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1. General

Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates. ^{1}H NMR (400 MHz,500MHz or 600MHz) and ^{13}C NMR (101 MHz, 126MHz or 151MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Or alternatively, ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*), are reported in Hertz (Hz). GC analyses were performed using a Shimadzu GC-2010ultragas chromatography–mass spectrometry instrument equipped with a Shimadzu AOC-20s autosampler.

2. General procedure for iodochlorination of alkynes

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NIS (0.3 mmol, 1.5 equiv.), LiCl (0.4 mmol, 2 equiv.) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at rt for 24 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4, and the solvent was removed in vacuum. The residue was purified by flash silica gel column chromatography (eluted with hexanes and ethyl acetate) to give the desired products.

3. General procedure for iodochlorination of aromatic alkynes

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NIS (0.3 mmol, 1.5 equiv.), LiCl (0.4 mmol, 2 equiv.) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at -10 ^{o}C for 18 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash silica gel column chromatography (eluted with hexanes and ethyl acetate) to give the desired products.

4. General procedure for iodochlorination of aliphatic alkynes

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NIS (0.3 mmol, 1.5 equiv.), LiCl (0.4 mmol, 2 equiv) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at -25 ^{o}C for 24 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel (eluted with hexanes and ethyl acetate) to give the desired products.

5. General procedure for iodochlorination alkynyl esters and sulfonyl alkynes

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NIS (0.4 mmol, 2 equiv.), LiCl (0.6 mmol, 3 equiv.) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at rt for 48 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous $Na_2SO_{4,}$ and the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel (eluted with hexanes and ethyl acetate) to give the desired products.

6. General procedure for diiodination

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NIS (0.3 mmol, 1.5 equiv.), LiI (0.4 mmol, 2equiv.) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at 0 ^{o}C and warm to rt for 24 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel (eluted with hexanes and ethyl acetate).

7. General procedure for iodobromination

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NIS (0.3 mmol, 1.5 equiv.), LiBr (0.4 mmol, 2 equiv) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at 0℃ for 24 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel (eluted with hexanes and ethyl acetate).

8. General procedure for dibromination

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NBS (0.24 mmol, 1.2 equiv.), LiBr (0.24 mmol, 1.2equiv.) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at 0℃ for 24 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel (eluted with hexanes and ethyl acetate).

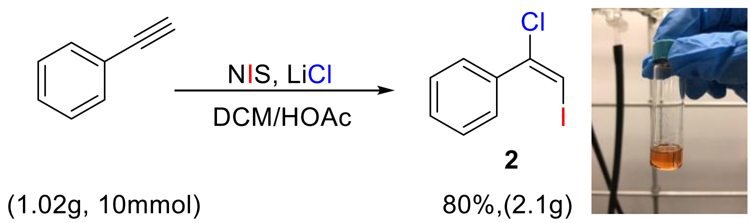
9. General procedure for chlorobromination

A 10 mL glass vial with a screw cap was charged with alkynes (0.2 mmol), NBS (0.24 mmol, 1.2 equiv.), LiCl (0.24 mmol, 1.2equiv.) and a solvent mixture of DCM (0.6 mL) and HOAc (0.4 mL). The reaction mixture was stirred at -40℃ for 24 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel (eluted with hexanes and ethyl acetate).

10. General procedure for Iodo-functionalization of alkynes

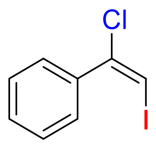
A 10 mL glass vial with a screw cap was charged with phenylacetylene (20.4mg, 0.2 mmol), NIS (0.24 mmol, 1.2 equiv.), Nucleophiles (0.24 mmol, 1.2 equiv.) and a solvent mixture of DCM (0.5 mL) and HOAc (0.5 mL). The reaction mixture was stirred at 0°C and warm to rt for 24 h. Upon completion, the reaction mixture was quenched with saturated NaCl solution and was extracted with EtOAc, the combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash column chromatography on silica gel (eluted with hexanes and ethyl acetate).

11. Gram-scale synthesis of 2

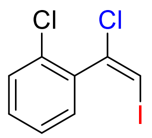


A 100 mL double neck flask equipped with a stir bar was charged with NIS (15 mmol, 3.37 g, 1.5 equiv.), and DCM (15 mL) then cool to -10°C. LiCl (20 mmol, 848 mg, 2 equiv.) was dissolved in the HOAc (25 ml) and slowly added to the reaction mixture for 45min. At the same time, to this flask, a solution of phenylacetylene (10 mmol,1.02g, 1 equiv.) in DCM (10 ml) was slowly added over a course of 45 min and the resulting solution was stirred for 2h. after the reaction was complete, the reaction mixture was filtered through a short plug of Celite. And the organic layer was diluted a saturated aqueous $Na_2S_2O_3$ solution and extracted with DCM. The combined organic layer was then washed with brine, and was dried over anhydrous Na_2SO_4. After the solvent was removed under a reduced pressure, the crude product was purified by silica gel column chromatography to give the desired product 3 (2.1 g, 80% yield).

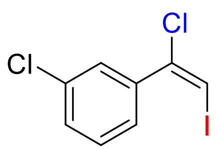
12. Characterization data of the products (compounds 2-105)



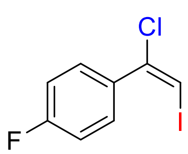
(*E*)-(1-chloro-2-iodovinyl)benzene (**2**). Colorless oil[1], 37.5 mg, 71% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.48 (m, 2H), 7.45 – 7.31 (m, 3H), 6.77 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.6, 134.1, 129.5, 128.95, 128.91, 128.3, 128.2, 72.9.



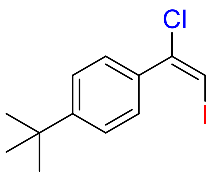
(*E*)-1-chloro-2-(1-chloro-2-iodovinyl)benzene (**3**). Yellow oil, 40.5 mg, 68% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.40 (m, 1H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 6.90 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.5, 132.5, 132.2, 130.7, 130.5, 129.99, 127.1, 78.3. IR (neat, cm^{-1}): 3072, 2925, 1588, 1470, 1438, 1149, 1052, 888, 742, 679. HRMS (EI$^+$) calcd. for $C_8H_5Cl_2I$ [M]$^+$: 297.8813 found: 297.8810.



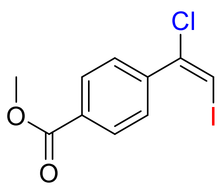
(*E*)-1-chloro-3-(1-chloro-2-iodovinyl)benzene (**4**). Yellow oil, 42.9 mg, 72% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (td, *J* = 1.8, 0.6 Hz, 1H), 7.44 – 7.32 (m, 3H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.3, 134.2, 132.5, 129.6, 129.1, 127.2, 74.2. IR (neat, cm^{-1}): 3064, 1561, 1470, 1414, 1247, 1160, 1080, 919, 881, 791. HRMS (EI$^+$) calcd. for $C_8H_5Cl_2I$ [M]$^+$: 297.8813 found: 297.8807.



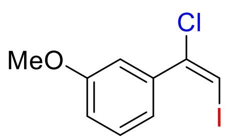
(*E*)-1-(1-chloro-2-iodovinyl)-4-fluorobenzene (**5**). Yellow oil, 47.4 mg, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.21 – 6.81 (m, 2H), 6.70 (s, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.74 – -121.56 (m, 1F). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.9 (d, *J* = 250.4 Hz), 133.6, 133.1, 131.1 (d, *J* = 8.6 Hz), 115.4 (d, *J* = 22.0 Hz), 73.4. IR (neat, cm^{-1}): 3069, 1893, 1605, 1499, 1231, 1158, 1097, 1015, 886, 836. HRMS (EI$^+$) calcd. for C_8H_5ClFI [M]$^+$: 281.9108 found: 281.9101.



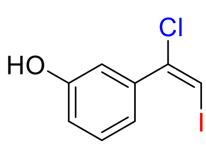
(*E*)-1-(tert-butyl)-4-(1-chloro-2-iodovinyl)benzene (**6**). Yellow oil, 49.9 mg, 78% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.7, 134.5, 134.2, 128.7, 125.2, 72.0, 34.9, 31.2. IR (neat, cm^{-1}): 3068, 2961, 2903, 2867, 1608, 1504, 1461, 1363, 1267, 1155. HRMS (EI$^+$) calcd. for $C_{12}H_{14}ClI$ [M]$^+$: 319.9829 found: 319.9823.



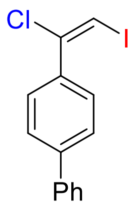
Methyl (*E*)-4-(1-chloro-2-iodovinyl)benzoate (**7**). Yellow oil, 34.0 mg, 53% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 141.9, 133.0, 130.9, 129.6, 129.1, 74.4, 52.3. IR (neat, cm^{-1}): 3066,2949,1031,1718, 1595,1434,1273,1179,1106,1018. HRMS (ESI$^+$) calcd. for $C_{10}H_9ClIO_2$ [M+H]$^+$: 322.9336. found: 322.9330.



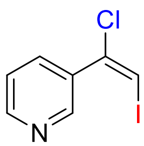
(*E*)-1-(1-chloro-2-iodovinyl)-3-methoxybenzene (**8**). Yellow oil, 47.0 mg, 80% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 8.0 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.07 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.95 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.77 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.3, 138.8, 133.9, 129.4, 121.3, 115.4, 114.3, 73.1, 55.4. IR (neat, cm^{-1}): 3070, 3007, 2939, 2835, 1578, 1484, 1282, 1226, 1041, 784. HRMS (EI$^+$) calcd. for C_9H_8ClIO [M]$^+$: 293.9303 found: 293.9302.



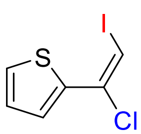
(*E*)-3-(1-chloro-2-iodovinyl)phenol (**9**). Yellow oil, 44.8 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.9 Hz, 1H), 7.12 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.01 (dd, *J* = 2.6, 1.7 Hz, 1H), 6.89 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 6.78 (s, 1H), 5.06 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.3, 139.1, 133.6, 129.7, 121.6, 116.6, 115.9, 73.2. IR (neat, cm^{-1}): ν = 3419, 1584, 1444, 1281, 1216, 954, 816, 784, 702, 666 cm^{-1}. HRMS (ESI-) calcd. for C_8H_5ClIO [M-H]$^-$ 278.9074, found 278.9068.



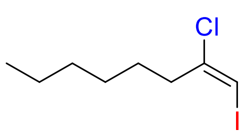
(E)-4-(1-chloro-2-iodovinyl)-1,1'-biphenyl (**10**). Yellow solid, 55 mg, 81% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 - 7.67 (m, 6H), 7.53 (t, J = 7.1 Hz, 2H), 7.46 - 7.43 (m, 1H), 6.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 140.2, 136.4, 133.9, 129.6, 129.0, 127.9, 127.3, 127.1, 127.0, 73.1.HRMS (ESI^{+}) calcd. for $C_{14}H_{10}ClI$ $[M]^{+}$ 339.9516, found 339.9510.



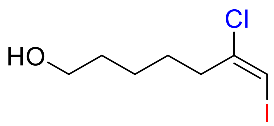
(E)-3-(1-chloro-2-iodovinyl)pyridine (**11**). Yellow oil, 38.7 mg, 73% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.70 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.70 (td, J = 7.7, 1.8 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.23 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 7.00 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 155.1, 149.8, 136.3, 123.8, 123.5, 121.7, 96.9. IR (neat, cm^{-1}): 3050, 1708, 1578, 1564, 1460, 1427, 1283, 1150, 1048, 991. HRMS (ESI^{+}) calcd. for C_7H_6ClIN $[M+H]^{+}$: 265.9233 found: 265.9233.



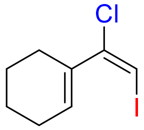
(E)-2-(1-chloro-2-iodovinyl)thiophene (**12**). Colorless oil, 37.8 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 (dd, J = 3.1, 1.2 Hz, 1H), 7.49 (dd, J = 5.2, 1.1 Hz, 1H), 7.32 (dd, J = 5.1, 3.0 Hz, 1H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 137.2, 129.2, 127.8, 127.6, 125.1, 71.0. IR (neat, cm^{-1}): 3072, 1566, 1418, 1261, 1122, 1043, 1048, 814,702. HRMS (EI^{+}) calcd. for C_6H_4ClIS $[M]^{+}$: 269.8767 found: 269.8761.



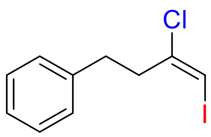
(E)-2-chloro-1-iodooct-1-ene (**13**). Colorless oil, 42.4 mg, 78% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 6.29 (s, 1H), 2.75 – 2.38 (m, 2H), 1.75 – 1.56 (m, 2H), 1.41 – 1.23 (m, 6H), 0.99 – 0.81 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 138.4, 72.1, 38.5, 31.5, 28.2, 26.6, 22.5, 14.1. IR (neat, cm^{-1}): 2964, 2925, 2100, 1498, 1466, 1310, 1247, 1083, 860, 651. HRMS (EI^{+}) calcd. for $C_8H_{14}ClI$ $[M]^{+}$: 271.9829 found: 271.9826.



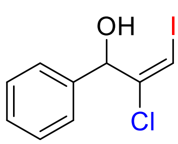
(*E*)-6-chloro-7-iodohept-6-en-1-ol (**14**). Yellow oil, 41.6 mg, 76% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.32 (s, 1H), 3.69 (t, *J* = 6.5 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 1.70-1.64 (m, 4H), 1.63 – 1.03 (m, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.0, 72.5, 62.8, 38.4, 32.5, 26.5, 24.6. IR (neat, cm^{-1}): ν = 3380, 2933, 2860, 1450, 1429, 1051, 774, 668 cm^{-1}. HRMS (EI$^+$) calcd. for $C_7H_{12}ClI_2$ [M]$^+$: 273.9621, found 273.9616.



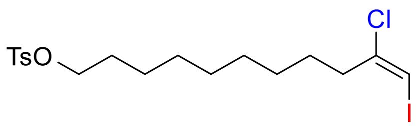
(*E*)-1-(1-chloro-2-iodovinyl)cyclohex-1-ene (**15**). Yellow oil, 39.7 mg, 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.34 (s, 1H), 5.98 (p, *J* = 2.0 Hz, 1H), 2.23 – 2.04 (m, 4H), 1.71 (qq, *J* = 5.1, 2.6 Hz, 2H), 1.67 – 1.59 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.0, 135.2, 132.3, 70.4, 25.8, 25.0, 22.2, 21.5. IR (neat, cm^{-1}): 3068, 2932, 2863, 1741, 1544, 1435, 1369, 1219, 1014, 923. HRMS (EI$^+$) calcd. for $C_8H_{10}ClI$ [M]$^+$: 267.9510, found: 267.9506.



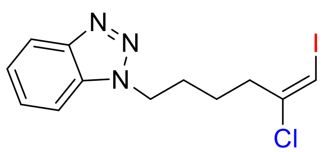
(*E*)-(3-chloro-4-iodobut-3-en-1-yl)benzene (**16**). Colorless oil, 53.7 mg, 92% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 2H), 7.21 – 7.14 (m, 3H), 6.27 (s, 1H), 2.98 – 2.36 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.0, 136.9, 128.6, 128.4, 126.3, 73.3, 40.6, 32.8. IR (neat, cm^{-1}): 3072, 3026, 2926, 2860, 1603, 1494, 1453, 1428, 1165, 1025. HRMS (EI$^+$) calcd. for $C_{10}H_{10}ClI$ [M]$^+$: 291.9516, found: 291.9512.



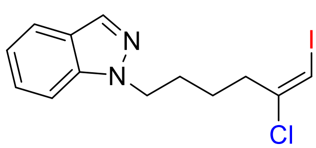
(*E*)-2-chloro-3-iodo-1-phenylprop-2-en-1-ol (**17**). Yellow oil, 45.9 mg, 78% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.47-7.21 (m, 3H), 6.70 (s, 1H), 5.57 (d, *J* = 5.9 Hz, 1H), 2.33 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.9, 128.5, 128.2, 125.7, 119.7, 110.6, 70.6. IR (neat, cm^{-1}): 3385, 3075, 3033, 1602, 1494, 1452, 1191, 1052, 784, 693. HRMS (EI$^+$) calcd. for C_9H_8ClIO [M]$^+$: 293.9308, found: 293.9303.



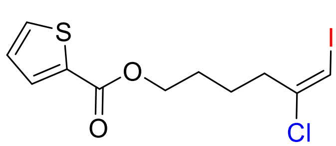
(*E*)-10-chloro-11-iodoundec-10-en-1-yl-4-methylbenzenesulfonate (**18**). Colorless oil, 77.4 mg, 80% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.29 (s, 1H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.61 – 2.52 (m, 2H), 2.46 (s, 3H), 1.73 – 1.51 (m, 4H), 1.38 – 1.15 (m, 10H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.6, 138.2, 133.2, 129.8, 127.9, 72.2, 70.7, 38.4, 29.2, 29.1, 28.8, 28.8, 28.3, 26.6, 25.3, 21.6 IR (neat, cm^{-1}): 2926, 2855, 1598, 1463, 1358, 1188, 1097, 951, 812. HRMS (ESI^{+}) calcd. for $C_{18}H_{26}ClIO_3SNa$ [M+Na]$^{+}$: 507.0233, found: 507.0227.



(*E*)-1-(5-chloro-6-iodohex-5-en-1-yl)-1H-benzo[d][1,2,3]triazole (**19**). Yellow oil, 56.3 mg, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.43 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.38 (s, 1H), 4.83 (t, *J* = 7.0 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.55 – 2.03 (m, 2H), 1.73 (dq, *J* = 10.3, 7.5 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3, 137.1, 126.2, 117.9, 73.3, 56.1, 37.7, 37.7, 28.7, 28.6, 23.7, 23.6. IR (neat, cm^{-1}): 3067, 2951, 2864, 1602, 1566, 1448, 1326, 1279, 1145, 1086. HRMS (ESI^{+}) calcd. for $C_{12}H_{14}ClIN_3$ [M+H]$^{+}$: 361.9921, found: 361.9920.

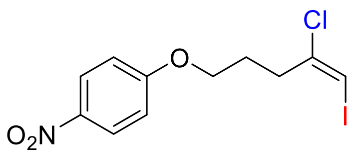


(*E*)-1-(5-chloro-6-iodohex-5-en-1-yl)-1H-indazole (**20**). Yellow oil, 59.8 mg, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.30 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.30 (s, 1H), 4.42 (t, *J* = 7.0 Hz, 2H), 2.60 (t, *J* = 7.3 Hz, 2H), 2.12 – 1.78 (m, 2H), 1.63 (tt, *J* = 10.2, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.4, 137.4, 132.9, 126.1, 124.0, 121.1, 120.4, 108.9, 73.0, 48.4, 37.8, 28.5, 23.9. IR (neat, cm^{-1}): 3067, 2972, 2948, 2870, 1741, 1466, 1428, 1368, 1219, 735. HRMS (EI^{+}) calcd. for $C_{13}H_{14}ClIN_2$ [M]$^{+}$: 359.9890, found: 359.9885.

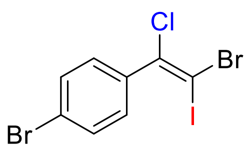


(*E*)-5-chloro-6-iodohex-5-en-1-yl thiophene-2-carboxylate (**21**). Colorless oil, 58.4 mg, 79% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10

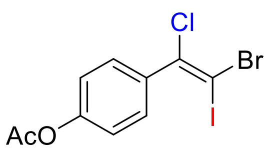
(dd, J = 5.0, 3.7 Hz, 1H), 6.33 (s, 1H), 4.46 – 4.05 (m, 2H), 2.65 (t, J = 7.0 Hz, 2H), 1.95 – 1.61 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1, 137.4, 133.7, 133.3, 132.2, 127.6, 72.9, 64.5, 37.9, 27.4, 23.1. IR (neat, cm^{-1}): 3074, 2958, 2857, 1703, 1522, 1417, 1257, 1090, 752, 721. HRMS (ESI$^+$) calcd. for $C_{13}H_{14}ClIN_2$ [M-I]$^+$: 243.0247, found: 243.0243.



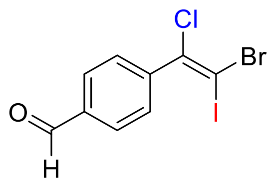
(*E*)-1-((4-chloro-5-iodopent-4-en-1-yl)oxy)-4-nitrobenzene (**22**). White solid, 60.2 mg, 82% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, J = 9.3 Hz, 2H), 6.97 (d, J = 9.2 Hz, 2H), 6.40 (s, 1H), 4.09 (t, J = 6.1 Hz, 2H), 2.83 (t, J = 7.1 Hz, 2H), 2.15 (td, J = 6.9, 1.0 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.8, 141.5, 136.6, 125.9, 114.5, 73.8, 66.8, 35.1, 26.1. IR (neat, cm^{-1}): 2926, 2855, 1598, 1463, 1358, 1188, 1174, 1097, 951, 812. HRMS (ESI$^+$) calcd. for $C_{11}H_{12}ClINO_3$ [M+H]$^+$: 367.9550, found: 367.9542.



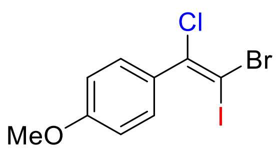
(*E*)-1-bromo-4-(2-bromo-1-chloro-2-iodovinyl)benzene (**23**). Yellow oil, 65.5 mg, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.5, 134.8, 131.8, 130.5, 123.9, 52.6. IR (neat, cm^{-1}): ν= 3084, 2922, 1909, 1573, 1480, 1391,1181, 1069, 1009, 828 HRMS (EI$^+$) calcd. for $C_8H_4Br_2ClI$ [M]$^+$: 419.7407, found: 419.7406.



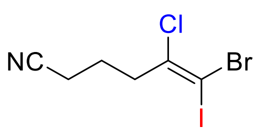
(*E*)-4-(2-bromo-1-chloro-2-iodovinyl)phenyl acetate (**24**). White solid, 72.8 mg, 91% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.9, 151.3, 130.2, 121.8, 52.4, 21.2. IR (neat, cm^{-1}): 2935, 1766, 1727, 1598, 1498, 1366, 1162, 1008, 898, 852. HRMS (EI$^+$) calcd. for $C_{10}H_7BrClIO_2$ [M]$^+$: 399.8363 found: 399.8355.



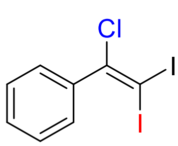
(*E*)-4-(2-bromo-1-chloro-2-iodovinyl)benzaldehyde (**25**). Yellow solid, 63.6 mg, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.3, 145.2, 136.6, 134.4, 129.9, 129.7, 53.3. IR (neat, cm^{-1}): 2828, 2553, 1682, 1605, 1428, 1278, 1205, 926, 864, 763. HRMS (EI^{+}) calcd. for $C_9H_5BrClIO$ [M]$^{+}$: 369.8248 found: 369.8251.



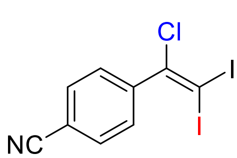
(*E*)-1-(2-bromo-1-chloro-2-iodovinyl)-4-methoxybenzene (**26**). White solid, 62.5 mg, 84% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.2, 136.0, 131.7, 130.3, 113.7, 55.2, 51.1. IR (neat, cm^{-1}): 3006, 2926, 2840, 1896, 1605, 1504, 1296, 1237, 1175, 1026. HRMS (EI^{+}) calcd. for $C_9H_7BrClIO$ [M]$^{+}$: 371.8408 found: 371.8408.



(*E*)-6-bromo-5-chloro-6-iodohex-5-enenitrile (**27**). Yellow oil, 57.2 mg, 86% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.99 – 2.59 (m, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.02 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.4, 118.8, 51.4, 40.6, 23.2, 16.2. IR (neat, cm^{-1}): 2925, 2247, 1561, 1452, 1424, 1177, 1093, 909, 795, 760. HRMS (ESI) calcd. for $C_6H_7BrClIN$ [M+H]$^{+}$ 333.8495, found 333.8489.

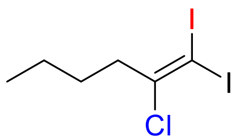


(1-Chloro-2,2-diiodovinyl)benzene (**28**)[2]. Yellow solid, 62.4 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (s, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.6, 139.6, 129.4, 128.6, 128.5, 14.2.

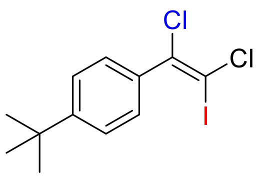


4-(1-Chloro-2,2-diiodovinyl)benzonitrile (**29**). Yellow oil, 71.3 mg, 86% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.6, 137.9, 132.2, 129.3, 117.9, 113.0, 16.2. IR (neat, cm^{1}): 3084,2221,1603,1496,1402,1018,841,726

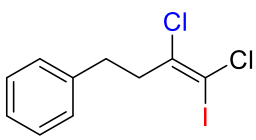
555cm^{-1}. HRMS (EI^{+}) calcd. for $C_9H_4ClI_2N$ [M]$^{+}$: 414.8116 found: 414.8112.



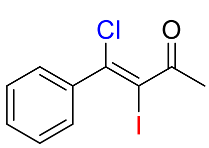
2-Chloro-1,1-diiodohex-1-ene (**30**). Yellow oil, 62.1 mg, 84% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.77 – 2.40 (m, 2H), 1.60 (q, *J* = 7.6, 6.8 Hz, 2H), 1.38 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.1, 41.3, 29.4, 21.7, 13.9, 10.7. IR (neat, cm^{-1}): 2960, 2929, 2869, 1567, 1456, 1296, 1125, 759, 731, 683. HRMS (EI^{+}) calcd. for $C_6H_{10}ClI_2$ [M]$^{+}$: 370.8560, found: 370.8555.



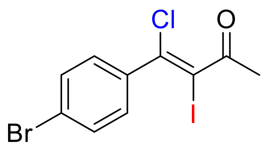
(*E*)-1-(tert-butyl)-4-(1,2-dichloro-2-iodovinyl)benzene (**31**). White solid, 48.8 mg, 69% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.9, 136.2, 133.6, 128.9, 125.4, 69.0, 34.8, 31.2. IR (neat, cm^{-1}): 2971, 2870, 1926, 1463, 1111, 937, 850, 818, 724, 676. HRMS (EI^{+}) calcd. for $C_{12}H_{13}Cl_2I$ [M]$^{+}$: 353.9439, found: 353.9429.



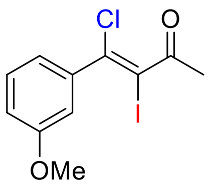
(*E*)-(3,4-dichloro-4-iodobut-3-en-1-yl)benzene (**32**). Yellow oil, 41.1 mg, 63% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.29 (m, 2H), 7.27 – 7.21 (m, 2H), 3.45 – 2.40 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.5, 135.2, 128.5, 126.4, 68.0, 43.6, 33.2. IR (neat, cm^{-1}): 3067, 2948, 2892, 2834, 1612, 1481, 1451, 1247, 1085, 967.HRMS (EI^{+}) calcd. for $C_{10}H_9Cl_2I$ [M]$^{+}$: 325.9126, found: 325.9121.



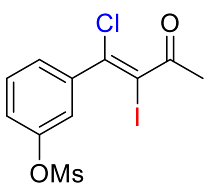
(*E*)-4-chloro-3-iodo-4-phenylbut-3-en-2-one (**33**)[3]. Yellow oil, 44.1 mg, 72% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.46 (m, 2H), 7.45 – 7.36 (m, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.9, 138.3, 131.0, 129.7, 128.7, 128.3, 92.1, 27.2. IR (neat, cm^{-1}): 3061, 2925, 1706, 1616, 1487, 1355, 1442, 1191, 766, 717. HRMS (ESI) Calculated for $C_{10}H_9ClIO$ [M+H]$^{+}$ 306.9386, found 306.9381.



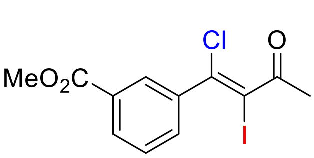
(E)-4-(4-bromophenyl)-4-chloro-3-iodobut-3-en-2-one (**34**). Yellow solid, 58.3 mg, 76% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 197.8, 137.2, 131.8, 130.5, 129.9, 124.2, 92.9, 27.3. IR (neat, cm^{-1}): 3082, 2957, 1922, 1700, 1605, 1479, 1348, 1188, 836, 728. HRMS (EI$^+$) calcd. for $C_{10}H_7BrClIO$ [M]$^+$: 383.8413, found: 383.8407.



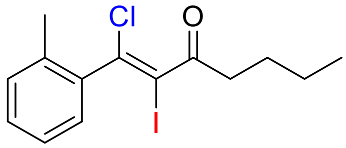
(E)-4-chloro-3-iodo-4-(3-methoxyphenyl)but-3-en-2-one (**35**). Yellow solid, 60.5 mg, 90% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 6.99 (t, J = 2.1 Hz, 1H), 6.95 (dd, J = 8.5, 2.3 Hz, 1H), 3.84 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 197.7, 159.0, 139.2, 130.5, 129.3, 120.8, 115.4, 113.8, 92.0, 55.1, 27.0. IR (neat, cm^{-1}): 2962, 2920, 2849, 1706, 1585, 1487, 1358, 1320, 1264, 1170. HRMS (EI$^+$) calcd. for $C_{11}H_{10}ClIO_2$ [M]$^+$: 335.9409, found: 335.9403.



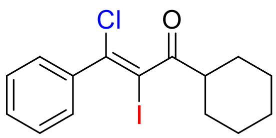
(E)-3-(1-chloro-2-iodo-3-oxobut-1-en-1-yl)phenylmethanesulfonate (**36**). Yellow oil, 59.2 mg, 74% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.45 (m, 2H), 7.45 – 7.41 (m, 1H), 7.36 (dt, J = 7.4, 2.1 Hz, 1H), 3.20 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 197.5, 148.6, 140.1, 130.2, 128.9, 127.8, 123.5, 122.6, 93.5, 37.6, 27.1. IR (neat, cm^{-1}): 3031, 2934, 1701, 1578, 1478, 1352, 1176, 1132, 962, 825. HRMS (EI$^+$) calcd. for $C_{11}H_{10}ClIO_4S$ [M]$^+$: 399.9028, found: 399.9027.



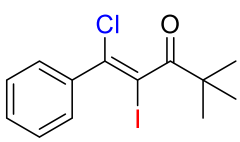
Methyl (E)-3-(1-chloro-2-iodo-3-oxobut-1-en-1-yl)benzoate (**37**). Yellow solid, 42.2 mg, 58% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.18 – 8.14 (m, 1H), 8.08 (ddd, J = 7.8, 1.7, 1.2 Hz, 1H), 7.66 (ddd, J = 7.7, 1.9, 1.2 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 3.94 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 197.7, 166.1, 138.8, 133.2, 130.8, 130.6, 130.1, 129.9, 128.7, 93.3, 52.4, 27.3. IR (neat, cm^{-1}): 2960, 2925, 1717, 1689, 1428, 1303, 1198, 1104, 1076, 728. HRMS (EI$^+$) calcd. for $C_{12}H_{10}ClIO_3$ [M]$^+$: 363.9358, found: 363.9356.



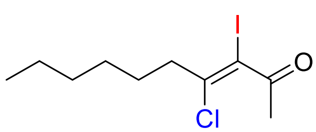
(E)-1-chloro-2-iodo-1-(o-tolyl)hept-1-en-3-one (**38**). Colorless oil, 59.4 mg, 82% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.70 (dd, J = 7.8, 1.3 Hz, 1H), 7.45 (td, J = 7.5, 1.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 2.85 – 2.76 (m, 2H), 2.62 (s, 3H), 1.78 – 1.63 (m, 2H), 1.47 (h, J = 7.4 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 192.5, 141.3, 136.5, 132.7, 132.4, 131.4, 125.8, 90.5, 41.0, 29.0, 21.9, 21.7, 13.9. IR (neat, cm^{-1}): 2960, 2925, 2859, 1672, 1452, 1233, 1031, 731. HRMS (EI^{+}) calcd. for $C_{14}H_{16}ClIO$ [M]$^{+}$: 361.9934, found: 361.9938.



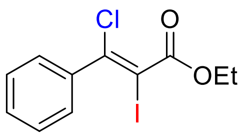
(E)-3-chloro-1-cyclohexyl-2-iodo-3-phenylprop-2-en-1-one (**39**). Yellow solid, 59.8 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.60 – 7.24 (m, 5H), 2.92 (tt, J = 11.5, 3.5 Hz, 1H), 2.00 (dd, J = 14.0, 2.4 Hz, 2H), 1.73 (ddd, J = 11.2, 5.5, 2.4 Hz, 2H), 1.69 – 1.52 (m, 1H), 1.43 (tdd, J = 12.8, 9.7, 3.4 Hz, 2H), 1.30 – 1.01 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 203.4, 138.7, 131.0, 129.7, 128.9, 128.4, 91.0, 48.8, 29.1, 25.8, 25.8. IR (neat, cm^{-1}): 2950, 2922, 2846, 1696, 1442, 1142, 1094, 1024, 717, 693. HRMS (EI^{+}) calcd. for $C_{15}H_{16}ClIO$ [M]$^{+}$: 373.9928, found: 373.9929.



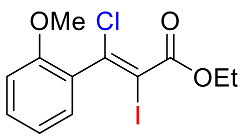
(E)-1-chloro-2-iodo-4,4-dimethyl-1-phenylpent-1-en-3-one (**40**). White solid, 59.2 mg, 85% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.51 – 7.47 (m, 2H), 7.46 – 7.40 (m, 3H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-d) δ 207.5, 138.1, 129.7, 129.3, 129.0, 128.4, 87.9, 44.2, 28.7. IR (neat, cm^{-1}): 2974, 2932, 2873, 1741, 1679, 1362, 1229, 1104, 735, 697. HRMS (EI^{+}) calcd. for $C_{13}H_{14}ClIO$ [M]$^{+}$: 347.9772, found: 347.9768.



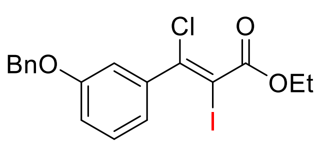
(E)-4-chloro-3-iododec-3-en-2-one (**41**). Yellow oil, 49.6 mg, 79% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 2.97 – 2.53 (m, 2H), 2.45 (s, 3H), 1.64 (p, J = 7.4 Hz, 2H), 1.47 – 1.13 (m, 6H), 1.15 – 0.49 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 197.9, 135.3, 91.5, 41.4, 31.5, 28.2, 27.6, 26.7, 22.5, 14.0. IR (neat, cm^{-1}): 2958, 2927, 2857, 1690, 1558, 1444, 1352, 1203, 1099, 734. HRMS (EI^{+}) calcd. for $C_{10}H_{16}ClIO$ [M]$^{+}$: 313.9885, found: 313.9889.



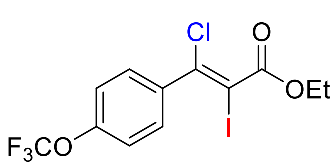
Ethyl (*E*)-3-chloro-2-iodo-3-phenylacrylate (**42**). [4] Yellow oil, 54.4 mg, 81% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 0H), 1.39 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.3, 138.7, 134.7, 129.8, 128.7, 128.6, 128.4, 81.2, 62.7, 13.9.



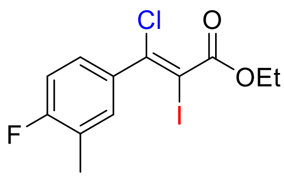
Ethyl (*E*)-3-chloro-2-iodo-3-(2-methoxyphenyl)acrylate (**43**). Yellow oil, 57.1 mg, 78% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.31 – 7.17 (m, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.4, 155.3, 133.1, 130.8, 129.3, 128.0, 120.1, 111.0, 84.2, 62.12, 62.07, 55.3, 13.5. IR (neat, cm^{-1}): 2976, 2941, 2838, 1724, 1595, 1491, 1236, 1024, 756, 672. HRMS (EI^{+}) calcd. for $C_{12}H_{12}ClIO_3$ [M]$^{+}$: 365.9514 found: 365.9511.



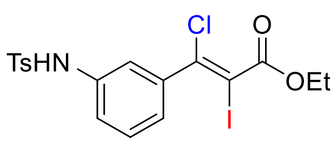
Ethyl (*E*)-3-(3-(benzyloxy)phenyl)-3-chloro-2-iodoacrylate (**44**). Yellow oil, 76.0 mg, 86% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.44 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 8.2 Hz, 2H), 7.12 – 7.06 (m, 2H), 7.04 (ddd, *J* = 8.3, 2.5, 1.0 Hz, 1H), 5.11 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.3, 158.5, 139.9, 136.5, 134.4, 129.6, 128.7, 128.1, 127.5, 121.3, 116.8, 114.9, 81.3, 70.2, 62.7, 14.0. IR (neat, cm^{-1}): 3032, 2981, 1724, 1578, 1454, 1226, 1175, 1026, 776, 691. HRMS (EI^{+}) calcd. for $C_{18}H_{16}ClIO_3$ [M]$^{+}$: 441.9833 found: 441.9823.



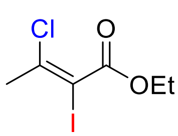
Ethyl (*E*)-3-chloro-2-iodo-3-(4-(trifluoromethoxy)phenyl)acrylate (**45**). Yellow oil, 65.5 mg, 78% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.89, (s, 3F). ^{13}C NMR (100 MHz, Chloroform-*d*) ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.9, 149.7, 136.9, 133.1, 130.5, δ 120.2 (q, J = 256.1 Hz), 120.43, 82.00, 62.65, 13.74. IR (neat, cm^{-1}): 2985, 1726, 1615, 1504, 1242, 1205, 1162, 1027, 902, 854. HRMS (EI^+) calcd. for $C_{12}H_9ClF_3IO_3$ $[M]^+$: 419.9232, found: 419.9232.



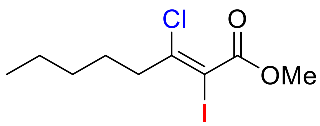
Ethyl (*E*)-3-chloro-3-(4-fluoro-3-methylphenyl)-2-iodoacrylate (**46**). Yellow oil, 62.6 mg, 85% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 (ddd, J = 16.2, 7.4, 2.3 Hz, 2H), 7.03 (t, J = 8.9 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.30 (d, J = 2.0 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.06 – -120.58 (m, 1F). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.1, 161.6 (d, J = 249.1 Hz), 134.3, 133.9, 132.0, 128.2, 125.2 (d, J = 17.6 Hz), 115.0 (d, J = 22.3 Hz), 81.2, 62.6, 14.4, 13.8. IR (neat, cm^{-1}): 3469, 3009, 2974, 2950, 1745, 1494, 1445, 1372, 1226, 1031. HRMS (EI^+) calcd. for $C_{12}H_{11}ClFIO_2$ $[M]^+$: 367.9471, found: 367.9469.



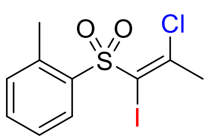
Ethyl (*E*)-3-chloro-2-iodo-3-(3-((4-methylphenyl) sulfonamido) phenyl)acrylate (**47**). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, J = 8.0 Hz, 2H), 7.19 – 6.65 (m, 6H), 4.22 (q, J = 7.0 Hz, 2H), 2.22 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.3, 144.3, 140.0, 137.0, 135.9, 133.9, 130.0, 129.8, 127.6, 125.6, 123.0, 121.7, 82.2, 63.0, 21.7, 14.1. IR (neat, cm^{-1}): 3252, 2982, 1709, 1597, 1465, 1392, 1231, 1154, 1090, 1028. HRMS (ESI^+) calcd. for $C_{18}H_{17}ClINO_4Na$ $[M+Na]^+$: 527.9509 found: 527.9500.



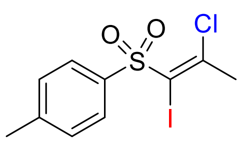
Ethyl (*E*)-3-chloro-2-iodobut-2-enoate (**48**)[4]. Colorless oil, 46.0 mg, 84% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 4.29 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.9, 135.0, 80.9, 62.5, 29.6, 13.9.



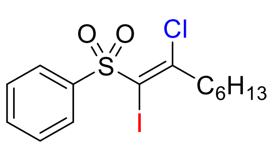
Methyl (*E*)-3-chloro-2-iodooct-2-enoate (**49**). Yellow oil, 56.2 mg, 89% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.84 (s, 3H), 2.75 – 2.42 (m, 2H), 1.77 – 1.57 (m, 2H), 1.42 – 1.18 (m, 4H), 0.98 – 0.70 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.4, 139.7, 79.5, 53.2, 41.7, 30.7, 26.4, 22.4, 13.9. IR (neat, cm^{-1}): 2955, 2929, 2864, 1731, 1614, 1432, 1242, 1021, 790, 674. HRMS (EI^{+}) calcd. for $C_9H_{14}ClIO_2$ [M]$^{+}$: 315.9722, found: 315.9717.



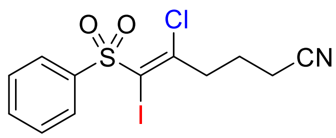
(*E*)-1-((2-chloro-1-iodoprop-1-en-1-yl)sulfonyl)-2-methylbenzene (**50**). White solid, 64.1 mg, 90% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 1H), 7.30 (t, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 3.38 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.0, 141.1, 134.0, 130.9, 130.2, 126.8, 126.7, 101.4, 41.0, 18.8. IR (neat, cm^{-1}): 2918, 2850, 1702, 1619, 1459, 1365, 1314, 1054, 797, 721. HRMS (EI^{+}) calcd. for $C_{10}H_{10}ClIO_2S$ [M]$^{+}$: 355.9129, found: 355.9126.



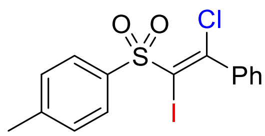
(*E*)-1-((2-chloro-1-iodoprop-1-en-1-yl)sulfonyl)-4-methylbenzene (**51**). White solid, 66.2 mg, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 2.58 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.1, 143.2, 136.0, 129.6, 128.8, 99.2, 34.9, 21.7. IR (neat, cm^{-1}): 2972, 1923, 1738, 1593, 1553, 1362, 1320, 1153, 856, 811. HRMS (EI^{+}) calcd. for $C_{10}H_{10}ClIO_2S$ [M]$^{+}$: 355.9129, found: 355.9124.



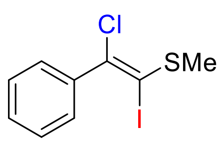
(*E*)-((2-chloro-1-iodooct-1-en-1-yl)sulfonyl)benzene (**52**). Yellow oil, 72.5 mg, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.92 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 3.10 – 2.18 (m, 2H), 1.58 (q, *J* = 7.7 Hz, 2H), 1.50 – 1.08 (m, 6H), 1.06 – 0.38 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.1, 139.3, 133.8, 128.9, 128.6, 98.3, 46.7, 31.4, 28.2, 26.9, 22.4, 14.0. IR (neat, cm^{-1}): ν = 3064, 2956, 2928, 2857, 1550, 1447, 1328, 1157, 1084, 849, 755, 717, 687, 591 cm^{-1}. HRMS (EI^{+}) calcd. for $C_{14}H_{18}ClIO_2S$ [M]$^{+}$: 411.9761, found: 411.9756.



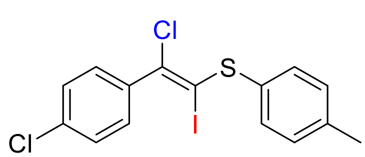
(*E*)-5-chloro-6-iodo-6-(phenylsulfonyl)hex-5-enenitrile (**53**). Yellow oil, 61.6 mg, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.96 (m, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 3.05 – 2.76 (m, 2H), 2.39 (t, *J* = 7.0 Hz, 2H), 2.08 – 1.87 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 138.8, 134.2, 129.1, 128.8, 118.4, 101.0, 45.3, 22.9, 16.4. IR (neat, cm^{-1}): ν = 3064, 2937, 2247, 1552, 1448, 1325, 1155, 1082, 830, 757, 717, 687, 590 cm^{-1}. HRMS (EI^{+}) calcd. for $C_{12}H_{11}ClINO_2S$ [M]$^{+}$: 394.9244, found: 394.9245.



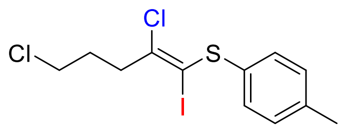
(*E*)-1-((2-chloro-1-iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (**54**). Yellow oil, 73.6 mg, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.35 (m, 1H), 7.34 – 7.27 (m, 2H), 7.23 – 7.15 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.6, 144.8, 136.1, 135.8, 130.0, 129.4, 128.8, 128.4, 128.0, 106.3, 21.7. IR (neat, cm^{-1}): ν = 3059, 2920, 2851, 1592, 1322, 1152, 1082, 811, 719, 692, 661, 610 cm^{-1}.HRMS (EI^{+}) calcd. for $C_{15}H_{12}ClIO_2S$ [M]$^{+}$: 417.9291, found: 417.9285.



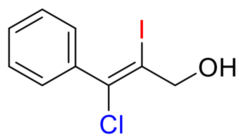
(*E*)-(2-chloro-1-iodo-2-phenylvinyl)(methyl)sulfane (**55**). Yellow oil, 52.7 mg, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 6.91 (m, 5H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.6, 129.1, 129.0, 129.0, 128.3, 128.2, 93.1, 18.5. IR (neat, cm^{-1}): 3056, 2922, 1594, 1556, 1436, 1070, 934, 834, 698 cm^{-1}. HRMS (EI^{+}) Calculated for C_9H_8ClIS[M]$^{+}$: 309.9081, found 309.9074.



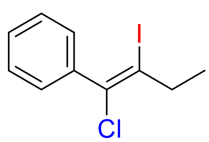
(*E*)-(2-chloro-2-(4-chlorophenyl)-1-iodovinyl)(p-tolyl)sulfane (**56**). Yellow oil, 70.5 mg, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.34 (s, 4H), 7.24 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.0, 139.6, 134.3, 133.8, 130.4, 130.1, 129.8, 128.5, 128.5, 94.2, 21.4. IR (neat, cm^{-1}): 3024, 2918, 1591, 1484, 1392, 1084, 1012, 830, 802, 726, 662 cm^{-1}.HRMS (EI^{+}) calcd. for $C_{15}H_{11}Cl_2IS$ [M]$^{+}$: 419.9003, found: 419.8994.



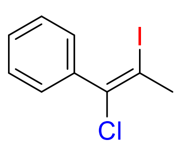
(*E*)-(2,5-dichloro-1-iodopent-1-en-1-yl)(phenyl)sulfane (**57**). Yellow oil, 57.3 mg, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 3.04 – 2.92 (m, 2H), 2.39 (s, 3H), 2.10 – 2.08 (m, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 132.6, 130.0, 128.7, 128.0, 104.1, 43.4, 40.8, 31.5, 21.3. IR (neat, cm^{-1}): 3025, 2924, 2855, 1602, 1494, 1083, 898, 805, 745, 698 cm^{-1}. HRMS (EI^{+}) calcd. for $C_{11}H_{13}Cl_2IS$ [M]$^{+}$: 385.9160, found 385.9166.



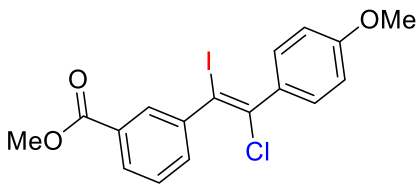
(*E*)-3-chloro-2-iodo-3-phenylprop-2-en-1-ol (**58**)[5]. Yellow solid, 44.1mg, 75% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.34 (m, 5H), 4.63 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.9, 130.4, 129.2, 128.9, 128.4, 101.3, 67.8. IR (neat, cm^{-1}): 3427, 3058, 2906, 1623, 1489, 1442, 1241, 1070, 1024, 873. HRMS (EI^{+}) Calculated for C_9H_8ClIO [M]$^{+}$ 293.9308, found 293.9311.



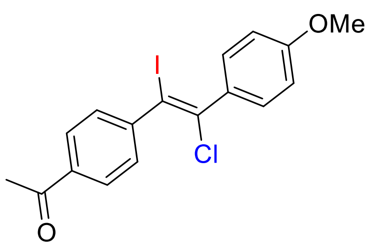
(*E*)-(1-chloro-2-iodobut-1-en-1-yl)benzene (**59**)[1]. Yellow oil, 47.9 mg, 82% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.32 (m, 5H), 2.91 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.3 Hz, 3H). IR (neat, cm^{-1}): ν = 3055, 2970, 2931, 2872, 1594, 1487, 1545, 1104, 1069, 875, 757, 694 cm^{-1}. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 129.2, 128.8, 128.3, 127.7, 102.8, 36.3, 13.1.



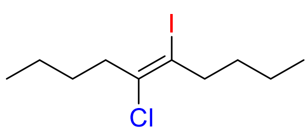
(*E*)-(1-chloro-2-iodoprop-1-en-1-yl)benzene (**60**)[1]. Colorless oil, 43.4 mg, 78% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.32 (m, 5H), 2.76 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.7, 129.1, 129.0, 128.8, 128.3, 92.0, 31.3.



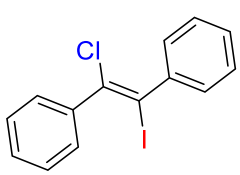
Methyl (*E*)-3-(2-chloro-1-iodo-2-(4-methoxyphenyl)vinyl)benzoate (**61**). White solid, 72.8 mg, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.36 (m, 3H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.3, 159.9, 143.1, 133.3, 133.1, 131.4, 130.5, 130.3, 129.3, 129.3, 128.4, 113.5, 91.2, 55.2, 52.1. IR (neat, cm^{-1}): 3068, 3019, 2952, 2839, 1725, 1602, 1506, 1438, 1292, 1230. HRMS (EI$^+$) calcd. for $C_{17}H_{14}ClIO_3$ [M]$^+$: 427.9676; found: 427.9670.



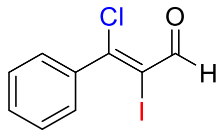
(*E*)-1-(4-(2-chloro-1-iodo-2-(4-methoxyphenyl)vinyl)phenyl)ethan-1-one (**62**). White solid, 75.8 mg, 92% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.3, 160.2, 147.5, 136.6, 133.3, 131.6, 130.7, 129.2, 128.4, 113.7, 91.1, 55.4, 26.7. IR (neat, cm^{-1}): 3069, 2952, 2839, 1725, 1607, 1603, 1438, 1292, 1231, 1174. HRMS (ESI$^+$) calcd. for $C_{17}H_{15}ClIO_2$ [M+H]$^+$: 412.9805 found: 412.9802.



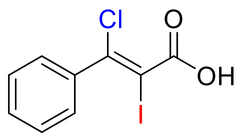
(*E*)-5-chloro-6-iododec-5-ene (**63**). Colorless oil, 54.0 mg, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.66 (q, *J* = 7.2 Hz, 4H), 1.67 – 1.45 (m, 4H), 1.43 – 1.25 (m, 4H), 0.94 (td, *J* = 7.3, 3.3 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 131.5, 99.1, 42.8, 41.6, 30.5, 29.2, 21.8, 21.5, 13.9. IR (neat, cm^{-1}): 2958, 2927, 2863, 1619, 1456, 1379, 1108, 1080, 933, 728. HRMS (EI$^+$) calcd. for $C_{10}H_{18}ClI$ [M]$^+$: 300.0136 found: 300.0113.



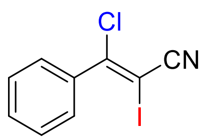
(*E*)-(1-chloro-2-iodoethene-1,2-diyl)dibenzene (**64**)[6]. White solid, 41.5 mg, 61% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.35 (m, 9H), 7.34 – 7.27 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.5, 141.5, 130.2, 128.9, 128.6, 128.3, 93.6. IR (neat, cm^{-1}): 3061, 3016, 1957, 1633, 1487, 1442, 1073, 836, 697, 655. HRMS (EI^+) calcd. for $C_{14}H_{10}ClI$ $[M]^+$: 339.9516 found: 339.9512.



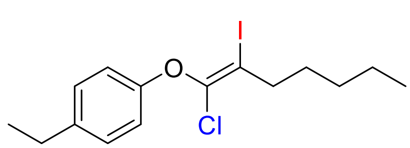
(*E*)-3-chloro-2-iodo-3-phenylacrylaldehyde (**65**). Yellow oil, 43.8 mg, 75% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.45 (s, 1H), 7.60 – 7.50 (m, 2H), 7.52 – 7.42 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.1, 149.1, 139.9, 130.8, 128.6, 128.5, 103.1. IR (neat, cm^{-1}): 3056, 2863, 1737, 1687, 1555, 1483, 1443, 1217, 1098, 877. HRMS (EI^+) calcd. for C_9H_6ClIO $[M]^+$: 291.9146 found: 291.9148.



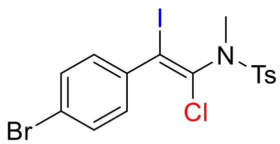
(*E*)-3-chloro-2-iodo-3-phenylacrylic acid (**66**). Yellow solid, 32.0 mg, 52% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.47 – 7.41 (m, 3H). (acid peak?) ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.3, 139.0, 137.0, 130.0, 128.6, 128.5, 80.2. IR (neat, cm^{-1}): 2915, 2810, 2633, 2518, 1686, 1574, 1445, 1407, 1264, 912. HRMS (EI^+) calcd. for $C_9H_6ClIO_2$ $[M]^+$: 307. 9096 found: 307.9093.



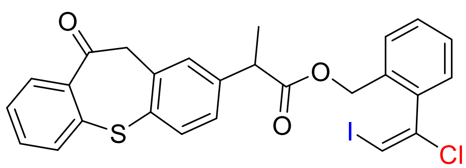
(*E*)-3-chloro-2-iodo-3-phenylacrylonitrile (**67**). Yellow oil, 24.8 mg, 43% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.37 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 136.9, 131.3, 128.7, 128.6, 116.7, 52.6. IR (neat, cm^{-1}): 2921, 2211, 1599, 1574, 1438, 1218, 1156, 896, 733, 693 cm^{-1}. HRMS (EI^+) calcd. for C_9H_5ClIN $[M]^+$: 288.9155 found: 288.9162.



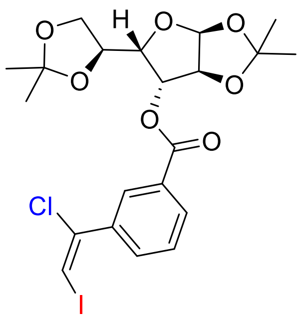
(*E*)-1-((1-chloro-2-iodohept-1-en-1-yl)oxy)-4-ethylbenzene (**68**). Yellow oil, 54.4 mg, 72% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 2.77 – 2.44 (m, 4H), 1.63 (dd, *J* = 9.1, 5.5 Hz, 2H), 1.40 (p, *J* = 4.0, 3.4 Hz, 4H), 1.26 (t, *J* = 7.6 Hz, 3H), 0.96 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.8, 140.0, 134.8, 129.0, 116.5, 86.8, 38.9, 30.6, 28.3, 28.2, 22.5, 15.6, 14.1. IR (neat, cm^{-1}): ν = 2958, 2926, 2856, 1604, 1503, 1203, 1166, 1049, 830, 727, 682 cm^{-1}.HRMS (EI^{+}) calcd. for $C_{15}H_{20}ClIO$ $[M]^{+}$: 378.0247 found: 378.0242.



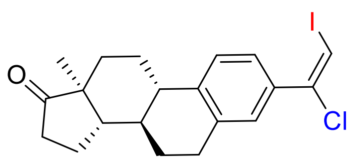
(*E*)-N-(2-(4-bromophenyl)-1-chloro-2-iodovinyl)-N,4-dimethylbenzenesulfonamide (**69**), Yellow solid, 75mg, 72% yield ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.01 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.7, 139.7, 134.4, 131.6, 130.4, 129.6, 129.6, 128.8, 123.2, 99.2, 77.3, 77.0, 76.8, 35.1, 21.7. IR (neat, cm^{-1}): 2931, 1574, 1356, 1173, 987, 771, 662, 554 cm^{-1}.HRMS (ESI^{+}) calcd. for $C_{16}H_{14}ClIBrNO_2SNa$ $[M+Na]^{+}$: 547.8560 found: 547.8554.



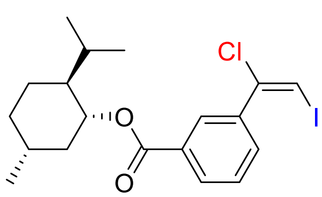
(*E*)-2-(1-chloro-2-iodovinyl)benzyl -2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (**70**). Yellow oil, 93.0 mg, 81% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.9, 4.0 Hz, 2H), 7.52 – 7.28 (m, 6H), 7.22 (ddd, *J* = 24.7, 7.0, 2.3 Hz, 2H), 6.79 (s, 1H), 5.16 (d, *J* = 17.2 Hz, 2H), 4.38 (s, 2H), 3.82 (d, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.3, 173.5, 142.5, 140.2, 137.9, 137.8, 136.2, 133.4, 133.2, 132.9, 132.5, 131.6, 131.5, 130.9, 129.8, 129.3, 129.1, 128.8, 128.7, 126.9, 126.5, 77.7, 64.2, 51.1, 45.2, 18.5. IR (neat, cm^{-1}): 3062, 2928, 1734, 1673, 1587, 1456, 1426, 1284, 1154, 1073, 886, 757, 684 cm^{-1}. HRMS (ESI^{+}) Calculated for $C_{26}H_{21}ClIO_3S$ $[M+H]^{+}$: 574.9944, found 574.9935.



(3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl-3-((*E*)-1-chloro-2-iodovinyl)benzoate (**71**). Yellow oil, 74.8 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (t, *J* = 1.8 Hz, 1H), 8.12 – 7.89 (m, 1H), 7.75 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 6.85 (s, 1H), 5.96 (d, *J* = 3.7 Hz, 1H), 5.50 (d, *J* = 2.9 Hz, 1H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.39 (ddd, *J* = 8.1, 5.8, 4.8 Hz, 1H), 4.32 (dd, *J* = 8.1, 2.9 Hz, 1H), 4.14 (dd, *J* = 8.6, 5.9 Hz, 1H), 4.09 (dd, *J* = 8.6, 4.9 Hz, 1H), 1.61 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 138.3, 133.9, 132.8, 130.6, 130.4, 129.8, 128.7, 112.4, 109.5, 105.2, 83.4, 80.0, 74.4, 72.6, 67.4, 26.8, 26.8, 26.2, 25.3. IR (neat, cm^{-1}): ν = 3447, 3069, 2987, 2860, 1729, 1630, 1378, 1234, 1156, 1077, 945, 844, 754, 673 cm^{-1}. HRMS (ESI$^+$) Calculated for $C_{21}H_{25}ClIO_7$ $[M+H]^+$: 551.0328, found 551.0325.

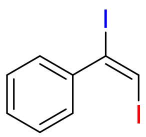


(8R,9S,13S,14S)-3-((*E*)-1-chloro-2-iodovinyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**72**). Yellow oil, 63.4 mg, 72% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (s, 2H), 7.30 (s, 1H), 6.74 (s, 1H), 3.07 – 2.89 (m, 2H), 2.54 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.35 (td, *J* = 10.8, 4.3 Hz, 1H), 2.25 – 1.90 (m, 4H), 1.73 – 1.62 (m, 2H), 1.59 – 1.44 (m, 4H) , 0.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.4, 136.6, 135.0, 134.2, 129.4, 126.4, 125.2, 72.2, 50.5, 48.0, 44.5, 37.9, 35.9, 31.6, 29.3, 26.4, 25.6, 21.6, 13.9. IR (neat, cm^{-1}): ν = 3053, 2918, 2851, 1737, 1402, 1033, 841, 822, 794, 705, 667 cm^{-1}. HRMS (ESI$^+$) Calculated for $C_{20}H_{23}ClIO$ $[M+H]^+$: 441.0482, found 441.0479.

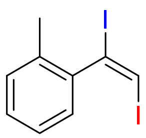


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl-3-((*E*)-1-chloro-2-iodovinyl)benzoate (**73**). Yellow oil, 62.4 mg, 70% yield.

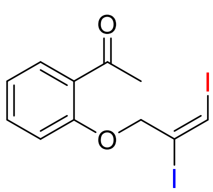
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.61 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 6.86 (s, 1H), 4.97 (td, *J* = 10.9, 4.4 Hz, 1H), 2.16 (d, *J* = 12.0 Hz, 1H), 2.00 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.62 – 1.53 (m, 2H), 1.27 – 1.05 (m, 3H), 0.95 (dd, *J* = 6.8, 4.3 Hz, 6H), 0.82 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 137.9, 133.1, 131.1, 130.5, 130.3, 128.4, 75.3, 73.9, 47.3, 41.0, 34.3, 31.5, 26.5, 23.7, 22.1, 20.8, 16.6. IR (neat, cm^{-1}): ν = 3068, 2954, 2925, 2868, 1717, 1454, 1293, 1237, 1107, 884, 781, 690 cm^{-1}. HRMS (ESI^+) Calculated for $C_{19}H_{25}ClIO_2$ $[M+H]^+$: 447.0588, found 447.0582.



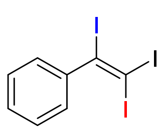
(*E*)-(1,2-diiodovinyl)benzene (**74**).[7] White solid, 53.4 mg, 75% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 5H), 7.26 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.1, 128.9, 128.5, 128.4, 96.1, 80.7.



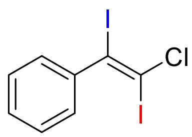
(*E*)-1-(1,2-diiodovinyl)-2-methylbenzene (**75**) .[8] Yellow solid, 57.7 mg, 78% yield. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.23 (m, 3H), 7.21 (ddd, *J* = 7.4, 1.6, 0.8 Hz, 1H), 7.11 (dd, *J* = 7.4, 1.7 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.9, 134.5, 130.6, 129.0, 127.6, 126.3, 96.2, 82.8, 19.5.



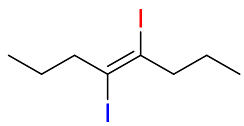
(*E*)-1-(2-((2,3-diiodoallyl)oxy)phenyl)ethan-1-one (**76**). Yellow oil, 59.9 mg, 70% yield. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.3, 1.9 Hz, 1H), 7.29 (s, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.94 – 6.83 (m, 1H), 4.85 (d, *J* = 1.0 Hz, 2H), 2.74 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.6, 156.5, 133.5, 130.7, 129.0, 121.7, 112.9, 96.9, 83.4, 75.5, 32.6. IR (neat, cm^{-1}): 3084, 2972, 2918, 1741, 1654, 1592, 1438, 1358, 1226, 1024. HRMS (ESI^+) Calculated for $C_{11}H_{10}I_2O_2$ $[M]^+$: 427.8770, found 427.8758.



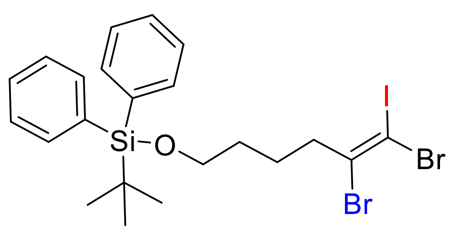
(1,2,2-triiodovinyl)benzene (**77**). Yellow solid, 86.7 mg, 90% yield. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.30 (m, 3H), 7.29 – 7.22 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.7, 128.7, 128.6, 127.4, 112.5, 22.5. IR (neat, cm^{-1}): 3049, 2919, 1972, 1951, 1482, 1439, 1276, 1069, 1027, 859. HRMS (EI^+) calcd. for $C_8H_5ClI_2$ $[M]^+$: 341. 389.8164, found: 389.8163.



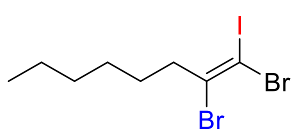
(*E*)-(2-chloro-1,2-diiodovinyl)benzene (**78**).[9] White solid, 66.3 mg, 85% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.32 (m, 3H), 7.32 – 7.22 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.9, 128.9, 128.6, 128.4, 100.5, 73.4.



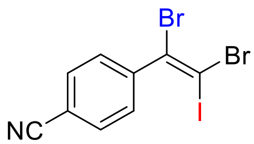
(*E*)-4,5-diiodooct-4-ene (**79**).[8] Colorless oil, 58.2 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.75 – 2.38 (m, 4H), 1.59 (h, *J* = 7.4 Hz, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 101.8, 52.3, 21.39, 12.59.



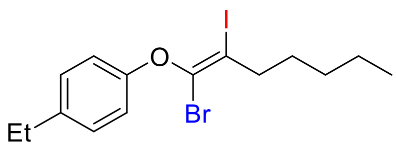
(*E*)-tert-butyl((5,6-dibromo-6-iodohex-5-en-1-yl)oxy)diphenylsilane (**80**). Colorless oil, 102.9 mg, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.58 (m, 4H), 7.51 – 7.31 (m, 6H), 3.71 (t, *J* = 6.1 Hz, 2H), 2.85 – 2.55 (m, 2H), 1.84 – 1.70 (m, 2H), 1.61 (dt, *J* = 8.6, 6.0 Hz, 2H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.5, 133.8, 131.0, 129.5, 127.5, 63.2, 49.5, 44.5, 31.1, 26.8, 24.1, 19.1. IR (neat, cm^{-1}): 3074, 2934, 2857, 1473, 1427, 1111, 1006, 825, 742, 700. HRMS (EI$^+$) calcd. for $C_{22}H_{27}Br_2IOSi$ [M-(H-^{t}Bu)+H]$^+$: 562.8539, found:562.8530.



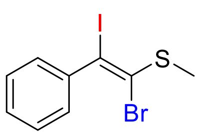
(*E*)-1,2-dibromo-1-iodooct-1-ene (**81**). Colorless oil, 63.8 mg, 81% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.74 – 2.56 (m, 2H), 1.62 (dq, *J* = 12.3, 7.6, 7.2 Hz, 2H), 1.44 – 1.26 (m, 6H), 1.02 – 0.74 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 131.3, 49.2, 44.9, 31.5, 28.1, 27.7, 22.5, 14.0. IR (neat, cm^{-1}): 2955, 2920, 2855, 1644, 1456, 1376, 1278, 1125, 777, 724. HRMS (EI$^+$) calcd. for $C_8H_{13}Br_2I$ [M]$^+$: 393.8423, found: 393.8420.



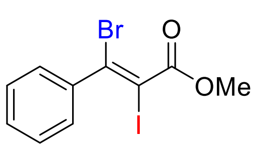
(*E*)-4-(1,2-dibromo-2-iodovinyl)benzonitrile (**82**). Yellow solid, 68.6mg, 84% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.3, 132.6, 129.7, 123.6, 118.1, 113.1, 55.2. IR (neat, cm^{-1}): 2916. 2221.1402.1600.1017.833.788. HRMS (EI$^+$) calcd. for $C_9H_4Br_2I$ [M]$^+$: 410.7755, found: 410.7750.



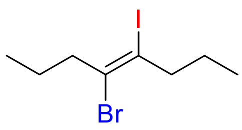
(*E*)-1-((1-bromo-2-iodohex-1-en-1-yl)oxy)-4-ethylbenzene (**83**). Yellow oil, 60.4 mg, 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 7.9 Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 4H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.40 (s, 4H), 1.26 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.9, 140.1, 129.0, 125.5, 116.7, 88.4, 40.7, 30.6, 28.2, 28.2, 22.5, 15.6, 14.0. IR (neat, cm^{-1}): ν = 2958, 2926, 2856, 1636, 1604, 1503, 1460, 1203, 1049, 830, 727, 682 cm^{-1}. HRMS (EI$^+$) calcd. for $C_{15}H_{20}BrIO$ [M]$^+$: 421.9742, found: 421.9740.



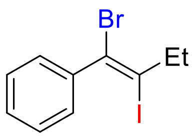
(*E*)-(1-bromo-2-iodo-2-phenylvinyl)(methyl)sulfane (**84**). Yellow oil, 60 mg, 85% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.25 (m, 5H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 128.7, 128.4, 128.3, 118.7, 94.9, 20.6. HRMS (EI$^+$) calcd. for C_9H_8BrIS [M]$^+$: 353.8575, found: 353.8570.



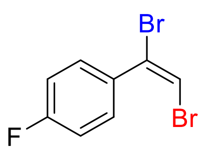
methyl (*E*)-3-bromo-2-iodo-3-phenylacrylate (**85**).[10] Yellow oil, 50 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.25 (m, 5H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.2, 140.6, 129.7, 128.6, 128.5, 123.1, 81.6, 53.5. IR (neat, cm^{-1}): 2951, 2253, 1726, 1613, 1432, 1243, 1205, 1017, 907, 727. MS (EI$^+$) calcd. for $C_{10}H_8BrIO_2$: 365.9, found: 365.9.



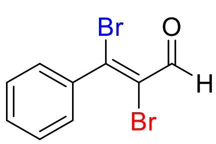
(E)-4-bromo-5-iodooct-4-ene (**86**).[10] Colorless oil, 44.2 mg, 70% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.75 – 2.70 (m, 2H), 2.69 – 2.65 (m, 2H), 1.86 – 1.36 (m, 4H), 1.01 – 0.90 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 122.6, 99.8, 47.5, 46.9, 21.6, 21.0, 13.0, 12.8. IR (neat, cm^{-1}): 2962, 2932, 2873, 1461, 1428, 1379, 1111, 1090, 885, 745. HRMS (EI$^+$) calcd. for $C_8H_{14}BrI$ [M]$^+$: 315.9318, found: 315.9315.



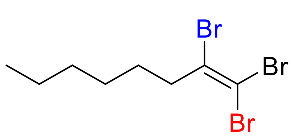
(E)-(1-bromo-2-iodobut-1-en-1-yl)benzene (**87**).[10] Yellow oil, 50.4 mg, 75% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.27 (m, 5H), 2.87 (q, J = 7.4 Hz, 2H), 1.19 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.9, 129.1, 128.6, 128.4, 116.8, 103.7, 39.4, 12.9. IR (neat, cm^{-1}): ν = 3050, 2972, 2933, 2872, 1594, 1544, 1104, 1069, 875, 758, 690 cm^{-1}.HRMS (EI$^+$) calcd. for $C_{10}H_{10}BrI$ [M]$^+$: 335.9011, found: 335.9009.



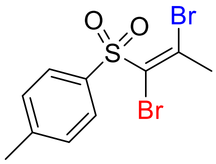
(E)-1-(1,2-dibromovinyl)-4-fluorobenzene (**88**).[11] Yellow oil, 25 mg, 45% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (dd, J = 8.8, 5.2 Hz, 2H), 7.08 (t, J = 8.7 Hz, 2H), 6.80 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.9 (d, J = 250.5 Hz), 133.1(d, J = 3.7 Hz), 131.3 (d, J = 8.4 Hz), 120.2, 115.4 (d, J = 22.1 Hz), 103.4. MS (EI) calcd. for $C_8H_5FBr_2$: 277.9, found: 277.9.



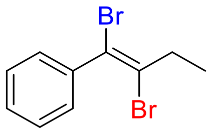
(E)-2,3-dibromo-3-phenylacrylaldehyde (**89**).[12] Yellow oil, 47.8 mg, 83% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.54 – 7.50 (m, 2H), 7.49 – 7.44 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 185.9, 139.2, 137.5, 130.6, 128.5, 128.5, 120.8. IR (neat, cm^{-1}): 3056, 2869, 1678, 1562, 1486, 1443, 1377, 1214, 1108, 717. HRMS (EI$^+$) calcd. for $C_9H_6Br_2O$ [M]$^+$: 287.8785, found: 287.8776.



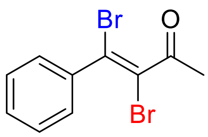
1,1,2-tribromooct-1-ene (**90**). Colorless oil, 62.9 mg, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.79 – 2.50 (m, 2H), 1.73 – 1.54 (m, 2H), 1.30 (p, J = 4.3, 3.3 Hz, 6H), 0.98 – 0.81 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 129.7, 86.7, 40.8, 31.3, 28.0, 27.4, 22.4, 14.0. IR (neat, cm^{-1}): 2955, 2926, 2857, 1455, 1378, 1125, 824, 802, 755, 724. HRMS (EI$^+$) calcd. for $C_8H_{13}Br_3$ [M]$^+$: 345.8542, found: 345.8538.



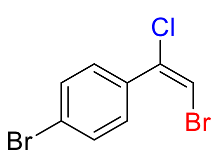
(*E*)-1-((1,2-dibromoprop-1-en-1-yl)sulfonyl)-4-methylbenzene (**91**). White solid, 50.7 mg, 72% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 2.61 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.4, 129.7, 128.8, 128.6, 120.9, 33.3, 21.8. IR (neat, cm^{-1}): 2932, 1922, 1595, 1560, 1327, 1305, 1153, 1080, 871, 811. HRMS (EI$^+$) calcd. for $C_{10}H_{10}Br_2O_2S$ [M]$^+$: 351.8763, found: 351.8762.



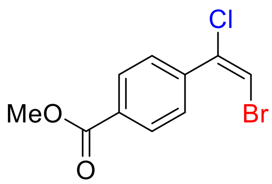
(*E*)-(1,2-dibromobut-1-en-1-yl)benzene (**92**).[11] Yellow oil, 35 mg, 61% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.32 (m, 5H), 2.90 (q, *J* = 7.4 Hz, 2H), 1.27 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*)) δ 140.9, 129.1, 128.6, 128.2, 124.9, 115.6, 35.1, 12.1. MS (EI) calcd. for $C_{10}H_{10}Br_2$: 287.9, found: 287.9.



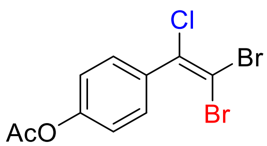
(*E*)-3,4-dibromo-4-phenylbut-3-en-2-one (**93**).[13] Colorless oil, 41.7 mg, 69% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.28 (m, 5H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.4, 138.5, 132.9, 130.3, 128.8, 128.7, 124.6, 29.3. IR (neat, cm^{-1}): 3062, 2920, 2852, 1701, 1568, 1487, 1443, 1353, 1228, 1186. HRMS (EI$^+$) calcd. for $C_{10}H_8Br_2O$ [M]$^+$: 301.8942, found: 301.8932.



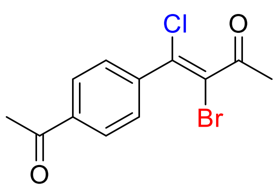
(*E*)-1-bromo-4-(2-bromo-1-chlorovinyl)benzene (**94**). Yellow oil, 28.2 mg, 48% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.67 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.4, 131.7, 131.5, 130.6, 123.8, 102.5. IR (neat, cm^{-1}): ν = 3072, 2923, 2854, 1505, 1477, 1066, 1008, 880, 824, 777, 725, 672, 626, cm^{-1}.HRMS (EI$^+$) calcd. for $C_8H_5Br_2Cl$ [M]$^+$: 293.8447, found: 293.8445.



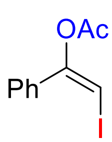
Methyl (*E*)-4-(2-bromo-1-chlorovinyl)benzoate (**95**). Yellow oil, 27.4 mg, 50% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 6.71 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.9, 139.4, 131.4, 130.5, 129.1, 128.6, 102.9, 52.0. IR (neat, cm^{-1}): ν = 3078, 2950, 1719, 1607, 1434, 1270, 1160, 771, 730, 697. HRMS (EI^{+}) calcd. for $C_{10}H_8BrClO_2$ [M]$^{+}$: 273.9396, found: 273.9389.



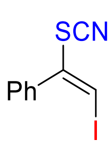
4-(2,2-Dibromo-1-chlorovinyl)phenyl acetate (**96**). Yellow oil, 66.1 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.0, 151.2, 134.6, 133.4, 130.2, 121.6, 89.6, 21.2. IR (neat, cm^{-1}): 2936, 1769, 1505, 1369, 1160, 1020, 898, 850, 791, 724. HRMS (EI^{+}) calcd. for $C_{10}H_7Br_2ClO_2$ [M]$^{+}$: 351.8496, found: 351.8491.



(*E*)-4-(4-acetylphenyl)-3-bromo-4-chlorobut-3-en-2-one (**97**). White solid, 24.6 mg, 41% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 2.63 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.9, 195.0, 140.6, 137.6, 129.0, 128.2, 116.0, 28.4, 26.6. IR (neat, cm^{-1}): 3009, 2915, 1713, 1683, 1599, 1401, 1358, 1268, 1195, 857. HRMS (EI^{+}) calcd. for $C_{12}H_{10}BrClO$ [M]$^{+}$: 299.9553, found: 299.9548.

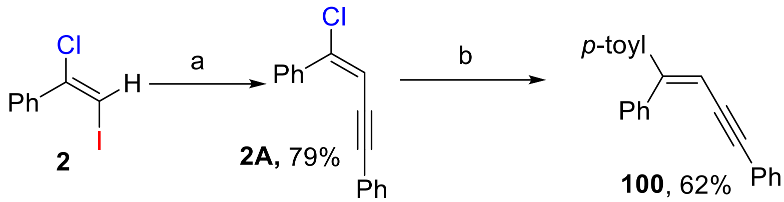


(*E*)-2-iodo-1-phenylvinyl acetate (**98**).[14] Colorless oil, 31.6 mg, 55% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.46 (m, 2H), 7.38 (dd, *J* = 5.1, 2.1 Hz, 3H), 6.34 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 151.2, 134.5, 129.5, 128.9, 128.2, 67.1, 20.8.



(*E*)-(2-iodo-1-thiocyanatovinyl)benzene (**99**)[15]. Colorless oil, 25.7 mg, 45% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 5H), 7.28 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.0, 131.0, 130.3, 129.1, 129.0, 109.3, 81.3.

13. Synthesis of 100



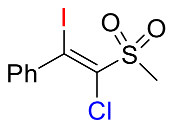
Sonogashira coupling. A mixture of **2** (52.8 mg, 0.2 mmol), phenylacetylene (28.6 mg, 0.28 mmol), $Pd(PPh_3)Cl_2$ (7 mg, 5mol%) and CuI (5.7 mg, 15 mol%) in dry toluene (0.6 mL) was added Et_3N (0.1 mL, 0.9 mmol). After stirring overnight at 80 °C under nitrogen, the reaction mixture was filtered through celite and the solvent was removed by rotary evaporation. The resulting residue was purified by chromatography on silica gel to give the desired product **2A** (37.6 mg, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.37 (m, 5H), 7.36 – 7.29 (m, 3H), 6.31 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.0, 136.1, 131.4, 129.7, 128.6, 128.6, 128.4, 128.4, 127.9, 123.0, 108.3, 94.7, 86.3. HRMS (EI$^+$) calcd. for $C_{16}H_{11}Cl$: 238.0549, found: 238.0546.

Suzuki coupling. A mixture of **2A** (23.8 mg, 0.1 mmol), *p*-Me-$C_6H_4B(OH)_2$ (20.4 mg, 0.15 mmol), $Pd(OAc)_2$ (2.3 mg, 10 mol%) and Cs_2CO_3 (65 mg, 0.2 mmol) in dry 1,4-dioxane (1 mL) was stirred at 90 °C under nitrogen for 8 h. After the completion of the reaction, the reaction mixture was filtered through celite and the solvent was removed by rotary evaporation. The resulting residue was purified by chromatography on silica gel to give the desired products **100** (18.2 mg, 62%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 5.9 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.30 – 7.19 (m, 7H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.21 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.7, 139.3, 138.5, 138.3, 131.3, 130.2, 129.0, 128.2, 128.1, 127.9, 123.7, 106.2, 93.3, 89.3, 21.2. HRMS (EI$^+$) calcd. for $C_{23}H_{18}$: 294.1409, found: 294.1414.

14. Synthesis of 101

To a 20 mL vial equipped a stirring bar, **55** (61.8 mg, 0.2 mmol), 77% *m*CPBA (90 mg, 0.4 mmol), and DCM (4 mL) were added at room temperature. Then the reaction mixture was stirred at room temperature for 3 hours and then saturated $NaHCO_3$ (15 mL) was added. The resulting mixture was extracted with DCM (3 × 20 mL). The combined organic extracts were concentrated under reduced pressure and purified by flash chromatography on silica gel to give the desired product **101** (54.5 mg, 80%).



(*E*)-(2-chloro-1-iodo-2-(methylsulfonyl)vinyl)benzene (**101**). White solid, 27.3 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.38 – 7.31 (m, 1H), 7.32 – 7.24 (m, 2H), 3.32 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.0, 130.4, 129.6, 128.6, 127.2, 101.0, 40.9. IR (neat, cm^{-1}): 3008, 2929, 1559, 1479, 1323, 1147, 978, 757, 706, 510 cm^{-1}. HRMS (EI^{+}) calcd. for $C_9H_8ClIO_2S$ [M]$^{+}$: 341.8978, found: 341.8973.

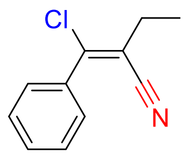
15. Synthesis of 58

To a solution of ester **42** (67.2 mg, 0.2 mmol, 1.0 eq) in DCM (2 mL) at 0 °C was added diisobutylaluminum hydride as a 1 M solution in hexanes (0.5 mL, 0.5 mmol). The reaction was warmed to room temperature and stirred for 2 h. Methanol (1 mL) was carefully added dropwise to quench the reaction. Ether (5 mL) and a saturated solution of Rochelle's salt (3 mL) were then introduced, and the resulting mixture was stirred until both layers became clear. The layers were separated, and the organic phase was dried over $NaSO_4$, filtered, and concentrated. Purification by column chromatography on silica gel eluting with 10 % EtOAc in hexanes gave the desired compound **58** (43mg,74%).

Using the same procedure, Aldehyde **65** could also be reduced to compound **58** (45.7mg, 78%)

16. Synthesis of 102

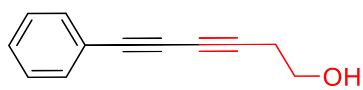
A mixture of **59** (0.2 mmol, 58 mg), $Zn(CN)_2$ (0.2mmol, 23 mg) and CuI (0.24 mmol, 45 mg) in DMF 1 mL was stirred at 100 ℃ for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (4ml), filtered through a short of silica gel. The organic oil was added to a saturated aqueous solution and washed with EtOAc (3 x 15 mL). The combined organic extracts were concentrated under reduced pressure and purified by flash chromatography on silica gel to give the desired product **102** (33.4 mg, 89%).



(*E*)-2-(chloro(phenyl)methylene)butanenitrile (**102**). Colorless oil,33.4mg, 89% yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.50 (m, 2H), δ 7.45 – 7.49 (m, 3H) 2.62 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 136.2, 130.7, 128.6, 128.5, 117.5, 113.7, 77.4, 77.1, 76.8, 26.3, 11.8. IR (neat, cm^{-1}): 2976, 2160, 1605, 1450, 1402, 906, 755, 693 cm^{-1}. MS (EI) calcd. for $C_{11}H_{10}ClN$: 191.1, found: 191.1.

17. Synthesis of 103

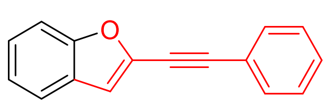
A mixture of **74** (0.2 mmol,71 mg), 3-butyn-1-ol (0.4 mmol, 28 mg), $Pd(OAc)_2$ (5 mol%, 2.2 mg), CuI (5 mol%, 2mg), Et_3N (0.2 mL), and THF (0.8 mL) was stirred under an argon atmosphere at rt for 24 h. Upon complete consumption of the starting material, the reaction mixture was filtered and evaporated. The residue was purified by flash column chromatography to afford products **103** (26.5 mg, 78% yield).



6-Phenylhexa-3,5-diyn-1-ol (**103**). Colorless oil, 26.5 mg, 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.41 (m, 2H), 7.36 – 7.27 (m, 3H), 3.79 (t, *J* = 6.3 Hz, 2H), 2.63 (t, *J* = 6.3 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 129.1, 128.4, 121.8, 81.1, 75.4, 74.0, 66.8, 60.8, 24.0. IR (neat, cm^{-1}):3324, 2285,1489, 1414,1375,1036, 946, 752, 686, 542 cm^{-1}. MS (EI) calcd. for $C_{12}H_{10}O$: 170.2, found: 170.2.

18. Synthesis of 104

A mixture of **74** (0.2 mmol,71 mg), 2-Ethynylphenol (0.4 mmol, 47 mg), $Pd(OAc)_2$ (2mol%,1 mg), CuI (5 mol%, 2 mg), Et_3N (0.2 mL), and THF (0.8 mL) was stirred under an argon atmosphere at r.t. for 18h.Then heat to 100℃ for 6h. Upon complete consumption of the starting material, Then the mixture was filtered and evaporated, the residue was purified by flash column chromatography to afford products **104** (26.1 mg, 61% yield).

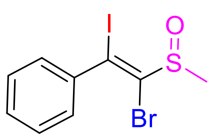


2-(Phenylethynyl)benzofuran (**104**), colorless oil, 26.6 mg, 61% yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.71 – 7.64 (m, 3H), 7.58

(dq, J = 8.3, 0.9 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.46 – 7.41 (m, 1H), 7.37 – 7.29 (m, 1H), 7.11 (s, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 154.9, 138.8, 131.7, 129.2, 128.5, 127.8, 125.6, 123.3, 121.9, 121.2, 111.6, 111.3, 95.1, 79.7. IR (neat, cm^{-1}): 3060, 2923, 1596, 1441, 1145, 970, 855,734, 687,645 cm^{-1}. MS (EI) calcd. for $C_{16}H_{10}O$: 218.1, found: 218.1.

19. Synthesis of 105

To a well-stirred solution of 85 (73mg,0.2mmol), in aqueous-acetonitrile (3:1, 1.2ml) was added dropwise a solution of Oxone (0.14mmol) in water (1.2ml). Stirring was continued and the reaction was monitored by TLC. Upon completion of the reaction, the mixture was diluted with chilled water. The resultant sulfoxide was extracted with ethyl acetate. The combined organic extracts were concentrated under reduced pressure and purified by flash chromatography on silica gel to give the desired product **105** (54 mg, 71%).



(*E*)-(2-bromo-1-iodo-2-(methylsulfinyl)vinyl)benzene (**105**). White solid, 54 mg, 71% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 6.87 (m, 5H), 2.65 (s, 3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.0, 131.3, 129.6, 128.6, 128.2, 99.3, 39.0. IR (neat, cm^{-1}): 2915, 2854, 1596, 1727, 1296, 1064, 943, 693 cm^{-1}. HRMS (EI$^+$) calcd. for C_9H_8BrIOS $[M]^+$: 369.8524, found: 369.8519.

20. Structure assignment of compound 18

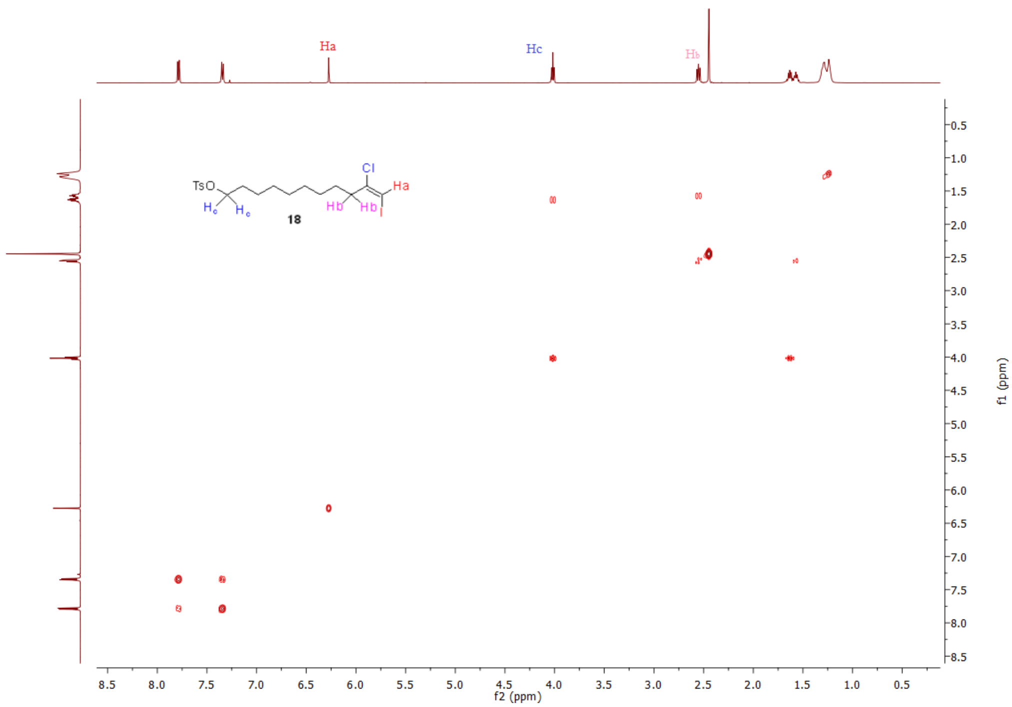


Figure S1. COSY of 18

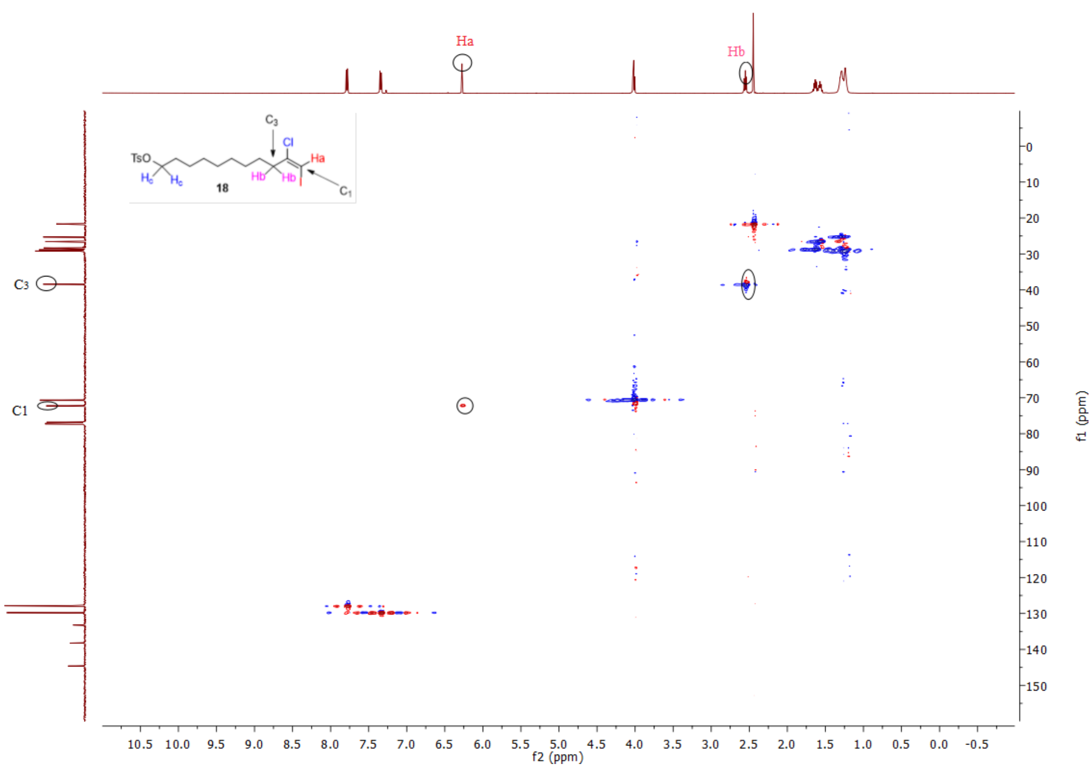


Figure S2. HSQC of 18

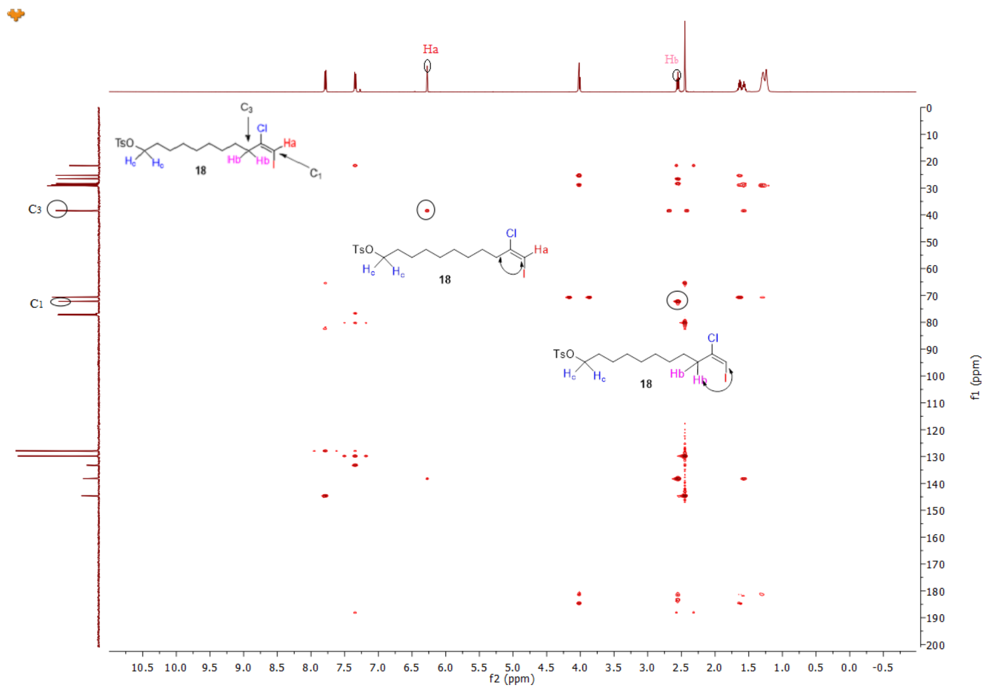


Figure S3. HMBC of **18.**

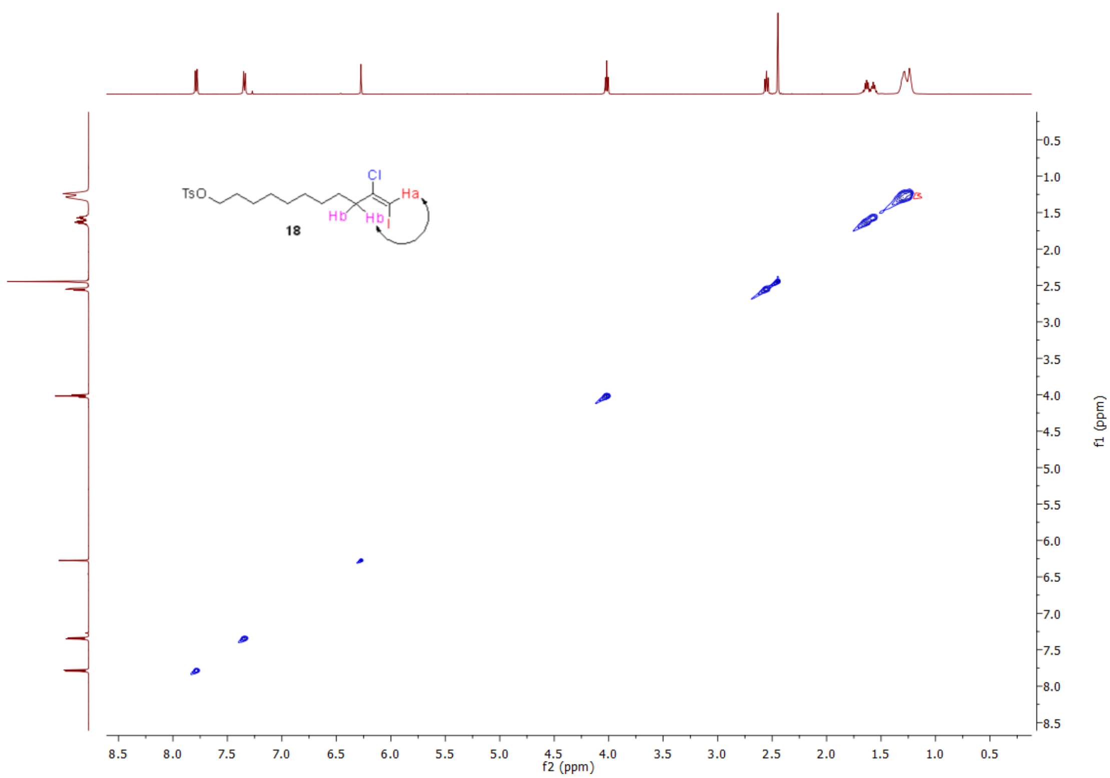


Figure S4. NOSEY of **18.**

The assignment of C_3 and C_1 were confirmed as indicated by the observation of a ^1H-^{13}C HSQC interaction (Figure S2). The interaction was observed between the H_a and C_3 as well as H_c and C_1 in the ^1H-^{13}C HMBC experiment (Figure 3) which indicated that the C_1 substituted with iodine. According to Zhu's report[16], the NOE effect was detected for the *Z*-1,2-dihaloalkenes compounds; in contrast, no enhancements were observed for the *E*-1,2-dihaloalkenes. Similarly, we have not observed the cross peak between the H_b and H_a in NOESY of **18** (Figure S4).

21. Structure assignment of compound 62

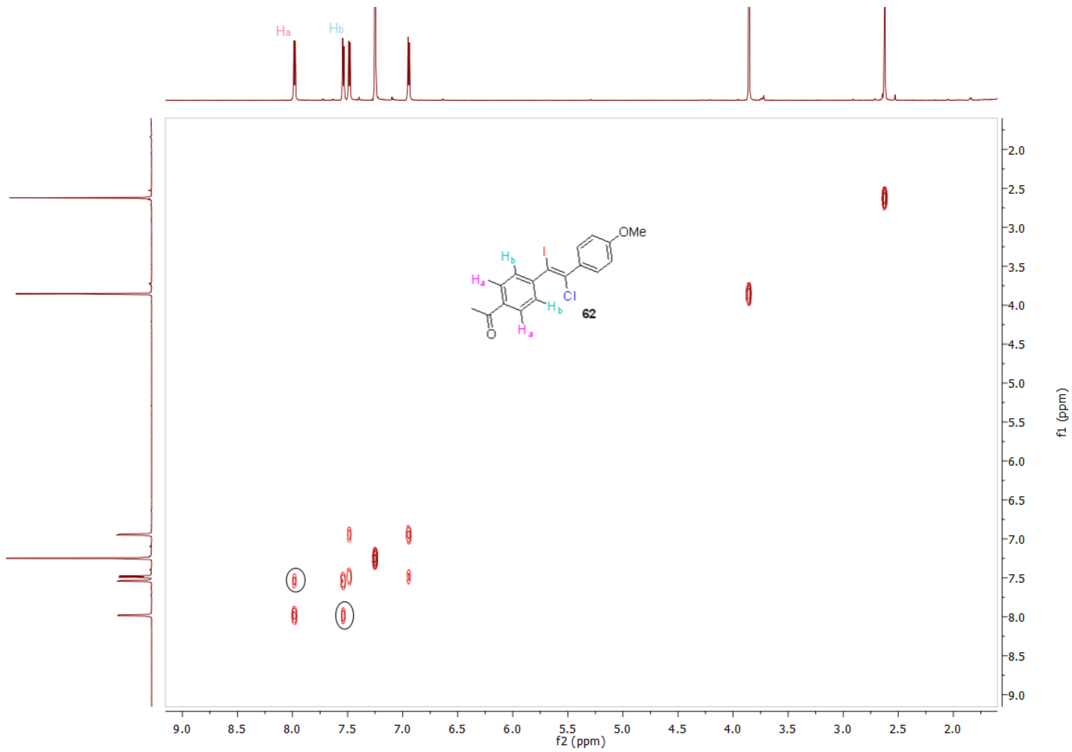


Figure S5. COSY of **62**

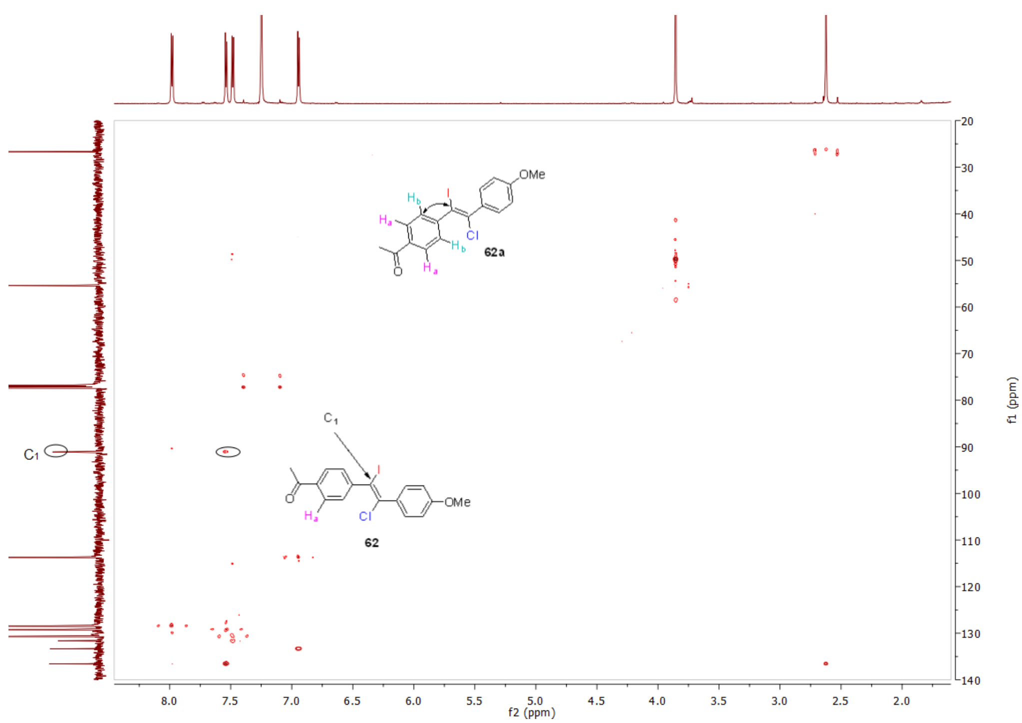


Figure S6. HMBC of **62.**

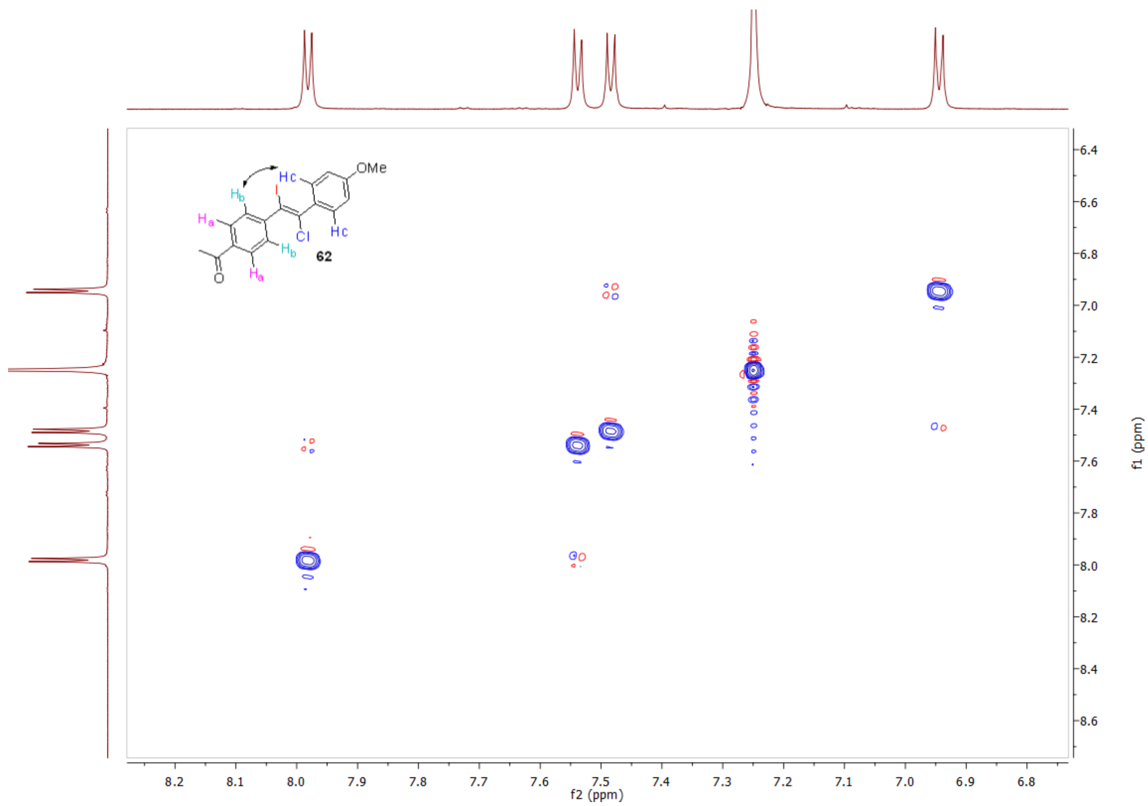


Figure S7. NOESY of **62**

The NMR peaks for Ha and H_b was assigned based on the H-H COSY analysis (Figure S5). In light of a previous report[17], the C_1 should exhibit a substantial upfield shift due to the iodine substitution (Figure S6). An interaction was observed between the H_b and C_1 in the ^{1}H-^{13}C HMBC experiment (Figure S6), which indicated that the C1 was substituted with iodine. A NOESY experiment was carried out, and we have not observed interaction between the H_b and H_c (Figure S7).

22. Structure assignment of compound 95

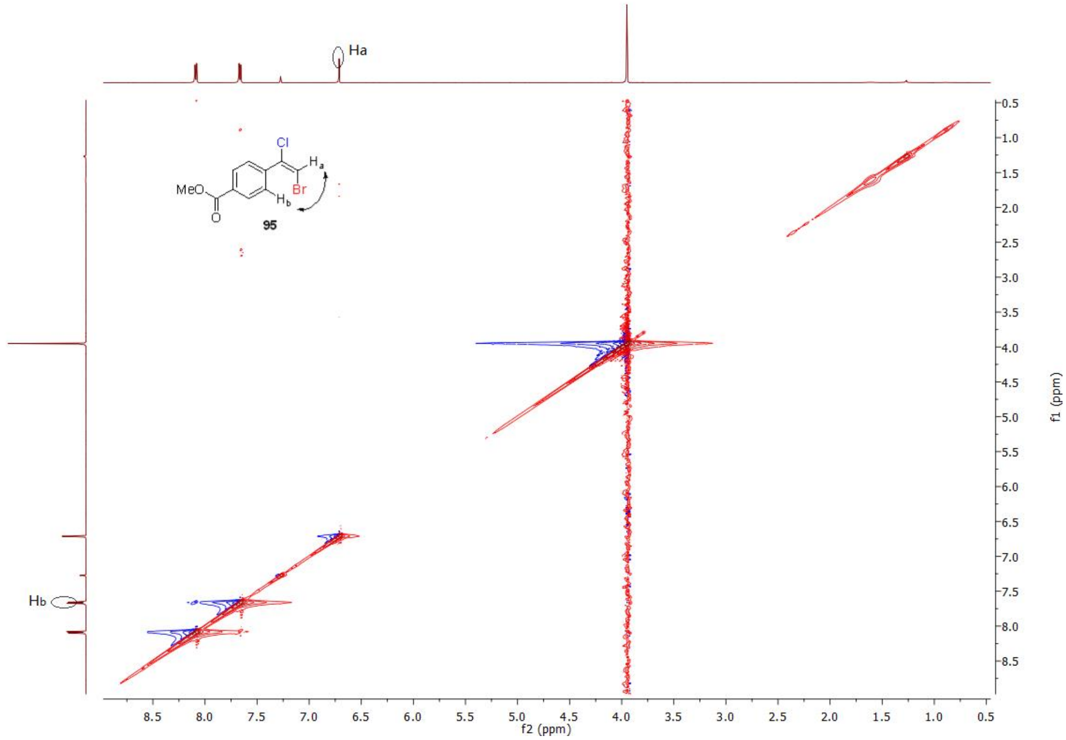
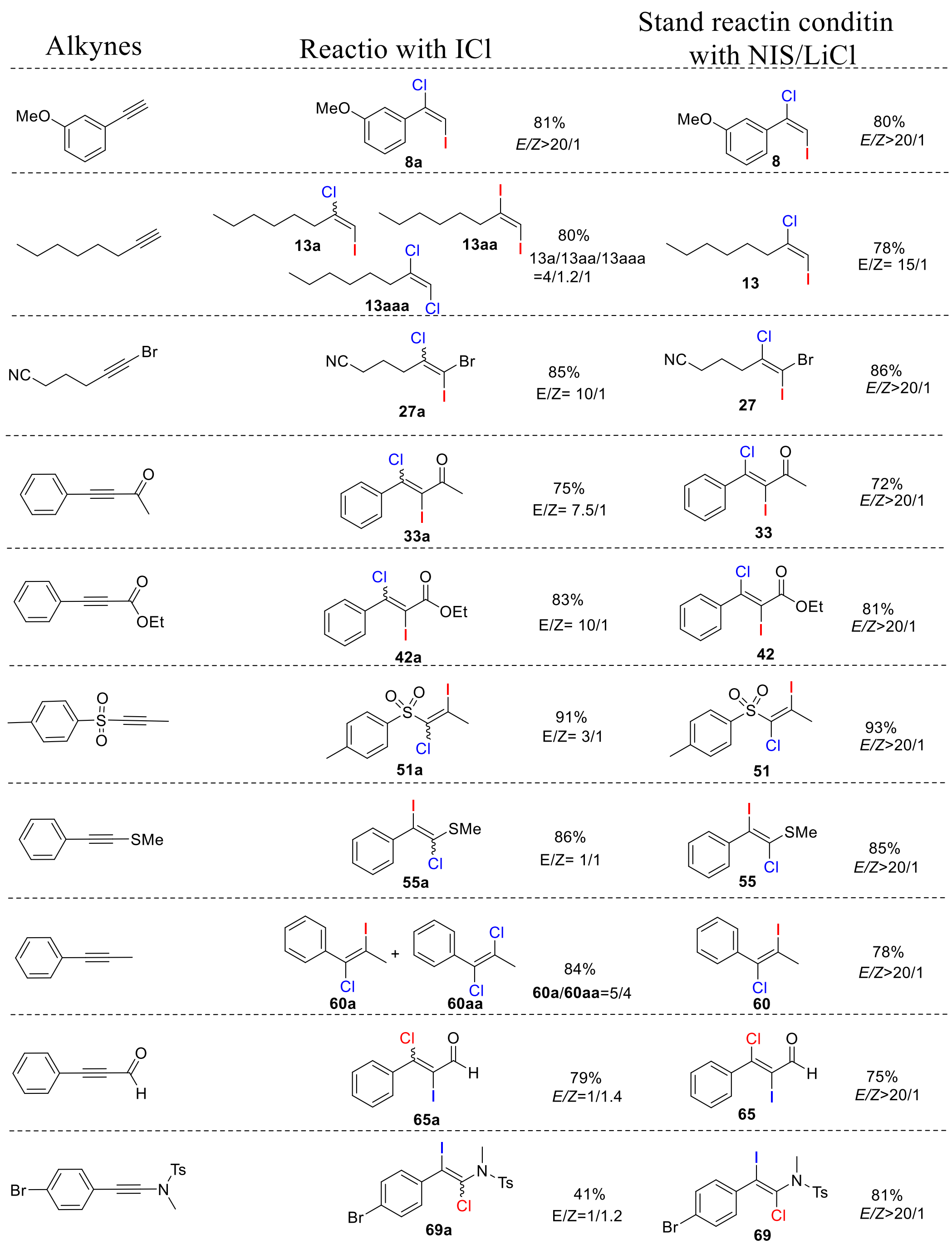


Figure S8. NOESY of **95**

A NOESY experiment was carried out, and we have not observed interaction between the H_b and H_a (Figure S8).

23. Comparison experiments



Note: all the experiments were carried out at the same reaction condition; the only difference was the ICl source. all the products were isolated by flash silica gel column chromatography. The Regio-isomer were confirmed by NMR and GC-MS, compound **13aaa** was determined by GC-MS, the NMR data of Compound **60aa**[18] consistent with the previous report.

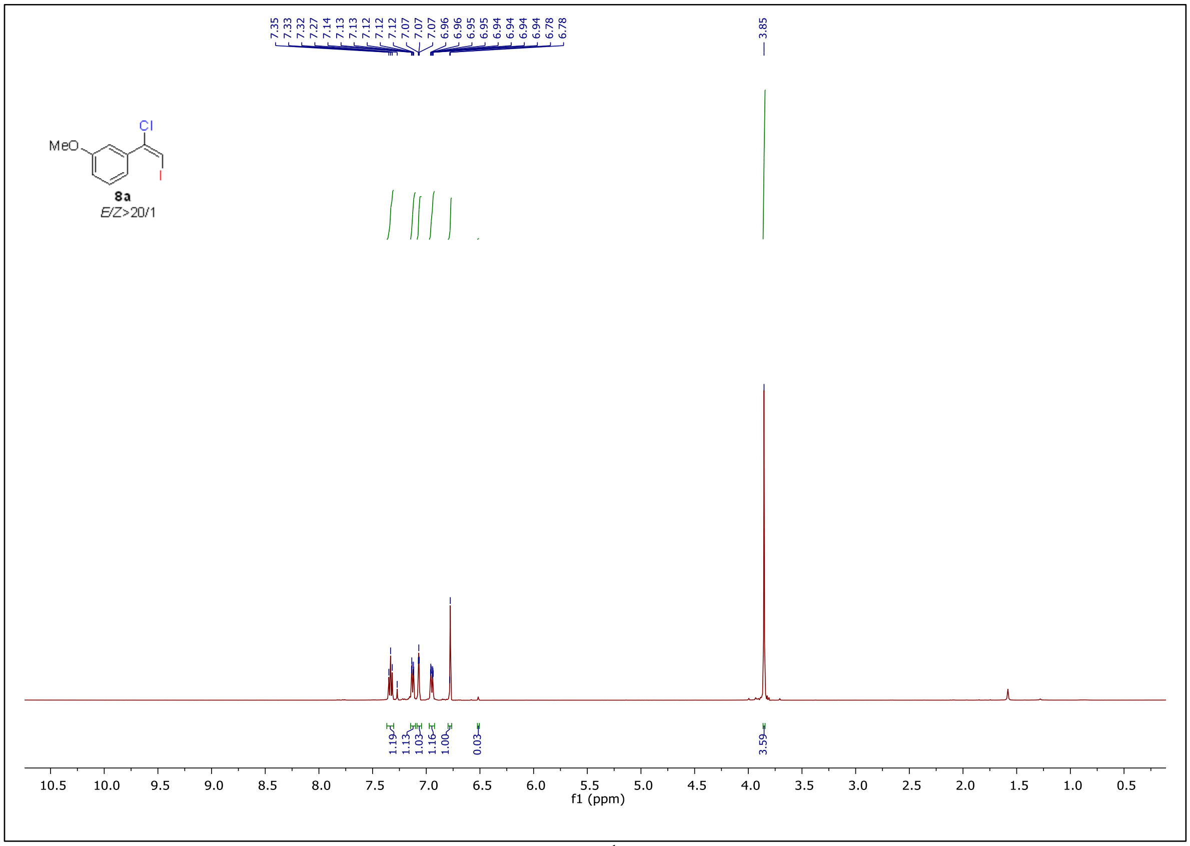


Figure S9. ^{1}H NMR of **8a**

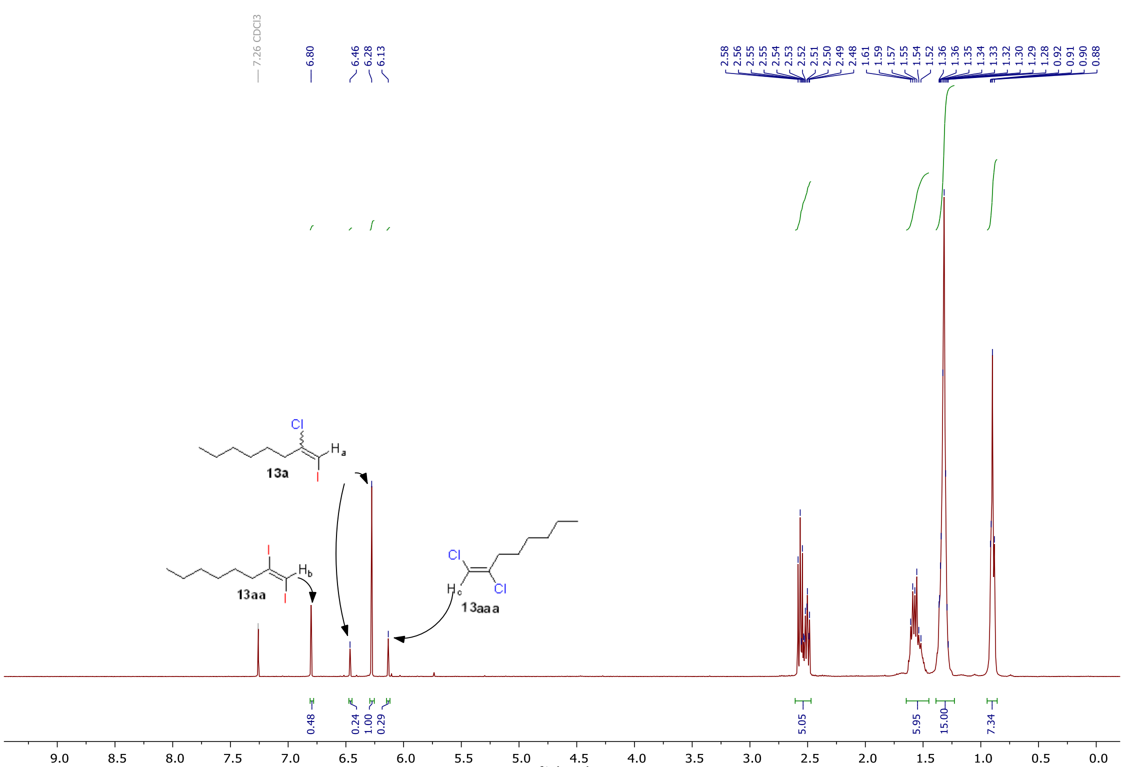


Figure S10. ^{1}H NMR of **13a**

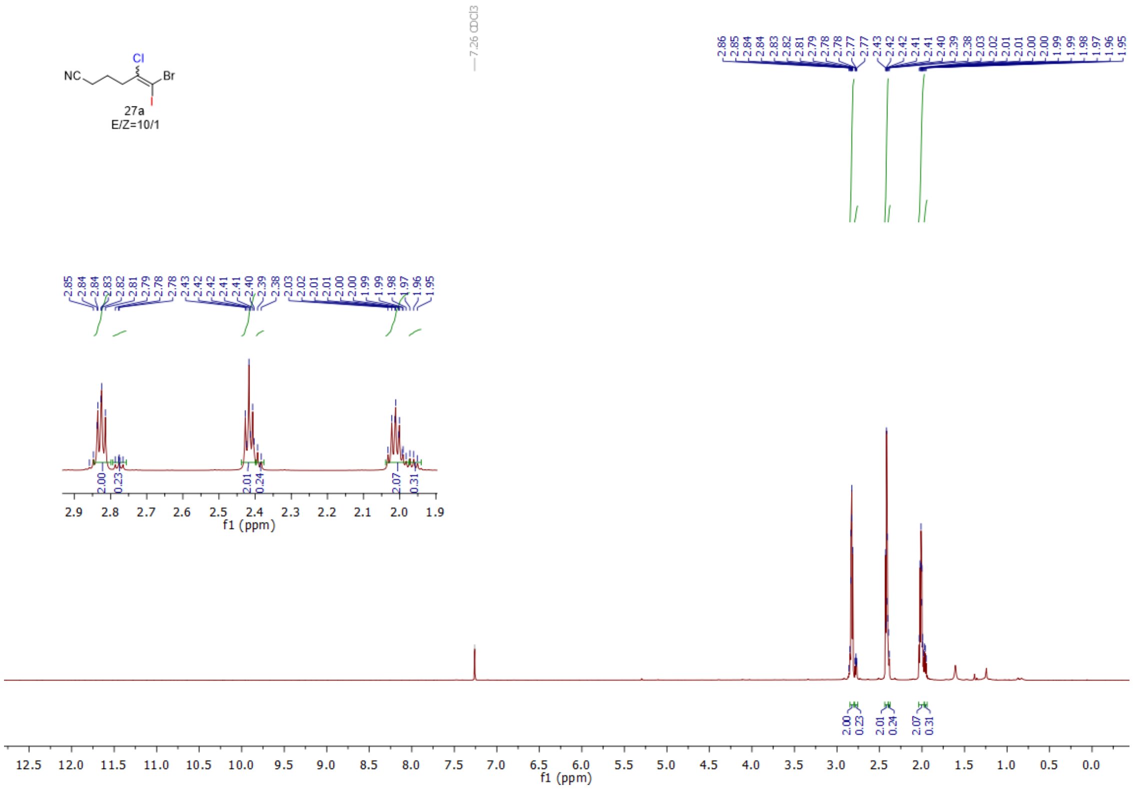


Figure S11. ^{1}H NMR of **27a**

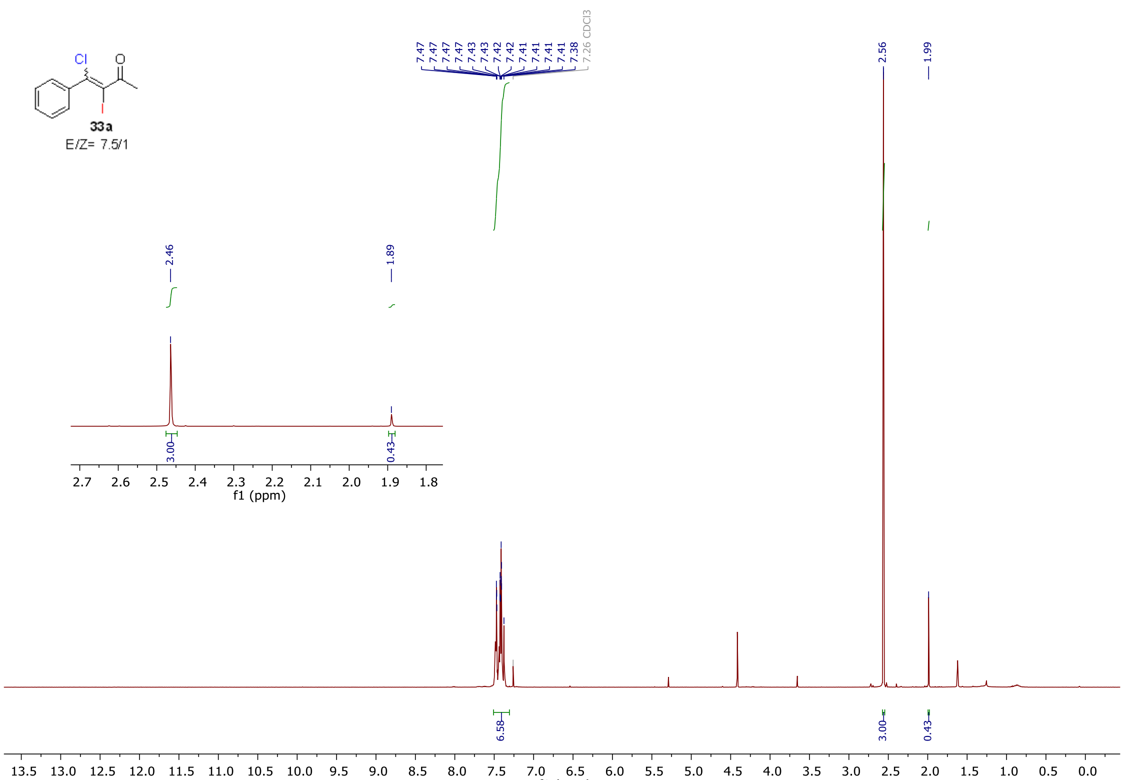


Figure S12. ^{1}H NMR of **33a**

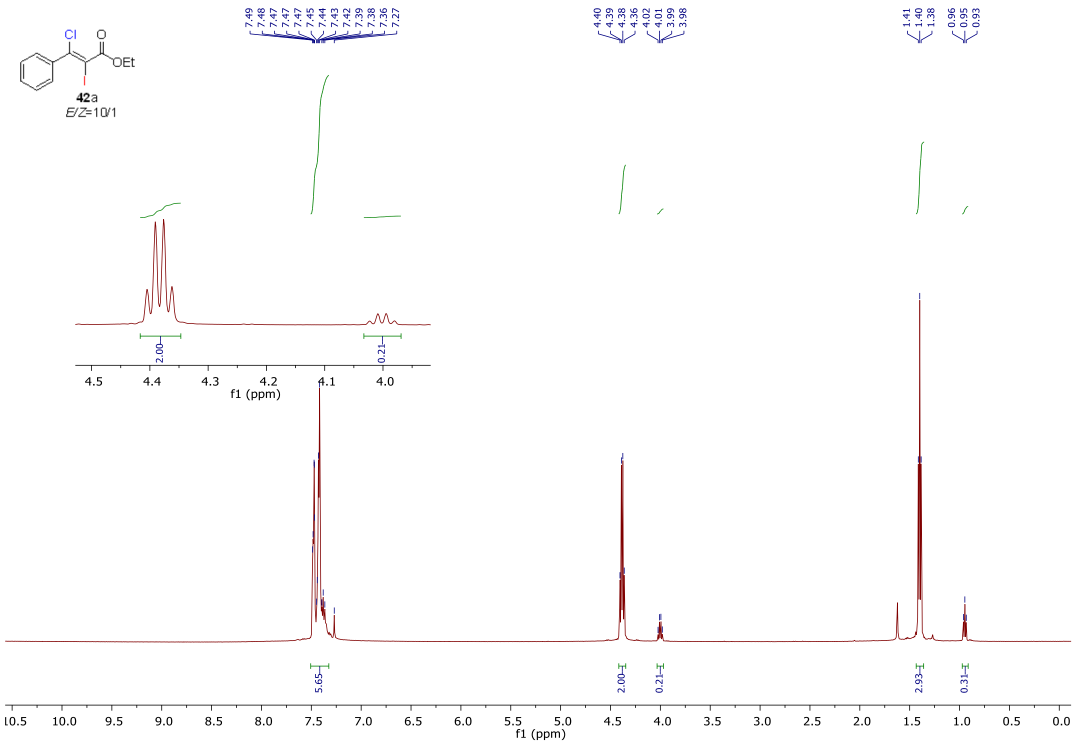


Figure S13. ^{1}H NMR of **42a**

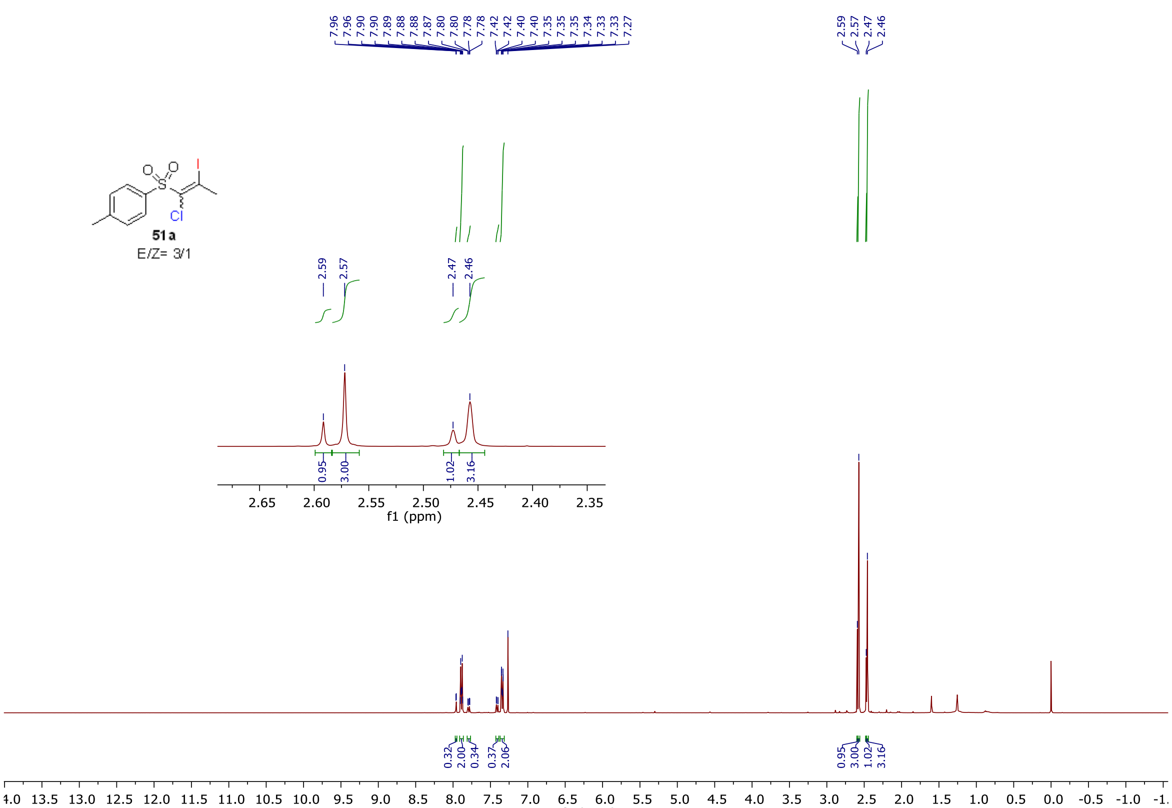


Figure S14. ^{1}H NMR of **51a**

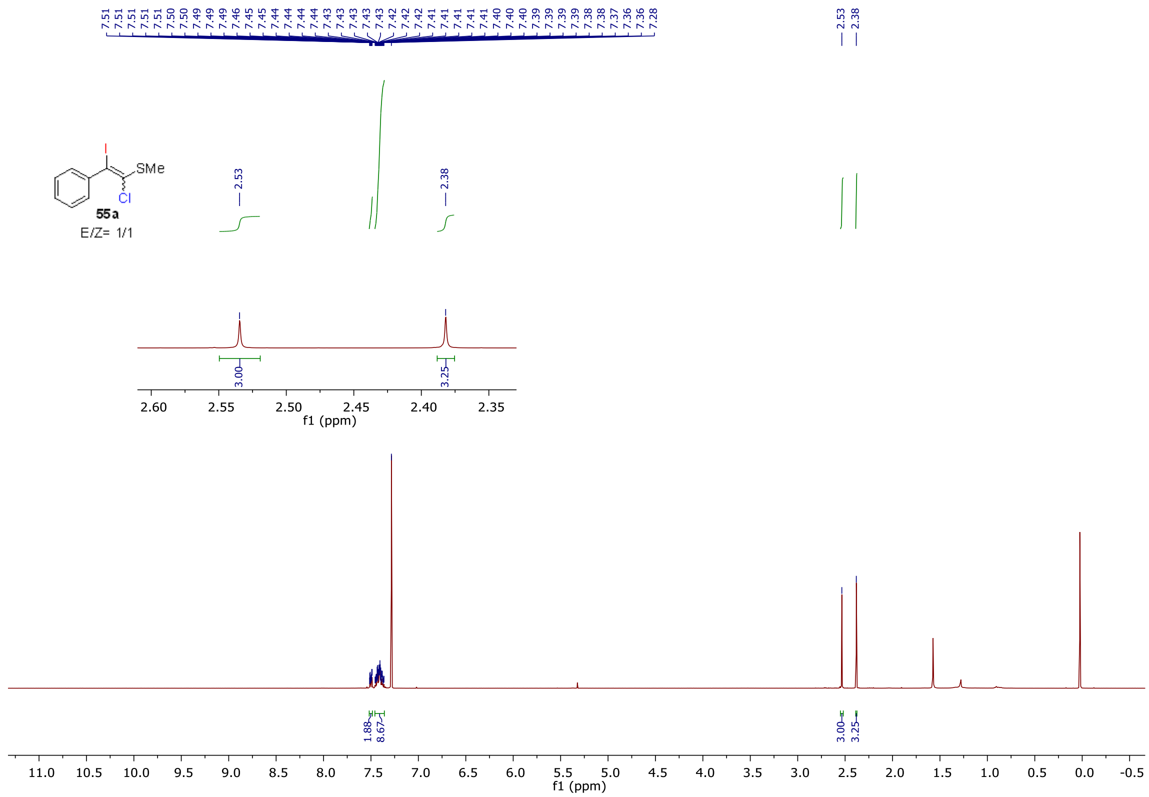


Figure S15. ^{1}H NMR of 55a

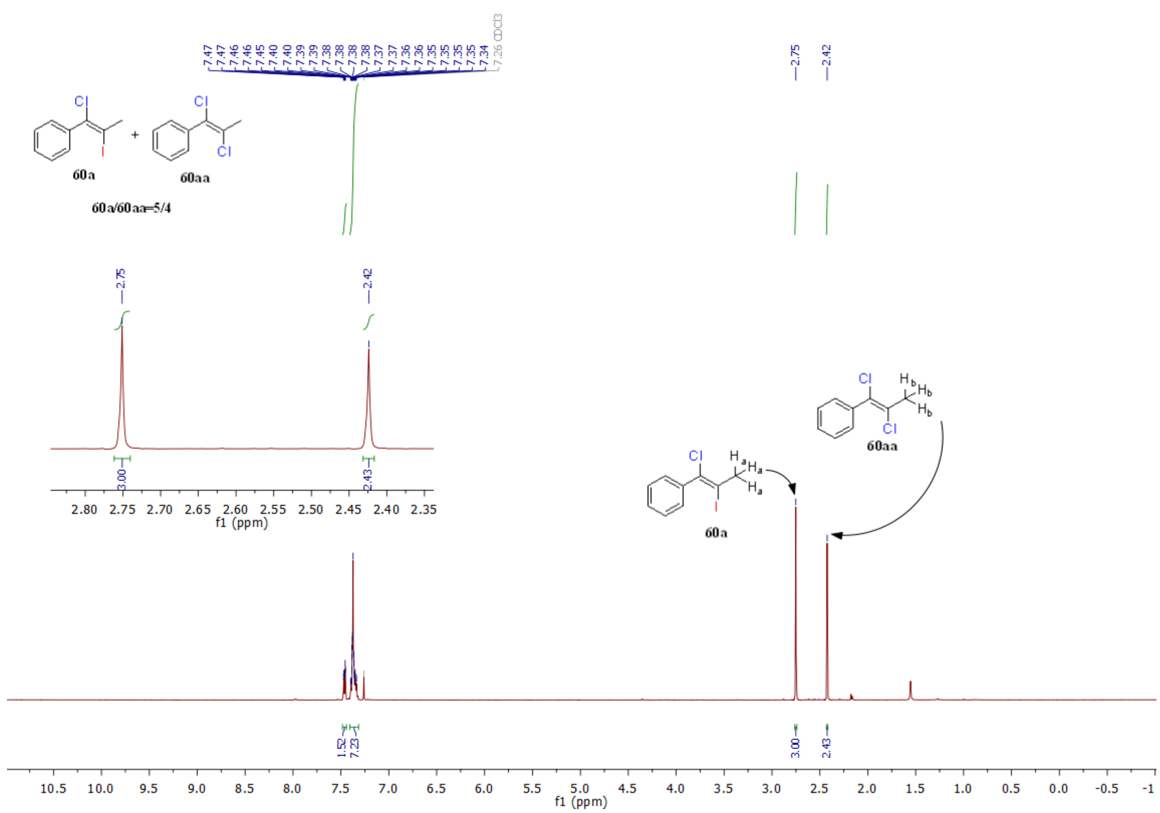


Figure S16. ^{1}H NMR of **60a**

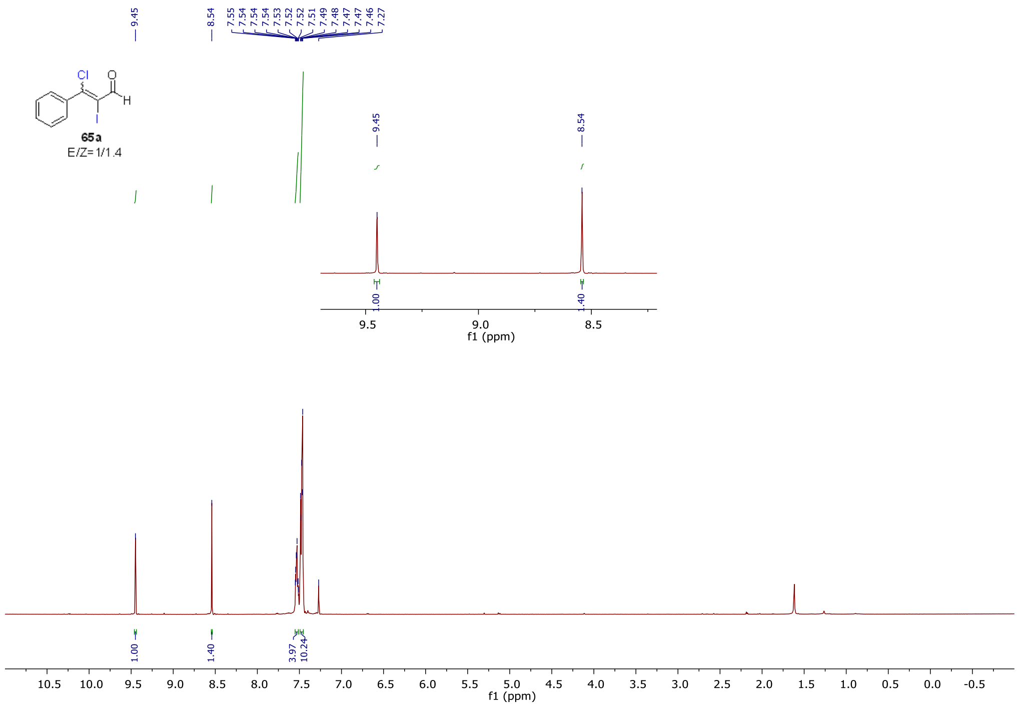


Figure S17. ^{1}H NMR of **65a**

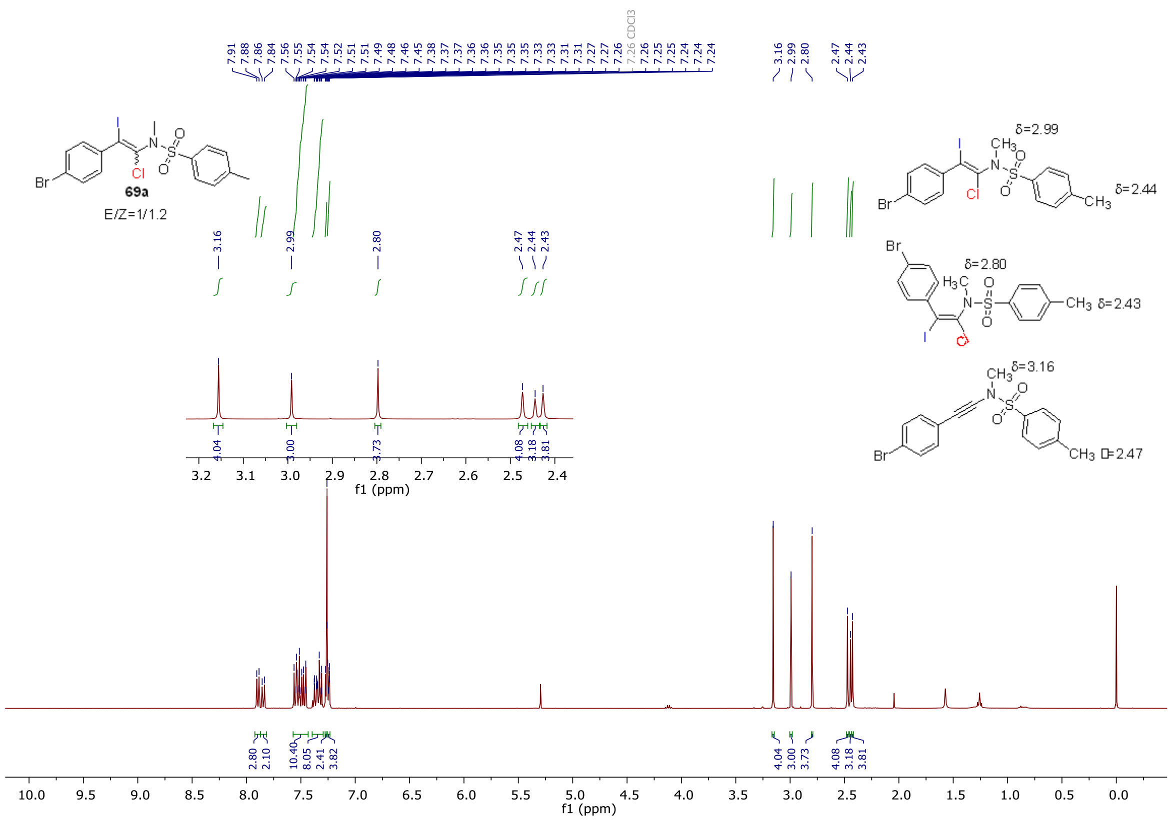


Figure S18. ^{1}H NMR of **69a**

24. The crystallographic data of 10

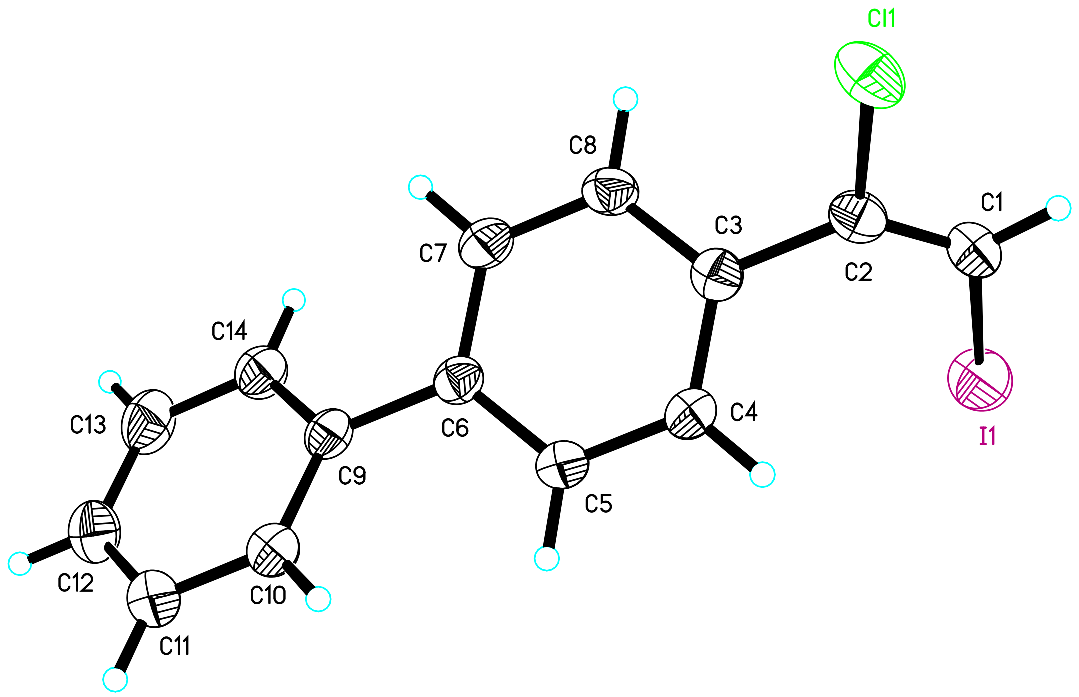


Table S1. Crystal data and structure refinement for mo_dd18319_0m.

