Supporting information

Electrophilic Trifluoromethylation by Copper-Catalyzed Addition of CF_3-Transfer Reagents to Alkenes and Alkynes

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General information

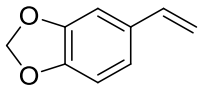
Trifluoromethylating agent **1a** was prepared by literature procedure from 2-iodobenzoic acid.[1] Starting material **3b** was prepared according to a literature procedure from piperonal.[2] All other chemicals were obtained from commercial suppliers and used without further preparations. All reactions were performed under air. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm ^{1}H, 77.16 ppm ^{13}C, external standard α,α,α-trifluorotoluene (-63.73 ppm) ^{19}F) using a 400 MHz instrument. HRMS data were recorded on an instrument using ESI technique except for compounds **6a** and **6b** that were ionized by APCI. All column chromatography was performed using silica gel (35-70 microns).

General procedure for trifluoromethyl additions

A 3 ml screwtop vial (temp. ≤ 60°C) or a 5 ml microwave vial (temp. > 60°C) equipped with a Teflon coated stirring bar was charged with copper iodide (1.9 mg, 0.01 mmol, 10 mol% or 19 mg, 0.1 mmol, 1 eq.), **1a** (47.4 mg, 0.15 mmol, 1.5 eq.), $CDCl_3$ (0.5 ml) and substrate (0.1 mmol, 1 eq.). The vial was sealed and heated for 18 h at the indicated temperature. After the reaction was finished the vial contents were concentrated under reduced pressure and purified by column chromatography. When 1 eq. of copper iodide was used the crude product was filtered through a celite plug before concentrating.

Compound characterization

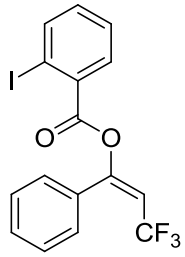
5-Ethenyl-1,3-Benzodioxole (3b)



This compound was synthesized according to a known literature procedure from piperonal.[2] Isolated by column chromatography (pentane) as a colorless oil (71 %). The NMR data obtained for **3b** are in agreement with literature values.[2] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.15 (1H, dd, $^{3}J_{HH}$ = 10.8 Hz, $^{4}J_{HH}$ = 0.6 Hz), 5.60 (1H, dd, $^{3}J_{HH}$ = 17.5 Hz, $^{4}J_{HH}$ = 0.7 Hz), 5.96 (2H, s) 6.65 (1H,

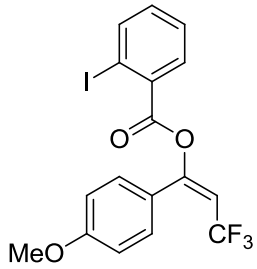
dd, $^{3}J_{HH}$ = 17.5 Hz, 10.8 Hz), 6.78 (1H, d, $^{3}J_{HH}$ = 8.0 Hz), 6.85 (1H, dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.6 Hz), 6.98 (1H, d, $^{4}J_{HH}$ = 1.6 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 101.1, 105.5, 108.3, 112.0, 121.1, 132.3, 136.5, 147.5, 148.1.

(E)-3,3,3-Trifluoro-1-phenylprop-1-en-1-yl 2-iodobenzoate (4a)



This compound was synthesized according to the general procedure at 100°C. Isolated by column chromatography (pentane: diethyl ether, 9:1) as white solids (55%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.97 (1H, q, $^{3}J_{HF}$ = 7.8 Hz), 7.21 (1H, td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.7 Hz), 7.43 (4H, m), 7.59 (2H, dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.8 Hz), 7.94 (1H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.6 Hz), 8.05 (1H, dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 0.8 Hz), ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.68 (d, $^{3}J_{HF}$ = 8.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 95.0, 110.3 (q, J_{CF} = 36.0 Hz), 122.6 (q, J_{CF} = 269.2 Hz), 128.3, 128.4, 128.7 (q, J_{CF} = 1.8 Hz), 130.6, 131.9, 132.3, 133.0, 133.8, 142.1, 157.1 (q, J_{CF} = 6.4 Hz), 163.4 Hz (q, J_{CF} = 1.0 Hz), HRMS (ESI): *m*/*z* calcd. for $[C_{16}H_{10}F_3IO_2+Na]^+$ 440.9570, found: 440.9588.

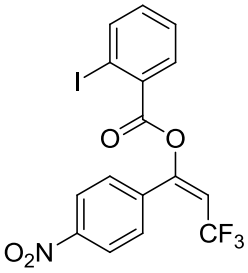
(E)-3,3,3-Trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl 2-iodobenzoate (4b)



This compound was synthesized according to the general procedure at 60°C. Isolated by column chromatography (pentane: diethyl ether, 6:1) as white solids (78%). ^{1}H NMR ($CDCl_3$, 400

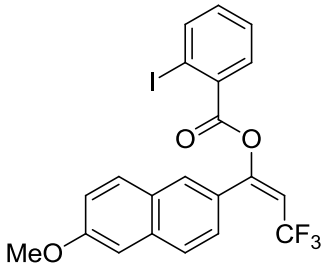
MHz): δ 3.83 (3H, s), 5.88 (1H, q, $^{3}J_{HF}$ = 7.9 Hz), 6.92 (2H, m), 7.21 (1H, td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.7 Hz), 7.45 (1H, td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.1 Hz), 7.53 (2H, m), 7.95 (1H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 1.7 Hz), 8.05 (1H, dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.0 Hz), ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.62 (d, $^{3}J_{HF}$ = 7.9 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 95.0, 109.2 (q, J_{CF} = 36.0 Hz), 113.9, 122.8 (q, J_{CF} = 269.0 Hz) 124.5, 128.3, 130.2 (q, J_{CF} = 2.0 Hz) 131.8, 133.1, 133.8, 142.1, 156.9 (q, J_{CF} = 6.4 Hz), 161.4, 163.5 (q, J_{CF} = 0.9 Hz), HRMS (ESI): *m*/*z* calcd. for $[C_{17}H_{12}F_3IO_3+Na]^+$ 470.9675, found: 470.9668.

(E)-3,3,3-Trifluoro-1-(4-nitrophenyl)prop-1-en-1-yl 2-iodobenzoate (4c)



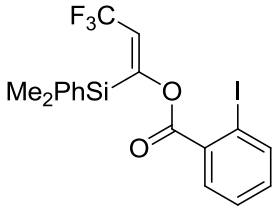
This compound was synthesized according to the general procedure at 100°C. Isolated by column chromatography (pentane: DCM 3:2) as white solids (78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.12 (q, $^{3}J_{HF}$ = 7.7 Hz), 7.24 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.7 Hz), 7.47 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.1 Hz), 7.77 (d, $^{3}J_{HH}$ = 8.8 Hz), 7.92 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.6 Hz), 8.06 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.0 Hz), 8.29 (d, $^{3}J_{HH}$ = 8.8 Hz), ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.82 (d, $^{3}J_{HF}$ = 7.7 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 95.1, 112.4 (q, J_{CF} = 36.3 Hz), 122.1 (q, J_{CF} = 269.7 Hz), 123.7, 128.4, 130.0 (q, J_{CF} = 1.9 Hz), 132.0, 132.3, 134.2, 138.3, 142.3, 149.0, 154.7 (q, J_{CF} = 6.3 Hz), 163.2 (q, J_{CF} = 0.9 Hz), HRMS (ESI): *m*/*z* calcd. for $[C_{16}H_9F_3INO_4+Na]^+$ 485.9421, found: 485.9415.

(E)-3,3,3-Trifluoro-1-(6-methoxynaphthalen-2-yl)prop-1-en-1-yl 2-iodobenzoate (4d)



This compound was synthesized according to the general procedure at 60°C. Isolated by column chromatography (pentane: diethyl ether, 6:1) as white solids (69%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.93 (3H, s), 7.13-7.23 (3H, m), 7.45 (1H, td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.1 Hz), 7.61 ($^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 1.6 Hz), 7.77 (2H, t, $^{3}J_{HH}$ = 9.1 Hz), 7.97 (1H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.7 Hz), 8.02 (1H, br. s.), 8.05 (1H, dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.0 Hz), ^{19}F NMR (376 MHz, $CDCl_3$): δ -55.51 (d, $^{3}J_{HF}$ = 7.9 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 95.0, 105.8, 110.0 (q, J_{CF} = 36.1 Hz), 119.8, 122.8 (q, J_{CF} = 269.2 Hz), 125.8 (q, J_{CF} = 1.8 Hz) 127.0, 127.3, 128.1, 128.3, 128.9 (q, J_{CF} = 1.9 Hz), 130.4, 131.9, 133.0, 133.8, 135.6, 142.1, 157.3 (q, J_{CF} = 6.4 Hz) 159.1, 163.5 (q, J_{CF} = 1.0 Hz), HRMS (ESI): *m*/*z* calcd. for $[C_{21}H_{14}F_3IO_3+Na]^+$ 520.9832, found: 520.9844.

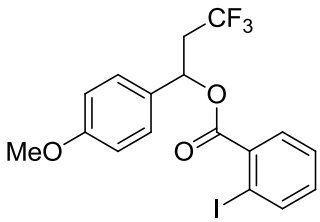
(Z)-1-(Dimethyl(phenyl)silyl)-3,3,3-trifluoroprop-1-en-1-yl 2-iodobenzoate (4e)



This compound was synthesized according to the general procedure at 120°C except heating was done by microwave irradiation for 30 min. Isolated by column chromatography (pentane: diethyl ether, 29:1) as white solids (53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.65 (6H, s), 6.31 (1H, q, $^{3}J_{HF}$ = 8.5 Hz), 7.11-7.16 (1H, m), 7.24-7.35 (XH, m), 7.58-7.62 (2H, m), 7.96-7.99 (1H, m), ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.29 (d, $^{3}J_{HF}$ = 8.6 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ -2.4 (q, J_{CF} = 2.4 Hz), 94.4, 122.9 (q, J_{CF} = 269.4 Hz), 124.0 (q, J_{CF} = 35.1 Hz), 127.9, 128.0, 129.8,

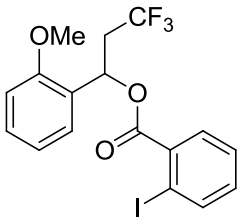
131.2, 133.2, 133.5, 134.6, 134.9 (q, J_{CF} = 0.9 Hz) 141.6, 164.7 (q, J_{CF} = 1.1 Hz), 167.7 (q, J_{CF} = 6.4 Hz), HRMS (ESI): *m/z* calcd. for $[C_{18}H_{16}F_3IO_2Si+Na]^+$ 498.9809, found: 498.9802.

3,3,3-Trifluoro-1-(4-methoxyphenyl)propyl 2-iodobenzoate (5a)



This compound was synthesized according to the general procedure at 60°C. Isolated by column chromatography (pentane: diethyl ether, 19:1) as a clear colorless oil (86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.66 (1H, dqd, $^3J_{HH}$ = 15.2 Hz, 4.5 Hz, $^3J_{HF}$ = 10.3 Hz), 3.00 (1H, dqd, $^3J_{HH}$ = 15.2 Hz, 8.9 Hz, $^3J_{HF}$ = 10.0 Hz), 3.81 (3H, s), 6.31 (1H, dd, $^3J_{HH}$ = 8.9 Hz, 4.4 Hz), 6.89-6.94 (2H, m), 7.14 (1H, td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz), 7.37-7.43 (3H, m), 7.81 (1H, dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz), 7.98 (1H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.1 Hz) ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.75 (t, $^3J_{HF}$ = 10.2 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.3 (q, J_{CF} = 28.2 Hz) 55.4, 70.8 (q, J_{CF} = 3.3 Hz) 94.3, 114.3, 125.3 (q, J_{CF} = 277.6 Hz) 128.1, 128.3, 130.2, 131.1, 133.0, 134.5, 141.6, 160.1, 165.0, HRMS (ESI): *m/z* calcd. for $[C_{17}H_{14}F_3IO_3+Na]^+$ 472.9832, found: 472.9814.

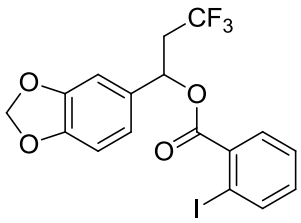
3,3,3-trifluoro-1-(2-methoxyphenyl)propyl 2-iodobenzoate (5b)



This compound was synthesized according to the general procedure at 120°C except heating was done by microwave irradiation for 1 h. Isolated by column chromatography (pentane: diethyl ether, 9:1) as a clear colorless oil (58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.66 – 2.92 (2H, m), 3.91 (3H, s), 6.68 (1H, dd, $^3J_{HH}$ = 9.0 Hz, 3.3 Hz), 6.92 (1H, d, $^3J_{HH}$ = 8.2 Hz), 6.97 (1H, td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 0.8 Hz) 7.16 (1H, td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz), 7.31 (1H, td, $^3J_{HH}$ = 7.9 Hz,

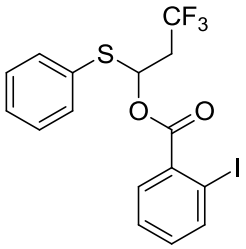
$^4J_{HH}$ = 1.7 Hz), 7.40 (1H, dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz), 7.44 (1H, dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.1 Hz) 7.93 (1H, dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz) 8.01 (1H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.0 Hz) ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.91 (t, $^3J_{HF}$ = 10.4 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.1 (q, J_{CF} = 28.1 Hz) 55.7, 66.8 (q, J_{CF} = 3.4 Hz) 94.5, 110.9, 120.9, 125.7 (q, J_{CF} = 277.8 Hz), 126.5, 126.7, 128.1, 129.8, 131.2, 133.0, 134.5, 141.7, 156.1, 164.8, HRMS (ESI): *m*/*z* calcd. for $[C_{17}H_{14}F_3IO_3+Na]^+$ 472.9832, found: 472.9837.

1-(Benzo[d][1,3]dioxol-5-yl)-3,3,3-trifluoropropyl 2-iodobenzoate (5c)



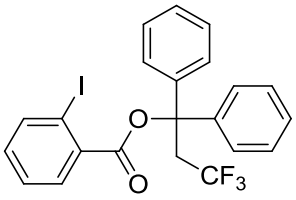
This compound was synthesized according to the general procedure at 60°C. Isolated by column chromatography (pentane: diethyl ether, 9:1) as a clear colorless oil (77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.63 (1H, dqd, $^3J_{HH}$ = 15.0 Hz, 4.5 Hz, $^3J_{HF}$ = 10.4 Hz), 3.00 (1H, dqd, $^3J_{HH}$ = 15.3 Hz, 8.9 Hz, $^3J_{HF}$ = 10.0 Hz), 5.98 (3H, s), 6.24 (1H, dd, $^3J_{HH}$ = 8.8 Hz, 4.4 Hz), 6.79-6.82 (1H, m), 6.93-6.97 (2H, m), 7.16 (1H, td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz), 7.41 (1H, td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.1 Hz), 7.83 (1H, dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz), 7.99 (1H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.0 Hz), ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.78 (t, $^3J_{HF}$ = 10.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.5 (q, J_{CF} = 28.4 Hz), 71.0 (q, J_{CF} = 3.3 Hz), 94.4, 101.5, 107.1, 108.6, 120.8, 125.3 (q, J_{CF} = 277.6 Hz), 128.1, 131.2, 132.0, 133.1, 134.3, 141.7, 148.21, 148.22, 164.9, HRMS (ESI): *m*/*z* calcd. for $[C_{17}H_{12}F_3IO_4+Na]^+$ 486.9625, found: 486.9611.

3,3,3-Trifluoro-1-(phenylthio)propyl 2-iodobenzoate (5d)



This compound was synthesized according to the general procedure at 60°C. Isolated by column chromatography (pentane: diethyl ether, 9:1) as a clear colorless oil (51%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.75 (2H, qd, $^{3}J_{HH}$ = 9.9 Hz, 6.6 Hz), 6.59 (1H, t, $^{3}J_{HH}$ = 6.4 Hz), 7.19 (1H, td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.6 Hz), 7.37-7.45 (4H, m), 7.56 (2H, m), 7.78 (1H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.5 Hz), 8.03 (1H, d, $^{3}J_{HH}$ = 7.9 Hz), ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.87 (t, $^{3}J_{HF}$ = 10.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.5 (q, J_{CF} = 29.3 Hz), 74.2 (q, J_{CF} = 3.2 Hz), 94.6, 124.9 (q, J_{CF} = 278.0 Hz), 128.1, 129.51, 129.52, 129.6, 131.1, 133.3, 133.7, 135.2, 141.9, 164.3, HRMS (ESI): *m*/*z* calcd. for $[C_{16}H_{12}F_3IO_2S+Na]^+$ 474.9447, found: 474.9448.

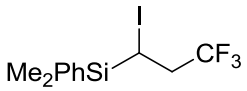
3,3,3-Trifluoro-1,1-diphenylpropyl 2-iodobenzoate (5e)



This compound was synthesized according to the general procedure at 120°C except heating was done by microwave irradiation for 30 min. Isolated by column chromatography (pentane: dichloromethane, 4:1) as colorless crystals (70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.92 (2H, q, $^{3}J_{HF}$ = 10.0 Hz), 7.20 (1H, td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.6 Hz), 7.27 (2H, t, $^{3}J_{HH}$ = 7.2 Hz), 7.34 (4H, t, $^{3}J_{HH}$ = 7.6 Hz), 7.43 (4H, d, $^{3}J_{HH}$ = 7.6 Hz), 7.50 (1H, td, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 0.9 Hz), 7.96 (1H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.6 Hz), 8.00 (1H, dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 0.8 Hz), ^{19}F NMR

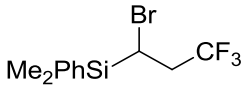
(376 MHz, $CDCl_3$): δ -59.59 (t, $^3J_{HF}$ = 10.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.3 (q, J_{CF} = 27.0 Hz), 83.1 (q, J_{CF} = 2.2 Hz), 94.1, 125.7, 125.8 (q, J_{CF} = 278.4 Hz), 127.8, 128.2, 128.6, 130.9, 132.9, 135.7, 141.6, 143.3, 165.0, HRMS (ESI): *m*/*z* calcd. for $[C_{22}H_{16}F_3IO_2+Na]^+$ 519.0045, found: 519.0053.

Dimethyl(phenyl)(3,3,3-trifluoro-1-iodopropyl)silane (6a)



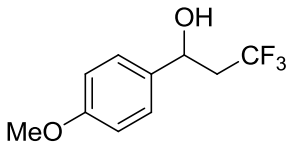
This compound was synthesized according to the general procedure at room temperature. Isolated by column chromatography (pentane: dichloromethane, 19:1) as a clear colorless oil (71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.52 (3H, s), 0.54 (3H, s), 2.44-2.69 (2H, m), 3.27 (1H, dd, $^3J_{HH}$ = 11.2 Hz, 2.5 Hz), 7.37-7.47 (3H, m), 7.51-7.56 (2H, m), ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.02 (t, $^3J_{HF}$ = 9.8 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ -4.5, -2.9, 2.1 (q, J_{CF} = 2.2 Hz), 38.4 (q, J_{CF} = 29.1 Hz), 126.2 (q, J_{CF} = 278.8 Hz), 128.4, 130.2, 134.2, 134.6, HRMS (APCI): *m*/*z* calcd. for $[C_{11}H_{13}F_3ISi]^-$ 356.9789, found: 356.9778.

Dimethyl(phenyl)(3,3,3-trifluoro-1-bromopropyl)silane (6b)



This compound was synthesized according to the general procedure at 60°C except 1 eq. (0.1 mmol) of CuBr was used. Isolated by column chromatography (pentane: dichloromethane, 29:1) as a clear colorless oil (52%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.49 (3H, s), 0.50 (3H, s), 2.38–2.62 (2H, m), 3.47 (1H, dd, $^3J_{HH}$ = 11.1 Hz, 2.5 Hz), 7.37-7.47 (3H, m), 7.52-7.56 (2H, m), ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.79 (t, $^3J_{HF}$ = 9.9 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.5, -4.0, 29.2 (q, J_{CF} = 2.4 Hz), 37.8 (q, J_{CF} = 29.2 Hz), 126.3 (q, J_{CF} = 278.8 Hz), 128.4, 130.3, 134.17, 134.4, HRMS (APCI): *m*/*z* calcd. for $[C_{11}H_{13}BrF_3Si]^-$ 310.9902, found: 310.9913.

3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-ol (7) by hydrolysis of 5a (Figure 2).



