Electronic Supplementary Material (ESI) for Chemical Communications.

Aminium Cation-Radical Catalysed Selective Hydration of (*E*)-Aryl Enynes

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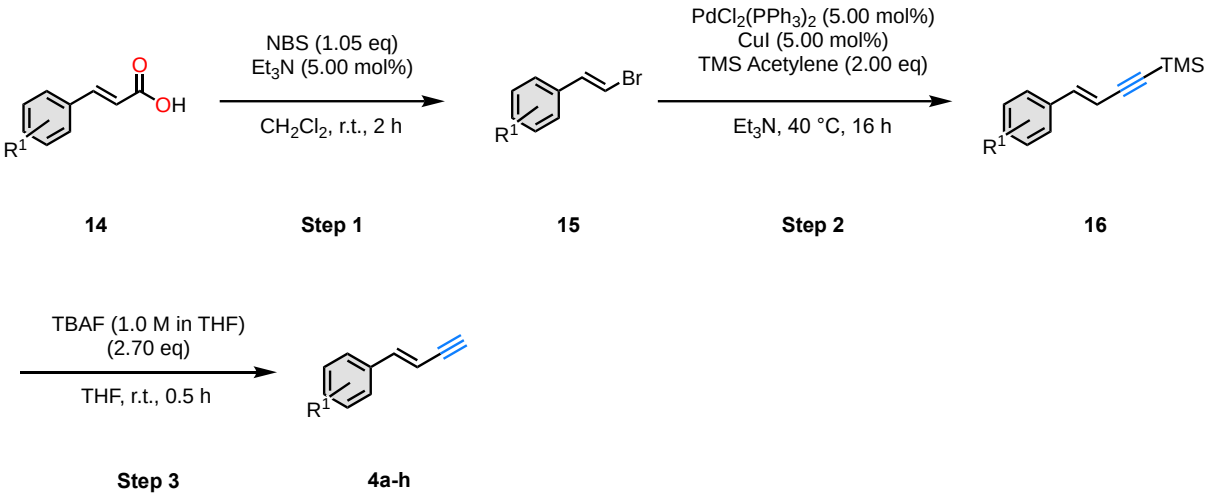
General Methods

Unless otherwise stated, all reactions were performed with reagent-grade solvents. All reagents and solvents were obtained from commercial sources and used without further purification. High purity acetone (max. 0.01%) was purchased from VWR Chemicals. Reactions were monitored using thin-layer chromatography (TLC) and visualized using UV light and stained using a basic $KMnO_4$ (potassium permanganate) solution. Flash column chromatography was performed using a Biotage® Isolera™ on Biotage® KP-Sil SNAP cartridges. Petrol refers to petroleum spirit (b.p. 40-60 °C). NMR spectra (^{1}H, ^{13}C, and ^{19}F) were recorded on Bruker Ascend™ 400 (400 MHz) and Ultrashield™ 500 PLUS (500 MHz) spectrometers as dilute solutions in the stipulated solvent. All chemical shifts (δ) are reported in parts per million (ppm) with ^{1}H and ^{13}C NMR referenced to solvent signals [^{1}H NMR: $CDCl_3$ (7.27); ^{13}C NMR: $CDCl_3$ (77.16)] Coupling constants (*J*) are reported in Hertz (Hz) and recorded after averaging. The multiplicity of the ^{1}H NMR signals are designated by one of the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, appt s=apparent singlet, appt d=apparent doublet, appt t=apparent triplet signal. Infra-red spectra were obtained using an Agilent Cary 660 FTIR spectrometer in ATR mode, with the peaks recorded as ν_{max}/cm^{-1}. HRMS were obtained using an Agilent 6530 accurate-massQ-TOF LC/MS in electrospray ionisation (ESI). Melting point data was collected using a Gallenkamp melting point apparatus. Single crystal X-ray diffraction data were collected on an XtaLAB Pro: Kappa single diffractometer.

General procedures for the synthesis of compounds 1, 4, 6 and 12

Synthesis of Enynes 1 and 4a-h



Step 1: The bromides **15** were synthesized using a catalytic Hunsdiecker reaction.[1]

A typical procedure: To a solution of the required cinnamic acid **14** (1.00 eq) in CH_2Cl_2 (3.00 mL/1.00 mmol) was added Et_3N (5.00 mol%) and stirred at room temperature for 5 minutes to which NBS (1.05 eq) was added and the solution stirred for a further 2 h. The solution was concentrated under reduced pressure, and the crude product was purified by flash column chromatography to obtain the analytically pure product.

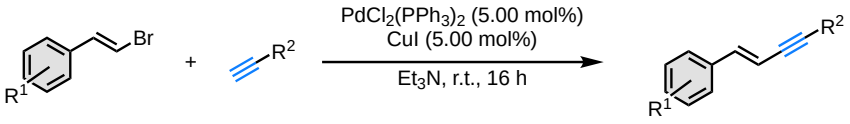
Step 2: TMS-protected enynes **16** were synthesized using a Sonogashira cross-coupling reaction.[2]

A typical procedure: To a solution of the required bromide **15** (1.00 eq) in Et_3N (5.00 mL/1.00 mmol) degassed with argon for 5 min was added $Pd(PPh_3)_2Cl_2$ (5.00 mol%) and CuI (5.00 mol%). The solution was stirred for 5 min at 40 °C followed by the addition of TMS acetylene (2.00 eq) and then stirred for a further 16 h at 40 °C. The resultant mixture was filtered through a pad of Celite®, concentrated under reduced pressure, and the crude product purified by flash column chromatography to obtain the analytically pure product.

Step 3: The enynes **1** and **4a-h** were synthesized by TMS deprotection using TBAF.[3]

A typical procedure: To a solution of the desired TMS protected enyne **16** (1.00 eq) in THF (10.0 mL/1.00 mmol) was added TBAF (1M in THF) (2.70 eq). The resultant solution was stirred for 30 min at room temperature and then concentrated under reduced pressure, dissolved in EtOAc, and washed with H_2O. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to obtain the analytically pure product.

Synthesis of Enynes 4i-q

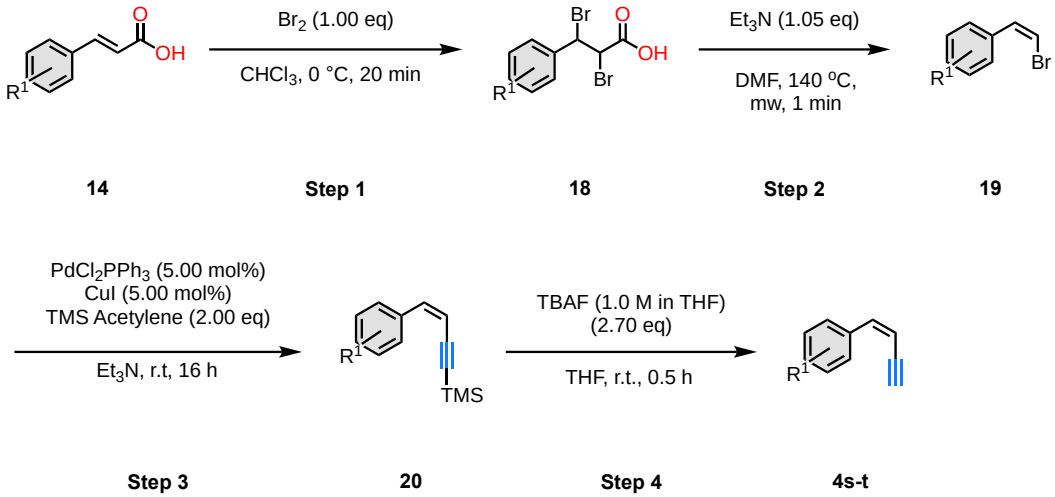


15 **17** **4i-q**

Enynes **4i-q** were synthesized by a Sonogashira cross-coupling reaction.[2]

A typical procedure: To a solution of the required bromide **15** (1.00 eq) in Et_3N (5.00 mL/1.00 mmol) degassed with argon for 5 min was added $PdCl_2(PPh_3)_2$ (5.00 mol%), and CuI (5.00 mol%). The solution was stirred at room temperature for 5 min, followed by the addition of the required alkyne **17** (1.10 eq) and stirred for a further 16 h. The resultant mixture was filtered through a pad of Celite®, concentrated under reduced pressure and the crude product purified by flash column chromatography to obtain the analytically pure product.

Synthesis of Enynes 4s-t



The bromides **19** were synthesized from the corresponding cinnamic acid **14**, *via* a two-step reaction procedure.

A typical procedure:[4]

Step 1: To a solution of the required cinnamic acid **14** (1.00 eq) in $CHCl_3$ (10.0 mL/1.00 mmol) at 0 ˚C was added bromine (1.00 eq) dropwise and the solution stirred for 20 mins. The resultant solution was stored in the refrigerator overnight, the precipitate filtered and washed twice with $CHCl_3$ to give the analytically pure product.

Step 2: To a solution of the required 2, 3-dibromo-3-phenylpropanoic acid derivative **18** (1.00 eq) in DMF (1.00 mL/1.00 mmol) was added Et_3N (1.05 eq). The reaction vial was sealed and irradiated with microwaves for 1 min at 140 ˚C. The reaction mixture was diluted with Et_2O and was washed with 5% LiCl in H_2O. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give the analytically pure product.

Step 3: The TMS-protected enynes **20** were synthesized by a Sonogashira cross-coupling reaction.[2]

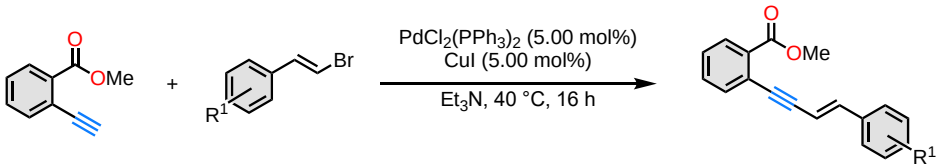
A typical procedure: To a solution of the required bromide **19** (1.00 eq) in Et_3N (5.00 mL/1.00 mmol) degassed with argon for 5 min was added $Pd(PPh_3)_2Cl_2$ (5.00 mol%) and CuI (5.00 mol%). The solution was stirred for 5 min at room temperature followed by the addition of TMS acetylene (2.00 eq) and

then stirred for a further 16 h. The resultant mixture was filtered through a pad of Celite®; the filtrate quenched with sat. $NH_4Cl_{(aq)}$ and extracted into Et_2O. The organic phase dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure, and the crude product purified by flash column chromatography to obtain the analytically pure product.

Step 4: Terminal enynes **4s-t** were synthesized by a TMS deprotection of enyne **20** using TBAF.[3]

A typical procedure: To a solution of the required TMS protected enyne **20** (1.00 eq) in THF (5.00 mL/1.00 mmol) was added TBAF (1M in THF) (2.70 eq). The resultant solution was stirred for 30 min at room temperature, then concentrated under reduced pressure, dissolved in EtOAc, and washed with H_2O. The organic phase over dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, and the crude product was purified by flash column chromatography to obtain the analytically pure product.

Synthesis of Enynes 12a-i



21 **15** **12a-i**

Enynes **12a-i** were synthesized by a Sonogashira cross-coupling reaction.[2]

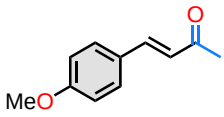
A typical procedure: To a solution of required bromide **15** (1.00 eq) in Et_3N (10.0 mL/1.00 mmol) degassed with argon for 5 min was added $PdCl_2(PPh_3)_2$ (5.00 mol%), and CuI (5.00 mol%). The solution was stirred at 40 °C for 5 min, followed by the addition of methyl 2-ethynylbenzoate **21** (1.00 eq) added and stirred for a further 16 h at 40 °C. The resultant mixture was filtered through a pad of Celite®, concentrated under reduced pressure, and the crude product purified by flash column chromatography to obtain the analytically pure product.

Synthesis and experimental data for compounds 2 and 5a-u

General procedure A

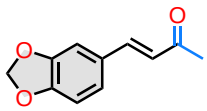
A solution of the required enyne (0.20 mmol, 1.00 eq) in acetone (1.00 mL) was degassed by purging with nitrogen for 5 min. A separate solution of acetone (1.00 mL) was degassed for 5 min, placed under nitrogen, heated to 40 °C and tris(4-bromophenyl)-ammoniumyl hexachloroantimonate (TBPA) (0.02 mmol, 0.10 eq) added. The enyne solution was added dropwise immediately after, and the solution stirred for 2 h at 40 °C. The reaction was quenched with sat. K_2CO_3 in methanol (1.00 mL), washed with brine (5.00 mL), and extracted into EtOAc (2 x 5.00 mL). The organic fractions were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure and the crude product purified by flash column chromatography.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-one (2)[6]



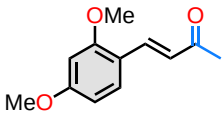
Following general procedure A, the title compound was isolated after purification by flash column chromatography (0-12% EtOAc in petroleum ether) as a white solid (26.0 mg, 74%). **m.p.** 75-77 °C (lit: 72-74 °C);[6] **IR** ν_{max} ($CDCl_3$)/cm^{-1}: 3011, 2841, 1664, 1602, 1512, 1250; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (m, 3H), 6.92 (m, 2H), 6.61 (d, *J* = 16.3 Hz, 1H), 3.85 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 198.7, 161.9, 143.6, 130.3, 127.3, 125.3, 114.7, 56.8, 27.7; **HRMS** (ESI) calculated for $C_{11}H_{13}O_2$ [M+H$^+$]: 177.0910, found 177.0909.

(*E*)-4-(Benzo[*d*][1,3]dioxol-5-yl)but-3-en-2-one (5a)[7]



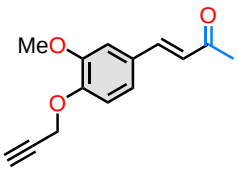
Following general procedure A, the title compound was isolated after purification by flash column chromatography (10% EtOAc in petroleum ether) as a yellow solid (29.0 mg, 76%). **m.p.** 107-108 °C (lit:110-113 °C);[7] **IR** υ_{max} (ATR)/cm^{-1}: 2901, 1660, 1624, 1501, 1237; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 16.2 Hz, 1H), 7.06 – 7.00 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 16.2 Hz, 1H), 6.01 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.3, 150.0, 148.6, 143.3, 129.0, 125.5, 124.9, 108.8, 106.7, 101.8, 27.7; **HRMS** (ESI) calculated for $C_{11}H_{14}O_2$ [M+H$^+$]: 191.0703, found 191.0706.

(*E*)-4-(2,4-dimethoxyphenyl)but-3-en-2-one (5b)[8]



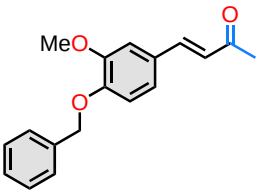
Following general procedure A, the title compound was isolated after purification by flash column chromatography (20% EtOAc in petroleum ether) as a colourless solid (31.0 mg, 76%). **m.p.** 77-78 °C (lit: 58.5-59.5 °C);[8] **IR** υ_{max} (ATR)/cm^{-1}: 2949, 2923, 2843, 1653, 1571, 1250; **^{1}H NMR** (400 MHz, $CDCl_3$) 7.81 (d, *J* = 16.4 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 6.68 (d, *J* = 16.4 Hz, 1H), 6.52 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 162.9, 159.6, 138.6, 129.7, 125.3, 116.2, 105.3, 98.2, 55.3, 55.3, 26.9; **HRMS** (ESI$^+$): calculated for $C_{12}H_{14}O_3$ [M+H$^+$]: 207.1016, found 207.1013.

(*E*)-4-(3-Methoxy-4-(prop-2-yn-1-yloxy)phenyl)but-3-en-2-one (5c)[9]



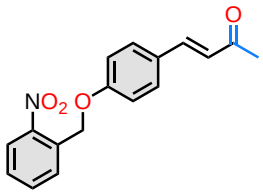
Following general procedure A, the title compound was isolated after purification by flash column chromatography (0-25% EtOAc in petroleum ether) as a brown solid (36.0 mg, 78%) **m.p.** 104-106 °C (lit: 110-111 °C);[9] **IR** υ_{max} (ATR)/cm^{-1}: 3256, 2616, 2128, 1671, 1512; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 16.2 Hz, 1H), 7.13 (appt dd, *J* = 8.3, 1.9 Hz, 1H), 7.09 (appt d, *J* = 1.8 Hz, 1H), 7.02 (appt d, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 16.2 Hz, 1H), 4.81 (d, *J* = 2.4 Hz, 2H), 3.92 (s, 3H), 2.54 (t, *J* = 2.4 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.5, 150.0, 149.1, 143.4, 128.6, 125.9, 122.6, 113.8, 110.4, 78.1, 76.4, 56.8, 56.1, 27.6; **HRMS** (ESI$^+$): calculated for $C_{14}H_{14}O_3Na$ [M+Na$^+$]: 253.0835, found 253.0831.

(*E*)-4-(4-(Benzyloxy)-3-methoxyphenyl)but-3-en-2-one (5d)



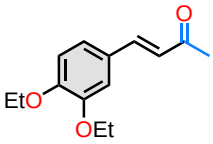
Following general procedure A, the title compound was isolated after purification by flash column chromatography (0-15% EtOAc in petroleum ether) as a brown solid (42.0 mg, 75%). **m.p.** 90-91 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2999, 2617, 1683, 1592, 1510; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 7.11 (appt d, *J* = 2.0 Hz, 1H), 7.08 (appt dd, *J* = 8.4, 2.0 Hz, 1H), 6.91 (appt d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 16.2 Hz, 1H), 5.20 (s, 2H), 3.93 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 150.7, 150.0, 143.6, 136.7, 128.8, 128.2, 127.9, 127.4, 125.5, 122.9, 113.6, 110.4, 71.0, 56.2, 27.5; **HRMS** (ESI$^+$): calculated for $C_{18}H_{18}O_3Na$ [M+Na$^+$]: calculated for 305.1148, found 305.1147.

(*E*)-4-(4-((2-nitrobenzyl)oxy)phenyl)but-3-en-2-one (5e)



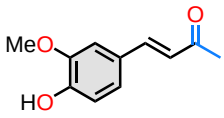
Following general procedure A, the title compound was isolated after purification by flash column chromatography (0-15% EtOAc in petroleum ether) as a brown solid (49.0 mg, 82%). **m.p.** 150 - 153 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2925, 2853, 1661, 1601, 1501; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 – 8.13 (m, 1H), 7.91 – 7.82 (m, 1H), 7.73 – 7.64 (m, 1H), 7.55 – 7.42 (m, 4H), 7.06 – 6.94 (m, 2H), 6.62 (d, *J* = 16.2 Hz, 1H), 5.53 (s, 2H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 160.2, 147.1, 143.0, 134.2, 133.4, 130.2, 128.7, 128.6, 128.1, 125.7, 125.3, 115.5, 67.0, 27.6; HRMS (ESI$^+$): calculated for $C_{17}H_{15}NO_4Na$ [M+Na$^+$]: calculated for 320.0893, found 320.0887.

