Supporting Information

Enantioselective Construction of Sterically Hindered Tertiary α-Aryl Ketones: A Catalytic Asymmetric Synthesis of Isoflavanones

Michael P. Carroll, Helge Muller-Bunz and Patrick J. Guiry*

Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland
E-mail: patrick.guiry@ucd.ie

Table of Contents

I. General Information

General Procedures. Unless otherwise noted, reactions were performed with rigorous exclusion of air and moisture, under an inert atmosphere of nitrogen in oven-dried glassware with magnetic stirring. N_2-flushed stainless steel cannulas or plastic syringes were used to transfer air- and moisture-sensitive reagents. Oxygen-free nitrogen was obtained from BOC gases. Evaporation *in vacuo* refers to the removal of volatiles on a Buchi rotary evaporator with integrated vacuum pump. Flash chromatography was carried out using Merck Kieselgel 60 F254 (230-400 mesh) silica gel. Thin-layer chromatography (TLC) was performed on Merck DC-Alufolien plates pre-coated with silica gel 60 F254. They were visualised with UV-light (254 nm) fluorescence quenching, or by charring with an acidic vanillin solution (vanillin, H_2SO_4, acetic acid in methanol).

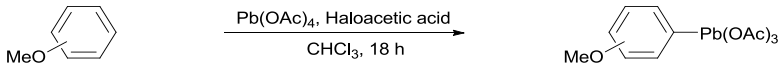
Materials. Commercial reagents were purchased from Sigma Aldrich, Acros, Apollo Scientific, Alfa Aesar, Strem or TCI, and were used as received with the following exceptions. Diethyl

ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene ($PhCH_3$) were dried by passing through activated alumina columns; tetrahydrofuran (THF) was freshly distilled under N_2 from sodium/benzophenone ketyl. Tris(dibenzylideneacetone)dipalladium(0) chloroform adduct was prepared *via* the method of Zalesskiy *et al.*[1] Lead(IV) tetraacetate was purchased from Aldrich and recrystallized from glacial acetic acid, then dried under vacuum (0.2 torr.) for 18 hours immediately prior to use. Hexamethyldisilazane (HMDS) was freshly distilled over calcium hydride before use. Quinap was purchased from Strem and stored in a desiccator under N_2. Quinazolinap and PHOX ligands were prepared according to previously described methods and were stored in a desiccator under N_2.[2,3] Allyl cyanoformate was prepared *via* a previously reported method.[4] Arylboronic acids used were either commercially available or made *via* lithium halogen exchange with the corresponding aryl bromide, and then quenched with triisopropyl borate. Arylstannanes were made via lithium halogen exchange with the corresponding aryl bromide and quenched with *n*-tributyltin chloride.

Instrumentation. ^{1}H NMR spectra were recorded on a 300 MHz Varian-Inova spectrometer, a 400 MHz Varian-Inova spectrometer, a 500 MHz Varian-Inova spectrometer or a 600 MHz Varian-Inova spectrometer. ^{13}C NMR spectra were recorded on a 400 MHz Varian-Inova spectrometer (101 MHz) or a 500 MHz Varian-Inova spectrometer (125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$ = δ 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon references of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). All ^{13}C spectra are ^{1}H decoupled. ^{19}F spectra were recorded on a 300 MHz Varian-Inova spectrometer (282 MHz); chemical shifts are reported in parts per million. ^{31}P spectra were recorded on a 300 MHz Varian-Inova spectrometer (162 MHz); chemical shifts are reported in parts per million. NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, dd, app., = apparent double doublet, t. app., = apparent triplet), coupling constant in Hertz (Hz), integration. Exact mass ESI mass spectra (HRMS) were measured on a micromass LCT orthogonal time of flight mass spectrometer with leucine enkephalin (Tyr-Gly-Phe-Leu) as an internal lock mass. FT-IR spectra were recorded on a Perkin-Elmer Infrared FT spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Optical rotation values were measured at room temperature with a Schmidt + Haensch UniPol 2000 polarimeter. $[\alpha]_D$ values are given in $degcm^3\ g^{-1}\ dm^{-1}$. Melting points were determined in open capillary tubes with a Gallenkamp melting point apparatus and are uncorrected. High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 series instrument with a binary pump and a diode array detector, using Chiralpak AS-H (25 cm x 0.46 cm), Chiralpak IB (25 cm x 0.46 cm) and Chiralpak IA (25 cm x 0.46 cm) columns. The Microanalytical Laboratory, University College Dublin, performed elemental analyses. X-ray diffraction was collected on an Agilent Technologies (former Oxford Diffraction) Super Nova A diffractometer at 100 K.

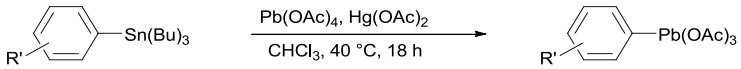
II. Preparation of Aryllead Triacetates

General procedure A for the preparation of aryllead triacetates (direct plumbation).[5]



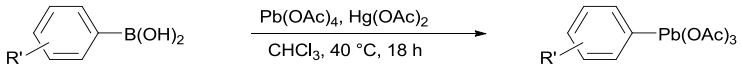
To a stirred solution of lead (IV) tetraacetate[6] (1 equiv.) and haloacetic acid (10 equiv.) in anhydrous $CHCl_3$ (0.3 M) at room temperature was added, dropwise over 15 min, arene (2.7 equiv.) in anhydrous $CHCl_3$ (3 M). The reaction mixture was stirred for 18 h and then washed with water (2 x 100 mL), the organic phase concentrated to a volume of ~10 mL and added dropwise to pentane (500 mL) wherein a yellow solid precipitated out. This yellow solid was stirred in a mixture of glacial acetic acid (0.22 M) and $CHCl_3$ (0.3 M) for 2 h. This solution was then washed with water (3 x 100 mL), dried with $MgSO_4$, concentrated to a volume of ~10 mL and added dropwise to pentane (500 mL). The aryllead triacetate, which precipitated as a bright yellow solid was filtered and dried in a dessicator over potassium hydroxide.

General procedure B for the preparation of aryllead triacetates (tin-lead exchange).[7]

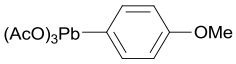


To a stirred solution of lead (IV) tetraacetate[6] (1 equiv.) and mercury (II) acetate[6] (5 mol. %) in anhydrous $CHCl_3$ (0.6 M) at 40 °C was added, aryltributylstannane (1 equiv.). The mixture was stirred at 40 °C for 18 h and then filtered through a plug of Celite, which was washed with $CHCl_3$ (2 x 40 mL). The chloroform filtrate was then reduced *in vacuo* to give a solid. Pentane (200 mL) was added and the aryllead triacetate precipitated as a yellow solid which was filtered and dried in a dessicator over potassium hydroxide.

General procedure C for the preparation of aryllead triacetates (boron-lead exchange).[8]



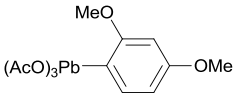
To a stirred solution of lead (IV) tetraacetate[6] (1 equiv.) and mercury (II) acetate[6] (5 mol. %) in anhydrous $CHCl_3$ (0.6 M) at 40 °C was added, aryl boronic acid (1 equiv.). The mixture was stirred at 40 °C for 18 h and then filtered through a plug of Celite, which was washed with $CHCl_3$. The organic filtrate was washed with water and the aqueous layer extracted with $CHCl_3$. The combined chloroform layers were filtered through a plug of Celite and concentrated in volume to ~ 100 mL. Pentane (500 mL) was added and the mixture kept at -20 °C for 2 days. The aryllead triacetate, which was deposited as a yellow solid, was filtered and dried in a dessicator over potassium hydroxide.



4-Methoxyphenyllead triacetate (S1). Prepared according to general procedure A using anisole and dichloroacetic acid. The title compound was isolated as a yellow solid (2.54 g, 60%) with spectral data in agreement with literature values.[9]

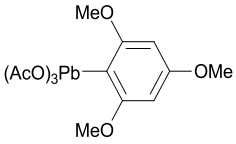
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.7 Hz, 2H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 397.2 Hz), 7.09 (d, J = 8.7 Hz, 2H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 128.8 Hz), 3.84 (s, 3H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 71.4 Hz), 2.12 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 128.8 Hz);

^{13}C NMR (125 MHz, $CDCl_3$): δ 180.4, 135.7, 132.5, 116.3, 116.2, 55.5, 19.9.



2,4-Dimethoxyphenyllead triacetate (S2). Prepared according to general procedure A using 1,3-dimethoxybenzene and monochloroacetic acid. The title compound was isolated as a yellow solid (2.75 g, 64%) with spectral data in agreement with literature values.[10]

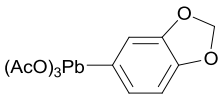
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 8.8 Hz, 1H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 396.4 Hz), 6.66 (dd, J = 8.8, 2.5 Hz, 1H), 6.56 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 2.09 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 126.2 Hz).



2,4,6-Trimethoxyphenyllead triacetate (S3). Prepared according to general procedure A using 1,3,5-trimethoxybenzene. The product was isolated as a yellow solid (3.82 g, 72%) with spectral data in agreement with literature values.[11]

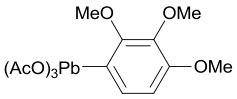
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.19 (s, 2H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 165.0 Hz), 3.86 (s, 6H), 3.82 (s, 3H), 2.07 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 128.4 Hz);

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.3, 164.8, 160.7, 92.1, 91.1, 56.4, 55.7, 20.2.

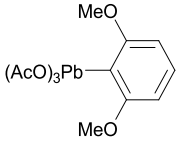


3,4-Methylenedioxyphenyllead triacetate (S4). Prepared according to general procedure B, and the title compound was isolated as a yellow solid (3.32 g, 61%) with spectral data in agreement with literature values.[12]

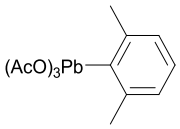
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 2H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 172.2 Hz), 2.12 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 129.0 Hz);
^{13}C NMR (101 MHz, $CDCl_3$): δ 180.4, 150.6, 129.7, 124.5, 112.7, 111.2, 109.8, 102.0, 20.5.



2,3,4-Trimethoxyphenyllead triacetate (S5). Prepared according to general procedure B, and the title compound was isolated as a yellow solid (2.43 g, 52%).
m.p. 154-156 °C;
IR (film) ν_{max} 3620, 3147, 2400, 1564 cm^{-1};
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.9 Hz, 1H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 393.4 Hz), 6.83 (d, *J* = 8.9 Hz, 1H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 153.6 Hz), 4.05 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 2.10 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 129.4 Hz);
^{13}C NMR (101 MHz, $CDCl_3$): δ 179.7, 157.2, 152.0, 146.7, 142.0, 126.0, 108.7, 61.7, 61.0, 55.8, 20.3;
Elemental Analysis Calculated For $C_{15}H_{20}O_9Pb$: C, 32.67; H, 3.66. Found: C, 32.43; H, 3.54.

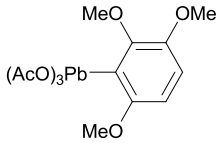


2,6-Dimethoxyahenyryllead triacetate (S6). Prepared according to general procedure B, and the title compound was isolated as a yellow solid (1.95 g, 58%).
m.p. 157-159 °C;
IR (film) ν_{max} 3155, 2981,2253, 1793 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 2H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 191.6 Hz), 3.89 (s, 6H), 2.09 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 65.30.0 Hz);
^{13}C NMR (101 MHz, $CDCl_3$): δ 179.4, 159.8, 133.9, 107.1, 54.07, 20.2;
Elemental Analysis Calculated For $C_{14}H_{18}O_8Pb$: C, 32.24; H, 3.48. Found: C, 32.35; H, 3.33.

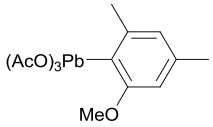


2,6-Dimethylphenyllead triacetate (S7). Prepared according to general procedure C, and the title compound was isolated as a yellow crystalline solid (6.11 g, 37%).
m.p. 181-183 °C;
IR (film) ν_{max} 2984, 2253, 1554, cm^{-1};

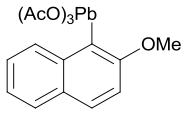
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 2H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 208.8 Hz), 2.63 (s, 6H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 33.6 Hz), 2.08 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 128.4 Hz);
^{13}C NMR (125 MHz, $CDCl_3$): δ 180.0, 167.4, 140.6, 131.4, 130.5, 22.6, 22.1;
Elemental Analysis Calculated For $C_{14}H_{18}O_6Pb$: C, 34.35; H, 3.71. Found: C, 34.23; H, 3.60.



2,3,6-Trimethoxyphenyllead triacetate (S8). Prepared according to general procedure C, and the title compound was isolated as a yellow crystalline solid (1.12 g, 52%).
m.p. 120-121 °C;
IR (film) ν_{max} 2344, 2839, 1560, 1485 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 1H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 243.2 Hz), 3.99 (s, 3H), 3.84 (s, 3H), 3.83 (3H, s) 2.09 (s, 3H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 129.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.6, 153.1, 151.0, 149.5, 147.9, 117.6, 107.0, 61.7, 57.1, 56.0, 20.1;
Elemental Analysis: Calculated for $C_{15}H_{20}O_9Pb$: C, 32.67; H, 3.66. Found C, 32.98; H, 3.35.

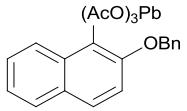


2-Methoxy-4,6-dimethylphenyllead triacetate (S9). Prepared according to general procedure C, and the title compound was isolated as a yellow crystalline solid (2.33 g, 34%).
m.p. 143-145 °C;
IR (film) ν_{max} 2941, 2361, 1576, 1399 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (s, 1H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 188.2 Hz), 6.67 (s, 1H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 209.0 Hz), 3.87 (s, 3H), 2.55 (s, 3H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 29.2 Hz), 2.34 (s, 3H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 17.0 Hz), 2.07 (s, 9H. ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 128.2 Hz);
^{13}C NMR (101 MHz, $CDCl_3$): δ 179.7, 157.2, 150.4, 143.4, 142.3, 126.6, 110.6, 56.4, 21.4, 20.6, 20.4.
Elemental Analysis: Calculated for $C_{15}H_{20}O_7Pb$: C, 34.68; H, 3.88. Found C, 34.60; H, 3.68.



2-Methoxynaphthyllead triacetate (S10). Prepared according to general procedure C, and the title compound was isolated as a yellow solid (0.78 g, 36%) with spectral data in agreement with literature values.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, app., 1H), 7.99 (d, app., *J* = 8.9 Hz, 1H), 7.85 (d, app., *J* = 8.2 Hz, 1H), 7.63 (m, 1H), 7.45 (t, app., *J* = 7.6 Hz, 1H), 7.34 (d, app., *J* = 8.9 Hz, 1H), 4.04 (s, 3H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 158.2 Hz), 2.11 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 128.4 Hz).



2-Benzyloxynaphthyllead triacetate (S11). Prepared according to general procedure C, and the title compound isolated as a yellow crystalline solid (1.3g, 22 % yield).

m.p. 157-159 °C;

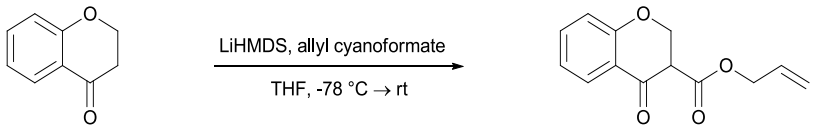
IR (film) ν_{max} 3583, 2368, 1594, 1560 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.63 (t, app., *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.46 – 7.23 (m, 6H), 5.36 (s, 2H), 2.00 (s, 9H, ^{207}Pb satellites gave $J_{H\text{-}Pb}$ = 128.8 Hz);

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.0, 155.2, 135.3, 134.6, 134.0, 131.5, 128.8, 128.7, 128.3, 127.6, 125.0, 124.6, 114.1, 109.9, 72.4, 18.5;

Elemental Analysis Calculated for $C_{23}H_{22}O_7Pb$: C, 44.73; H, 3.59. Found: C, 44.88; H, 3.37.

III. Procedure for the synthesis of allyl 4-oxochroman-3-carboxylate.



S12 **S13**

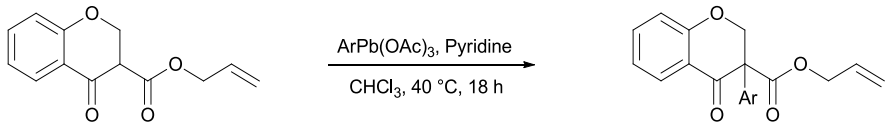
*n*BuLi (16 mL, 2.5 M in hexanes, 40 mmol) was added dropwise to a well stirred solution of HMDS (8.3 mL, 40 mmol) in THF (50 mL) at 0 °C. The solution was stirred for 30 min at this temperature before cooling to – 78 °C. 4-Chromanone **S12** (3g, 20 mmol) in THF (50 mL) was then added drop wise. After 60 min allyl cyanoformate (11.1g, 100 mmol) was added drop wise and the reaction mixture stirred at -78 °C for 30 min. The reaction was then allowed to warm to room temperature and quenched with a saturated aqueous NH_4Cl solution (150 mL). The mixture was then extracted with Et_2O (3 x 70 mL), the combined organic layers dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude oil was purified *via* column chromatography

(pentane/Et_2O, 4/1) to give the title compound as a pale orange oil (3.3g, 72% yield) consisting of a mixture of keto and enol tautomers with spectral data in agreement with literature values.[4]

R_f = 0.72 (pentane/Et_2O, 4/1);

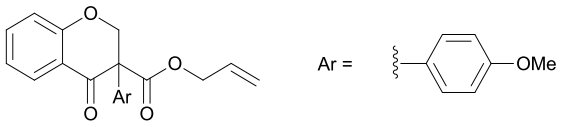
^{1}H NMR (300 MHz, $CDCl_3$): δ (keto tautomer) 7.93 (dd, app., *J* = 7.9, 1.6 Hz, 0.7 H), 7.50 (ddd, *J* = 8.3, 7.5, 2 Hz, 0.7H), 7.05 (t, app., *J* = 8.0 Hz, 0.7H), 6.99 (d, app., *J* = 8.3 Hz, 0.7H), 5.91 (m, 0.7H), 5.34 (m, 0.7H), 5.25 (m, 0.7H), 4.81 (dd, *J* = 11.6, 8.4 Hz, 0.7H), 4.69 (m, 1.4H), 4.64 (dd, *J* = 11.6, 4.5 Hz, 0.7H), 3.77 (dd, *J* = 8.4, 4.4 Hz, 0.7H); δ (enol tautomer) 11.92 (s, 0.3H), 7.66 (dd, app., *J* = 7.7, 1.5 Hz, 0.3H), 7.32 (m, 0.3H), 6.88 (d, app., *J* = 4.1 Hz, 0.3H), 5.99 (m, 0.6H), 5.36 (d, ap., *J* = 17.2 Hz, 0.3H), 5.30 (m, 0.3H), 4.97 (s, 0.6H), 4.71 (m, 0.6H).

IV. General procedure for the preparation of allyl 3-aryl-4-oxochroman-3-carboxylates.



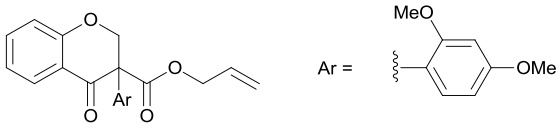
S13

To a stirred solution of allyl 4-oxochroman-3-carboxylate **S13** (1 equiv.) and aryllead triacetate (1.1 equiv.) in anhydrous $CHCl_3$ (0.6 M), was added dropwise anhydrous pyridine (3.3 equiv.). The resulting mixture was heated at 40 °C for 18 h. The reaction mixture was diluted with $CHCl_3$ (50 mL) and washed with 6% H_2SO_4 (2 x 50 mL). The aqueous phase was extracted with $CHCl_3$ (2 x 50 mL) and the combined organic extracts were washed with water (2 x 50 mL), dried over $MgSO_4$ and reduced *in vacuo* to give an orange oil. The crude oil was then purified *via* column chromatography.



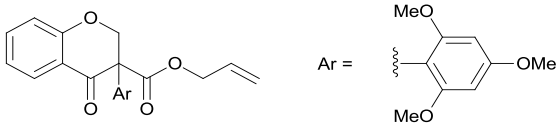
Allyl 3-(4-methoxyphenyl)-4-oxochroman-3-carboxylate (S14). Prepared according to the general procedure and the title compound was isolated as a white solid (0.457 g, 63%) with spectral data in agreement with literature values.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, app., *J* = 8.8 Hz, 1H), 7.45 (t, app., *J* = 7.6 Hz, 1H), 7.26 (m, 2H), 7.02 (d, app., *J* = 8.8 Hz, 1H), 6.90 (m, 3H), 5.83 (m, 1H), 5.20 (m, 2H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.92 (d, *J* = 12.0 Hz, 1H), 4.67 (m, 2H), 3.77 (s, 3H).



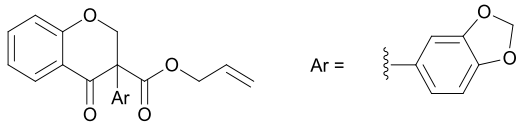
Allyl 3-(2,4-dimethoxyphenyl)-4-oxochroman-3-carboxylate (S15). Prepared according to the general procedure and the title compound was isolated as a white solid (0.378 g, 60%) with spectral data in agreement with literature values.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.48 (t, app., *J* = 8.3 Hz, 1H), 7.07 (t, app., *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.34 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.86 (m, 1H), 5.20 (m, 2H), 5.11 (d, *J* = 11.5 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.70 (m, 2H), 3.76 (s, 6H).



Allyl 4-oxo-3-(2,4,6-trimethoxyphenyl)chroman-3-carboxylate (S16). Prepared according to the general procedure and the title compound was isolated as a white solid (0.908 g, 80%) with spectral data in agreement with literature values.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.41 (ddd, *J* = 8.7, 7.5, 1.7 Hz, 1H), 7.03 (t, app., *J* = 7.5 Hz, 1H), 6.92 (d, app., *J* = 8.7 Hz, 1H), 6.10 (s, 2H), 5.88 (m, 1H), 5.21 (m, 2H), 4.97 (d, *J* = 11.5 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 5.5 Hz, 2H), 3.77 (s, 3H), 3.54 (s, 6H).



Allyl 3-(benzo[d][1,3]dioxol-5-yl)-4-oxochroman-3-carboxylate (S17). Prepared according to the general procedure and the title compound was isolated as a white solid (0.481 g, 78%).

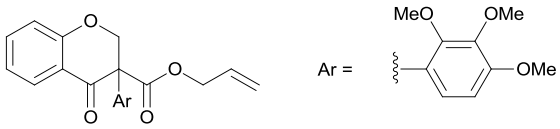
R_f = 0.34 (pentane/EtOAc, 5/1);

IR (film) ν_{max} 2898, 1735, 1691, 1607 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (t, app., *J* = 7.7 Hz, 1H), 7.04 (dd, *J* = 11.1, 3.9 Hz, 1H), 6.93 (d, app., *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 1.5 Hz, 1H), 6.78 (m, 2H), 5.94 (m, 2H), 5.82 (m, 1H), 5.21 (m, 2H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.67 (m, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 188.2, 168.2, 160.6, 147.9, 147.6, 136.1, 131.1, 128.1, 126.1, 121.9, 121.2, 120.2, 118.6, 117.6, 108.5, 108.3, 101.3, 71.7, 66.5, 61.6;

HRMS: (ESI-TOF) calculated for $C_{20}H_{16}O_6Na$ ([M + Na^+]) 375.0845, found 375.0847.



Allyl 4-oxo-3-(2,3,4-trimethoxyphenyl)chroman-3-carboxylate (S18). Prepared according to the general procedure and the title compound was isolated as a pale oil (0.371 g, 80%) after chromatography.

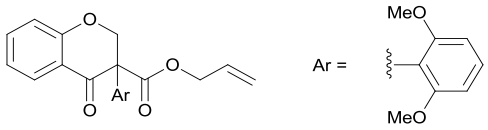
R_f = 0.43 (pentane/EtOAc, 4/1);

IR (film) ν_{max} 2947, 2254, 1734, 1695, 1606 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, app., *J* = 7.8 Hz, 1H), 7.48 (t, app, *J* = 7.8 Hz, 1H), 7.07 (t, app, *J* = 7.5 Hz, 1H), 6.95 (d, app, *J* = 7.5 Hz), 6.59 (d, *J* = 8.7 Hz, 1H), 6.52 (d, *J* = 8.7 Hz, 1H), 5.86 (m, 1H), 5.22 (m, 2H), 5.01 (d, *J* = 11.3 Hz, 1H), 4.89 (d, *J* = 11.3Hz, 1H), 4.76 (dd, *J* = 13.3, 4.4 Hz 1H), 4.68 (dd, *J* = 13.3, 4.4 Hz, 1H), 3.83 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 188.7, 168.6, 161.2, 154.1, 151.8, 142.1, 135.8, 131.3, 127.8, 122.7, 121.7, 121.0, 118.4, 117.8, 106.0, 72.3, 65.8, 61.3, 60.5, 60.2, 55.9;

HRMS: (ESI-TOF) calculated for $C_{22}H_{23}O_7$ ([M + H^+]) 399.1444, found 399.1434.



Allyl 3-(2,6-dimethoxyphenyl)-4-oxochroman-3-carboxylate (S19). Prepared according to the general procedure and the title compound was isolated as a white solid (0.384 g, 86%).

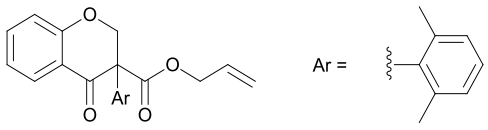
R_f = 0.27 (pentane/EtOAc, 4/1);

IR (film) ν_{max} 2253, 1735, 1692, 1607 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, app., *J* = 7.64 Hz, 1H), 7.42 (t, app., *J* = 7.64 Hz, 1H), 7.22 (m, 1H), 7.05 (t, *J* = 8.43 Hz, 1H), 6.92 (d, app., *J* = 8.43 Hz, 1H), 6.55(d, app., *J* = 8.31 Hz, 2H), 5.88 (m, 1H), 5.19 (m, 2H), 5.01 (d, *J* = 11.5 Hz, 1H), 4.92 (d, *J* = 11.5 Hz, 1H), 4.69 (d, *J* = 4.97, 2H), 3.56 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 188.2, 168.9, 160.8, 158.4, 134.6, 132.0, 129.6, 127.4, 122.2, 121.3, 117.9, 117.4, 113.7, 105.7, 72.0, 66.0, 59.0, 55.7;

HRMS: (ESI-TOF) calculated for $C_{21}H_{20}O_6Na$ ([M + Na^+]) 391.1158, found 391.1160.



Allyl 3-(2,6-dimethylphenyl)-4-oxochroman-3-carboxylate (S20). Prepared according to the general procedure and the title compound was isolated as a clear oil (0.306g, 70%).

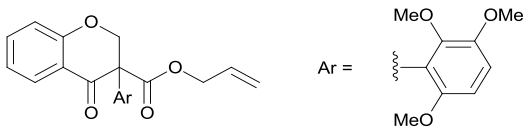
R_f = 0.37 (cyclohexane/methanol, 50/1);

IR (film) ν_{max} 2938, 2435 1728, 1693, 1605 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, app., *J* = 7.88 Hz, 1H), 7.49 (t, app., *J* = 7.88 Hz, 1H), 7.13 – 6.94 (5H, m), 5.83 (m, 1H), 5.19 (m, 2H), 5.04 (d, *J* = 12.3 Hz, 1H), 4.71 (m, 3H), 2.24 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 188.1, 169.0, 160.7, 137.7, 136.6, 133.3, 130.9, 130.6, 128.3, 127.7, 121.7, 120.3, 118.8, 117.9, 71.4, 66.6, 64.0, 23.4.

HRMS: (ESI-TOF) calculated for $C_{21}H_{20}O_4Na$ ([M + Na^+]) 359.1259, found 359.1255.



Allyl 4-oxo-3-(2,3,6-trimethoxyphenyl)chroman-3-carboxylate (S21). Prepared according to the general procedure and the title compound was isolated as a white solid (0.217 g, 84%).

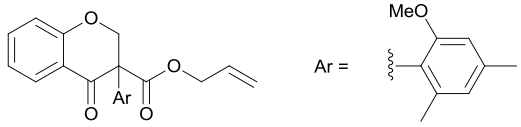
R_f = 0.30 (pentane/EtOAc, 3/1);

IR (film) ν_{max} 2939, 1734, 1691, 1608 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.41 (t, app., *J* = 8.2 Hz, 1H), 7.03 (t, app., *J* = 8.2 Hz, 1H), 6.91 (d, app., *J* = 8.2 Hz, 1H), 5.88 (m, 1H), 5.23 (m, 2H), 5.08 (d, *J* = 11.5 Hz, 1H), 4.91 (d, *J* = 11.5 Hz, 1H), 4.73 (dd, *J* = 13.4, 5.4 Hz, 1H), 4.65 (dd, *J* = 13.4, 5.4 Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 3.51 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 187.6, 168.6, 160.8, 151.8, 148.5, 147.3, 134.7, 131.9, 127.4, 122.0, 121.5, 119.6, 117.8, 117.4, 112.5, 106.7, 72.3, 66.0, 60.1, 59.5, 56.1, 56.0;

HRMS: (ESI-TOF) calculated for $C_{22}H_{22}O_5Na$ ([M + H^+]) 367.1545, found 367.1561.



Allyl 3-(2-methoxy-4,6-dimethylphenyl)-4-oxochroman-3-carboxylate (S22). Prepared according to the general procedure and the title compound isolated as a white solid (0.238 g, 75%).

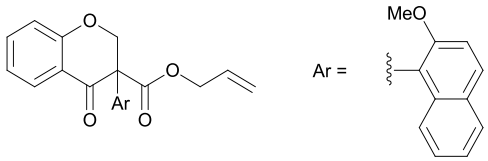
R_f = 0.66 (pentane/EtOAc, 4/1);

IR (film) ν_{max} 2938, 1730, 1692, 1606, cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, app., *J* = 8.0 Hz, 1H), 7.45 (t, app., *J* = 7.5 Hz, 1H), 7.04 (t, app., *J* = 7.5 Hz, 1H), 6.95 (d, app., *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 6.57 (s, 1H), 5.87 (m, 1H), 5.25 (d, *J* = 16.9 Hz, 1H), 5.16 (d, *J* = 11.1 Hz, 1H), 4.97 (d, *J* = 11.7 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.69 (m, 2H), 3.55 (s, 3H), 2.27 (s, 3H), 2.13 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 188.3, 169.1, 160.8, 157.5, 138.8, 138.0, 135.3, 131.5, 127.8, 126.4, 121.4, 121.3, 121.2, 118.4, 117.7, 111.5, 71.8, 66.0, 61.2, 55.5, 21.6, 21.1;

HRMS: (ESI-TOF) calculated for $C_{22}H_{23}O_5$ ([M + H^+]) 367.1545, found 367.1561.



Allyl 3-(2-methoxynaphthalen-1-yl)-4-oxochroman-3-carboxylate (S23). Prepared according to the general procedure and the title compound was isolated as a white solid (0.222 g, 89%).

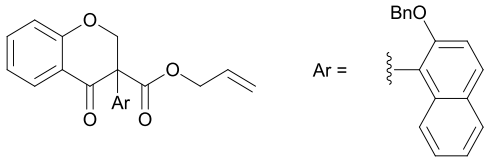
R_f = 0.58 (pentane/EtOAc, 4/1);

IR (film) ν_{max} 2942, 2383, 1724, 1690, 1605 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, app., *J* = 7.8 Hz, 1H), 7.81 (d, app., *J* = 8.8 Hz, 2H), 7.58 (d, app., *J* = 8.3 Hz, 1H), 7.44 (dd, app., *J* = 16.8, 8.8 Hz, 2H), 7.36 (m, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.10 (t, app., *J* = 7.8 Hz, 1H), 6.92 (d, app., *J* = 8.3 Hz, 1H), 5.77 (m, 1H), 5.15 (m, 4H), 4.74 (dd, *J* = 13.2, 5.6 Hz, 1H), 4.66 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.48 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 188.0, 169.9, 160.7, 155.7, 134.9, 132.2, 131.4, 131.1, 130.6, 129.5, 127.6, 126.7, 123.6, 121.9, 121.6, 118.5, 117.9, 117.5, 115.4, 72.5, 66.5, 60.9, 56.7;

HRMS: (ESI-TOF) calculated for $C_{22}H_{23}O_5$ ([M + H^+]) 367.1545, found 367.1561.



Allyl 3-(2-(benzyloxy)naphthalen-1-yl)-4-oxochroman-3-carboxylate (24). Prepared according to the general procedure and the title compound isolated as a white solid (0.563 g, 80%).

R_f = 0.57 (pentane/EtOAc, 3/1);

IR (film) ν_{max} 2931, 2876, 1724, 1691, 1605 cm^{-1};

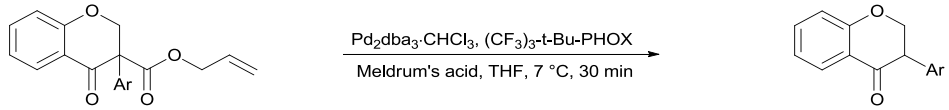
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, app., *J* = 8.0 Hz, 1H), 7.74 (d, app., *J* = 8.7 Hz, 1H), 7.59 (d, app., *J* = 8.7 Hz, 1H), 7.38 (m, 3H), 7.26 (m, 3H), 7.14 (m, 3H), 6.88 (m, 2H), 5.74 (m, 1H), 5.25 (m, 1H), 5.12 (m, 3H), 4.92 (d, *J* = 12.6 Hz, 1H), 4.81 (d, *J* = 12.6 Hz, 1H), 4.67 (dd, *J* = 13.2, 5.5 Hz, 1H), 4.57 (dd, *J* = 13.2, 5.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 187.8, 169.8, 160.7, 155.1, 136.3, 134.8, 132.5, 131.4, 131.1, 130.6, 129.4, 128.3, 127.9, 127.8, 127.2, 126.7, 123.6, 123.4, 121.8, 121.5, 118.4, 117.9, 117.3, 116.3, 72.6, 66.4, 61.1;

HRMS: (ESI-TOF) calculated for $C_{30}H_{25}O_5$ ([M + H^+]) 465.1702, found 465.1712.

V. General Procedure for the Preperation of Isoflavanones.

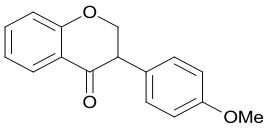
Representative Procedure for the Enantioselective Synthesis of Isoflavanones



Pd_2dba_3 (5.7 mg, 0.006 mmol) (*S*)-$(CF_3)_3$-*t*-Bu-PHOX (9.2 mg, 0.015 mmol) and freshly distilled THF (2 mL) were added to a flame dried 10 mL Schlenck tube and the resulting mixture stirred at 40 °C for 30 min. The reaction mixture was then cooled to 7 °C for 10 min before a THF solution (3 mL) of β-ketoester substrate (50 mg, 0.125 mmol) and Meldrum's acid (45 mg, 0.312 mmol) was added. The reaction mixture was stirred at 7 °C for 30 min before being filtered through a pad of silica and the solvent was removed *in vacuo* to give an orange oil. The orange oil was then purified by column chromatography.

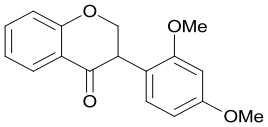
General Procedure for the Racemic Synthesis of Isoflavanones

Racemic isoflavanones were prepared in a manner analogous to the enantioselective procedure using 1,2-Bis(diphenylphosphino)ethane (0.125 equiv.) as an achiral ligand.