Identification code	mo_dd18319_0m	
Empirical formula	C14 H10 Cl I	
Formula weight	340.57	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.7863(4) Å	= 90°.
	b = 9.7114(3) Å	= 100.442(2)°.

	c = 13.7154(5) Å	= 90°.
Volume	1281.91(8) Å^3	
Z	4	
Density (calculated)	1.765 Mg/m^3	
Absorption coefficient	2.676 mm^{-1}	
F(000)	656	
Crystal size	0.170 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.116 to 25.988°.	
Index ranges	-10<=h<=12, -11<=k<=10, -16<=l<=14	
Reflections collected	6080	
Independent reflections	2478 [R(int) = 0.0201]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5529	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2478 / 0 / 146	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.0956	
R indices (all data)	R1 = 0.0474, wR2 = 0.1017	
Extinction coefficient	0.0055(15)	
Largest diff. peak and hole	1.069 and -0.788 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_dd18319_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	7537(1)	10197(1)	3302(1)	78(1)
Cl(1)	8203(1)	7305(1)	722(1)	63(1)
C(1)	7781(4)	9237(5)	1995(3)	55(1)
C(2)	7857(4)	7890(4)	1879(3)	47(1)
C(3)	7684(4)	6774(4)	2581(3)	43(1)
C(4)	6471(4)	6649(4)	2952(3)	51(1)
C(5)	6295(4)	5596(4)	3591(3)	49(1)
C(6)	7339(4)	4628(4)	3894(3)	41(1)
C(7)	8554(4)	4758(4)	3504(3)	48(1)
C(8)	8719(4)	5803(4)	2862(3)	48(1)
C(9)	7159(4)	3508(4)	4593(3)	42(1)
C(10)	5864(4)	2960(4)	4629(3)	52(1)
C(11)	5697(5)	1921(5)	5286(4)	63(1)
C(12)	6827(5)	1410(5)	5927(4)	68(1)
C(13)	8114(5)	1929(5)	5894(4)	69(1)
C(14)	8298(4)	2968(4)	5239(3)	53(1)

Table S3. Bond lengths [Å] and angles [°] for mo_dd18319_0m.

I(1)-C(1)	2.072(5)
Cl(1)-C(2)	1.774(4)
C(1)-C(2)	1.322(6)
C(1)-H(1)	0.9300
C(2)-C(3)	1.480(5)
C(3)-C(4)	1.379(5)
C(3)-C(8)	1.387(5)
C(4)-C(5)	1.378(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.395(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.396(6)
C(6)-C(9)	1.481(5)
C(7)-C(8)	1.372(6)
C(7)-H(7)	0.9300
C(8)-H(8)	0.9300
C(9)-C(10)	1.383(6)
C(9)-C(14)	1.394(5)
C(10)-C(11)	1.382(6)
C(10)-H(10)	0.9300
C(11)-C(12)	1.375(7)
C(11)-H(11)	0.9300
C(12)-C(13)	1.365(7)

C(12)-H(12)	0.9300
C(13)-C(14)	1.384(6)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(2)-C(1)-I(1)	124.6(3)
C(2)-C(1)-H(1)	117.7
I(1)-C(1)-H(1)	117.7
C(1)-C(2)-C(3)	129.1(4)
C(1)-C(2)-Cl(1)	116.7(3)
C(3)-C(2)-Cl(1)	114.2(3)
C(4)-C(3)-C(8)	118.2(4)
C(4)-C(3)-C(2)	120.8(3)
C(8)-C(3)-C(2)	121.0(3)
C(5)-C(4)-C(3)	121.0(4)
C(5)-C(4)-H(4)	119.5
C(3)-C(4)-H(4)	119.5
C(4)-C(5)-C(6)	121.4(4)
C(4)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3
C(7)-C(6)-C(5)	117.0(4)
C(7)-C(6)-C(9)	121.6(3)
C(5)-C(6)-C(9)	121.4(3)
C(8)-C(7)-C(6)	121.4(4)
C(8)-C(7)-H(7)	119.3
C(6)-C(7)-H(7)	119.3

C(7)-C(8)-C(3)	121.1(4)
C(7)-C(8)-H(8)	119.5
C(3)-C(8)-H(8)	119.5
C(10)-C(9)-C(14)	117.7(4)
C(10)-C(9)-C(6)	121.5(3)
C(14)-C(9)-C(6)	120.8(3)
C(11)-C(10)-C(9)	121.4(4)
C(11)-C(10)-H(10)	119.3
C(9)-C(10)-H(10)	119.3
C(12)-C(11)-C(10)	120.3(4)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	119.0(4)
C(13)-C(12)-H(12)	120.5
C(11)-C(12)-H(12)	120.5
C(12)-C(13)-C(14)	121.4(4)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-H(13)	119.3
C(13)-C(14)-C(9)	120.2(4)
C(13)-C(14)-H(14)	119.9
C(9)-C(14)-H(14)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for mo_dd18319_0m. The anisotropic displacement factor exponent takes the form: -2 ^{2}[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	98(1)	57(1)	88(1)	-15(1)	38(1)	-5(1)
Cl(1)	74(1)	71(1)	47(1)	-2(1)	17(1)	-18(1)
C(1)	56(2)	54(2)	59(2)	8(2)	17(2)	-5(2)
C(2)	40(2)	53(2)	46(2)	-2(2)	6(2)	-8(2)
C(3)	44(2)	42(2)	43(2)	-4(2)	6(2)	-4(2)
C(4)	42(2)	47(2)	63(2)	8(2)	12(2)	9(2)
C(5)	43(2)	50(2)	57(2)	6(2)	16(2)	6(2)
C(6)	42(2)	40(2)	42(2)	-5(2)	8(2)	1(2)
C(7)	38(2)	52(2)	53(2)	-1(2)	3(2)	7(2)
C(8)	36(2)	54(2)	55(2)	-1(2)	11(2)	-2(2)
C(9)	48(2)	38(2)	41(2)	-6(2)	8(2)	5(2)
C(10)	49(2)	50(2)	59(2)	5(2)	10(2)	5(2)
C(11)	62(3)	53(3)	77(3)	10(2)	20(2)	2(2)
C(12)	78(3)	57(3)	72(3)	20(2)	17(3)	8(2)
C(13)	77(3)	62(3)	64(3)	16(2)	2(2)	17(3)
C(14)	52(2)	54(2)	52(2)	2(2)	6(2)	5(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)for mo_dd18319_0m.

	x	y	z	U(eq)
H(1)	7840	9793	1453	66
H(4)	5761	7286	2768	61
H(5)	5463	5528	3825	59
H(7)	9267	4124	3683	58
H(8)	9539	5861	2610	57
H(10)	5089	3298	4202	63
H(11)	4817	1566	5295	76
H(12)	6716	720	6377	82
H(13)	8883	1578	6320	83
H(14)	9184	3307	5230	63

Table S6. Torsion angles [°] for mo_dd18319_0m.

I(1)-C(1)-C(2)-C(3)	5.3(7)
I(1)-C(1)-C(2)-Cl(1)	-175.2(2)
C(1)-C(2)-C(3)-C(4)	58.2(6)
Cl(1)-C(2)-C(3)-C(4)	-121.4(4)
C(1)-C(2)-C(3)-C(8)	-123.7(5)
Cl(1)-C(2)-C(3)-C(8)	56.7(4)
C(8)-C(3)-C(4)-C(5)	0.6(6)
C(2)-C(3)-C(4)-C(5)	178.7(4)
C(3)-C(4)-C(5)-C(6)	0.7(7)

C(4)-C(5)-C(6)-C(7)	-1.4(6)
C(4)-C(5)-C(6)-C(9)	179.0(4)
C(5)-C(6)-C(7)-C(8)	0.9(6)
C(9)-C(6)-C(7)-C(8)	-179.6(4)
C(6)-C(7)-C(8)-C(3)	0.4(6)
C(4)-C(3)-C(8)-C(7)	-1.1(6)
C(2)-C(3)-C(8)-C(7)	-179.2(4)
C(7)-C(6)-C(9)-C(10)	-149.3(4)
C(5)-C(6)-C(9)-C(10)	30.2(5)
C(7)-C(6)-C(9)-C(14)	30.6(5)
C(5)-C(6)-C(9)-C(14)	-149.9(4)
C(14)-C(9)-C(10)-C(11)	0.5(6)
C(6)-C(9)-C(10)-C(11)	-179.6(4)
C(9)-C(10)-C(11)-C(12)	0.3(7)
C(10)-C(11)-C(12)-C(13)	-1.0(8)
C(11)-C(12)-C(13)-C(14)	0.9(8)
C(12)-C(13)-C(14)-C(9)	-0.1(7)
C(10)-C(9)-C(14)-C(13)	-0.6(6)
C(6)-C(9)-C(14)-C(13)	179.5(4)

Symmetry transformations used to generate equivalent atoms:

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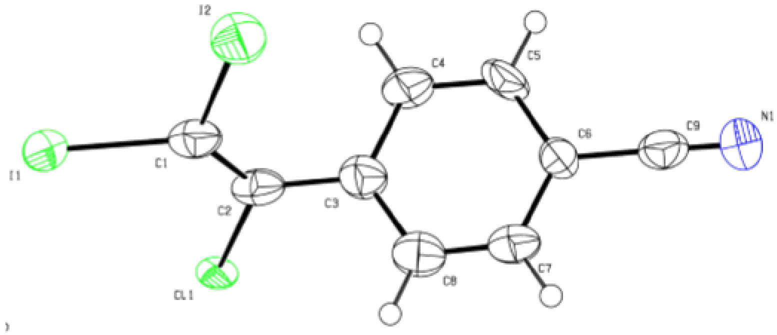

Table S7. Crystal data and structure refinement for 20190815ZH_ZNZ1296_0m_a.

Identification code	20190815ZH_ZNZ1296_0m_a	
Empirical formula	$C_9 H_4ClI_2N$	
Formula weight	415.38	
Temperature	213(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.9634(5) Å	= 90°.
	b = 8.7445(5) Å	= 102.017(2)°.
	c = 14.8139(8) Å	= 90°.
Volume	1135.67(11) $Å^3$	
Z	4	
Density (calculated)	2.429 Mg/m^3	
Absorption coefficient	31.101 mm^{-1}	
F(000)	752	
Crystal size	0.160 x 0.110 x 0.080 mm^3	
Theta range for data collection	5.140 to 52.989°.	
Index ranges	-10<=h<=10, -10<=k<=9, -17<=l<=17	
Reflections collected	8960	
Independent reflections	2009 [R(int) = 0.0629]	
Completeness to theta = 52.989°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2009 / 0 / 118	
Goodness-of-fit on F^2	1.113	
Final R indices [I>2sigma(I)]	R1 = 0.0758, wR2 = 0.2343	
R indices (all data)	R1 = 0.0787, wR2 = 0.2384	
Extinction coefficient	n/a	
Largest diff. peak and hole	4.078 and -2.259 e.$Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)for 20190815ZH_ZNZ1296_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	10113(1)	7798(1)	610(1)	43(1)
I(2)	9376(1)	9150(1)	2713(1)	58(1)
Cl(1)	6847(3)	5692(3)	465(2)	30(1)
N(1)	2804(15)	6525(19)	4570(9)	60(3)
C(1)	8657(17)	7731(16)	1561(10)	46(3)
C(5)	6076(17)	6209(17)	3682(9)	45(3)
C(6)	4570(14)	6681(15)	3422(8)	36(3)
C(9)	3569(16)	6600(17)	4084(10)	46(3)
C(2)	7418(15)	6918(15)	1477(10)	41(3)
C(3)	6424(16)	6802(17)	2152(10)	46(3)
C(4)	7013(16)	6310(17)	3069(10)	46(3)
C(7)	4022(17)	7236(19)	2537(11)	51(4)
C(8)	4909(18)	7266(19)	1908(11)	58(4)

Table S9. Bond lengths [Å] and angles [°] for 20190815ZH_ZNZ1296_0m_a.

I(1)-C(1)	2.110(16)	C(4)-C(5)-C(6)	119.6(11)
I(2)-C(1)	2.099(15)	C(4)-C(5)-H(5)	120.2
Cl(1)-C(2)	1.828(14)	C(6)-C(5)-H(5)	120.2
N(1)-C(9)	1.096(19)	C(5)-C(6)-C(7)	119.9(12)
C(1)-C(2)	1.30(2)	C(5)-C(6)-C(9)	119.7(11)
C(5)-C(4)	1.36(2)	C(7)-C(6)-C(9)	120.3(12)
C(5)-C(6)	1.387(19)	N(1)-C(9)-C(6)	178.9(17)
C(5)-H(5)	0.9400	C(1)-C(2)-C(3)	126.6(14)
C(6)-C(7)	1.388(19)	C(1)-C(2)-Cl(1)	119.0(12)
C(6)-C(9)	1.462(19)	C(3)-C(2)-Cl(1)	114.2(10)
C(2)-C(3)	1.47(2)	C(8)-C(3)-C(4)	119.1(13
C(3)-C(8)	1.39(2)	C(8)-C(3)-C(2)	119.9(13)
C(3)-C(4)	1.42(2)	C(4)-C(3)-C(2)	120.9(12)
C(4)-H(4)	0.9400	C(5)-C(4)-C(3)	120.0(12)
C(7)-C(8)	1.34(2)	C(5)-C(4)-H(4)	120.0
C(7)-H(7)	0.9400	C(3)-C(4)-H(4)	120.0
C(8)-H(8)	0.9400	C(8)-C(7)-C(6)	121.2(13)
C(2)-C(1)-I(2)	120.7(12)	C(8)-C(7)-H(7)	119.4
C(2)-C(1)-I(1)	125.8(12)	C(6)-C(7)-H(7)	119.4
I(2)-C(1)-I(1)	113.5(7)	C(7)-C(8)-C(3)	120.0(14)
C(3)-C(8)-H(8)	120.0	C(7)-C(8)-H(8)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2$x 10^3) for 20190815ZH_ZNZ1296_0m_a. The anisotropicdisplacement factor exponent takes the form: $-2\ \ ^{2}[\ h^{2}\ a^{*2}U^{11} + ... + 2\ h\ k\ a^{*}\ b^{*}\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	34(1)	51(1)	41(1)	4(1)	4(1)	0(1)
I(2)	58(1)	61(1)	52(1)	-14(1)	5(1)	-21(1)
Cl(1)	30(1)	33(1)	22(1)	-6(1)	-4(1)	-19(1)
N(1)	50(7)	90(11)	43(7)	2(7)	18(6)	1(7)
C(1)	41(7)	46(8)	44(7)	8(6)	-5(6)	1(6)
C(5)	58(8)	51(8)	25(6)	18(5)	5(6)	8(6)
C(6)	38(6)	41(6)	28(6)	1(5)	8(5)	-4(5)
C(9)	37(7)	51(8)	44(7)	9(6)	-2(6)	3(6)
C(2)	38(7)	36(6)	42(7)	3(5)	-8(5)	-7(5)
C(3)	45(7)	50(7)	41(7)	8(6)	6(6)	9(6)
C(4)	39(7)	48(8)	49(8)	11(6)	1(6)	20(6)
C(7)	39(7)	65(10)	44(8)	10(7)	-3(6)	13(6)
C(8)	51(10)	69(10)	50(9)	21(8)	4(7)	16(8)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 20190815ZH_ZNZ1296_0m_a.

	x	y	z	U(eq)
H(5)	6448	5821	4278	54
H(4)	8050	6055	3254	56
H(7)	3014	7596	2374	61
H(8)	4505	7602	1304	69

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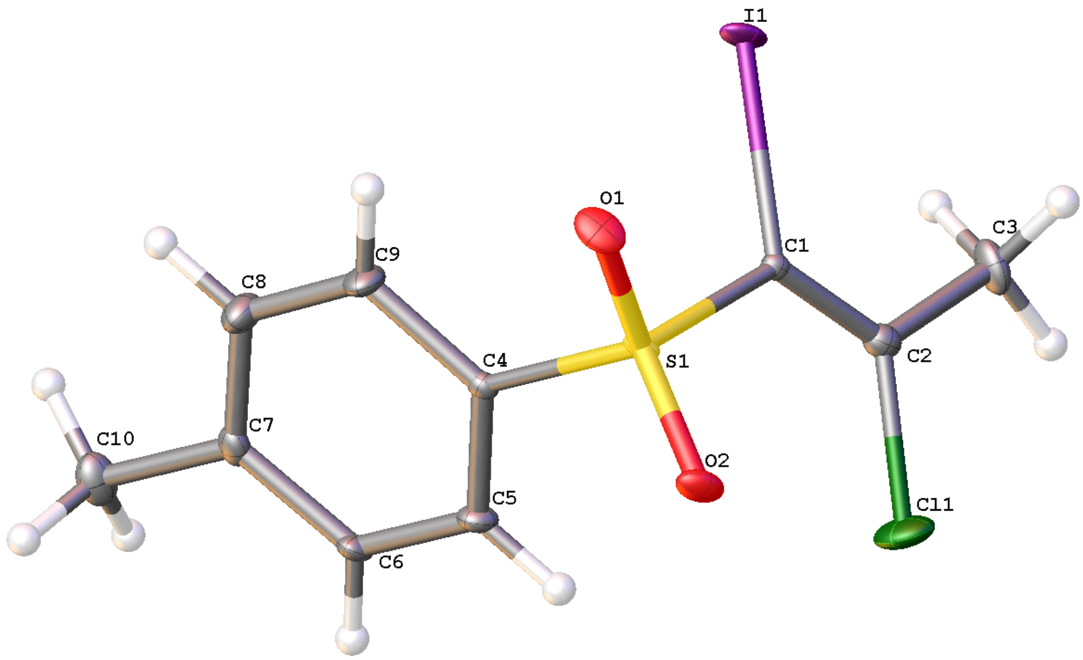

Table S12. Crystal data and structure refinement for 1903044365_0m.

Identification code	1903044365_0m
Empirical formula	$C_{10}H_{10}ClIO_2S$
Formula weight	356.59
Temperature/K	170.01
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.4648(5)
b/Å	7.3253(3)
c/Å	15.0403(7)
α/°	90
β/°	106.584(2)
γ/°	90
Volume/Å^3	1210.59(9)
Z	4
ρ_{calc}g/cm^3	1.957
μ/mm^{-1}	16.539
F(000)	688.0
Crystal size/mm^3	0.15 × 0.12 × 0.08
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	9.944 to 109.862
Index ranges	$-12 \leq h \leq 13$, $-8 \leq k \leq 8$, $-18 \leq l \leq 18$
Reflections collected	9888

Independent reflections	2287 [R_{int} = 0.0444, R_{sigma} = 0.0363]
Data/restraints/parameters	2287/120/139
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0602, wR_2 = 0.1618
Final R indexes [all data]	R_1 = 0.0608, wR_2 = 0.1628
Largest diff. peak/hole / e Å^{-3}	3.12/-3.80

Table S13. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1903044365_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	4216.9(3)	7041.9(4)	2987.5(2)	13.7(3)
Cl1	3625.7(15)	1421(2)	4233.3(10)	22.8(4)
S1	4702.5(13)	2839.2(15)	2520.3(9)	6.9(4)
O1	4548(4)	3804(6)	1661(2)	15.7(9)
O2	4210(4)	1016(5)	2475(3)	14.1(8)
C1	4095(4)	4253(7)	3257(3)	6.8(9)
C2	3653(5)	3686(8)	3940(4)	11.5(10)
C3	3149(5)	4952(9)	4535(4)	17.8(12)
C4	6260(5)	2767(7)	3115(4)	7.8(9)
C5	6695(5)	1517(8)	3834(4)	12.4(9)
C6	7907(5)	1483(8)	4309(4)	11.7(9)
C7	8725(5)	2690(8)	4088(4)	12.3(10)
C8	8276(5)	3936(8)	3373(4)	17.0(10)
C9	7055(5)	4004(8)	2881(4)	15.2(10)
C10	10063(6)	2620(10)	4579(4)	18.3(12)

Table S14. Anisotropic Displacement Parameters (Å^2×10^3) for 1903044365_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	13.6(3)	3.7(3)	20.7(3)	-1.19(9)	-0.22(16)	0.11(9)
Cl1	34.7(9)	13.7(8)	22.2(7)	8.6(5)	11.7(6)	-1.0(6)
S1	8.5(6)	4.6(6)	5.6(5)	-1.1(3)	-1.4(4)	1.9(4)
O1	17(2)	20(2)	6.4(17)	-0.5(14)	-2.9(15)	5.2(16)
O2	13.9(15)	7.3(14)	17.5(14)	-2.3(11)	-1.1(12)	-0.6(12)
C1	6.5(12)	6.5(12)	6.9(11)	-0.5(9)	0.9(9)	0.1(9)
C2	11.2(13)	10.3(13)	12.0(12)	-0.4(9)	1.7(9)	0.4(9)
C3	14(3)	26(3)	16(2)	-5(2)	7(2)	6(2)
C4	8.4(12)	7.1(12)	7.7(12)	-0.2(8)	2.2(9)	1.3(9)
C5	13(2)	9(2)	14(2)	4.0(18)	2.4(18)	2.1(19)

C6	10(2)	8(2)	16(2)	3.5(18)	2.1(18)	2.3(18)
C7	10(2)	12(2)	16(2)	-3.9(19)	5.1(19)	0.8(19)
C8	14(2)	17(2)	20(2)	5.9(19)	4.7(19)	-2.2(19)
C9	15(2)	13(2)	18(2)	8.3(18)	4.9(18)	0.3(19)
C10	12(3)	22(3)	19(3)	-6(3)	2(2)	-1(3)

Table S15. Bond Lengths for 1903044365_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C1	2.095(5)	C4	C5	1.396(7)
Cl1	C2	1.719(6)	C4	C9	1.400(7)
S1	O1	1.439(4)	C5	C6	1.370(8)
S1	O2	1.444(4)	C6	C7	1.396(8)
S1	C1	1.796(5)	C7	C8	1.392(8)
S1	C4	1.754(6)	C7	C10	1.502(9)
C1	C2	1.335(7)	C8	C9	1.385(8)
C2	C3	1.515(7)			

Table S16. Bond Angles for 1903044365_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	117.8(2)	C3	C2	Cl1	113.6(4)
O1	S1	C1	107.5(2)	C5	C4	S1	120.1(4)
O1	S1	C4	108.6(2)	C5	C4	C9	120.3(5)
O2	S1	C1	110.3(2)	C9	C4	S1	119.6(4)
O2	S1	C4	108.9(2)	C6	C5	C4	120.1(5)
C4	S1	C1	102.8(2)	C5	C6	C7	121.0(5)
S1	C1	I1	112.6(2)	C6	C7	C10	121.5(5)
C2	C1	I1	120.9(4)	C8	C7	C6	118.3(5)
C2	C1	S1	126.4(4)	C8	C7	C10	120.2(5)
C1	C2	Cl1	122.5(4)	C9	C8	C7	122.1(5)
C1	C2	C3	123.9(5)	C8	C9	C4	118.3(5)

Table S17. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1903044365_0m.

Atom	*x*	*y*	*z*	U(eq)
H3A	2396.49	5516.43	4154.59	27
H3B	3747.32	5905.61	4798.24	27
H3C	2975.39	4253.95	5038.97	27
H5	6149.66	688.41	3993.86	15
H6	8196.08	626.36	4796.85	14
H8	8824.19	4766.29	3218.79	20
H9	6765.25	4867.3	2396.53	18
H10A	10184.34	2295.51	5231.01	27
H10B	10426.83	3817.91	4541.48	27
H10C	10451.16	1701.29	4283.87	27

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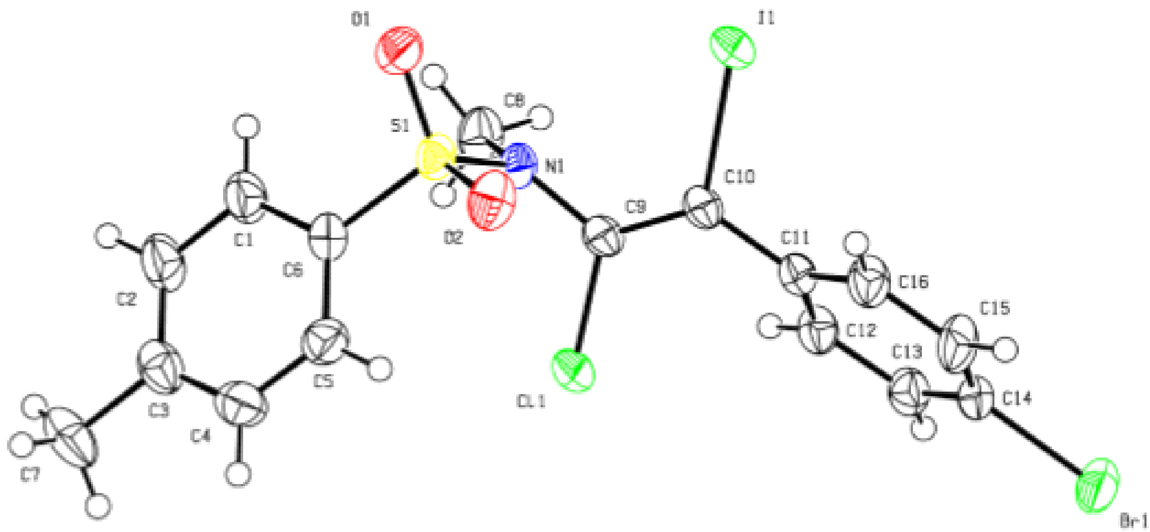

Table S18. Crystal data and structure refinement for 20190730ZH_ZNZ3043_0m_a.

Identification code	20190730ZH_ZNZ3043_0m_a	
Empirical formula	C16 H14 Br Cl I N O2 S	
Formula weight	526.60	
Temperature	210(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 33.9978(13) Å	a= 90°.
	b = 9.0203(4) Å	b= 103.9310(10)°.
	c = 12.2264(5) Å	g = 90°.
Volume	3639.2(3) Å^3	
Z	8	
Density (calculated)	1.922 Mg/m^3	
Absorption coefficient	12.854 mm^{-1}	
F(000)	2032	
Crystal size	0.160 x 0.140 x 0.110 mm^3	
Theta range for data collection	4.663 to 52.998°.	
Index ranges	-40<=h<=40, -10<=k<=10, -14<=l<=14	
Reflections collected	17095	
Independent reflections	3162 [R(int) = 0.0572]	
Completeness to theta = 52.998°	98.3 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3667 and 0.1101
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3162 / 0 / 210
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.1027
R indices (all data)	R1 = 0.0385, wR2 = 0.1034
Extinction coefficient	n/a
Largest diff. peak and hole	1.450 and -0.729 e.Å^{-3}

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)for 20190730ZH_ZNZ3043_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	4627(1)	-2042(1)	8703(1)	47(1)
C(1)	2767(1)	6803(5)	3085(3)	42(1)
Cl(1)	3333(1)	2771(1)	5358(1)	43(1)
I(1)	4580(1)	5077(1)	5866(1)	40(1)
N(1)	3660(1)	5115(3)	4536(3)	30(1)
O(1)	3567(1)	7828(3)	4366(2)	44(1)
S(1)	3421(1)	6578(1)	4870(1)	31(1)
C(2)	2365(1)	6554(5)	2543(3)	48(1)
O(2)	3473(1)	6485(3)	6062(2)	42(1)
C(3)	2103(1)	5866(4)	3092(4)	42(1)
C(4)	2245(1)	5467(5)	4205(4)	44(1)
C(5)	2645(1)	5682(4)	4768(3)	38(1)
C(6)	2908(1)	6347(4)	4197(3)	33(1)
C(7)	1667(1)	5589(6)	2483(4)	53(1)
C(8)	3631(2)	4813(5)	3342(3)	42(1)
C(9)	3743(1)	3914(4)	5281(3)	28(1)
C(10)	4110(1)	3575(4)	5889(3)	29(1)
C(11)	4235(1)	2222(4)	6564(3)	29(1)
C(12)	4173(1)	831(4)	6062(3)	34(1)
C(13)	4298(1)	-447(5)	6697(3)	35(1)

C(14)	4473(1)	-299(4)	7824(3)	34(1)
C(15)	4537(1)	1062(5)	8344(3)	44(1)
C(16)	4420(1)	2326(4)	7712(3)	38(1)

Table S20. Bond lengths [Å] and angles [°] for 20190730ZH_ZNZ3043_0m_a.

Br(1)-C(14)	1.905(4)	C(14)-C(15)	1.375(6)
C(1)-C(2)	1.384(6)	C(15)-C(16)	1.382(6)
C(1)-C(6)	1.391(5)	C(15)-H(15)	0.9400
C(1)-H(1)	0.9400	C(16)-H(16)	0.9400
Cl(1)-C(9)	1.756(3)	C(2)-C(1)-C(6)	119.3(4)
I(1)-C(10)	2.101(3)	C(2)-C(1)-H(1)	120.3
N(1)-C(9)	1.400(5)	C(6)-C(1)-H(1)	120.3
N(1)-C(8)	1.465(5)	C(9)-N(1)-C(8)	117.3(3)
N(1)-S(1)	1.651(3)	C(9)-N(1)-S(1)	119.5(2)
O(1)-S(1)	1.429(3)	C(8)-N(1)-S(1)	118.5(3)
S(1)-O(2)	1.428(3)	O(2)-S(1)-O(1)	121.07(18)
S(1)-C(6)	1.752(4)	O(2)-S(1)-N(1)	105.00(16)
C(2)-C(3)	1.385(6)	O(1)-S(1)-N(1)	106.40(17)
C(2)-H(2)	0.9400	O(2)-S(1)-C(6)	109.67(17)
C(3)-C(4)	1.378(6)	O(1)-S(1)-C(6)	107.43(17)
C(3)-C(7)	1.509(5)	N(1)-S(1)-C(6)	106.34(17)
C(4)-C(5)	1.380(6)	C(1)-C(2)-C(3)	121.1(4)
C(4)-H(4)	0.9400	C(1)-C(2)-H(2)	119.4
C(5)-C(6)	1.397(5)	C(3)-C(2)-H(2)	119.4
C(5)-H(5)	0.9400	C(4)-C(3)-C(2)	118.7(4)
C(7)-H(7A)	0.9700	C(4)-C(3)-C(7)	121.0(4)
C(7)-H(7B)	0.9700	C(2)-C(3)-C(7)	120.3(4)
C(7)-H(7C)	0.9700	C(3)-C(4)-C(5)	121.8(4)
C(8)-H(8A)	0.9700	C(3)-C(4)-H(4)	119.1
C(8)-H(8B)	0.9700	C(5)-C(4)-H(4)	119.1
C(8)-H(8C)	0.9700	C(4)-C(5)-C(6)	118.9(4)
C(9)-C(10)	1.326(5)	C(4)-C(5)-H(5)	120.6
C(10)-C(11)	1.477(5)	C(6)-C(5)-H(5)	120.6
C(11)-C(12)	1.390(5)	C(1)-C(6)-C(5)	120.2(3)

C(11)-C(16)	1.396(5)	C(1)-C(6)-S(1)	119.7(3)
C(12)-C(13)	1.398(6)	C(5)-C(6)-S(1)	120.1(3)
C(12)-H(12)	0.9400	C(3)-C(7)-H(7A)	109.5
C(13)-C(14)	1.370(6)	C(3)-C(7)-H(7B)	109.5
C(13)-H(13)	0.9400	H(7A)-C(7)-H(7B)	109.5
C(3)-C(7)-H(7C)	109.5	C(16)-C(11)-C(10)	120.3(3)
H(7A)-C(7)-H(7C)	109.5	C(11)-C(12)-C(13)	120.3(3)
H(7B)-C(7)-H(7C)	109.5	C(11)-C(12)-H(12)	119.8
N(1)-C(8)-H(8A)	109.5	C(13)-C(12)-H(12)	119.8
N(1)-C(8)-H(8B)	109.5	C(14)-C(13)-C(12)	118.6(4)
H(8A)-C(8)-H(8B)	109.5	C(14)-C(13)-H(13)	120.7
N(1)-C(8)-H(8C)	109.5	C(12)-C(13)-H(13)	120.7
H(8A)-C(8)-H(8C)	109.5	C(13)-C(14)-C(15)	122.2(4)
H(8B)-C(8)-H(8C)	109.5	C(13)-C(14)-Br(1)	118.8(3)
C(10)-C(9)-N(1)	124.0(3)	C(15)-C(14)-Br(1)	119.0(3)
C(10)-C(9)-Cl(1)	119.2(3)	C(14)-C(15)-C(16)	119.1(3)
N(1)-C(9)-Cl(1)	116.7(2)	C(14)-C(15)-H(15)	120.5
C(9)-C(10)-C(11)	127.4(3)	C(16)-C(15)-H(15)	120.5
C(9)-C(10)-I(1)	117.4(3)	C(15)-C(16)-C(11)	120.4(4)
C(11)-C(10)-I(1)	115.1(2)	C(15)-C(16)-H(16)	119.8
C(12)-C(11)-C(16)	119.3(3)	C(11)-C(16)-H(16)	119.8
C(12)-C(11)-C(10)	120.4(3)		

Symmetry transformations used to generate equivalent atoms:

Table S21. Anisotropic displacement parameters ($Å^2$x 10^3) for 20190730ZH_ZNZ3043_0m_a. The anisotropicdisplacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	46(1)	43(1)	51(1)	16(1)	10(1)	14(1)
C(1)	32(2)	58(3)	35(2)	9(2)	3(2)	5(2)
Cl(1)	24(1)	40(1)	58(1)	10(1)	-3(1)	-7(1)
I(1)	25(1)	41(1)	50(1)	5(1)	1(1)	-7(1)
N(1)	28(2)	34(2)	22(1)	3(1)	-2(1)	1(1)
O(1)	42(2)	37(2)	48(2)	10(1)	-1(1)	-5(1)
S(1)	33(1)	31(1)	26(1)	1(1)	-2(1)	0(1)
C(2)	33(2)	66(3)	38(2)	4(2)	-1(2)	6(2)
O(2)	52(2)	42(2)	27(1)	-5(1)	0(1)	6(1)
C(3)	32(2)	36(2)	54(2)	-9(2)	4(2)	4(2)
C(4)	36(2)	37(2)	60(3)	0(2)	17(2)	-2(2)
C(5)	40(2)	34(2)	41(2)	4(2)	12(2)	3(2)
C(6)	30(2)	34(2)	32(2)	2(1)	4(1)	6(2)
C(7)	28(2)	53(3)	73(3)	-21(2)	1(2)	-2(2)
C(8)	44(3)	55(3)	25(2)	2(2)	6(2)	11(2)
C(9)	25(2)	31(2)	27(2)	-4(1)	1(1)	-5(1)
C(10)	24(2)	32(2)	27(2)	-4(1)	0(1)	-2(1)
C(11)	23(2)	32(2)	30(2)	1(1)	1(1)	0(1)
C(12)	30(2)	36(2)	32(2)	-1(2)	1(1)	2(2)
C(13)	31(2)	34(2)	41(2)	1(2)	7(2)	6(2)
C(14)	25(2)	34(2)	42(2)	11(2)	7(2)	7(2)
C(15)	45(2)	49(3)	29(2)	6(2)	-9(2)	6(2)
C(16)	36(2)	36(2)	36(2)	-2(2)	-4(2)	0(2)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)for 20190730ZH_ZNZ3043_0m_a.

	x	y	z	U(eq)
H(1)	2941	7275	2706	51
H(2)	2269	6857	1791	57
H(4)	2066	5037	4591	52
H(5)	2738	5386	5524	46
H(7A)	1495	6329	2708	80
H(7B)	1586	4610	2673	80
H(7C)	1641	5651	1676	80
H(8A)	3860	4213	3269	63
H(8B)	3633	5741	2943	63
H(8C)	3381	4284	3024	63
H(12)	4046	750	5291	41
H(13)	4262	-1388	6358	42
H(15)	4658	1130	9119	53
H(16)	4465	3263	8057	46

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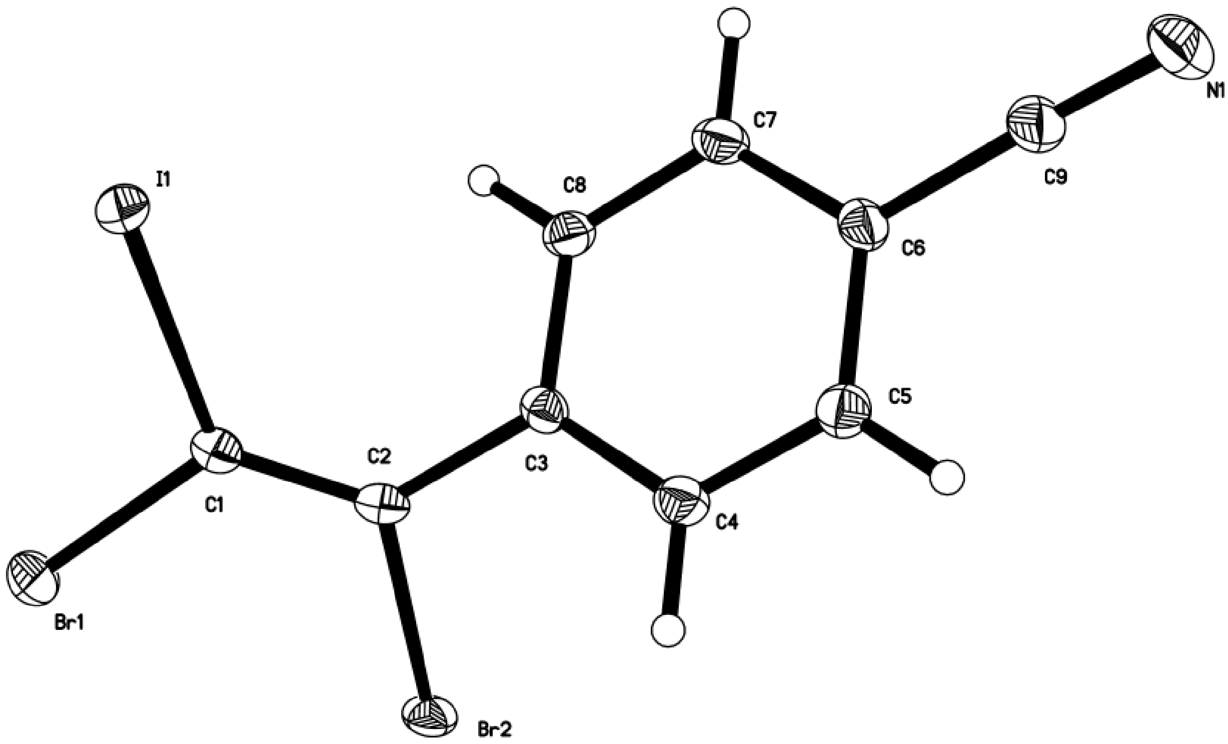

Table S23. Crystal data and structure refinement for 20191027LI_ZNZ4686_0m_a.

Identification code	20191027LI_ZNZ4686_0m_a	
Empirical formula	C9 H4 Br2 I N	
Formula weight	412.85	
Temperature	190(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 4.16110(10) Å	= 90°.
	b = 18.3564(5) Å	= 101.6520(10)°.
	c = 13.9941(4) Å	= 90°.
Volume	1046.88(5) Å^3	
Z	4	
Density (calculated)	2.619 Mg/m^3	
Absorption coefficient	22.185 mm^{-1}	
F(000)	752	
Crystal size	0.120 x 0.110 x 0.090 mm^3	
Theta range for data collection	3.501 to 52.982°.	

Index ranges	-4<=h<=4, -21<=k<=21, -16<=l<=15
Reflections collected	7688
Independent reflections	1836 [R(int) = 0.0356]
Completeness to theta = 52.982°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1836 / 0 / 118
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0241, wR2 = 0.0628
R indices (all data)	R1 = 0.0256, wR2 = 0.0637
Extinction coefficient	n/a
Largest diff. peak and hole	1.001 and -0.558 e.Å^{-3}

Table S24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 20191027LI_ZNZ4686_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2132(1)	786(1)	4153(1)	34(1)
Br(2)	716(1)	2460(1)	3322(1)	29(1)
C(1)	3810(10)	1604(2)	4908(3)	26(1)
C(2)	3245(9)	2282(2)	4599(3)	24(1)
C(3)	4412(9)	2962(2)	5141(3)	22(1)
C(4)	5860(10)	3510(2)	4686(3)	28(1)
C(5)	7032(10)	4133(2)	5181(3)	28(1)
C(6)	6749(9)	4227(2)	6150(3)	26(1)
C(7)	5224(11)	3685(2)	6614(3)	29(1)
C(8)	4069(10)	3063(2)	6104(3)	26(1)
C(9)	8065(11)	4872(3)	6668(3)	33(1)
I(1)	6811(1)	1298(1)	6235(1)	27(1)
N(1)	9160(11)	5388(2)	7049(3)	48(1)

Table S25. Bond lengths [Å] and angles [°] for 20191027LI_ZNZ4686_0m_a.

Br(1)-C(1)	1.887(4)
Br(2)-C(2)	1.910(4)
C(1)-C(2)	1.323(6)
C(1)-I(1)	2.095(4)
C(2)-C(3)	1.490(6)
C(3)-C(4)	1.391(6)
C(3)-C(8)	1.396(5)
C(4)-C(5)	1.375(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.395(6)
C(5)-H(5)	0.9500
C(6)-C(7)	1.408(6)
C(6)-C(9)	1.438(6)
C(7)-C(8)	1.379(6)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-N(1)	1.135(6)
C(2)-C(1)-Br(1)	123.0(3)
C(2)-C(1)-I(1)	125.2(3)
Br(1)-C(1)-I(1)	111.7(2)
C(1)-C(2)-C(3)	127.1(4)
C(1)-C(2)-Br(2)	119.6(3)
C(3)-C(2)-Br(2)	113.2(3)
C(4)-C(3)-C(8)	118.9(4)
C(4)-C(3)-C(2)	119.9(3)
C(8)-C(3)-C(2)	121.1(4)
C(5)-C(4)-C(3)	120.9(4)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	120.1(4)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	119.7(4)
C(5)-C(6)-C(9)	119.5(4)

C(7)-C(6)-C(9)	120.8(4)
C(8)-C(7)-C(6)	119.2(4)
C(8)-C(7)-H(7)	120.4
C(6)-C(7)-H(7)	120.4
C(7)-C(8)-C(3)	121.1(4)
C(7)-C(8)-H(8)	119.4
C(3)-C(8)-H(8)	119.4
N(1)-C(9)-C(6)	177.4(5)

Symmetry transformations used to generate equivalent atoms:

Table S26. Anisotropic displacement parameters ($Å^2$x 10^3) for 20191027LI_ZNZ4686_0m_a. The anisotropic displacement factor exponent takes the form: $-2\ ^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	44(1)	26(1)	30(1)	-7(1)	0(1)	-6(1)
Br(2)	34(1)	34(1)	17(1)	-2(1)	-2(1)	5(1)
C(1)	30(2)	27(2)	21(2)	-4(2)	3(2)	-2(2)
C(2)	23(2)	32(2)	17(2)	-2(2)	3(2)	0(2)
C(3)	22(2)	22(2)	22(2)	-2(2)	2(2)	4(2)
C(4)	31(2)	29(2)	24(2)	-1(2)	7(2)	3(2)
C(5)	28(2)	27(2)	26(2)	1(2)	2(2)	-1(2)
C(6)	27(2)	23(2)	26(2)	-2(2)	-4(2)	3(2)
C(7)	34(2)	32(2)	21(2)	-3(2)	5(2)	5(2)
C(8)	29(2)	28(2)	21(2)	2(2)	4(2)	3(2)
C(9)	34(2)	30(2)	29(2)	-1(2)	-7(2)	-1(2)
I(1)	31(1)	27(1)	22(1)	1(1)	-1(1)	2(1)
N(1)	62(3)	38(2)	37(2)	-9(2)	-10(2)	-6(2)

Table S27. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 20191027LI_ZNZ4686_0m_a.

	x	y	z	U(eq)
H(4)	6041	3453	4024	33
H(5)	8037	4501	4863	33
H(7)	4992	3746	7271	35
H(8)	3023	2698	6414	31

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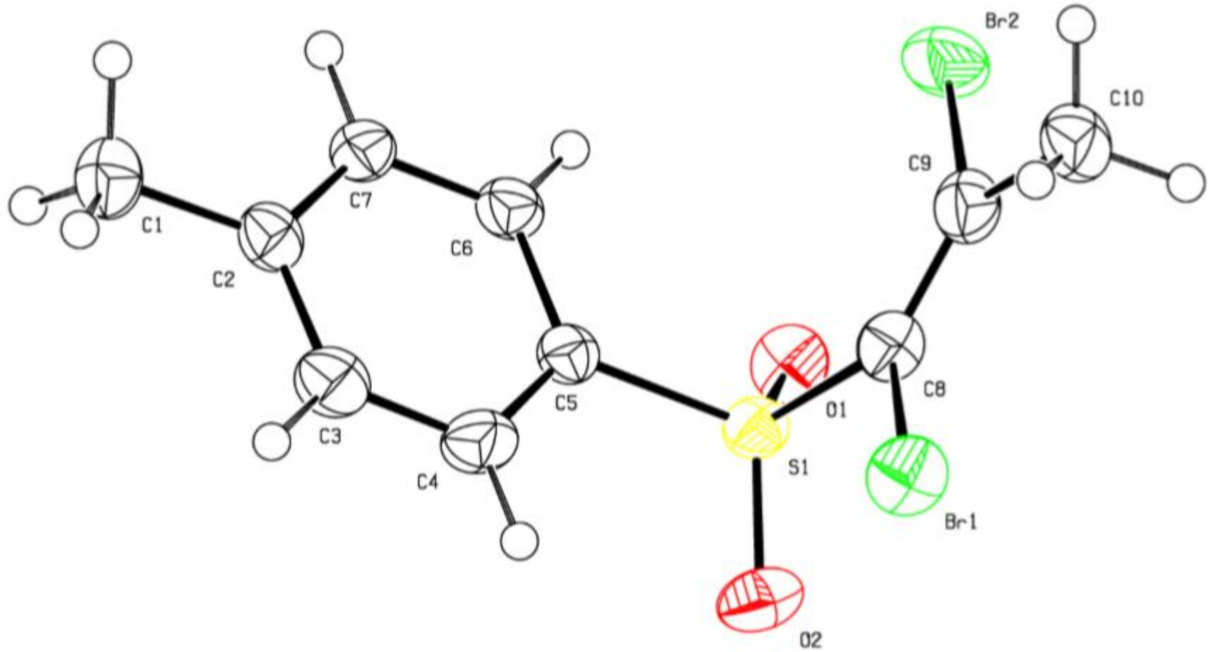

Table S28. Crystal data and structure refinement for 20191031LI_ZNZ2648_0m_a.

Identification code	20191031LI_ZNZ2648_0m_a	
Empirical formula	C9 H8 Br I O S	
Formula weight	371.02	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.6374(3) Å	= 90°.
	b = 10.8292(5) Å	= 92.333(2)°.
	c = 18.2279(10) Å	= 90°.
Volume	1111.86(10) $Å^3$	
Z	4	
Density (calculated)	2.216 Mg/m^3	
Absorption coefficient	6.621 mm^{-1}	
F(000)	696	
Crystal size	0.120 x 0.110 x 0.090 mm^3	
Theta range for data collection	2.923 to 28.329°.	
Index ranges	-7<=h<=7, -14<=k<=13, -24<=l<=22	
Reflections collected	10610	

Independent reflections	2748 [R(int) = 0.0233]
Completeness to theta = 25.242°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3343 and 0.2350
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2748 / 0 / 119
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0183, wR2 = 0.0452
R indices (all data)	R1 = 0.0202, wR2 = 0.0459
Extinction coefficient	n/a
Largest diff. peak and hole	0.697 and -1.019 e.$Å^{-3}$

Table S29. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for 20191031LI_ZNZ2648_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	9844(1)	5622(1)	3852(1)	29(1)
Br(1)	3946(1)	2825(1)	2857(1)	27(1)
S(1)	6007(1)	5358(1)	2374(1)	25(1)
O(1)	3627(3)	5347(2)	1994(1)	34(1)
C(7)	7362(3)	4183(2)	3677(1)	22(1)
C(8)	6020(3)	4160(2)	3064(1)	21(1)
C(6)	7396(3)	3258(2)	4274(1)	23(1)
C(5)	5572(4)	3234(2)	4766(1)	30(1)
C(1)	9284(4)	2440(2)	4372(1)	28(1)
C(9)	7977(4)	4598(2)	1777(1)	35(1)
C(4)	5650(4)	2398(2)	5340(2)	36(1)
C(3)	7527(4)	1585(2)	5434(1)	35(1)
C(2)	9336(4)	1604(2)	4941(2)	33(1)

Table S30. Bond lengths [Å] and angles [°] for 20191031LI_ZNZ2648_0m_a.

I(1)-C(7)	2.1098(19)
Br(1)-C(8)	1.8885(19)
S(1)-O(1)	1.4852(16)
S(1)-C(9)	1.788(2)
S(1)-C(8)	1.806(2)
C(7)-C(8)	1.323(3)
C(7)-C(6)	1.479(3)
C(6)-C(1)	1.390(3)
C(6)-C(5)	1.393(3)
C(5)-C(4)	1.384(3)
C(5)-H(5)	0.9500
C(1)-C(2)	1.377(3)
C(1)-H(1)	0.9500
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(4)-C(3)	1.382(3)
C(4)-H(4)	0.9500
C(3)-C(2)	1.386(4)
C(3)-H(3)	0.9500
C(2)-H(2)	0.9500
O(1)-S(1)-C(9)	106.46(11)
O(1)-S(1)-C(8)	107.26(10)
C(9)-S(1)-C(8)	96.21(11)
C(8)-C(7)-C(6)	126.73(18)
C(8)-C(7)-I(1)	119.65(15)
C(6)-C(7)-I(1)	113.59(14)
C(7)-C(8)-S(1)	124.04(16)
C(7)-C(8)-Br(1)	120.73(16)
S(1)-C(8)-Br(1)	115.23(11)
C(1)-C(6)-C(5)	119.1(2)
C(1)-C(6)-C(7)	120.88(19)
C(5)-C(6)-C(7)	119.91(19)
C(4)-C(5)-C(6)	119.9(2)

C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(2)-C(1)-C(6)	120.6(2)
C(2)-C(1)-H(1)	119.7
C(6)-C(1)-H(1)	119.7
S(1)-C(9)-H(9A)	109.5
S(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
S(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(3)-C(4)-C(5)	120.7(2)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(4)-C(3)-C(2)	119.4(2)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(1)-C(2)-C(3)	120.3(2)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S31. Anisotropic displacement parameters ($Å^2 x 10^3$) for 20191031LI_ZNZ2648_0m_a. The anisotropicdisplacement factor exponent takes the form: $-2\ ^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	33(1)	28(1)	27(1)	1(1)	-3(1)	-10(1)
Br(1)	26(1)	27(1)	29(1)	-5(1)	0(1)	-6(1)
S(1)	25(1)	25(1)	23(1)	2(1)	-1(1)	1(1)
O(1)	24(1)	42(1)	36(1)	8(1)	-4(1)	6(1)
C(7)	22(1)	22(1)	21(1)	-1(1)	3(1)	-3(1)
C(8)	22(1)	21(1)	21(1)	-2(1)	3(1)	-1(1)
C(6)	24(1)	22(1)	22(1)	0(1)	-1(1)	-5(1)

C(5)	24(1)	34(1)	31(1)	6(1)	2(1)	1(1)
C(1)	29(1)	23(1)	32(1)	-3(1)	4(1)	-1(1)
C(9)	28(1)	50(1)	26(1)	4(1)	7(1)	6(1)
C(4)	31(1)	44(1)	34(1)	10(1)	7(1)	-4(1)
C(3)	40(1)	30(1)	35(1)	13(1)	-4(1)	-8(1)
C(2)	34(1)	22(1)	42(2)	2(1)	-3(1)	1(1)

Table S32. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)for 20191031LI_ZNZ2648_0m_a.

	x	y	z	U(eq)
H(5)	4276	3791	4708	36
H(1)	10550	2459	4043	33
H(9A)	7367	3771	1659	52
H(9B)	9553	4529	2020	52
H(9C)	8090	5077	1323	52
H(4)	4400	2382	5674	43
H(3)	7578	1019	5832	42
H(2)	10616	1037	4996	39

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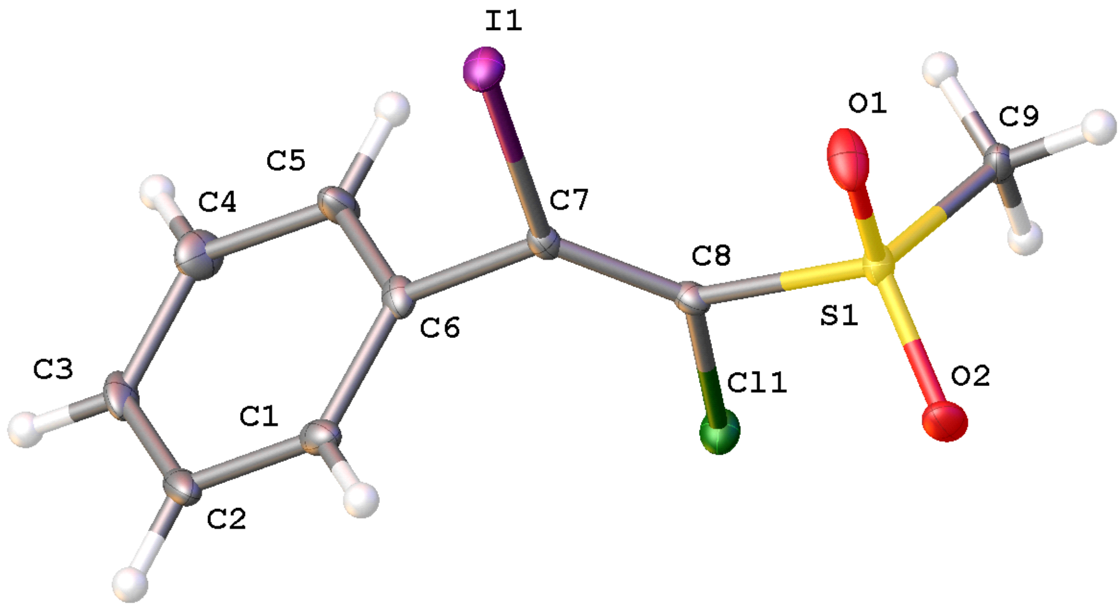

Table S33. Crystal data and structure refinement for 1904226483_0m.

Identification code	1904226483_0m
Empirical formula	$C_9H_8ClIO_2S$
Formula weight	342.56
Temperature/K	169.97
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.09320(10)
b/Å	10.3240(2)
c/Å	29.7405(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2177.90(6)
Z	8
ρ_{calc}g/cm^3	2.089
μ/mm^{-1}	18.365
F(000)	1312.0
Crystal size/mm^3	0.12 × 0.05 × 0.01
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	12.026 to 109.868
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 12$, $-36 \le l \le 36$
Reflections collected	20107
Independent reflections	2064 [R_{int} = 0.0384, R_{sigma} = 0.0195]

Data/restraints/parameters	2064/0/128
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0204, wR_2 = 0.0502
Final R indexes [all data]	R_1 = 0.0209, wR_2 = 0.0507
Largest diff. peak/hole / e Å^{-3}	0.41/-0.89

Table S32. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1904226483_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	9881.0(2)	7686.2(2)	6371.7(2)	21.90(8)
Cl1	4164.4(7)	6100.5(5)	5798.1(2)	20.32(13)
S1	7925.6(8)	5664.4(5)	5440.2(2)	16.63(13)
O1	9878(2)	5901(2)	5527.5(6)	30.3(5)
O2	7304(3)	4341.2(16)	5415.3(5)	27.1(4)
C1	5277(3)	6684(2)	6929.8(8)	20.3(5)
C2	4096(4)	7104(3)	7271.6(8)	24.7(5)
C3	3404(3)	8351(3)	7270.1(8)	26.1(5)
C4	3872(4)	9186(2)	6923.8(9)	28.1(6)
C5	5063(3)	8774(3)	6582.0(9)	24.6(6)
C6	5783(3)	7526(2)	6585.6(7)	16.6(5)
C7	7118(3)	7085(2)	6230.1(7)	15.3(4)
C8	6559(3)	6405(2)	5876.7(7)	15.9(4)
C9	7244(4)	6487(2)	4951.9(7)	22.2(5)

Table S33. Anisotropic Displacement Parameters (Å^2×10^3) for 1904226483_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	15.83(11)	26.42(12)	23.45(11)	-4.30(6)	-1.32(5)	-2.15(5)
Cl1	14.2(3)	25.3(3)	21.5(3)	-5.1(2)	-1.1(2)	0.4(2)
S1	18.0(3)	17.0(3)	14.9(2)	-2.44(19)	2.00(19)	2.8(2)
O1	16.7(9)	48.0(13)	26.1(9)	-12.2(9)	0.8(7)	5.3(7)
O2	39.9(11)	14.9(8)	26.6(8)	-1.6(7)	8.9(8)	3.4(7)
C1	22.6(12)	20.3(13)	18.2(11)	-2.3(10)	-1.8(9)	-2.4(9)
C2	23.0(13)	33.1(14)	18.1(11)	0.0(10)	3.2(10)	-8.4(11)
C3	17.1(11)	38.0(15)	23.4(11)	-12.6(11)	6.5(10)	-3.9(10)
C4	26.1(13)	22.3(13)	36.0(13)	-5.7(10)	6.5(11)	5.0(10)
C5	26.7(14)	21.6(14)	25.4(13)	1.8(10)	7.6(10)	1.5(9)
C6	14.8(12)	19.2(11)	15.7(10)	-3.5(8)	0.6(9)	-1.5(9)
C7	14.1(11)	15.4(10)	16.4(10)	2.0(9)	0.9(9)	1.5(9)
C8	13.7(10)	17.0(11)	17.0(10)	0.2(8)	1.3(8)	0.2(8)
C9	31.1(13)	19.7(11)	15.8(10)	-0.3(9)	2.0(9)	-0.2(10)

Table S34. Bond Lengths for 1904226483_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C7	2.099(2)	C1	C6	1.390(3)
Cl1	C8	1.743(2)	C2	C3	1.378(4)
S1	O1	1.4304(18)	C3	C4	1.383(4)
S1	O2	1.4373(18)	C4	C5	1.389(3)
S1	C8	1.791(2)	C5	C6	1.386(3)
S1	C9	1.750(2)	C6	C7	1.490(3)
C1	C2	1.387(3)	C7	C8	1.325(3)

Table S35. Bond Angles for 1904226483_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	117.95(12)	C6	C5	C4	120.2(2)
O1	S1	C8	108.65(11)	C1	C6	C7	119.7(2)
O1	S1	C9	109.58(12)	C5	C6	C1	119.5(2)
O2	S1	C8	106.07(10)	C5	C6	C7	120.8(2)
O2	S1	C9	109.48(11)	C6	C7	I1	111.14(15)
C9	S1	C8	104.18(11)	C8	C7	I1	126.55(17)
C2	C1	C6	120.0(2)	C8	C7	C6	122.3(2)
C3	C2	C1	120.3(2)	Cl1	C8	S1	110.69(12)
C2	C3	C4	120.0(2)	C7	C8	Cl1	119.57(17)
C3	C4	C5	120.0(2)	C7	C8	S1	129.72(18)

Table S36. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1904226483_0m.

Atom	*x*	*y*	*z*	U(eq)
H1	5741.12	5820.48	6930.93	24
H2	3761.06	6528.89	7507.83	30
H3	2606.9	8637.66	7506.67	31
H4	3378.84	10041.4	6919.81	34
H5	5385.8	9349	6344.9	29
H9A	7414.33	7420.14	4995.44	33
H9B	5915.25	6303.84	4887.93	33
H9C	8021.67	6195.93	4698.85	33

31. The crystallographic data of 105

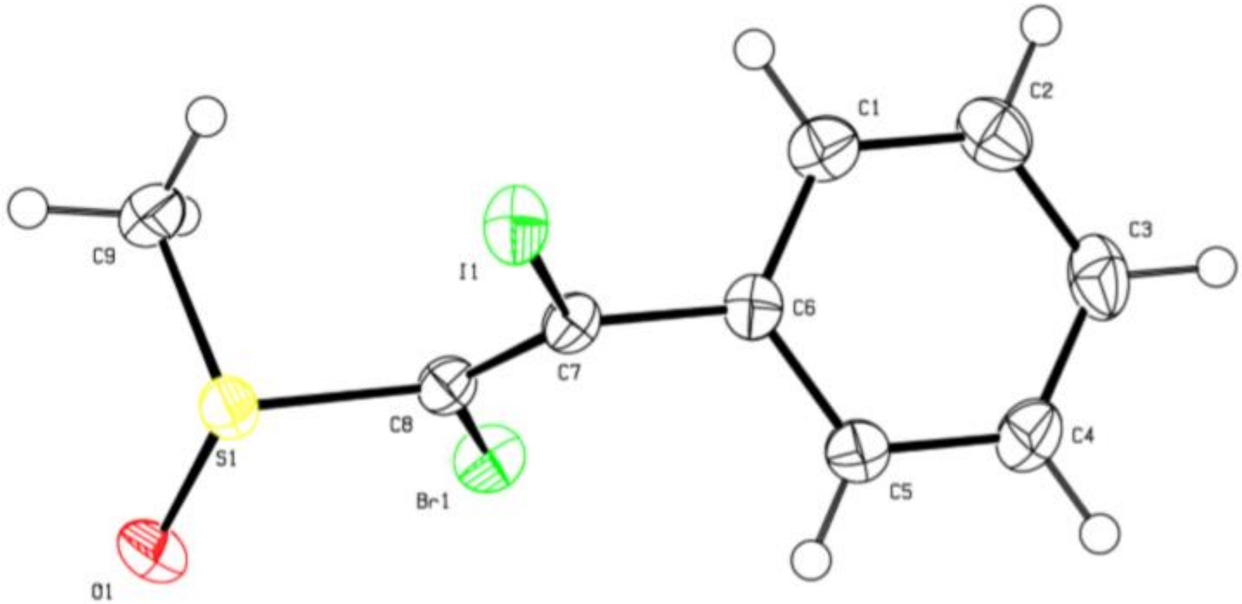

Table S37. Crystal data and structure refinement for 20191031LI_ZNZ2648_0m_a.

Identification code	20191031LI_ZNZ2648_0m_a	
Empirical formula	C9 H8 Br I O S	
Formula weight	371.02	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.6374(3) Å	= 90°.
	b = 10.8292(5) Å	= 92.333(2)°.
	c = 18.2279(10) Å	= 90°.
Volume	1111.86(10) $Å^3$	
Z	4	
Density (calculated)	2.216 Mg/m^3	
Absorption coefficient	6.621 mm^{-1}	
F(000)	696	
Crystal size	0.120 x 0.110 x 0.090 mm^3	
Theta range for data collection	2.923 to 28.329°.	
Index ranges	-7<=h<=7, -14<=k<=13, -24<=l<=22	
Reflections collected	10610	
Independent reflections	2748 [R(int) = 0.0233]	

Completeness to theta = 25.242°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.3343 and 0.2350
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2748 / 0 / 119
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0183, wR2 = 0.0452
R indices (all data)	R1 = 0.0202, wR2 = 0.0459
Extinction coefficient	n/a
Largest diff. peak and hole	0.697 and -1.019 e.Å^{-3}

Table S38. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)for 20191031LI_ZNZ2648_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	9844(1)	5622(1)	3852(1)	29(1)
Br(1)	3946(1)	2825(1)	2857(1)	27(1)
S(1)	6007(1)	5358(1)	2374(1)	25(1)
O(1)	3627(3)	5347(2)	1994(1)	34(1)
C(7)	7362(3)	4183(2)	3677(1)	22(1)
C(8)	6020(3)	4160(2)	3064(1)	21(1)
C(6)	7396(3)	3258(2)	4274(1)	23(1)
C(5)	5572(4)	3234(2)	4766(1)	30(1)
C(1)	9284(4)	2440(2)	4372(1)	28(1)
C(9)	7977(4)	4598(2)	1777(1)	35(1)
C(4)	5650(4)	2398(2)	5340(2)	36(1)
C(3)	7527(4)	1585(2)	5434(1)	35(1)
C(2)	9336(4)	1604(2)	4941(2)	33(1)

Table S39. Bond lengths [Å] and angles [°] for 20191031LI_ZNZ2648_0m_a.

I(1)-C(7)	2.1098(19)
Br(1)-C(8)	1.8885(19)
S(1)-O(1)	1.4852(16)
S(1)-C(9)	1.788(2)
S(1)-C(8)	1.806(2)
C(7)-C(8)	1.323(3)
C(7)-C(6)	1.479(3)
C(6)-C(1)	1.390(3)
C(6)-C(5)	1.393(3)
C(5)-C(4)	1.384(3)
C(5)-H(5)	0.9500
C(1)-C(2)	1.377(3)
C(1)-H(1)	0.9500
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(4)-C(3)	1.382(3)
C(4)-H(4)	0.9500
C(3)-C(2)	1.386(4)
C(3)-H(3)	0.9500
C(2)-H(2)	0.9500
O(1)-S(1)-C(9)	106.46(11)
O(1)-S(1)-C(8)	107.26(10)
C(9)-S(1)-C(8)	96.21(11)
C(8)-C(7)-C(6)	126.73(18)
C(8)-C(7)-I(1)	119.65(15)
C(6)-C(7)-I(1)	113.59(14)
C(7)-C(8)-S(1)	124.04(16)
C(7)-C(8)-Br(1)	120.73(16)
S(1)-C(8)-Br(1)	115.23(11)
C(1)-C(6)-C(5)	119.1(2)
C(1)-C(6)-C(7)	120.88(19)
C(5)-C(6)-C(7)	119.91(19)

C(4)-C(5)-C(6)	119.9(2)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(2)-C(1)-C(6)	120.6(2)
C(2)-C(1)-H(1)	119.7
C(6)-C(1)-H(1)	119.7
S(1)-C(9)-H(9A)	109.5
S(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
S(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(3)-C(4)-C(5)	120.7(2)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(4)-C(3)-C(2)	119.4(2)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(1)-C(2)-C(3)	120.3(2)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S40. Anisotropic displacement parameters ($Å^2$x 10^3) for 20191031LI_ZNZ 2648_0m_a. The anisotropic displacement factor exponent takes the form: -2 ^{2}[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	33(1)	28(1)	27(1)	1(1)	-3(1)	-10(1)
Br(1)	26(1)	27(1)	29(1)	-5(1)	0(1)	-6(1)
S(1)	25(1)	25(1)	23(1)	2(1)	-1(1)	1(1)
O(1)	24(1)	42(1)	36(1)	8(1)	-4(1)	6(1)
C(7)	22(1)	22(1)	21(1)	-1(1)	3(1)	-3(1)
C(8)	22(1)	21(1)	21(1)	-2(1)	3(1)	-1(1)

C(6)	24(1)	22(1)	22(1)	0(1)	-1(1)	-5(1)
C(5)	24(1)	34(1)	31(1)	6(1)	2(1)	1(1)
C(1)	29(1)	23(1)	32(1)	-3(1)	4(1)	-1(1)
C(9)	28(1)	50(1)	26(1)	4(1)	7(1)	6(1)
C(4)	31(1)	44(1)	34(1)	10(1)	7(1)	-4(1)
C(3)	40(1)	30(1)	35(1)	13(1)	-4(1)	-8(1)
C(2)	34(1)	22(1)	42(2)	2(1)	-3(1)	1(1)

Table S41. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)for 20191031LI_ZNZ2648_0m_a.

	x	y	z	U(eq)
H(5)	4276	3791	4708	36
H(1)	10550	2459	4043	33
H(9A)	7367	3771	1659	52
H(9B)	9553	4529	2020	52
H(9C)	8090	5077	1323	52
H(4)	4400	2382	5674	43
H(3)	7578	1019	5832	42
H(2)	10616	1037	4996	39

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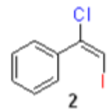
33. Copies of NMR Spectra

Figure S19. ^{1}H-NMR of **2**



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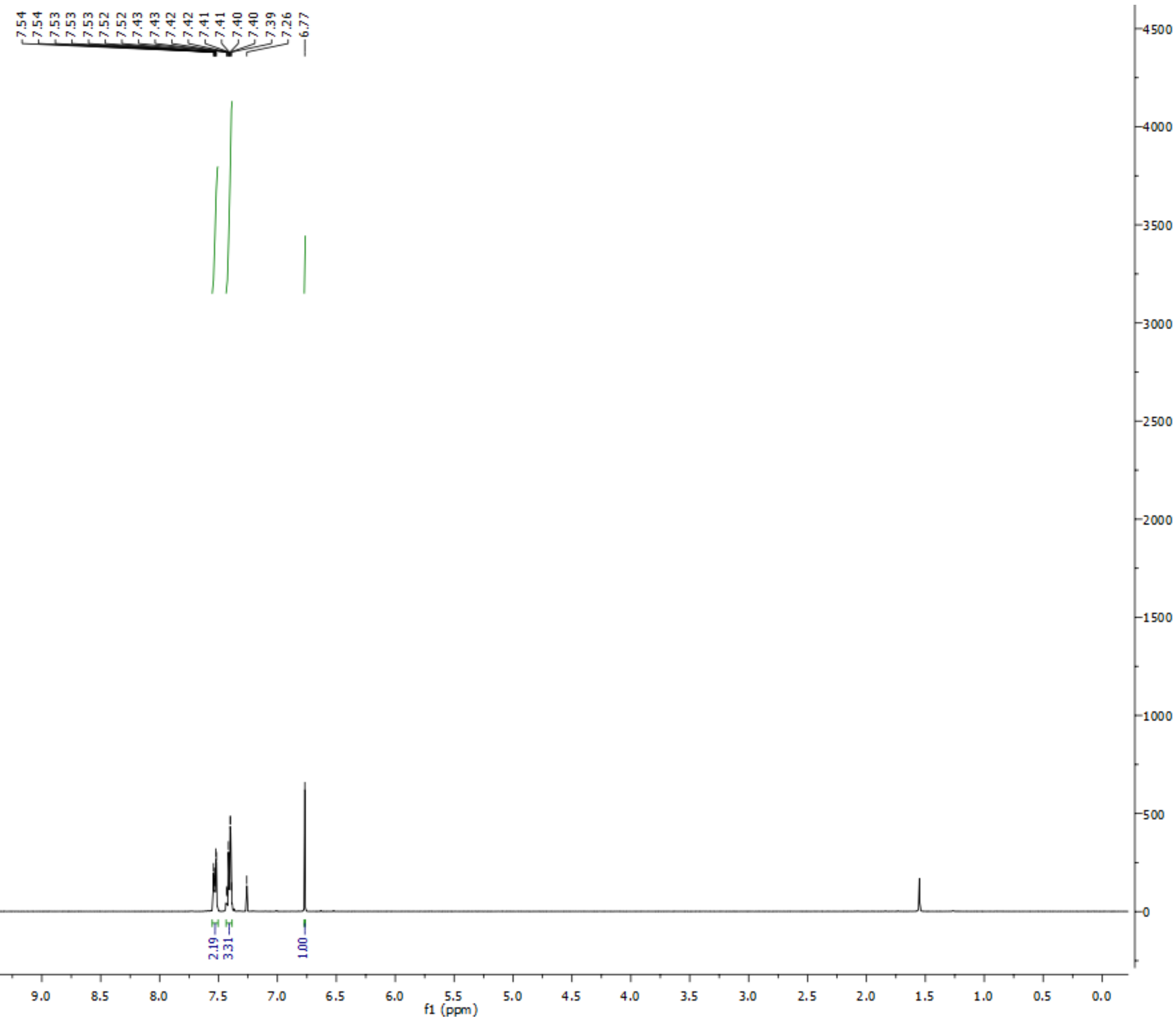

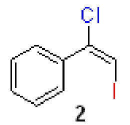

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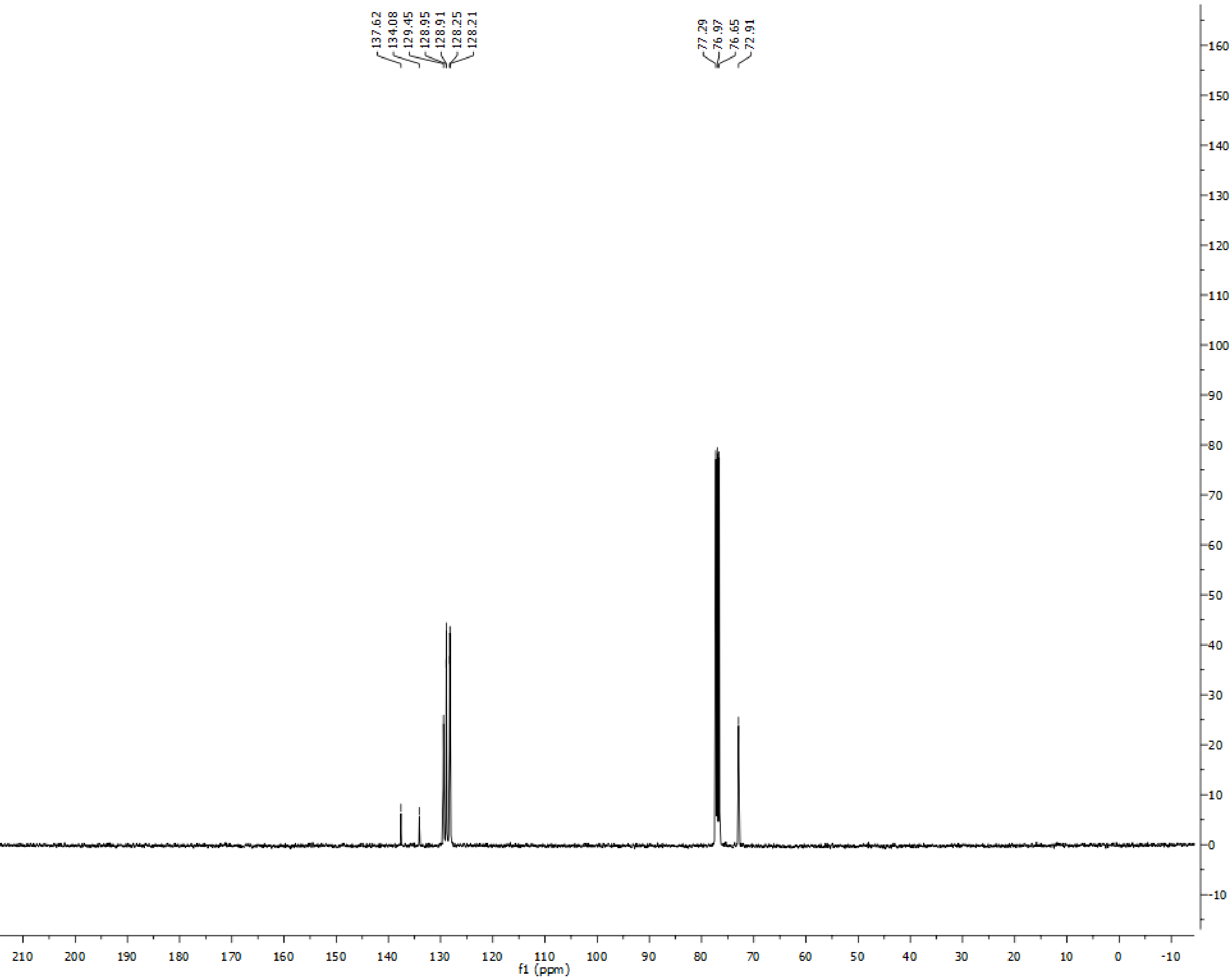
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134.08
129.45
128.95
128.91
128.25
128.21
77.29
76.97
76.65
72.91
f1 (ppm)

Figure S21. ^{1}H-NMR of **3**

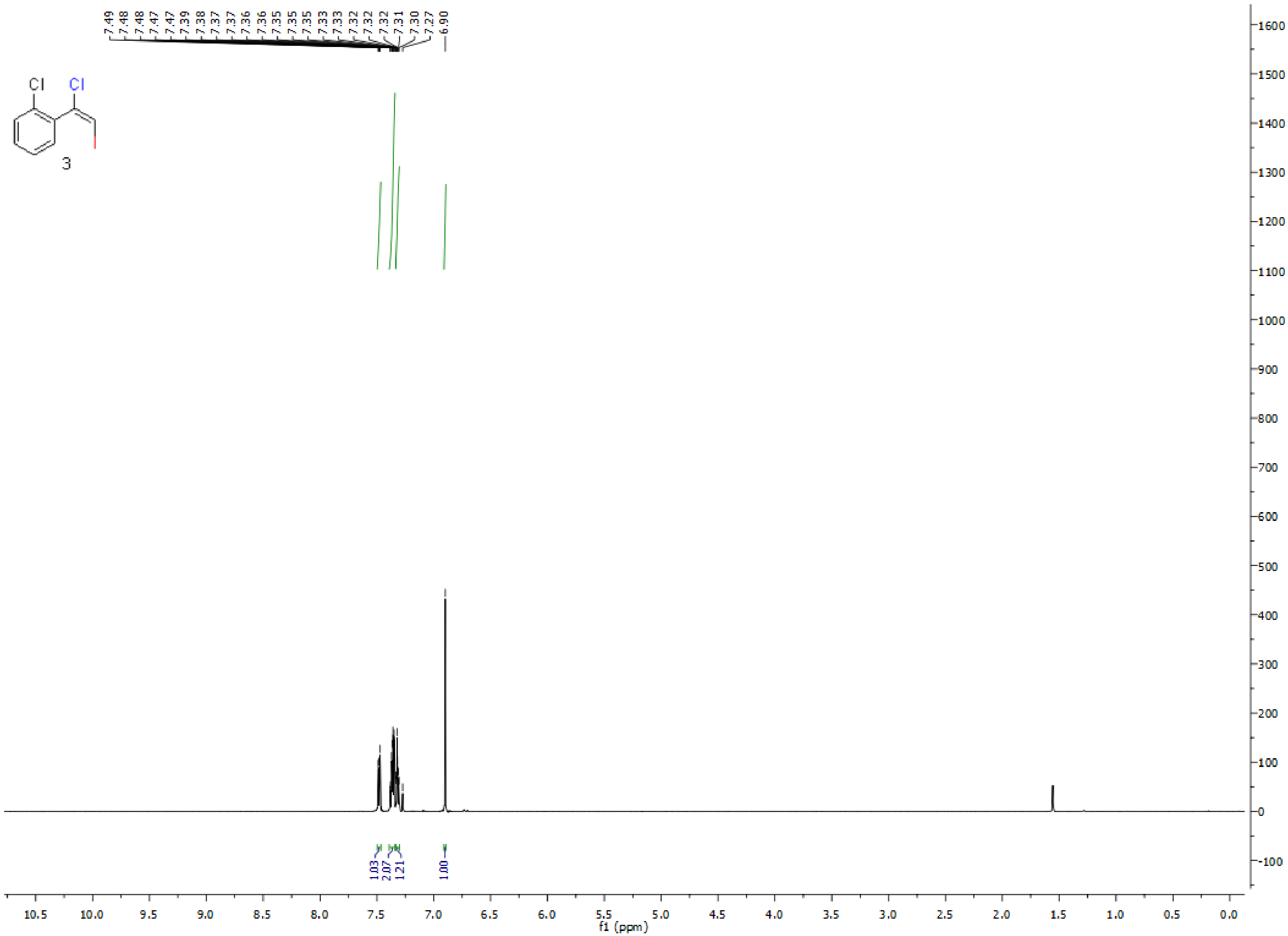
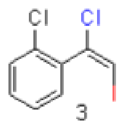


Figure S22. ^{13}C-NMR of **3**



3

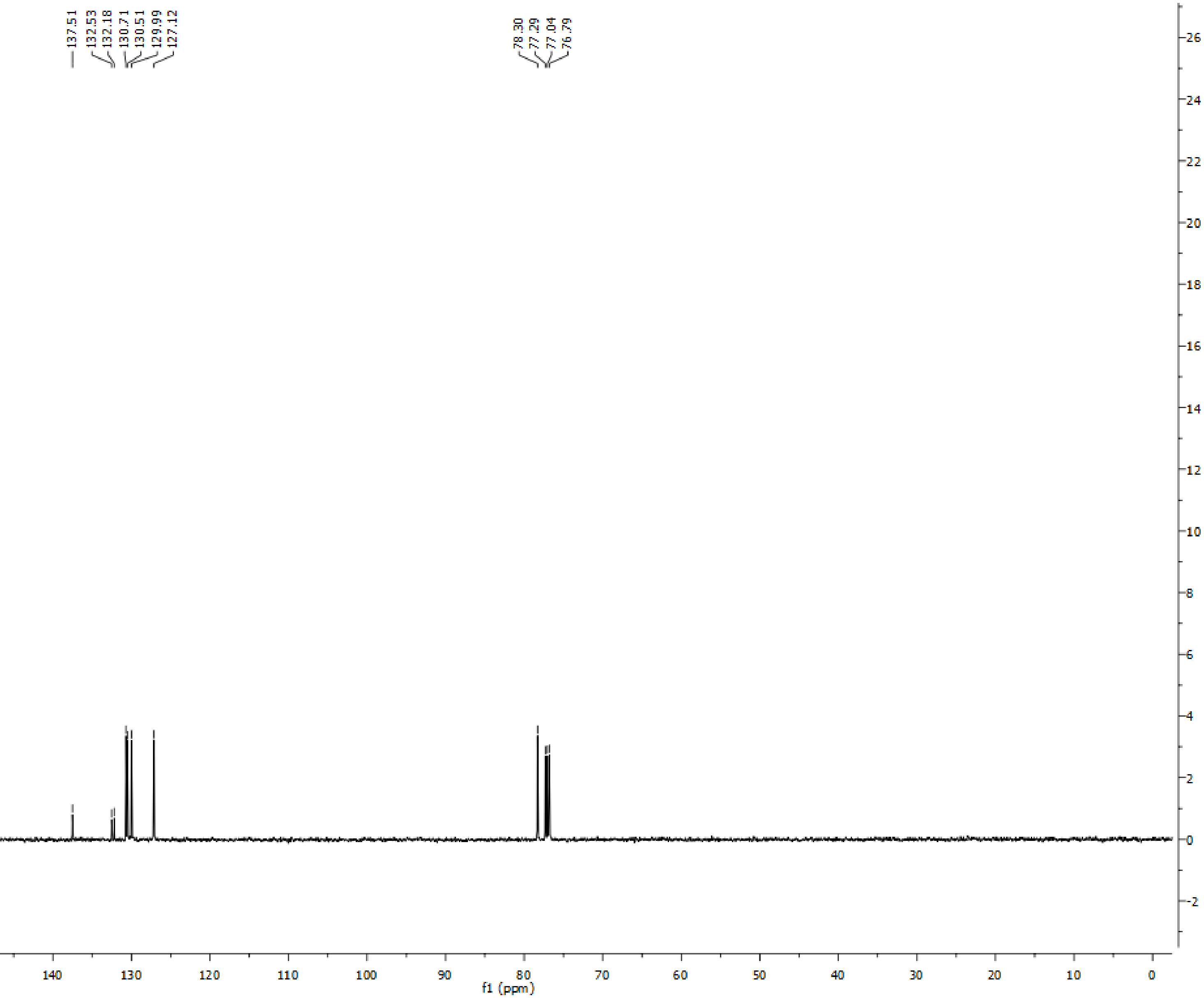
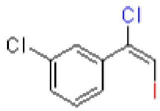


Figure S23. ^{1}H-NMR of **4**



4

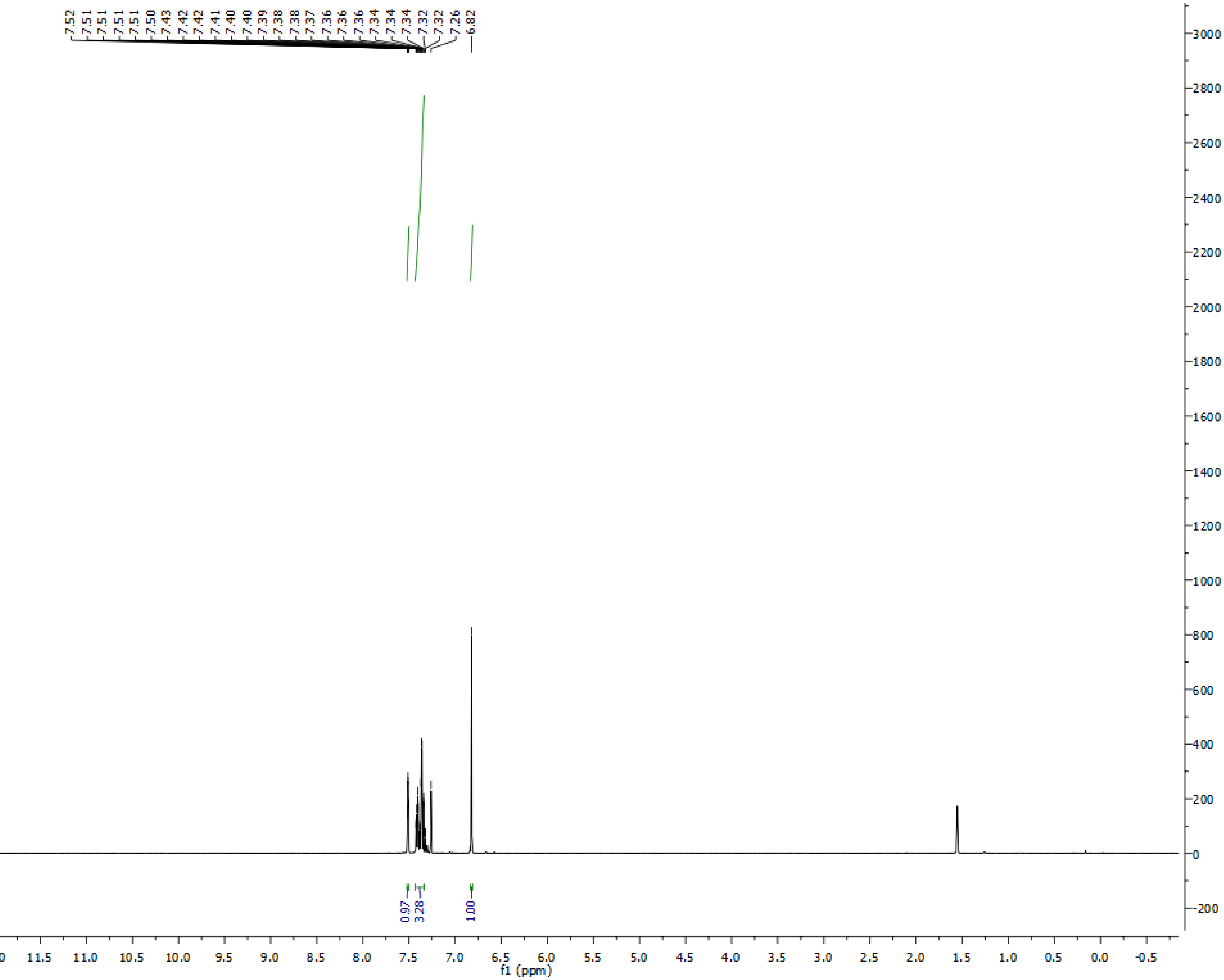


Figure S24. ^{13}C-NMR of **4**

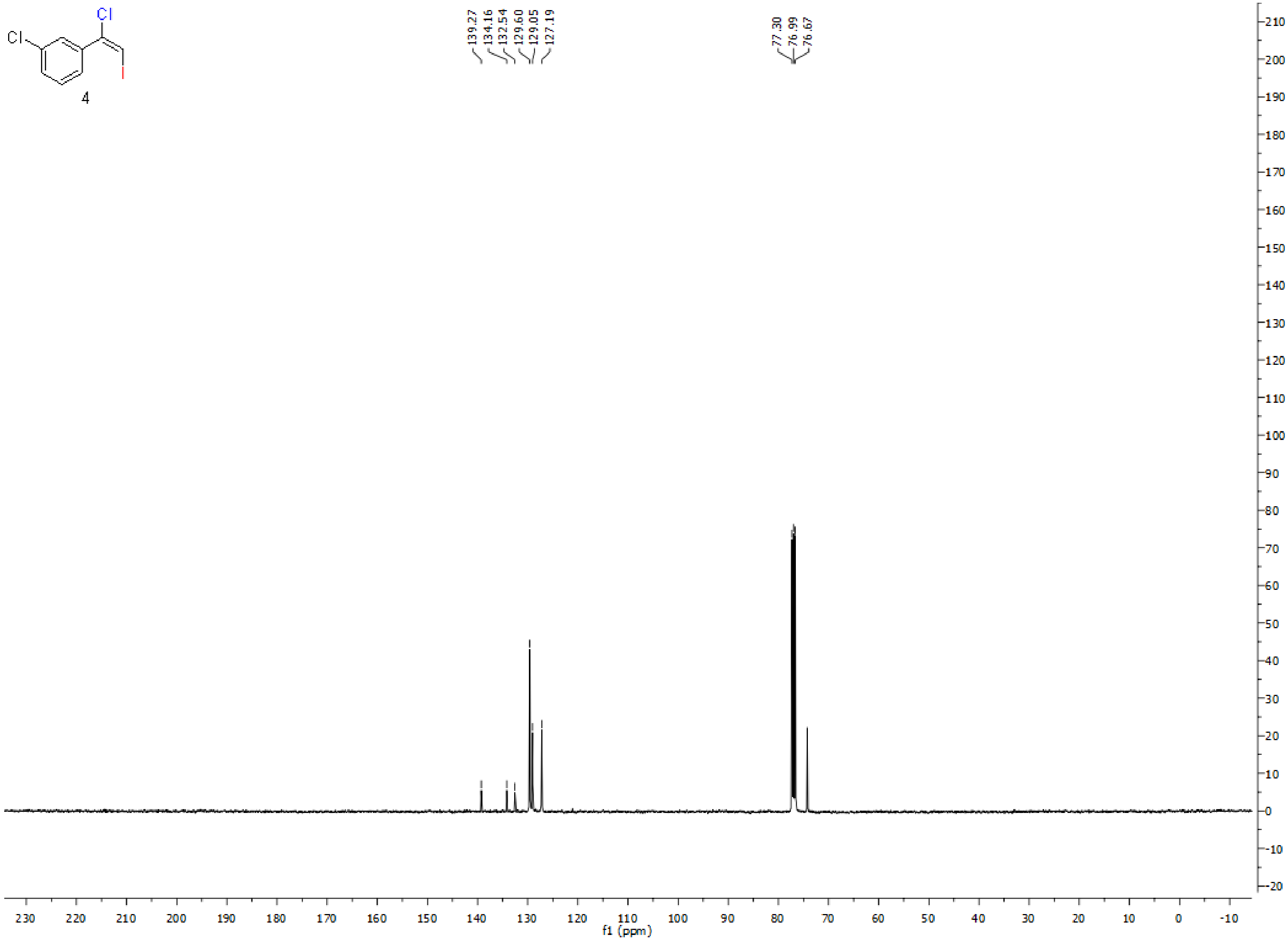
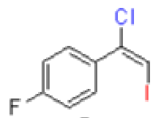


Figure S25. ^{1}H-NMR of **5**



5

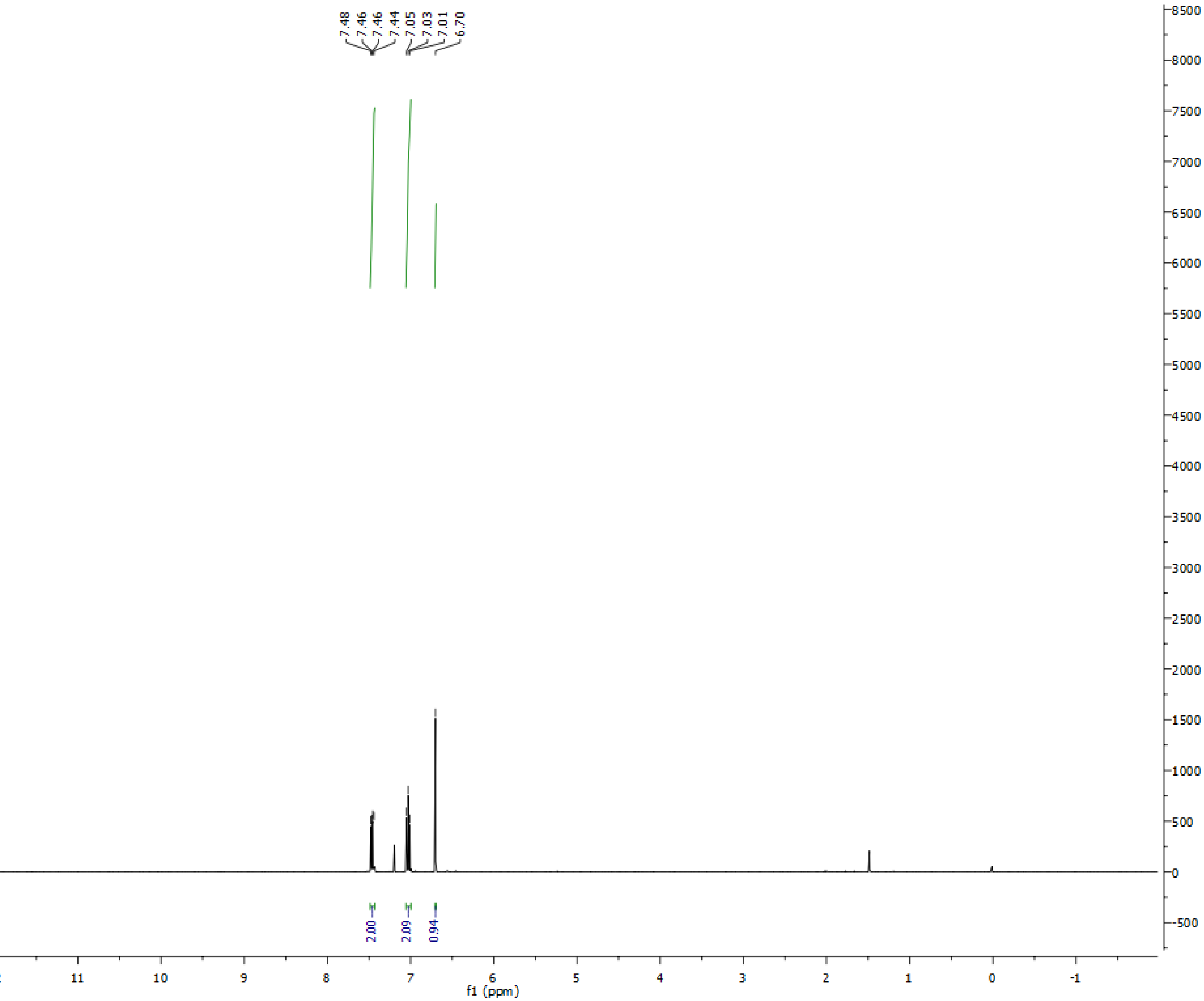
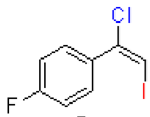


Figure S26. ^{19}F-NMR of **5**



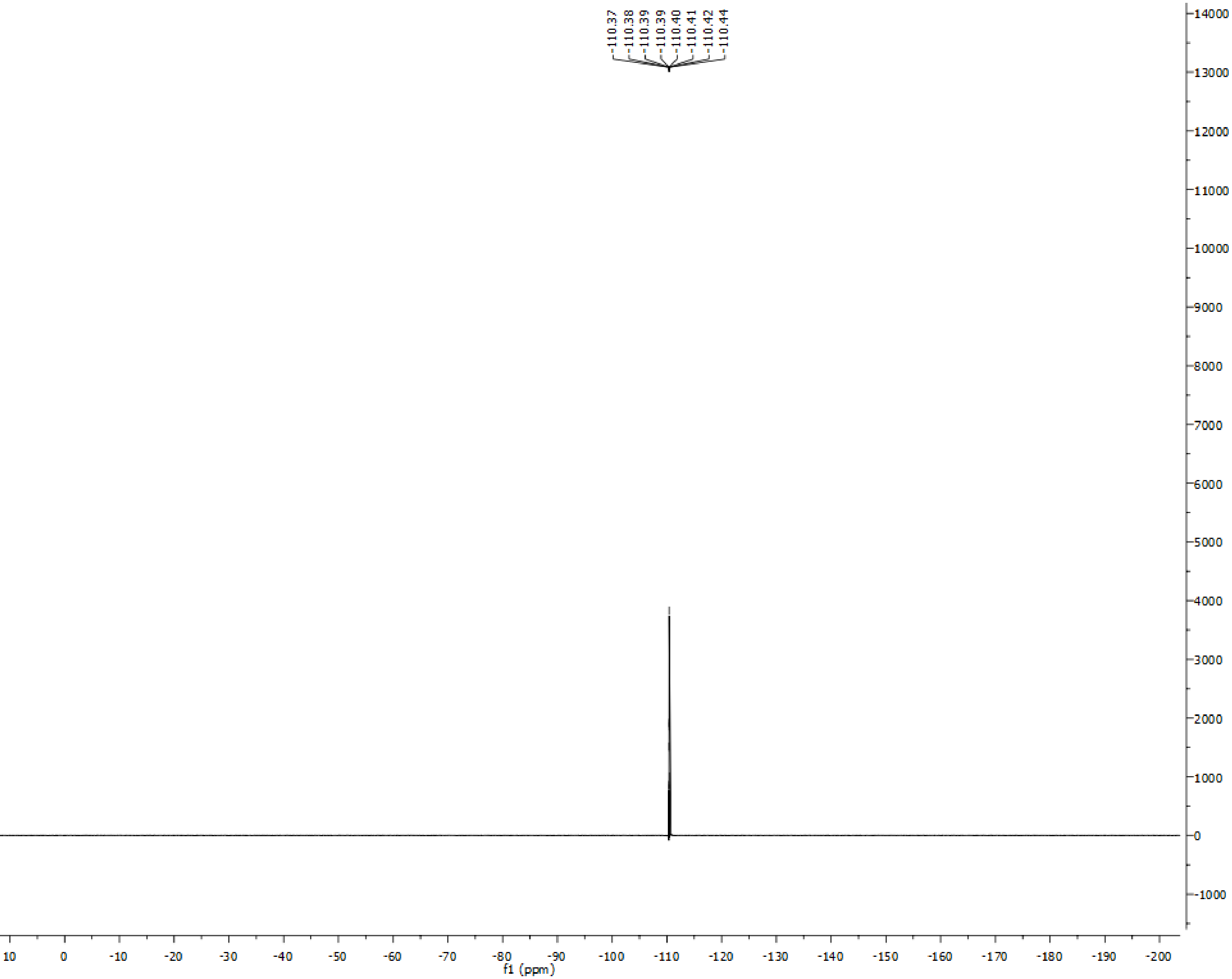
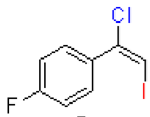


Figure S27. ^{13}C-NMR of **5**



5

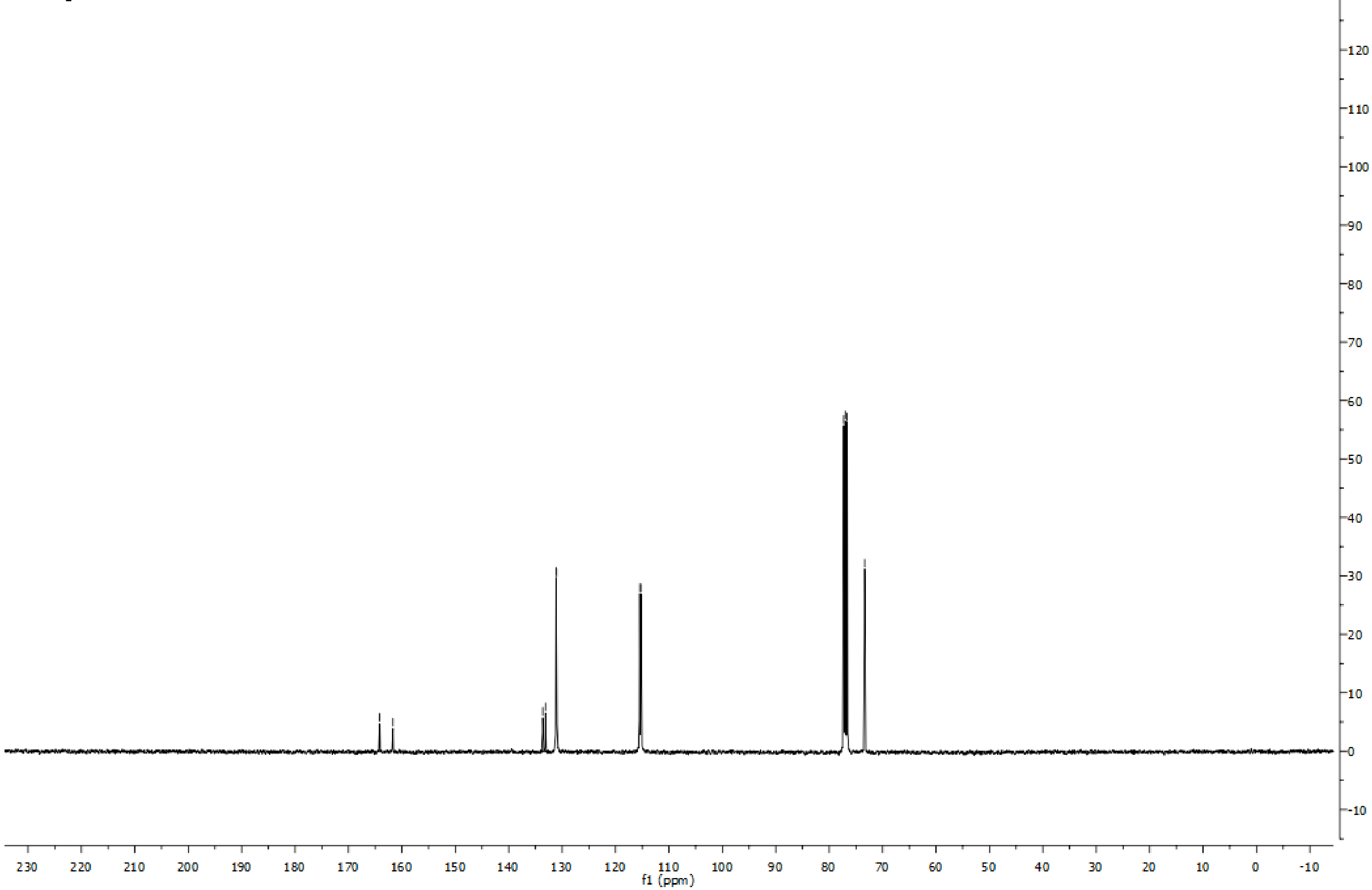


Figure S28. ^{1}H-NMR of **6**

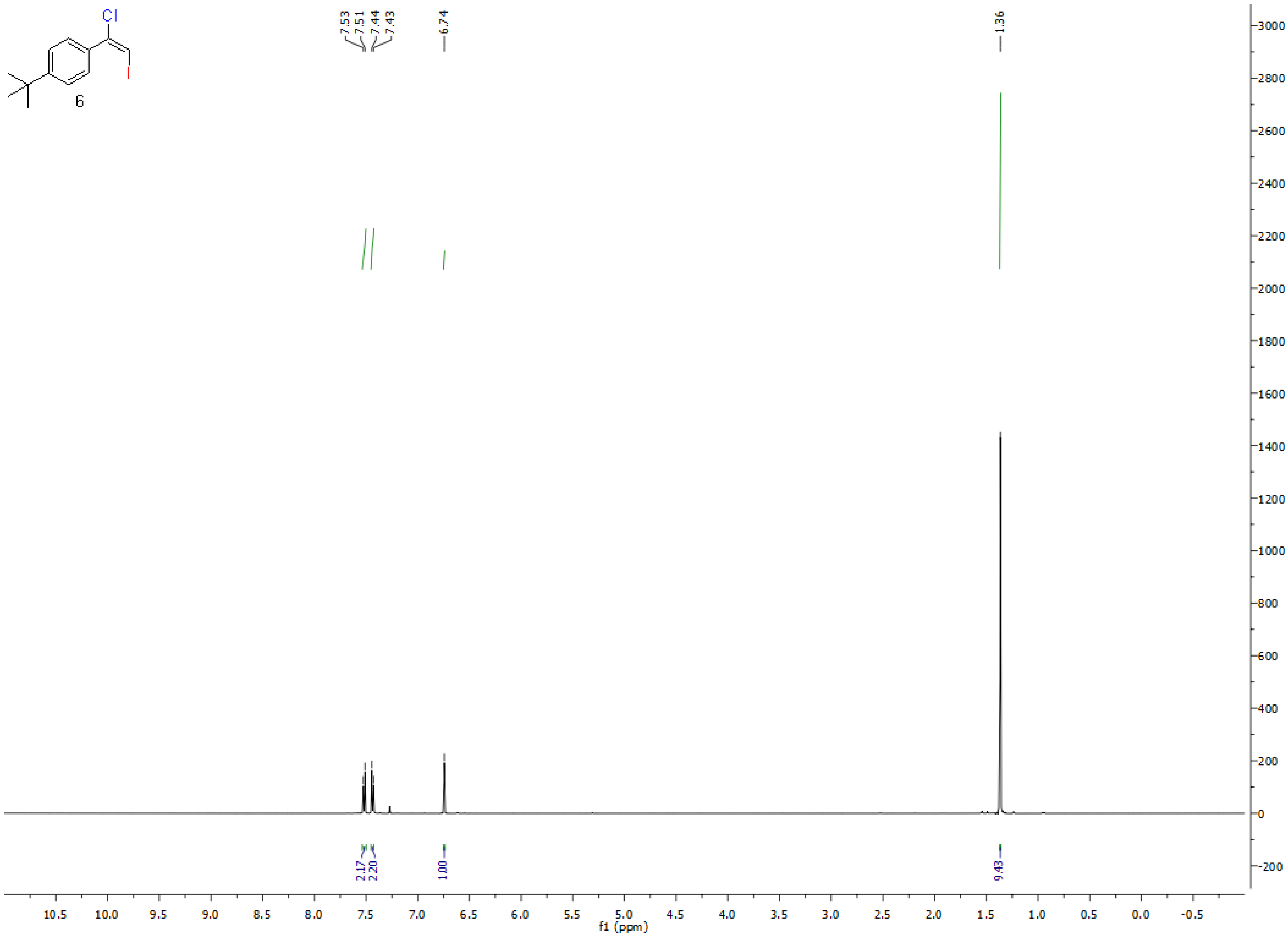
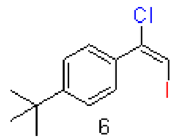


