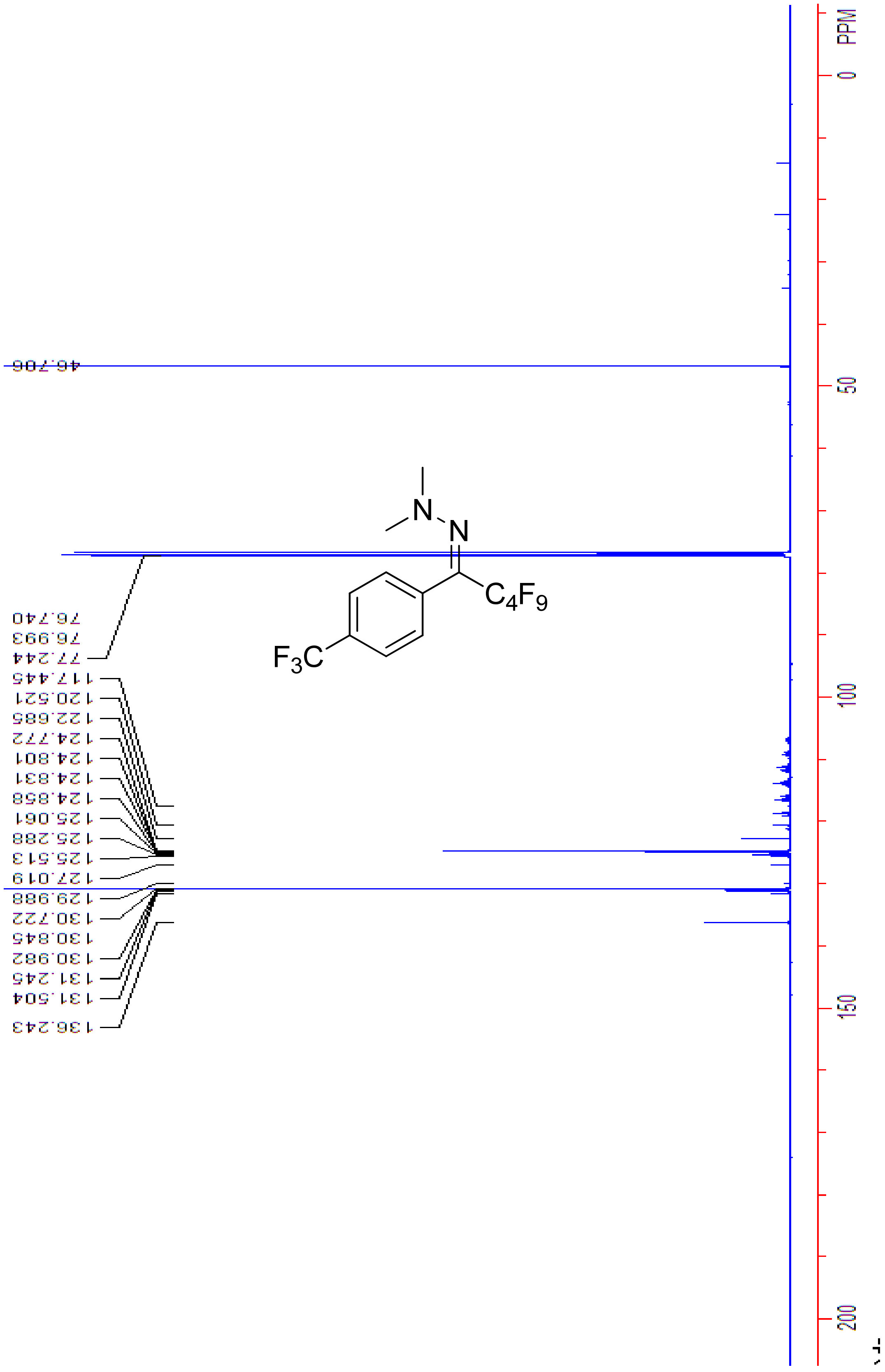


^{1}H NMR spectrum of **3ak**



^{13}C NMR spectrum of **3ak**



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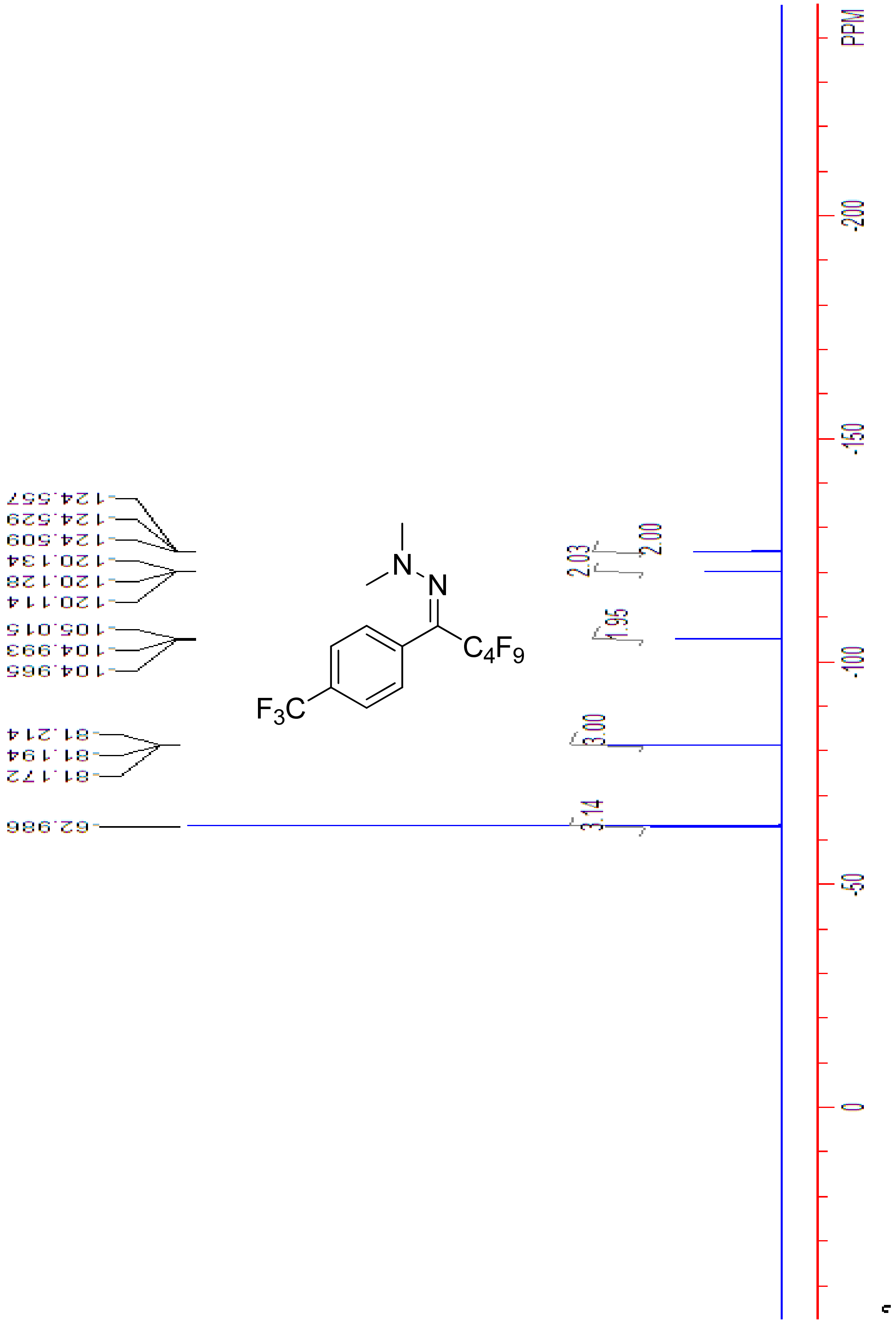
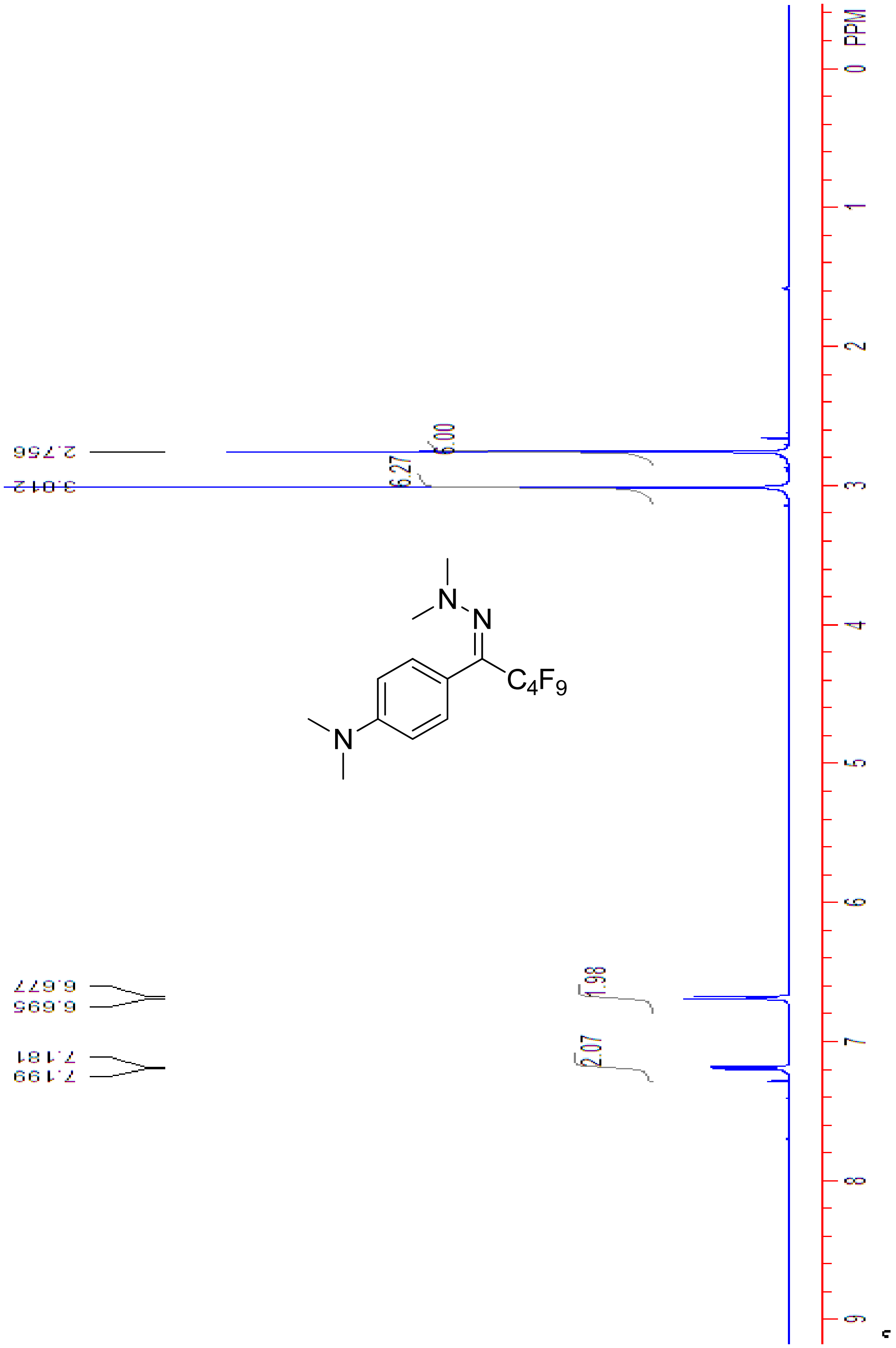
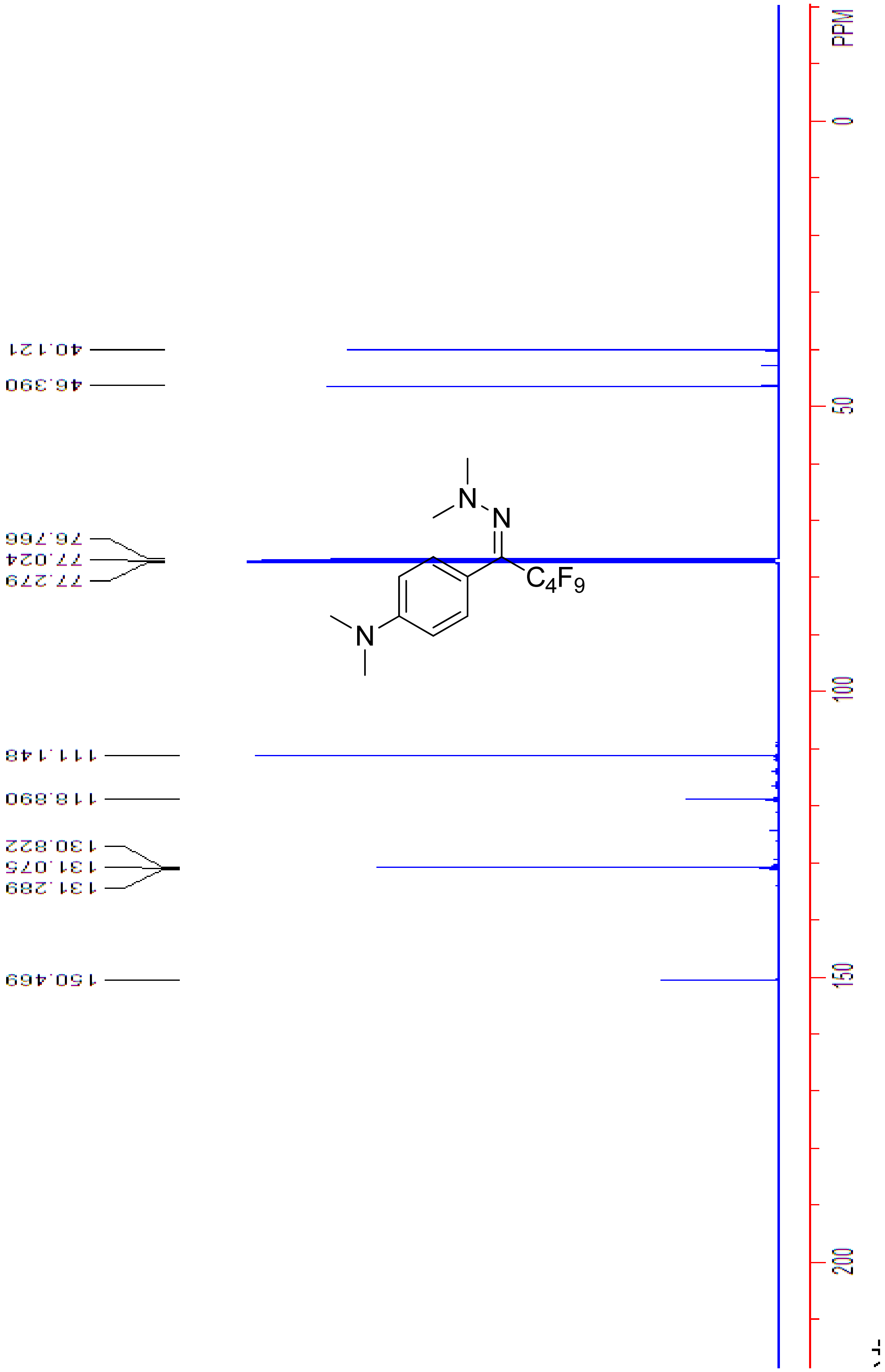