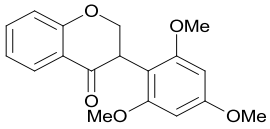
4'-Methoxyisoflavanone (S25). Prepared according to the general procedure and the title compound was isolated as a white solid (0.037 g, 98%) with spectral data in agreement with literature values.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.9, 1.6 1H), 7.20 (d, app., *J* = 8.7 Hz, 1H), 7.05 (d, app., *J* = 7.9 Hz, 1H), 7.00 (d, app., *J* = 8.7 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.64 (dd, *J* = 10.2, 4.2 Hz, 2H), 3.95 (m, 1H), 2.90 (s, 3H).



2',4'-Dimethoxyisoflavanone (S26). Prepared according to the general procedure and the title compound was isolated as a white solid (0.031 g, 85%) with spectral data in agreement with literature values.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49 (t, app., *J* = 7.8 Hz, 1H), 7.03 (m, 3H), 6.48 (m, 2H), 4.61 (t, app., *J* = 11.5, 5.5 Hz, 1H), 4.50 (dd, *J* =11.5, 5.5 Hz, 1H), 4.30 (dd, *J* = 12.0, 5.5 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H).

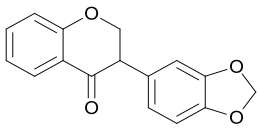


2',4',6'-Trimethoxyisoflavanone (S27). Prepared according to the general procedure and the title compound was isolated as a white solid (0.034 g, 92%) with spectral data in agreement with literature values.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 (t, app., *J* = 8.2 Hz, 1H), 7.02 (m, 2H), 6.16 (s, 2H), 4.69 (m, 2H), 4.35 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 190.5, 161.8, 161.5, 159.2, 136.2, 127.6, 121.7, 121.0, 117.6, 104.2, 91.3, 69.7, 55.7, 55.3, 43.5;

$[\alpha]_D^{20}$ = -62.7 $deg cm^3 g^{-1} dm^{-1}$ (*c* = 1.7 $g cm^{-3}$ in $CHCl_3$) for 92% *ee*.



3'4'-Methylenedioxyisoflavanone (S28). Prepared according to the general procedure and the title compound was isolated as a white solid (0.036 g, 72%).

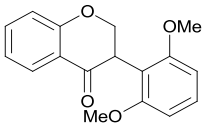
R_f = 0.27 (pentane/EtOAc, 8/1)

IR (film) ν_{max} 3055, 1689, 1606, 1452 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): 7.95 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.4, 1.6, 1.2 Hz, 1H), 7.04 (t, ap., *J* = 7.9 Hz, 1H), 7.00 (d, app., *J* = 8.4 Hz, 1H), 6.76 (m, 3H), 5.93 (m, 2H), 4.62 (m, 2H), 3.90 (dd, *J* = 8.9, 5.3 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$): 192.1, 161.4, 148.0, 147.2, 136.0, 128.5, 127.7, 121.9, 121.6, 120.9, 117.8, 108.9, 108.6, 101.1, 71.5, 51.9;

HRMS: (ESI-TOF) calculated for $C_{16}H_{12}O_4$ ([M + H^+]) 268.0736, found 268.0741



2',6'-Dimethoxyisoflavanone (S29). Prepared according to the general procedure and the title compound was isolated as a white solid (0.031 g, 83%).

R_f = 0.30 (pentane/EtOAc, 7/1);

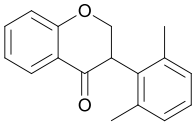
IR (film) ν_{max} 3155, 2962, 1739, 1719 1475 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 (t, app., *J* = 7.8 Hz, 1H), 7.25 (m, 1H), 7.02 (m, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.76 (m, 2H), 4.38 (m, 1H), 3.75 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.5, 161.8, 158.5, 135.0, 129.1, 127.6, 121.7, 121.1, 117.7, 111.7, 104.4, 69.4, 55.8, 43.7 ;

HRMS: (ESI-TOF) calculated for $C_{17}H_{16}O_4Na$ ([M + Na^+]) 307.0946, found 307.0938.

$[\alpha]_D^{20}$ = -84.0 $degcm^3g^{-1}dm^{-1}$ (*c* = 0.2 gcm^{-3} in $CHCl_3$) for 85% *ee*.



2',6'-Dimethylisoflavanone (S30). Prepared according to the general procedure and the title compound was isolated as a white solid (0.033 g, 86%).

R_f = 0.61 (pentane/EtOAc, 4/1);

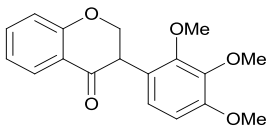
IR (film) ν_{max} 2963, 1689, 1605, 1496 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, app., *J* = 8.3 Hz, 1H), 7.52 (t, app., *J* = 8.3 Hz, 1H), 7.08 (m, 5H), 4.62 (m, 2H), 4.46 (dd, *J* = 9.0, 4.4 Hz, 1H), 2.31 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.0, 161.6, 137.3, 135.9, 131.4, 129.1, 127.8, 127.6, 121.6, 121.3, 117.9, 69.2, 49.6, 21.7;

HRMS: (ESI-TOF) calculated for $C_{17}H_{16}O_2$ ([M + Na^+]) 275.1048, found 275.1047.

$[\alpha]_D^{20}$ = -4.7 $degcm^3g^{-1}dm^{-1}$ (*c* = 1.0 gcm^{-3} in $CHCl_3$) for 71% *ee*.



2',3',4'-Trimethoxyisoflavanone (S31). Prepared according to the general procedure and the title compound isolated as a pale oil (0.032 g, 87%).

R_f = 0.59 (pentane/EtOAc, 2/1);

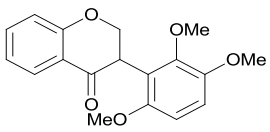
IR (film) ν_{max} 3007, 2941, 1690, 1604, 1464 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.50 (t, app., *J* = 7.8 Hz, 1H), 7.04 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 4.63 (m, 1H), 4.50 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.23 (dd, *J* = 12.3, 5.6 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.7, 161.8, 153.6, 151.9, 142.3, 135.6, 127.6, 124.3, 121.5, 121.4, 121.1, 117.8, 107.3, 71.1, 60.7, 60.6, 55.9, 48.7;

HRMS: (ESI-TOF) calculated for $C_{18}H_{20}O_5$ ([M + H^+]) 315.1232, found 315.1224.

$[\alpha]_D^{20}$ = -20.8 degcm^{3}g^{-1}dm^{-1} (*c* = 2.0 gcm^{-3} in $CHCl_3$) for 51% *ee*.



2',3',6'-Trimethoxyisoflavanone (S32). Reaction performed on a 38 mg scale. Prepared according to the general procedure and the title compound isolated as a white solid (0.027 g, 90%).

R_f = 0.51 (pentane/EtOAc, 4/1);

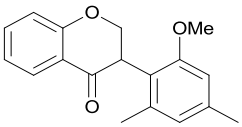
IR (film) ν_{max} 2941, 1691, 1605, 1487, 1458 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 (t, app., *J* = 8.3 Hz, 1H), 7.04 (t, app., *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.60 (d, *J* = 9.0 Hz, 1H), 4.78 (dd, *J* = 13.1, 10.4 Hz, 1H), 4.68 (dd, *J* = 13.1, 5.6 Hz, 1H), 4.38 (dd, *J* = 10.4, 5.6 Hz, 1H) 3.82 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 192.5, 161.9, 160.4, 152.1, 148.4, 147.1, 136.2, 127.5, 121.6, 121.2, 118.2, 117.8, 112.4, 106.2, 69.7, 56.2, 56.1, 44.6;

HRMS: (ESI-TOF) calculated for $C_{18}H_{20}O_5$ ([M + H^+]) 315.1232, found 315.1223.

$[\alpha]_D^{20}$ = -69.5 degcm^{3}g^{-1}dm^{-1} (*c* = 0.12 gcm^{-3} in $CHCl_3$) for 85% *ee*.



2'-Methoxy-4',6'-dimethylisoflavanone (S33). Performed on a 13 mg scale. Prepared according to the general procedure and the title compound isolated as a clear oil (0.012 g, 93%).

R_f = 0.64 (pentane/EtOAc, 4/1);

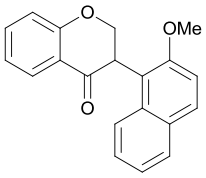
IR (film) ν_{max} 2361, 1700, 1654, 1605, 1477 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, app., *J* = 8.0 Hz, 1H), 7.48 (t, app., *J* = 7.7 Hz, 1H), 7.05 (t, app., *J* = 7.7 Hz, 1H), 7.00 (d, app., *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 6.59 (s, 1H), 4.76 (m, 1H), 4.36 (m, 2H), 3.66 (s, 3H), 2.31 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.3, 161.1, 157.4, 147.7, 138.5, 138.2, 135.2, 130.8, 127.6, 124.1, 121.3, 117.7, 110.6, 69.3, 55.5, 42.8, 29.9, 21.4;

HRMS: (ESI-TOF) calculated for $C_{18}H_{18}O_3Na$ ([M + Na^+]) 305.1154, found 305.1147;

$[\alpha]_D^{20}$ = -5.8 degcm^{3}g^{-1}dm^{-1} (*c* = 0.11 gcm^{-3} in $CHCl_3$) for 75% *ee*.



2'-Methoxynaphthylisoflavanone (S34). Prepared according to the general procedure and the title compound was isolated as a white solid (0.035g, 89%).

R_f = 0.58 (pentane/EtOAc, 3/1);

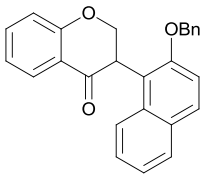
IR (film) ν_{max} 2932, 1653, 1560, 1436 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, app., *J* = 7.6 Hz, 1H), 7.85 (m, 3H), 7.51 (m, 2H), 7.37 (t, app., *J* = 7.5 Hz, 1H), 7.30 (d, app., *J* = 9.0 Hz, 1H), 7.09 (t, app., *J* = 7.6 Hz 1H), 7.06 (d, app., *J* = 8.4 Hz, 1H), 4.96 (s, 1H), 4.87 (m, 1H), 4.50 (m, 1H), 3.83 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.4, 161.8, 155.2, 136.4, 134.8, 130.0, 129.6, 128.9, 127.7, 127.0, 123.6, 121.8, 121.5, 117.8, 117.7, 114.8, 114.0, 69.5, 56.4, 46.0;

HRMS: (ESI-TOF) calculated for $C_{20}H_{16}O_3$ ([M + H^+]) 304.1099, found 304.1104

$[\alpha]_D^{20}$ = -144.7 $degcm^3g^{-1}dm^{-1}$ (*c* = 0.1 gcm^{-3} in $CHCl_3$) for 89% *ee*.



2'-Benzyloxynaphthylisoflavanone (S35). Prepared according to the general procedure and the title compound was isolated as a white solid (0.065 g, 81%).

R_f = 0.30 (pentane/EtOAc, 8/1);

IR (film) ν_{max} 2353, 2338, 1690, 1604, 1478 cm^{-1};

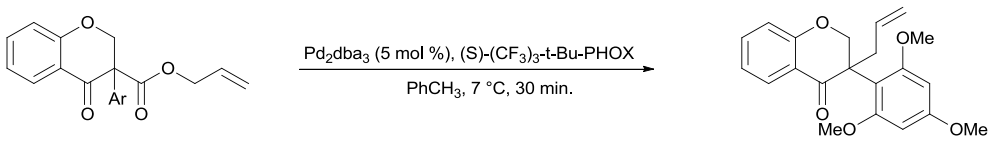
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (m, 3H), 7.48 (m, 2H), 7.29 (m, 7H), 7.00 (m, 2H), 5.14 (m, 2H), 4.98 (s, ap., 1H), 4.87 (dd, *J* = 13.3, 10.7 Hz, 1H), 4.46 (dd, *J* = 10.7, 5.7 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.3, 161.6, 154.3, 136.5, 133.1, 130.0, 129.7, 128.9, 128.3, 127.8, 127.3, 127.0, 123.7, 121.8, 121.4, 122.6, 117.7, 116.9, 114.8, 71.4, 69.4, 46.1;

HRMS: (ESI-TOF) calculated for $C_{26}H_{20}O_3$ ([M + H^+]) 381.1491, found 381.1497;

$[\alpha]_D^{20}$ = -56.3 $degcm^3g^{-1}dm^{-1}$ (*c* = 1.4 gcm^{-3} in $CHCl_3$) for 87% *ee*.

VI. Synthesis of 3-Allyl-3-(2,4,6-trimethoxyphenyl)chroman-4-one



S16 **S36**

Pd_2dba_3 (5.6 mg, 0.006 mmol) and (*S*)-$(CF_{3)3}$-*t*-Bu-PHOX (9.2 mg, 0.015 mmol) and anhydrous $PhCH_3$ (2 mL) were added to a flame dried 10 mL Schlenck flask and the resulting mixture heated at 40 °C for 30 min. The mixture was then cooled to 7 °C for 10 min before allyl 4-oxo-3-(2,4,6-trimethoxyphenyl)chroman-3-carboxylate (50 mg, 0.125 mmol) in anhydrous $PhCH_3$ (3 mL) was added. The reaction mixture was then stirred at this temperature for 30 min before being filtered through a pad of silica and the solvent being removed *in vacuo* to give an orange oil which was purified *via* column chromatography (Pentane/ CH_2Cl_2, 1/3) to give the product as a white solid (34 mg, 77%)

R_f = 0.37 (pentane/CH_2Cl_2, 1/3);

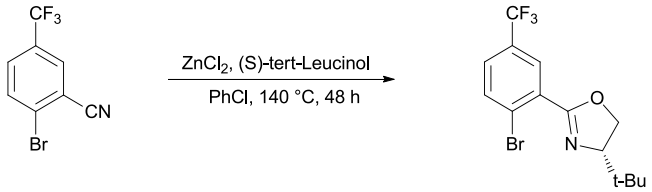
IR (film) ν_{max} 2964, 1691, 1608, 1480, 1464 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, app., *J* = 7.8 Hz, 1H), 7.35 (t, app., *J* = 7.5 Hz, 1H), 6.99 (t, app., *J* = 7.5 Hz, 1H), 6.84 (d, app., *J* = 8.03 Hz, 1H), 6.08 (s, 2H), 5.91 (m, 1H), 5.10 (d, *J* = 11.4 Hz, 1H), 4.92 (m, 2H), 4.09 (d, *J* = 11.4 Hz, 1H), 3.75 (s, 3H), 3.63 (s, 6H), 3.04 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.69 (*J* = 14.2, 6.8 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.6, 159.4, 159.2, 158.9, 134.2, 132.7, 126.6, 121.3, 119.9, 115.9, 115.4, 106.5, 91.3, 72.8, 54.5, 54.1, 50.6, 36.1;

HRMS: (ESI-TOF) calculated for $C_{21}H_{23}O_5$ ([M + H^+]) 355.1545, found 355.1534;

VII. Synthesis of (*S*)-$(CF_3)_3$-*t*-Bu-PHOX



S37 **S38**

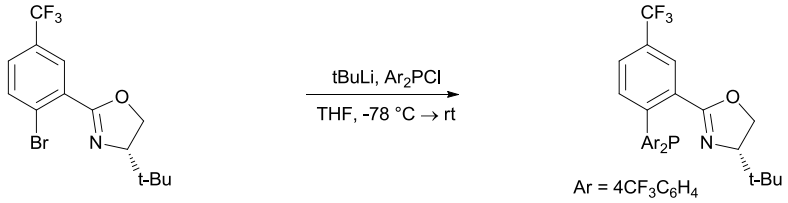
(*S*)-2-(2-Bromo-5-(trifluoromethyl)phenyl)-4-*tert*-4,5-dihydrooxazole. 2-Bromo-5-(trifluoromethyl)benzonitrile (2.0 g, 8 mmol), and (*S*)-*tert*-Leucinol (0.94 g, 8 mmol) were dissolved in anhydrous chlorobenzene (8 mL) in a dry 50 mL Schlenck flask. The reaction mixture was heated to 60 °C in an oil bath and $ZnCl_2$ (1.6 mL, 1.6 mmol, 1M in diethyl ether) was added drop wise. The temperature of the oil bath was increased to 140 °C and the reaction stirred under N_2 for 48 hours. After this time the reaction was cooled to room temperature and the solvent removed *in vacuo* to produce a brown oil which was purified *via* column chromatography (pentane/EtOAc, 9/1) to give the title compound as a pale yellow oil (2.44 g, 87%) with spectral data in agreement with literature values.[14]

R_f = 0.67 (pentane/EtOAc, 9/1);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.9 Hz, 1H), 4.41 (m, 1H), 4.28 (t, ap. *J* = 8.4 Hz, 1H), 4.14 (m, 1H), 1.00 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.4, 134.4, 130.9, 128.2, 127.8, 125.9, 124.7, 69.1, 33.9, 25.8, 22.3, 13.9;

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.86.



S38 **S39**

(*S*)-2-(Bis(4-(trifluoromethyl)phenyl)phosphine)-5-(trifluoro)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole. (*S*)-2-(2-Bromo-5-(trifluoromethyl)phenyl)-4-*tert*-4,5-dihydrooxazole (0.738g, 2.1 mmol) was dissolved in THF (10.5 mL) at -78 °C. *t*BuLi (2.88 mL, 1.6M in hexanes, 4.62 mmol) was added drop wise. The reaction mixture was stirred at -78 °C for 1h before chlorobis[4-(trifluoromethyl)phenyl]phosphine (1g, 2.8 mmol) was added drop wise. The reaction was allowed to warm to room temperature and stirred for 1h. The reaction mixture was then poured into a separatory funnel containing saturated aqueous NH_4Cl solution (20 mL). The phases were separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine (40 mL) dried over $MgSO_4$ and the solvent reduced *in vacuo* to give an orange oil which was purified *via* column chromatography to give the title compound as a white solid (0.989 g, 76%) with spectral data in agreement with literature values.[14]

R_f = 0.41 (Pentane/CH_2Cl_2, 5/1);

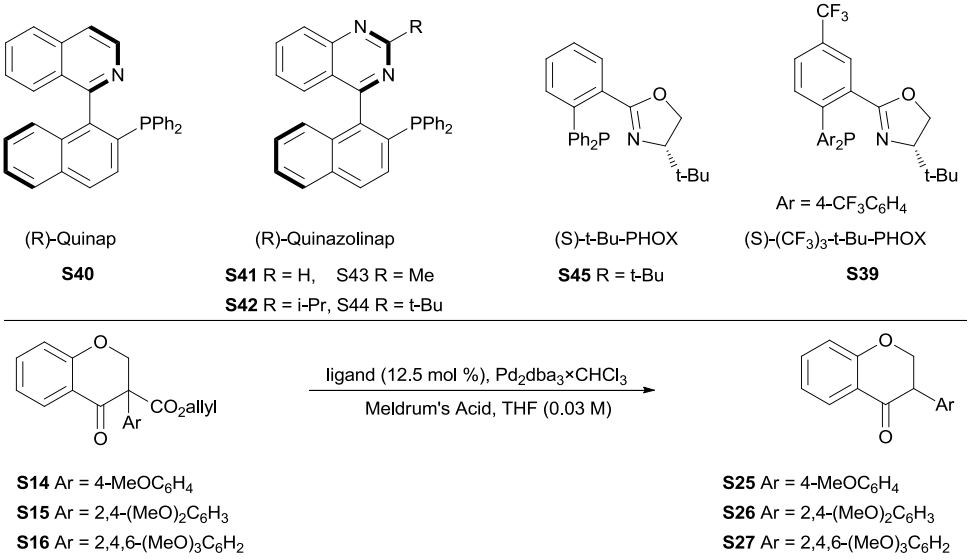
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.58 (m, 5H), 7.32 (m, 4H), 6.96 (dd, *J* = 8.4, 1.9 Hz, 1H), 4.24 (t, ap., *J* = 9.4 Hz, 1H), 4.09 (t, ap., *J* = 8.6 Hz, 1H), 3.94 (t, ap., *J* = 9.4 Hz, 1H), 2.17 (s, 9H);

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.96;

^{31}P NMR (162 MHz, $CDCl_3$): δ -7.11.

VIII. Optimization of Decarboxylative Protonation Reaction

Table S.1 *Screening of P,N-ligands and optimization of decarboxylative protonation conditions.*

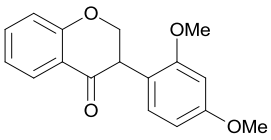
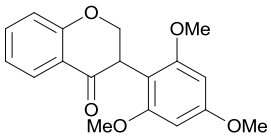
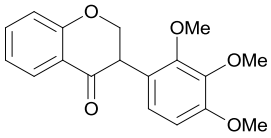
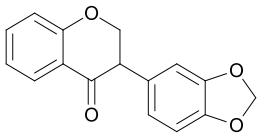
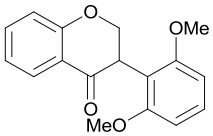
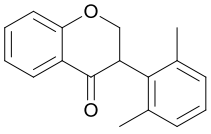
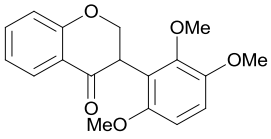


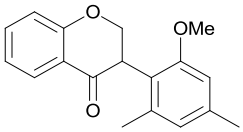
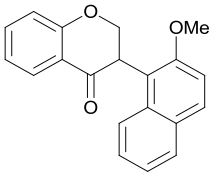
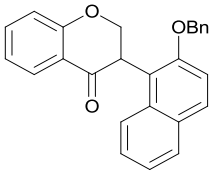
entry	ligand	substrate	temp.(°C)	time(h)	conv.[a] (%)	ee[b], (%)
1	S39	S14	rt	1	100	13
2	S40	S14	rt	1	>85	7
3	S41	S14	rt	1	100	4
4	S41	S14	0	12	<10	nd
5	S42	S14	rt	1	100	nd
6	S43	S14	rt	1	100	nd
7	S44	S14	rt	1	100	7
8	S44	S15	rt	1	100	19
9	S38	S16	rt	1	100	78(*R*)[c]
10	S38	S16	0	1	100	89(*R*)[c]
11	S38	S16	7	0.5	100	92(*R*)[c]
12	S38	S16	rt	0.5	100	78(*R*)[c]
13	S38	S15	7	0.5	100	35
14[d]	S38	S16	7	1	100	73
15	S38	S16	-20	48	0	nd

[a]Determined by HPLC or ^{1}H NMR spectroscopy. [b]Determined by chiral phase HPLC. [c]Determined by x-ray crystallography. [d]2.5 mol% of Pd_2dba_3 used.

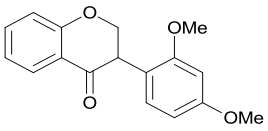
IX. Methods for determination of Enantiomeric excess

Table S.2 *Methods utilised for determination of enantiomeric excess.*

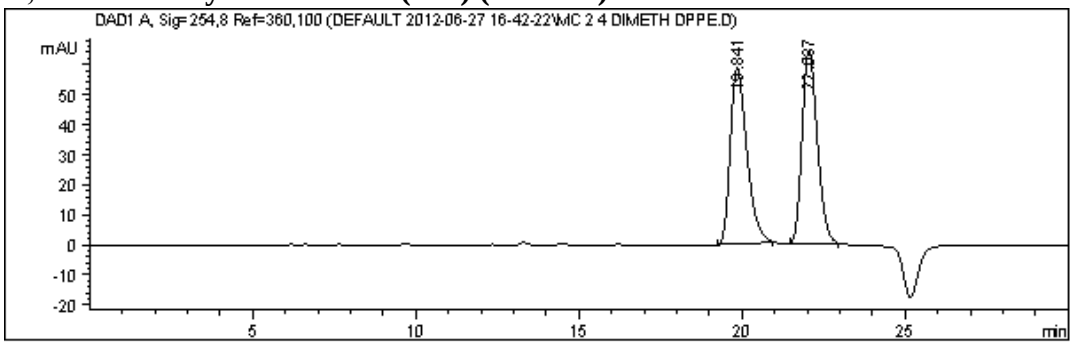
Entry	Product	Assay Conditions	retention time (min) of major enantiomer	retention time (min) of minor enantiomer	% *ee*
1		HPLC Chiralpak – ASH 96/4, Heptane/EtOH Isocratic, 1mL/min	22.05	19.67	35
2		HPLC Chiralpak – ASH 96/4, Heptane/EtOH Isocratic, 0.6mL/min	17.67	19.88	92
3		HPLC Chiralpak – IA 96/4, Heptane/EtOH Isocratic, 1mL/min	22.50	15.32	51
4		HPLC Chiralpak – IB 99/1, Heptane/EtOH Isocratic, 1mL/min	16.23	18.96	23
5		HPLC Chiralpak – IB 96/4, Heptane/EtOH Isocratic, 1mL/min	11.76	10.16	85
6		HPLC Chiralpak – IB 995/005, Heptane/EtOH Isocratic, 1mL/min	15.42	10.71	71
7		HPLC Chiralpak – IB 96/4, Heptane/EtOH Isocratic, 1mL/min	10.04	8.49	85

8		HPLC Chiralpak – IB 96/4, Heptane/EtOH Isocratic, 1mL/min	7.78	5.73	75
9		HPLC Chiralpak – IB 85/15, Heptane/EtOH Isocratic, 1mL/min	8.30	6.49	89
10		HPLC Chiralpak – IB 85/15, Heptane/EtOH Isocratic, 1mL/min	10.59	7.46	87

X. HPLC Chromatograms



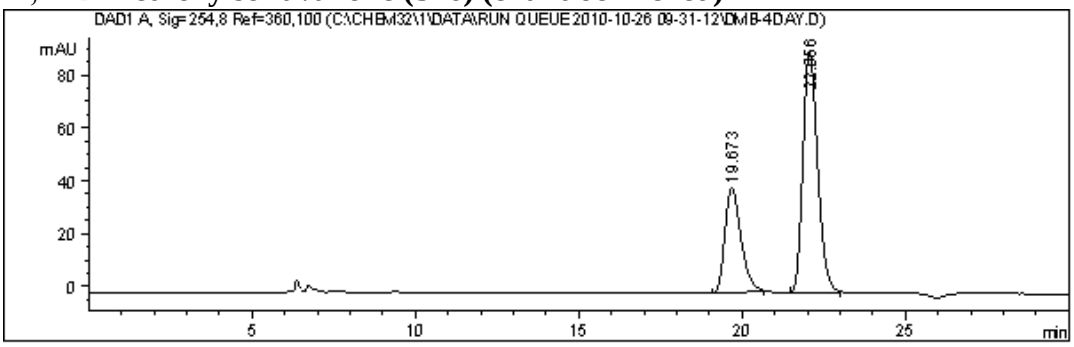
2',4'-Dimethoxyisoflavanone (S26) (racemic)



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

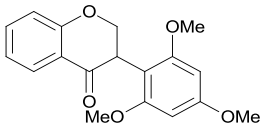
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.841	BB	0.5449	2081.65186	58.53414	49.8441
2	22.037	BB	0.5009	2094.67725	64.49146	50.1559
Totals :				4176.32910	123.02560	

2',4'-Dimethoxyisoflavanone (S26) (enantioenriched)

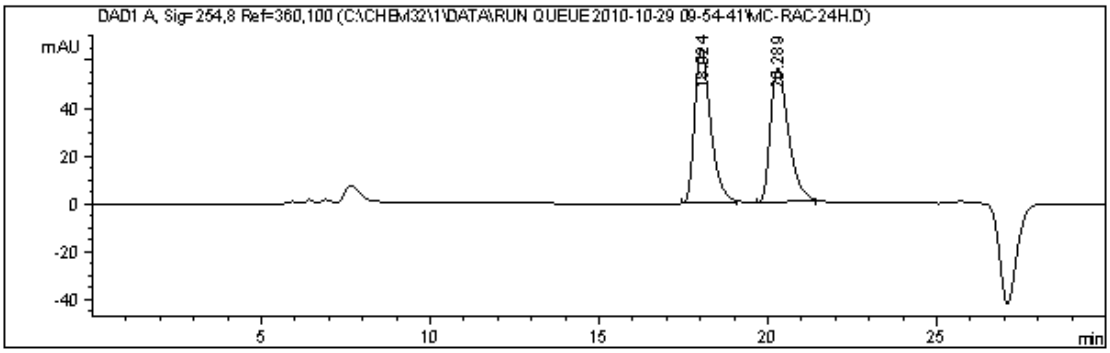


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.673	BB	0.5302	1362.26831	39.51256	32.2641
2	22.056	BB	0.4838	2859.97583	91.71723	67.7359
Totals :				4222.24414	131.22979	



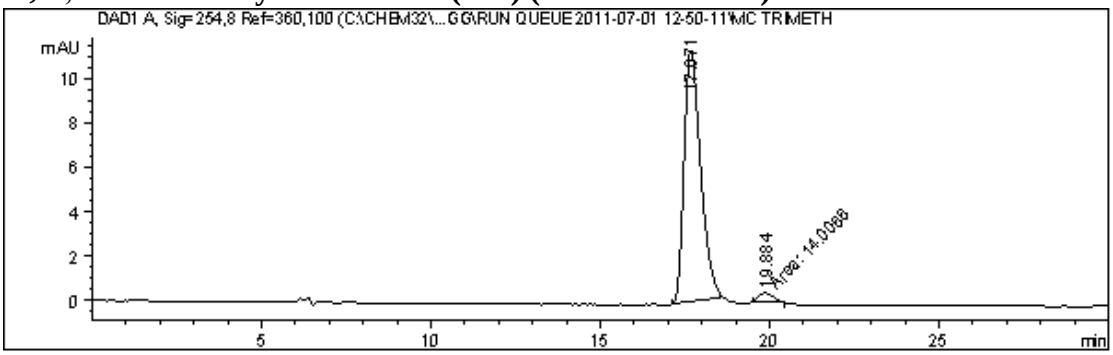
2,'4',6'-Trimethoxyisoflavanone (S27) (racemic)



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

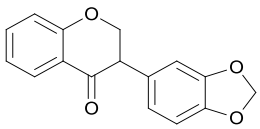
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.024	BB	0.5013	2144.19434	64.92616	50.5148
2	20.289	BB	0.5718	2100.49487	56.22941	49.4852
Totals :				4244.68921	121.15556	

2',4',6'-Trimethoxyisoflavanone (S27) (enantioenriched)

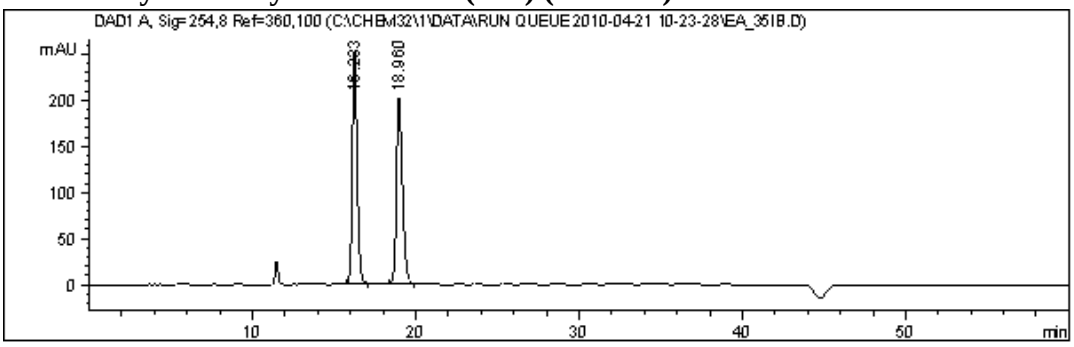


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.671	BB	0.5119	385.15936	11.34926	96.4910
2	19.884	MM	0.5227	14.00665	4.46575e-1	3.5090
Totals :				399.16601	11.79583	



3’4’-Methylenedioxyisoflavanone (S28) (racemic)

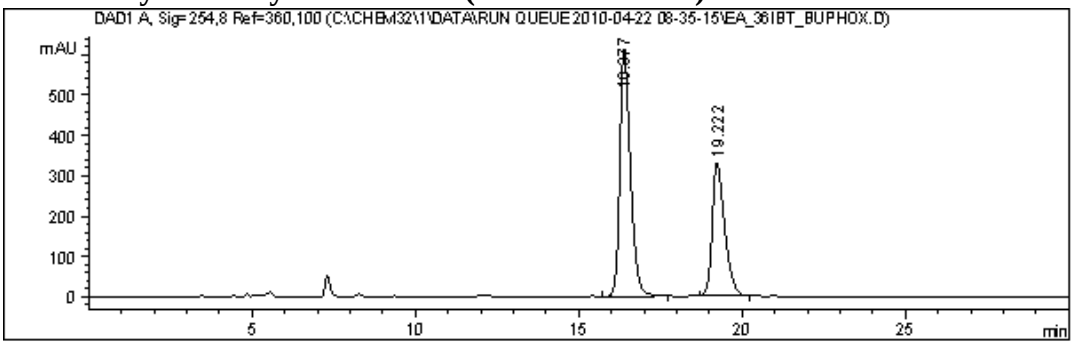


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.233	BB	0.3100	5161.76318	253.00961	50.1812
2	18.960	BB	0.3812	5124.48438	202.55074	49.8188

Totals : 1.02862e4 455.56035

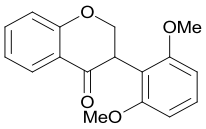
3’4’-Methylenedioxyisoflavanone (enantioenriched)



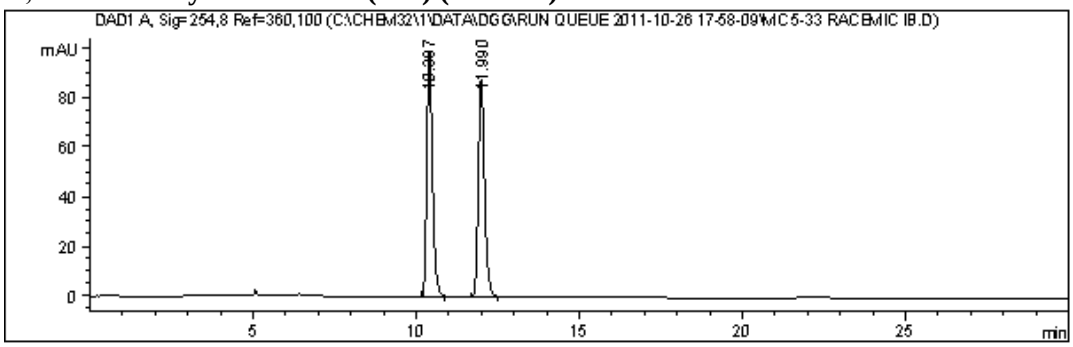
Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.377	VB	0.3393	1.38451e4	613.37476	61.2656
2	19.222	BB	0.3962	8753.41895	331.40079	38.7344

Totals : 2.25986e4 944.77554



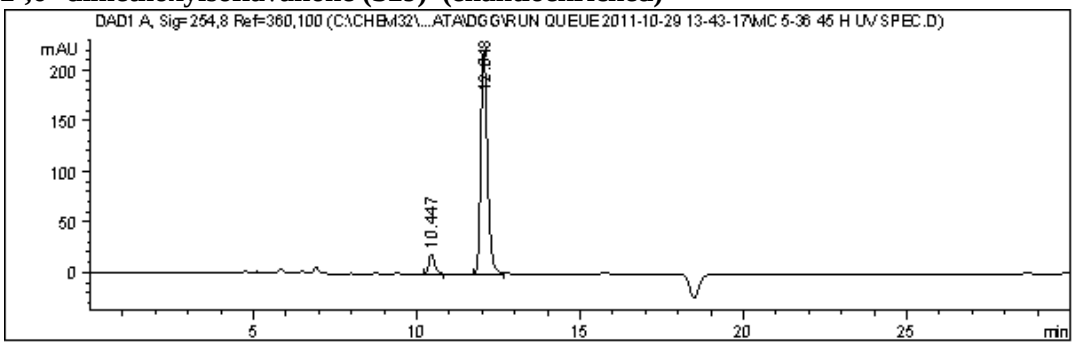
2',6'-Dimethoxyisoflavanone (S29) (racemic)