(*E*)-4-(3,4-diethoxyphenyl)but-3-en-2-one (5f)[10]



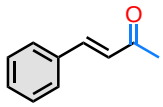
Following general procedure A, the title compound was isolated after purification by flash column chromatography (0-30% EtOAc in petroleum ether) as a brown solid (38.0 mg, 81%). **m.p.** 89-90 °C (lit: 86 °C)[10]; **IR** ν_{max} (ATR)/cm^{-1}: 2887, 1835, 1642, 1592, 1514; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 16.2 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.87 (appt d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 16.2 Hz, 1H), 4.17 – 4.08 (m, 4H), 2.36 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 151.4, 149.0, 143.8, 127.3, 125.2, 123.1, 112.8, 112.0, 64.8, 64.6, 27.5, 14.9, 14.8; **HRMS** (ESI$^+$): calculated for $C_{14}H_{18}O_3Na$ [M+Na$^+$]: 257.1148, found 257.1147.

(*E*)-4-(4-Hydroxy-3-methoxyphenyl)but-3-en-2-one (5g)[11]



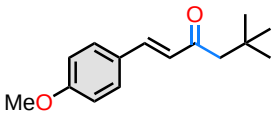
Following general procedure A, the title compound was isolated after purification by flash column chromatography (0-12% EtOAc in petroleum ether) as a brown solid (30.0 mg, 79%). **m.p.** 110-113 °C (lit: 118-120 °C);[11] **IR** ν_{max} (ATR)/cm^{-1}: 3288, 2924, 2853, 1637, 1582, 1517; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 16.2 Hz, 1H), 7.09 (appt dd, *J* = 8.2, 1.9 Hz, 1H), 7.06 (appt d, *J* = 1.9 Hz, 1H), 6.93 (appt d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 16.2 Hz, 1H), 3.94 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, 148.4, 147.0, 143.9, 127.1, 125.2, 123.7, 115.0, 109.4, 56.1, 27.5; **HRMS** (ESI$^+$): calculated for $C_{11}H_{12}O_3Na$ [M+Na$^+$]: 215.0679, found 215.0670.

(*E*)-4-Phenylbut-3-en-2-one (5h)[12]



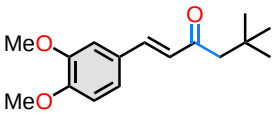
Following general procedure A, the title compound was isolated after purification by flash column chromatography (0-12% EtOAc in petroleum ether) as a colourless solid (14.0 mg, 48%). **m.p.** 44-47 °C (lit: 40-42 °C);[12] **IR** υ_{max} (ATR)/cm^{-1}: 3011, 1667, 1626, 1609, 1577; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (m, 3H), 7.42 (m, 3H), 6.73 (d, *J* = 16.3 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.6, 143.8, 134.7, 130.8, 129.3, 128.7, 127.6, 24.0; **HRMS** (ESI$^+$): calculated for $C_{10}H_{11}O$ [M+H$^+$]: 147.0804, found 147.0798.

(*E*)-1-(4-Methoxyphenyl)-5,5-dimethylhex-1-en-3-one (5i)



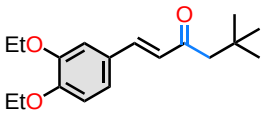
Following a modified general procedure A (heated to 50 °C), the title compound was isolated after purification by flash column chromatography (10% EtOAc in petroleum ether) as a colourless solid (41 mg, 88%). **m.p.** 58-60 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2956, 2871, 2038, 1685, 1597; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 3H), 6.91 (appt d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 2.52 (s, 2H), 1.06 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 161.6, 142.0, 130.1, 127.5, 125.7, 114.5, 55.5, 53.9, 31.8, 30.2; **HRMS** (ESI$^+$): calculated for $C_{15}H_{20}O_2Na$ [M+Na$^+$]: 255.1356, found 255.1354.

(*E*)-1-(3,4-Dimethoxyphenyl)-5,5-dimethylhex-1-en-3-one (5j)



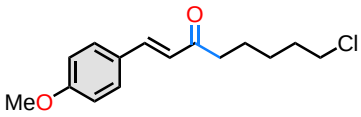
Following a modified general procedure A (heated to 50 °C), the title compound was isolated after purification by flash column chromatography (0-15% EtOAc in petroleum ether) as a yellow solid (39.0 mg, 75%). **m.p**. 48-50 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2953, 2866, 1635, 1596, 1510; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 16.0 Hz, 1H), 7.13 (appt dd, *J* = 8.3, 2.0 Hz, 1H), 7.07 (appt d, *J* = 2.0 Hz, 1H), 6.87 (appt d, *J* = 8.3 Hz, 1H), 6.62 (d, 1H), 3.92 (s, 3H), 3.91 (s, 3H) 2.53 (s, 2H), 1.07 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.3, 151.4, 149.4, 142.4, 127.8, 126.1, 123.1, 111.3, 110.0, 56.1, 56.1, 53.6, 31.8, 30.2; **HRMS** (ESI$^+$): calculated for $C_{16}H_{23}O_3$ [M+H$^+$]: 263.1642, found 263.1643.

(*E*)-1-(3,4-diethoxyphenyl)-5,5-dimethylhex-1-en-3-one (5k)



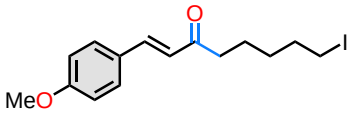
Following a modified general procedure A (heated to 50 °C), the title compound was isolated after purification by flash column chromatography (10-20% EtOAc in petroleum ether) as a yellow solid (48.0 mg, 83%). **m.p**. 55-57 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2955, 2870, 1678, 1593, 1510; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 16.0 Hz, 1H), 7.10 (appt dd, *J* = 8.3, 2.0 Hz, 1H), 7.07 (appt d, *J* = 2.0 Hz, 1H), 6.86 (appt d, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 4.16 – 4.09 (appt qd, *J* = 7.0, 1.9 Hz, 4H), 2.52 (s, 2H), 1.46 (appt td, *J* = 7.0, 1.4 Hz, 6H), 1.06 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.3, 151.3, 149.0, 142.5, 127.6, 125.9, 123.0, 112.9, 112.3, 64.8, 64.6, 53.6, 31.7, 30.2, 14.9, 14.8; **HRMS** (ESI$^+$): calculated for $C_{18}H_{26}O_3Na$ [M+Na$^+$]: 313.1774, found 313.1769.

***(E)*-8-Chloro-1-(4-methoxyphenyl)oct-1-en-3-one (5i)**



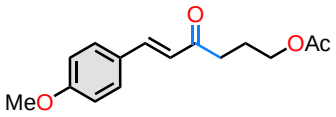
Following a modified general procedure A (performed on a 0.66 mmol scale at 50 °C for 3 h), the title compound was isolated after purification by flash column chromatography (20% EtOAc in petroleum ether) as a pale yellow oil (64.0 mg, 69%). **IR** ν_{max} (ATR)/cm^{-1}: 2935, 1604, 1510, 1247; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 3H), 6.99 – 6.86 (m, 2H), 6.63 (d, *J* = 16.1 Hz, 1H), 3.84 (s, 3H), 3.55 (t, *J* = 6.8 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 1.82 (dq, *J* = 8.1, 6.8 Hz, 2H), 1.76 – 1.66 (m, 2H), 1.56 – 1.46 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.0, 161.5, 142.2, 129.9, 127.1, 123.9, 114.4, 55.4, 44.8, 40.4, 32.4, 26.6, 23.5; **HRMS** (ESI$^+$): calculated for $C_{15}H_{20}ClO_2$ [M+H$^+$] 267.1146, found 267.1141.

***(E)*-8-Iodo-1-(4-methoxyphenyl)oct-1-en-3-one (5m)**



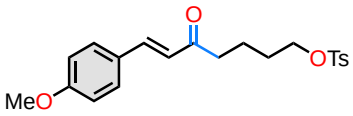
Following a modified general procedure A (performed on a 0.29 mmol scale at 50 °C for 3 h), the title compound was isolated after purification by flash column chromatography (20% EtOAc in petroleum ether) as a pale yellow oil (63.0 mg, 60%). **IR** ν_{max} (ATR)/cm^{-1}: 2930, 1649, 1604, 1250; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 3H), 6.91 (appt d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 16.1 Hz, 1H), 3.85 (s, 3H), 3.21 (t, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.78 – 1.65 (m, 2H), 1.54 – 1.43 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.0, 161.6, 142, 130.0, 127.1, 124.0, 114.4, 55.4, 40.4, 33.3, 30.2, 23.2, 6.8; **HRMS** (ESI^+) calculated for $C_{15}H_{20}IO_2$ [M+H^+] 359.0503, found 359.0497.

***(E)*-6-(4-Methoxyphenyl)-4-oxohex-5-en-1-yl acetate (5n)**



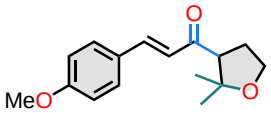
Following general procedure A (performed on a 0.41 mmol scale at 50 °C for 3 h), the title compound was isolated after purification by flash column chromatography (20% EtOAc in petroleum ether) as a yellow oil (33.0 mg, 31%). **IR** ν_{max} (ATR)/cm^{-1}: 2966, 1726, 1683, 1599, 1513, 1253; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 3H), 6.92 (appt d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 16.1 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.08 – 1.99 (m, 5H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 171.0, 161.6, 142.4, 130.0, 127.0, 123.8, 114.4, 63.8, 55.4, 36.9, 23.2, 20.9; **HRMS** (ESI^+) calculated for $C_{15}H_{19}O_4$ [M+H^+] 263.1278, found 263.1280.

(*E*)-7-(4-Methoxyphenyl)-5-oxohept-6-en-1-yl 4-methylbenzenesulfonate (5o)



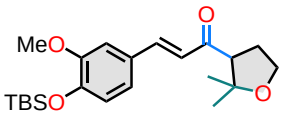
Following general procedure A (performed at 50 °C for 3 h), the title compound was isolated after purification by flash column chromatography (0-35% EtOAc in petroleum ether) as a yellow oil (48.0 mg, 62%). **IR** ν_{max} (ATR)/cm^{-1}: 2925, 2854, 1923, 1680, 1597; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (appt d, *J* = 8.3 Hz, 2H), 7.48 (m, 3H), 7.33 (appt d, *J* = 7.9 Hz, 2H), 4.09 – 4.02 (m, 2H), 3.84 (s, 3H), 2.65 – 2.57 (m, 2H), 2.43 (s, 3H), 1.75 – 1.67 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.6, 161.8, 144.9, 142.6, 130.1, 130.0, 128.0, 127.2, 123.9, 114.6, 70.3, 55.5, 39.6, 28.4, 21.7, 20.3; **HRMS** (ESI$^+$) calculated for $C_{21}H_{24}O_5SNa$ [M+Na$^+$] 411.1237, found 411.1236.

(*E*)-1-(2,2-Dimethyltetrahydrofuran-3-yl)-3-(4-methoxyphenyl)prop-2-en-1-one (5p)



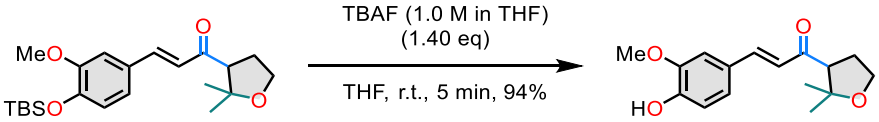
Following general procedure A (performed on a 0.62 mmol scale at 45 °C for 3 h), the title compound was isolated after purification by flash column chromatography (20-30% EtOAc in petroleum ether) as a pale yellow oil (69.0 mg, 43%). **IR** ν_{max} (ATR)/cm^{-1}: 2973, 1593, 1510, 1171; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.9 Hz, 1H), 7.56 – 7.51 (m, 2H), 6.96 – 6.90 (m, 2H), 6.71 (d, *J* = 15.9 Hz, 1H), 4.02 (ddd, *J* = 8.6, 8.6, 4.5 Hz, 1H), 3.90 (ddd, *J* = 8.6, 7.9, 7.6 Hz, 1H), 3.85 (s, 3H), 3.24 (dd, *J* = 8.5, 8.2 Hz, 1H), 2.55 (dddd, *J* = 12.7, 8.6, 8.5, 7.6 Hz, 1H), 2.10 (dddd, *J* = 12.7, 8.2, 7.9, 4.5 Hz, 1H), 1.48 (s, 3H), 1.09 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, 161.9, 143.0, 130.3, 127.2, 123.7, 114.6, 82.1, 65.7, 59.0, 55.5, 29.1, 29.0, 23.7; **HRMS** (ESI$^+$) calculated for $C_{16}H_{20}NaO_3$ [M+Na$^+$] 283.1305, found 283.1302.

(*E*)-3-(4-((*tert*-Butyldimethylsilyl)oxy)-3-methoxyphenyl)-1-(2,2-dimethyltetrahydrofuran-3-yl)prop-2-en-1-one (5q)



Following general procedure A (performed on a 0.94 mmol scale at 50 °C for 3 h), the title compound was isolated after purification by flash column chromatography (10-30% EtOAc in petroleum ether) as a pale yellow oil (107 mg, 29%). **IR** ν_{max} (ATR)/cm^{-1} 2929, 1681, 1591, 1507, 1283; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 15.9 Hz, 1H), 7.09 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 4.03 (ddd, *J* = 8.6, 8.6, 4.6 Hz, 1H), 3.95 – 3.89 (m, 1H), 3.86 (s, 3H), 3.27 (dd, *J* = 8.5, 8.2 Hz, 1H), 2.55 (dddd, *J* = 12.7, 8.6, 8.5, 7.7 Hz, 1H), 2.10 (dddd, *J* = 12.7, 8.2, 8.0, 4.6 Hz, 1H), 1.49 (s, 3H), 1.10 (s, 3H), 1.01 (s, 9H), 0.19 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.7, 151.4, 148.2, 143.5, 128.4, 124.1, 122.8, 121.4, 111.5, 82.1, 65.7, 58.7, 55.7, 29.1, 29.1, 25.8, 23.8, 18.6, −4.5; **HRMS** (ESI$^+$) calculated for $C_{22}H_{35}O_4Si$ [M+H$^+$] 391.2299, found 391.2300.

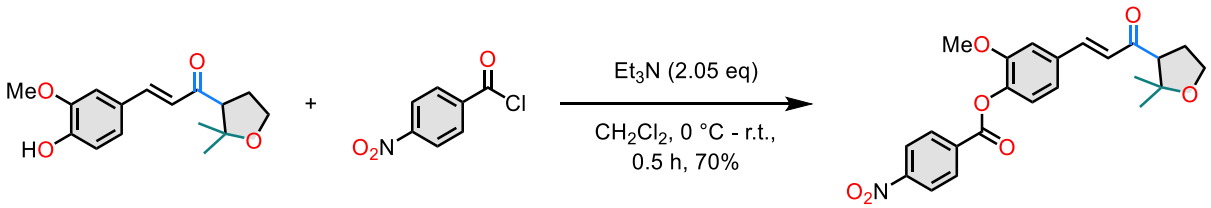
(*E*)-1-(2,2-Dimethyltetrahydrofuran-3-yl)-3-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-one



To a solution of (*E*)-tert-butyl(4-(2-(6,6-dimethyl-2,7-dioxabicyclo[3.2.0]heptan-1-yl)vinyl)-2-methoxyphenoxy)dimethylsilane (27.0 mg , 0.0700 mmol) in THF (1.00 mL) at room temperature was added TBAF (1M in THF, 104 µL, 0.100 mmol) and the resultant solution stirred for 5 min. The reaction mixture was diluted with EtOAc (25.0 mL) and washed with water (25.0 mL). The aqueous phase was washed with EtOAc (25.0 mL), the organic phases combined, dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure and the crude product purified through a short silica pad (100% EtOAc) to obtain the analytically pure product as a pale yellow oil (18.0 mg, 94%). **IR** ν_{max} (ATR)/cm^{-1}: 3328, 2970, 1582, 1512, 1272; **^{1}H NMR** ($CDCl_3$, 400 MHz): 7.57 (d, *J* = 15.8 Hz, 1H), 7.16 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.08 (d, *J* = 1.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 15.8 Hz, 1H), 5.98 (s, 1H), 4.05

(ddd, *J* = 8.5, 8.3, 4.6 Hz, 1H), 3.97 (s, 3H), 3.92 (ddd, *J* = 8.3, 8.1, 8.0 Hz, 1H), 3.28 (dd, *J* = 8.3, 8.2 Hz, 1H), 2.57 (dddd, *J* = 12.7, 8.5, 8.3, 8.1 Hz, 1H), 2.18 – 2.06 (dddd, *J* = 12.7, 8.2, 8.0, 4.6, 1H), 1.50 (s, 3H), 1.12 (s, 3H); **^{13}C NMR** ($CDCl_3$, 101 MHz): 198.5, 148.4, 146.8, 143.4, 126.9, 123.6, 123.4, 114.9, 109.8, 82.0, 65.5, 58.6, 56.0, 28.9, 28.9, 23.6; **HRMS** (ESI^+) calculated for $C_{16}H_{21}O_4$ [M+H^+] 277.1434, found 277.1435.

(*E*)-4-(3-(2,2-Dimethyltetrahydrofuran-3-yl)-3-oxoprop-1-en-1-yl)-2-methoxyphenyl 4-nitrobenzoate (5r)



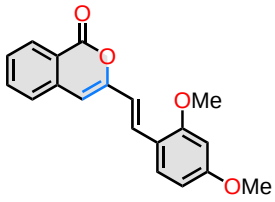
To a solution of (*E*)-4-(2-(6,6-dimethyl-2,7-dioxabicyclo[3.2.0]heptan-1-yl)vinyl)-2-methoxyphenol (54.0 mg, 0.190 mmol) in CH_2Cl_2 (2.50 mL) at 0 °C was added triethylamine (54.0 µL, 0.390 mmol), followed by a solution of 4-nitrobenzoyl chloride (36.0 mg, 0.190 mmol) in CH_2Cl_2 (2.50 mL). The resultant solution was stirred at 0 °C for 5 min, then 25 min at room temperature. The reaction was then diluted with CH_2Cl_2 (50.0 mL) and washed with water (50.0 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure and the crude product purified by flash column chromatography (50% EtOAc in petroleum ether) to obtain the analytically pure product as a colourless solid (58.0 mg, 70%). m.p. 132 °C. **IR** ν_{max} (ATR)/cm^{-1}: 2973, 1744, 1607, 1254; **^{1}H NMR** ($CDCl_3$, 400 MHz): 8.42 – 8.35 (m, 4H), 7.61 (d, *J* = 15.9 Hz, 1H), 7.26 – 7.18 (m, 3H), 6.80 (d, *J* = 15.9 Hz, 1H), 4.05 (ddd, *J* = 8.7, 8.4, 4.5 Hz, 1H), 3.93 (ddd, *J* = 8.7, 7.8, 7.9 Hz, 1H), 3.89 (s, 3H), 3.28 (dd, *J* = 8.2, 8.0 Hz, 1H), 2.58 (dddd, *J* = 12.6, 8.2, 8.4, 7.9 Hz, 1H), 2.14 (dddd, *J* = 12.6, 8.0, 7.8, 4.5 Hz, 1H), 1.50 (s, 3H), 1.12 (s, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz): 198.5, 162.6, 151.4, 151.0, 142.2, 141.4, 134.5, 133.9, 131.5, 126.3, 123.7, 123.2, 121.4, 111.9, 82.0, 65.5, 58.9, 56.0, 28.9, 28.8, 23.6; **HRMS** (ESI^+) calculated for $C_{23}H_{23}NNaO_7$ [M+Na^+] 448.1367, found 448.1371.

