Supporting Information

Fluorous Aryl Diazirine Photoaffinity Labeling Reagents

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Experimental Section

All of the solvents were purchased from suppliers as anhydrous grade. 4-(3-(trifluoromethyl)-3H-diazirin-3-yl) benzoic acid was purchased from Chem-Impex international Inc.. Methyl 4-(hydroxymethyl)benzoate, 1-Iodo-perfluoropropane, 1-Iodo-perfluorohexane, isopropylmagnesium chloride solution and other chemicals were purchased from Acros or Sigma-Aldrich.

^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 1% TMS) solutions on Gemini-300 MHz, Inova-400 MHz or Inova-500 MHz spectrometer. HPLC analyses were performed on a Thermo Betasil C18 reversed phased column (150 x 4.6 mm, 5 μm) with SHIMADZU LC-6AD system. Mass spectra and high-resolution mass spectra were obtained from an apex-Qe (Qh-FTICR) mass spectrometer (Bruker Daltonics, Billerica, MA).

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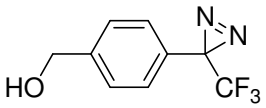
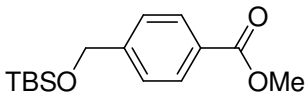


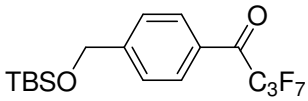
(4-(3-(trifluoromethyl)-3*H*-diazirin-3-yl)phenyl)methanol (1a)[1]

A solution of 4-(3-(trifluoromethyl)-3H-diazirin-3-yl) benzoic acid (6.0 mg, 26 μmol) and sodium borohydride (3.0 mg, 78 μmol) in THF (60 μL) was added to a vial at 0 ^{o}C. Boron trifluoride etherate (11.0 mg, 78 μmol) in THF (50 μL) was then added dropwise and the mixture was stirred at 0 ^{o}C. After 16 h, saturated NH_4Cl solution was added. The mixture was extracted with dichloromethane and the layers were separated. The aqueous layer was further extracted with CH_2Cl_2 three times. The combined organic layers were dried over sodium sulfate and concentrated under vacuum. The residue was purified through flash chromatography (pure CH_2Cl_2) over silica gel to yield compound **1a** as colorless oil (3.2 mg, 57 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.70 (t, J = 6.0 Hz, 1H), 4.72 (d, J = 5.6 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H).



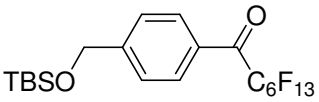
methyl 4-((*tert*-butyldimethylsilyloxy)methyl)benzoate (3)[2]

Compound **3** was prepared from methyl 4-(hydroxymethyl)benzoate by following the literature protocol[3]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 6H), 0.95 (s, 9H), 3.90 (s, 3H), 4.79 (s, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –5.35, 18.34, 25.86, 51.94, 64.47, 125.62, 128.70, 129.55, 146.74, 167.03.



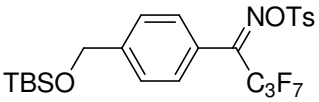
1-(4-((tert-butyldimethylsilyloxy)methyl)phenyl)-2,2,3,3,4,4,4-heptafluorobutan-1-one (5b)

A schlenk tube was charged with 2.0 M isopropylmagnesium chloride solution (2.75 mL, 5.50 mmol, in THF) and dry ether (6.0 mL) under Ar at -78 ^{o}C. 1-Iodo-perfluoropropane (1.48 g, 5.00 mmol) was added dropwise in 15 min under vigorous stirring. After another 45 min compound **3** (0.70 g, 2.50 mmol) was added dropwise in 15 min. The resulting mixture was stirred at the same temperature for 1 h and then warmed to 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for an additional hour and saturated NH_4Cl solution was added followed by ethyl acetate. The layers were separated and the aqueous layer was further extracted with EtOAc three times. The combined organic fractions were dried over sodium sulfate and concentrated under vacuum. The residue was purified through flash chromatography (Hex : EA = 95 : 5) over silica gel to yield compound **5b** as colorless oil (0.54 g, 51 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.13 (s, 6H), 0.97 (s, 9H), 4.83 (s, 2H), 7.50 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ –5.37, 18.37, 25.86, 64.23, 126.08, 130.38 (t, J = 3.5 Hz), 149.99, 182.86 (t, J = 25.2 Hz); ^{19}F ($CDCl_3$, 376 MHz) –80.67, –113.98, –125.93; HRMS (ESI) for $C_{17}H_{22}F_7O_2Si$: calcd 419.1277; found 419.2775.



1-(4-((tert-butyldimethylsilyloxy)methyl)phenyl)-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-one (5c)

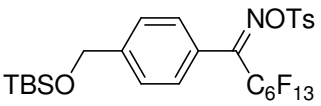
This was prepared in a similar manner to **5b.** Compound **3** (1.31 g) was used to afford **5b** (1.39 g, 53%) as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 6H), 0.97 (s, 9H), 4.86 (s, 2H), 7.52 (d, J = 8.7 Hz, 2H), 8.07 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ –5.61, 18.37, 25.75, 64.30, 126.12, 130.43, 150.11 182.89 (t, J = 25.9 Hz); ^{19}F ($CDCl_3$, 376 MHz) –81.30, –113.16, –121.38, –121.56, –123.23, –126.54; HRMS (ESI) for $C_{22}H_{22}F_{13}O_2Si$: calcd 569.1181; found 569.1192.



1-(4-((tert-butyldimethylsilyloxy)methyl)phenyl)-2,2,3,3,4,4,4-heptafluorobutan-1-one O-tosyl oxime (6b)

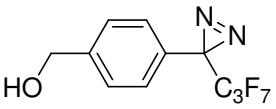
Ketone **5b** (523 mg, 1.25 mmol), EtOH (1.25 mL), pyridine (2.50 mL) and $NH_2OH{\cdot}HCl$ (130 mg, 1.88 mmol) were successively added to a flask at room temperature. The resulting solution was heated and stirred at 85 ^{o}C for 4 h. The solvent was then removed under reduced pressure. The resulting residue was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated under vacuum to generate the crude oxime product as light yellow oil. Pyridine (2.5 mL) and TsCl (286 mg, 1.50 mmol) were then added to the crude oxime residue at room temperature. The resulting solution was heated and stirred at 85 ^{o}C for 16 h. The solvent was then removed under

reduced pressure and the resulting residue was suspended with brine and extracted with CH_2Cl_2. The combined organic layers were dried over sodium sulfate and concentrated under vacuum. The residue was purified through flash chromatography (Hex : EA = 95 : 5) over silica gel to yield compound **5b** as light yellow oil (367 mg, 50 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.04 (s, 6H), 0.87 (s, 9H), 2.41 (s, 3H), 4.71 (s, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ –5.35, 18.39, 21.77, 25.90, 64.23, 123.16, 125.95, 128.39, 129.28, 129.75, 131.23, 145.32, 146.06, 155.14 (t, *J* = 24.5 Hz); ^{19}F ($CDCl_3$, 376 MHz) –80.58, –110.74, –124.78; HRMS (ESI) for $C_{24}H_{29}F_7NO_4SSi$: calcd 588.1475; found 588.1476.



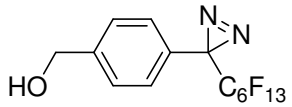
1-(4-((tert-butyldimethylsilyloxy)methyl)phenyl)-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptan-1-one O-tosyl oxime (6c)

This was prepared in a similar manner to **6b.** Compound **5c** (1.25 g, 2.2 mmol) was used to generate **6c** (760 mg, 47%) as light yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.12 (s, 6H), 0.96 (s, 9H), 2.47 (s, 3H), 4.78 (s, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ –5.36, 18.38, 21.70, 25.90, 64.23, 123.23, 125.94, 128.37, 129.25, 129.72, 131.26, 145.30, 146.04, 155.39 (t, *J* = 25.7 Hz); ^{19}F ($CDCl_3$, 376 MHz) –81.29, –109.92, –120.41, –121.62, –123.27, –126.61; HRMS (ESI) for $C_{27}H_{29}F_{13}NO_4SSi$: calcd 738.1379; found 738.1401.



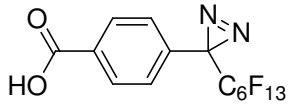
(4-(3-(perfluoropropyl)-3*H*-diazirin-3-yl)phenyl)methanol (1b)

Compound **5b** (360 mg, 0.61 mmol), EtOH (1 mL) and liquid ammonia (ca. 1 mL) were added successively to a sealed tube at -78 ^{o}C. The reaction mixture was slowly warmed to room temperature with stirring for 12 h. The white solid in the reaction was filtered off and the filtrate was concentrated under vacuum. The resulting residue was then suspended with methanol (1 mL) and Et_3N (92.6 mg, 0.92 mmol) at 0 ^{o}C. Iodine was slowly added until red color remained. The reaction mixture was then stirred for 1 h at room temperature and the solvent was removed under reduced pressure. The residue was dissolved in THF (1 mL) and TBAF (0.92 mL, 1.0 M in THF) was added. The reaction mixture stirred at room temperature for 1 h. Evaporation of the solvent and flash chromatography (Hex : EA = 1 : 1) over silica gel gave compound **1b** as colorless oil (120 mg, 62 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.89 (br, 1H), 4.59 (s, 2H), 7.28–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.25 (t, *J* = 27.8 Hz), 64.19, 127.16, 128.30, 142.91, ^{19}F ($CDCl_3$, 376 MHz) –81.27, –110.79, –125.16; HRMS (ESI) for $C_{11}H_7F_7N_2ONa$: calcd 339.0344; found 339.1993.



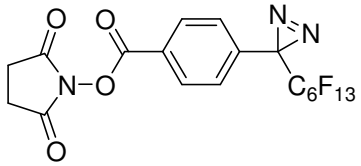
(4-(3-(perfluorohexyl)-3*H*-diazirin-3-yl)phenyl)methanol (1c)

This was prepared in a similar manner to **1b.** Compound **5c** (760 mg) was used to yield **1c** (342 mg, 75%) as light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.66 (s, 2H), 7.35 (apparent s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.55 (t, *J* = 28.2 Hz), 64.40, 127.25, 128.41, 142.93, ^{19}F ($CDCl_3$, 376 MHz) –81.32, –109.95, –120.67, –122.45, –123.31, –126.61; HRMS (ESI) for $C_{14}H_8F_{13}O$: calcd 439.0368; found 439.0366.



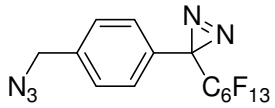
4-(3-(perfluorohexyl)-3*H*-diazirin-3-yl)benzoic acid (9)

Compound **1c** (210 mg, 0.45 mmol), dioxane (0.5 mL), KOH (0.2 N, 2.25 mL), and potassium permanganate (107 mg, 0.68 mmol) were added successively to a vial at room temperature. After 14 h, the reaction mixture was acidified with HCl (2.0 N, 3.0 mL) and extracted with CH_2Cl_2. The extract was dried over sodium sulfate and concentrated. To the residue were added dioxane (0.5 mL), 0.2 N KOH (4.5 mL) and potassium permanganate (214 mg, 1.35 mmol) successively at room temperature. After 6 h, the reaction mixture was acidified with HCl (2.0 N, 3.0 mL) and extracted with CH_2Cl_2 three times. The combined organic layers were dried over sodium sulfate and concentrated under vacuum to give compound **9** as white solid (183 mg, 85 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45 (d, *J* = 8.7 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.48 (t, *J* = 29.0 Hz), 128.24, 130.66, 130.70, 134.76, 170.28; ^{19}F ($CDCl_3$, 376 MHz) –81.28; –109.60, –120.62, –122.43, –123.29, –126.60; HRMS (ESI) for $C_{14}H_6F_{13}O_2$: calcd 453.0160; found 453.1702.



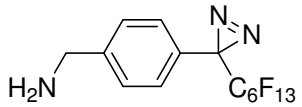
2, 5-dioxopyrrolidin-1-yl 4-(3-(perfluorohexyl)-3*H*-diazirin-3-yl)benzoate (10)

Compound **9** (20 mg, 42 μmol), CH_2Cl_2 (0.2 mL), and N-hydroxysuccinimide (5.3 mg, 46 μmol) were successively added to a vial at room temperature. A solution of dicyclohexylcarbodiimide (DCC) (9.5 mg, 46 μmol) in CH_2Cl_2 (0.1 mL) was then added dropwise. After 2 h, the solvent was removed under reduced pressure. The residue was purified through flash chromatography (Hex : EA = 4 : 1) over silica gel to yield compound **10** as white powder (19 mg, 78 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.92 (s, 4H), 7.50 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.65, 27.40 (t, *J* = 30.0 Hz), 126.69, 128.52, 131.03, 135.93, 160.90, 168.89; ^{19}F ($CDCl_3$, 376 MHz) –81.26; –109.53, –120.61, –122.42, –123.26, –126.58. HRMS (ESI) for $C_{18}H_8F_{13}NO_4Na$: calcd 572.0143; found 572.0139.



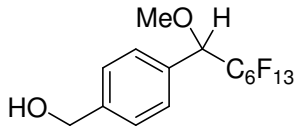
3-(4-(azidomethyl)phenyl)-3-(perfluorohexyl)-3*H*-diazirine (11)

Compound **1c** (20 mg, 43 μmol), CH_2Cl_2 (0.2 mL), and triethylamine (10.9 mg, 108 μmol) were added successively to a flask at room temperature. Methanesulfonyl chloride (9.9 mg, 86 μmol) was then added dropwise to the reaction mixture. After 16 h, water was added and the mixture was extracted with CH_2Cl_2 three times. The combined organic layers were dried over sodium sulfate and concentrated under vaccum. To the residue was added DMF (0.2 mL), tetrabutylammonium iodide (1.6 mg, 4.3 μmol) and sodium azide (3.0 mg, 45μmol) successively and the mixture was stirred at room temperature. After 4 h, water was added and the mixture was extracted with ethyl acetate three times. The combined organic layers were dried over sodium sulfate and concentrated under vacuum. The residue was purified through flash chromatography (Hex : EA = 95 : 5) over silica gel to give compound **11** as light yellow oil (19 mg, 90 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.37 (s, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.49 (t, *J* = 30.0 Hz), 54.09, 128.57, 128.72, 129.23, 137.70; ^{19}F ($CDCl_3$, 376 MHz) –81.30; –109.96, –120.68, –122.44, –123.29, –126.61; HRMS (ESI) for $C_{14}H_6F_{13}O_2$: calcd 453.0160; found 453.1702.



(4-(3-(perfluorohexyl)-3*H*-diazirin-3-yl)phenyl)methanamine (12)

Compound **11** (19 mg, 39 μmol), THF (100 μL), water (10 μL) and triphenylphosphine (12.3 mg, 47 μmol) were added successively to a vial. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed and the residue was purified through flash chromatography (CH_2Cl_2 : MeOH = 9 : 1) over silica gel to yield compound **12** as light yellow oil (14 mg, 77 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 2H), 7.34 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.58 (t, *J* = 28.4 Hz), 45.90, 127.66, 128.42, 145.35; ^{19}F ($CDCl_3$, 376 MHz) –81.29, –110.00, –120.68, –122.47, –123.31, –126.61; HRMS (ESI) for $C_{14}H_9F_{13}N_3$: calcd 466.0589; found 466.0590.

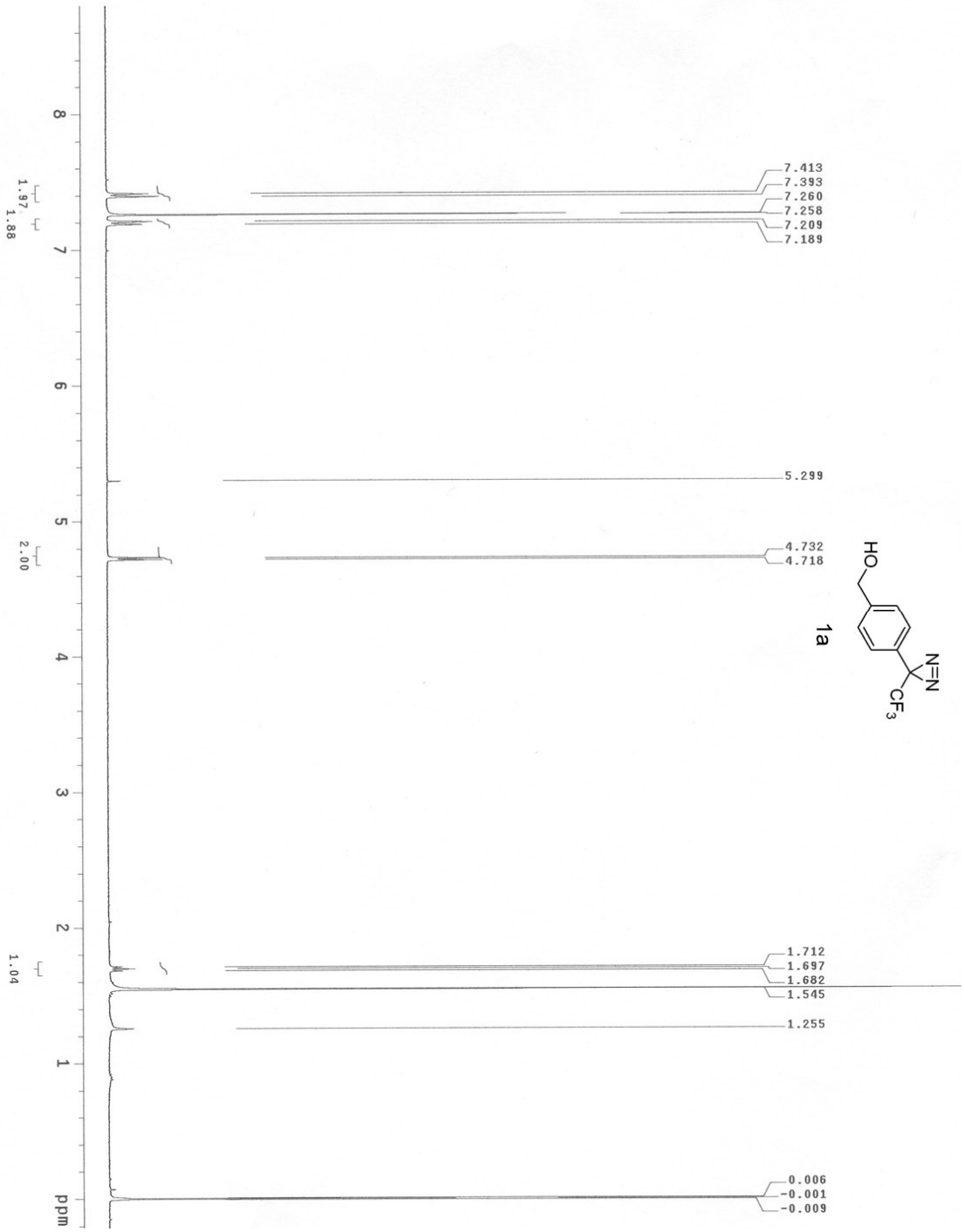


(4-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-methoxyheptyl)phenyl)methanol (13)

Diazirine **1c** (0.28 μmol) in methanol (0.4 mL) was added to a vial at room temperature. The sample was first irradiated with light at 365 nm (8 watt, 1 cm distance) for 5 min and then light at 312 nm (8 watt, 1 cm distance) for 5 min. The resulting reaction mixture sample was

subjected to HPLC analysis and FSPE.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.67 (t, *J* = 5.6 Hz, 1H), 3.34 (s, 3H), 4.67 (dd, *J* = 19.6 Hz, 4.8 Hz, 1H), 4.75 (d, *J* = 6.4 Hz, 2H), 7.44 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 57.59, 64.90, 80.38 (q), 127.03, 129.12, 130.86, 142.48; HRMS (ESI) for $C_{15}H_{11}F_{13}O_2Na$: calcd 493.0449; found 493.0450.