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

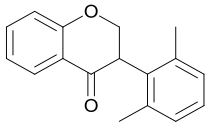
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.397	BB	0.1826	1192.01501	98.93672	50.3005
2	11.990	BB	0.2025	1177.77087	87.79649	49.6995

2',6'-dimethoxyisoflavanone (S29) (enantioenriched)

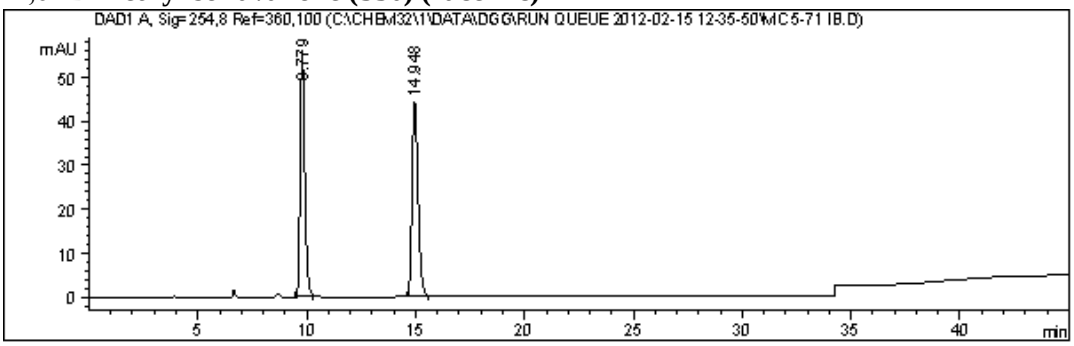


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.447	BB	0.1860	243.51949	20.00692	7.1954
2	12.048	BB	0.2180	3140.87573	220.73814	92.8046



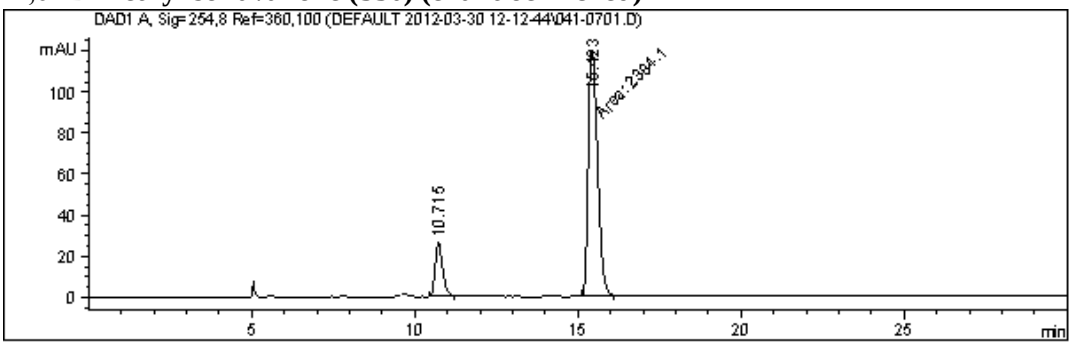
2',6'-Dimethylisoflavanone (S30) (racemic)



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

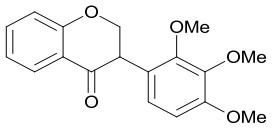
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.779	BB	0.2211	825.20447	56.27131	49.3131
2	14.948	BB	0.2935	848.19470	44.27385	50.6869

2',6'-Dimethylisoflavanone (S30) (enantioenriched)

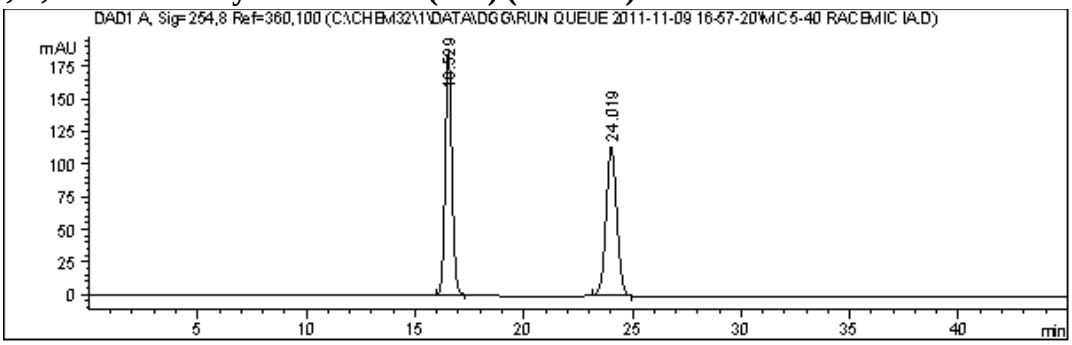


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.715	BB	0.2406	418.55402	26.17146	14.9342
2	15.423	MM	0.3314	2384.10181	119.89255	85.0658



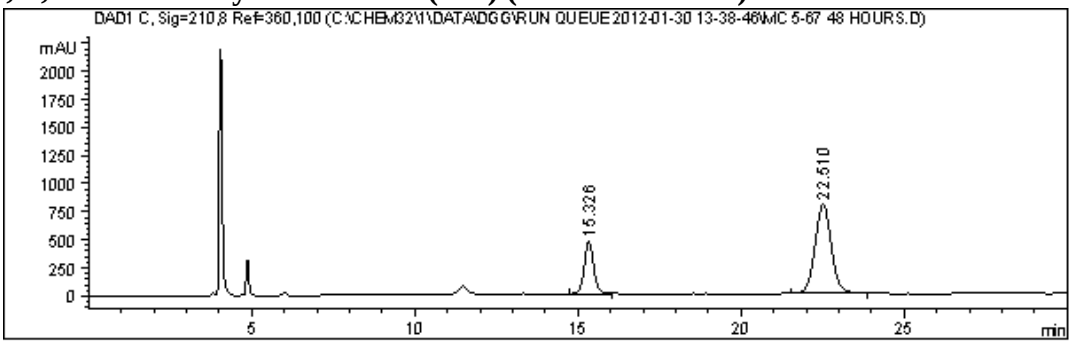
2’,3’,4’-Trimethoxyisoflavanone (S31) (racemic)



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

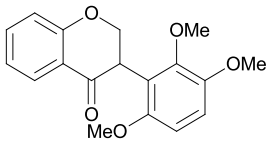
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.529	BB	0.3289	4057.20801	188.64003	50.9320
2	24.019	BB	0.5271	3908.72266	114.27161	49.0680

2’,3’,4’-Trimethoxyisoflavanone (S31) (enantioenriched)

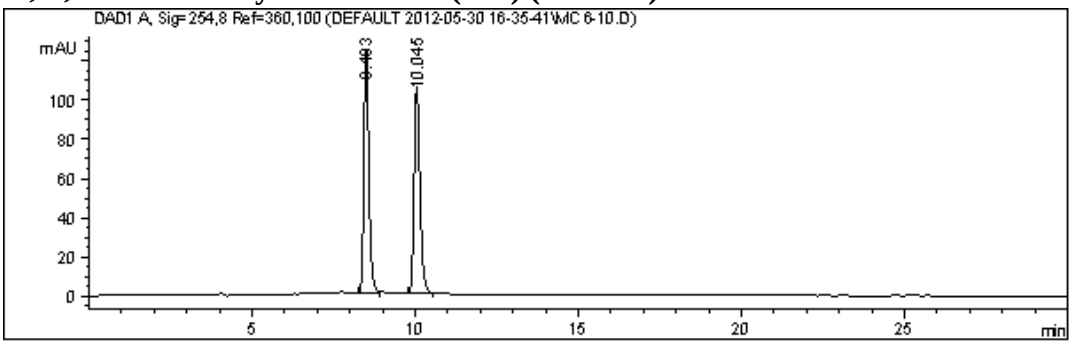


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.326	BB	0.3041	9185.74316	461.77859	24.8890
2	22.510	BB	0.5424	2.77211e4	791.92230	75.1110



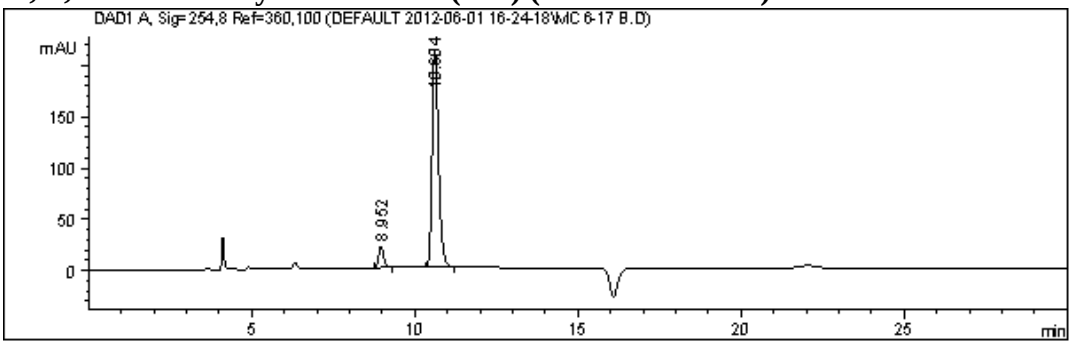
2’,3’,6’-Trimethoxyisoflavanone (S32) (racemic)



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

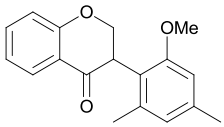
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.493	BB	0.1584	1304.60791	124.30222	49.8592
2	10.045	BB	0.1889	1311.97473	105.62945	50.1408

2’,3’,6’-Trimethoxyisoflavanone (S32) (enantioenriched)

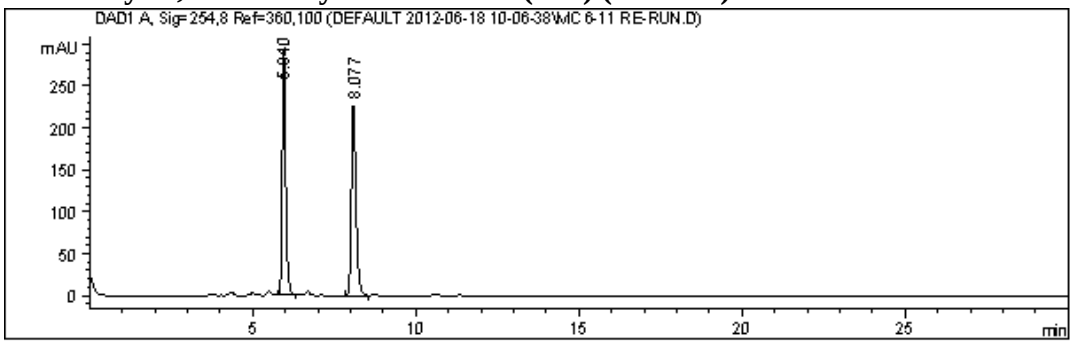


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.952	BB	0.1699	236.12476	21.21287	7.5199
2	10.604	BB	0.2095	2903.86548	212.39406	92.4801



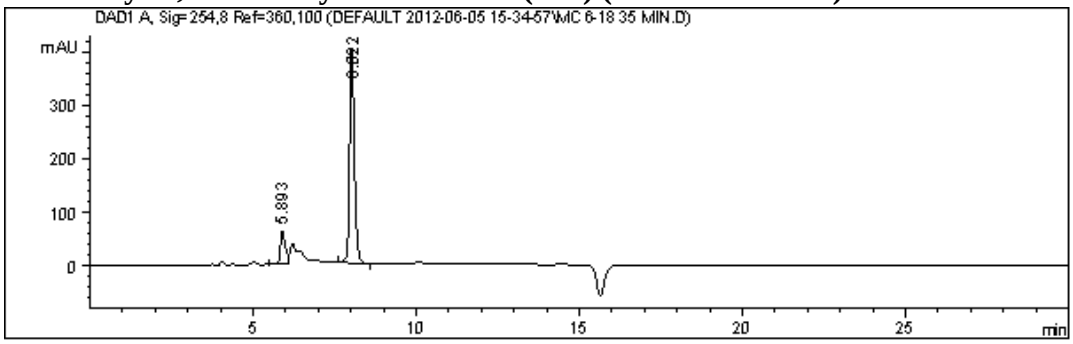
2'-Methoxy-4',6'-dimethylisoflavanone (S33) (racemic)



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

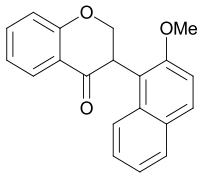
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.940	VB	0.1124	2172.69800	293.23044	49.1385
2	8.077	BB	0.1512	2248.87939	227.73228	50.8615
Totals :				4421.57739	520.96272	

2'-Methoxy-4',6'-dimethylisoflavanone (S33) (enantioenriched)

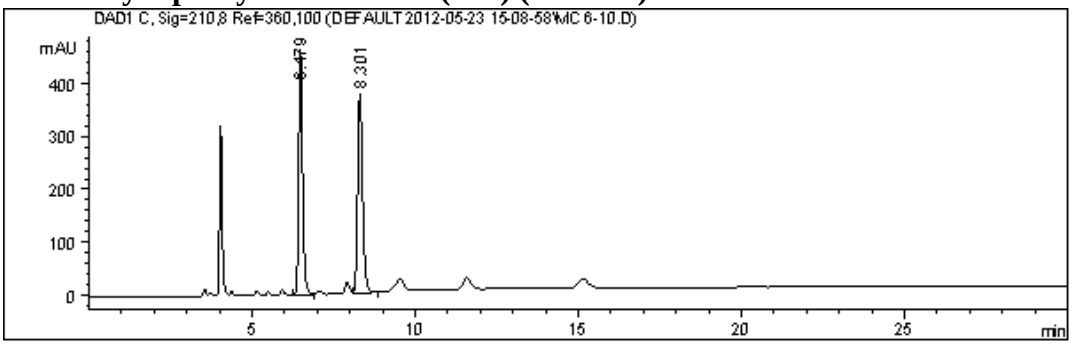


Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.893	VV	0.1451	620.90015	62.93204	13.1788
2	8.022	BB	0.1548	4090.47070	401.73419	86.8212
Totals :				4711.37085	464.66624	



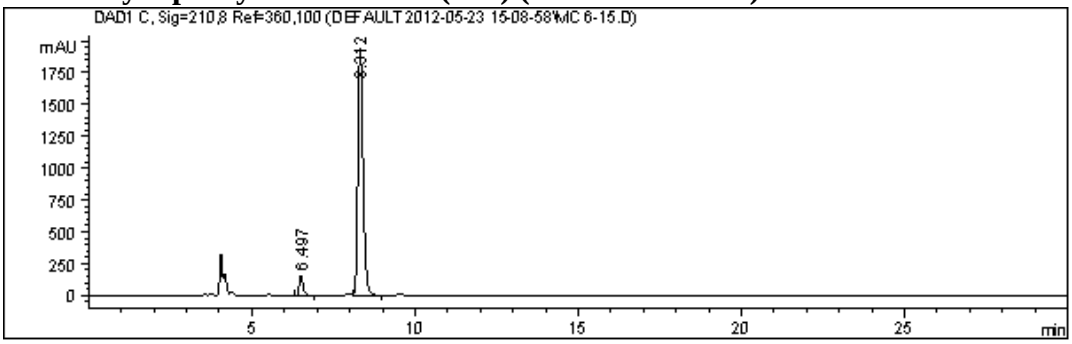
2'-Methoxynaphthylisoflavanone (S34) (racemic).



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

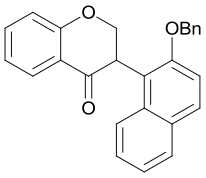
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.479	VV	0.1246	3850.03955	465.04099	49.1212
2	8.301	VB	0.1614	3987.79907	377.08331	50.8788

2'-Methoxynaphthylisoflavanone (S34) (enantioenriched).

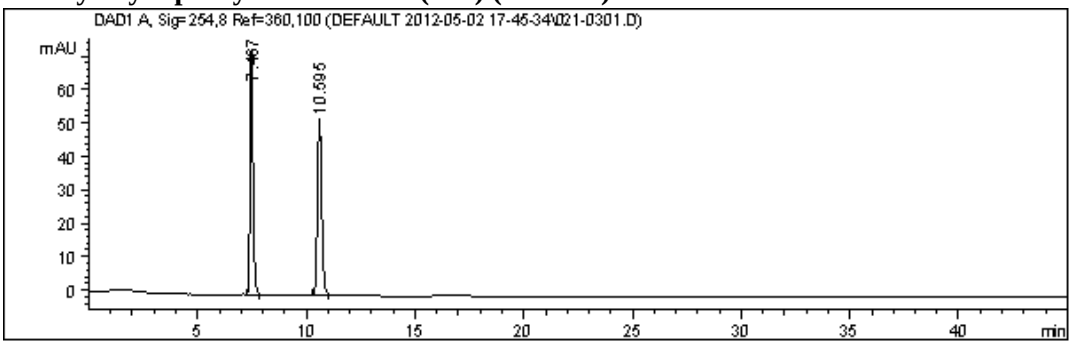


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.497	VB	0.1249	1309.36975	157.60234	5.7639
2	8.312	VB	0.1705	2.14073e4	1944.12097	94.2361



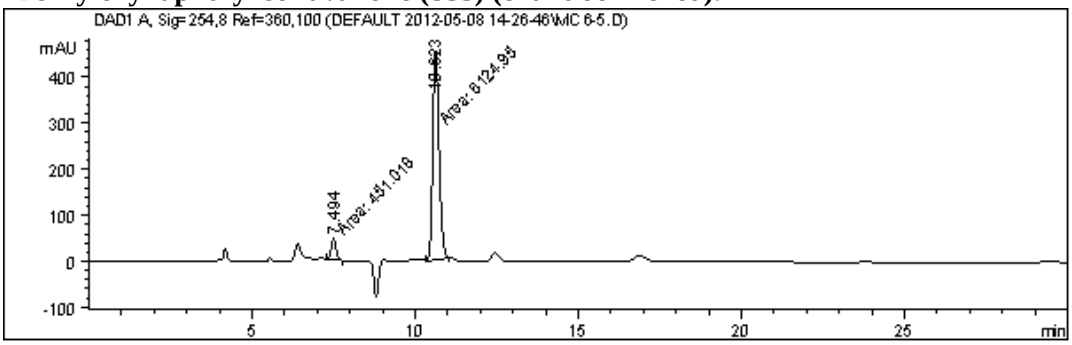
2'-Benzyloxynaphthylisoflavanone (S35) (racemic).



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.467	BB	0.1472	712.69965	73.45382	49.8148
2	10.595	BB	0.2091	717.99786	52.66039	50.1852

2'-Benzyloxynaphthylisoflavanone (S35) (enantioenriched).



Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.494	MM	0.1649	451.01822	45.58456	6.8586
2	10.623	MM	0.2236	6124.95410	456.53607	93.1414

XI. X-Ray Single-Crystal Data for (*R*)-2',4',6'-Trimethoxyisoflavanone S27

A single crystal of **(***R*)-2',4',6'-Trimethoxyisoflavanone **S27**, suitable for X-ray diffraction was obtained by slow diffusion of diethyl ether into a saturated solution of the isoflavanone in chloroform.

Table S.3 *Crystal data and structure refinement for (R)-2',4',6'-Trimethoxyisoflavanone* ***S27***

Empirical formula	$C_{18}\ H_{18}\ O_5$
Formula weight	314.32
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1$ (#4)
Unit cell dimensions	a = 9.2264(1) Å α= 90°. b = 6.84999(9) Å β= 99.843(1)°. c = 12.2116(2) Å γ = 90°.
Volume	760.421(18) $Å^3$
Z	2
Density (calculated)	1.373 Mg/m^3
Absorption coefficient	0.828 mm^{-1}
F(000)	332
Crystal size	0.3109 x 0.1595 x 0.1000 mm^3
Theta range for data collection	3.67 to 77.09°.
Index ranges	–11<=h<=11, –8<=k<=8, –
Reflections collected	6757
Independent reflections	3111 [R(int) = 0.0155]
Completeness to theta = 77.00°	99.1 %
Absorption correction	Analytical
Max. and min. transmission	0.941 and 0.859
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	3111 / 1 / 211
Goodness–of–fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0767
R indices (all data)	R1 = 0.0302, wR2 = 0.0785
Absolute structure parameter	0.06(12)
Largest diff. peak and hole	0.199 and –0.192 e.$Å^{-3}$

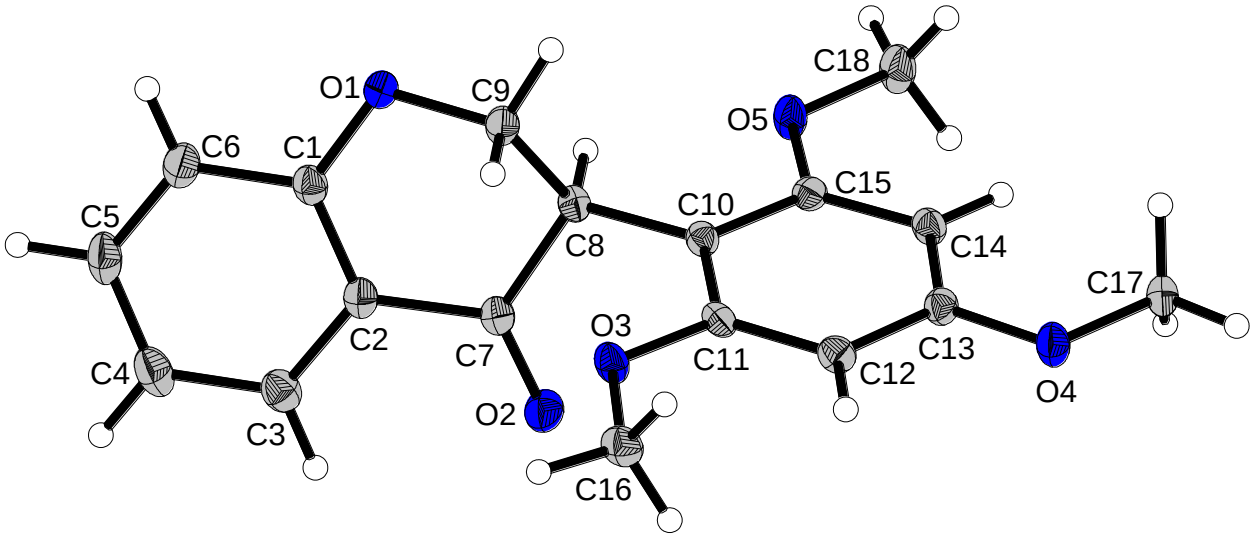


Figure S.1 ORTEP drawing (50 % probability thermal ellipsoids) of the molecular structure of (*R*)-2',4',6'-Trimethoxyisoflavanone **S27**

Table S.4 *Atomic coordinates [(x,y,z), x 10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x 10^3) for (R)-2',4',6'-Trimethoxyisoflavanone* ***S27***

Atom	x	y	z	U(eq)*
C(1)	–1496(1)	7305(2)	574(1)	17(1)
O(1)	–635(1)	8914(1)	791(1)	20(1)
C(2)	–1200(1)	5540(2)	1148(1)	16(1)
C(3)	–2130(1)	3936(2)	861(1)	20(1)
C(4)	–3334(1)	4086(2)	20(1)	25(1)
C(5)	–3616(1)	5849(2)	–554(1)	24(1)
C(6)	–2714(1)	7454(2)	–282(1)	22(1)
C(7)	160(1)	5304(2)	1984(1)	15(1)
O(2)	481(1)	3768(1)	2462(1)	21(1)
C(8)	1162(1)	7089(2)	2139(1)	15(1)
C(9)	260(1)	8960(2)	1884(1)	19(1)
C(10)	2134(1)	7140(2)	3268(1)	14(1)
C(11)	1537(1)	7148(2)	4250(1)	15(1)
O(3)	33(1)	7103(2)	4094(1)	18(1)
C(16)	–650(1)	7112(2)	5062(1)	20(1)
C(12)	2413(1)	7174(2)	5298(1)	17(1)
C(13)	3939(1)	7186(2)	5369(1)	16(1)

O(4)	4729(1)	7205(2)	6421(1)	20(1)
C(17)	6299(1)	7243(2)	6524(1)	19(1)
C(14)	4582(1)	7168(2)	4418(1)	16(1)
C(15)	3670(1)	7142(2)	3380(1)	14(1)
O(5)	4220(1)	7084(2)	2410(1)	19(1)
C(18)	5785(1)	7086(3)	2485(1)	23(1)

*U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table S5. *Bond lengths [Å] and angles [°] for (R)-2',4',6'-Trimethoxyisoflavanone* ***S27***

C(1)–O(1)	1.3581(16)
C(1)–C(2)	1.4009(18)
C(1)–C(6)	1.4017(15)
O(1)–C(9)	1.4446(14)
C(2)–C(3)	1.4011(17)
C(2)–C(7)	1.4842(15)
C(3)–C(4)	1.3824(17)
C(3)–H(3)	0.9500
C(4)–C(5)	1.399(2)
C(4)–H(4)	0.9500
C(5)–C(6)	1.3845(19)
C(5)–H(5)	0.9500
C(6)–H(6)	0.9500
C(7)–O(2)	1.2149(16)
C(7)–C(8)	1.5251(17)
C(8)–C(10)	1.5110(13)
C(8)–C(9)	1.5313(17)
C(8)–H(8)	1.0000
C(9)–H(9A)	0.9900
C(9)–H(9B)	0.9900
C(10)–C(15)	1.4003(14)
C(10)–C(11)	1.4025(14)
C(11)–O(3)	1.3686(12)

C(11)–C(12)	1.3928(14)
O(3)–C(16)	1.4318(13)
C(16)–H(16A)	0.9800
C(16)–H(16B)	0.9800
C(16)–H(16C)	0.9800
C(12)–C(13)	1.3961(14)
C(12)–H(12)	0.9500
C(13)–O(4)	1.3645(12)
C(13)–C(14)	1.3906(15)
O(4)–C(17)	1.4331(13)
C(17)–H(17A)	0.9800
C(17)–H(17B)	0.9800
C(17)–H(17C)	0.9800
C(14)–C(15)	1.3968(14)
C(14)–H(14)	0.9500
C(15)–O(5)	1.3663(12)
O(5)–C(18)	1.4314(13)
C(18)–H(18A)	0.9800
C(18)–H(18B)	0.9800
C(18)–H(18C)	0.9800

O(1)–C(1)–C(2)	123.04(10)
O(1)–C(1)–C(6)	117.01(11)
C(2)–C(1)–C(6)	119.94(11)
C(1)–O(1)–C(9)	114.89(9)
C(1)–C(2)–C(3)	119.52(10)
C(1)–C(2)–C(7)	120.52(10)
C(3)–C(2)–C(7)	119.73(11)
C(4)–C(3)–C(2)	120.54(12)
C(4)–C(3)–H(3)	119.7
C(2)–C(3)–H(3)	119.7
C(3)–C(4)–C(5)	119.57(12)

C(3)–C(4)–H(4)	120.2
C(5)–C(4)–H(4)	120.2
C(6)–C(5)–C(4)	120.85(11)
C(6)–C(5)–H(5)	119.6
C(4)–C(5)–H(5)	119.6
C(5)–C(6)–C(1)	119.58(12)
C(5)–C(6)–H(6)	120.2
C(1)–C(6)–H(6)	120.2
O(2)–C(7)–C(2)	122.19(11)
O(2)–C(7)–C(8)	122.79(10)
C(2)–C(7)–C(8)	114.90(10)
C(10)–C(8)–C(7)	112.62(10)
C(10)–C(8)–C(9)	112.52(10)
C(7)–C(8)–C(9)	110.42(8)
C(10)–C(8)–H(8)	107.0
C(7)–C(8)–H(8)	107.0
C(9)–C(8)–H(8)	107.0
O(1)–C(9)–C(8)	111.98(10)
O(1)–C(9)–H(9A)	109.2
C(8)–C(9)–H(9A)	109.2
O(1)–C(9)–H(9B)	109.2
C(8)–C(9)–H(9B)	109.2
H(9A)–C(9)–H(9B)	107.9
C(15)–C(10)–C(11)	117.04(9)
C(15)–C(10)–C(8)	121.51(9)
C(11)–C(10)–C(8)	121.44(9)
O(3)–C(11)–C(12)	122.89(10)
O(3)–C(11)–C(10)	114.73(9)
C(12)–C(11)–C(10)	122.37(9)
C(11)–O(3)–C(16)	117.68(8)
O(3)–C(16)–H(16A)	109.5
O(3)–C(16)–H(16B)	109.5

H(16A)–C(16)–H(16B)	109.5
O(3)–C(16)–H(16C)	109.5
H(16A)–C(16)–H(16C)	109.5
H(16B)–C(16)–H(16C)	109.5
C(11)–C(12)–C(13)	118.50(10)
C(11)–C(12)–H(12)	120.7
C(13)–C(12)–H(12)	120.7
O(4)–C(13)–C(14)	123.43(9)
O(4)–C(13)–C(12)	115.36(9)
C(14)–C(13)–C(12)	121.22(10)
C(13)–O(4)–C(17)	116.85(8)
O(4)–C(17)–H(17A)	109.5
O(4)–C(17)–H(17B)	109.5
H(17A)–C(17)–H(17B)	109.5
O(4)–C(17)–H(17C)	109.5
H(17A)–C(17)–H(17C)	109.5
H(17B)–C(17)–H(17C)	109.5
C(13)–C(14)–C(15)	118.74(9)
C(13)–C(14)–H(14)	120.6
C(15)–C(14)–H(14)	120.6
O(5)–C(15)–C(14)	122.14(9)
O(5)–C(15)–C(10)	115.73(9)
C(14)–C(15)–C(10)	122.13(9)
C(15)–O(5)–C(18)	117.68(8)
O(5)–C(18)–H(18A)	109.5
O(5)–C(18)–H(18B)	109.5
H(18A)–C(18)–H(18B)	109.5
O(5)–C(18)–H(18C)	109.5
H(18A)–C(18)–H(18C)	109.5
H(18B)–C(18)–H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S6. *Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (R)-2',4',6'-Trimethoxyisoflavanone* ***S27***[*]

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	13(1)	23(1)	15(1)	–1(1)	4(1)	–1(1)
O(1)	17(1)	20(1)	20(1)	5(1)	–2(1)	–2(1)
C(2)	13(1)	21(1)	14(1)	–2(1)	3(1)	1(1)
C(3)	20(1)	23(1)	19(1)	–3(1)	4(1)	–3(1)
C(4)	19(1)	33(1)	21(1)	–7(1)	3(1)	–7(1)
C(5)	16(1)	40(1)	15(1)	–4(1)	1(1)	–1(1)
C(6)	17(1)	31(1)	17(1)	2(1)	2(1)	2(1)
C(7)	14(1)	17(1)	15(1)	–2(1)	2(1)	1(1)
O(2)	22(1)	15(1)	24(1)	0(1)	–2(1)	2(1)
C(8)	13(1)	17(1)	16(1)	0(1)	1(1)	0(1)
C(9)	17(1)	17(1)	20(1)	1(1)	–2(1)	–1(1)
C(10)	13(1)	13(1)	17(1)	0(1)	1(1)	1(1)
C(11)	12(1)	13(1)	20(1)	–1(1)	3(1)	–1(1)
O(3)	11(1)	23(1)	19(1)	–1(1)	4(1)	–1(1)
C(16)	16(1)	24(1)	23(1)	0(1)	8(1)	0(1)
C(12)	16(1)	18(1)	17(1)	–1(1)	5(1)	–1(1)
C(13)	16(1)	15(1)	16(1)	–1(1)	0(1)	0(1)
O(4)	15(1)	29(1)	15(1)	–1(1)	1(1)	–2(1)
C(17)	14(1)	23(1)	18(1)	1(1)	–2(1)	–1(1)
C(14)	12(1)	16(1)	19(1)	0(1)	2(1)	0(1)
C(15)	14(1)	13(1)	16(1)	1(1)	3(1)	1(1)
O(5)	11(1)	32(1)	15(1)	1(1)	3(1)	1(1)
C(18)	12(1)	40(1)	19(1)	2(1)	4(1)	2(1)

[*] The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Table S7. *Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (R)-2',4',6'-Trimethoxyisoflavanone* ***S27***

Atom	x	y	z	U(eq)
H(3)	–1930	2736	1247	24
H(4)	–3967	2998	–167	29
H(5)	–4437	5947	–1138	29
H(6)	–2920	8649	–672	26
H(8)	1827	6992	1574	18
H(9A)	–384	9134	2448	22
H(9B)	934	10093	1935	22
H(16A)	–310	5982	5528	30
H(16B)	–1721	7046	4837	30
H(16C)	–387	8315	5484	30
H(12)	1982	7184	5951	20
H(17A)	6635	6045	6207	29
H(17B)	6742	7334	7311	29
H(17C)	6594	8377	6124	29
H(14)	5622	7174	4474	19
H(18A)	6190	8293	2845	35
H(18B)	6032	7005	1737	35
H(18C)	6204	5961	2925	35

Table S8. *Torsion angles [°] for (R)-2',4',6'-Trimethoxyisoflavanone* ***S27***

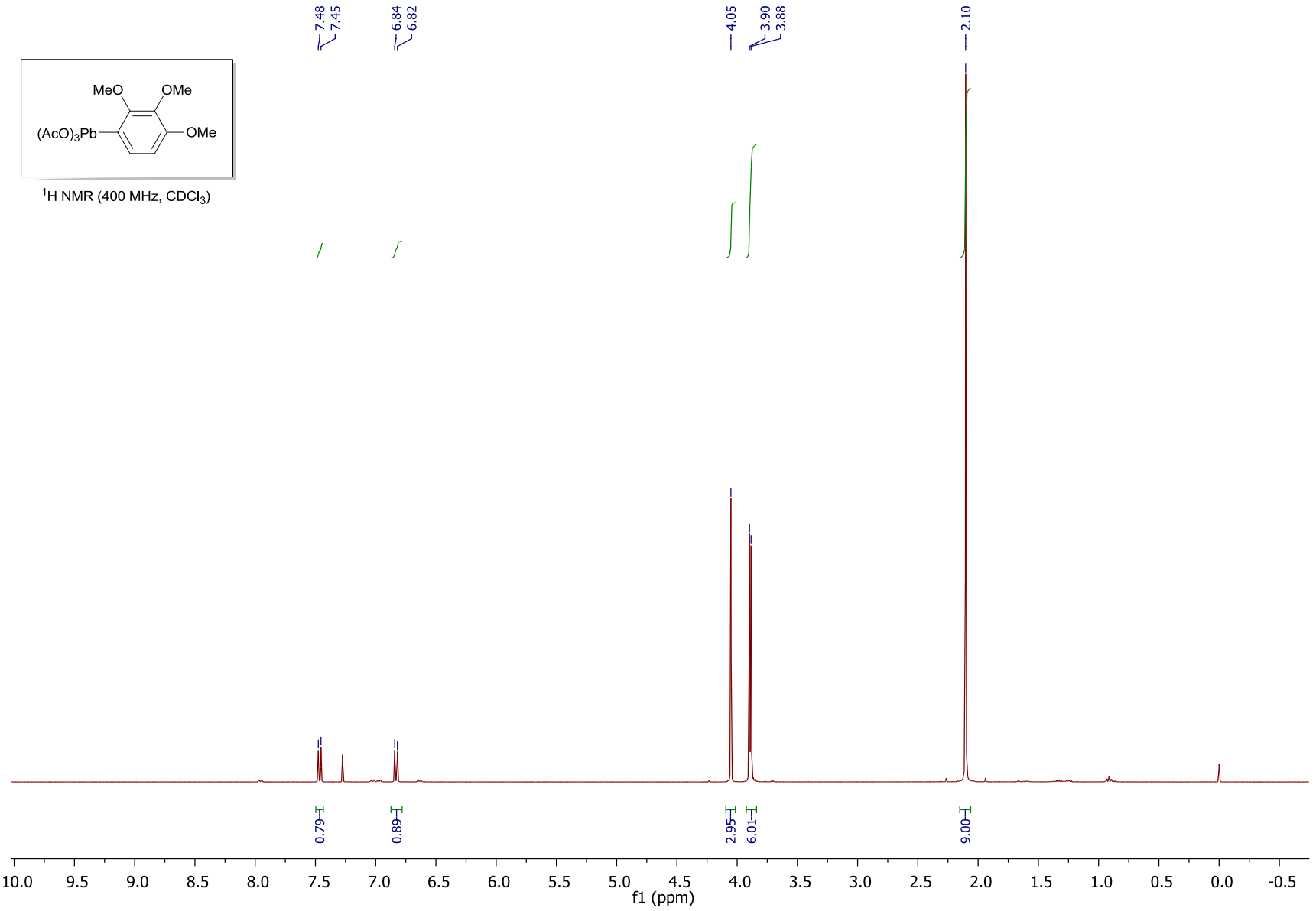
C(2)–C(1)–O(1)–C(9)	–22.04(15)
C(6)–C(1)–O(1)–C(9)	159.05(10)
O(1)–C(1)–C(2)–C(3)	–178.96(10)
C(6)–C(1)–C(2)–C(3)	–0.09(17)
O(1)–C(1)–C(2)–C(7)	–4.49(17)
C(6)–C(1)–C(2)–C(7)	174.39(10)
C(1)–C(2)–C(3)–C(4)	–0.15(17)