Synthesis and experimental data for compounds 13a-i

General procedure B

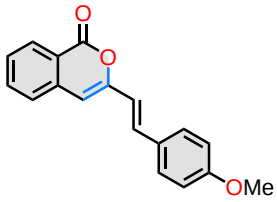
A solution of the required 1,4-diarylenyne (0.20 mmol, 1.00 eq) in acetone (1.50 mL) was degassed with nitrogen for 5 min followed by the addition of TBPA (0.02 mmol, 0.10 eq.), and the resultant solution stirred for 1 h at 50 °C. The reaction was quenched by the addition of sat. K_2CO_3 in methanol (1.00 mL), diluted with brine (10 mL) and extracted between EtOAc (2 x 10.0mL). The organic phases were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure and the crude product purified by flash column chromatography.

(*E*)-3-(2,4-Dimethoxystyryl)-1*H*-isochromen-1-one (13a)



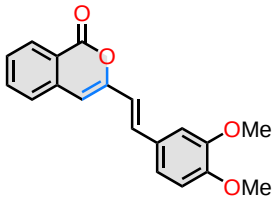
Following general procedure B, the title compound was isolated after purification by flash column chromatography (10-30% EtOAc in petroleum ether) as a yellow solid (51.0 mg, 82%). **m.p.** 129-131 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2924, 2854, 1729, 1601, 1558; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (appt d, *J* = 7.9 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.46 – 7.40 (m, 2H), 7.39 (appt d, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 16.1 Hz, 1H), 6.52 (appt dd, *J* = 8.5, 2.4 Hz, 1H), 6.47 (appt d, *J* = 2.4 Hz, 1H), 6.40 (s, 1H), 3.90 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5, 161.7, 159.3, 153.9, 138.2, 134.8, 130.0, 129.3, 128.6, 127.7, 125.7, 120.8, 118.2, 105.3, 104.6, 98.7, 55.6, 55.6; **HRMS** (ESI) calculated for $C_{19}H_{16}O_4$ [M+H$^+$]: 309.1121, found 309.1122.

(*E*)-3-(4-Methoxystyryl)-1*H*-isochromen-1-one (13b)[13]



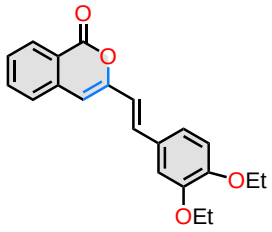
Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-10% EtOAc in petroleum ether) as a yellow solid (41.0 mg, 73%). **m.p.** 58-60 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2926, 2853, 2191, 1728, 1600; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (m, 1H), 7.71 – 7.63 (m, 1H), 7.50 – 7.38 (m, 5H), 6.94 – 6.88 (m, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.41 (s, 1H), 3.84 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 160.5, 153.2, 138.0, 134.9, 132.8, 130.0, 128.8, 128.7, 127.9, 125.8, 120.9, 117.4, 114.5, 105.0, 55.5; **HRMS** (ESI$^+$): calculated for $C_{18}H_{15}O_2Na$ [M+Na$^+$]: 301.0835, found 301.0836.

(*E*)-3-(3,4-Dimethoxystyryl)-1*H*-isochromen-1-one (13c)



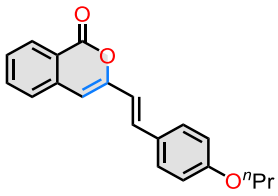
Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-12% EtOAc in petroleum ether) as a yellow solid (54.0 mg, 88%). **m.p.** 140-141 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2928, 2834, 1721, 1650, 1513; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (appt d, *J* = 8.0 Hz, 1H), 7.67 (appt td, *J* = 7.8, 1.3 Hz, 1H), 7.48 – 7.36 (m, 3H), 7.10 (appt dd, *J* = 8.4, 1.8 Hz, 1H), 7.05 (appt d, *J* = 1.9 Hz, 1H), 6.87 (appt d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.42 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 153.0, 150.1, 149.3, 137.9, 134.9, 133.0, 129.9, 129.0, 128.0, 125.8, 121.1, 120.8, 117.6, 111.4, 109.4, 105.1, 56.1, 56.0; **HRMS** (ESI$^+$): calculated for $C_{20}H_{19}O_4$ [M+H$^+$]: 309.1121, found 309.1121.

(*E*)-3-(3,4-Diethoxystyryl)-1*H*-isochromen-1-one (13d)



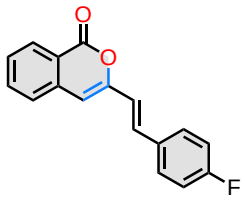
Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-40% EtOAc in petroleum ether) as a yellow solid (48.0 mg, 72%). **m.p**. 168-169 °C; **IR** ν_{max} (ATR)/cm^{-1}: 3444, 2978,2927, 2872, 1726; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 – 8.22 (m, 1H), 7.70 – 7.62 (m, 1H), 7.47 – 7.33 (m, 3H), 7.09 – 7.02 (m, 2H), 6.89 – 6.84 (m, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.40 (s, 1H), 4.18 – 4.07 (m, 4H), 1.51 – 1.42 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 153.1, 149.9, 148.9, 137.9, 134.9, 133.1, 129.9, 128.9, 127.9, 125.8, 121.1, 120.8, 117.4, 113.2, 111.7, 105.0, 64.7, 64.6, 15.0, 14.9; **HRMS** (ESI$^+$): calculated for $C_{21}H_{20}O_4Na$ [M+Na$^+$]: 359.1254, found 359.1270.

(*E*)-3-(4-Propoxystyryl)-1*H*-isochromen-1-one (13e)



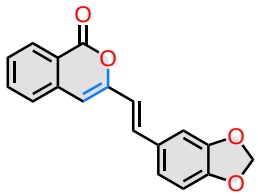
Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-15% EtOAc in petroleum ether) as a yellow solid (40.0 mg, 66%). **m.p.** 114-115 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2962, 2926, 2874, 1730, 1709; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (appt d, *J* = 7.9 Hz, 1H), 7.67 (appt td, *J* = 7.8, 1.2 Hz, 1H), 7.49 – 7.36 (m, 5H), 6.90 (appt d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.40 (s, 1H), 3.95 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.76 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 160.1, 153.2, 138.0, 134.9, 132.9, 130.0, 128.7, 128.6, 127.9, 125.8, 120.8, 117.3, 115.0, 104.9, 69.8, 22.7, 10.6; **HRMS** (ESI$^+$): calculated for $C_{20}H_{18}O_3Na$ [M+Na$^+$]: 329.1148, found 329.1139.

(*E*)-3-(4-Fluorostyryl)-1*H*-isochromen-1-one (13f)[13]



Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-25% EtOAc in petroleum ether) as a yellow solid (53.0 mg, 72%). **m.p**. 141-143 °C; **IR** ν_{max} (ATR)/cm^{-1}: 2923, 2854, 1721, 1596, 1508; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (appt d, *J* = 7.9 Hz, 1H), 7.73 – 7.65 (appt td, *J* = 7.8, 1.3 Hz, 1H), 7.55 – 7.37 (m, 5H), 7.12 – 7.03 (m, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.46 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 249.5 Hz), 162.1, 152.6, 137.7, 135.0, 132.3 (d, *J* = 3.5 Hz), 131.9, 130.0, 128.9 (d, *J* = 8.2 Hz), 128.3, 125.9, 121.1, 119.4 (d, *J* = 2.5 Hz), 116.1 (d, *J* = 21.8 Hz), 105.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.9; **HRMS** (ESI^+): calculated for $C_{17}H_{11}FO_2Na$ [$M+Na^+$]: 289.0635, found 289.0642.

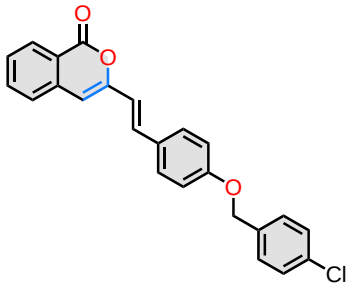
(*E*)-3-(2-(Benzo[*d*][1,3]dioxol-5-yl)vinyl)-1*H*-isochromen-1-one (13g)



Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-20% EtOAc in petroleum ether) as a yellow solid (35.0 mg, 60%). **m.p.** 180 °C (decomposed). **IR** ν_{max} (ATR)/cm^{-1}: 3087, 2924, 2096, 1719, 1655; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (appt d, *J* = 7.9 Hz, 1H), 7.68 (appt td, *J* = 7.7, 1.3 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.43 – 7.33 (m, 2H), 7.04 (appt d, *J* = 1.6 Hz, 1H), 6.99 (appt dd, *J* = 8.0, 1.6 Hz, 1H), 6.82 (appt d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.41 (s, 1H), 6.00 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 153.0, 148.6, 148.5, 137.9, 135.0,

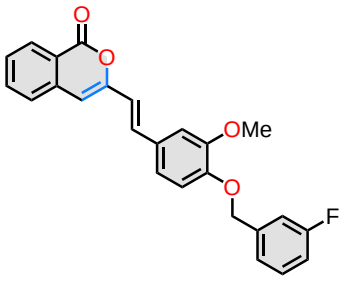
132.8, 130.5, 130.0, 128.0, 125.8, 123.1, 120.9, 117.9, 108.8, 105.9, 105.3, 101.5; **HRMS** (ESI^+): calculated for $C_{18}H_{13}O_4Na$ [M+Na^+]: 315.0628, found 315.0631.

(*E*)-3-(4-((4-Chlorobenzyl)oxy)styryl)-1*H*-isochromen-1-one (13h)



Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-15% EtOAc in petroleum ether) as a yellow solid (48.0 mg, 62%). **m.p.** 175-176 °C; **IR** ν_{max} (ATR)/cm^{-1}: 3038, 1726,1629, 1603; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (appt d, *J* = 7.9 Hz, 1H), 7.67 (appt t, *J* = 7.6 Hz, 1H), 7.49 – 7.34 (m, 9H), 6.96 (appt d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.41 (s, 1H), 5.06 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 159.3, 153.1, 137.9, 135.4, 135.0 134.1, 132.6, 130.0, 129.3, 129.0, 128.9, 128.8, 128.0, 125.8, 120.9, 117.7, 115.4, 105.1, 69.5; **HRMS** (ESI^+): calculated for $C_{24}H_{18}ClO_3Na$ [M+Na^+]: 389.0939, found 389.0942.

(*E*)-3-(4-((3-Fluorobenzyl)oxy)-3-methoxystyryl)-1*H*-isochromen-1-one (13i)

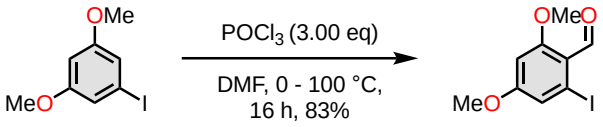


Following general procedure B, the title compound was isolated after purification by flash column chromatography (0-20% EtOAc in petroleum ether) as a yellow solid (37.0 mg, 70%). **m.p.** 113-115 °C; **IR** ν_{max} (ATR)/cm^{-1}: 3066, 2924, 2853, 1722, 1592; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (appt d, *J* = 7.8 Hz,

1H), 7.67 (appt td, *J* = 7.6, 1.3 Hz, 1H), 7.49 – 7.30 (m, 4H), 7.23 – 7.15 (m, 2H), 7.09 – 6.96 (m, 3H), 6.86 (appt d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.43 (s, 1H), 5.17 (s, 2H), 3.95 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 246.3 Hz), 162.3, 153.0, 150.0, 148.9, 139.6 (d, *J* = 7.3 Hz), 137.9, 135.0, 132.9, 130.3 (d, *J* = 8.2 Hz), 130.0, 129.8, 128.0, 125.8, 122.7 (d, *J* = 2.9 Hz), 120.9, 120.8, 118.9, 115.0 (d, *J* = 21.2 Hz), 114.4 – 114.1 (m), 110.2, 105.2, 70.4, 56.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.8. **HRMS** (ESI^+): calculated for $C_{25}H_{19}FO_4Na$ [$M+Na^+$]: 425.1160, found 425.1161.

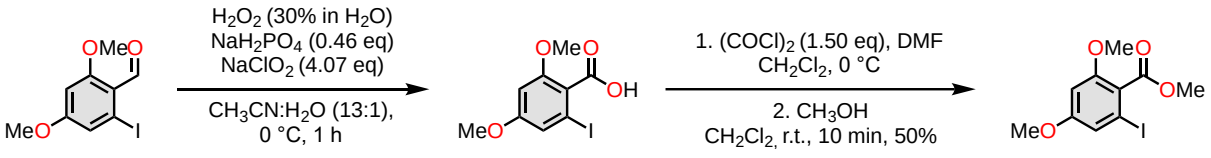
Synthesis and experimental data for compounds 12j and 13j

2-Iodo-4,6-dimethoxybenzaldehyde[14]



To a solution of 1-iodo-3,5-methoxybenzene (2.40 g, 9.09 mmol) in anhydrous DMF (15.0 mL) was added $POCl_3$ (2.55 mL, 27.3 mmol, 3.00 eq) dropwise at 0 °C. The solution was stirred at 0 °C for 5 min and then heated to 100 °C for 16 h. The reaction mixture was cooled to room temperature then poured into ice cold water (100 mL), the resultant precipitate collected by filtration and washed with water (2 x 10.0 mL) to obtain the analytically pure product as a light brown solid (2.19 g, 83%). **m.p.** 78-79 °C (lit: 81-82 °C)[14]; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 1595, 1422, 1206, 1157; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.1 (s, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.6, 164.6, 163.3, 119.2, 118.3, 99.2, 98.6, 56.0, 56.0; **HRMS** (ESI^+): calculated for $C_8H_{10}IO_2$ [$M+H^+$]: 264.9720, found 264.9724.

Methyl 2-iodo-4,6-dimethoxybenzoate[15]



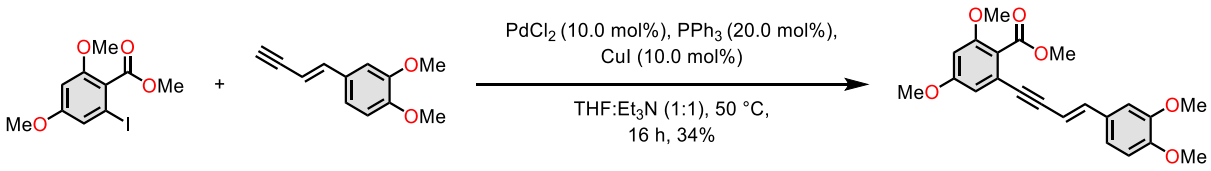
Step 1 **Step 2**

Step 1: To a solution of 2-iodo-4,6-dimethoxybenzaldehyde (2.00 g, 6.85 mmol) in an CH_3CN:H_2O mixture (13:1) (86.0 mL) was added NaH_2PO_4 (374 mg, 3.16 mmol, 0.46 eq), $NaClO_2$ (2.52 g, 27.9 mmol, 4.07 eq) and H_2O_2 (30% in H_2O, 1.71 mL) successively at 0 °C and vigorously stirred for 1 h. The solution was diluted with H_2O (75.0 mL) and extracted into EtOAc (2 x 75.0 mL). The organic phases were

combined, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure, and the crude product was used directly into the next step without further purification.

Step 2: To a solution of crude 2-iodo-4,6-dimethoxybenzoic acid in CH_2Cl_2 (50.0 mL) at 0 °C was added $(COCl)_2$ (885 µL, 10.3 mmol, 1.50 eq) followed by the 1 drop of DMF. The reaction mixture was stirred until the effervescence ceased and then concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (40.0 mL) and CH_3OH (5.0 mL) and stirred for 10 min. The solution was concentrated under reduced pressure and the crude product purified by flash column chromatography (0-25% EtOAc in petroleum ether) to obtain the analytically pure product as a colourless solid (1.10 g, 50% over steps 1 and 2). **m.p.** 71-72 °C (lit: 72-74 °C);[15] **IR** ν_{max} (ATR)/cm^{-1}: 3019, 2399, 1732, 1599, 1558; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 2.1 Hz, 1H), 6.43 (d, *J* = 2.1 Hz, 1H), 3.91 (s, 3H), 3.79 (appt d, *J* = 4.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 161.7, 158.0, 123.5, 115.3, 99.1, 93.0, 56.2, 55.8, 52.8; **HRMS** (ESI^+): calculated for $C_{10}H_{11}IO_4$ [$M+H^+$]: 322.9775, found 322.9773.

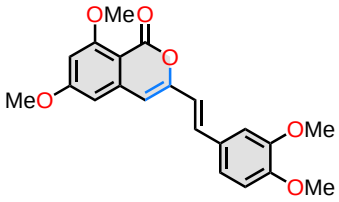
Methyl (*E*)-2-(4-(3,4-dimethoxyphenyl)but-3-en-1-yn-1-yl)-4,6-dimethoxybenzoate (12j)



To a solution of methyl 2-iodo-4,6-dimethoxybenzoate (600 mg, 1.86 mmol) in anhydrous THF (20.0 mL) and Et_3N (20.0 mL) degassed with argon for 5 min was added $PdCl_2$ (33.0 mg, 0.190 mmol, 10.0 mol%), PPh_3 (98.0 mg, 0.370 mmol, 20.0 mol%) and CuI (35.0 mg, 0.190 mmol, 10.0 mol%) successively at room temperature. The solution was then degassed with argon for a further 5 mins followed by the addition of *(E)*-4-(but-1-en-3-yn-1-yl)-1,2-dimethoxybenzene (421 mg, 2.24 mmol, 1.20 eq). The reaction mixture was heated at 50 °C and stirred for 16 h. The resultant solution was cooled to room temperature, filtered through a short pad of Celite® and concentrated under reduced pressure. The crude residue purified by flash column chromatography (0-30% EtOAc in petrol) to obtain the

analytically pure product as a brown paste (242 mg, 34%). **IR** ν_{max} (ATR)/cm^{-1}: 3018, 1734, 1719, 1463, 1456; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 – 6.93 (m, 3H), 6.83 (appt d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 6.20 (d, *J* = 16.2 Hz, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 3.82 (s, 3H), 3.82 (appt d, *J* = 1.7 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.5, 161.5, 158.1, 150.1, 149.3, 142.1, 129.4, 123.9, 120.3, 118.8, 111.3, 108.6, 108.0, 105.7, 99.6, 92.6, 88.5, 56.2, 56.1, 56.0, 55.7, 52.5; **HRMS** (ESI$^+$): calculated for $C_{22}H_{23}O_6$ [M+H$^+$]: 383.1489, found 383.1488.

