Aminodifluorosulfinium-Salts: Selective Fluorination Reagents with Enhanced Thermal Stability and Ease of Handling

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General Methods.

The ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded with a 300 MHz NMR spectrometer. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra were referenced to TMS with respect to the residual proton in the deuterated solvents. Chemical shifts for ^{19}F NMR spectra were referenced to $CFCl_3$ using 0.05% trifluorotoluene in benzene-d6 for calibration. High-resolution mass spectra were obtained on a LC/MS spectrometer using atmospheric pressure photoionization ionization (APPI). An HPLC fitted with an μ-Bondpack C-18 3.9x300 mm column, auto-injector and diode array detector provided information on reaction progress and assay yield. Relevant HPLC parameters include 0.05% TFA in H_2O/MeOH mobile phase, 22 °C column temperature, and monitoring at 210 nm. An HPLC fitted with an Chiralcel OJ 250 x 4.6 mm column, auto-injector and diode array detector provided information on enantiomeric excess. Relevant HPLC parameters include Hexanes/Ethanol/2-propanol/TFA 1000:20:5:1, 25 °C column temperature, and monitoring at 215 nm. Melting points were obtained from a capillary apparatus and are uncorrected. Differential scanning calorimetry data were collected using 40 mL gold plated high pressure crucible and the samples were crimped closed. The typical ramp tests were conducted using the following parameters; hold sample at 30 °C for 10 minutes followed by a ramp from 30 °C to 300 °C at 5 °C/min while isothermal tests used the following; ramping from 30 °C to 90 °C at 5 °C/min, once at 90°C holding for 80 hours. The ARC experiments, accelerating rate calorimetry, were undertaken in titanium test cells. The ARC tests were conducted under a "heat –wait – search" mode between the range of 30 to 300 °C with heating at 5 °C/min, 10 °C steps, a 20 minute wait time and a detection limit of 0.02 °C/min. Powder x-ray diffraction (XPRD) data was acquired using the following parameters: voltage 40 kV, current 40.0 mA, scan range (2θ) 5 to 35°, scan step size 0.01° and antiscattering slit 1 mm. Column chromatography purifications were carried out on silica gel 40-63 μm flash

chromatography packing (60 Å pore diameter). DAST and Deoxo-Fluor were purchased from Aldrich.

Preparation of dialkylaminodifluorosulfinium salts

Preparation of XtalFluor-E (1) using DAST and HBF_4. To a solution of diethylaminosulfur trifluoride (4.1 mL, 31 mmol) in anhydrous diethyl ether (50 mL) at room temperature was added, dropwise and under nitrogen, neat tetrafluoroboric acid diethyl ether complex (4.2 mL, 31 mmol) over a period of 30 min, while keeping the reaction temperature below 30˚C. The resulting suspension was stirred an additional 20 min, then filtered under a blanket of nitrogen. The solid material was rinsed twice with diethyl ether (2x25 mL), then dried under vacuum to provide diethylaminodifluorosulfinium tetrafluoroborate (6.7 g, 96%) as an off-white solid: mp 77-84 ˚C. All spectral data were consistent with those reported in the manuscript.

Preparation of diethylaminodifluorosulfinium trifluoromethanesulfonate (3). To an ice-cold solution of diethylaminosulfur trifluoride (2.45 mL, 18.6 mmol) in anhydrous diethyl ether (30 mL) was added, dropwise and under nitrogen, neat trifluoromethanesulfonic acid (1.65 mL, 18.6 mmol) over a period of 5 min at room temperature. The resulting suspension was stirred for an additional 30 min at the same temperature, then filtered under a blanket of nitrogen. The solid material was rinsed twice with diethyl ether (2x20 mL), then dried under vacuum to provide **3** (4.4 g, 81%) as a white solid: mp 97-101 ˚C; ^{1}H NMR (CD_3CN, 300 MHz) δ 3.91 (m, 4H), 1.38 (t, J = 7.0 Hz, 6H); ^{19}F NMR (CD_3CN, 282 MHz) δ 12.5 (s, 2F), -79.8 (s, 3F); ^{13}C NMR (CD_3CN, 75 MHz) δ 121.4 (q, J = 320.0 Hz), 48.3 (br), 12.4.

Reaction Profiles of XtalFluor without additives

Reaction of Hydrocinnamyl Alcohol with Diethylaminodifluorosulfinium Tetrafluoroborate in Acetonitrile: To a stirred suspension of XtalFluor-M (362 mg, 1.5 mmol) in acetonitrile (3.0 mL) at room temperature was added 3-phenylpropanol (131 μL, 1.0 mmol). After 1.5 h, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 minutes, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography using DCM/MeOH (100/1) to provide 3-phenylpropanol (25 mg, 19%) and acetamide **5** (33 mg, 25%) as clear oils. Characterization for compound **5**: [1] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31-7.08 (m, 5H), 5.60 (brs, 1H), 3.25 (q, J = 6.8 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H), 1.91 (s, 3H), 1.76 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1, 141.4, 128.5, 128.3, 126.0, 38.3, 33.3, 31.1, 23.3.

Reaction of Hydrocinnamyl Alcohol with Diethylaminodifluorosulfinium Tetrafluoroborate in Dichloromethane: To a stirred suspension of XtalFluor-E (687 mg, 3 mmol) in dichloromethane (3.0 mL) at room temperature was added 3-phenylpropanol (262 μL, 2.0 mmol). After 5 min, no remaining starting material was observed by HPLC. The reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 minutes, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography (hexanes, then 10% EtOAc in hexanes) to provide fluoride **6** (88 mg, 32%), ether **7** (127 mg, 25%) and sulfinate **8** (51 mg, 8%) as a clear oils; Characterization for

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compound **7**:[2] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.37-7.18 (m, 10H), 3.46 (t, *J* = 6.5 Hz, 4H), 2.76 (t, *J* = 7.5 Hz, 4H), 1.95 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.3, 128.8, 128.6, 126.1, 70.2, 32.7, 31.7; Characterization for compound **8**:[3] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.15 (m, 10H), 4.10-3.88 (m, 4H), 2.72 (t, *J* = 7.6 Hz, 4H), 2.06-1.93 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.1, 128.8, 128.7, 126.4, 61.7, 32.1, 31.3.

General Fluorination Procedures

General Procedure A: To a solution of triethylamine trihydrofluoride (2.0 mmol) in dichloromethane (3.0 mL) was added XtalFluor-E or XtalFluor-M (1.5 mmol) followed by the substrate (1.0 mmol) (see Tables 2-4 for the initial reaction temperature). After 30 min of stirring under nitrogen, the reaction mixture was allowed to warm to room temperature if previously cooled. Upon reaction completion, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography.

General Procedure B: To a solution of triethylamine trihydrofluoride (2.0 mmol) and triethylamine (1.0 mmol) in dichloromethane (3.0 mL) were successively added XtalFluor-E or XtalFluor-M (1.5 mmol) and the substrate (1.0 mmol) (see Tables 2-4 for the initial reaction temperature). After 30 min of stirring under nitrogen, the reaction mixture was allowed to warm to room temperature if previously cooled. Upon reaction completion, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15

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[3] Kiasat, A. R.; Kazemi, F.; Khosravian, F. *Phosphorus, Sulfur and Silicon* **2004**, *179*, 431.

min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography.

General Procedure C: To a solution of substrate (1.0 mmol) and DBU (1.5 mmol) in dichloromethane (3.0 mL) was added XtalFluor-E or XtalFluor-M (1.5 mmol) (see Tables 2 for the initial reaction temperature). After 30 min of stirring under nitrogen, the reaction mixture was allowed to warm to room temperature if previously cooled. Upon reaction completion, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography.

General Procedure D: To a solution of triethylamine trihydrofluoride (1.0 mmol) in 1,2-dichloroethane (2.0 mL) was added XtalFluor-E or XtalFluor-M (1.5 mmol) followed by the substrate (1.0 mmol), and the reaction mixture was heated to reflux. Upon reaction completion, the reaction mixture was quenched at room temperature with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography.

Fluorinations Examples using XtalFluor-E and XtalFluor-M

1-Fluoro-3-phenylpropane (6).[4] According to General Procedure C, fluorination of 3-phenylpropanol with XtalFluor-E, followed by flash chromatography using pentane, provided the title compound (106 mg, 76%) as a clear oil. Characterization for compound **6**:[4] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.19 (m, 5H), 4.47 (dt, $^{2}J_{H\text{-}F}$ = 47.3 Hz, $^{3}J_{H\text{-}H}$ = 5.9 Hz, 2H), 2.76 (t, 7.3 Hz, 2H), 2.11-1.95 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -220.6 (tt, $^{2}J_{H\text{-}F}$ = 47.6 Hz, $^{3}J_{H\text{-}F}$ = 23.0 Hz, 2F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.2, 128.6, 128.6, 126.1, 83.2 (d, $^{1}J_{C\text{-}F}$ = 165.4 Hz), 32.2 (d, $^{2}J_{C\text{-}F}$ = 20.2 Hz), 31.4 (d, $^{3}J_{C\text{-}F}$ = 5.6 Hz);

2-Fluoro-4-phenylbutane (10).[5] According to General Procedure C, fluorination of 4-phenyl-2-butanol with XtalFluor-E, followed by flash chromatography using pentane, provided the title compound (110 mg, 72%) admixed with 4-phenylbutene (6.25:1 ratio respectively) as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35-7.11 (m, 5H), 4.62 (dm, $^{2}J_{H\text{-}F}$ = 48.4 Hz, 1H), 2.89-2.49 (m, 2H), 2.14-1.63 (m, 2H), 1.31 (dd, $^{3}J_{H\text{-}F}$ = 23.8 Hz, $^{3}J_{H\text{-}H}$ = 6.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -174.4 (m, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.4, 128.3, 125.9, 89.9 (d, $^{1}J_{C\text{-}F}$ = 165.2 Hz), 38.6 (d, $^{2}J_{C\text{-}F}$ = 20.6 Hz), 31.3 (d, $^{3}J_{C\text{-}F}$ = 5.2 Hz) 20.9 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz).

Fluorocyclooctane (12).[6] According to General Procedure B, fluorination of cyclooctanol with XtalFluor-E, followed by flash chromatography using pentane, provided the title compound (105 mg, 81%) of admixed with cyclooctene (12.1:1 ratio respectively) as a clear oil. Major compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.63 (dm, $^{2}J_{H\text{-}F}$ = 45.9 Hz, 1H), 1.96-1.42 (m, 16H);

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[6] (a) Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574. (b) Beaulieu, F.; Beauregard, L.-P.; Courchesne, G.; Couturier, M.; LaFlamme, F.; L'Heureux, A. *Org. Lett.* **2009**, *11*, 5050.

^{19}F NMR ($CDCl_3$, 282 MHz) δ -159.7 (brs, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 95.0 (d, $^1J_{C\text{-}F}$ = 163.4 Hz), 32.3 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 27.4, 25.3, 22.2 (d, $^3J_{C\text{-}F}$ = 9.8 Hz).

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl fluoride (16).[7,5a] According to General Procedure C, fluorination of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose with XtalFluor-E, without any further purification, provided the title compound (519 mg, 96%, β : α anomers in a 1.1:1 ratio respectively) as a foam. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.47-7.15 (m, 20H), 5.61 (dd, $^2J_{H\text{-}F}$ = 53.2 Hz, $^3J_{H\text{-}H}$ = 2.3 Hz, 0.48H, α-anomer), 5.31 (dd, $^2J_{H\text{-}F}$ = 51.8 Hz, $^3J_{H\text{-}H}$ = 6.4 Hz, 0.52H, β-anomer), 5.07-4.48 (m, 8H), 4.11-3.54 (m, 6H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -138.0 (dd, $^1J_{F\text{-}H}$ = 53.4 Hz, $^2J_{F\text{-}H}$ = 10.6 Hz, β-F), -149.44 (dd, $^1J_{F\text{-}H}$ = 54.4 Hz, $^2J_{F\text{-}H}$ = 25.8 Hz, α-F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.5, 138.3, 138.1, 137.9, 137.5, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 112.8 (d, $^1J_{C\text{-}F}$ = 215.2 Hz, β-anomer), 108.6 (d, $^1J_{C\text{-}F}$ = 228.7 Hz, α-anomer), 83.6, 83.4, 81.7, 81.5, 81.4, 79.5, 79.2, 77.5, 77.1, 77.0, 77.7, 75.9, 75.5, 75.2, 75.0, 74.9, 74.8, 74.5, 73.6, 73.5, 72.7, 68.4, 67.8.

3β-Fluoro-dehydroisoandrosterone (18).[8] To a stirred suspension of XtalFluor-E (344 mg, 1.5 mmol) in dichloromethane (3.0 mL) was added triethylamine trihydrofluoride (652 μL, 4.0 mmol) followed by androstenolone (288 mg, 1.0 mmol) at rt. After 16 h, the reaction mixture was quenched with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography using hexanes/EtOAc (9/1) to provide the title compound (222 mg, 77%) as a white solid: mp

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[8] (a) Rozen, S.; Faust, Y.; Ben-Yakov, H. *Tetrahedron Lett.* **1979**, *20*, 1823. (b) Boutin, N.E.; Robert, D.U.; Cambon, A.R. *Bull. Soc. Chim. Fr.* **1974**, 2862.

143-144 ˚C (lit.[9] mp 152-154 ˚C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.29 (brm, 1H), 4.25 (dm, $^2J_{H\text{-}F}$ = 49.3 Hz, 1H), 2.43-2.26 (m, 3H), 2.08-1.28 (m, 12H), 1.24-1.08 (m, 2H), 1.01-0.81 (m, 5H), 0.76 (s, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -168.5 (dm, $^2J_{H\text{-}F}$ = 48.1 Hz, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 220.9, 139.7 (d, $^3J_{C\text{-}F}$ = 12.0 Hz), 122.4, 92.6 (d, $^1J_{C\text{-}F}$ = 175 Hz), 51.8, 50.2, 47.6, 39.5 (d, $^2J_{C\text{-}F}$ = 19.4 Hz), 36.8, 36.4 (d, $^3J_{C\text{-}F}$ = 10.9 Hz), 35.9 , 31.6, 31.5, 28.9 (d, $^2J_{C\text{-}F}$ = 18.6 Hz), 22.0, 20.5, 19.5, 13.7

2-Fluoro-2-methyl-1-phenylpropan-1-one (20).[5a] According to General Procedure C, fluorination of 2-hydroxy-2-methyl-1-phenylpropan-1-one with XtalFluor-E, followed by flash chromatography using pentane, provided the title compound (155 mg, 93%) admixed with 2-methyl-1-phenylprop-2-en-1-one (4.1:1 ratio respectively) as a clear oil; Major compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.61-7.38 (m, 3H), 1.69 (d, $^3J_{H\text{-}F}$ = 21.7 Hz, 6H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -143.6 (m, $^3J_{H\text{-}F}$ = 23.2 Hz, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.8 (d, $^2J_{C\text{-}F}$ = 27.2 Hz), 133.1, 129.9 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 128.3, 127.1, 99.8 (d, $^1J_{C\text{-}F}$ = 180.6 Hz), 25.7 (d, $^2J_{C\text{-}F}$ = 23.7 Hz).

Ethyl 2-fluoro-2-methylpropanoate (22).[10] According to General Procedure B, fluorination of ethyl 2-hydroxy-2-methylpropanoate with XtalFluor-M, followed by flash chromatography using pentane, provided the title compound (96 mg, 72%) admixed with ethyl methacrylate (21:1 ratio respectively) as a clear oil; Major compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.20 (q, *J* = 7.2 Hz, 2H), 1.54 (d, $^3J_{H\text{-}F}$ = 21.2 Hz, 6H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz)

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δ -147.6 (m, $^{3}J_{H\text{-}F}$ = 21.3 Hz, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.3 (d, $^{2}J_{C\text{-}F}$ = 25.2 Hz), 92.6 (d, $^{1}J_{C\text{-}F}$ = 181.6 Hz), 61.5, 24.9 (d, $^{2}J_{C\text{-}F}$ = 24.3 Hz), 14.0.

3-Fluoro-3,7-dimethylocta-1,6-diene (24).[11] According to General Procedure B, fluorination of geraniol with XtalFluor-M, followed by flash chromatography using pentane, provided the title compound (155 mg, 88%) as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.88 (td, *J* = 17.7, 11.3 Hz, 1H), 5.26 (d, *J* = 17.7 Hz, 1H), 5.15-5.05 (m, 2H), 2.20-1.95 (m, 2H), 1.68 (s, 3H), 1.77-1.63 (m, 2H), 1.60 (s, 3H), 1.41 (d, $^{3}J_{H\text{-}F}$ = 21.5 Hz, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -149.0 (m, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.9 (d, $^{2}J_{C\text{-}F}$ = 23.3 Hz), 132.0, 123.9, 113.6 (d, $^{3}J_{C\text{-}F}$ = 10.7 Hz), 96.1 (d, $^{1}J_{C\text{-}F}$ = 169.4 Hz), 40.4 (d, $^{2}J_{C\text{-}F}$ = 23.3 Hz), 25.8, 25.4 (d, $^{2}J_{C\text{-}F}$ = 25.2 Hz), 22.4 (d, $^{3}J_{C\text{-}F}$ = 4.7 Hz), 17.7.

4-*tert*-Butyl-1,1-difluorocyclohexane (28).[12,6b] According to General Procedure B, fluorination of 4-*tert*-butyl-cyclohexanone with XtalFluor-E, followed by flash chromatography using pentane, provided the title compound admixed with 4-*tert*-butyl-1-fluorocyclohex-1-ene in a 62:1 ratio (160 mg, 91%) as a clear oil; Major compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.14-2.05 (m, 2H), 1.83-1.54 (m, 4H), 1.33-1.24 (m, 2H), 1.11-1.06 (m, 1H), 0.86 (s, 9H). ^{19}F NMR ($CDCl_3$, 282 MHz) δ -91.9 (d, $^{2}J_{F\text{-}F}$ = 231.8 Hz, 1F), 103.5 (dtt, $^{2}J_{F\text{-}F}$ = 234.9 Hz, $^{3}J_{H\text{-}F}$ = 36.7, 12.1 Hz, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 124.0 (t, $^{1}J_{C\text{-}F}$ = 238.9 Hz), 46.8, 34.4 (dd, $^{2}J_{C\text{-}F}$ = 25.4, 21.8 Hz), 32.5, 27.8, 24.0 (d, $^{3}J_{C\text{-}F}$ = 9.8 Hz).

***N*-Boc-4-amino-1,1-difluorocyclohexane (30).**[13] According to General Procedure D, fluorination of *N*-Boc-4-amino-cyclohexan-1-one with XtalFluor-E, followed by flash

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chromatography using hexanes/EtOAc (9/1) provided the title compound (144 mg, 61%) admixed with *N*-Boc-4-amino-1-fluorocyclohex-1-ene (5.1:1 ratio respectively) as pale yellow solid; mp 119-122 °C. Major compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.61 (brs, 1H), 3.51 (brs, 1H), 2.06-1.60 (m, 6H), 1.54-1.31 (m, 2H), 1.37 (s, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -95.0 (d, $^{2}J_{F\text{-}F}$ = 242.4 Hz, 1F), -100.8 (d, $^{2}J_{F\text{-}F}$ = 248.3 Hz, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.2, 122.5 (d, $^{1}J_{C\text{-}F}$ = 242.7 Hz), 79.3, 47.3, 32.0 (t, $^{2}J_{C\text{-}F}$ = 25.2 Hz), 28.8 (d, $^{3}J_{C\text{-}F}$ = 9.8 Hz), 28.3.

8,8-Difluoro-1,4-dioxaspiro[4.5]decane (34).[6b] To a stirred suspension of XtalFluor-M (482 mg, 2.0 mmol) in dichloromethane (1.9 mL) was added triethylamine trihydrofluoride (163 µL, 1.0 mmol) followed by 1,4-dioxaspiro[4.5]decan-8-one (156 mg, 1.0 mmol) at r.t. After 24 h, the reaction mixture was quenched with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography using hexanes/EtOAc (9/1) to provide the title compound (136 mg, 76%) as a white solid; mp 40-44 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.92 (s, 4H), 2.09-1.96 (m, 4H), 1.86-1.74 (m, 4H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -100.2 (s, 2F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 123.0 (t, $^{1}J_{C\text{-}F}$ = 240.4 Hz), 107.4, 64.6, 31.5 (t, $^{2}J_{C\text{-}F}$ = 25.0 Hz), 31.2 (t, $^{3}J_{C\text{-}F}$ = 5.4 Hz).

***N*-Cbz-4,4-difluoropiperidine (38).** According to General Procedure B, fluorination of *N*-Cbz-4-oxopiperidine with XtalFluor-E, followed by flash chromatography using hexanes/EtOAc (9/1), provided the title compound (207 mg, 81%) admixed with *N*-Cbz-4-fluoro-1,2,3,6-tetrahydropyridine (13:1 ratio respectively) as a clear oil; Major compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43-7.28 (m, 5H), 5.13 (s, 2H), 3.67-3.56 (m, 4H), 2.04-1.84 (m, 4H); ^{19}F NMR

($CDCl_3$, 282 MHz) δ -97.9 (m, $^3J_{H\text{-}F}$ = 13.3 Hz, 2F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.9, 136.4, 128.6, 128.2, 128.0, 121.6 (t, $^1J_{C\text{-}F}$ = 242.5 Hz), 67.5, 40.9 (t, $^3J_{C\text{-}F}$ = 5.3 Hz), 33.9 (t, $^2J_{C\text{-}F}$ = 20.3 Hz); HRMS-APPI calcd for $C_{13}H_{16}F_2NO_2$ $[M^*]^+$ 256.1140, found 256.1144.

Ethyl 2,2-difluoro-2-phenylacetate (40).[14] To a stirred suspension of XtalFluor-E (687 mg, 3.0 mmol) in dichloromethane (3.0 mL) was added triethylamine trihydrofluoride (652 μL, 4.0 mmol) and triethylamine (278 μL, 2.0 mmol) followed by ethyl 2-oxo-2-phenylacetate (159 μL, 1.0 mmol) at rt. After 24 h, the reaction mixture was quenched with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography using hexanes/EtOAc (9/1) to provide the title compound (174 mg, 87%) as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66-7.58 (d, *J* = 7.3 Hz, 2H), 7.52-7.40 (m, 3H), 4.29 (q, *J* = 7.3 Hz, 2H), 1.29 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -103.9 (s, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.2 (t, $^2J_{C\text{-}F}$ = 35 Hz), 132.8 (t, $^2J_{C\text{-}F}$ = 24.9 Hz) 131.0, 128.6, 125.4 (t, $^3J_{C\text{-}F}$ = 6 Hz), 113.4 (t, $^1J_{C\text{-}F}$ = 251.5 Hz), 63.1, 13.8.

(2,2-Difluoropropoxy)benzene (42).[10] According to General Procedure B, fluorination of 1-phenoxypropan-2-one with XtalFluor-E, followed by flash chromatography using hexanes/EtOAc (20/1) provided the title compound (152 mg, 88%) as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 4.12 (t, $^3J_{H\text{-}F}$ = 11.2 Hz, 2H), 1.29 (t, $^3J_{H\text{-}F}$ = 18.9 Hz, 3H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -98.1 (m, 2F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.9, 129.6, 121.8, 121.6 (t, $^1J_{C\text{-}F}$ = 238.8 Hz), 114.6, 69.5 (t, $^2J_{C\text{-}F}$ = 35.0 Hz), 20.9 (t, $^2J_{C\text{-}F}$ = 26.3 Hz).

[14] Fukuara, T.; Hara, S. *Synlett* **2009**, 198.

3-Phenylpropanoyl fluoride (44).[6b] According to General Procedure A, fluorination of 3-phenylpropanoic acid with XtalFluor-E, followed by flash chromatography using pentane, provided the title compound (143 mg, 94%) as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30-7.17 (m, 5H), 2.96 (t, J = 7.6 Hz, 2H), 2.79 (t, J = 7.6 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ 44.8 (s, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.0 (d, $^{1}J_{C\text{-}F}$ = 180.2 Hz), 139.1, 128.9, 128.5, 127.0, 34.7 (d, $^{2}J_{C\text{-}F}$ = 50.7 Hz), 30.2.

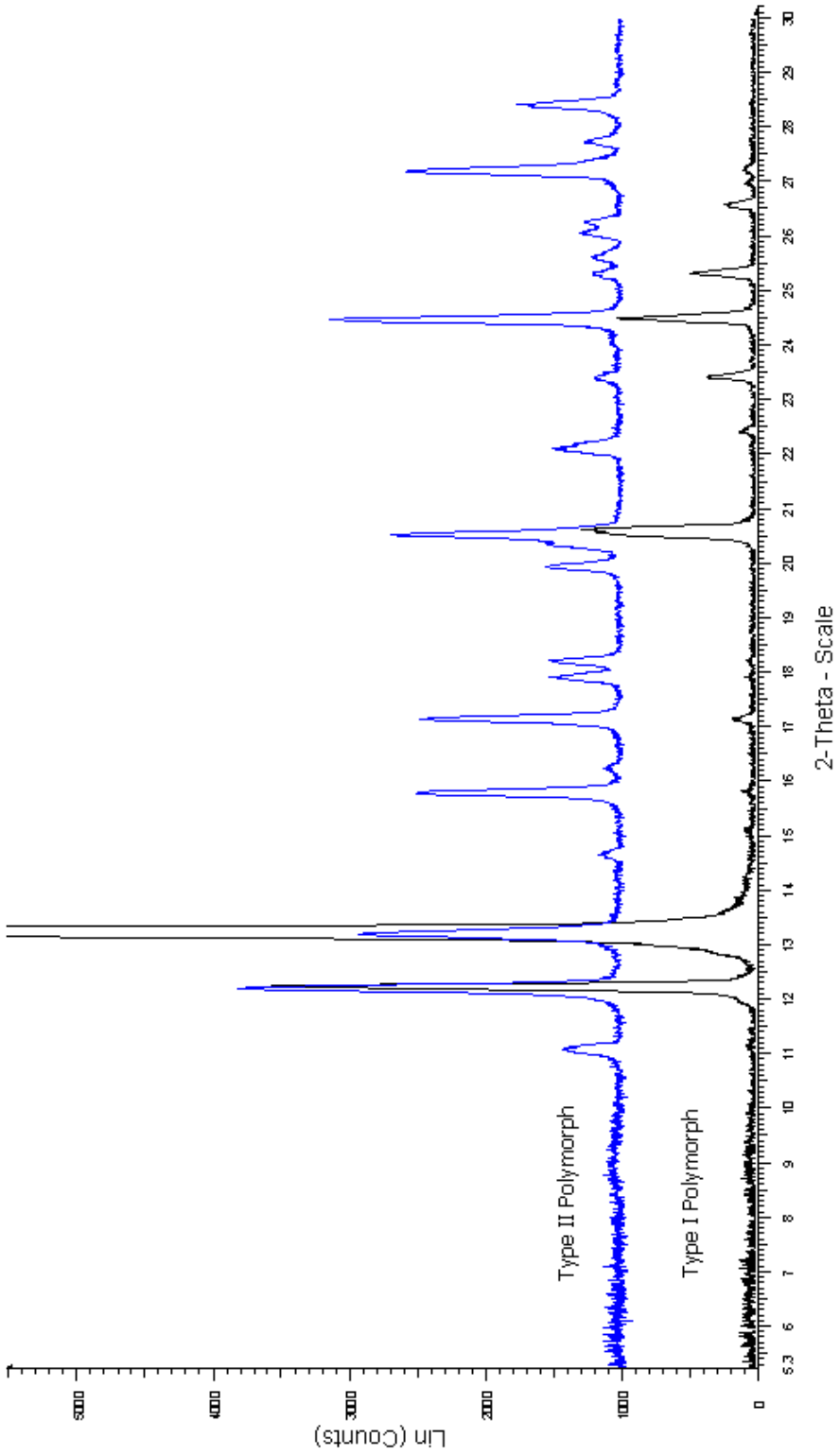
Benzoyl fluoride (46).[6b,10] According to General Procedure A, fluorination of benzoic acid with XtalFluor-E, followed by flash chromatography using pentane, provided the title compound (110 mg, 89%) as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.94 (d, J = 7.8, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 8.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ 17.5 (s, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.3 (d, $^{1}J_{C\text{-}F}$ = 344.3 Hz), 135.5, 131.5 (d, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 129.2, 125.0 (d, $^{2}J_{C\text{-}F}$ = 60.4 Hz).

(Fluoromethyl)(phenyl)sulfane (48).[15] To a stirred suspension of XtalFluor-E (687 mg, 3.0 mmol) in dichloromethane (3.0 mL) was added triethylamine trihydrofluoride (652 μL, 4.0 mmol) followed by methylphenylsulfoxide (140 mg, 1.0 mmol) at r.t. After 24 h, the reaction mixture was quenched with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel to provide the title compound (139 mg, 98%) as a clear oil; Major compound: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62-7.47 (m, 2H), 7.42-7.28 (m, 3H), 5.73 (d, $^{2}J_{H\text{-}F}$ = 53.3 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -181.6 (t, $^{2}J_{H\text{-}F}$ = 53.3 Hz, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.4, 130.6, 129.2, 127.8, 85.7 (d, $^{1}J_{C\text{-}F}$ = 215.9 Hz).

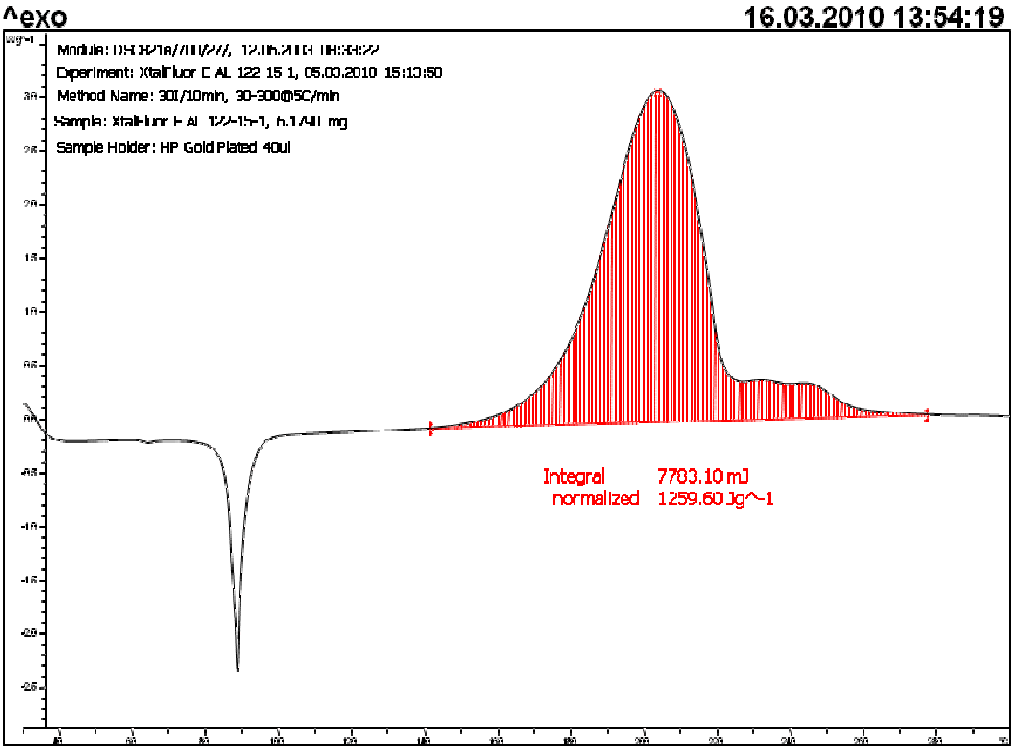
[15] (a) Zhang, W.; Zhu, L.; Hu, J. *Tetrahedron* **2007**, *63*, 10569. (b) Fuchigami, T.; Konno, A.; Kakagawa, K.; Shimojo, M. *J. Org. Chem.* **1994**, *59*, 5937.

2-Fluoro-4-phenylbutanenitrile (50). To a stirred solution of 3-phenylpropanal (132 μL, 1.0 mmol), potassium cyanide (3.3 mg, 0.05 mmol), 18-crown-6 (13 mg, 0.05 mmol) in dichloromethane (3.0 mL) was added trimethylsilylcyanide (125 μL, 1.0 mmol). The solution was stirred at rt for 30 min and then XtalFluor-M (362 mg, 1.5 mmol) and triethylamine trihydrofluoride (326 μL, 2.0 mmol) were successively added. After 24 h, the reaction mixture was quenched with a 5% aqueous sodium bicarbonate solution, stirred for 15 min, and the resulting mixture was extracted twice using dichloromethane. The organic phases were combined, dried over magnesium sulfate and filtered through a pad of silica gel. Solvents were evaporated and the resulting crude material was purified by silica gel flash chromatography using hexanes/EtOAc (9/1) to provide the title compound (148 mg, 91%) as a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39-7.20 (m, 5H), 5.08 (dt, $^{2}J_{H-F}$ = 47.3 Hz, $^{3}J_{H-H}$ = 7.1 Hz, 1H), 2.88 (t, J = 7.1 Hz, 2H), 2.47-2.15 (m, 4H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -189.4 (m, 1F); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.7, 128.8, 128.5, 126.9, 116.0 (d, $^{2}J_{C-F}$ = 31.3 Hz), 78.7 (d, $^{1}J_{C-F}$ = 181.9 Hz), 35.2 (d, $^{2}J_{C-F}$ = 22.2 Hz), 29.9 (d, $^{3}J_{C-F}$ = 4.4 Hz); HRMS-APPI calcd for $C_{10}H_{10}FN$ $[M^{*}]^{+}$ 163.0797, found 163.0797.