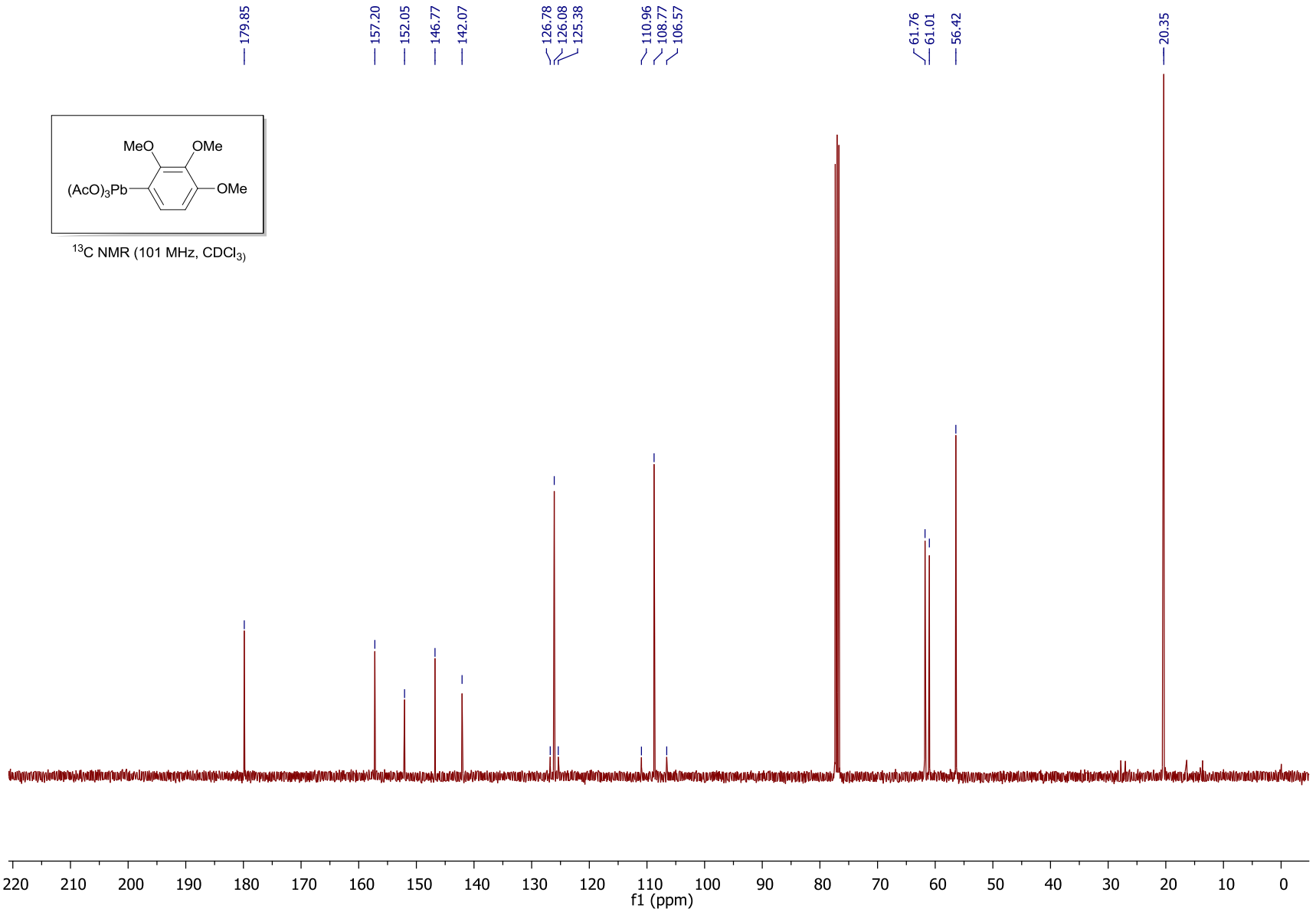
C(7)–C(2)–C(3)–C(4)	–174.67(11)
C(2)–C(3)–C(4)–C(5)	0.58(18)
C(3)–C(4)–C(5)–C(6)	–0.78(18)
C(4)–C(5)–C(6)–C(1)	0.54(18)
O(1)–C(1)–C(6)–C(5)	178.83(10)
C(2)–C(1)–C(6)–C(5)	–0.11(17)
C(1)–C(2)–C(7)–O(2)	–176.75(11)
C(3)–C(2)–C(7)–O(2)	–2.29(17)
C(1)–C(2)–C(7)–C(8)	–0.57(15)
C(3)–C(2)–C(7)–C(8)	173.90(10)
O(2)–C(7)–C(8)–C(10)	–28.17(16)
C(2)–C(7)–C(8)–C(10)	155.67(9)
O(2)–C(7)–C(8)–C(9)	–154.89(11)
C(2)–C(7)–C(8)–C(9)	28.95(13)
C(1)–O(1)–C(9)–C(8)	51.98(13)
C(10)–C(8)–C(9)–O(1)	178.45(9)
C(7)–C(8)–C(9)–O(1)	–54.77(12)
C(7)–C(8)–C(10)–C(15)	120.06(12)
C(9)–C(8)–C(10)–C(15)	–114.35(13)
C(7)–C(8)–C(10)–C(11)	–58.62(16)
C(9)–C(8)–C(10)–C(11)	66.97(15)
C(15)–C(10)–C(11)–O(3)	–178.67(12)
C(8)–C(10)–C(11)–O(3)	0.06(18)
C(15)–C(10)–C(11)–C(12)	0.58(19)
C(8)–C(10)–C(11)–C(12)	179.31(12)
C(12)–C(11)–O(3)–C(16)	0.90(18)
C(10)–C(11)–O(3)–C(16)	–179.86(12)
O(3)–C(11)–C(12)–C(13)	178.92(12)
C(10)–C(11)–C(12)–C(13)	–0.3(2)
C(11)–C(12)–C(13)–O(4)	–179.80(12)
C(11)–C(12)–C(13)–C(14)	–0.1(2)
C(14)–C(13)–O(4)–C(17)	1.1(2)

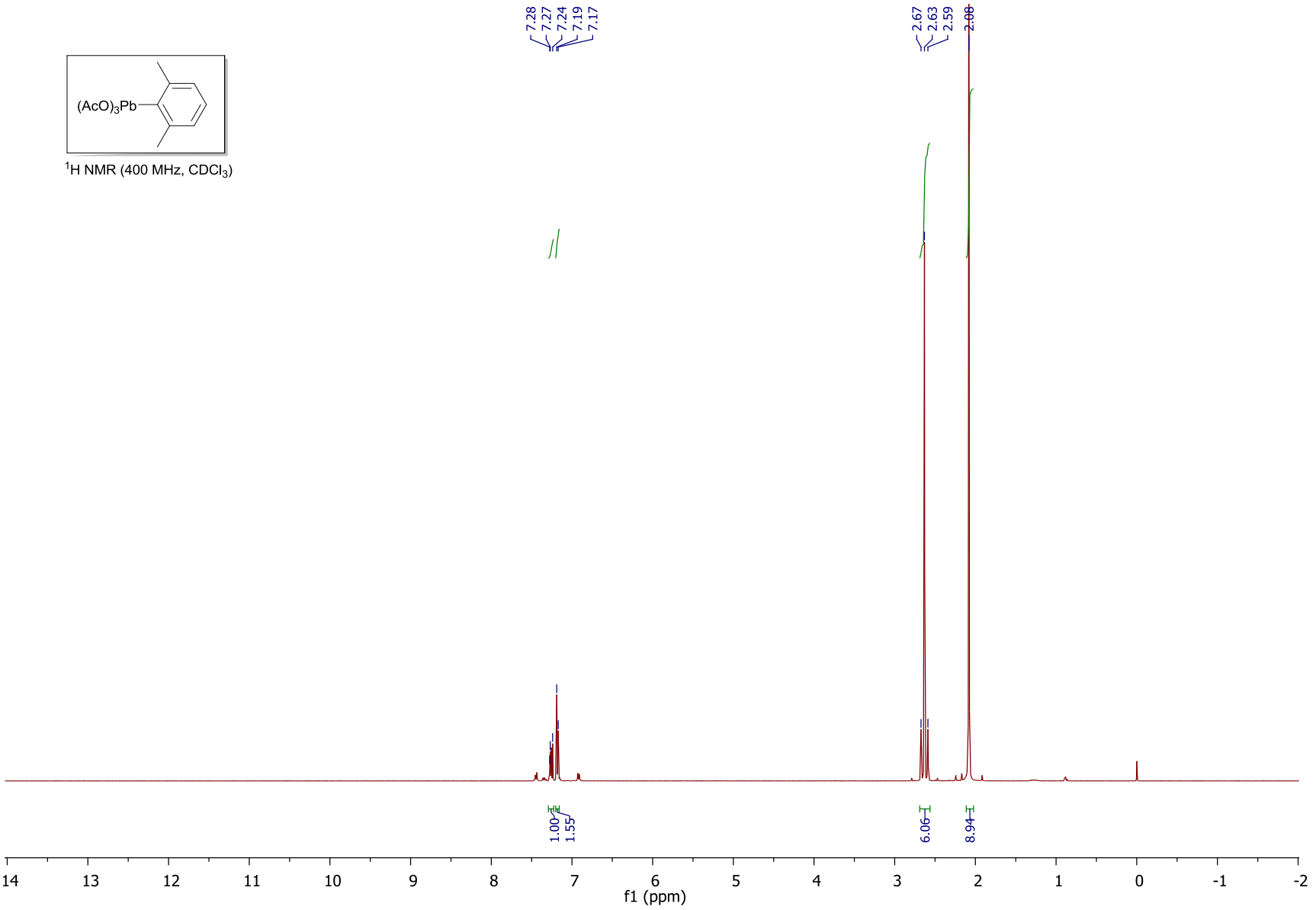
C(12)–C(13)–O(4)–C(17)	–179.21(12)
O(4)–C(13)–C(14)–C(15)	179.80(12)
C(12)–C(13)–C(14)–C(15)	0.1(2)
C(13)–C(14)–C(15)–O(5)	–178.63(12)
C(13)–C(14)–C(15)–C(10)	0.2(2)
C(11)–C(10)–C(15)–O(5)	178.37(12)
C(8)–C(10)–C(15)–O(5)	–0.36(18)
C(11)–C(10)–C(15)–C(14)	–0.56(19)
C(8)–C(10)–C(15)–C(14)	–179.29(13)
C(14)–C(15)–O(5)–C(18)	–1.14(19)
C(10)–C(15)–O(5)–C(18)	179.93(12)

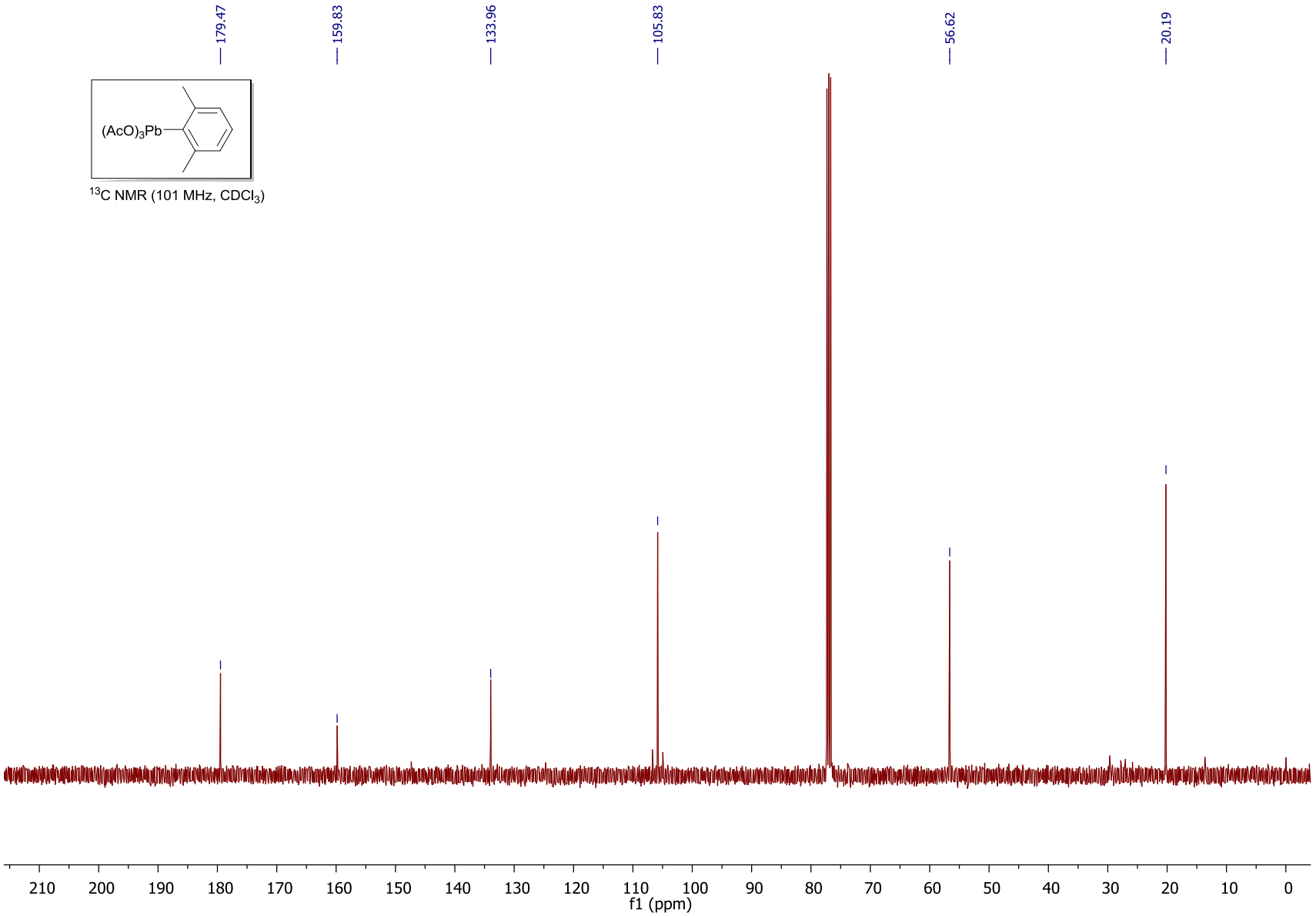
Symmetry transformations used to generate equivalent atoms:

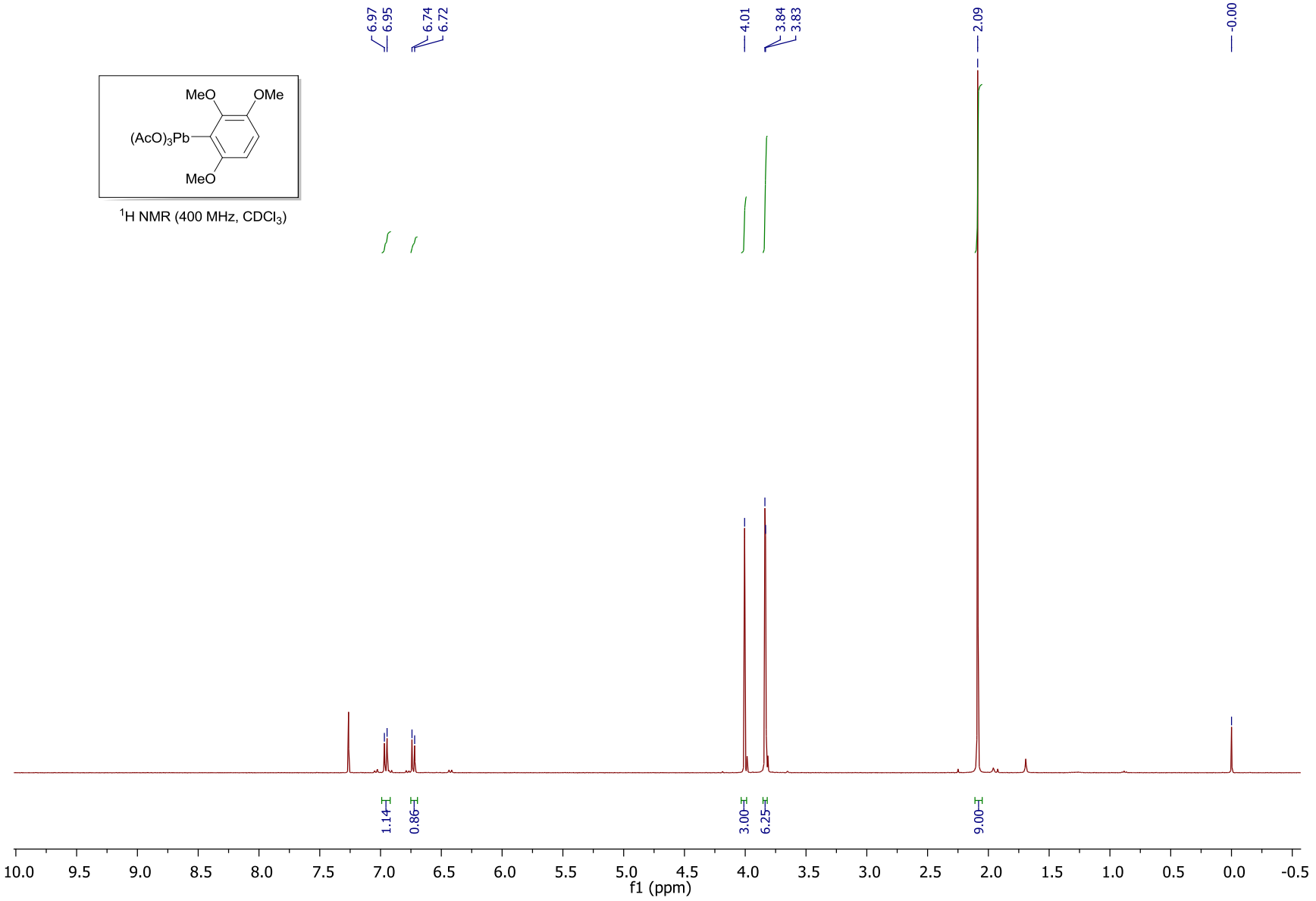
XII. NMR spectra

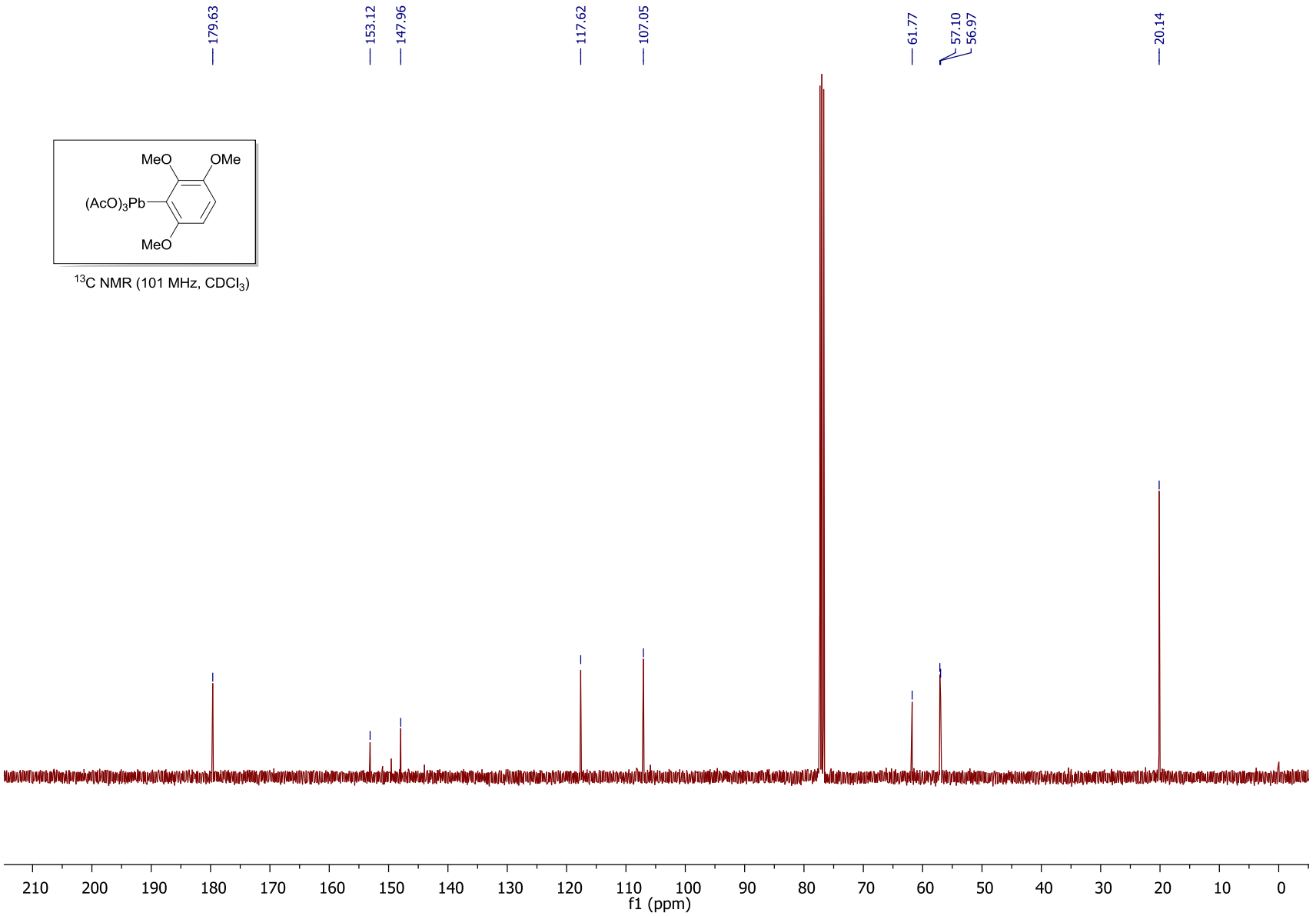


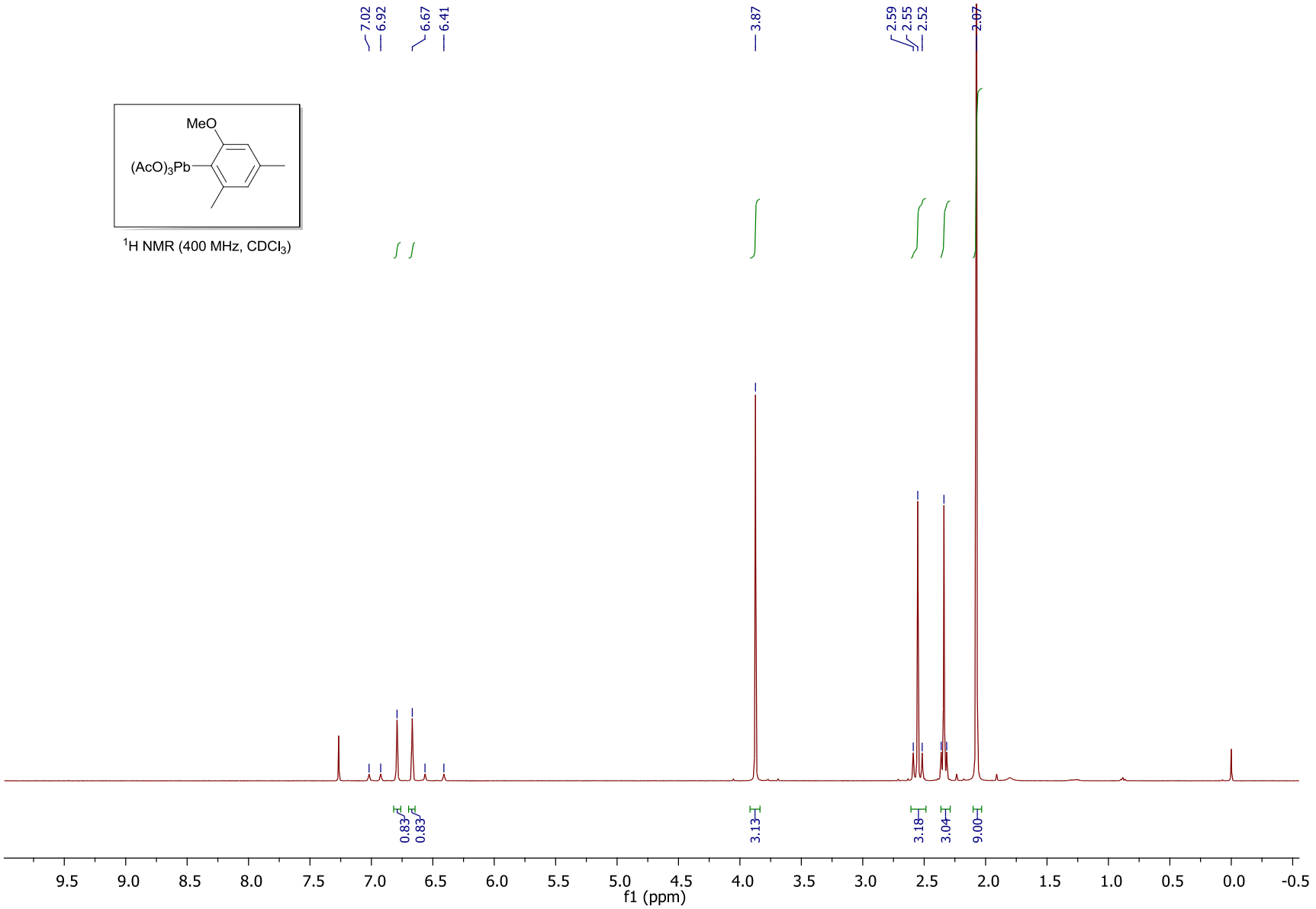



(AcO)3Pb
1H NMR (400 MHz, CDCl3)
7.28
7.27
7.24
7.19
7.17
2.67
2.63
2.59
2.08
1.00
1.55
6.06
8.94
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