1. Husain, S. S.; Nirthanan, S.; Ruesch, D.; Solt, K.; Cheng, Q.; Li, G.; Arevalo, E.; Olsen, R. W.; Raines, D. E.; Forman, S. A.; Cohen, J. B.; Miller, K. W. *J. Med. Chem.* **2006,** *49,* 4818-4825
2. Brink, G.-J.; Arends, I. W. C. E.; Hoogenraad, M.; Verspui, G.; Sheldon, R. A. *Adv. Synth. Catal.* **2003**, *345*, 1341-1352
3. Melancon, B. J.; Perl, N. R.; Taylor, R. E. *Org. Lett.*, **2007**, *9*, 1425-1428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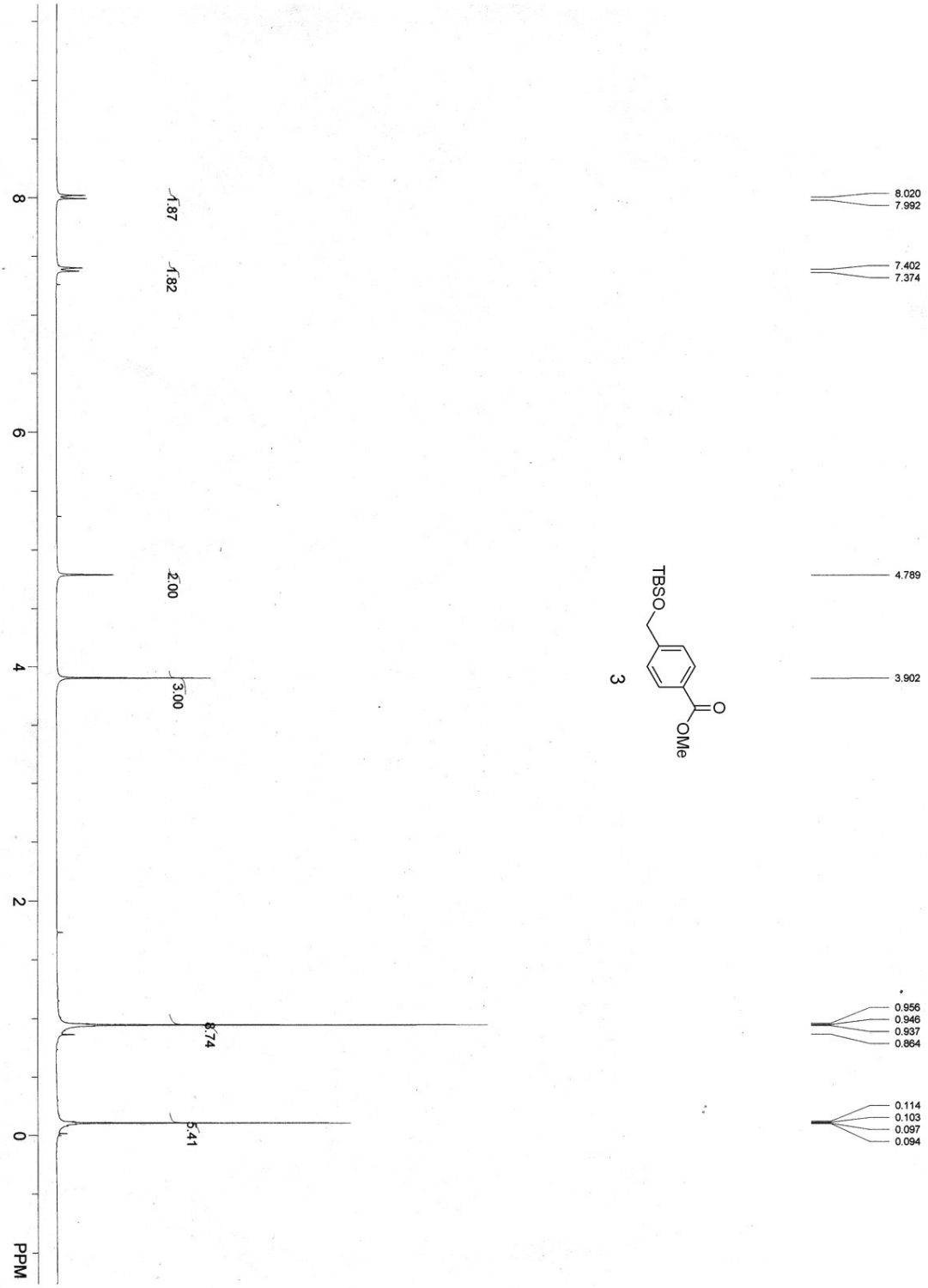
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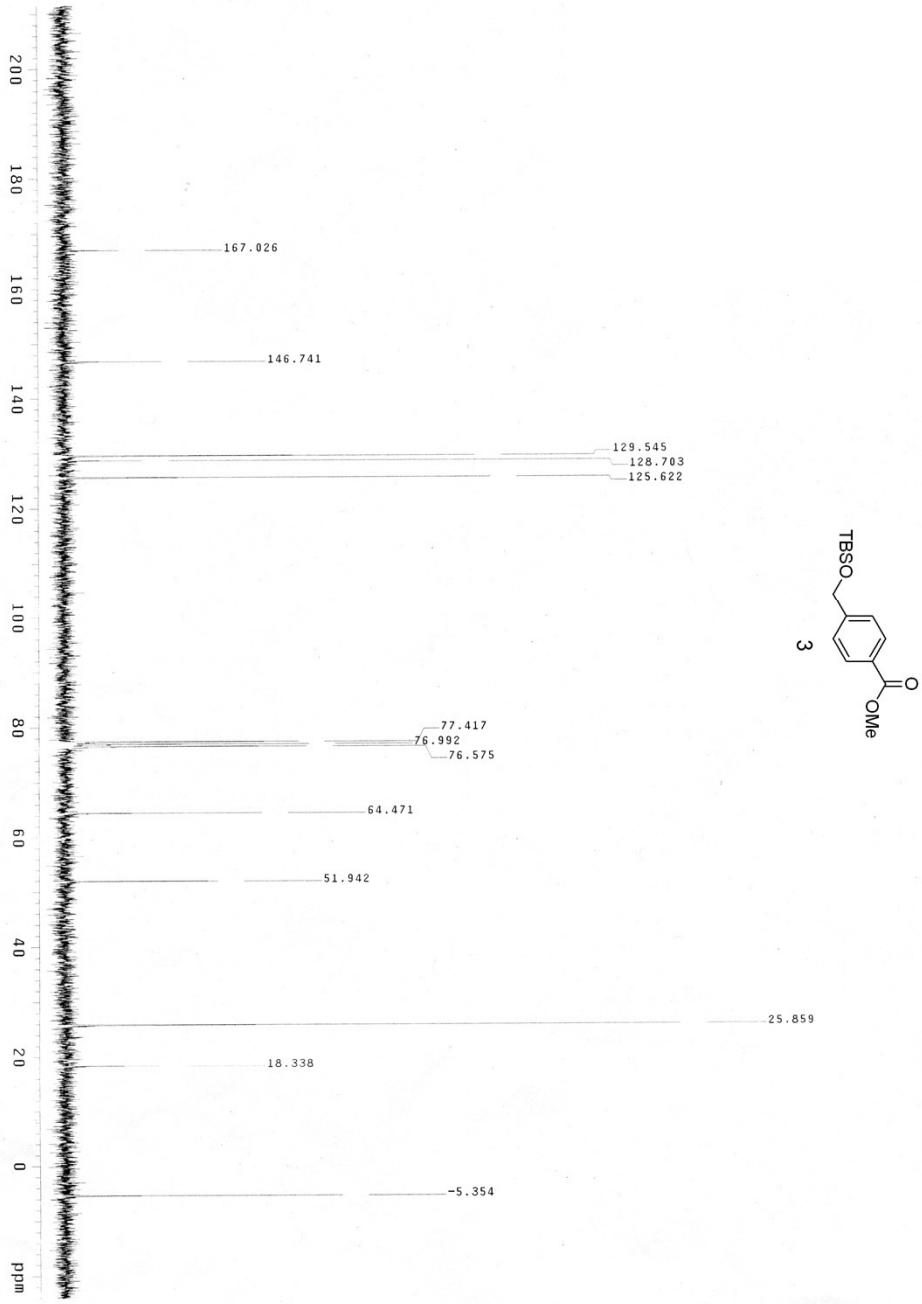
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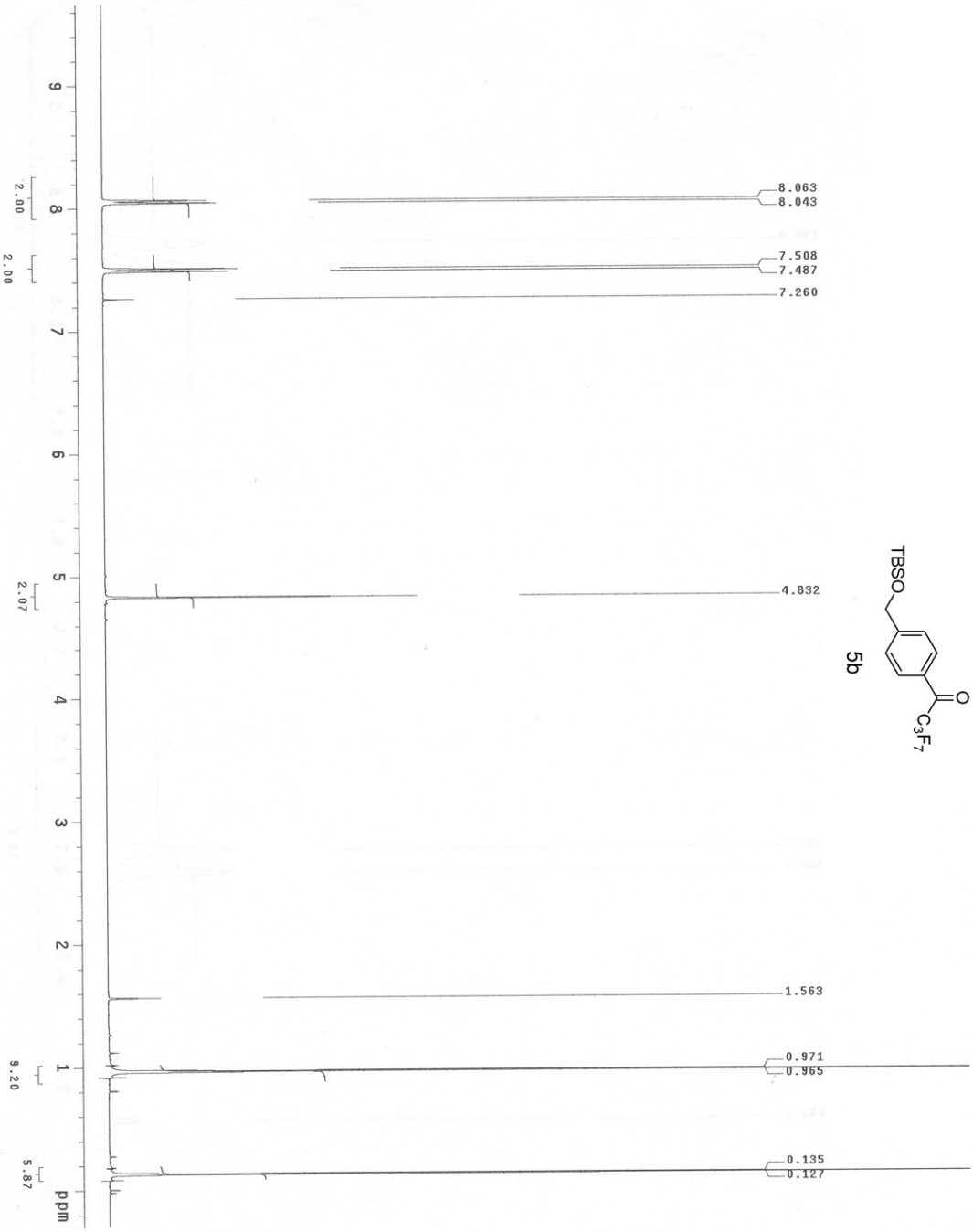
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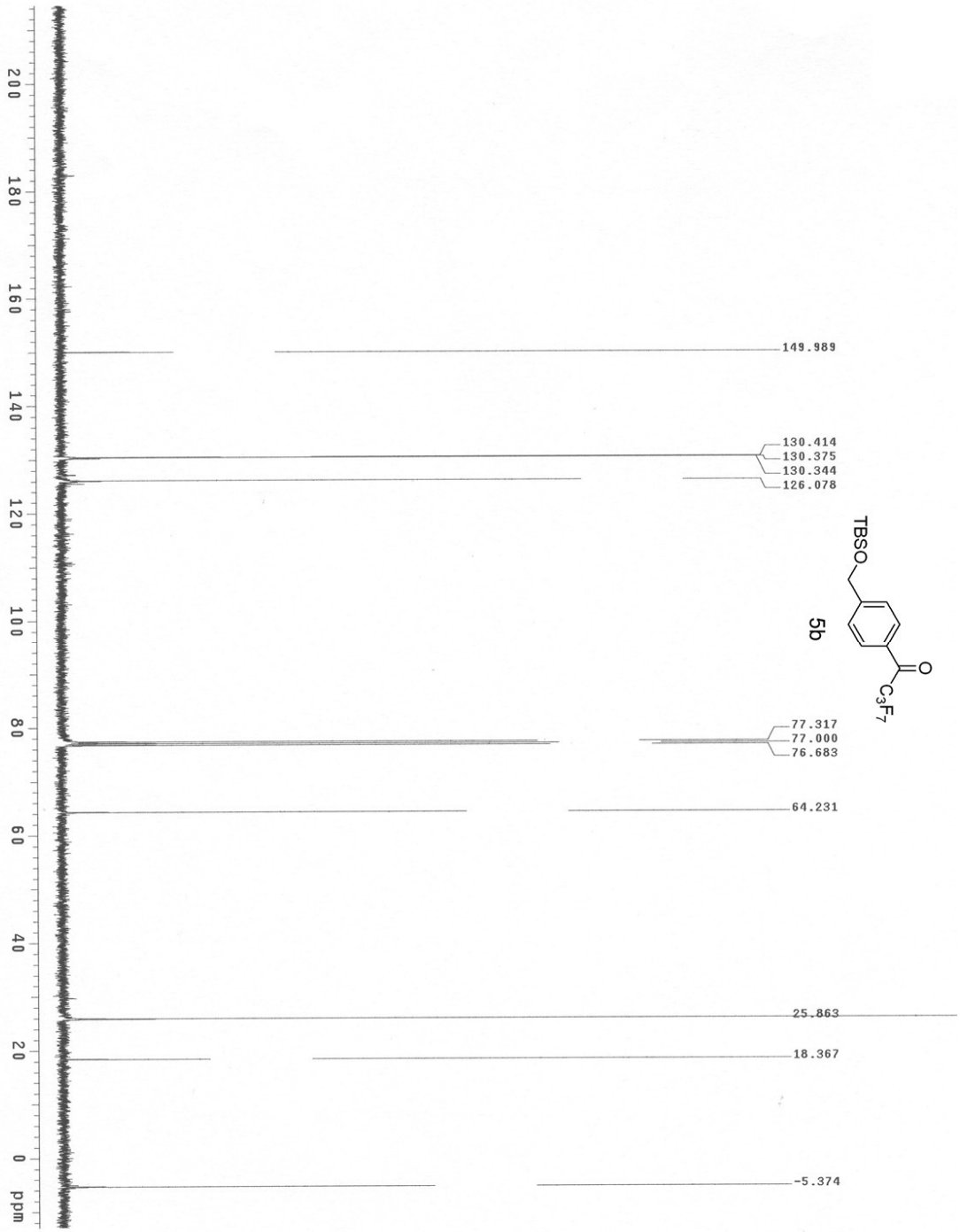
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O
C3F7
77.317
77.000
76.683
64.231
25.863
18.367
-5.374
200
180
160
140
120
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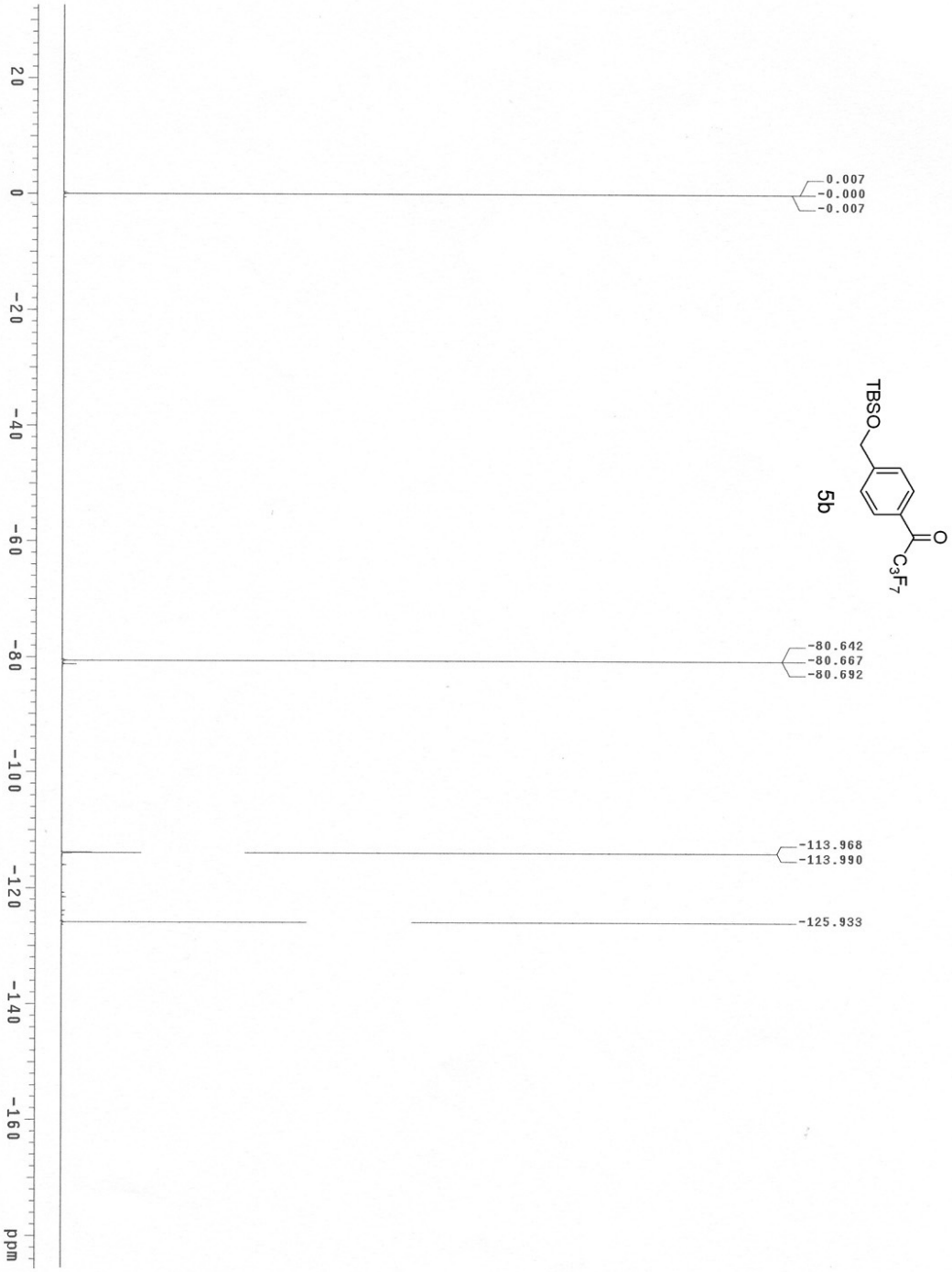
80
60
40
20
0
ppm