Figure S29. ^{13}C-NMR of **6**



6

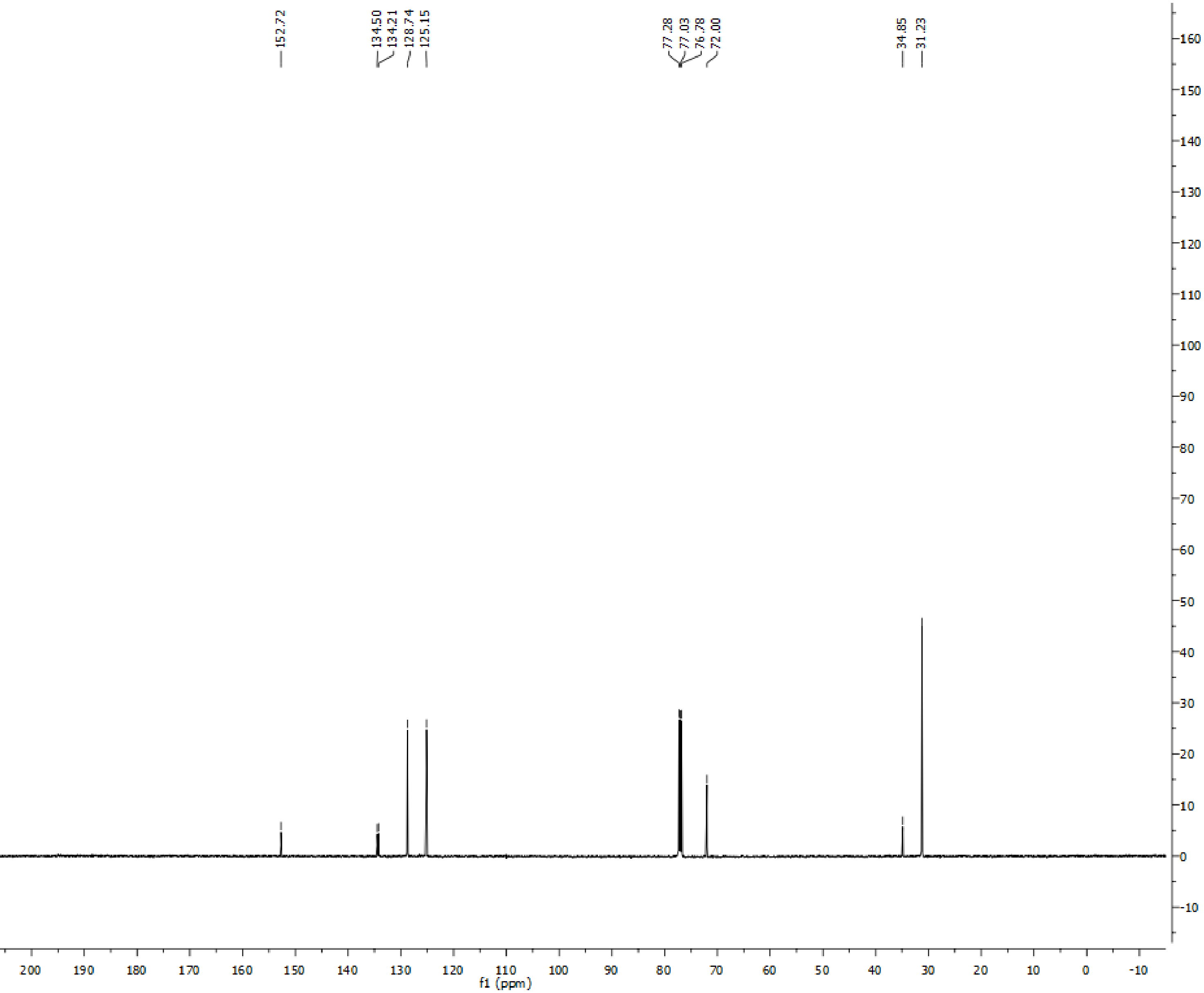


Figure S30. ^{1}H-NMR of **7**

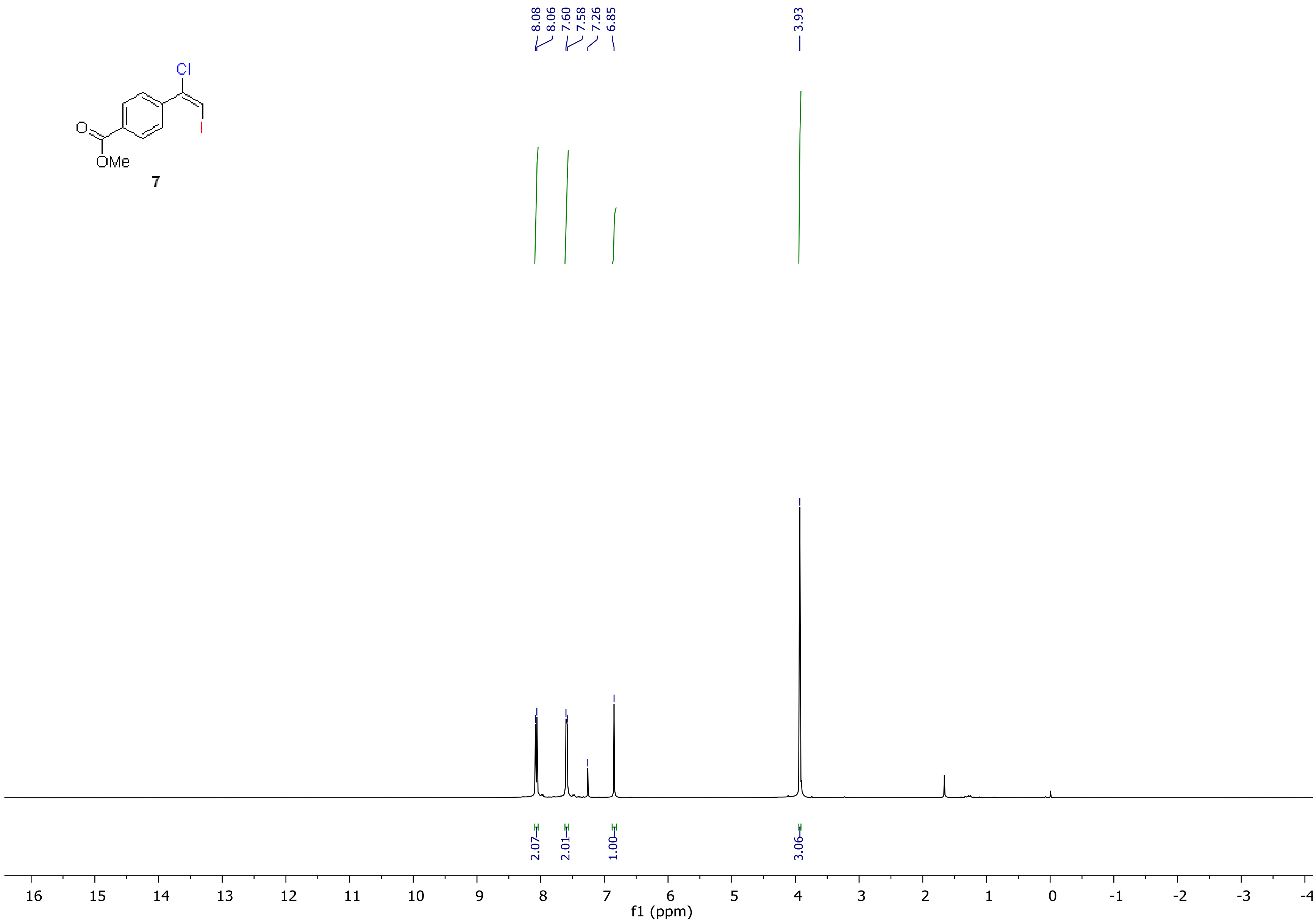


Figure S31. ^{13}C-NMR of **7**

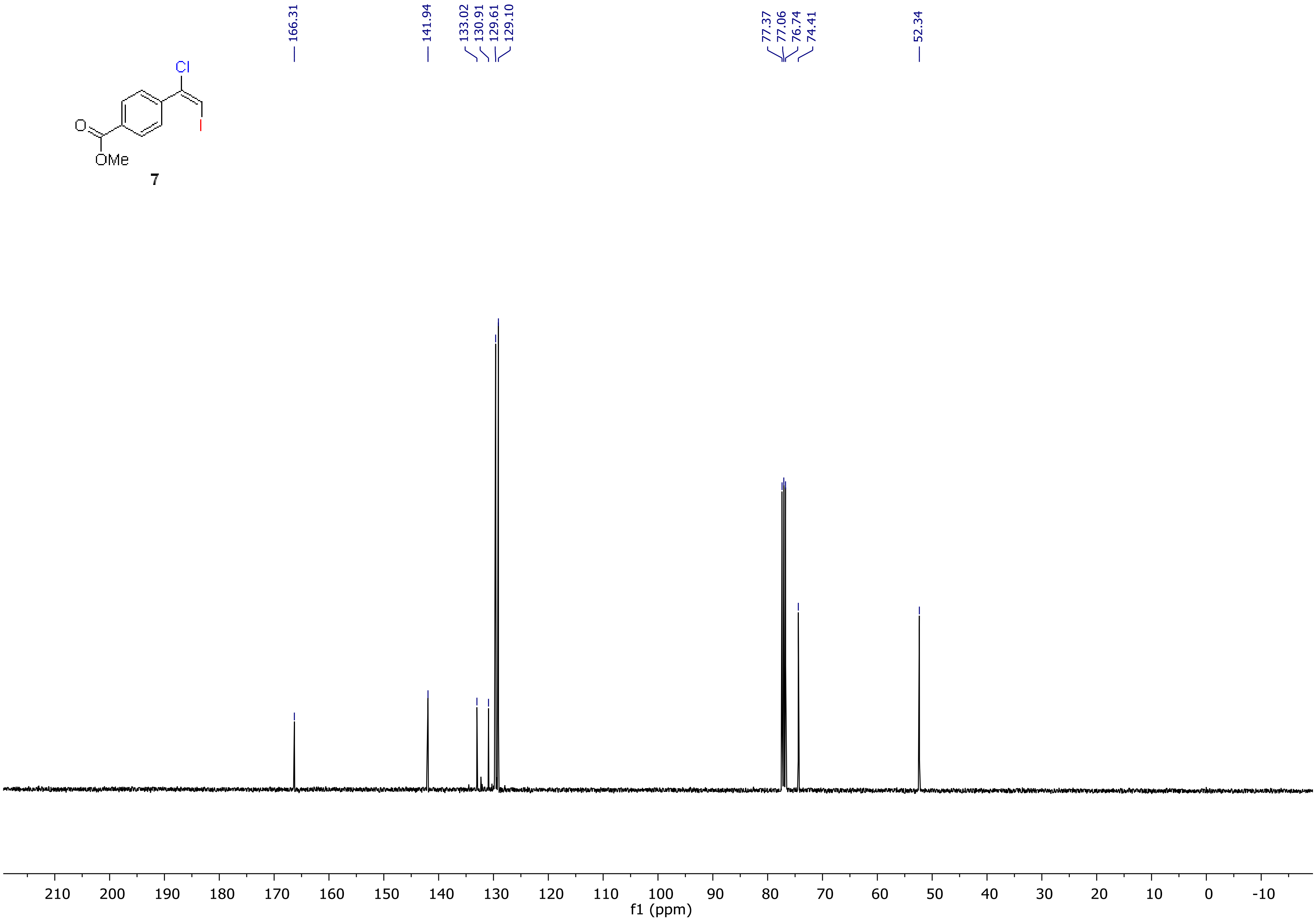


Figure S32. ^{1}H-NMR of **8**

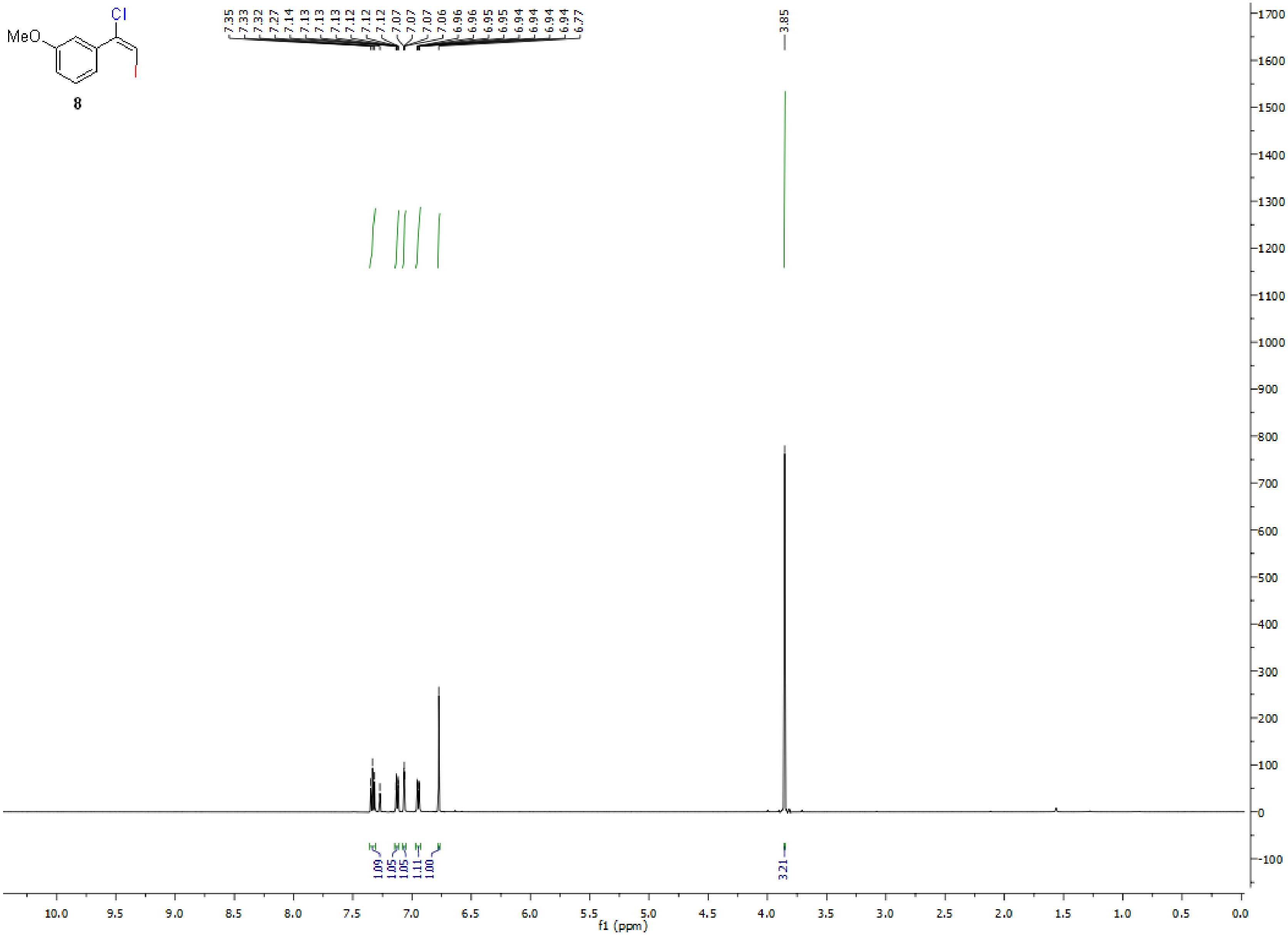
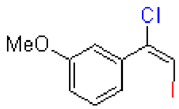


Figure S33. ^{13}C-NMR of **8**



8

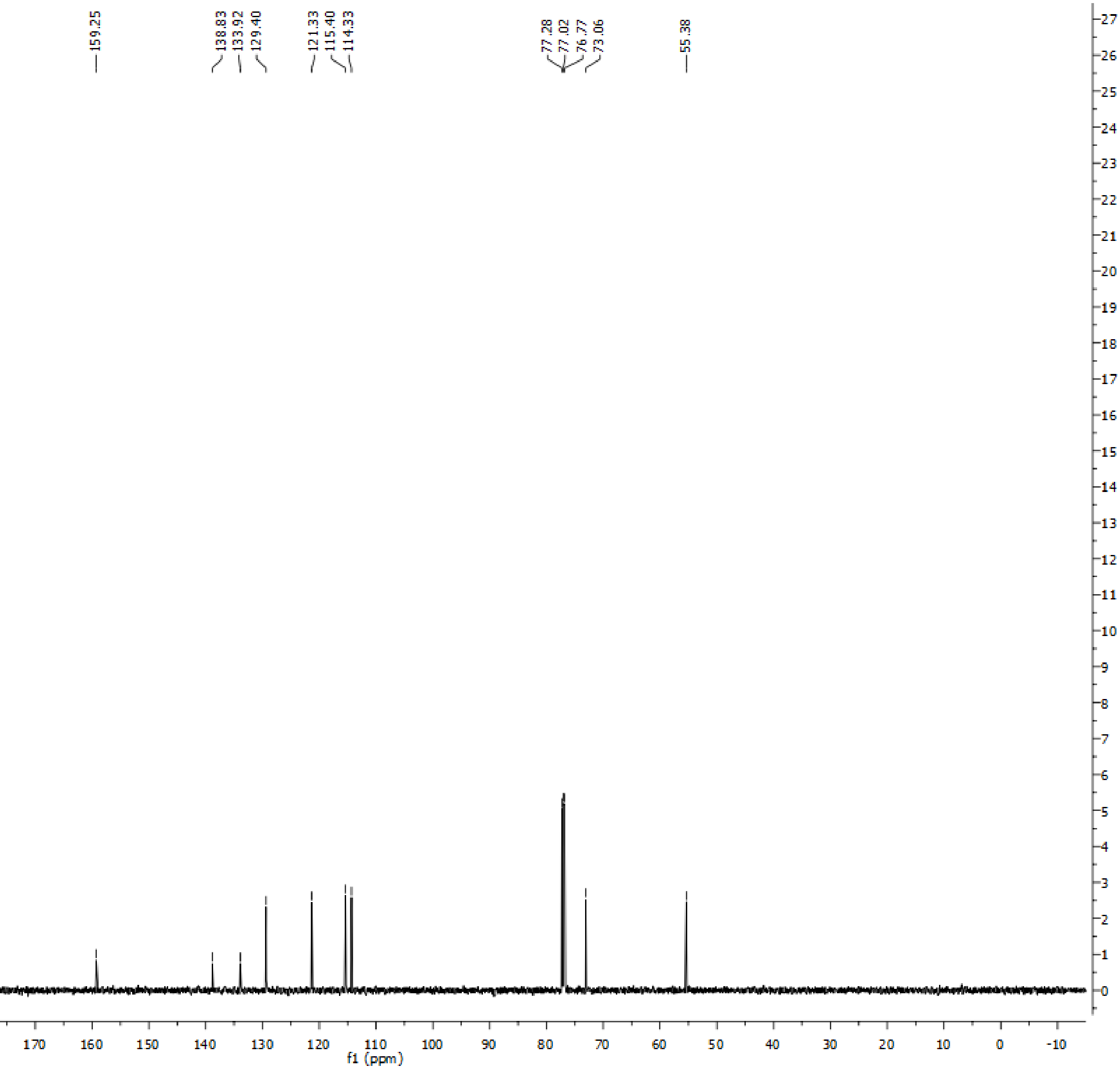


Figure S34. ^{1}H-NMR of **9**

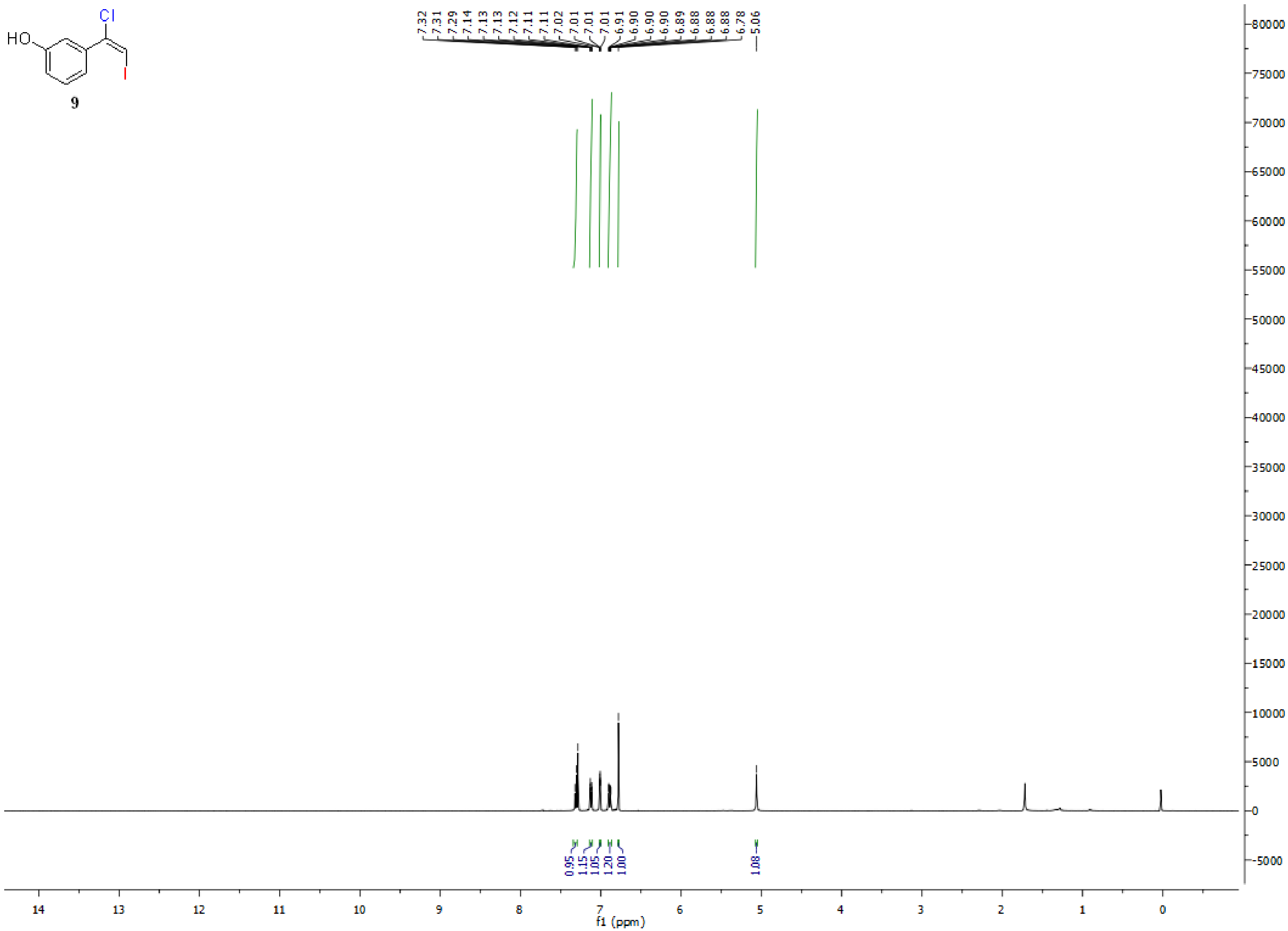
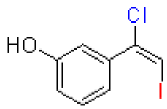


Figure S35. ^{13}C-NMR of **9**



9

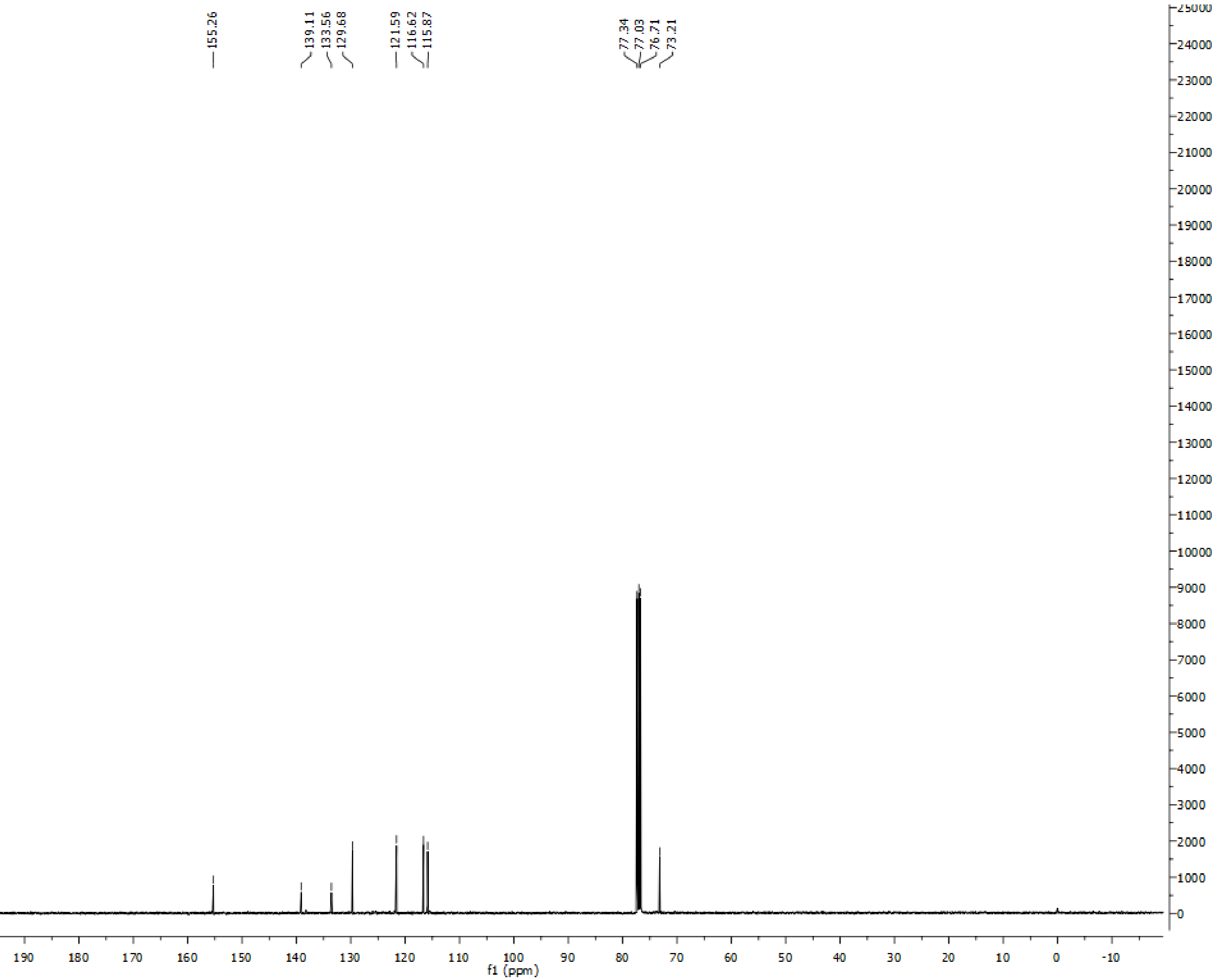
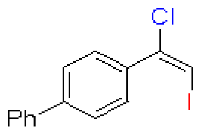


Figure S36. [1]H-NMR of **10**



10

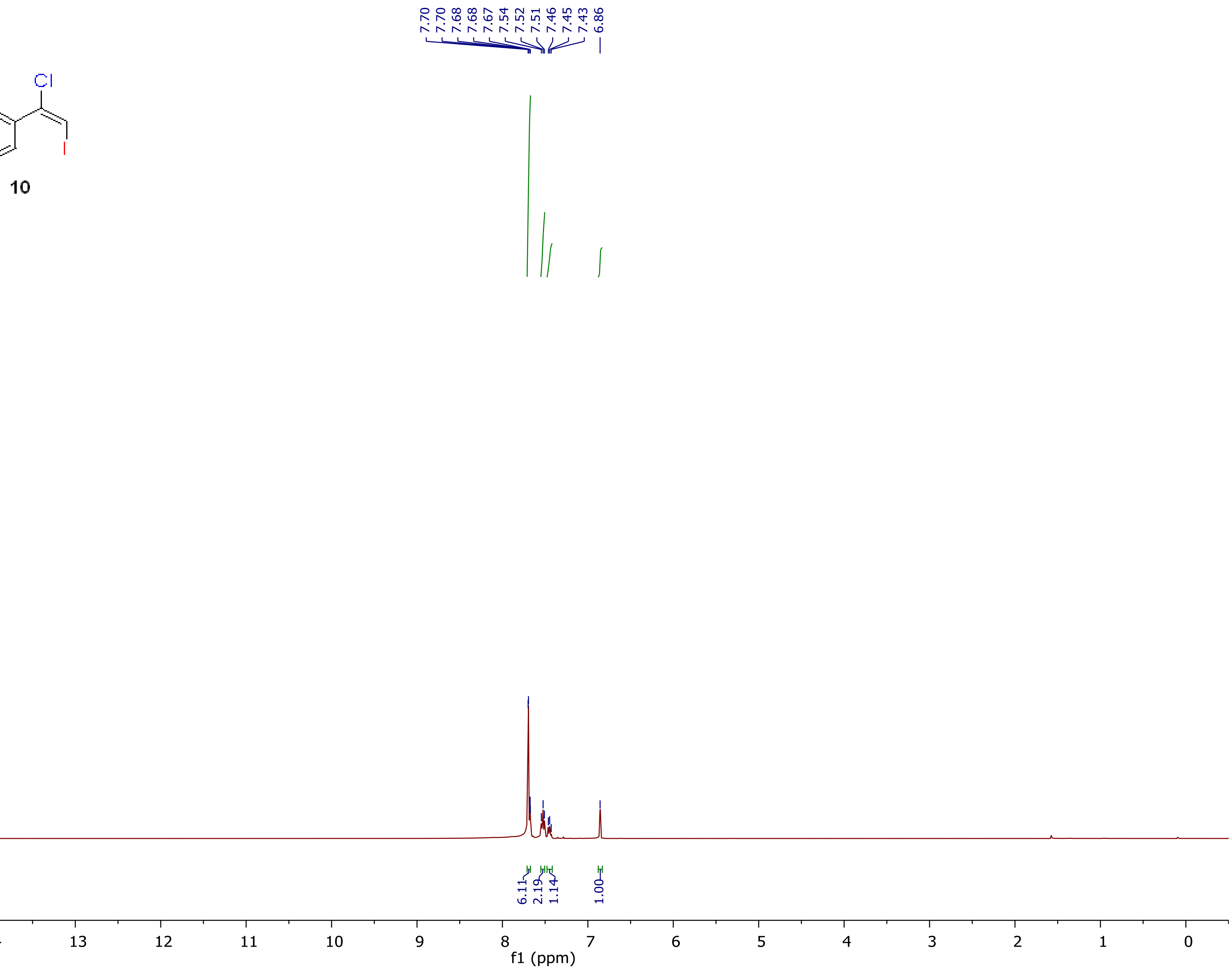
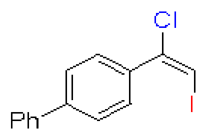


Figure S37. ^{13}C-NMR of **10**



10

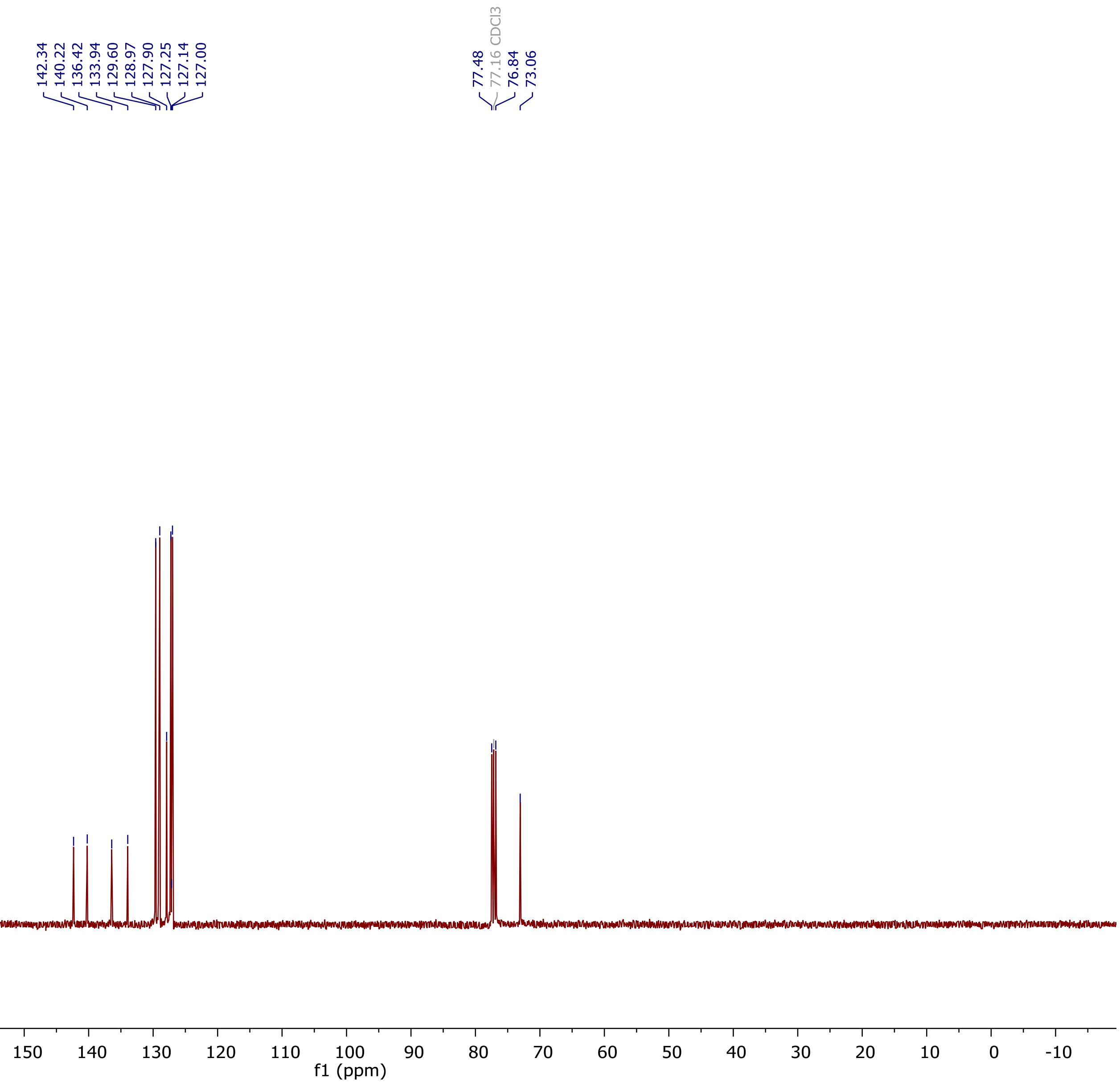


Figure S38. ^{1}H-NMR of **11**

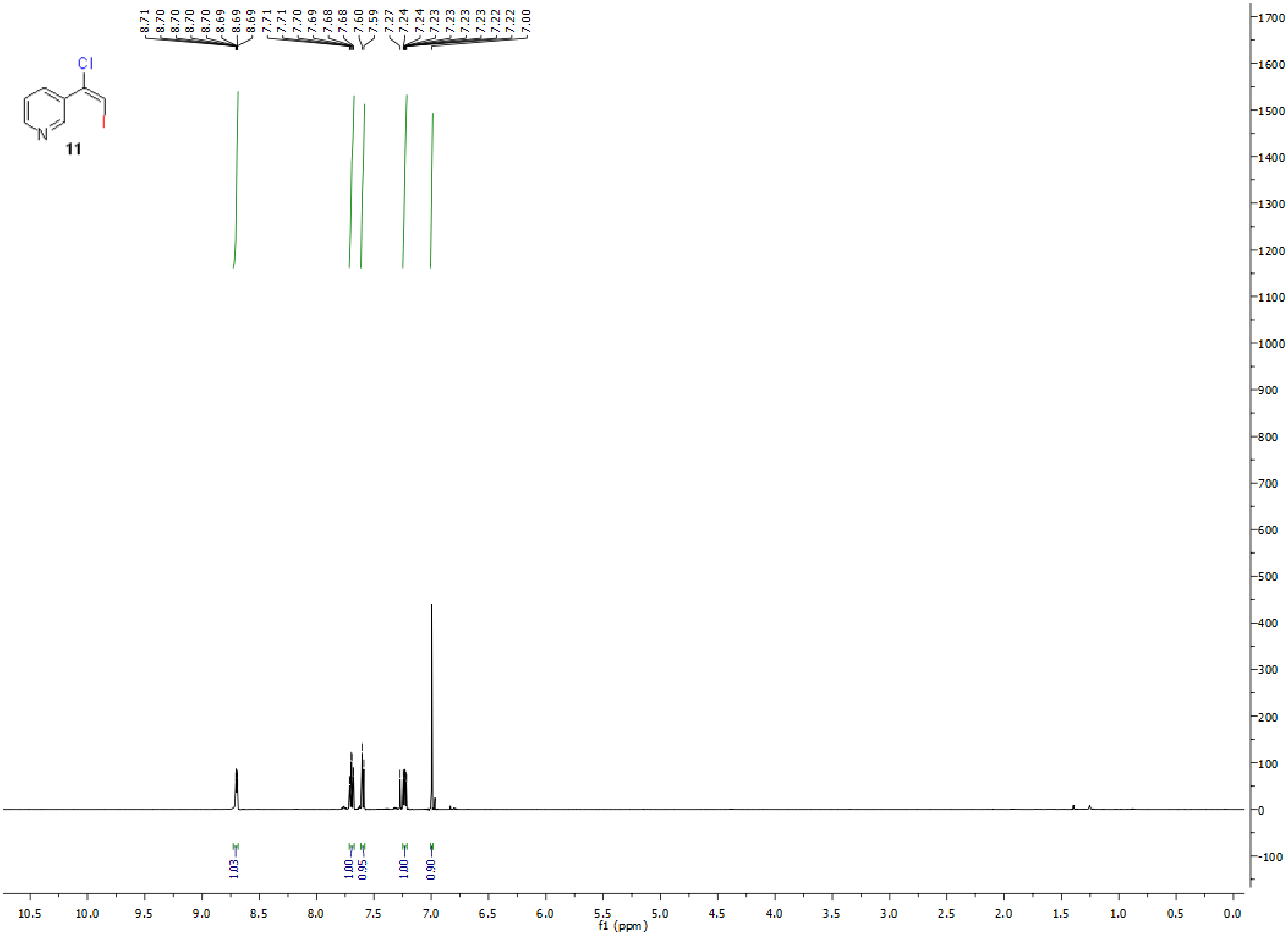
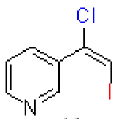


Figure S39. ^{13}C-NMR of **11**



11

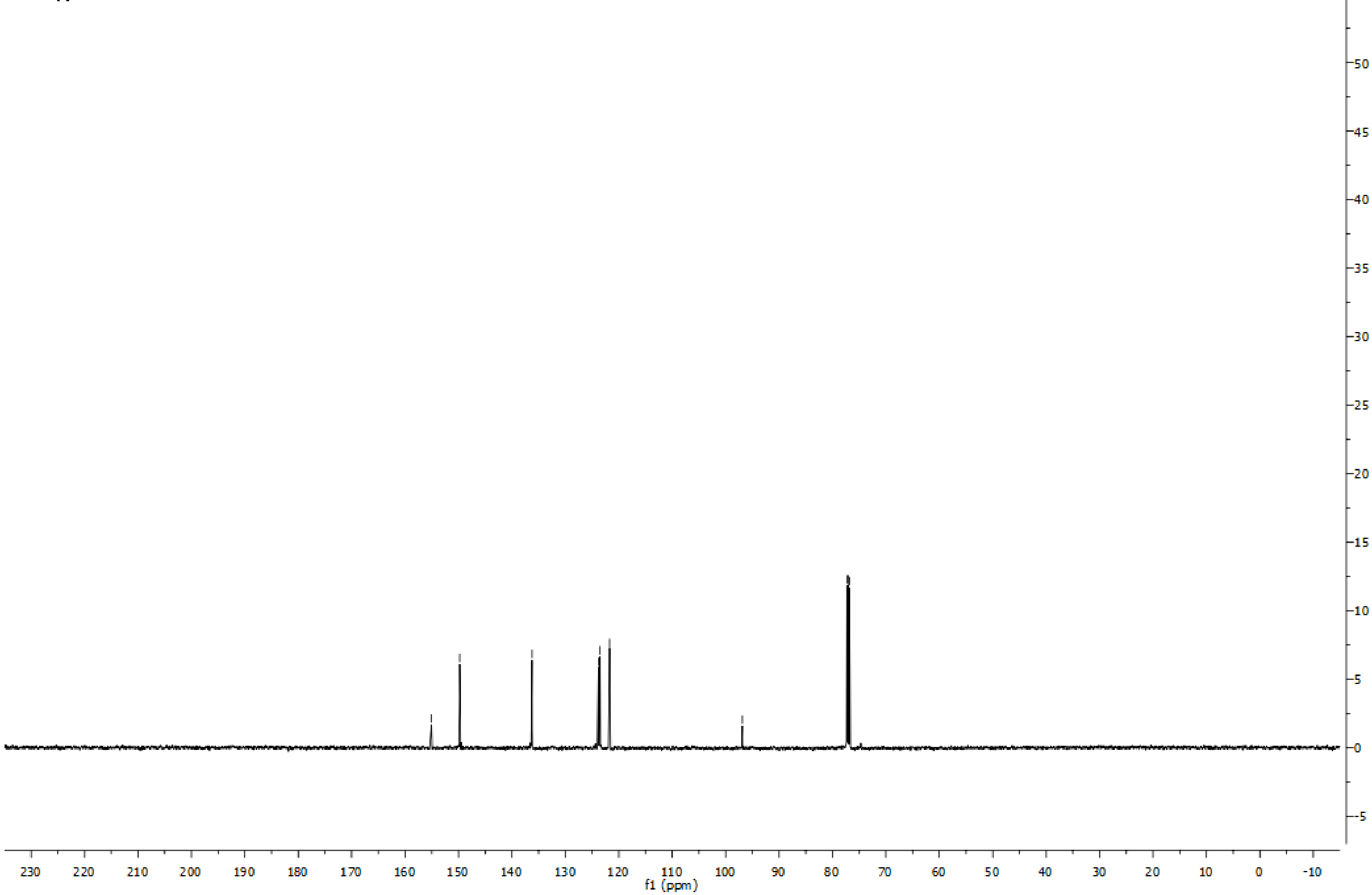


Figure S40. ^{1}H-NMR of **12**

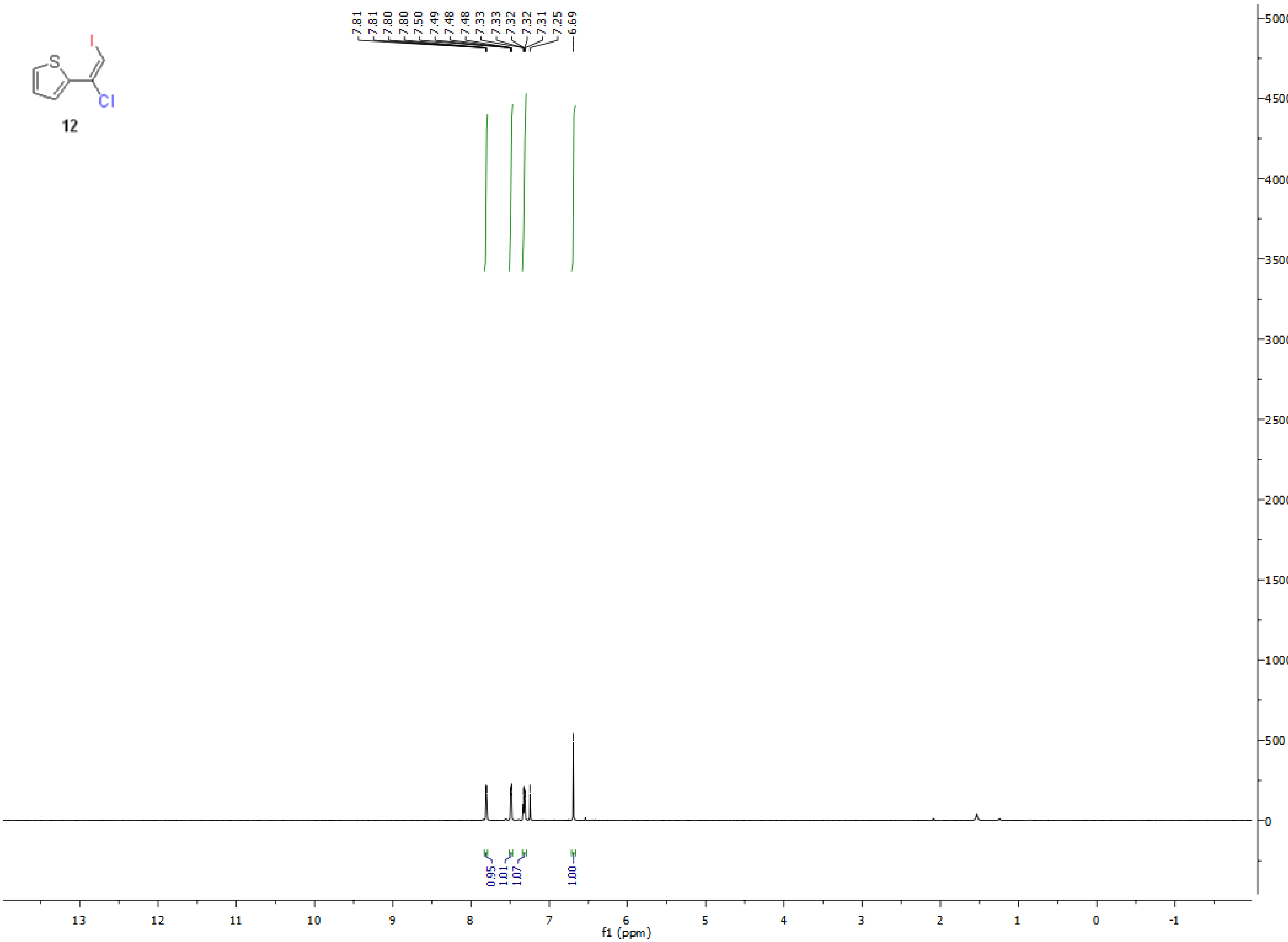
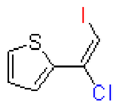


Figure S41. ^{13}C-NMR of **12**



12

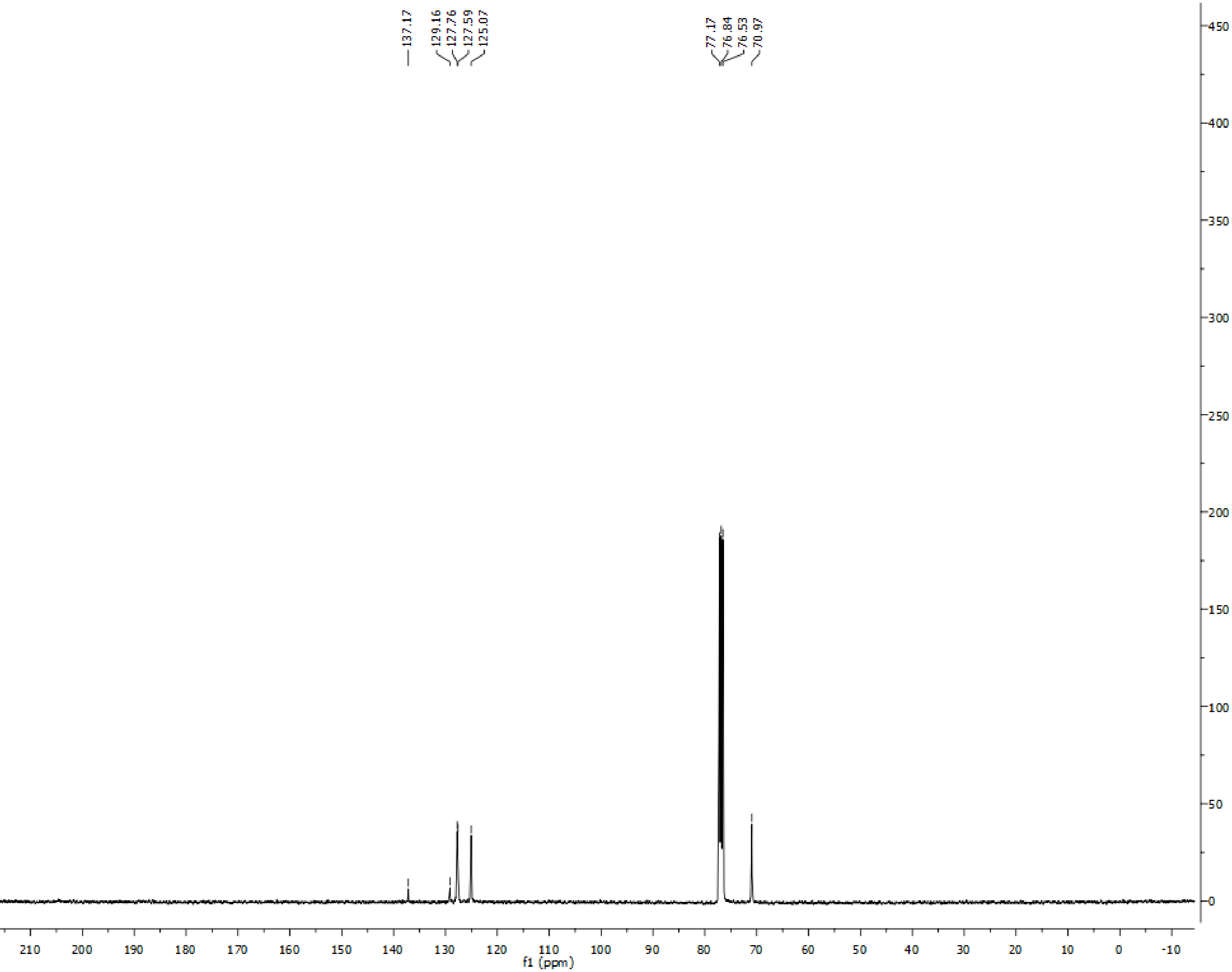


Figure S42. ^{1}H-NMR of **13**

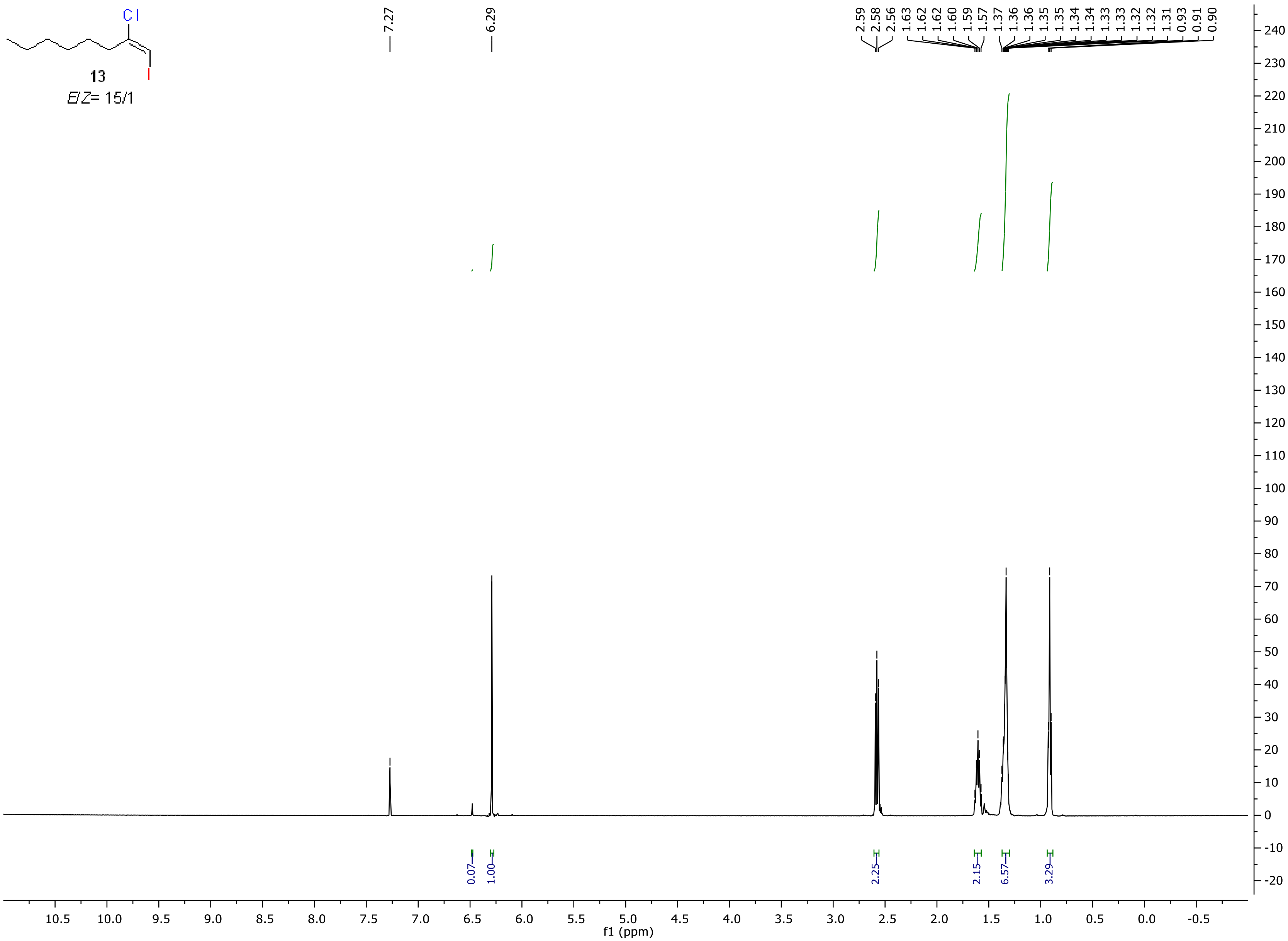
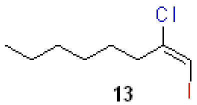


Figure S43. ^{13}C-NMR of **13**



13

E/Z= 15/1

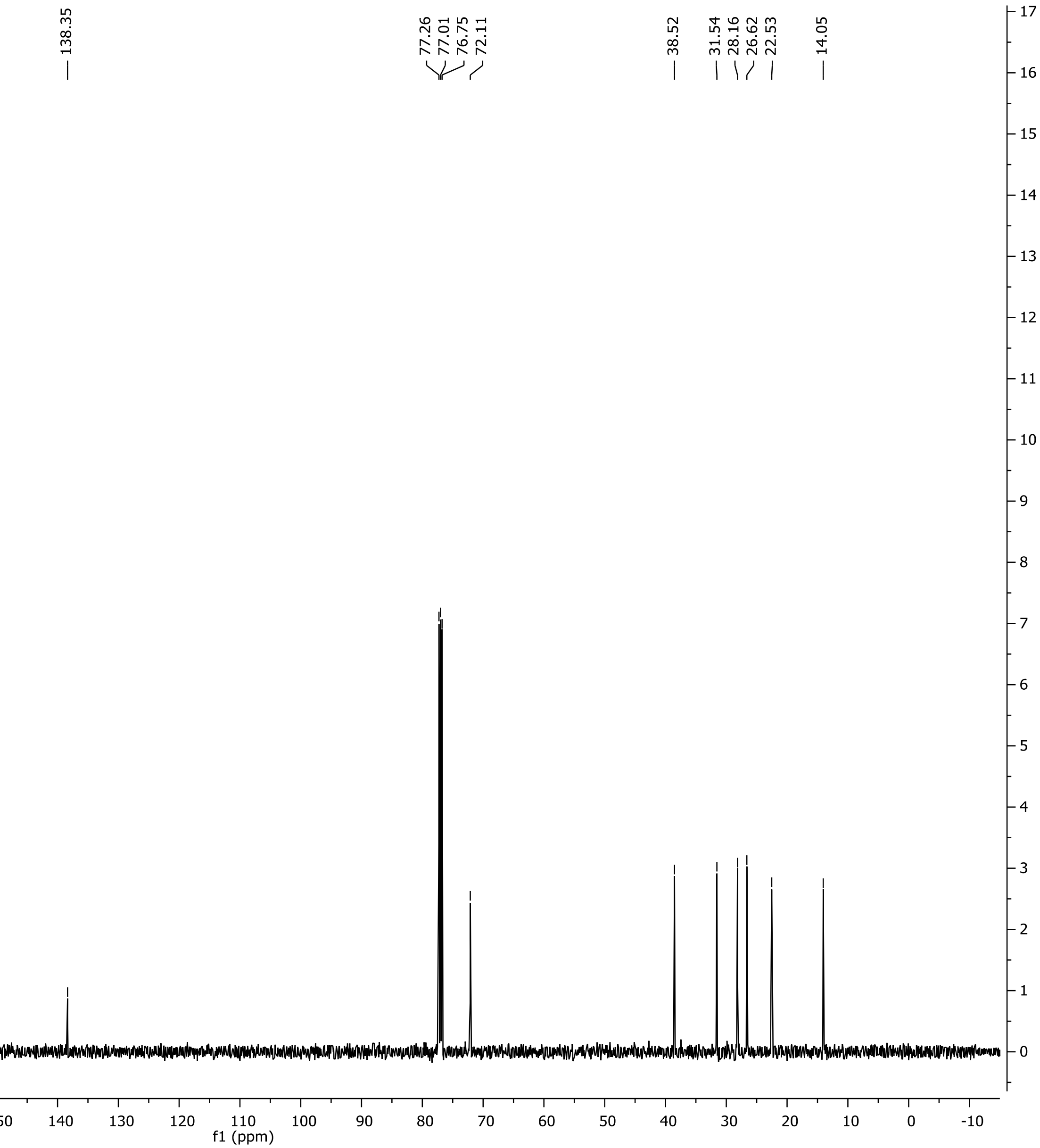


Figure S44. ^{1}H-NMR of **14**

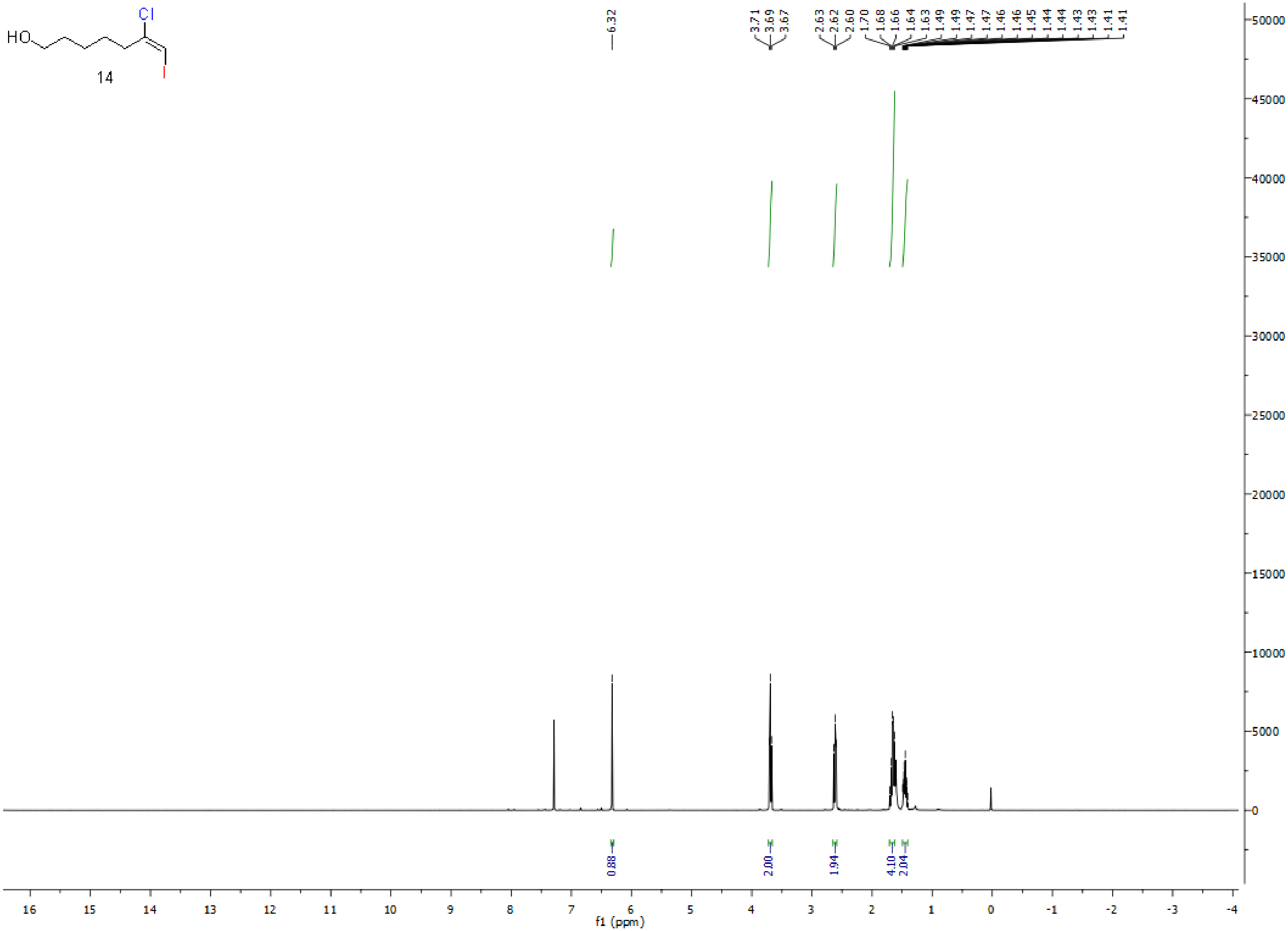
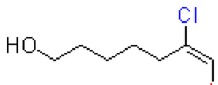


Figure S45. ^{13}C-NMR of **14**



14

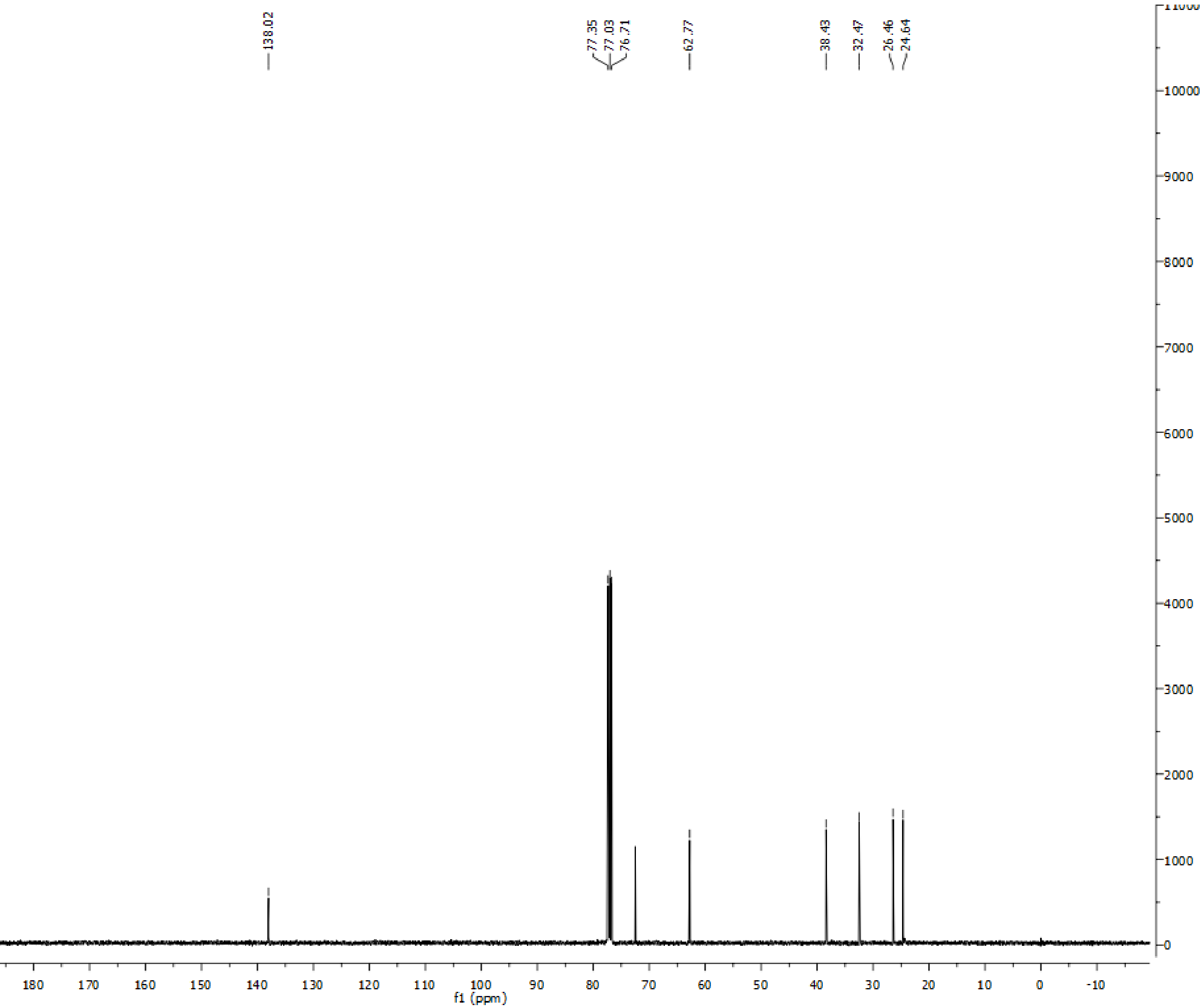
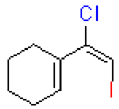


Figure S46. ^{1}H-NMR of **15**



15

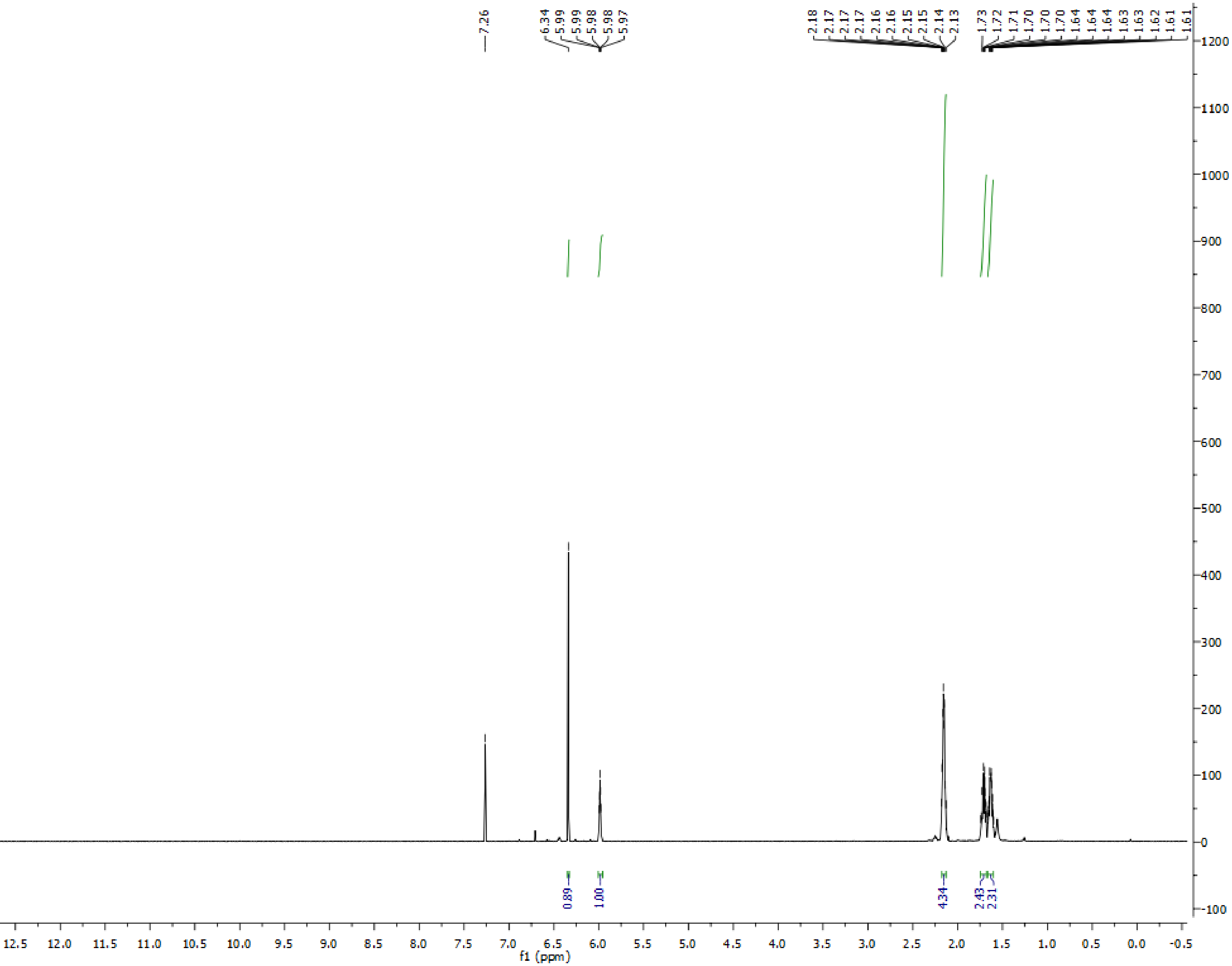
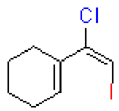


Figure S47. ^{13}C-NMR of **15**



15

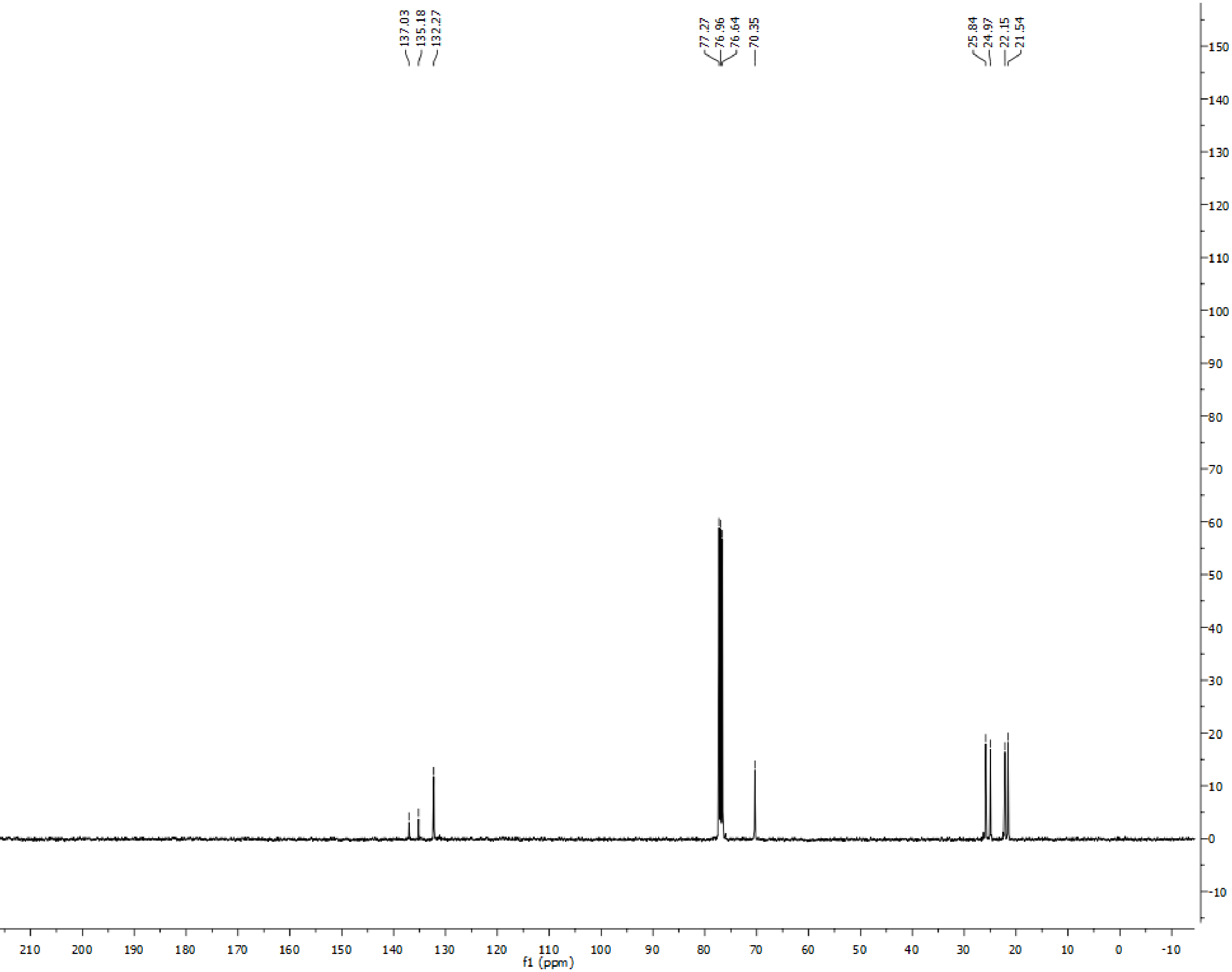
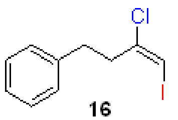


Figure S48. ^{1}H-NMR of **16**



16

E/*Z*= 16/11

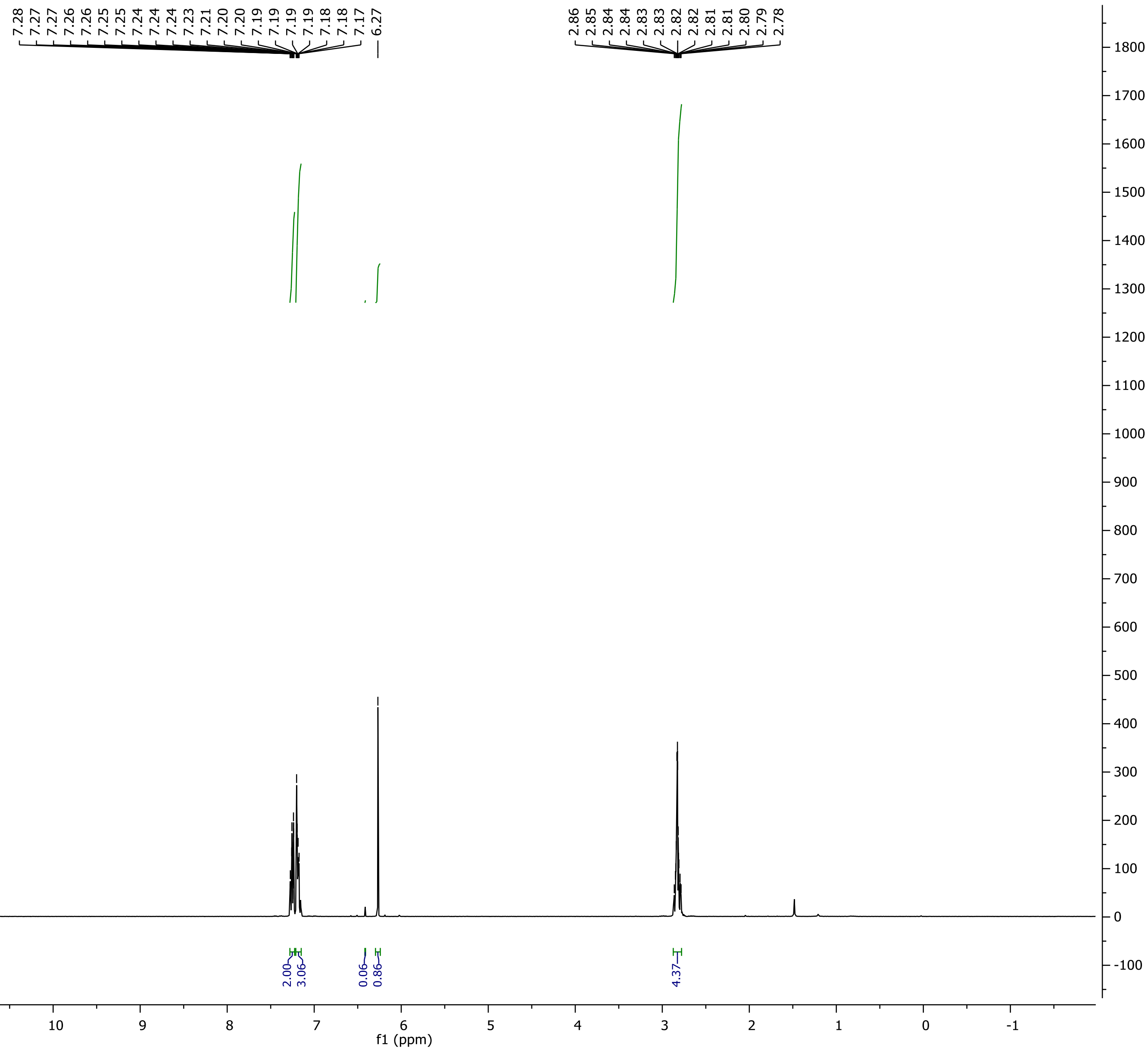
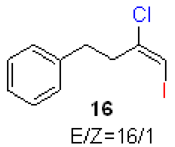


Figure S49. ^{13}C-NMR of **16**



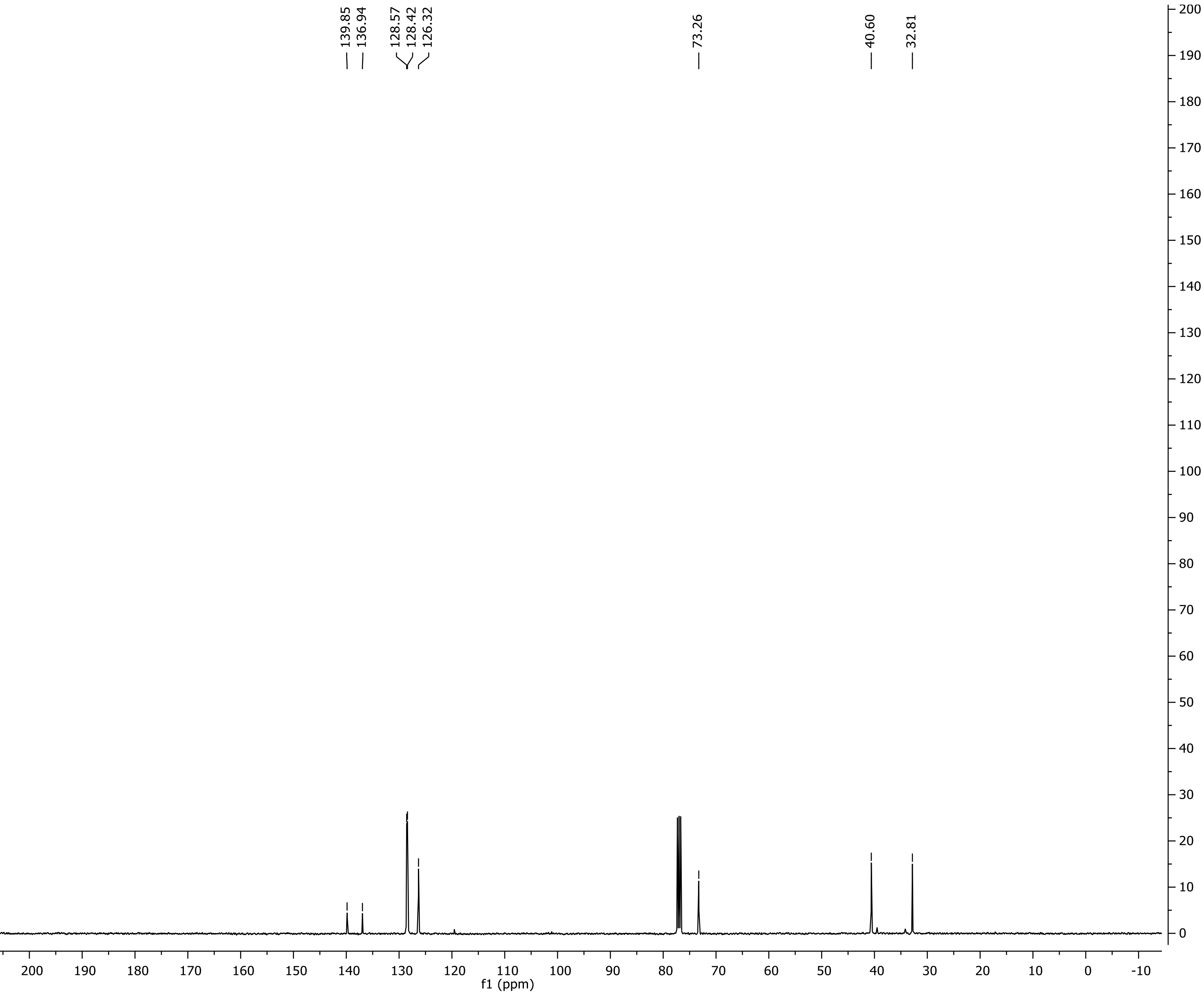
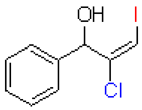


Figure S50. [1]H-NMR of **17**



17
E/Z= 33/1

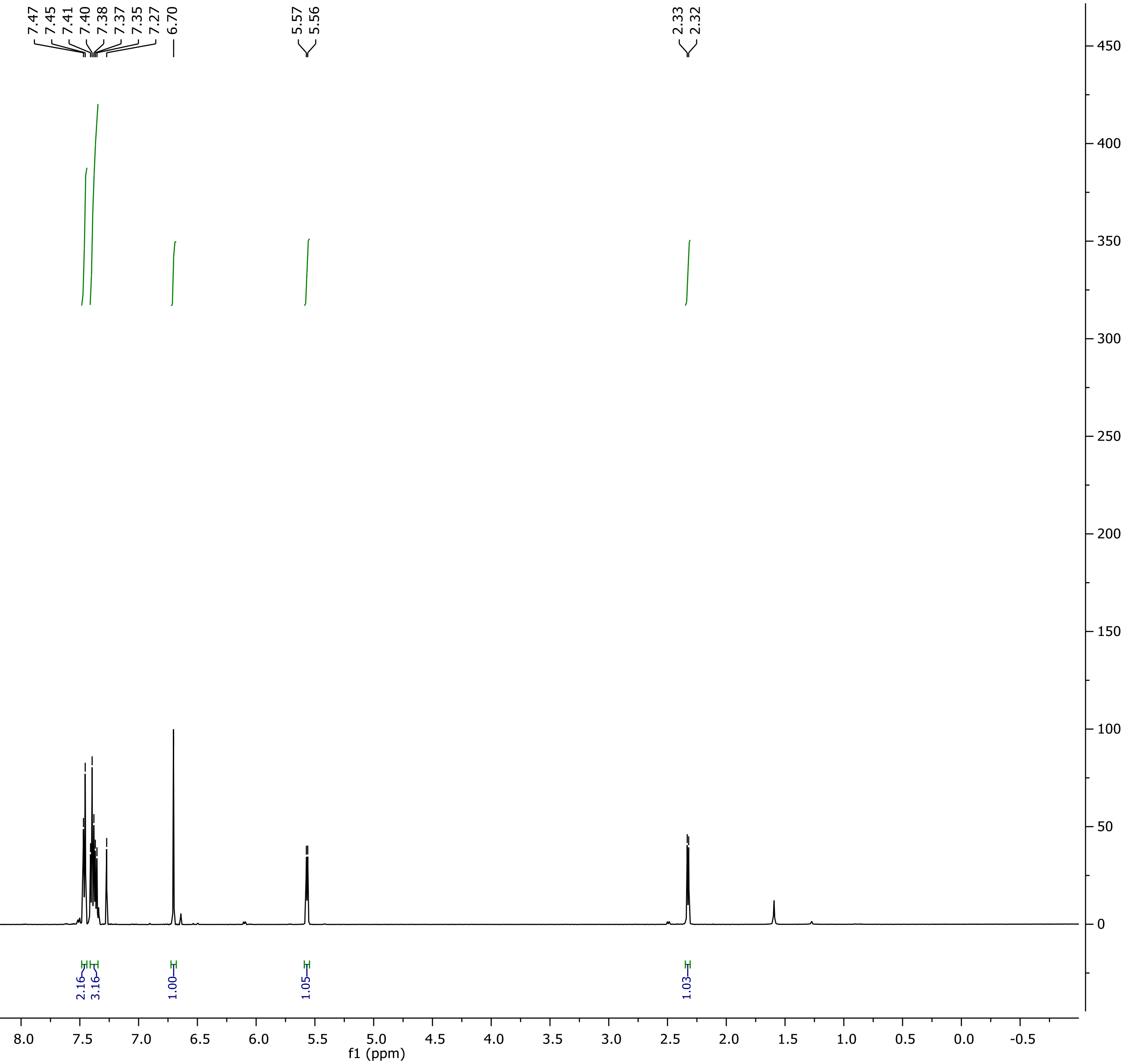


Figure S51. ^{13}C-NMR of **17**

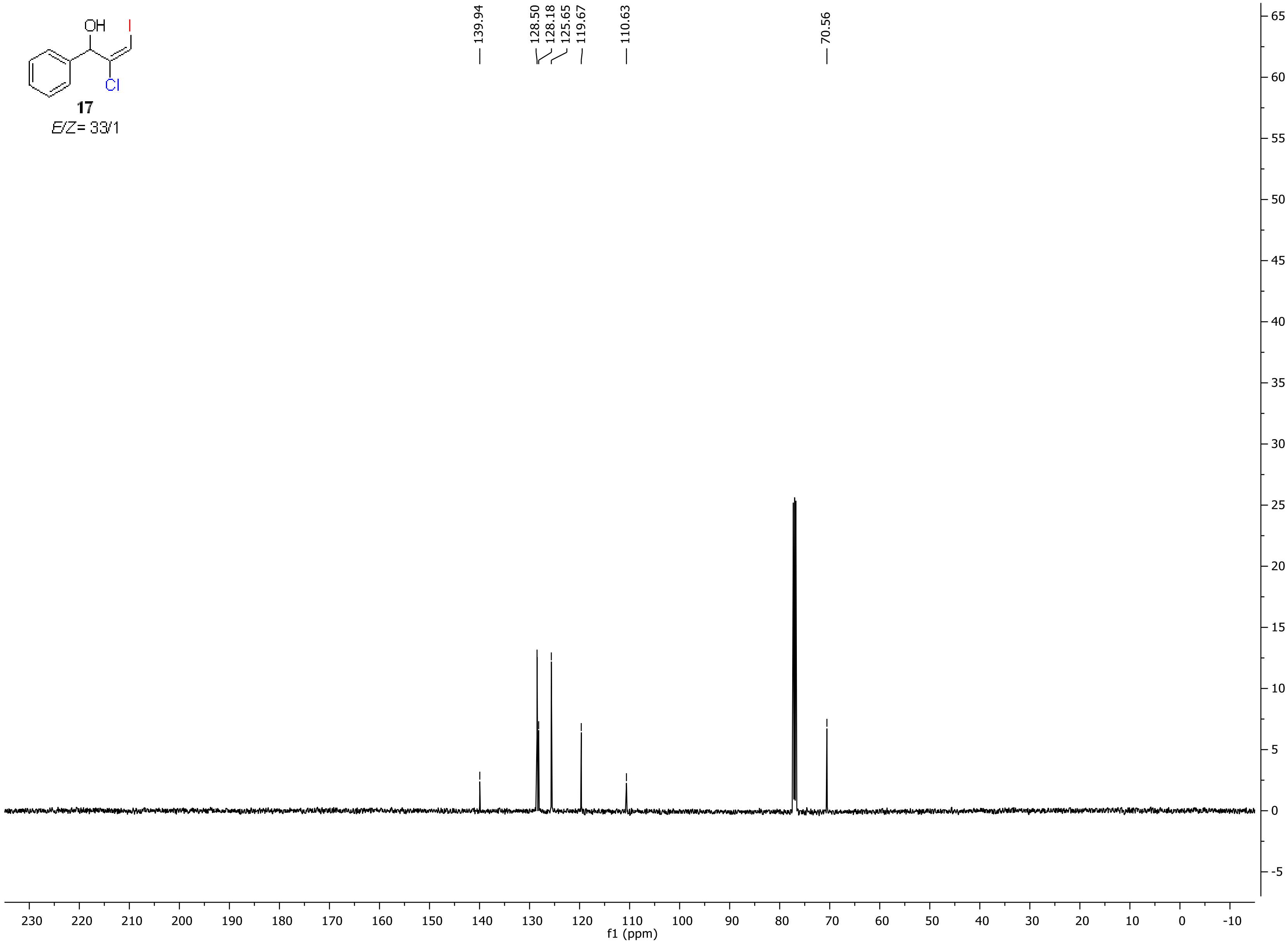


Figure S52. ^{1}H-NMR of **18**

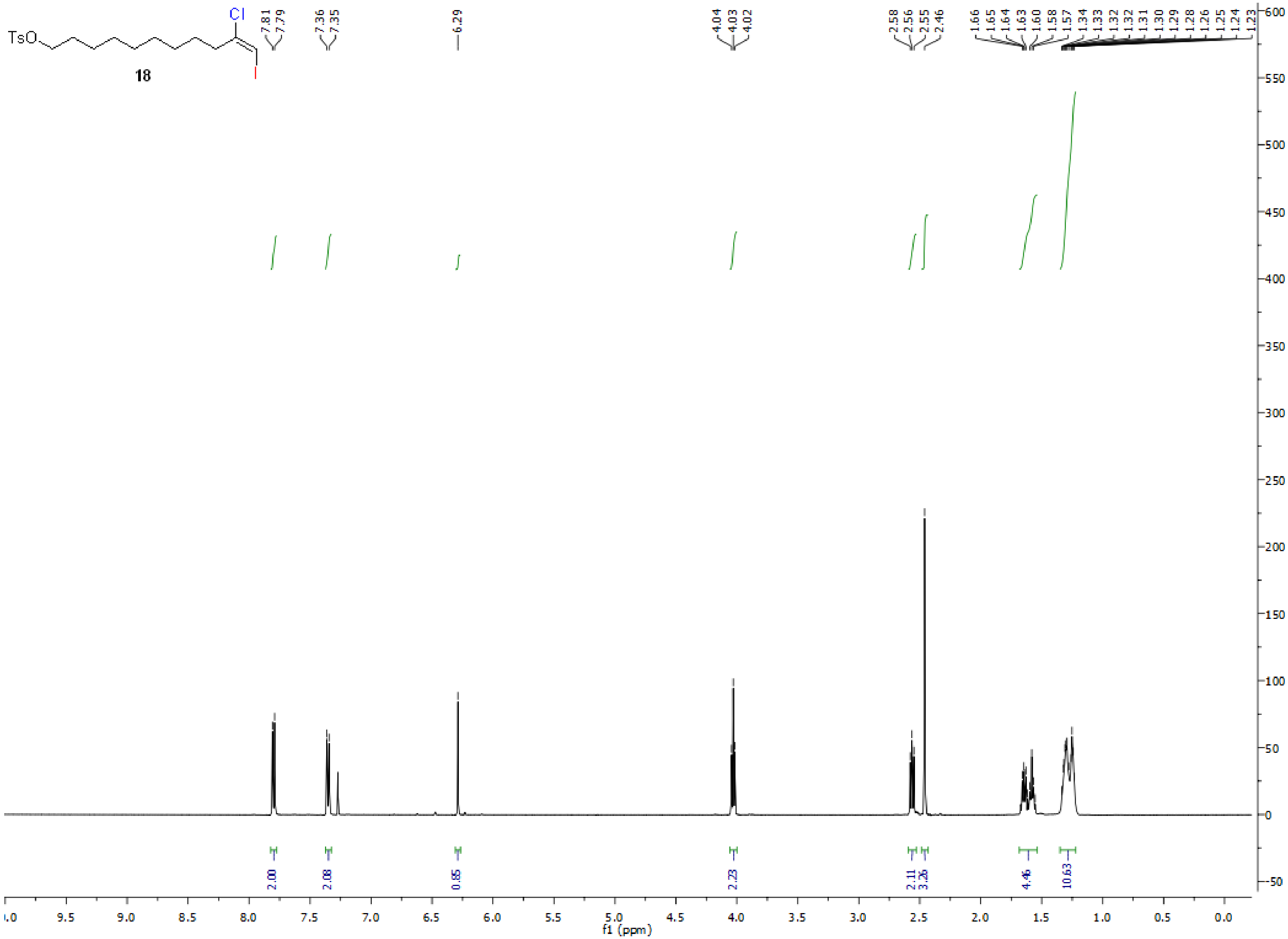


Figure S53. ^{13}C-NMR of **18**

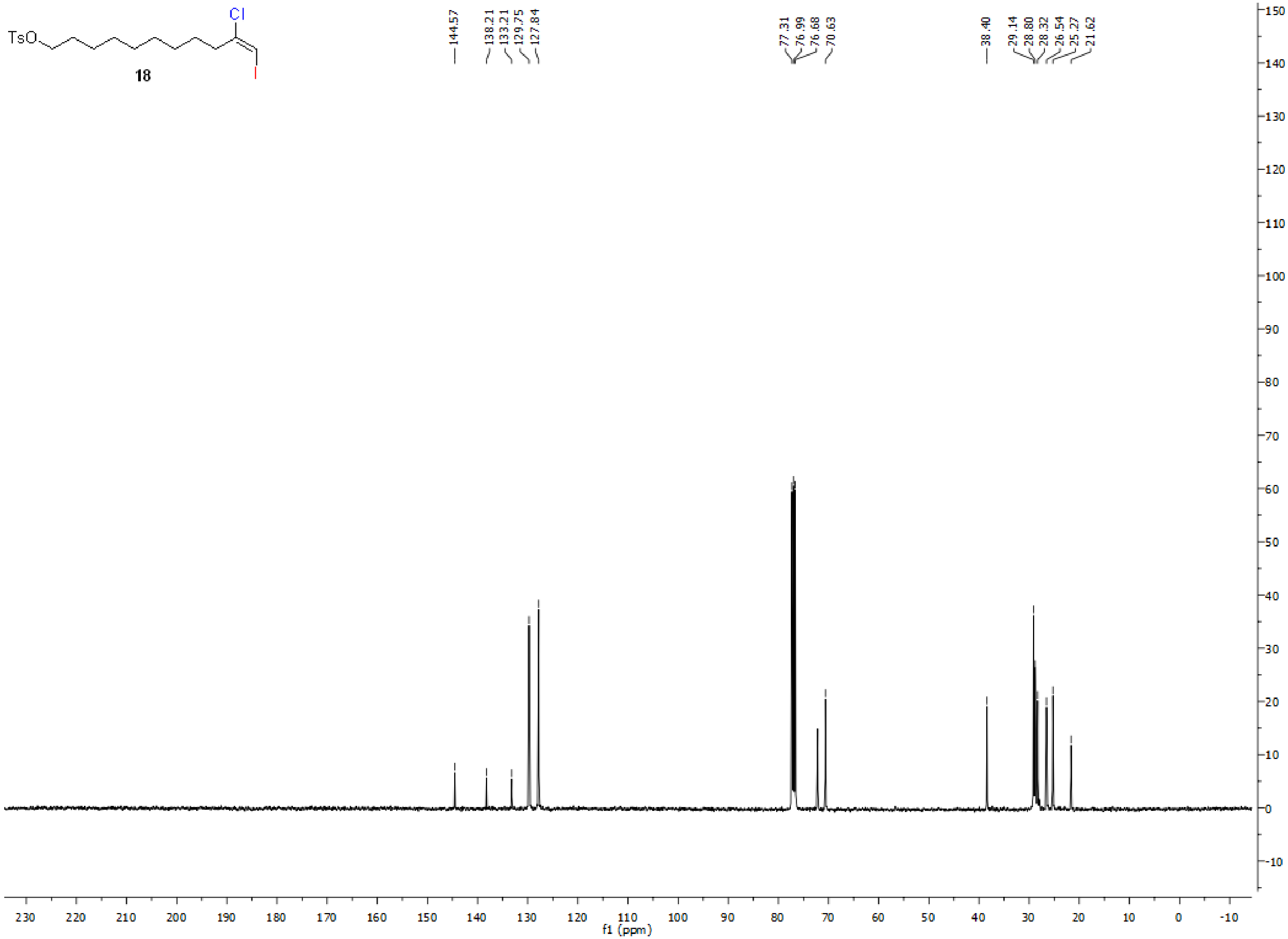
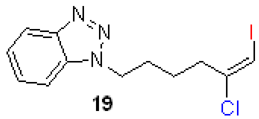


Figure S54. ^{1}H-NMR of **19**



19

E/Z= 17/1

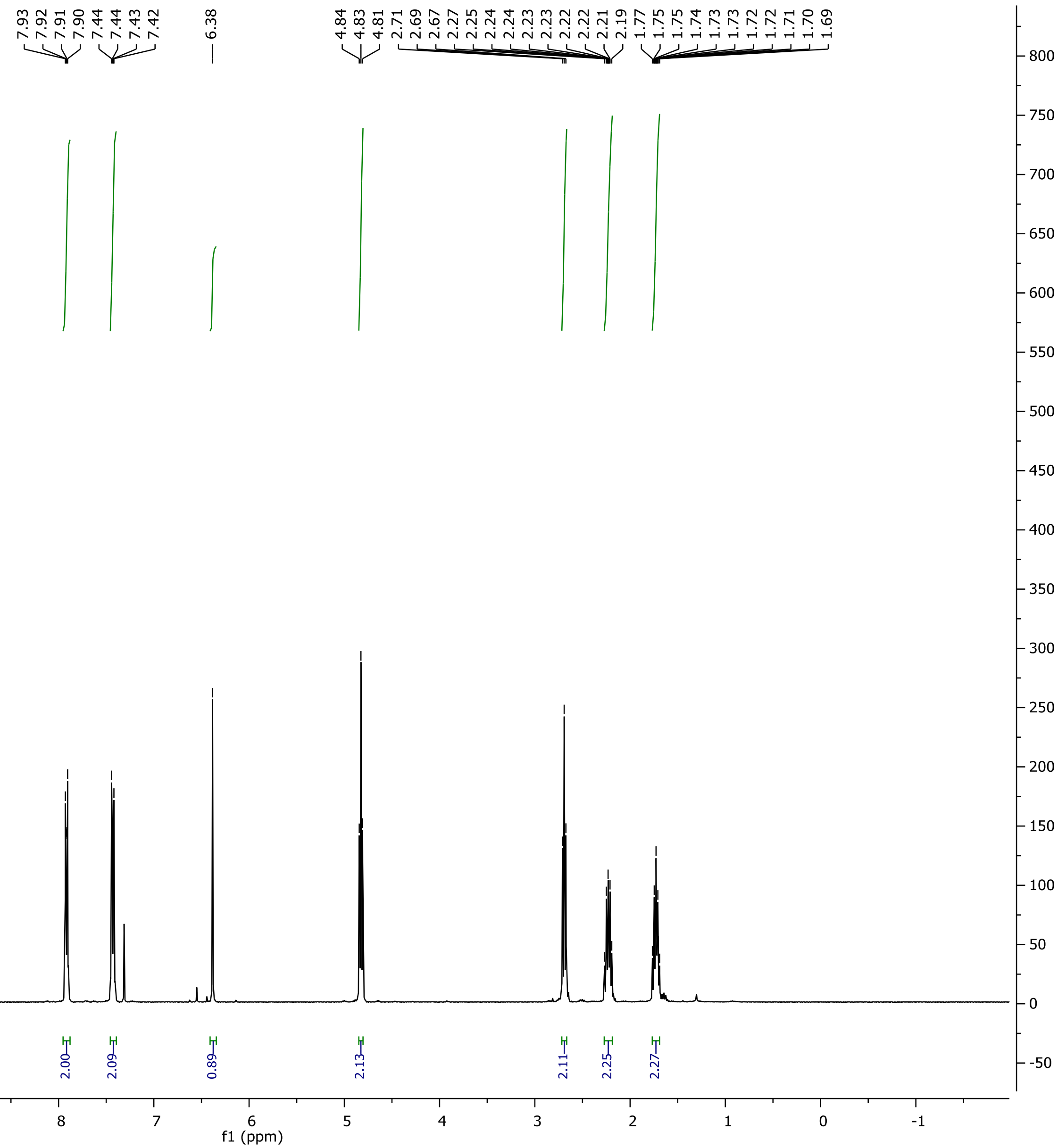
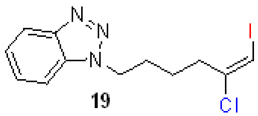


Figure S55. ^{13}C-NMR of **19**



19

E/Z= 17/1

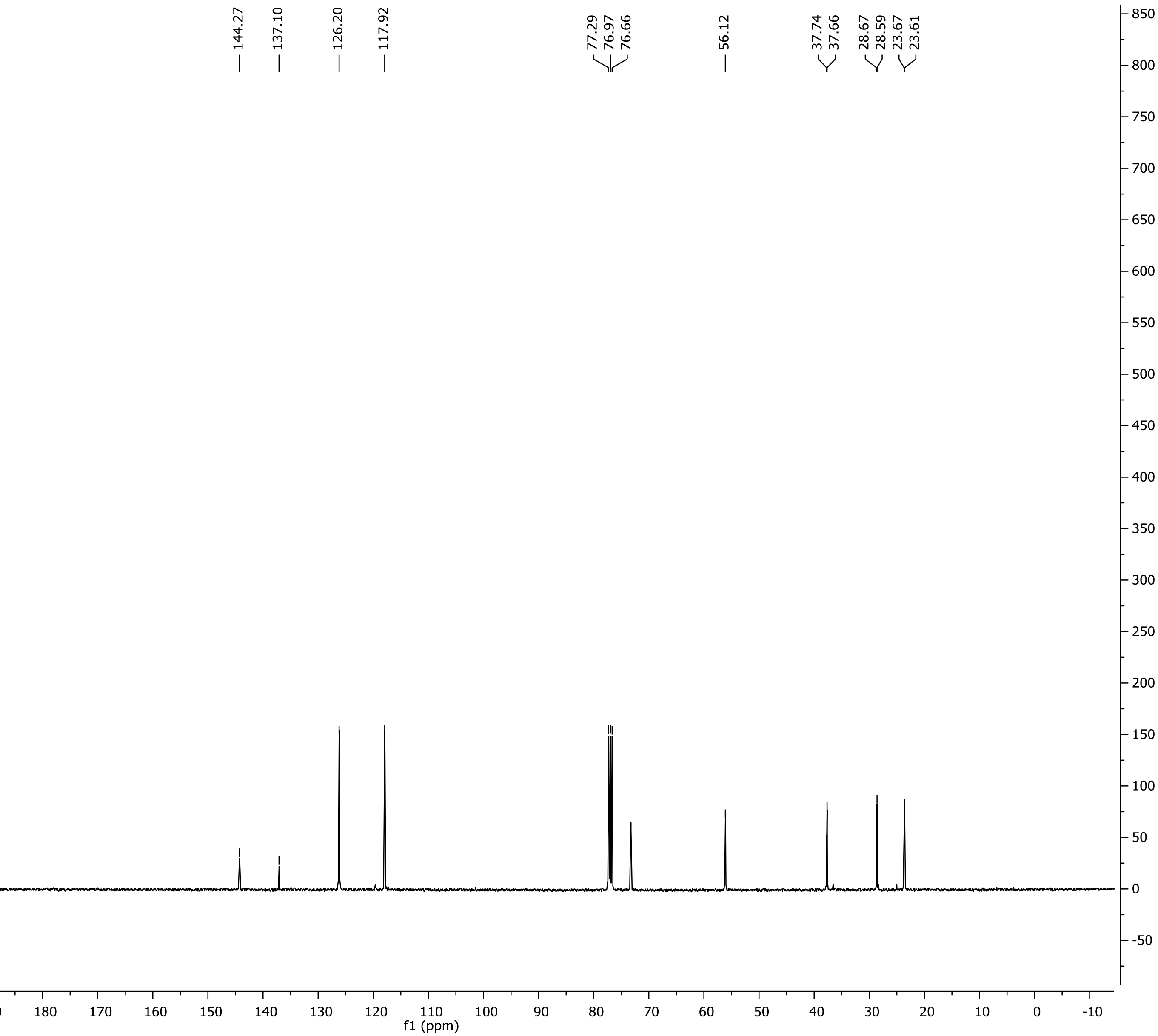


Figure S56. ^{1}H-NMR of **20**

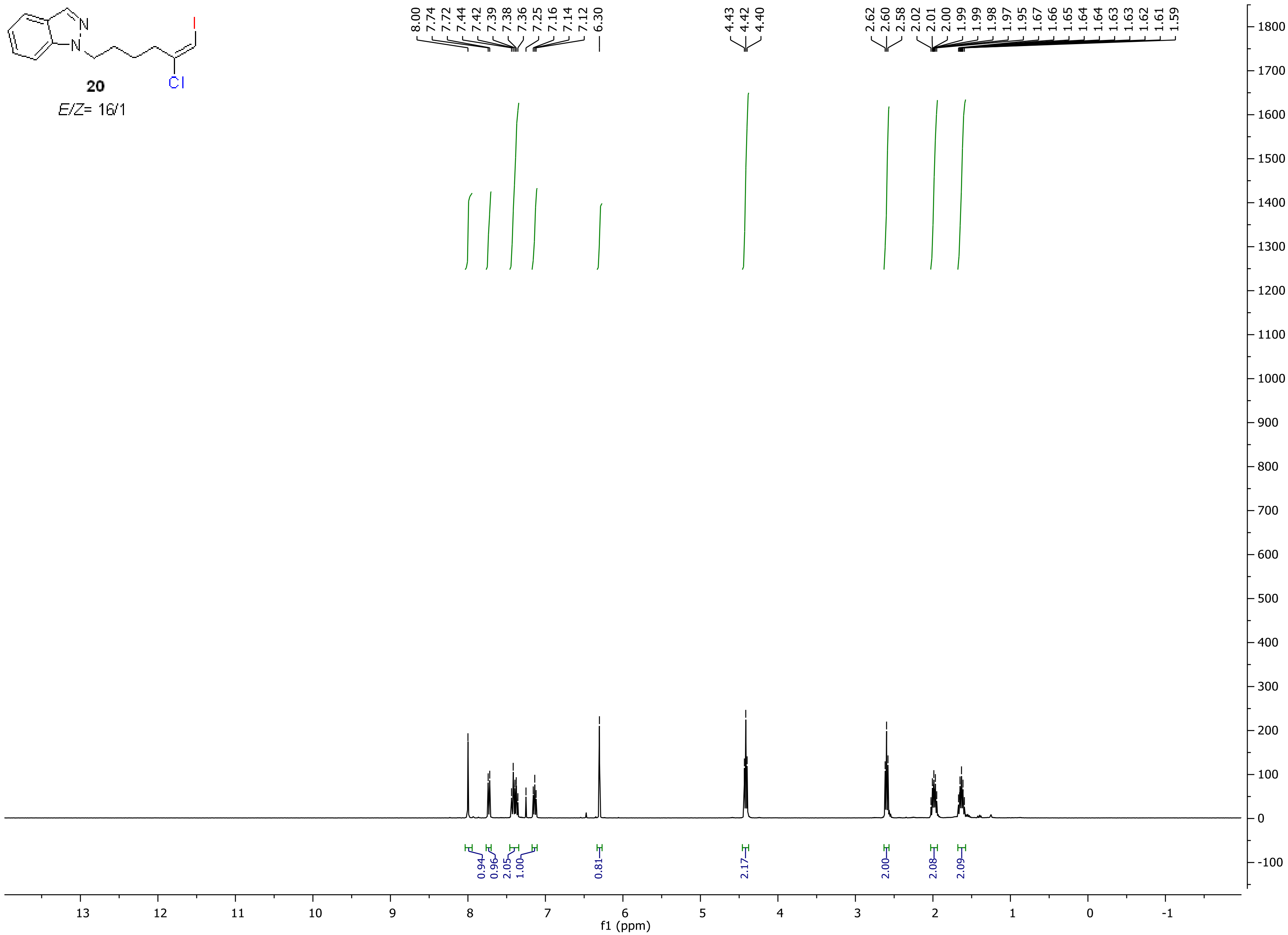


Figure S57. ^{13}C-NMR of **20**

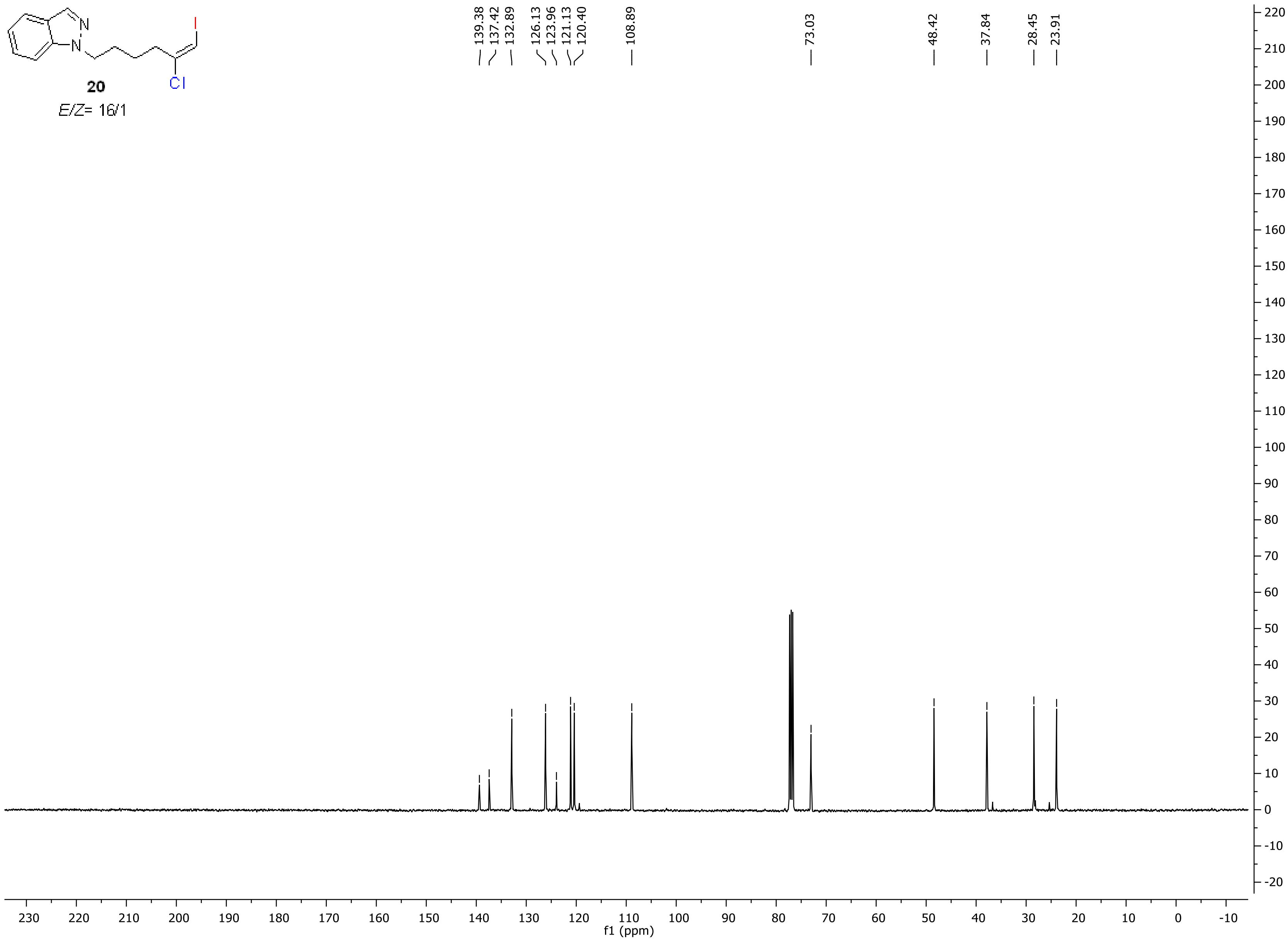
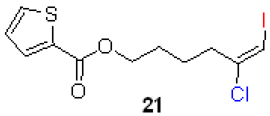


Figure S58. ^{1}H-NMR of **21**



21

E/Z= 15/1

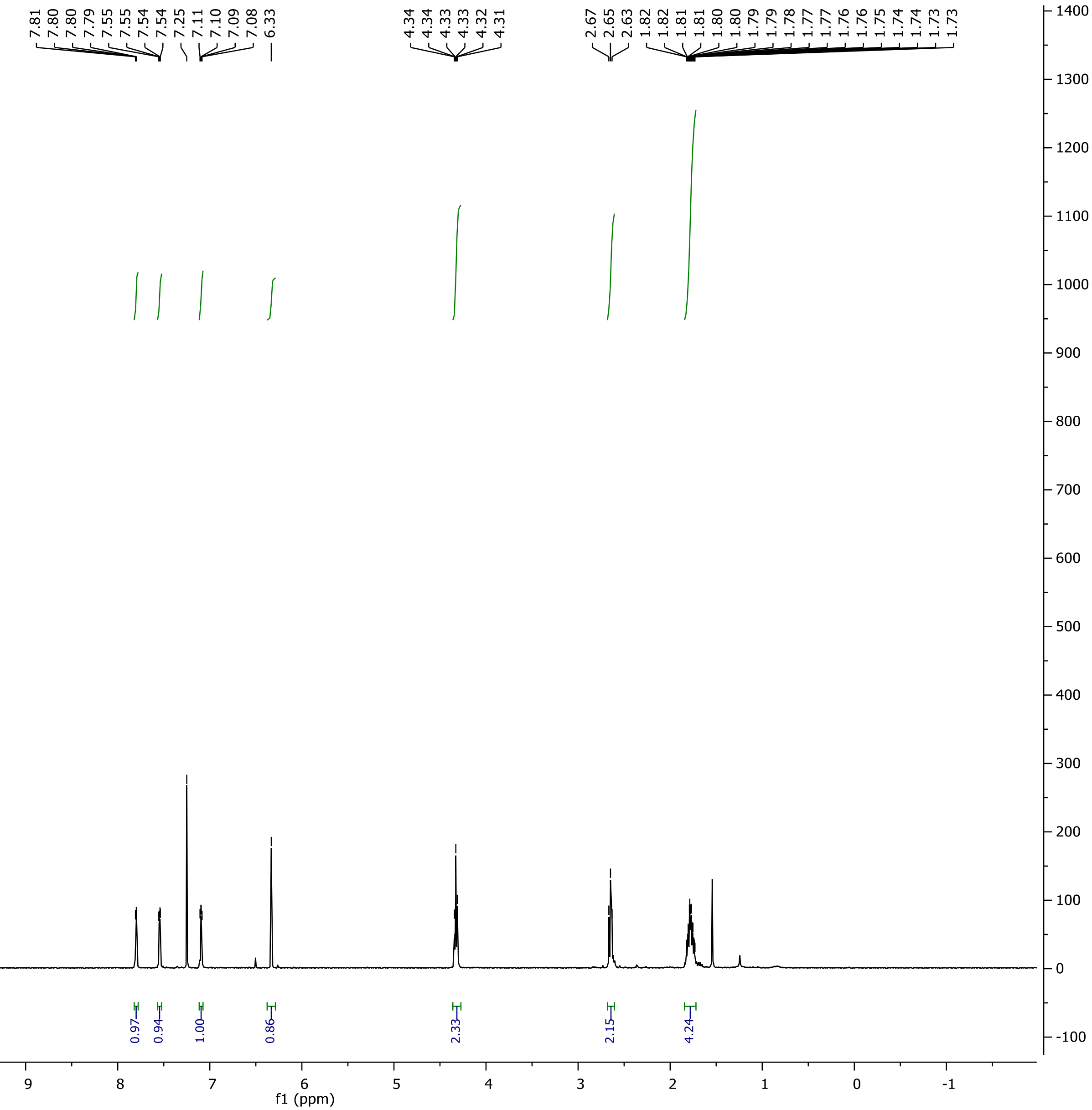


Figure S59. ^{13}C-NMR of **21**

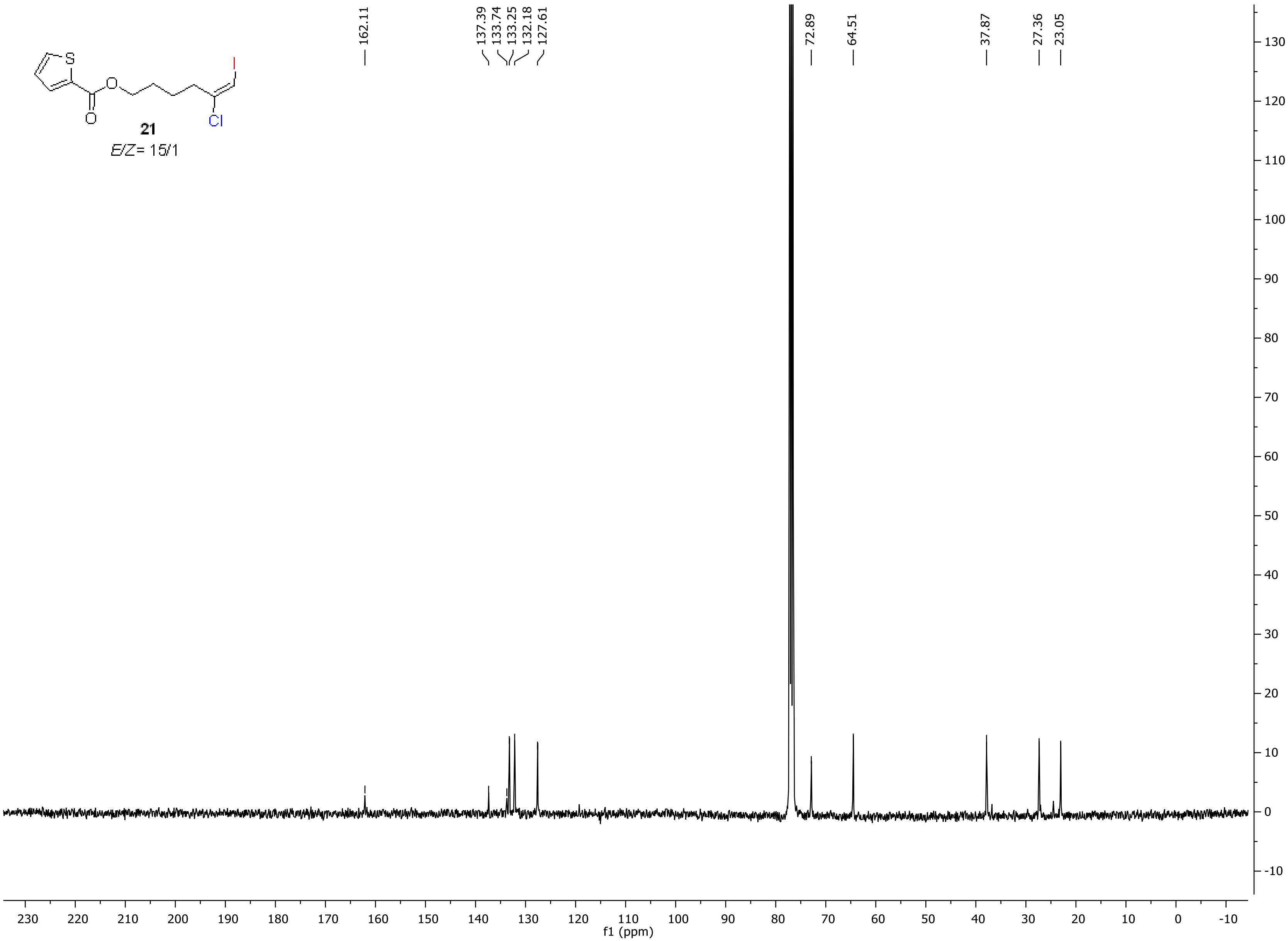


Figure S60. ^{1}H-NMR of **22**

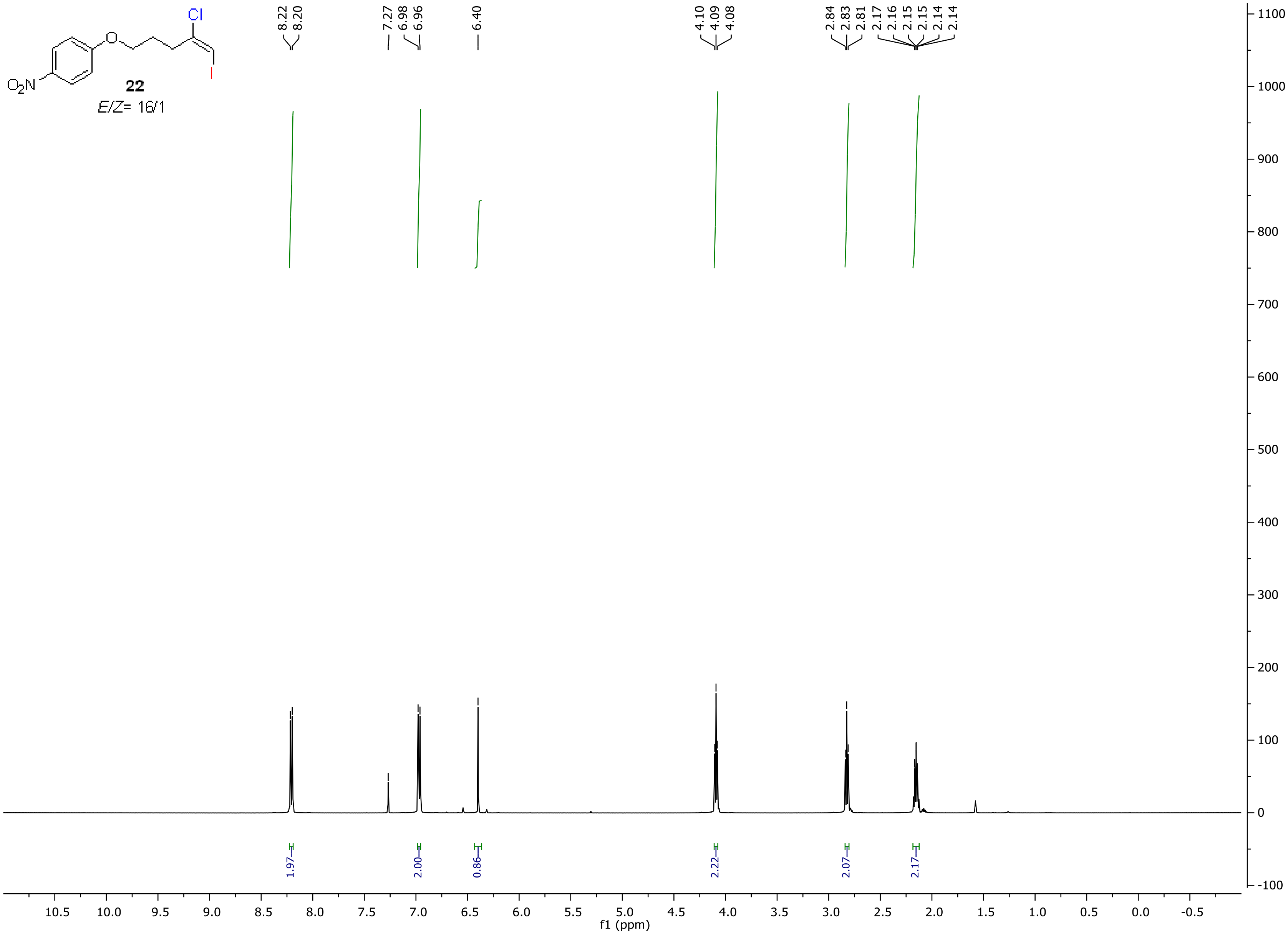
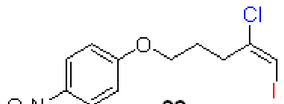


Figure S61. ^{13}C-NMR of **22**



22
E/Z= 16/1

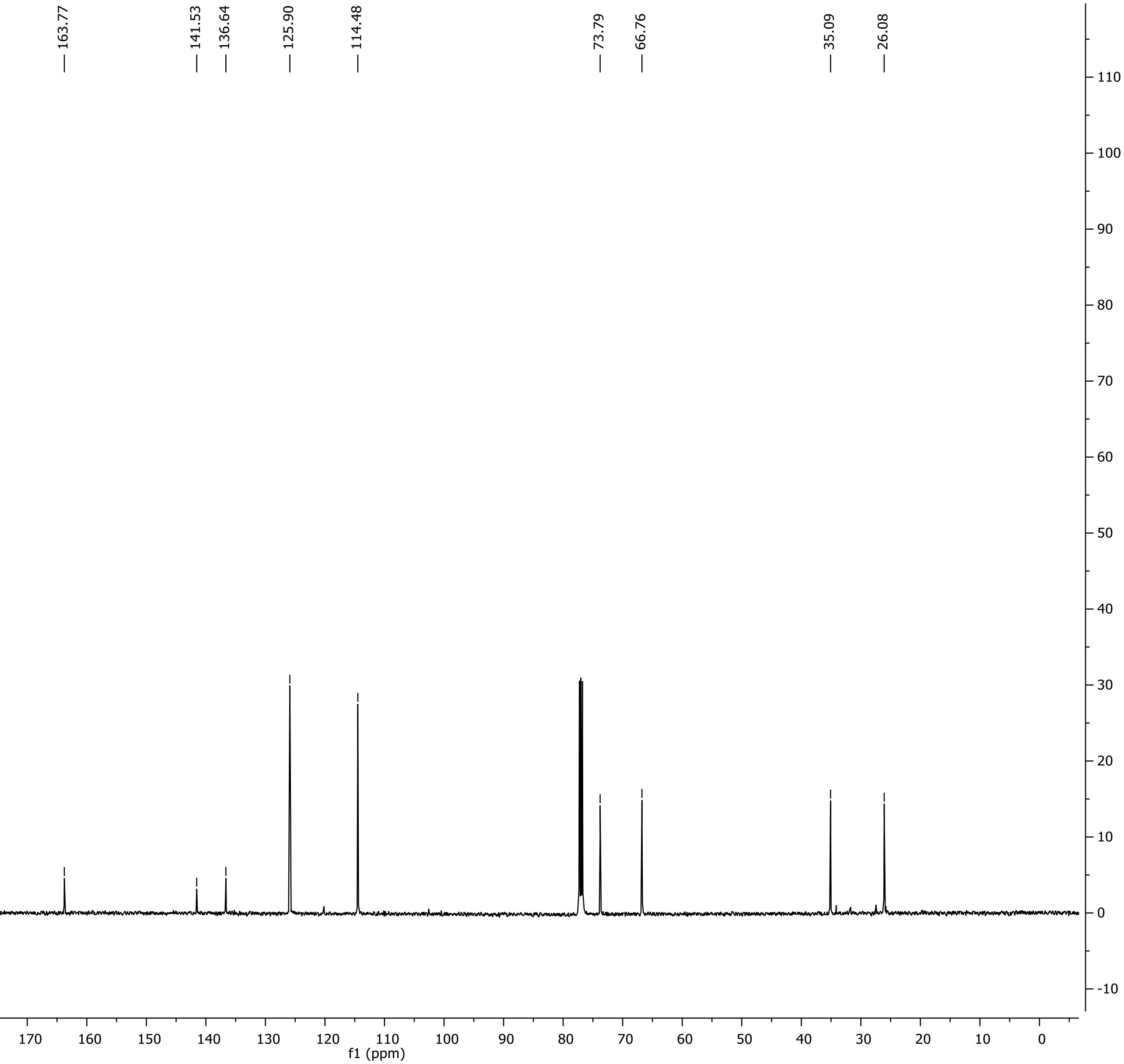
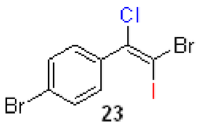


Figure S62. ^{1}H-NMR of **23**



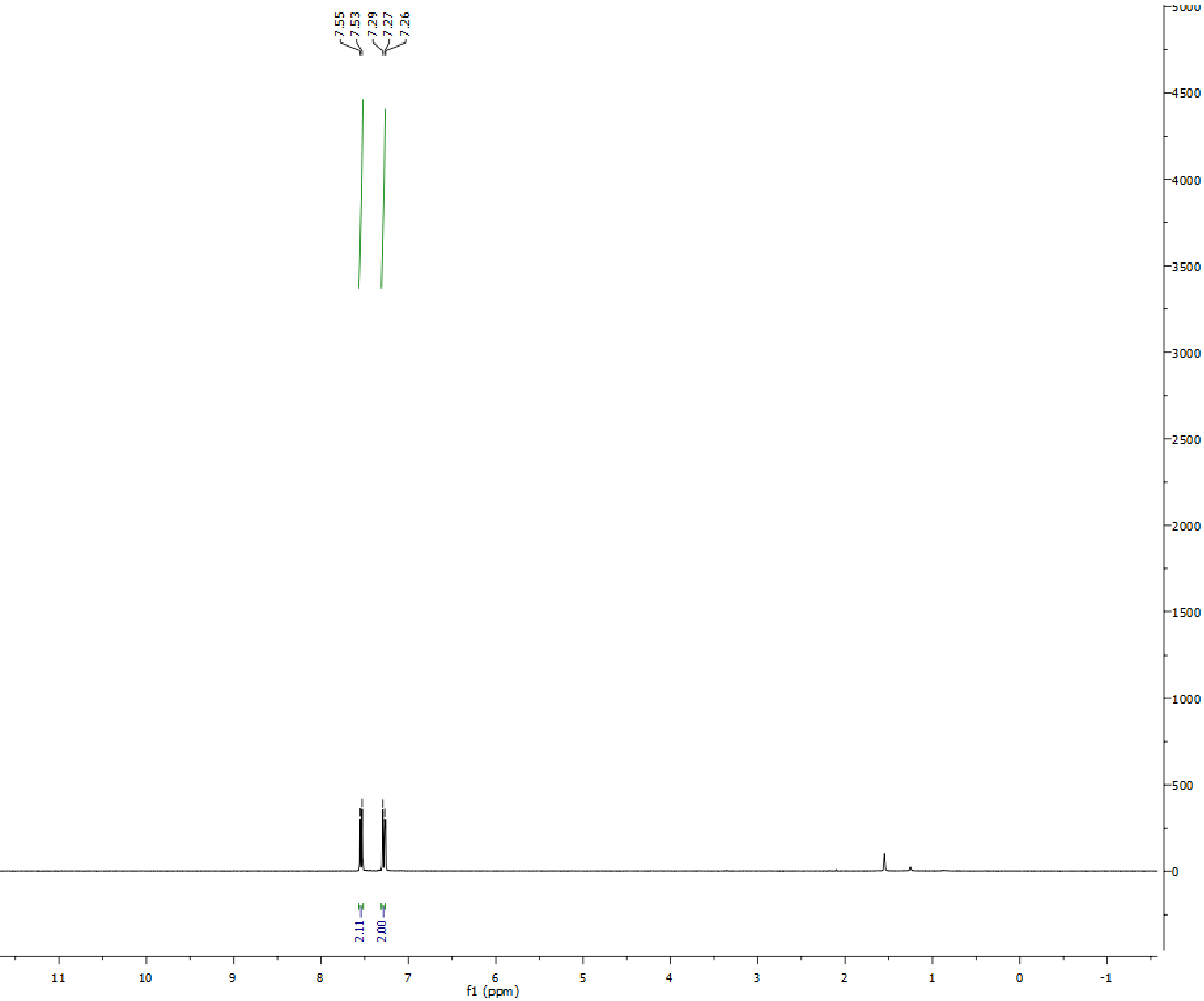
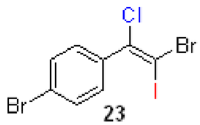