XPRD of XtalFluor-E



DSC of XtalFluor-E



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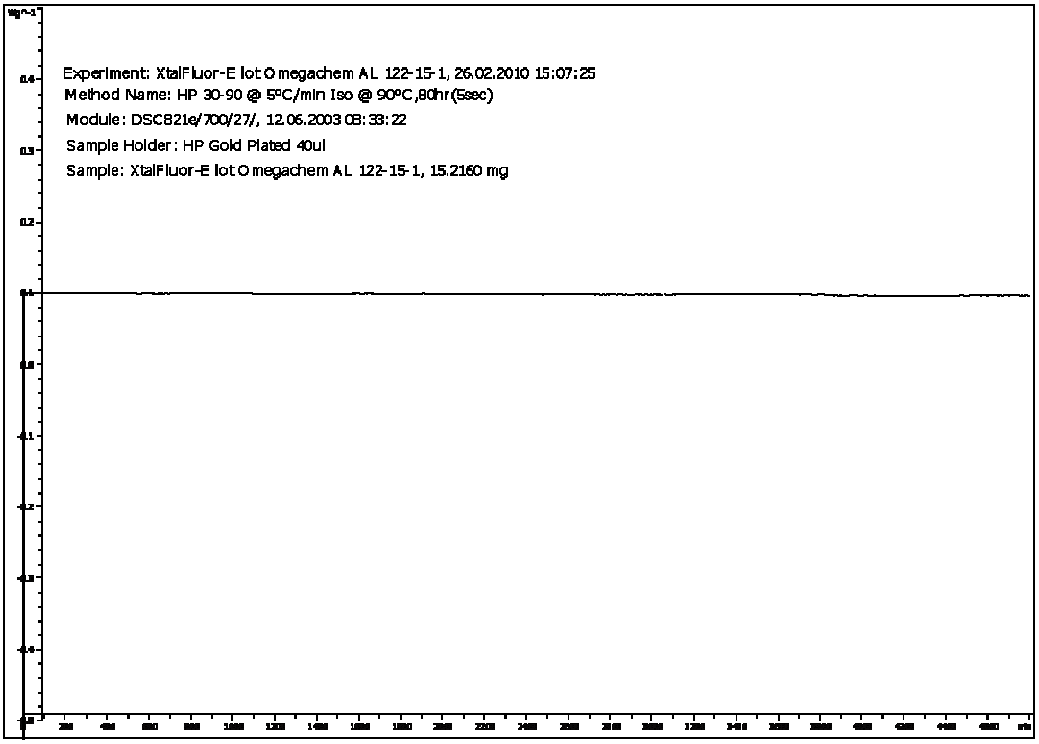
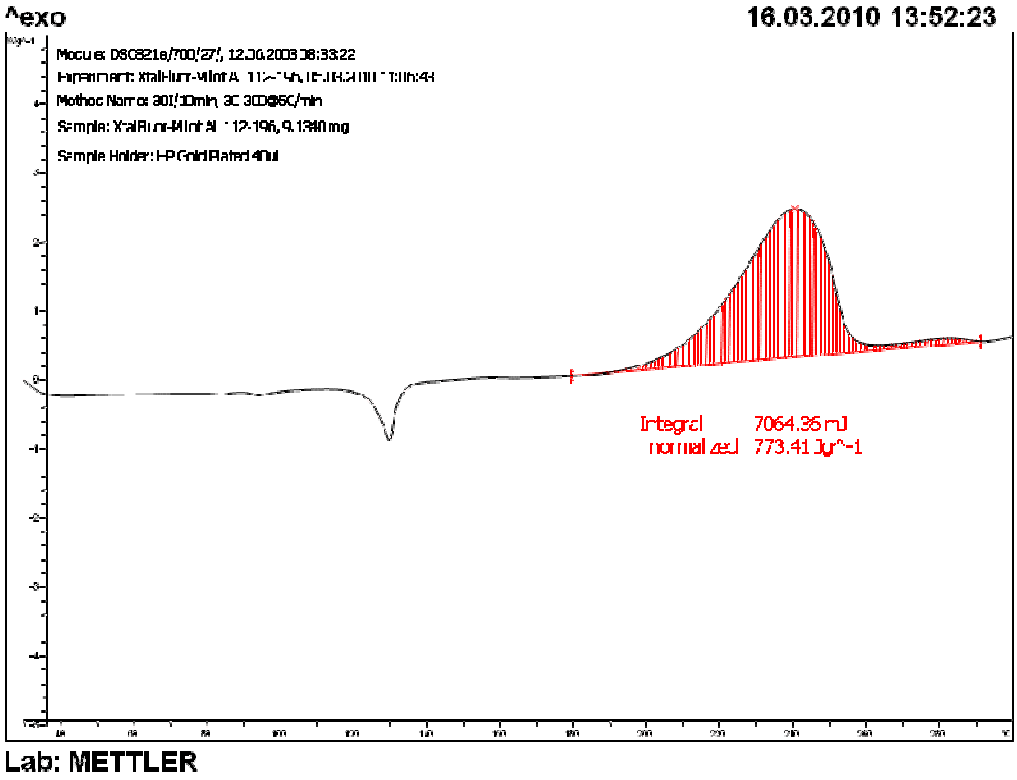
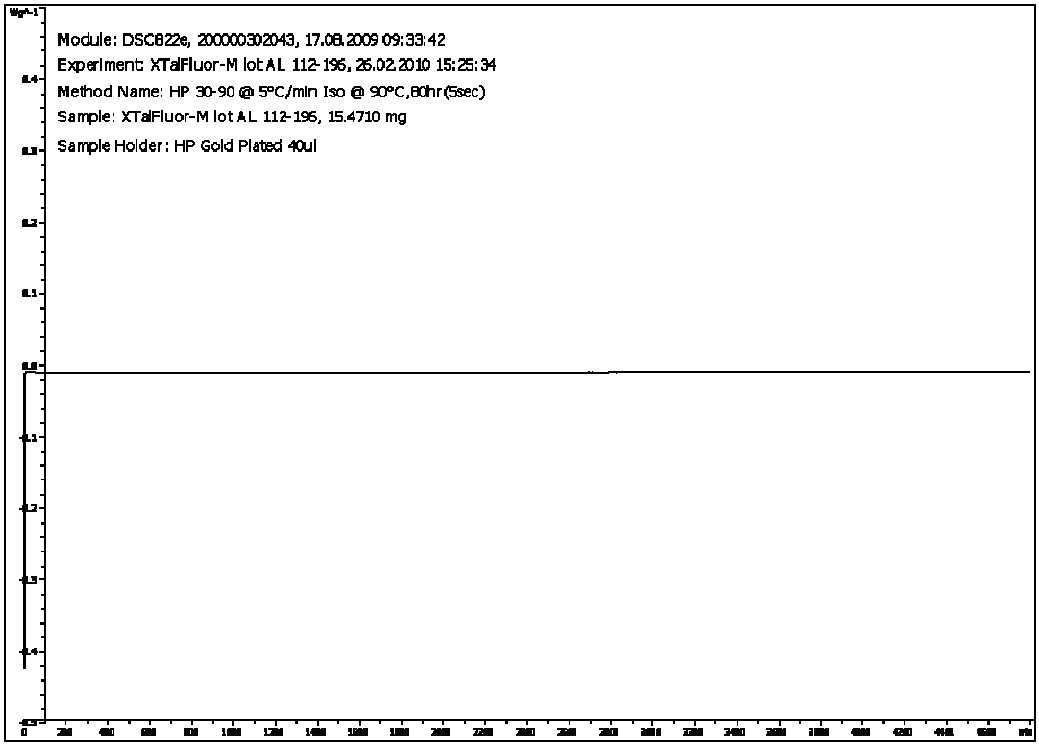


DSC of XtalFluor-M



Isothermal Calorimetry of XtalFluor-M



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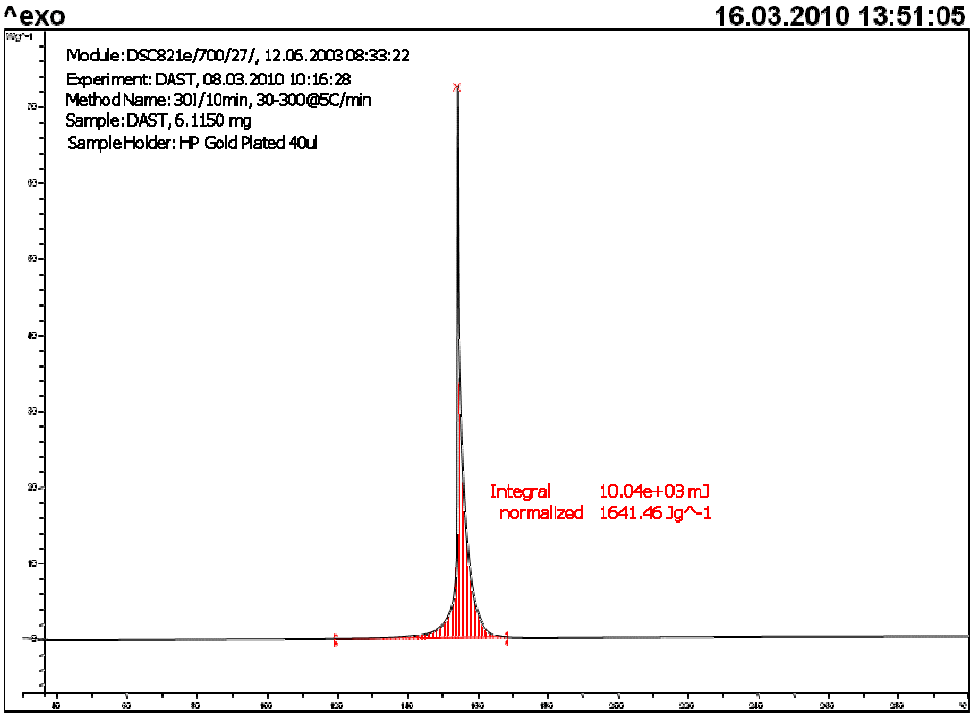
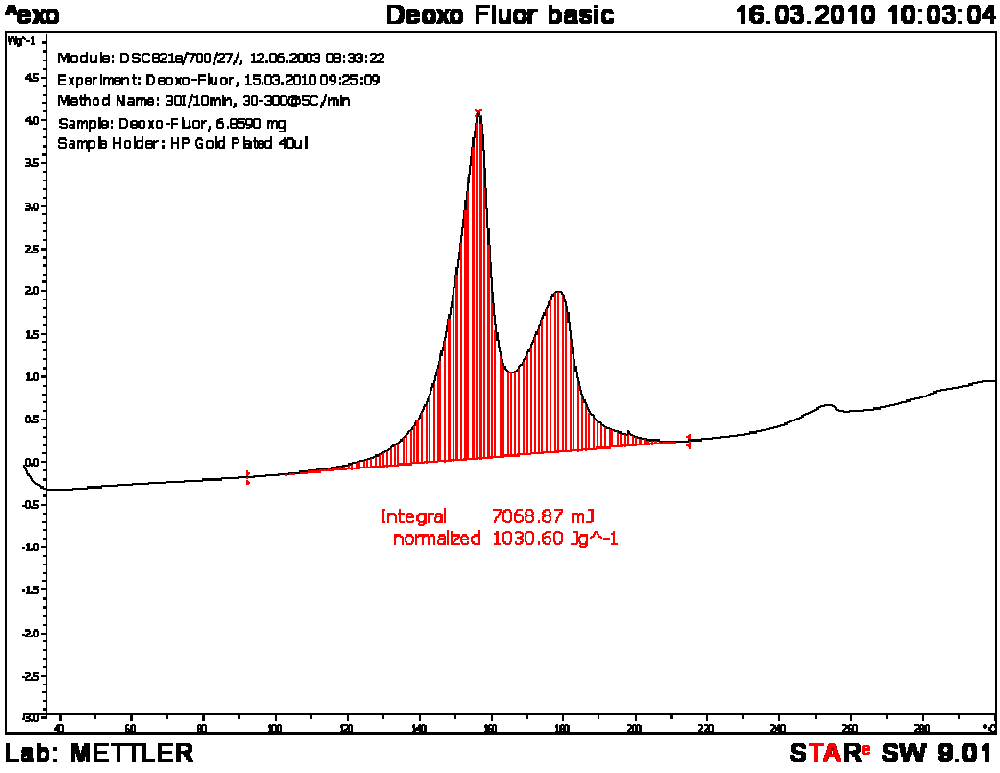


DSC of Deoxo-Fluor



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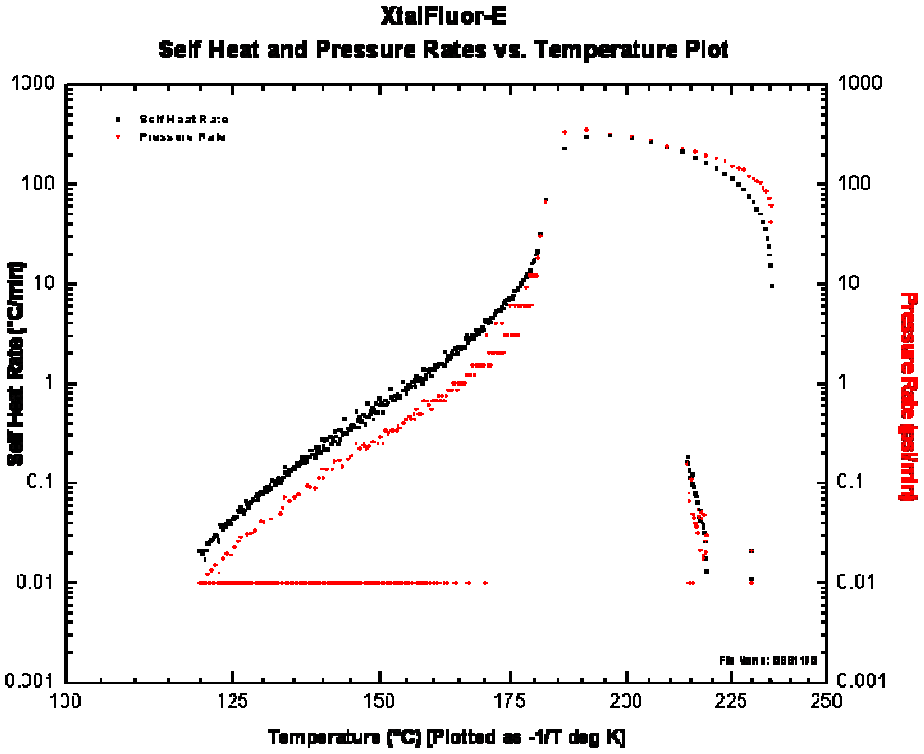

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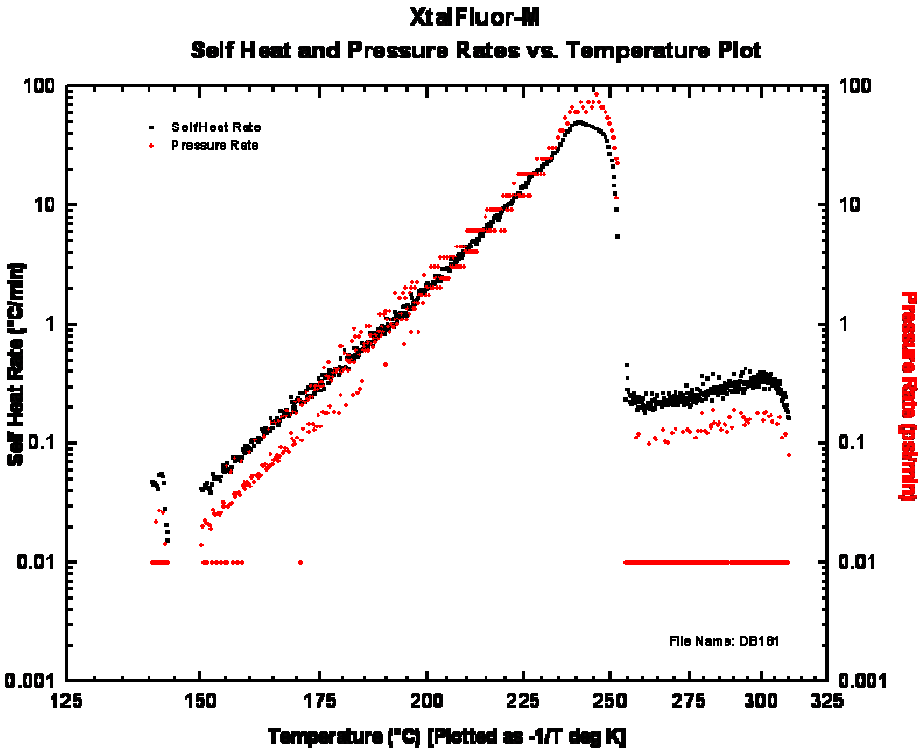

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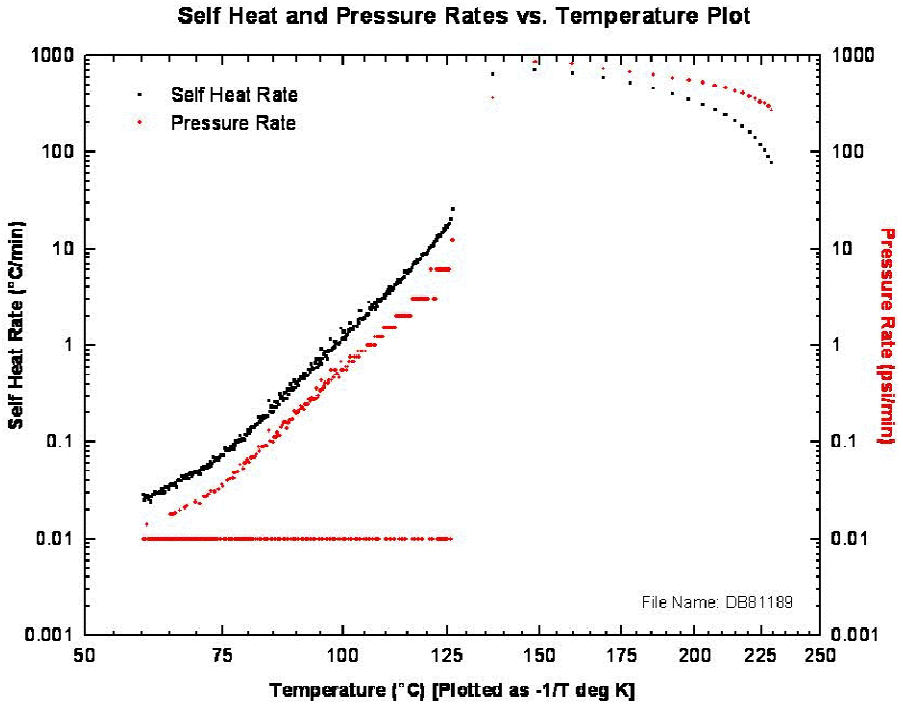

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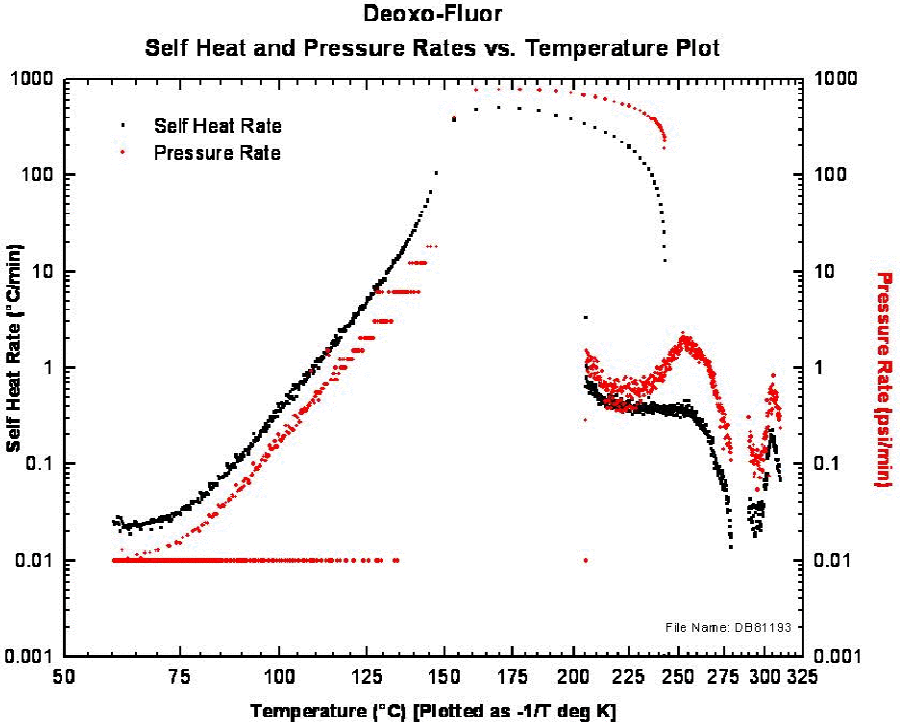
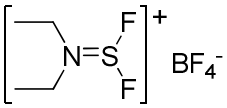


^{1}H, ^{13}C and ^{19}F-NMR of all compounds



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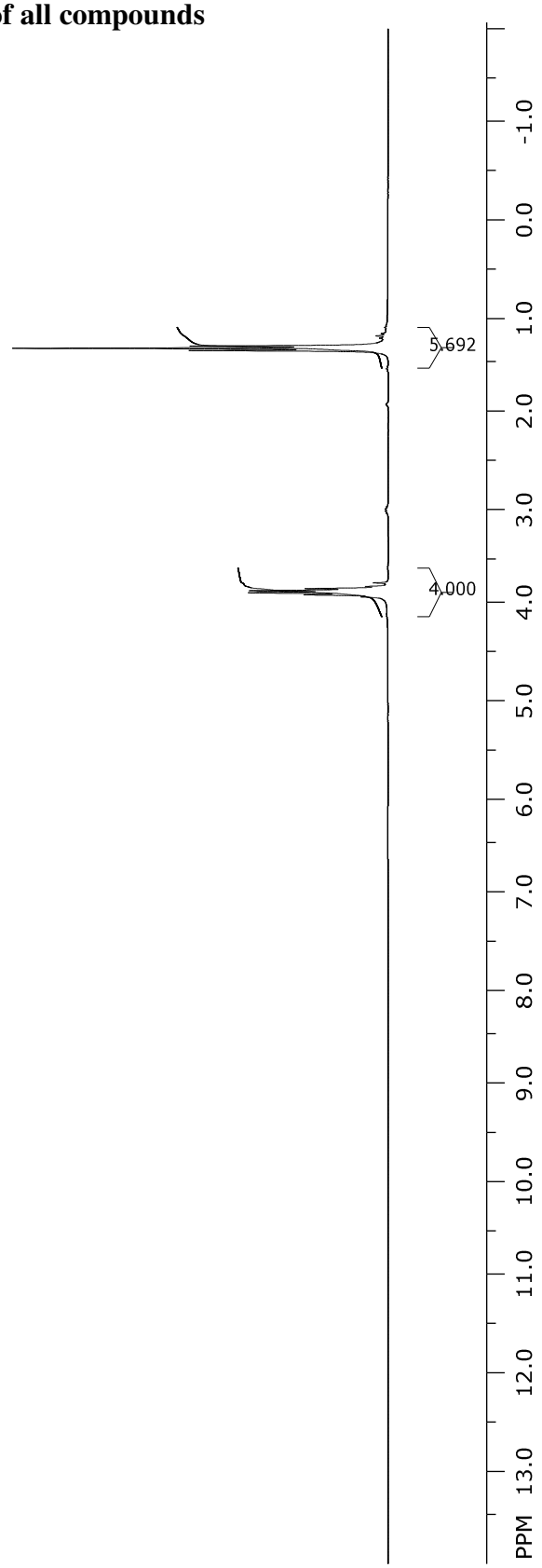

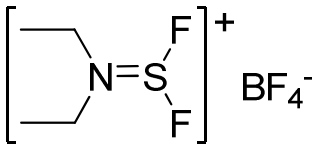
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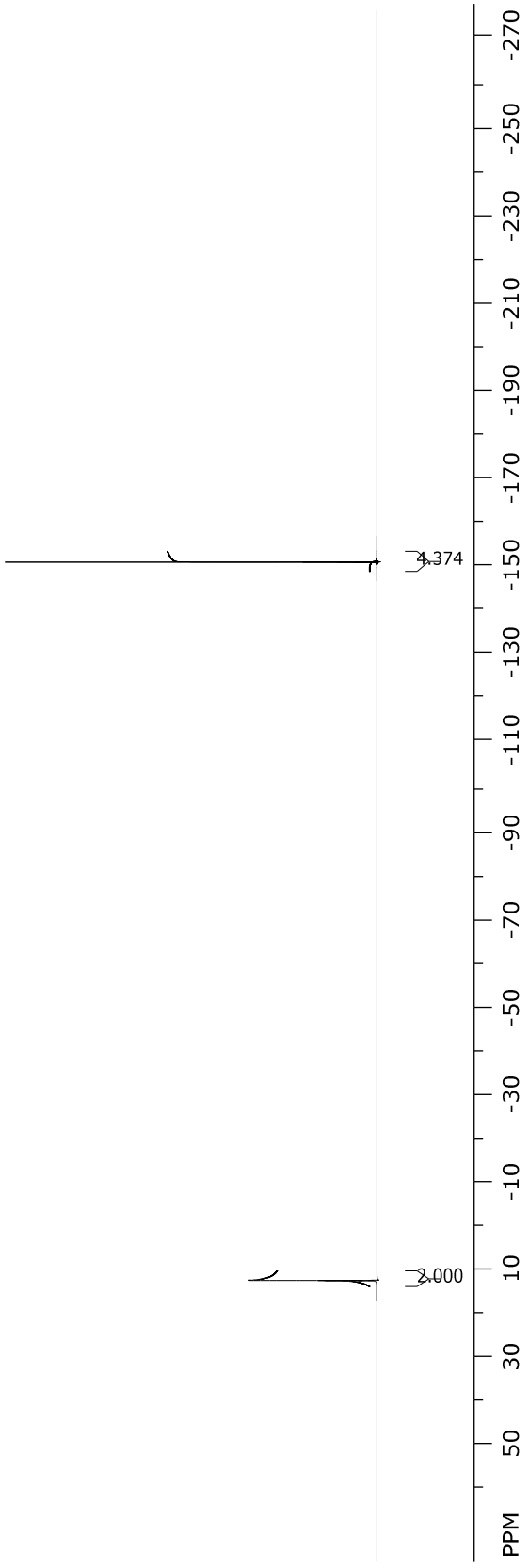
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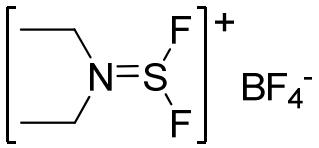

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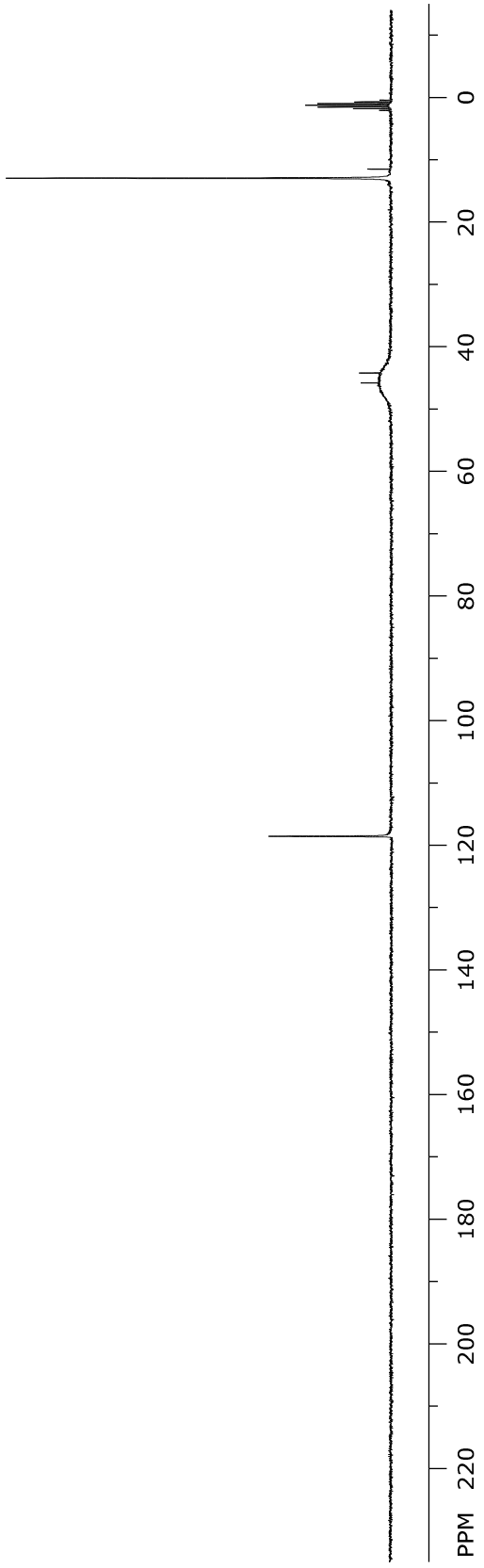

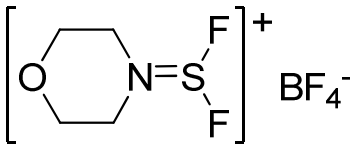

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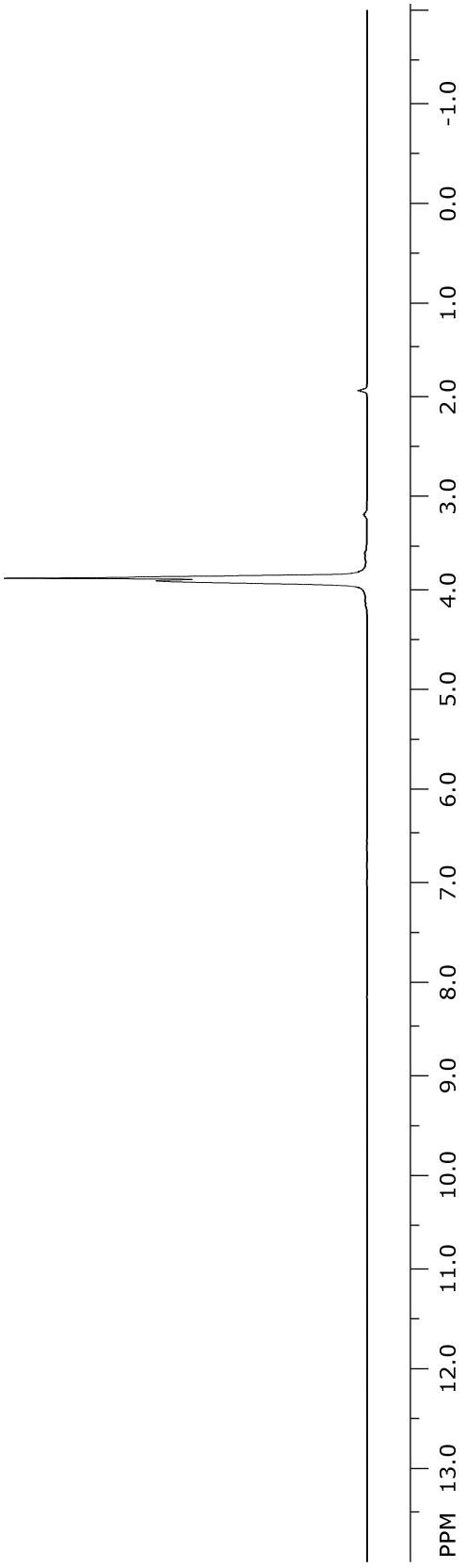

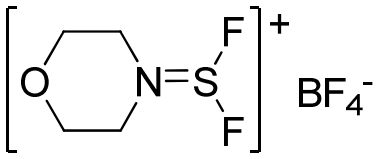
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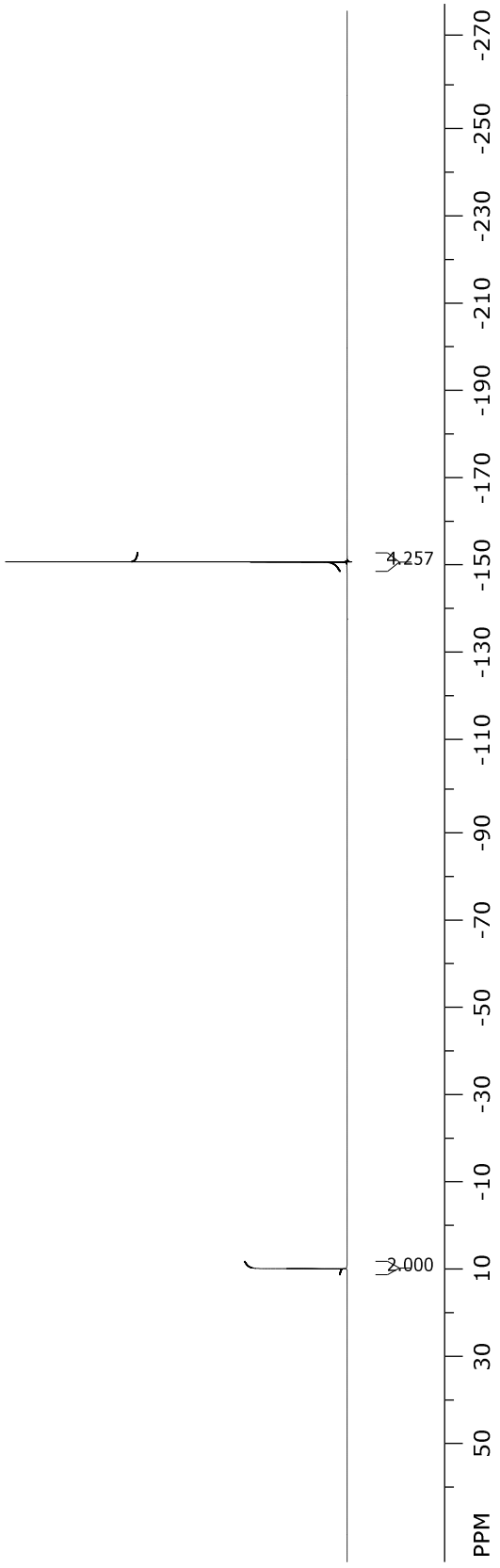
N=S
F
F
+
BF4-

2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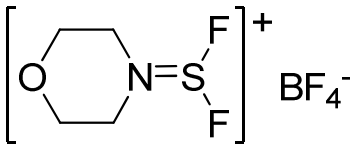

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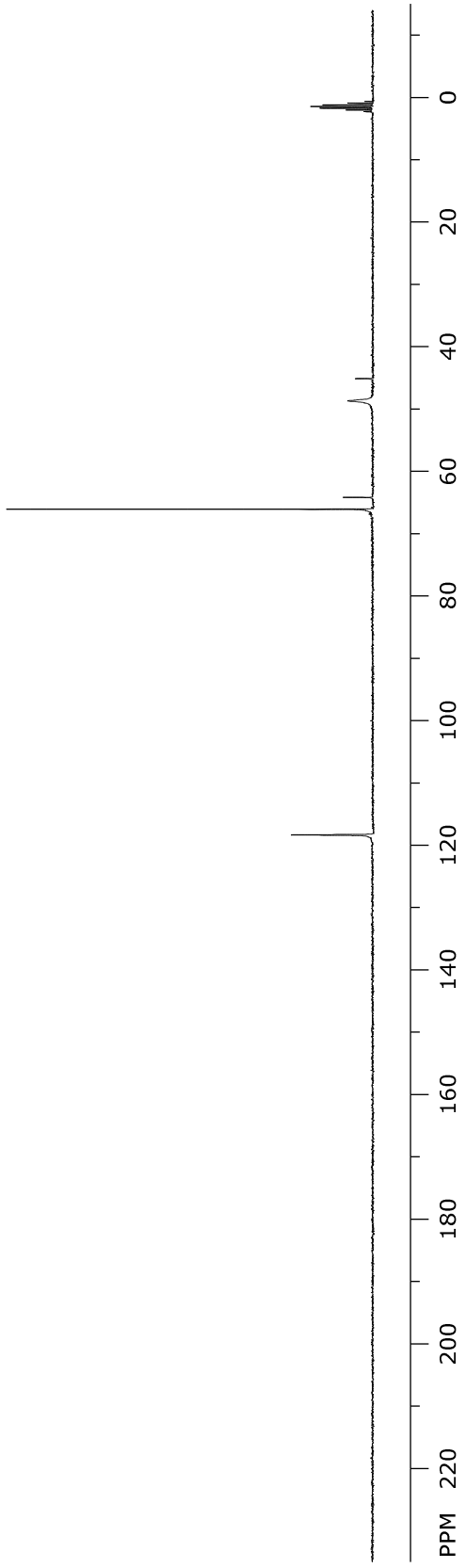