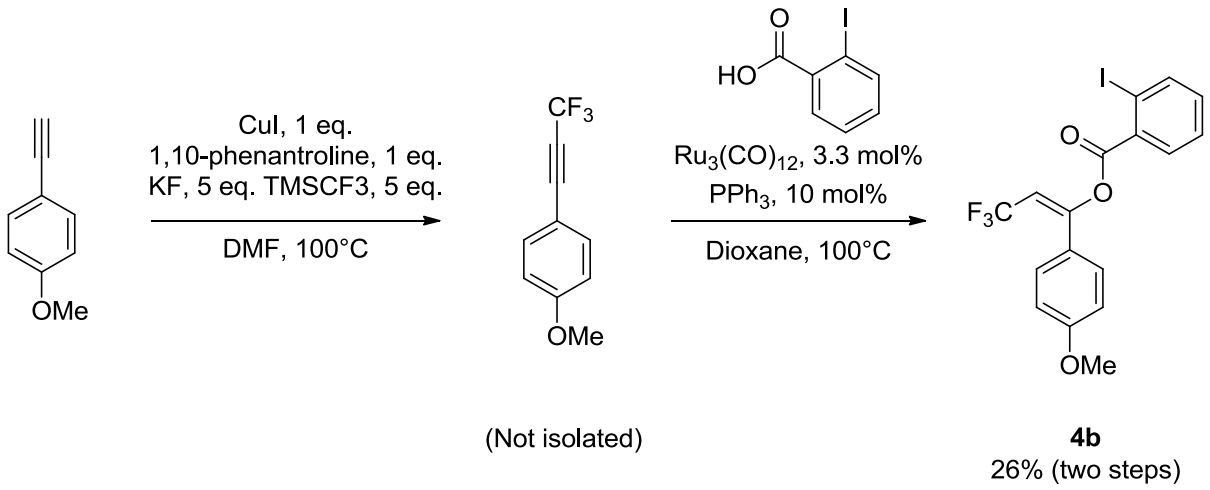
Compund **5a** was synthesized according to the general procedure on a 1 mmol scale at 60°C. Upon reaction completion the solvent was evaporated from the crude reaction mixture and K_2CO_3 (345 mg, 2.5 mmol, 2.5 eq.) and MeOH (7 mL) was added. The mixture was stirred at rt for 4 h, then neutralized with 1M HCl. The aqueous layer was extracted with diethyl ether (3X10 mL), dried over anhydrous $MgSO_4$, filtered and evaporated. Column chromatography (DCM) yielded 7 as a pale yellow oil (77% overall yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.32-2.66 (3H, m), 3.79 (3H, s), 4.97 (1H, dd, $^3J_{HH}$ = 8.7 Hz, 4.0 Hz), 6.88 (2H, dt, $^3J_{HH}$ = 9.6 Hz, $^4J_{HH}$ = 2.5 Hz), 7.26 (2H, dt, $^3J_{HH}$ = 9.5 Hz, $^4J_{HH}$ = 2.5 Hz), ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.70 (t, $^3J_{HF}$ = 10.7 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.7 (q, J_{CF} = 26.8 Hz), 55.3, 68.4 (q, J_{CF} = 3.3 Hz), 114.2, 126.0 (q, J_{CF} = 277.4 Hz), 127.1, 134.7, 159.6, HRMS (ESI): *m*/*z* calcd. for $[C_{10}H_{11}F_3O_2+Na]^+$ 243.0603, found: 243.0611.

Competition experiments

To a 3 ml screwtop vial equipped with a Teflon coated stirring bas was added copper iodide (19.0 mg, 0.1 mmol, 1eq.), **1a (**28.4 mg, 0.09 mmol 0.9 eq.), $CDCl_3$ (0.5 mL) and 1 eq. each of competing substrates. The vial was screwed shut and stirred in an oil bath at 60°C for 18h. The crude reaction mixture was centrifuged and an aliquot of the supernatant was analyzed by NMR. The ratio of products was determined by ^{19}F NMR. The competive trifluromethyl-benzoyloxylation of **2b** vs. **2a** gave a ratio of **4b** vs. **4a** = 1: 0.5; the reaction of **2b** vs. **3a** gave a ratio of **4b** vs. **5a** = 1: 4; while the the reaction of **3a** vs. **3b** gave a ratio of **5a** vs. **5b** = 1: 3.

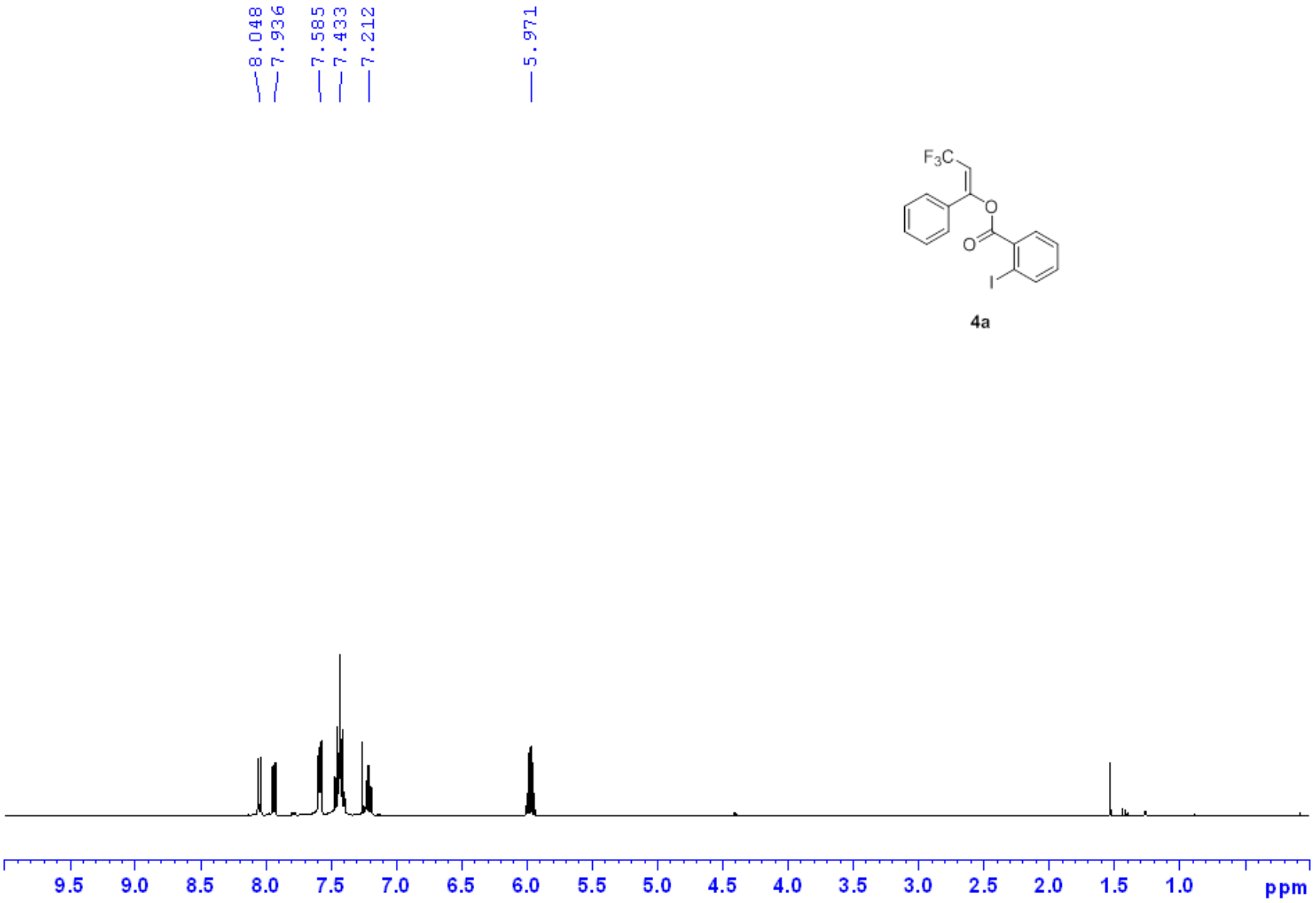
Authentic synthesis of 4b through an alternative pathway

To determine the geometry of the double bond in the alkene products, compound **4b** was synthesized from **2b** in two steps via alternative literature procedures.[3,4] In the first step the alkyne proton was exchanged for a trifluoromethyl group by a procedure reported by Qing and Chu.[3] Subsequently, this trifluoromethyl-acetylene derivative was reacted with 2-iodobenzoic acid in an E-selective Ru-catalyzed reaction reported by Itoh and co-workers.[4] The product was isolated as a white solid (26% over two steps). All spectroscopic data for this product are identical to compound **4b** synthesized by the above general procedure (entries 3-4). Based on this authenitic synthesis, we assigned the double bond of products **4a-e** as indicated above and in Table 1.



References

1. Stanek, K.; Koller, R.; Togni, A. *J. Org. Chem.* **2008**, *73*, 7678–7685
2. Aslam, S. N.; Stevenson, P.C.; Phythian, S. J.; Veitch, N. C.; Hall, D.R. *Tetrahedron*, **2006**, *62*, 4214-4226
3. Chu, L.; Qing, F.-L. *J. Am. Chem. Soc.*, **2010**, *132*, 7262–7263
4. Kawatsura, M.; Namioka, J.; Kajita, K.; Yamamoto, M.; Tsuji, H.; Itoh, T. *Org. Lett.*, **2011**, *13*, 3285–3287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7.212
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O
O
I
4a
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8.0
7.5
7.0
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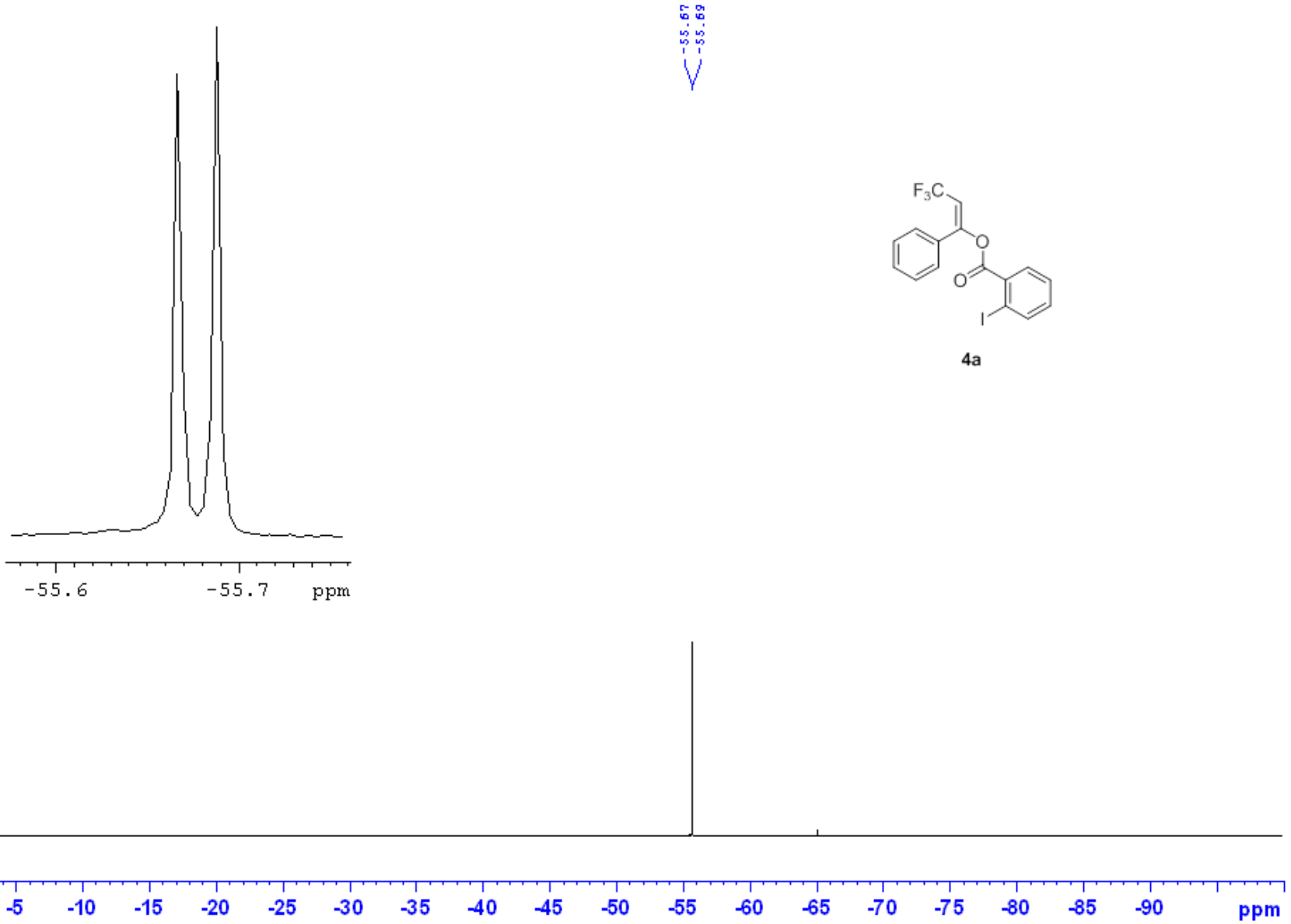
1.0
ppm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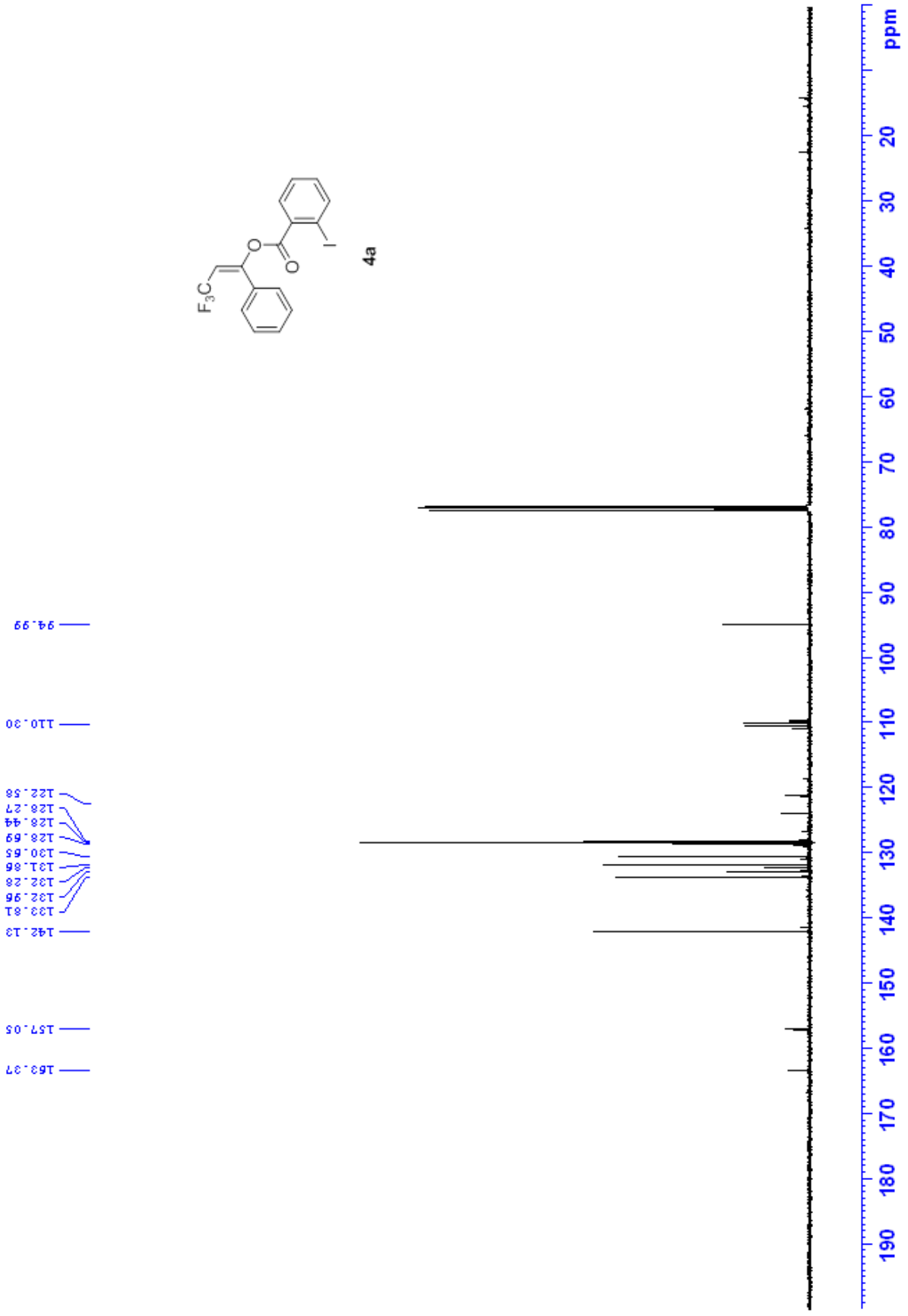
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132.96
133.81
142.13
157.05
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170
180
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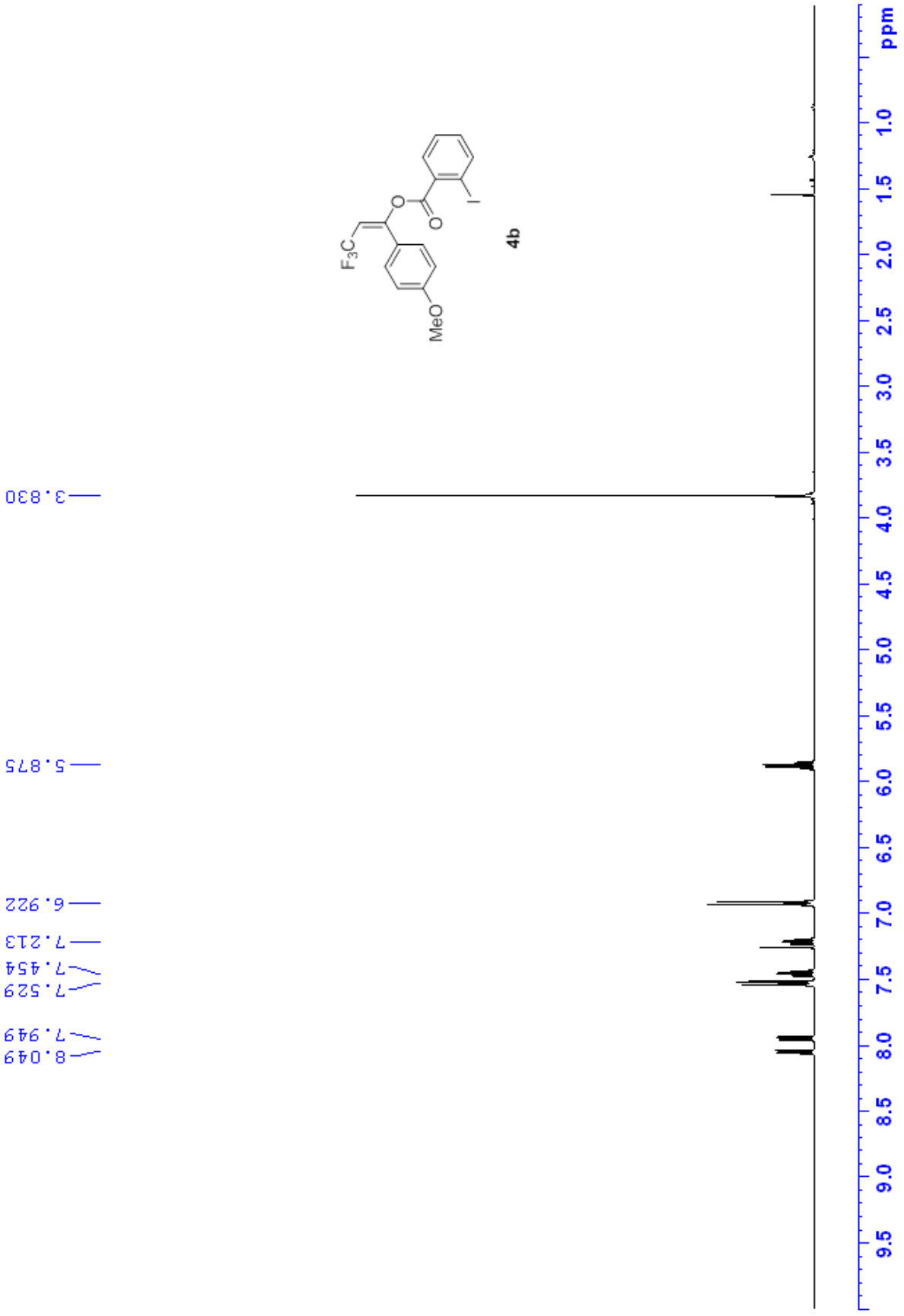
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4b
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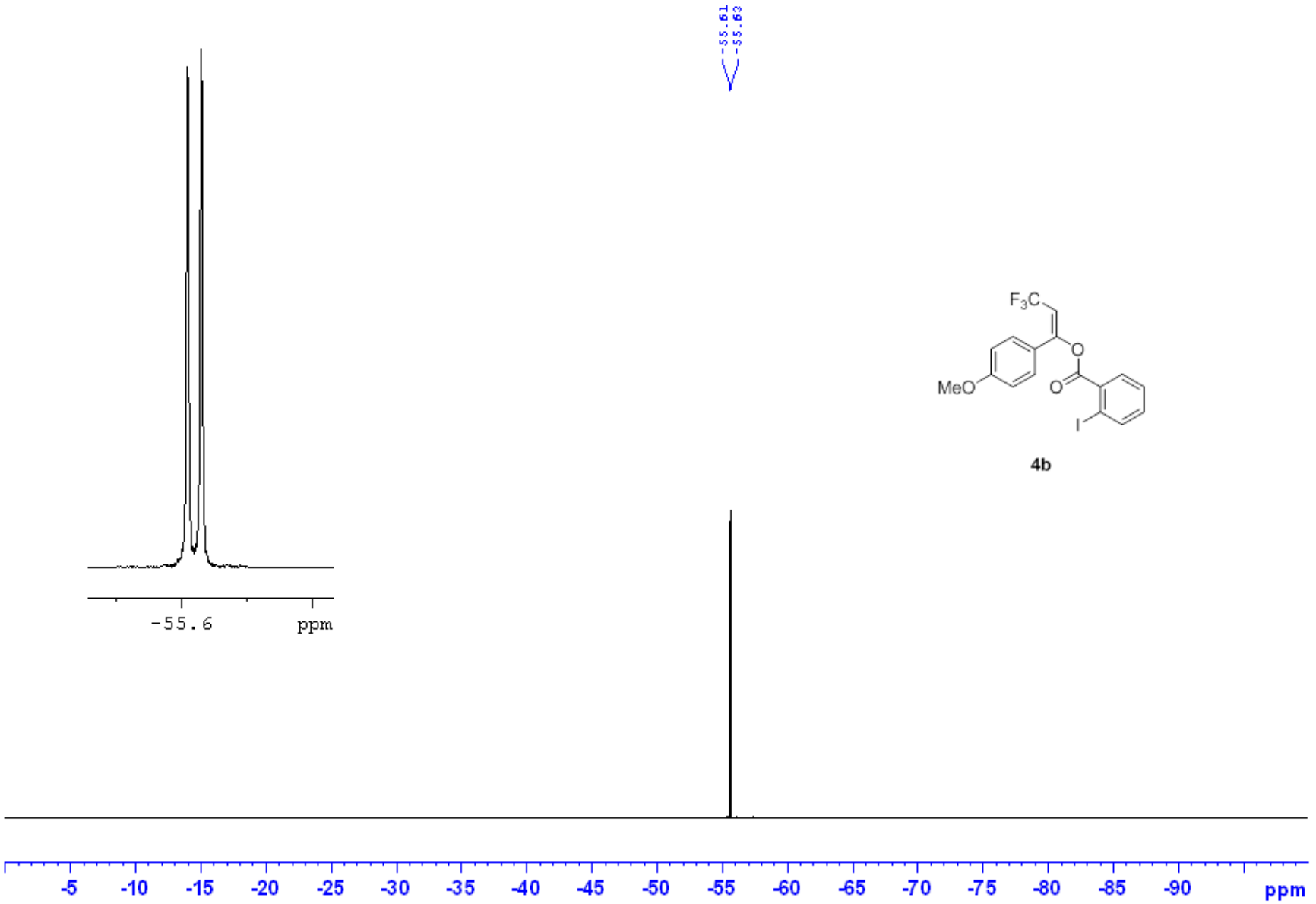
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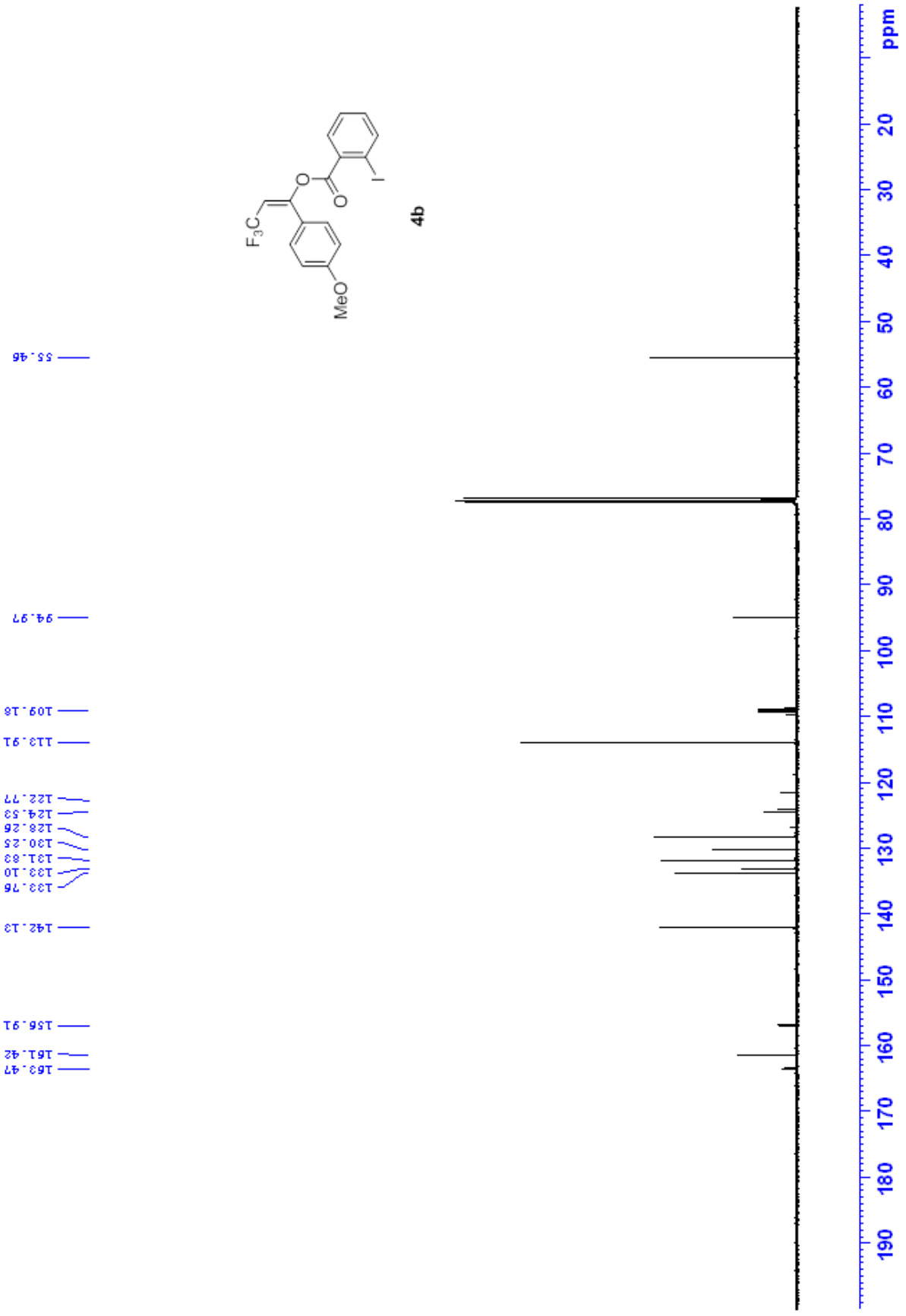
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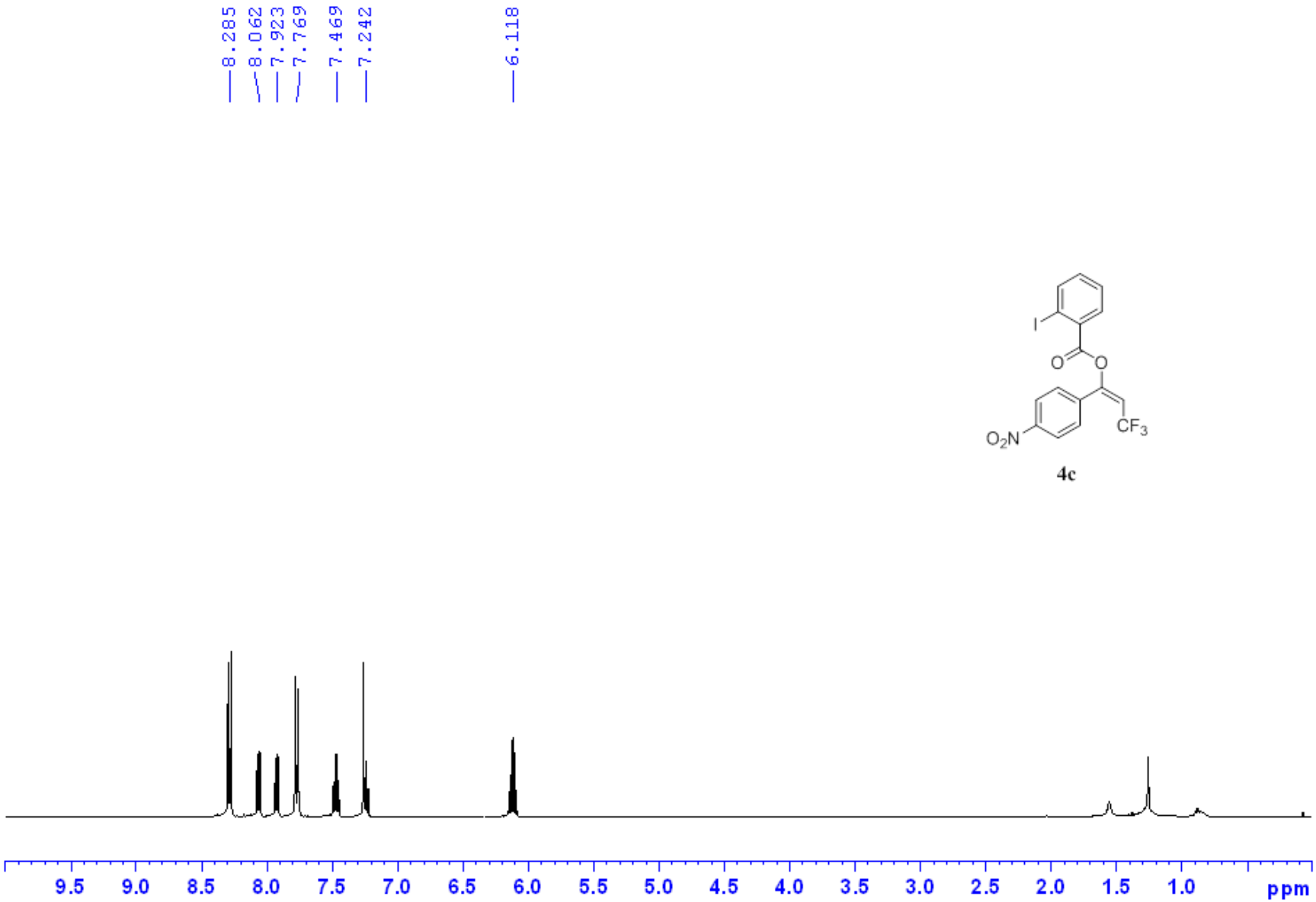
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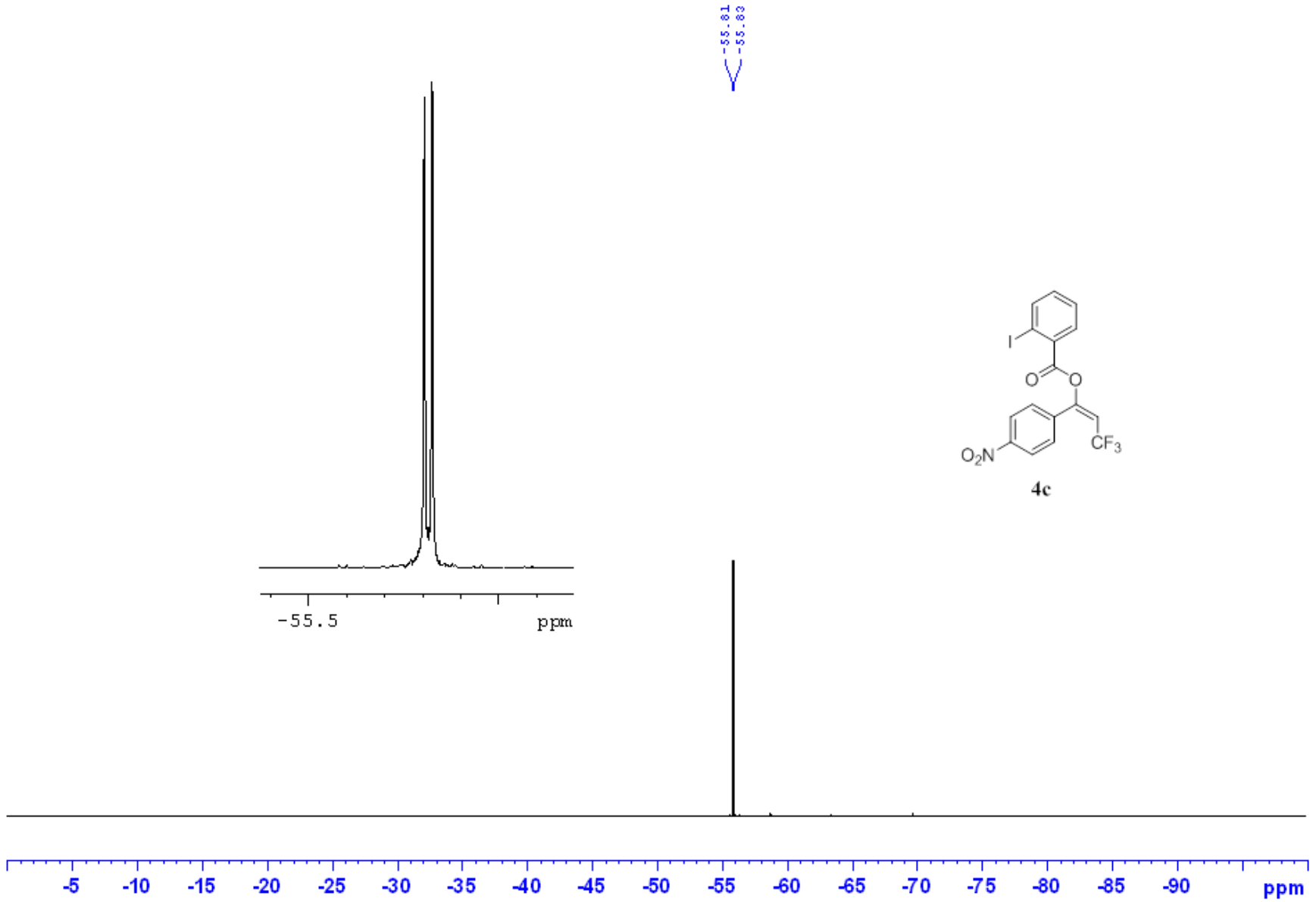
ppm