(*E*)-3-(3,4-dimethoxystyryl)-6,8-dimethoxy-1*H*-isochromen-1-one (13j)



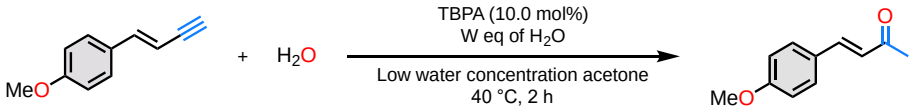
Following modified general procedure B (performed on a 0.66 mmol scale for 7 h), the crude product was purified by flash column chromatography (0-60% EtOAc in petrol) to yield the title compound (**13j**) as a yellow solid (69 mg, 30%). **m.p.** 98-100 °C. **IR** υ_{max} (ATR)/cm^{-1} 2931, 2840, 1715, 1595, 1563, 1514, 1455, 1207. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 15.9 Hz, 1H), 7.11 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.05 (d, *J* = 1.7 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H), 6.38 (d, *J* = 2.2 Hz, 1H), 6.27 (s, 1H), 3.99 (s, 3H), 3.94 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 163.6, 158.9, 153.8, 150.1, 149.3, 142.5, 133.4, 129.1, 121.0, 117.4, 111.4, 109.6, 105.3, 103.6, 100.4, 98.7, 56.5, 56.1, 56.0, 55.8; **HRMS** (ESI+): calculated for $C_{21}H_{21}O_6$ [M+H+]: 369.1333, found 369.1331.

NMR experiments

General Procedure for the Investigation into the Effect of Water Content on the Hydration Reaction

A solution of the required enyne (0.20 mmol, 1.00 eq) and the stipulated equivalents of H_2O in low water concentration (max. 0.01%, purchased from VWR Chemicals) acetone (1.00 mL) was degassed by purging with argon for 5 min. A separate solution of low water concentration acetone (1.00 mL) was degassed by purging with argon for 5 min, placed under argon, heated to 40 °C and tris(4-bromophenyl)-ammoniumyl hexachloroantimonate (TBPA) (0.02 mmol, 0.10 eq) added. The enyne solution was added dropwise immediately after, and the solution stirred for 2 h at 40 °C. The reaction was quenched with sat. K_2CO_3 in methanol (1.00 mL), washed with brine (5.00 mL), and extracted into EtOAc (2 x 5.00 mL). The organic fractions were combined, dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure, and the percentage conversion determined by quantitative ^1H NMR using hexamethyldisiloxane (HMDSO) as an internal standard.

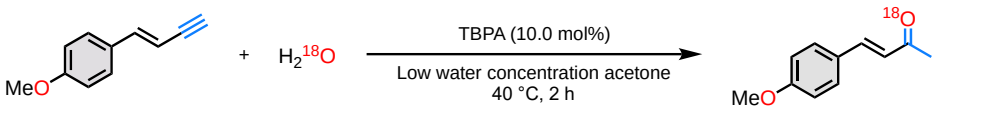
Table S1. The effect of water content on the hydration reaction



Entry	Water equivalents added	Percentage conversion/%[a]
1	0.00	28
2	1.00	78
3	2.00	60
4	3.00	30
5	4.00	26
6	5.00	7

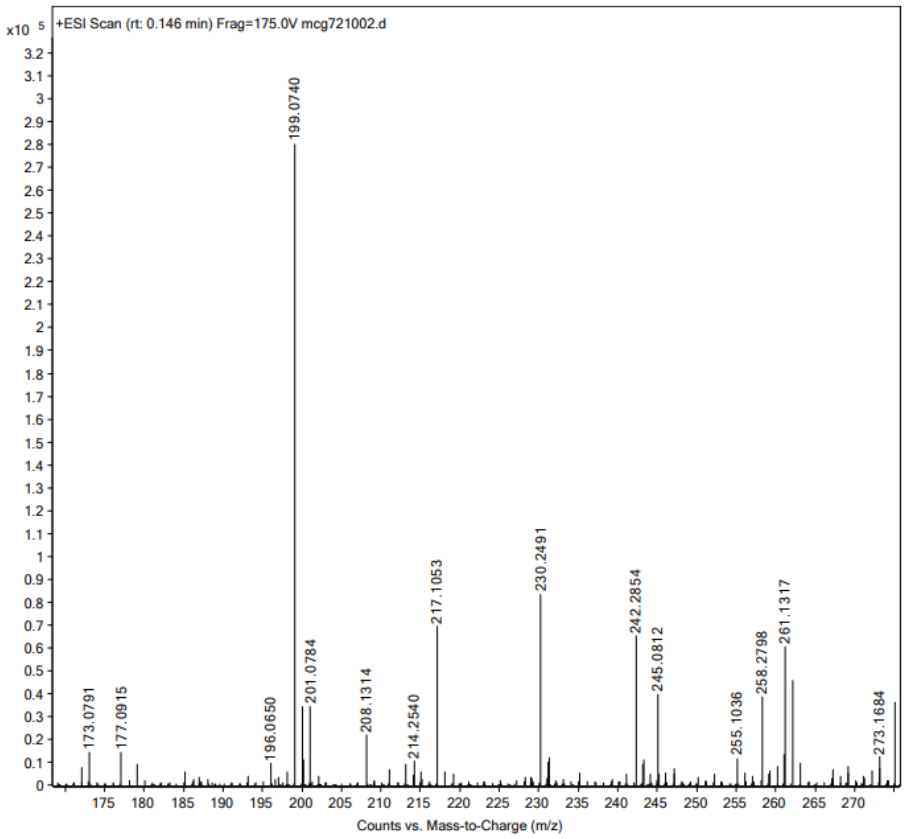
[a] Percentage conversion determined by quantitative ^1H NMR using hexamethyldisiloxane (HMDSO) as an internal standard.

Labelling experiments



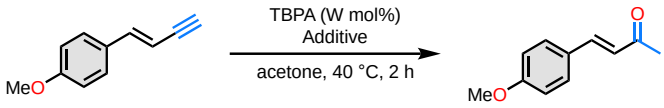
$C_{11}H_{12}O_2Na$ [M+Na$^+$] calculated 199.0730, found 199.0740
$C_{11}H_{12}O^{18}ONa$ [M+Na$^+$] calculated 201.0772, found 201.0784

Figure S1. Mass Spectrum of Labelling Experiment with $H_2{}^{18}O$



Control experiments

Table S2. Control experiments to support the cation-radical mechanistic pathway



Entry	W (mol%)	Additive	Percentage yield/%[a]
1	0	tris(4-bromophenyl)amine (10 mol%)	0
2	10	2,6-di-*tert*-butyl-4-methylpyridine (20 mol%)	68
3	10	TEMPO (20 mol%)	0
4[b]	10	—	43

[a] The reactions were performed on a 0.20 mmol scale of enyne; isolated yields. [b] Reaction performed under an atmosphere of oxygen.

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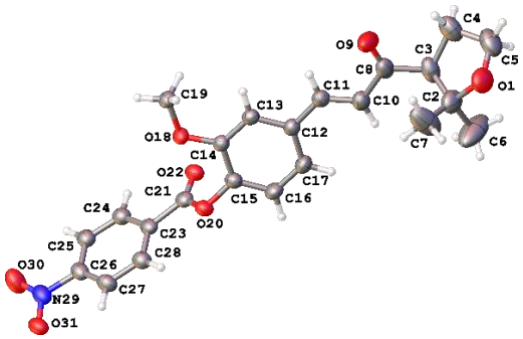
X-ray Crystallography Data

X-ray data of structure **5r** (CCDC2059518)



Datablock: abjemc

Bond precision: C-C = 0.0030 A Wavelength=1.54184

Cell: a=6.85821(12) b=12.4948(3) c=15.2391(3)
alpha=72.5999(17) beta=78.0024(16) gamma=89.0863(16)
Temperature: 120 K

	Calculated	Reported
Volume	1217.40(5)	1217.39(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C23 H23 N O7, C H2 Cl2	C23 H23 N O7, C H2 Cl2
Sum formula	C24 H25 Cl2 N O7	C24 H25 Cl2 N O7
Mr	510.35	510.35
Dx,g cm-3	1.392	1.392
Z	2	2
Mu (mm-1)	2.785	2.785
F000	532.0	532.0
F000'	535.03	
h,k,lmax	8,15,19	8,15,19
Nref	5172	5011
Tmin,Tmax	0.607,0.761	0.887,0.947
Tmin'	0.393	

Correction method= # Reported T Limits: Tmin=0.887 Tmax=0.947
AbsCorr = GAUSSIAN

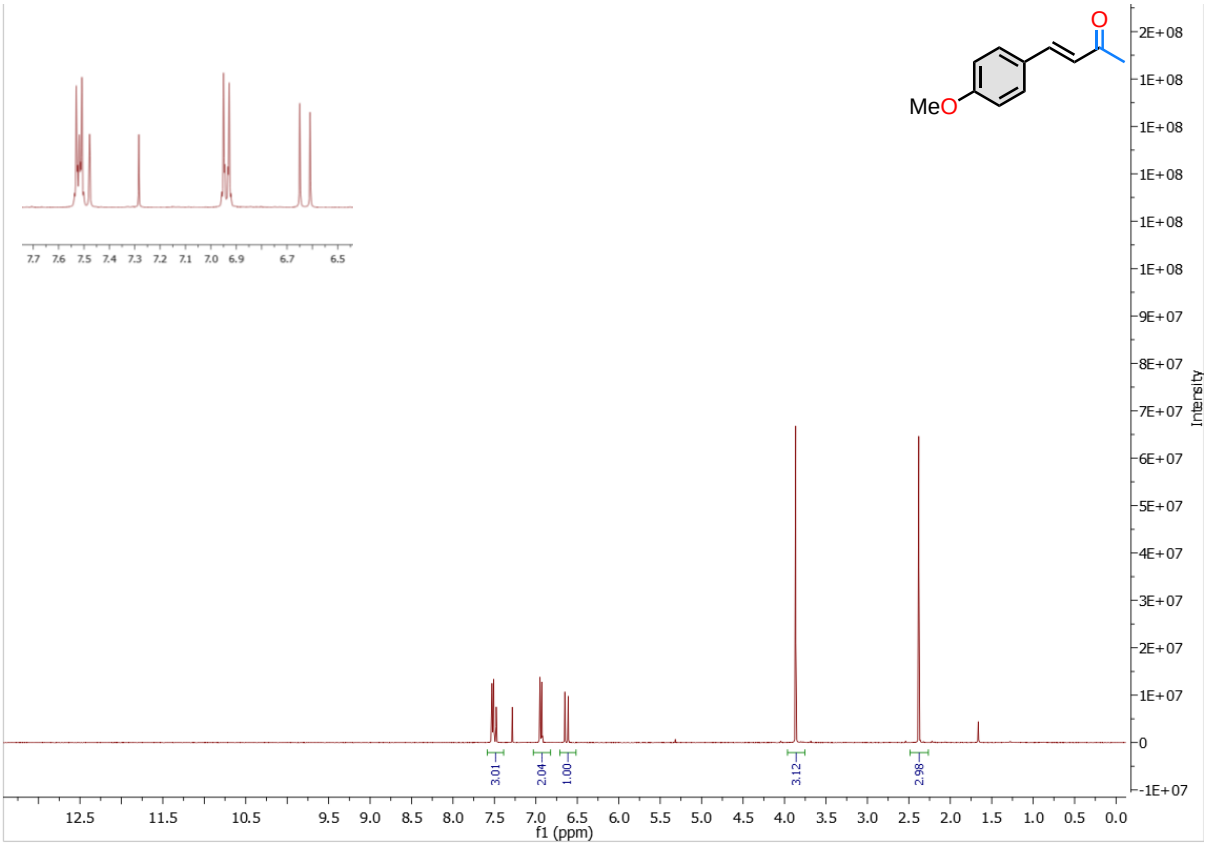
Data completeness= 0.969 Theta(max)= 77.388

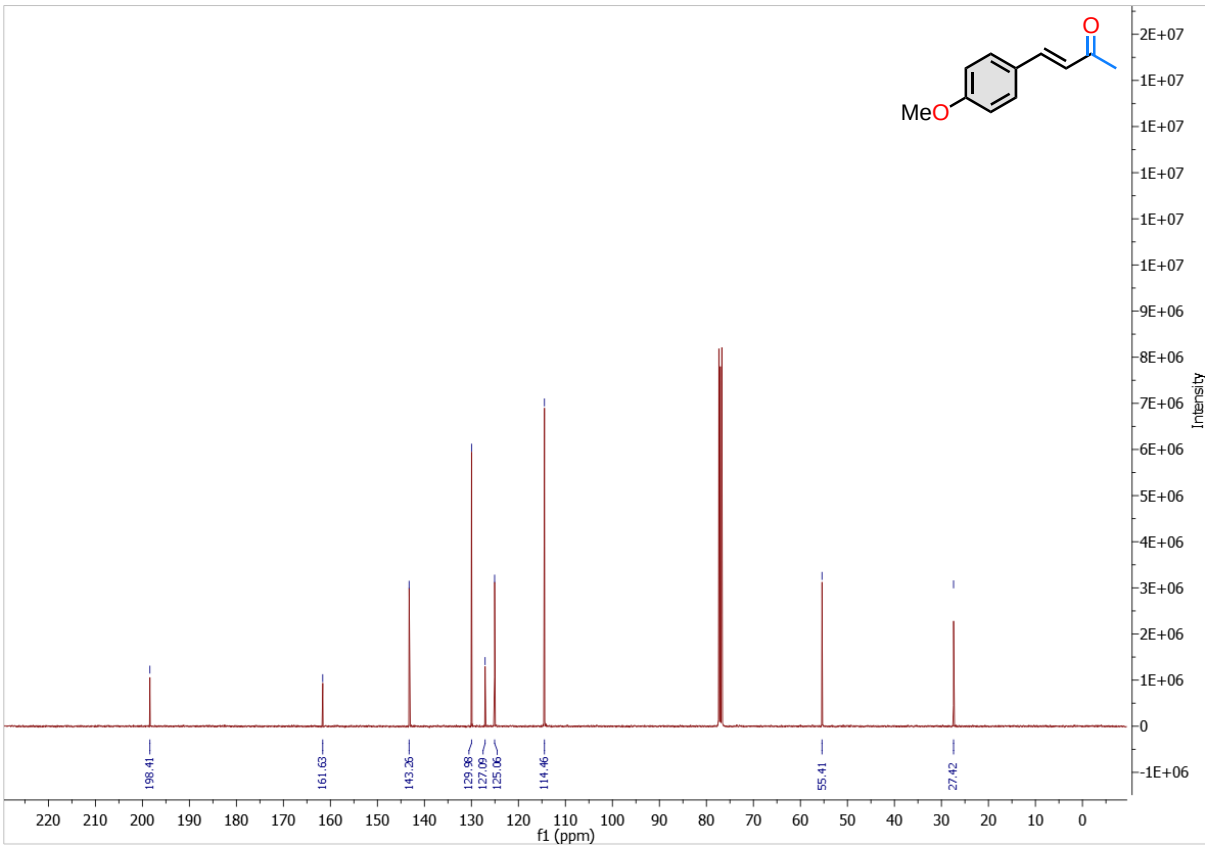
R(reflections)= 0.0532(4599) wR2(reflections)= 0.1339(5011)

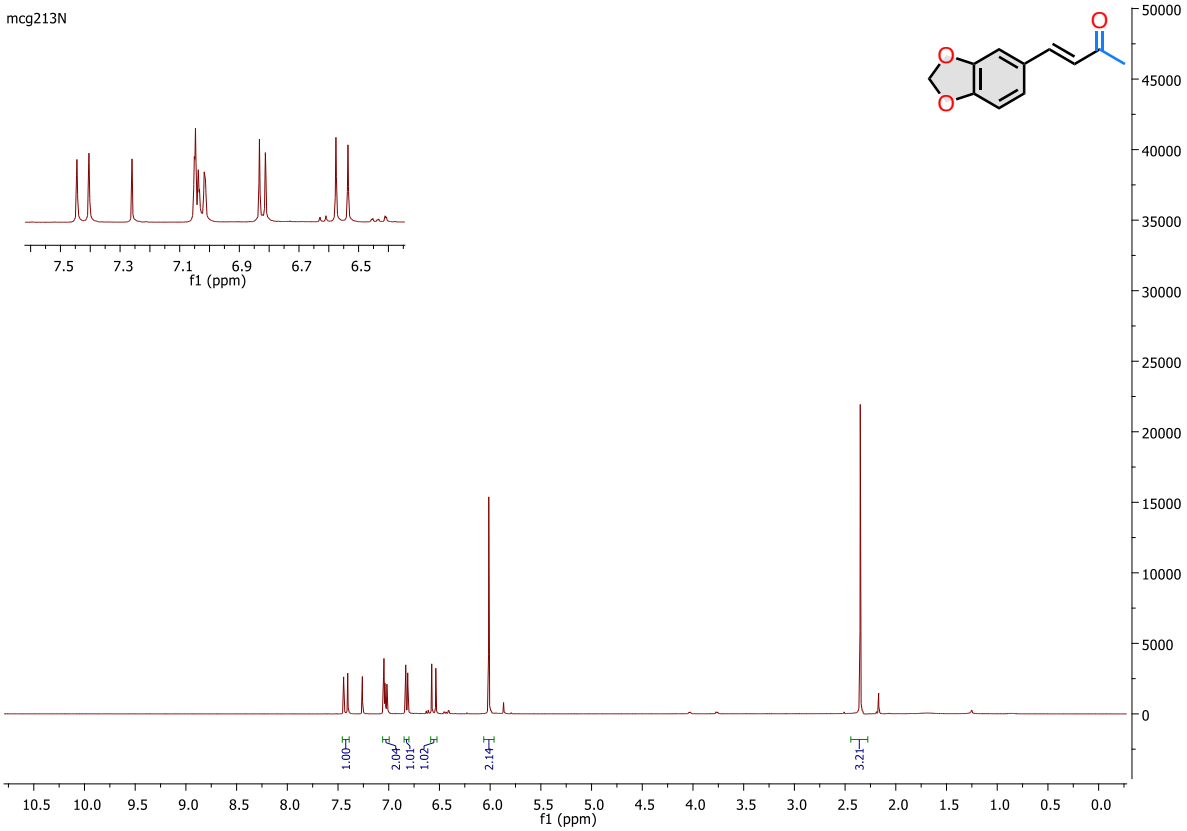
S = 1.053 Npar= 394

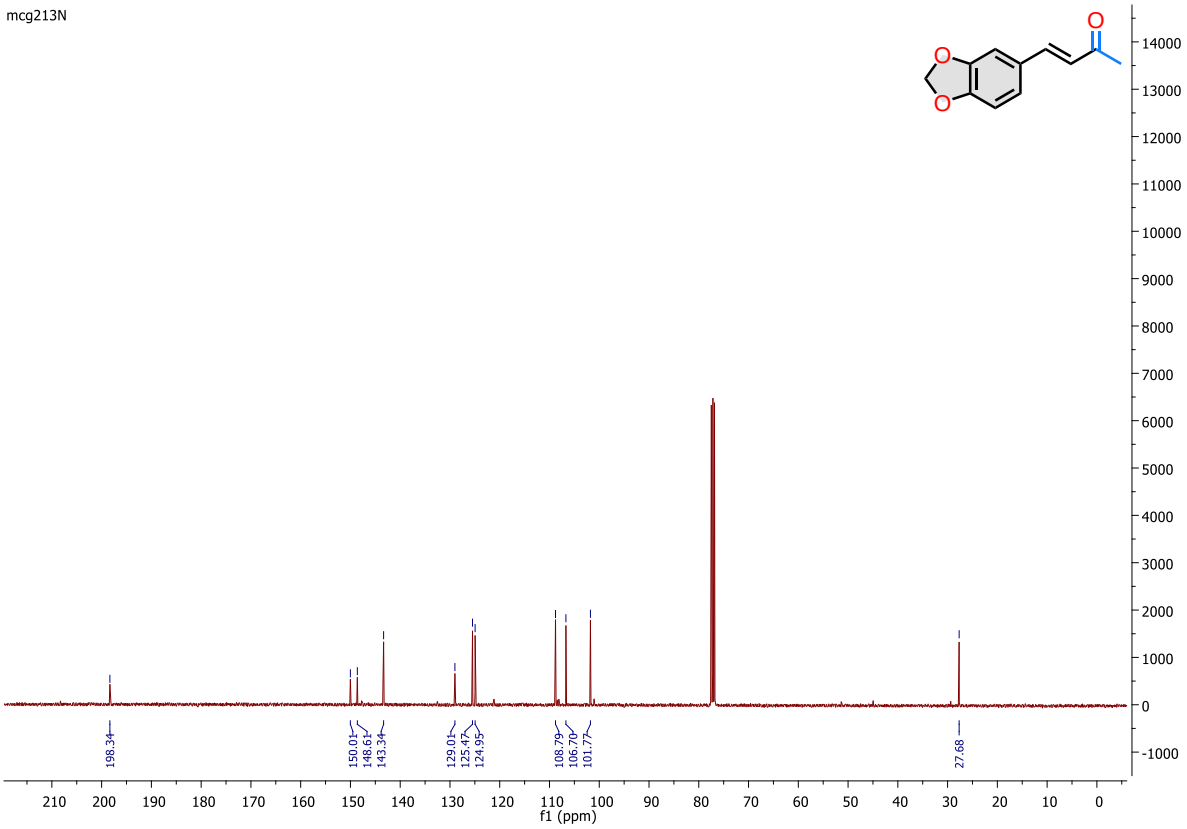
The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