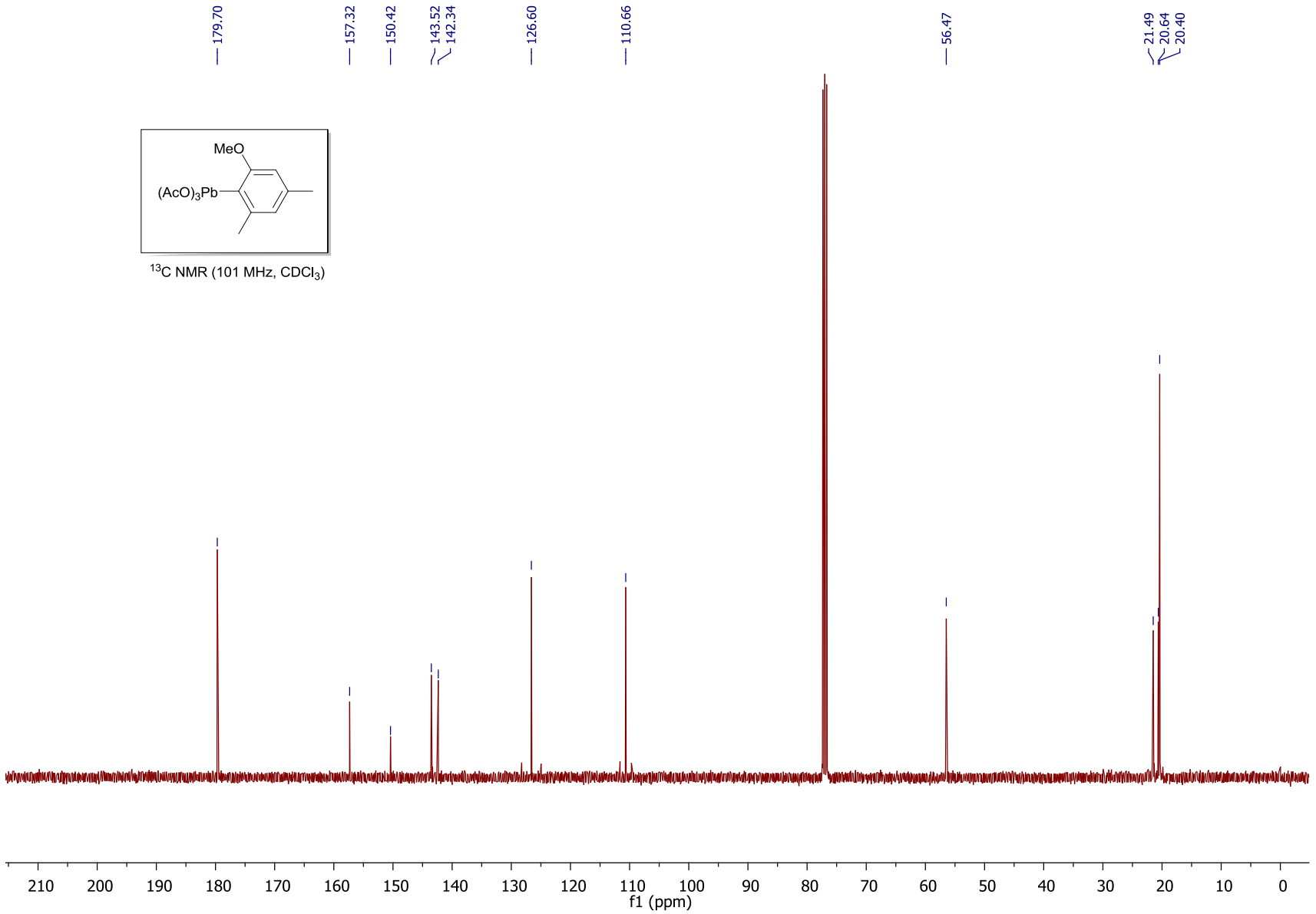


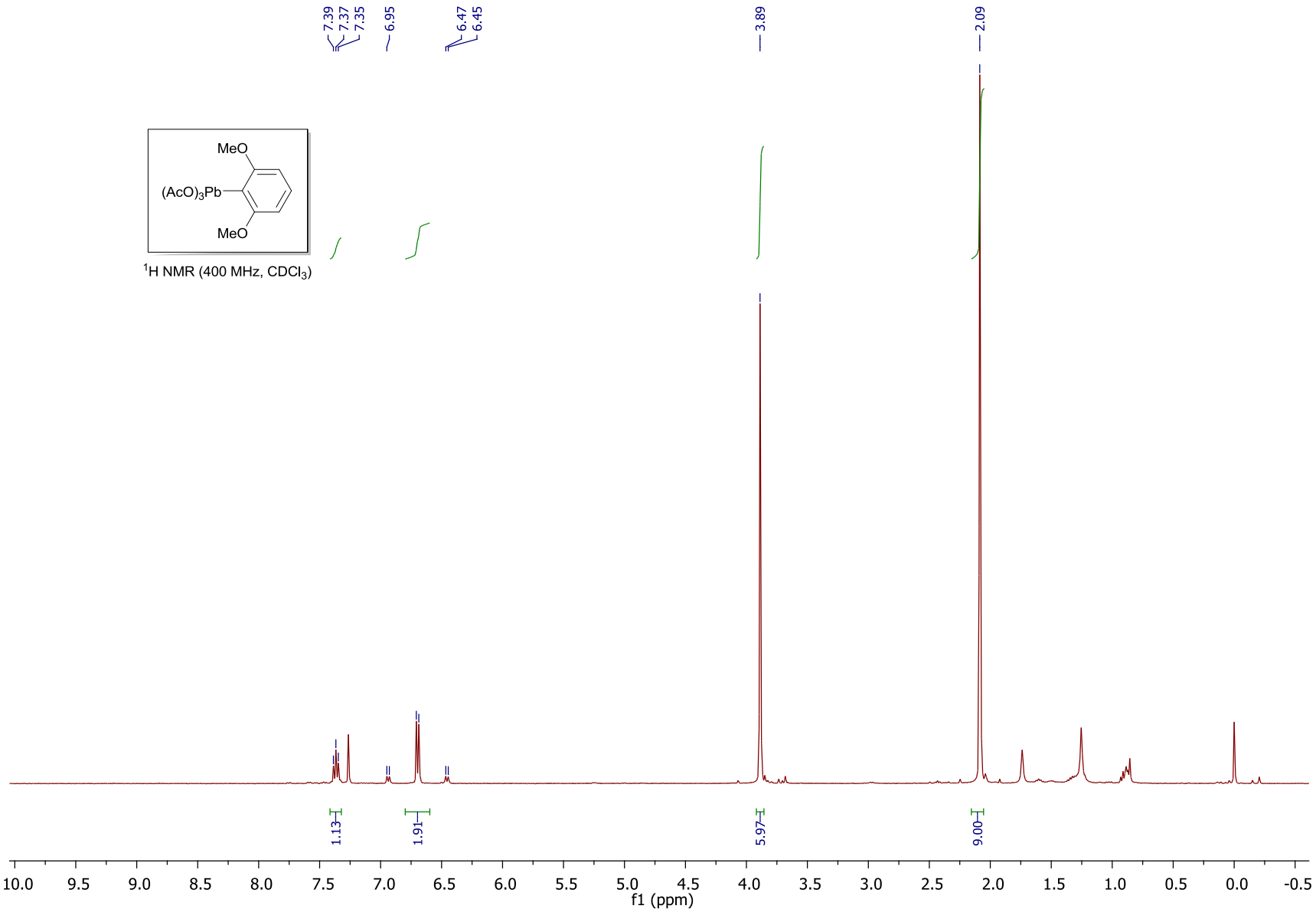


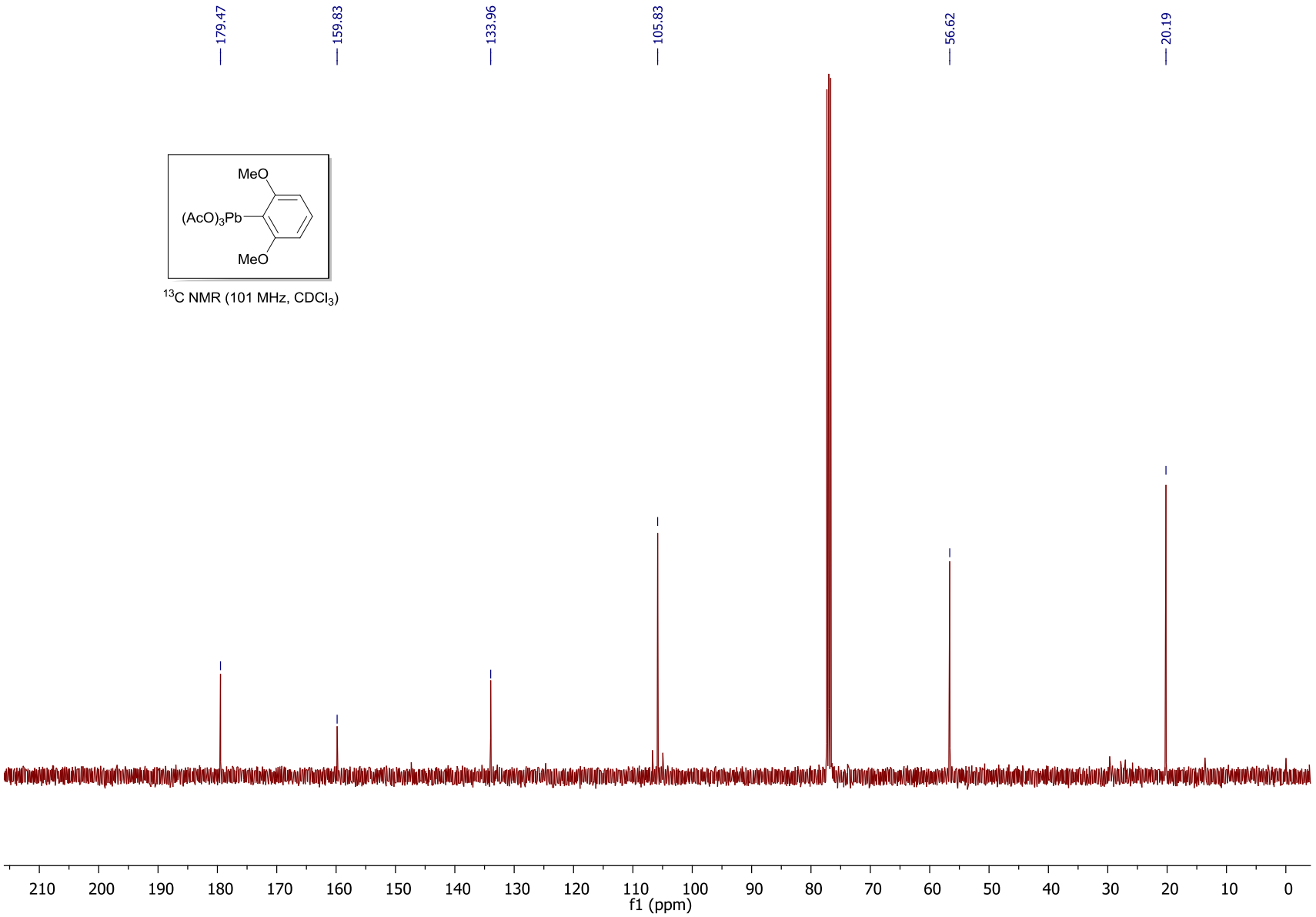


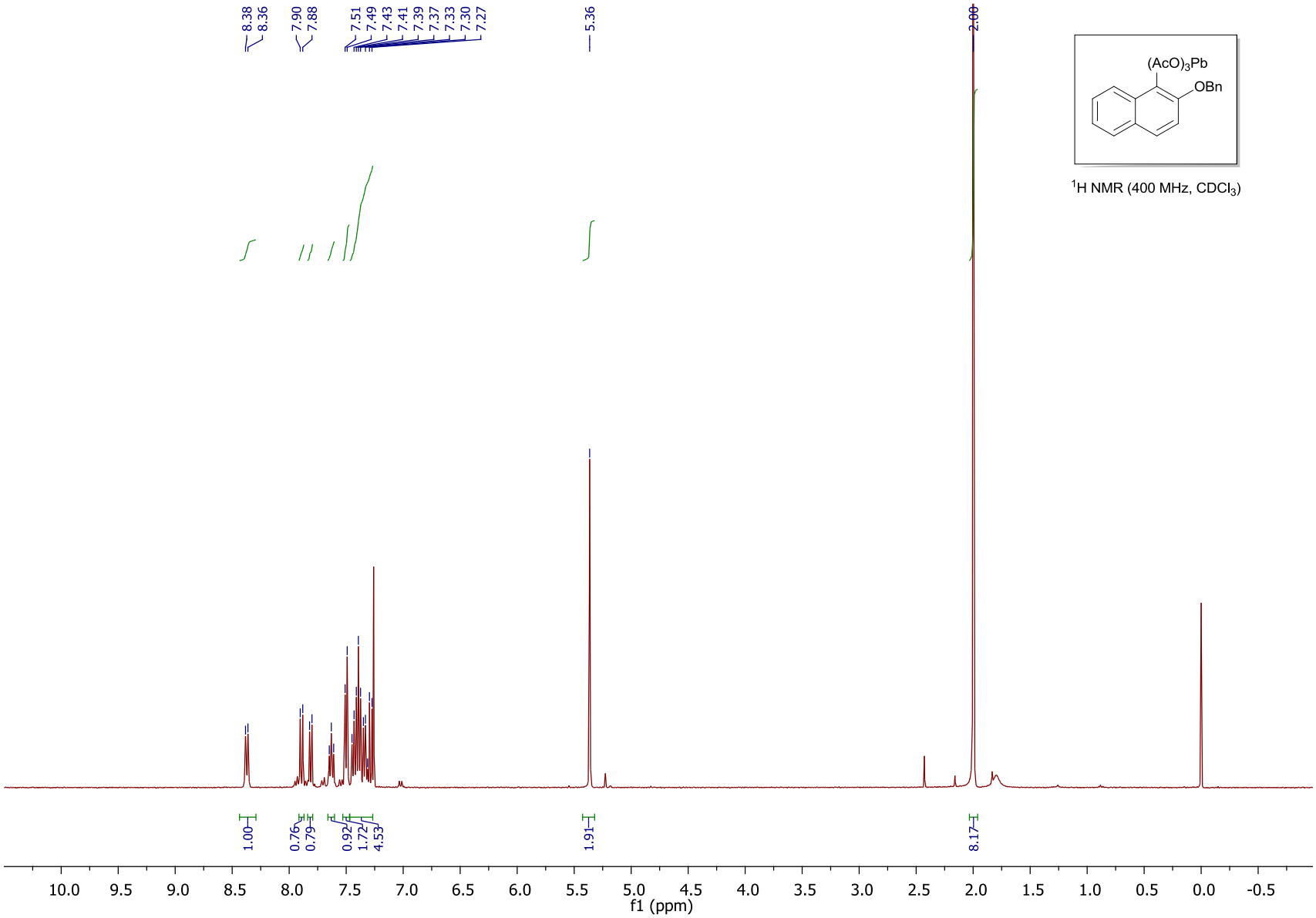


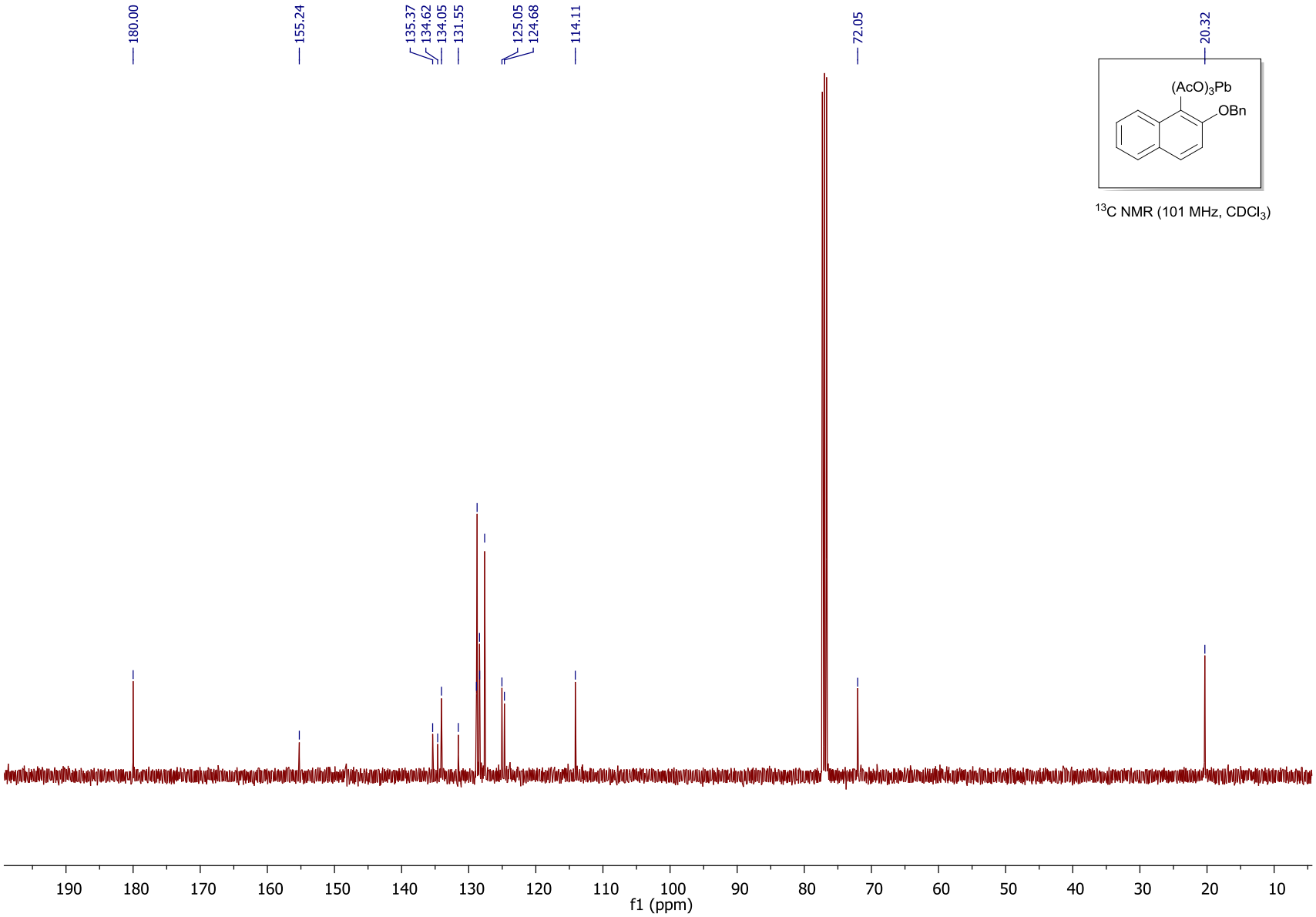
^{1}H NMR (400 MHz, $CDCl_3$)

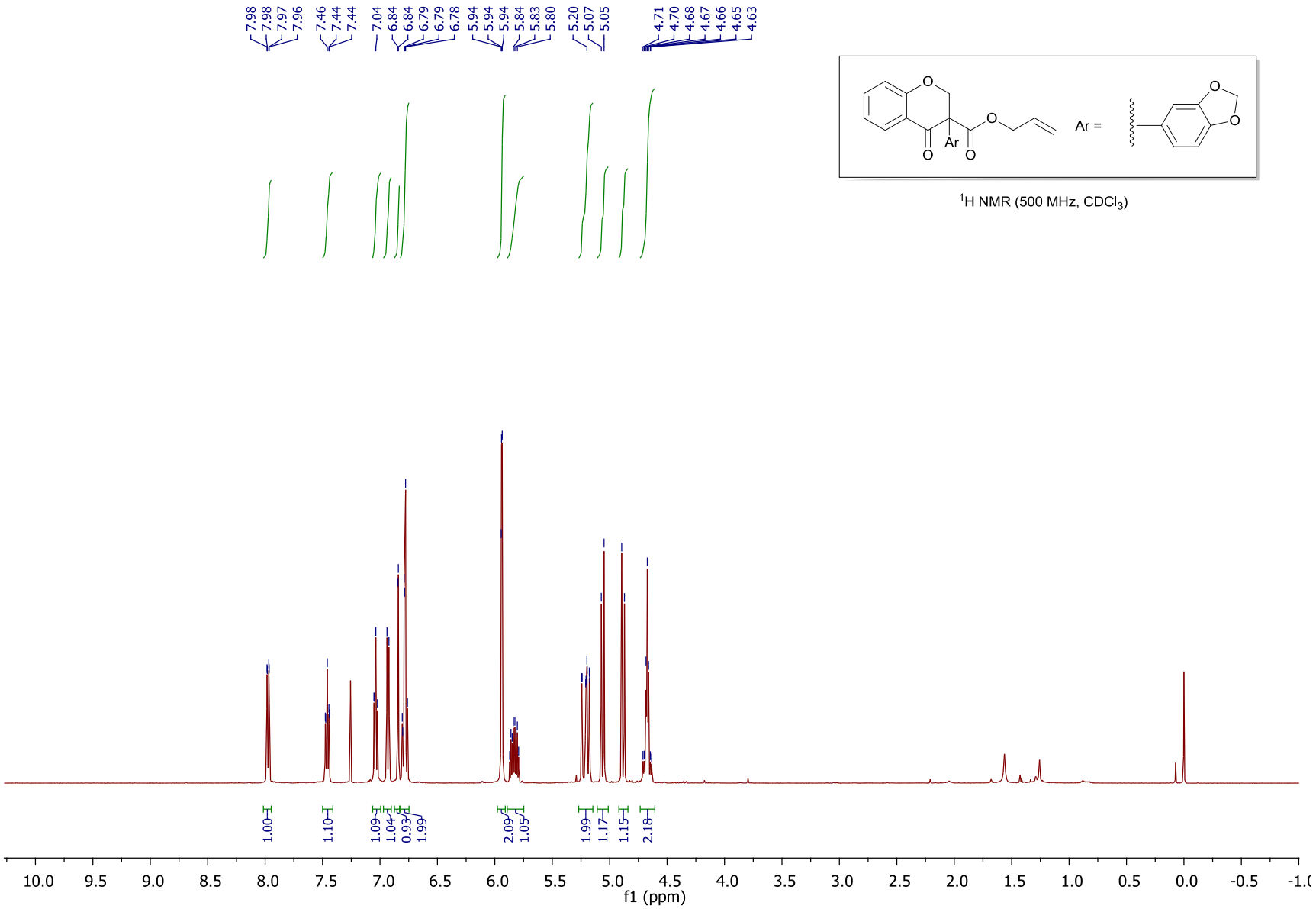




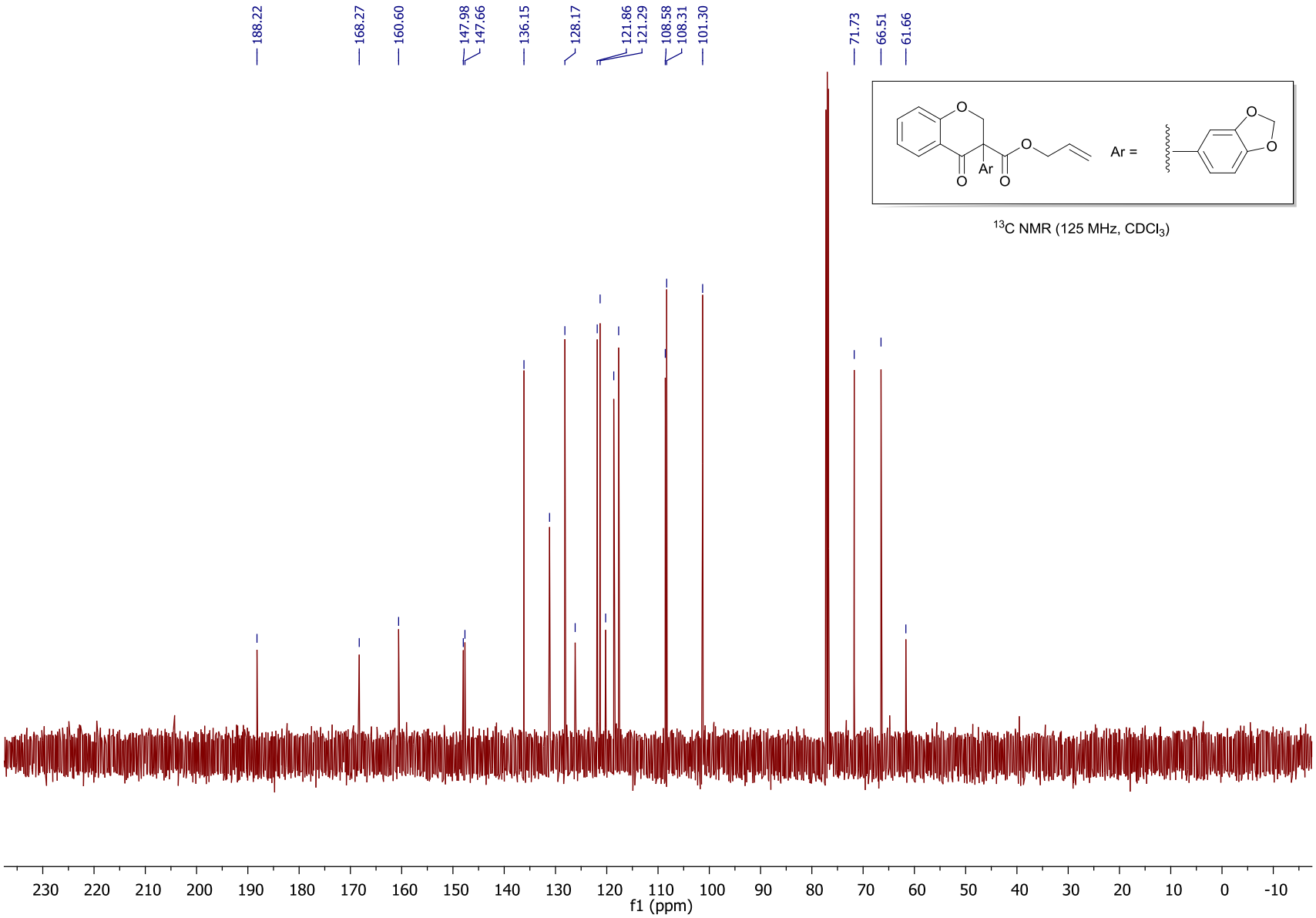


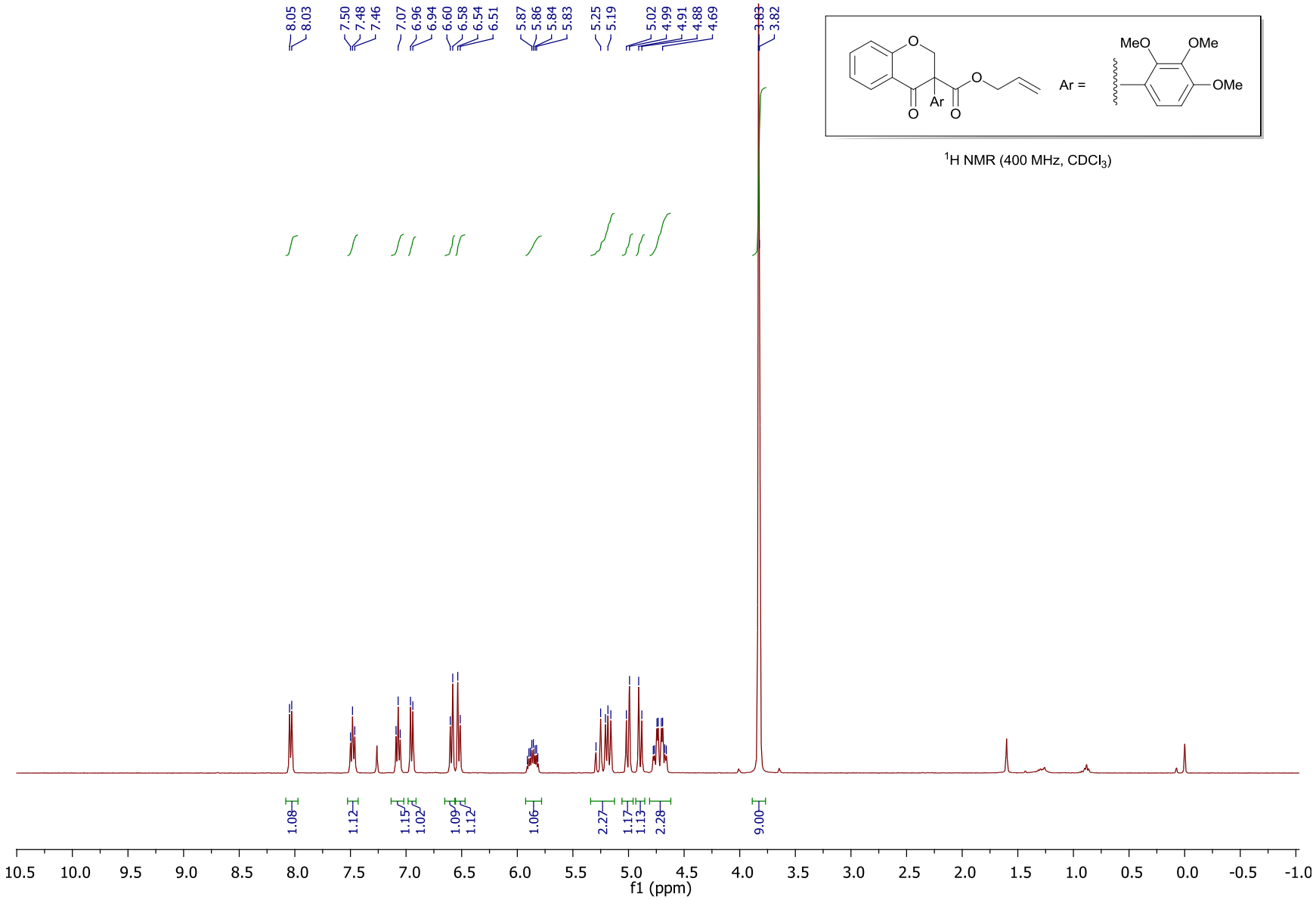




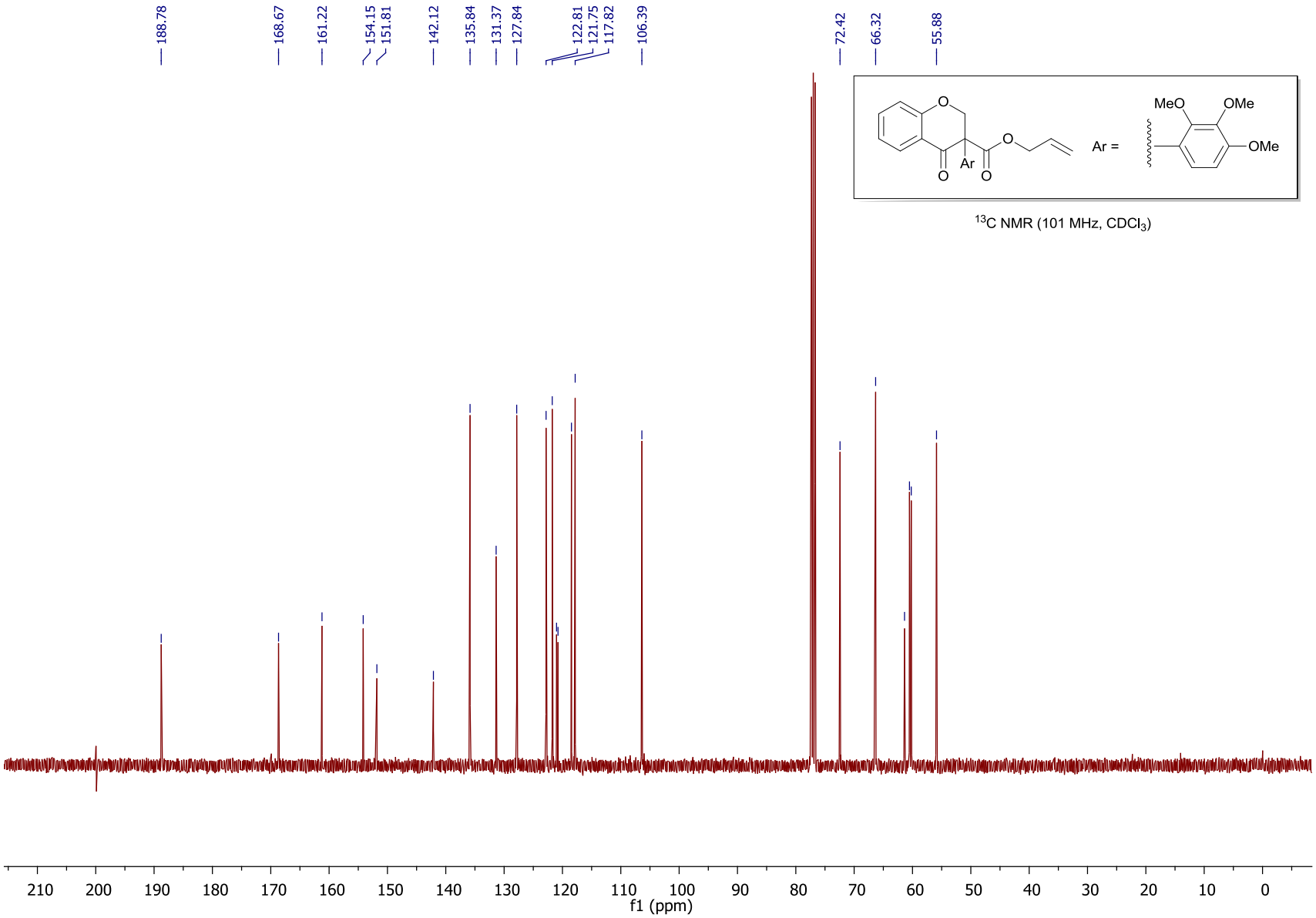


^{1}H NMR (500 MHz, $CDCl_3$)

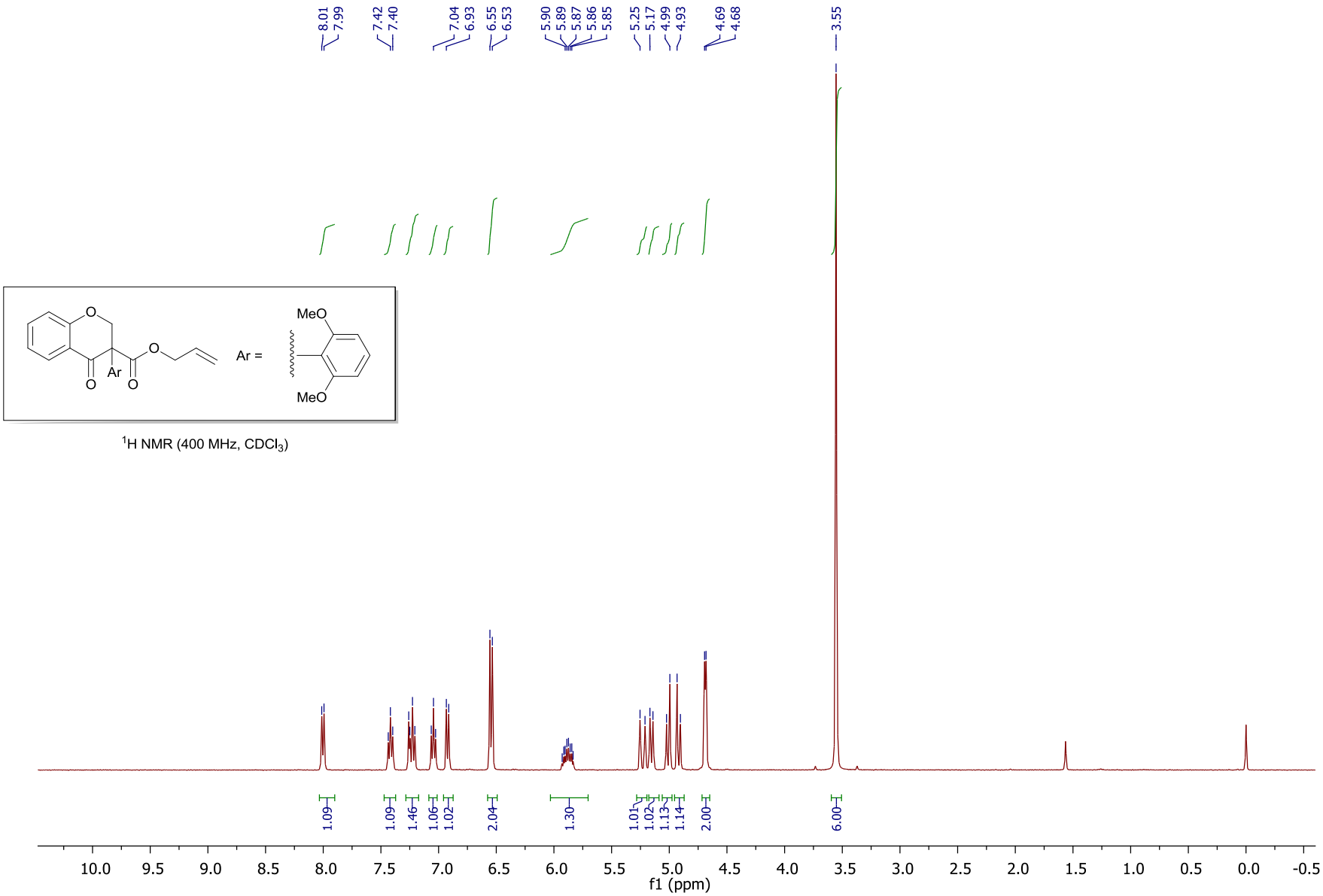




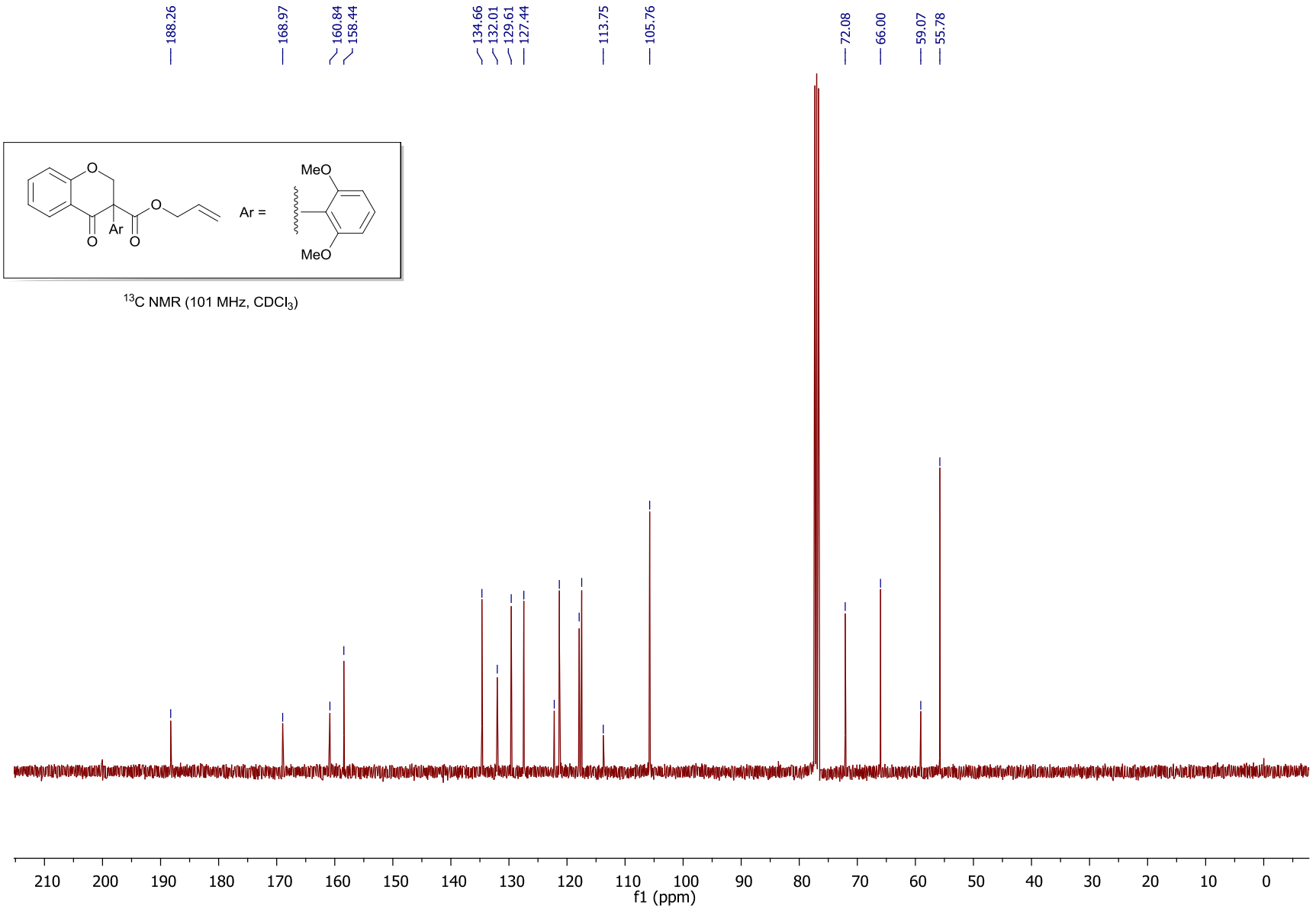
^{1}H NMR (400 MHz, $CDCl_3$)



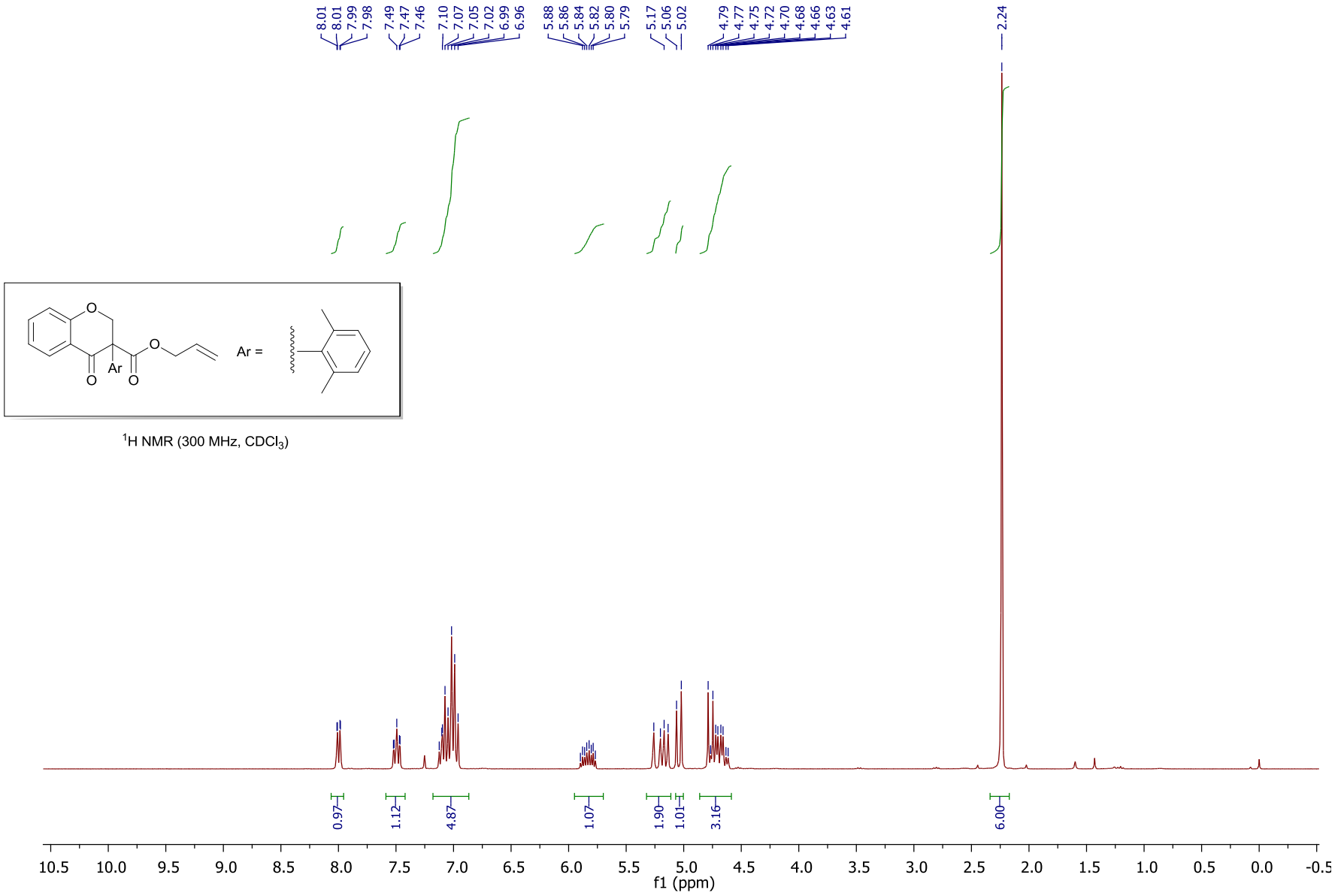
^{13}C NMR (101 MHz, $CDCl_3$)