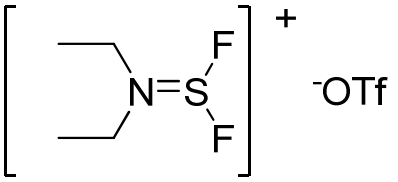
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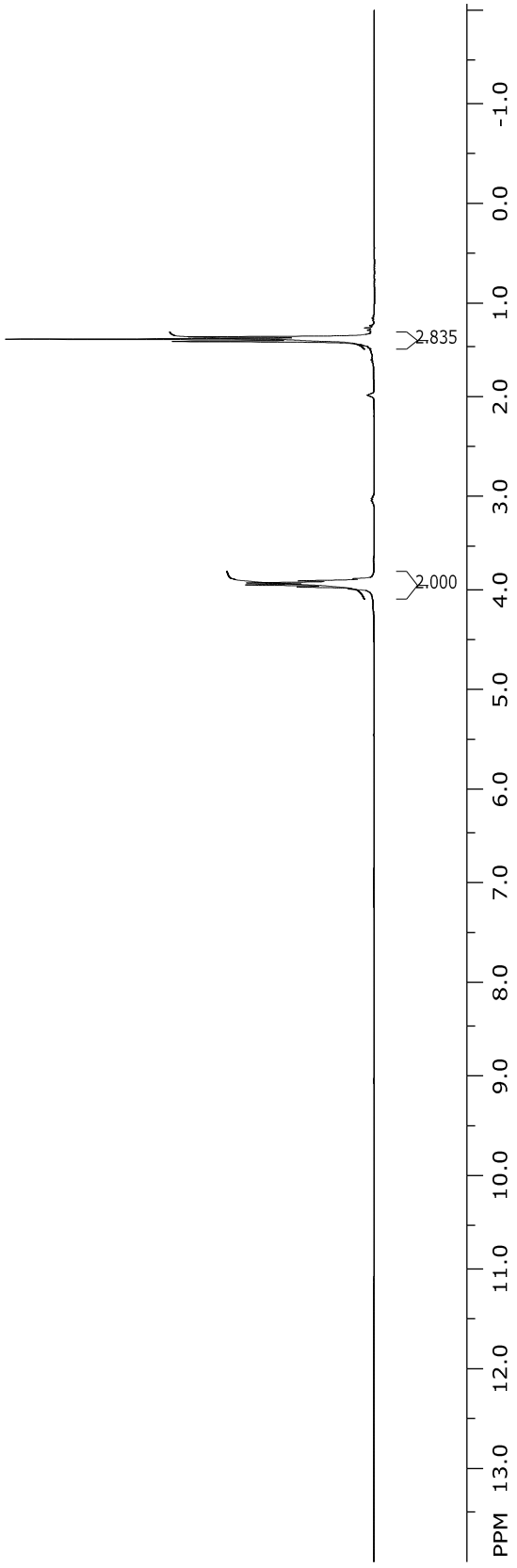
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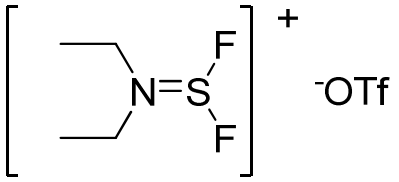
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+
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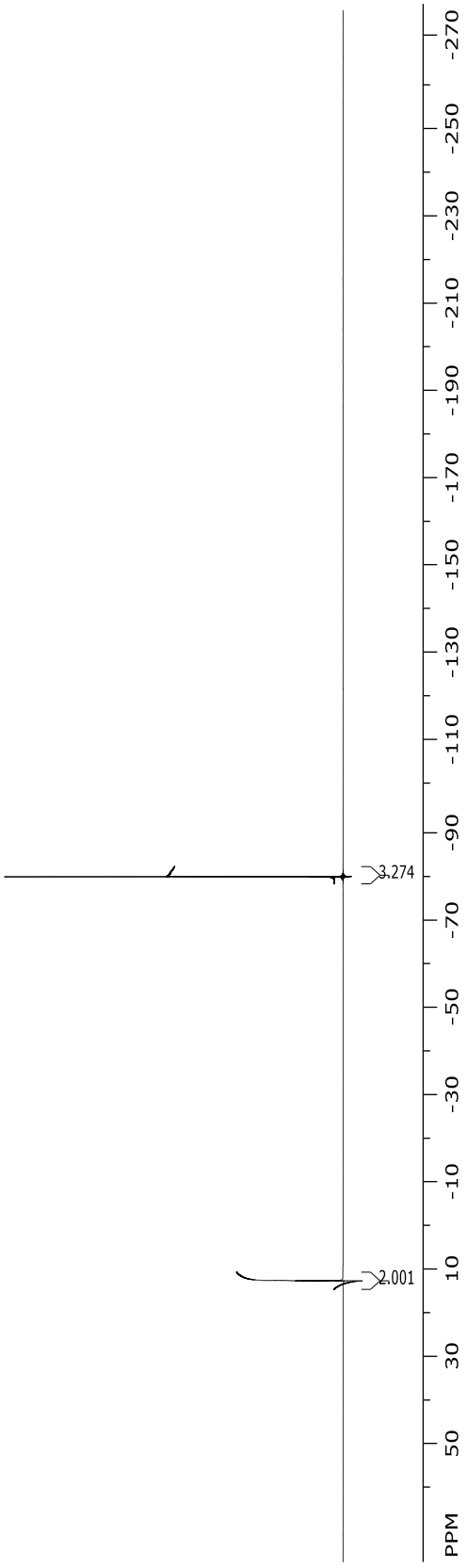
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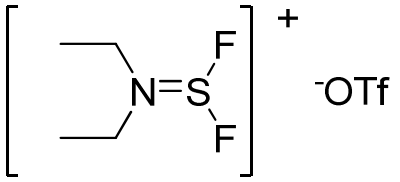

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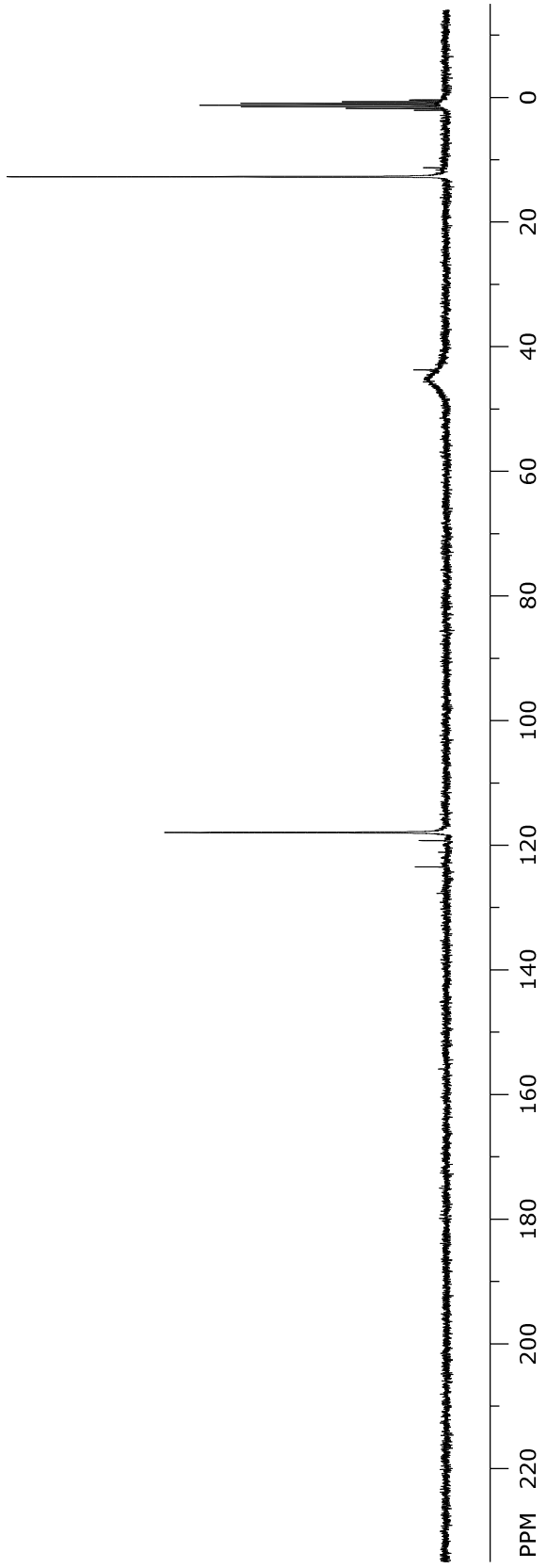

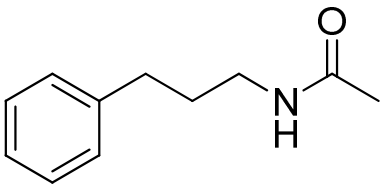
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N
H

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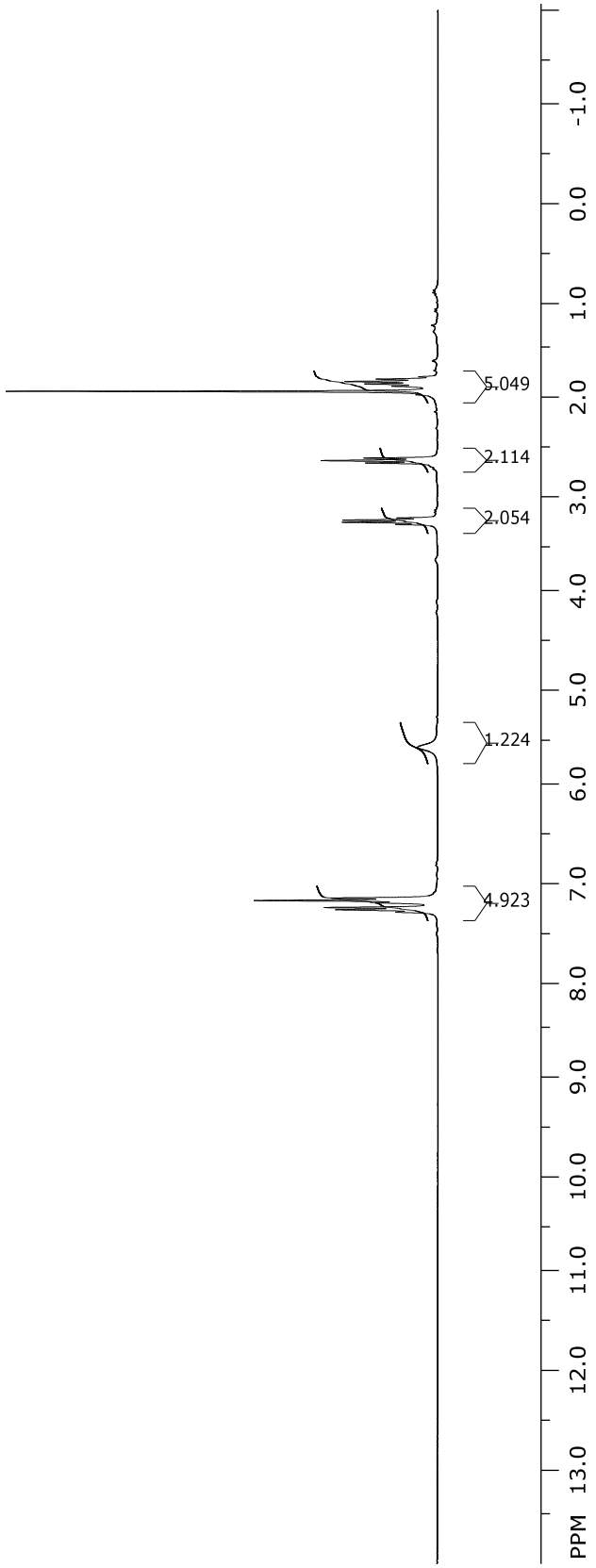
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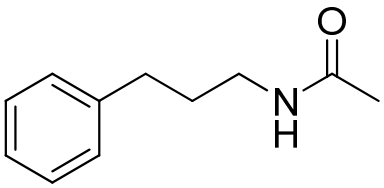

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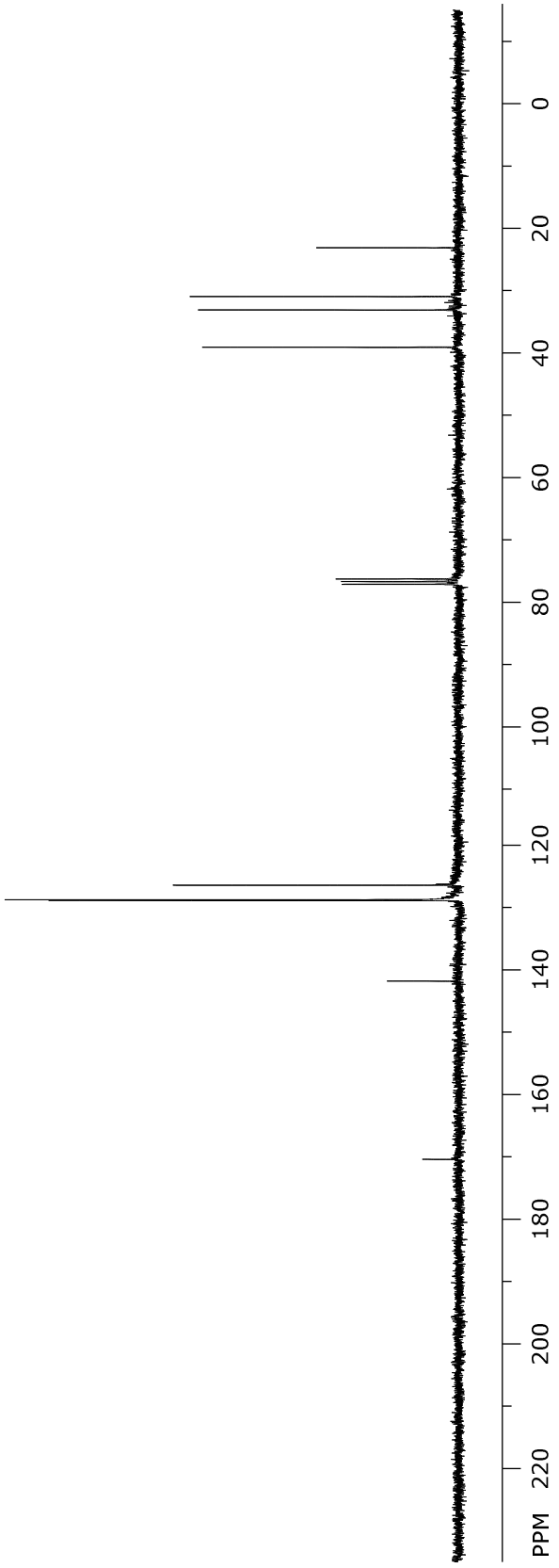

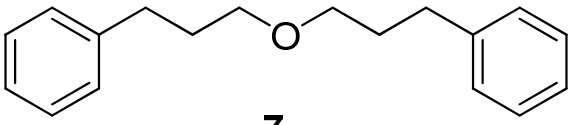

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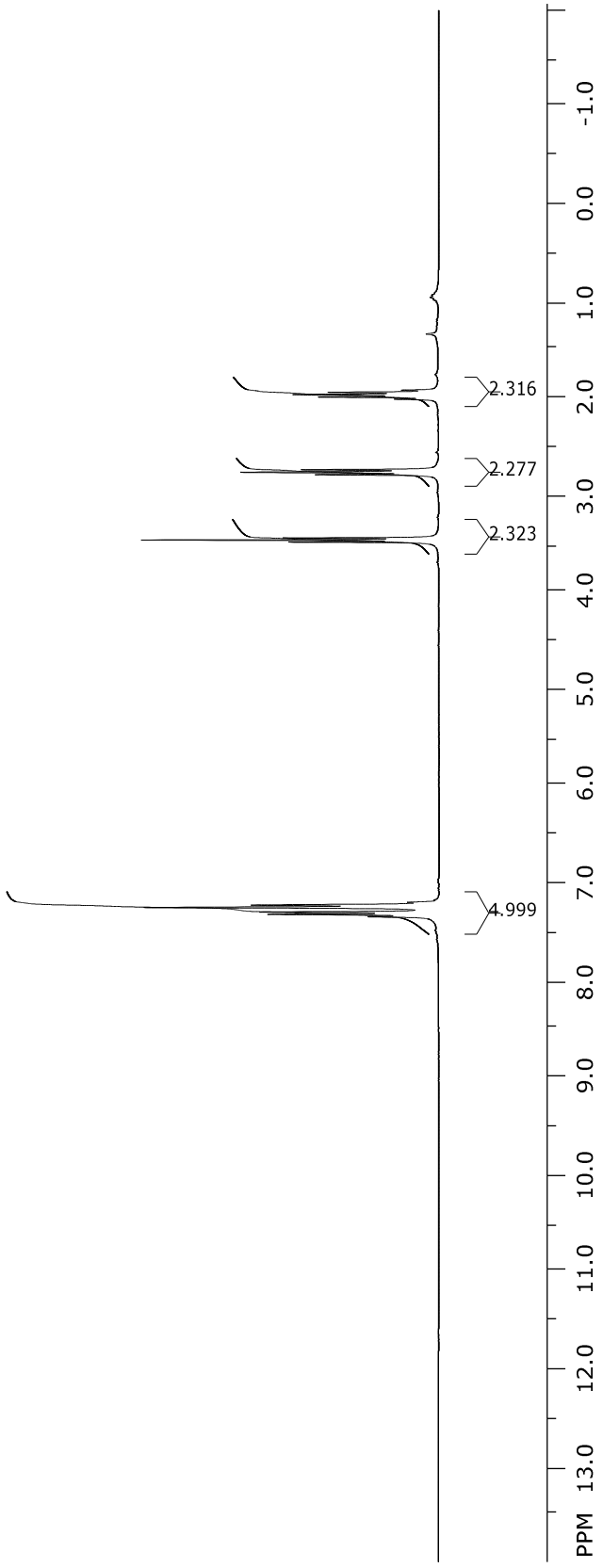
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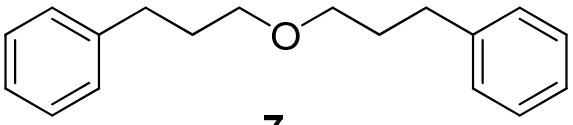

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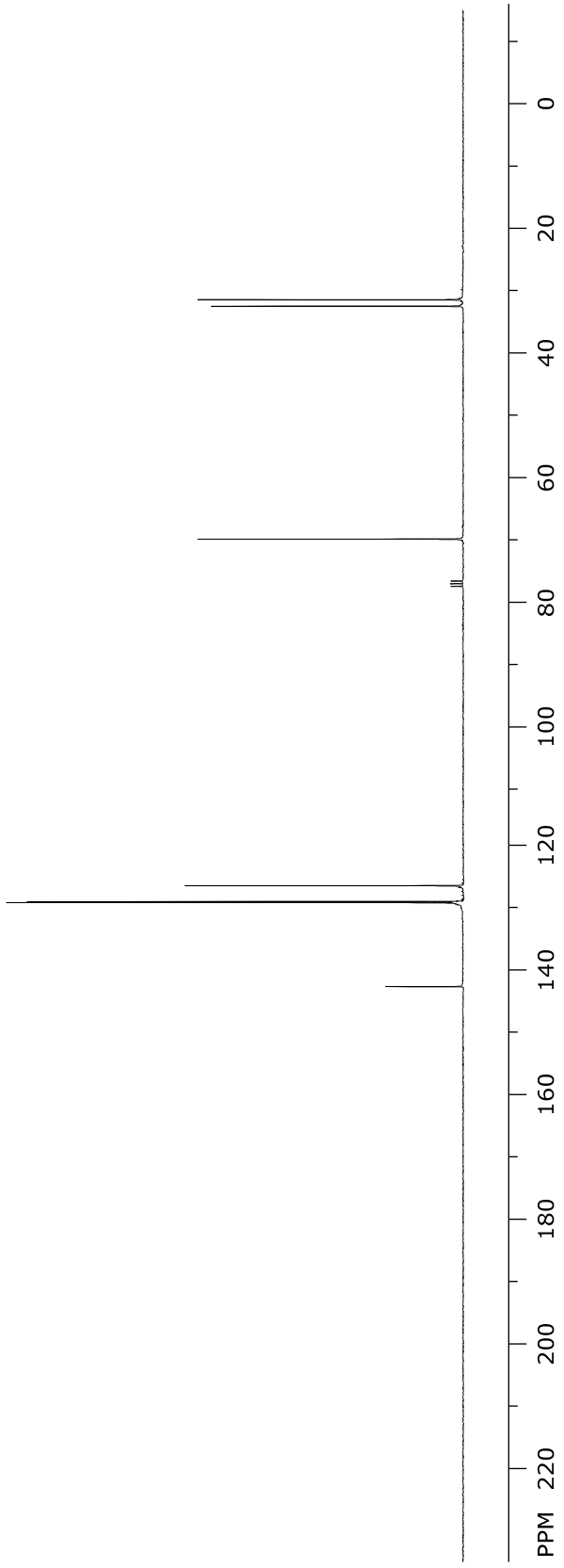
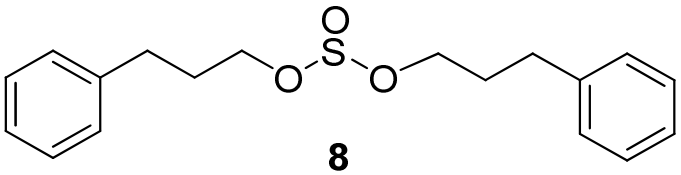
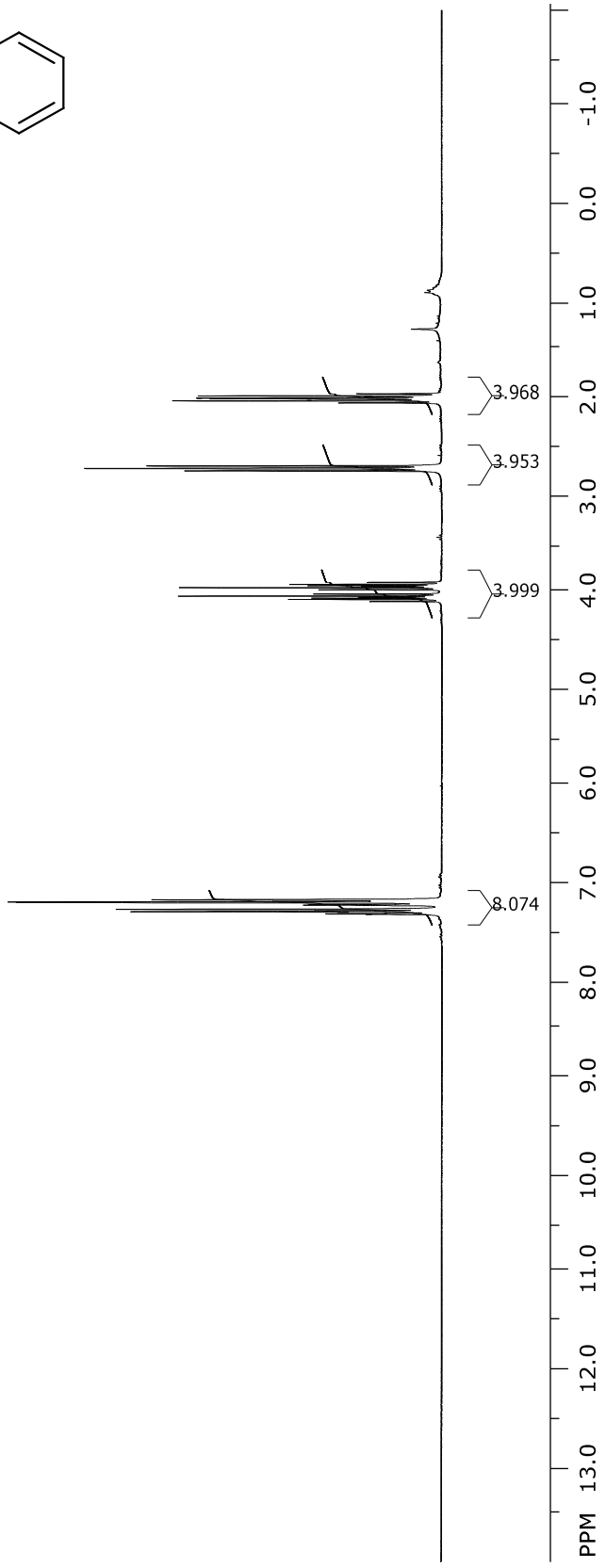



O
S
O
O

8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3.953
3.999
8.074
-1.0
0.0
1.0
2.0
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5.0
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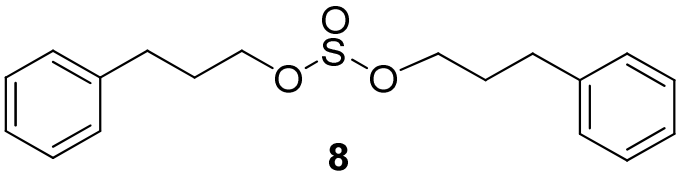
9.0
10.0
11.0
12.0
13.0
PPM



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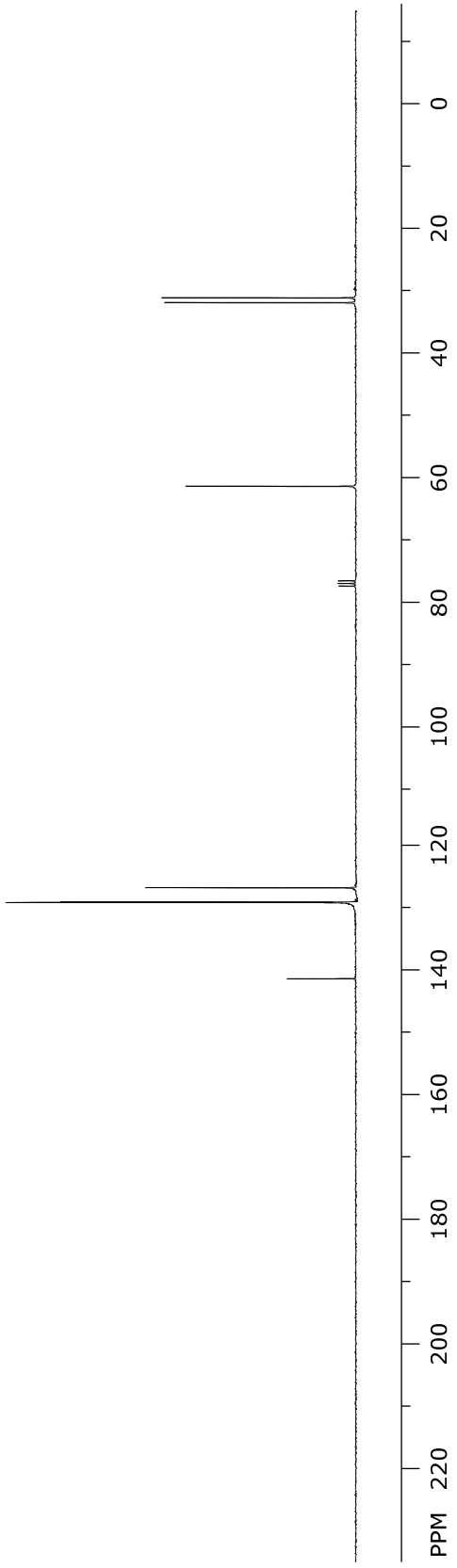

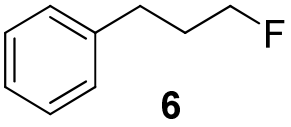
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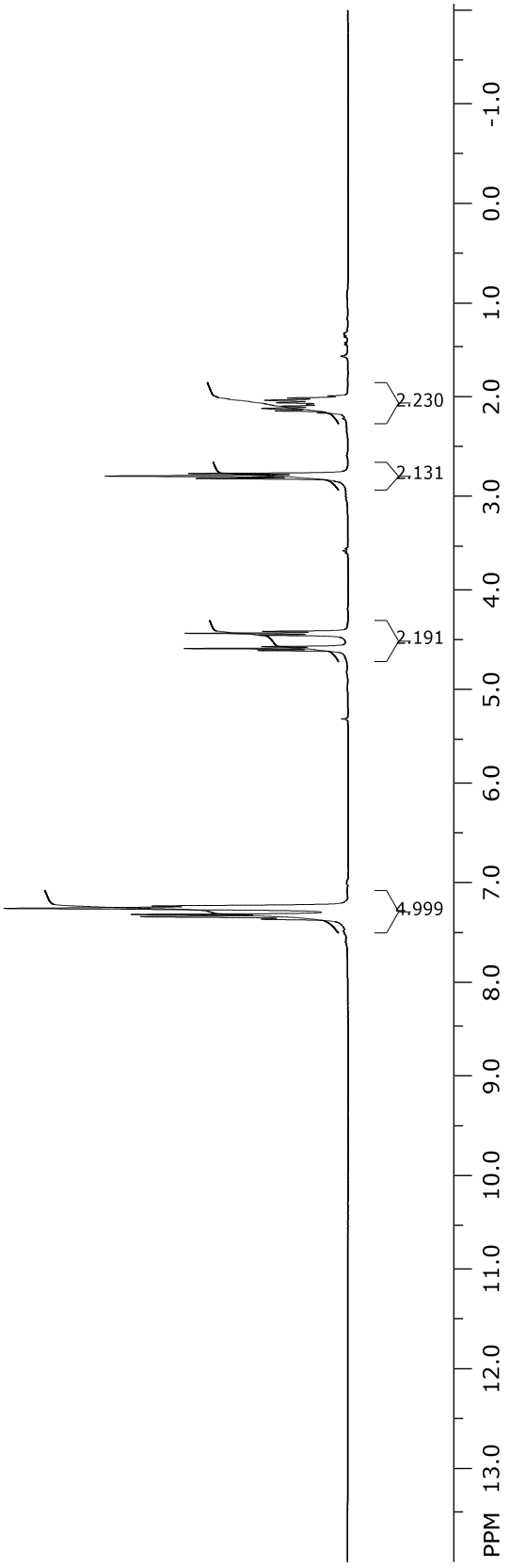
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2.131
2.191
4.999
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0.0
1.0
2.0
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5.0
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7.0
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10.0
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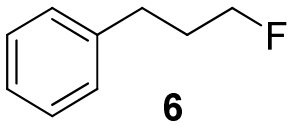
12.0
13.0
PPM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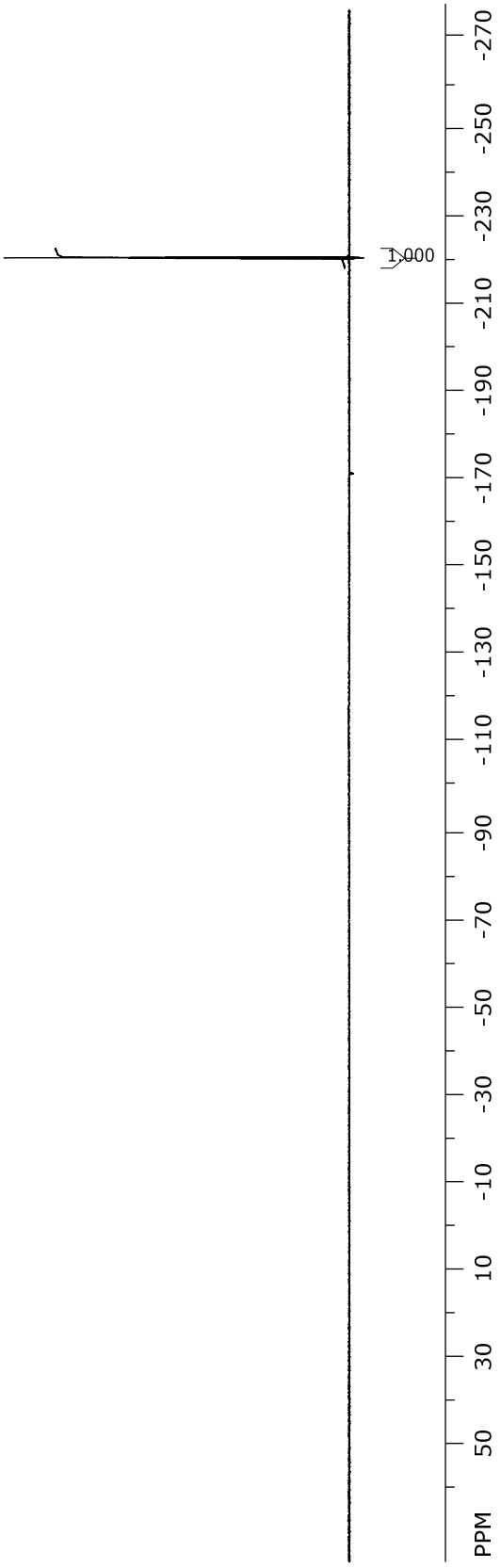
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PPM
50
30
10
-10
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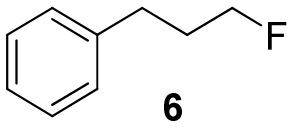
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270



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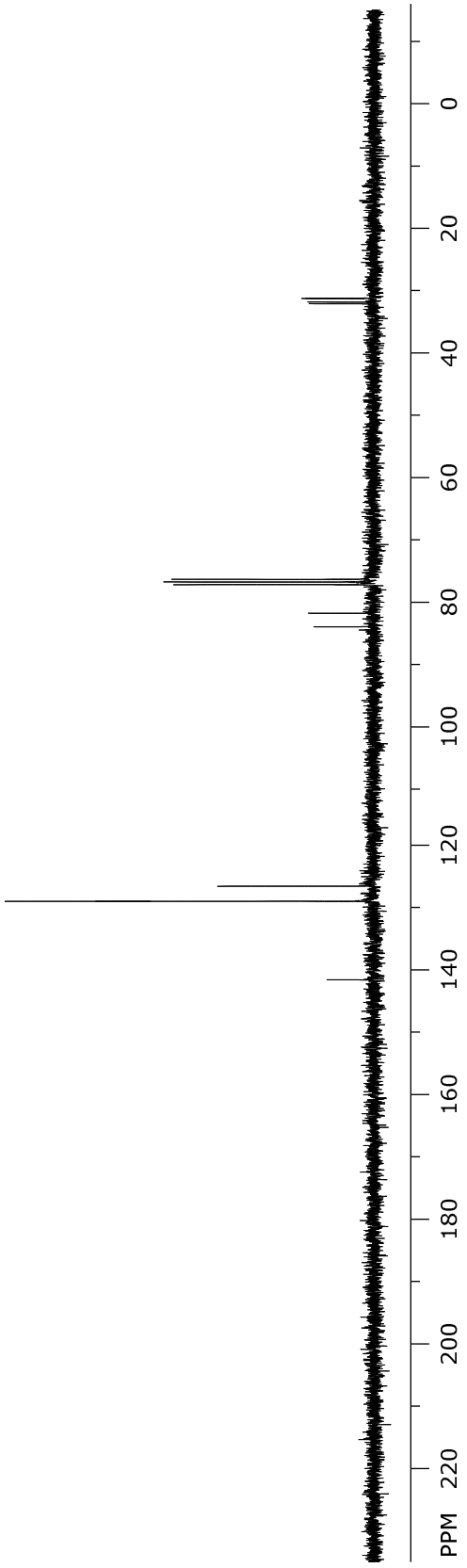

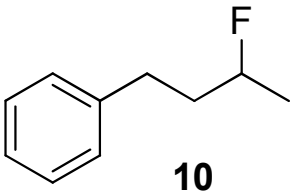
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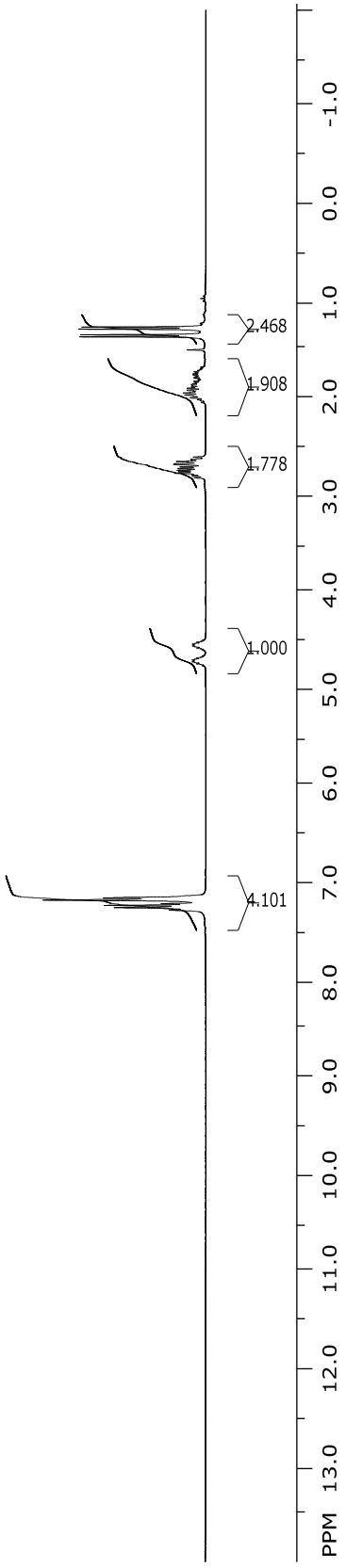
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1.778
1.000
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0.0
1.0
2.0
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5.0
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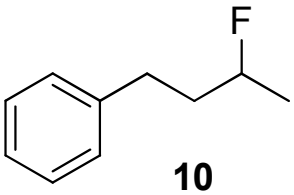
PPM



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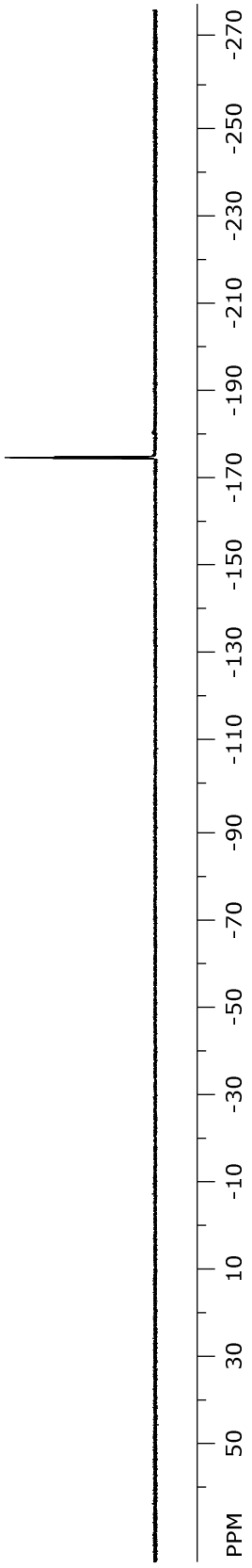

