Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Visible Light-Induced Transformation of Aldehydes to Esters, Carboxylic Anhydrides and Amides

Silvia Gaspa,[a] Inês Raposo,[a] Leonor Pereira,[a] Gabriele Mulas,[a] Pier Carlo Ricci,[b] Andrea Porcheddu[c] and Lidia De Luca[a] *

[a] Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari, via Vienna 2, 07100 Sassari, Italy

[b] Dipartimento di Fisica, Università degli Studi di Cagliari, Cittadella Universitaria, 09042 Monserrato, Italy

[c] Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Cittadella Universitaria, 09042 Monserrato, Italy

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Experimental Section:

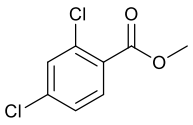
General Information

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, $KMnO_4$, 2,4-DNP and cerium ammonium molybdate staining. The reactions were conducted with Abet tech sun 2000 simulator (under 100 mW/cm^2 simulated AM 1.5G irradiance). For irradiation with blue light OSRAM Oslon SSL 80 LDCQ7P-1U3U (blue, λ max = 455 nm, I max = 1000 mA, 1.12 W) was used. ^{1}H 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). Elemental analyses were measured on a Perkin-Elmer Elemental Analyzer 2400-CHN. 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. For the determination of the quantum yield a Stabilized laser diode Oxxius-450 (λ= 450 ± 5 nm) was utilized as excitation source. Newport model 1918-C power meter for the determination of the irradiation beam and transmitted. Arex Digital as plate stirrer.

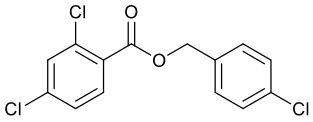
General Procedure for esters 5a-s under solar simulator irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under solar simulator irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of aldehyde). Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and an alcohol (1.0 mmol) was dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol) and then DMAP (10% mol) at once. After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the alcohol (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

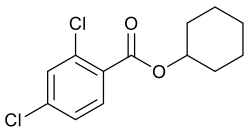
Compound characterizations:



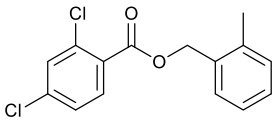
Methyl 2,4-dichlorobenzoate (5a): Yellow oil; (0.201 g, 98 % yield); R_f = 0.3 (hexane/ethyl acetate 4.7/0.3). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.92 (s, 3H).[1] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 138.3, 134.9, 132.5, 131.0, 128.2, 126.9, 52.5.[1]



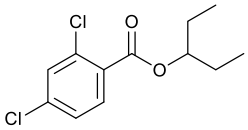
4-chlorobenzyl 2,4-dichlorobenzoate (5b): White solid; (0.293 g, 93 % yield); m.p.= 69-70 °C; R_f = 0.276 (hexane/ethyl acetate 4.7/0.3). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.41 – 7.33 (m, 4H), 7.29 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.32 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4, 138.6, 135.1, 134.4, 133.8, 132.6, 131.1, 129.8, 128.8, 127.9, 127.0, 66.6. *Anal. Calcd. for* $C_{14}H_9Cl_3O_2$: C, 53.29; H, 2.87. Found: C, 53.27; H, 2.84.



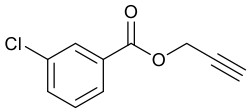
Cyclohexyl 2,4-dichlorobenzoate (5c): Colorless oil; (0.218 g, 80 % yield); R_f = 0.44 (hexane/ethyl acetate 4.7/0.3). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 5.04 (tt, *J* = 8.6, 3.9 Hz, 1H), 1.94 (dt, *J* = 9.1, 5.0 Hz, 2H), 1.79 (dq, *J* = 14.6, 4.8 Hz, 2H), 1.64 – 1.54 (m, 3H), 1.49 – 1.31 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4, 137.9, 134.6, 132.3, 130.9, 129.2, 126.9, 74.3, 31.5, 25.4, 23.6. *Anal. Calcd. for* $C_{13}H_{14}Cl_2O_2$: C, 57.16; H, 5.17. Found: C, 57.17; H, 5.15.



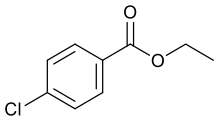
2-methylbenzyl 2,4-dichlorobenzoate (5d):[2] Colorless oil; (0.283 g, 96 % yield); R_f = 0.4 (hexane/ethyl acetate 4.7/0.3). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.29 – 7.20 (m, 4H), 5.38 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 164.5, 138.4, 137.1, 135.1, 133.3, 132.6, 131.1, 130.4, 129.6, 128.8, 128.2, 127.0, 126.1, 65.9, 19.0.



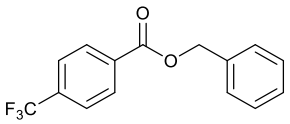
Pentan-3-yl 2,4-dichlorobenzoate (5e): Yellow oil; (0.201 g, 77 % yield); R_f = 0.41 (hexane/ethyl acetate 4.7/0.3). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.04 (p, *J* = 6.2 Hz, 1H), 1.71 (p, *J* = 7.3 Hz, 4H), 0.97 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.7, 137.8, 134.5, 132.1, 130.8, 129.2, 126.8, 78.6, 26.3, 9.6. *Anal. Calcd. for* $C_{12}H_{14}Cl_2O_2$: C, 55.19; H, 5.40. Found: C, 55.21; H, 5.42.



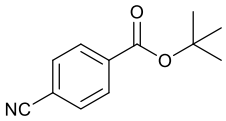
Prop-2-yn-1-yl 3-chlorobenzoate (5f): Colorless oil; (0.156 g, 80 % yield); R_f = 0.486 (hexane/ethyl acetate 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.54 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 4.92 (d, *J* = 2.5 Hz, 2H), 2.54 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.6, 134.6, 133.3, 131.1, 129.8, 129.7, 127.9, 75.3, 52.8. *Anal. Calcd. for* $C_{10}H_7ClO_2$: C, 61.72; H, 3.63. Found: C, 61.75; H, 3.66.



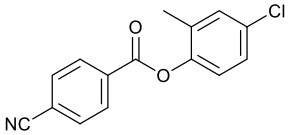
Ethyl 4-chlorobenzoate (5g):[3] Colorless oil; (0.131 g, 71 % yield); R_f = 0.49 (hexane/ethyl acetate 4.8/0.2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.6, 139.1, 130.8, 128.9, 128.6, 61.1, 14.2.



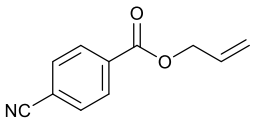
Benzyl 4-(trifluoromethyl)benzoate (5h):[4] Yellow oil; (0.224 g, 80 % yield); R_f = 0.303 (hexane/ethyl acetate 4.8/0.2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.36 (m, 3H), 5.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 135.6, 134.5 (d, J_{C-F} = 32.4 Hz), 133.3 (d, J_{C-F} = 0.9 Hz), 130.1, 128.7, 128.5, 128.3, 125.4 (q, J_{C-F}= 3.7 Hz), 123.6 (d, J_{C-F} = 271.6 Hz), 67.2.



***Tert*-butyl 4-cyanobenzoate (5i)**: White solid; (0.122 g, 60 % yield); R_f = 0.39 (hexane/ethyl acetate 4.5/0.5); m.p.= 77-78°C.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 1.60 (s, 9H).[6] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.0, 135.8, 132.0, 129.9, 118.1, 115.8, 82.4, 28.1.[6]

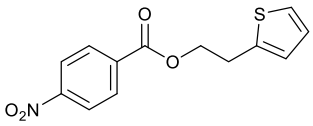


4-chloro-2-methylphenyl 4-cyanobenzoate (5j): White solid; (0.256 g, 94 % yield); m.p.= 116-118°C; R_f = 0.424 (hexane/ethyl acetate 4.2/0.8). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 7.03 (dd, *J* = 8.7, 2.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.5, 148.8, 137.7, 133.1, 132.4, 131.9, 130.6, 129.9, 123.8, 120.1, 117.7, 117.2, 20.2. *Anal. Calcd. for* $C_{15}H_{10}ClNO_2$: C, 66.31; H, 3.71; N, 5.16. Found: C, 66.33; H, 3.75; N, 5.20.

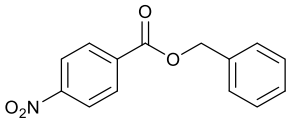


Allyl 4-cyanobenzoate (5k):[7] Yellow oil; (0.161 g, 86 % yield); R_f = 0.27 (hexane/ethyl acetate 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 6.03 (ddt, *J* = 16.4, 11.0, 5.8 Hz, 1H), 5.41 (d, *J* = 17.1 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 4.85 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz,

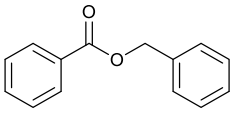
$CDCl_3$) δ: 164.5, 133.9, 132.2, 131.5, 130.1, 119.0, 117.9, 116.4, 66.3.



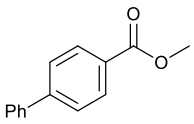
2-(thiophen-2-yl)ethyl 4-nitrobenzoate (5l): Colorless oil; (0.130 g, 47 % yield); R_f = 0.47 (hexane/ethyl acetate 4.2/0.8). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 5.2 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.92 (d, *J* = 3.4 Hz, 1H), 4.60 (t, *J* = 6.5 Hz, 2H), 3.33 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.5, 150.6, 139.5, 135.5, 130.8, 127.0, 125.7, 124.3, 123.6, 66.0, 29.3. *Anal. Calcd. for* $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05. Found: C, 56.33; H, 3.96; N, 5.09.



Benzyl 4-nitrobenzoate (5m): Yellow solid; (0.211 g, 82 % yield); R_f = 0.516 (hexane/ethyl acetate 4.2/0.8); m.p.= 81-83°C .[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 – 8.22 (m, 4H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.36 (m, 3H), 5.41 (s, 2H).[9] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4, 150.5, 135.4, 135.2, 130.7, 128.6, 128.5, 128.3, 123.4, 67.5.[9]

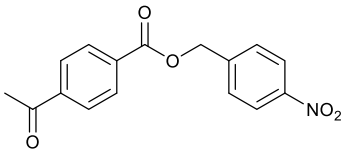


Benzyl benzoate (5n):[10] Colorless oil; (0.159 g, 75 % yield); R_f = 0.448(hexane/ethyl acetate 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.31 (m, 7H), 5.36 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.5, 136.1, 133.1, 130.2, 129.8, 128.6, 128.4, 128.3, 128.2, 66.7.

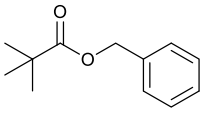


Methyl [1,1'-biphenyl]-4-carboxylate (5o): White solid; (0.170 g, 80 % yield); m.p= 117 °C;[11] R_f = 0.303

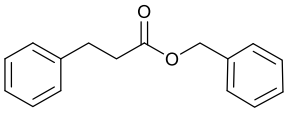
(hexane/ethyl acetate 4.8/0.2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.3 Hz, 2H), 7.65 (dd, *J* = 14.7, 7.9 Hz, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 3.95 (s, 3H).[12] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 145.5, 139.9, 130.0, 128.9, 128.8, 128.1, 127.2, 126.9, 52.0.[12]



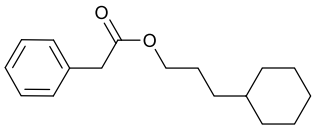
4-Nitrobenzyl 4-acetylbenzoate (5p):[13] White solid; (0.254 g, 85 % yield); m.p= 168-169 °C; R_f = 0.227 (hexane/ethyl acetate 3.5:1.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (d, *J* = 8.0 Hz, 2H), 8.17 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 5.49 (s, 2H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.3, 165.2, 147.8, 142.8, 140.6, 133.2, 130.0, 128.5, 128.3, 123.9, 65.6, 26.9.



Benzyl pivalate (5q):[14] Yellow oil; (0.177 g, 92 % yield); R_f = 0.5 (hexane/ethyl acetate 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 – 7.31 (m, 5H), 5.11 (s, 2H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.3, 136.4, 128.4, 127.9, 127.6, 65.9, 38.8, 27.2.



Benzyl 3-phenylpropanoate (5r):[15] Colorless oil; (0.194 g, 81 % yield); R_f = 0.5 (hexane/ethyl acetate 4.3/0.7). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 – 7.24 (m, 10H), 5.18 (s, 2H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.5, 140.3, 135.8, 128.4, 128.4, 128.2, 128.2, 128.1, 126.1, 66.1, 35.7, 30.8.

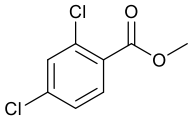


3-Cyclohexylpropyl 2-phenylacetate (5s):[13] Colorless oil; (0.221 g, 85 % yield); R_f = 0.548 (hexane/ethyl acetate 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 – 7.22 (m, 5H), 4.05 (t, *J* = 6.7 Hz, 2H), 3.59 (s, 2H), 1.68 – 1.57 (m, 7H), 1.24 – 1.10 (m, 6H), 0.88 - 0.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.6, 134.3, 129.3, 128.5, 127.0, 65.3, 41.5, 37.3, 33.5, 33.3, 26.7, 26.4, 26.0.

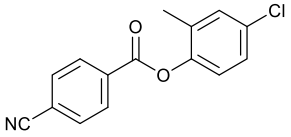
General Procedure for esters 5a, 5j, 5n, 5o and 5q under blue LED irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred and irradiated using a blue LED (455 nm) for 8 h at 25 °C under Ar (the reaction was monitored by TLC until disappearance of aldehyde). Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and an alcohol (1.0 mmol) was dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol) and then DMAP (10% mol) at once. After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the alcohol (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

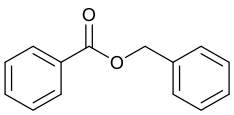
Compound characterizations:



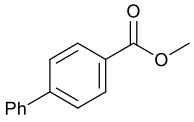
Methyl 2,4-dichlorobenzoate (5a): Yellow oil; (0.154 g, 75 % yield).



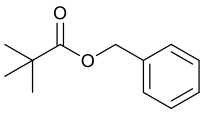
4-chloro-2-methylphenyl 4-cyanobenzoate (5j): White solid; (0.212 g, 78 % yield).



Benzyl benzoate (5n): Colorless oil; (0.148 g, 70 % yield).



Methyl [1,1'-biphenyl]-4-carboxylate (5o): White solid; (0.146 g, 69 % yield).

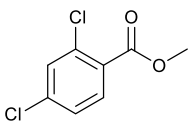


Benzyl pivalate (5q): Yellow oil; (0.157 g, 82 % yield).

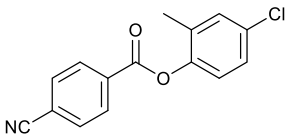
General Procedure for esters 5a, 5j, 5n, 5o and 5q under sun light irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under sun light irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of aldehyde). Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and an alcohol (1.0 mmol) was dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol) and then DMAP (10% mol) at once. After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the alcohol (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

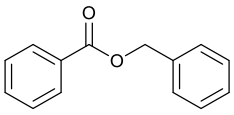
Compound characterizations:



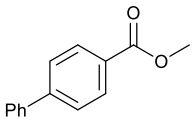
Methyl 2,4-dichlorobenzoate (5a): Yellow oil; (0.199 g, 97 % yield).



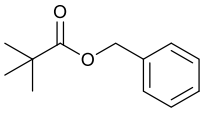
4-chloro-2-methylphenyl 4-cyanobenzoate (5j): White solid; (0.250 g, 92 % yield).



Benzyl benzoate (5n): Colorless oil; (0.157 g, 74 % yield).



Methyl [1,1'-biphenyl]-4-carboxylate (5o): White solid; (0.167 g, 79 % yield).

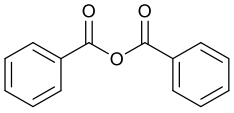


Benzyl pivalate (5q): Yellow oil; (0.175 g, 91 % yield).

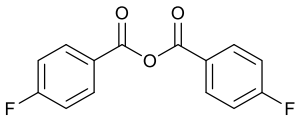
General Procedure for anhydrides 7a-g under solar simulator irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under solar simulator irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of 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 dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol). After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

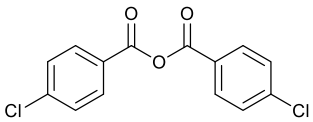
Compound characterizations:



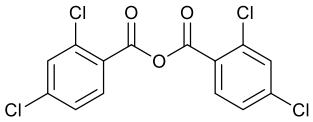
Benzoic anhydride (7a): Colorless oil; (0.181 g, 80 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, J = 7.6 Hz, 4H), 7.67 (t, J = 7.4 Hz, 2H), 7.52 (t, J = 7.5 Hz, 4H).[16] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.2, 134.4, 130.4, 128.8, 128.7.[16]



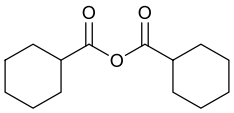
4-fluorobenzoic anhydride (7b):[17] White solid; (0.256 g, 98 % yield); mp 113-115 °C; R_f = 0.62 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 – 8.16 (m, 4H), 7.23 - 7.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7 (d, J_{C-F} = 255 Hz), 161.2, 133.3 (d, J_{C-F} = 9 Hz), 125.0 (d, J_{C-F} = 3 Hz), 116.5 (d, J_{C-F} = 11 Hz).



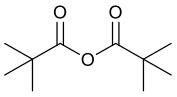
4-chlorobenzoic anhydride (7c):[16] White solid; (0.224 g, 76 % yield); mp 180-182 °C; R_f = 0.56 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.2 Hz, 4H), 7.51 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 141.4, 131.9, 129.4, 127.1.



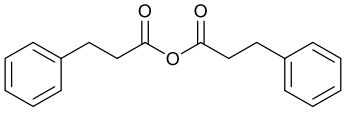
2,4-dichlorobenzoic anhydride (7d):[18] White solid; (0.186 g, 51 % yield); mp 119-120 °C R_f = 0.4 (hexane/ethyl acetate 4.5/0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 2.0 Hz, 2H), 7.38 (dd, *J* = 8.5, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 140.4, 136.2, 133.6, 131.6, 127.5, 126.0.



Cyclohexanecarboxylic anhydride (7e):[19] Colorless oil; (0.216 g, 91 % 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.



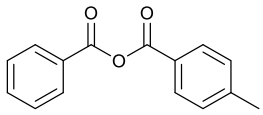
Pivalic anhydride (7f): Yellow oil; (0.178 g, 96 % yield); R_f = 0.58 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (s, 18H).[20] ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 39.9, 26.3.[21]



3-phenylpropanoic anhydride (7g):[22] Colorless oil; (0.223 g, 79 % 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.

General Procedure for anhydrides 7h under solar simulator irradiation:

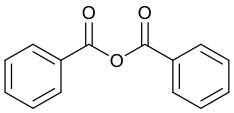


In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of benzaldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under solar simulator irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of aldehyde). Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and 4-methylbenzoic acid (1.0 mmol) was dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol). After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid (monitored by TLC, the reaction is usually complete in about 1 h). Then 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 benzoic 4-methylbenzoic anhydride (7h): Colorless oil; (0.202 g, 75 % Benzoic 4-methylbenzoic anhydride and 25 % of benzoic anhydride); R_f = 0.39 (Hexane/EtOAc, 4.5:0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 – 8.13 (m, 2H), 8.04 (d, J = 8.3 Hz, 2H), 7.70 – 7.62 (m, 1H), 7.52 (m, 2H), 7.31 (d, J = 7.7 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4, 162.3, 162.2, 145.6, 134.5, 134.4, 130.5, 130.4, 130.4, 129.5, 128.8, 128.8, 128.7, 128.2, 125.9, 21.7. HRMS (HESI-FTORBITRAP) calcd for $C_{15}H_{12}NaO_3$ $[M+Na]^+$: 263,0679, found 263,0679.

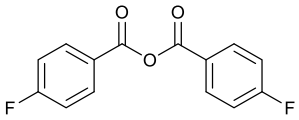
General Procedure for anhydrides 7a, 7b and 7e under blue LED irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under blue LED irradiation for 8 hours under Ar (the reaction was monitored by TLC until disappearance of 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 dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol). After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

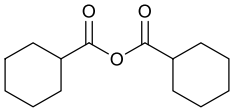
Compound characterizations:



Benzoic anhydride (7a): Colorless oil; (0.158 g, 70 % yield).



