Supporting Information

Synthesis of *n*-alkyl terminal halohydrin esters from acid halides and cyclic ethers or thioethers under solvent- and catalyst-free conditions

Kunuru Venkatesham, Dokuburra Chanti Babu, Tatipamula Vinay Bharadwaj, Richard A. Bunce, Chitturi Bhujanga Rao* and Yenamandra Venkateswalu*†

Natural Products Laboratory, Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad, India, 500 007. E-mail: cbrchem@gmail.com; Fax: 91-40-27160512; Tel: + 91-40-27193167

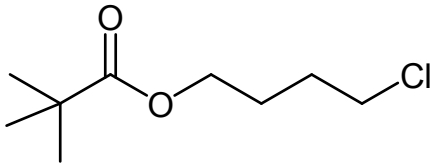
Table of Contents

General Information:

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp or I_2 stain. All products were characterized by their NMR and MS spectra. ^{1}H and ^{13}C NMR was recorded at 300 MHz, in $CDCl_3$ using TMS as the internal standard, chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane.

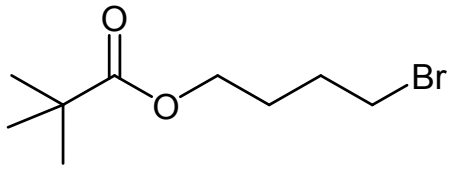
General Experimental Procedure:

The reaction was carried out by simple addition of organic acid halide (1.1 mmol) to heterocyclic ether (1.0 mmol) in a 10-mL round-bottomed flask under solvent- and catalyst-free conditions at rt. The reaction mixture was stirred at room temperature and monitored by TLC. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and washed with saturated aqueous $NaHCO_3$ (5 mL). The resulting solution was extracted again with EtOAc (10 mL) and the combined organic layers were dried over Na_2SO_4. The mixture was then concentrated *in vacuo* to yield the corresponding product. Column chromatography was performed if needed, but generally, the products required no further purification.



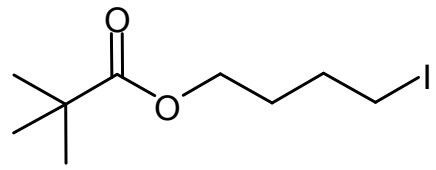
4-Chlorobutyl pivalate (**3a**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (t, 2H, *J* = 6.04 Hz), 3.55 (t, 2H, *J* = 6.7 Hz), 1.85 (m, 2H), 1.69 (m, 2H), 1.18 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.7, 64.2, 44.9, 28.8, 27.4, 27.1 (3C), 25.3.; **IR**: ν 2941, 1727, 1114, 769 cm^{-1}; **MS** (ESI): *m/z* 215 (M+Na); **HRMS**: *m/z* **Calcd**: 215.0815 ($C_9H_{17}ClO_2$+Na); **Found**: 215.0809.



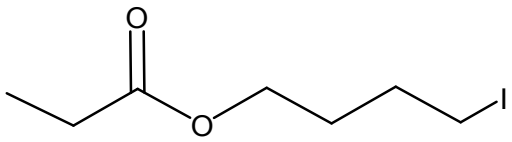
4-Bromobutyl pivalate (**3b**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.08 (t, 2H, *J* = 6.4 Hz), 3.43 (t, 2H, *J* = 6.4 Hz), 1.93 (quintet, 2H, *J* = 6.4 Hz), 1.79 (t, 2H, *J* = 6.4 Hz), 1.19 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.3, 63.2, 38.6, 33.0, 29.2, 27.2, 27.0 (3C).; **IR**: ν 2965, 1728, 1155, 771 cm^{-1}; **MS** (ESI): *m/z* 259 (M+Na); **HRMS:** *m/z* **Calcd**: 259.0309 ($C_9H_{17}BrO_2$+Na); **Found**: 259.0301.



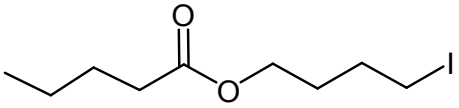
4-Iodobutyl pivalate (**3c**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.08 (t, 2H, *J* = 6.4 Hz), 3.21 (t, 2H, *J* = 6.4 Hz), 1.90 (m, 2H), 1.75 (m, 2H), 1.20 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.4, 62.9, 38.9, 29.8, 29.1, 27.0 (3C), 6.1. **IR**: ν 2964, 1727, 1154, 770 cm^{-1}; **MS** (ESI): *m/z* 307 (M+Na); **HRMS**: *m/z* **Calcd**: 307.0171 ($C_9H_{17}IO_2$+Na); **Found**: 307.0157.



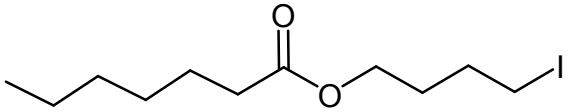
4-Iodobutyl propionate (**11**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.09 (t, 2H, *J* = 6.4 Hz), 3.20 (t, 2H, *J* = 6.7 Hz), 2.31 (q, 2H, *J* = 7.5 Hz), 1.89 (m, 2H), 1.76 (m, 2H), 1.13 (t, 2H, *J* = 7.5 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.2, 62.9, 29.9, 29.5, 27.4, 9.0, 5.8. **IR**: ν 2955, 1736, 1184, 747 cm^{-1}; **MS** (ESI): *m/z* 278 (M+Na); **HRMS**: *m/z* **Calcd**: 278.9858 ($C_7H_{13}IO_2$+Na); **Found**: 278.9836.



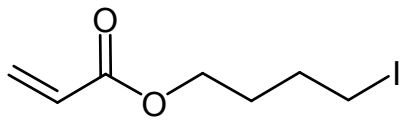
4-Iodobutyl pentanoate (**12**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.09 (t, 2H, *J* = 6.4 Hz), 3.22 (t, 2H, *J* = 6.8 Hz), 2.31 (t, 2H, *J* = 7.3 Hz), 1.90 (m, 2H), 1.75 (m, 2H), 1.60 (m, 2H), 1.34 (m, 2H), 0.92 (t, 3H, J = 7.3 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.7, 62.9, 33.9, 29.9, 29.4, 26.9, 22.1, 13.6, 5.9; **IR**: ν 2961, 1733, 1180, 758 cm^{-1}; **MS** (ESI): *m/z* 307 (M+Na); **HRMS**: *m/z* **Calcd**: 307.0171 ($C_9H_{17}IO_2$+Na); **Found**: 307.0163.



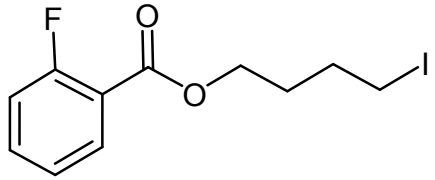
4-Iodobutyl heptanoate (**13**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.08 (t, 2H, *J* = 6.0 Hz), 3.20 (t, 2H, *J* = 7.5 Hz), 2.28 (t, 2H, *J* = 7.5 Hz), 1.89 (m, 2H), 1.74 (m, 2H), 1.59 (m, 2H), 1.28 (m, 2H), 0.87 (t, 3H, *J* = 6.7 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.3, 62.6, 34.0, 34.0, 29.8, 29.3, 28.5, 24.6, 22.2, 13.7, 5.5.; **IR**: ν 2955, 1736, 1168, 727 cm^{-1}; **MS** (ESI): *m/z* 335 (M+Na), **HRMS**: *m/z* **Calcd**: 335.0484 ($C_{11}H_{21}IO_2$+Na); **Found**: 335.0477.



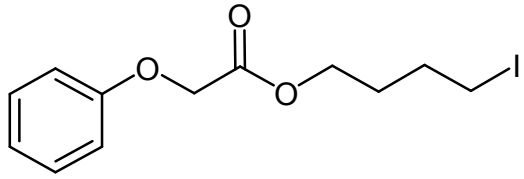
4-Iodobutyl acrylate (**14**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.41 (dd, 1H, *J* = 1.5, 17.3 Hz), 6.11 (dd, 1H, *J* = 10.5, 17.3, Hz), 5.82 (dd, 1H, *J* = 1.5, 10.5 Hz), 4.19 (t, 2H, *J* = 6.0 H), 3.22 (t, 2H *J* = 6.7 Hz), 1.92 (m, 2H), 1.81 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.2, 133.3, 130.8, 63.3, 29.9, 29.4, 5.7.; **IR**: ν 2956, 1724, 1192, 809 cm^{-1}; **MS** (ESI): *m/z* = 276 (M+Na); **HRMS**: *m/z* **Calcd**: 276.9701 ($C_7H_{11}IO_2$+Na); **Found**: 276.9694.



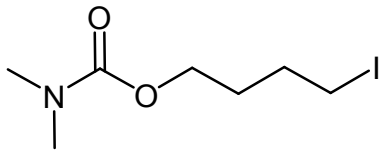
4-Iodobutyl 2-fluorobenzoate (**15**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (t d, 1H, *J* = 1.8, 7.5 Hz), 7.52 (m, 1H), 7.28-7.10 (br m, 2H), 4.36 (t, 2H, *J* = 6.0 Hz), 3.26 (t, 2H, *J* = 6.6 Hz), 2.09-1.85 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 163.5, 160.1, 134.4, 134.3, 131.9, 123.8, 116.7, 63.9, 29.9, 29.4, 5.8; **IR**: ν 2957, 1722, 1298, 757 cm^{-1}; **MS** (ESI): *m/z* 344 (M+Na); **HRMS**: *m/z* **Calcd**: 344.9763 ($C_{11}H_{12}FIO_2$+Na); **Found**: 344.9748.



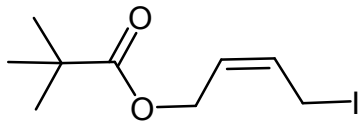
4-Iodobutyl 2-phenoxyacetate (**16**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (m, 2H), 7.00 (t, 1H, *J* = 7.3 Hz), 6.92 (d, 2H, *J*= 7.9 Hz), 4.64 (s, 2H), 4.23 (t, 2H, *J* = 6.0 Hz), 3.16 (t, 2H, *J* = 6.4 Hz), 1.80 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.1, 157.5, 129.4 (2C), 121.6, 114.7 (2C), 65.0, 63.1, 29.5, 29.3, 5.7.; **IR**: ν 2957, 1758, 1195, 755 cm^{-1}; **MS** (ESI): *m/z* 356 (M+Na); **HRMS**: *m/z* **Calcd:** 356.9963 ($C_{12}H_{15}IO_3$+Na); **Found**: 356.9951.



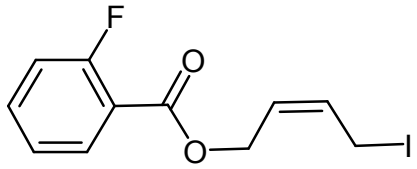
4-Iodobutyl dimethylcarbamate (**17**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.08 (t, 2H, *J* = Hz), 3.21 (t, 2H, *J* = Hz), 2.89 (s, 6H), 1.90 (m, 2H), 1.73 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 156.3, 63.9, 36.2 (2C), 35.7, 29.9, 29.8, 5.9.; **IR**: ν 2939, 1703, 1190, 768 cm^{-1}; **MS** (ESI): *m/z* 293 (M+Na); **HRMS**: *m/z* **Calcd**: 293.9967 ($C_7H_{14}INO_2$+Na); **Found**: 293.9958.



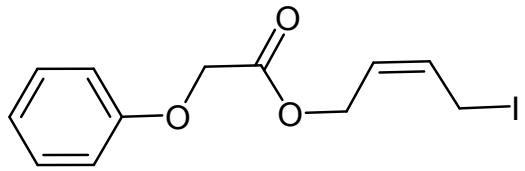
(*Z*)-4-Iodobut-2-en-1-yl pivalate (**22**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99 (m, 1H), 5.79 (m, 1H), 4.54 (m, 2H), 3.86 (dd, 2H, *J* = 0.7, 7.9 Hz), 1.21 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.0, 131.1, 127.8, 63.3, 38.7, 27.1 (3C), 3.9.; **IR**: ν 2924, 1730, 1153, 769 cm^{-1}; **MS** (ESI): *m/z* 305 (M+Na); **HRMS**: *m/z* **Calcd**: 305.0014 ($C_9H_{15}IO_2$+Na); **Found**: 305.0006.



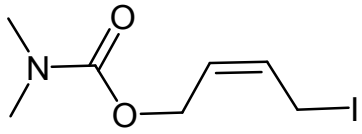
(*Z*)-4-Iodobut-2-en-1-yl 2-fluorobenzoate (**23**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (td, 1H, *J* = 1.8, 7.6 Hz), 7.53 (m, 1H), 7.21 (td, 1H, *J* = 1.0, 7.7 Hz), 7.14 (ddd, 1h, *J* = 0.9, 8.3, 10.8 Hz), 6.12 (m, 1H), 5.91 (m, 1H), 4.83 (d, 2H, *J* = 5.9 Hz), 3.89 (dd, 2H, *J* = 0.6, 7.9 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 163.5, 160.0, 134.4, 31.9 (2C), 131.8, 127.0, 123.8, 116.7, 64.1, 3.6.; **IR**: ν 2927, 1723, 1125, 757 cm^{-1}; **MS** (ESI): *m/z* 342 (M+Na); **HRMS**: *m/z* **Calcd**: 342.9607 ($C_{11}H_{10}FIO_2$+Na); **Found**: 342.9582.



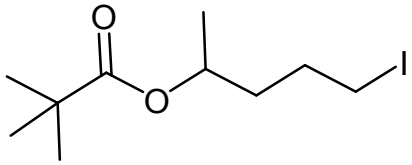
(*Z*)-4-Iodobut-2-en-1-yl 2-phenoxyacetate (**24**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (t, 2H, *J* = 7.4 Hz), 7.00 (t, 1H, *J*= 7.3 Hz), 6.91 (d, 2H, *J* = 7.7 Hz), 6.01 (m, 1H), 5.78 (m, 1H), 4.68 (d, 2H, *J* = 6.1 Hz), 4.65 (s, 2H), 3.85 (d, 2H, *J* = 7.9 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.5, 157.5, 132.6, 129.5 (2C), 126.4, 121.7, 114.5 (2C), 65.1, 64.2,3.3. **IR**: ν 2924, 1738, 1213, 755 cm^{-1}; **MS** (ESI): *m/z* 354 (M+Na); **HRMS**: *m/z* **Calcd**: 354.9807 ($C_{12}H_{13}IO_3$+Na); **Found**: 354.9778.



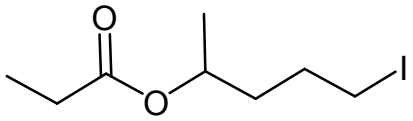
(*Z*)-4-Iodobut-2-en-1-yl dimethylcarbamate (**25**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.97 (m, 1H), 5.81 (m, 1H), 4.56 (d, 2H, *J* = 5.6 Hz), 3.85 (d, 2H, *J* = 7.7 Hz), 2.91 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 156.1, 130.6, 128.5, 64.3, 36.4, 35.8, 4.1. **IR**: ν 2924, 1632, 1187, 767 cm^{-1}; **MS** (ESI): *m/z* = 291 (M+Na); **HRMS**: *m/z* **Calcd**: 291.9810 ($C_7H_{12}IO_2$+Na); **Found**: 291.9802.



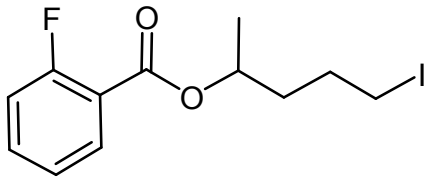
5-Iodopentan-2-yl pivalate (**26**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.95 (m, 1H), 3.18 (t, 2H, *J* = 6.7 Hz), 2.31 (q, 2H, *J* = 7.7 Hz), 1.84 (m, 2H), 1.66 (m, 2H), 1.23 (s, 9H), 1.13 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.7, 68.5, 36.0, 28.8, 28.3, 26.6 (3C), 19.4, 5.8. ; **IR**: ν 2974, 1725, 1166, 770 cm^{-1}; **MS** (ESI): *m/z* 321 (M+Na); **HRMS**: *m/z* **Calcd**: 321.0327 ($C_{10}H_{19}IO_2$+Na); **Found**: 321.0317.



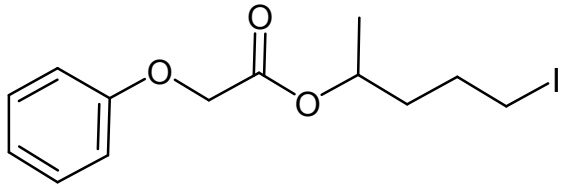
5-Iodopentan-2-yl propionate (**27**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.92 (m, 1H), 3.18 (t, 2H, *J* = 6.7 Hz), 2.29 (q, 2H, *J* = 7.7 Hz), 1.84 (m, 2H), 1.65 (m, 2H), 1.21 (d, 3H, *J* = 6.2 Hz), 1.13 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.8, 69.3, 36.5, 29.2, 27.6, 19.8, 9.0, 6.1; **IR**: ν 2957, 1741, 1172, 745 cm^{-1}; **MS** (ESI): *m/z* 271 (M+H), 293 (M+Na), **HRMS**: m/z **Calcd**: 271.0195 ($C_8H_{15}IO_2$+H); **Found**: 271. 0190.



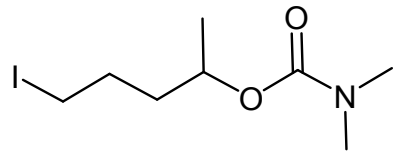
5-Iodopentan-2-yl 2-fluorobenzoate (**28**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (qd, 1H, *J* = 1.5, 7.9 Hz), 7.52 (m, 1H), 7.28-7.10 (br m, 2H), 5.21 (m, 1H), 3.22 (t, 2H, *J* = 6.6 Hz), 1.99-1.71 (br m, 4H), 1.36 (d, 3H, *J* = 6.2 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 163.8, 160.7, 134.1, 131.8 (2C), 123.8, 116.9, 70.8, 36.6, 29.1, 19.9, 6.2.; **IR**: ν 2957, 1722, 1298, 757 cm^{-1}; **MS** (ESI): *m/z* 358 (M+Na); **HRMS**: *m/z* **Calcd**: 358.9920 ($C_{12}H_{14}FIO_2$+Na); **Found**: 358.9896.



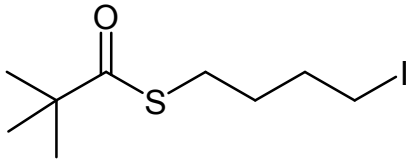
5-Iodopentan-2-yl 2-phenoxyacetate (**29**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (t, 2H, *J* = 8.1 Hz), 6.99 (t, 1H, *J* = 7.3 Hz), 6.91(dd, 2H, *J* = 0.9, 7.5 Hz), 5.07 (m, 1H), 4.64 (s, 2H), 4.61 (s, 3H), 3.13 (t, 2H, *J* = 6.4 Hz), 1.84-1.60 (m, 4H), 1.26 (d, 3H, *J* = 6.2 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.5, 157.6, 129.4 (2C), 121.6, 114.4 (2C), 71.1, 65.3, 36.4, 28.8, 19.8, 5.9; **IR**: ν 2931, 1757, 1198, 754 cm^{-1}; **MS** (ESI): *m/z* 371 (M+Na); **HRMS**: *m/z* **Calcd**: 371.0120 ($C_{13}H_{17}IO_3$+Na); **Found**: 371.0104.



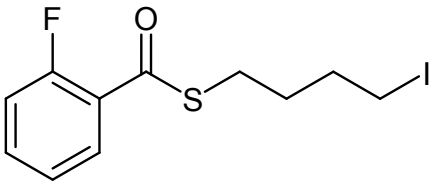
5-Iodopentan-2-yl dimethylcarbamate (**30**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.81 (m, 1H), 3.19 (t, 2H, *J* = 6.8 Hz), 2.90 (s, 6H), 1.92-1.80 (m, 2H), 1.77-1.62 (m, 2H), 1.23 (d, 3H, *J* = 6.2 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 156.0, 70.3, 36.7, 35.6, 29.2, 20.3, 6.4.; **IR**: ν 2930, 1702, 1191, 769 cm^{-1}; **MS** (ESI): *m/z* 308 (M+Na); **HRMS**: *m/z* **Calcd**: 308.0123 ($C_8H_{16}NIO_2$+Na); **Found**: 308.0111.



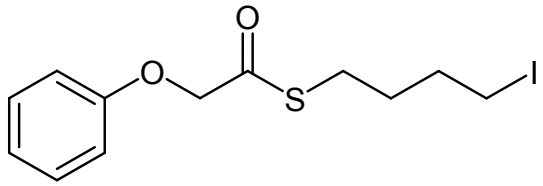
S-4-Iodobutyl 2,2-dimethylpropanethioate (**31**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.18 (t, 2H, *J* = 6. 7 Hz), 2.84 (t, 2H, *J* = 6.7 Hz), 1.89 (m, 2H), 2.33 (m, 2H)., 1.22 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 206.6, 46.3, 32.3, 30.3, 27.3 (3C), 26.8, 5.7.; **IR**: ν 2967, 1702, 1101, 713 cm^{-1}; **MS** (ESI): *m/z* 322 (M+Na); **HRMS**: *m/z* **Calcd** = 322.9942 ($C_9H_{17}IOS$+Na); **Found**: 322.9936.



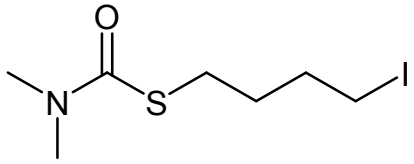
S-4-Iodobutyl 2-fluorobenzothioate (**32**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (t, 1H, *J* = 6.7 Hz), 7.50 (q, 1H, *J* = 6.7 Hz), 7.26 - 7.12 (m, 2H), 3.22 (t, 2H, *J* = 6.7 Hz), 3.09 (t, 2H, *J* = 7.5 Hz), 1.97 (m, 2H), 1.81 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 188.4, 159.3, 134.2, 129.4 (2C), 129.0, 116.5, 32.2, 30.0, 27.9, 5.7.; **IR**: ν 2932, 1669, 1197, 917, 765 cm^{-1}; **MS** (ESI): *m/z* 360 (M+Na); **HRMS**: *m/z* **Calcd**: 360.9535 ($C_{11}H_{12}FIOS$+Na); **Found**: 360.9517.



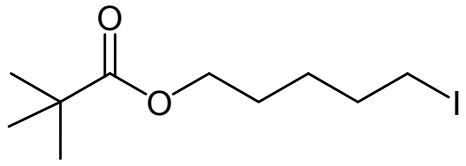
S-4-Iodobutyl 2-phenoxyethanethioate (**33**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (t, 2H, *J* = 7.5 Hz), 7.02 (t, 1H, *J* = 7.5 Hz), 6.91 (d, 2H, *J* = 8.3 Hz), 4.68 (s, 2H), 3.17 (t, 2H, *J* = 6.7 Hz), 2.95 (t, 2H, *J* = 7.5 Hz), 1.89 (m, 2H), 1.71 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 198.1, 157.5, 129.5 (2C), 121.9, 114.7 (2C), 72.6, 32.1, 30.0, 26.7, 5.5.; **IR**: ν 2927, 1680, 1216, 754 cm^{-1}; **MS** (ESI): *m/z* 372 (M+Na); **HRMS**: *m/z* **Calcd**: 372.9735 ($C_{12}H_{15}IO_2S$+Na); **Found**: 372.9709.



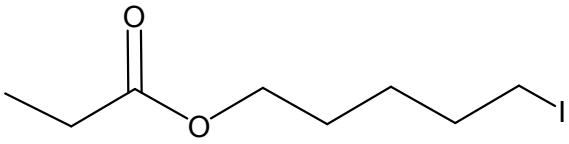
S-4-Iodobutyl dimethylcarbamothioate (**34**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.19 (t, 2H, *J* = 7.5 Hz), 3.00 (s, 6H), 2.91 (t, 2H, *J* = 7.5Hz), 1.92, (m, 2H), 1.72 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.1, 36.8, 35.0 (2C), 28.8, 28.7, 5.8.; **IR**: ν 2930, 1652, 1099, 687 cm^{-1}; **MS** (ESI): *m/z* 309 (M+Na); **HRMS**: *m/z* **Calcd**: 309.9738 ($C_7H_{14}INOS$+Na); **Found**: 309.9707.



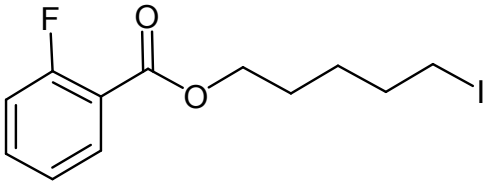
5-Iodopentyl pivalate (**35**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.06 (t, 2H, *J* = 6.0 Hz), 3.19 (t, 2H, *J* = 6.7 Hz), 1.84 (m, 2H), 1.65 (m, 2H), 1.47 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.5, 63.9, 38.6, 32.8, 27.5, 27.1, 26.9 (3C), 6.4.; **IR**: ν 2963, 1727, 1156, 770 cm^{-1}; **MS** (ESI): *m/z* 321 (M+Na); **HRMS**: *m/z* **Calcd**: 321.0327 ($C_{10}H_{19}IO_2$+Na); **Found**: 321.0317.



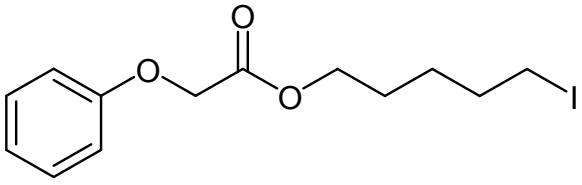
5-Iodopentyl propionate (**36**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.07 (t, 2H, *J* = 6.4 Hz), 3.19 (t, 2H, *J* = 6.7 Hz), 2.31 (q, 2H, *J* = 7.5 Hz), 1.85 (m, 2H), 1.65 (m, 2H), 1.47 (m, 2H), 1.14 (t, 3H, *J* = 7.5 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.4, 63.8, 32.8, 27.4 (2C), 26.8, 9.0, 6.5.; **IR**: ν 2940, 1736, 1186, 770 cm^{-1}; **MS** (ESI): *m/z* 271 (M+H), 293 (M+Na); **HRMS**: *m/z* **Calcd**: 271.0195 ($C_8H_{15}IO_2$+H); **Found**: 271.0190.



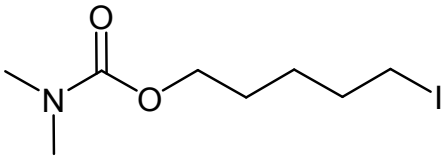
5-Iodopentyl 2-fluorobenzoate (**37**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (t d, 1H, *J* = 1.5, 7.5 Hz), 7.51 (m, 1H), 7.23-7.10 (m, 2H), 4.34 (t, 2H, *J* = 6.7 Hz), 3.21 (t, 2H, *J* = 6.7 Hz), 1.90 (m, 2H), 1.80 (m, 2H), 1.58 (m, 2H); **^{13}C NMR** (300 MHz, $CDCl_3$): δ 163.6, 160.0, 134.4, 131.9 (2C), 123.8, 116.7, 64.8, 32.8, 27.4, 26.9, 6.5. ; **IR**: ν 2937, 1726, 1298, 757 cm^{-1}; **MS** (ESI): *m/z* = 358 (M+Na); **HRMS**: *m/z* **Calcd**: 358.9920 ($C_{12}H_{14}FIO_2$+Na); **Found**: 358. 9896.



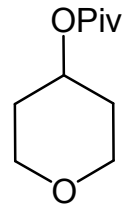
5-Iodopentyl 2-phenoxyacetate (**38**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (m, 2H, *J* = 7.9 Hz), 6.99 (t, 1H, *J* = 7.9 Hz), 6.91 (d, 2H, *J* = 7.9Hz), 4.63 (s, 2H), 4.21 (t, 2H, *J* = 5.9Hz), 3.14 (t, 2H, *J* = 6.9 Hz), 1.81 (m, 2H), 1.67 (m, 2H), 1.42 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.9, 157.7, 129.4 (2C), 121.6, 114.5 (2C), 65.2, 64.7, 32.7, 27.3, 26.6, 6.2.; **IR**: ν 2935, 1758, 1194, 754 cm^{-1}; **MS** (ESI): *m/z* 371 (M+Na); **HRMS**: *m/z* **Calcd** = 371.0120 ($C_{13}H_{17}IO_3$+Na); **Found**: 371.0104.



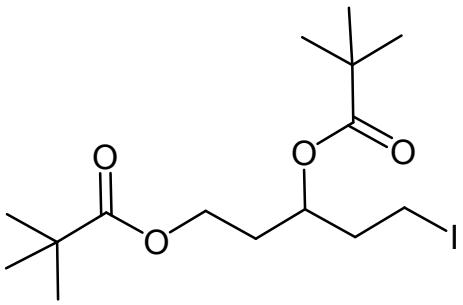
5-Iodopentyl dimethylcarbamate (**39**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (t, 2H, *J* = 6.4 Hz), 3.18 (t, 2H, *J* = 6.9 Hz), 2.89 (s, 6H), 1.84 (m, 2H), 1.64 (m, 2H), 1.47 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 156.5, 64.7, 36.2, 35.7, 32.8, 27.8, 26.7, 6.6.; **IR**: ν 2934, 1704, 1189, 769 cm^{-1}; **MS** (ESI): *m/z* 308 (M+Na); **HRMS**: *m/z* **Calcd**: 308.0123 ($C_8H_{16}NIO_2$+Na); **Found**: 308. 0111.



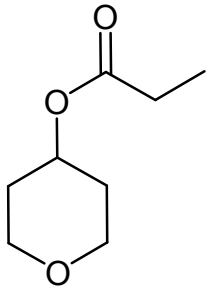
Tetrahydro-2*H*-pyran-4-yl pivalate (**41**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.92 (m, 1H), 3.87 (m, 2H), 3.57(m, 2H), 1.90 (m, 2H), 1.66 (m, 2H), 1.20 (s, 9H).; **MS** (ESI): *m/z* 209 (M+Na).



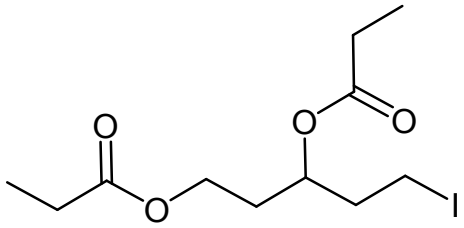
5-iodopentane-1,3-dipivalate (**42**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.01 (m, 1H), 4.08 (t, 2H, *J* = 75. Hz), 3.12 (t, 2H, *J* = 7.5 Hz), 2.15 (m, 2H), 1.91(m, 2H), 1.19 (s, 18H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.3, 177.1, 70.7, 60.1, 38.5, 32.6, 27.1 (6C), 5.0; **IR**: ν 2970, 1728, 1150, 767 cm^{-1}; **MS** (ESI): *m/z* 421 (M+Na); **HRMS**: *m/z* **calcd** = 421.0852 ($C_{15}H_{27}IO_4$+Na); **Found**: 421.0837.



Tetrahydro-2*H*-pyran-4-yl propionate (**43**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.94 (m, 1H), 3.90 (m, 2H), 3.54 (m, 2H), 2.33 (q, 2H, *J* = 7.6 Hz), 1.90 (m, 2H), 1.66 (m, 2H), 1.14 (t, 3H, *J* = 7.6 Hz). **MS** (ESI): *m/z* 181 (M+Na).



