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Supporting Information

Anhydrides from aldehydes or alcohols *via* an oxidative cross coupling

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Experimental Section:

General Information

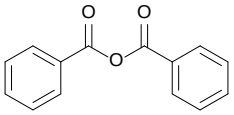
All reagents and solvents were as obtained by commercial source. All the reactions were run under Argon atmosphere using standard techniques. All solvents were dried by usual methods and distilled under Argon. Aldehydes were fresh distilled before use. Column chromatography was generally performed on silica gel (pore size 60 Å, 32-63 nm particle size) and reactions were monitored by thin-layer chromatography (TLC) analysis was performed with Merck Kieselgel 60 F254 plates and visualized using UV light at 254 nm, $KMnO_4$ and 2,4-DNP staining. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance III 400 spectrometer (400 MHz or 100 MHz, respectively) using $CDCl_3$ solutions and TMS as an internal standard. Chemical shifts are reported in parts per million (ppm, d) relative to internal tetramethylsilane standard (TMS, d 0.00). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet; dd, doublet of doublets; br, broad. The coupling constants, J, are reported in Hertz (Hz). The IR spectra were recorded on a Jasco FTIR-480 Plus Fourier Transform spectrometer. High resolution mass spectra HRMS (HESI-FT-ORBITRAP) were recorded on a Q-Exactive Thermo Scientific mass spectrometer. Melting points were determined in open capillary tubes and are uncorrected.

General Procedure from aldehydes

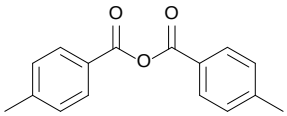
TCCA (256 mg, 1.1 mmol) was portionwise added over a period of 1-2 min to a solution of an aldehyde (1.1 mmol) in 3.25 mL dichloromethane, under dry argon atmosphere and at room temperature. The resulting suspension was stirred at room temperature and under dry argon. The reaction was monitored by TLC until disappearance of the aldehyde. Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and a carboxylic acid (1.0 mmol) was portionwise added, followed by dropwise addition of NEt_3 (202 mg, 2.0 mmol). After completion of the additions, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid, monitored by TLC. For the products **5a-5f**, the solvent was evaporated under reduced pressure and the residue purified by flash chromatography.

For the products **5g-5j** the reaction mixture was washed three times with a solution of 5 % HCl and then three times with a solution of 5 % $NaHCO_3$; the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure providing the desired anhydride.

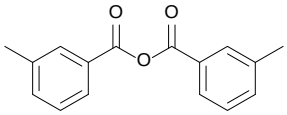
Compound characterizations



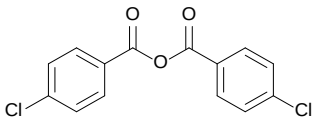
Benzoic anhydride 5a: Colorless oil; (221 mg, 0.98 mmol, 98 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, *J* = 7.6 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 4H).[1] ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 134.4, 130.4, 128.8, 128.7.[1] IR (neat, cm^{-1}): ν = 2923, 2852, 1786, 1725, 1599, 1452, 1280, 1040, 997, 701.[2]



4-methylbenzoic anhydride 5b: White solid; (155 mg, 0.61 mmol, 61 % yield); mp 95 – 97 °C;[1] R_f = 0.45 (Hexane/EtOAc, 4.5:05). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 7.7 Hz, 4H), 7.31 (d, *J* = 7.8 Hz, 4H), 2.45 (s, 6H).[1] ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 145.5, 130.6, 129.5, 126.2, 21.8.[1] IR (neat, cm^{-1}): ν = 3050, 2952, 2924, 1775, 1712, 1610, 1411, 1301, 1226, 1211, 1172, 1052, 1016, 824, 751. [3]

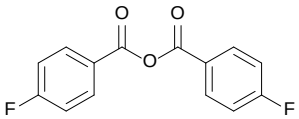


3-methylbenzoic anhydride 5c: White solid; (157 mg, 0.62 mmol, 62 % yield); mp 65-67 °C;[4] R_f = 0.44 (Hexane/EtOAc, 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.95 (m, 4H), 7.48 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 6H).[1] ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 138.8, 135.3, 131.0, 128.8, 128.7, 127.7, 21.3.[1] IR (neat, cm^{-1}): ν = 3031, 2922, 2865, 1785, 1723, 1607, 1589, 1487, 1381, 1285, 1250, 1153, 1031, 998, 743.[4]

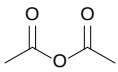


4-chlorobenzoic anhydride 5d:[1] White solid; (215 mg, 0.73 mmol, 73 % yield); mp 180-182 °C; R_f = 0.56 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.2 Hz, 4H), 7.51 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 141.4, 131.9, 129.4, 127.1. IR (neat,

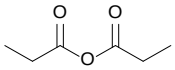
cm^{-1}): ν = 2924, 1785, 1721, 1592, 1487, 1401, 1291, 1175, 1092, 1011, 743.[3]



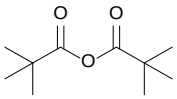
4-fluorobenzoic anhydride 5e:[4] White solid; (243 mg, 0.93 mmol, 93 % yield); mp 113-115 °C; R_f = 0.62 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 – 8.16 (m, 4H), 7.23 - 7.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7 (d, J_{C-F} = 255 Hz), 161.2, 133.3 (d, J_{C-F} = 9 Hz), 125.0 (d, J_{C-F} = 3 Hz), 116.5 (d, J_{C-F} = 11 Hz). IR (neat, cm^{-1}): ν = 3114, 3086, 2925, 1786, 1721, 1606, 1507, 1306, 1239, 1223, 1157, 844, 759.



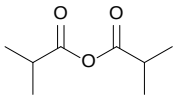
Acetic anhydride 5g: Colorless oil, (85 mg, 0.83 mmol, 83 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.18 (s, 1H).[11] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 22.0.[12] IR (neat, cm^{-1}): ν = 3031, 2948, 1839, 1755, 1438, 1379.



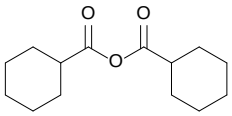
Propionic anhydride 5h:[13] Colorless oil, (111 mg, 0.85 mmol, 85 % yield); R_f = 0.61 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (q, J = 7.4 Hz, 4H), 1.17 (t, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 28.6, 8.3. IR (neat, cm^{-1}): ν = 2986, 2948, 2660, 1716, 1467, 1240, 1080.



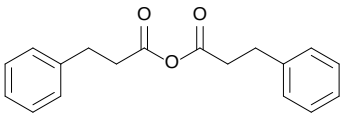
Pivalic anhydride 5i: Yellow oil; (143 mg, 0.77 mmol, 77 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (s, 18H).[5] ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 39.9, 26.3.[6] IR (neat, cm^{-1}): ν = 2977, 1701, 1484, 1415, 1305, 1201, 937, 869.



Isobutyric anhydride 5j: Yellow oil; (73 mg, 0.46 mmol, 46 % yield); R_f = 0.63 (Hexane/EtOAc, 4.6:0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (dt, *J* = 14.0, 7.0 Hz, 2H), 1.20 (d, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 35.0, 18.1. IR (neat, cm^{-1}): ν = 2979, 2939, 2880, 1812, 1746, 1471, 1388, 1020, 964, 738. HRMS (HESI-FT-ORBITRAP) calcd for $C_8H_{14}NaO_3$ $[M+Na]^+$: 181,0835, found 181,0834.



Cyclohexanecarboxylic anhydride 5k:[7] Colorless oil; (166 mg, 0.70 mmol, 70 % yield); R_f = 0.55 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (tt, *J* = 11.1, 3.7 Hz, 2H), 1.96 - 1.93 (m, 4H), 1.82 – 1.72 (m, 4H), 1.68 – 1.59 (m, 2H), 1.51 - 1.43 (m, 4H), 1.34 – 1.21 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 43.9, 28.4, 25.5, 25.1. IR (neat, cm^{-1}): ν = 2934, 2857, 1810, 1742, 1451, 1308, 1239, 1140, 1084, 1066, 992, 922.



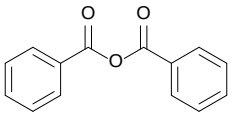
3-phenylpropanoic anhydride 5l:[8] Colorless oil; (220 mg, 0.78 mmol, 50 % yield); R_f = 0.57 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 - 7.25 (m,4H), 7.20 - 7.15 (m, 6H), 2.92 (t, *J* = 7.7 Hz, 4H), 2.70 (t, *J* = 7.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 139.4, 128.5, 128.2, 126.4, 36.6, 30.0. IR (neat, cm^{-1}): ν = 3087, 3029, 2927, 1817, 1747, 1604, 1497, 1455, 1046, 749.

General Procedure from benzylic alcohols

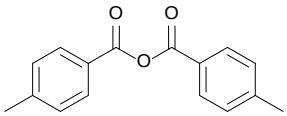
TCCA (256 mg, 1.1 mmol) was portionwise added over a period of 1-2 min to a solution of a benzylic alcohol (1.1 mmol) in 3.25 mL dichloromethane under dry argon atmosphere and at room temperature. The resulting suspension was stirred at room temperature and under dry argon. The reaction was monitored by TLC until disappearance of the alcohol. Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and a carboxylic acid (1.0 mmol) was portionwise added, followed by dropwise addition of NEt_3 (202 mg, 2.0 mmol). After completion of

the additions, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid, monitored by TLC. For the products **5a**, **5b**, **5m**, **5d**, **5n**, **5e** and **5o** the solvent was evaporated under reduced pressure and the residue purified by flash chromatography.

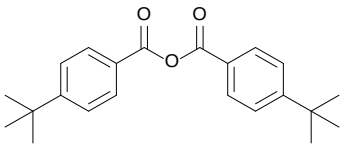
Compound characterizations



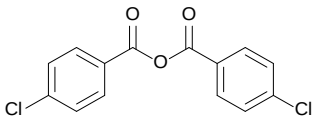
Benzoic anhydride 5a: (197 mg, 0.87 mmol, 87 % yield).



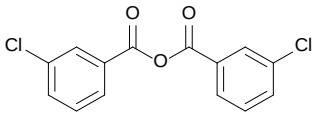
4-methylbenzoic anhydride 5b: (139 mg, 0.55 mmol, 55 % yield).



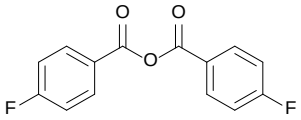
4-(*tert*-butyl)benzoic anhydride 5m:[9] Colorless oil; (253 mg, 0.75 mmol, 75 % yield); R_f = 0.43 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8.1 Hz, 4H), 7.53 (d, *J* = 8.1 Hz, 4H), 1.36 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5, 158.5, 130.5, 126.2, 125.9, 35.3, 31.0. IR (neat, cm^{-1}): ν = 2964, 2906, 2869, 1785, 1723, 1607, 1410, 1226, 1179, 1043, 765.



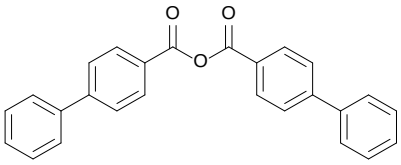
4-chlorobenzoic anhydride 5d: (209 mg, 0.71 mmol, 71 % yield)



3-chlorobenzoic anhydride 5n: White solid; (206 mg, 0.70 mmol, 64 % yield); mp 94-96 °C;[1] R_f = 0.4 (Hexane/EtOAc, 4.2:0.8). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (s, 2H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.68 – 7.65 (m, 2H), 7.49 (t, *J* = 7.9 Hz, 2H).[1] ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 135.2, 134.7, 130.4, 130.3, 128.6.[1] IR (neat, cm^{-1}): ν = 3073, 2926, 1792, 1575, 1471, 1424, 1277, 1202, 1039, 998, 736.[2]



4-fluorobenzoic anhydride 5e: (230 mg, 0.88 mmol, 88 % yield).



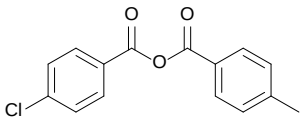
[1,1'-biphenyl]-4-carboxylic anhydride 5o:[4] White solid; (295 mg, 0.78 mmol, 78 % yield); mp 138 – 140 °C; R_f = 0.158 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 4H), 7.78 (d, *J* = 8.4 Hz, 4H), 7.68 (d, *J* = 7.2 Hz, 4H), 7.53 (t, *J* = 7.4 Hz, 4H), 7.46 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 147.3, 139.6, 131.2, 129.1, 128.6, 127.6, 127.5, 127.4 IR (neat, cm^{-1}): ν = 3032, 2943, 1779, 1717, 1605, 1486, 1450, 1406, 1227, 1175, 1001, 744.

General Procedure for mixed anhydrides 5p-5x:

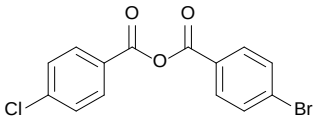
TCCA (256 mg, 1.1 mmol) was portionwise added over a period of 1-2 min to a solution of an aldehyde or a benzylic alcohol (1.1 mmol) in 3.25 mL dichloromethane under dry argon atmosphere and at room temperature. The resulting suspension was stirred at room temperature and under dry argon. The reaction was monitored by TLC until disappearance of the aldehyde or the alcohol. Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and a carboxylic acid (1.0 mmol) was portionwise added, followed by dropwise addition of NEt_3 (202 mg, 2.0 mmol). After completion of the additions, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid, monitored by TLC. For the products **5p**, **5q** and **5r**, the solvent was evaporated under reduced pressure and the residue purified by flash

chromatography. For the products **5s**-**5x** the reaction mixture was washed three times with a solution of 5% HCl and then three times with a solution of 5% $NaHCO_3$; the organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure providing the desired anhydride.

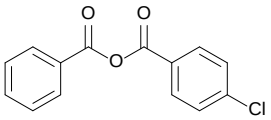
Compound characterizations



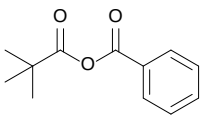
4-chlorobenzoic 4-methylbenzoic anhydride 5p: White solid; (209 mg, 78 % 4-chlorobenzoic 4-methylbenzoic anhydride and 22 % of 4-methylbenzoic anhydride); mp 100-104 °C; R_f = 0.46 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 2H), 8.04 - 8.01 (m, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.33 - 7.30 (m, 2H), 2.45 (s, 3H). The ^{1}H NMR spectrum indicates about 78 % of 4-chlorobenzoic 4-methylbenzoic anhydride and about 22 % of 4-methylbenzoic anhydride ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.1, 161.6, 145.8, 141.1, 131.8, 130.6, 129.6, 129.2, 127.4, 125.8, 21.8. ^{13}C NMR signals display the presence of 4-chlorobenzoic 4-methylbenzoic anhydride and 4-methylbenzoic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 2917, 1789, 1717, 1609, 1592, 1400, 1222, 1171, 1063, 1007, 843, 1063, 1007, 843, 739. HRMS (HESI-FT-ORBITRAP) calcd for $C_{15}H_{11}ClNaO_3$ $[M+Na]^+$: 297,0289, found 297,0286.



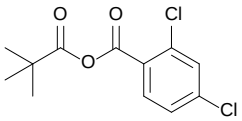
4-bromobenzoic 4-chlorobenzoic anhydride 5q: White solid; (247 mg, 89 % 4-bromobenzoic 4-chlorobenzoic anhydride and 11 % 4-bromobenzoic anhydride); mp 212-216 °C; R_f = 0.51 (Hexane/EtOAc, 4.6:0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H). The ^{1}H NMR spectrum indicates about 89 % of 4-bromobenzoic 4-chlorobenzoic anhydride and about 11 % of 4-bromobenzoic anhydride[10]. ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 161.3, 141.4, 132.4, 131.9, 131.9, 130.2, 129.4, 127.5, 127.1. ^{13}C NMR signals display the presence of 4-bromobenzoic 4-chlorobenzoic anhydride and 4-bromobenzoic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3078, 3101, 1785, 1719, 1590, 1482, 1340, 1251, 1090, 844. HRMS (HESI-FT-ORBITRAP) calcd for $C_{14}H_8BrClNaO_3$ $[M+Na]^+$: 360,9238, found 360,9234.



Benzoic 4-chlorobenzoic anhydride 5r: White solid; (218 mg, 89 % benzoic 4-chlorobenzoic anhydride and 11 % benzoic anhydride); mp 105-111 °C; R_f = 0.48 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.48 (m, 4H). The ^{1}H NMR spectrum indicates about 89 % of benzoic 4-chlorobenzoic anhydride and about 11 % of benzoic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0, 161.5, 141.1, 134.6, 131.8, 130.5, 129.2, 128.9, 128.5, 127.2. ^{13}C NMR signals display the presence of benzoic 4-chlorobenzoic anhydride and benzoic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3071, 1784, 1722, 1598, 1451, 1401, 1212, 1173, 1039, 997, 701. HRMS (HESI-FT-ORBITRAP) calcd for $C_{14}H_9ClNaO_3$ $[M+Na]^+$: 283,0132, found 283,0128.

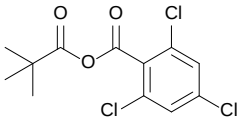


Benzoic pivalic anhydride 5s: Colorless oil; (156 mg, 93 % benzoic pivalic anhydride and 7 % pivalic anhydride); R_f = 0.41 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 1.35 (s, 9H). The ^{1}H NMR spectrum indicates about 93 % of benzoic pivalic anhydride and about 7 % of pivalic anhydride ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 162.2, 134.1, 130.1, 128.8, 128.5, 40.1, 26.3. ^{13}C NMR signals display the presence of benzoic pivalic anhydride and pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3065, 2978, 2937, 1802, 1733, 1601, 1480, 1542, 1240, 1067, 1011, 912, 700. HRMS (HESI-FT-ORBITRAP) calcd for $C_{12}H_{14}NaO_3$ $[M+Na]^+$: 229,0835, found 229,0834.