4-fluorobenzoic anhydride (7b): White solid; (0.210 g, 80 % yield).

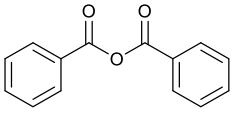


Cyclohexanecarboxylic anhydride (7e): Colorless oil; (0.190 g, 80 % yield).

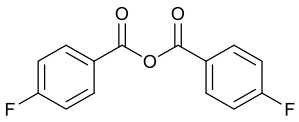
General Procedure for anhydrides 7a, 7b and 7e under sun light irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under sun light irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of 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 dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol). After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the carboxylic acid (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

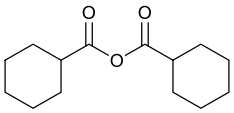
Compound characterizations:



Benzoic anhydride (7a): Colorless oil; (0.176 g, 78 % yield).



4-fluorobenzoic anhydride (7b): White solid; (0.252 g, 96 % yield).

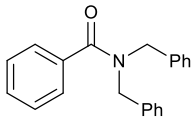


Cyclohexanecarboxylic anhydride (7e): Colorless oil; (0.219 g, 92 % yield).

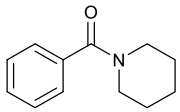
General Procedure for amides 9a-h under solar simulator irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under solar simulator irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of aldehyde). Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and an amine (1.0 mmol) was dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol). After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the amine (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

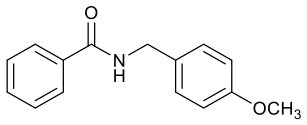
Compound characterizations:



***N,N*-dibenzylbenzamide (9a)**:[23] White solid; (0.235 g, 78 % yield); mp 112-113 °C R_f = 0.353 (hexane/ethyl acetate 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 – 7.48 (m, 2H), 7.41 – 7.28 (m, 11H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.71 (s, 2H), 4.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 136.9, 136.4, 136.1, 129.6, 128.8, 128.7, 128.5, 128.4, 127.6, 127.5, 127.0, 126.7, 51.5, 46.8.

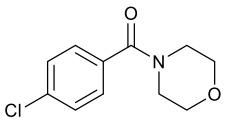


Phenyl(piperidin-1-yl)methanone (9b):[24] Yellow oil; (0.147 g, 81 % yield); R_f = 0.258 (hexane/ethyl acetate 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (s, 5H), 3.71 (br, s, 2H), 3.34 (br, s, 2H), 1.68 (br, s, 4H), 1.52 (br, s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 136.5, 129.3, 128.4, 126.8, 48.8, 43.1, 26.6, 25.6, 24.6.

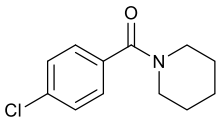


N-(4-methoxybenzyl)benzamide (9c): White solid; (0.188 g, 78 % yield); mp 83-84 °C [25] R_f = 0.353

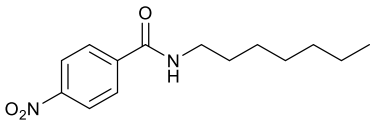
(hexane/ethyl acetate 3/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 7.9 Hz, 2H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.53 (s, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 3.78 (s, 3H).[26] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.3, 159.1, 134.5, 131.4, 130.3, 129.3, 128.5, 126.9, 114.1, 55.3, 43.6.[26]



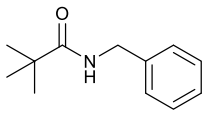
(4-chlorophenyl)(morpholino)methanone (9d):[27] White solid; (0.187 g, 83 % yield); mp 73-75 °C R_f = 0.258 (hexane/ethyl acetate 2/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 – 7.30 (m, 4H), 3.65 - 3.40 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.2, 135.8, 133.5, 128.7, 128.5, 66.6, 48.0, 42.6.



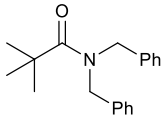
(4-chlorophenyl)(piperidin-1-yl)methanone (9e):[28] White solid; (0.159 g, 71 % yield); mp 70-71 °C R_f = 0.258 (hexane/ethyl acetate 2/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 – 7.30 (m, 4H), 3.68 (s, 2H), 3.33 (s, 2H), 1.71 – 1.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 135.5, 134.8, 128.5, 128.2, 48.6, 43.1, 26.4, 25.8, 24.4.



***N*-heptyl-4-nitrobenzamide (9f)**:[29] White solid; (0.180 g, 68 % yield); mp 77-79 °C R_f = 0.234 (hexane/ethyl acetate 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 8.9 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 6.16 (br, 1H), 3.50 – 3.46 (m, 2H), 1.64-1.58 (m, 2H), 1.58 - 1.36 (m, 2H), 1.33-1.25 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5, 149.6, 140.4, 128.0, 123.8, 40.5, 31.7, 29.5, 28.9, 26.9, 22.6, 14.0.



***N*-benzylpivalamide (9g)**:[30] White solid; (0.155 g, 81 % yield); mp 81-82 °C R_f = 0.21 (hexane/ethyl acetate 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 – 7.20 (m, 5H), 6.03 (s, 1H), 4.41 (d, *J* = 5.6 Hz, 2H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.2, 138.6, 128.6, 127.5, 127.3, 43.5, 38.6, 27.6.

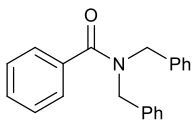


***N*,*N*-dibenzylpivalamide (9h)**:[31] Colorless oil; (0.219 g, 78 % yield); R_f = 0.323 (hexane/ethyl acetate 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 – 7.27 (m, 6H), 7.16 (d, *J* = 7.4 Hz, 4H), 4.62 (s, 4H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.0, 137.2, 128.6, 127.2, 49.6, 39.2, 28.7.

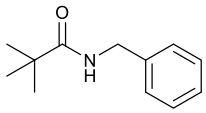
General Procedure for amides 9a and 9g under blue LED irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under blue LED irradiation for 8 hours under Ar (the reaction was monitored by TLC until disappearance of aldehyde). Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and an amine (1.0 mmol) was dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol). After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the amine (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

Compound characterizations:



***N*,*N*-dibenzylbenzamide (9a)**: White solid; (0.208 g, 69 % yield).

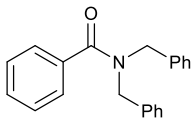


***N*-benzylpivalamide (9g)**: White solid; (0.115 g, 60 % yield).

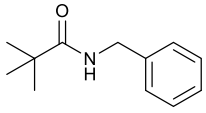
General Procedure for amides 9a and 9g under sun light irradiation:

In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of an aldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under sun light irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of aldehyde). Then the reaction mixture was cooled to 0 °C, stirred under an inert atmosphere of dry argon and an amine (1.0 mmol) was dropwise added via syringe followed by dropwise addition of NEt_3 (2.0 mmol). After completion of the addition, the reaction mixture left to stir at room temperature until disappearance of the amine (monitored by TLC, the reaction is usually complete in about 1 h). Then the solvent was removed under vacuum, and the residue purified by flash chromatography.

Compound characterizations:

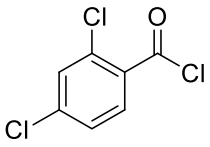


***N*,*N*-dibenzylbenzamide (9a)**: White solid; (0.232 g, 77 % yield).



***N*-benzylpivalamide (9g)**: White solid; (0.153 g, 80 % yield).

Characterization of 2,4-dichlorobenzoyl chloride 3:

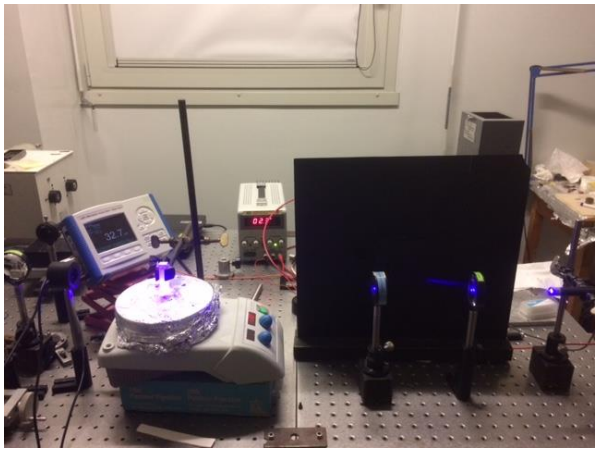


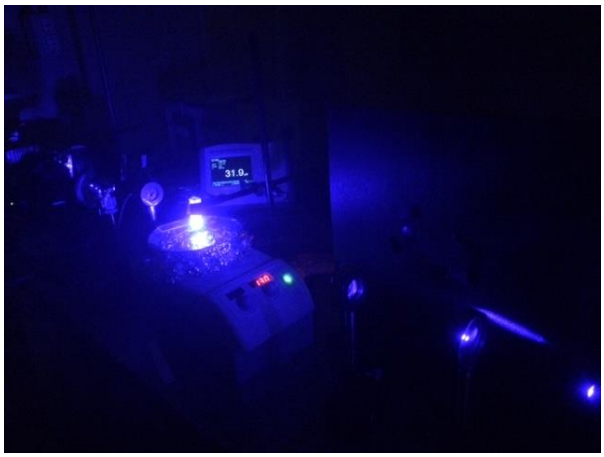
In a round bottom flask of 10 mL, equipped with a condenser, TCCA (0.37 mmol) was added to a solution of 2,4-dichlorobenzaldehyde (1.1 mmol) in 1 mL dichloromethane under Ar atmosphere and at room temperature. The resulting suspension was stirred under solar simulator irradiation for 4 hours under Ar (the reaction was monitored by TLC until disappearance of 2,4-dichlorobenzaldehyde). The mixture of reaction was filtered on Celite, then the solvent was removed under vacuum and the residue was distilled. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.0 Hz, 1H).[32] ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.1, 140.7, 135.0, 134.6, 131.4, 131.0, 127.4.[32]

Determination of quantum yield:

A quartz cuvette was charged with 1 mL dichloromethane, TCCA (0.37 mmol) and benzaldehyde (1.1 mmol). The vial was fitted with a Teflon cap. The reaction mixture was stirred and simultaneously irradiated by using a Stabilized laser diode Oxxius-450 (λ= 450 ± 5 nm) at room temperature for 3600s and the photon flux was measured. The laser beam was expanded and then parallelized by using a telescopic arrangement of two convergent lens. The final beam dimension was set in 5.5 ± 0.2 mm in order to cover the whole solution inside a 10x10 mm quartz cuvette. The cuvette with solvent and a stirring bar was placed in the beam (8 mw/cm^2) and the transmitted power focalized with a third convergent lens, was measured by a calibrated power meter (Newport model 1918-C) horizontal to the cuvette. The content of the cuvette was changed to the reaction mixture and the transmitted power was measured after different times. The yield of benzoyl chloride formed was determined by ^{1}H NMR spectroscopy. The quantum yield is calculated using the following equation:[33]

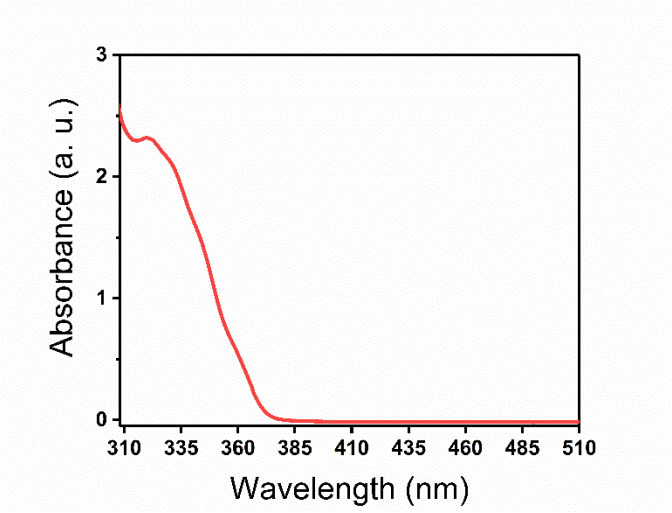
$$\phi = \frac{n_{Product}}{N_{ph}} = \frac{0.209*10^3\ \mu mol}{70\ \mu mol} = 3$$





UV-Vis Spectra:

TCCA (0.37 mmol) in 10 mL dichloromethane and benzaldehyde (1.1 mmol).



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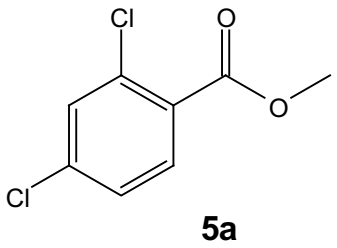
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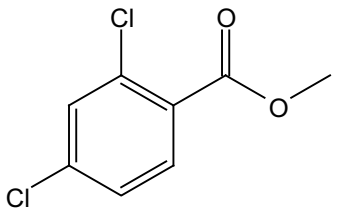
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5a

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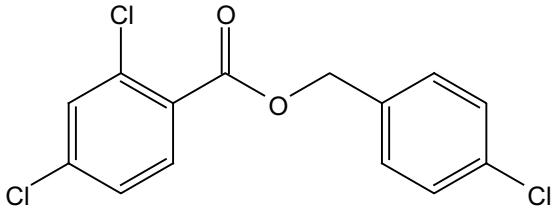
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5b

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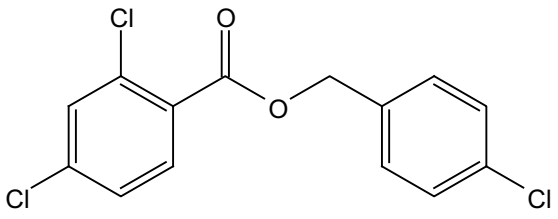
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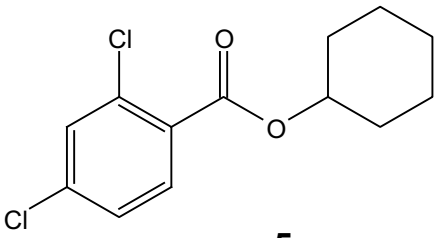
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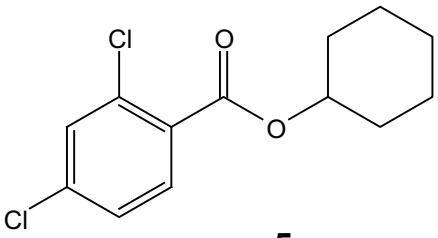
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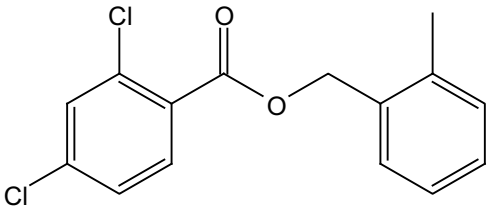
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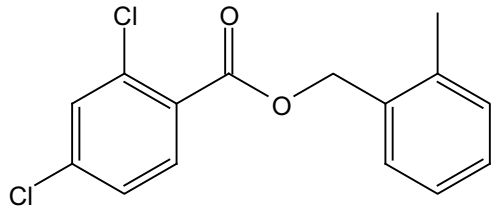
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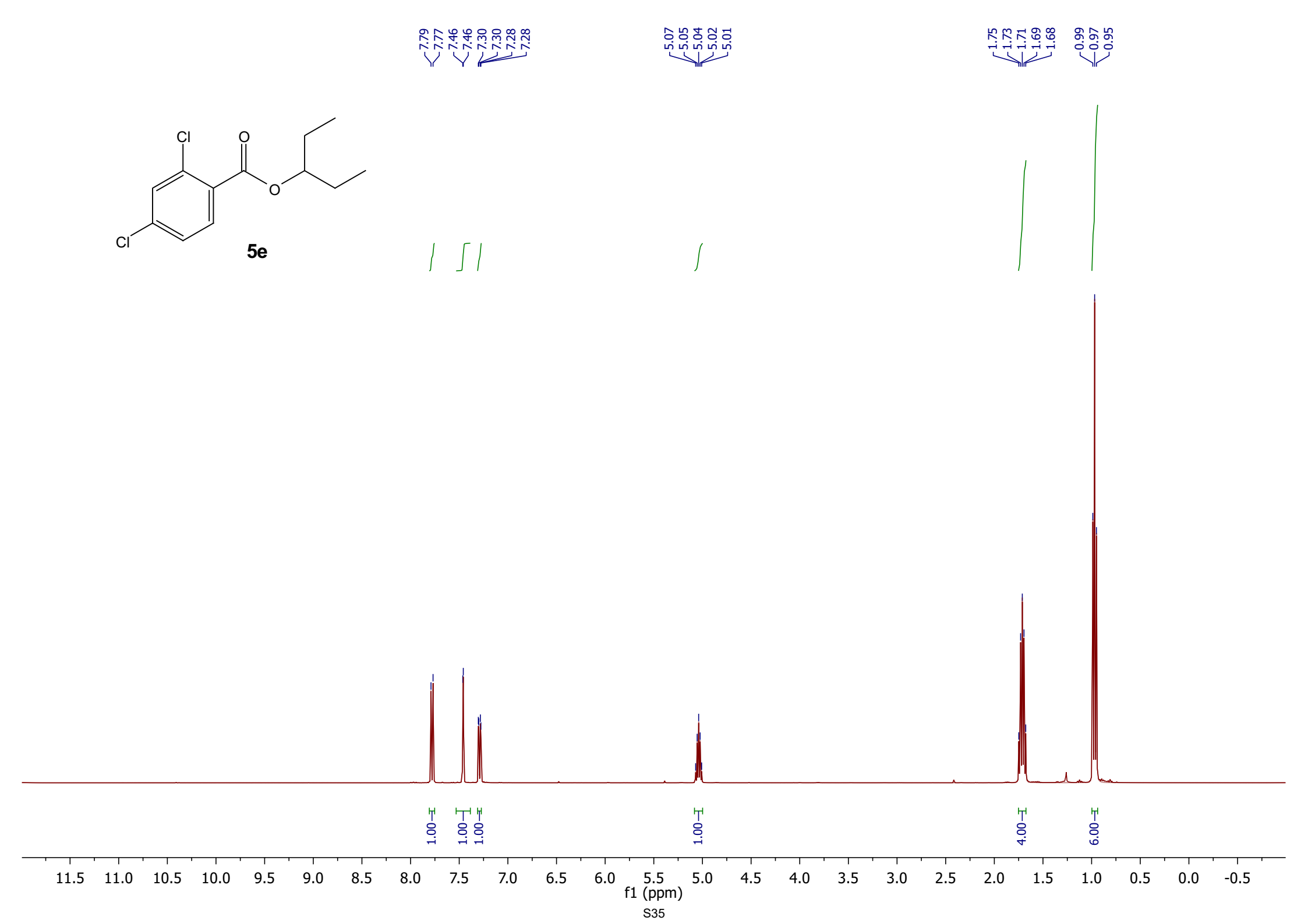
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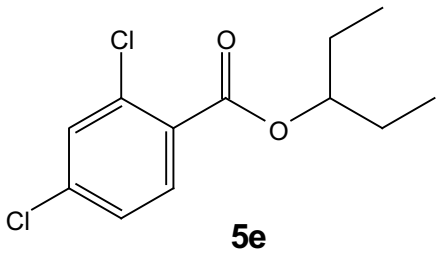
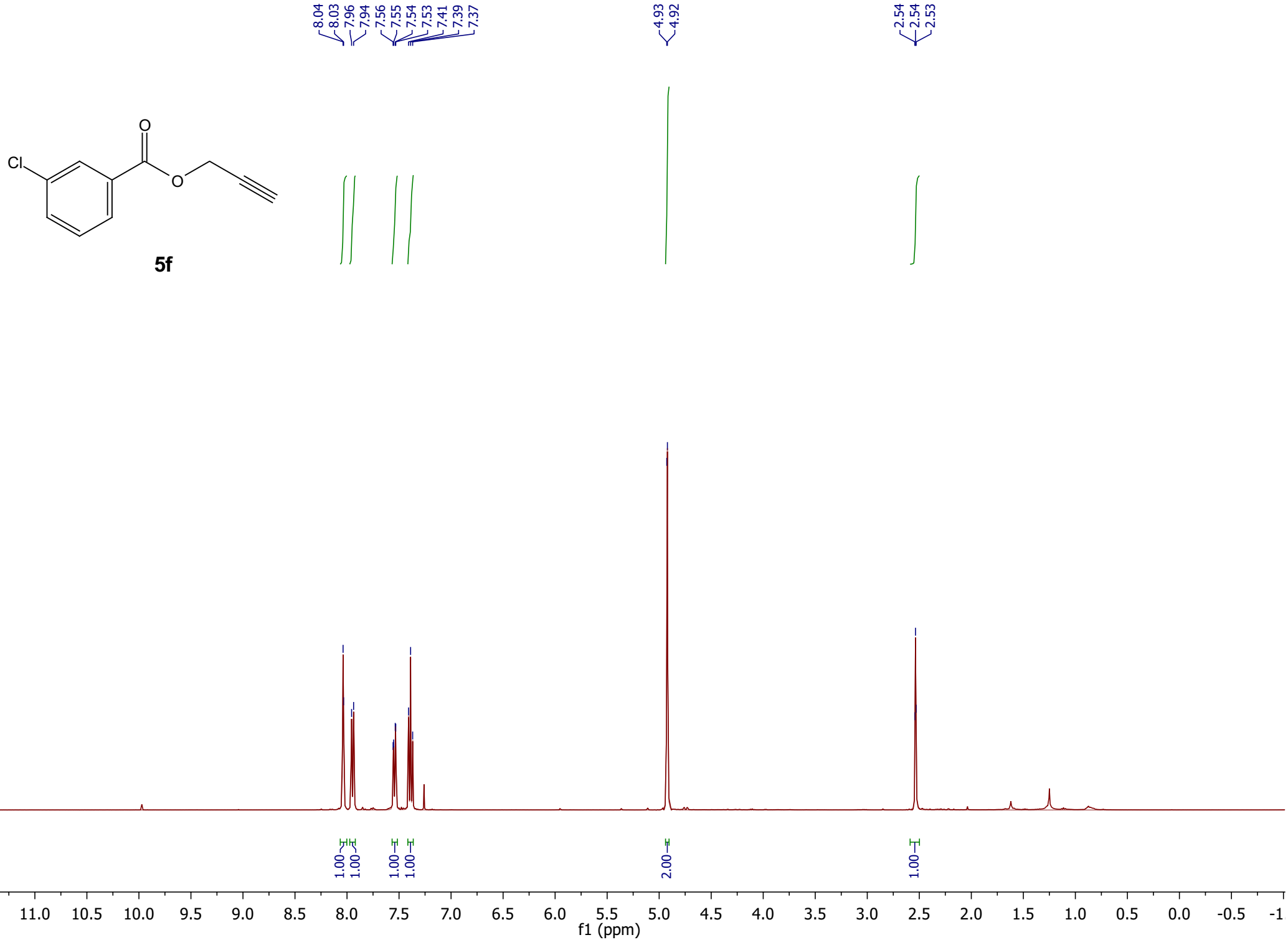
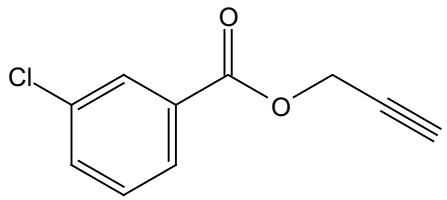
1.73
1.71
1.69
1.68
0.99
0.97
0.95
Cl
O
O
Cl
5e
1.00
1.00
1.00
1.00
4.00
6.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Cl
O
O
Cl