5-Iodopentane-1,3-dipropionate (**44**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.05 (m, 1H), 4.10 (t, 2H, *J* = 6.4 Hz), 3.11 (m, 2H), 2.34 (qd, 4H, *J* = 2.2, 7.5 Hz), 2.16 (m, 2H), 1.92 (q, 2H, *J* = 6.4 Hz), 1.14 (td, 6H, *J* = 2.0, 7.5 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 174.2, 173.8, 70.9, 60.1, 38.4, 32.6, 27.4 (2C), 9.0 (2C), -0.49 (CH_2-I). **MS** (ESI): *m/z* 365 (M+Na); **HRMS**: *m/z* **Calcd**: 365.0226 ($C_{11}H_{19}IO_4$+Na); **Found**: 365.0217.

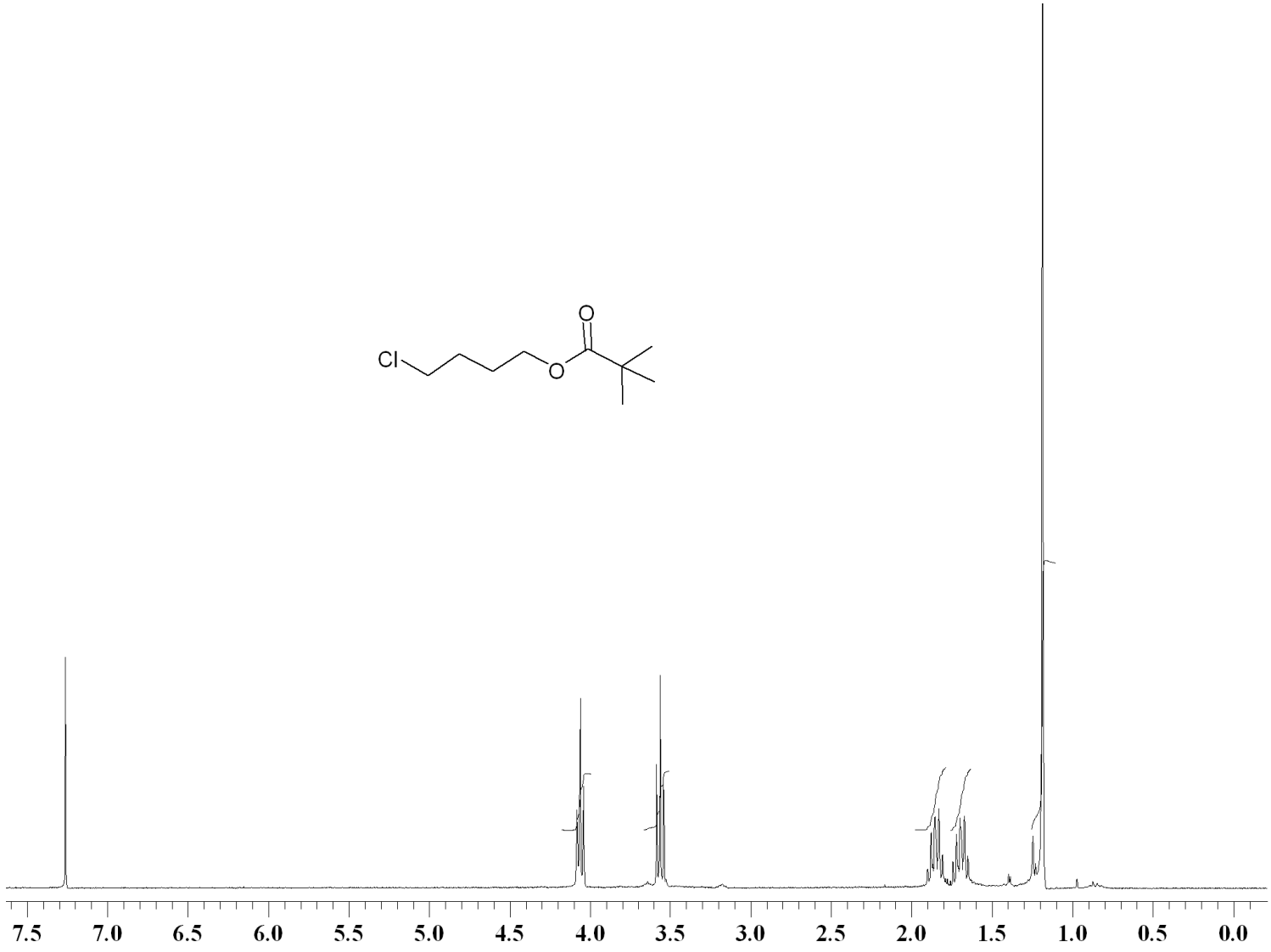


Fig: ^{1}H NMR of compound **3a**

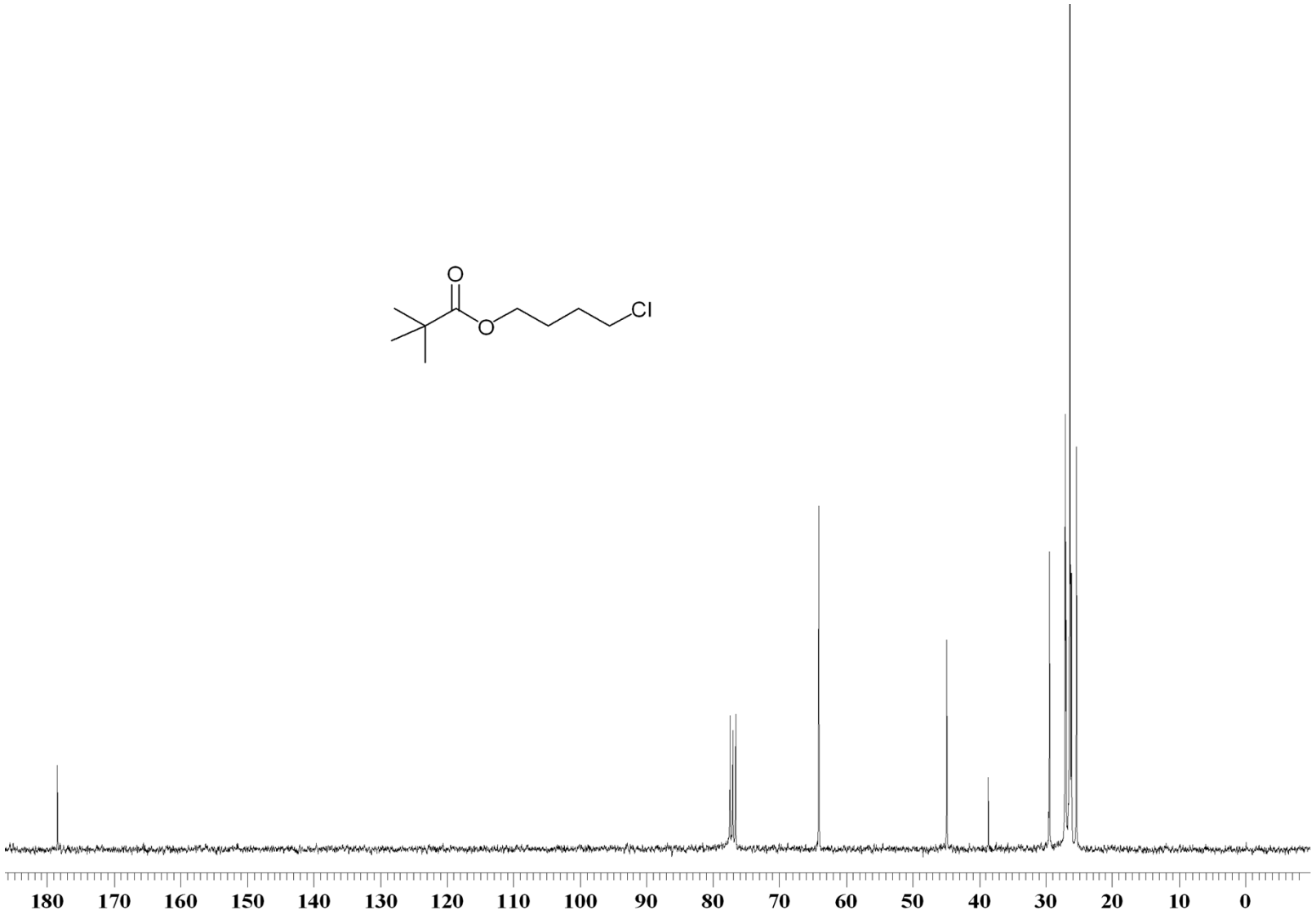


Fig: ^{13}C NMR of compound **3a**

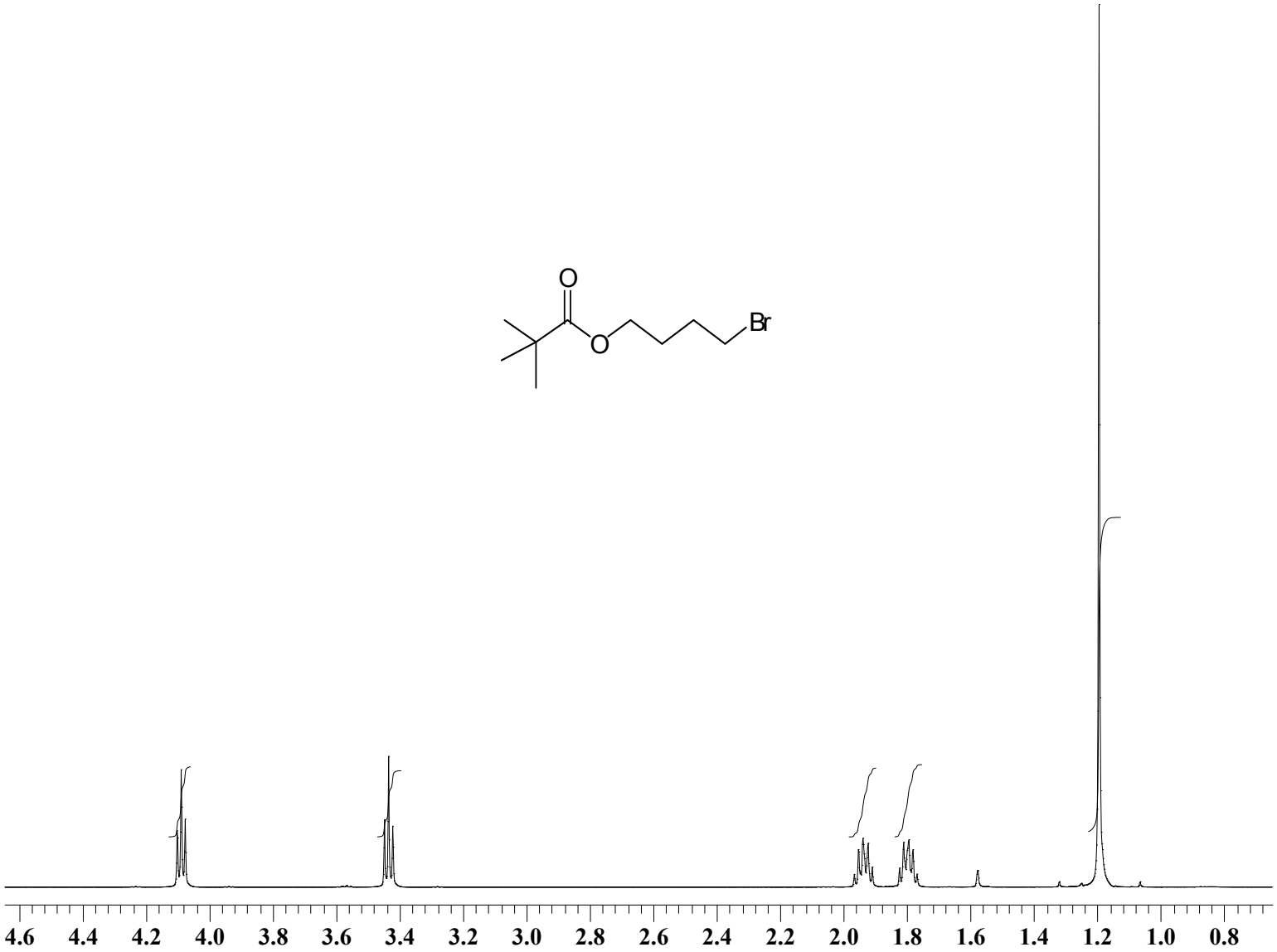


Fig: ^{1}H NMR of compound **3b**