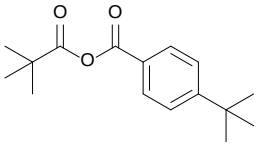


2,4-dichlorobenzoic pivalic anhydride 5t: Colorless oil; (228 mg, 88 % 2,4-dichlorobenzoic pivalic anhydride and 12 % pivalic anhydride); R_f = 0.66 (Hexane/EtOAc, 4.6:0.4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 1.32 (s, 9H). The ^{1}H NMR spectrum indicates about 88 % of 2,4-dichlorobenzoic pivalic anhydride and about 12 % of pivalic anhydride.^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.0, 160.2, 139.6, 135.5, 133.1, 131.2, 127.1, 126.7, 39.9, 26.3. ^{13}C NMR signals display the presence of benzoic 2,4-dichlorobenzoic anhydride and pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3096, 2978, 2937, 1806, 1738, 1585, 1479, 1376, 1231, 1054, 1001, 734. HRMS (HESI-FT-ORBITRAP)

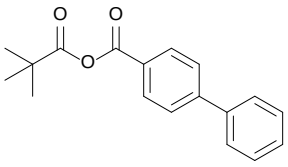
calcd for $C_{12}H_{12}Cl_2NaO_3$ [M+Na]$^+$: 297,0056, found 297,0054.



2,4,6-trichlorobenzoic pivalic anhydride 5u: Colorless oil; (262 mg, 89 % 2,4,6-trichlorobenzoic pivalic anhydride and 11 % pivalic anhydride); R_f = 0.44 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 2H), 1.28 (s, 9H). The ^{1}H NMR spectrum indicates about 89 % of 2,4,6-trichlorobenzoic pivalic anhydride and about 11 % of pivalic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 159.2, 136.7, 132.6, 130.6, 128.1, 40.0, 26.3. ^{13}C NMR signals display the presence of 2,4,6-trichlorobenzoic pivalic anhydride and pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3083, 2978, 2937, 1818, 1751, 1579, 1550, 1480, 1371, 1237, 1098, 998, 961. HRMS (HESI-FT-ORBITRAP) calcd for $C_{12}H_{11}Cl_3NaO_3$ [M+Na]$^+$: 330,9666, found 330,9667.

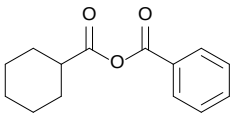


4-(*tert*-butyl)benzoic pivalic anhydride 5v: Colorless oil; (197 mg, 91 % of 4-(*tert*-butyl)benzoic pivalic anhydride and 9 % of pivalic anhydride); R_f = 0.44 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 1.35 (s, 9H), 1.33 (s, 9H). he ^{1}H NMR spectrum indicates about 91 % of 4-(*tert*-butyl)benzoic pivalic anhydride and about 9 % of pivalic anhydride.^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 162.2, 158.1, 130.1, 126.1, 125.6, 40.0, 35.0, 30.8, 26.4. ^{13}C NMR signals display the presence of benzoic 4-(*tert*-butyl)benzoic pivalic anhydride and of pivalic anhydride in the carbonyl region. IR (neat, cm^{-1}): ν = 3061, 2968, 2908, 1802, 1731, 1608, 1461, 1409, 1365, 1252, 1070, 1000, 849. HRMS (HESI-FT-ORBITRAP) calcd for $C_{16}H_{22}NaO_3$ [M+Na]$^+$: 285,1461, found 285,1457.



[1,1'-biphenyl]-4-carboxylic pivalic anhydride 5w: Yellow solid; (240 mg, 95 % [1,1'-biphenyl]-4-carboxylic pivalic anhydride and 5 % pivalic anhydride.); mp 86 – 91 °C; R_f = 0.56 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5

Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.48 - 7.37 (m, 3H), 1.37 (s, 9H). The ^{1}H NMR spectrum indicates about 95 % of [1,1'-biphenyl]-4-carboxylic pivalic anhydride and about 5 % of pivalic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 162.1, 146.8, 139.3, 130.6, 128.8, 128.3, 127.4, 127.1, 127.0, 40.1, 26.34. ^{13}C NMR signals display the presence of [1,1'-biphenyl]-4-carboxylic pivalic anhydride and pivalic anhydride.in the carbonyl region. IR (neat, cm^{-1}): ν = 3060, 3032, 2977, 2936, 1780, 1728, 1607, 1480, 1406, 1279, 1250, 1071, 1000, 748. HRMS (HESI-FT-ORBITRAP) calcd for $C_{18}H_{18}NaO_3$ $[M+Na]^+$: 305,1148, found 305,1148.



Benzoic cyclohexanecarboxylic anhydride 5x: Colorless oil; (198 mg, 89 % benzoic cyclohexanecarboxylic anhydride 7 % cyclohexanecarboxylic anhydride and 4 % benzoic anhydride.); R_f = 0.56 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.57 (dd, *J* = 10.9, 8.8 Hz, 1H), 2.05 (d, *J* = 13.0 Hz, 2H), 1.81 - 1.78 (m, 2H), 1.67 – 1.53 (m, 3H), 1.38 - 1.24 (m, 3H). The ^{1}H NMR spectrum indicates about 89% of benzoic cyclohexanecarboxylic anhydride, about 7 % of cyclohexanecarboxylic anhydride and about 4 % of benzoic anhydride. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 162.5, 134.3, 130.3, 128.7, 44.1, 28.4, 25.5, 25.1. ^{13}C NMR signals display the presence of benzoic cyclohexanecarboxylic anhydride, of cyclohexanecarboxylic anhydride and of benzoic anhydride.in the carbonyl region. IR (neat, cm^{-1}): ν = 3064, 2935, 2857, 1806, 1731, 1600, 1452, 1263, 1235, 994, 701. HRMS (HESI-FT-ORBITRAP) calcd for $C_{14}H_{16}NaO_3$ $[M+Na]^+$: 255,0992, found 255,0990.

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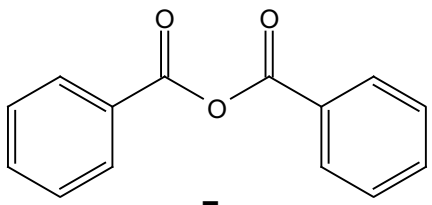

5a

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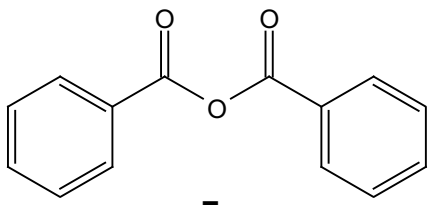
7.65
7.54
7.52
7.51
4.00
2.00
4.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



5a

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30
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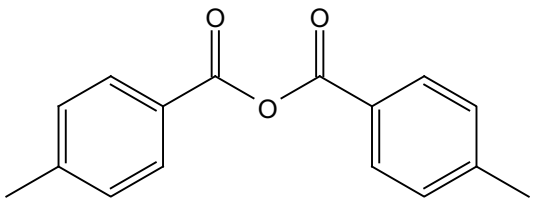
-10
f1 (ppm)



5b

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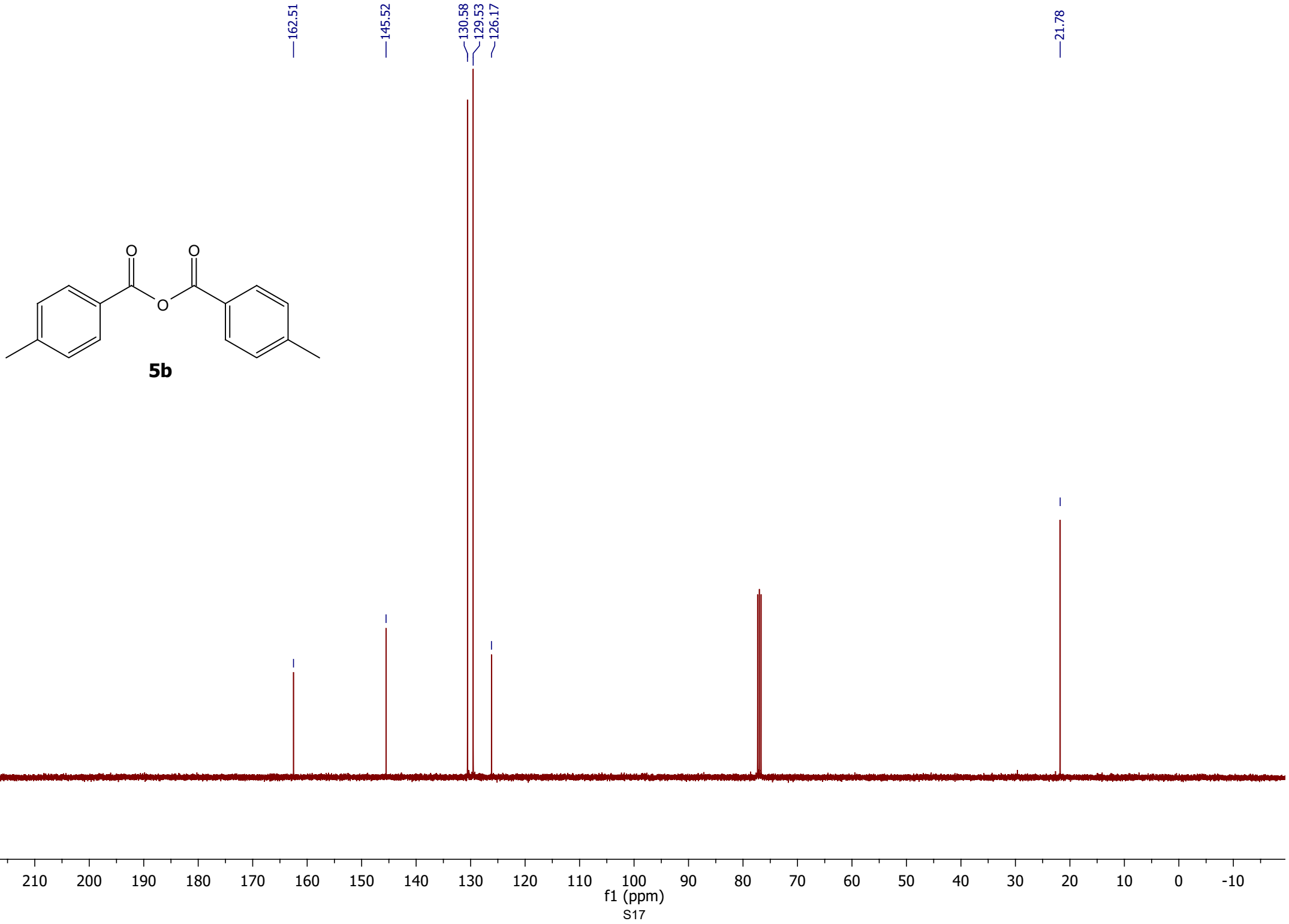
8.02
7.32
7.30
2.45
0.00
4.00
4.00
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.17
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O
O
5b
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200
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180
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160
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140
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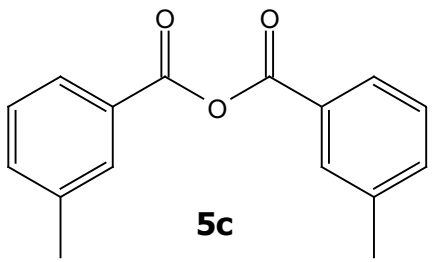
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5c