4c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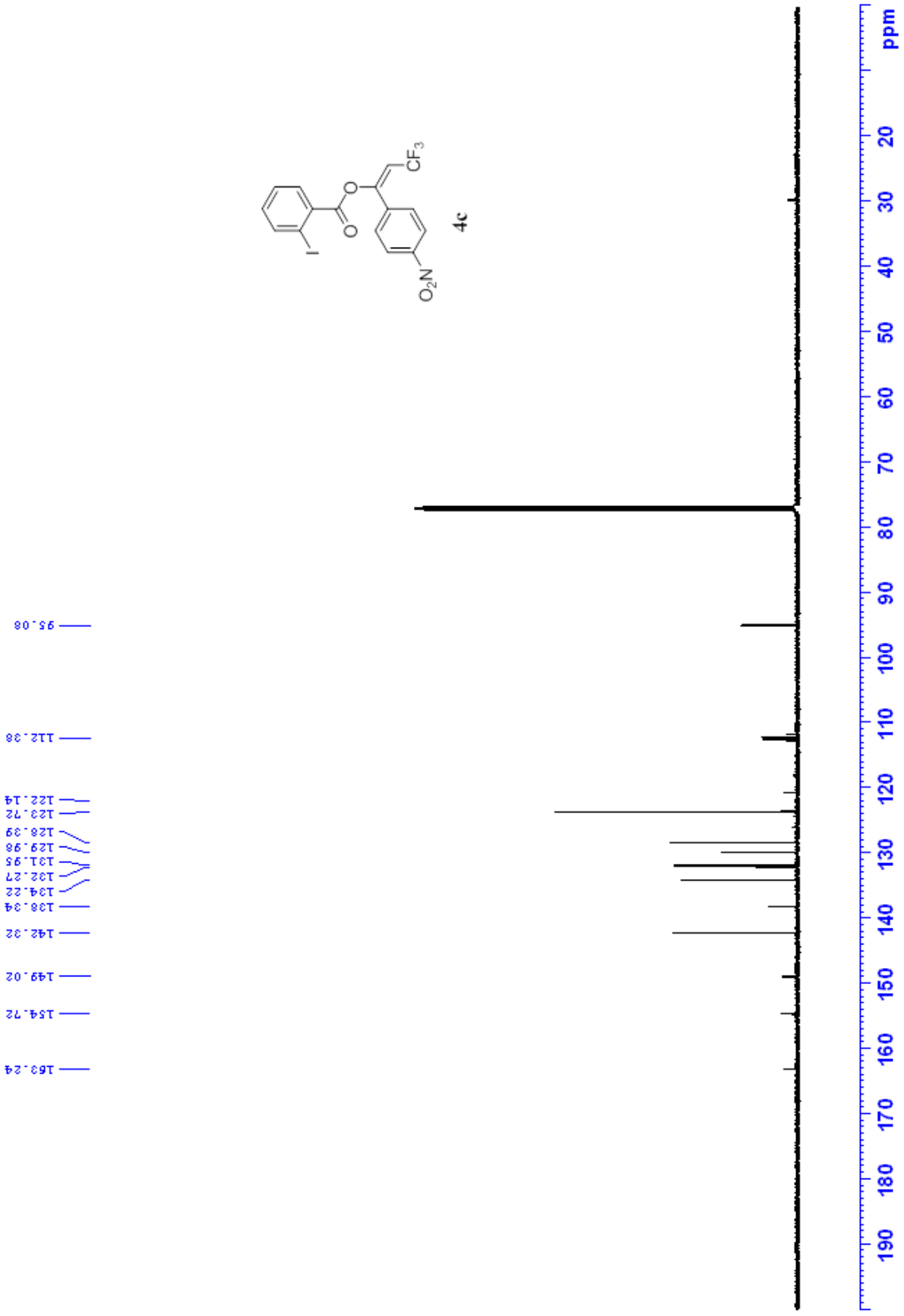
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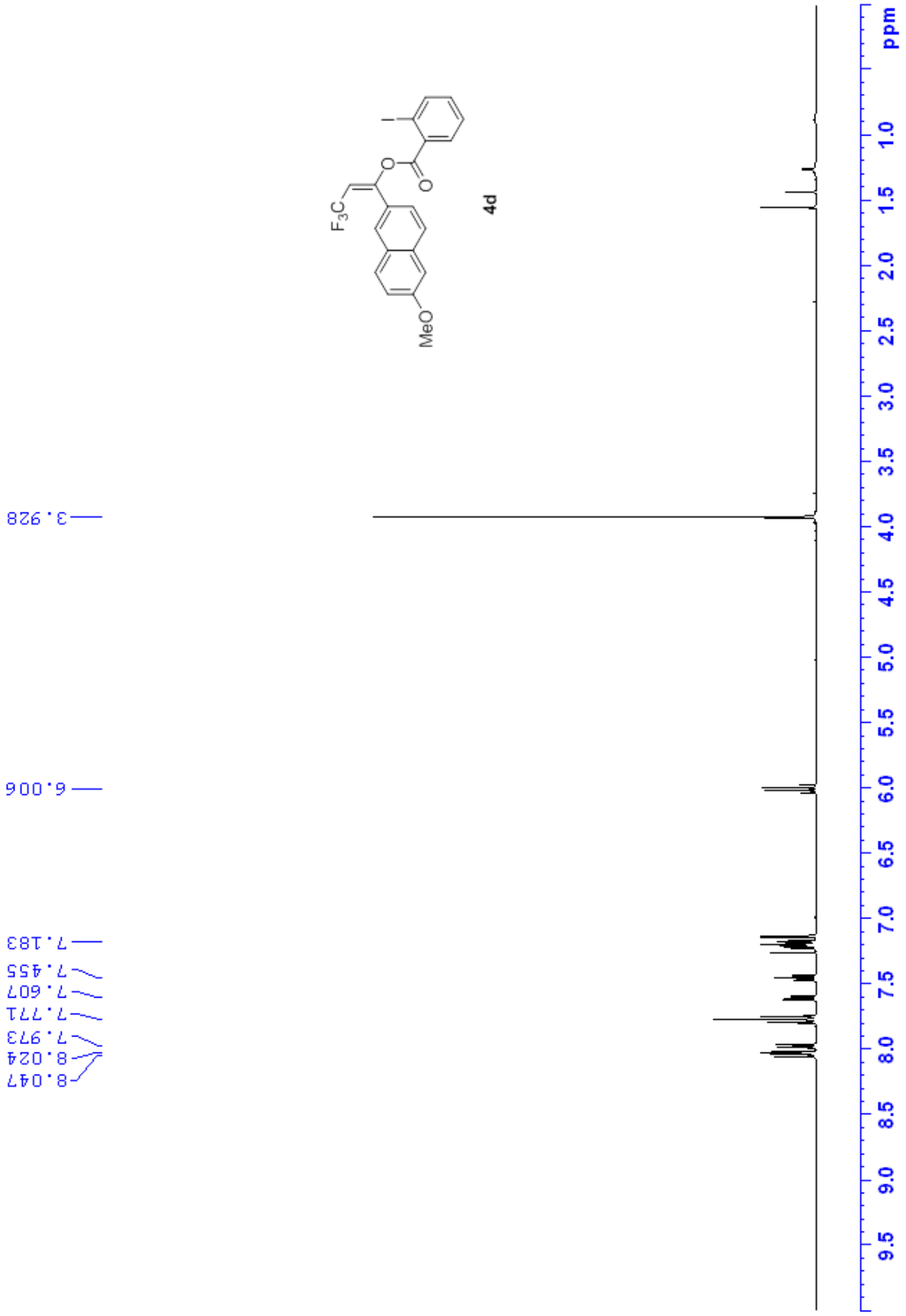
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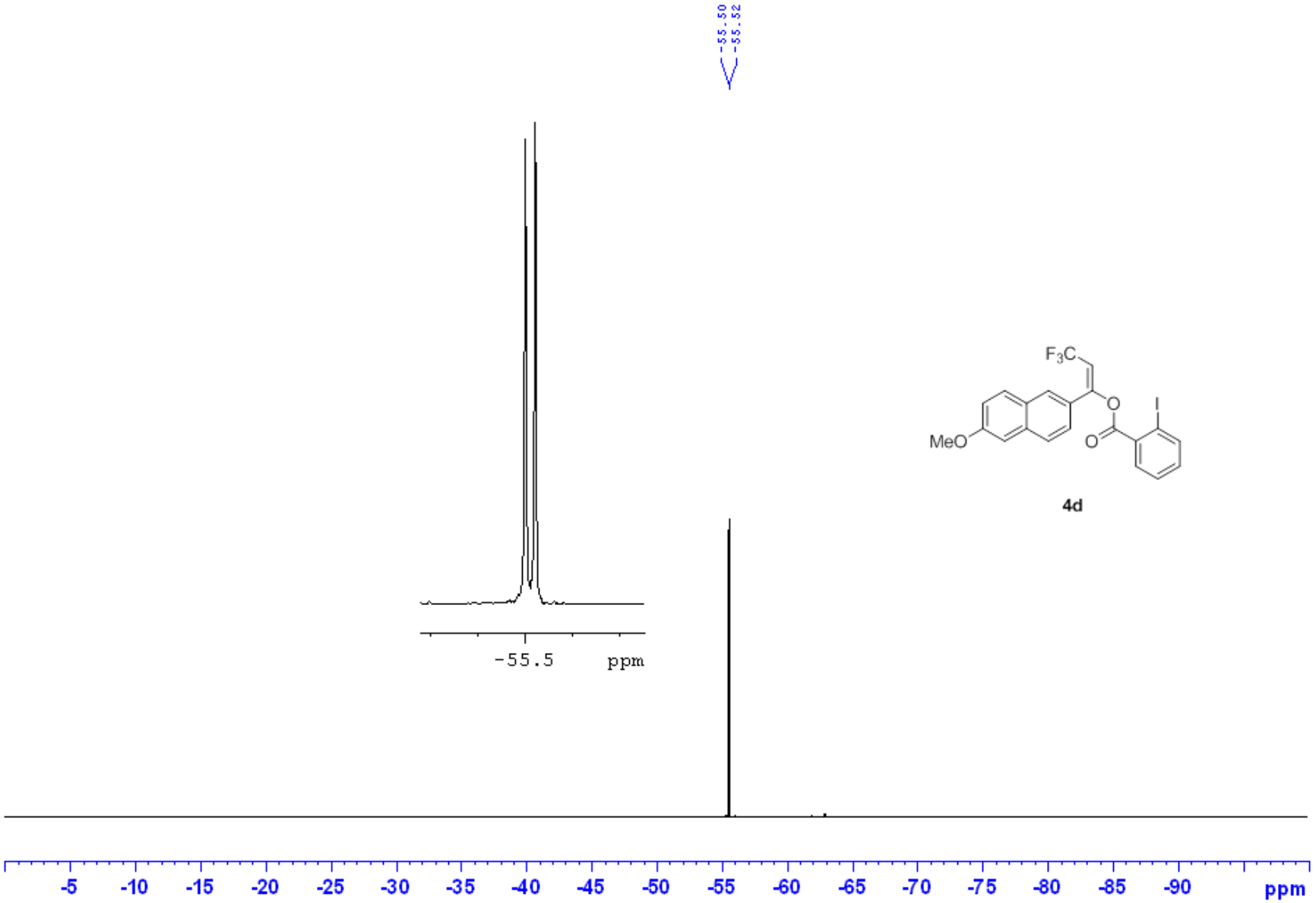
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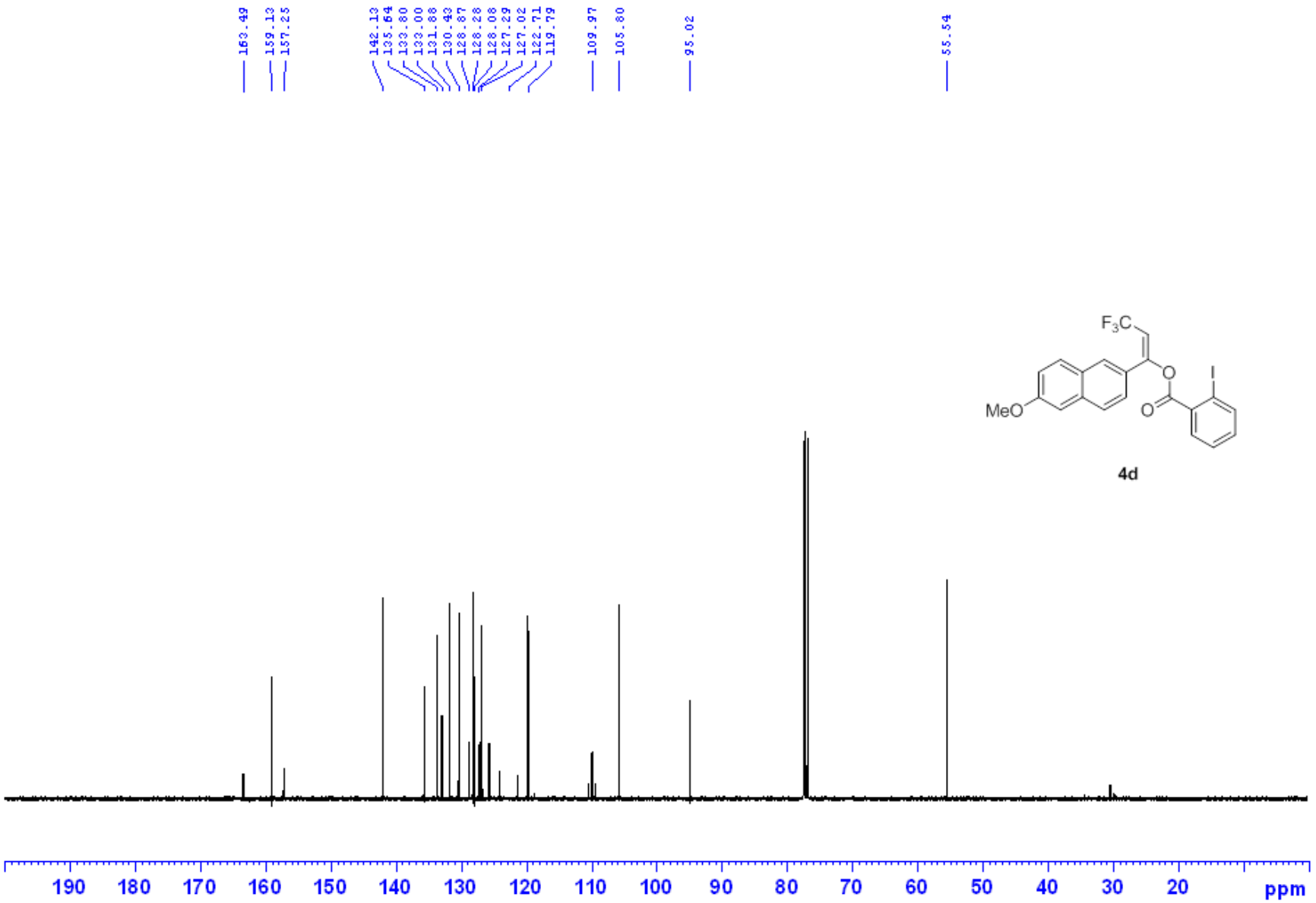
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122.71
119.79
109.97
105.80
95.02
55.54
F3C
O
O
I
MeO
4d
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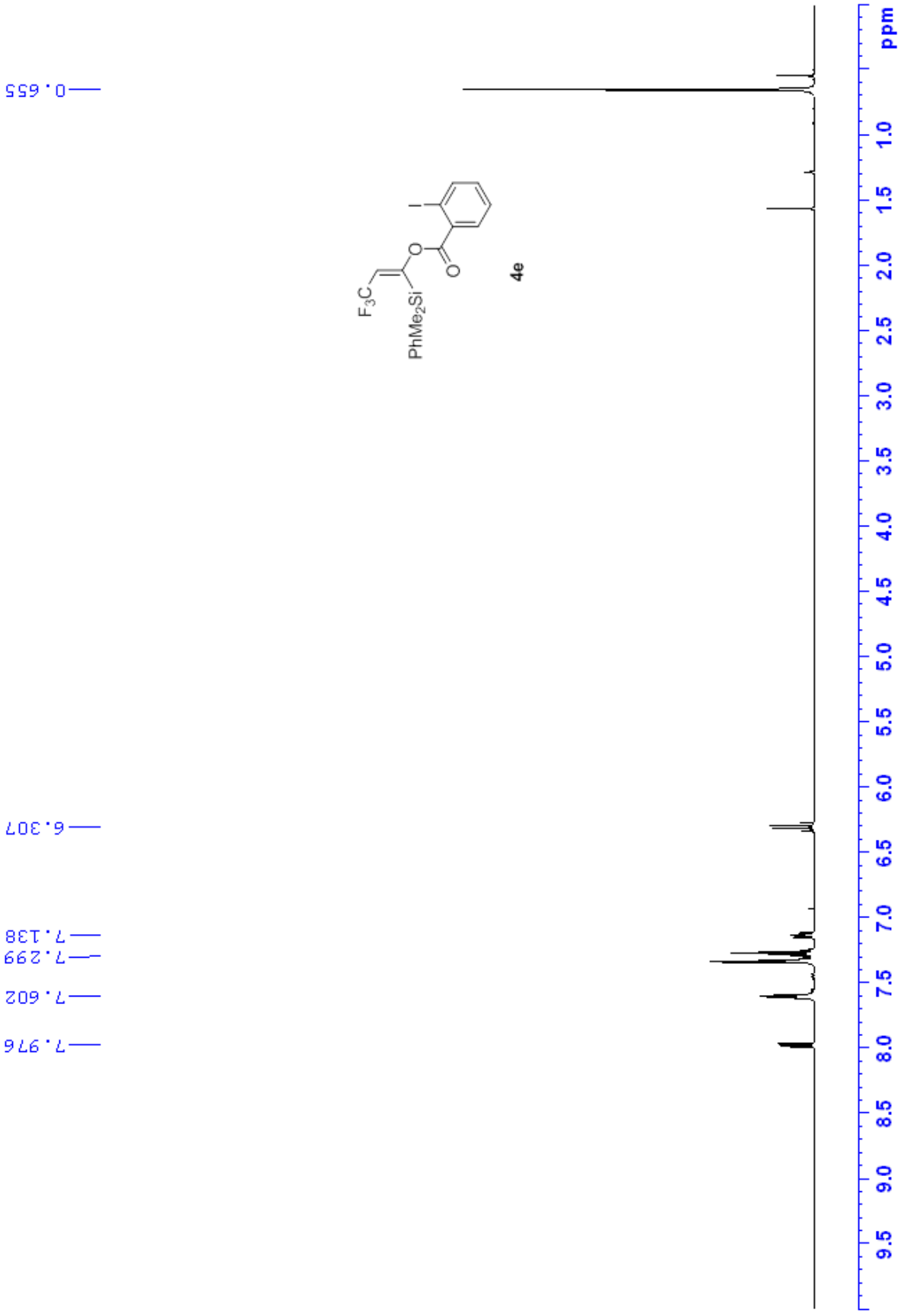
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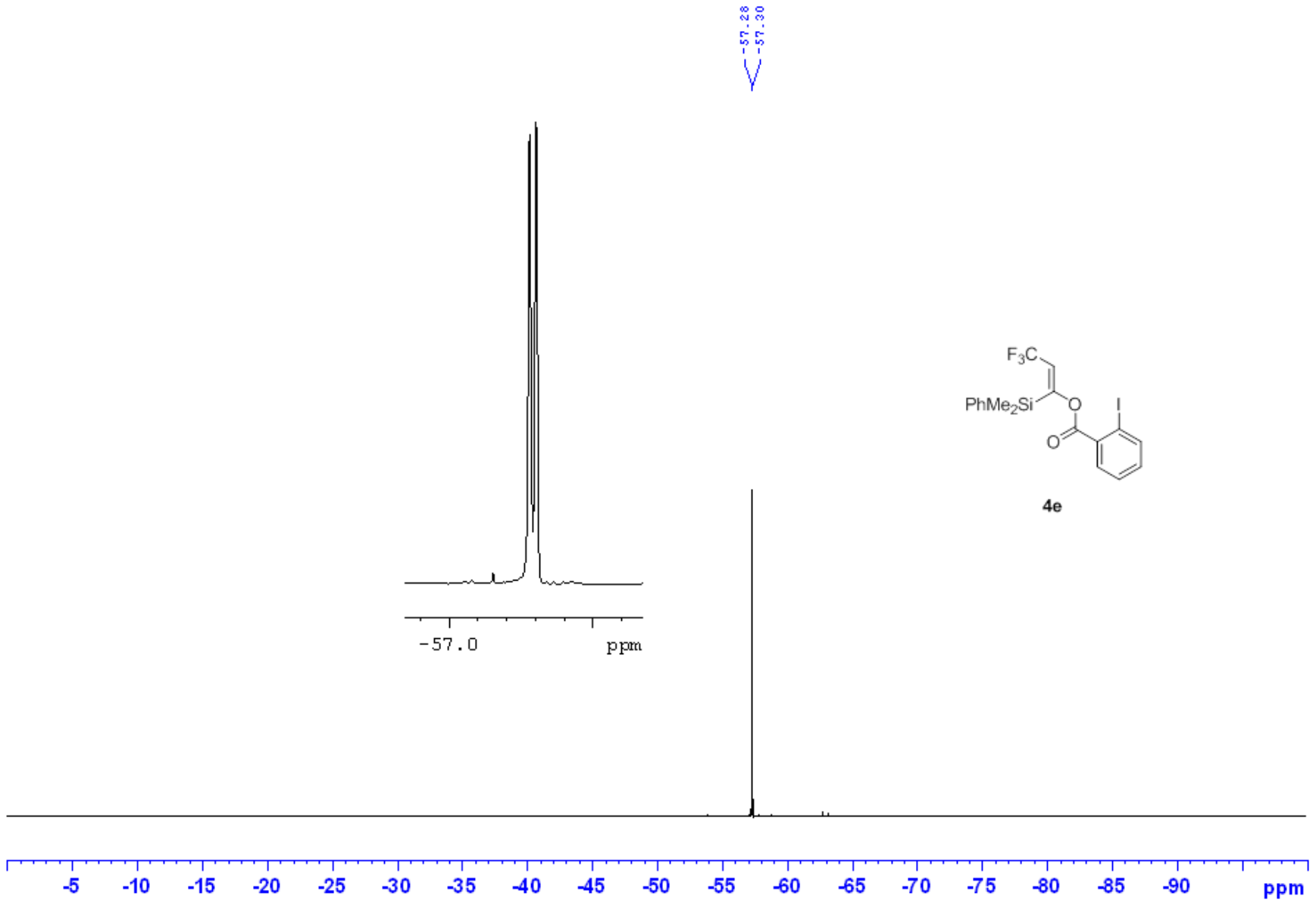