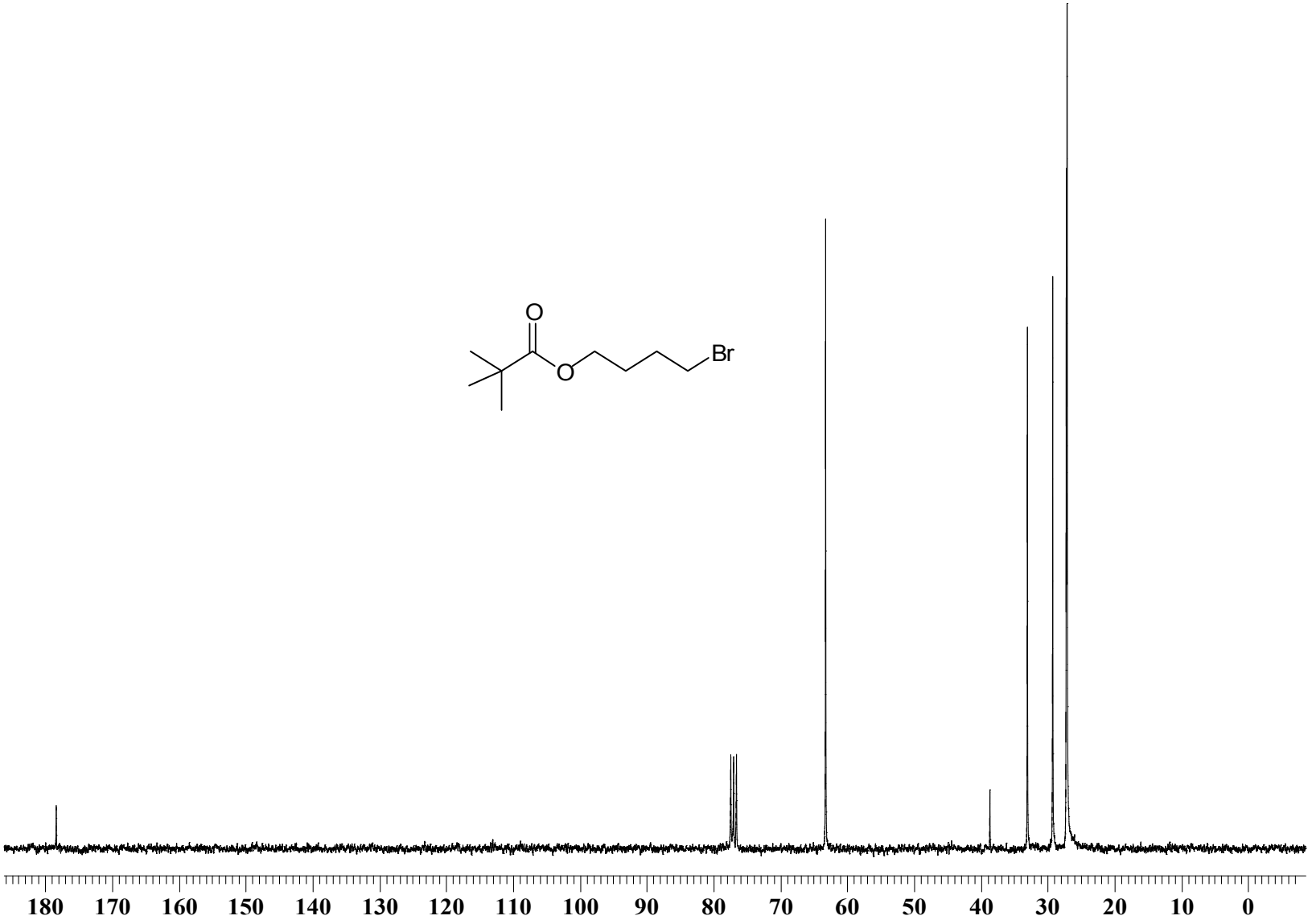


Fig: ^{13}C NMR of compound **3b**

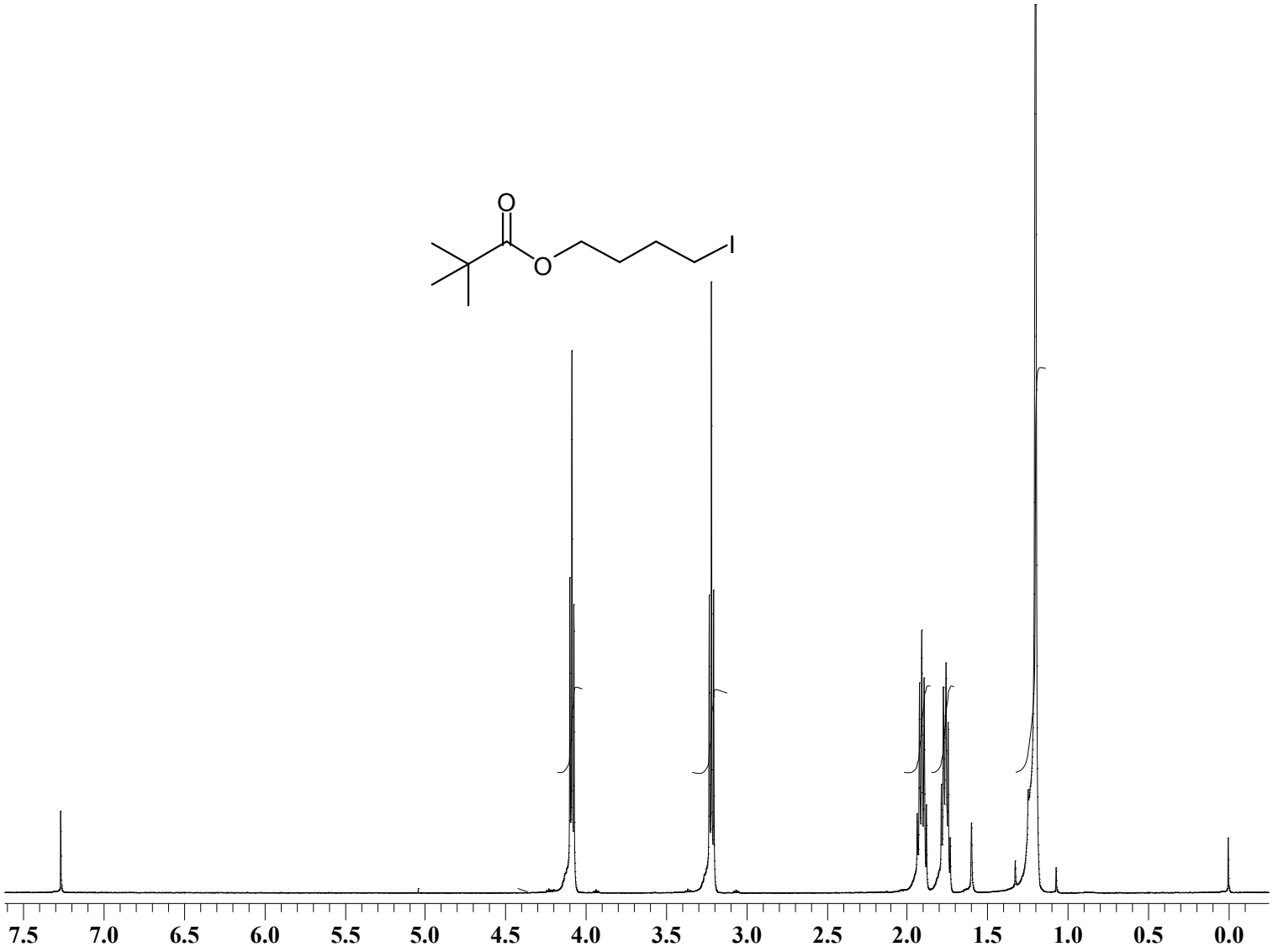


Fig: ^{1}H NMR of compound **3c**

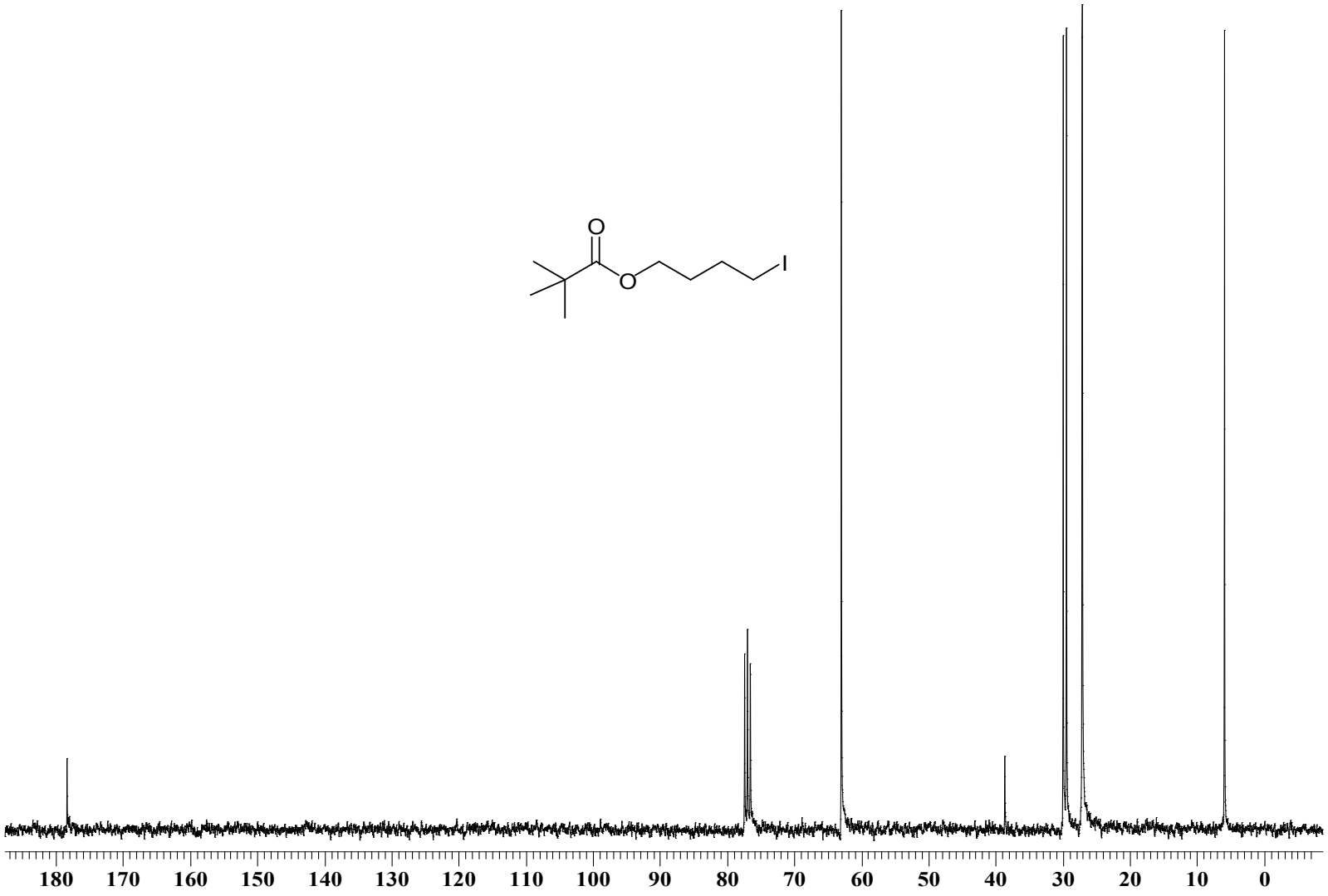


Fig: ^{13}C NMR of compound **3c**

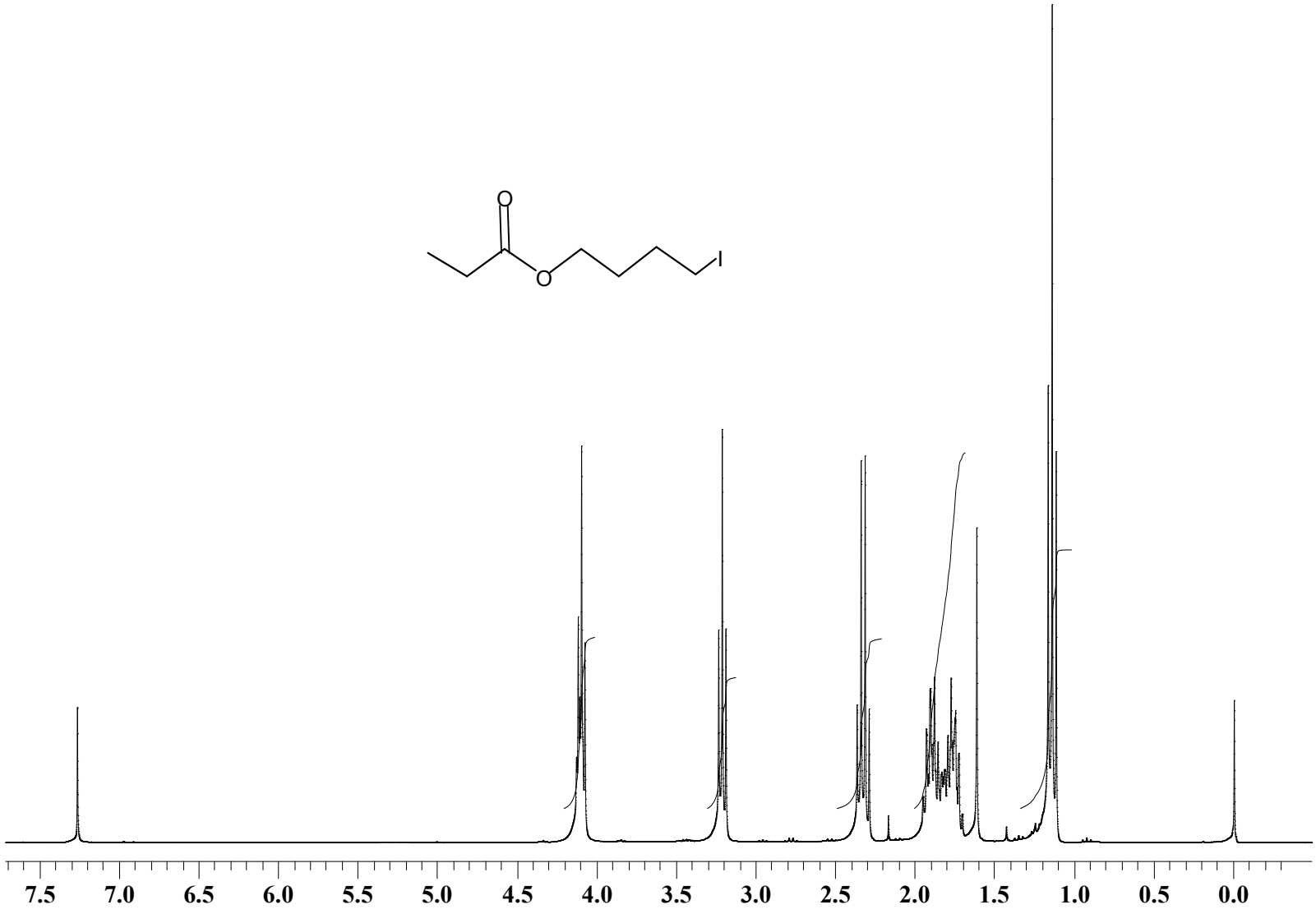


Fig: ^{1}H NMR of compound **11**

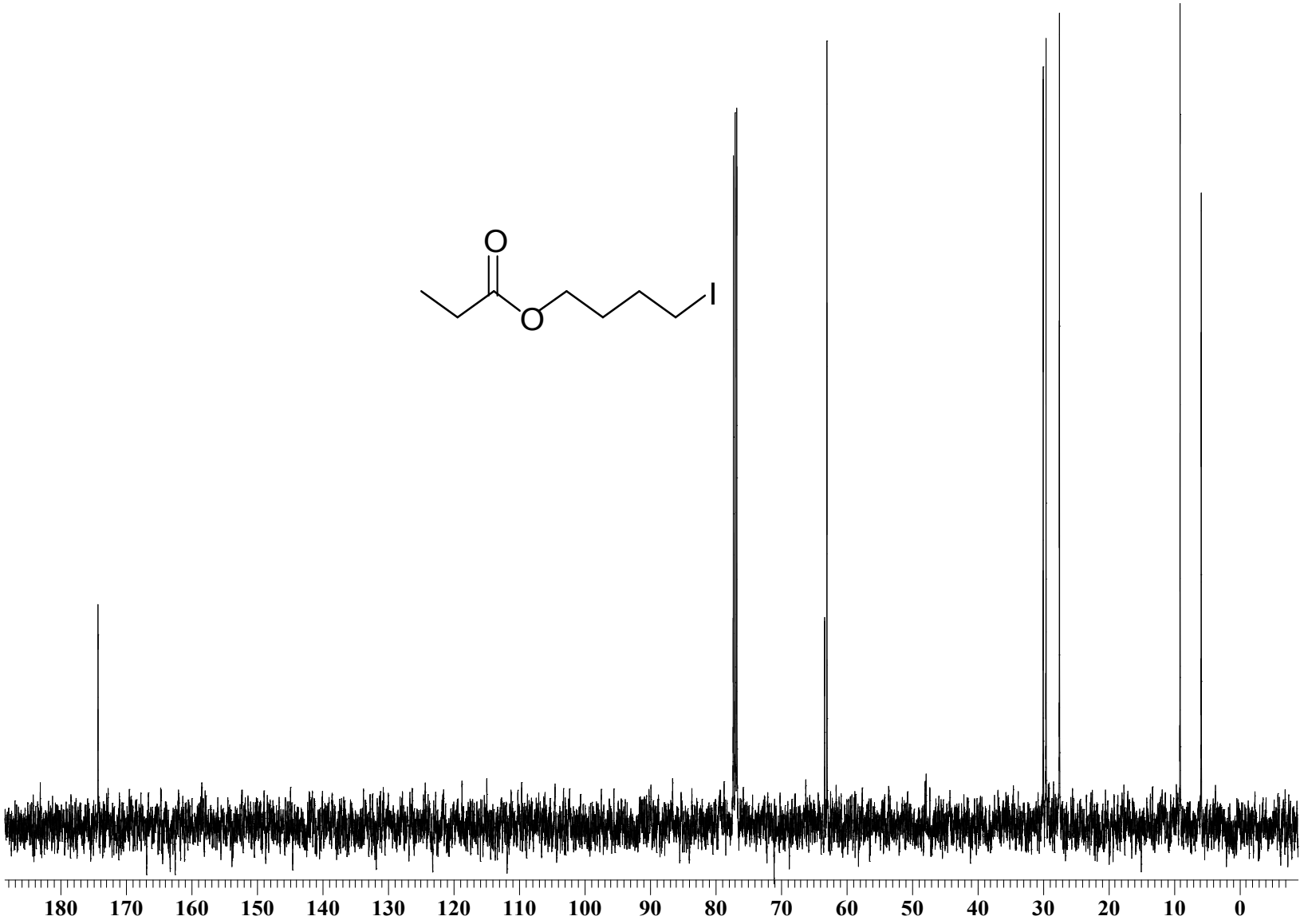


Fig: ^{13}C NMR of compound **11**

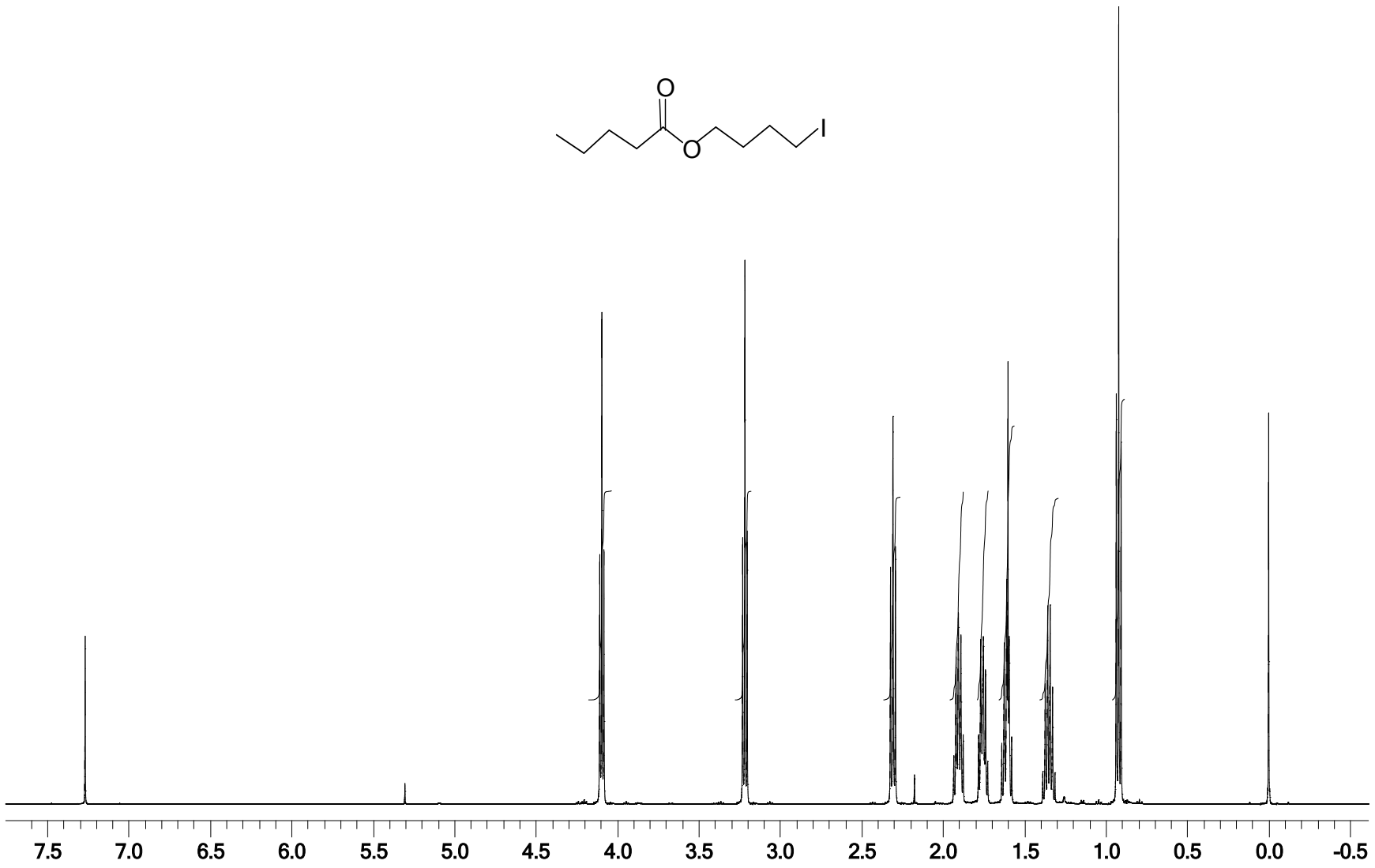


Fig: ^{1}H NMR of compound **12**

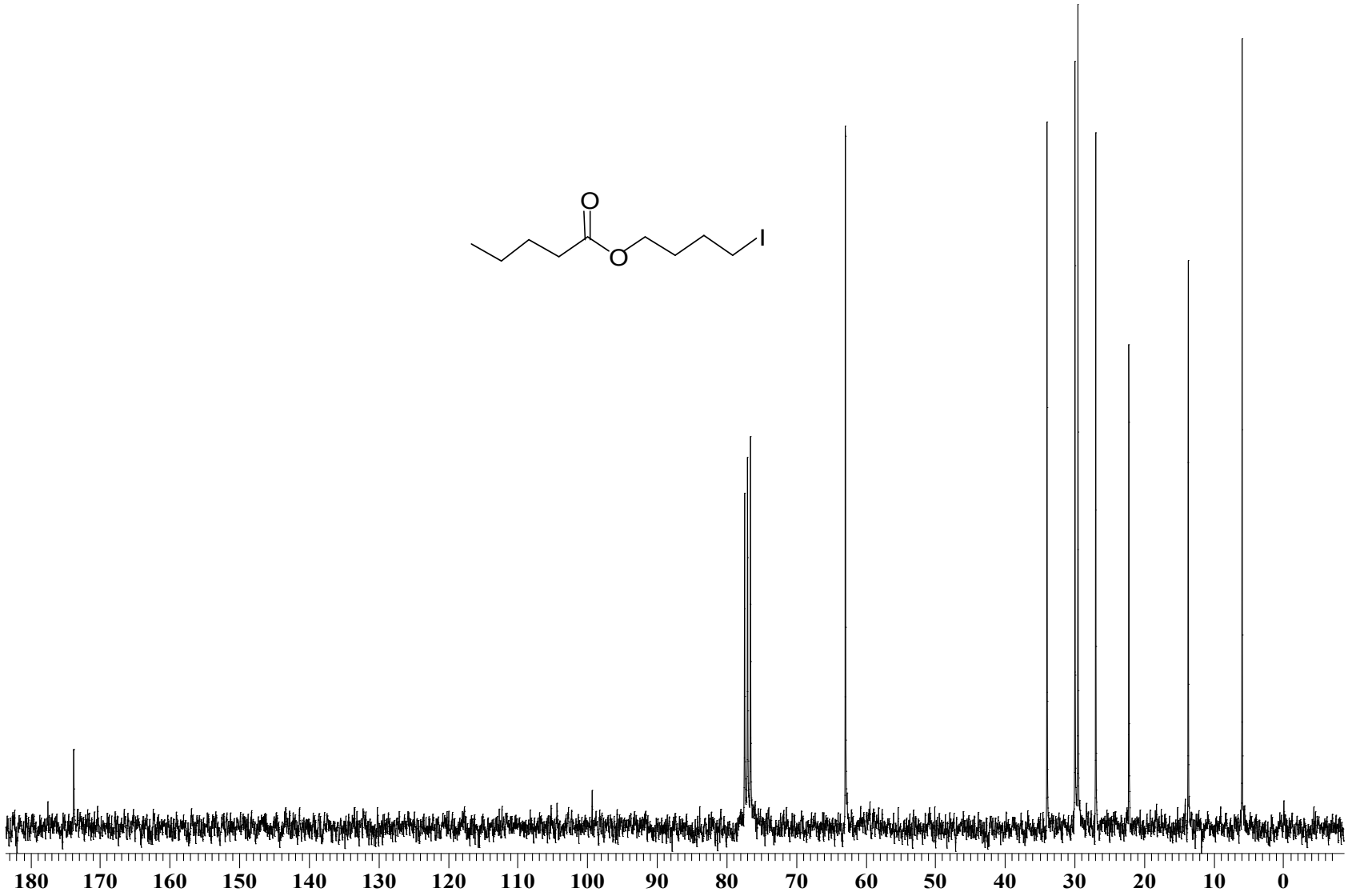


Fig: ^{13}C NMR of compound **12**

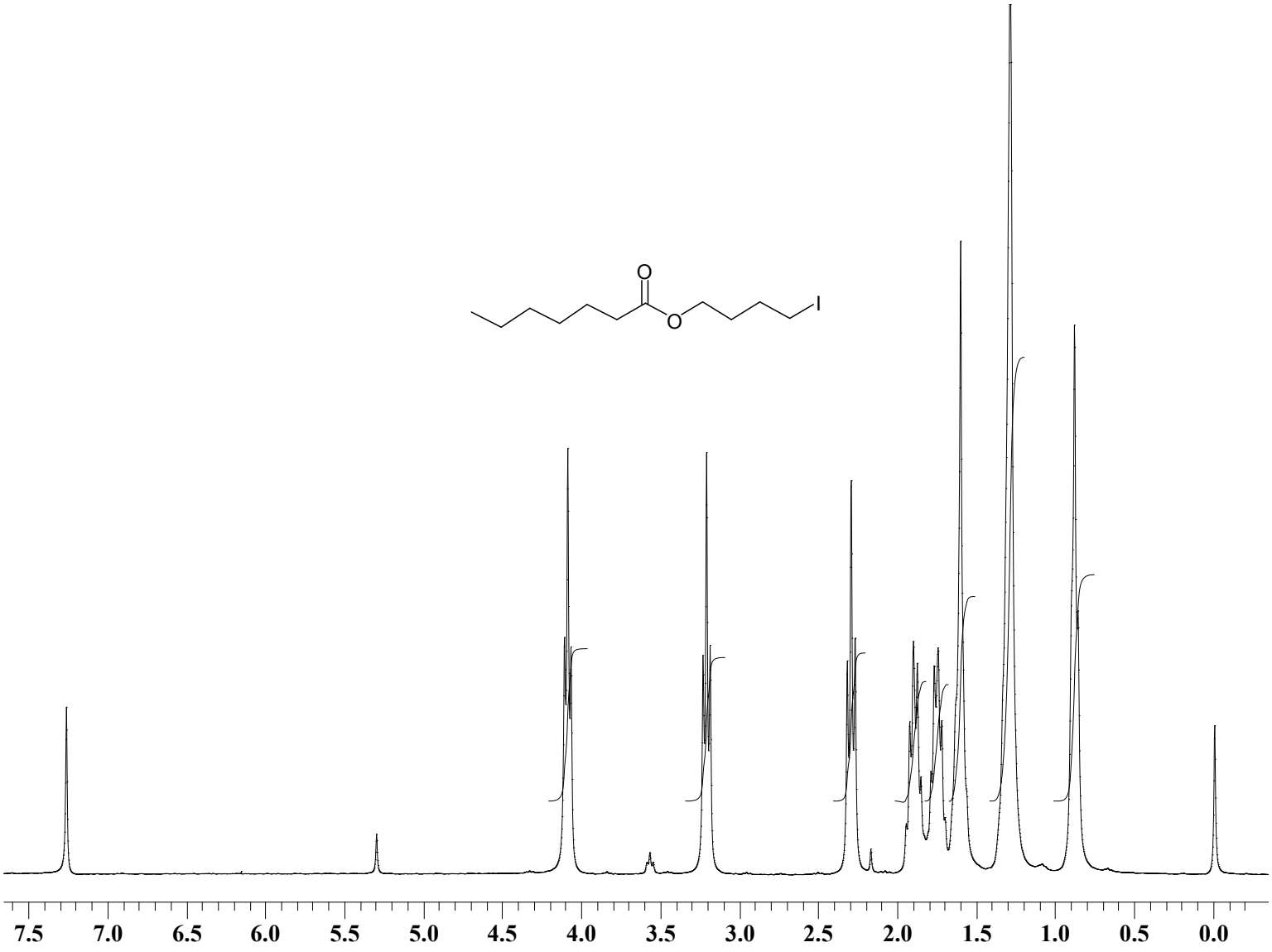


Fig: ^{1}H NMR of compound **13**

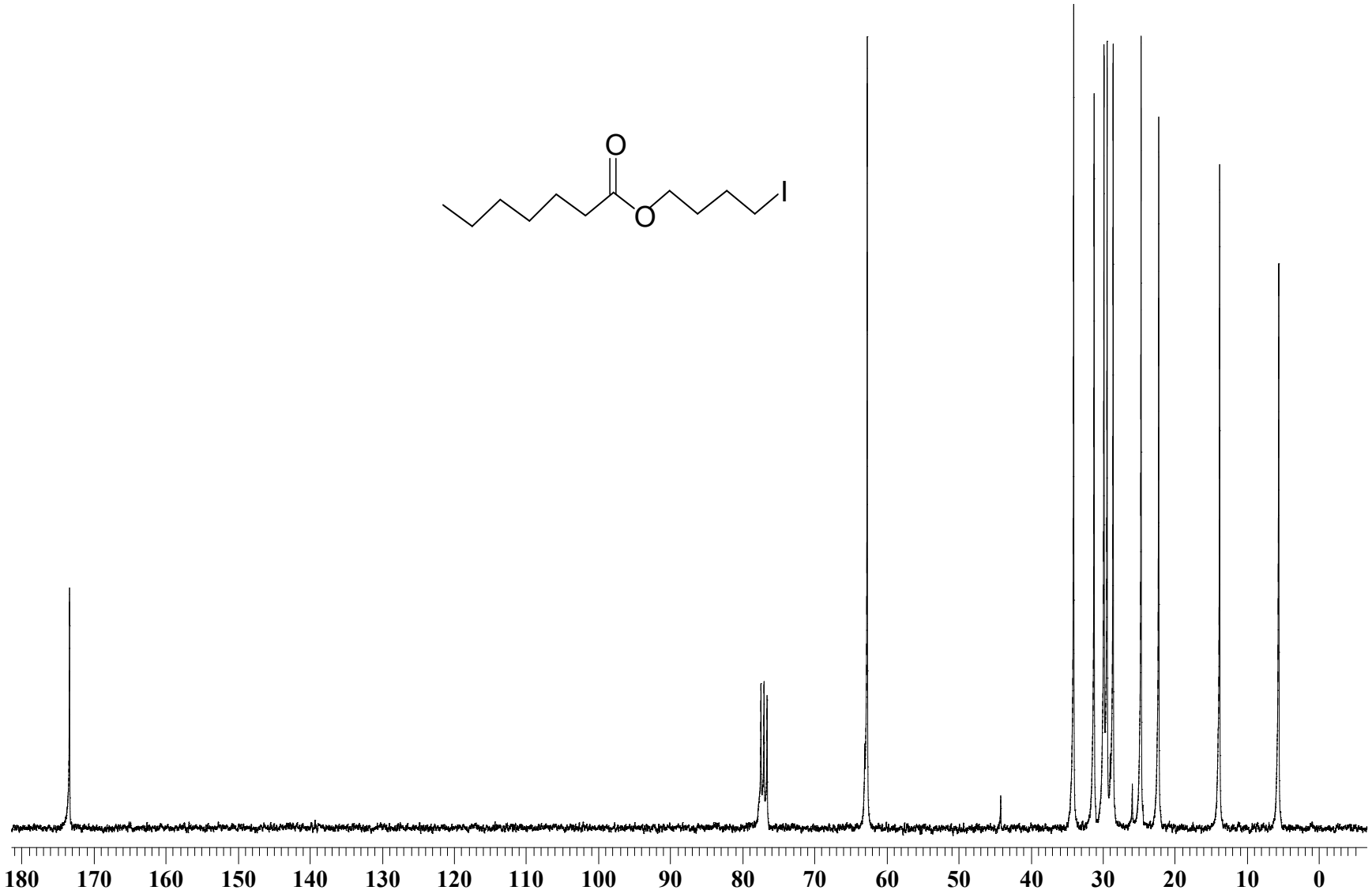


Fig: ^{13}C NMR of compound **13**

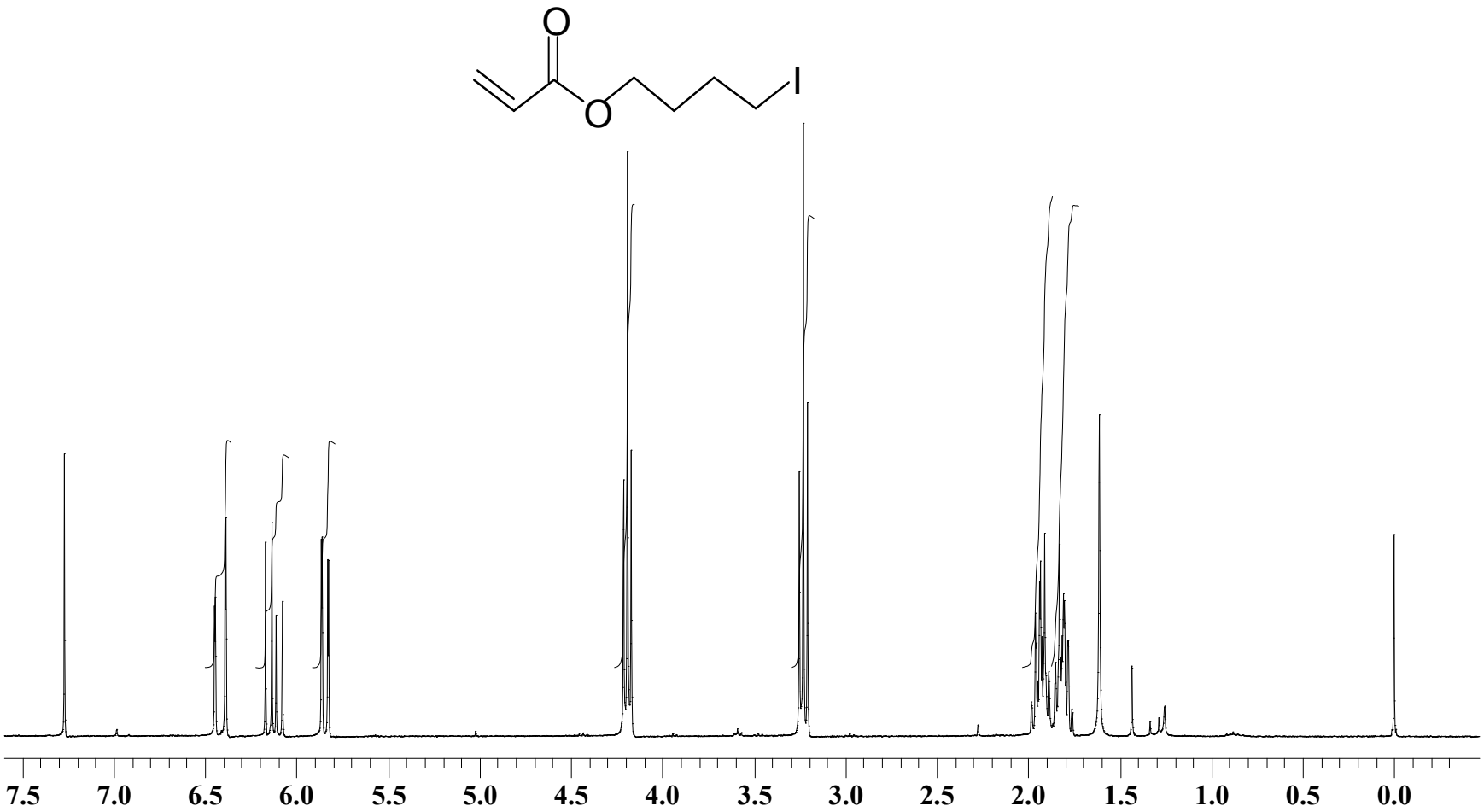