0.007
-0.000
-0.007
TBSO
O
C_3F_7
5b
-80.642
-80.667
-80.692
-113.968
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-125.933
20
0
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-40
-60
-80
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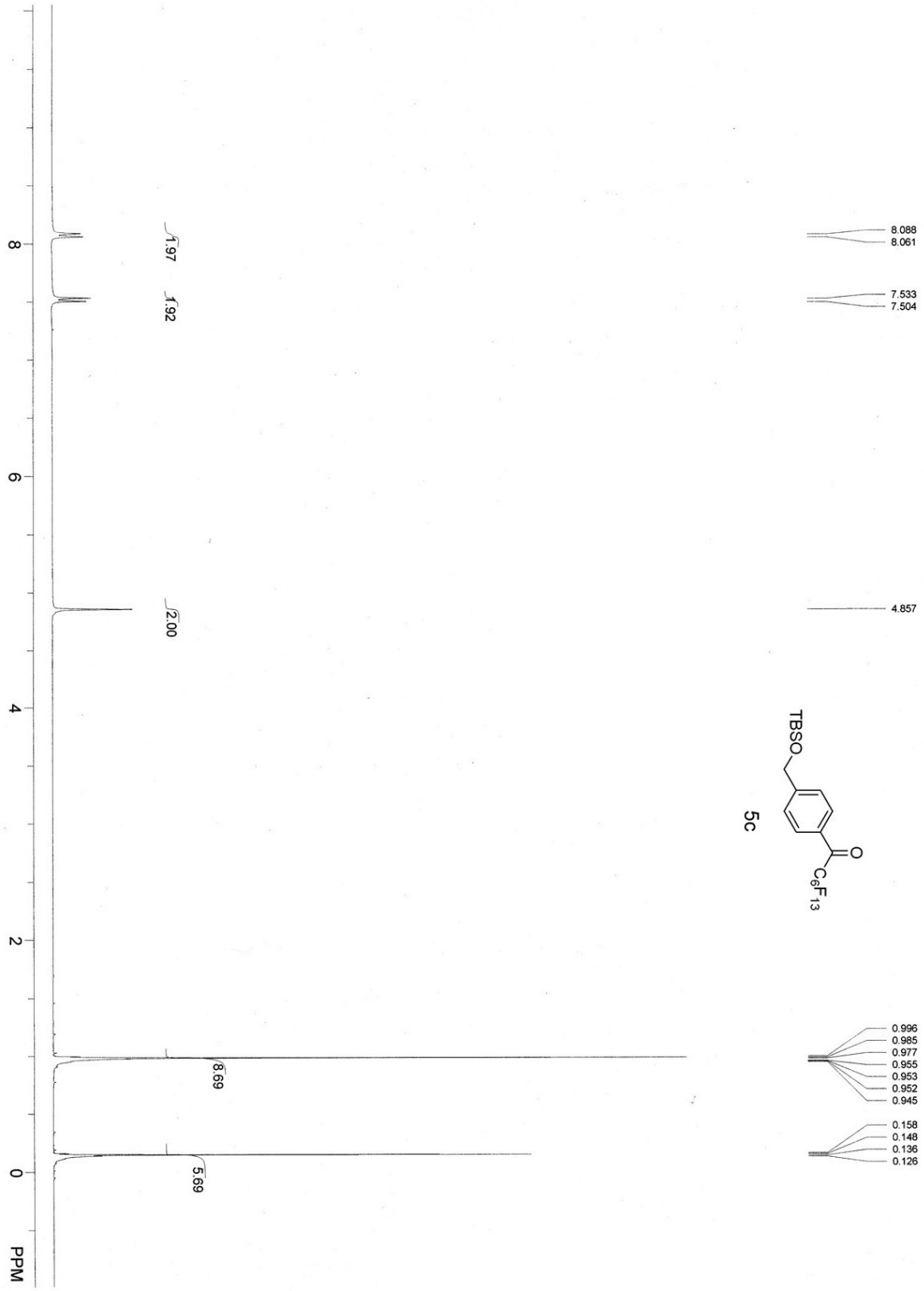
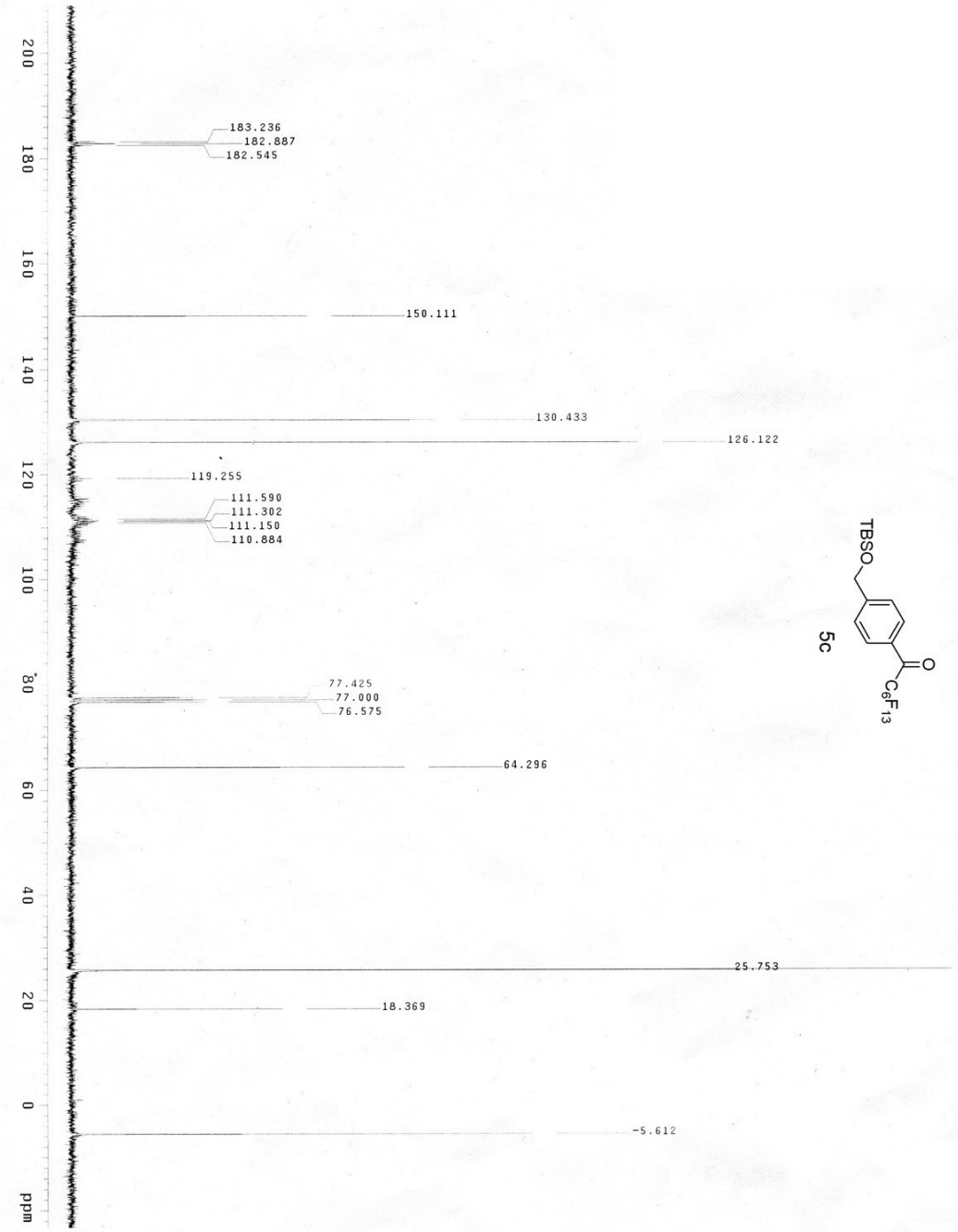
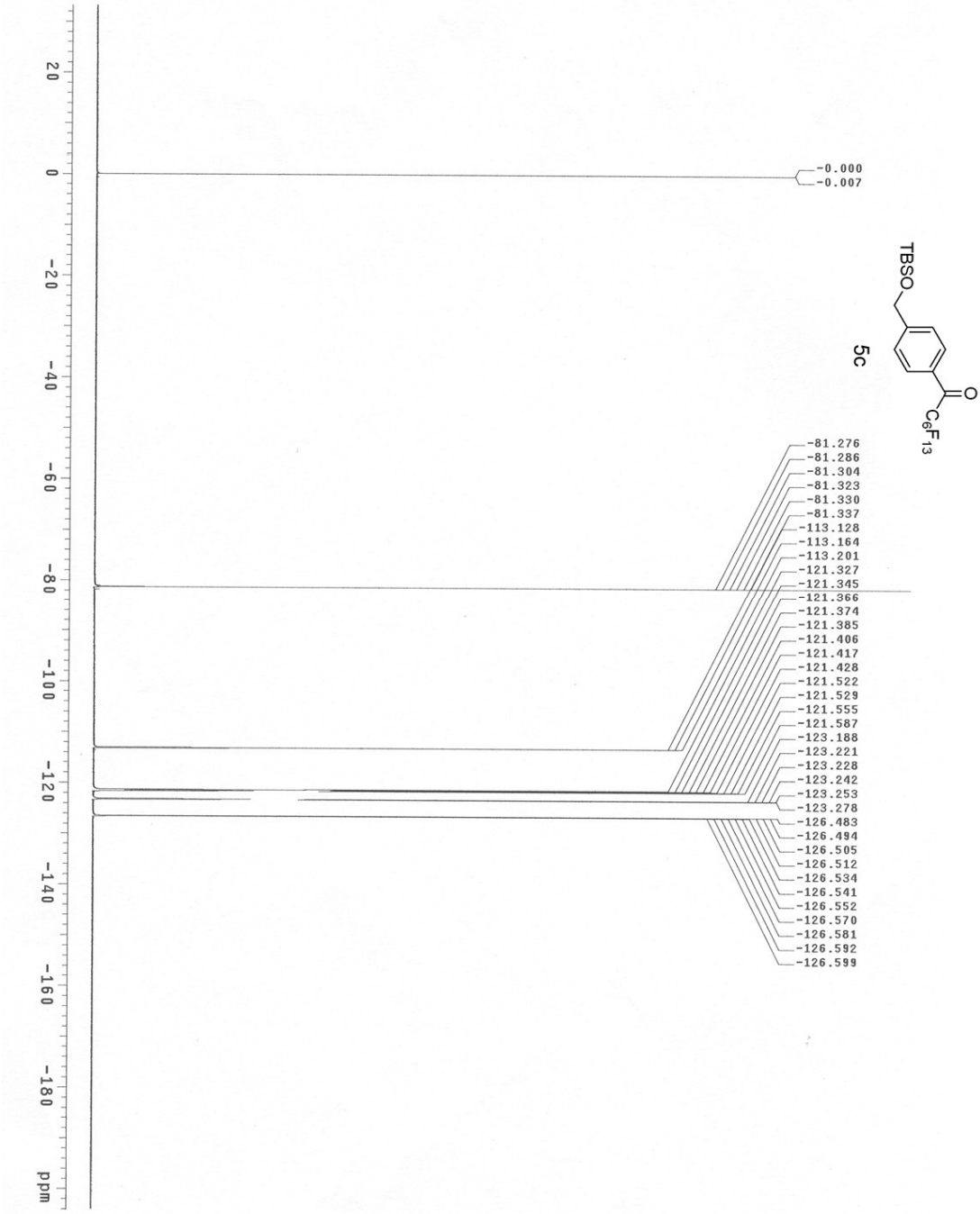
-140
-160
ppm


8.088
8.061
7.533
7.504
4.857
0.996
0.985
0.977
0.955
0.953
0.952
0.945
0.158
0.148
0.136
0.126
TBSO
O
C6F13
5c
1.97
1.92
2.00
8.69
5.69
8
6
4
2
0
PPM


183.236
182.887
182.545
150.111
130.433
126.122
119.255
111.590
111.302
111.150
110.884
77.425
77.000
76.575
64.296
25.753
18.369
-5.612
ppm
200
180
160
140
120
100
80
60
40
20
0
TBSO
O
C_6F_{13}
5c


TBSO
O
C6F13
5c
-0.000
-0.007
-81.276
-81.286
-81.304
-81.323
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-81.337
-113.128
-113.164
-113.201
-121.327
-121.345
-121.366
-121.374
-121.385
-121.406
-121.417
-121.428
-121.522
-121.529
-121.555
-121.587
-123.188
-123.221
-123.228
-123.242
-123.253
-123.278
-126.483
-126.494
-126.505
-126.512
-126.534
-126.541
-126.552
-126.570
-126.581
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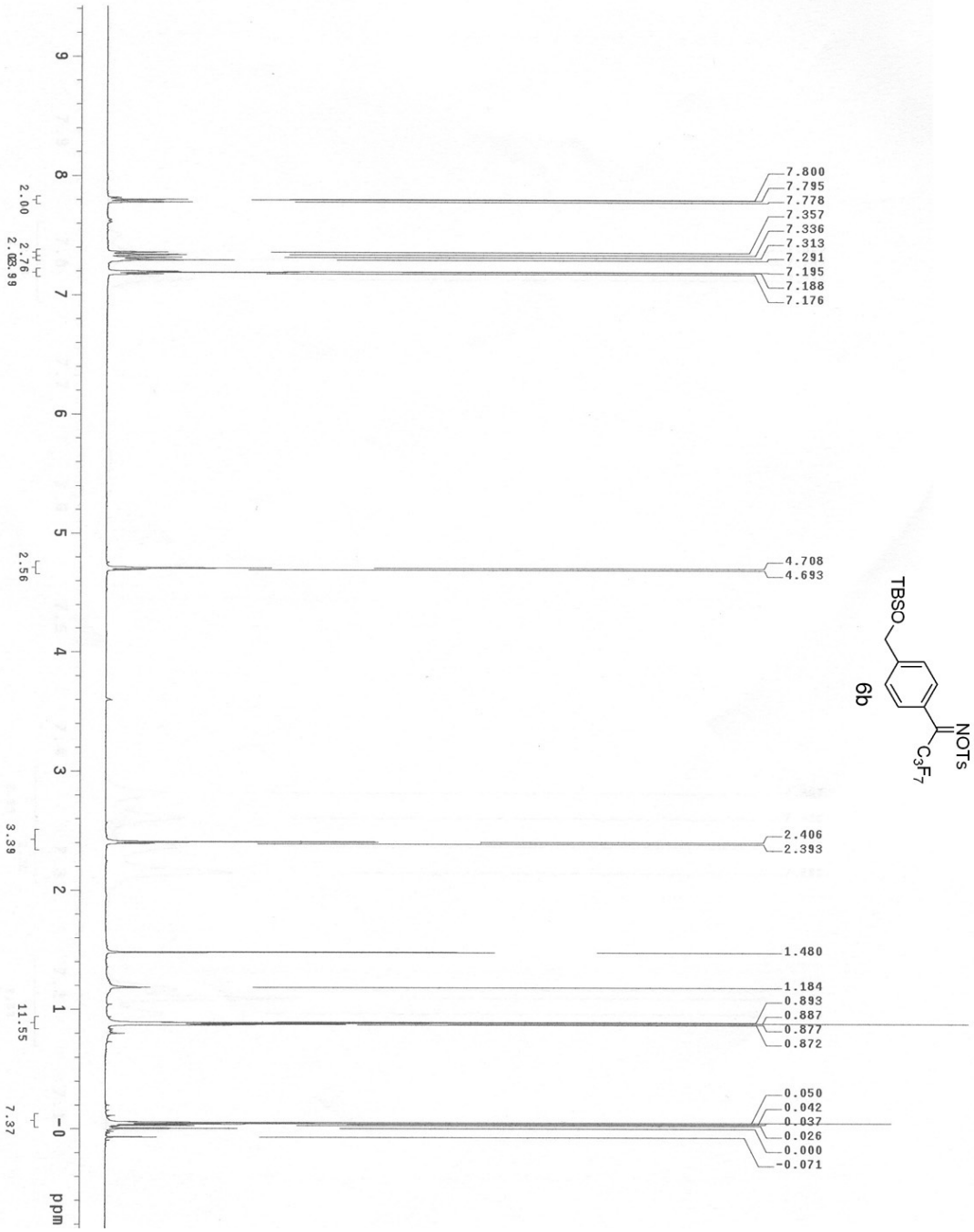
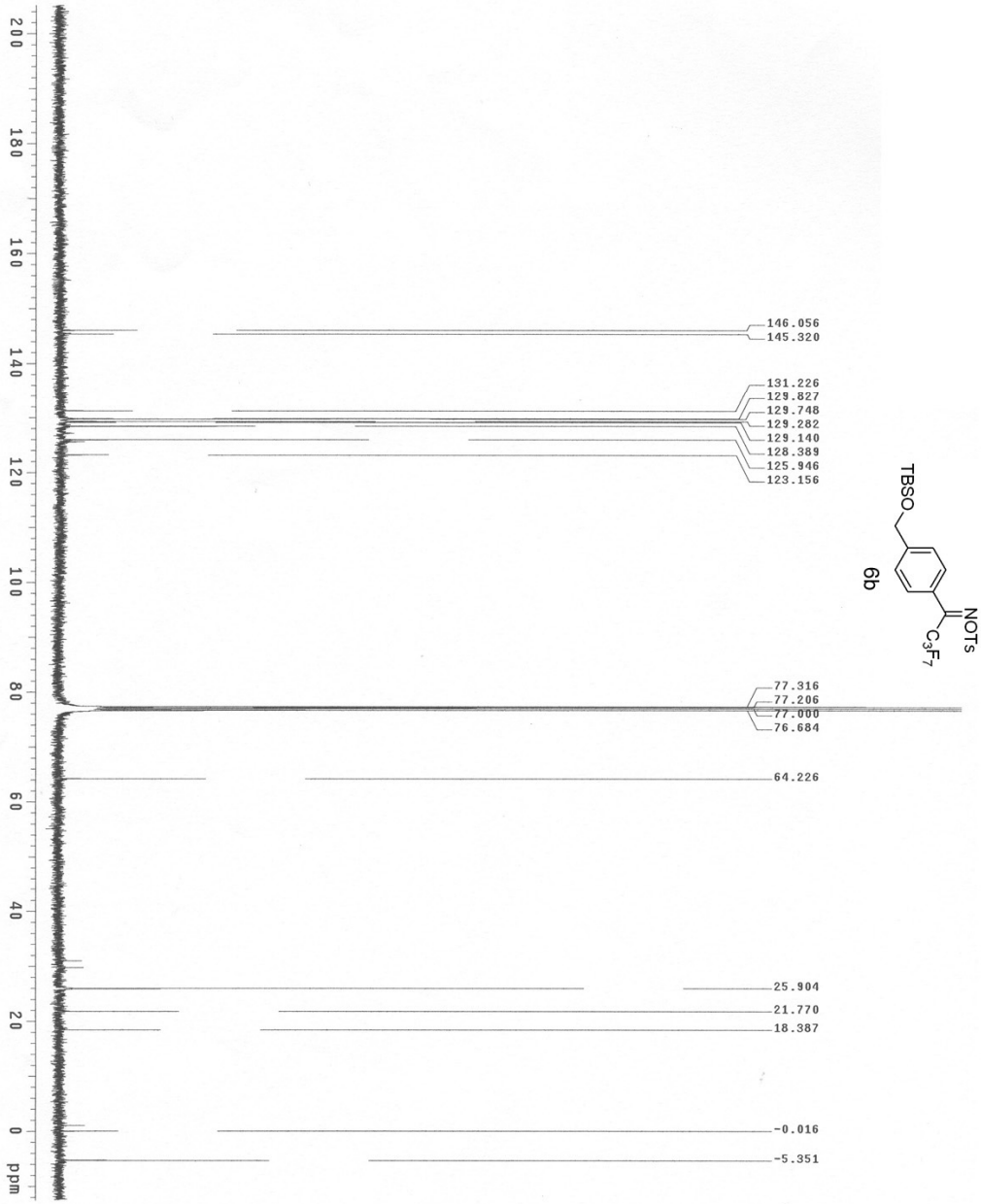
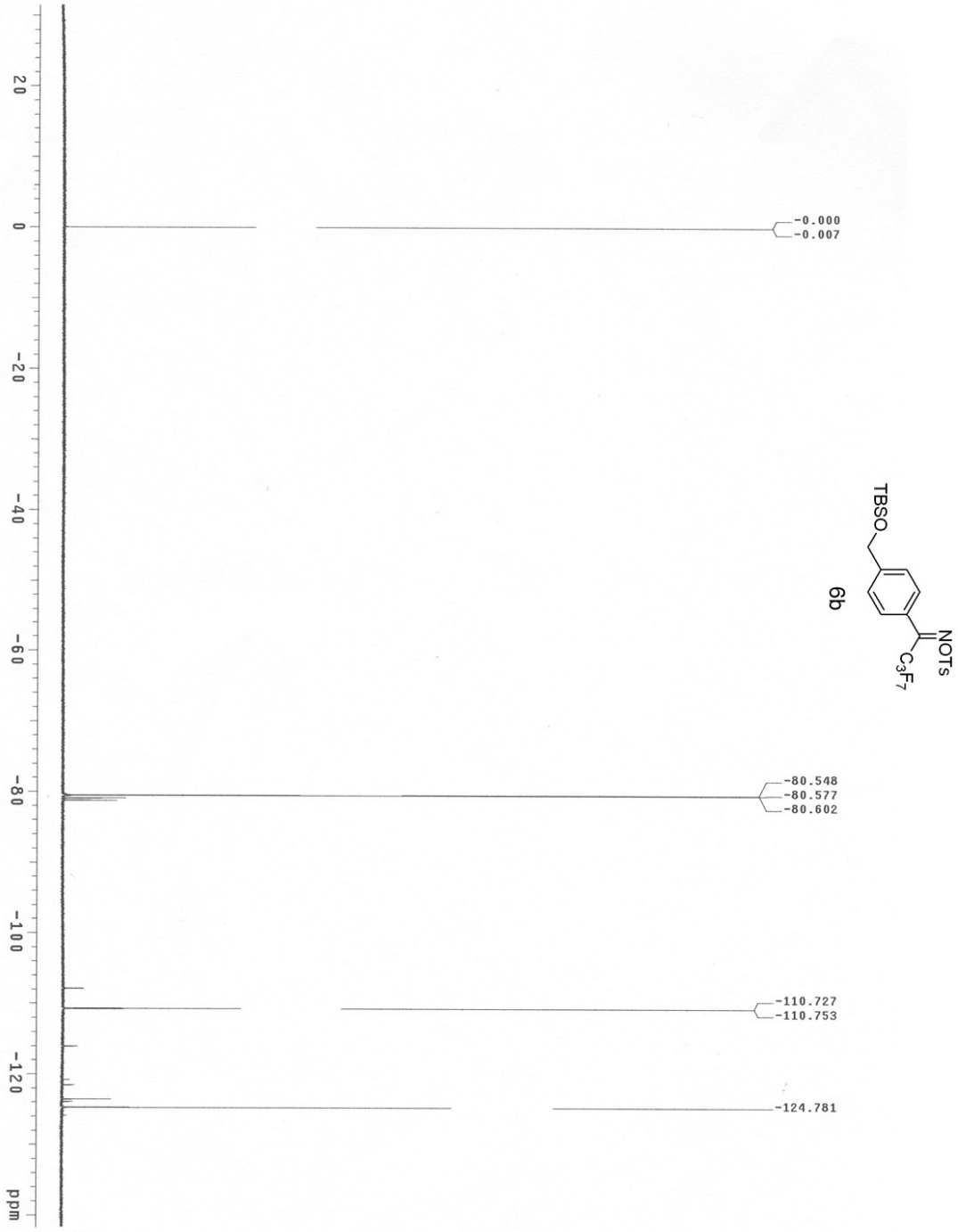
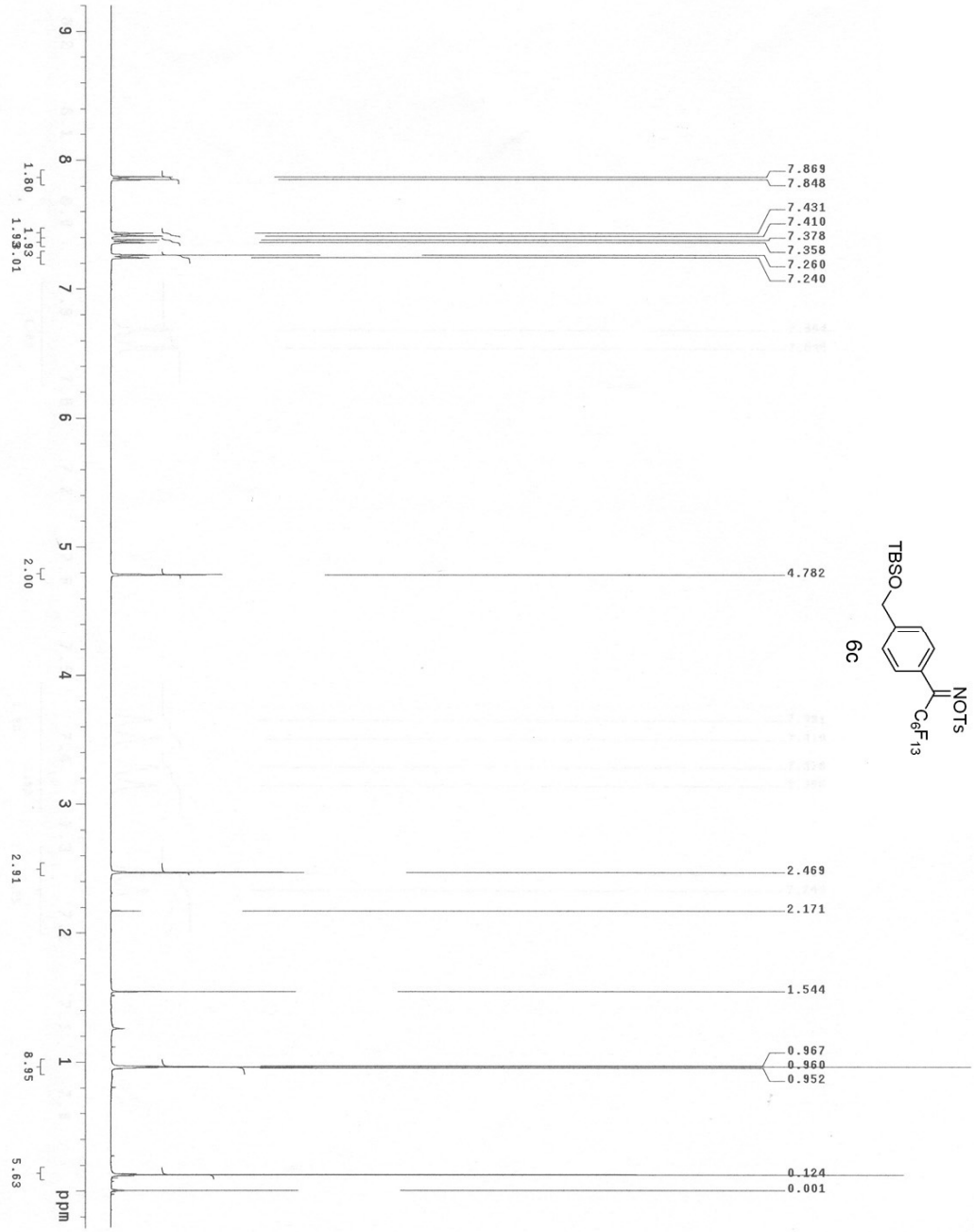
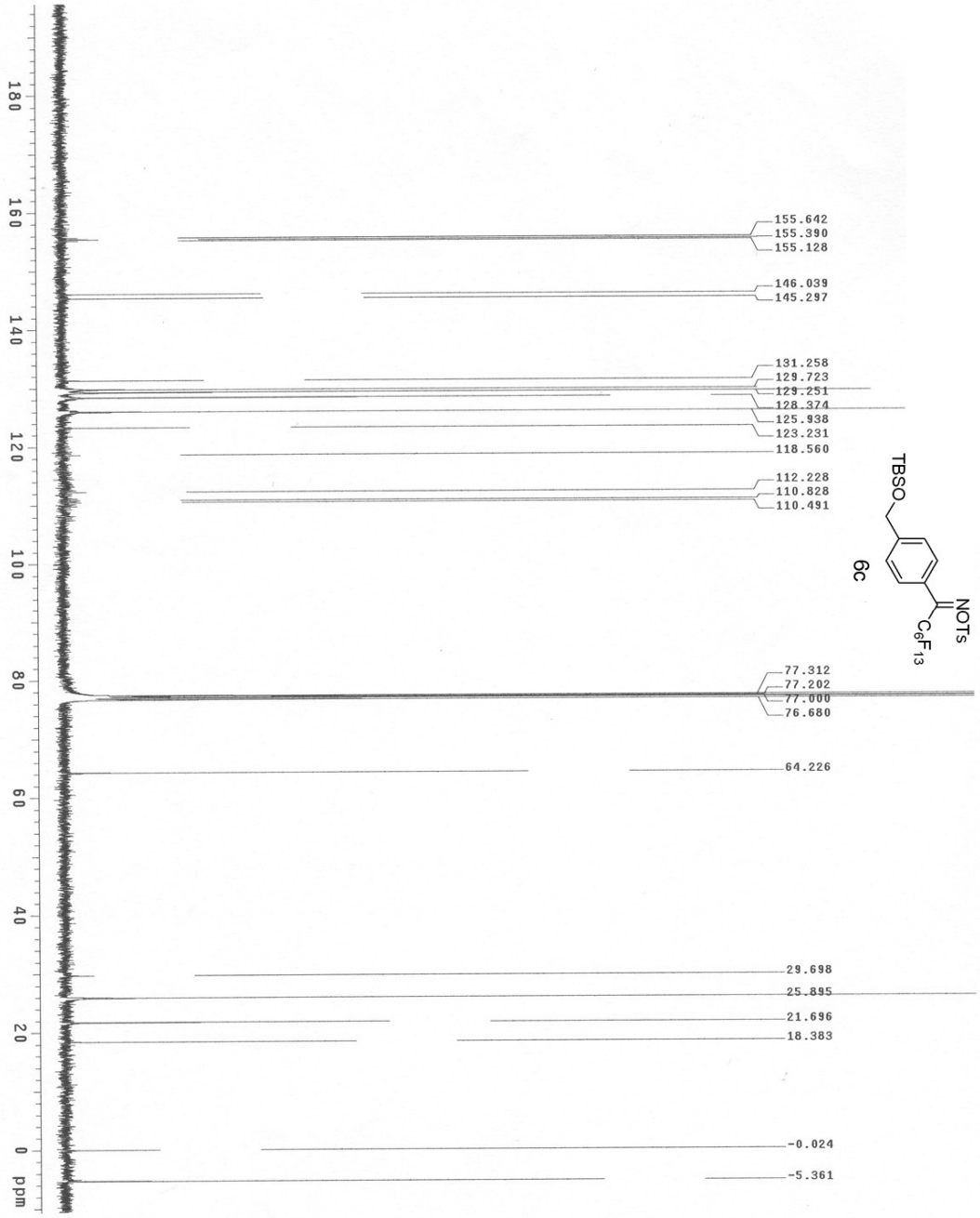
-60
-80
-100
-120
-140
-160
-180
ppm