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7.49
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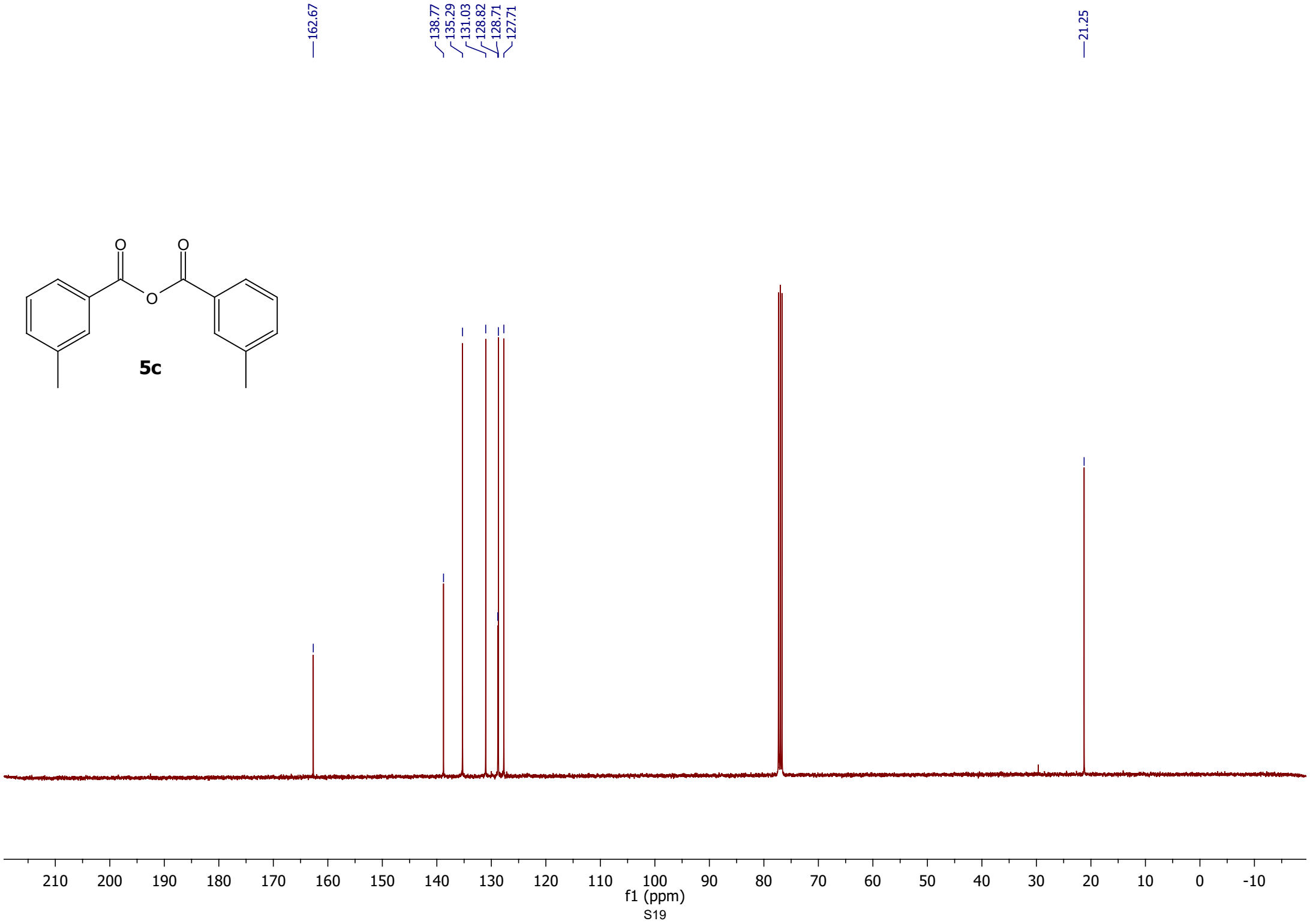
7.43
7.41
7.39
2.45
4.00
2.00
2.00
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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127.71
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O
O
5c
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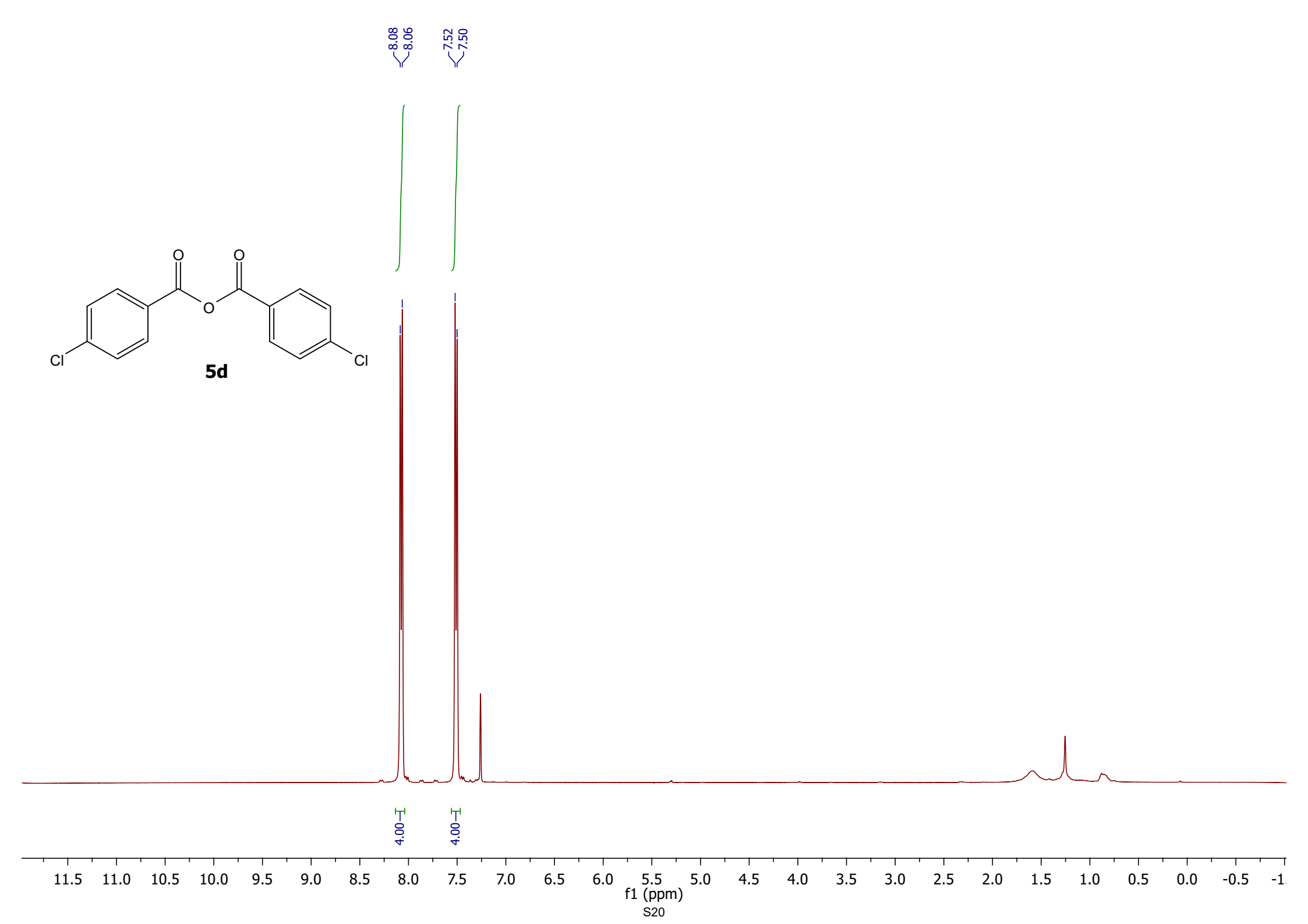
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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Cl
5d
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9.0
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8.0
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7.0
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5.5
5.0
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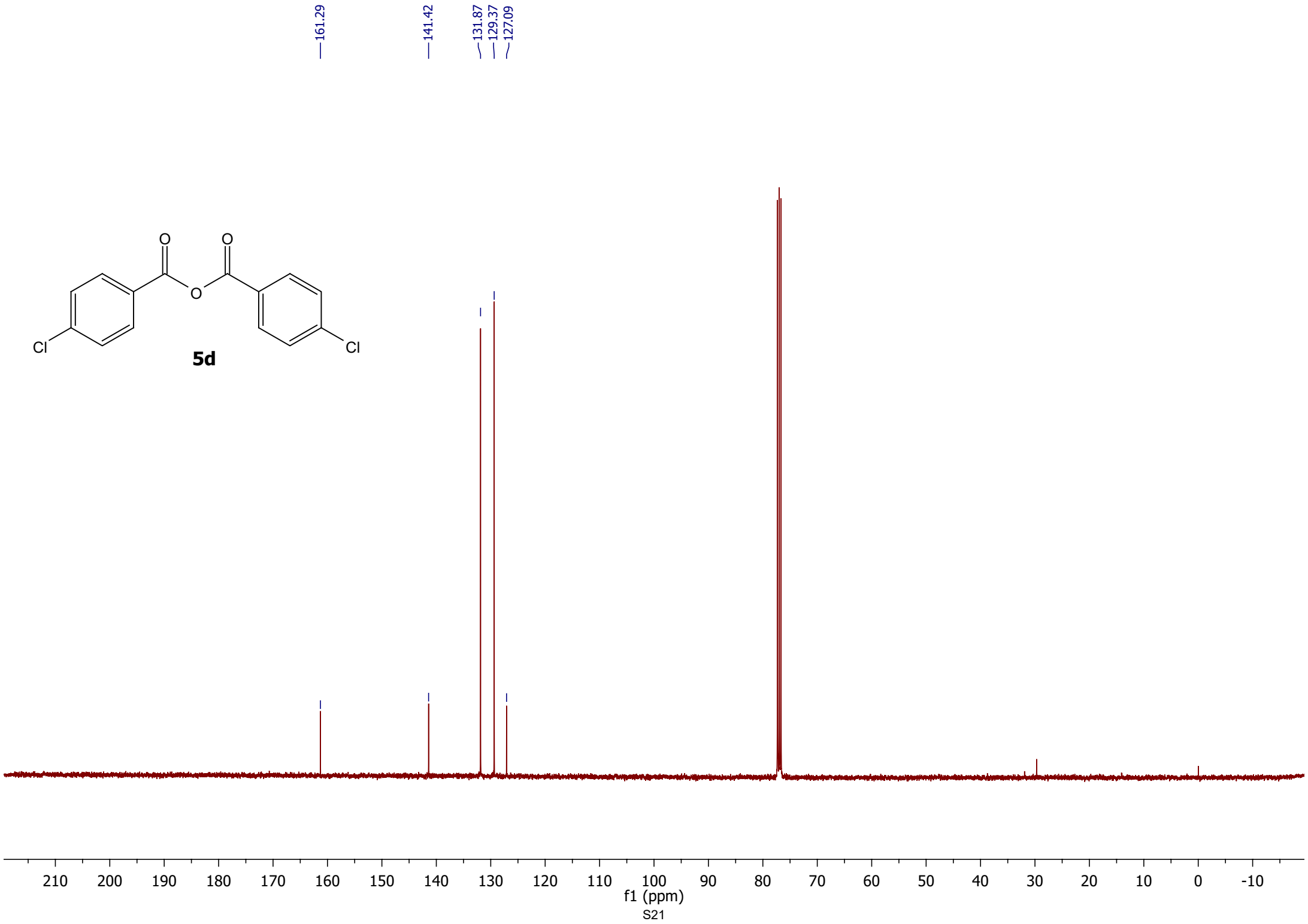
f1 (ppm)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Cl
Cl
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40
30
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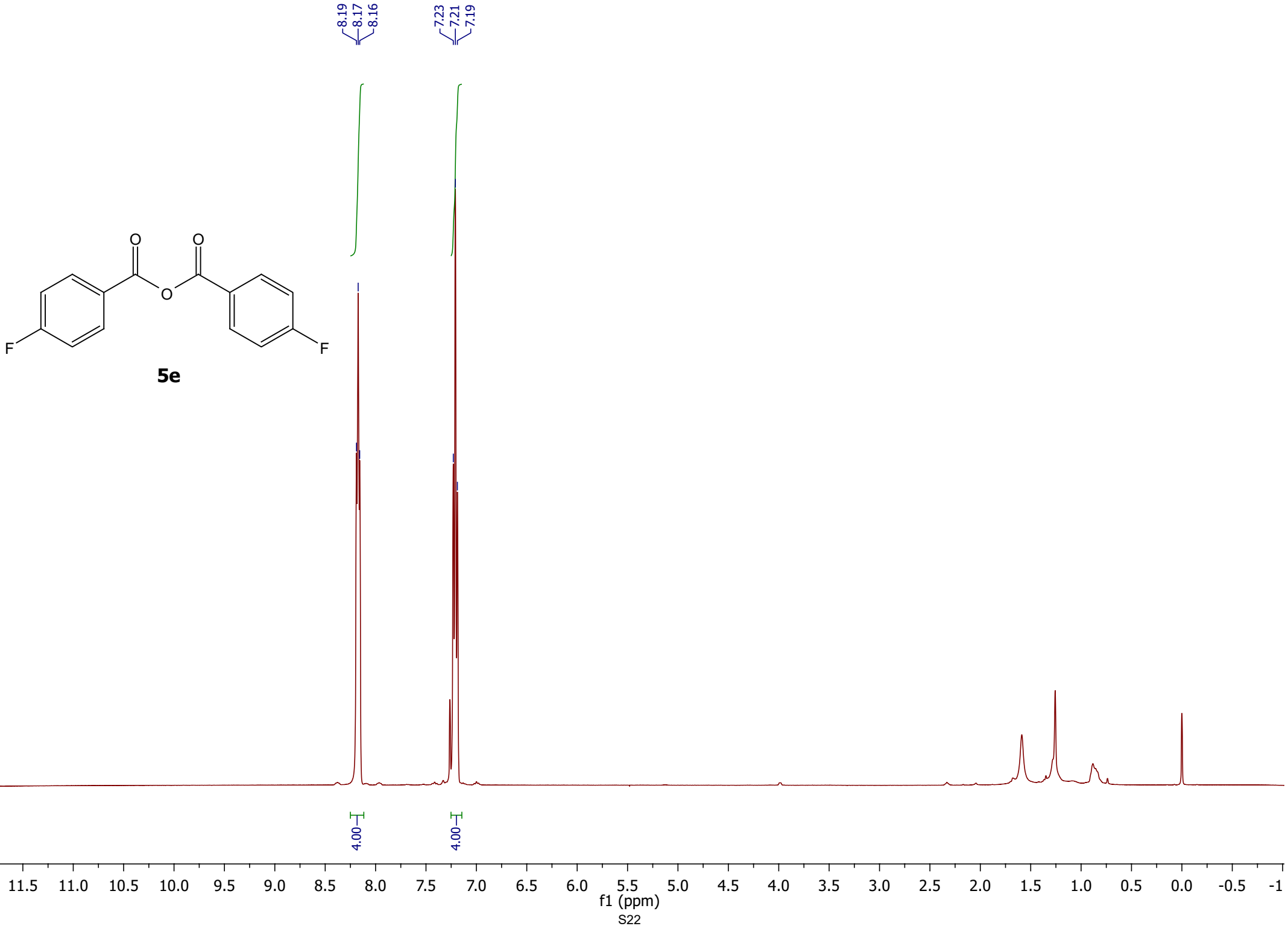
f1 (ppm)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7.19
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O
O
F
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5e
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4.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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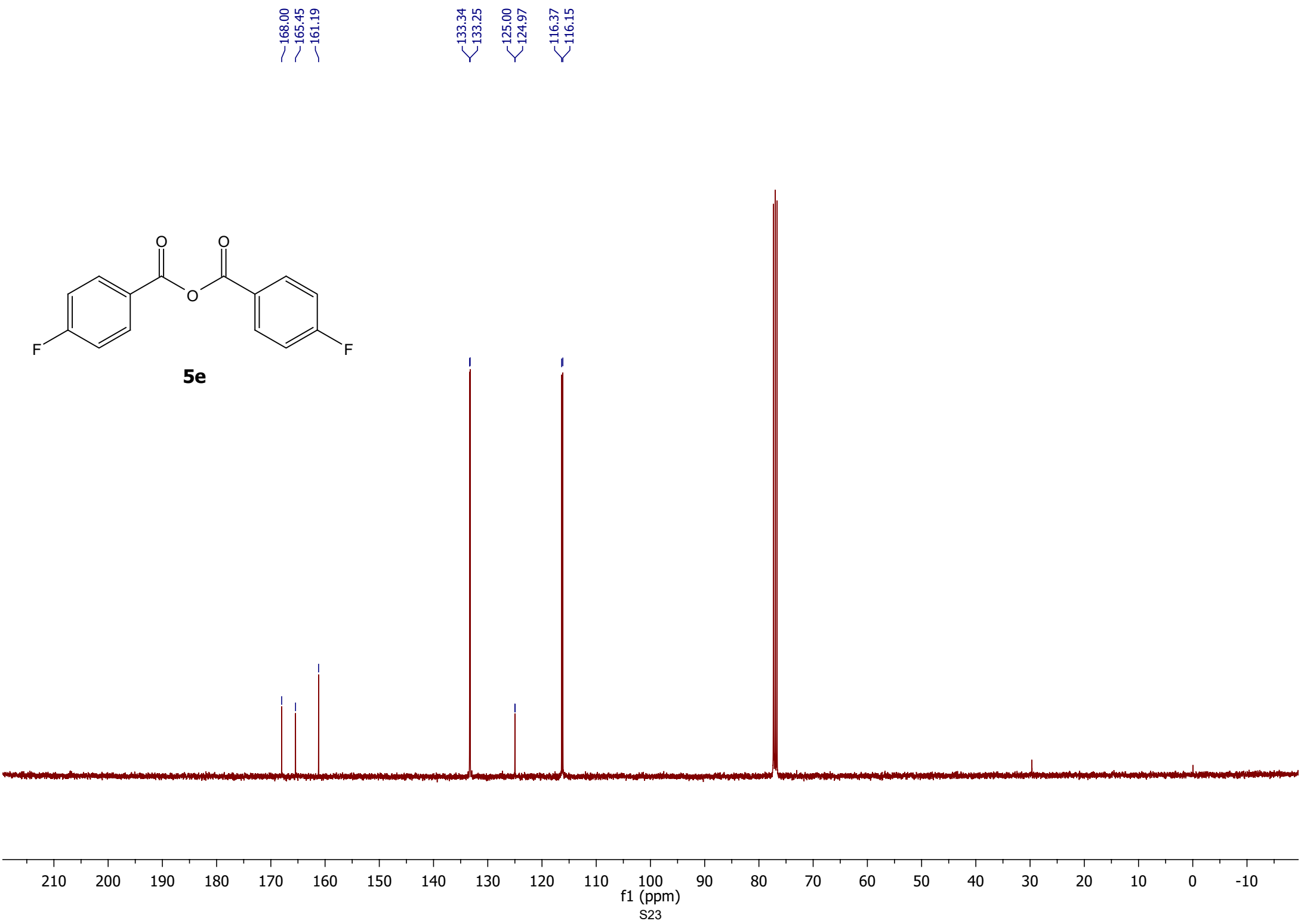
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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F
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200
190
180
170
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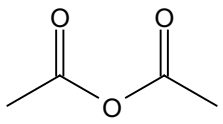
f1 (ppm)



5g

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200
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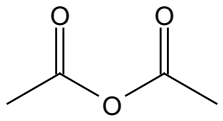

5g

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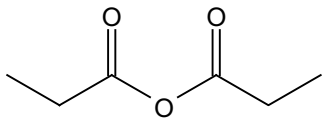
f1 (ppm)



5h

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6.00
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12
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10
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8
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6
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4
3
2
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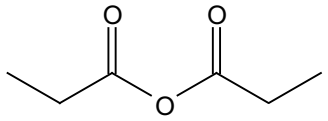
0
-1
f1 (ppm)



5h

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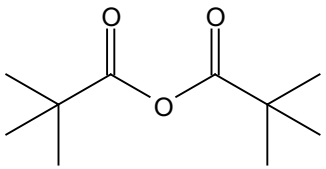
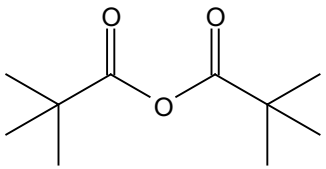
28.65
8.32
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



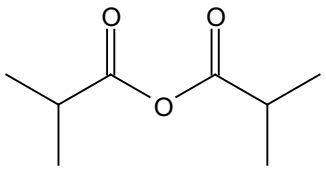
5i

1.19
18.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



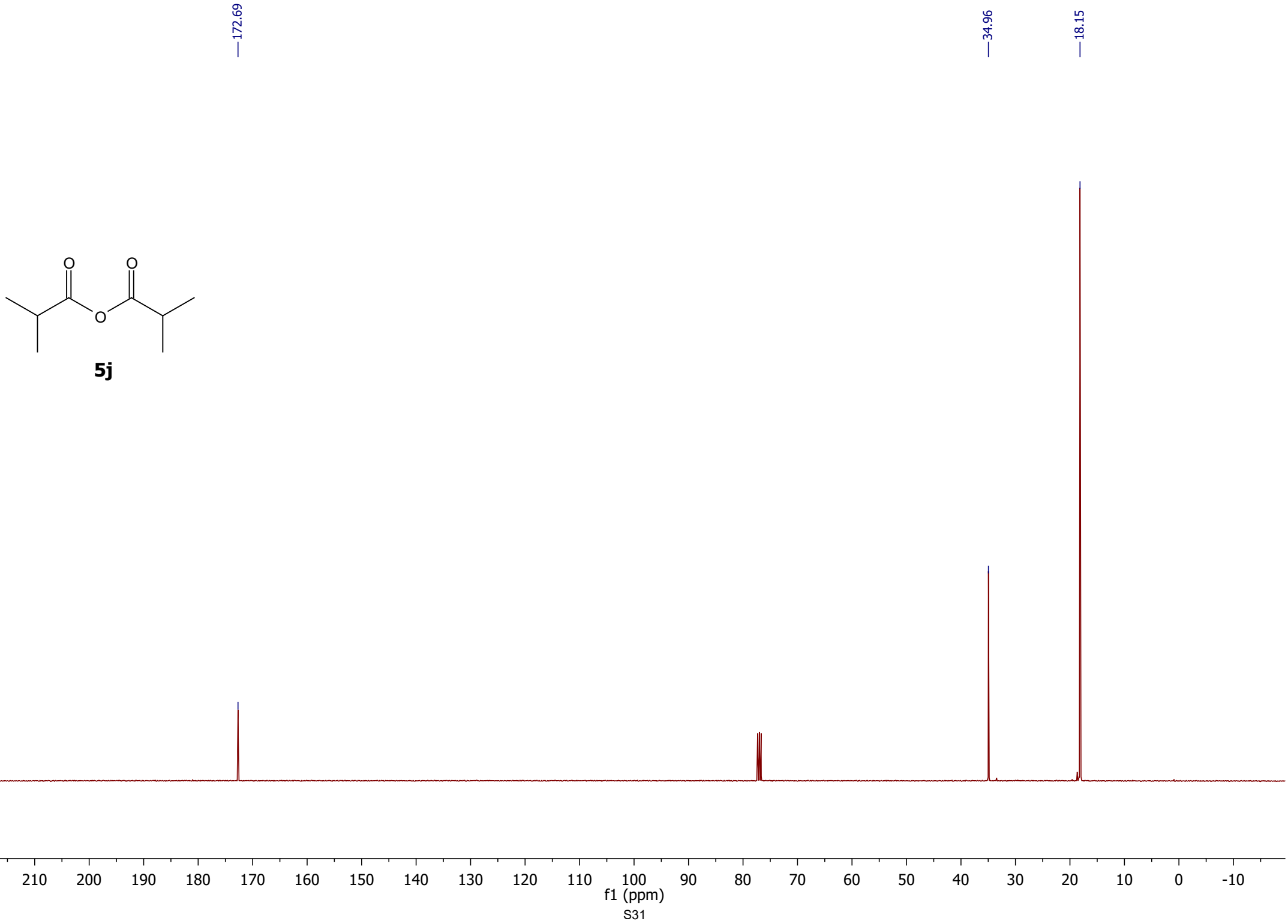
5i

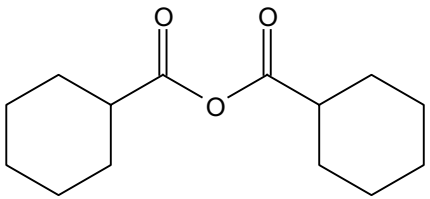
173.72
39.96
26.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5j

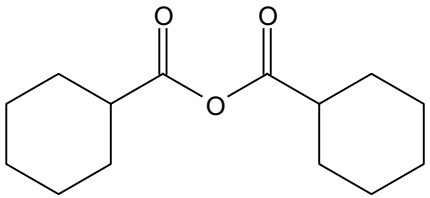
2.66
2.64
2.63
2.61
2.59
1.21
1.19
2.00
12.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


172.69
34.96
18.15
O
O
O
5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



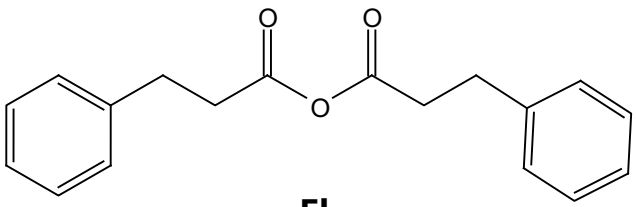
5k

2.43
2.42
2.41
2.40
2.39
2.38
2.37
2.36
2.36
1.96
1.96
1.93
1.93
1.79
1.78
1.77
1.76
1.75
1.64
1.63
1.62
1.51
1.49
1.43
1.33
1.30
1.27
1.25
1.24
2.00
4.00
4.00
2.00
4.00
6.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