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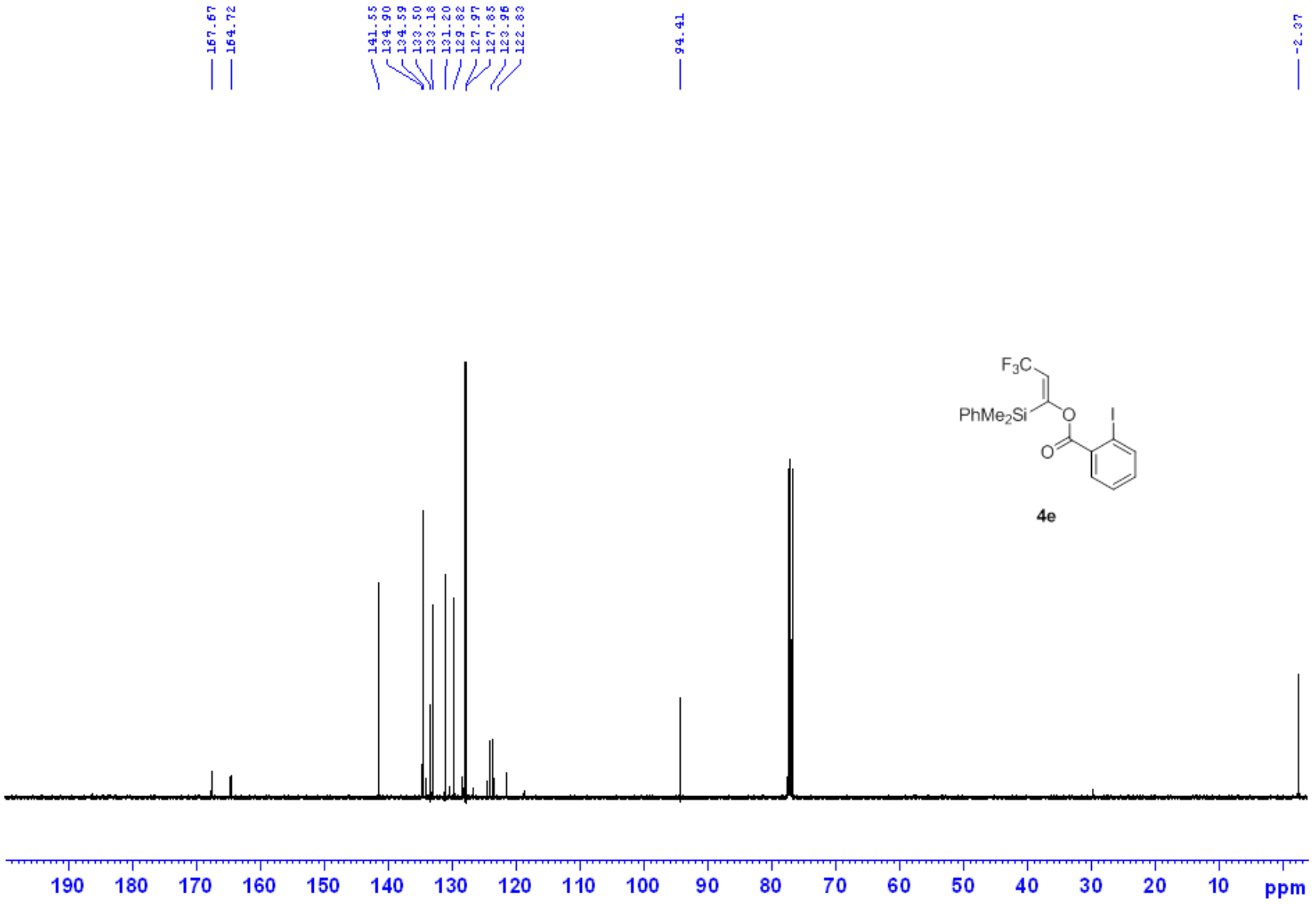
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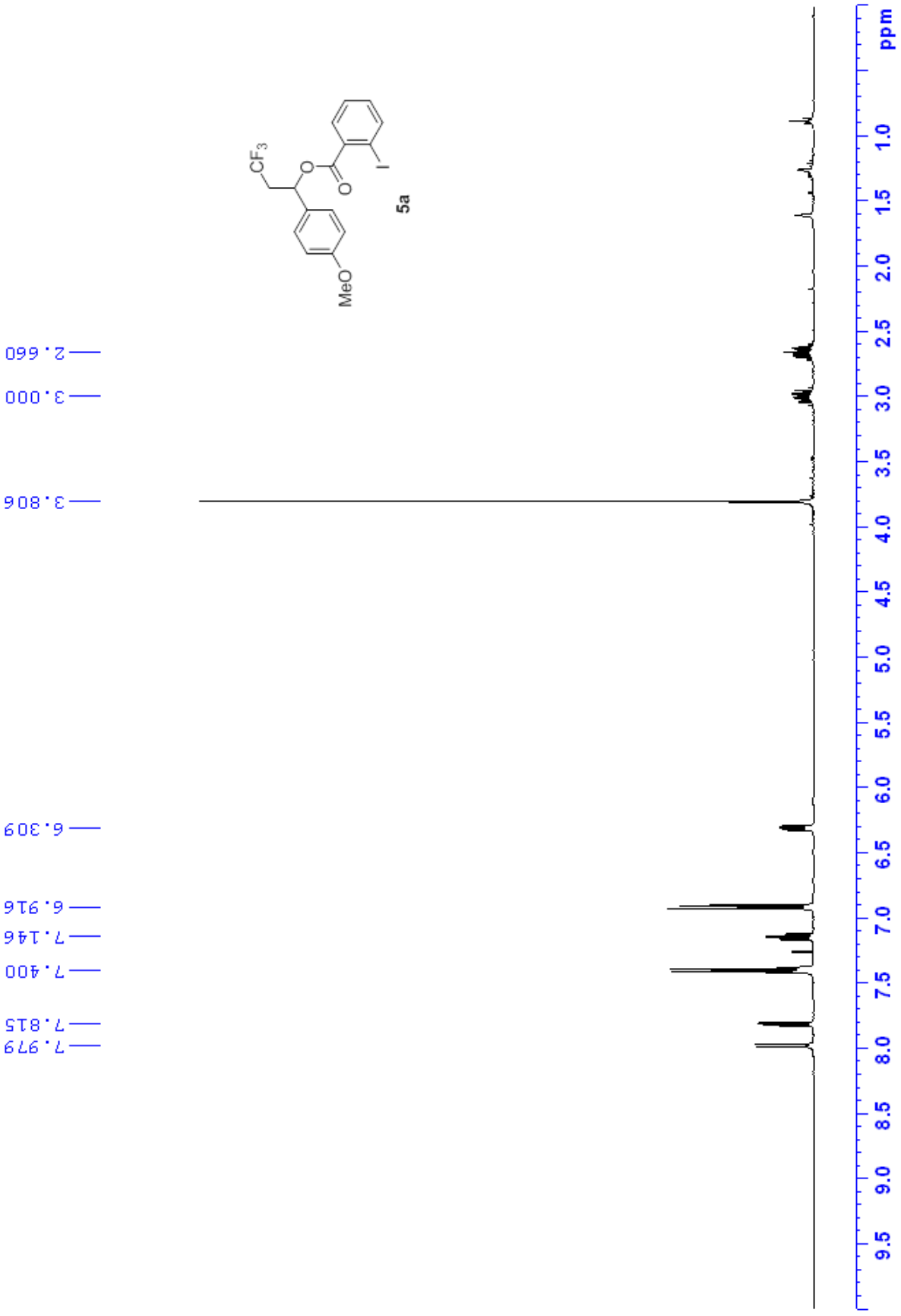
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CF3
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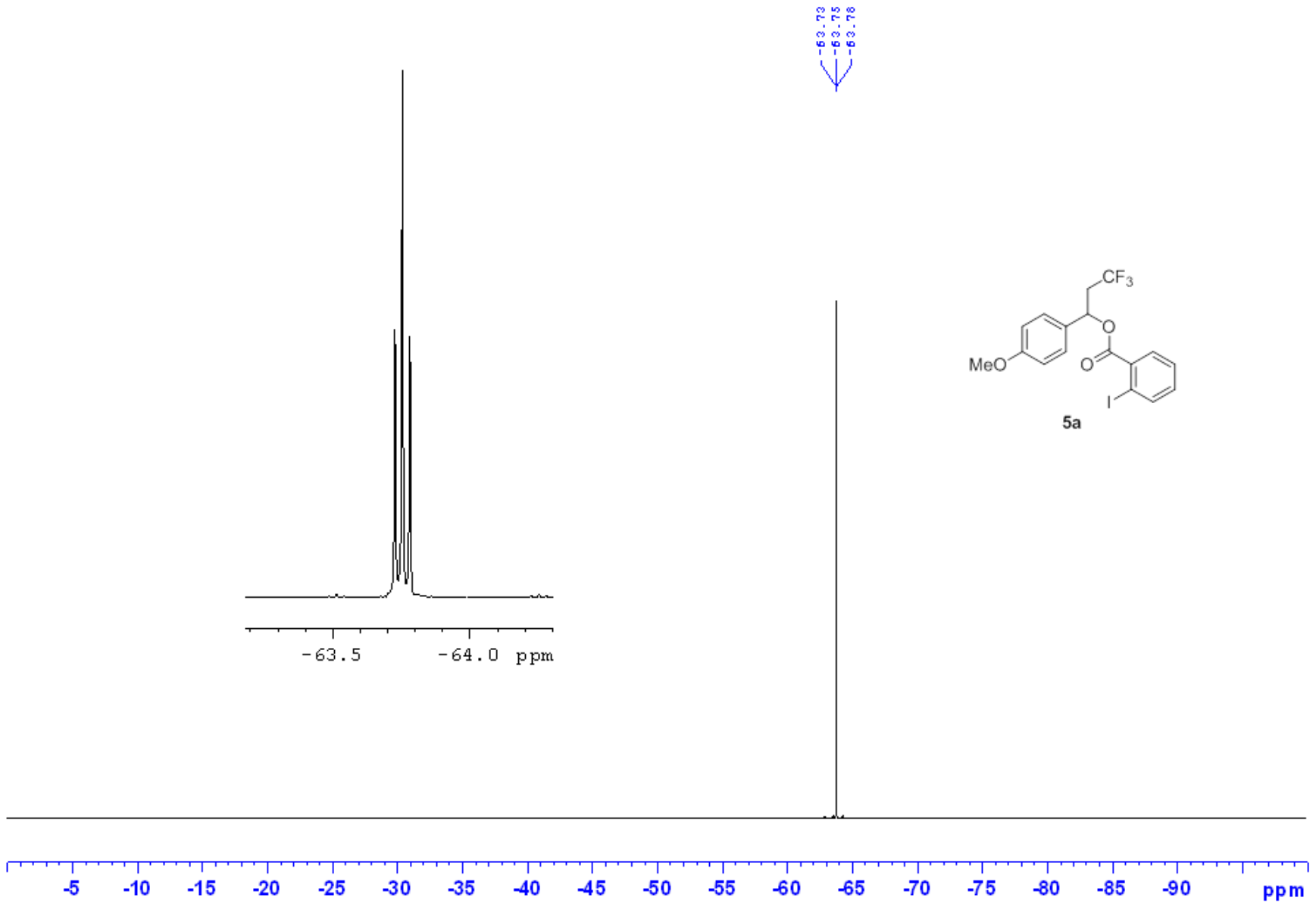
O
I
MeO
5a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I
5a
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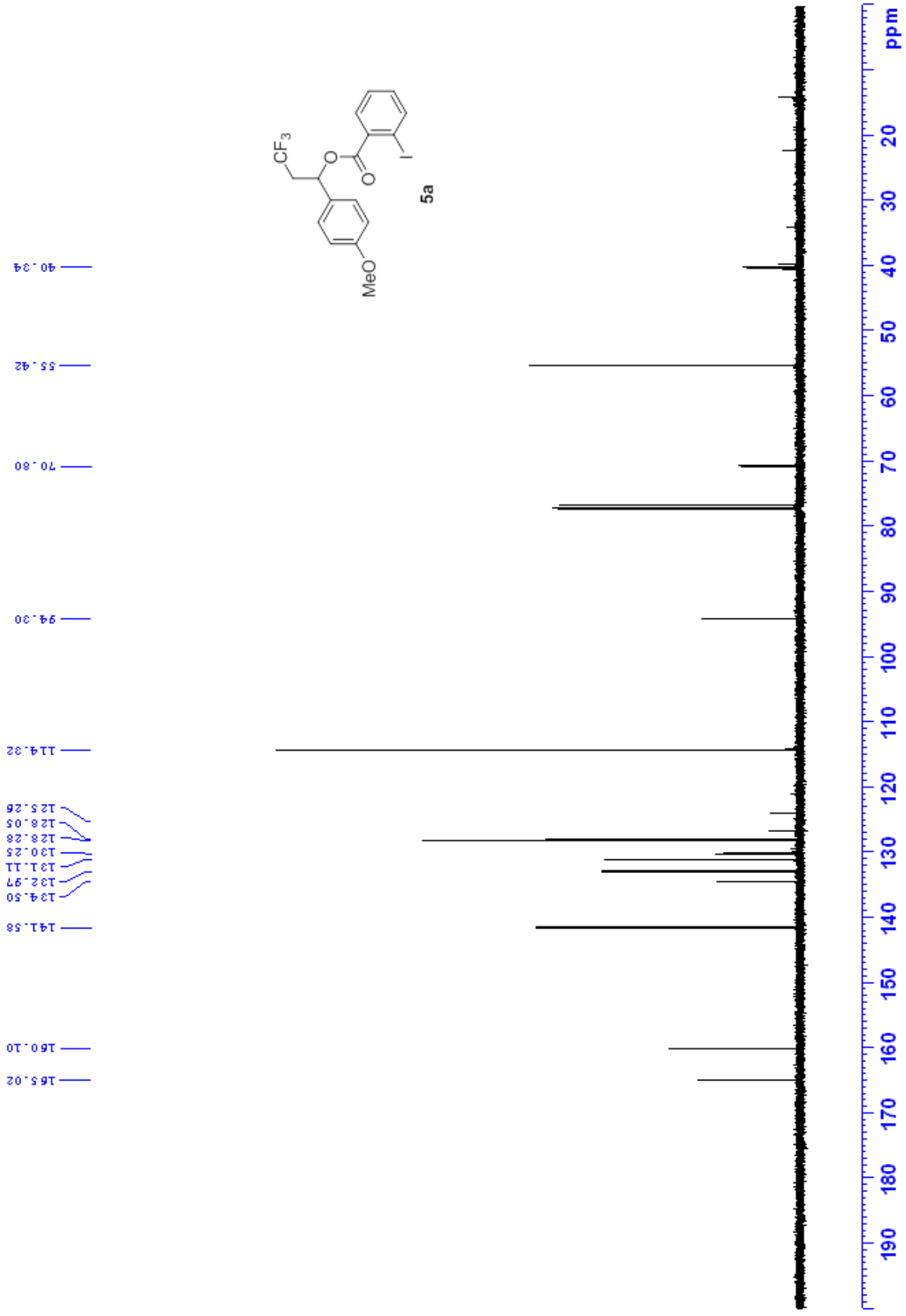
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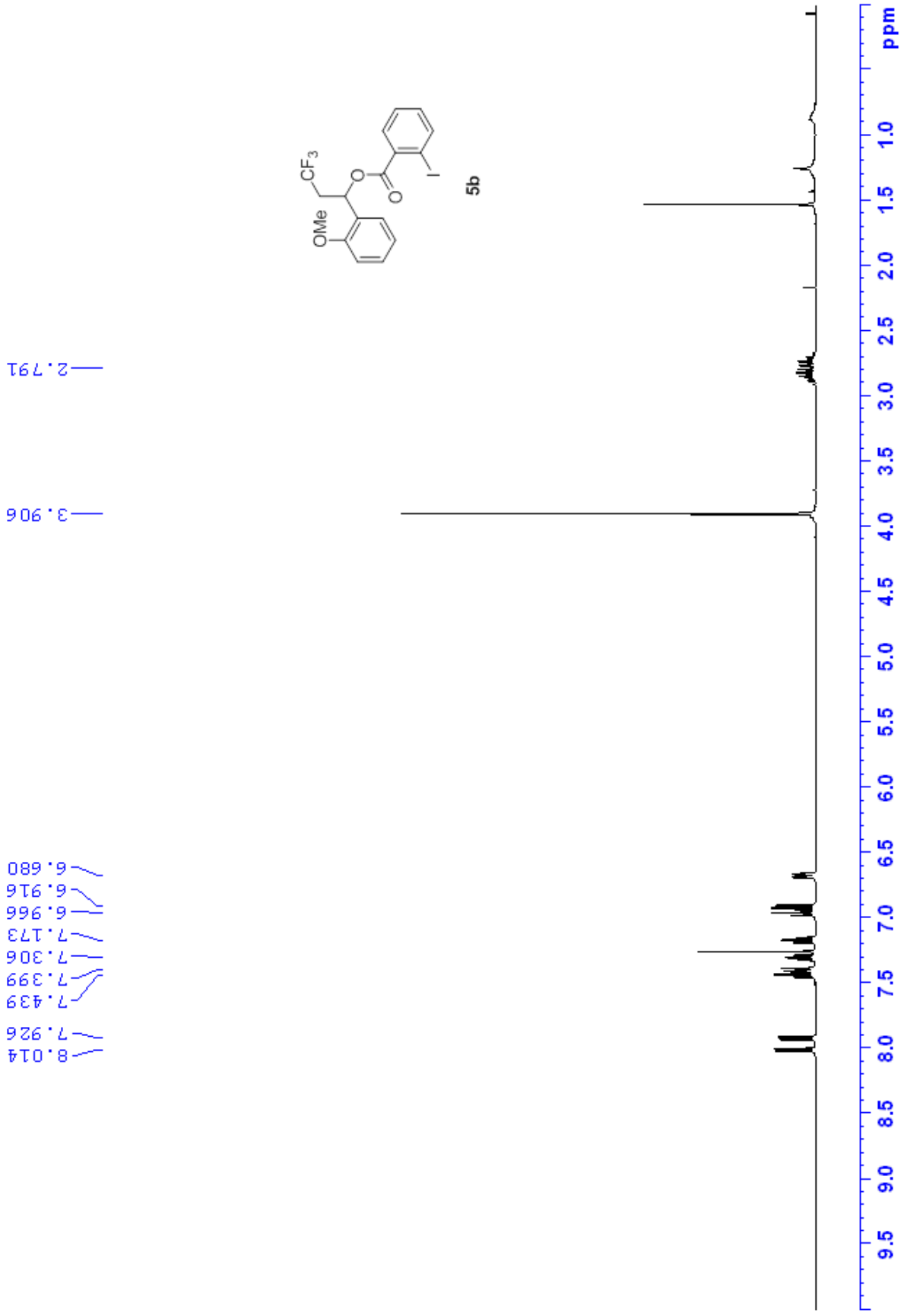
