

Electronic Supplementary Information

Study on the Selectivity in the Electrophilic Monofluorination of 2,3-Allenates with SelectfluorTM: An Efficient Synthesis of 4-Fluoro-2(5H)-furanones and 3-Fluoro-4-oxo-2(E)-alkenoates†

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General experimental methods:

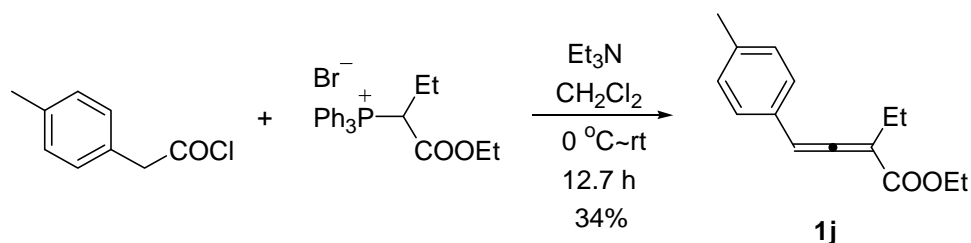
¹H, ¹³C, and ¹⁹F NMR spectra were recorded on instruments operated at 300, 75, and 282 MHz, respectively, in CDCl₃. Chemical shifts (δ) are given in parts per million (ppm) with the residual peak of CHCl₃ at 7.260 ppm as the internal standard. Infrared spectra were recorded from thin films of pure samples on sodium chloride plates for liquid or in the form of KBr discs for solid samples. Mass and HRMS spectra were carried out in EI, ESI, or MALDI mode. Thin layer chromatography was performed on pre-coated glassback plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel (10-40 μ). MeCN used in the formation of 3-fluoro-4-oxo-2(E)-alkenoates was refluxed in the presence of calcium hydride for 10 hours and distilled right before use. For convenience and accuracy, 45 μL of water was pre-added into 50 mL of anhydrous MeCN to prepare the solvent for the formation of 3-fluoro-4-oxo-2(E)-alkenoates. SelectfluorTM used in the formation of **3a-j** was purchased from Tian Jin You Long Sci-Tech Development Co.,Ltd. in China; for those purchased from Alfa Aesar, about 2% of 3-chloro-4-oxo-2(E)-alkenoates were

formed together with 3-fluoro-4-oxo-2(*E*)-alkenoates in our experiments.

Synthesis of starting materials

Compounds **1a**,^{1a} **1e-g**,^{1a} **1p**,^{1a} **1b**,^{1b} **1c-d**,^{1c} **1k**,^{1c} **1h**,^{1d} **1i**,^{1e} **1m**,^{1f} **1n**,^{1g} **1o**,^{1h} **1s**,^{1h} **1t**,^{1h} **1r**¹ⁱ as well as new compounds **1j**, **1l**, and **1q** were prepared following the known procedure.^{1j}

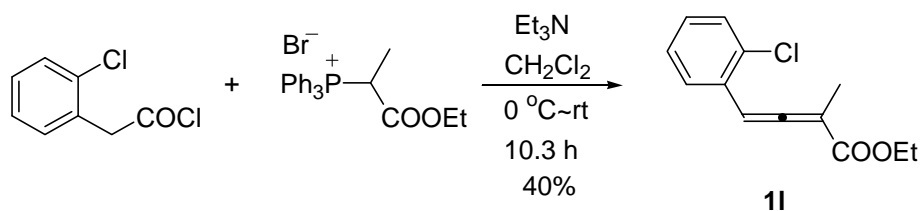
(1) Ethyl 2-ethyl-4-(*p*-tolyl)-2,3-butadienoate (**1j**)



Typical procedure: To a stirred solution of (1-ethoxycarbonyl-propyl)triphenylphosphonium bromide (4.61 g, 10.1 mmol) and triethyl amine (3.10 mL, $d = 0.725\text{ g/mL}$, 2.25 g, 22.3 mmol) in 20 mL of CH_2Cl_2 at $0\text{ }^\circ\text{C}$ was added *p*-tolylacetyl chloride (1.85 g, 11.0 mmol) dropwise. Then this reaction system was allowed to rise to room temperature. After 12.7 h, CH_2Cl_2 was evaporated and the residue mixture was washed with petroleum ether/ Et_2O ($v/v = 1/1$). Filtration, evaporation, and purification by chromatography (petroleum ether/ethyl acetate = 100/1) on silica gel afforded ethyl 2-ethyl-4-(*p*-tolyl)-2,3-butadienoate **1j** (0.779 g, 34%): liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.22-7.12 (m, 4H), 6.54 (t, $J = 3.3\text{ Hz}$, 1H), 4.21 (qd, $J = 7.1\text{ Hz}$ and 1.5 Hz , 2H), 2.50-2.28 (m, 5H), 1.26 (t, $J = 7.1\text{ Hz}$, 3H), 1.08 (t, $J = 7.4\text{ Hz}$, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 211.5, 166.8, 137.5, 129.6, 129.5, 127.0, 106.0, 98.6, 61.0, 22.2, 21.2, 14.3, 12.4; IR (neat) ν (cm^{-1}) 2970, 2925, 2871, 1944, 1712, 1514, 1453, 1366, 1250, 1178, 1128, 1101, 1045; MS (70 eV, EI) m/z (%): 231 ($\text{M}^+ + 1$, 13.58), 230 (M^+ , 82.22), 142 (100); HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$ (M^+): 230.1307. Found: 230.1305.

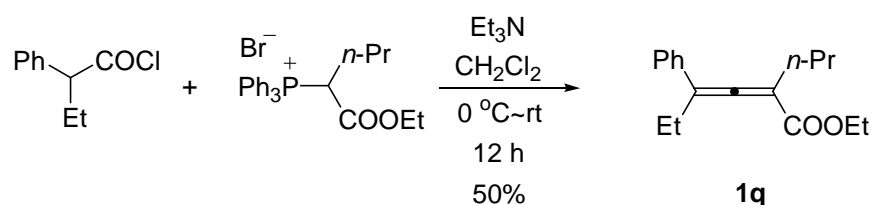
The following compounds were prepared according to this typical procedure.

(2) Ethyl 4-(2-chlorophenyl)-2-methyl-2,3-butadienoate (**1l**)



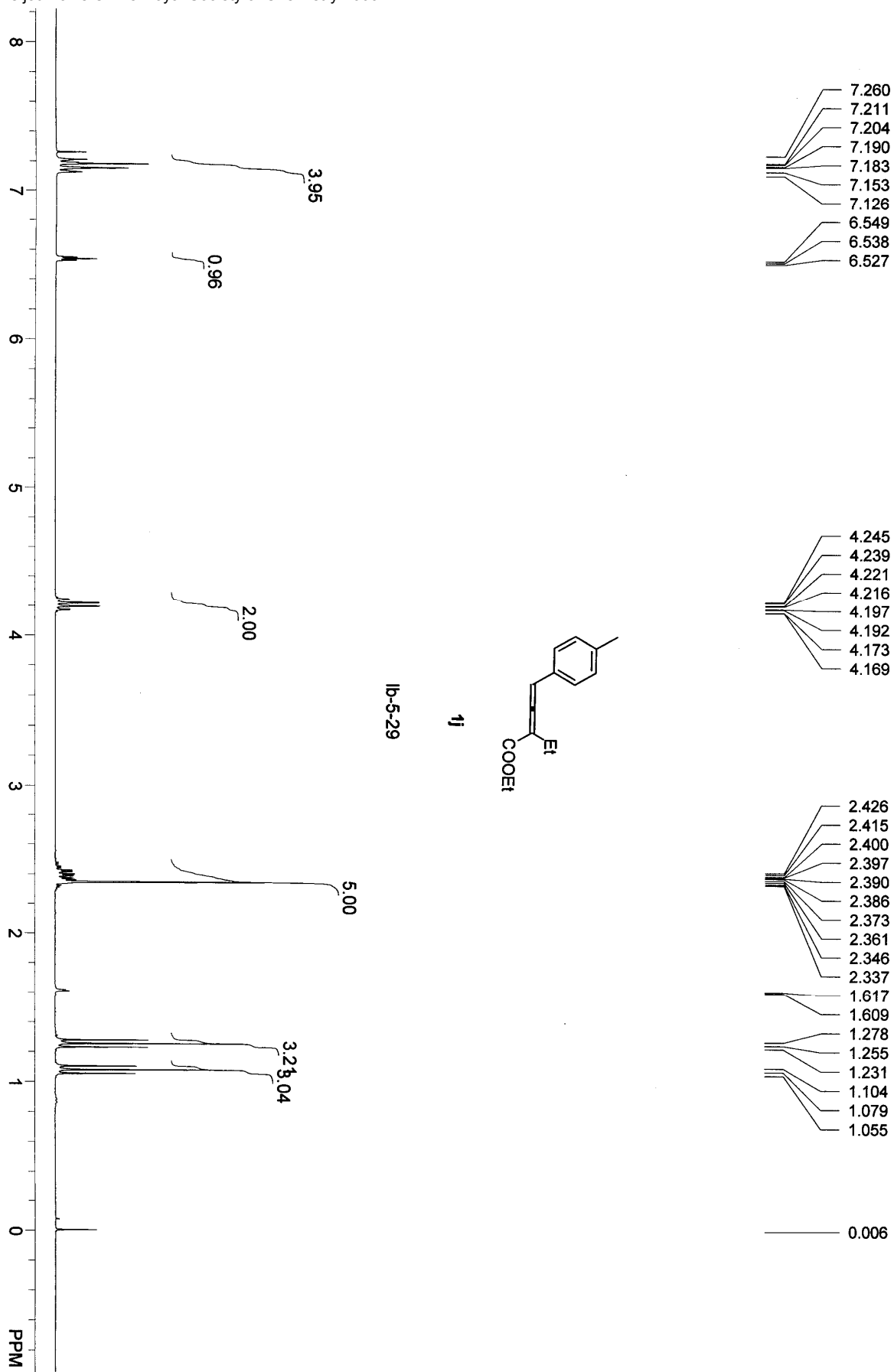
The reaction of 2-(2-chlorophenyl)acetyl chloride (6.07 g, 32.1 mmol), (1-ethoxycarbonyl)ethyltriphenylphosphonium bromide (13.3 g, 30.1 mmol), and triethyl amine (9.0 mL, $d = 0.725$ g/mL, 6.53 g, 64.6 mmol) in 60 mL of CH_2Cl_2 afforded **1l** (2.88 g, 40%): liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.33 (m, 2H), 7.26-7.13 (m, 2H), 6.90 (q, $J = 3.2$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 2.00 (d, $J = 3.2$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.0, 166.8, 132.4, 130.5, 129.8, 128.9, 128.6, 126.9, 99.6, 93.7, 61.2, 15.0, 14.2; IR (neat) ν (cm^{-1}) 3069, 2982, 2919, 1949, 1714, 1588, 1564, 1479, 1443, 1368, 1268, 1121, 1049, 1031; MS (70 eV, EI) m/z (%): 238 ($\text{M}^+(\text{}^{37}\text{Cl})$, 10.98), 236 ($\text{M}^+(\text{}^{35}\text{Cl})$, 32.53), 128 (100); HRMS calcd for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{}^{35}\text{Cl}$ (M^+): 236.0604. Found: 236.0603.

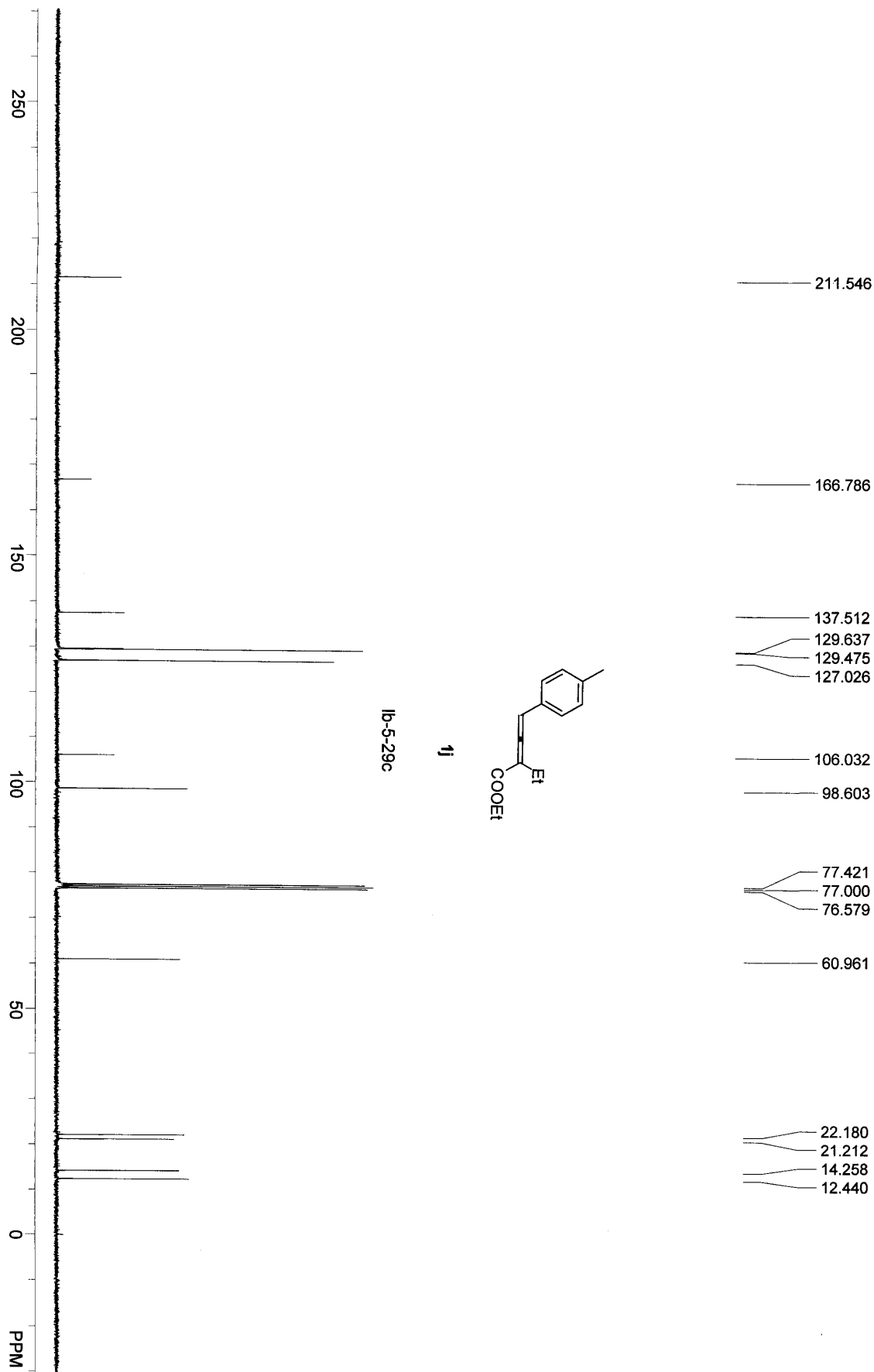
(3) Ethyl 4-phenyl-2-propyl-2,3-hexadienoate (**1q**)

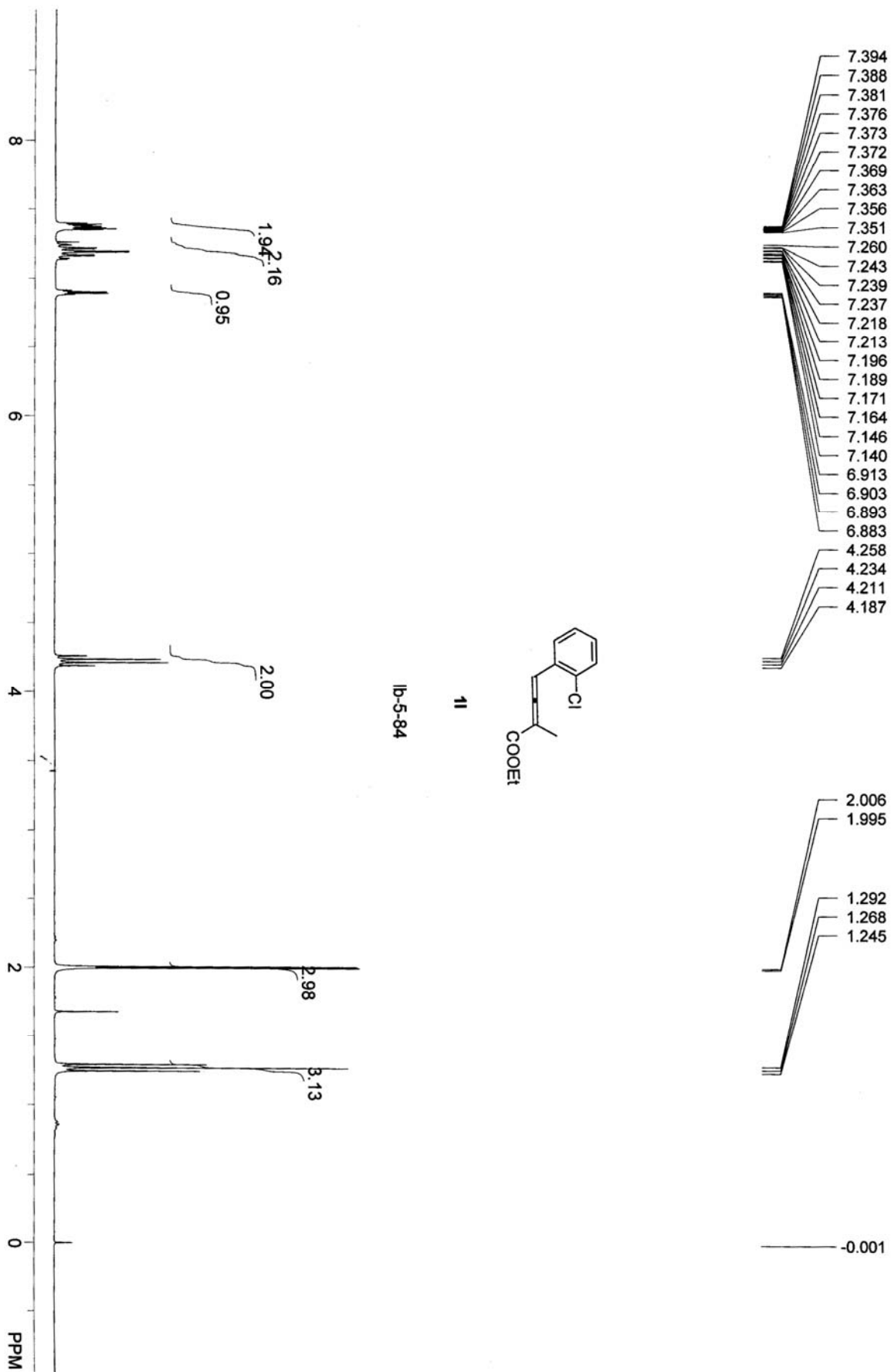


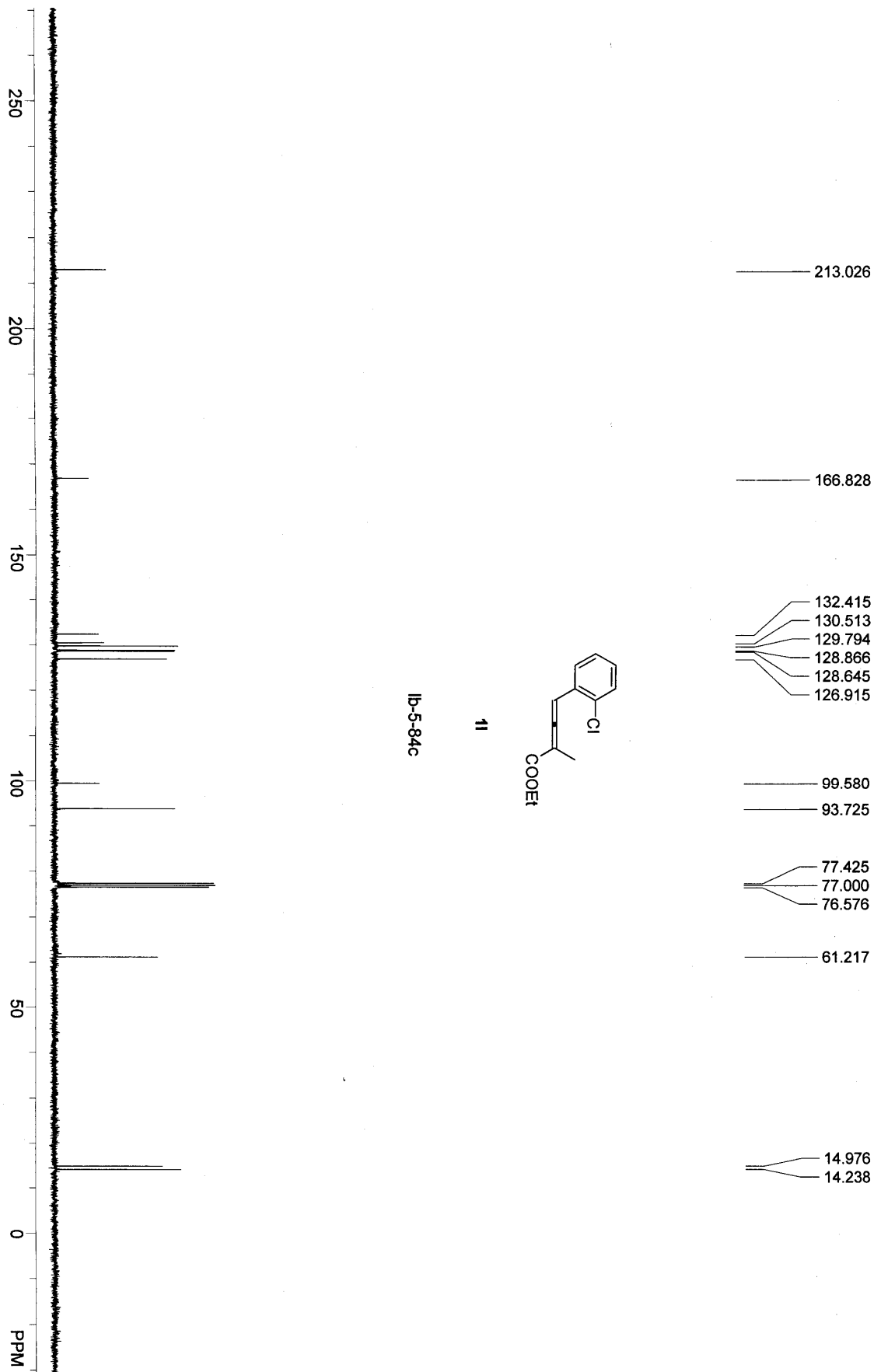
The reaction of 2-phenylbutanoyl chloride (18.3 g, 100 mmol), (1-ethoxycarbonyl)butyltriphenylphosphonium bromide (47.9 g, 100 mmol), and triethyl amine (20.3 g, 201 mmol) in 150 mL of CH_2Cl_2 afforded **1q** (12.8 g, 50%): liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.42-7.28 (m, 4H), 7.27-7.20 (m, 1H), 4.30-4.10 (m, 2H), 2.54 (q, $J = 7.4$ Hz, 2H), 2.33 (t, $J = 7.6$ Hz, 2H), 1.57-1.42 (m, 2H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.16 (t, $J = 7.4$ Hz, 3H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 210.8, 167.5, 135.4, 128.4, 127.2, 126.1, 111.3, 104.0, 60.7, 31.0, 23.2, 21.5, 14.3, 13.9, 12.4; IR (neat) ν (cm^{-1}) 3085, 3060, 3030, 2965, 2933, 2873, 1941, 1712, 1598, 1494, 1455, 1377, 1366, 1249, 1130, 1088, 1069, 1039; MS (70 eV, EI) m/z (%): 259 (M^++1 , 10.18), 258 (M^+ , 53.01), 129 (100); HRMS calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2$ (M^+): 258.1620. Found: 258.1621.

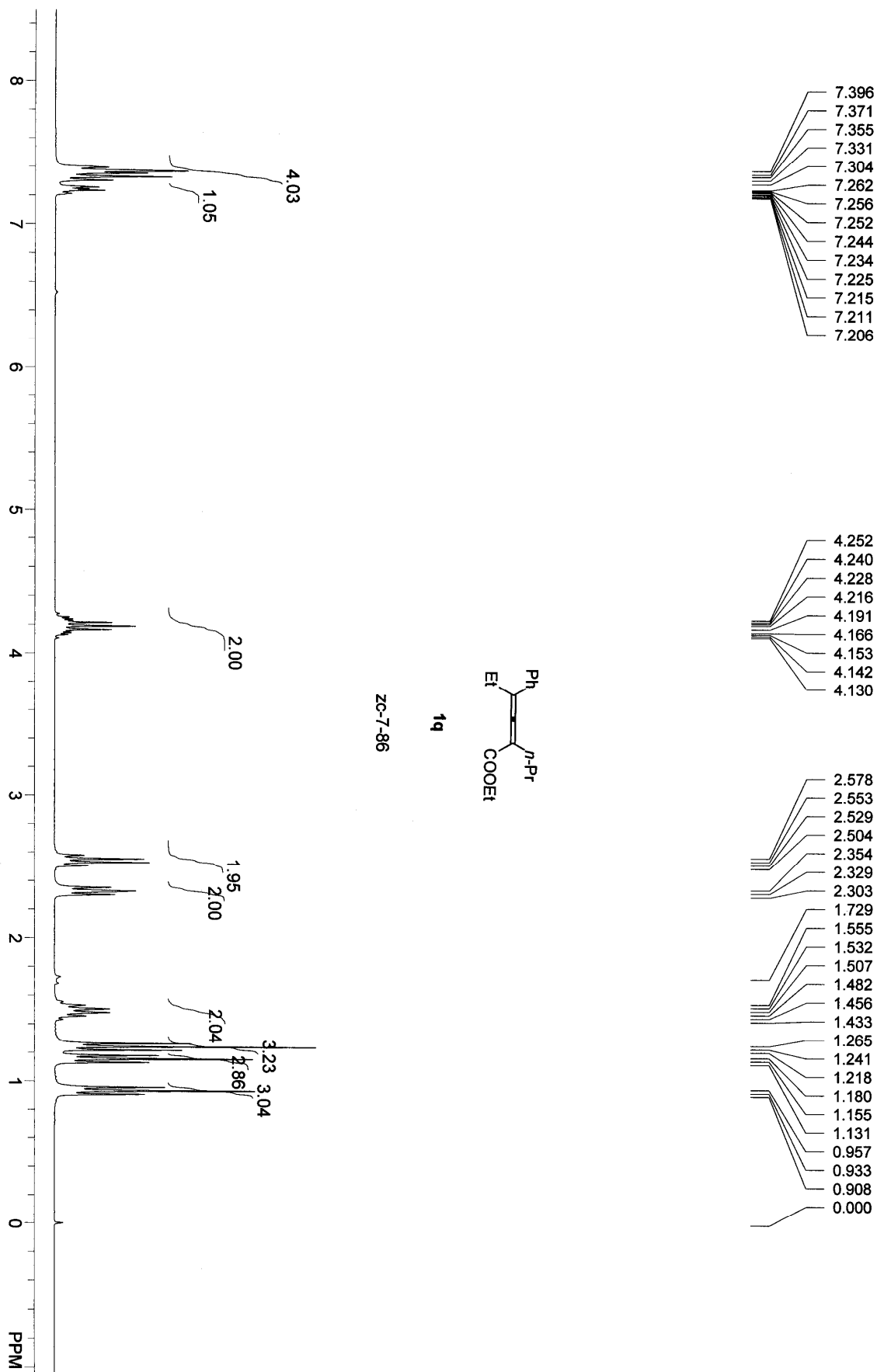
- (1) (a) P. Nanayakkara, H. Alper *J. Org. Chem.* **2004**, *69*, 4686. (b) Z. Lu, G. Chai, S. Ma *Angew. Chem; Int. Ed.* **2008**, *47*, 6045. (c) C. Fu, S. Ma *Eur. J. Org. Chem.* **2005**, 3942. (d) G. Chen, C. Fu, S. Ma *J. Org. Chem.* **2006**, *71*, 9877. (e) W. H. Pirkle, M. E. Koscho, *J. Chromatogr. A* **1997**, *761*, 65. (f) H.-J. Bestmann, H. Hartung *Chem. Ber.* **1966**, *99*, 1198; (g) G. Chen, C. Fu, S. Ma *Tetrahedron* **2006**, *62*, 4444; (h) B. M. Trost, A. B. Pinkerton, M. Seidel, *J. Am. Chem. Soc.* **2001**, *123*, 12466. (i) W. S. Wadsworth, W. D. Emmons, *J. Am. Chem. Soc.* **1961**, *83*, 1733. (j) R. W. Lang, H.-J. Hansen, *Org. Synth.* **1984**, *62*, 202.