5e

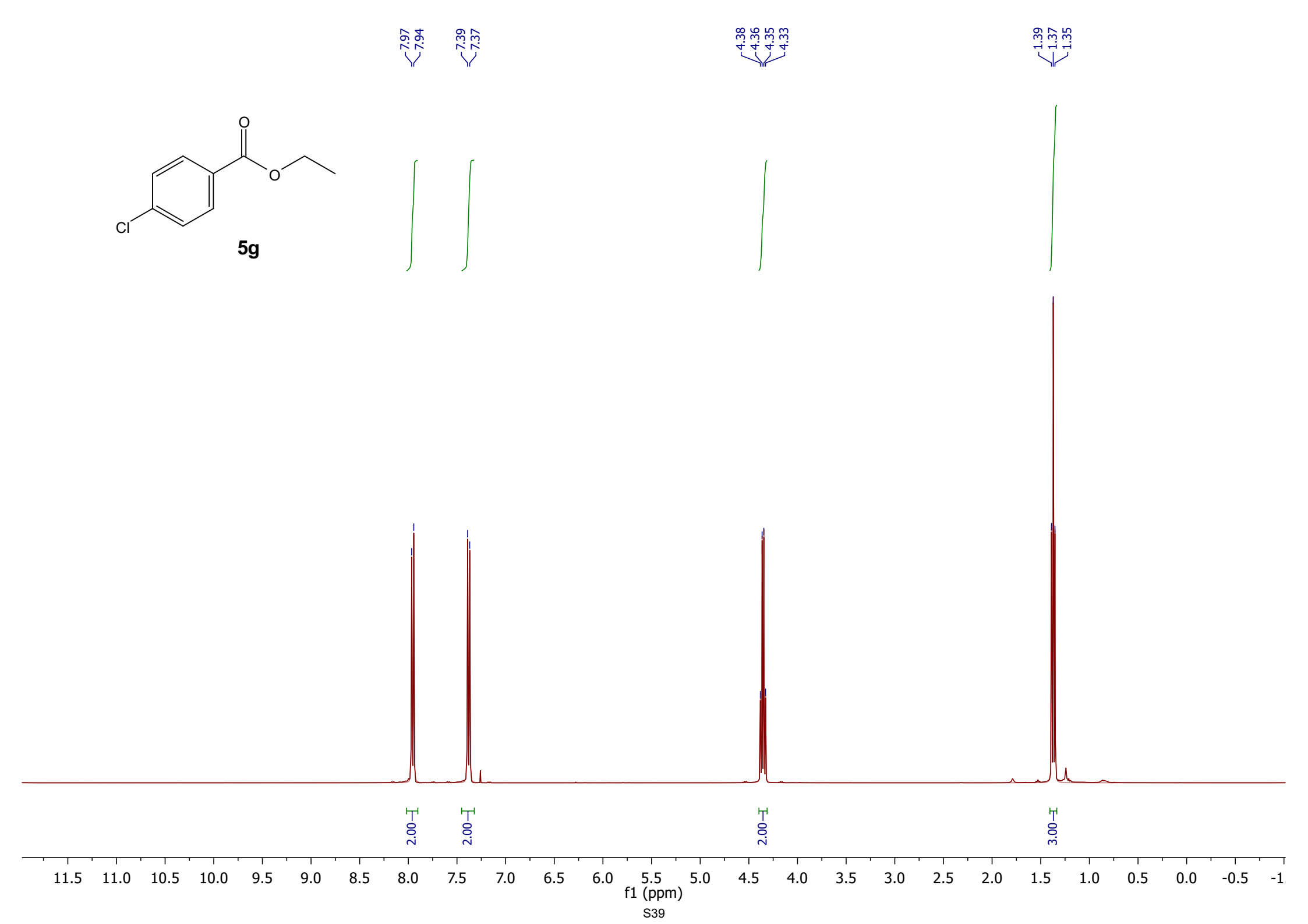
164.69
137.80
134.54
132.13
130.79
129.20
126.84
78.56
26.33
9.59
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

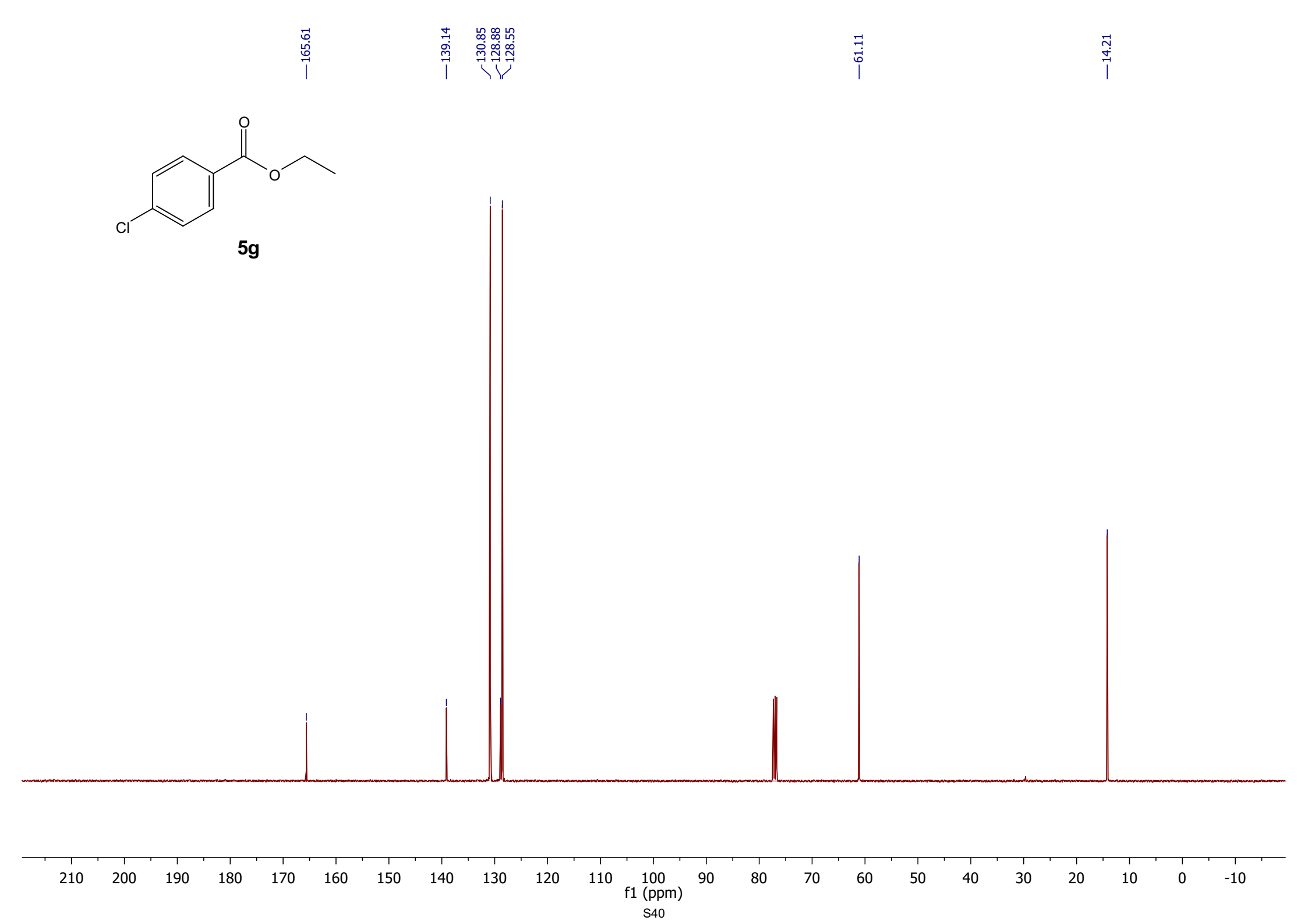

8.04
8.03
7.96
7.94
7.56
7.55
7.54
7.53
7.41
7.39
7.37
4.93
4.92
2.54
2.54
2.53
Cl
O
O
5f
1.00
1.00
1.00
1.00
2.00
1.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

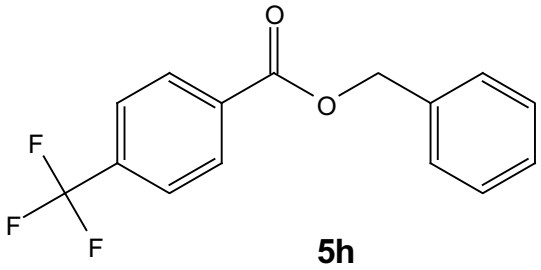

O
Cl
O

5f

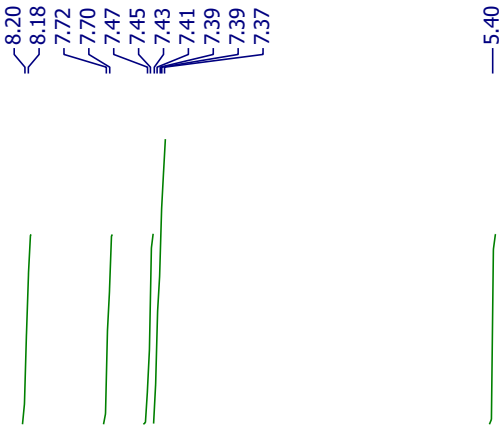
164.55
134.59
133.34
131.09
129.81
129.73
127.89
75.30
52.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

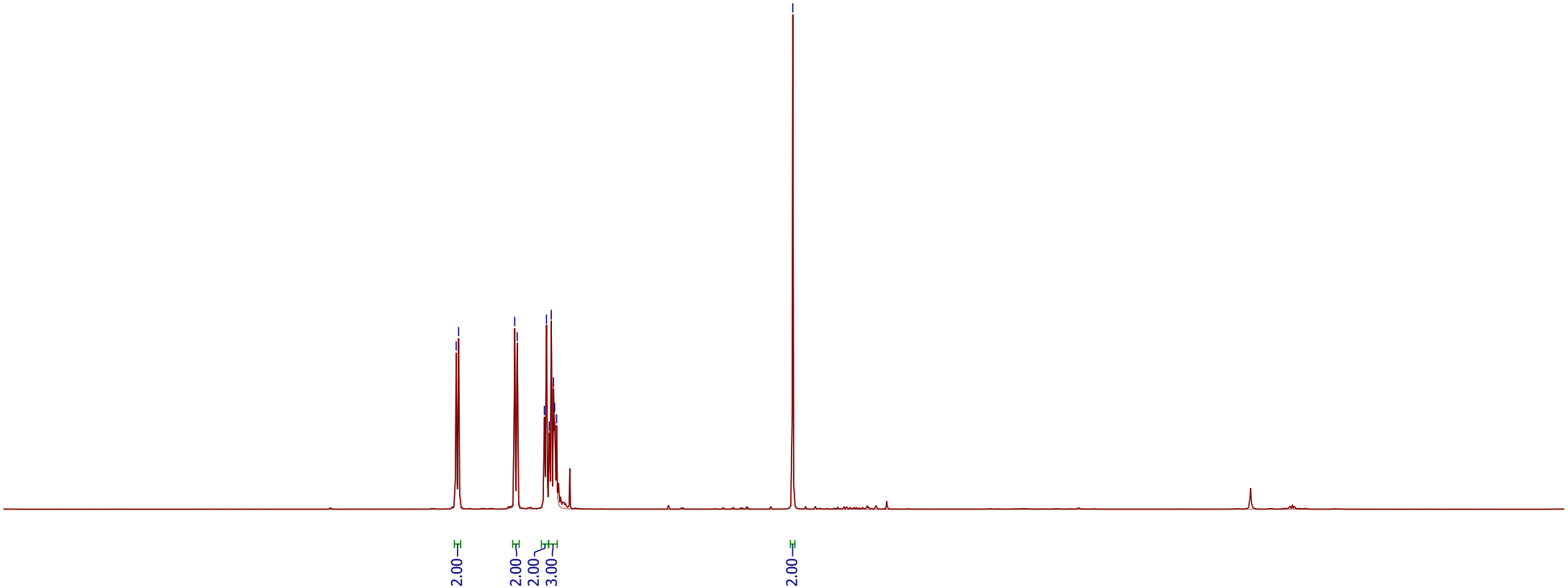

7.97
7.94
7.39
7.37
4.38
4.36
4.35
4.33
1.39
1.37
1.35
O
O
Cl
5g
2.00
2.00
2.00
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

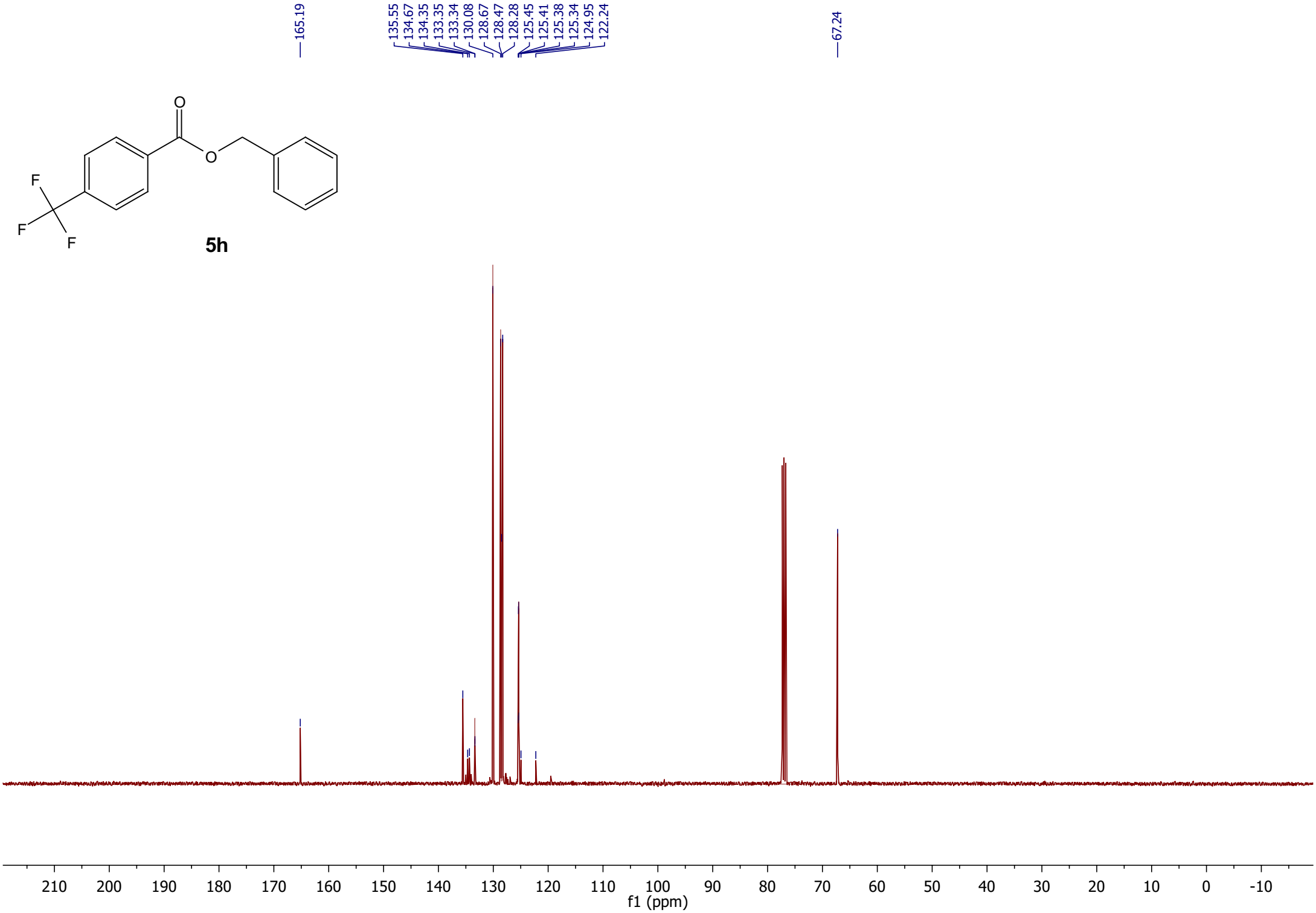

165.61
139.14
130.85
128.88
128.55
61.11
14.21
O
O
Cl
5g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

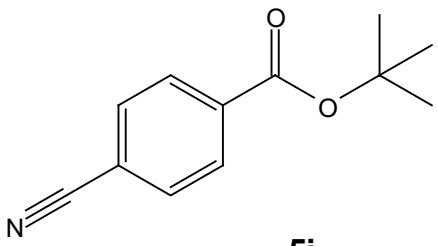

O
O
F
F
F

5h


8.20
8.18
7.72
7.70
7.47
7.45
7.43
7.41
7.39
7.39
7.37
5.40

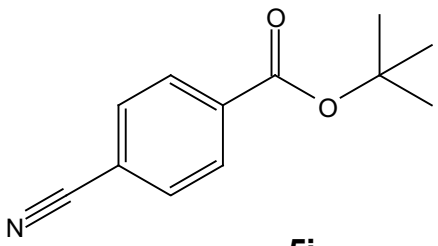

2.00
2.00
2.00
3.00
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


165.19
135.55
134.67
134.35
133.35
133.34
130.08
128.67
128.47
128.28
125.45
125.41
125.38
125.34
124.95
122.24
67.24
O
O
F
F
F
5h
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
N