7.800
7.795
7.778
7.357
7.336
7.313
7.291
7.195
7.188
7.176
4.708
4.693
2.406
2.393
1.480
1.184
0.893
0.887
0.877
0.872
0.050
0.042
0.037
0.026
0.000
-0.071
2.00
2.76
2.99
2.56
3.39
11.55
7.37
ppm
TBSO
NOTs
C_3F_7
6b


146.056
145.320
131.226
129.827
129.748
129.282
129.140
128.389
125.946
123.156
77.316
77.206
77.000
76.684
64.226
25.904
21.770
18.387
-0.016
-5.351
ppm
200
180
160
140
120
100
80
60
40
20
0
TBSO
NOTs
C_3F_7
6b


TBSO
NOTs
C_3F_7
6b
-0.000
-0.007
-80.548
-80.577
-80.602
-110.727
-110.753
-124.781
20
0
-20
-40
-60
-80
-100
-120
ppm


7.869
7.848
7.431
7.410
7.378
7.358
7.260
7.240
4.782
2.469
2.171
1.544
0.967
0.960
0.952
0.124
0.001
ppm
TBSO
NOTs
C_6F_{13}
6c


155.642
155.390
155.128
146.039
145.297
131.258
129.723
129.251
128.374
125.938
123.231
118.560
112.228
110.828
110.491
77.312
77.202
77.000
76.680
64.226
29.698
25.895
21.696
18.383
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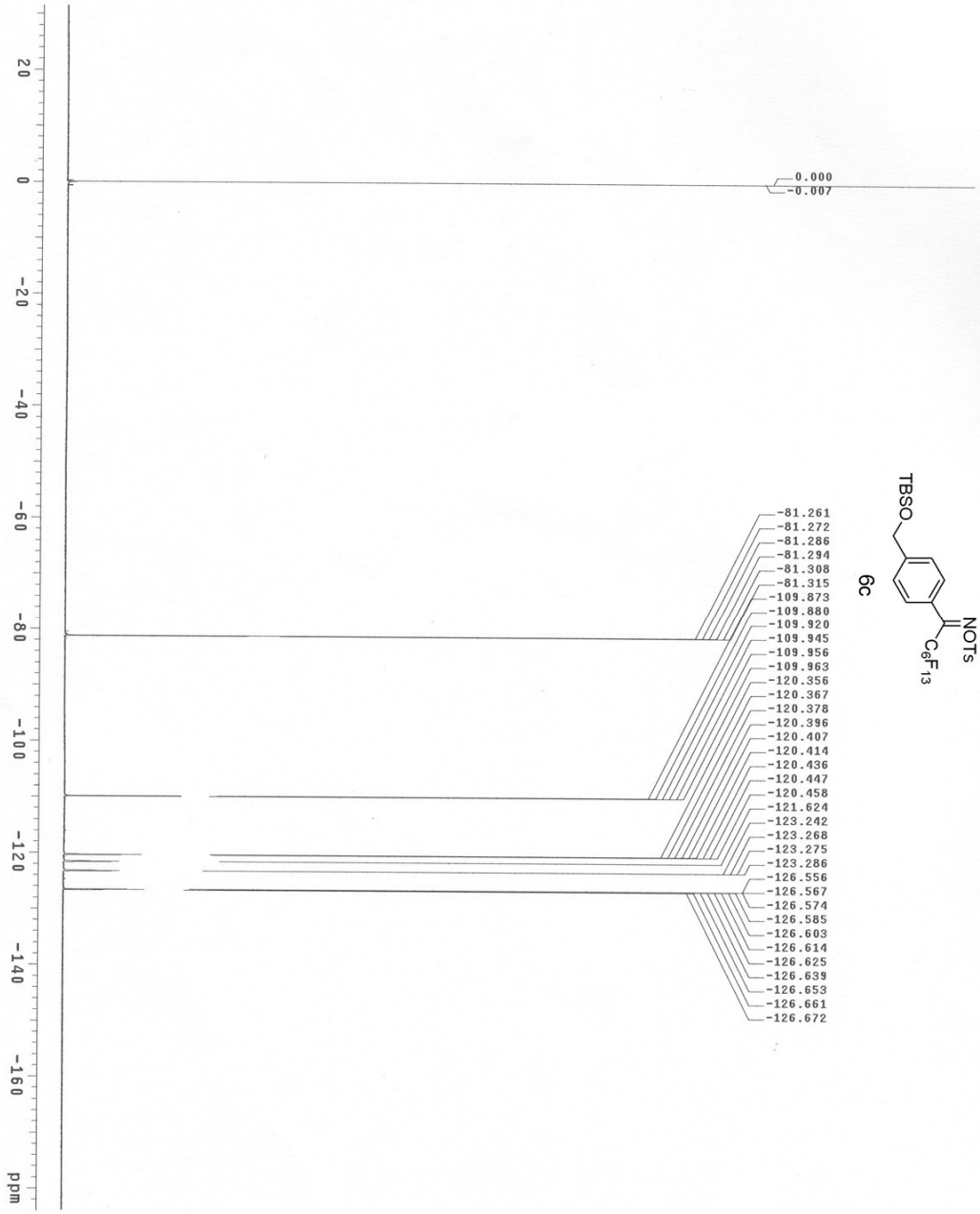
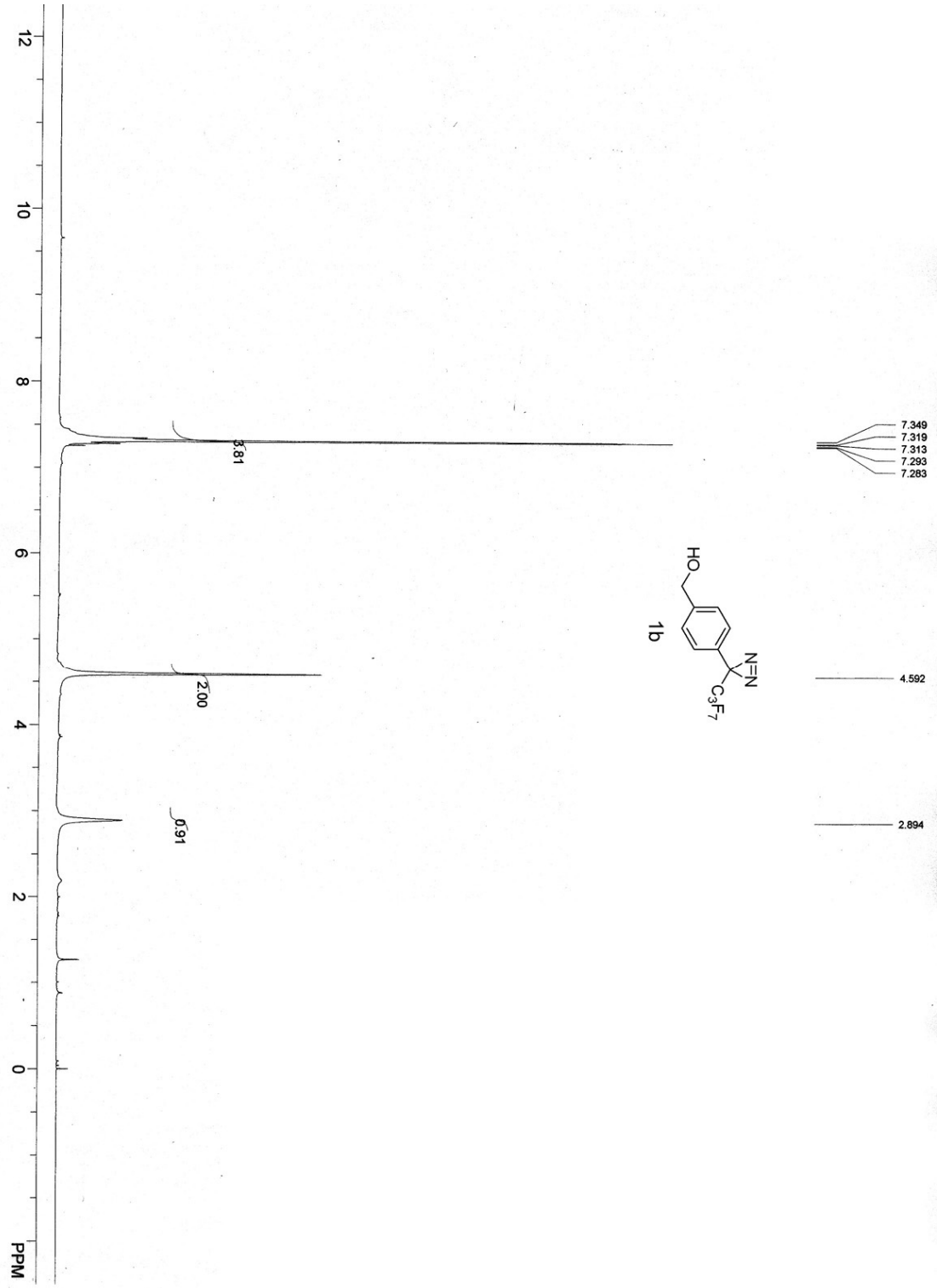
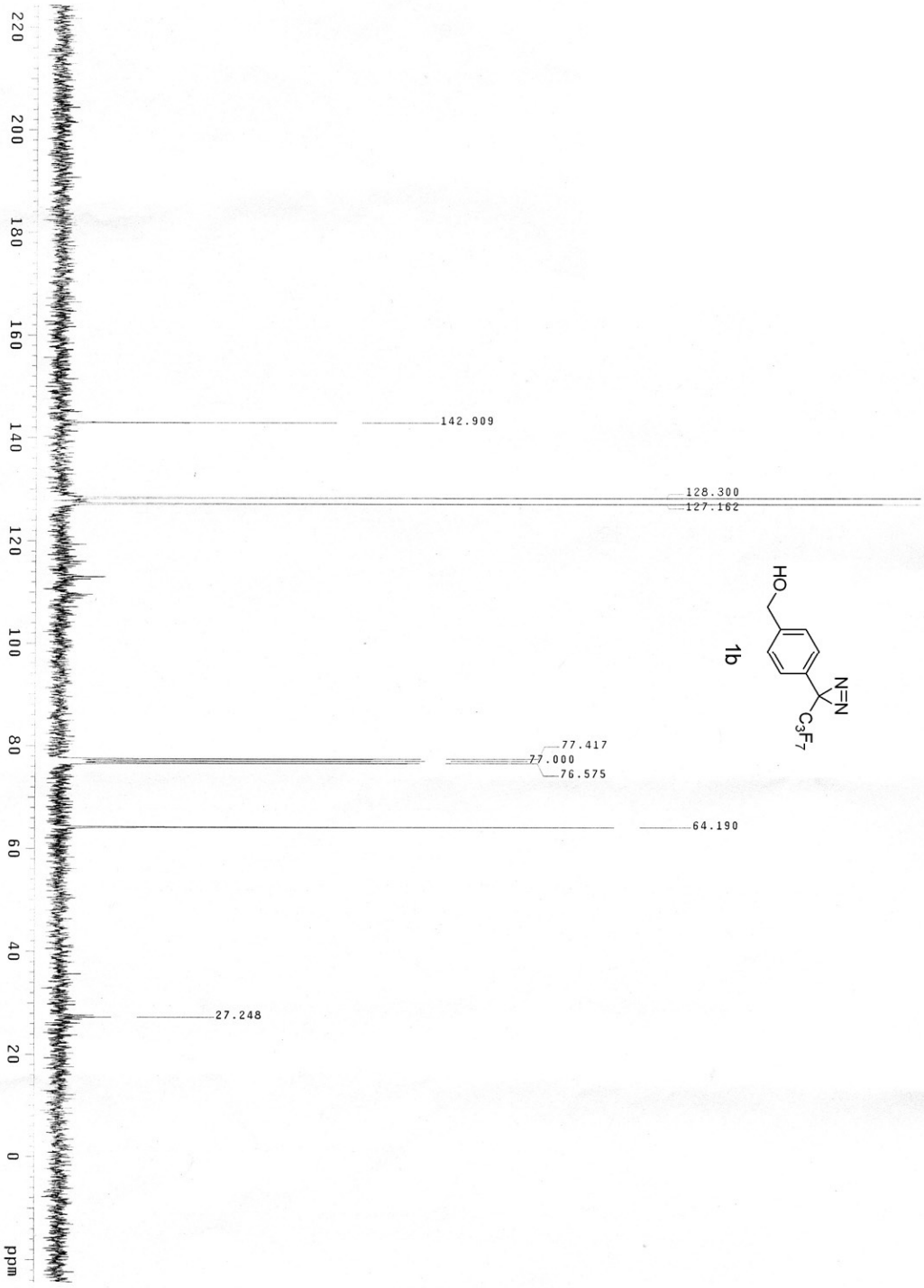
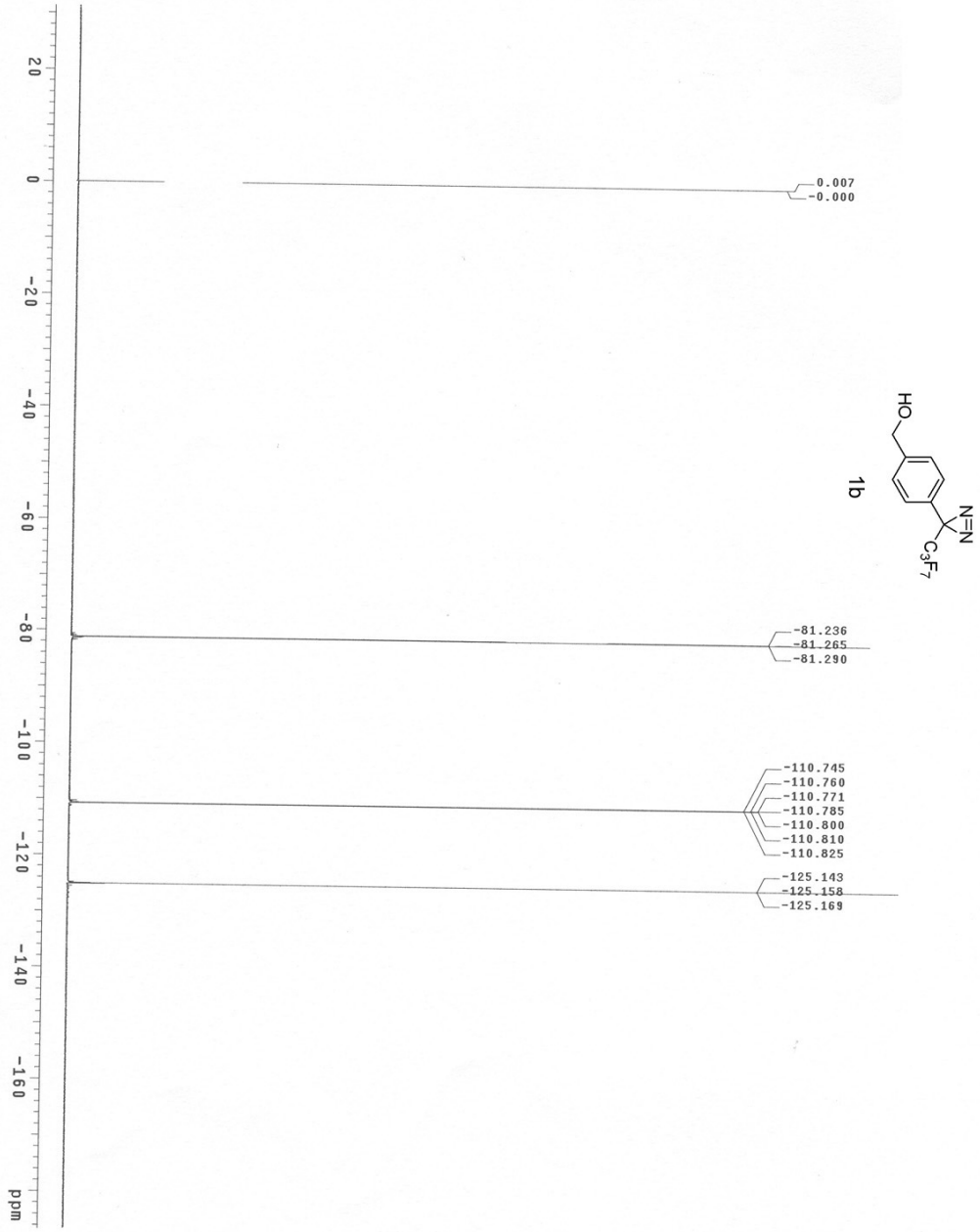
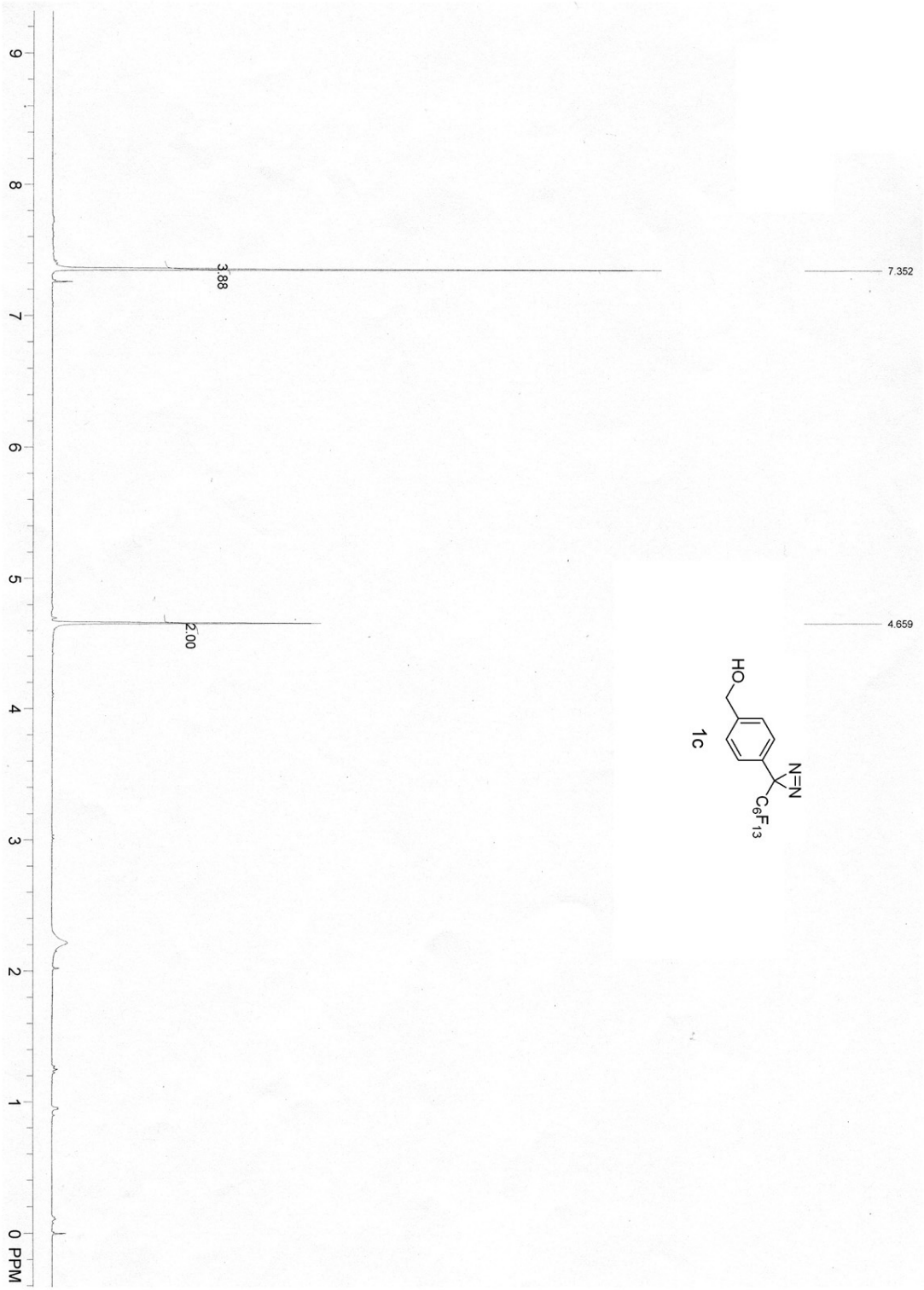
-5.361
ppm
TBSO
NOTs
C_6F_{13}
6c