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O
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OMe
ppm
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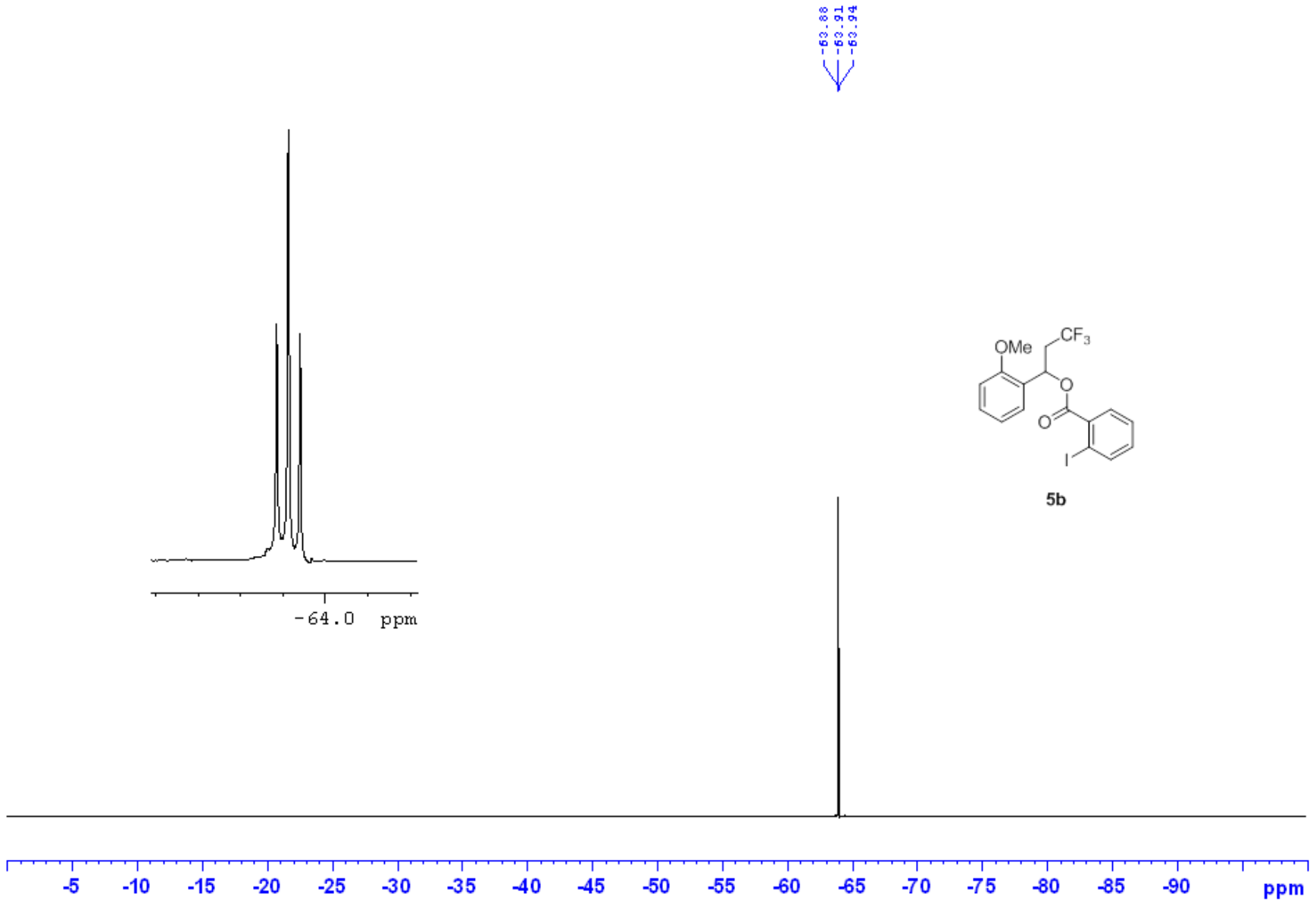
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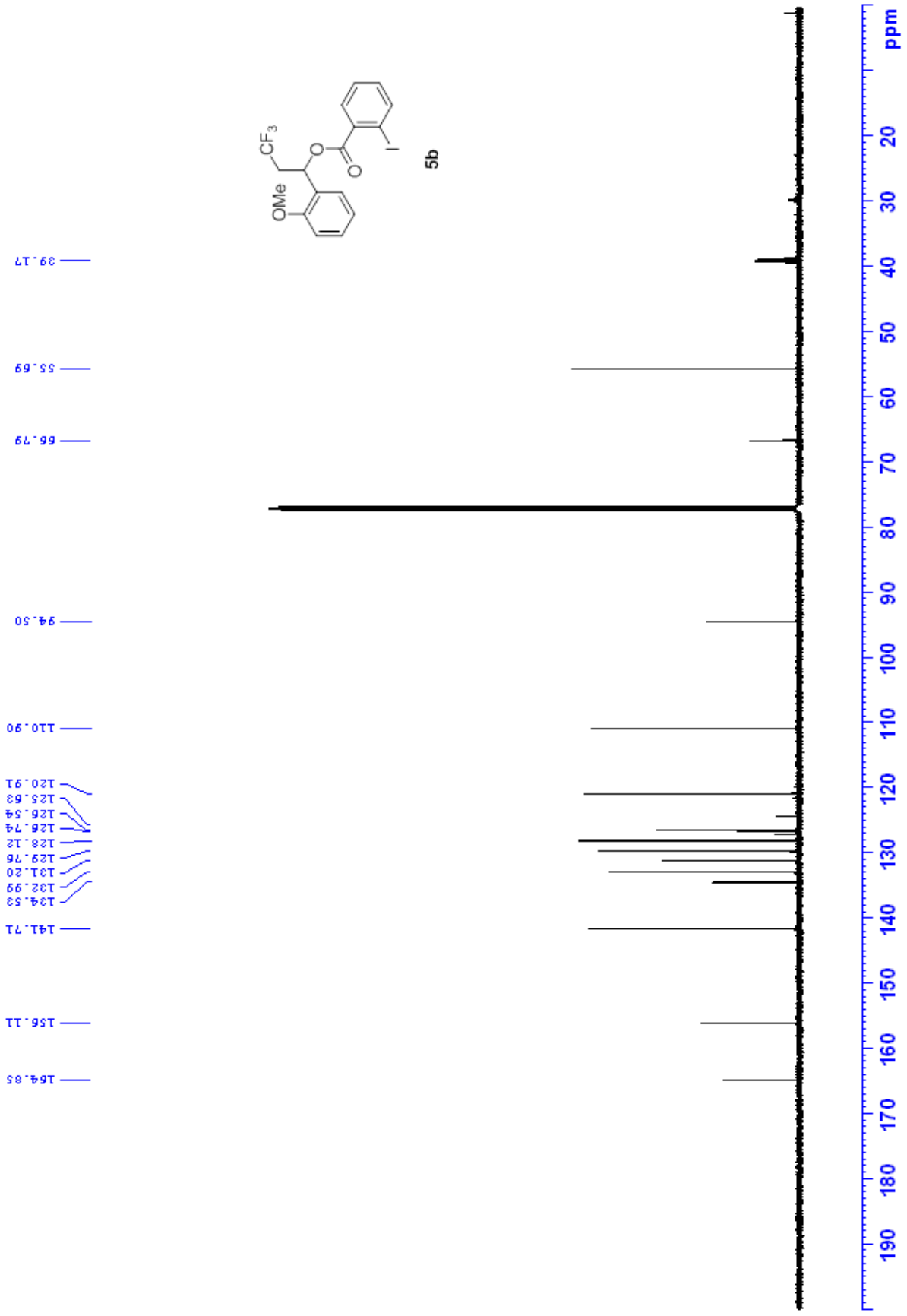
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OMe
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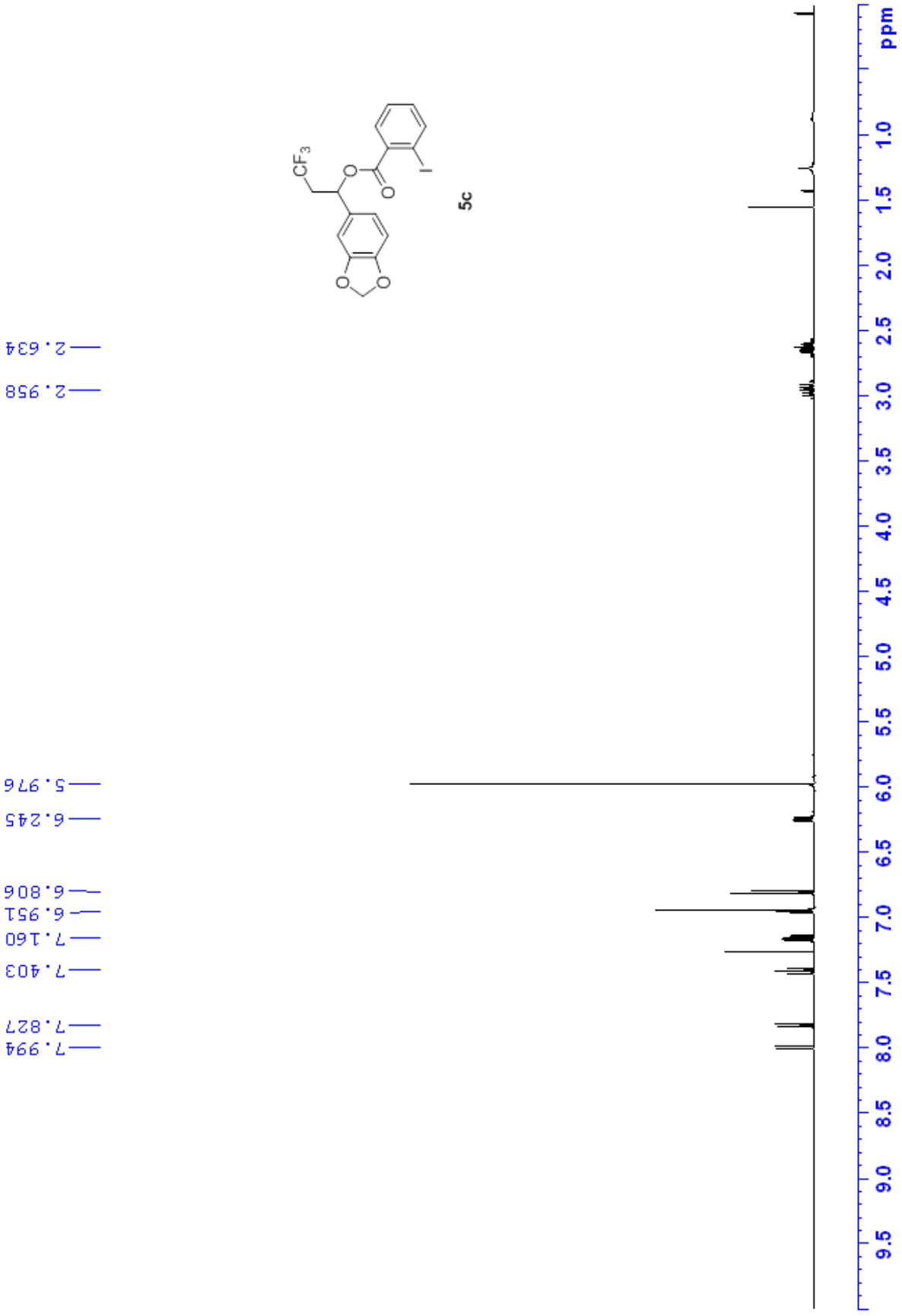
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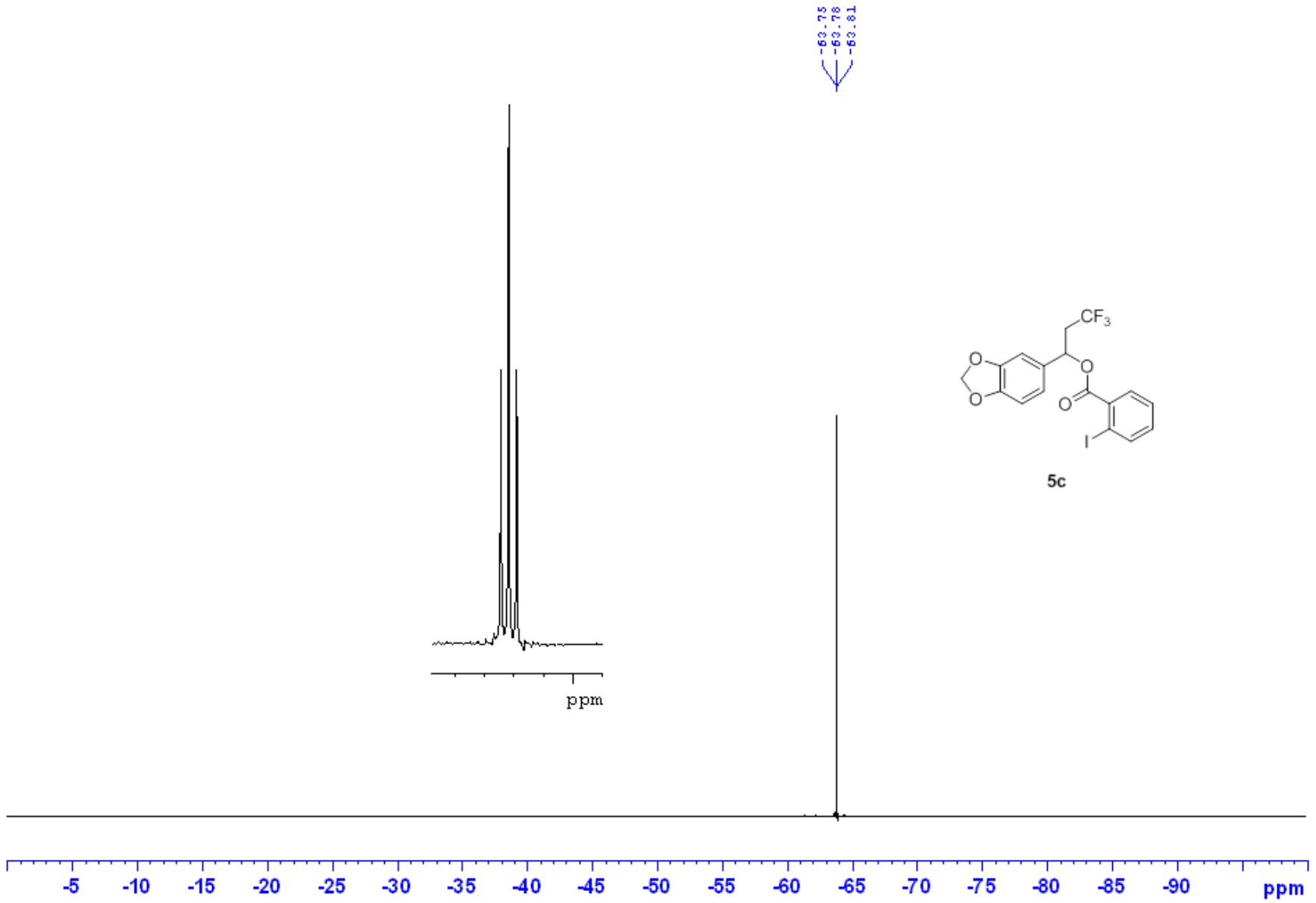
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O
O
O
O
I
5c
ppm
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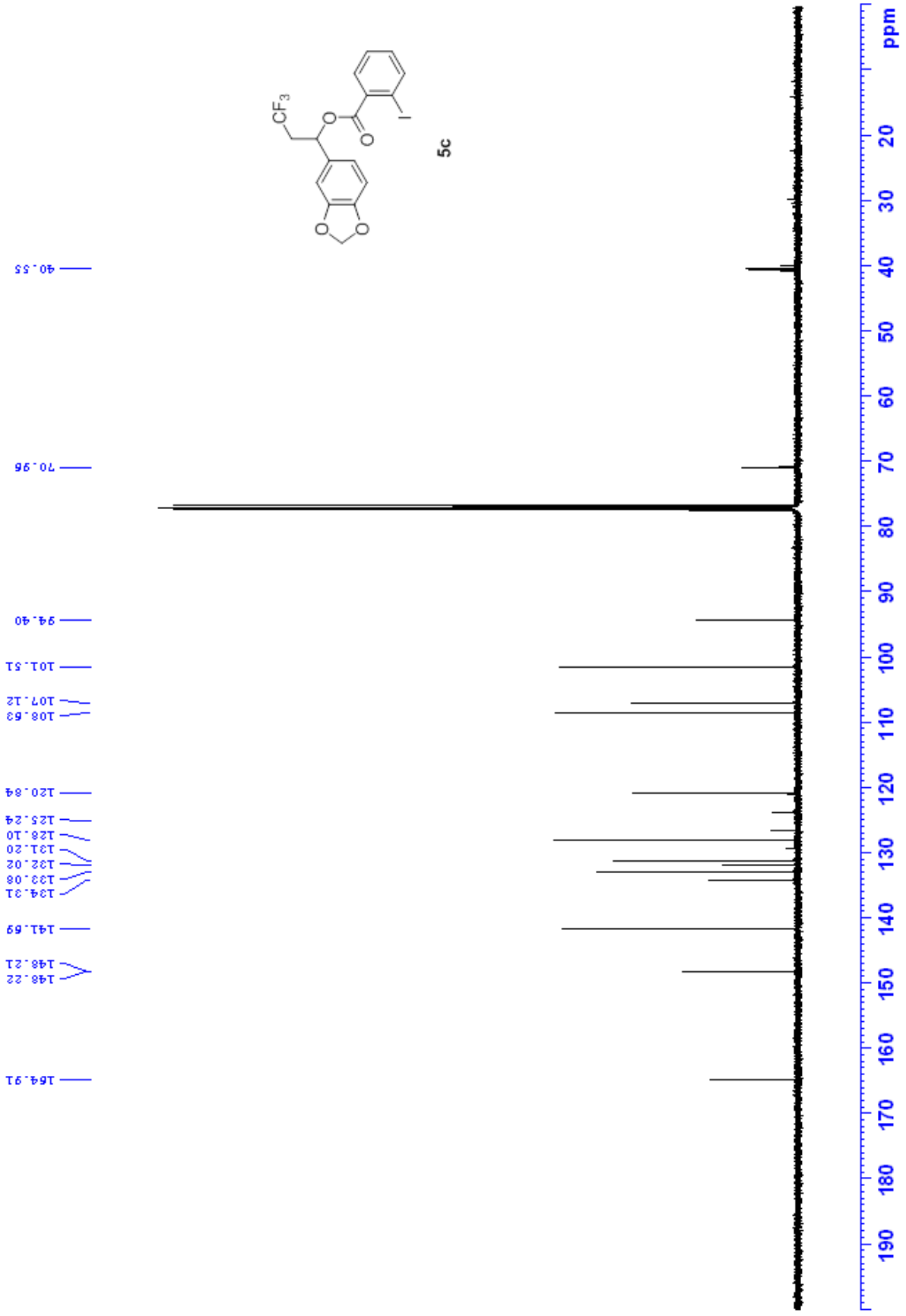