Fig: ^{1}H NMR of compound **14**

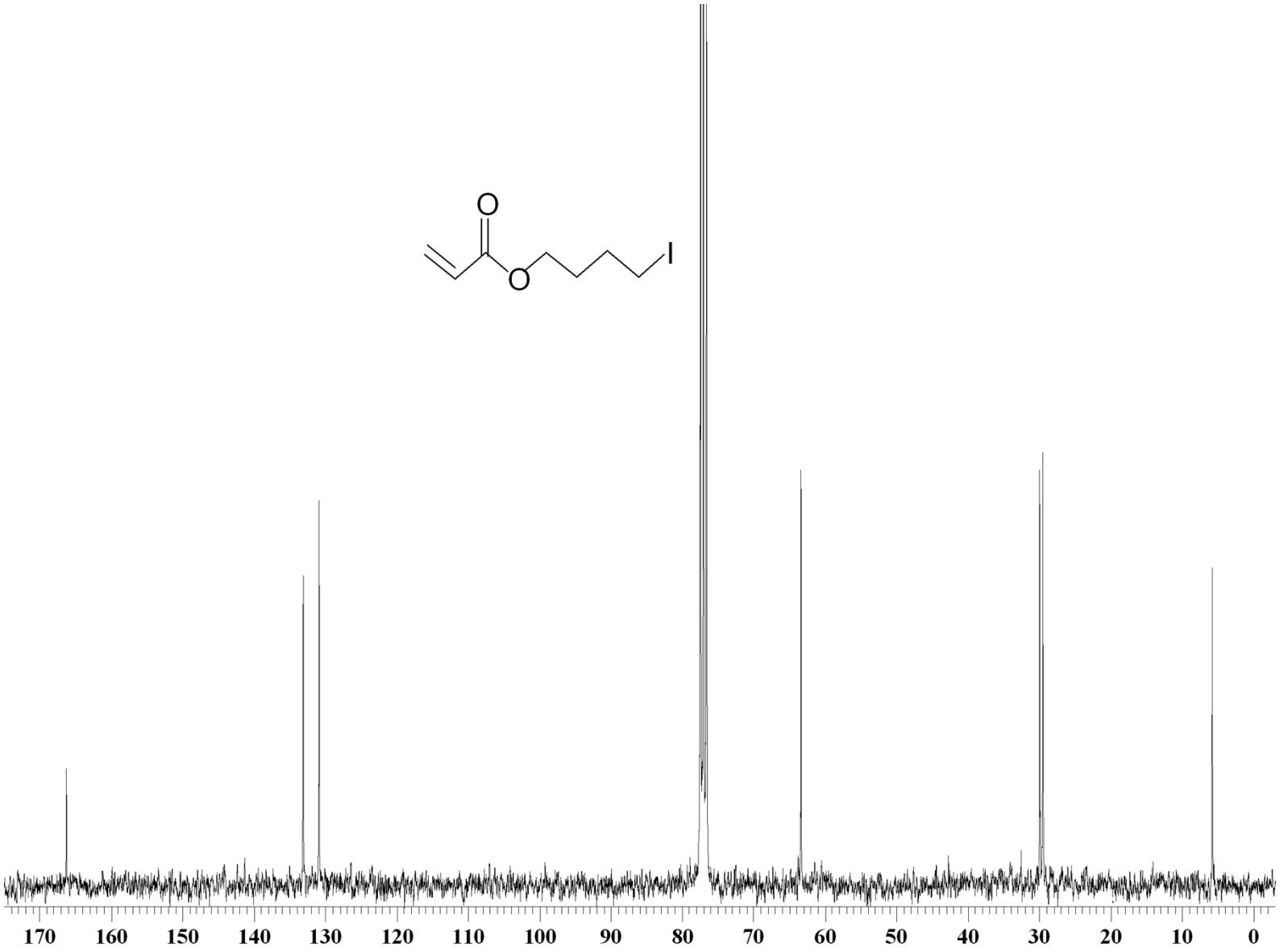


Fig: ^{13}C NMR of compound **14**

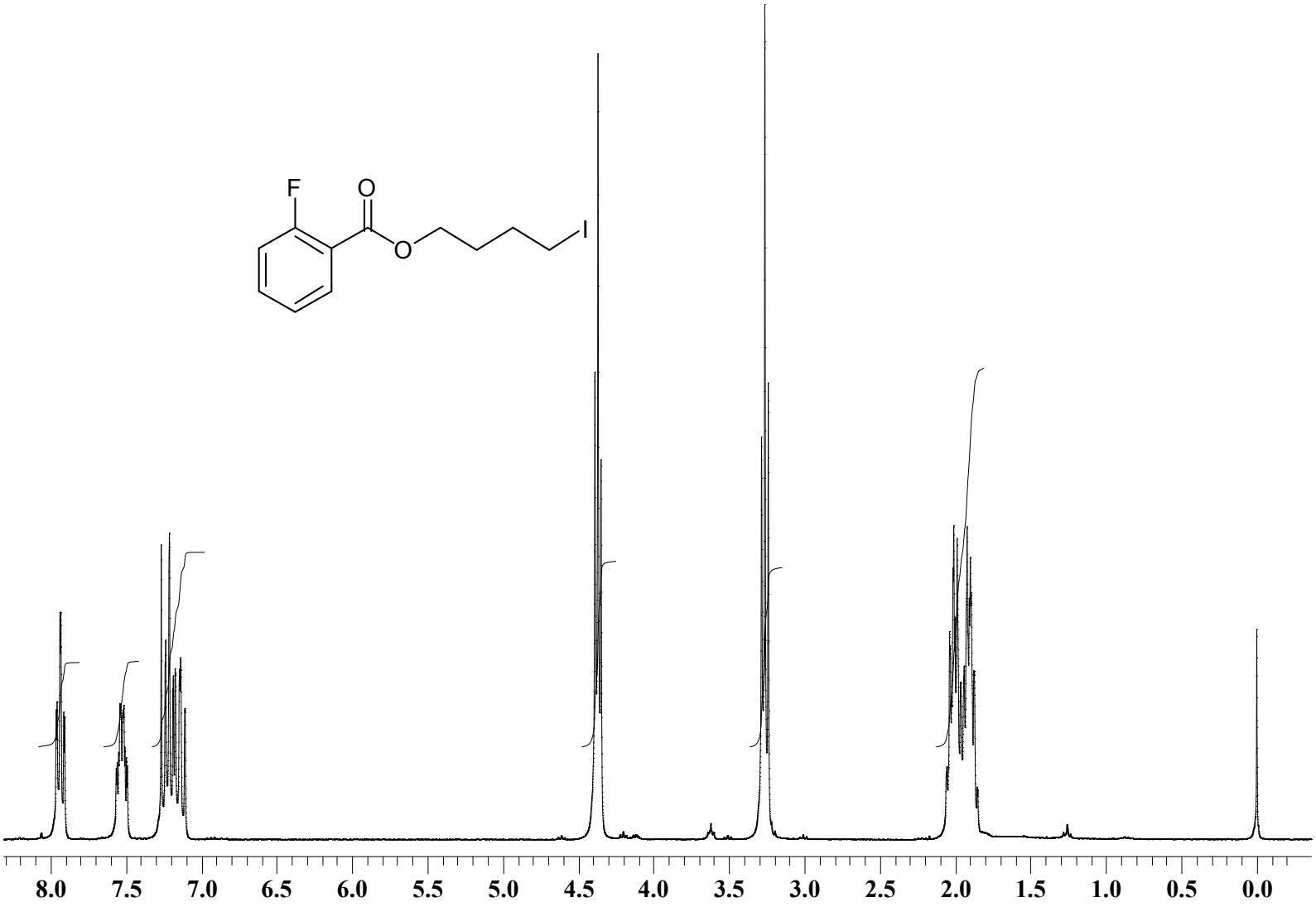


Fig: ^{1}H NMR of compound **15**

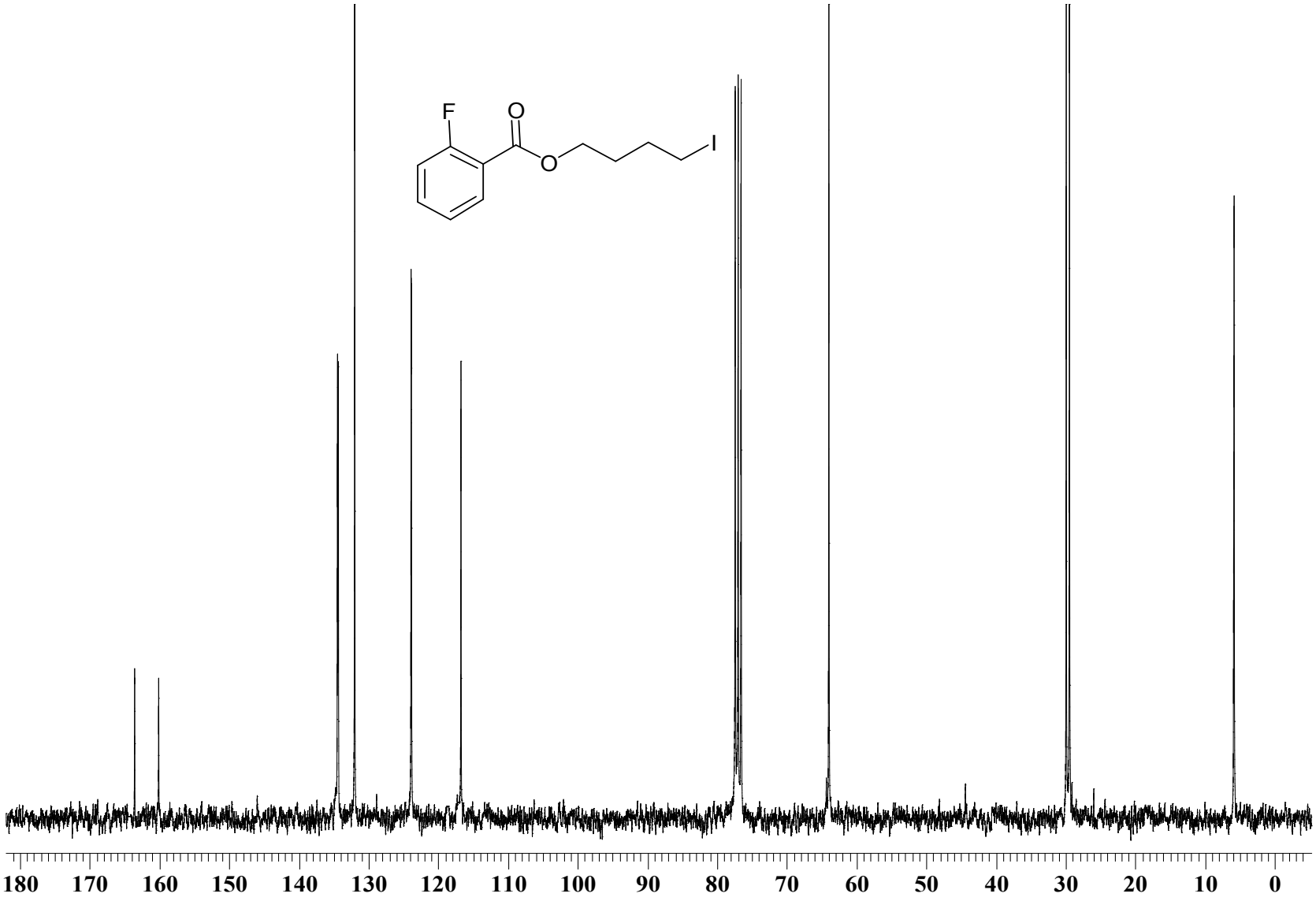


Fig: ^{13}C NMR of compound **15**

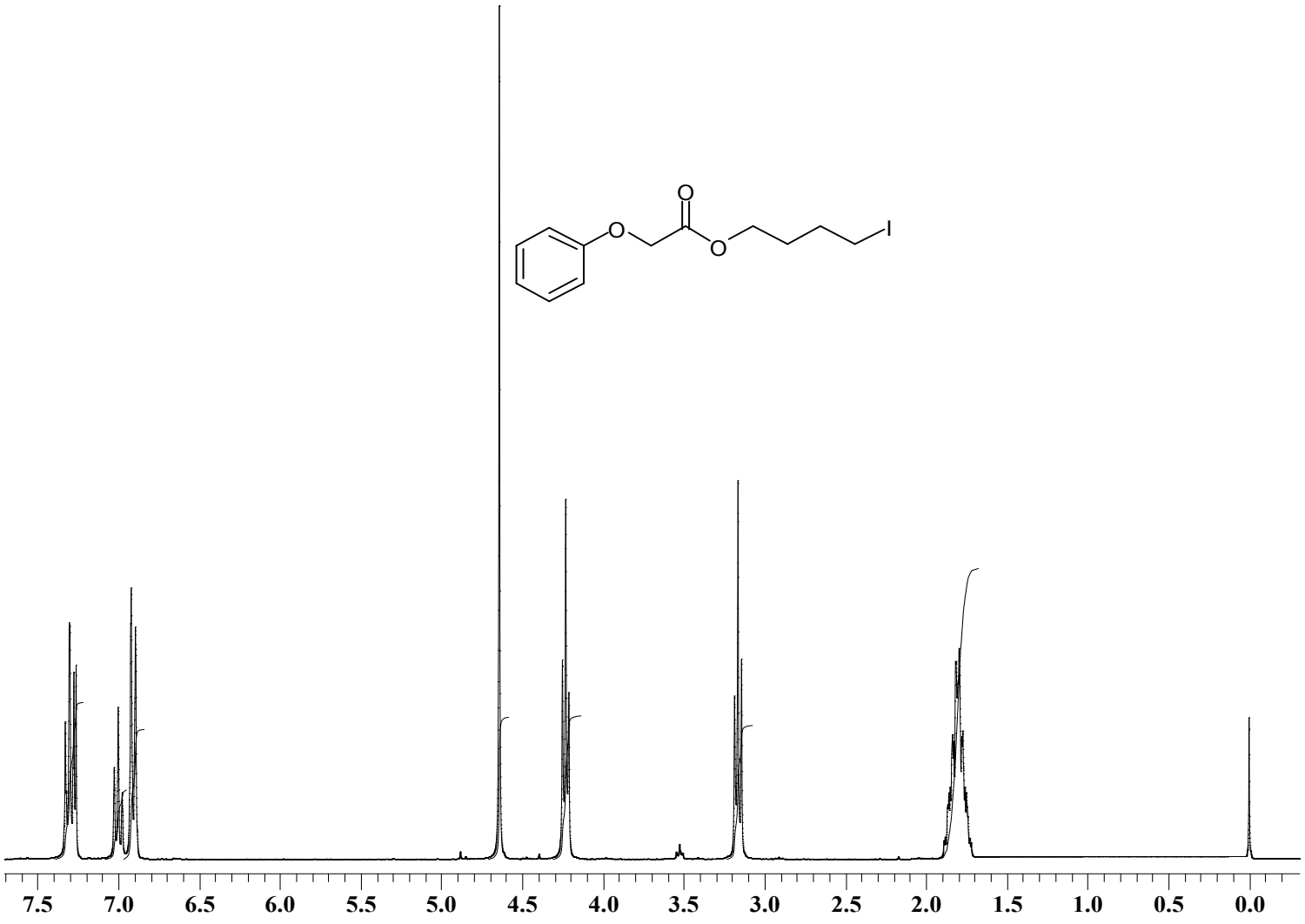


Fig: ^{1}H NMR of compound **16**

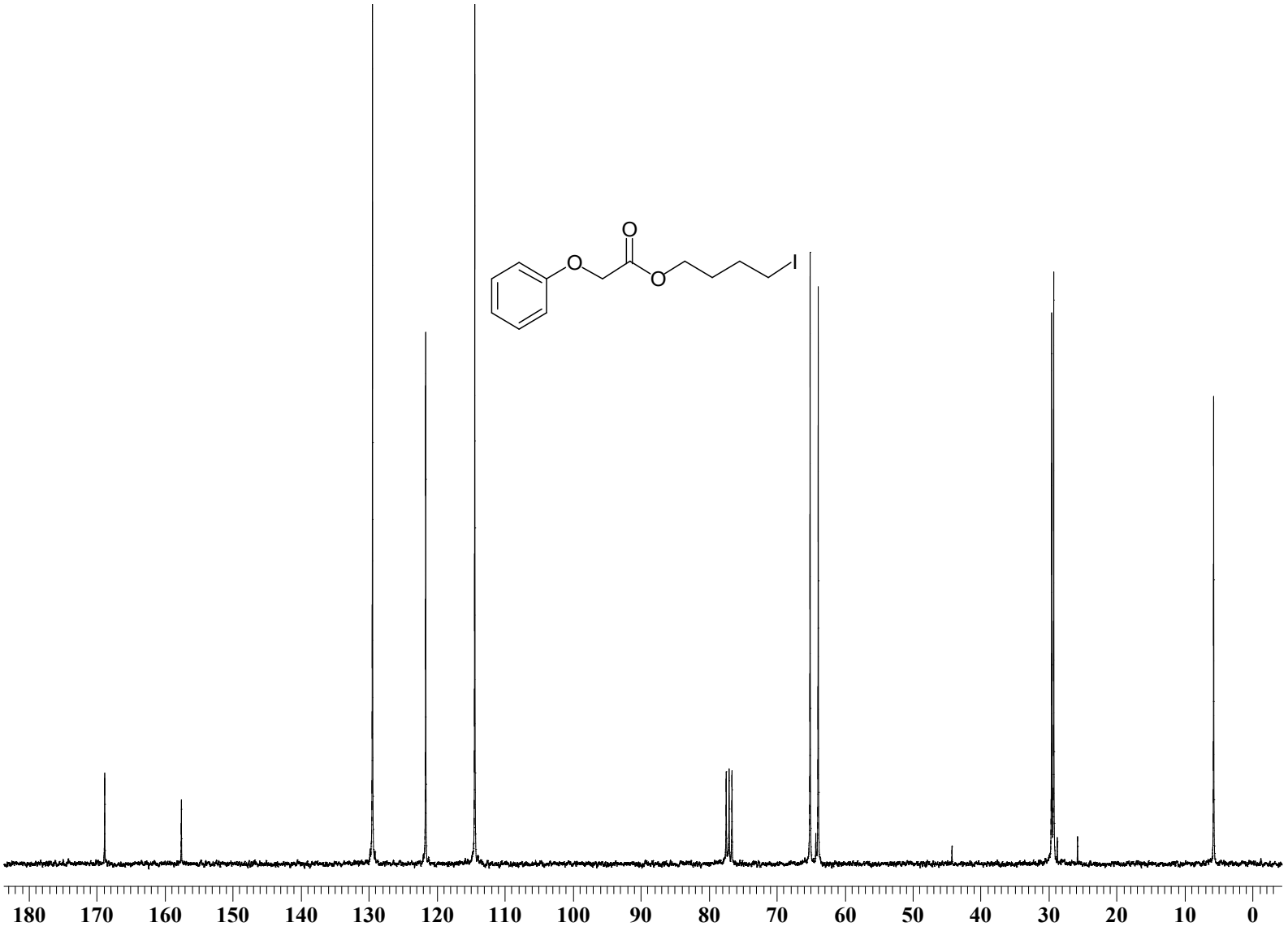


Fig: ^{13}C NMR of compound **16**

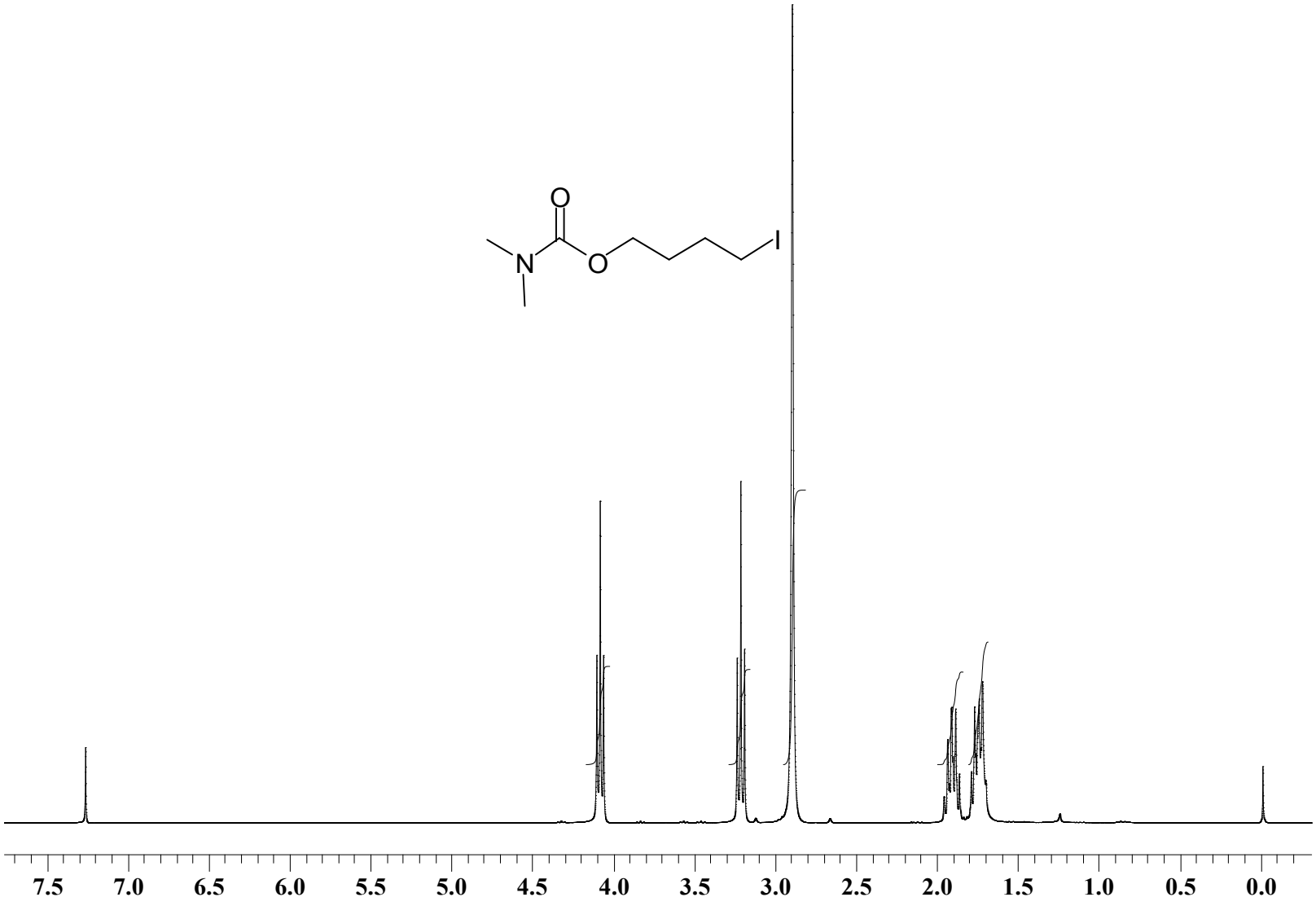


Fig: ^{1}H NMR of compound **17**

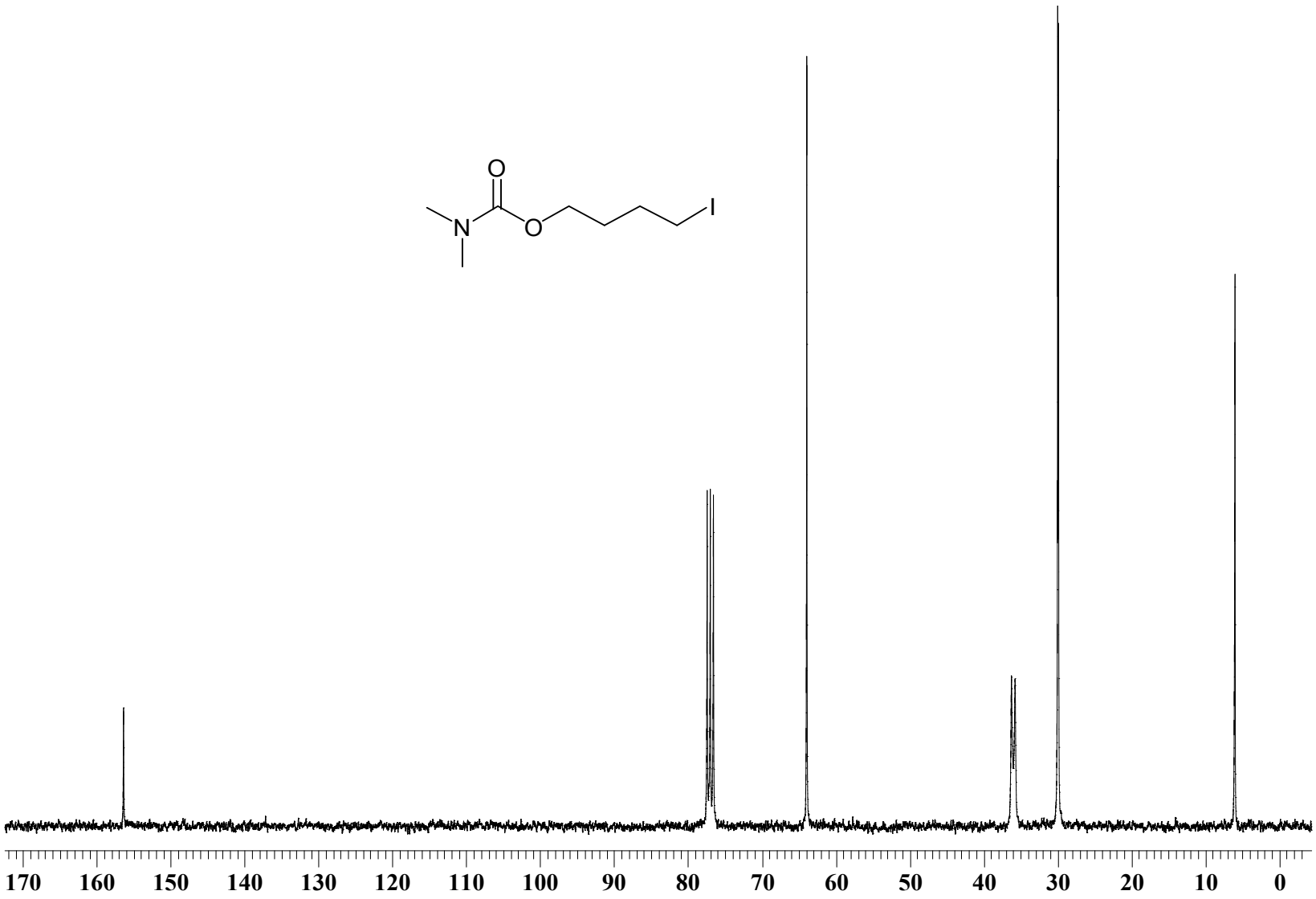


Fig: ^{13}C NMR of compound **17**

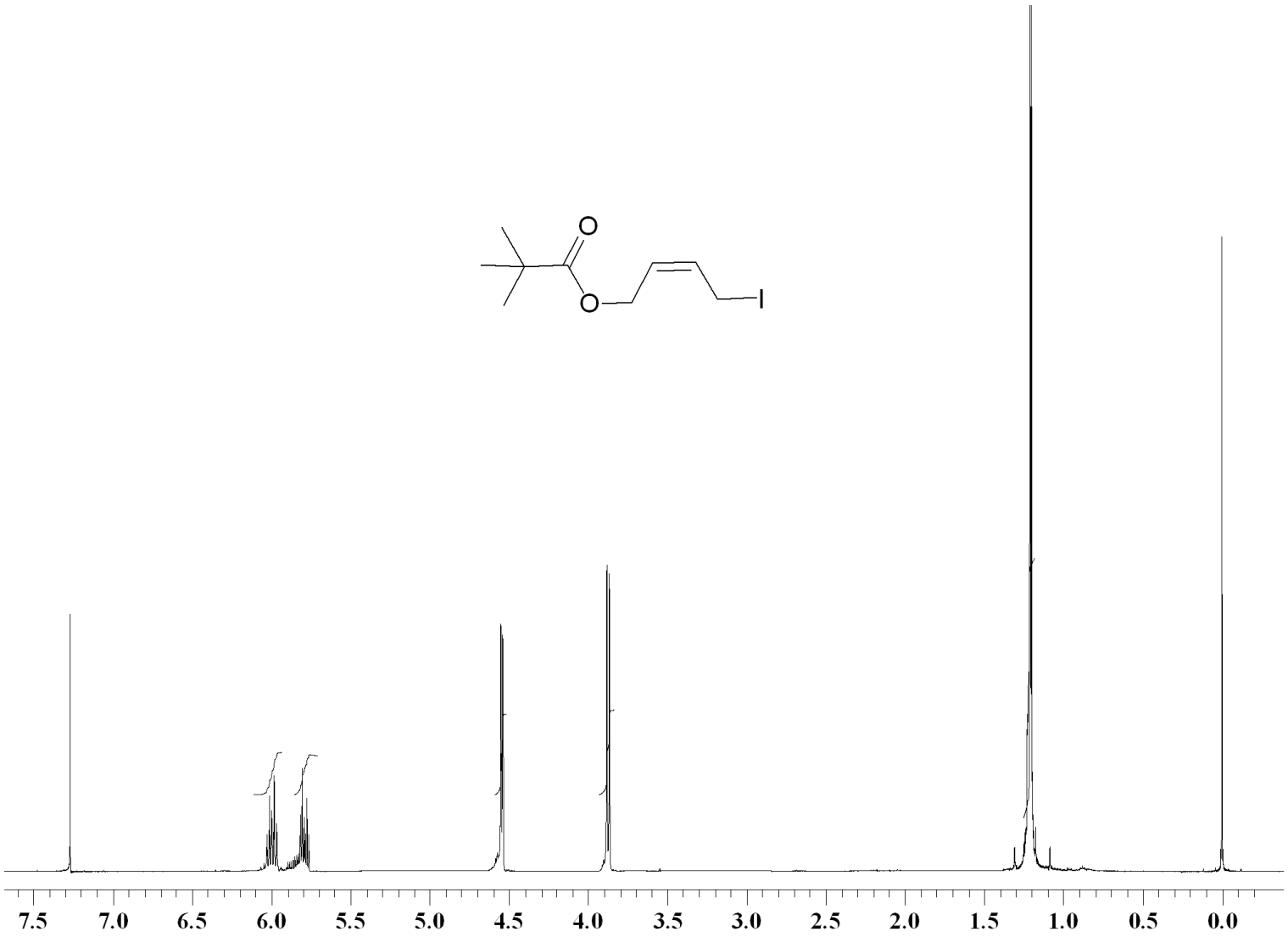


Fig: ^{1}H NMR of compound **22**

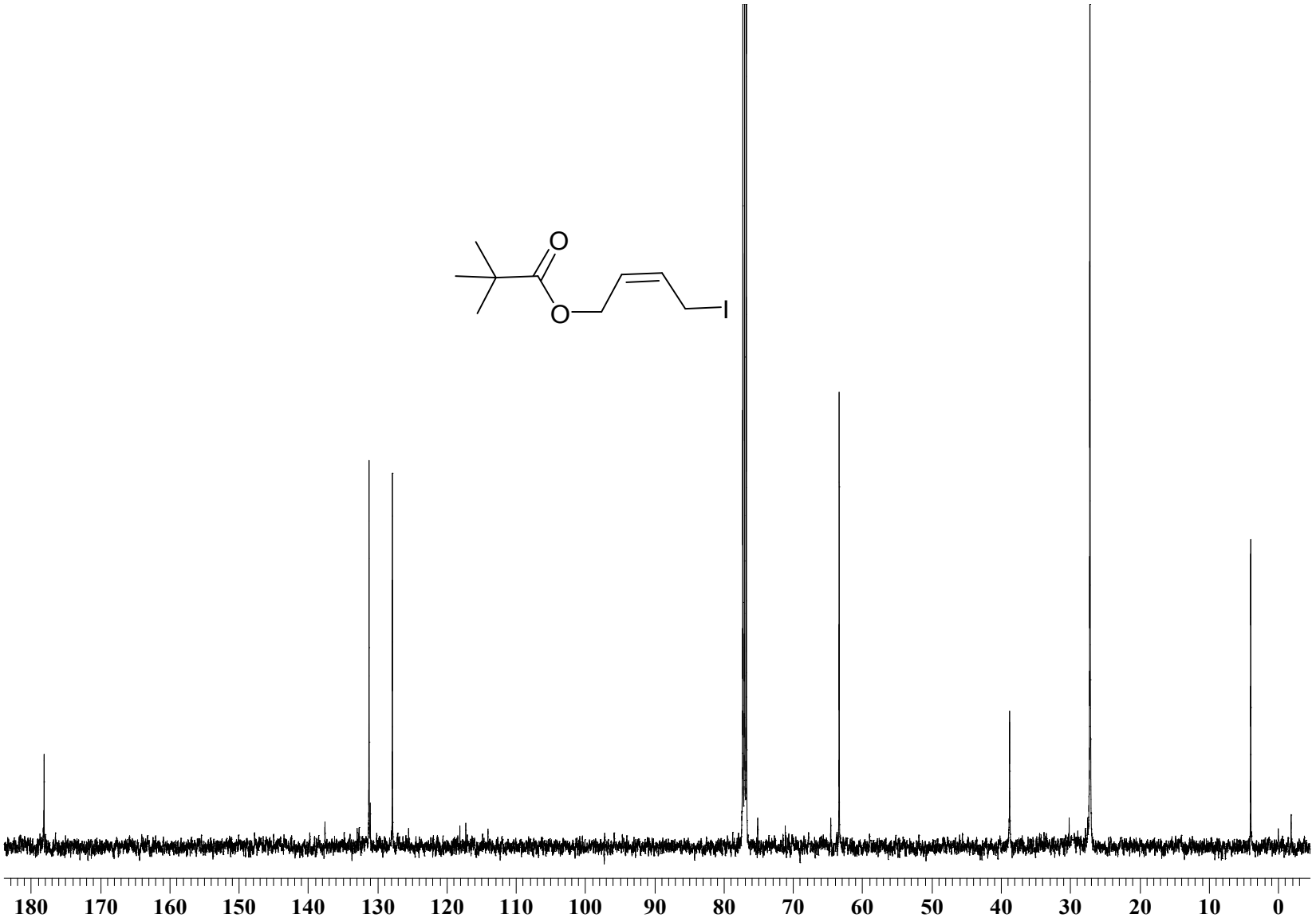