Figure S63. ^{13}C-NMR of **23**



23

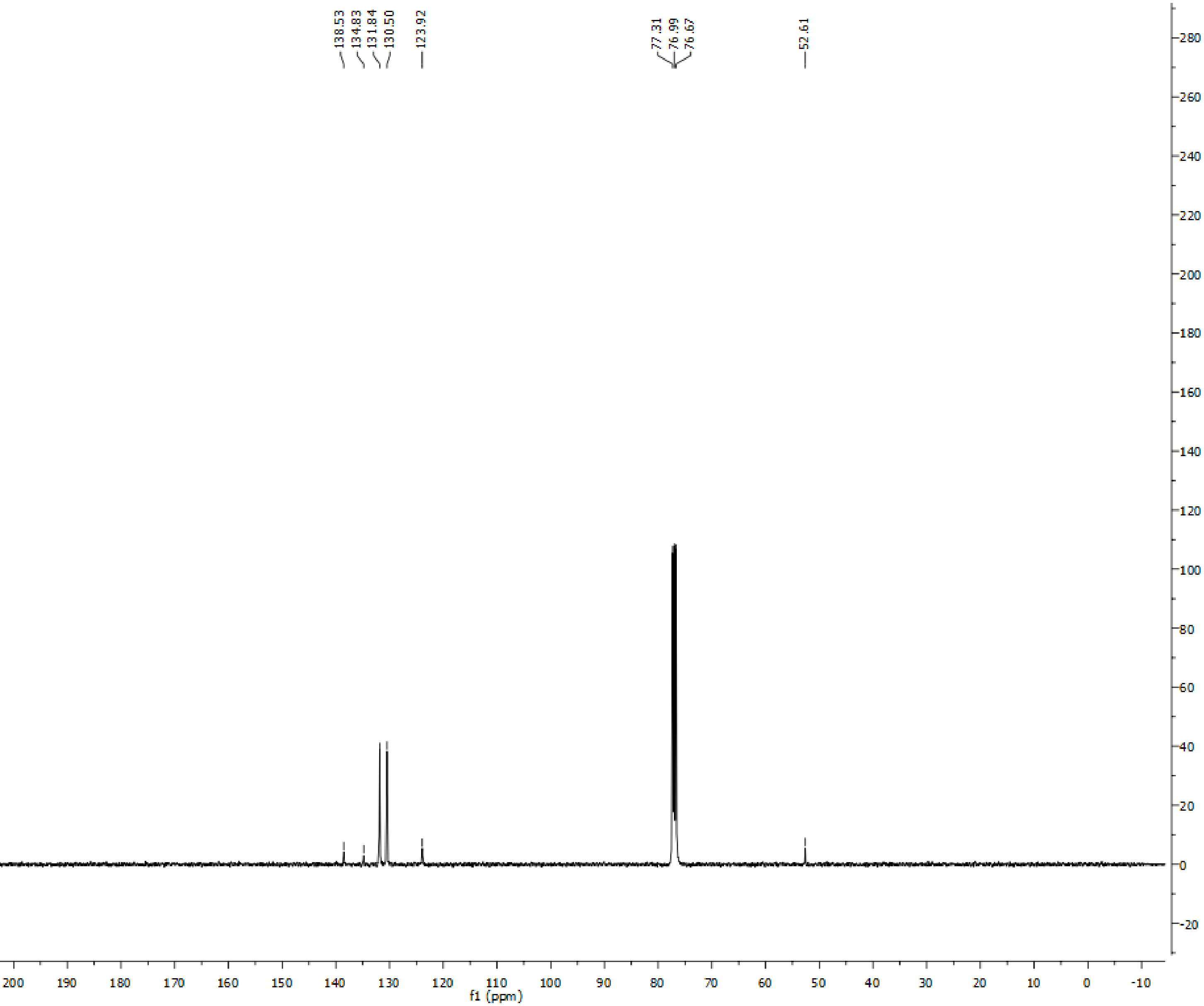


Figure S64. ^{1}H-NMR of **24**

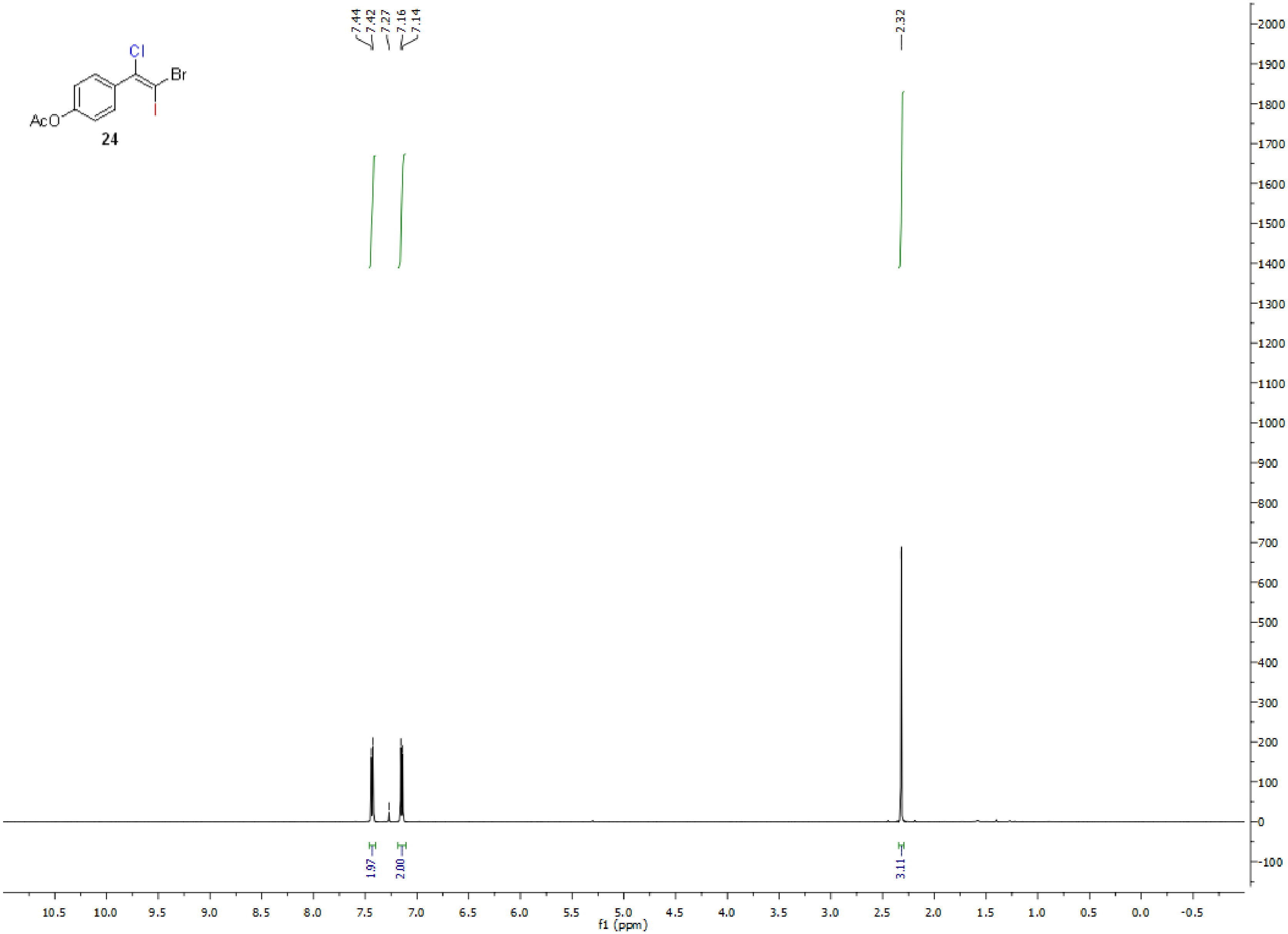


Figure S65. ^{13}C-NMR of **24**

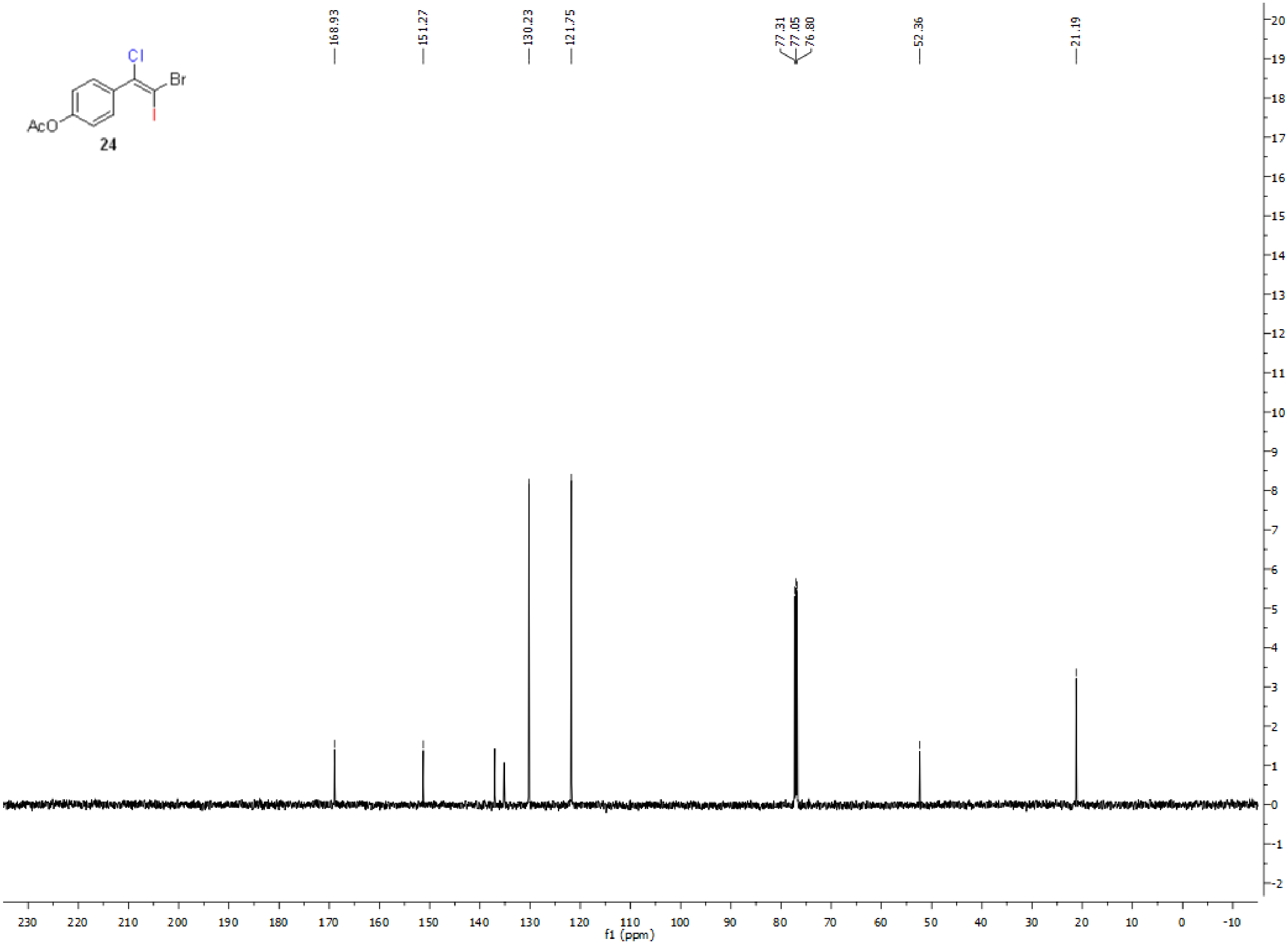
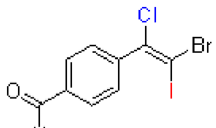


Figure S66. ^{1}H-NMR of **25**



25

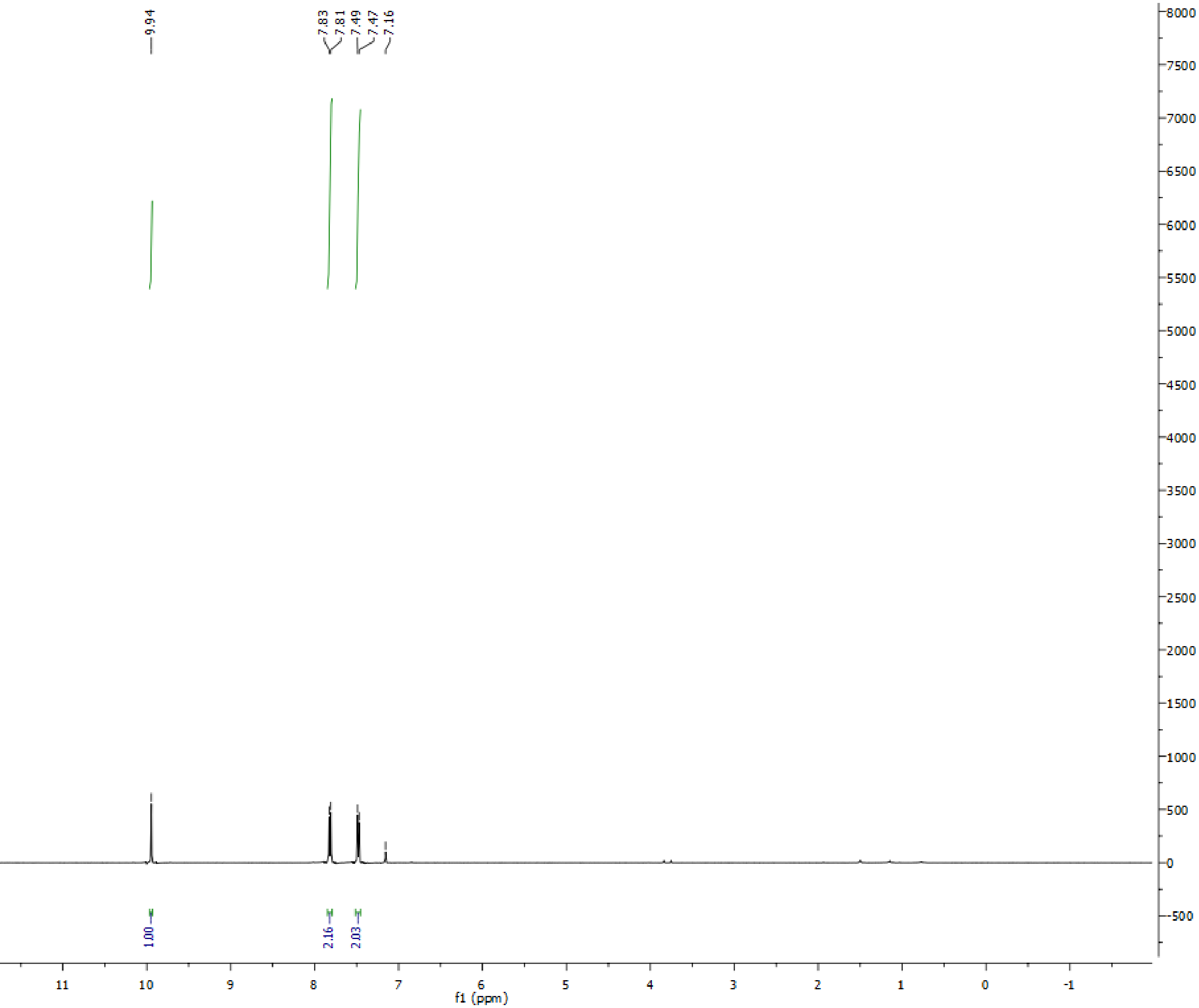


Figure S67. ^{13}C-NMR of **25**

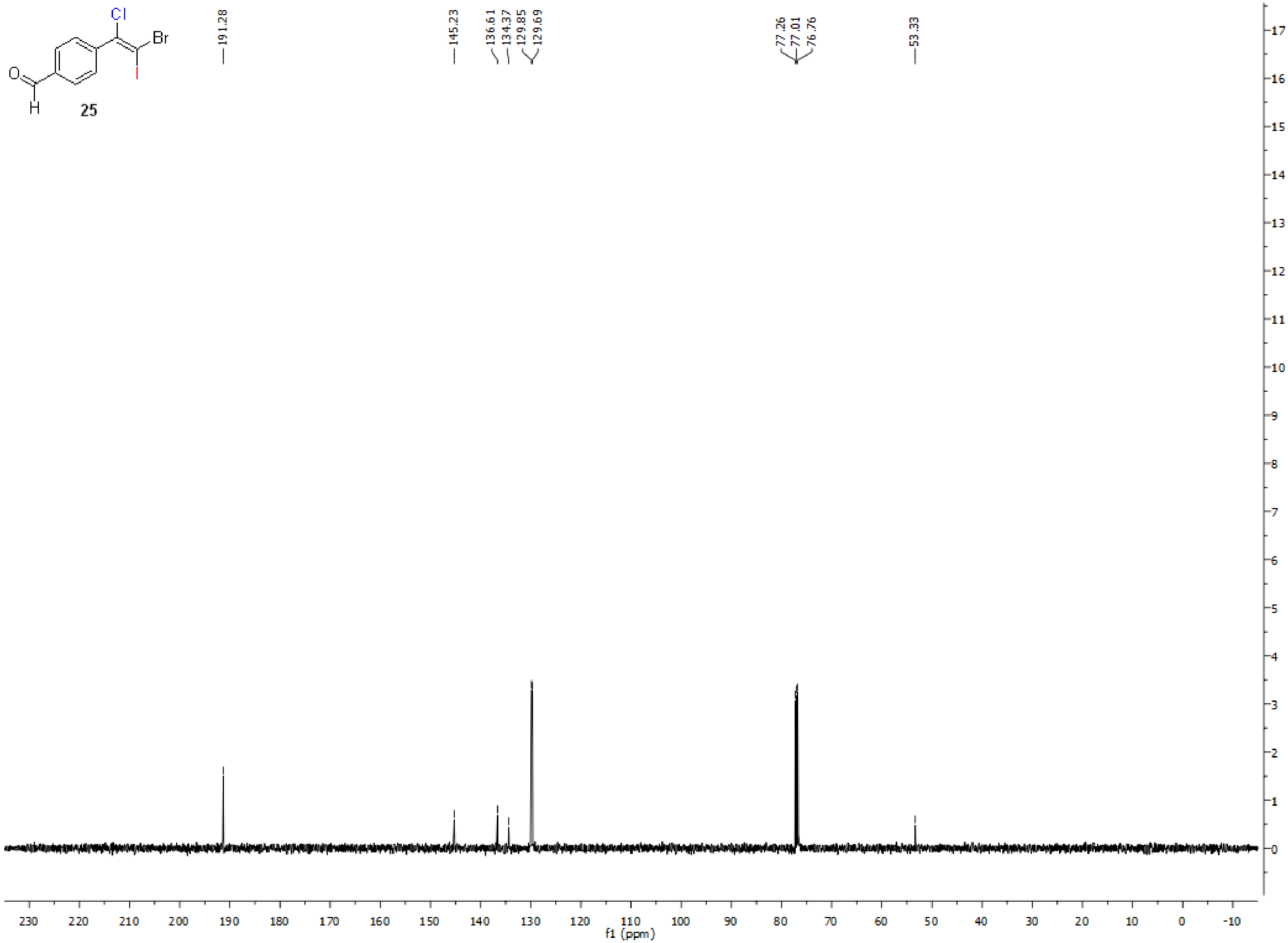


Figure S68. ^{1}H-NMR of **26**

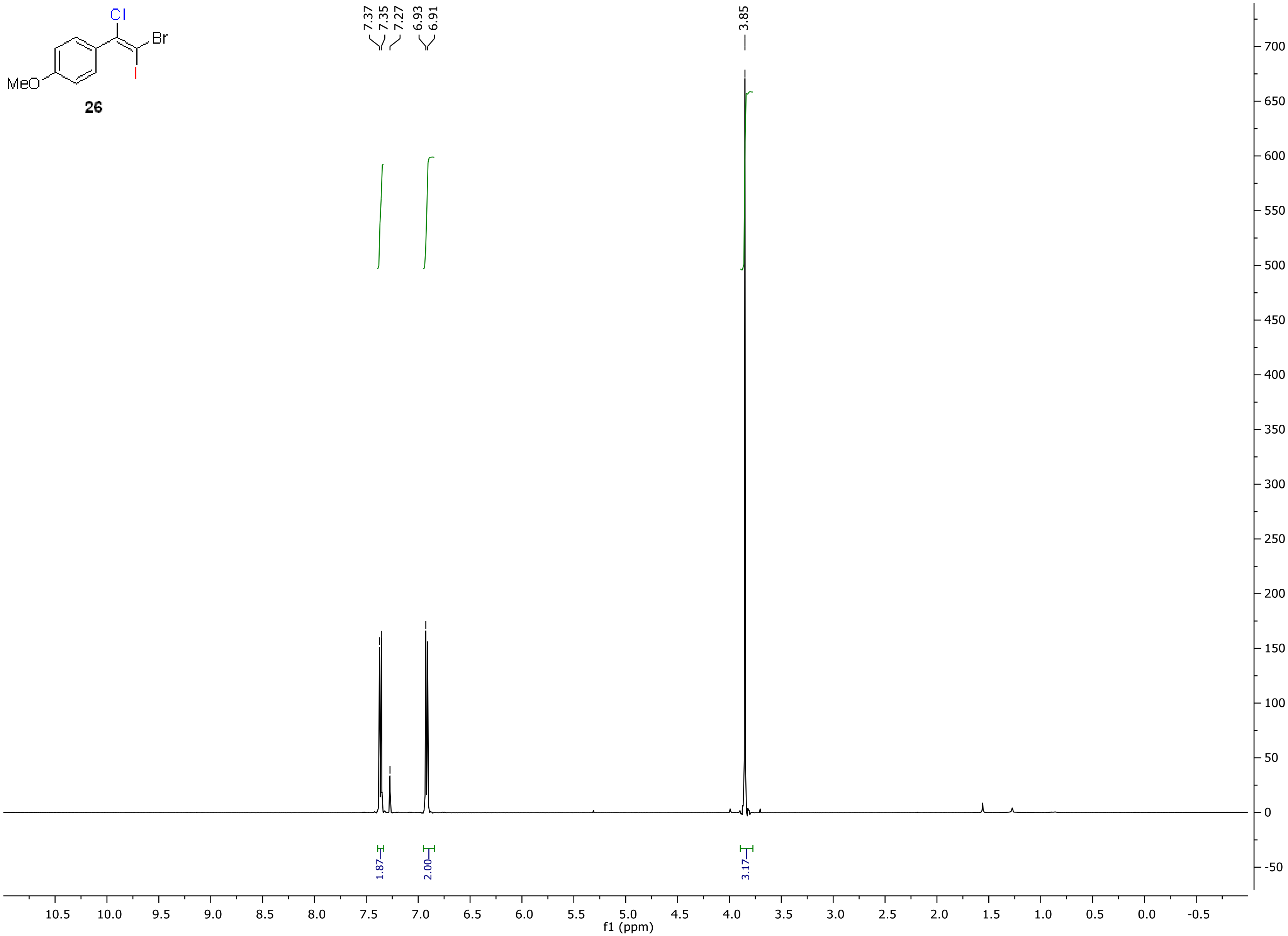


Figure S69. ^{13}C-NMR of **26**

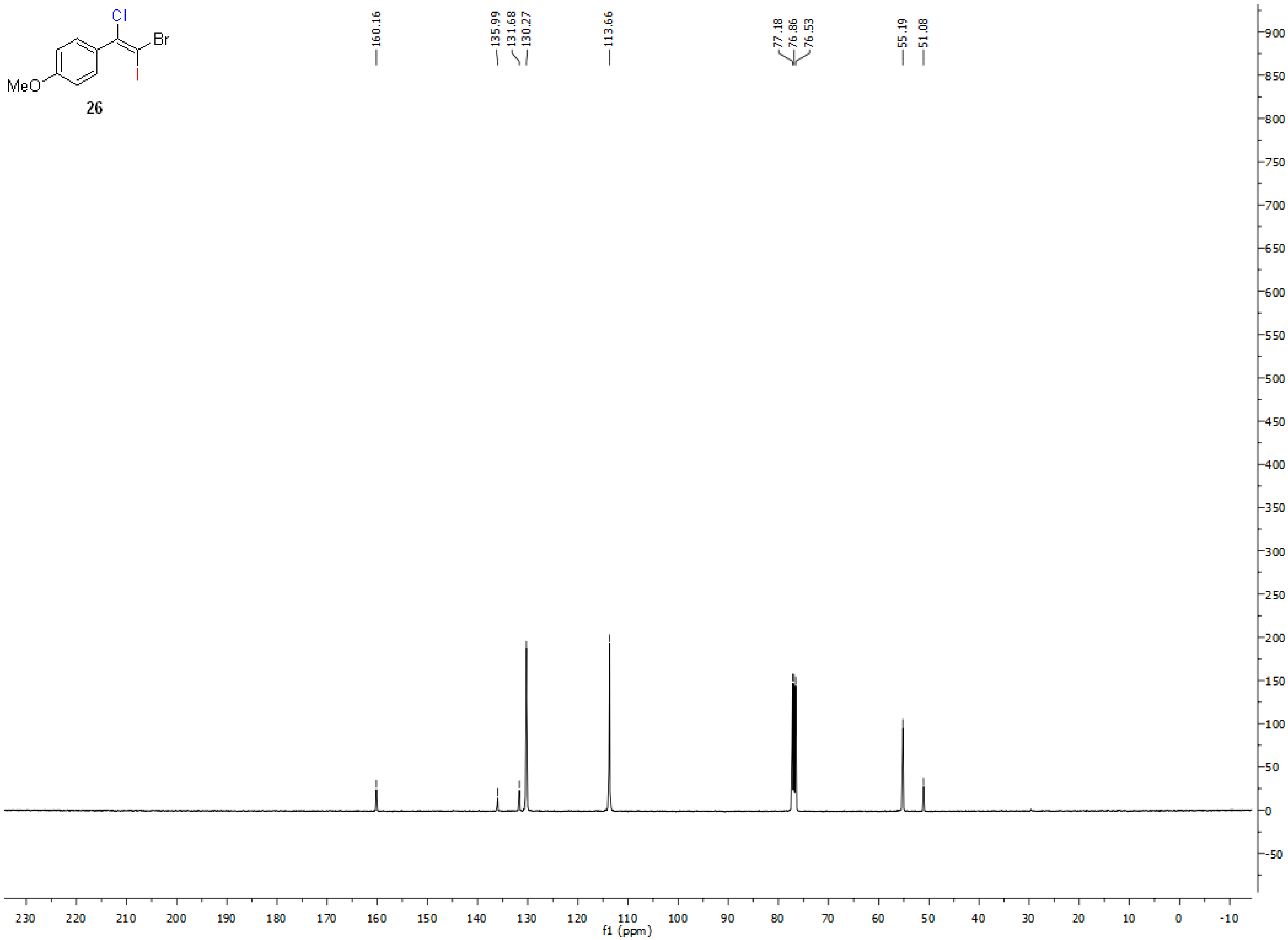


Figure S70. ^{1}H-NMR of **27**

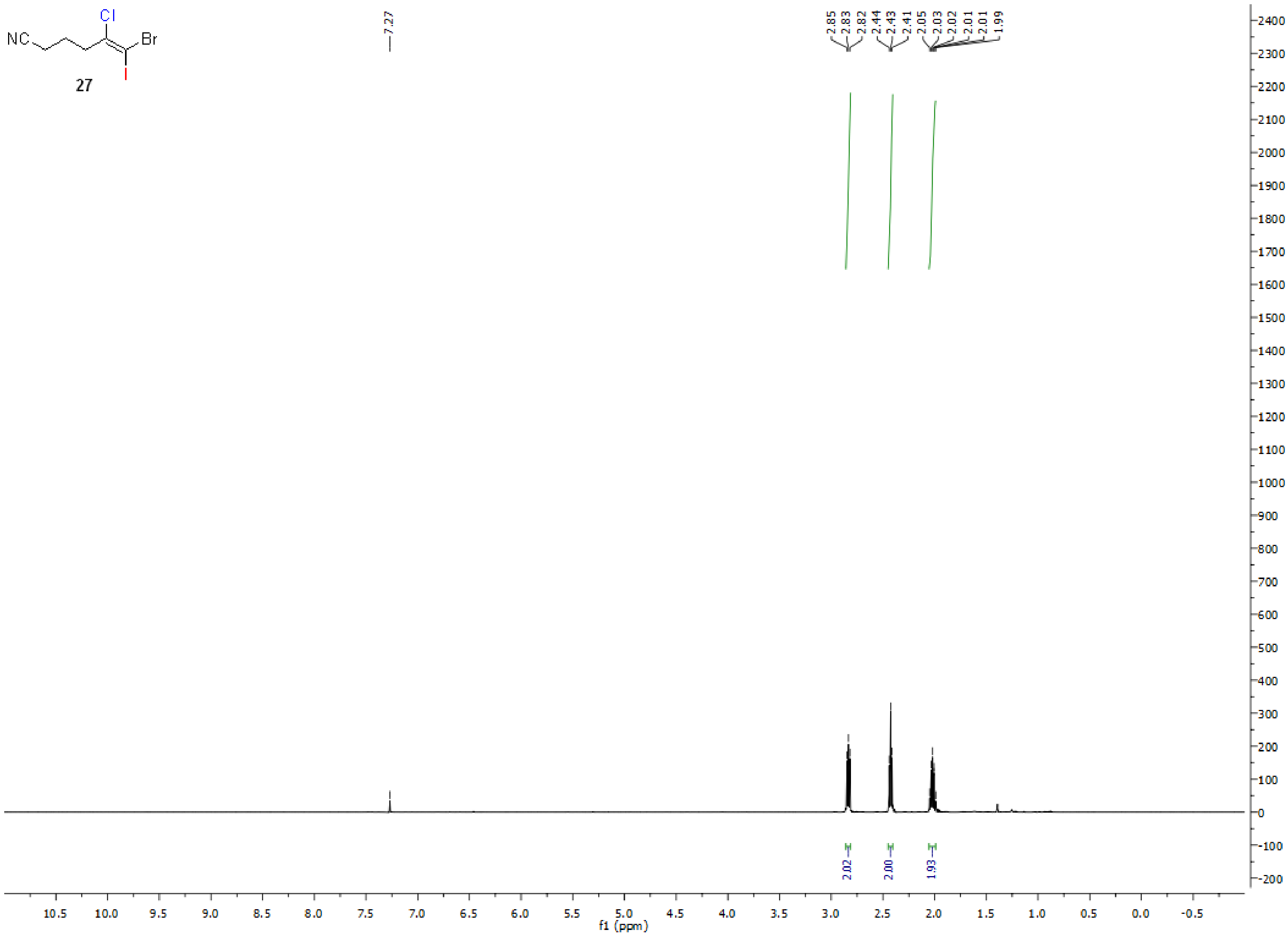


Figure S71. ^{13}C-NMR of **27**

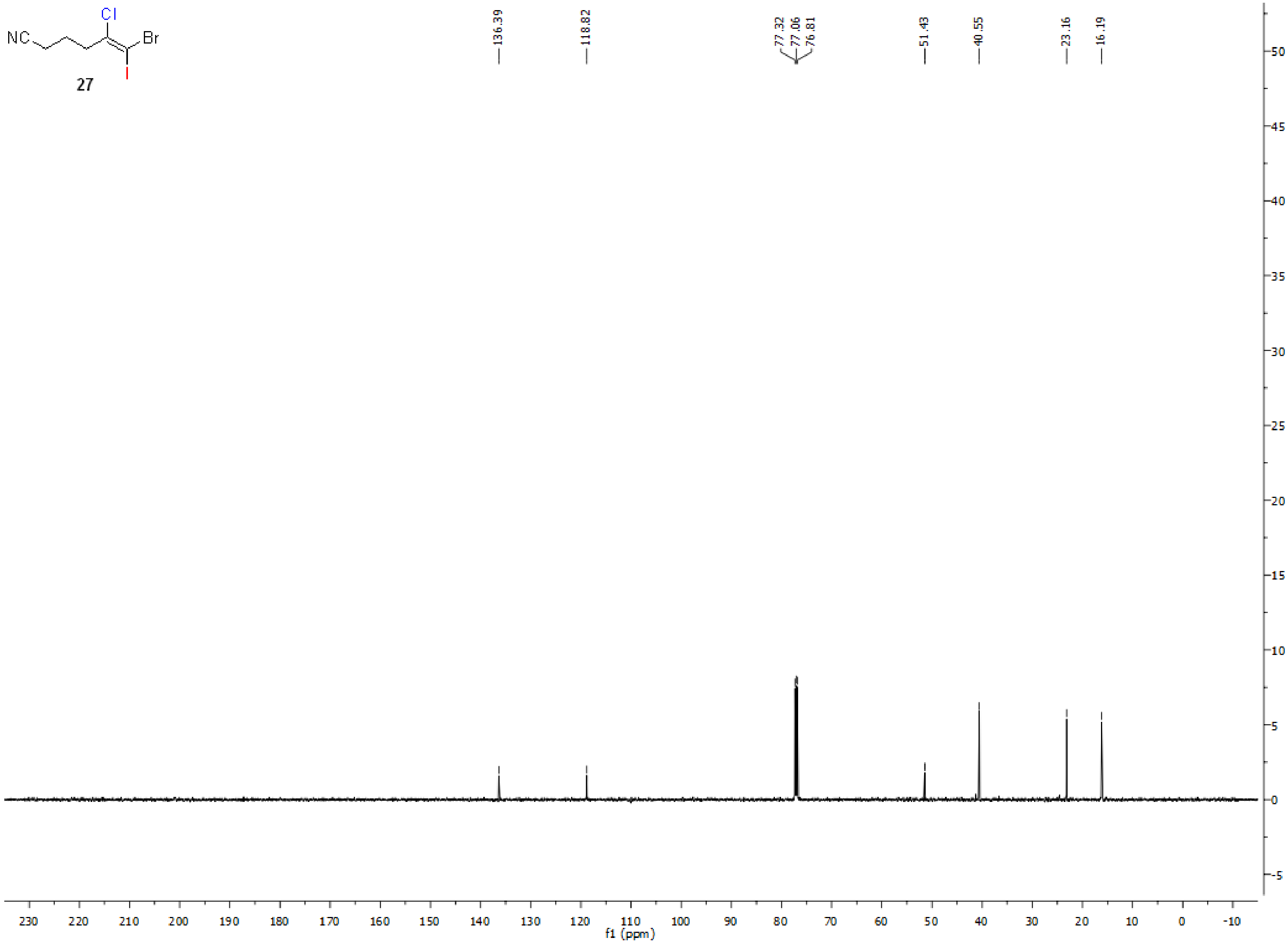


Figure S72. ^{1}H-NMR of **28**

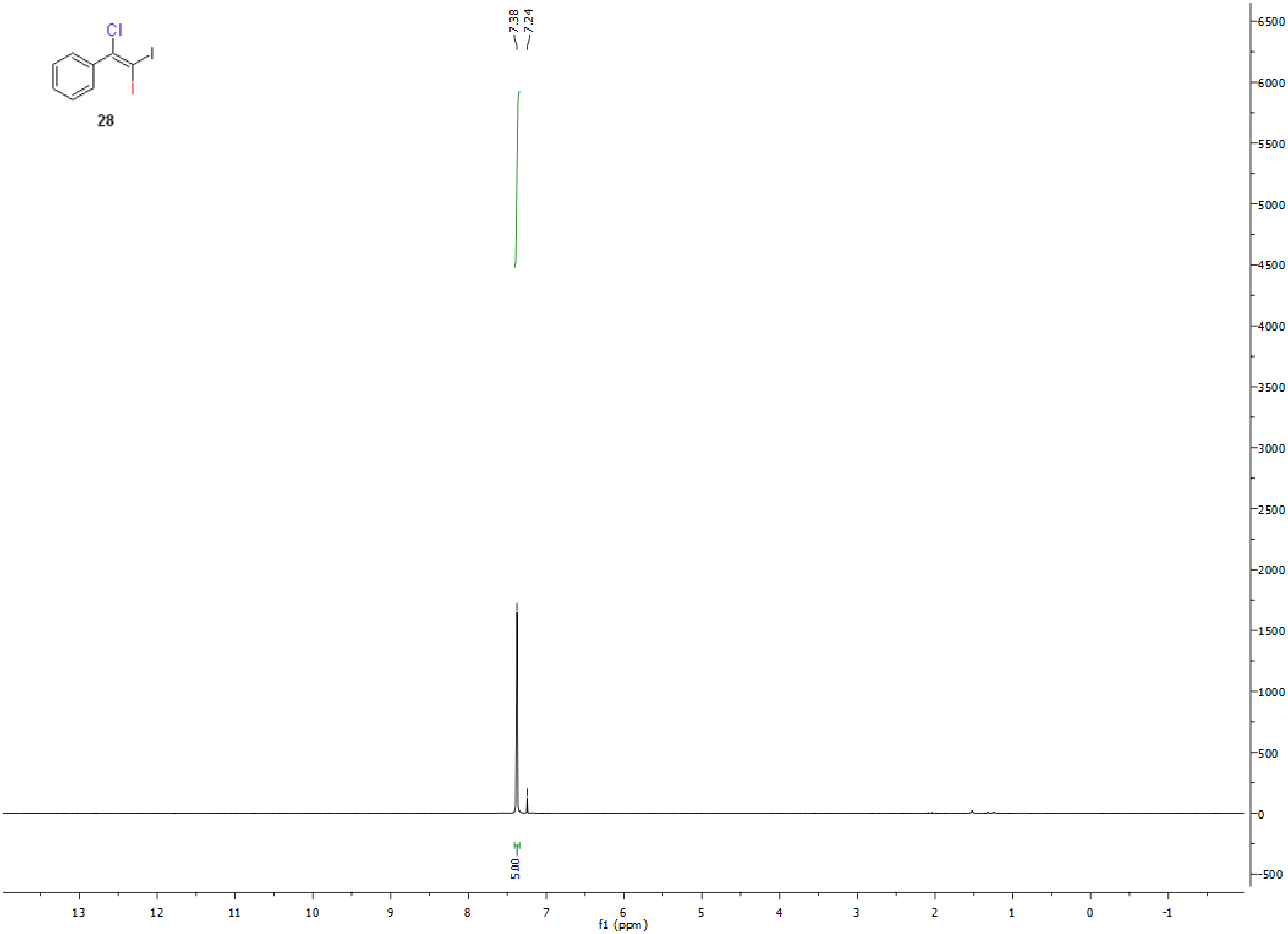
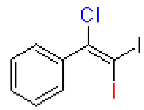


Figure S73. ^{13}C-NMR of **28**



28

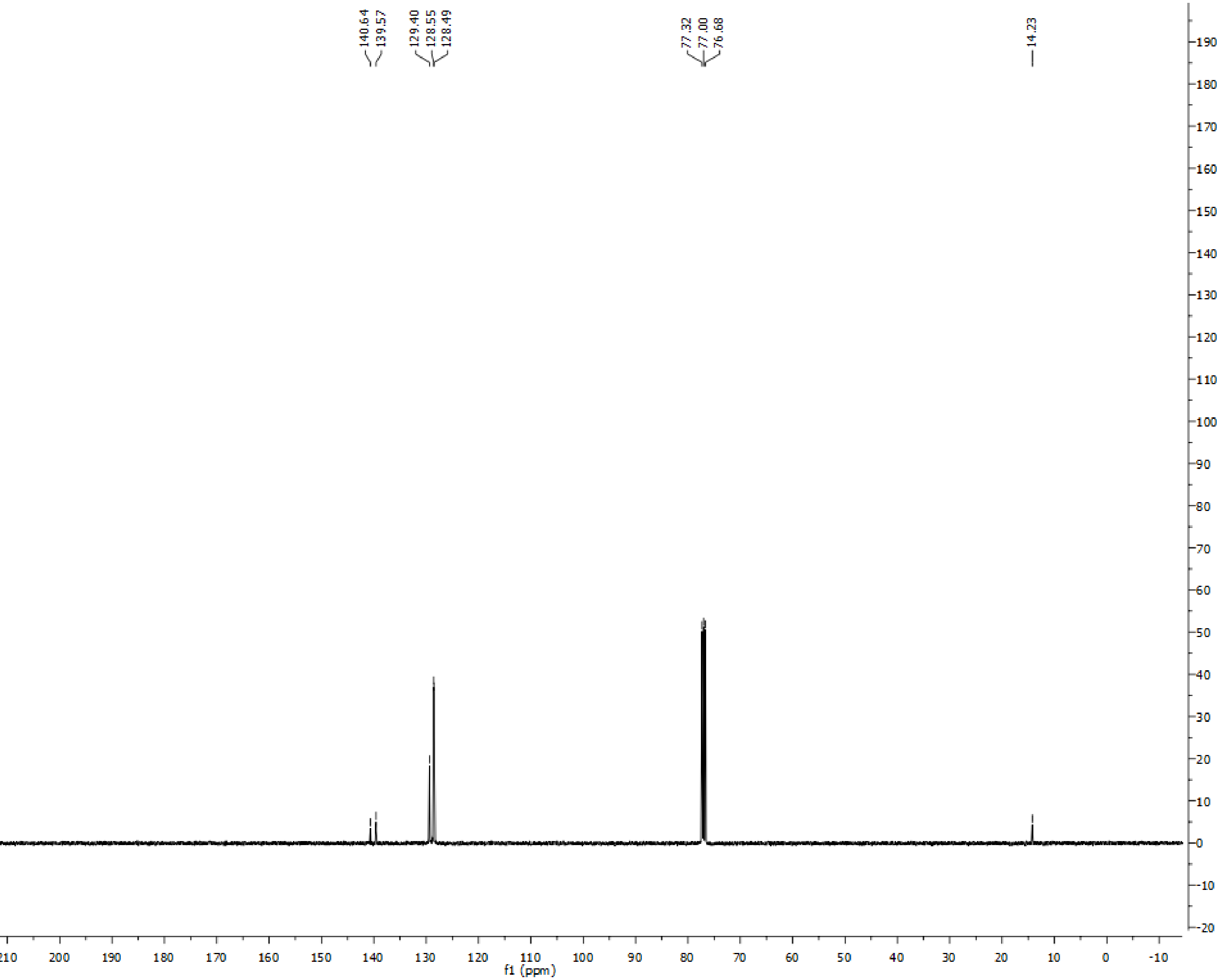


Figure S74. ^{1}H-NMR of **29**

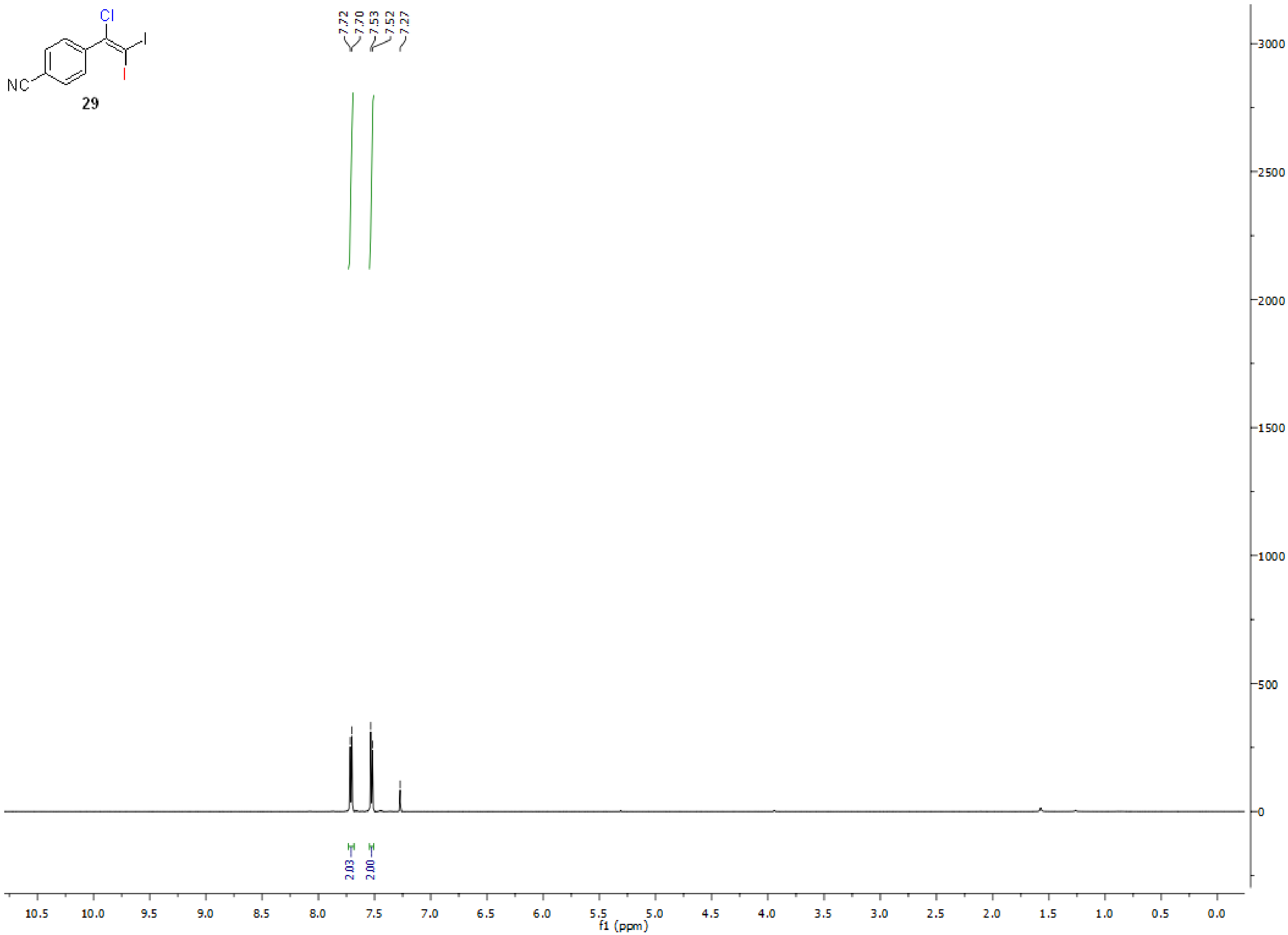
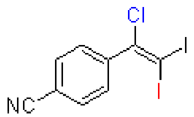


Figure S75. ^{13}C-NMR of **29**



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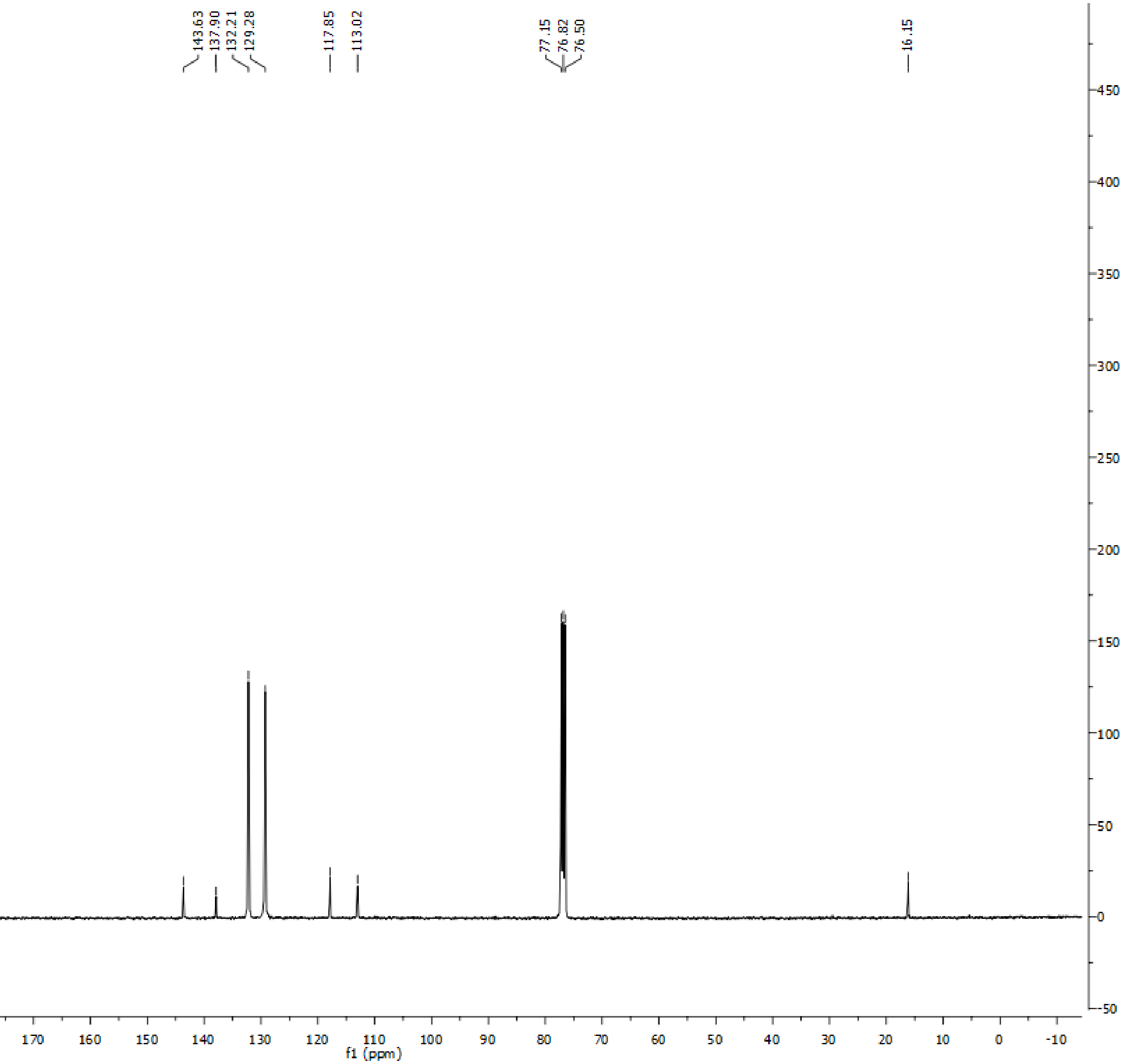
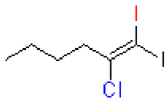


Figure S76. [1]H-NMR of **30**



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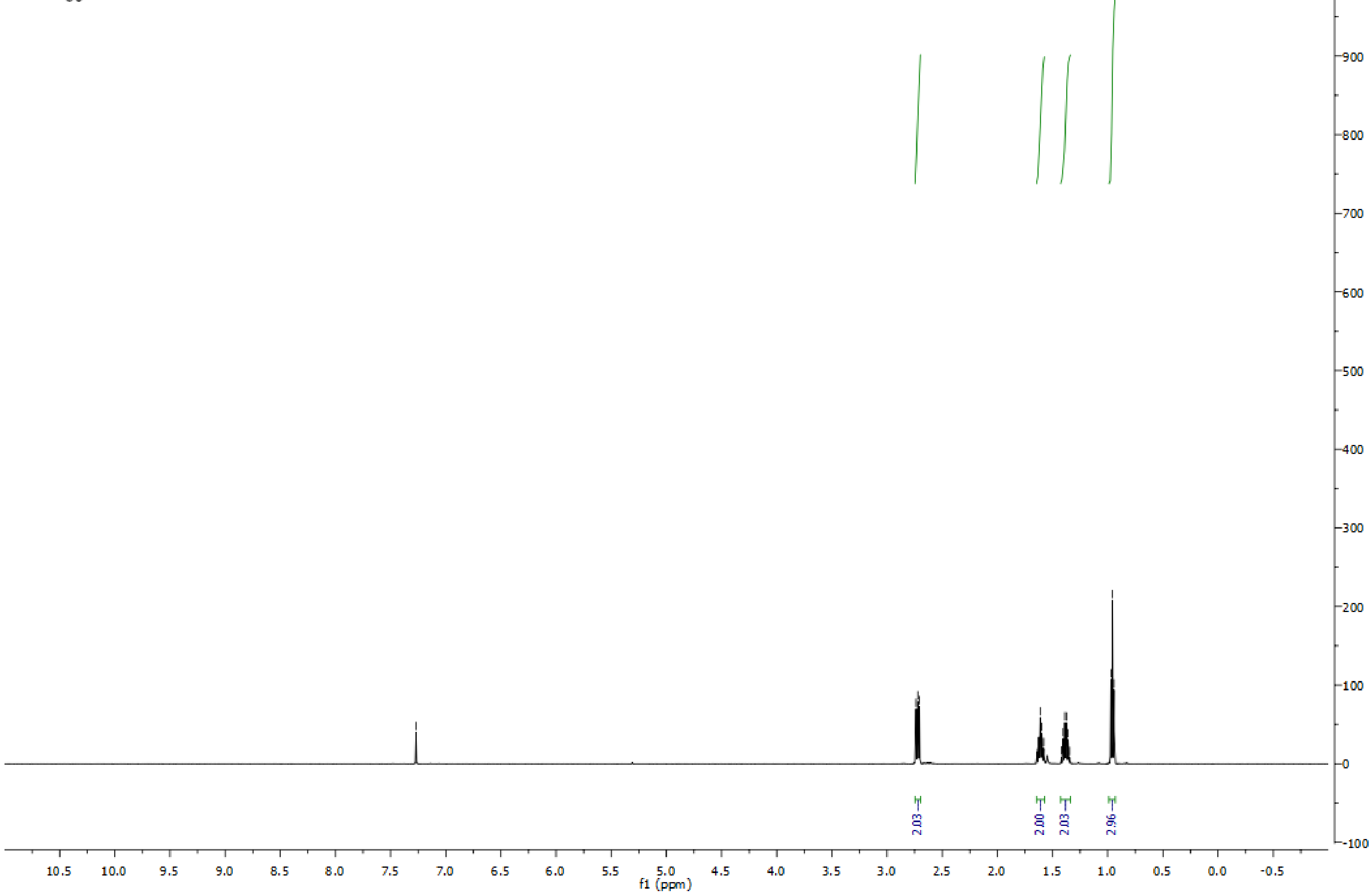


Figure S77. ^{13}C-NMR of **30**

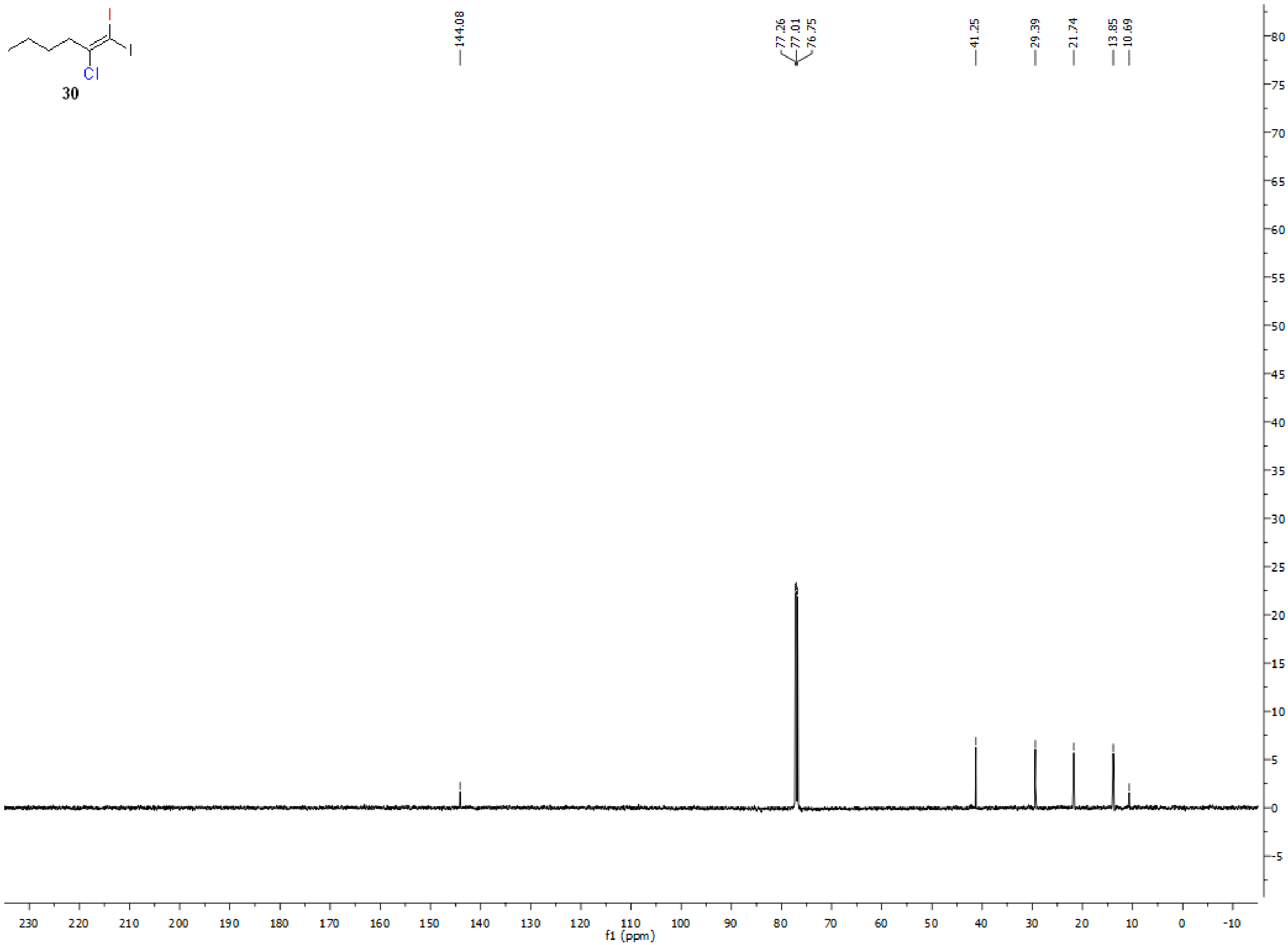


Figure S78. ^{1}H-NMR of **31**

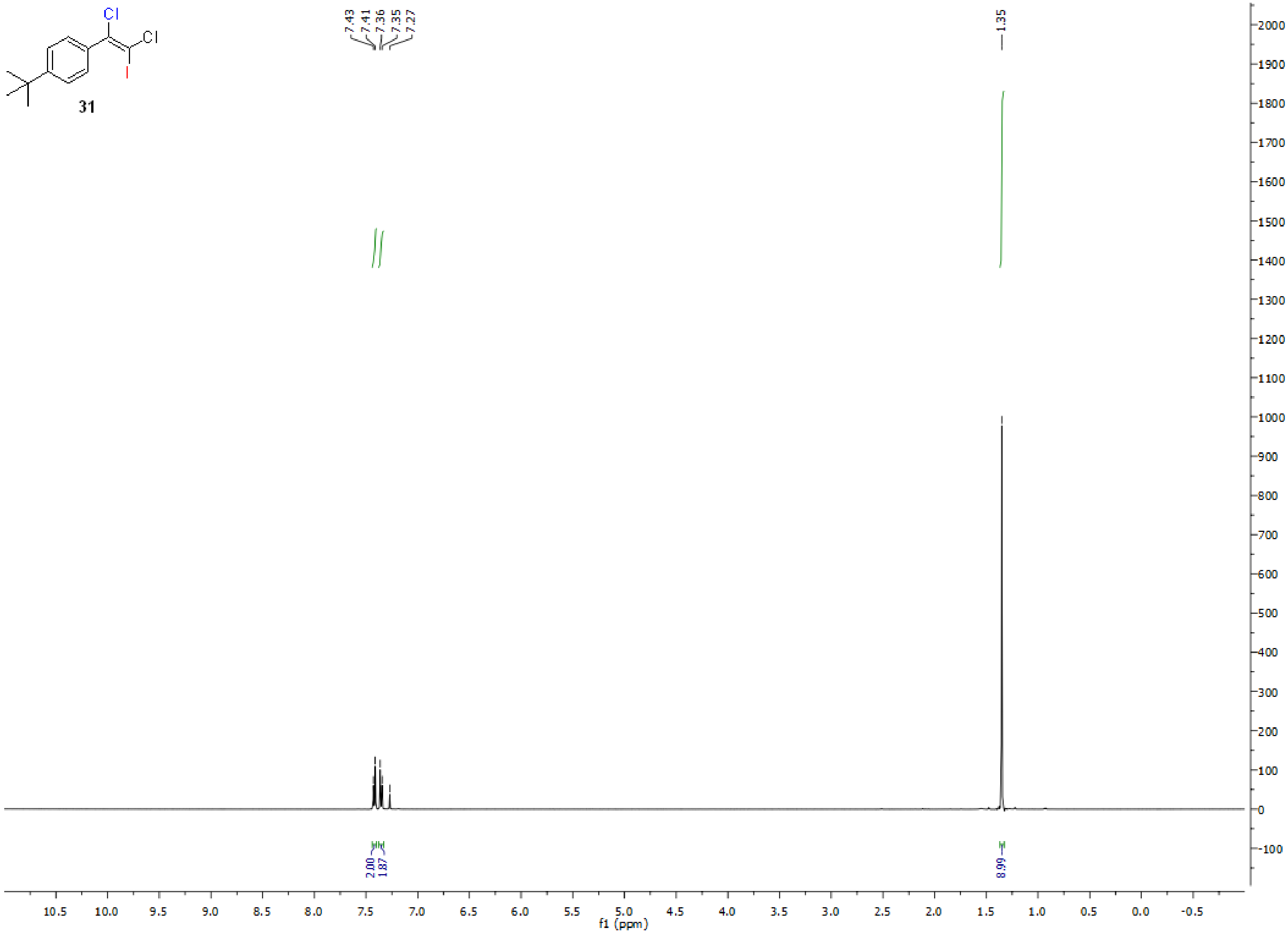
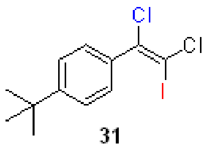


Figure S79. ^{13}C-NMR of **31**



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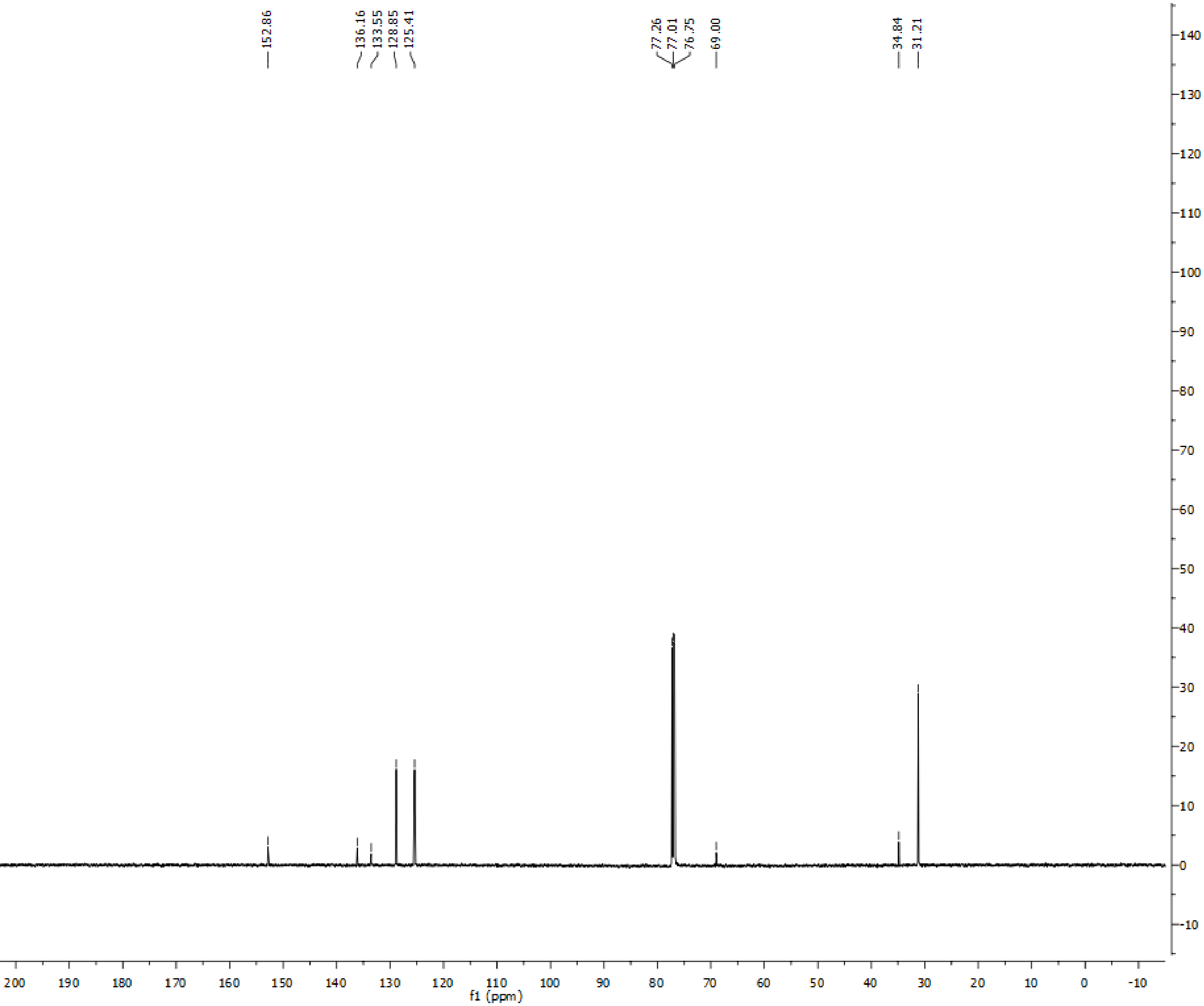


Figure S80. ^{1}H-NMR of **32**

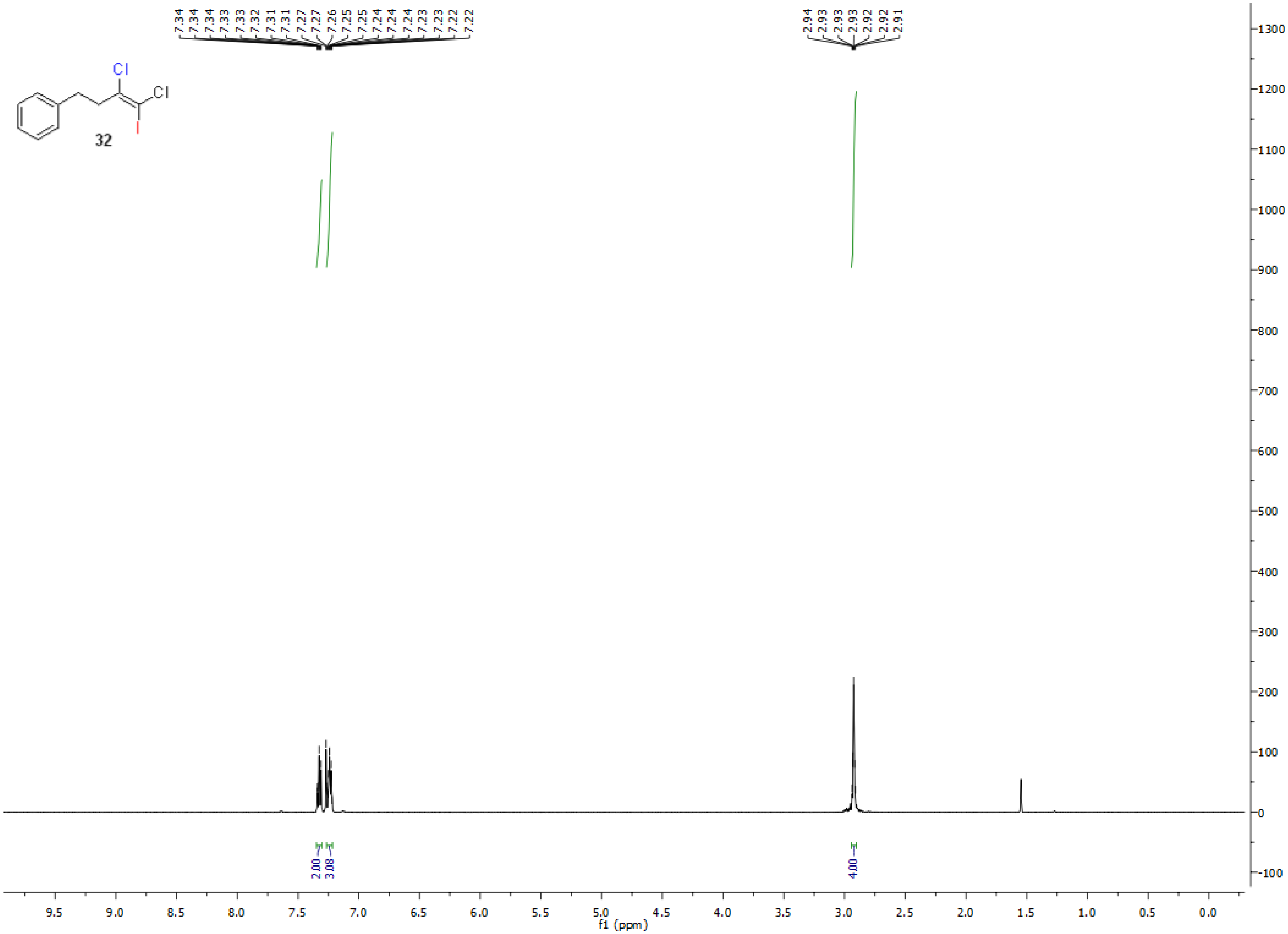


Figure S81. ^{13}C-NMR of **32**

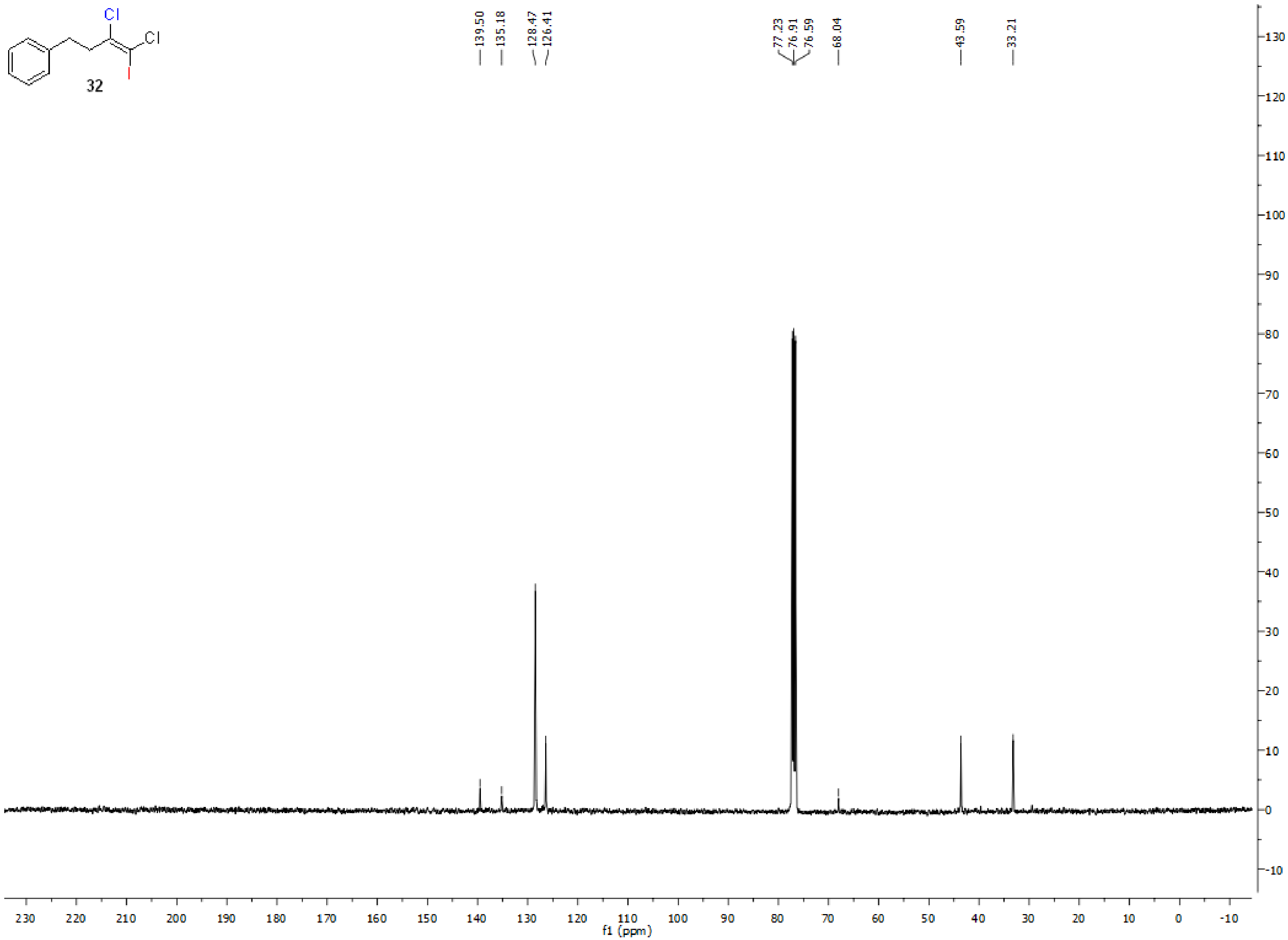
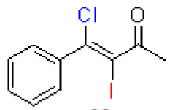


Figure S82. ^{1}H-NMR of **33**



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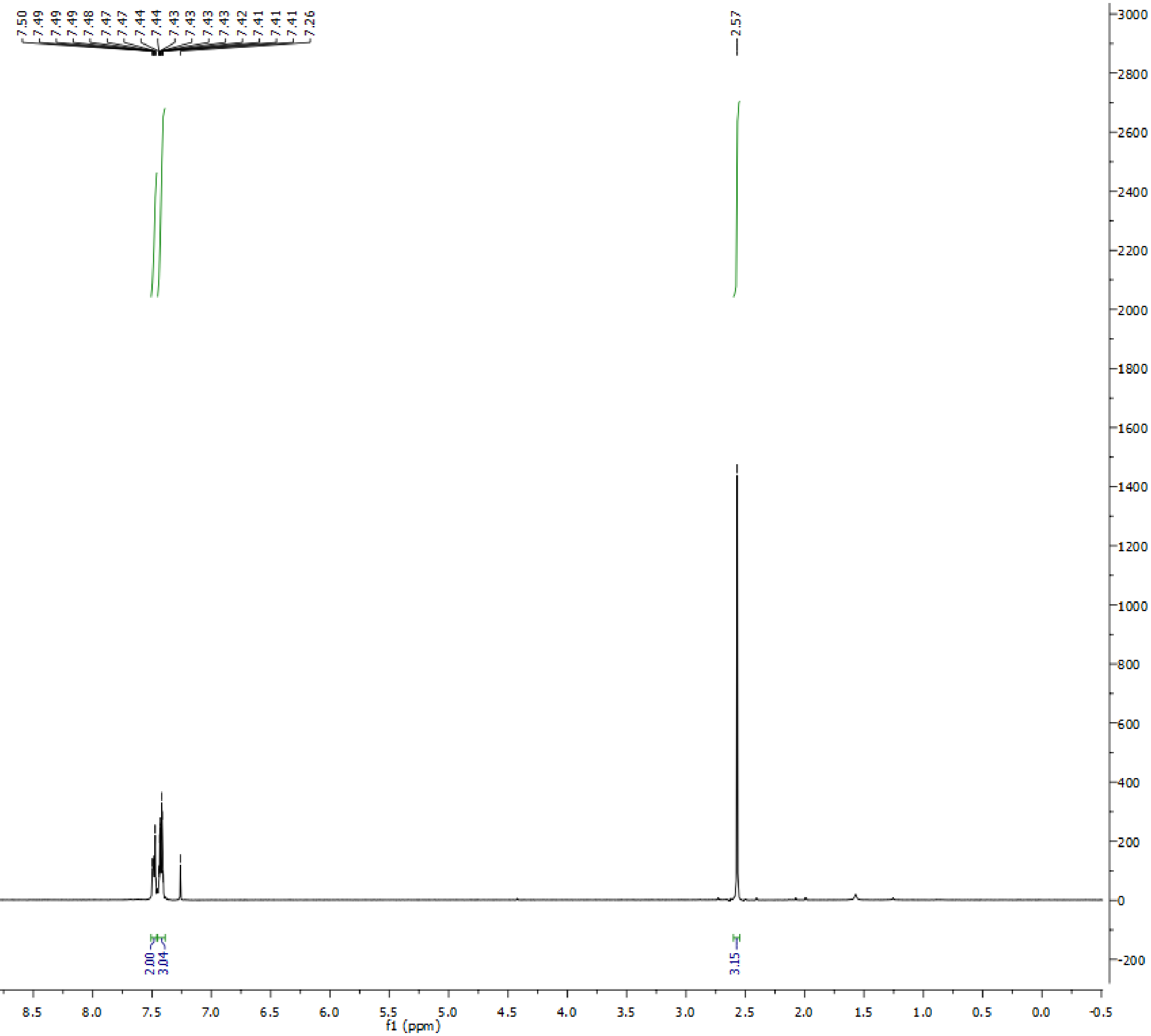
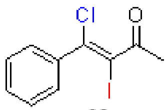


Figure S83. ^{13}C-NMR of **33**



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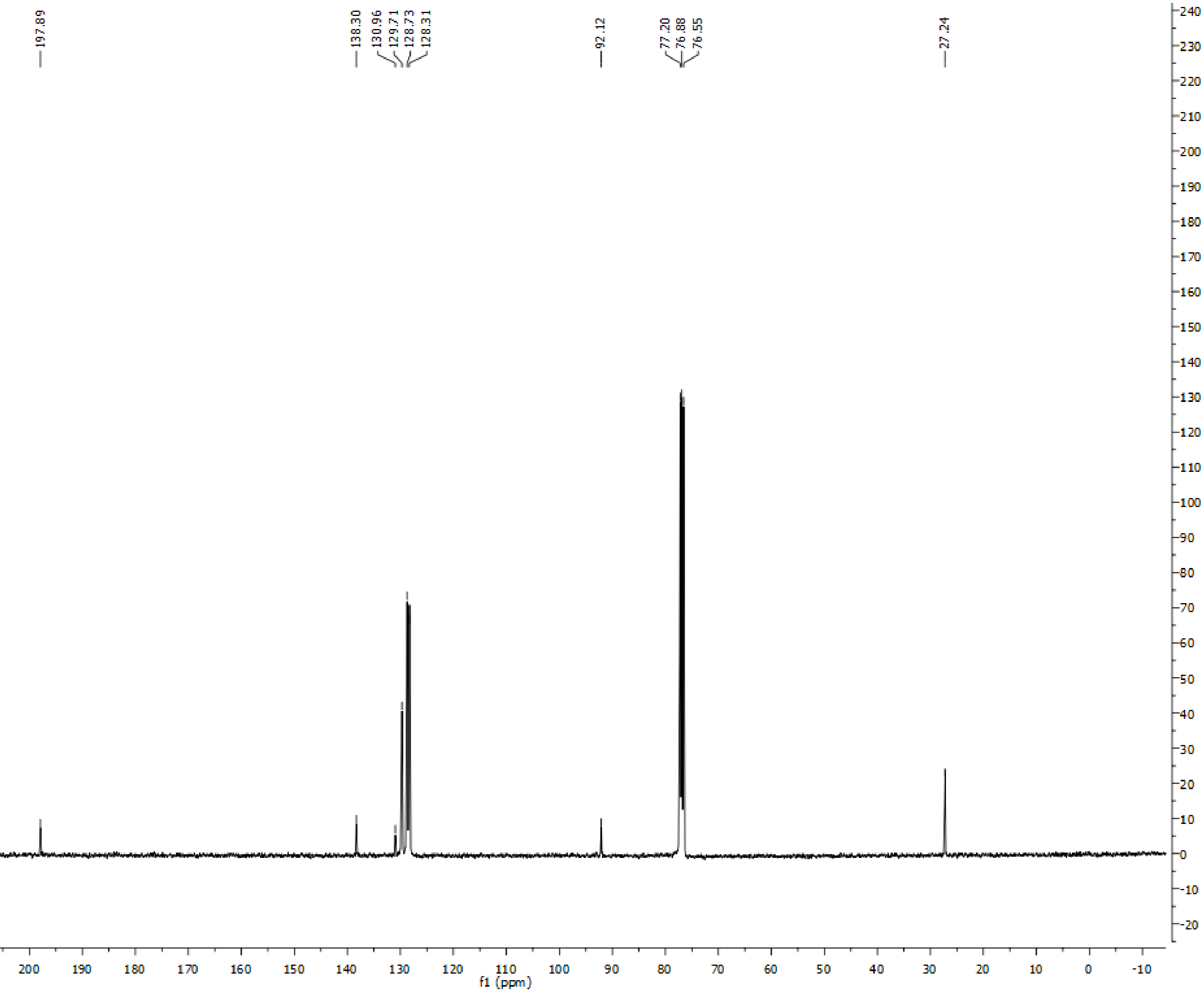
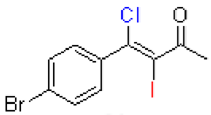


Figure S84. ^{1}H-NMR of **34**



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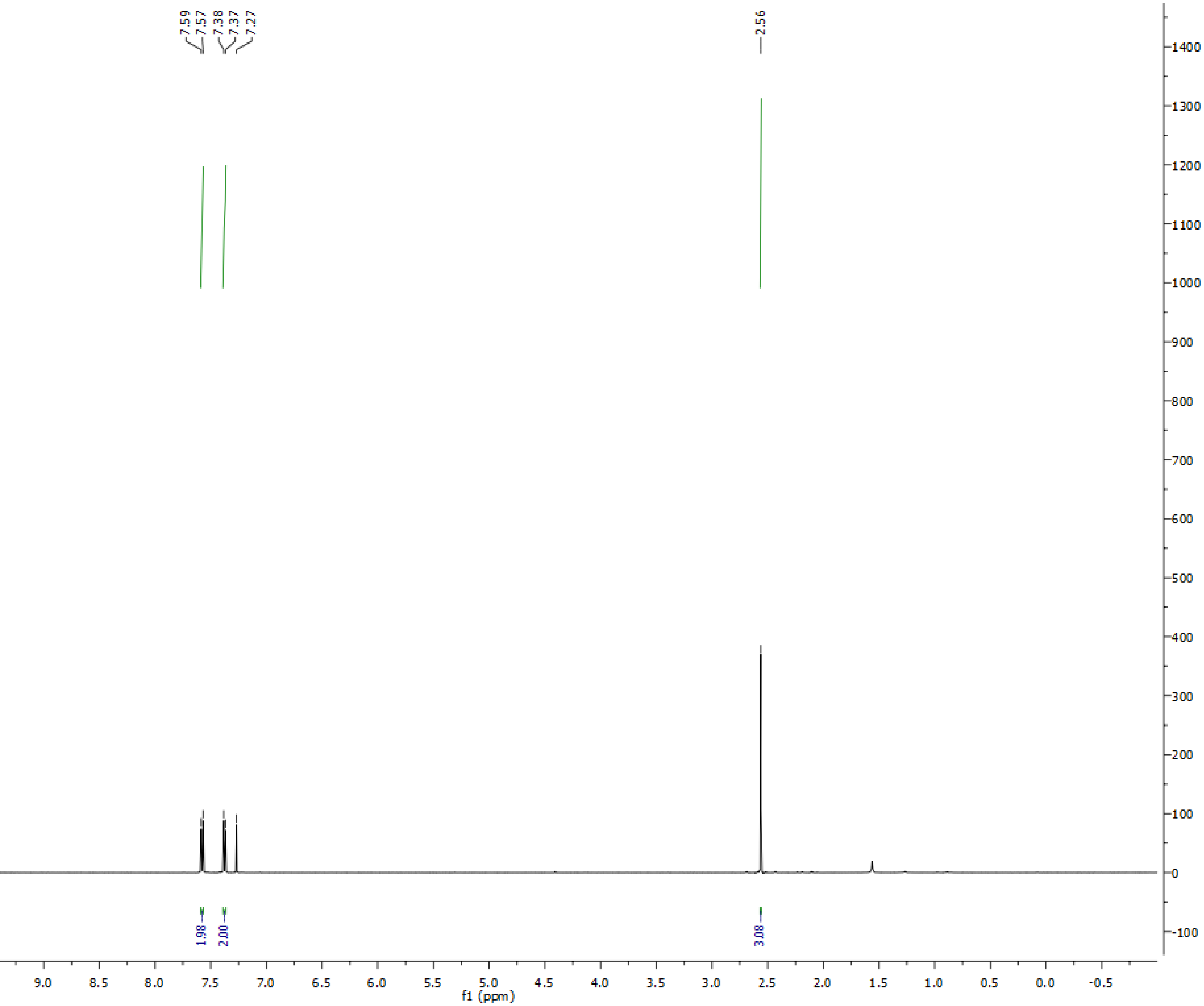
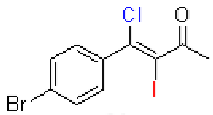


Figure S85. ^{13}C-NMR of **34**



34

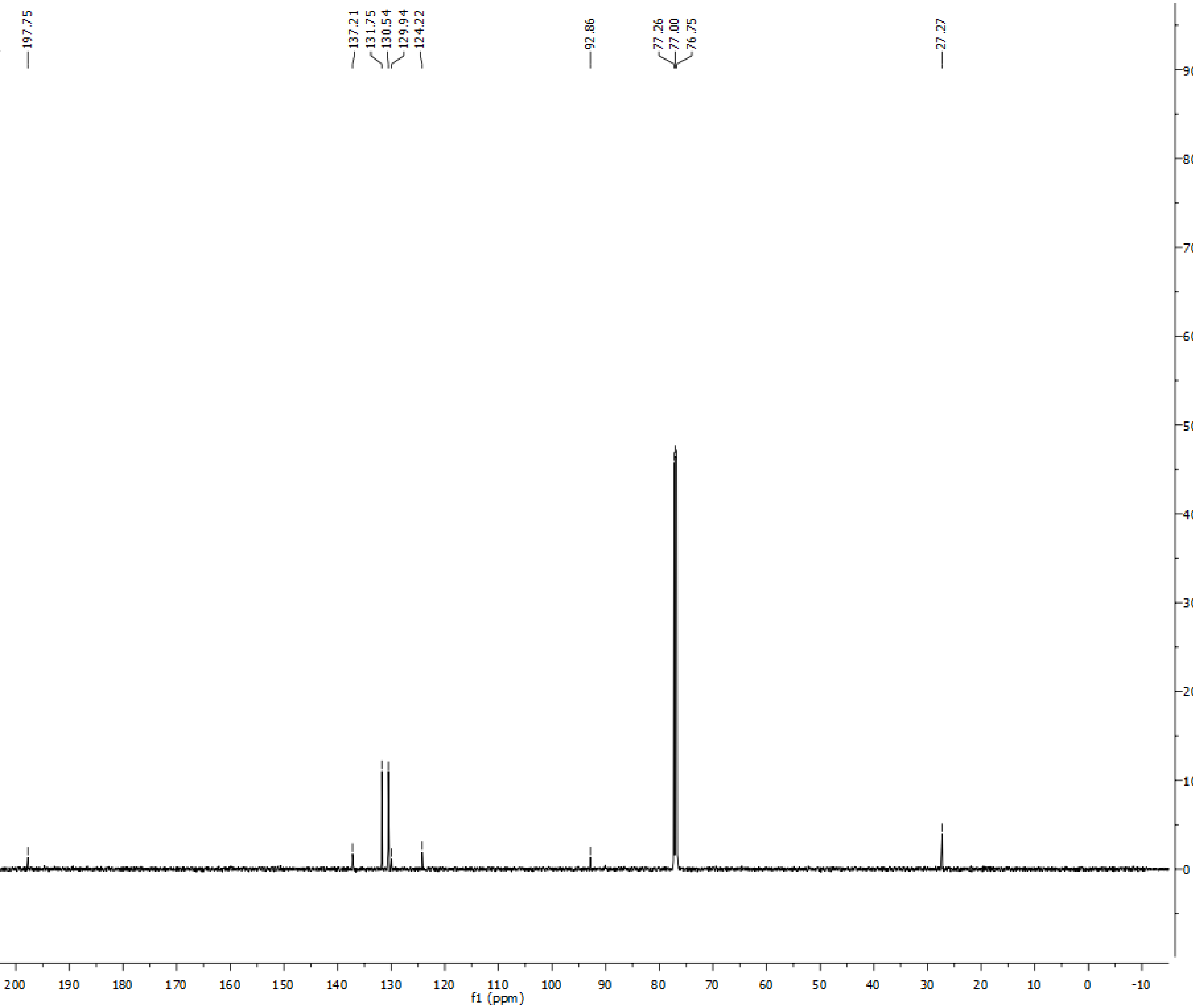


Figure S86. ^{1}H-NMR of **35**

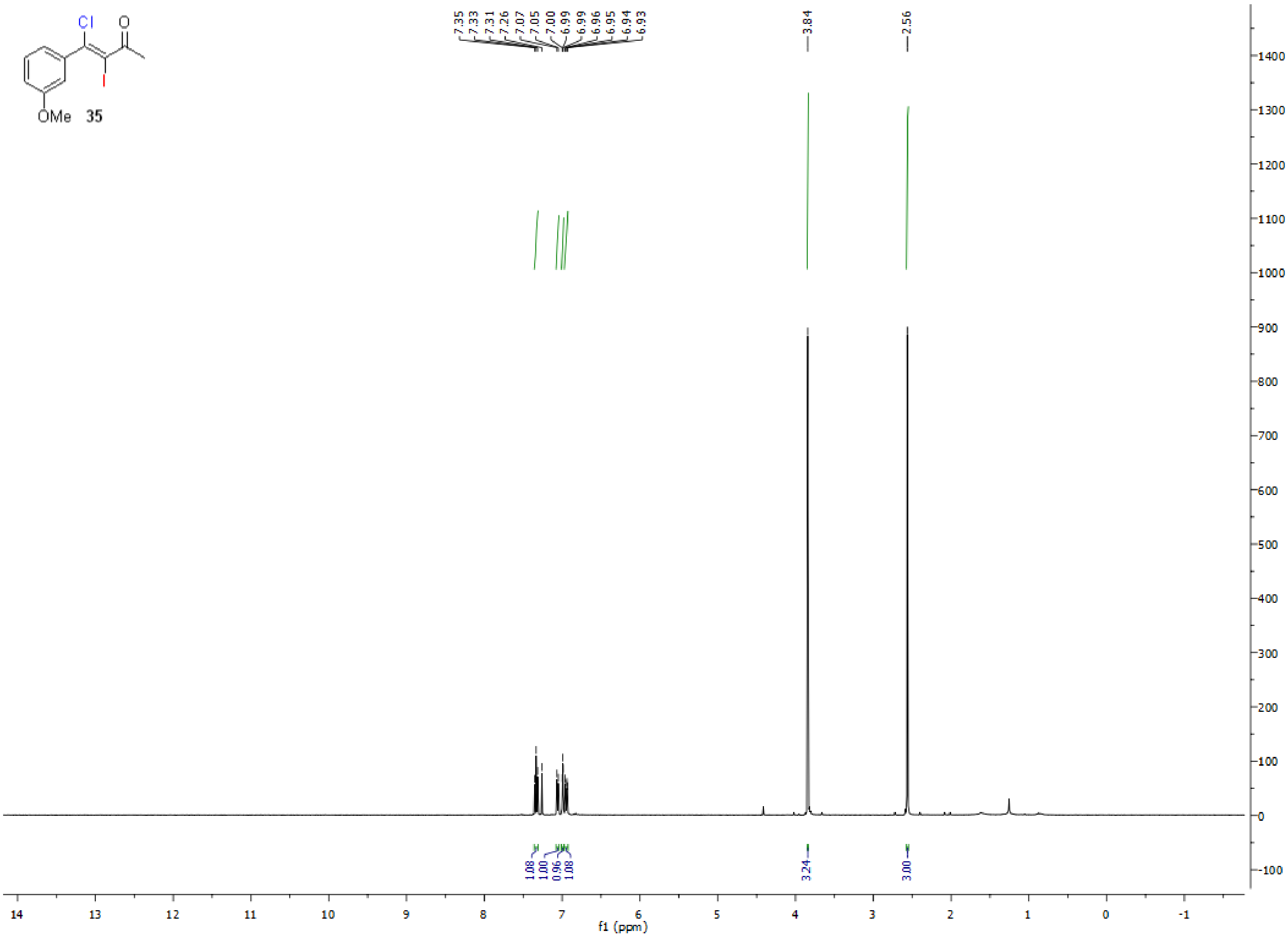
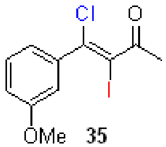


Figure S87. ^{13}C-NMR of **35**



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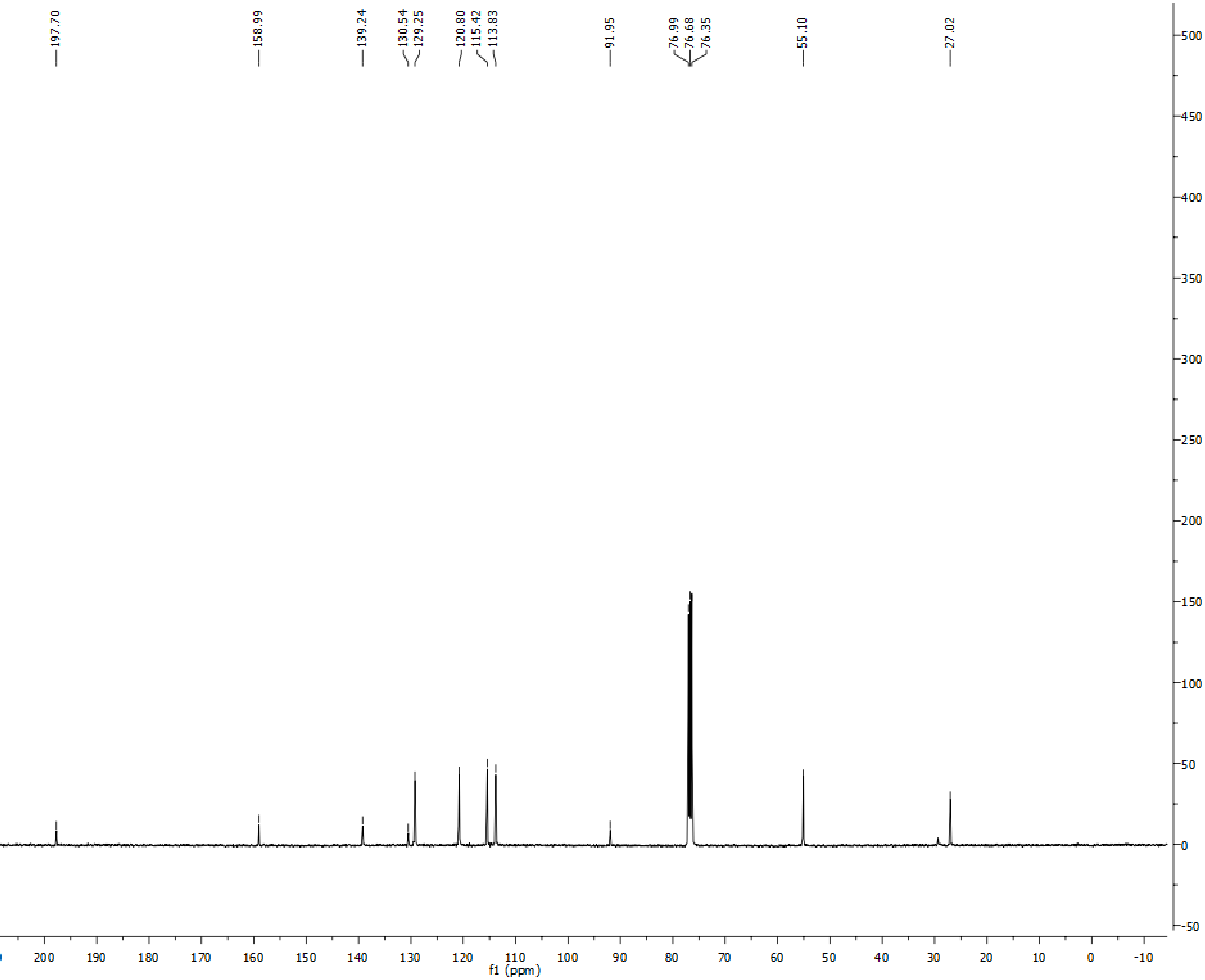
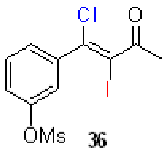


Figure S88. ^{1}H-NMR of **36**



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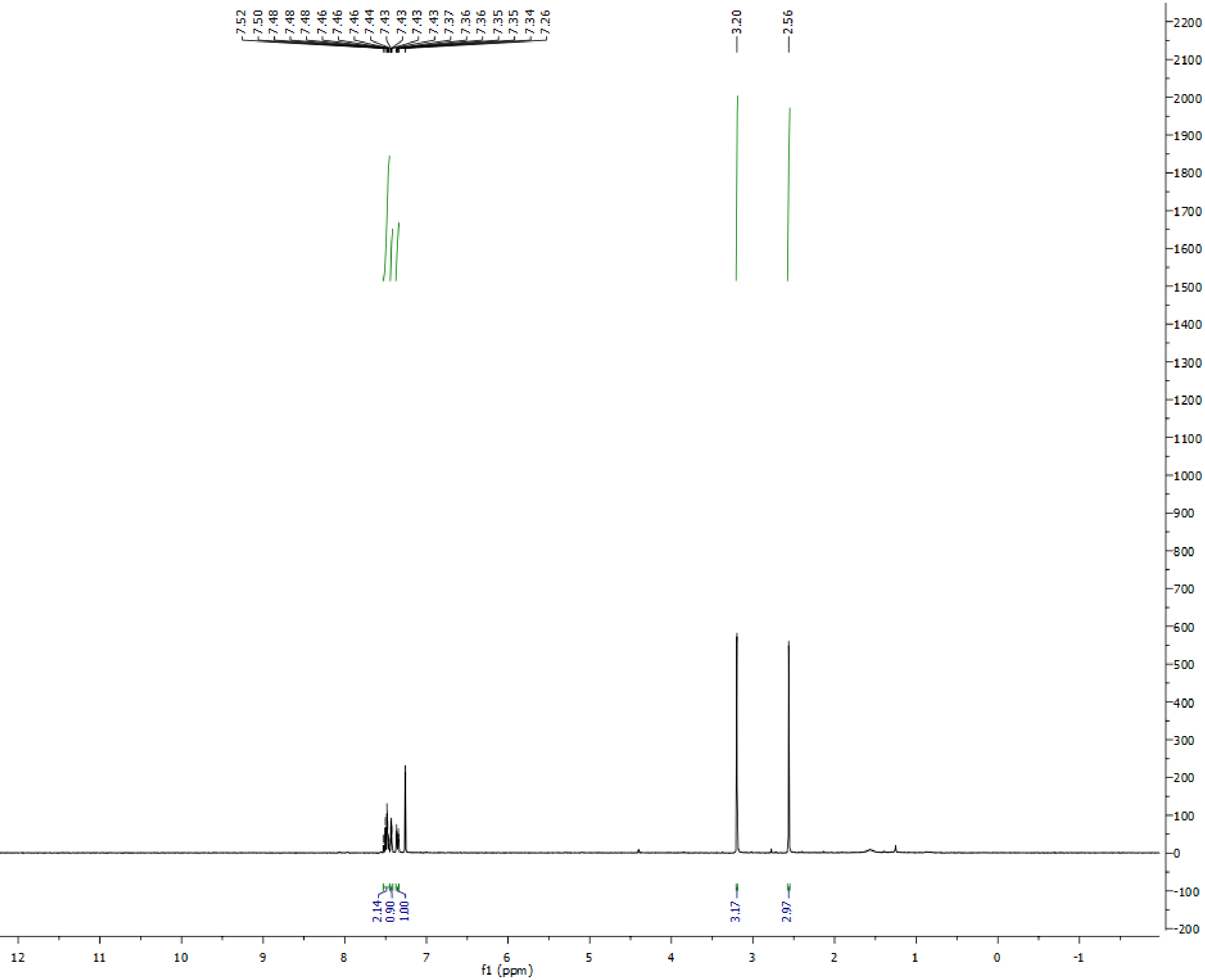


Figure S89. ^{13}C-NMR of **36**

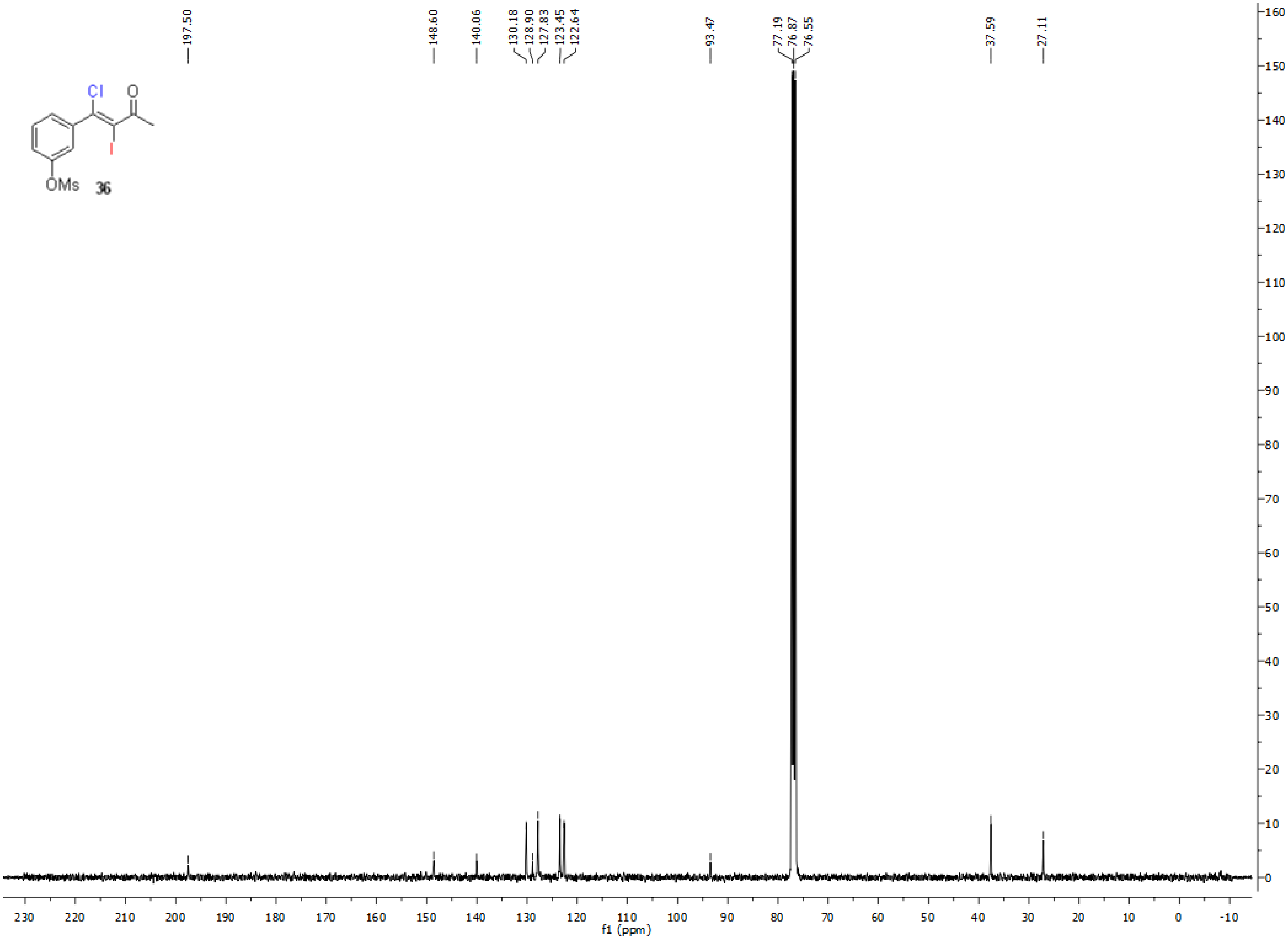


Figure S90. ^{1}H-NMR of **37**

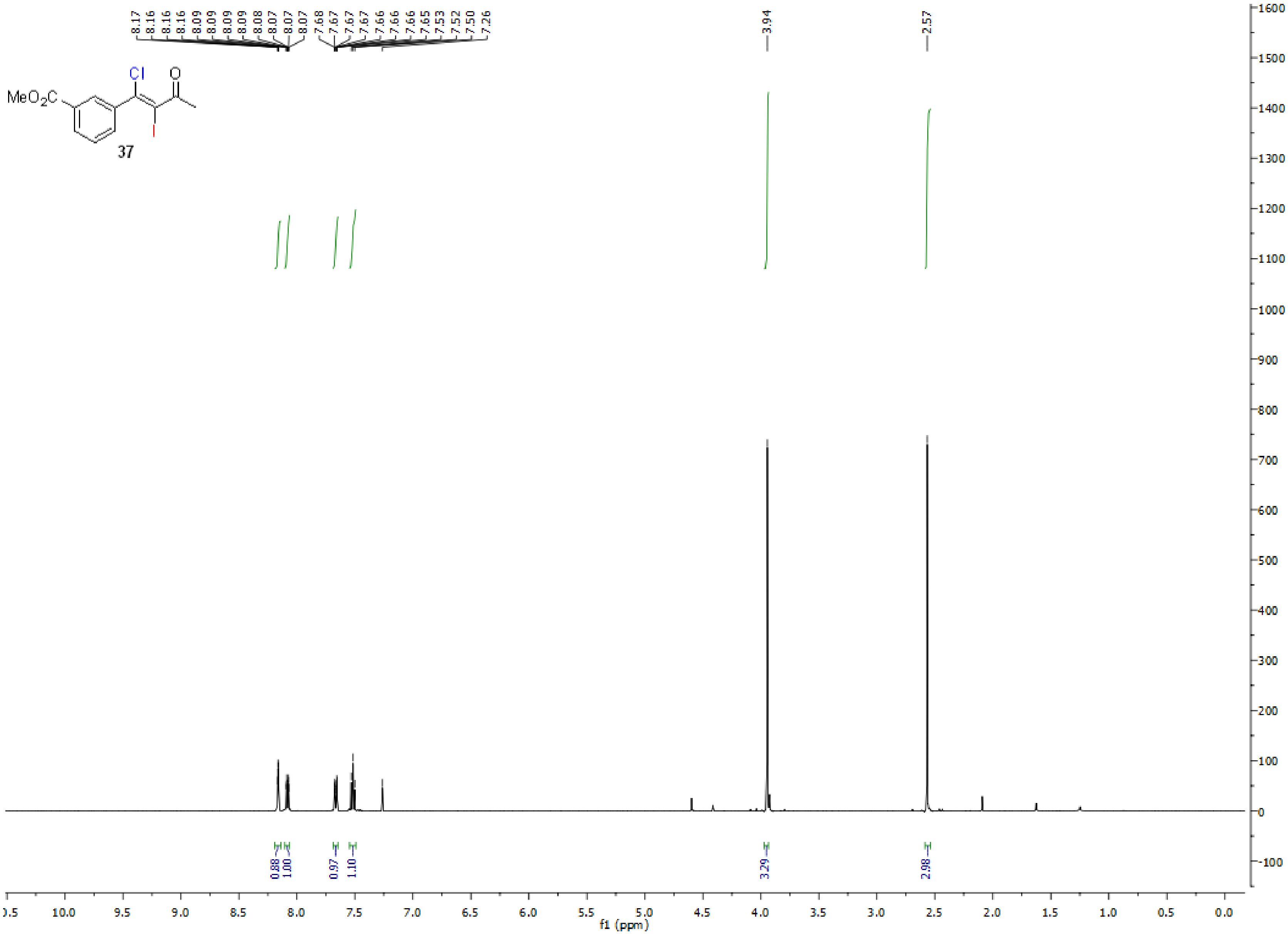


Figure S91. ^{13}C-NMR of **37**

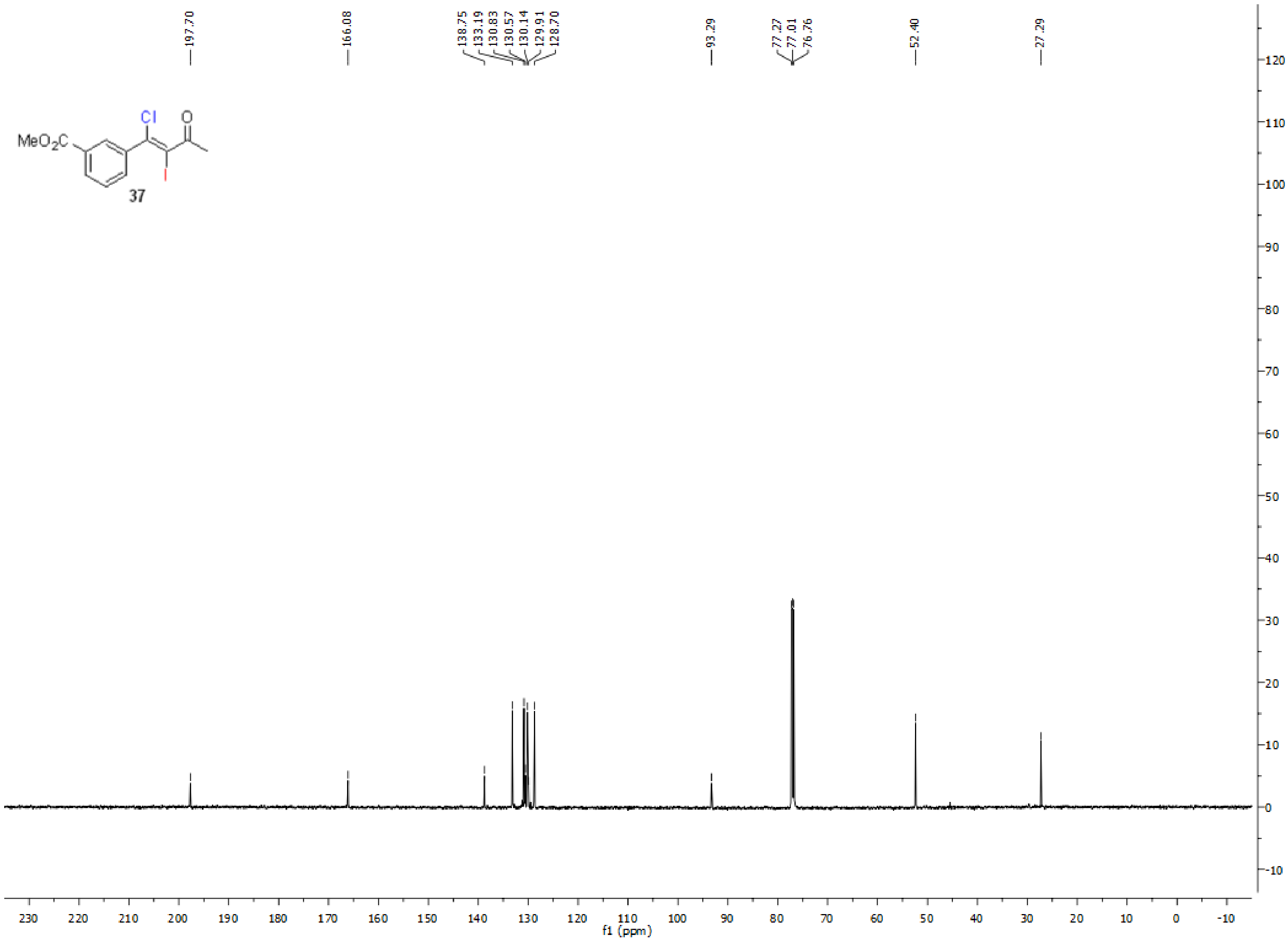


Figure S92. ^{1}H-NMR of **38**

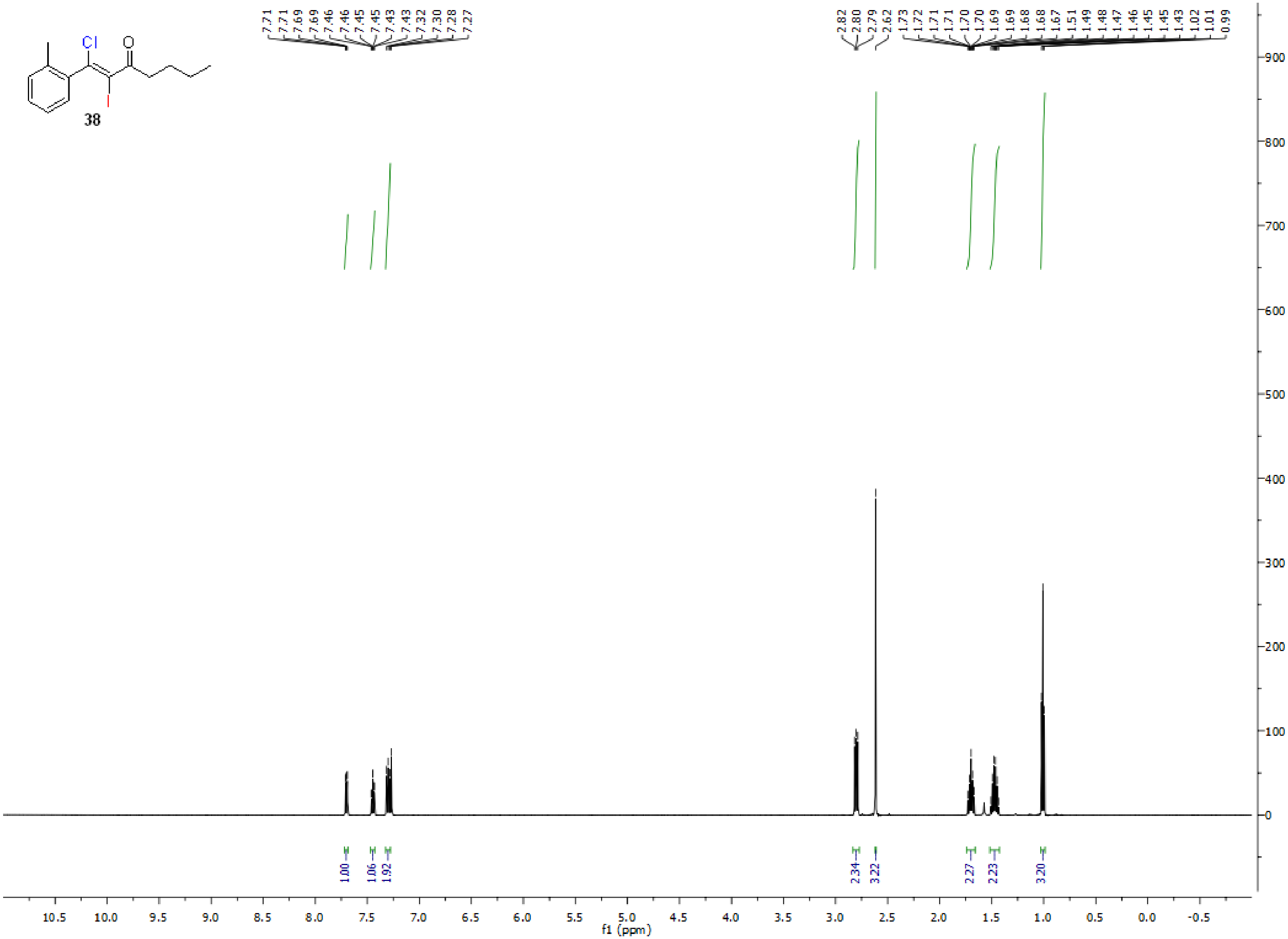
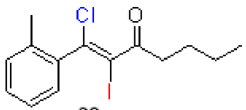


Figure S93. ^{13}C-NMR of **38**



38

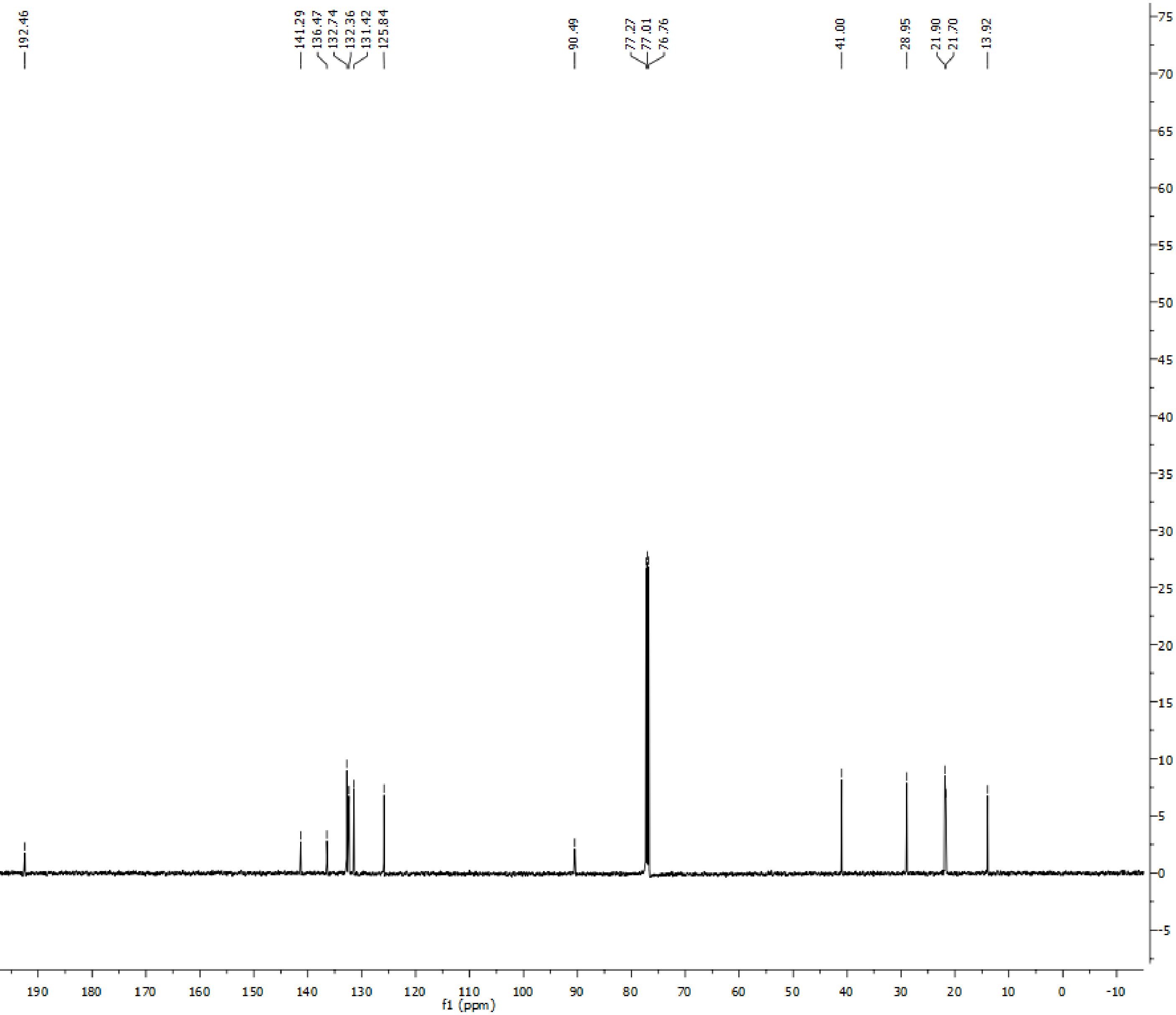


Figure S94. ^{1}H-NMR of **39**

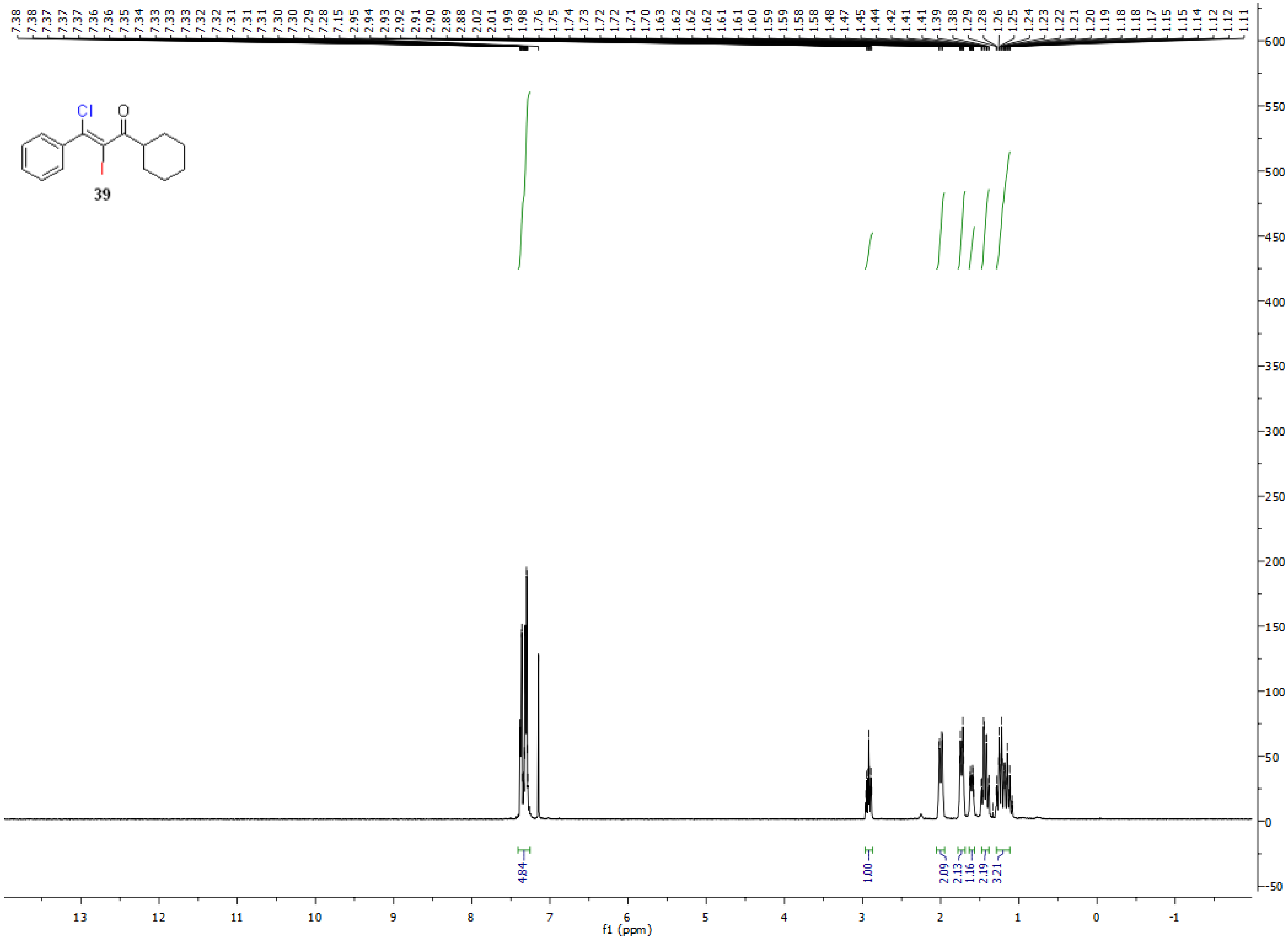


Figure S95. ^{13}C-NMR of **39**

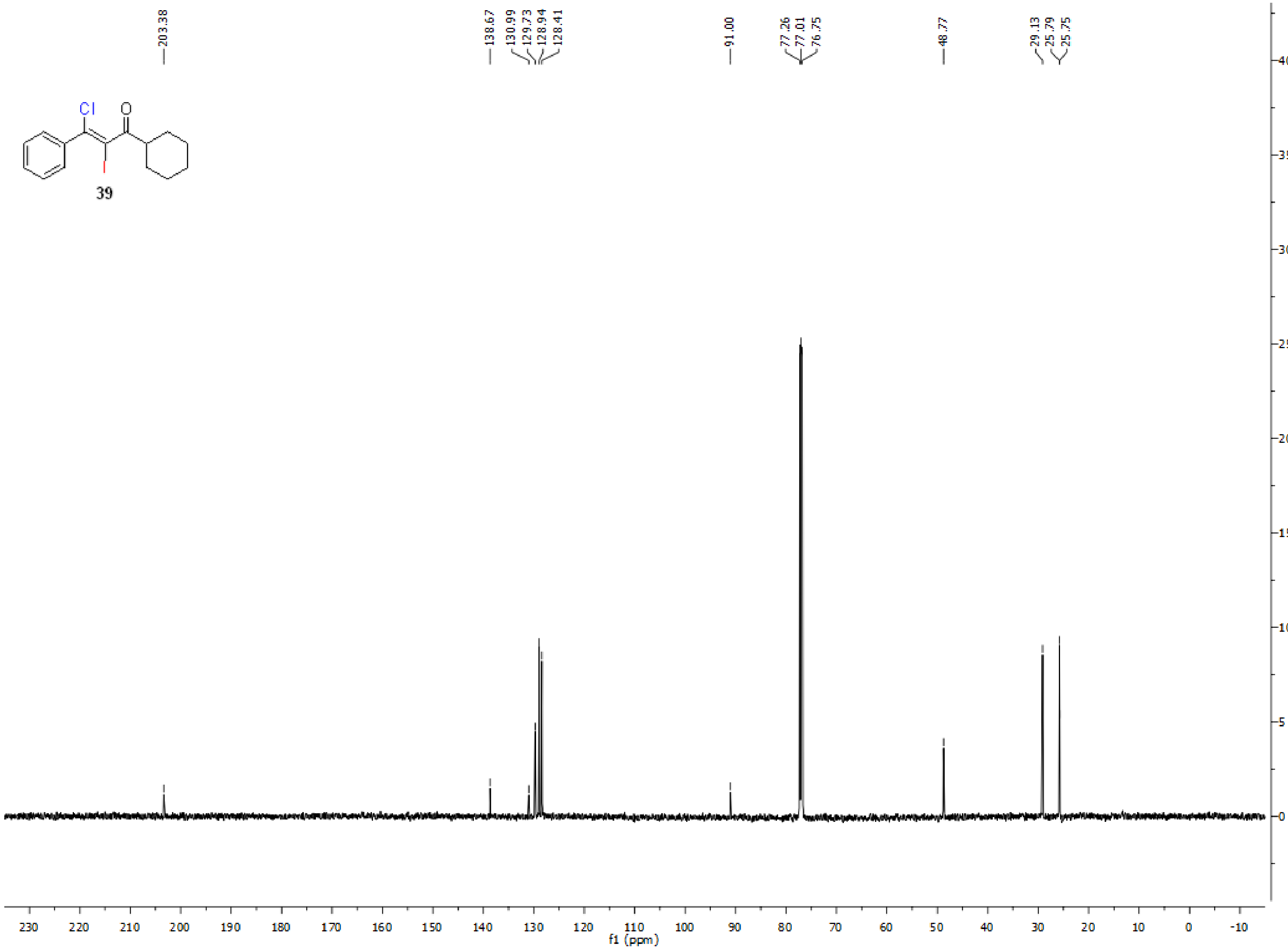
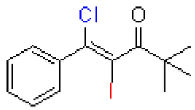


Figure S96. ^{1}H-NMR of **40**



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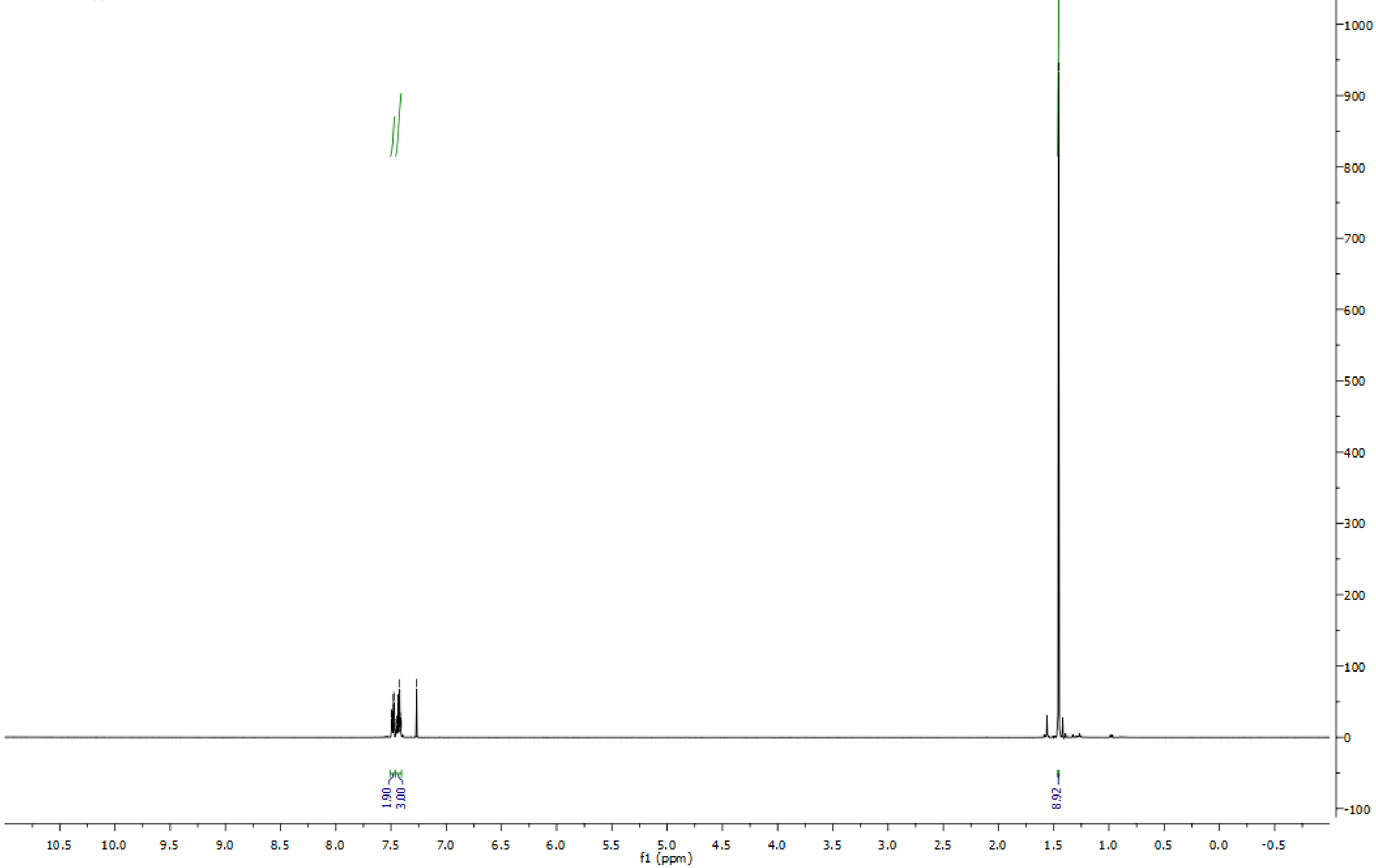
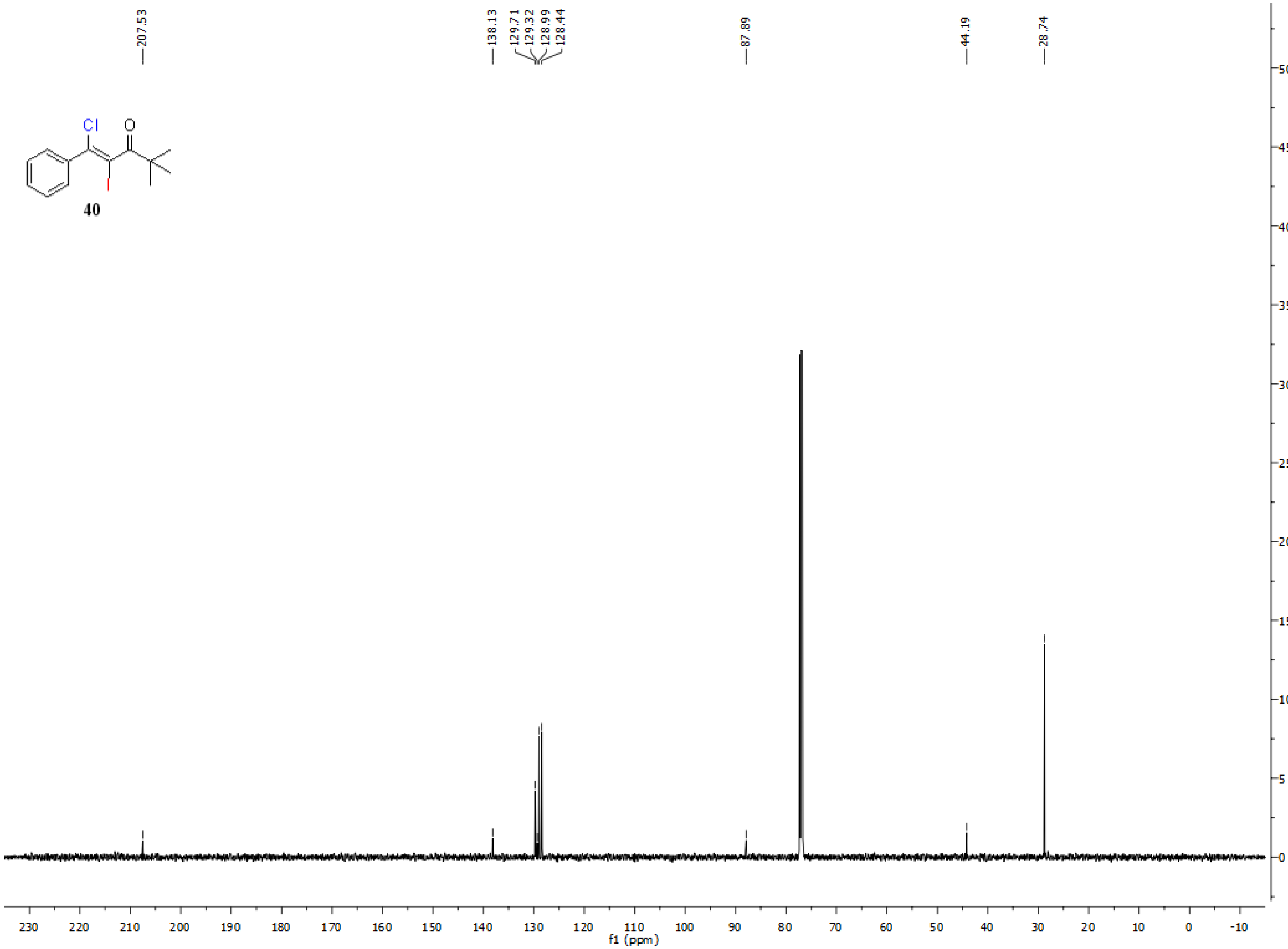
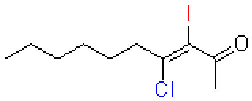