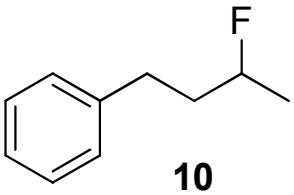

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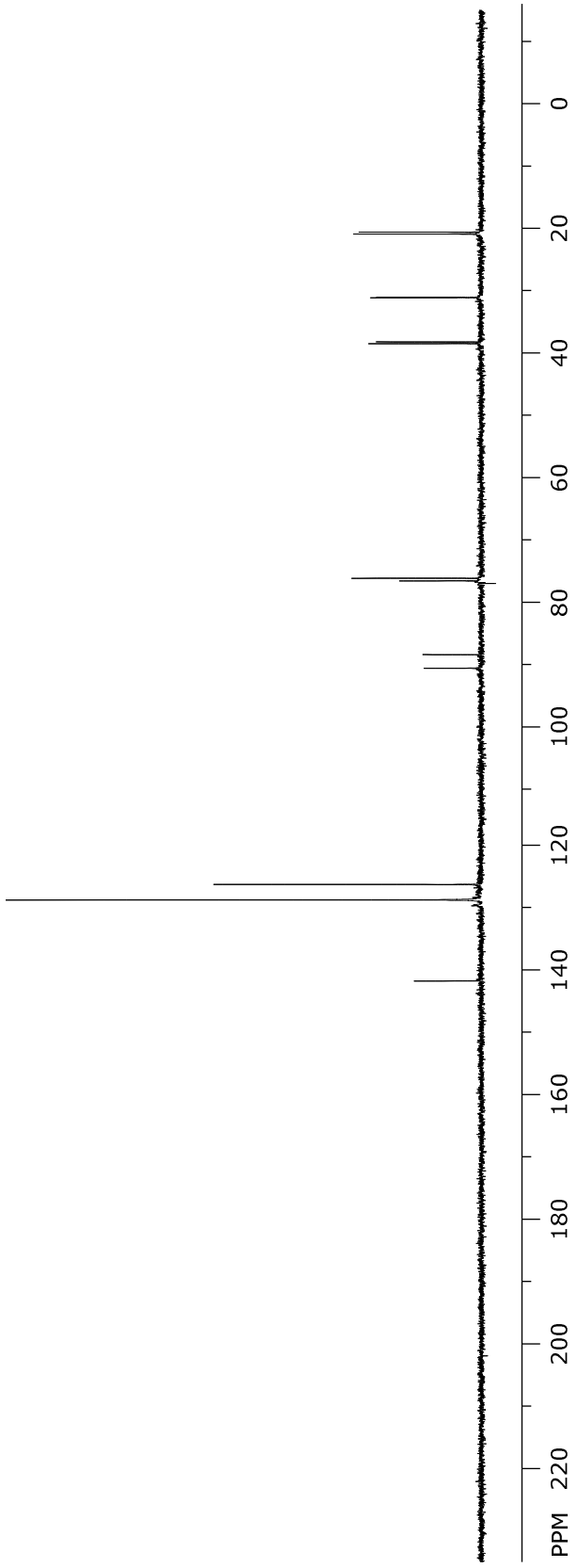

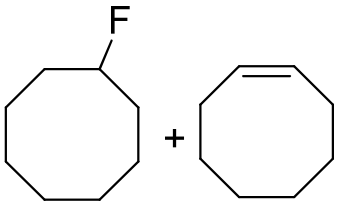
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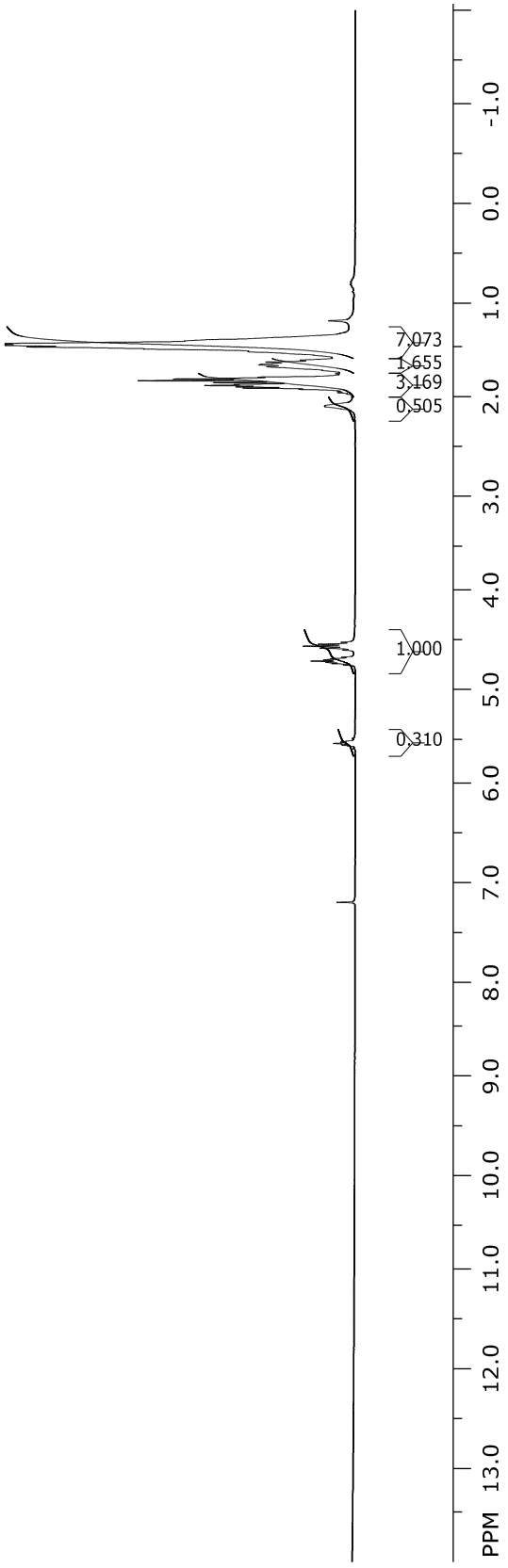
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3.169
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1.000
0.310
-1.0
0.0
1.0
2.0
3.0
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5.0
6.0
7.0
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10.0
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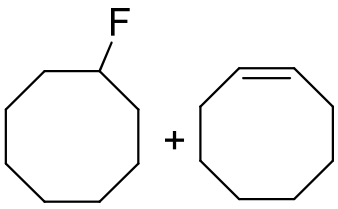
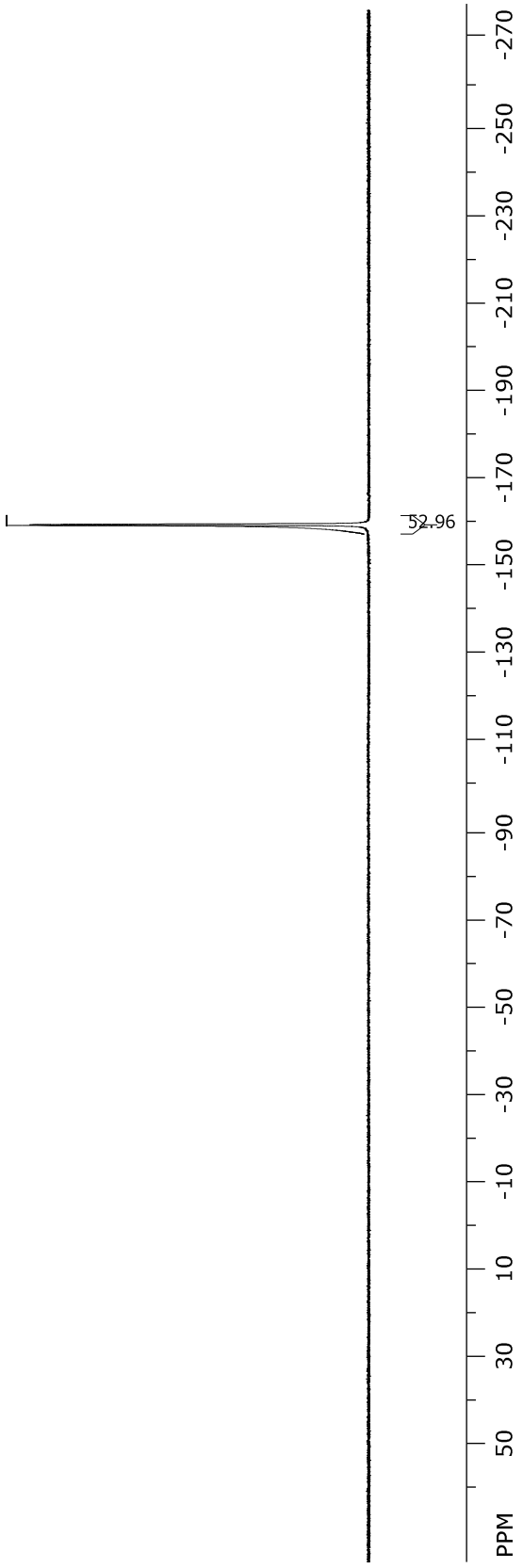
12.0
13.0
PPM


F
+

12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-270
-250
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-190
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-150
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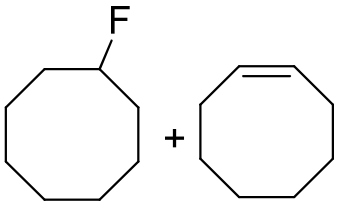
-110
-90
-70
-50
-30
-10
10
30
50
PPM



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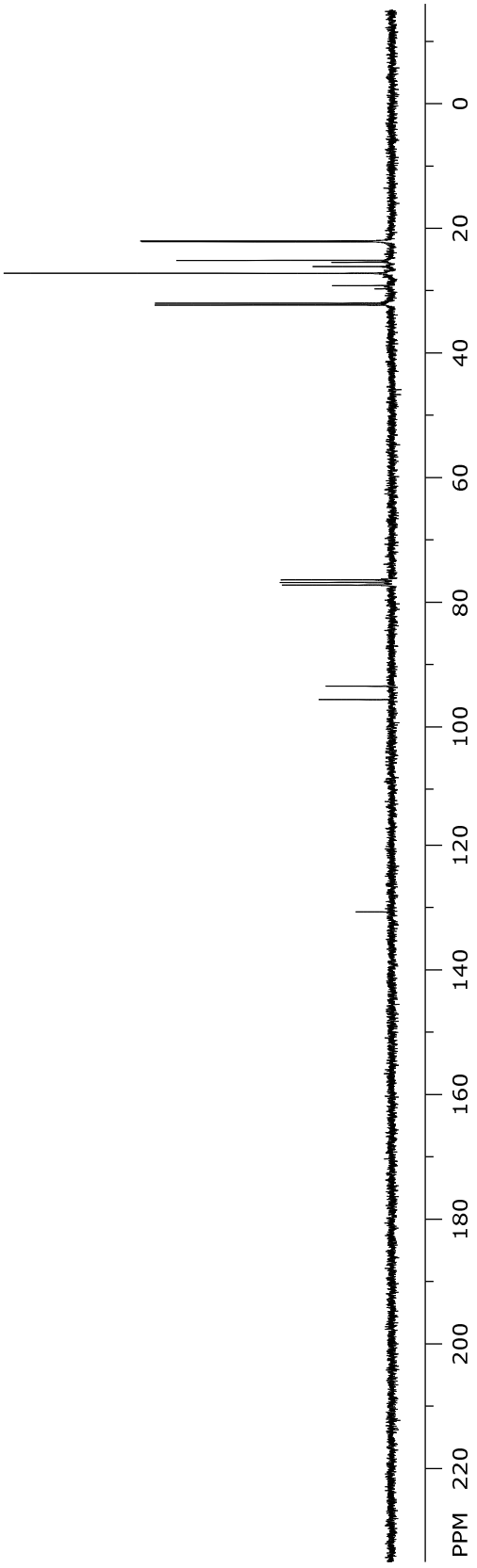
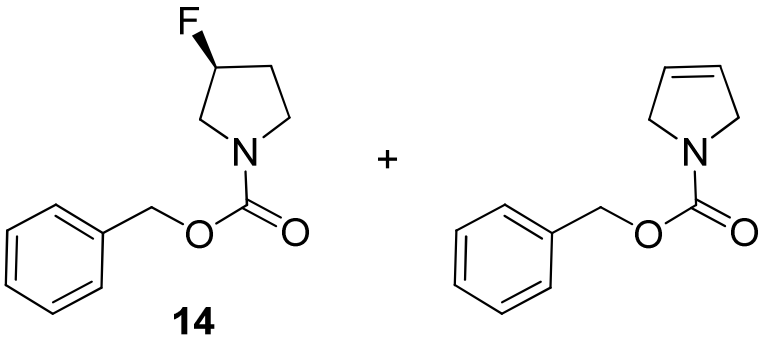
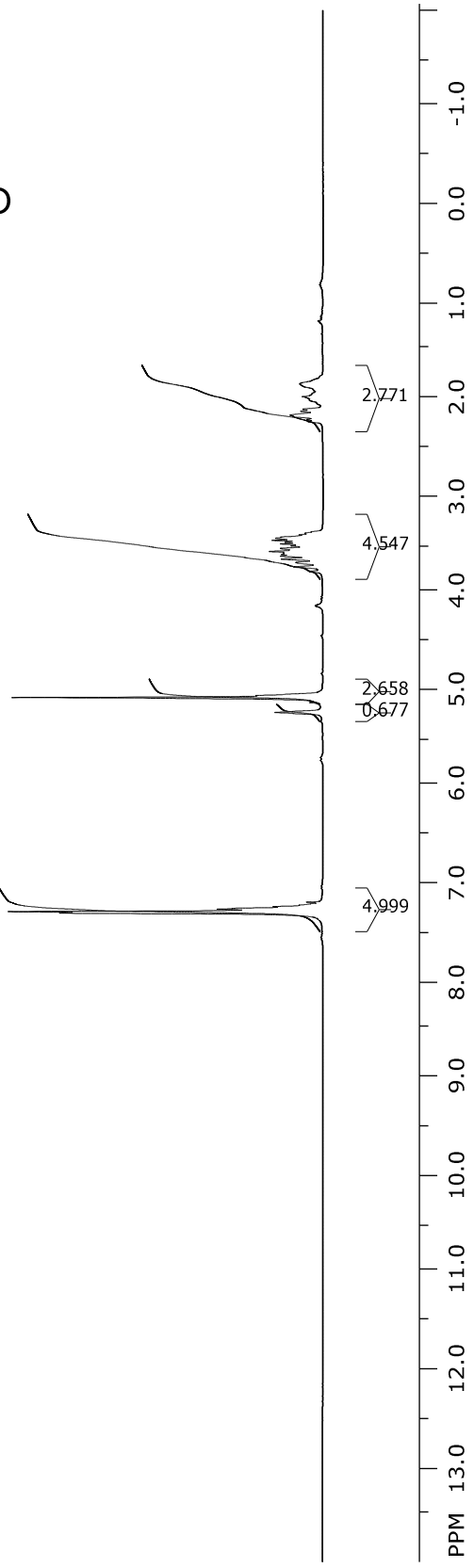



F
N
O
O
14
+
N
O
O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1.0
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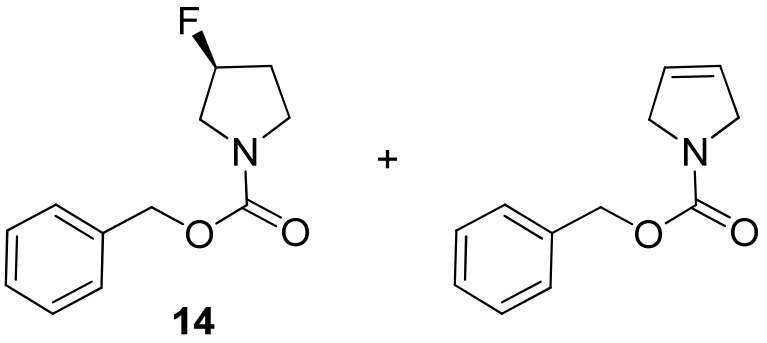
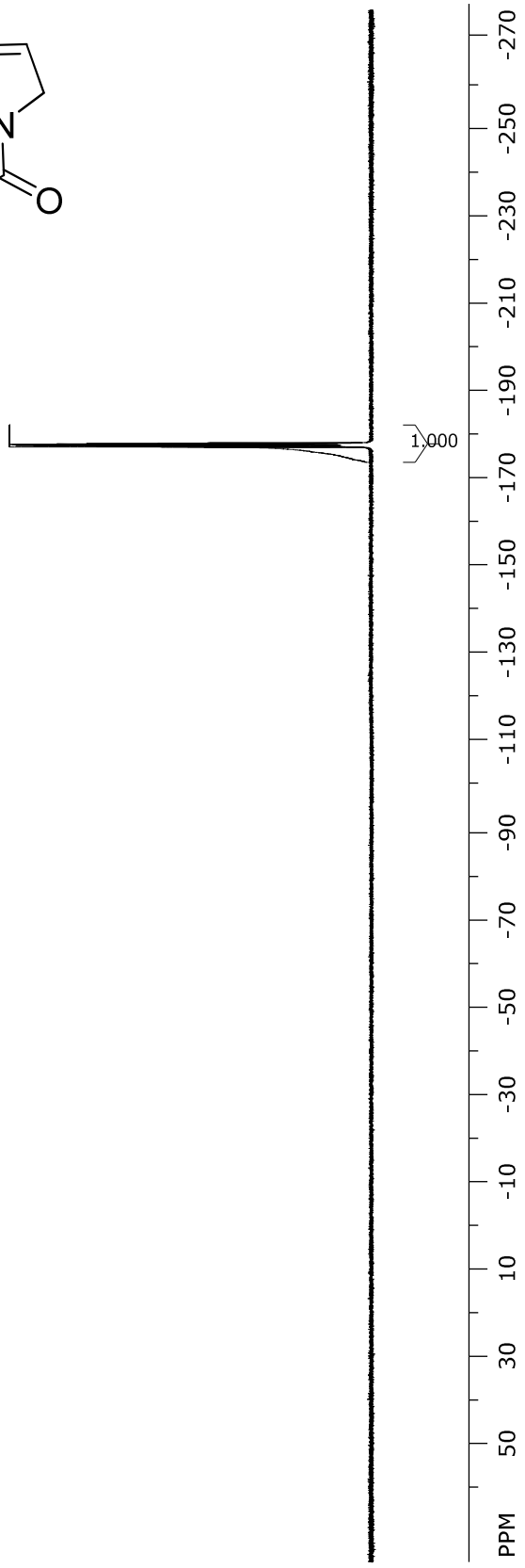
13.0
PPM


F
N
O
O
14
+
N
O
O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-270
-250
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-210
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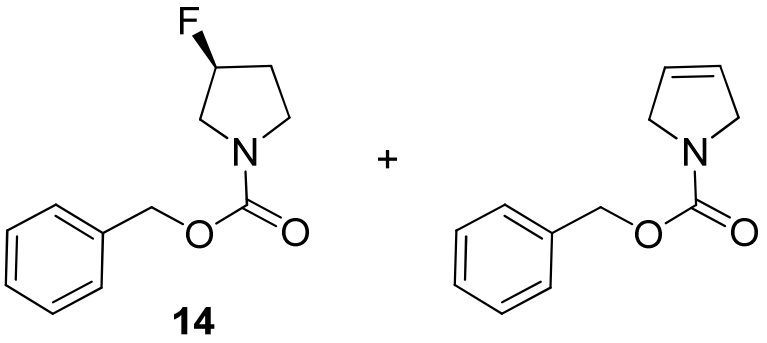
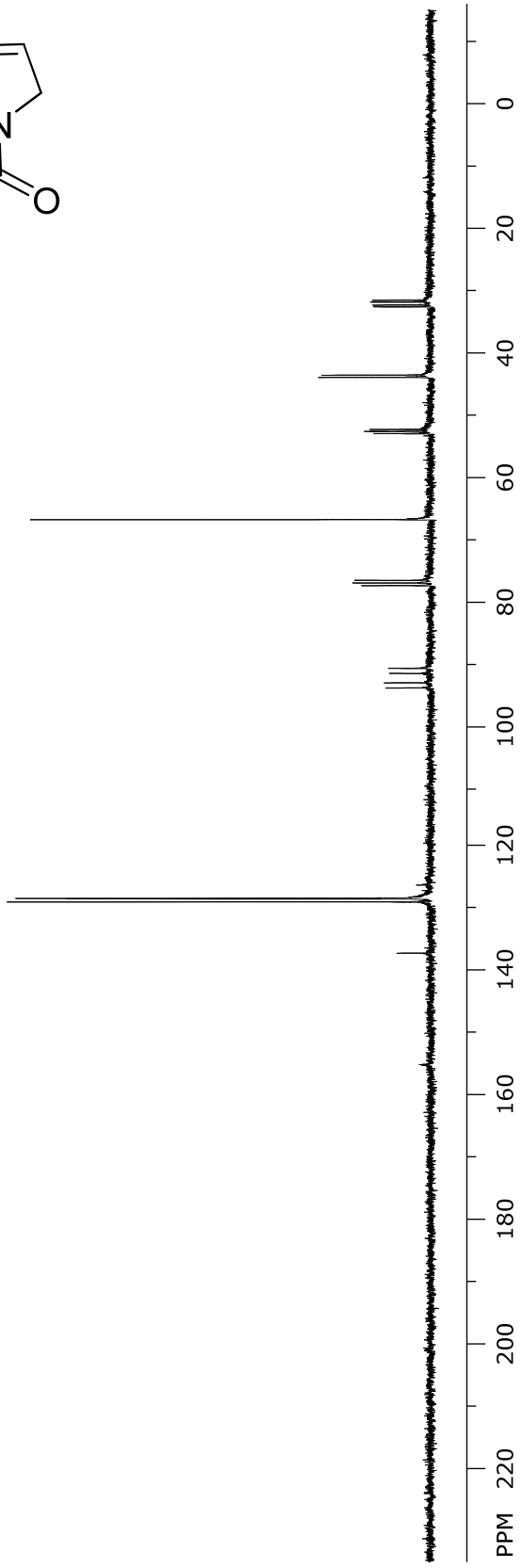
-170
-150
-130
-110
-90
-70
-50
-30
-10
10
30
50
PPM


F
N
O
O
14
+
N
O
O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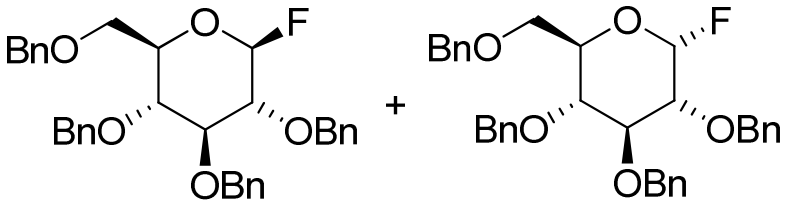
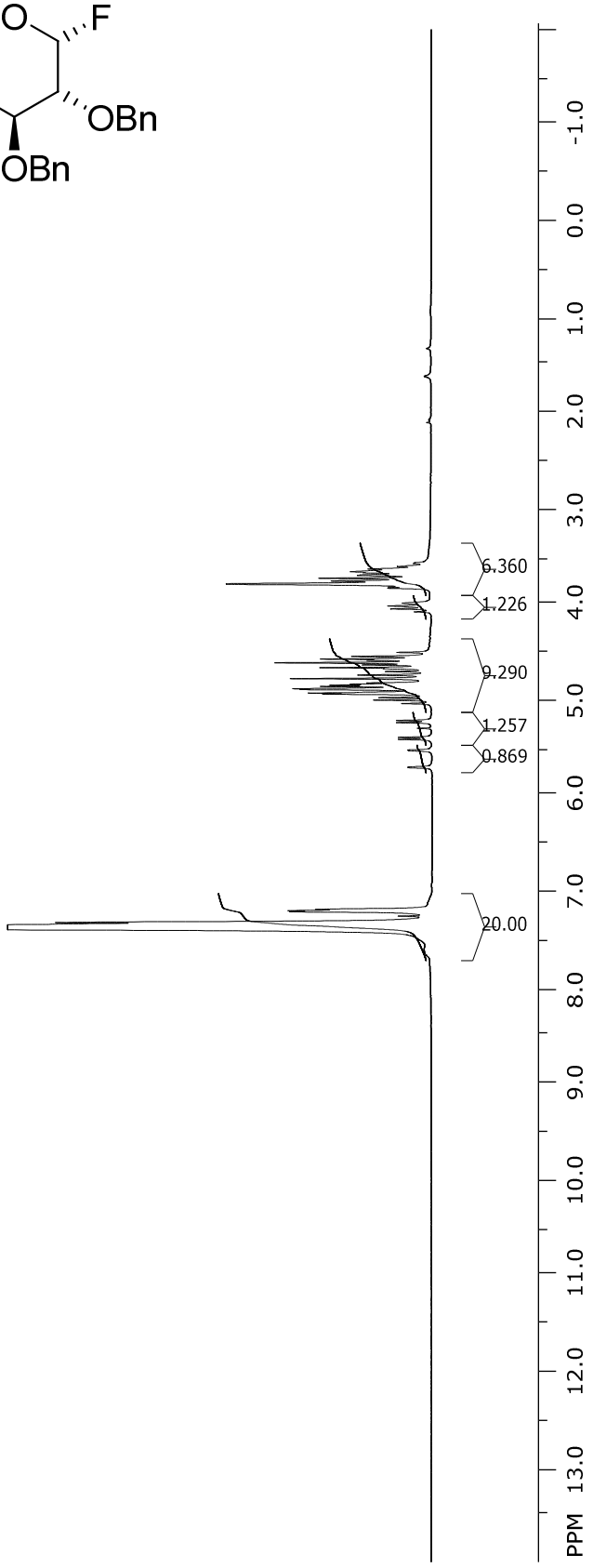
60
80
100
120
140
160
180
200
220
PPM


BnO
O
F
BnO
OBn
OBn
+
BnO
O
F
BnO
OBn
OBn

16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1.257
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20.00
PPM
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12.0
11.0
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7.0
6.0
5.0
4.0
3.0
2.0
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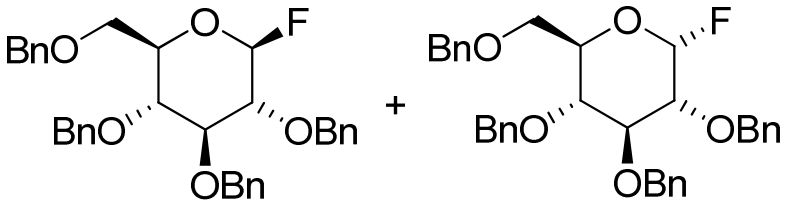
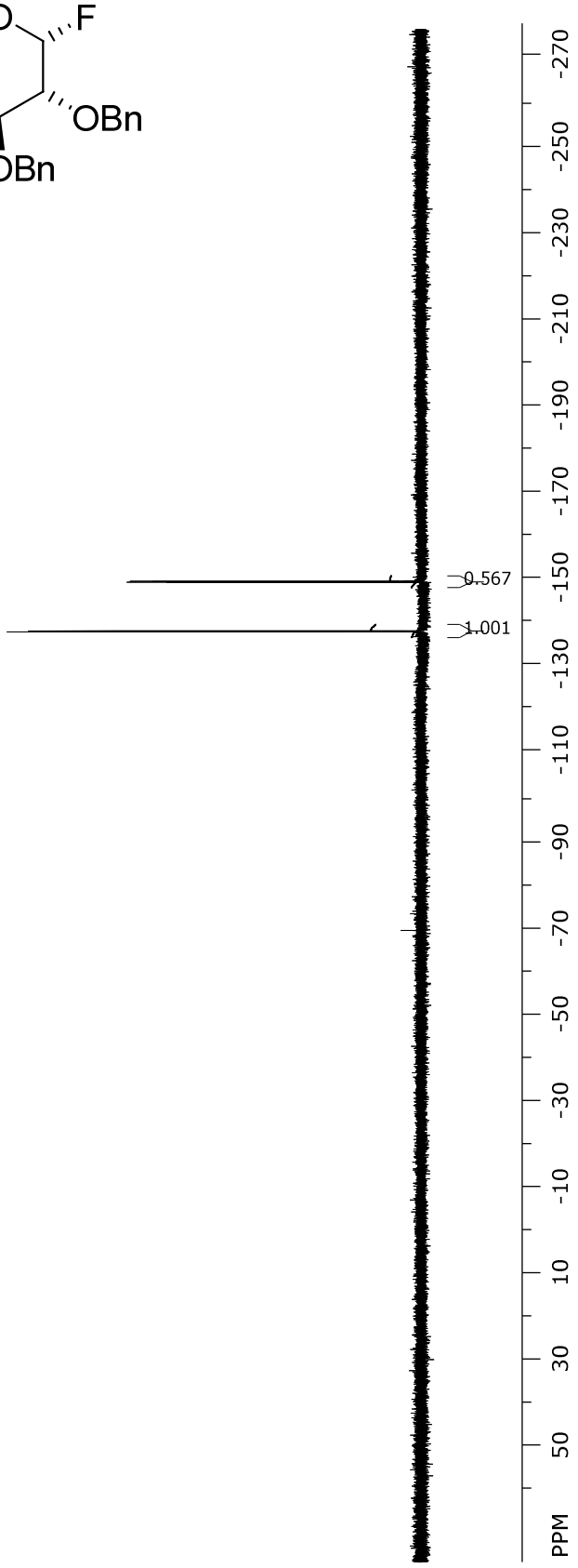
0.0
-1.0


BnO
O
F
BnO
OBn
OBn
+
BnO
O
F
BnO
OBn
OBn

16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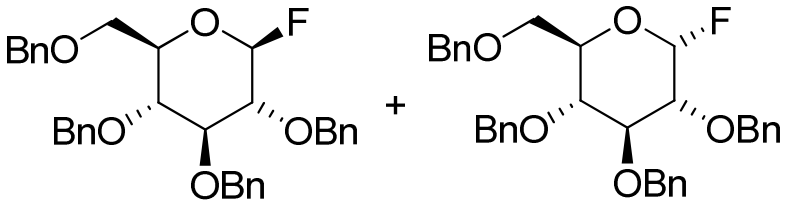
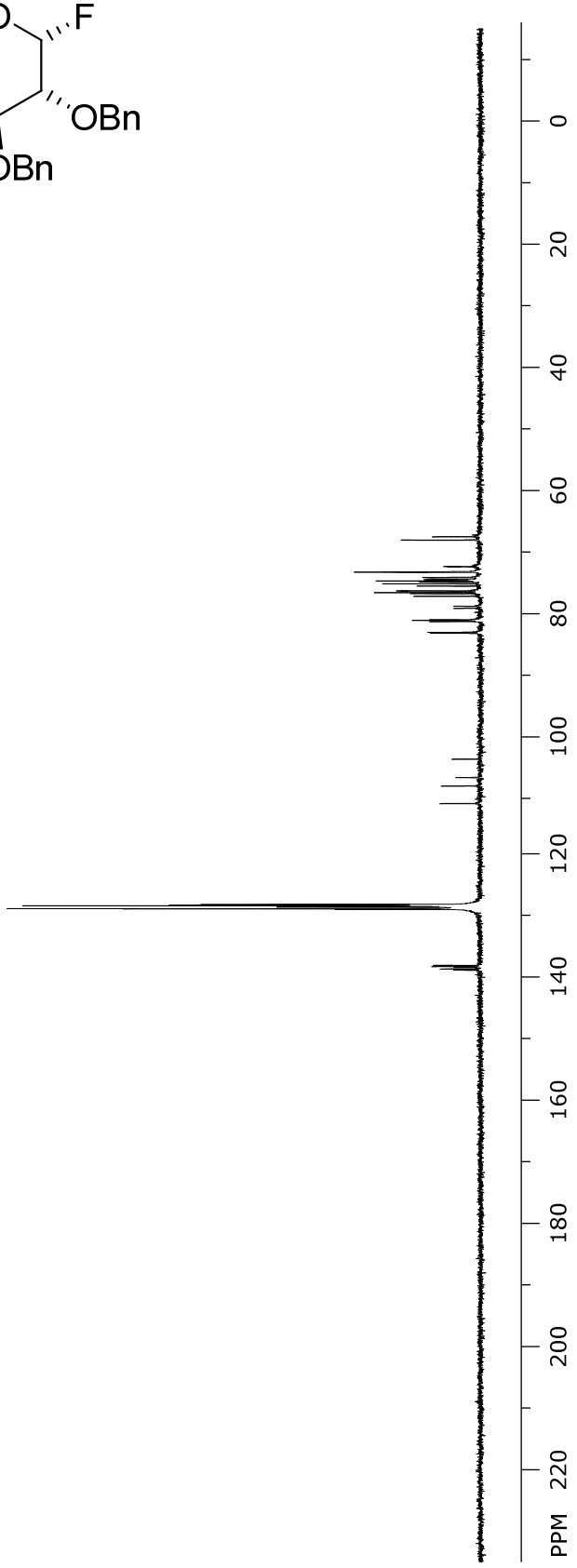
-150
-130
-110
-90
-70
-50
-30
-10
10
30
50
PPM


BnO
O
F
BnO
OBn
OBn
+
BnO
O
F
BnO
OBn
OBn

16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100
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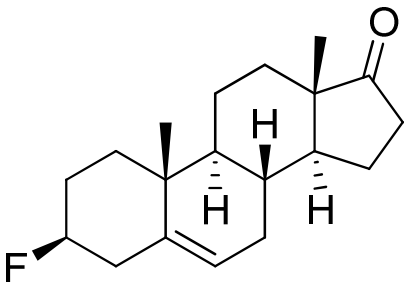
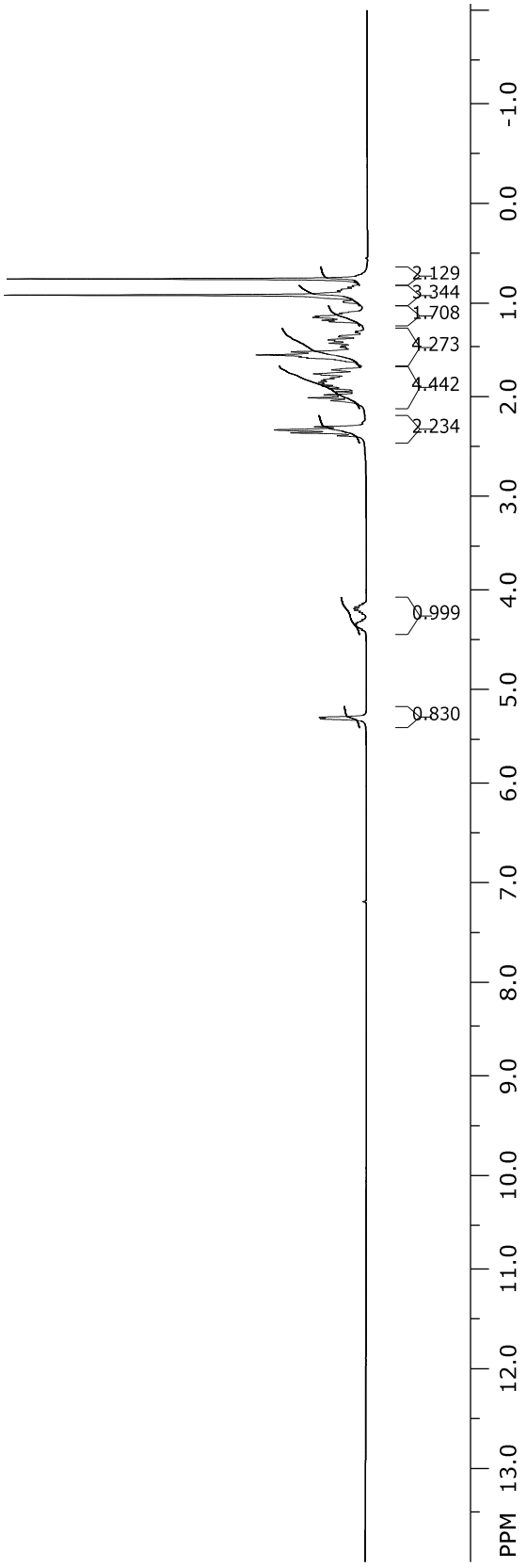
PPM