ppm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O
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I
O
O
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128.10
131.20
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148.22
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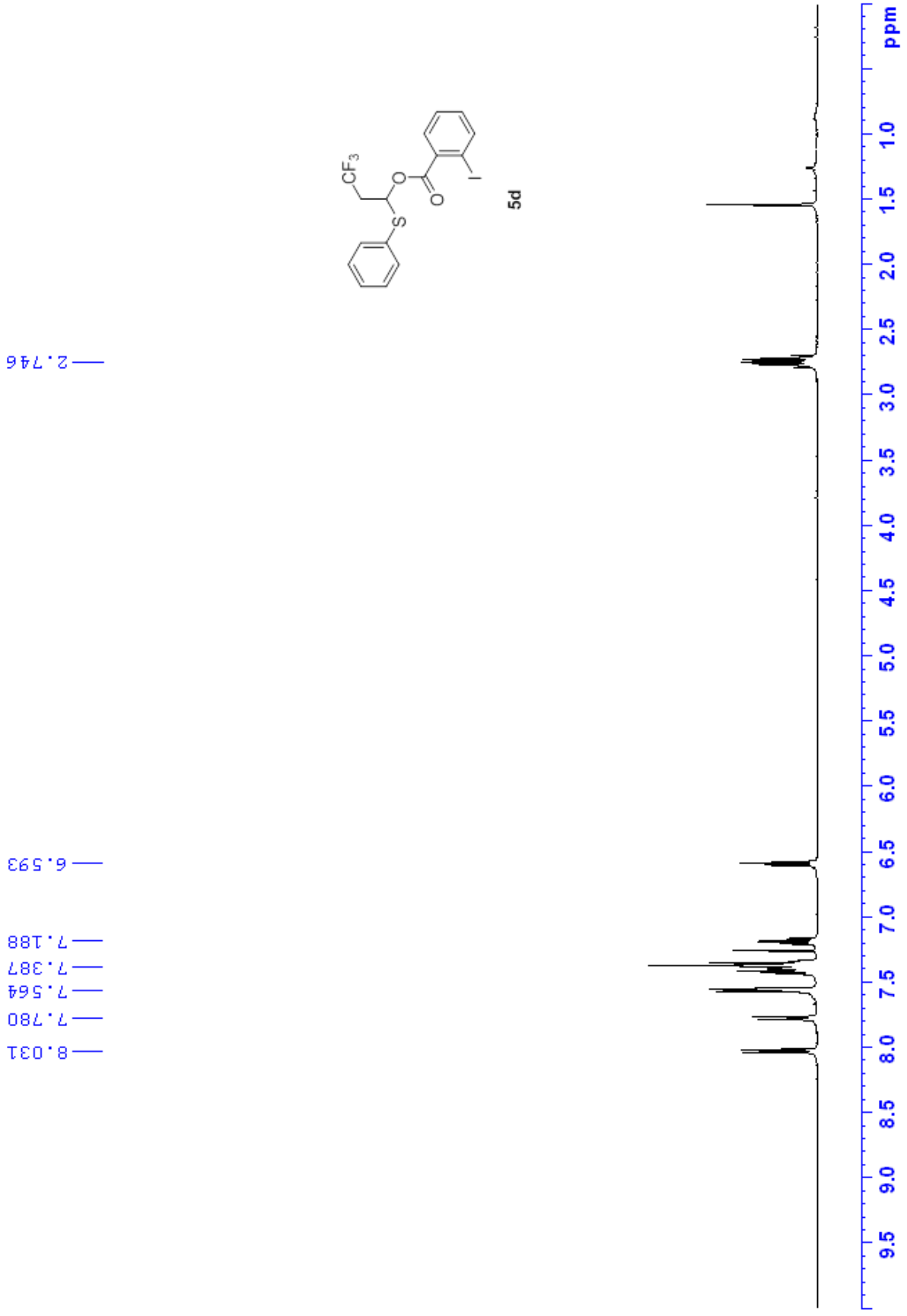
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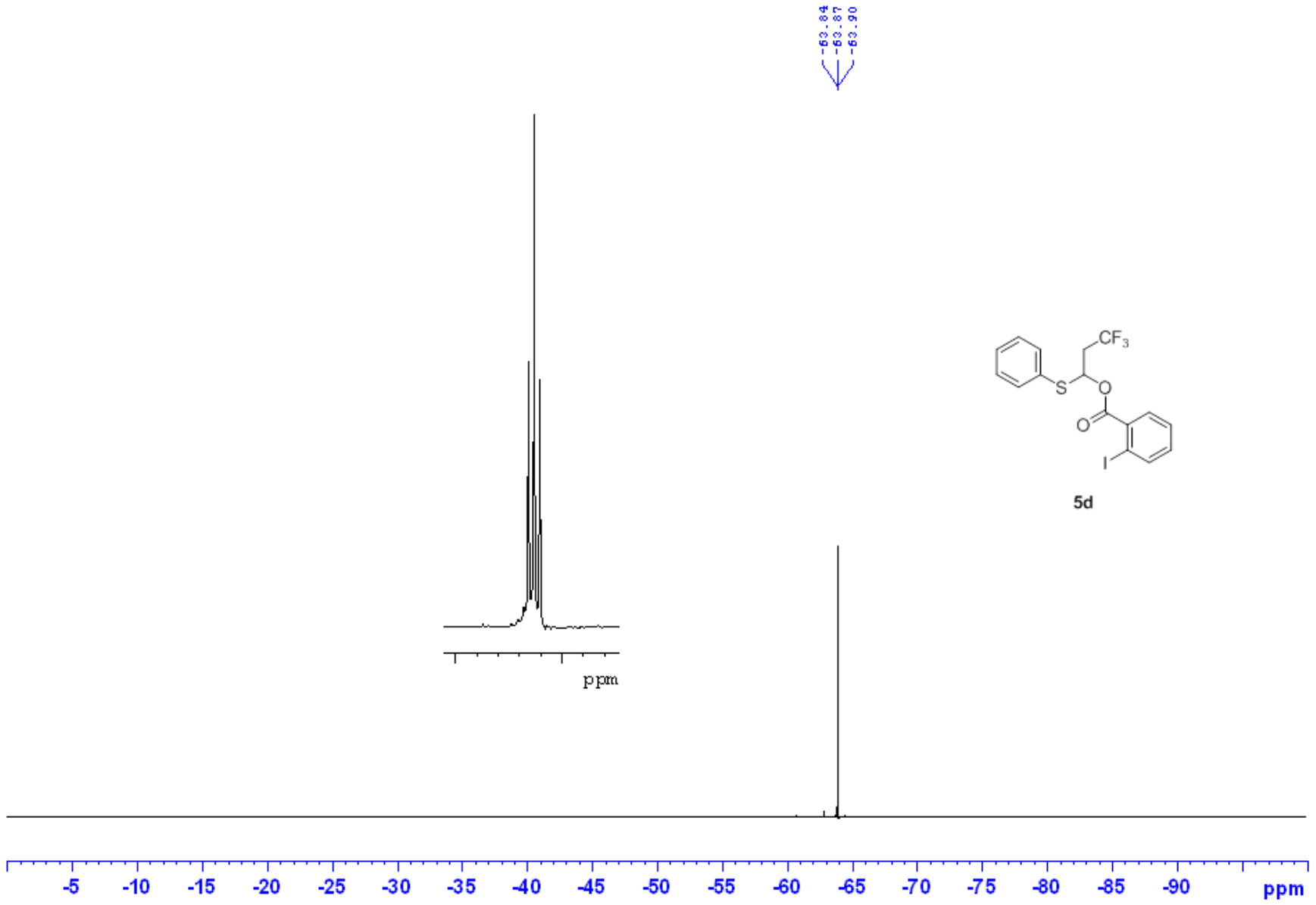
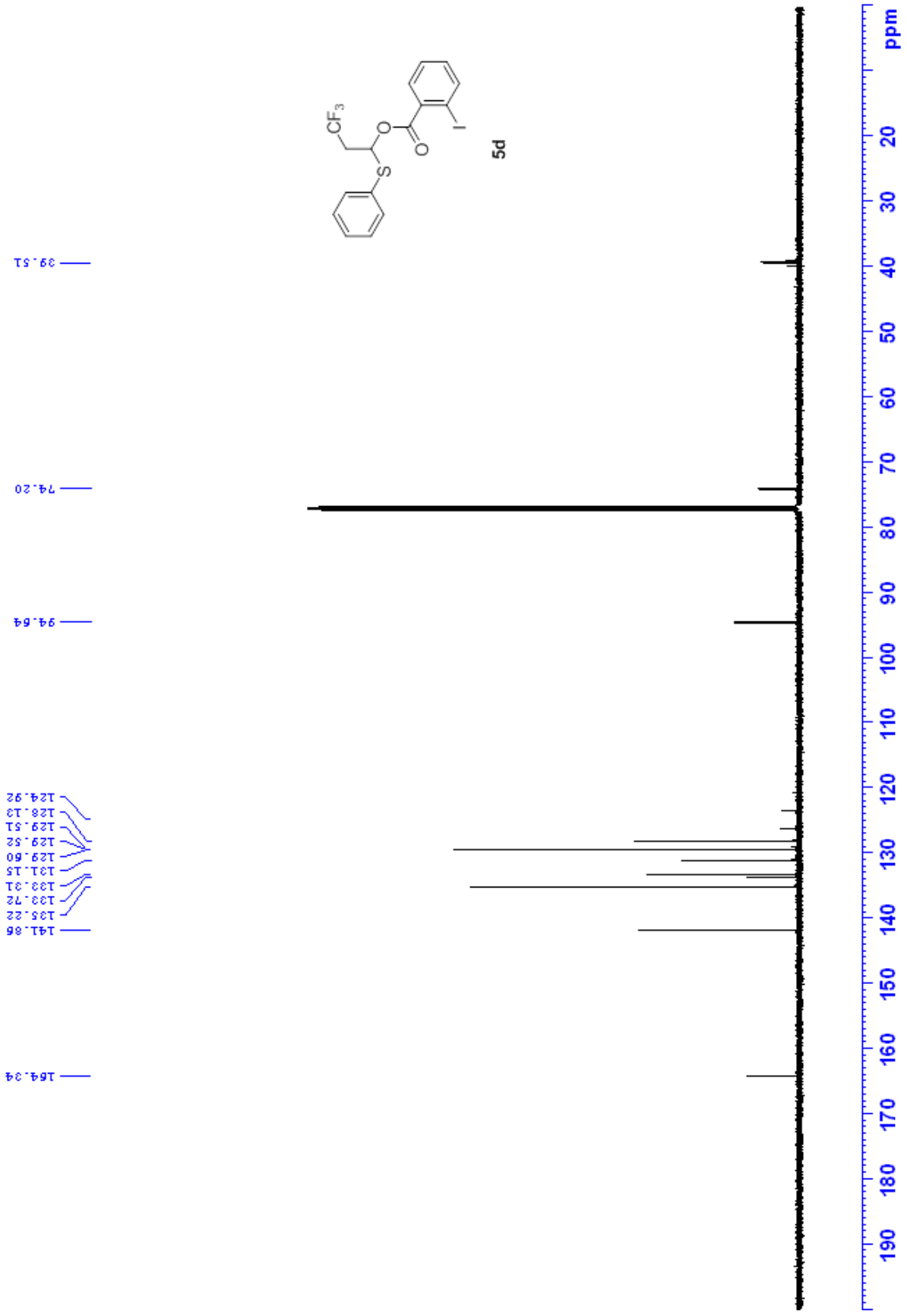
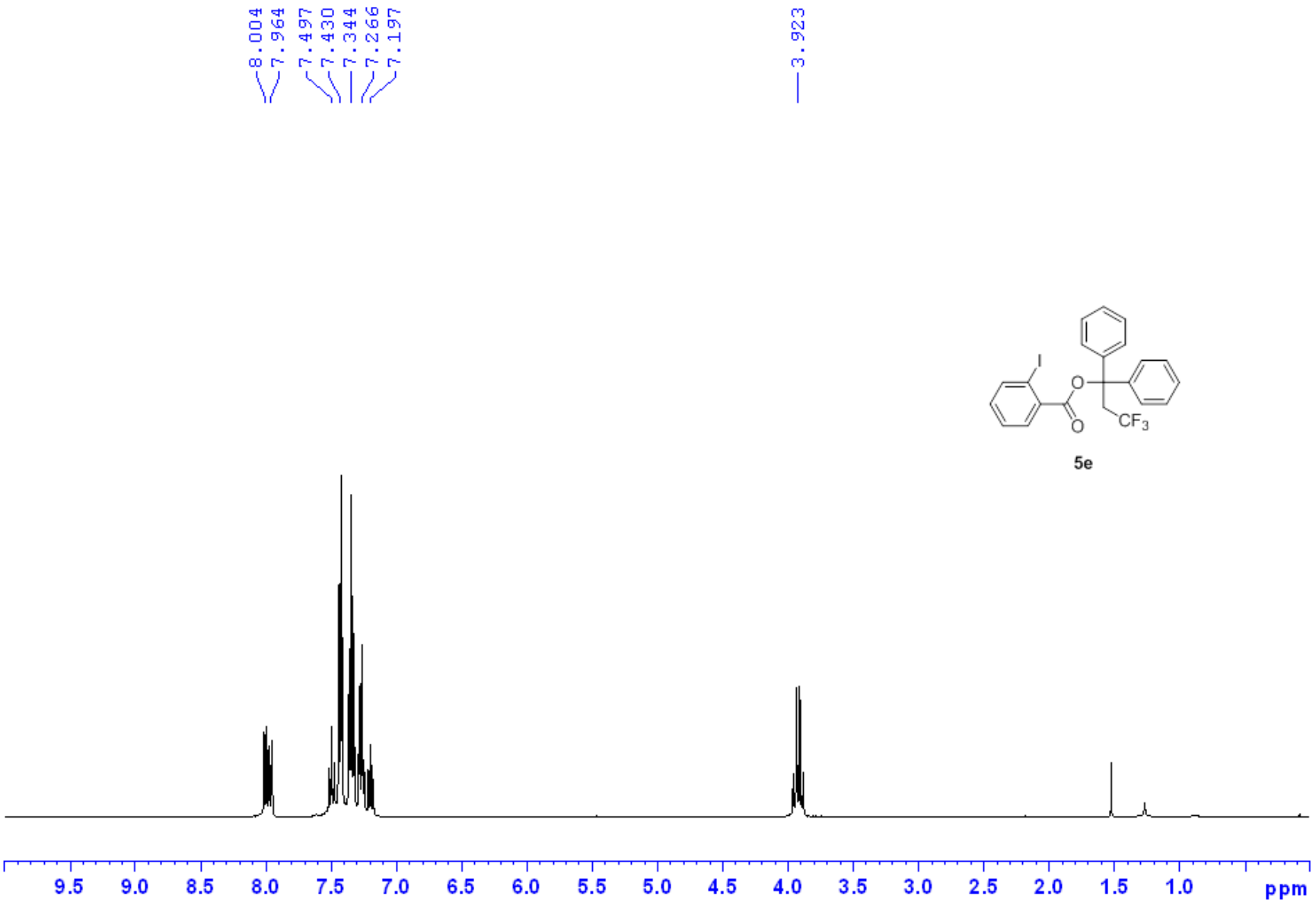
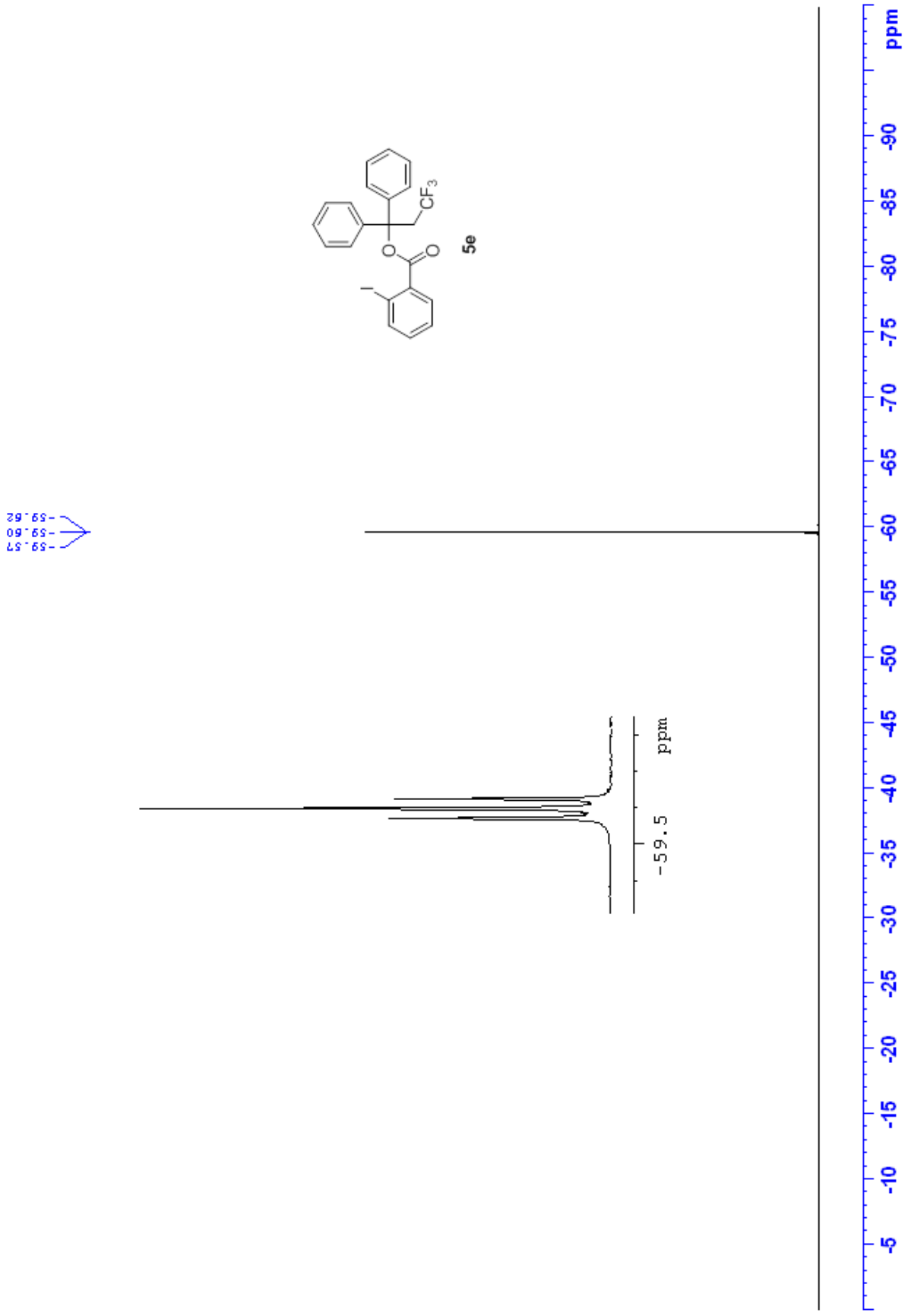
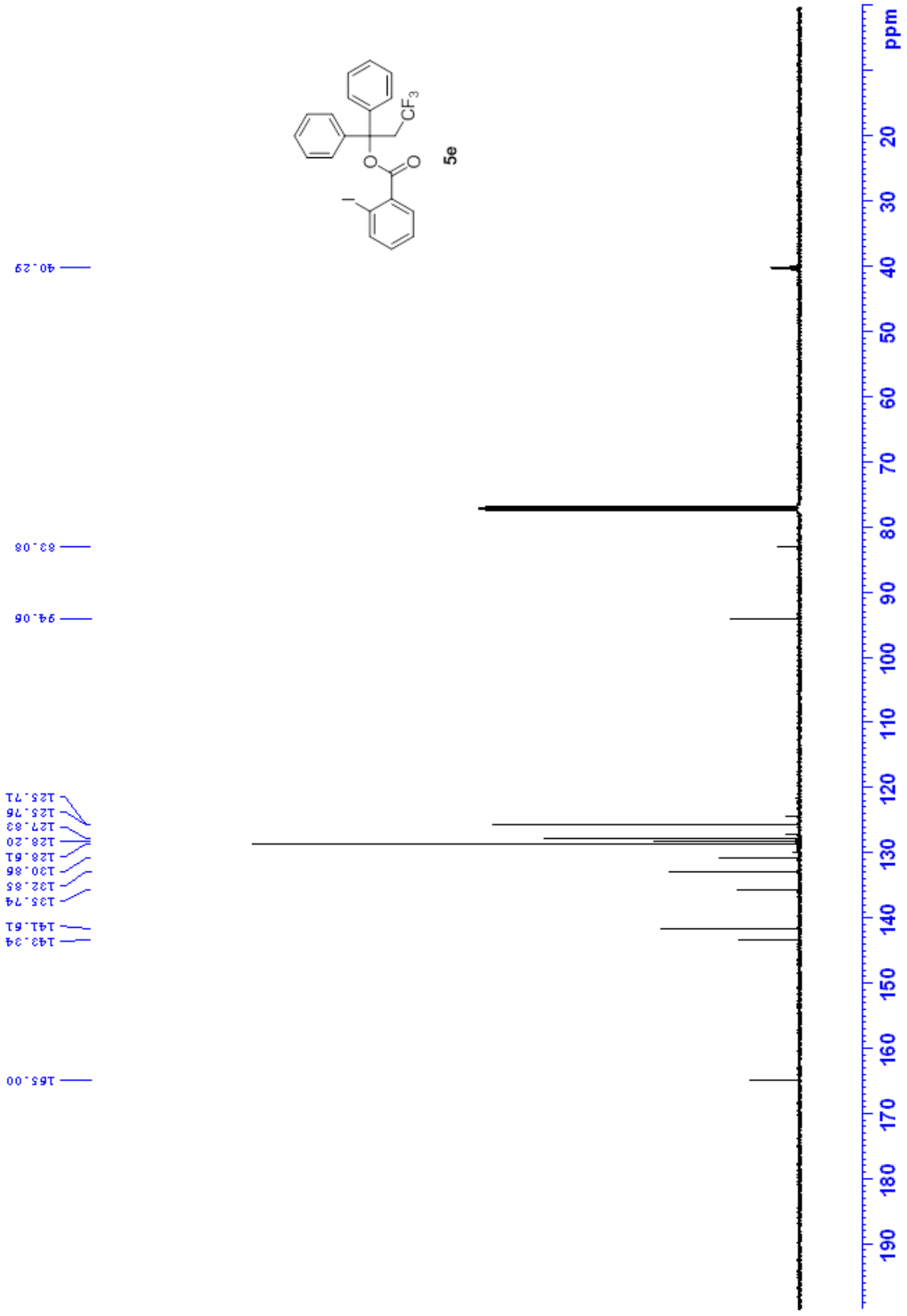
8.031
ppm