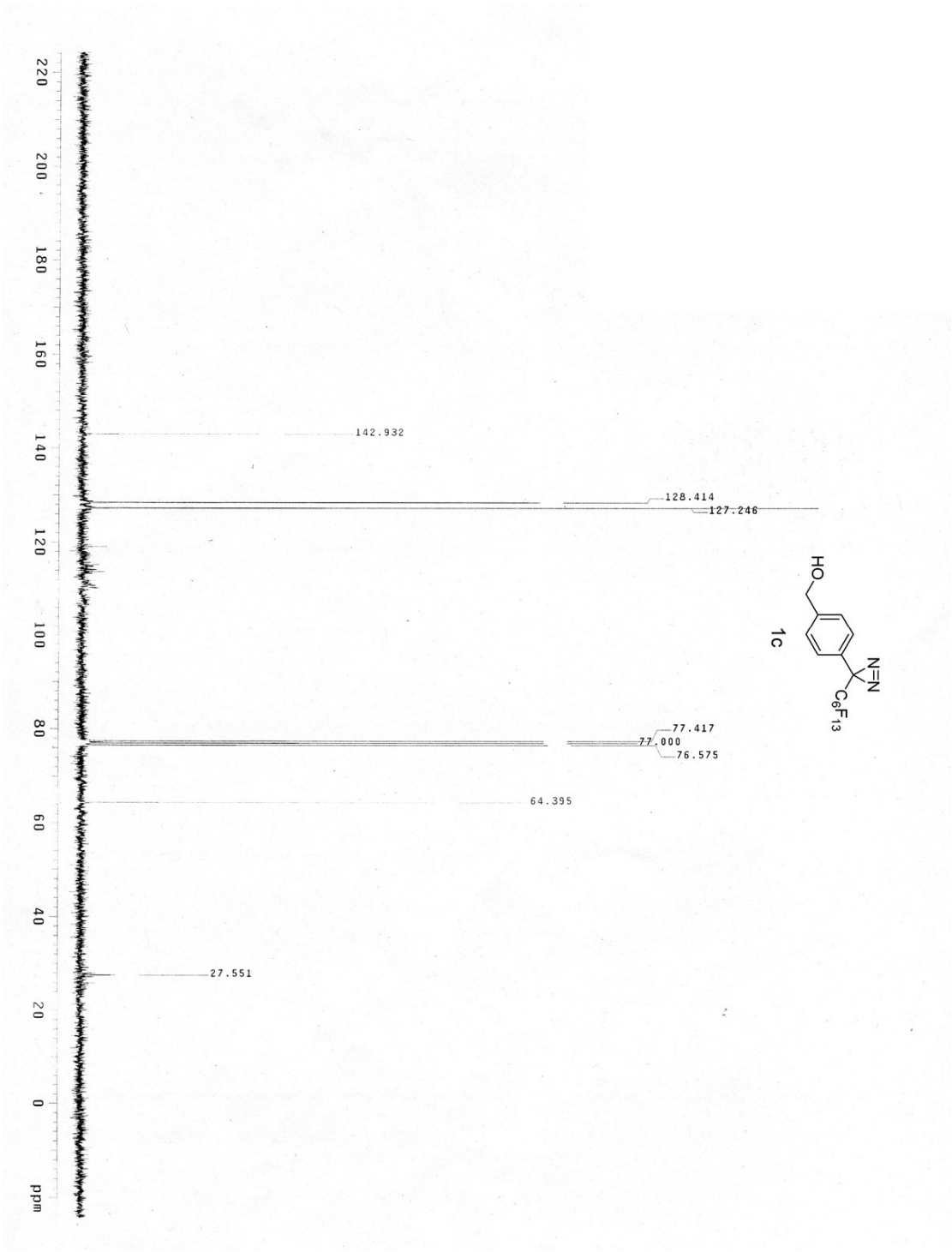

TBSO
NOTs
C_6F_{13}
6c
0.000
-0.007
-81.261
-81.272
-81.286
-81.294
-81.308
-81.315
-109.873
-109.880
-109.920
-109.945
-109.956
-109.963
-120.356
-120.367
-120.378
-120.396
-120.407
-120.414
-120.436
-120.447
-120.458
-121.624
-123.242
-123.268
-123.275
-123.286
-126.556
-126.567
-126.574
-126.585
-126.603
-126.614
-126.625
-126.639
-126.653
-126.661
-126.672
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm

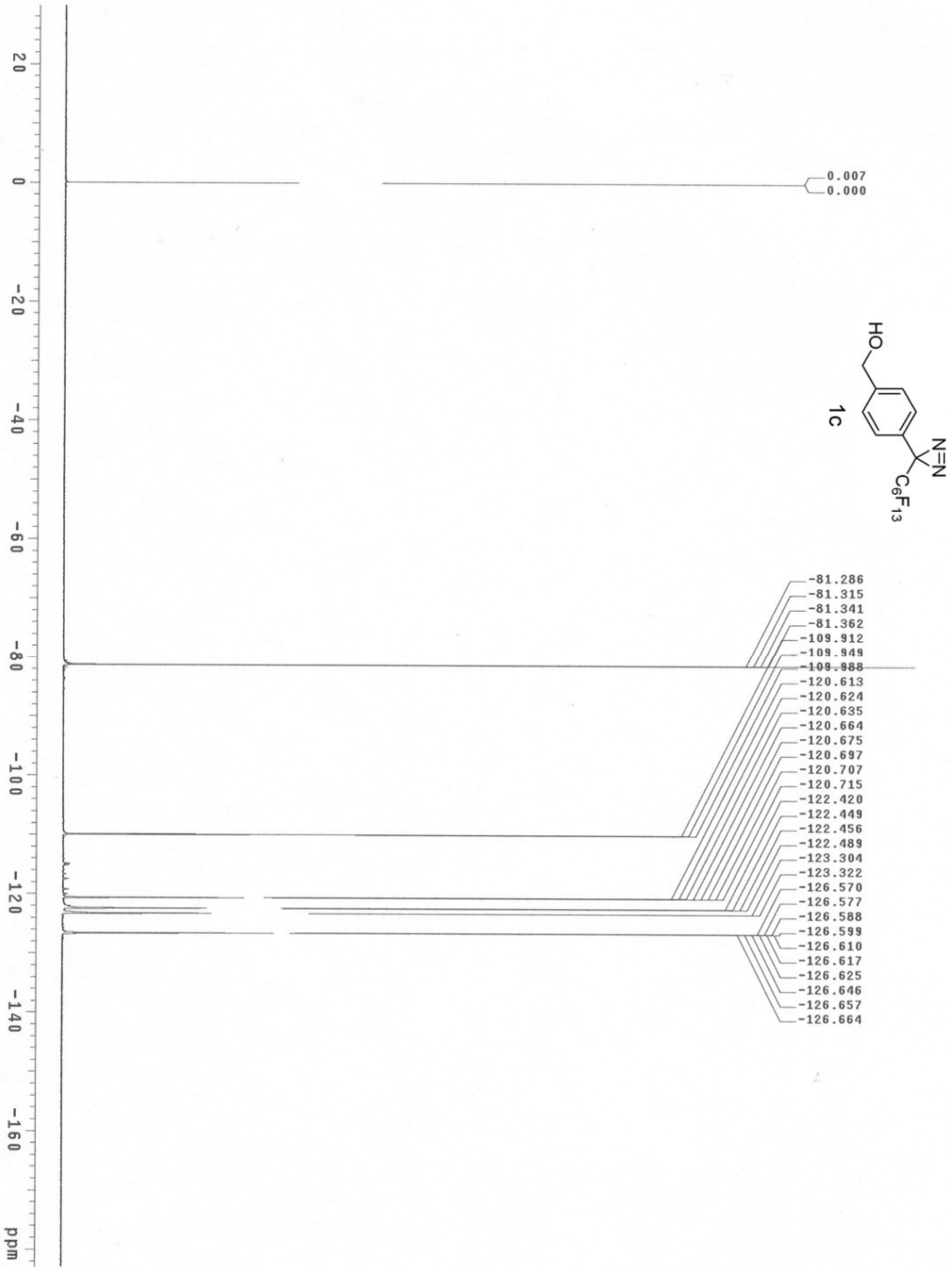

7.349
7.319
7.313
7.293
7.283
4.592
2.894
3.81
2.00
0.91
HO
N=N
C3F7
1b
12
10
8
6
4
2
0
PPM

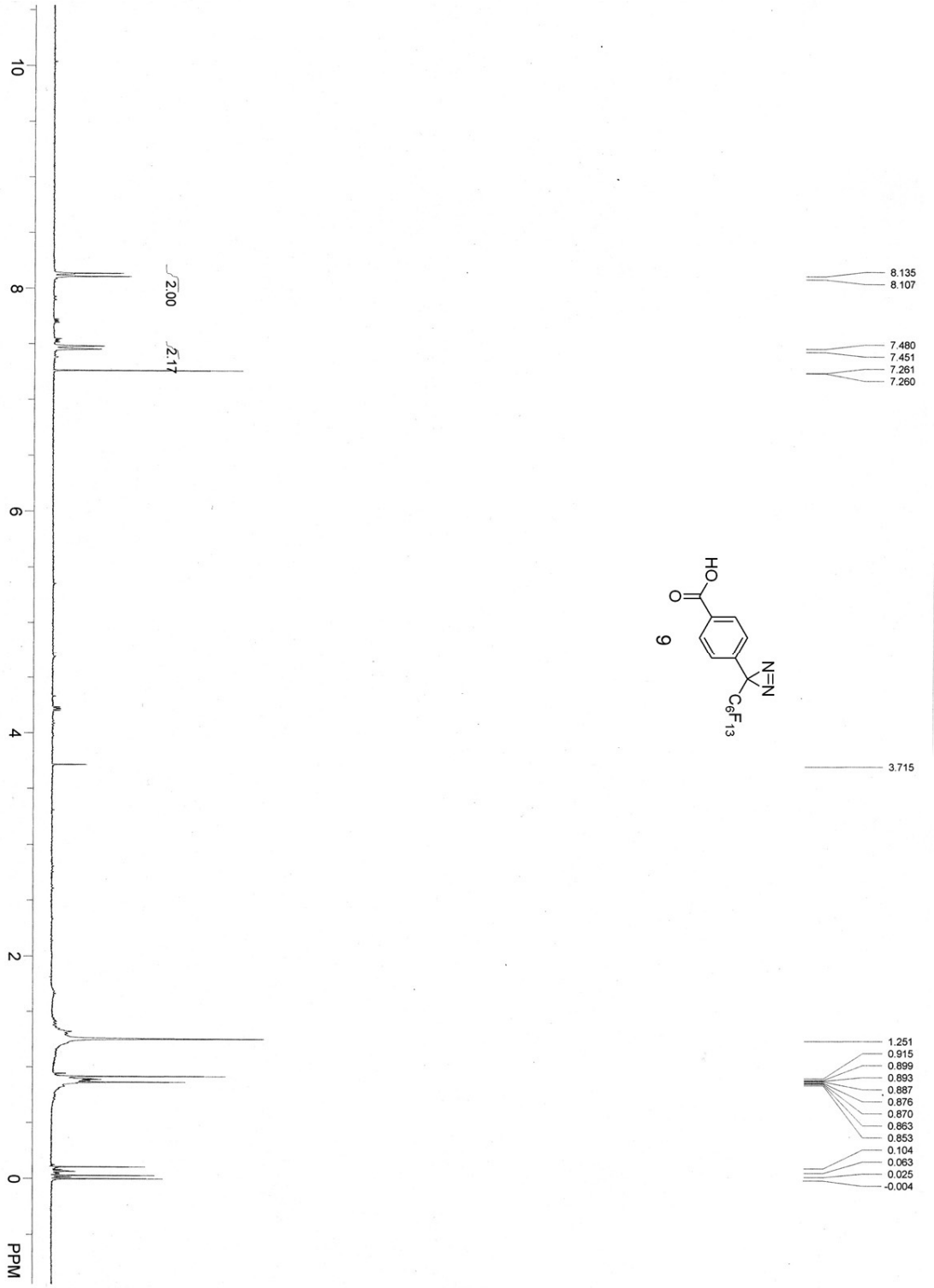

142.909
128.300
127.162
77.417
77.000
76.575
64.190
27.248
ppm
220
200
180
160
140
120
100
80
60
40
20
0
HO
N=N
C3F7
1b

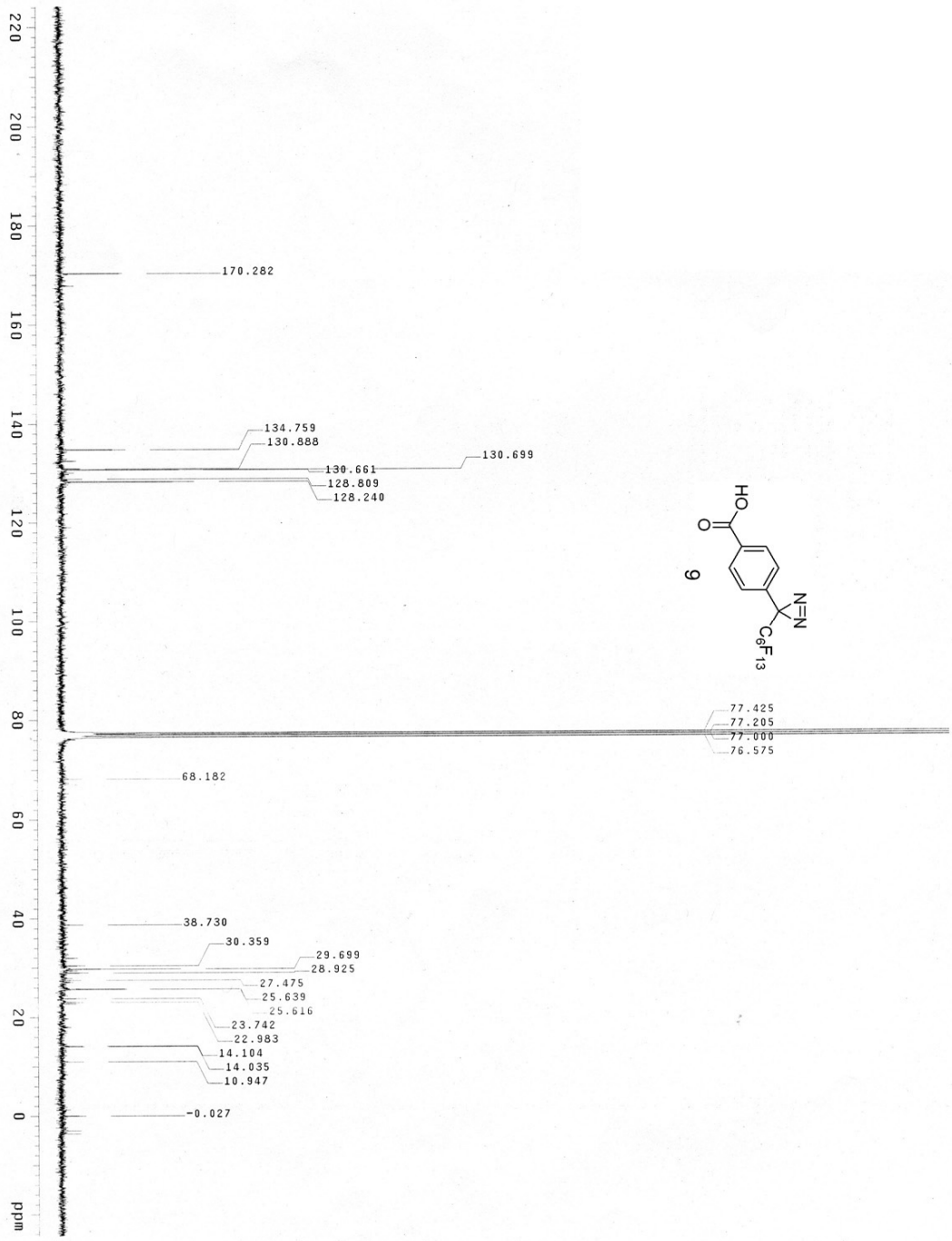

0.007
-0.000
-81.236
-81.265
-81.290
-110.745
-110.760
-110.771
-110.785
-110.800
-110.810
-110.825
-125.143
-125.158
-125.169
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm
HO
N=N
C3F7
1b

