CHEMISTRY
A European Journal

Supporting Information

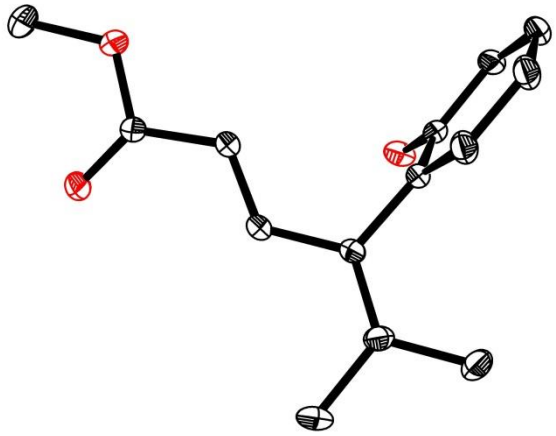
Iron- or Palladium-Catalyzed Reaction Cascades Merging Cycloisomerization and Cross-Coupling Chemistry

Filipe Gomes, Pierre-Georges Echeverria, and Alois Fürstner*[a]

chem_201803360_sm_miscellaneous_information.pdf

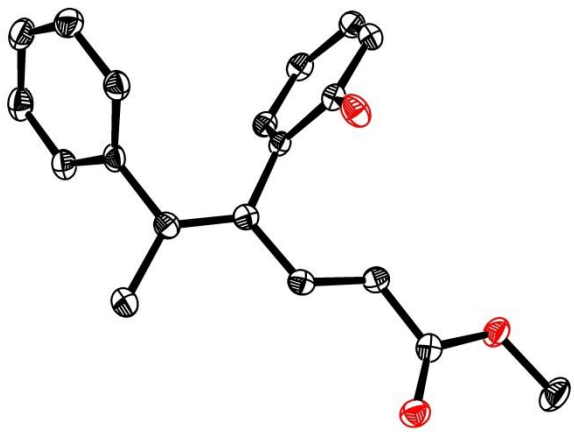
SUPPORTING CRYSTALLOGRAPHIC DATA

A crystallographic abstract for compound **3f** is already contained in the Supporting Information of our preliminary Communication (**CCDC 1478953**).[1]



Figures S1. Structure of compound **3a** in the solid state

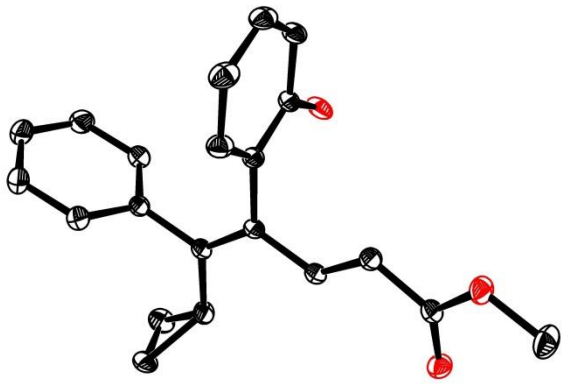
X-ray Crystal Structure Analysis of Compound 3a: $C_{14}H_{16}O_3$, M_r = 232.27 g · mol^{-1}, yellow block, crystal size 0.21 x 0.13 x 0.13 mm, monoclinic, space group $P2_1/n$, a = 7.3650(18) Å, b = 8.112(2) Å, c = 20.679(5) Å, β = 99.872(5)°, V = 1217.2(5) Å^3, T = 100 K, Z = 4, D_{calc} = 1.268 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.088 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker-AXS APEX-II diffractometer, 1.999 < θ < 31.356°, 336568 measured reflections, 4091 independent reflections, 3636 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.060 [$I > 2\sigma(I)$], wR_2 = 0.184, 159 parameters, H atoms riding, S = 1.119, residual electron density +0.5 / -0.5 e Å^{-3}. **CCDC 1850024**



[1] P.-G. Echeverria, A. Fürstner, *Angew. Chem. Int. Ed*. **2016**, *55*, 1188-11192; Angew. Chem. 2016, 128, 11354-11358.

Figures S2. Structure of compound **9a** in the solid state

X-ray Crystal Structure Analysis of Compound 9a: $C_{19}H_{18}O_3$, M_r = 294.33 g · mol^{-1}, colorless block, crystal size 0.17 x 0.14 x 0.05 mm, monoclinic, space group $P2_1/n$, a = 8.9933(3) Å, b = 20.3822(6) Å, c = 9.6130(3) Å, β = 116.7750(10)°, V = 1573.17(9) Å^3, T = 100 K, Z = 4, D_{calc} = 1.243 g · cm^3, λ = 1.54178 Å, $\mu(Cu\text{-}K_\alpha)$ = 0.669 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.92, T_{max} = 0.97), Bruker AXS X8 Proteum diffractometer, 4.338 < θ < 67.370°, 37092 measured reflections, 2757 independent reflections, 2476 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.034 [$I > 2\sigma(I)$], wR_2 = 0.089, 202 parameters, H atoms riding, S = 1.031, residual electron density +0.2 / -0.2 e Å^{-3}. **CCDC 1850025**



Figures S3. Structure of compound **9b** in the solid state

X-ray Crystal Structure Analysis of Compound 9b: $C_{21}H_{20}O_3$, M_r = 320.37 g · mol^{-1}, colorless block, crystal size 0.16 x 0.12 x 0.12 mm, monoclinic, space group $P2_1/c$, a = 10.0865(10) Å, b = 16.984(3) Å, c = 10.087(7) Å, β = 92.660(19)°, V = 1726.2(13) Å^3, T = 100 K, Z = 4, D_{calc} = 1.233 g · cm^3, λ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.081 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.99, T_{max} = 0.99), Bruker-AXS APEX-II diffractometer, 3.039 < θ < 30.999°, 28763 measured reflections, 5467 independent reflections, 4746 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.049 [$I > 2\sigma(I)$], wR_2 = 0.139, 219 parameters, H atoms riding, S = 1.049, residual electron density +0.6 / -0.3 e Å^{-3}. **CCDC 1850023**

GENERAL

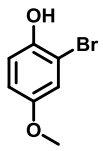
All reactions were carried out under Ar in glassware dried with a heat gun under vacuum (Schlenk line). The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, toluene (Na/K), MeOH (Mg, stored over MS 3Å); DMF, CH_3CN , NEt_3 and pyridine were dried by an adsorption solvent purification system based on molecular sieves. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM® SIL/UV254); Flash chromatography: Merck silica gel 60 (40–63 μm or 15–40 μm (fine)) with predistilled or HPLC grade solvents. NMR: Spectra were recorded on Bruker DPX 300, AV 400 or AV 500 spectrometers in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as reference and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers (ν) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan).

Unless stated otherwise, all commercially available compounds (Alfa Aesar, Sigma-Aldrich) were used as received. $Fe(acac)_3$ (> 99.9%) was purchased from Sigma-Aldrich. The Grignard reagents (Alfa Aesar, Sigma-Aldrich) were titrated prior to use according to a literature procedure.[2]

SUBSTRATES

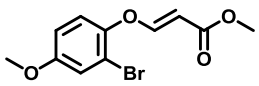
For the preparation of the substrates, see the Supporting Information of our preliminary Communication;[1] additional substrates were prepared as follows:

2-Bromo-4-methoxyphenol (S1). Bromine (267 µL, 5.23 mmol) was added dropwise at 0°C to a solution of 4-methoxyphenol (0.59 g, 4.75 mmol) in dichloromethane (16 mL). The mixture was stirred for 15 min at 0°C and then for 75 min at room temperature. The reaction was quenched with saturated aqueous Na_2SO_3 and the aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic layers were washed with water (20 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was engaged in the next step without further purification. The spectroscopic data correspond to those reported in the literature.[3] Colorless oil (90%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.01 (d, *J* = 2.9 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 6.80 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.16 – 5.09 (m, 1H), 3.75 (s, 3H).



$C_7H_7BrO_2$
203,04 g/mol

Methyl (*E*)-3-(2-bromo-4-methoxyphenoxy)acrylate (S2). DABCO (52.5 mg, 0.468 mmol) was added in one portion to a mixture of **S1** (950 mg, 4.68 mmol) and methyl propiolate (416 µL, 4.68 mmol) in CH_2Cl_2 (47 mL) at 0 °C. The mixture was stirred at room temperature for 1 h before the solvent was removed in vacuo. The residue



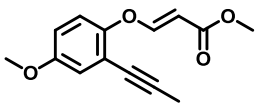
$C_{11}H_{11}BrO_4$
287,11 g/mol

[2] A. Krasovskiy, P. Knochel, *Synthesis* **2006**, 890-891.

[3] a) P. Bachu, J. Sperry, M. A. Brimble, *Tetrahedron* **2008**, *64*, 3343-3350; b) S. Kajigaeshi, T. Kakinami, T. Okamoto, H. Nakamura, M. Fujikawa, *Bull. Chem. Soc. Jpn.***1987**, *60*, 4187-4189.

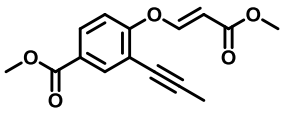
was purified by flash chromatography (hexanes/EtOAc, 90:10) to give the product as a yellow solid (645 mg, 48%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 12.3 Hz, 1H), 7.13 (d, *J* = 3.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.85 (dd, *J* = 8.9, 3.0 Hz, 1H), 5.36 (d, *J* = 12.4 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 160.5, 157.7, 146.1, 121.5, 118.8, 115.0, 114.7, 101.2, 56.0, 51.5; IR (neat, cm^{-1}) 3087, 3003, 2949, 2839, 1710, 1646, 1629, 1486, 1436, 1250, 1196, 1110, 1035, 839; MS (EI) *m/z* (%) 39 (3), 63 (13), 79 (10), 107 (7), 128 (9), 148 (10), 176 (29), 188 (23), 201 (26), 207 (100), 257 (15), 286 (71); HRMS (ESIpos) calcd. for $C_{11}H_{11}BrNaO_4^+$ $[M+Na]^+$ 308.9733, found: 308.9734;

Methyl (*E*)-3-(4-methoxy-2-(prop-1-yn-1-yl)phenoxy)acrylate (10). A Schlenk flask was charged with propargyllithium (205.1 mg, 4.46 mmol) and $ZnCl_2$ (607.6 mg, 4.46 mmol). THF (15 mL) was added and the resulting suspension was stirred for 15 min at ambient temperature before it was cannulated into another Schlenk flask containing a solution of **S2** (640 mg, 2.23 mmol) and Pd(dppf)Cl_2 (182.0 mg, 0.22 mmol) in THF (30 mL). The mixture was stirred at reflux temperature for 7 h before it was allowed to reach ambient temperature. The mixture was filtered through a pad of silica (rinsing with *tert*-butyl methyl ether), the combined filtrates were evaporated and the reside was purified by flash chromatography to give the title compound as a yellow oil (480 mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 12.3 Hz, 1H), 7.13 – 6.88 (m, 2H), 6.81 (dd, *J* = 8.9, 3.1 Hz, 1H), 5.39 (d, *J* = 12.3 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 161.2, 156.8, 149.9, 120.5, 117.9, 117.2, 115.3, 100.5, 92.0, 74.4, 55.8, 51.4, 4.7; IR (neat, cm^{-1}) 3080, 2999, 2951, 2916, 2839, 2239, 1714, 1647, 1495, 1436, 1200, 1128, 1035; MS (GC-EI) *m/z* (%) 50 (4), 63 (8), 77 (14), 89 (21), 102 (19), 115 (61), 128 (27), 144 (43), 155 (33), 171 (52), 186 (44), 203 (53), 215 (100), 231 (31), 246 (43); HRMS (EI) calcd. for $C_{14}H_{14}O_4$ 246.0887, found: 246.0888.



$C_{14}H_{14}O_4$
246,26 g/mol

Methyl (*E*)-4-((3-methoxy-3-oxoprop-1-en-1-yl)oxy)-3-(prop-1-yn-1-yl)benzoate (12). Prepared analogously from methyl (*E*)-3-iodo-4-((3-methoxy-3-oxoprop-1-en-1-yl)oxy)benzoate as a white solid (83 mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 2.2 Hz, 1H), 7.91 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.76 (d, *J* = 12.2 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 5.59 (d, *J* = 12.2 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 165.7, 159.1, 158.2, 135.6, 130.5, 126.9, 117.7, 116.0, 103.1, 93.0, 73.6, 52.3, 51.5, 4.6; IR (neat, cm^{-1}) 3082, 2995, 2952, 2243, 1721, 1651, 1436, 1308, 1220, 1139, 1098, 765; MS (EI) *m/z* (%) 39 (29), 51 (58), 59 (100), 77 (61), 85 (42), 102 (65), 115 (39), 128 (75), 155 (69), 183 (36), 199 (16), 214 (21), 231 (13), 242 (46), 259 (6), 274 (7); HRMS (ESIpos) calcd. for $C_{15}H_{14}NaO_5^+$ $[M+Na]^+$ 297.0733, found: 297.0735.



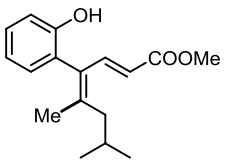
$C_{15}H_{14}O_5$
274,27 g/mol

IRON CATALYZED REACTION CASCADES

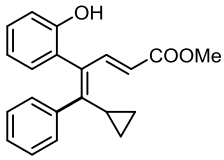
General Procedure. $Fe(acac)_3$ (5-20 mol%) was added to a Schlenk flask containing a solution of the 1,6-enyne in THF (0.01 M). The orange mixture was cooled to –30 °C before a solution of the Grignard reagent in THF or Et_2O (2 equiv) was added dropwise, resulting in an immediate color change to dark brown or dark green. Stirring was continued at –30 °C until TLC indicated complete consumption of the starting material. The reaction was then quenched with EtOH (1 mL). The mixture was concentrated, the residue suspended in CH_2Cl_2 and the mixture filtered through a pad of silica, eluting with hexane/EtOAc (1:1). The combined filtrates were evaporated and the residue was purified by flash chromatography to afford the desired product in analytically pure form.

For the analytical and spectral data of compounds **3a**, **3b**, **3c**, **3d**, **3f**, **3g**, **5a**, **5b**, **7**, **9a**, **15**, **17**, **19a, 21**, **23**, **26**, **34**, **36**, **39**, **40**, see the Supporting Information of our preliminary Communication.[1]

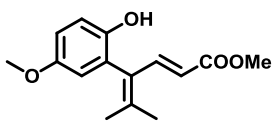
Compound 3e. Pale yellow oil (73%, *E/Z* = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 15.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.95 – 6.89 (m, 3H), 5.32 (d, *J* = 15.4 Hz, 1H), 4.83 (bs, 1H), 3.69 (s, 3H), 2.46 (dd, *J* = 13.1, 7.4 Hz, 1H), 2.37 (dd, *J* = 13.1, 7.4 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.66 (s, 3H), 0.99 (dd, *J* = 7.8, 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 152.4, 151.0, 141.6, 130.4, 129.4, 129.2, 124.9, 120.8, 119.1, 115.4, 51.5, 43.0, 27.9, 22.8, 22.3, 22.0; IR (neat) 3401, 2954, 2928, 2869, 1688, 1605, 1486, 1447, 1435, 1367, 1289, 1195, 1166, 1136, 1106, 1067, 1036, 1023, 975, 910, 864, 828, 809, 753, 731, 694, 647, 632, 608, 546, 508, 458, 435 cm^{-1}; MS (EI) *m/z* (%) = 31 (6), 43 (17), 55 (9), 65 (6), 77 (17), 91 (12), 115 (20), 128 (35), 145 (38), 157 (28), 171 (100), 185 (92), 199 (45), 217 (33), 231 (26), 274 (28); HRMS (ESIpos): calcd for $C_{17}H_{22}O_3Na$: 297.14611; found: 297.14630.



Compound 9b. Yellow waxy solid (74%, *E/Z* = 98:2 after 30 min reaction time); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 15.4 Hz, 1H), 7.11 – 7.01 (m, 3H), 6.98 (td, *J* = 7.9, 1.8 Hz, 1H), 6.89 (dd, *J* = 8.0, 2.0 Hz, 2H), 6.76 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.68 – 6.65 (m, 2H), 5.52 (d, *J* = 15.4 Hz, 1H), 4.94 (s, 1H), 3.73 (s, 3H), 2.39 (tt, *J* = 8.3, 5.2 Hz, 1H), 0.93 (d, *J* = 8.7 Hz, 2H), 0.49 – 0.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 155.1, 152.3, 141.6, 137.4, 131.4, 130.6, 129.6, 128.8, 128.6, 128.1, 127.2, 127.0, 125.1, 120.6, 120.1, 115.1, 51.6, 14.3, 7.1 (2C); IR (neat) 3401, 3057, 3010, 2950, 1689, 1607, 1578, 1486, 1447, 1437, 1360, 1282, 1196, 1170, 1113, 1079, 1032, 977, 912, 865, 843, 802, 754, 731, 704, 648, 626, 600, 575, 548, 506 cm^{-1}; MS (ESIneg) *m/z* = 319 ([M-H]), 539 ([2M-H]); HRMS (ESIneg): calcd for $C_{21}H_{19}O_3$: 319.13397; found: 319.13409.

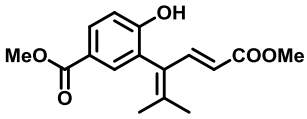


Compound 11. Pale yellow oil (89%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 15.4 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.79 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.46 (d, *J* = 3.0 Hz, 1H), 5.36 (d, *J* = 15.3 Hz, 1H), 4.56 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 2.14 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 153.6, 147.4, 146.8, 141.6, 128.5, 125.3, 119.2, 116.3, 115.5, 114.7, 55.8, 51.6, 23.8, 20.8; IR (neat, cm^{-1}) 3419, 2953, 2923, 2853, 1698, 1609, 1492, 1434, 1293, 1204, 1165, 1039; MS (EI) *m/z* (%) 43 (4), 55 (3), 77 (5), 91

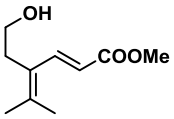


(6), 115 (9), 187 (32), 215 (49), 230 (37), 247 (15), 262 (100); HRMS (ESIpos) calcd. for $C_{15}H_{18}O_4Na^+$ $[M+Na]^+$ 285.1097, found: 285.1099.

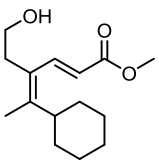
Compound 13. Pale yellow oil (94%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93-7.97 (m, 2H), 7.65 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 5.63 (s, 1H), 5.26 (d, *J* = 15.4 Hz, 1H), 3.87 (s, 3H), 3.69 (s, 3H), 2.15 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 166.8, 157.0, 148.2, 141.5, 132.7, 131.3, 127.4, 124.6, 122.8, 119.1, 115.6, 51.9, 51.6, 23.7, 20.7; IR (neat, cm^{-1}) 3376, 2953, 1716, 1609, 1436, 1270, 1198, 1170, 1118, 976, 772; MS (EI) *m/z* (%) 290 (31), 275 (16), 258 (100), 243 (50), 231 (25), 230 (46), 226 (10), 217 (10), 215 (15), 211 (23), 199 (28), 171 (16), 128 (13); HRMS (ESIpos) calcd. for $C_{16}H_{18}O_5Na$: 313.10463; found: 313.10464.



Compound 19b. Pale yellow oil (64%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 15.6 Hz, 1H), 5.87 (d, *J* = 15.7 Hz, 1H), 3.75 (s, 3H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 7.3 Hz, 2H), 1.98 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 144.7, 142.8, 126.7, 115.4, 61.4, 51.6, 31.7, 22.7, 21.3; IR (neat, cm^{-1}) 3417, 2952, 2887, 1716, 1706, 1615, 1435, 1312, 1150, 1042, 857; MS (EI) *m/z* (%) 41 (26), 55 (34), 59 (15), 67 (41), 79 (100), 91 (66), 107 (43), 124 (8), 139 (11), 151 (8), 169 (10), 184 (8); HRMS (ESIpos) calcd. for $C_{10}H_{16}NaO_3$ $[M+Na]^+$ 207.0992M; found: 207.0992

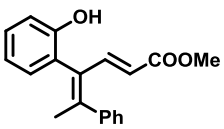


Compound 19c. Pale yellow oil (72%, *Z*/*E* = 73:27). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.91 (d, *J* = 15.6 Hz, 1H), 5.91 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H), 3.62 (t, *J* = 7.4 Hz, 2H), 2.94 – 2.83 (m, 1H), 2.59 (t, *J* = 7.4 Hz, 2H), 1.82 (s, 3H), 1.80 – 1.63 (m, 4H), 1.54 – 1.28 (m, 5H), 1.23 – 1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 168.6, 153.5, 141.8, 125.4, 115.5, 61.2, 51.5, 41.4, 32.0, 31.1 (2C), 26.2 (2C), 26.0, 15.8; IR (neat, cm^{-1}) 3426, 2927, 2853, 1716, 1698, 1610, 1435, 1376, 1297, 1258, 1237, 1195, 1159, 1041, 1022, 977, 912, 889, 858, 819, 795, 765, 733, 647, 619, 590, 569, 548, 537, 507, 489, 473 cm^{-1}; MS (EI) *m/z* (%) 31 (40), 41 (42), 55 (54), 67 (73), 79 (79), 91 (82), 105 (54), 119 (35), 133 (24), 139 (100), 147 (30), 161 (22), 169 (90), 178 (26), 192 (5), 205 (2), 220 (21).



PALLADIUM CATALYZED REACTION CASCADES

Representative Procedure. Methyl (2*E*,4*E*)-4-(2-hydroxyphenyl)-5-phenylhexa-2,4-dienoate (40a). A degassed mixture of 1,4-dioxane (1.1 mL) and water (2.2 mL) was added to a solution of enyne **1** (108.1 mg, 0.50 mmol), phenylboronic acid (121.9 mg, 1.0 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), SPhos (82.1 mg, 0.2 mmol), and potassium phosphate (169.8 mg, 0.8 mmol) in EtOAc (0.49 mL) under Ar. The mixture was stirred at 90°C for 30 min when TLC indicated full conversion. The mixture was extracted with *tert*-butyl methyl ether, the combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc, 95:5 → 90:10) to afford the title compound as a yellow oil (114.9 mg, 78%). ^{1}H NMR

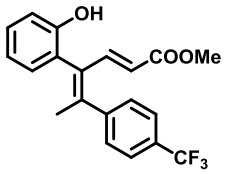


$C_{19}H_{18}O_3$
MW 294,35 g/mol

(400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 15.6 Hz, 1H), 7.49 – 7.35 (m, 3H), 7.33 – 7.27 (m, 3H), 7.06 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.00 (ddd, *J* = 8.1, 6.1, 1.2 Hz, 2H), 5.41 (dd, *J* = 15.5, 0.8 Hz, 1H), 4.88 (s, 1H), 3.62 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 152.7, 150.6, 143.7, 141.2, 130.6, 130.3, 129.7, 128.7, 128.6, 128.4, 124.4, 121.1, 120.3, 115.9, 51.6, 23.8; IR (neat, cm^{-1}) 3388, 2949, 1715, 1687, 1614, 1447, 1288, 1172, 754, 703; MS (EI) *m/z* (%) 77 (19), 91 (12), 103 (21), 115 (36), 128 (24), 142 (25), 165 (39), 178 (31), 189 (47), 202 (67), 219 (100), 234 (76), 247 (55), 262 (26), 279 (12), 294 (23); HRMS (GC-EI) calcd. for $C_{19}H_{18}O_3$ 294.1251, found: 294.1250.

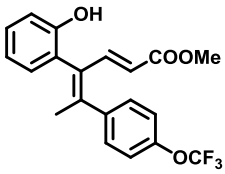
The following compounds were prepared analogously:

Methyl (2*E*,4*E*)-4-(2-hydroxyphenyl)-5-(4-(trifluoromethyl)phenyl)hexa-2,4-dienoate (40b). Yellow solid (84%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.7 – 7.6 (m, 2H), 7.5 (d, *J* = 15.5 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.3 (ddd, *J* = 8.2, 7.2, 1.9 Hz, 1H), 7.2 – 6.9 (m, 3H), 5.4 (dd, *J* = 15.5, 0.8 Hz, 1H), 5.0 (s, 1H), 3.6 (s, 3H), 2.0 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 152.7, 148.3, 145.0, 142.9, 131.8, 130.6, 130.3 (q, ^{2}J = 32.7 Hz), 129.9, 129.1, 125.7 (q, ^{3}J = 3.8 Hz), 124.1 (q, ^{1}J = 272.2 Hz), 124.0, 121.2, 121.2, 116.1, 51.7, 23.7; ^{19}F NMR (282 MHz, Chloroform-*d*) δ −66.4; IR (neat, cm^{-1}) 3400, 2955, 1718, 1615, 1578, 1464, 1448, 1325, 1166, 1123, 1079, 1016, 843, 754; MS (EI) *m/z* (%) 59 (2), 77 (4), 107 (9), 131 (10), 189 (10), 218 (12), 233 (12), 259 (8), 287 (29), 302 (67), 315 (63), 331 (17), 362 (100); HRMS (ESIpos) calcd. for $C_{20}H_{17}F_3NaO_3^+$ $[M+Na]^+$ 385.1022, found: 385.1023.



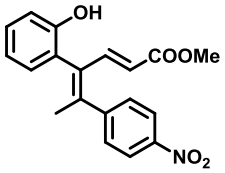
$C_{20}H_{17}F_3O_3$
MW 362,11 g/mol

Methyl (2*E*,4*E*)-4-(2-hydroxyphenyl)-5-(4-(trifluoromethoxy)phenyl)hexa-2,4-dienoate (40c). Yellow solid (80%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 15.5 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.11 – 6.94 (m, 3H), 5.42 (dd, *J* = 15.4, 0.8 Hz, 1H), 5.01 (s, 1H), 3.63 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 152.7, 149.1, 148.5, 143.2, 139.8, 131.3, 130.6, 130.3, 129.8, 124.2, 121.2, 121.0, 120.8, 116.1, 55.2, 51.7, 23.8; ^{19}F NMR (282 MHz, Chloroform-*d*) δ −57.7; IR (neat, cm^{-1}) 3392, 2951, 2852, 1687, 1609, 1589, 1505, 1447, 1437, 1250, 1203, 1111, 855, 754, 732; MS (EI) *m/z* (%) 43 (2), 107 (8), 131 (8), 189 (15), 215 (15), 233 (18), 291 (8), 303 (28), 318 (71), 331 (50), 347 (17), 378 (100); HRMS (ESIpos) calcd. for $C_{20}H_{17}F_3NaO_4^+$ $[M+Na]^+$ 401.0971, found: 401.0978.



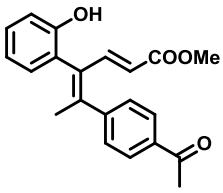
$C_{20}H_{17}F_3O_4$
MW 378,11 g/mol

Methyl (2*E*,4*E*)-4-(2-hydroxyphenyl)-5-(4-nitrophenyl)hexa-2,4-dienoate (40d). Yellow solid (61%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 15.4 Hz, 1H), 7.30 (ddd, *J* = 8.1, 7.0, 2.1 Hz, 1H), 7.13 – 6.95 (m, 3H), 5.46 (dd, *J* = 15.5, 0.8 Hz, 1H), 3.63 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.5, 152.6, 148.2, 147.6, 146.9, 142.3, 132.6, 130.6, 130.0, 129.8, 124.0, 123.7, 121.9, 121.4, 116.2, 51.8, 23.5; IR (neat, cm^{-1}) 3399, 3077, 2951, 2850, 1691, 1595, 1517, 1448, 1344, 1292, 1171, 1110, 857, 756; MS (EI) *m/z* (%) 59 (3), 107 (9), 131 (11), 165 (7), 189 (212), 218 (26), 262 (14), 279 (39), 322 (100), 339 (91); HRMS (ESIpos) calcd. for $C_{19}H_{17}NNaO_5^+$ $[M+Na]^+$ 362.0999, found: 362.0999



$C_{19}H_{17}NO_5$
MW 339,11 g/mol

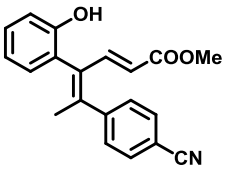
Methyl (2*E*,4*E*)-5-(4-acetylphenyl)-4-(2-hydroxyphenyl)hexa-2,4-dienoate (40e). Yellow solid (68%);



$C_{21}H_{20}O_4$
MW 336,14 g/mol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 7.88 (m, 2H), 7.51 (d, *J* = 15.4 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.30 (ddd, *J* = 8.1, 7.2, 1.9 Hz, 1H), 7.09 – 6.96 (m, 3H), 5.43 (dd, *J* = 15.5, 0.8 Hz, 1H), 4.88 (s, 1H), 3.62 (s, 3H), 2.65 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.8, 167.6, 152.7, 148.8, 146.2, 143.0, 136.7, 131.5, 130.6, 129.9, 129.0, 128.7, 124.0, 121.3, 121.1, 116.1, 51.7, 26.8, 23.6; IR (neat, cm^{-1}) 3366, 2950, 2924, 2849, 1682, 1604, 1486, 1448, 1403, 1358, 1266, 1169, 1015, 839, 736, 600; MS (EI) *m/z* (%) 43 (50), 77 (4), 115 (7), 131 (10), 165 (6), 189 (12), 233 (19), 247 (19), 261 (44), 277 (49), 289 (46), 304 (100), 321 (9), 336 (36); HRMS (ESIpos) calcd. for $C_{21}H_{20}NaO_4^+$ $[M+Na]^+$ 359.1254, found: 359.1259.