Fig: ^{13}C NMR of compound **22**

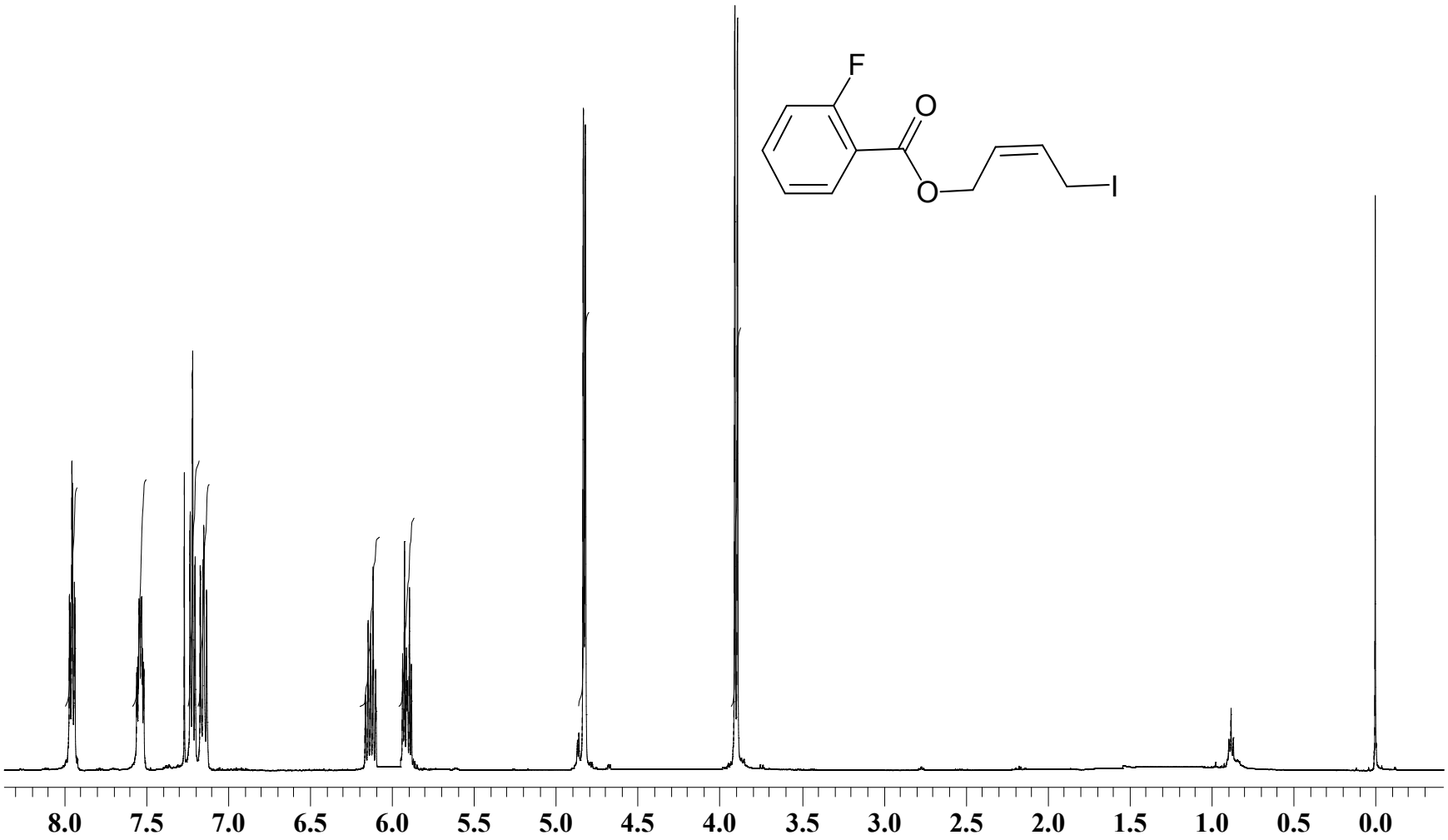


Fig: ^{1}H NMR of compound **23**

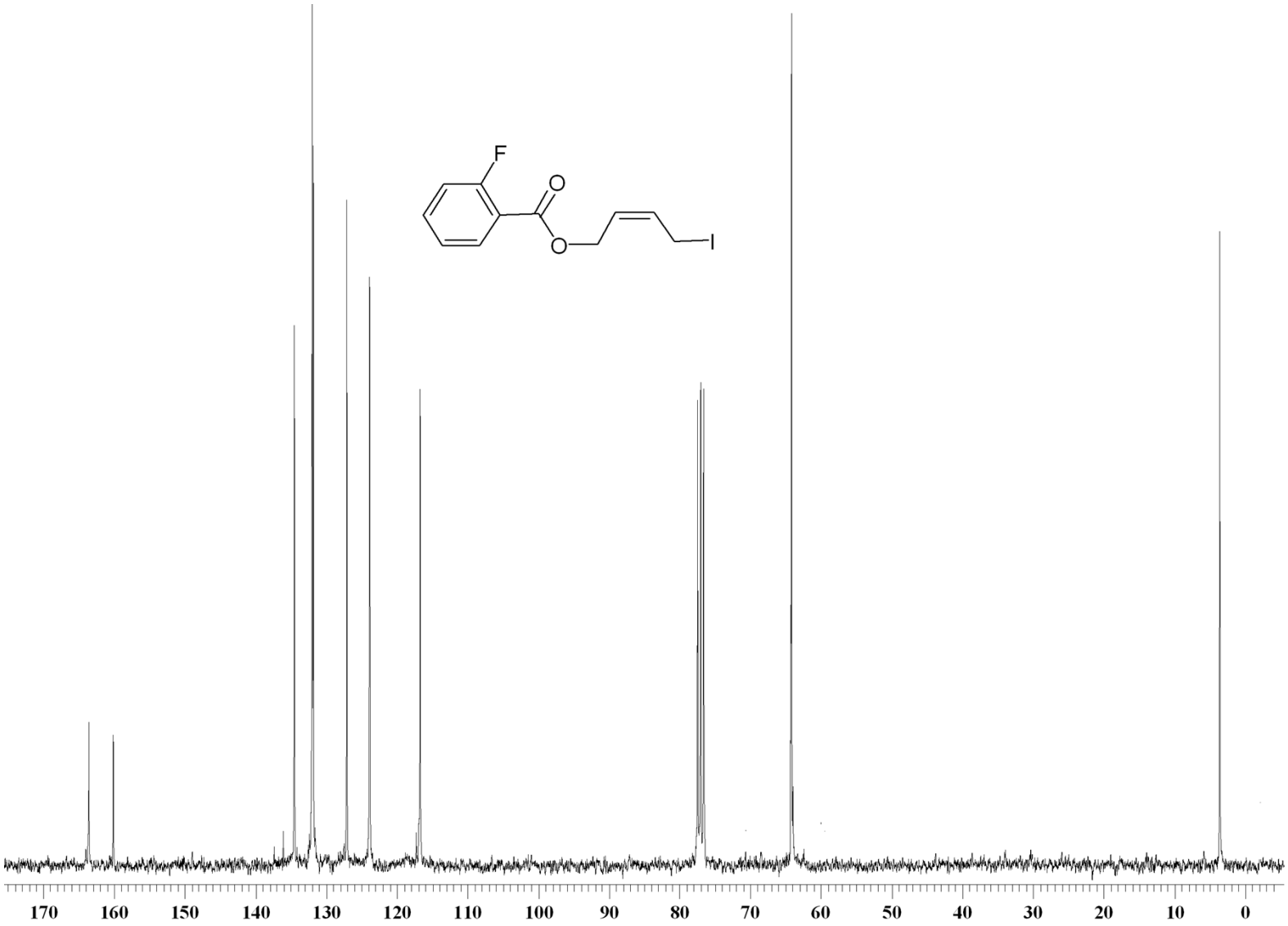


Fig: ^{13}C NMR of compound **23**

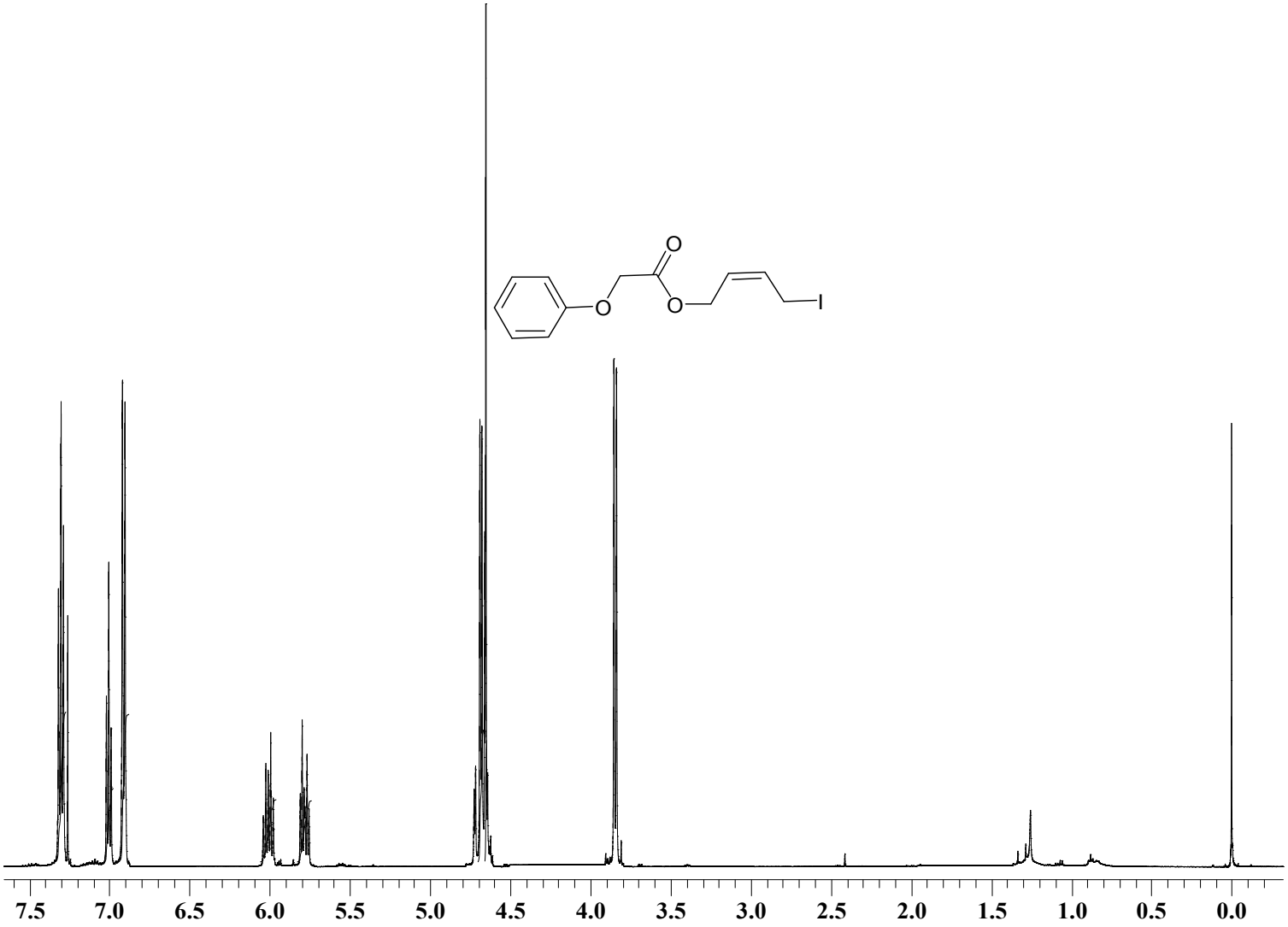


Fig: ^{1}H NMR of compound **24**

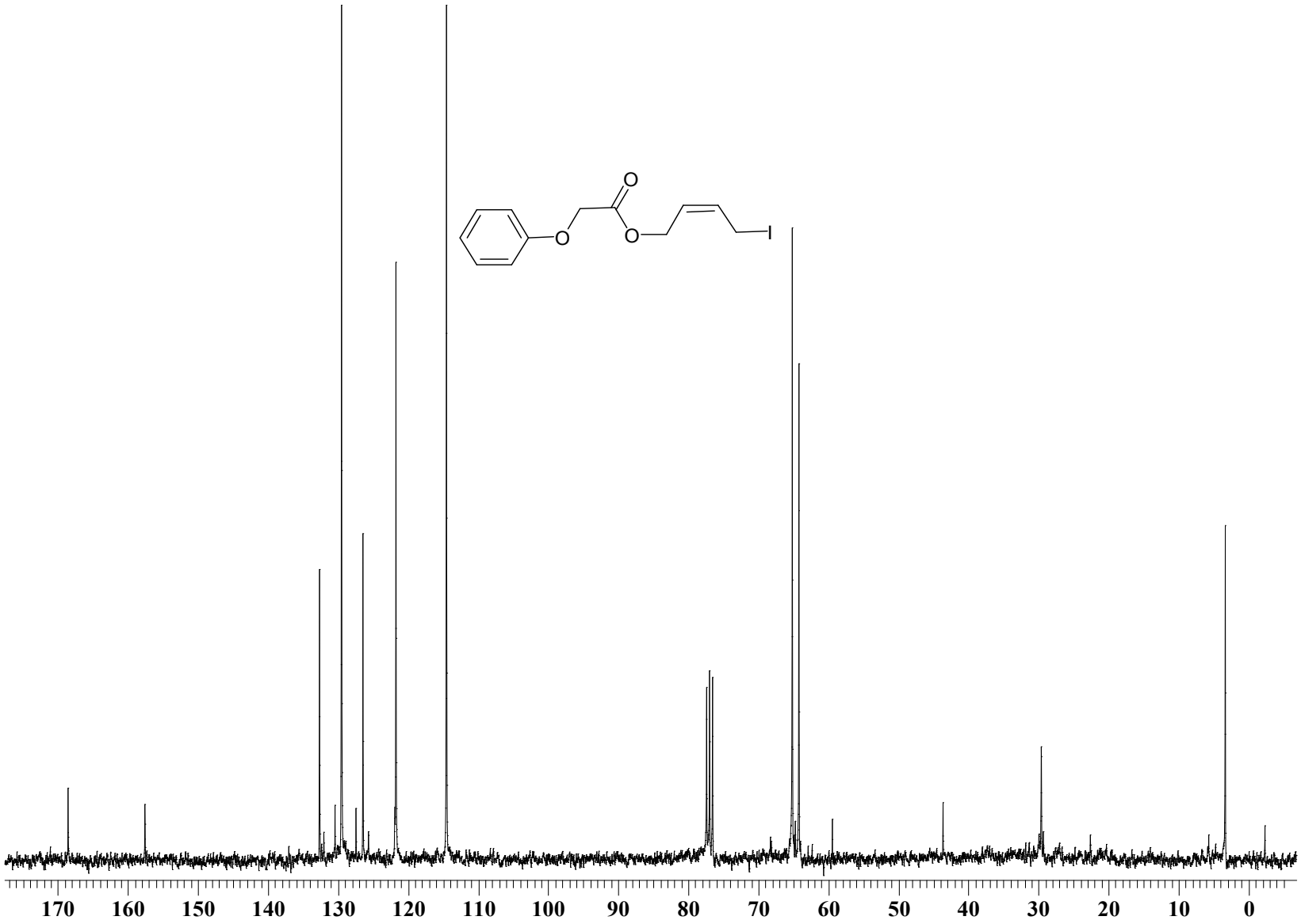


Fig: ^{13}C NMR of compound **24**

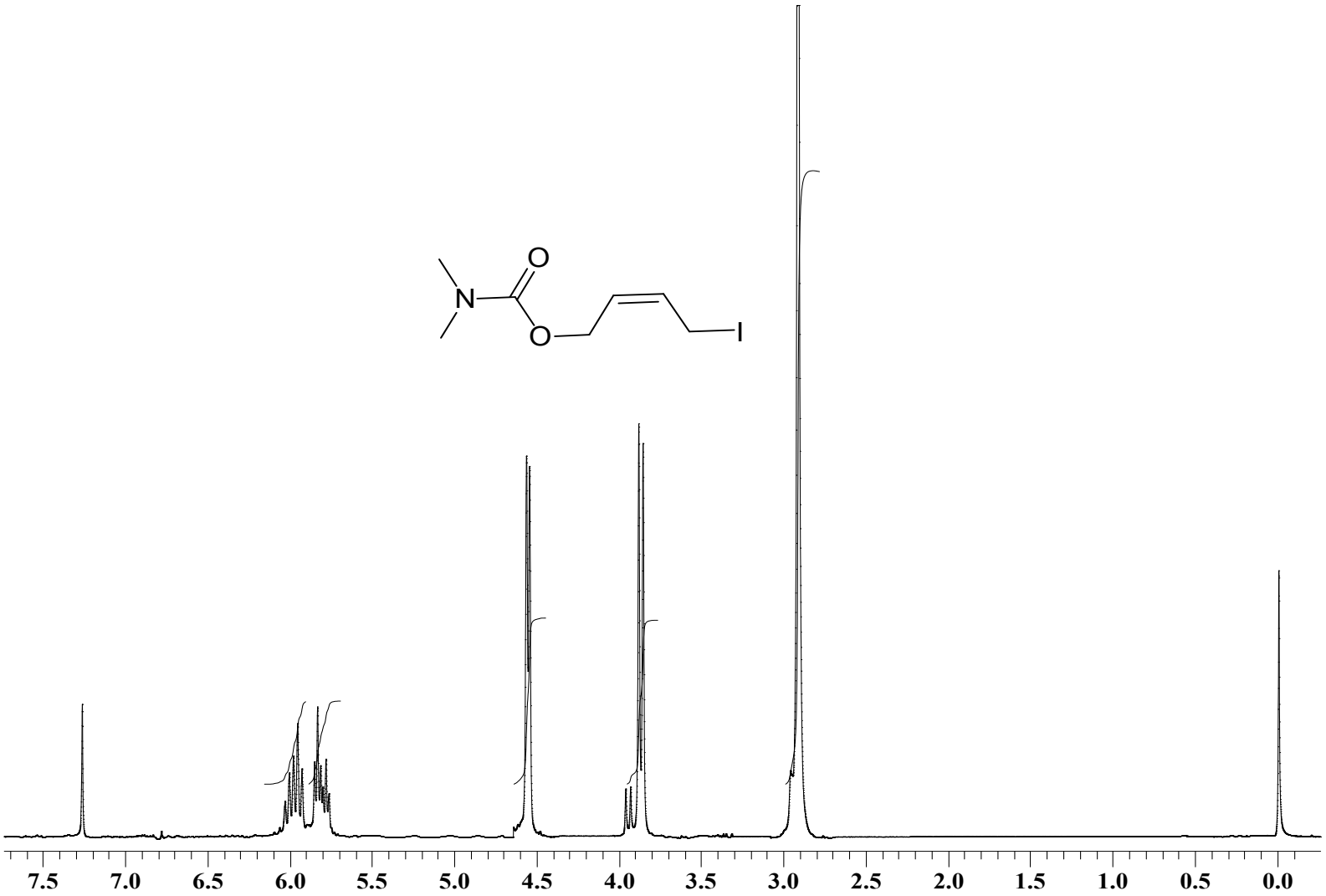


Fig: ^{1}H NMR of compound **25**

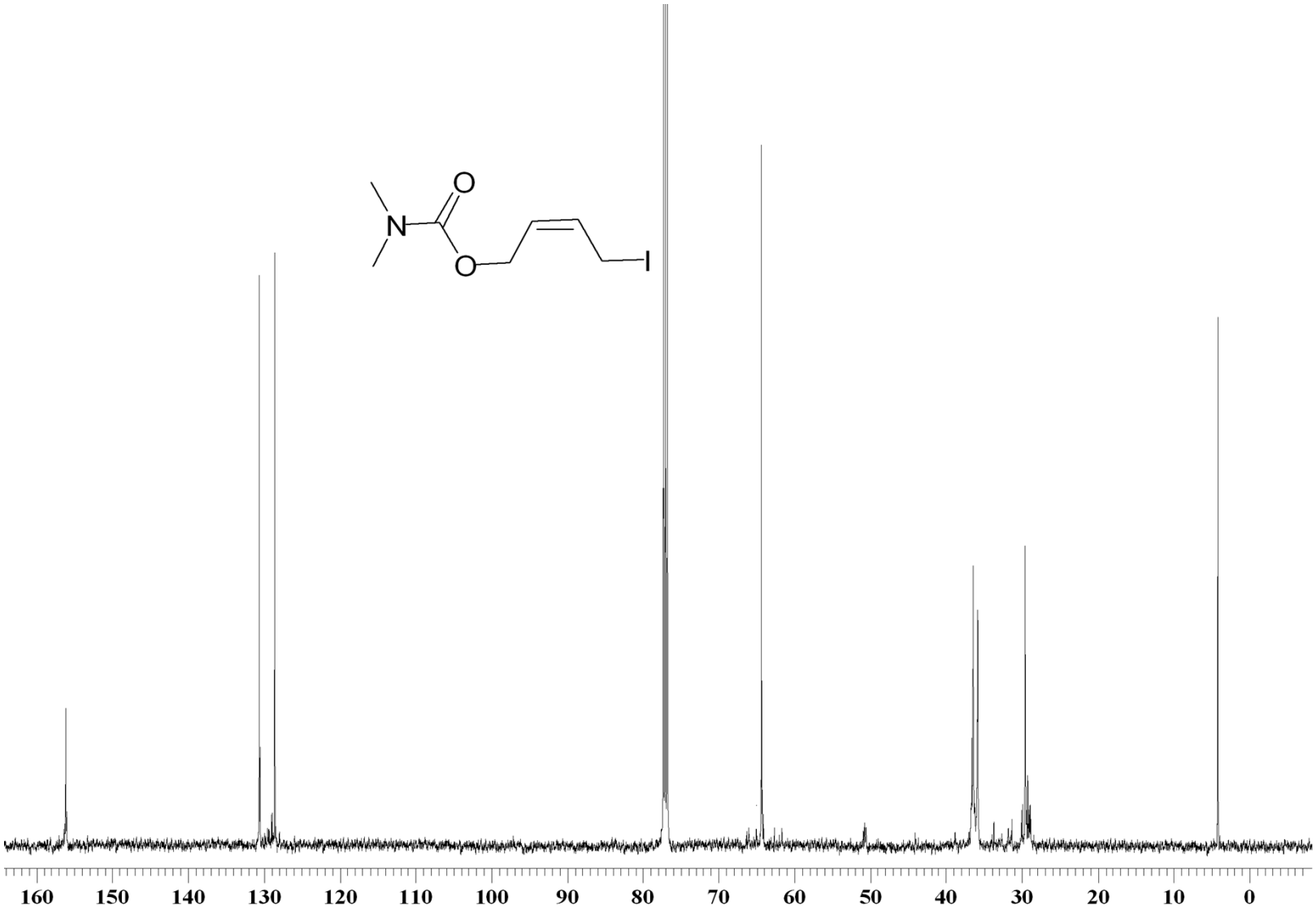


Fig: ^{13}C NMR of compound **25**

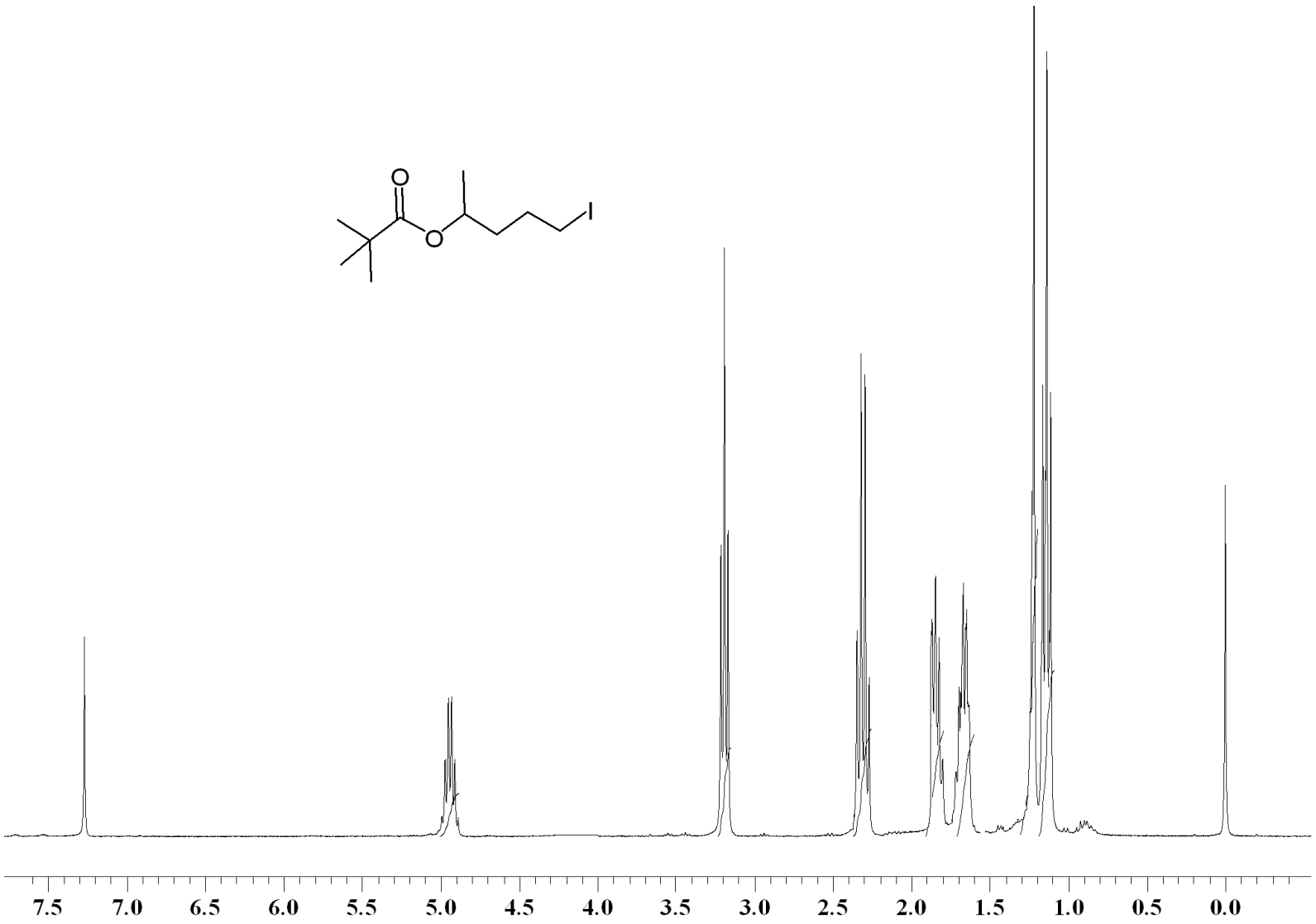


Fig: ^{1}H NMR of compound **26**

Fig: ^{13}C NMR of compound **26**

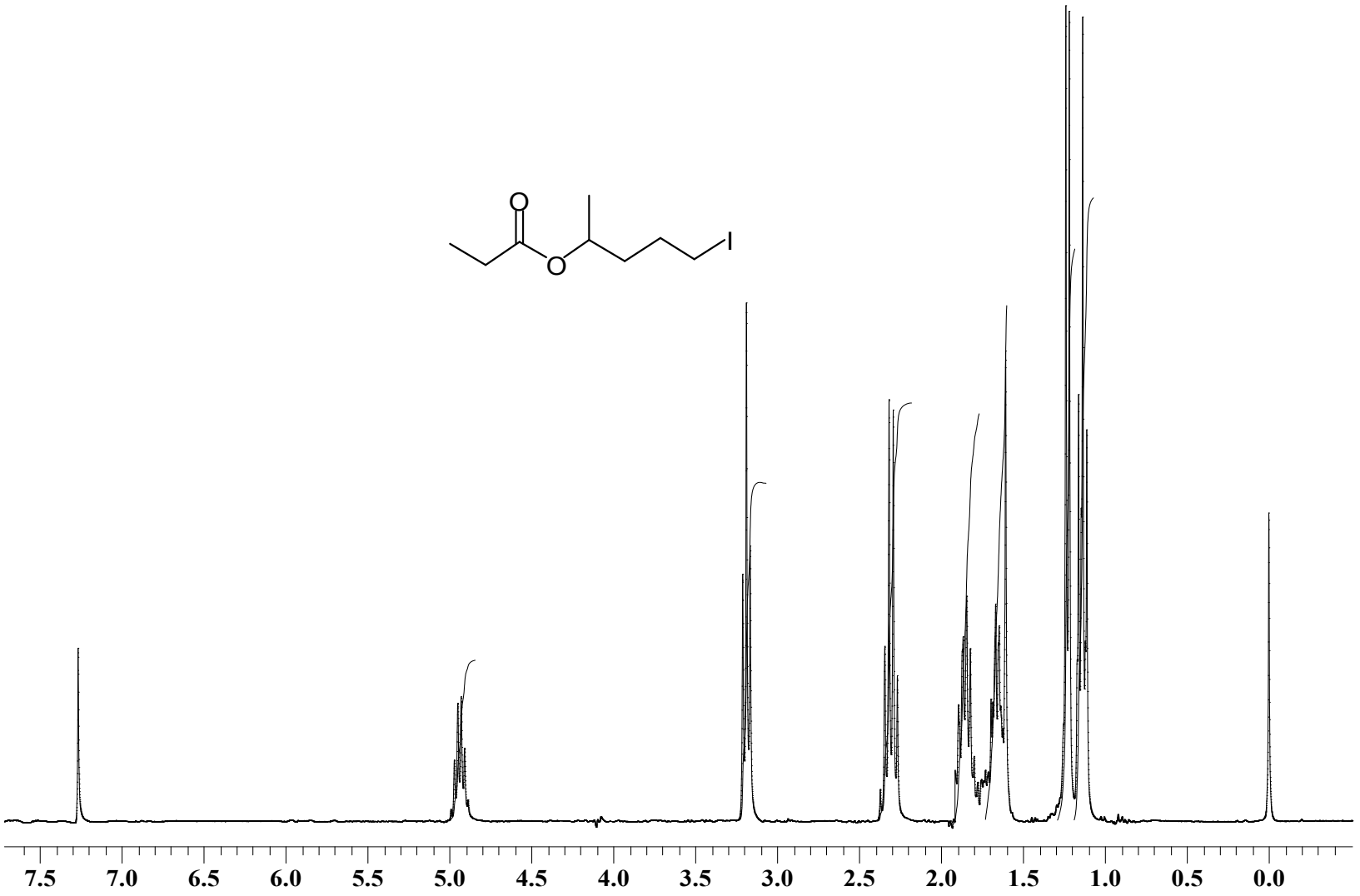


Fig: ^{1}H NMR of compound **27**

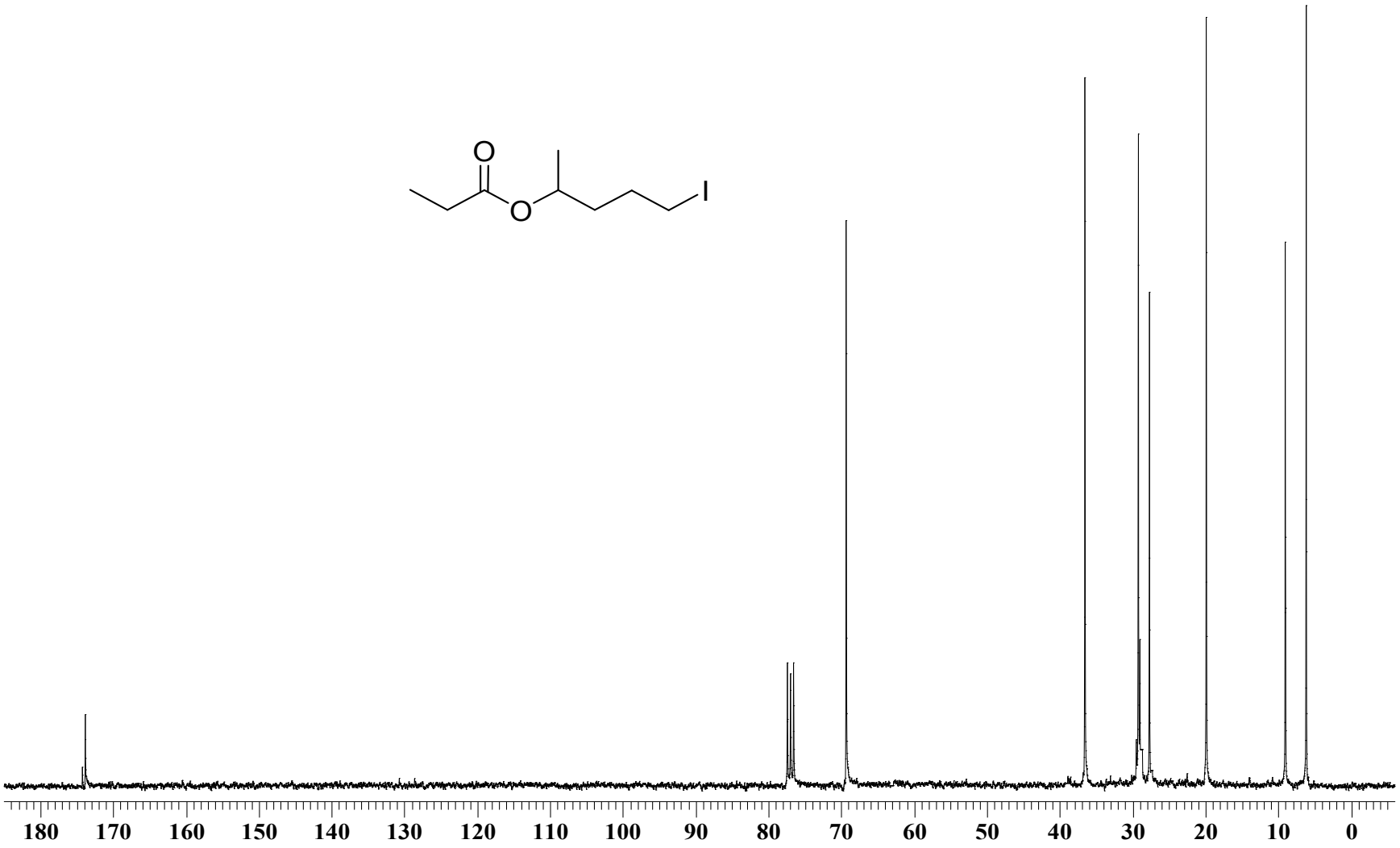