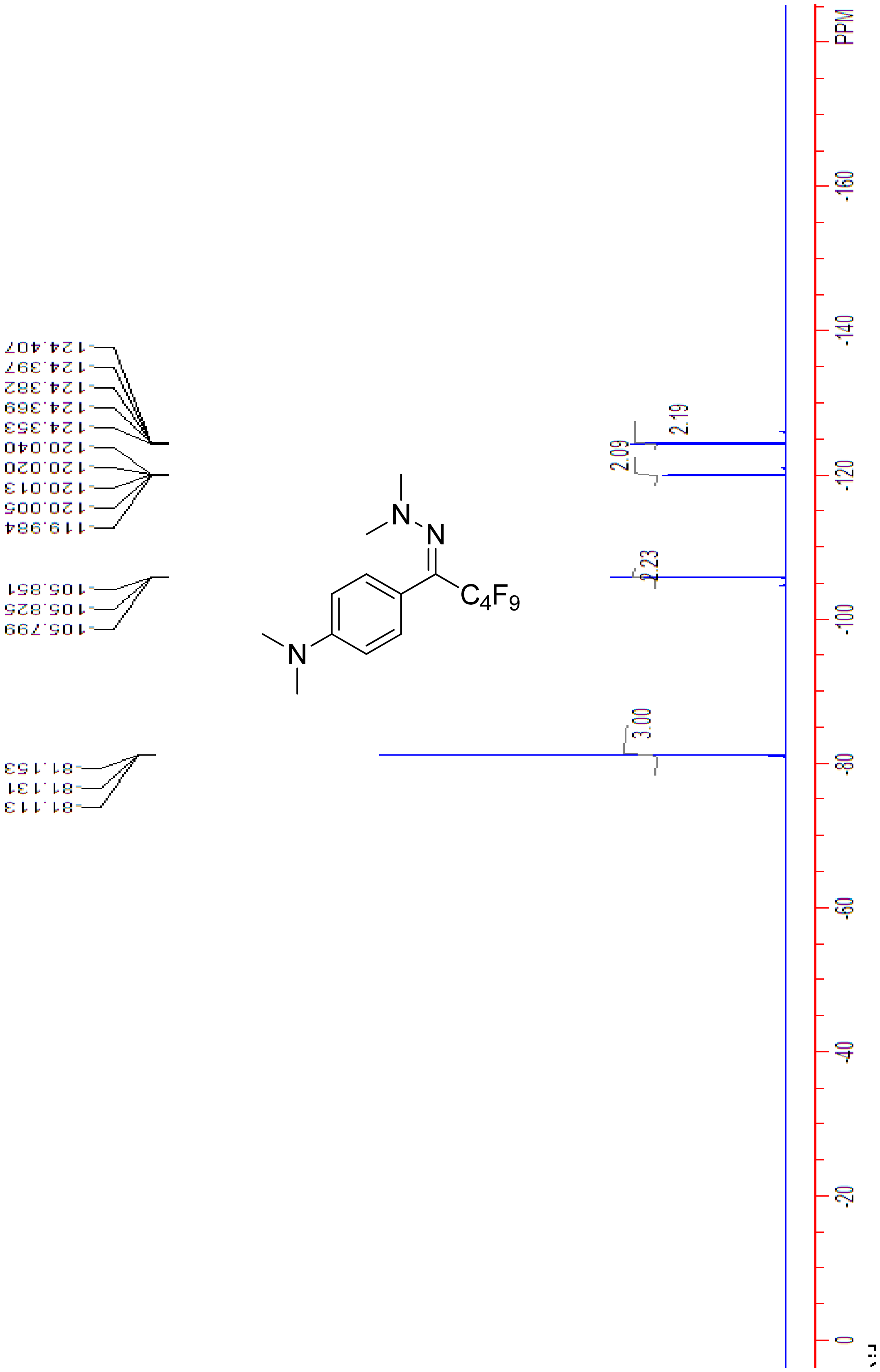
^{1}H NMR spectrum of **3al**



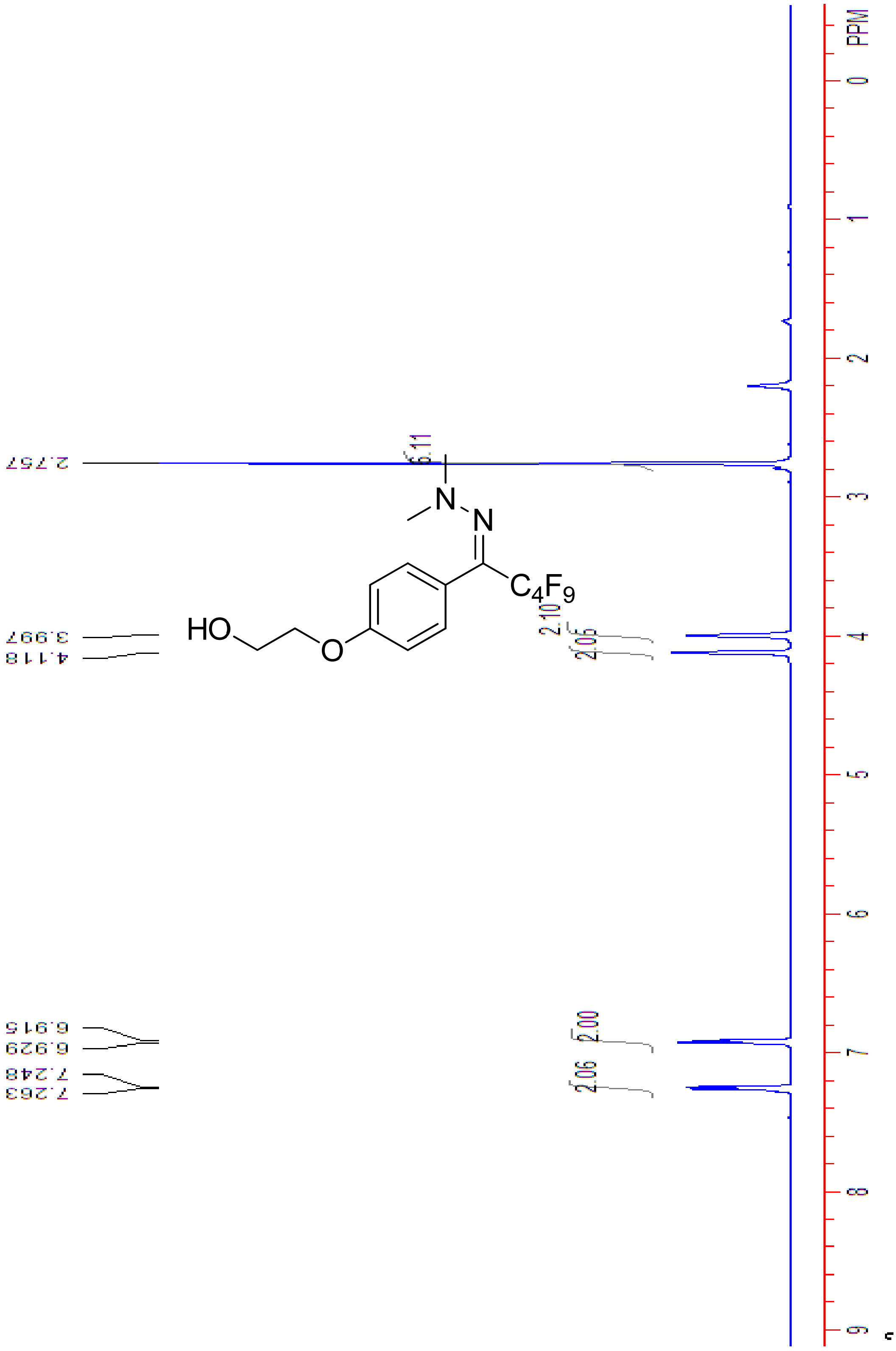
^{13}C NMR spectrum of **3al**



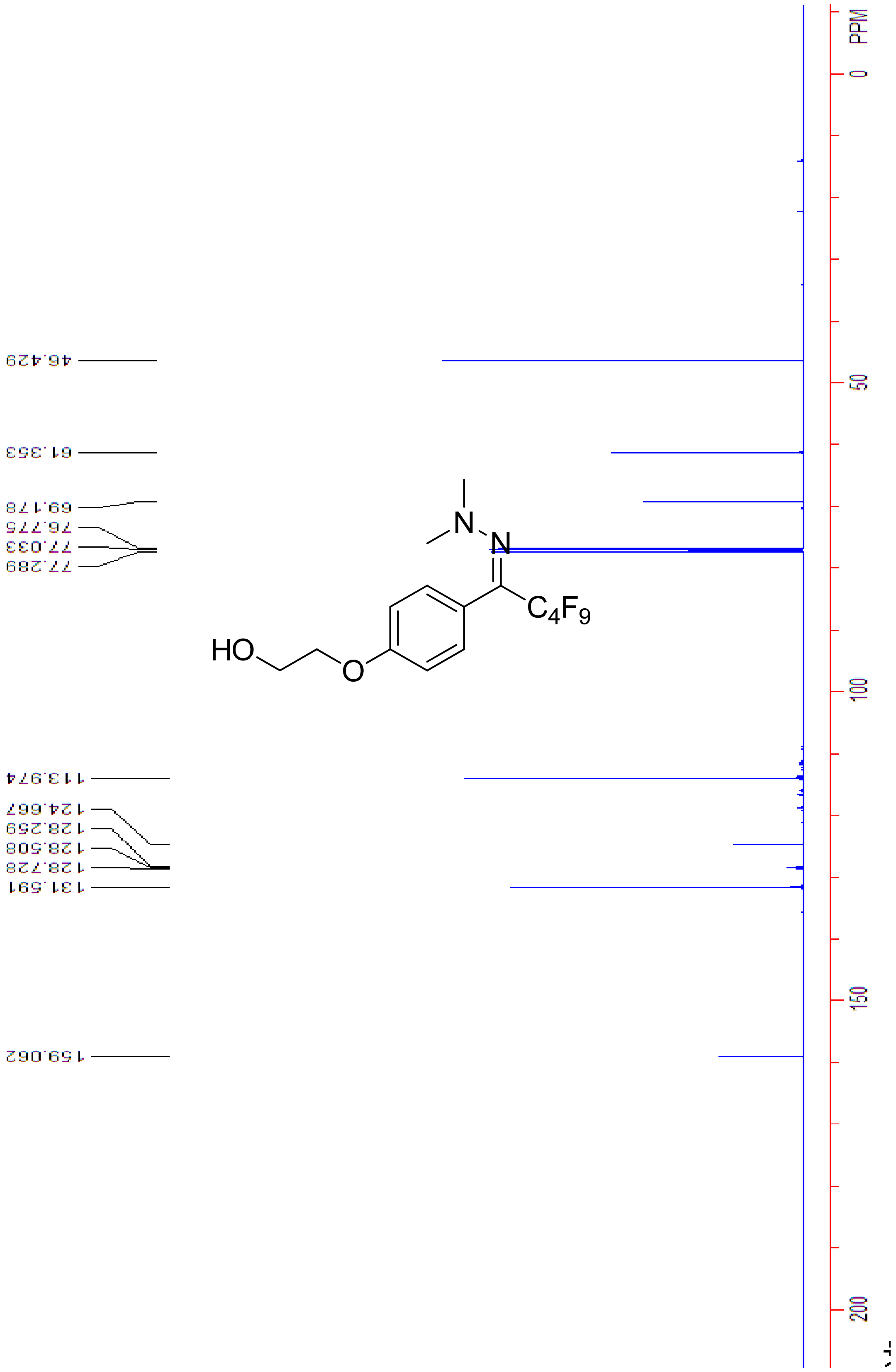
^{19}F NMR spectrum of **3al**



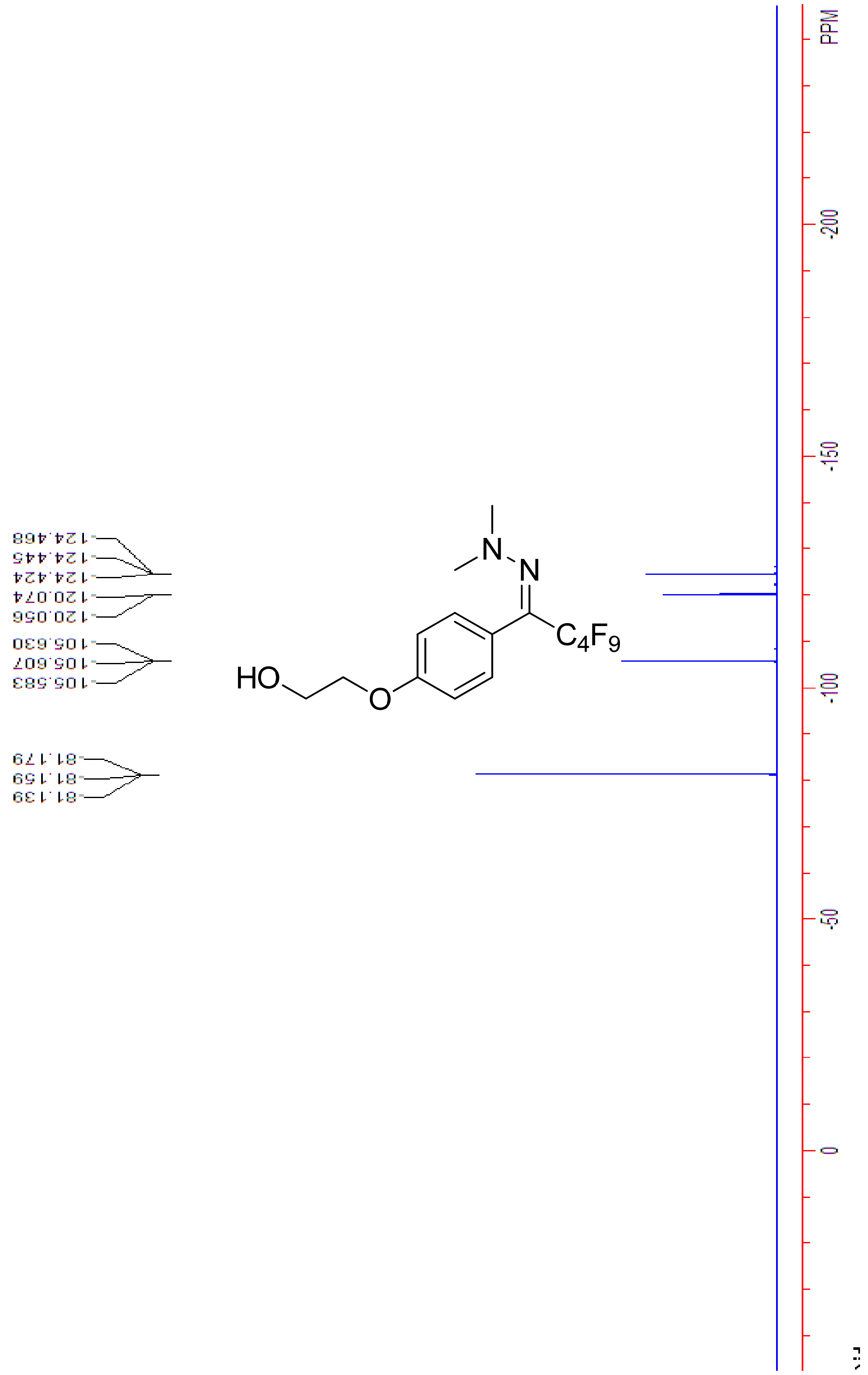
^{1}H NMR spectrum of **3am**



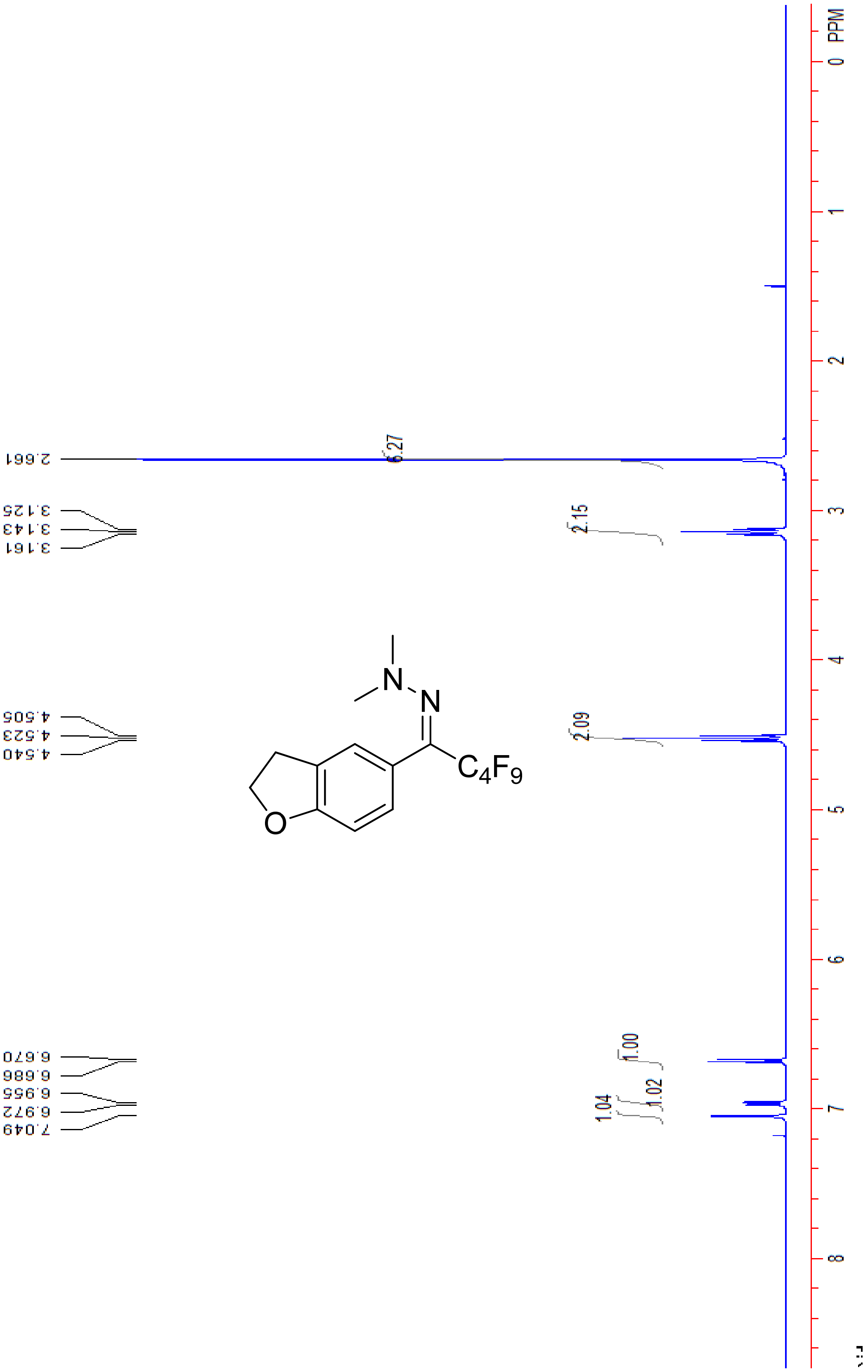
^{13}C NMR spectrum of **3am**



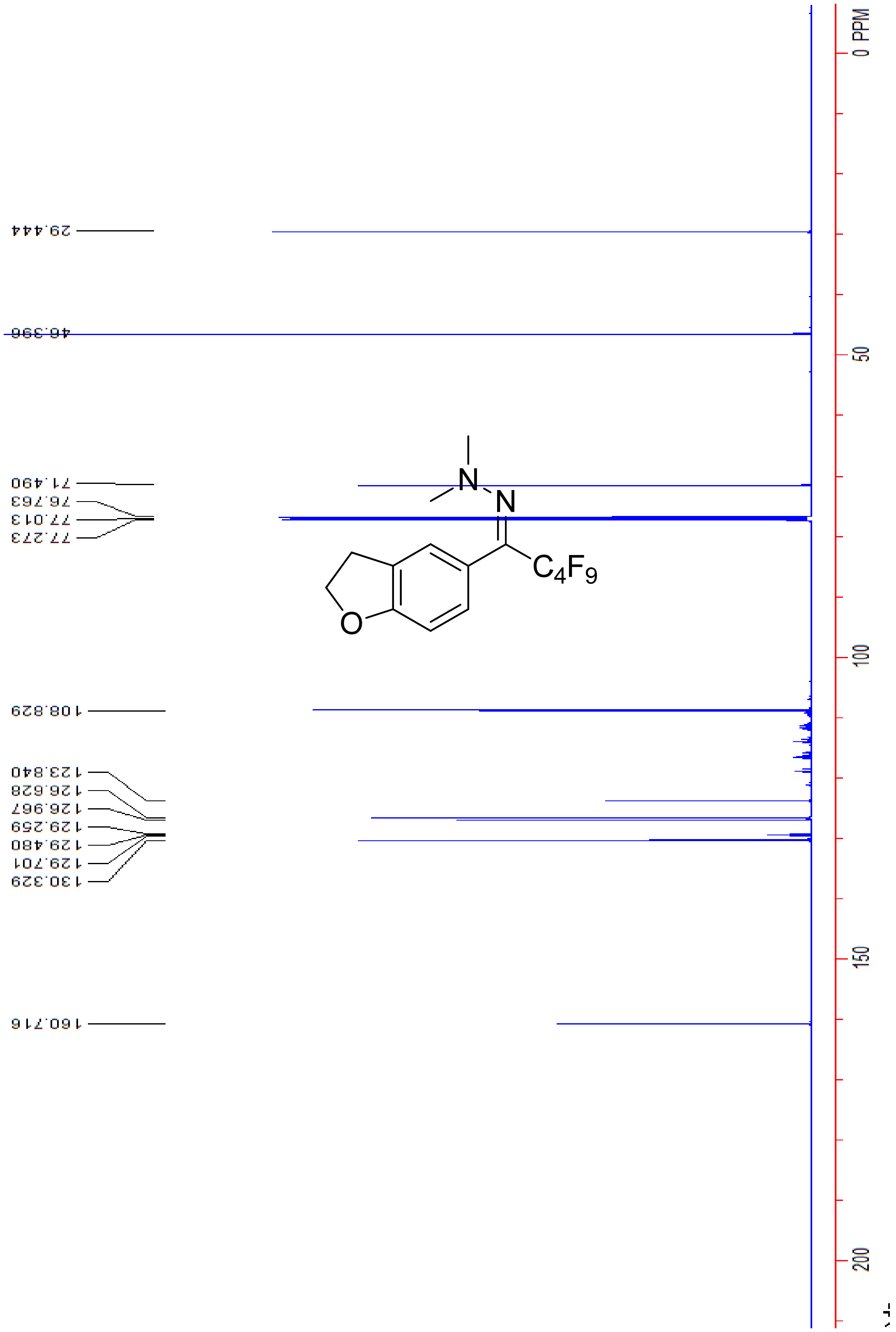
^{19}F NMR spectrum of **3am**



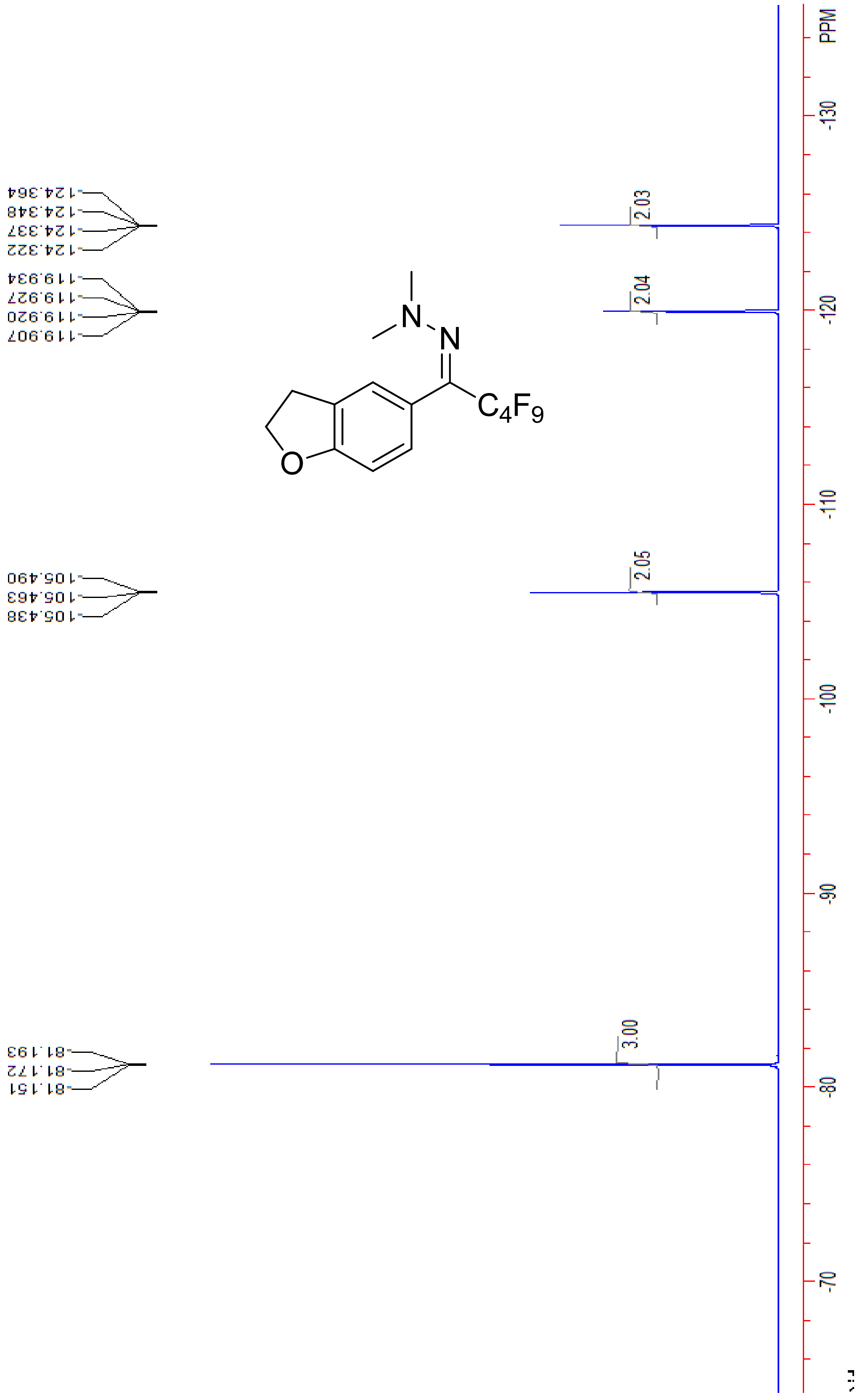
^{1}H NMR spectrum of **3an**



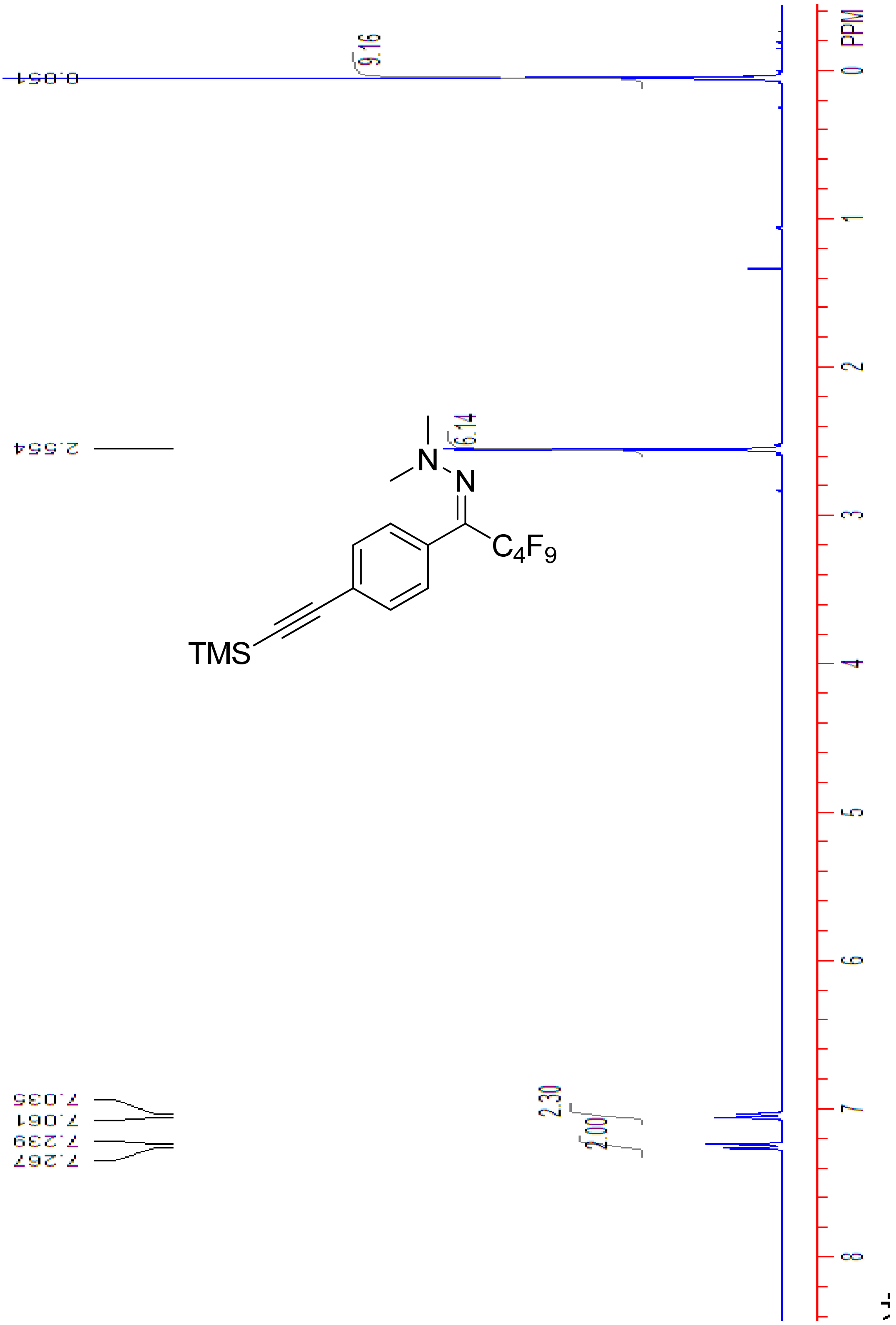
^{13}C NMR spectrum of **3an**



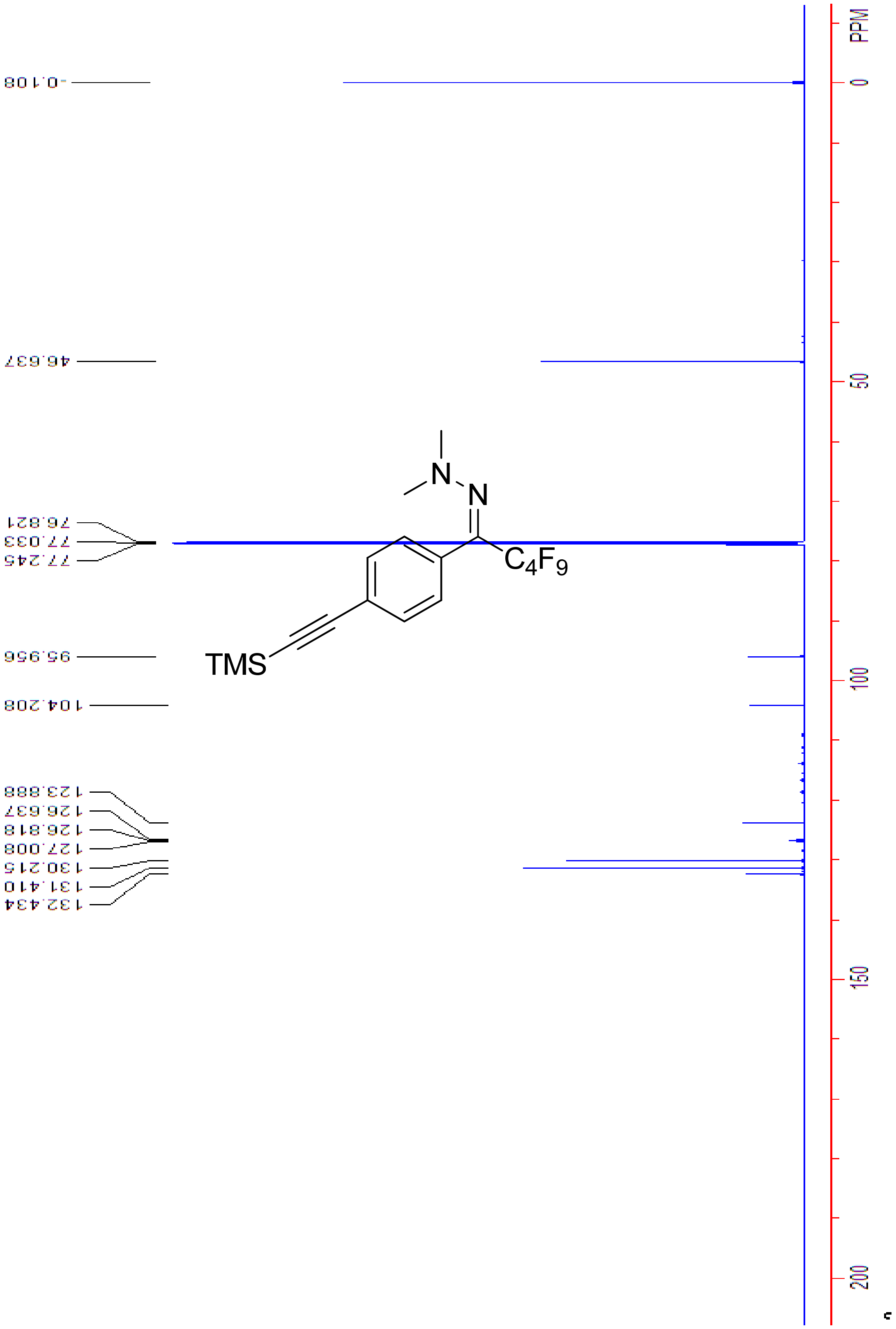