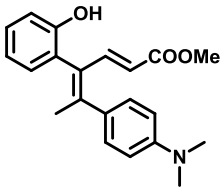
Methyl (2*E*,4*E*)-5-(4-cyanophenyl)-4-(2-hydroxyphenyl)hexa-2,4-dienoate (40f). Yellow solid (64%);



$C_{20}H_{17}NO_3$
MW 319,12 g/mol

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.30 (ddd, *J* = 8.1, 6.9, 2.2 Hz, 1H), 7.09 – 6.95 (m, 3H), 5.44 (dd, *J* = 15.5, 0.9 Hz, 1H), 3.63 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 152.7, 147.4, 146.2, 142.5, 132.5, 132.3, 130.6, 130.0, 129.6, 123.8, 121.6, 121.3, 118.7, 116.2, 112.0, 51.8, 23.5; IR (neat, cm^{-1}) 3402, 2950, 2363, 2229, 1690, 1607, 1448, 1289, 1170, 844, 746, 573; MS (EI) *m/z* (%) 39 (6), 77 (19), 128 (52), 190 (55), 216 (52), 227 (36), 246 (100), 272 (84), 304 (55), 319 (51); HRMS (ESIpos) calcd. for $C_{20}H_{17}NNaO_3^+$ $[M+Na]^+$ 342.1101, found: 342.1107.

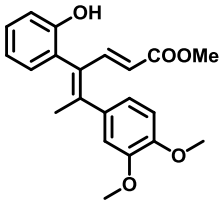
Methyl (2*E*,4*E*)-5-(4-(dimethylamino)phenyl)-4-(2-hydroxyphenyl)hexa-2,4-dienoate (40g). Yellow



$C_{21}H_{23}NO_3$
MW 337,17 g/mol

solid (67%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 15.5 Hz, 1H), 7.30 – 7.20 (m, 3H), 7.05 (ddd, *J* = 7.3, 1.9, 0.6 Hz, 1H), 6.98 (td, *J* = 7.8, 7.4, 1.1 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.37 (dd, *J* = 15.5, 0.8 Hz, 1H), 4.89 (s, 1H), 3.64 (s, 3H), 3.02 (s, 6H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 152.7, 151.2, 150.6, 144.8, 130.7, 130.2, 129.5, 128.5, 128.4, 125.3, 121.0, 118.9, 115.7, 111.9, 51.5, 40.5, 23.4; IR (neat, cm^{-1}) 3391, 3034, 2981, 2947, 2913, 2854, 2806, 1686, 1606, 1520, 1446, 1356, 1280, 1195, 1167, 1122, 819, 755; MS (EI) *m/z* (%) 42 (1), 77 (2), 121 (8), 139 (15), 165 (2), 189 (3), 219 (7), 248 (6), 264 (49), 278 (100), 290 811), 306 (6), 322 (10), 337 (79); HRMS (ESIpos) calcd. for $C_{21}H_{23}NNaO_3^+$ $[M+Na]^+$ 360.1570, found: 360.1574.

Methyl (2*E*,4*E*)-5-(3,4-dimethoxyphenyl)-4-(2-hydroxyphenyl)hexa-2,4-dienoate (40h). Yellow oil

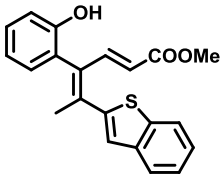


$C_{21}H_{22}O_5$
MW 354,15 g/mol

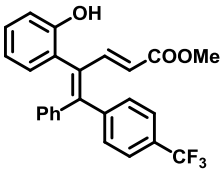
(67%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 15.5 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.05 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.99 (ddd, *J* = 8.1, 4.6, 1.2 Hz, 2H), 6.94 – 6.85 (m, 2H), 6.83 (d, *J* = 1.9 Hz, 1H), 5.40 (dd, *J* = 15.5, 0.8 Hz, 1H), 4.86 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.63 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 152.7, 150.2, 149.3, 148.9, 144.0, 133.7, 130.6, 130.0, 129.6, 124.7, 121.8, 121.1, 119.9, 115.9, 112.0, 111.1, 56.2, 56.1, 51.6, 23.7; IR (neat, cm^{-1}) 3430, 3060, 2999, 2950, 2838, 1696, 1604, 1509, 1447, 1248, 1168, 1140, 1023, 859, 810, 755, 733, 606; MS (EI) *m/z* (%) 77 (2), 89 (2), 115 (3), 131 (4), 147 (8), 165 (7), 202 (7), 219 (5), 248

(8), 264 (13), 281 (49), 295 (84), 307 (7), 323 (5), 339 (18), 354 (100); HRMS (ESIpos) calcd. for $C_{21}H_{22}NaO_5^+$ $[M+Na]^+$ 377.1359, found: 377.1361.

Methyl (2*E*,4*E*)-5-(benzo[b]thiophen-2-yl)-4-(2-hydroxyphenyl)hexa-2,4-dienoate (40i). Yellow oil (74%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 15.5 Hz, 1H), 7.97 – 7.78 (m, 2H), 7.50 – 7.34 (m, 3H), 7.30 (ddd, *J* = 8.0, 7.3, 1.9 Hz, 1H), 7.09 – 6.93 (m, 3H), 5.53 (dd, *J* = 15.4, 0.8 Hz, 1H), 4.89 (s, 1H), 3.67 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 152.6, 143.3, 142.9, 141.7, 140.4, 139.6, 132.7, 130.6, 129.9, 125.7, 125.2, 124.9, 124.5, 124.2, 122.3, 121.7, 121.2, 116.1, 51.7, 24.3; IR (neat, cm^{-1}) 3402, 3057, 2950, 2851, 1712, 1607, 1436, 1285, 1172, 750; MS (EI) *m/z* (%) 44 (1), 77 (1), 89 (1), 115 (5), 145 (8), 198 (11), 221 (3), 258 (11), 276 (22), 291 (100), 319 (4), 335 (6), 350 (49); HRMS (ESIpos) calcd. for $C_{21}H_{18}NaO_3S^+$ $[M+Na]^+$ 373.0869, found: 373.0870.



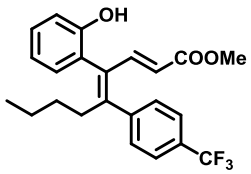
$C_{21}H_{18}O_3S$
MW 350,10 g/mol



$C_{25}H_{19}F_3O_3$
MW 424,13 g/mol

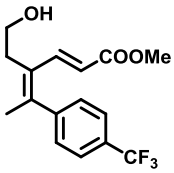
Methyl (2*E*,4*E*)-4-(2-hydroxyphenyl)-5-phenyl-5-(4-(trifluoromethyl)phenyl)-penta-2,4-dienoate (41). Yellow solid (85%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.57 (m, 3H), 7.44 – 7.35 (m, 2H), 7.20 – 7.05 (m, 4H), 6.98 – 6.90 (m, 3H), 6.84 – 6.72 (m, 2H), 5.68 (d, *J* = 15.5 Hz, 1H), 4.88 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 153.1, 150.4, 144.4, 143.8, 140.8, 133.1, 131.9, 131.4, 130.6 (q, ^2J = 32.2 Hz), 130.1, 129.8, 128.3, 128.0, 125.4 (q, ^3J = 4.0 Hz), 125.2, 124.1 (q, ^1J = 262.0 Hz), 122.7, 121.1, 116.1, 51.8; ^{19}F NMR (282 MHz, Chloroform-*d*) δ −62.6; IR (neat, cm^{-1}) 3400, 3058, 2952, 2932, 2853, 1713, 1688, 1614, 1448, 1322, 1166, 1123, 1064, 753, 699; MS (EI) *m/z* (%) 57 (3), 77 (4), 105 (8), 131 (10), 172 (8), 219 (11), 247 (9), 278 (10), 315 (8), 345 (16), 364 (86), 392 (17), 424 (100); HRMS (ESIpos) calcd. for $C_{25}H_{19}F_3NaO_3^+$ $[M+Na]^+$ 447.1178, found: 447.1179.

Methyl (2*E*,4*E*)-4-(2-hydroxyphenyl)-5-(4-(trifluoromethyl)phenyl)nona-2,4-dienoate (42). Yellow oil (54%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 7.9, 1.0 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.30 (ddd, *J* = 8.1, 7.2, 1.9 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.04 – 6.96 (m, 2H), 5.40 (d, *J* = 15.5 Hz, 1H), 4.74 (s, 1H), 3.62 (s, 3H), 2.30 (dt, *J* = 8.8, 6.1 Hz, 2H), 1.21 – 1.03 (m, 4H), 0.67 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 153.7, 152.6, 143.7, 142.9, 131.3, 130.7, 130.3 (q, ^2J = 32.7 Hz), 129.9, 129.4, 125.7 (q, ^3J = 3.7 Hz), 124.2 (q, ^1J = 272.2 Hz), 123.8, 121.4, 121.1, 116.0, 51.7, 36.4, 30.2, 22.6, 13.7; ^{19}F NMR (282 MHz, Chloroform-*d*) δ −62.6; IR (neat, cm^{-1}) 3400, 3065, 3034, 2956, 1690, 1615, 1448, 1323, 1287, 1167, 1126, 850, 755; MS (EI) *m/z* (%) 41 (2), 57 (2), 77 (2), 107 (6), 131 (9), 159 (7), 189 (8), 287 (15), 301 (46), 315 (100), 361 (23), 373 (9), 404 (75); HRMS (ESIpos) calcd. for $C_{23}H_{23}F_3NaO_3^+$ $[M+Na]^+$ 427.1492, found: 427.1491.



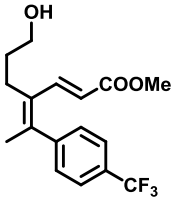
$C_{23}H_{23}F_3O_3$
MW 404,16 g/mol

Methyl (2*E*,4*Z*)-4-(2-hydroxyethyl)-5-(4-(trifluoromethyl)phenyl)hexa-2,4-dienoate (43). Colorless oil (56%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.6 (d, *J* = 12.7 Hz, 1H), 7.6 (d, *J* = 8.2 Hz, 2H), 7.5 (d, *J* = 8.2 Hz, 2H), 5.8 (m, 1H), 5.2 (d, *J* = 12.6 Hz, 1H), 4.0 (t, *J* = 6.6 Hz, 2H), 3.7 (s, 3H), 2.6 (q, *J* = 6.6 Hz, 2H), 2.1 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 162.4, 146.8, 137.0, 129.0 (q, ^{2}J = 32.2 Hz), 126.0, 125.2 (q, ^{3}J = 3.4 Hz), 124.5, 124.3 (q, ^{1}J = 272.1 Hz), 96.4, 70.2, 51.2, 28.6, 16.0; ^{19}F NMR (282 MHz, Chloroform-*d*) δ −62.4; IR (neat, cm^{-1}) 2951, 1713, 1626, 1326, 1119, 835; MS (EI) *m/z* (%) 41 (5), 59 (4), 85 (2), 129 (18), 143 (81), 159 (46), 165 (17), 185 (47), 197 (52), 213 (100), 239 (7), 254 (4), 282 (16), 314 (1); HRMS (ESIpos) calcd. for $C_{16}H_{17}F_3NaO_3^+$ $[M+Na]^+$ 337.1022, found: 337.1020.



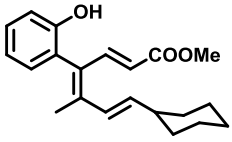
$C_{16}H_{17}F_3O_3$
MW 314,11 g/mol

Methyl (2*E*,4*Z*)-7-hydroxy-4-(1-(4-(trifluoromethyl)phenyl)ethylidene)hept-2-enoate (44). Colorless oil (58%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 12.7 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 5.80 (t, *J* = 7.3 Hz, 1H), 5.21 (d, *J* = 12.6 Hz, 1H), 3.89 (t, *J* = 6.2 Hz, 2H), 3.70 (s, 3H), 2.44 – 2.25 (m, 2H), 2.04 (s, 3H), 1.88 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 162.7, 147.2, 135.4, 128.9 (d, *J* = 32.3 Hz), 128.8, 126.0, 125.3 (q, *J* = 3.8 Hz), 124.4 (d, *J* = 271.6 Hz), 96.4, 70.4, 51.3, 28.7, 25.1, 15.9; IR (neat, cm^{-1}) 2952, 1710, 1624, 1324, 1120, 1068, 829; MS (EI) *m/z* (%) 43 (11), 55 (11), 81 (4), 115 (13), 129 (23), 142 (10), 159 (51), 185 (35), 199 (44), 211 (100), 228 (32), 254 (8), 268 (7), 296 (15), 328 (4); HRMS (ESIpos) calcd. for $C_{17}H_{19}F_3NaO_3^+$ $[M+Na]^+$ 351.1178, found: 351.1180.



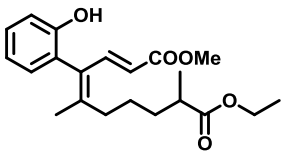
$C_{17}H_{19}F_3O_3$
MW 328,33 g/mol

Methyl (2*E*,4*E*,6*E*)-7-cyclohexyl-4-(2-hydroxyphenyl)-5-methylhepta-2,4,6-trienoate (45). White solid (63%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 15.3 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.03 – 6.88 (m, 4H), 6.02 (dd, *J* = 15.5, 7.5 Hz, 1H), 5.35 (d, *J* = 15.3 Hz, 1H), 4.87 (s, 1H), 3.70 (s, 3H), 2.28 – 2.09 (m, 1H), 1.86 – 1.65 (m, 8H), 1.46 – 1.10 (m, 5H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 152.8, 144.7, 143.2, 140.8, 130.6, 129.5, 129.0, 125.1, 124.6, 120.9, 119.7, 115.7, 51.7, 42.1, 33.0, 33.0, 26.2, 26.0, 17.8; IR (neat, cm^{-1}) 3411, 2999, 2923, 2850, 1697, 1600, 1484, 1448, 1304, 1174, 970, 755; MS (EI) *m/z* (%) 41 (15), 83 (13), 131 (19), 171 (46), 185 (72), 211 (52), 253 (53), 266 (15), 295 (4), 311 (15), 326 (100); HRMS (ESIpos) calcd. for $C_{21}H_{26}NaO_3^+$ $[M+Na]^+$ 349.1774, found: 349.1772.



$C_{21}H_{26}O_3$
MW 326,19 g/mol

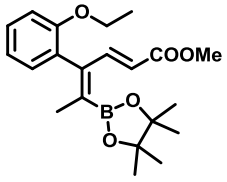
10-Ethyl 1-methyl (2*E*,4*E*)-4-(2-hydroxyphenyl)-5,9-dimethyldeca-2,4-dienedioate (46). Pale yellow oil (67%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 15.3 Hz, 1H), 7.23 (ddd, *J* = 8.3, 6.9, 2.1 Hz, 1H), 7.00 – 6.87 (m, 3H), 5.35 (d, *J* = 15.3 Hz, 1H), 4.84 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 2.66 – 2.42 (m, 3H), 1.67 (s, 3H), 1.65 – 1.51 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 167.7, 152.6, 150.6, 141.0, 130.4, 129.2, 129.0, 124.8, 120.7, 119.7, 115.6, 60.2, 51.2, 39.4, 33.9, 33.3, 26.5, 21.5, 17.0, 14.2; IR (neat, cm^{-1}) 3436, 2977, 2942, 2875, 1731, 1714, 1615, 1448, 1290, 1168,



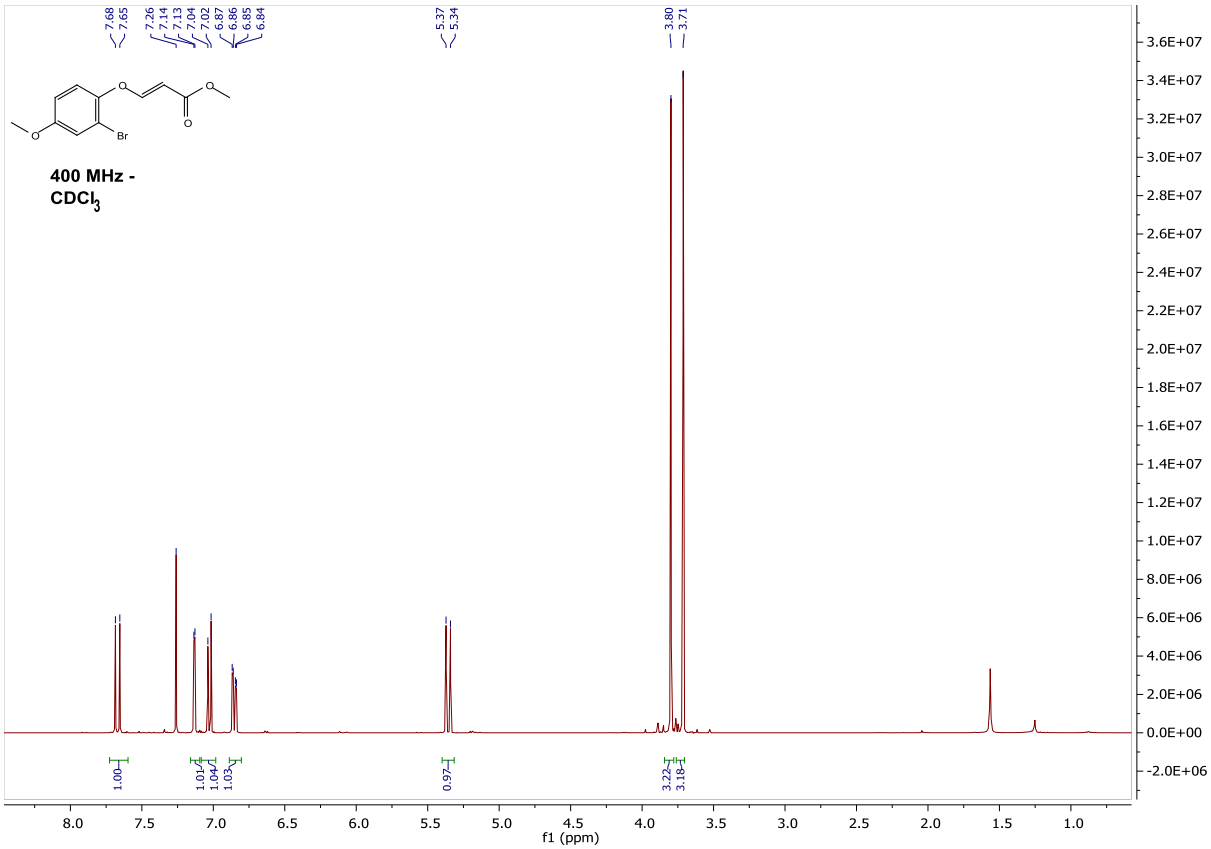
$C_{21}H_{28}O_5$
MW 360,45 g/mol

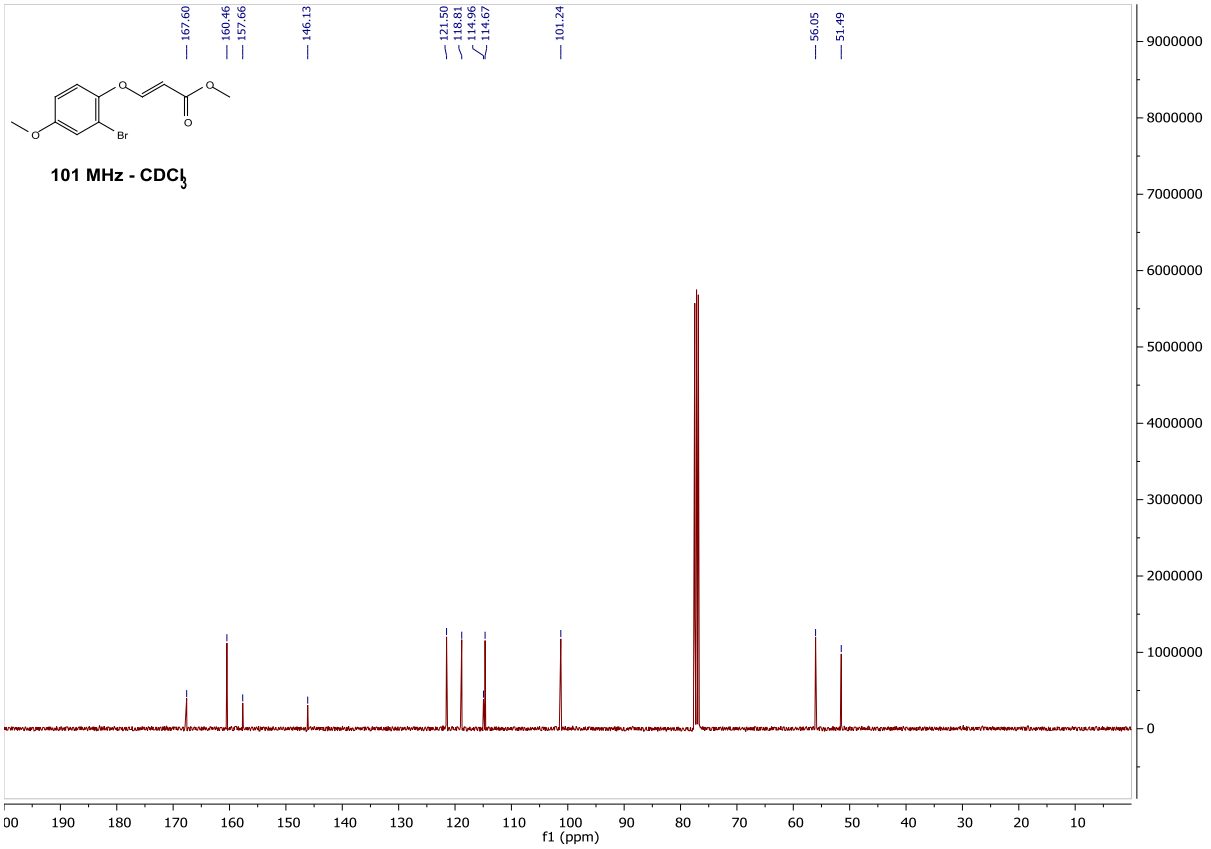
755; MS (EI) *m/z* (%) 43 (3), 55 (5), 69 (4), 91 (3), 107 (9), 128 (13), 157 (12), 171 (40), 185 (100), 199 (24), 217 (39), 231 (24), 242 (13), 259 (7), 270 (58), 284 (7), 301 (71), 312 (40), 344 (17); HRMS (ESIpos) calcd. for $C_{21}H_{28}NaO_5^+$ $[M+Na]^+$ 383.1829, found: 383.1828.

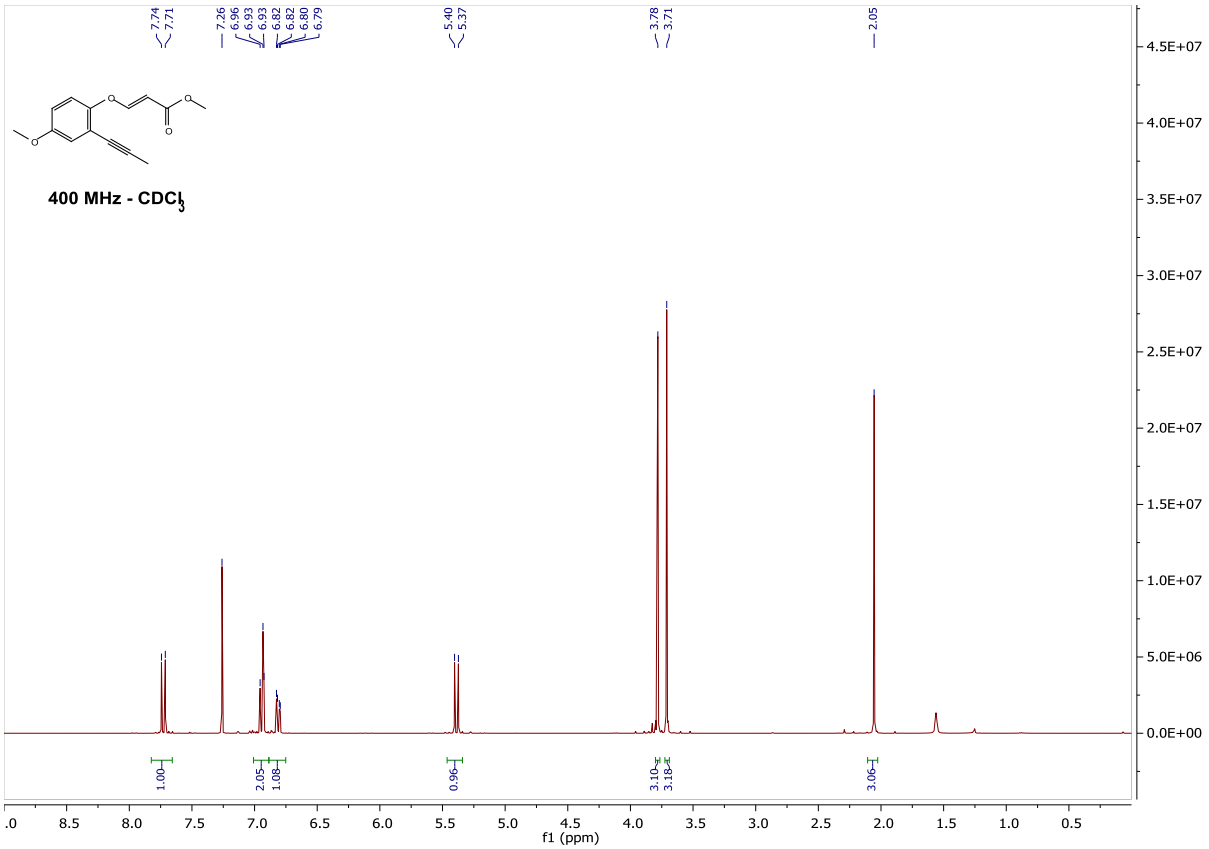
Methyl (2*E*,4*Z*)-4-(2-ethoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-2,4-dienoate (48). A solution of MeLi·LiBr (126 µL, 2.2 M in Et_2O) was added to a solution of B_2pin_2 (70.5 mg, 0.278 mmol) in THF (2mL) under Ar. The resulting mixture was stirred for 1 h at ambient temperature before it was transferred into a cold (0°C) solution of enyne **1** (20 mg, 0.0925 mmol), $Pd_2(dba)_3$ (16.9 mg, 0.0185 mmol), and triethyloxonium tetrafluoroborate (54.3 mg, 0.278 mmol) in THF (0.01 M). The cooling bath was removed and the resulting mixture was stirred at ambient temperature for 10 min. For work up, all volatile materials were evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 90:10 to 85:15), followed by preparative HPLC (250 mm Nucleodur C18-HT, 10 µm, ∅ 4.6 mm, MeCN/H_2O = 90:10, 1.0 mL/min) to give the title compound as a white solid (70%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 15.4 Hz, 1H), 7.30 – 7.22 (m, 1H), 6.96 – 6.89 (m, 3H), 5.31 (dd, *J* = 15.4, 0.8 Hz, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 3.69 (s, 3H), 1.65 (s, 3H), 1.37 (s, 12H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.5, 155.7, 147.7, 147.1, 130.6, 128.8, 127.7, 120.6, 119.5, 112.5, 84.0, 63.9, 51.4, 25.0, 19.6, 14.9; IR (neat, cm^{-1}) 2984, 1717, 1617, 1351, 1282, 1271, 1169, 1139; MS (EI) *m/z* (%) 43 (6), 59 (5), 83 (9), 101 (4), 115 (15), 141 (21), 157 (13), 185 (84), 199 (26), 217 (100), 227 (23), 243 (52), 272 (7), 285 (22), 313 (13), 343 (45), 372 (49); HRMS (ESIpos) calcd. for $C_{21}H_{29}B_1NaO_5^+$ $[M+Na]^+$ 395.2000, found: 395.2006.