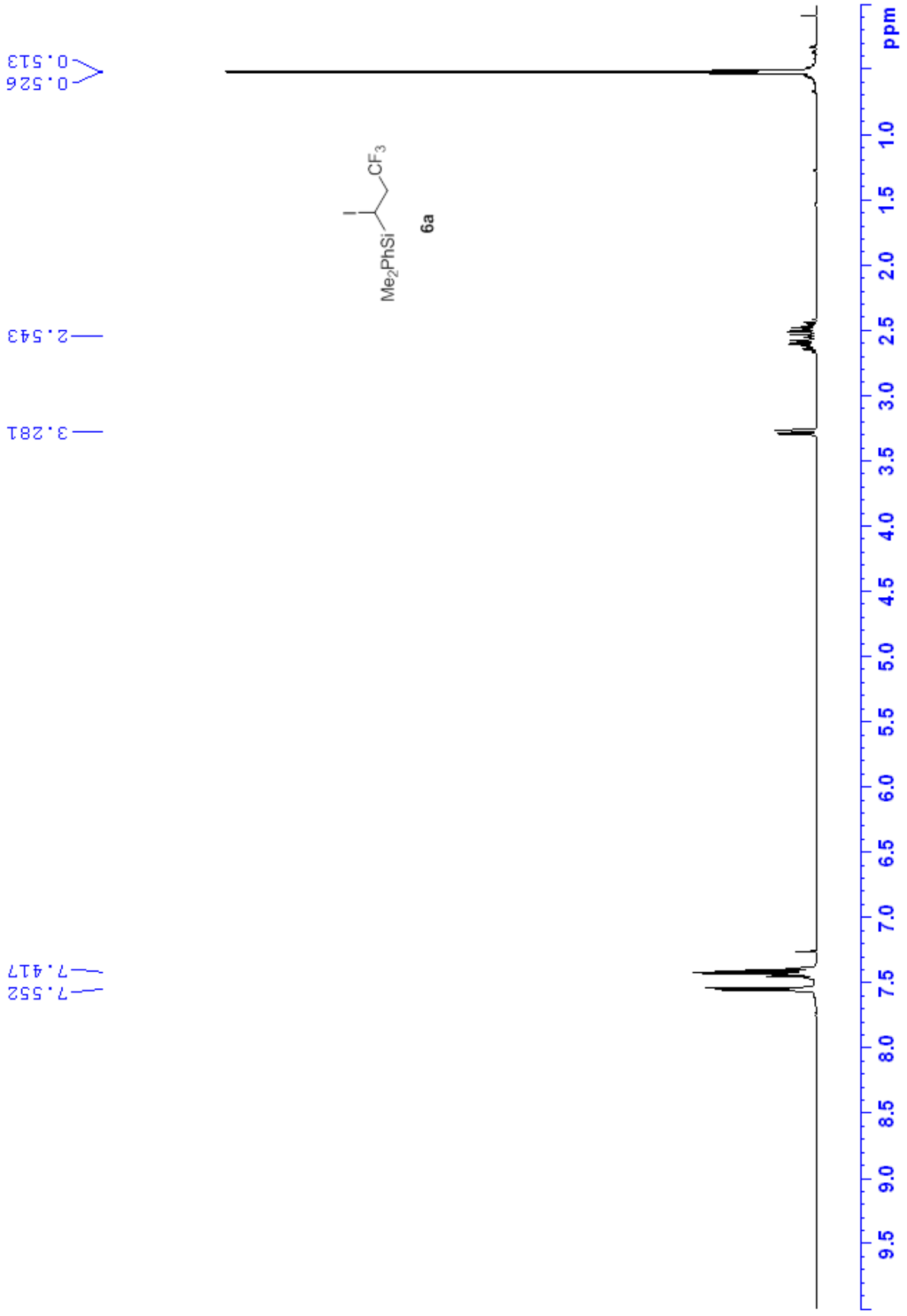

-63.84
-63.87
-63.90
CF3
S
O
O
I
5d
ppm
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
ppm

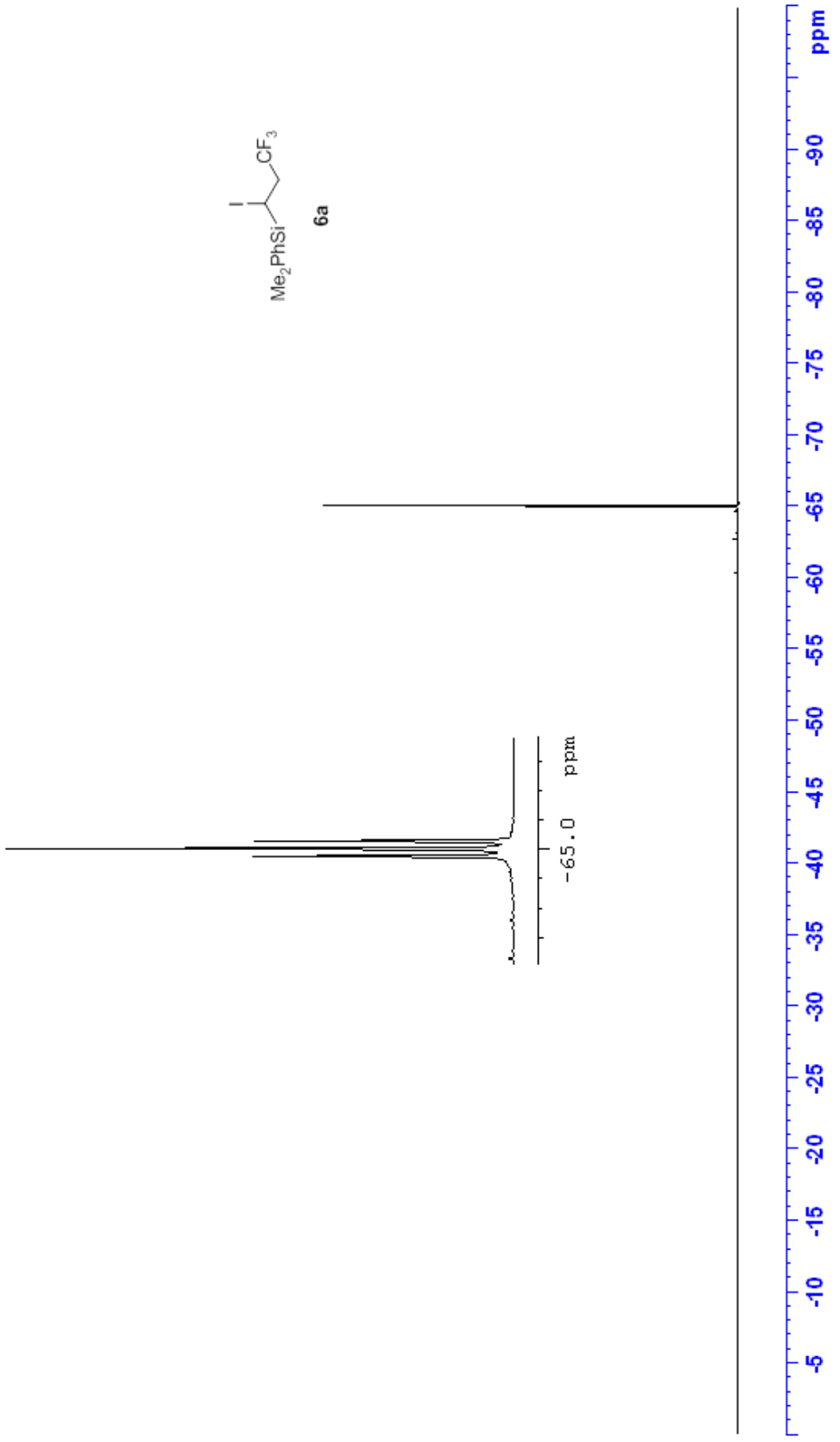

5d
39.51
74.20
94.64
124.92
126.13
129.51
129.52
129.60
131.15
133.31
133.72
135.22
141.86
164.34
ppm

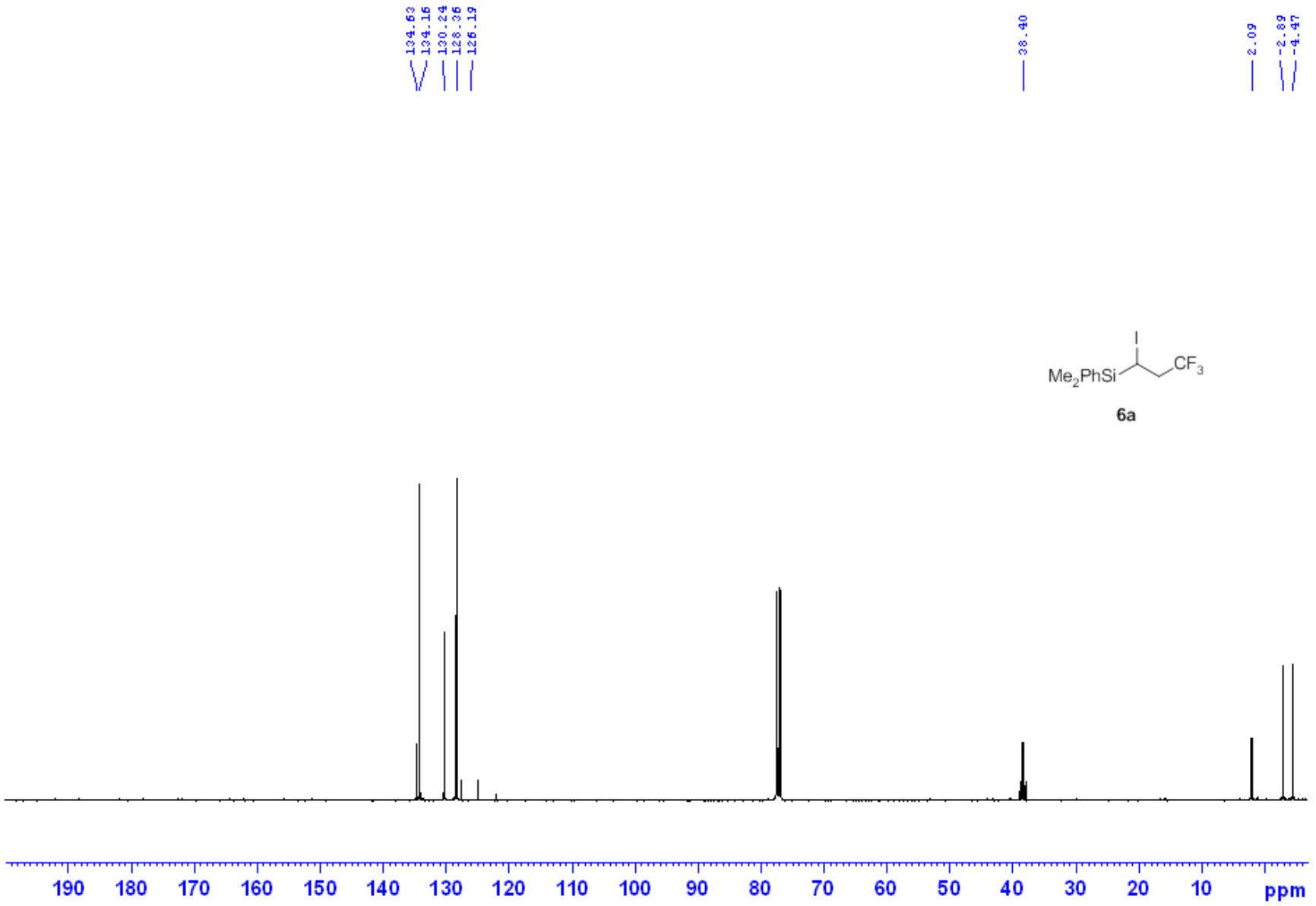

8.004
7.964
7.497
7.430
7.344
7.266
7.197
3.923
I
O
O
CF3
5e
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

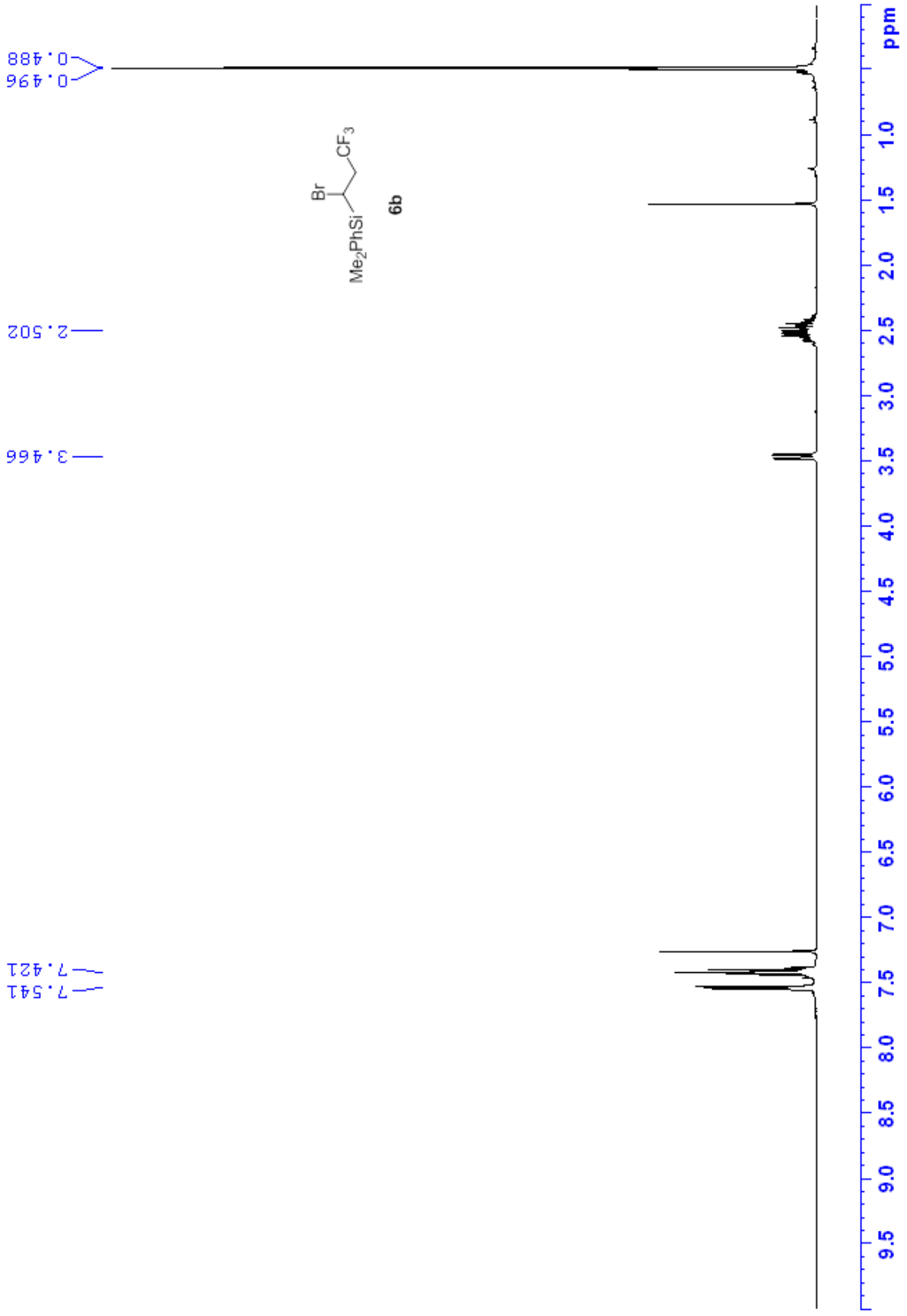

-59.57
-59.60
-59.62
5e
-59.5
ppm
ppm
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90