O
H
H
H
F

18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4.442
2.234
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0.830
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1.0
2.0
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5.0
6.0
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10.0
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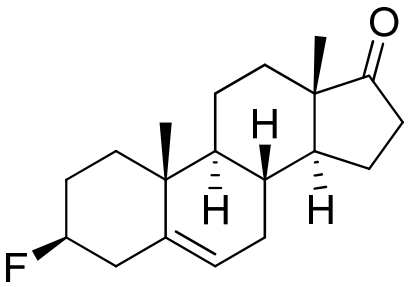
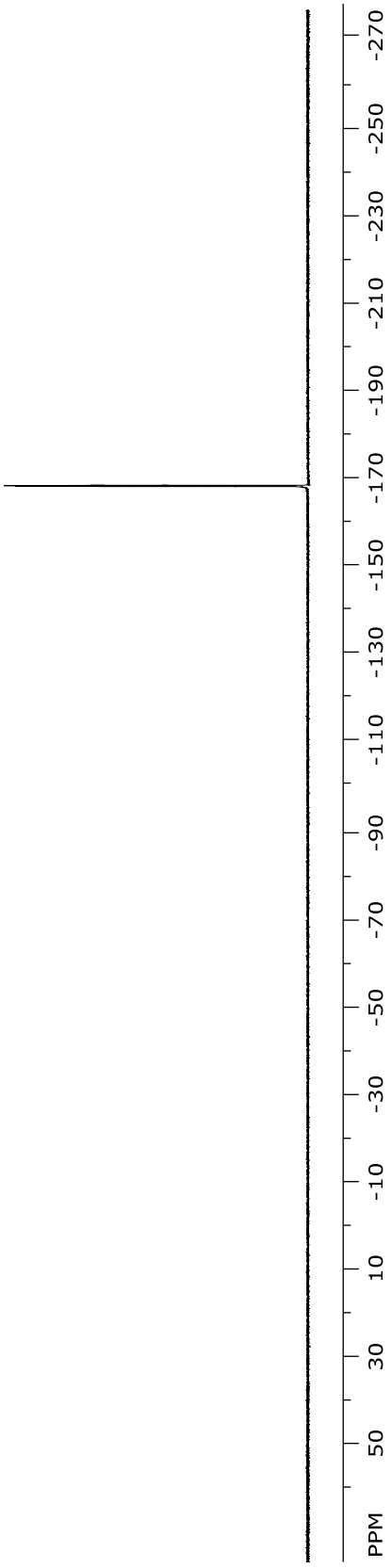
PPM


O
H
H
H
F

18


PPM
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-10
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-130
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-190
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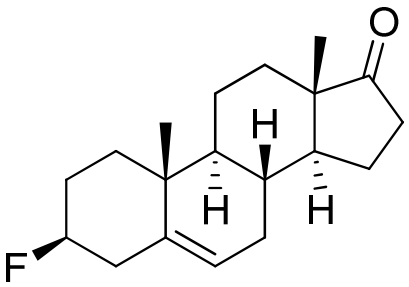
-230
-250
-270



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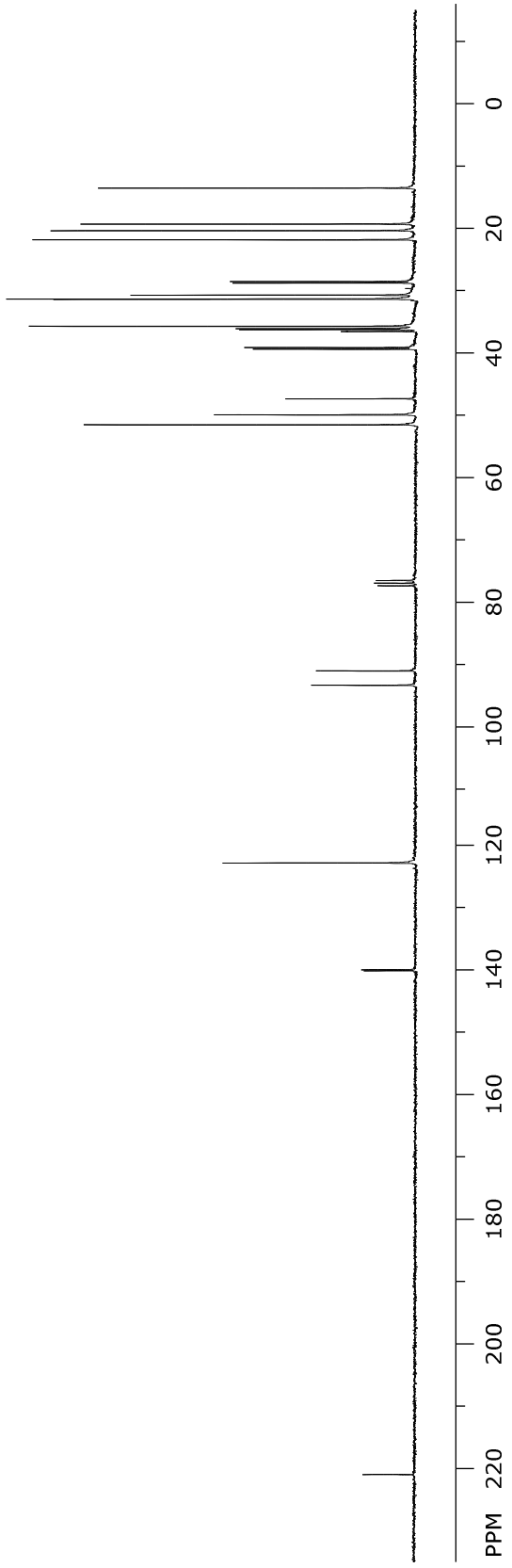
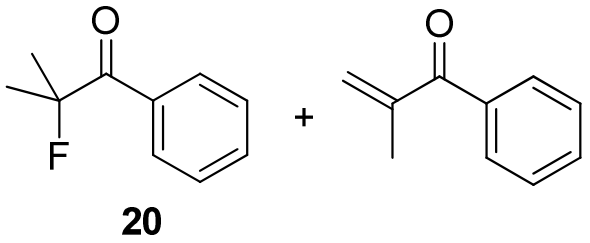
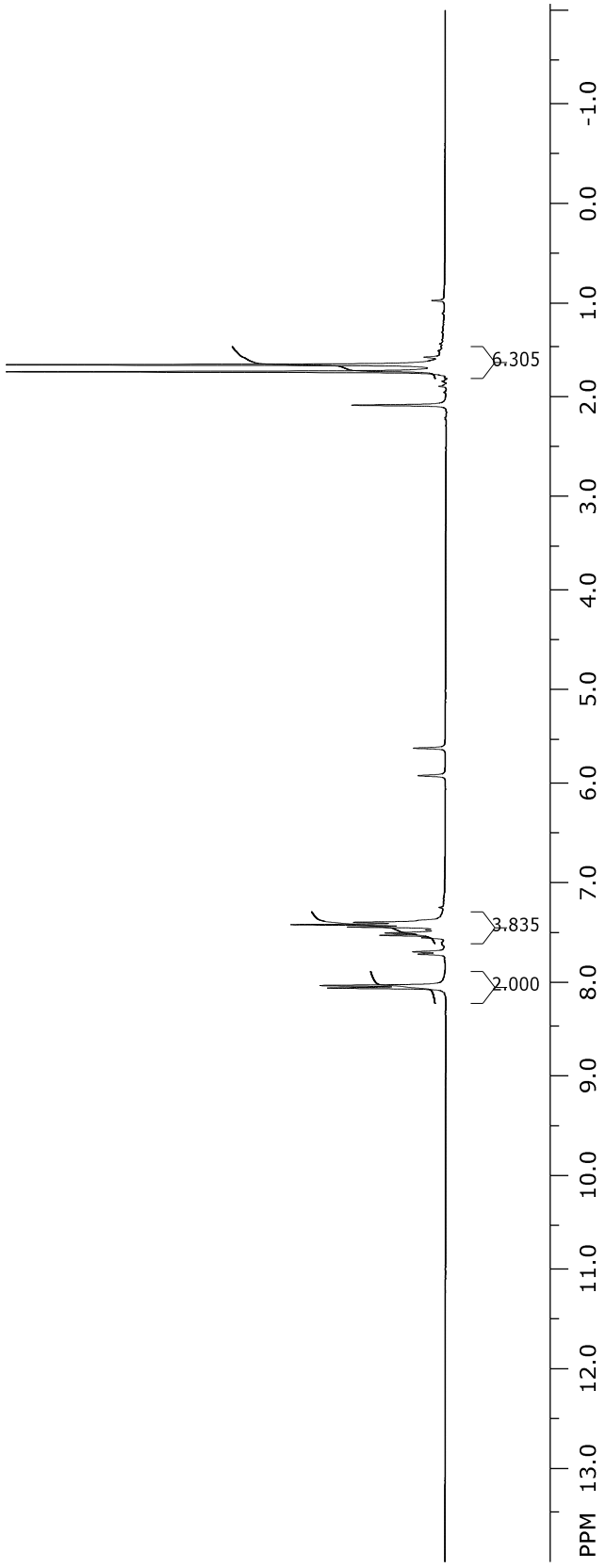



O
F
+
O

20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1.0
2.0
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5.0
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8.0
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10.0
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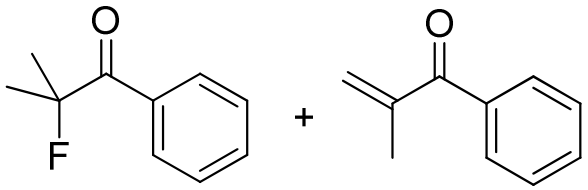
13.0
PPM



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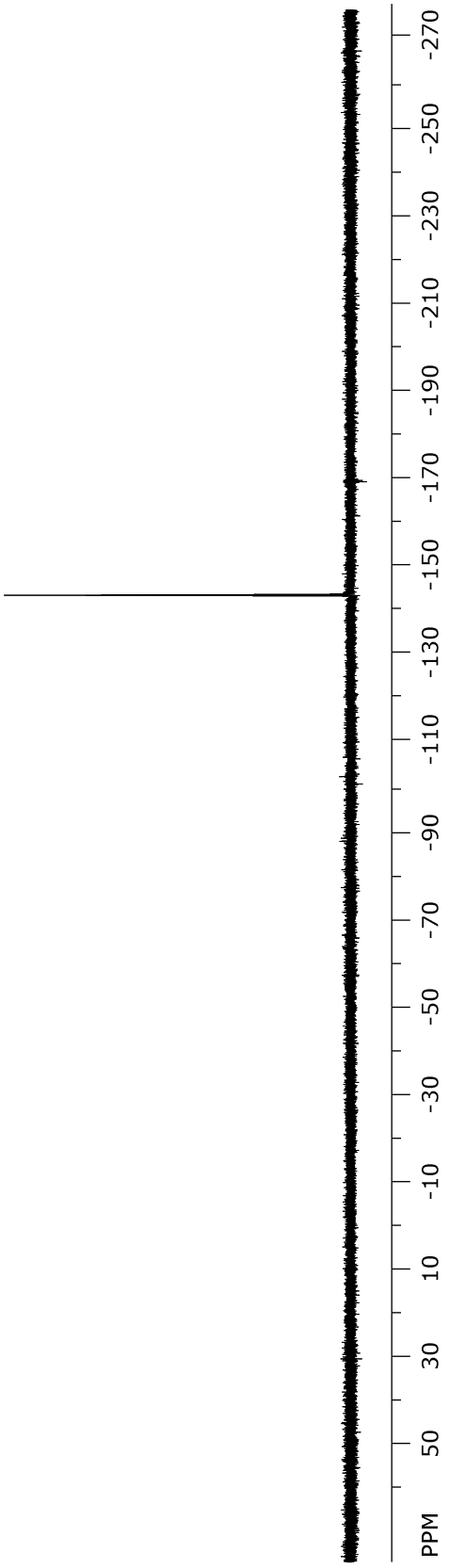

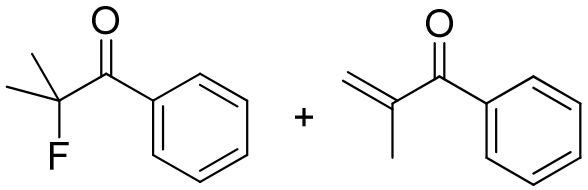

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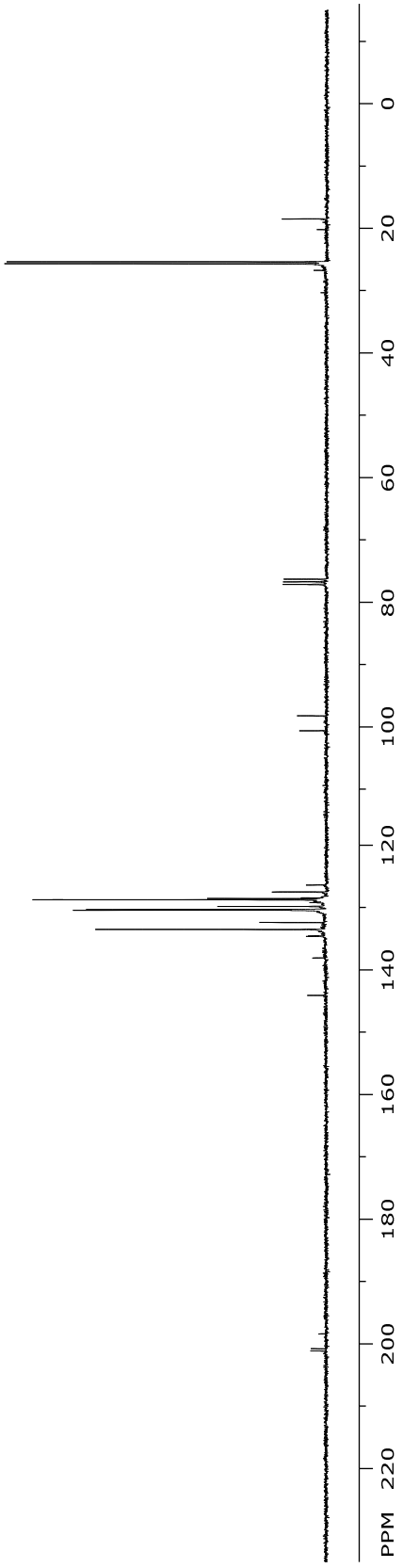
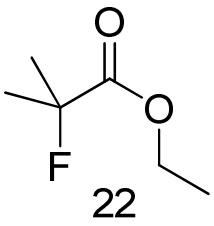
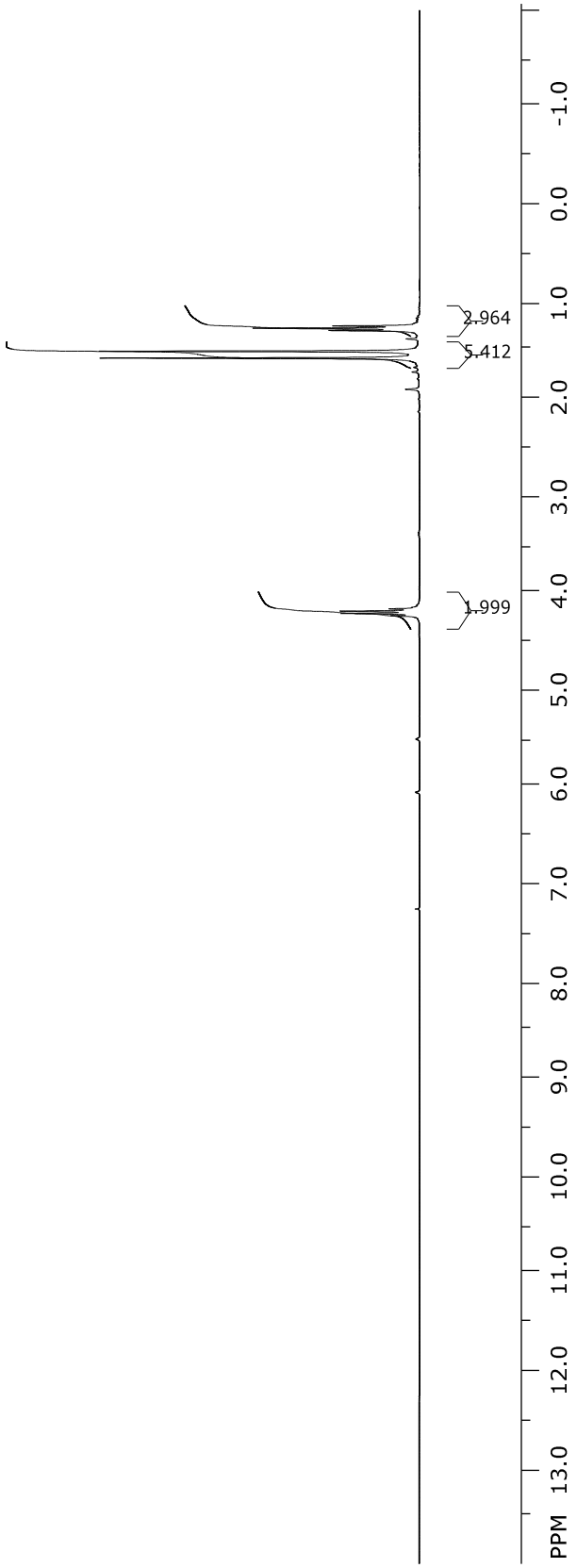



O
O
F

22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1.0
2.0
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4.0
5.0
6.0
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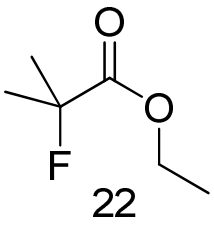
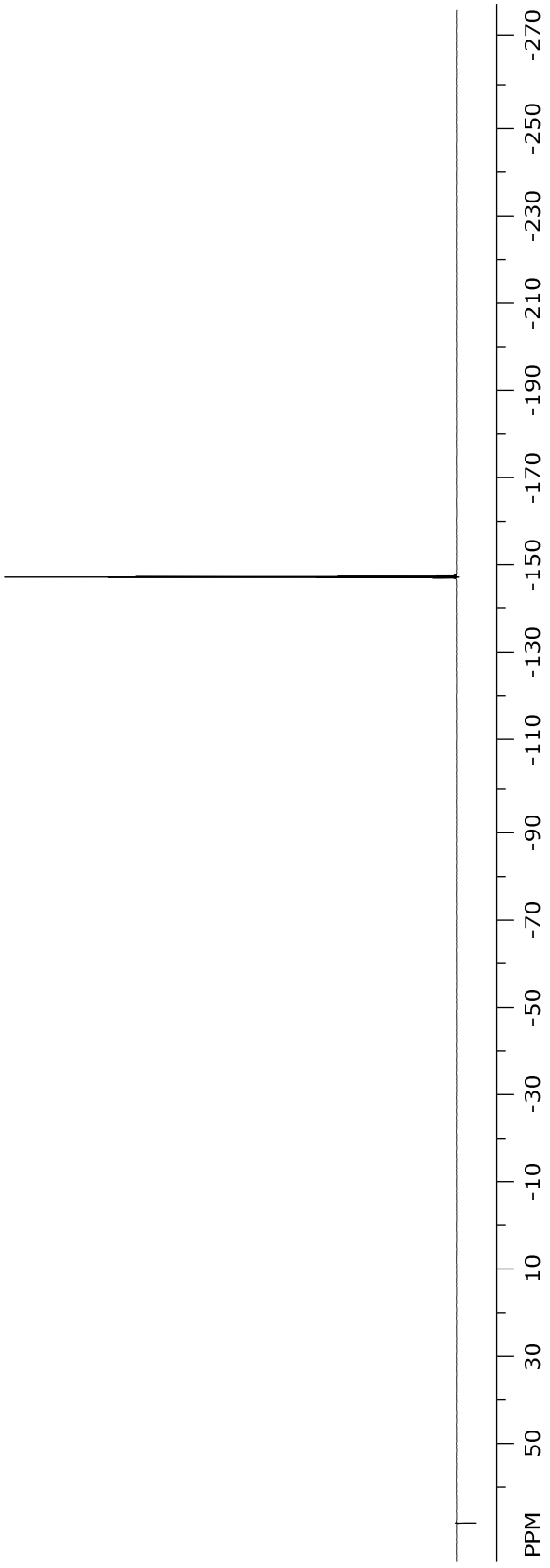
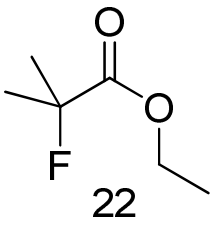
10.0
11.0
12.0
13.0
PPM



22





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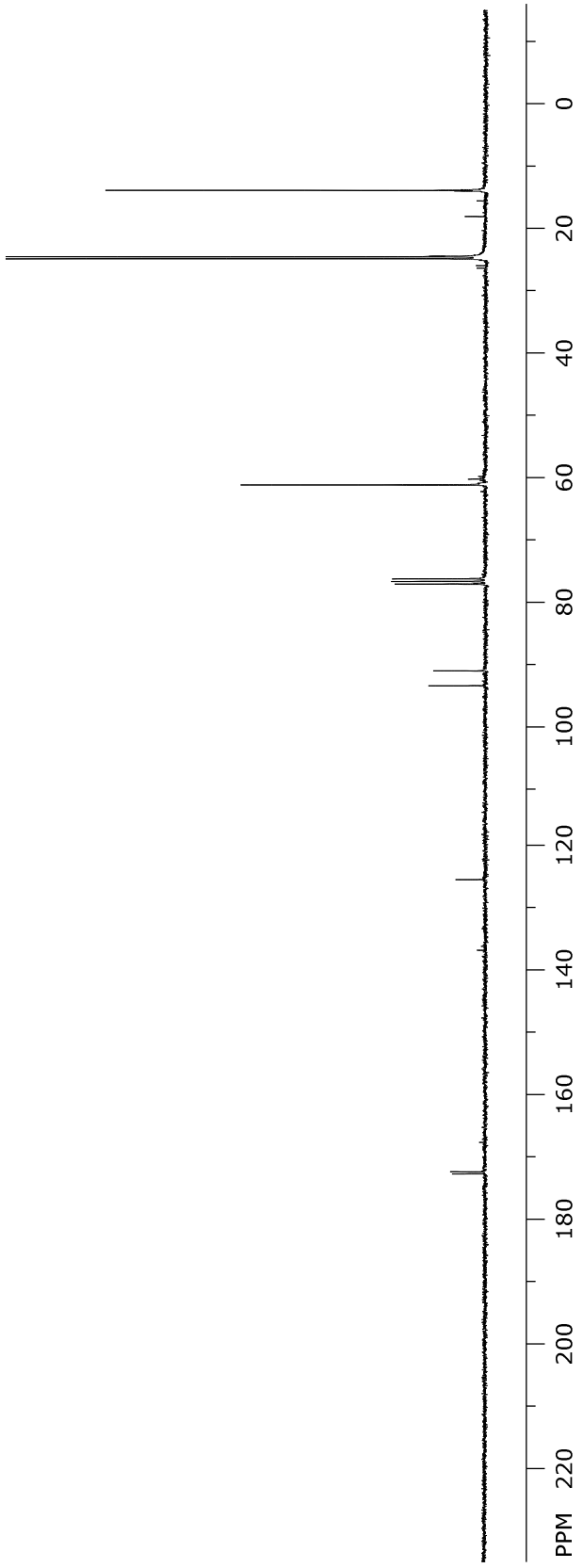

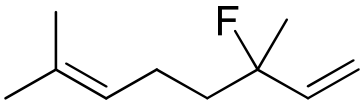
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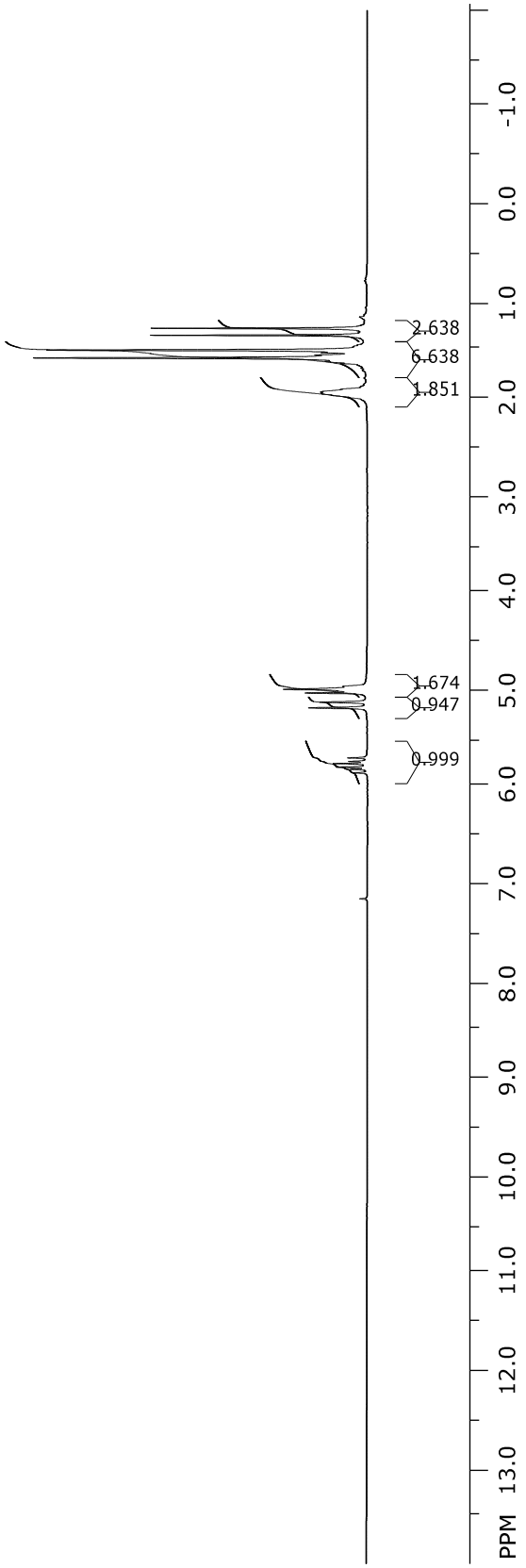
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0.947
0.999
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0.0
1.0
2.0
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5.0
6.0
7.0
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10.0
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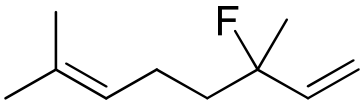
12.0
13.0
PPM



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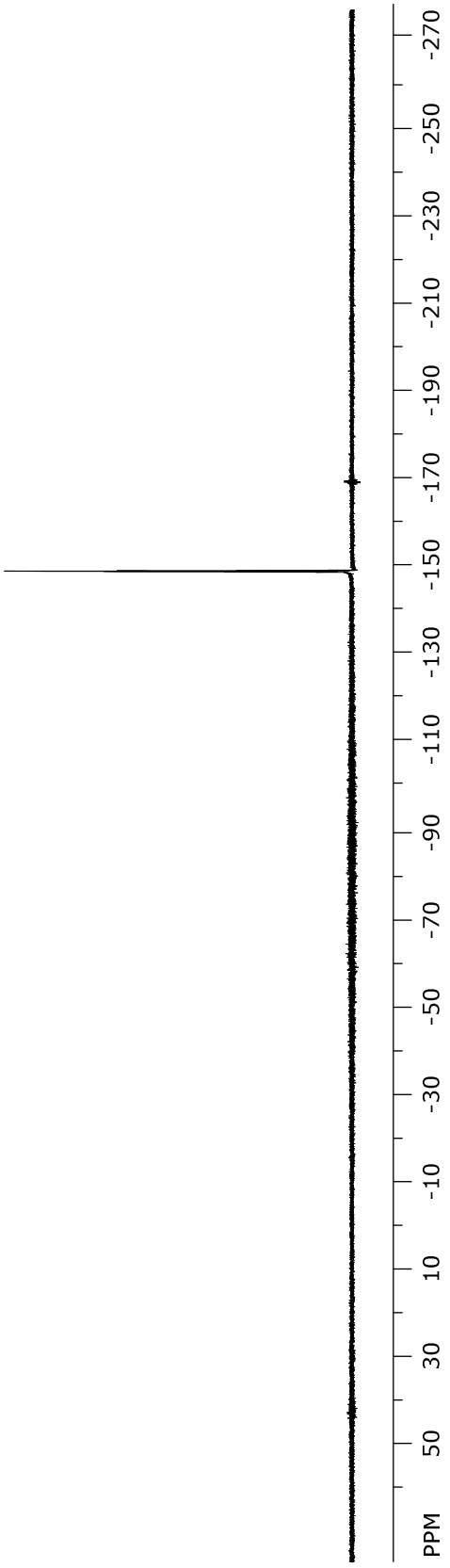

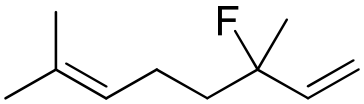

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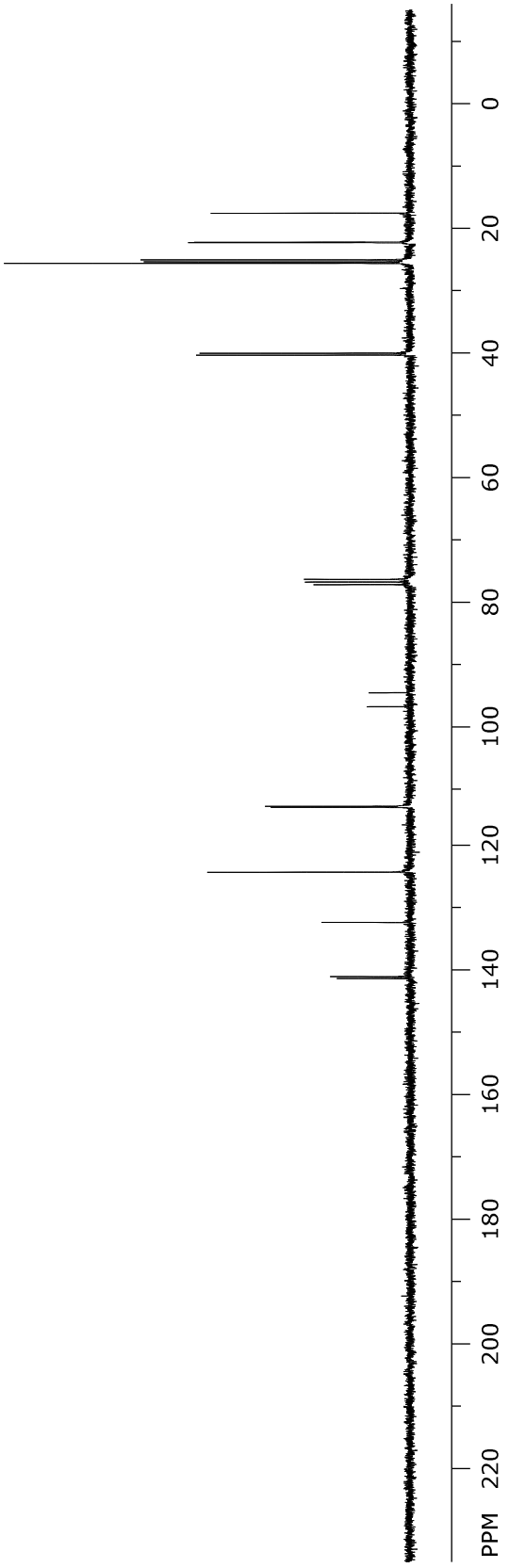

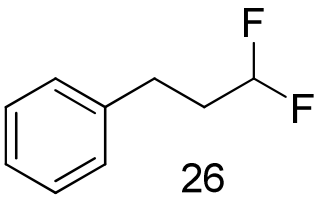
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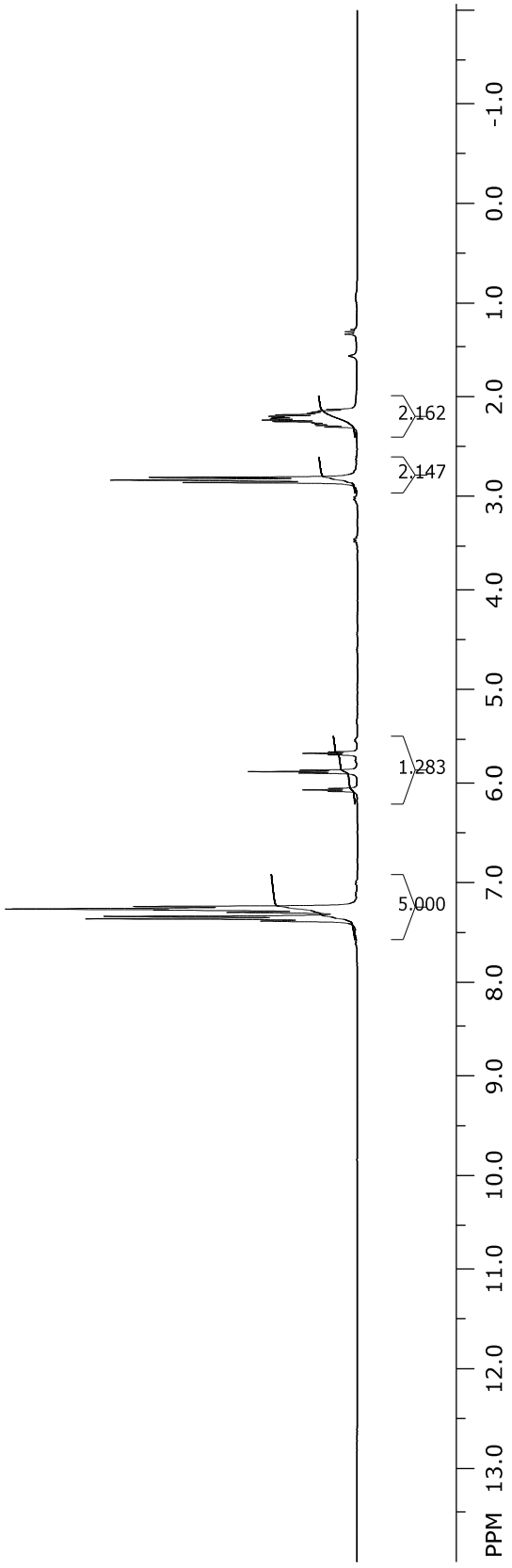
F

26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2.147
1.283
5.000
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0.0
1.0
2.0
3.0
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5.0
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7.0
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9.0
10.0
11.0
12.0
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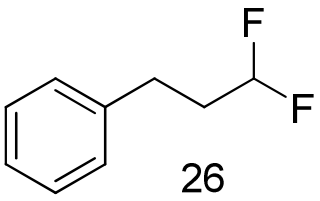
PPM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F

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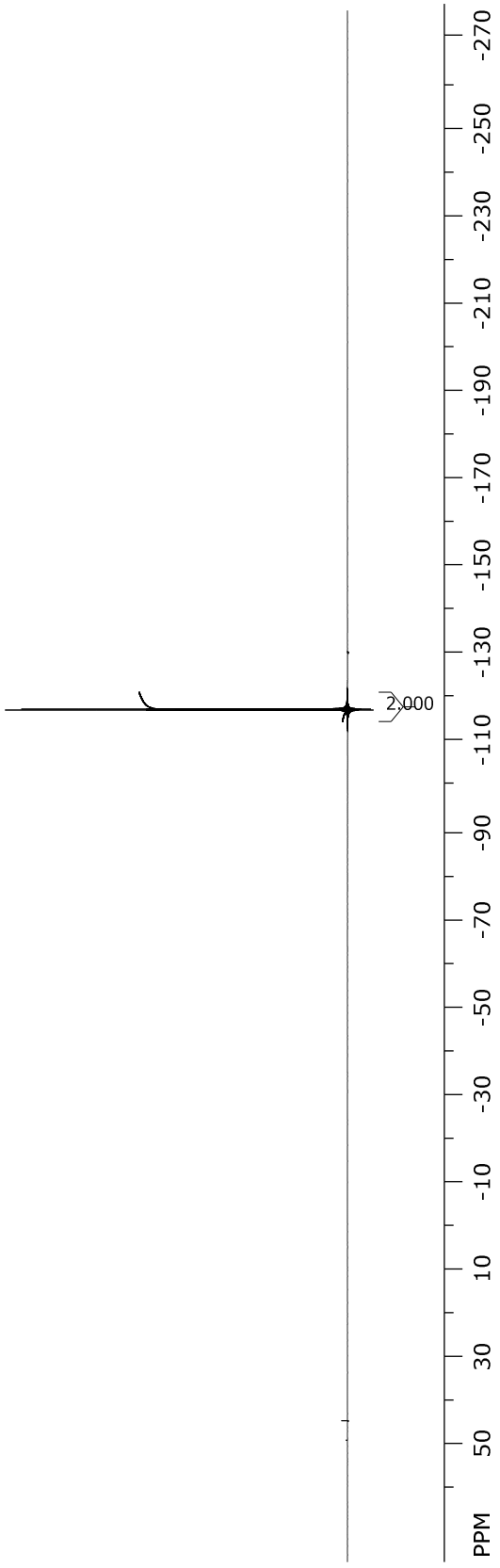
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-50
-30
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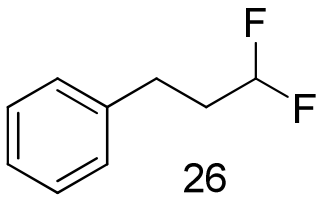
10
30
50
PPM