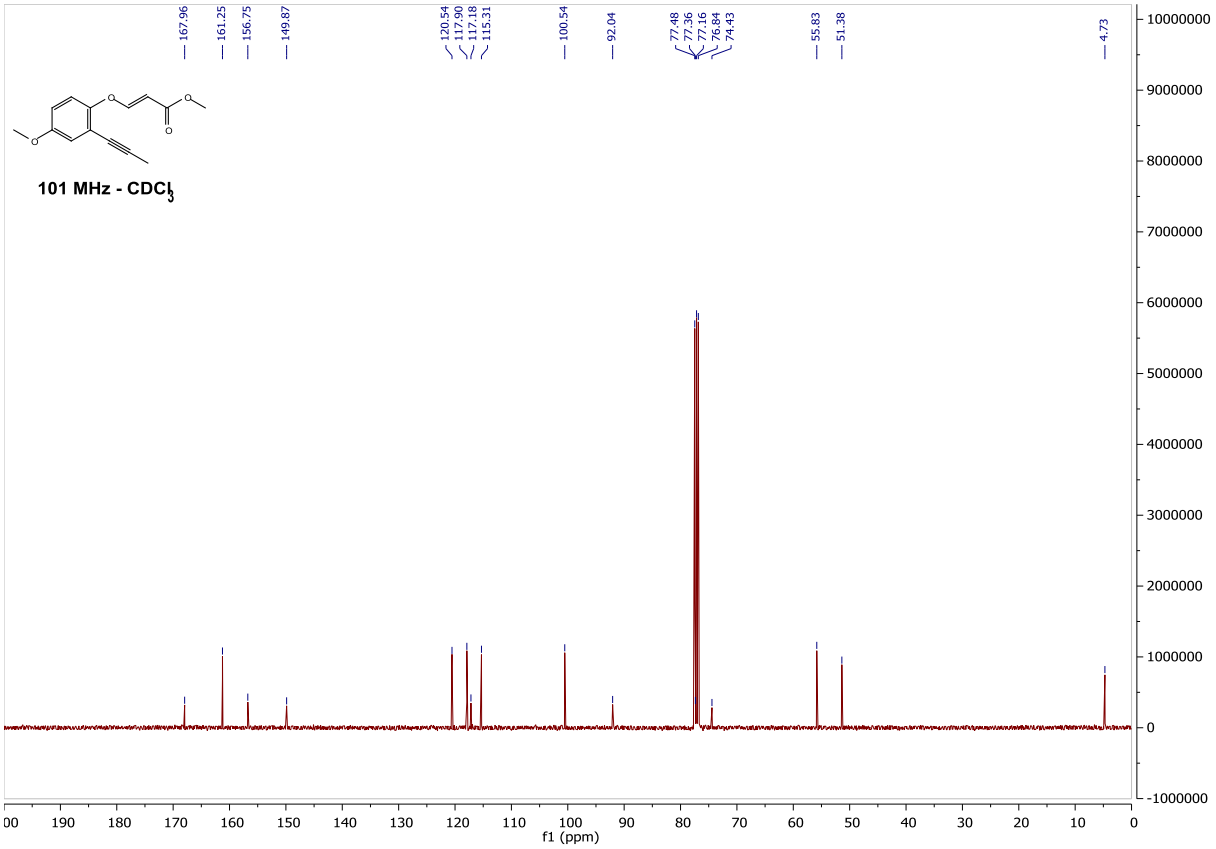


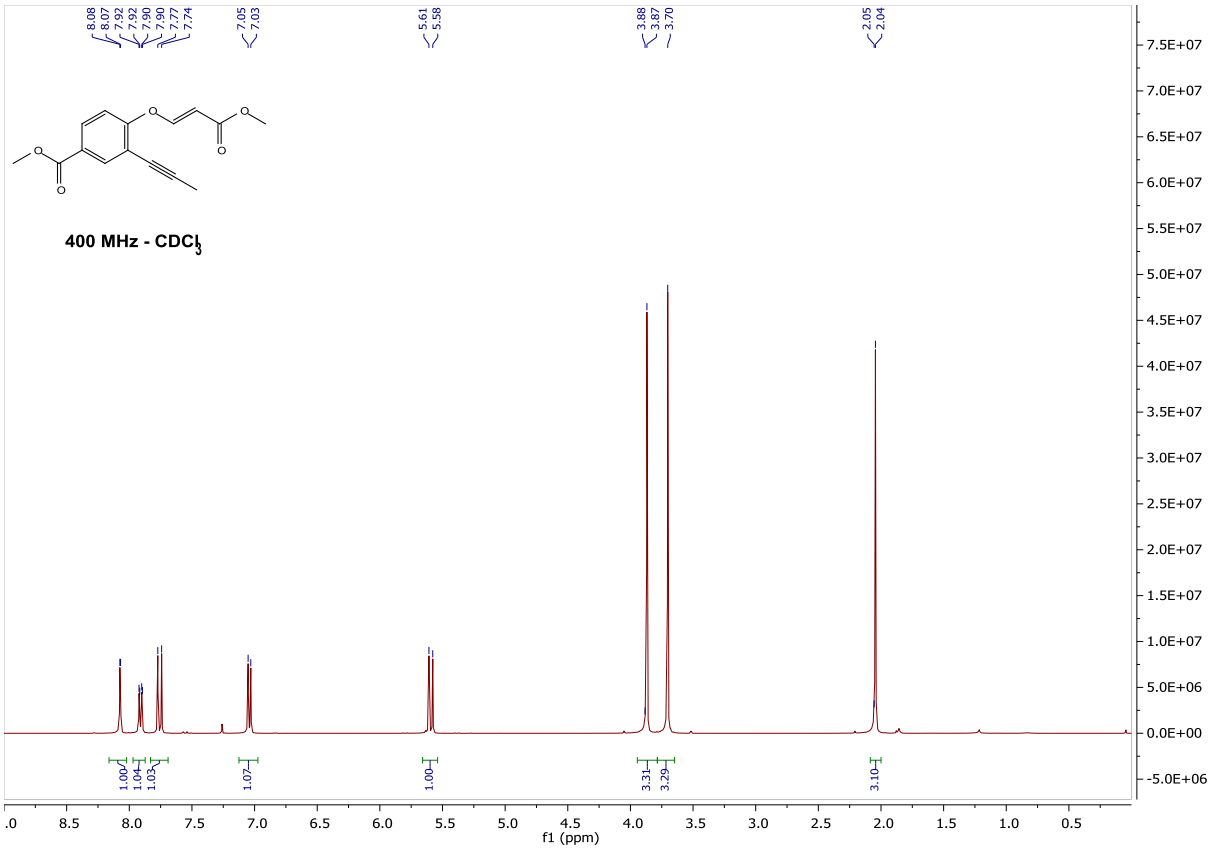
$C_{21}H_{29}BO_5$
MW 372,27 g/mol

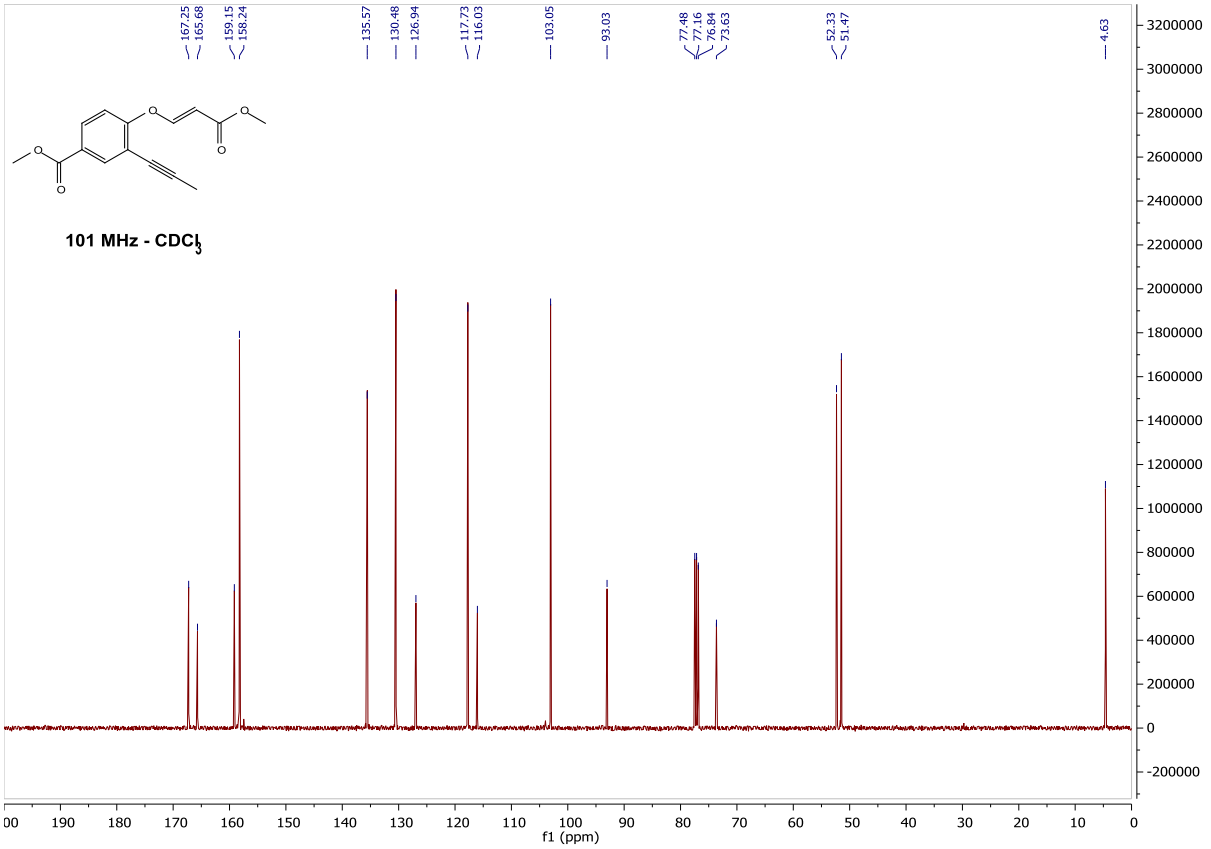

7.68
7.65
7.26
7.14
7.13
7.04
7.02
6.87
6.86
6.85
6.84
5.37
5.34
3.80
3.71
400 MHz -
CDCl3
1.00
1.01
1.04
1.03
0.97
3.22
3.18
f1 (ppm)

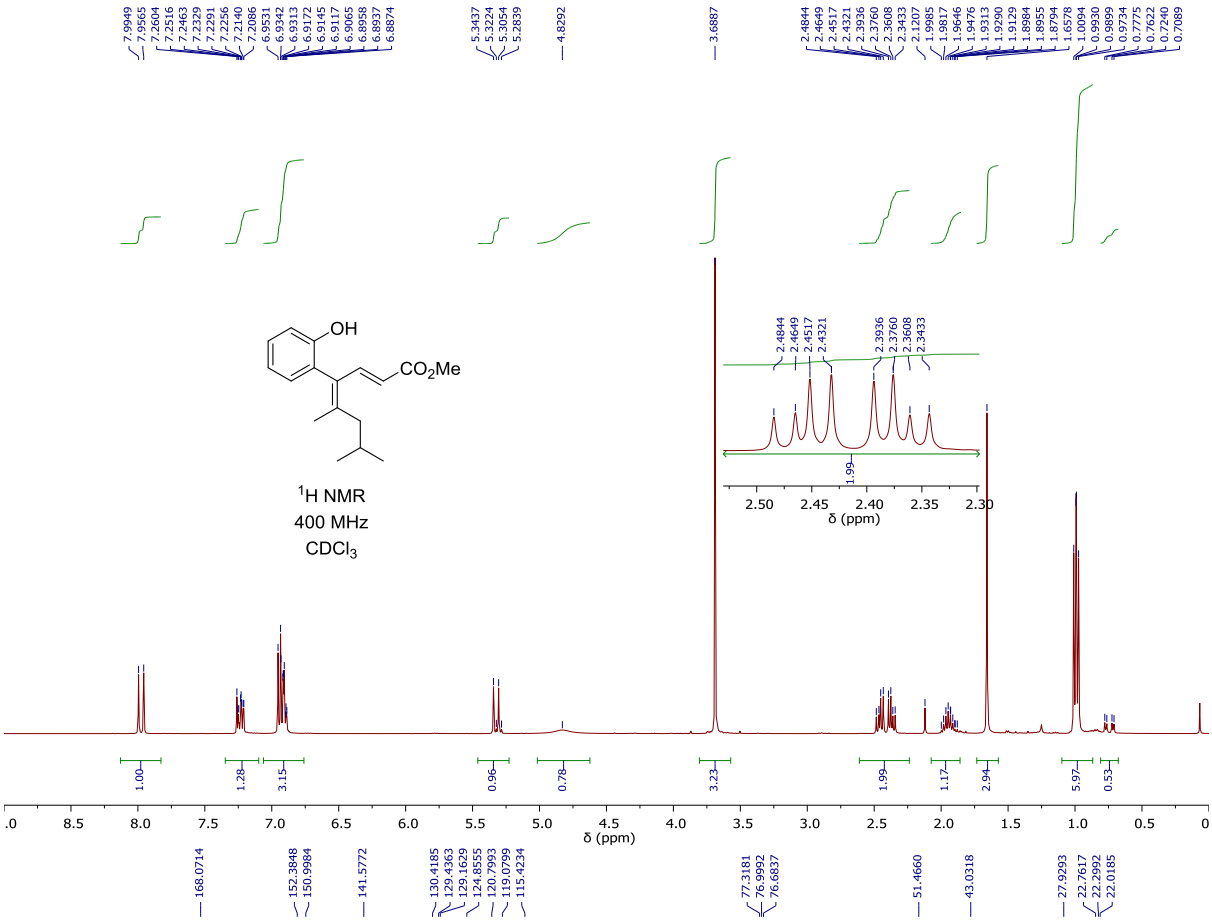

167.60
160.46
157.66
146.13
121.50
118.81
114.96
114.67
101.24
56.05
51.49
101 MHz - CDCl3
f1 (ppm)

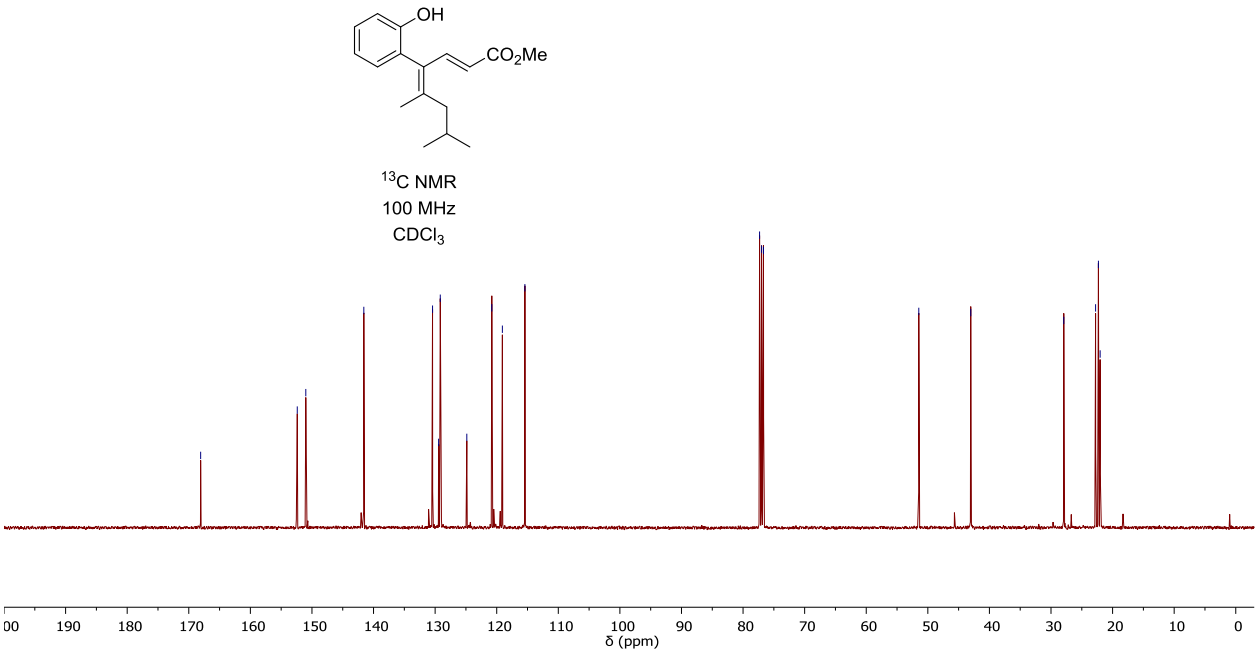

400 MHz - CDCl3
7.74
7.71
7.26
6.96
6.93
6.82
6.80
6.79
5.40
5.37
3.78
3.71
2.05
1.00
2.05
1.08
0.96
3.10
3.18
3.06
f1 (ppm)

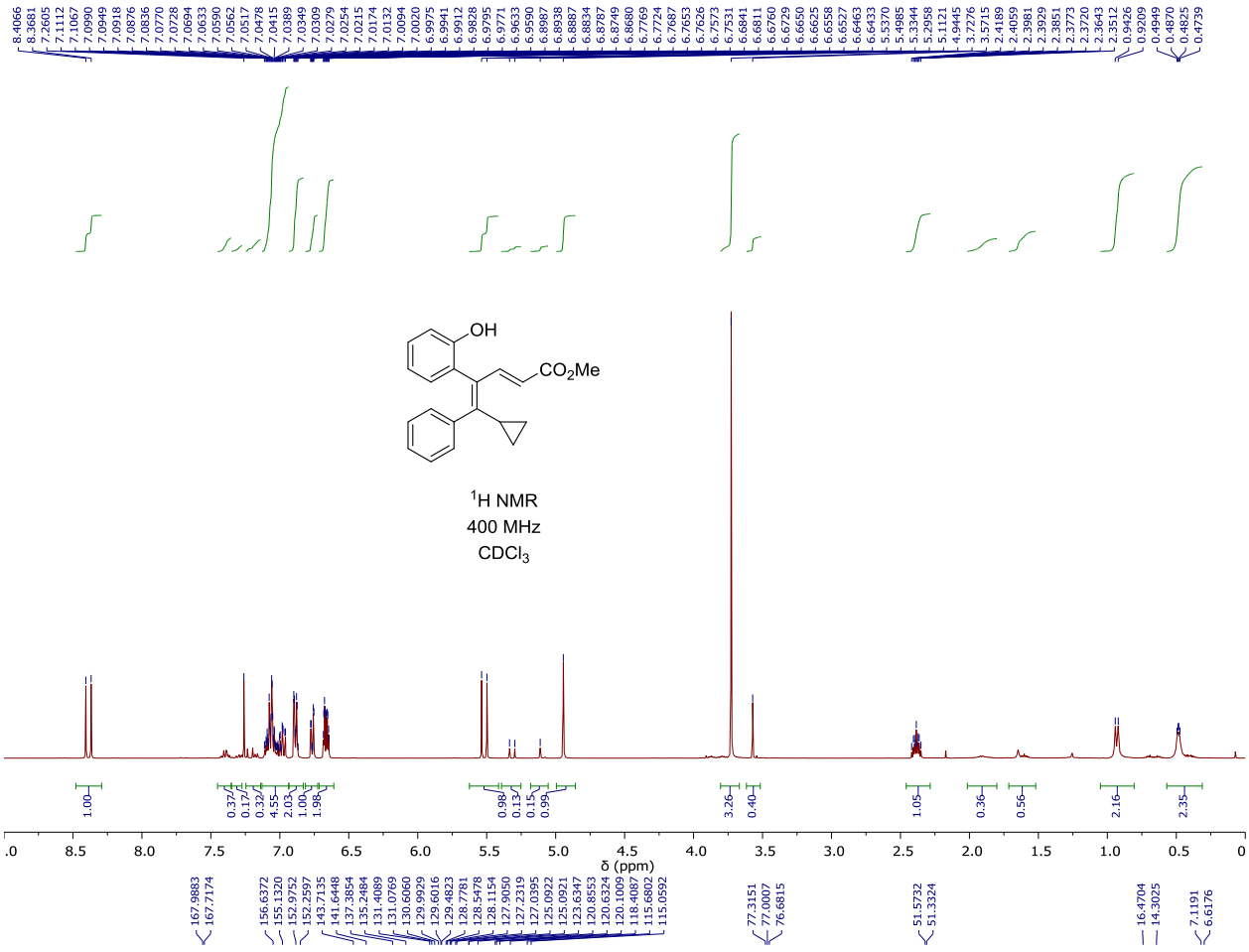

101 MHz - CDCl3
167.96
161.25
156.75
149.87
120.54
117.90
117.18
115.31
100.54
92.04
77.48
77.36
77.16
76.84
74.43
55.83
51.38
4.73
f1 (ppm)

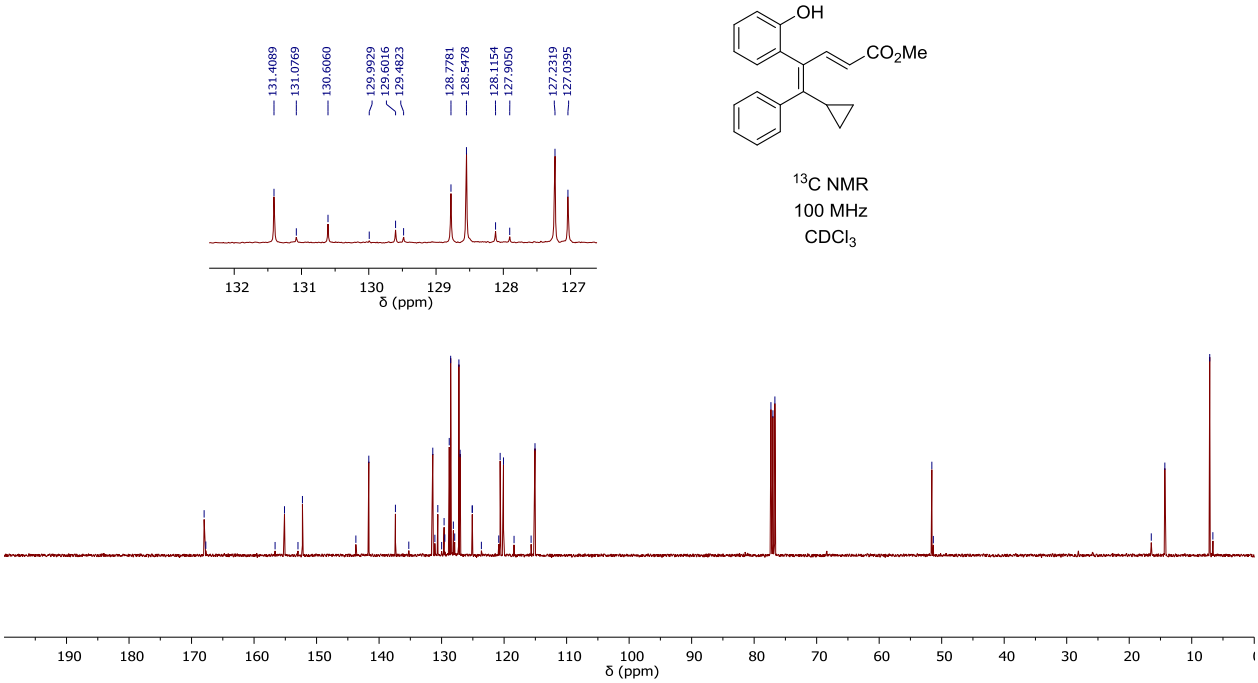

8.08
8.07
7.92
7.92
7.90
7.90
7.77
7.74
7.05
7.03
5.61
5.58
3.88
3.87
3.70
2.05
2.04
400 MHz - CDCl3
1.00
1.04
1.03
1.07
1.00
3.31
3.29
3.10
f1 (ppm)

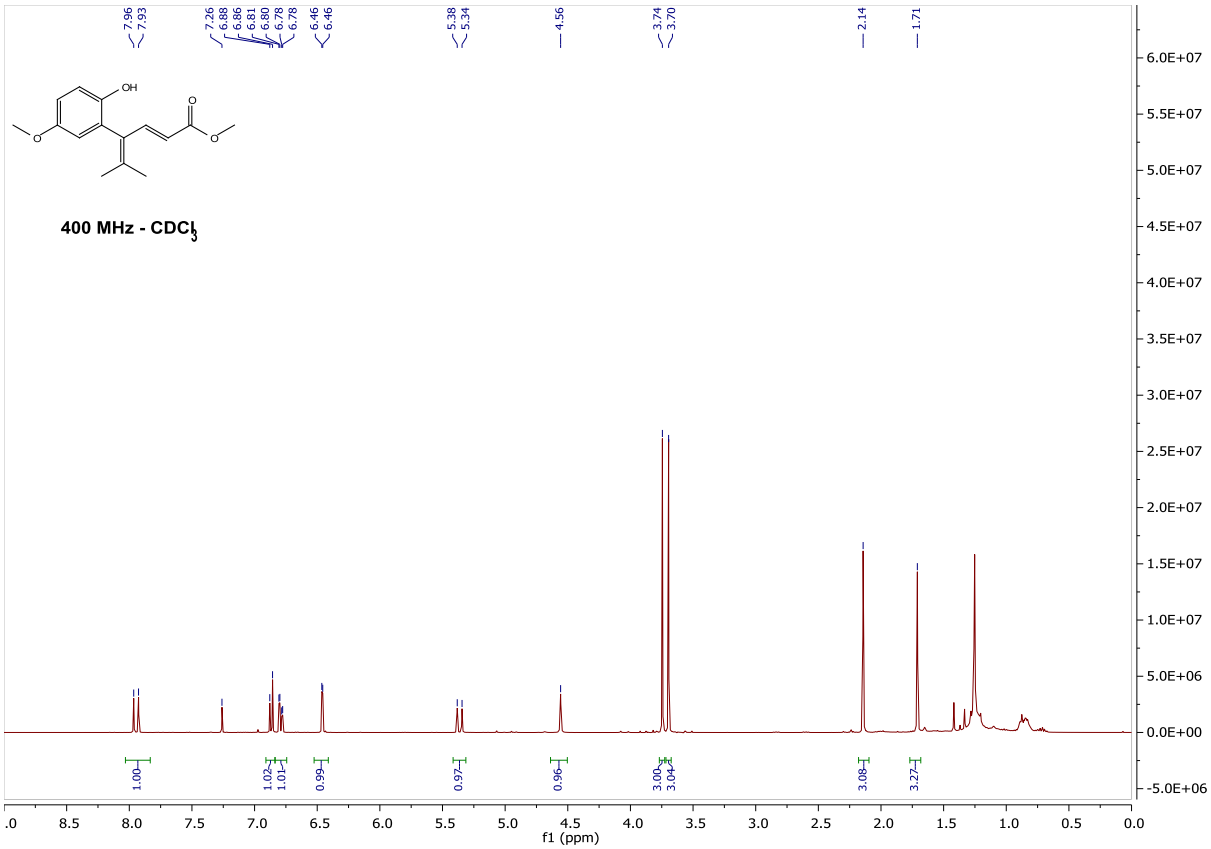

167.25
165.68
159.15
158.24
135.57
130.48
126.94
117.73
116.03
103.05
93.03
77.48
77.16
76.84
73.63
52.33
51.47
4.63
101 MHz - CDCl3
f1 (ppm)