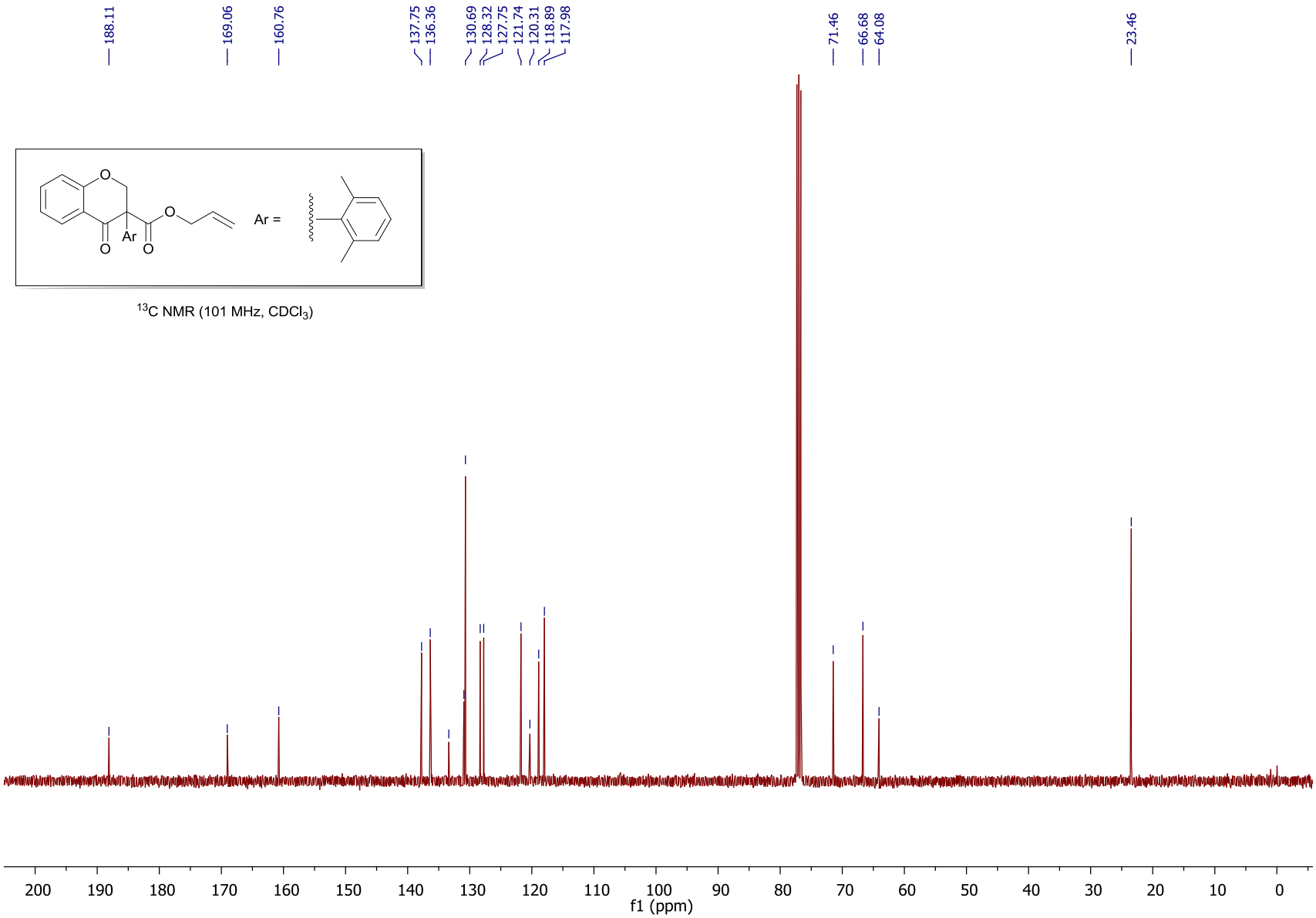
^{1}H NMR (400 MHz, $CDCl_3$)



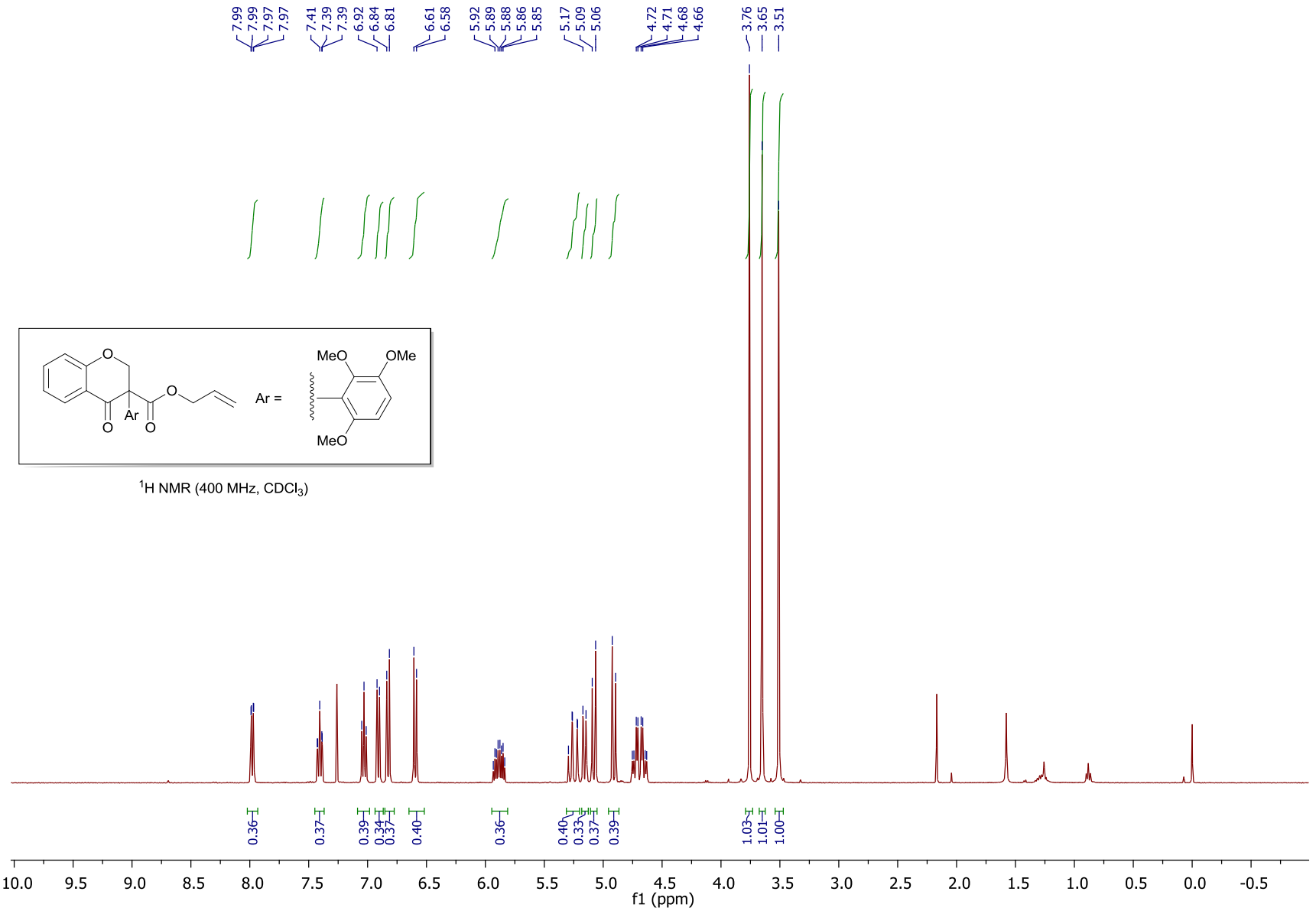
^{13}C NMR (101 MHz, $CDCl_3$)



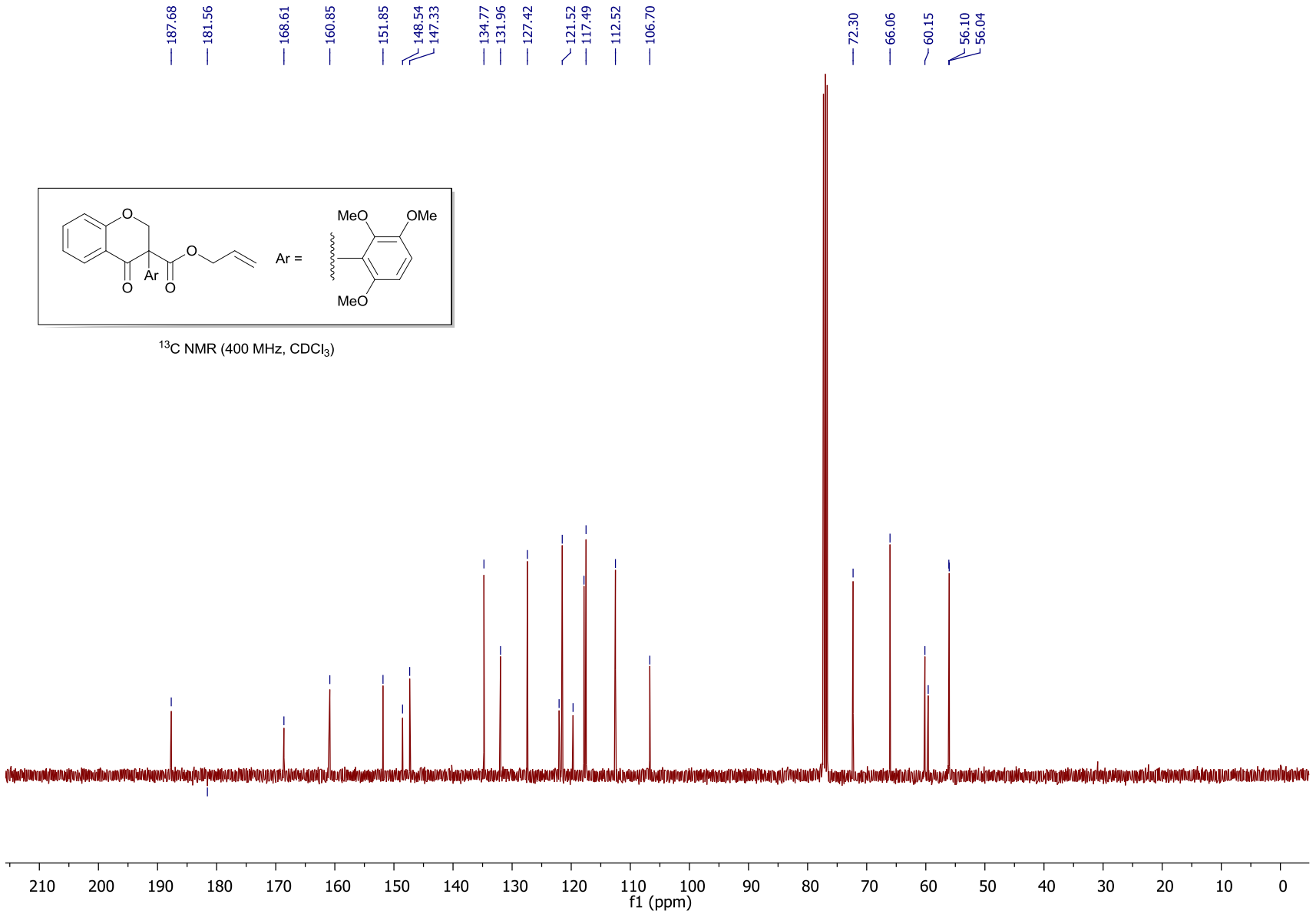
^{1}H NMR (300 MHz, $CDCl_3$)



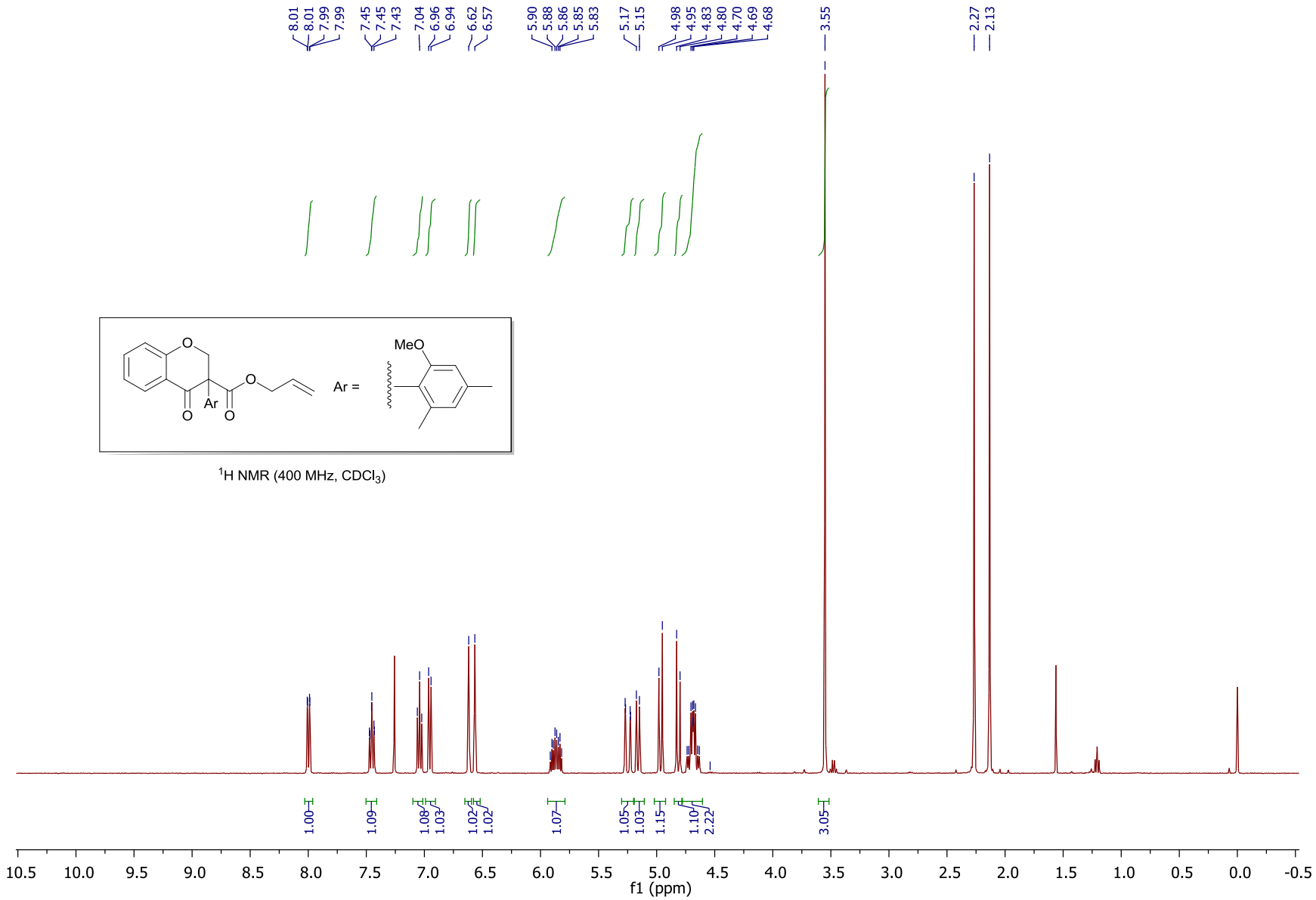
^{13}C NMR (101 MHz, $CDCl_3$)



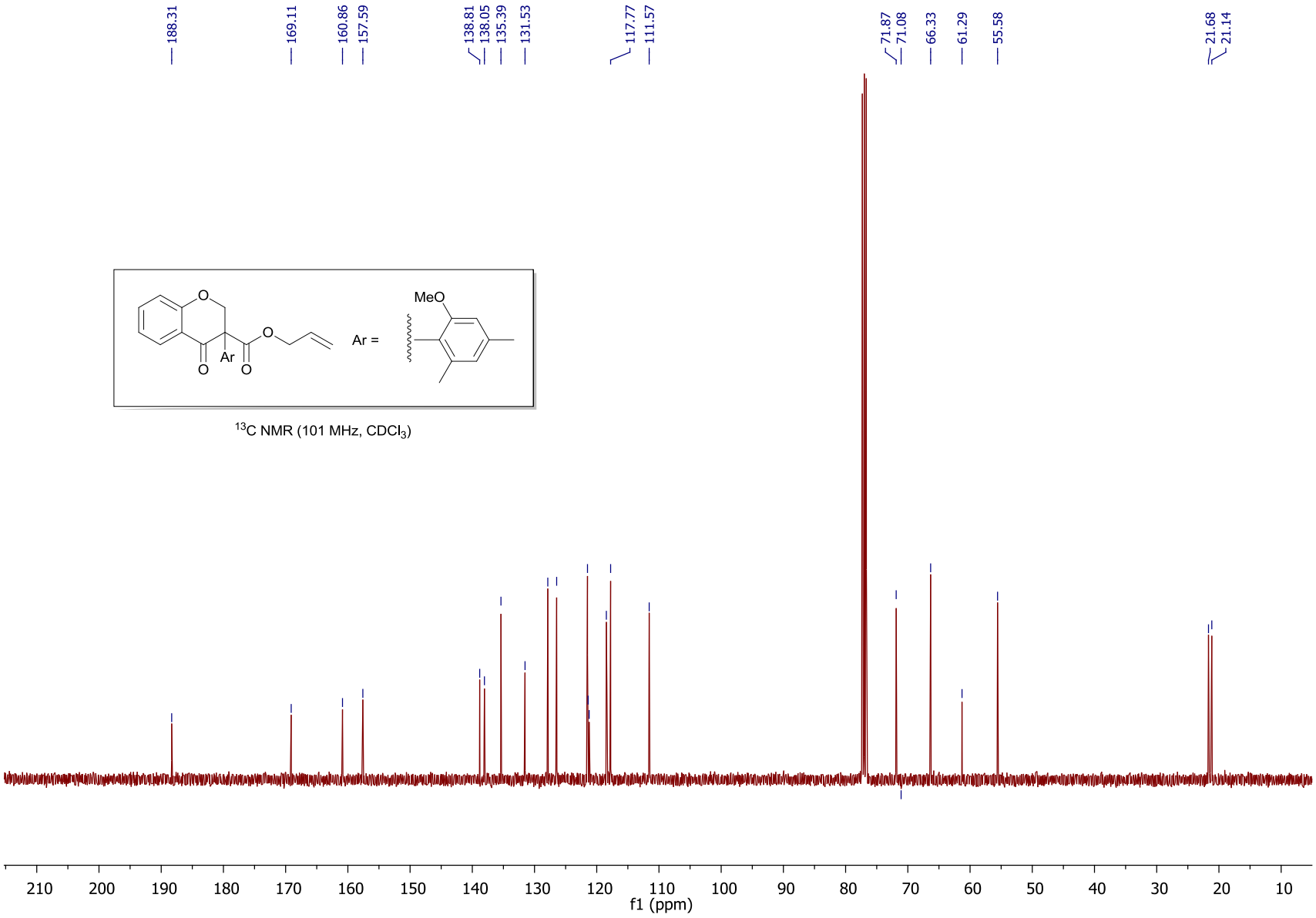
^{1}H NMR (400 MHz, $CDCl_3$)



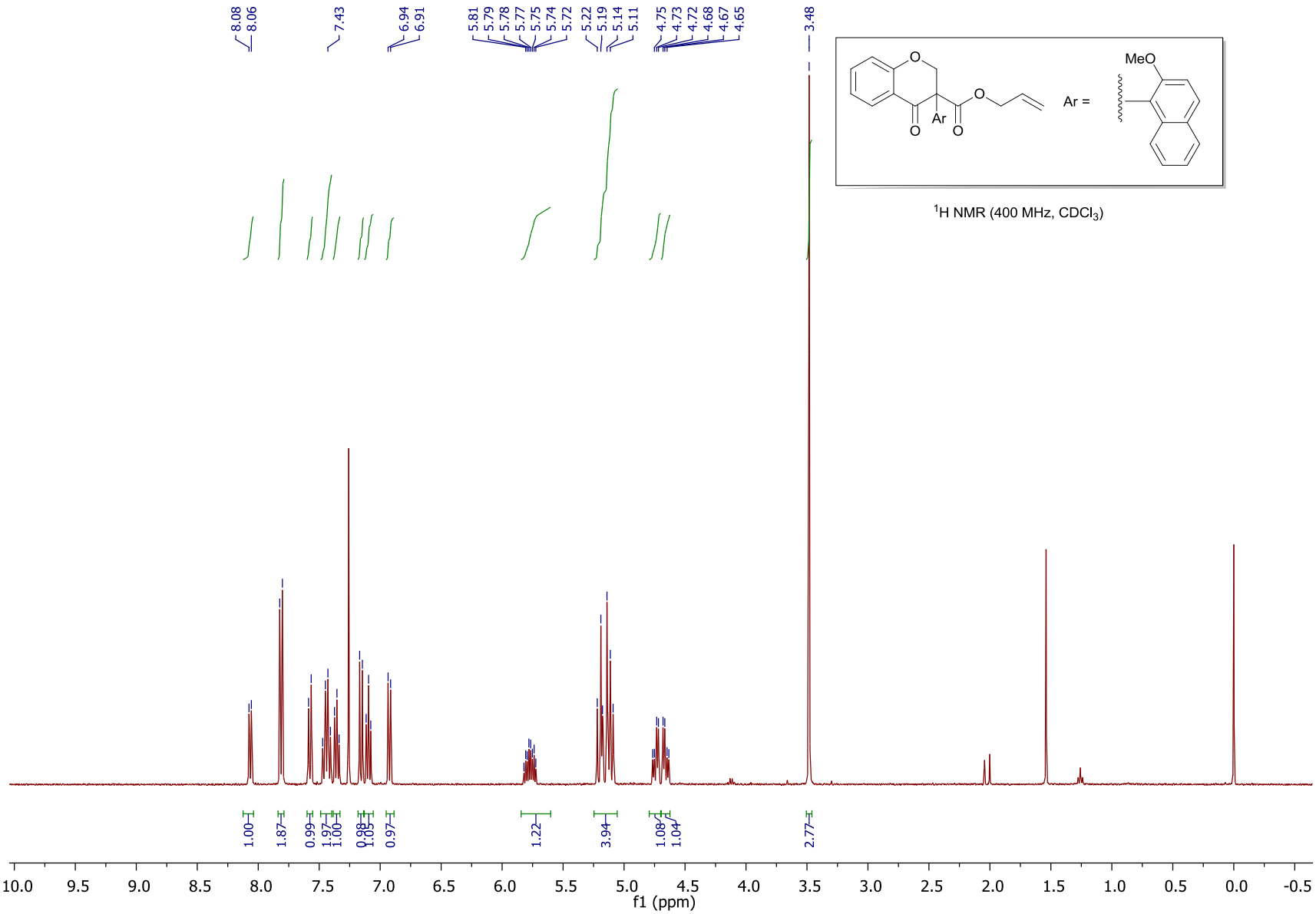
^{13}C NMR (400 MHz, $CDCl_3$)



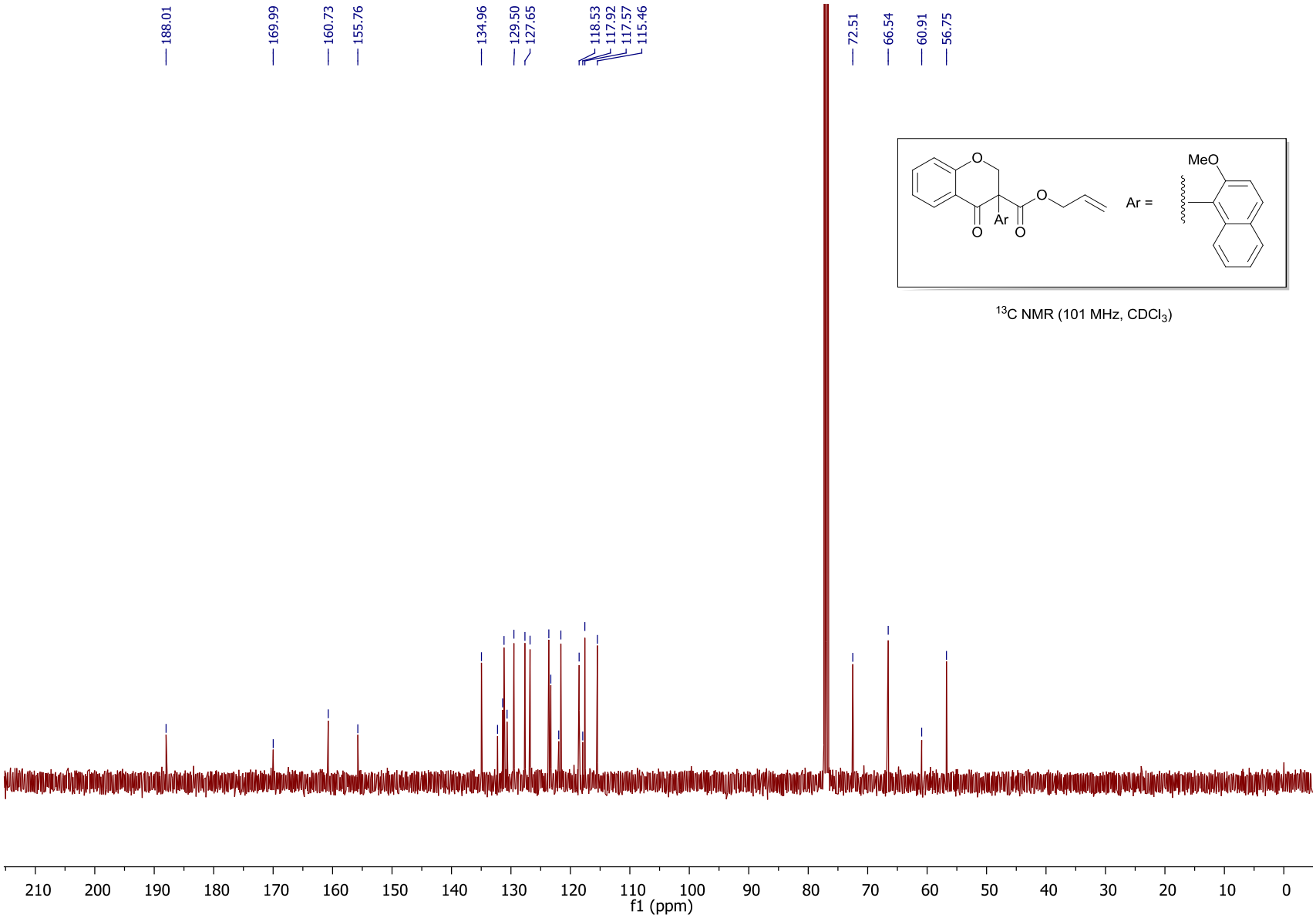
^{1}H NMR (400 MHz, $CDCl_3$)



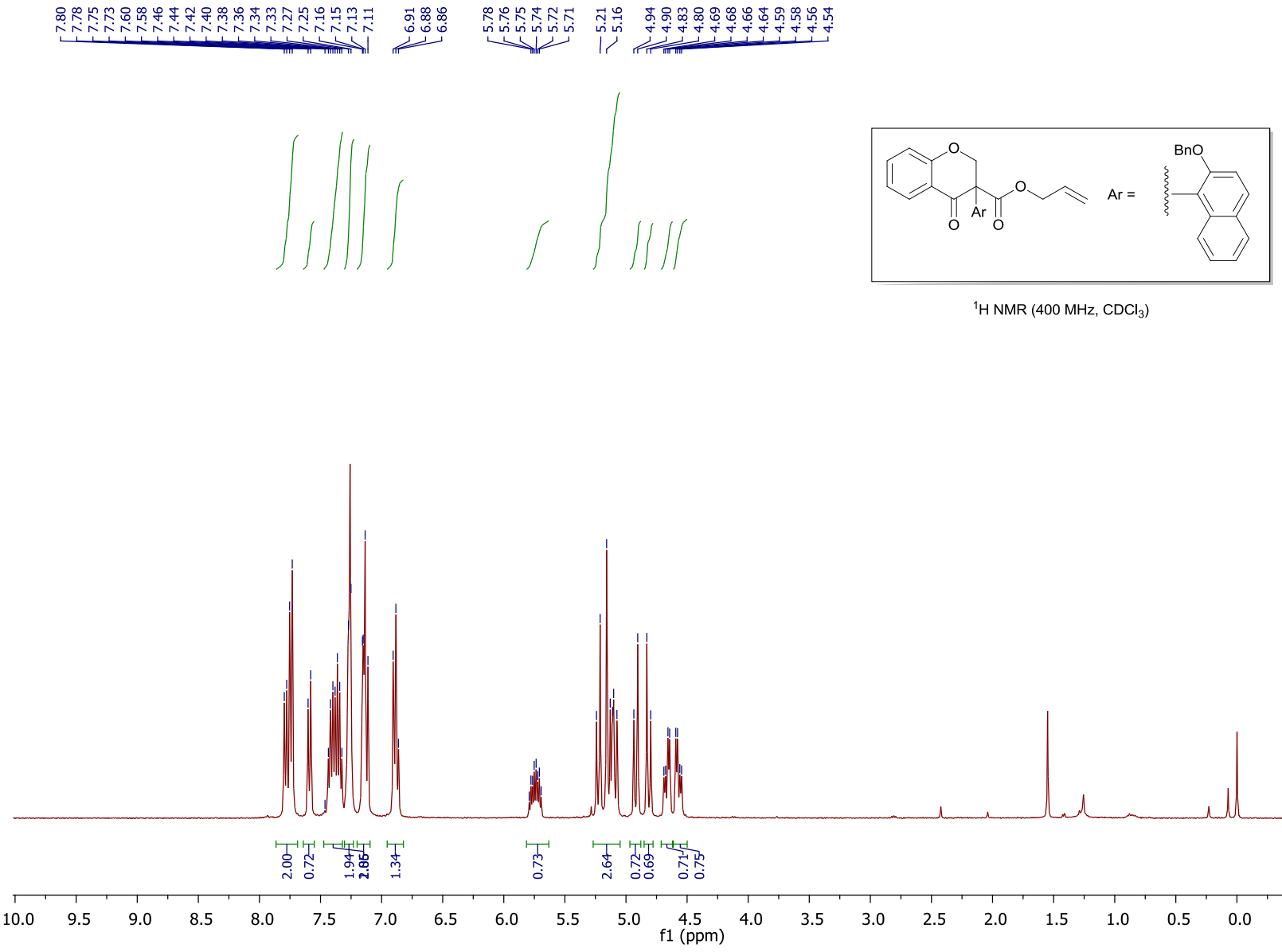
^{13}C NMR (101 MHz, $CDCl_3$)



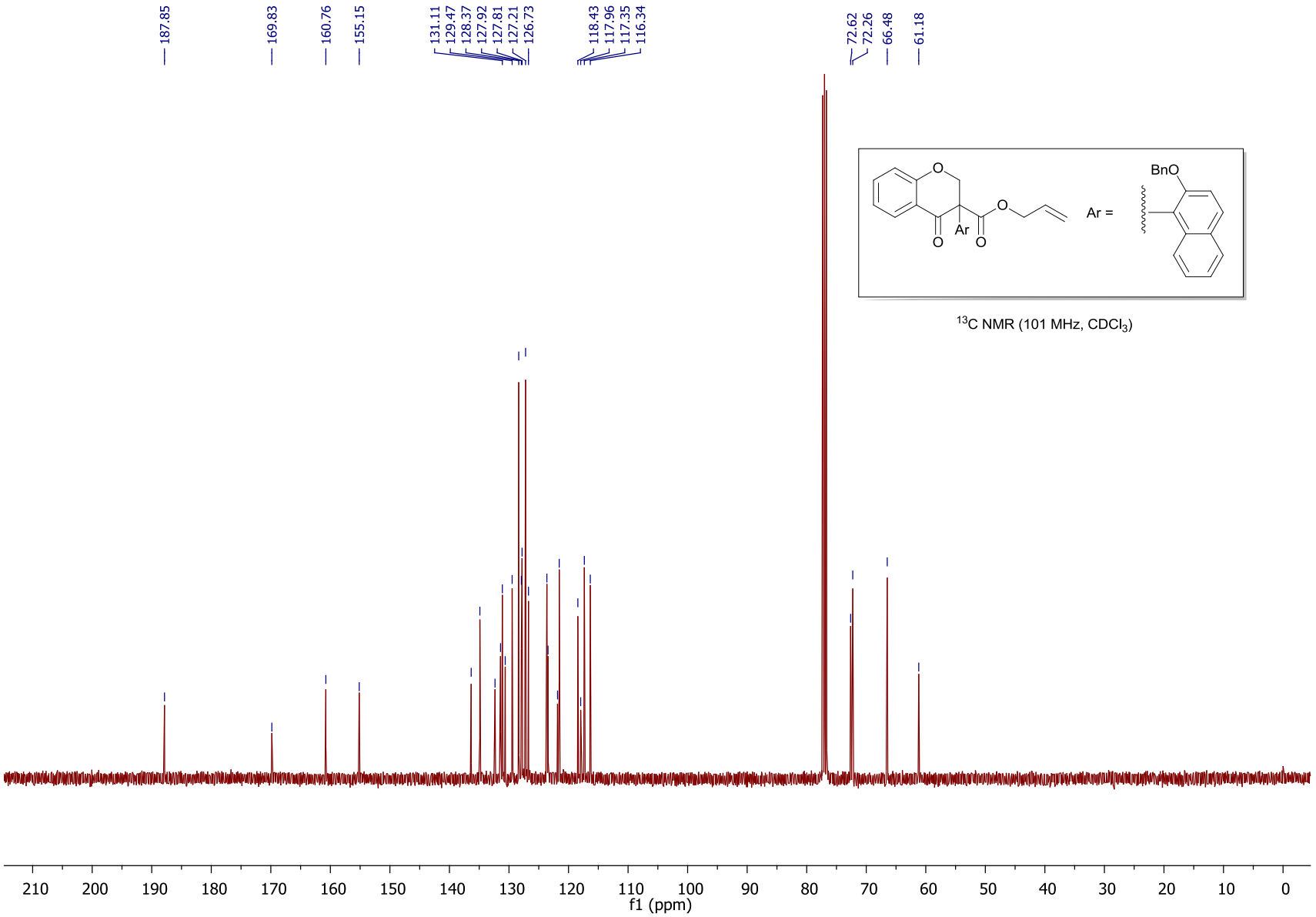
^{1}H NMR (400 MHz, $CDCl_3$)