^{19}F NMR spectrum of **3an**



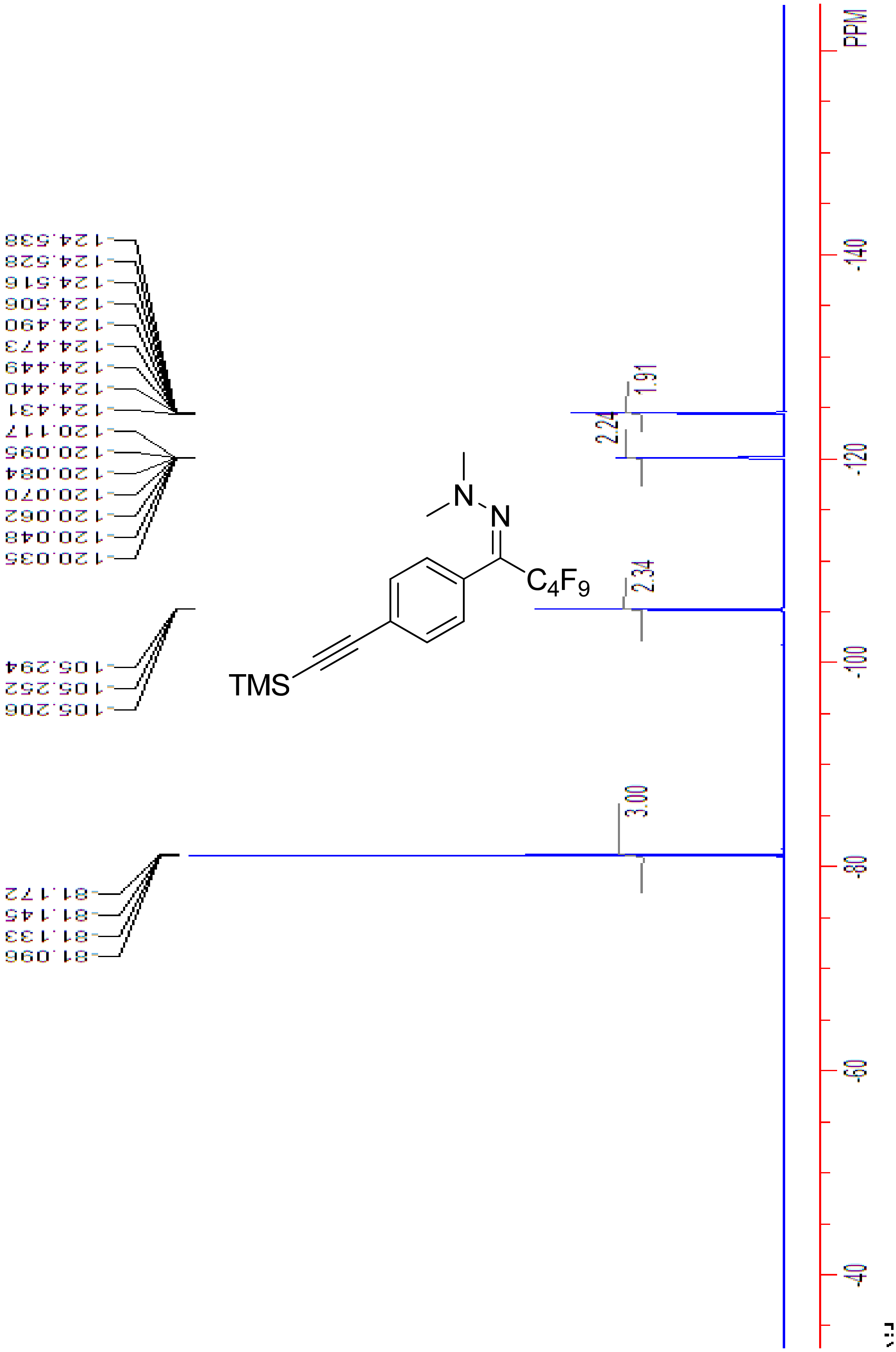
^{1}H NMR spectrum of **3ao**



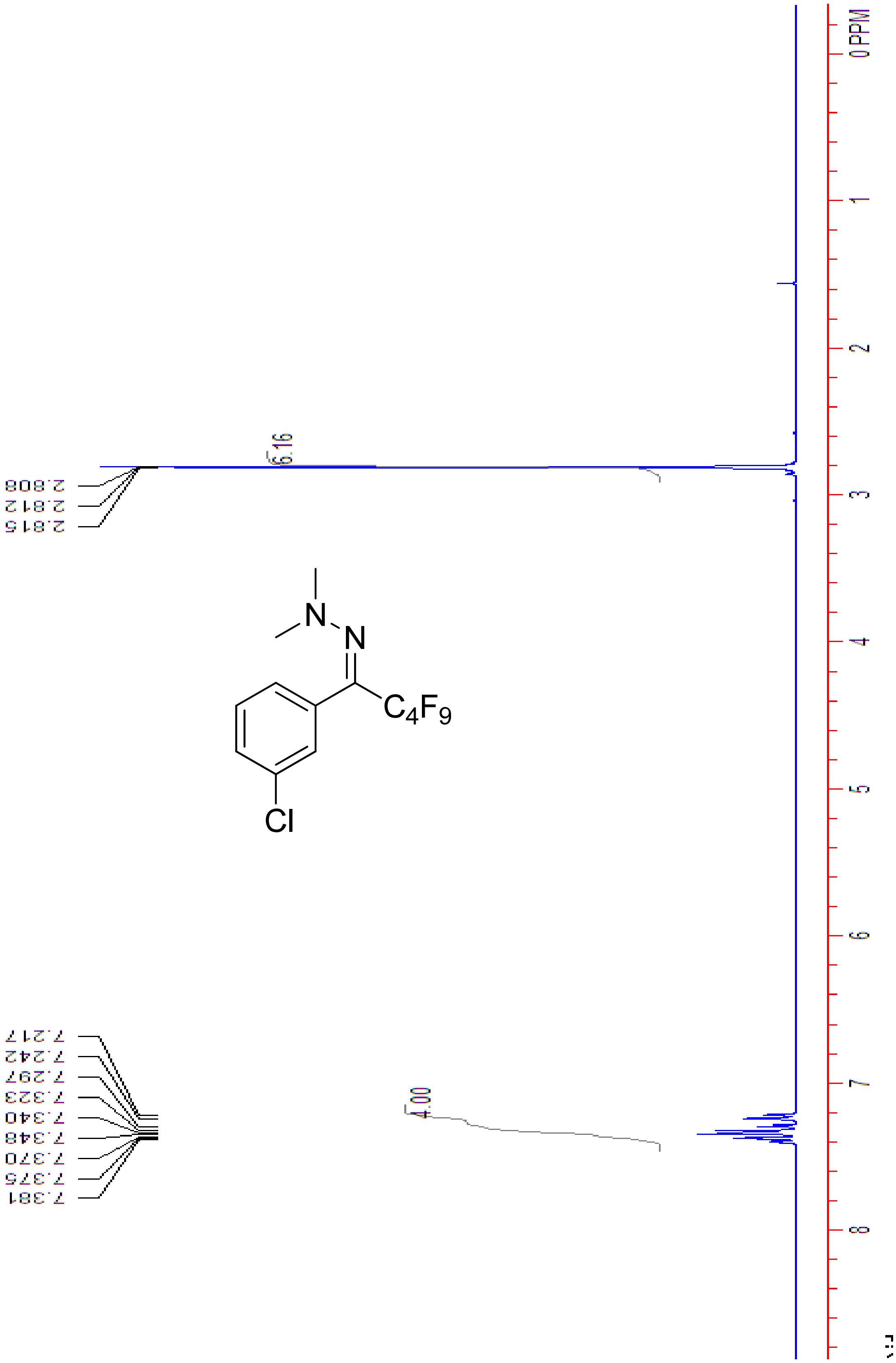
^{13}C NMR spectrum of **3ao**



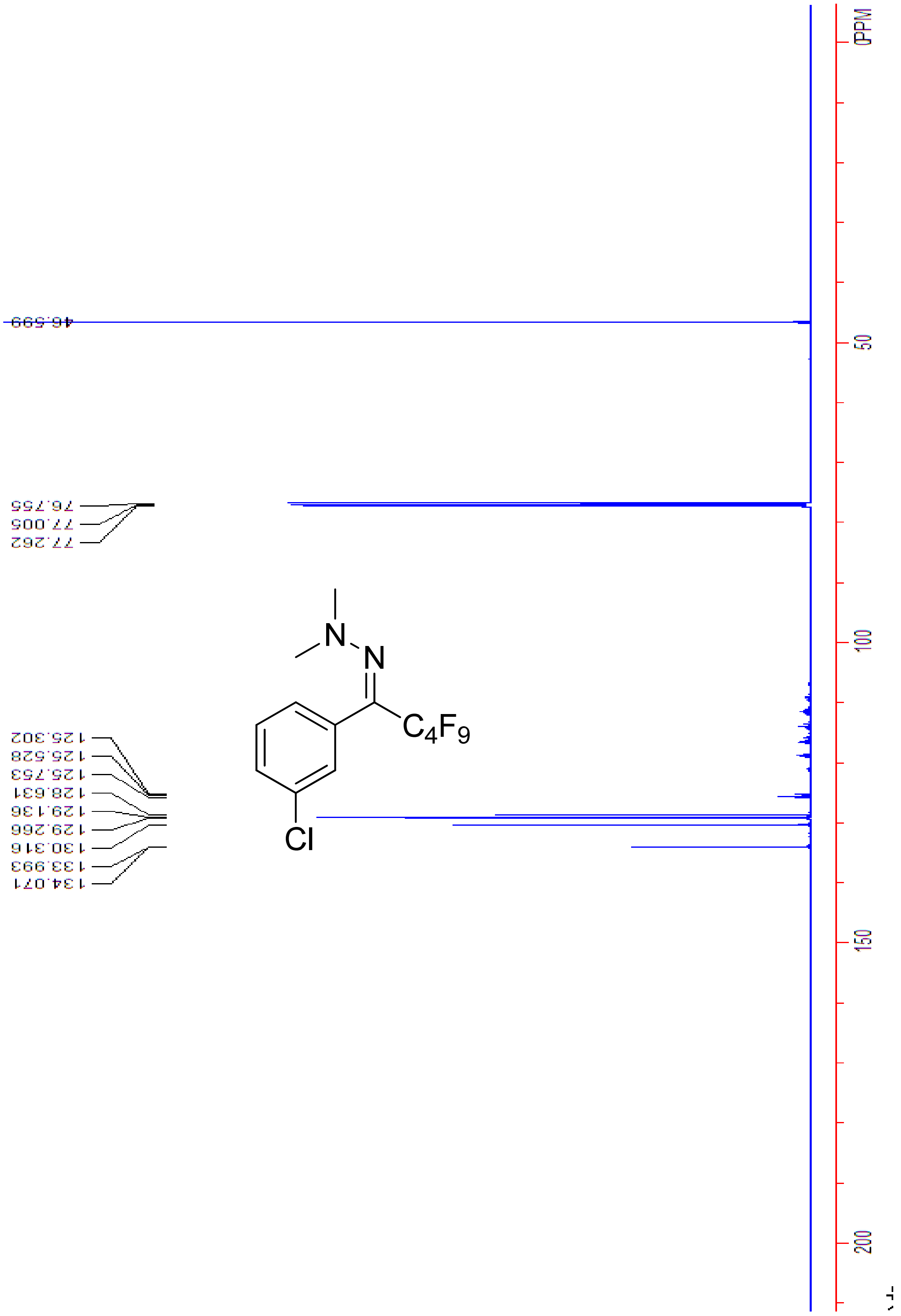
^{19}F NMR spectrum of **3ao**



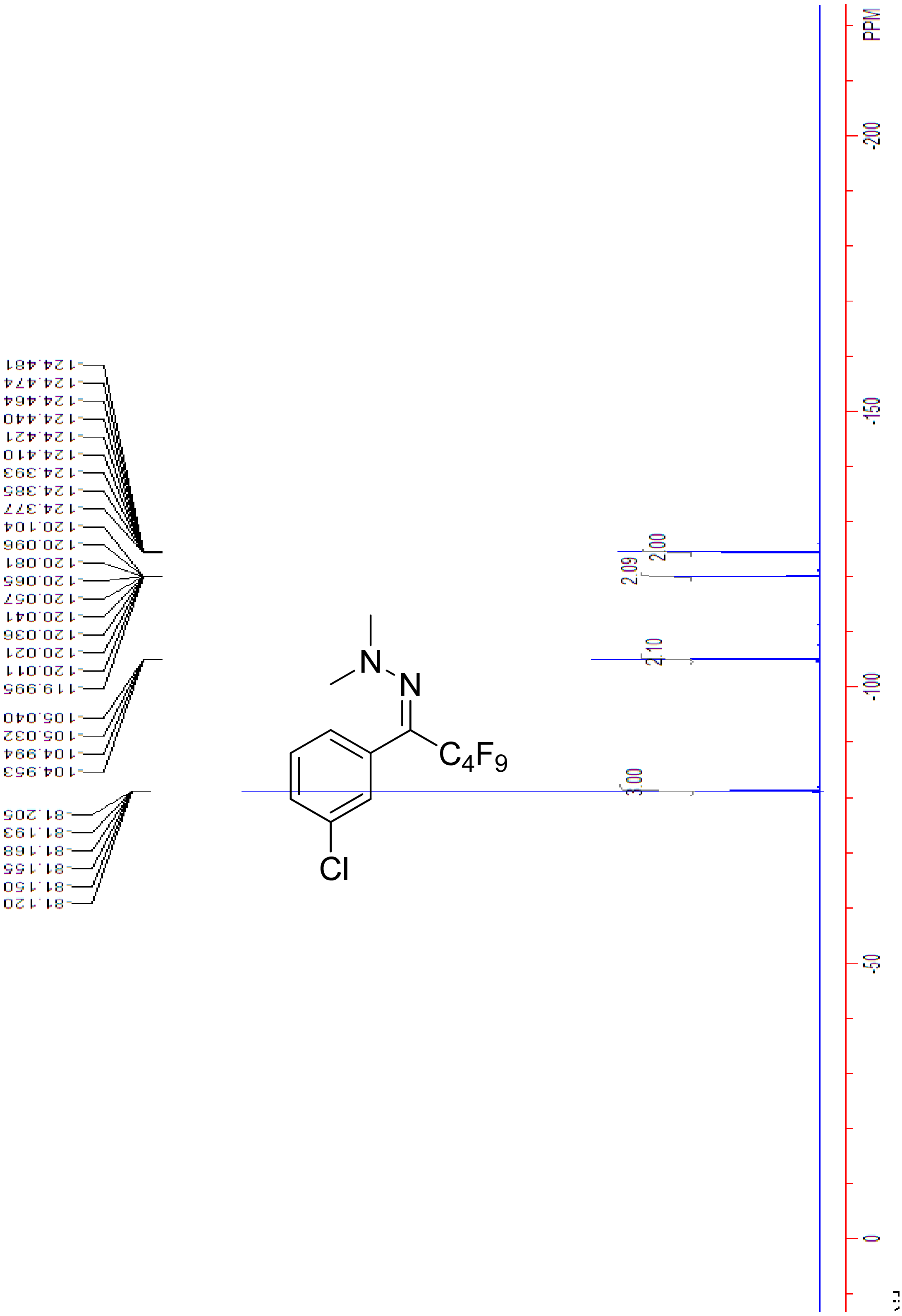
^{1}H NMR spectrum of **3ap**



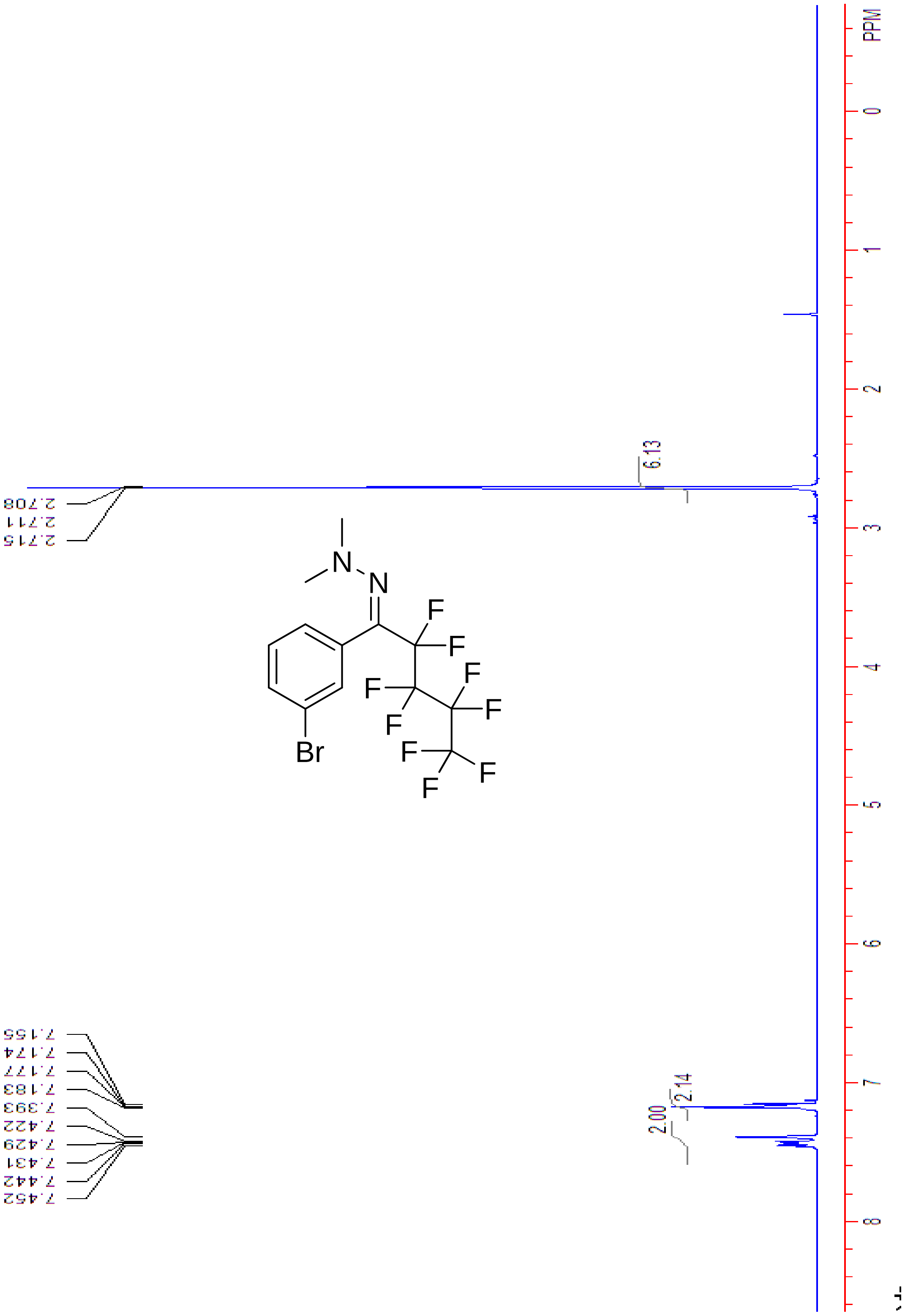
^{13}C NMR spectrum of **3ap**



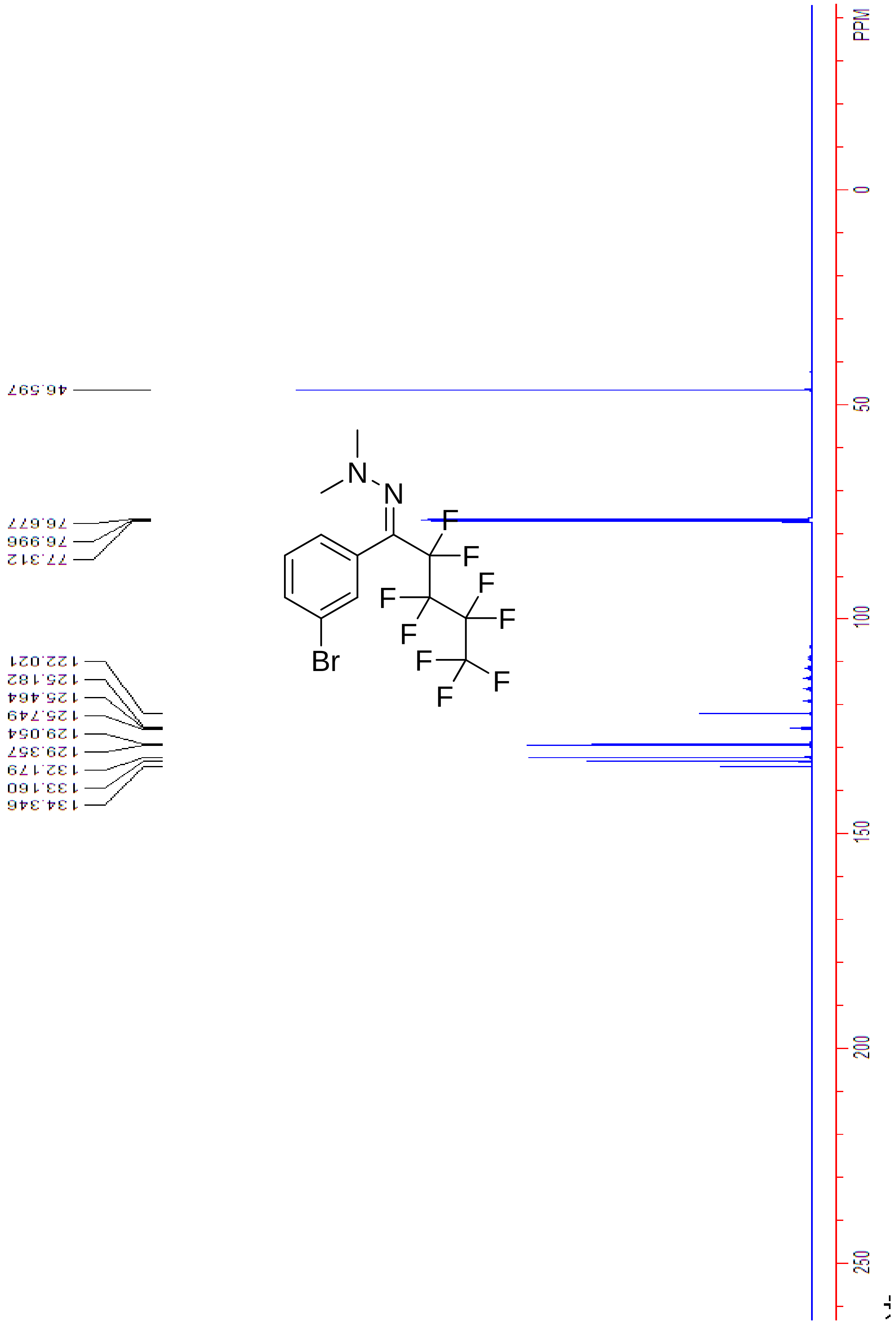
^{19}F NMR spectrum of **3ap**



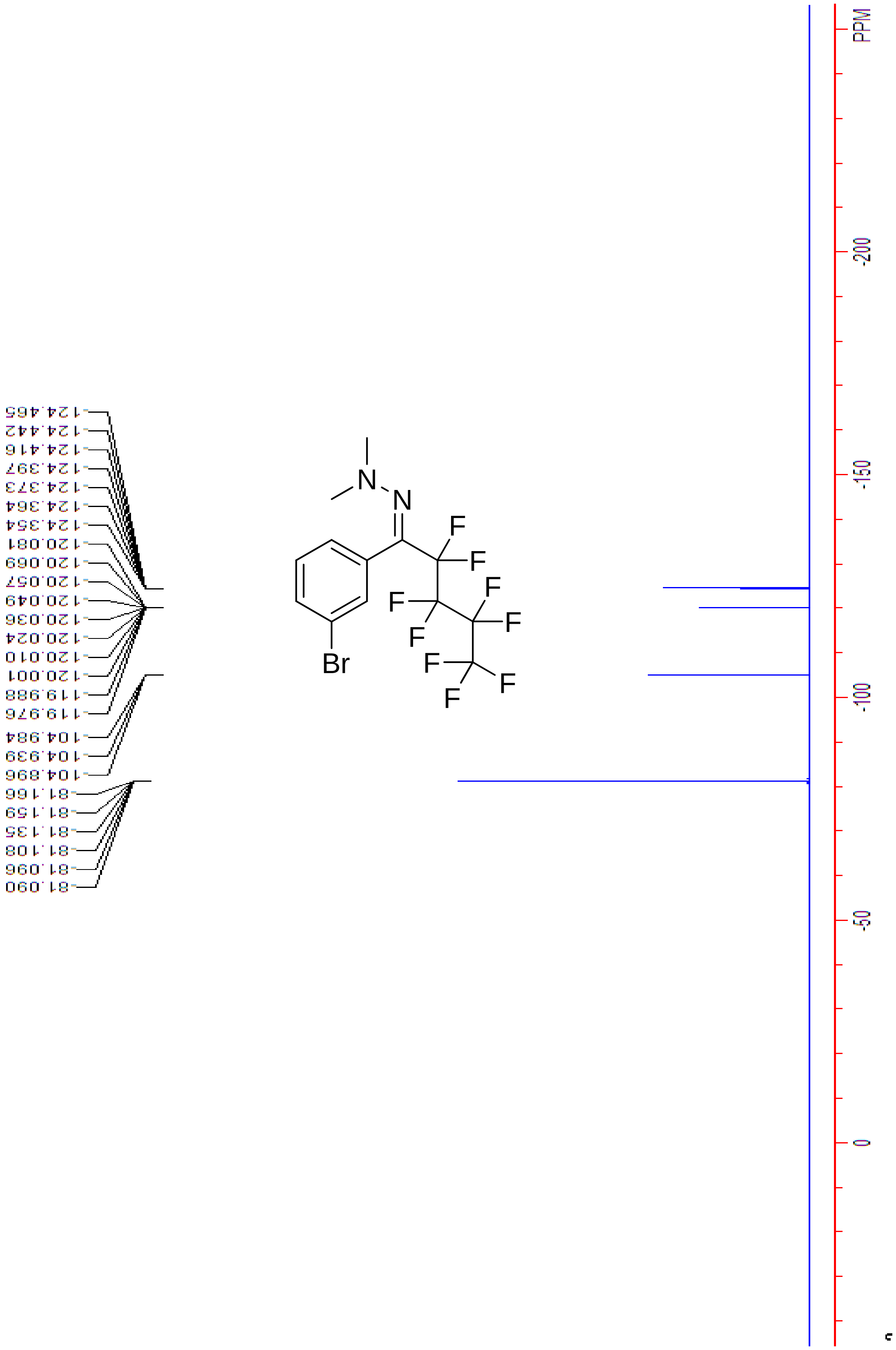
^{1}H NMR spectrum of **3aq**



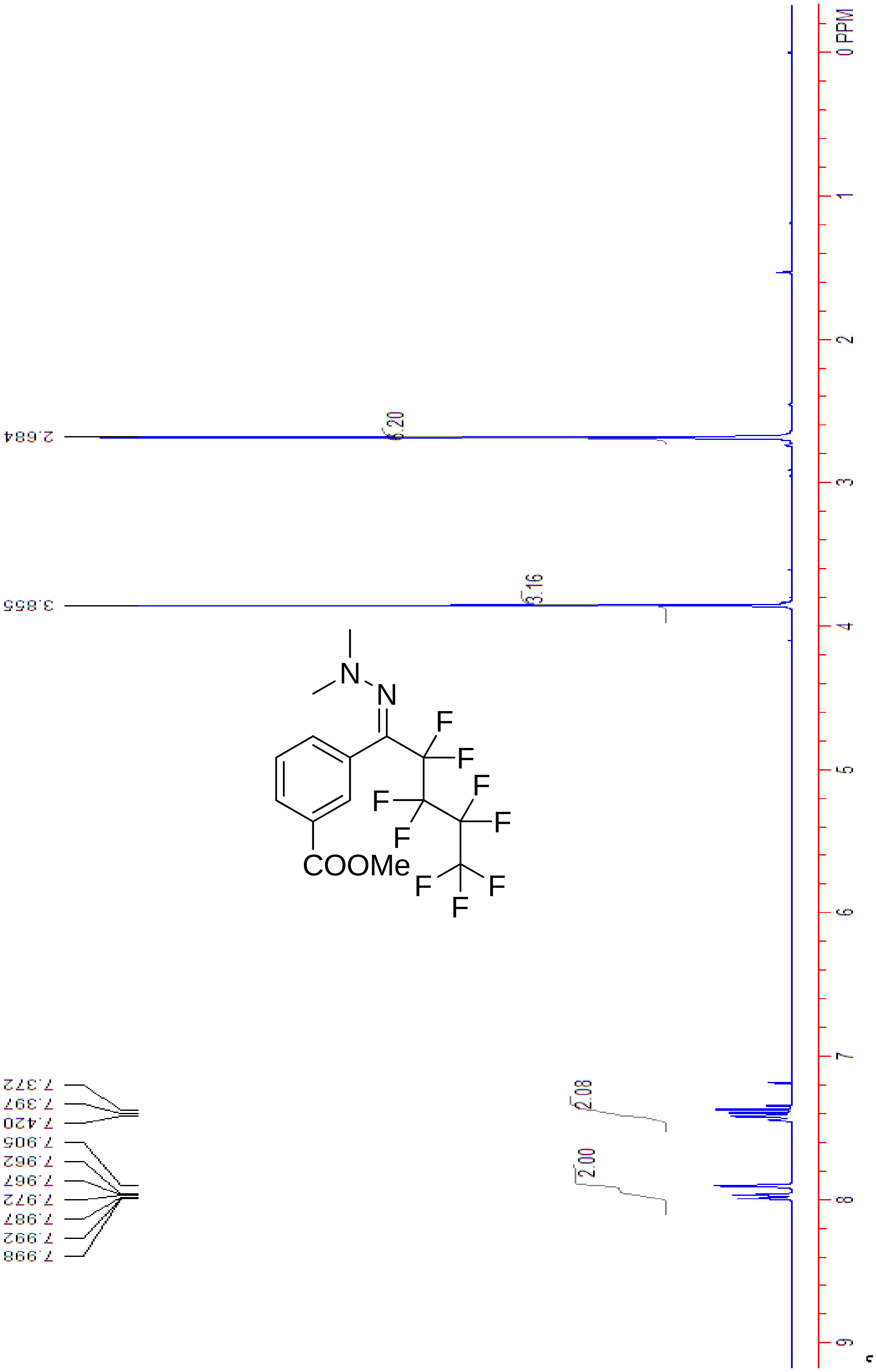
^{13}C NMR spectrum of **3aq**



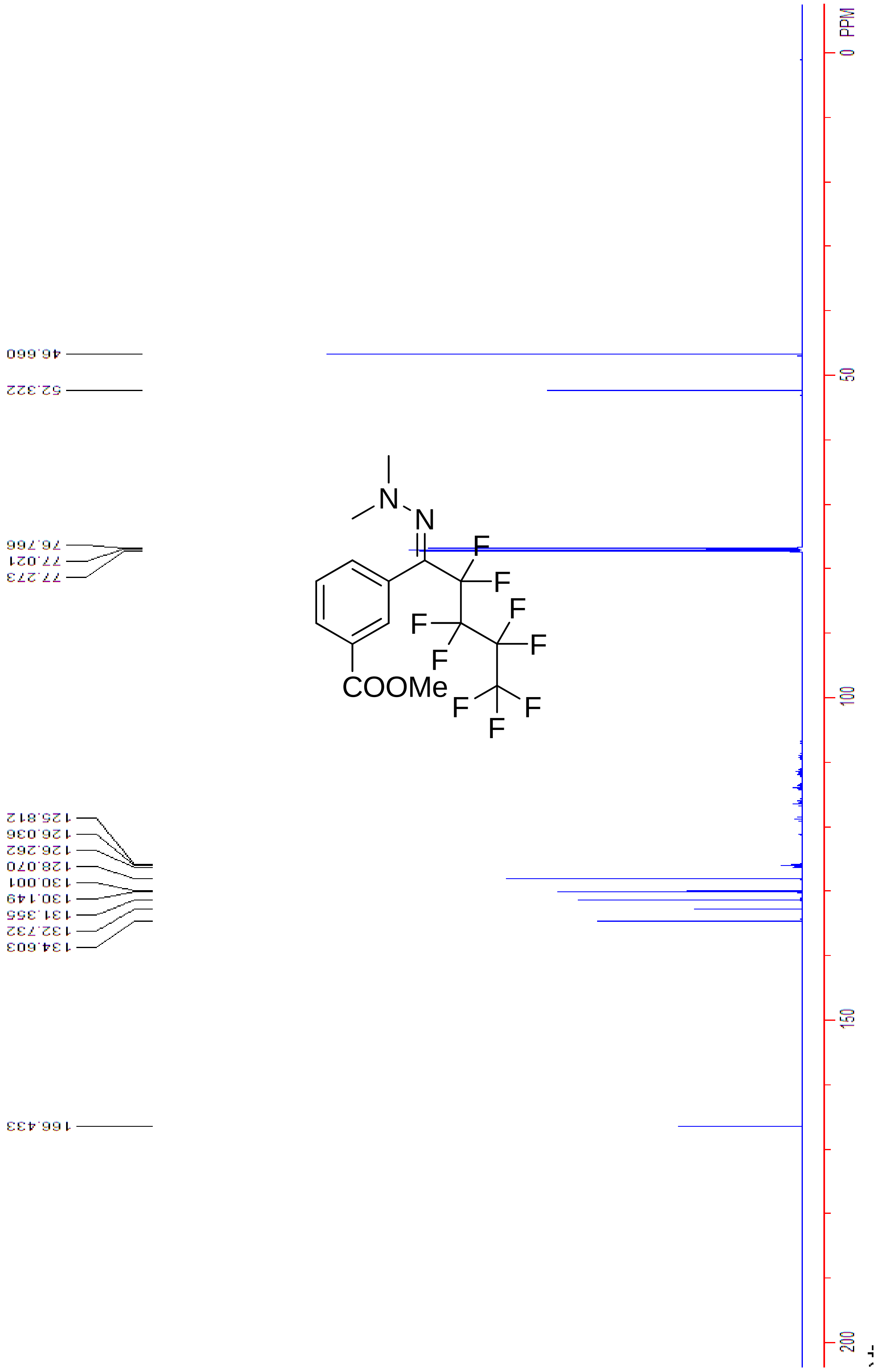