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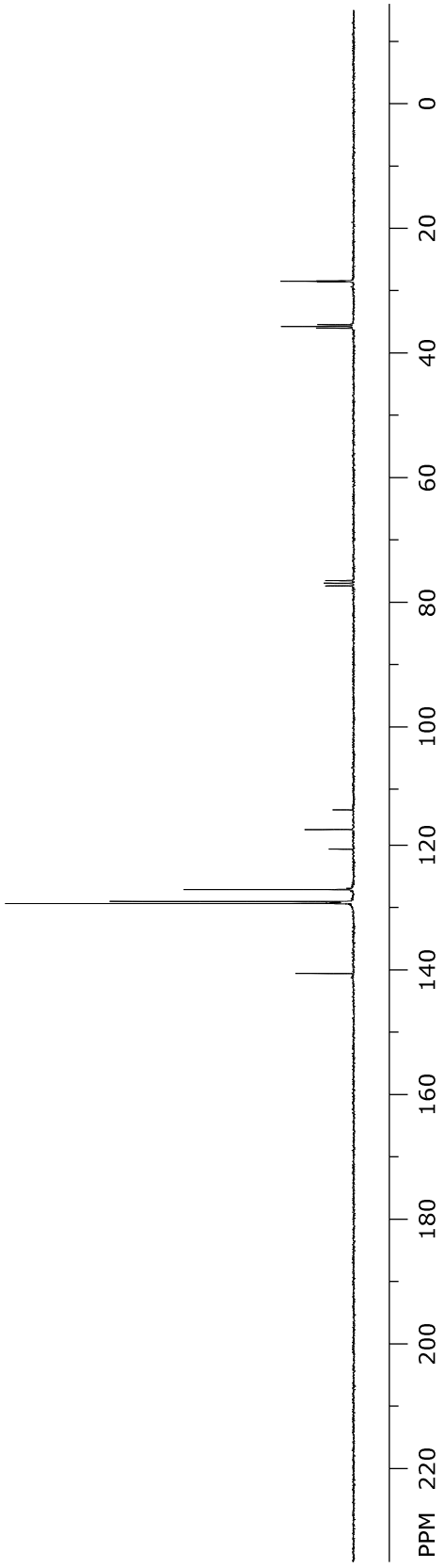
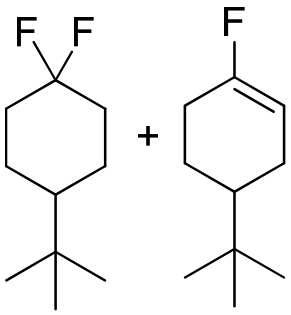
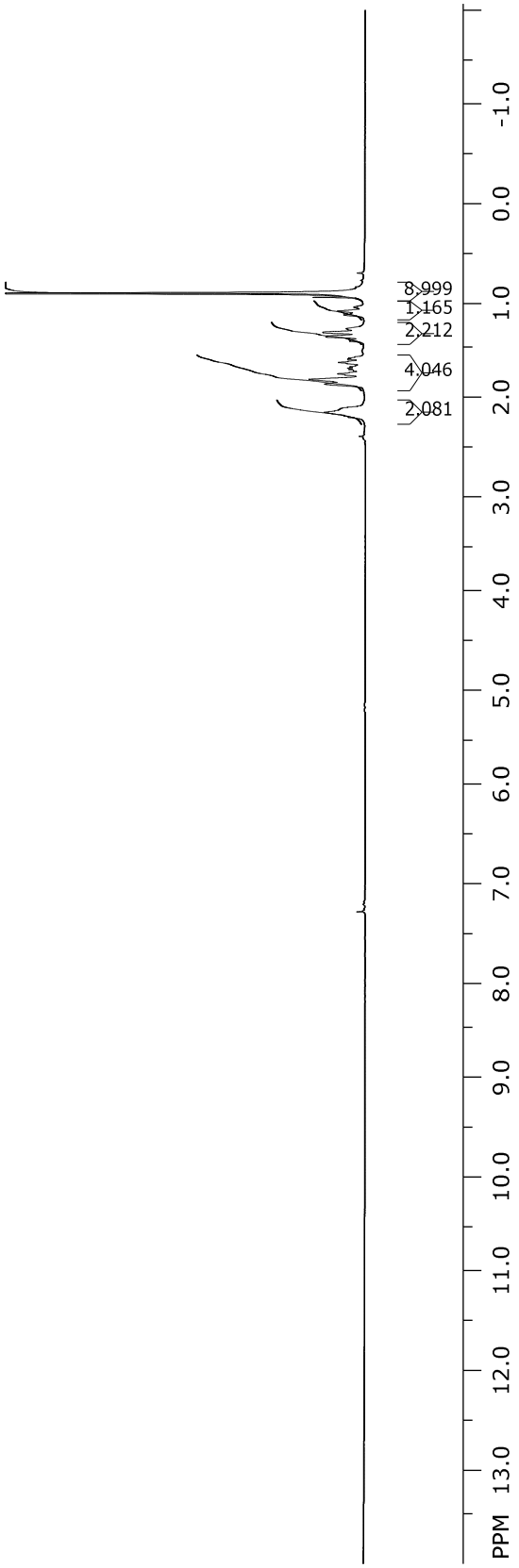



F
F
+
F

28


8.999
1.165
2.212
4.046
2.081
-1.0
0.0
1.0
2.0
3.0
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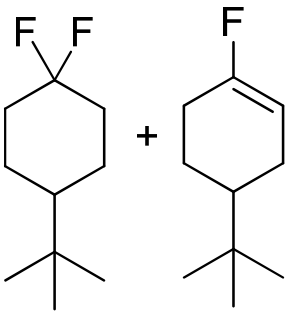
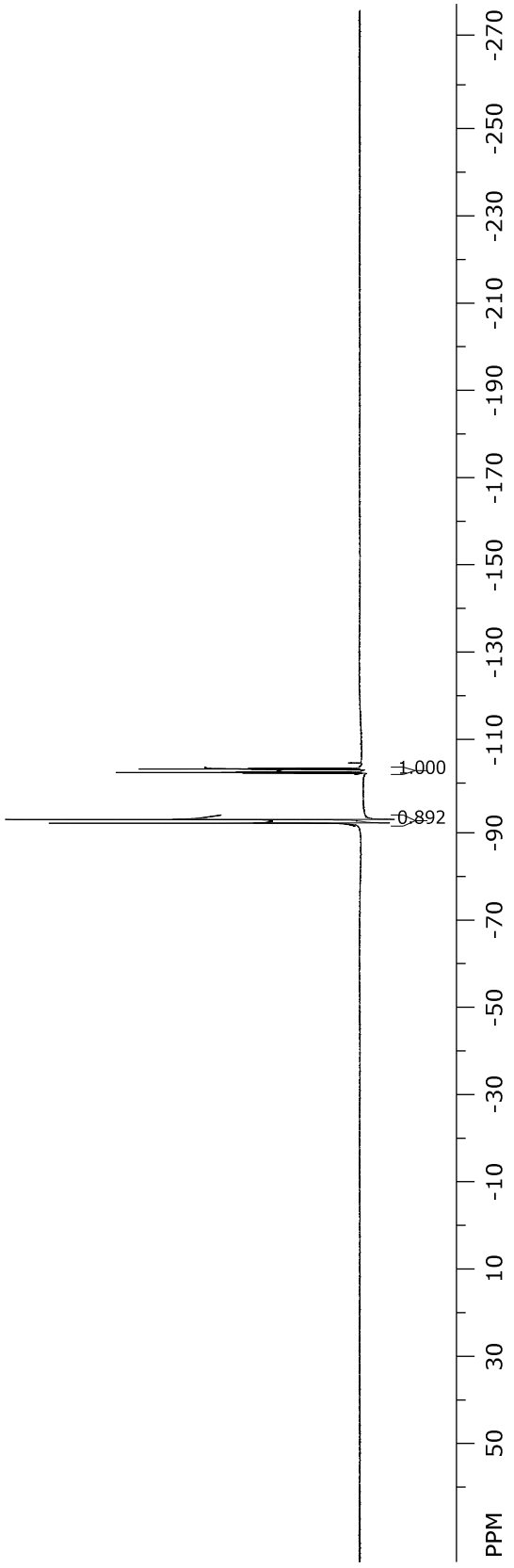
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
PPM


F F
F
+

28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0.892
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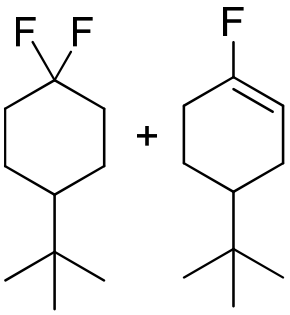
-150
-130
-110
-90
-70
-50
-30
-10
10
30
50
PPM



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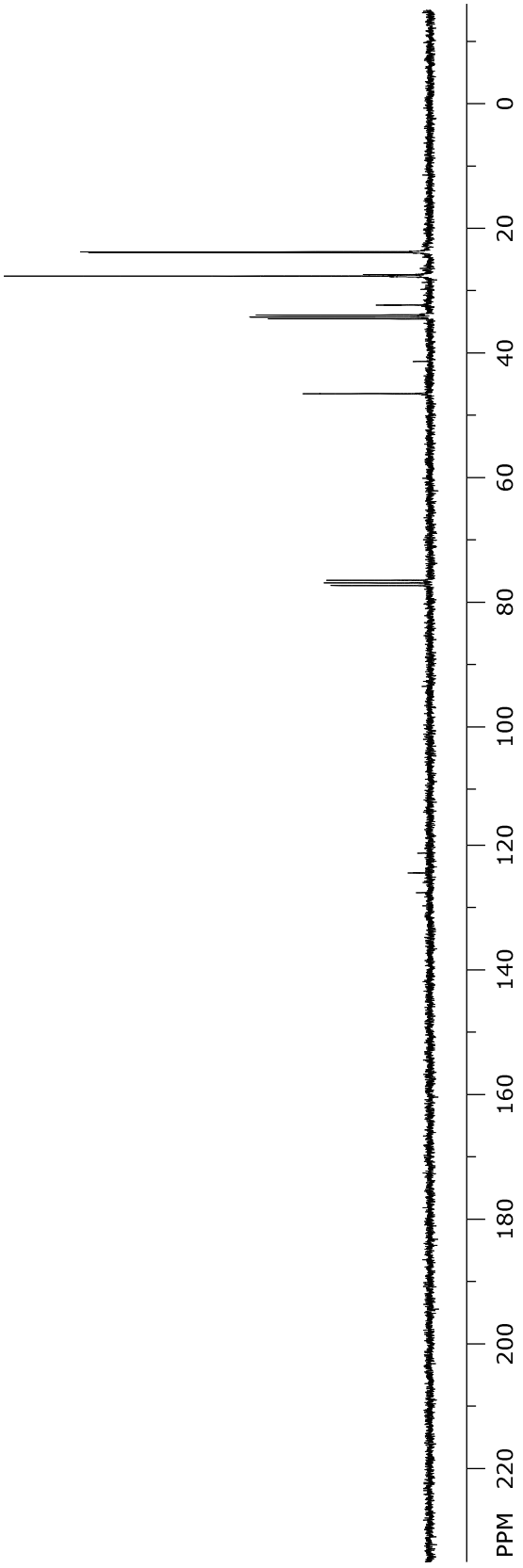
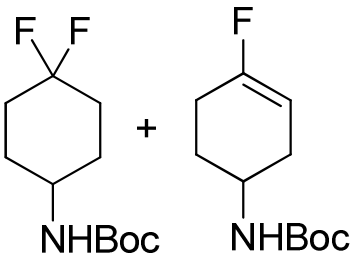
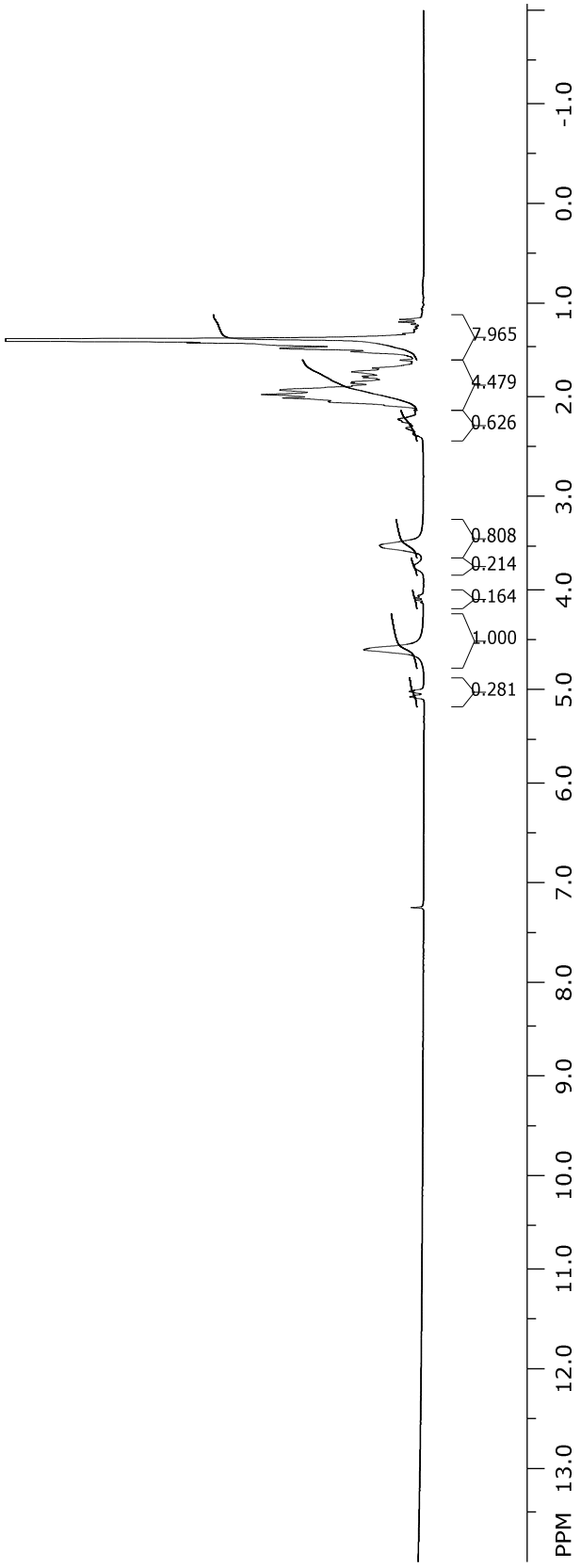



F F
+
F
NHBoc
NHBoc

30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4.479
0.626
0.808
0.214
0.164
1.000
0.281
-1.0
0.0
1.0
2.0
3.0
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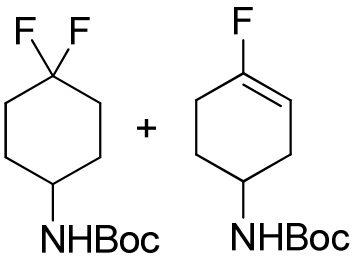
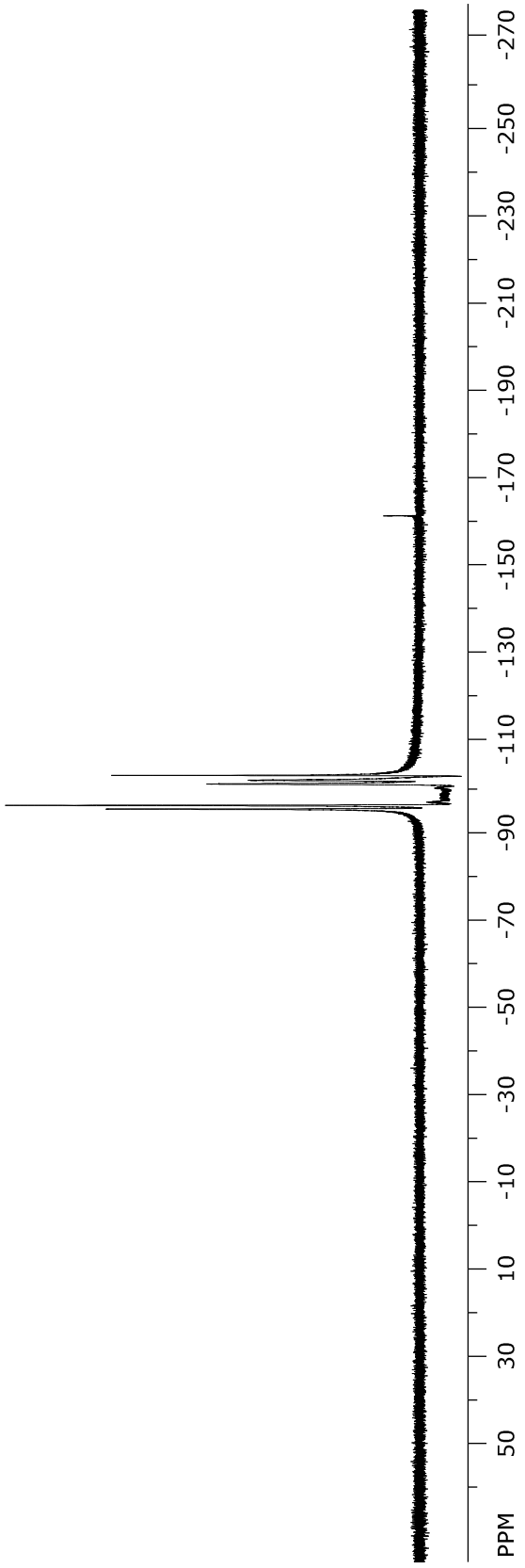
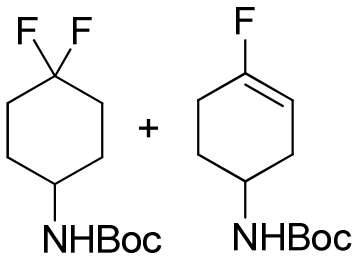
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
PPM


F F
+
F
NHBoc
NHBoc

30


-270
-250
-230
-210
-190
-170
-150
-130
-110
-90
-70
-50
-30
-10
10
30
50
PPM



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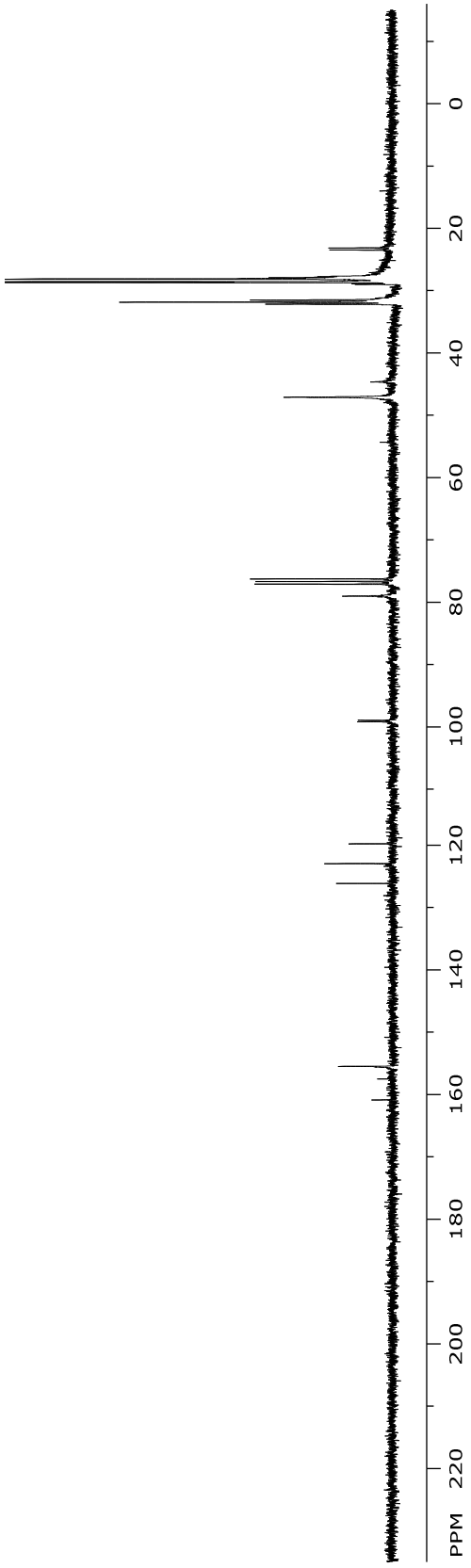
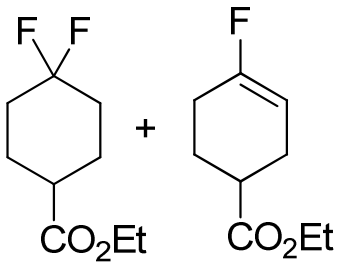
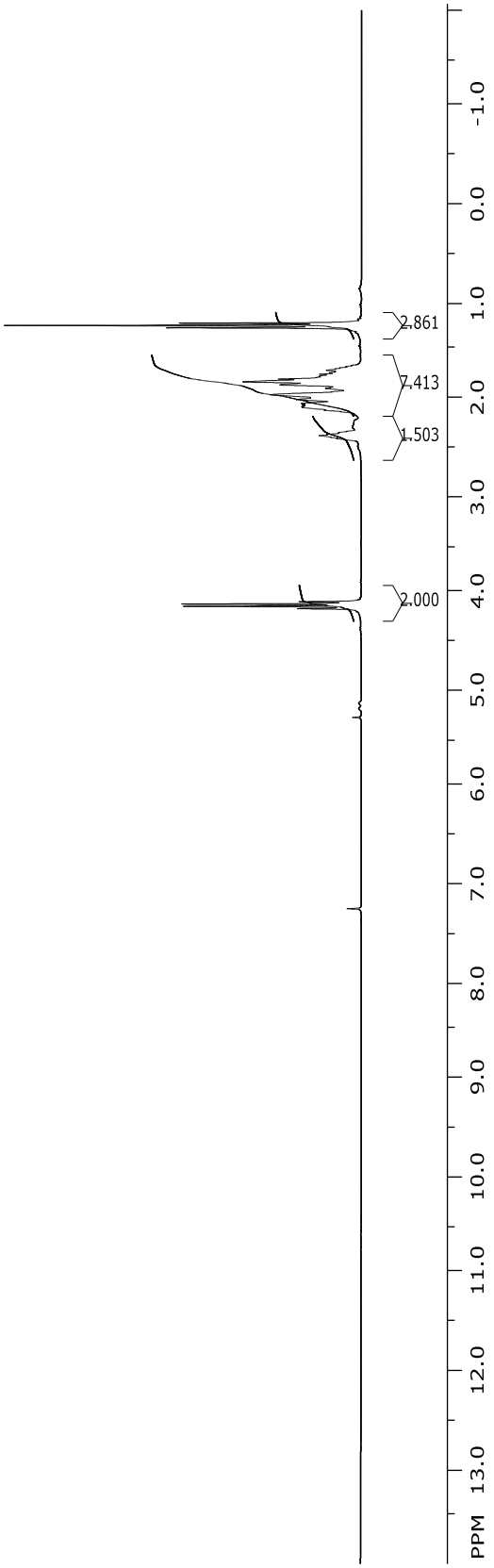



F F
+
F
CO2Et
CO2Et

32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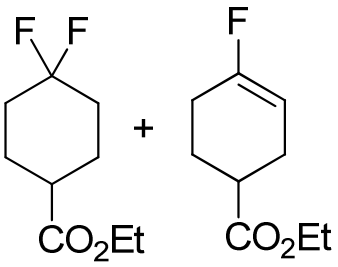
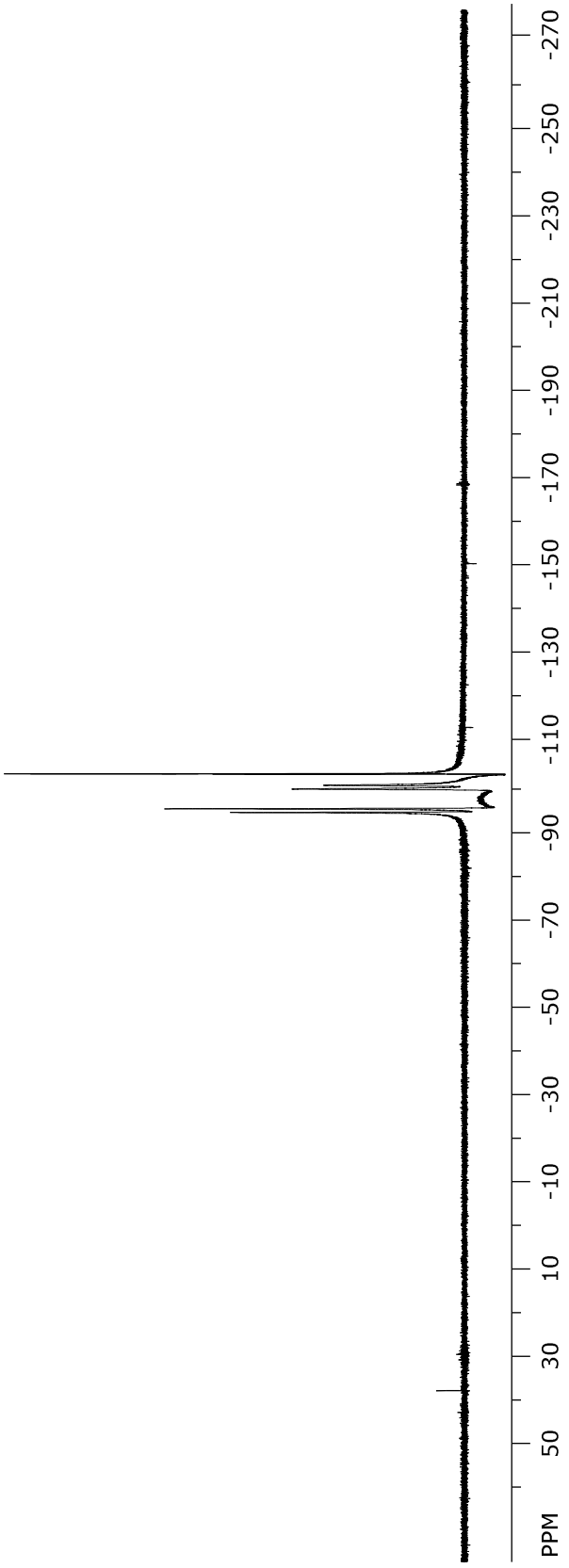
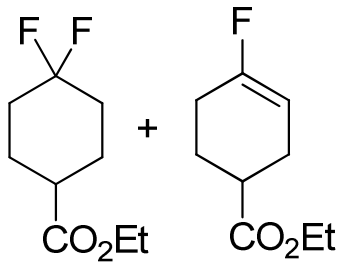
7.413
1.503
2.000
-1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
PPM

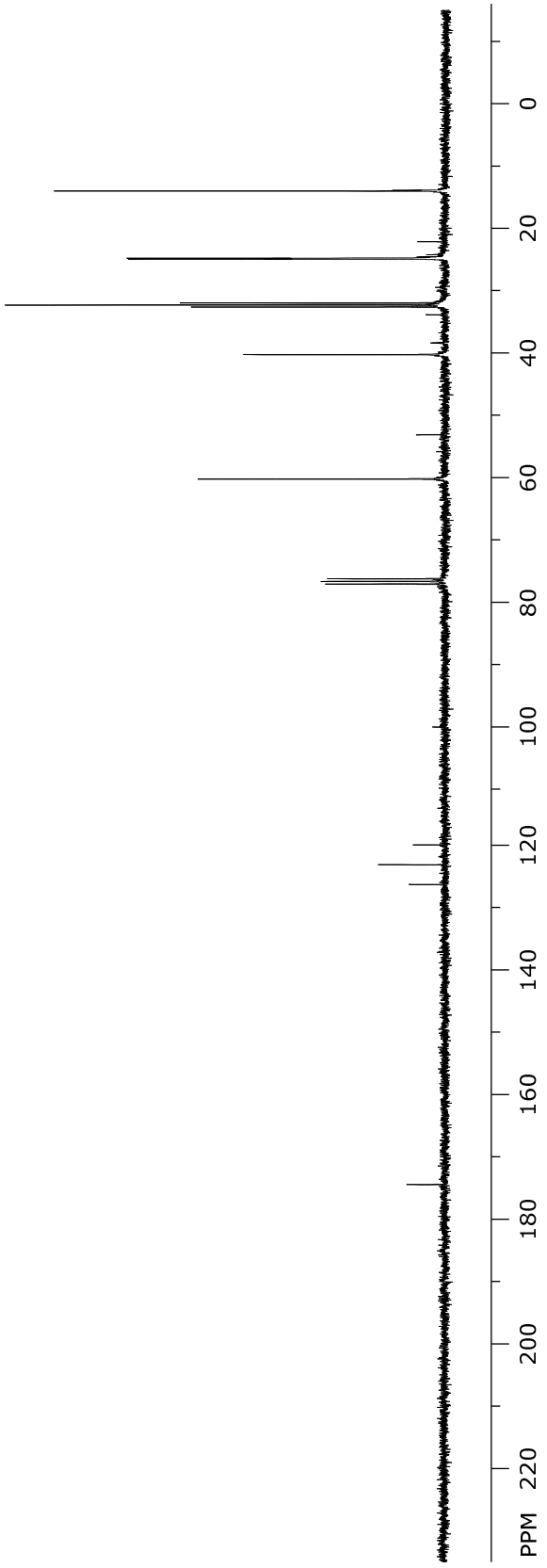

F F
+
F
CO2Et
CO2Et

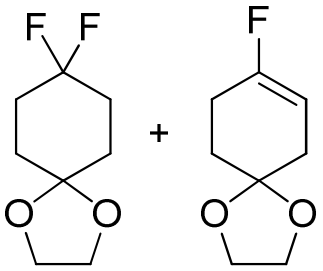
32


-270
-250
-230
-210
-190
-170
-150
-130
-110
-90
-70
-50
-30
-10
10
30
50
PPM

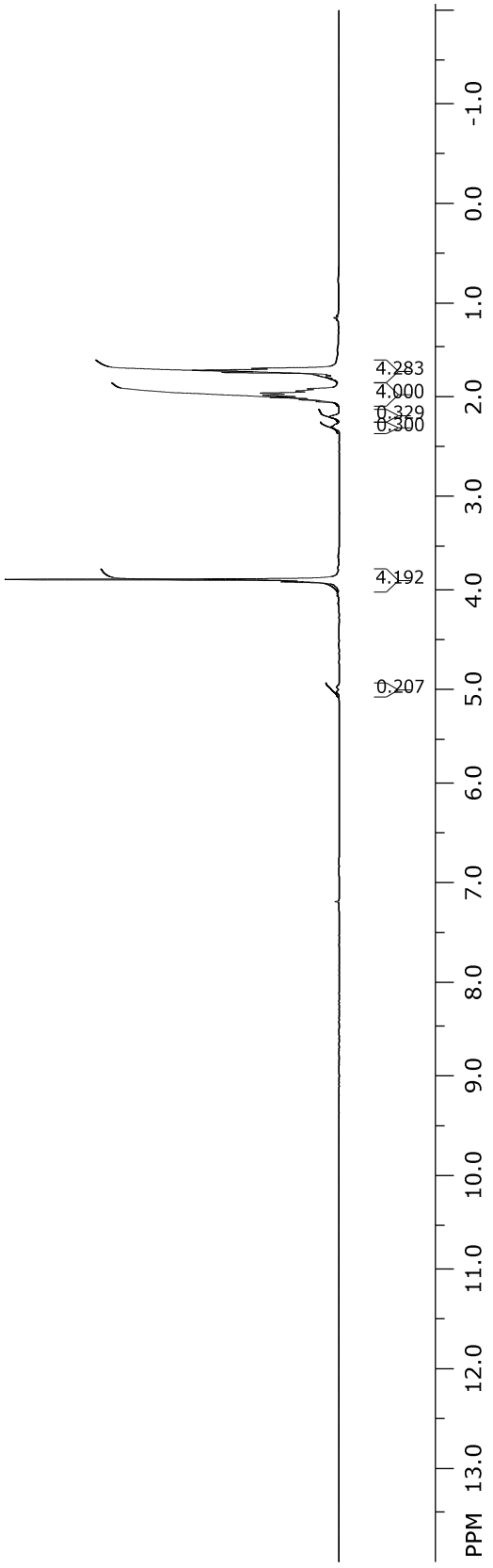


32




F
F
F
O
O
O
O

34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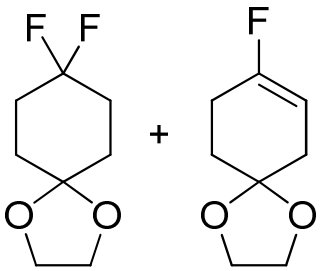
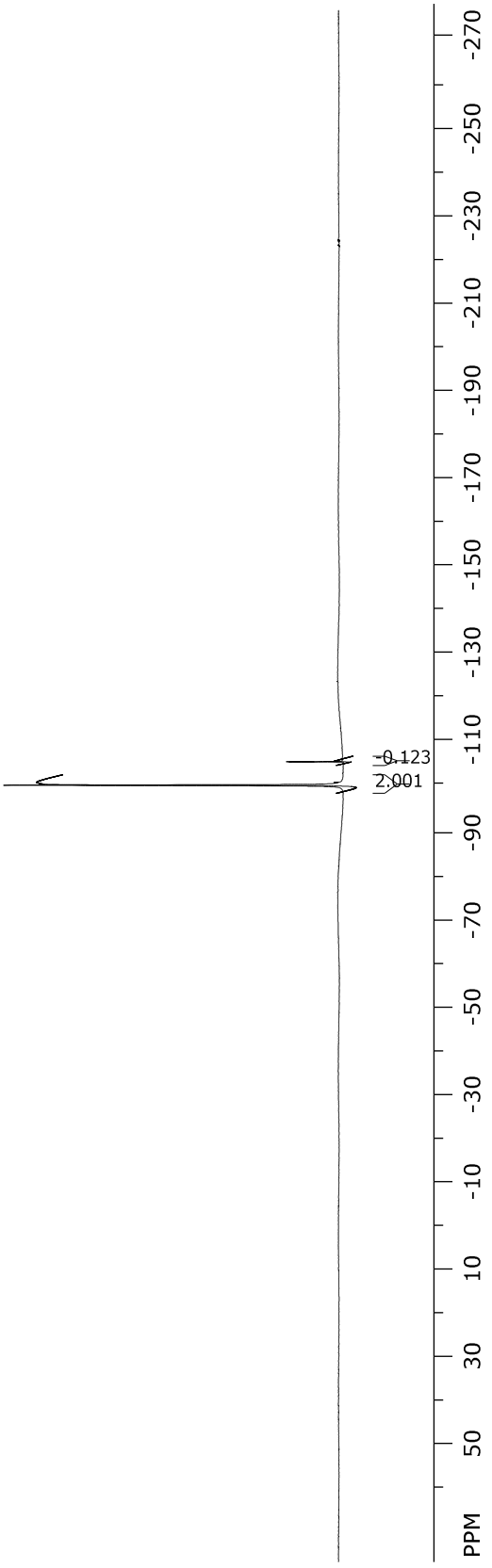
4.192
0.207
-1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
PPM


F
F
F
O
O
O
O

34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-270
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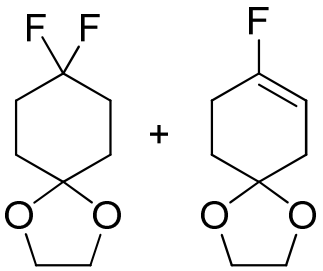
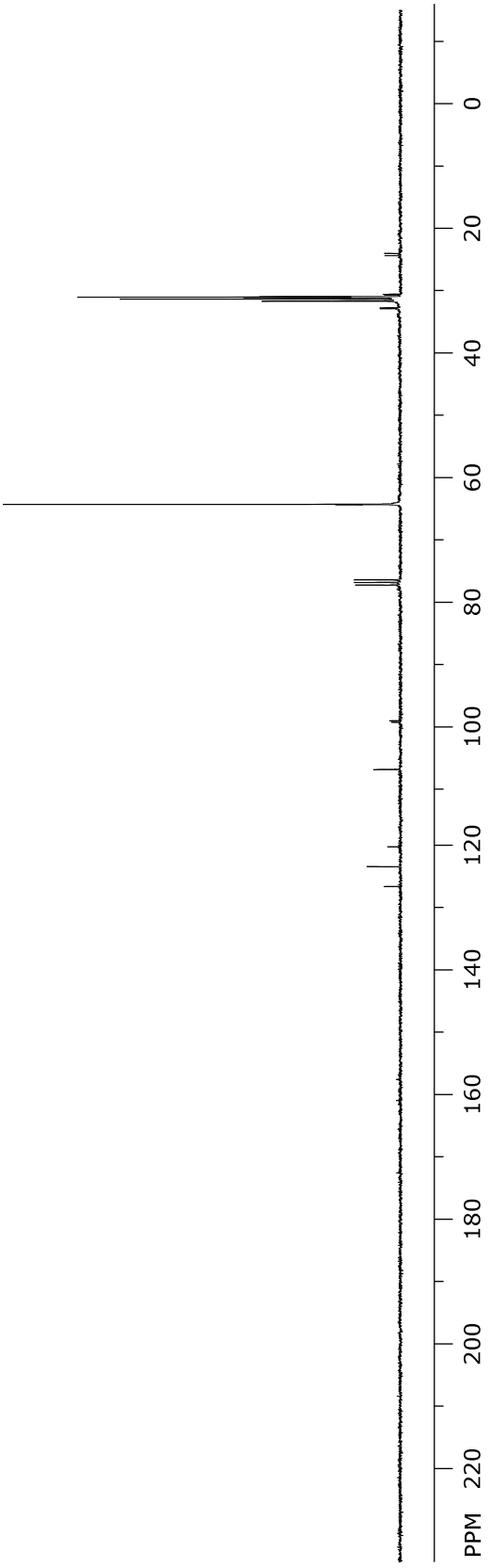
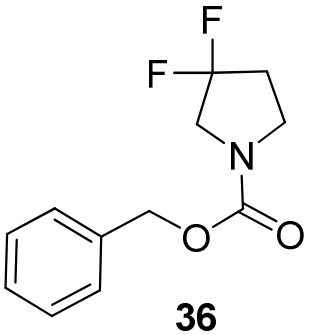
-190
-170
-150
-130
-110
-90
-70
-50
-30
-10
10
30
50
PPM