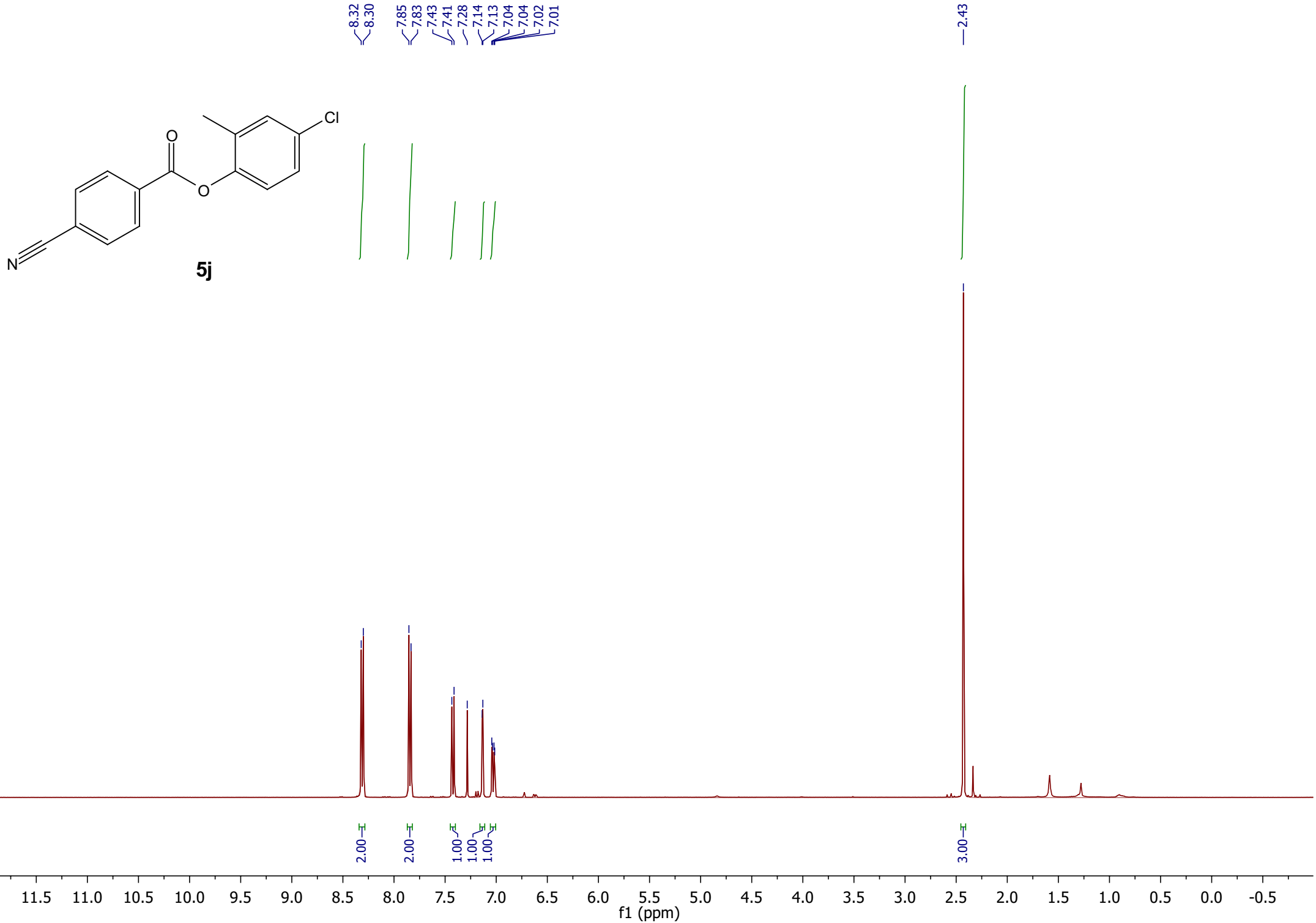
5i

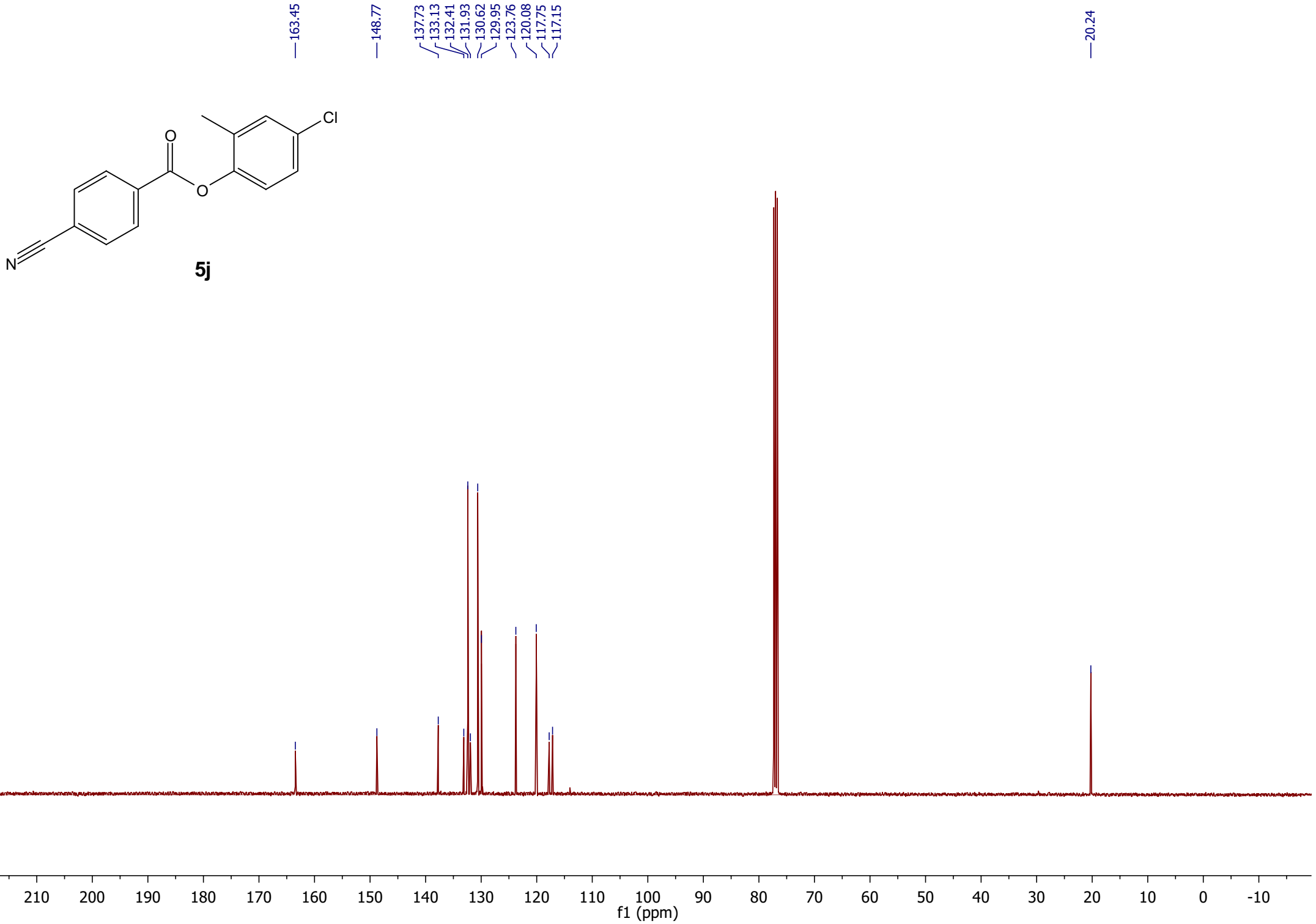
8.08
8.06
7.72
7.70
1.60
2.00
2.00
9.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

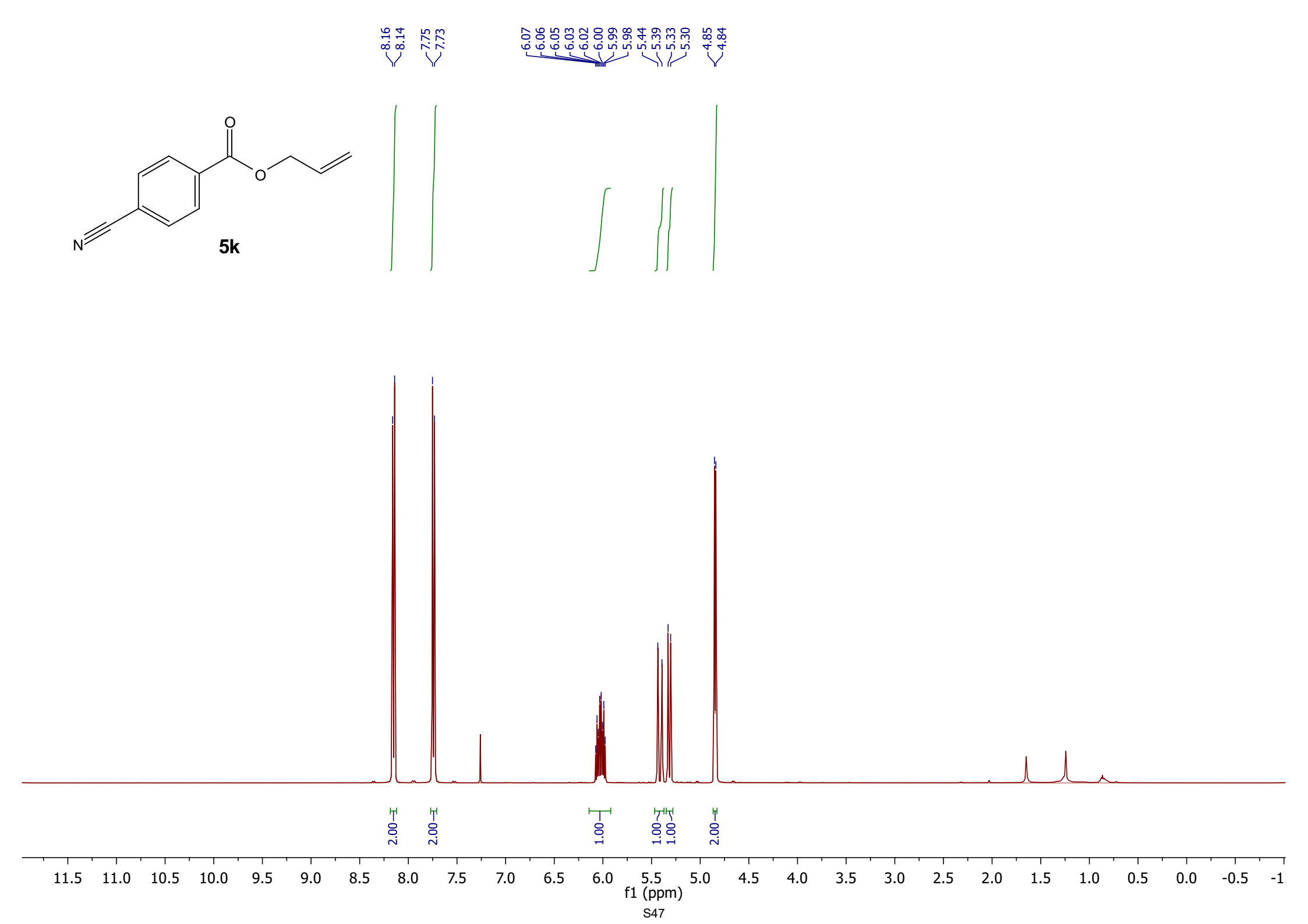

O
O
N

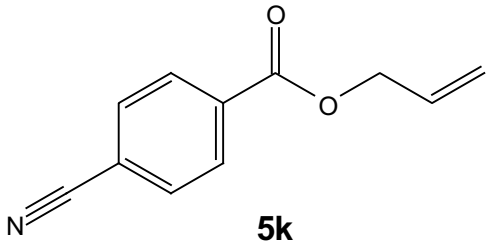
5i

163.96
135.83
132.02
129.91
118.12
115.84
82.36
28.07
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)


8.32
8.30
7.85
7.83
7.43
7.41
7.28
7.14
7.13
7.04
7.04
7.02
7.01
2.43
Cl
O
O
N
5j
2.00
2.00
1.00
1.00
1.00
3.00
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)

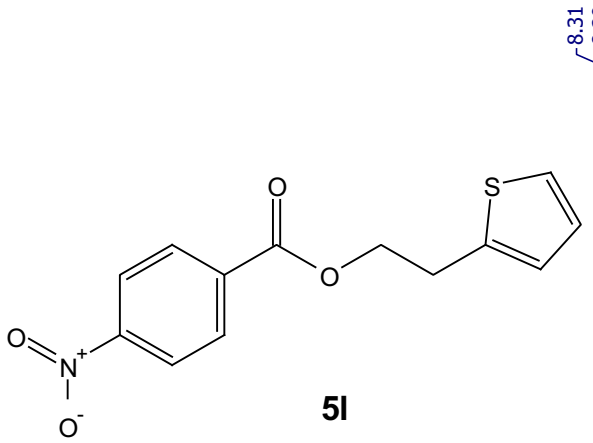

163.45
148.77
137.73
133.13
132.41
131.93
130.62
129.95
123.76
120.08
117.75
117.15
20.24
Cl
O
O
N
5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.16
8.14
7.75
7.73
6.07
6.06
6.05
6.03
6.02
6.00
5.99
5.98
5.44
5.39
5.33
5.30
4.85
4.84
O
O
N
5k
2.00
2.00
1.00
1.00
1.00
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)


O
O
N

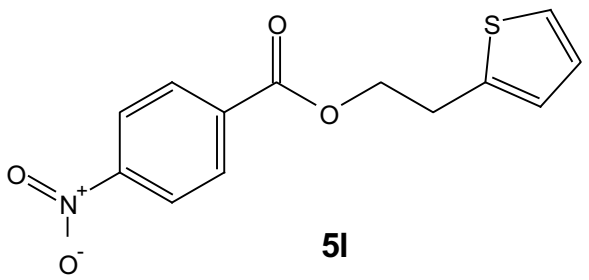
5k

164.53
133.92
132.17
131.53
130.08
118.98
117.89
116.41
66.25
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
S
O
O
N+
O-

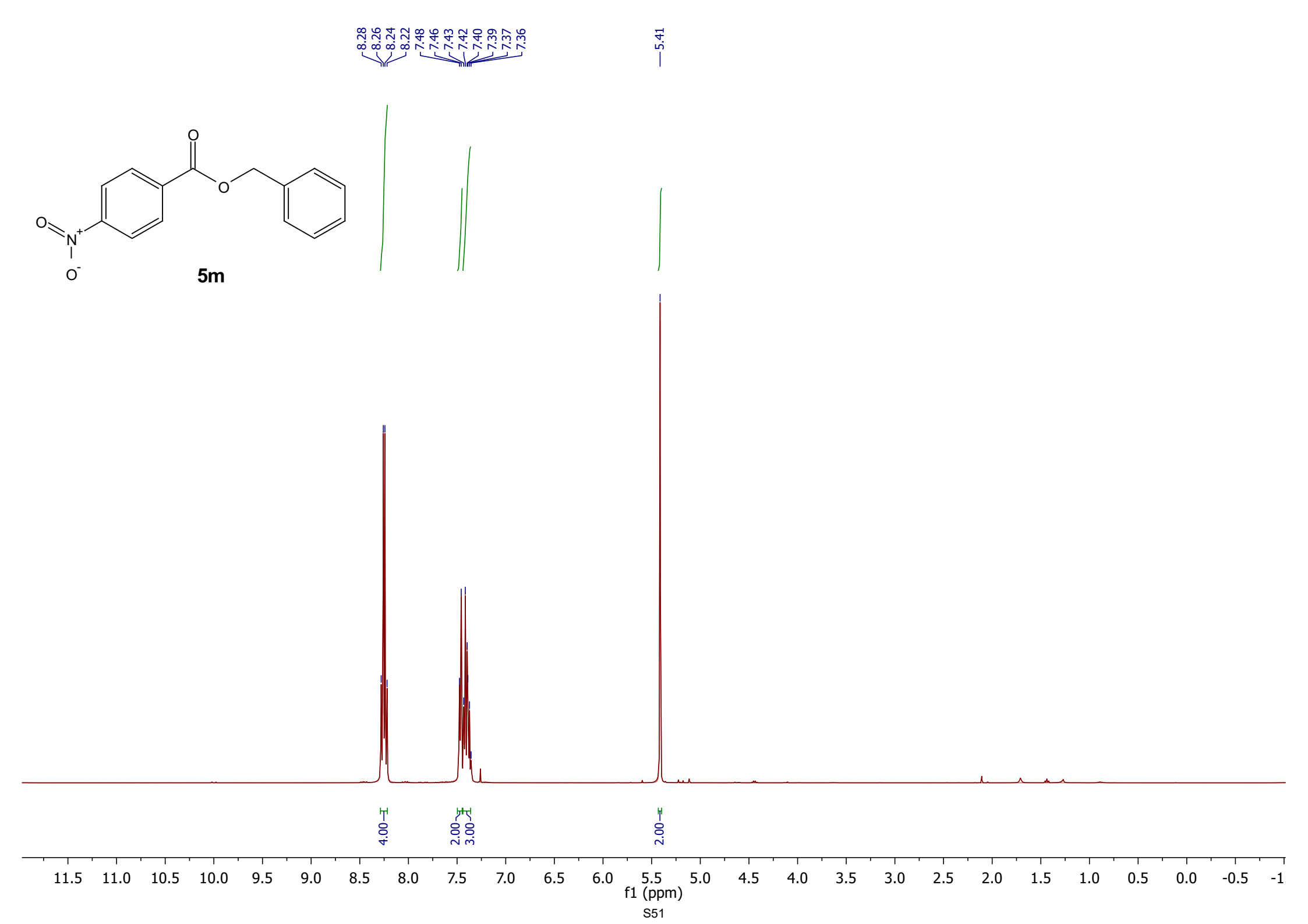
5l

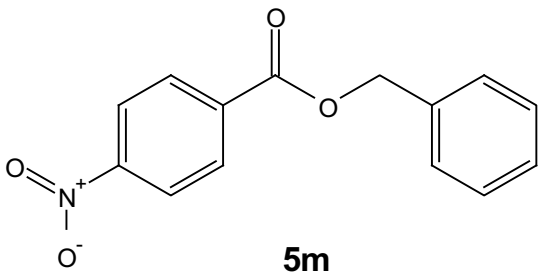
8.31
8.29
8.23
8.21
7.20
7.18
6.98
6.97
6.96
6.92
6.91
4.61
4.60
4.58
3.35
3.33
3.31
2.00
2.00
1.00
1.00
1.00
2.00
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
S
O
O
N+
O-

5l

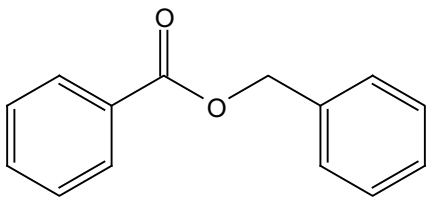
164.50
150.59
139.48
135.47
130.76
126.98
125.73
124.29
123.57
66.02
29.31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.28
8.26
8.24
8.22
7.48
7.46
7.43
7.42
7.40
7.39
7.37
7.36
5.41
O
O
O
N+
O-
5m
4.00
2.00
3.00
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)


O
O
O
N+
O-

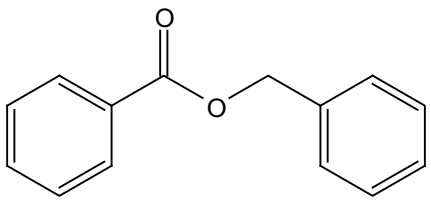
5m

164.40
150.47
135.39
135.18
130.70
128.64
128.53
128.32
123.43
67.53
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)