^{19}F NMR spectrum of **3aq**



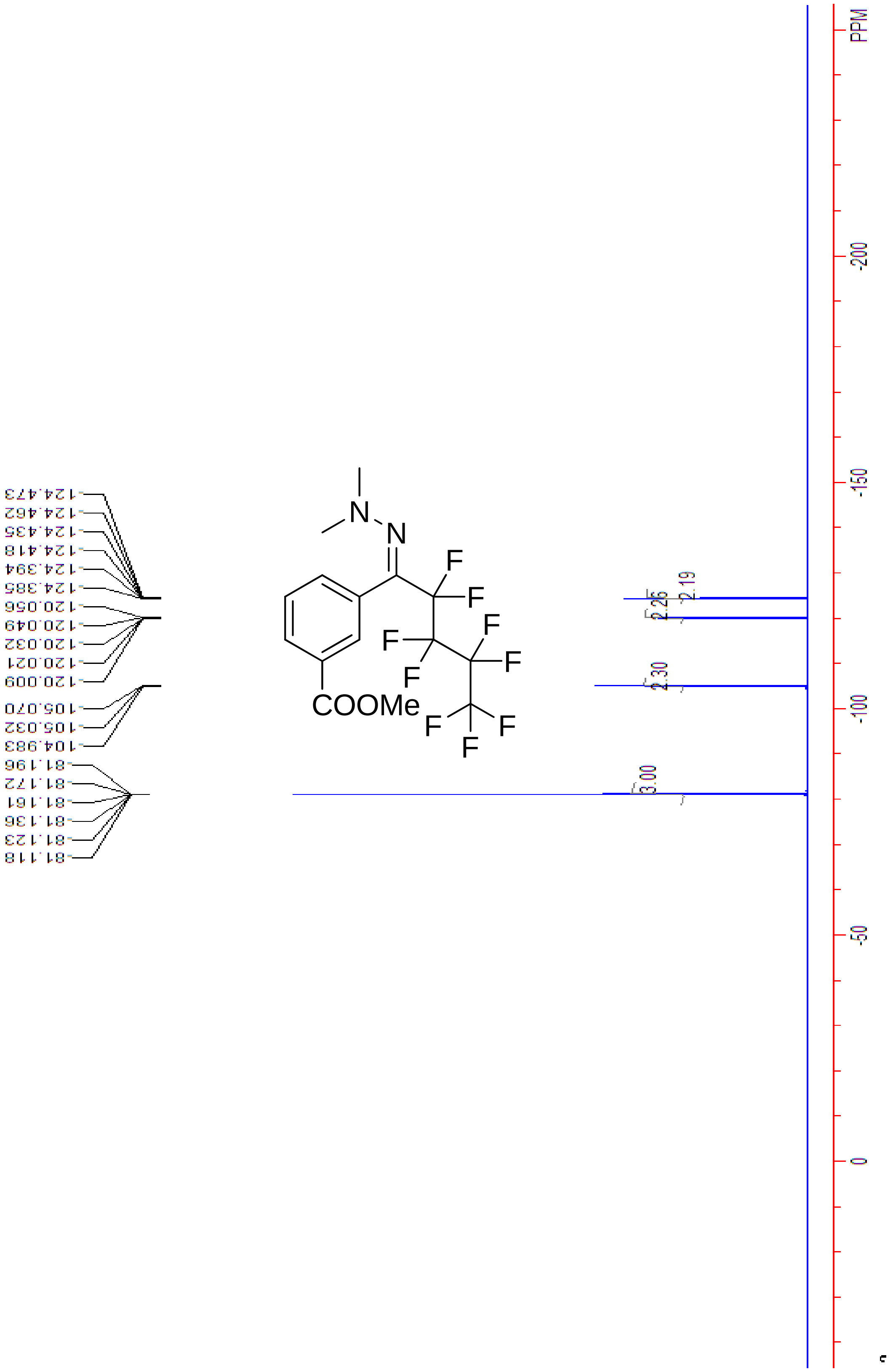
^{1}H NMR spectrum of **3ar**



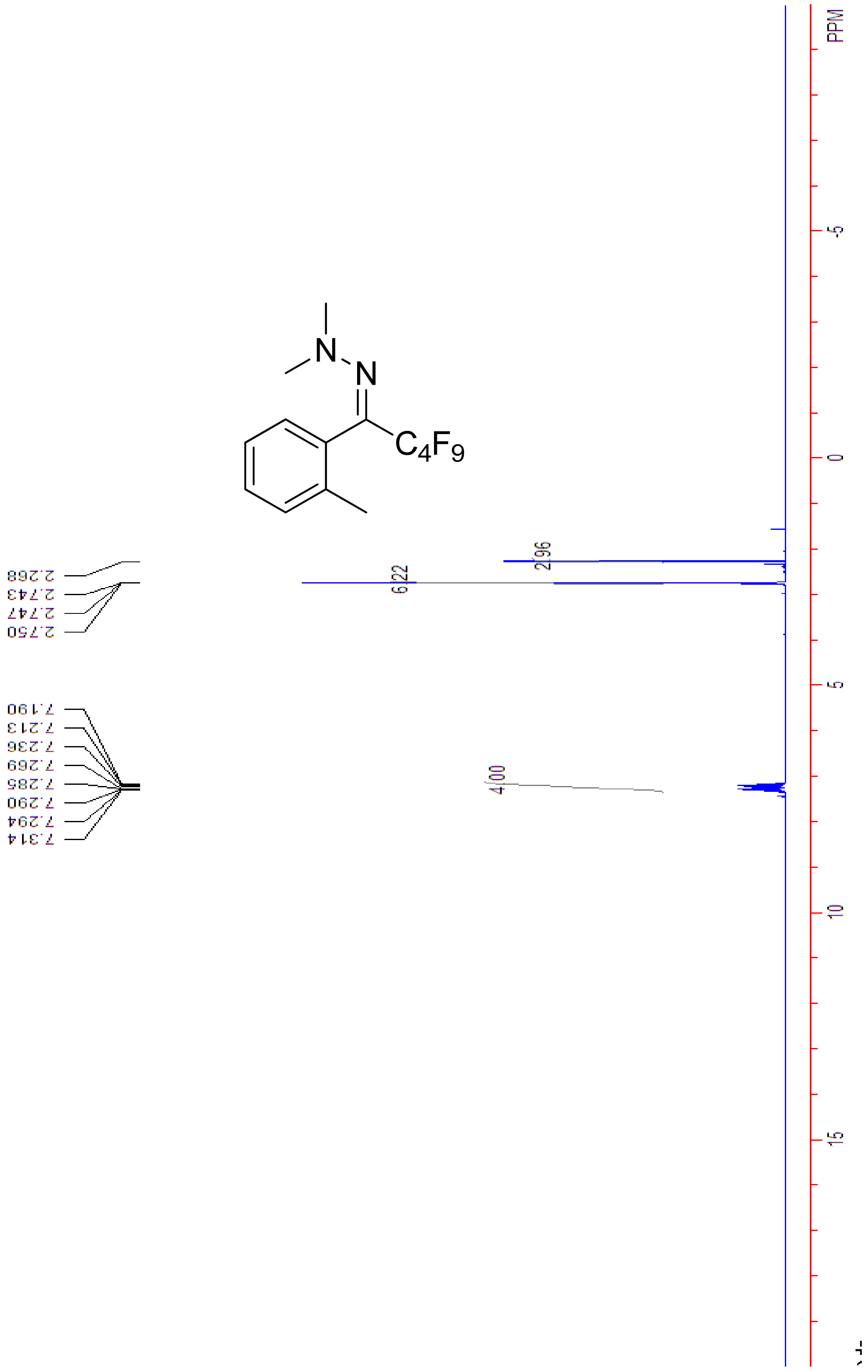
^{13}C NMR spectrum of **3ar**



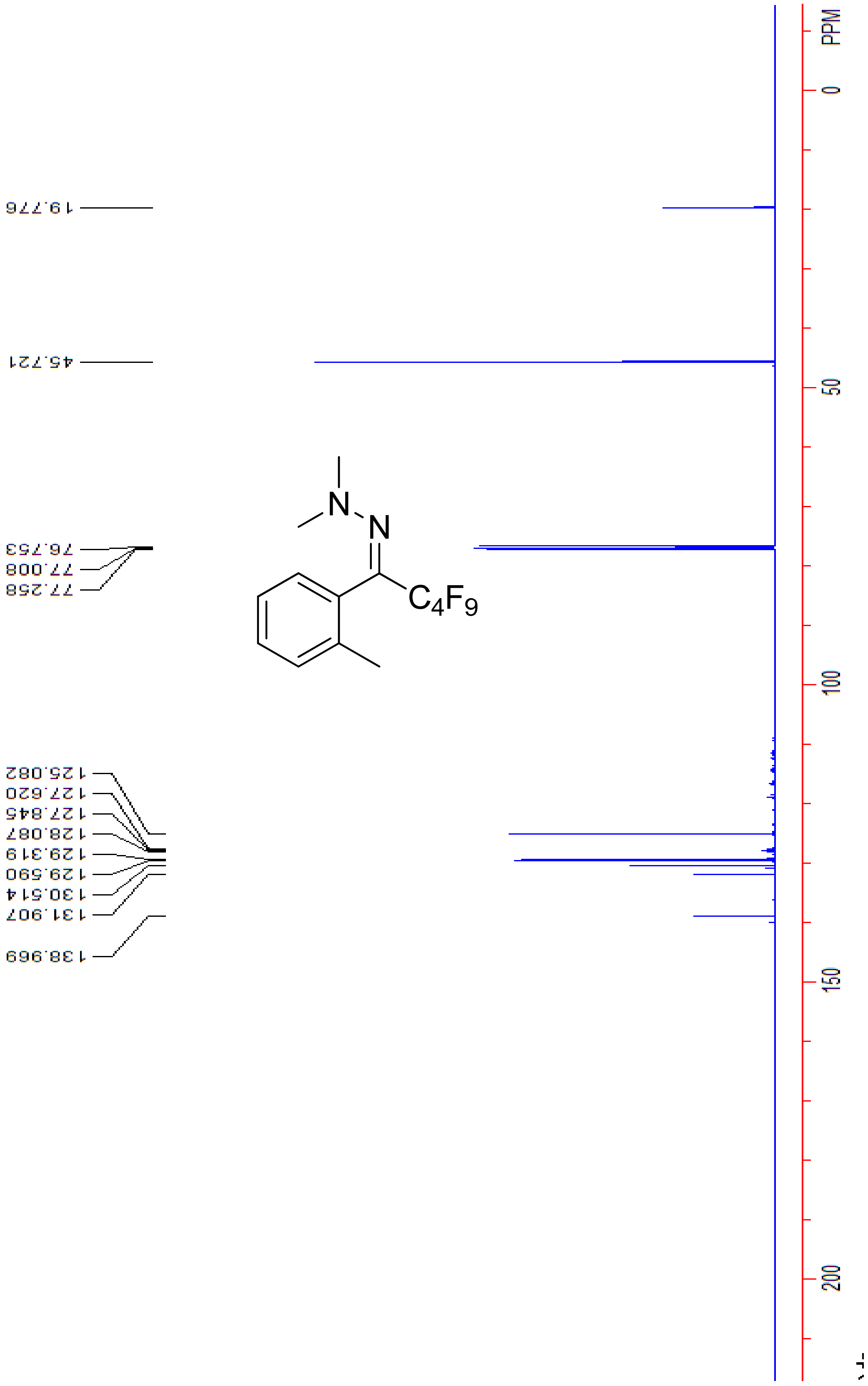
^{19}F NMR spectrum of **3ar**



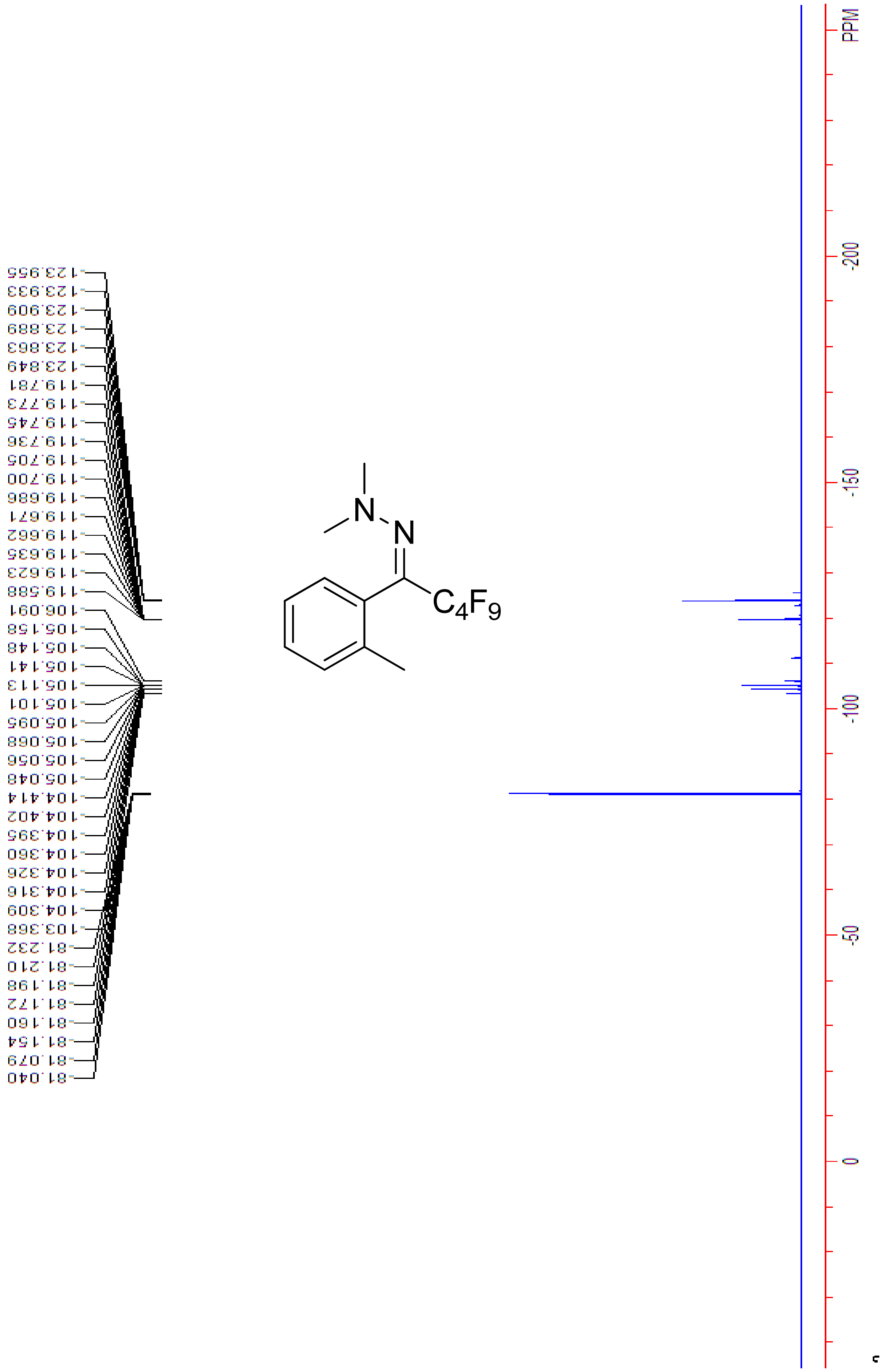
^{1}H NMR spectrum of **3as**



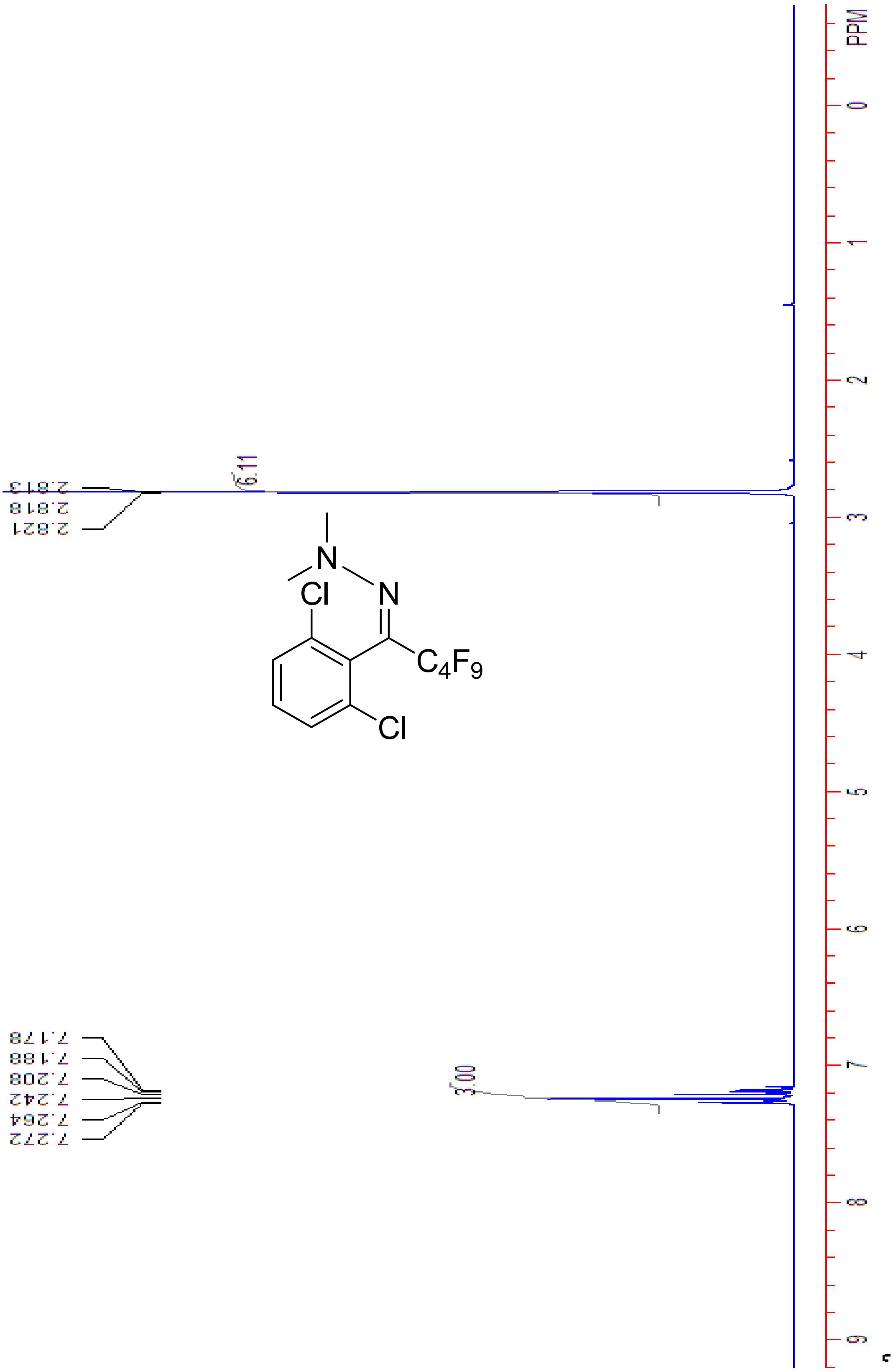
^{13}C NMR spectrum of **3as**



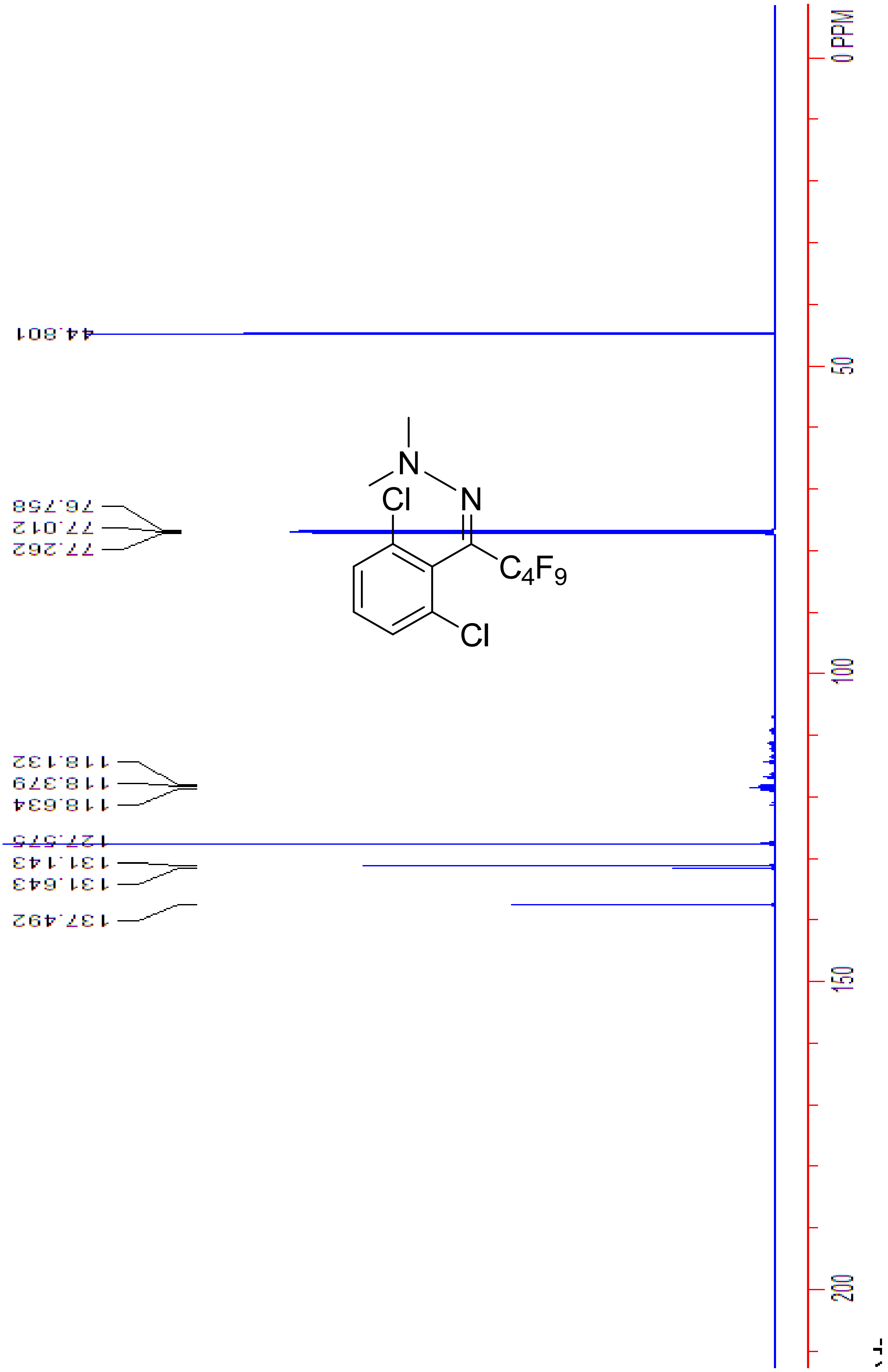
^{19}F NMR spectrum of **3as**



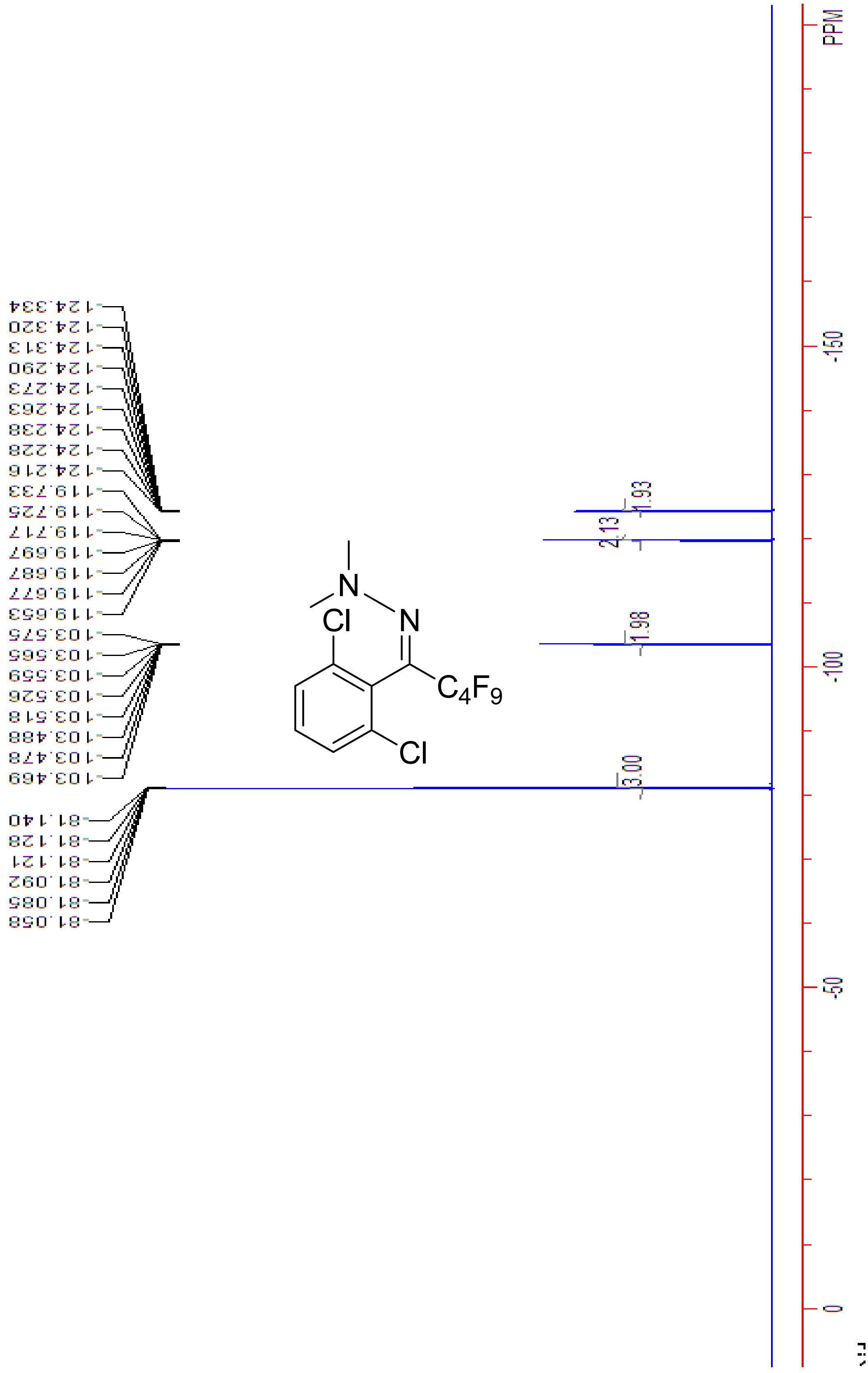
^{1}H NMR spectrum of **3at**



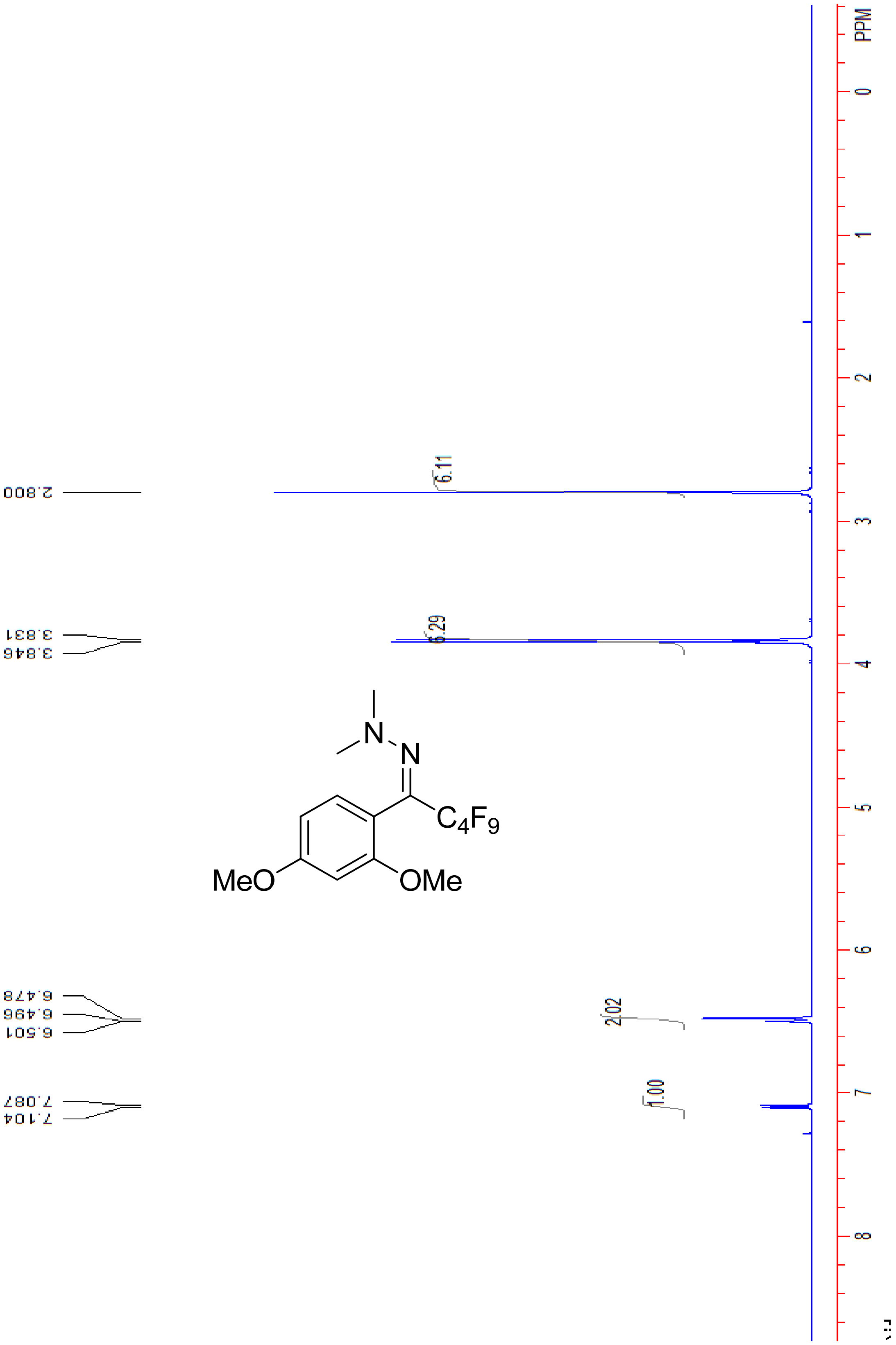
^{13}C NMR spectrum of **3at**