Figure S97. ^{13}C-NMR of **40**



40

Figure S98. ^{1}H-NMR of **41**



41

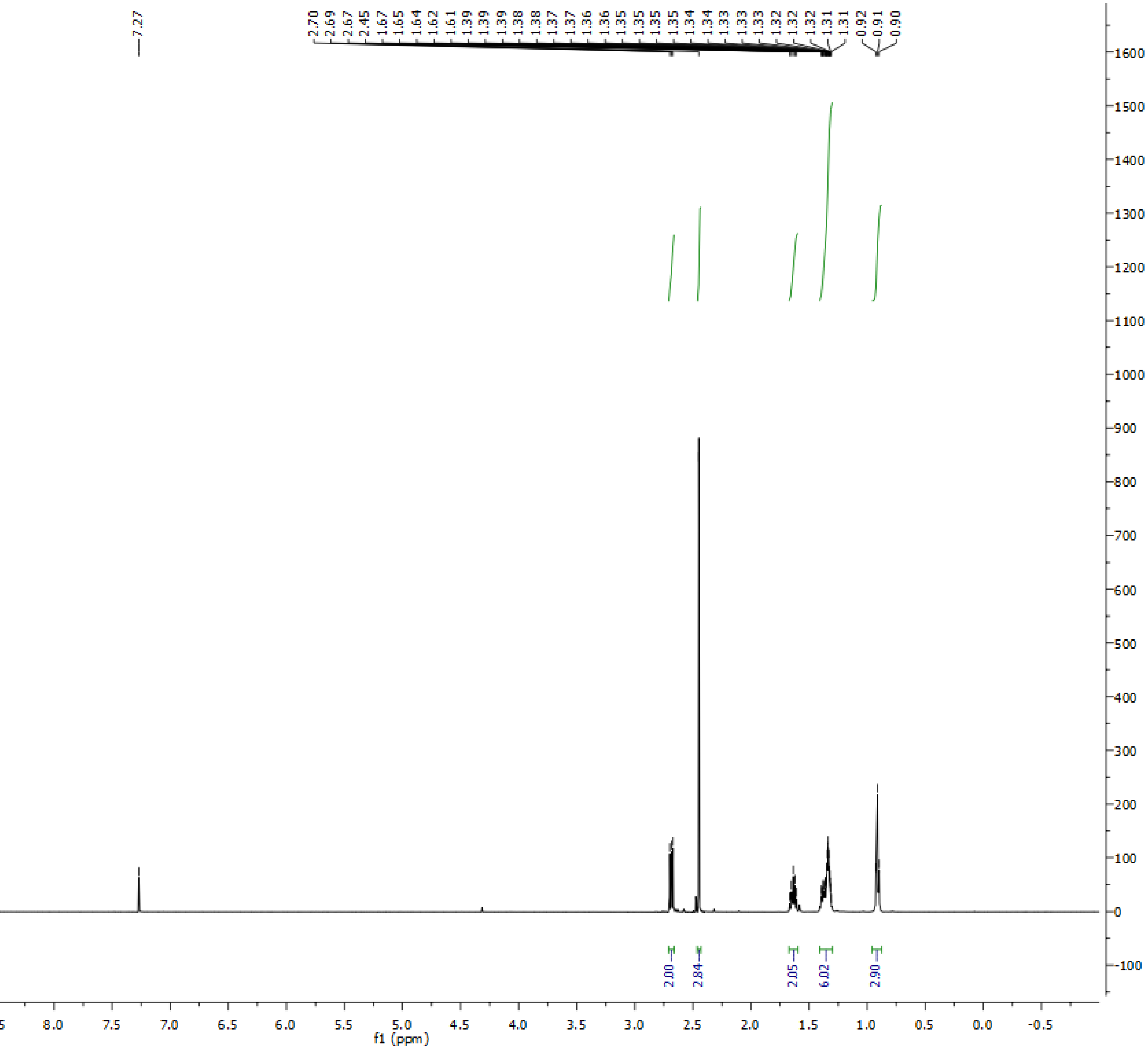


Figure S99. ^{13}C-NMR of **41**

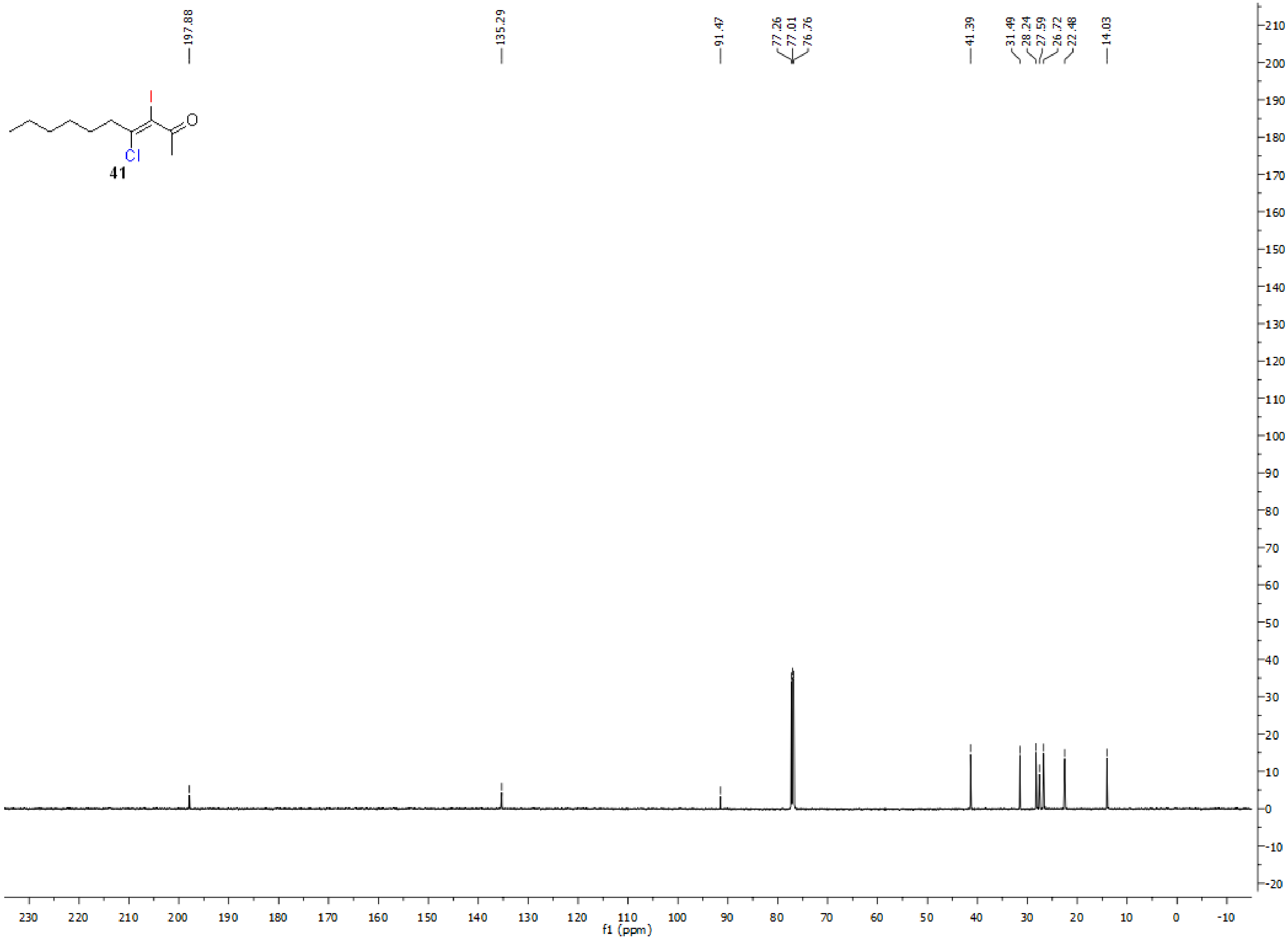


Figure S100. ^{1}H-NMR of **42**

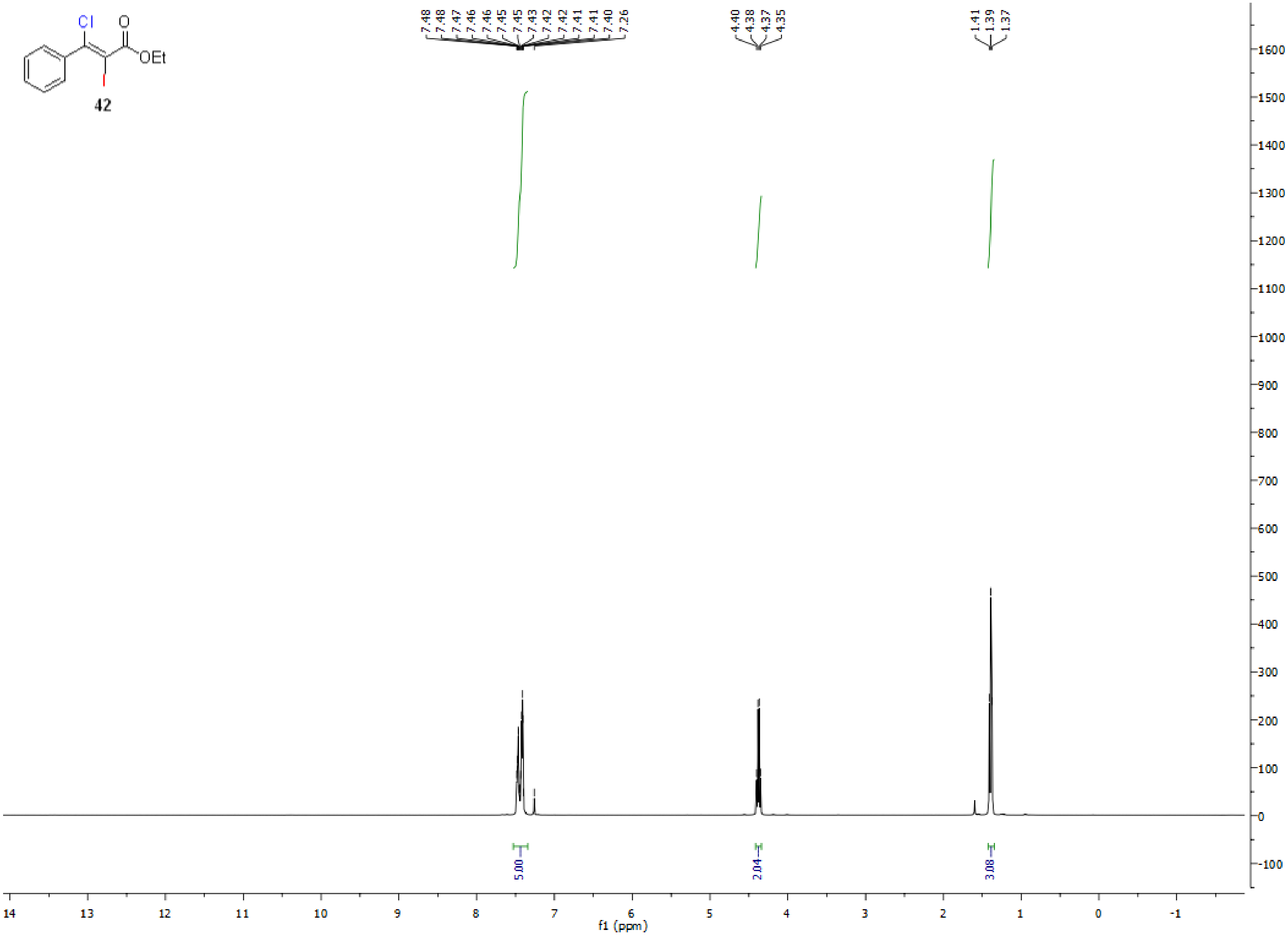


Figure S101. ^{13}C-NMR of **42**

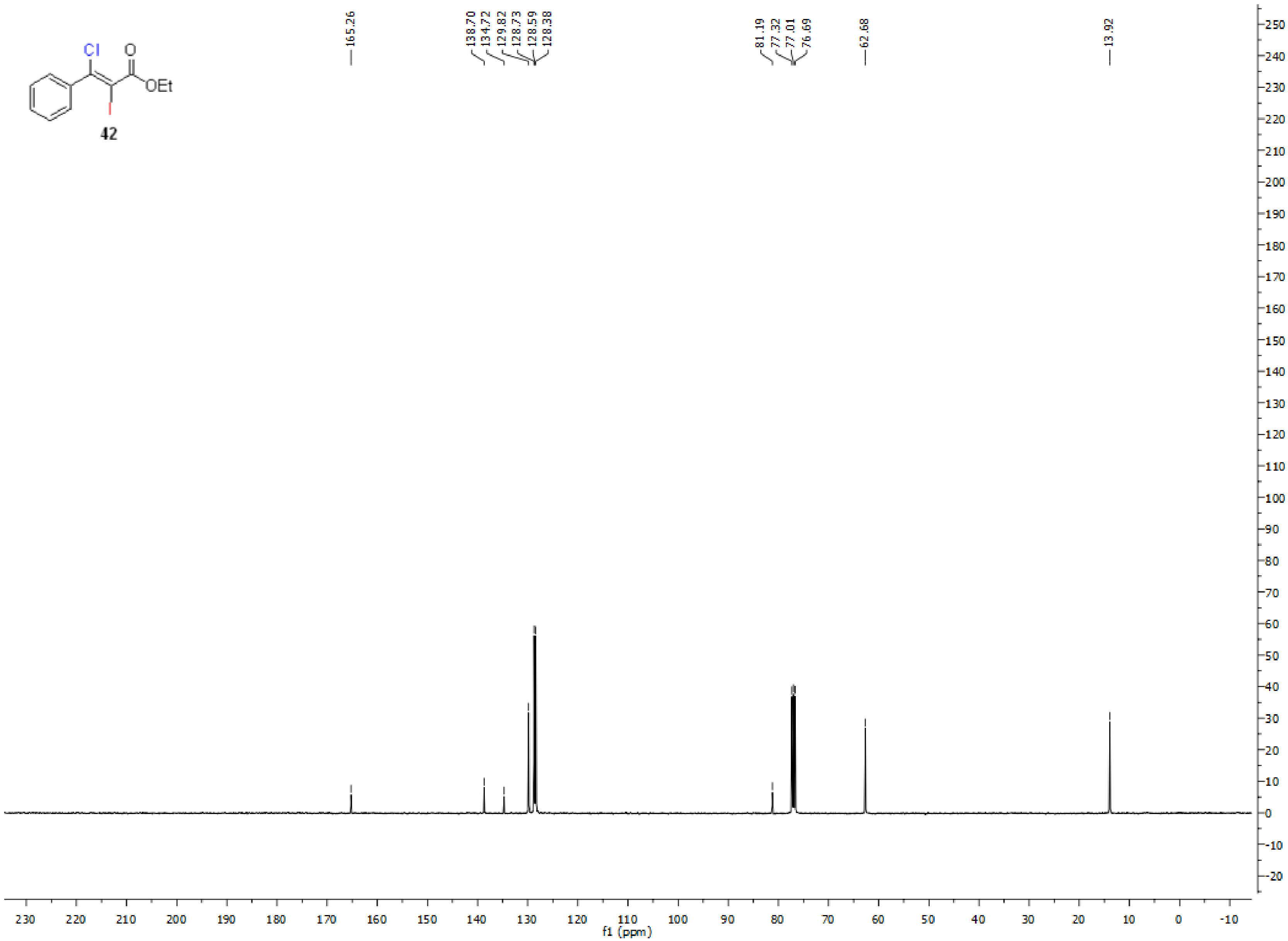
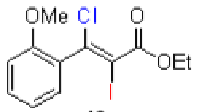


Figure S102. ^{1}H-NMR of **43**



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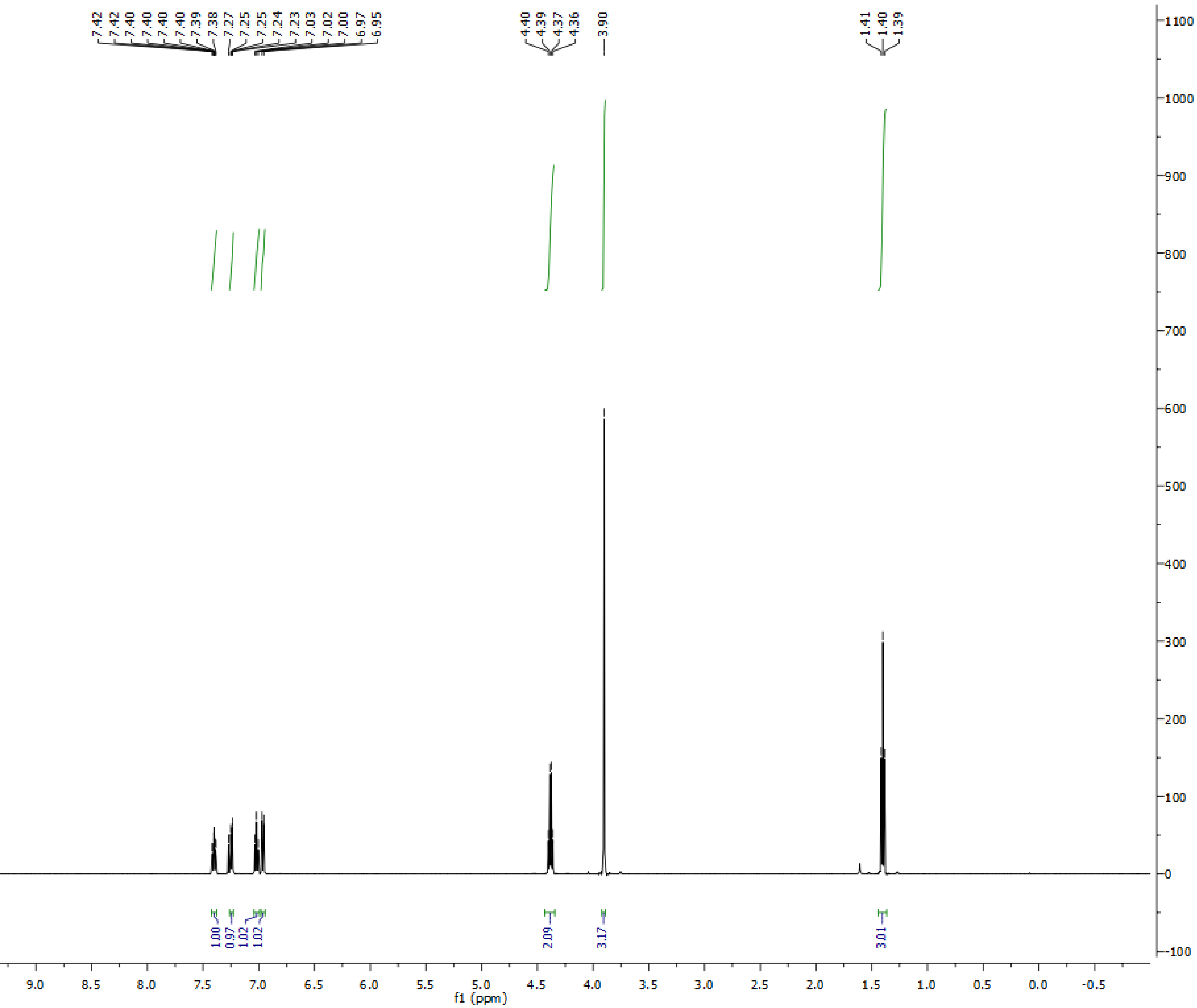
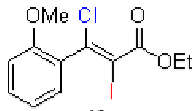


Figure S103. ^{13}C-NMR of **43**



43

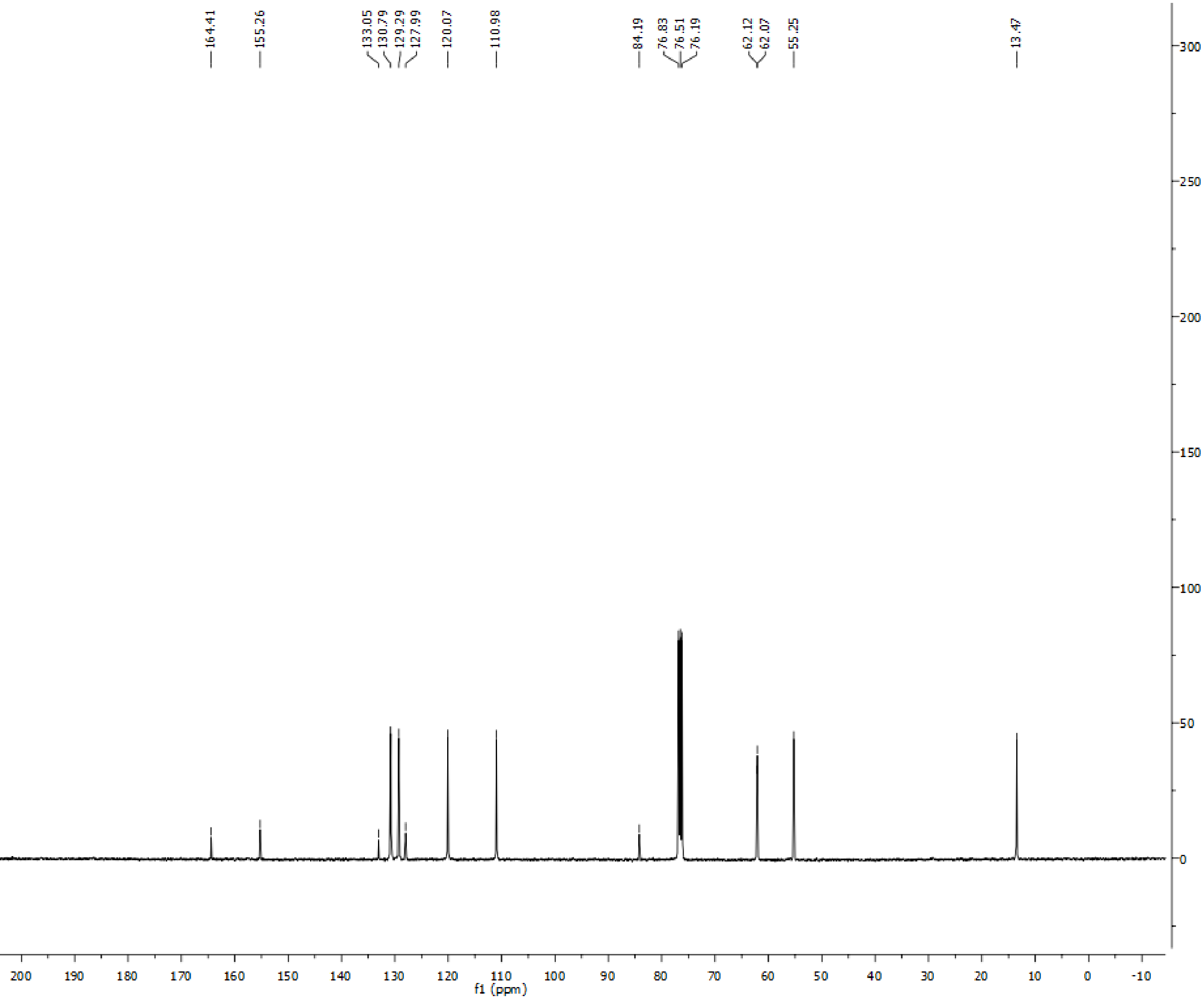


Figure S104. ^{1}H-NMR of **44**

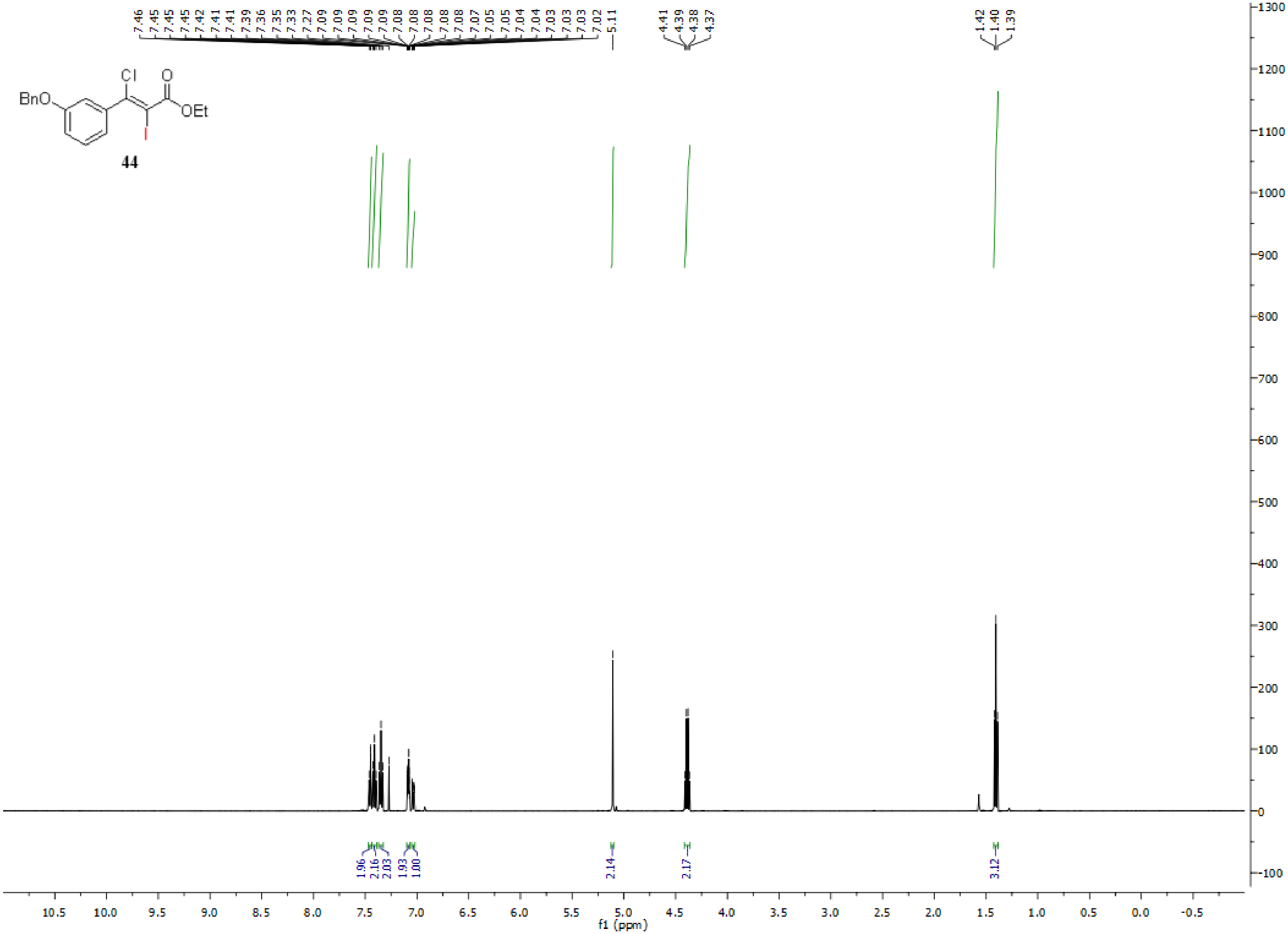


Figure S105. ^{13}C-NMR of **44**

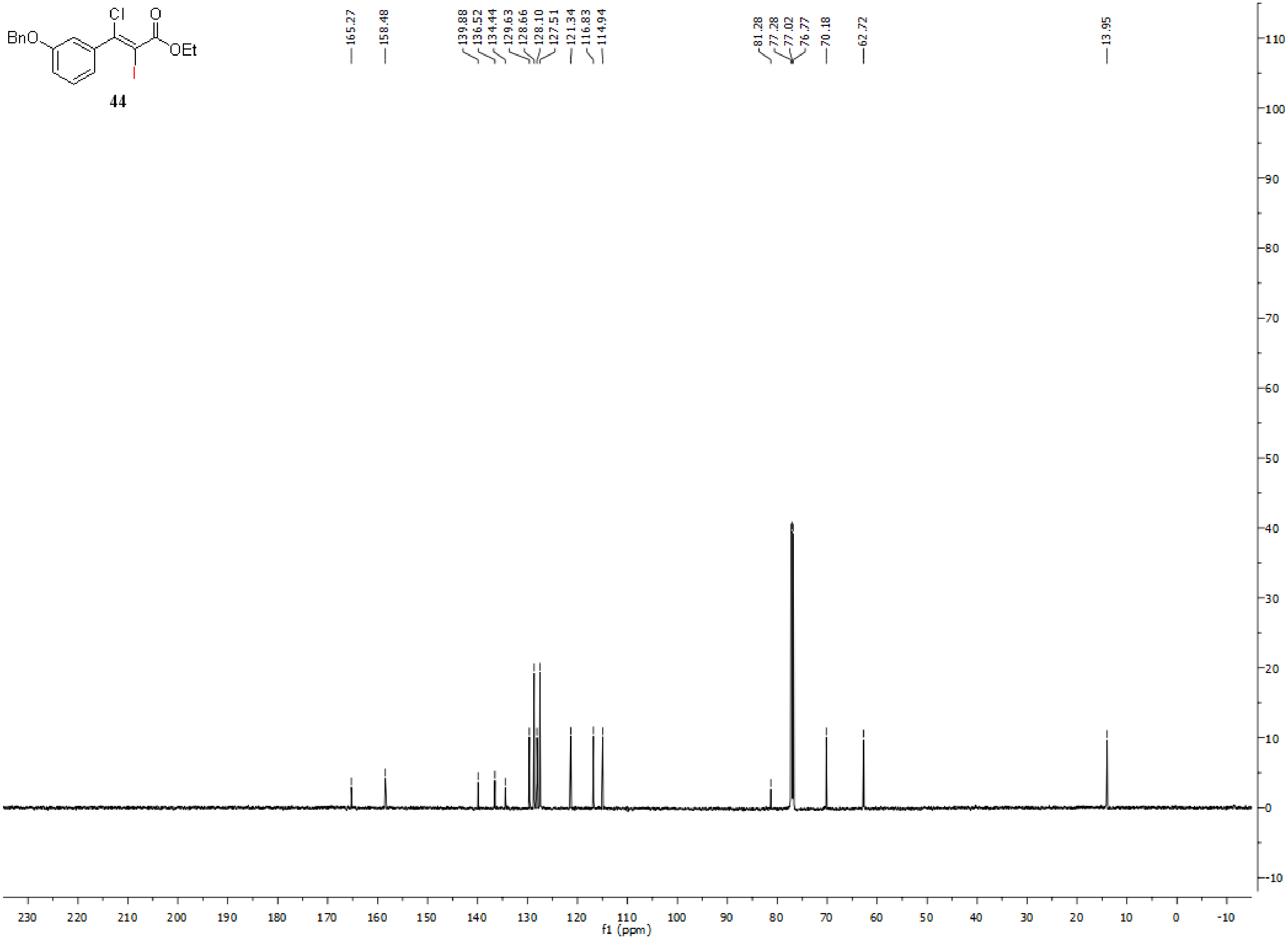


Figure S106. ^{1}H-NMR of **45**

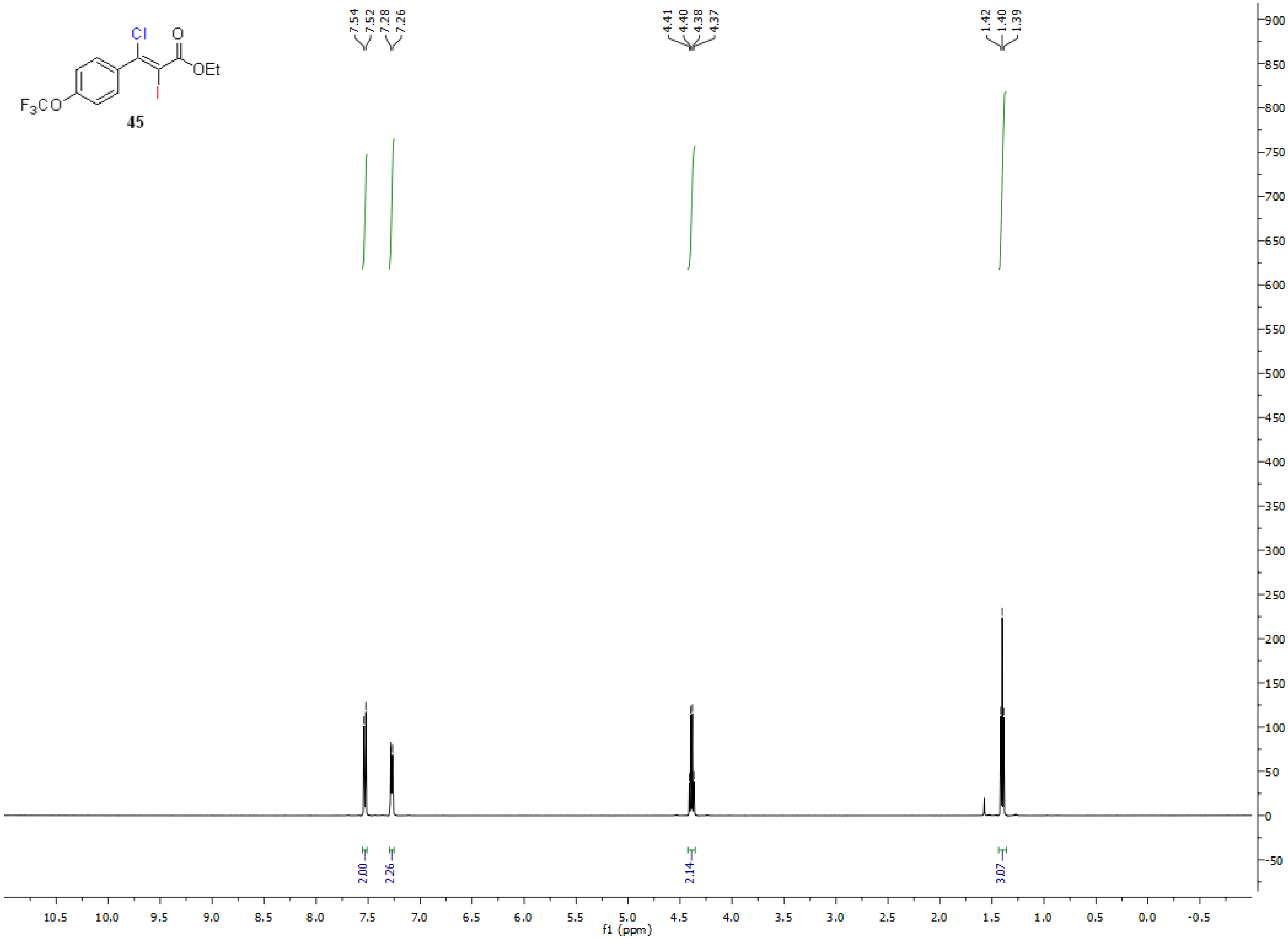
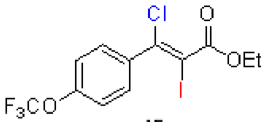


Figure S107. ^{19}F-NMR of **45**



45

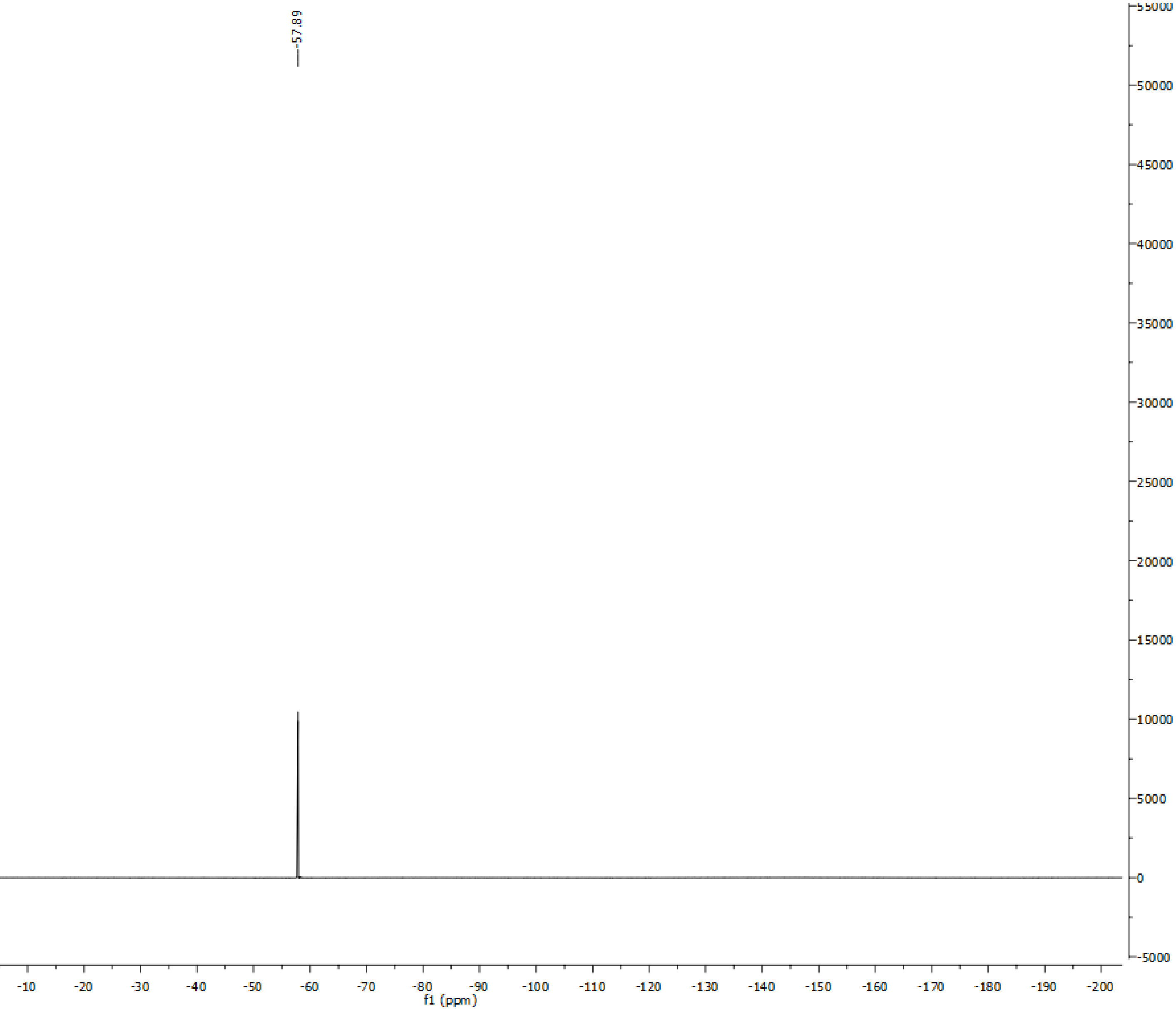


Figure S108. ^{13}C-NMR of **45**

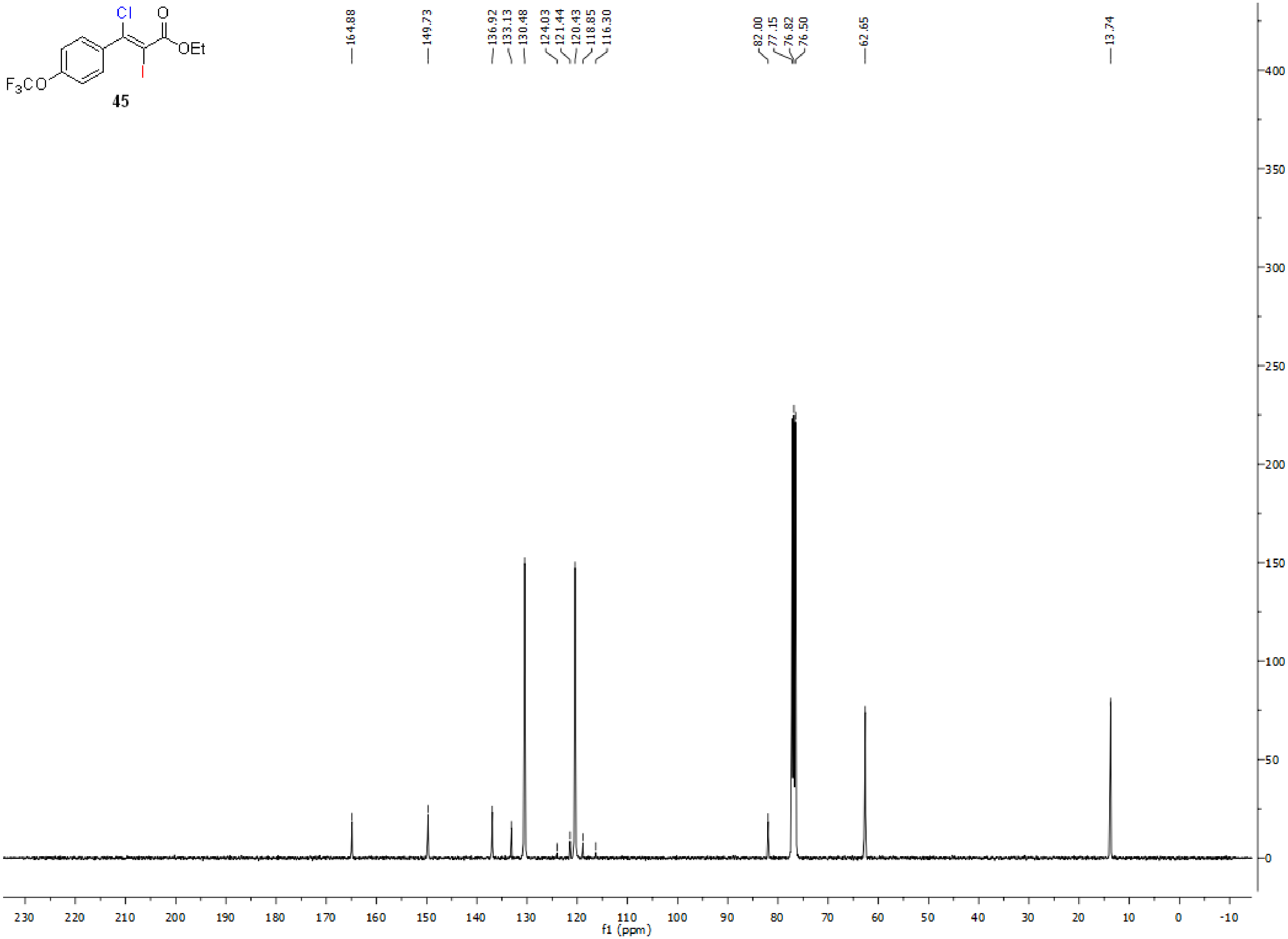
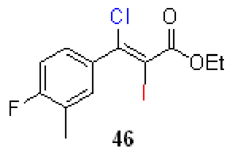


Figure S109. ^{1}H-NMR of **46**



46

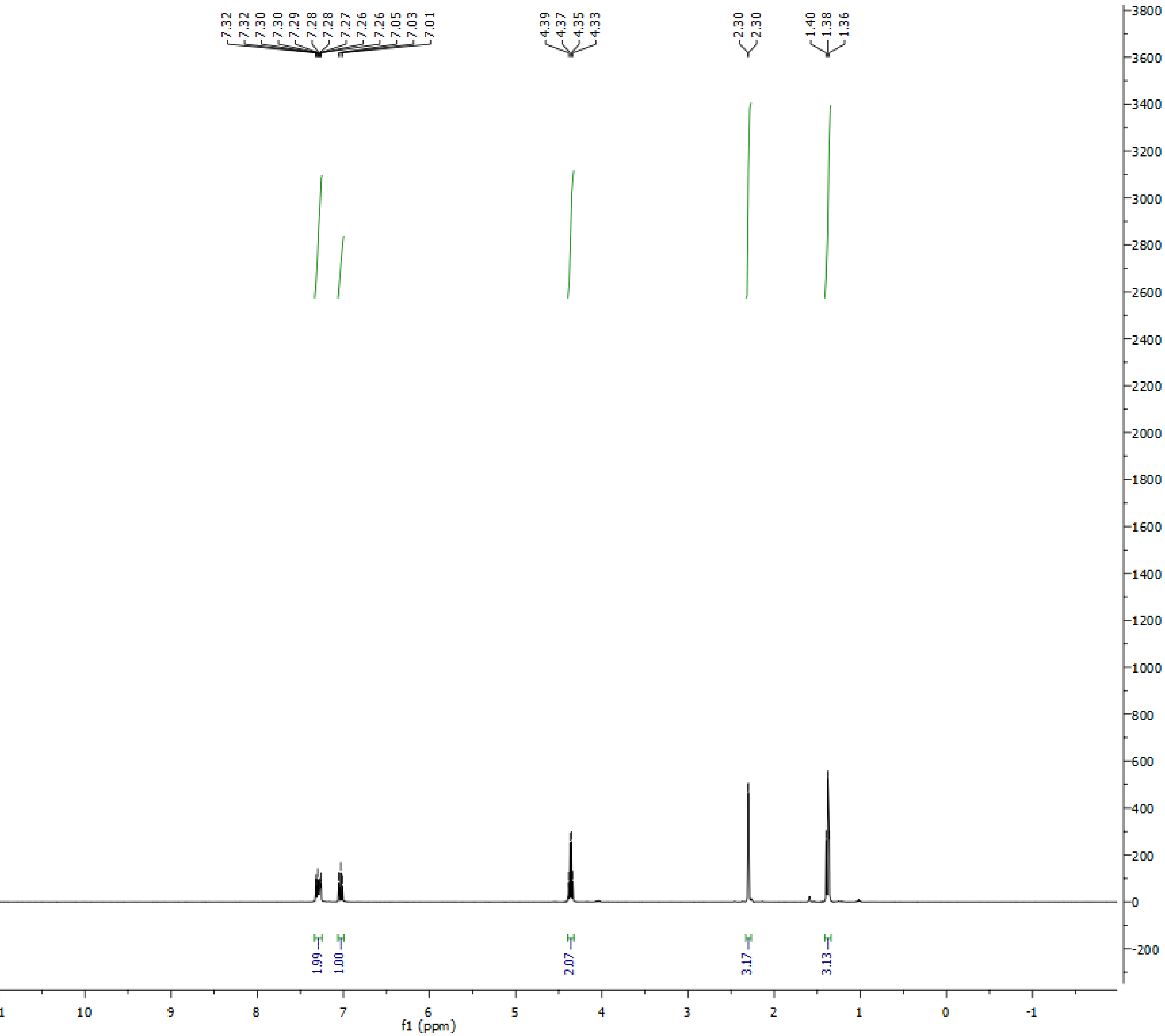


Figure S110. ^{19}F-NMR of **46**

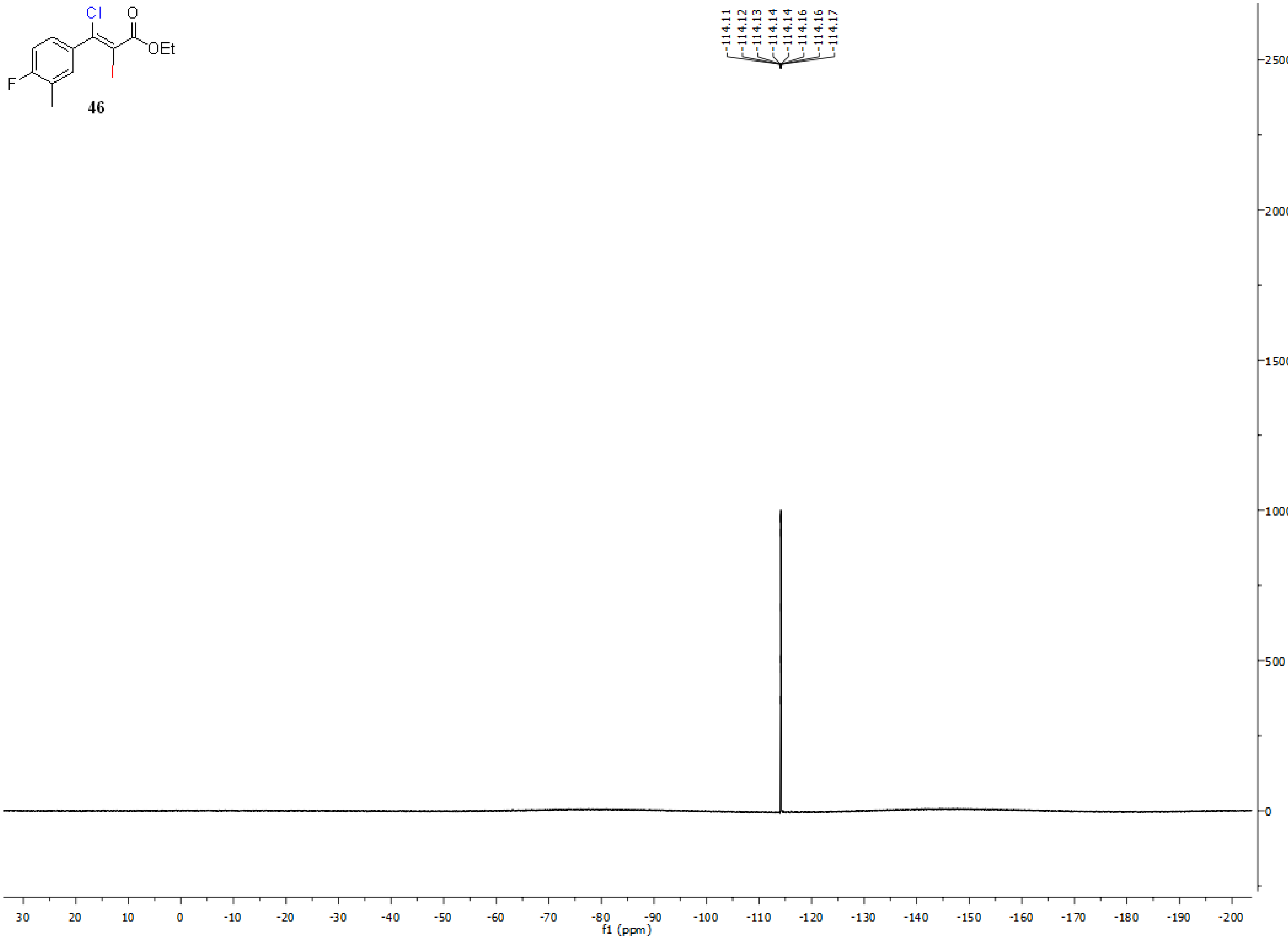
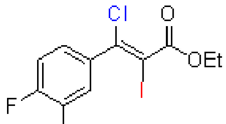


Figure S111. ^{13}C-NMR of **46**



46

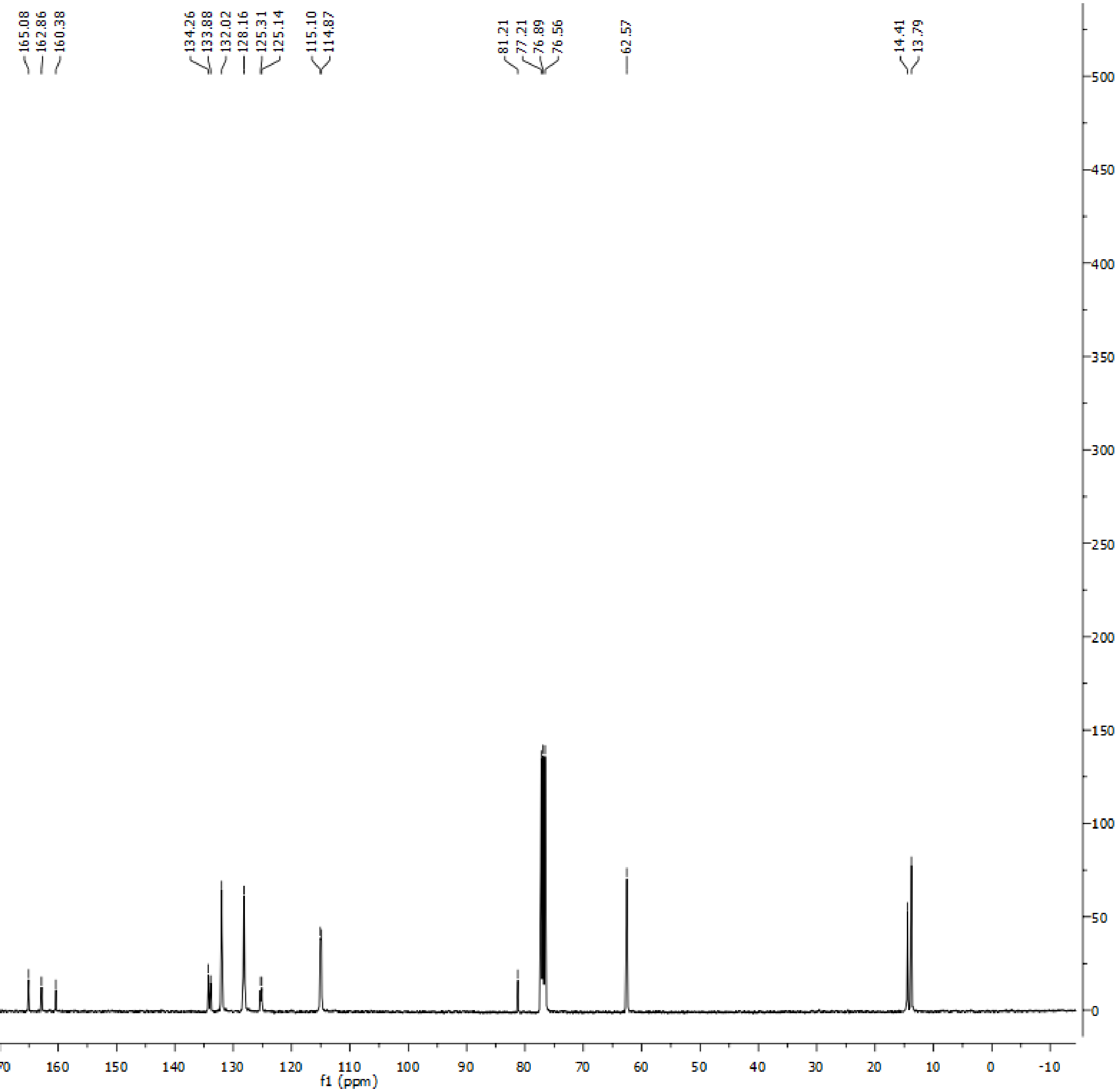
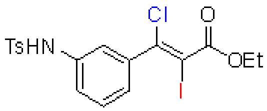


Figure S112. ^{1}H-NMR of **47**



47

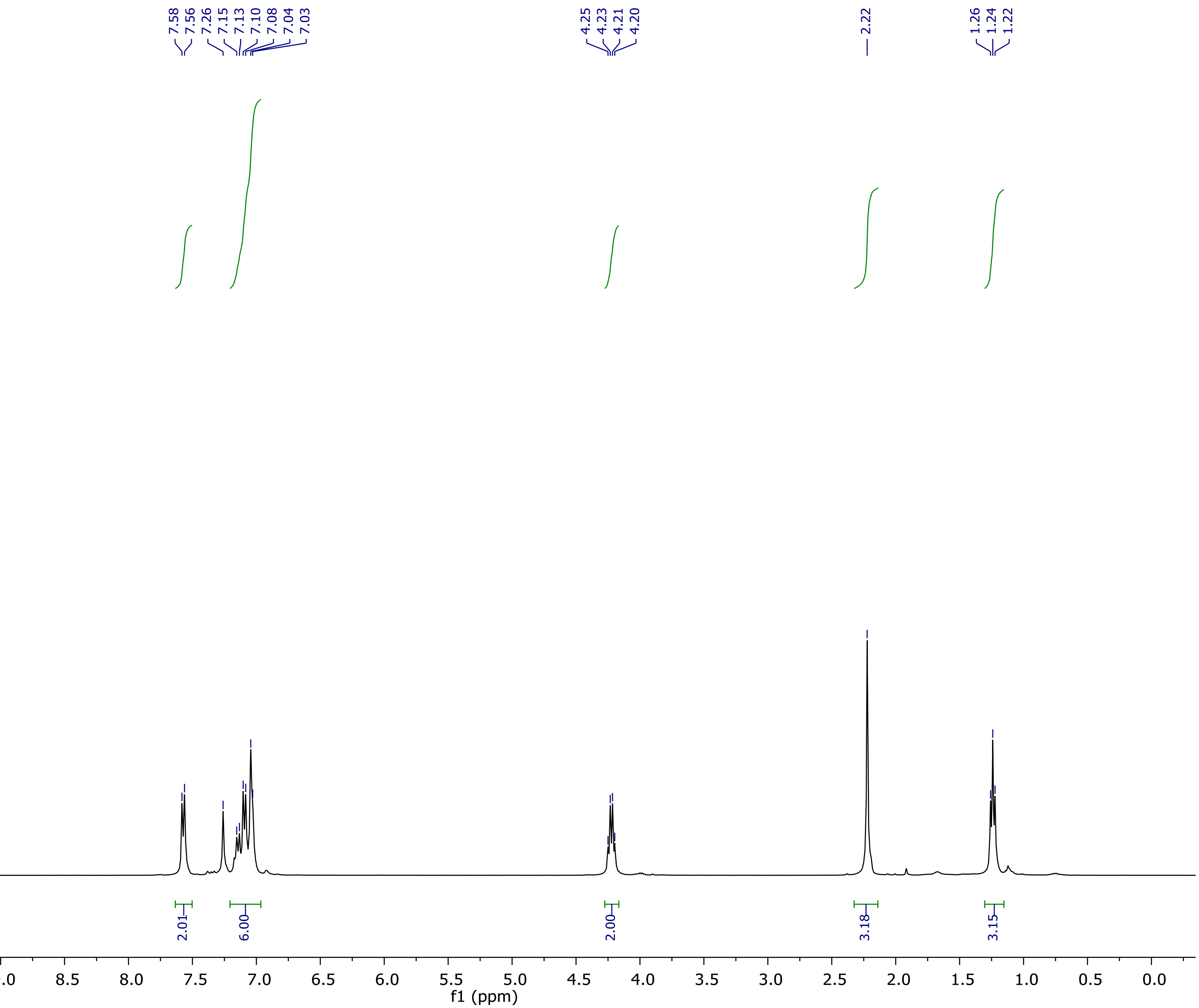


Figure S113. ^{13}C-NMR of **47**

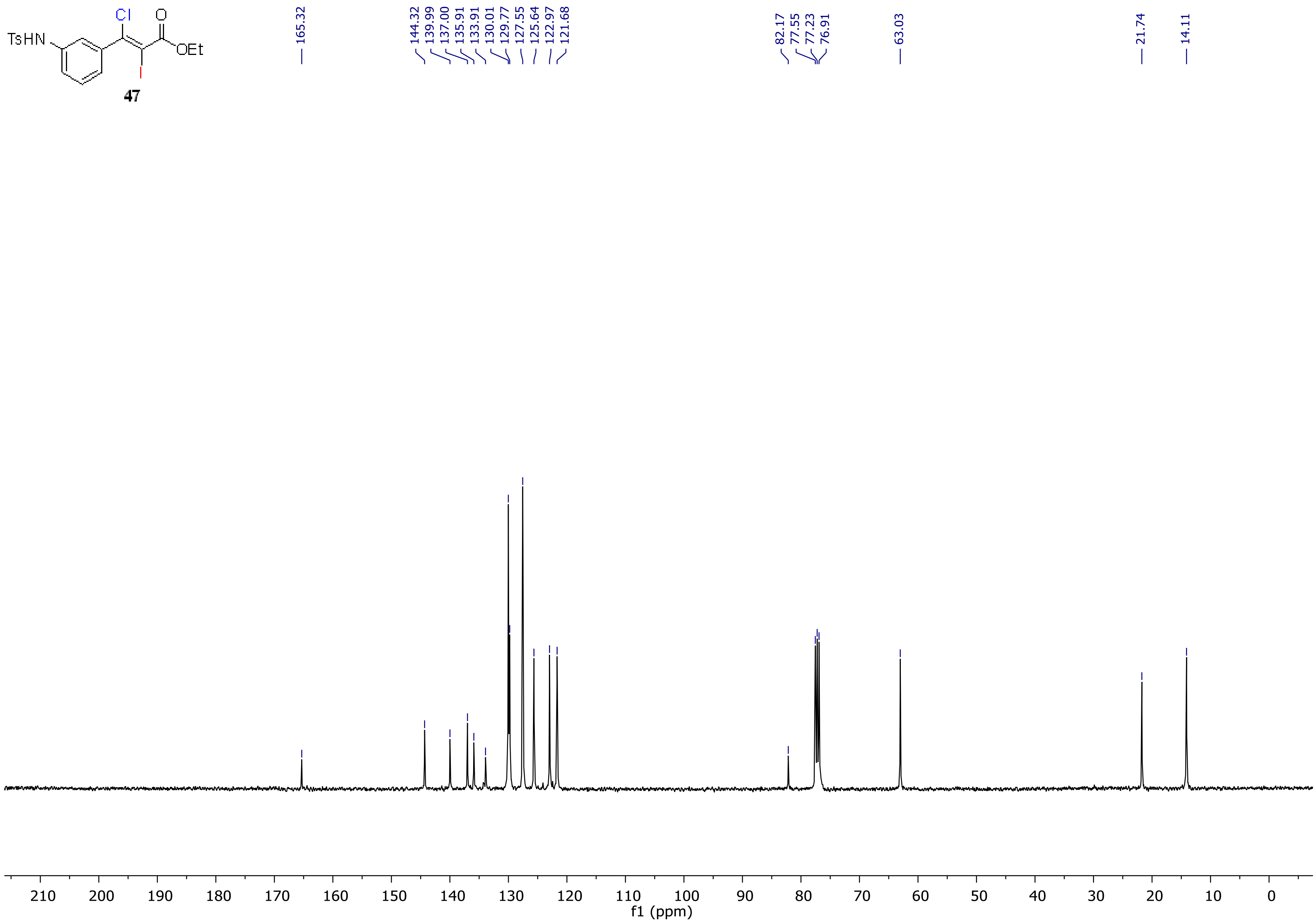


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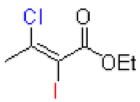
Figure S114. ^{1}H-NMR of **48**



48

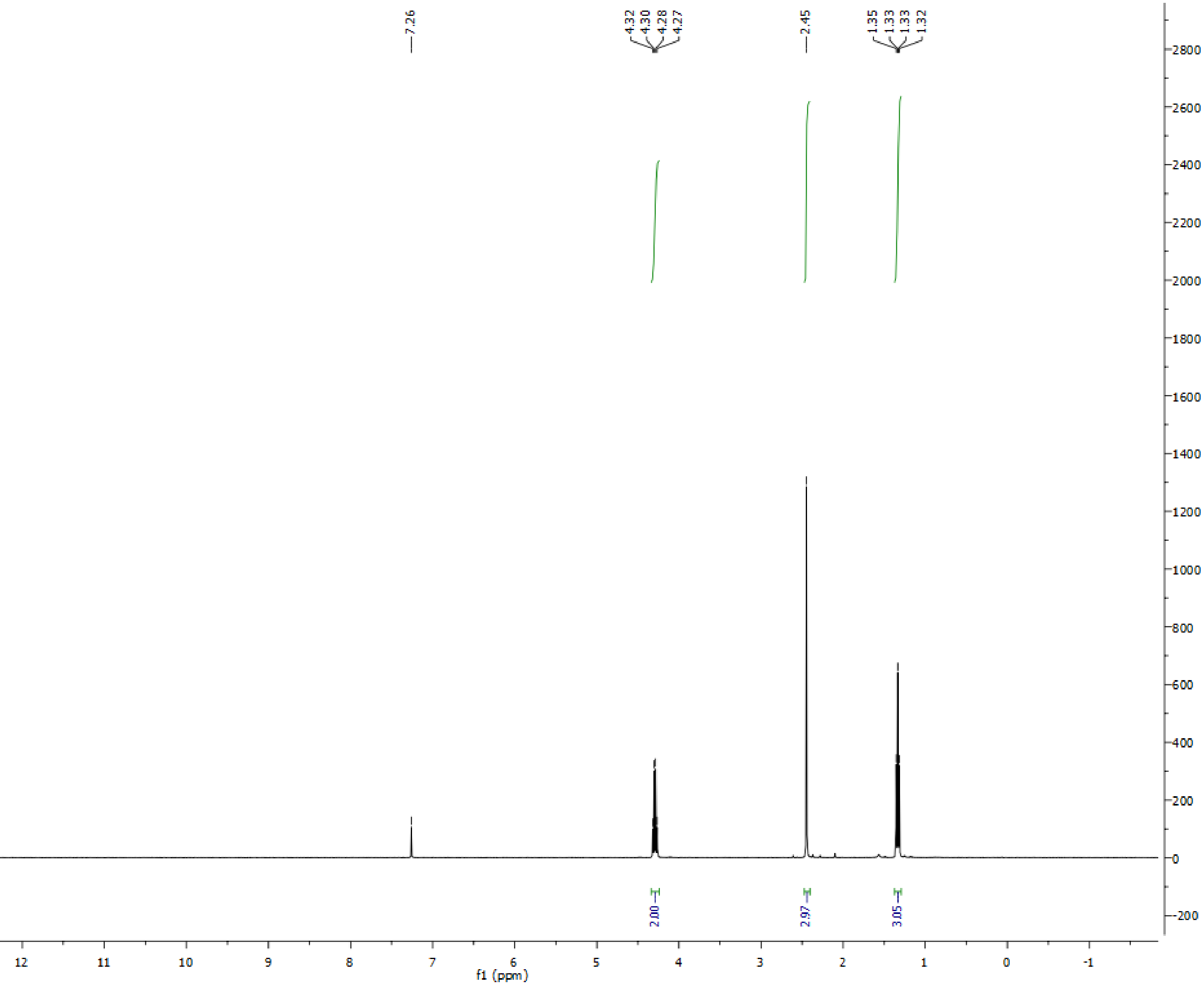


Figure S115. ^{13}C-NMR of **48**

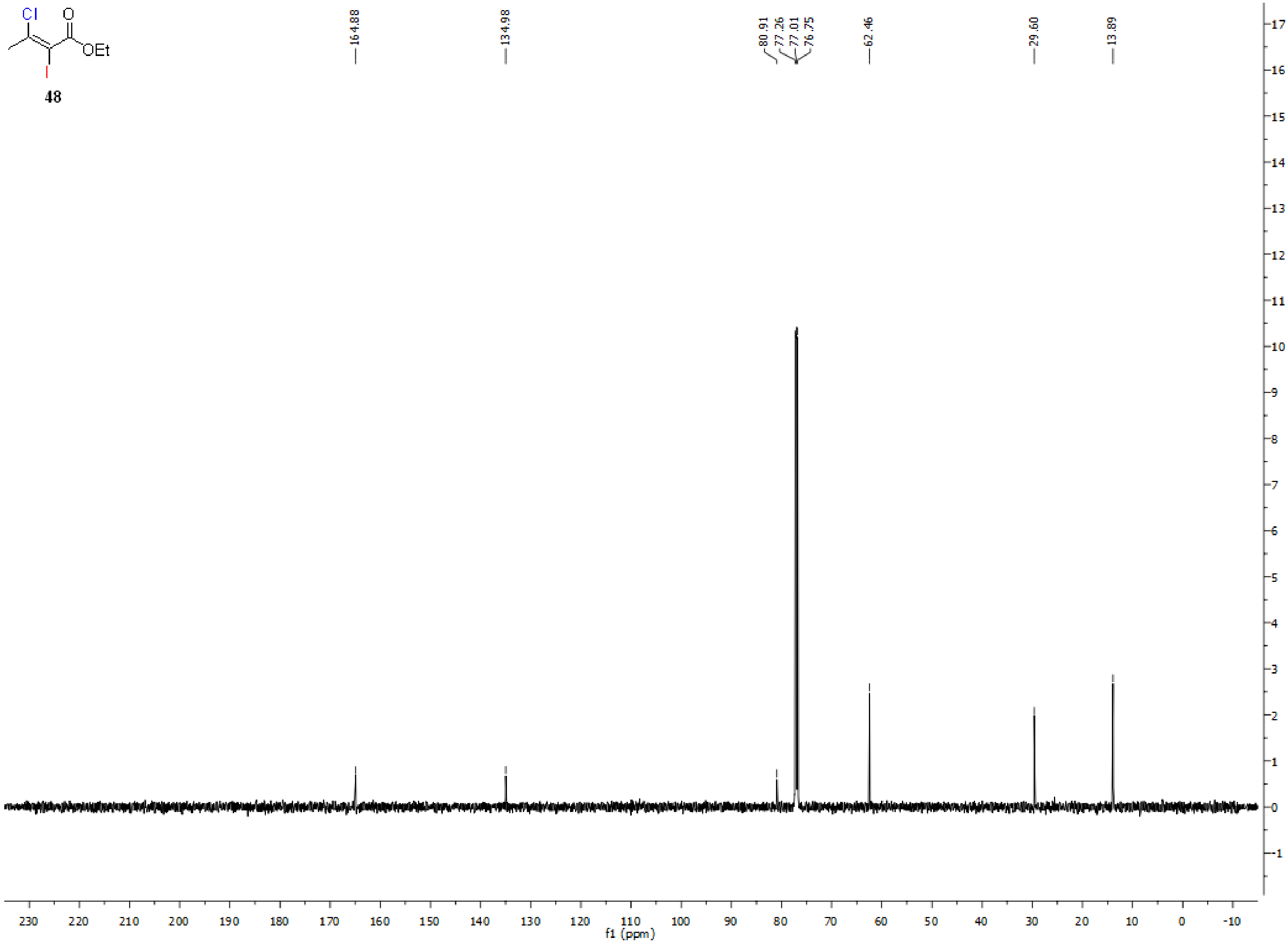
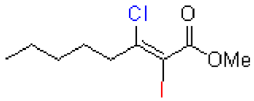


Figure S116. ^{1}H-NMR of **49**



49

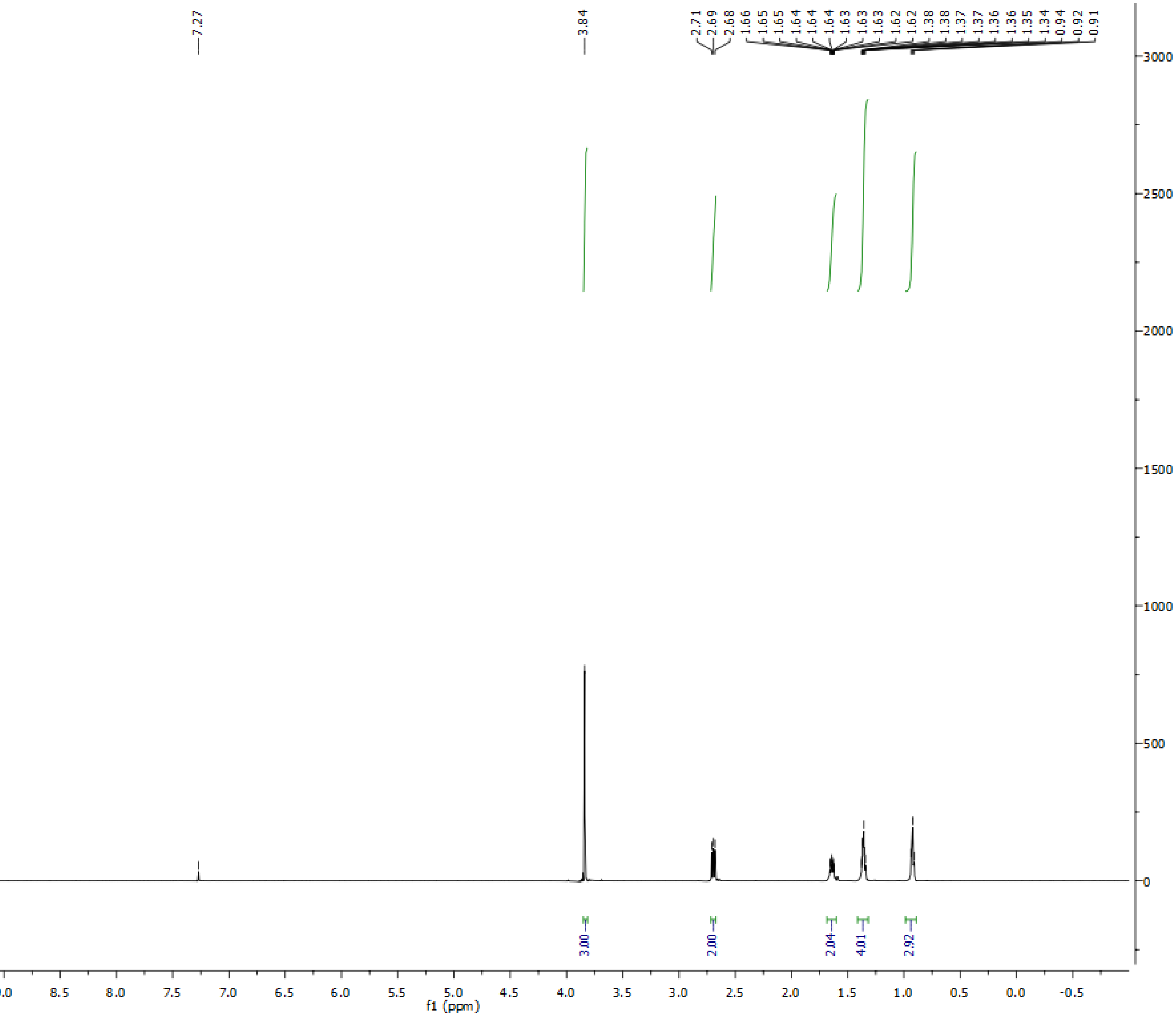
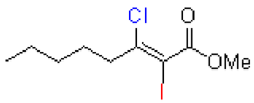


Figure S117. ^{13}C-NMR of **49**



49

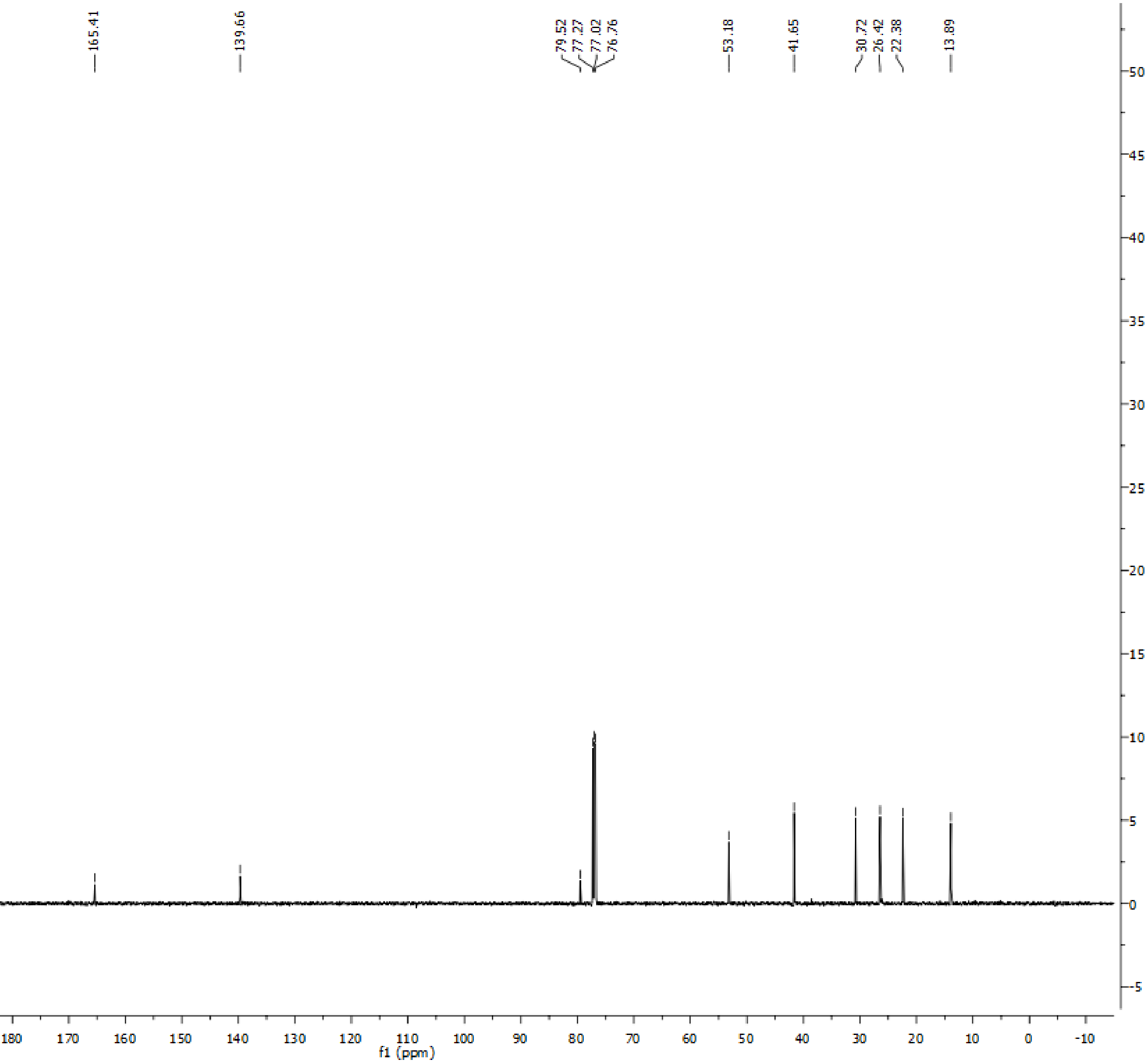
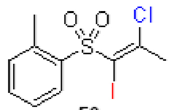


Figure S118. ^{1}H-NMR of **50**



50

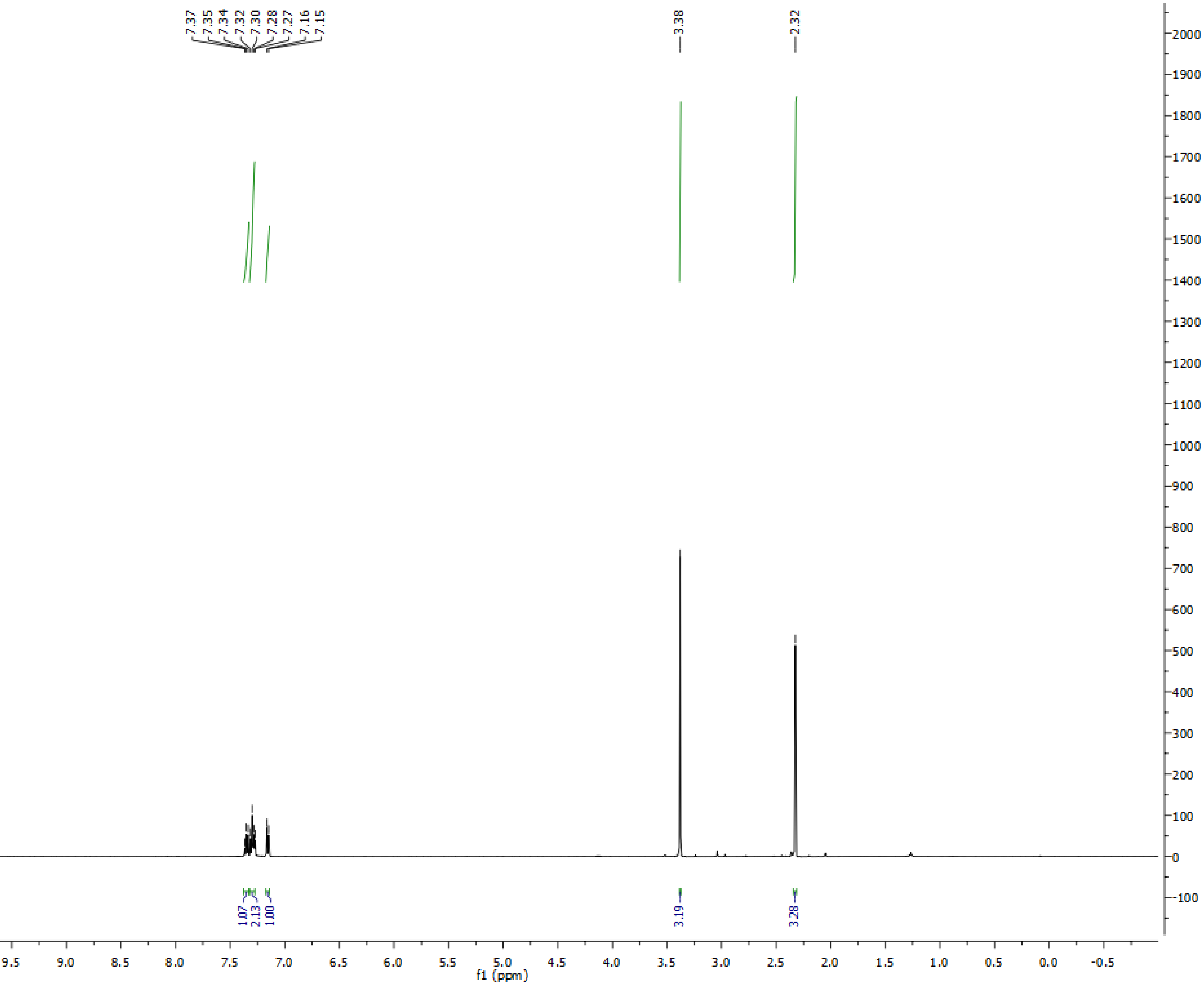
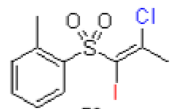


Figure S119. ^{13}C-NMR of **50**



50

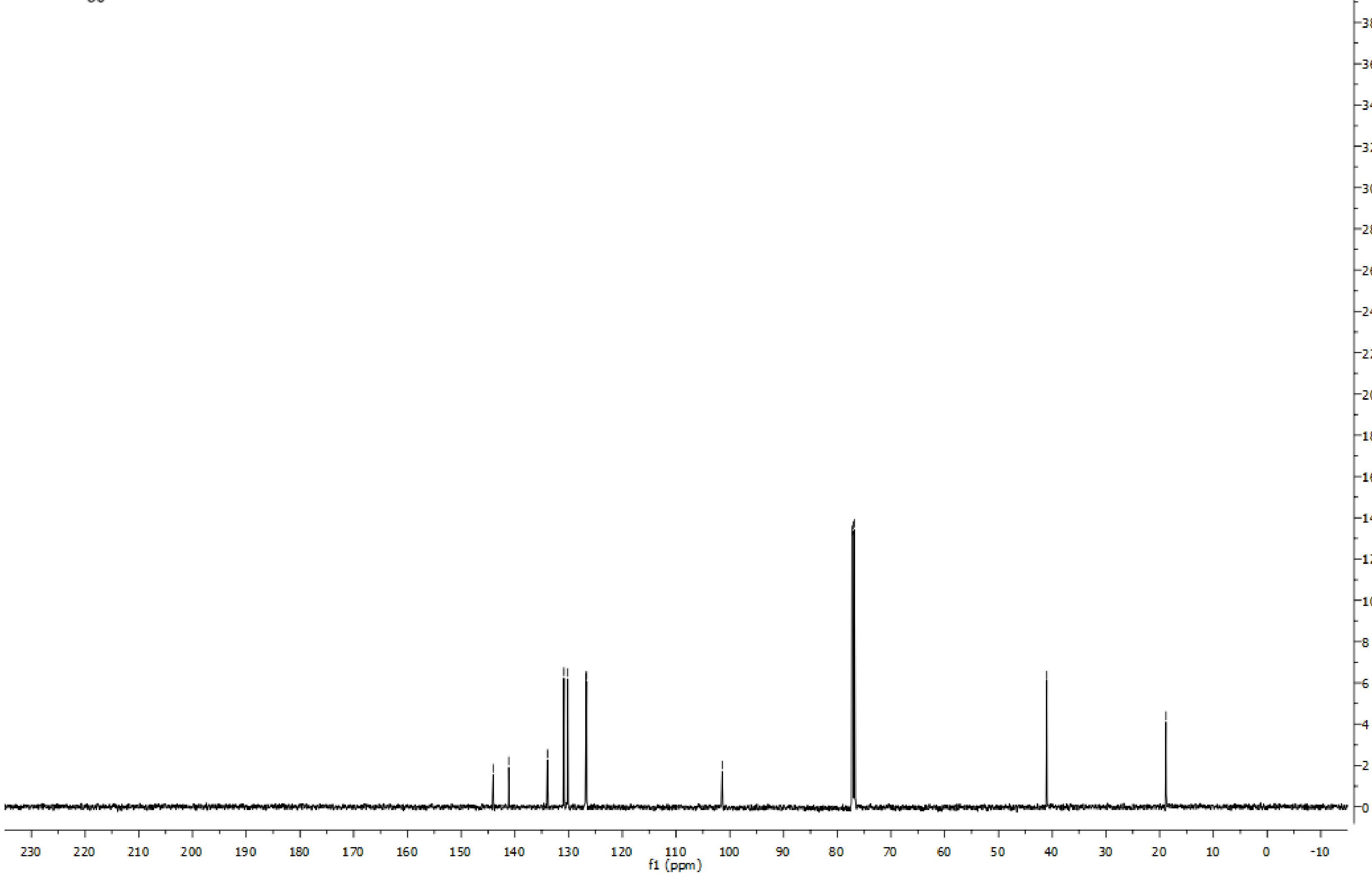
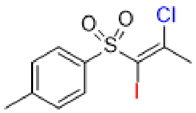


Figure S120. ^{1}H-NMR of **51**



51

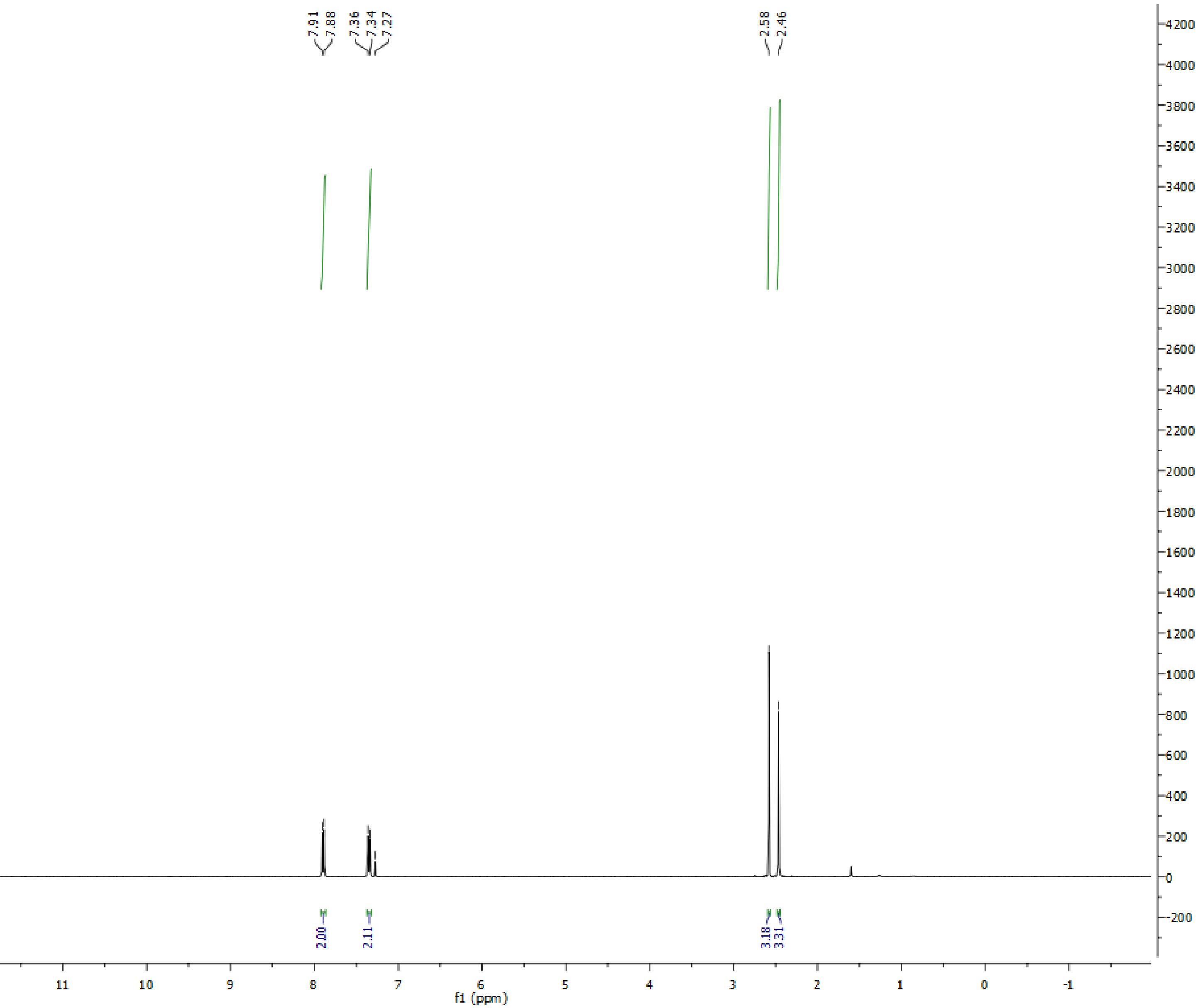
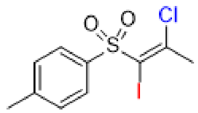


Figure S121. ^{13}C-NMR of **51**



51

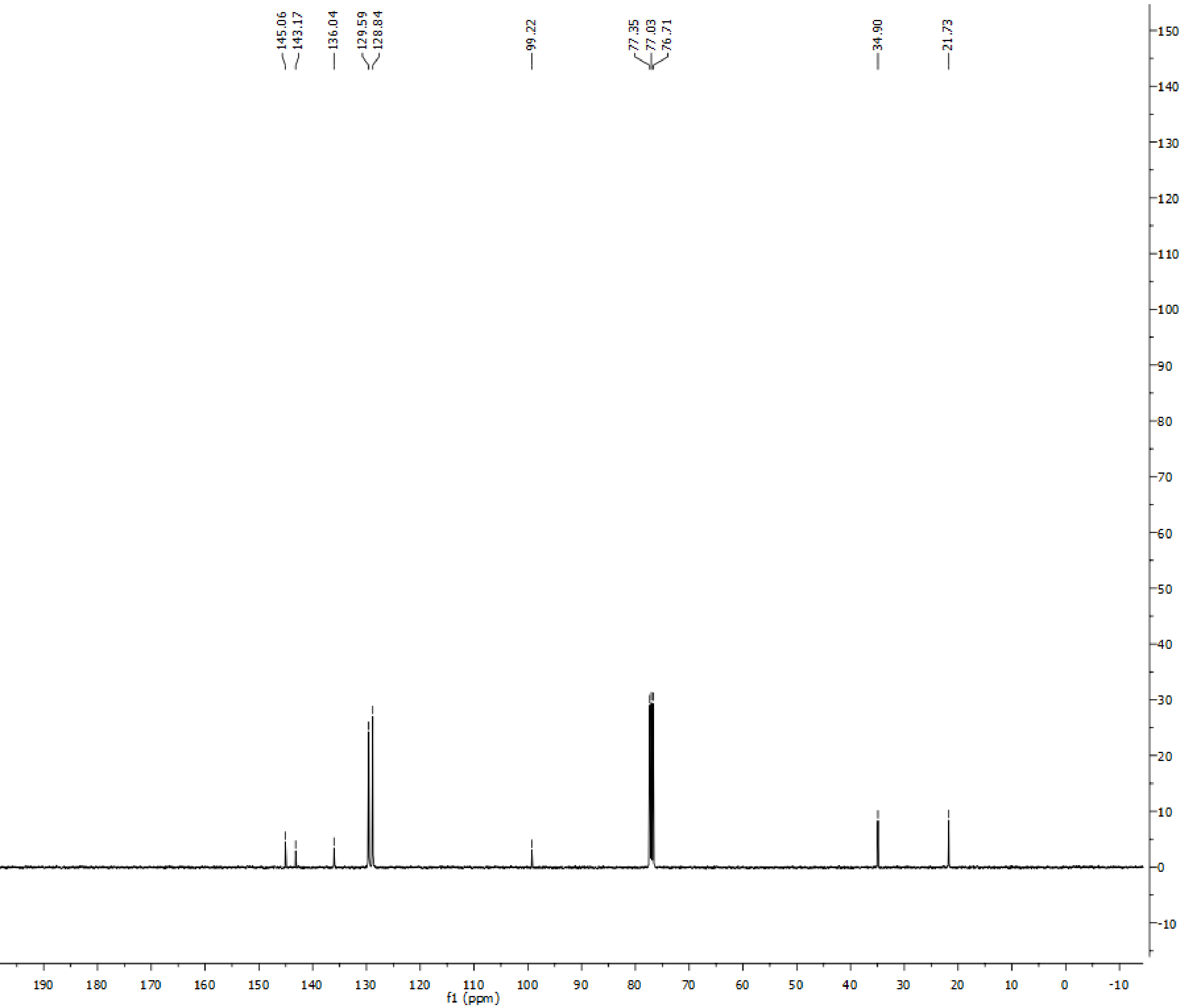


Figure S122. ^{1}H-NMR of **52**

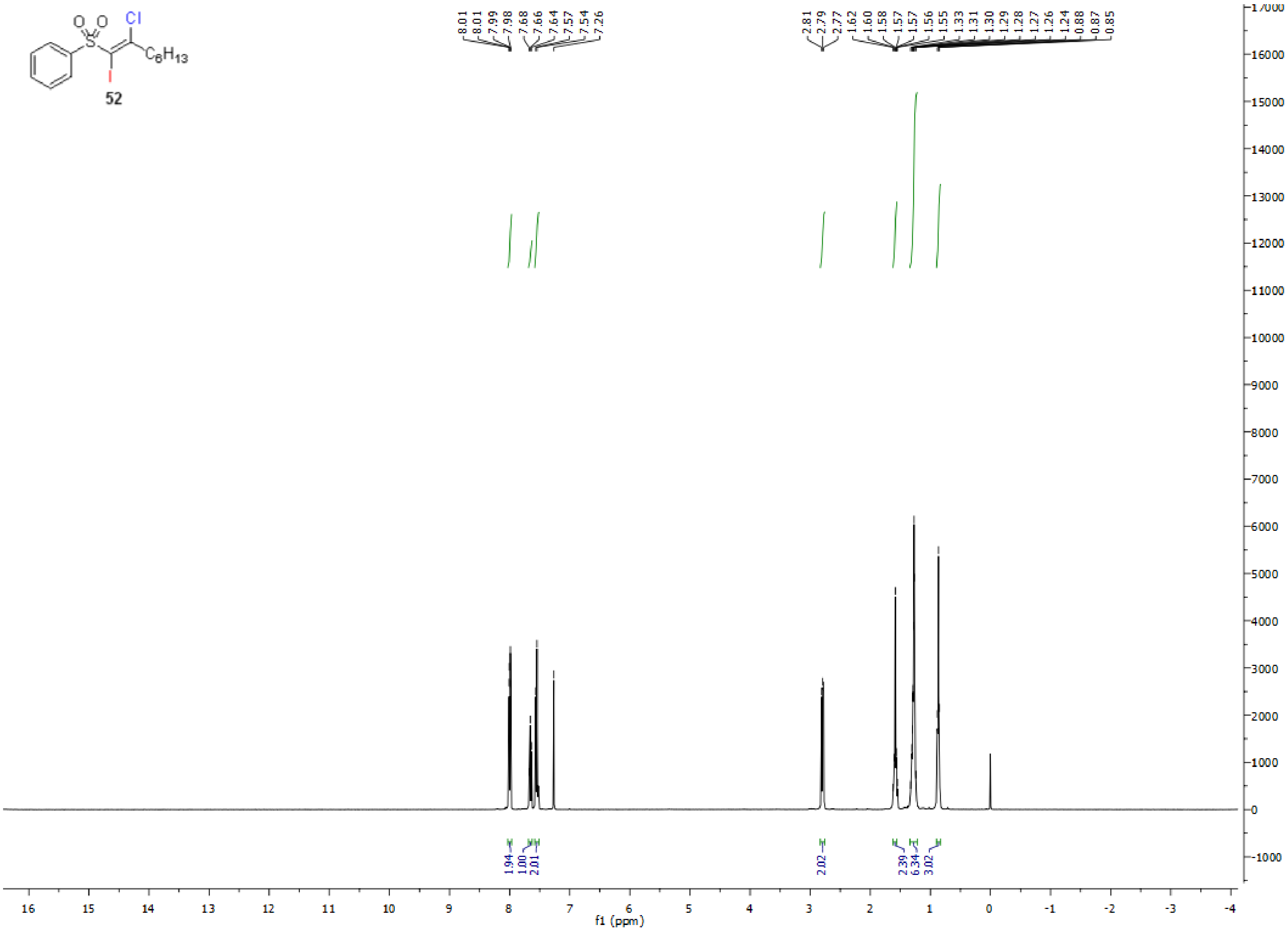
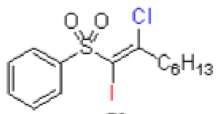


Figure S123. ^{13}C-NMR of **52**



52

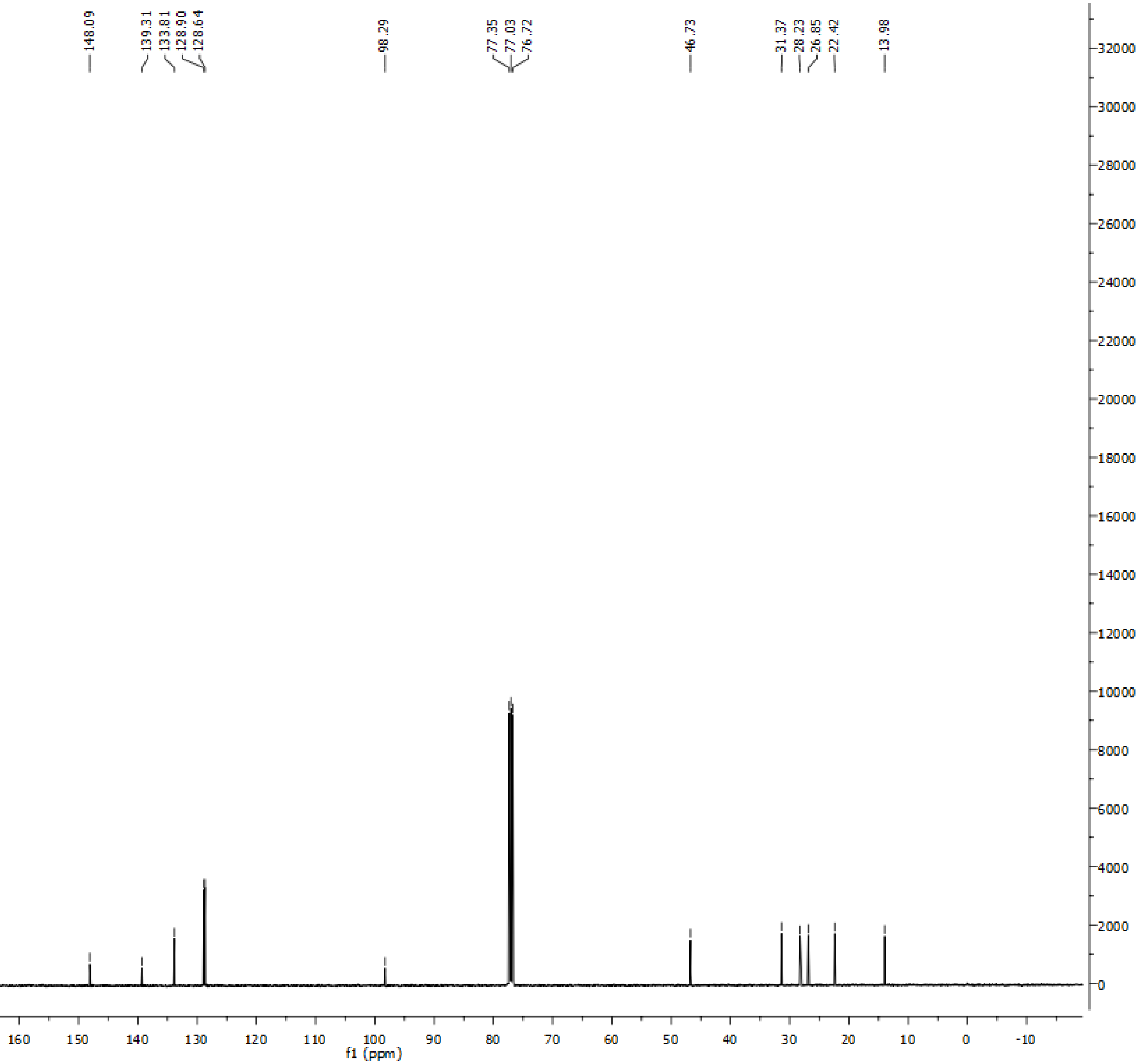
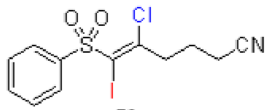


Figure S124. ^{1}H-NMR of **53**



53

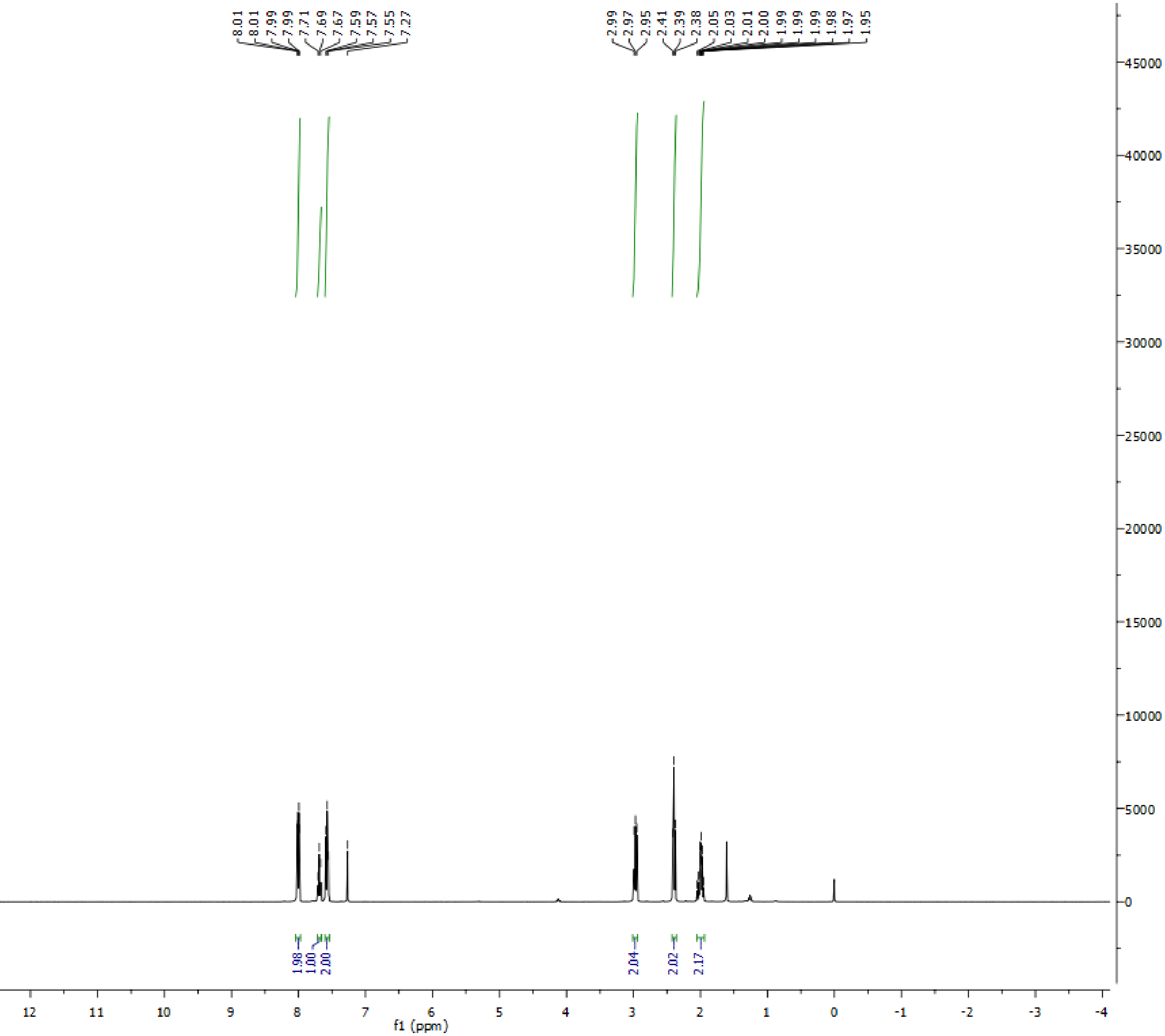
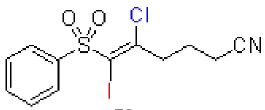


Figure S125. ^{13}C-NMR of **53**



53

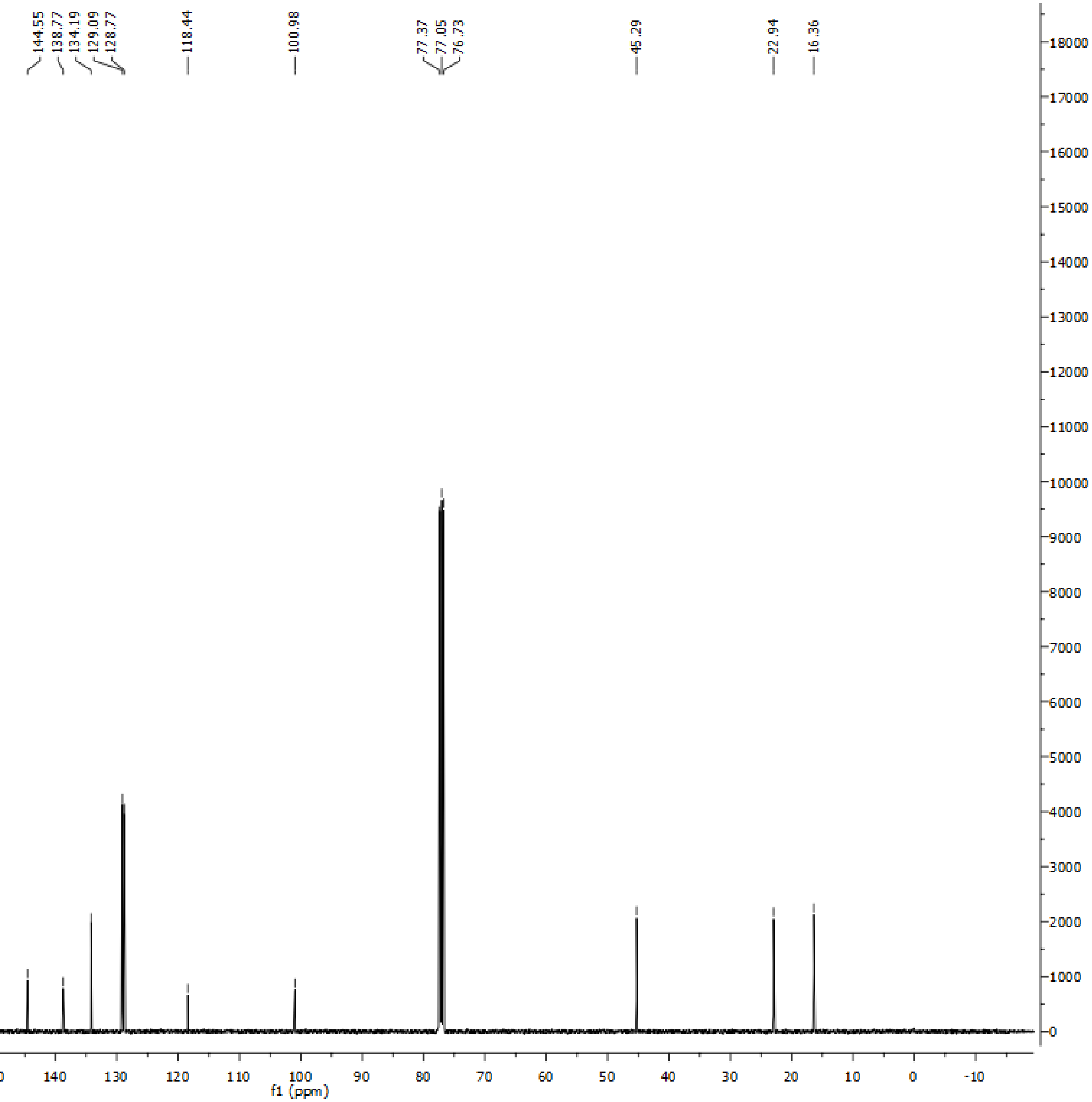


Figure S126. ^{1}H-NMR of **54**

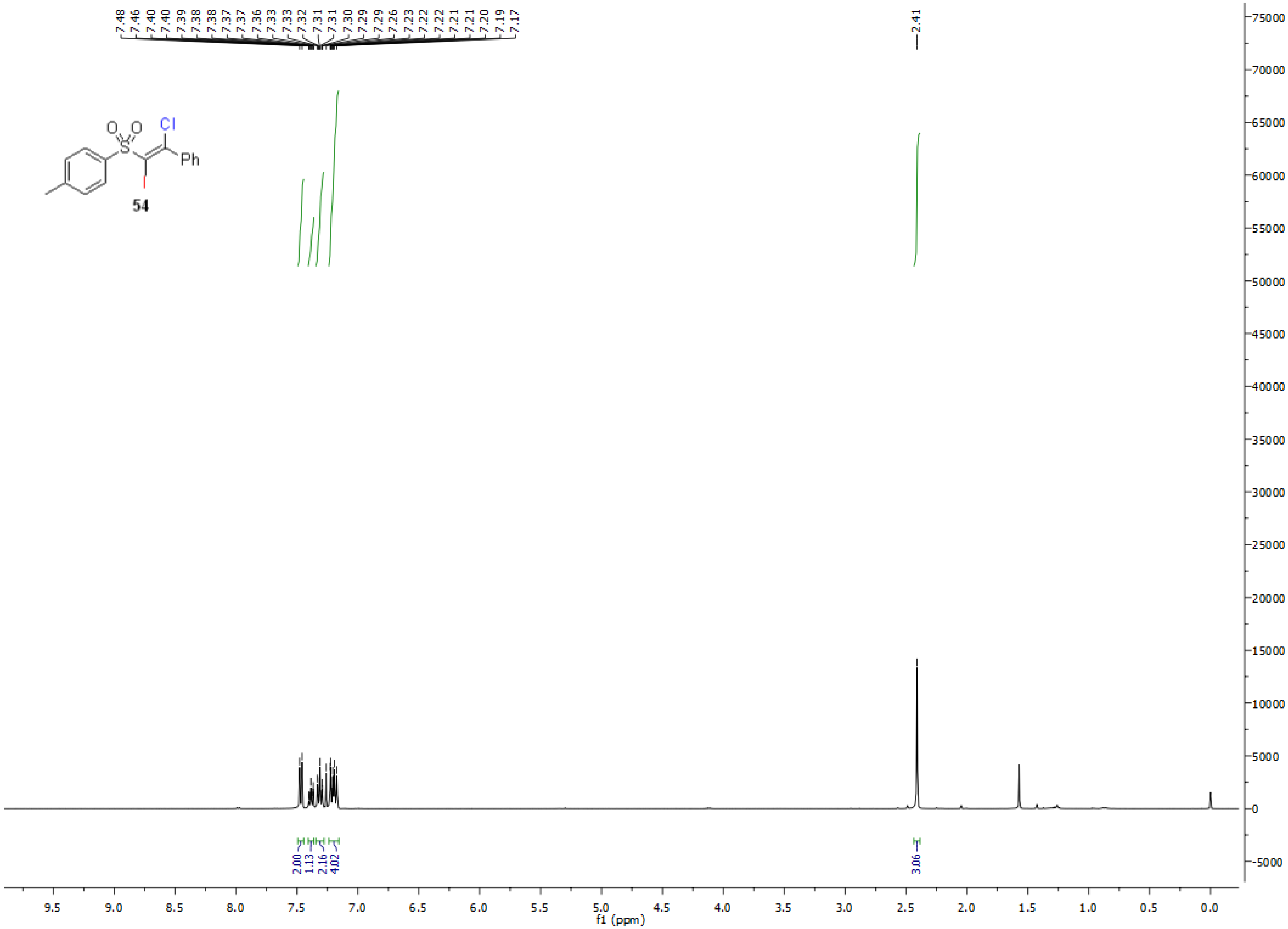
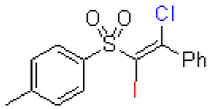


Figure S127. ^{13}C-NMR of **54**



54

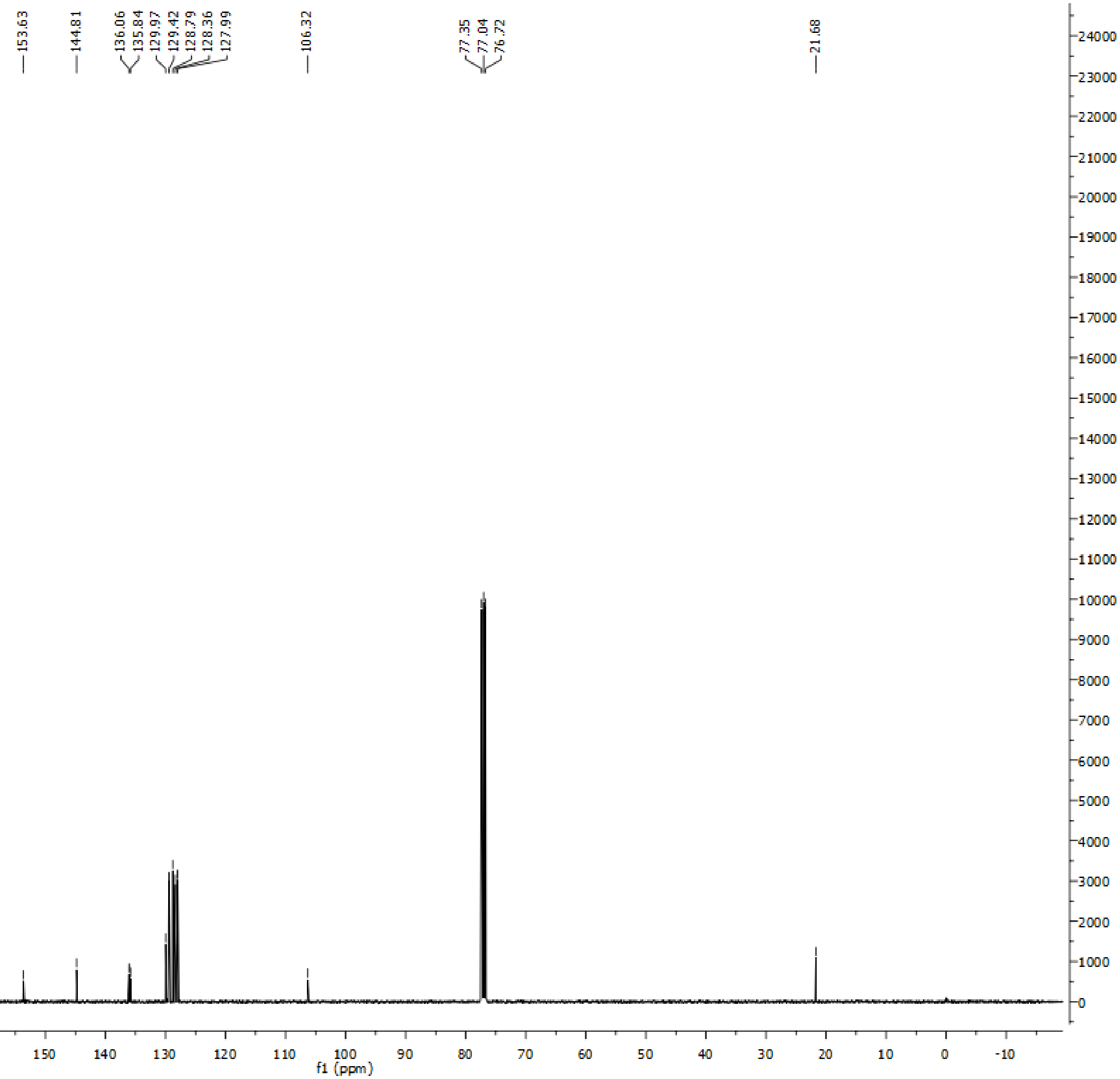
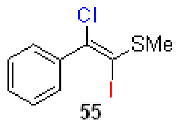


Figure S128. ^{1}H-NMR of **55**



55

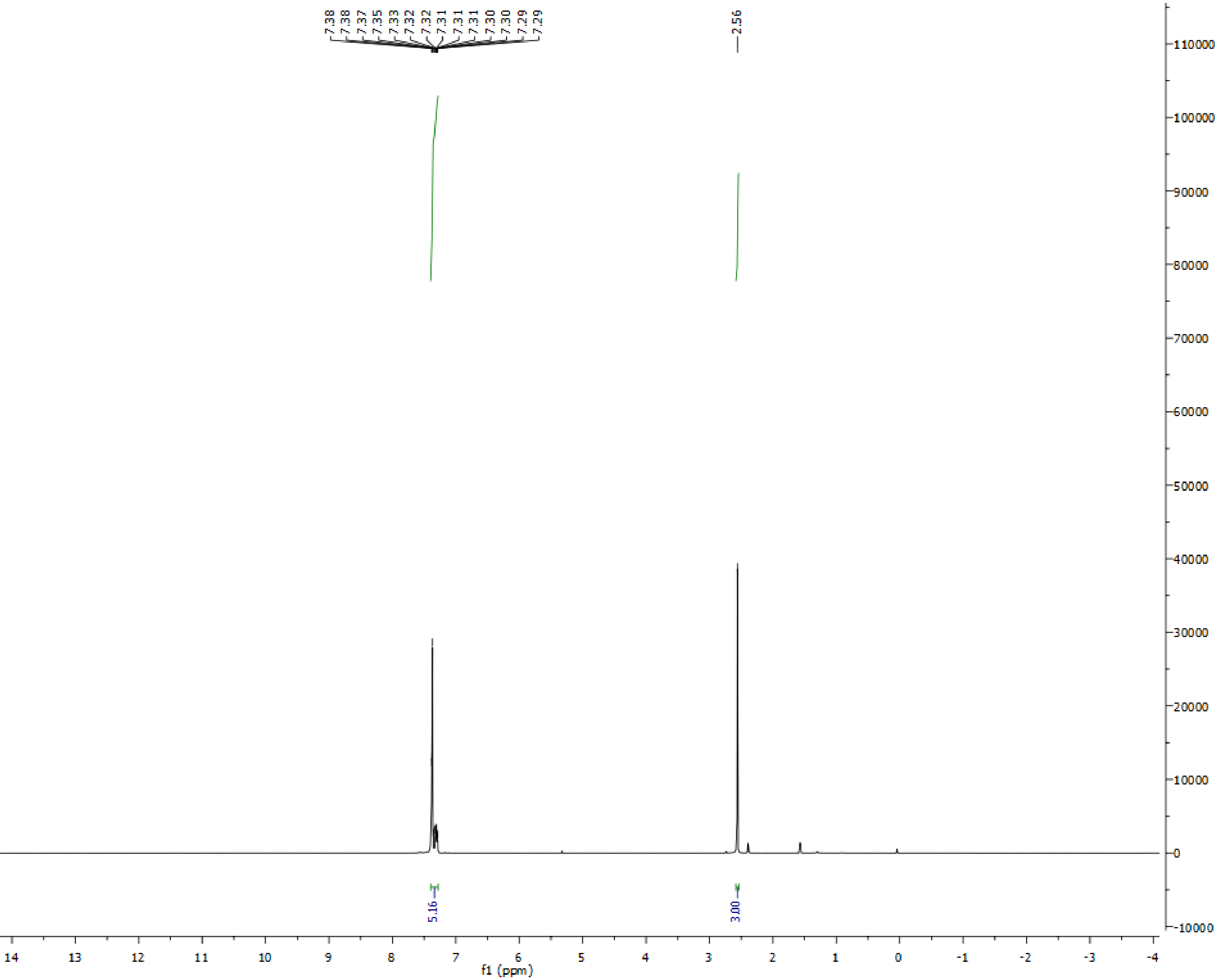


Figure S129. ^{13}C-NMR of **55**

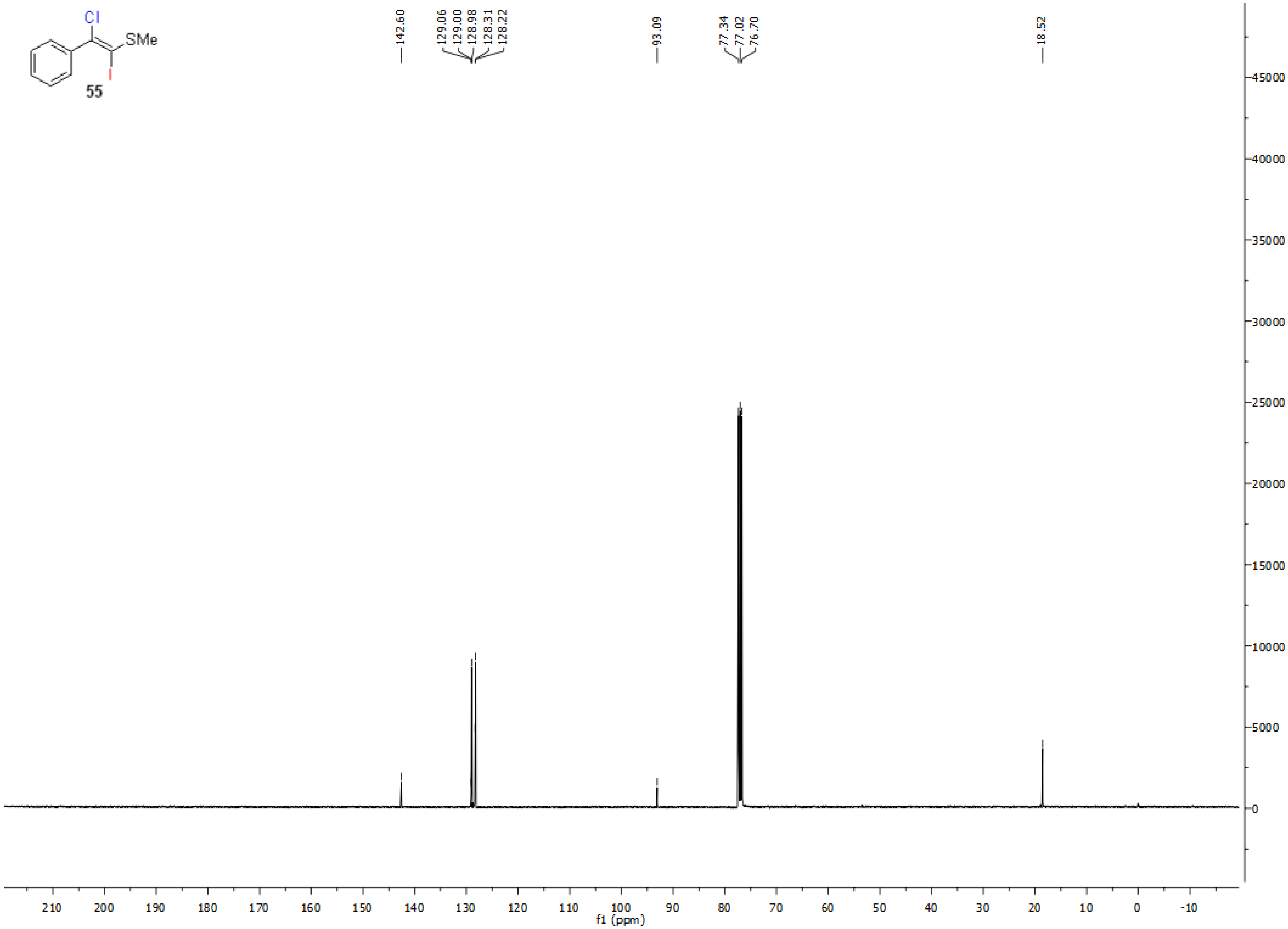
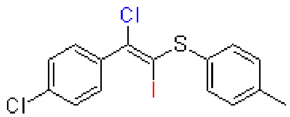


Figure S130. ^{1}H-NMR of **56**



56

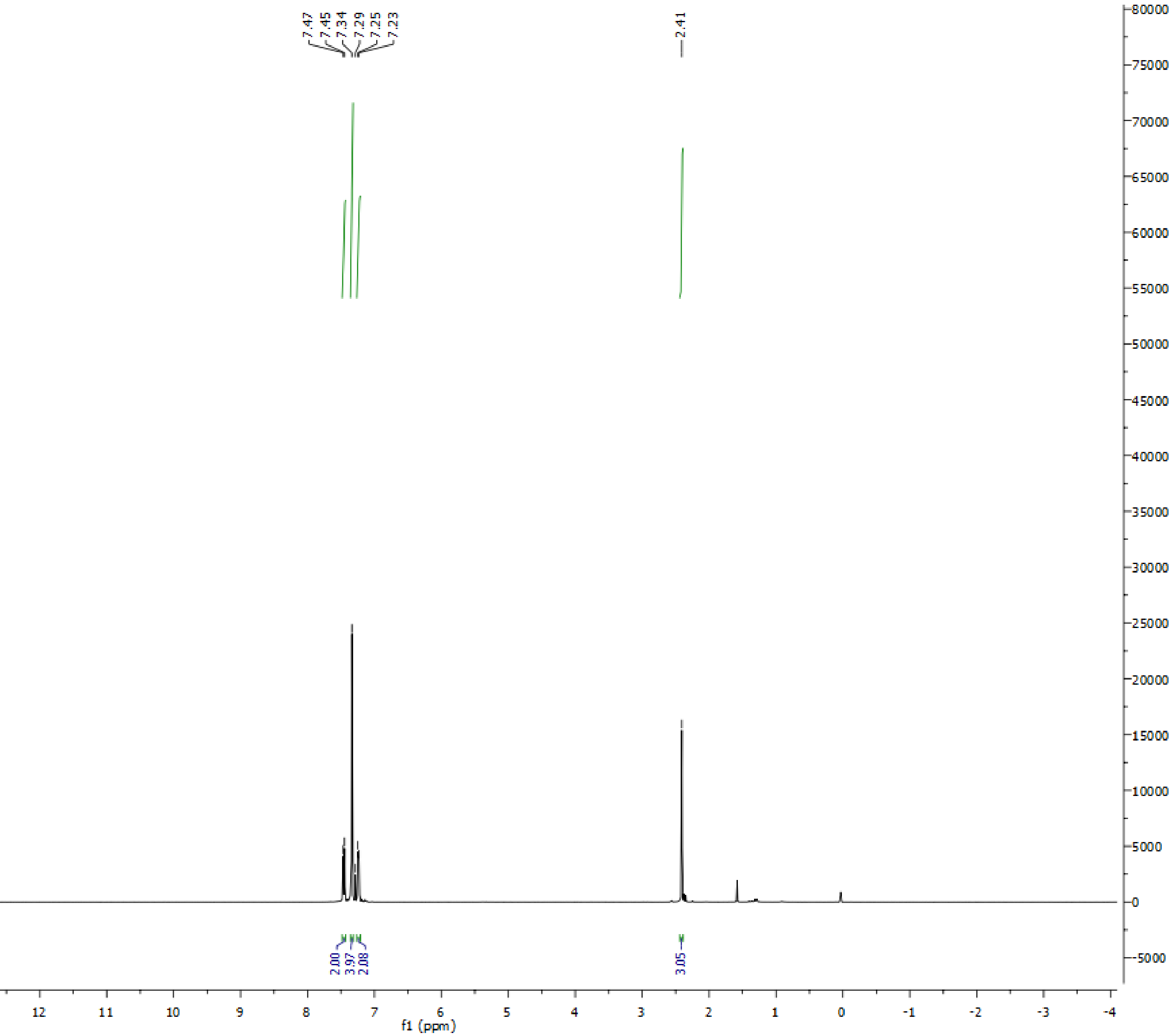
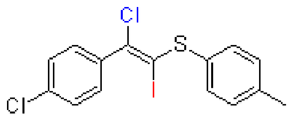