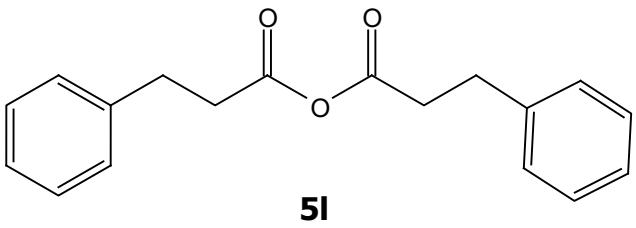
5k

171.80
43.90
28.35
25.53
25.10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



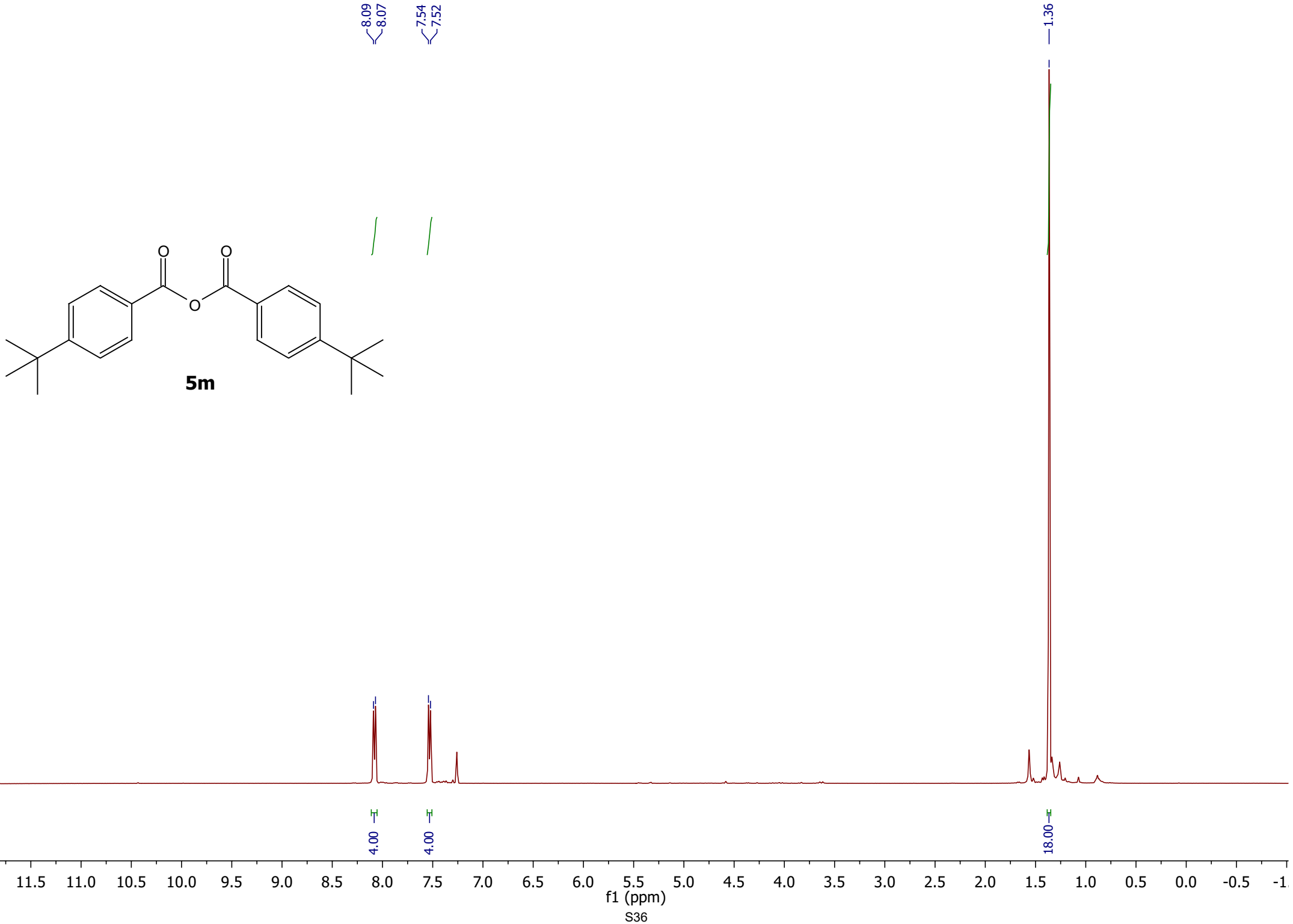
5l

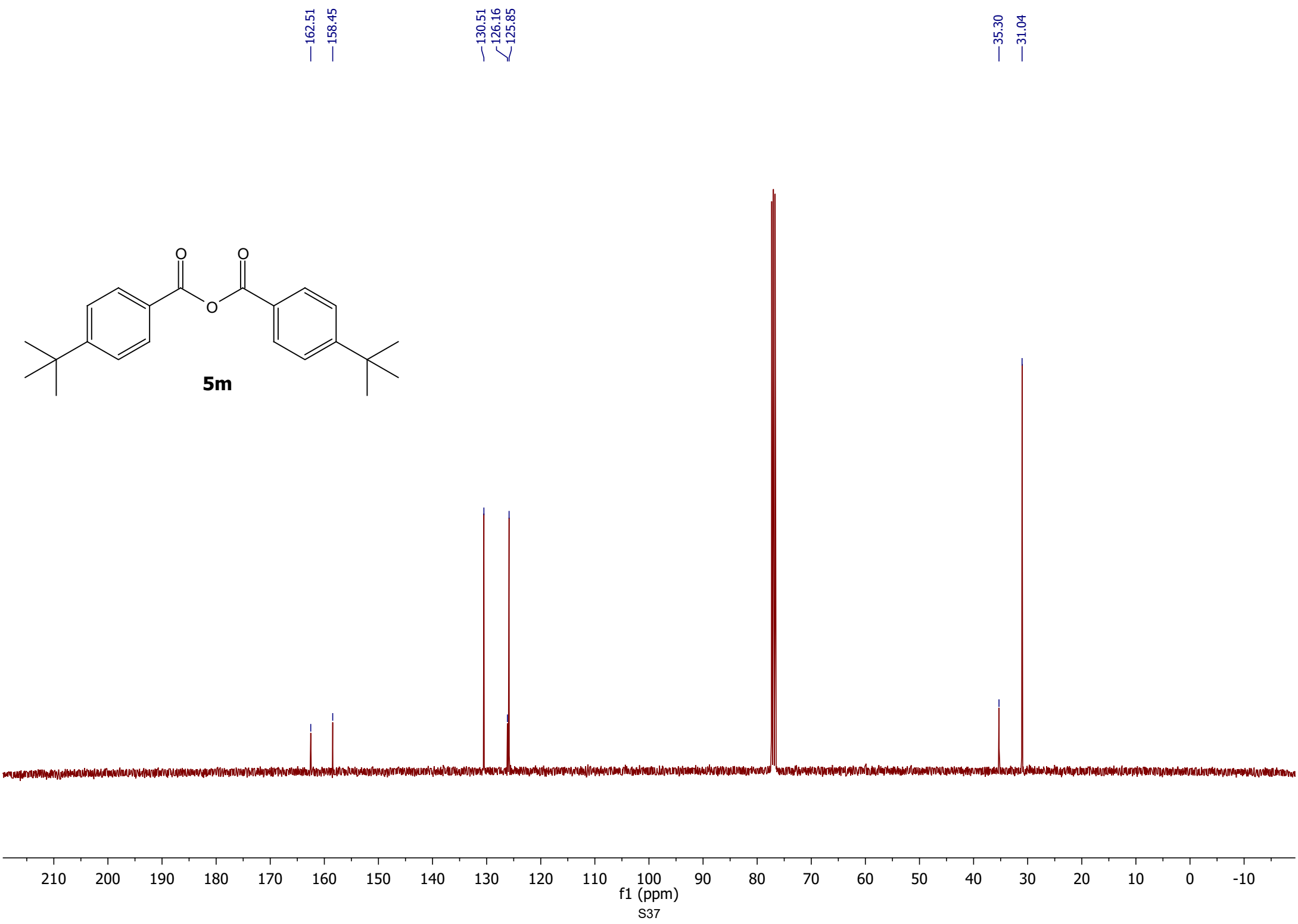
7.28
7.26
7.25
7.20
7.18
7.17
7.15
2.94
2.92
2.90
2.72
2.70
2.68
4.00
6.00
4.00
4.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

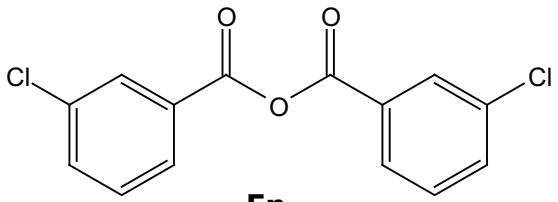


5l

168.37
139.45
128.47
128.15
126.39
36.62
30.02
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

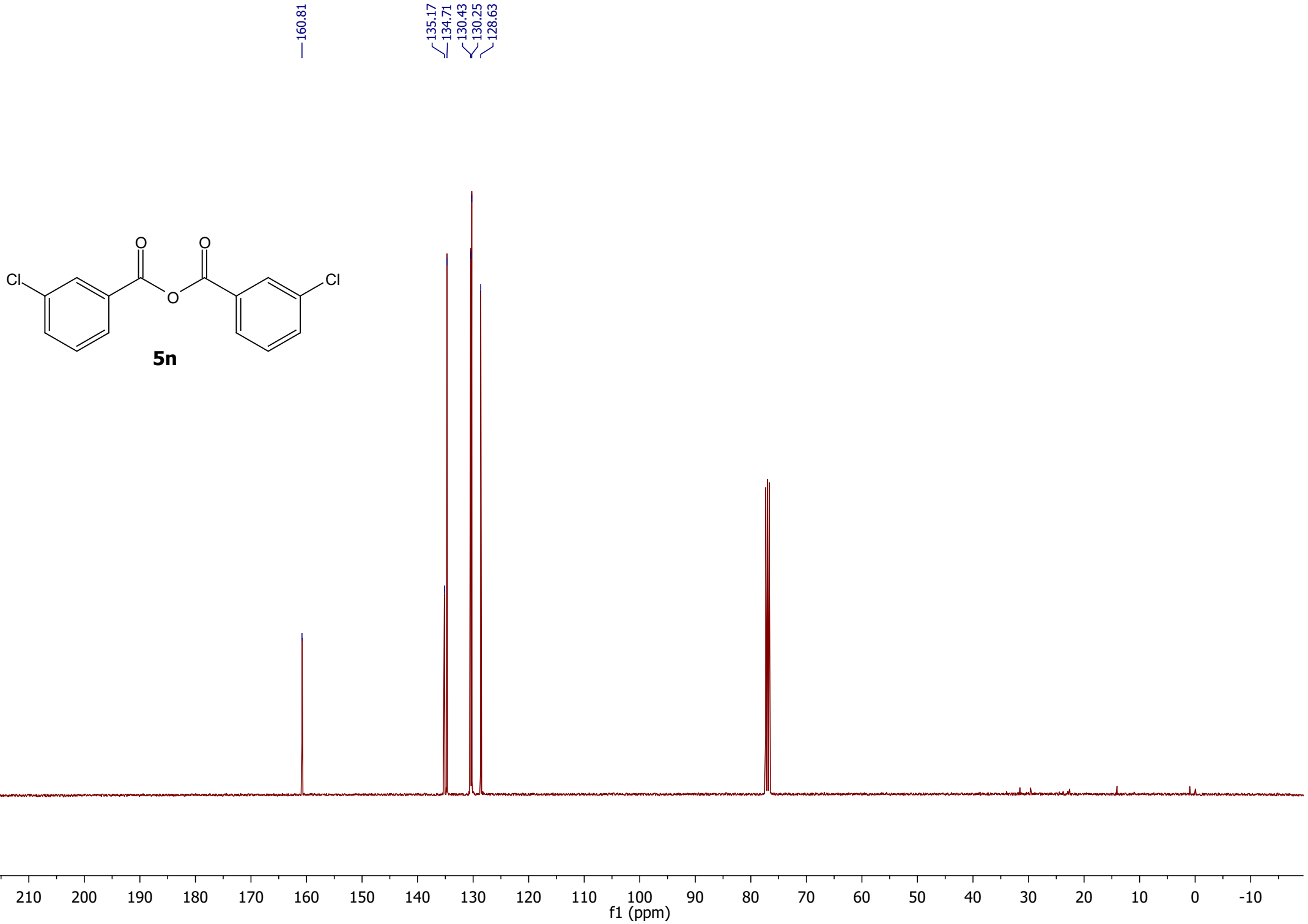

8.09
8.07
7.54
7.52
1.36
O
O
O
5m
4.00
4.00
18.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

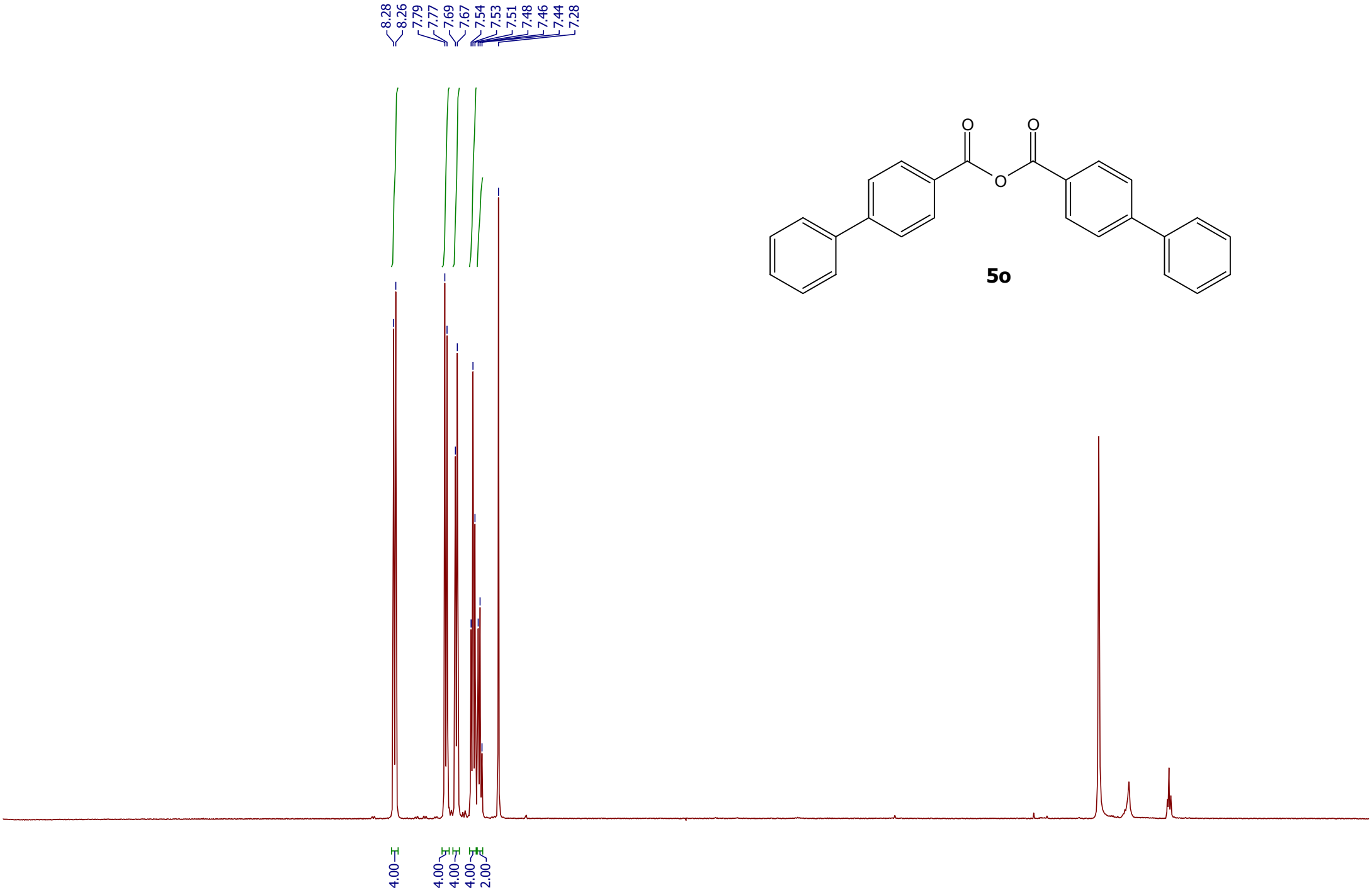

162.51
158.45
130.51
126.16
125.85
35.30
31.04
O
O
O
5m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