Fig: ^{13}C NMR of compound **27**

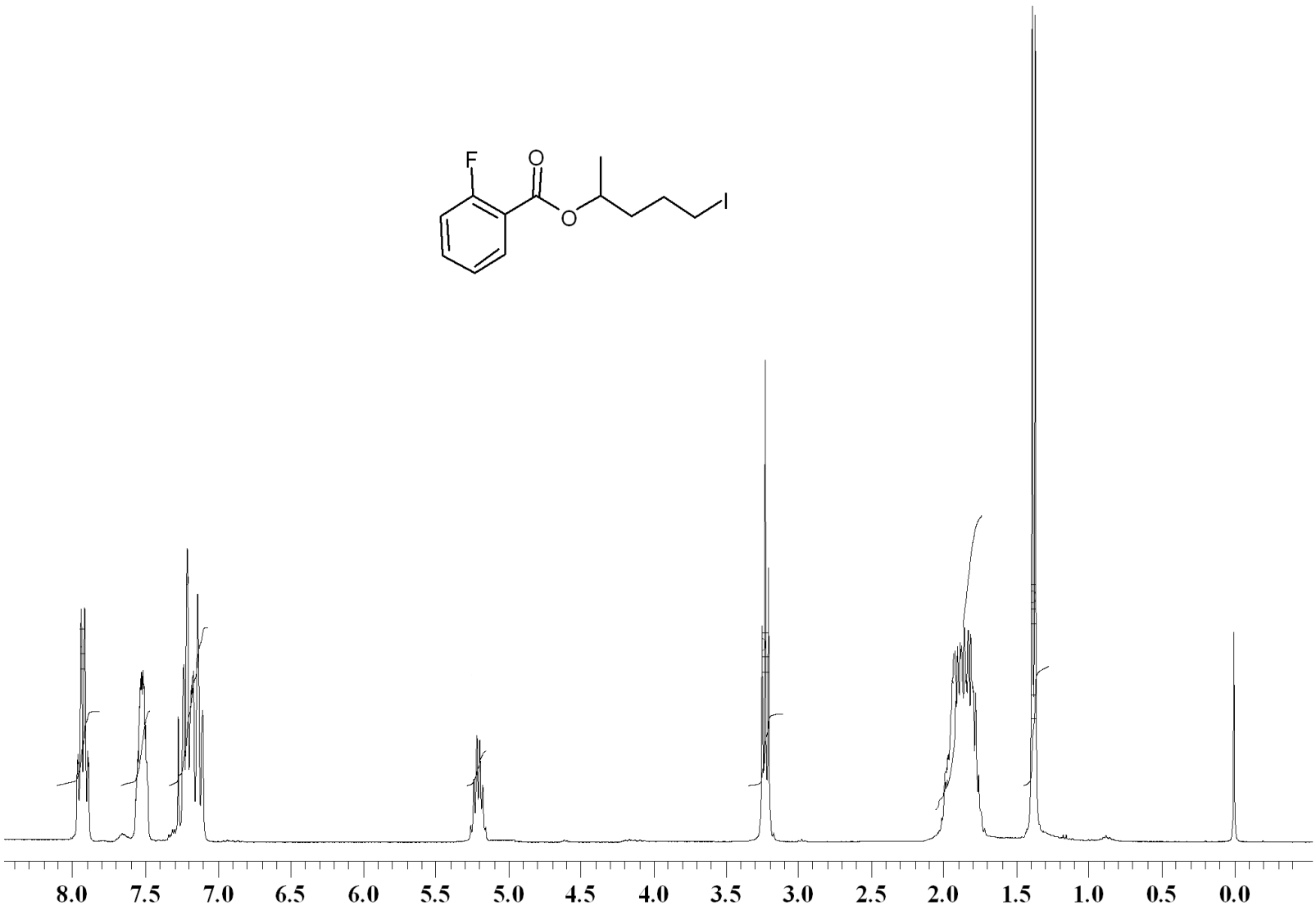


Fig: ^{1}H NMR of compound **28**

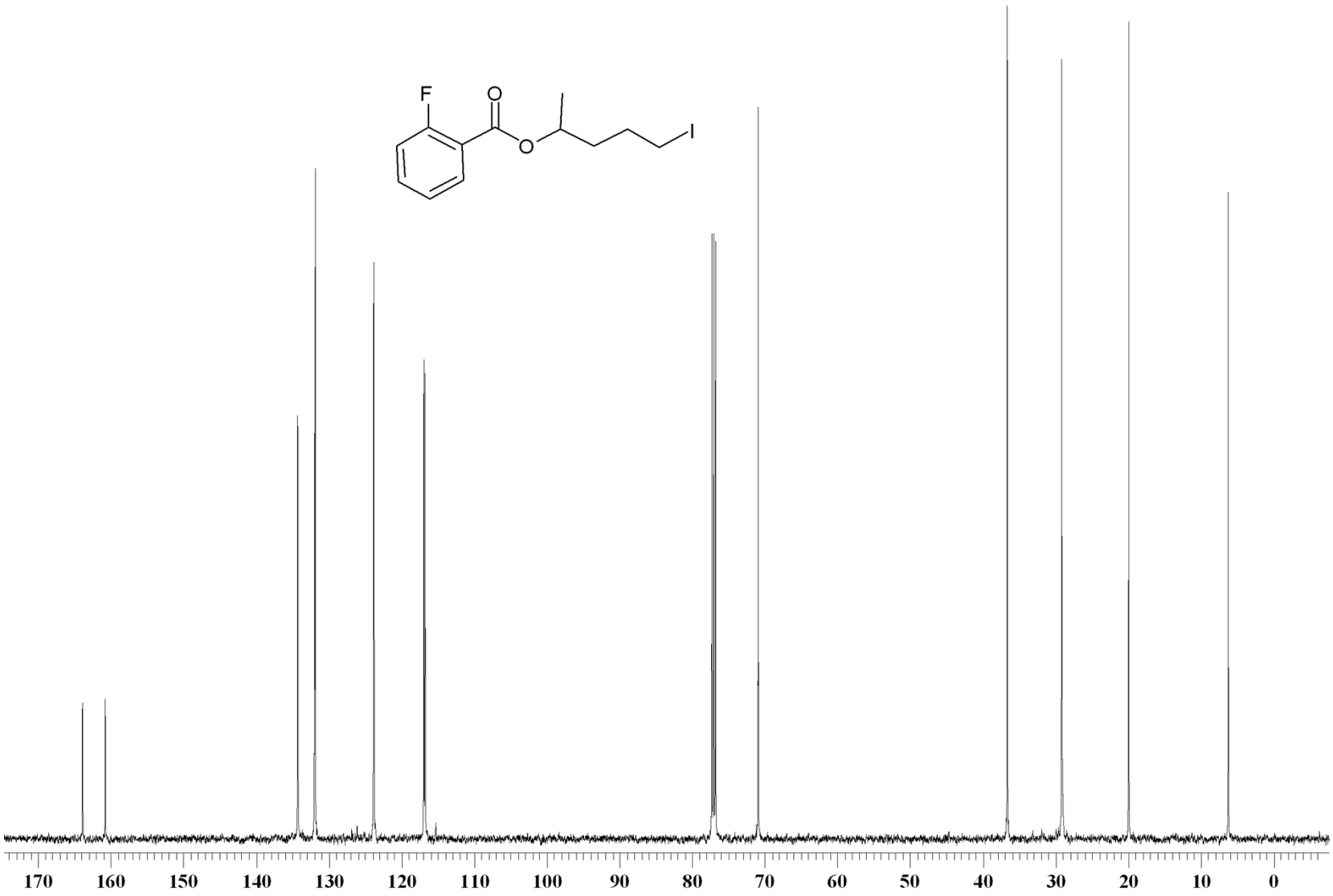


Fig: ^{13}C NMR of compound **28**

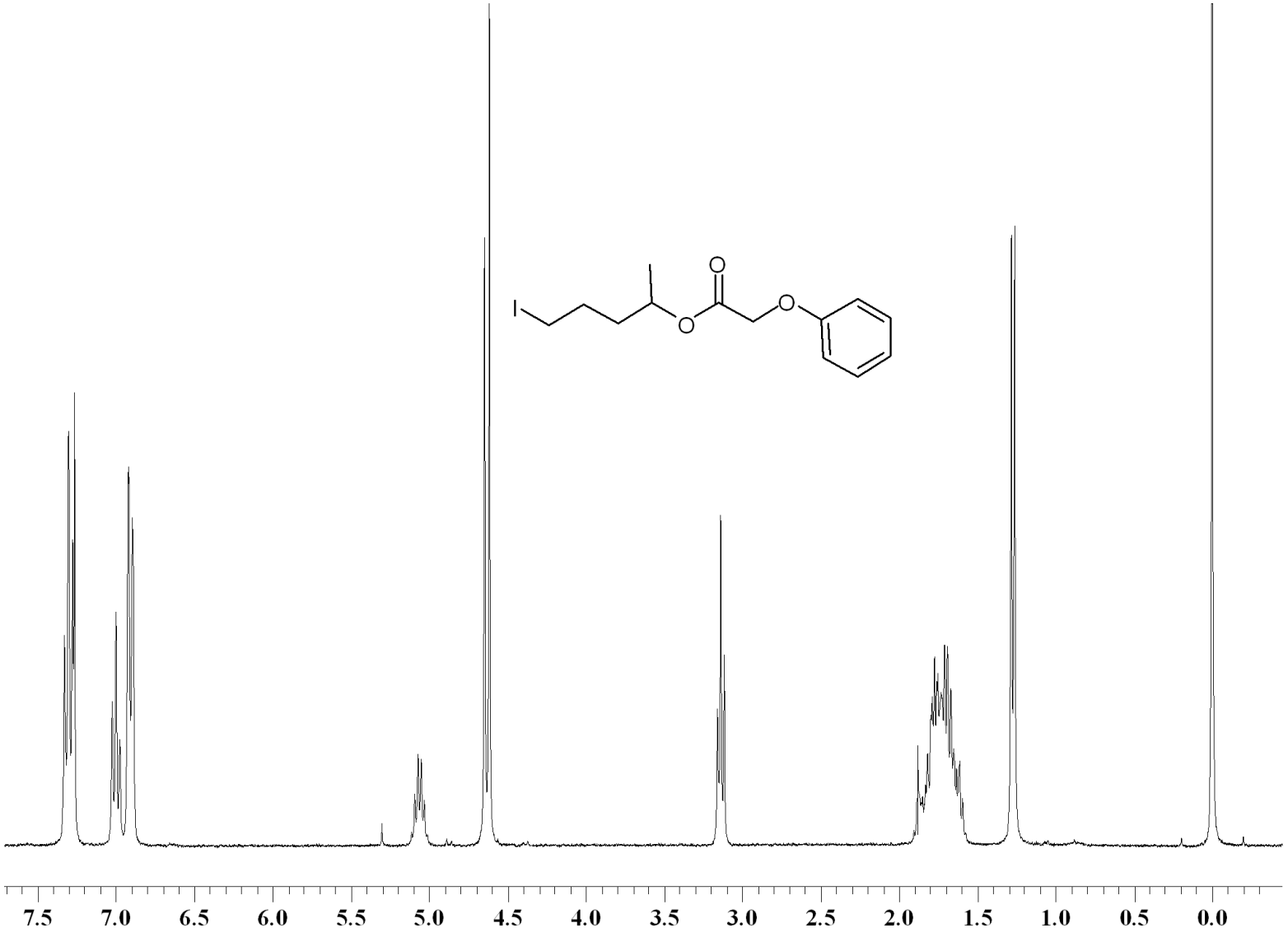


Fig: ^{1}H NMR of compound **29**

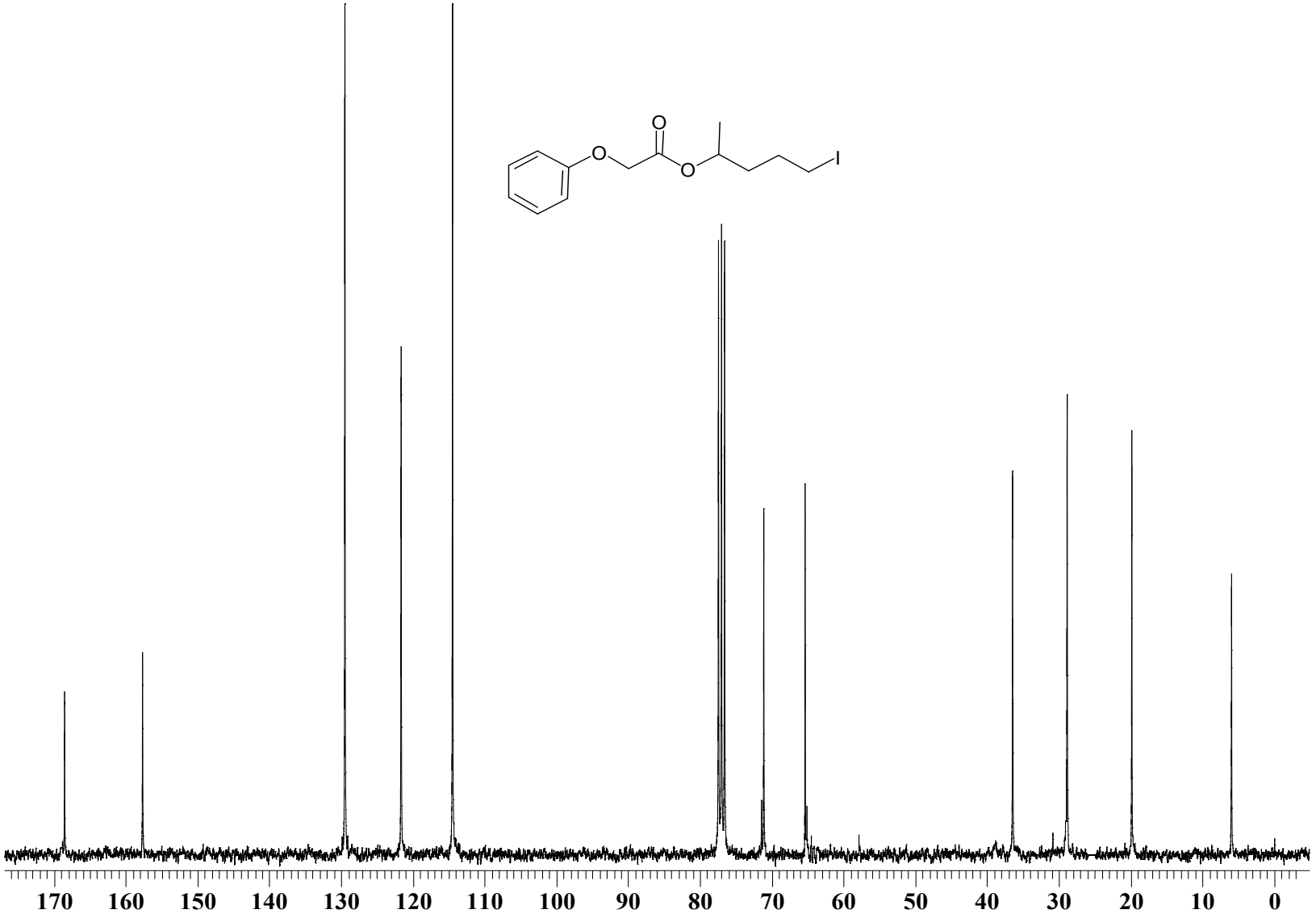


Fig: ^{13}C NMR of compound **29**

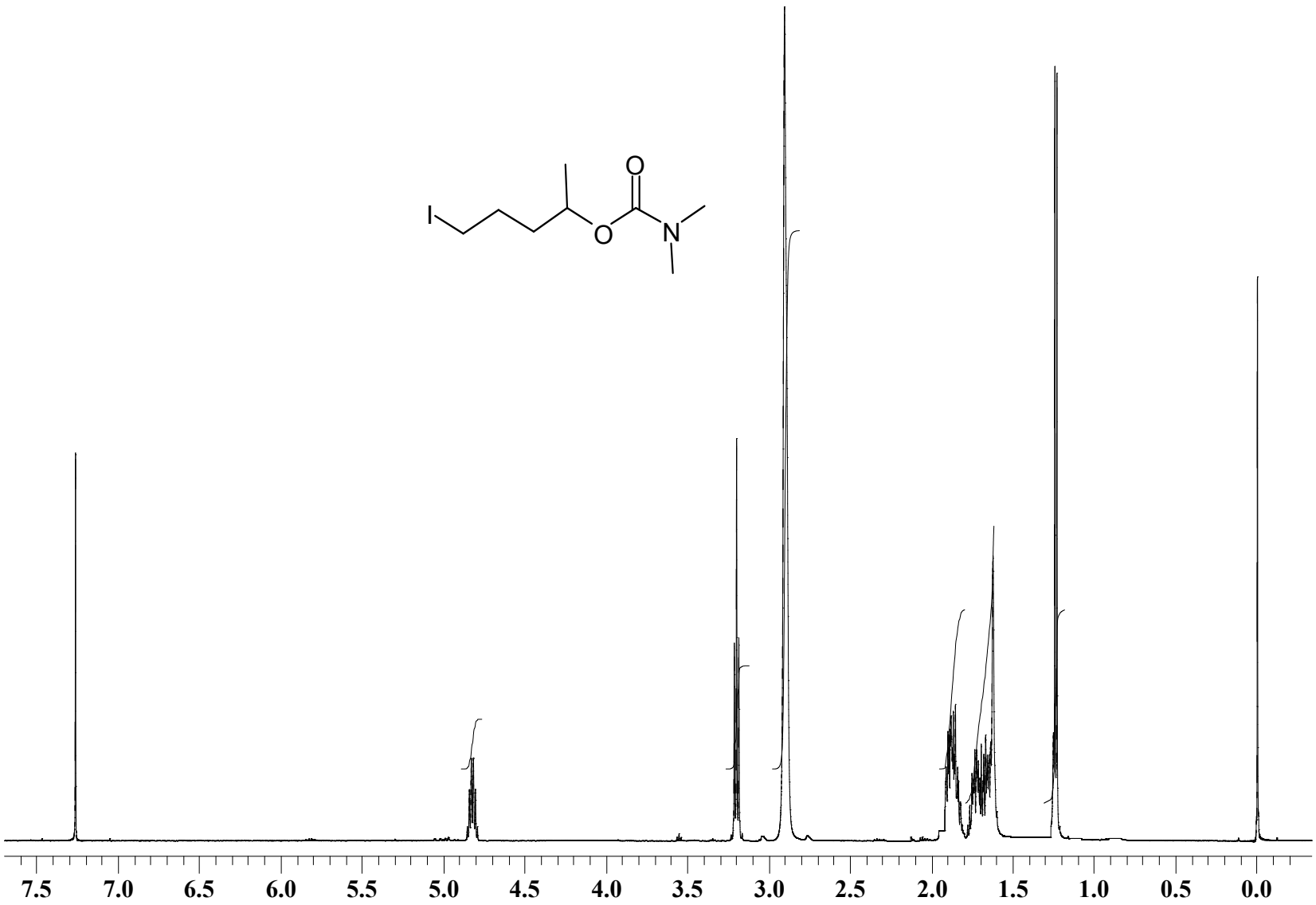


Fig: ^{1}H NMR of compound **30**

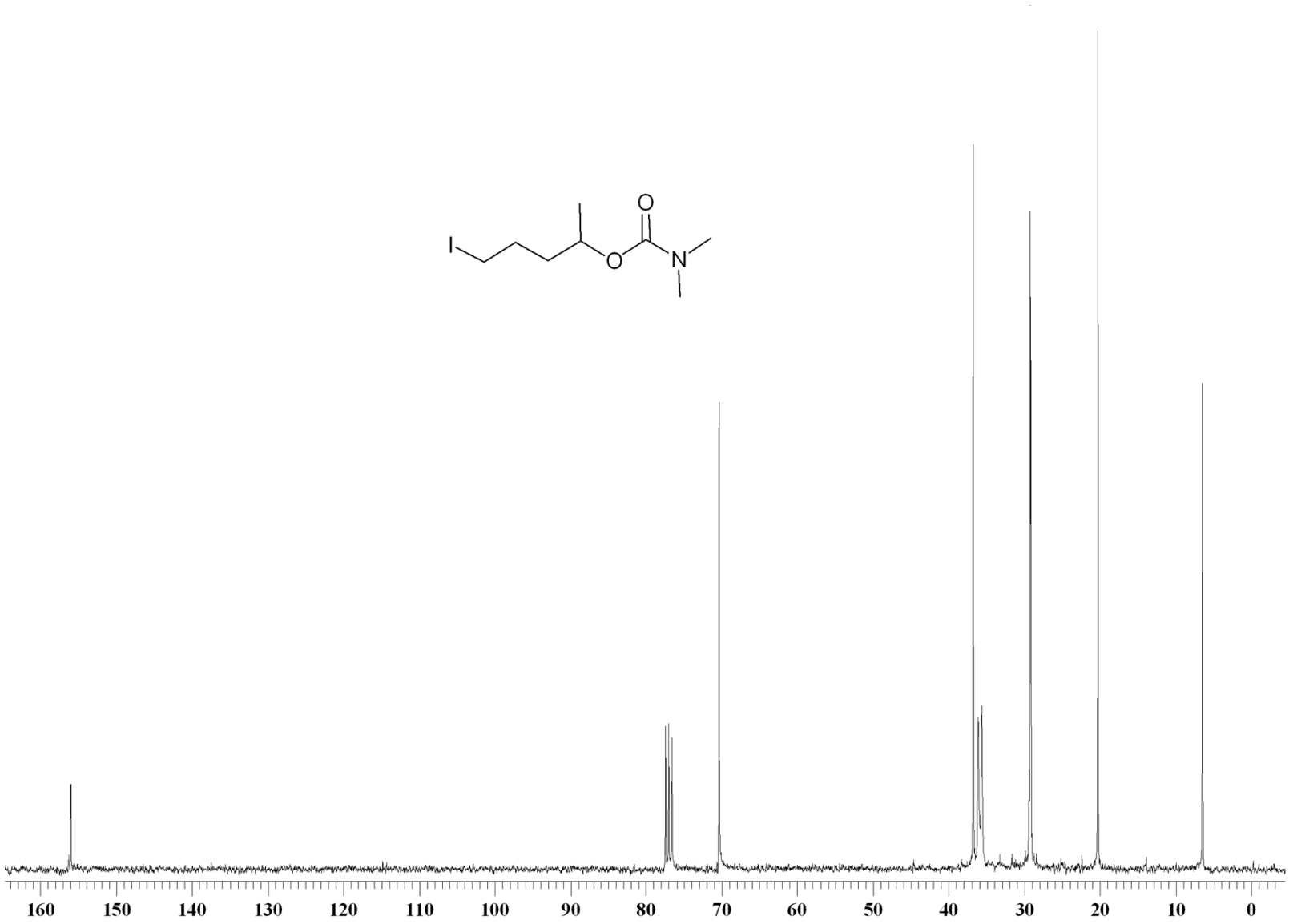


Fig: ^{13}C NMR of compound **30**

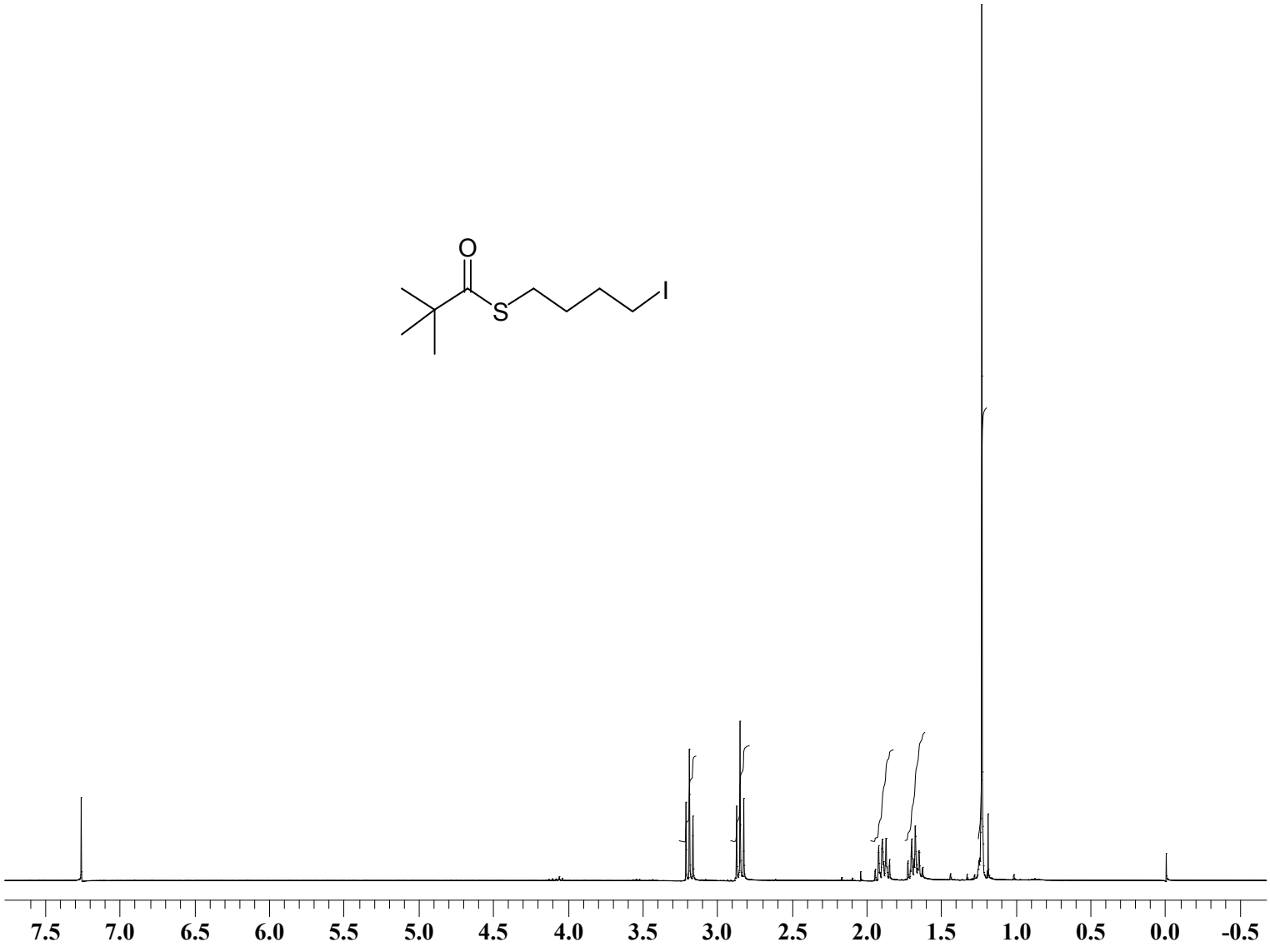


Fig: ^{1}H NMR of compound **31**

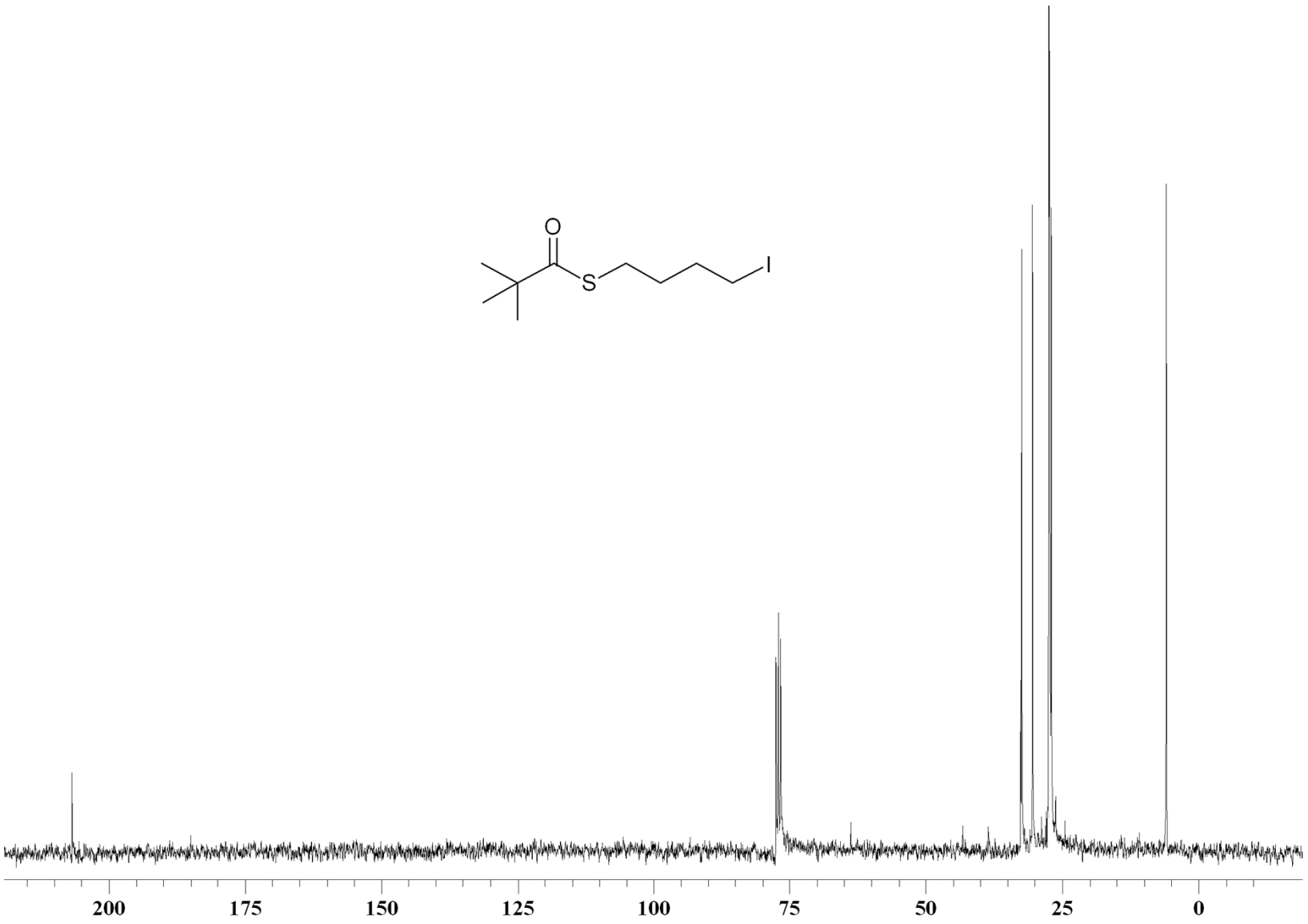


Fig: ^{13}C NMR of compound **31**

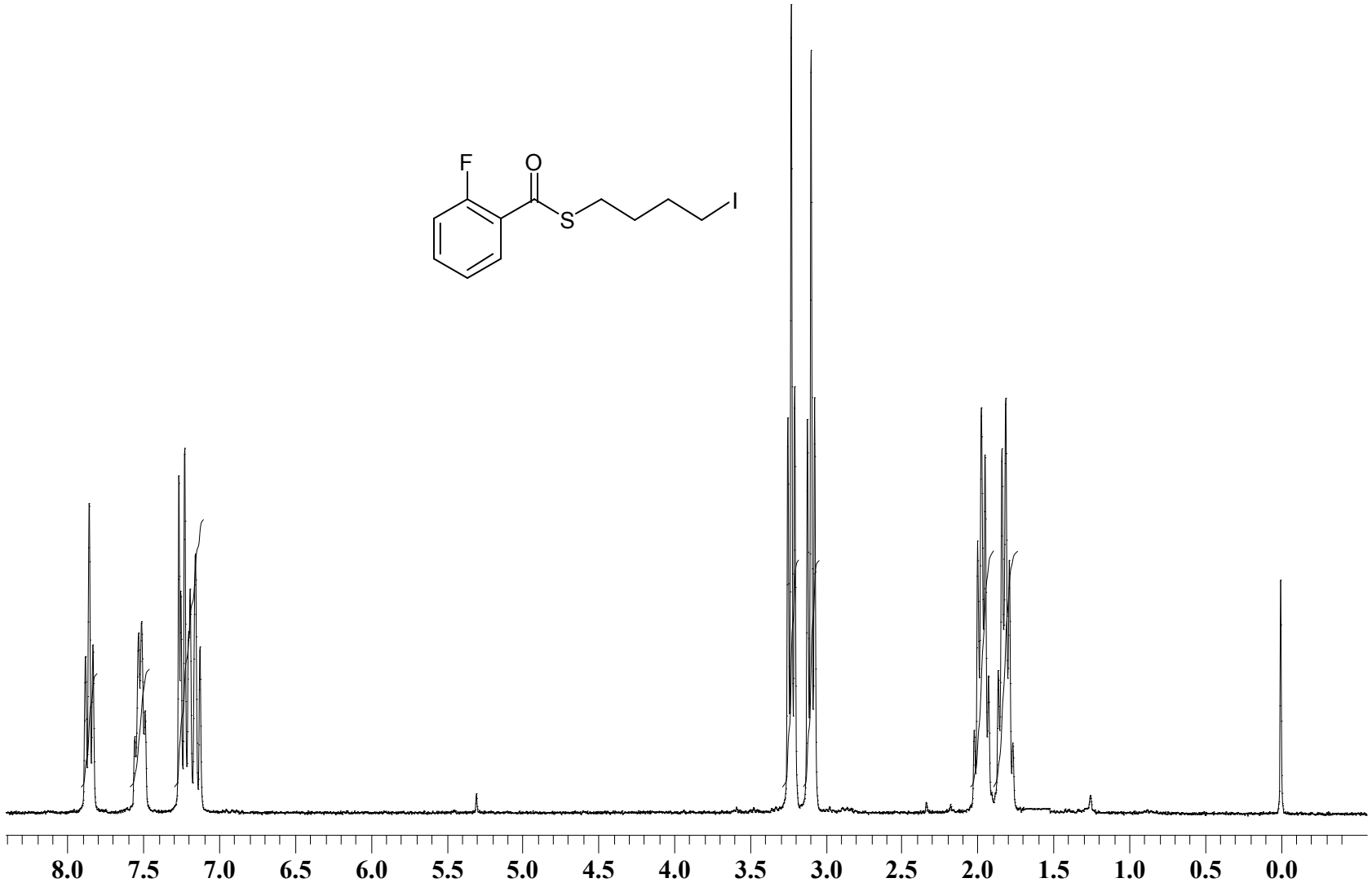


Fig: ^{1}H NMR of compound **32**