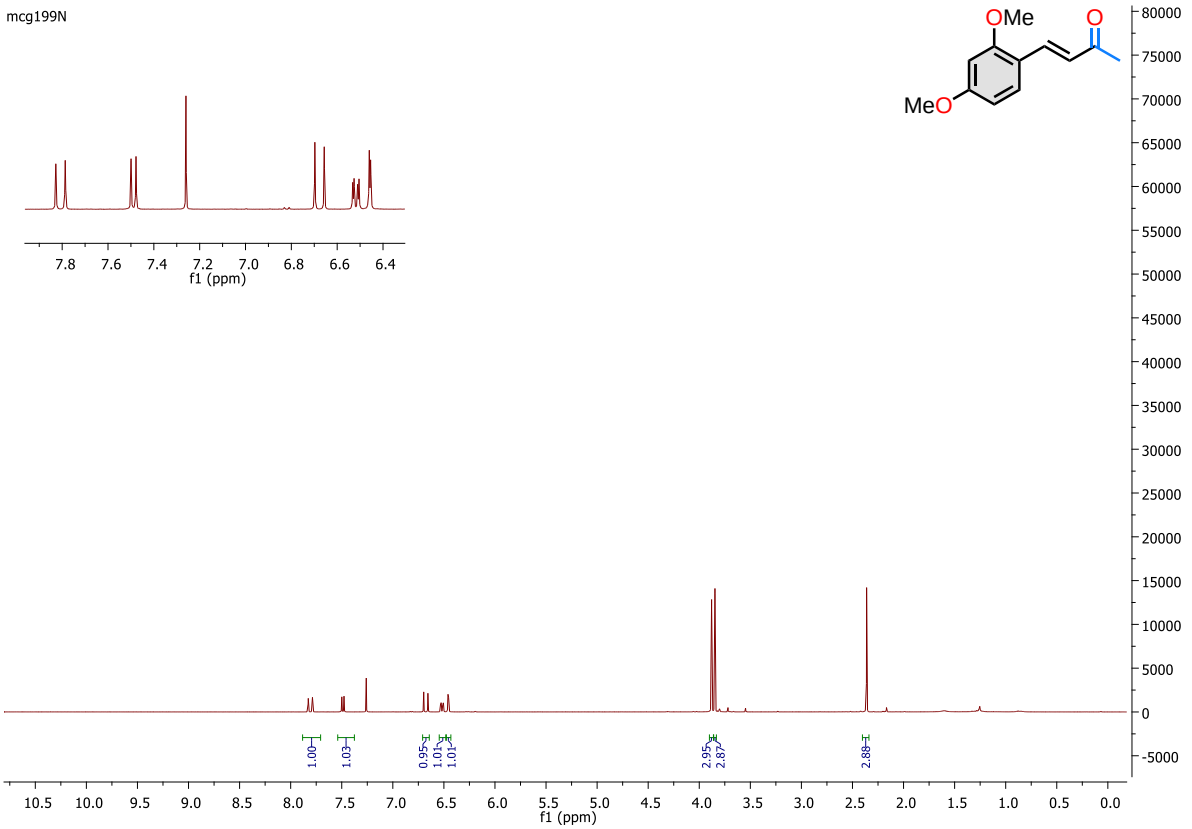
^{1}H, ^{13}C and ^{19}F NMR spectra

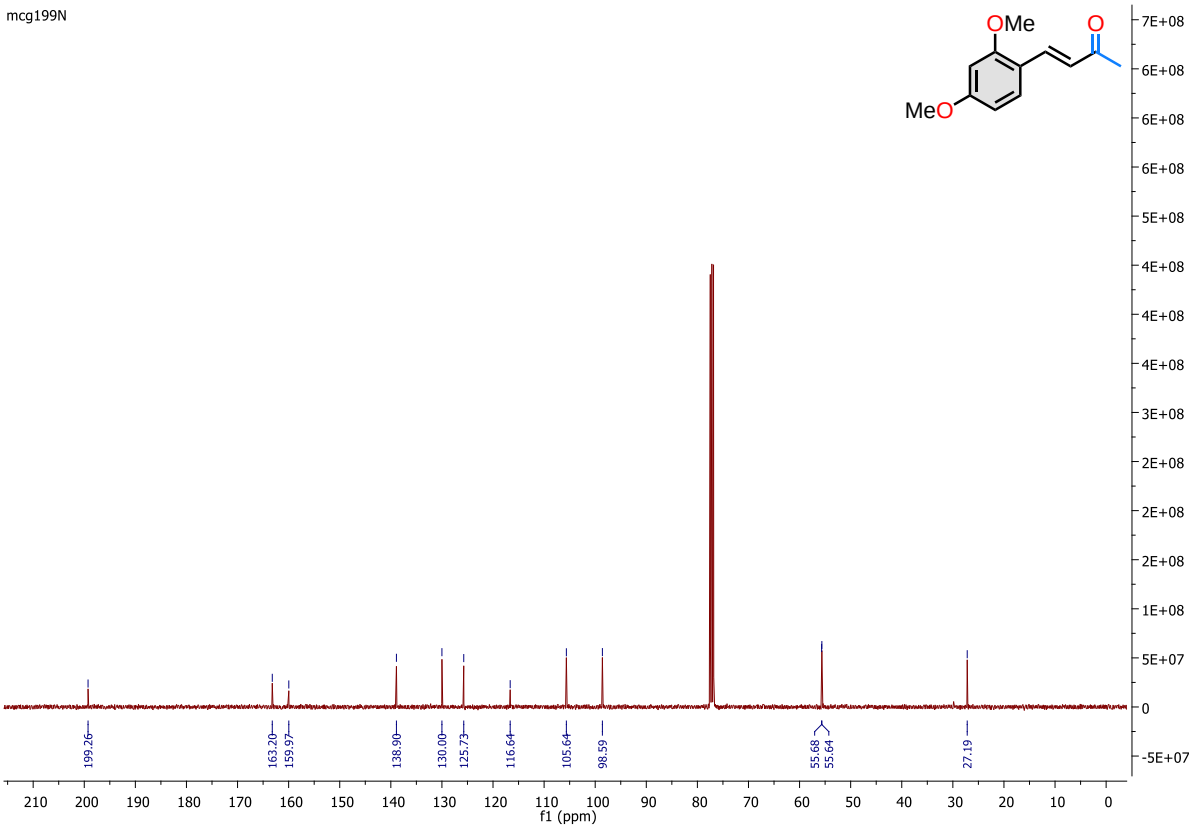


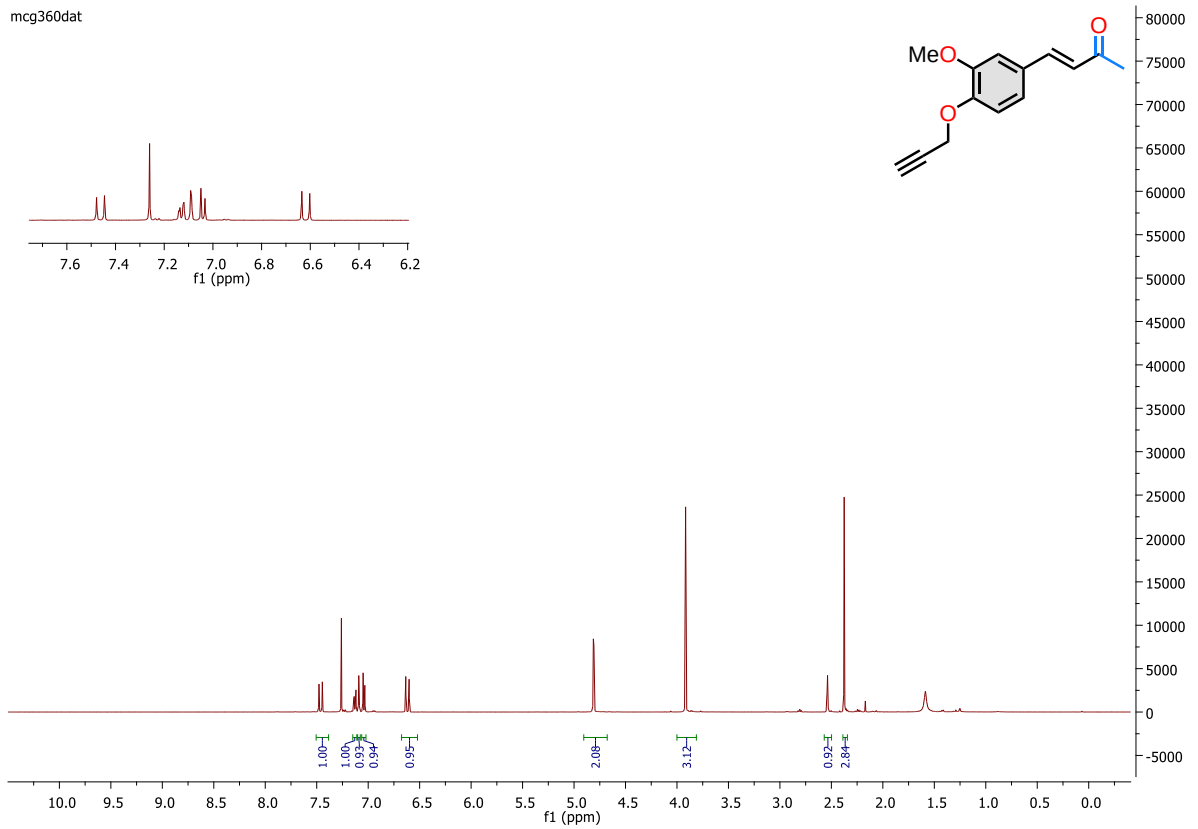


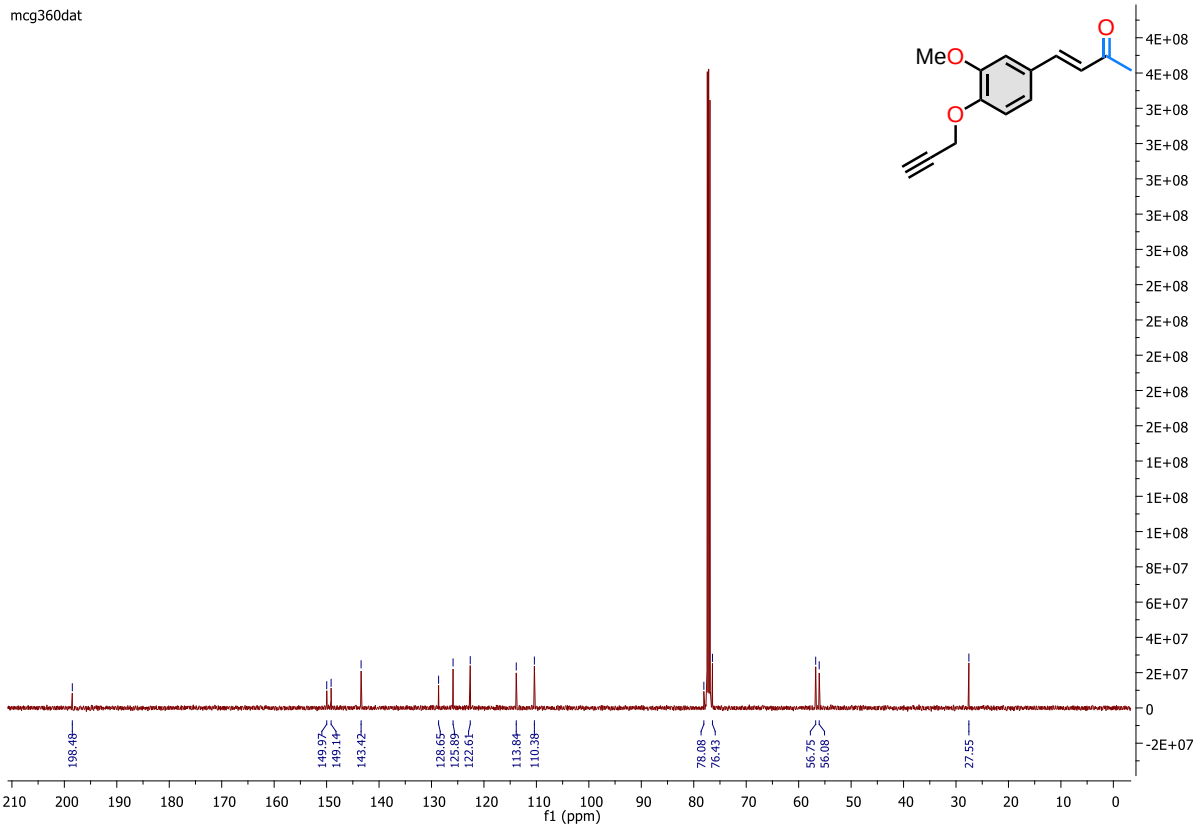

mcg213N
7.5
7.3
7.1
6.9
6.7
6.5
f1 (ppm)
1.00
2.04
1.01
1.02
2.14
3.21
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

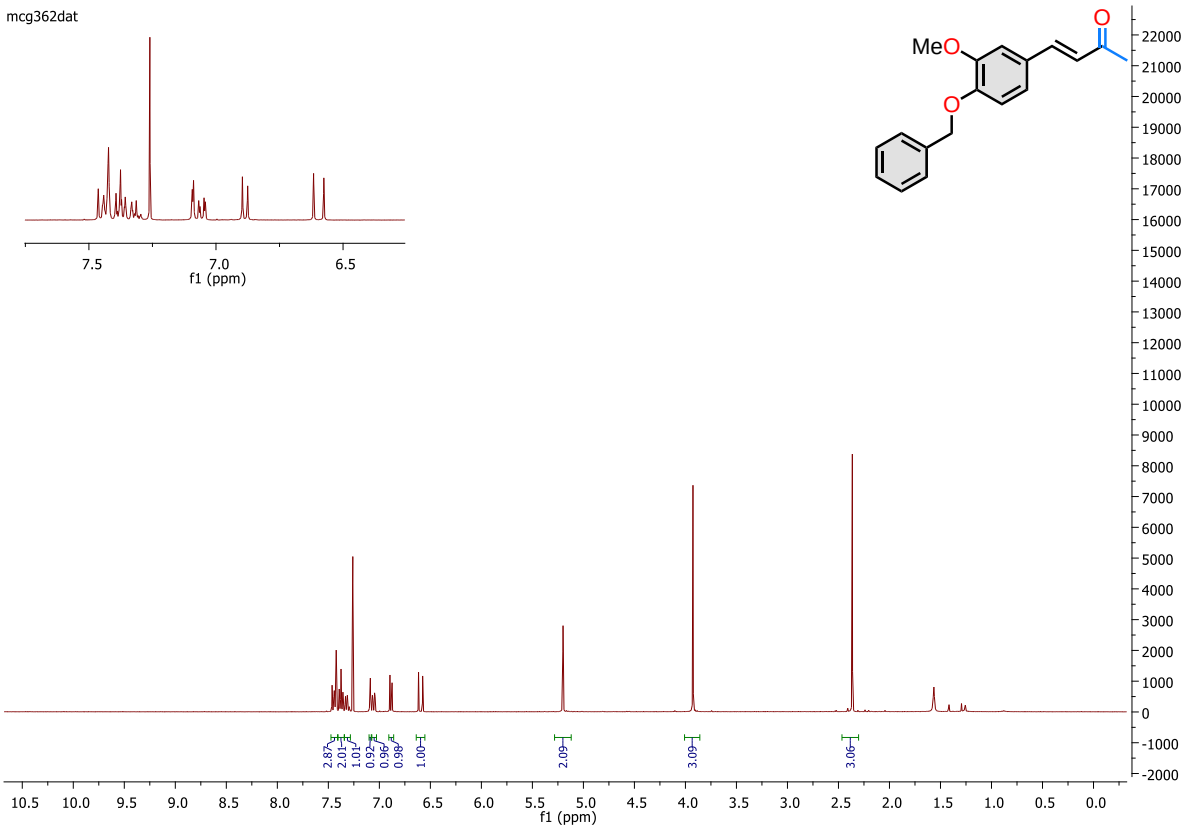

mcg213N
198.34
150.01
148.62
143.34
129.01
125.47
124.95
108.79
106.70
101.77
27.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