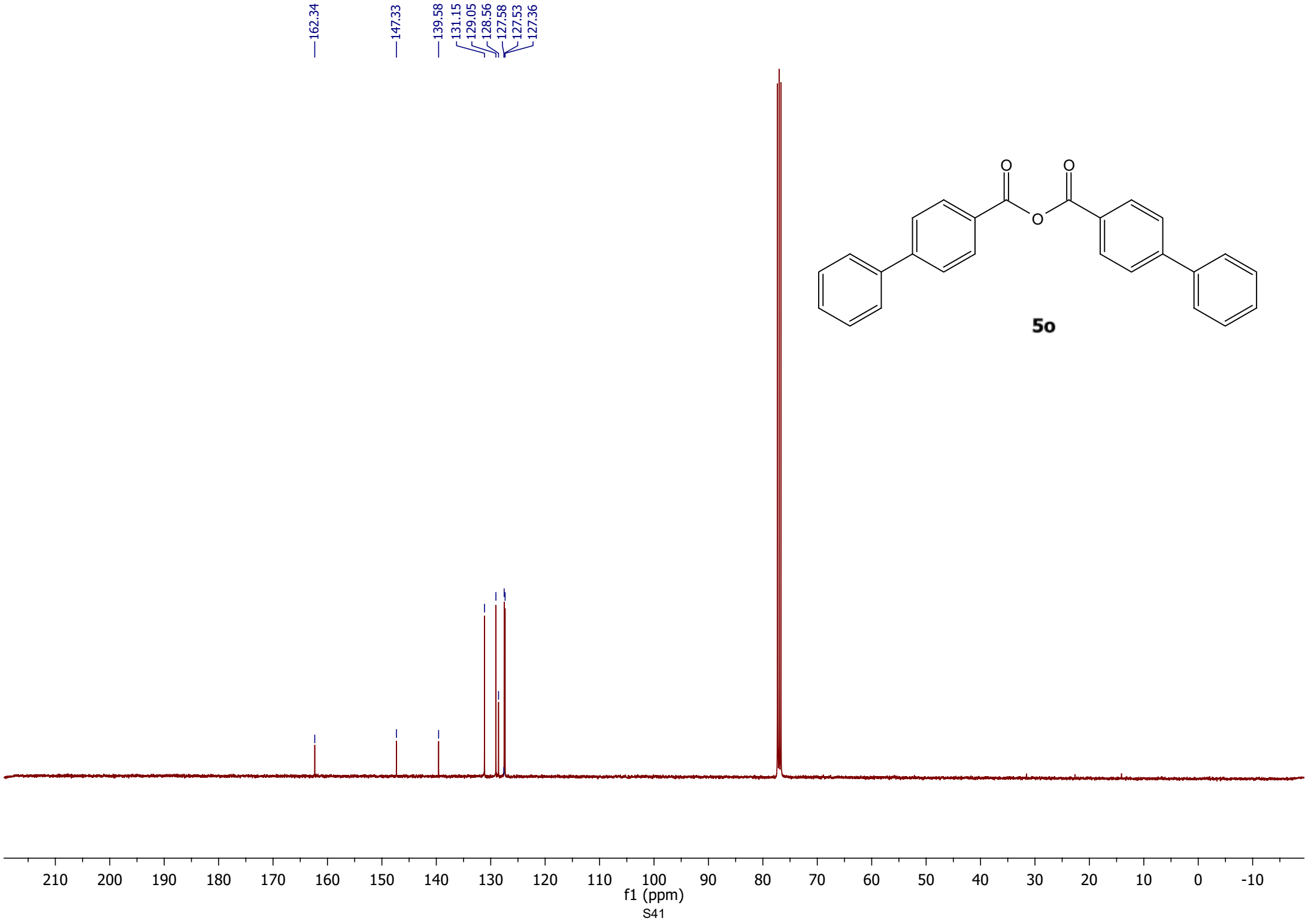

O
O
Cl
O
Cl

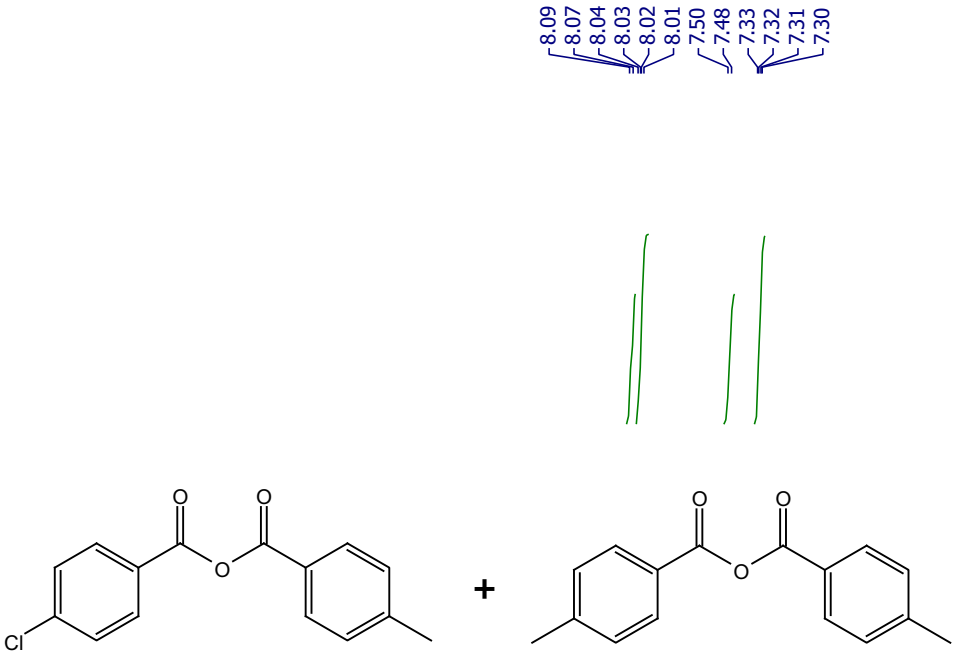
5n

8.11
8.05
8.03
7.68
7.68
7.67
7.66
7.66
7.65
7.51
7.49
7.48
2.00
2.00
2.00
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

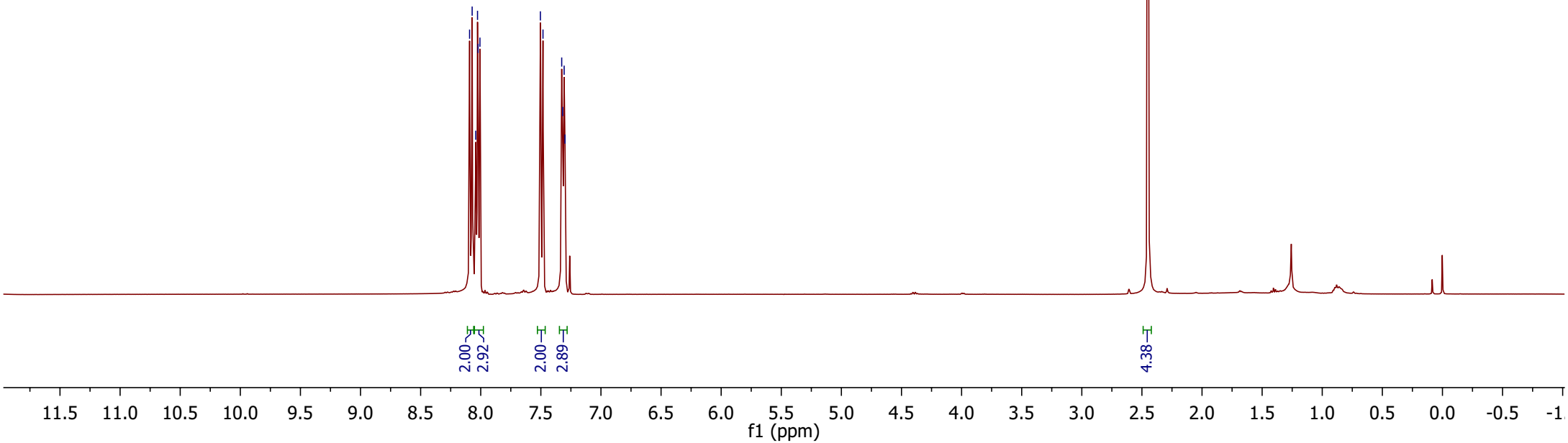

160.81
135.17
134.71
130.43
130.25
128.63
Cl
Cl
O
O
O
5n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

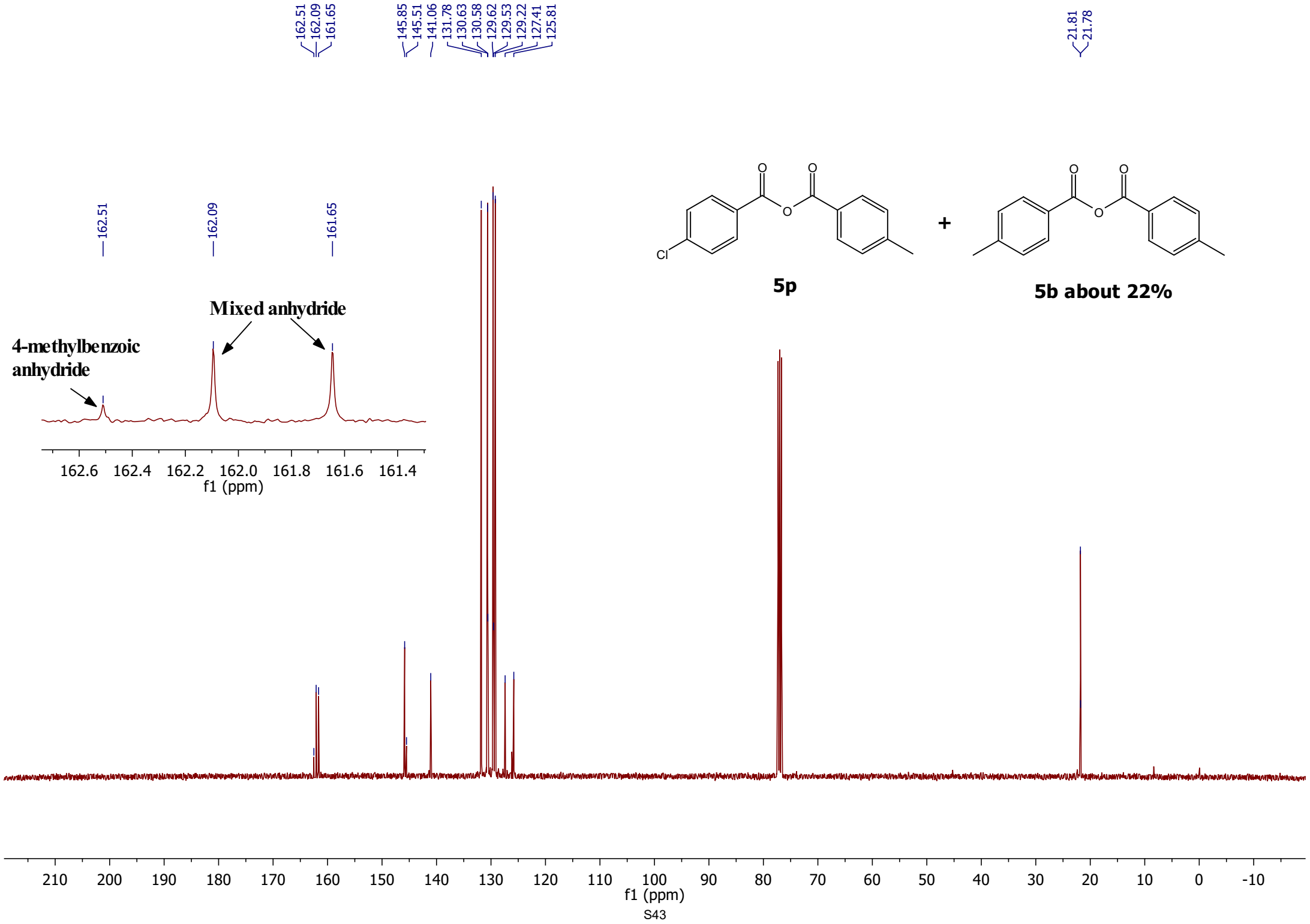

8.28
8.26
7.79
7.77
7.69
7.67
7.54
7.53
7.51
7.48
7.46
7.44
7.28
O
O
O
5o
4.00
4.00
4.00
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

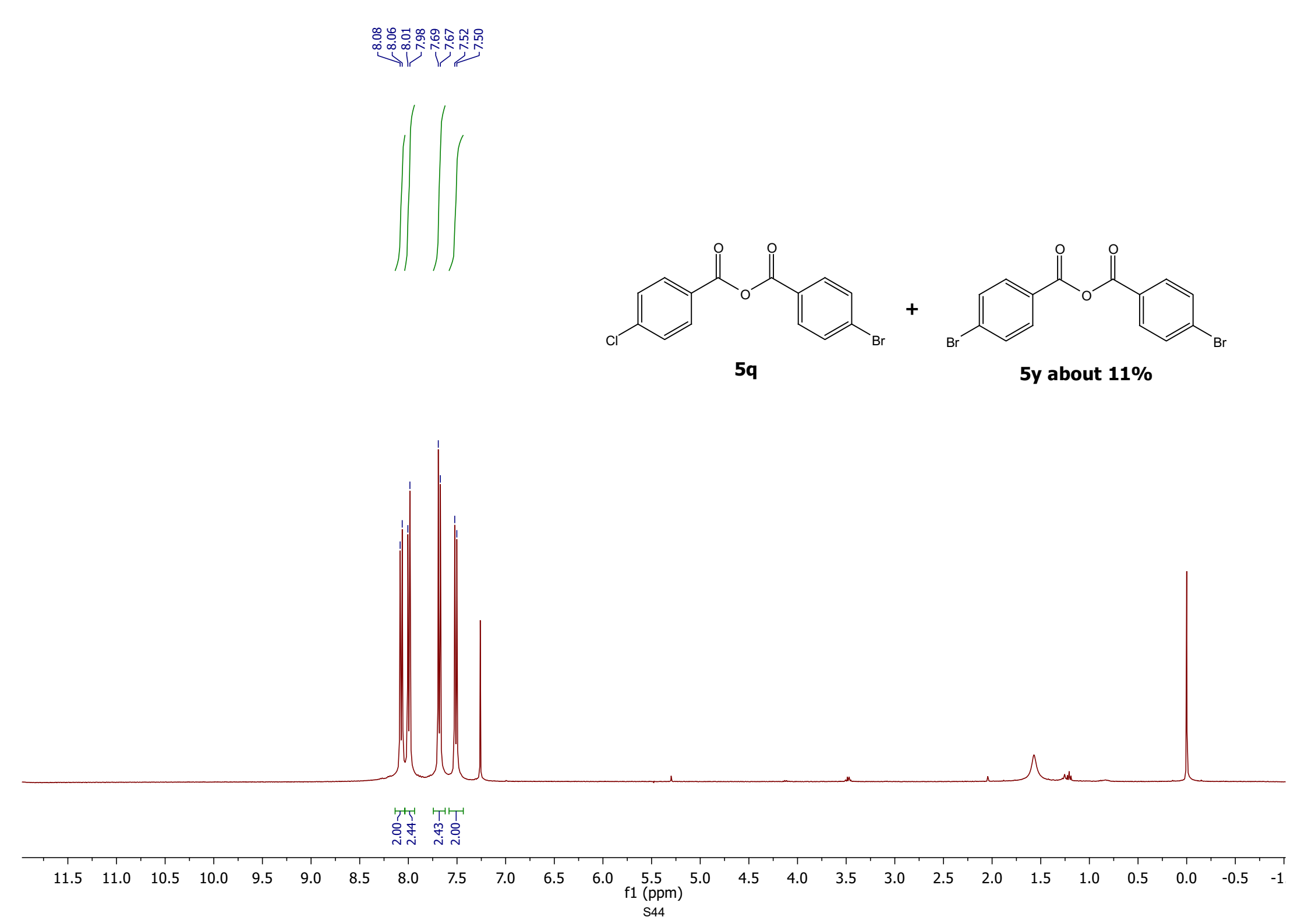

162.34
147.33
139.58
131.15
129.05
128.56
127.58
127.53
127.36
O
O
O
5o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