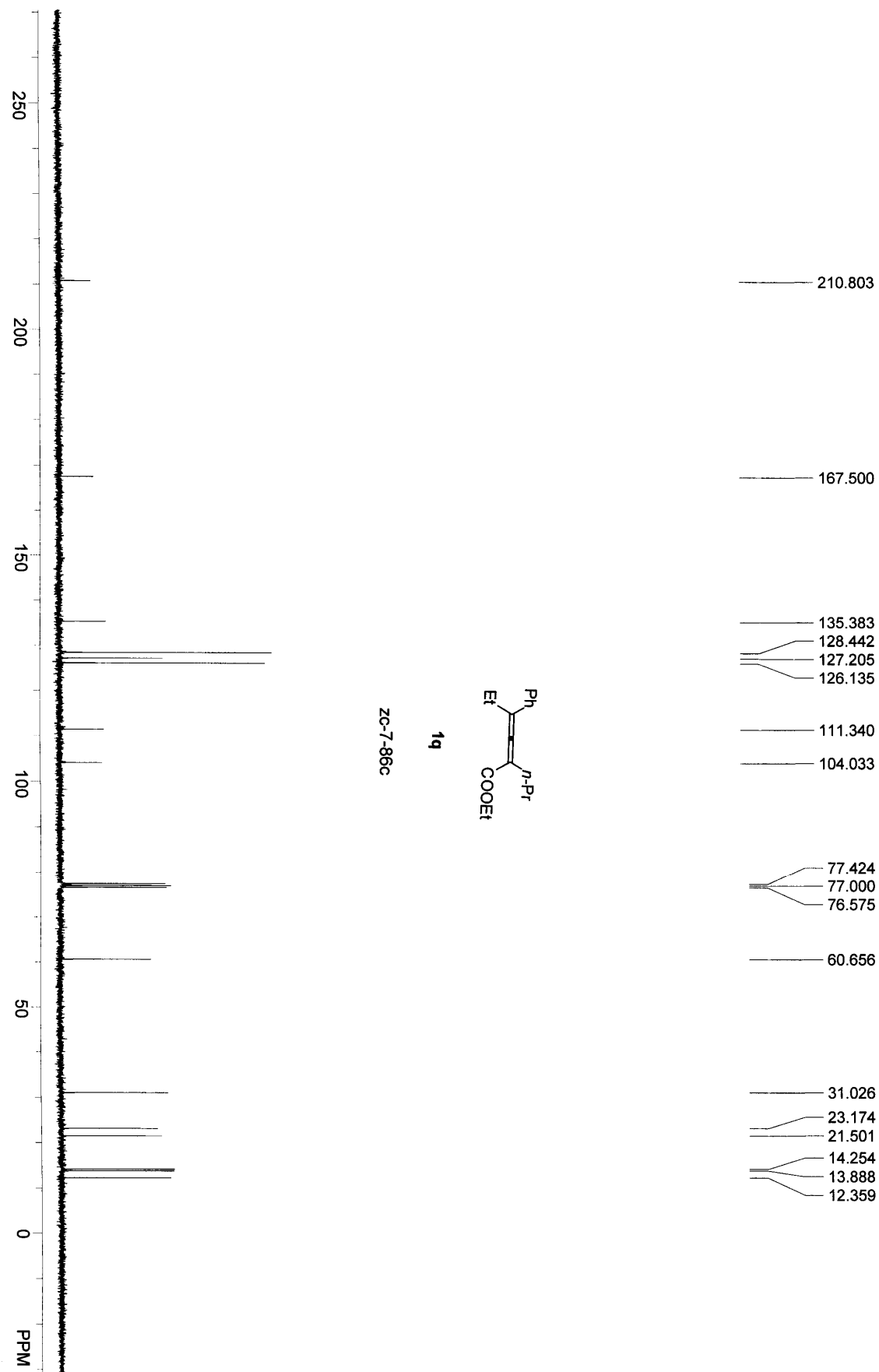


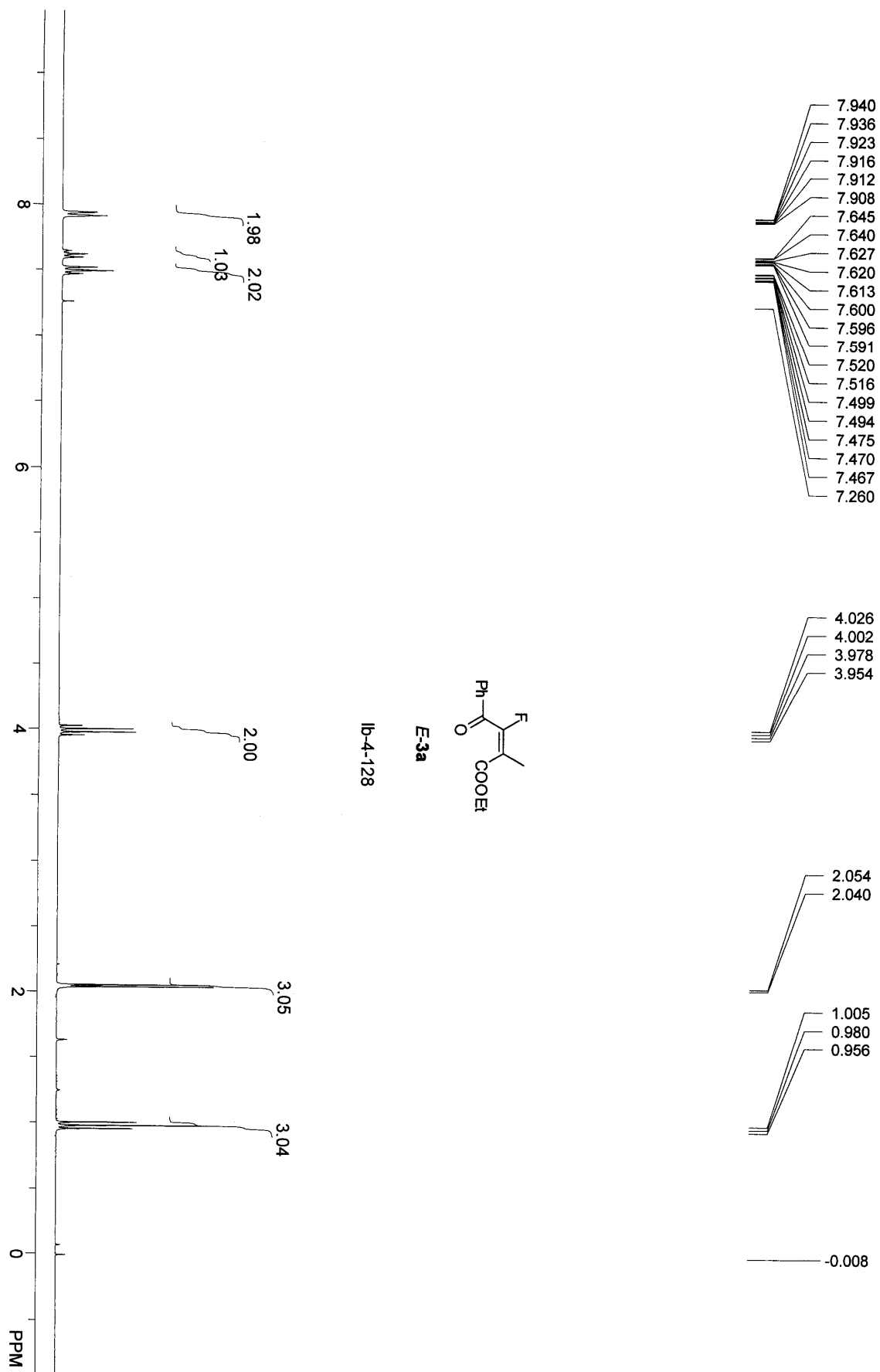


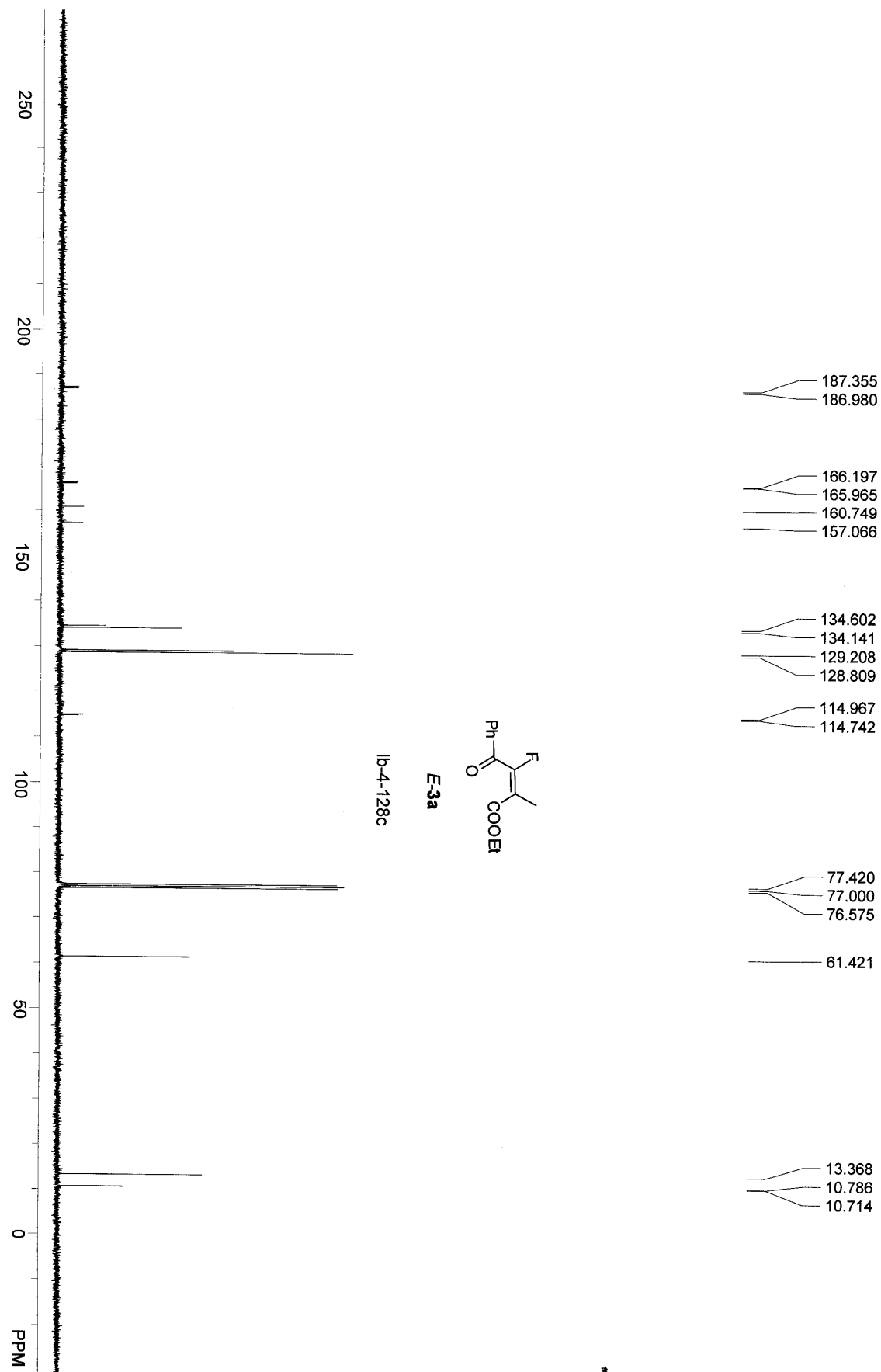


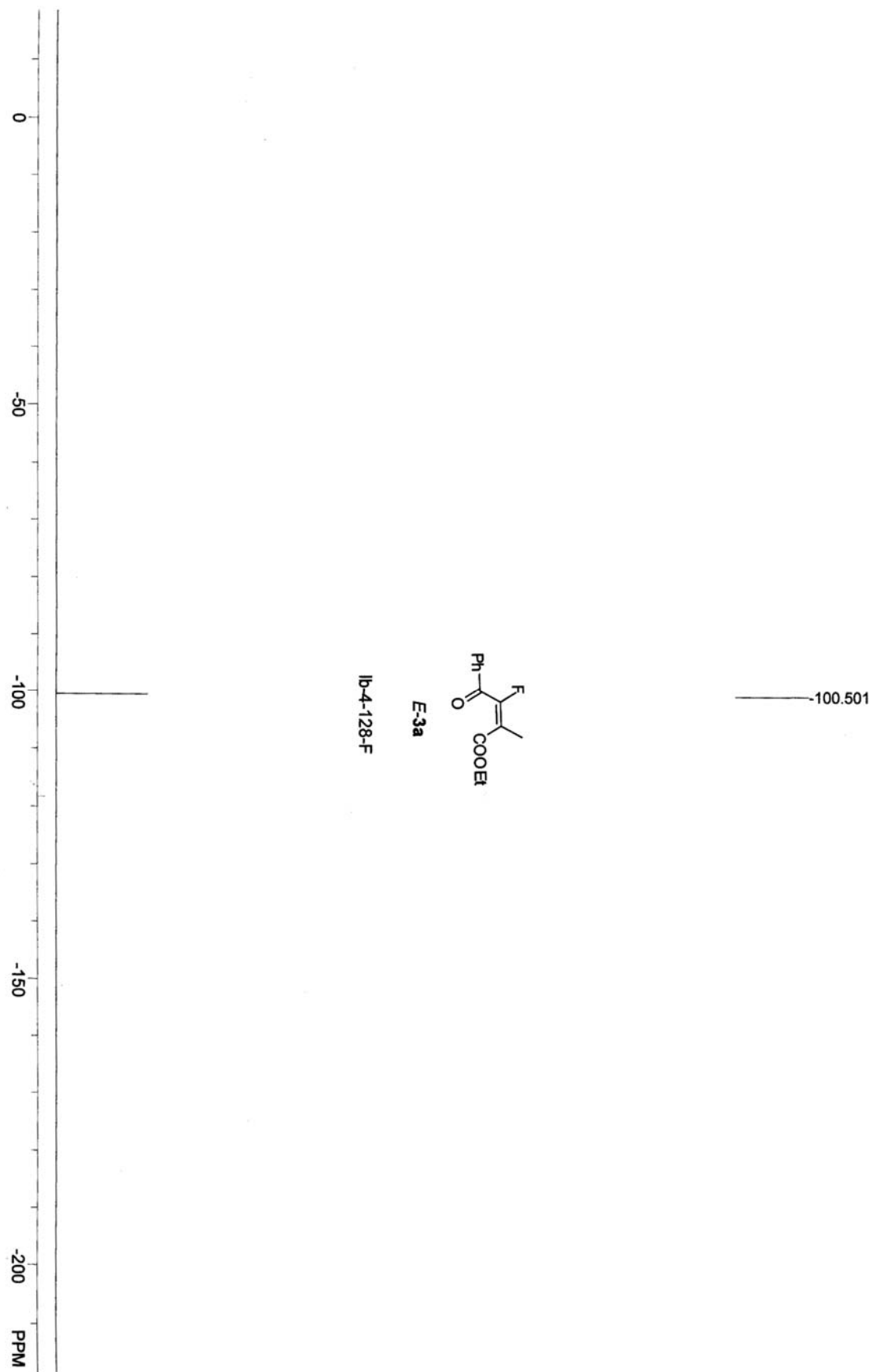




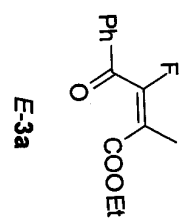
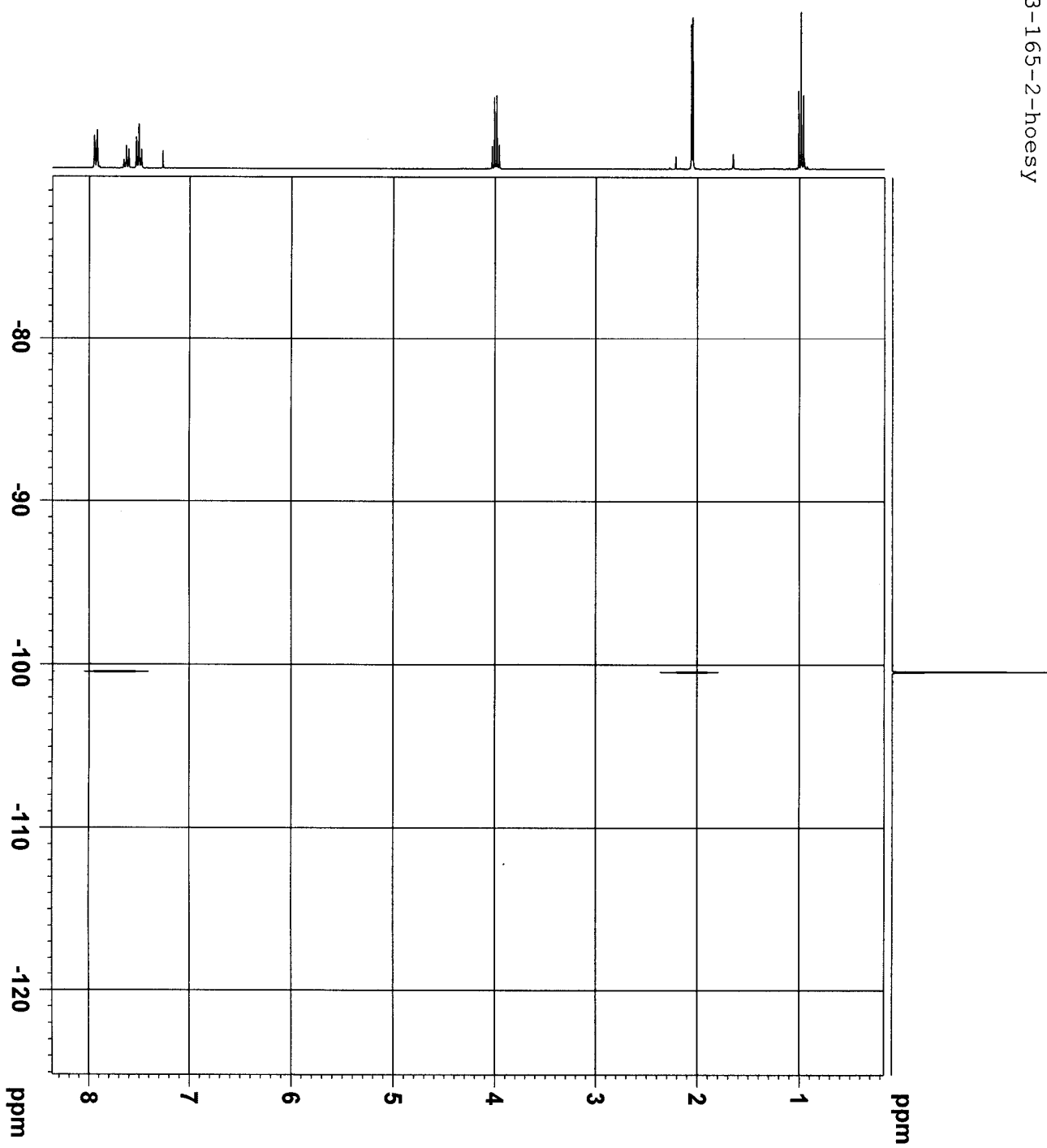


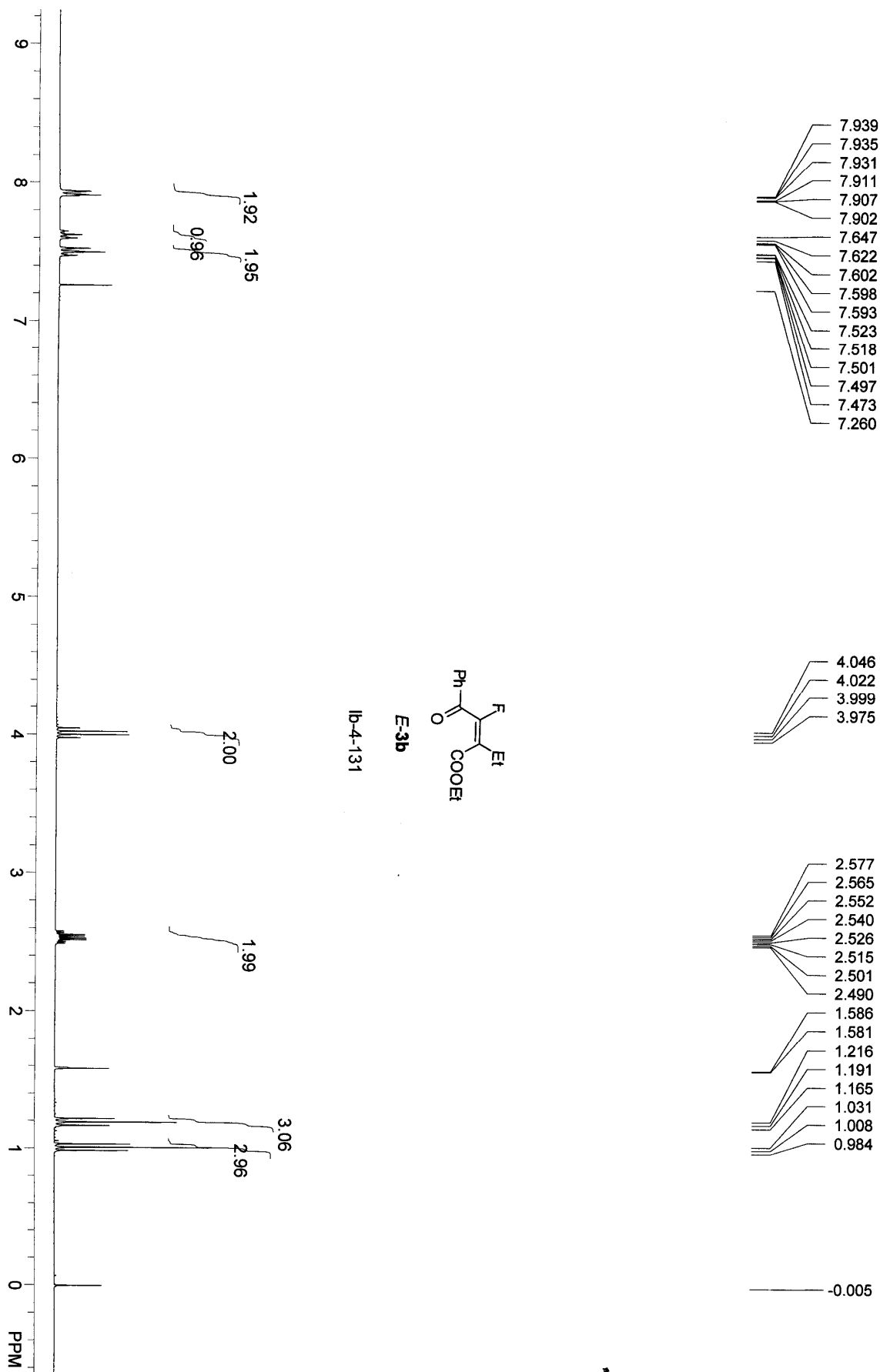


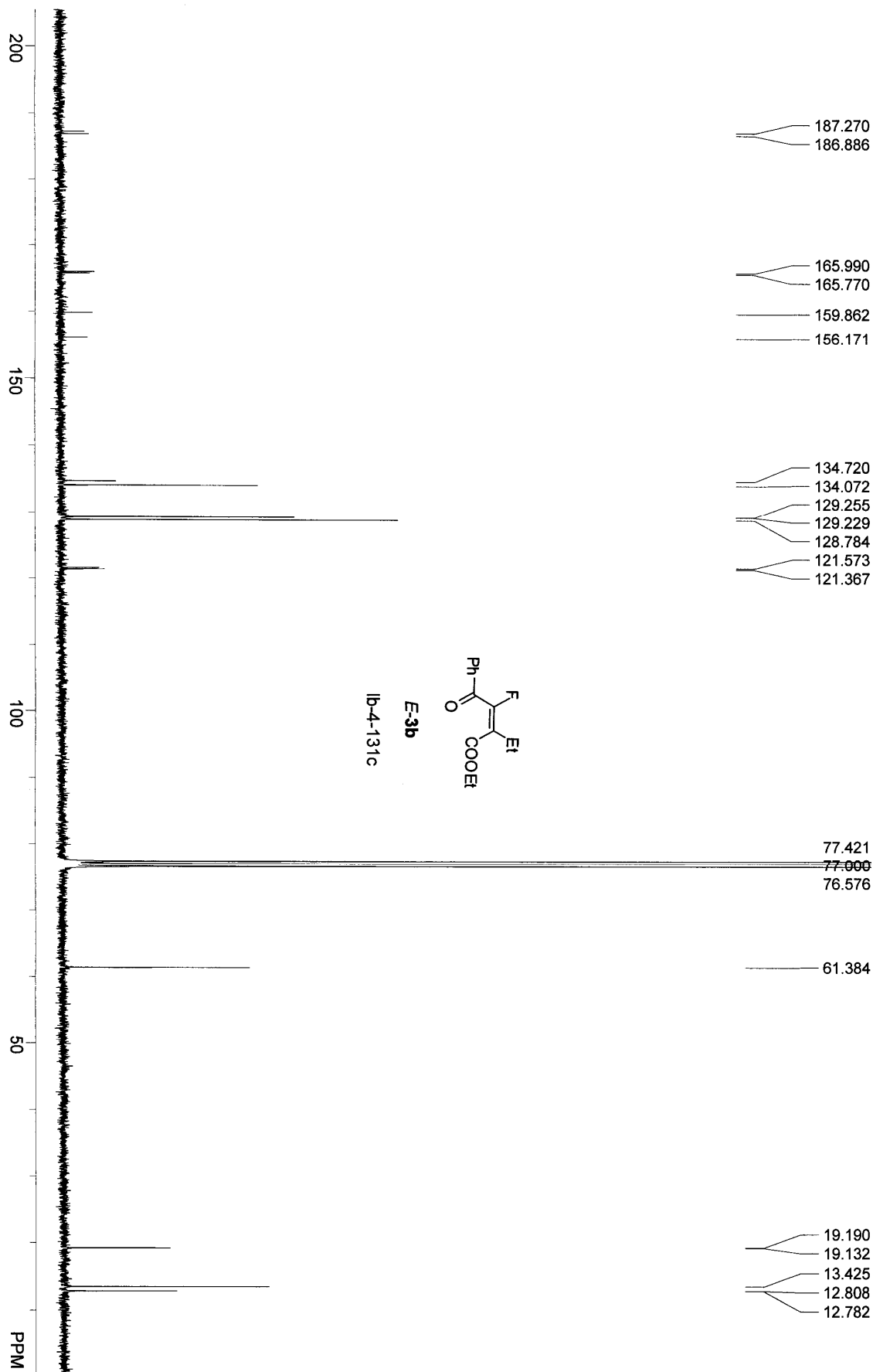


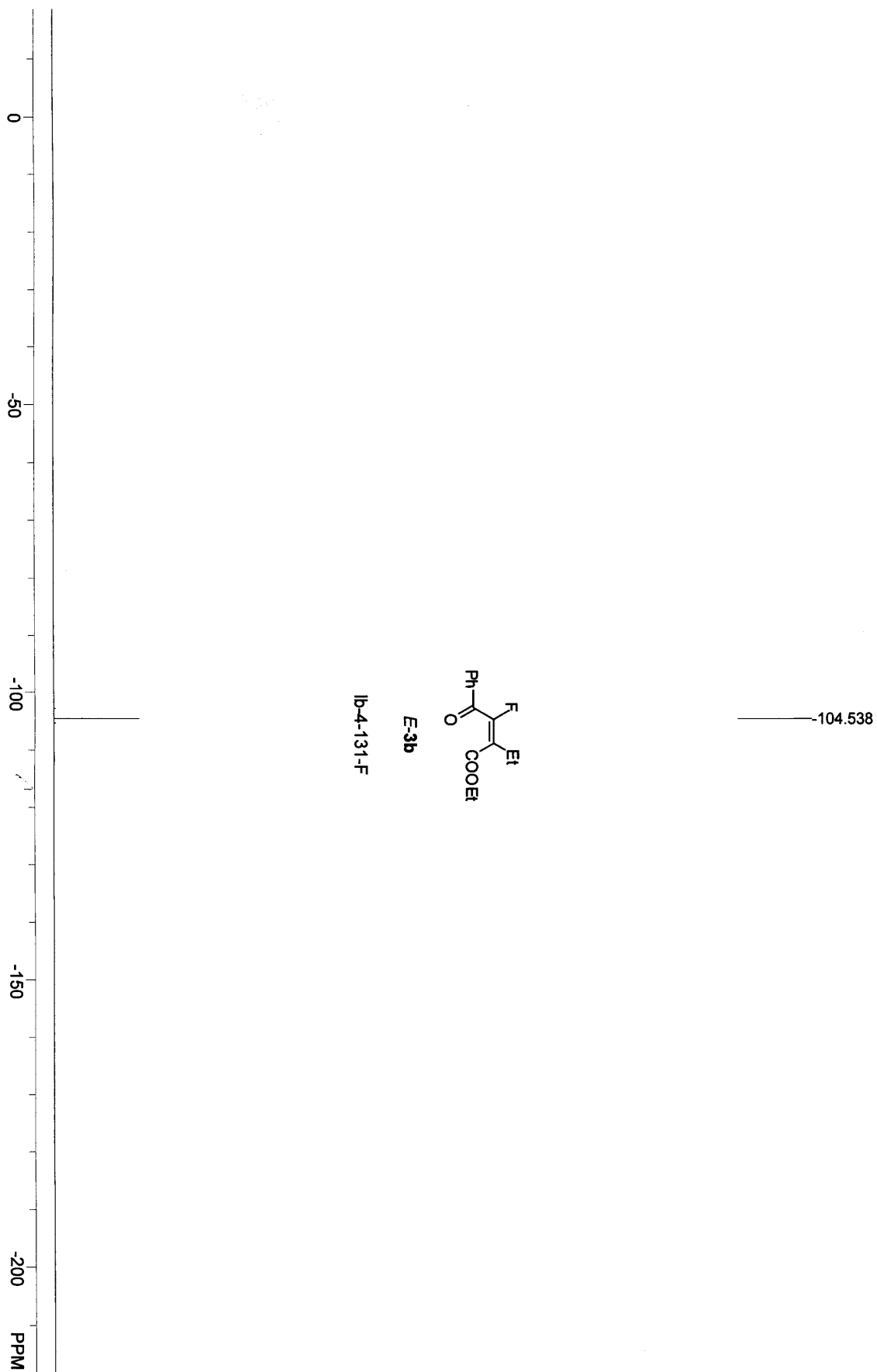


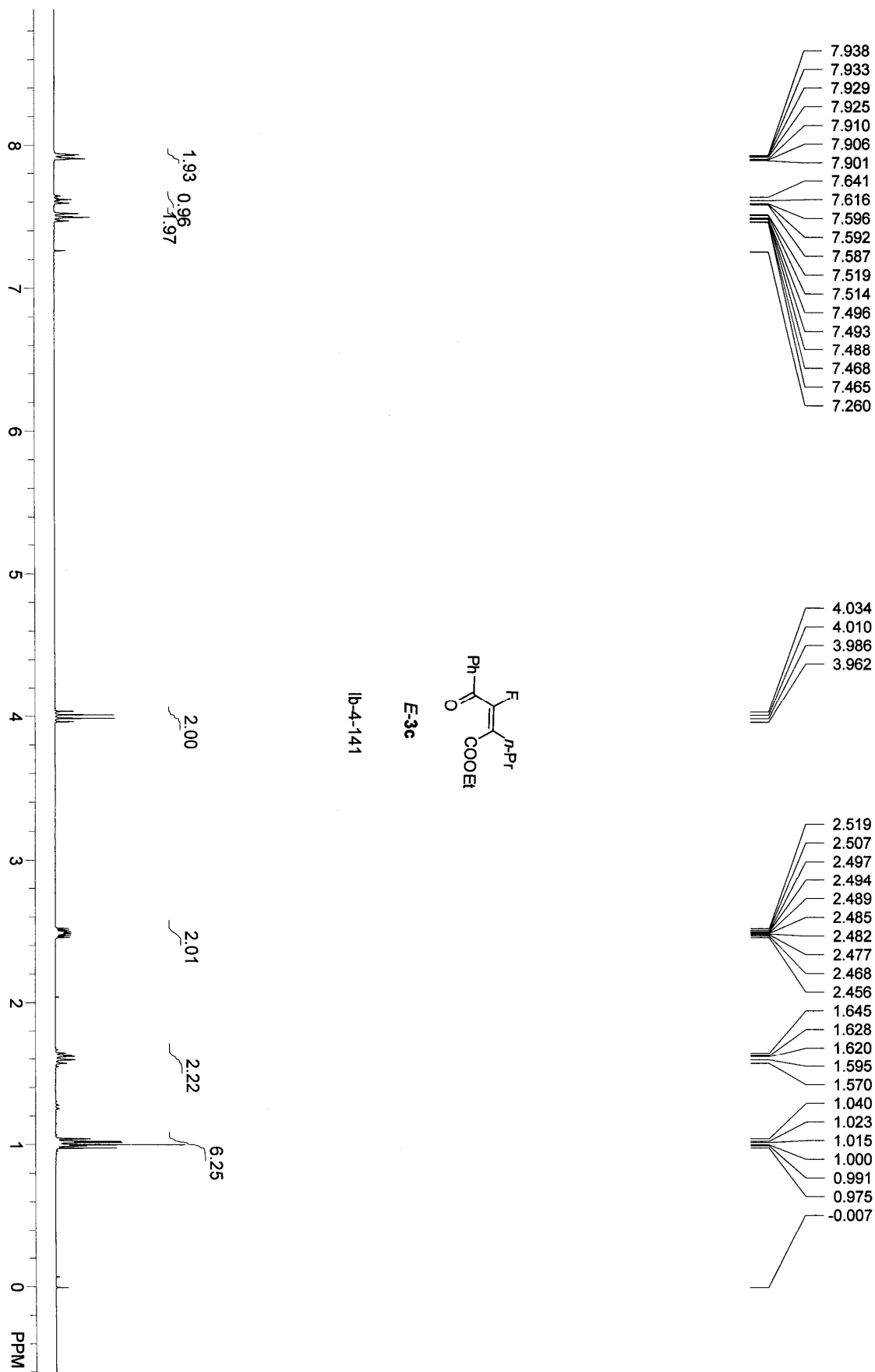
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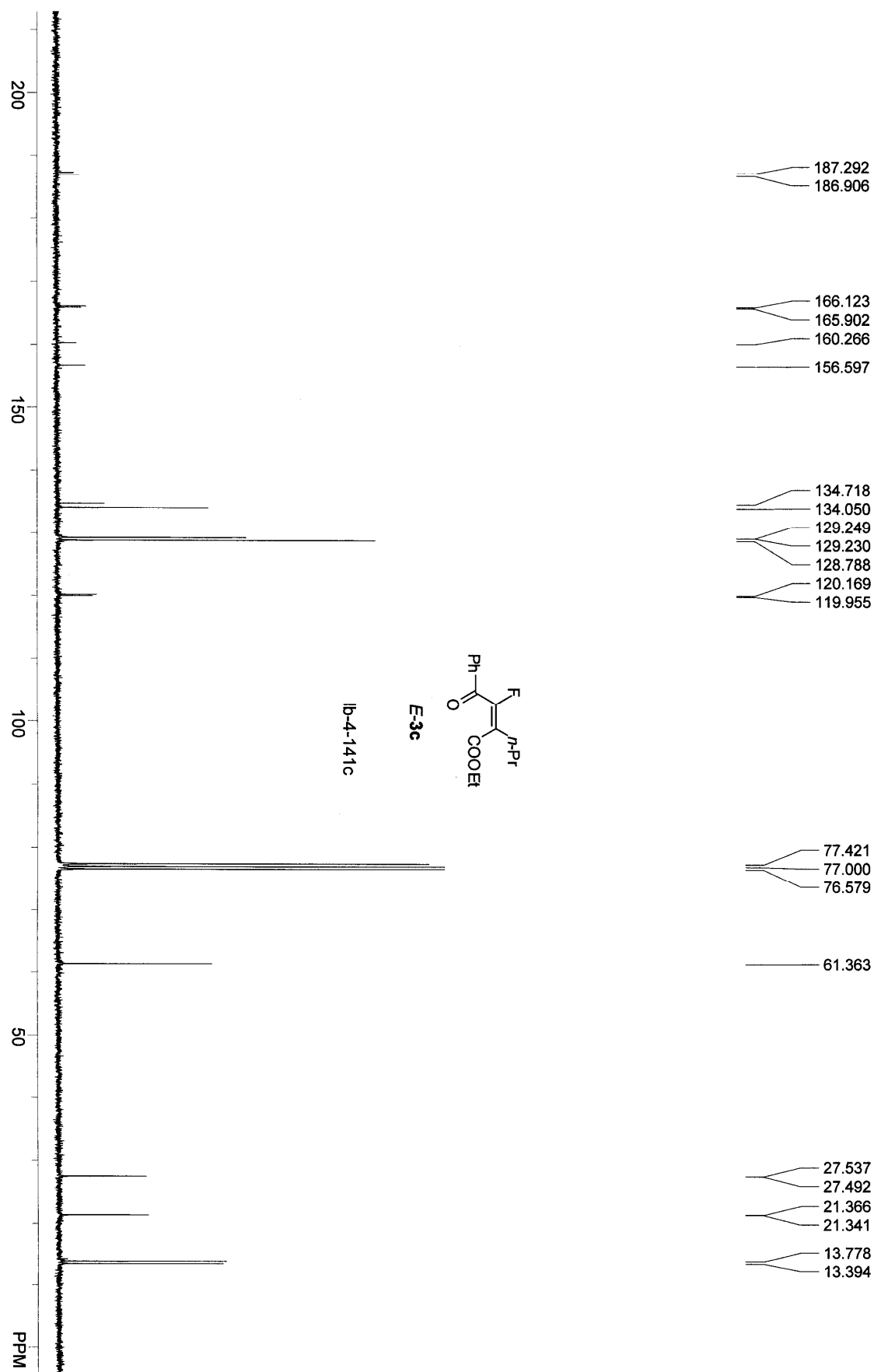