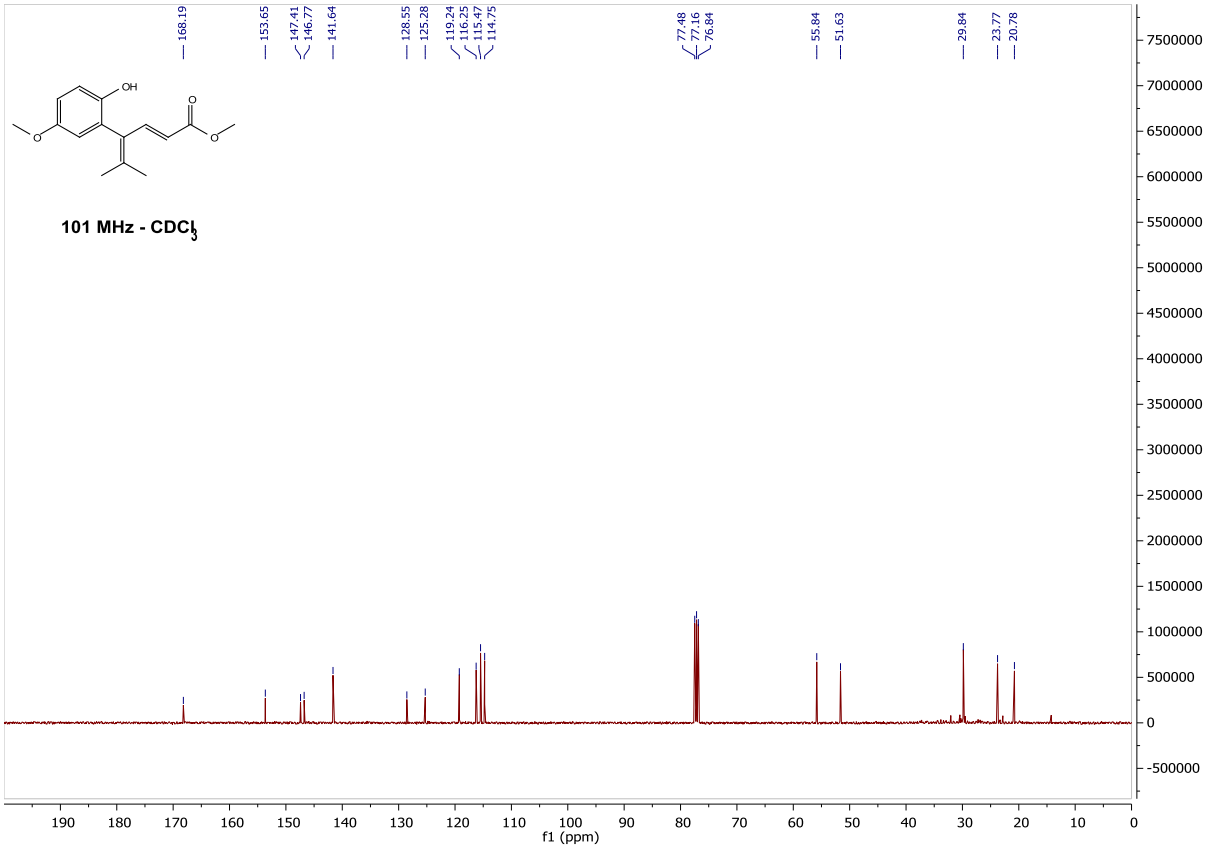

OH
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

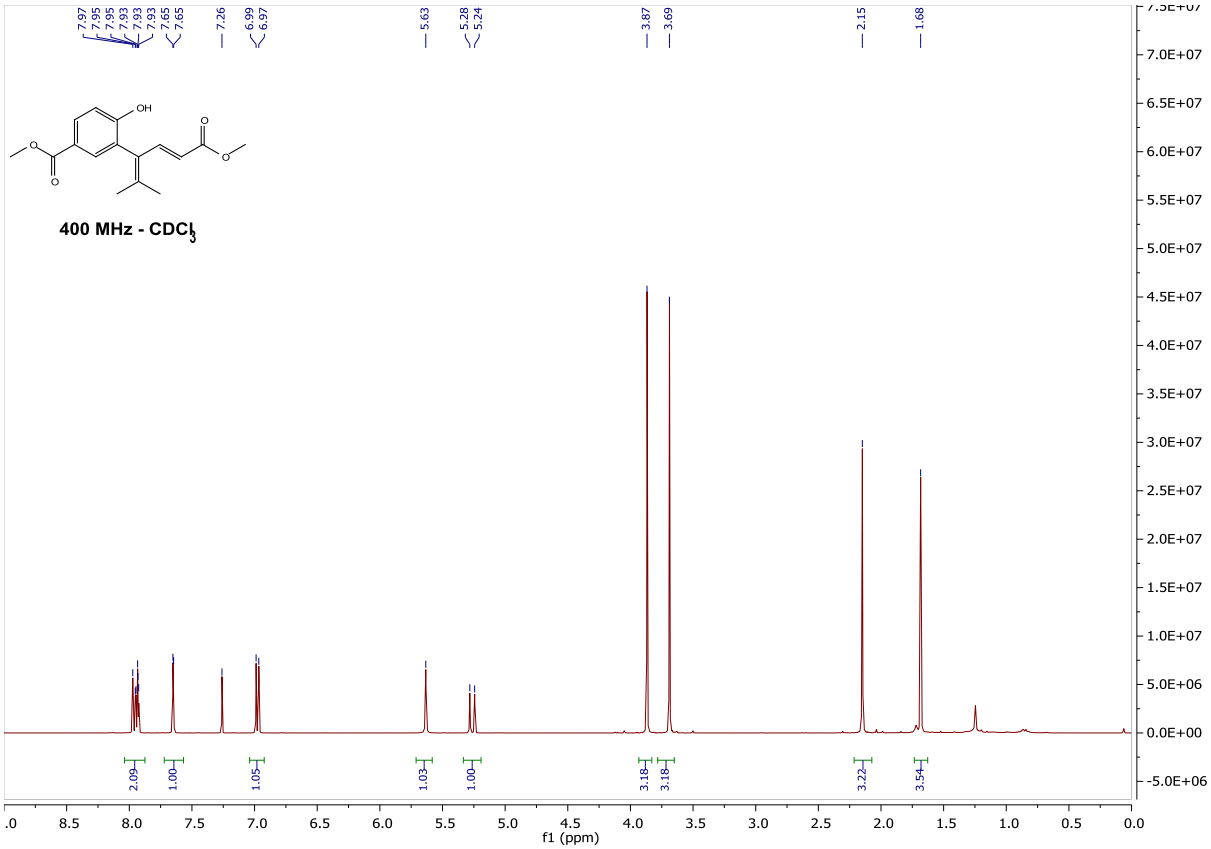

OH
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)

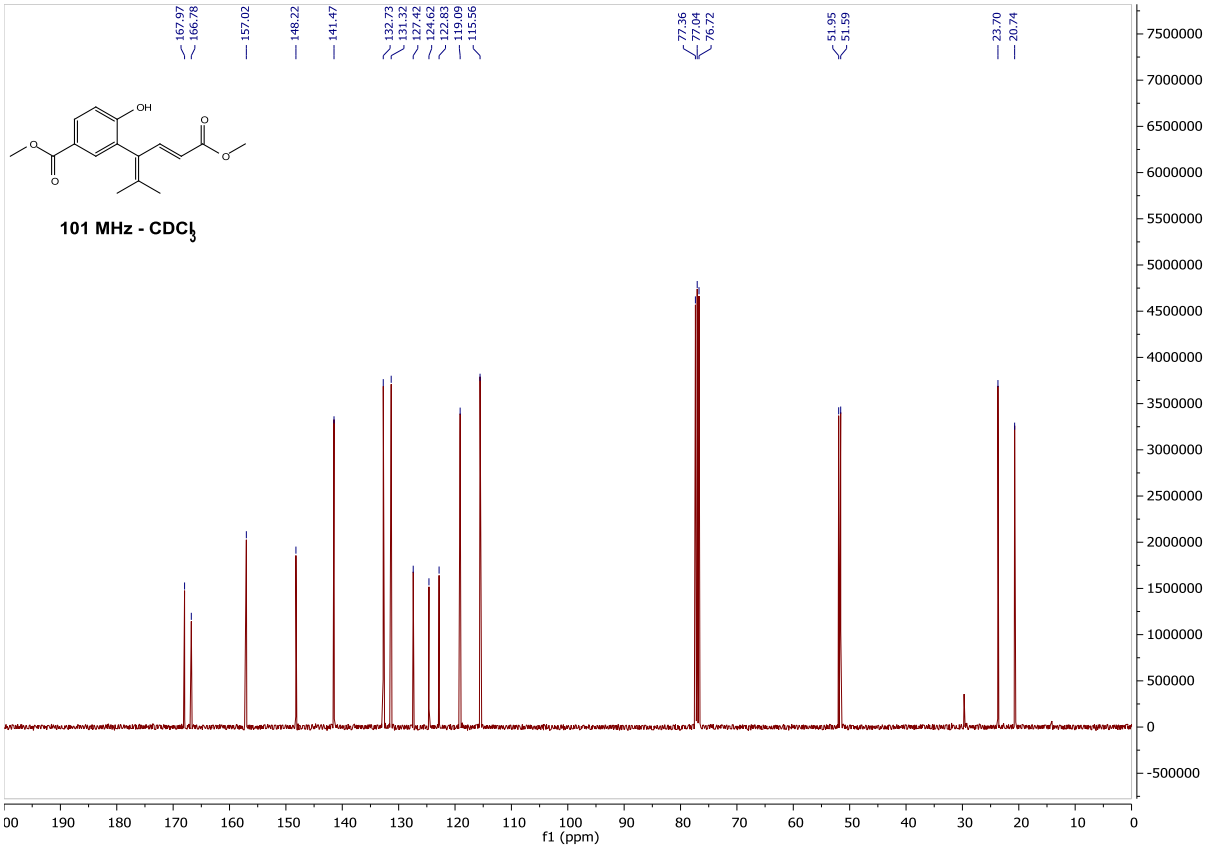

OH
CO2Me
1H NMR
400 MHz
CDCl3
δ (ppm)

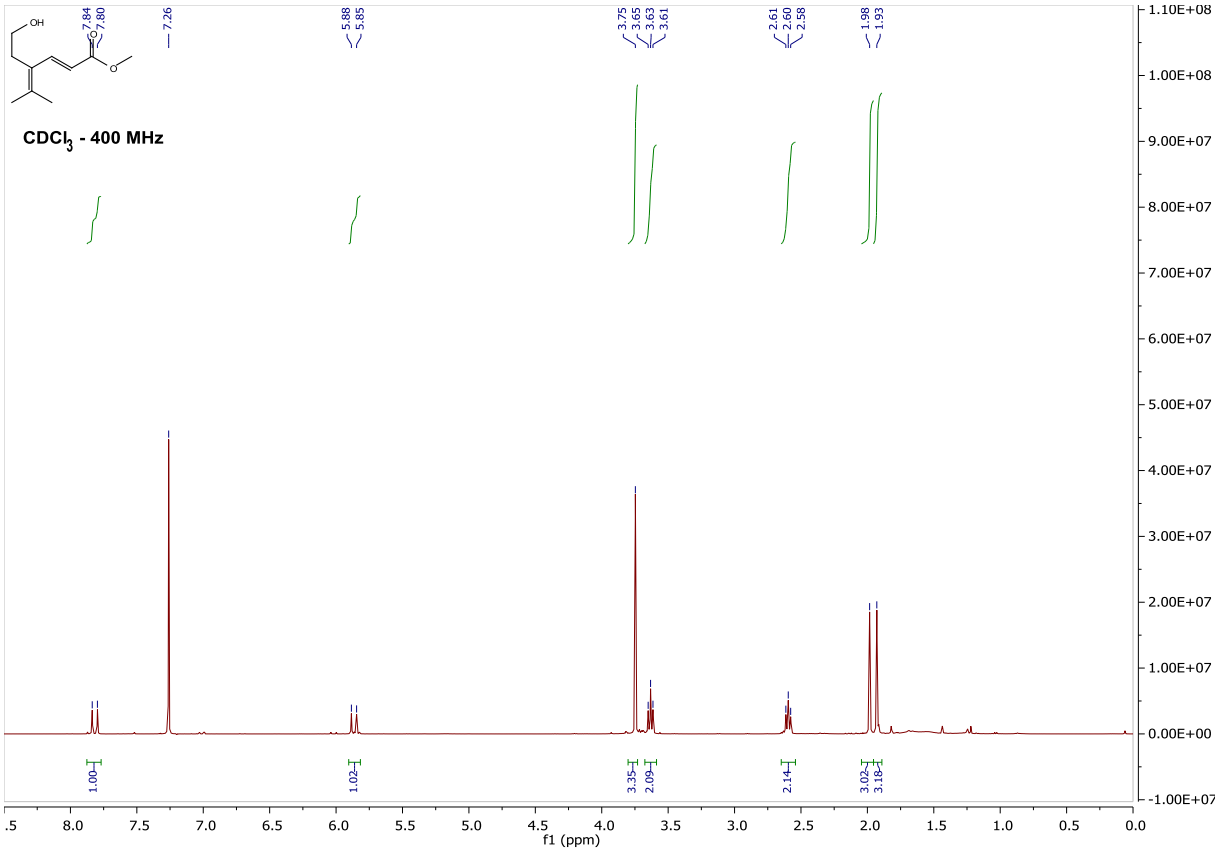

OH
CO2Me
13C NMR
100 MHz
CDCl3
δ (ppm)

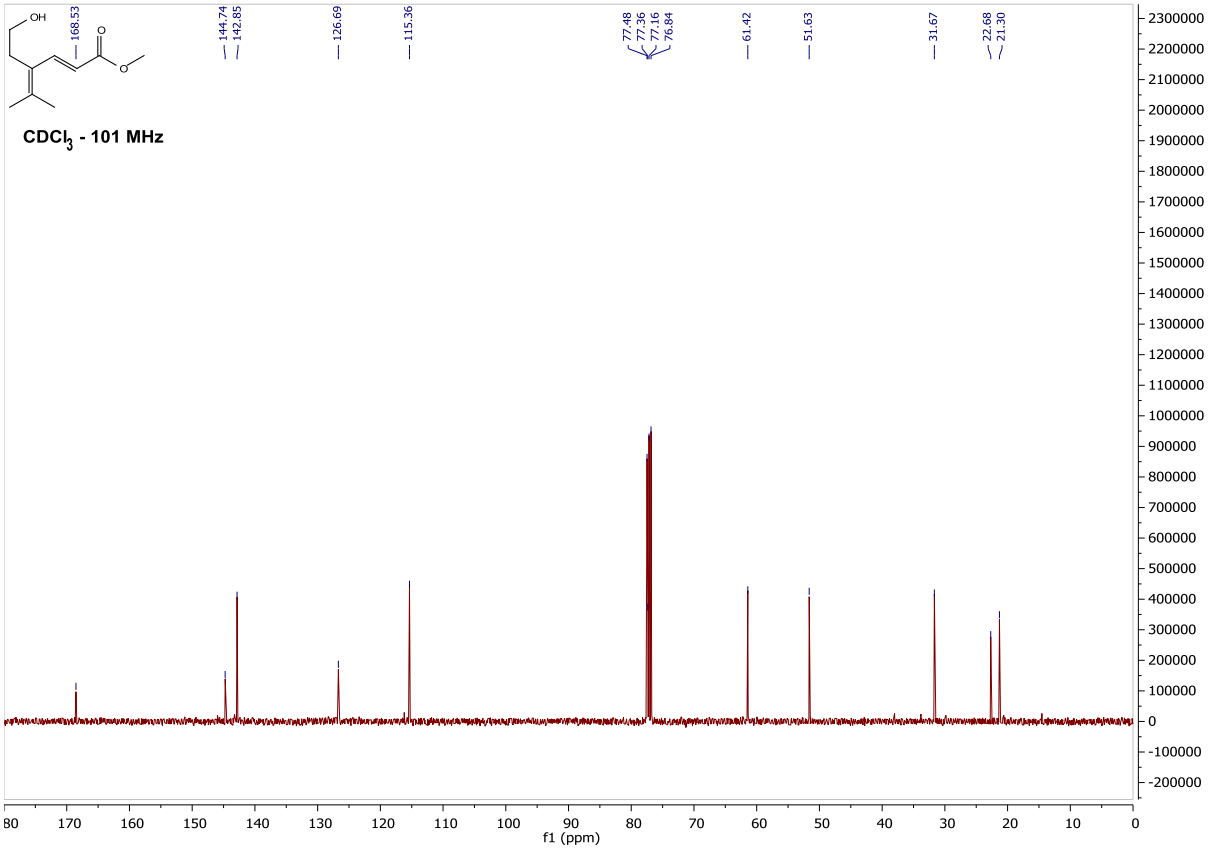

400 MHz - CDCl3
7.96
7.93
7.26
6.88
6.86
6.81
6.80
6.78
6.78
6.46
6.46
5.38
5.34
4.56
3.74
3.70
2.14
1.71
1.00
1.02
1.01
0.99
0.97
0.96
3.00
3.04
3.08
3.27
f1 (ppm)

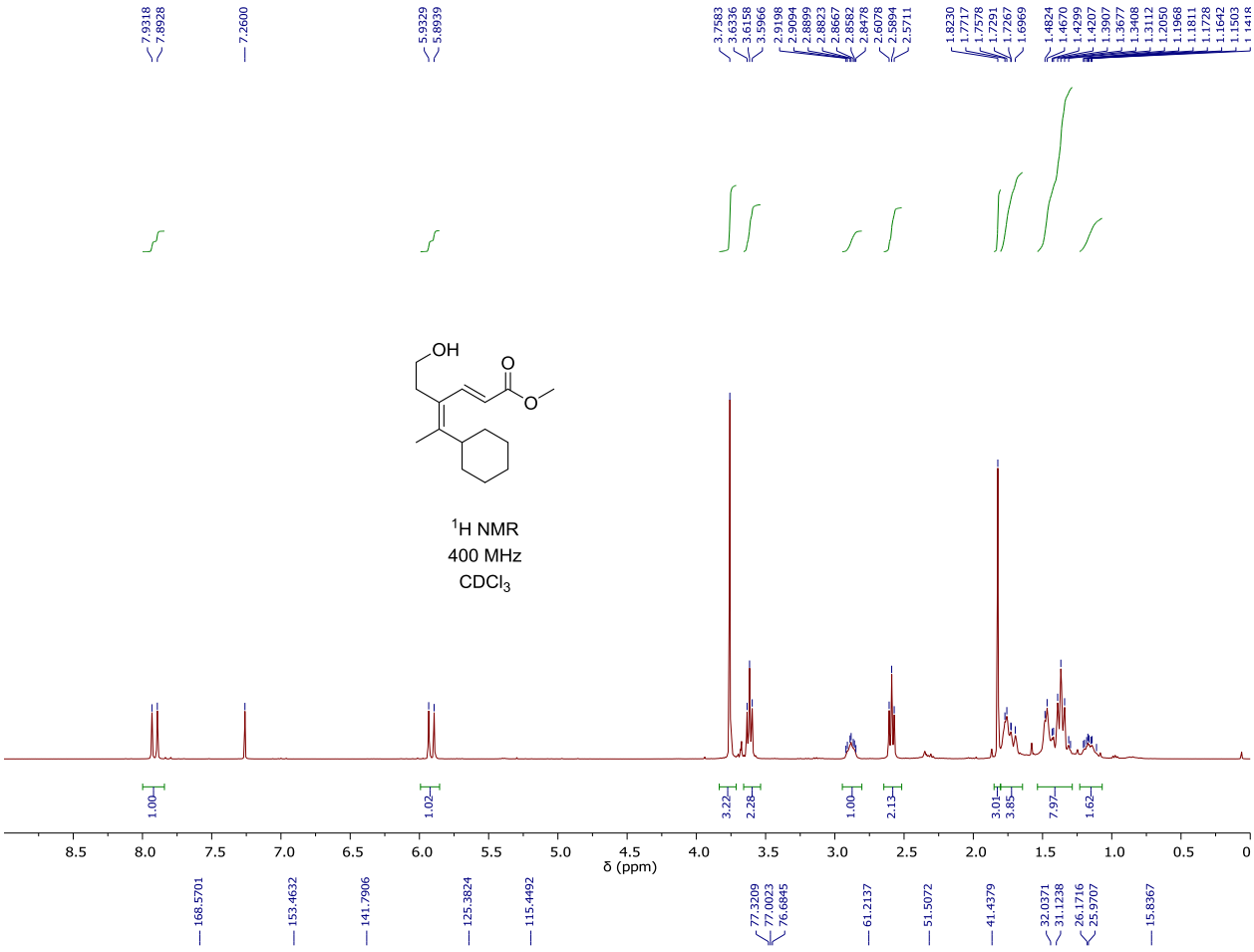

101 MHz - CDCl3
168.19
153.65
147.41
146.77
141.64
128.55
125.28
119.24
116.25
115.47
114.75
77.48
77.16
76.84
55.84
51.63
29.84
23.77
20.78
f1 (ppm)

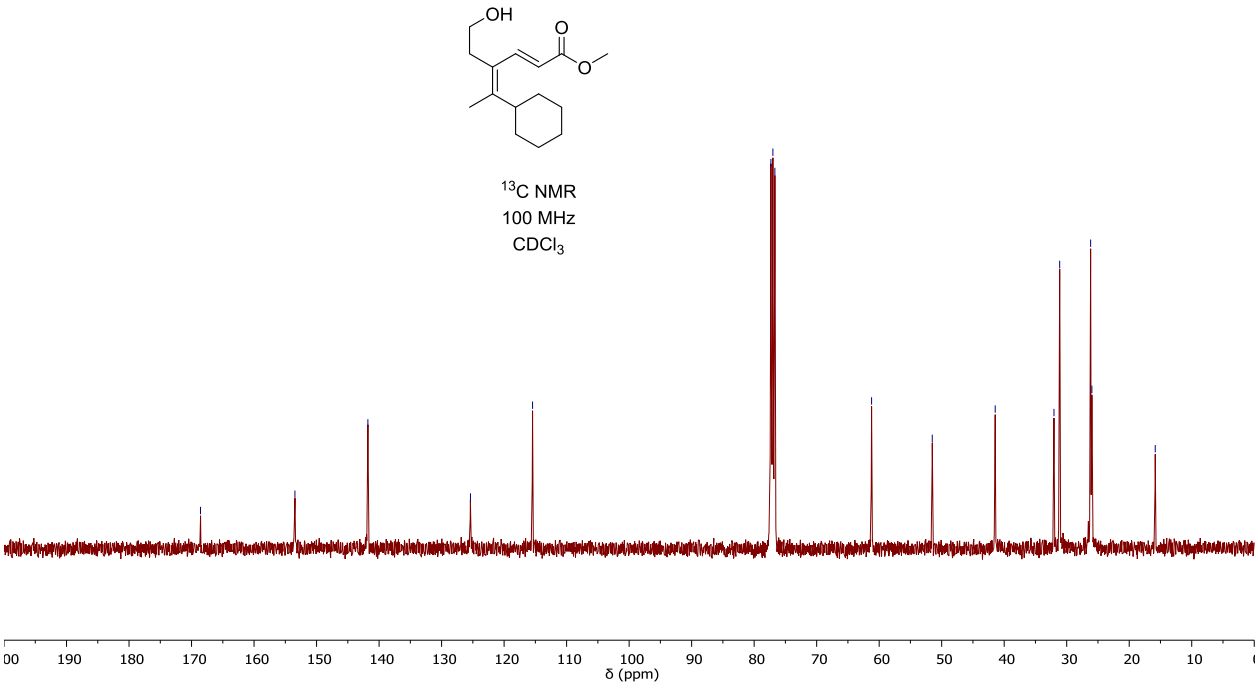

400 MHz - CDCl3
7.97
7.95
7.95
7.93
7.93
7.93
7.65
7.65
7.26
6.99
6.97
5.63
5.28
5.24
3.87
3.69
2.15
1.68
2.09
1.00
1.05
1.03
1.00
3.18
3.18
3.22
3.54
f1 (ppm)

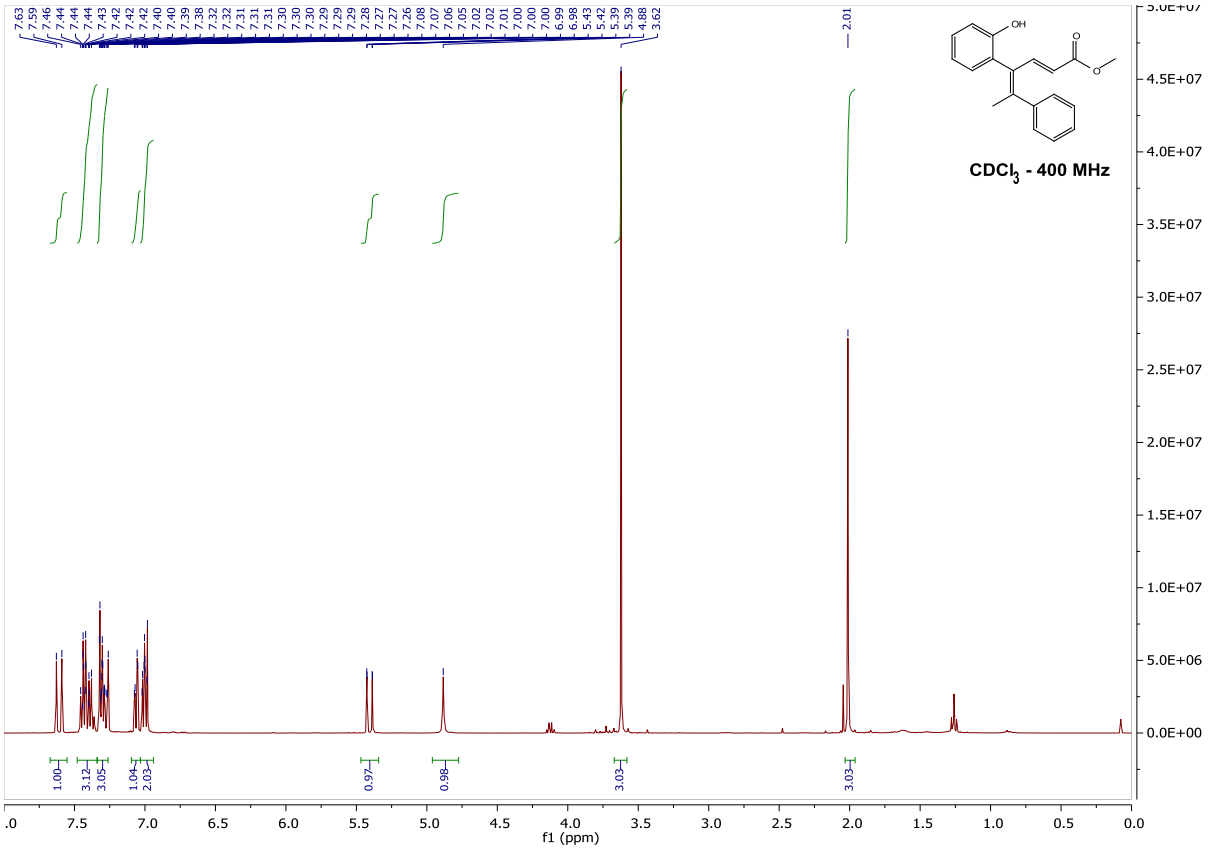

101 MHz - CDCl3
167.97
166.78
157.02
148.22
141.47
132.73
131.32
127.42
124.62
122.83
119.09
115.56
77.36
77.04
76.72
51.95
51.59
23.70
20.74
f1 (ppm)

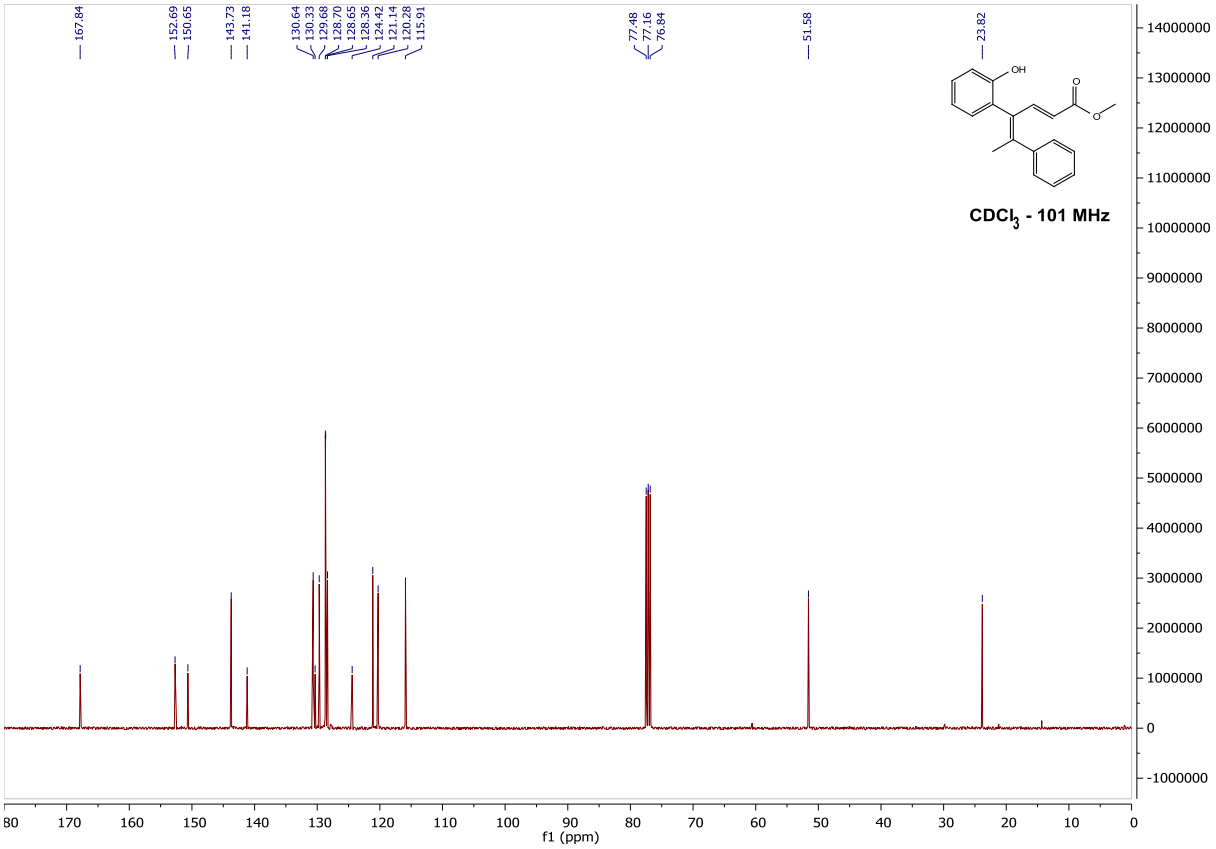

CDCl3 - 400 MHz
7.84
7.80
7.26
5.88
5.85
3.75
3.65
3.63
3.61
2.61
2.60
2.58
1.98
1.93
1.00
1.02
3.35
2.09
2.14
3.02
3.18
f1 (ppm)