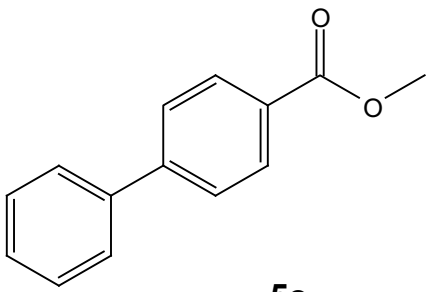
5n

8.08
8.06
7.55
7.53
7.51
7.45
7.43
7.41
7.39
7.37
7.35
7.34
7.32
5.35
2.00
1.00
7.00
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 -1.0
f1 (ppm)



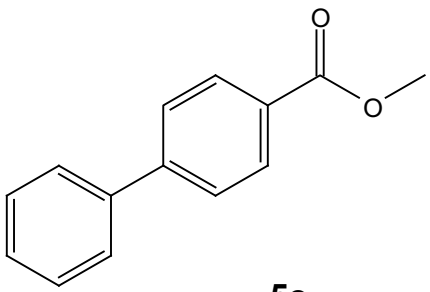
5n

166.34
136.01
132.95
130.08
129.63
128.53
128.30
128.16
128.09
66.60
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

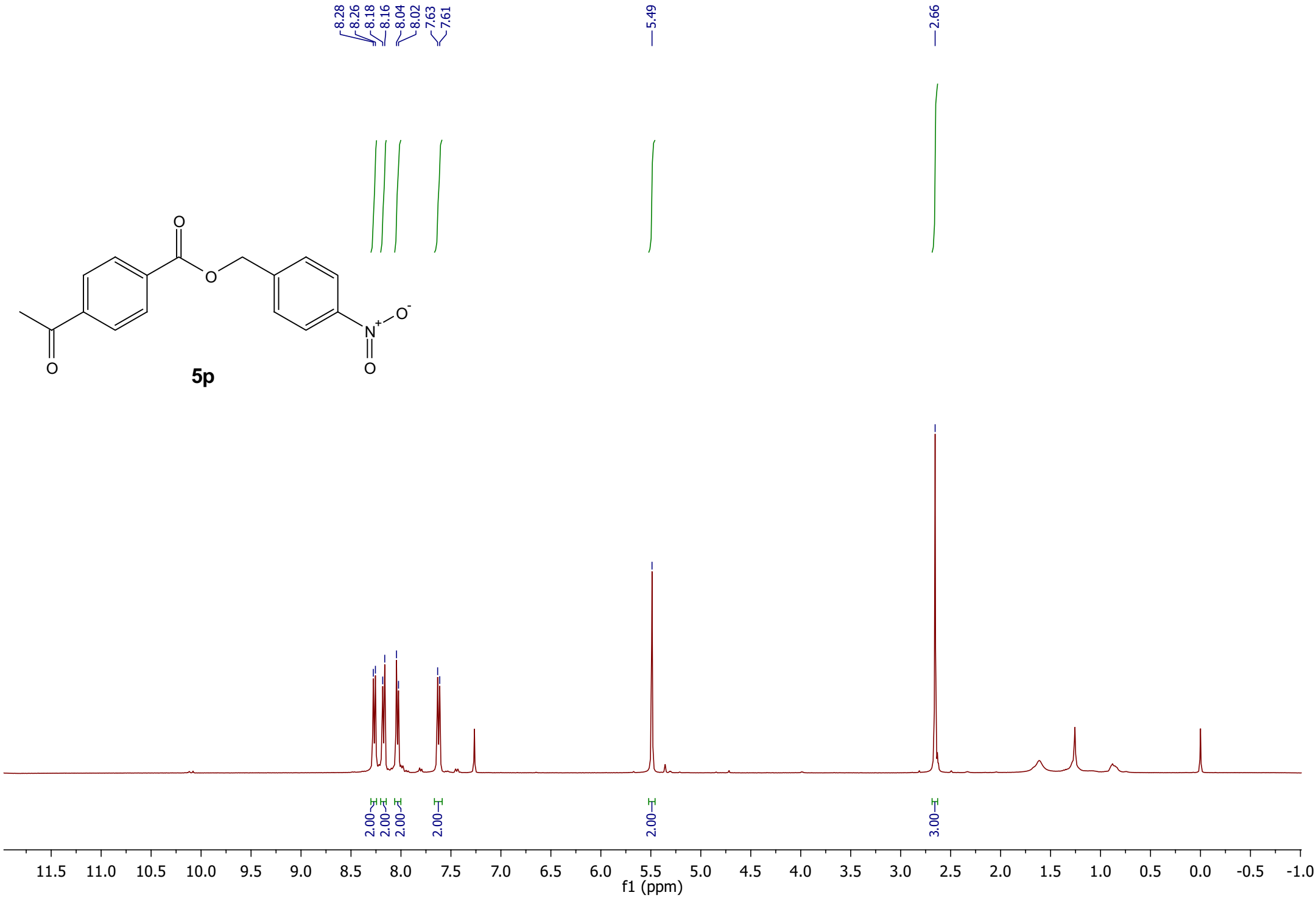
5o

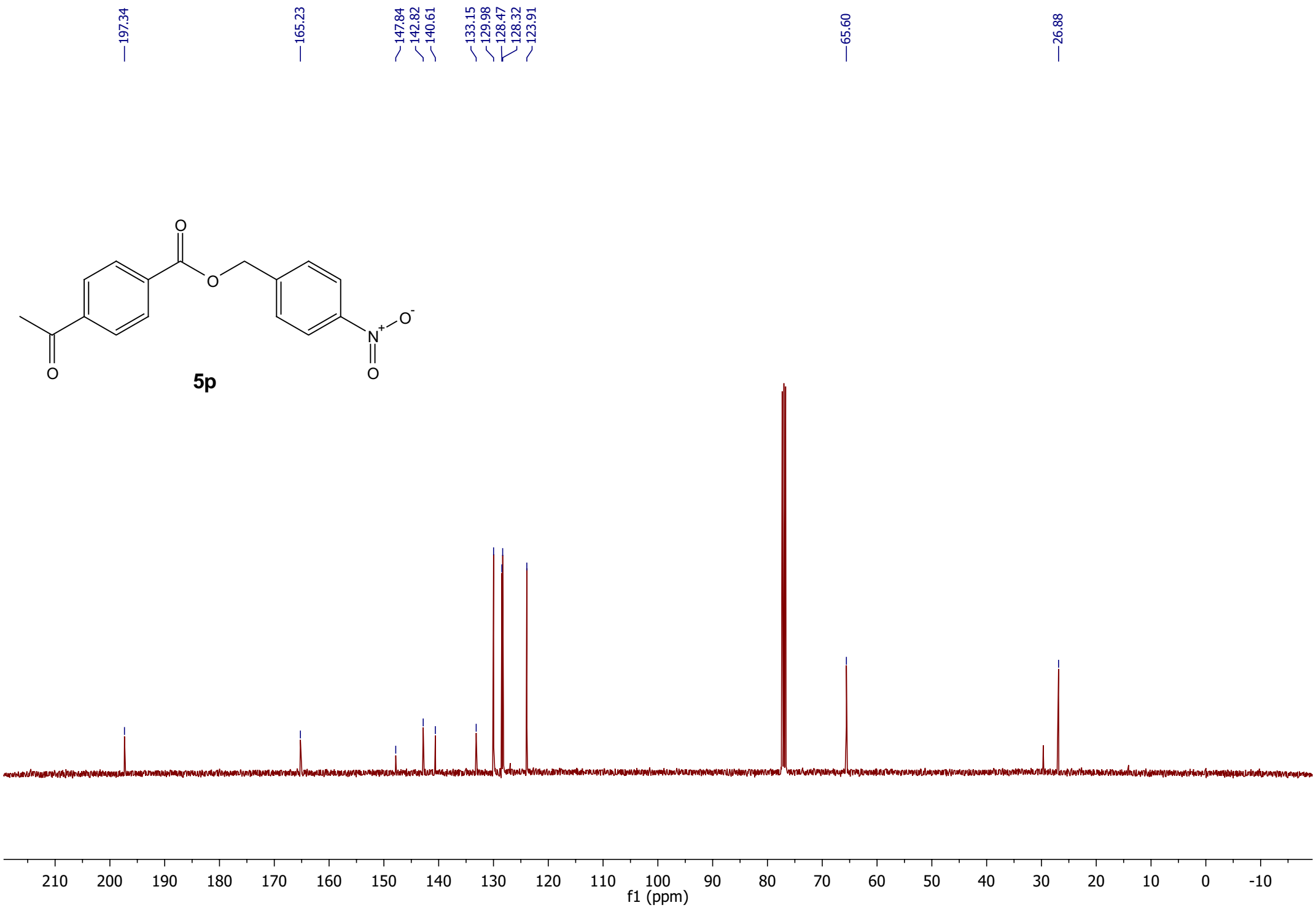
8.13
8.11
7.68
7.66
7.64
7.62
7.49
7.47
7.45
7.42
7.40
7.38
3.95
2.00
4.00
2.00
1.00
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

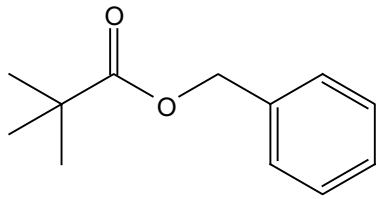

O
O

5o

166.89
145.53
139.90
130.02
128.93
128.84
128.06
127.19
126.95
52.02
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)

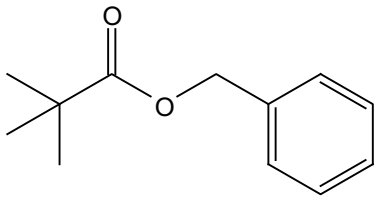

8.28
8.26
8.18
8.16
8.04
8.02
7.63
7.61
5.49
2.66
O
O
O
O
N+
O-
O
5p
2.00
2.00
2.00
2.00
2.00
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


197.34
165.23
147.84
142.82
140.61
133.15
129.98
128.47
128.32
123.91
65.60
26.88
O
O
O
N+
O-
O
5p
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)



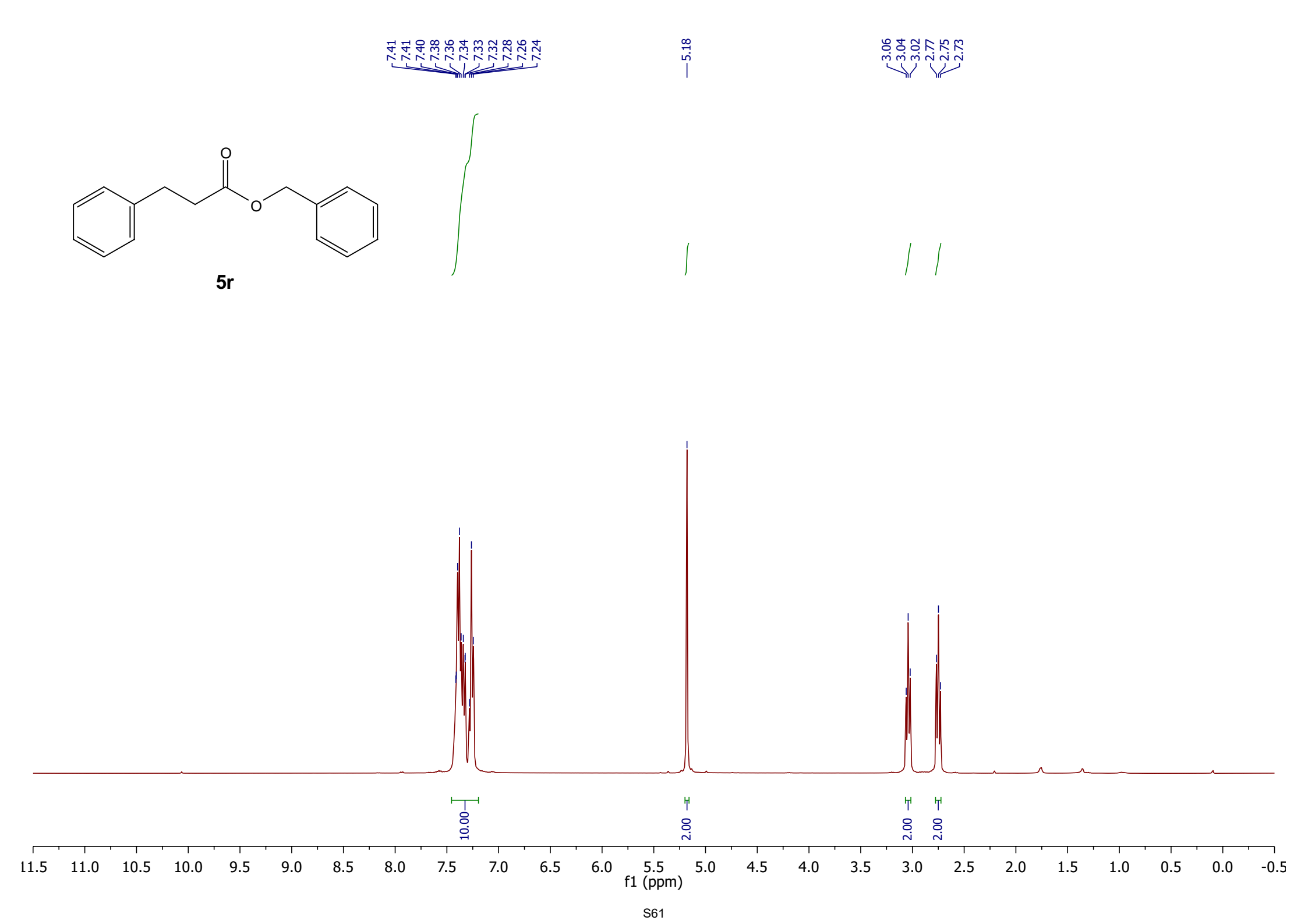
5q

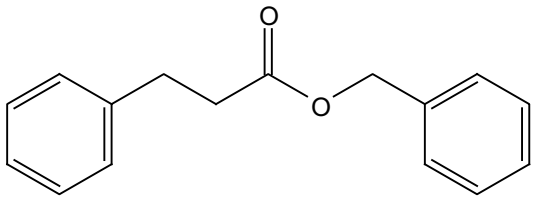
7.36
7.34
7.32
7.30
5.11
1.23
5.00
2.00
9.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



5q

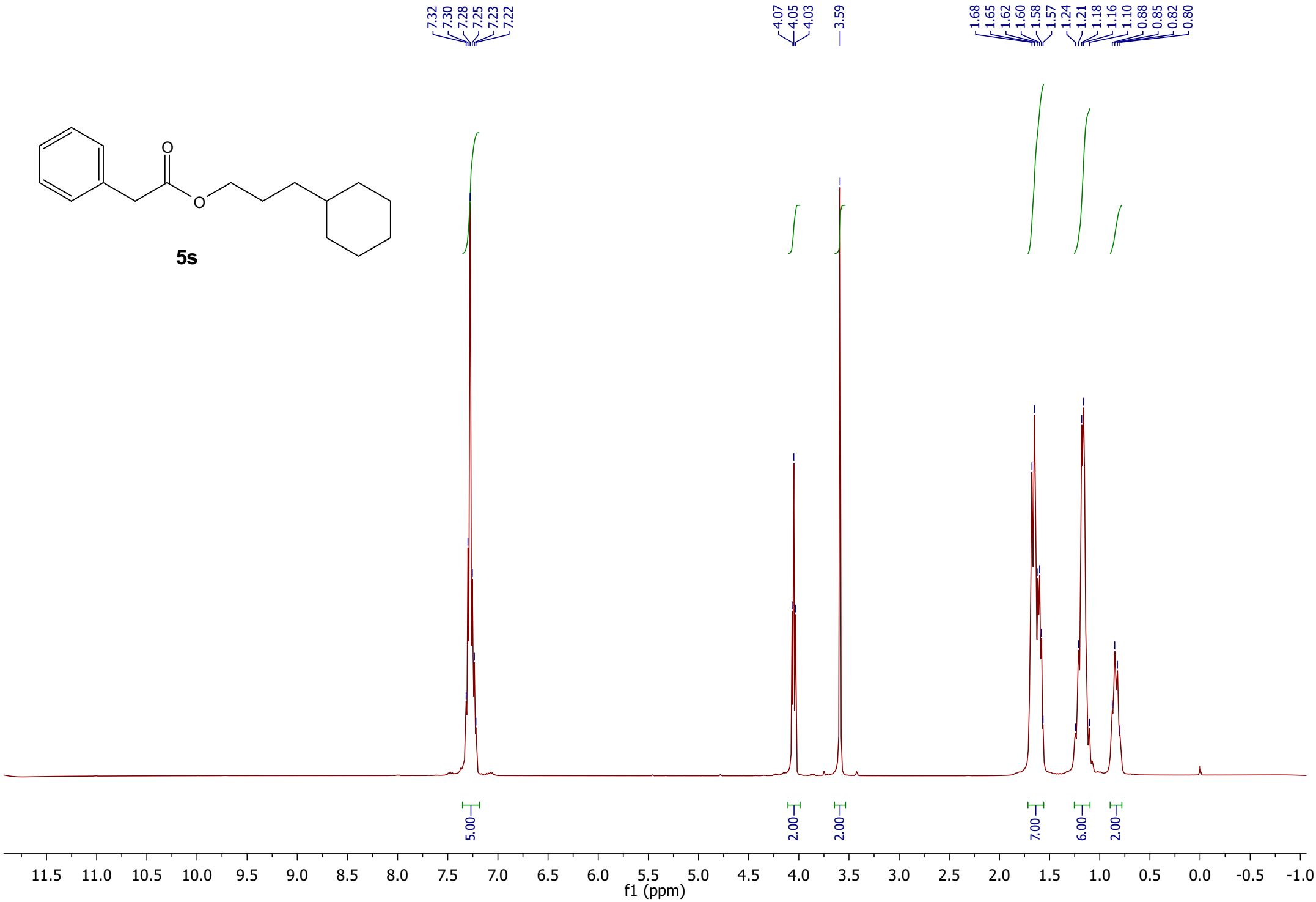
178.29
136.44
128.45
127.91
127.63
65.97
38.76
27.15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

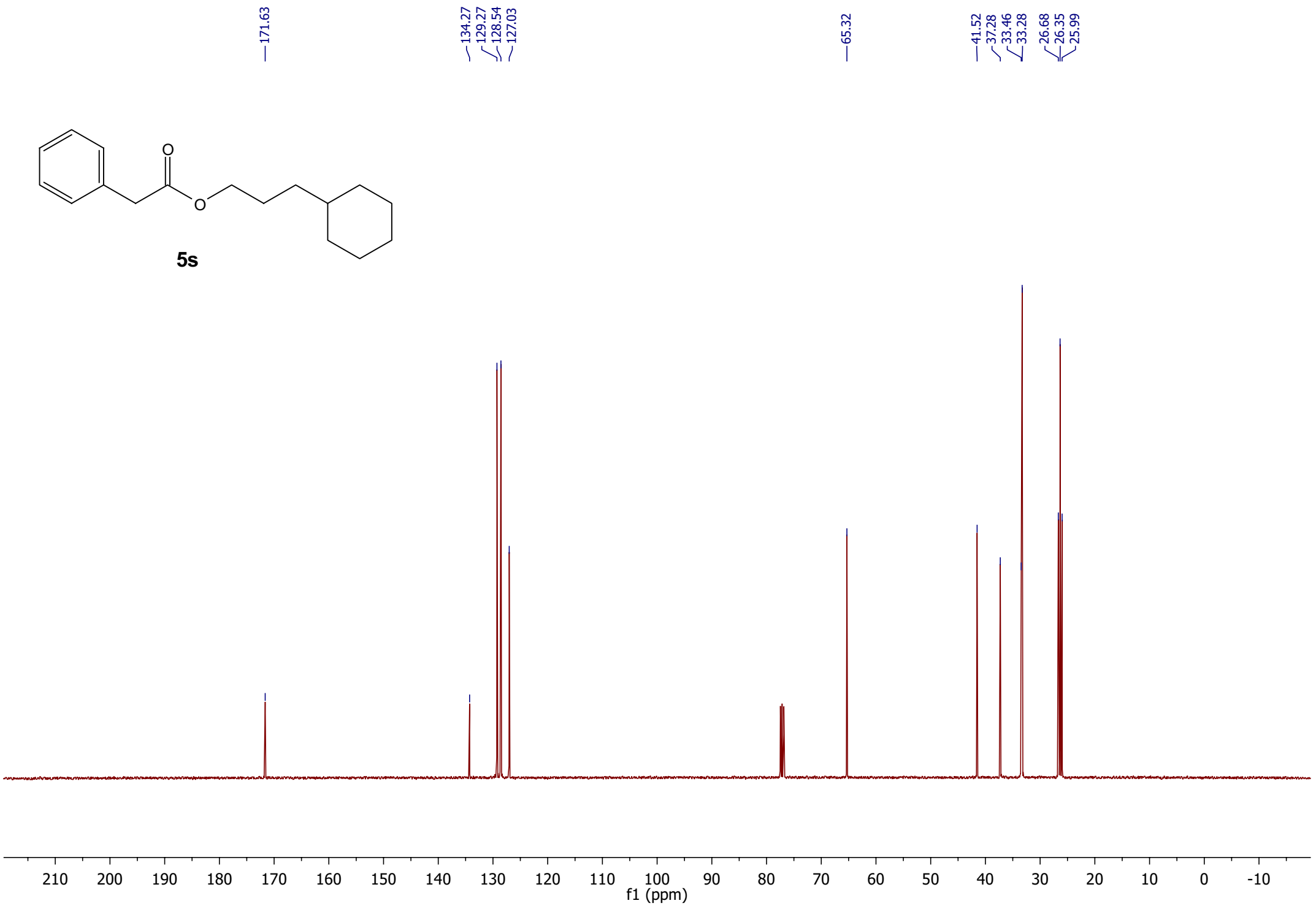

7.41
7.41
7.40
7.38
7.36
7.34
7.33
7.32
7.28
7.26
7.24
5.18
3.06
3.04
3.02
2.77
2.75
2.73
O
O
5r
10.00
2.00
2.00
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