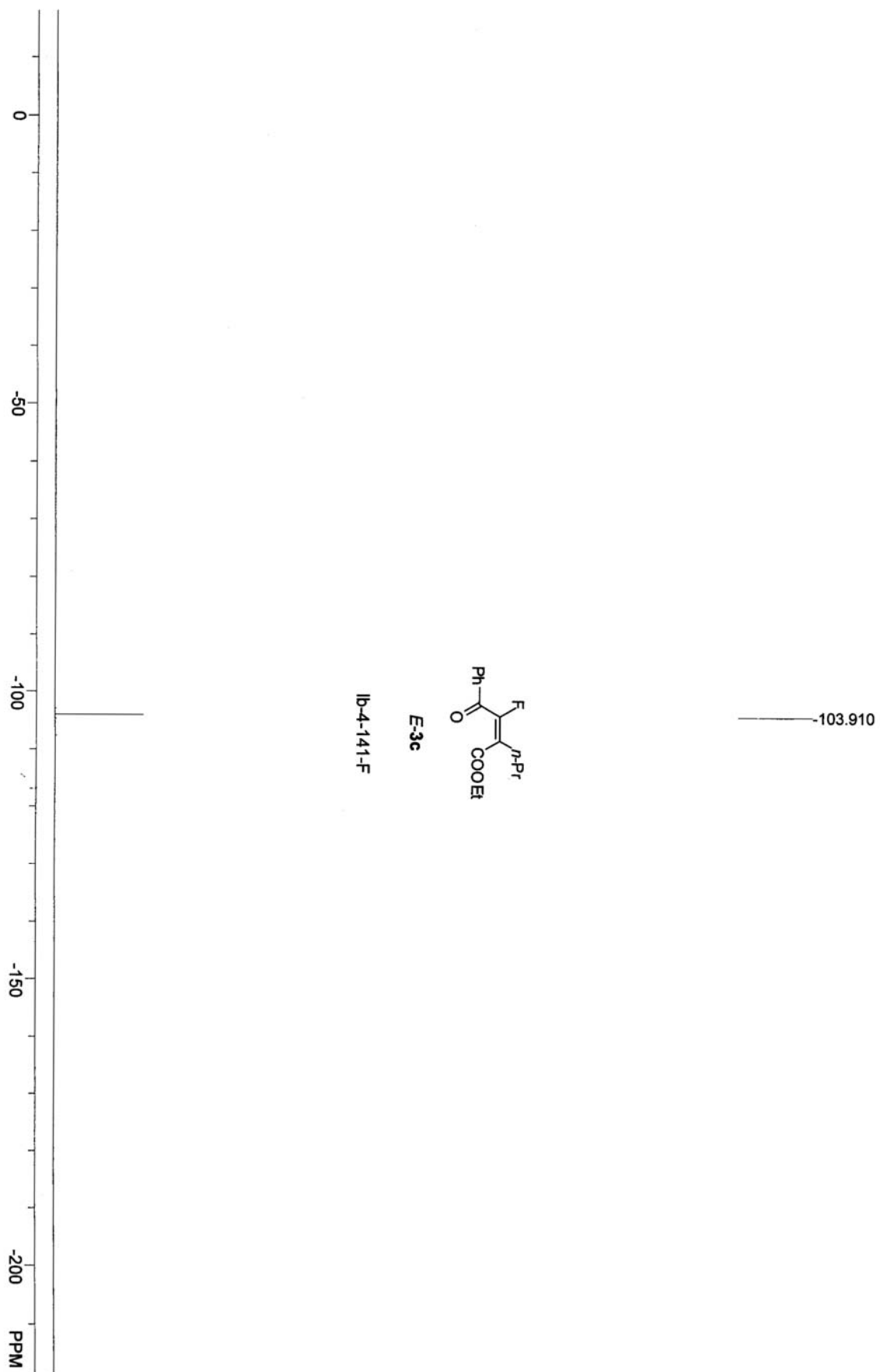


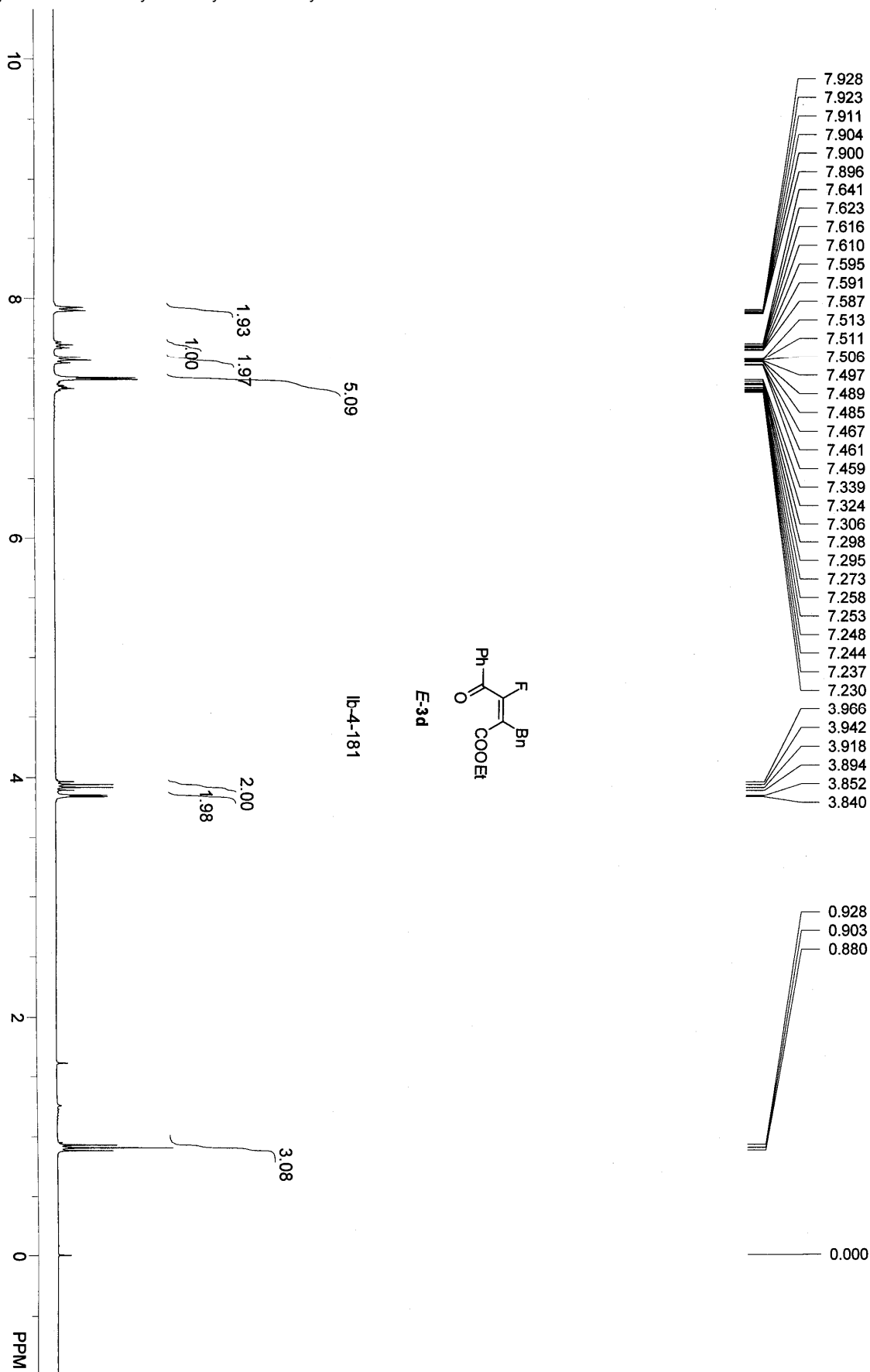


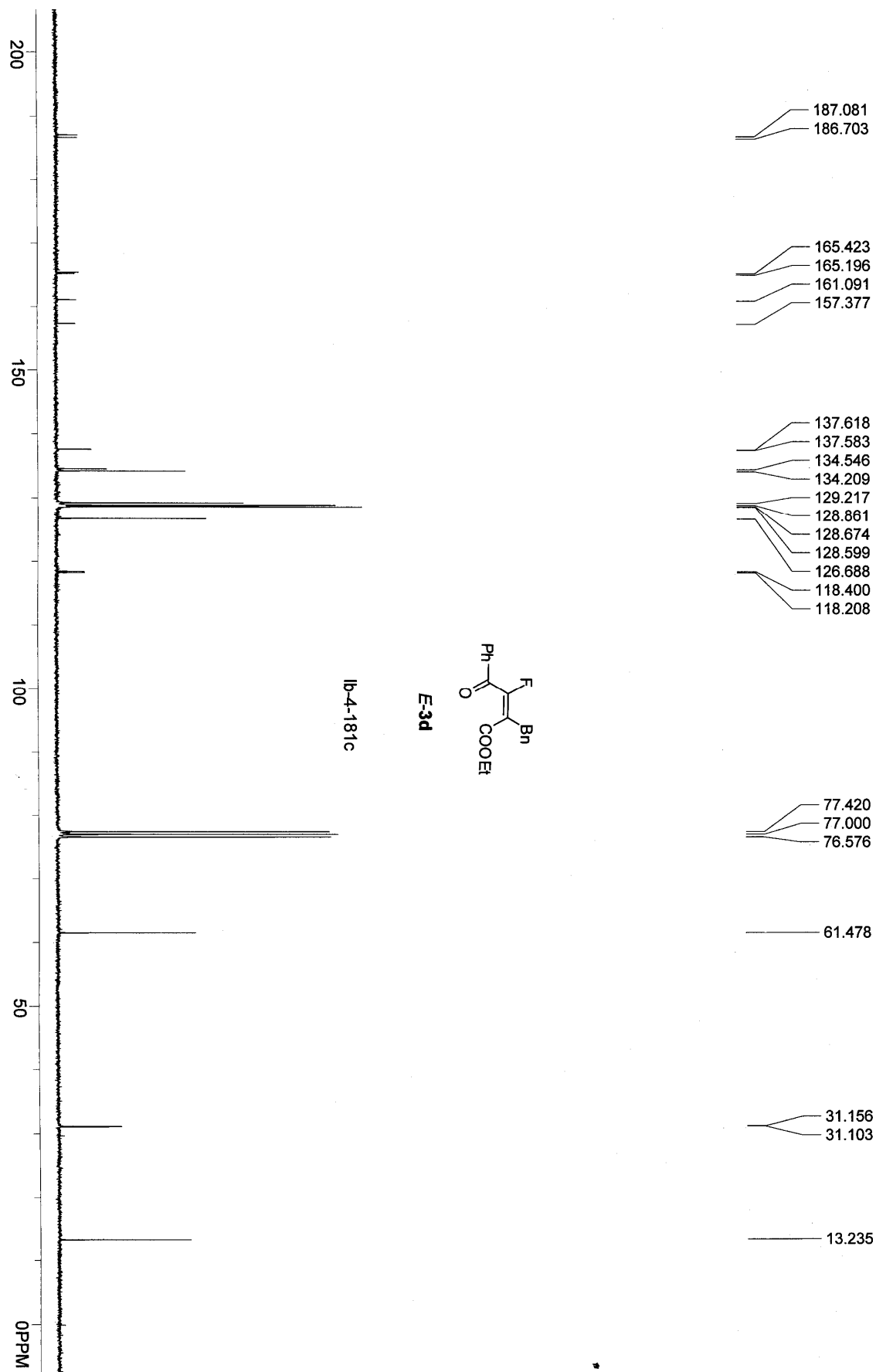


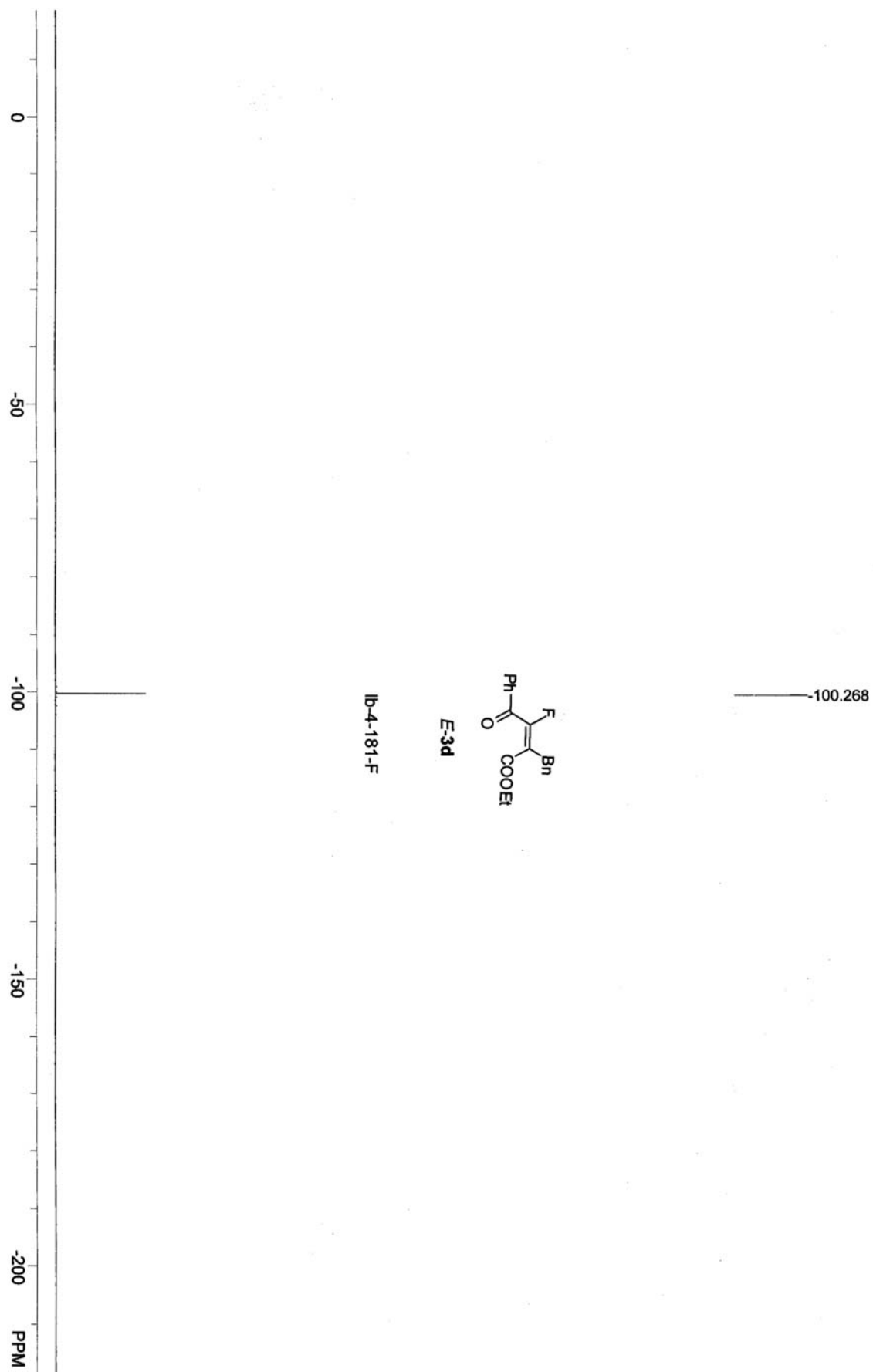


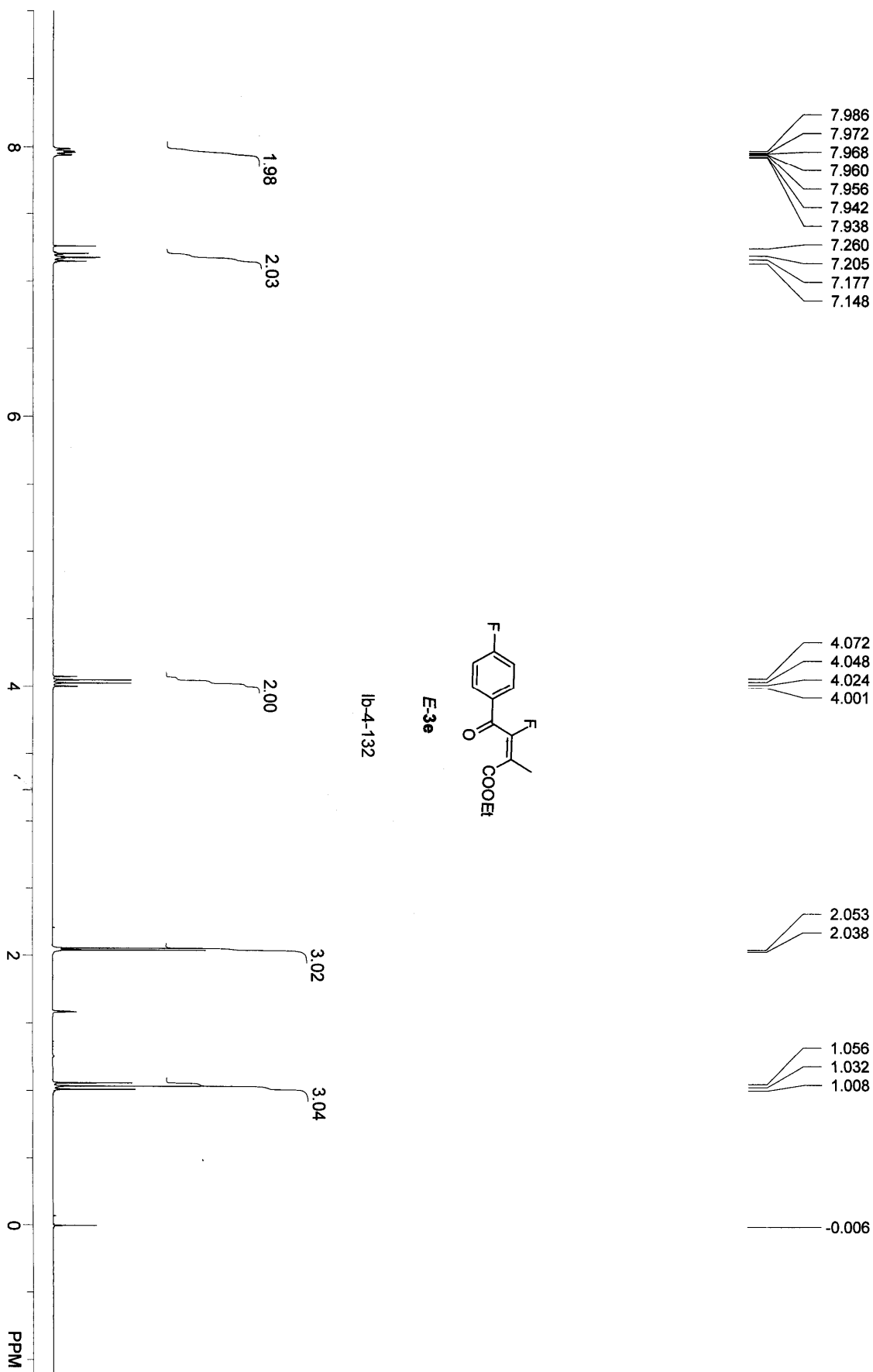


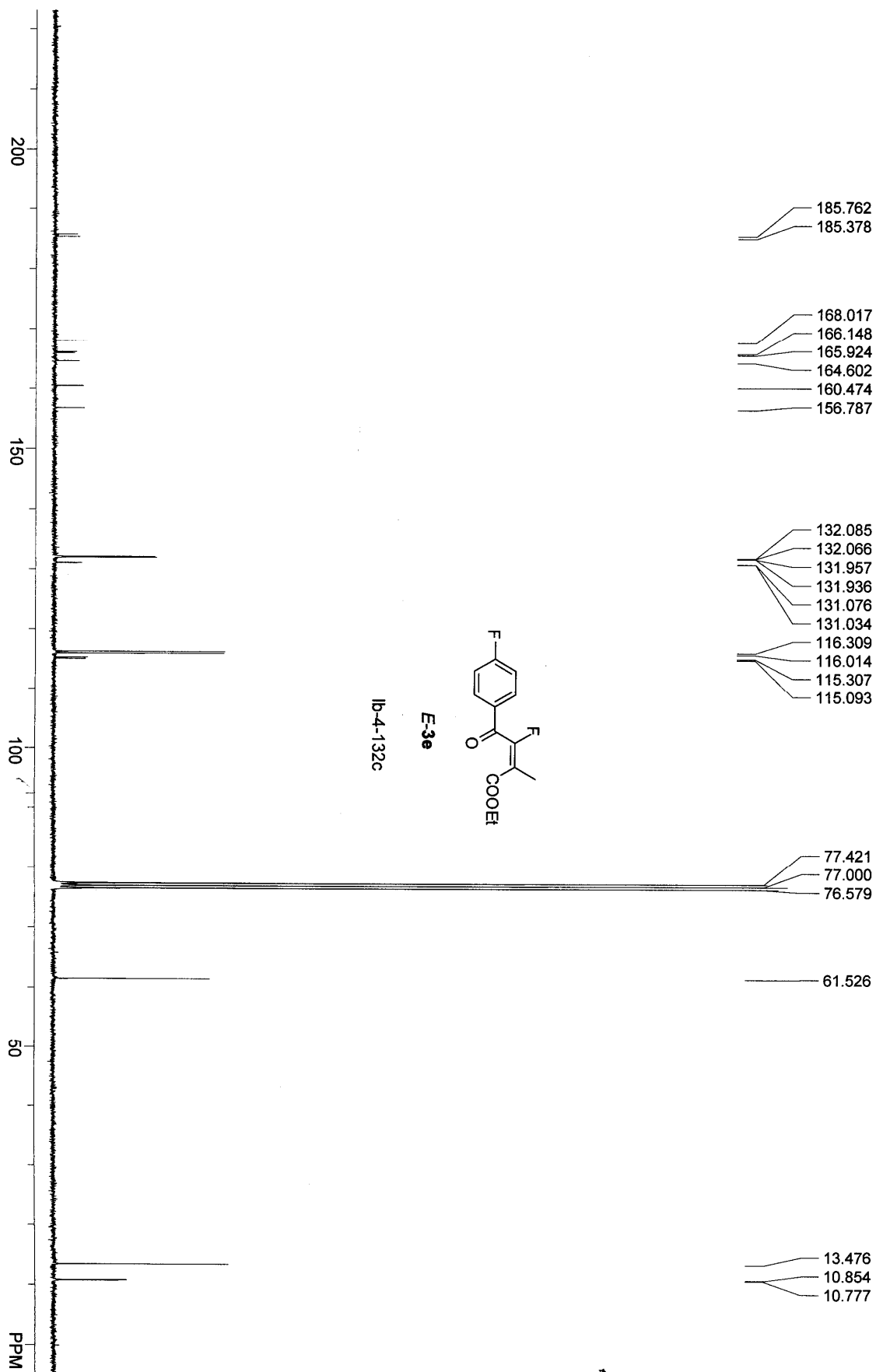




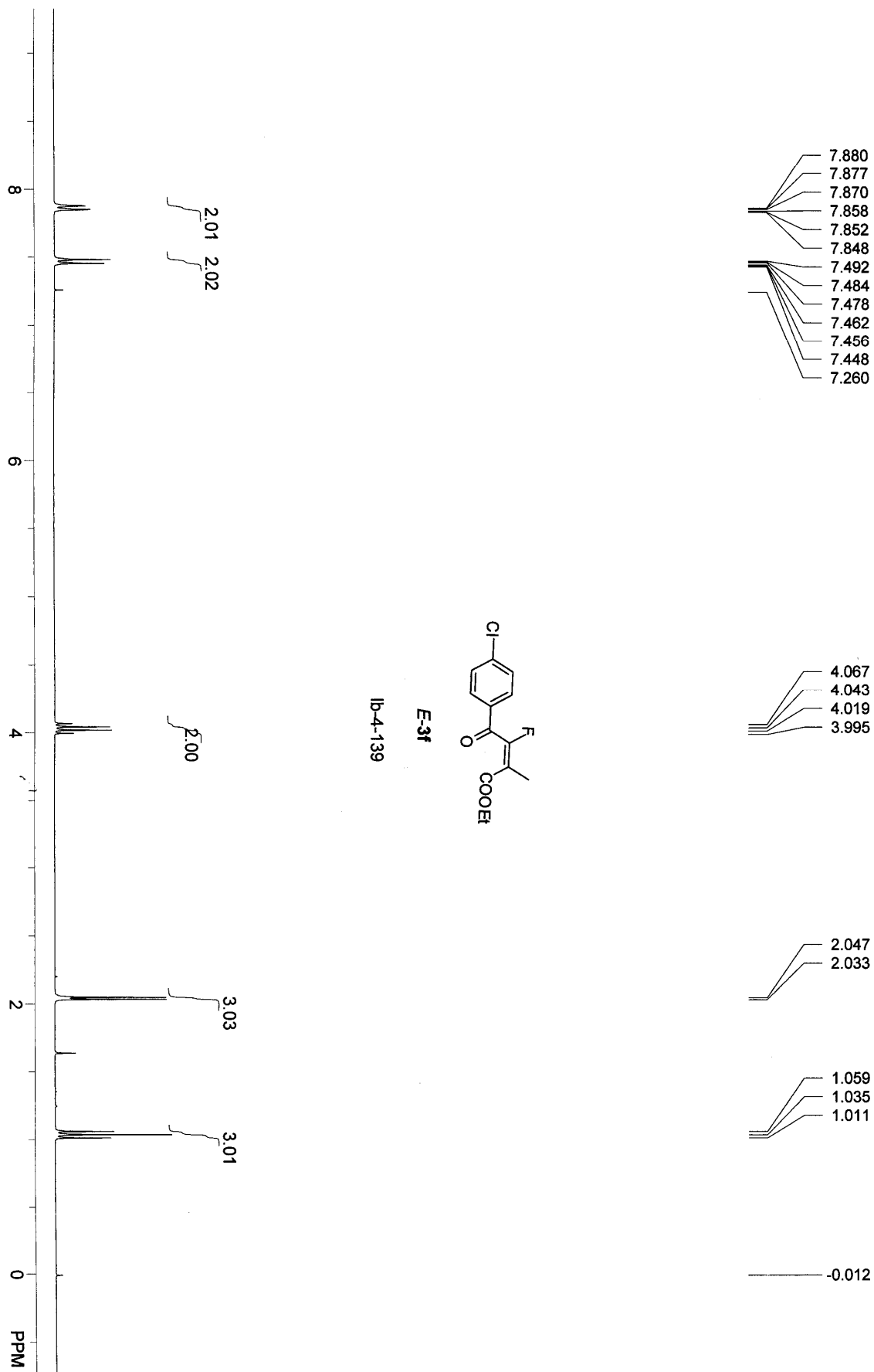


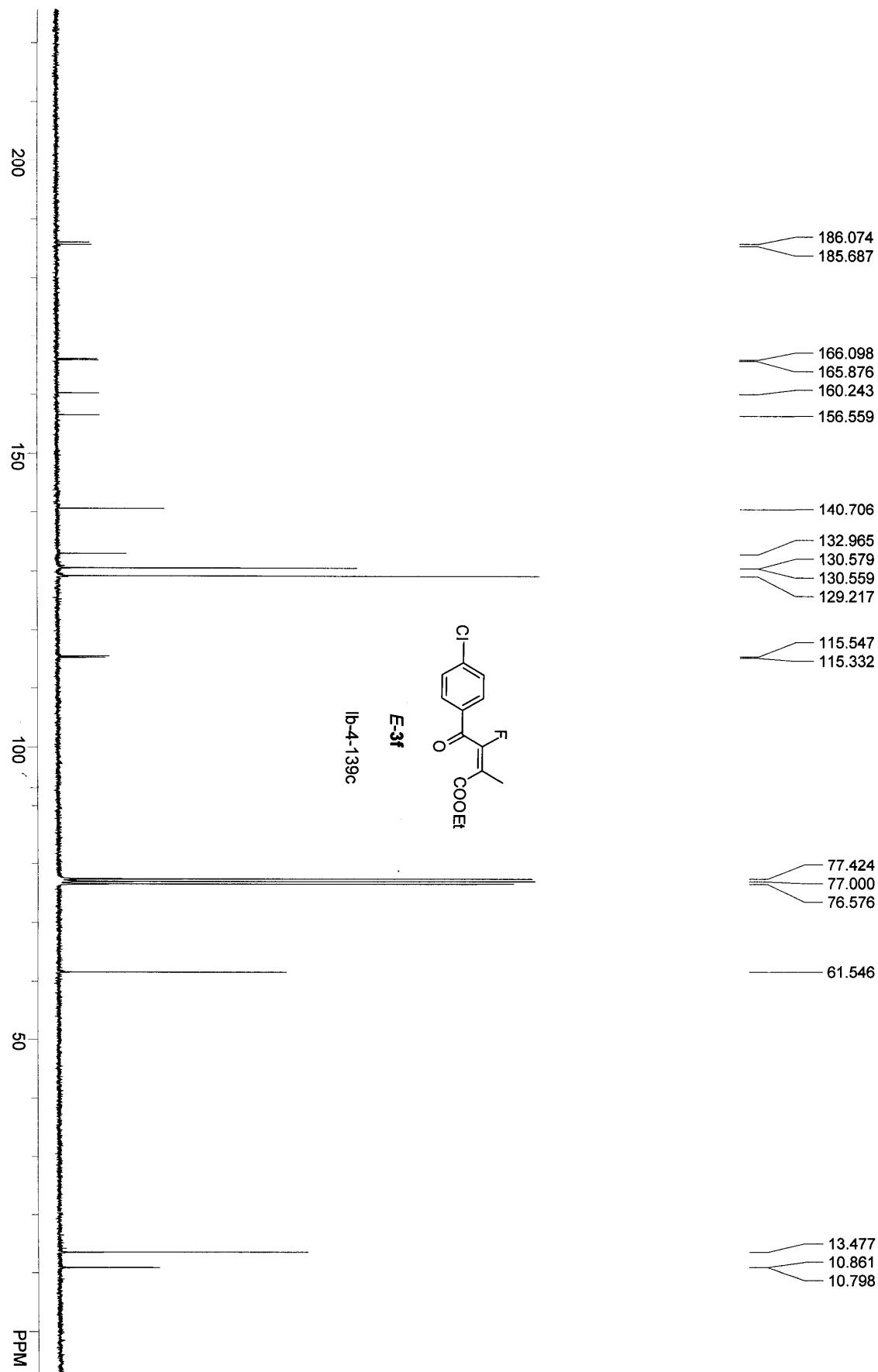


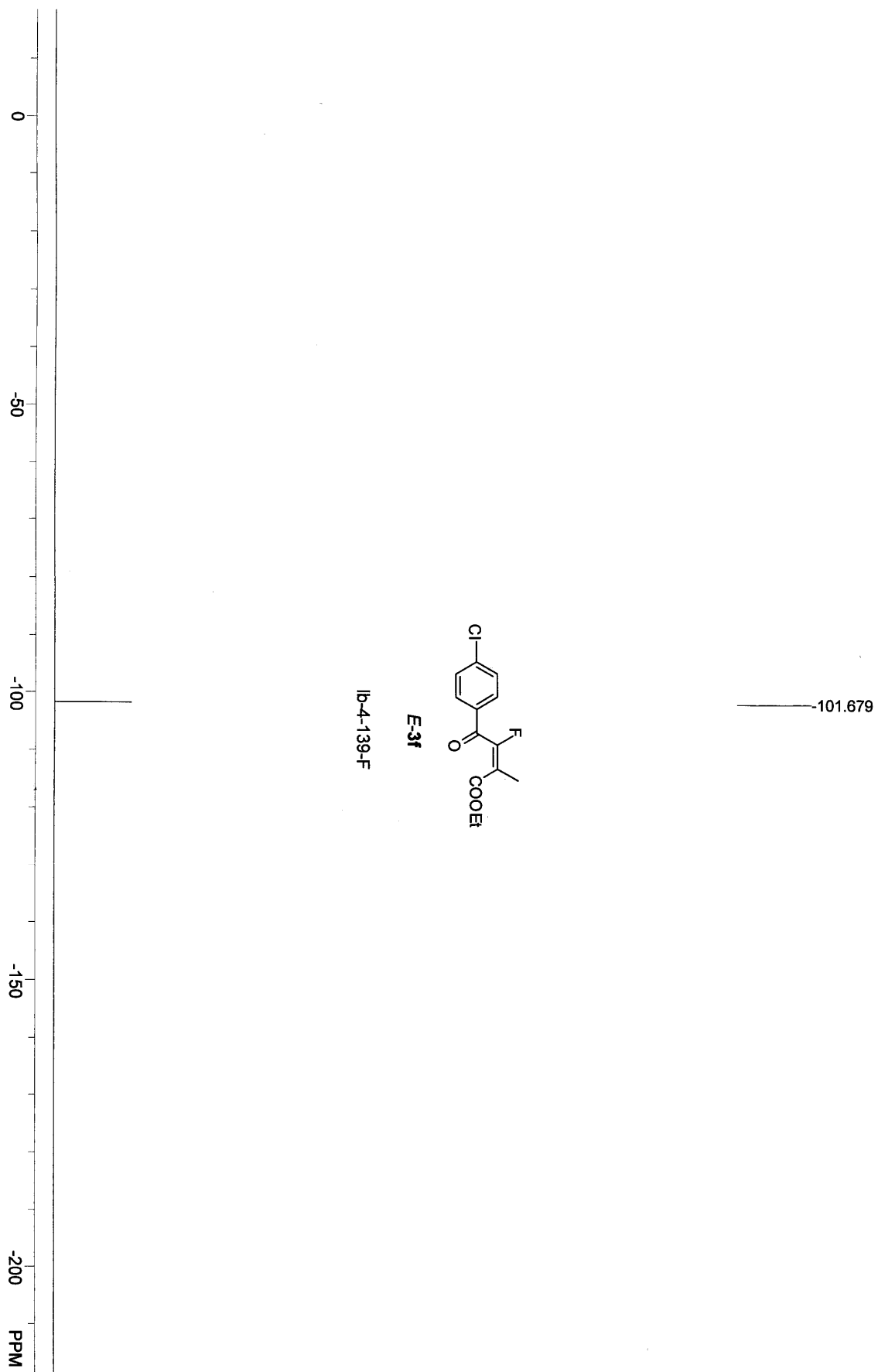


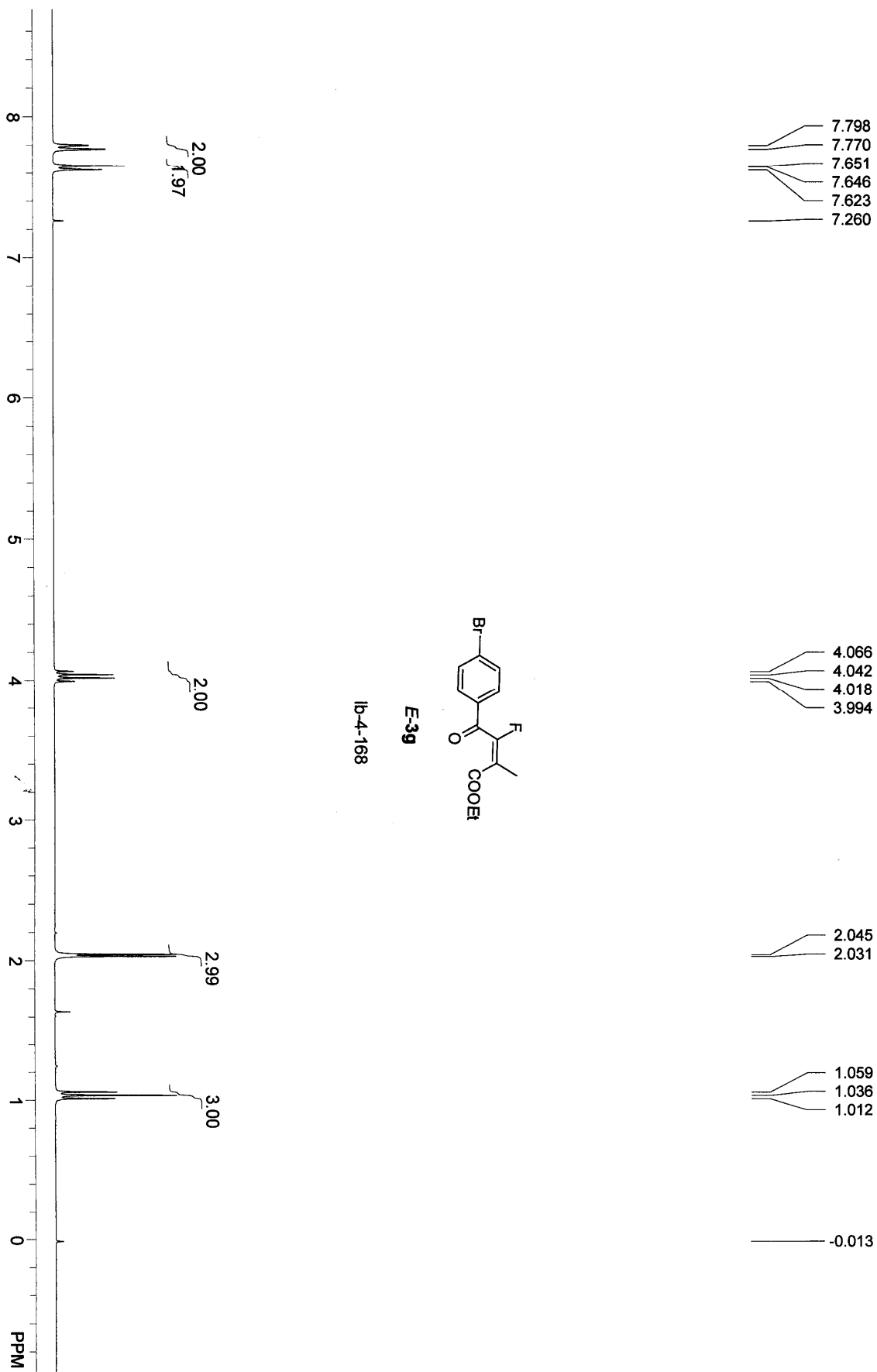


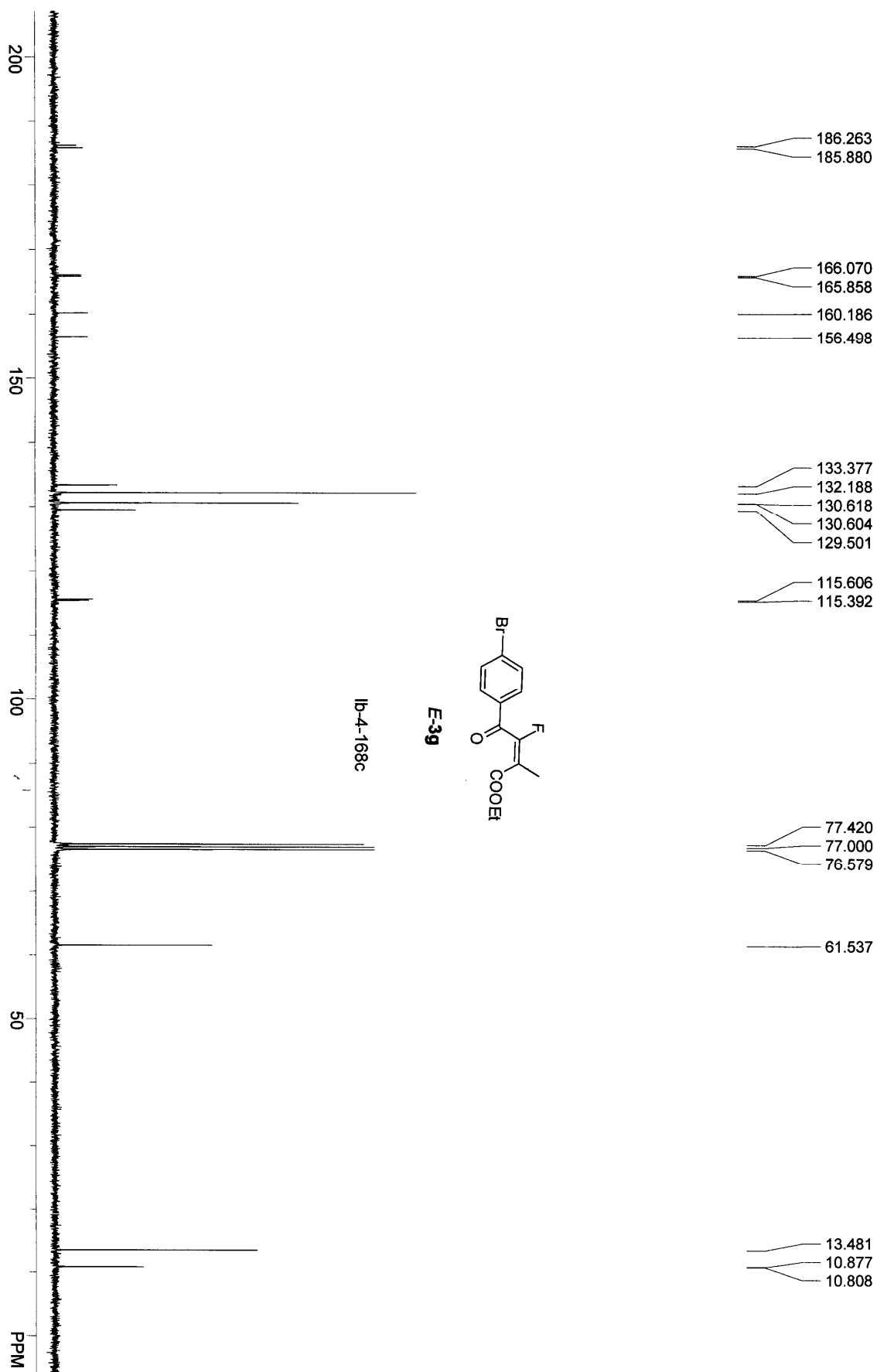