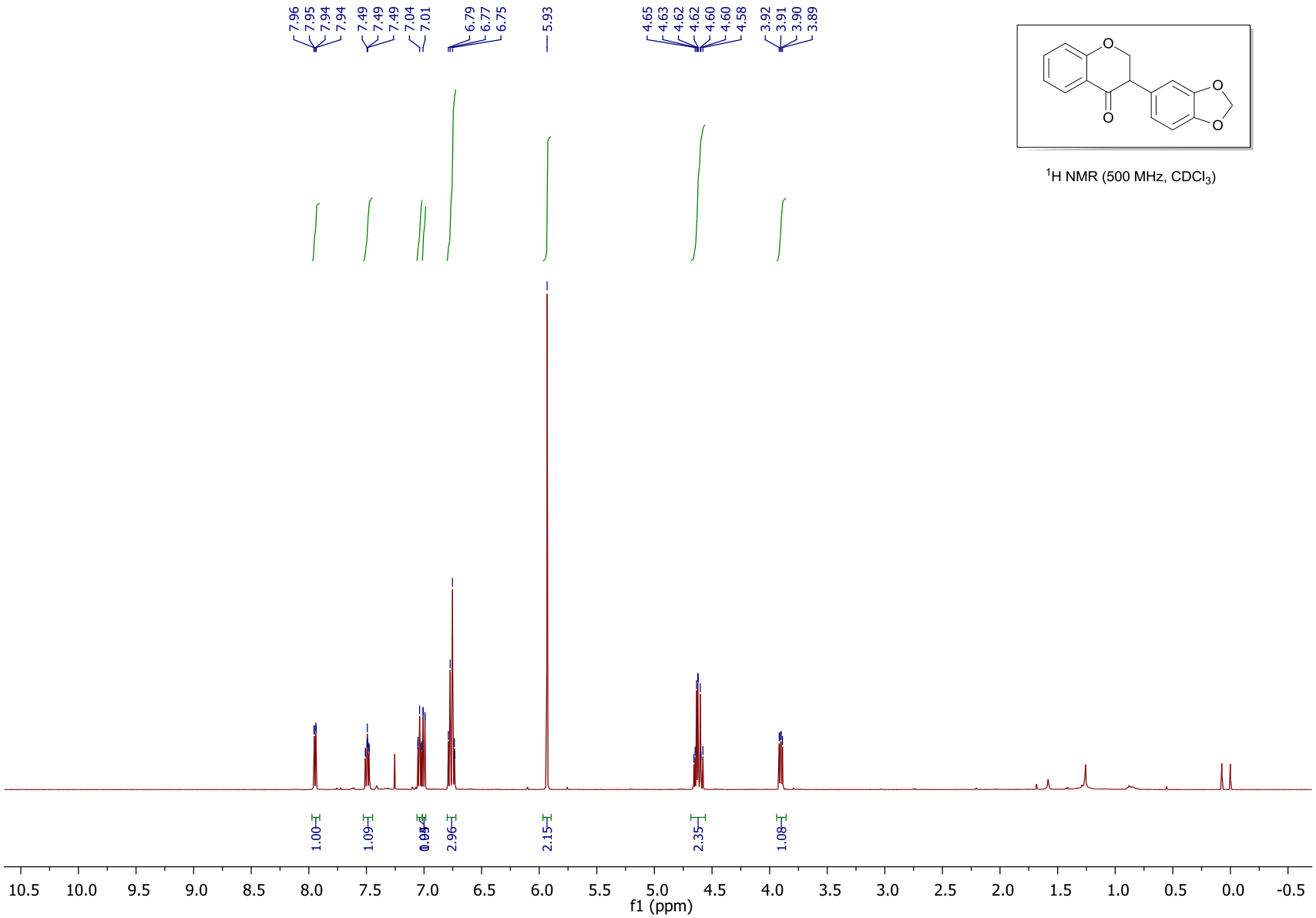


^{13}C NMR (101 MHz, $CDCl_3$)

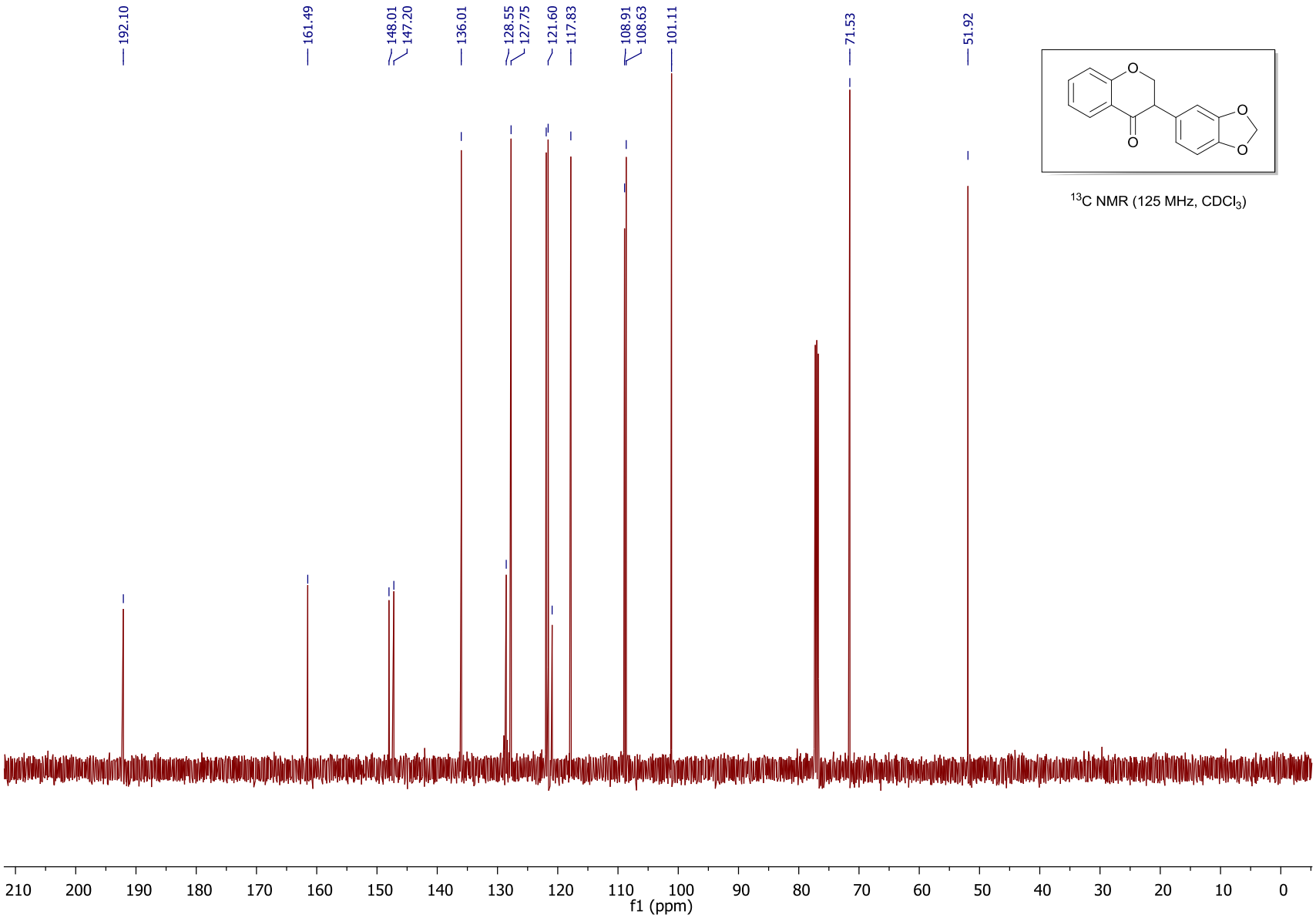


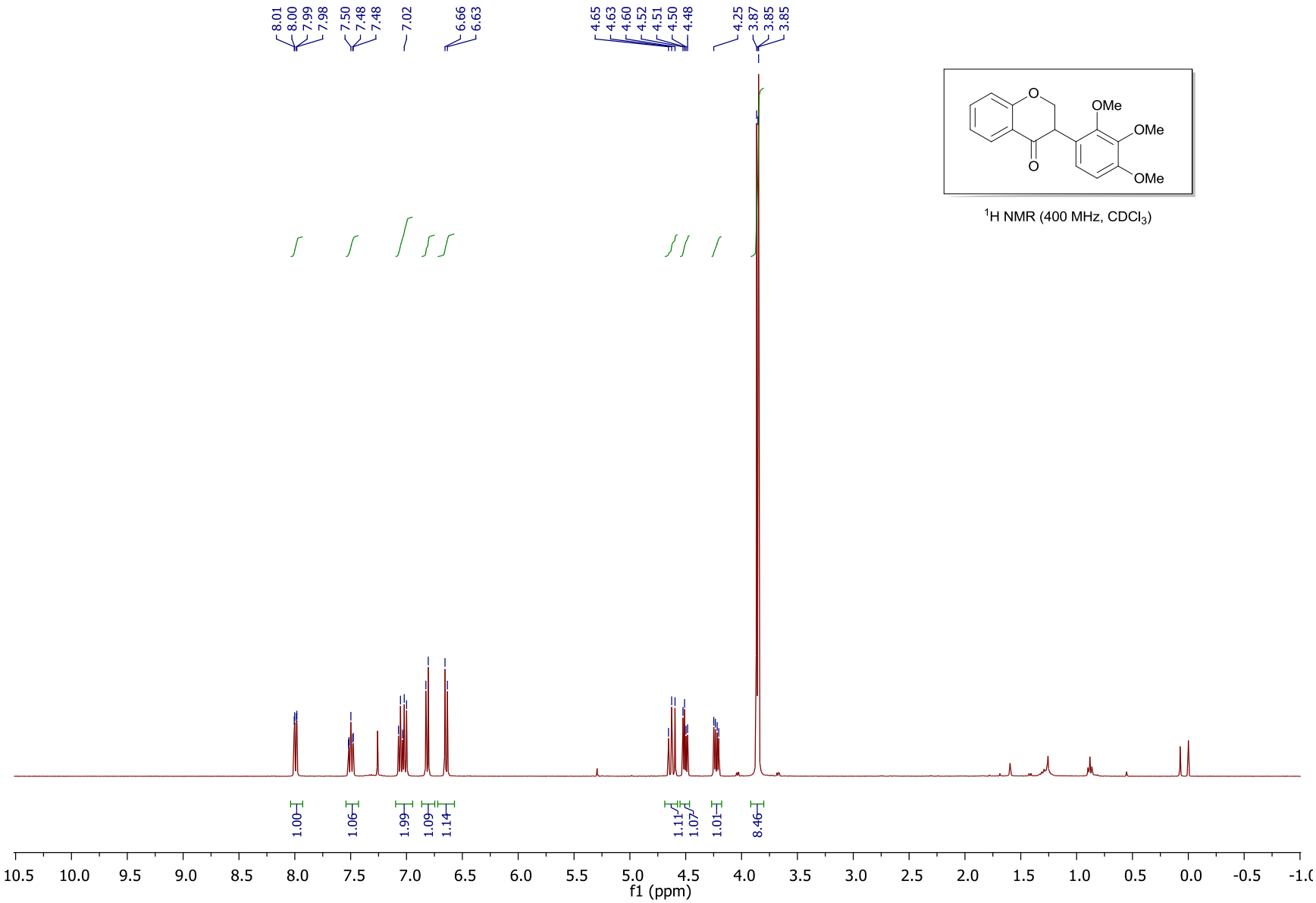
^{1}H NMR (400 MHz, $CDCl_3$)



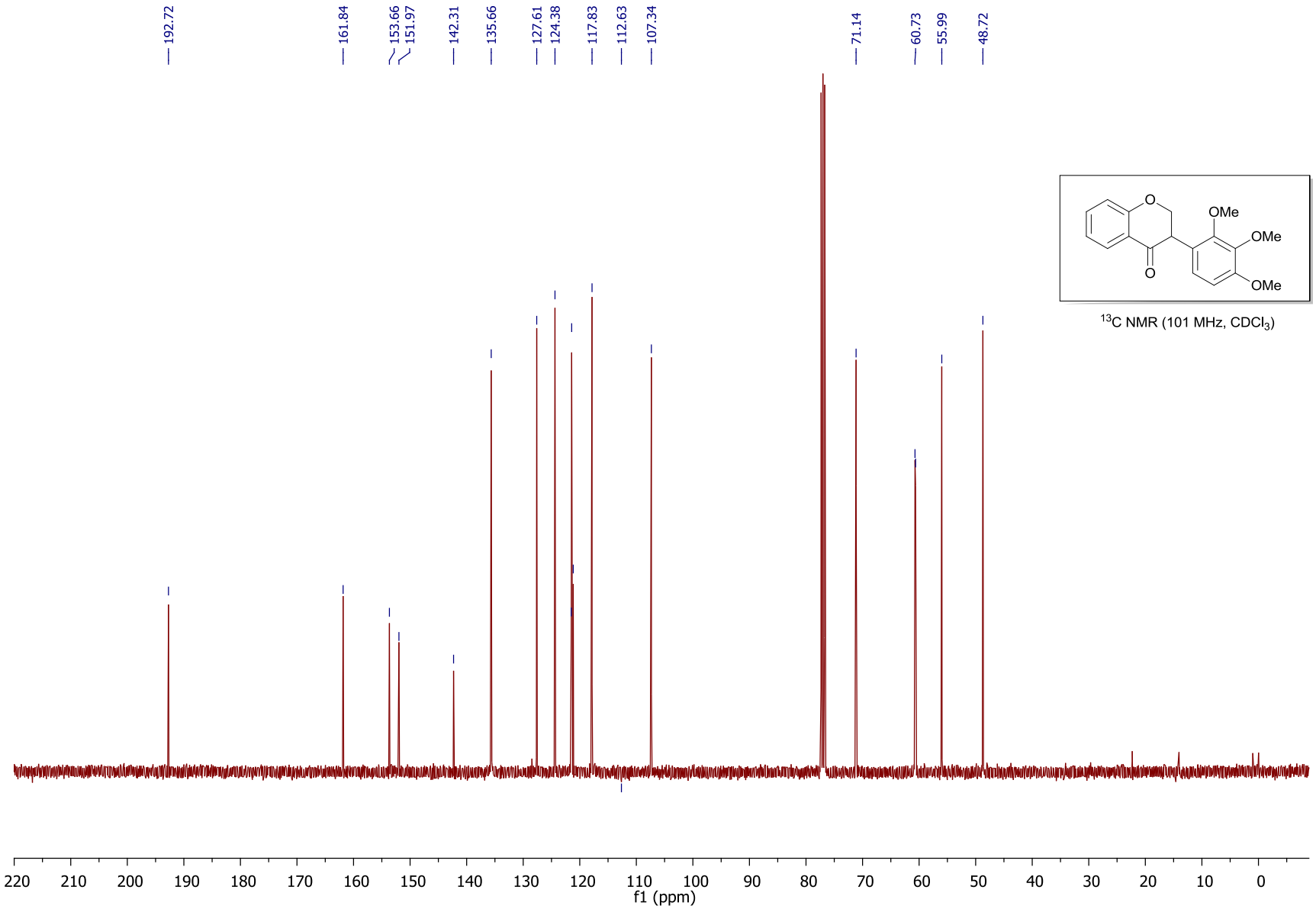


^{1}H NMR (500 MHz, $CDCl_3$)

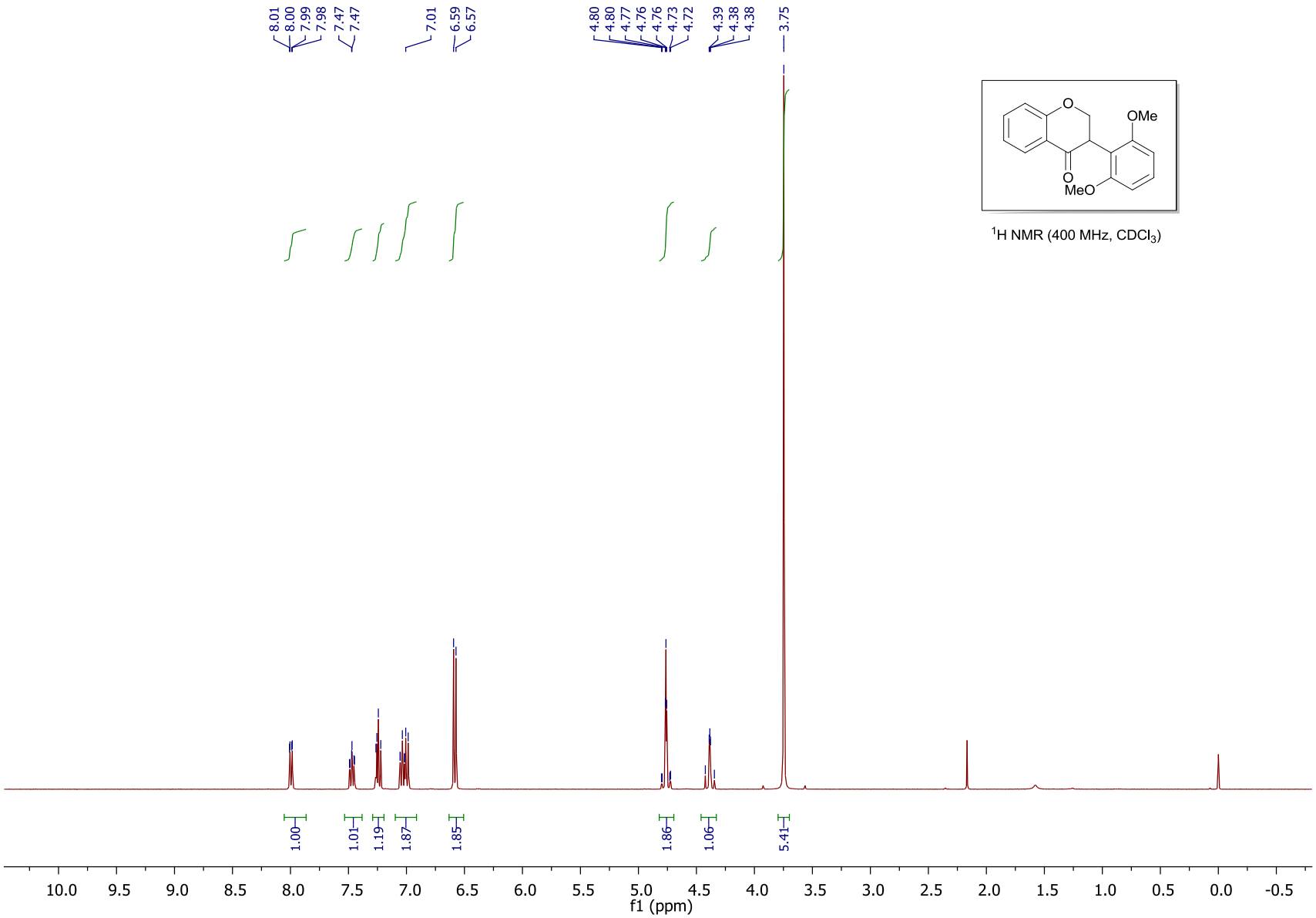




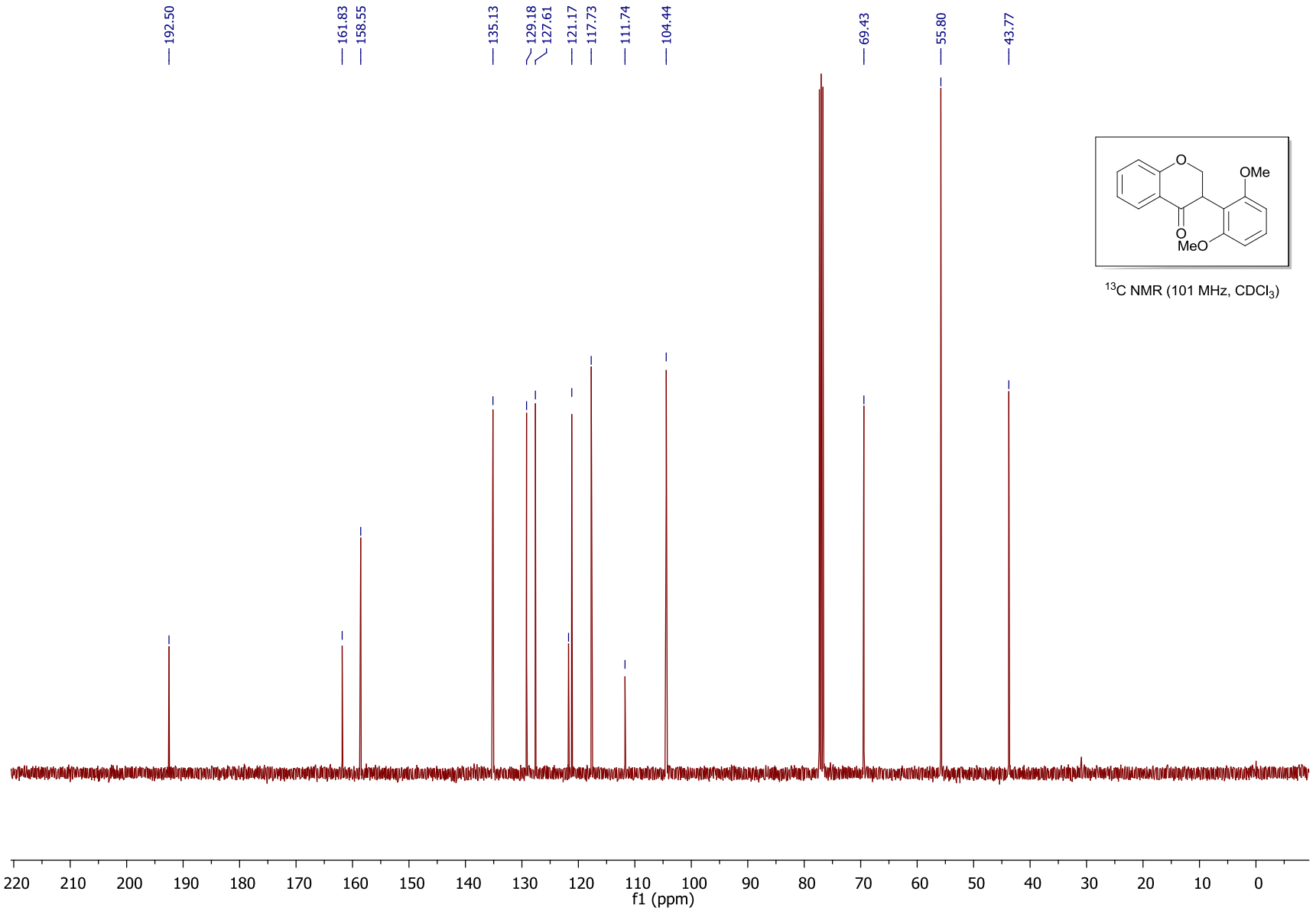
^{1}H NMR (400 MHz, $CDCl_3$)



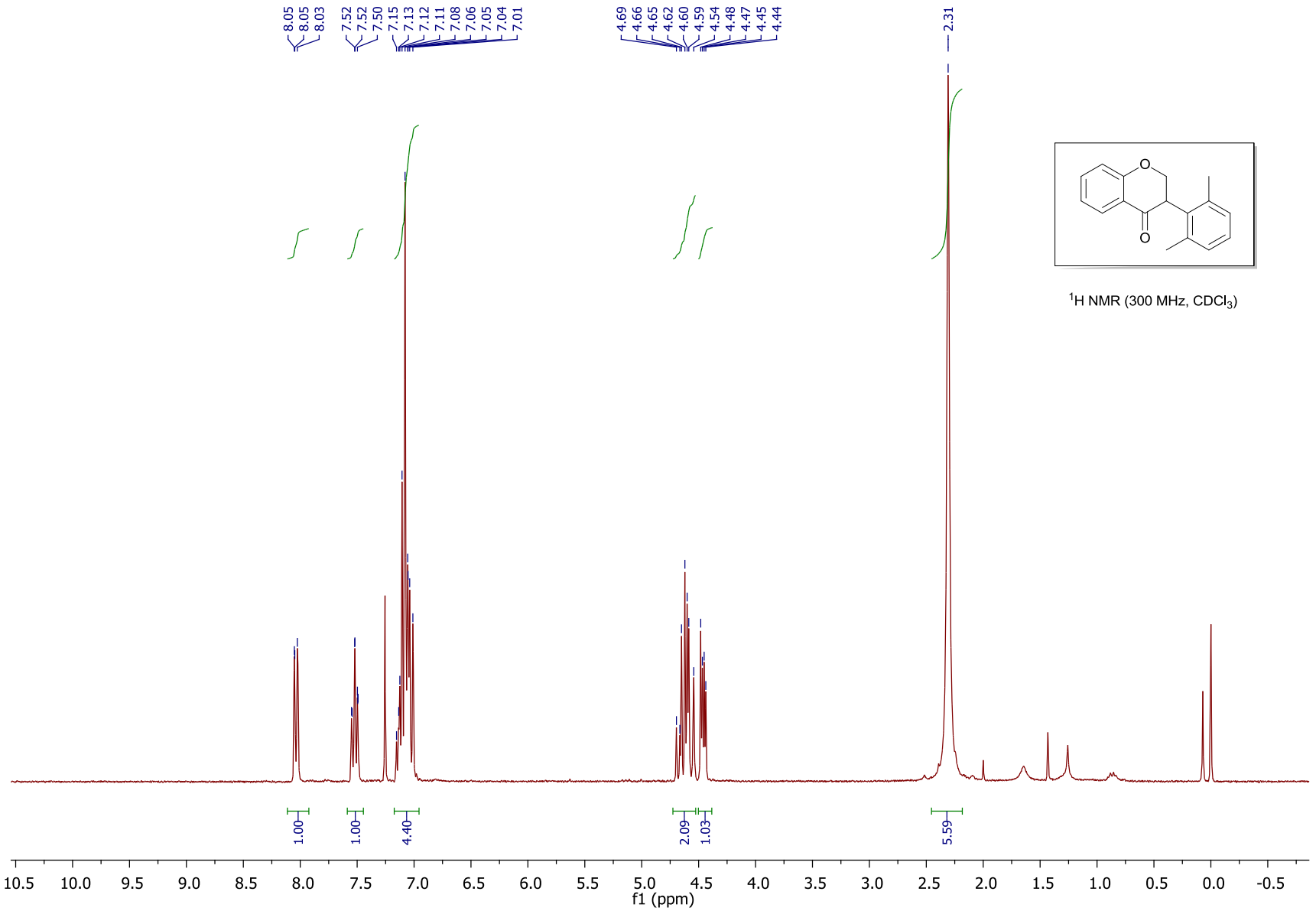
^{13}C NMR (101 MHz, $CDCl_3$)



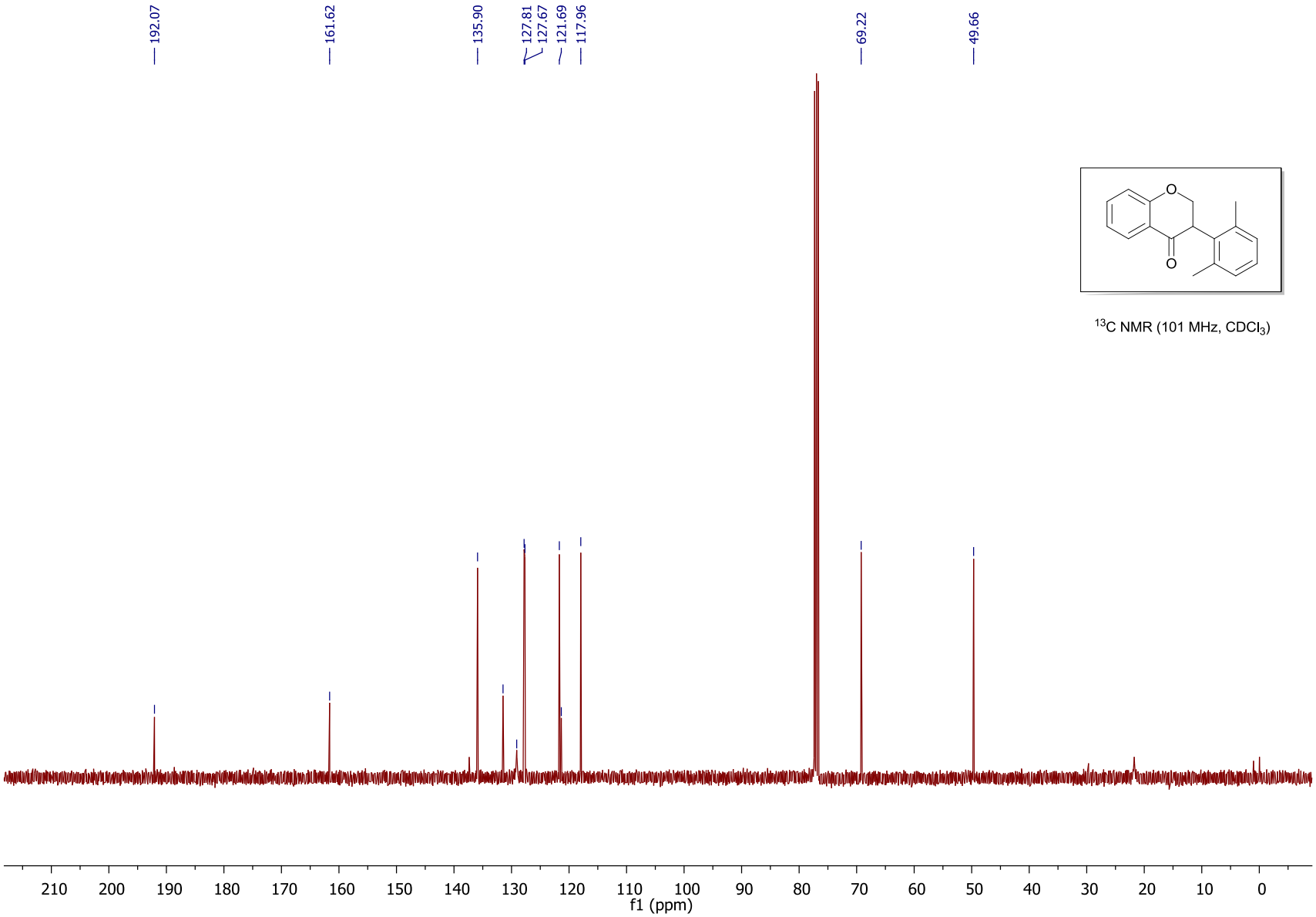
^{1}H NMR (400 MHz, $CDCl_3$)

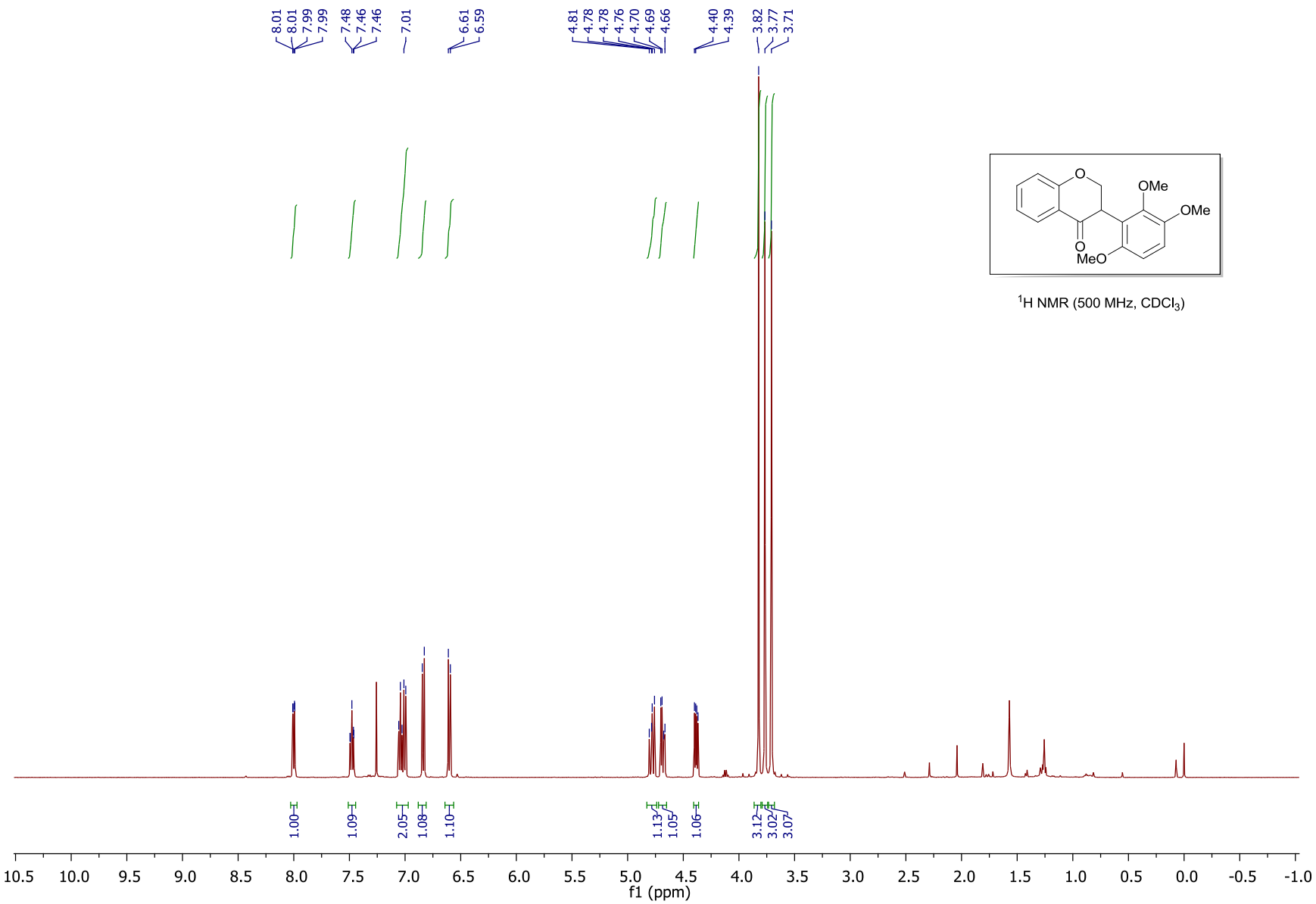


^{13}C NMR (101 MHz, $CDCl_3$)