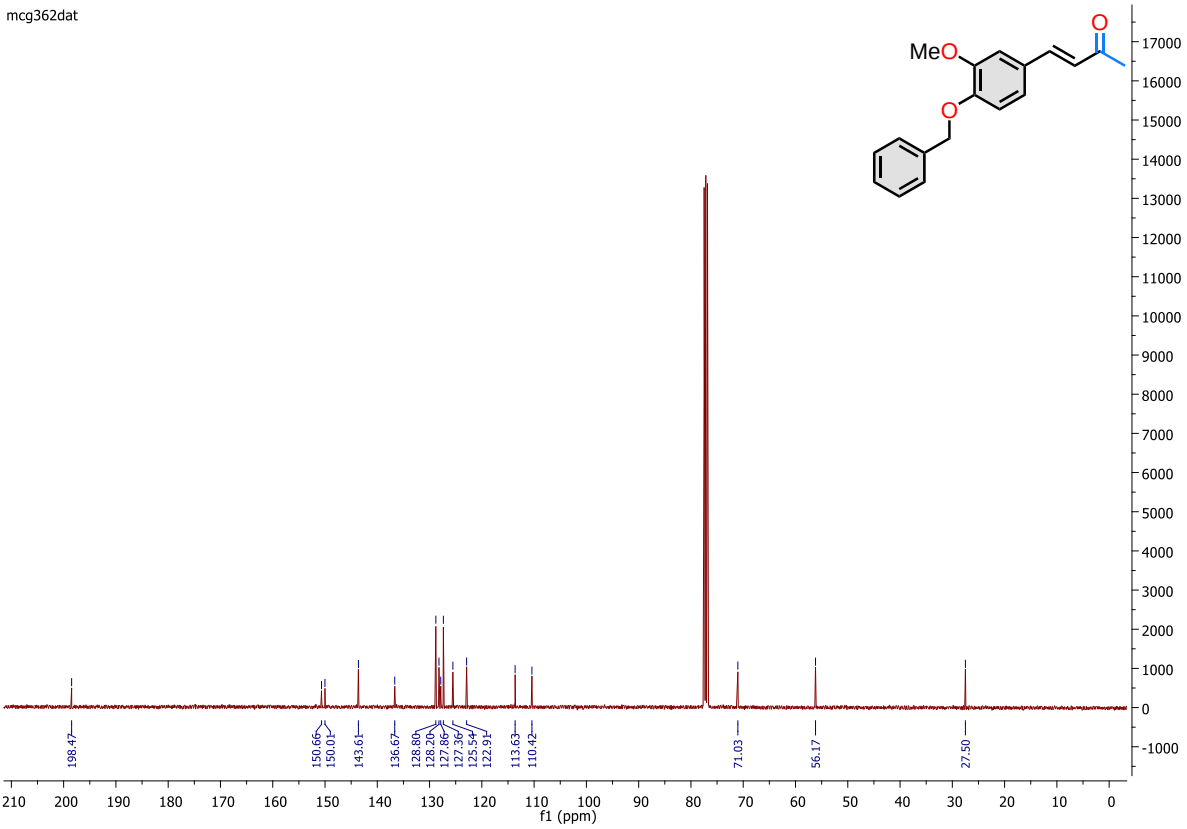

mcg199N
OMe
O
MeO
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)
1.00
1.03
0.95
1.01
1.01
2.95
2.87
2.88
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

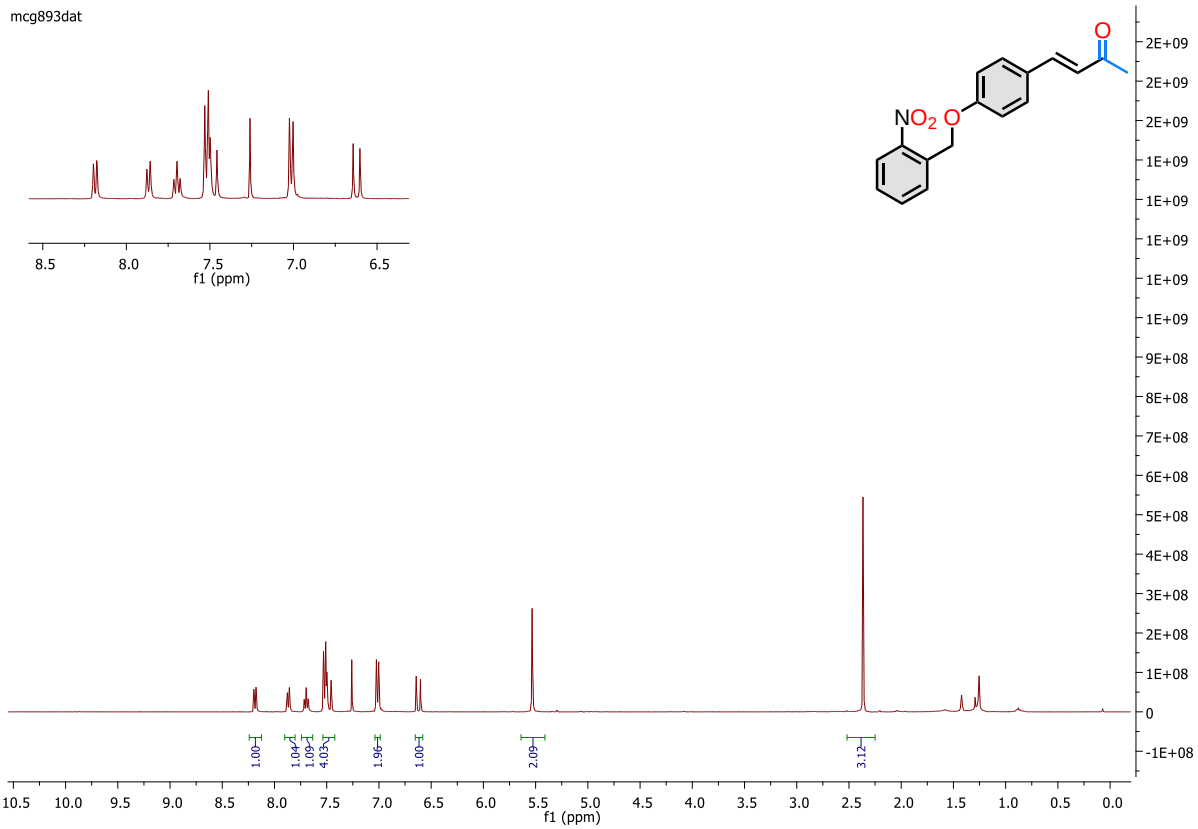

mcg199N
OMe
O
MeO
199.26
163.20
159.97
138.90
130.00
125.73
116.64
105.64
98.59
55.68
55.64
27.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

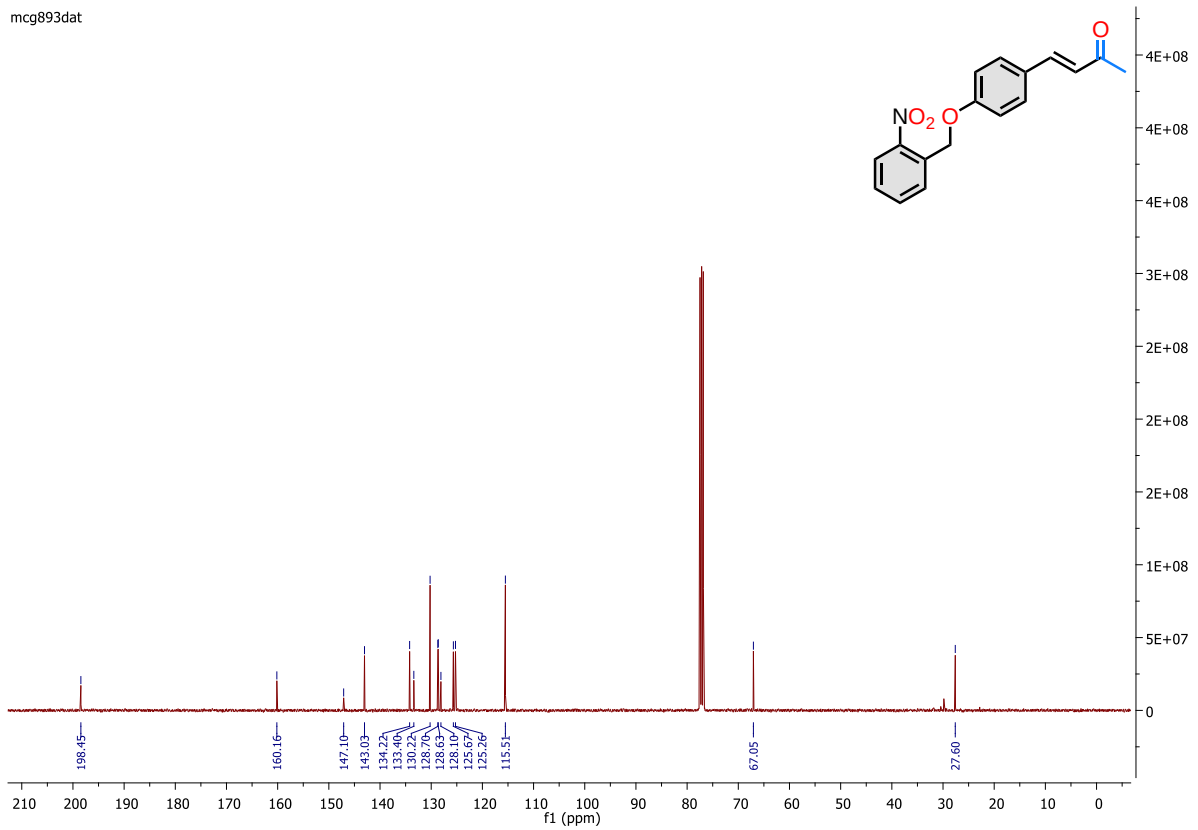

mcg360dat
MeO
O
O
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)
1.00 1.00 0.93 0.94 0.95 2.00 3.12 0.92 2.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

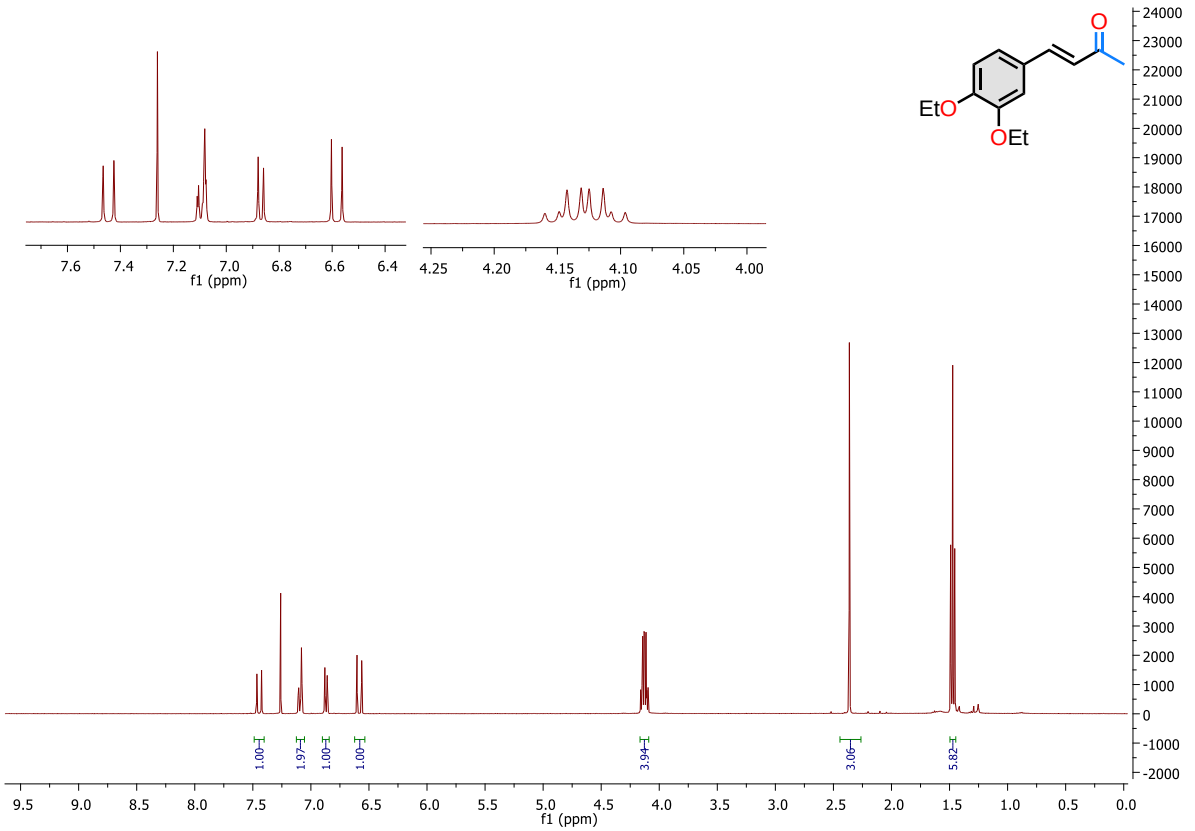

mcg360dat
MeO
O
O
198.48
149.97 149.14 143.42 128.65 125.89 122.61 113.84 110.38 78.08 76.43 56.75 56.08 27.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

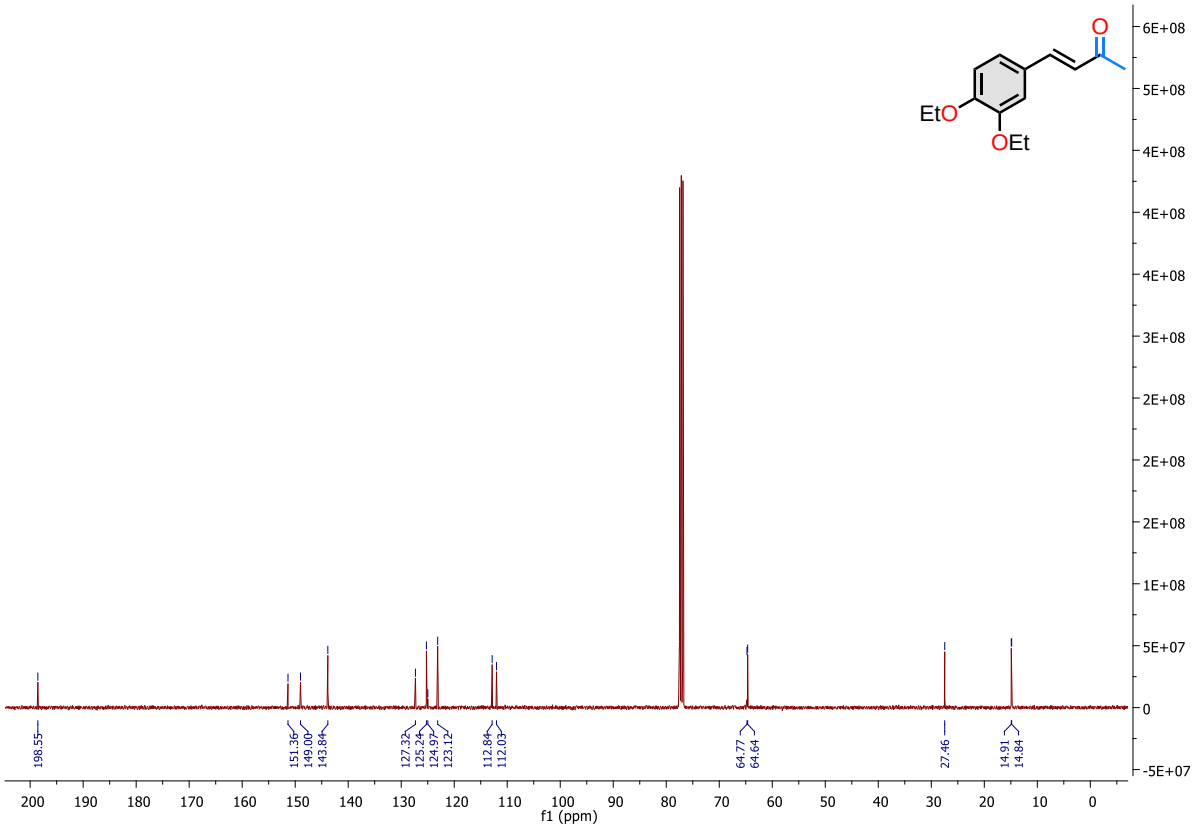

mcg362dat
MeO
O
O
7.5
7.0
6.5
f1 (ppm)
2.87
2.01
1.01
0.92
0.96
0.98
1.00
2.09
3.09
3.06
f1 (ppm)

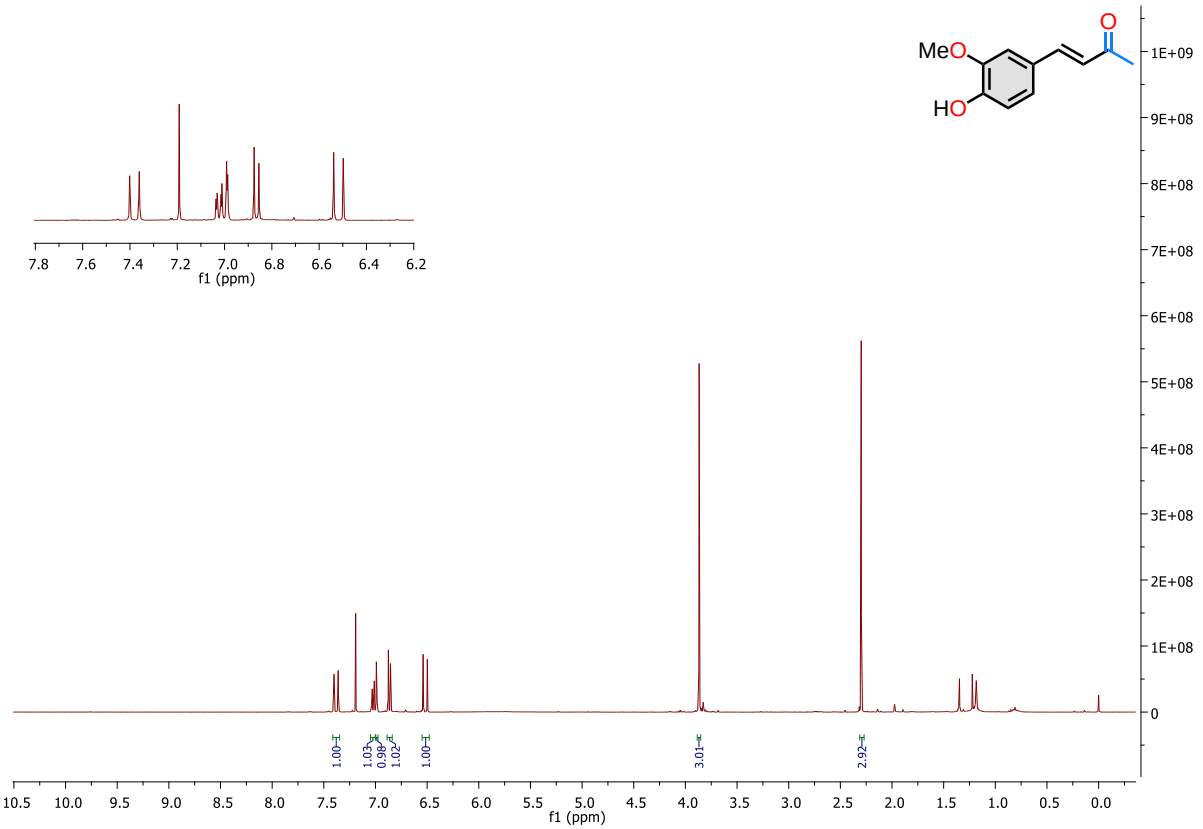

mcg362dat
MeO
O
O
198.47
150.66
150.01
143.61
136.67
128.80
128.20
127.86
127.39
125.54
122.91
113.63
110.42
71.03
56.17
27.50
f1 (ppm)