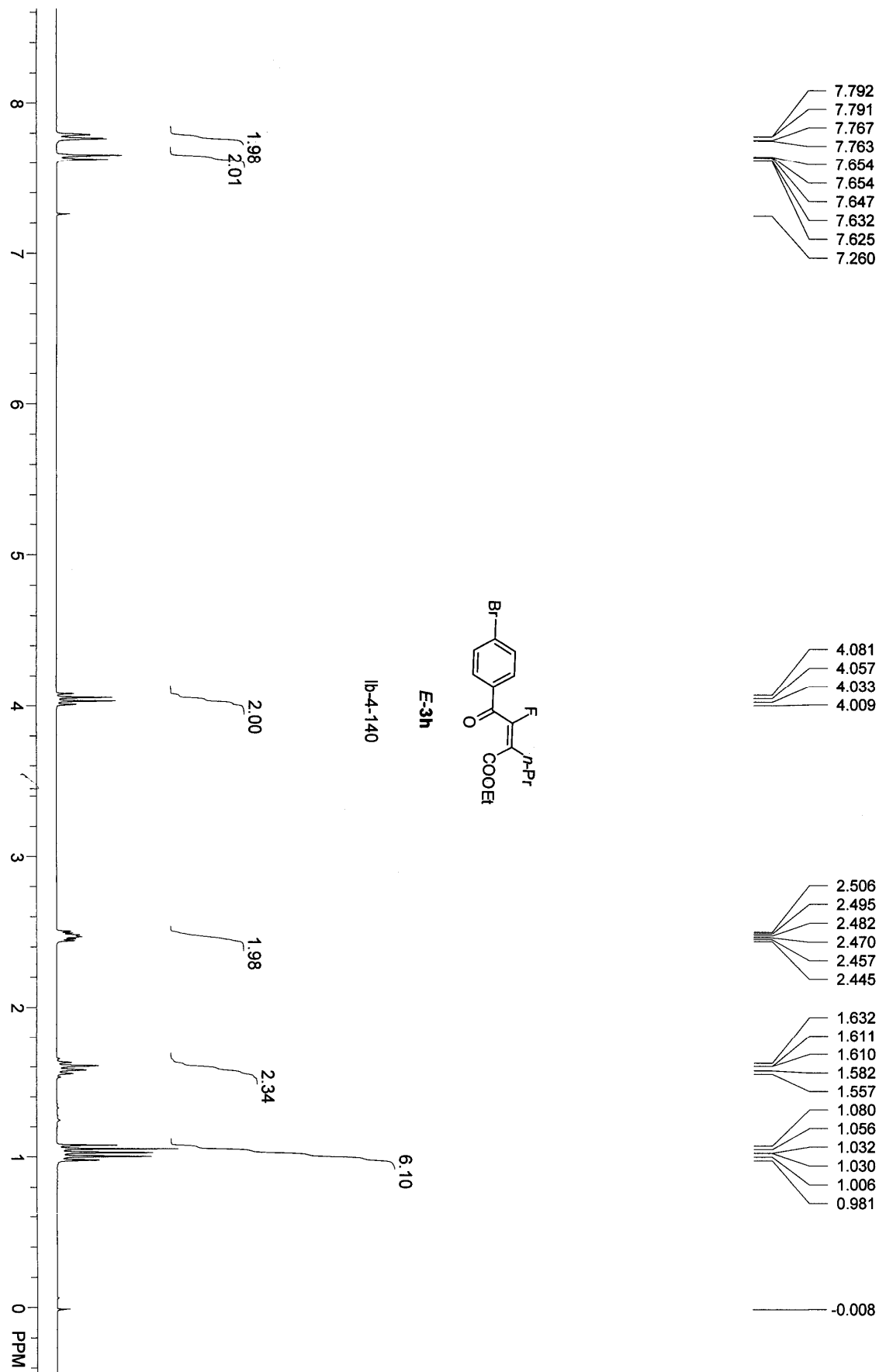


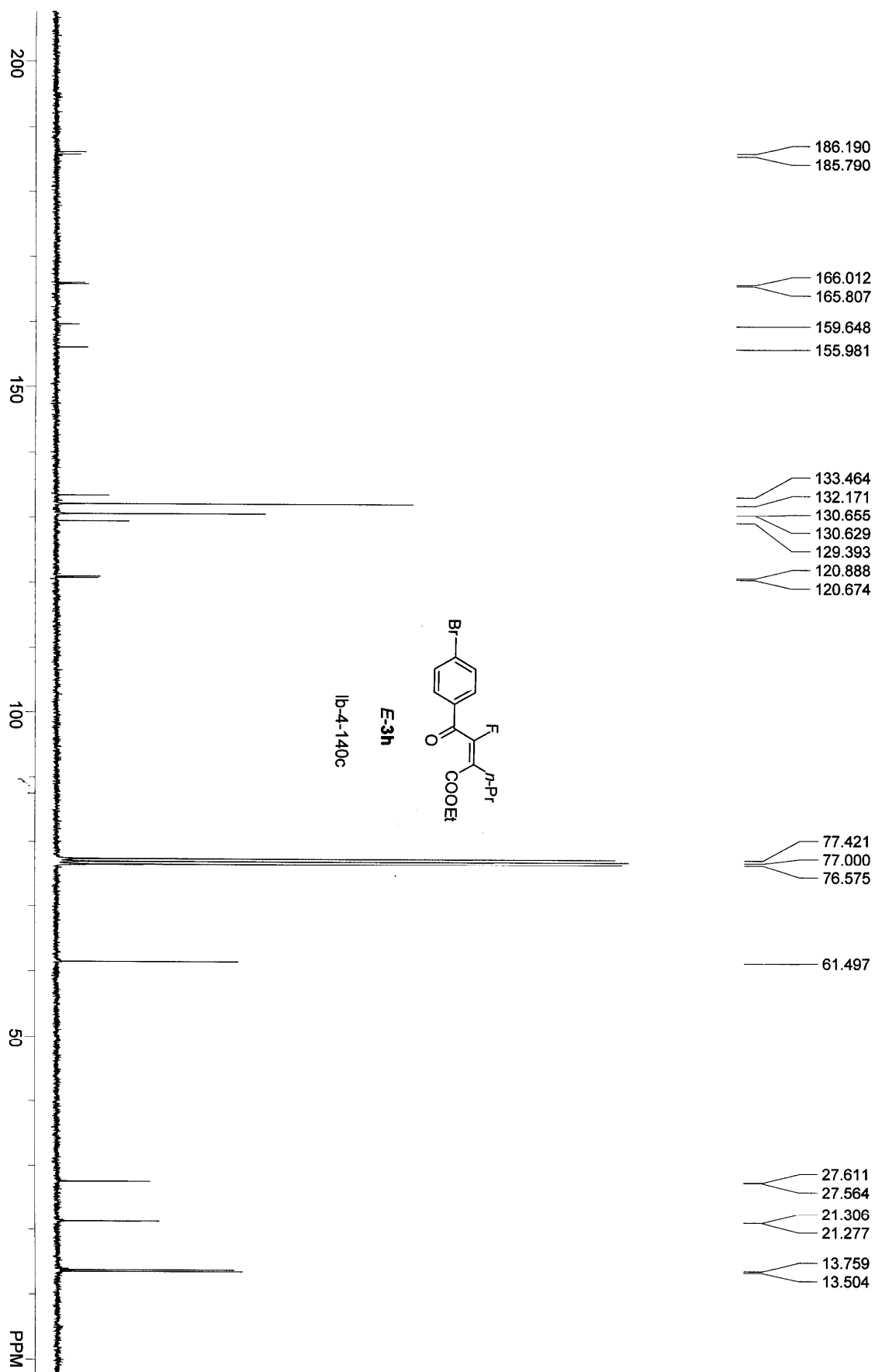


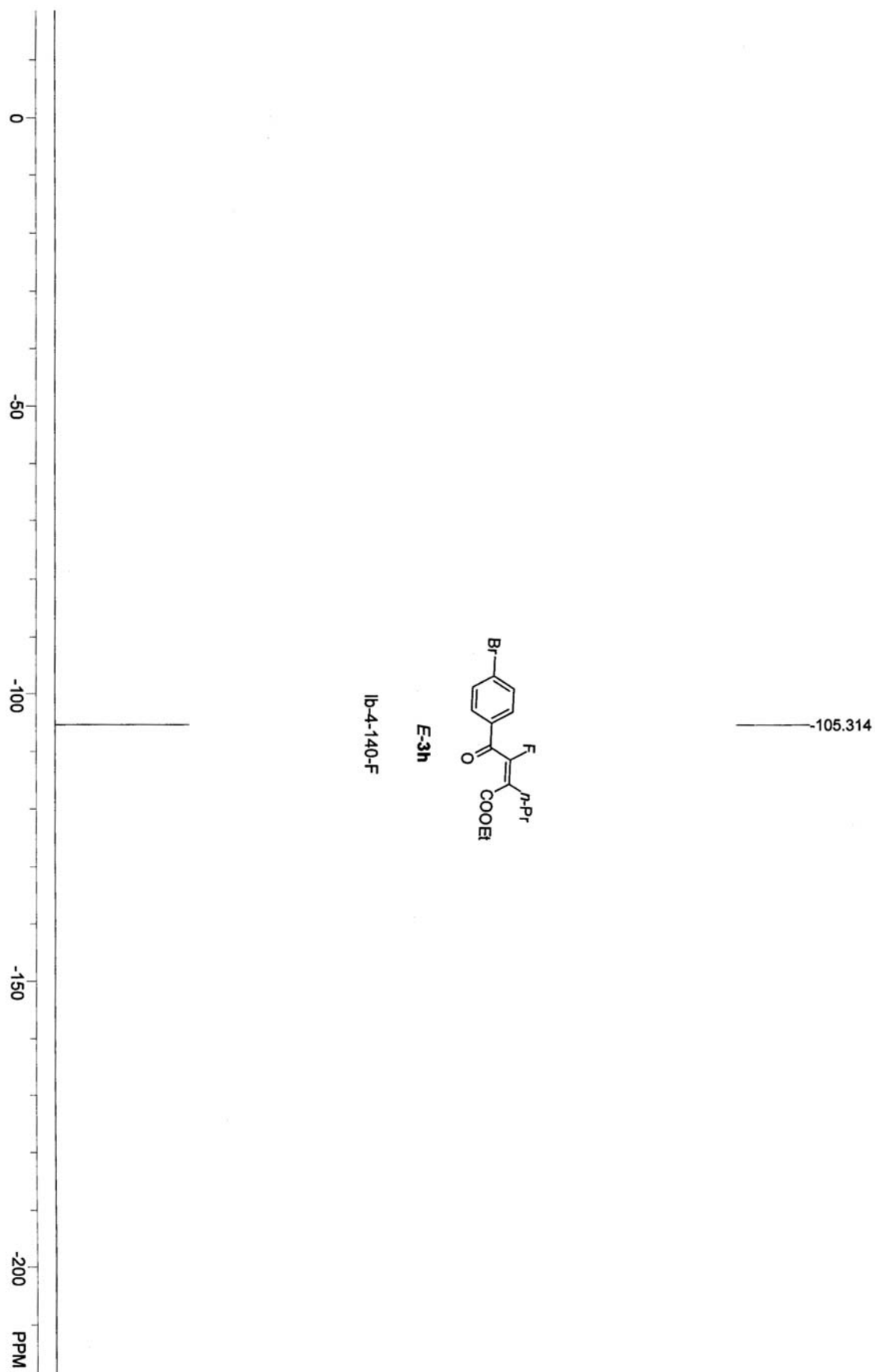


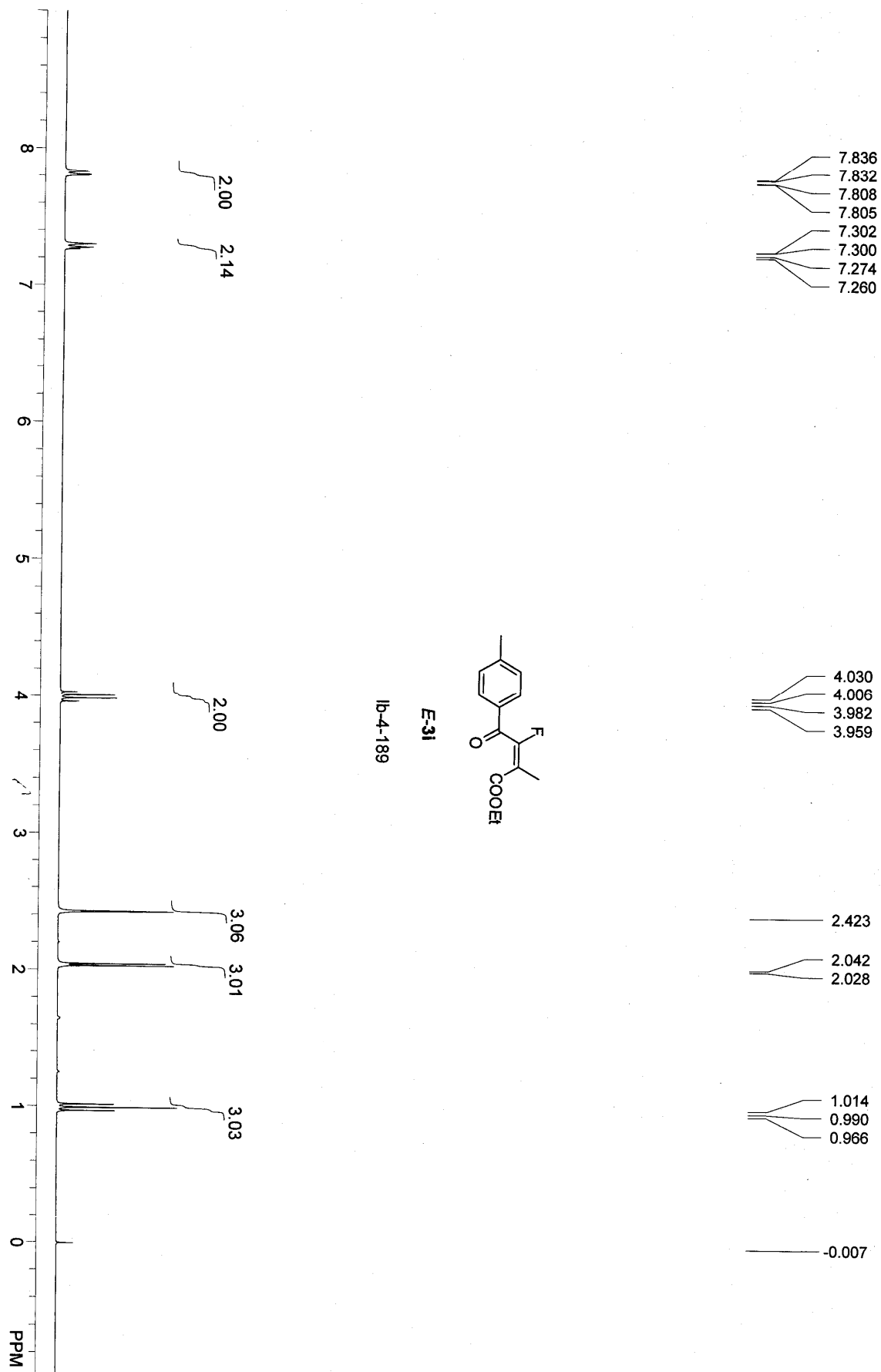


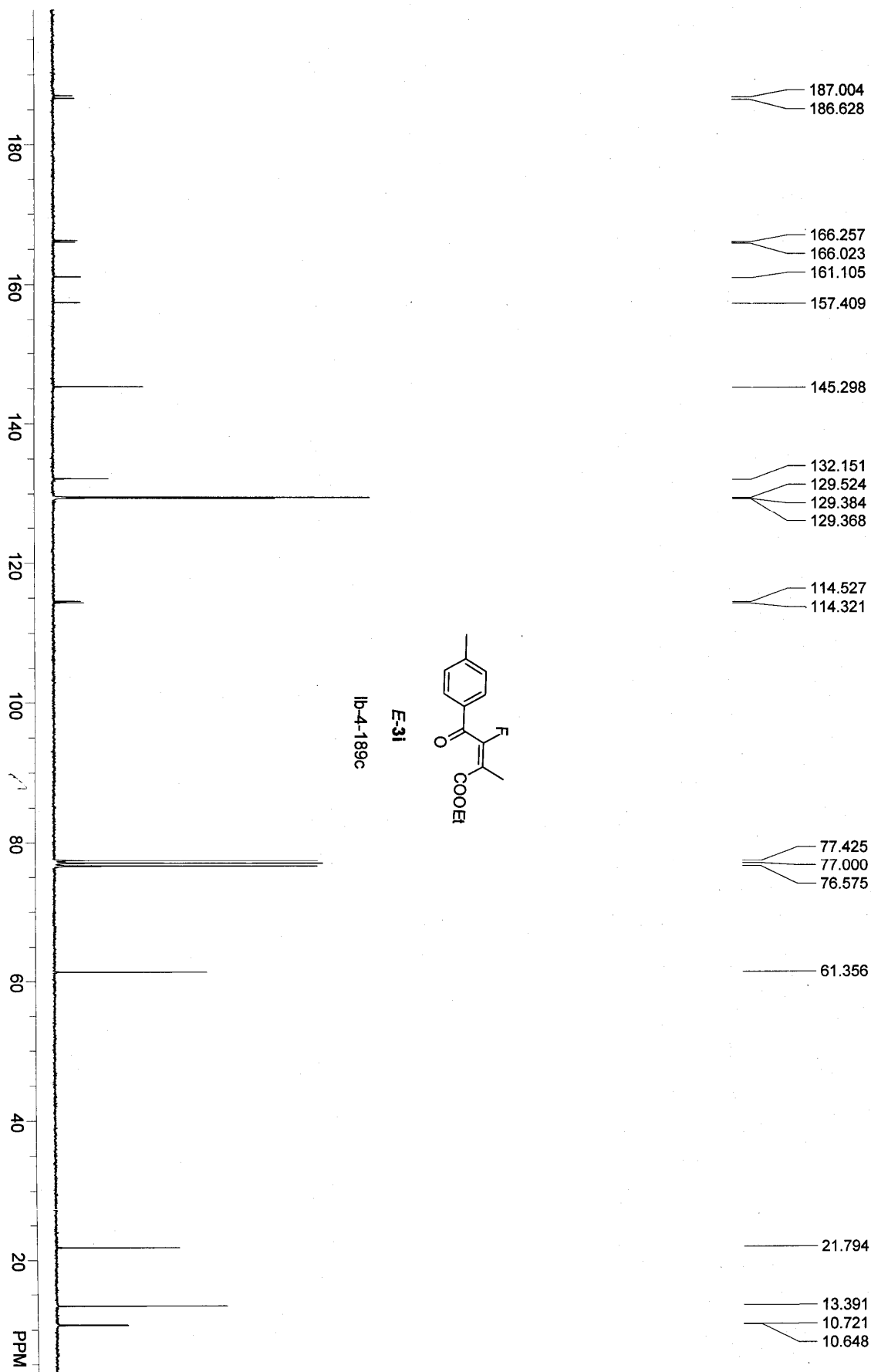


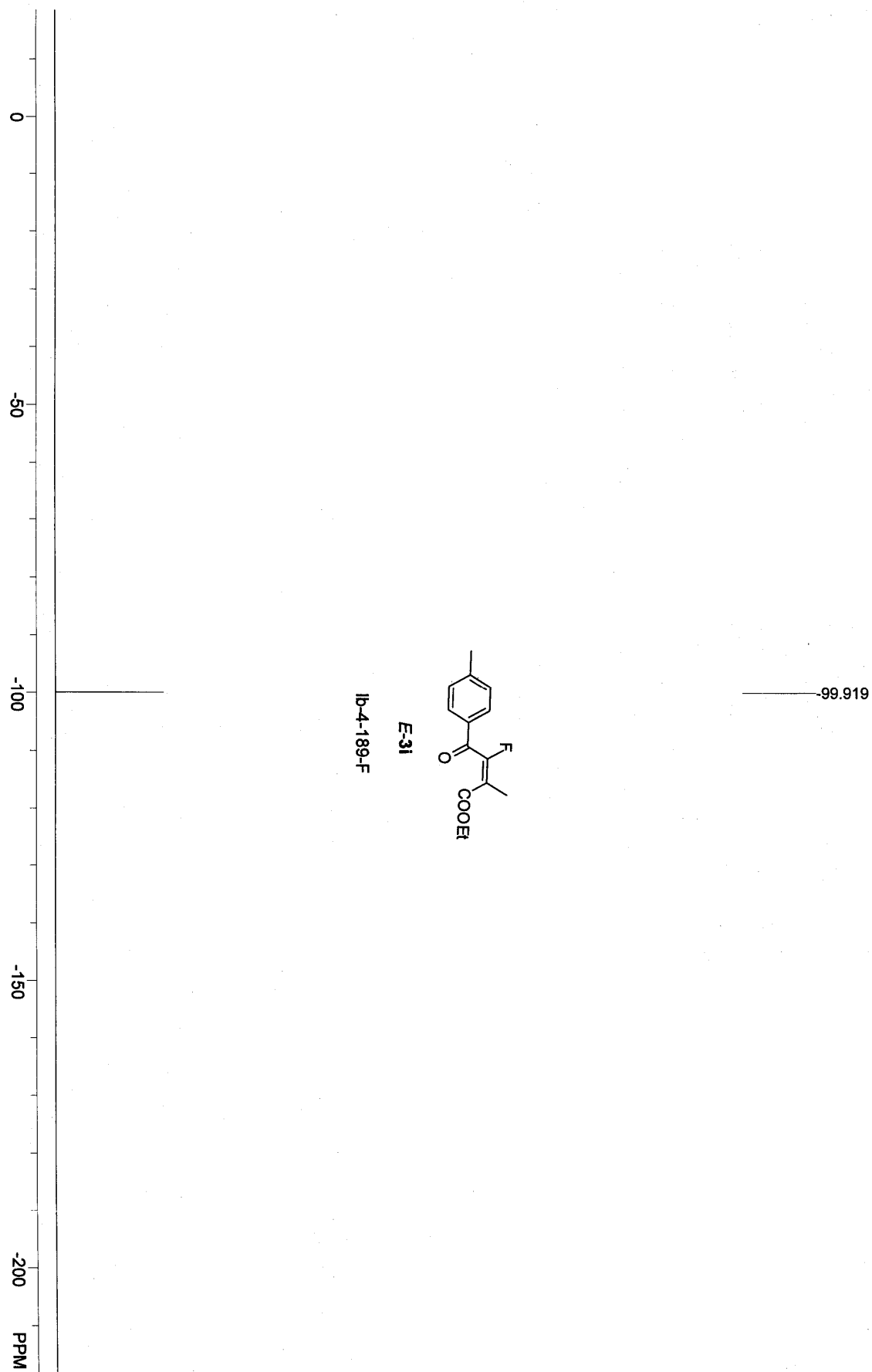


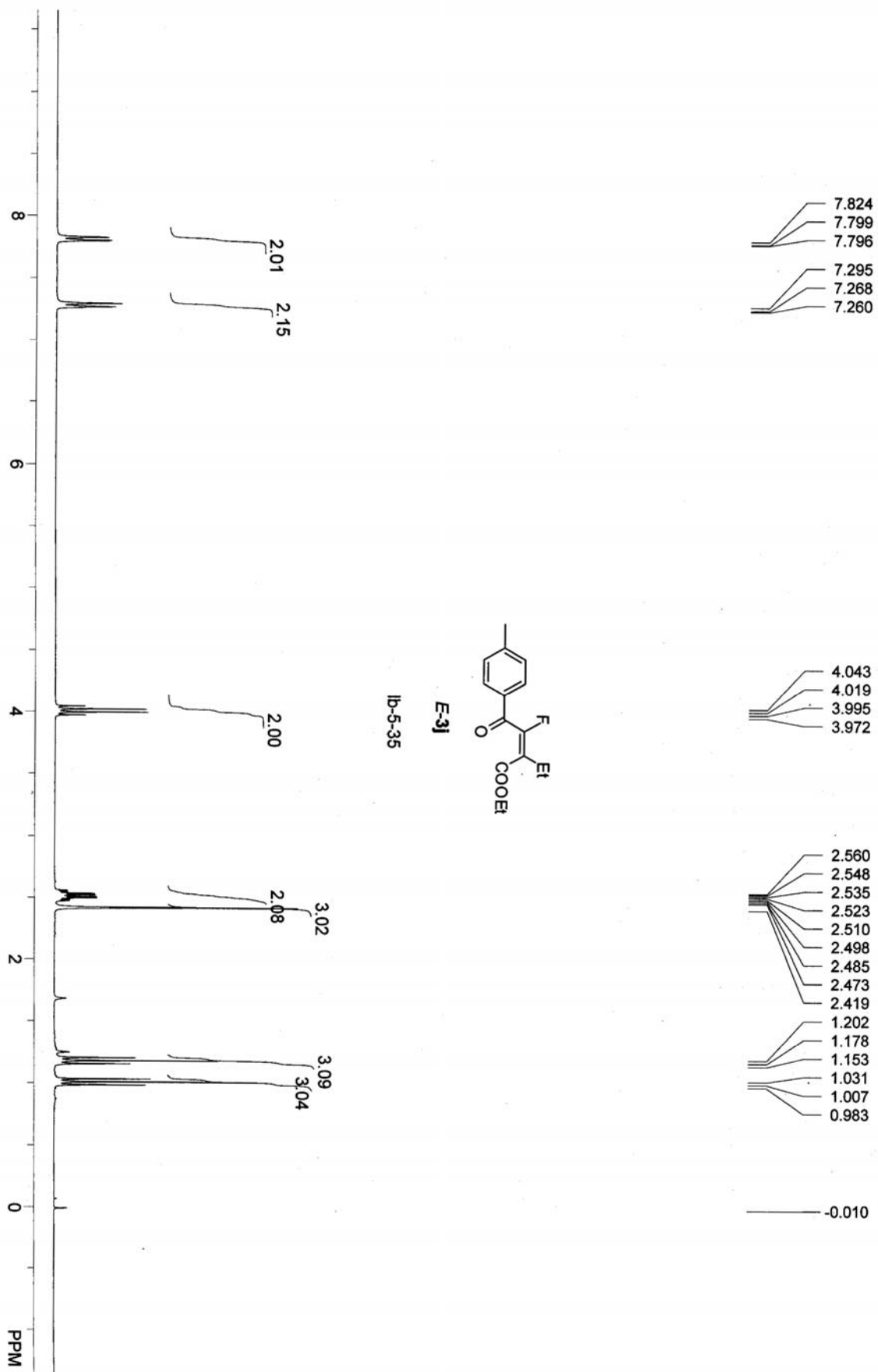


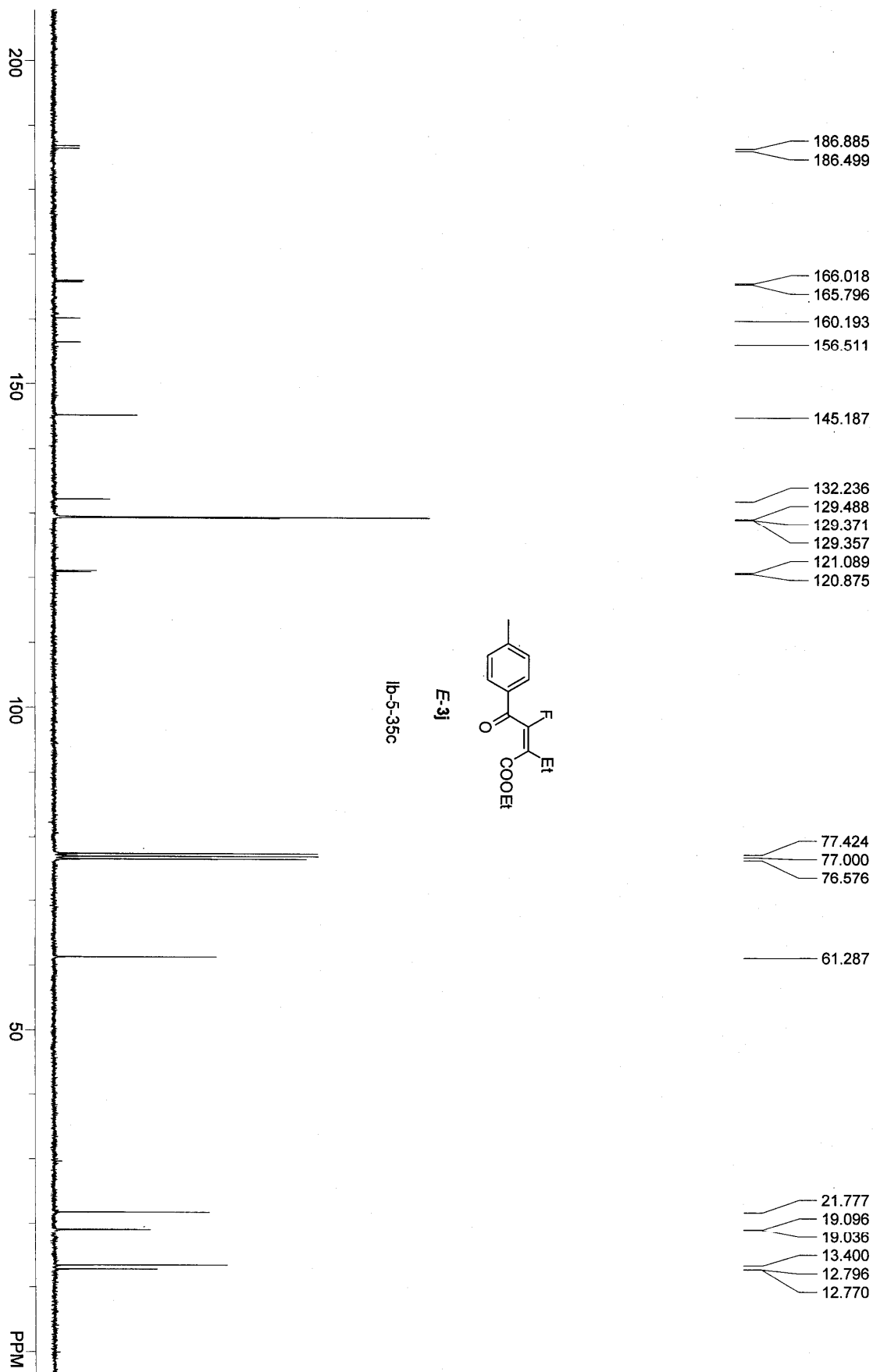


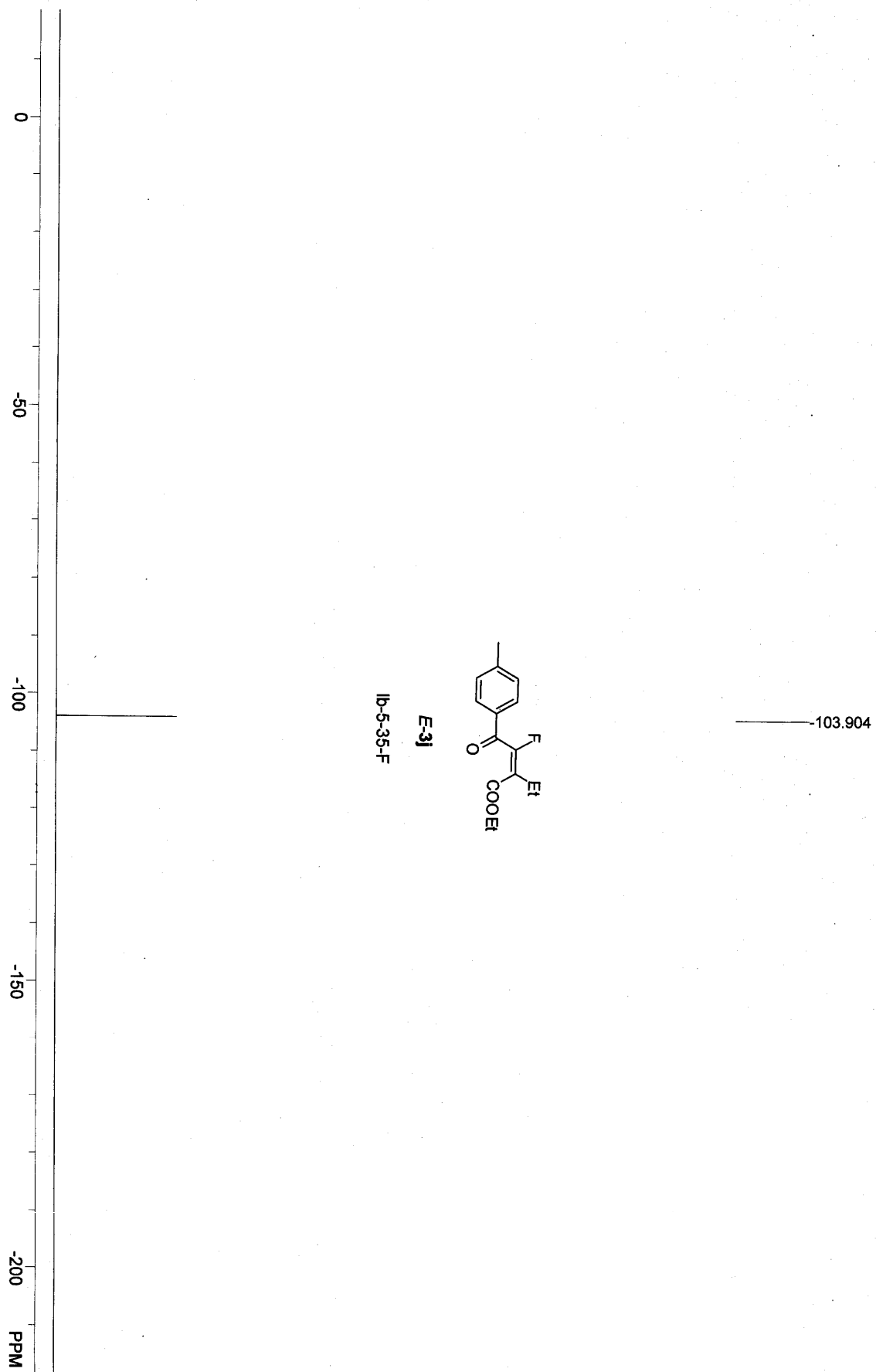


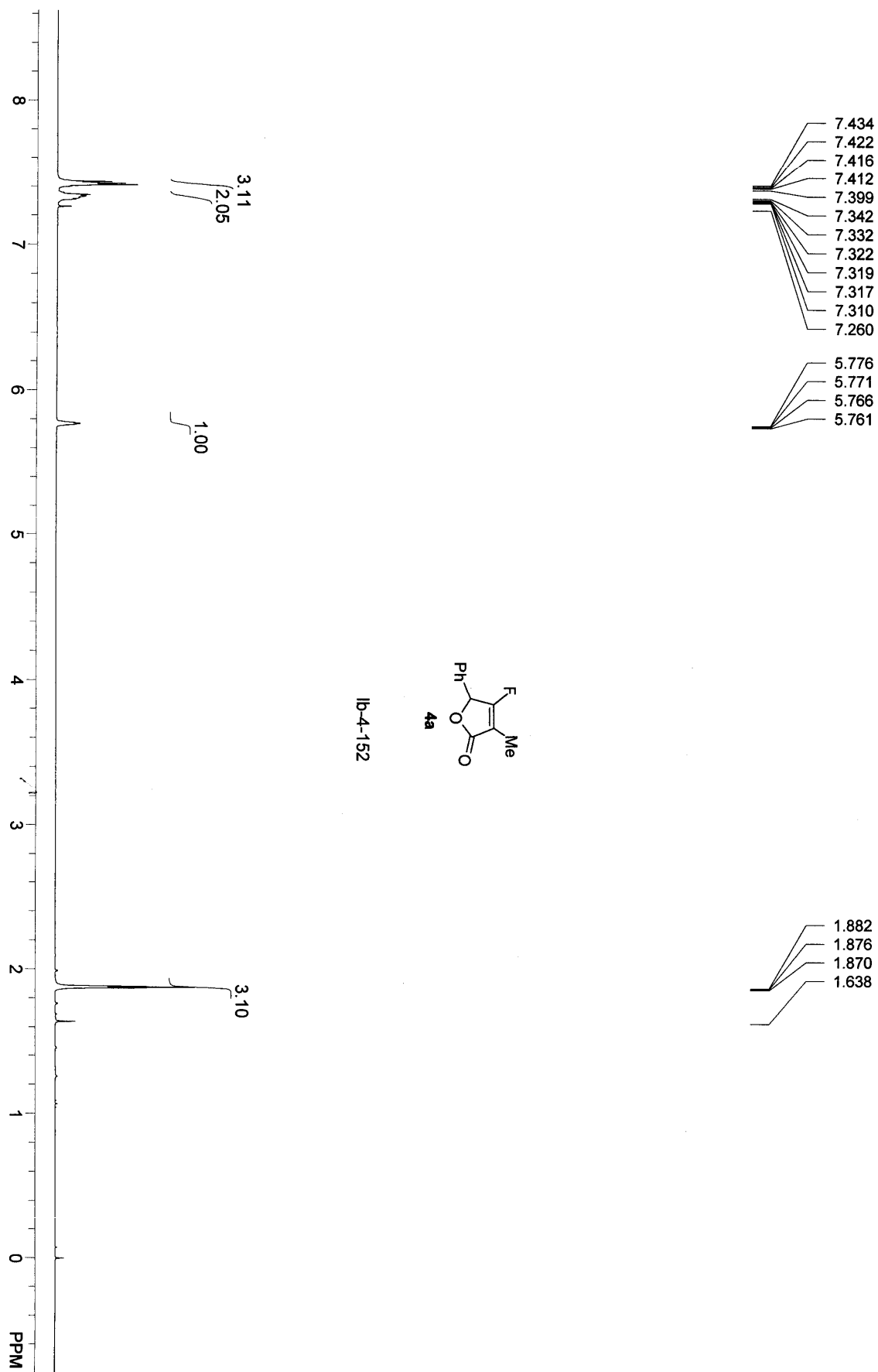