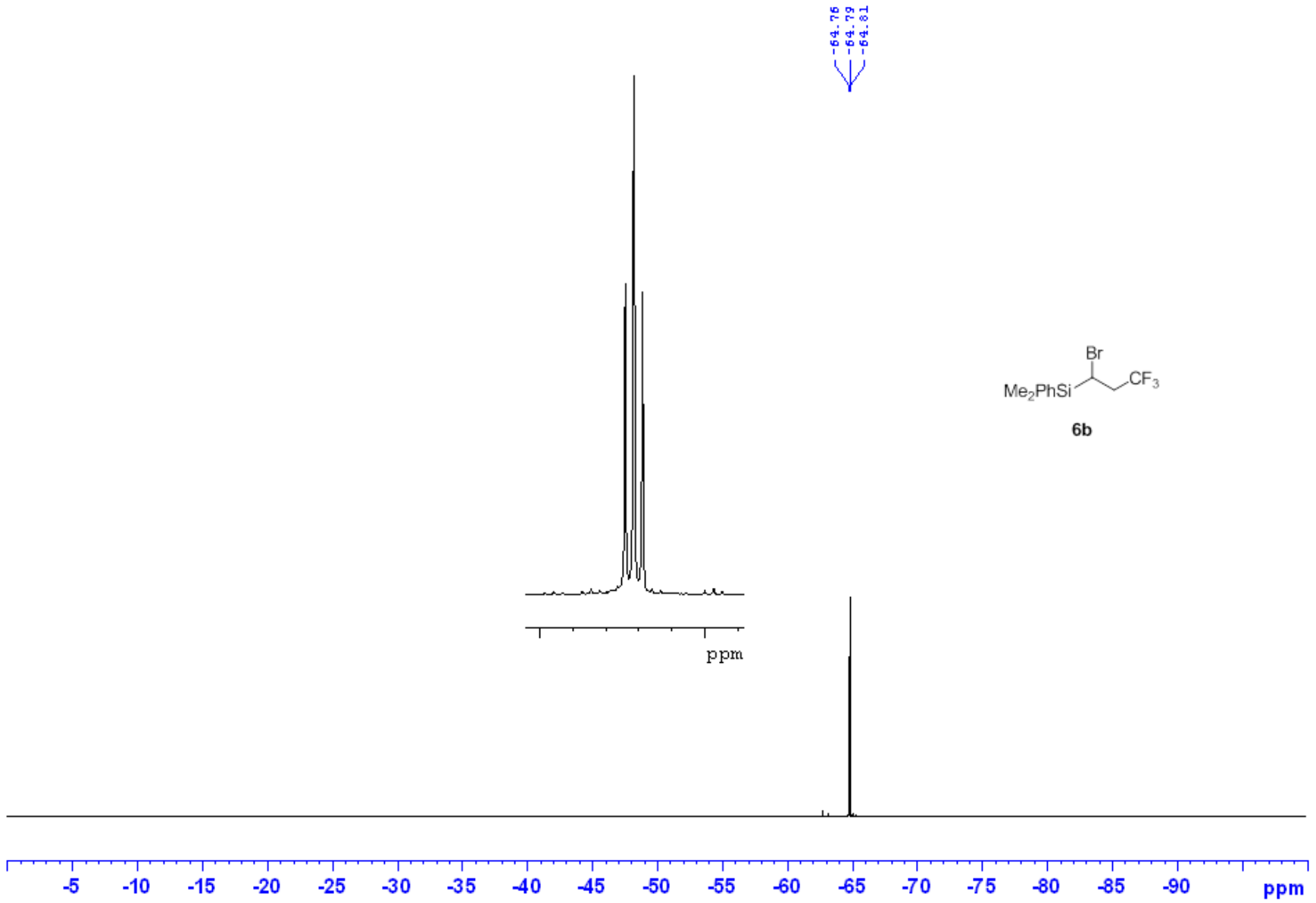

5e
40.29
83.08
94.06
125.71
125.76
127.63
128.20
128.61
130.86
132.85
135.74
141.61
143.34
165.00
ppm

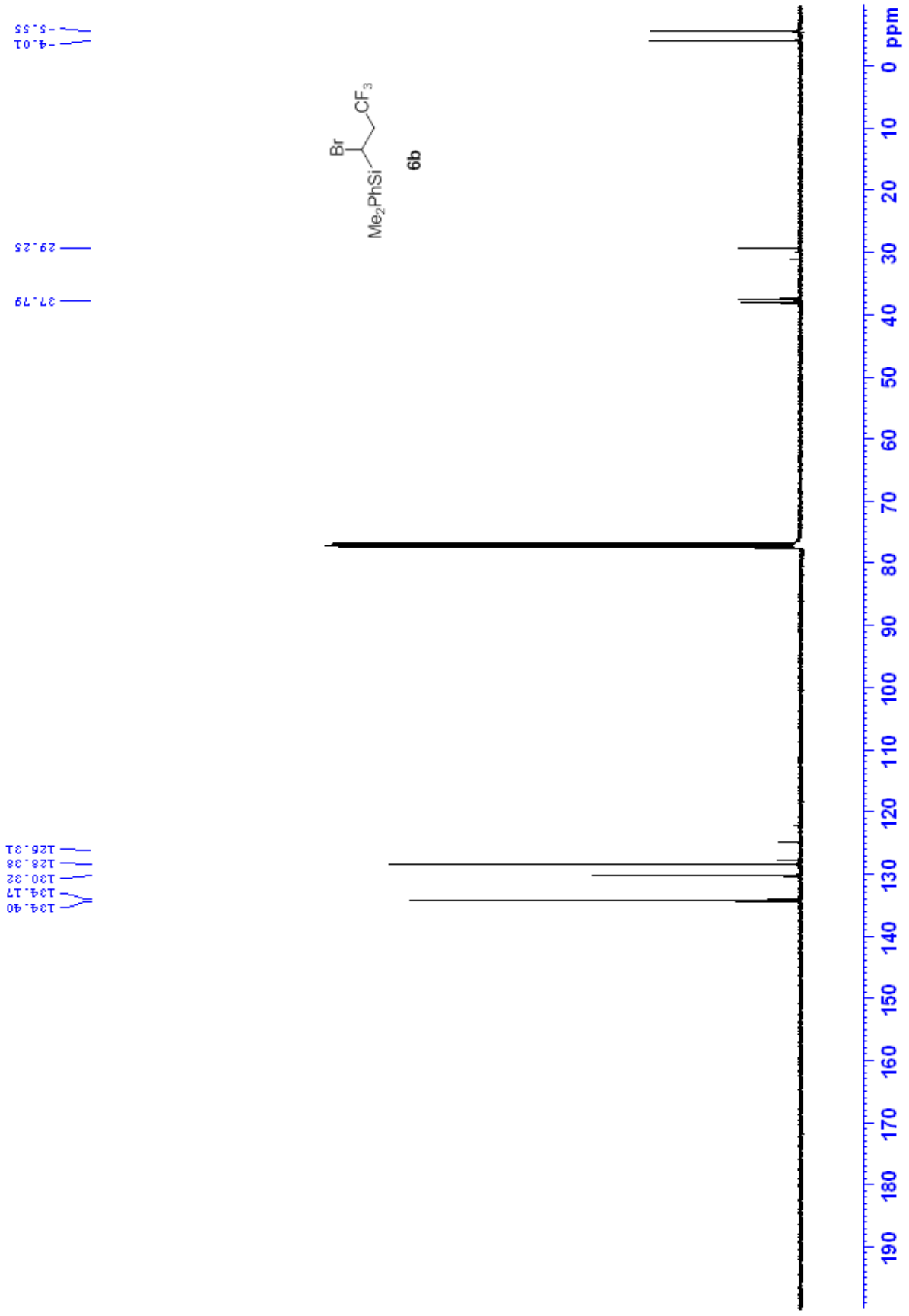

0.513
0.526
2.543
3.281
7.417
7.552
Me2PhSi
CF3
6a
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

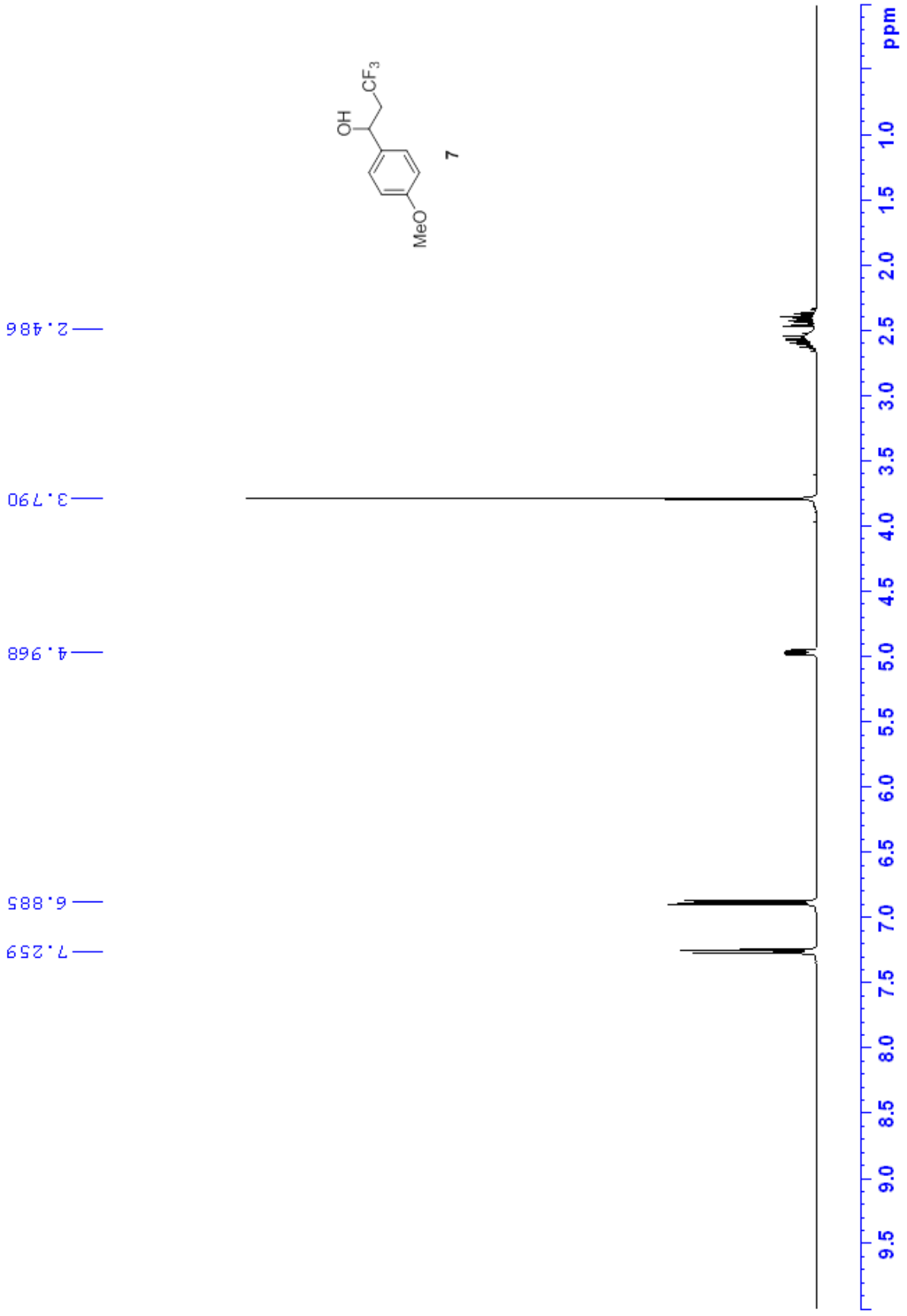

Me2PhSi
CF3
I
6a
-65.0
ppm
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
ppm

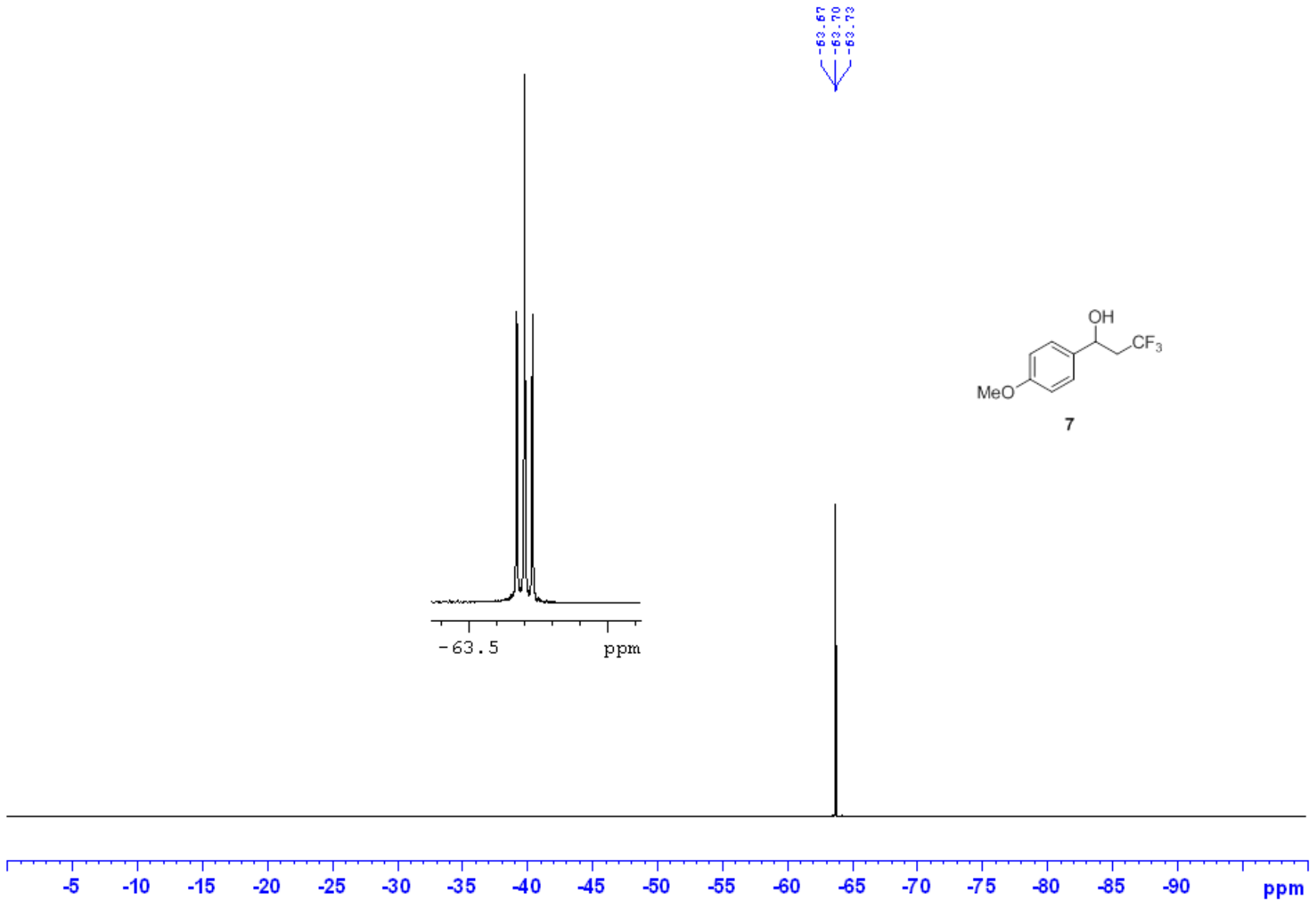

134.63
134.16
130.24
128.36
126.19
38.40
2.09
-2.89
-4.47
Me2PhSi
CF3
I
6a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

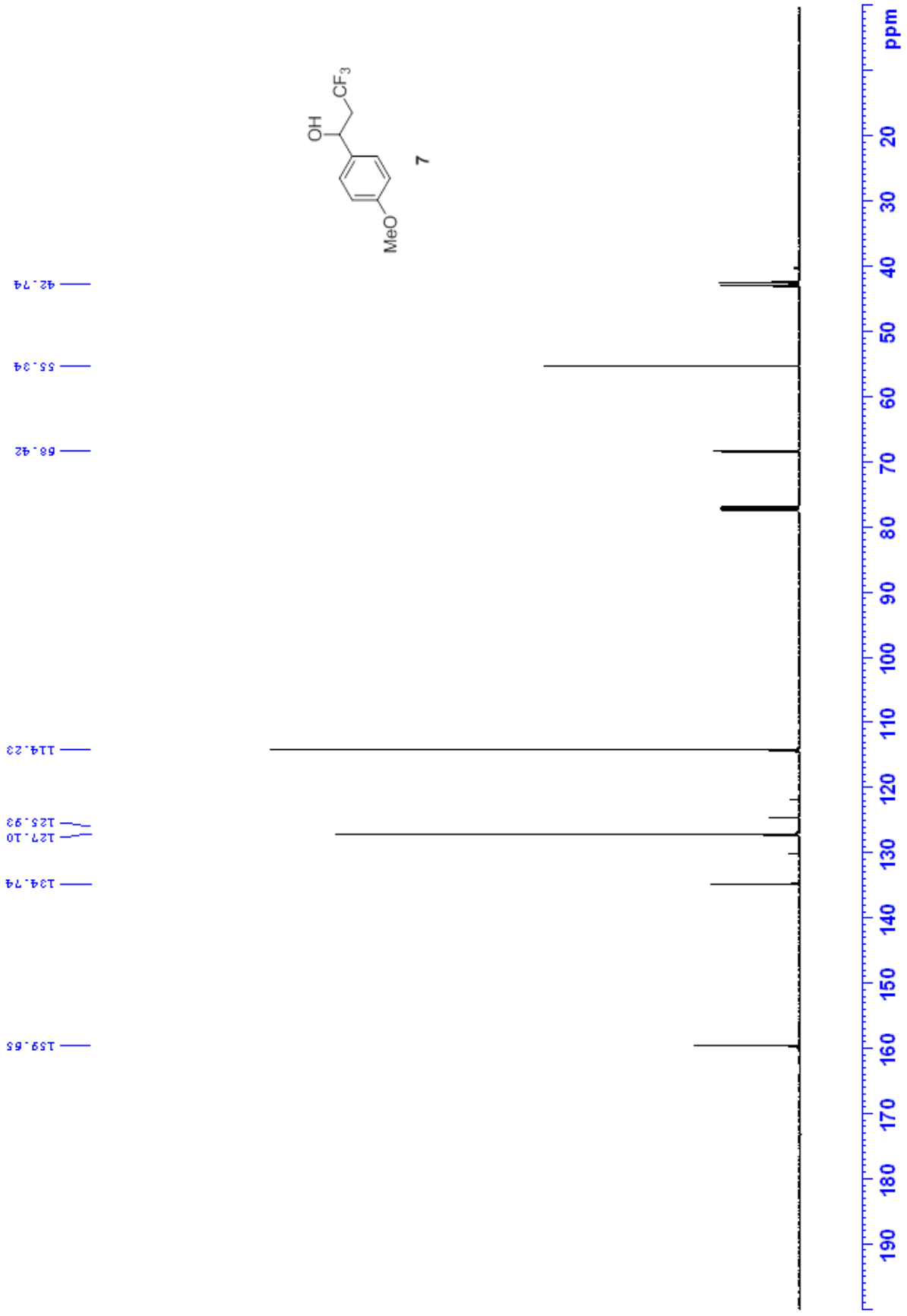

0.488
0.496
2.502
3.466
7.421
7.541
Br
CF3
Me2PhSi
6b
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5


-64.76
-64.79
-64.81
ppm
Br
Me2PhSi
CF3
6b
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
ppm


-5.55
-4.01
29.25
37.79
134.40
134.17
130.32
128.38
128.31
Br
CF3
Me2PhSi
6b
0 ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190


OH
CF3
MeO
7
2.486
3.790
4.968
6.885
7.259
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5


-63.67
-63.70
-63.73
OH
CF3
MeO
7
-63.5
ppm
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
ppm


OH
CF3
MeO
7
42.74
55.34
68.42
114.23
125.93
127.10
134.74
159.65
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190