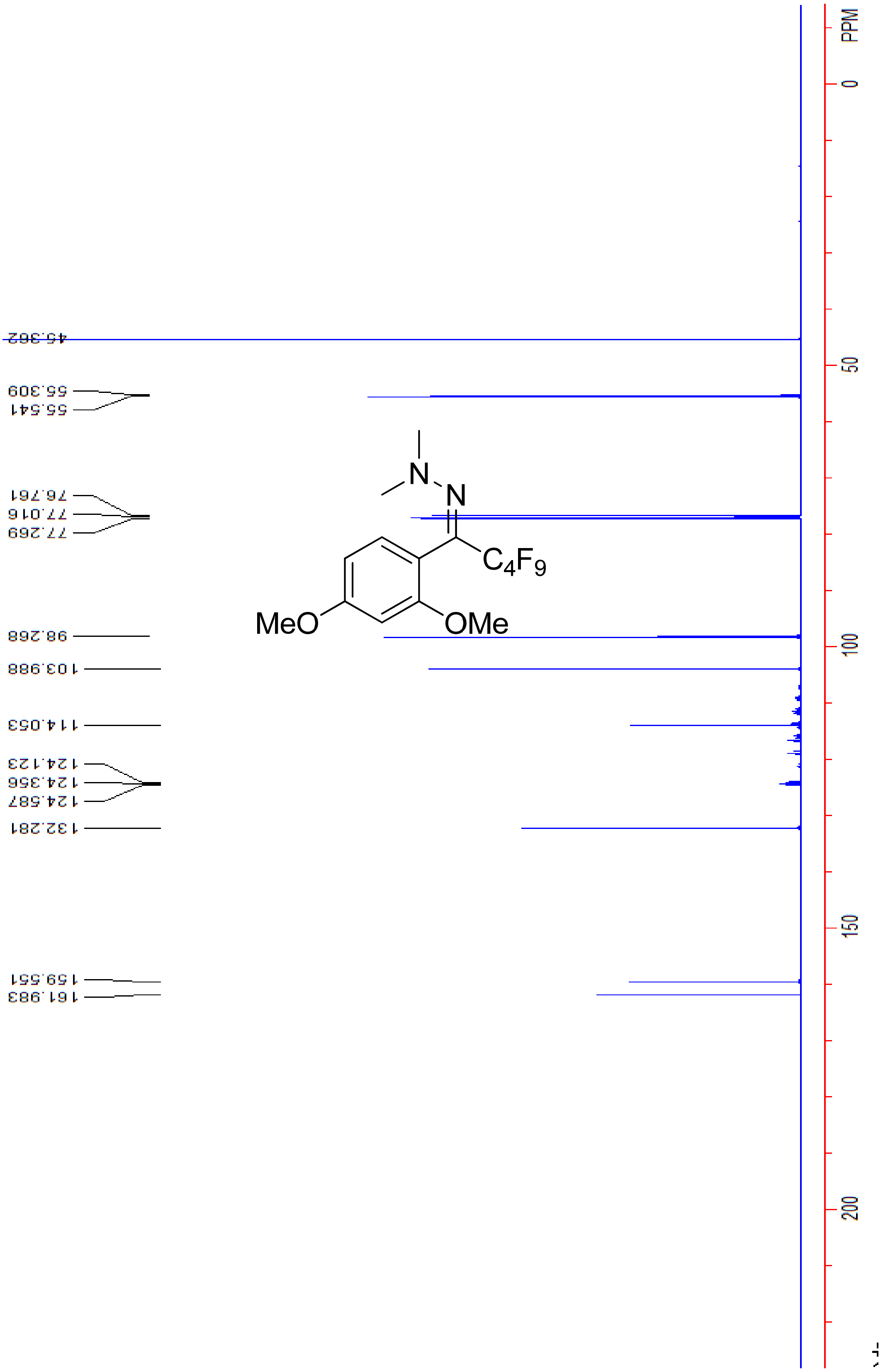
^{19}F NMR spectrum of **3at**



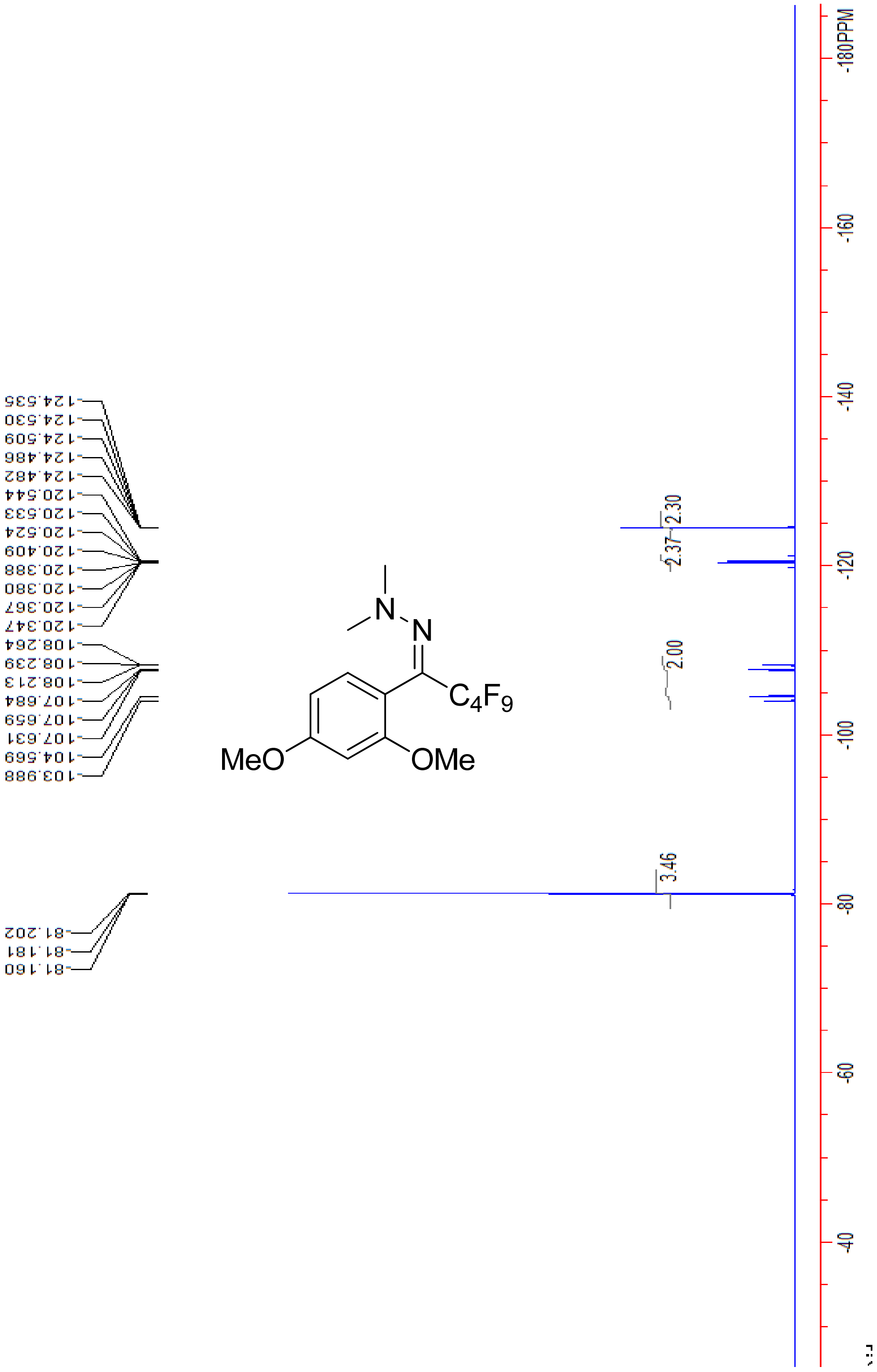
^{1}H NMR spectrum of **3au**



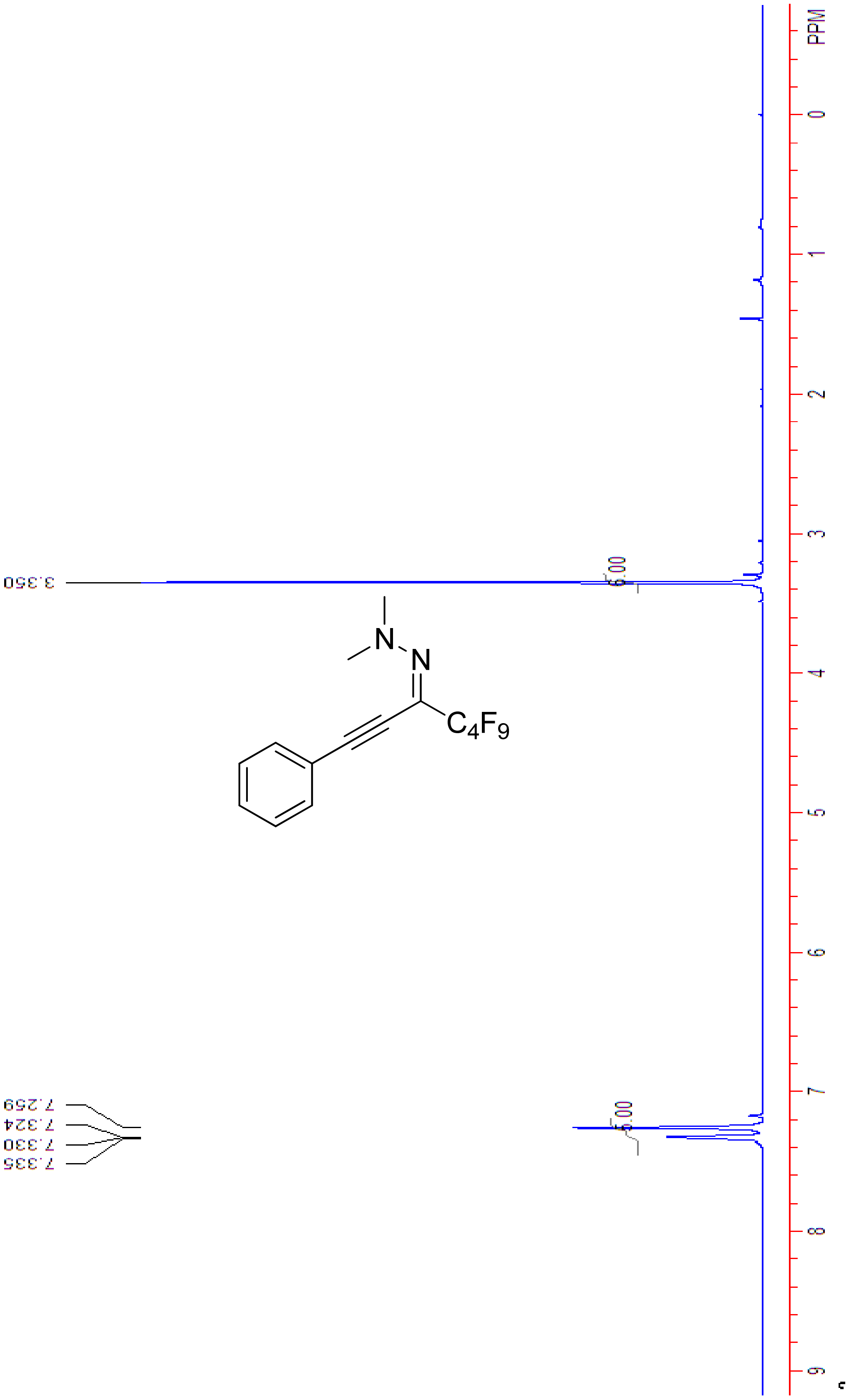
^{13}C NMR spectrum of **3au**



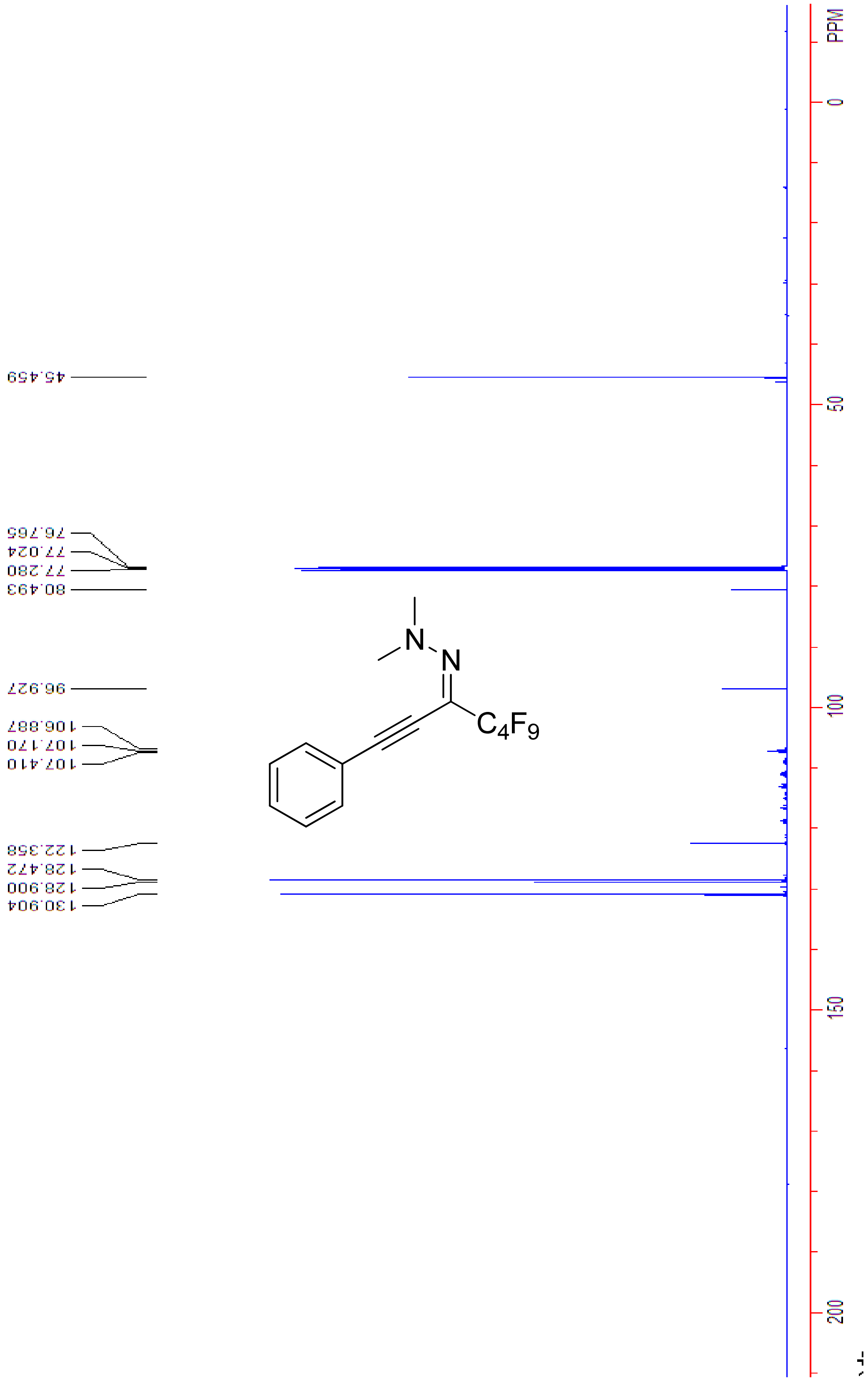
^{19}F NMR spectrum of **3au**



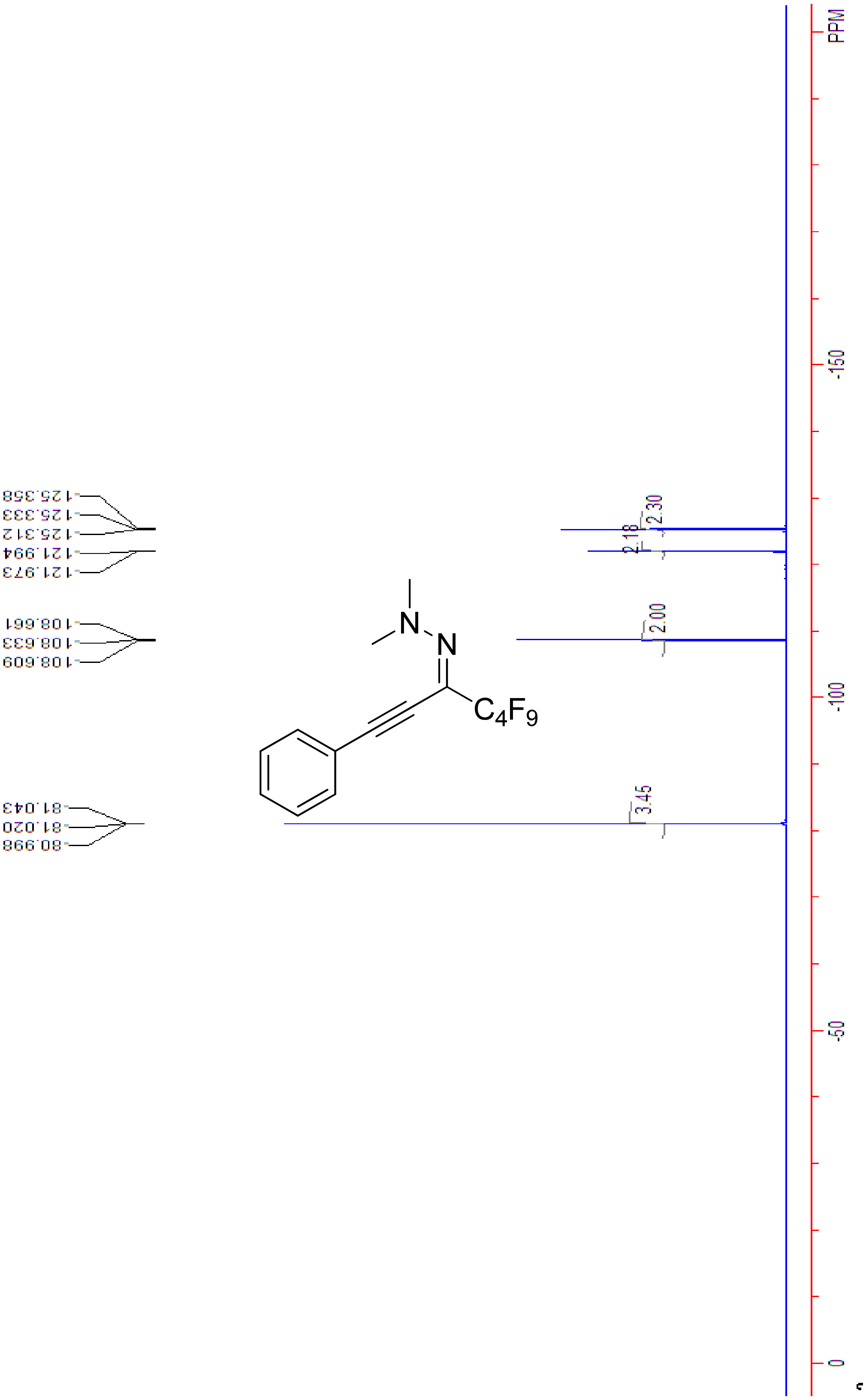
^{1}H NMR spectrum of **4a**



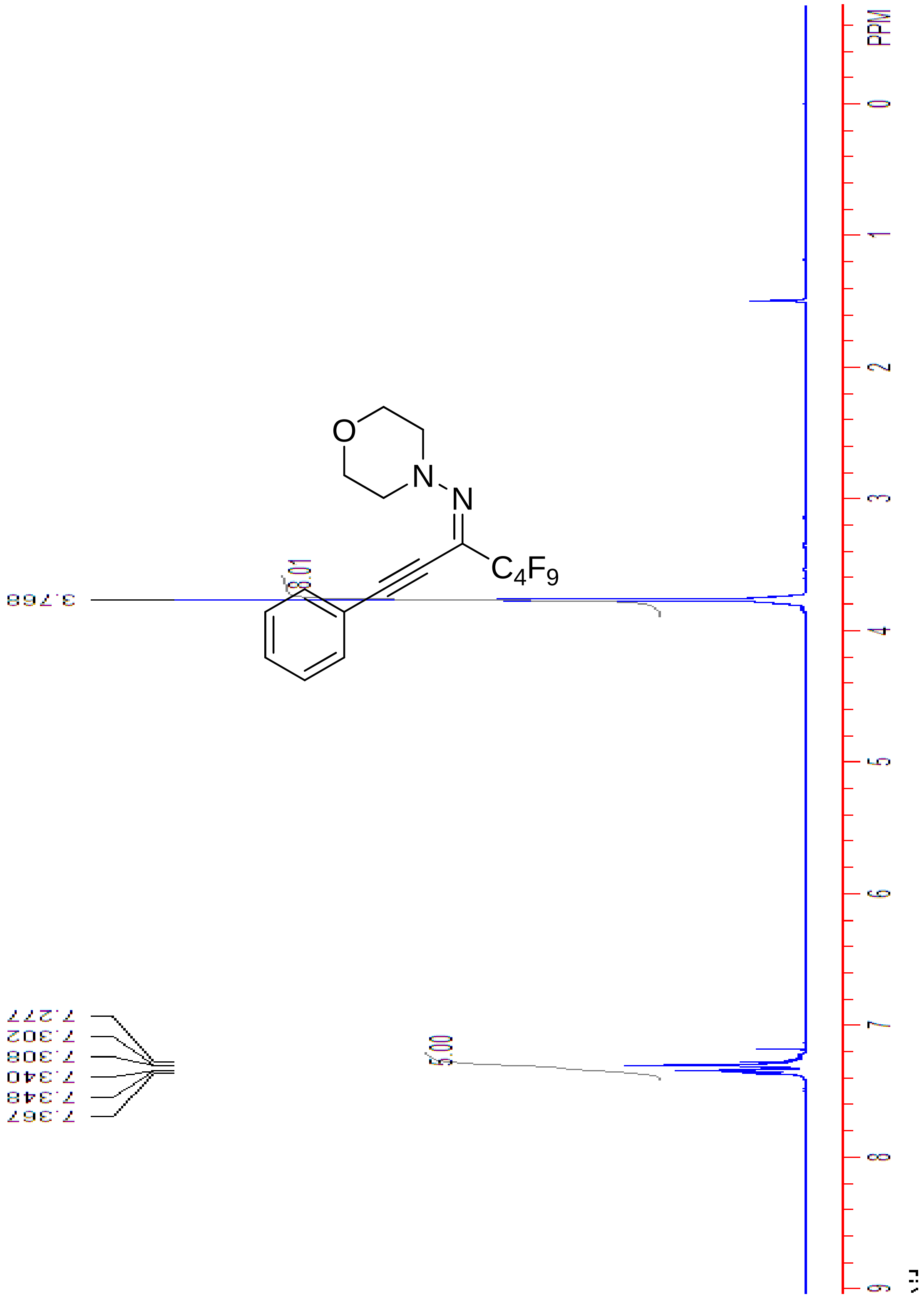
^{13}C NMR spectrum of **4a**



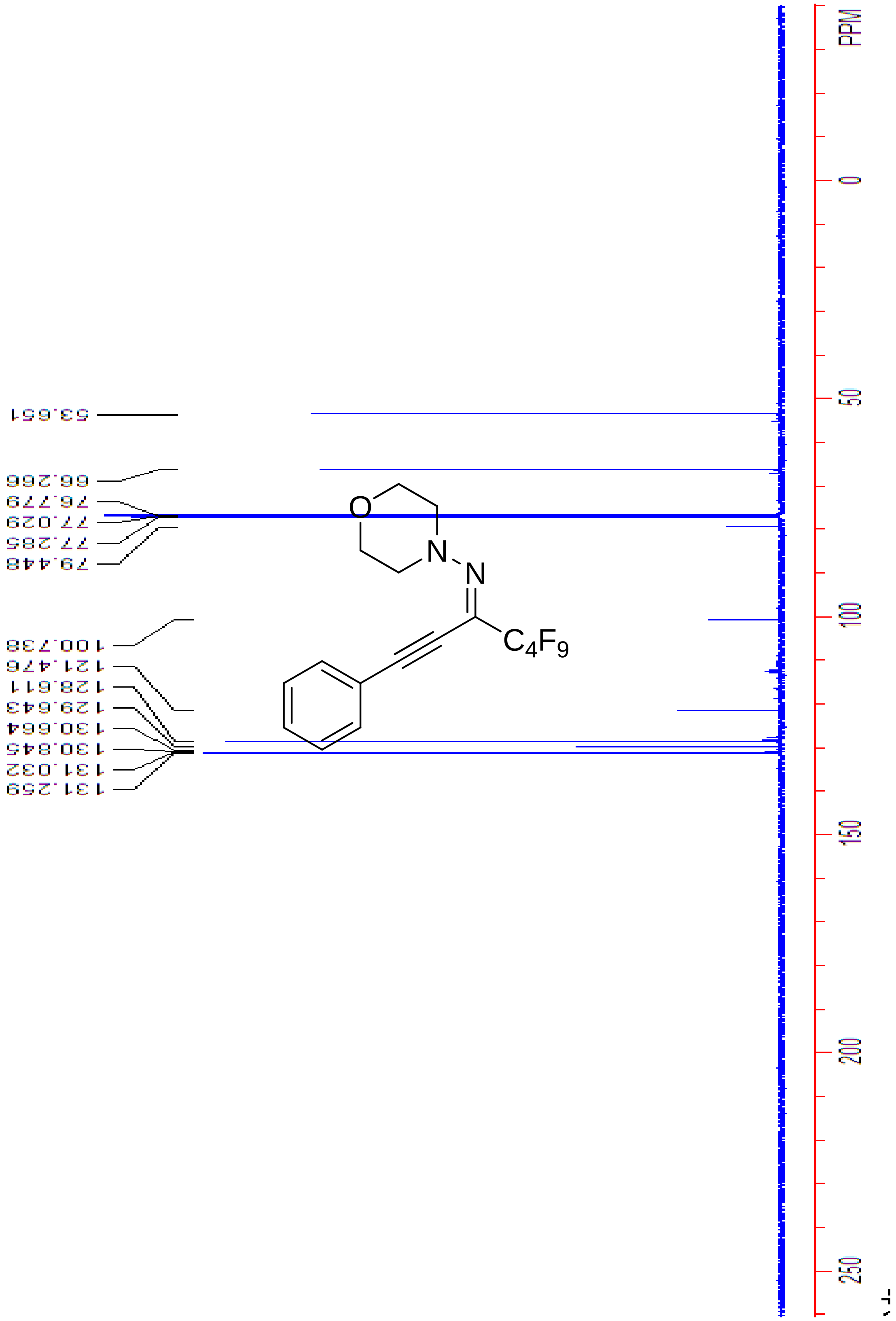
^{19}F NMR spectrum of **4a**



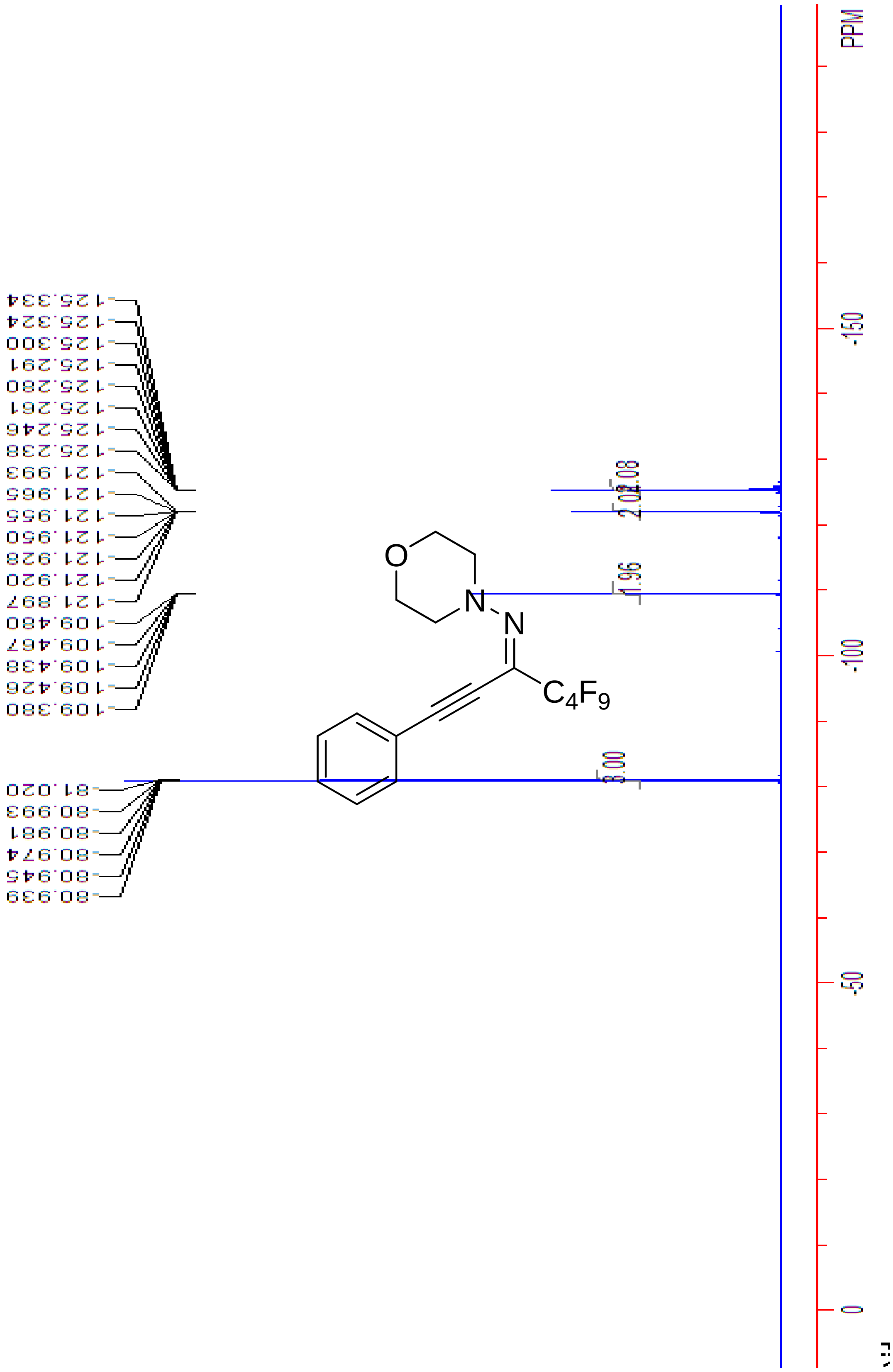
^{1}H NMR spectrum of **4b**



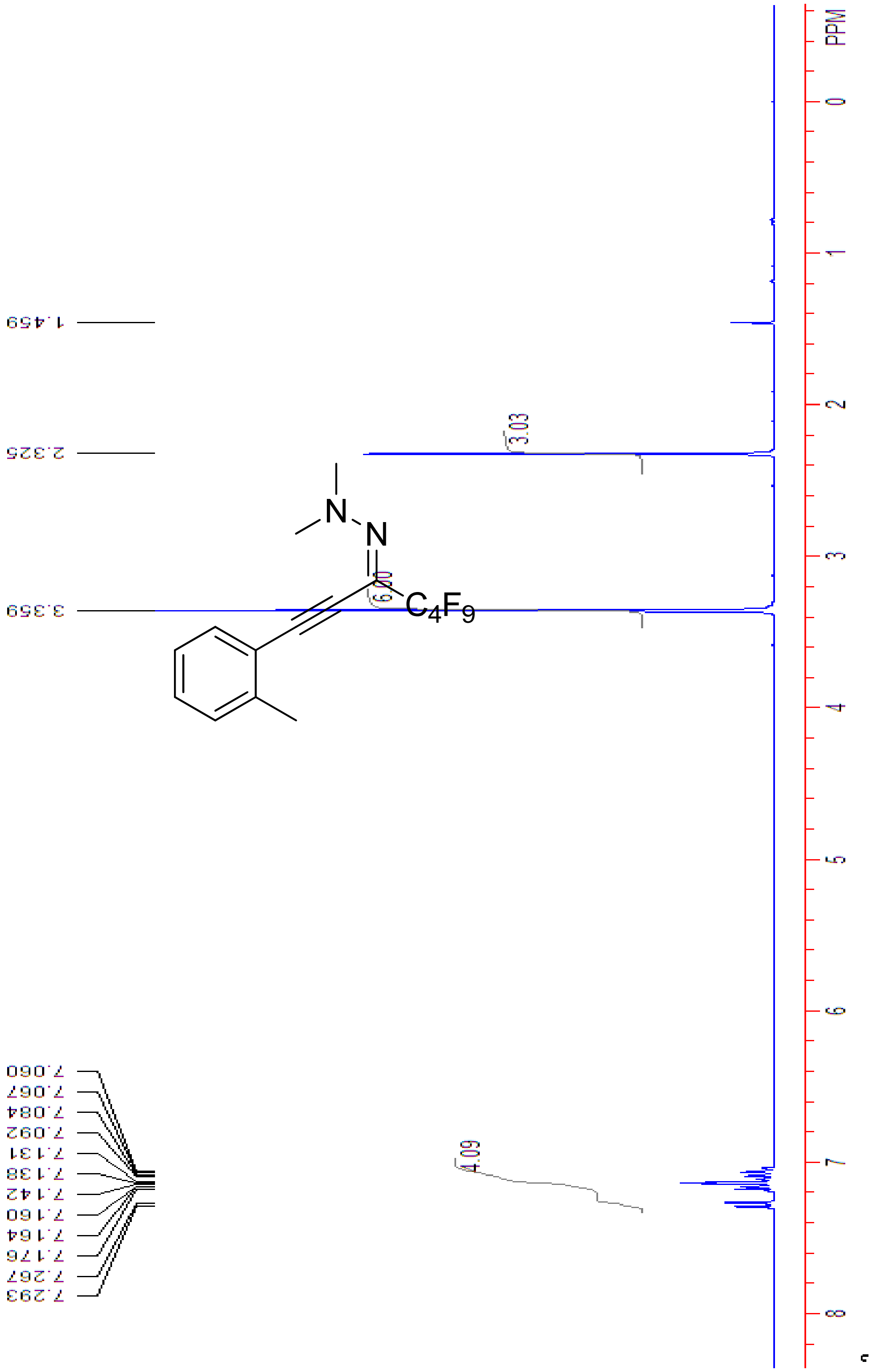
^{13}C NMR spectrum of **4b**