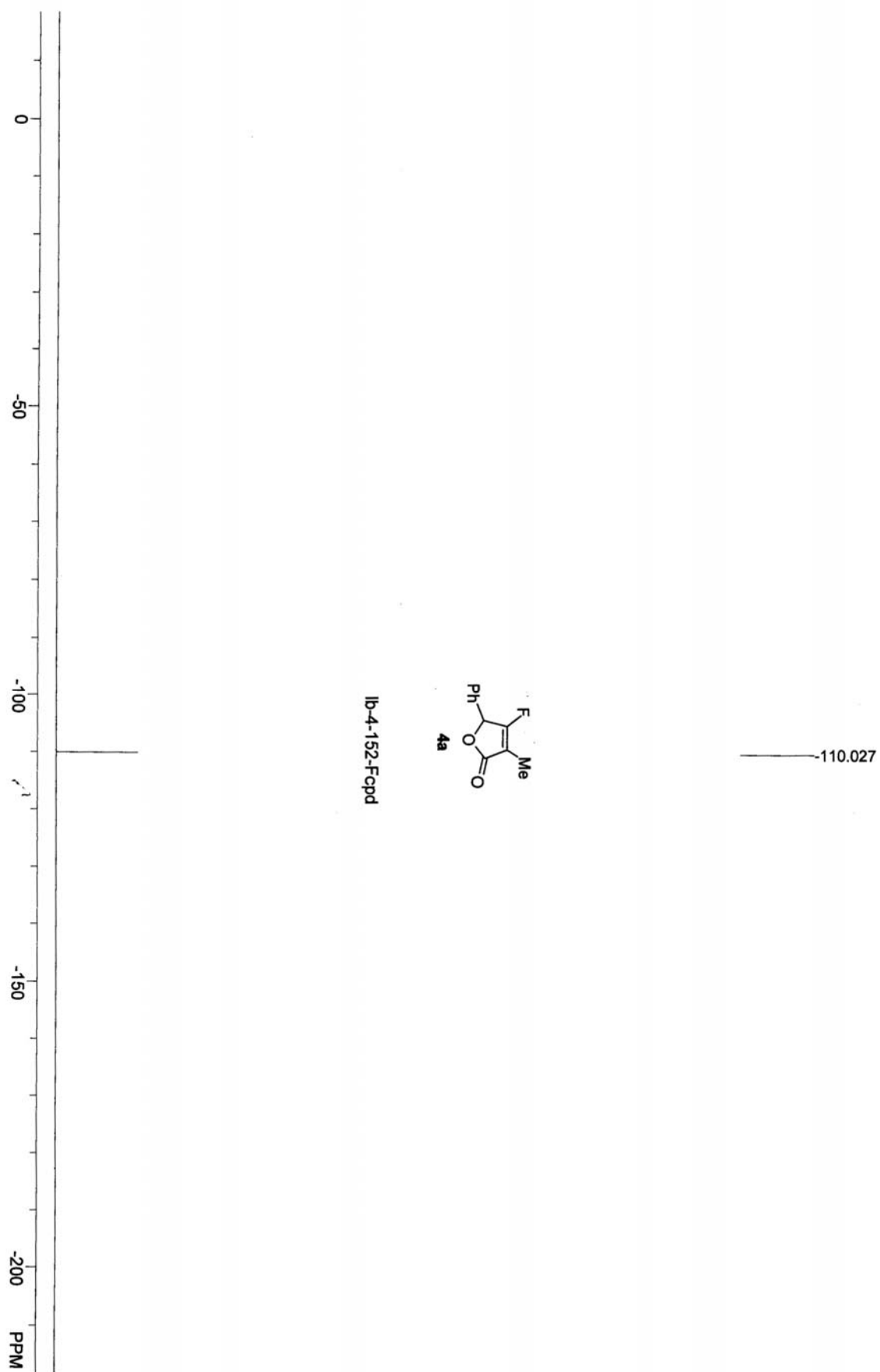


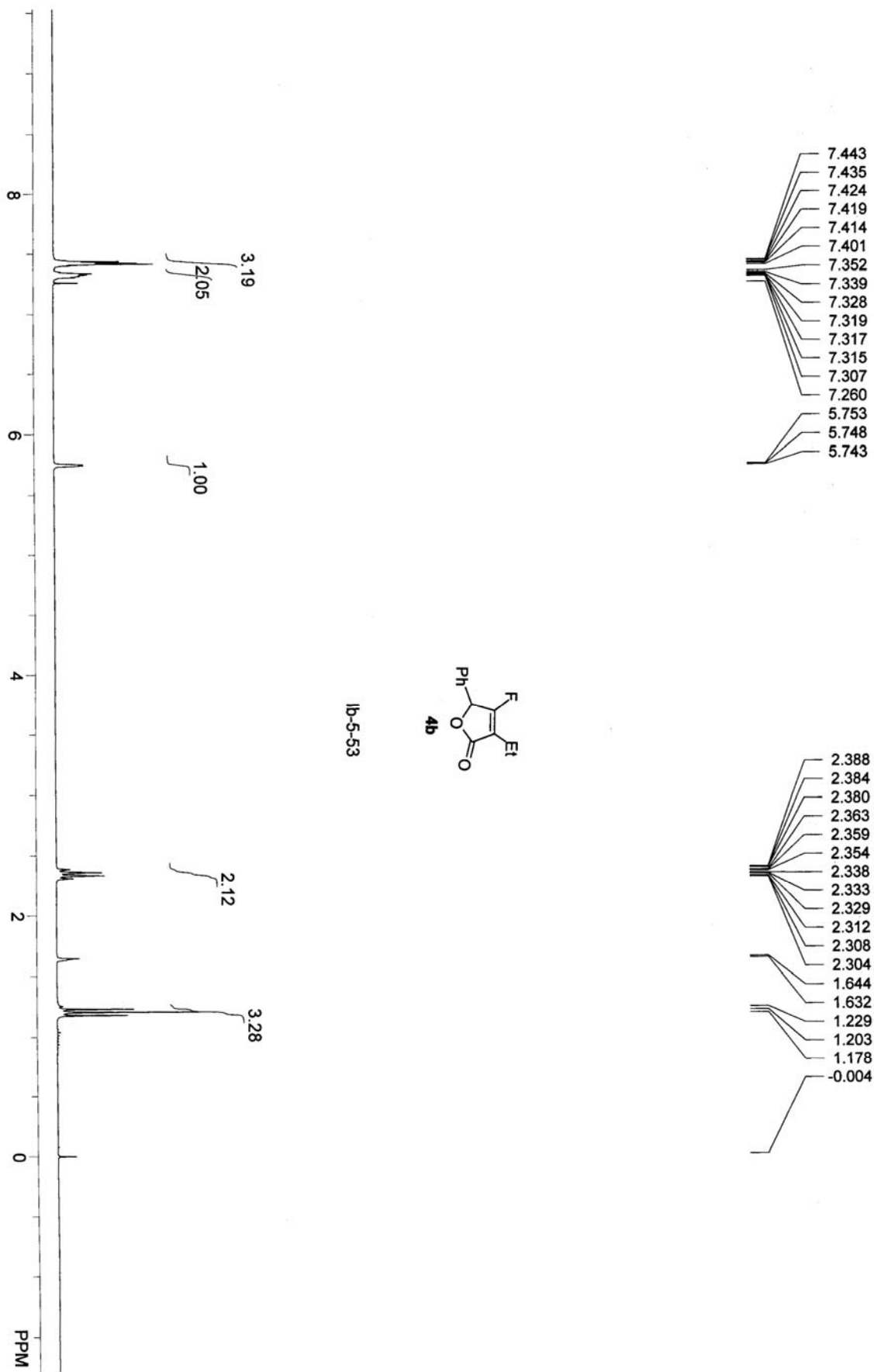


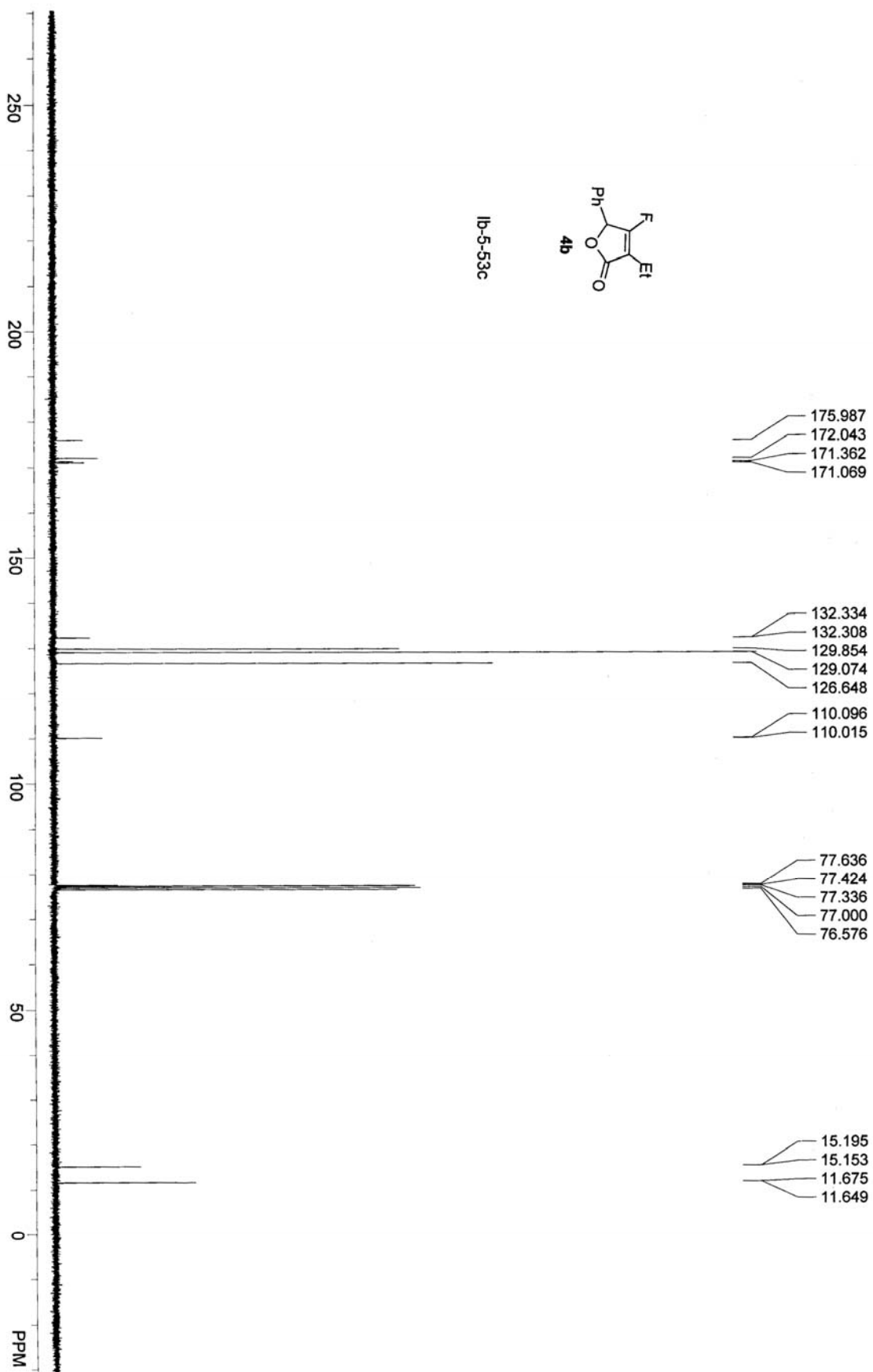


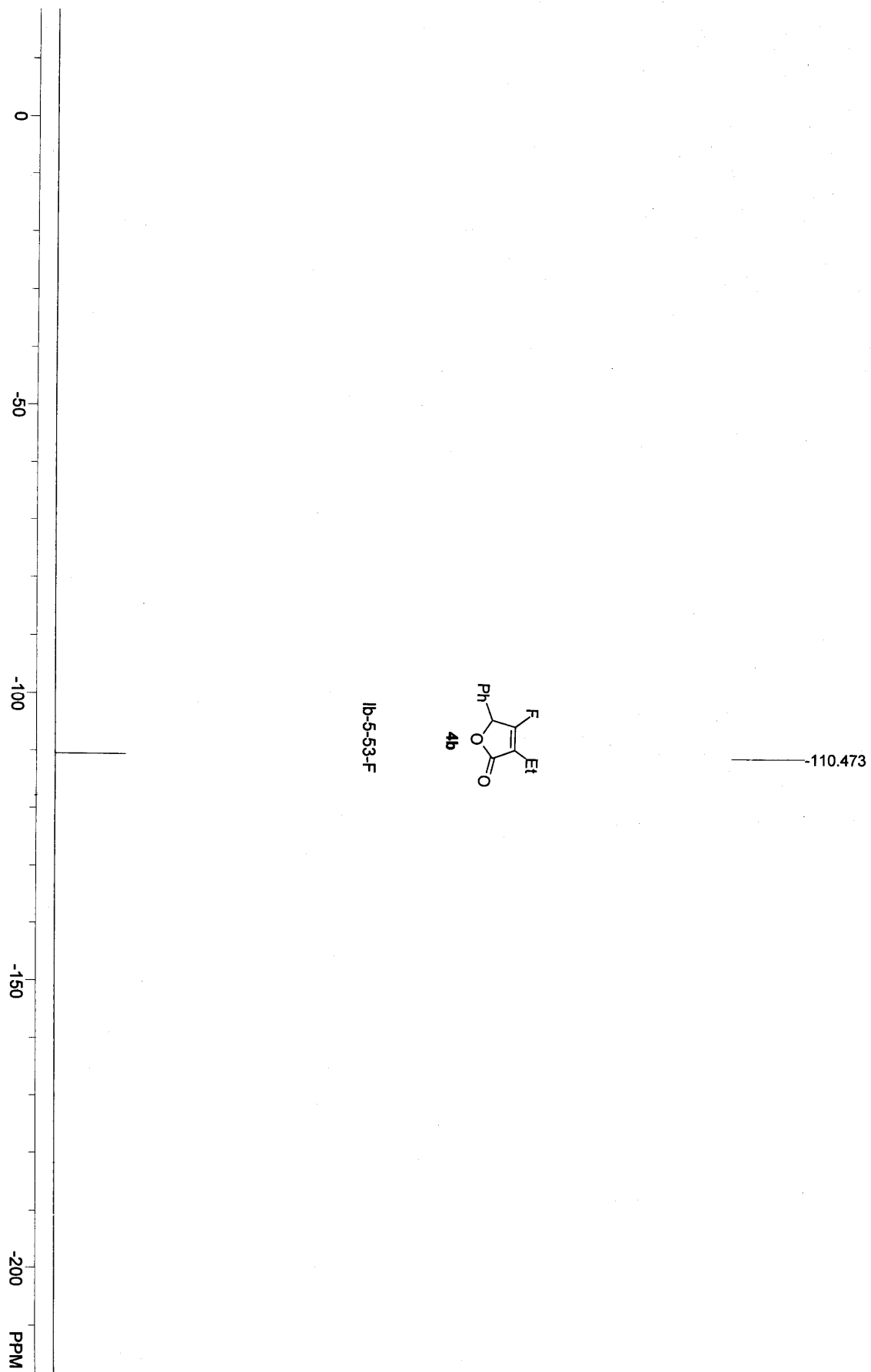


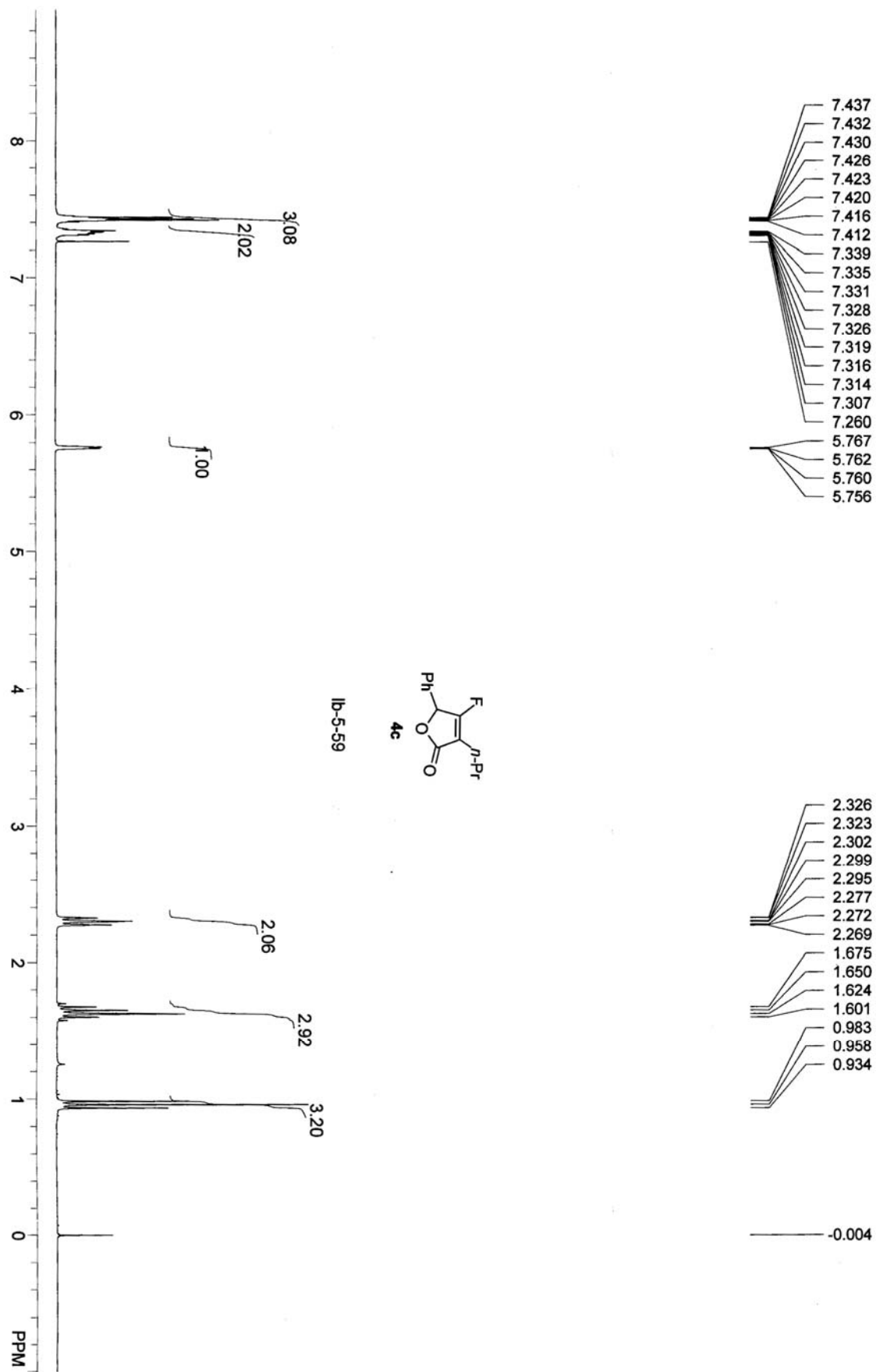


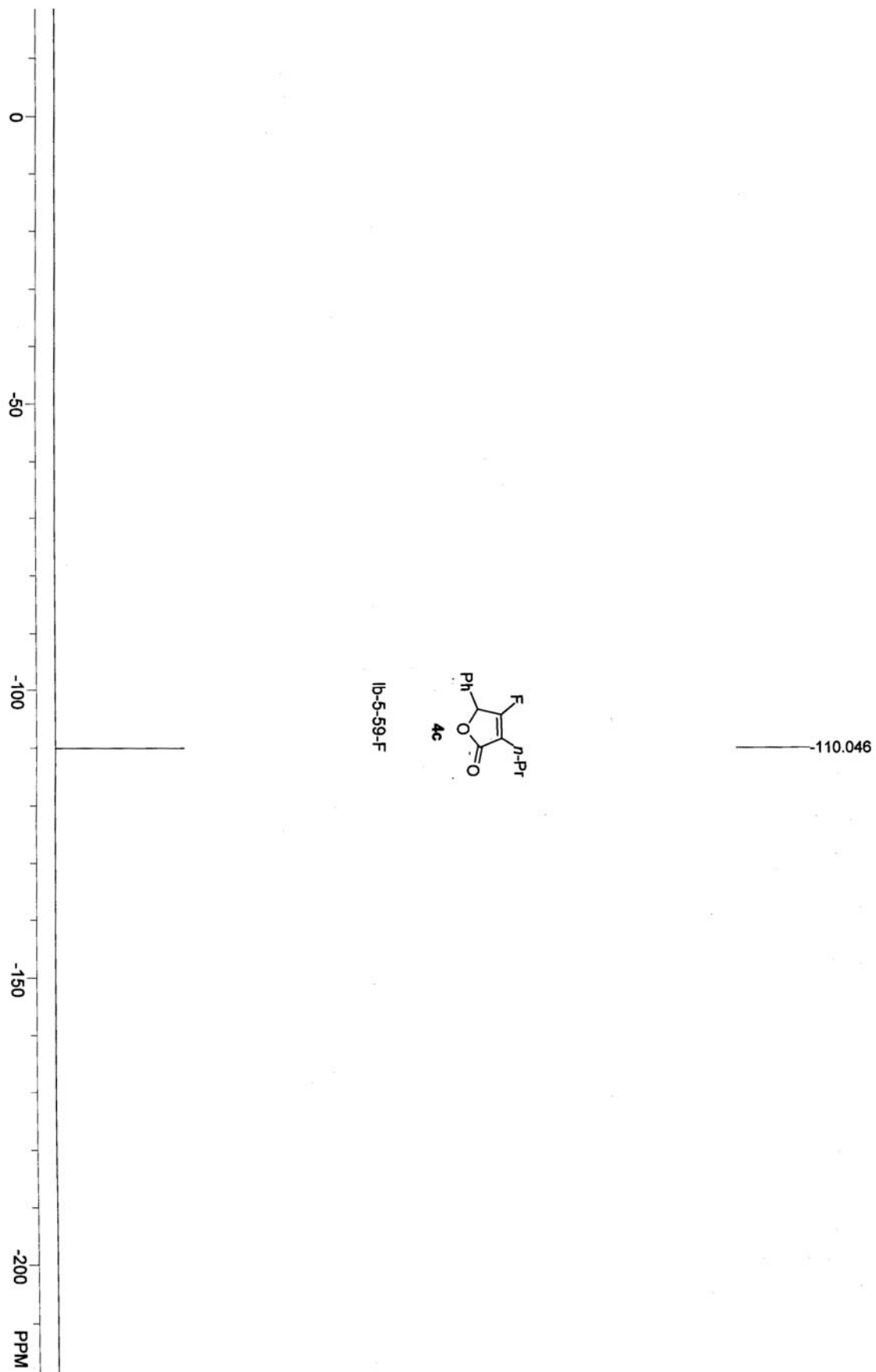


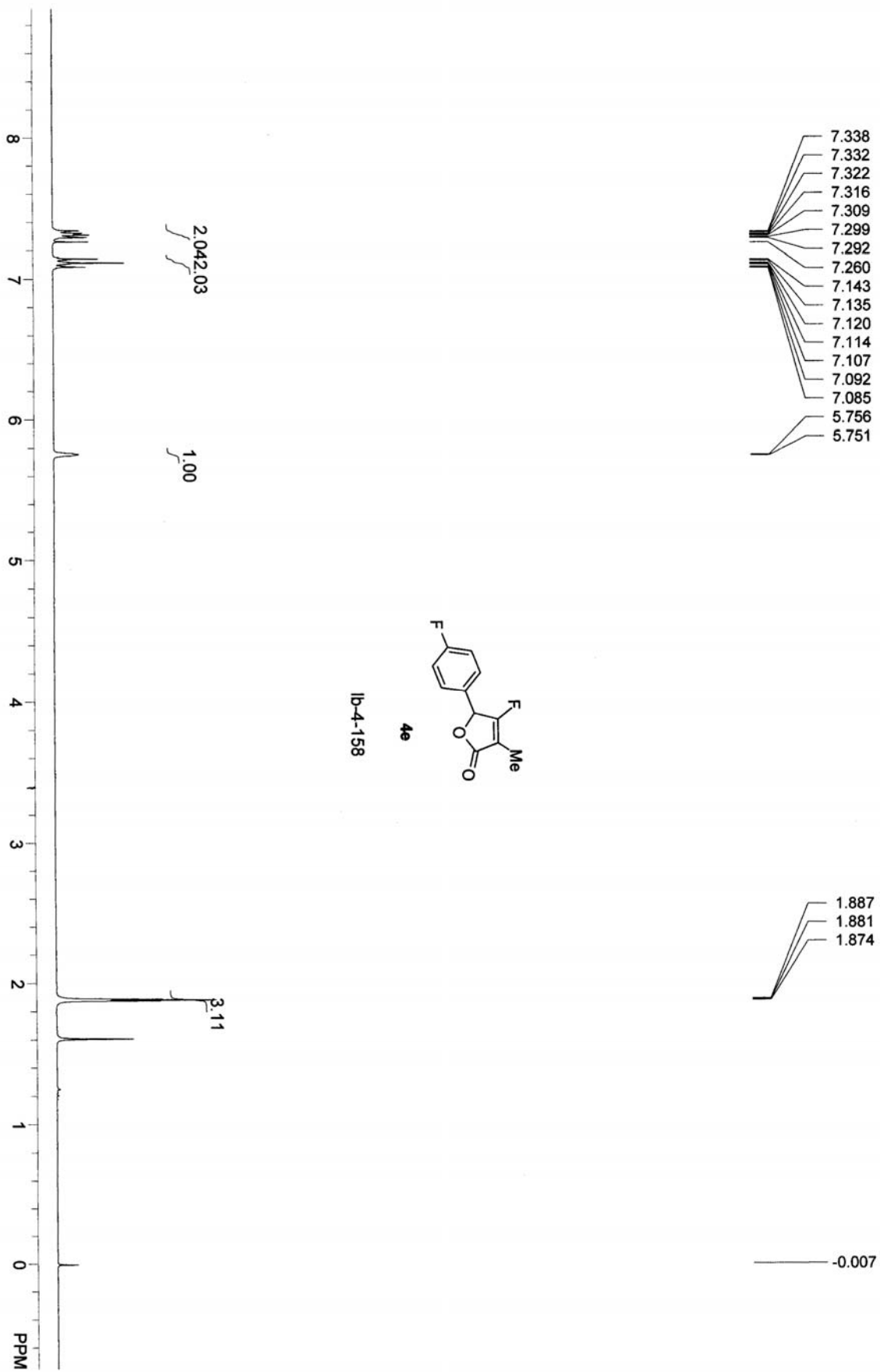


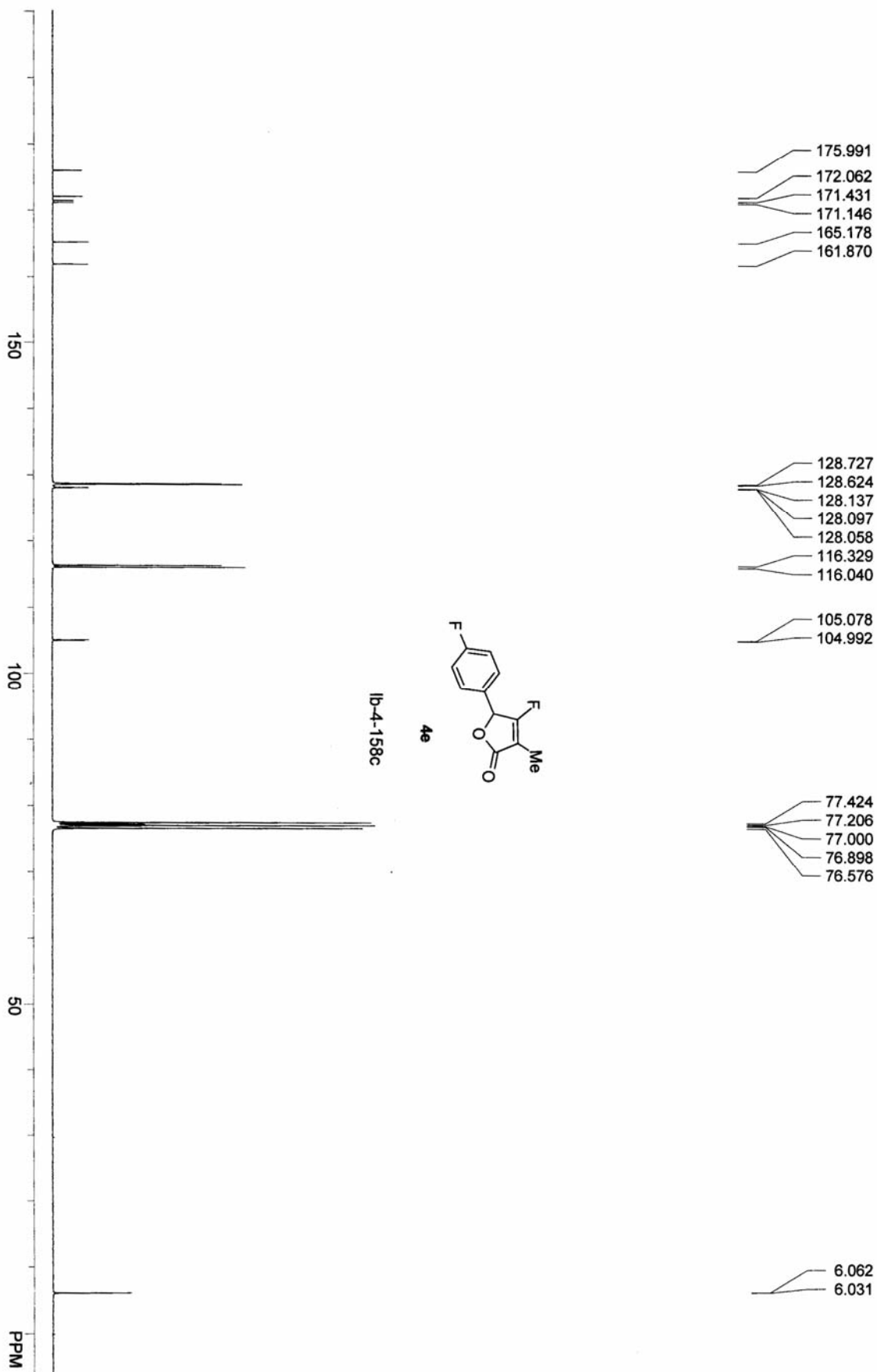


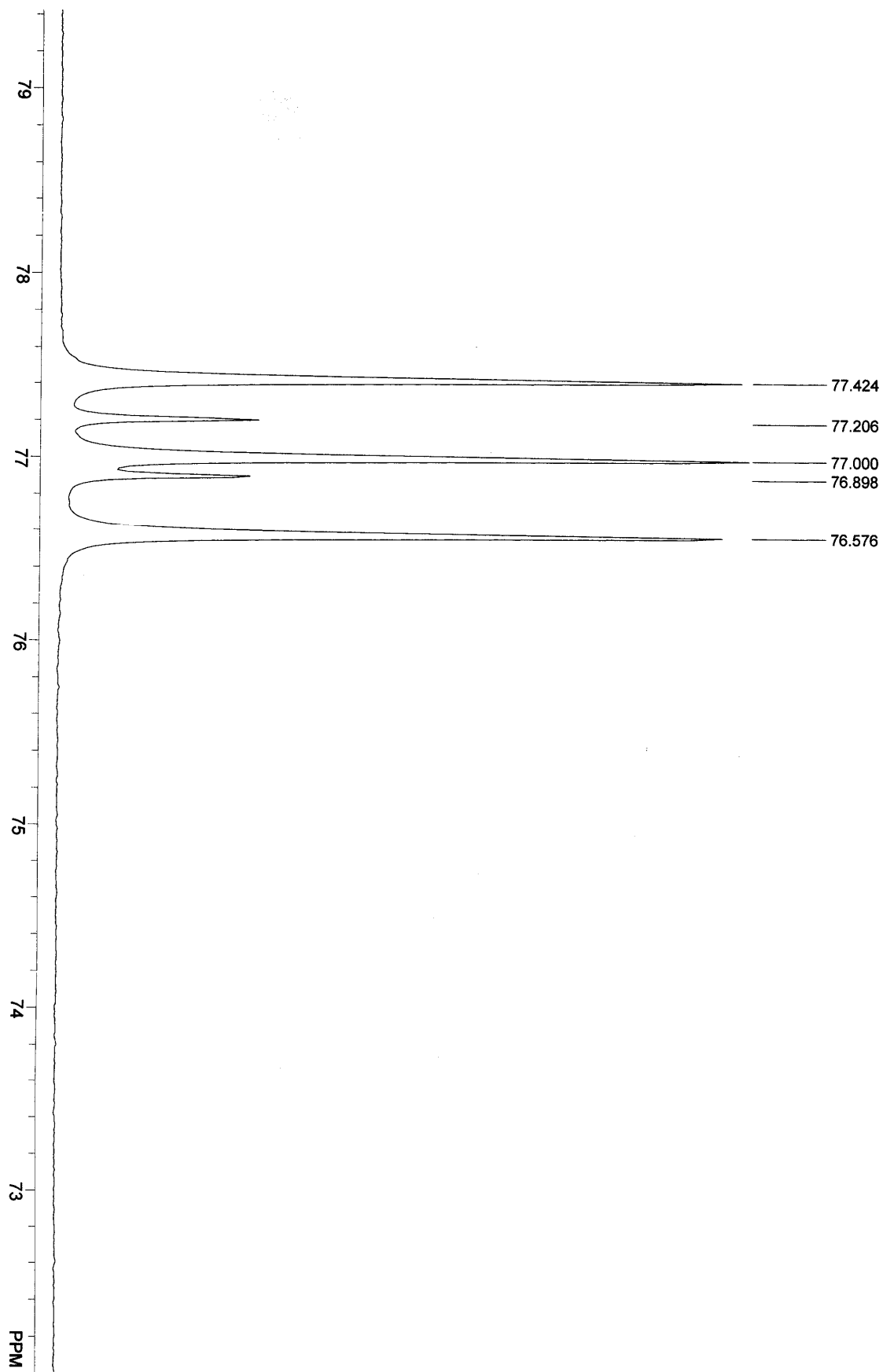


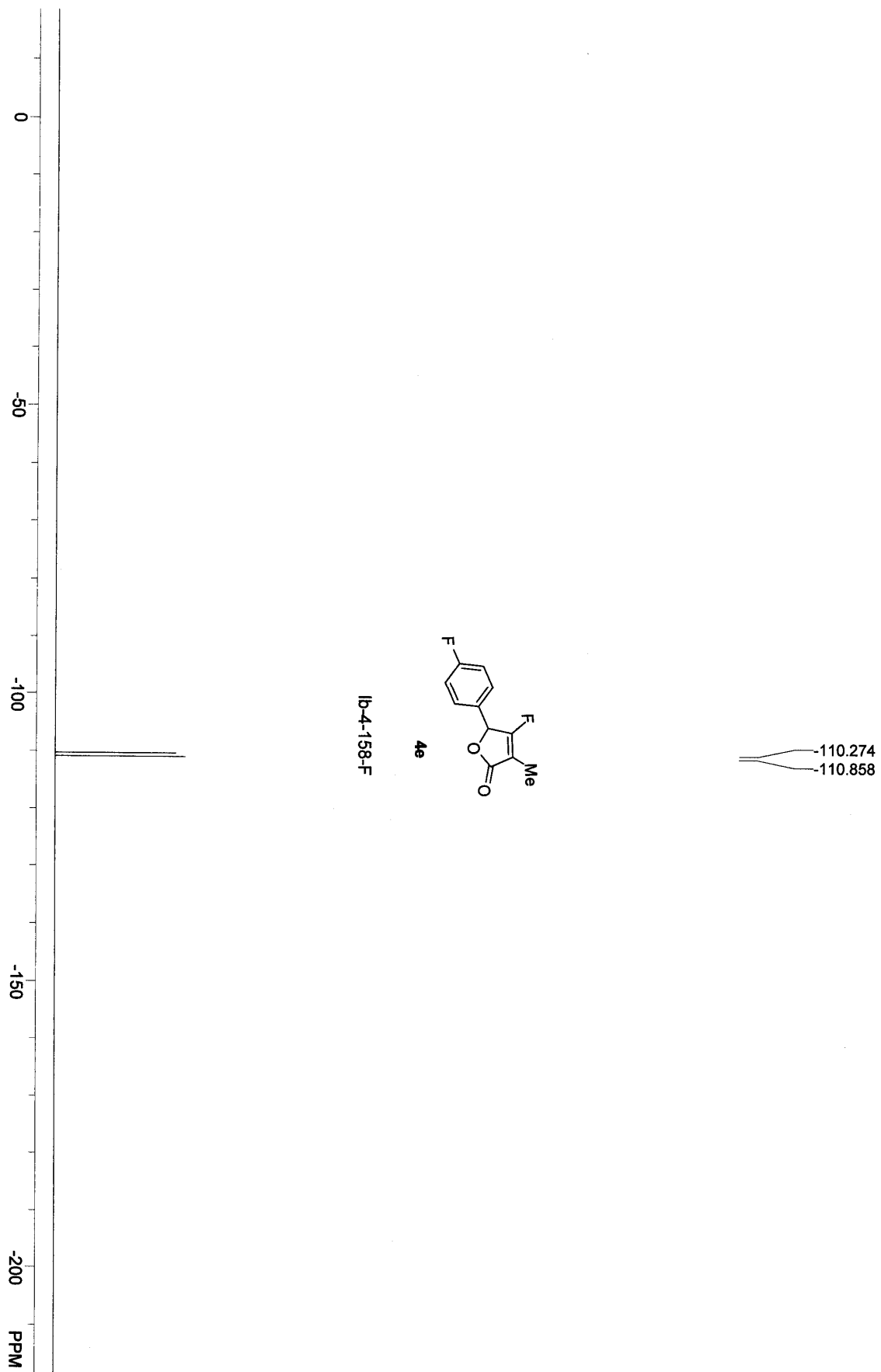


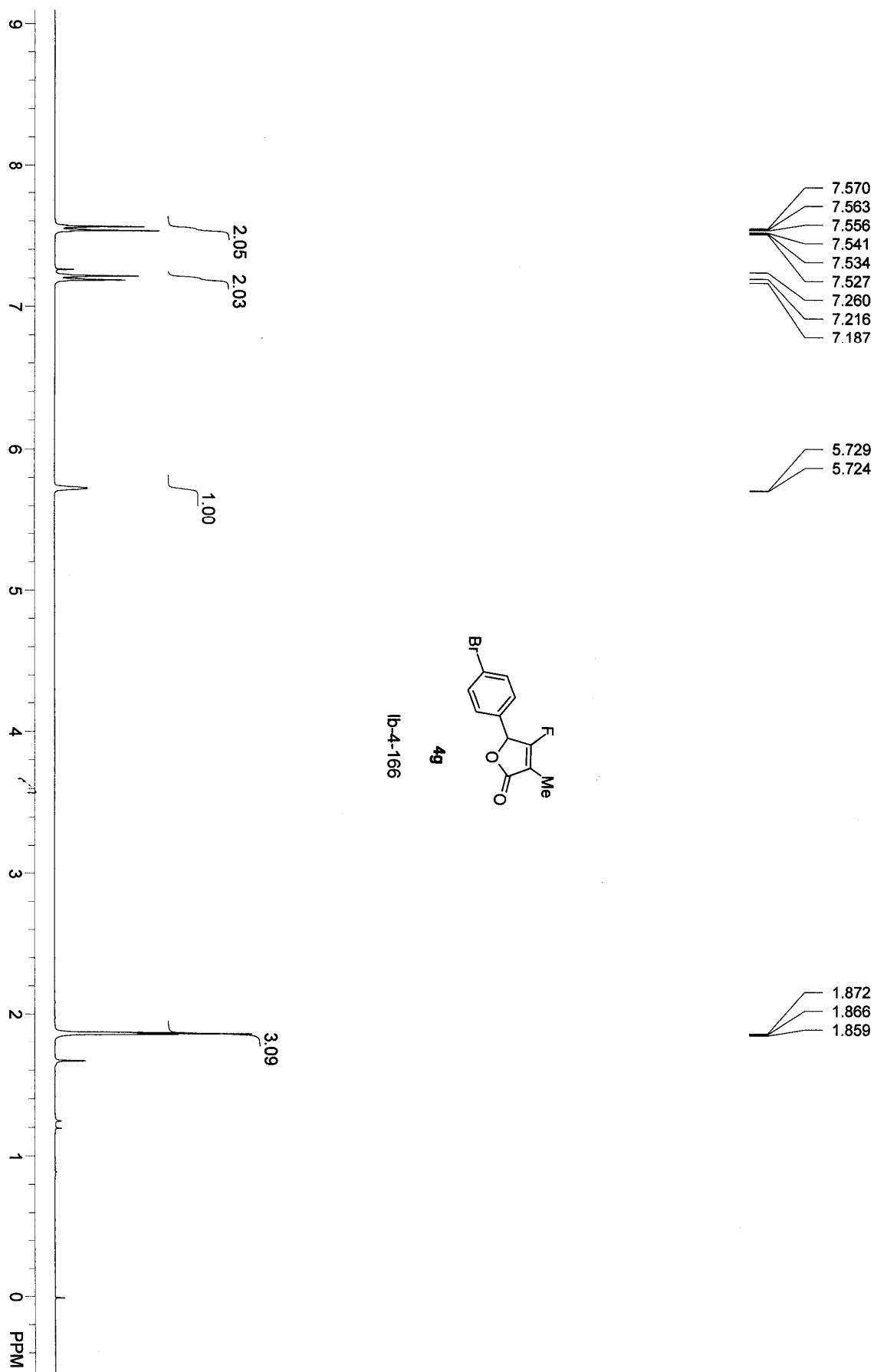