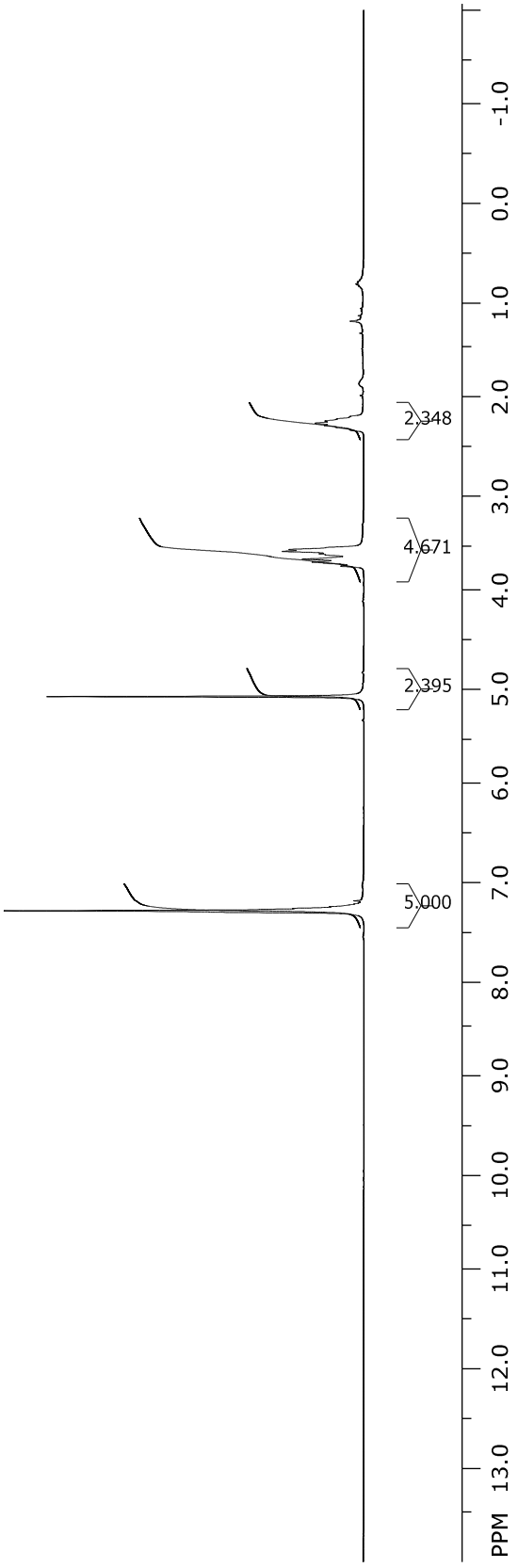


34




F
F
N
O
O

36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4.671
2.395
5.000
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1.0
2.0
3.0
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5.0
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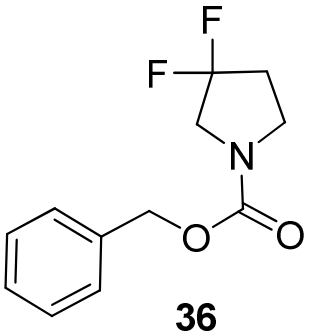
10.0
11.0
12.0
13.0
PPM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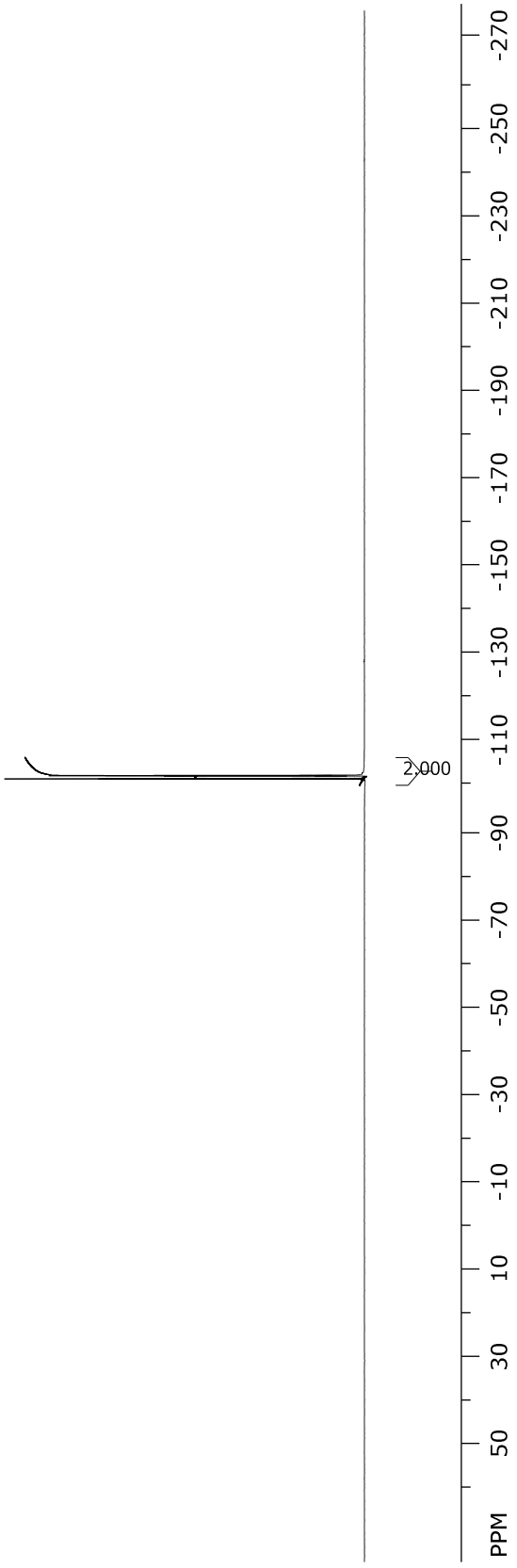
F
N
O
O

36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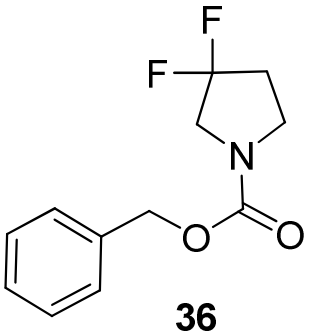
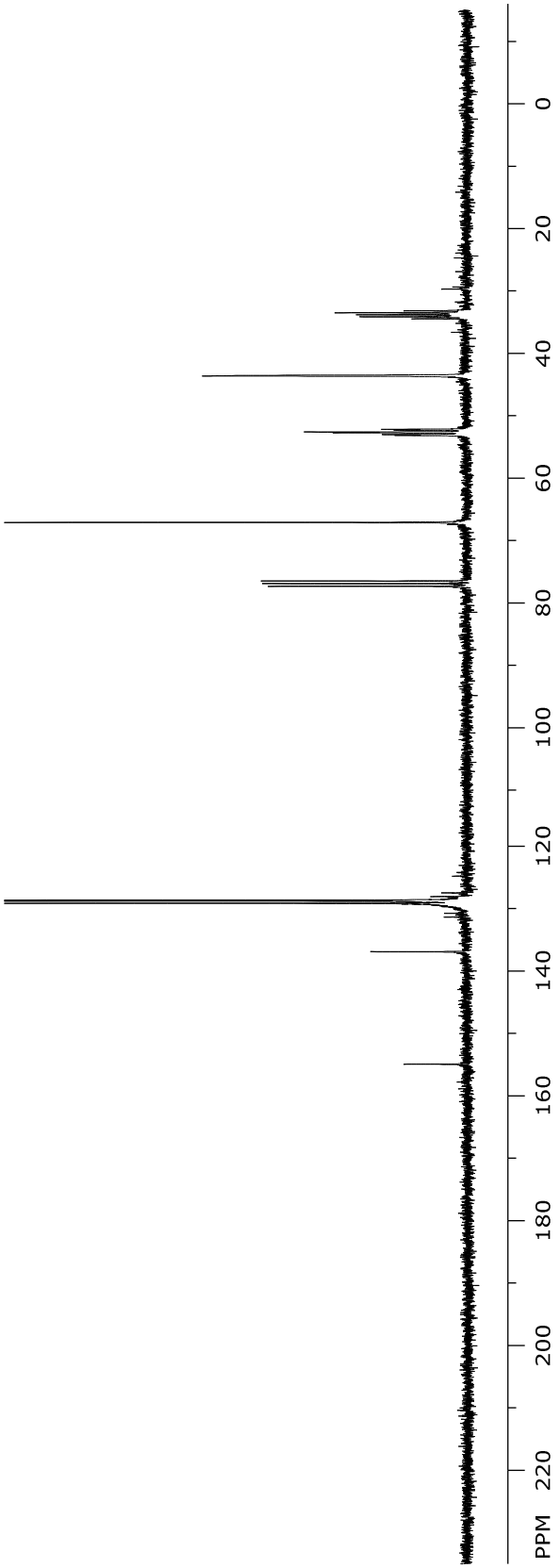
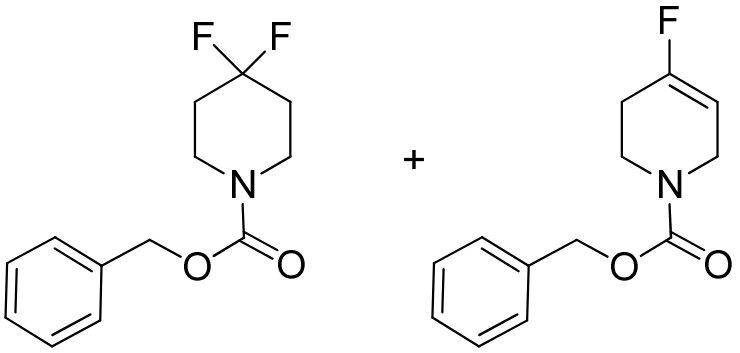
-90
-70
-50
-30
-10
10
30
50
PPM

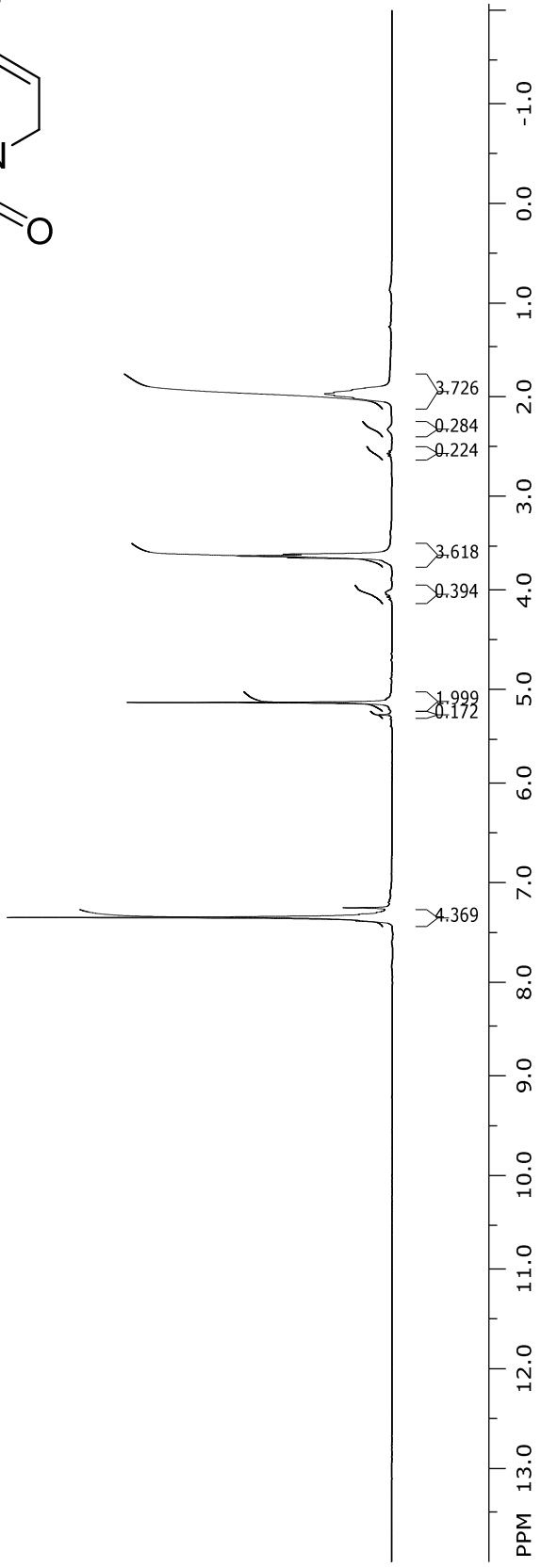


36




F
F
N
O
O
+
F
N
O
O

38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0.394
1.999
0.172
4.369
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0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
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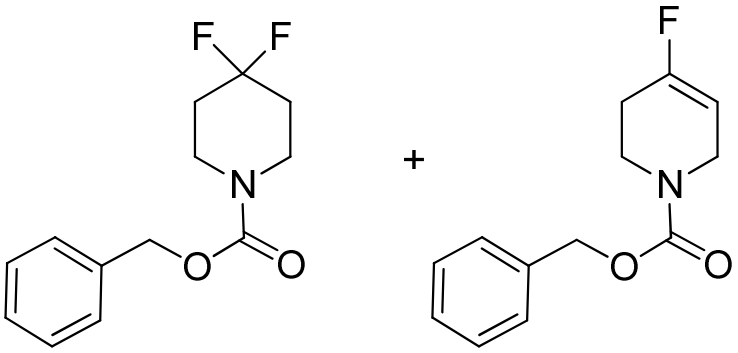
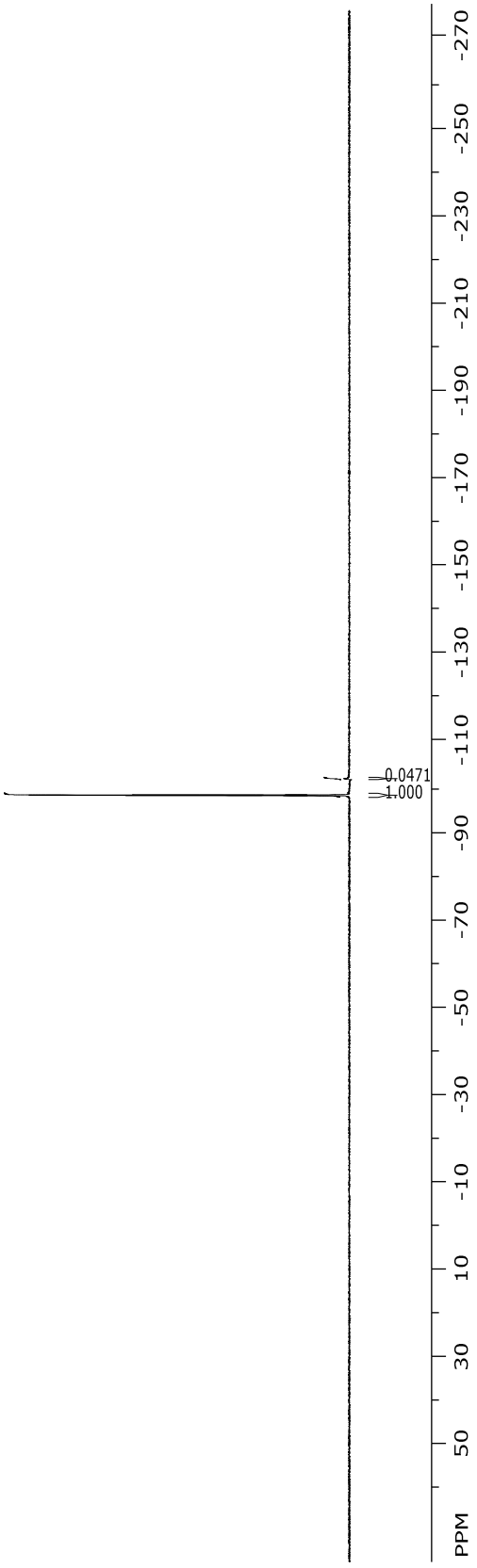
13.0
PPM


F
F
N
O
O
+
F
N
O
O

38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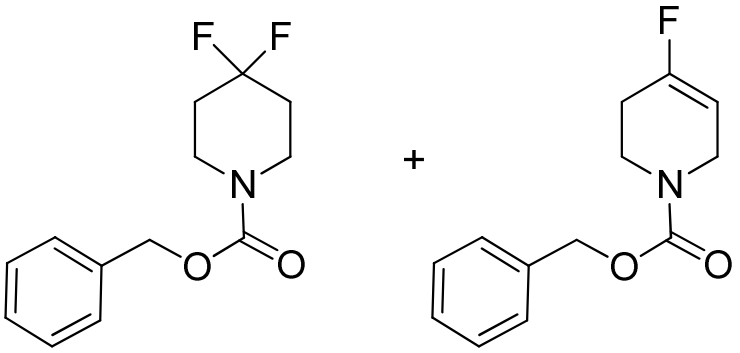
-130
-110
-90
-70
-50
-30
-10
10
30
50
PPM



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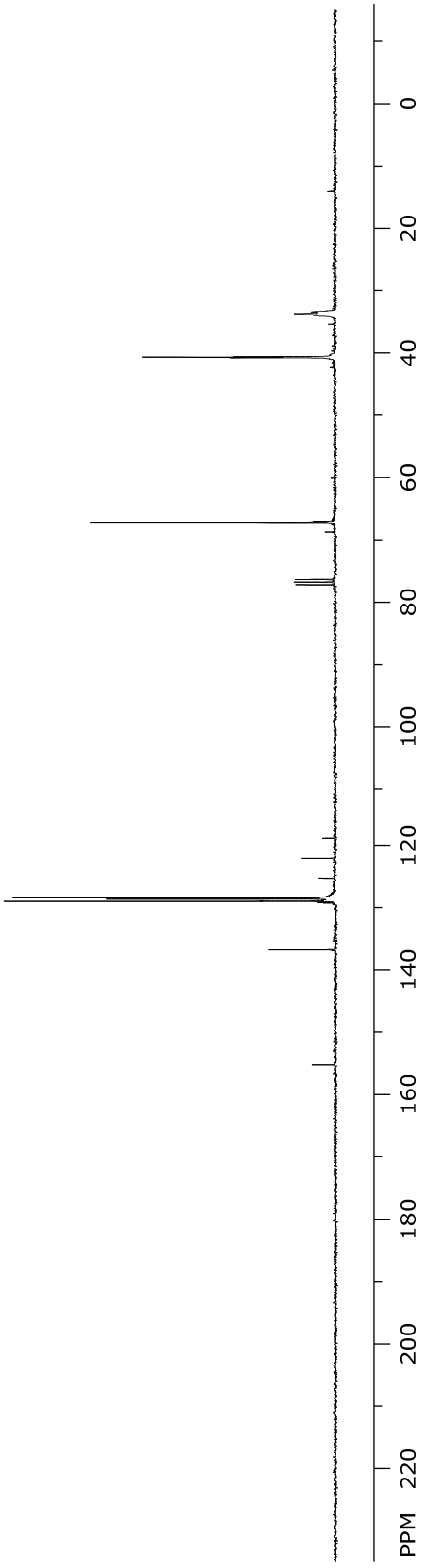

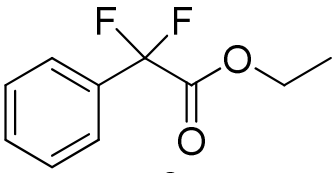
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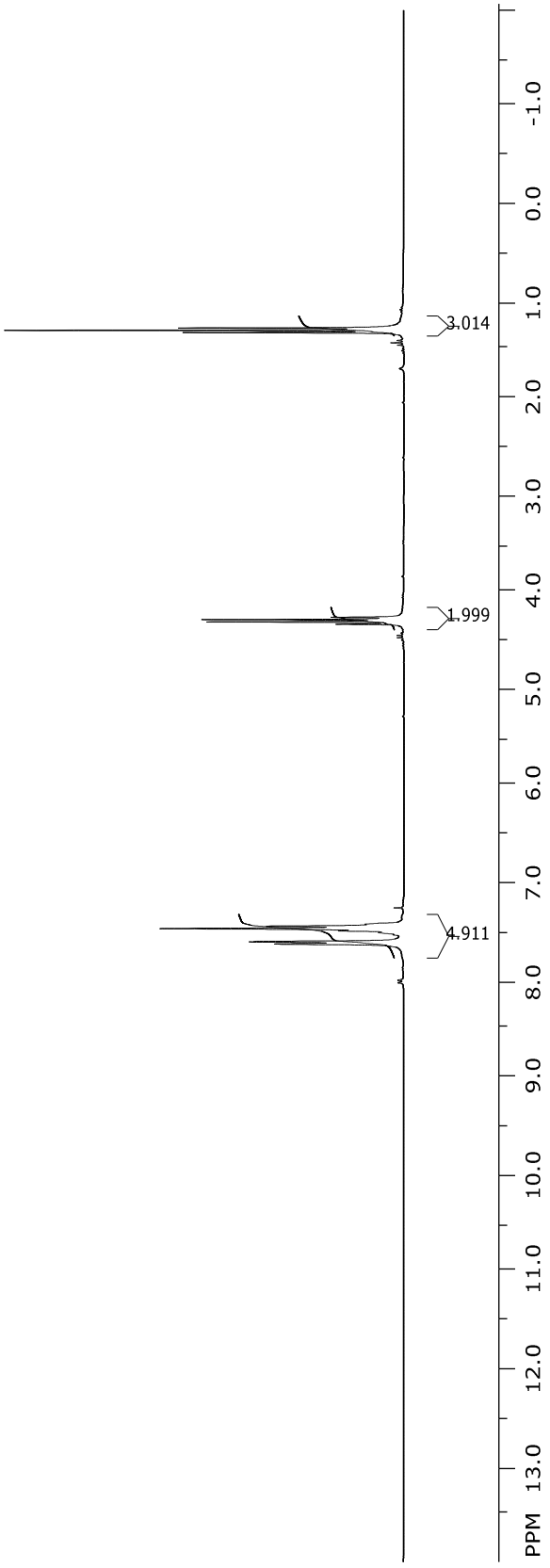
O

40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10.0
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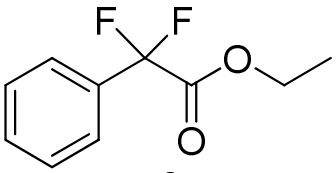
PPM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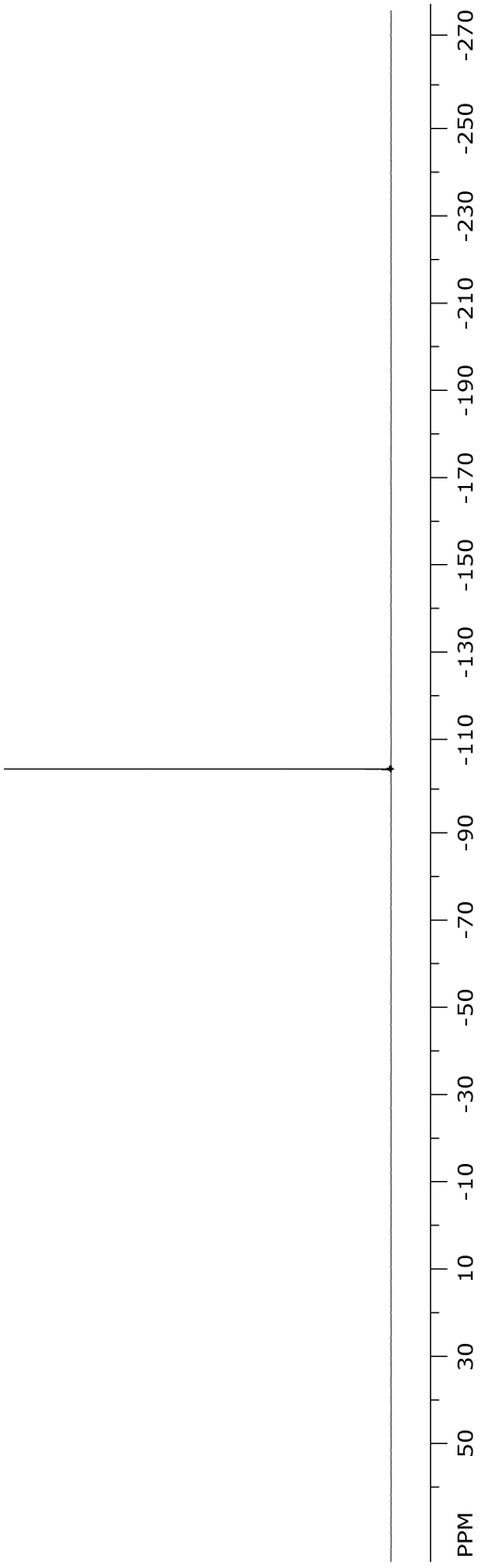
PPM
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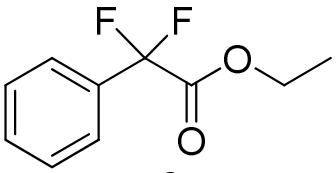

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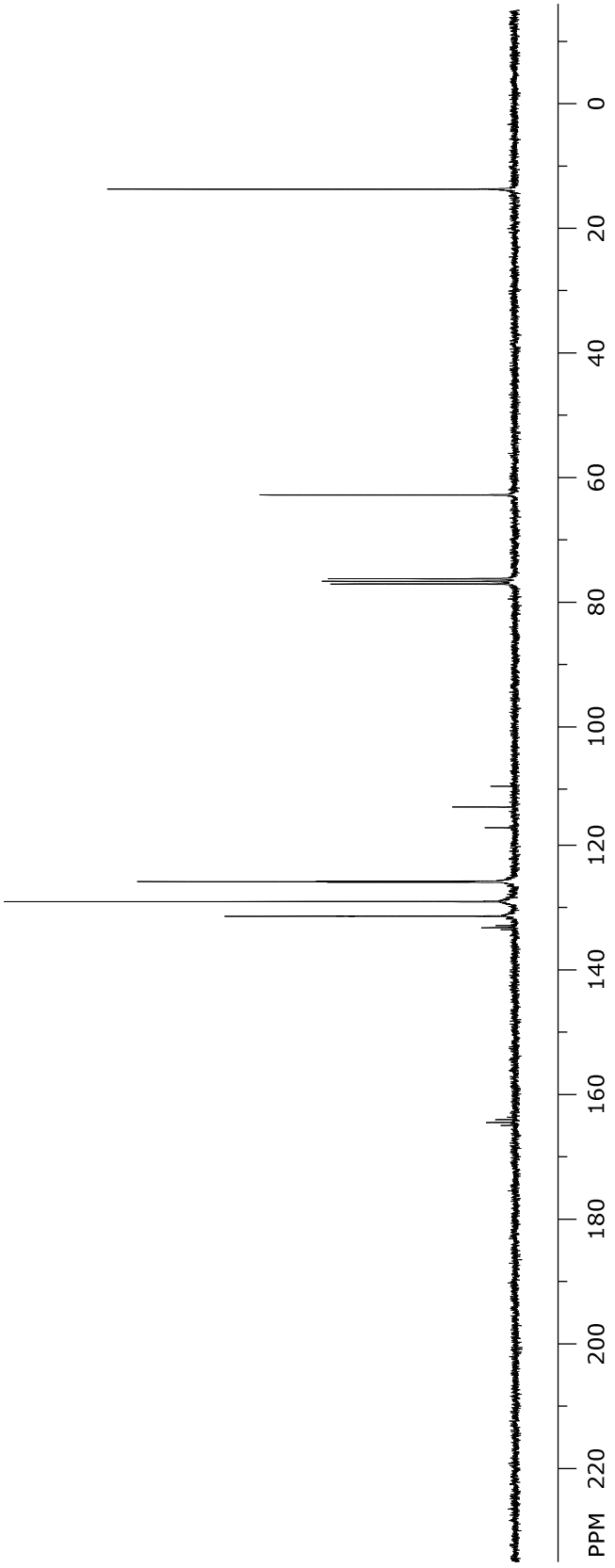

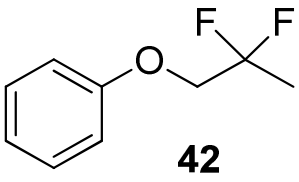
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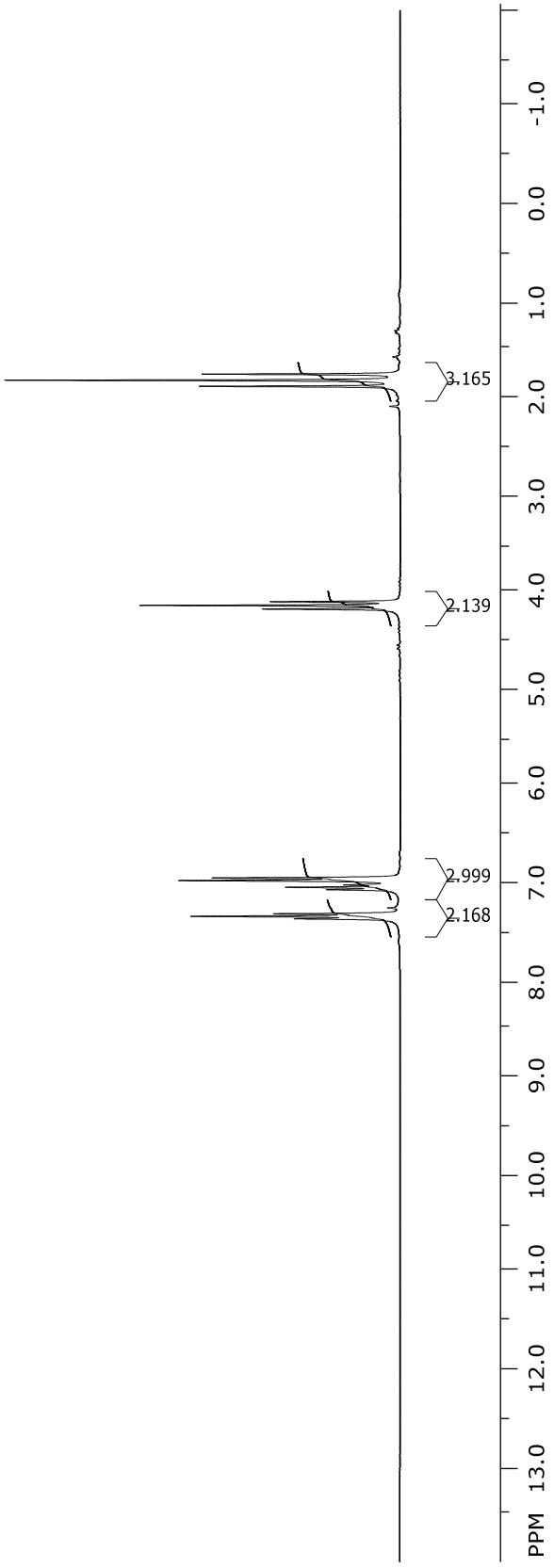
42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2.139
2.999
2.168
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0.0
1.0
2.0
3.0
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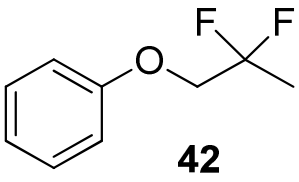
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
PPM



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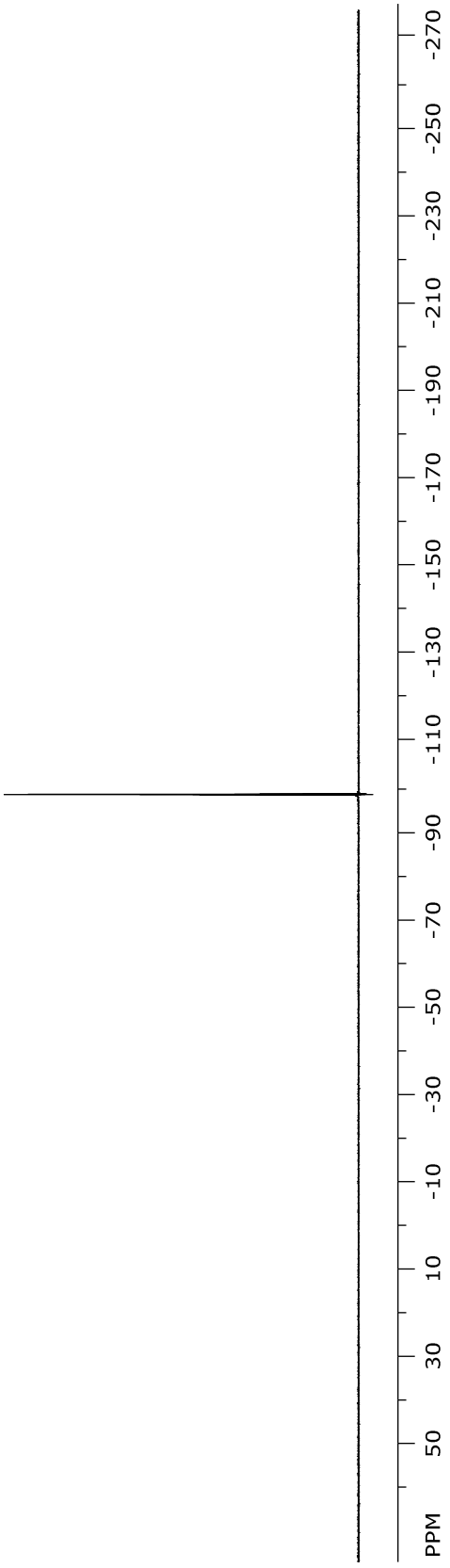

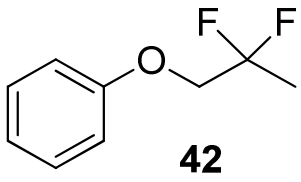

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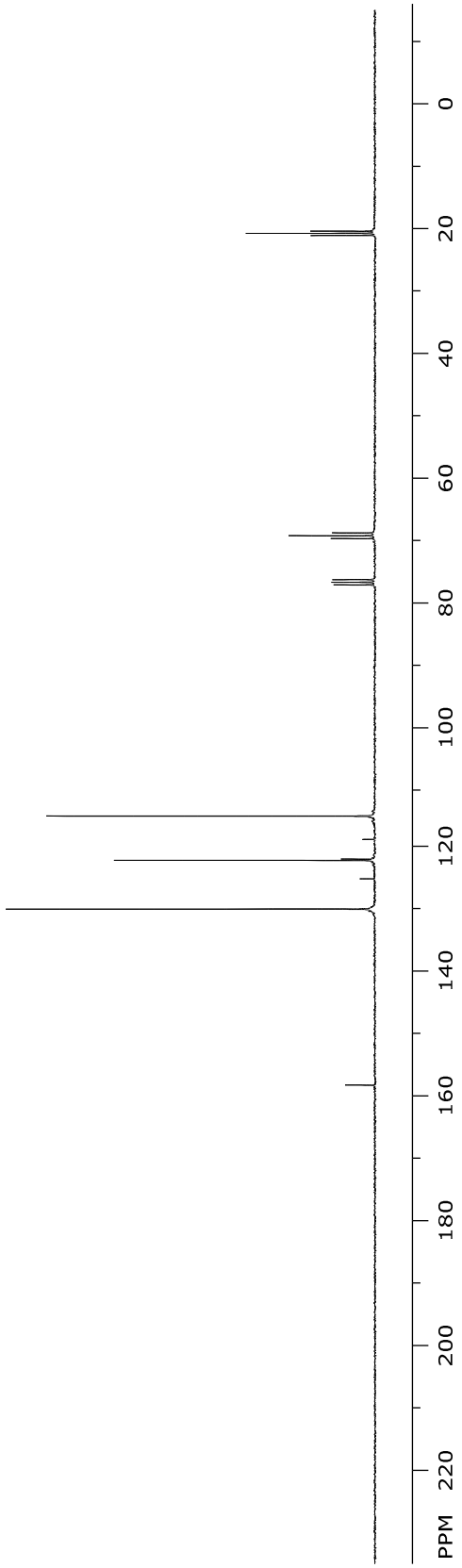