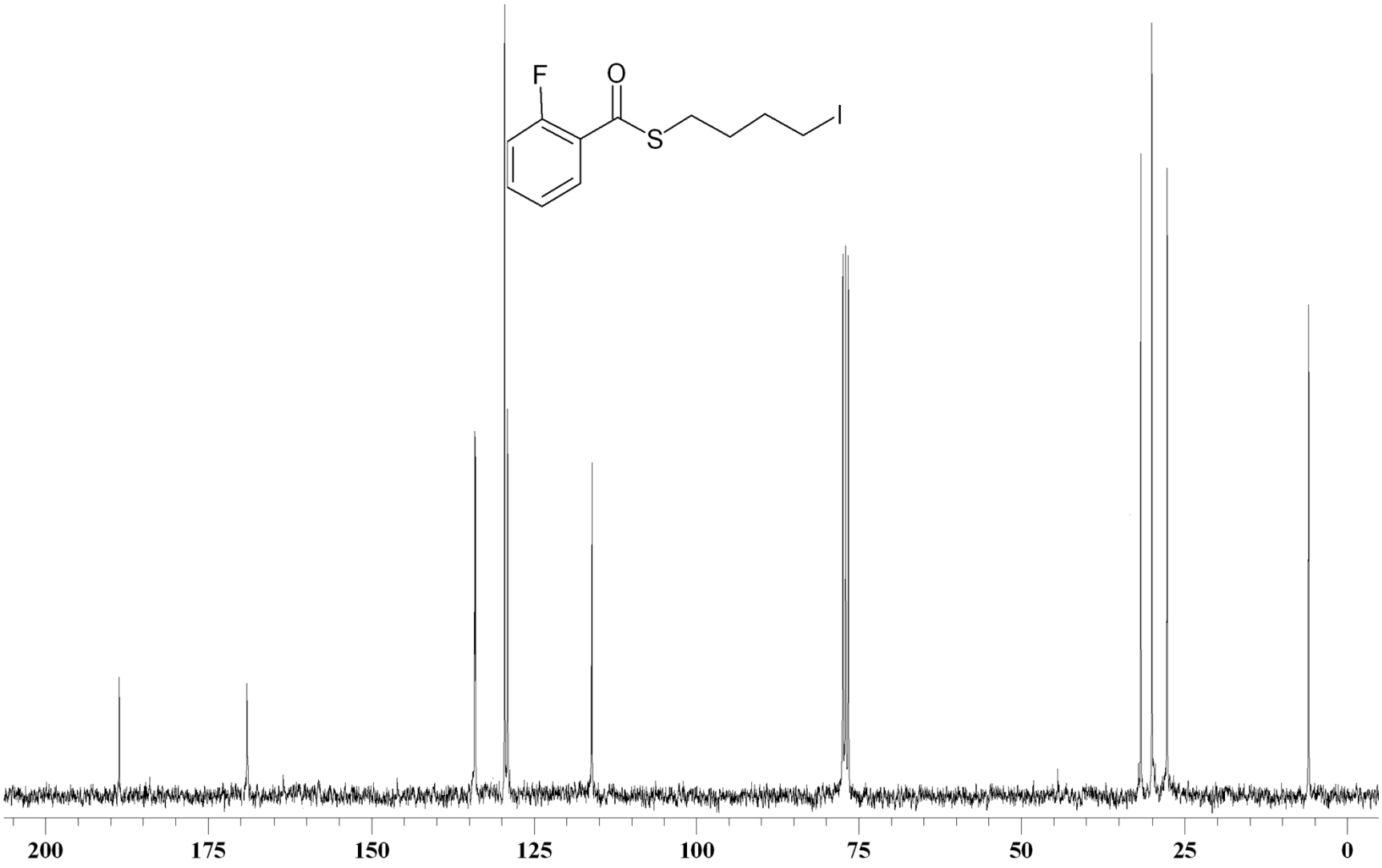


Fig: ^{13}C NMR of compound **32**

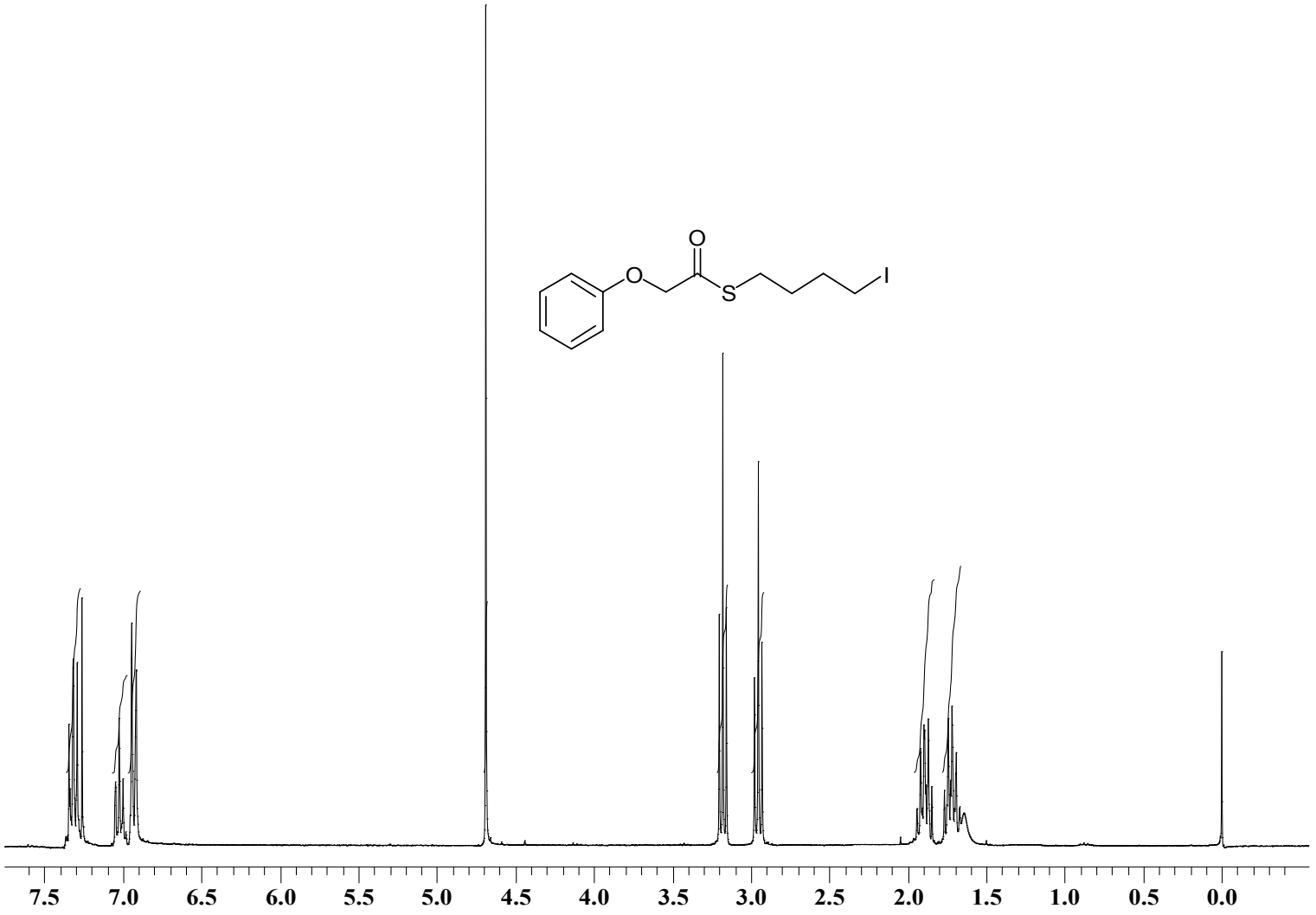


Fig: ^{1}H NMR of compound **33**

Fig: ^{13}C NMR of compound **33**

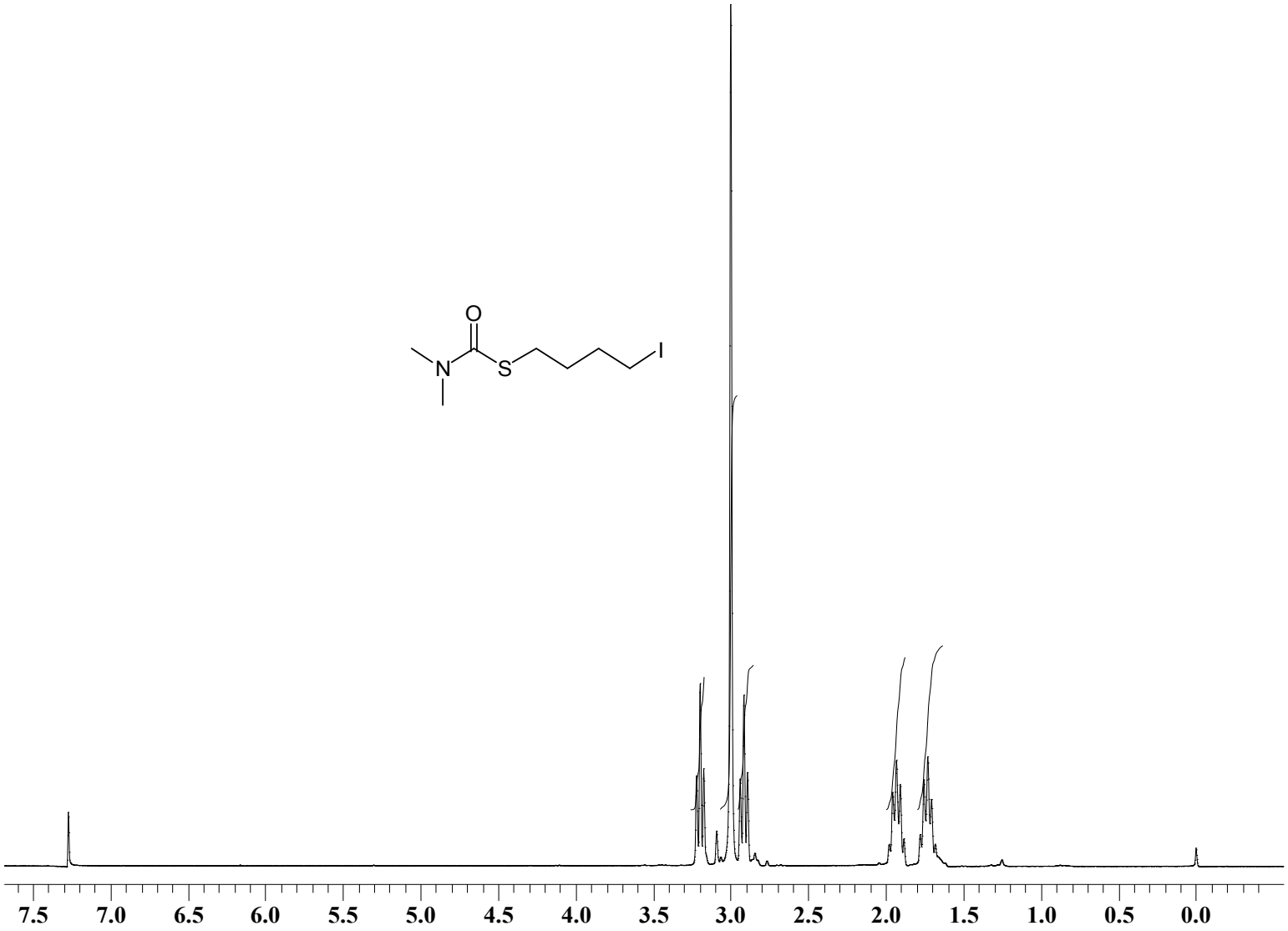


Fig: ^{1}H NMR of compound **34**

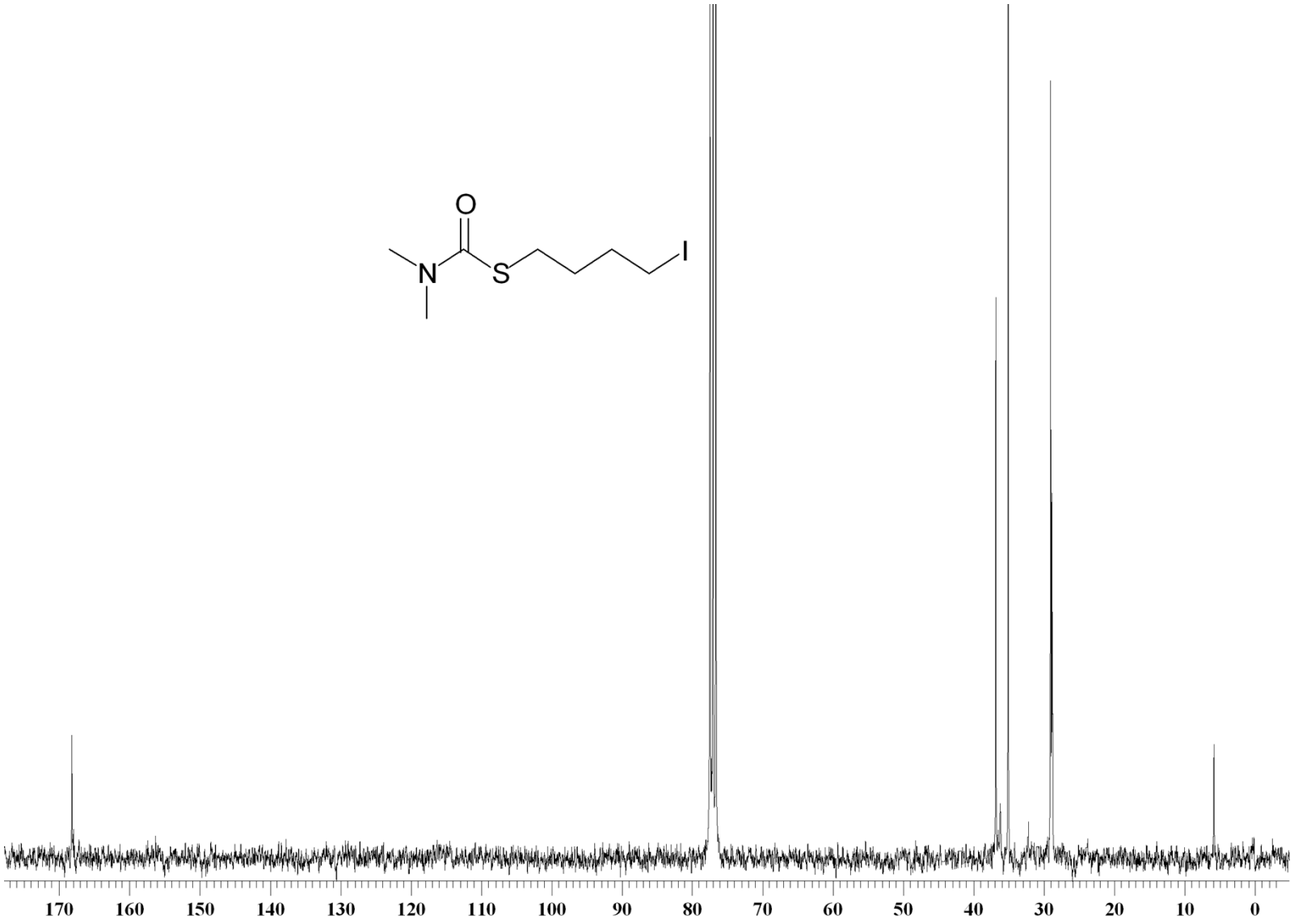


Fig: ^{13}C NMR of compound **34**

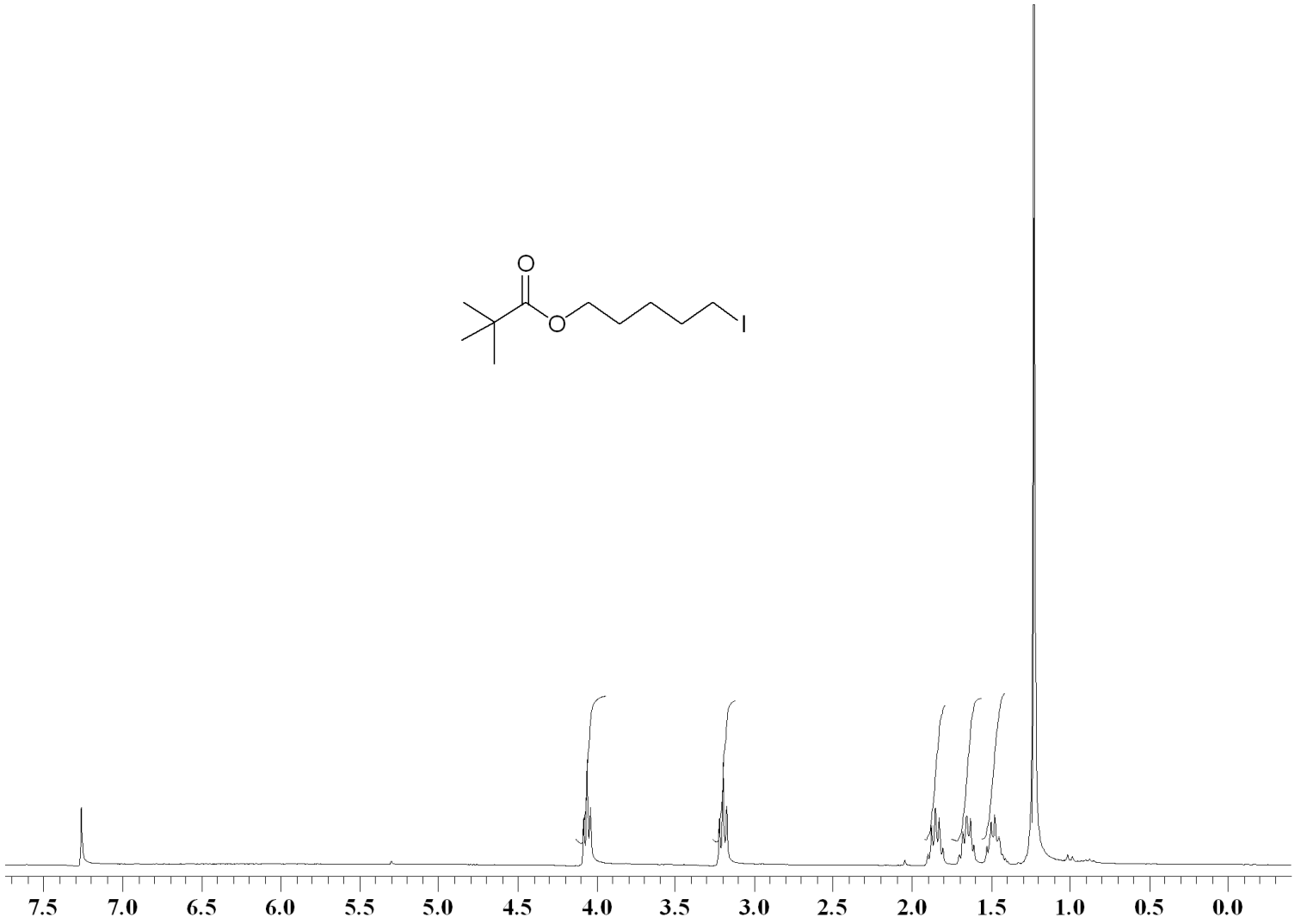


Fig: ^{1}H NMR of compound **35**

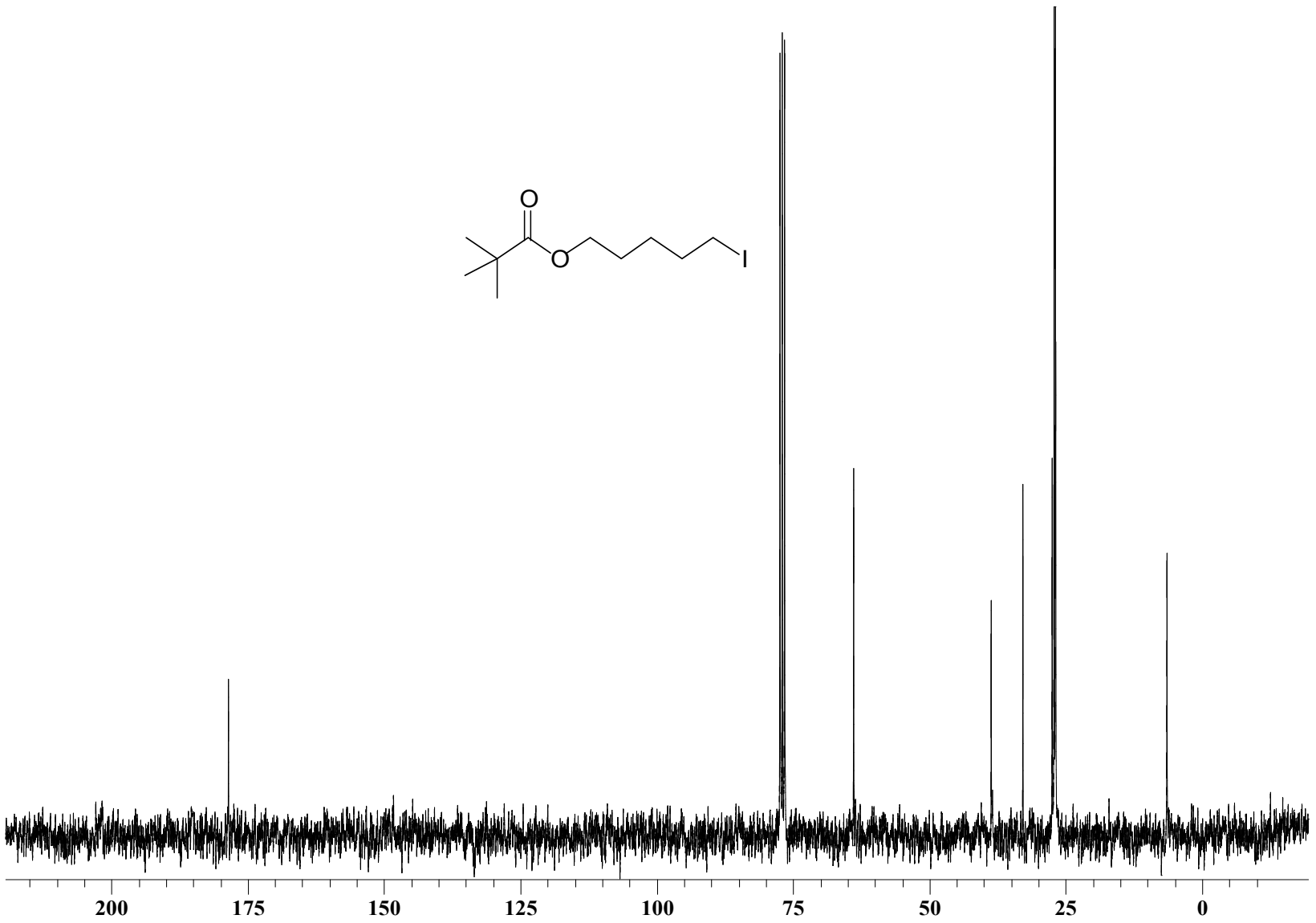


Fig: ^{13}C NMR of compound **35**

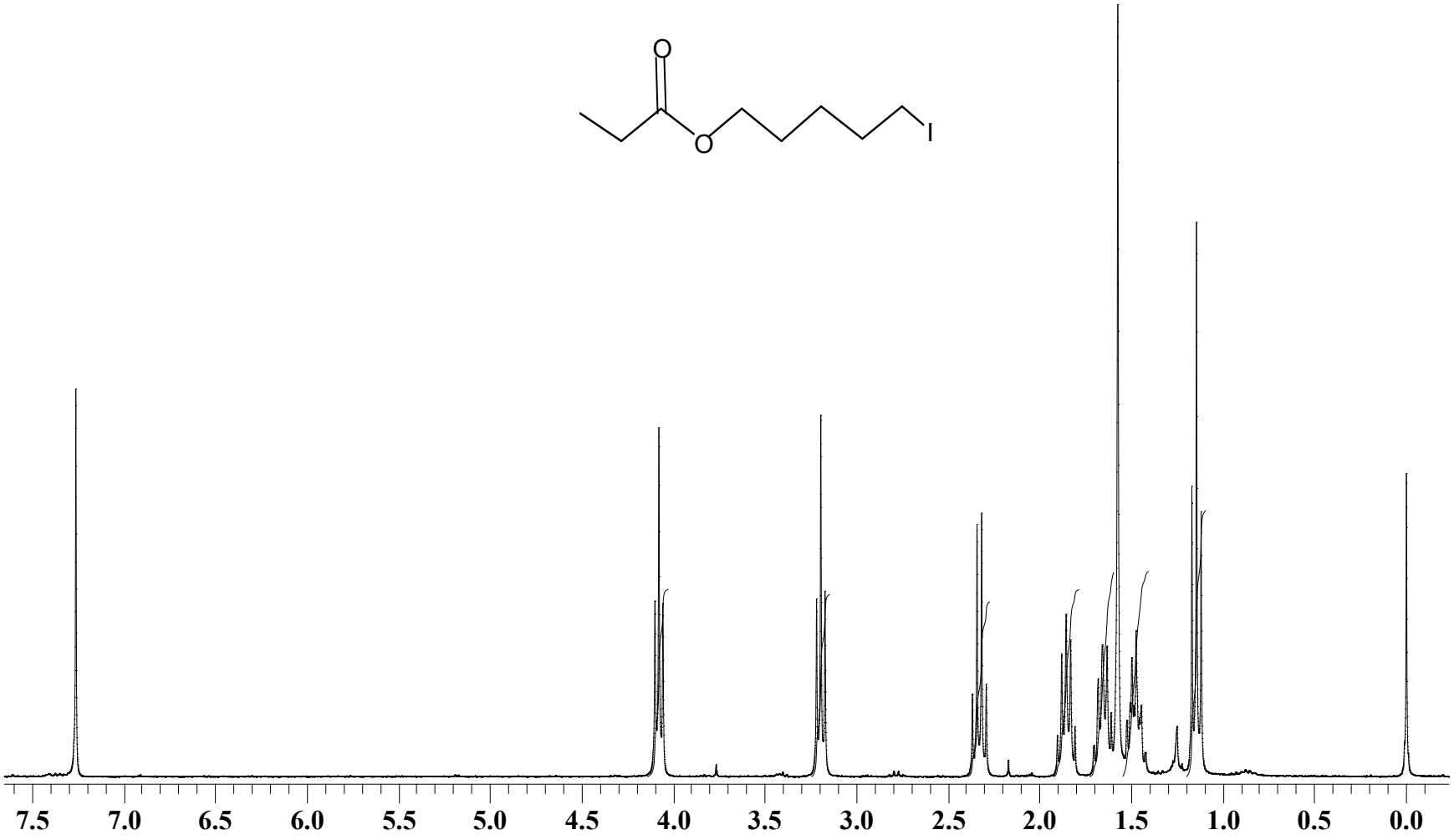


Fig: ^{1}H NMR of compound **36**

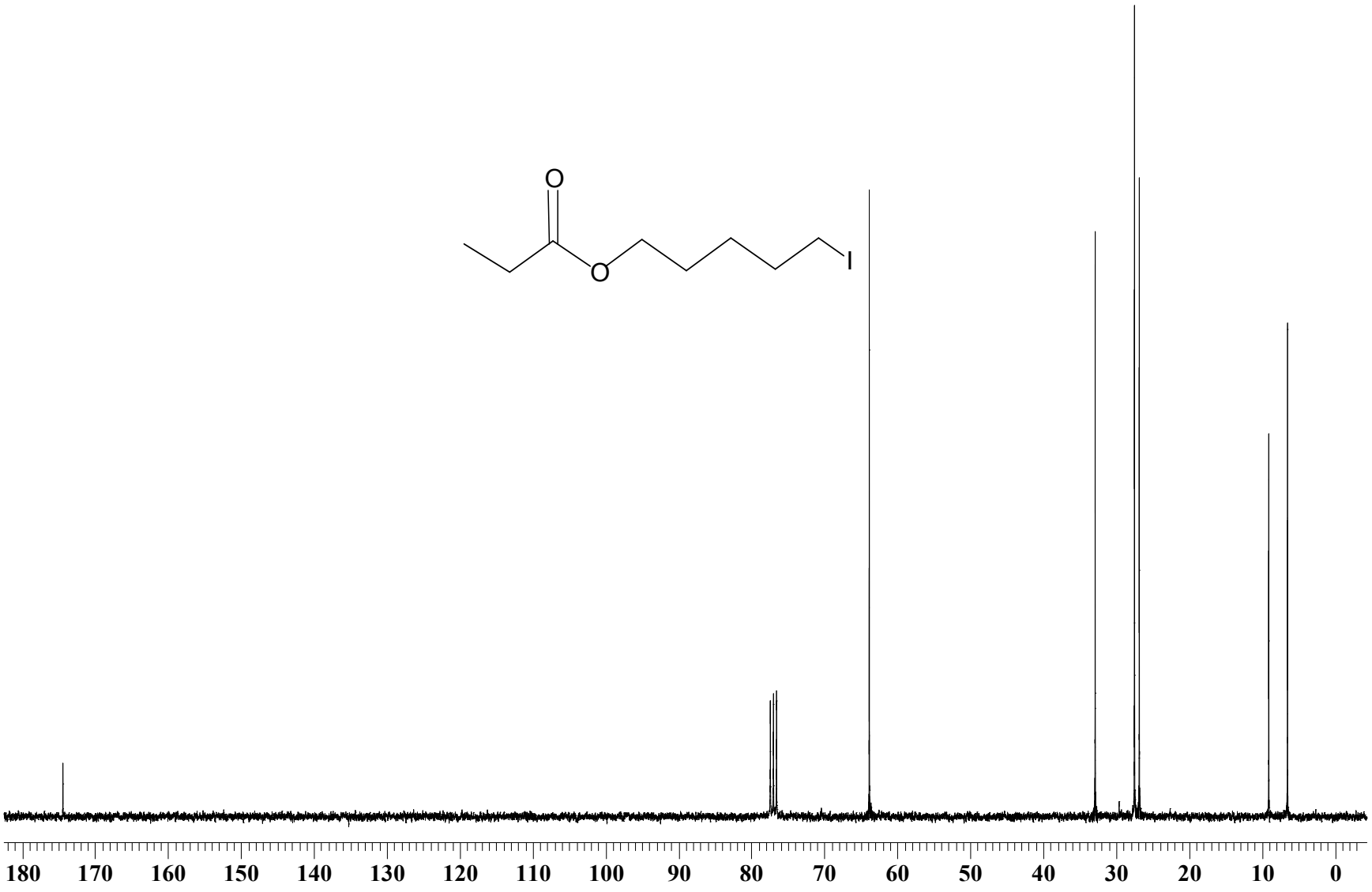


Fig: ^{13}C NMR of compound **36**

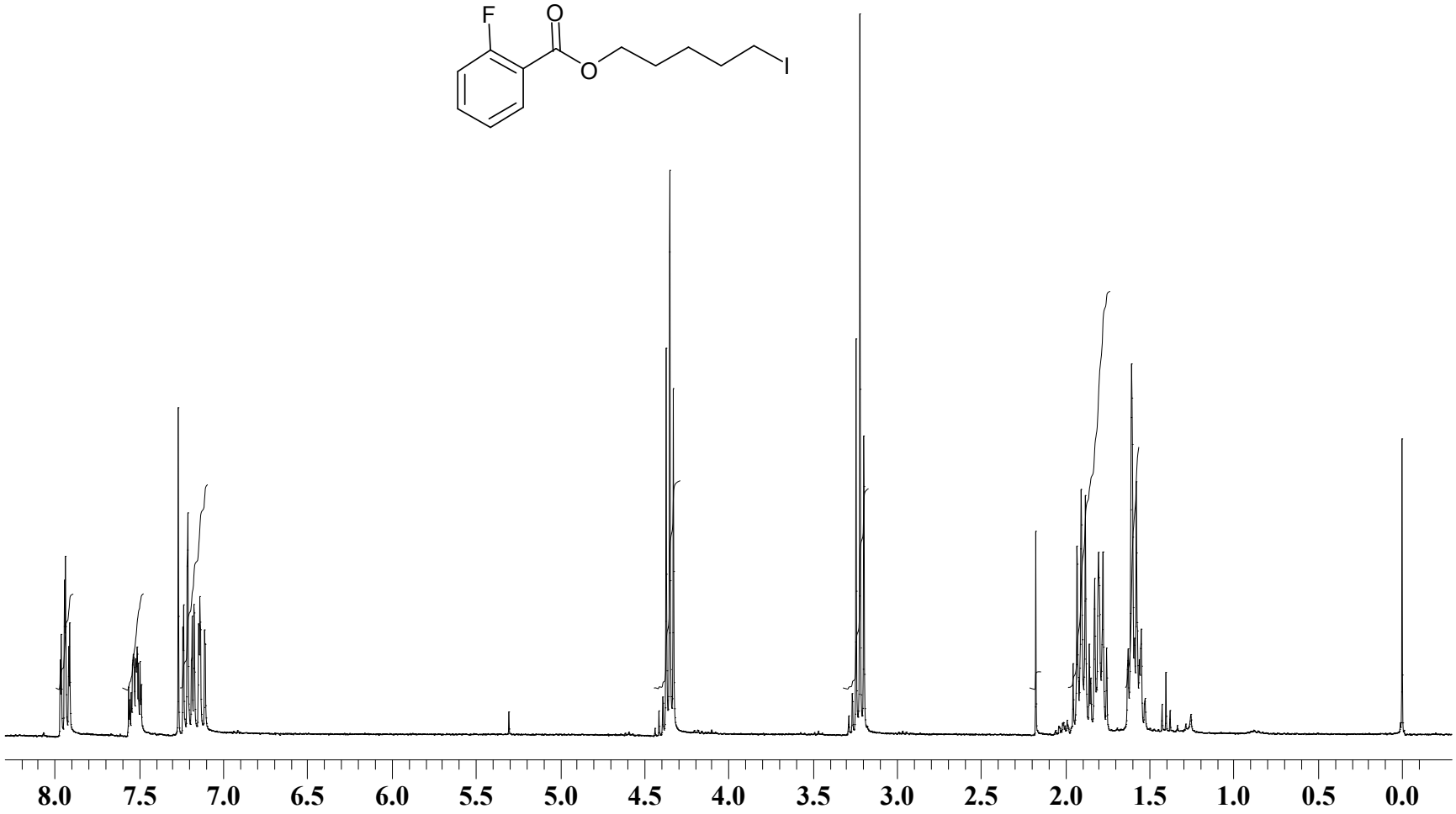