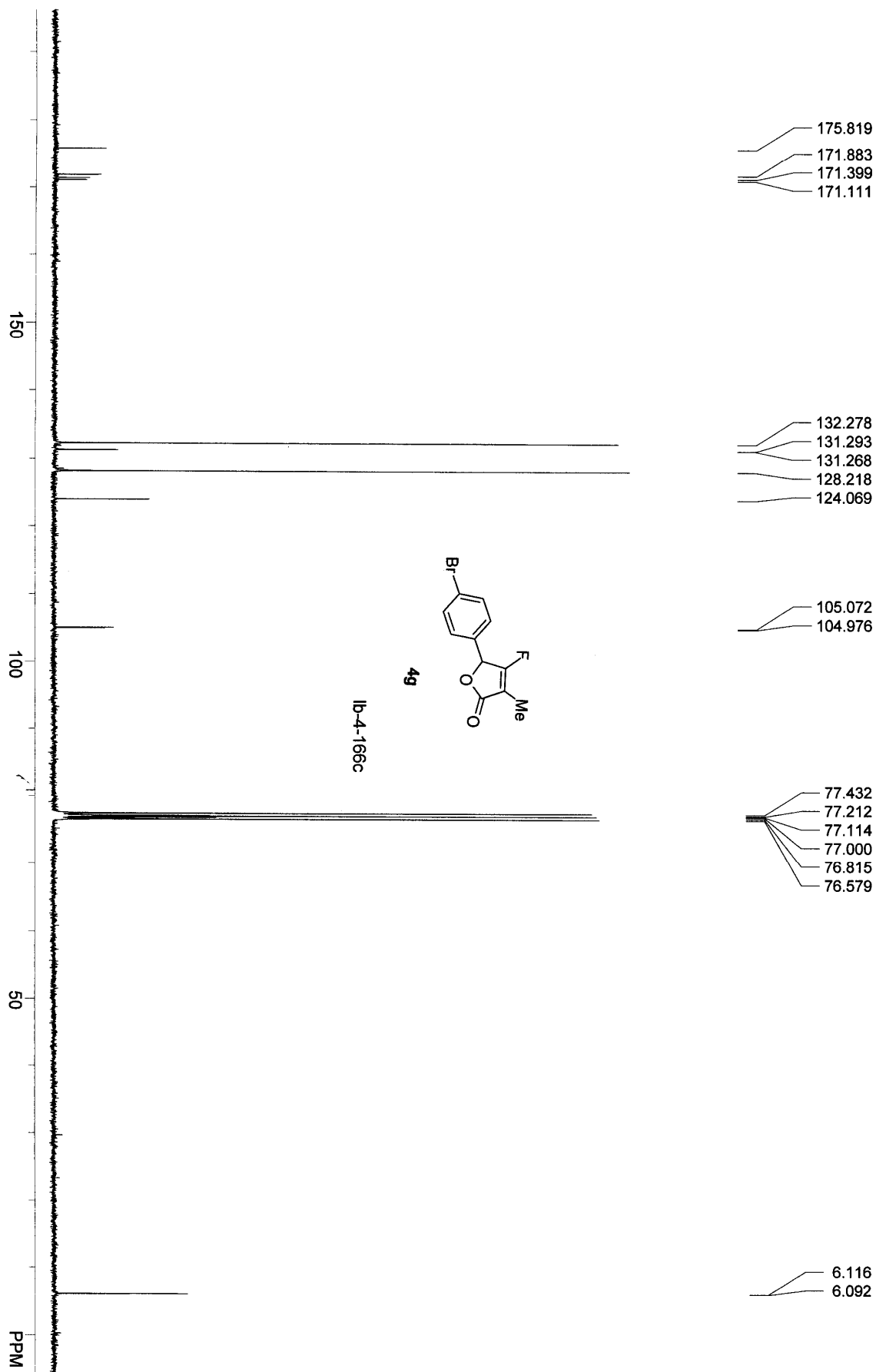


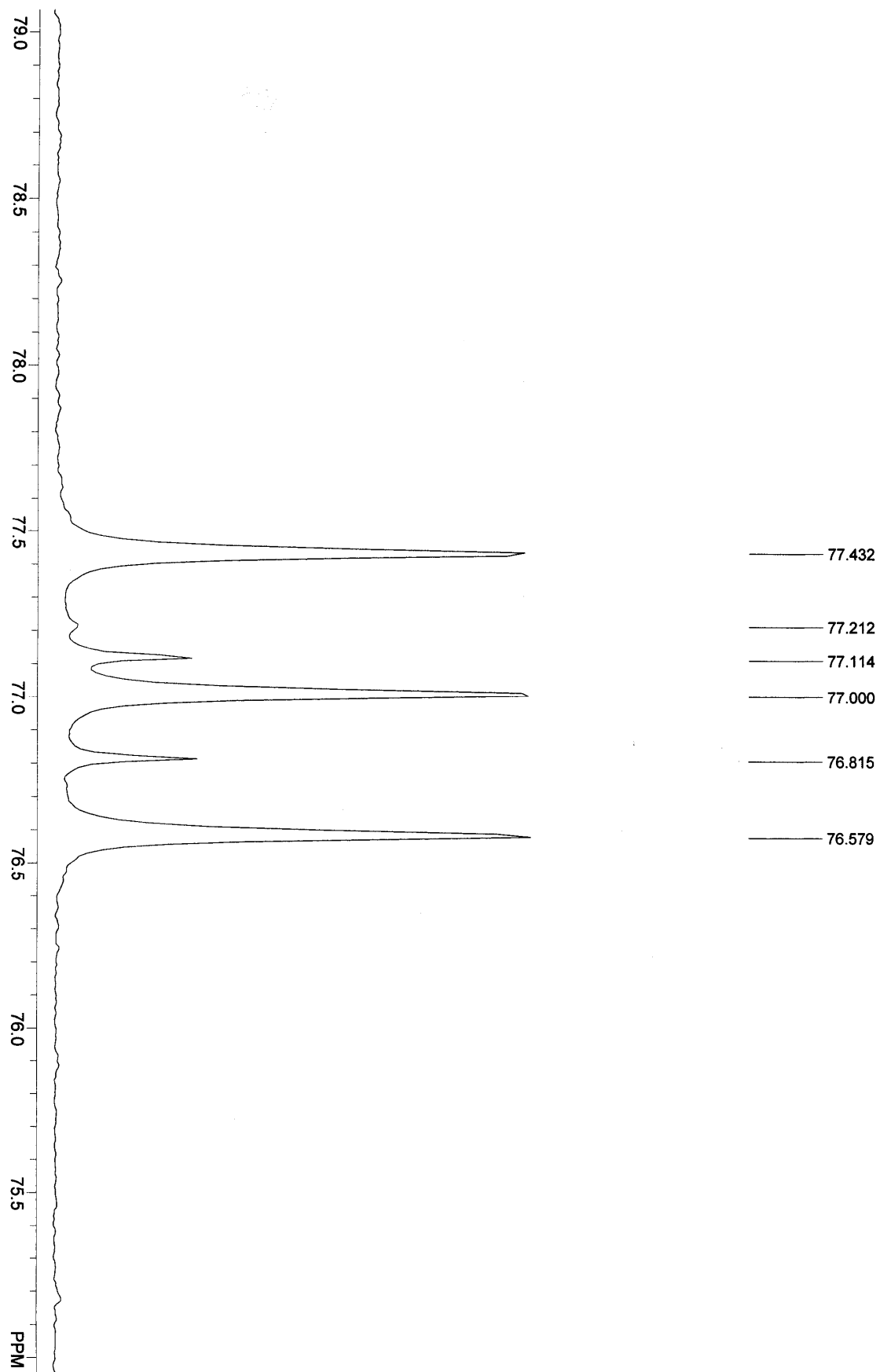


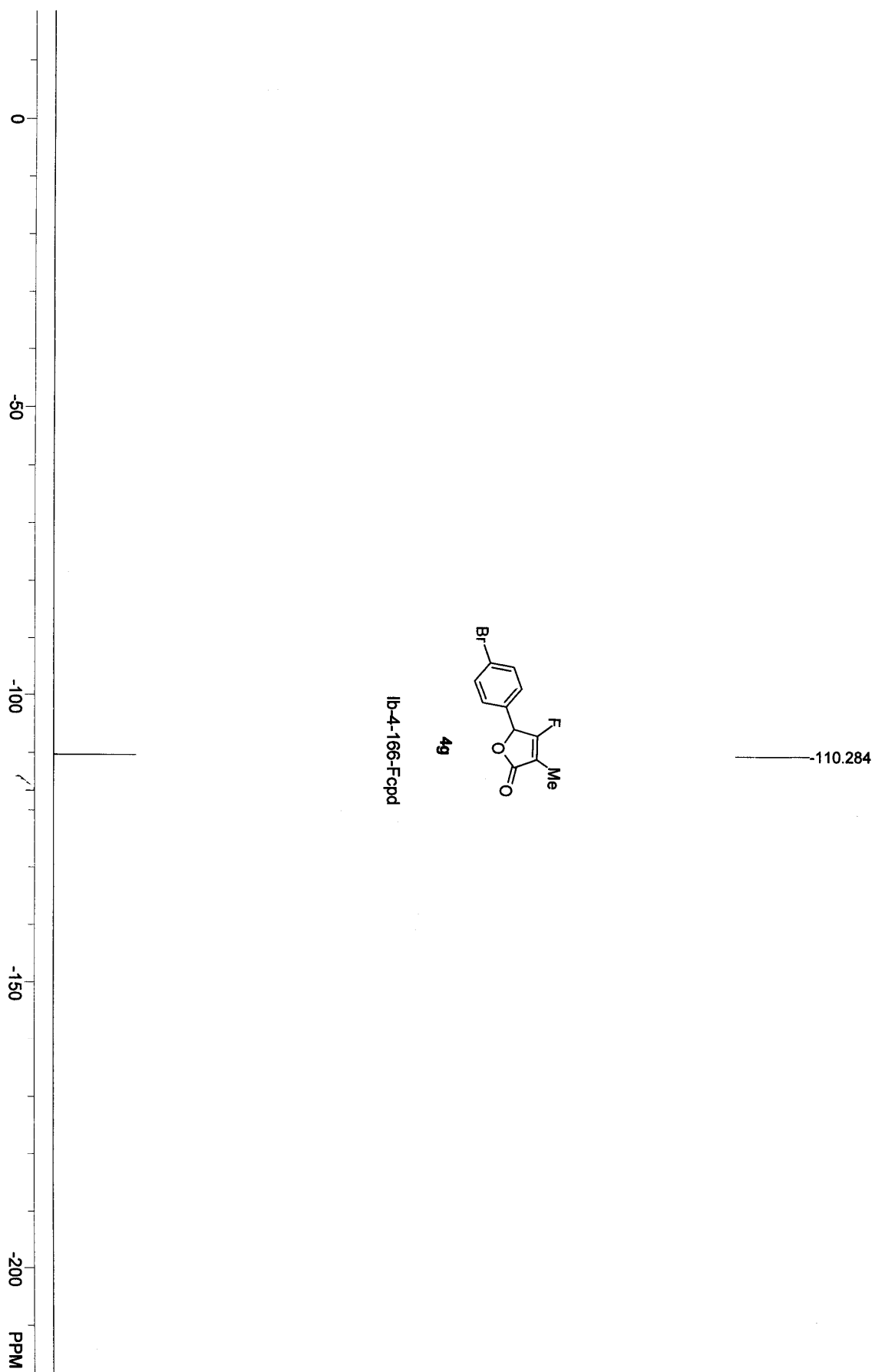


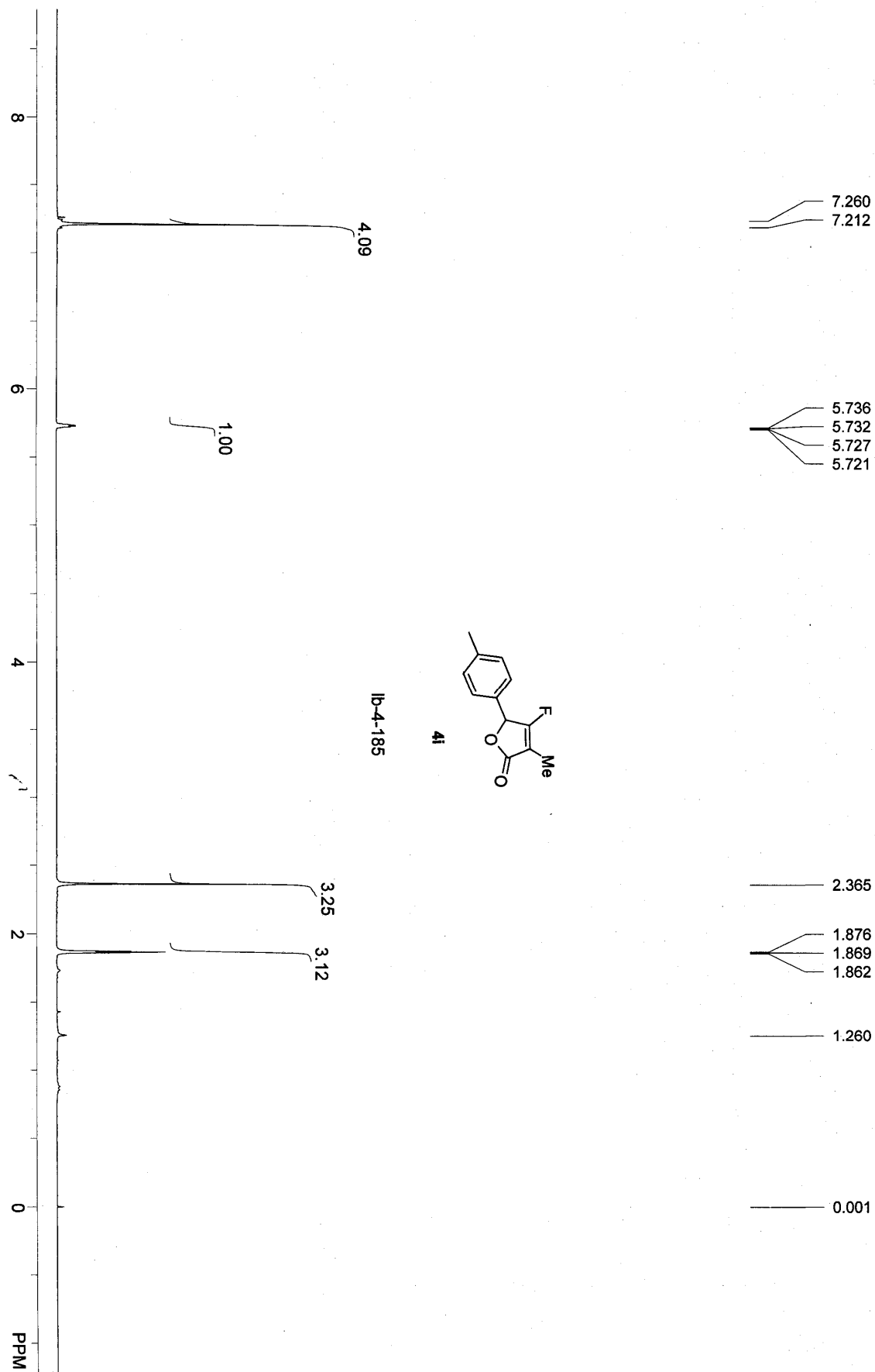


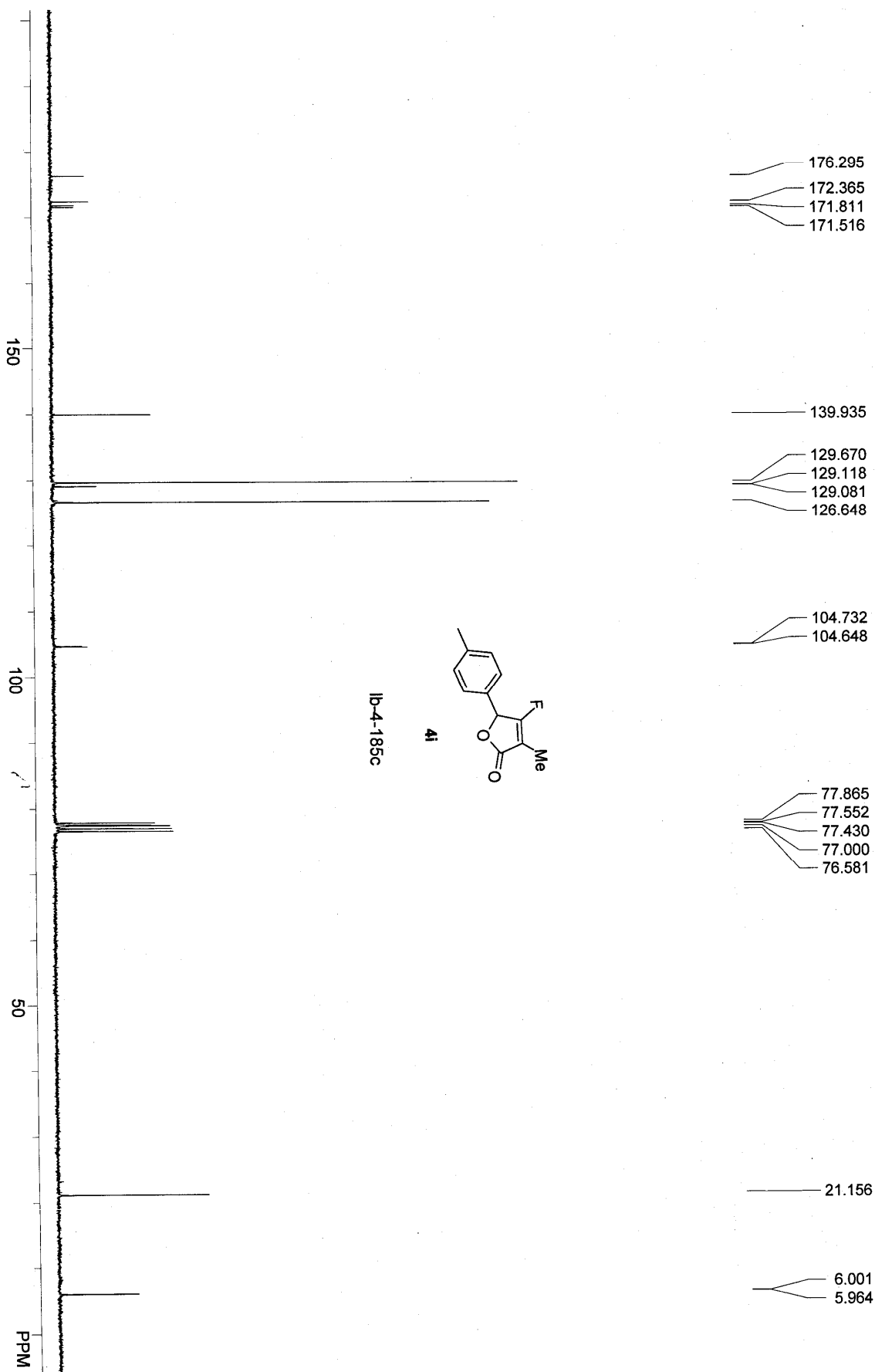


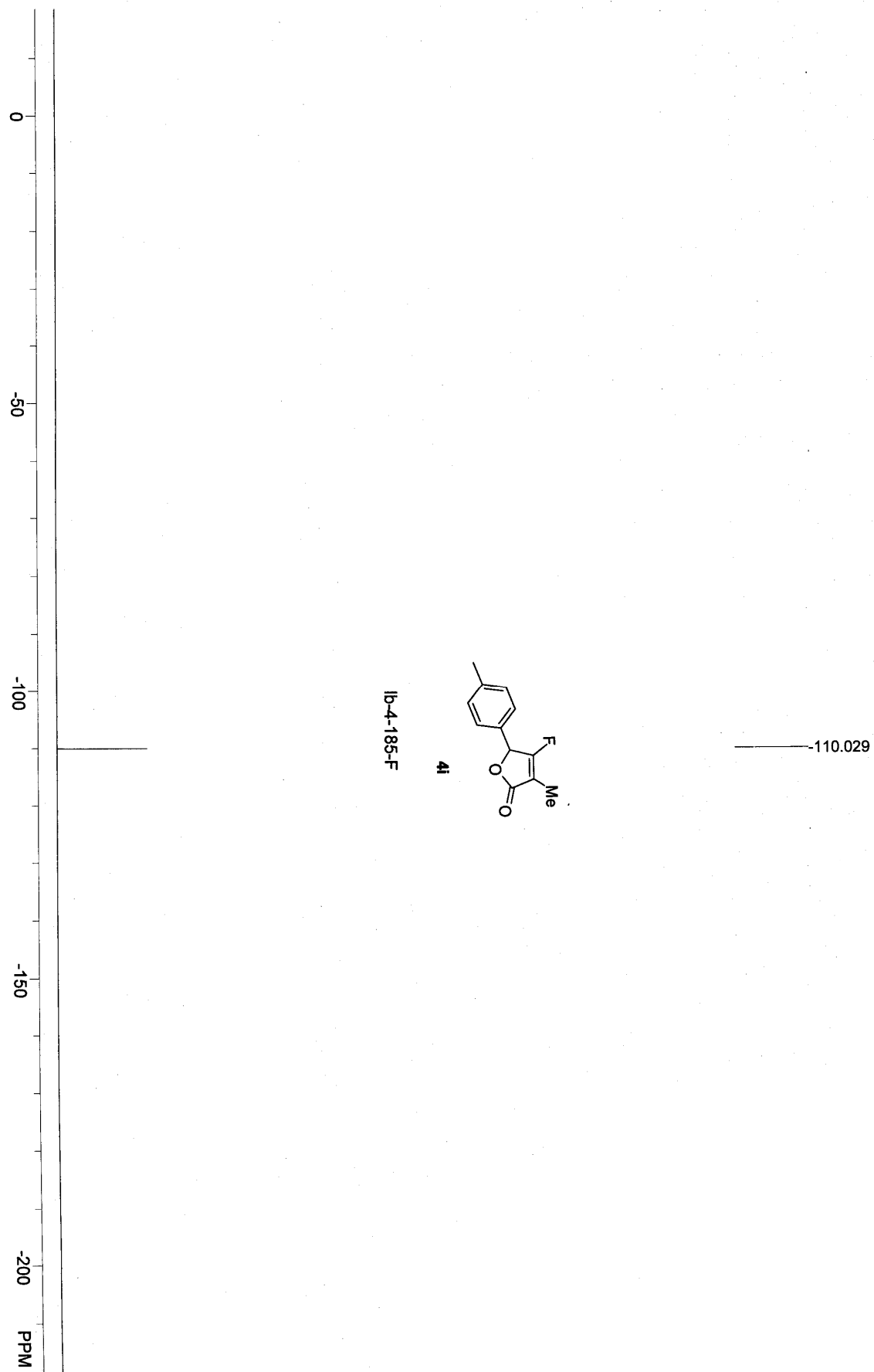


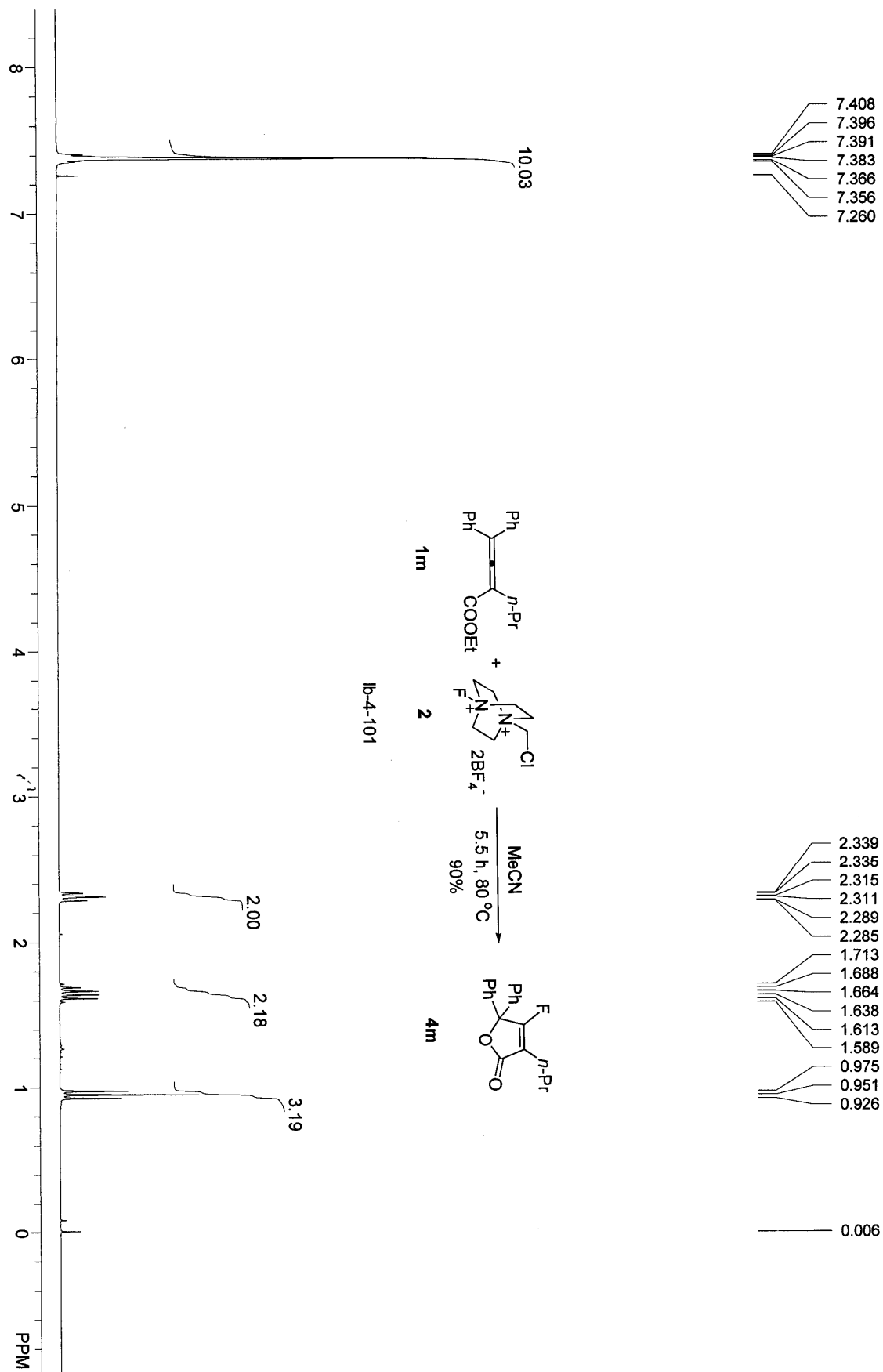


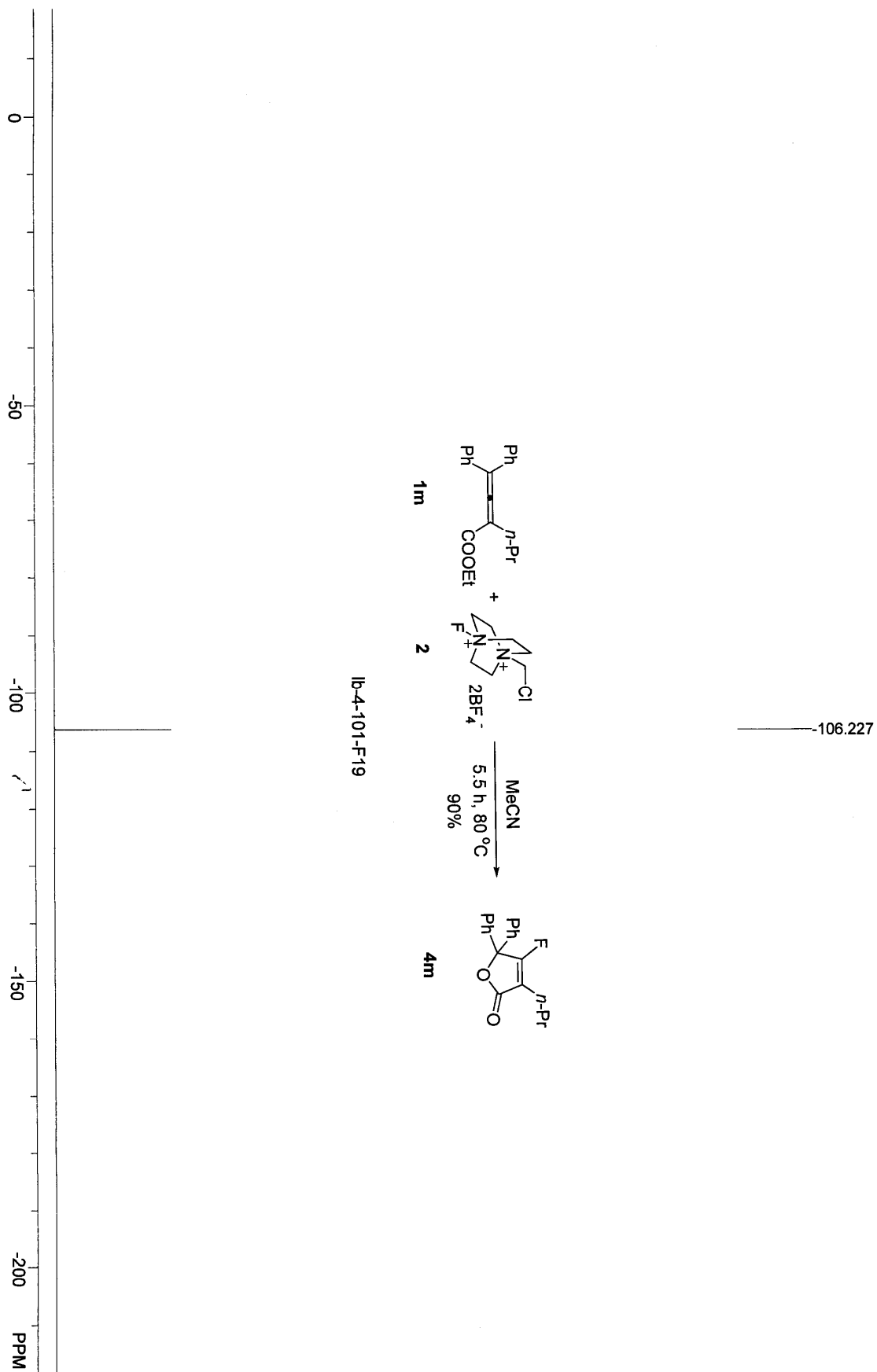


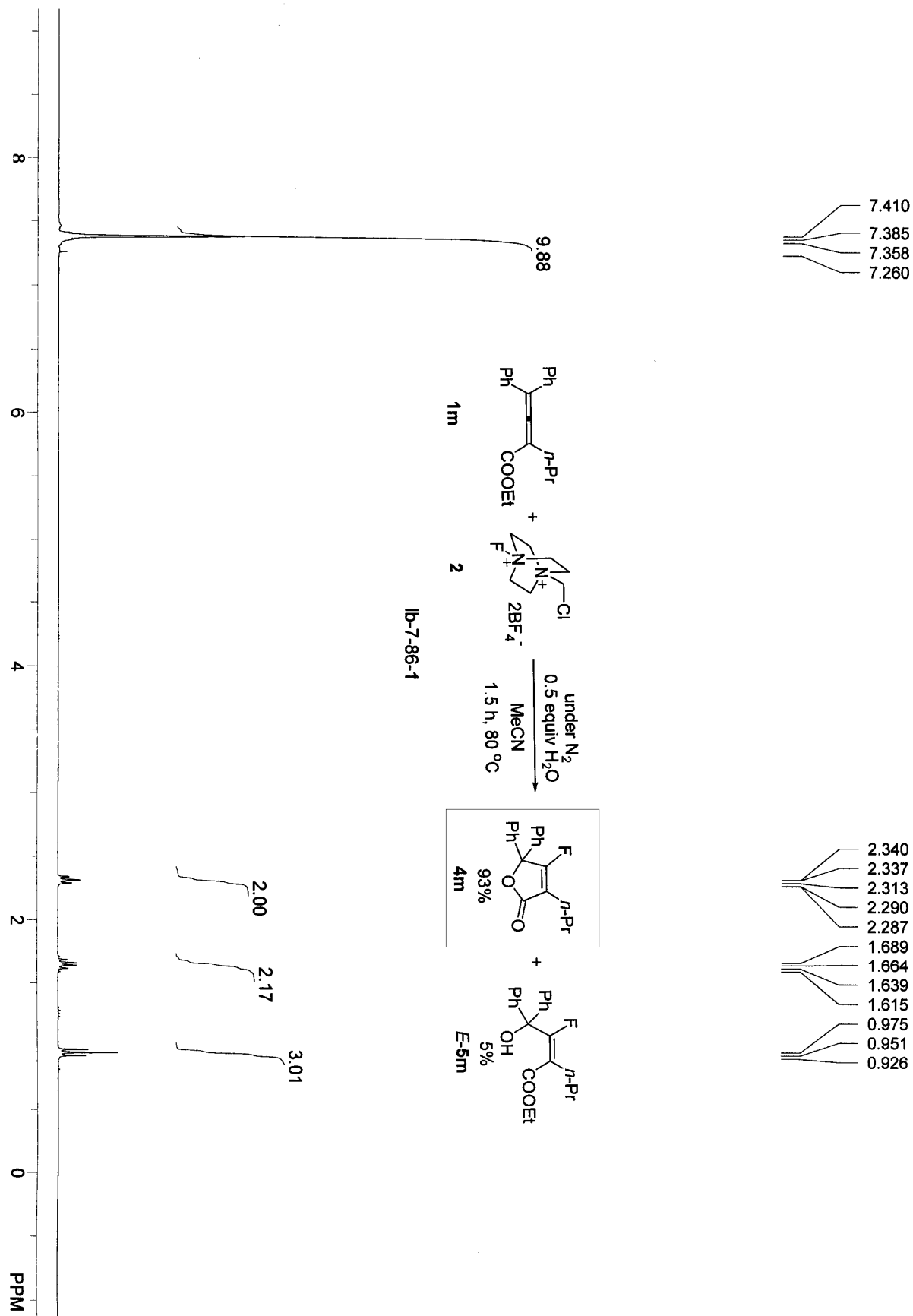


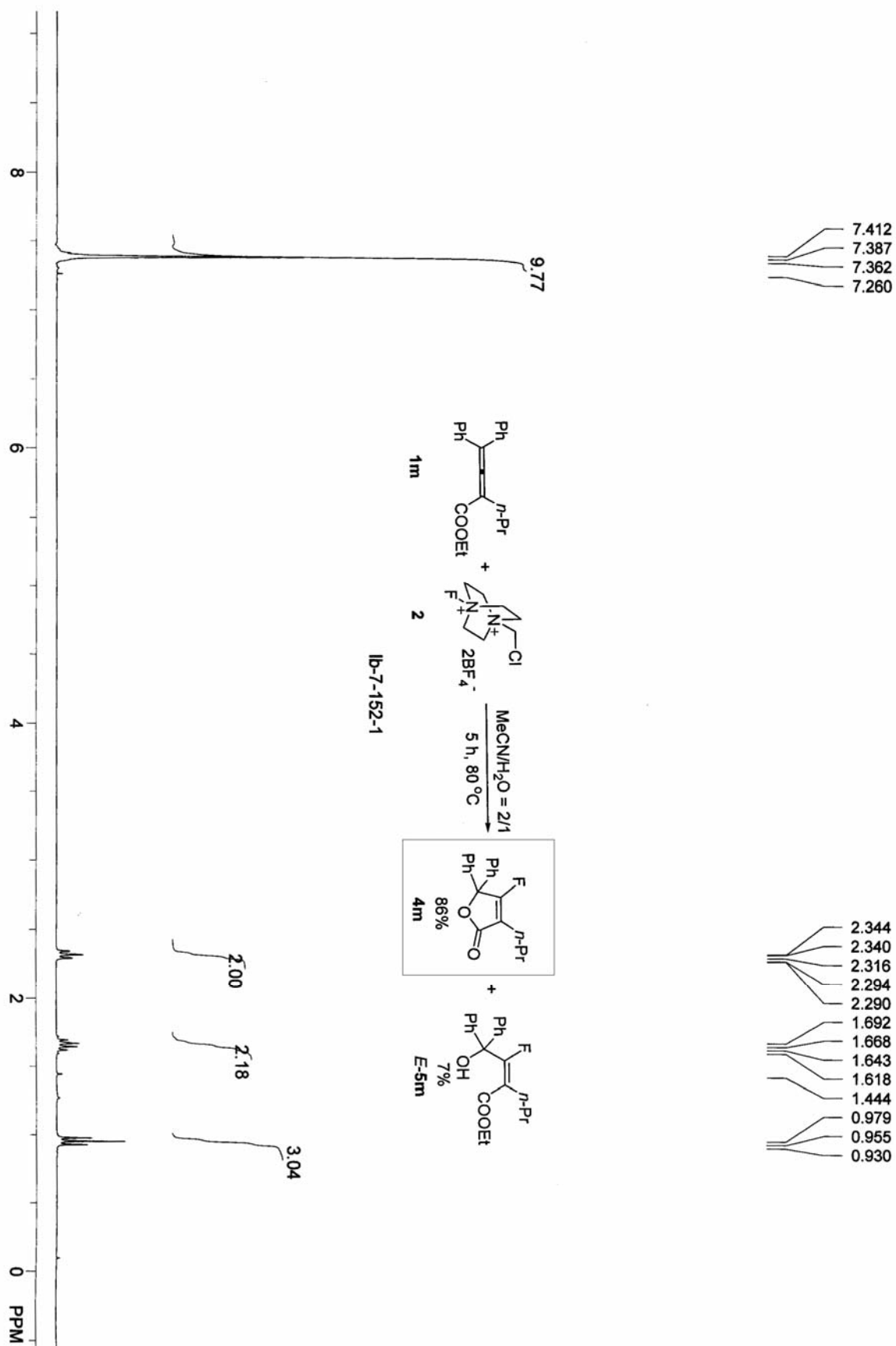


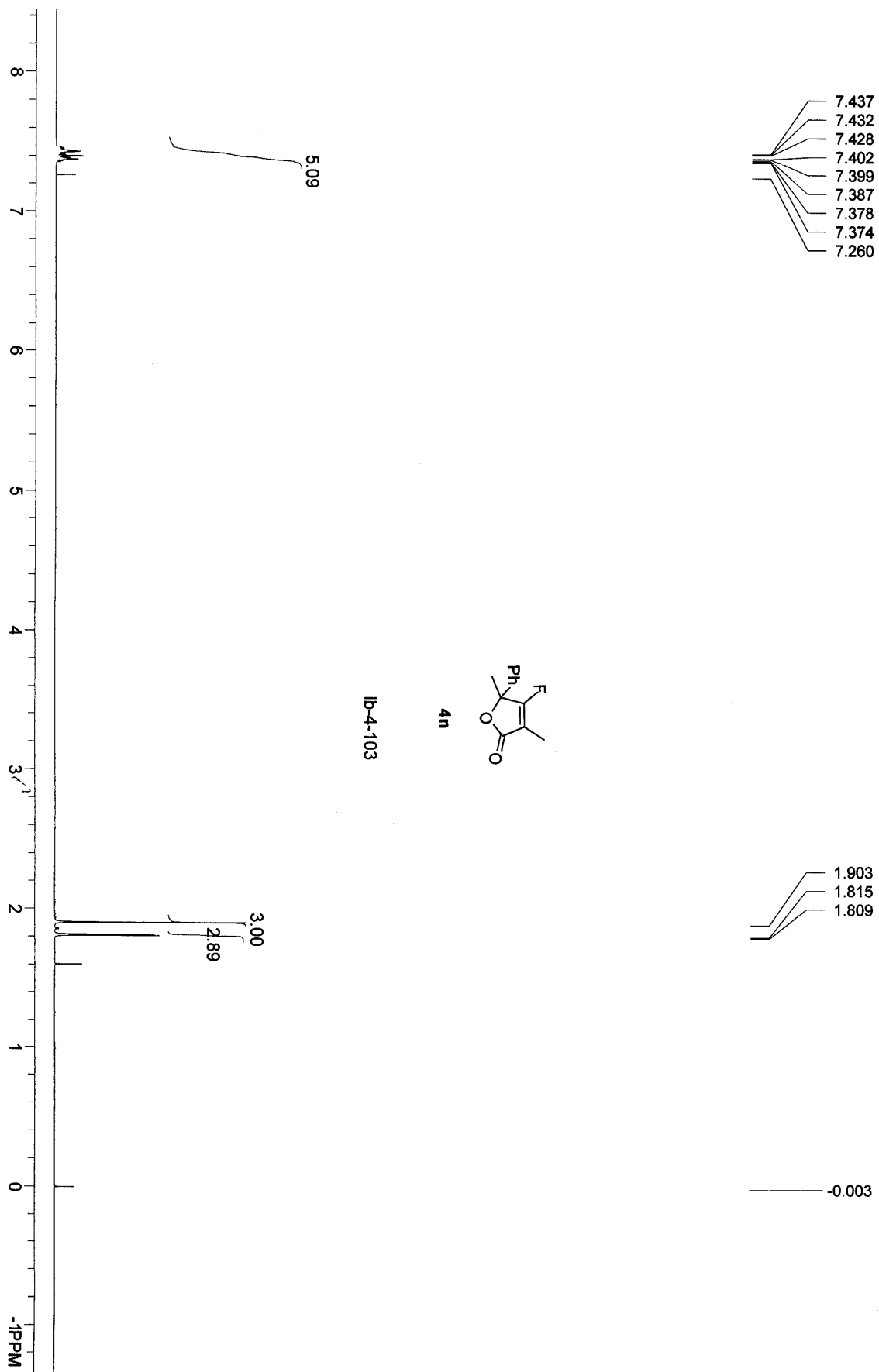