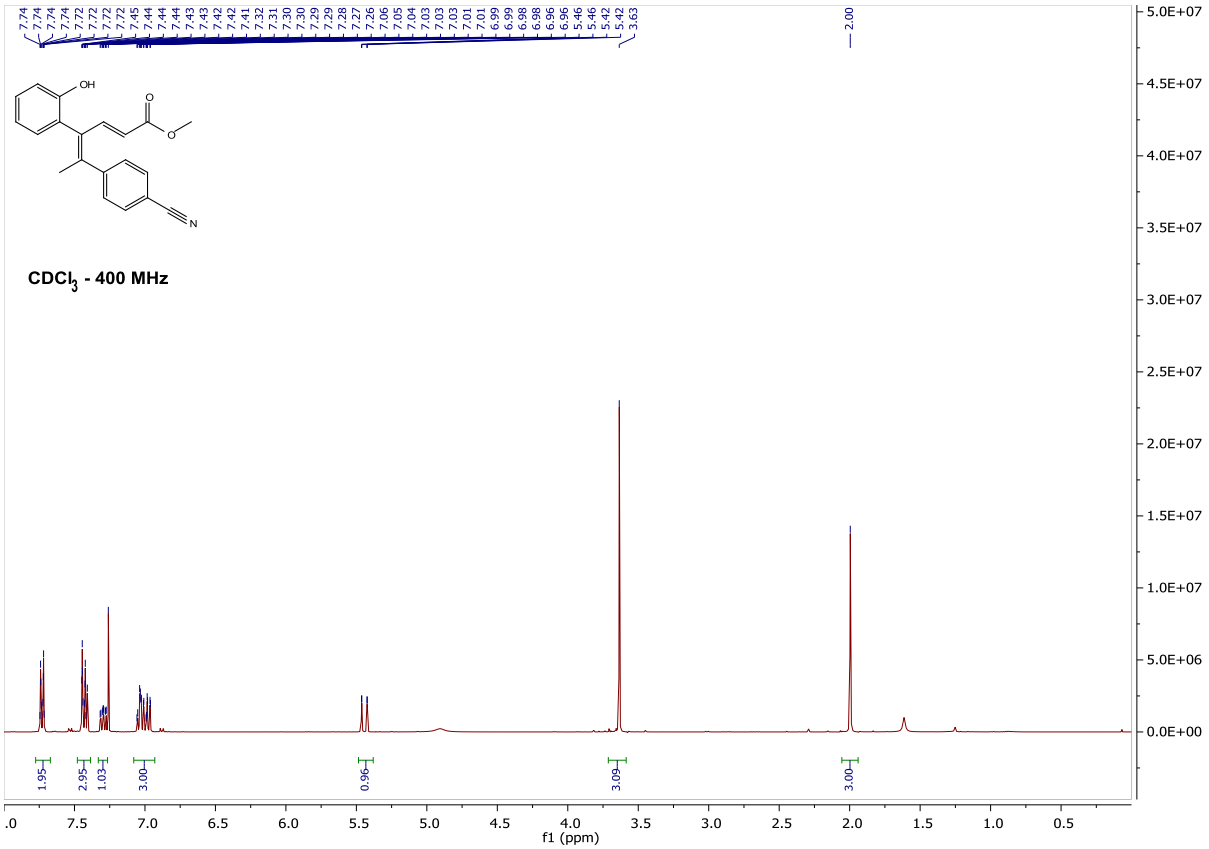

CDCl3 - 101 MHz
168.53
144.74
142.85
126.69
115.36
77.48
77.36
77.16
76.84
61.42
51.63
31.67
22.68
21.30
f1 (ppm)

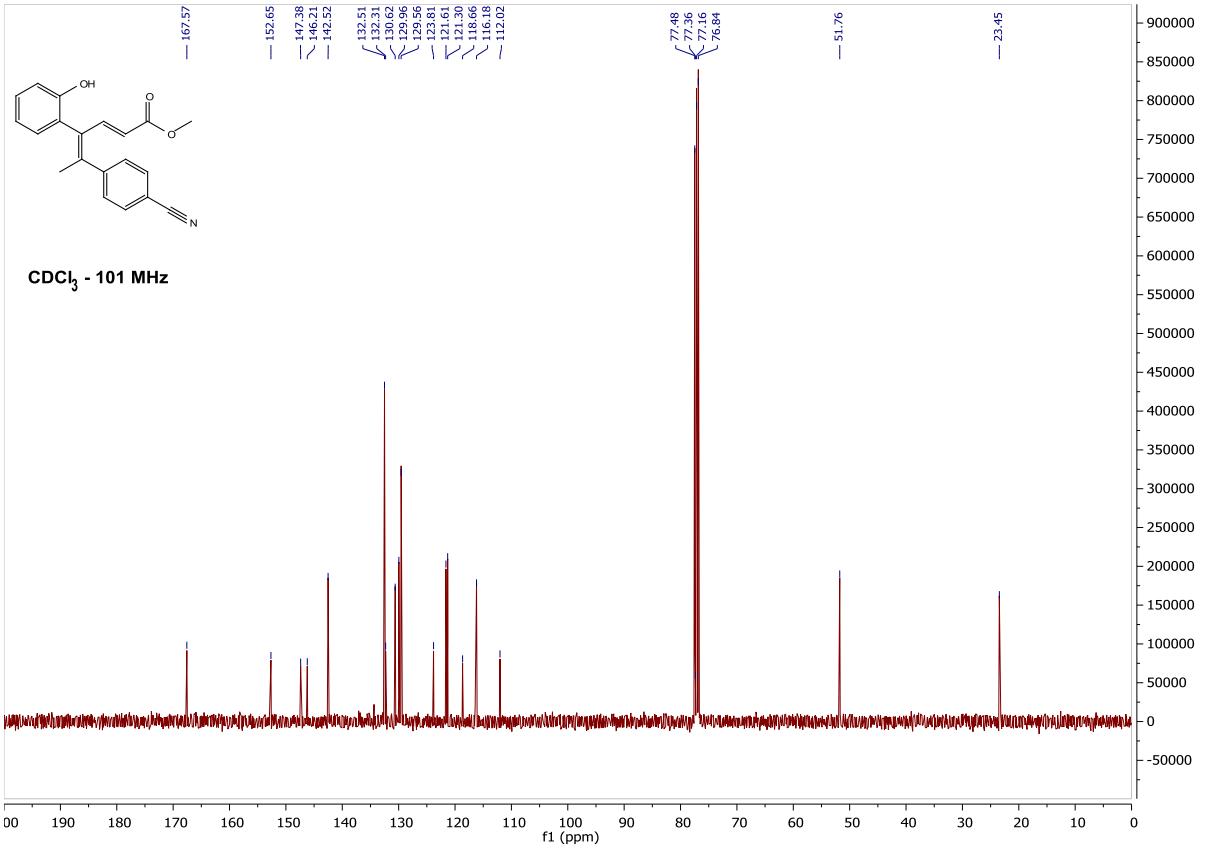

7.9318
7.8928
7.2600
5.9329
5.8939
3.7583
3.6336
3.6158
3.5966
2.9198
2.9094
2.8899
2.8823
2.8667
2.8582
2.8478
2.6078
2.5894
2.5711
1.8230
1.7717
1.7578
1.7291
1.7267
1.6969
1.4824
1.4670
1.4299
1.4207
1.3907
1.3677
1.3408
1.3112
1.2050
1.1968
1.1811
1.1728
1.1642
1.1503
OH
O
O
^{1}H NMR
400 MHz
$CDCl_3$
1.00
1.02
3.22
2.28
1.00
2.13
3.01
3.85
7.97
1.62
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
δ (ppm)
168.5701
153.4632
141.7906
125.3824
115.4492
77.3209
77.0023
76.6845
61.2137
51.5072
41.4379
32.0371
31.1238
26.1716
25.9707
15.8367

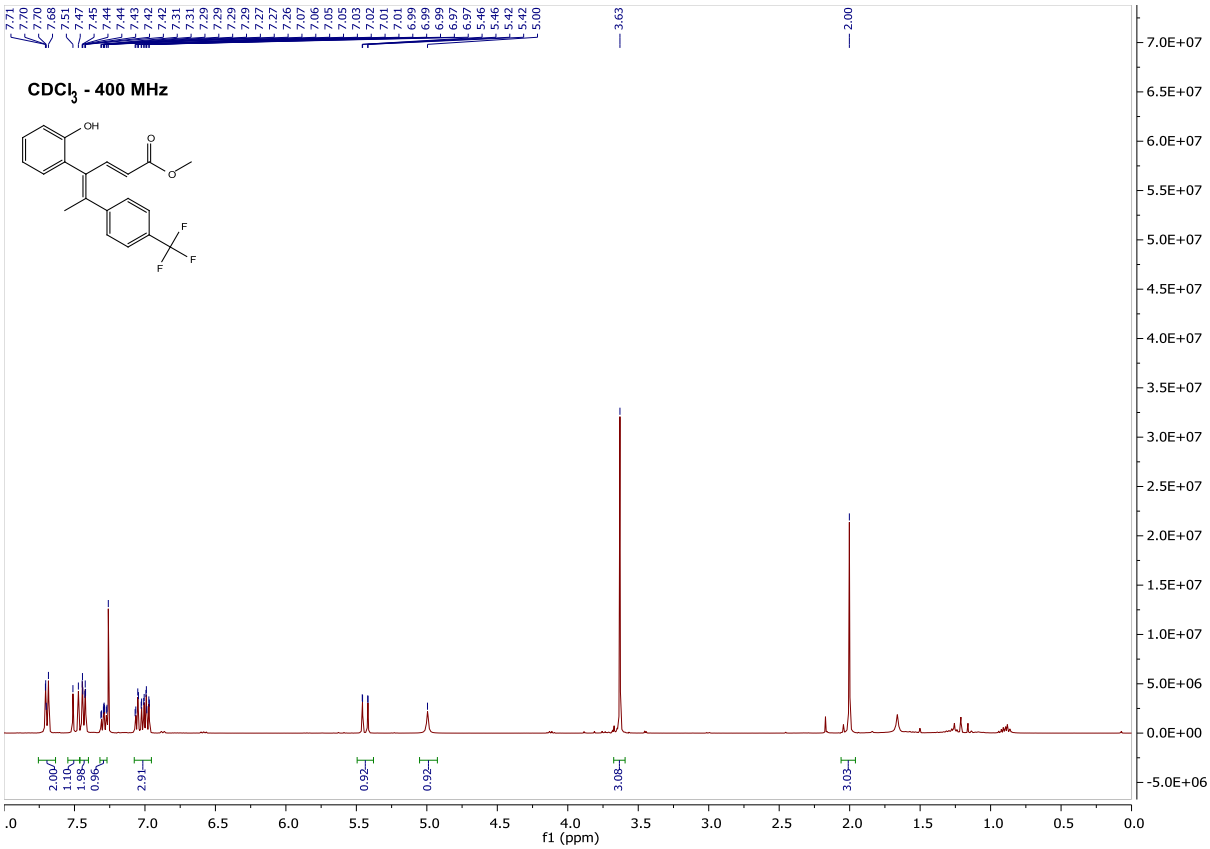

OH
O
O
^{13}C NMR
100 MHz
$CDCl_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ (ppm)

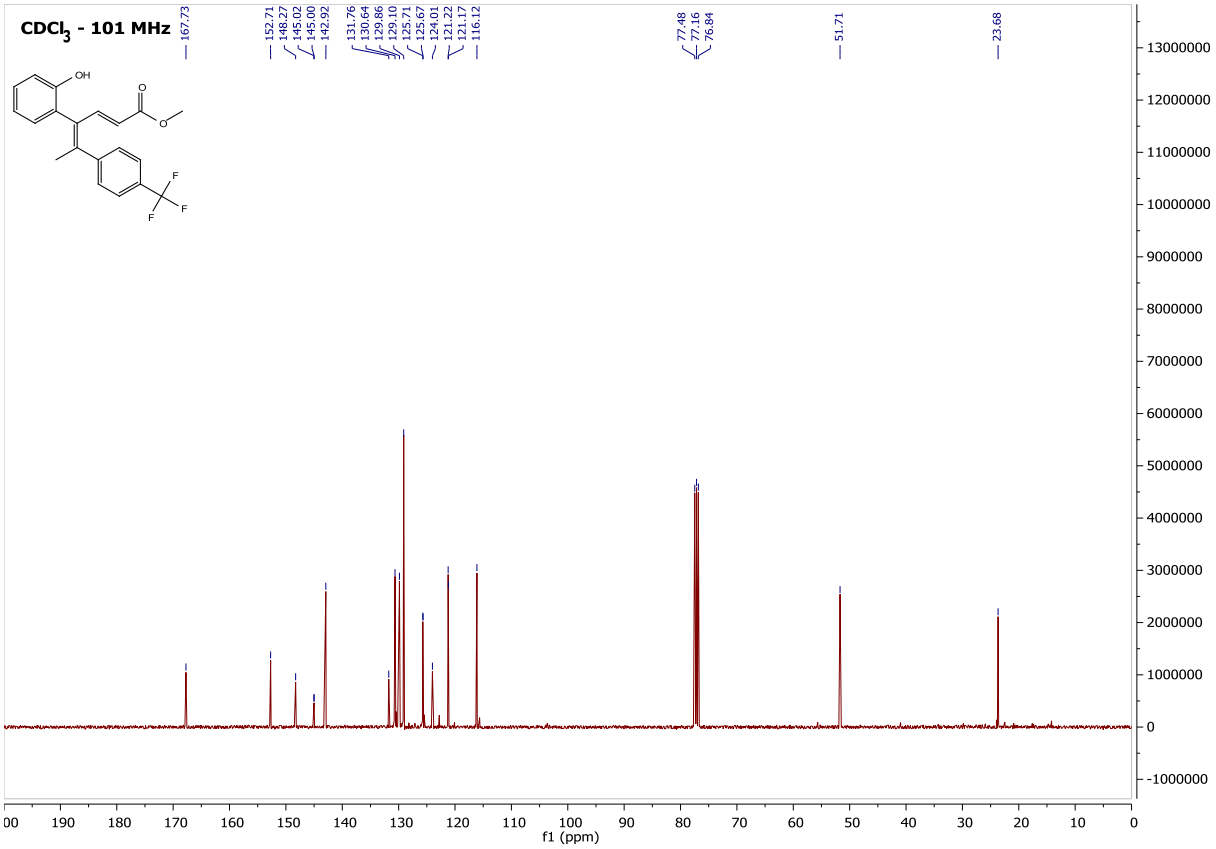

CDCl3 - 400 MHz
f1 (ppm)


CDCl3 - 101 MHz
f1 (ppm)

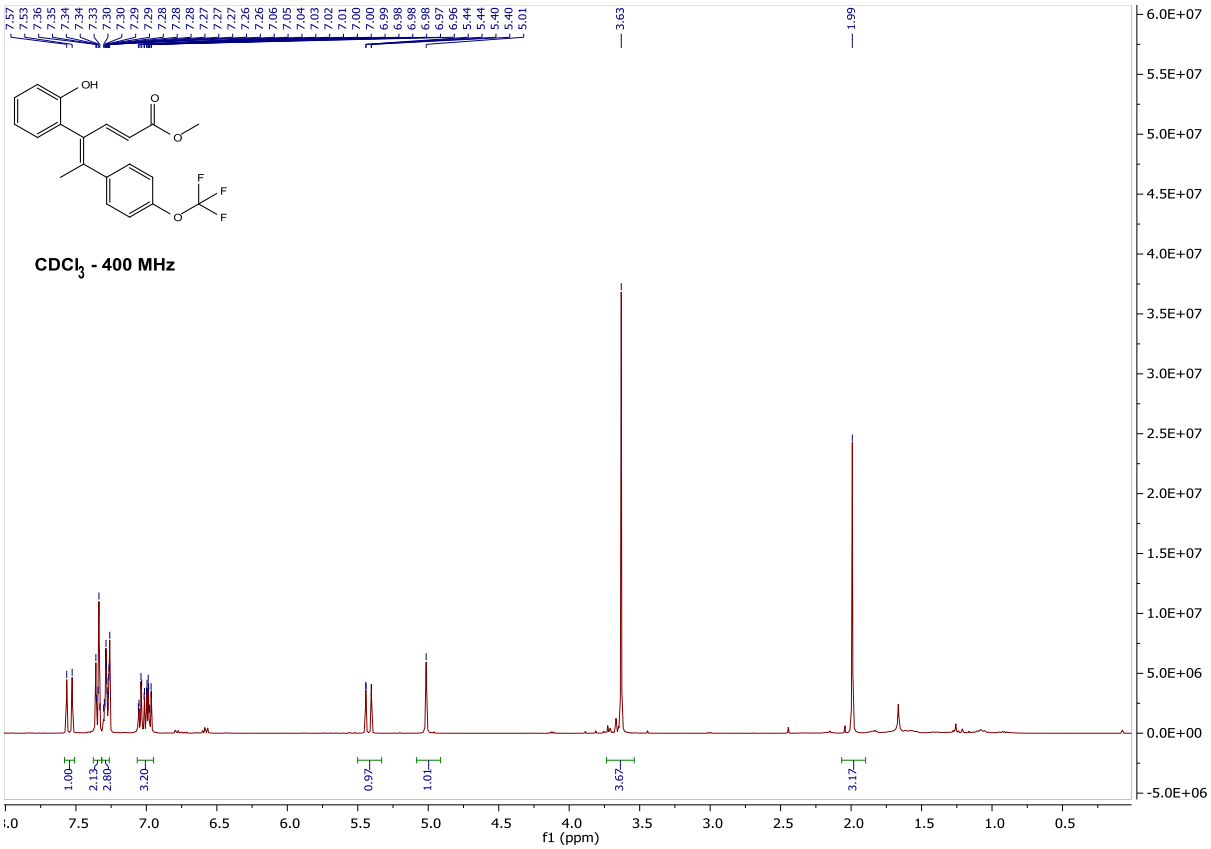

CDCl3 - 400 MHz
f1 (ppm)

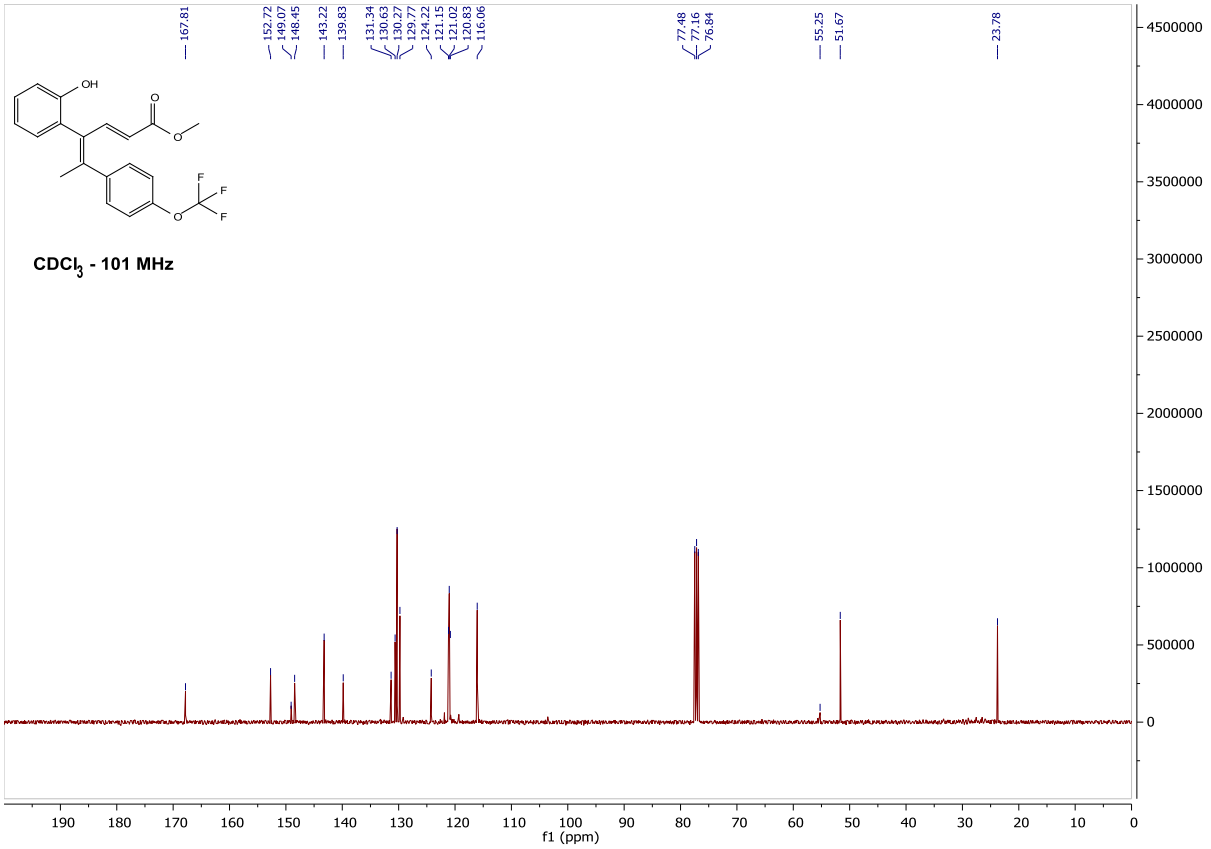

CDCl3 - 101 MHz
f1 (ppm)

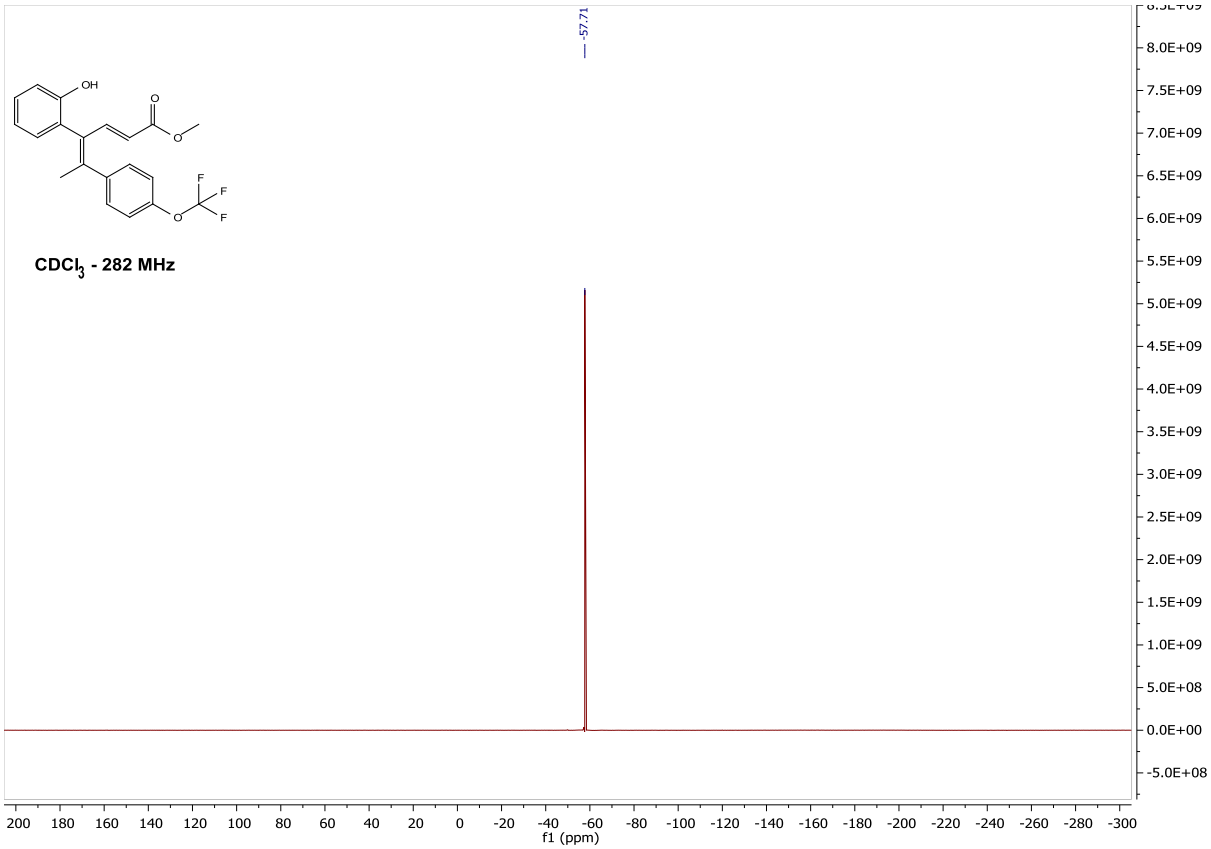

CDCl3 - 400 MHz
OH
O
O
F
F
F
7.71
7.70
7.70
7.68
7.51
7.47
7.45
7.44
7.44
7.43
7.42
7.42
7.31
7.31
7.29
7.29
7.29
7.29
7.27
7.27
7.26
7.07
7.06
7.05
7.05
7.03
7.02
7.01
7.01
6.99
6.99
6.99
6.97
6.97
5.46
5.46
5.42
5.42
5.00
3.63
2.00
2.00
1.10
1.98
0.96
2.91
0.92
0.92
3.08
3.03
f1 (ppm)

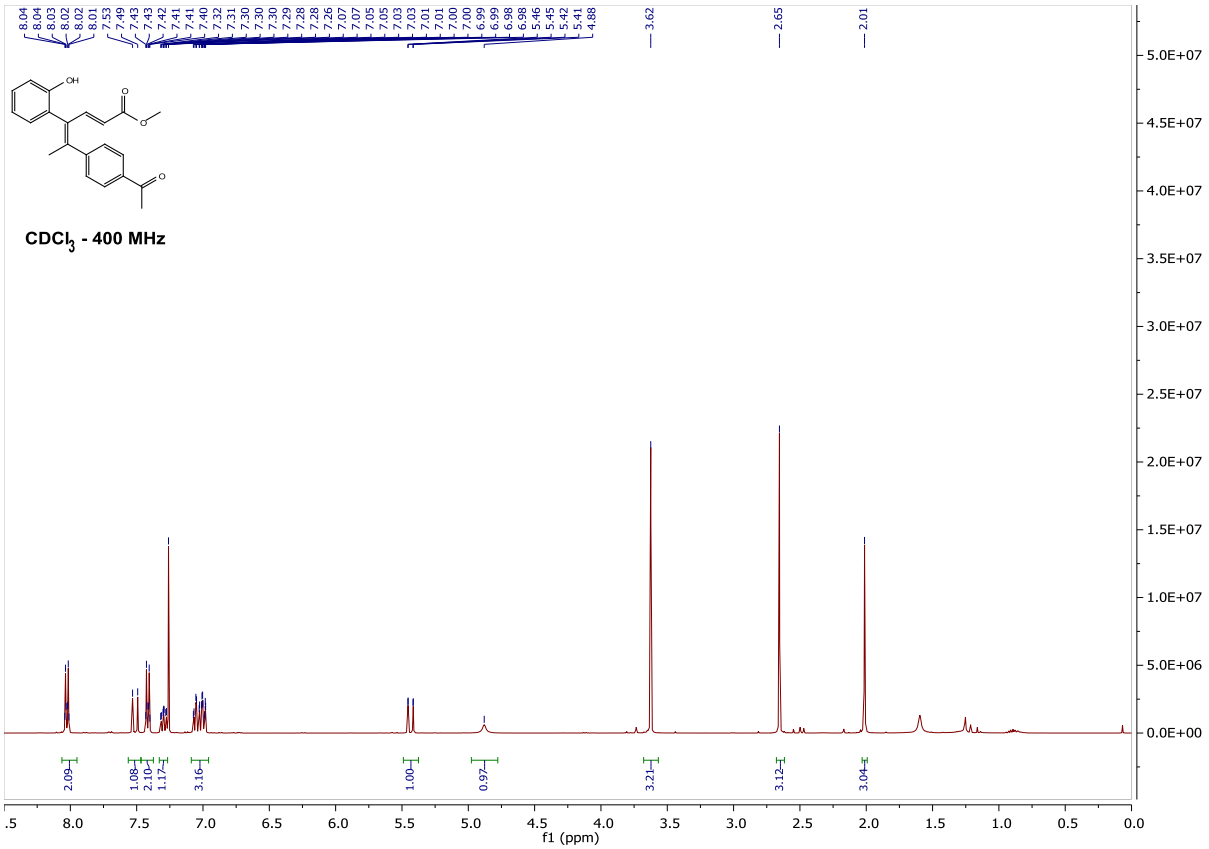

CDCl3 - 101 MHz
OH
O
O
F
F
F
167.73
152.71
148.27
145.02
145.00
142.92
131.76
130.64
129.86
129.10
125.71
125.67
124.01
121.22
121.17
116.12
77.48
77.16
76.84
51.71
23.68
f1 (ppm)