Fig: ^{1}H NMR of compound **37**

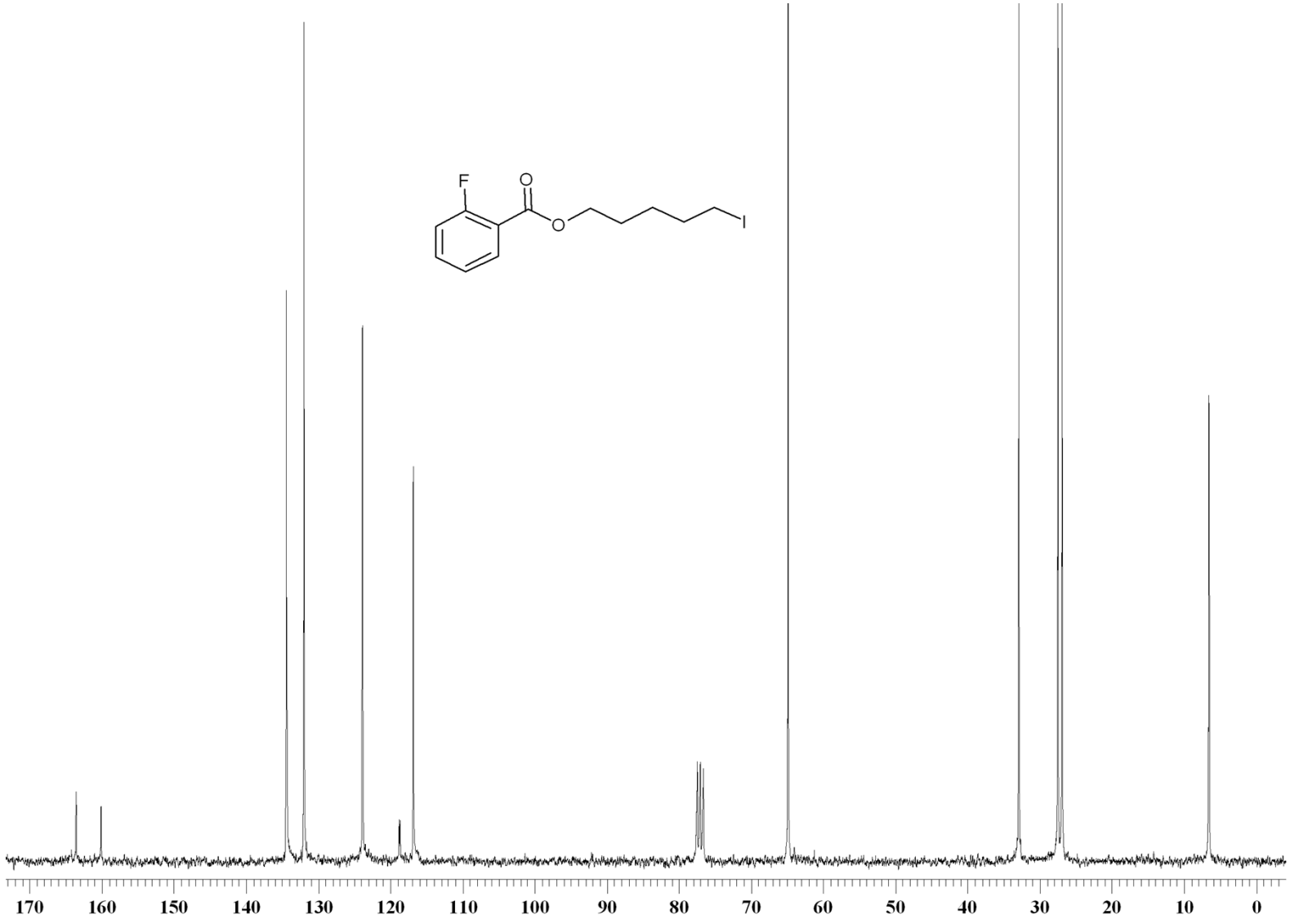


Fig: ^{13}C NMR of compound **37**

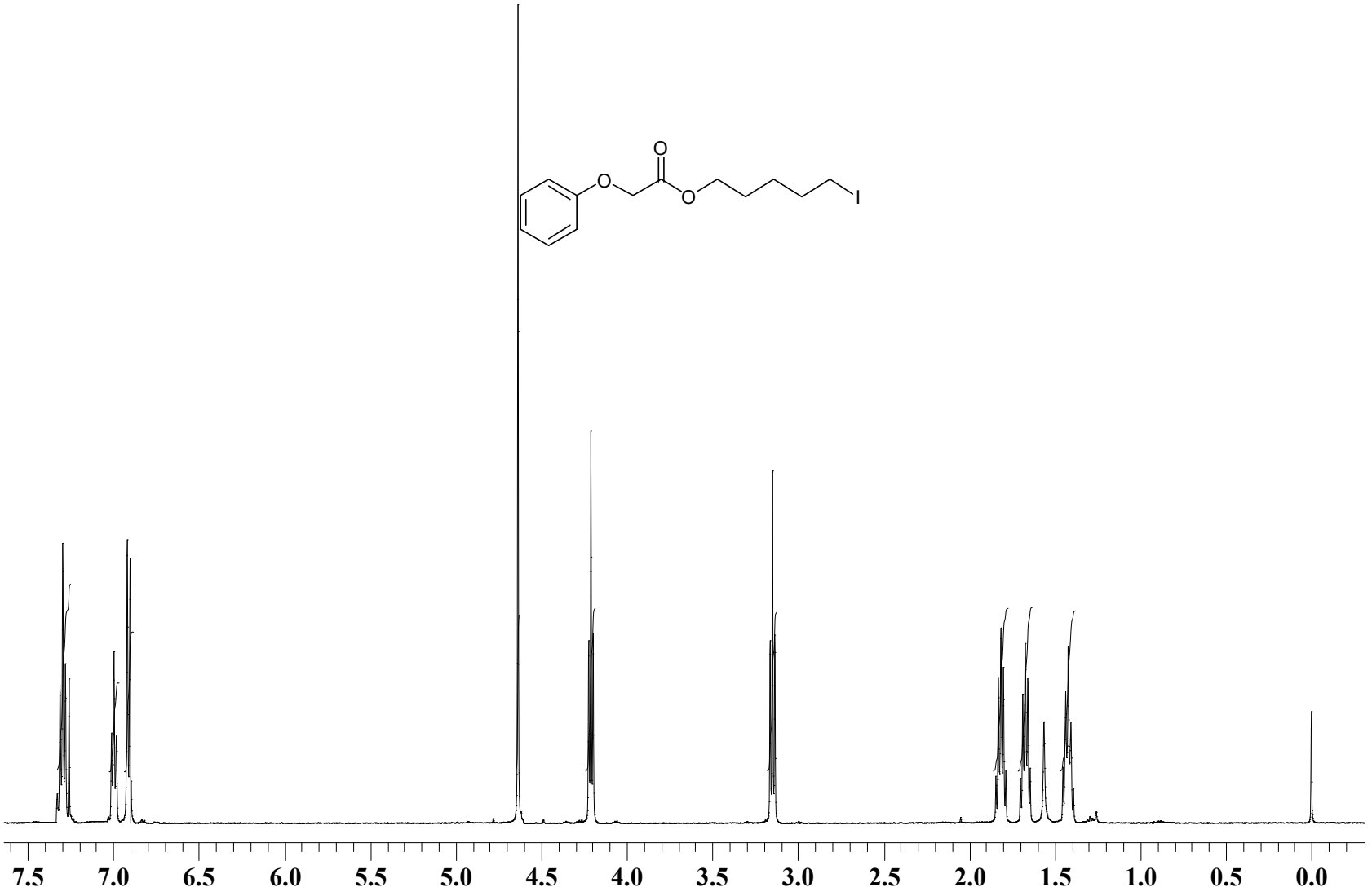


Fig: ^{1}H NMR of compound **38**

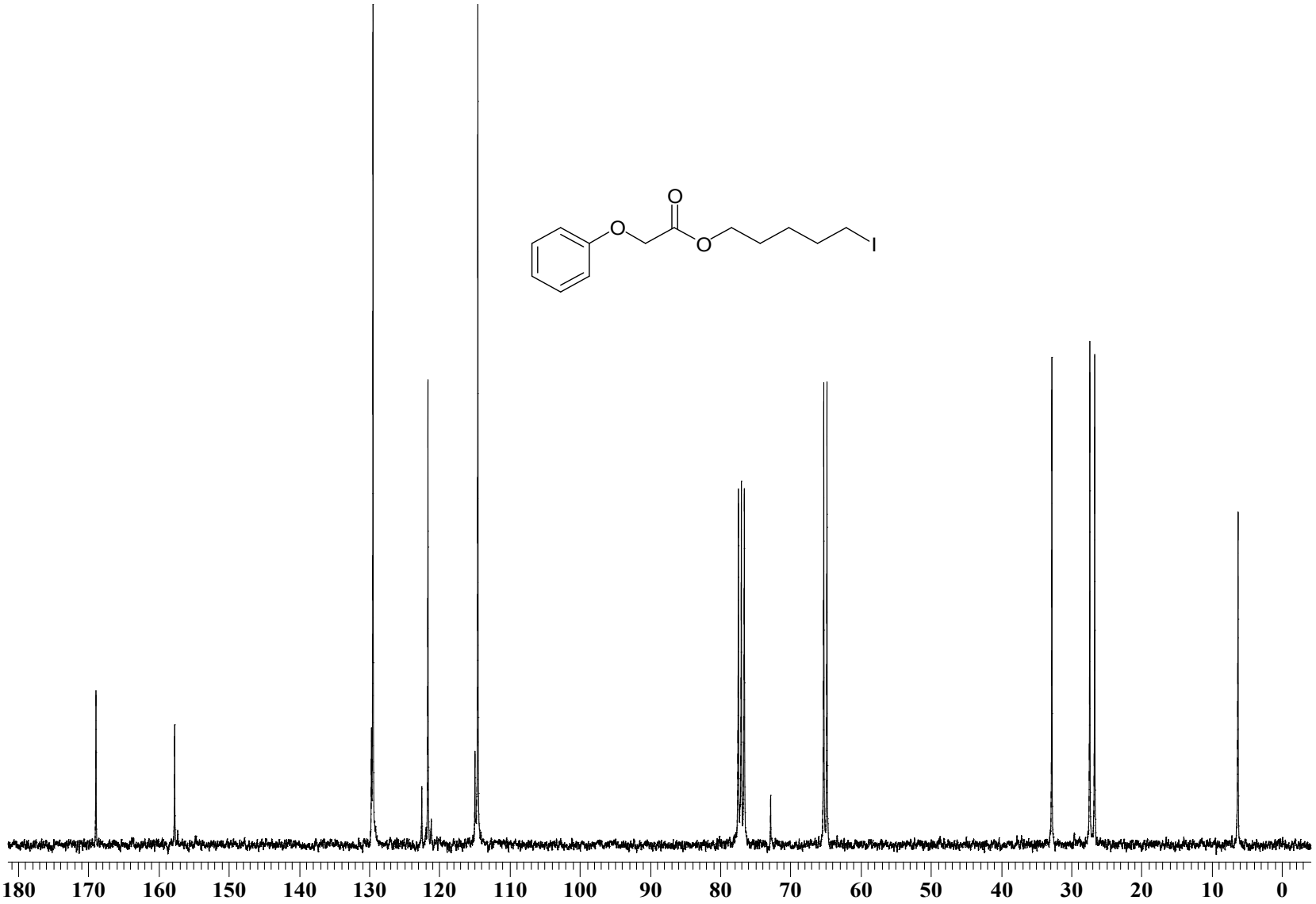


Fig: ^{13}C NMR of compound **38**

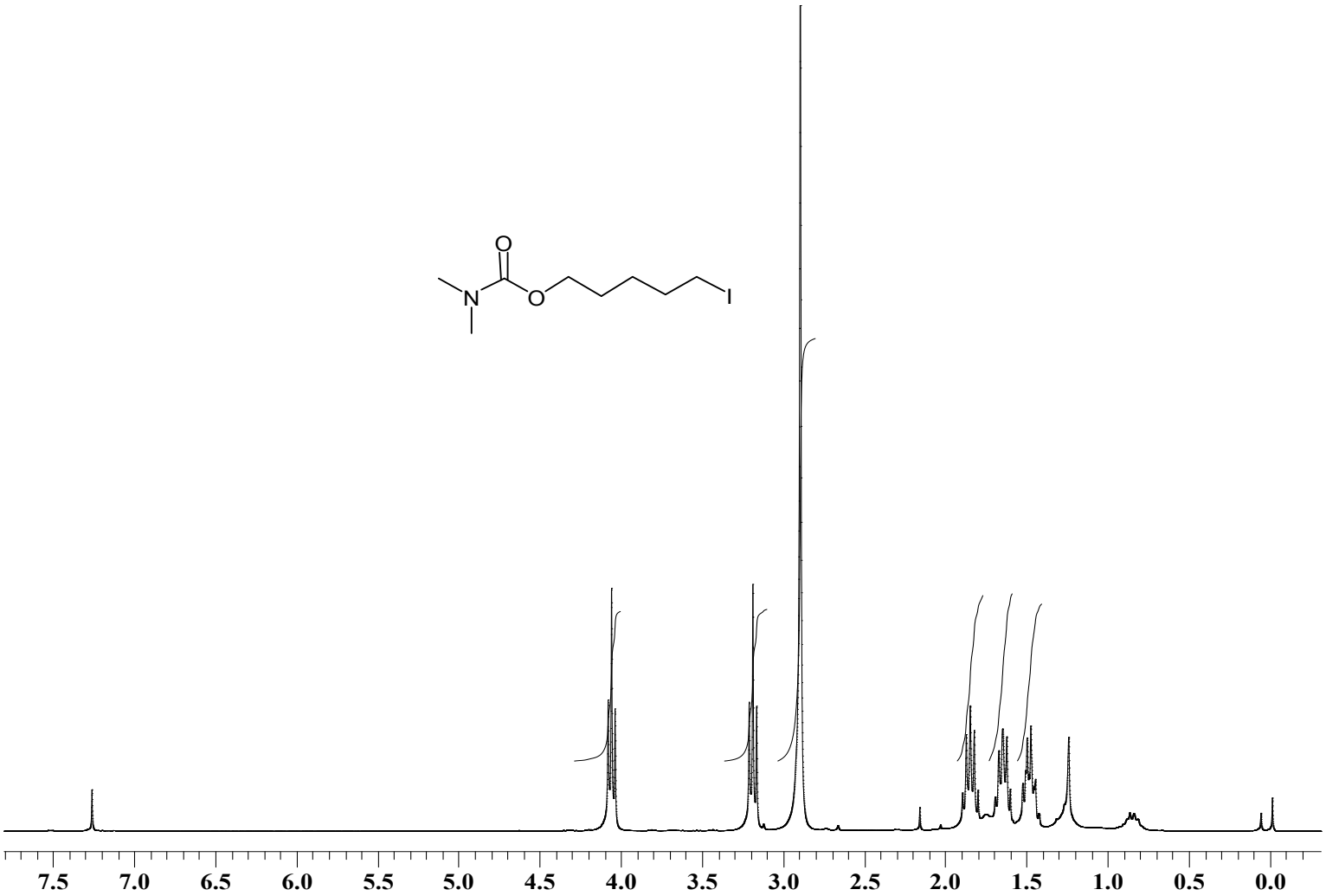


Fig: ^{1}H NMR of compound **39**

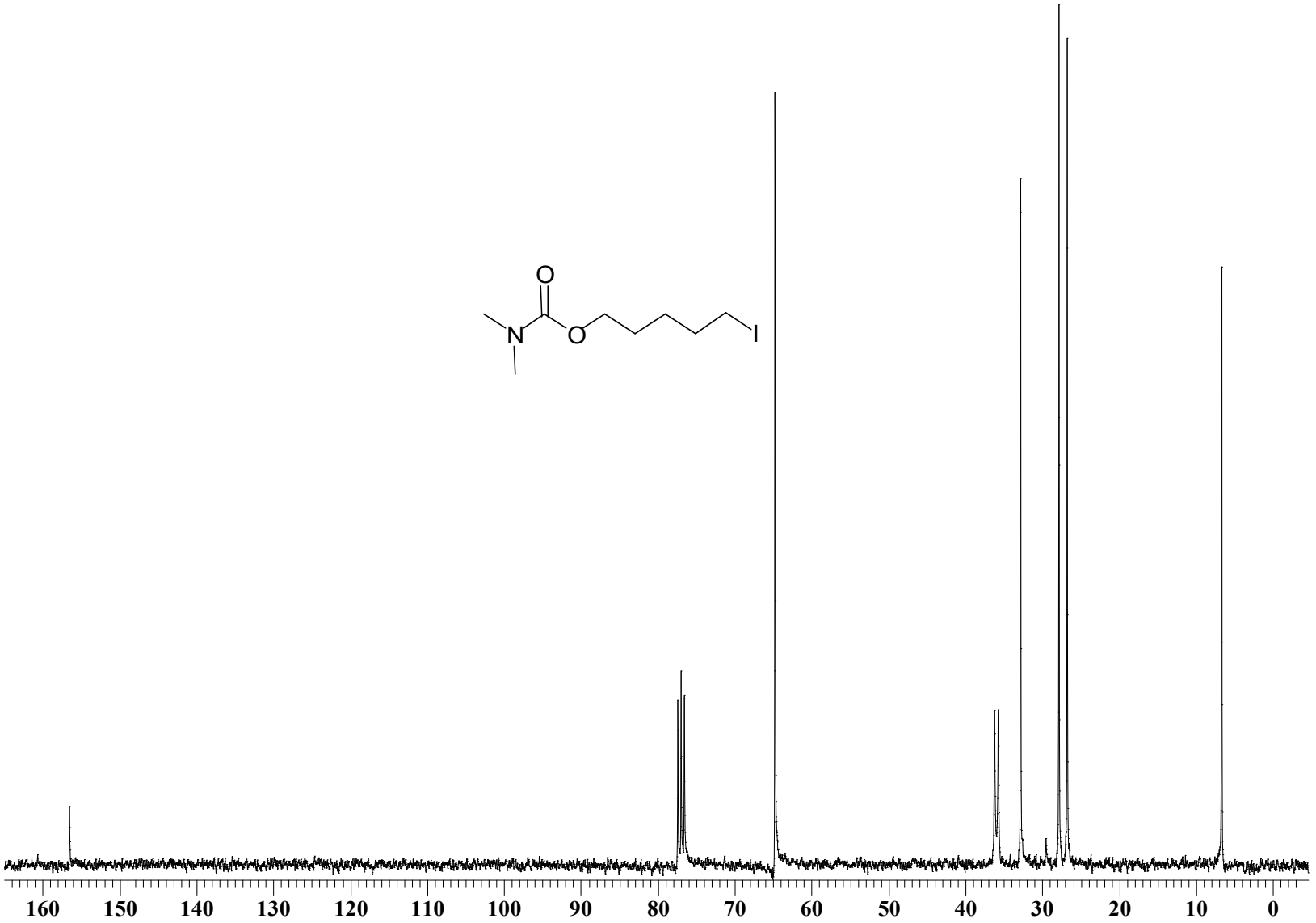


Fig: ^{13}C NMR of compound **39**

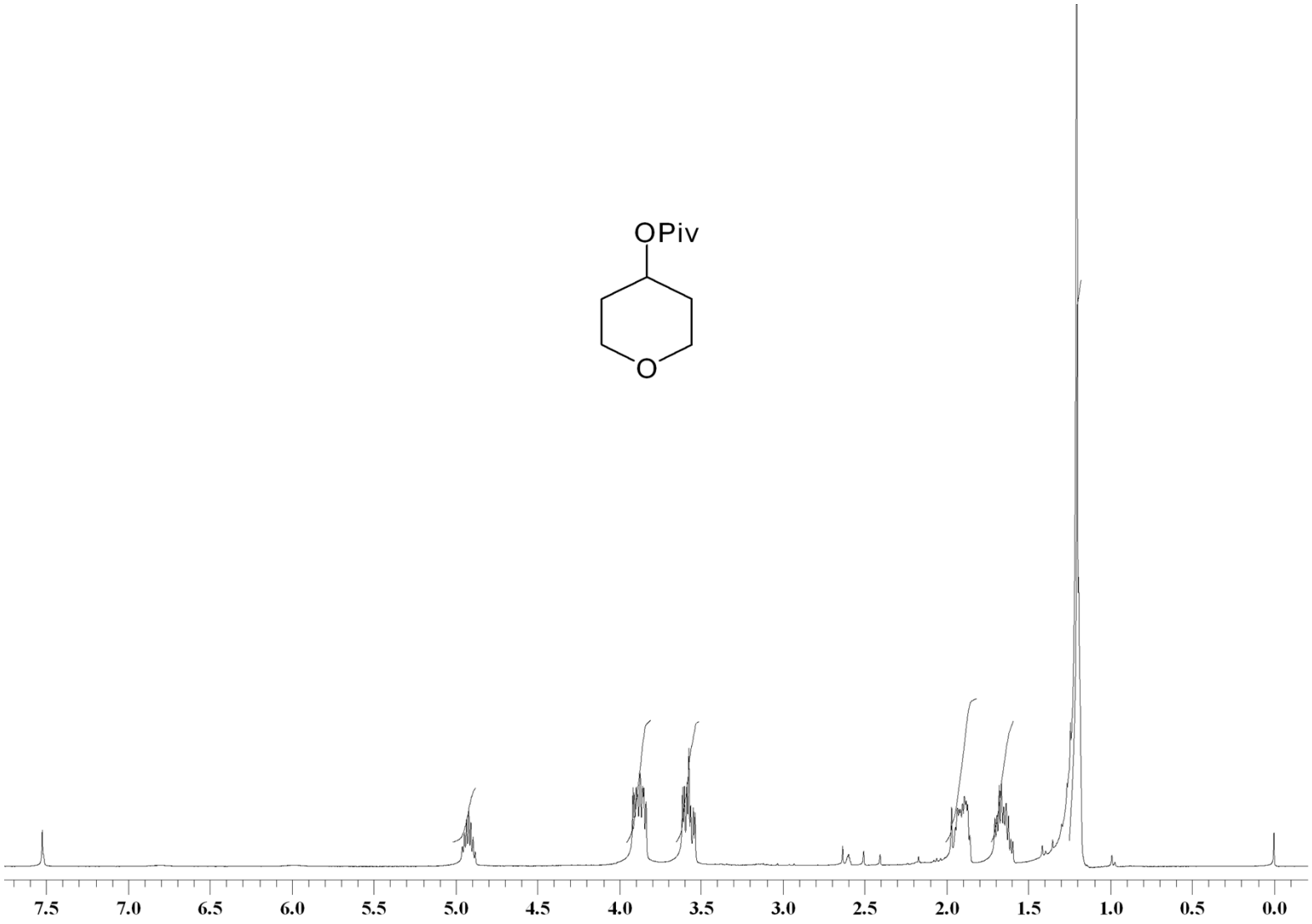


Fig: ^{1}H NMR of compound **42**

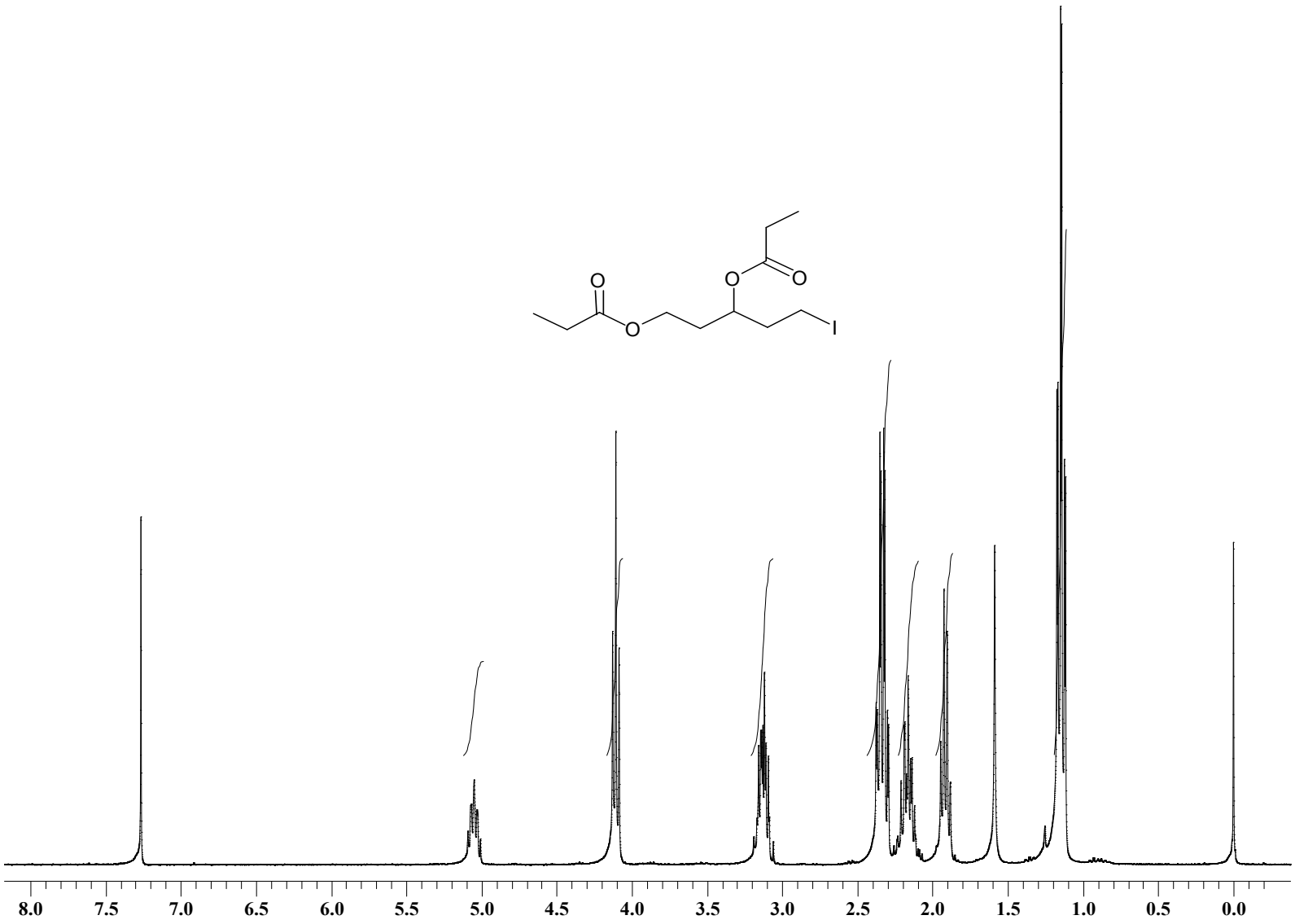


Fig: ^{1}H NMR of compound **44**

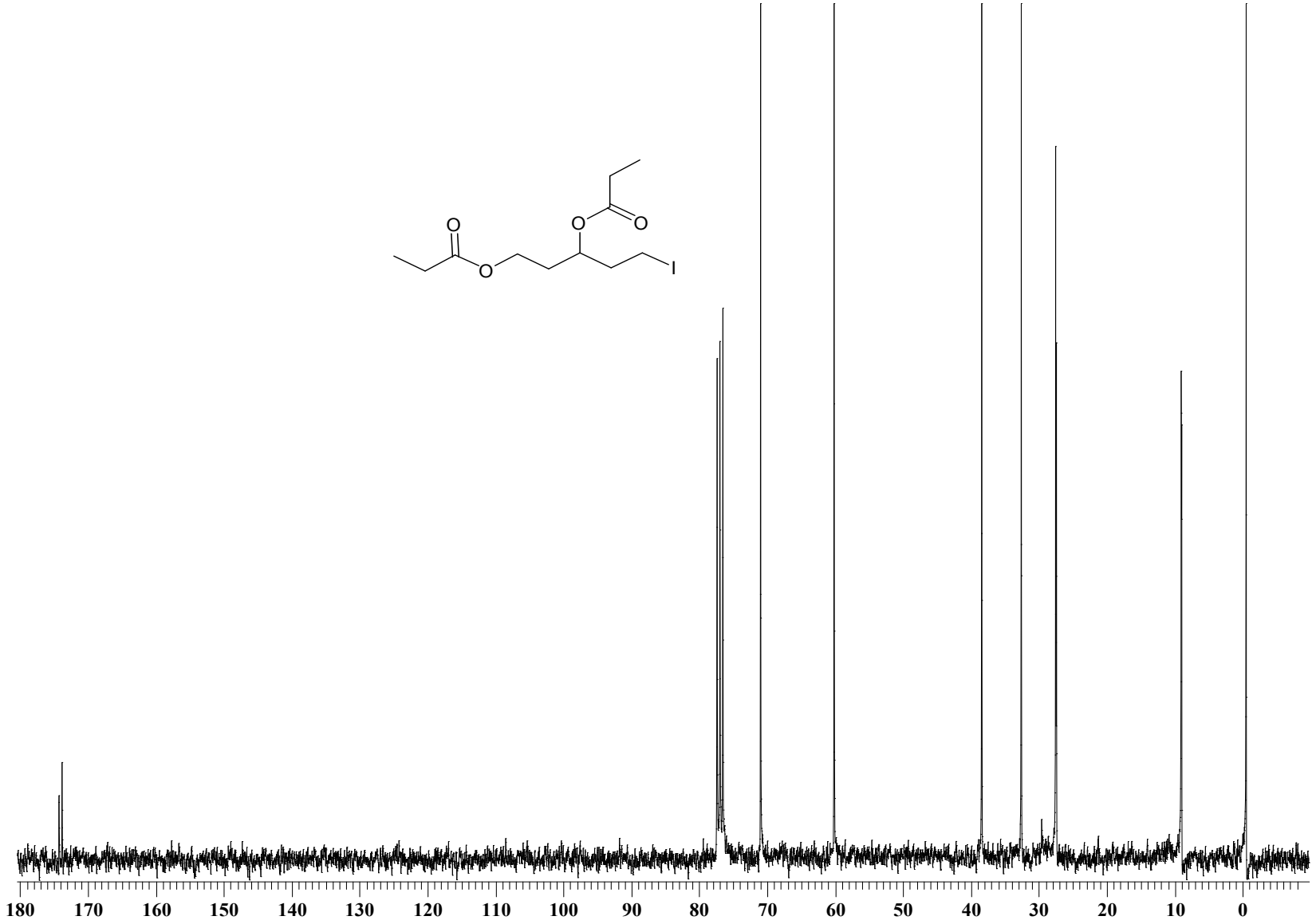


Fig: ^{13}C NMR of compound **44**

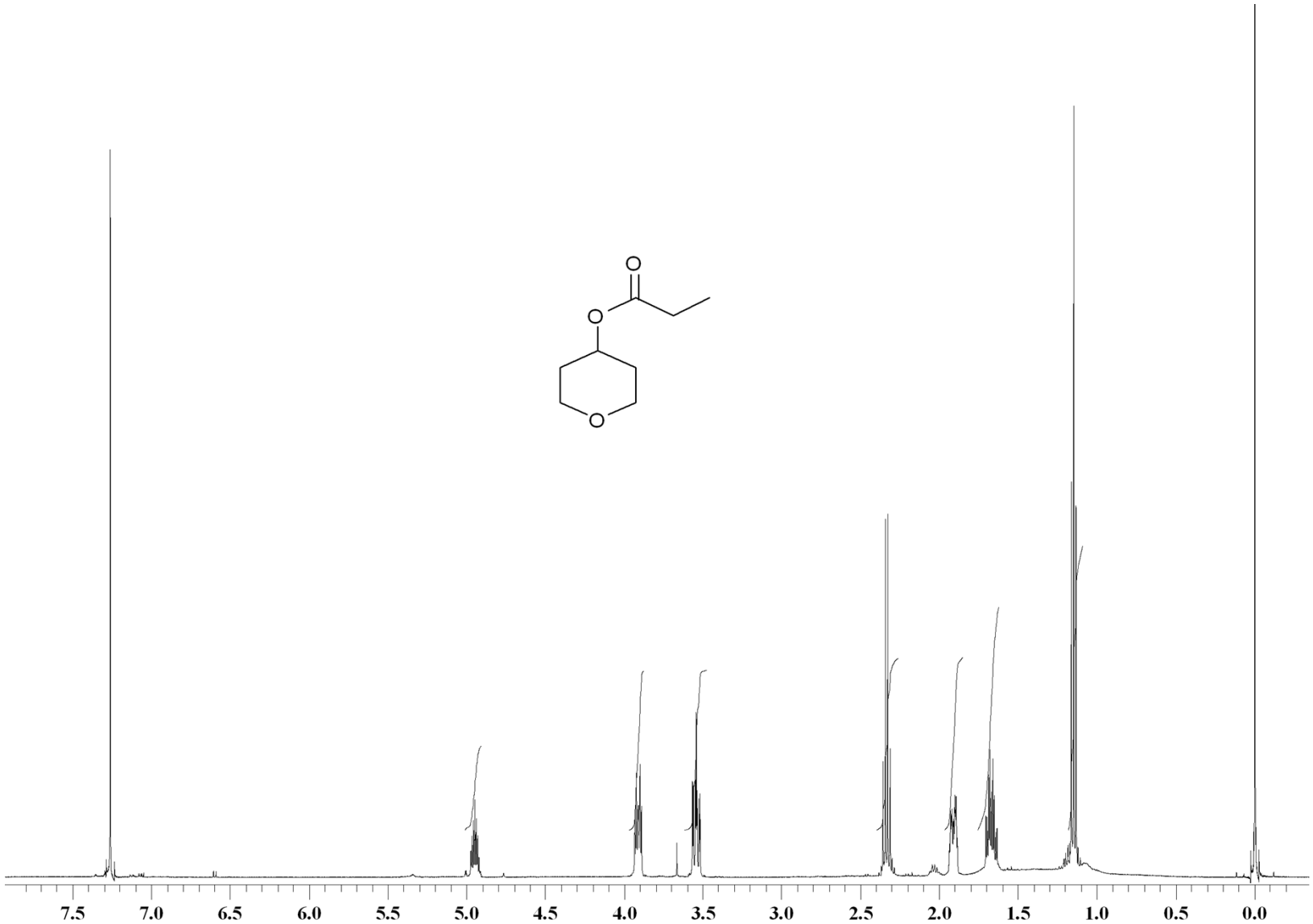


Fig: ^{1}H NMR of compound **43**