Figure S131. ^{13}C-NMR of **56**



56

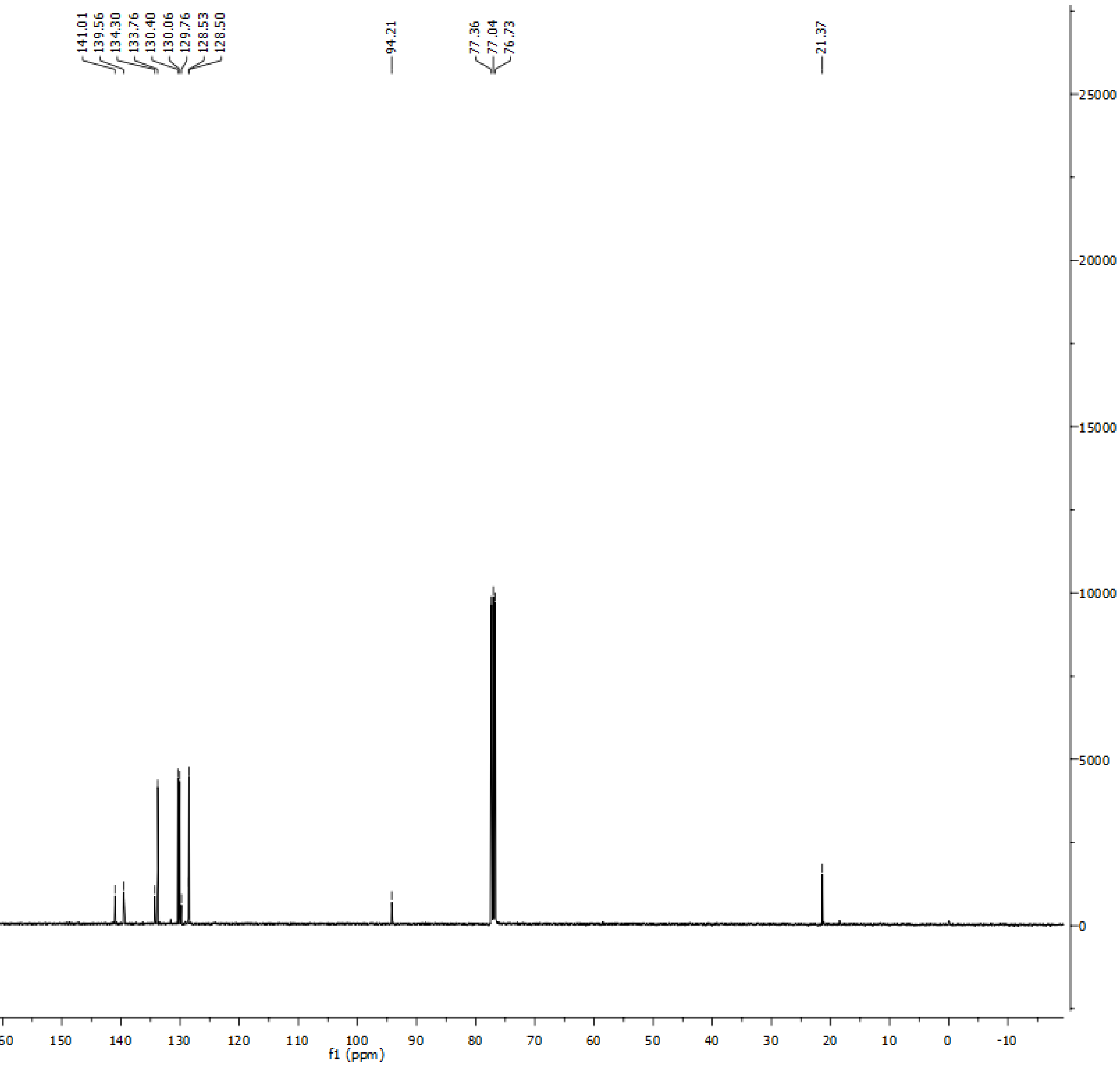


Figure S132. ^{1}H-NMR of **57**

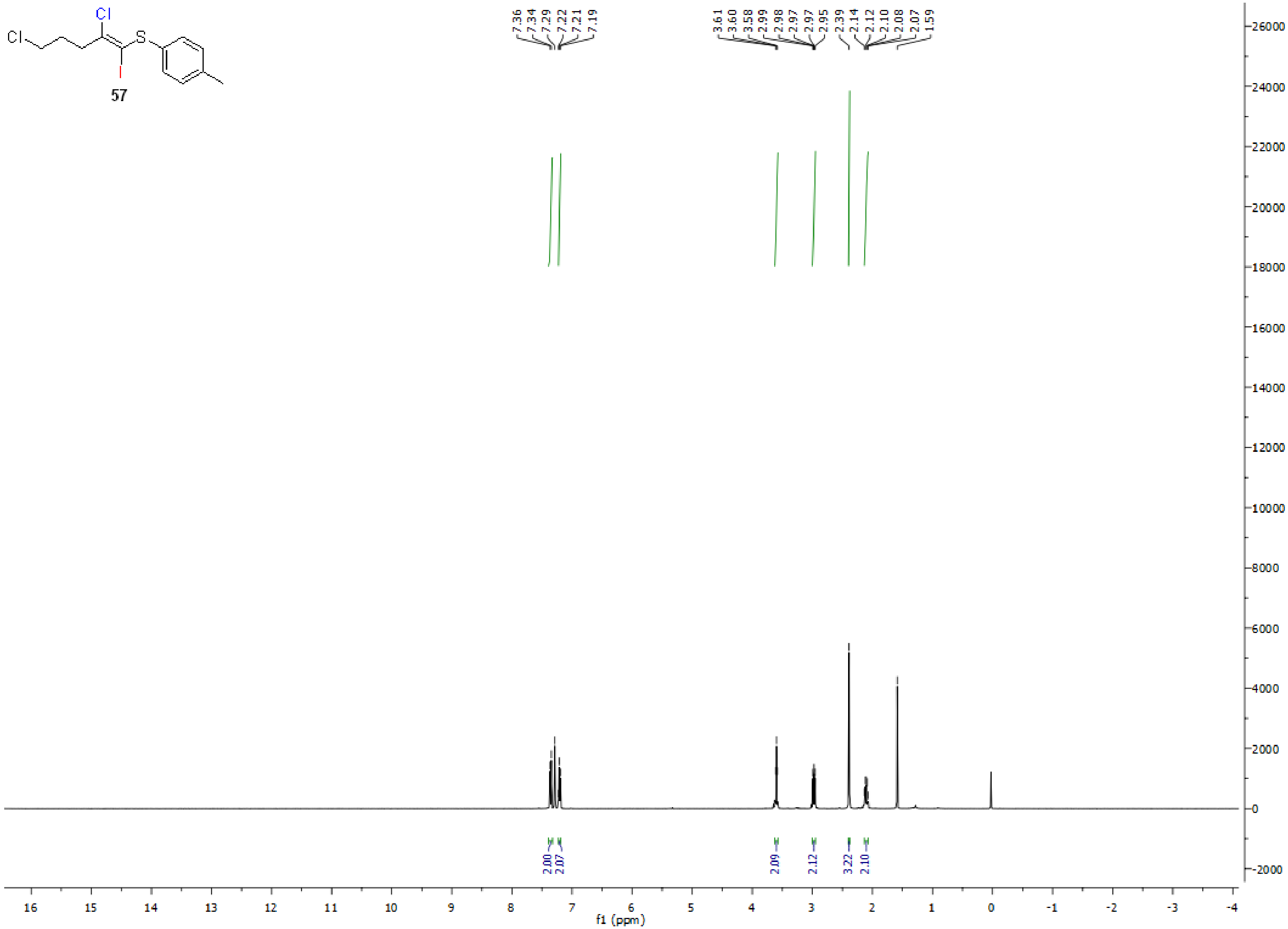
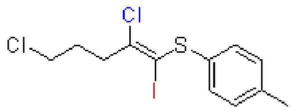


Figure S133. ^{13}C-NMR of **57**



57

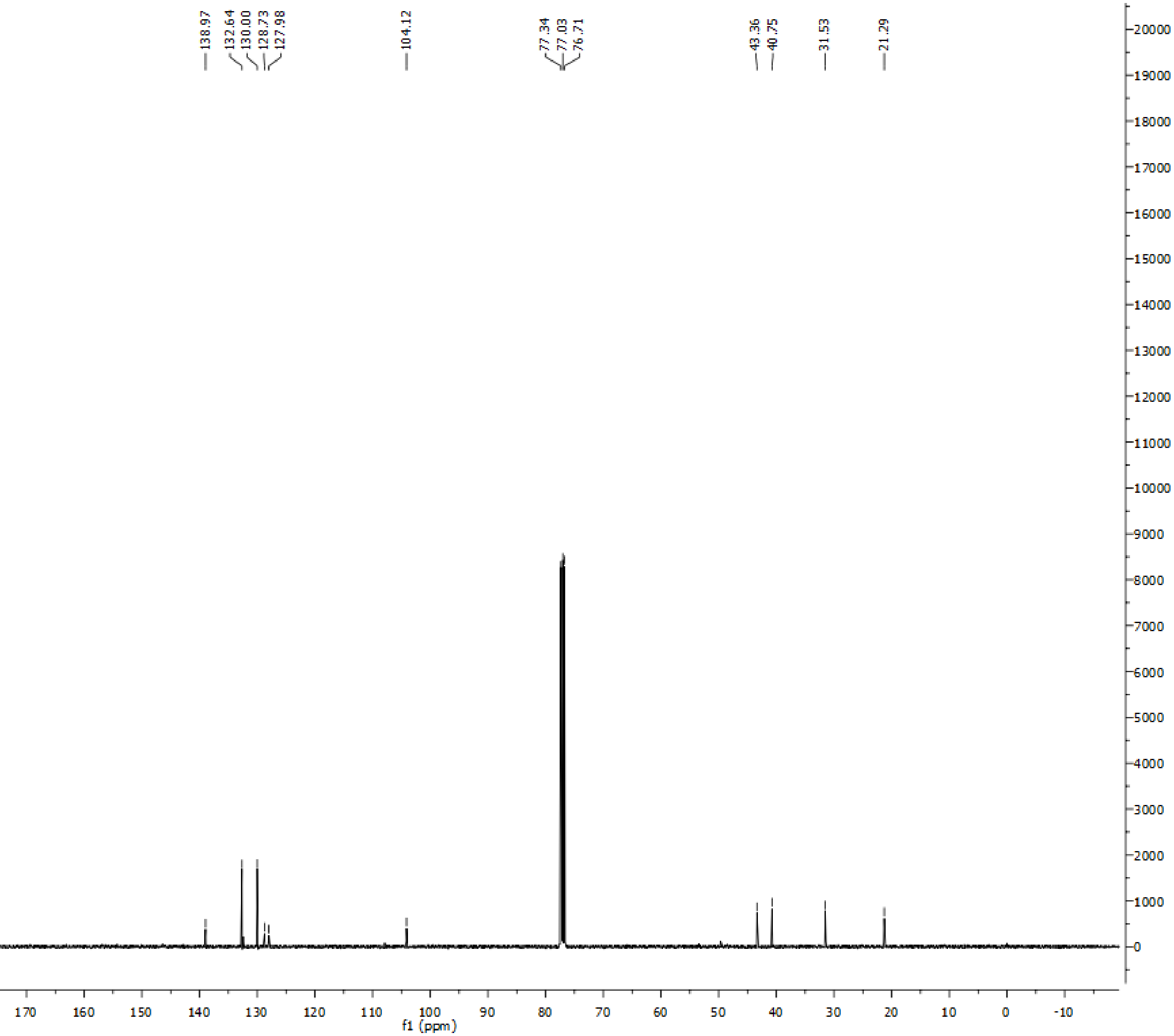
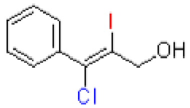


Figure S134. ^{1}H-NMR of **58**



58

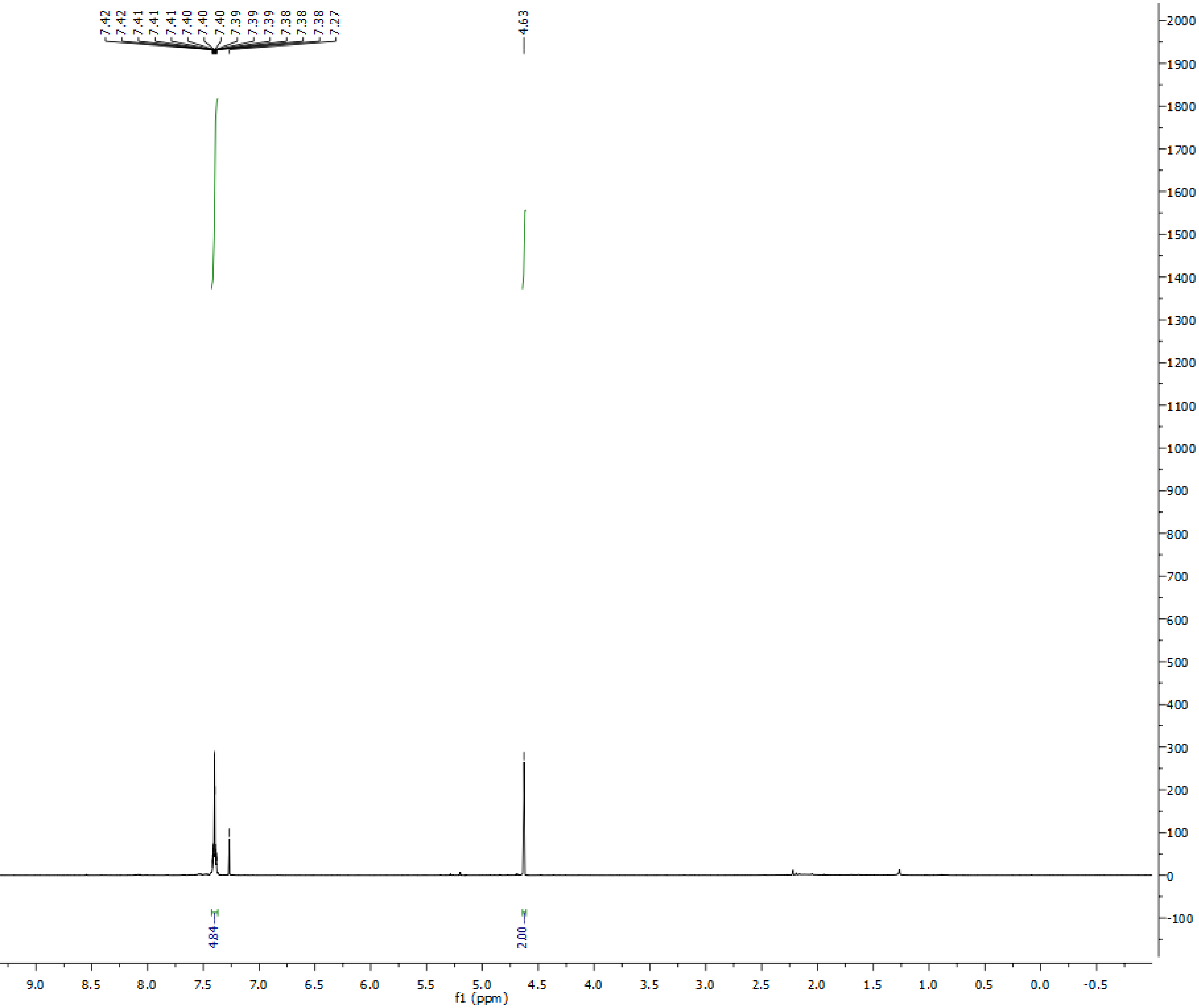
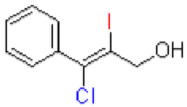


Figure S135. ^{13}C-NMR of **58**



58

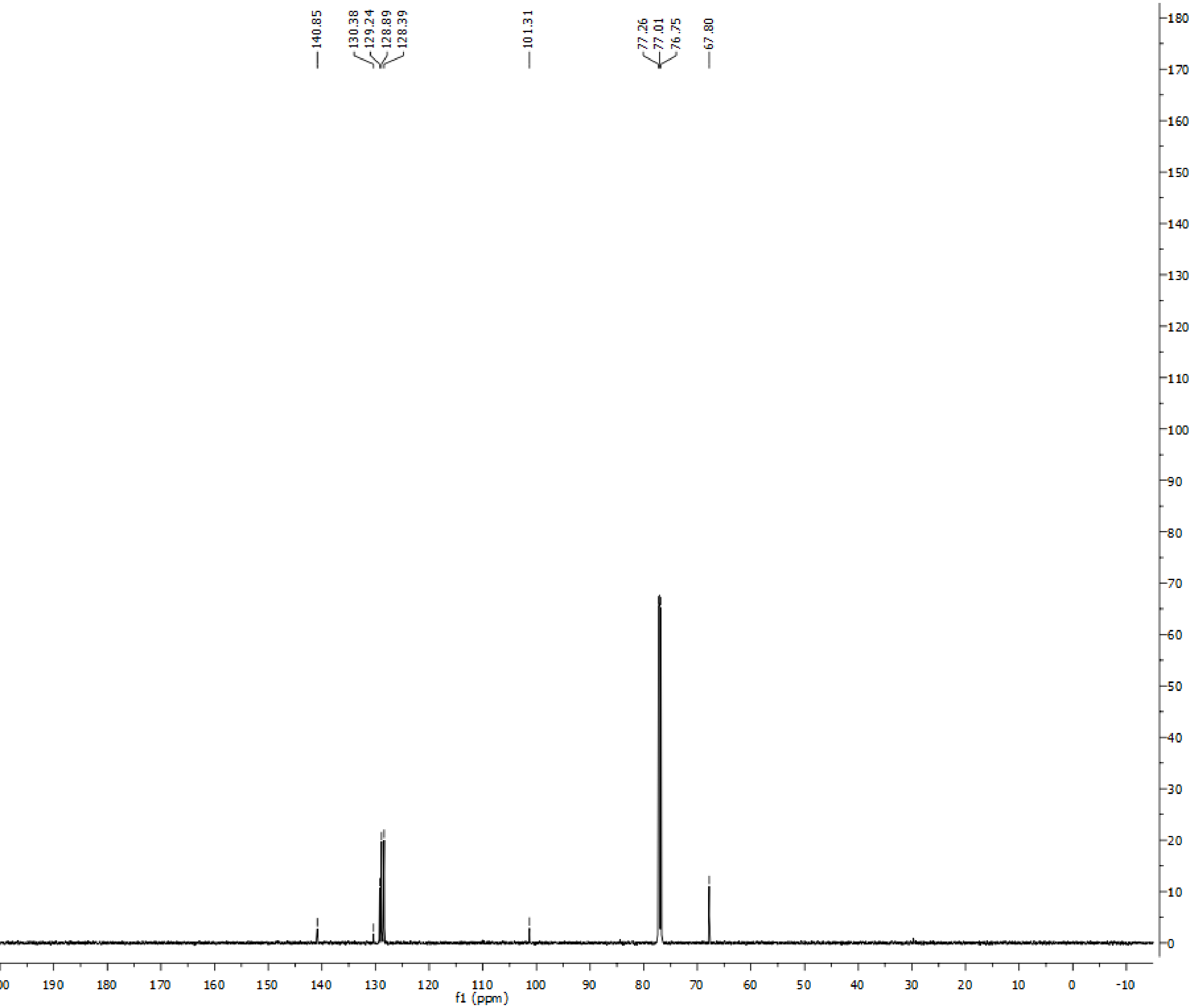
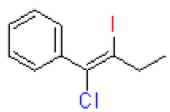


Figure S136. ^{1}H-NMR of **59**



59

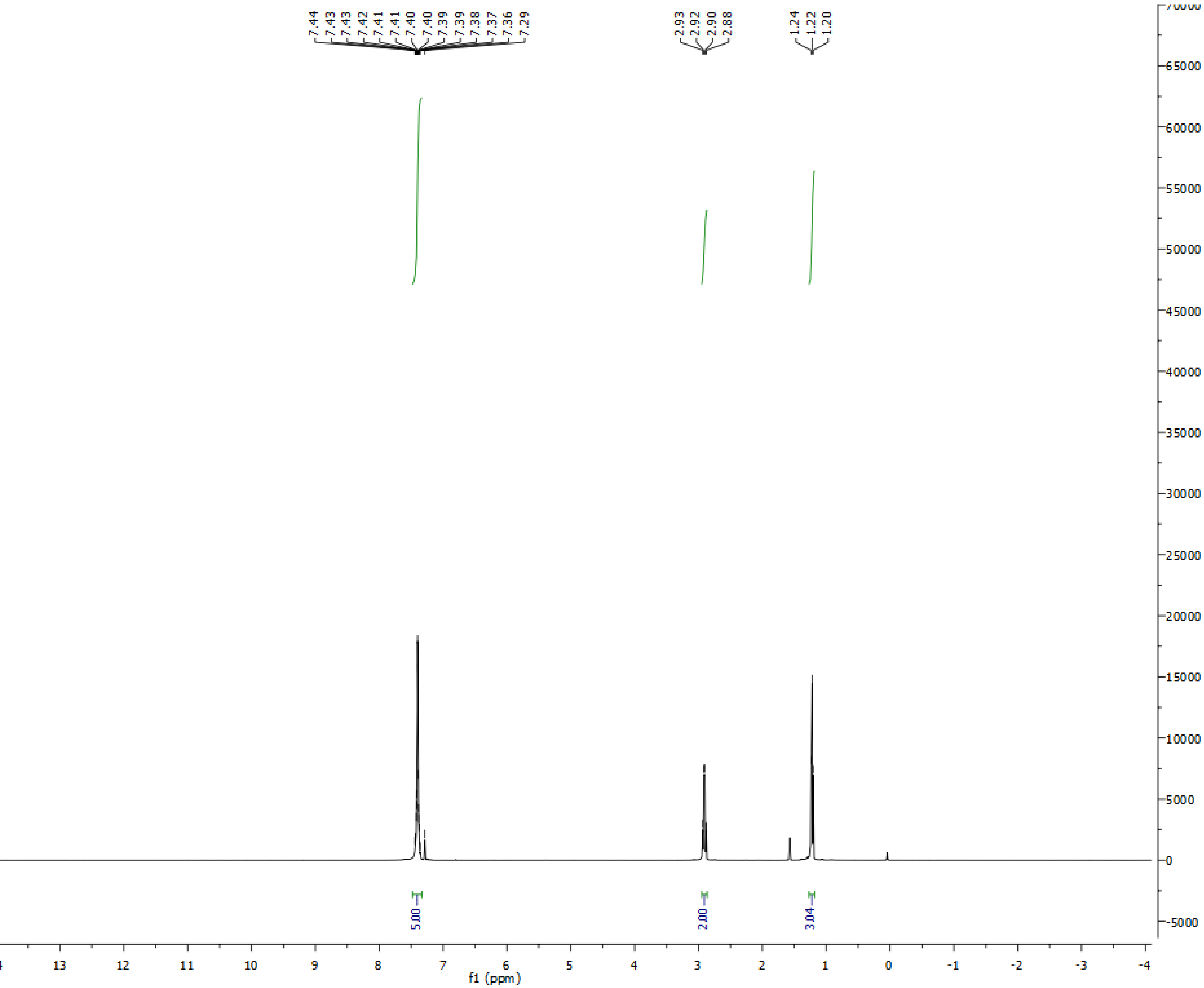
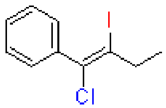


Figure S137. ^{13}C-NMR of **59**



59

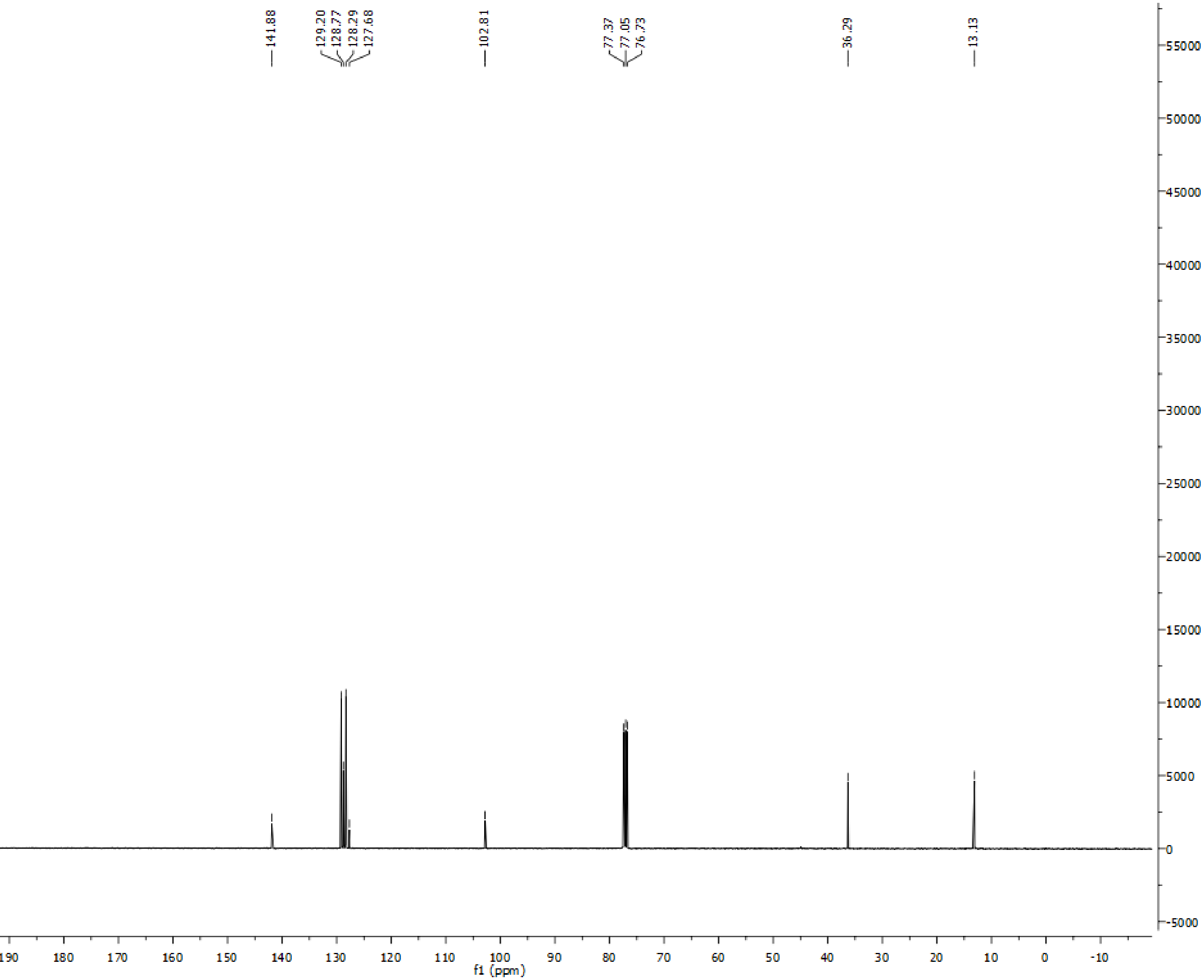
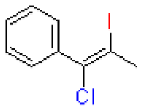


Figure S138. ^{1}H-NMR of **60**



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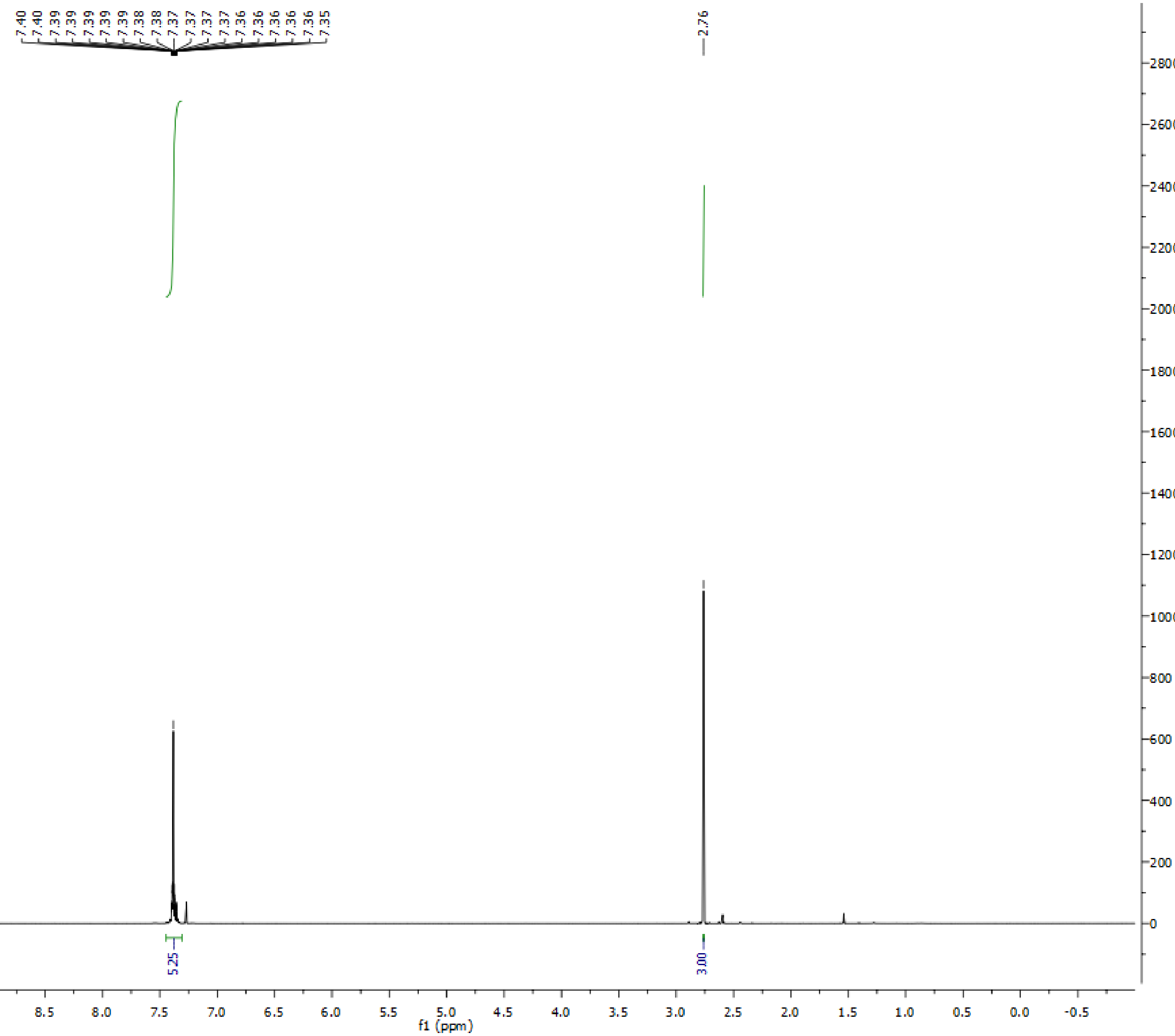
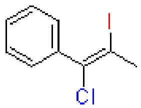


Figure S139. ^{13}C-NMR of **60**



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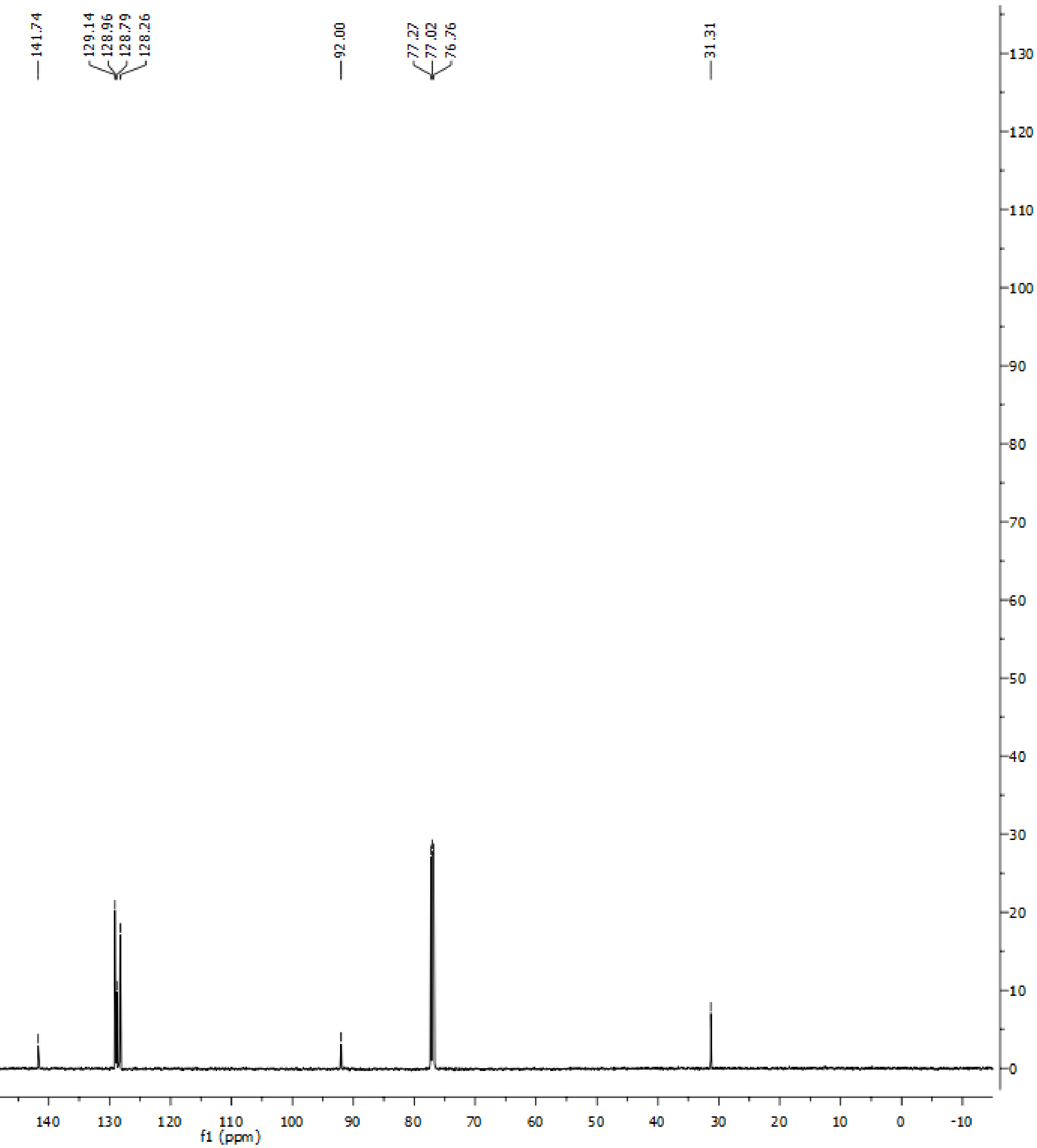
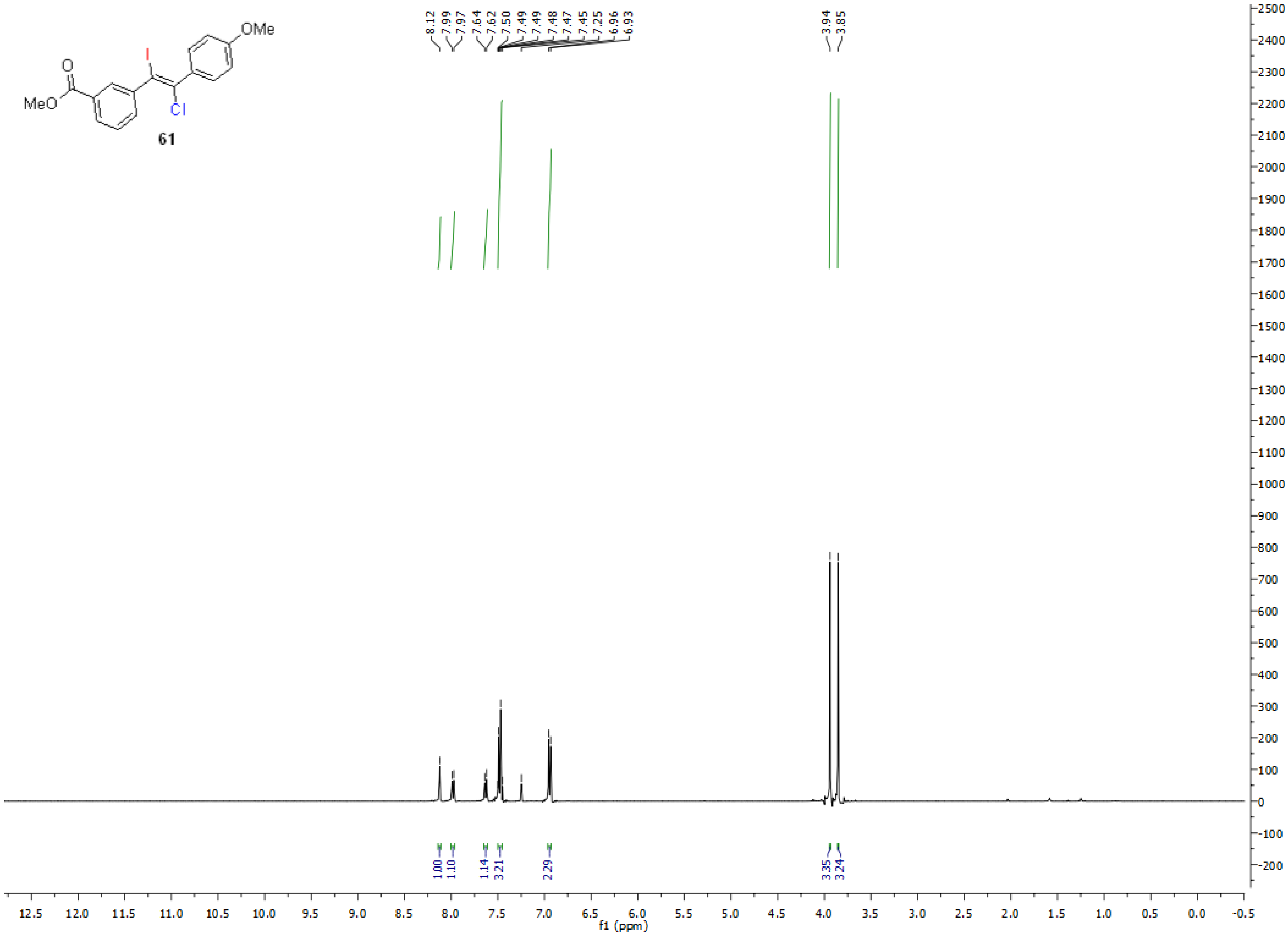


Figure S140. ^{1}H-NMR of **61**



61

Figure S141. ^{13}C-NMR of **61**

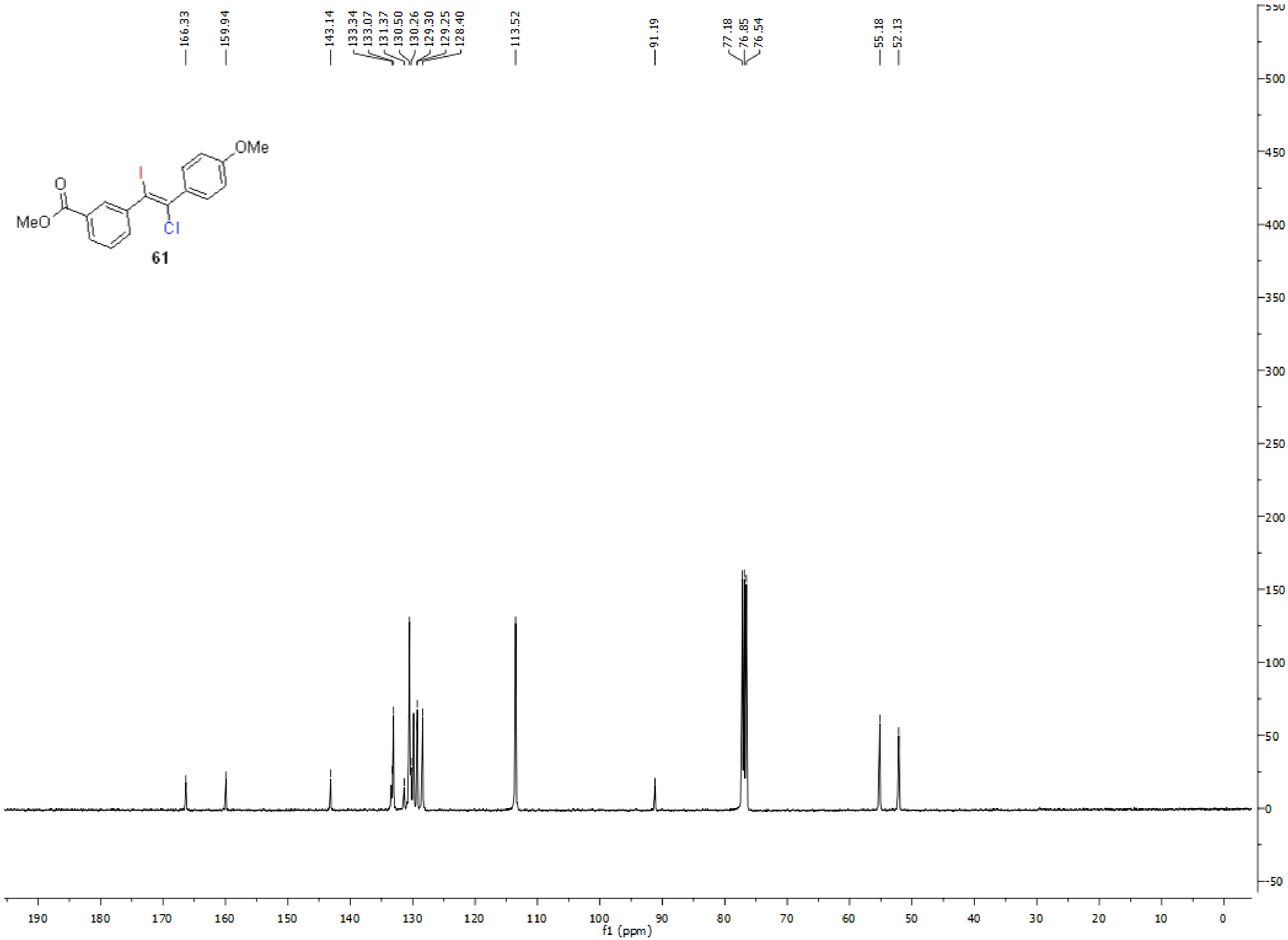


Figure S142. ^{1}H-NMR of **62**

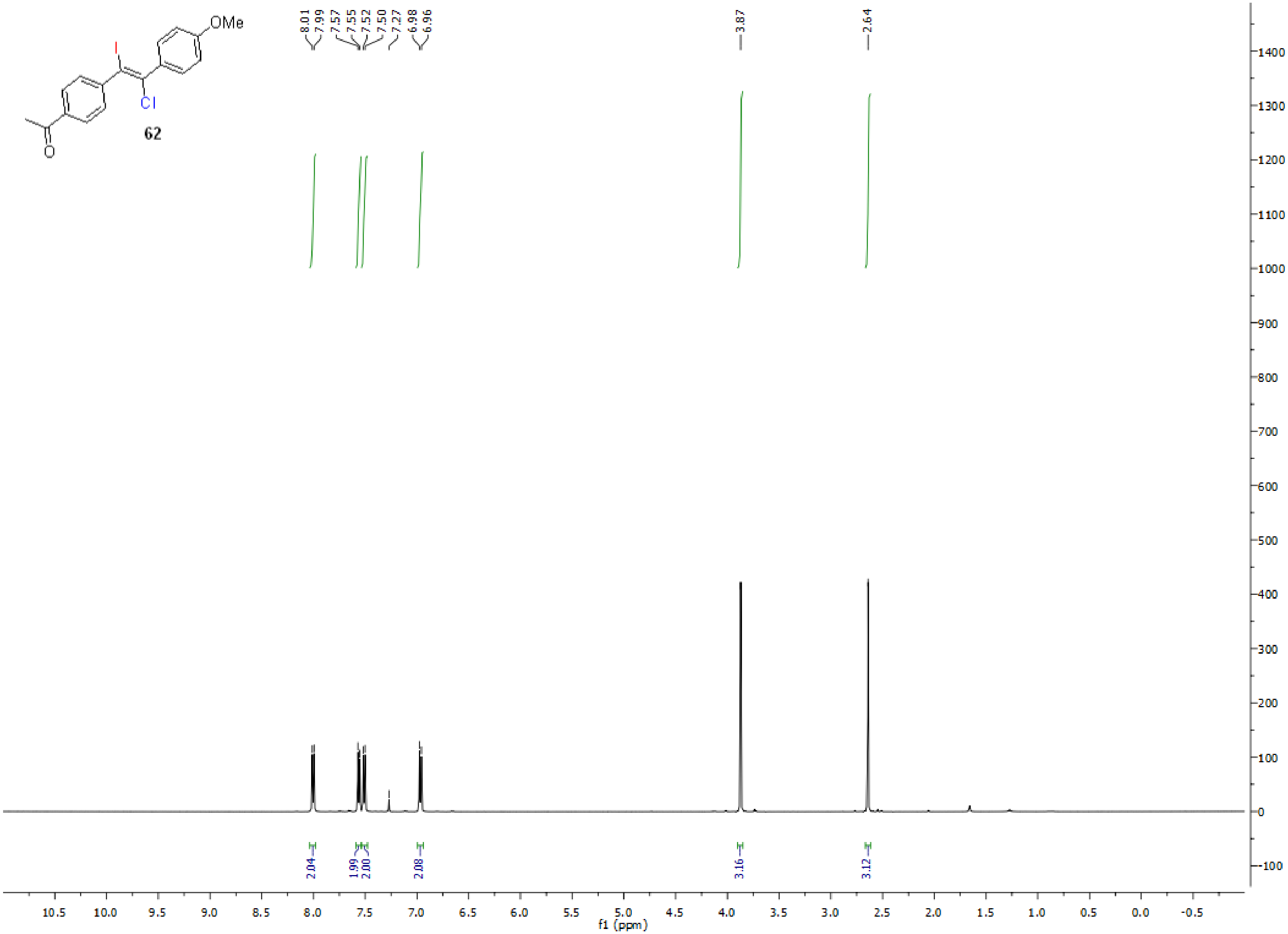


Figure S143. ^{13}C-NMR of **62**

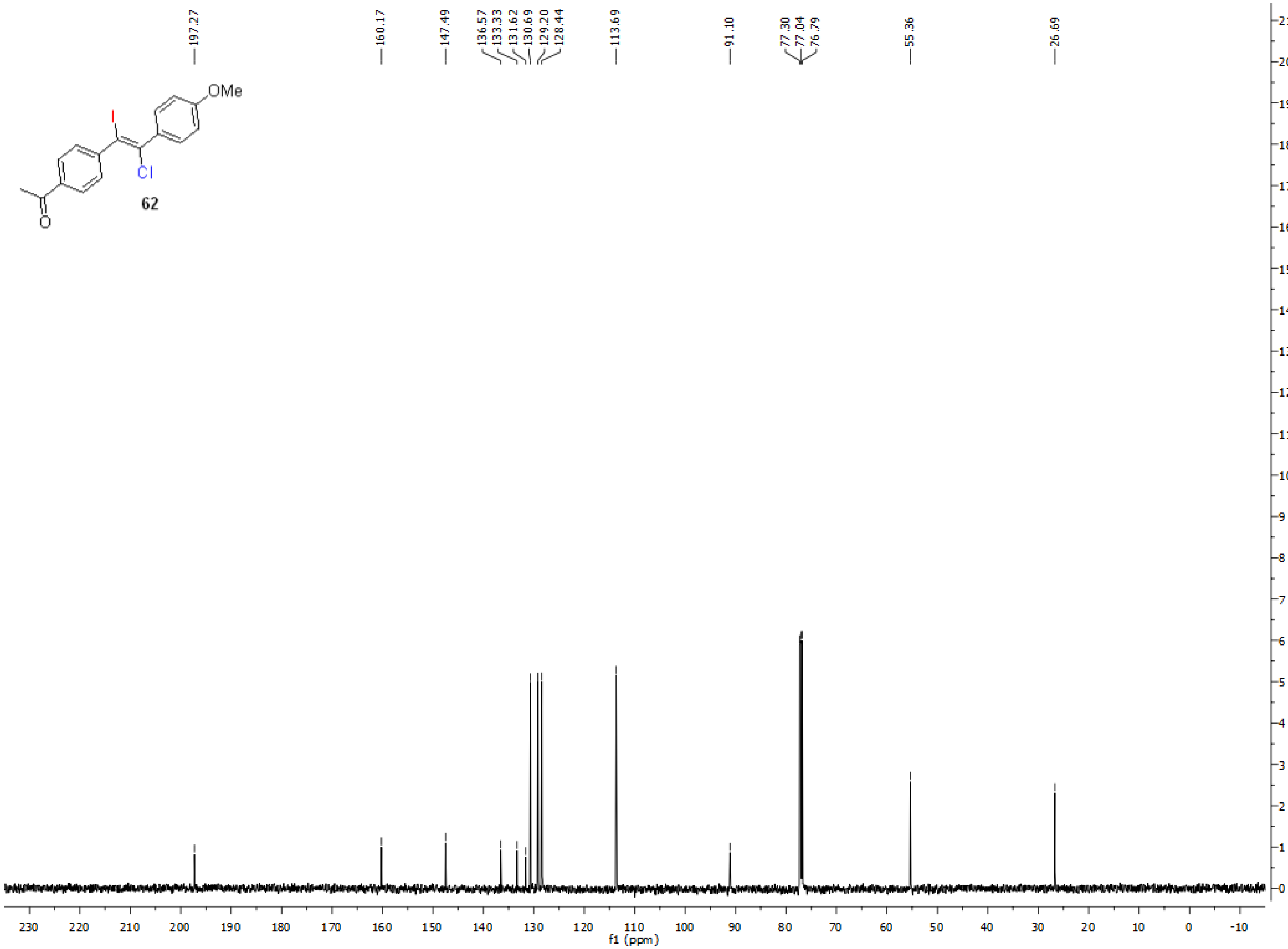
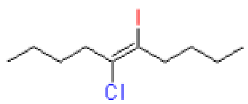


Figure S144. ^{1}H-NMR of **63**



63

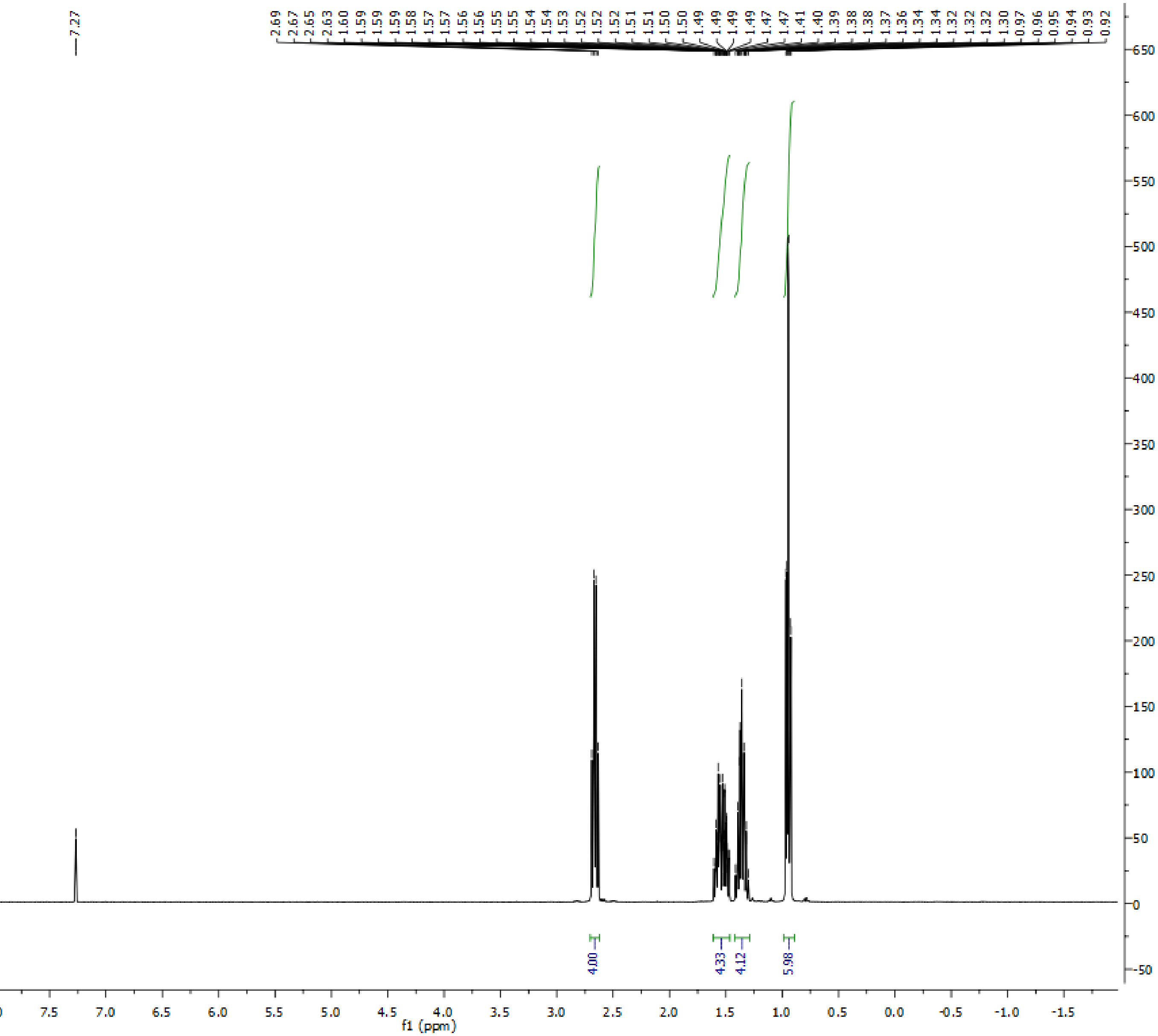
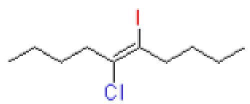


Figure S145. ^{13}C-NMR of **63**



63

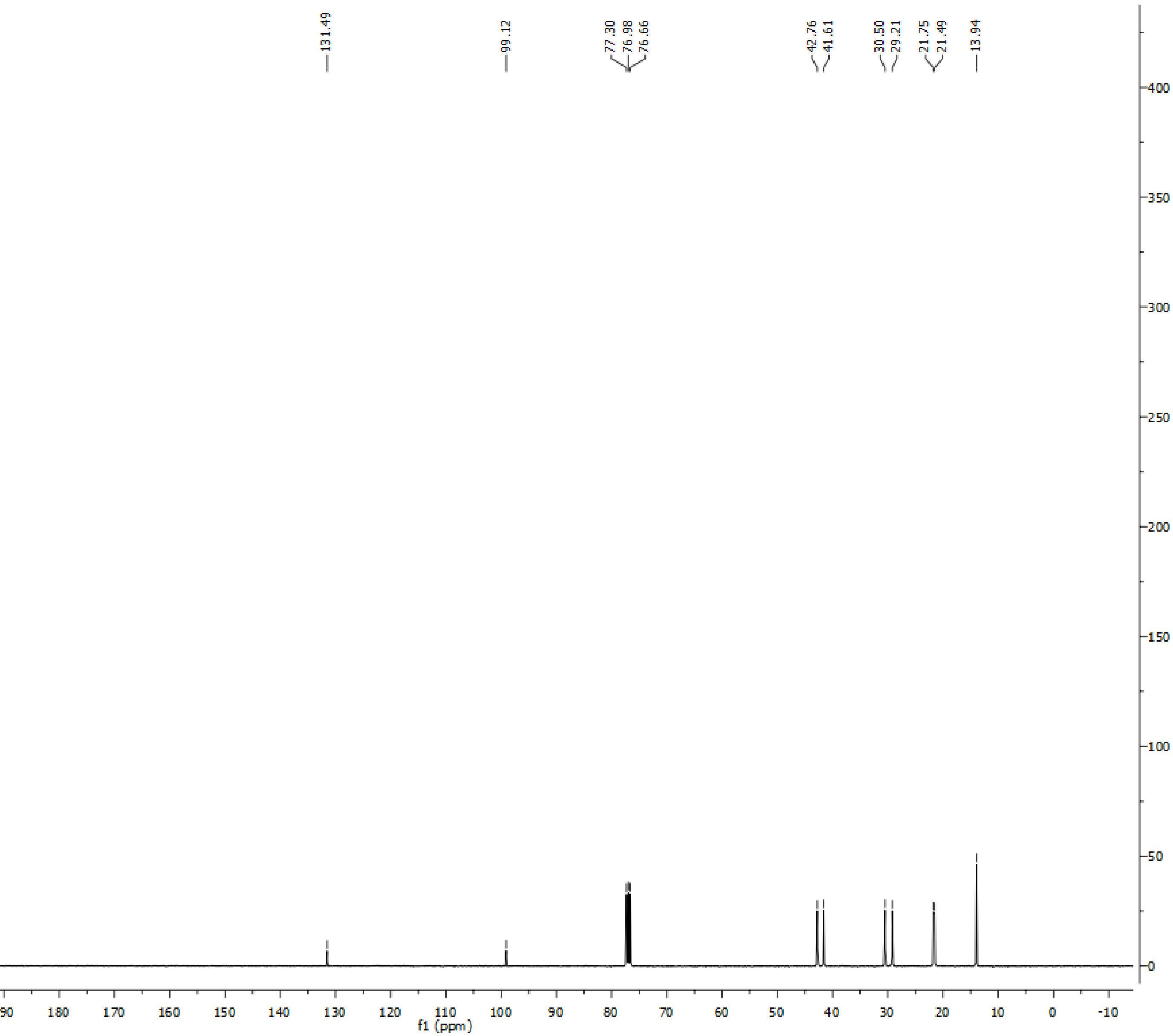
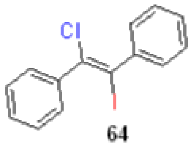


Figure S146. ^{1}H-NMR of **64**



64

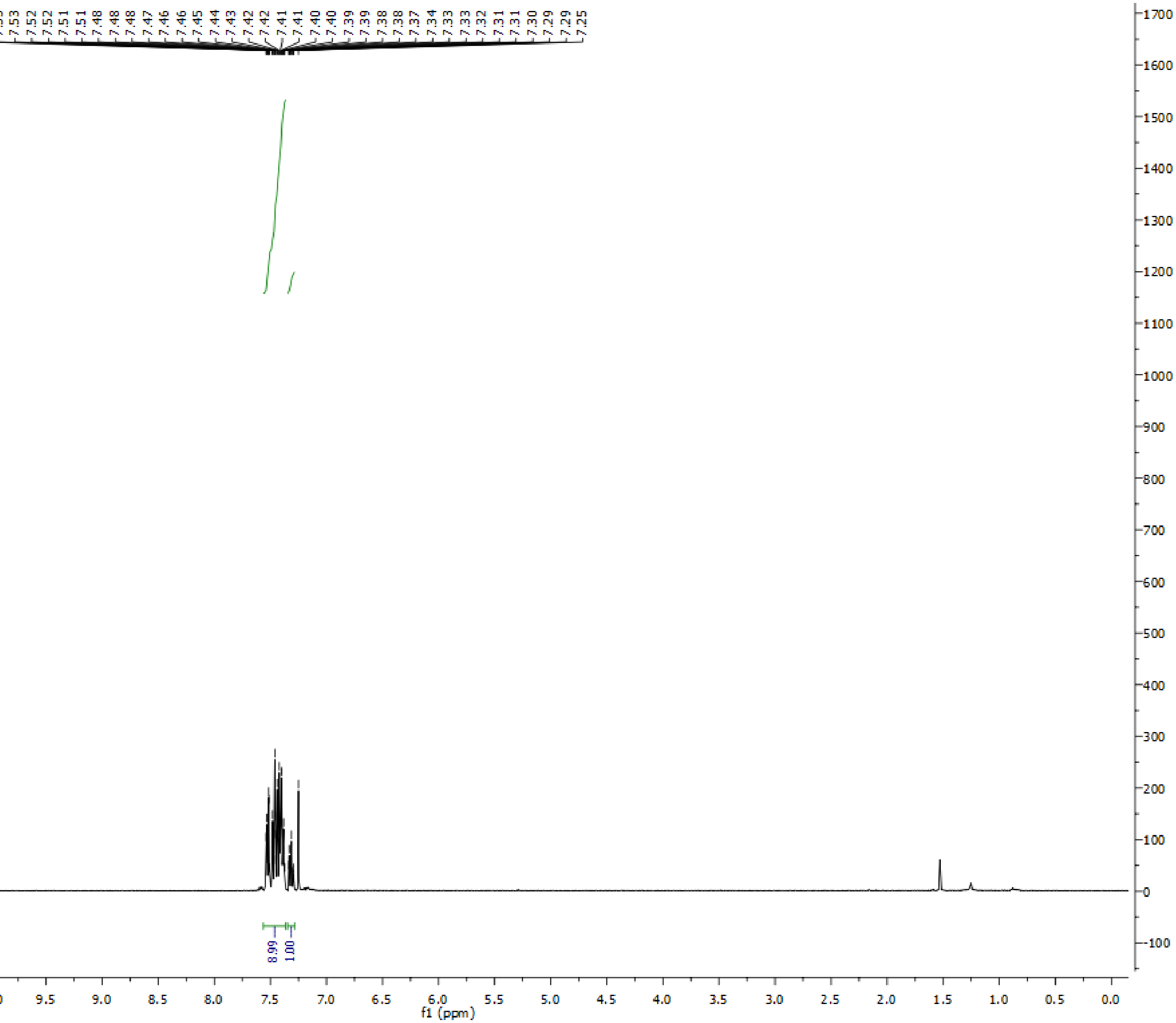
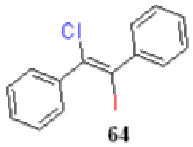


Figure S147. ^{13}C-NMR of **64**



64

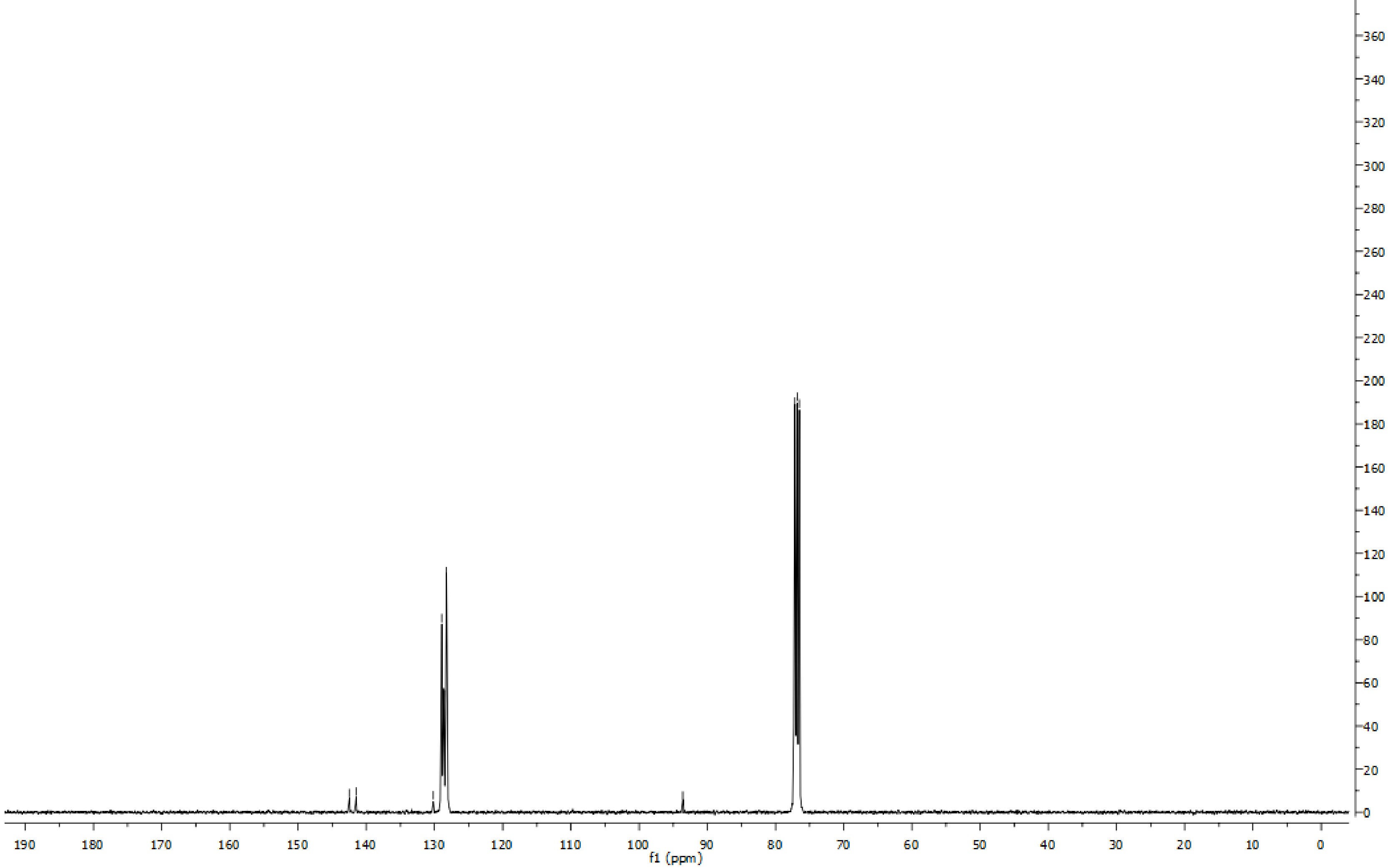


Figure S148. [1]H-NMR of **65**

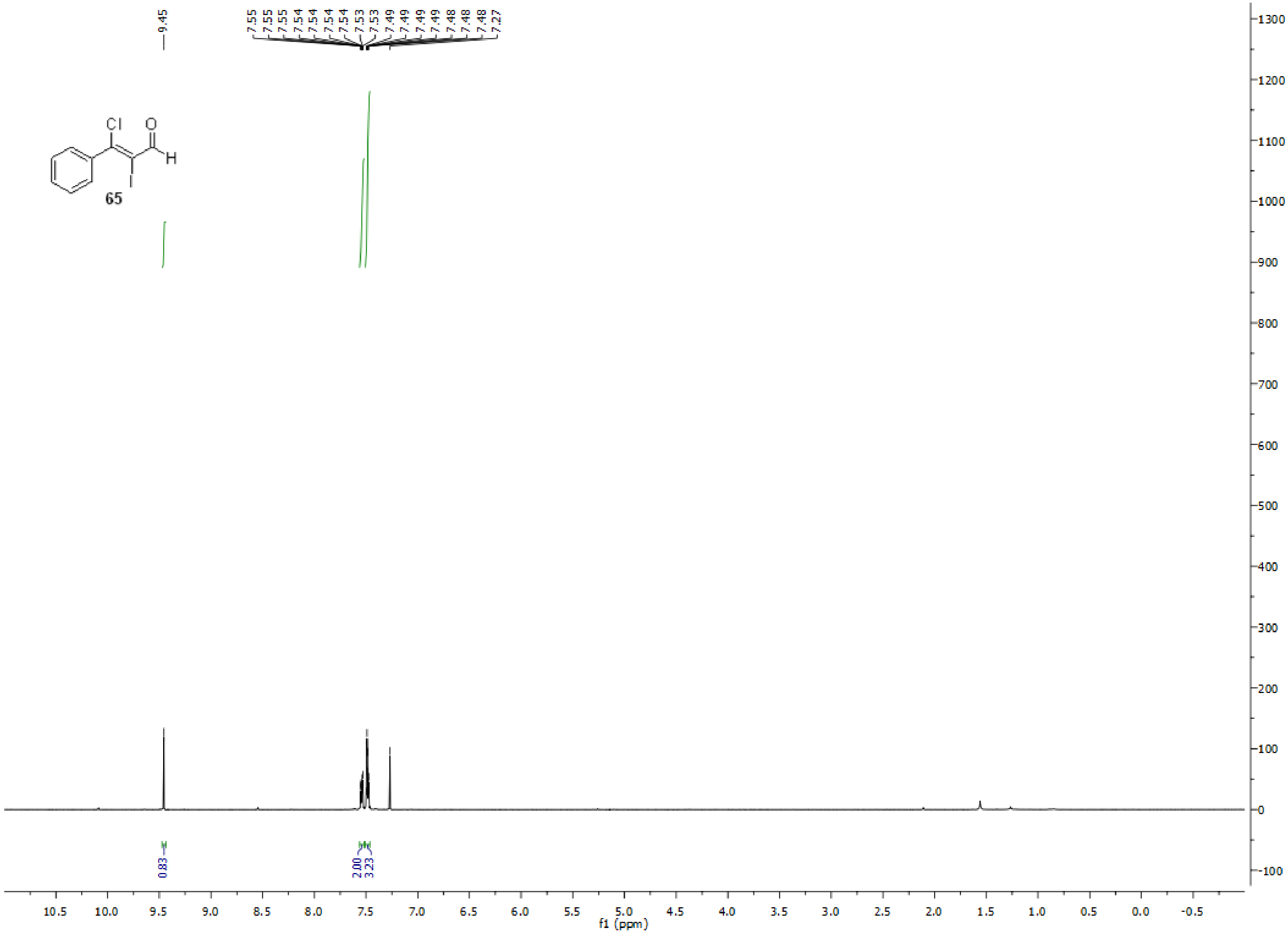


Figure S149. ^{13}C-NMR of **65**

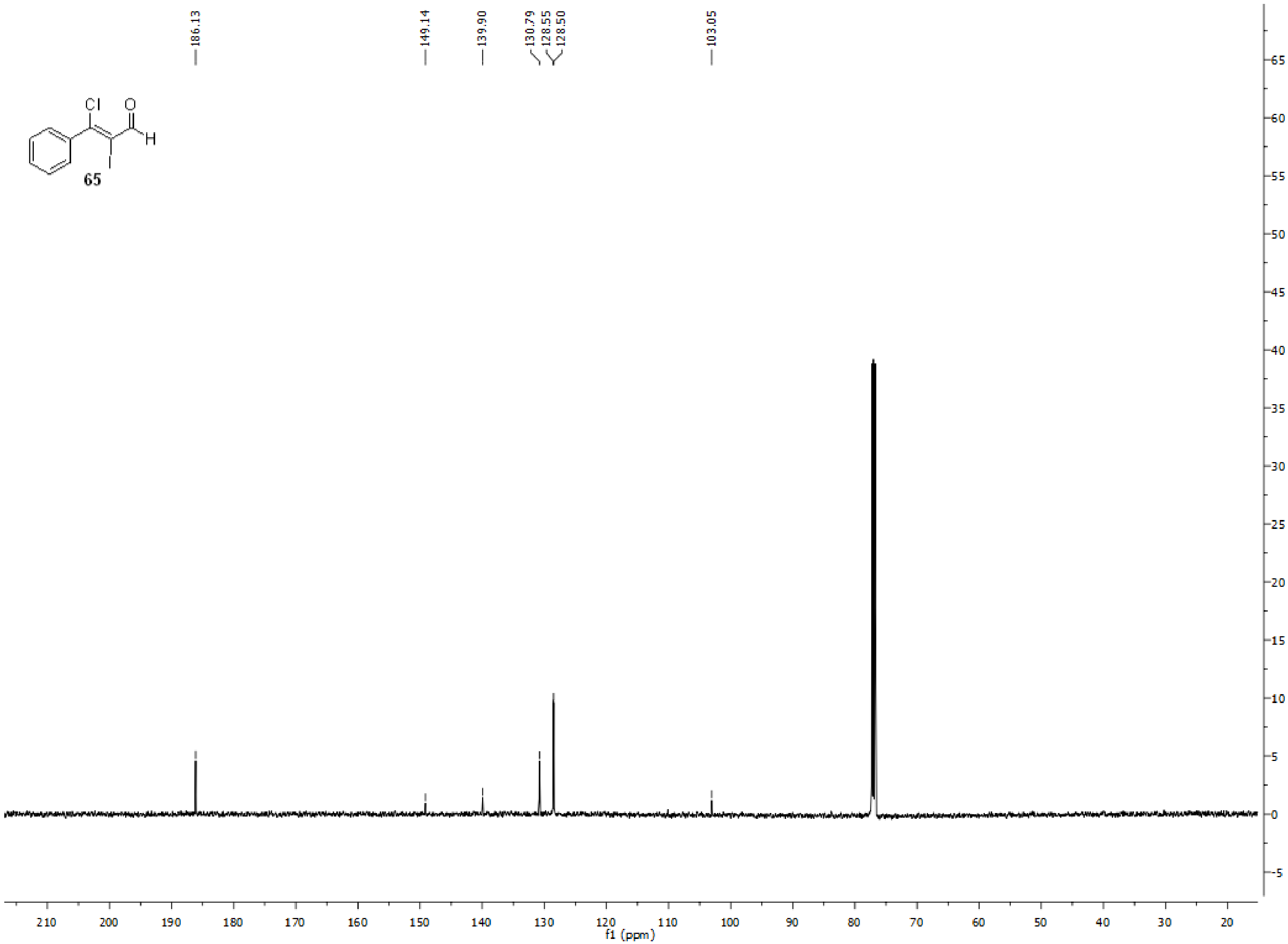


Figure S150. ^{1}H-NMR of **66**

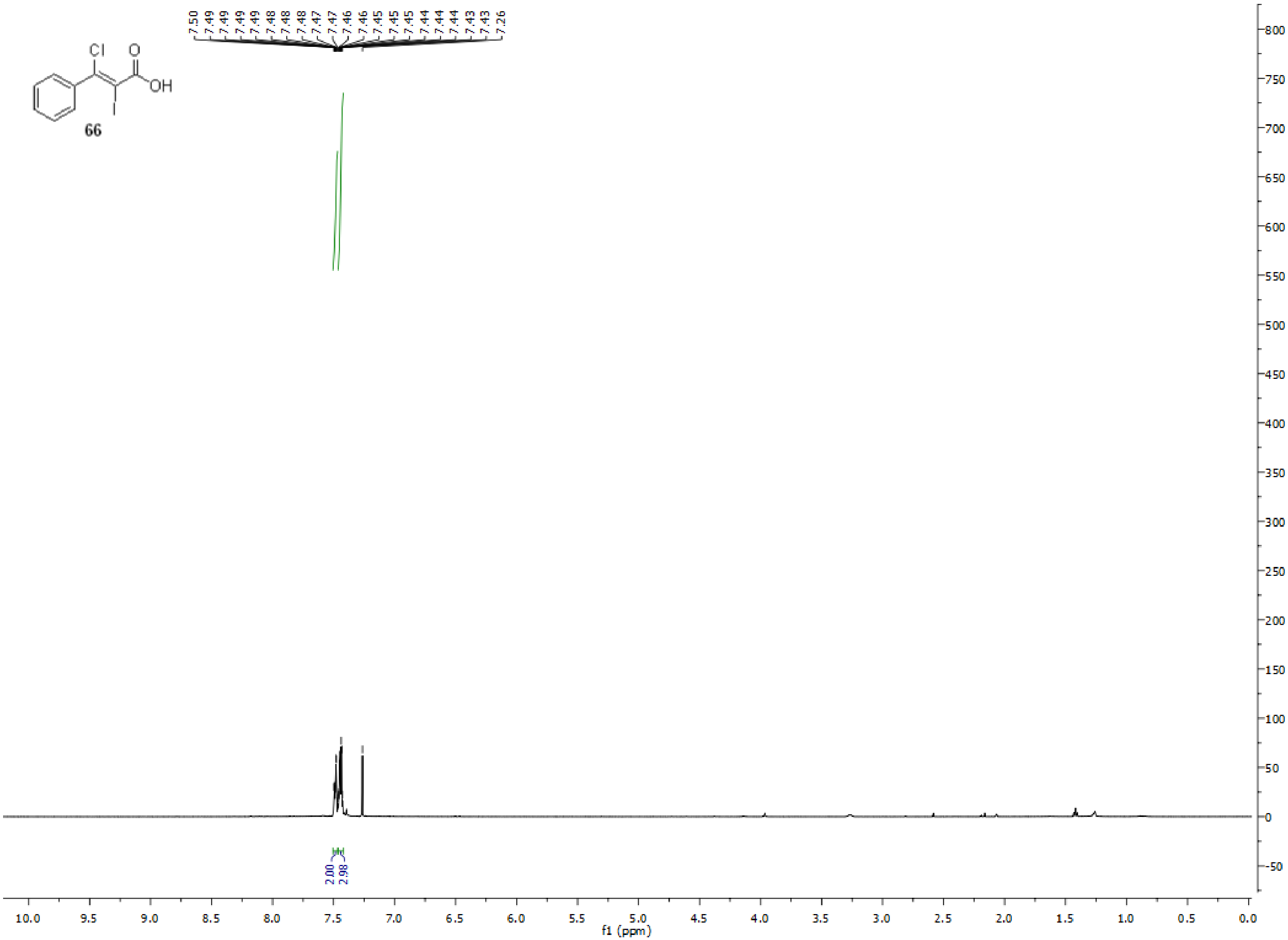


Figure S151. ^{13}C-NMR of **66**

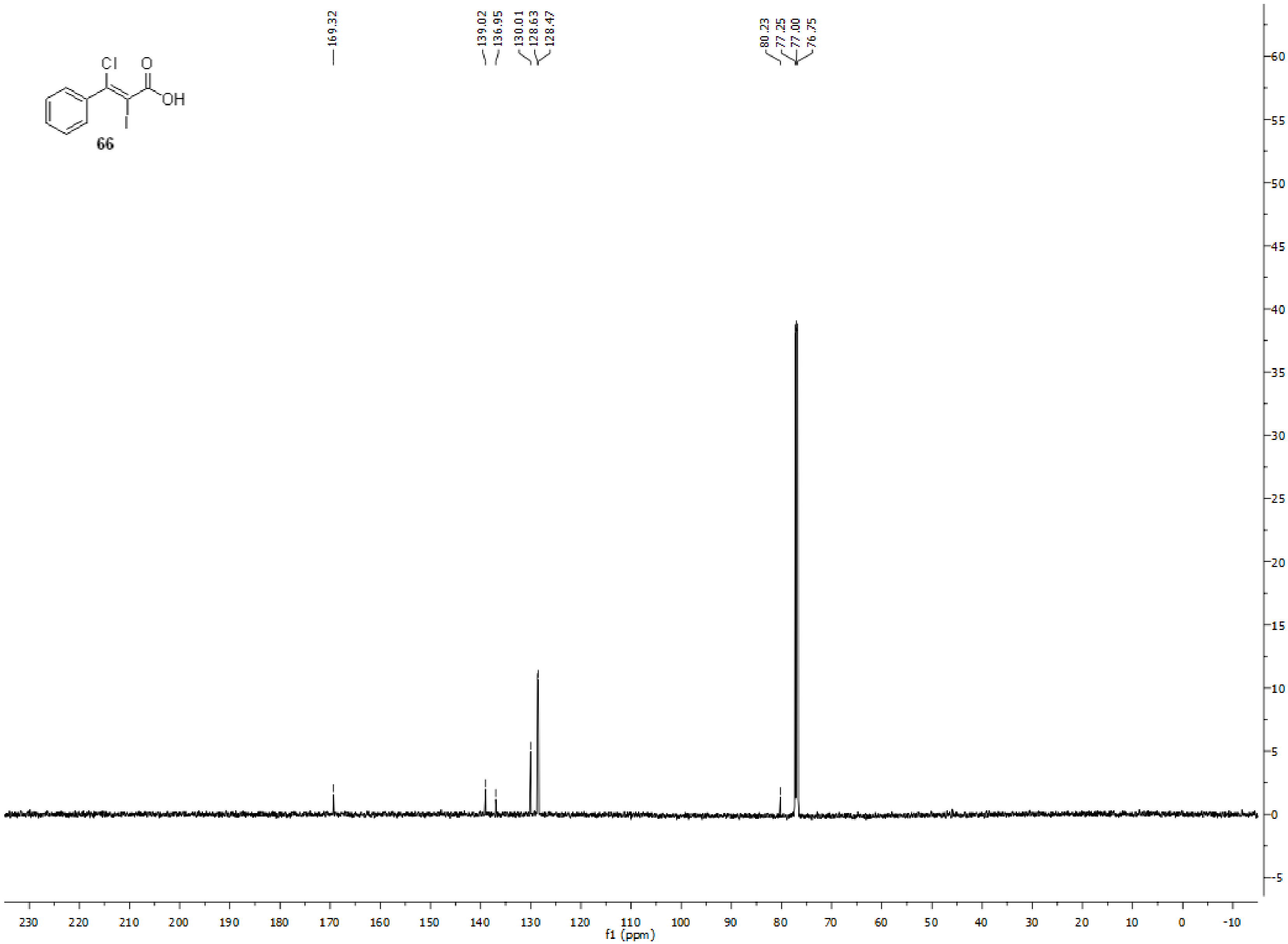
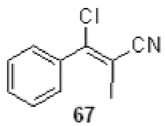


Figure S152. ^{1}H-NMR of **67**



67

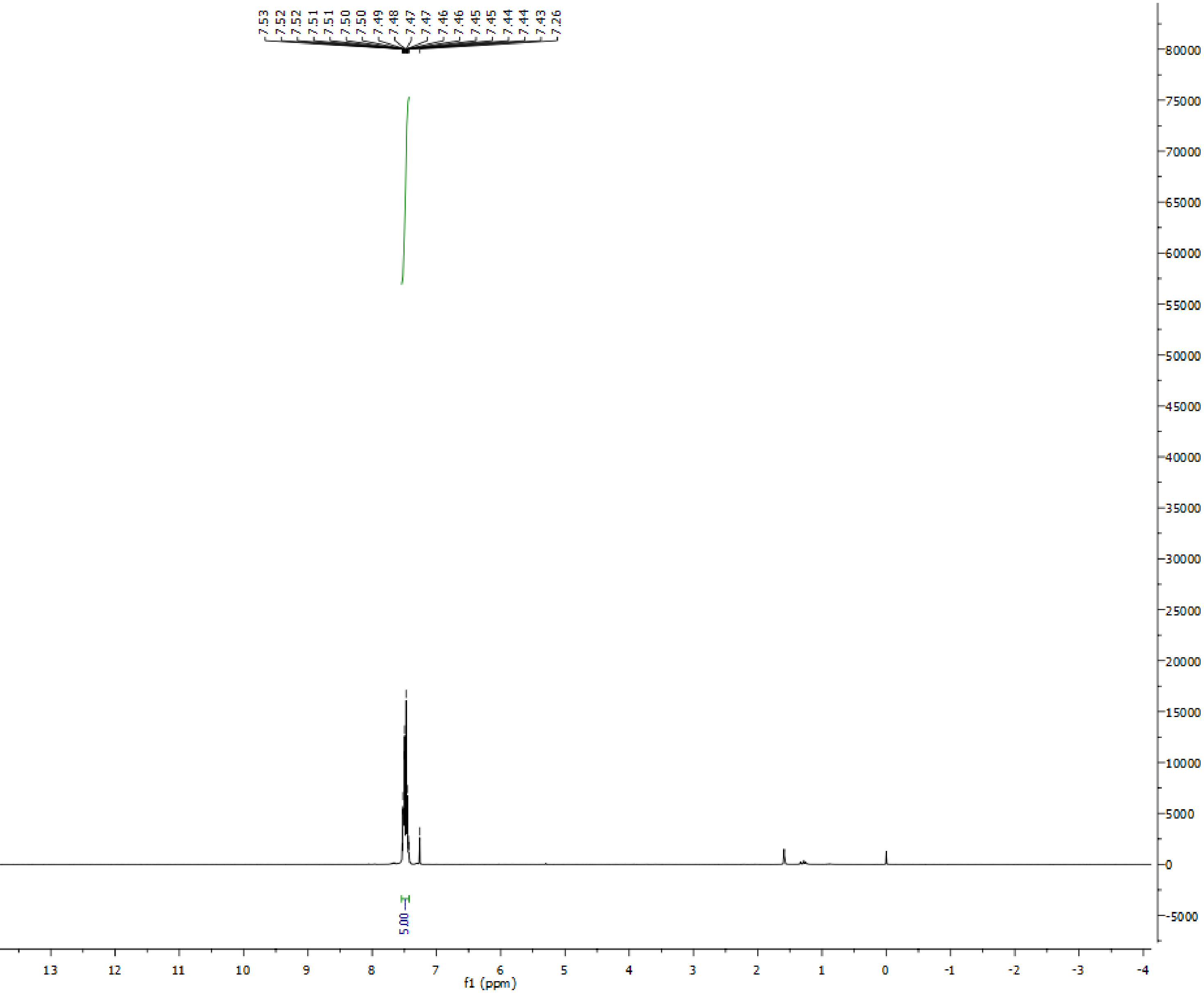


Figure S153. ^{13}C-NMR of **67**

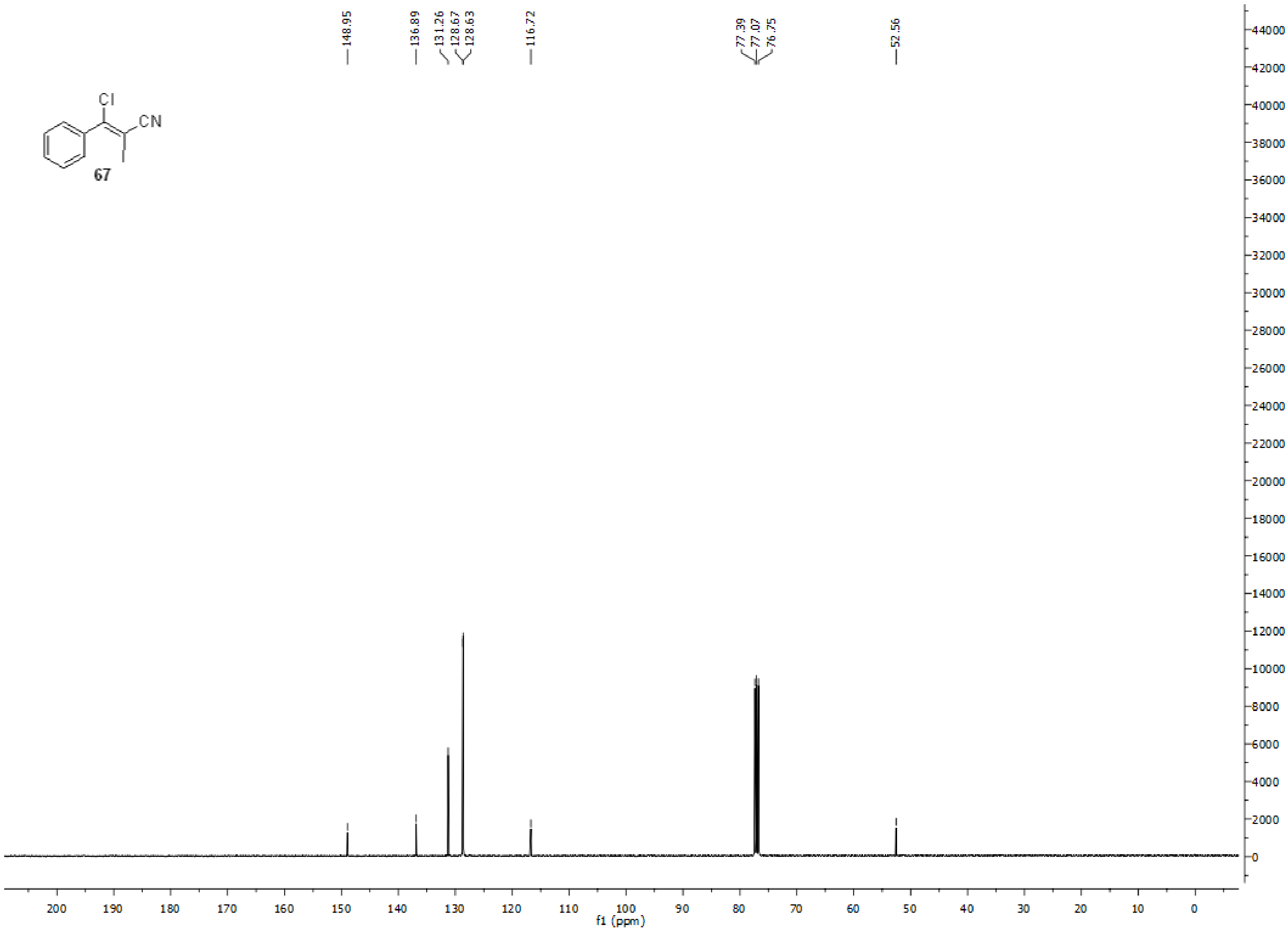
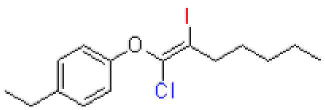


Figure S154. ^{1}H-NMR of **68**



68

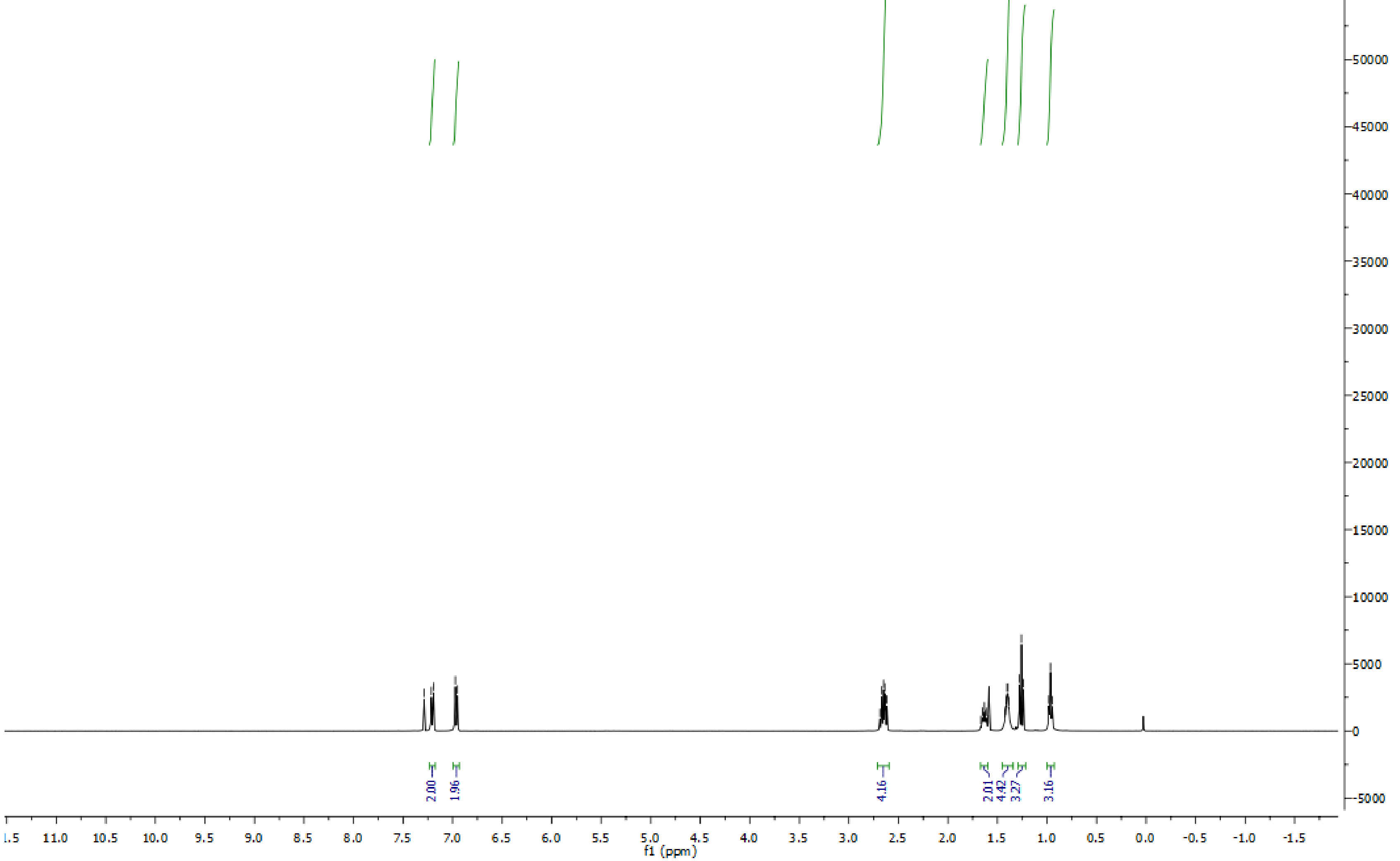


Figure S155. ^{13}C-NMR of **68**

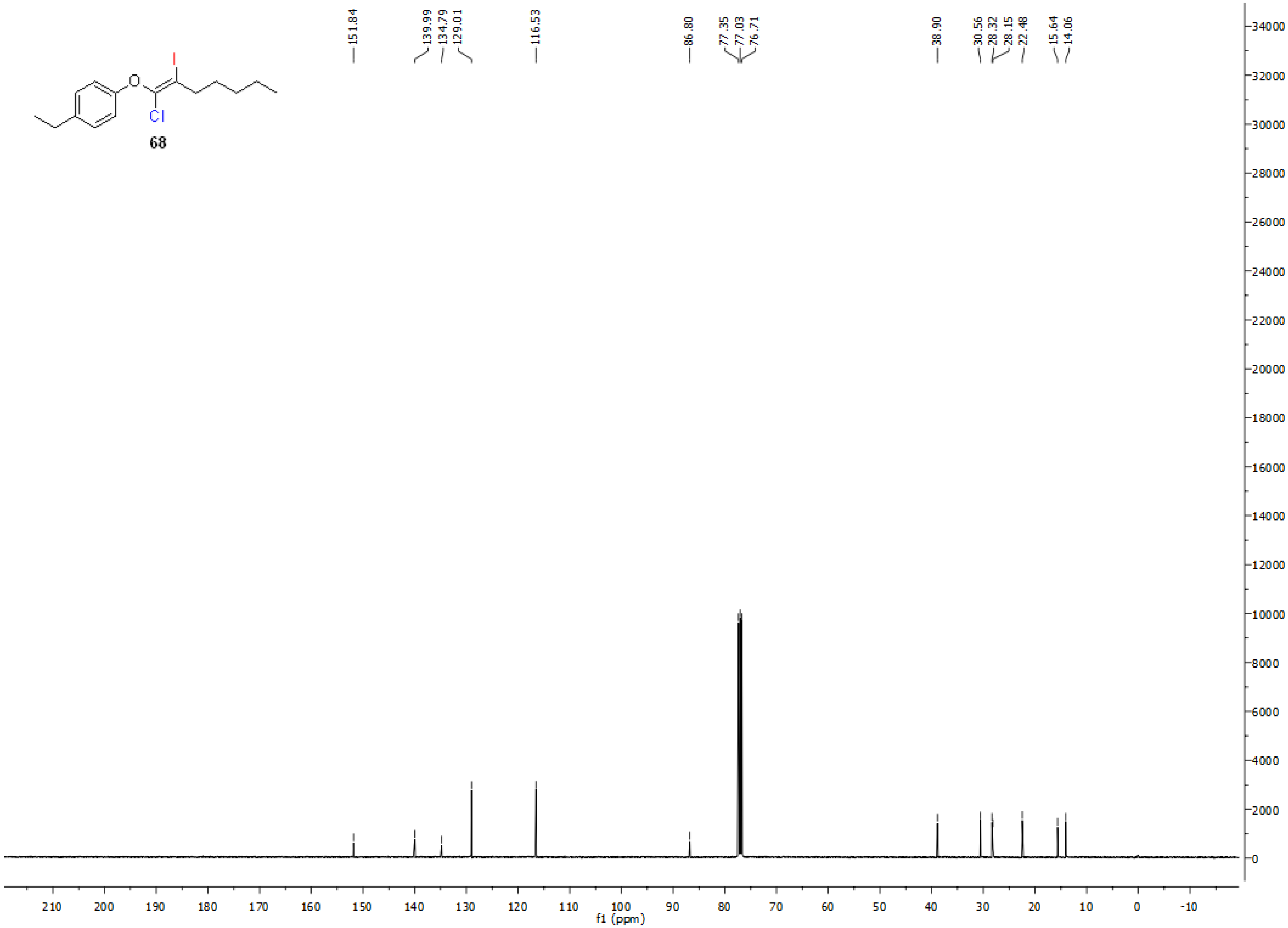
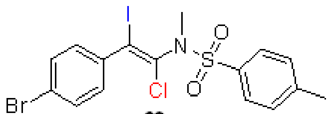


Figure S156. ^{1}H-NMR of **69**



69

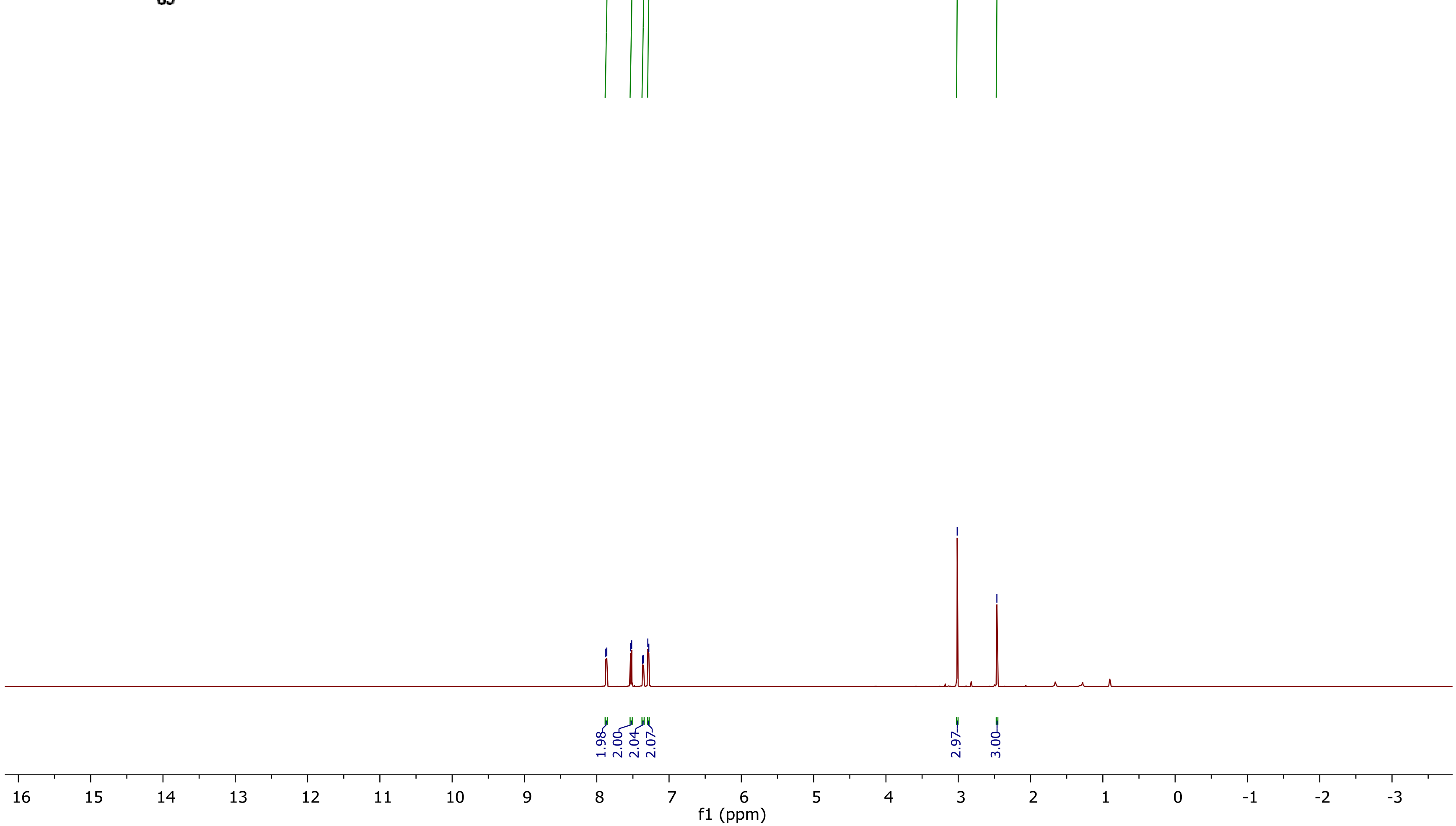
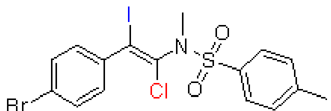


Figure S157. ^{13}C-NMR of **69**



69

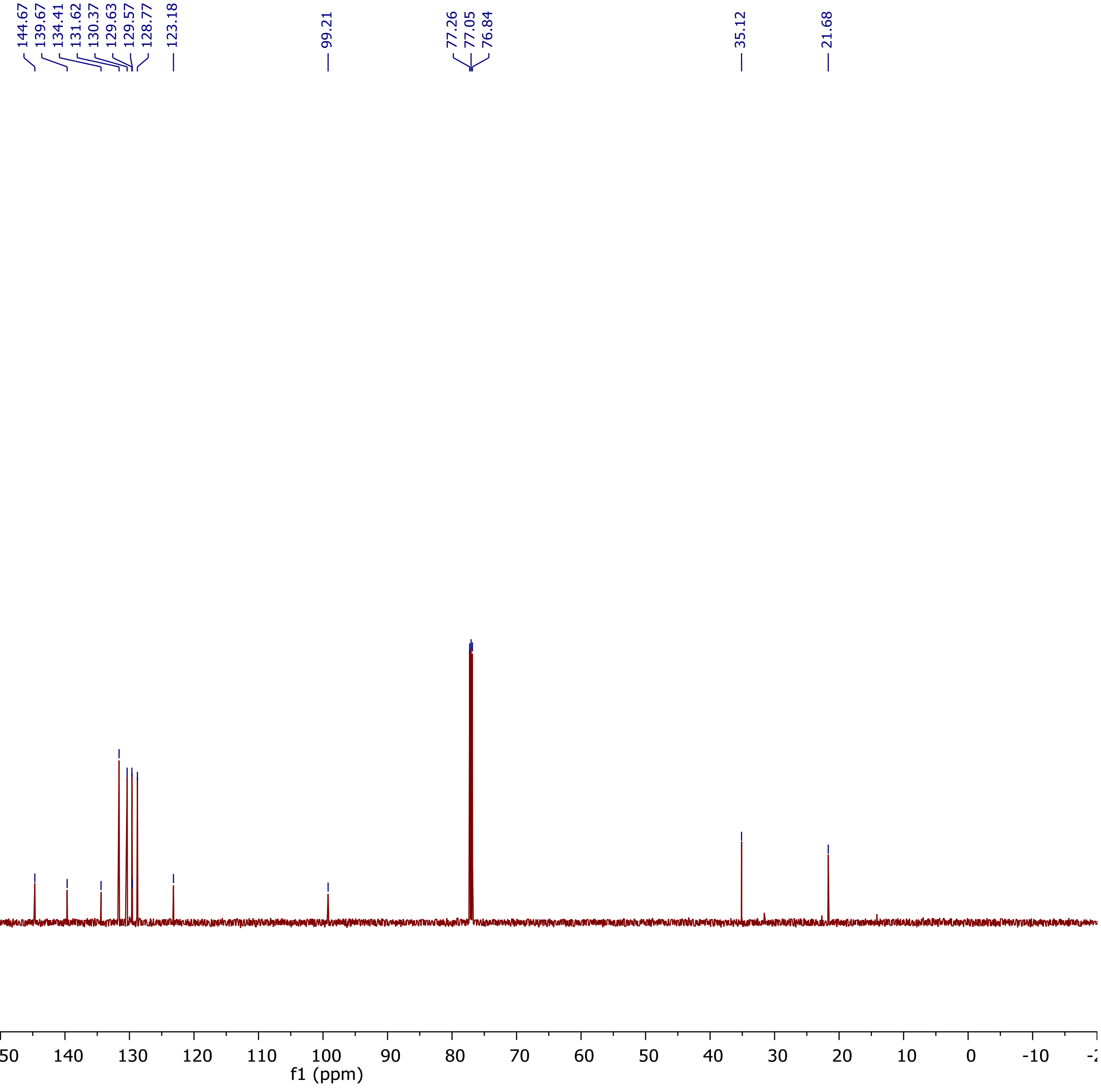


Figure S158. ^{1}H-NMR of **70**

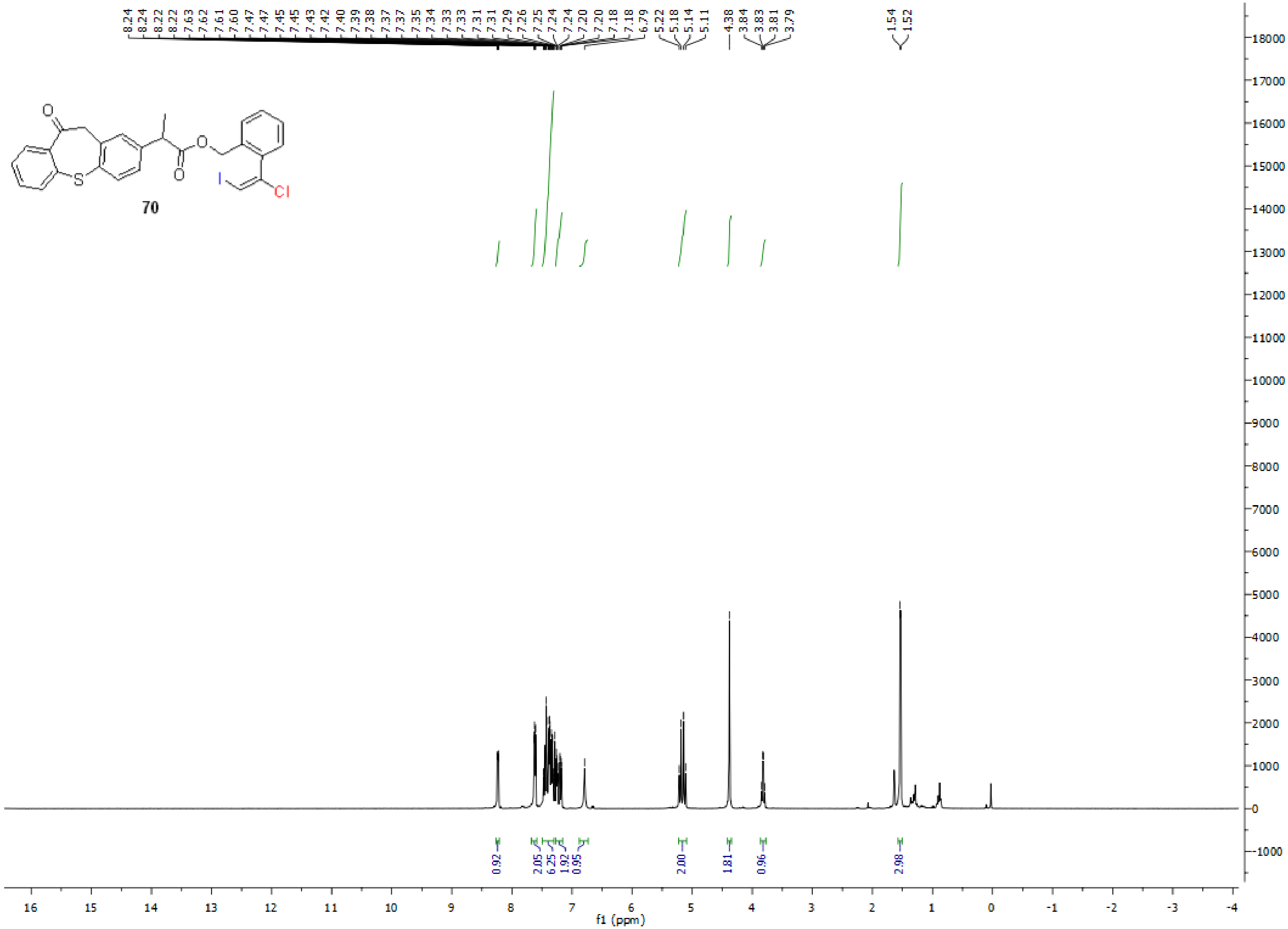


Figure S159. ^{13}C-NMR of **70**

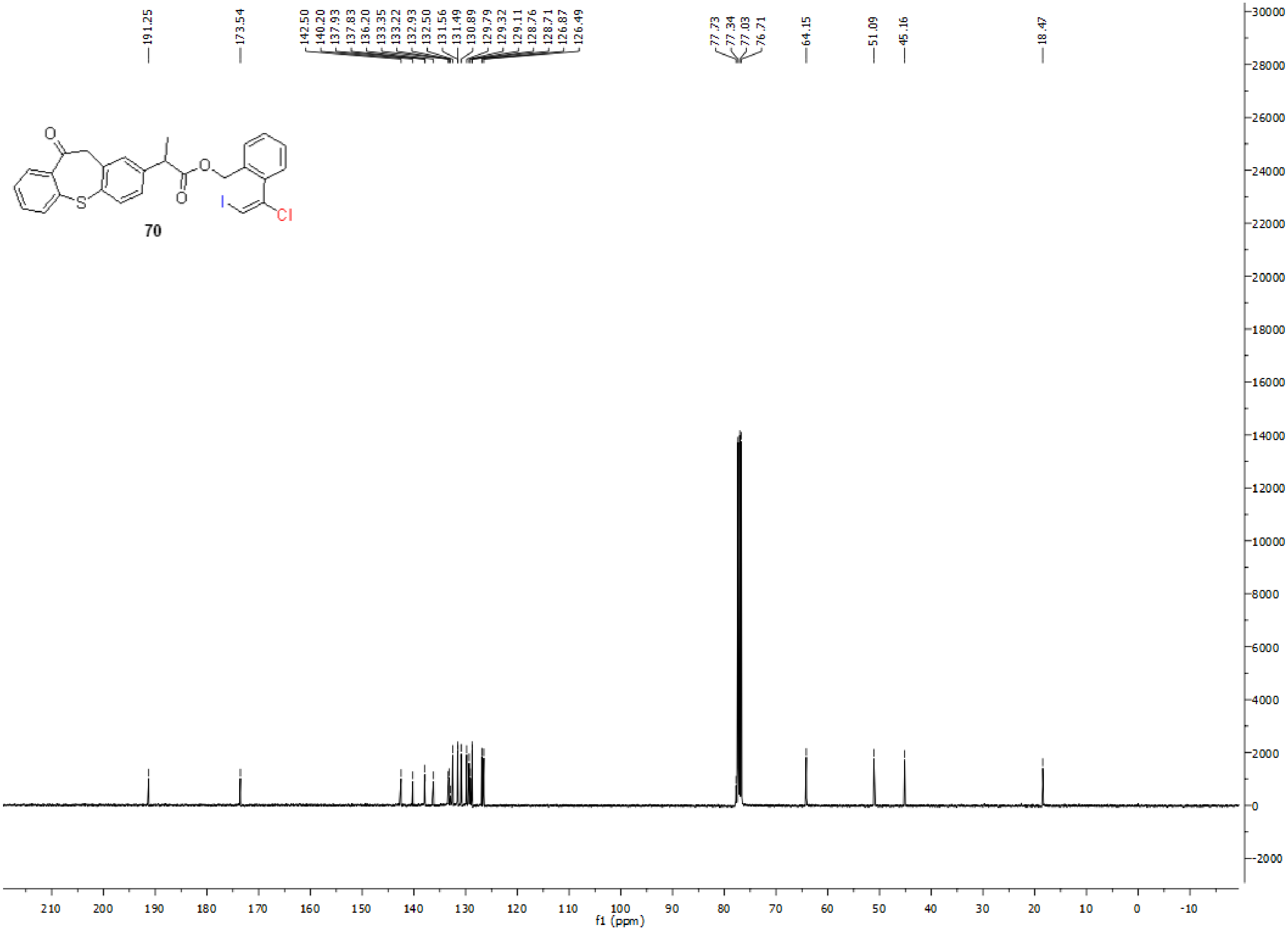
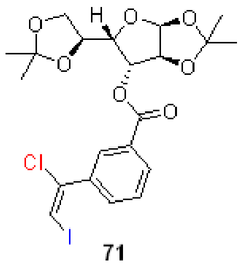


Figure S160. [1]H-NMR of **71**



71

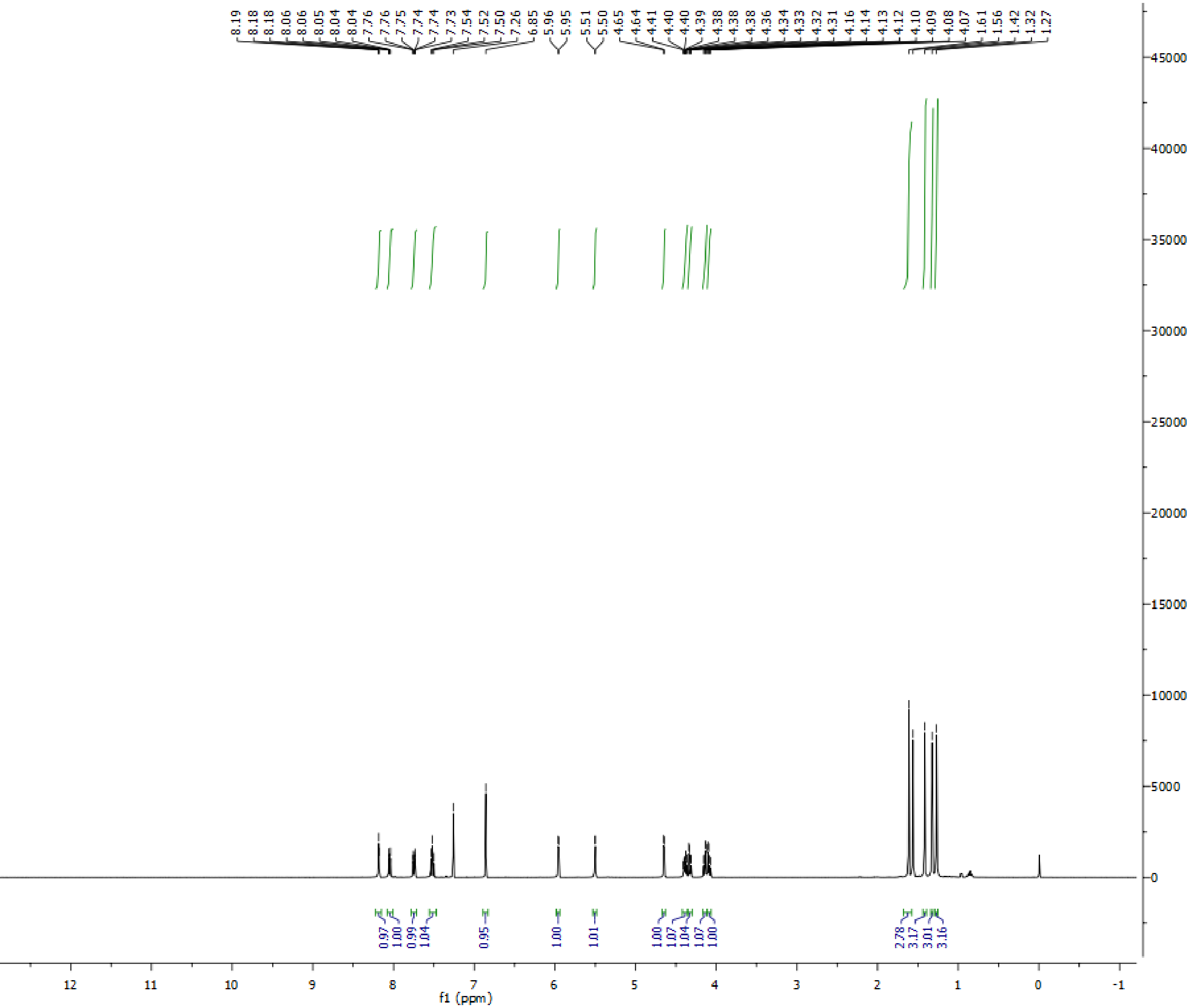
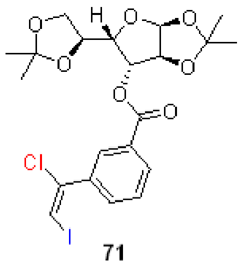


Figure S161. ^{13}C-NMR of **71**



71

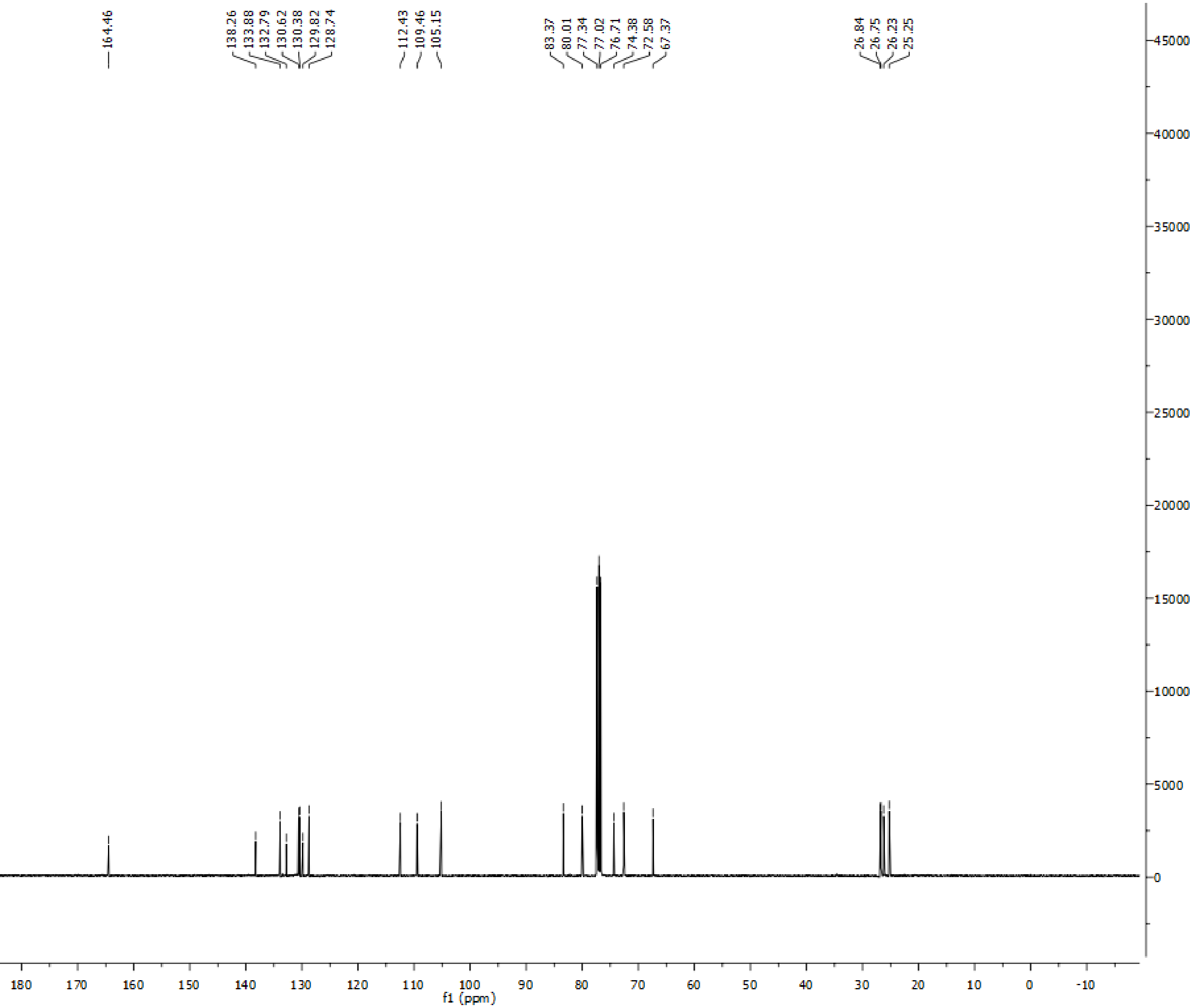


Figure S162. ^{1}H-NMR of **72**

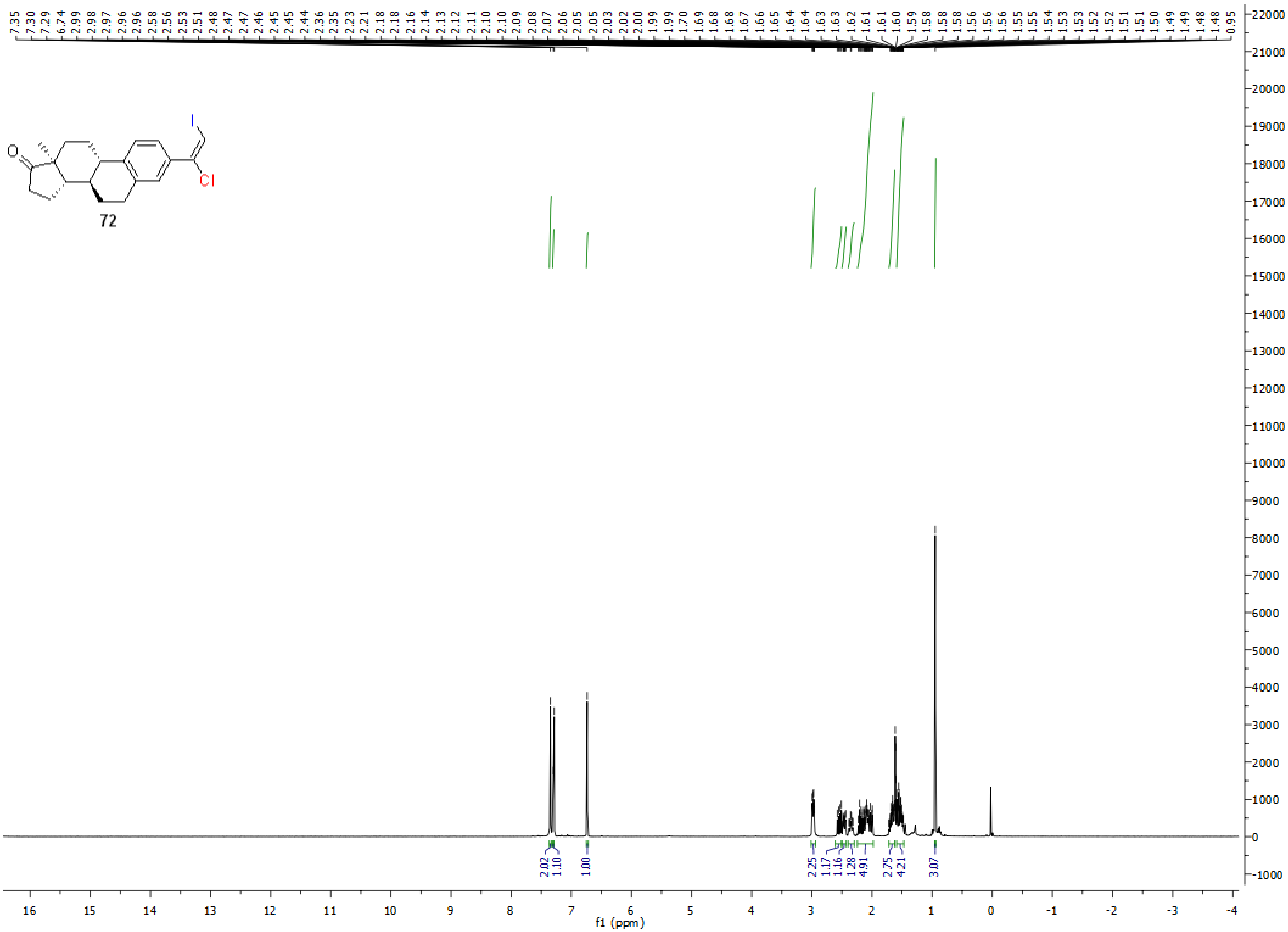


Figure S163. ^{13}C-NMR of **72**

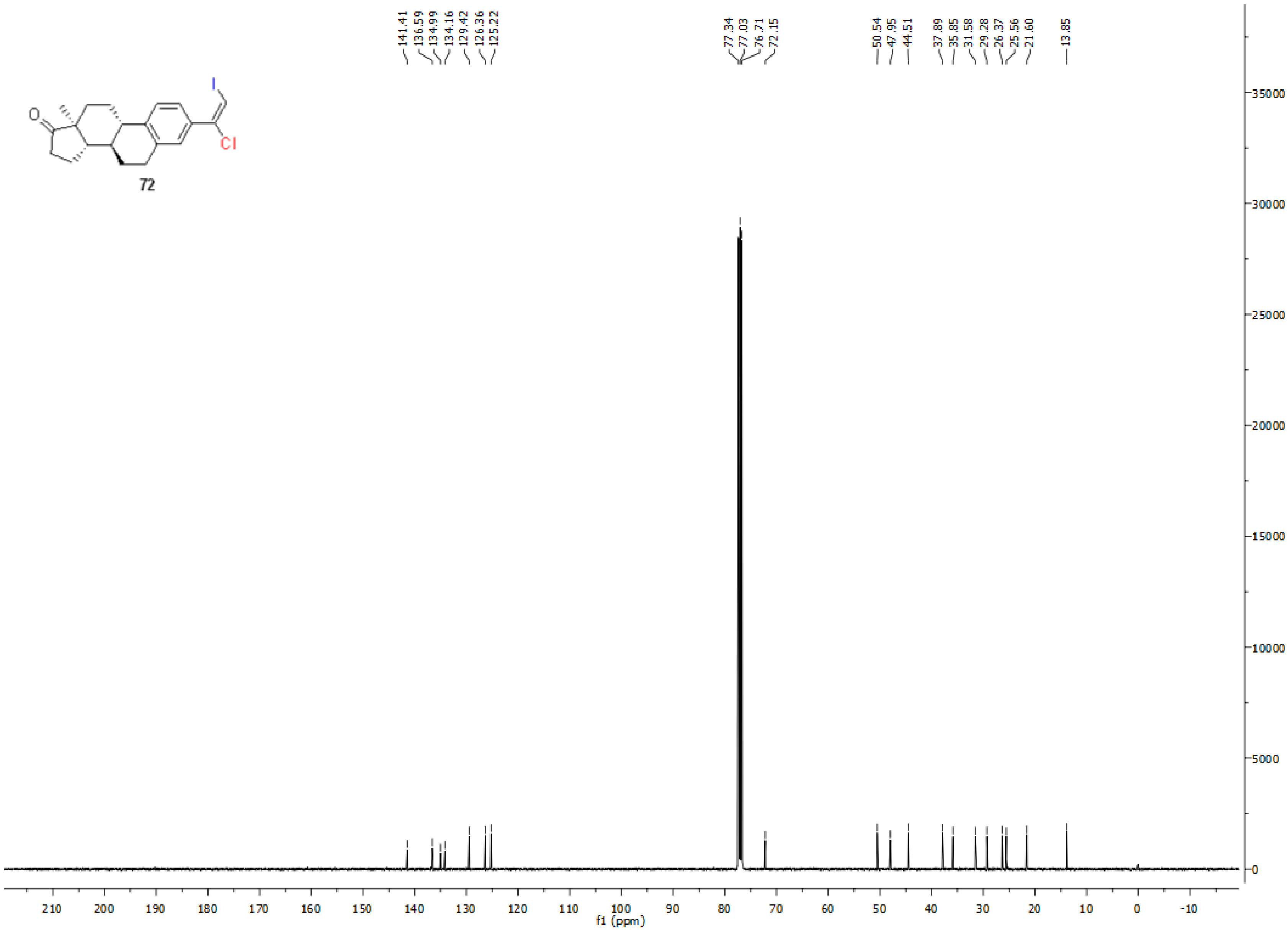


Figure S164. ^{1}H-NMR of **73**

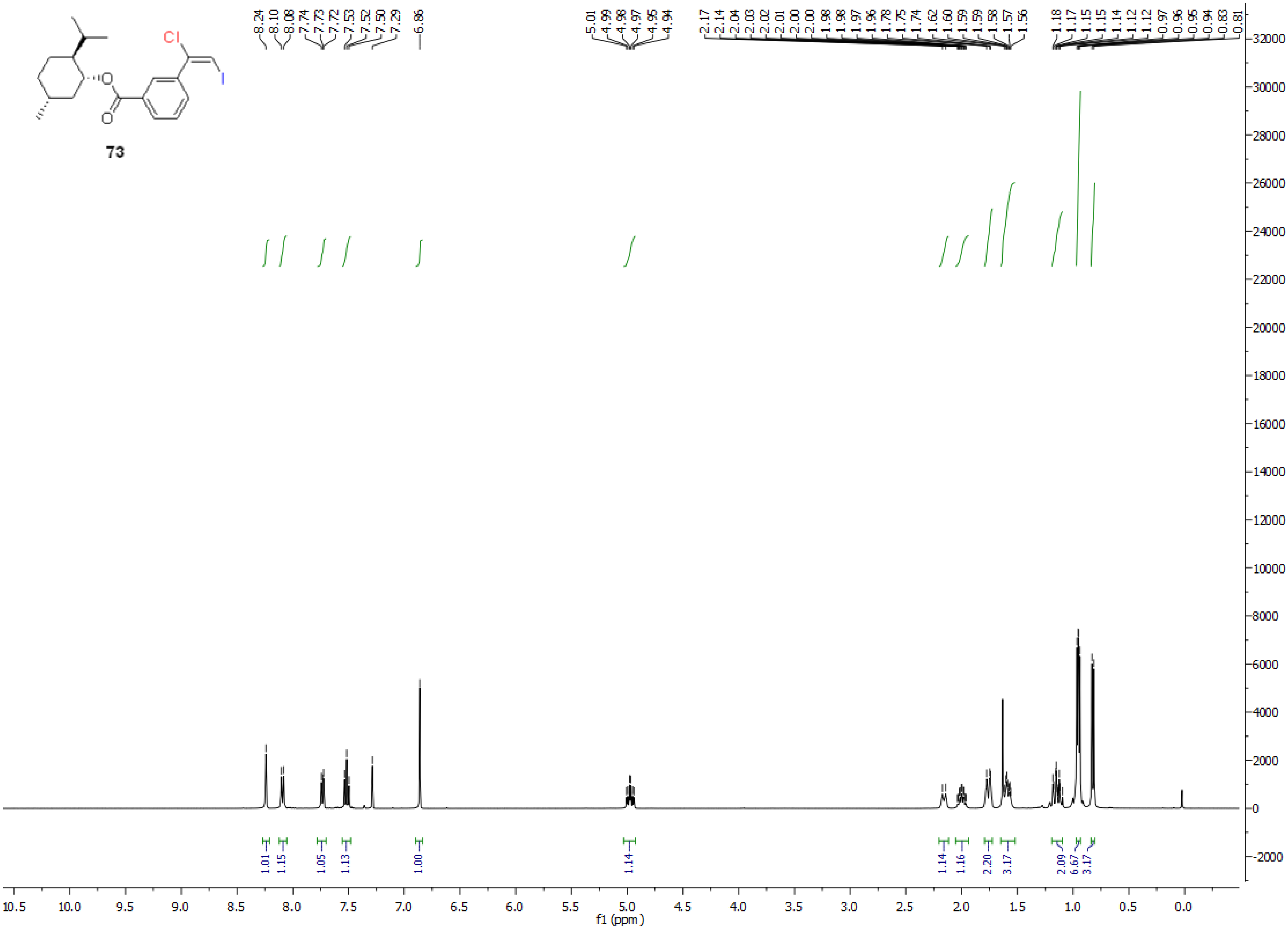
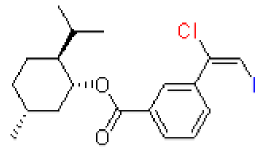