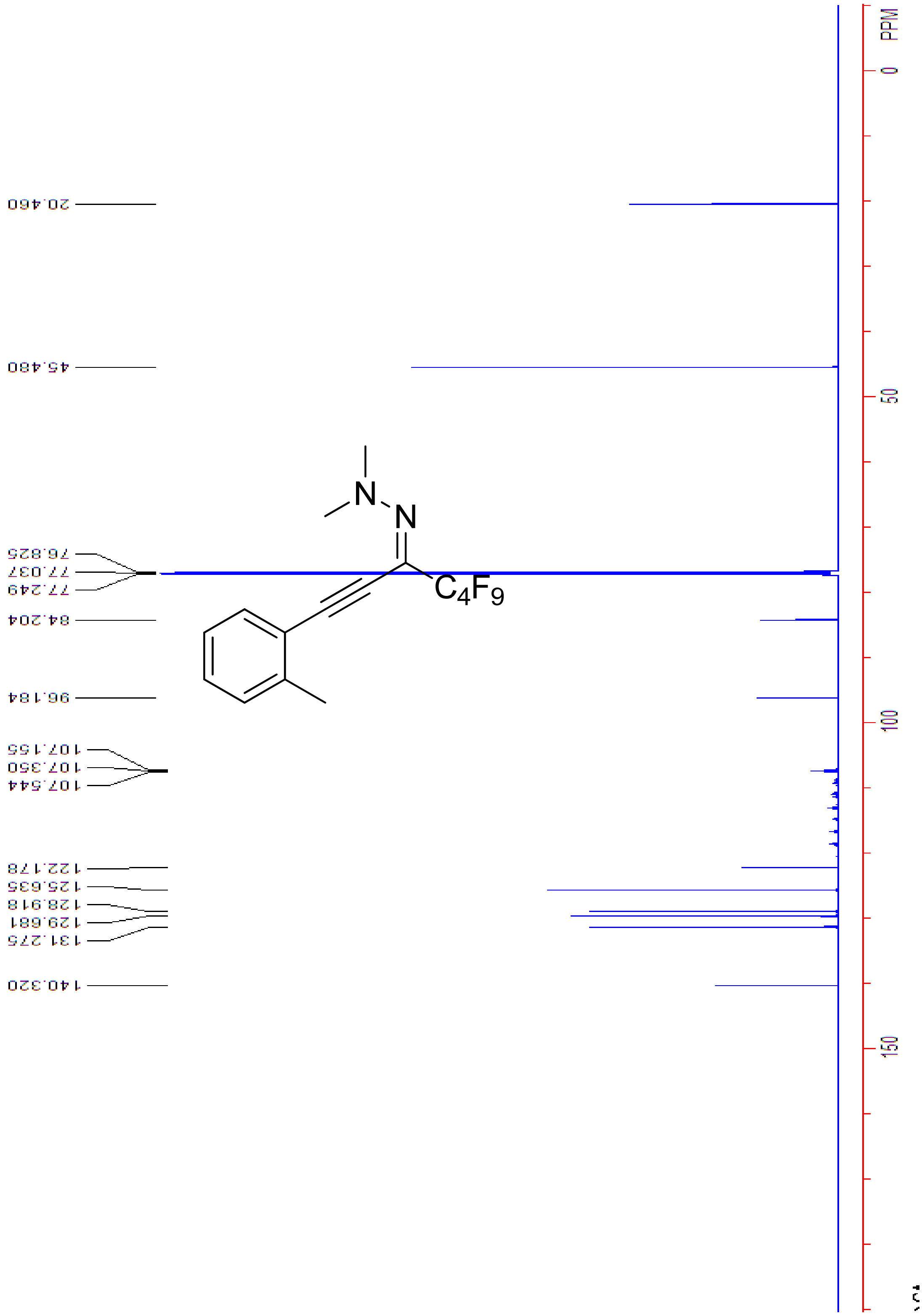
^{19}F NMR spectrum of **4b**



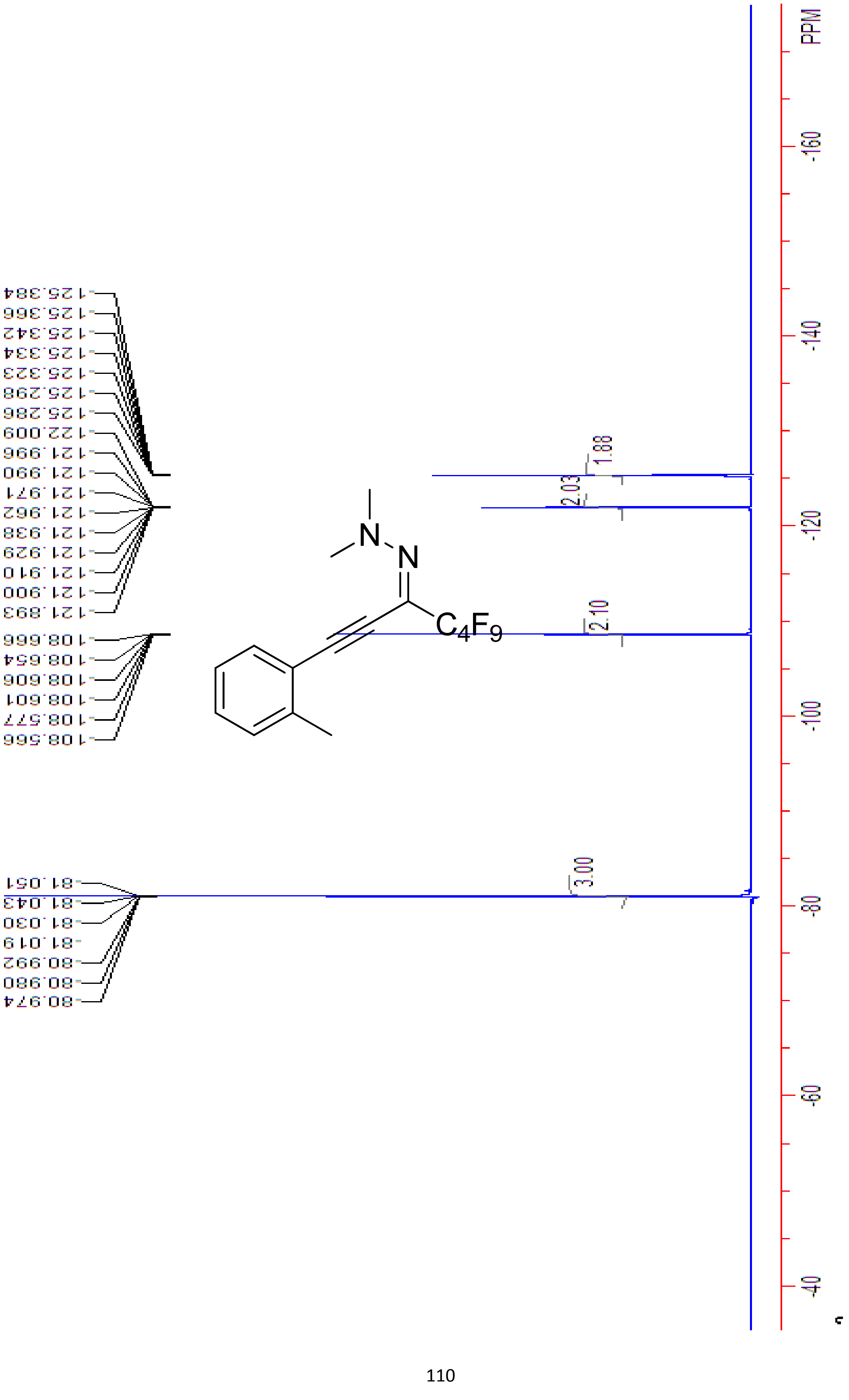
^{1}H NMR spectrum of **4c**



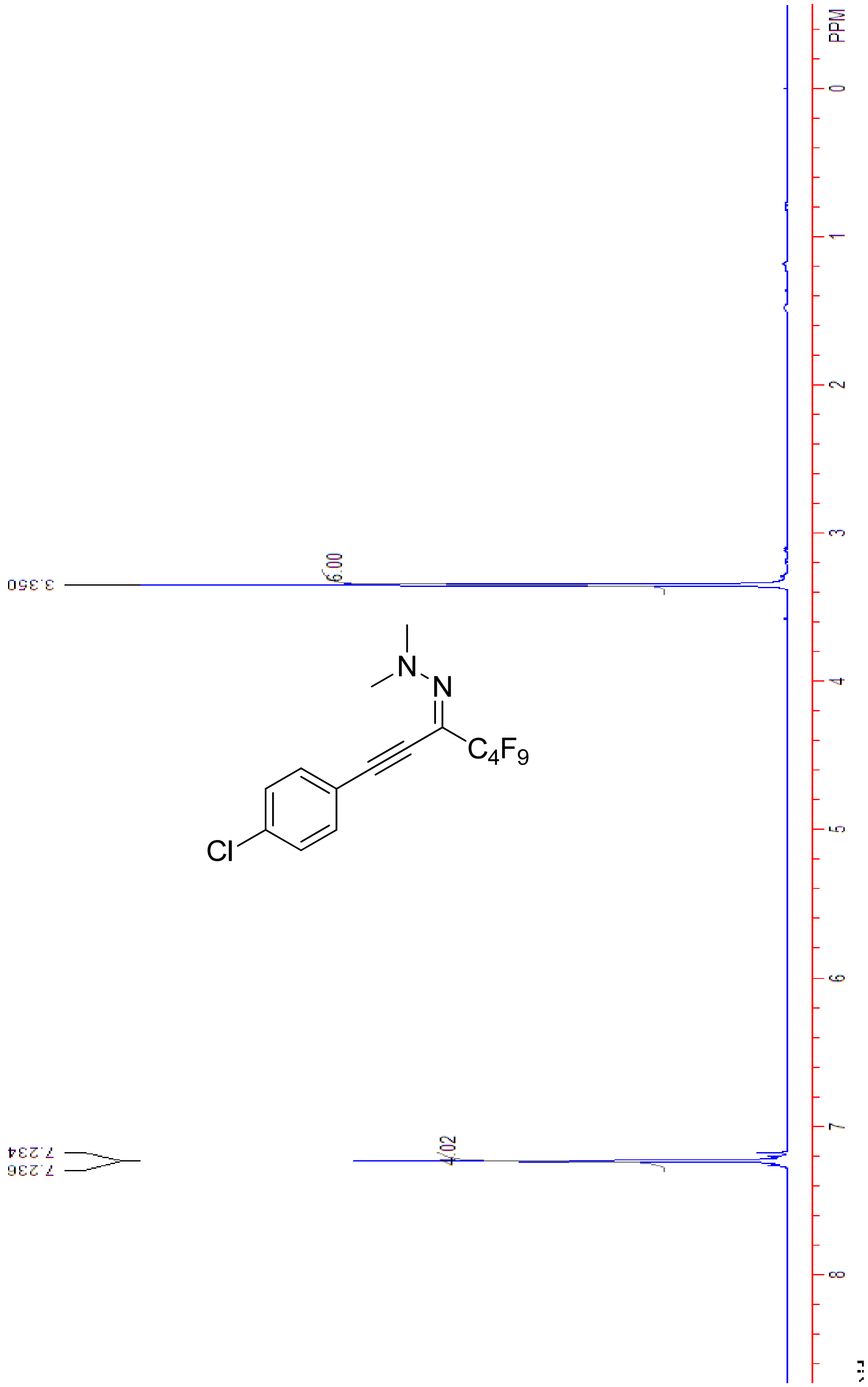
^{13}C NMR spectrum of **4c**



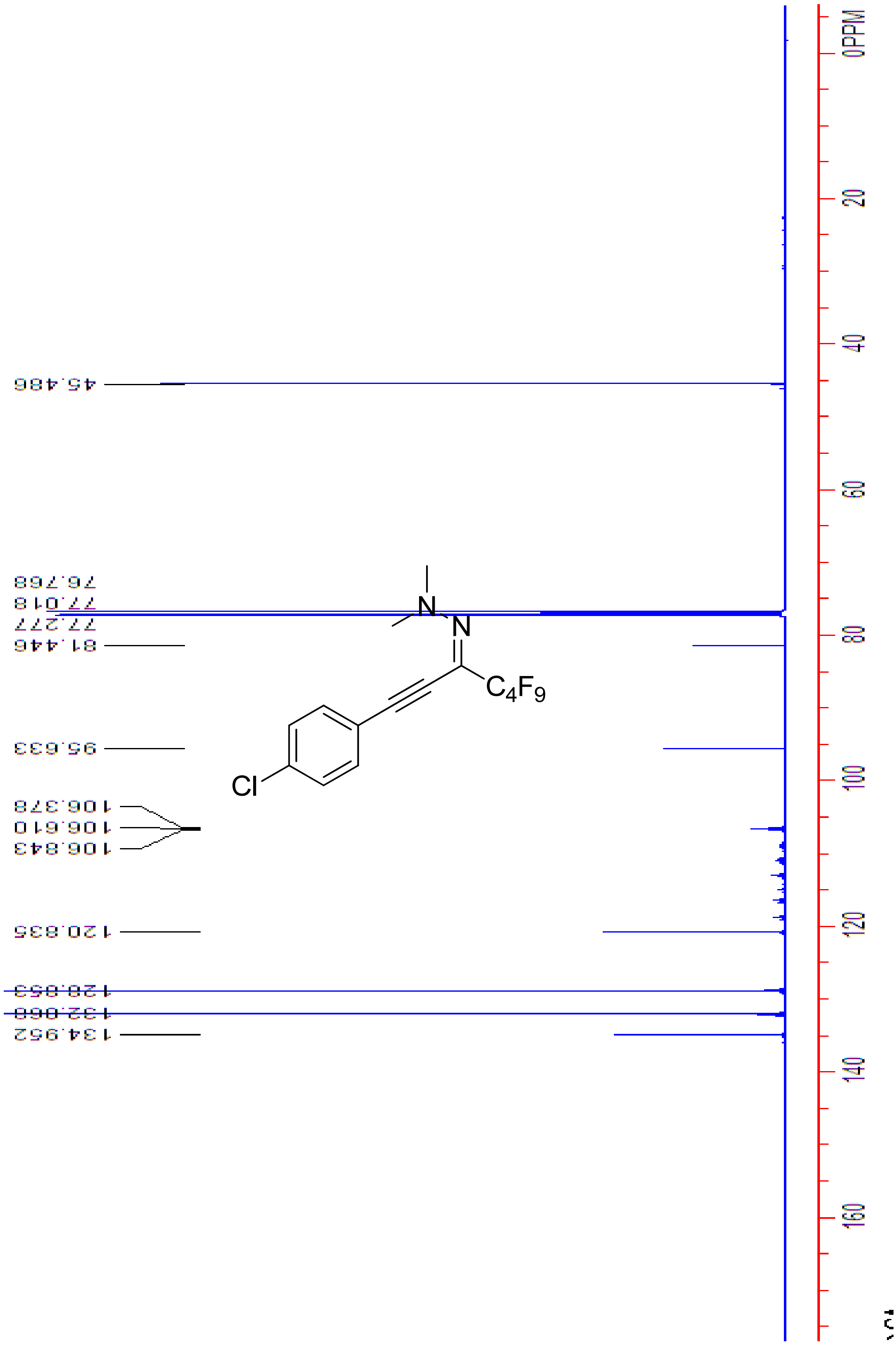
^{19}F NMR spectrum of **4c**



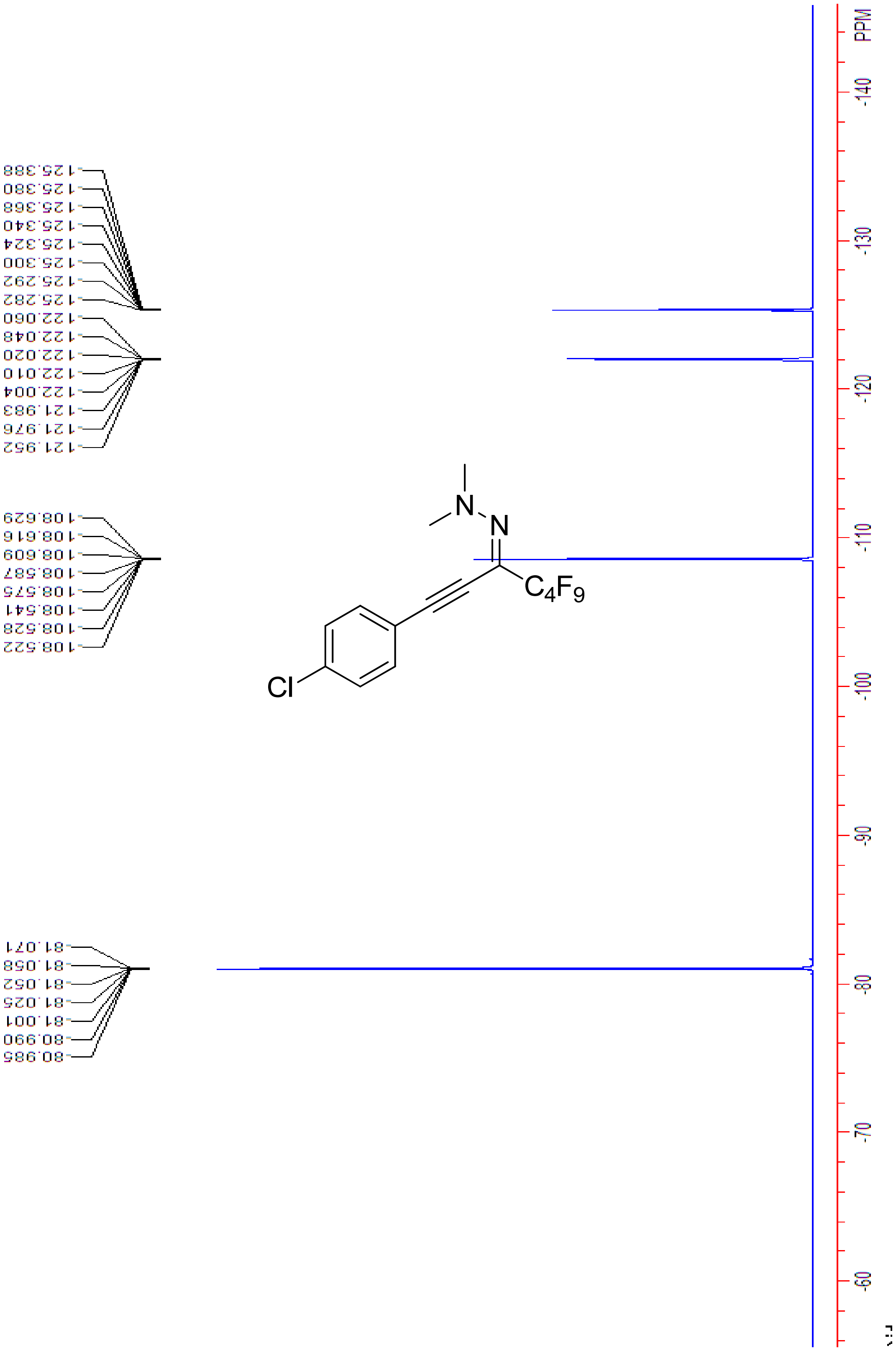
^{1}H NMR spectrum of **4d**



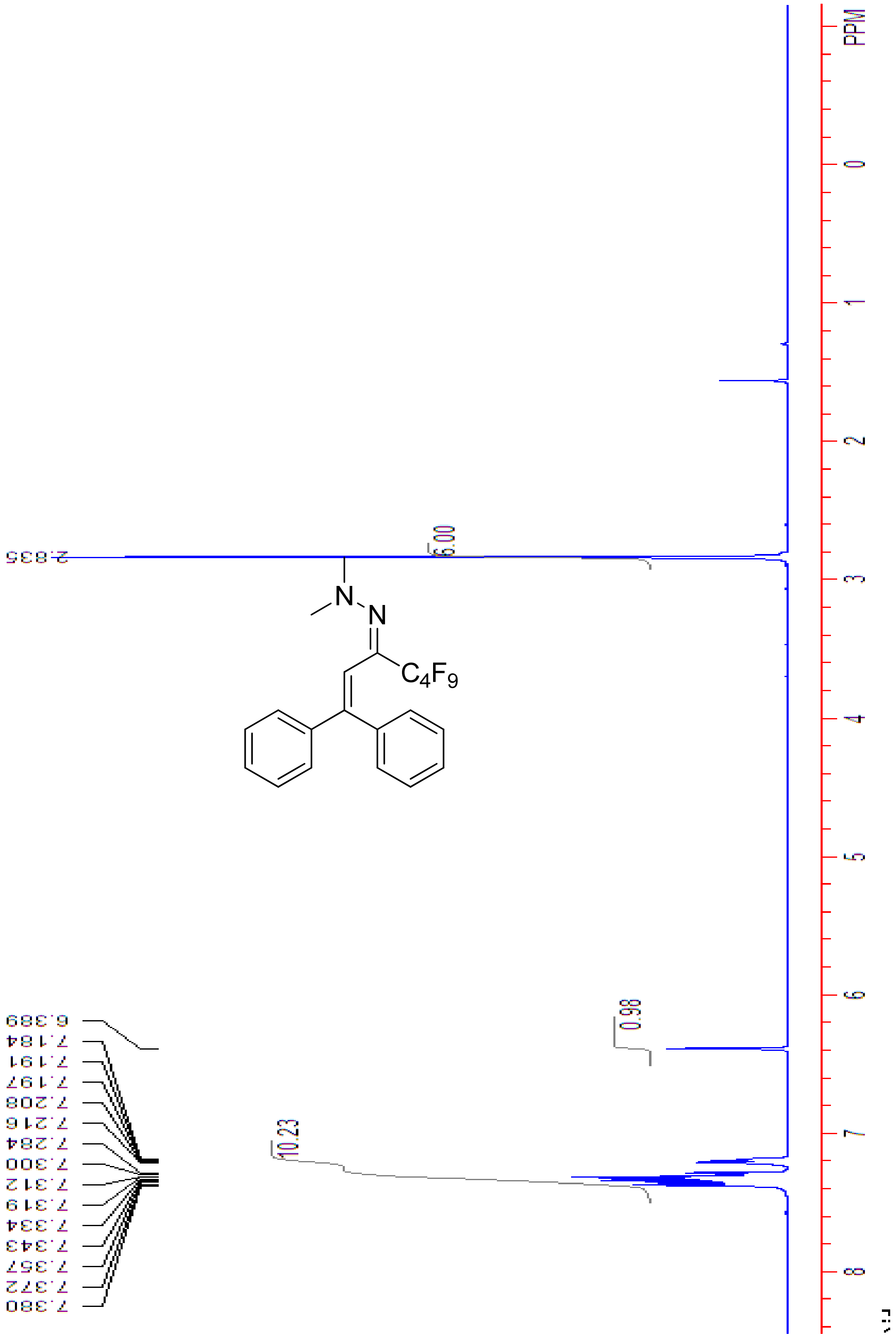
^{13}C NMR spectrum of **4d**



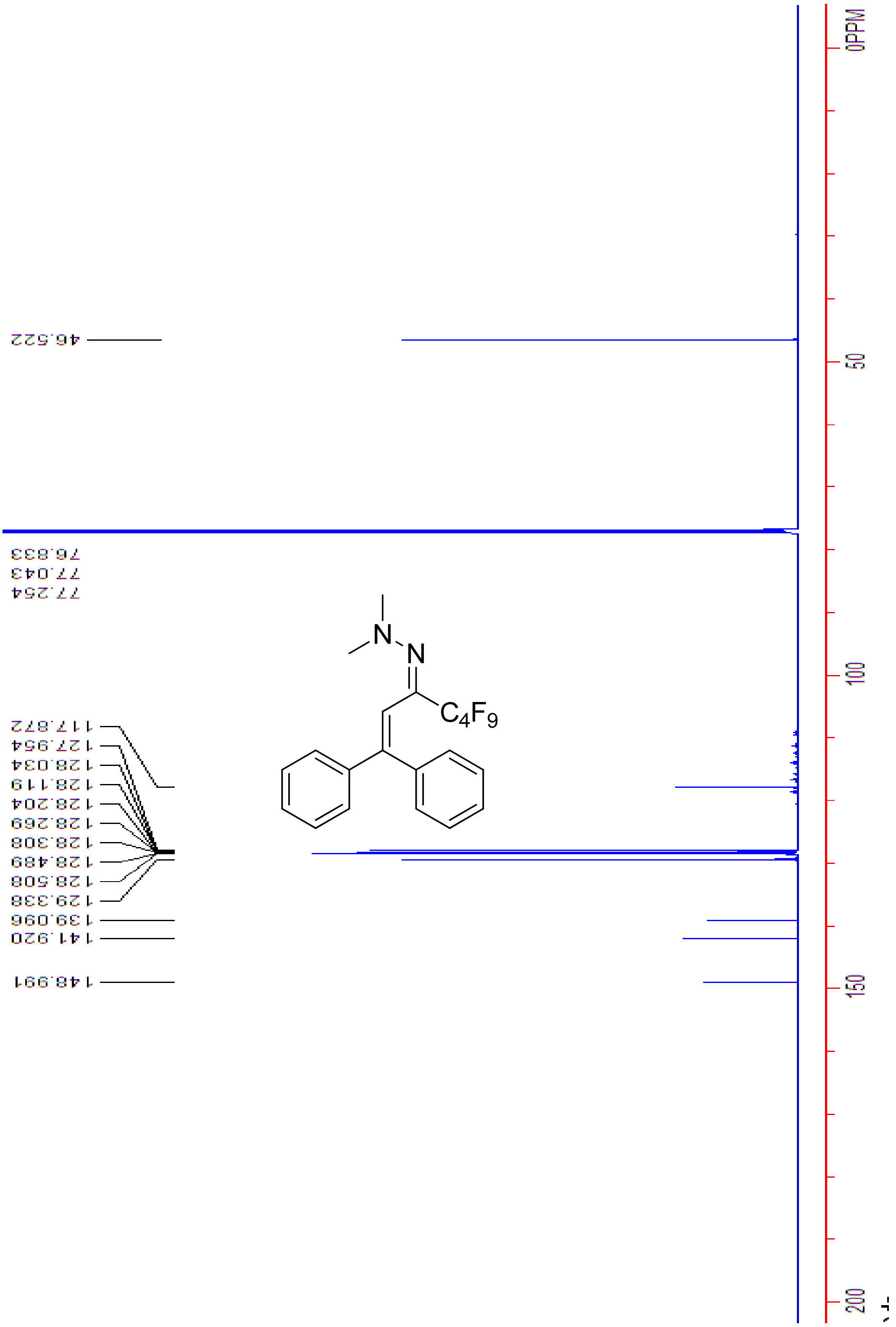
^{19}F NMR spectrum of **4d**



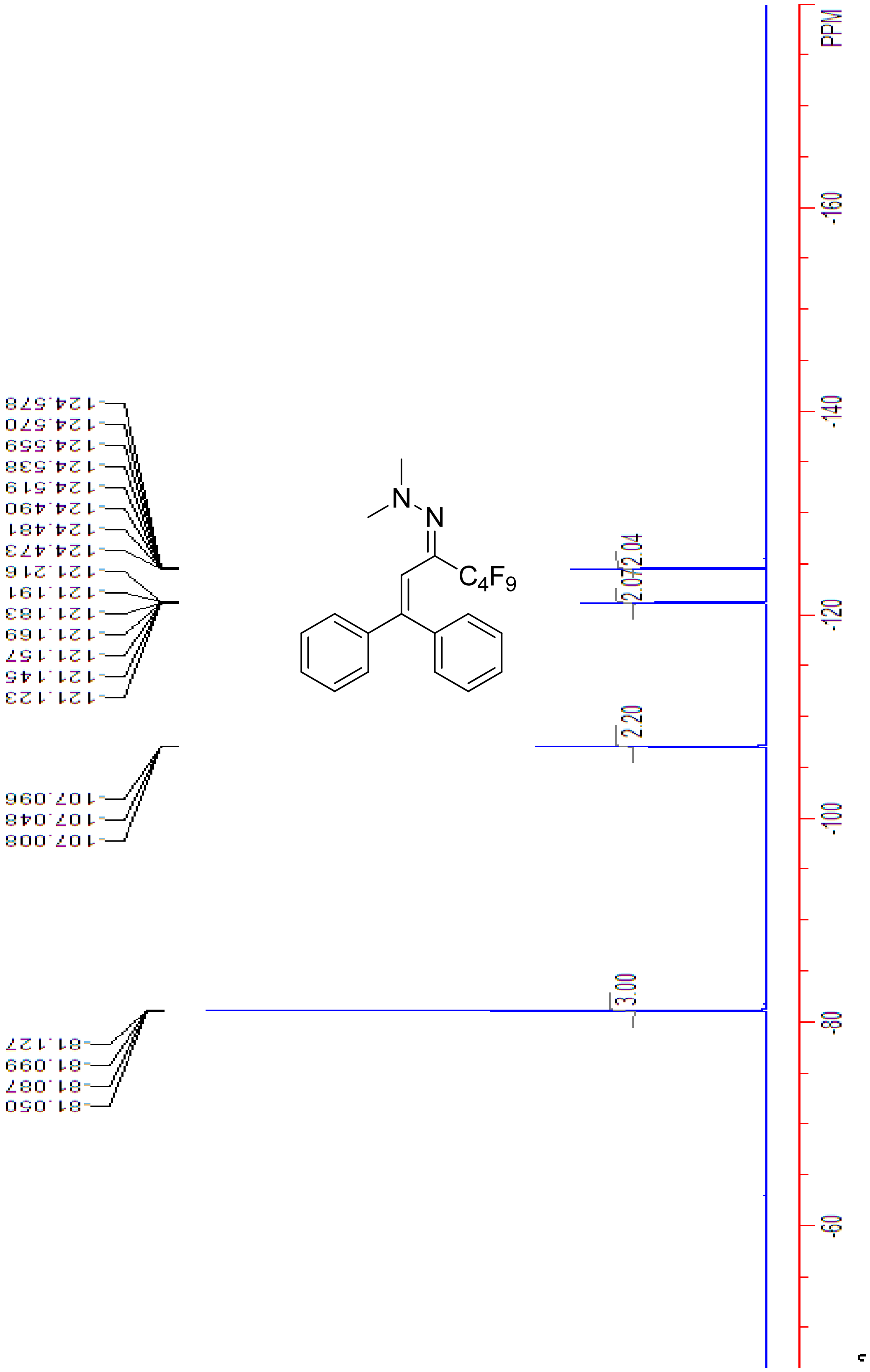
^{1}H NMR spectrum of **4e**



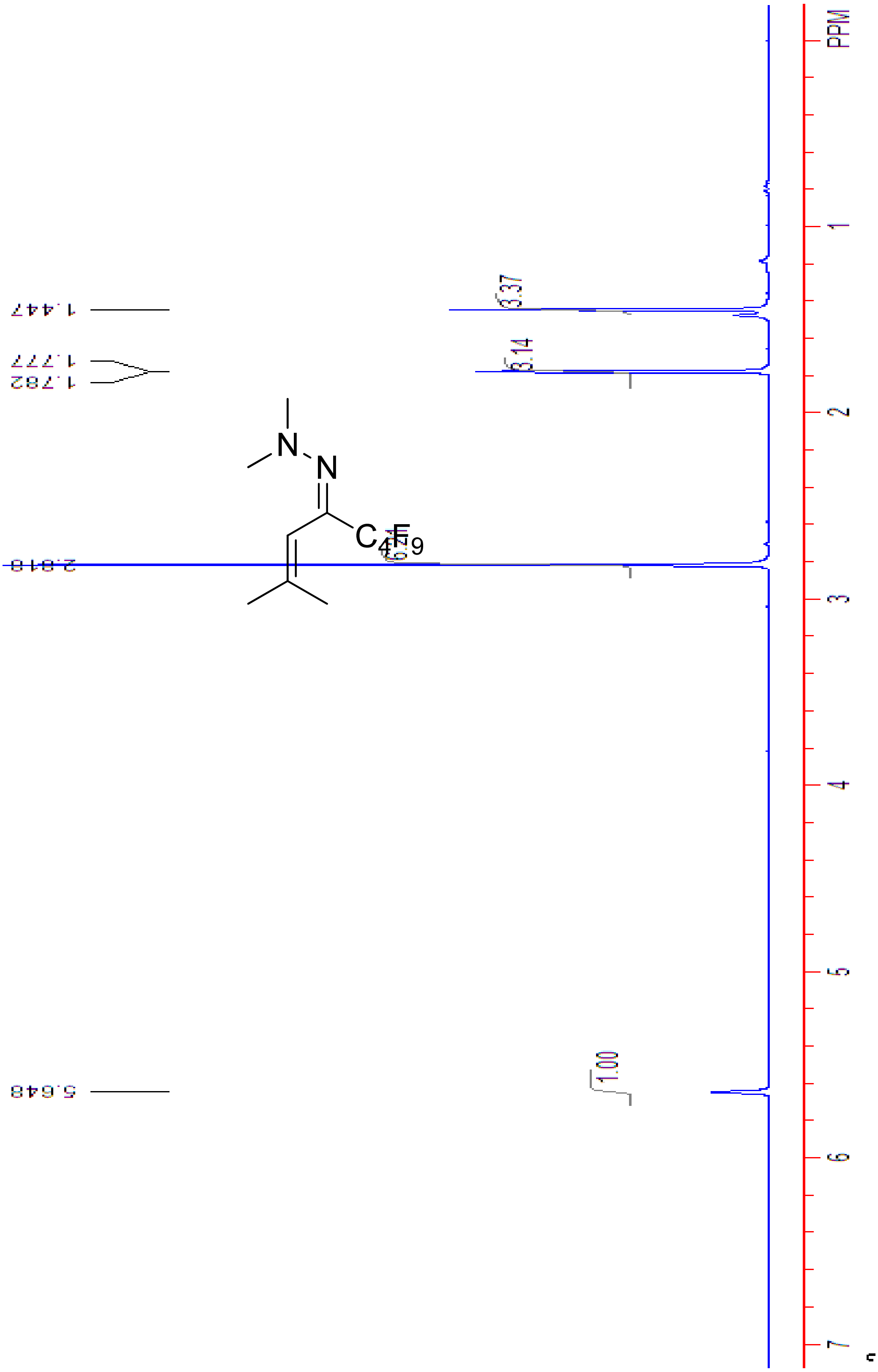
^{13}C NMR spectrum of **4e**