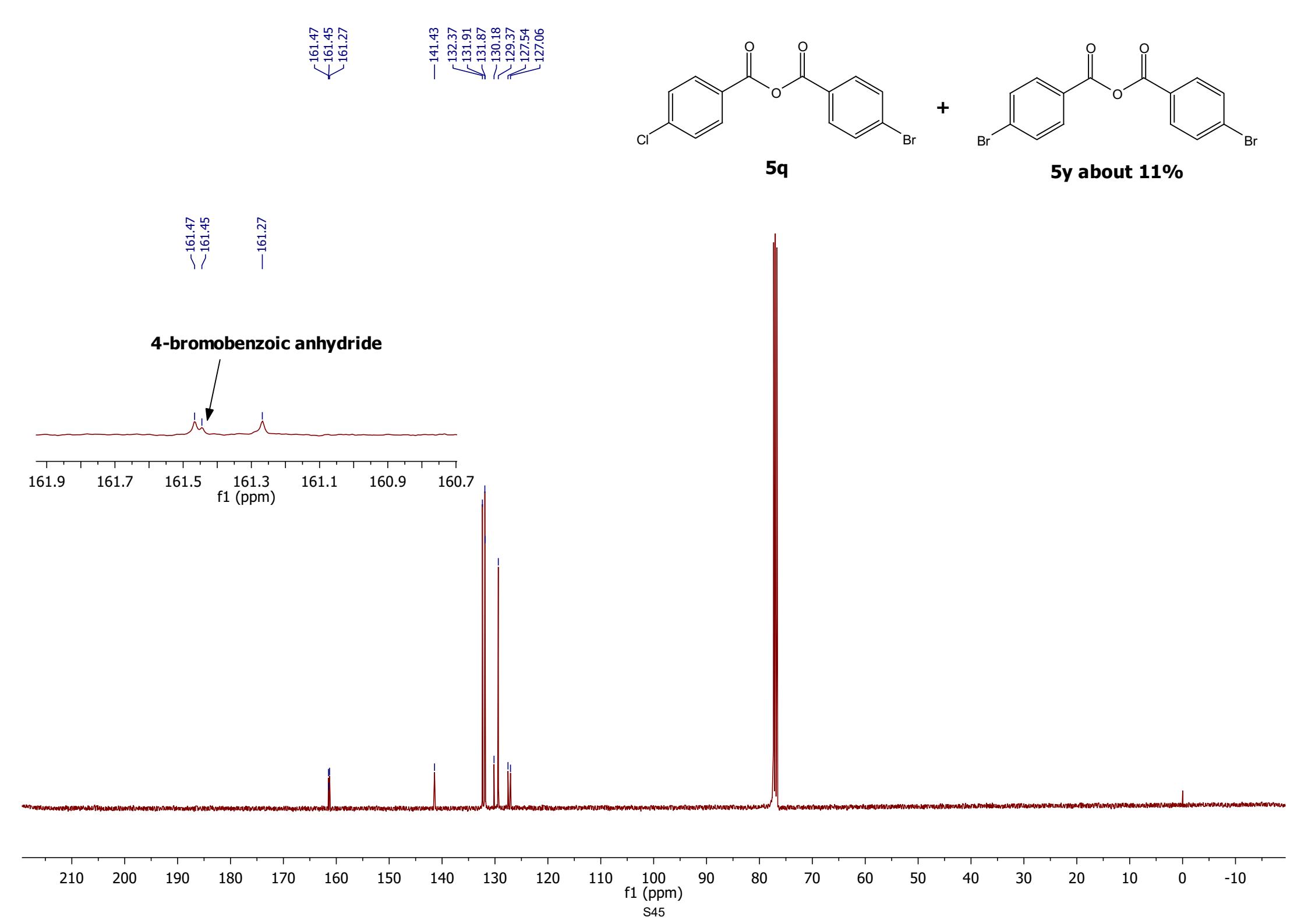


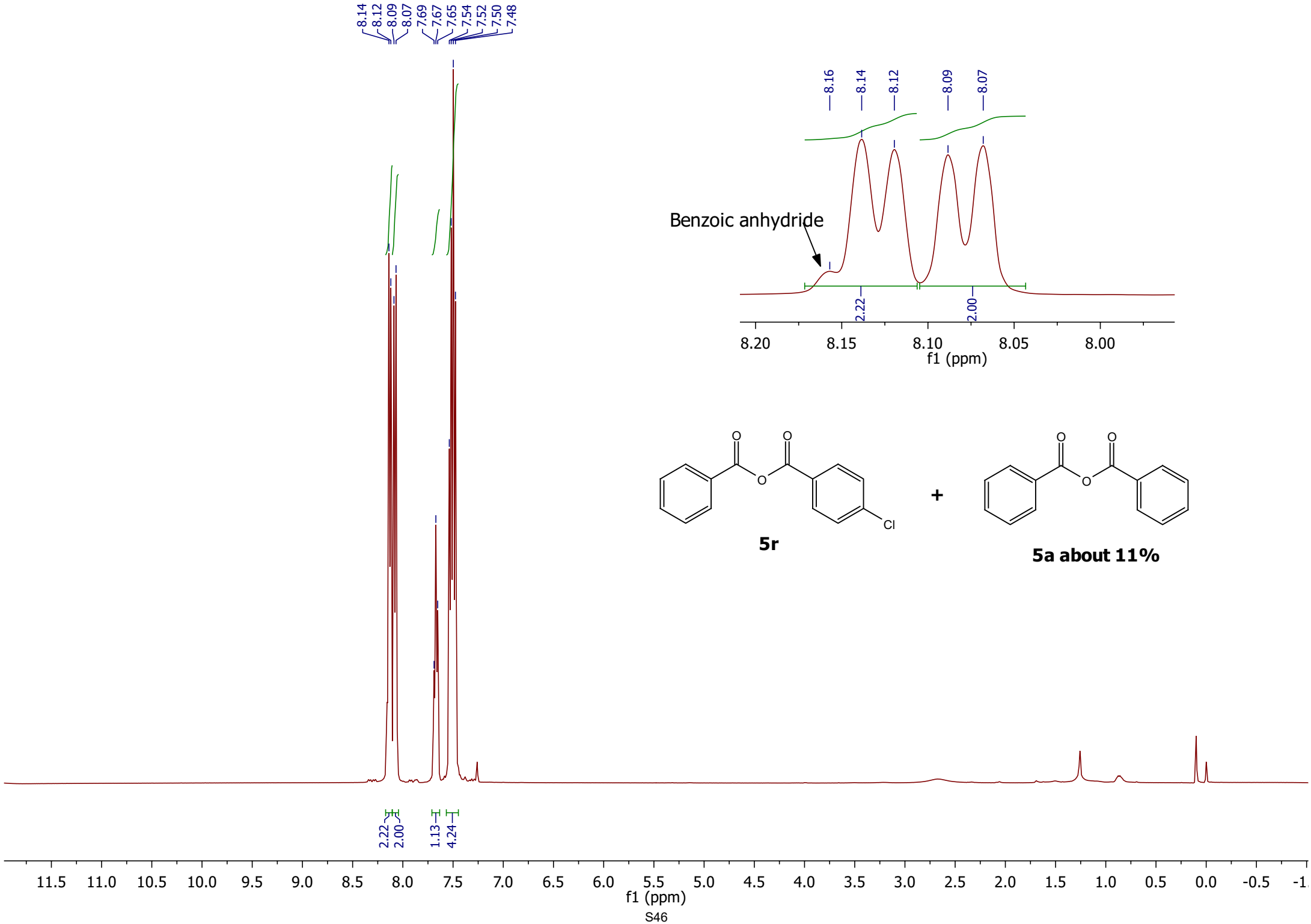
5p **5b about 22%**

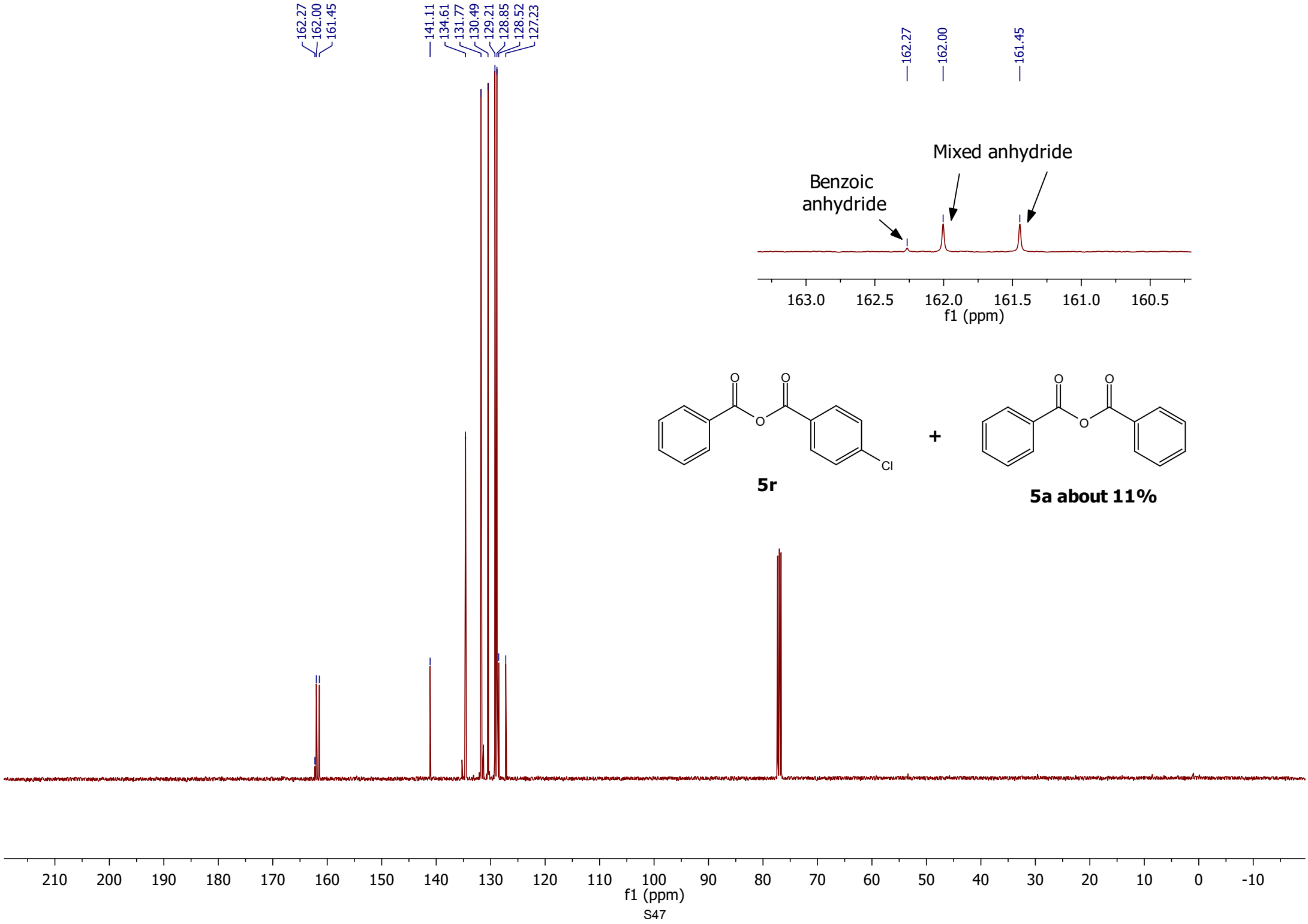


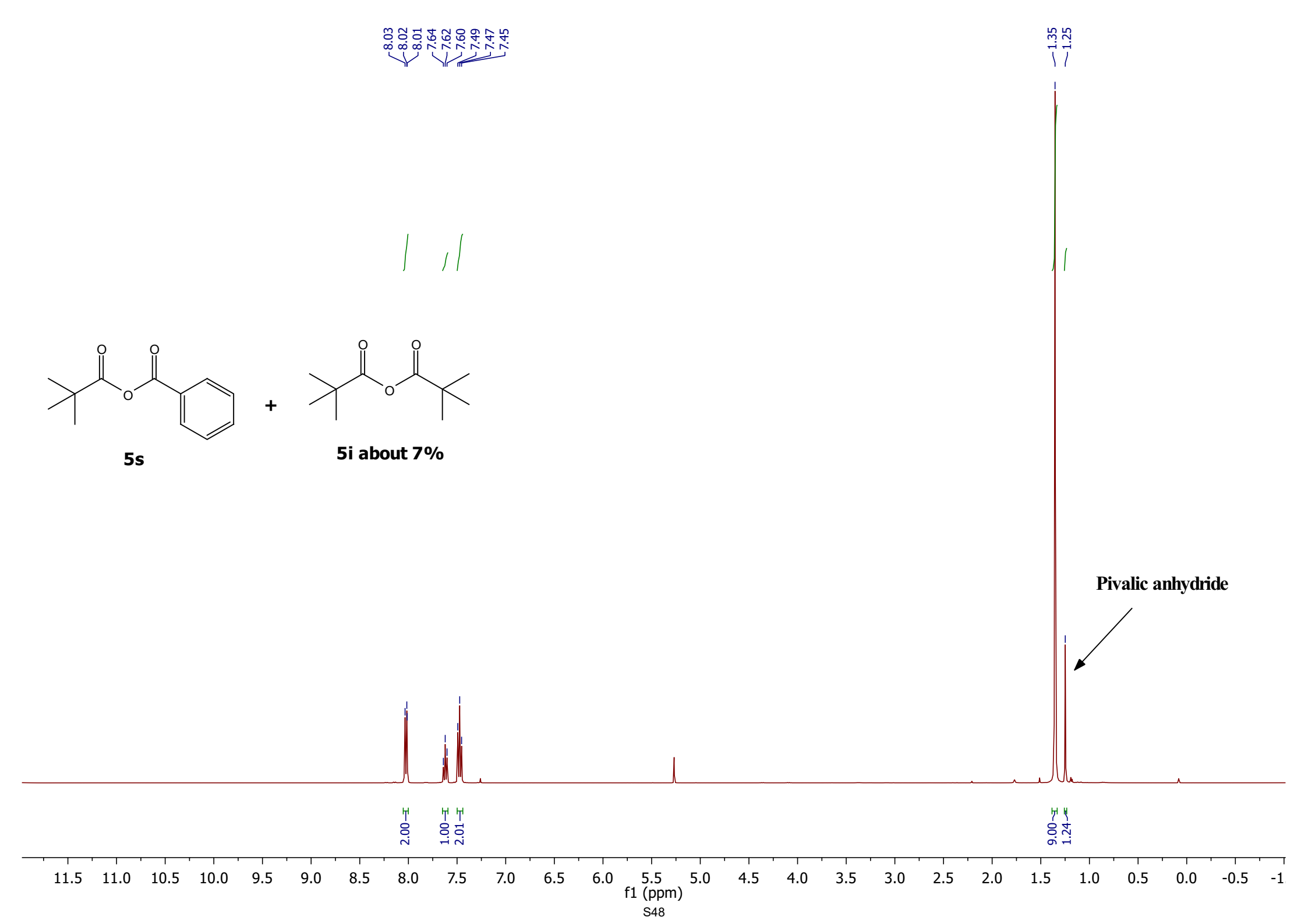

162.51
162.09
161.65
145.85
145.51
141.06
131.78
130.63
130.58
129.62
129.53
129.22
127.41
125.81
21.81
21.78
Mixed anhydride
4-methylbenzoic anhydride
162.6 162.4 162.2 162.0 161.8 161.6 161.4
f1 (ppm)
Cl
5p
+
5b about 22%
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

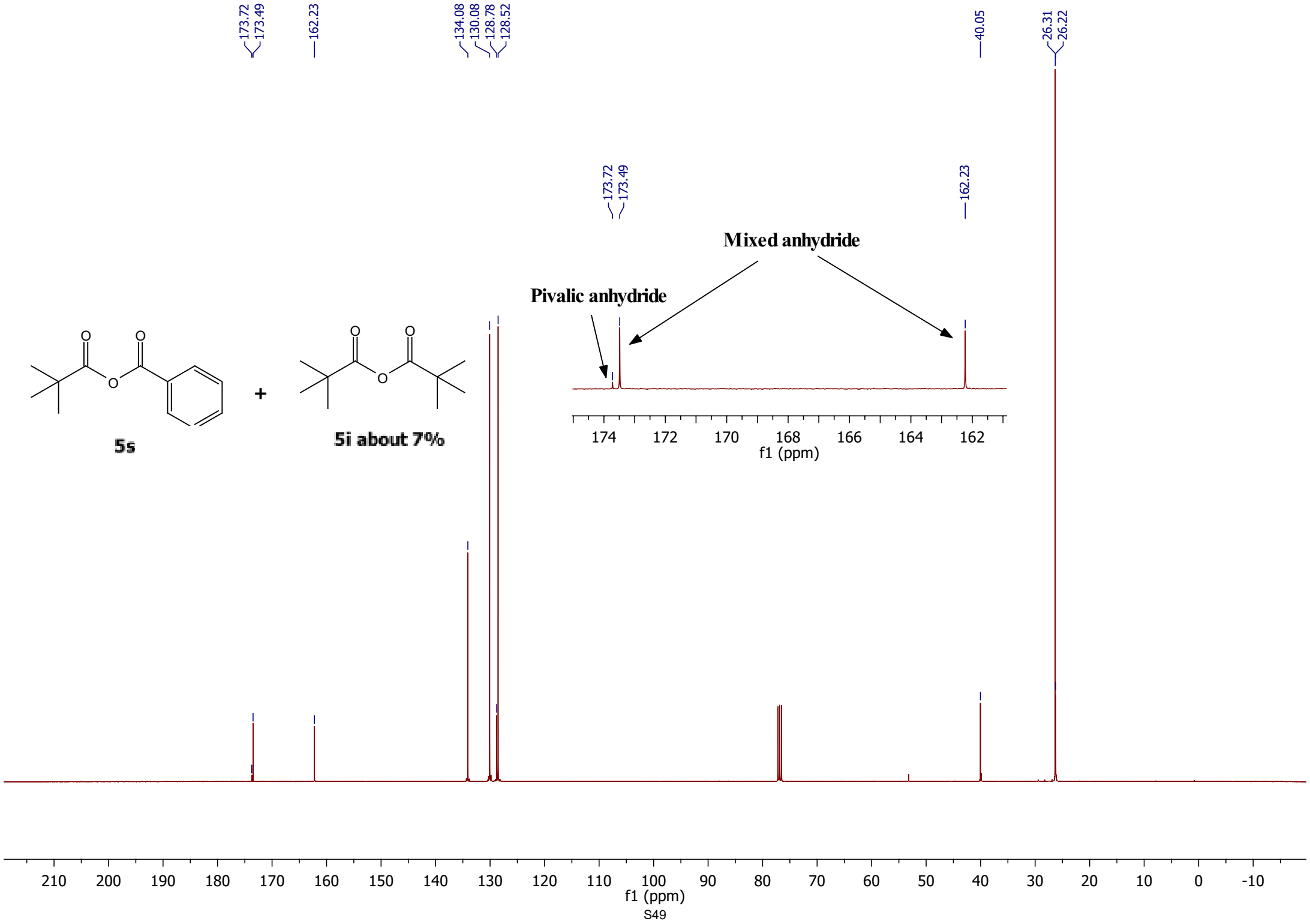

8.08
8.06
8.01
7.98
7.69
7.67
7.52
7.50
O
O
O
Cl
Br
+
O
O
O
Br
Br
5q
5y about 11%
2.00
2.44
2.43
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

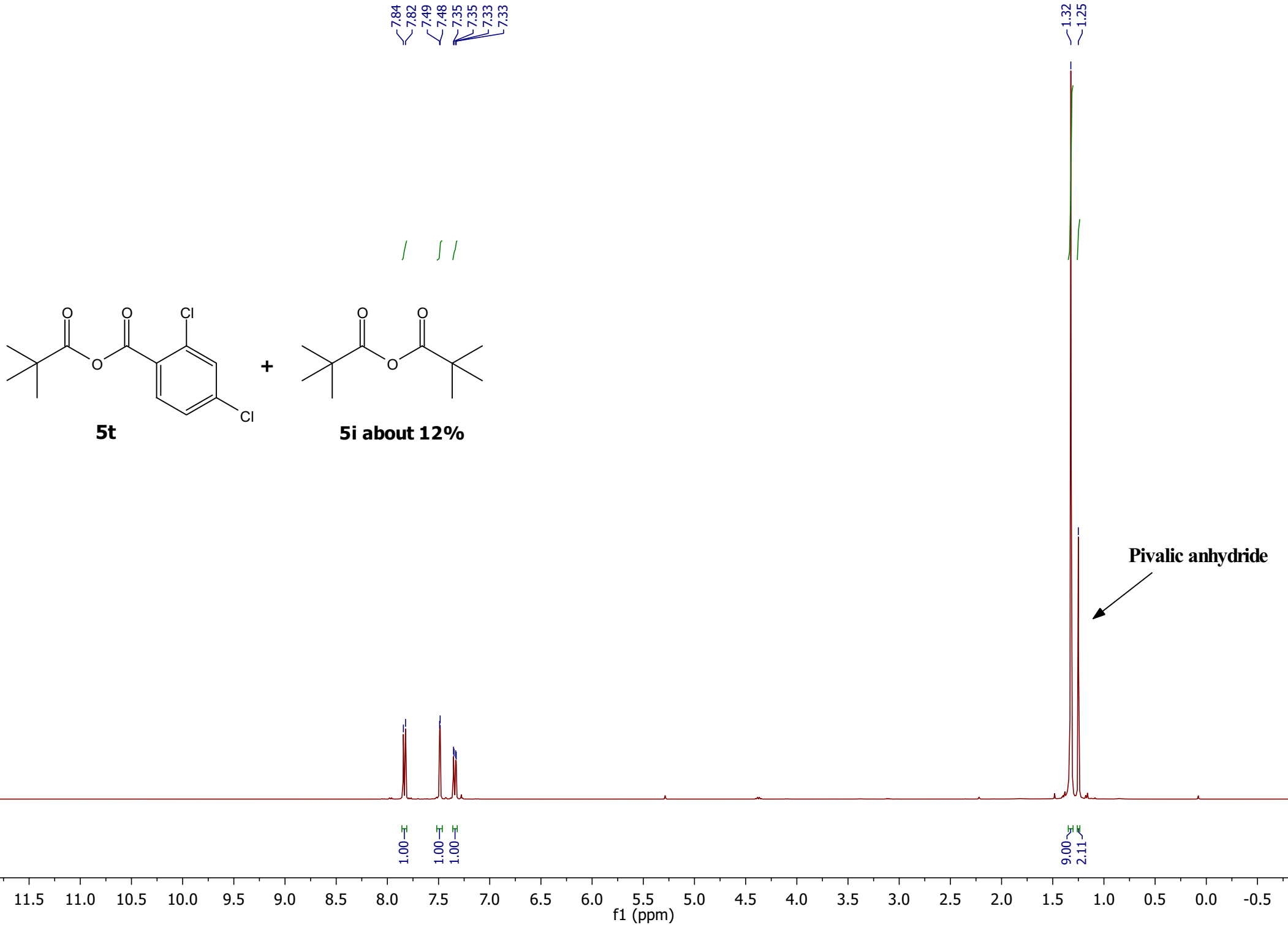

161.47
161.45
161.27
141.43
132.37
131.91
131.87
130.18
129.37
127.54
127.06
Cl
Br
5q
+
Br
Br
5y about 11%
161.47
161.45
161.27
4-bromobenzoic anhydride
161.9
161.7
161.5
161.3
161.1
160.9
160.7
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