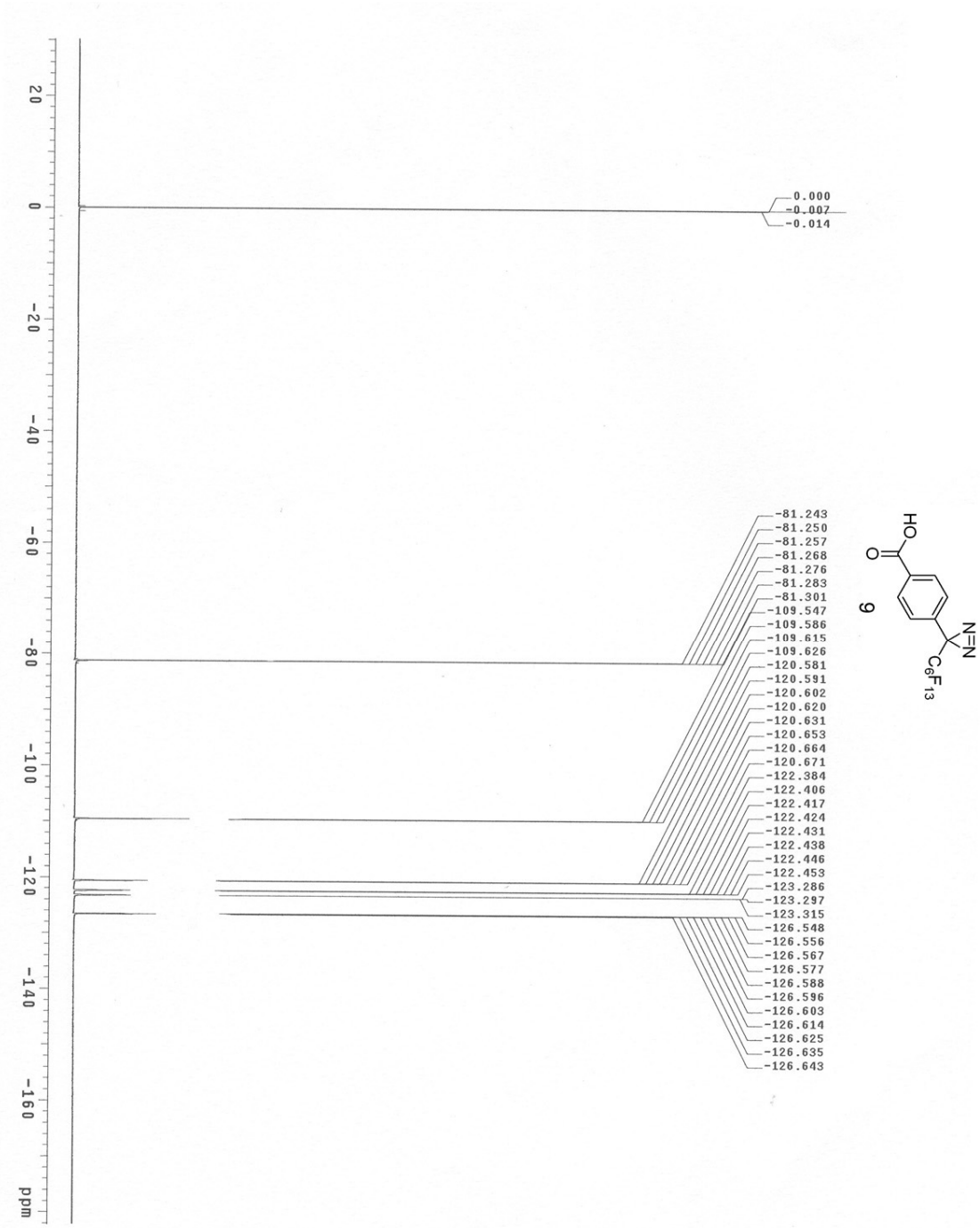

7.352
4.659
HO
N=N
C_6F_{13}
1c
3.88
2.00
9
8
7
6
5
4
3
2
1
0 PPM

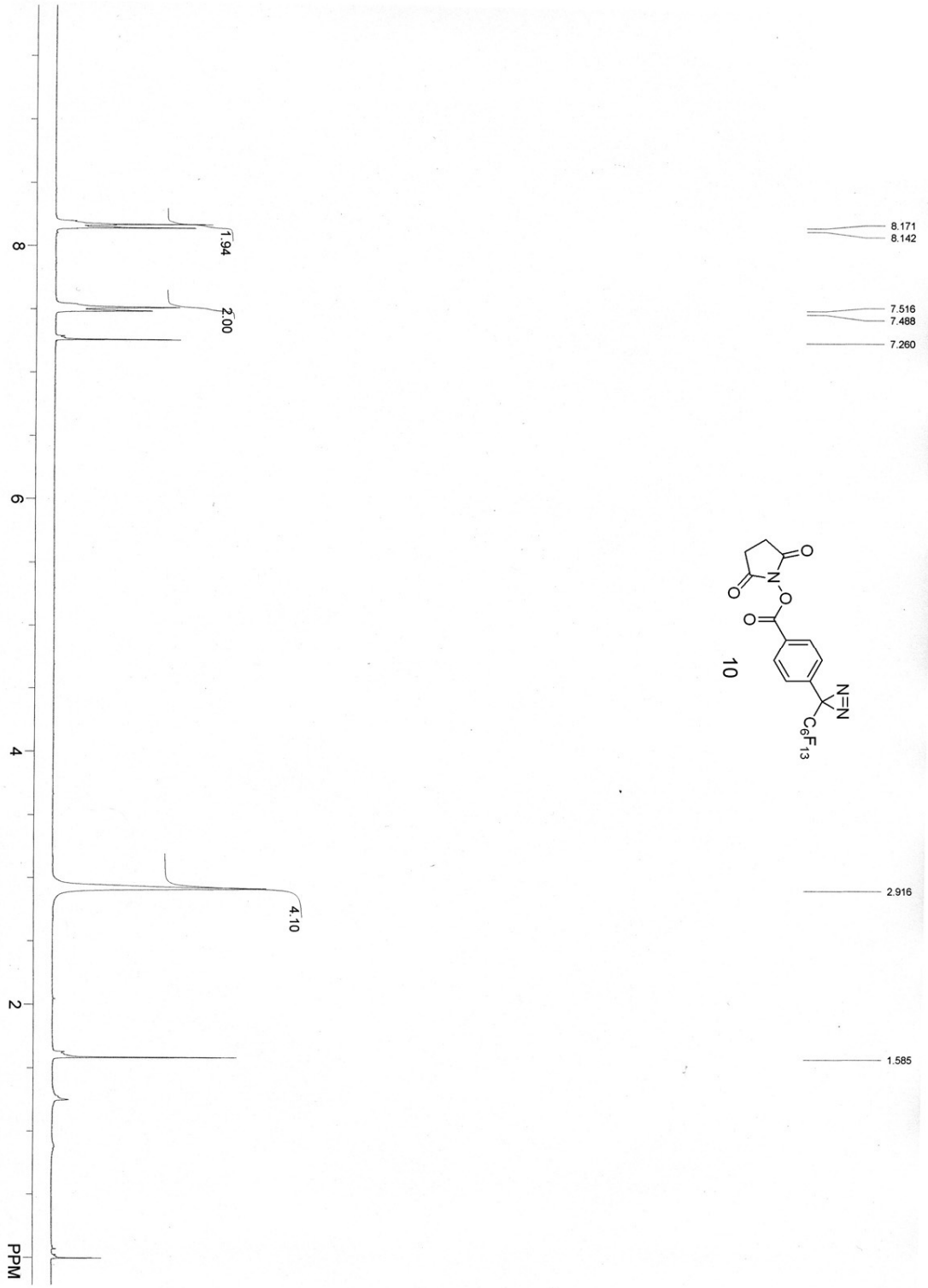

142.932
128.414
127.246
77.417
77.000
76.575
64.395
27.551
220
200
180
160
140
120
100
80
60
40
20
0
ppm
HO
N=N
C6F13
1c

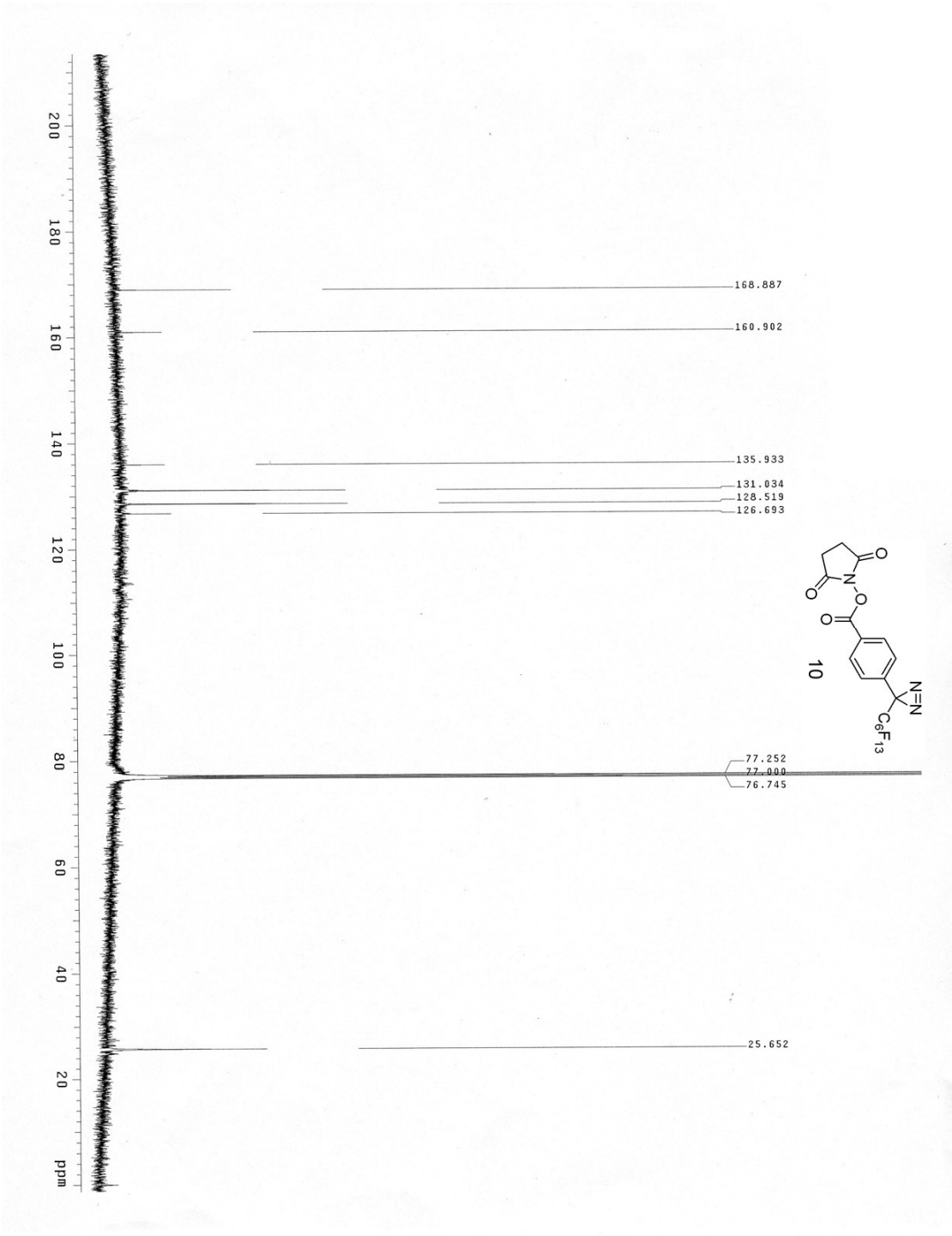

0.007
0.000
HO
N=N
C6F13
1c
-81.286
-81.315
-81.341
-81.362
-109.912
-109.949
-109.988
-120.613
-120.624
-120.635
-120.664
-120.675
-120.697
-120.707
-120.715
-122.420
-122.449
-122.456
-122.489
-123.304
-123.322
-126.570
-126.577
-126.588
-126.599
-126.610
-126.617
-126.625
-126.646
-126.657
-126.664
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm

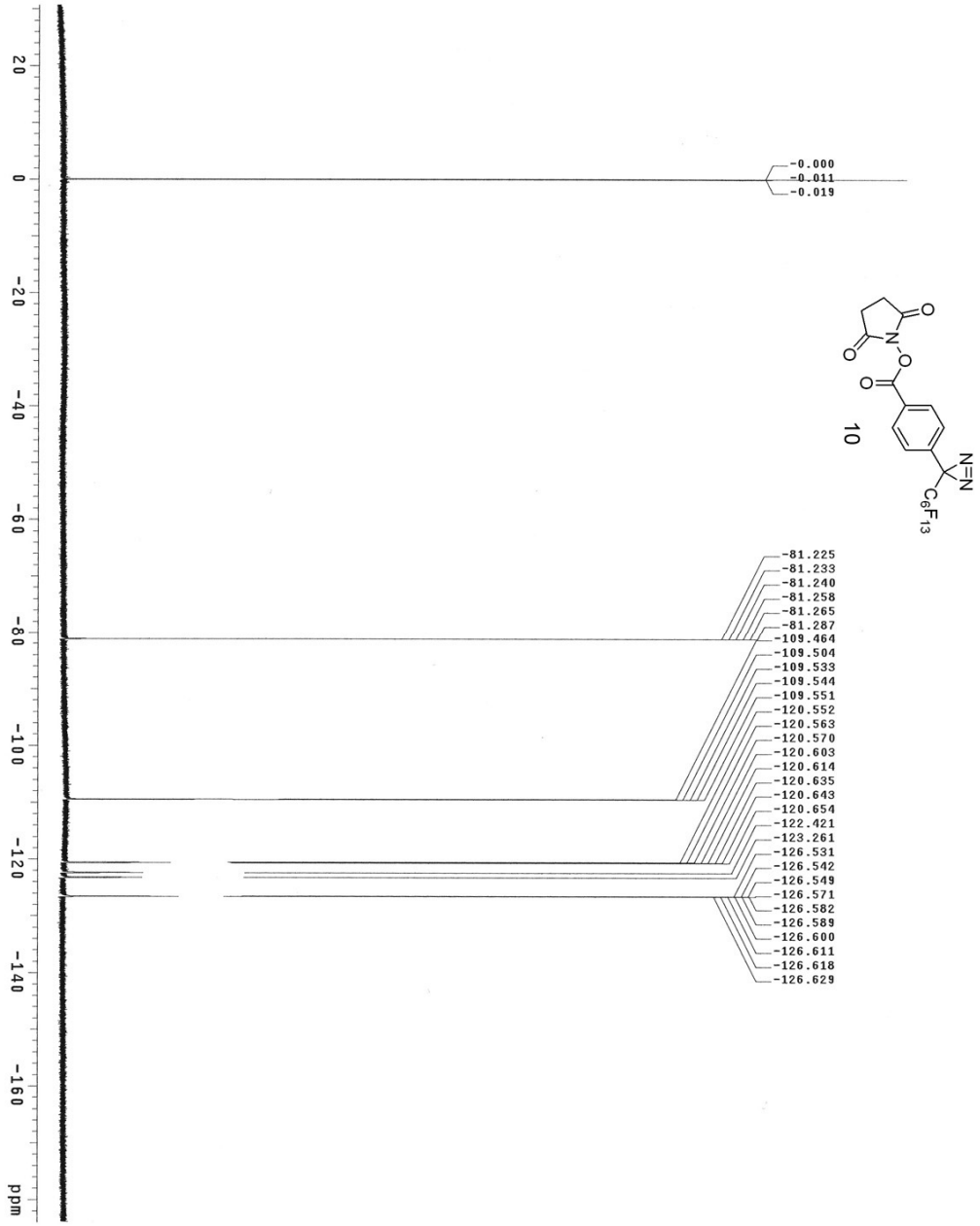

8.135
8.107
7.480
7.451
7.261
7.260
3.715
1.251
0.915
0.899
0.893
0.887
0.876
0.870
0.863
0.853
0.104
0.063
0.025
-0.004
2.00
2.17
HO
O
N=N
C6F13
9
10
8
6
4
2
0
PPM


170.282
134.759
130.888
130.661
130.699
128.809
128.240
77.425
77.205
77.000
76.575
68.182
38.730
30.359
29.699
28.925
27.475
25.639
25.616
23.742
22.983
14.104
14.035
10.947
-0.027
ppm
220
200
180
160
140
120
100
80
60
40
20
0
HO
O
N=N
C6F13
6


0.000
-0.007
-0.014
-81.243
-81.250
-81.257
-81.268
-81.276
-81.283
-81.301
-109.547
-109.586
-109.615
-109.626
-120.581
-120.591
-120.602
-120.620
-120.631
-120.653
-120.664
-120.671
-122.384
-122.406
-122.417
-122.424
-122.431
-122.438
-122.446
-122.453
-123.286
-123.297
-123.315
-126.548
-126.556
-126.567
-126.577
-126.588
-126.596
-126.603
-126.614
-126.625
-126.635
-126.643
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm
HO
O
N=N
C_6F_{13}
9


8.171
8.142
7.516
7.488
7.260
2.916
1.585
10
N=N
C6F13
O
N
O
O
O
1.94
2.00
4.10
8
6
4
2
PPM


168.887
160.902
135.933
131.034
128.519
126.693
77.252
77.000
76.745
25.652
10
N=N
C6F13
O
N
O
O
O
200
180
160
140
120
100
80
60
40
20
ppm


-0.000
-0.011
-0.019
10
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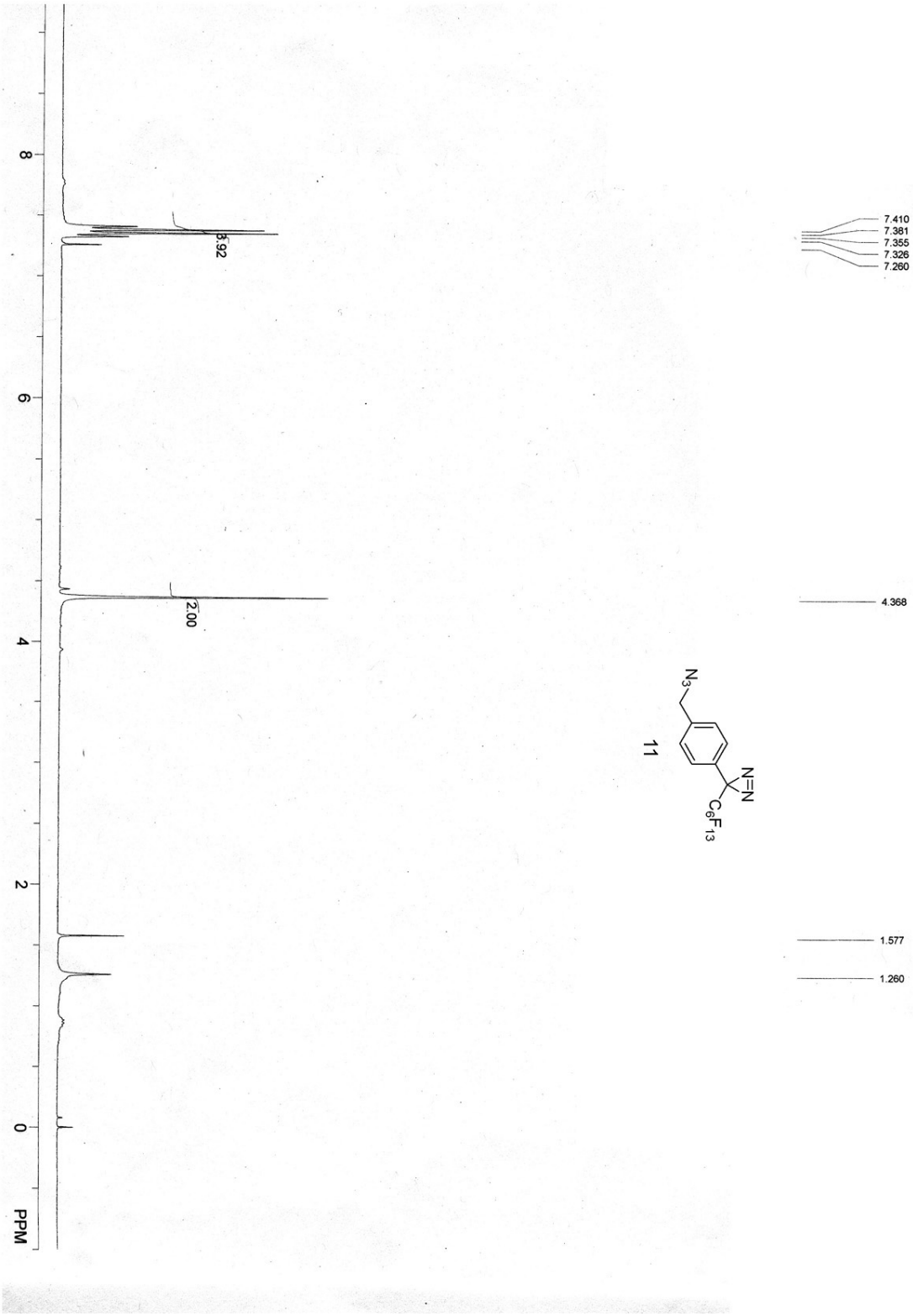
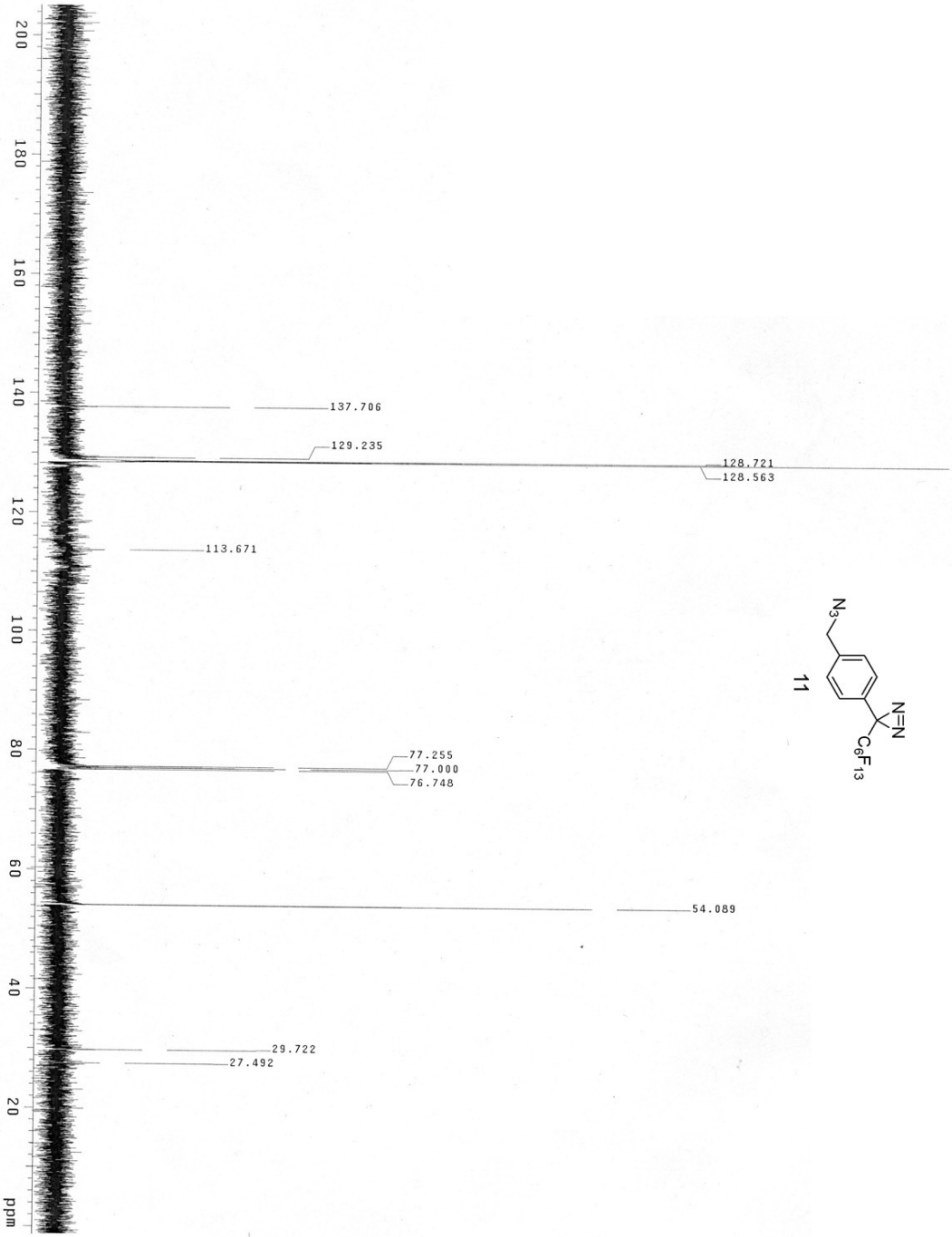
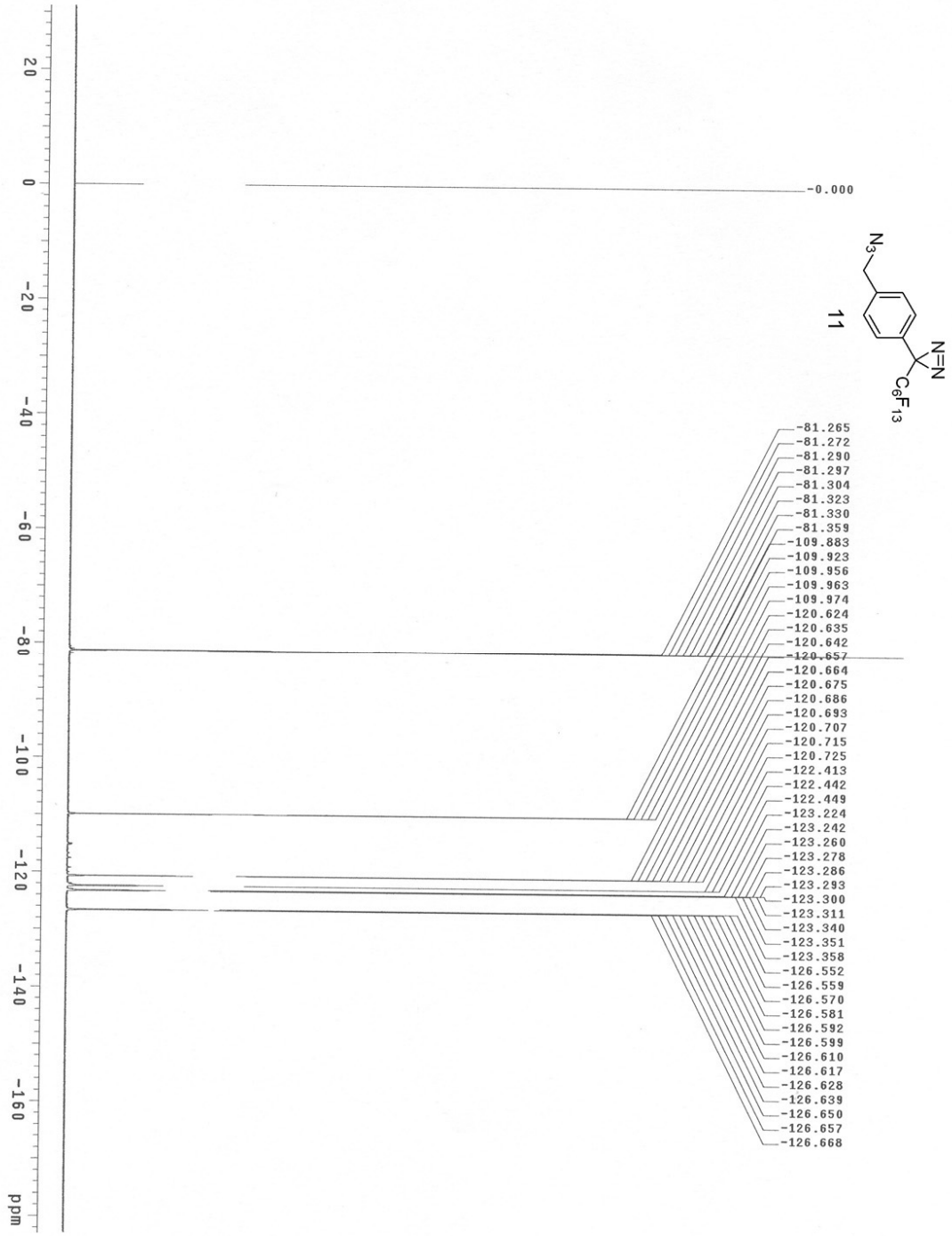
C6F13
-81.225
-81.233
-81.240
-81.258
-81.265
-81.287
-109.464
-109.504
-109.533
-109.544
-109.551
-120.552
-120.563
-120.570
-120.603
-120.614
-120.635
-120.643
-120.654
-122.421
-123.261
-126.531
-126.542
-126.549
-126.571
-126.582
-126.589
-126.600
-126.611
-126.618
-126.629
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm