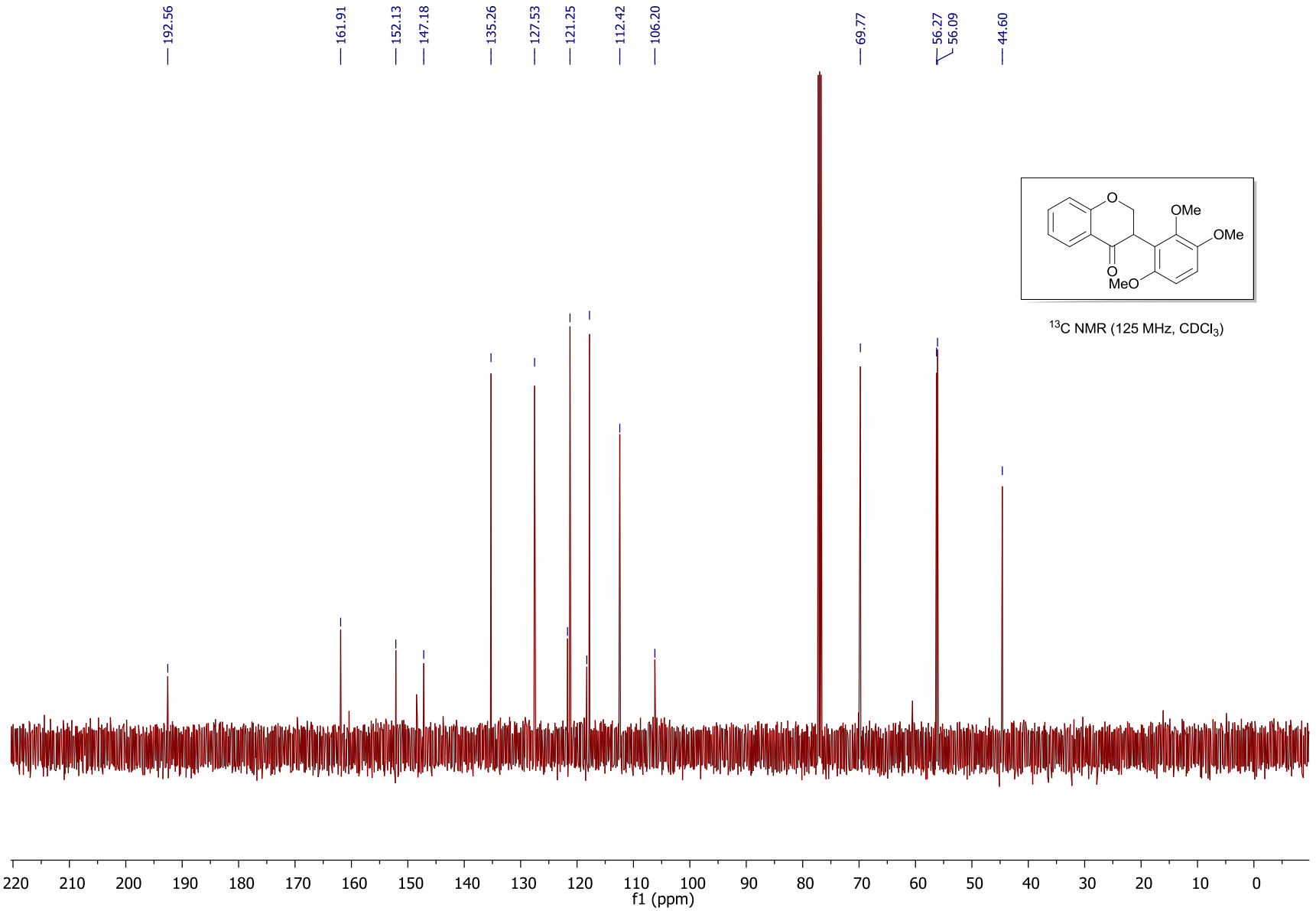


^{1}H NMR (300 MHz, $CDCl_3$)

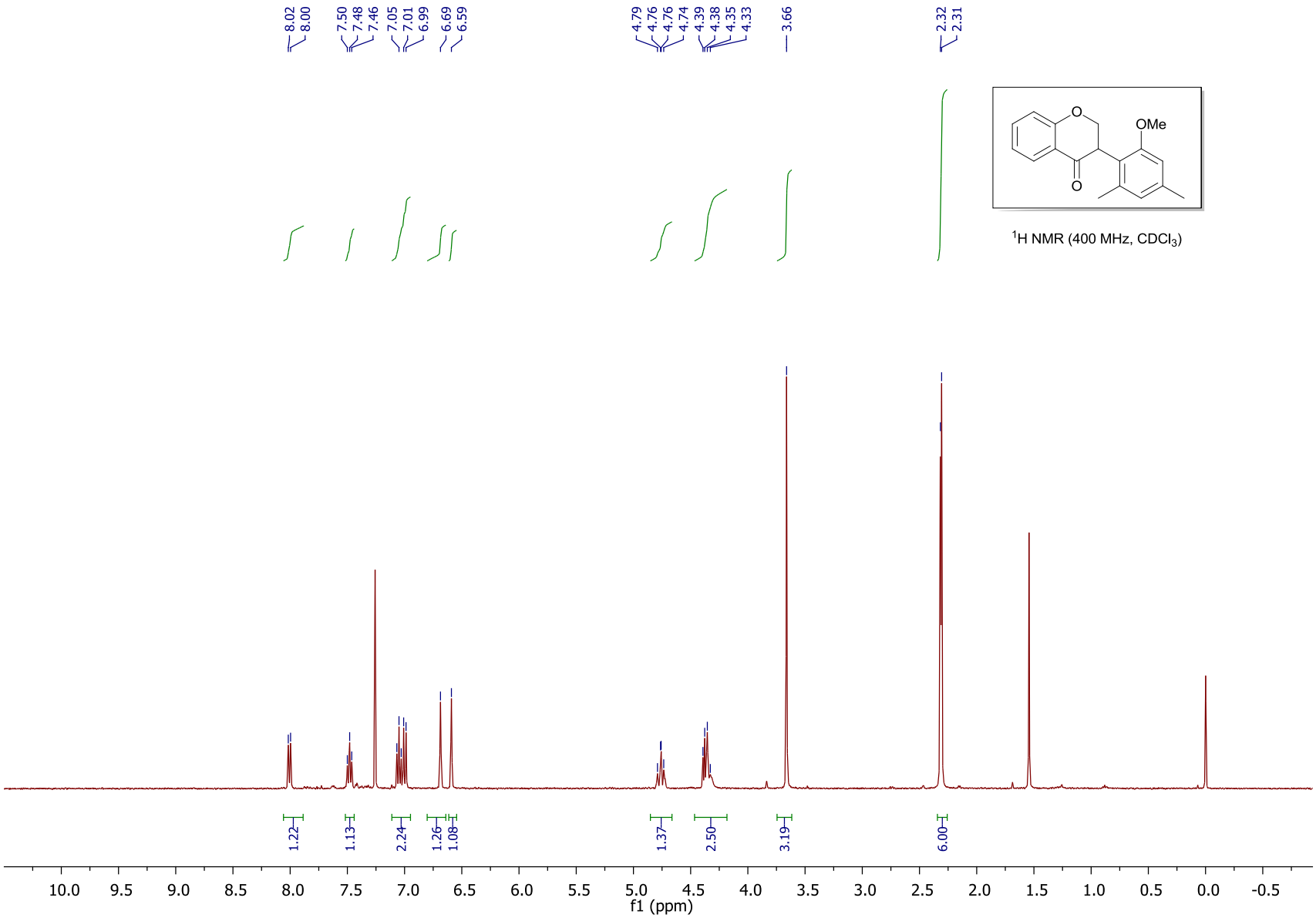


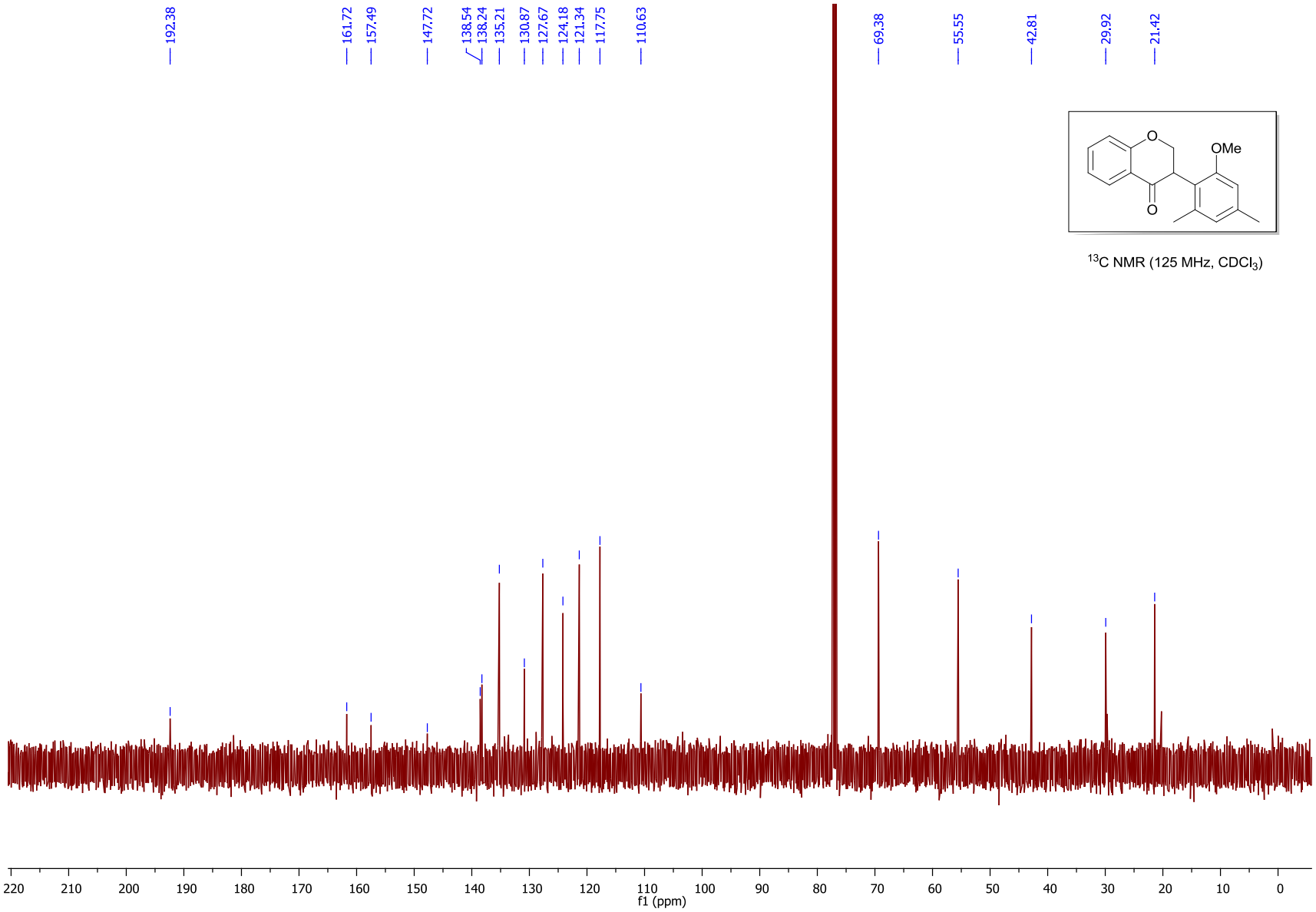


^{1}H NMR (500 MHz, $CDCl_3$)

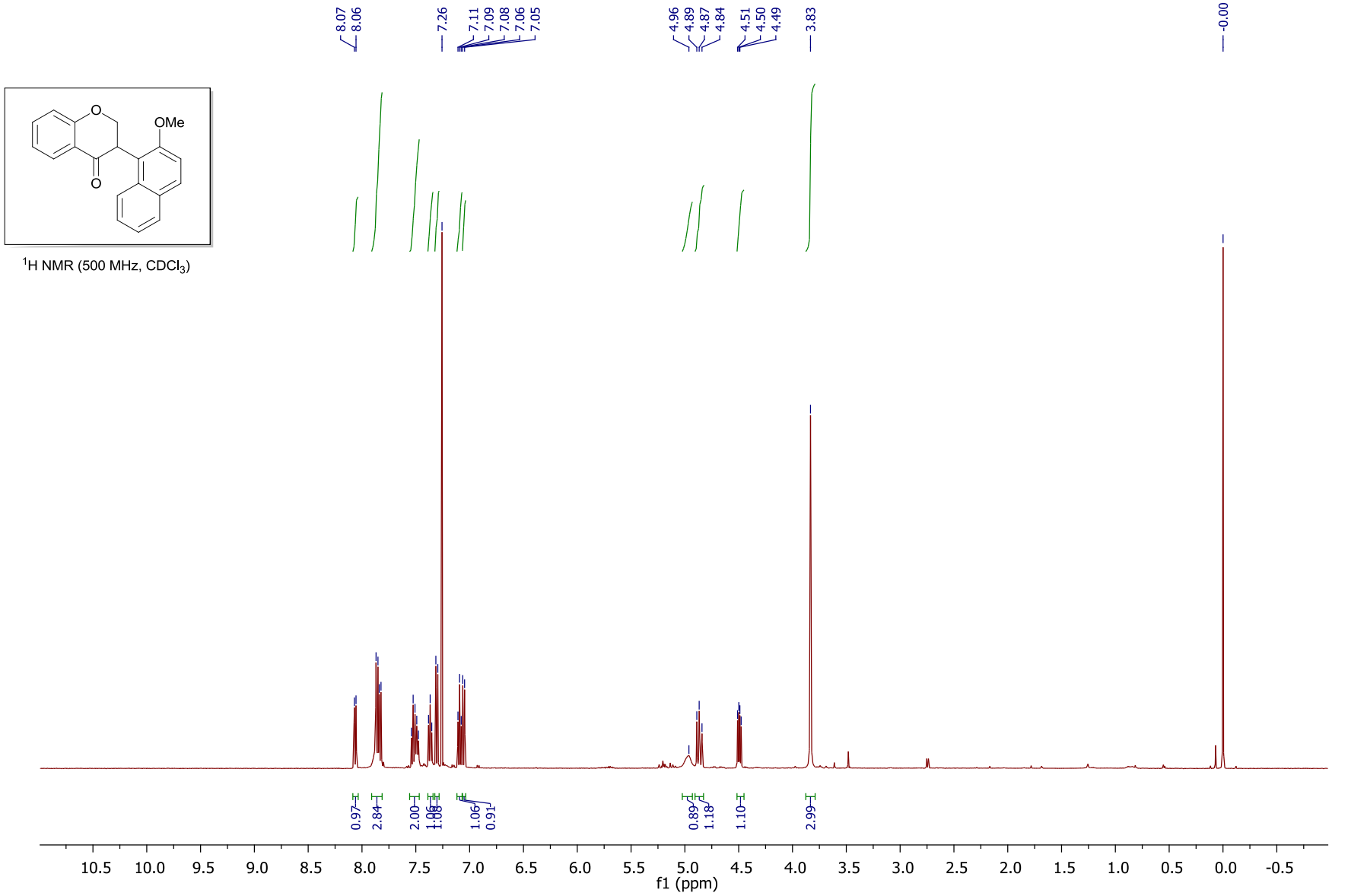


^{13}C NMR (125 MHz, $CDCl_3$)

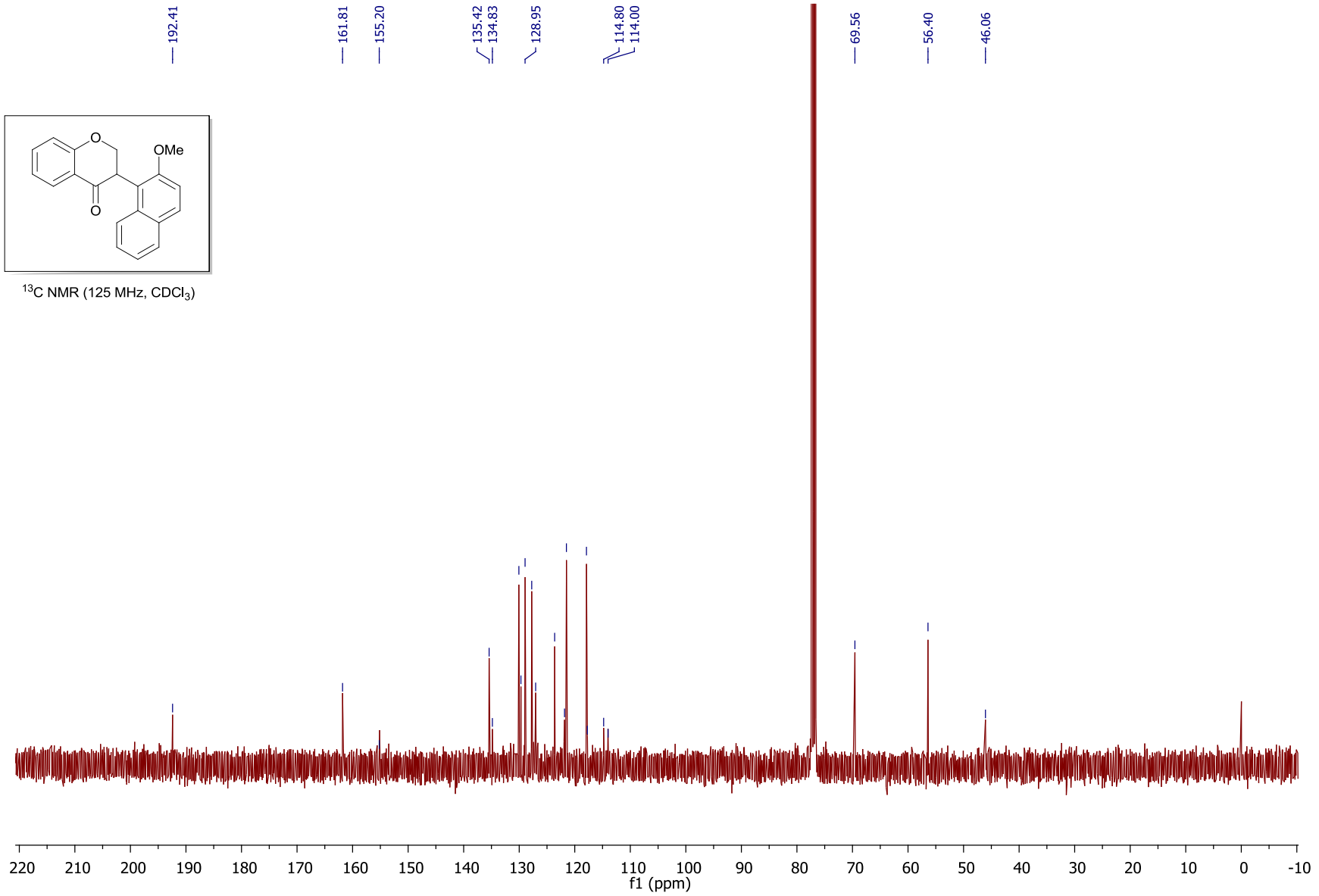




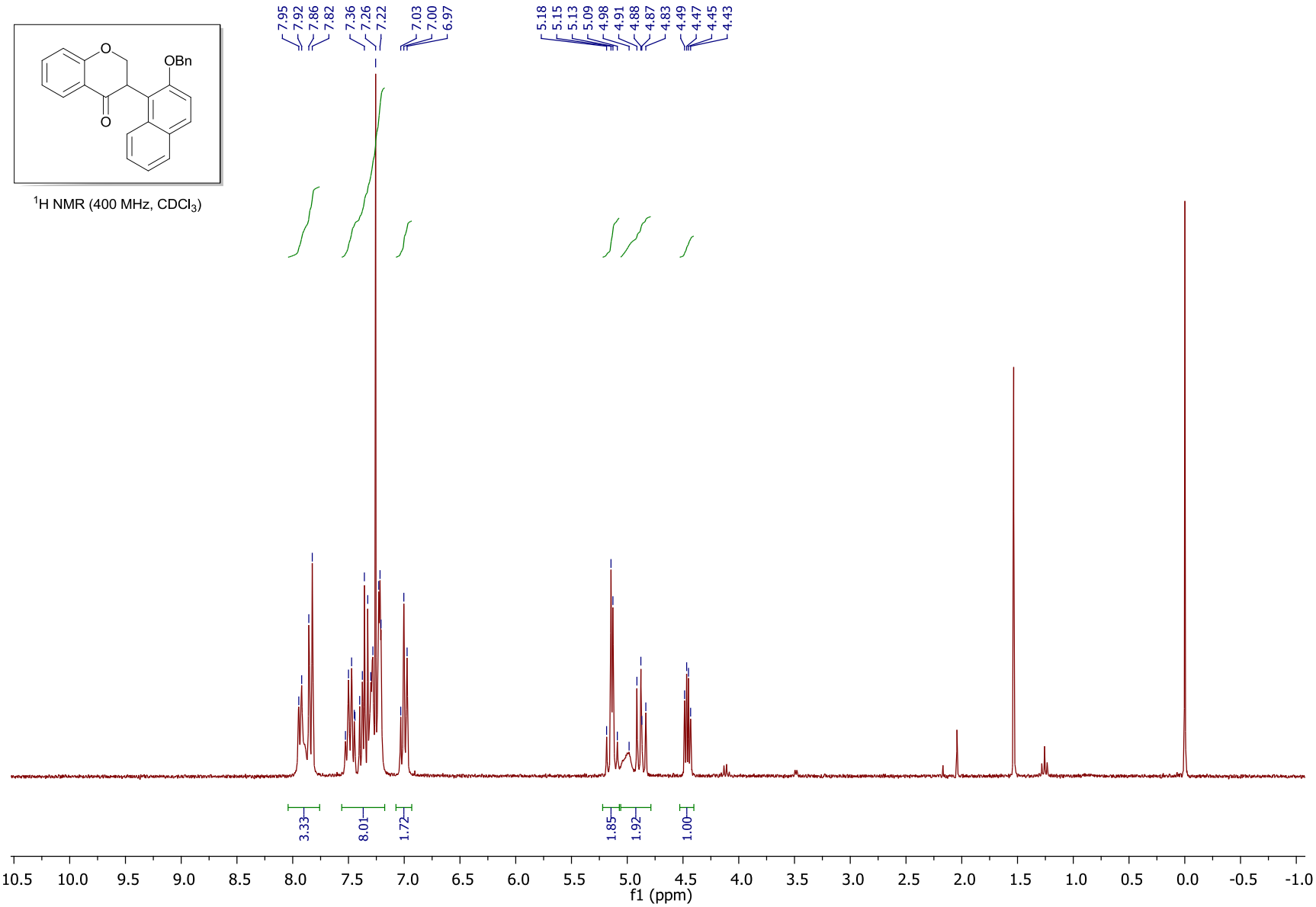
^{13}C NMR (125 MHz, $CDCl_3$)

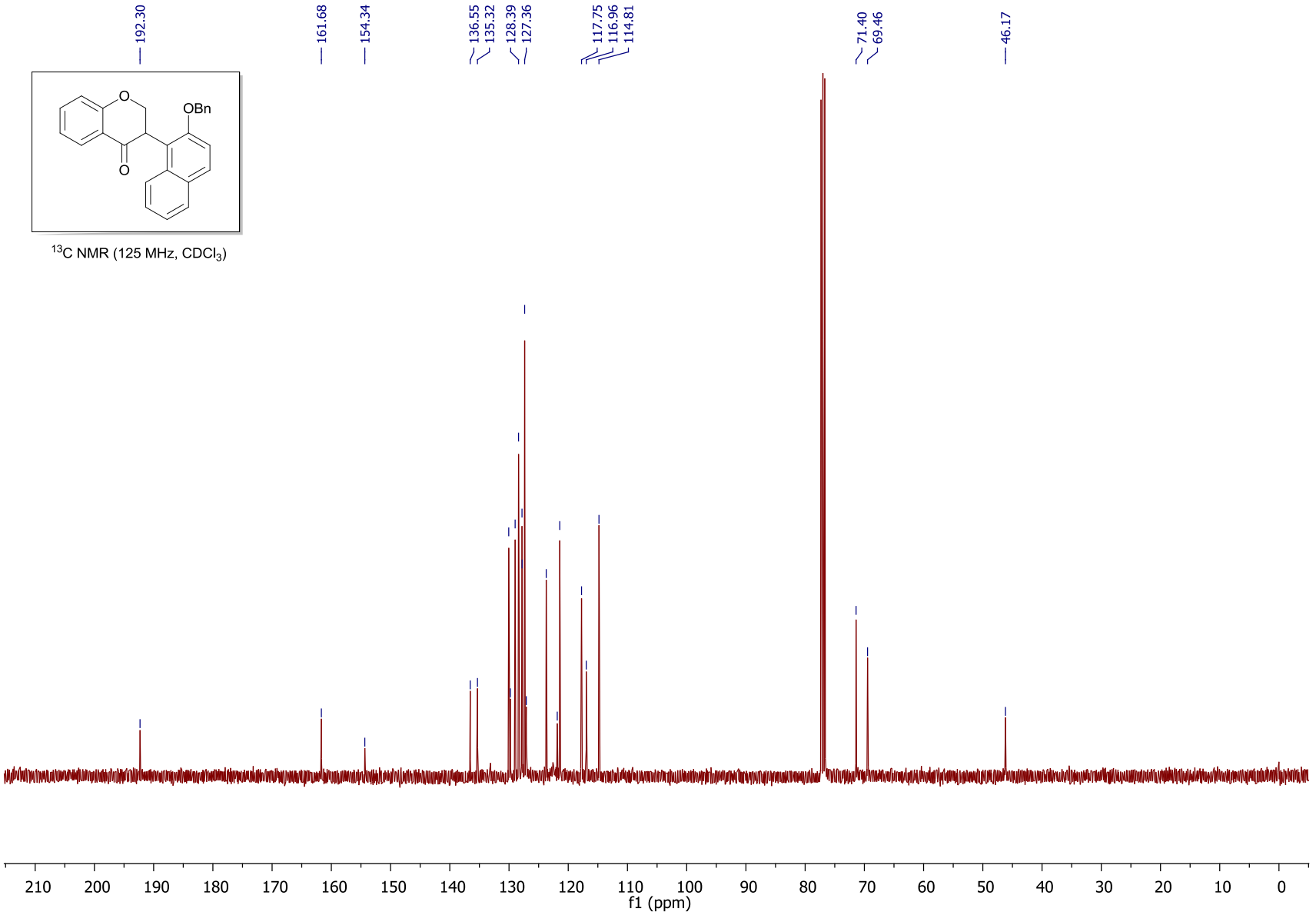


^{1}H NMR (500 MHz, $CDCl_3$)

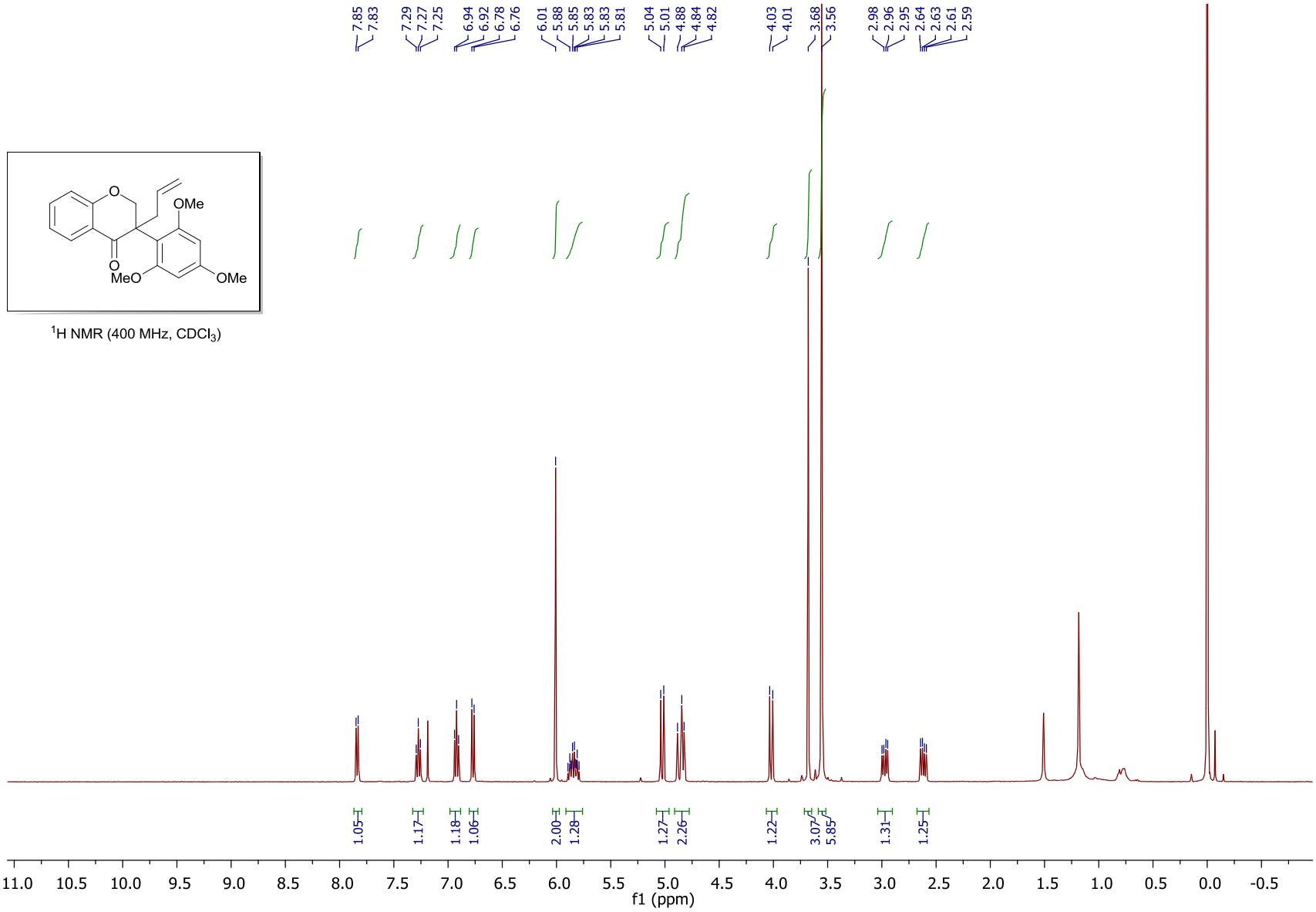


^{13}C NMR (125 MHz, $CDCl_3$)

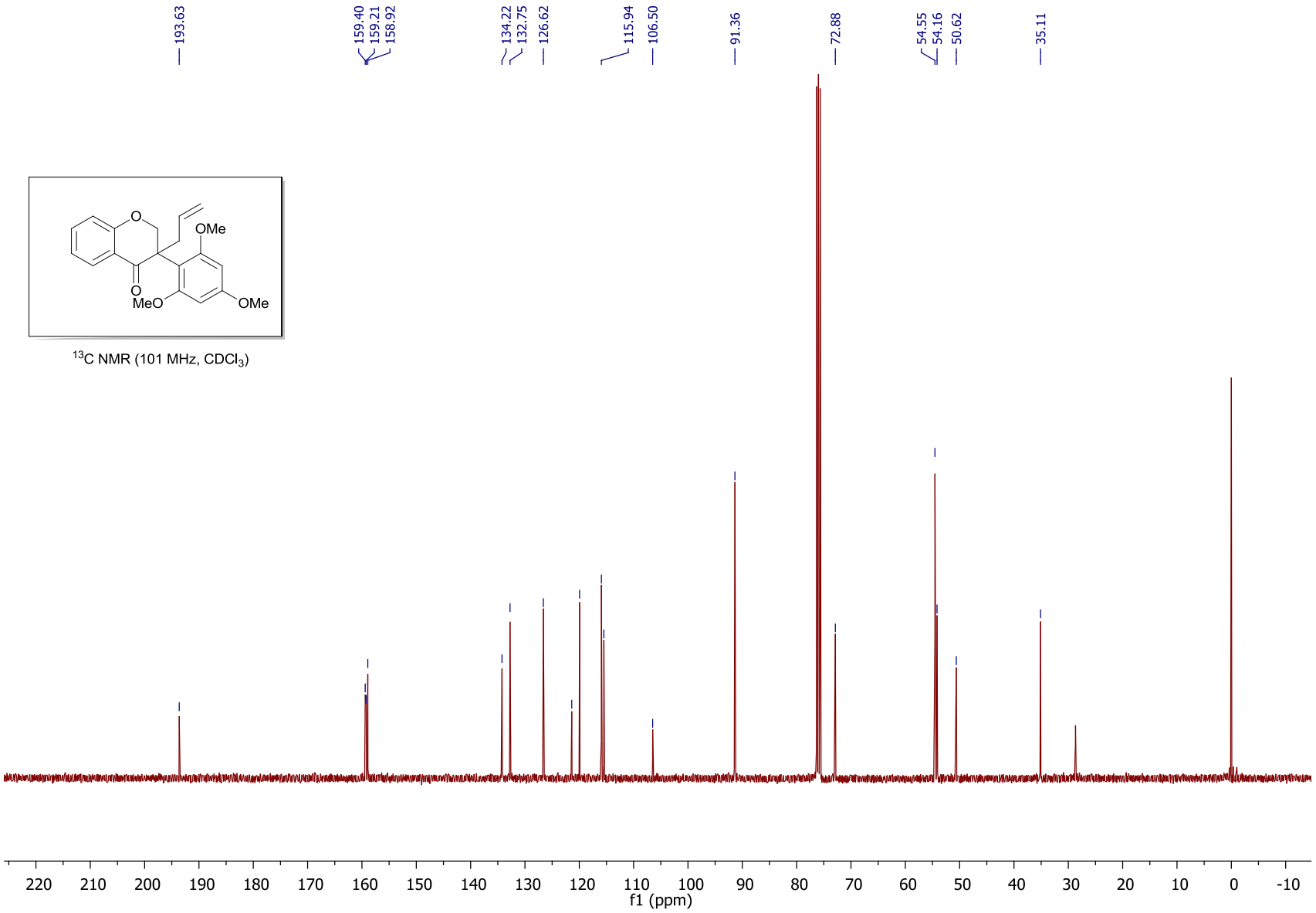




^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

XIII. Reference

(1) Zalesskiy, S. S.; Ananikov, V. P. *Organometallics* **2012**, *31*, 2302.
(2) Connolly, D. J.; Lacey, P. M.; McCarthy, M.; Saunders, C. P.; Carroll, A.-M.; Goddard, R.; Guiry, P. J. *J. Org. Chem.* **2004**, *69*, 6572.
(3) Tani, K.; Behenna, D. C.; McFadden, R. M.; Stoltz, B. M. *Org. Lett.* **2007**, *9*, 2529.
(4) Donnelly, D. M. X.; Finet, J.-P.; Rattigan, B. A. *J. Chem. Soc., Perkin T. 1* **1993**, 1729.
(5) P. Guiry, P. McCormack. Science of Synthesis; M.G. Moloney Ed.; Thieme: New York **2003**, *5*, 673-675
(6) $Pb(OAc)_4$ and $Hg(OAc)_2$ are both cumulative toxins and should be handled with care. For further safety information, see http://ww.hazard.com/msds/.
(7) Kozyrod, R.; Morgan, J.; Pinhey, J. *Aust. J. Chem.* **1985**, *38*, 1147.
(8) Morgan, J.; Pinhey, J. T. *J. Chem. Soc., Perk. T. 1* **1990**, 715.
(9) Harvey, D. R.; Norman, R. O. C. *J. Chem. Soc. (Resumed)* **1964**, 4860.
(10) Preuß, F. R.; Janshen, I. *Arch. Pharm. (Weinheim, Ger.)* **1960**, *293*, 933.
(11) Willemsens, L. C.; De Vos, D.; Spierenburg, J.; Wolters, J. *J. Organomet. Chem.* **1972**, *39*, C61.
(12) Barton, D. H. R.; Donnelly, D. M. X.; Finet, J.-P.; Guiry, P. J. *J. Chem. Soc., Perkin T. 1* **1991**, 2095.
(13) Kano, T.; Ohyabu, Y.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **2002**, *124*, 5365.
(14) White, D. E.; Stewart, I. C.; Grubbs, R. H.; Stoltz, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 810.