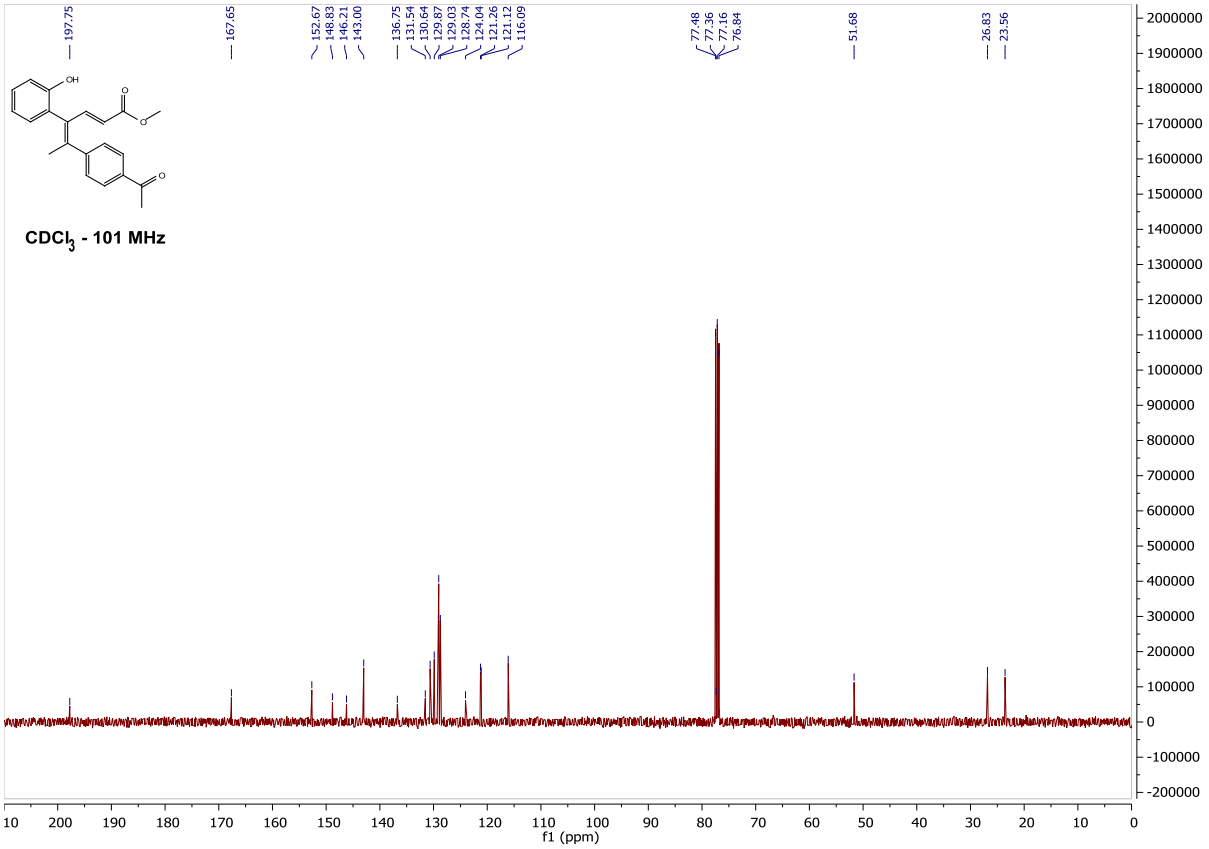

CDCl3 - 282 MHz
OH
O
O
F
F
F
-62.59
A (s)
-62.59
1.00
2.4E+10
2.2E+10
2.0E+10
1.8E+10
1.6E+10
1.4E+10
1.2E+10
1.0E+10
8.0E+09
6.0E+09
4.0E+09
2.0E+09
0.0E+00
-2.0E+09
-4.0E+09
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

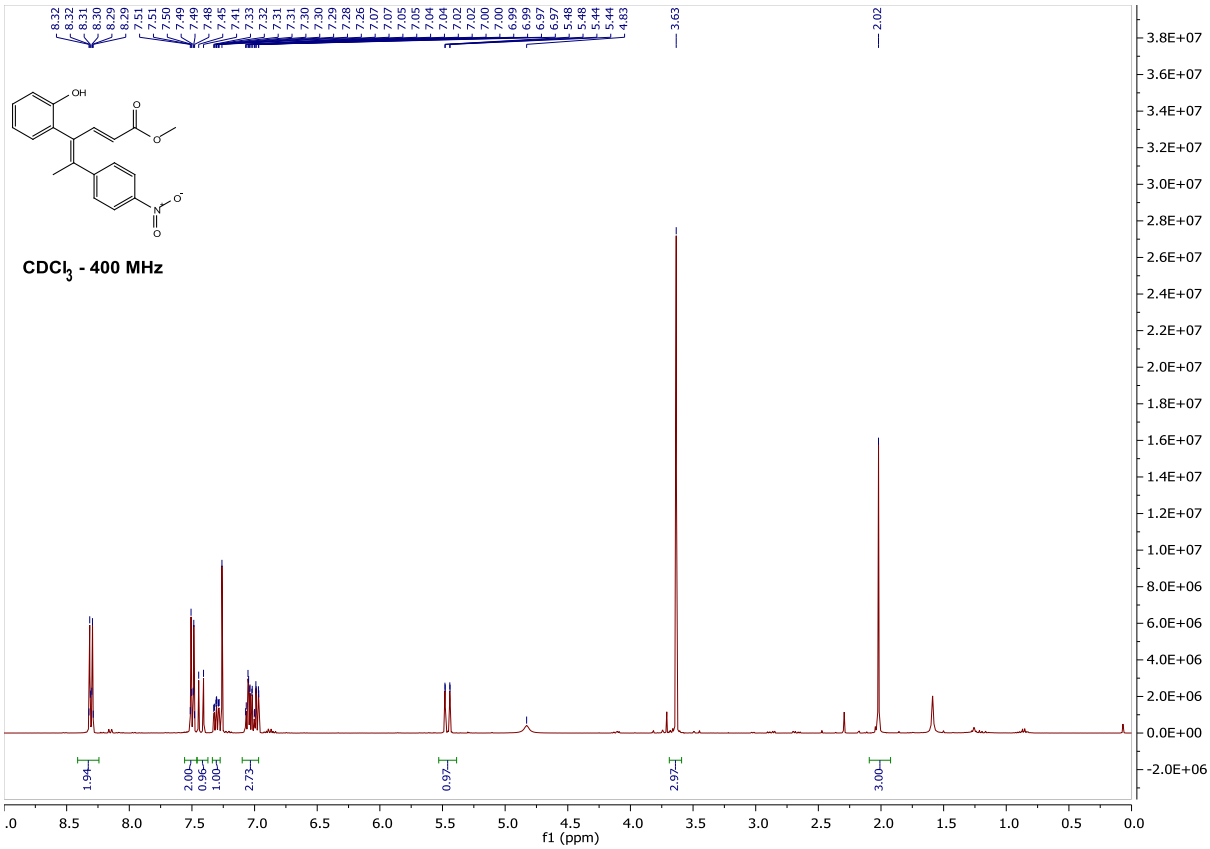

CDCl3 - 400 MHz
f1 (ppm)

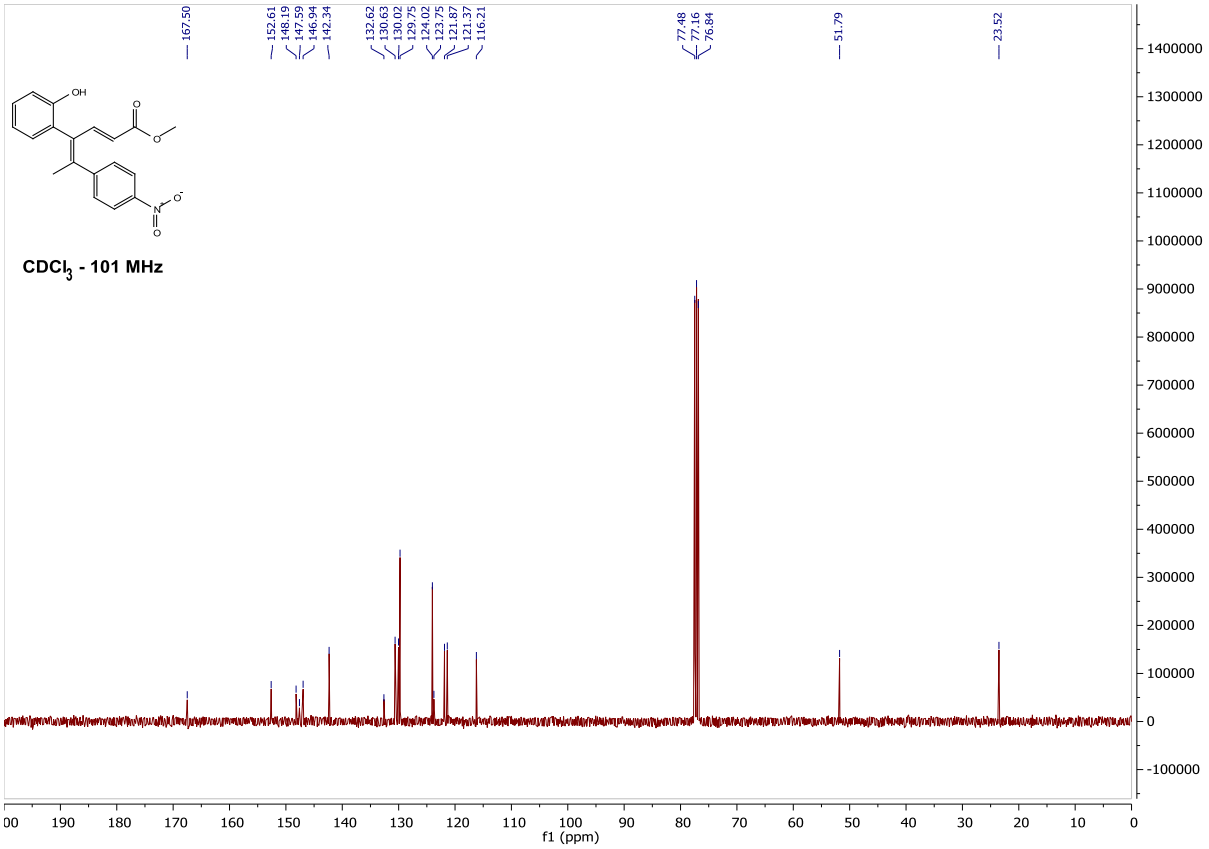

CDCl3 - 101 MHz
f1 (ppm)

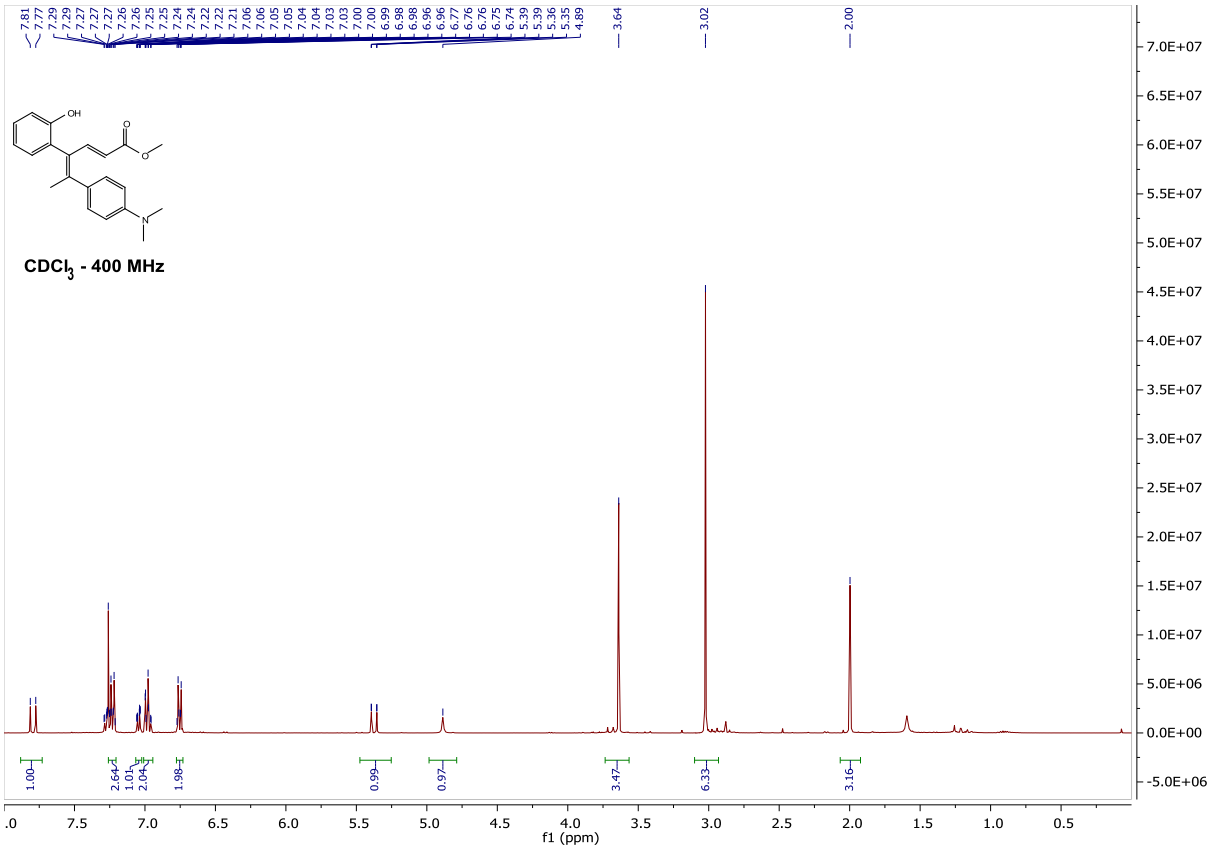

-57.71
OH
O
O
F
F
F
O
CDCl3 - 282 MHz
8.0E+09
7.5E+09
7.0E+09
6.5E+09
6.0E+09
5.5E+09
5.0E+09
4.5E+09
4.0E+09
3.5E+09
3.0E+09
2.5E+09
2.0E+09
1.5E+09
1.0E+09
5.0E+08
0.0E+00
-5.0E+08
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

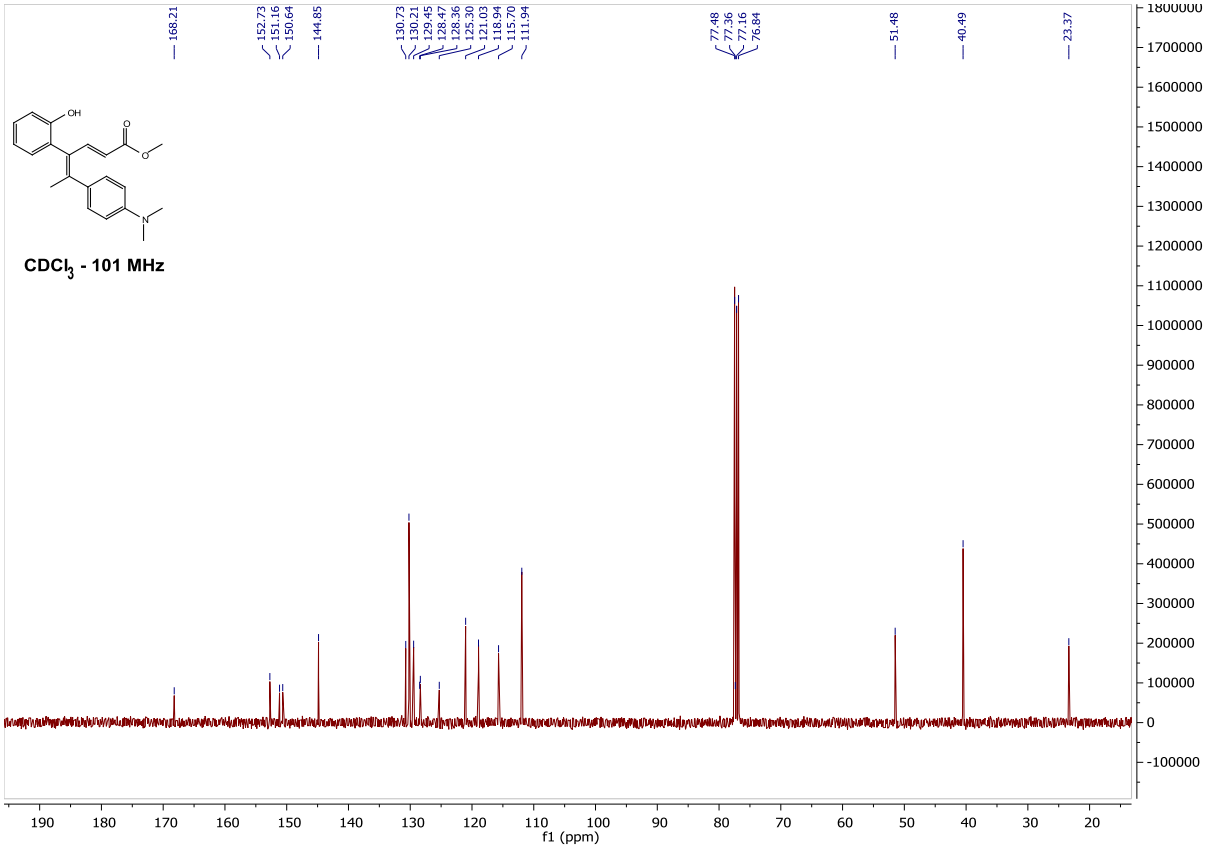

CDCl3 - 400 MHz
f1 (ppm)

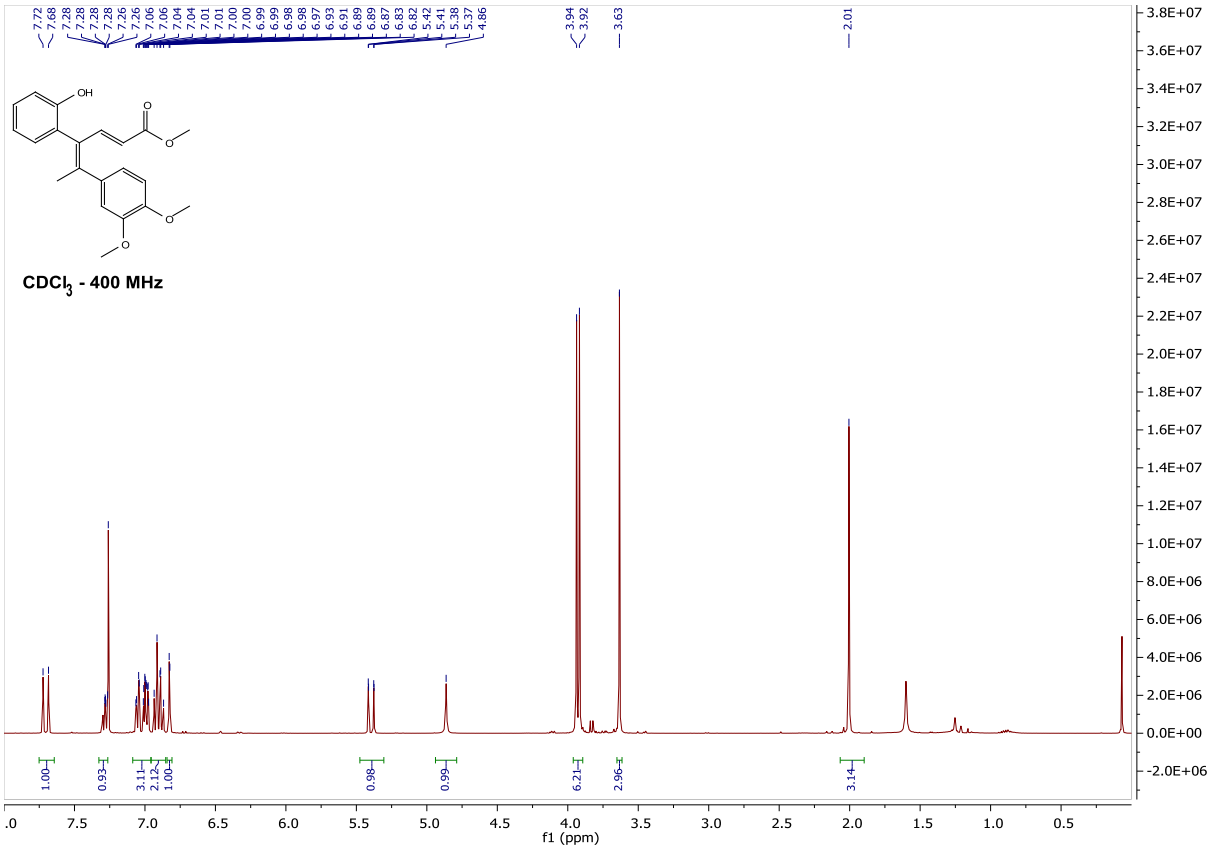

CDCl3 - 101 MHz
f1 (ppm)

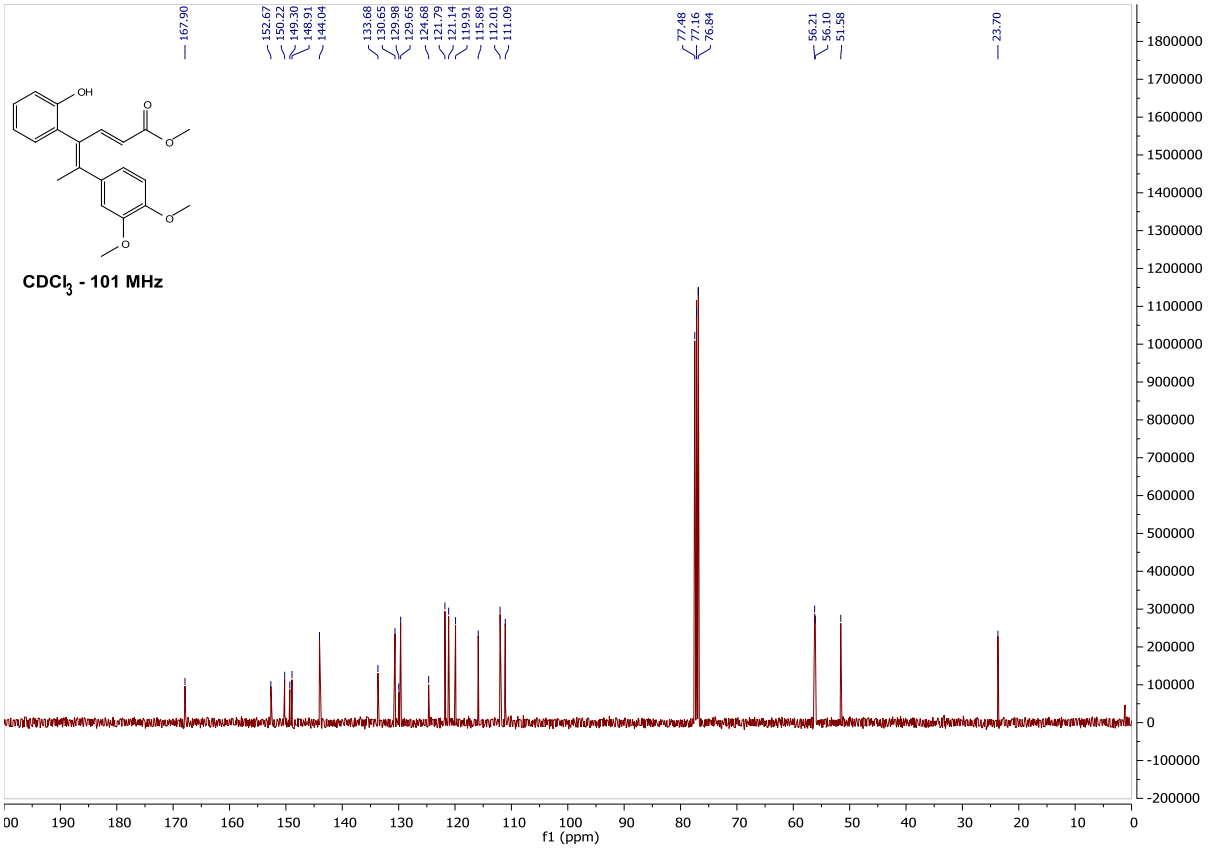

CDCl3 - 400 MHz
f1 (ppm)

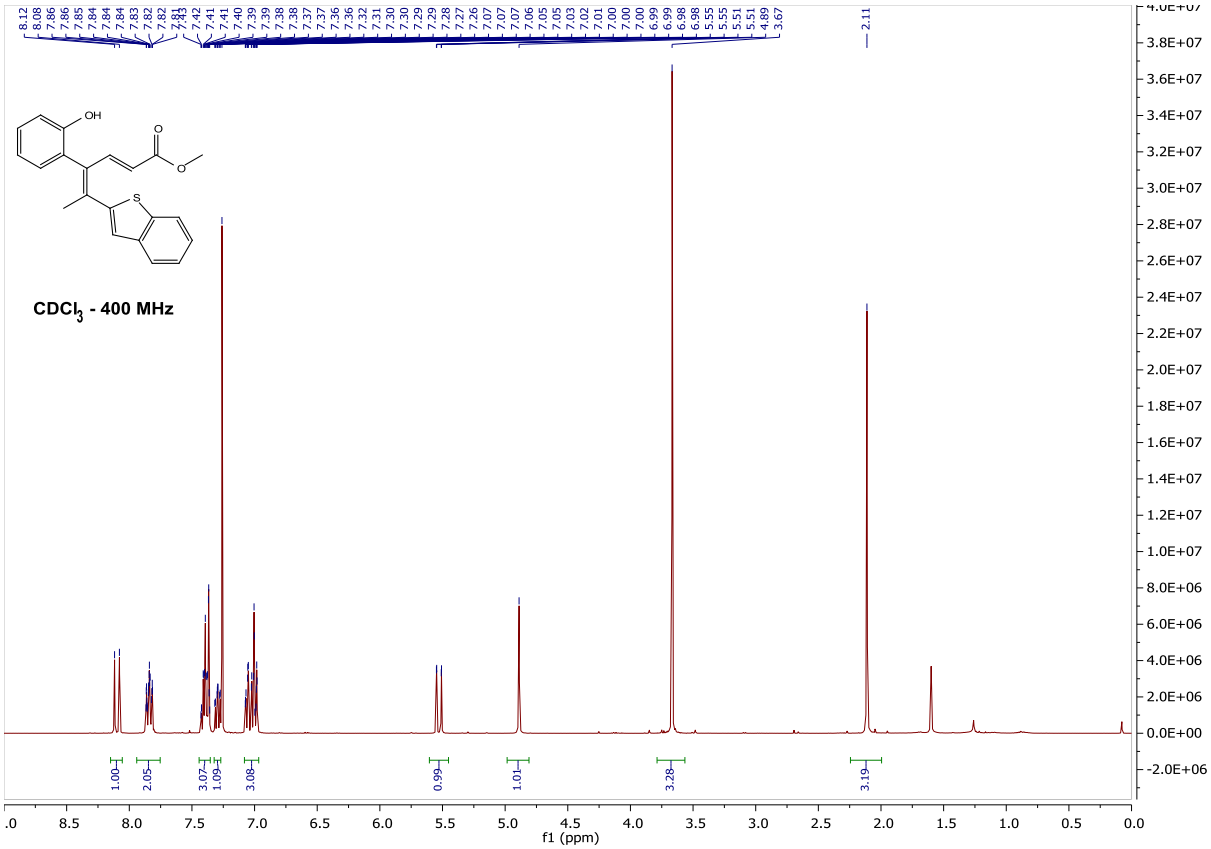

CDCl3 - 101 MHz
f1 (ppm)

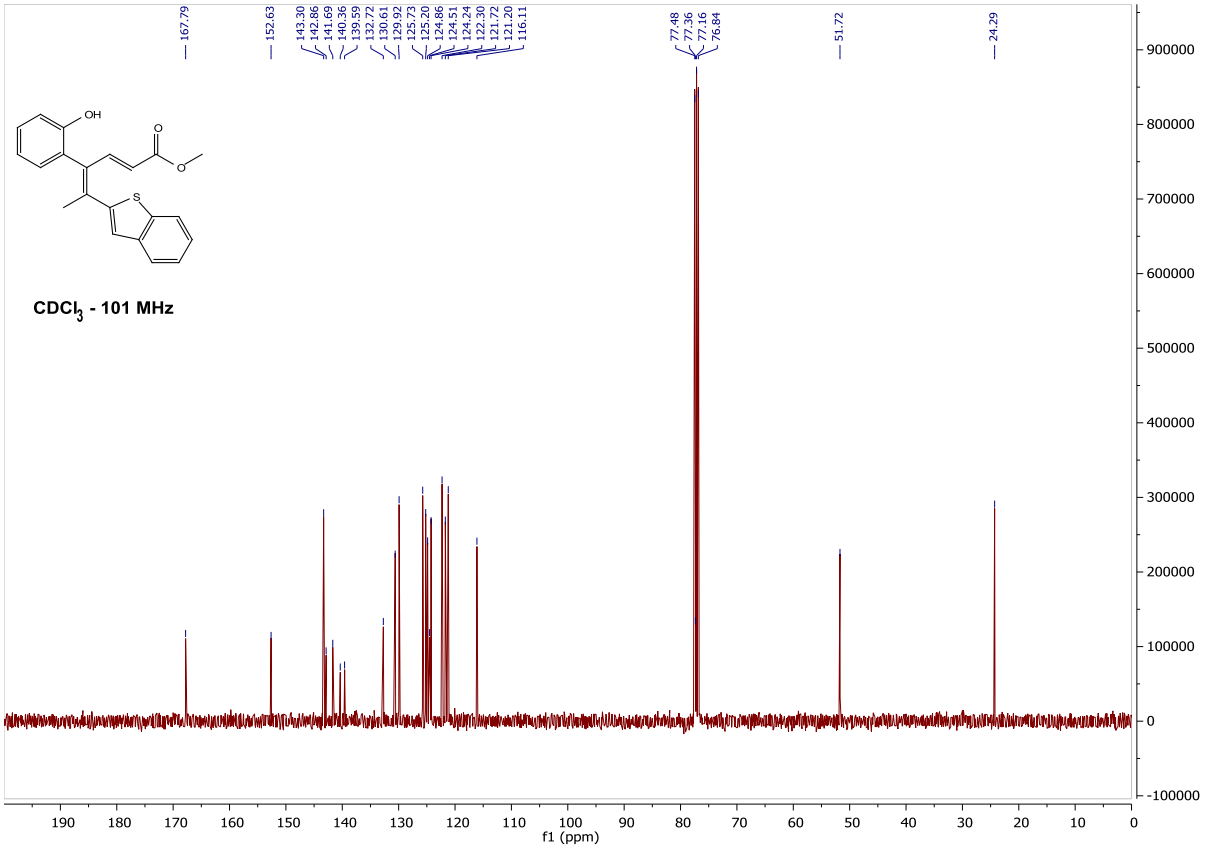

CDCl3 - 400 MHz
f1 (ppm)