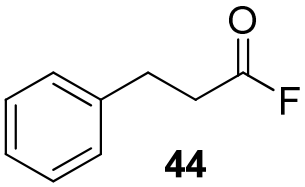
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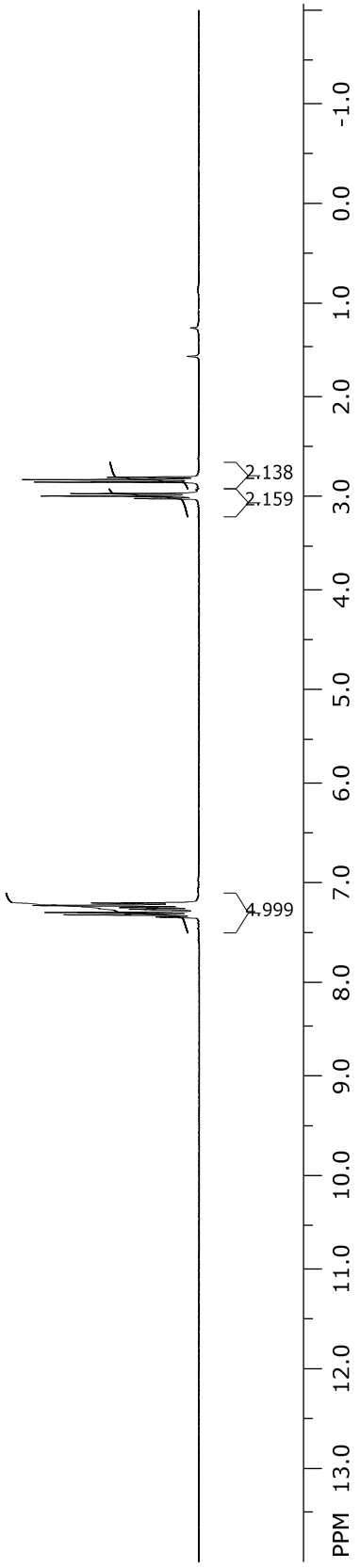
44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2.0
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10.0
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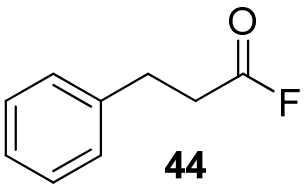
PPM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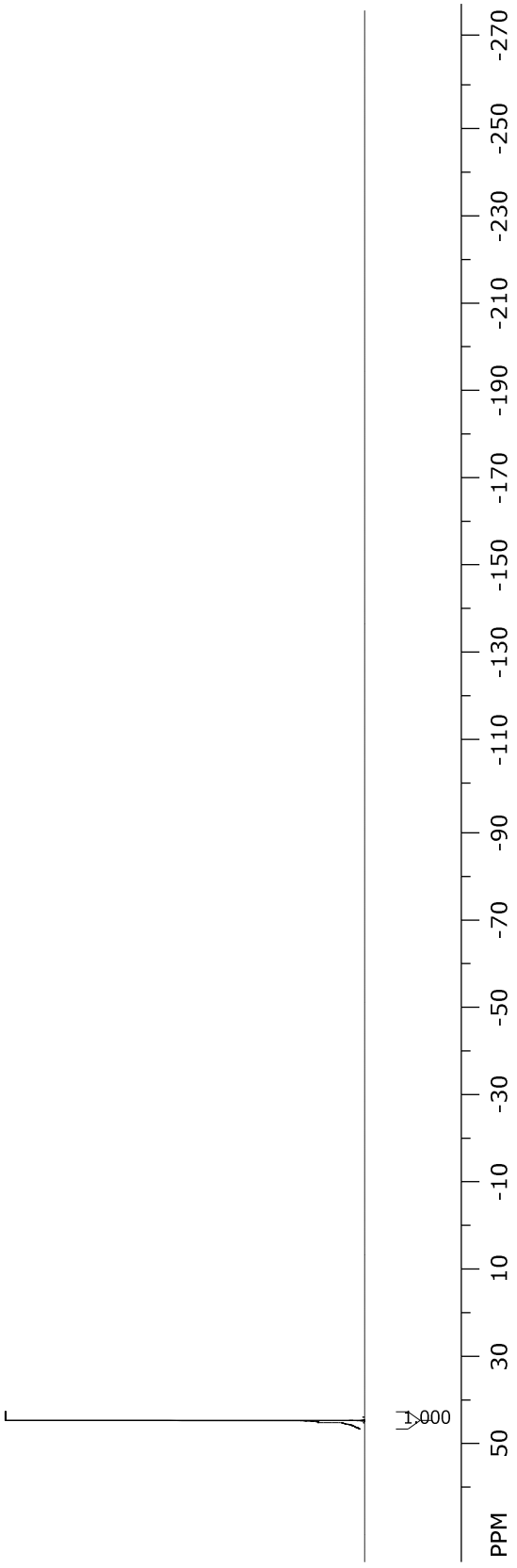
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-250
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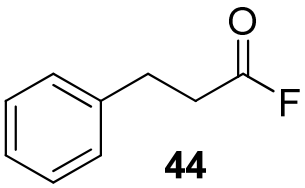
PPM



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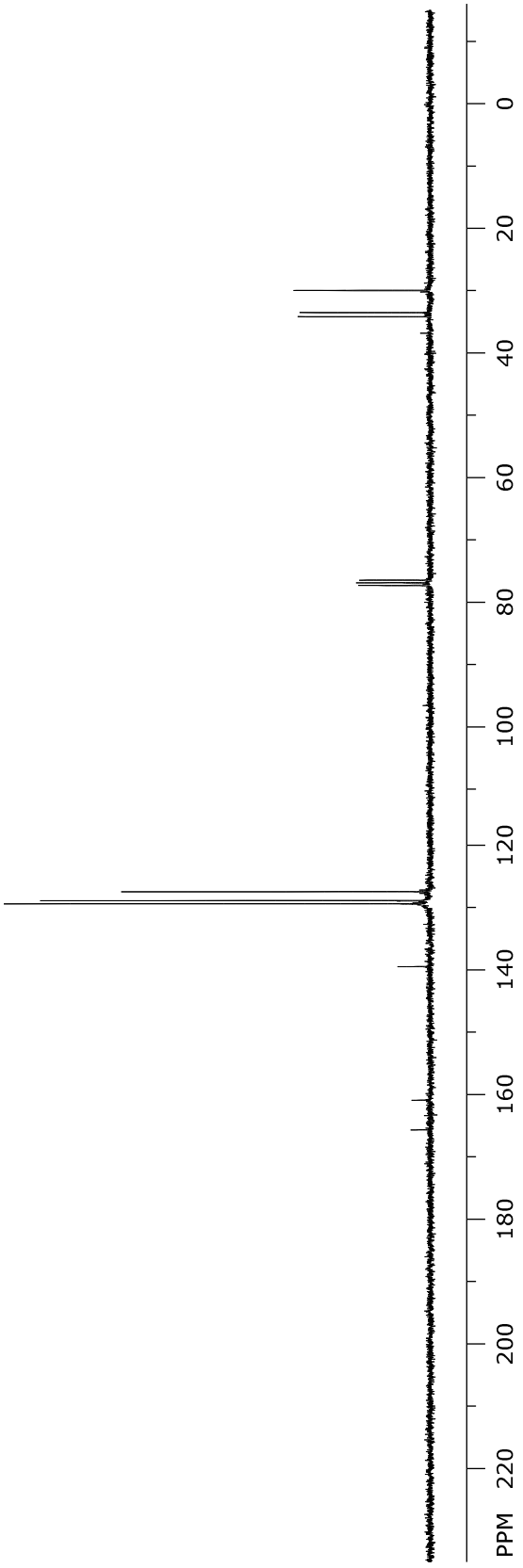

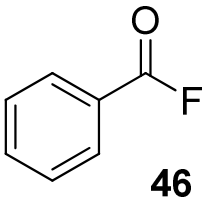
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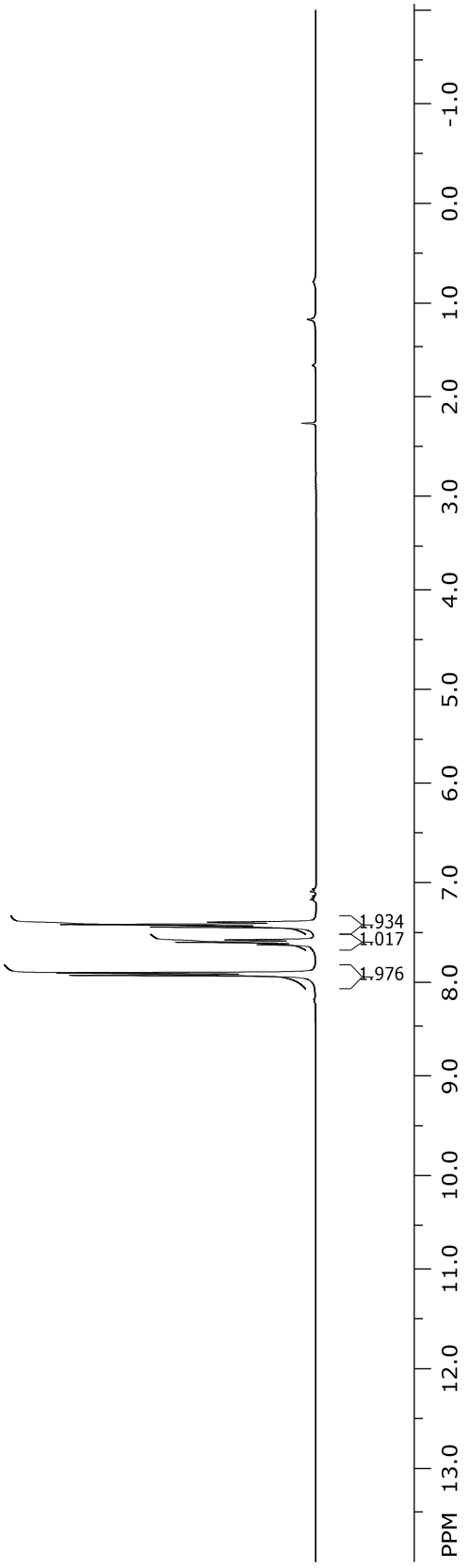
F

46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1.976
13.0
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11.0
10.0
9.0
8.0
7.0
6.0
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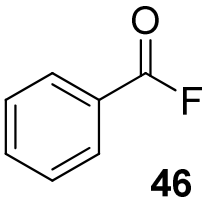
4.0
3.0
2.0
1.0
0.0
-1.0
PPM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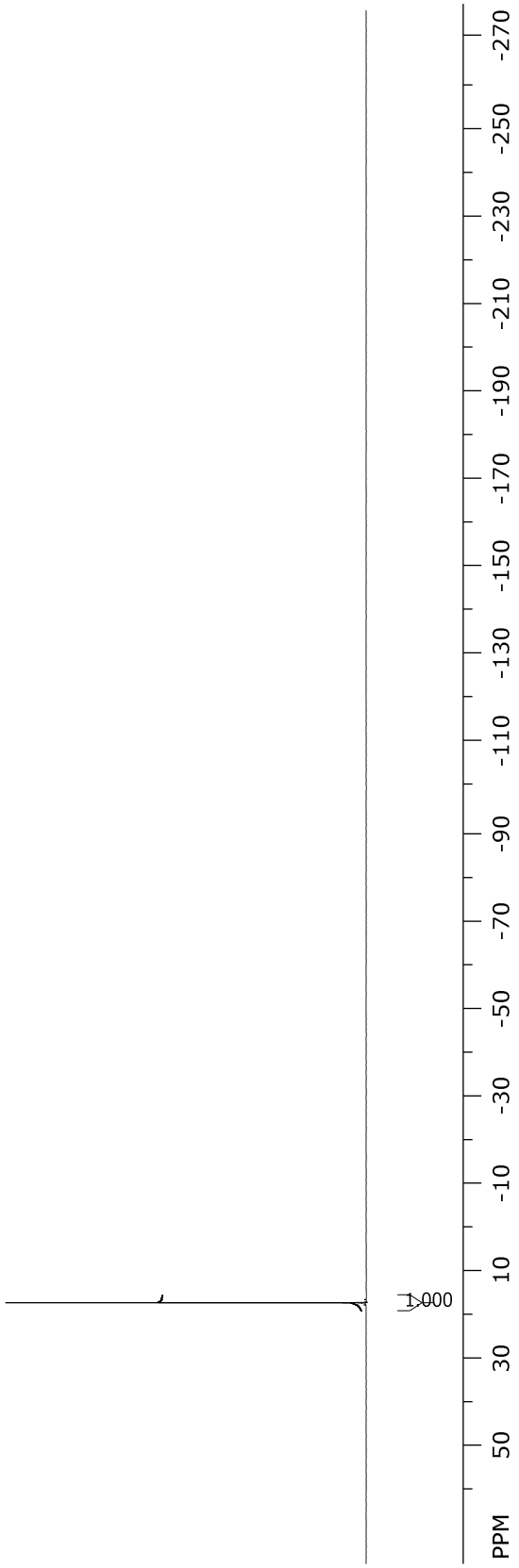
F

46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PPM
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-10
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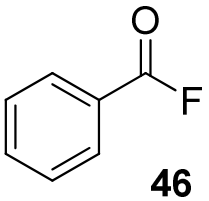
-230
-250
-270



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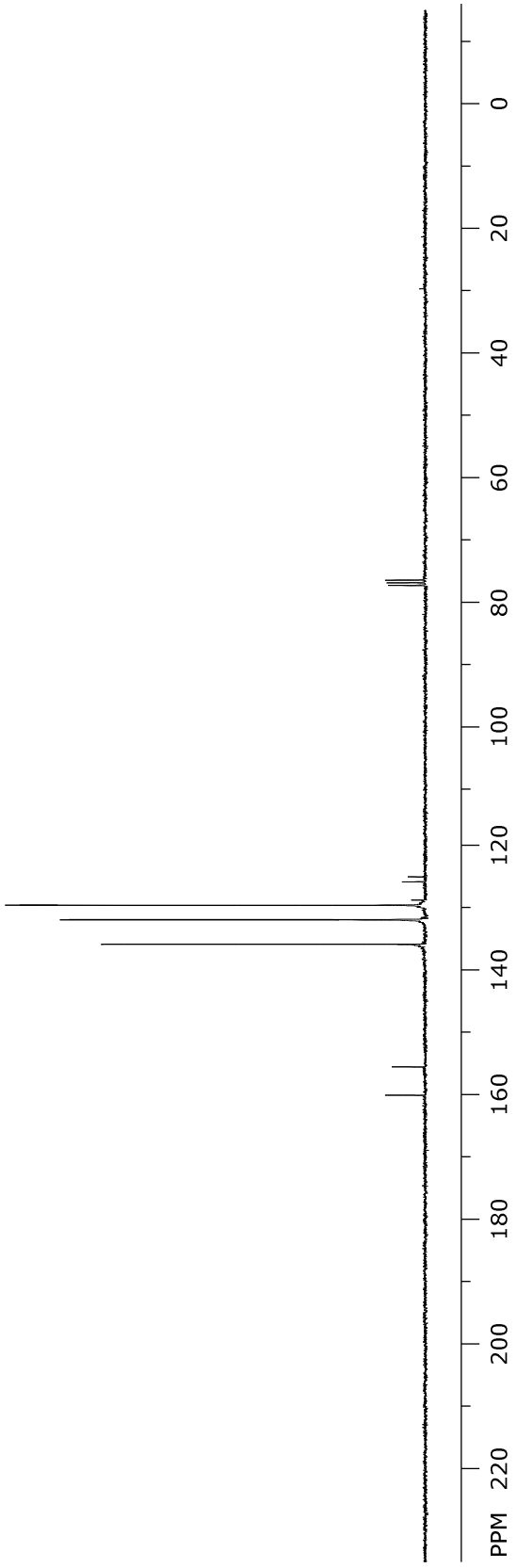

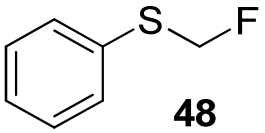

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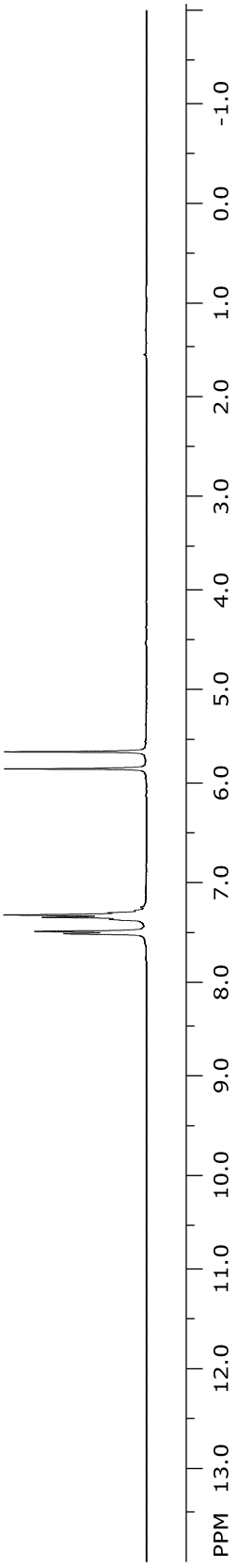

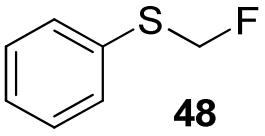

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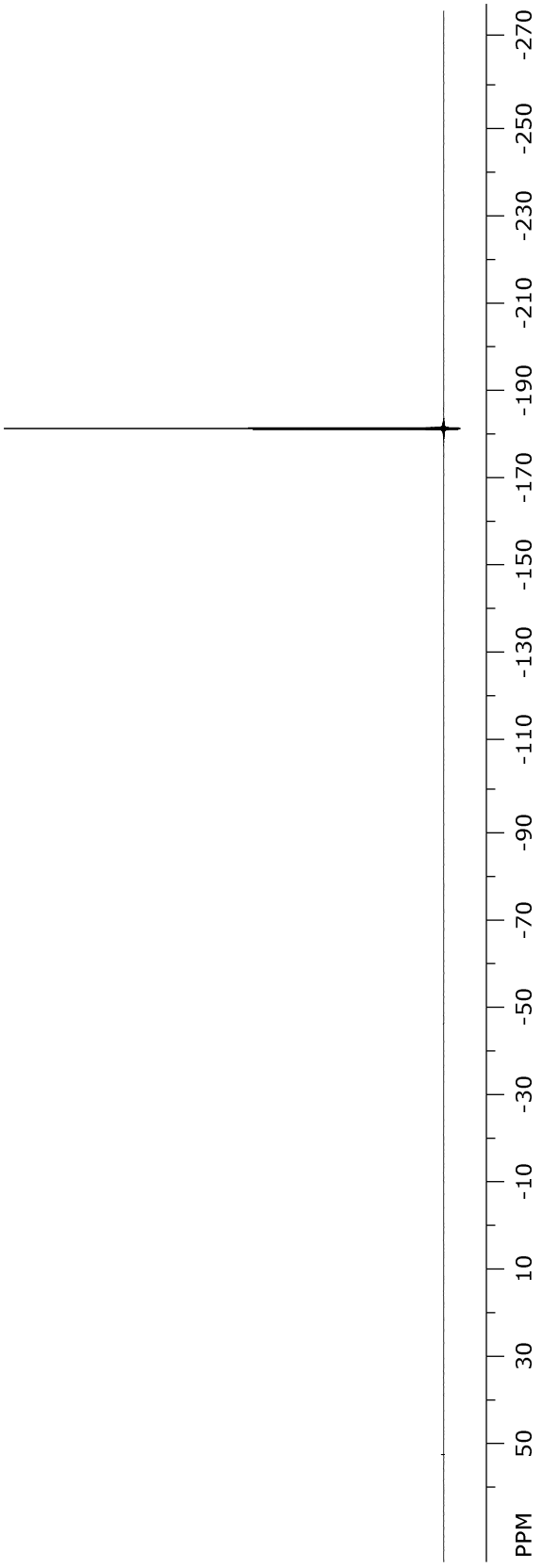

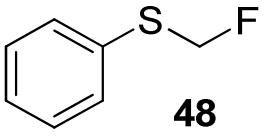

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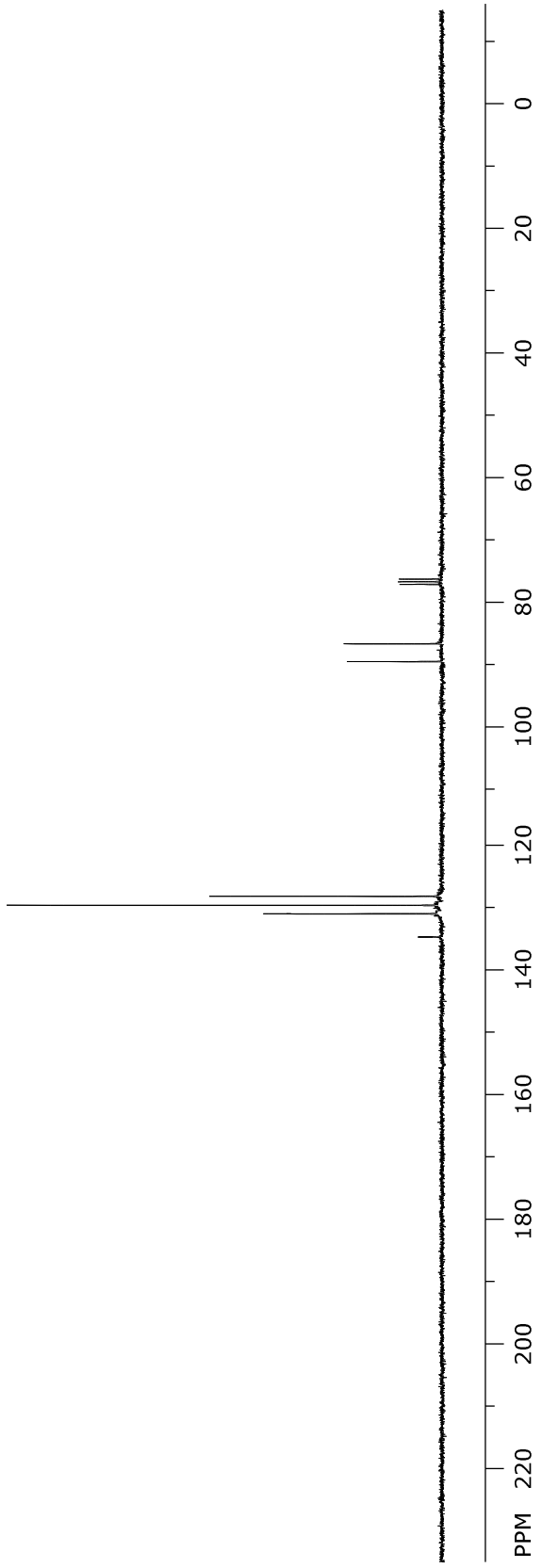

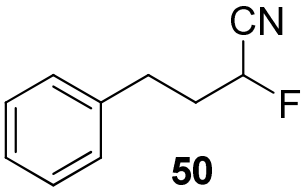
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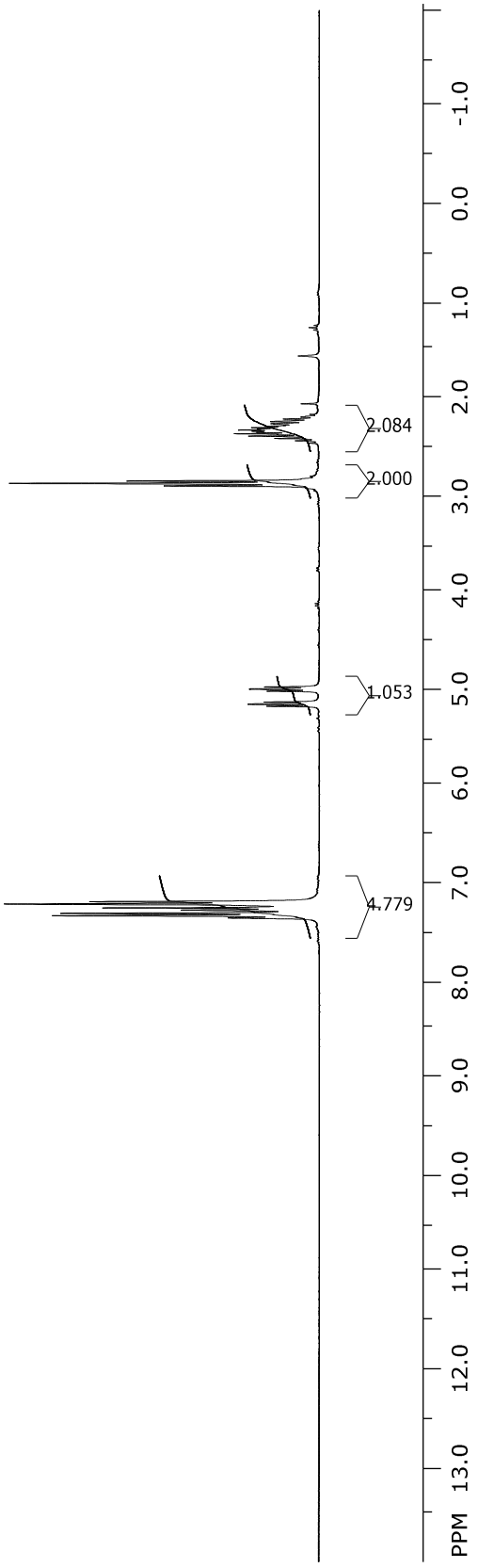
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2.0
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10.0
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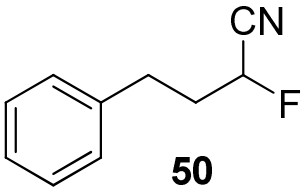
13.0
PPM



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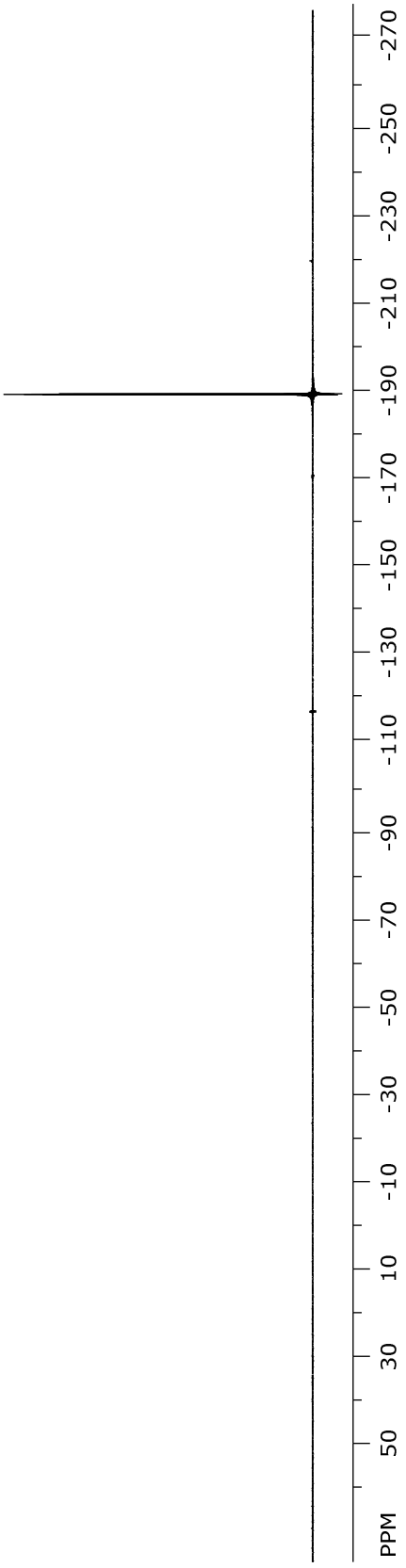

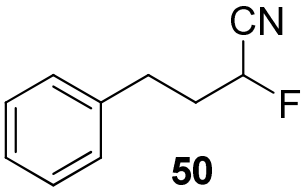

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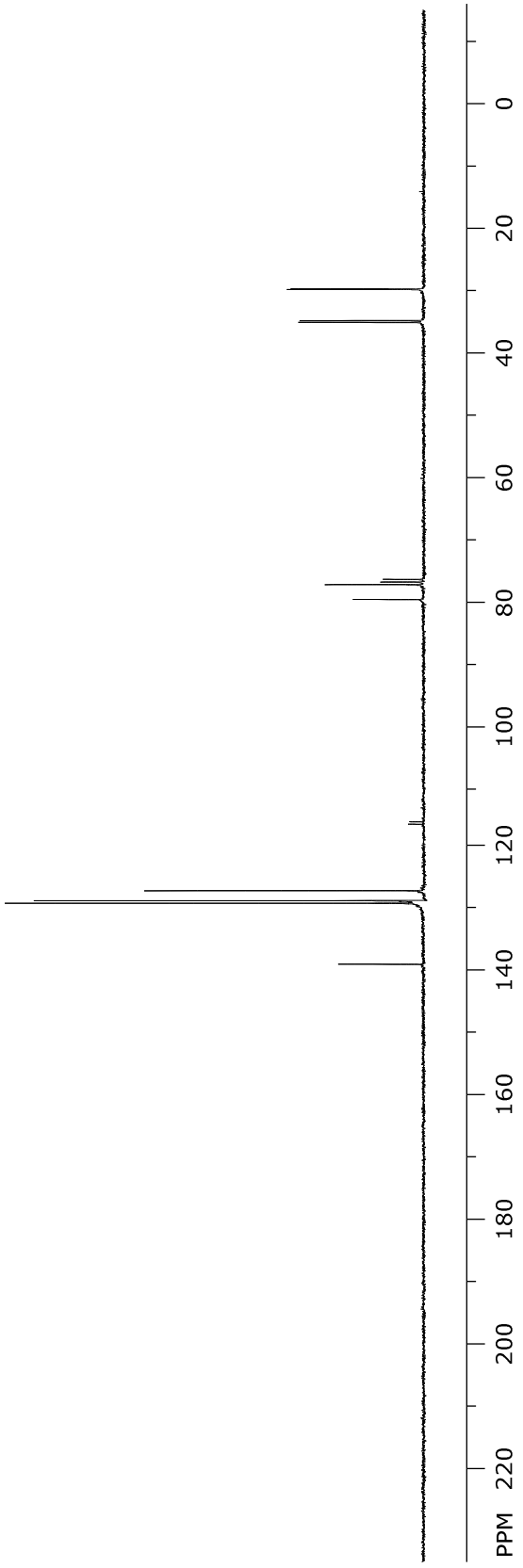
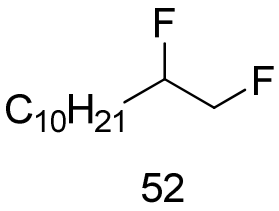
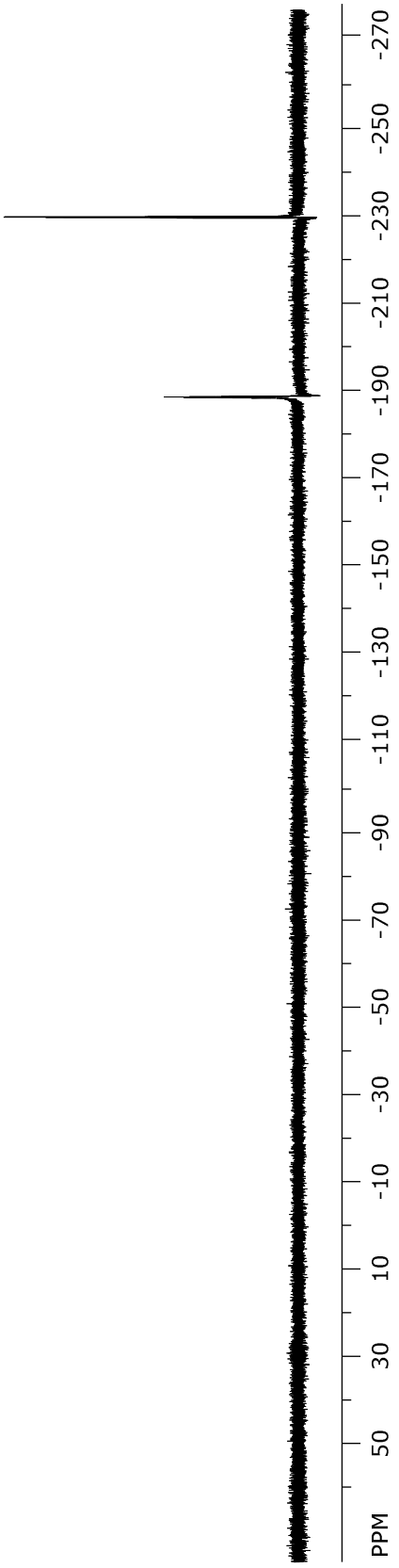



F
F
$C_{10}H_{21}$

52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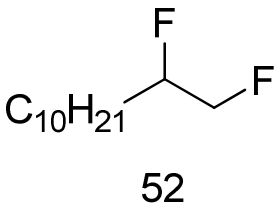
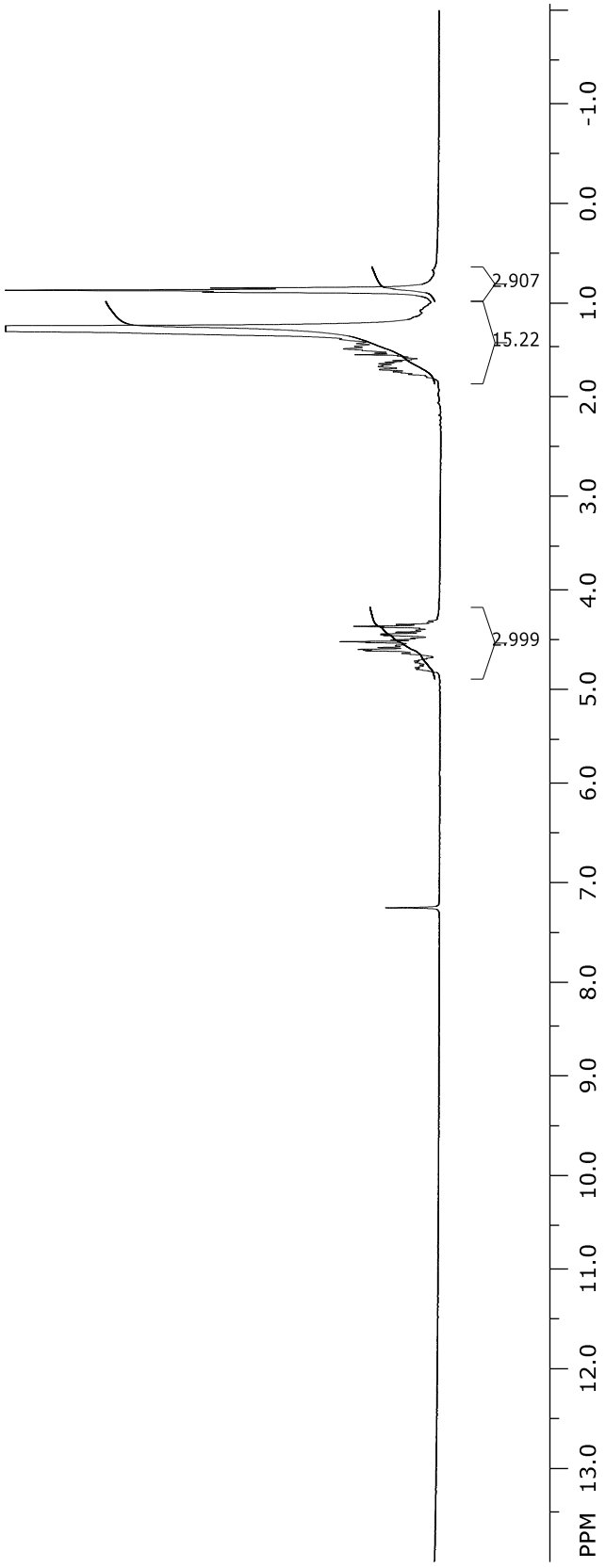
-70
-50
-30
-10
10
30
50
PPM


F
F
$C_{10}H_{21}$

52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1.0
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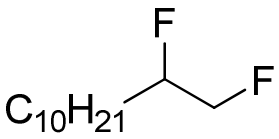
PPM



52