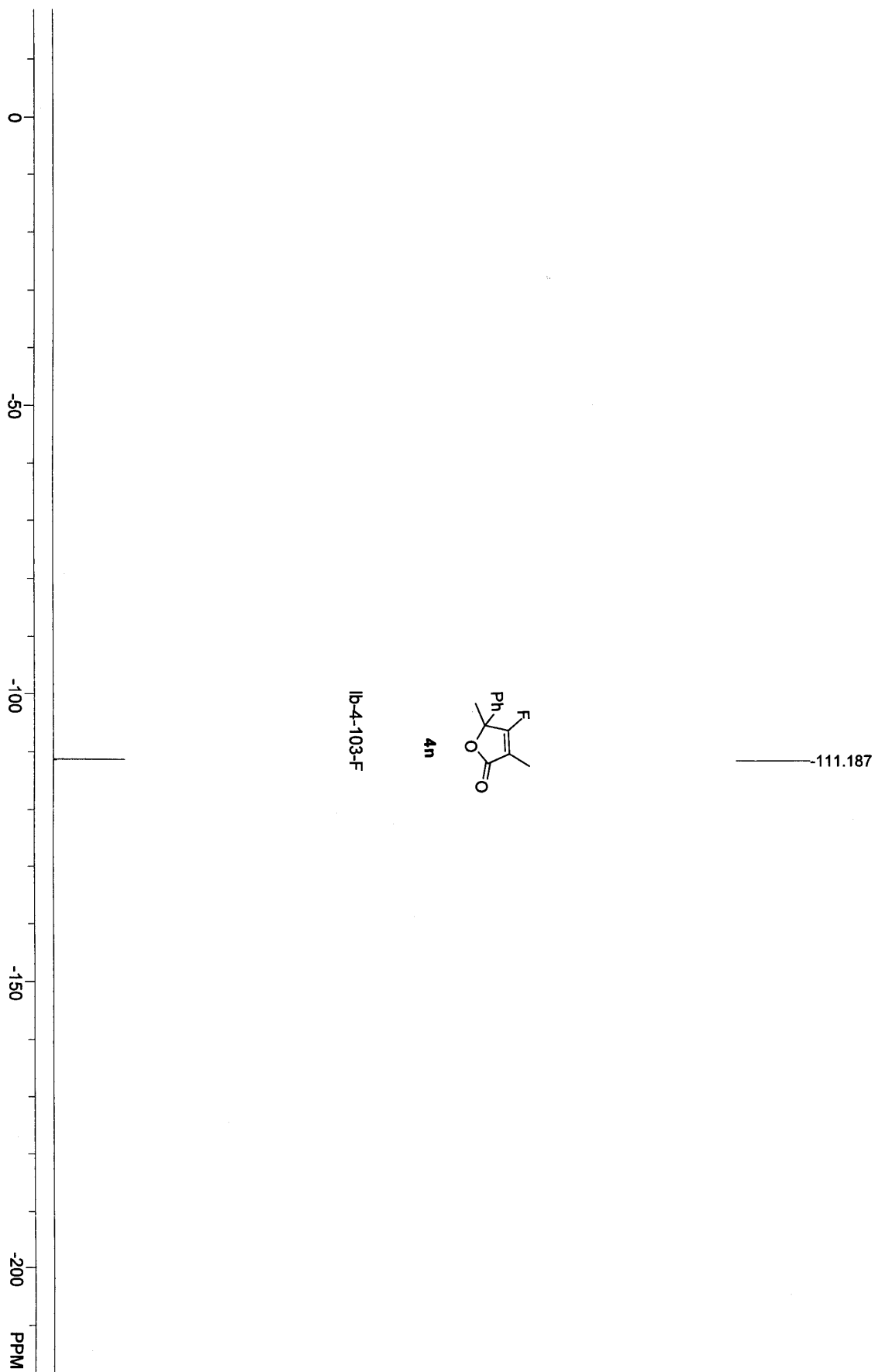


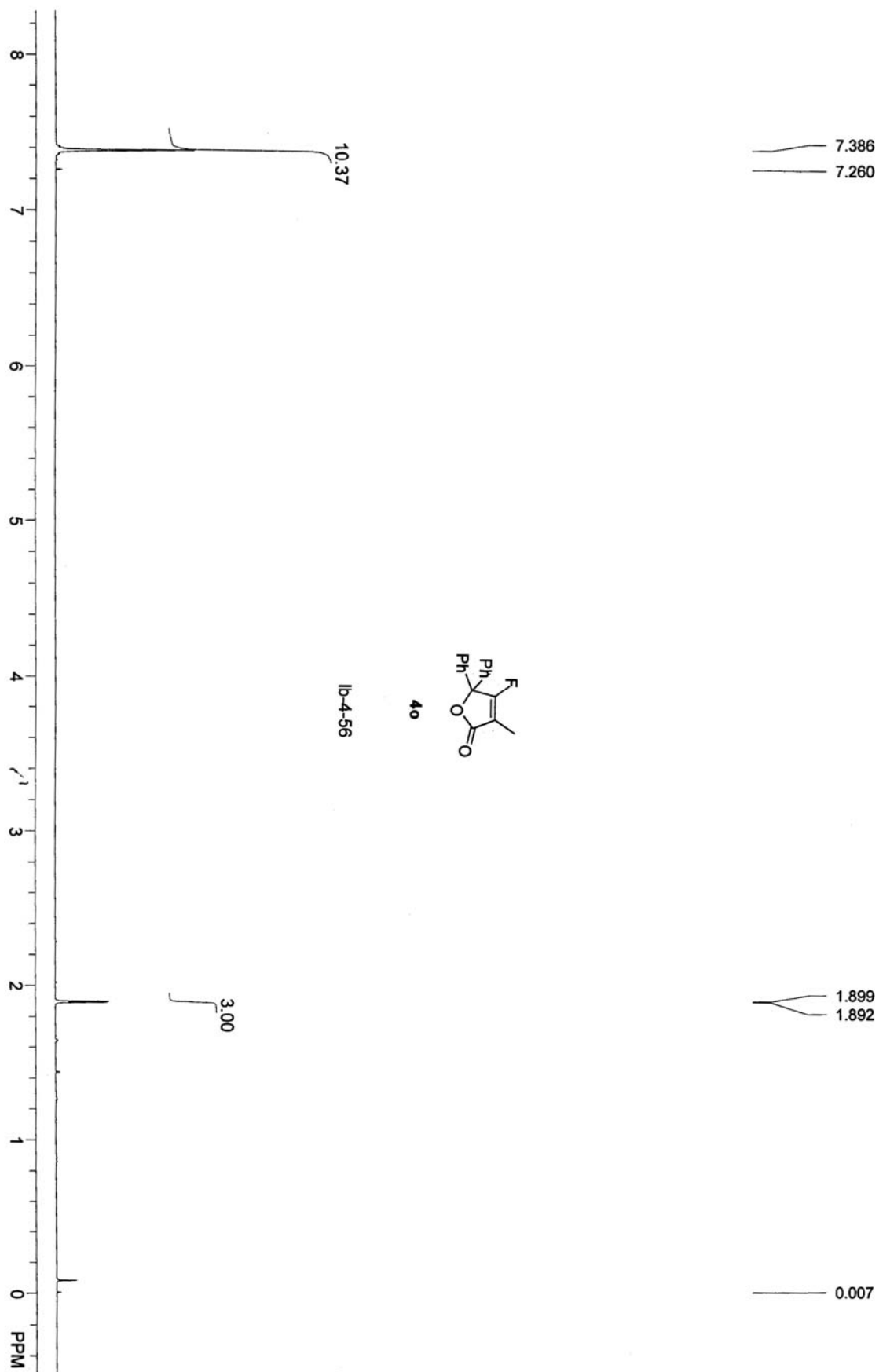


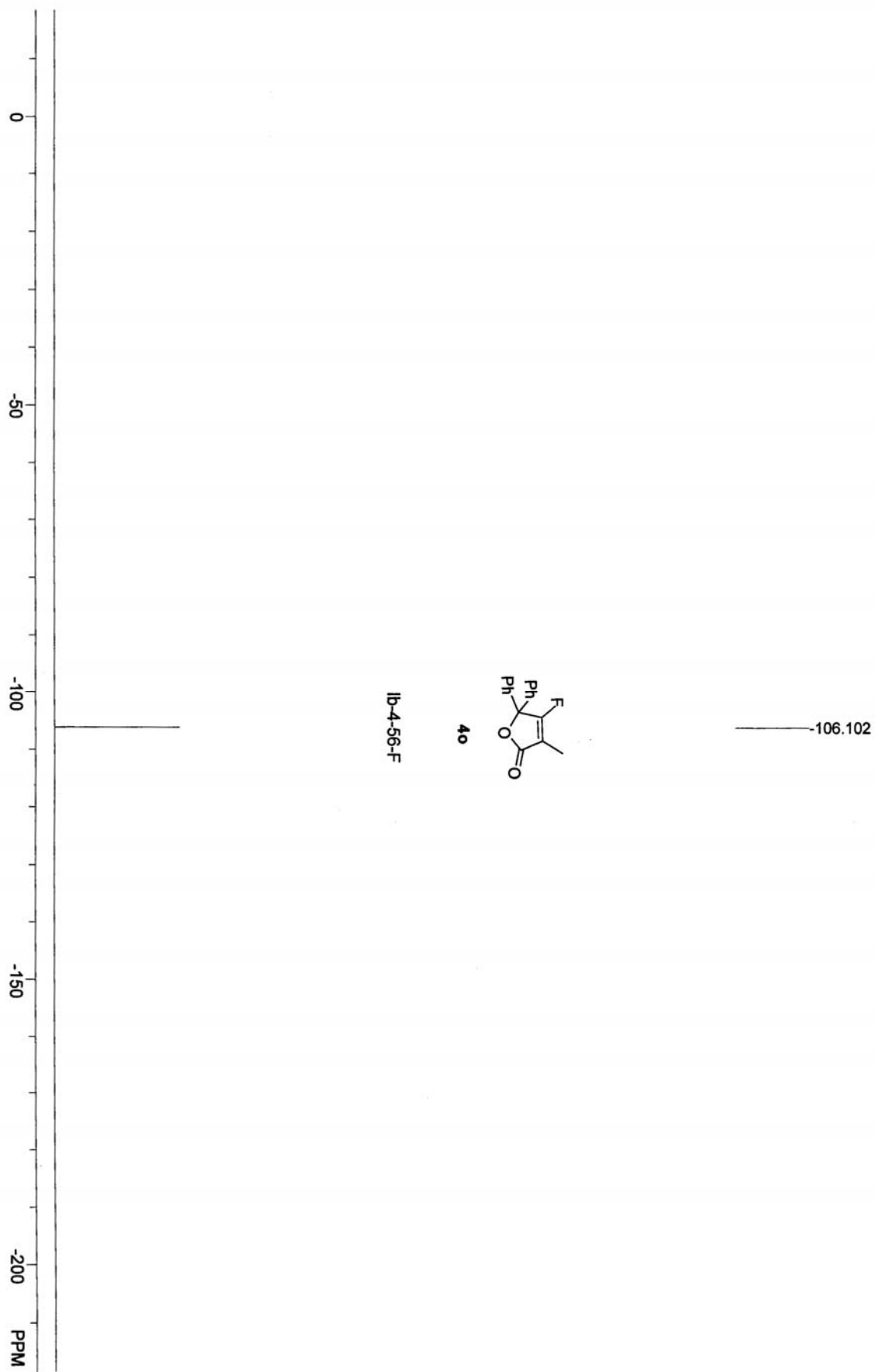


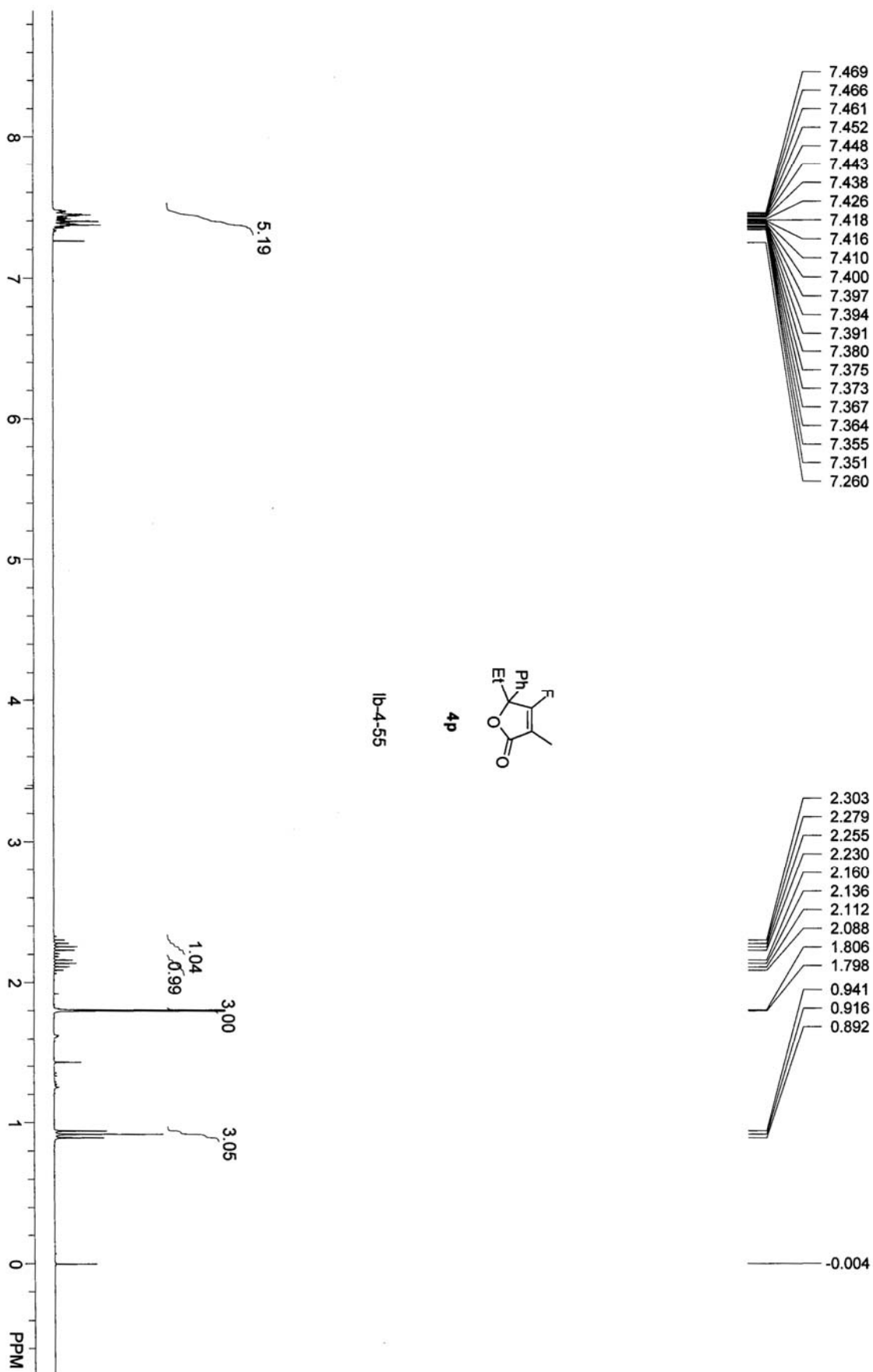


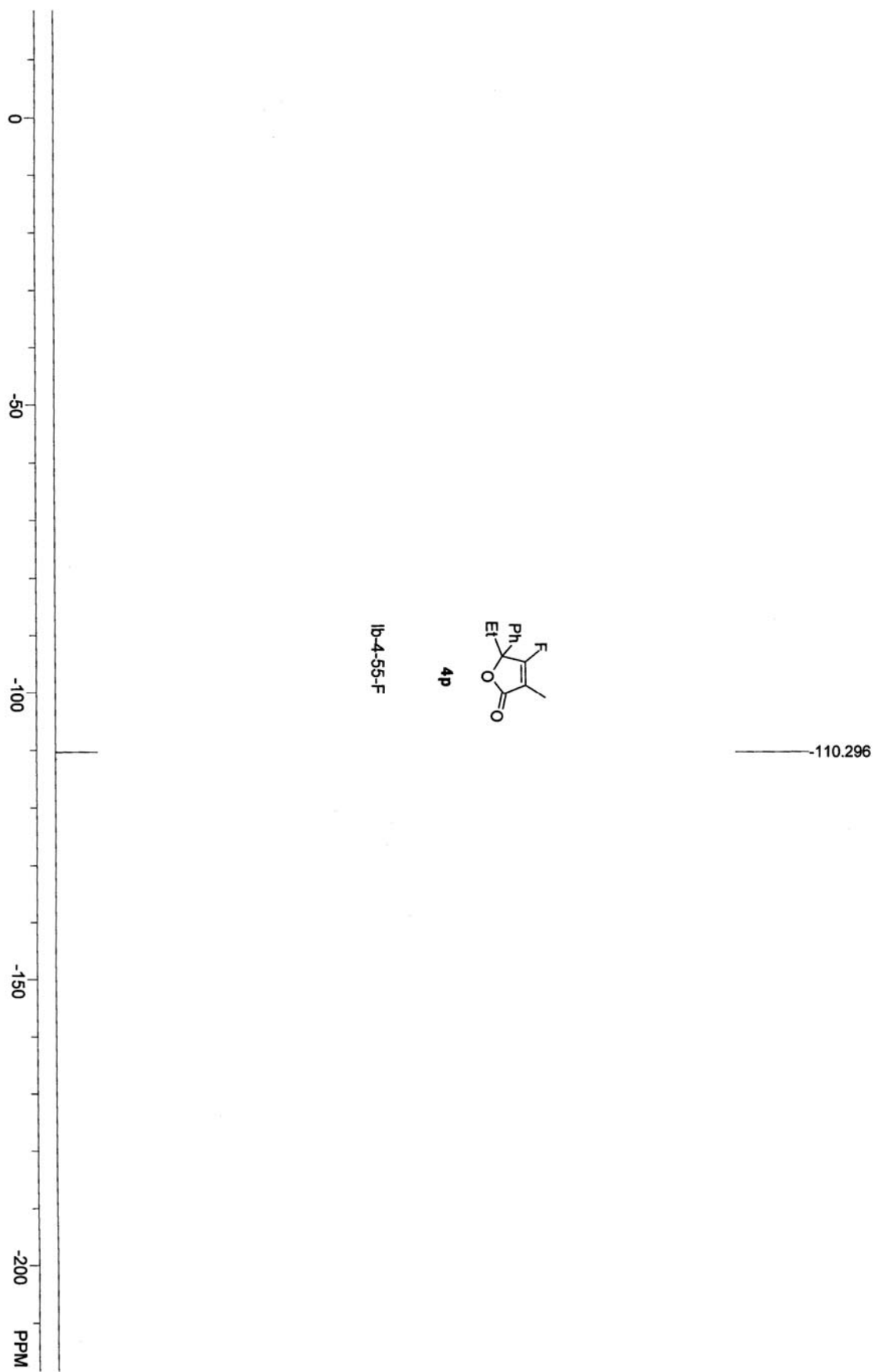


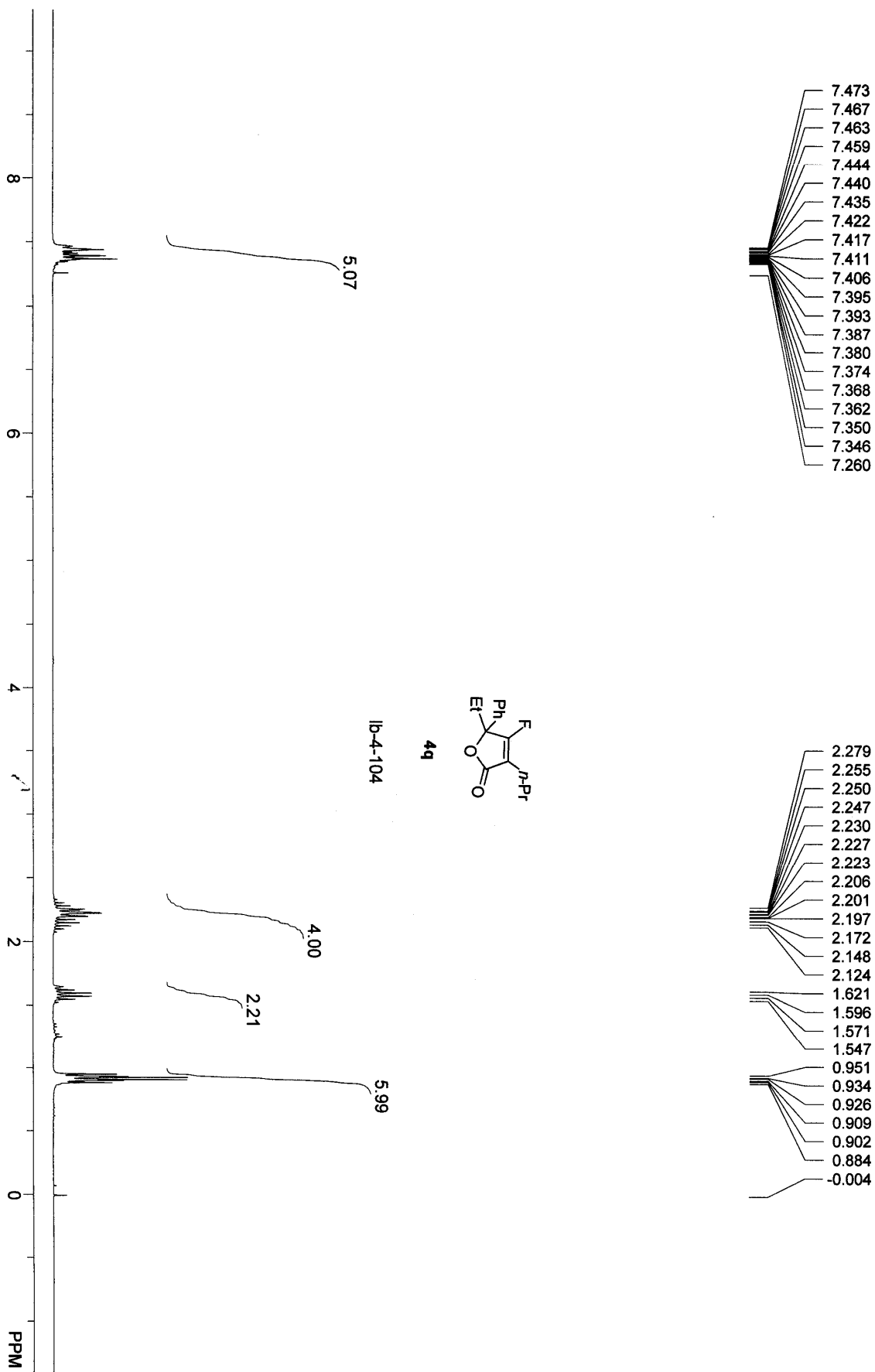


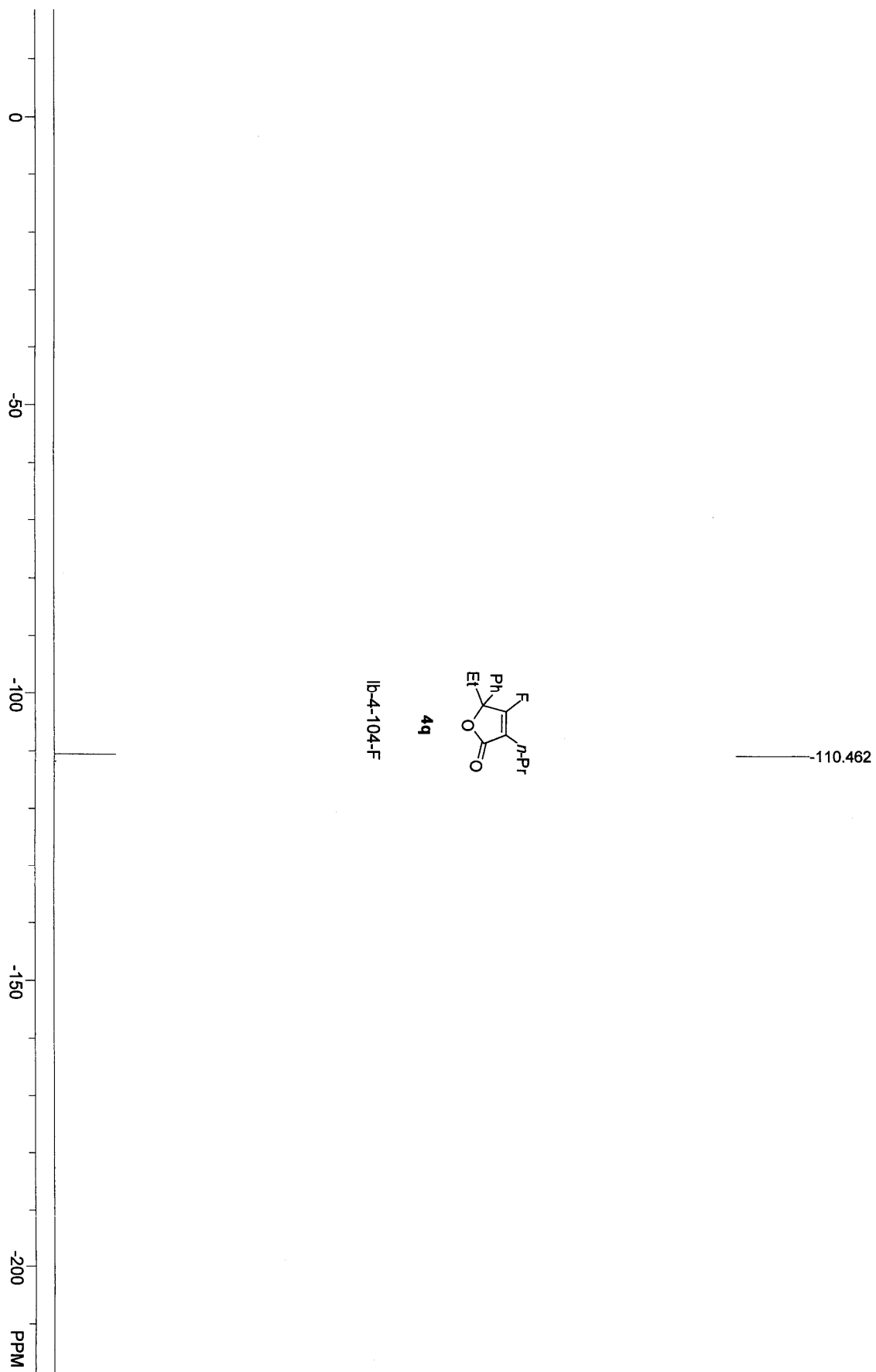


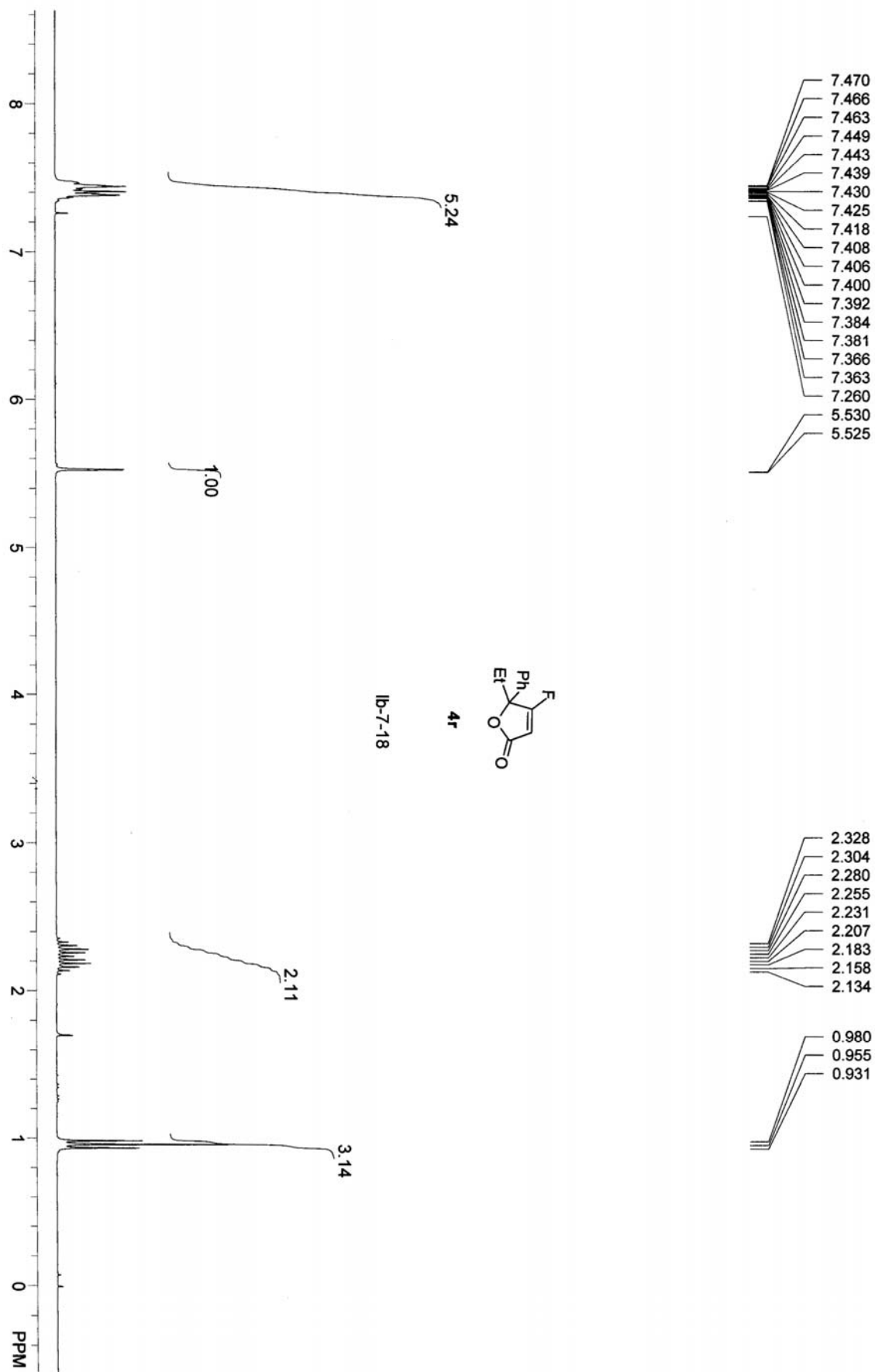


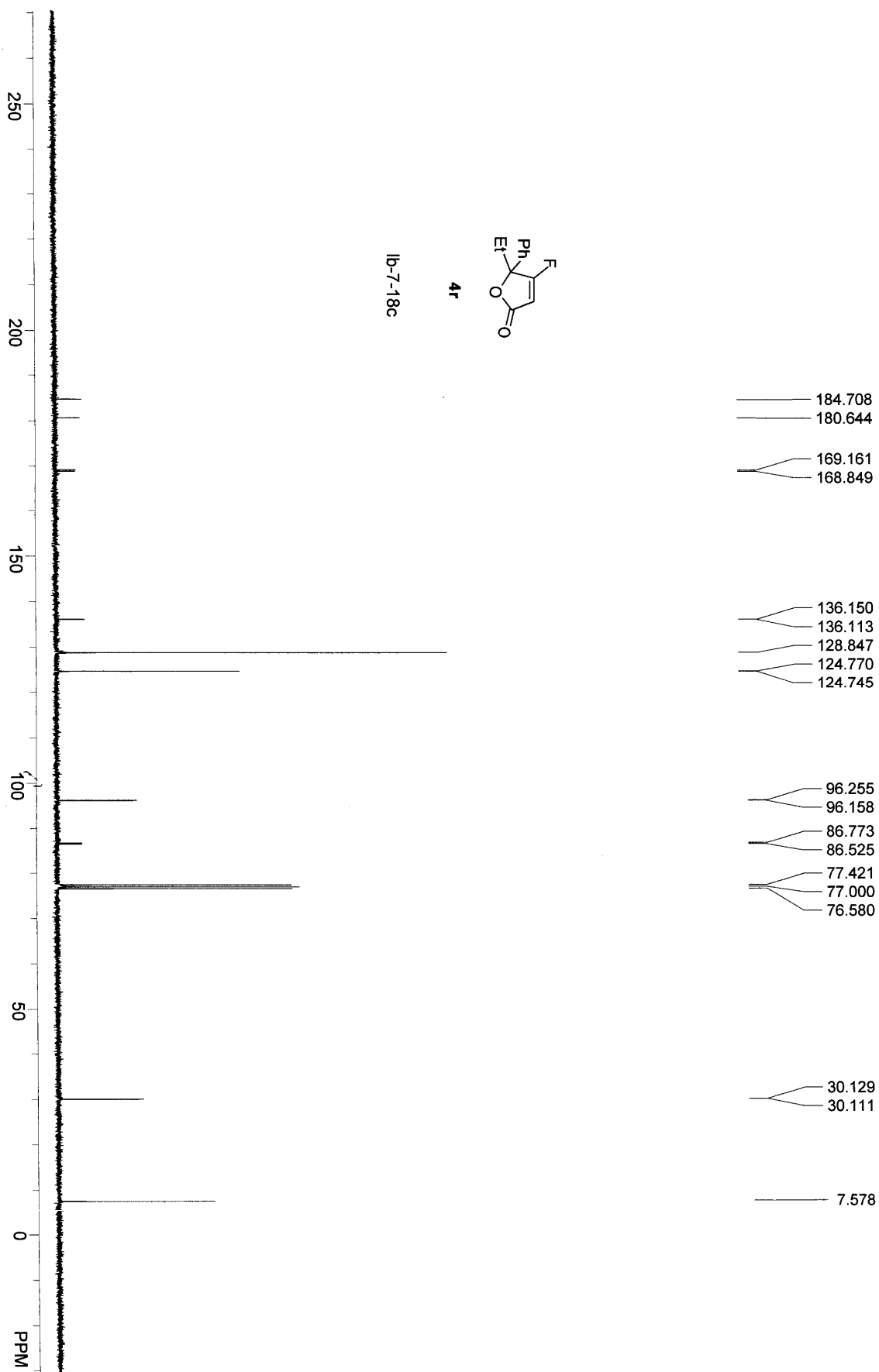


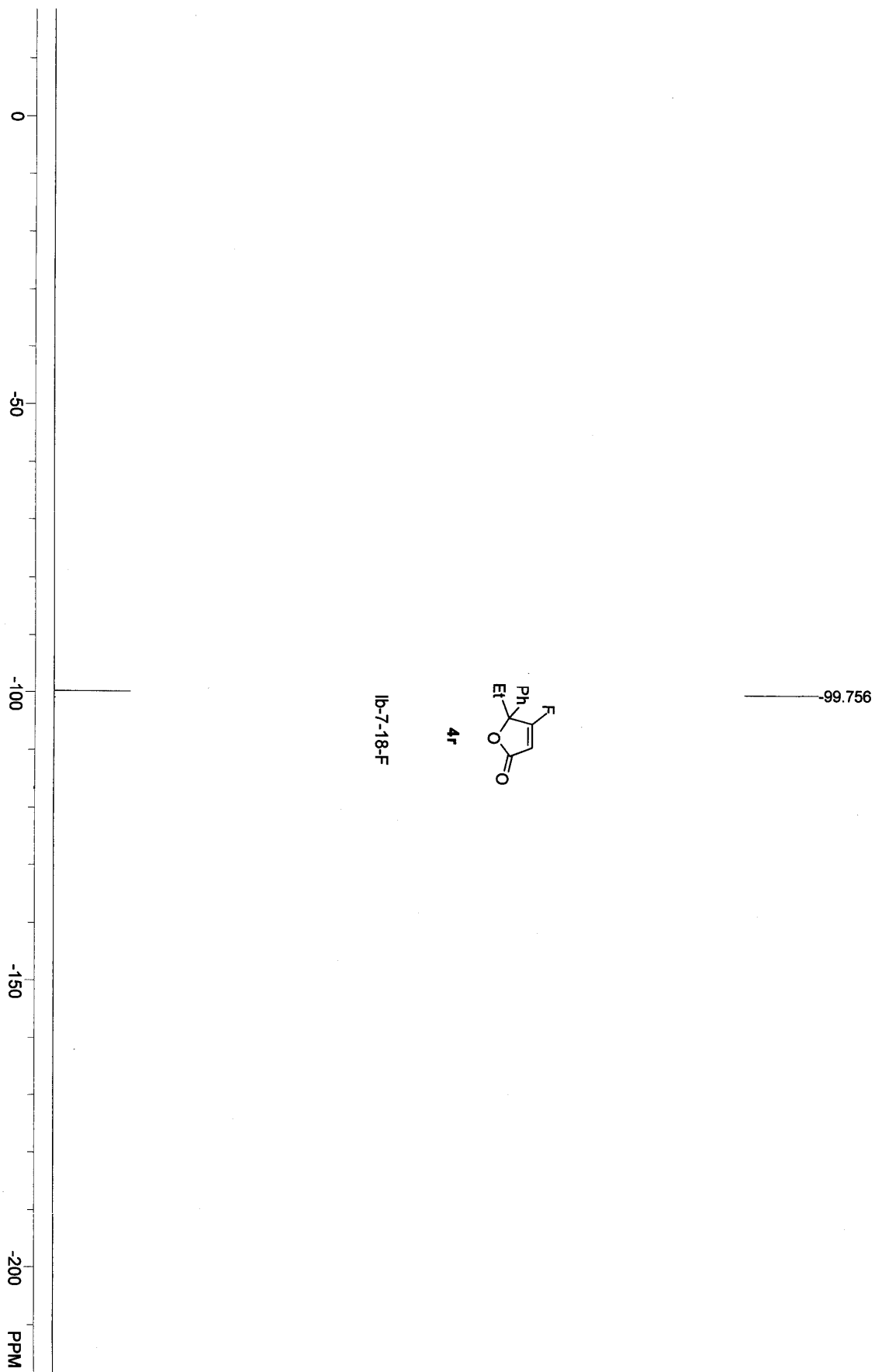


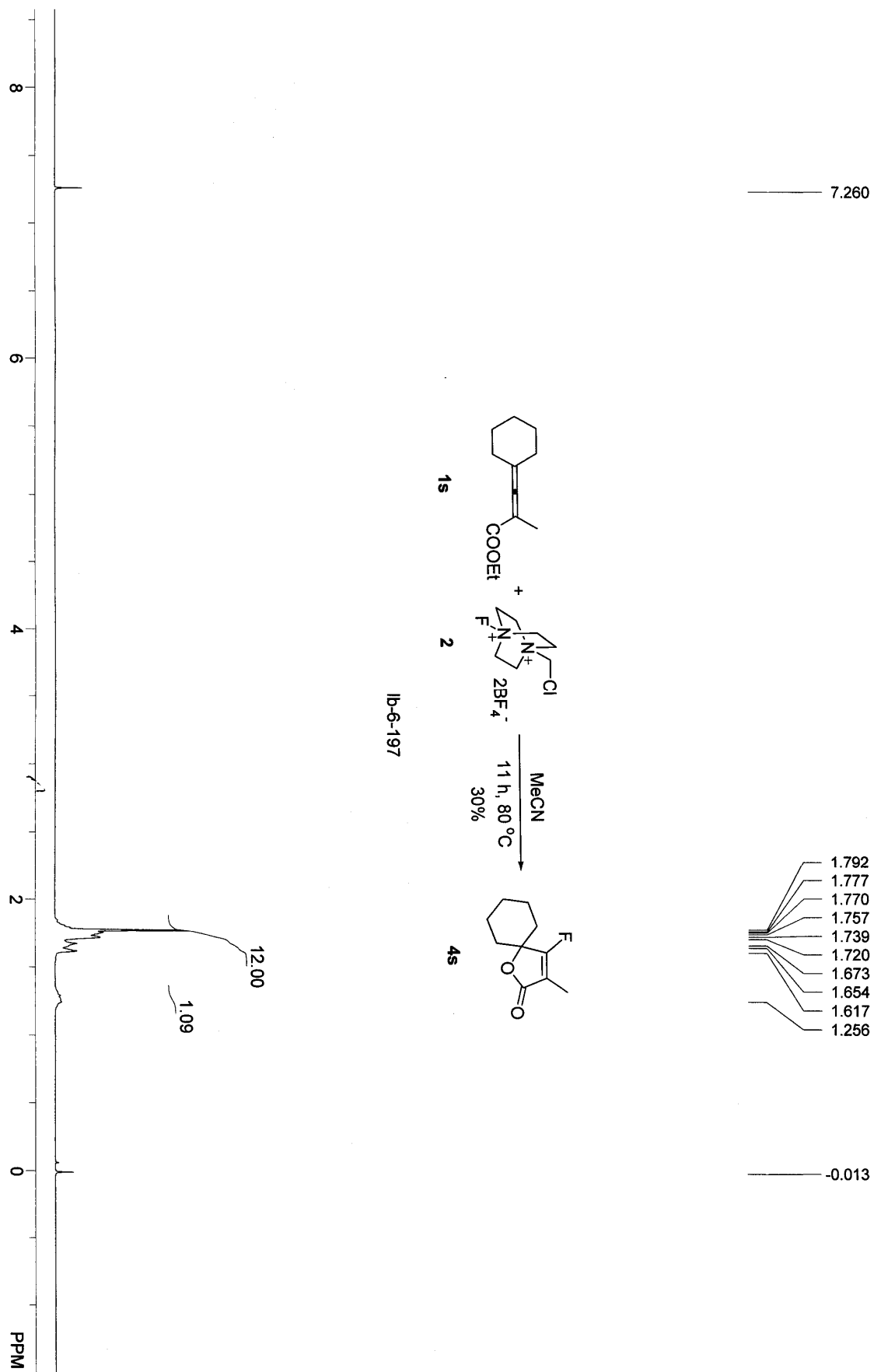