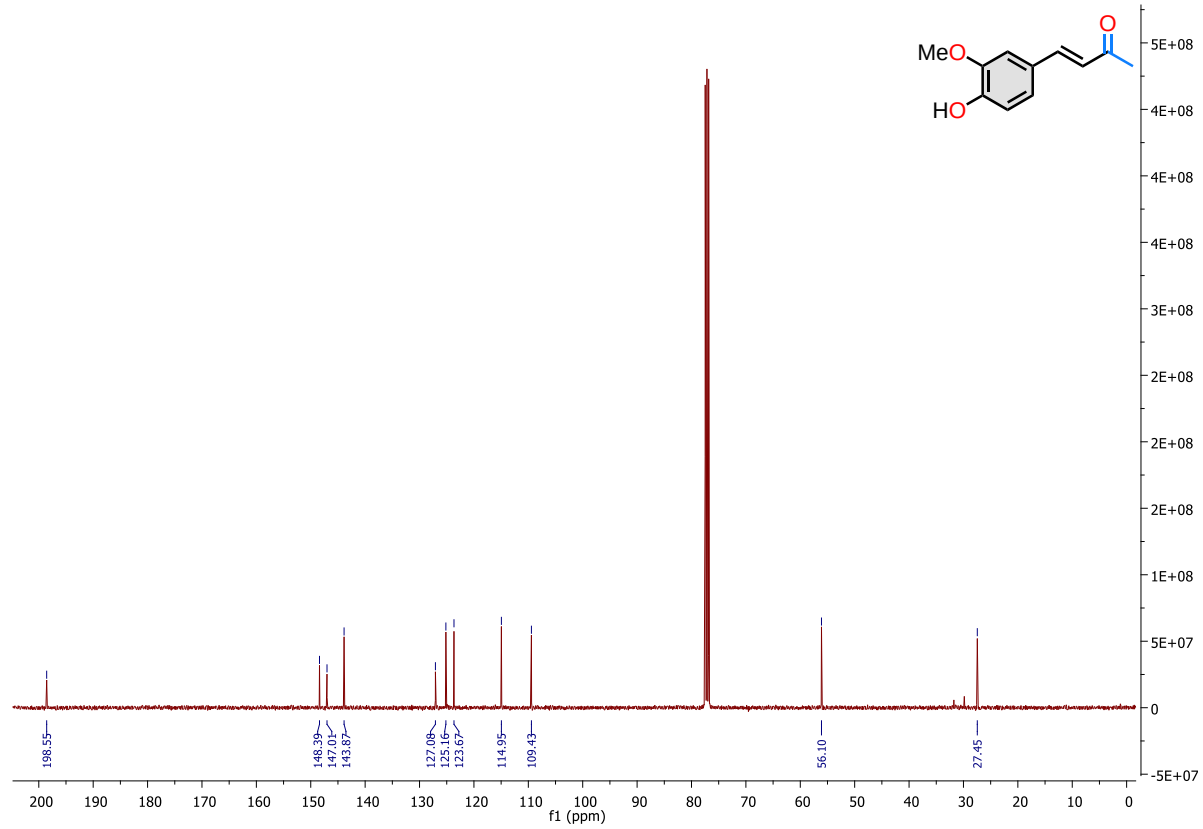

mcg893dat
O
NO2 O
8.5
8.0
7.5
7.0
6.5
f1 (ppm)
1.00
1.04
1.09
4.03
1.96
1.00
2.09
3.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

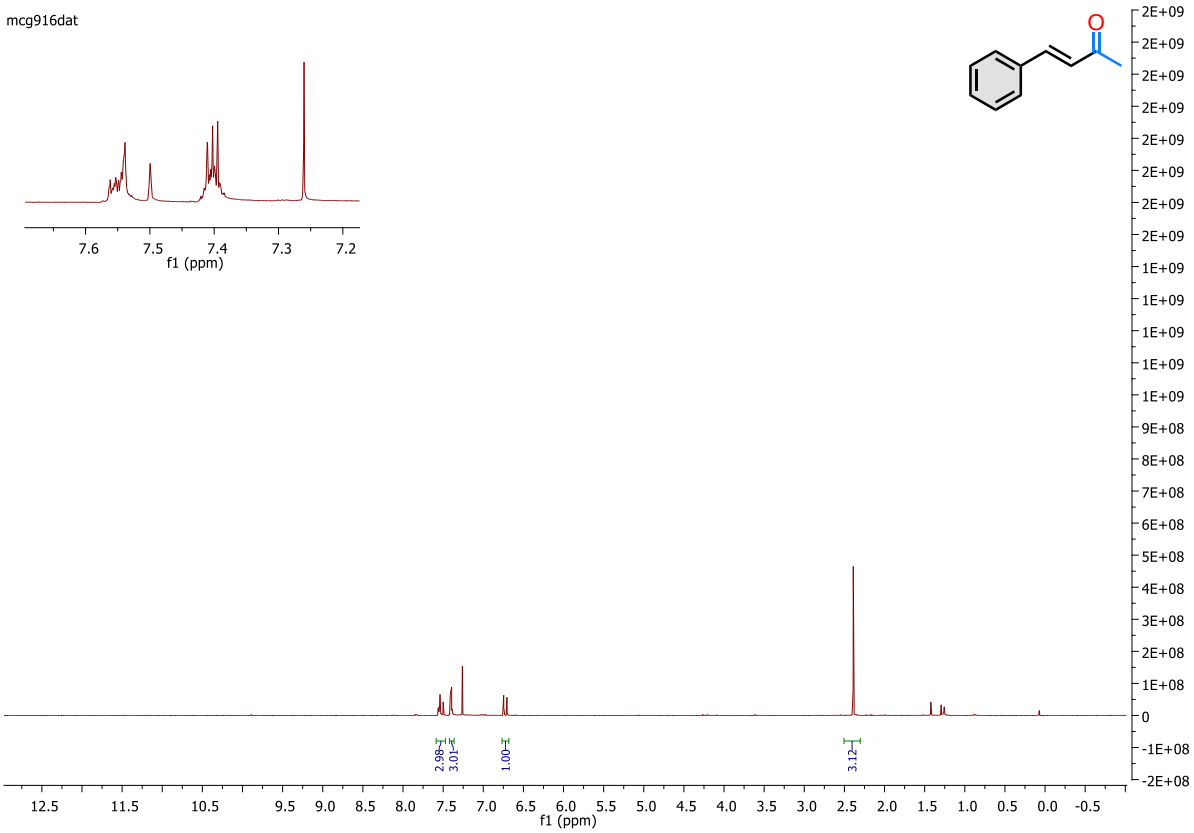

mcg893dat
O
NO2 O
198.45
160.16
147.10
143.03
134.22
133.46
130.22
128.76
128.63
128.10
125.67
125.26
115.51
67.05
27.60
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

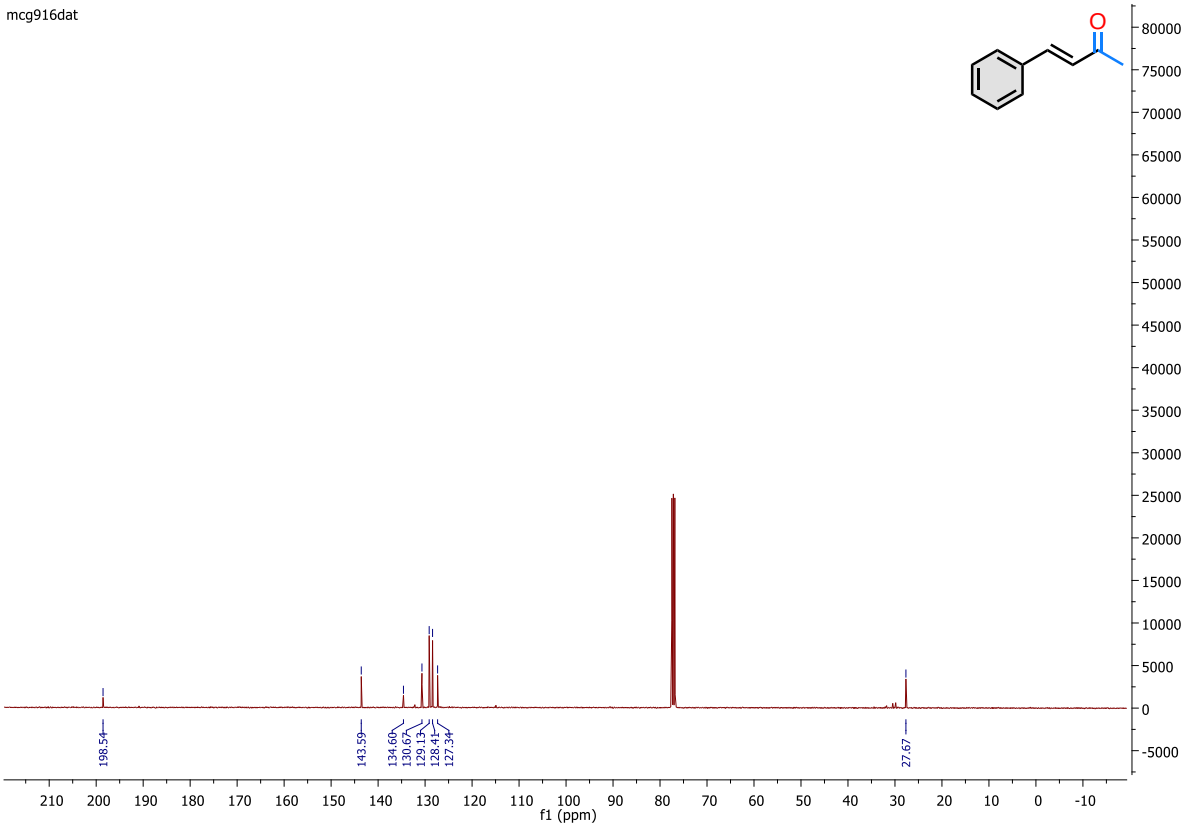

O
EtO
OEt
f1 (ppm)
1.00
1.97
1.00
1.00
3.94
3.06
5.82

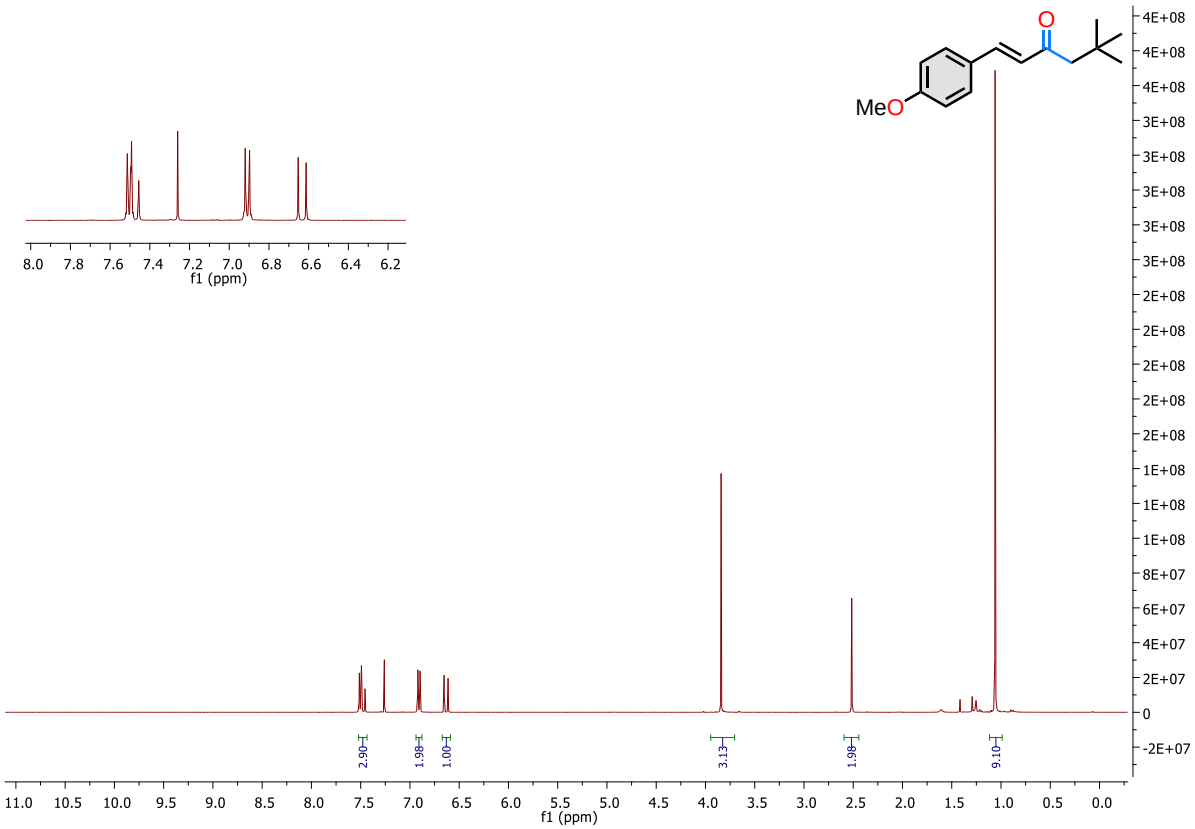

O
EtO
OEt
f1 (ppm)
198.55
151.36
149.00
143.84
127.32
125.24
124.97
123.12
112.84
112.03
64.77
64.64
27.46
14.91
14.84

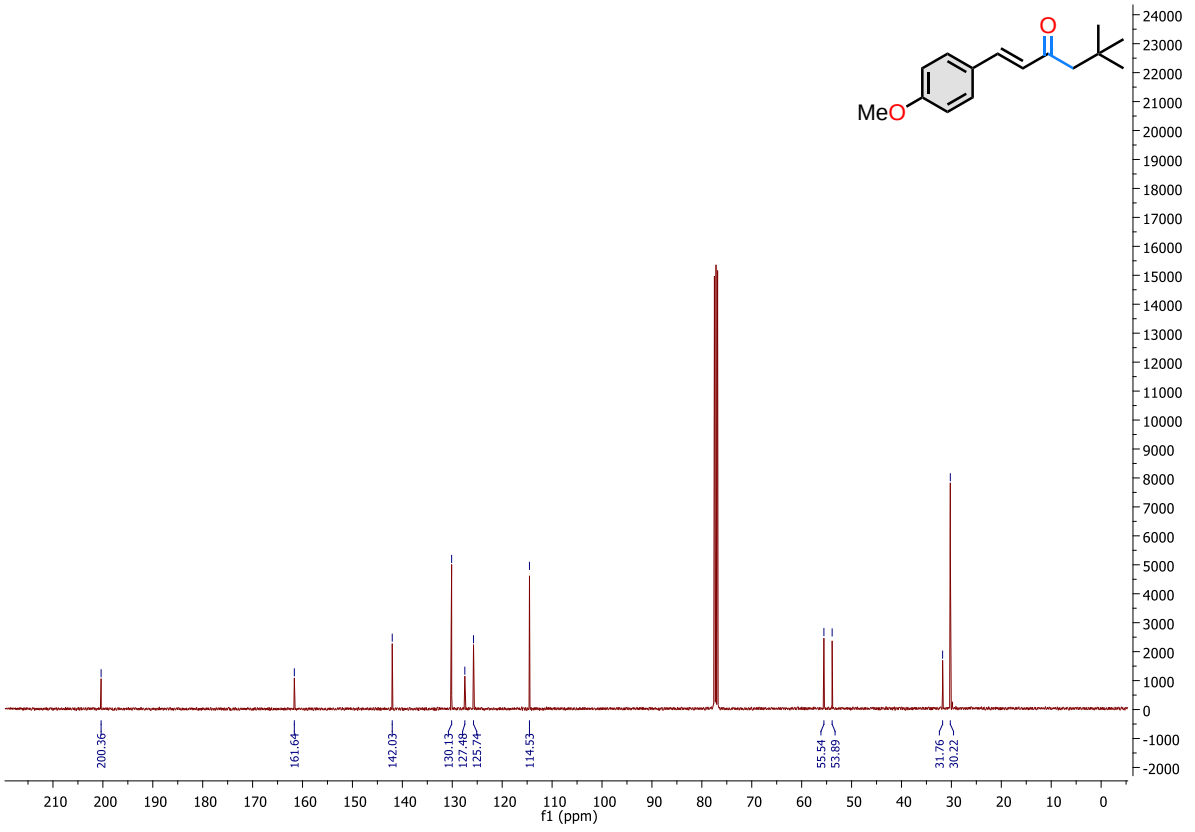

MeO
HO
O
f1 (ppm)
1.00
1.03
0.98
1.02
1.00
3.01
2.92

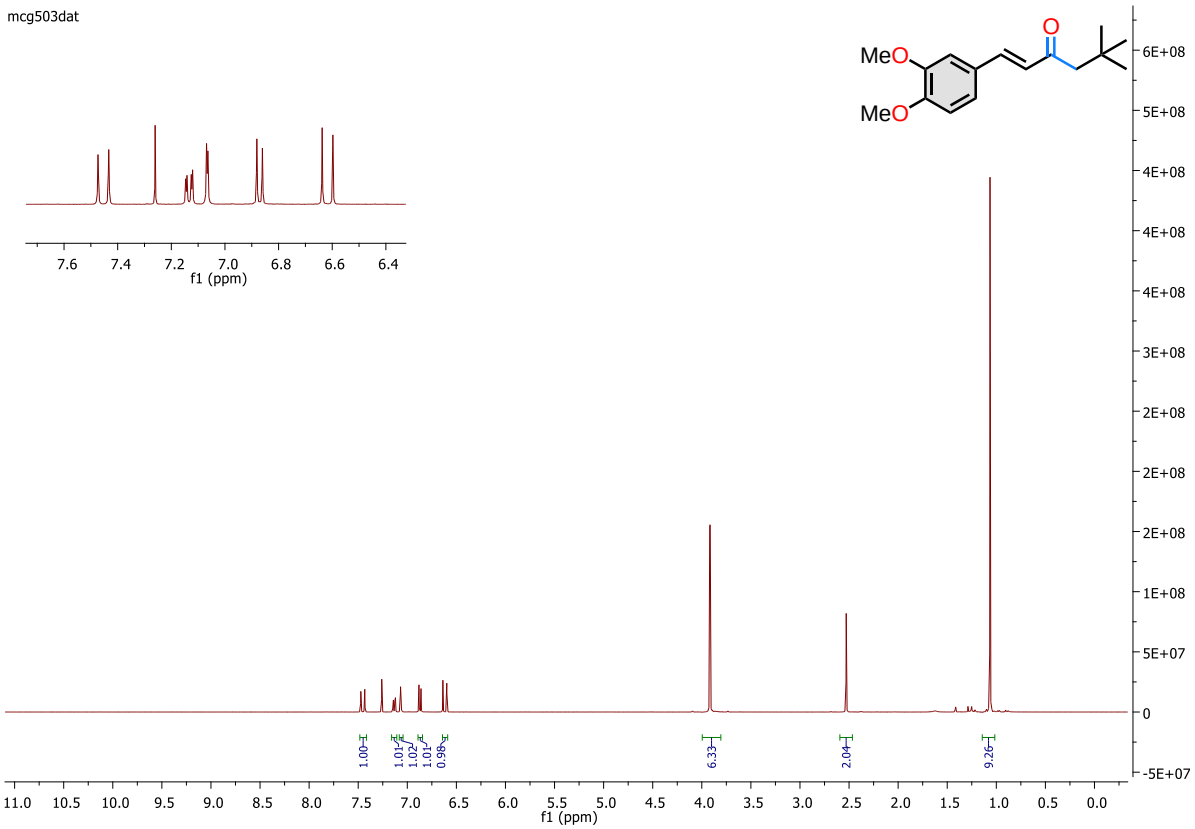

MeO
HO
O
f1 (ppm)
198.55
148.39
147.01
143.87
127.08
125.16
123.67
114.95
109.43
56.10
27.45