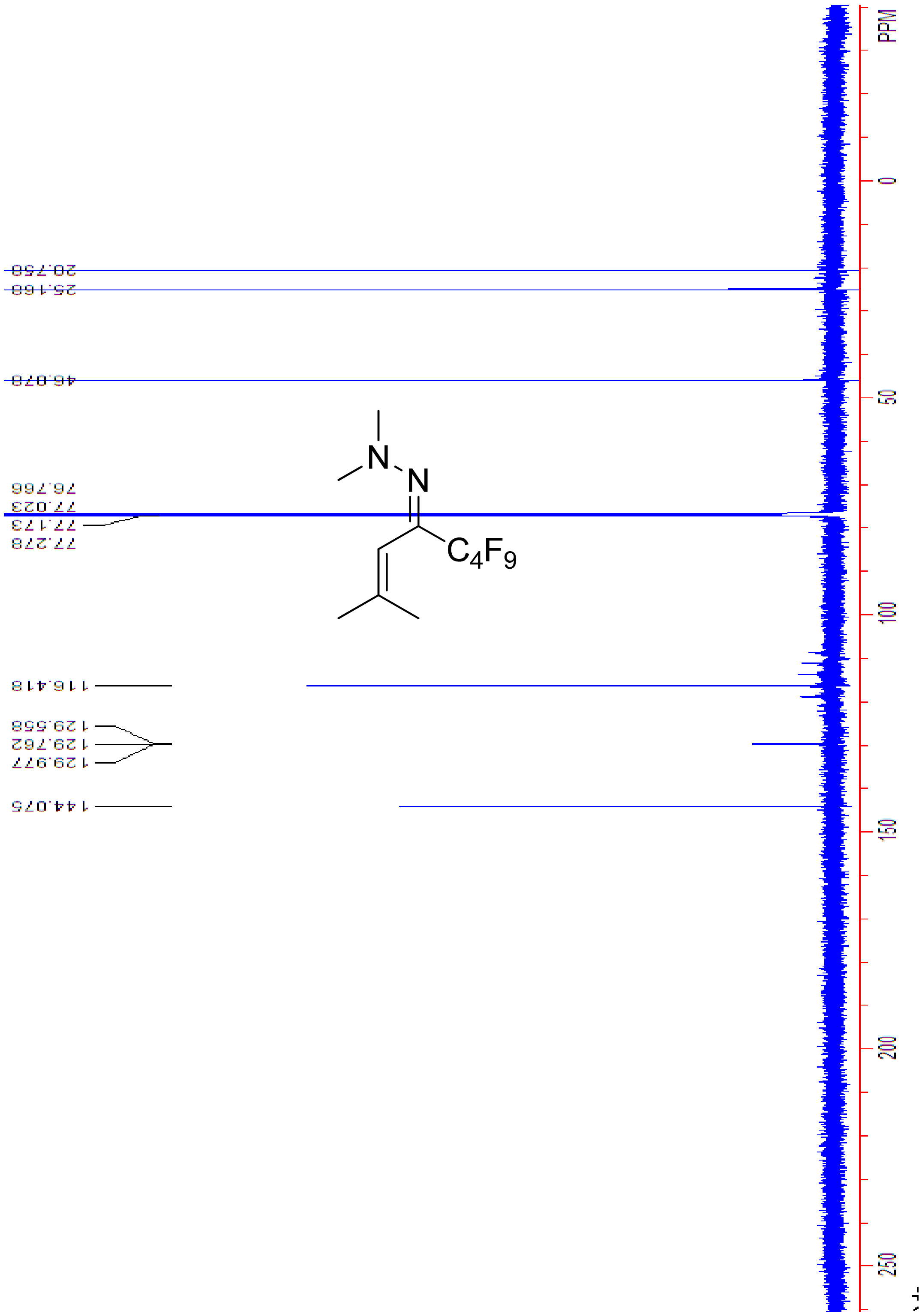
^{19}F NMR spectrum of **4e**



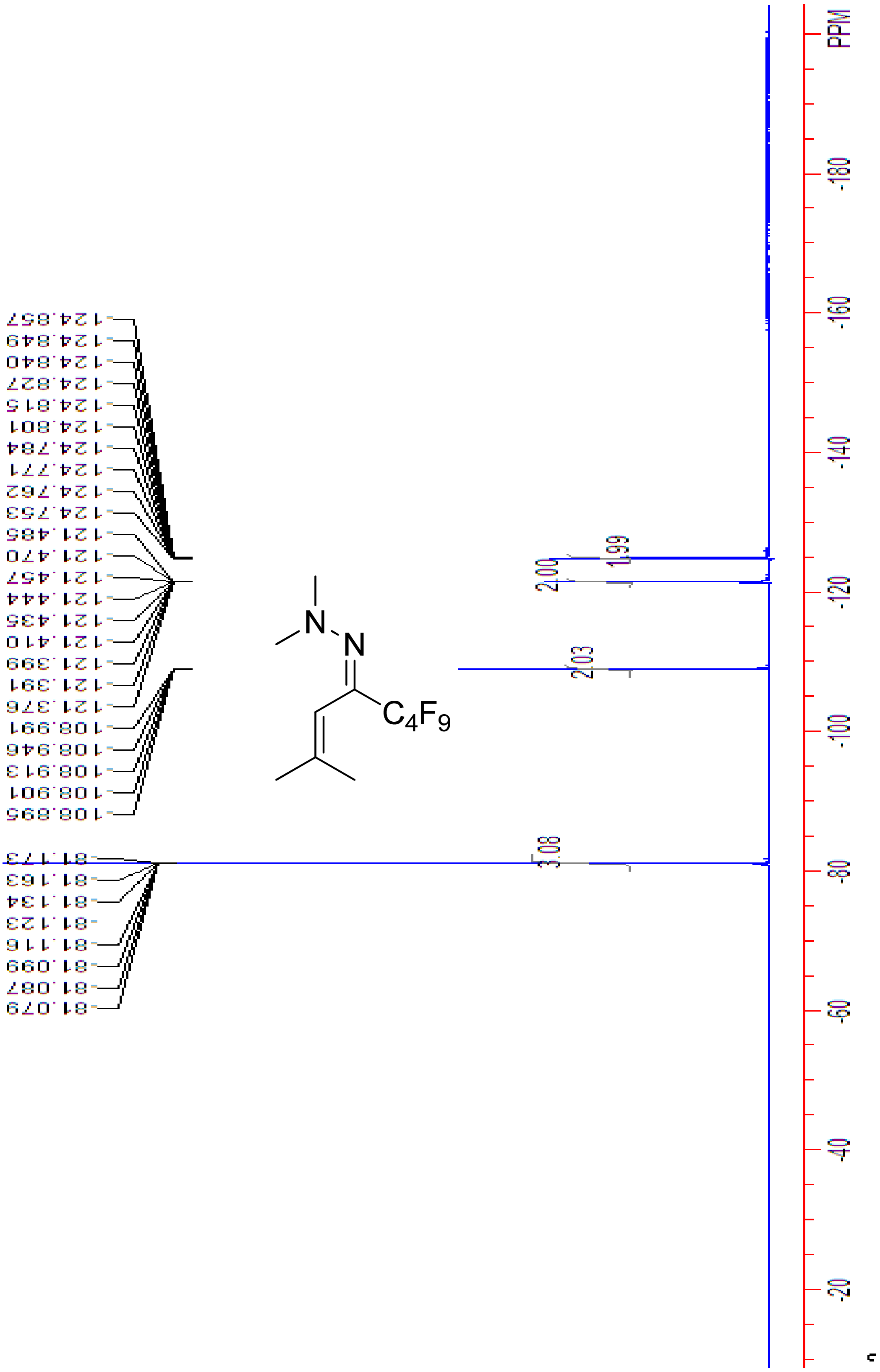
^{1}H NMR spectrum of **4f**



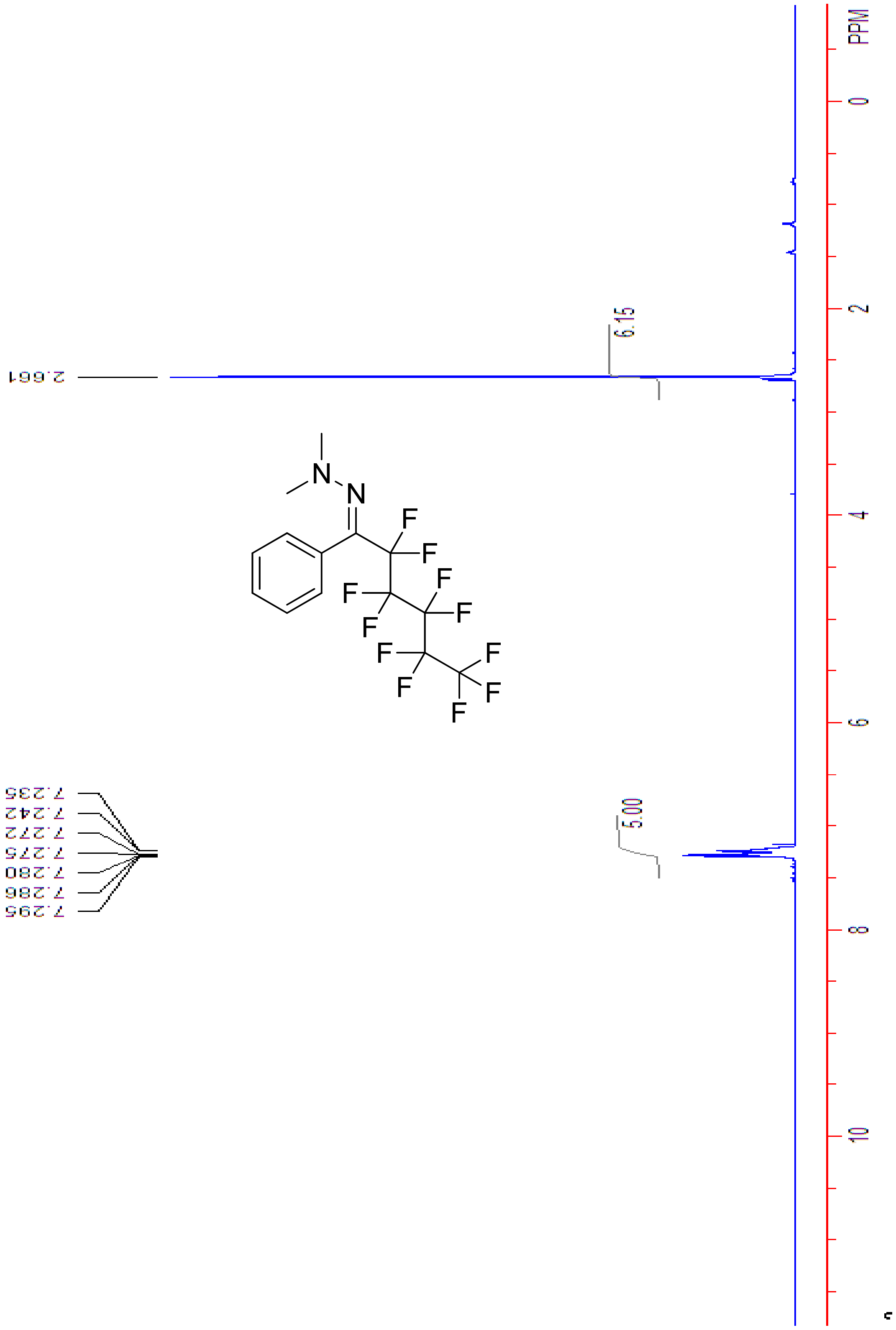
^{13}C NMR spectrum of **4f**



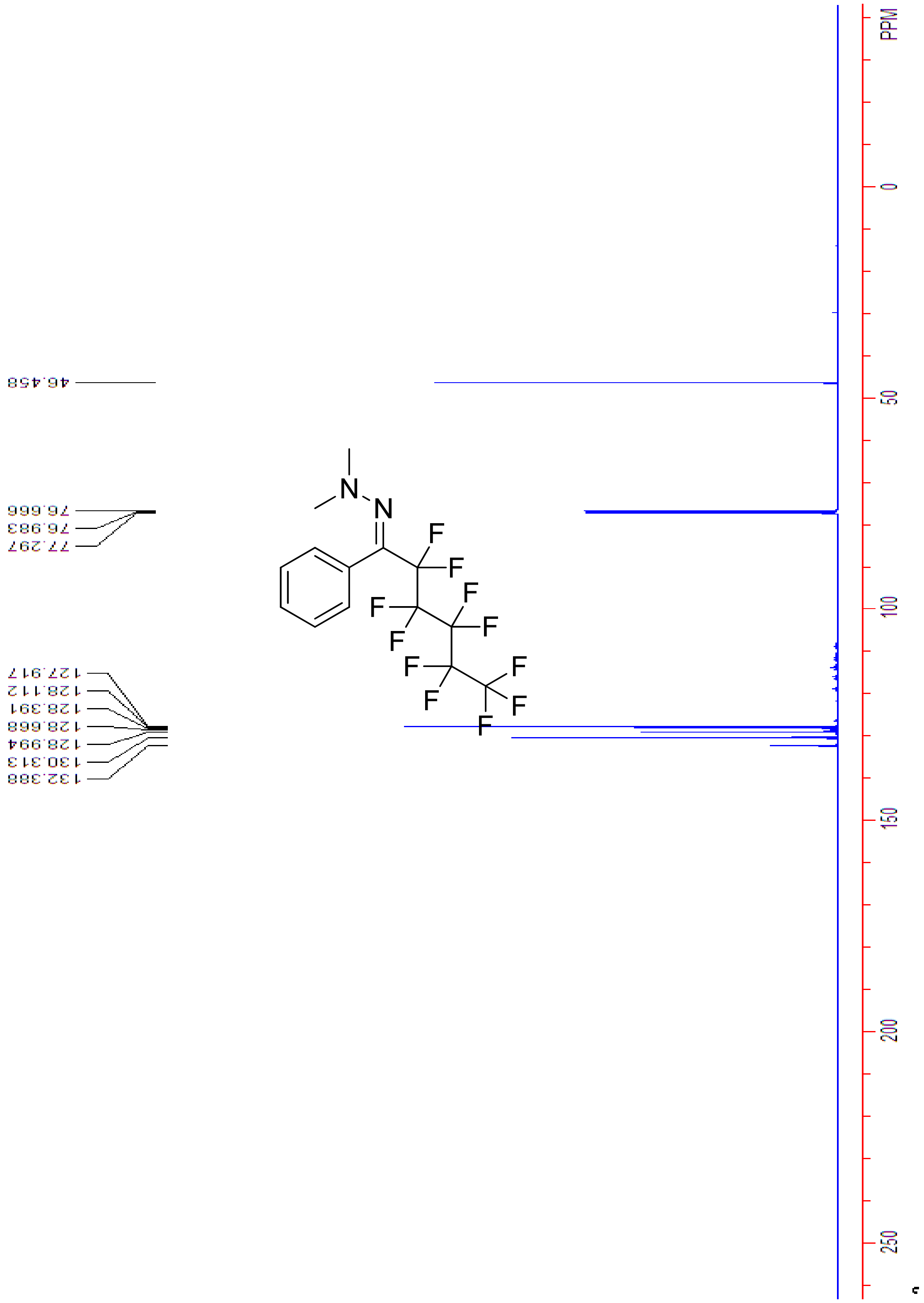
^{19}F NMR spectrum of **4f**



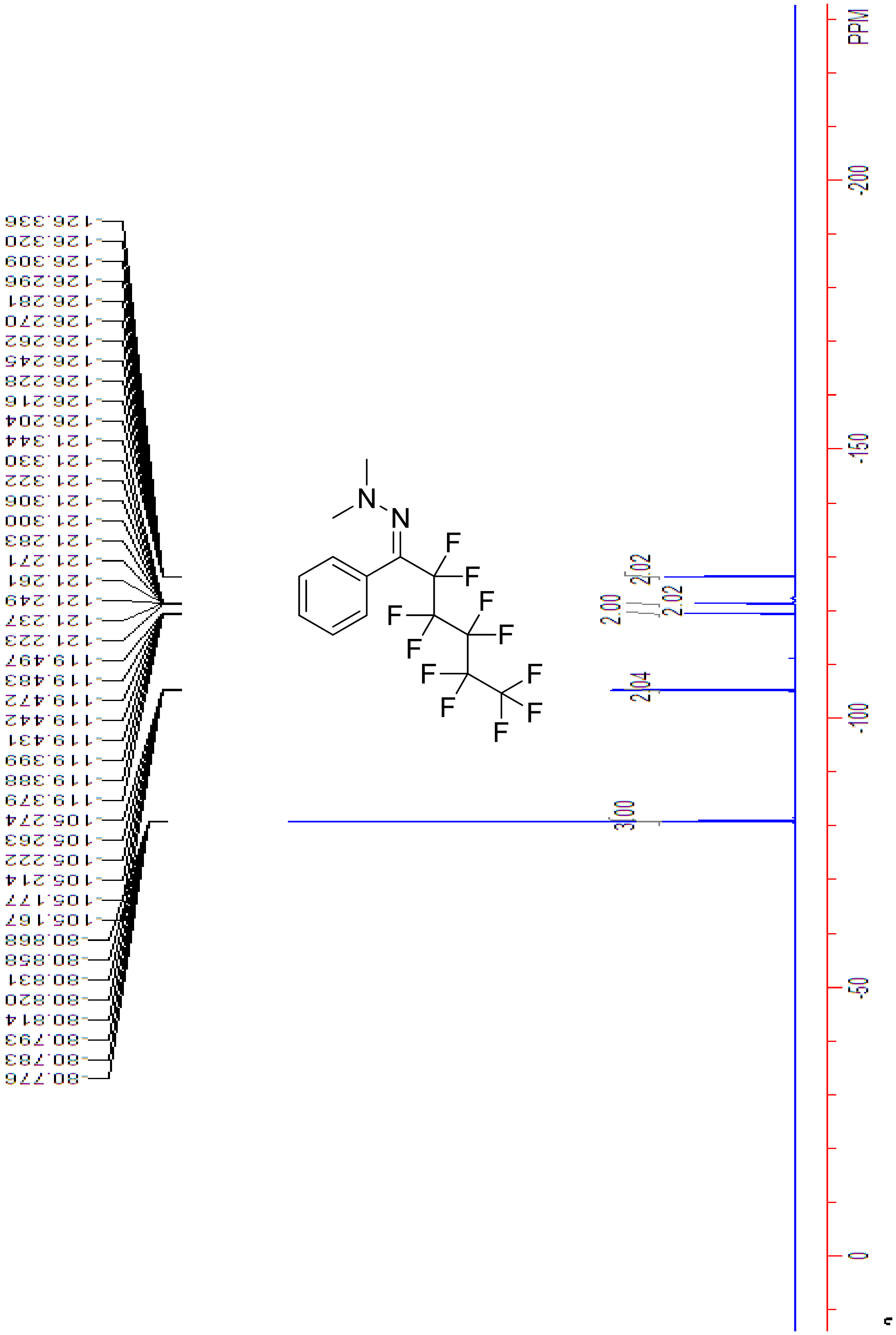
^{1}H NMR spectrum of **3ba**



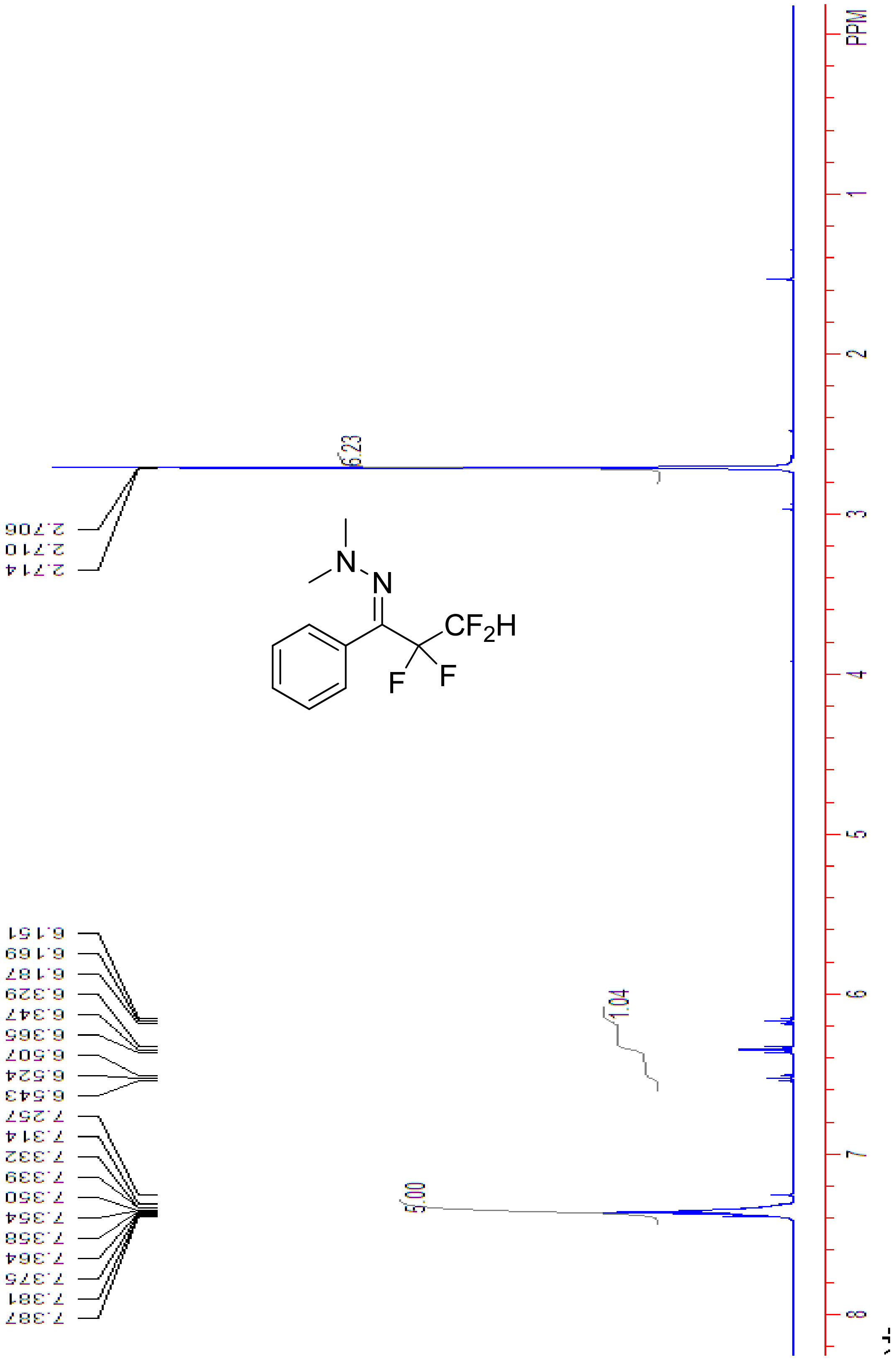
^{13}C NMR spectrum of **3ba**



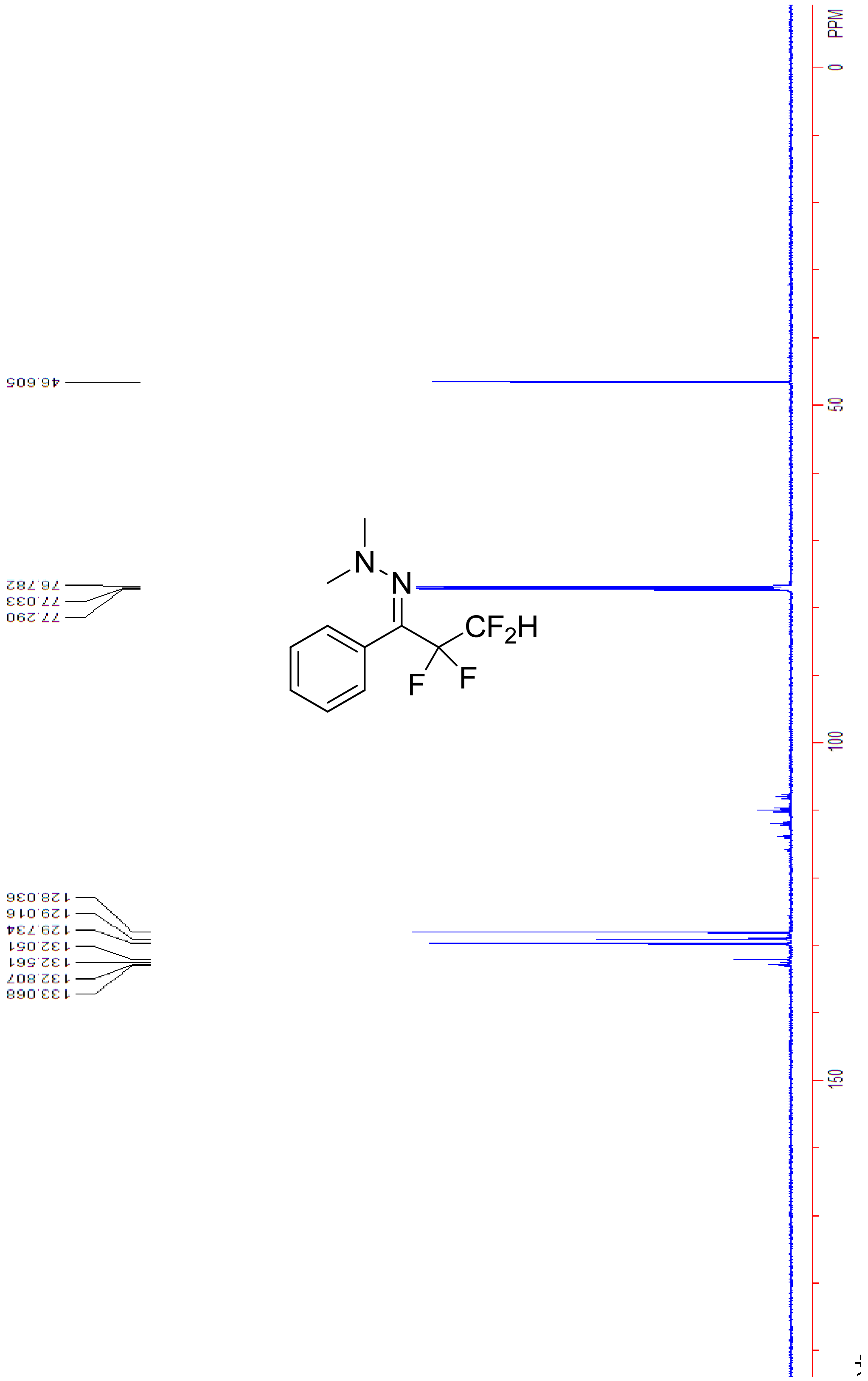
^{19}F NMR spectrum of **3ba**



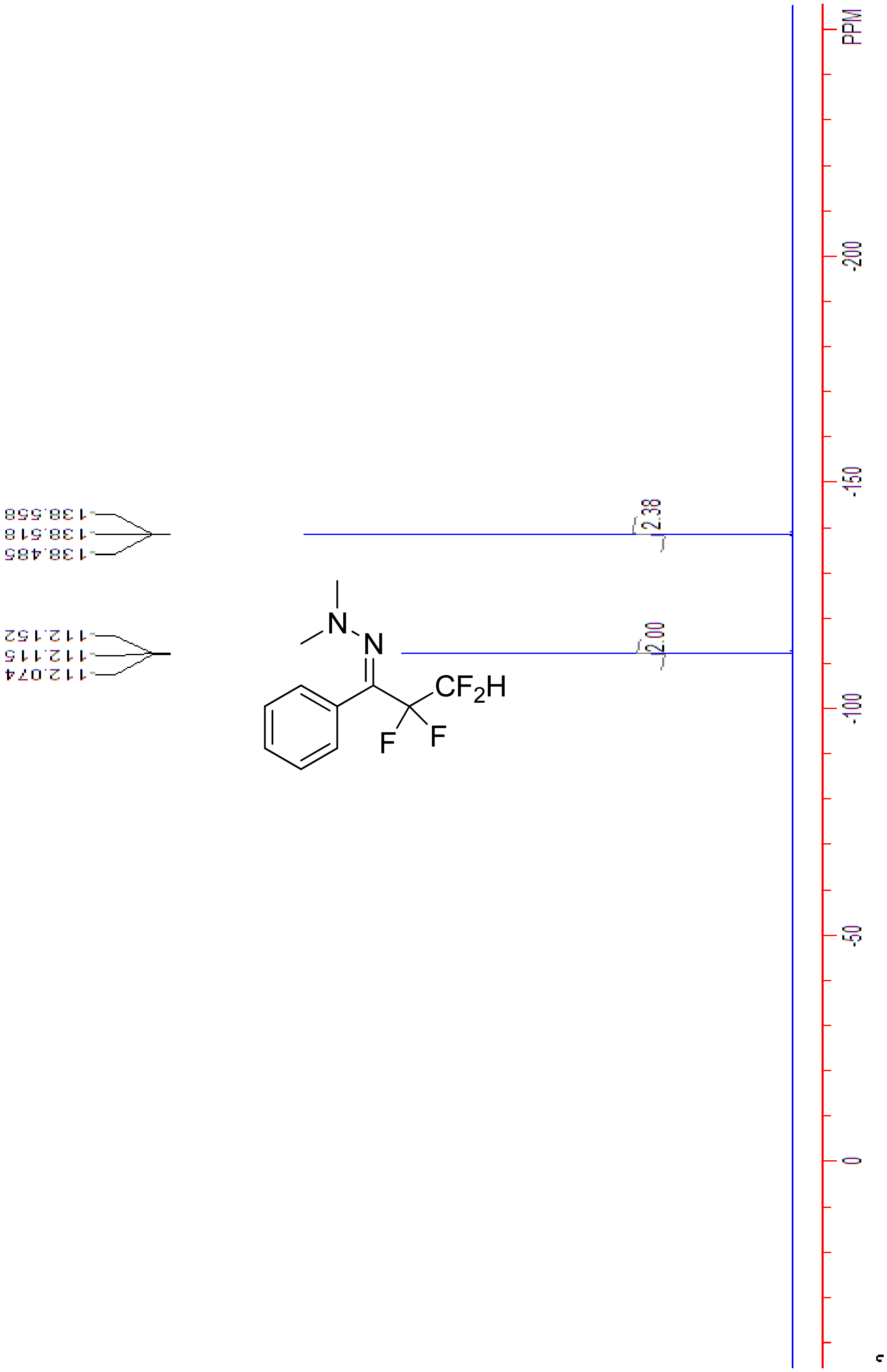
^{1}H NMR spectrum of **3da**



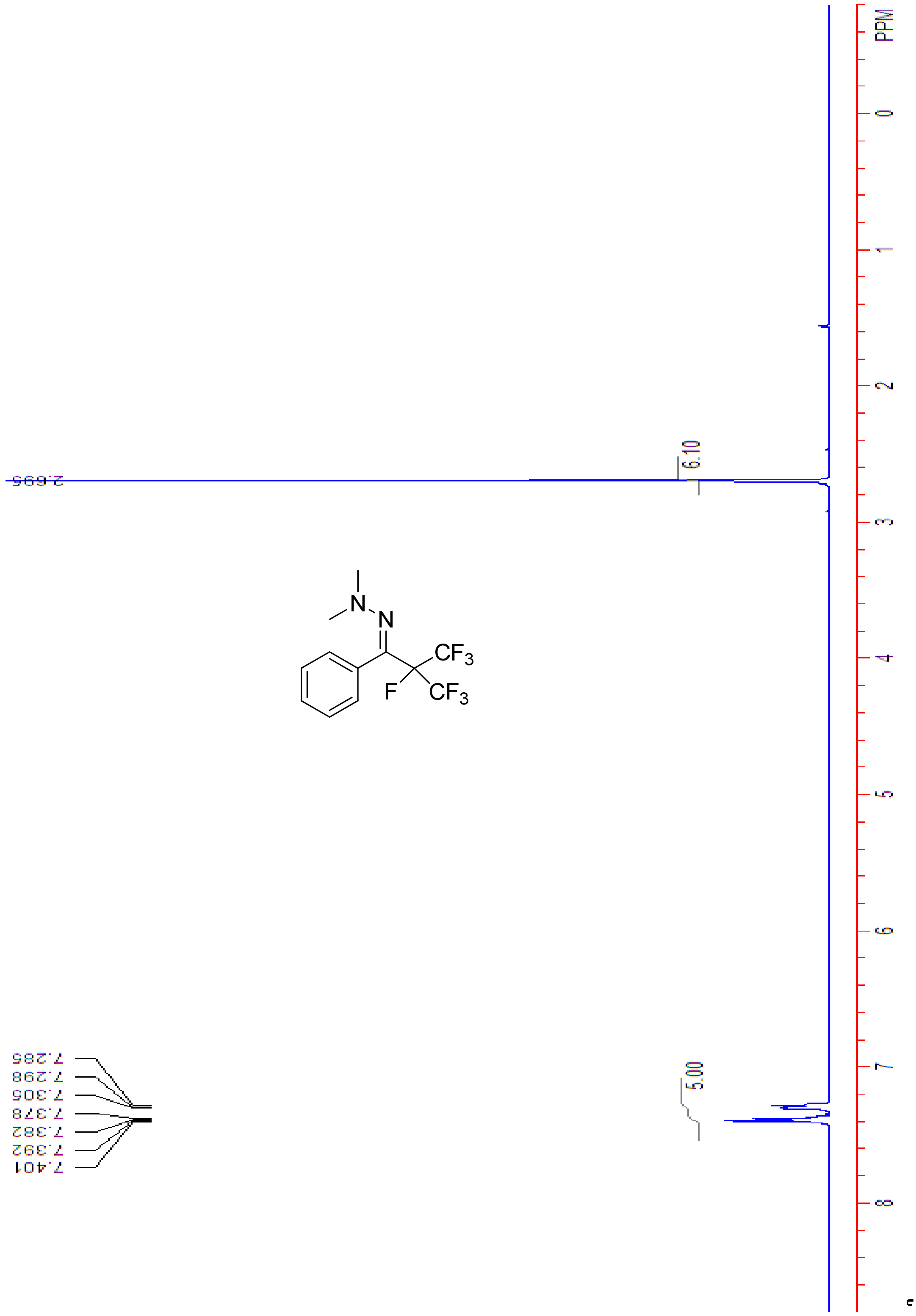