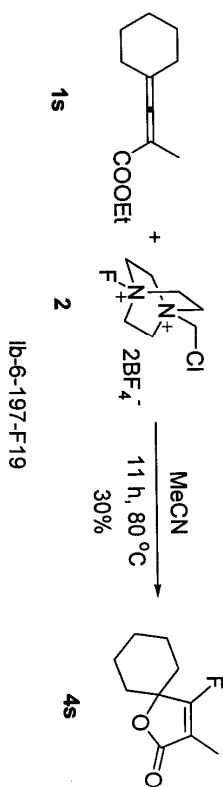
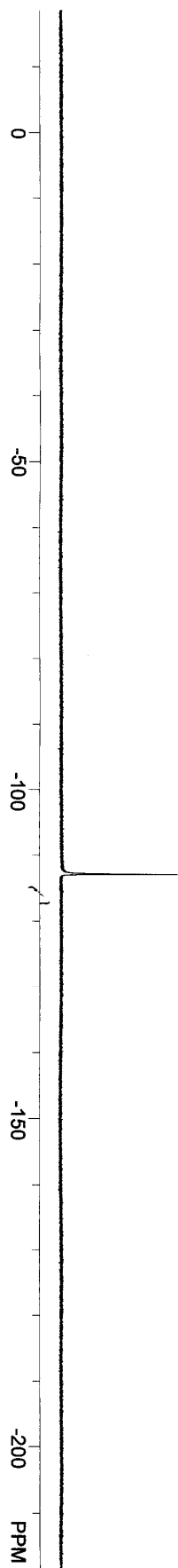




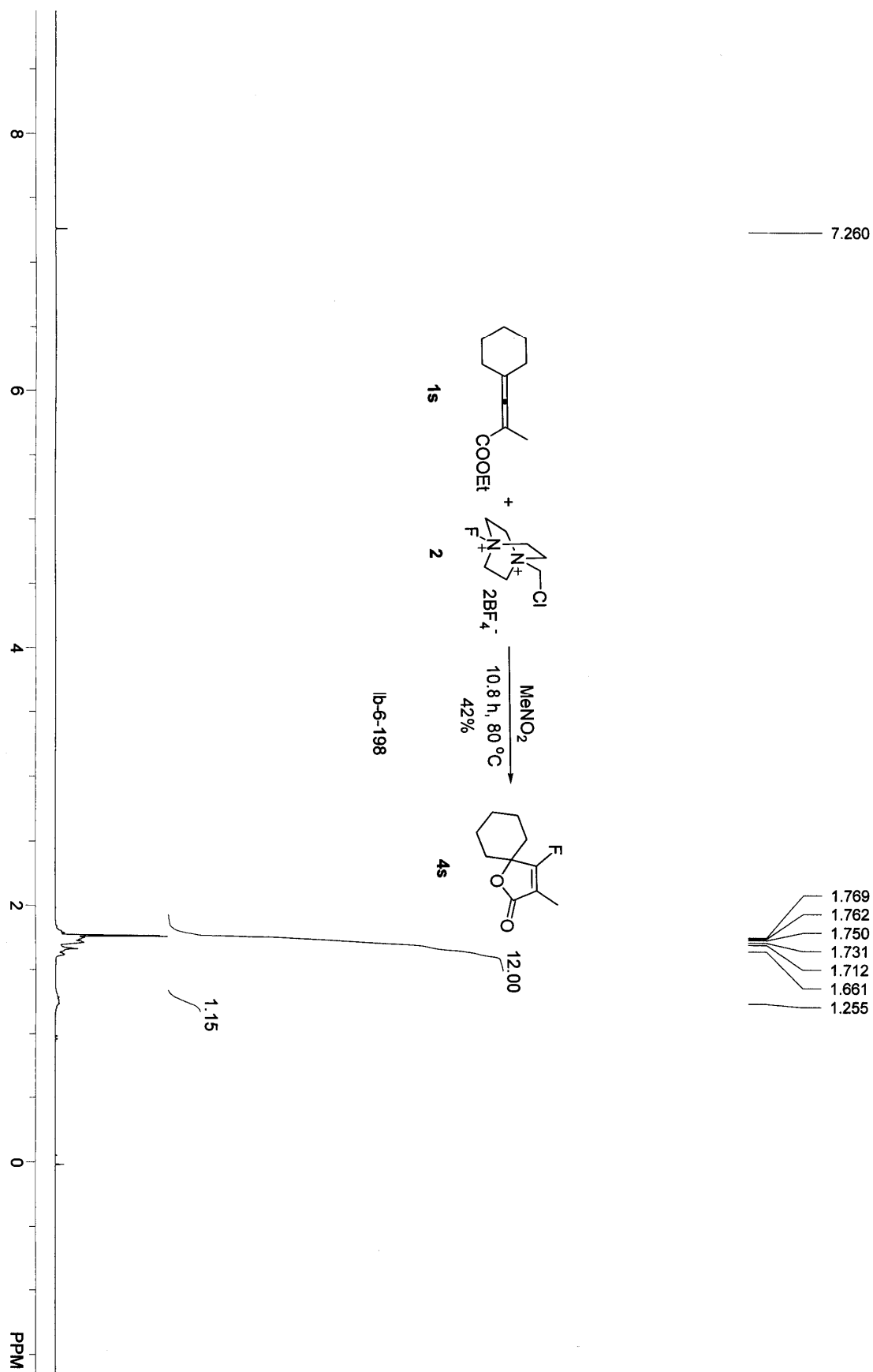


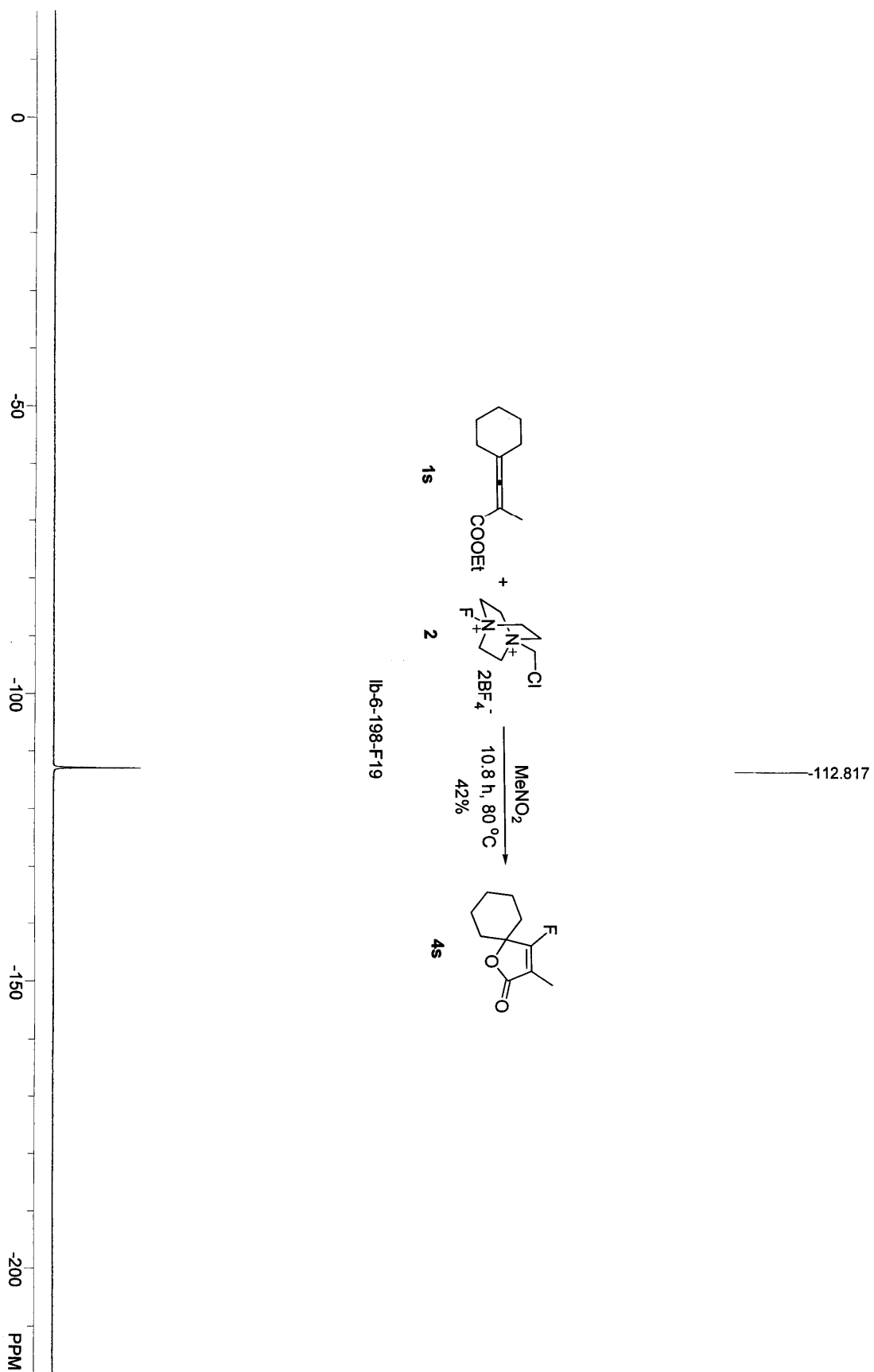


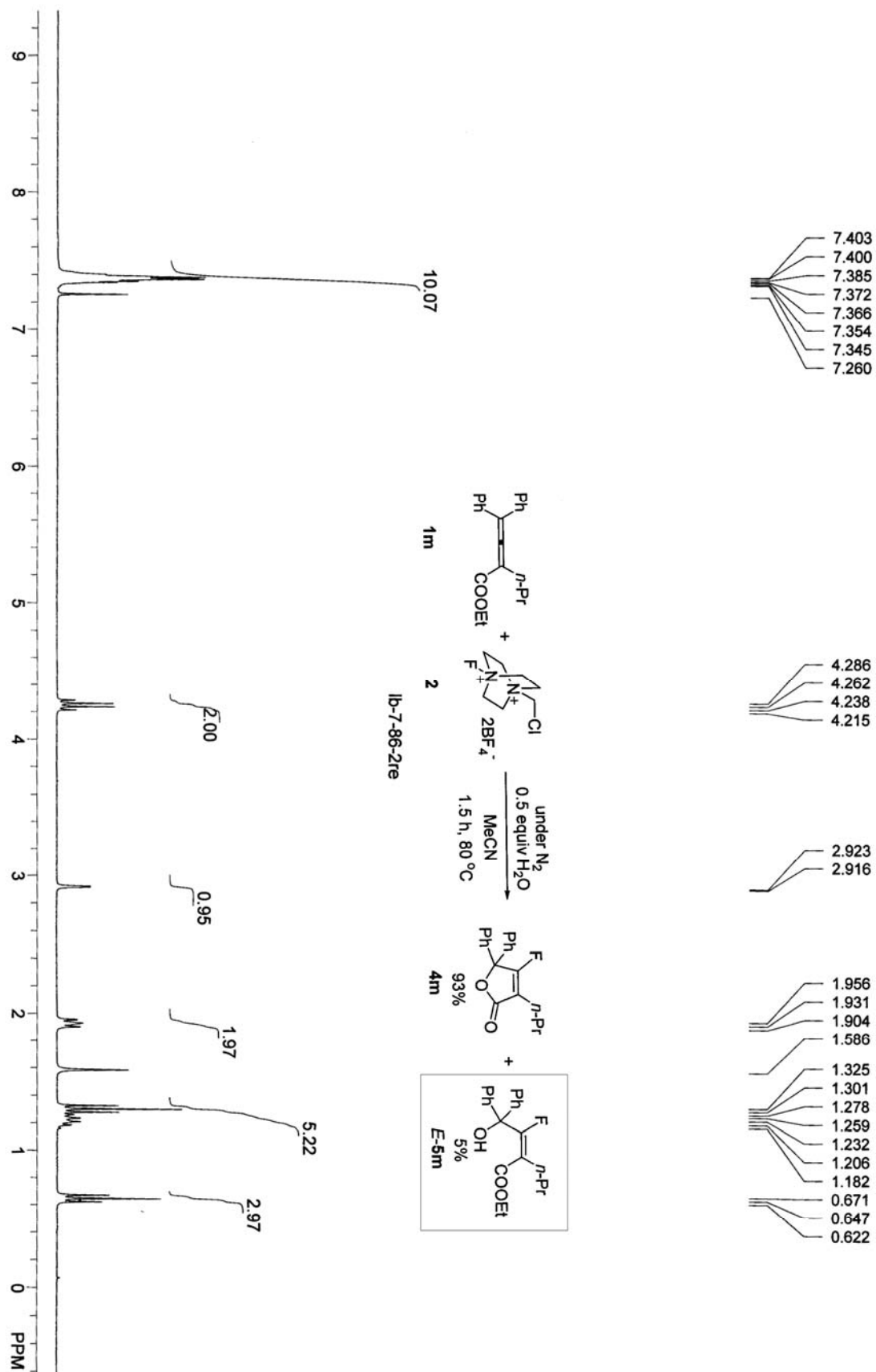


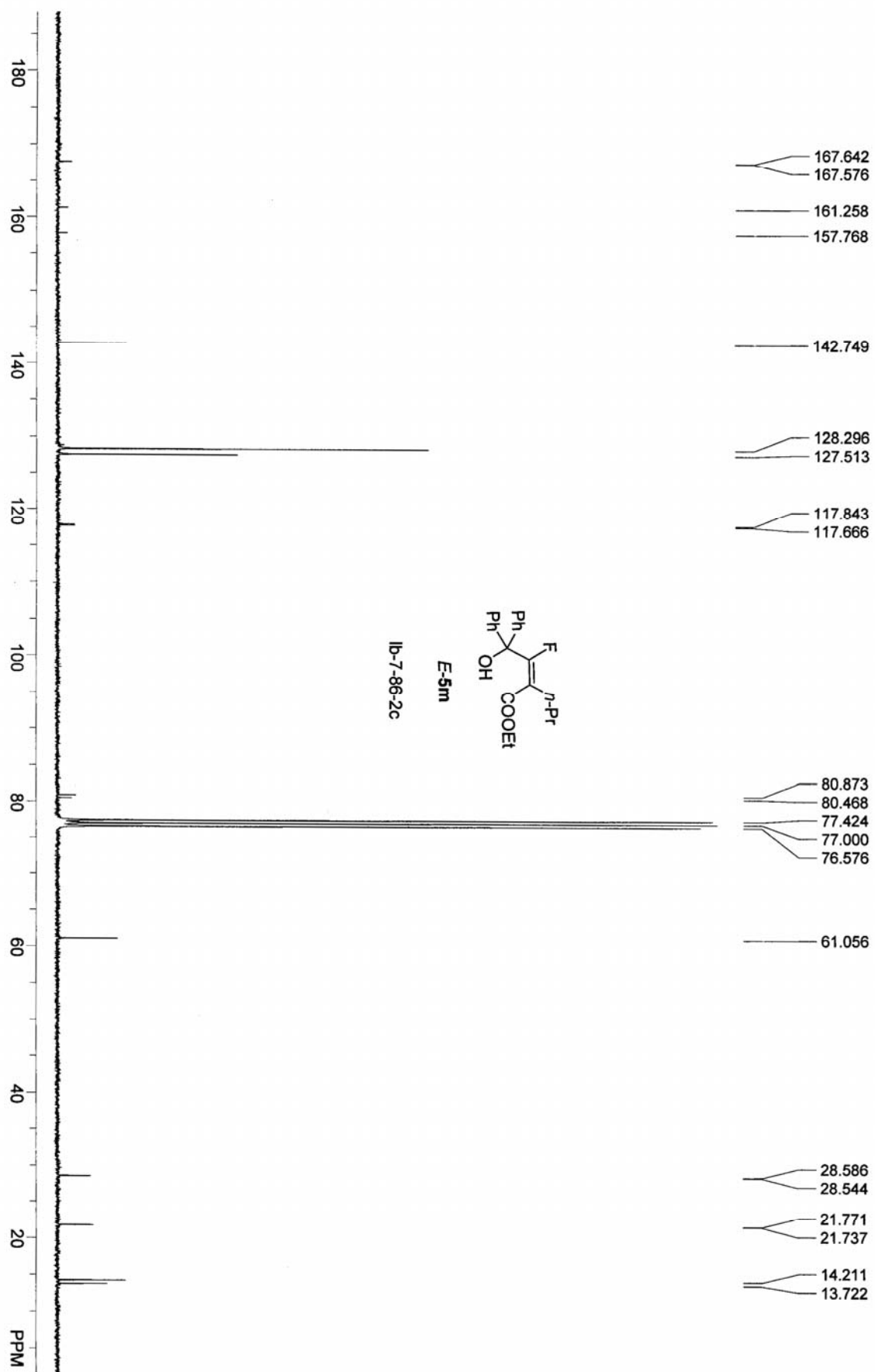


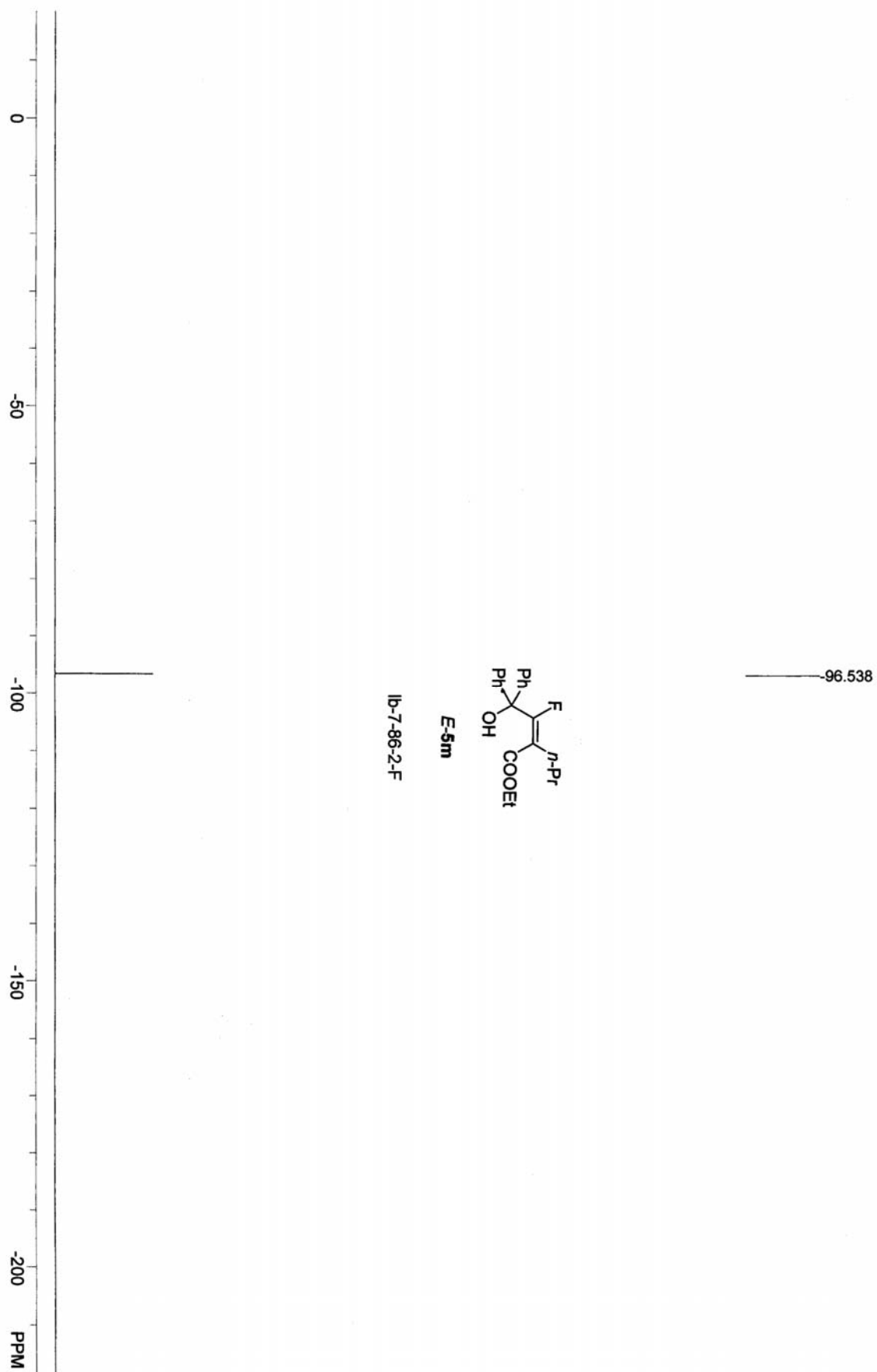
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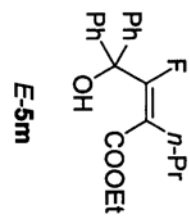












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