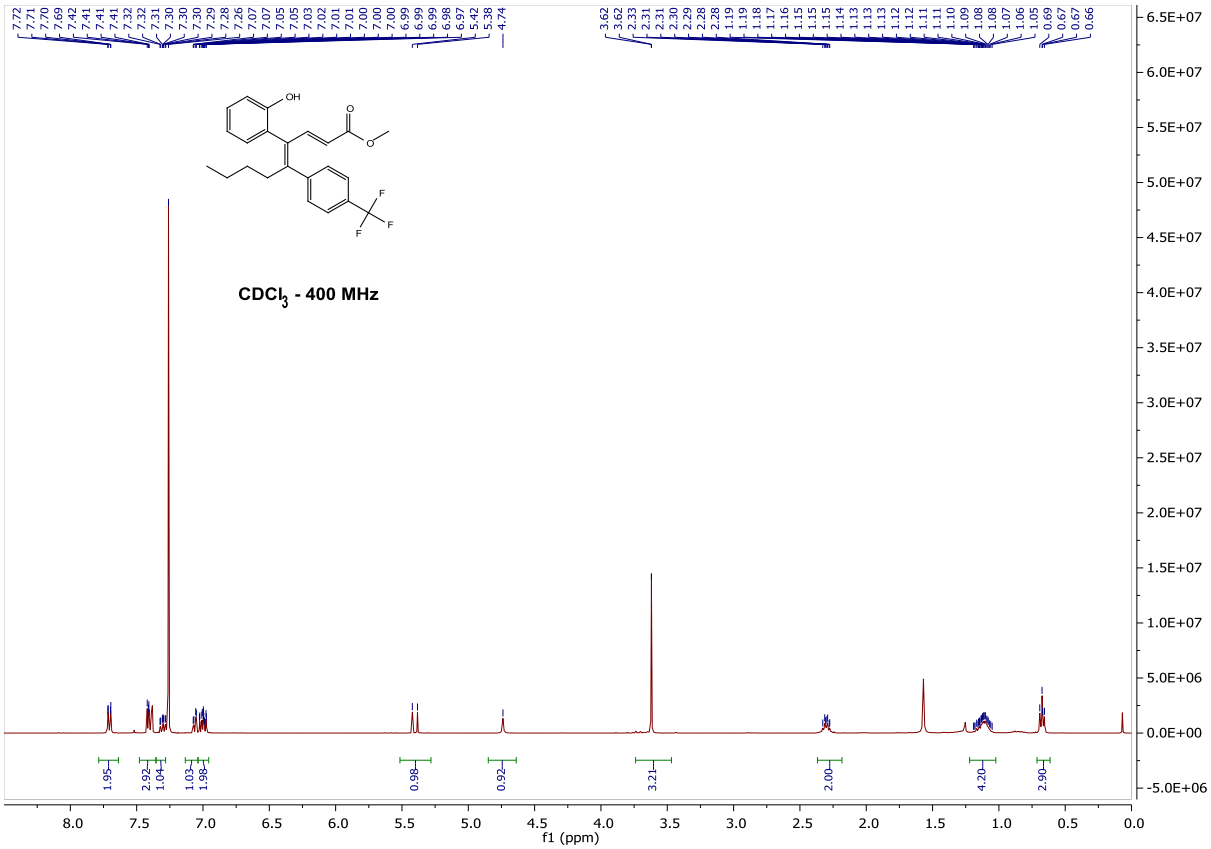

CDCl3 - 101 MHz
f1 (ppm)

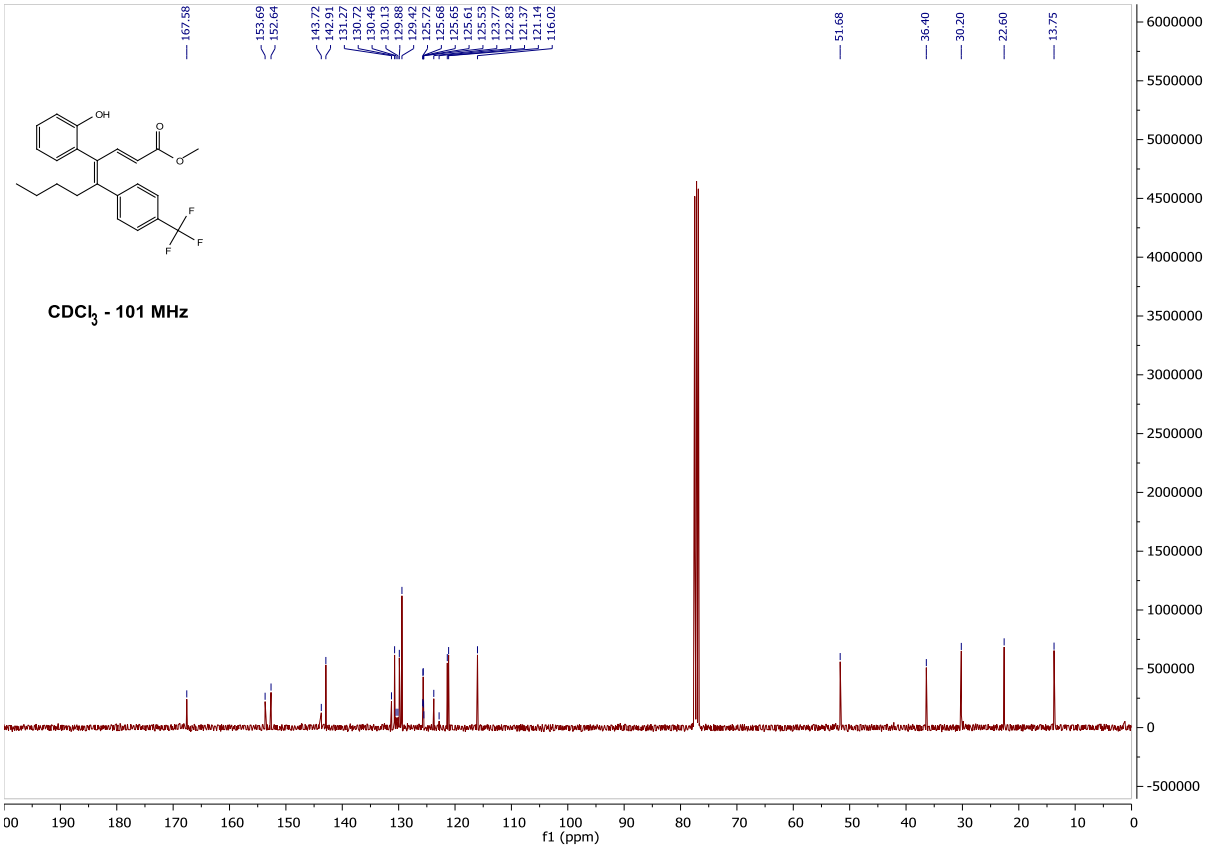

CDCl3 - 400 MHz
f1 (ppm)

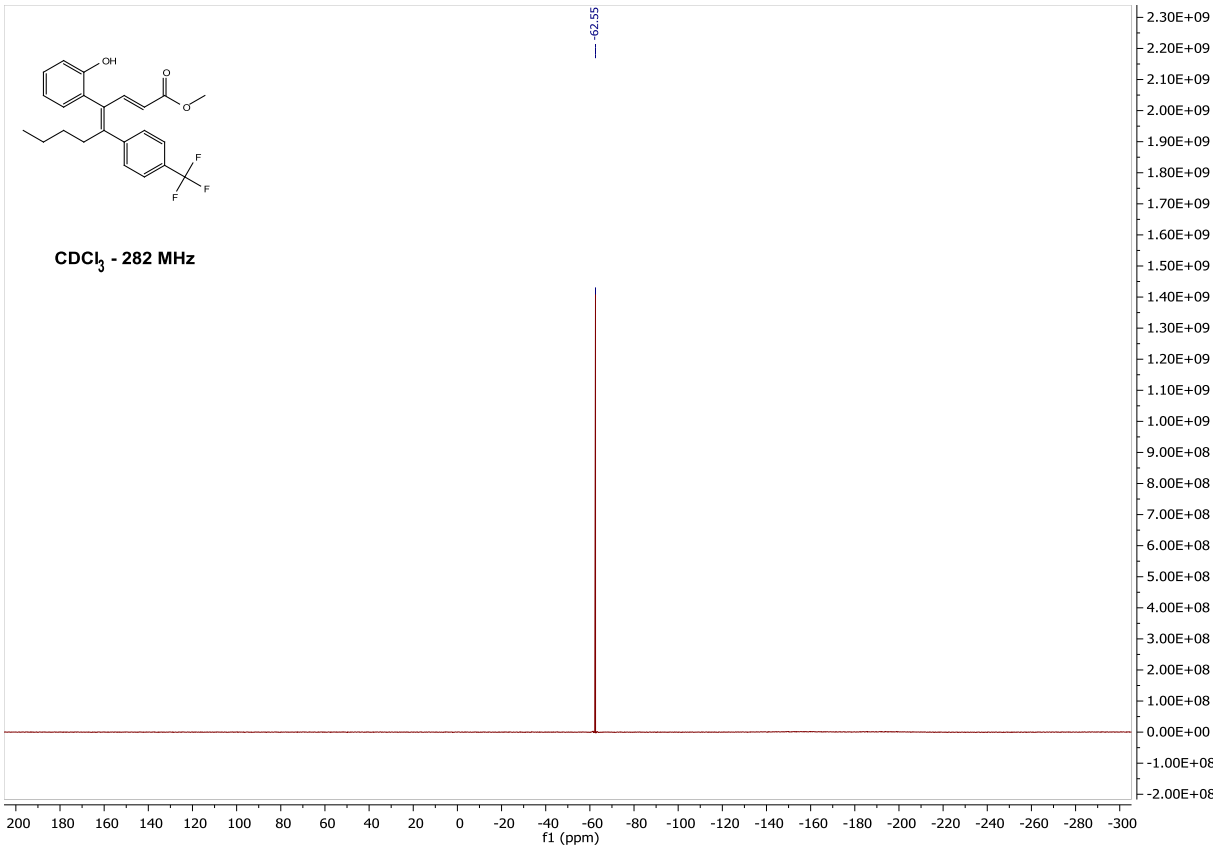

CDCl3 - 101 MHz
f1 (ppm)

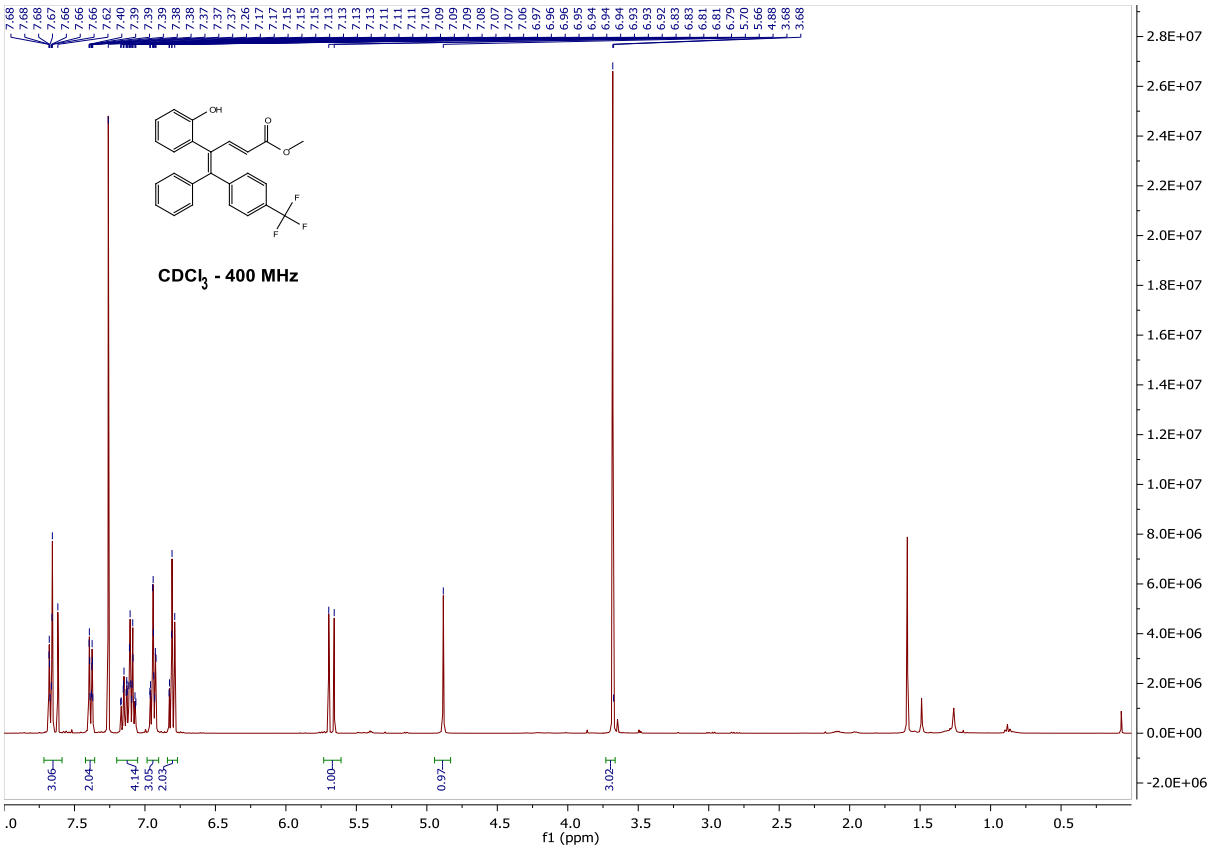

CDCl3 - 400 MHz
f1 (ppm)

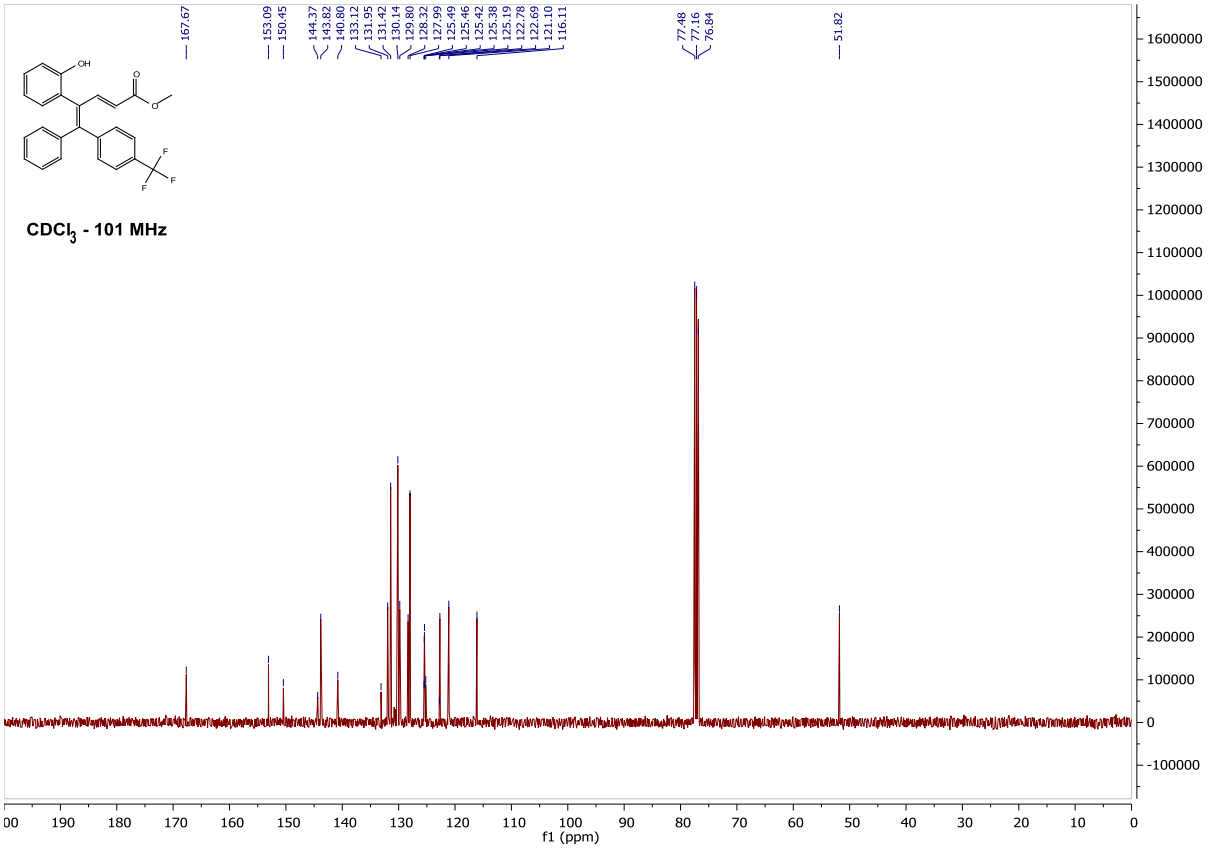

CDCl3 - 101 MHz
f1 (ppm)

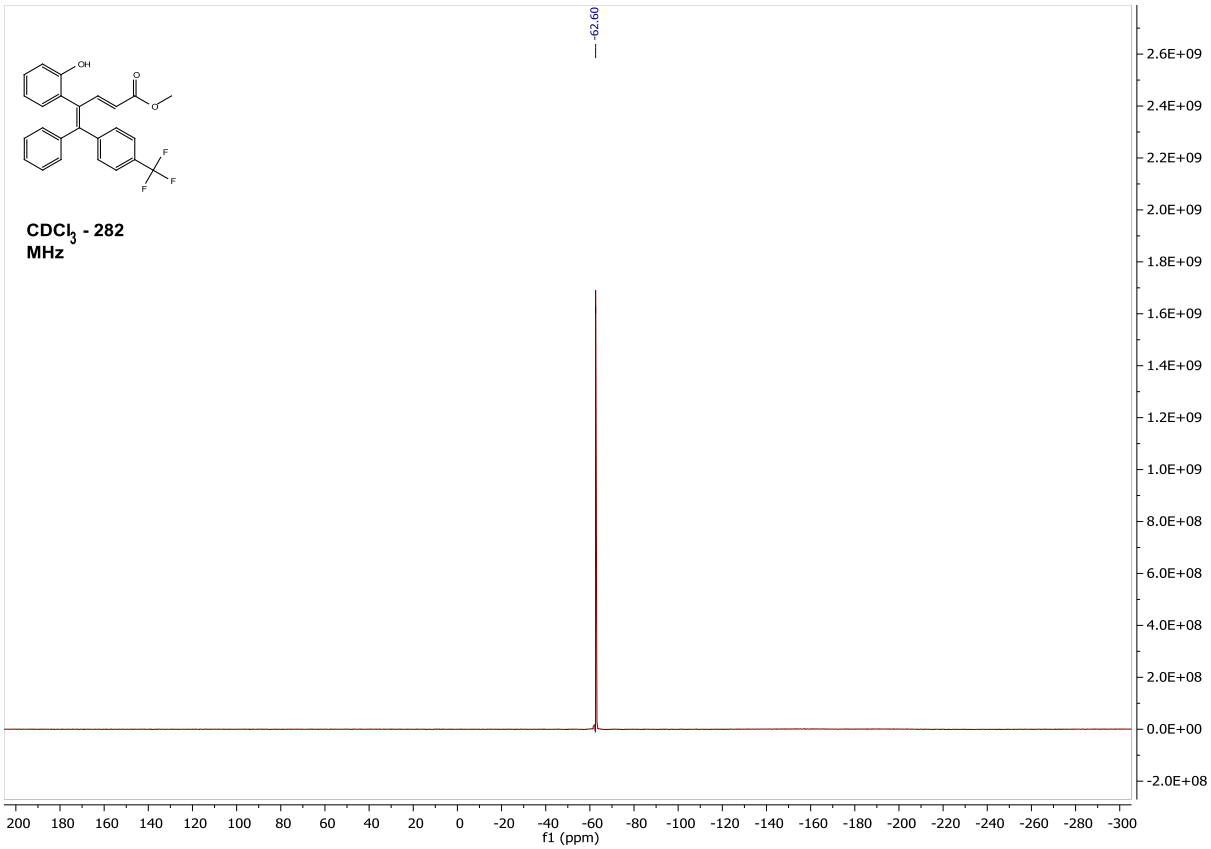

CDCl3 - 400 MHz
f1 (ppm)

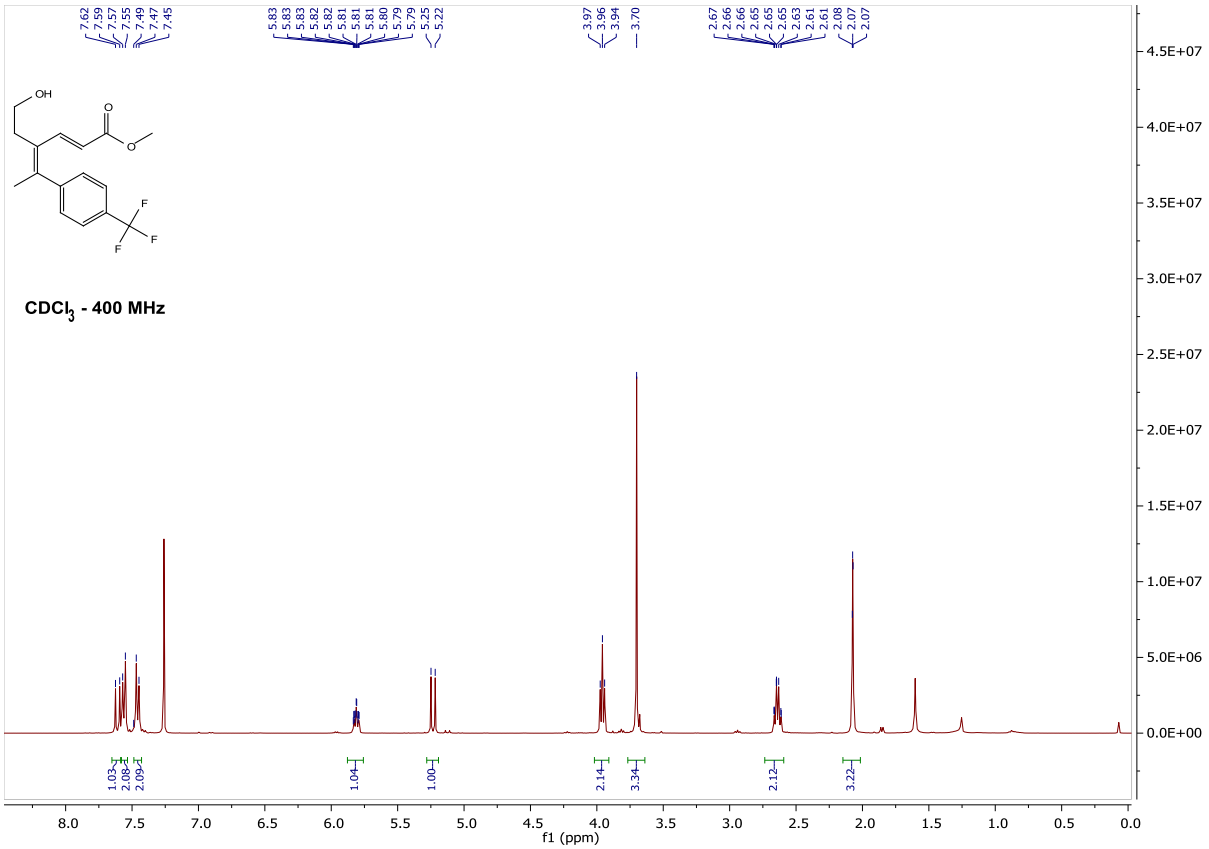

CDCl3 - 101 MHz
f1 (ppm)

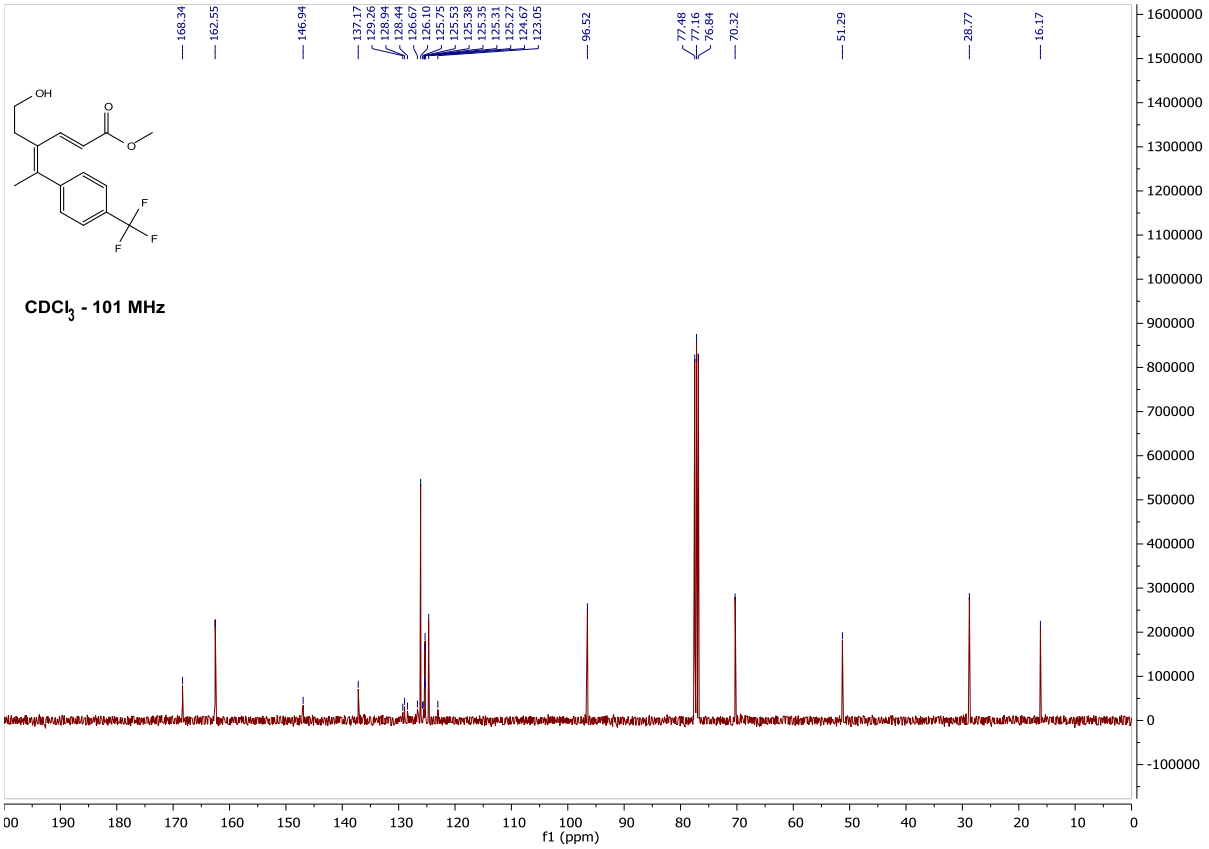

-62.55
CDCl3 - 282 MHz
OH
O
O
F
F
F
2.30E+09
2.20E+09
2.10E+09
2.00E+09
1.90E+09
1.80E+09
1.70E+09
1.60E+09
1.50E+09
1.40E+09
1.30E+09
1.20E+09
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
-2.00E+08
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

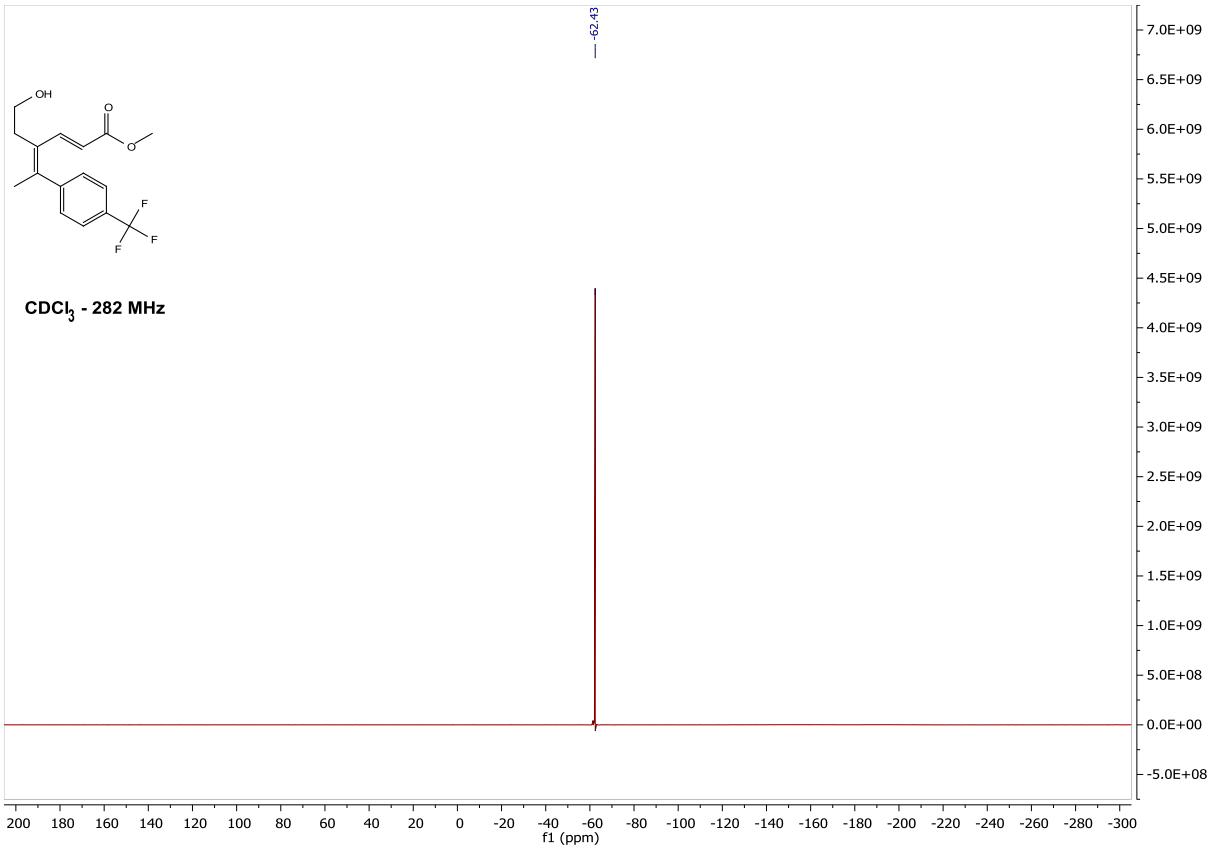

CDCl3 - 400 MHz
f1 (ppm)