Figure S165. ^{13}C-NMR of



73

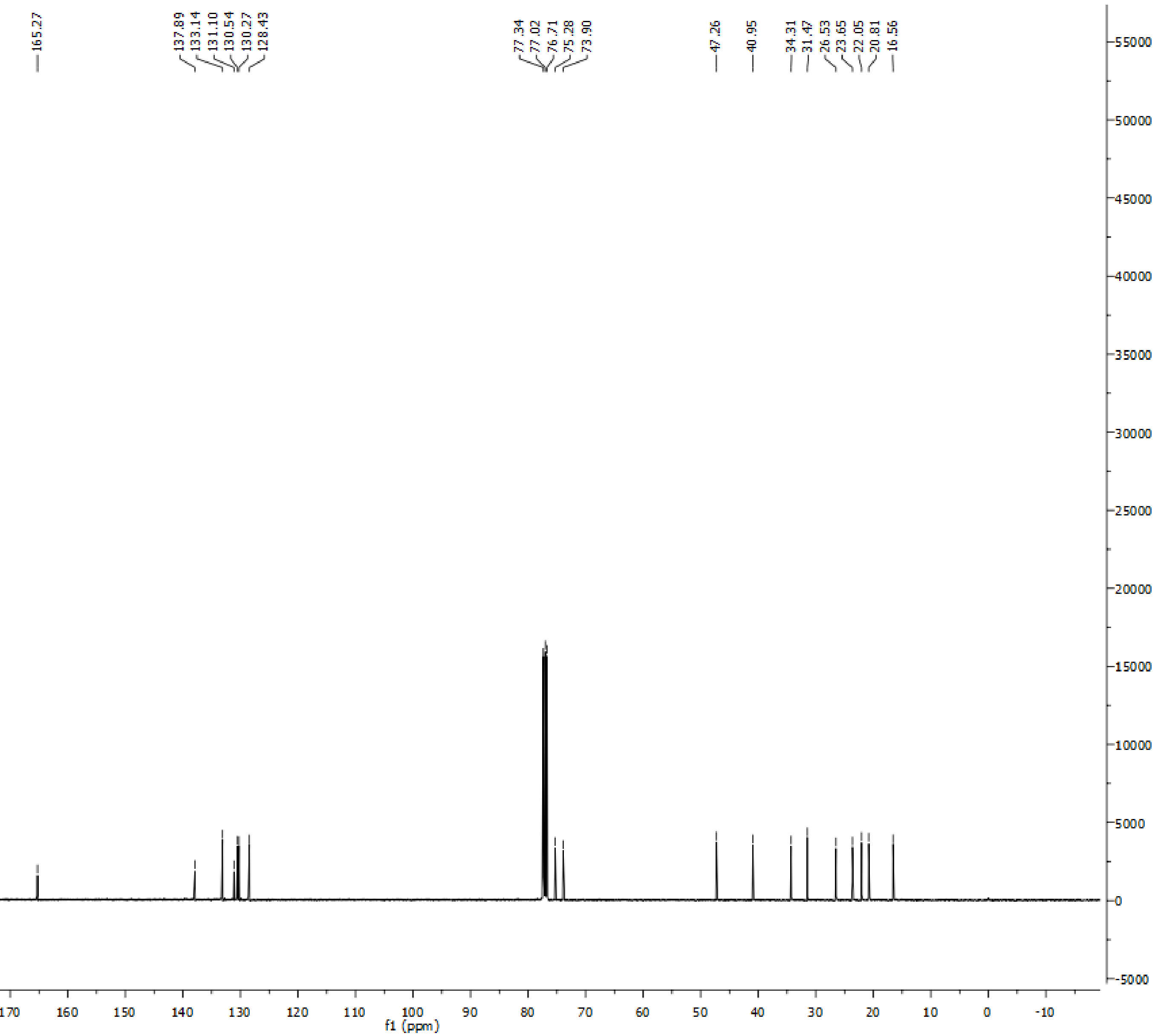
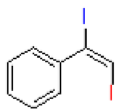


Figure S166. ^{1}H-NMR of **74**



74

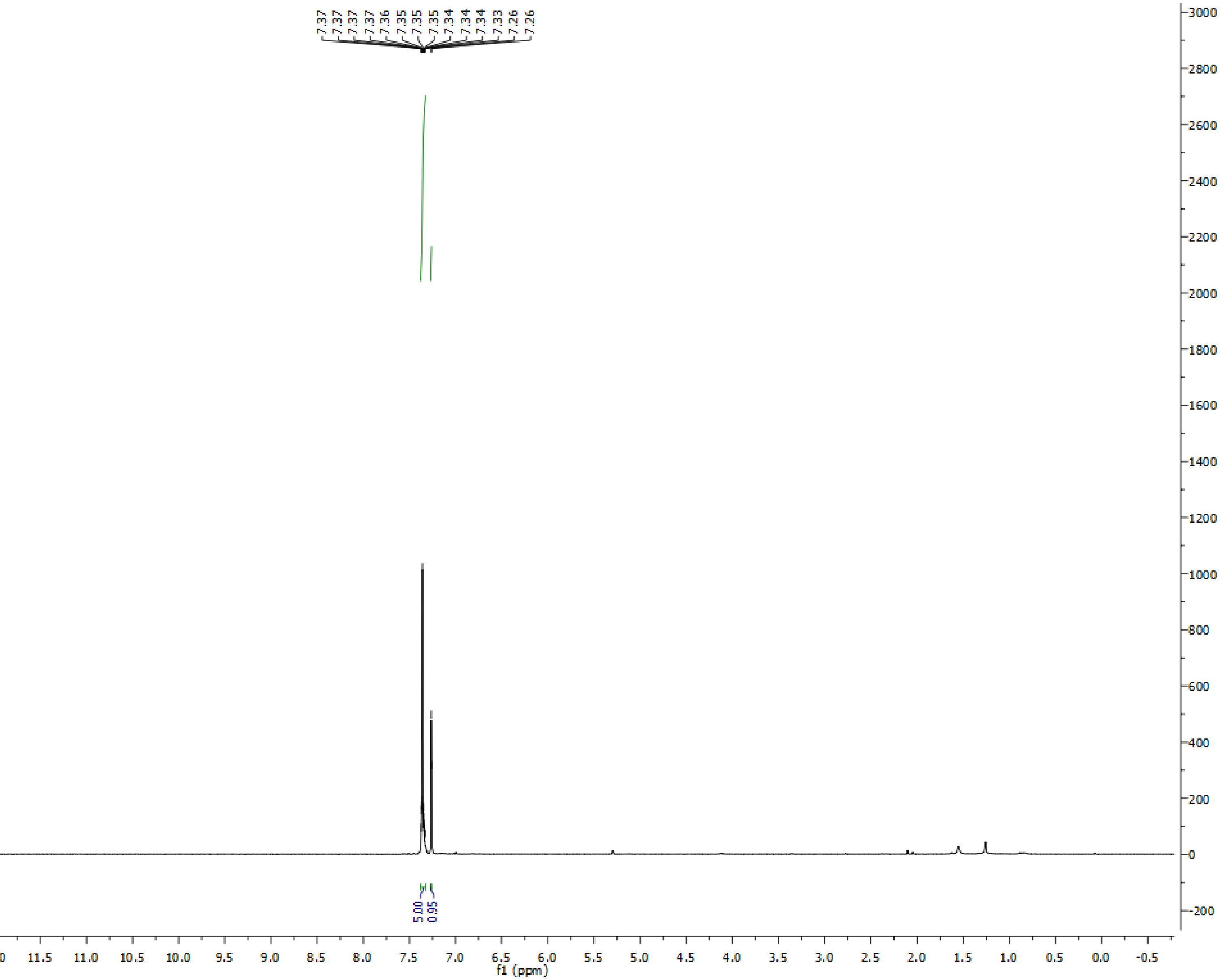
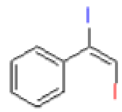


Figure S167. ^{13}C-NMR of **74**



74

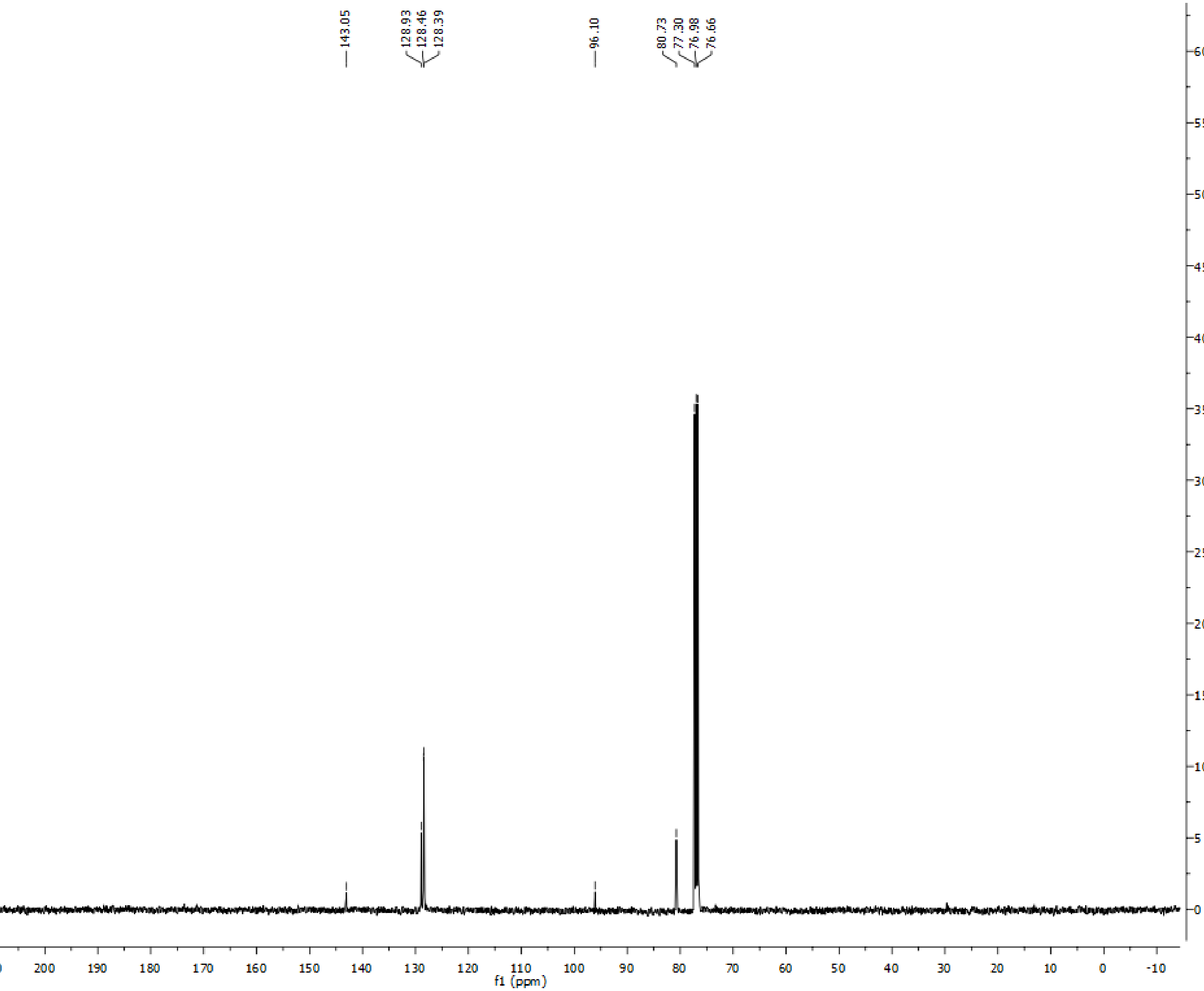
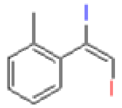


Figure S168. ^{1}H-NMR of **75**



75

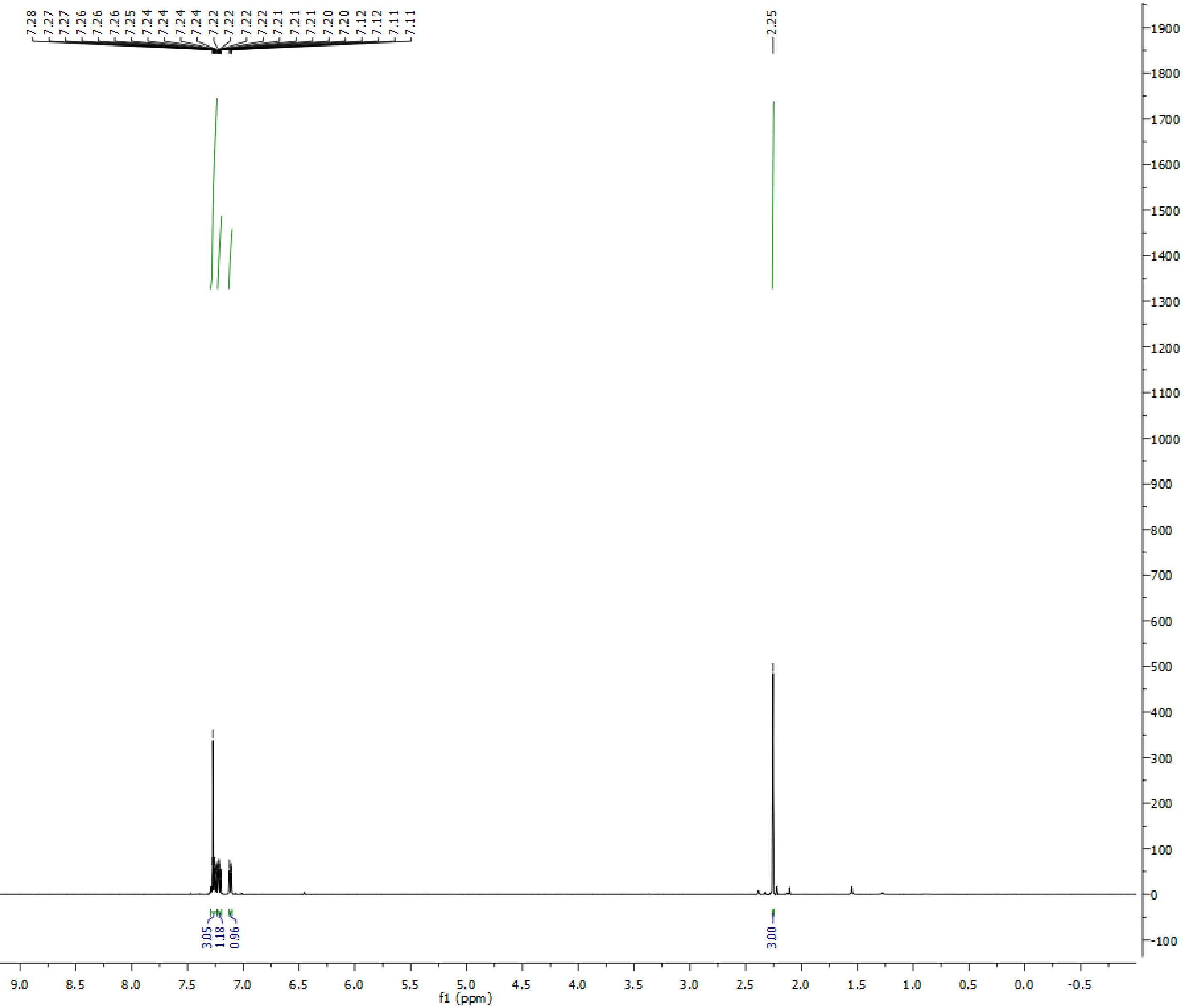
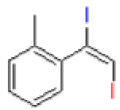


Figure S169. ^{13}C-NMR of **75**



75

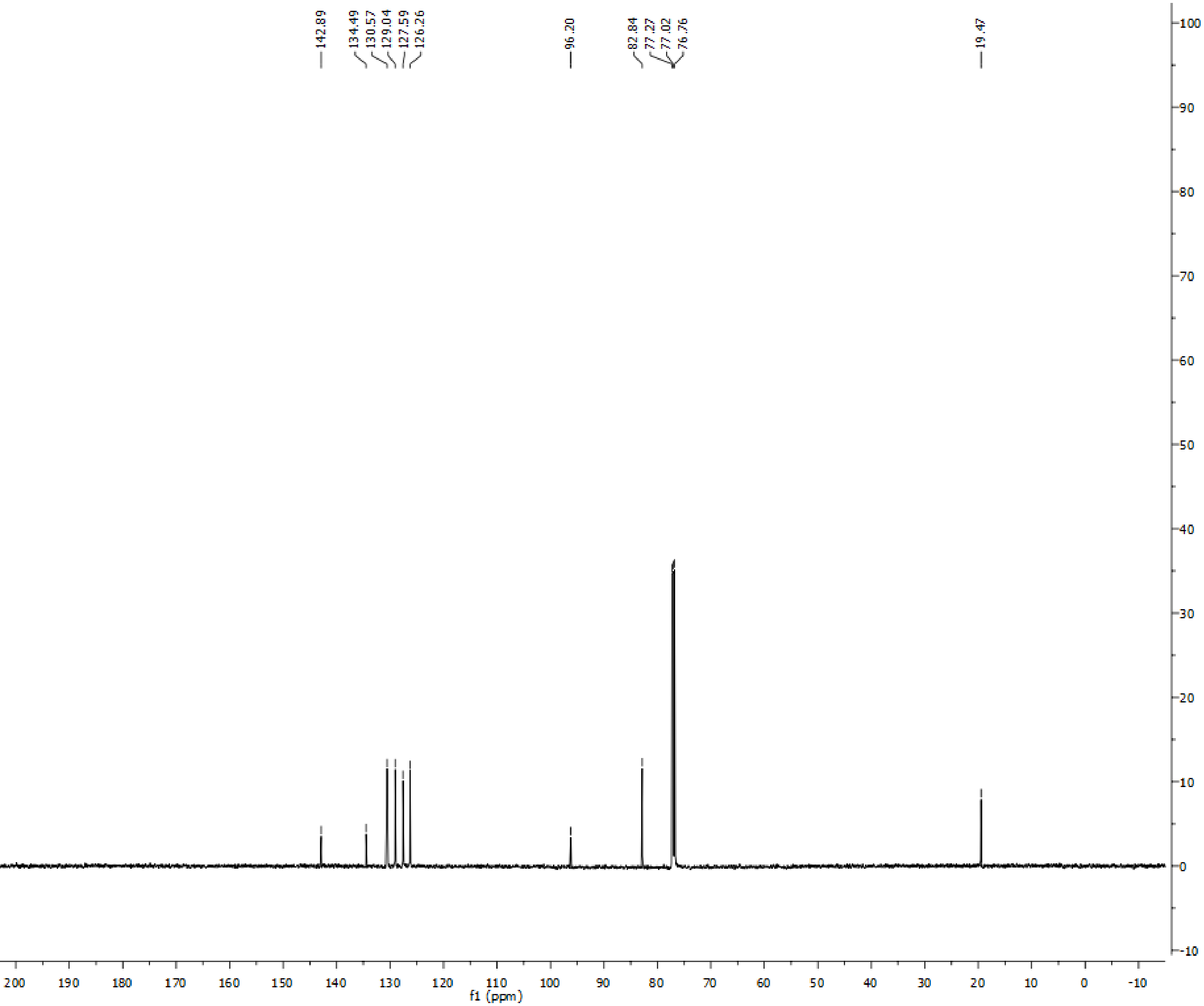


Figure S170. ^{1}H-NMR of **76**

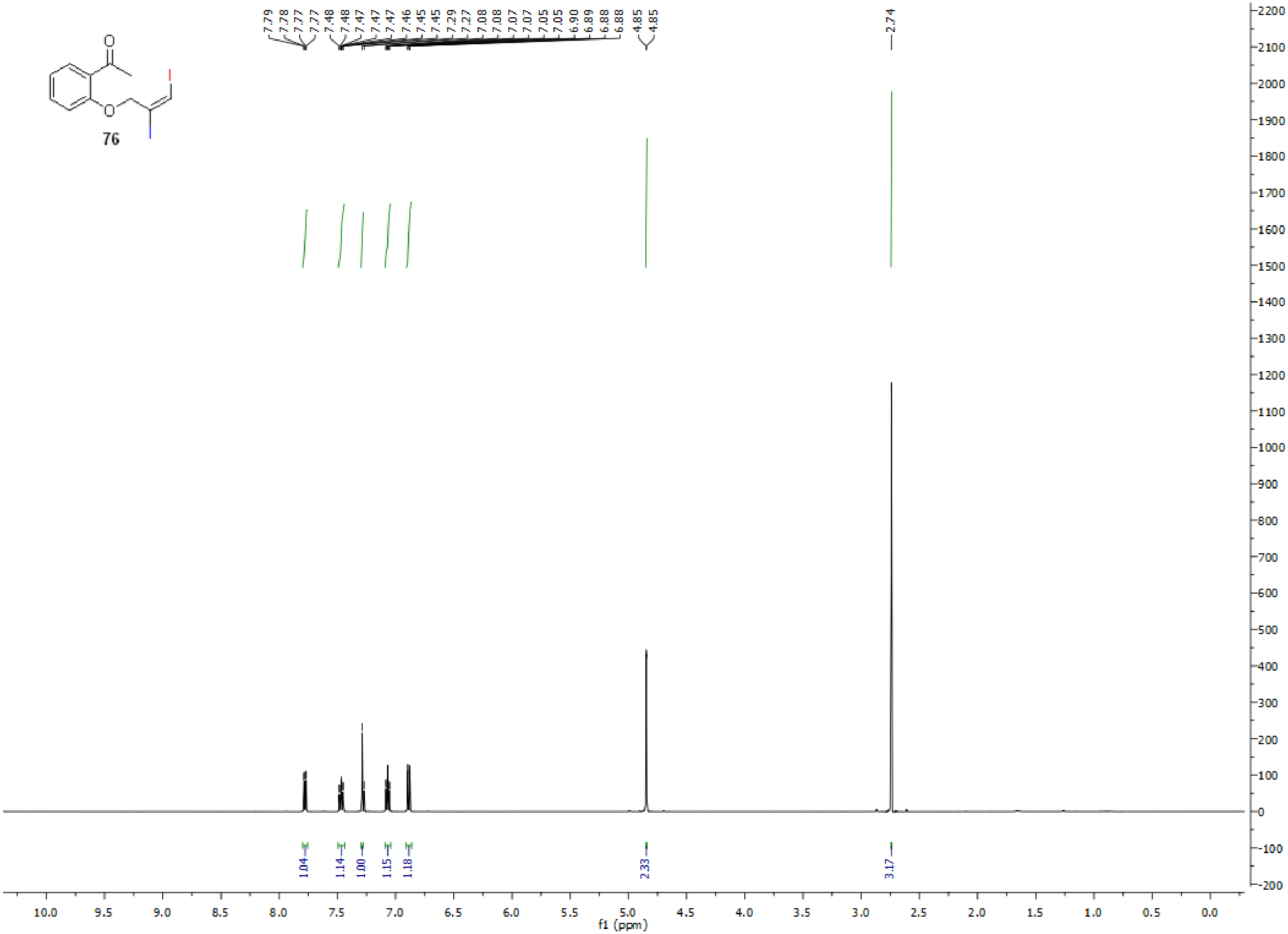


Figure S171. ^{13}C-NMR of **76**

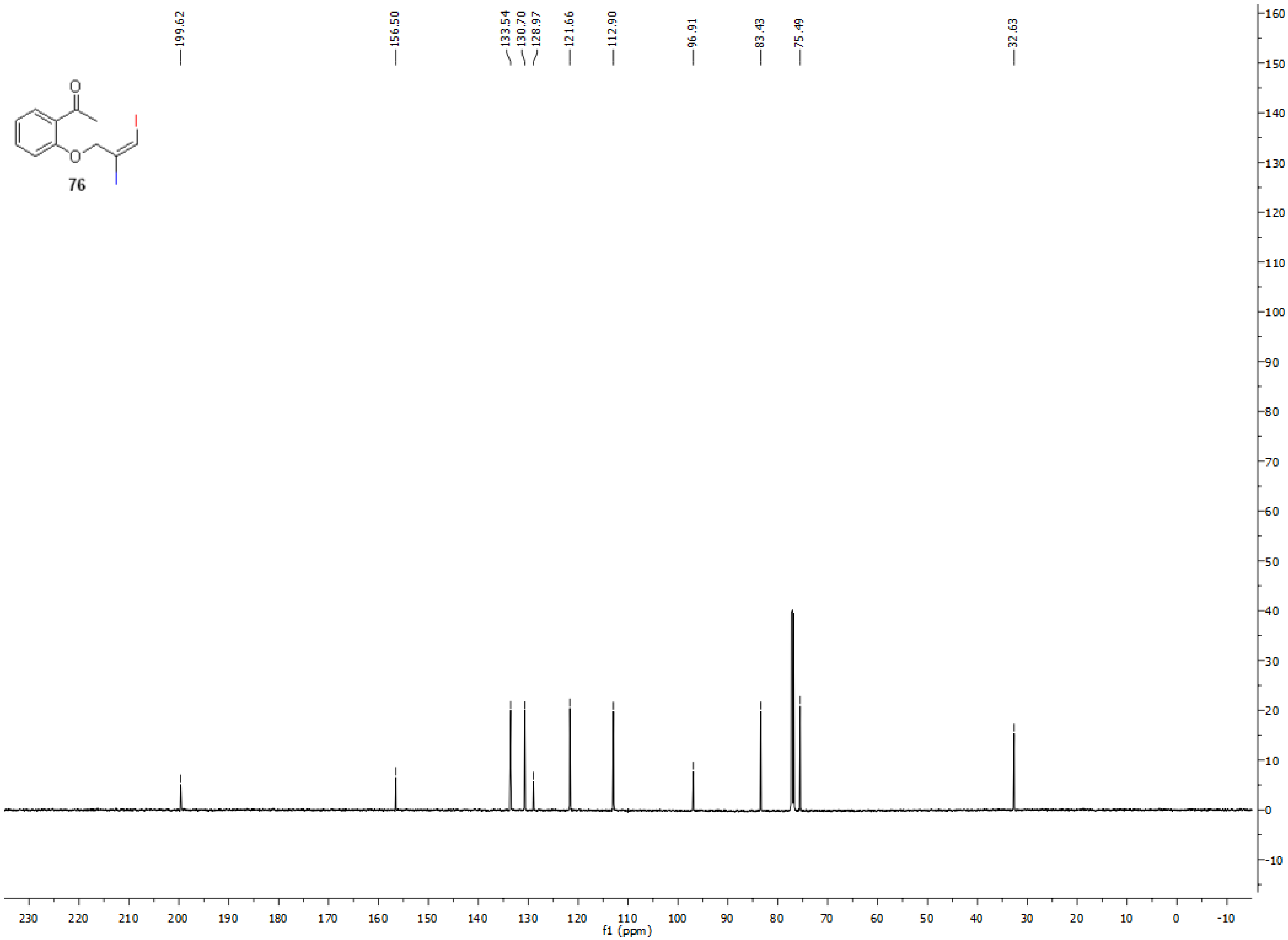


Figure S172. ^{1}H-NMR of **77**

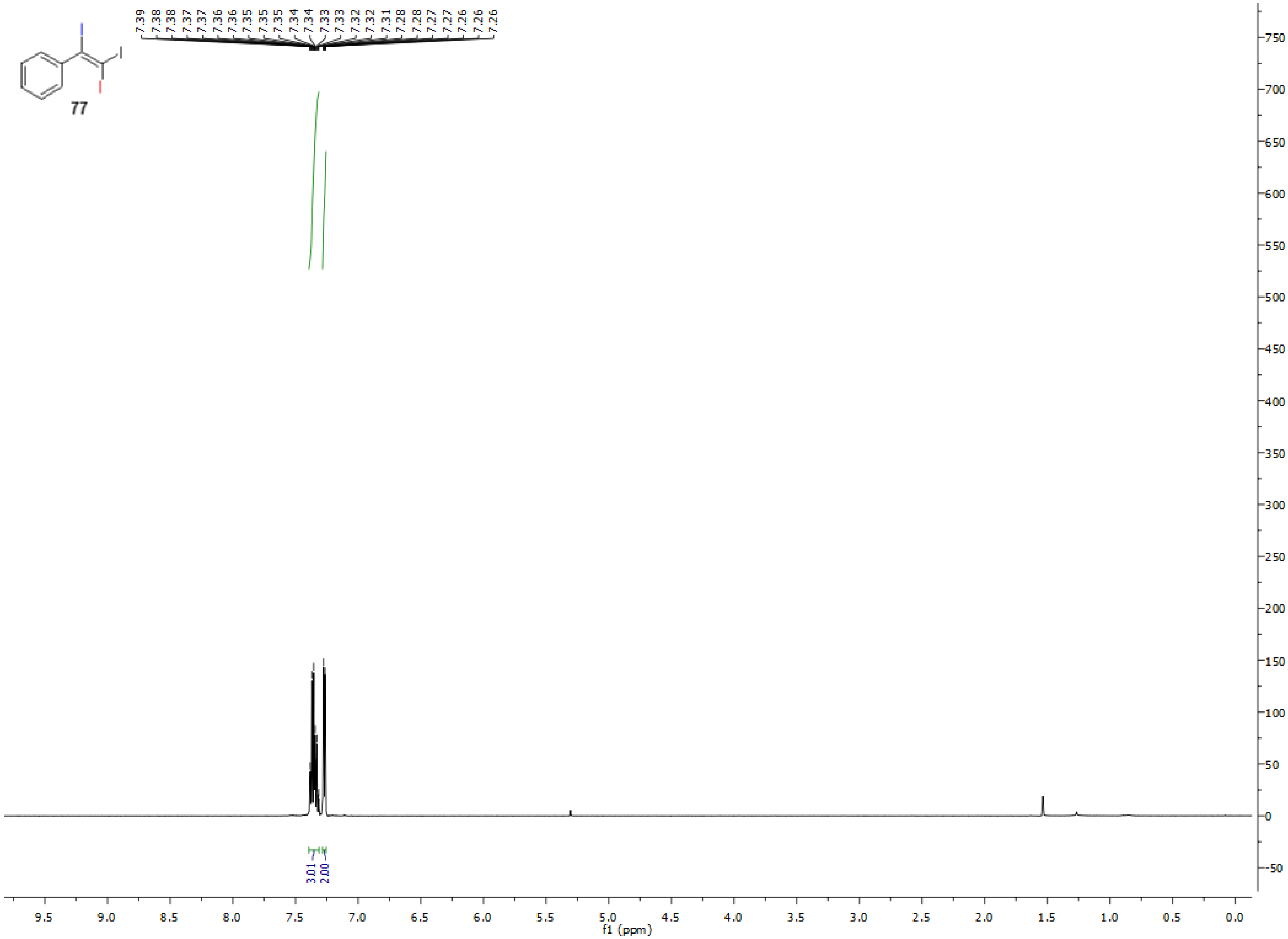
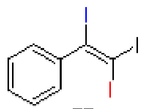


Figure S173. ^{13}C-NMR of **77**



77

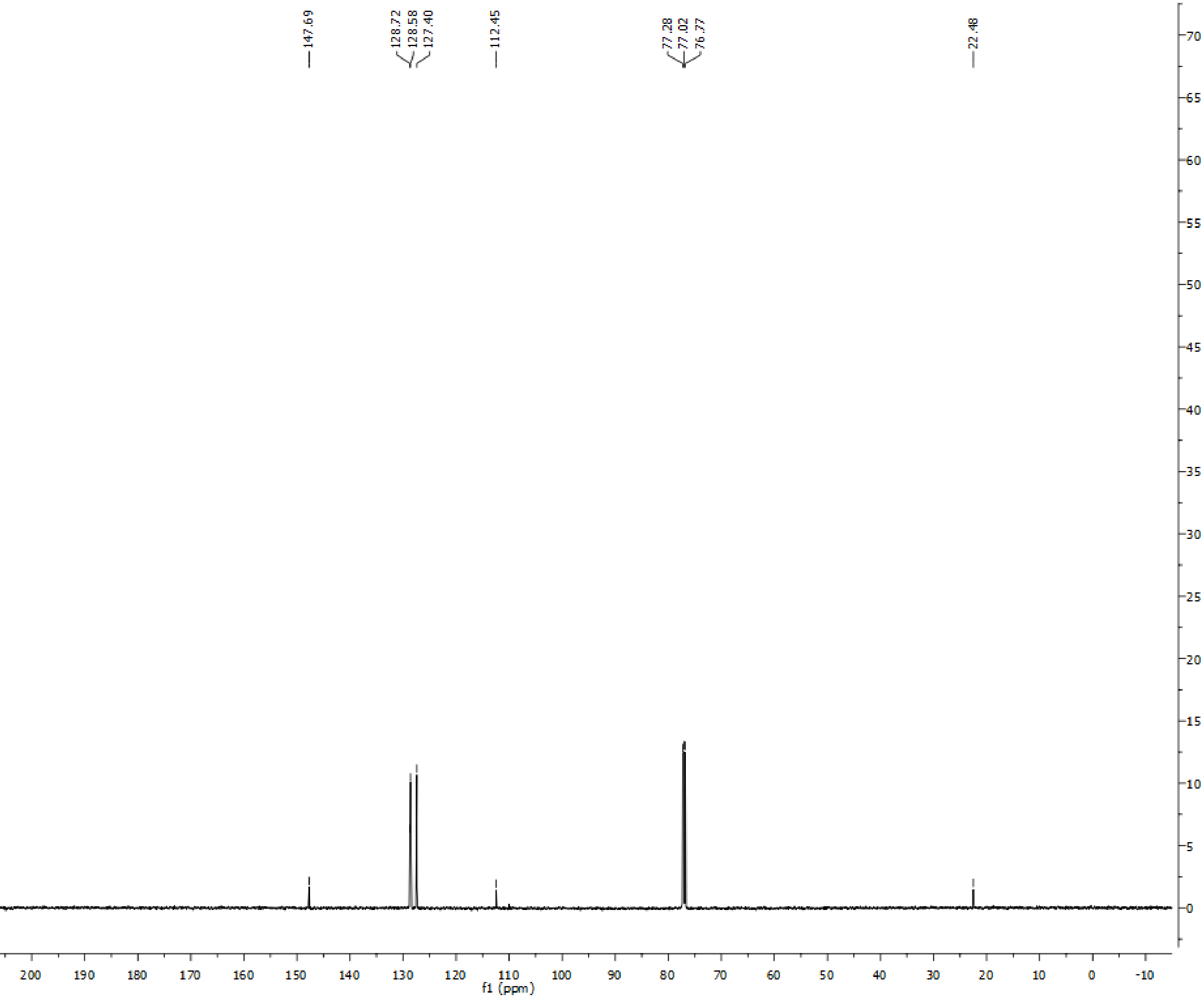


Figure S174. ^{1}H-NMR of **78**

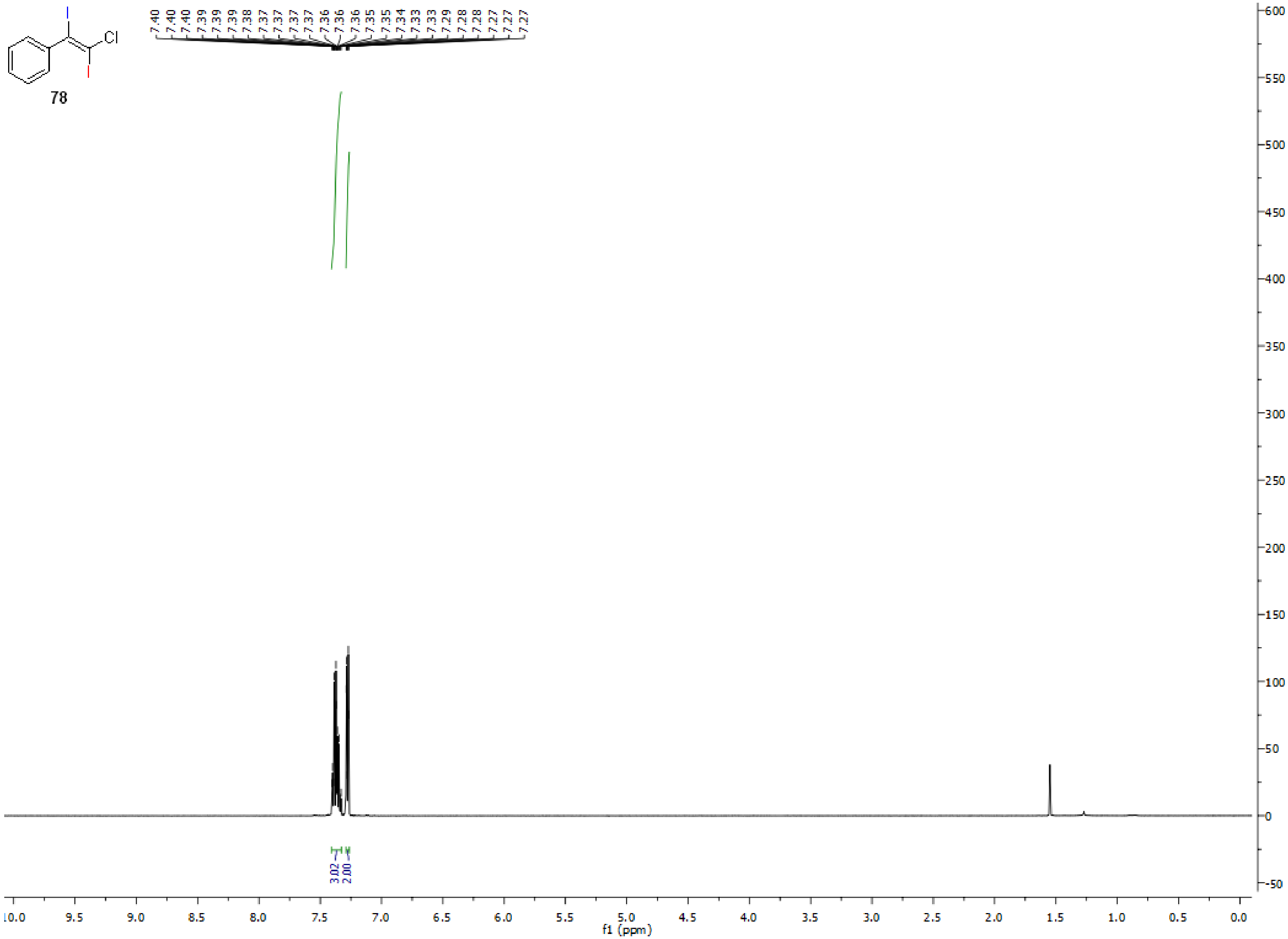
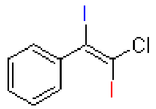


Figure S175. ^{13}C-NMR of **78**



78

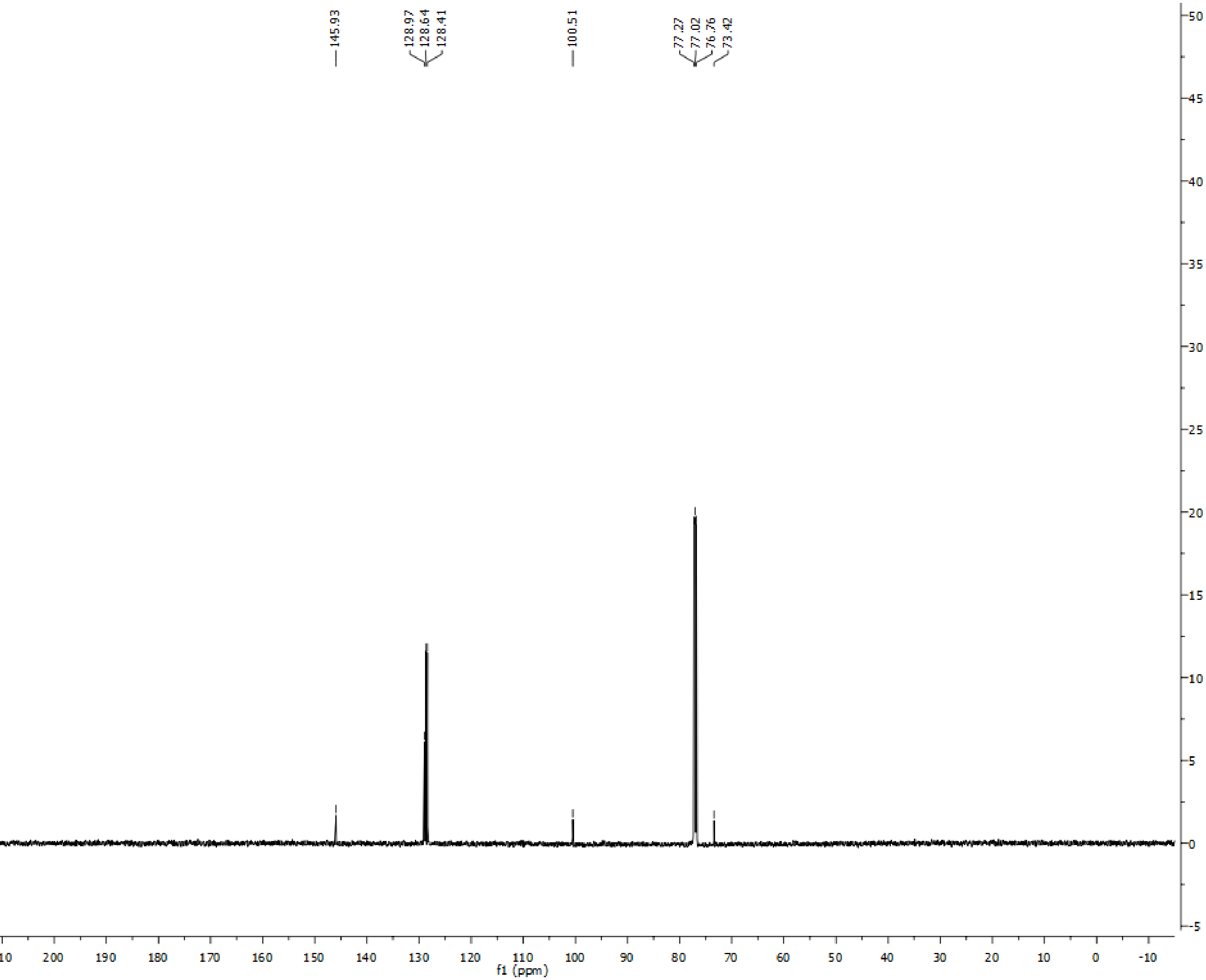
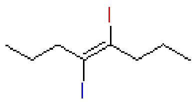


Figure S176. [1]H-NMR of **79**



79

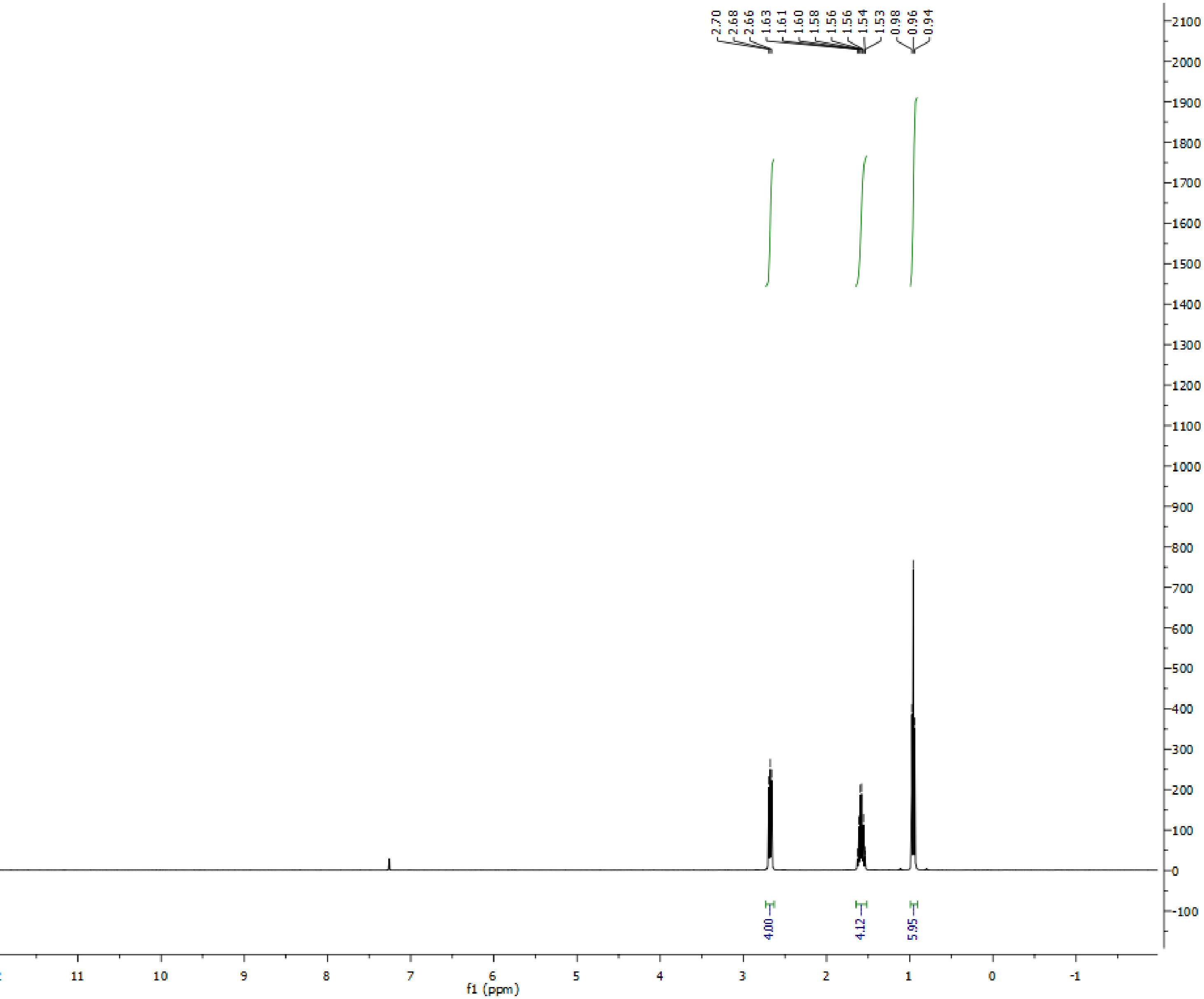
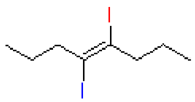


Figure S177. ^{13}C-NMR of **79**



79

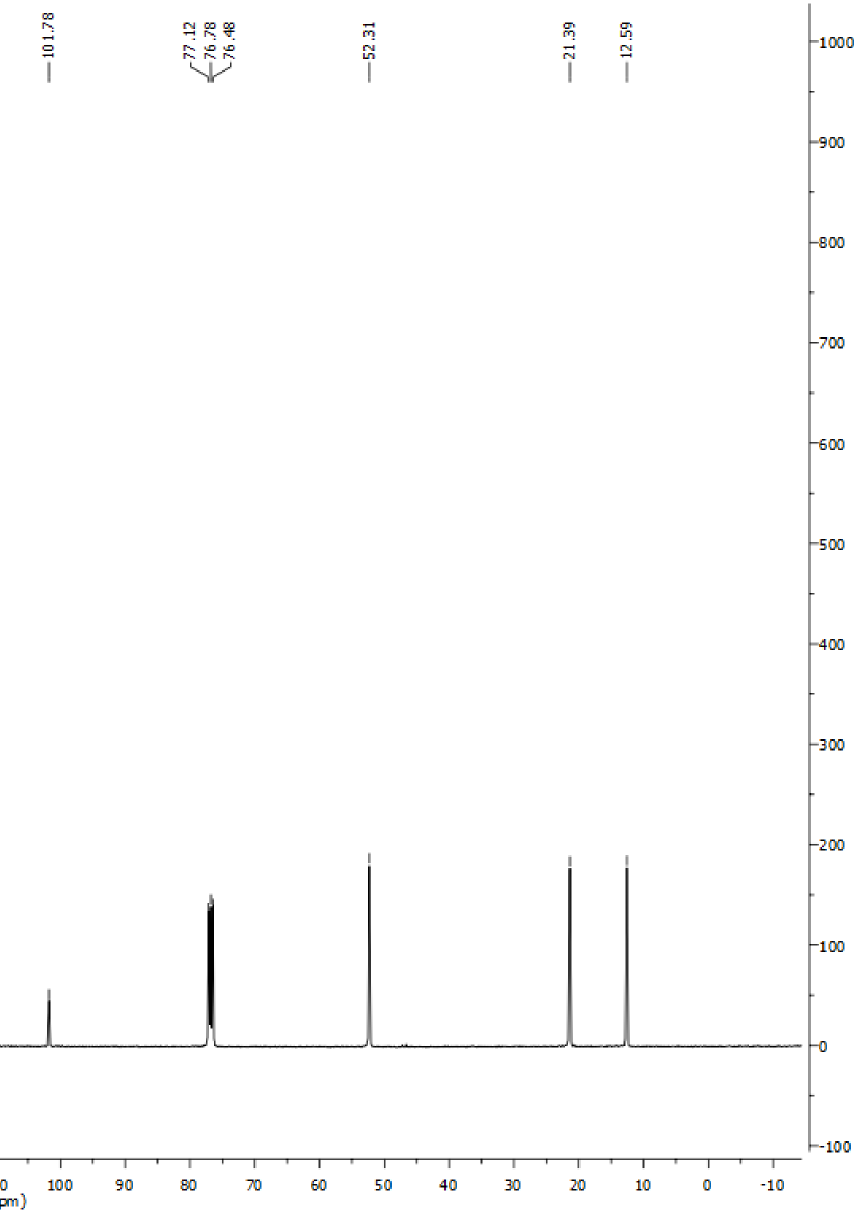


Figure S178. ^{1}H-NMR of **80**

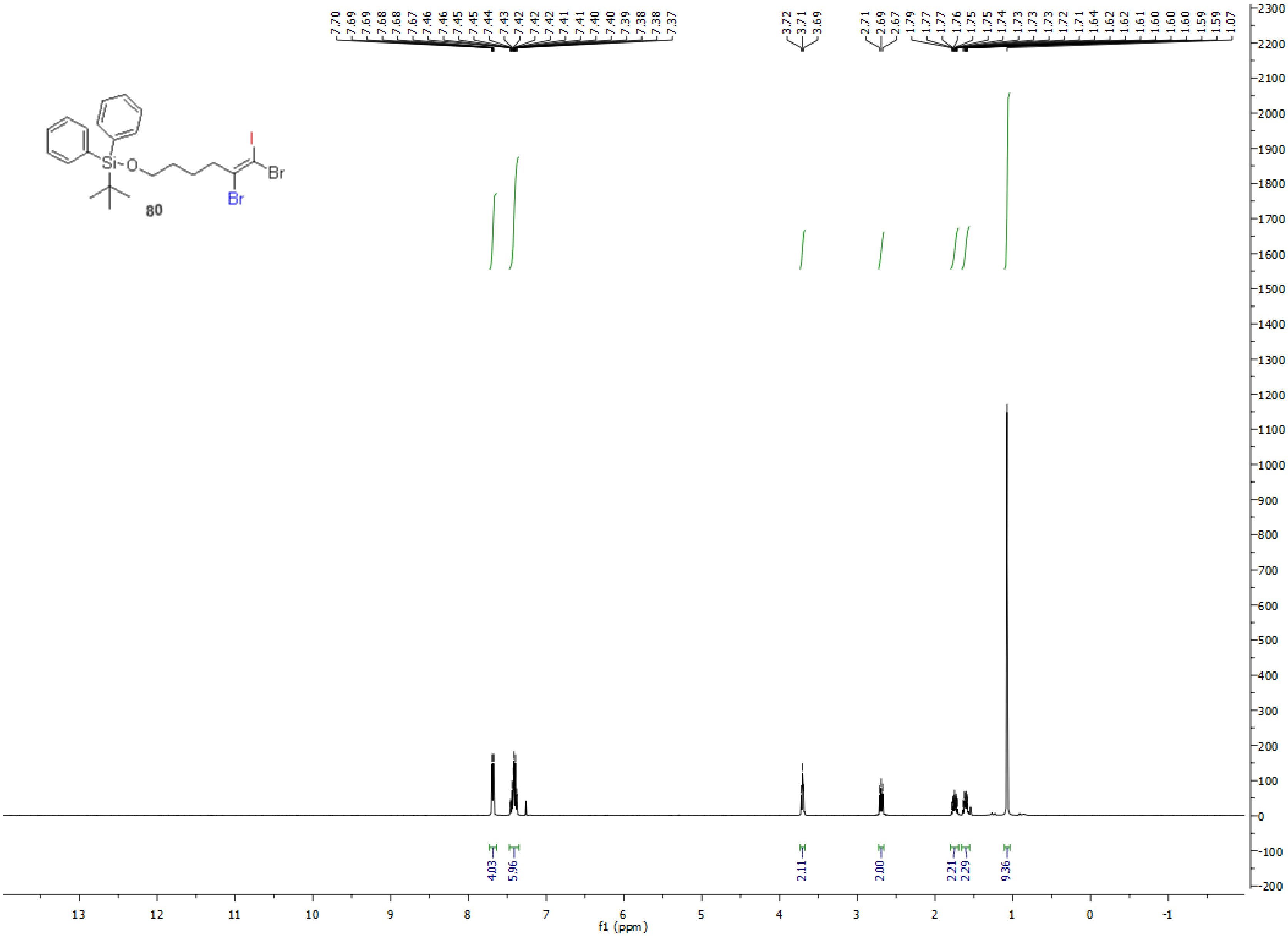
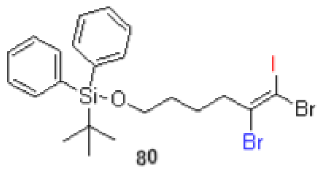


Figure S179. ^{13}C-NMR of **80**


80

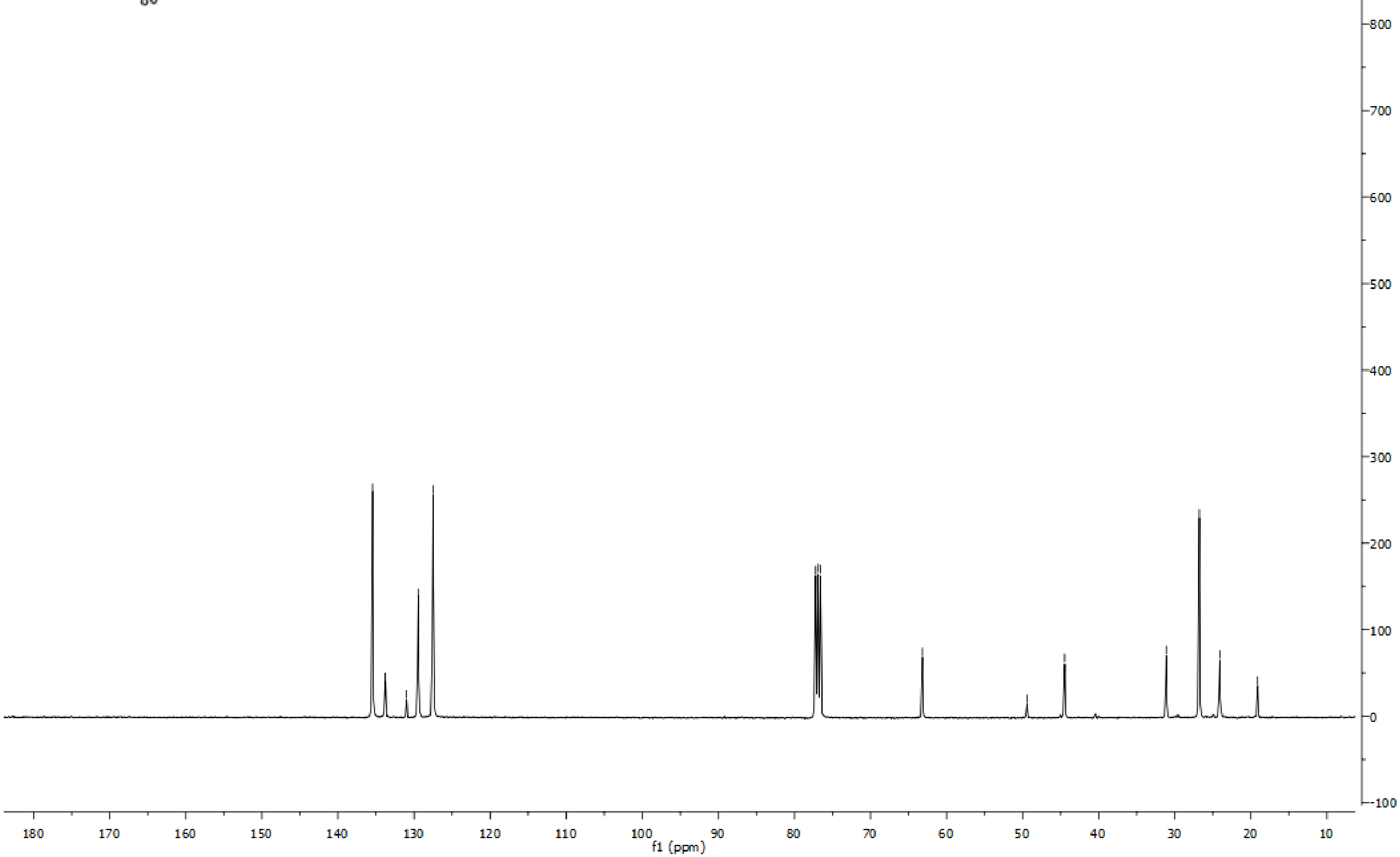
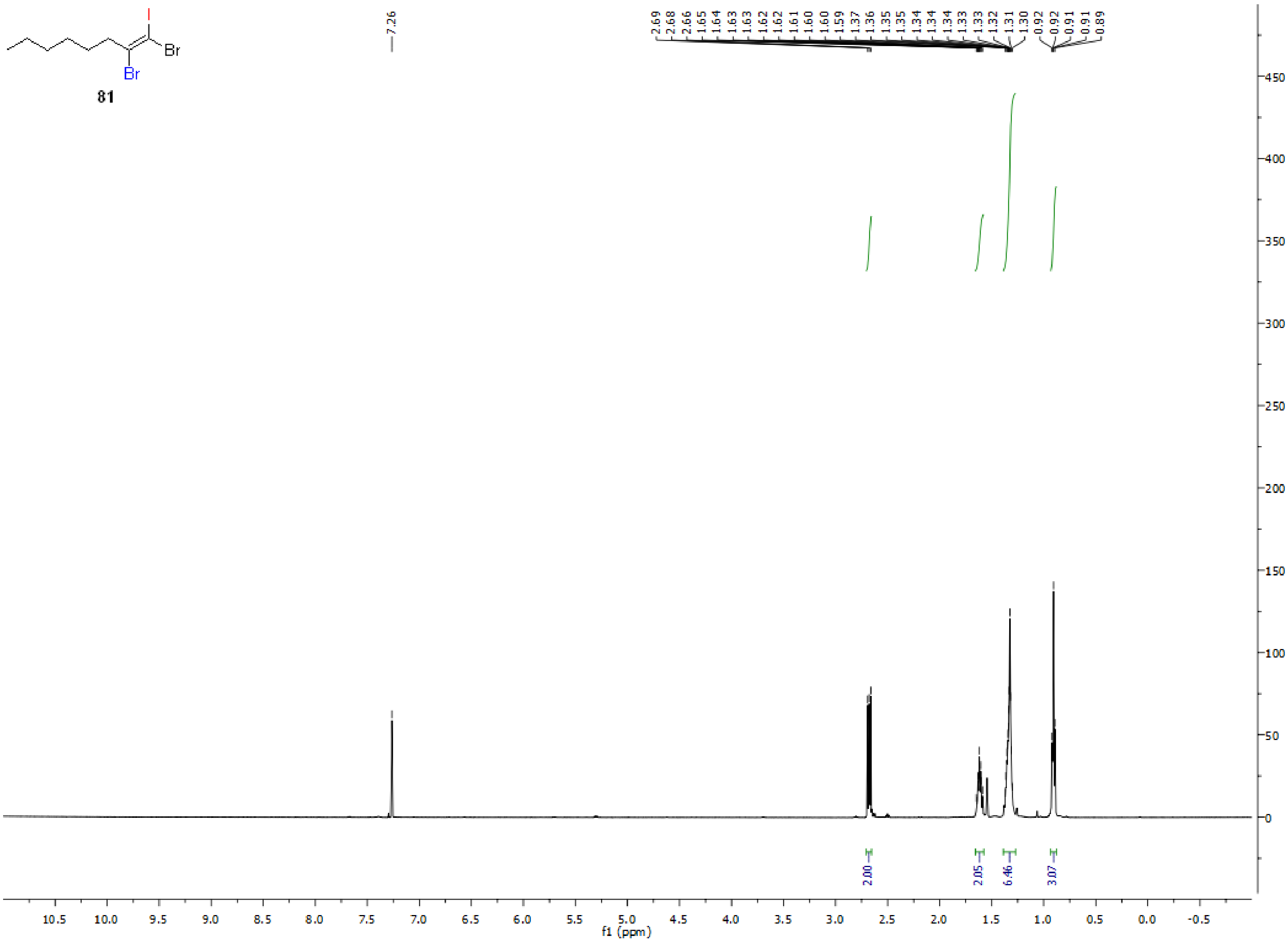
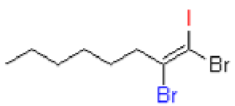


Figure S180. [1]H-NMR of **81**



81

Figure S181. ^{13}C-NMR of **81**



81

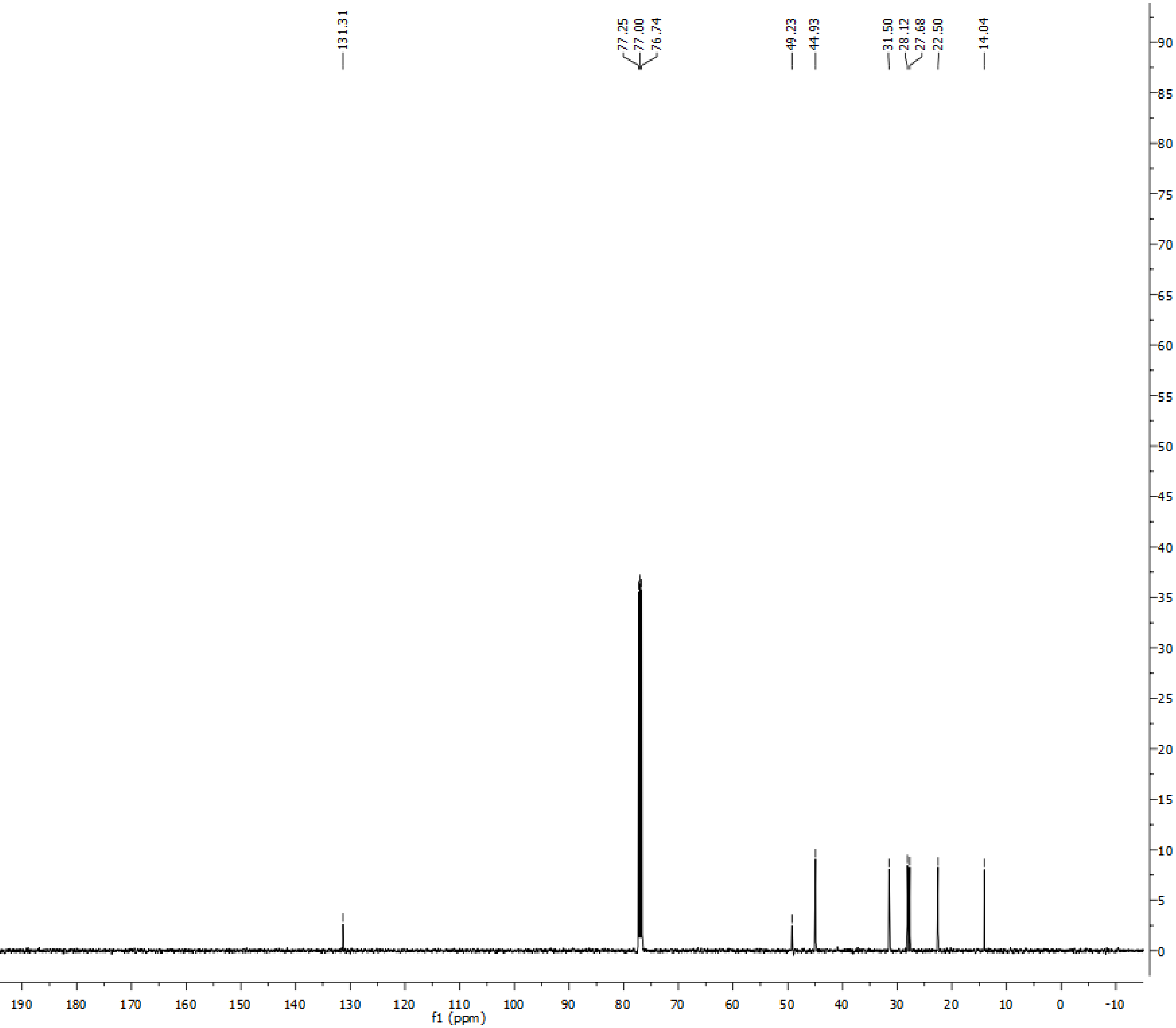
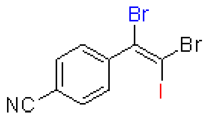


Figure S182. [1]H-NMR of **82**



82

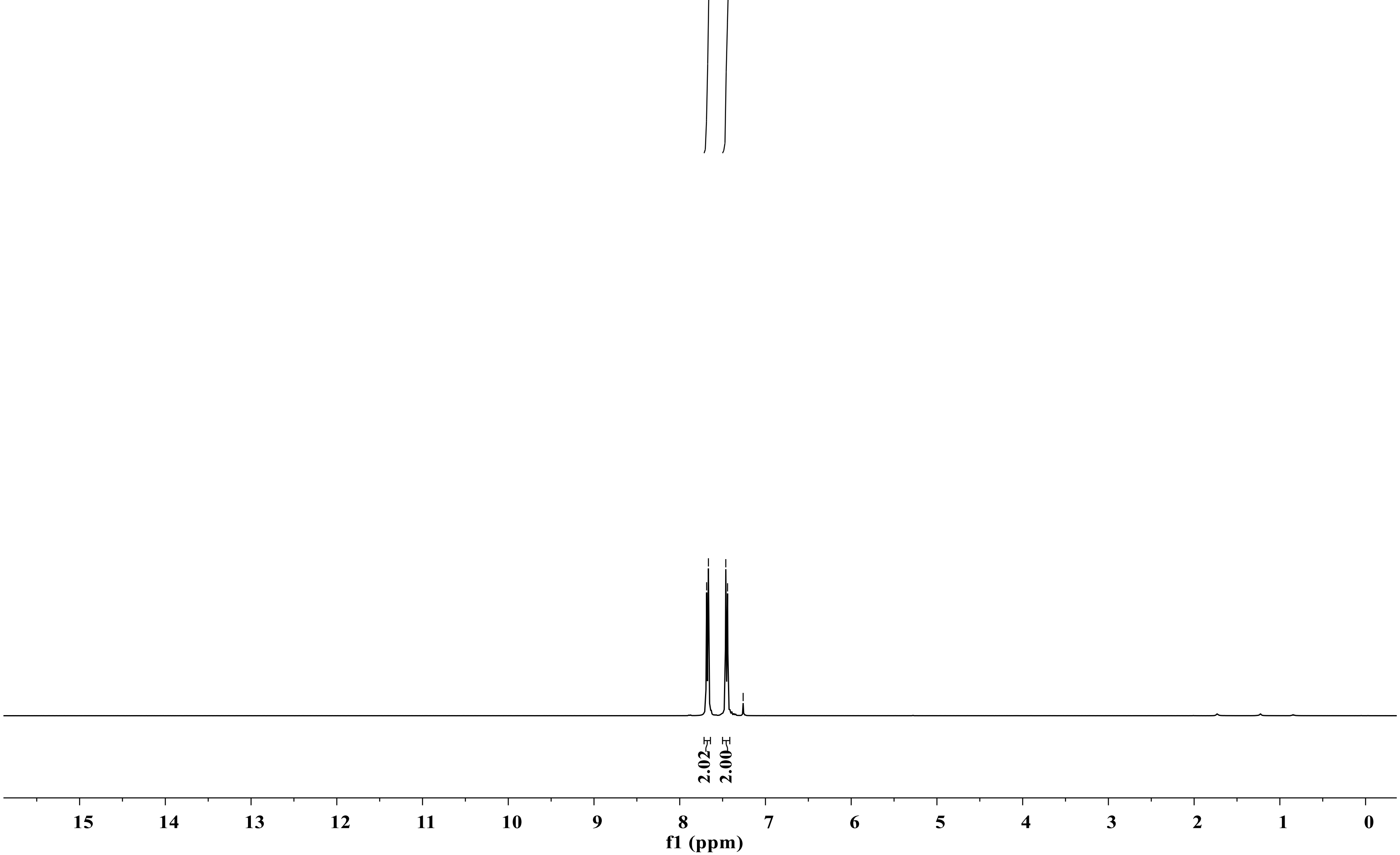


Figure S183. ^{13}C-NMR of **82**

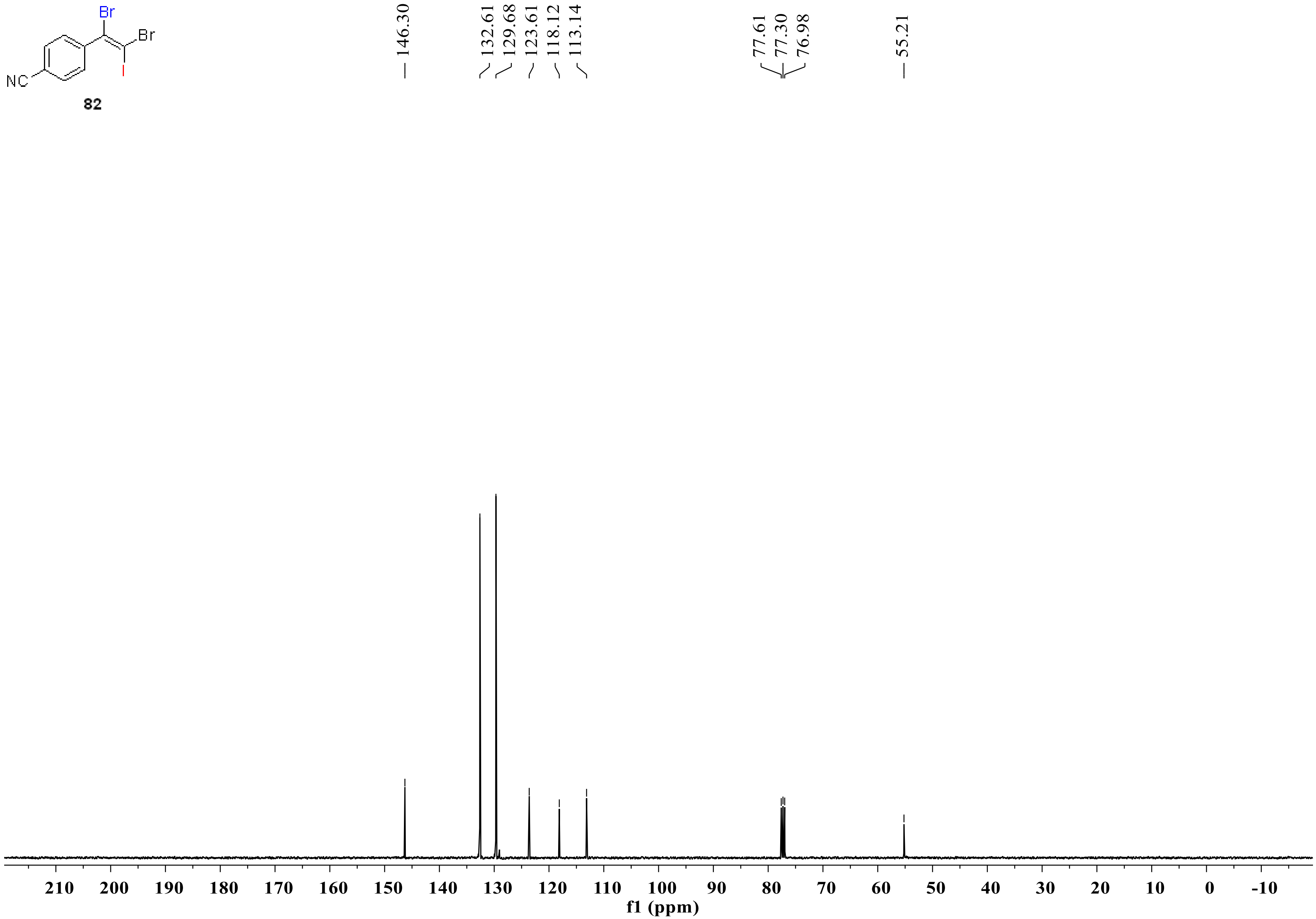
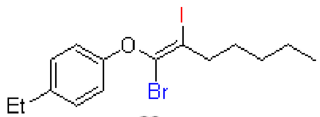


Figure S184. ^{1}H-NMR of **83**



83

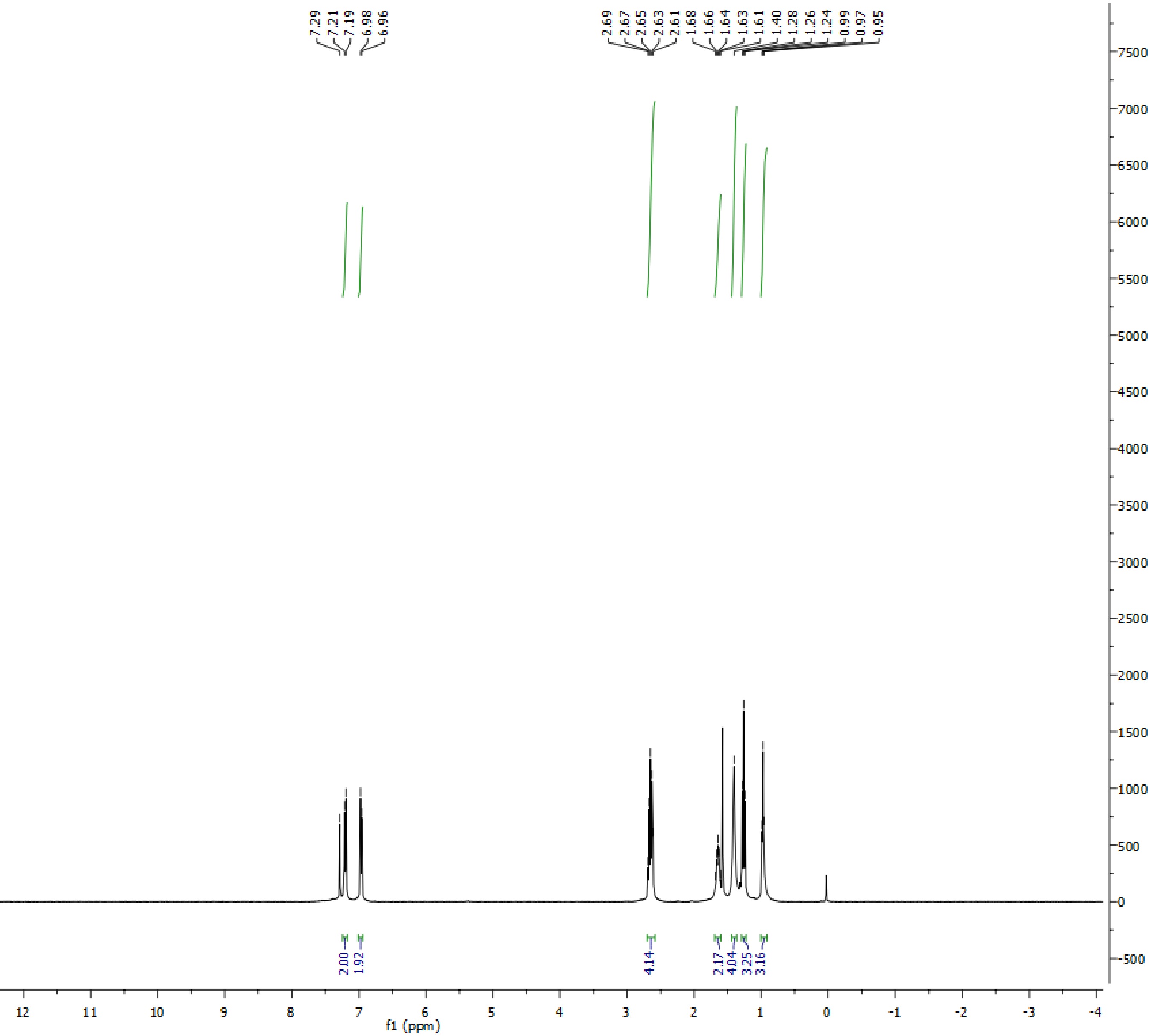
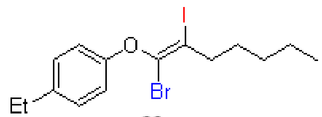


Figure S185. ^{13}C-NMR of **83**



83

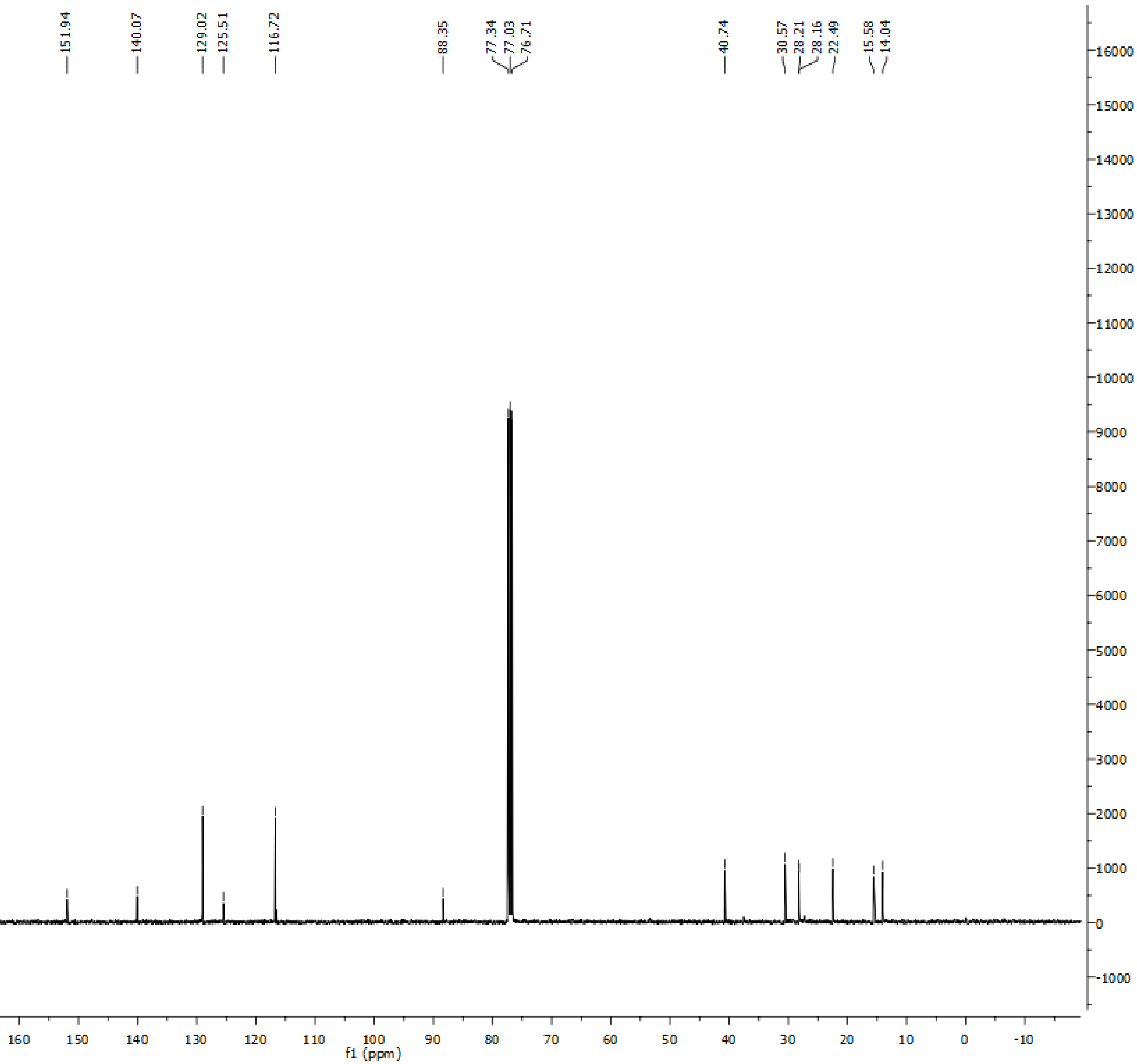
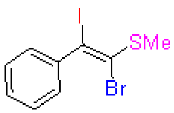


Figure S186. ^{1}H-NMR of **84**



84

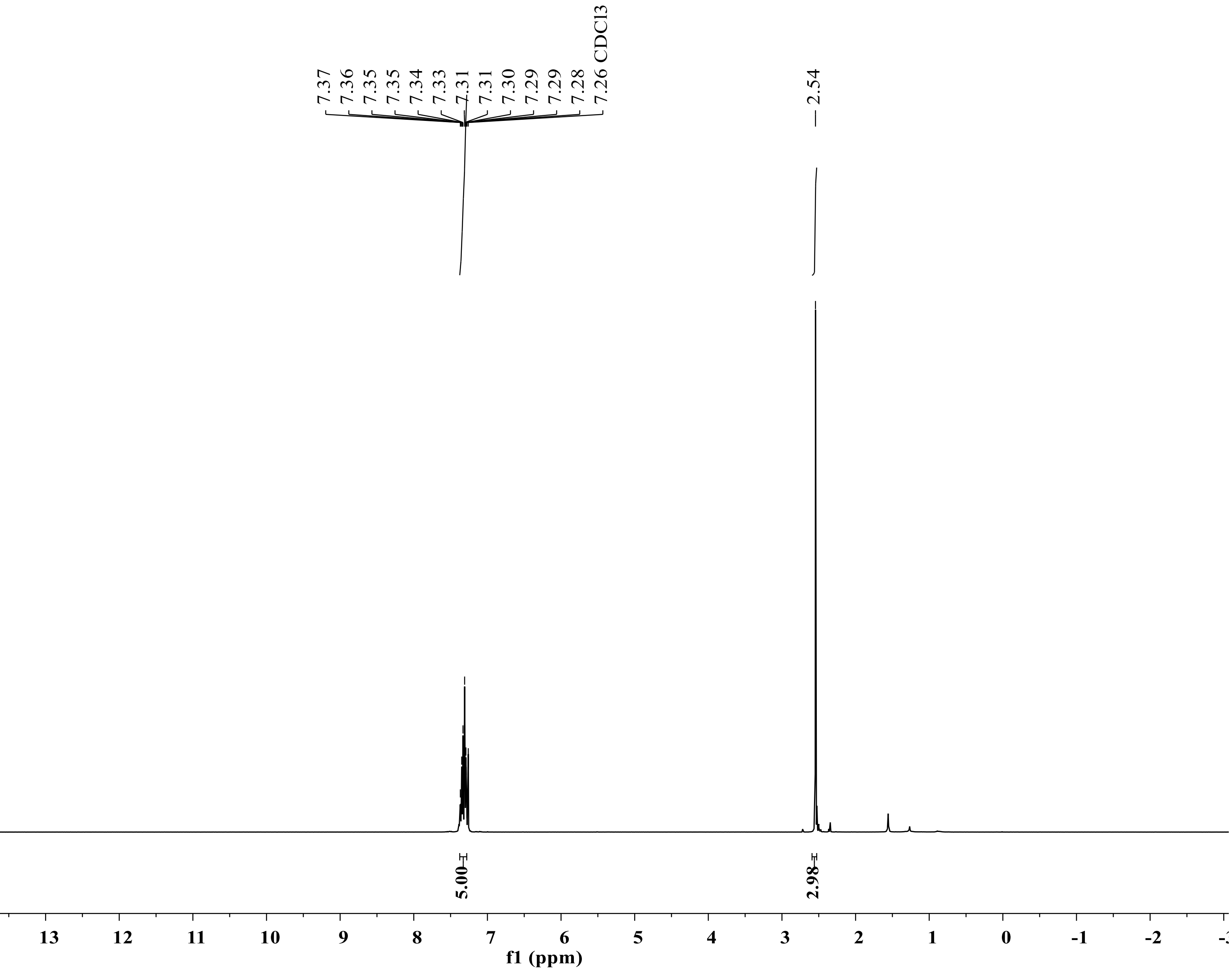
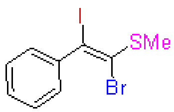


Figure S187. ^{13}C-NMR of **84**



84

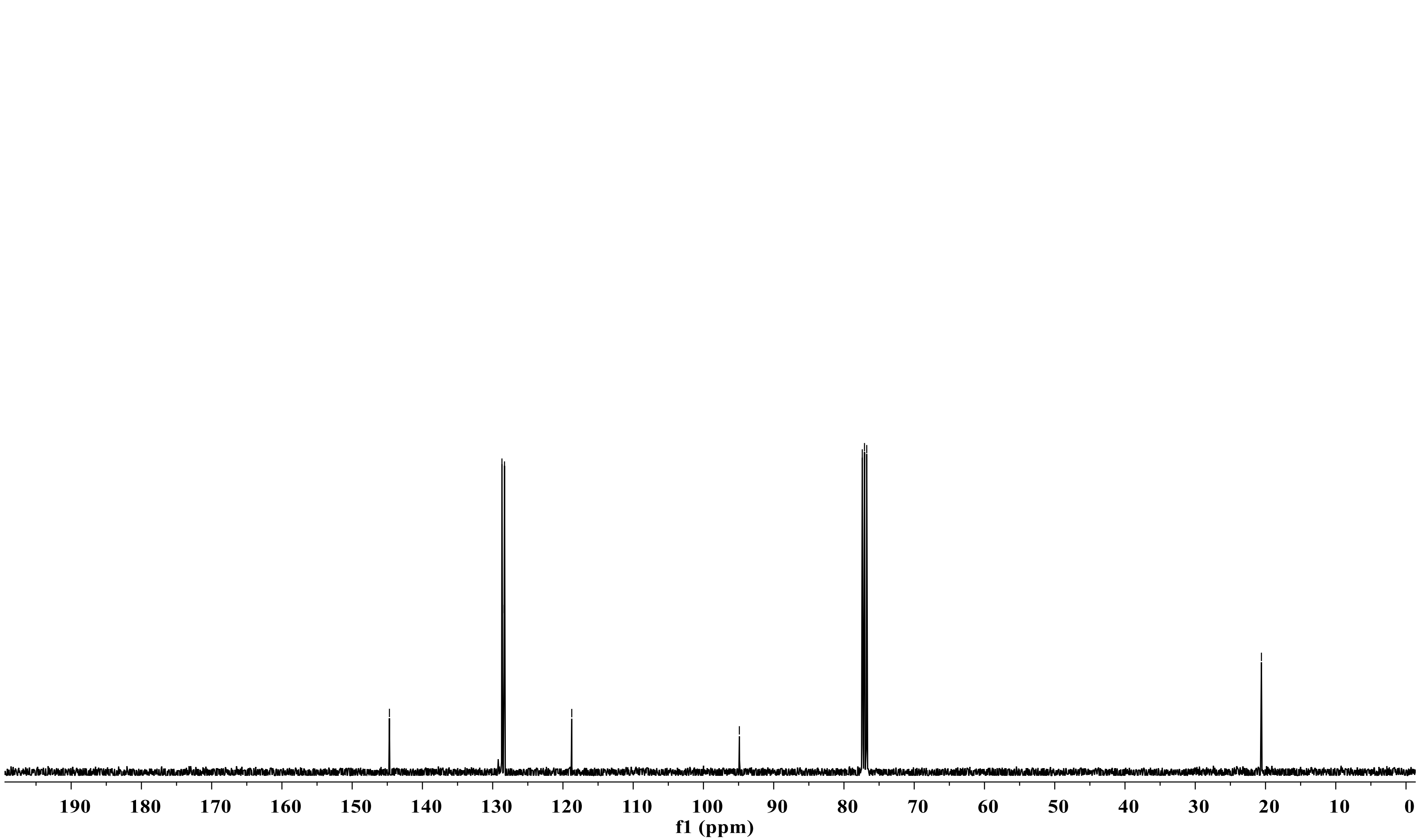
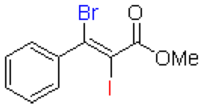


Figure S188. ^{1}H-NMR of **85**



85

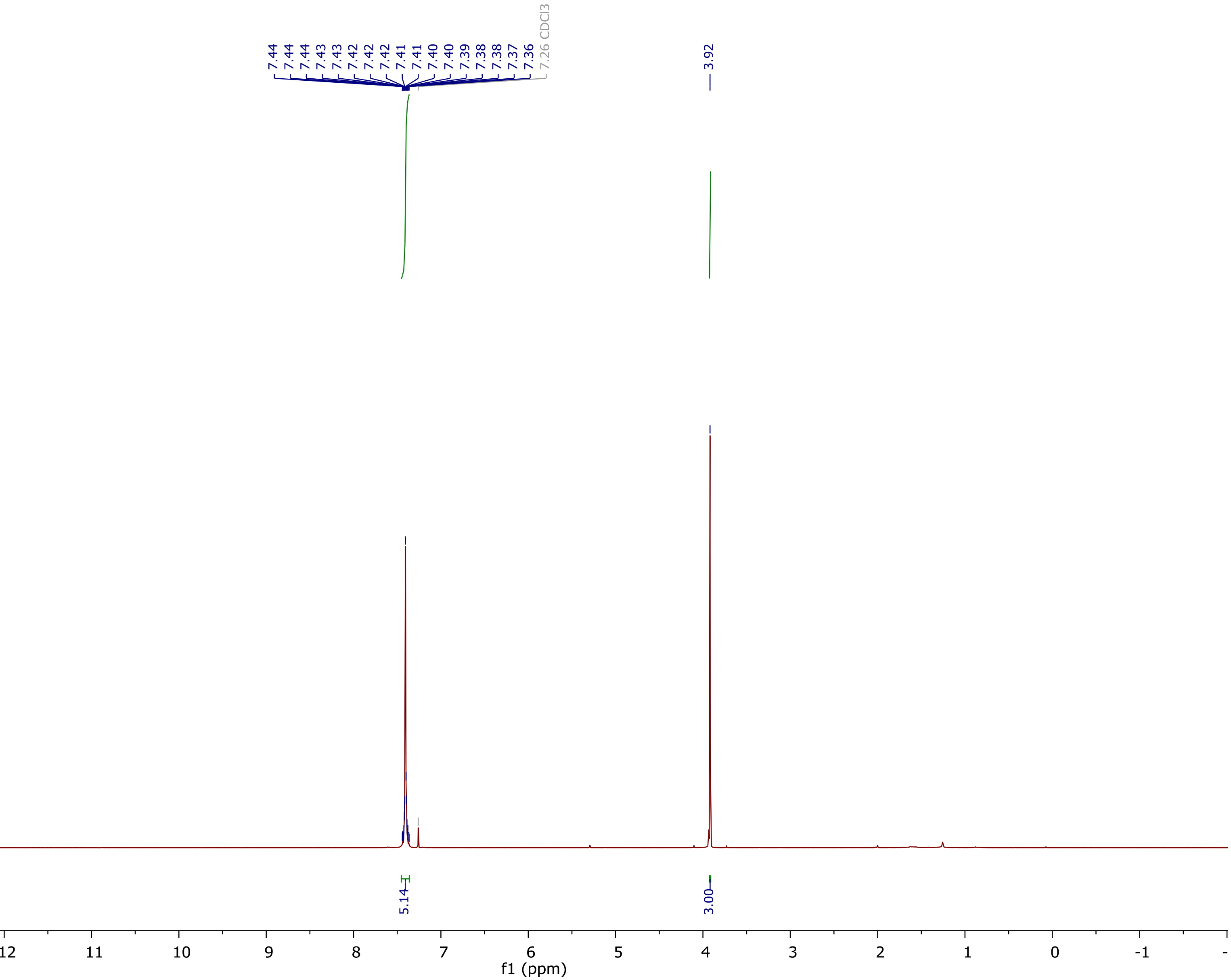
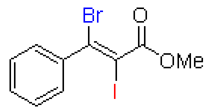


Figure S189. ^{13}C-NMR of **85**



85

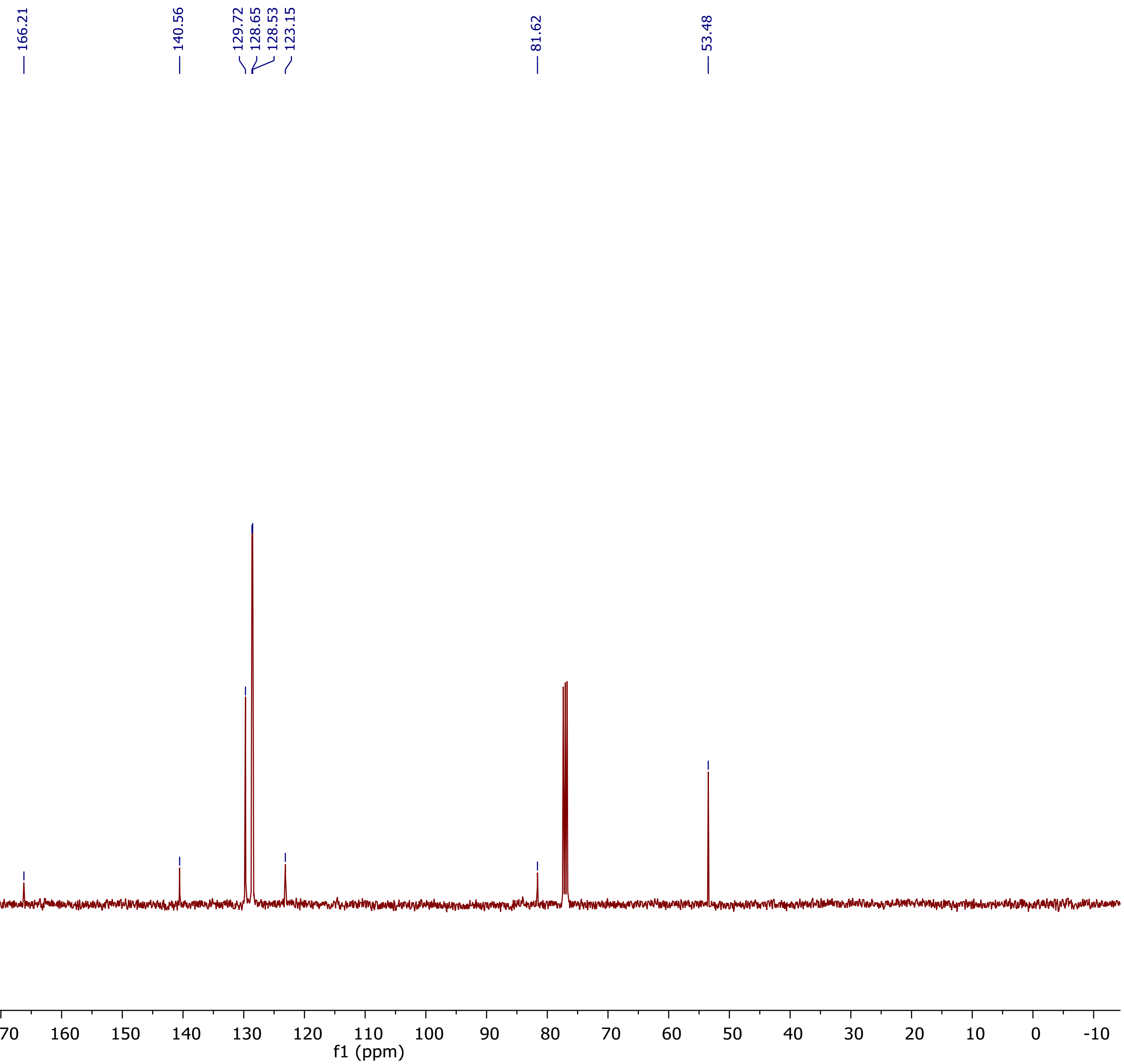
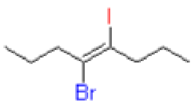


Figure S190. ^{1}H-NMR of **86**



86

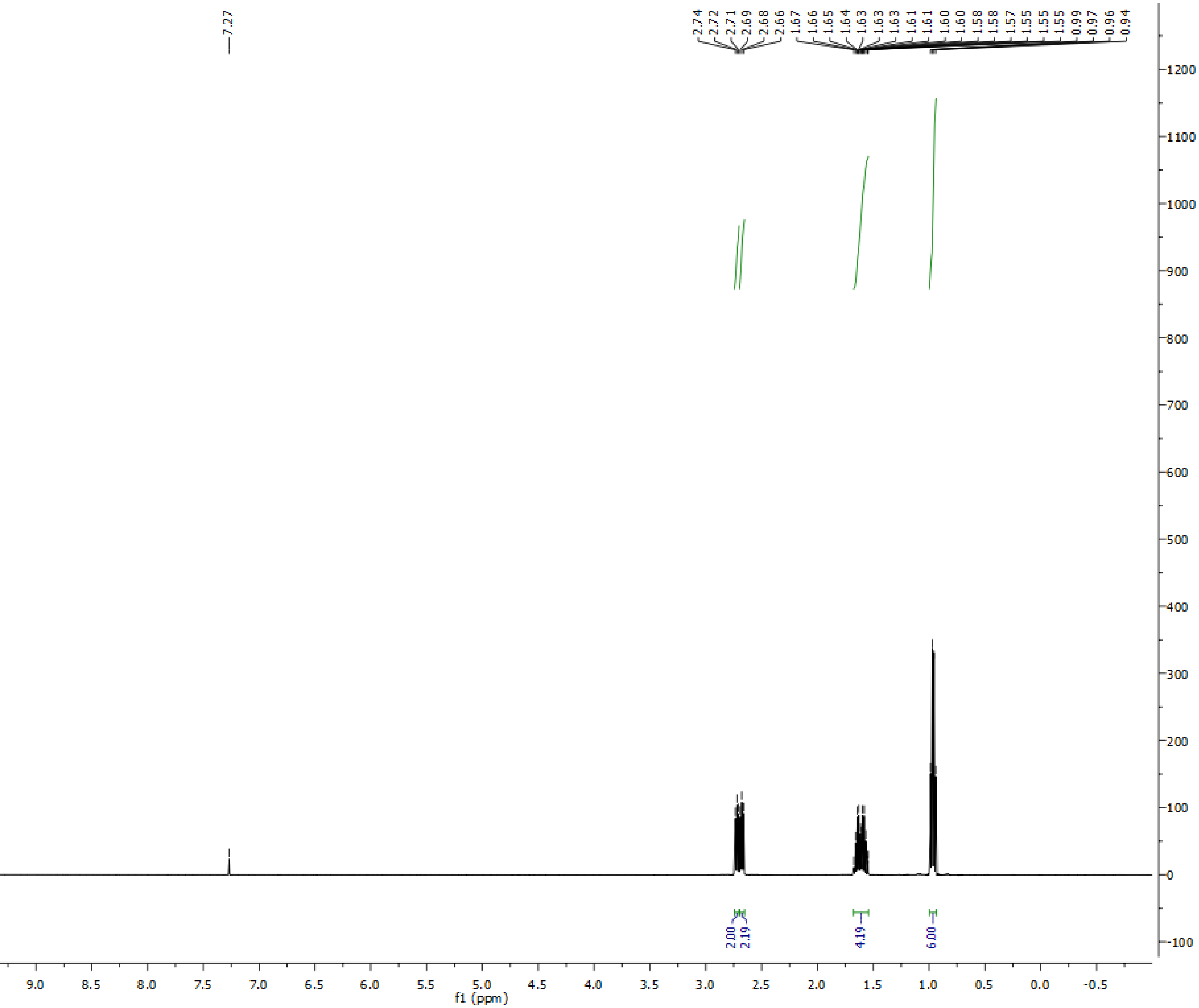
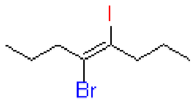


Figure S191. ^{13}C-NMR of **86**



86

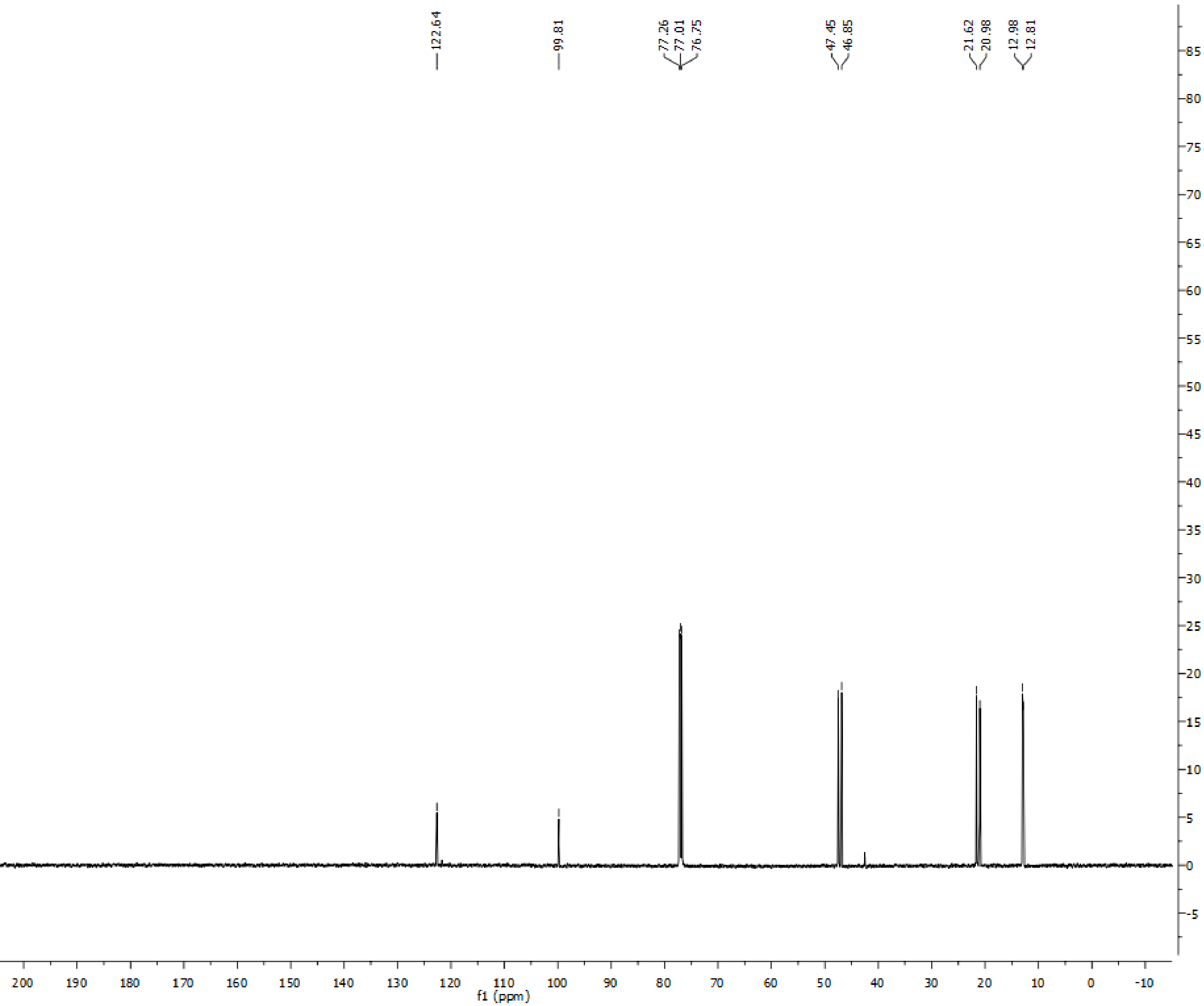
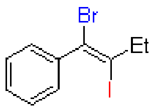


Figure S192. ^{1}H-NMR of **87**


87

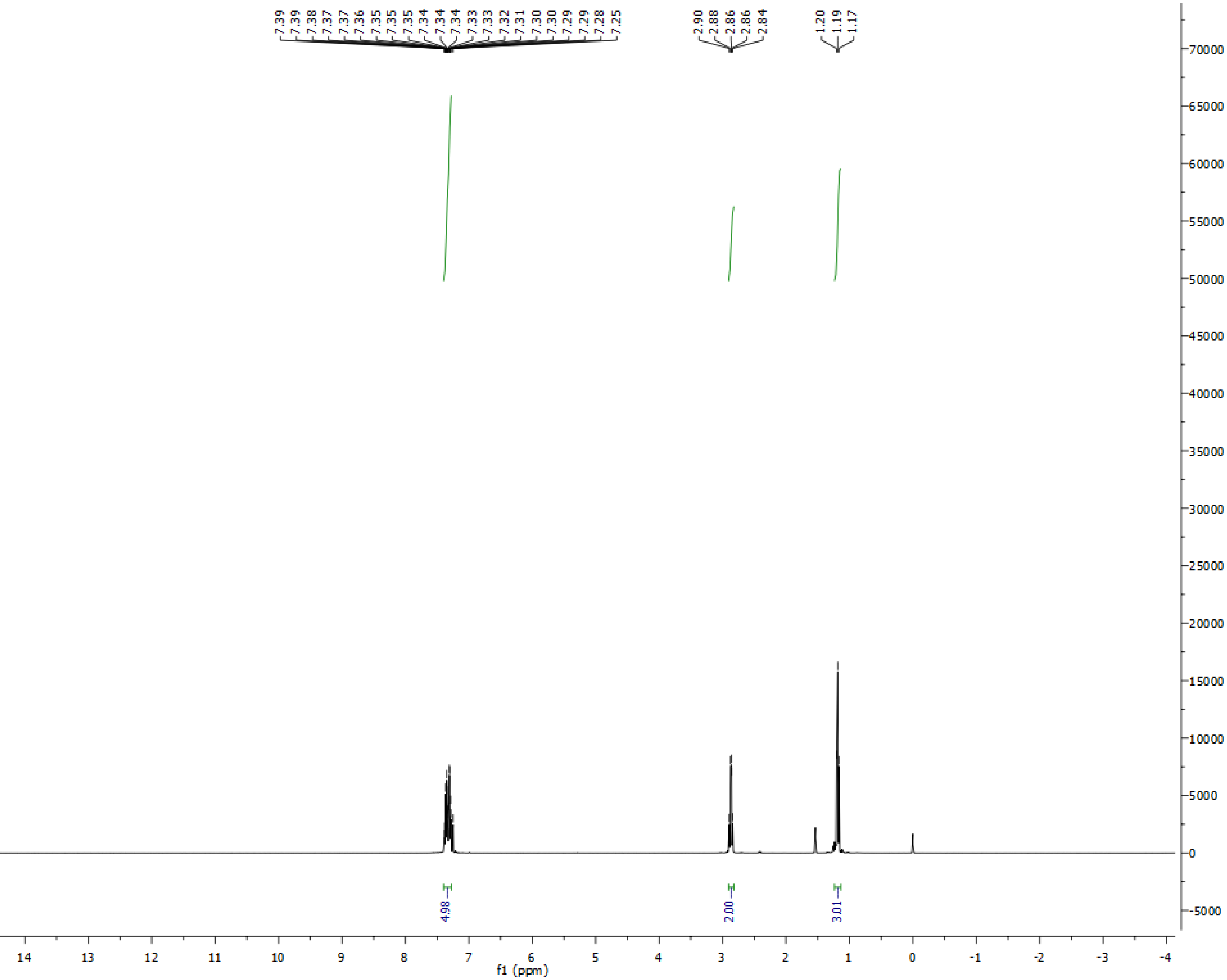
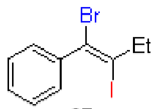


Figure S193. ^{13}C-NMR of **87**



87

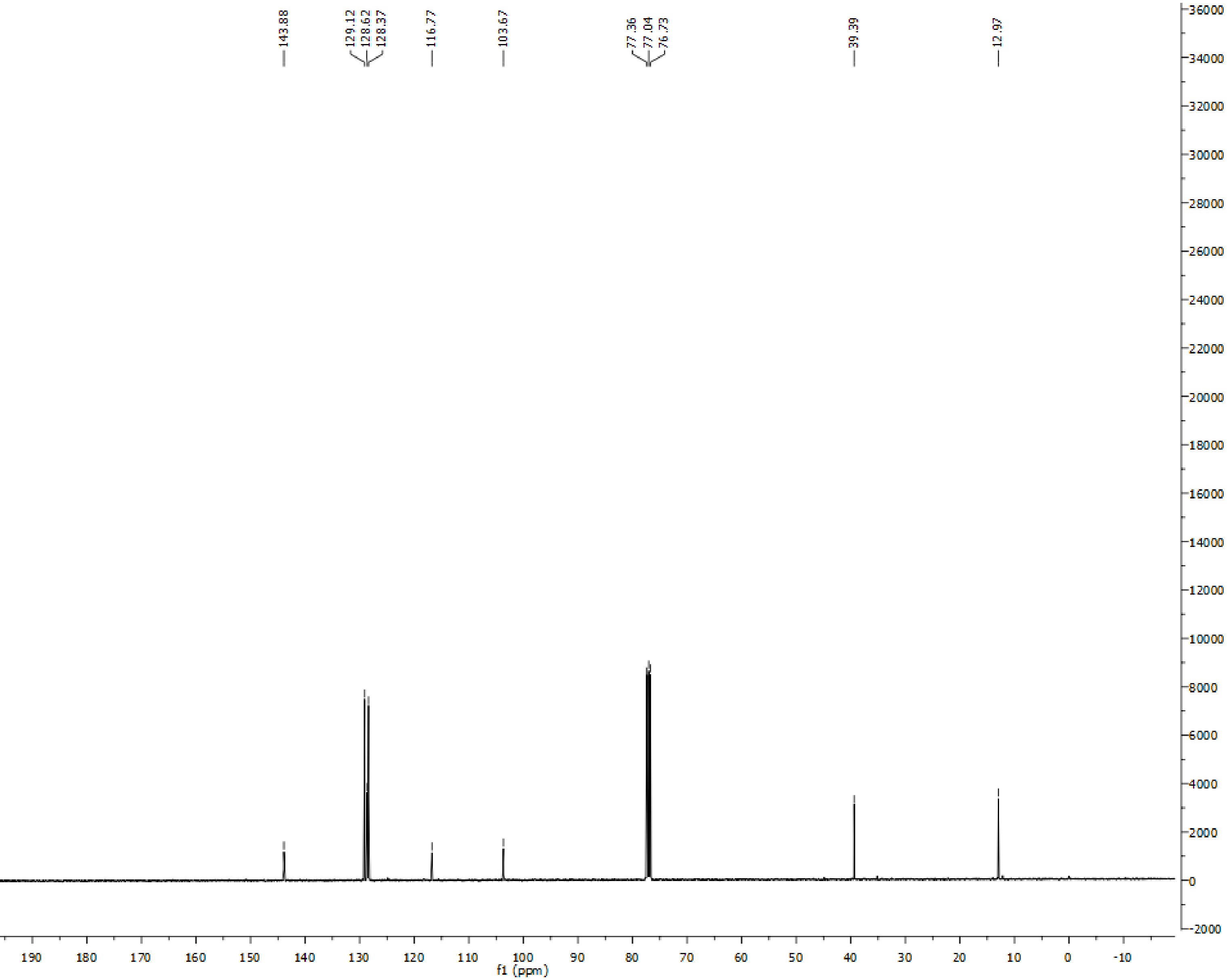
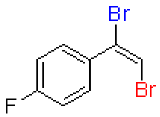


Figure S194. ^{1}H-NMR of **88**



88

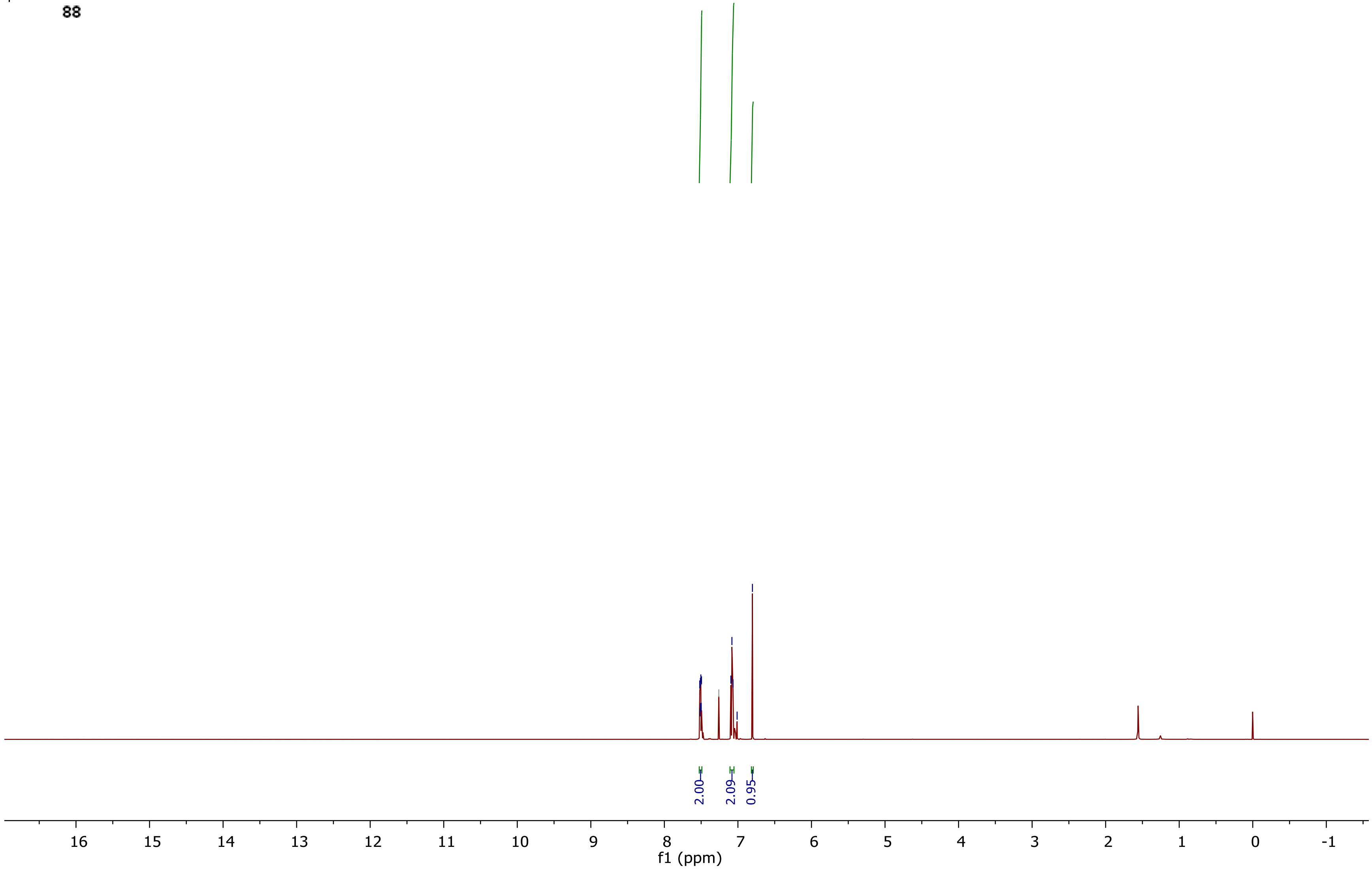
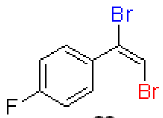


Figure S195. ^{13}C-NMR of **88**



88

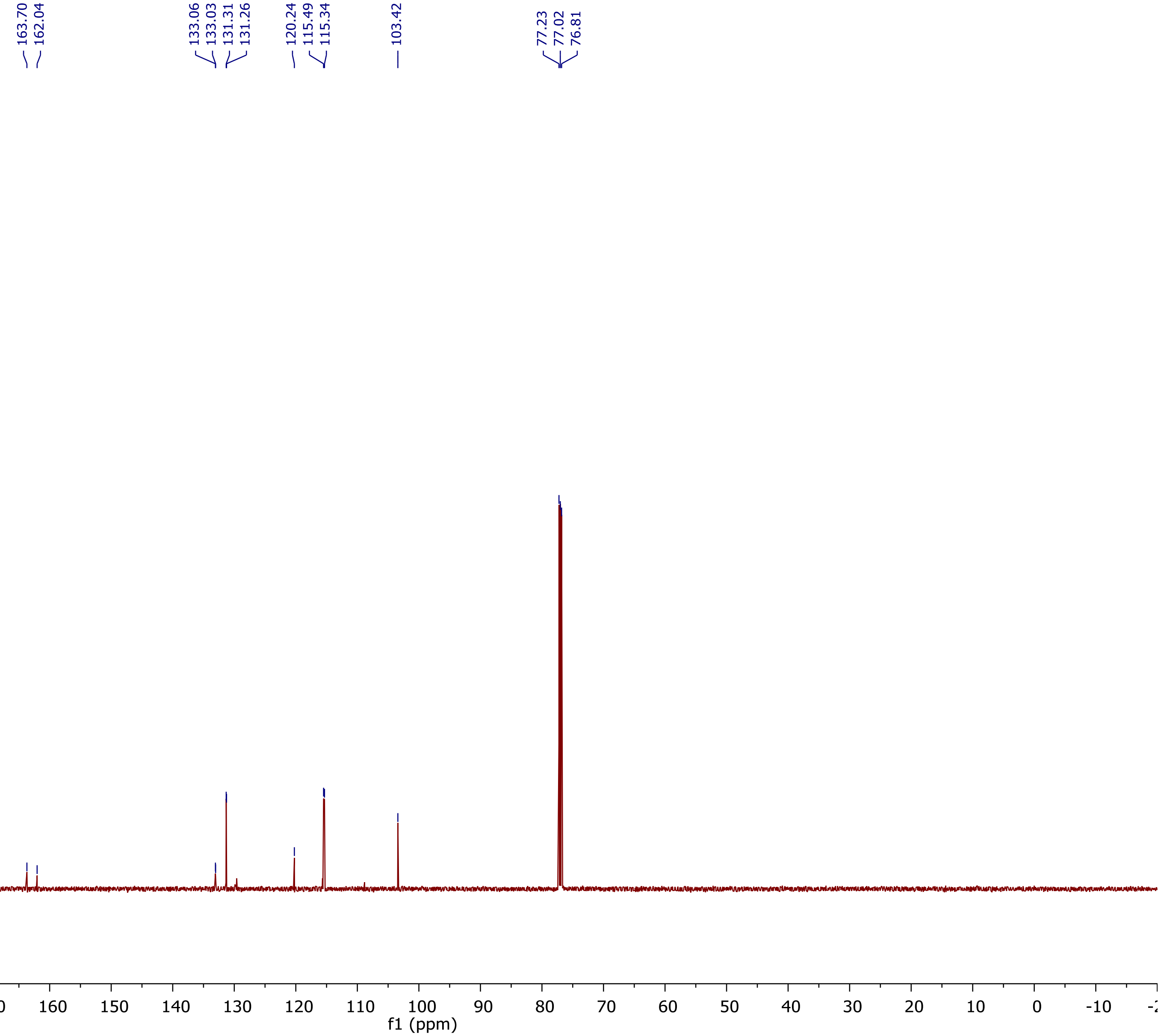


Figure S196. ^{1}H-NMR of **89**

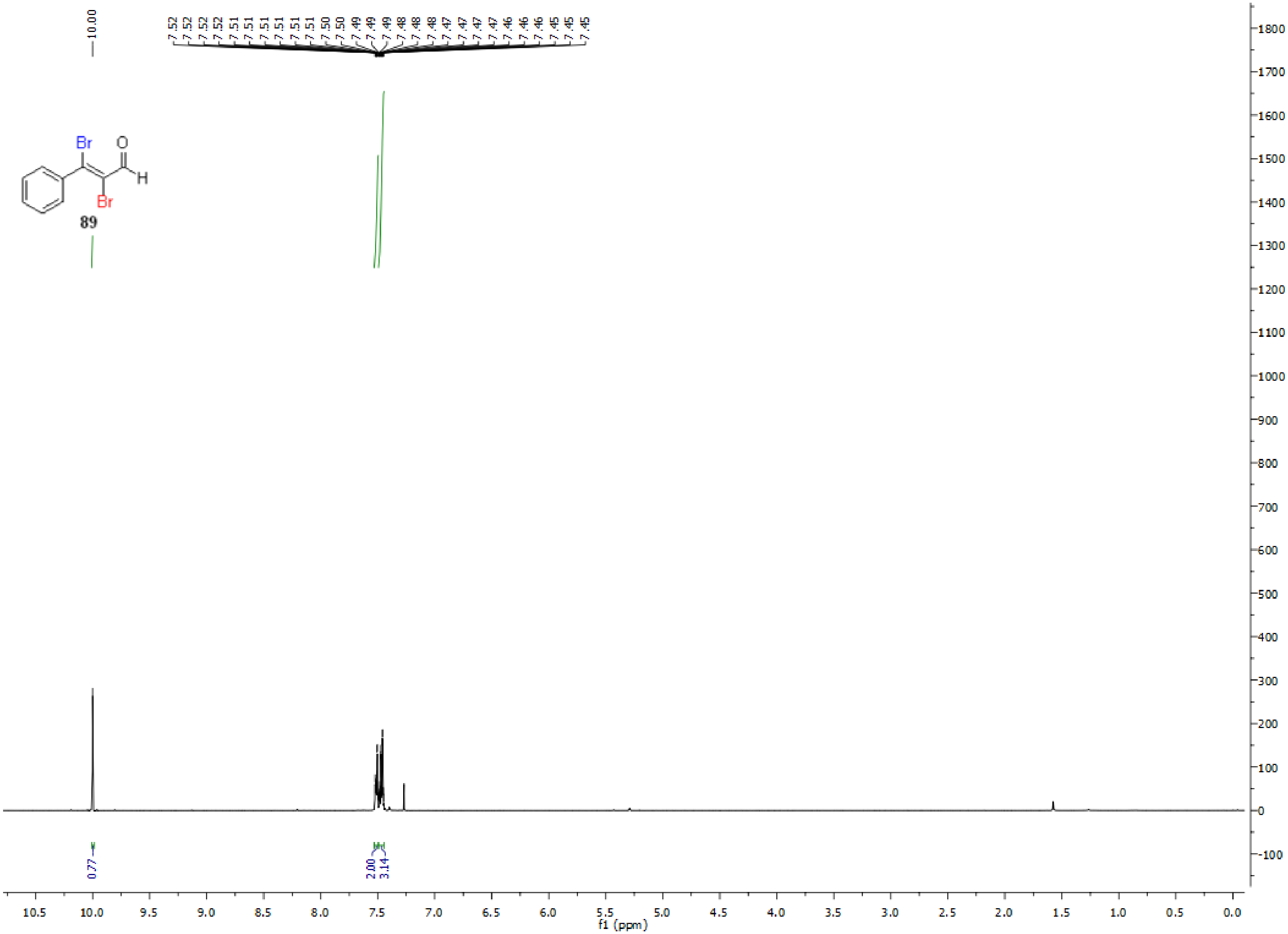


Figure S197. ^{13}C-NMR of **89**

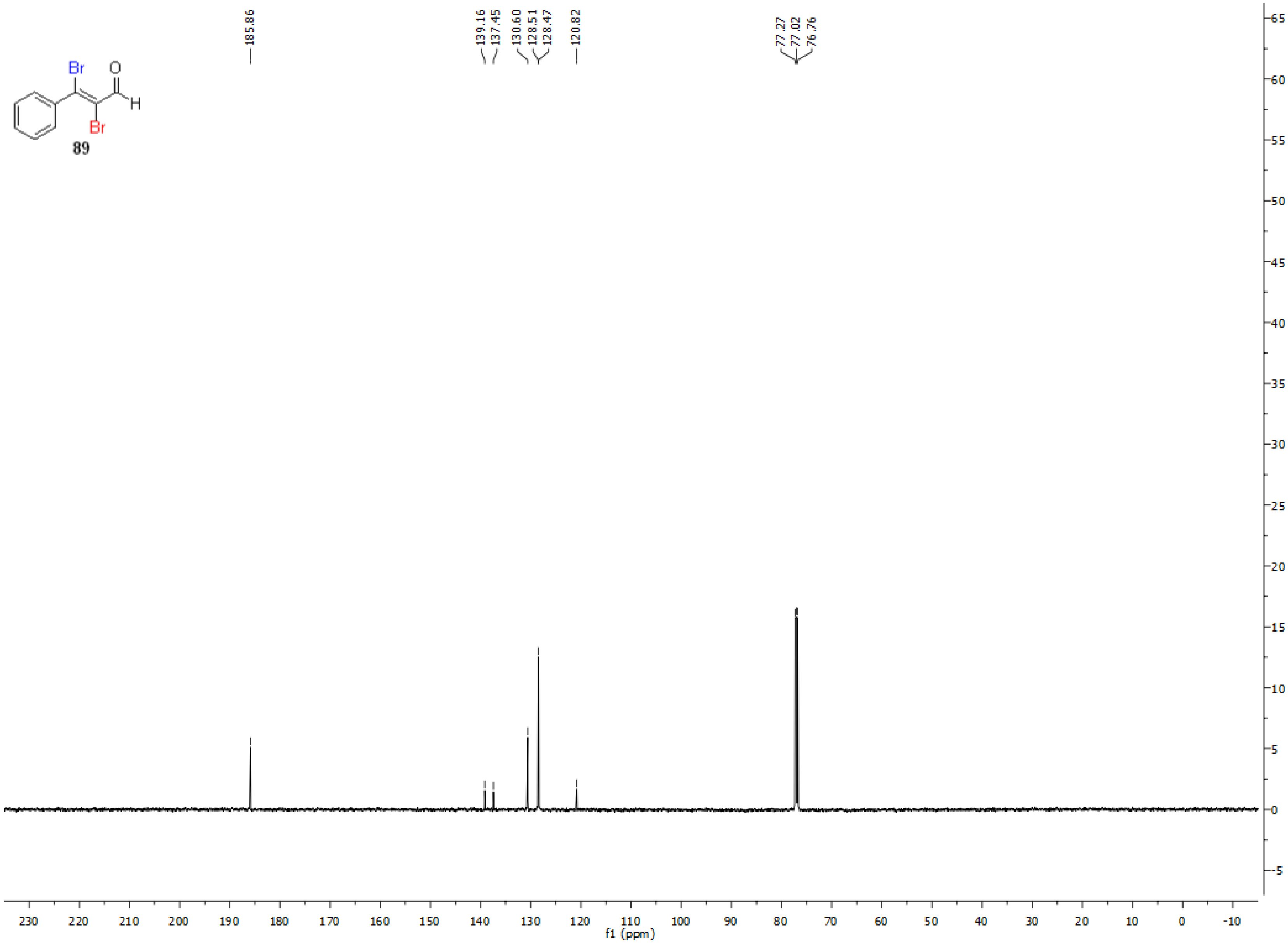
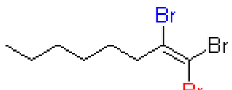