^{13}C NMR spectrum of **3da**



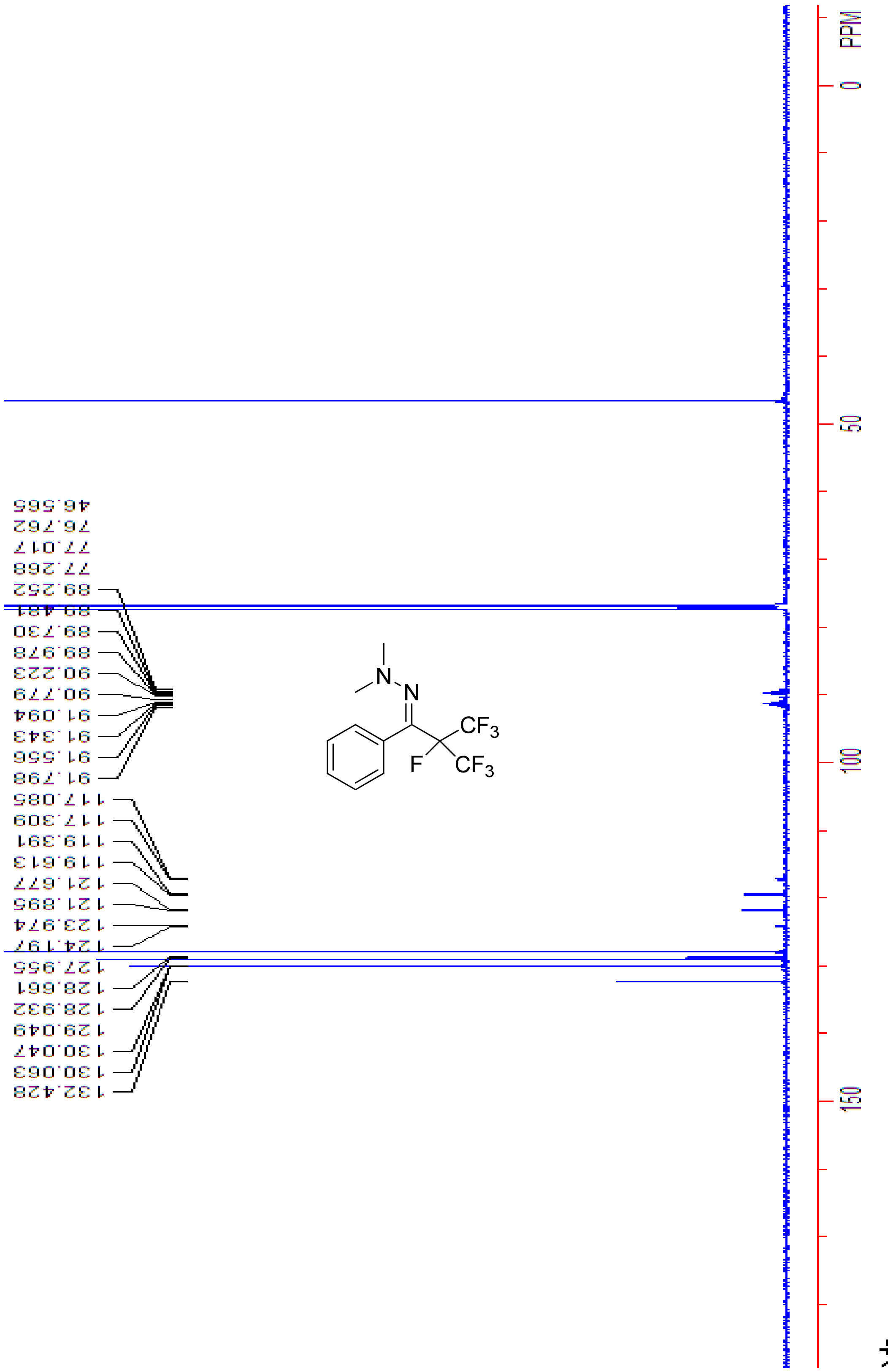
^{19}F NMR spectrum of **3da**



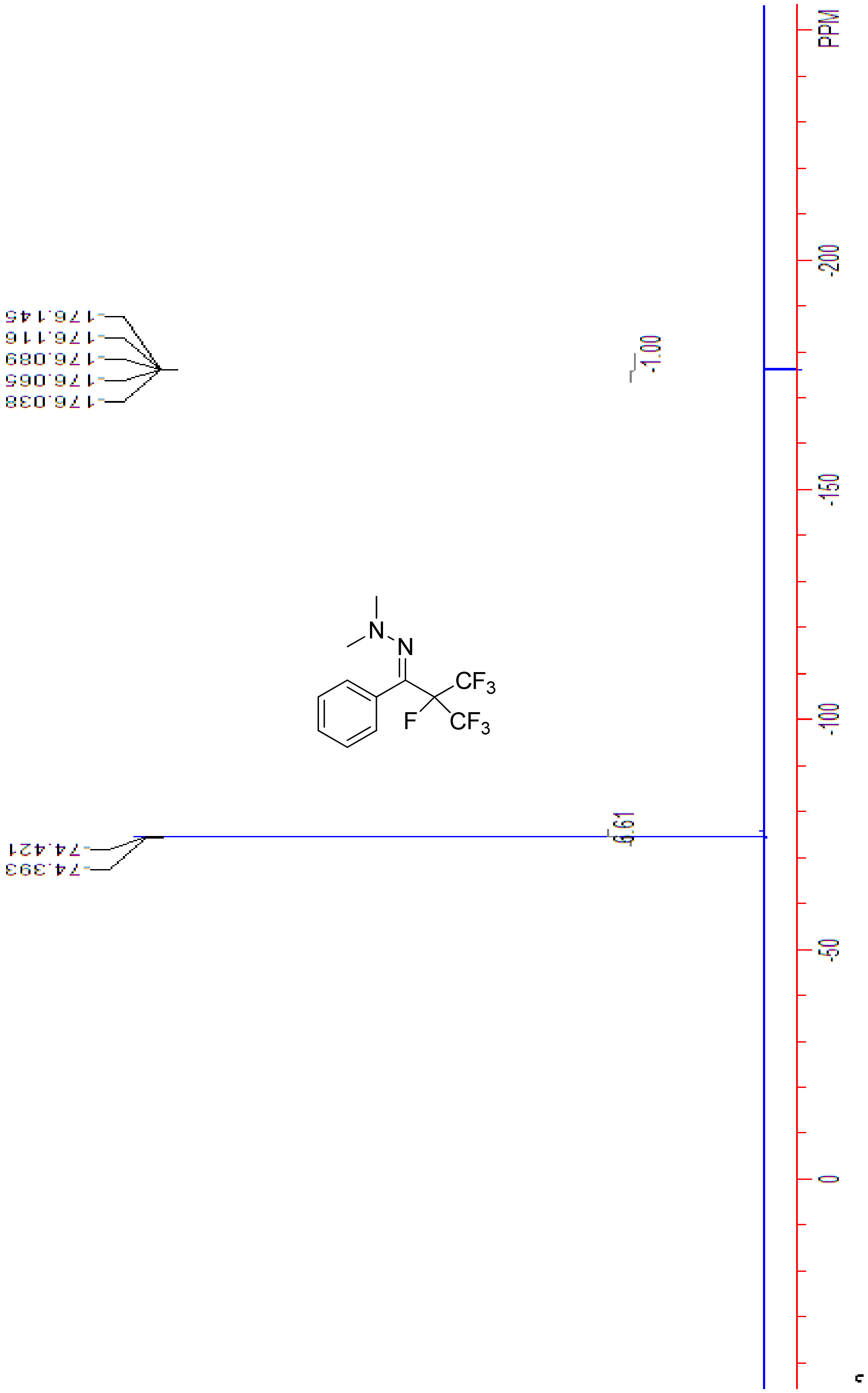
^{1}H NMR spectrum of **3ea**



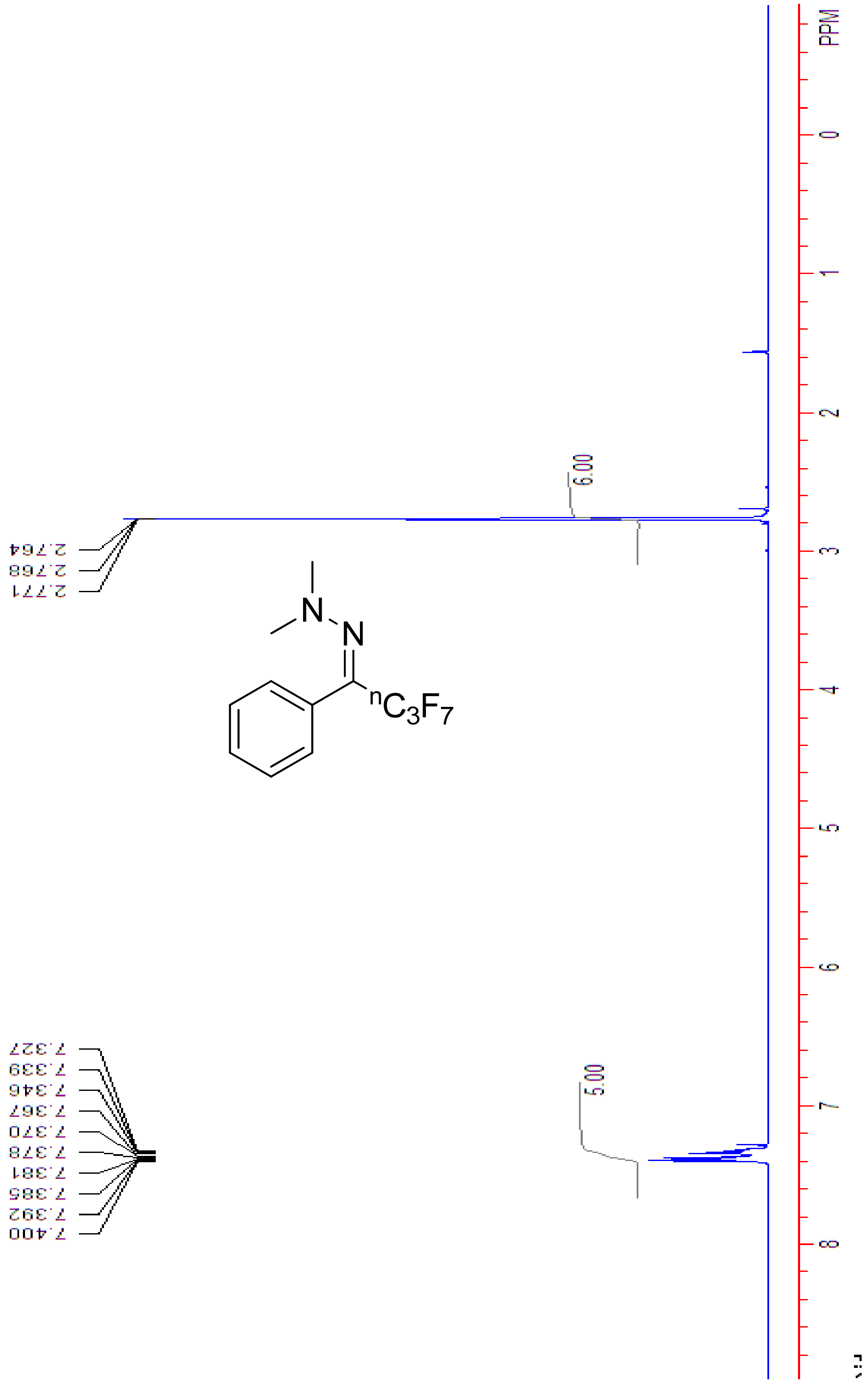
^{13}C NMR spectrum of **3ea**



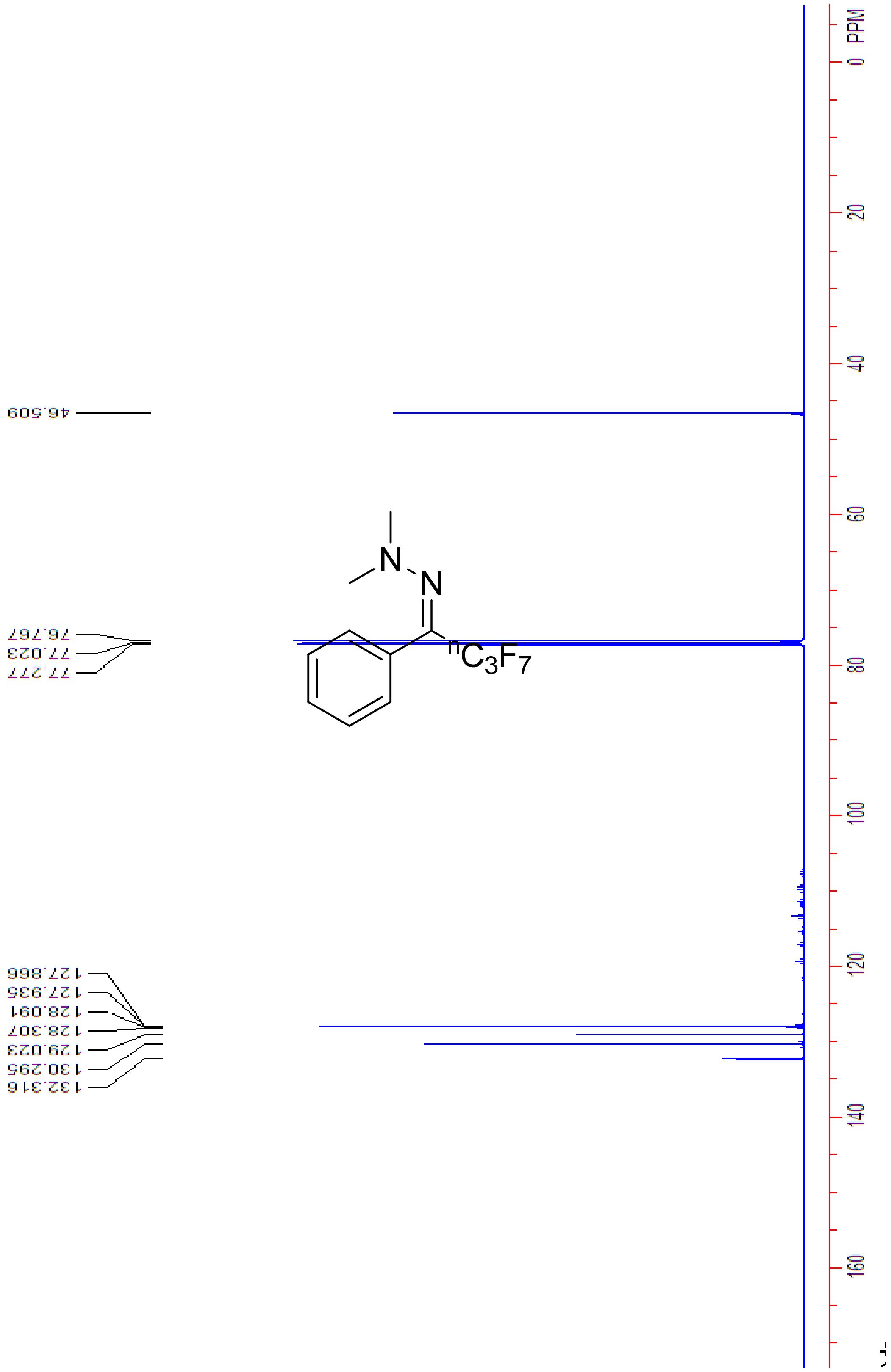
^{19}F NMR spectrum of **3ea**



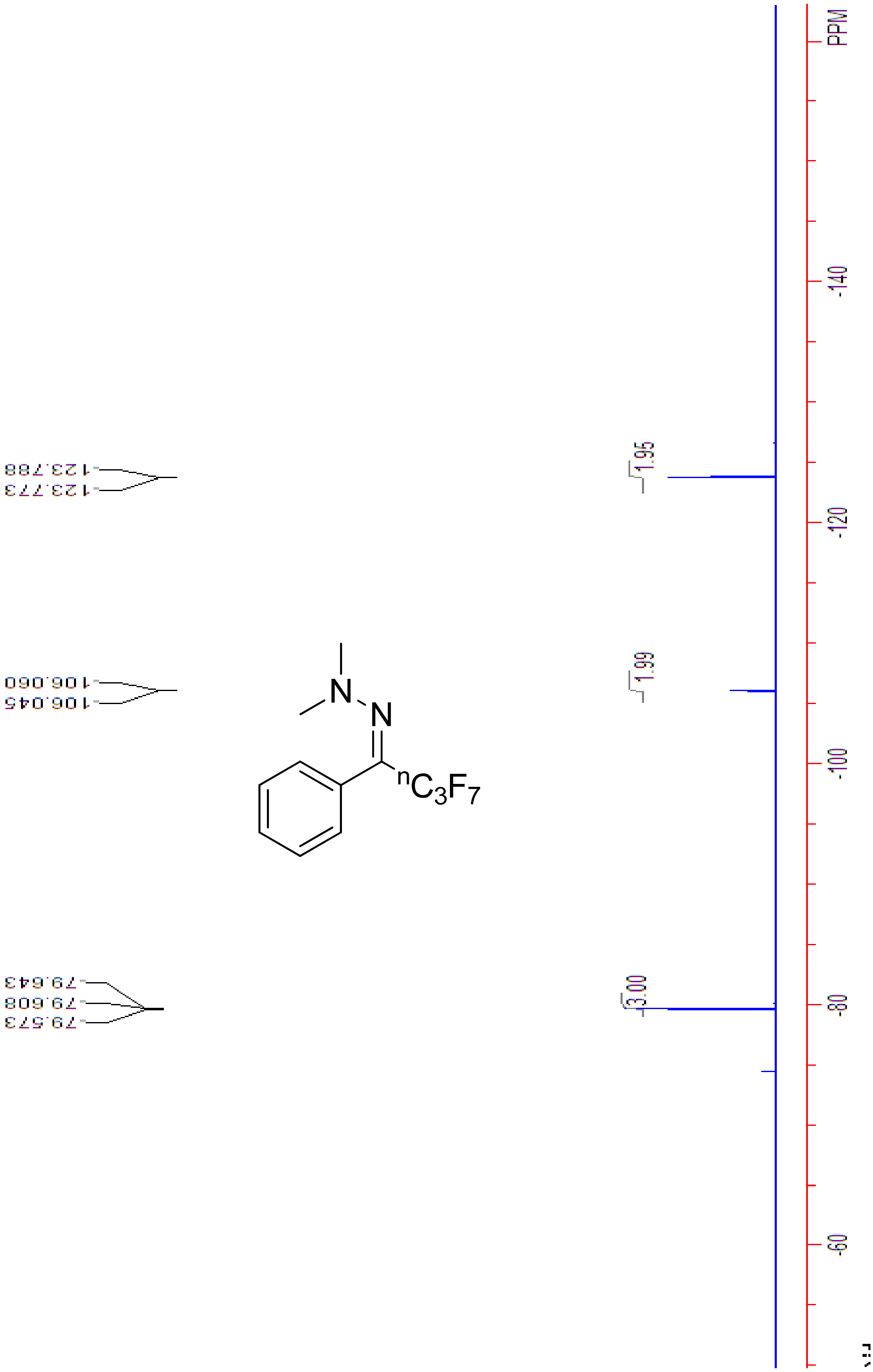
^{1}H NMR spectrum of **3fa**



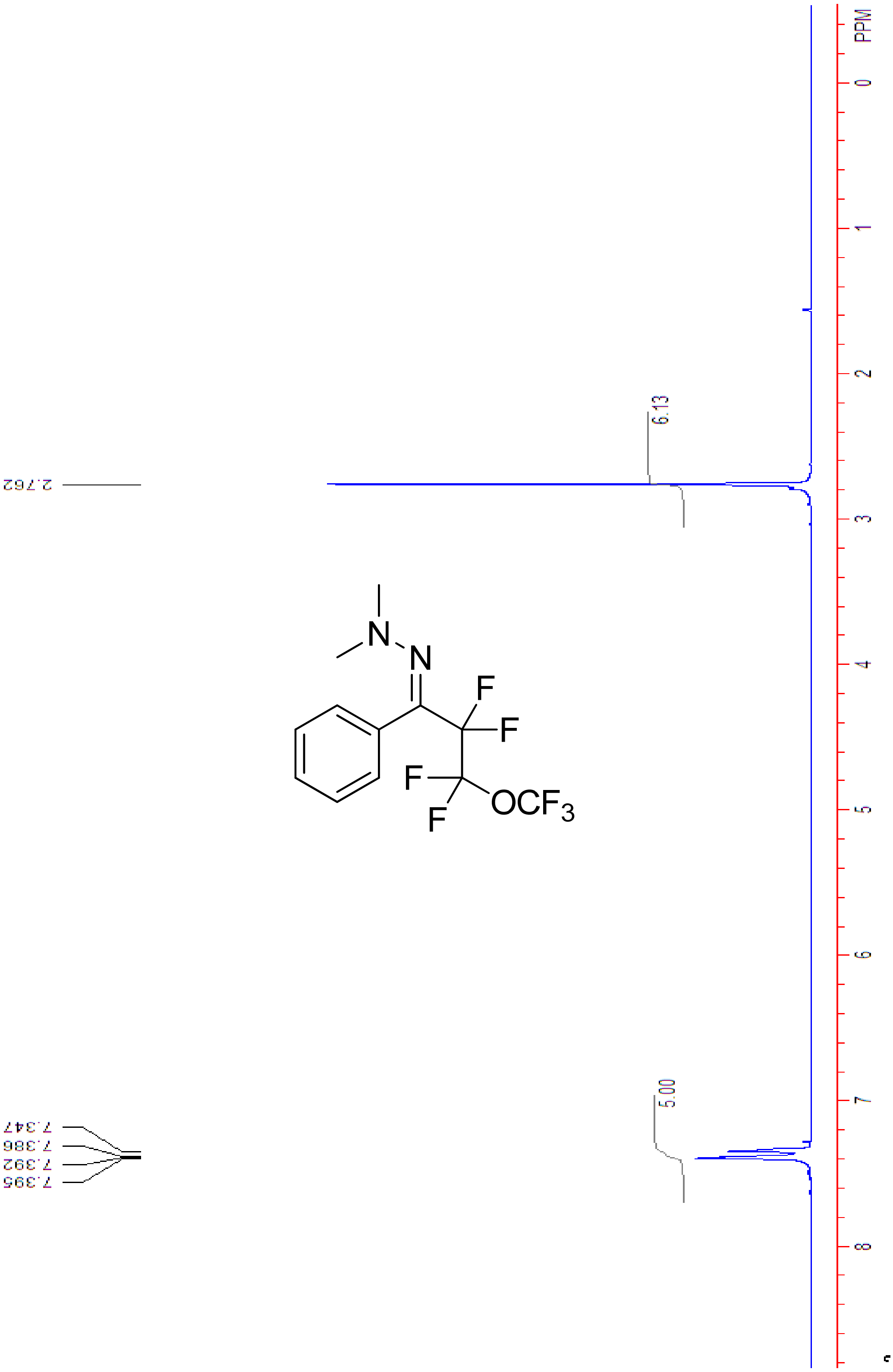
^{13}C NMR spectrum of **3fa**



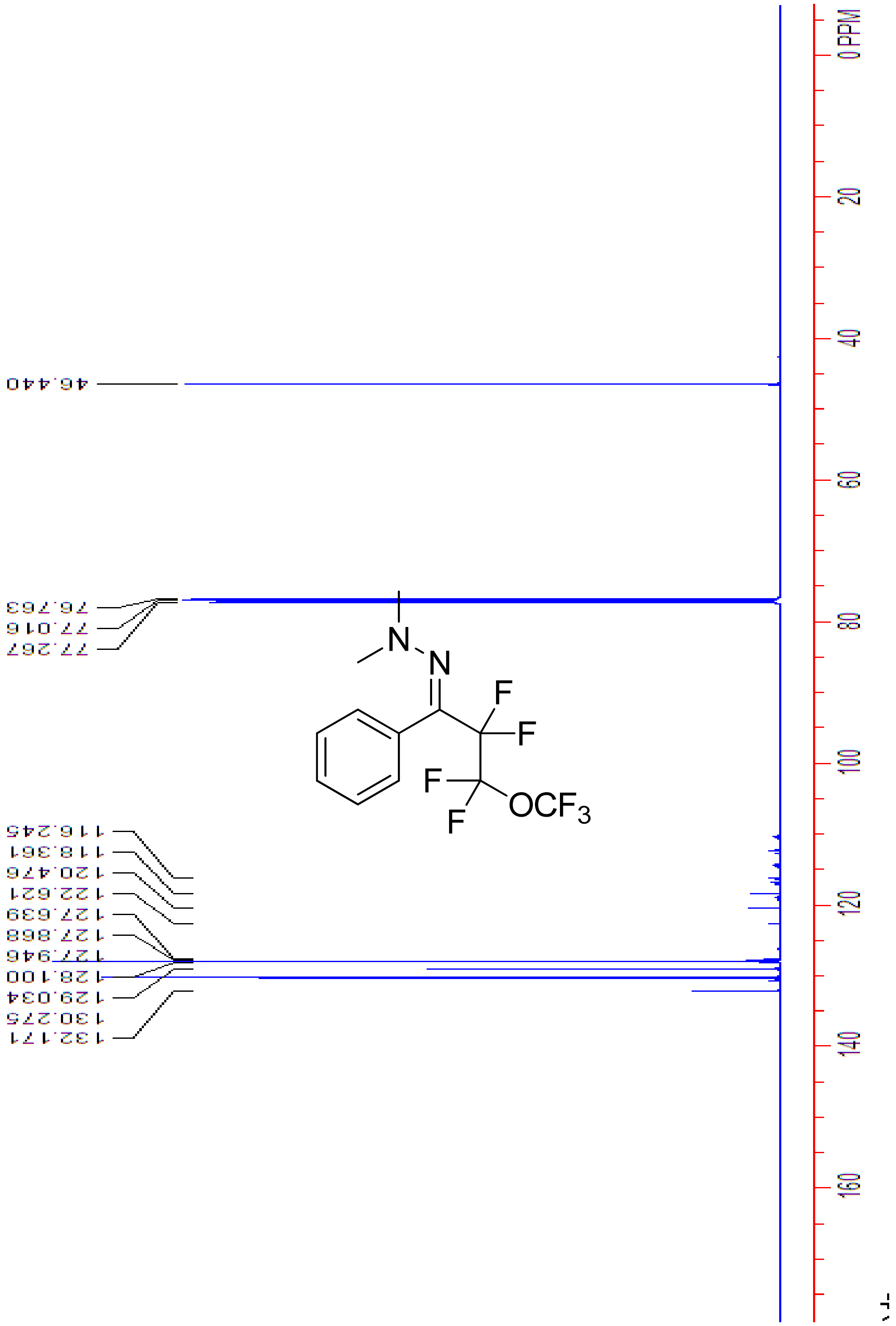
^{19}F NMR spectrum of **3fa**



^{1}H NMR spectrum of **3ha**



^{13}C NMR spectrum of **3ha**



^{19}F NMR spectrum of **3ha**