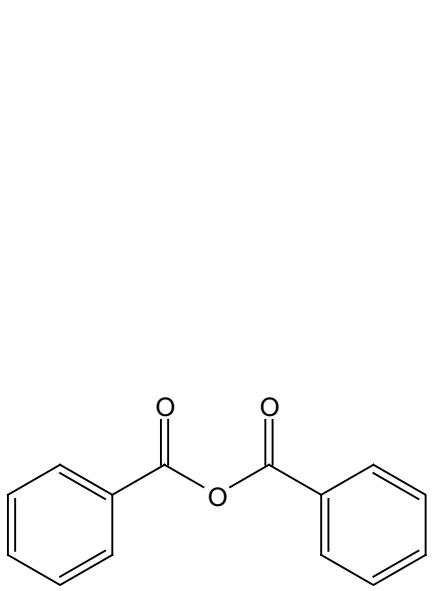


5r

172.50
140.27
135.83
128.39
128.36
128.25
128.17
128.06
126.13
66.09
35.72
30.80
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)

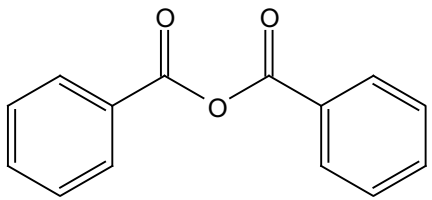

7.32
7.30
7.28
7.25
7.23
7.22
4.07
4.05
4.03
3.59
1.68
1.65
1.62
1.60
1.58
1.57
1.24
1.21
1.18
1.16
1.10
0.88
0.85
0.82
0.80
O
O
5s
5.00
2.00
2.00
7.00
6.00
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


171.63
134.27
129.27
128.54
127.03
65.32
41.52
37.28
33.46
33.28
26.68
26.35
25.99
O
O
5s
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)



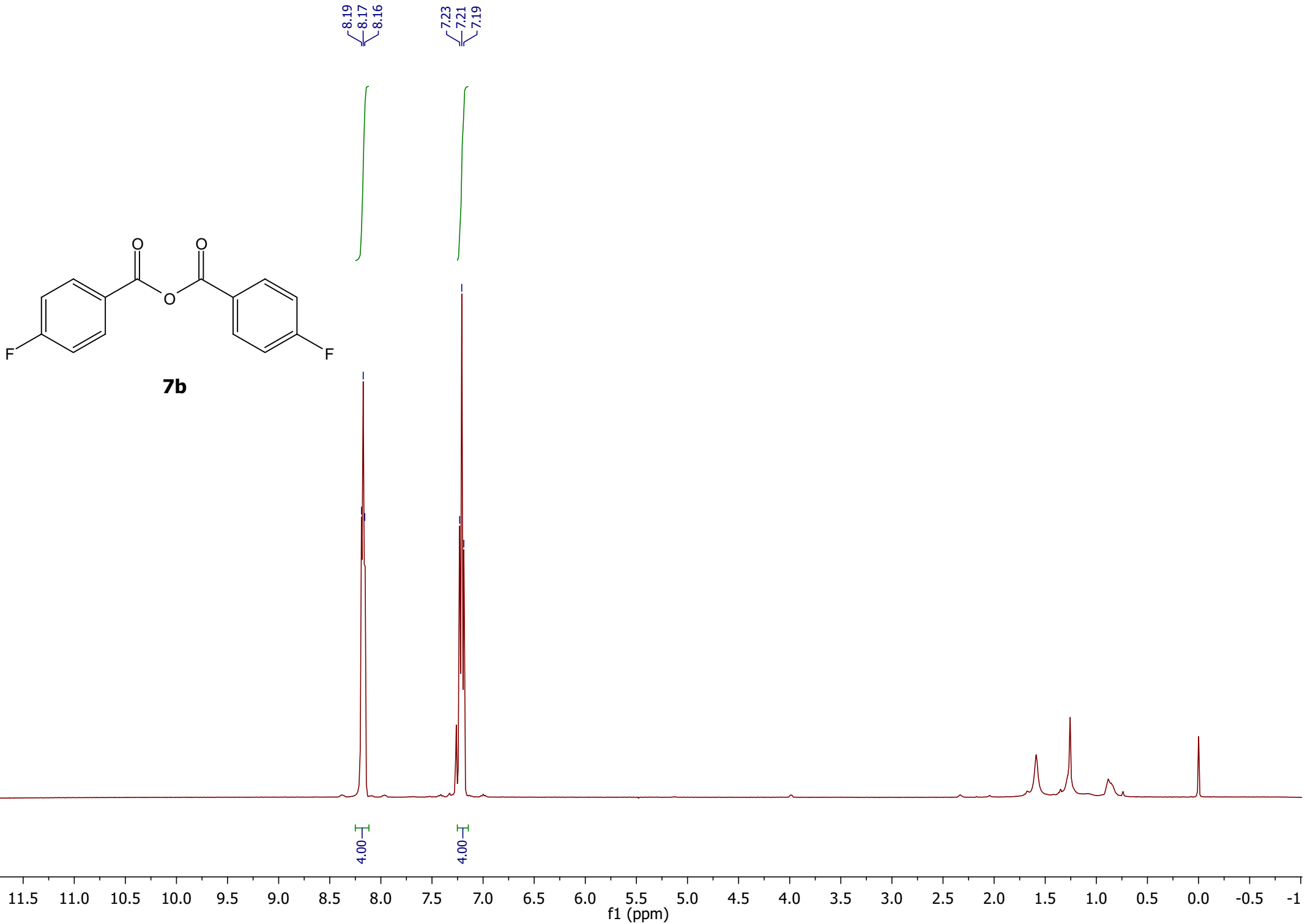
7a

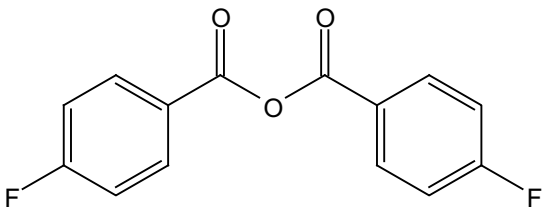
8.17
8.15
7.69
7.67
7.65
7.54
7.52
7.51
4.00
2.00
4.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



7a

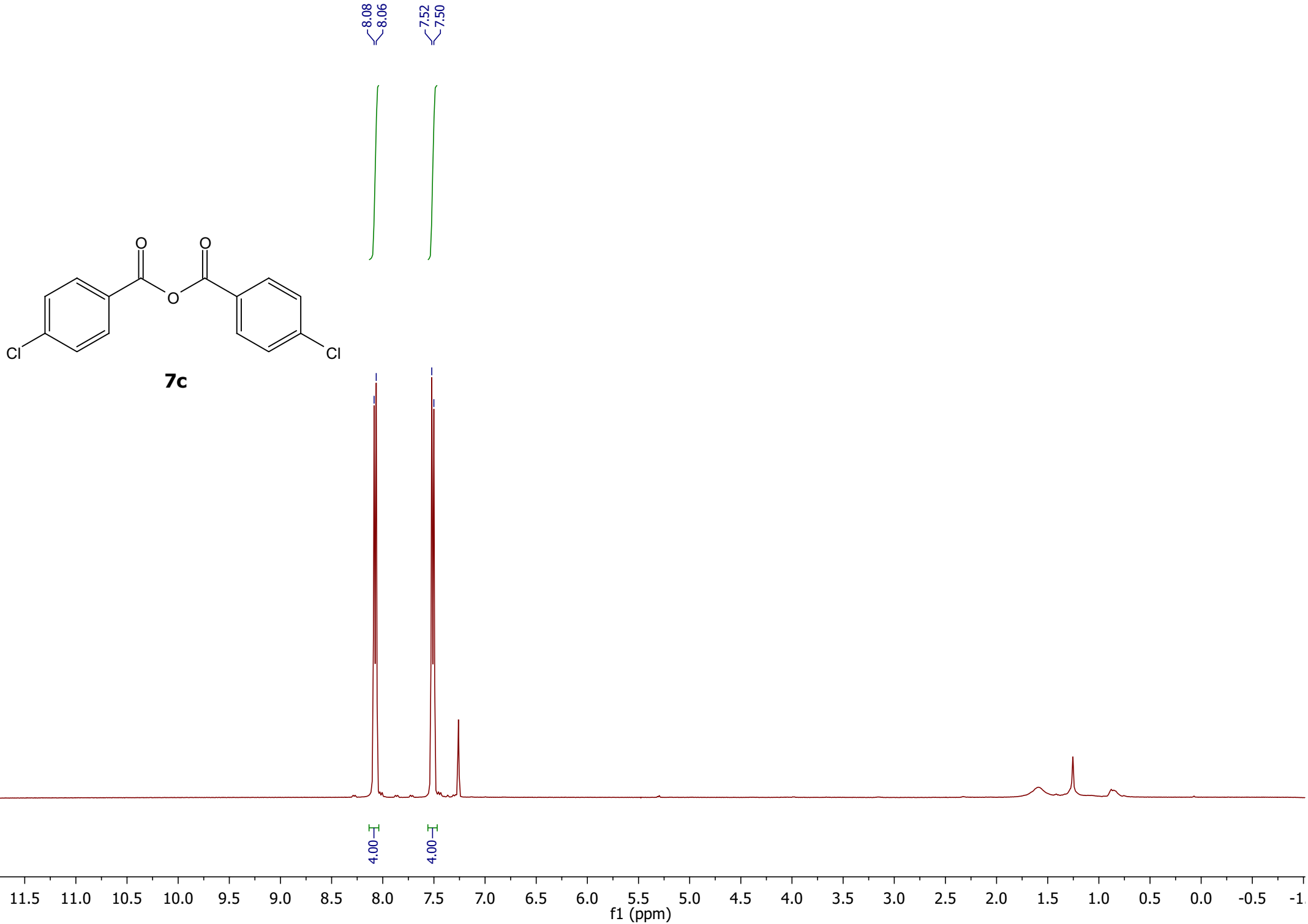
162.23
134.44
130.40
128.76
128.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

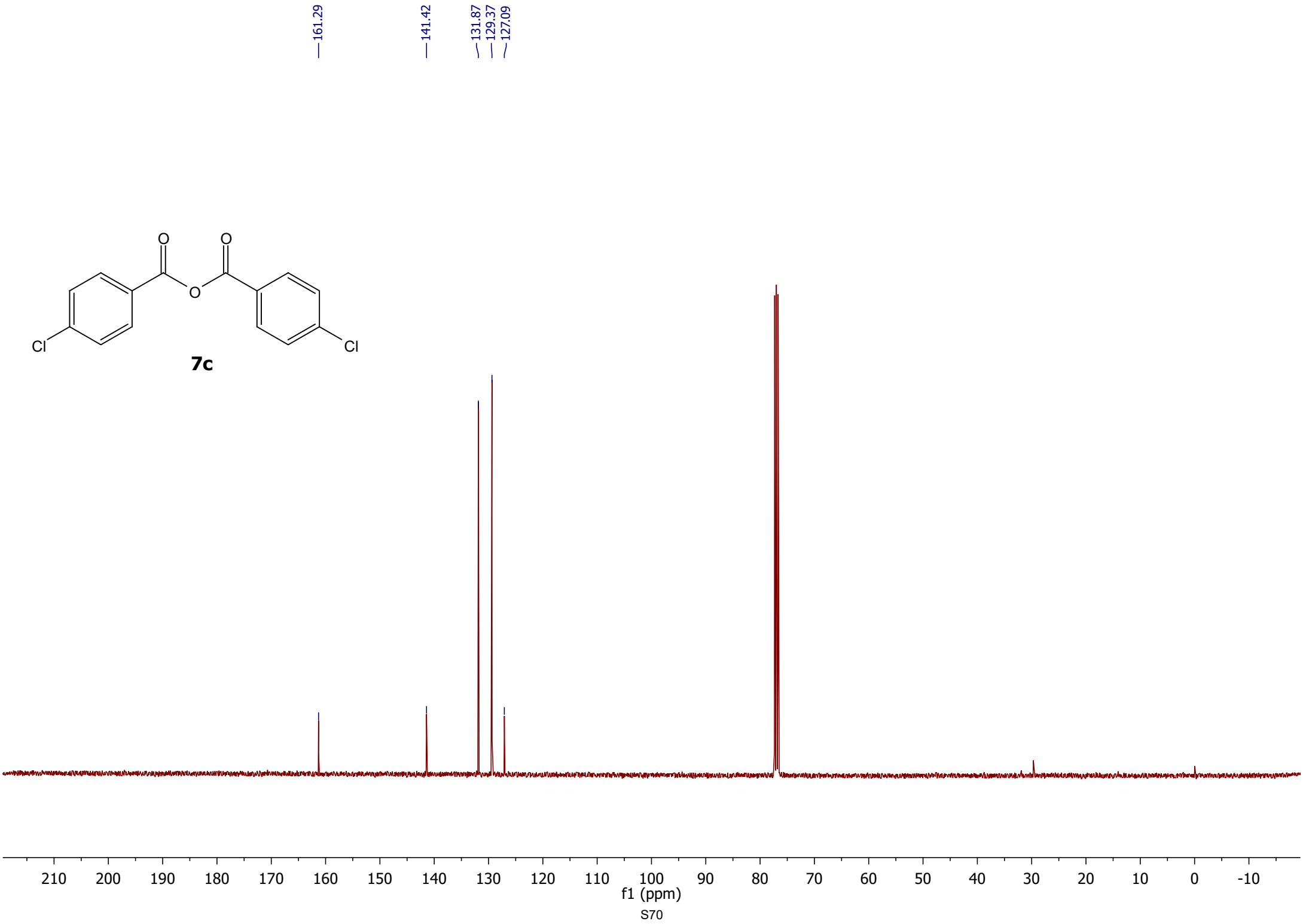

8.19
8.17
8.16
7.23
7.21
7.19
O
O
O
F
F
7b
4.00
4.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

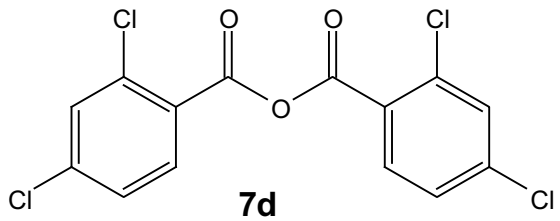

O
O
O
F
F

7b

168.00
165.45
161.19
133.34
133.25
125.00
124.97
116.37
116.15
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)

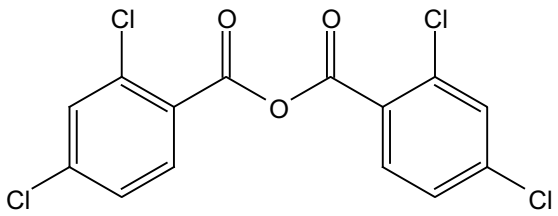

8.08
8.06
7.52
7.50
O
O
O
Cl
Cl
7c
4.00
4.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


161.29
141.42
131.87
129.37
127.09
O
O
O
Cl
Cl
7c
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)


Cl
O
O
Cl
O
Cl
Cl

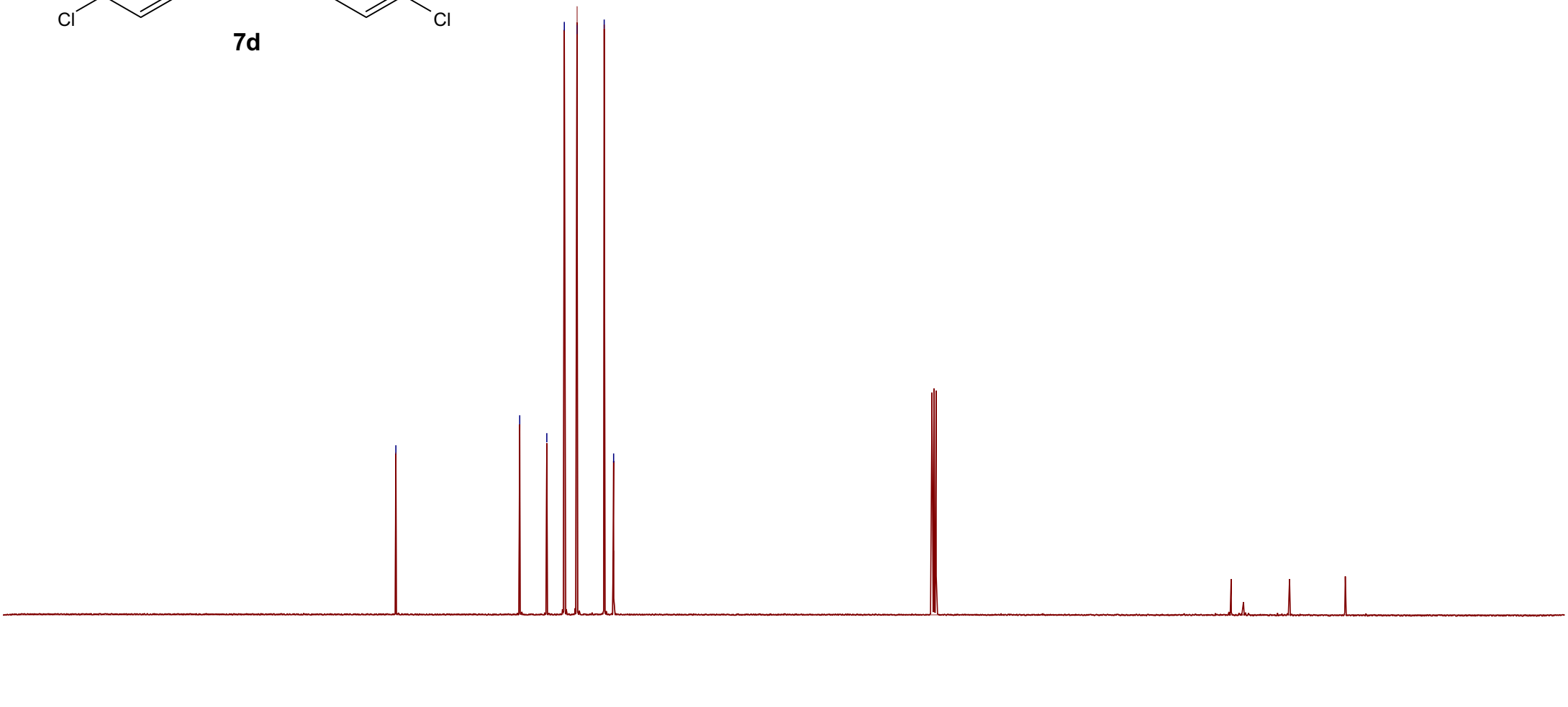
7d

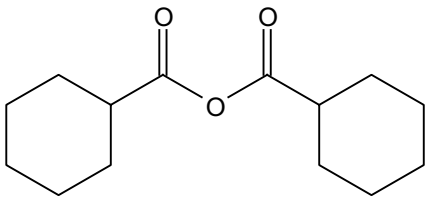
7.98
7.96
7.54
7.54
7.39
7.39
7.37
7.37
2.00
2.00
2.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