Figure S198. [1]H-NMR of **90**



90

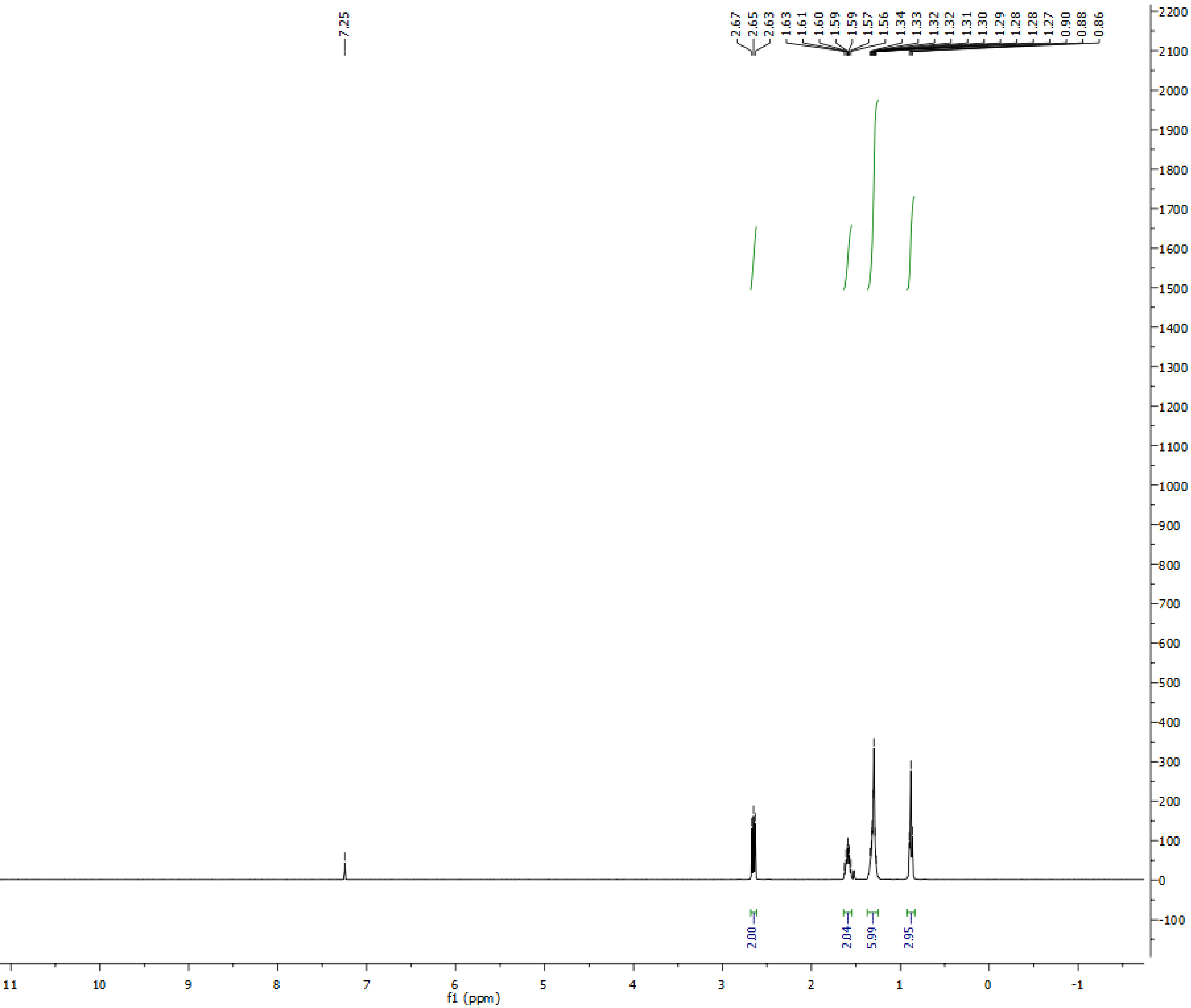
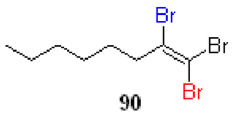


Figure S199. ^{13}C-NMR of **90**



90

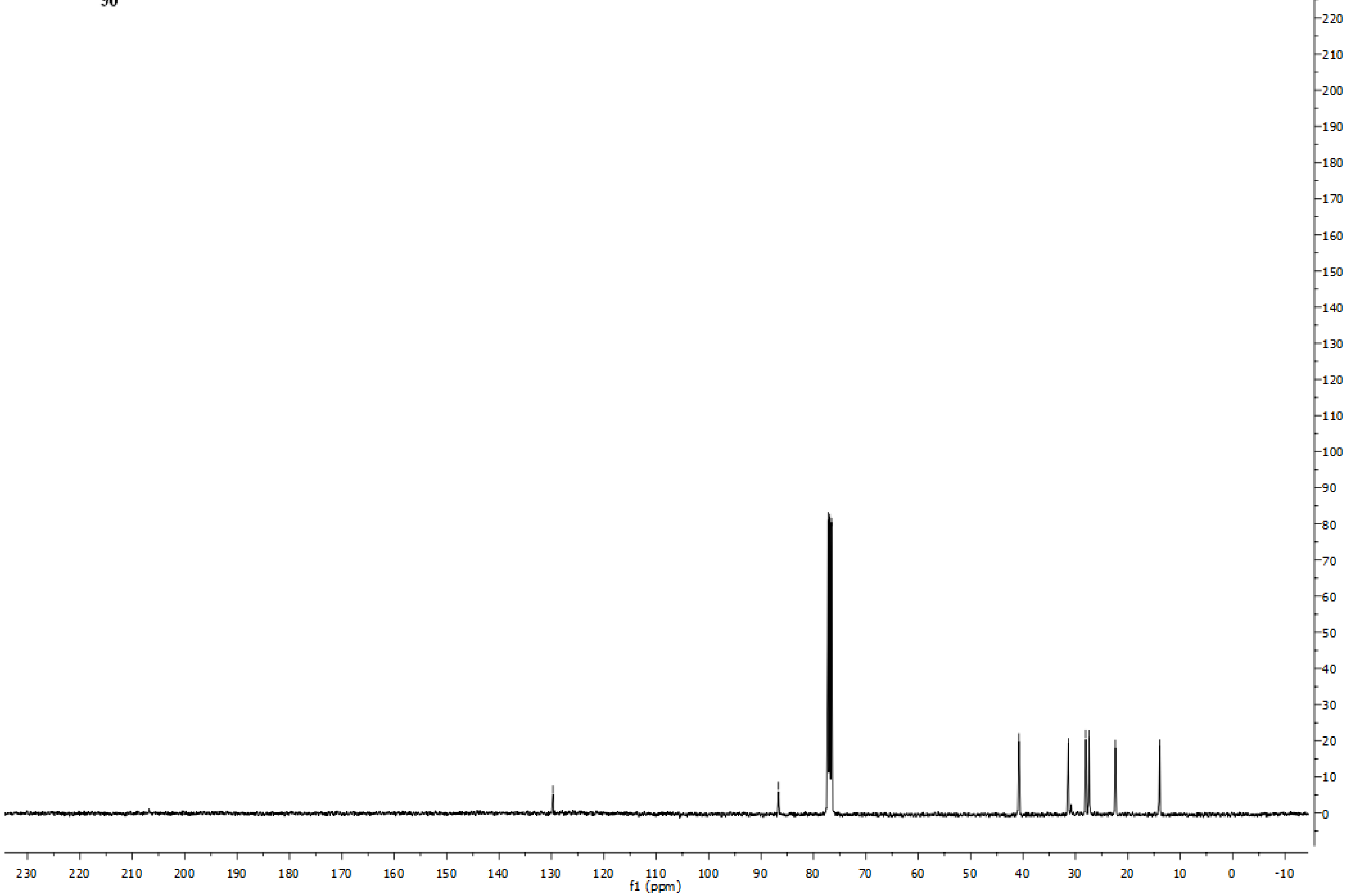


Figure S200. ^{1}H-NMR of **91**

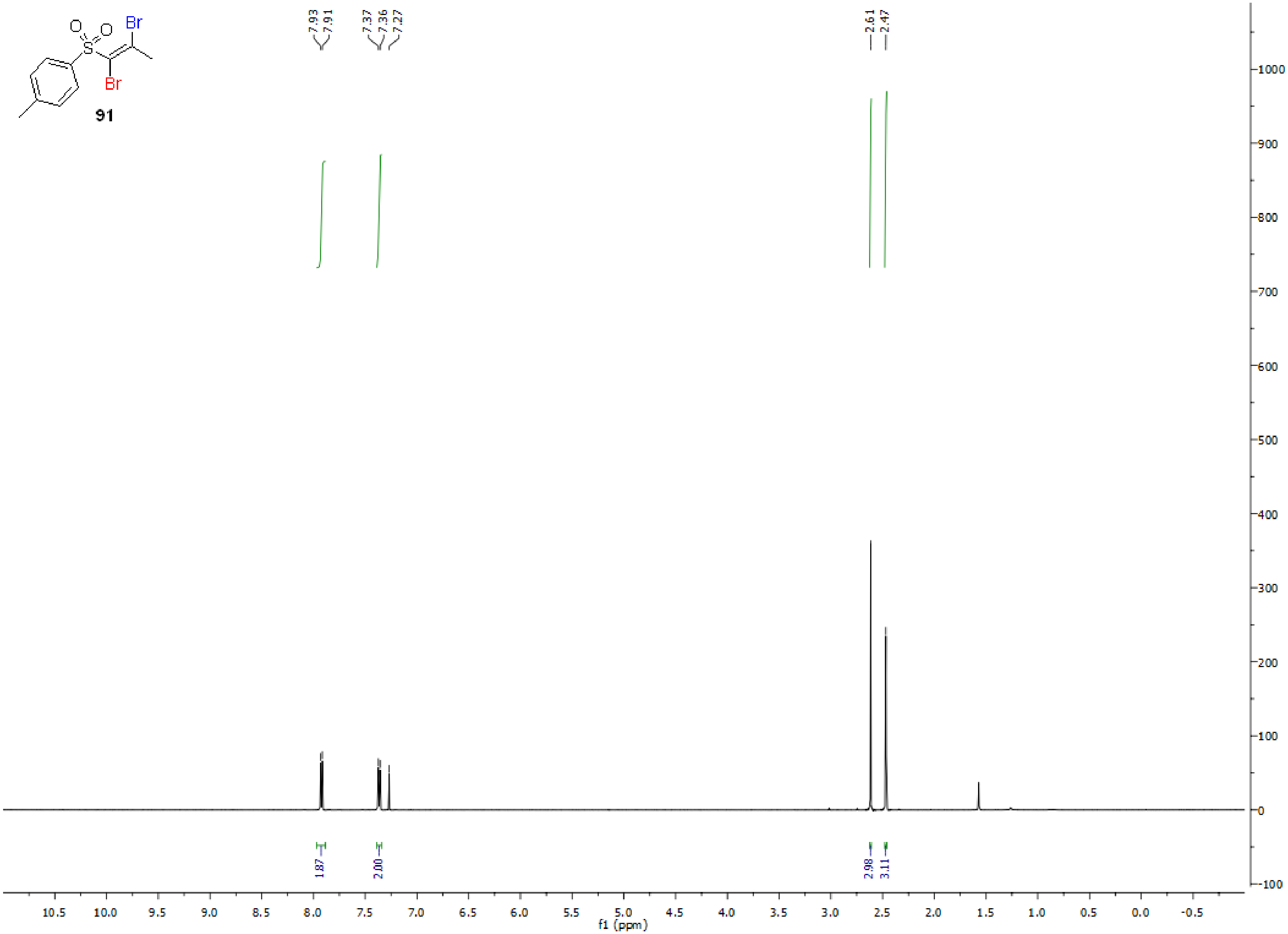
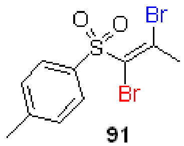


Figure S201. ^{13}C-NMR of **91**



91

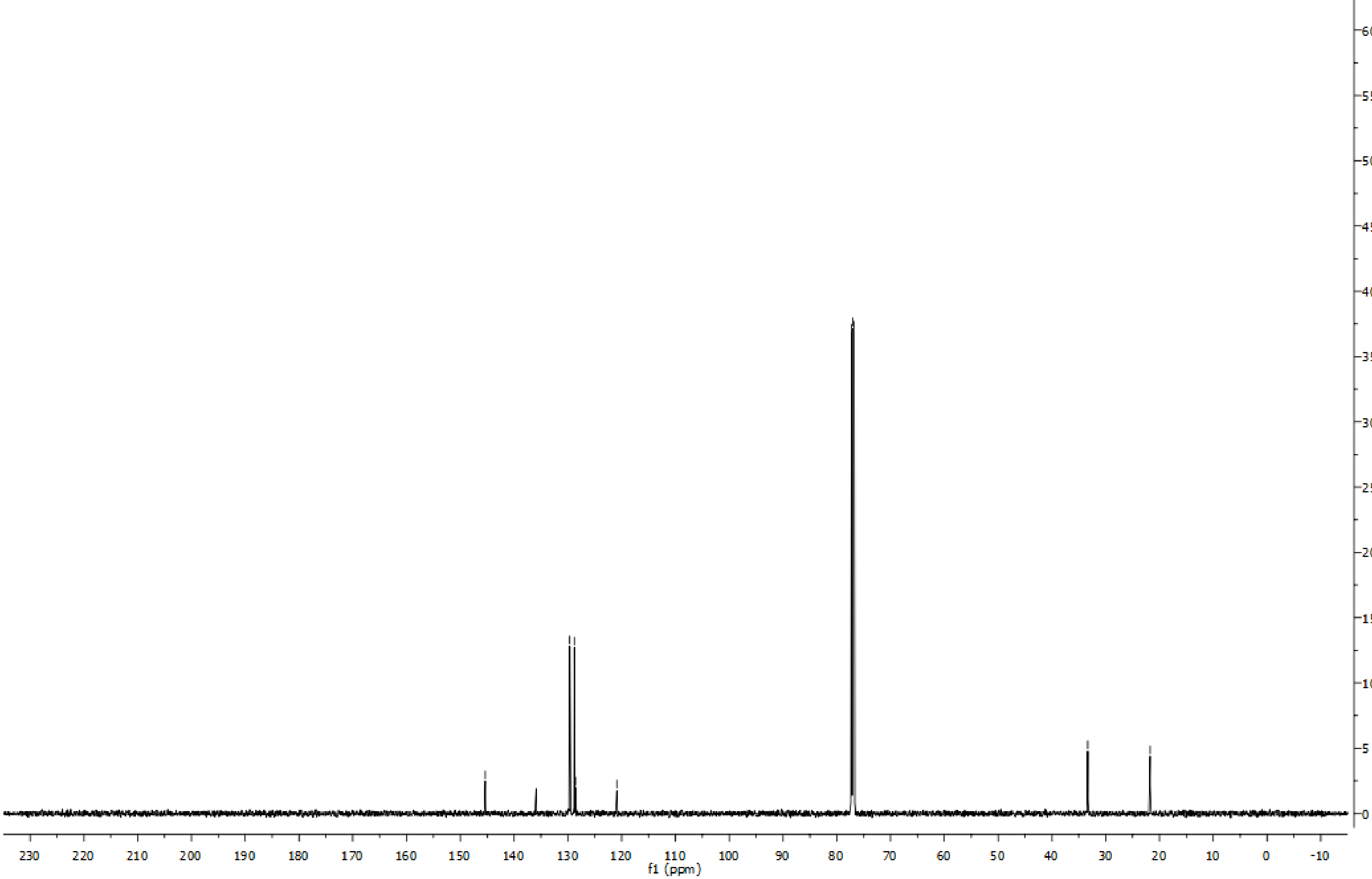
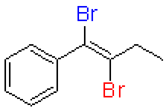


Figure S202. ^{1}H-NMR of **92**



92

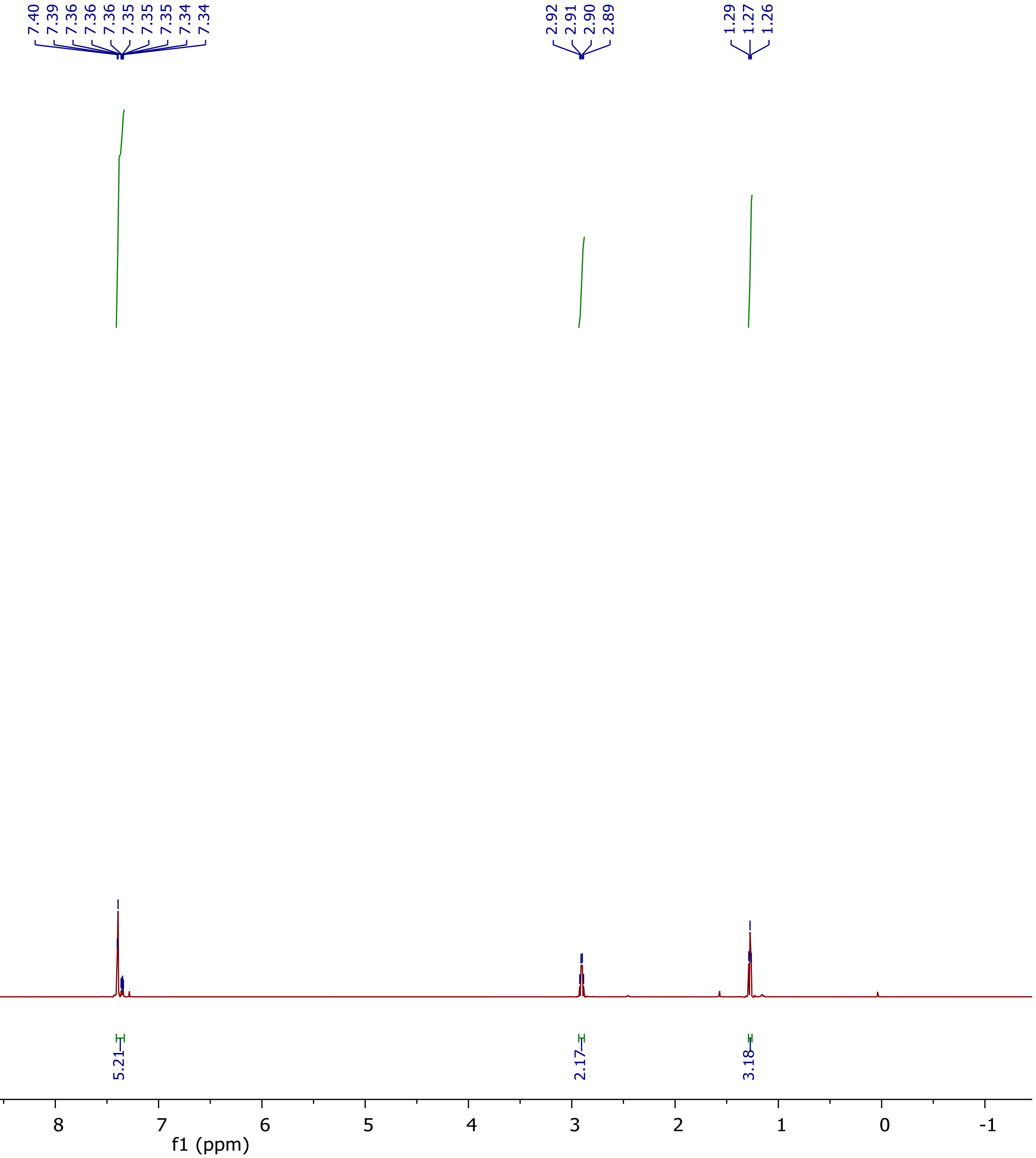
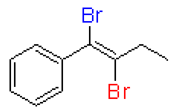


Figure S203. ^{13}C-NMR of **92**



92

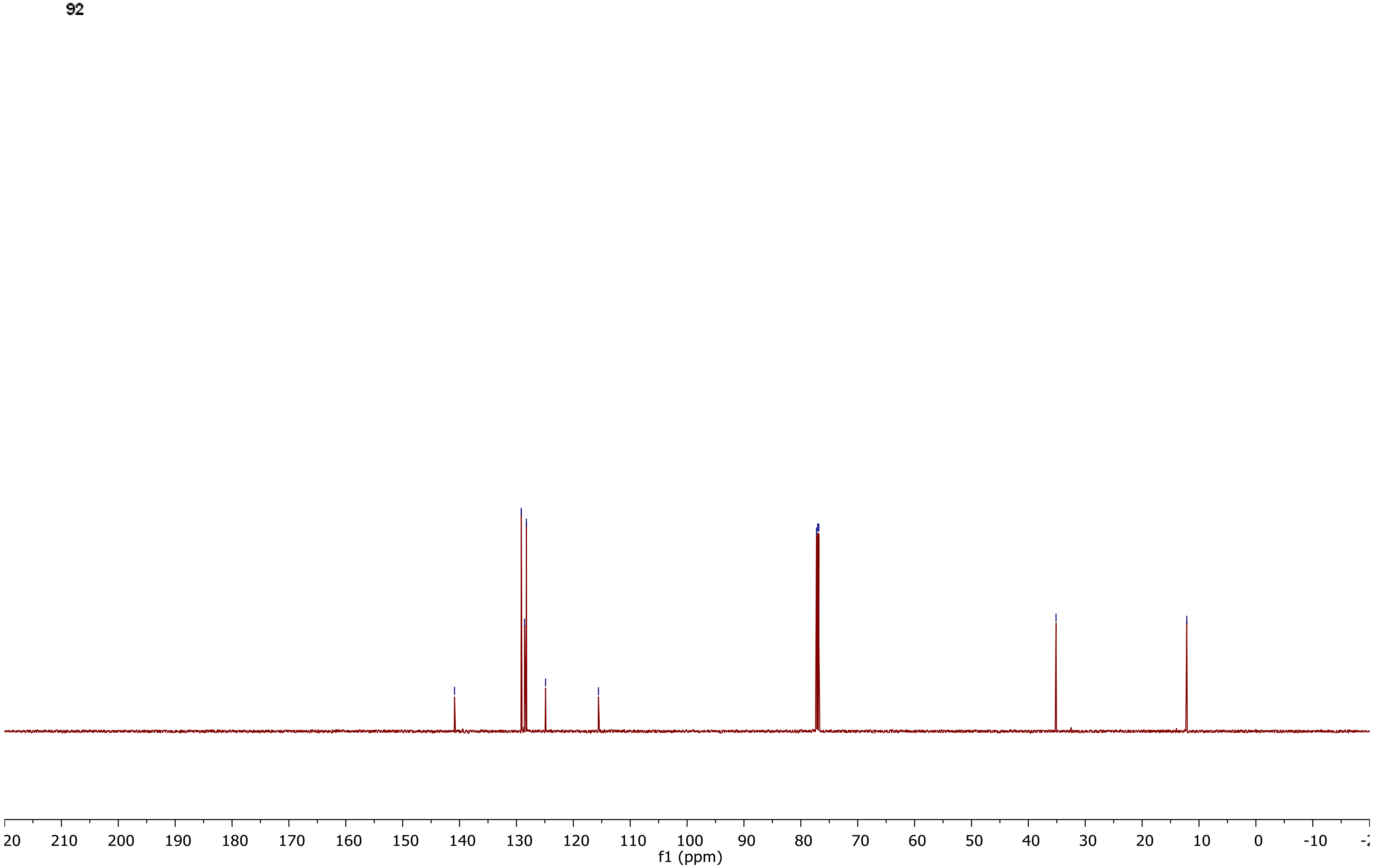
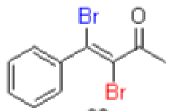


Figure S204. ^{1}H-NMR of **93**



93

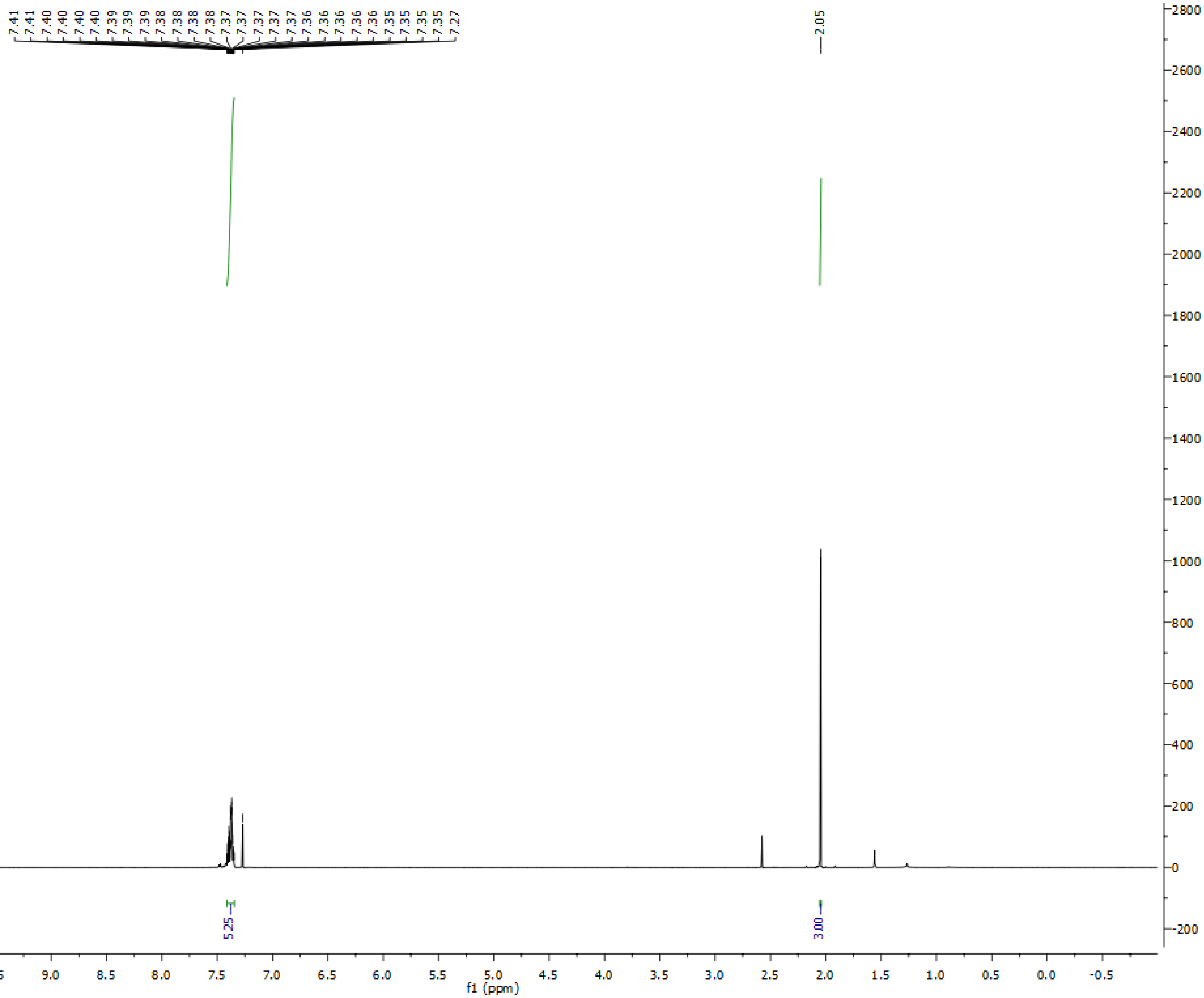


Figure S205. ^{13}C-NMR of **93**

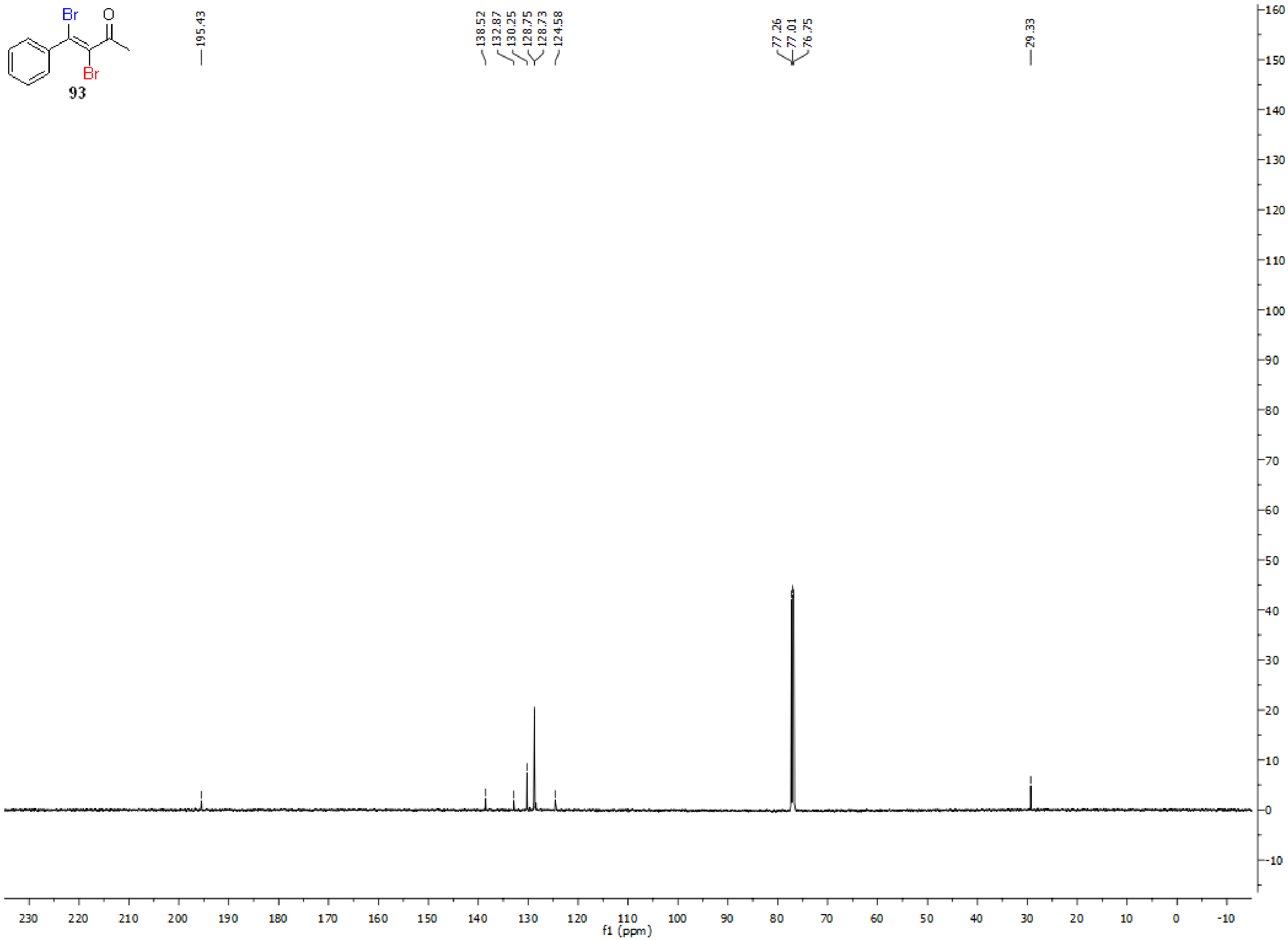
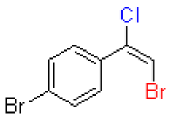


Figure S206. ^{1}H-NMR of **94**



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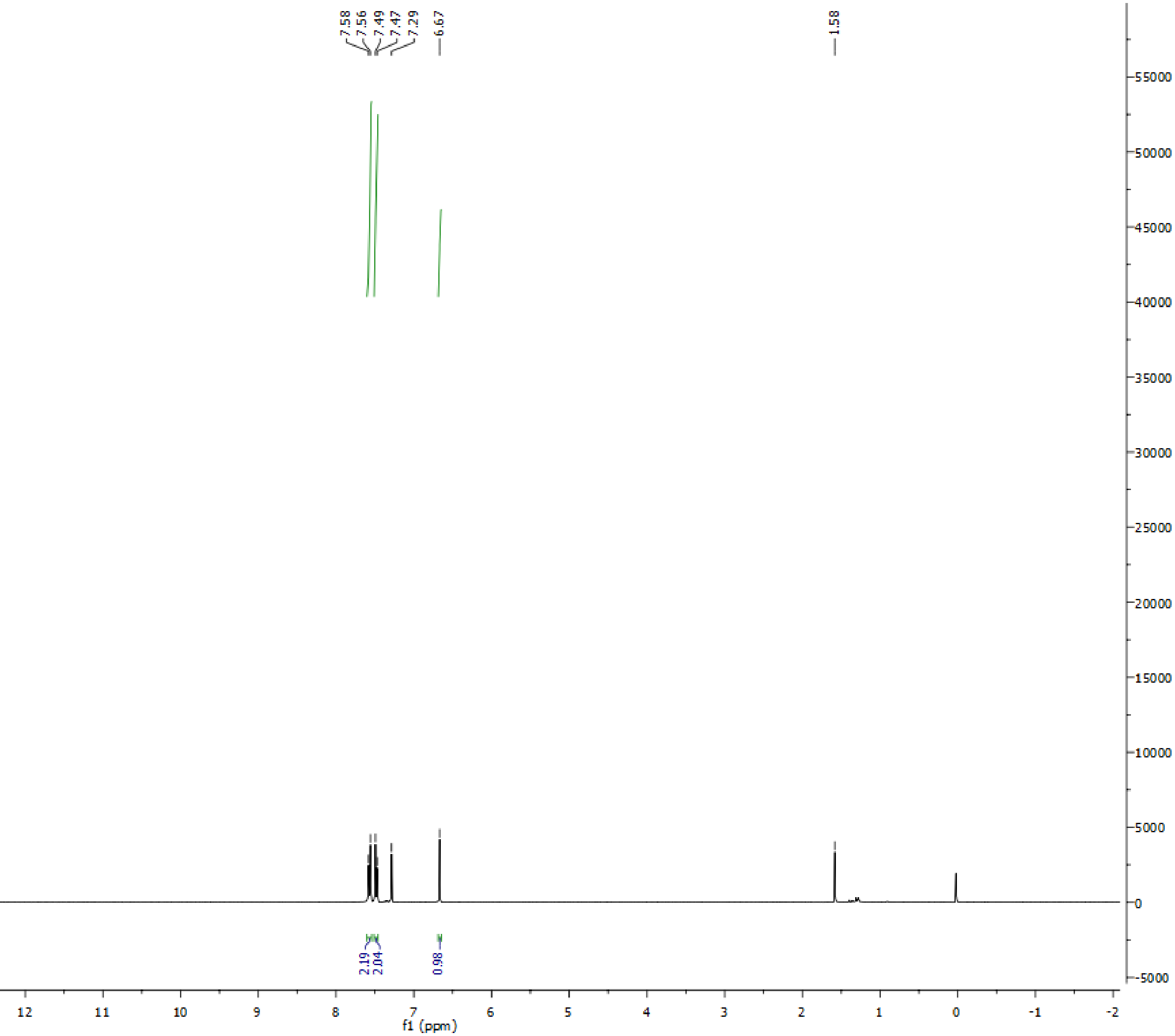
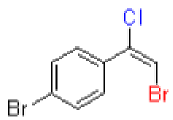


Figure S207. ^{13}C-NMR of **94**



94

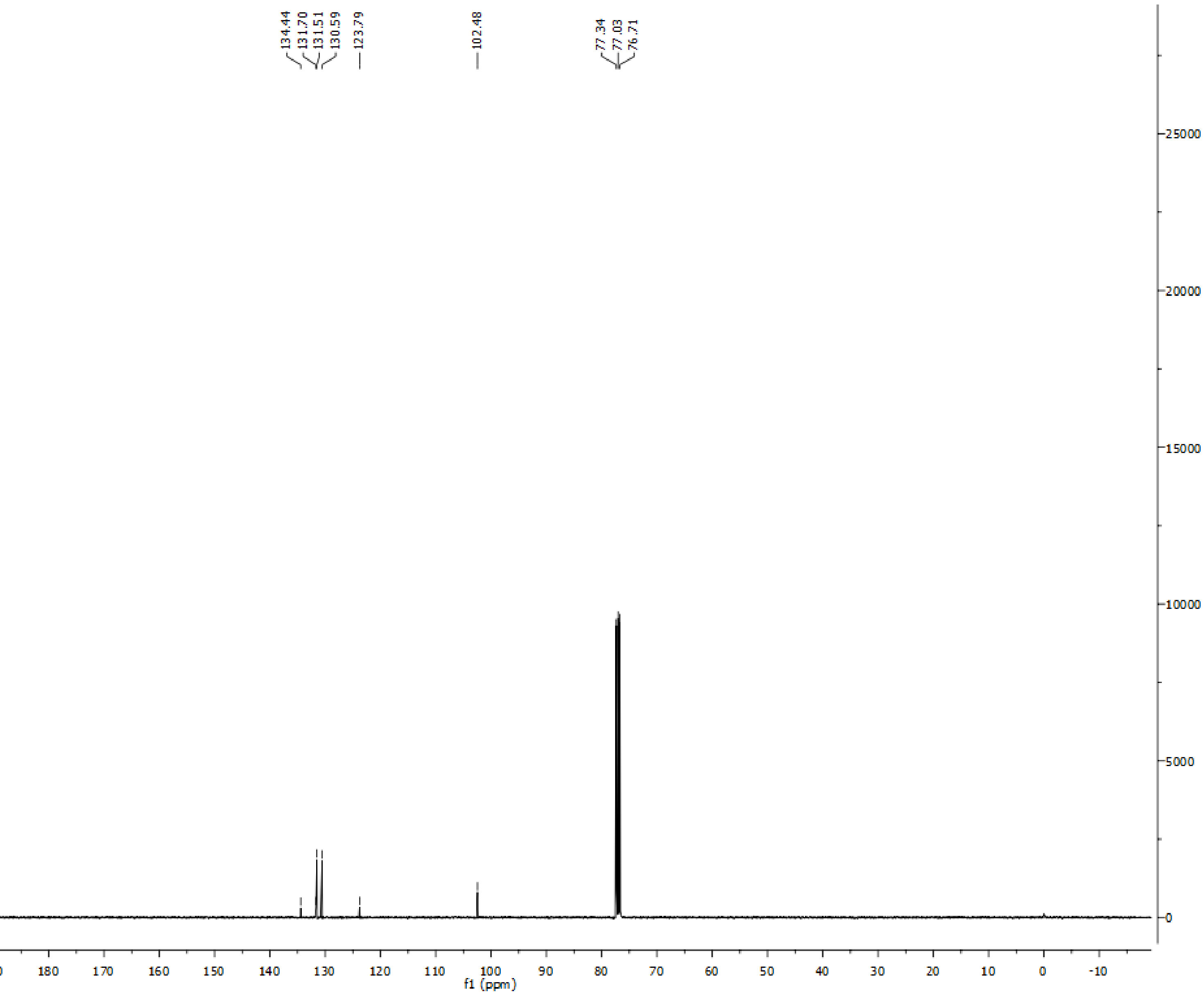


Figure S208. ^{1}H-NMR of **95**

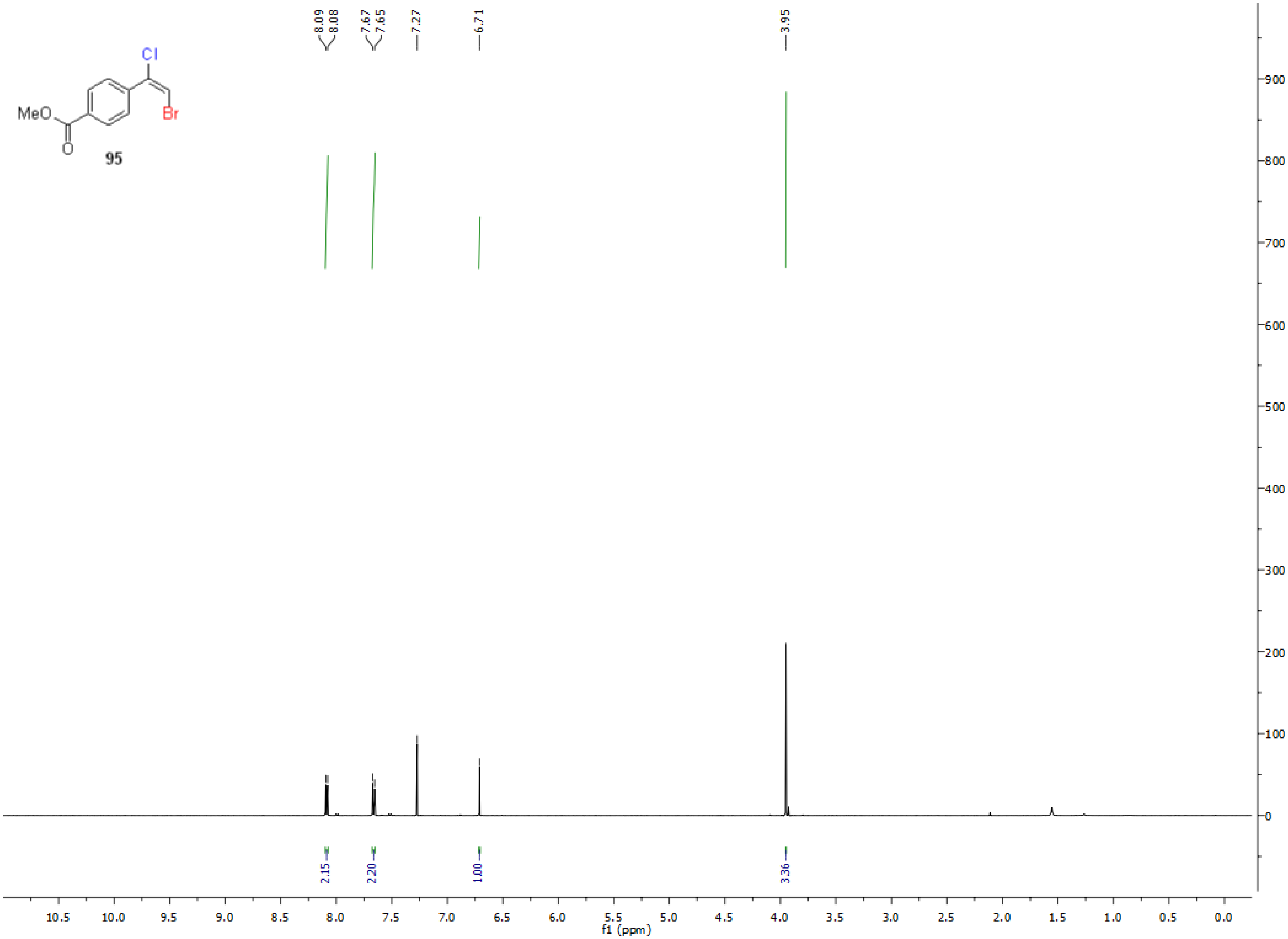
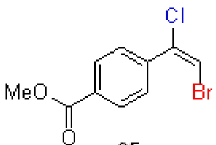


Figure S209. ^{13}C-NMR of **95**



95

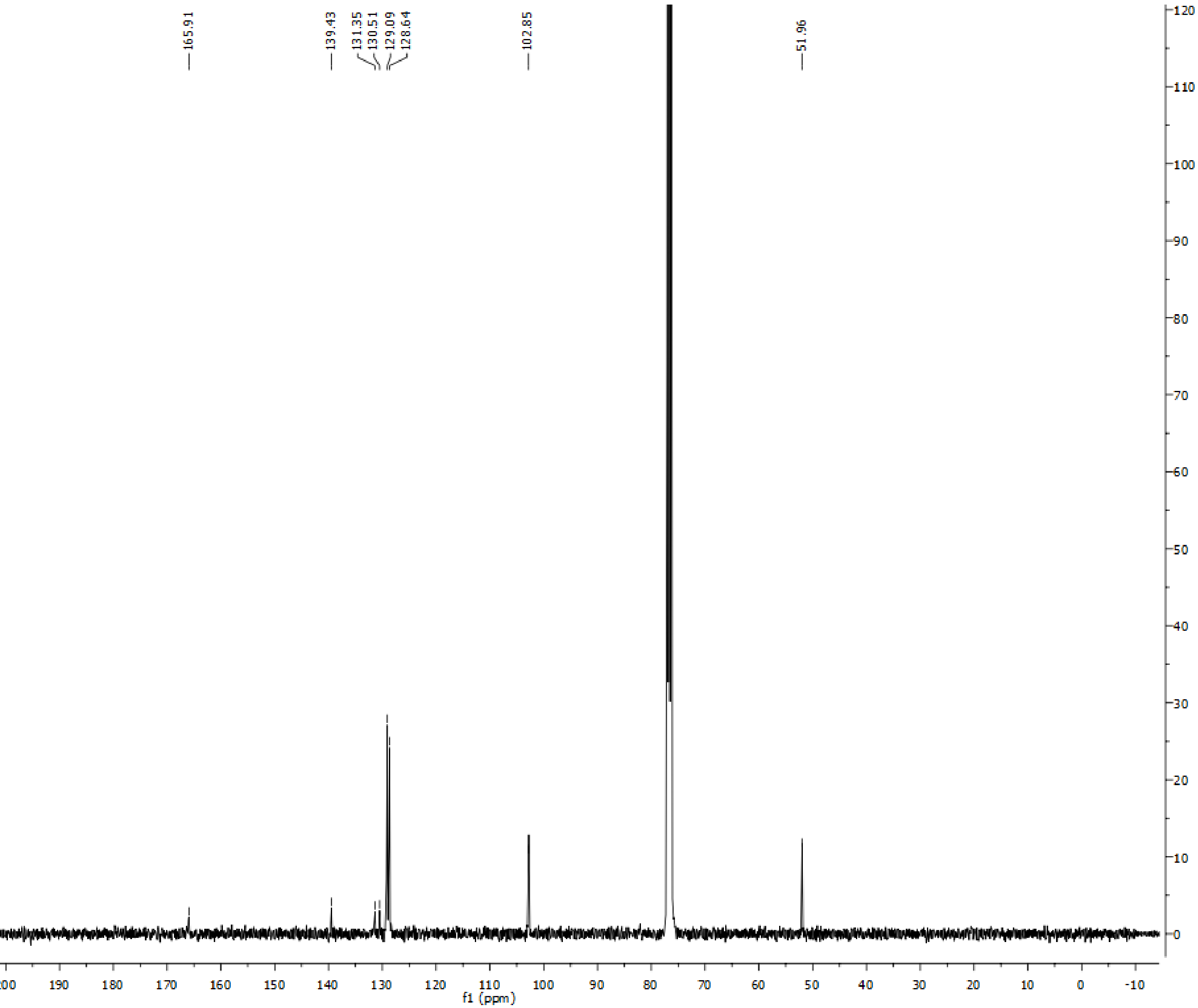
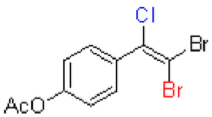


Figure S210. [1]H-NMR of **96**



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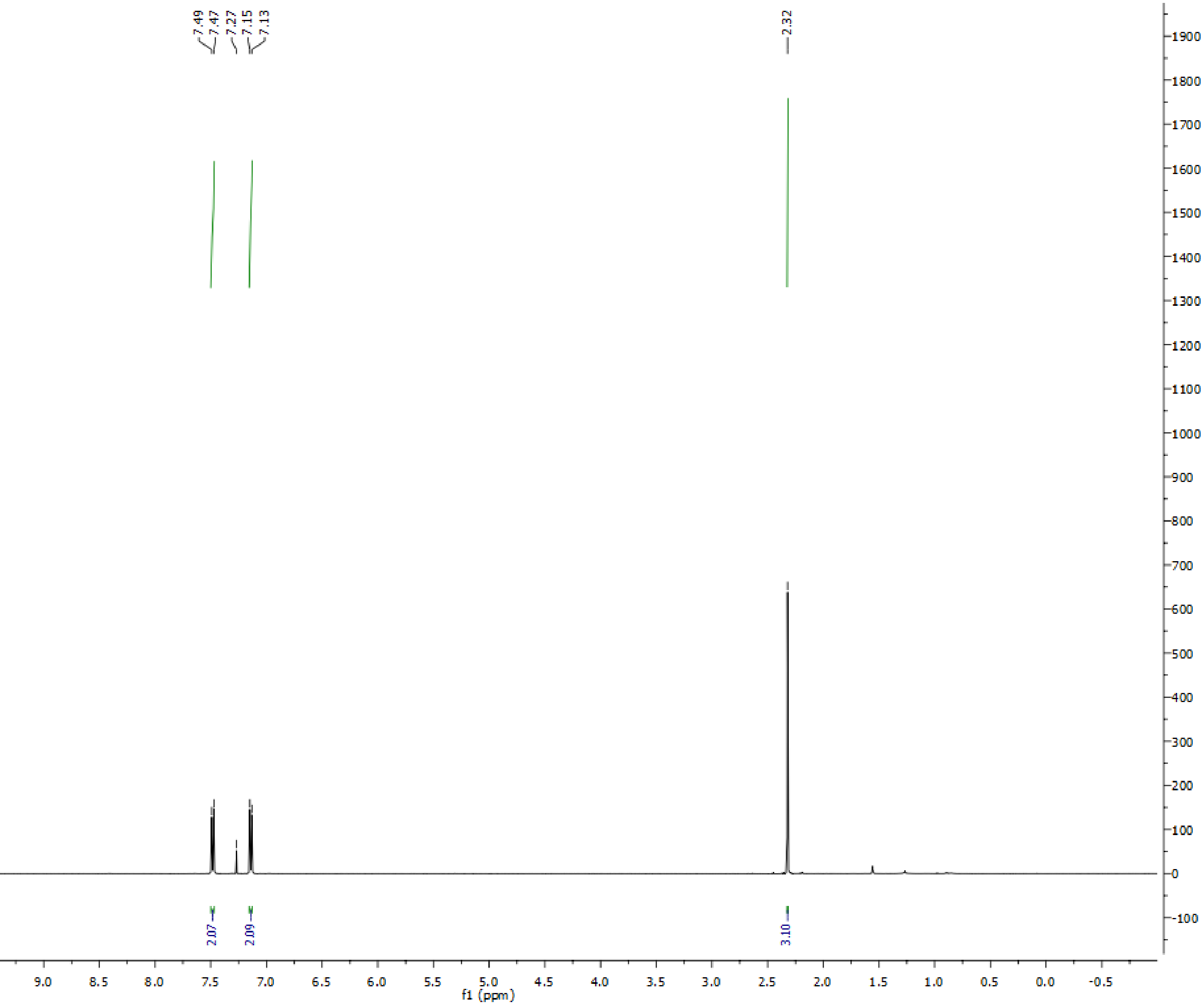
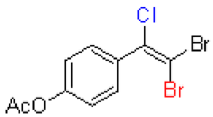


Figure S211. ^{13}C-NMR of **96**



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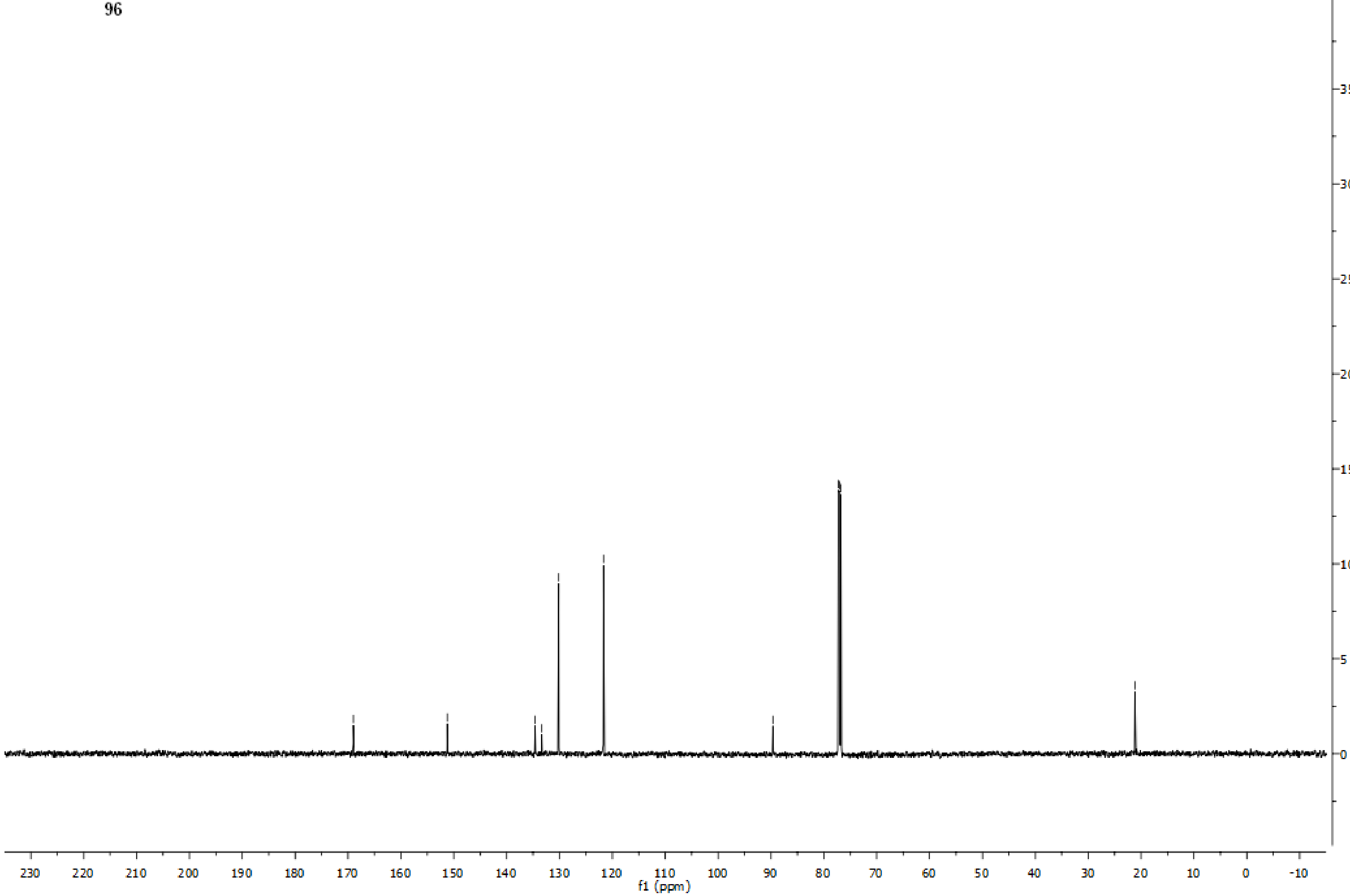


Figure S212. ^{1}H-NMR of **97**

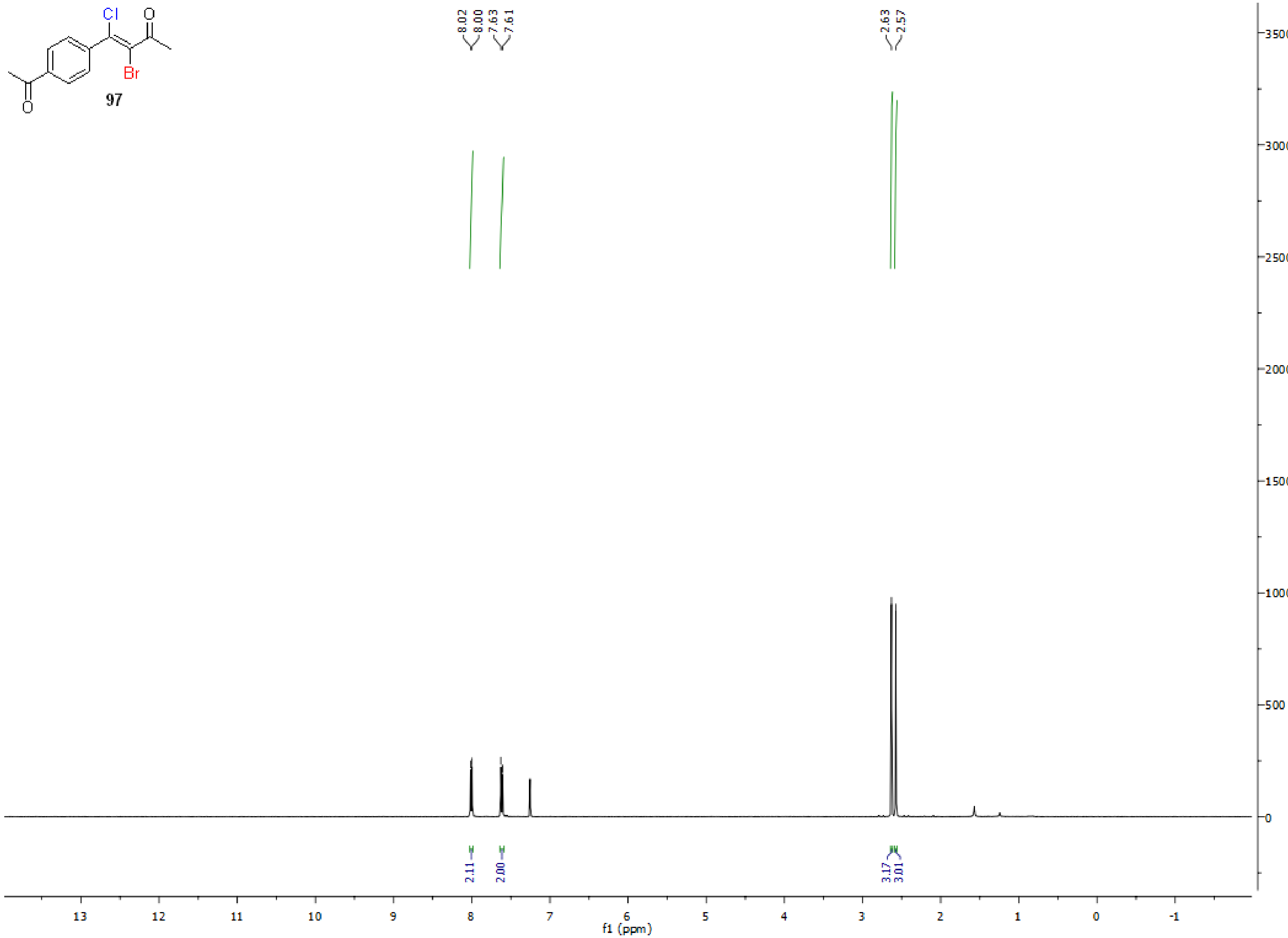


Figure S213. ^{13}C-NMR of **97**

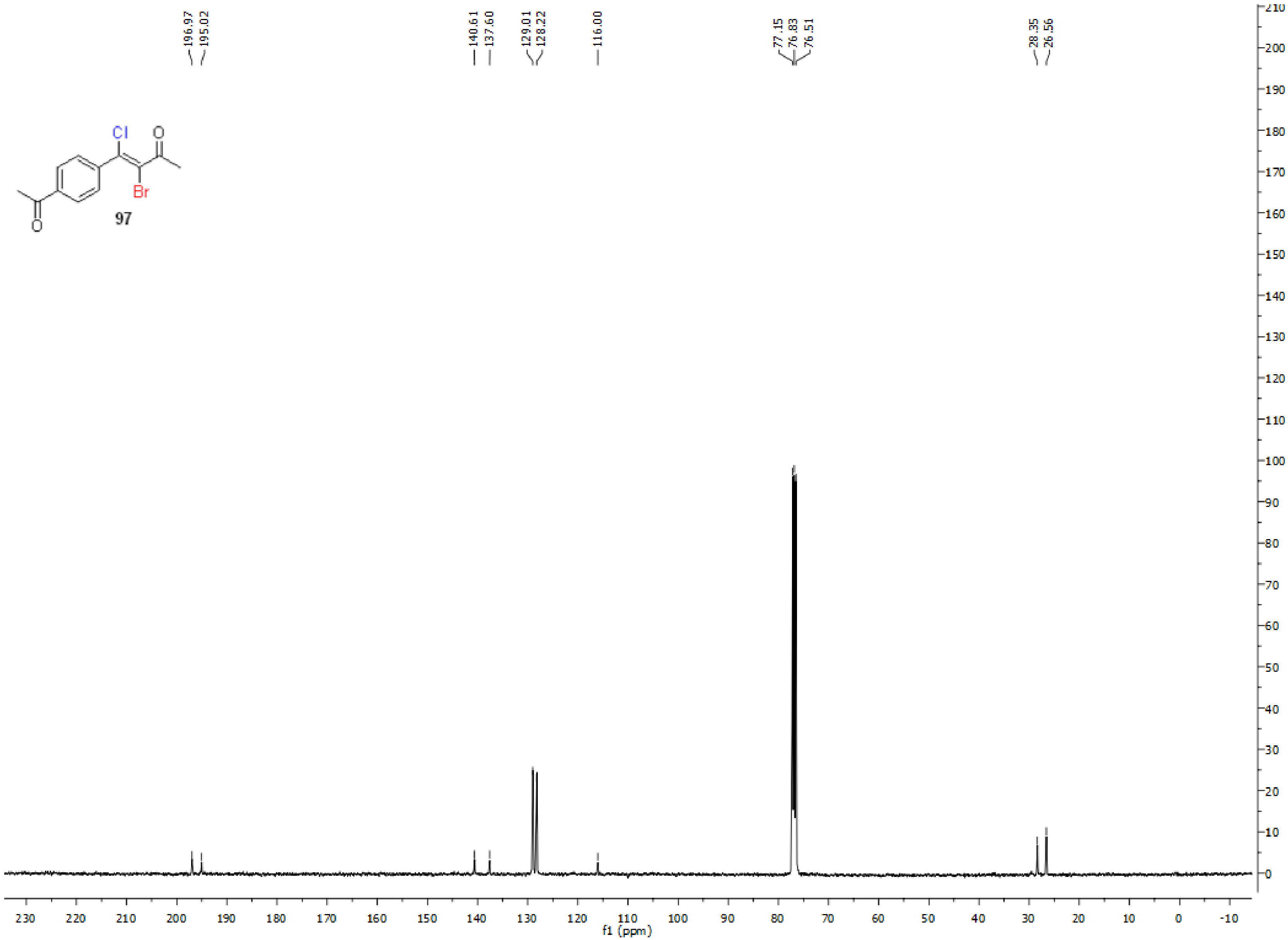
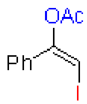


Figure S214. ^{1}H-NMR of **98**



98

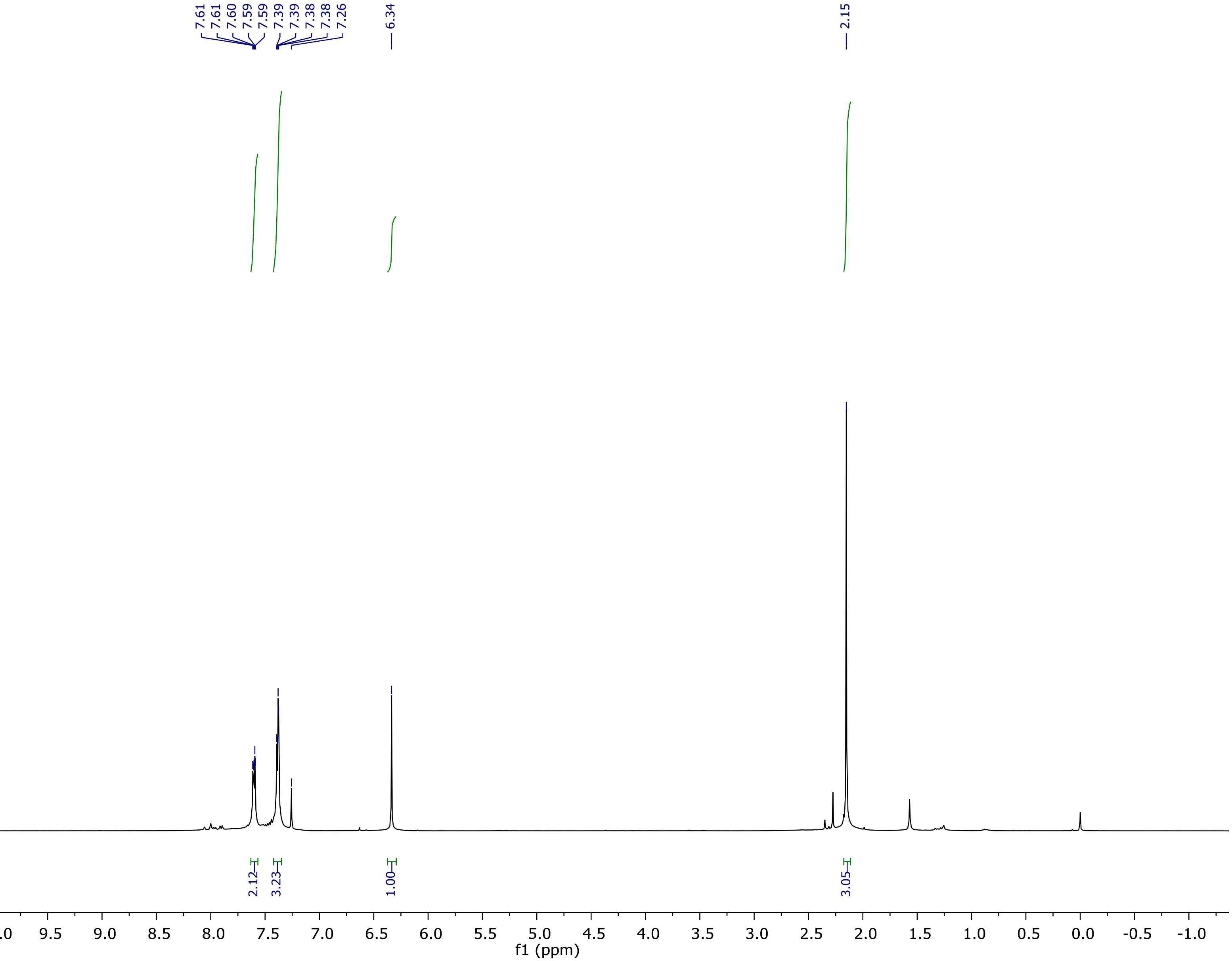
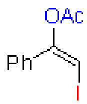


Figure S215. ^{13}C-NMR of **98**



98

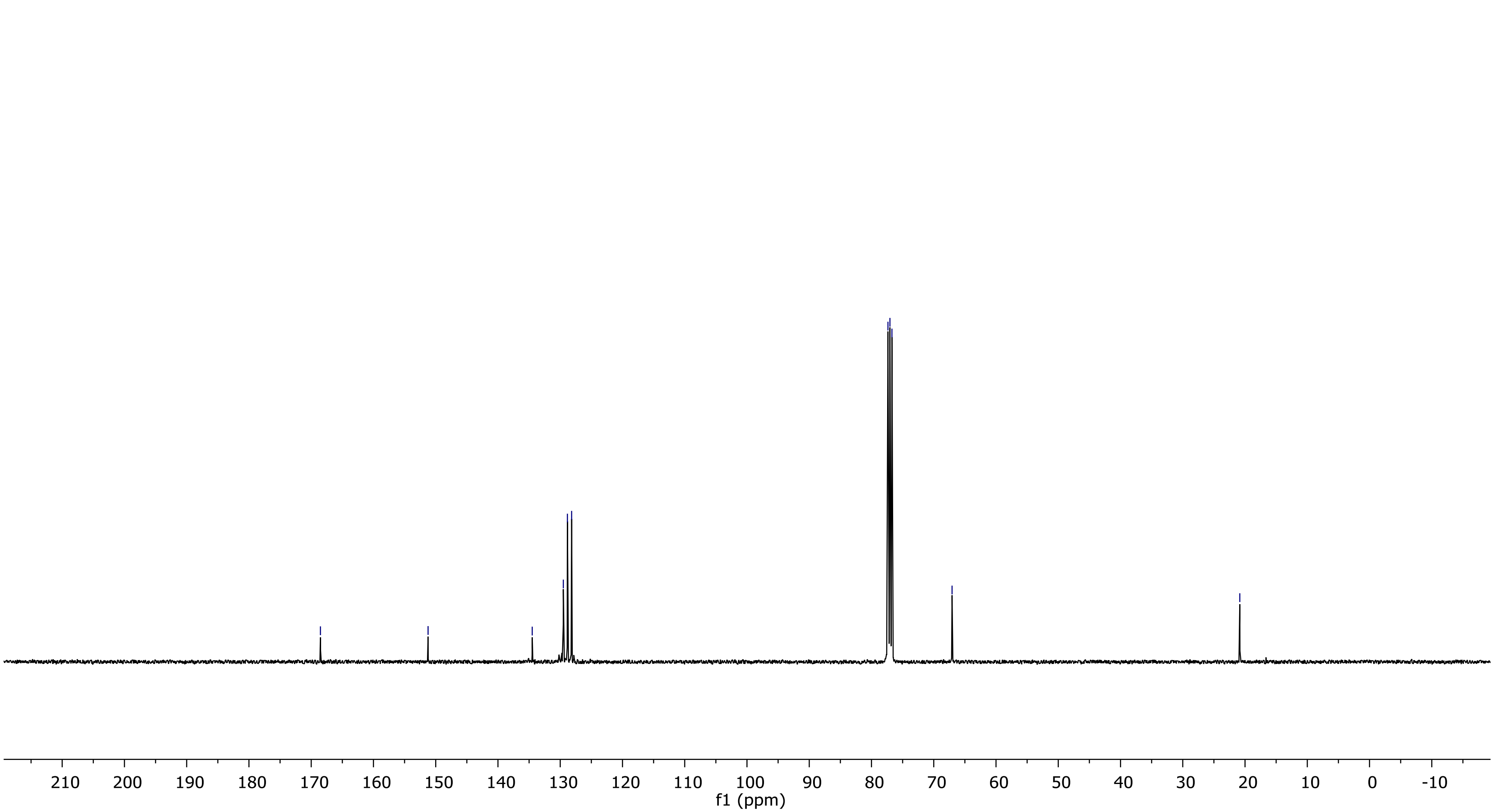
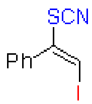


Figure S216. ^{1}H-NMR of **99**



99

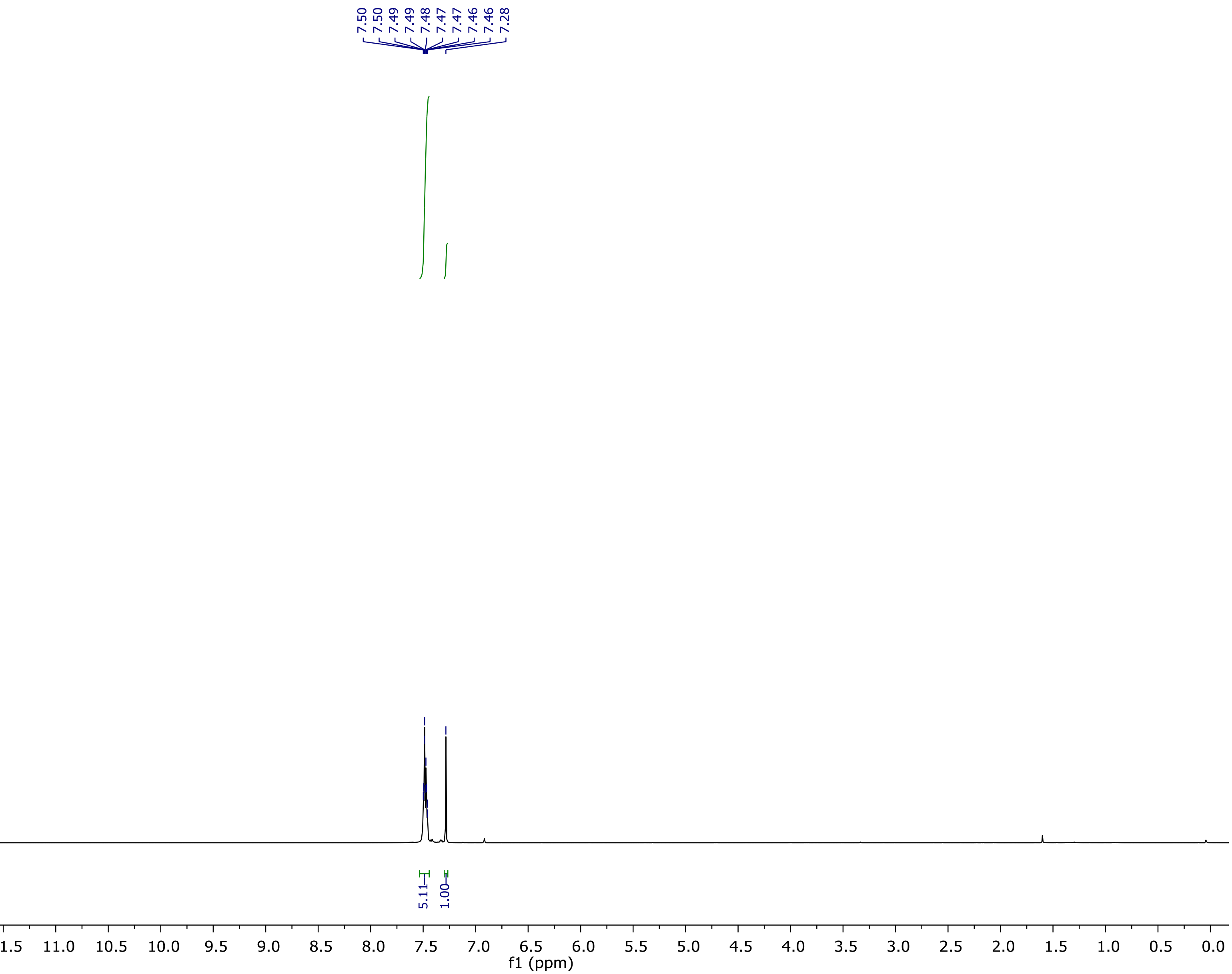


Figure S217. ^{13}C-NMR of **99**

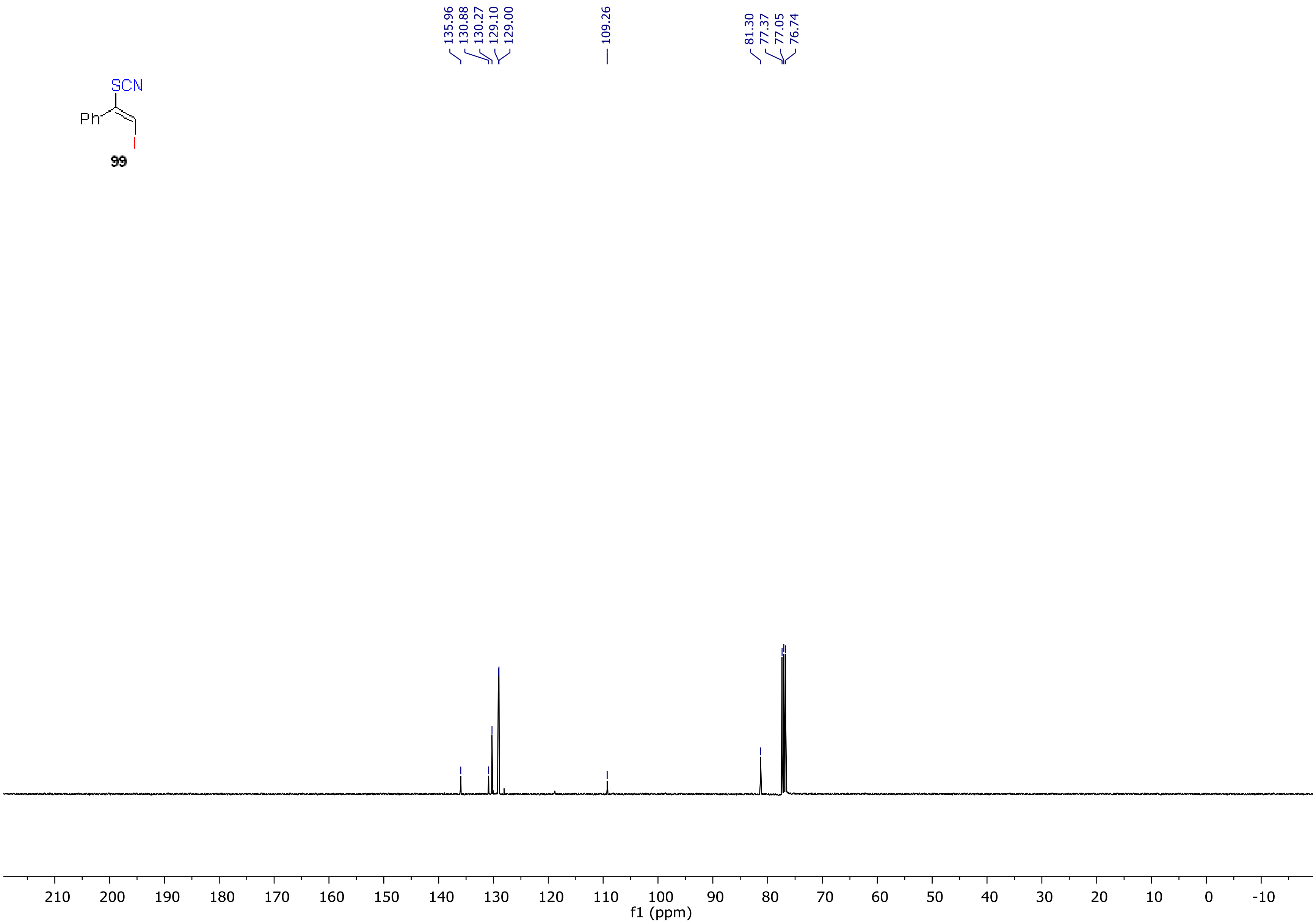
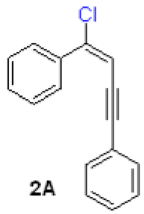


Figure S218. ^{1}H-NMR of **2A**



2A

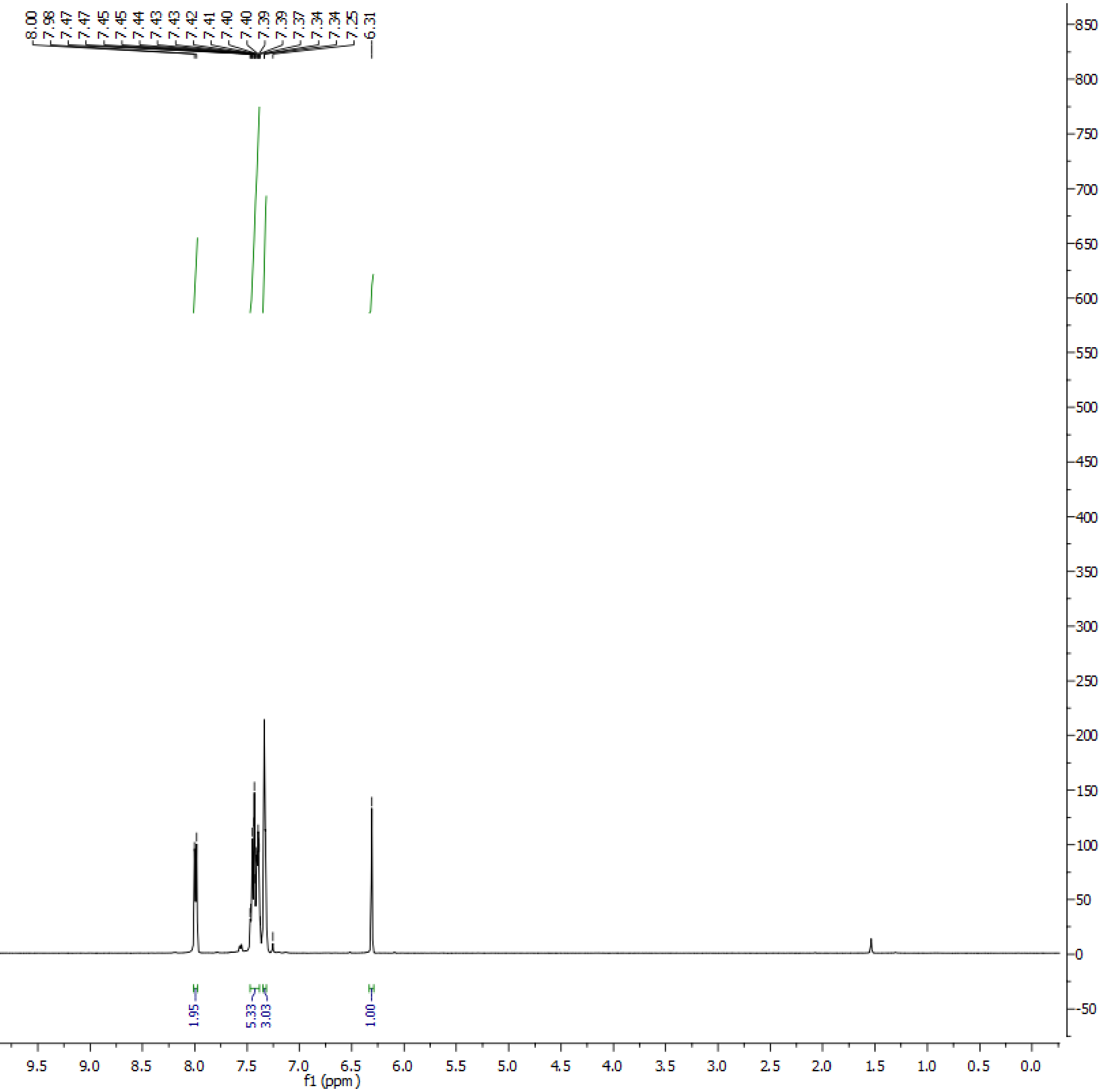


Figure S219. ^{13}C-NMR of **2A**

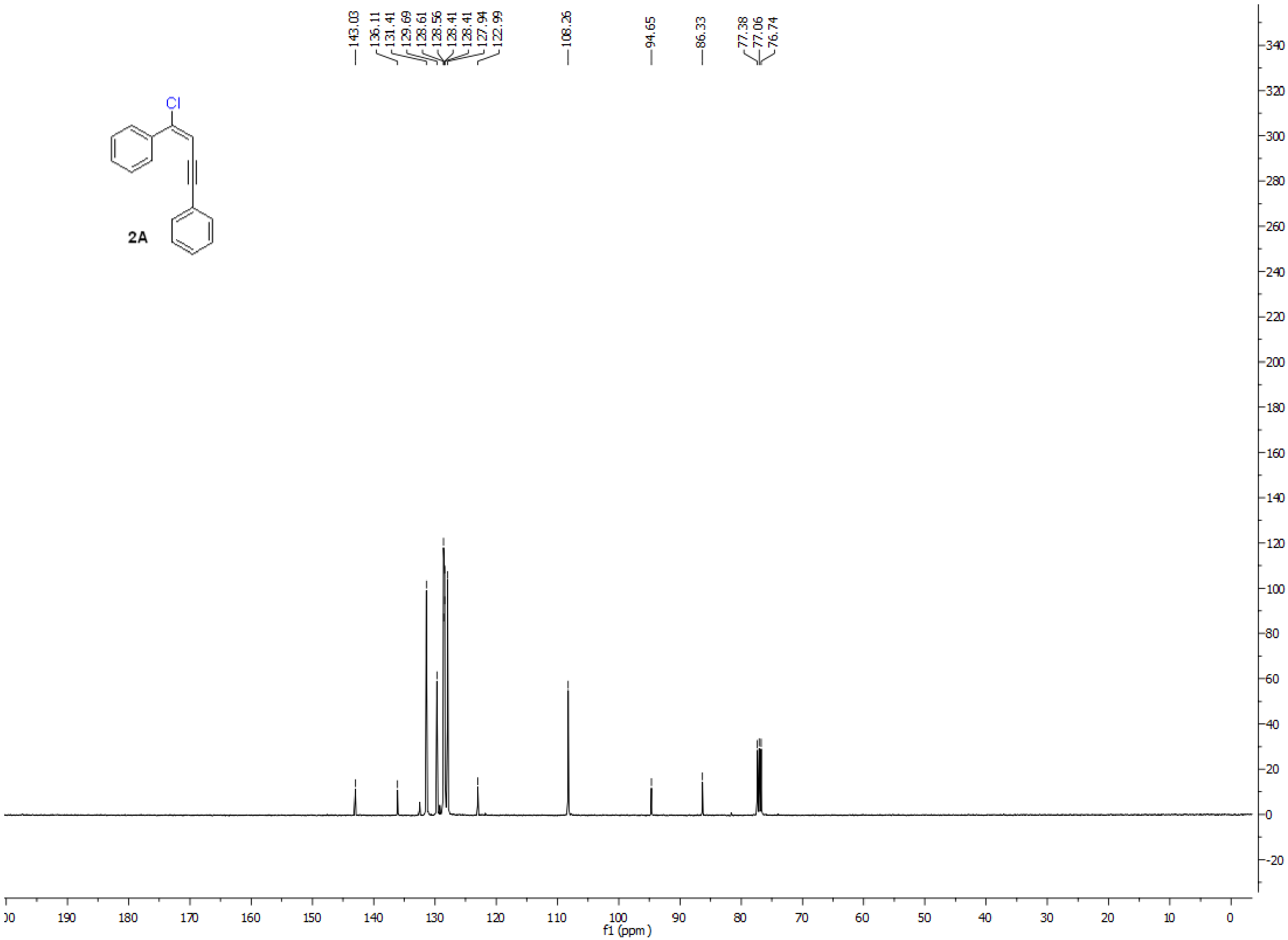


Figure S220. ^{1}H-NMR of **100**

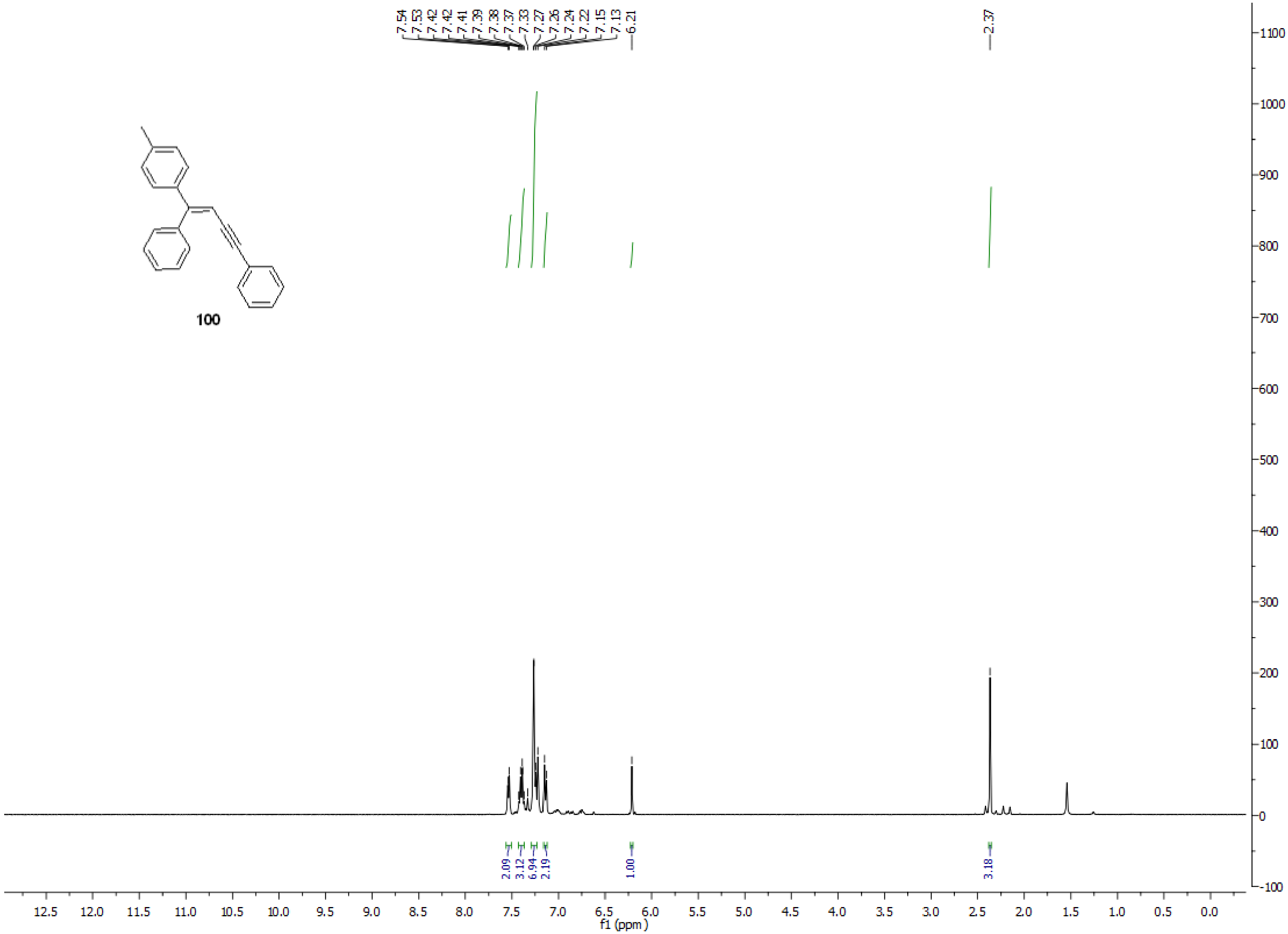
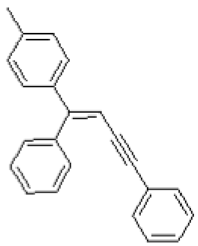


Figure S221. ^{13}C-NMR of **100**



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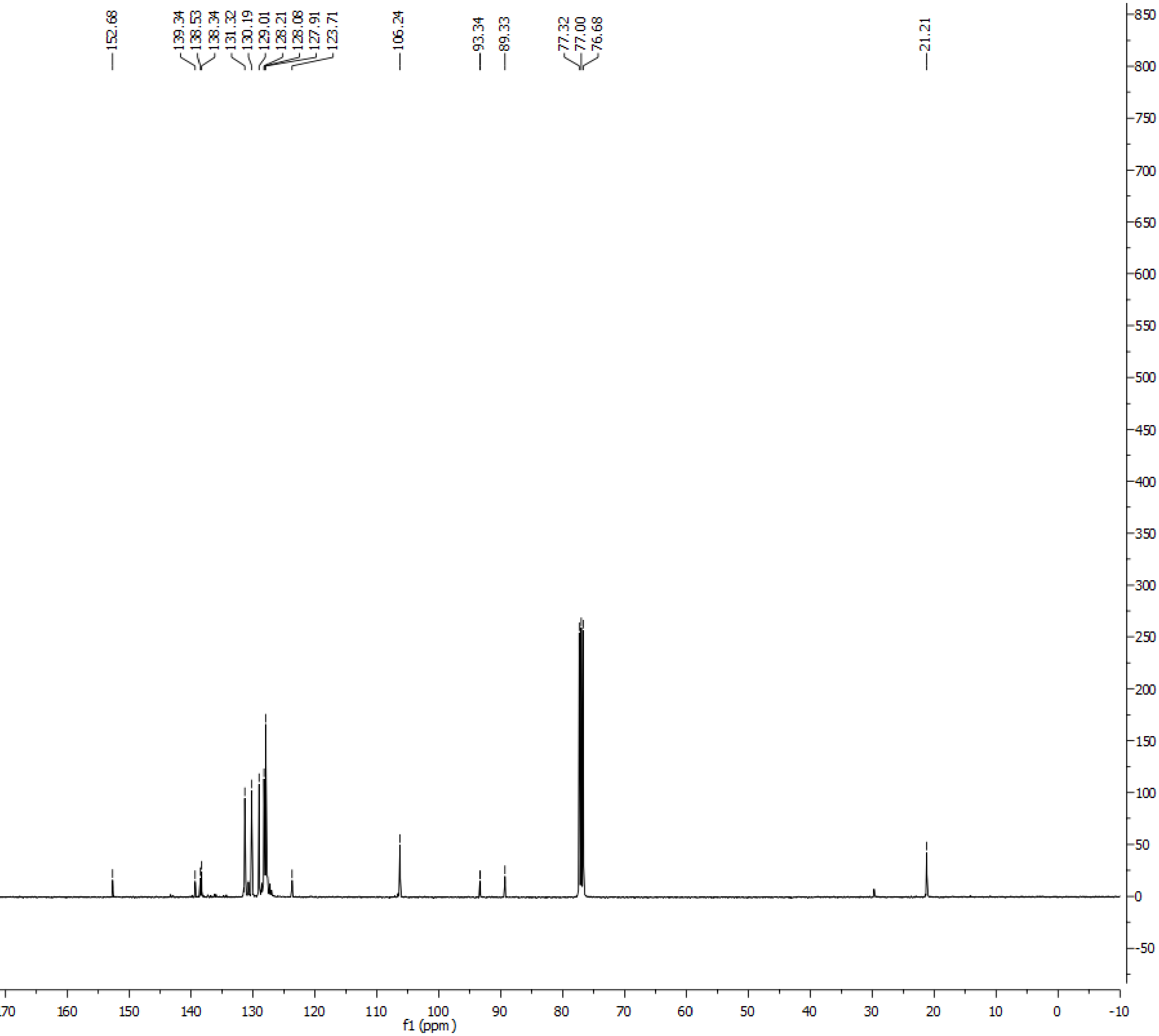
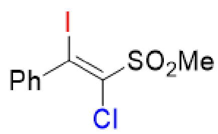
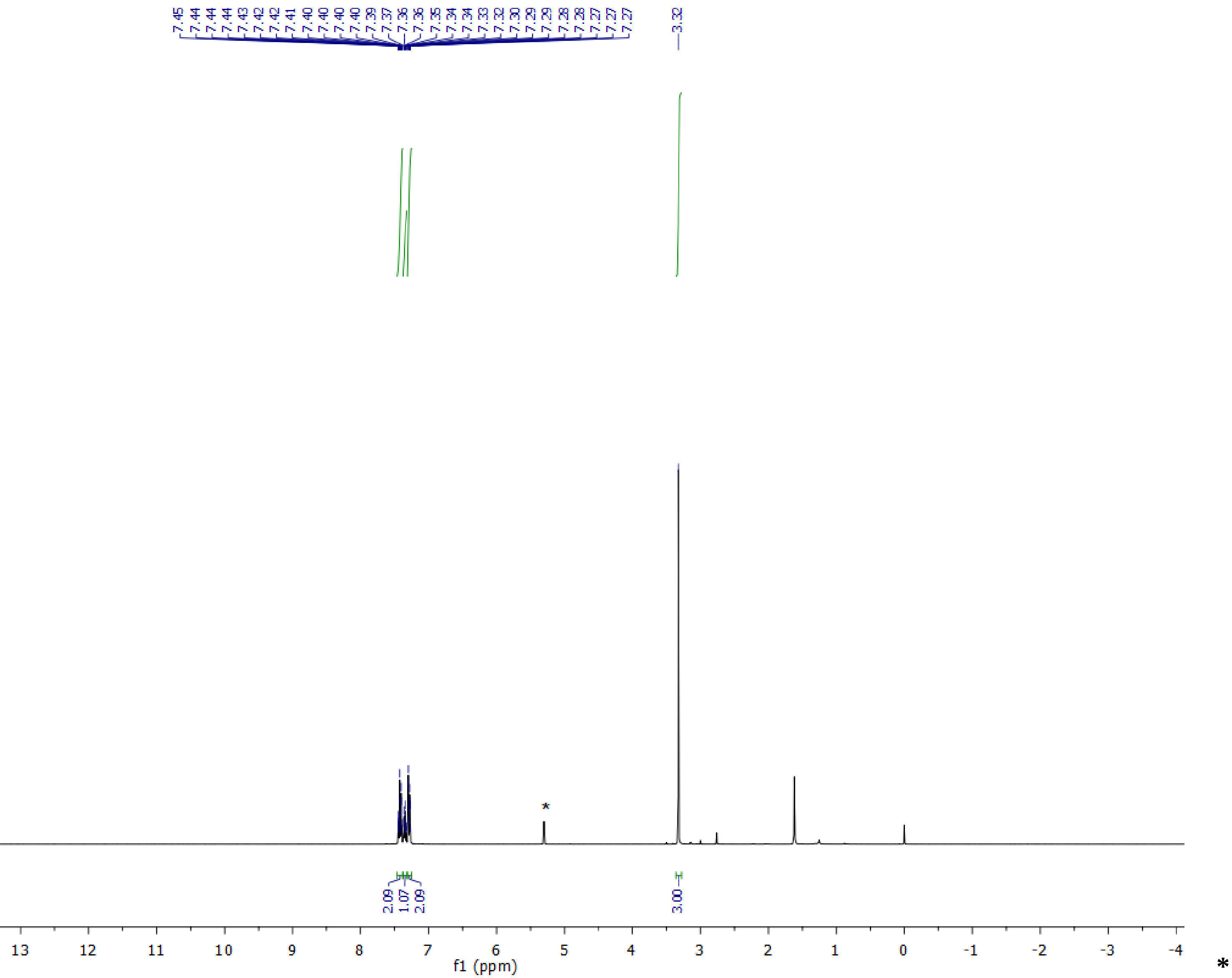


Figure S222. ^{1}H-NMR of **101**

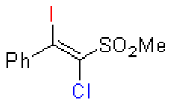


101



* DCM

Figure S223. ^{13}C-NMR of **101**



101

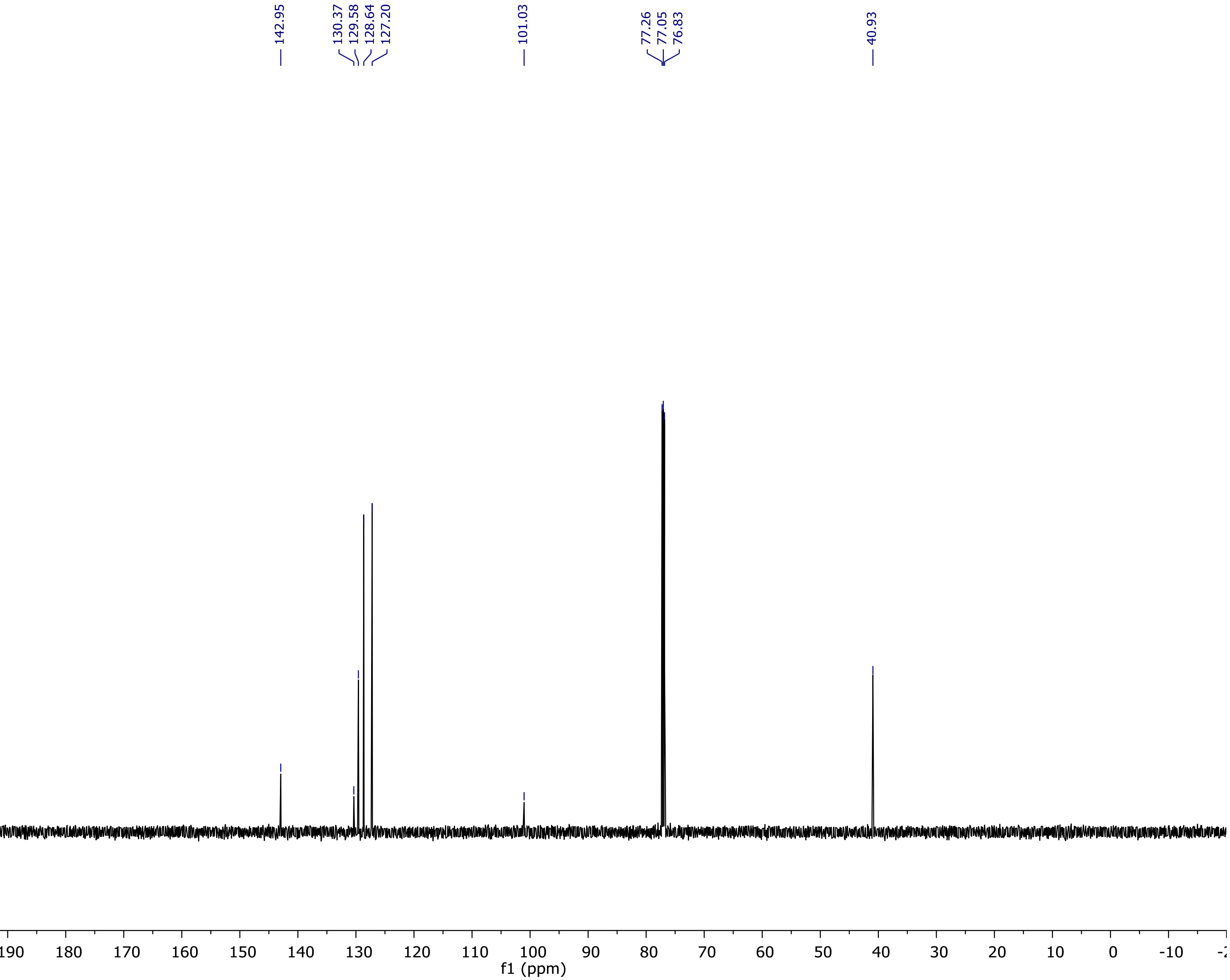
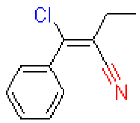


Figure S224. ^{1}H-NMR of **102**



102

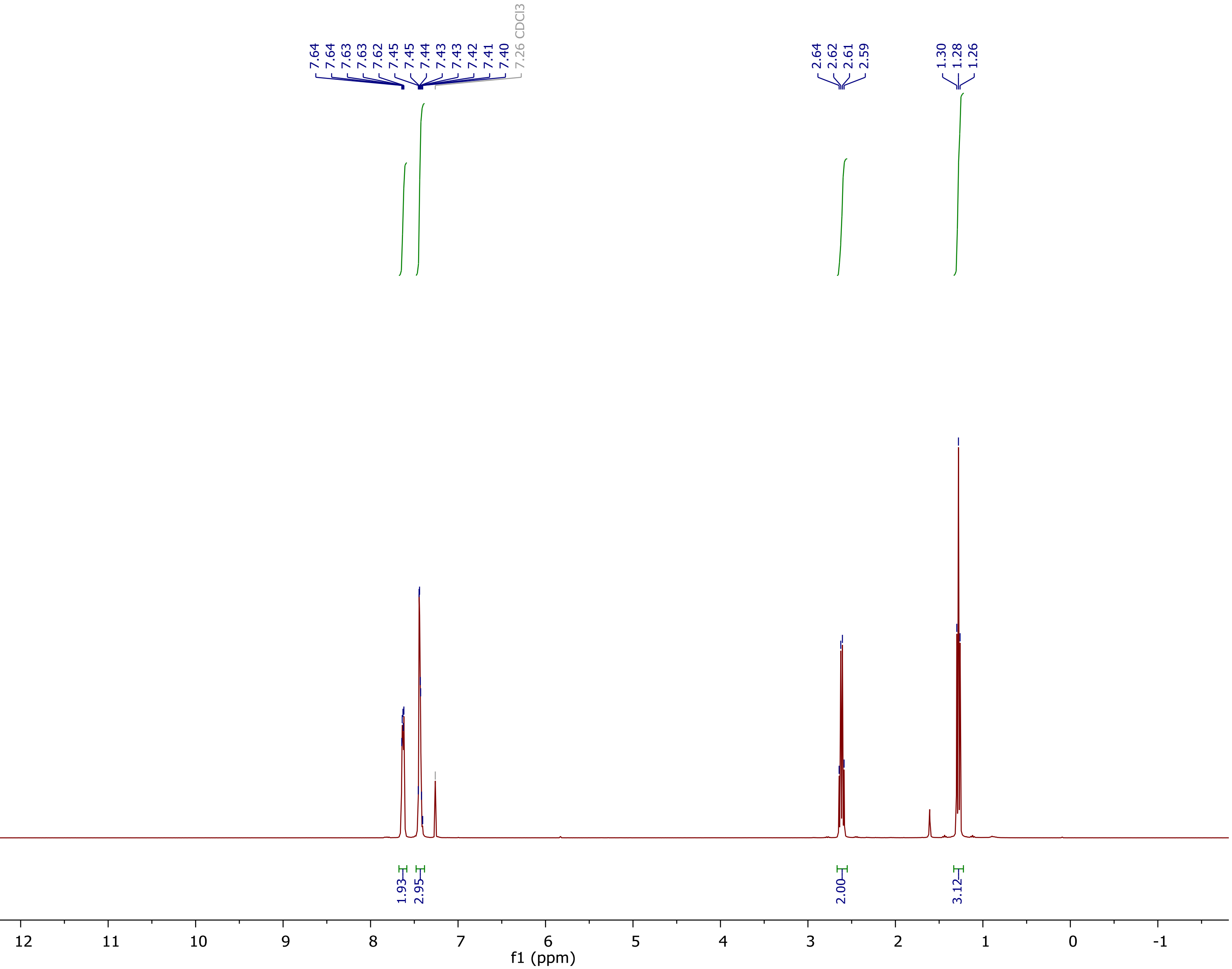
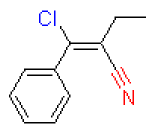


Figure S225. ^{13}C-NMR of **102**



102

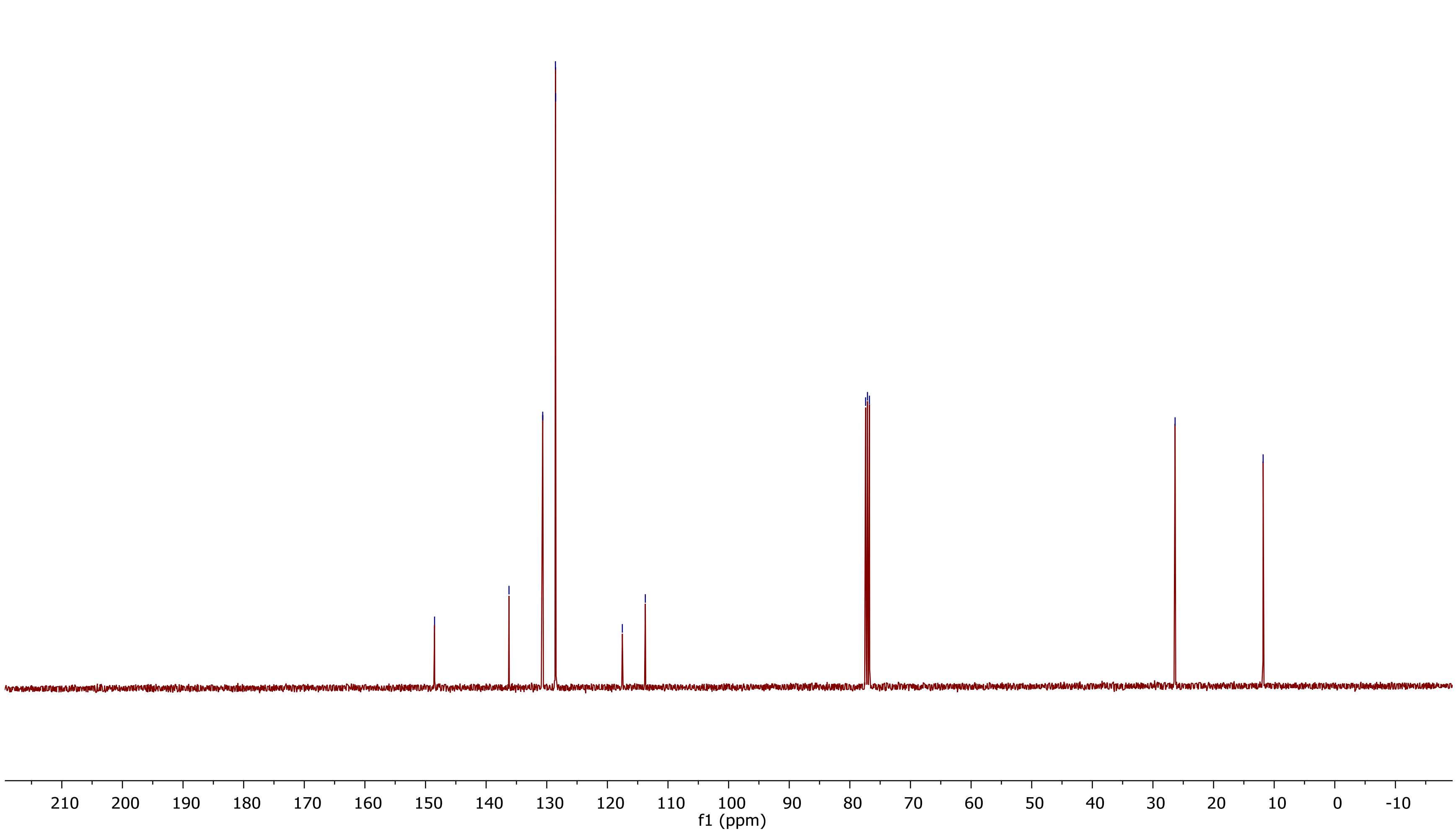


Figure S226. ^{1}H-NMR of **103**

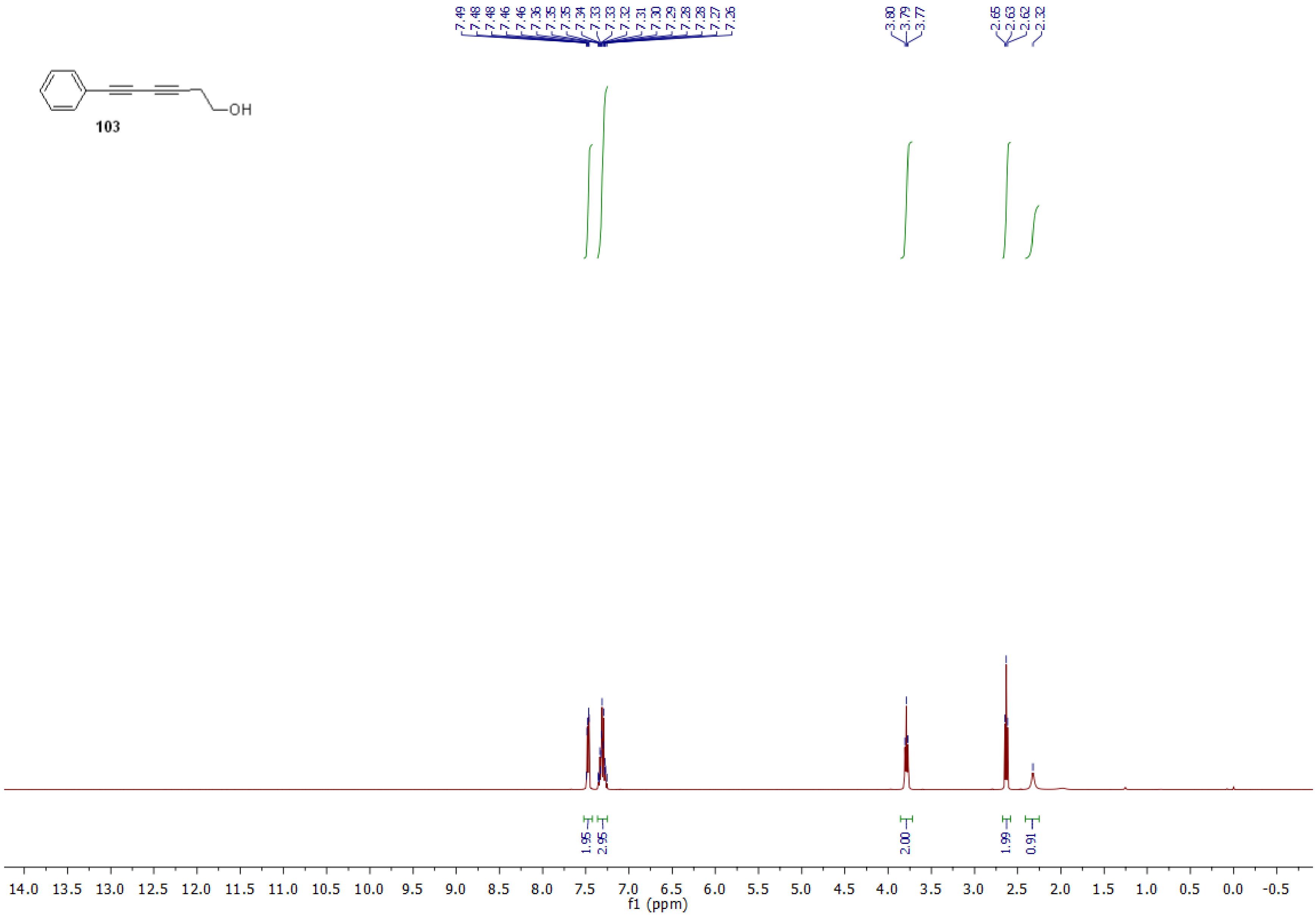
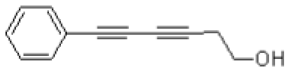


Figure S227. ^{13}C-NMR of **103**



103

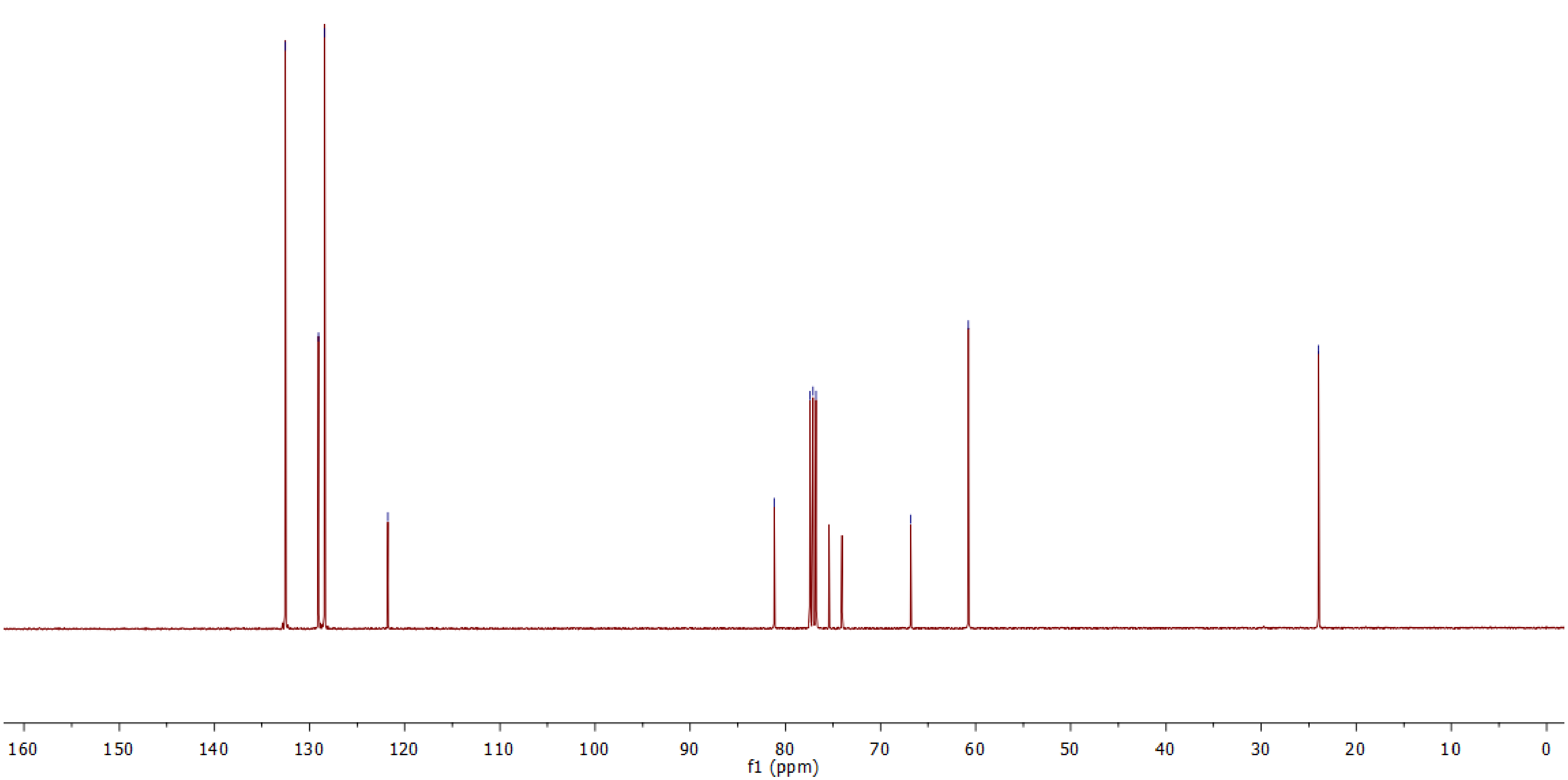
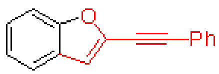


Figure S228. ^{1}H-NMR of **104**



104

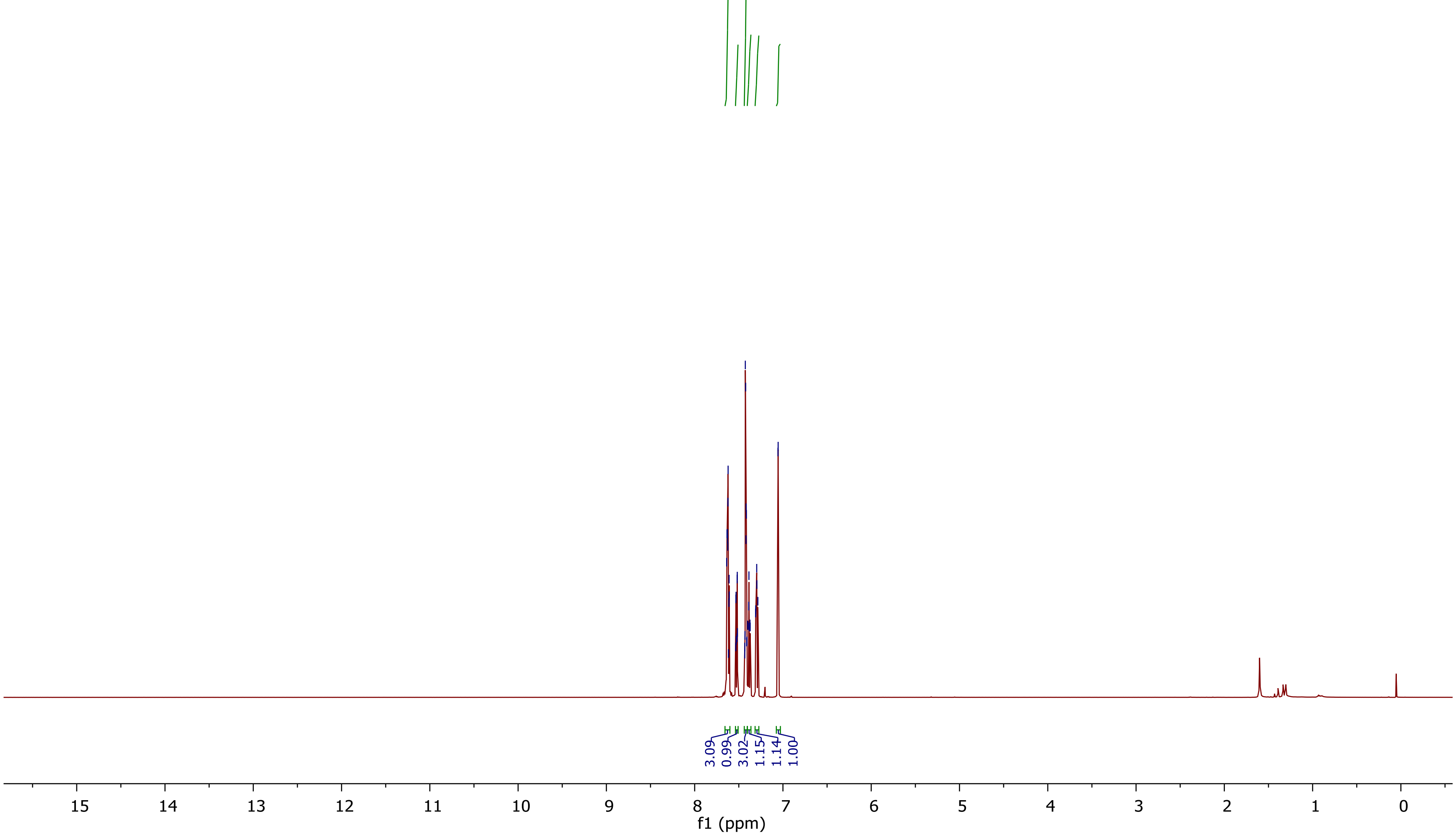
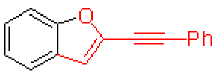


Figure S229. ^{13}C-NMR of **104**



104

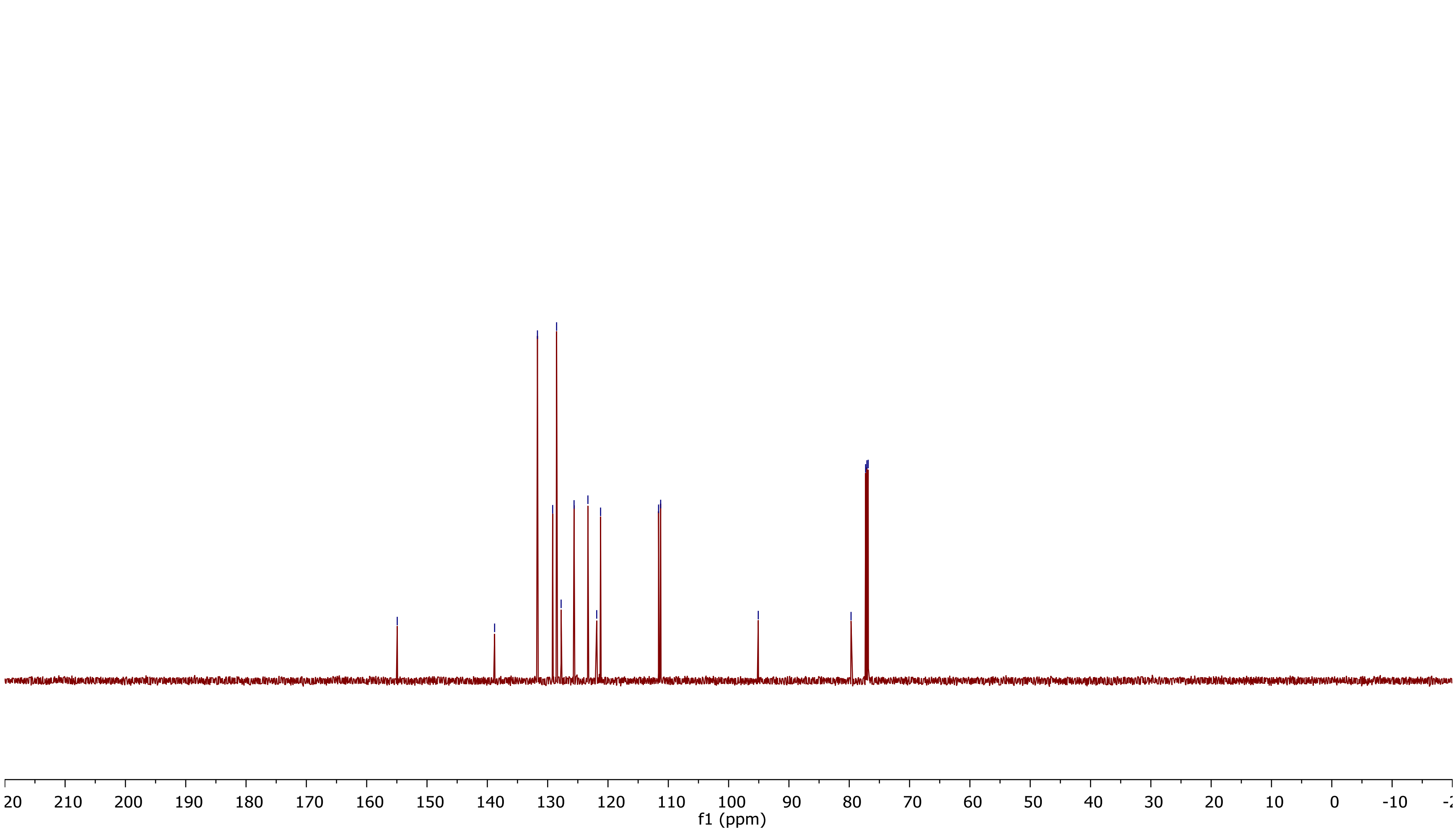
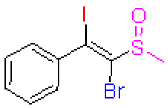


Figure S230. [1]H-NMR of **105**



105

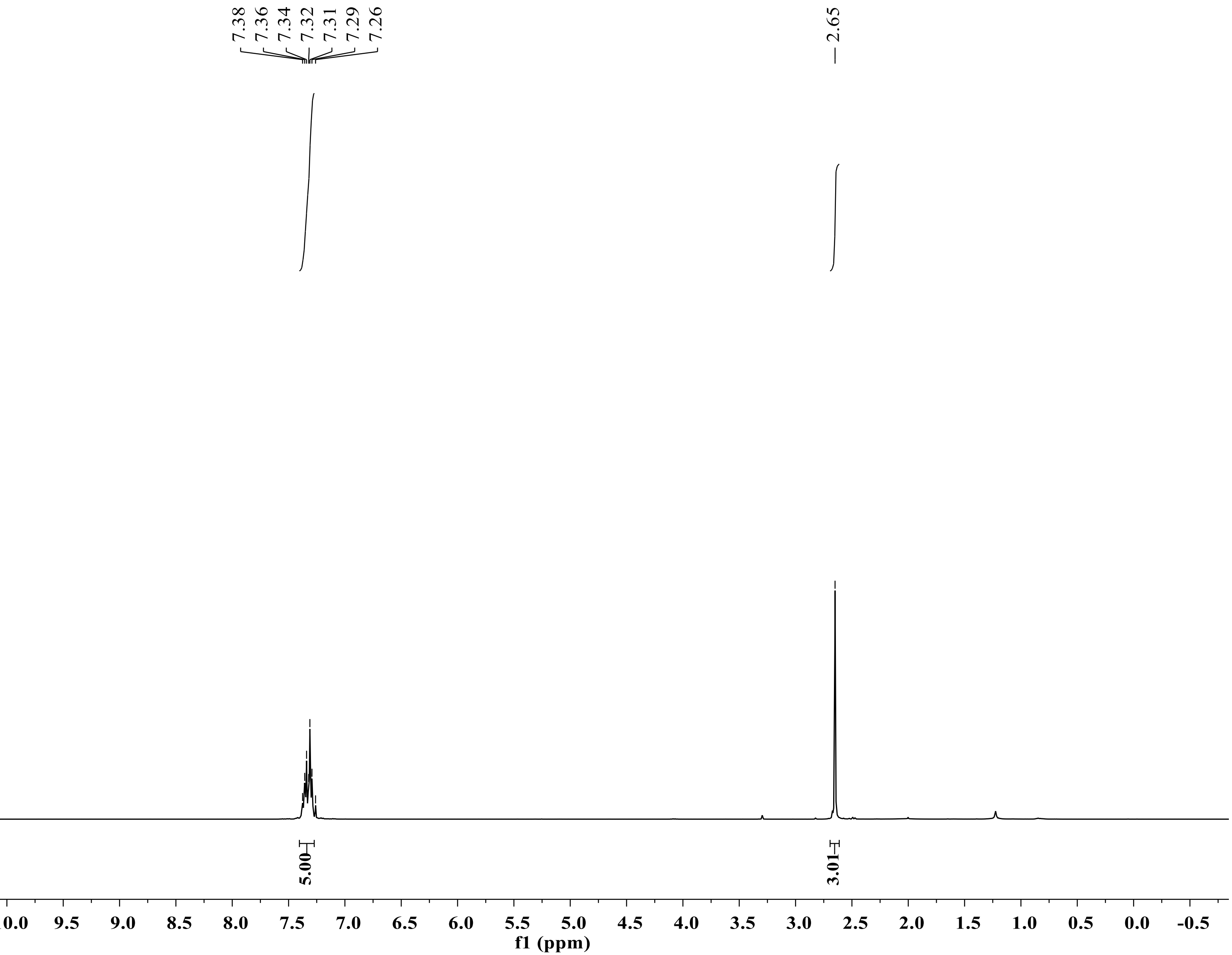
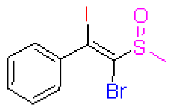


Figure S231. ^{13}C-NMR of **105**



105