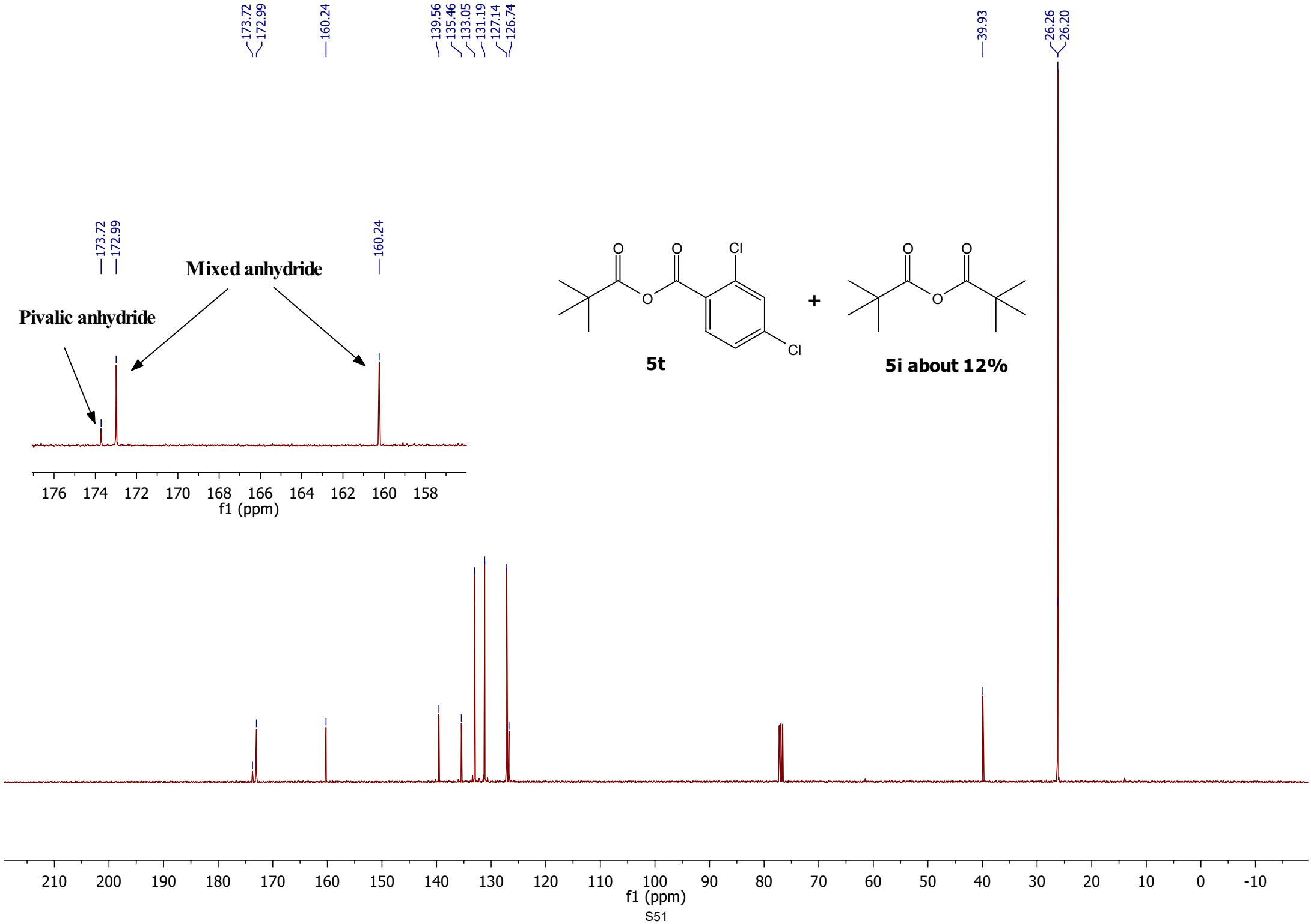

8.14
8.12
8.09
8.07
7.69
7.67
7.65
7.54
7.52
7.50
7.48
8.16
8.14
8.12
8.09
8.07
Benzoic anhydride
2.22
2.00
8.20
8.15
8.10
8.05
8.00
f1 (ppm)
O
O
O
O
Cl
5r
+
O
O
O
5a about 11%
2.22
2.00
1.13
4.24
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

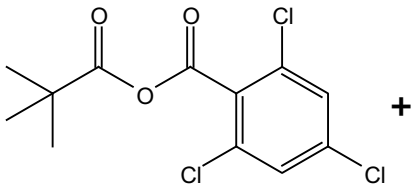

162.27
162.00
161.45
141.11
134.61
131.77
130.49
129.21
128.85
128.52
127.23
Mixed anhydride
Benzoic anhydride
163.0
162.5
162.0
161.5
161.0
160.5
f1 (ppm)
Cl
5r
+
5a about 11%
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.03
8.02
8.01
7.64
7.62
7.60
7.49
7.47
7.45
1.35
1.25
5s
+
5i about 7%
Pivalic anhydride
2.00
1.00
2.01
9.00
1.24
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


173.72
173.49
162.23
134.08
130.08
128.78
128.52
40.05
26.31
26.22
Mixed anhydride
Pivalic anhydride
5s
+
5i about 7%
f1 (ppm)
f1 (ppm)

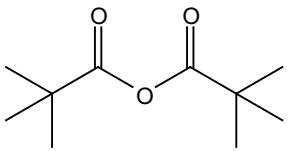

7.84
7.82
7.49
7.48
7.35
7.35
7.33
7.33
1.32
1.25
O
O
Cl
O
Cl
5t
+
O
O
O
5i about 12%
Pivalic anhydride
1.00
1.00
1.00
9.00
2.11
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


173.72
172.99
160.24
139.56
135.46
133.05
131.19
127.14
126.74
39.93
26.26
26.20
Mixed anhydride
Pivalic anhydride
O
O
Cl
Cl
5t
+
O
O
5i about 12%
176 174 172 170 168 166 164 162 160 158
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