7.410
7.381
7.355
7.326
7.260
4.368
1.577
1.260
3.92
2.00
8
6
4
2
0
PPM
11
N=N
C6F13
N3


137.706
129.235
128.721
128.563
113.671
77.255
77.000
76.748
54.089
29.722
27.492
ppm
200
180
160
140
120
100
80
60
40
20
11
N3
N=N
C6F13


N=N
C6F13
N3
11
-0.000
-81.265
-81.272
-81.290
-81.297
-81.304
-81.323
-81.330
-81.359
-109.883
-109.923
-109.956
-109.963
-109.974
-120.624
-120.635
-120.642
-120.657
-120.664
-120.675
-120.686
-120.693
-120.707
-120.715
-120.725
-122.413
-122.442
-122.449
-123.224
-123.242
-123.260
-123.278
-123.286
-123.293
-123.300
-123.311
-123.340
-123.351
-123.358
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-126.570
-126.581
-126.592
-126.599
-126.610
-126.617
-126.628
-126.639
-126.650
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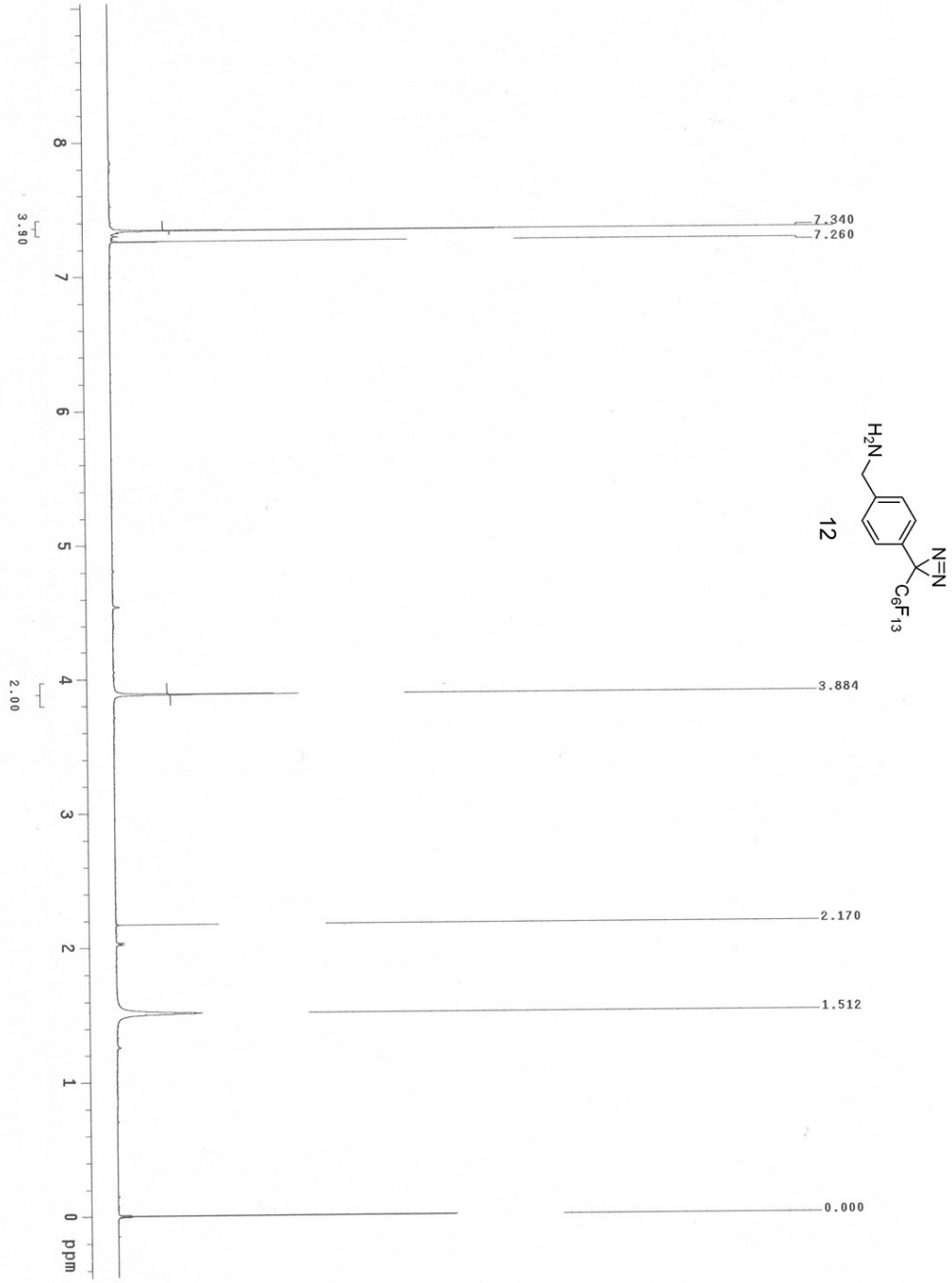
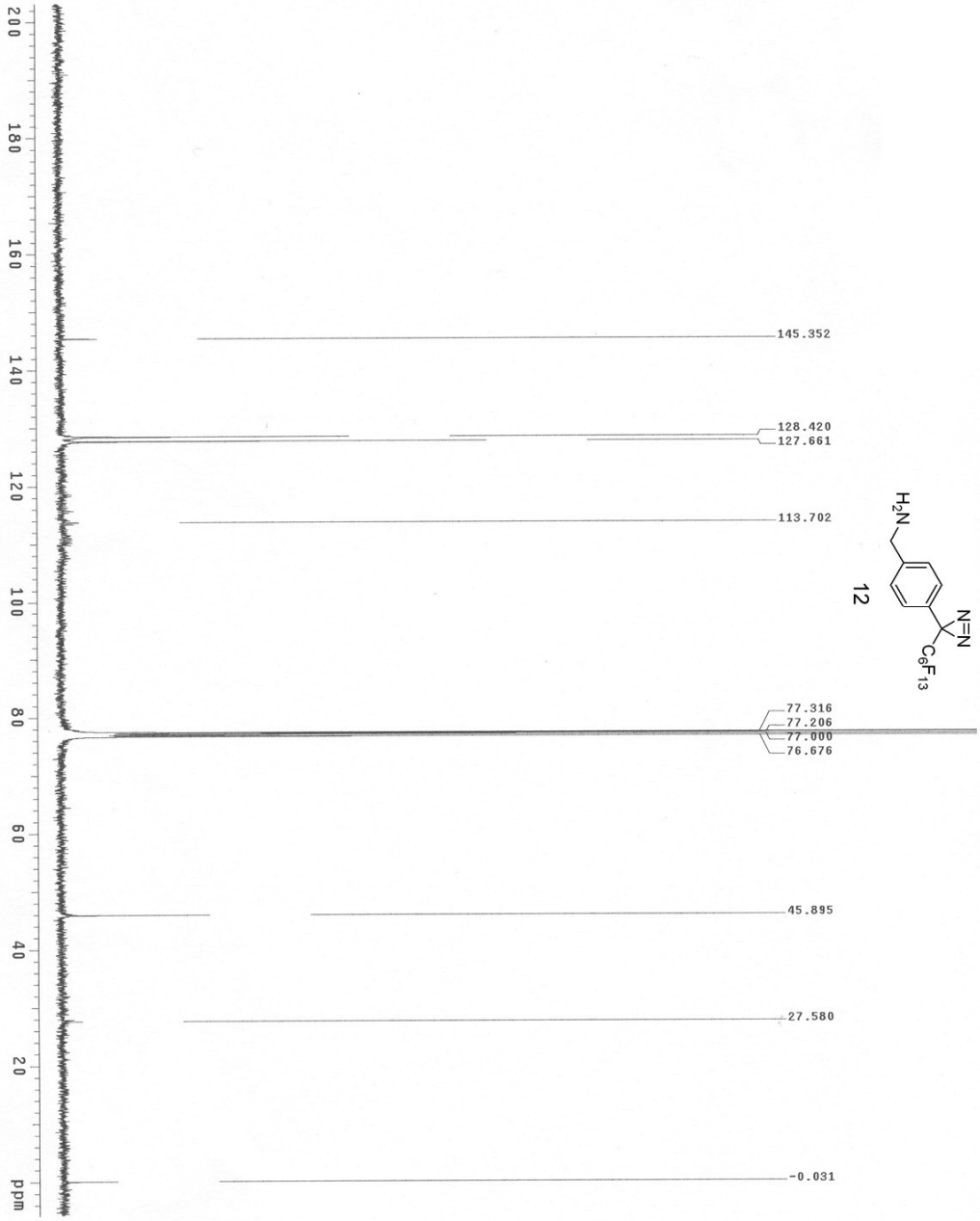
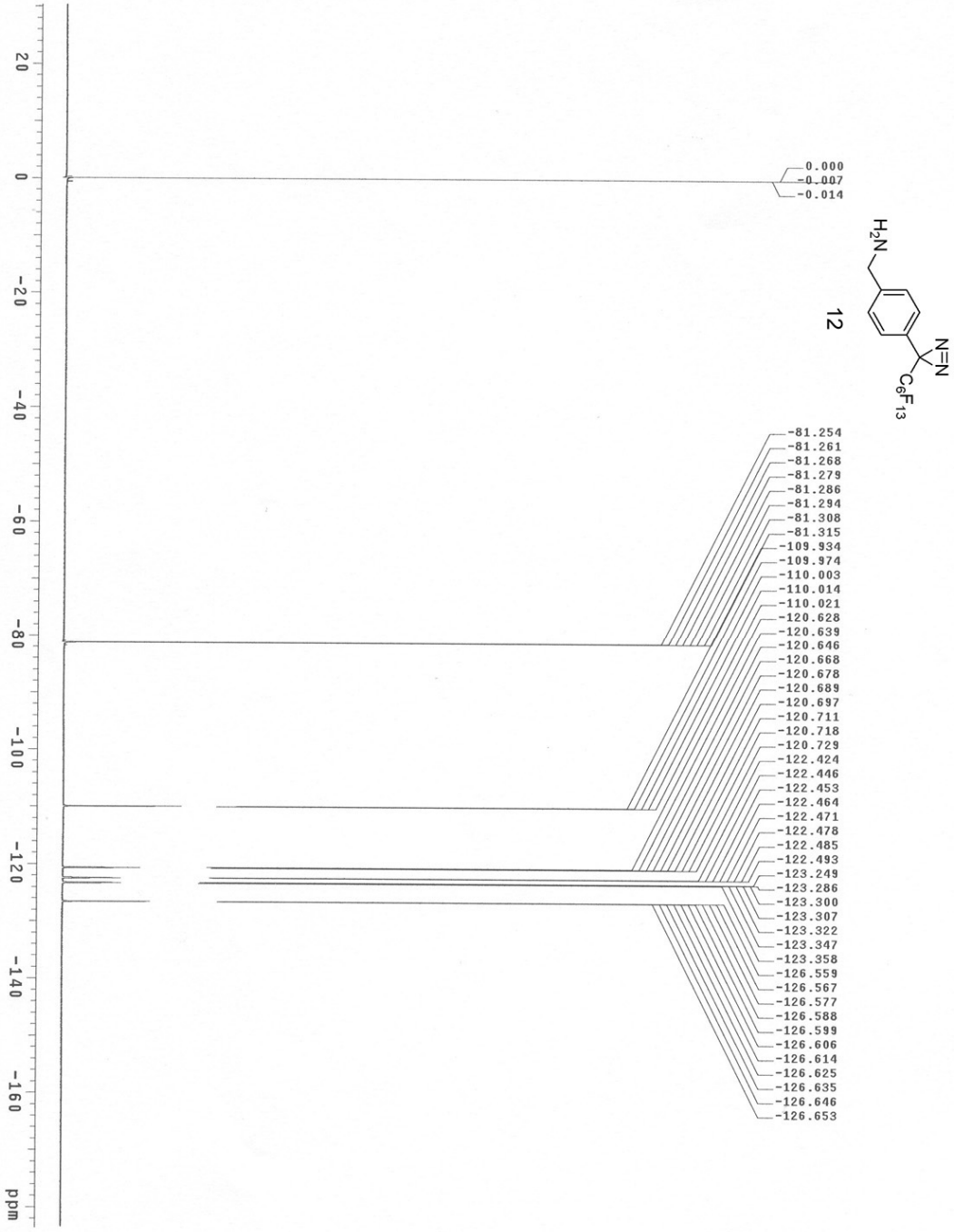
-126.668
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm


7.340
7.260
3.884
2.170
1.512
0.000
3.90
2.00
ppm
12
N=N
C_6F_{13}
H_2N


145.352
128.420
127.661
113.702
77.316
77.206
77.000
76.676
45.895
27.580
-0.031
ppm
200
180
160
140
120
100
80
60
40
20
H2N
N=N
C6F13
12