7d

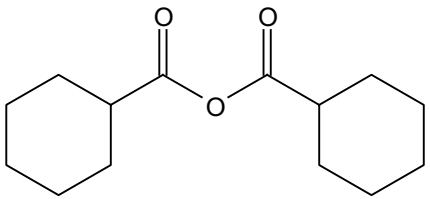
159.32
140.38
136.23
133.56
131.62
127.45
126.01





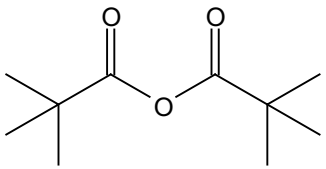
7e

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)



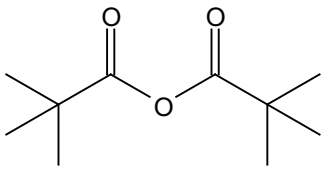
7e

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)



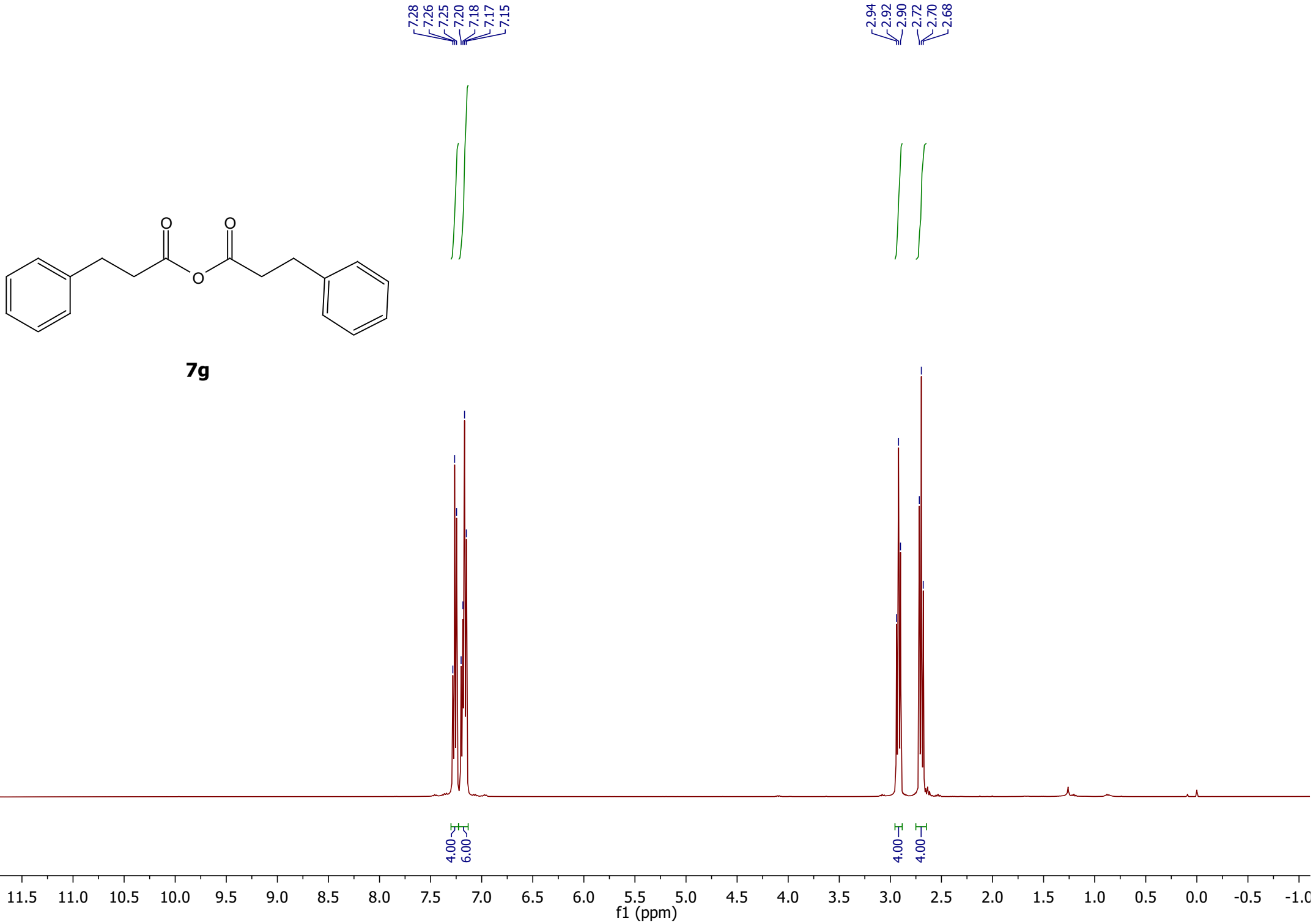
7f

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)

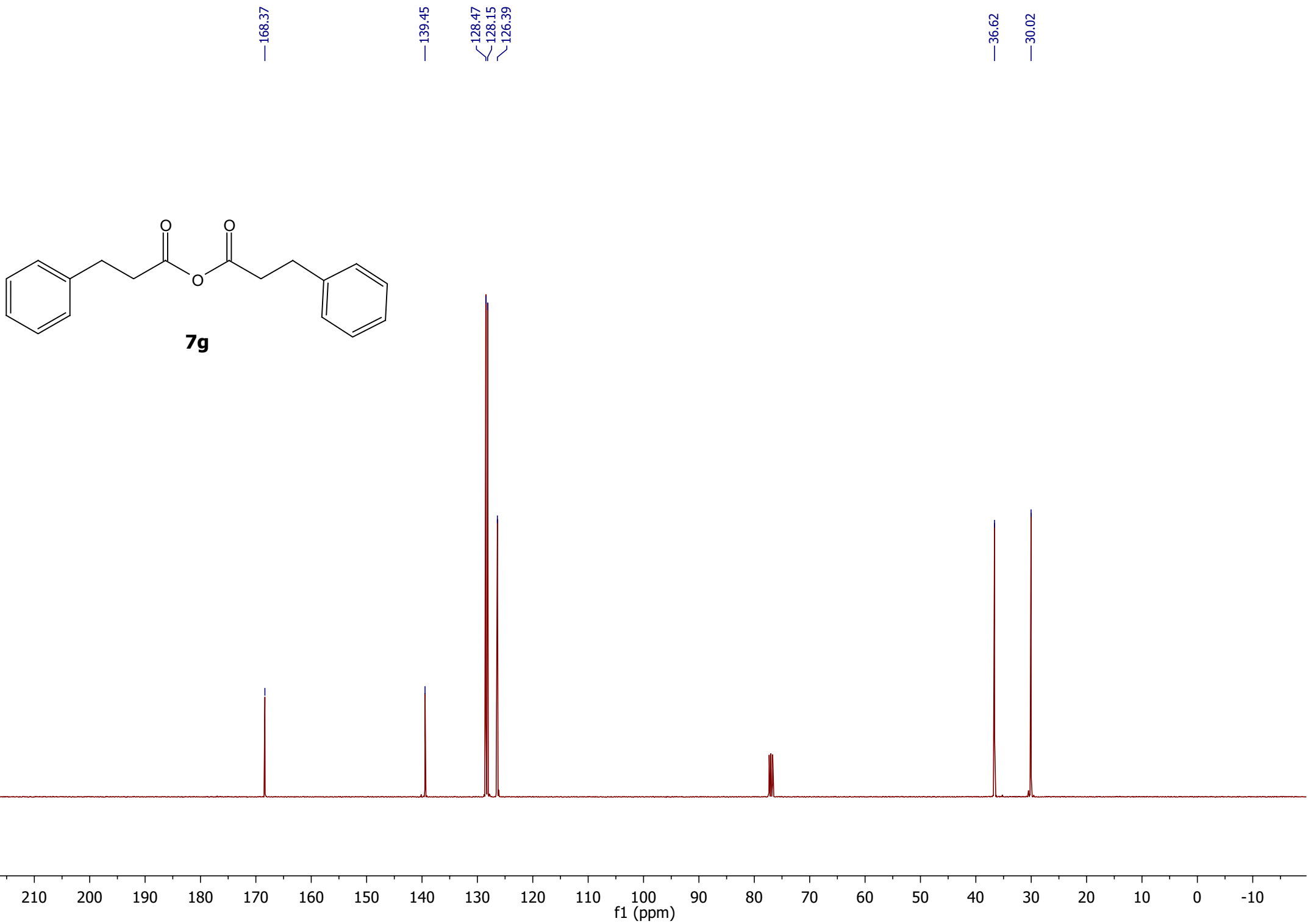


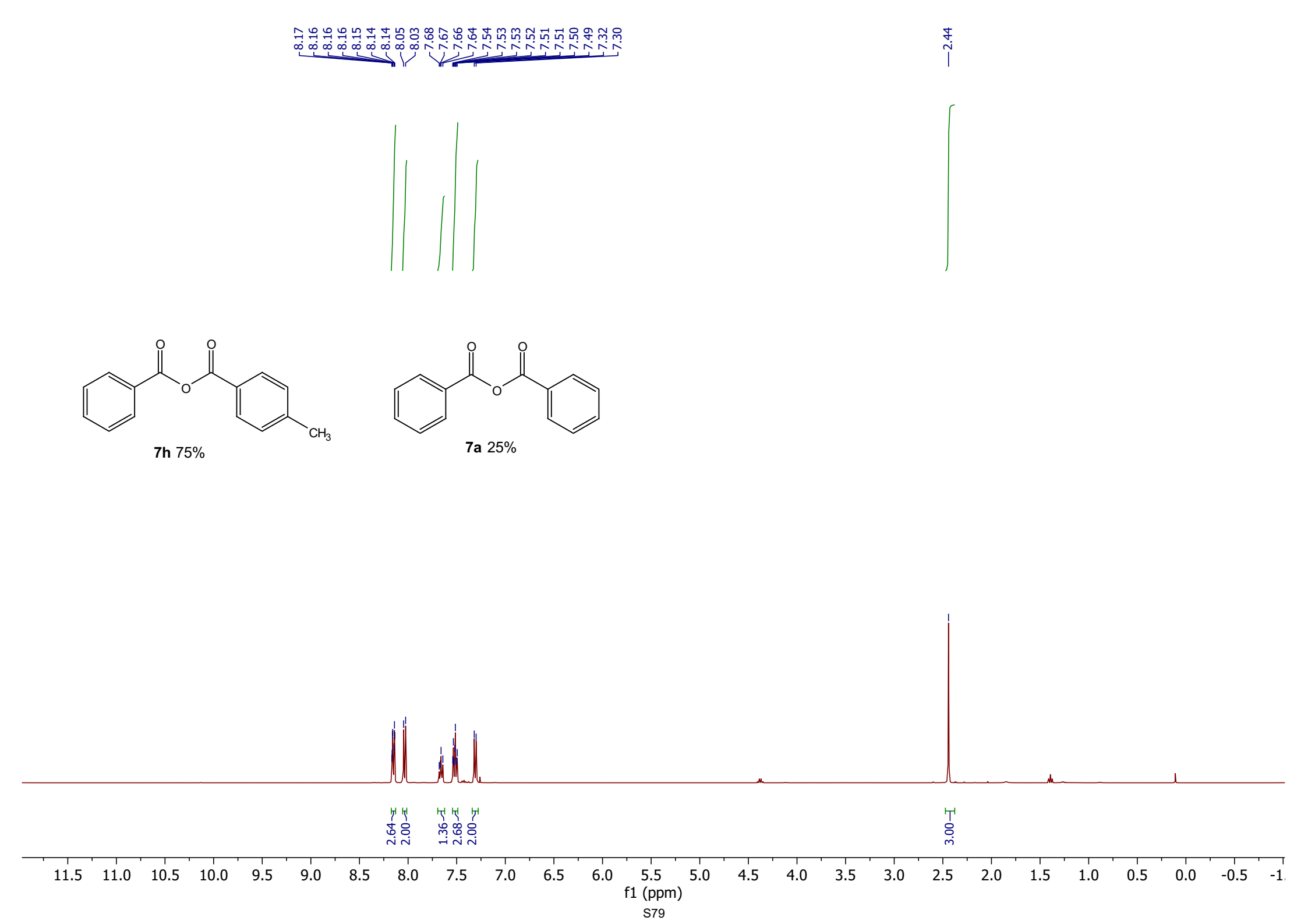
7f

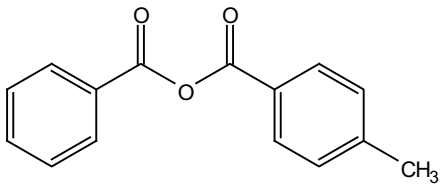
173.72
39.96
26.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


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
O
O
O
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)

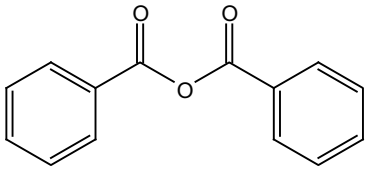
7g


168.37
139.45
128.47
128.15
126.39
36.62
30.02
O
O
O
7g
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)


8.17
8.16
8.16
8.16
8.15
8.14
8.14
8.05
8.03
7.68
7.67
7.66
7.64
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.32
7.30
2.44
O
O
O
CH3
7h 75%
O
O
O
7a 25%
2.64
2.00
1.36
2.68
2.00
3.00
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)

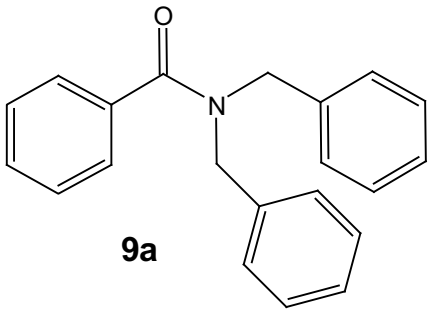

O
O
O
CH3

7h 75%


O
O
O

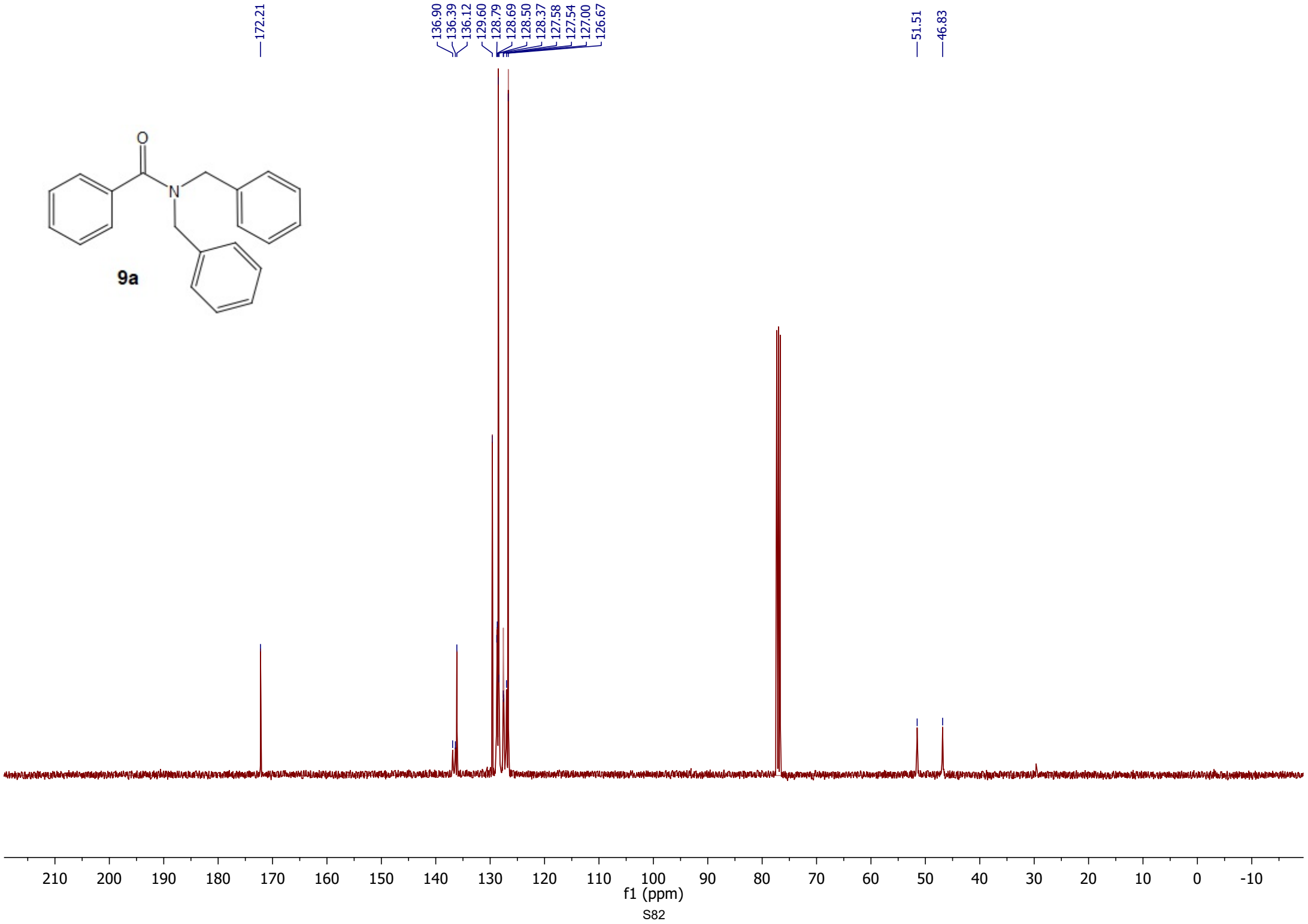
7a 25%

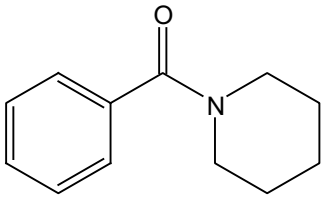
162.39
162.29
162.25
145.61
134.45
134.35
130.53
130.42
130.39
129.51
128.83
128.78
128.74
128.19
125.95
21.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
N