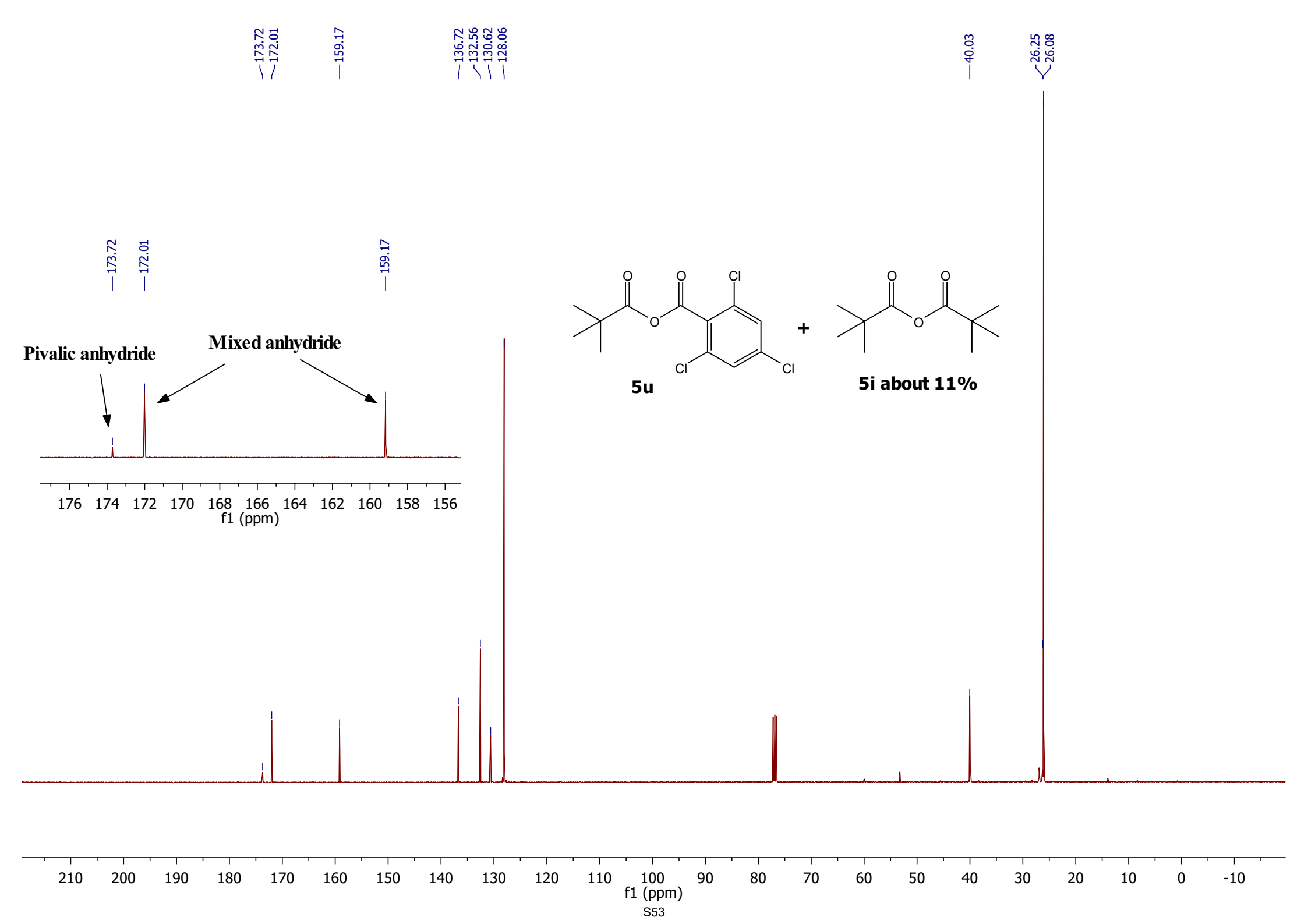


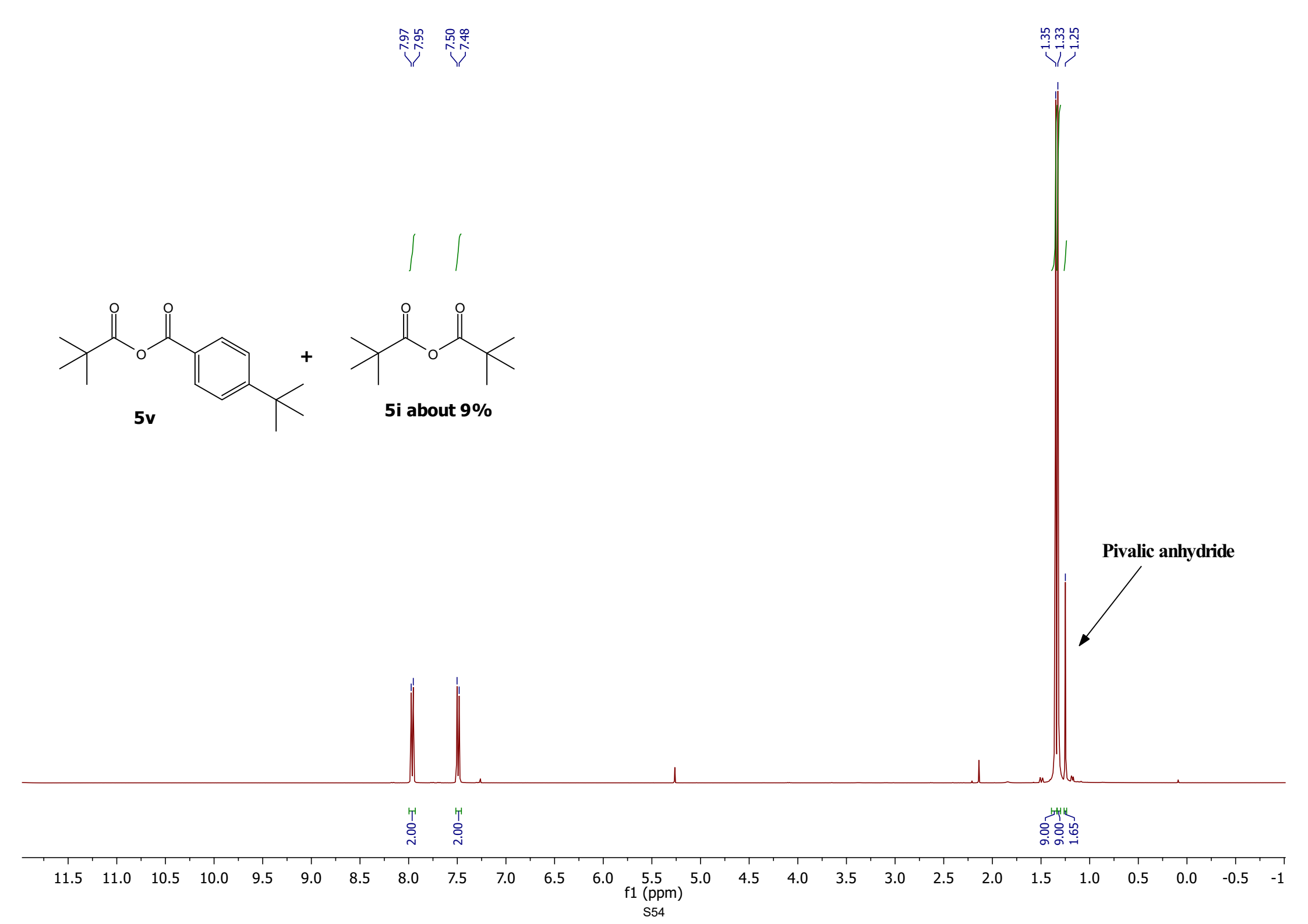
5u

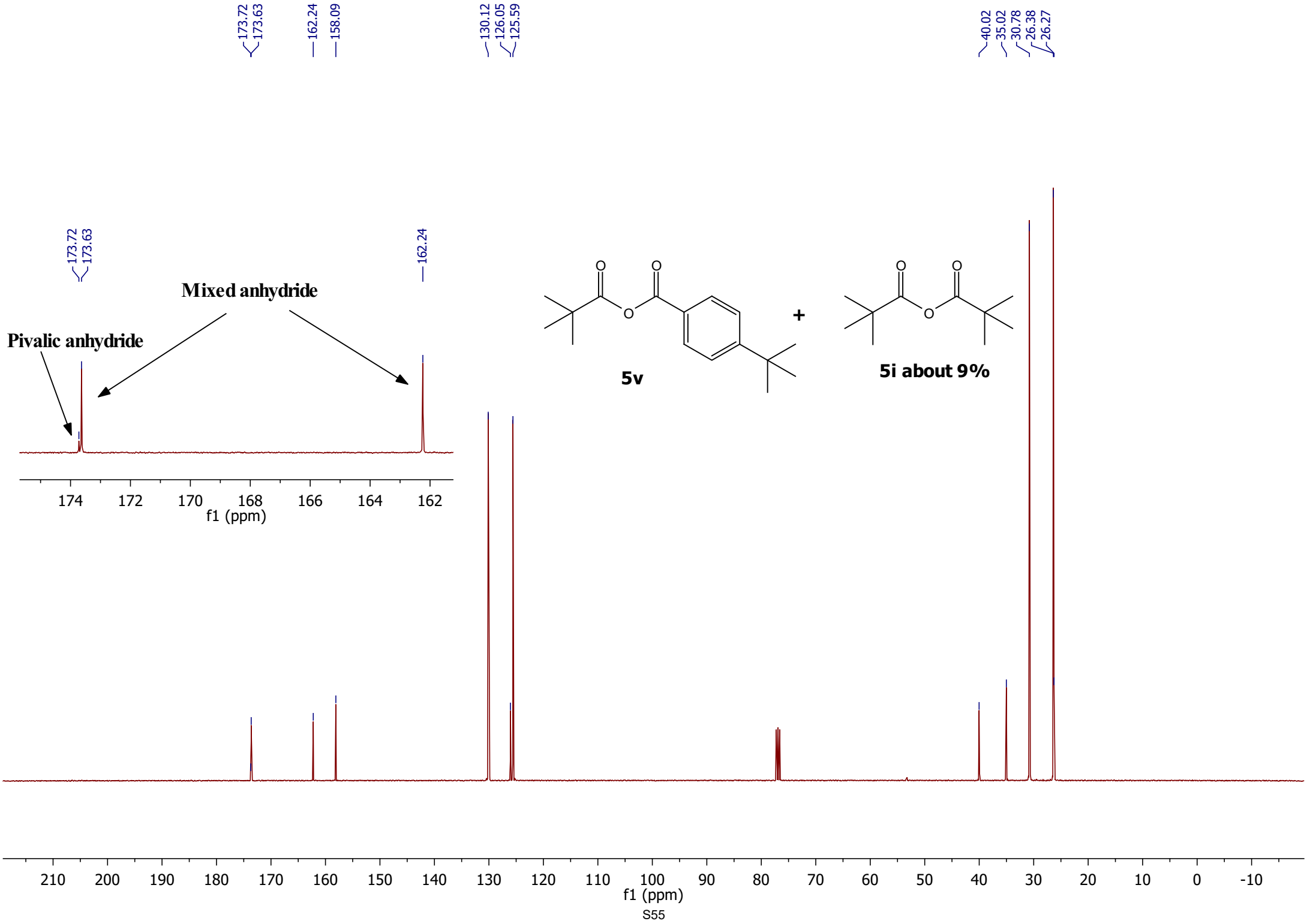
+

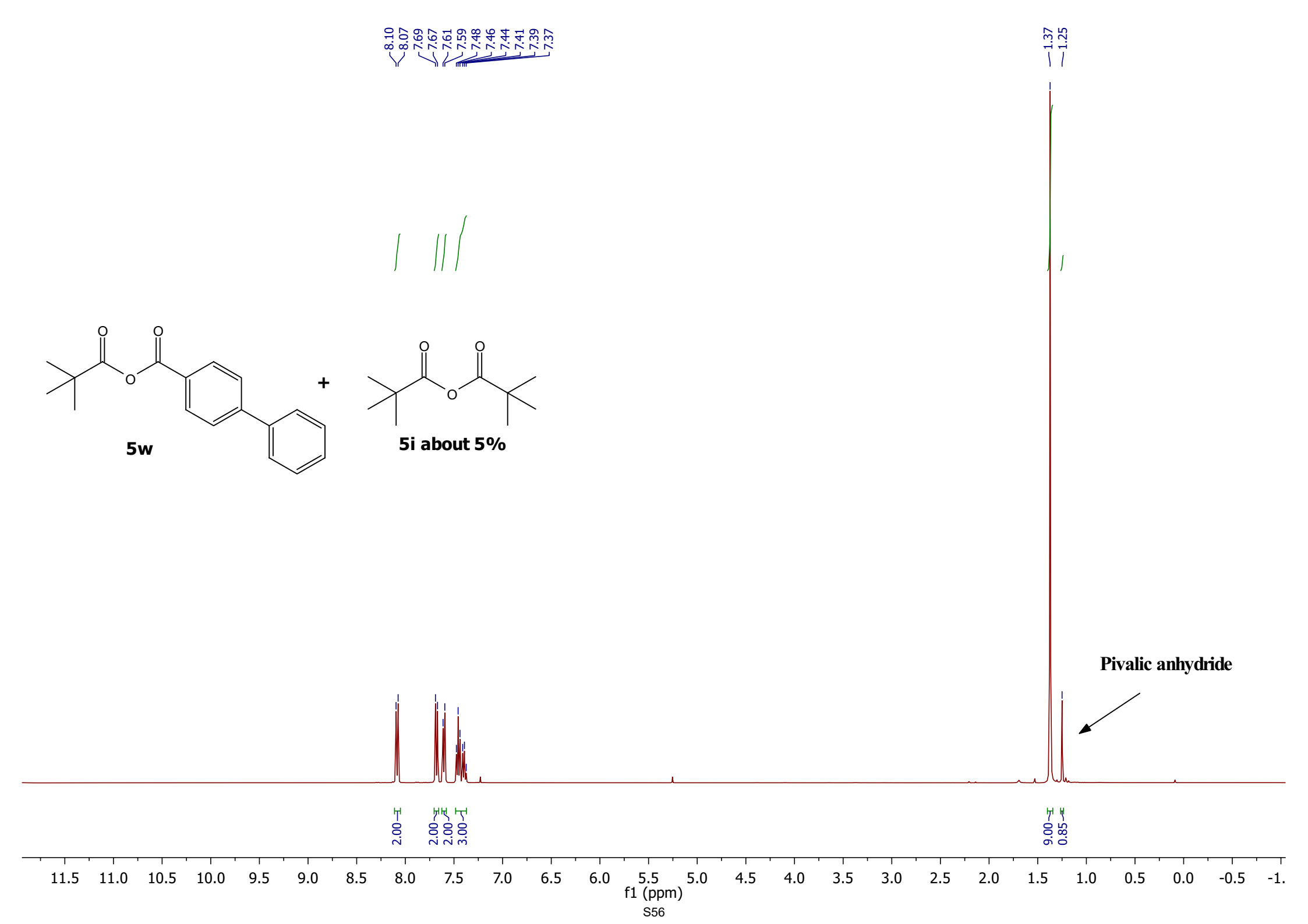


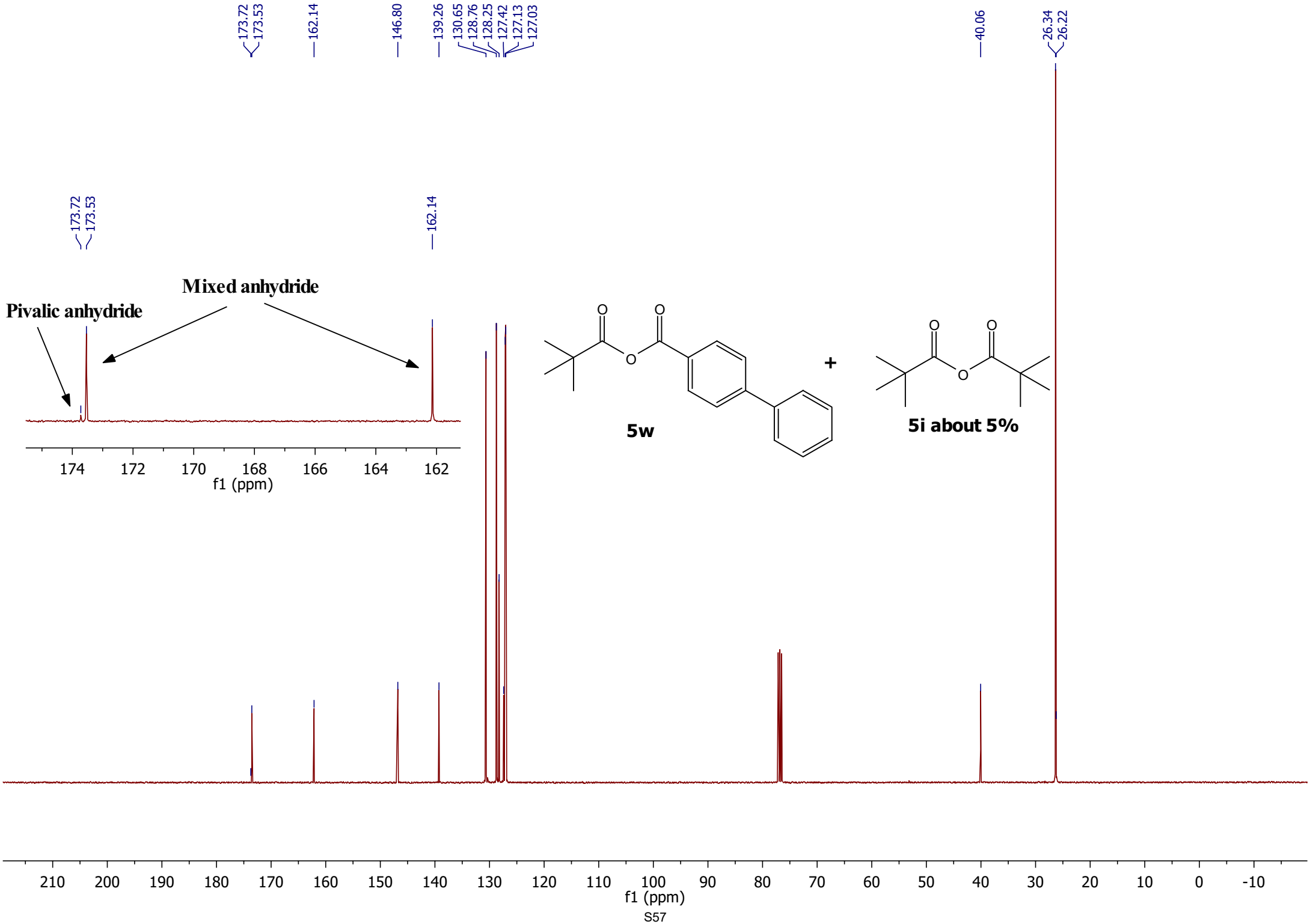
5i about 11%

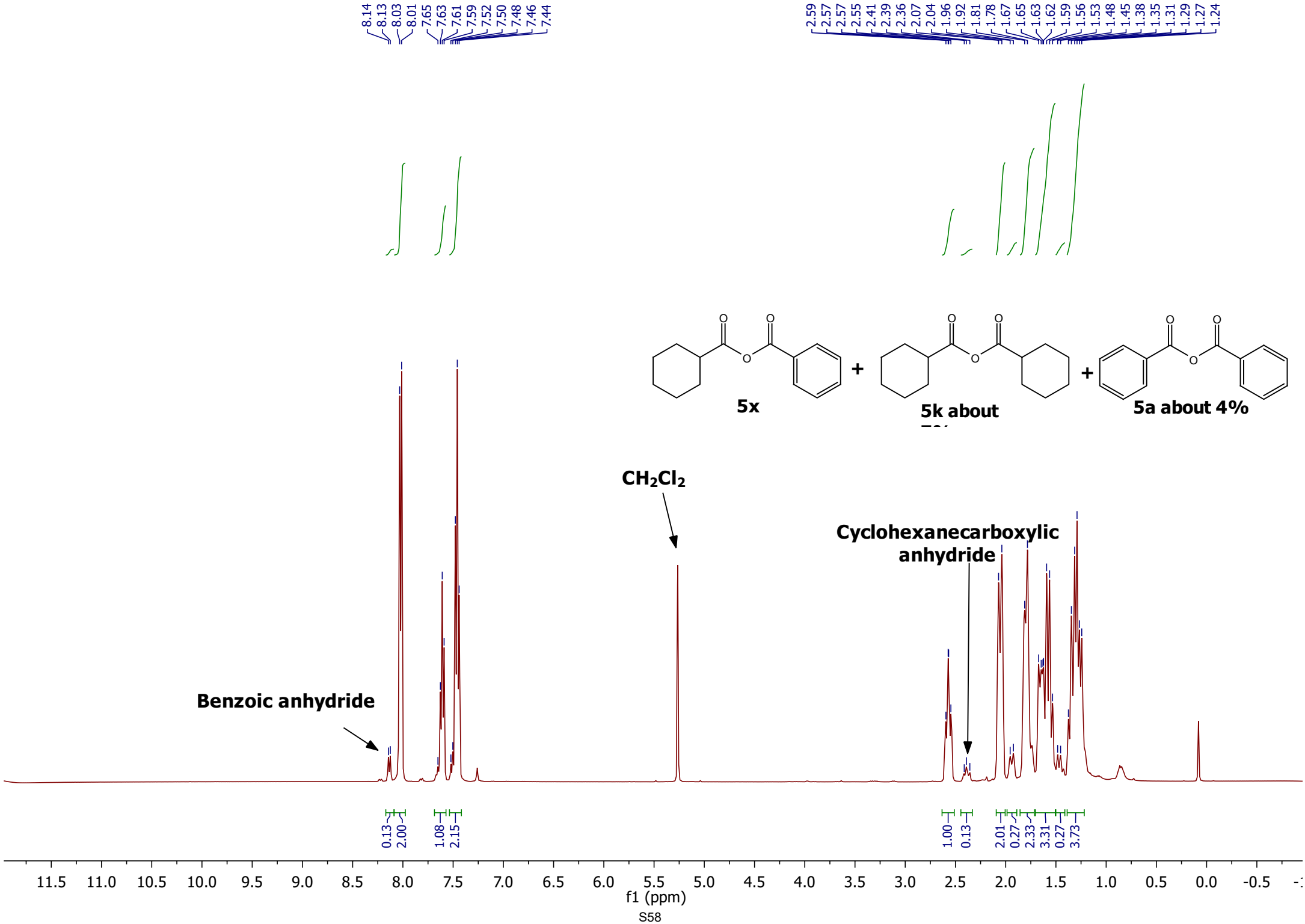

173.72
172.01
159.17
136.72
132.56
130.62
128.06
40.03
26.25
26.08
Pivalic anhydride
Mixed anhydride
f1 (ppm)
5u
5i about 11%
f1 (ppm)

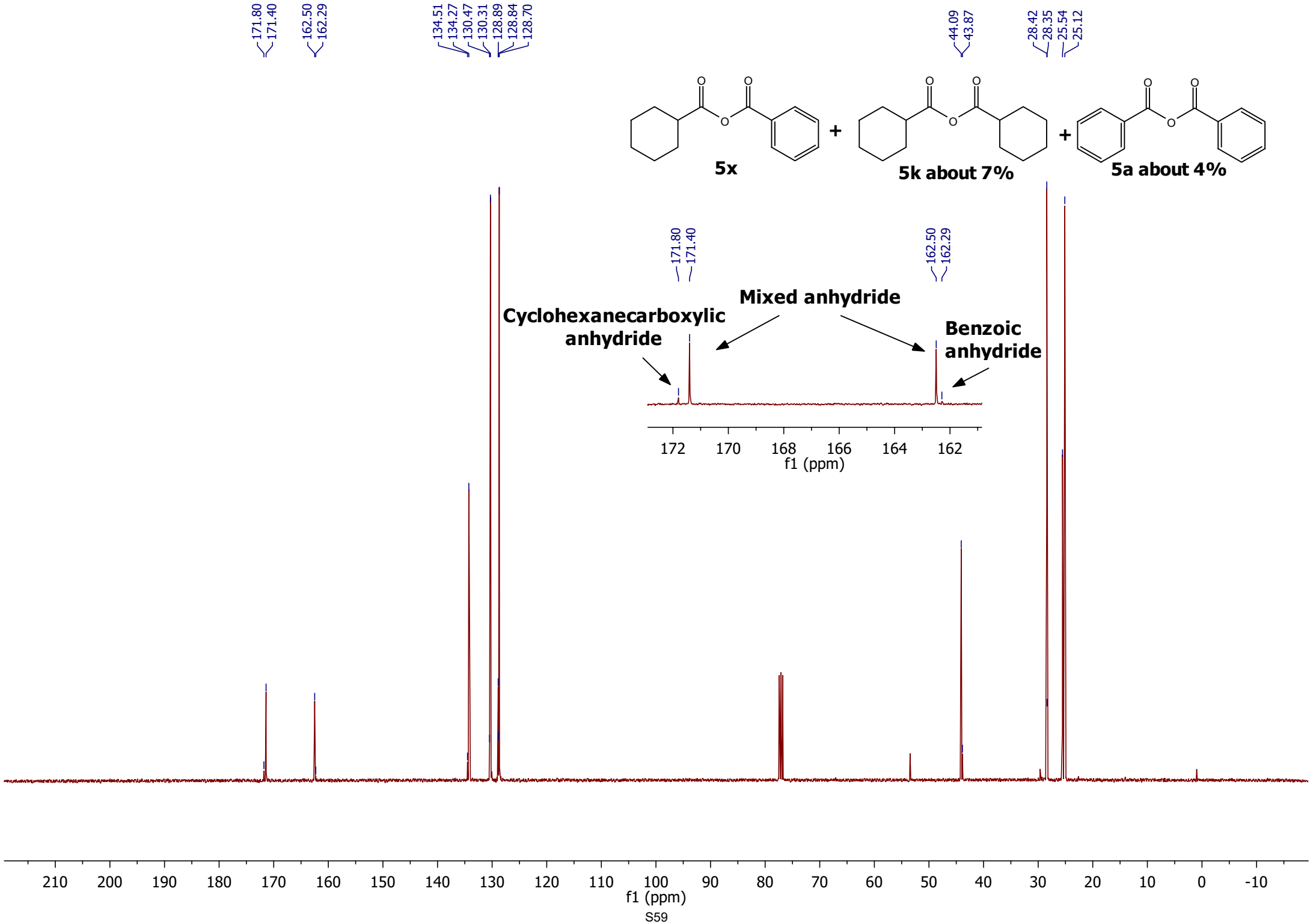

7.97
7.95
7.50
7.48
1.35
1.33
1.25
5v
+
5i about 9%
Pivalic anhydride
2.00
2.00
9.00
9.00
1.65
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


173.72
173.63
162.24
158.09
130.12
126.05
125.59
40.02
35.02
30.78
26.38
26.27
Mixed anhydride
Pivalic anhydride
5v
+
5i about 9%
f1 (ppm)
f1 (ppm)


8.10
8.07
7.69
7.67
7.61
7.59
7.48
7.46
7.44
7.41
7.39
7.37
1.37
1.25
5w
+
5i about 5%
Pivalic anhydride
2.00
2.00
2.00
3.00
9.00
0.85
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


173.72
173.53
162.14
146.80
139.26
130.65
128.76
128.25
127.42
127.13
127.03
40.06
26.34
26.22
Pivalic anhydride
Mixed anhydride
5w
+
5i about 5%
f1 (ppm)
f1 (ppm)


8.14
8.13
8.03
8.01
7.65
7.63
7.61
7.59
7.52
7.50
7.48
7.46
7.44
2.59
2.57
2.57
2.55
2.41
2.39
2.36
2.07
2.04
1.96
1.92
1.81
1.78
1.67
1.65
1.63
1.62
1.59
1.56
1.53
1.48
1.45
1.38
1.35
1.31
1.29
1.27
1.24
5x
+
5k about
+
5a about 4%
CH2Cl2
Cyclohexanecarboxylic anhydride
Benzoic anhydride
0.13
2.00
1.08
2.15
1.00
0.13
2.01
0.27
2.33
3.31
0.27
3.73
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


171.80
171.40
162.50
162.29
134.51
134.27
130.47
130.31
128.89
128.84
128.70
44.09
43.87
28.42
28.35
25.54
25.12
5x
5k about 7%
5a about 4%
Cyclohexanecarboxylic anhydride
Mixed anhydride
Benzoic anhydride
172
170
168
166
164
162
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)