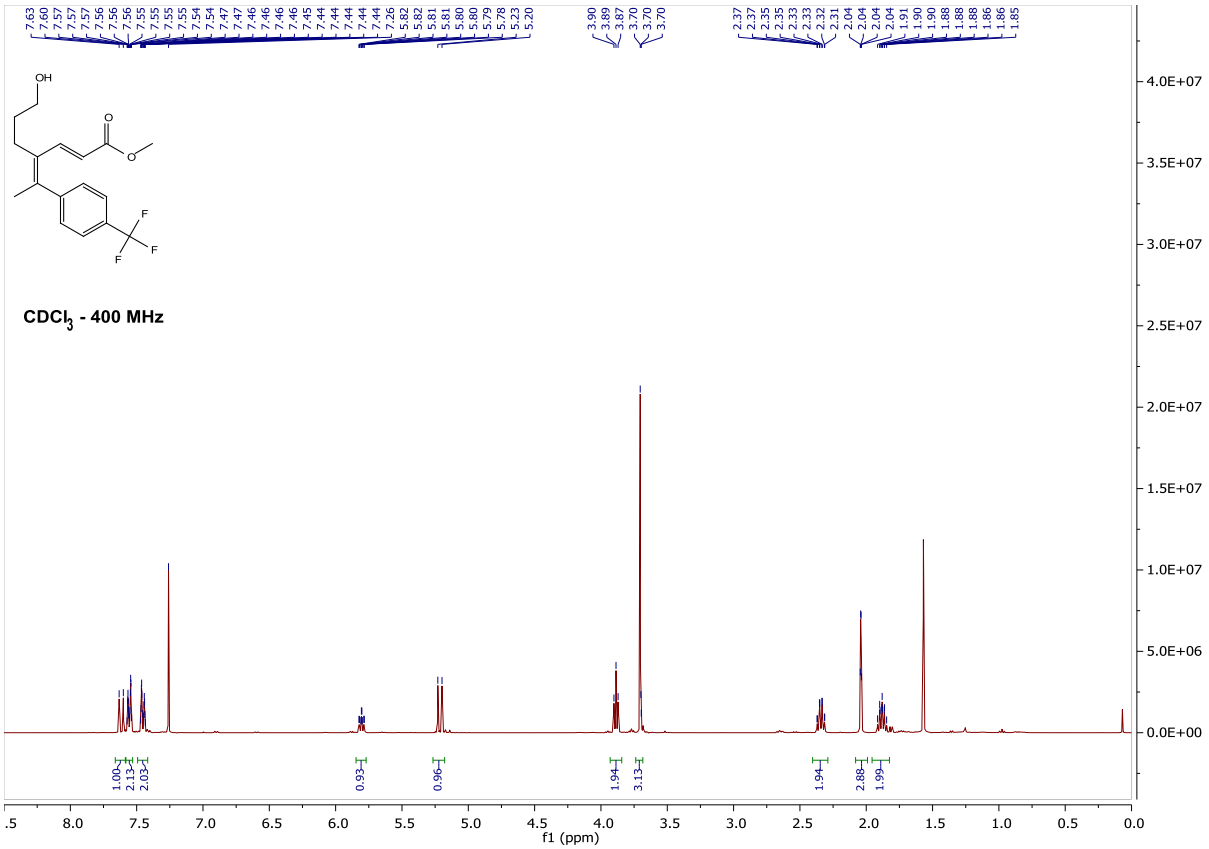

CDCl3 - 101 MHz
f1 (ppm)

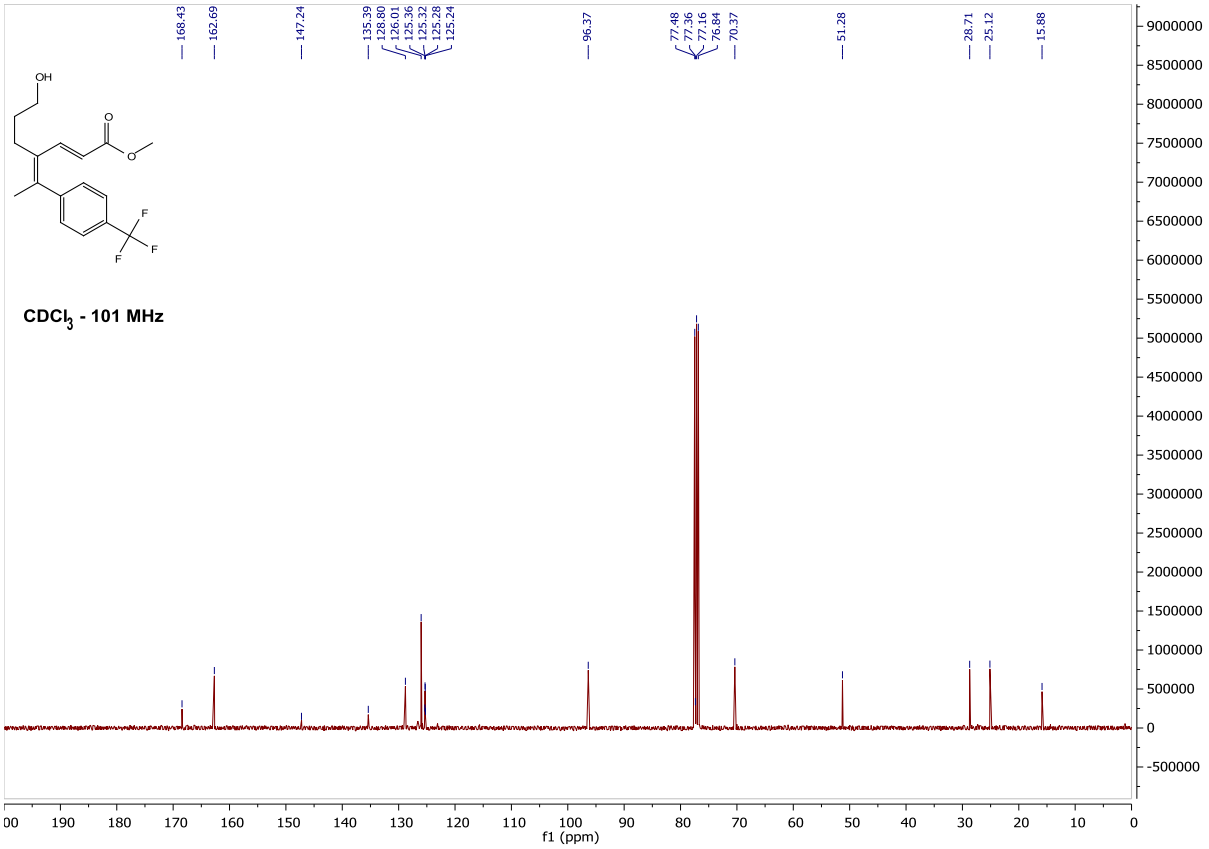

-62.60
CDCl3 - 282 MHz
2.6E+09
2.4E+09
2.2E+09
2.0E+09
1.8E+09
1.6E+09
1.4E+09
1.2E+09
1.0E+09
8.0E+08
6.0E+08
4.0E+08
2.0E+08
0.0E+00
-2.0E+08
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

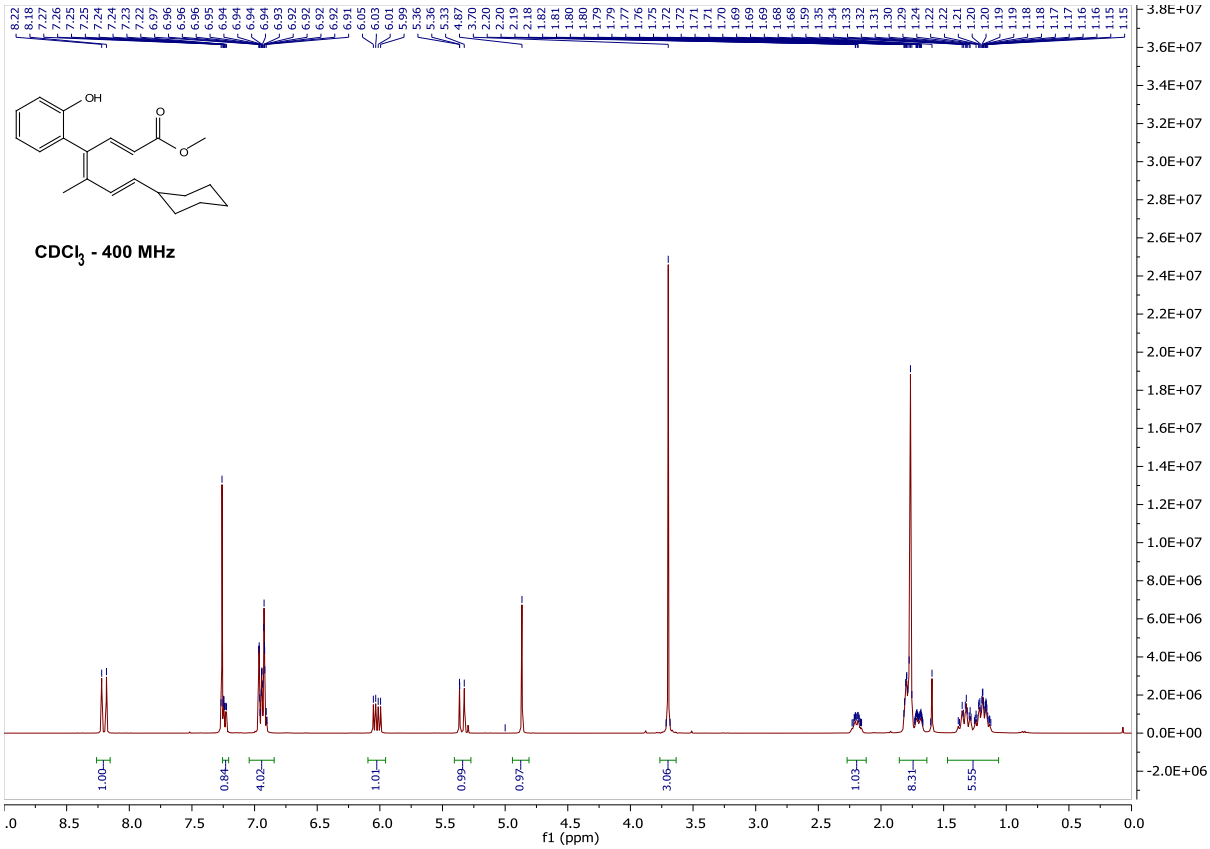

CDCl3 - 400 MHz
f1 (ppm)

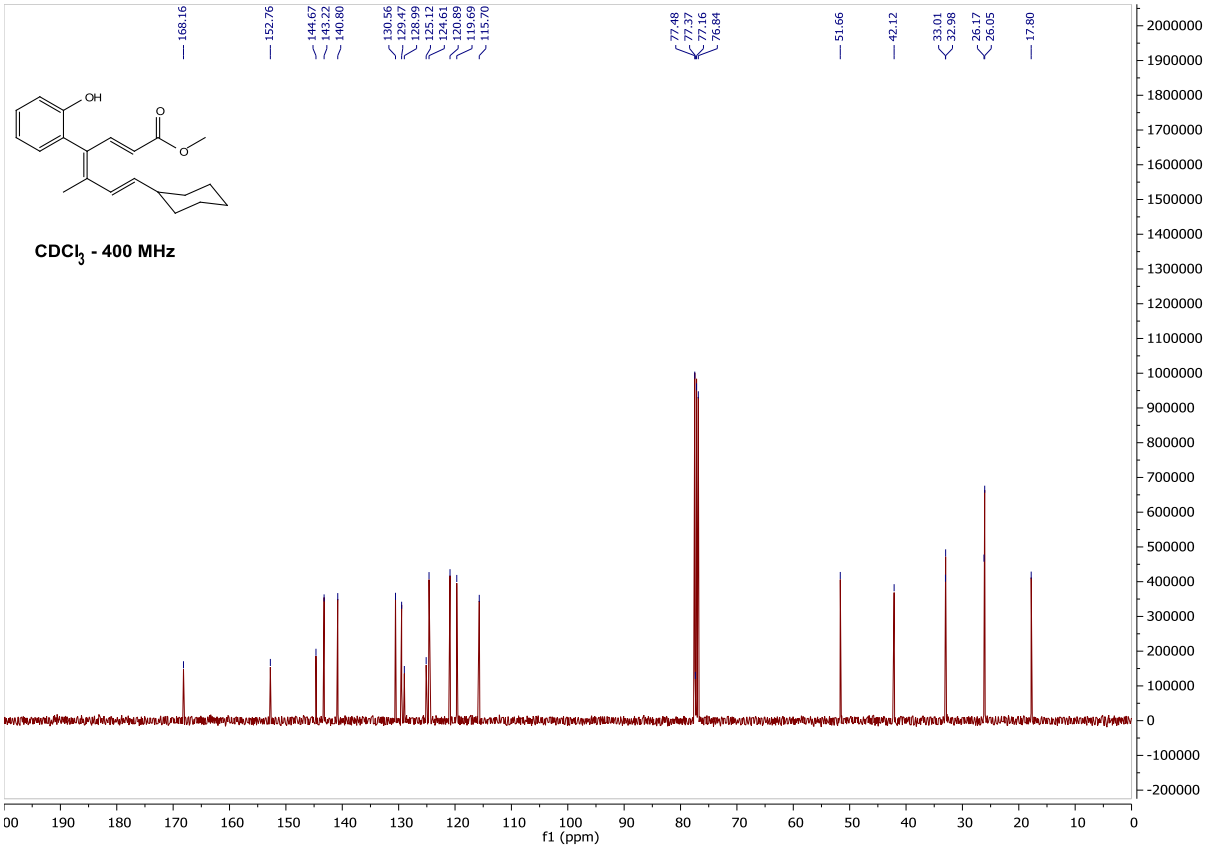

CDCl3 - 101 MHz
f1 (ppm)

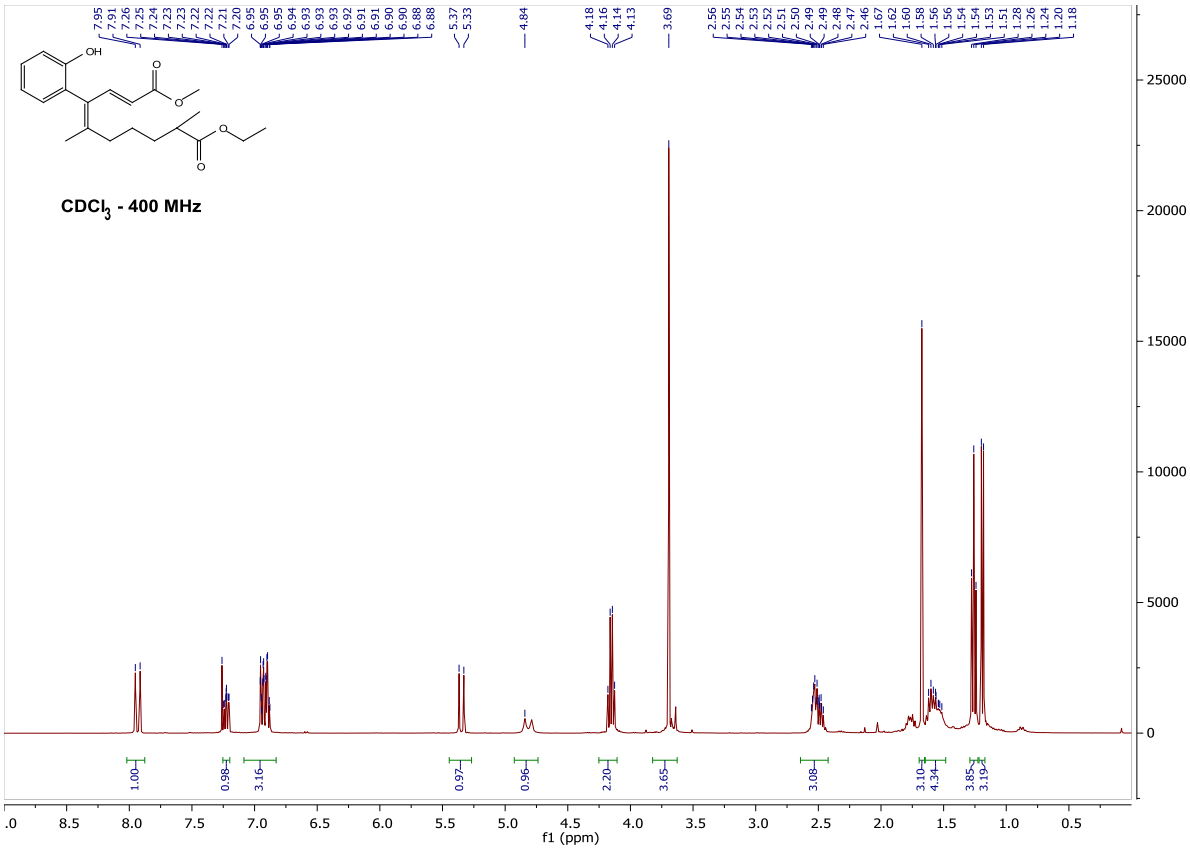

-62.43
OH
O
O
F
F
F
CDCl3 - 282 MHz
7.0E+09
6.5E+09
6.0E+09
5.5E+09
5.0E+09
4.5E+09
4.0E+09
3.5E+09
3.0E+09
2.5E+09
2.0E+09
1.5E+09
1.0E+09
5.0E+08
0.0E+00
-5.0E+08
200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

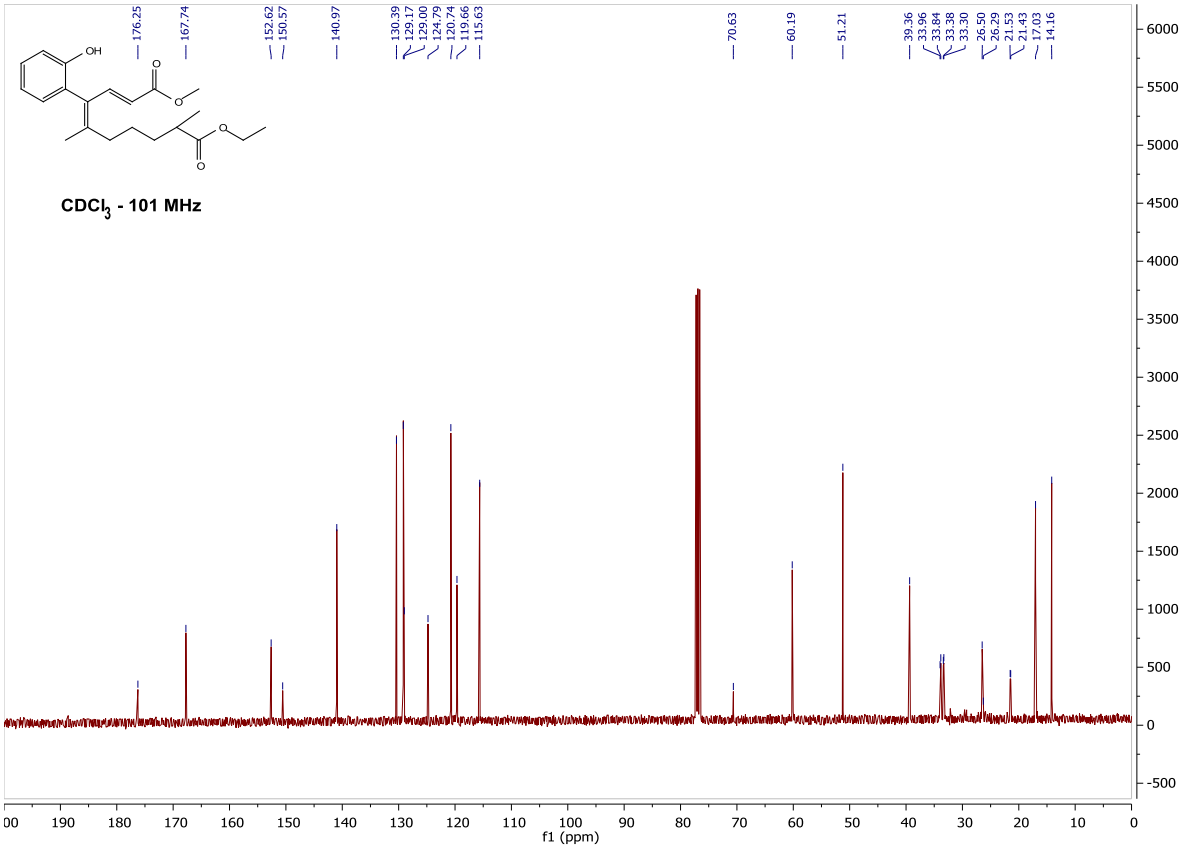

CDCl3 - 400 MHz
f1 (ppm)

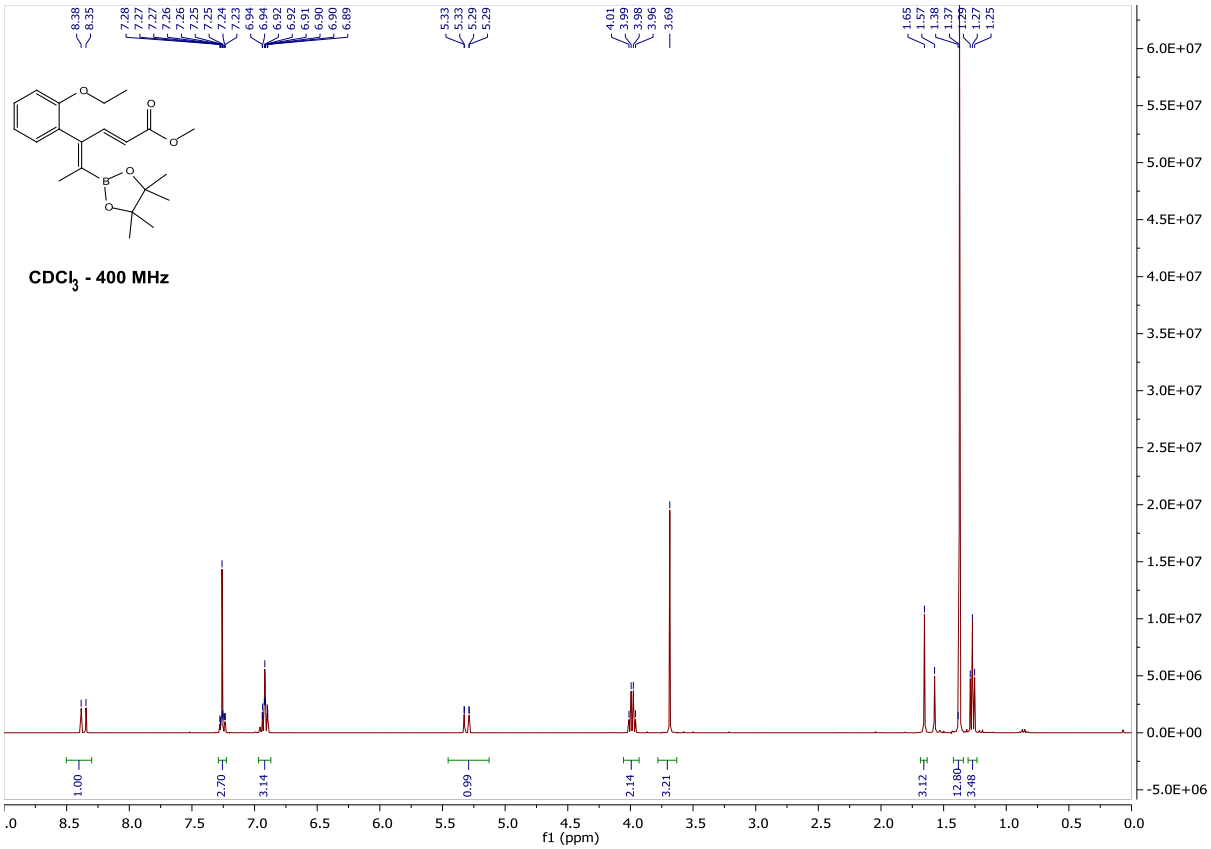

CDCl3 - 101 MHz
f1 (ppm)

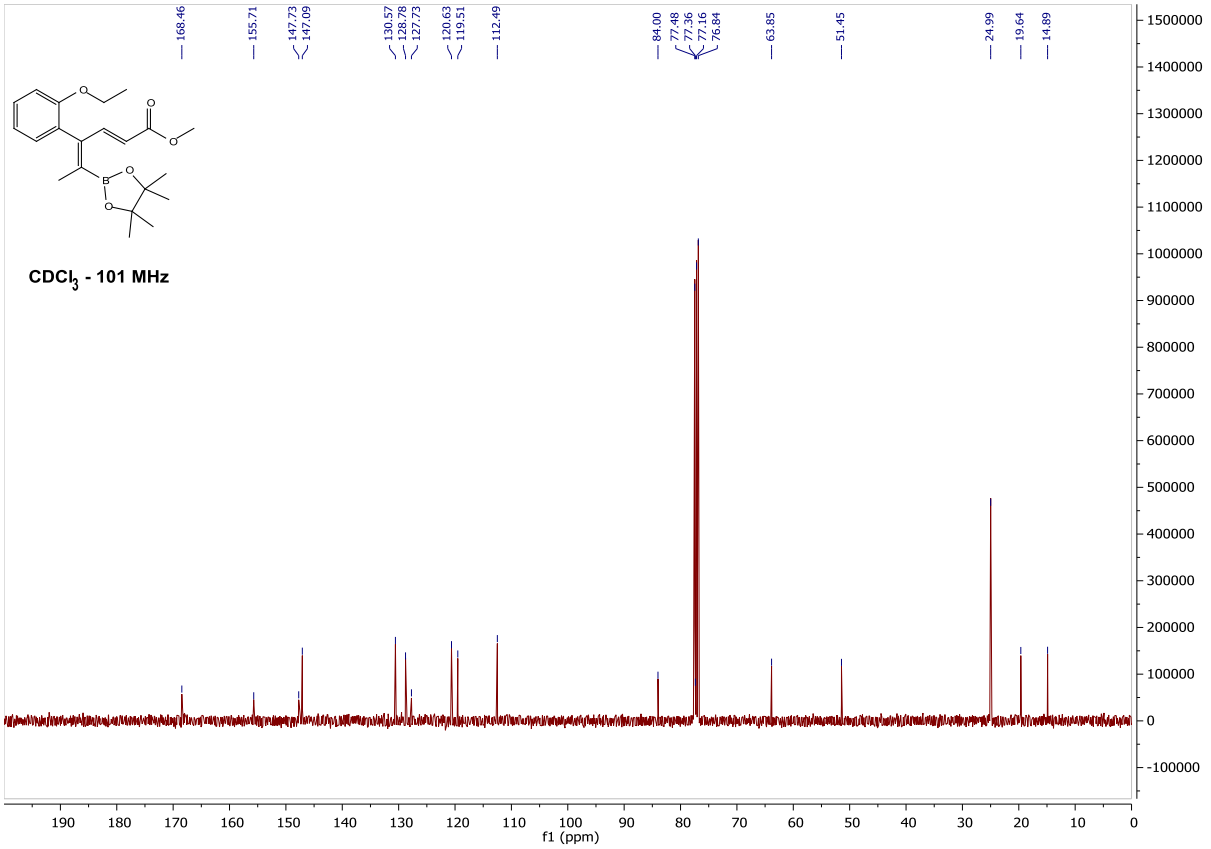

CDCl3 - 400 MHz
OH
O
O
f1 (ppm)


CDCl3 - 400 MHz
OH
O
O
f1 (ppm)


CDCl3 - 400 MHz
f1 (ppm)


CDCl3 - 101 MHz
f1 (ppm)


CDCl3 - 400 MHz
f1 (ppm)


CDCl3 - 101 MHz
f1 (ppm)