9a

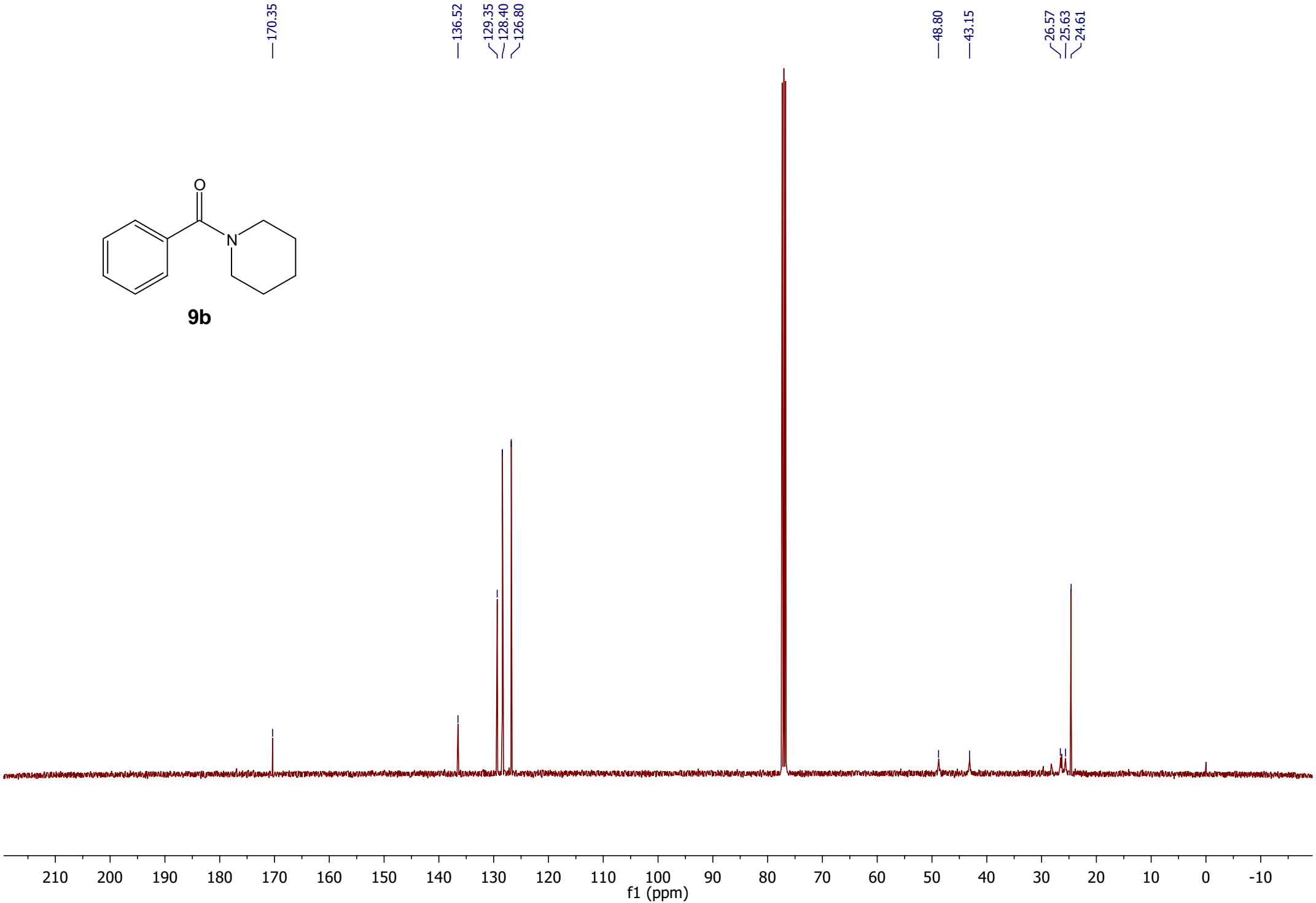
7.51
7.50
7.49
7.39
7.38
7.36
7.34
7.32
7.30
7.29
7.15
7.14
4.71
4.41
2.00
11.00
2.00
2.00
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

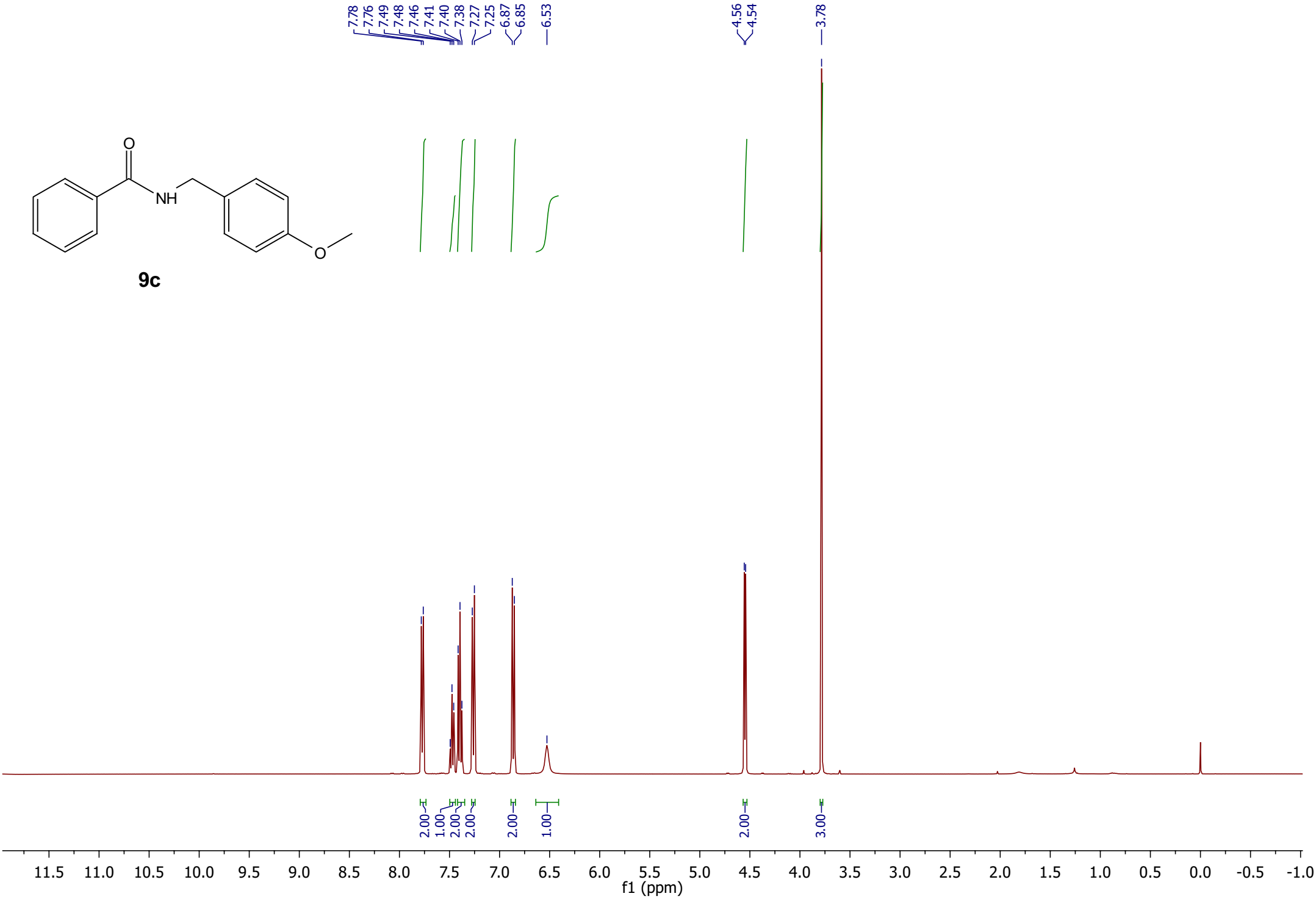

172.21
136.90
136.39
136.12
129.60
128.79
128.69
128.50
128.37
127.58
127.54
127.00
126.67
51.51
46.83
O
N
9a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

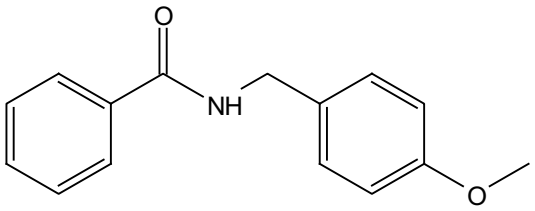

O
N

9b

7.39
3.71
3.34
1.68
1.52
5.00
2.00
2.00
4.01
2.01
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)

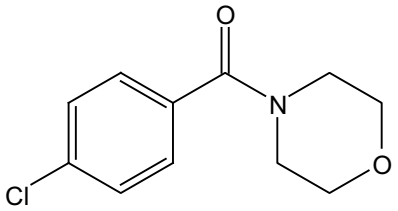

170.35
136.52
129.35
128.40
126.80
48.80
43.15
26.57
25.63
24.61
O
N
9b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.78
7.76
7.49
7.48
7.46
7.41
7.40
7.38
7.27
7.25
6.87
6.85
6.53
4.56
4.54
3.78
O
NH
O
9c
2.00
1.00
2.00
2.00
2.00
1.00
2.00
3.00
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)


O
NH
O

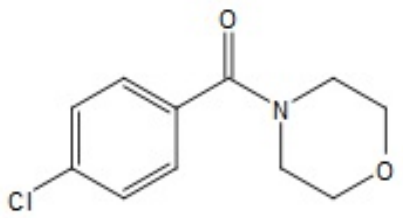
9c

167.23
159.03
134.40
131.41
130.25
129.21
128.48
126.90
114.08
55.25
43.54
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
N
O
Cl

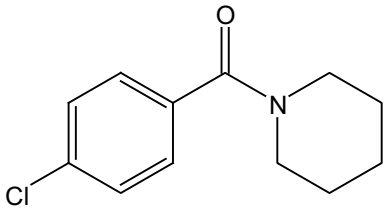
9d

7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
3.65
3.42
3.40
4.00
8.00
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)


O
N
O
Cl

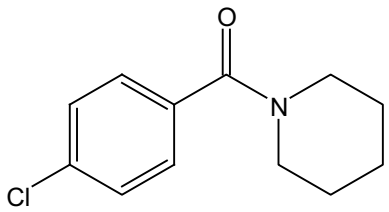
9d

169.15
135.81
133.49
128.68
128.51
66.64
48.03
42.56
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
N
Cl

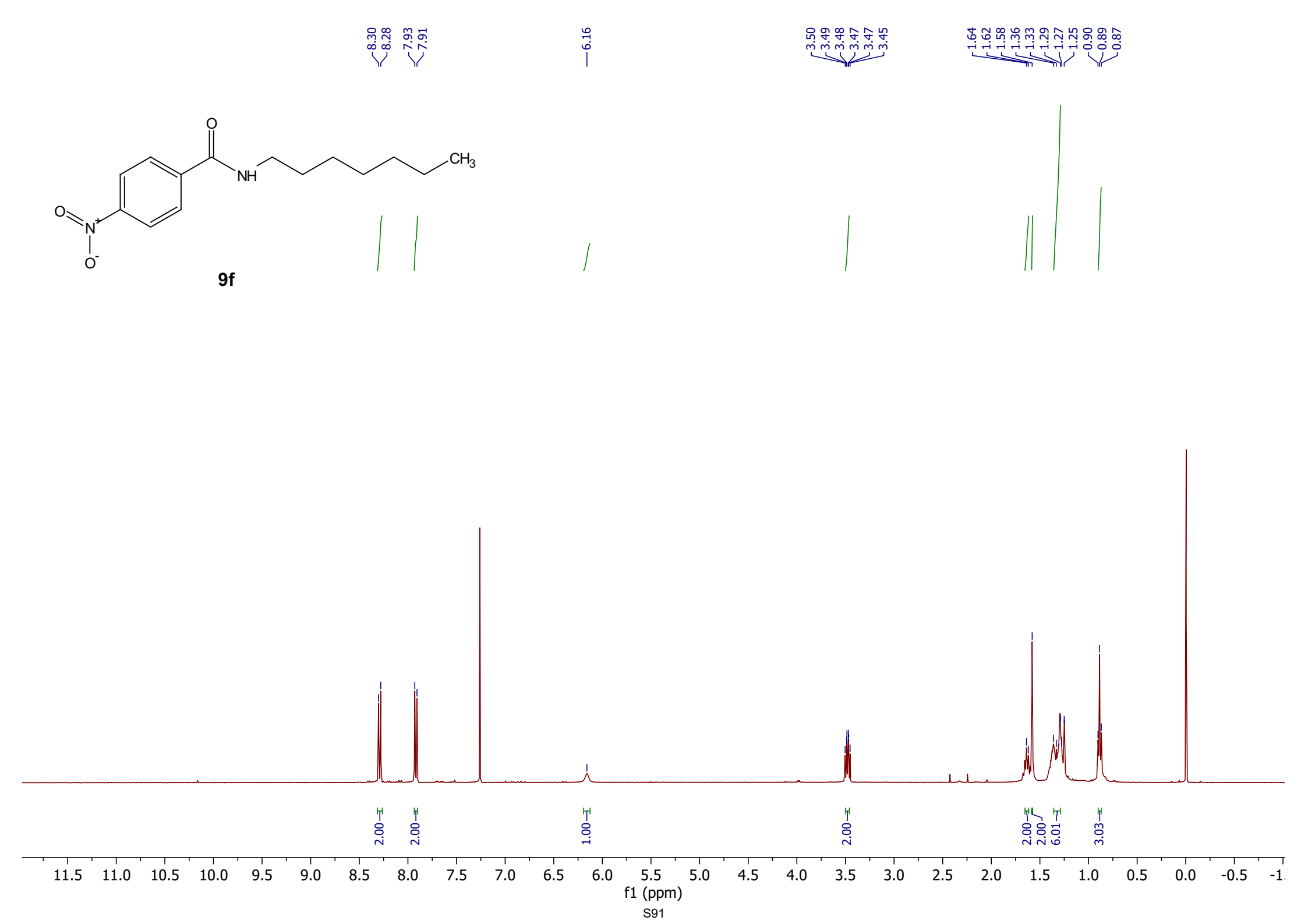
9e

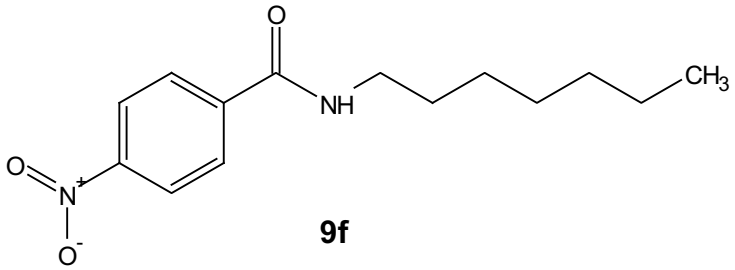
7.39
7.39
7.38
7.36
7.36
7.36
7.35
7.35
7.34
7.32
7.32
7.31
3.68
3.33
1.69
1.67
1.65
1.54
4.00
2.00
2.00
6.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.
f1 (ppm)


O
N
Cl

9e

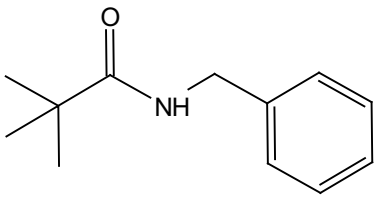
169.06
135.25
134.76
128.52
128.24
48.58
43.12
26.37
25.77
24.39
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1(
f1 (ppm)


8.30
8.28
7.93
7.91
6.16
3.50
3.49
3.48
3.47
3.47
3.45
1.64
1.62
1.58
1.36
1.33
1.29
1.27
1.25
0.90
0.89
0.87
O
NH
CH3
O
N+
O-
9f
2.00
2.00
1.00
2.00
2.00
2.00
6.01
3.03
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)


O
NH
CH3
O
N+
O-

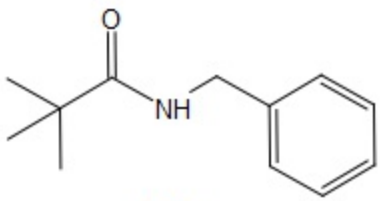
9f

165.46
149.47
140.39
128.03
123.80
40.45
31.69
29.51
28.93
26.91
22.56
14.04
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
NH

9d

7.33
7.31
7.29
7.27
7.25
7.24
7.23
6.03
4.42
4.40
1.21
5.00
0.93
2.00
9.00
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)

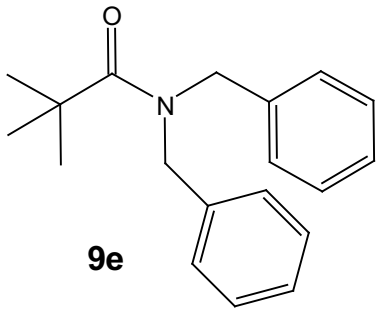


9d

178.23
138.61
128.61
127.53
127.31
43.49
38.64
27.55

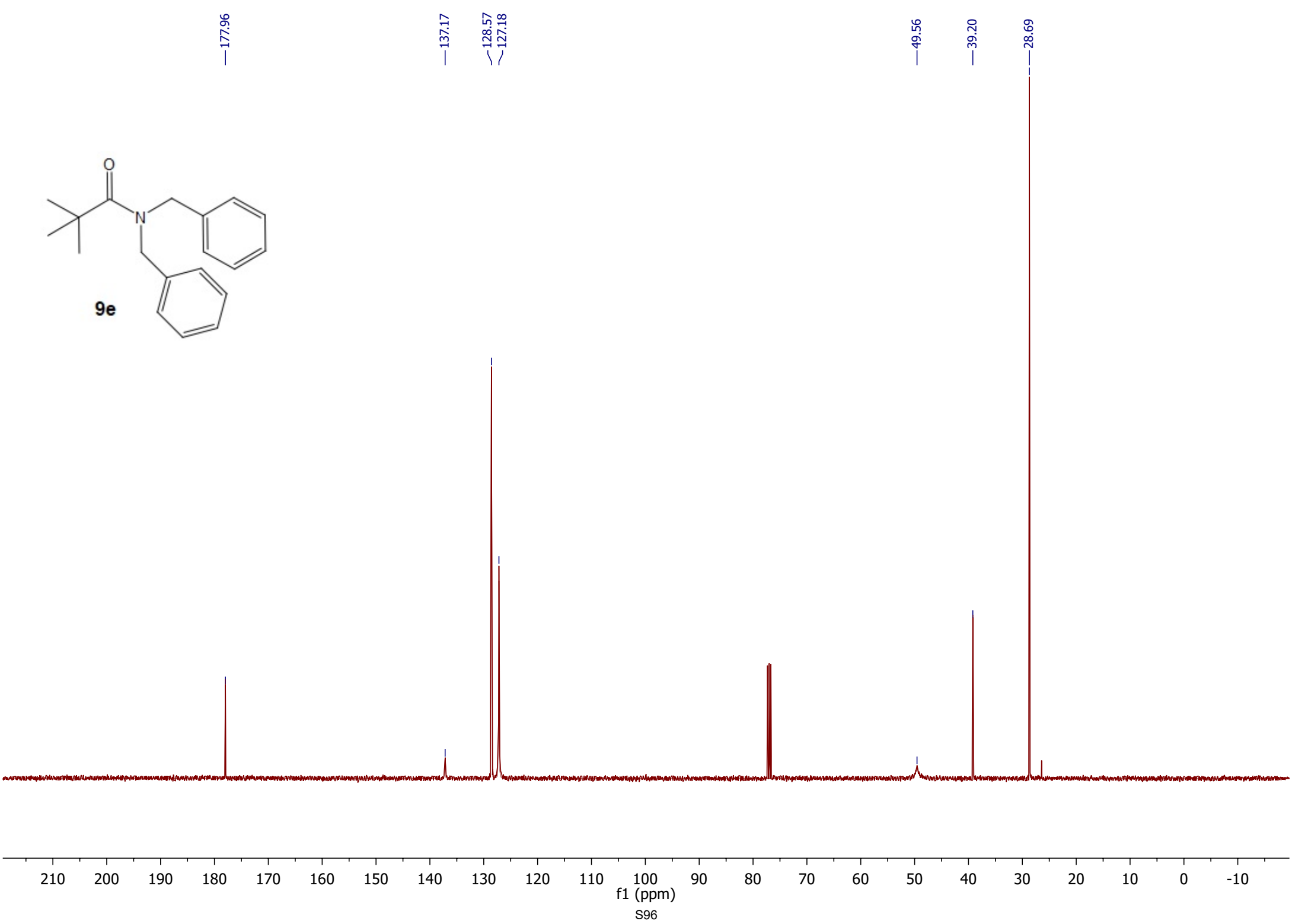
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

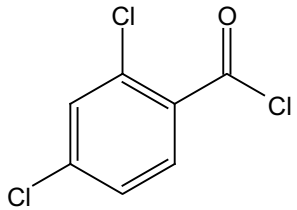
f1 (ppm)


O
N

9e

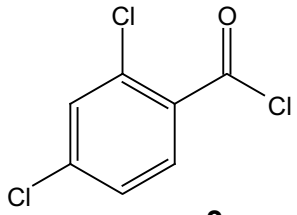
7.36
7.34
7.32
7.30
7.28
7.17
7.15
4.62
1.38
6.00
4.00
4.00
9.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.96
137.17
128.57
127.18
49.56
39.20
28.69
O
N
9e
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)


Cl
O
Cl
Cl

3

8.08
8.06
7.53
7.52
7.42
7.41
7.39
7.39
1.00
1.00
1.00
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)


Cl
O
Cl
Cl

3

164.10
140.75
134.99
134.58
131.44
130.98
127.42
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)