N=N
C6F13
H2N
12
0.000
-0.007
-0.014
-81.254
-81.261
-81.268
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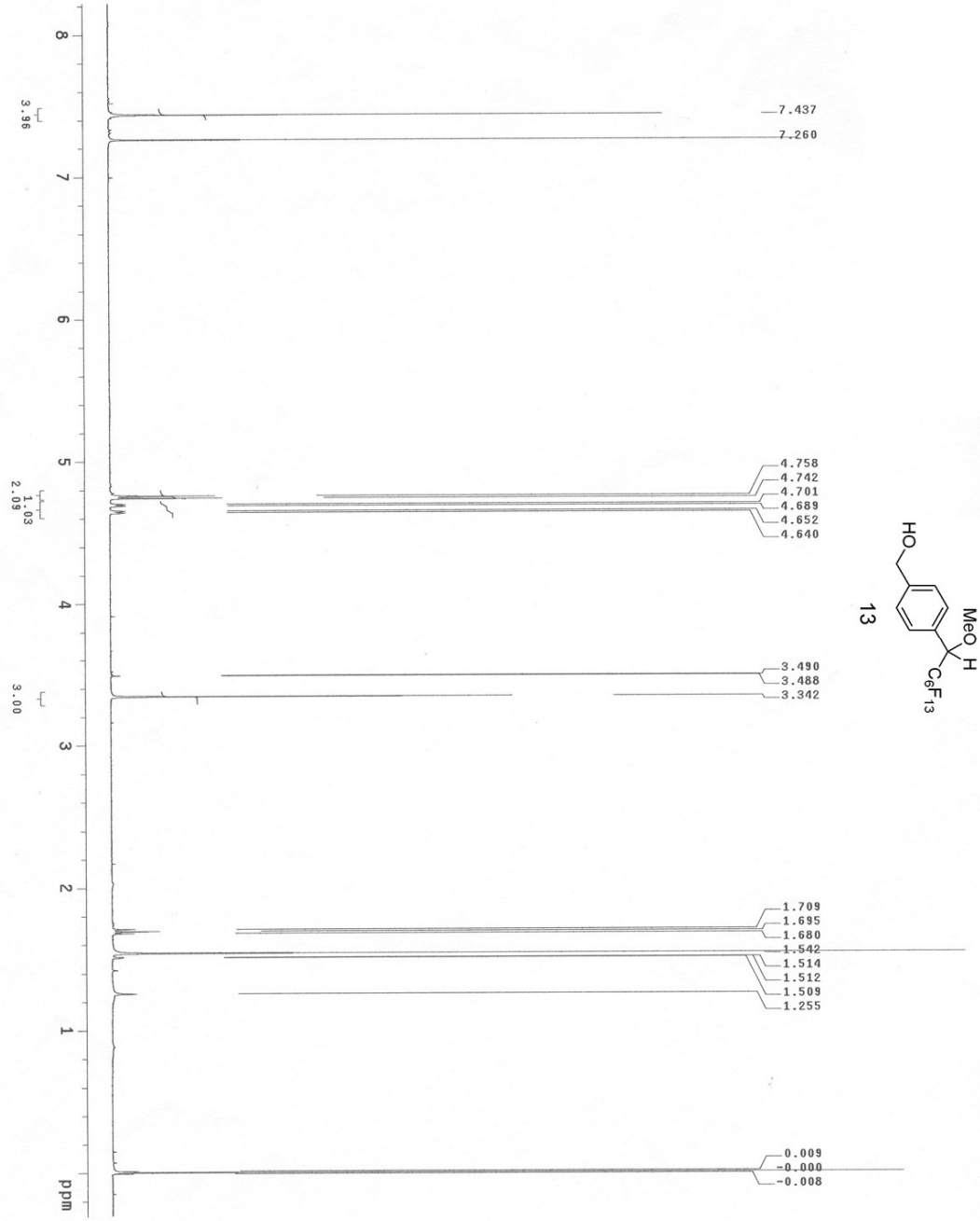
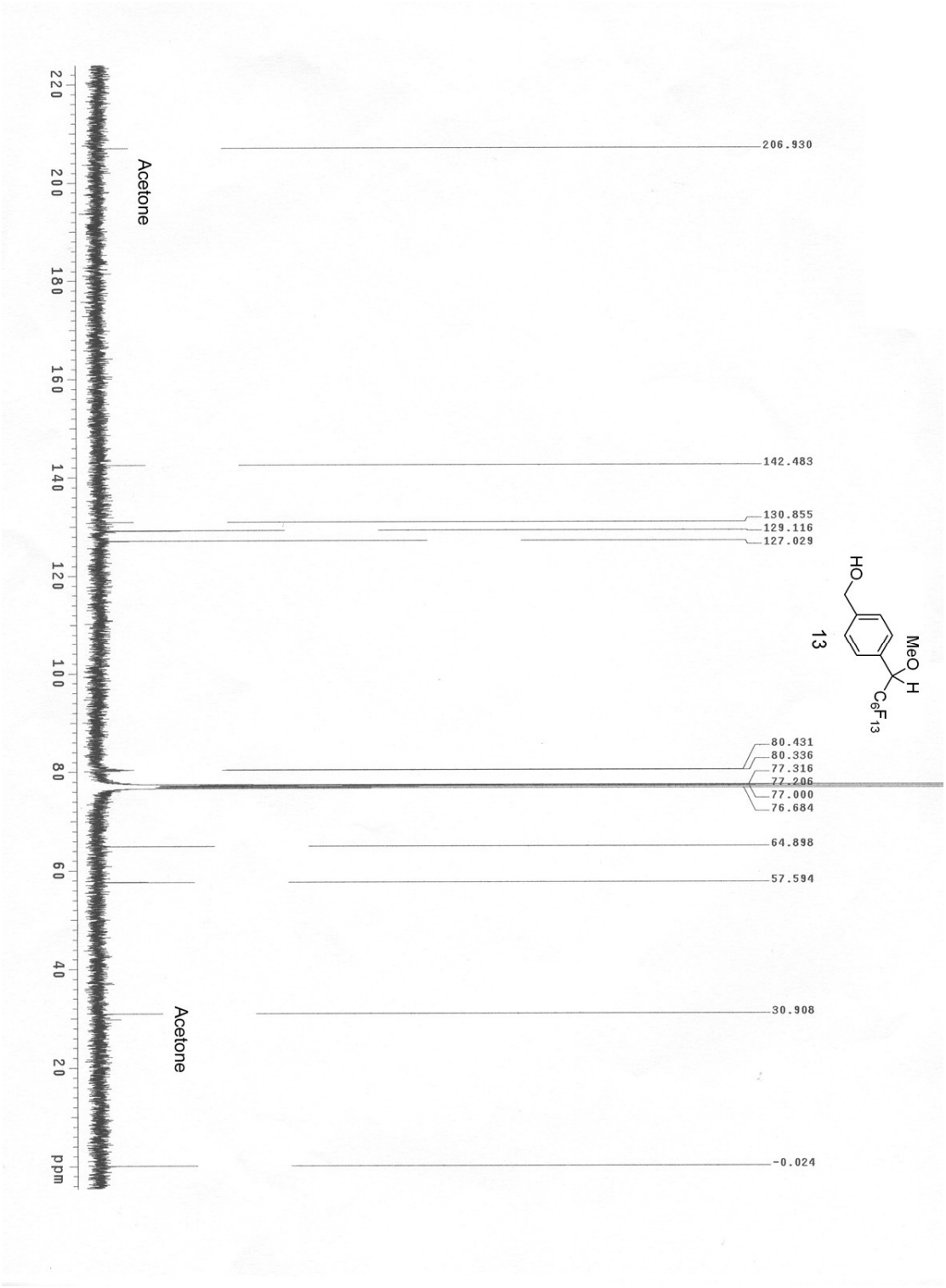
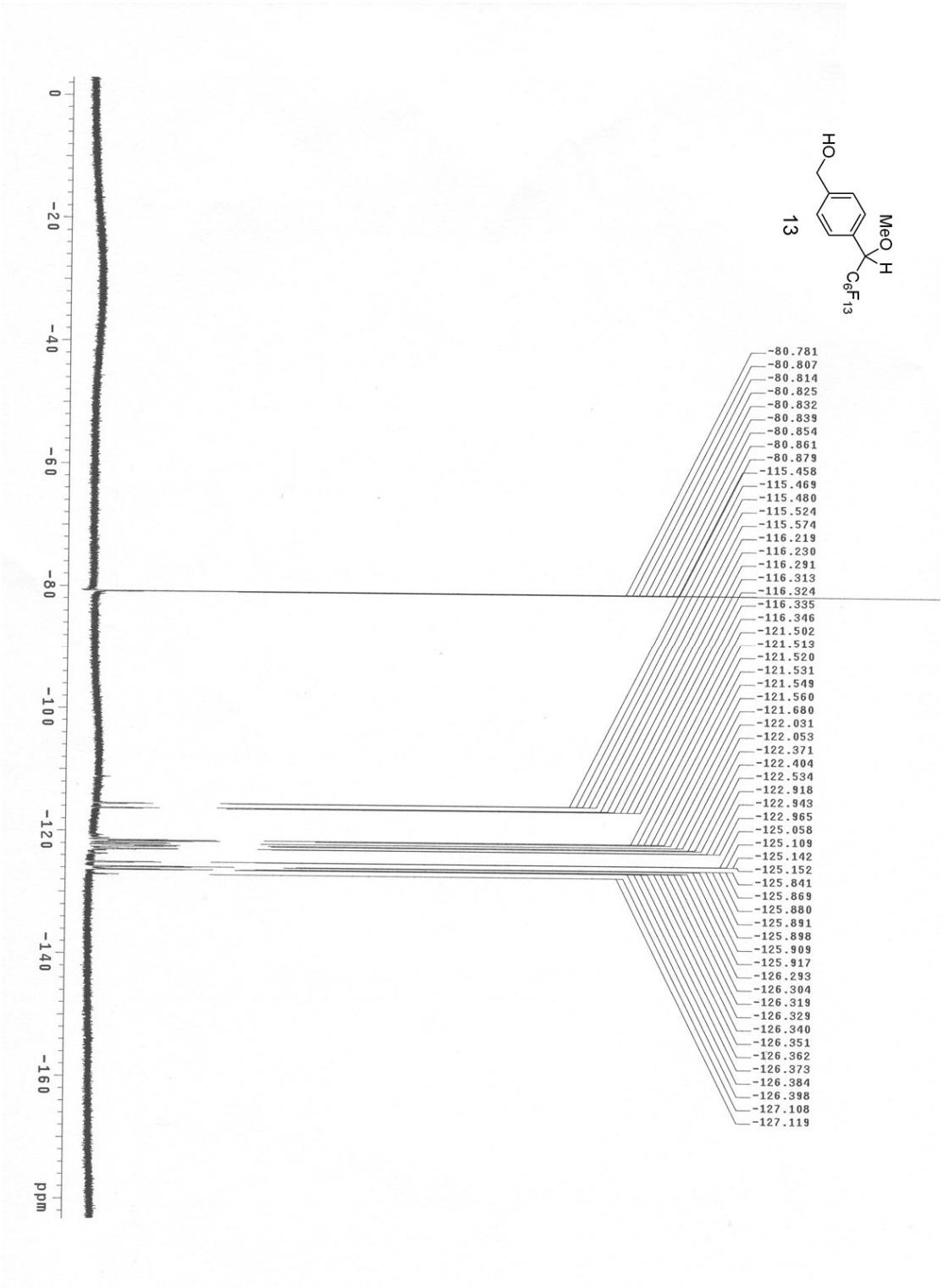
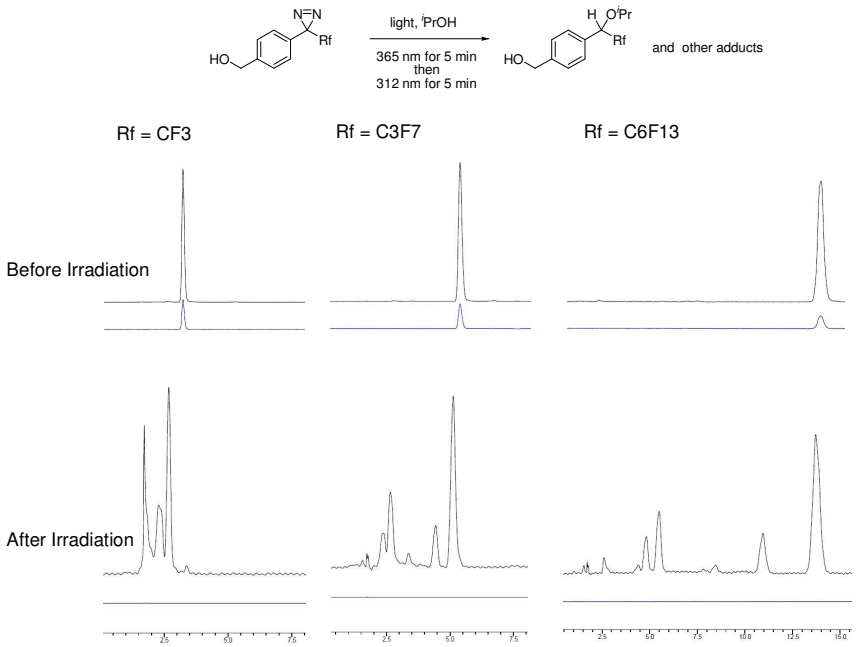
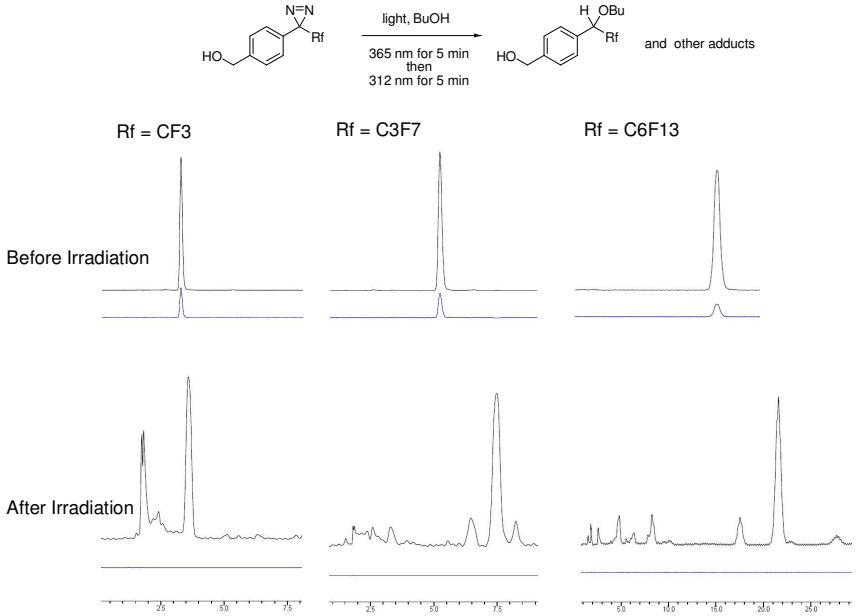
-81.286
-81.294
-81.308
-81.315
-109.934
-109.974
-110.003
-110.014
-110.021
-120.628
-120.639
-120.646
-120.668
-120.678
-120.689
-120.697
-120.711
-120.718
-120.729
-122.424
-122.446
-122.453
-122.464
-122.471
-122.478
-122.485
-122.493
-123.249
-123.286
-123.300
-123.307
-123.322
-123.347
-123.358
-126.559
-126.567
-126.577
-126.588
-126.599
-126.606
-126.614
-126.625
-126.635
-126.646
-126.653
20
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm


7.437
7.260
4.758
4.742
4.701
4.689
4.652
4.640
3.490
3.488
3.342
1.709
1.695
1.680
1.542
1.514
1.512
1.509
1.255
0.009
-0.000
-0.008
3.96
1.03
2.09
3.00
ppm
HO
MeO
H
C6F13
13

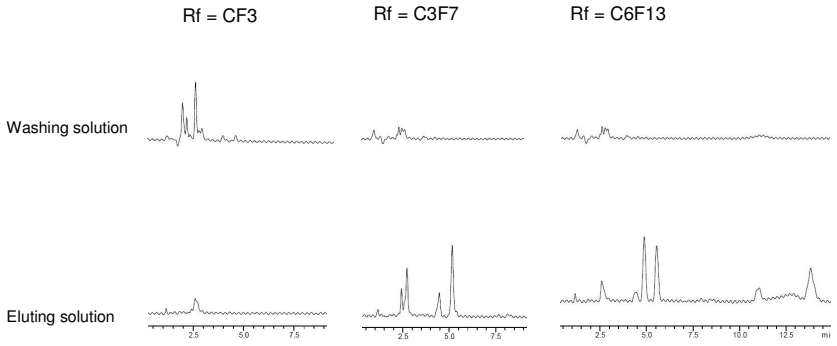

206.930
142.483
130.855
129.116
127.029
80.431
80.336
77.316
77.206
77.000
76.684
64.898
57.594
30.908
-0.024
Acetone
Acetone
13
HO
MeO H
C6F13
ppm

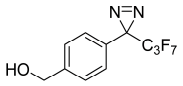

MeO
H
HO
C_6F_{13}
13
-80.781
-80.807
-80.814
-80.825
-80.832
-80.839
-80.854
-80.861
-80.879
-115.458
-115.469
-115.480
-115.524
-115.574
-116.219
-116.230
-116.291
-116.313
-116.324
-116.335
-116.346
-121.502
-121.513
-121.520
-121.531
-121.549
-121.560
-121.680
-122.031
-122.053
-122.371
-122.404
-122.534
-122.918
-122.943
-122.965
-125.058
-125.109
-125.142
-125.152
-125.841
-125.869
-125.880
-125.891
-125.898
-125.909
-125.917
-126.293
-126.304
-126.319
-126.329
-126.340
-126.351
-126.362
-126.373
-126.384
-126.398
-127.108
-127.119
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm


N=N
Rf
HO
light, iPrOH
365 nm for 5 min
then
312 nm for 5 min
H OiPr
Rf
HO
and other adducts
Rf = CF3
Rf = C3F7
Rf = C6F13
Before Irradiation
After Irradiation

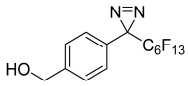

N=N
Rf
HO
light, BuOH
365 nm for 5 min
then
312 nm for 5 min
H OBu
Rf
HO
and other adducts
Rf = CF3
Rf = C3F7
Rf = C6F13
Before Irradiation
After Irradiation

FSPE of irradiated produtcts in ^{i}PrOH



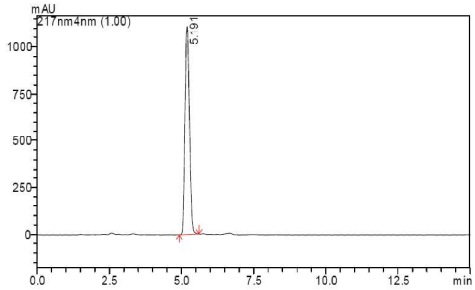


1b

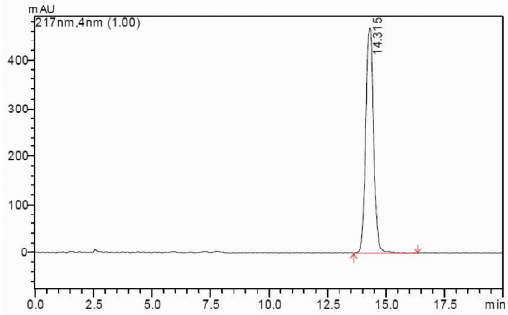


1c

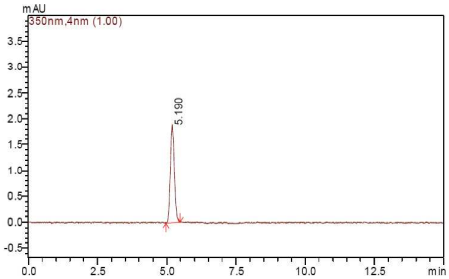
217 nm detection



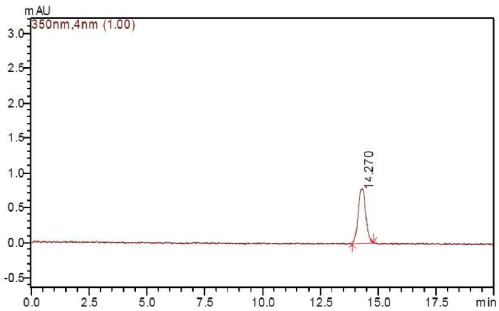
217 nm detection

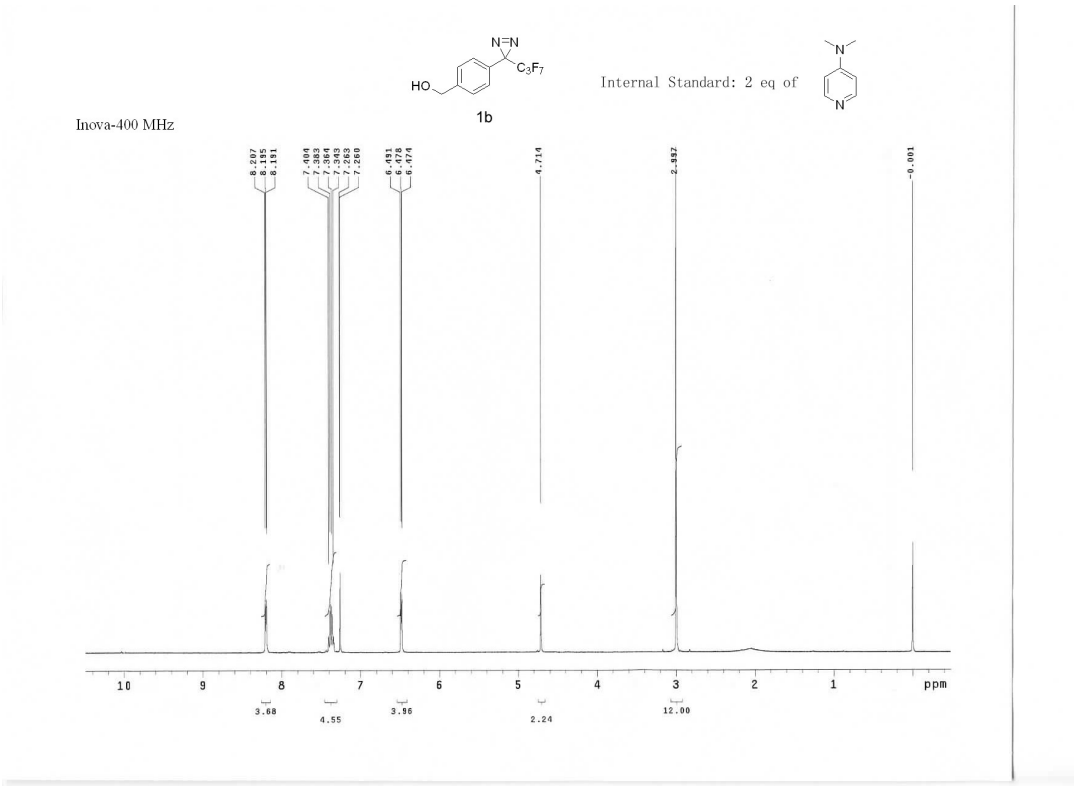


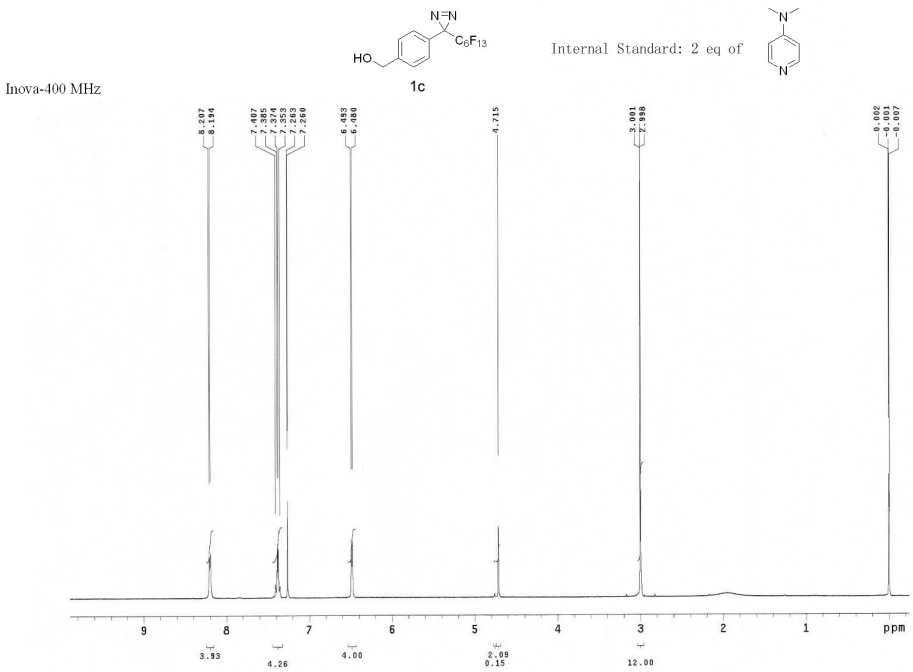
350 nm detection



350 nm detection




N=N
C3F7
HO
1b
Internal Standard: 2 eq of
Inova-400 MHz
8.207
8.195
8.181
7.404
7.383
7.366
7.343
7.263
7.260
6.481
6.478
6.474
4.714
2.992
-0.001
10
9
8
7
6
5
4
3
2
1
ppm
3.68
4.55
3.96
2.24
12.00


N=N
C6F13
HO
1c
Internal Standard: 2 eq of
Inova-400 MHz
8.207
8.194
7.407
7.385
7.374
7.353
7.263
7.260
6.483
6.480
4.715
3.001
2.998
0.002
-0.001
-0.007
9
8
7
6
5
4
3
2
1
ppm
3.93
4.26
4.00
2.09
0.15
12.00