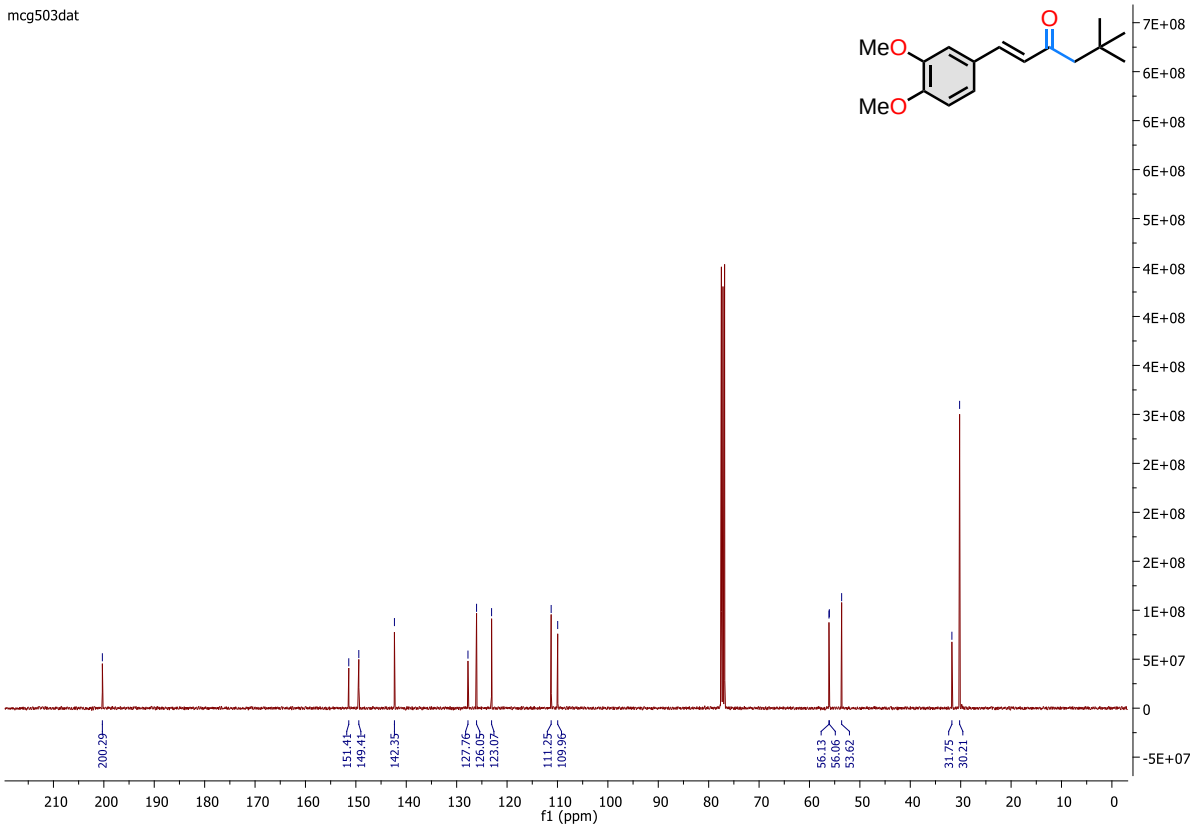

mcg916dat
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
O
2.98
3.01
1.00
3.12
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

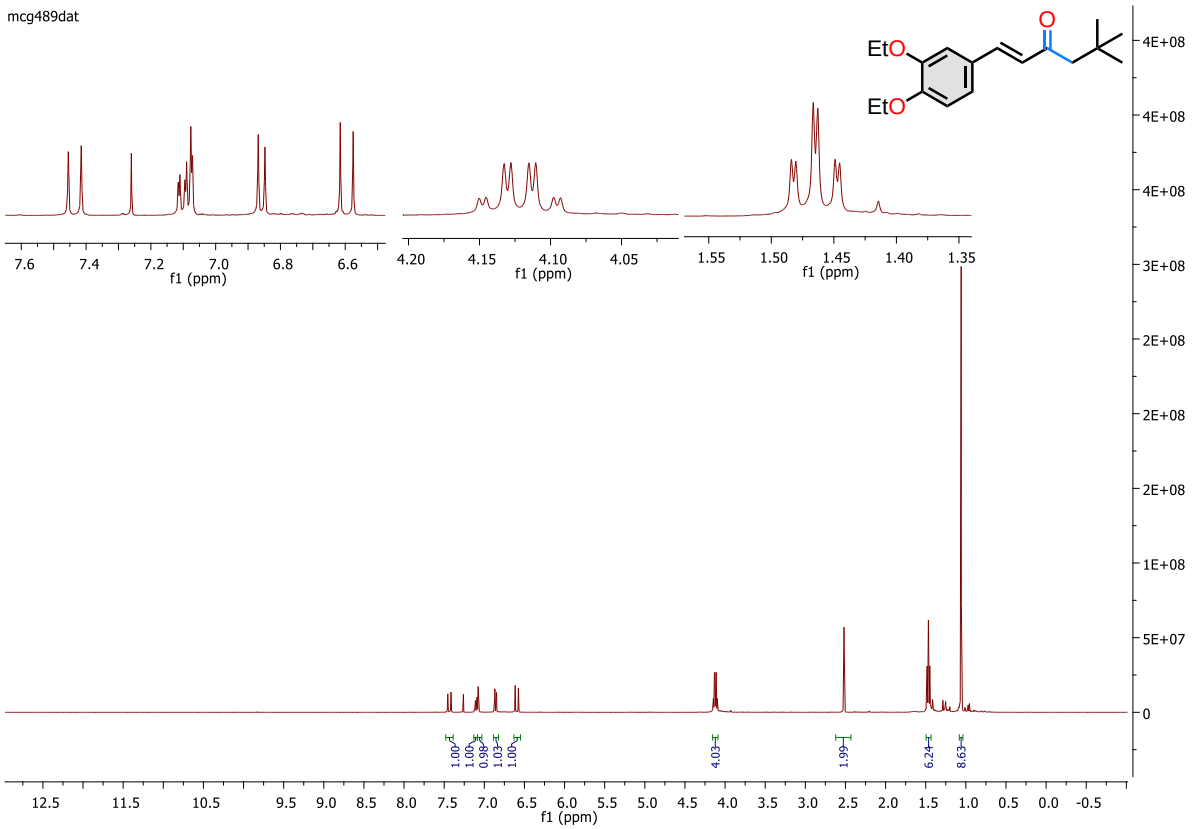

mcg916dat
O
198.54
143.59
134.60
130.67
129.13
128.41
127.34
27.67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

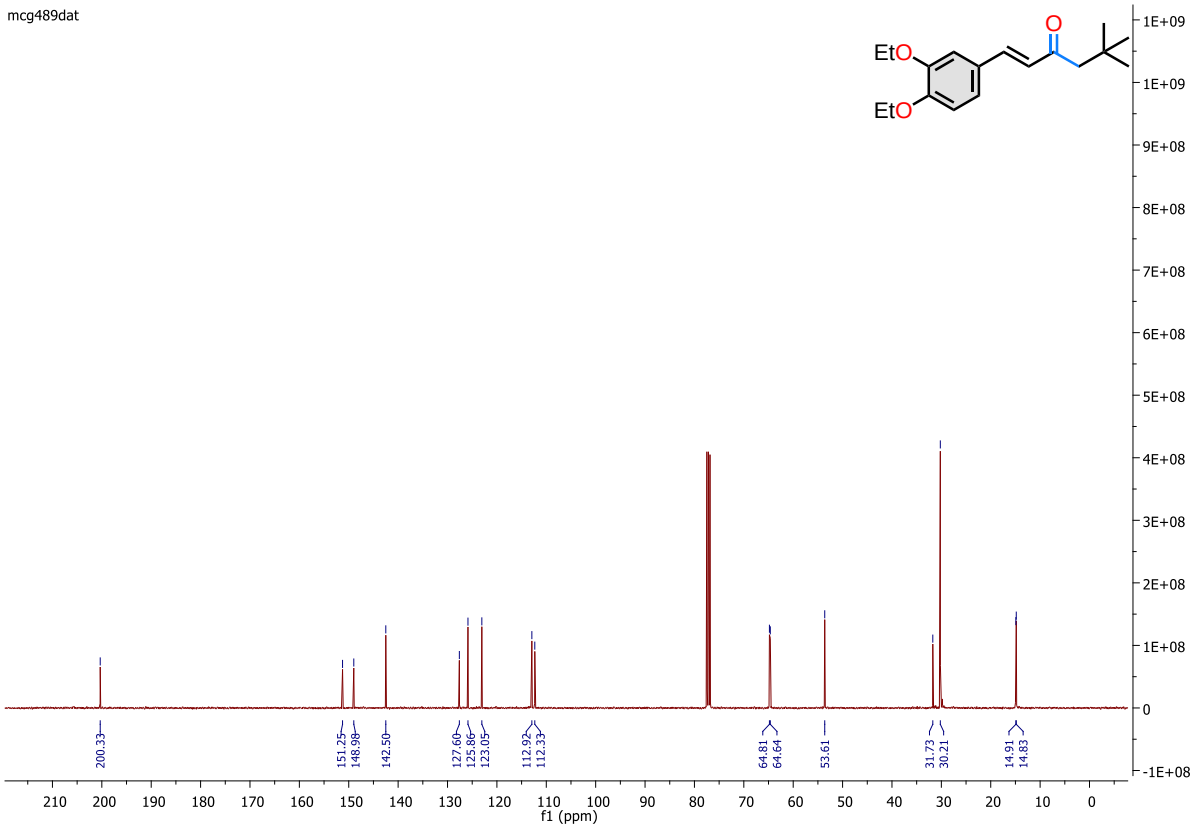

MeO
O
f1 (ppm)
2.90
1.98
1.00
3.13
1.98
9.10

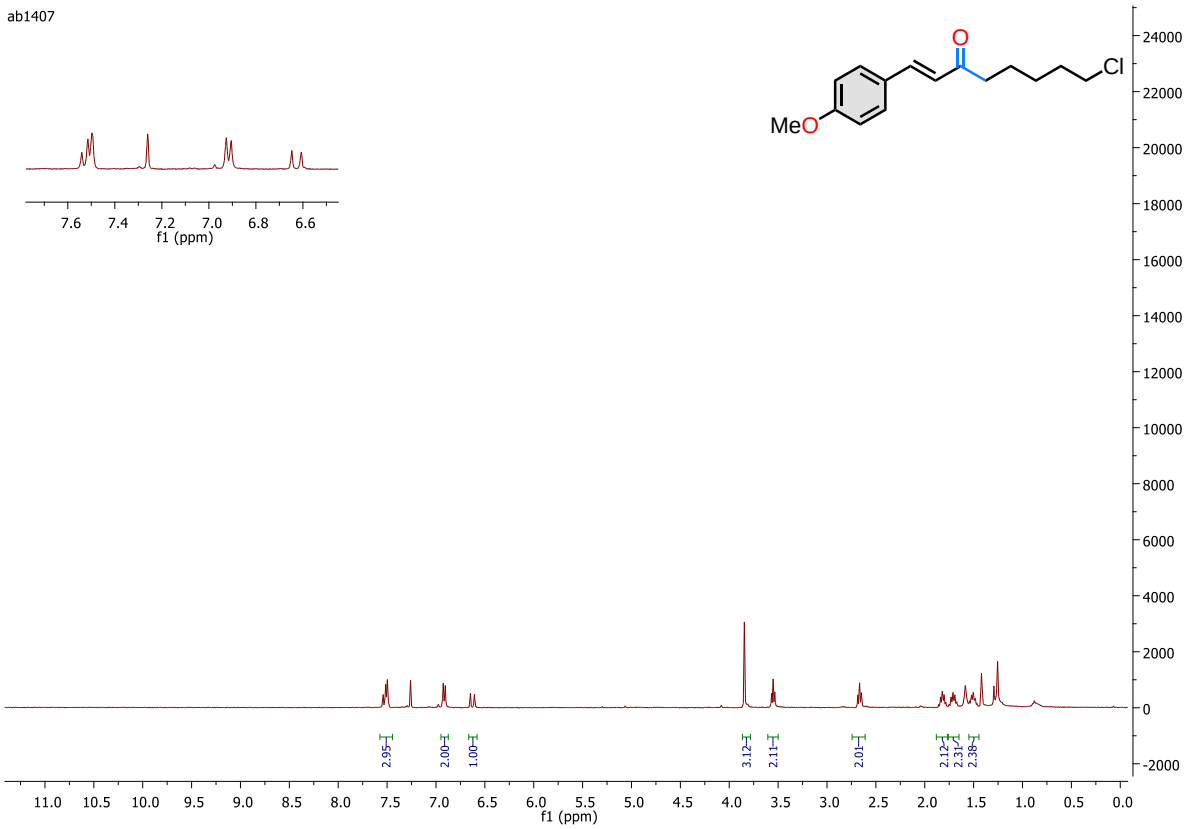

MeO
O
f1 (ppm)
200.36
161.64
142.03
130.13
127.48
125.74
114.53
55.54
53.89
31.76
30.22

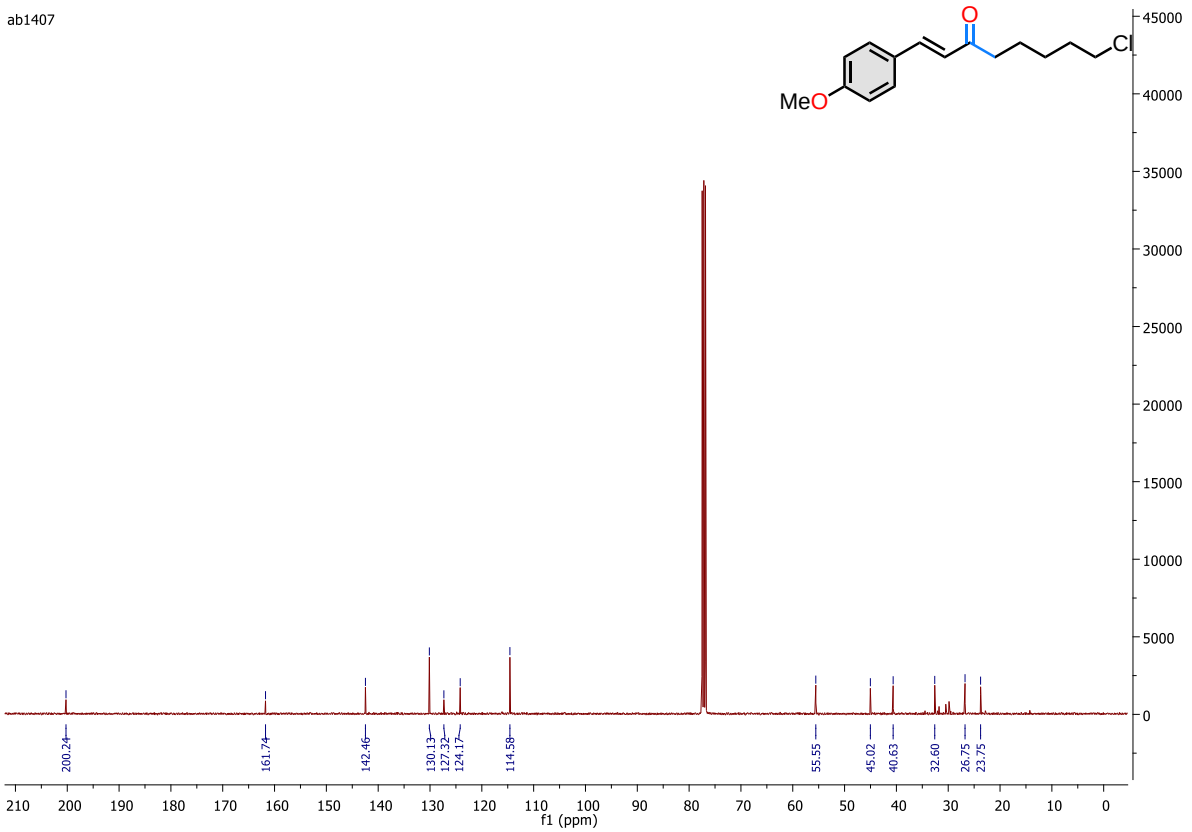

mcg503dat
MeO
MeO
O
f1 (ppm)
1.00
1.01
1.02
1.01
0.98
6.33
2.04
9.26

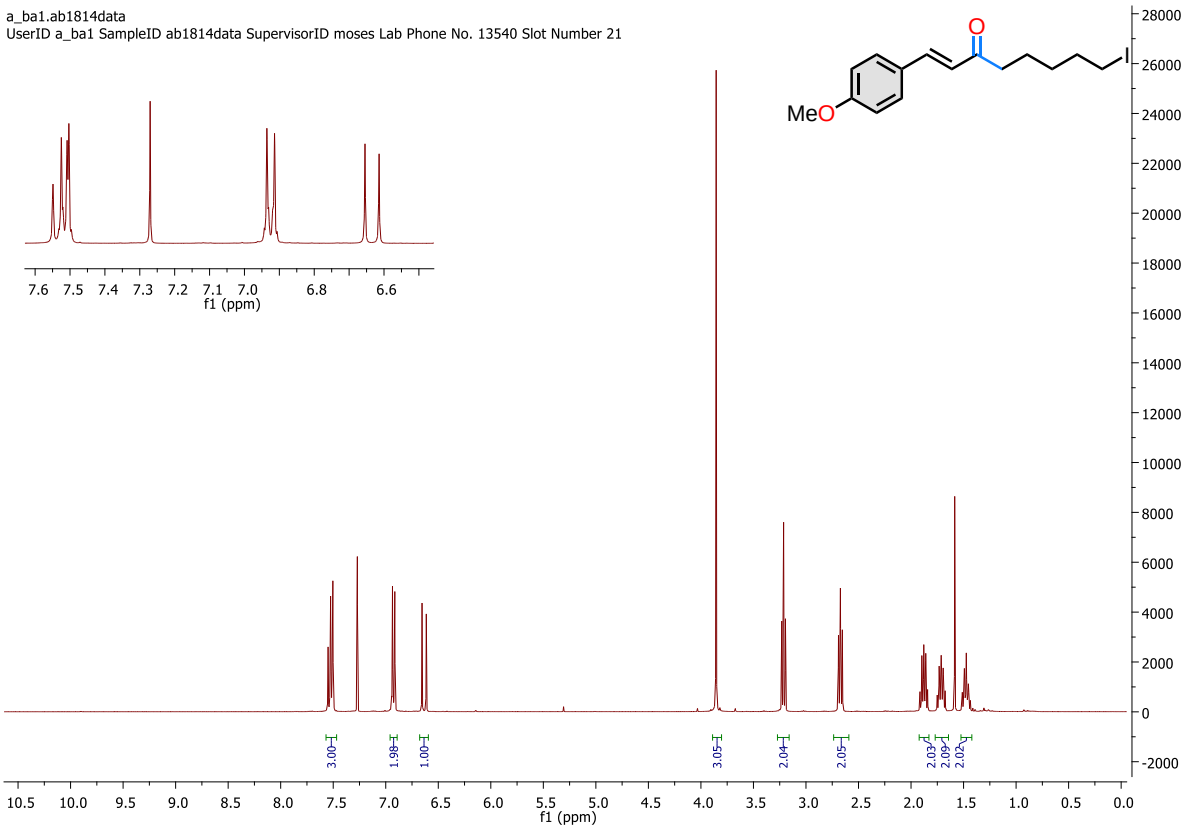

mcg503dat
MeO
MeO
O
f1 (ppm)
200.29
151.41
149.41
142.35
127.76
126.05
123.07
111.25
109.96
56.13
56.06
53.62
31.75
30.21

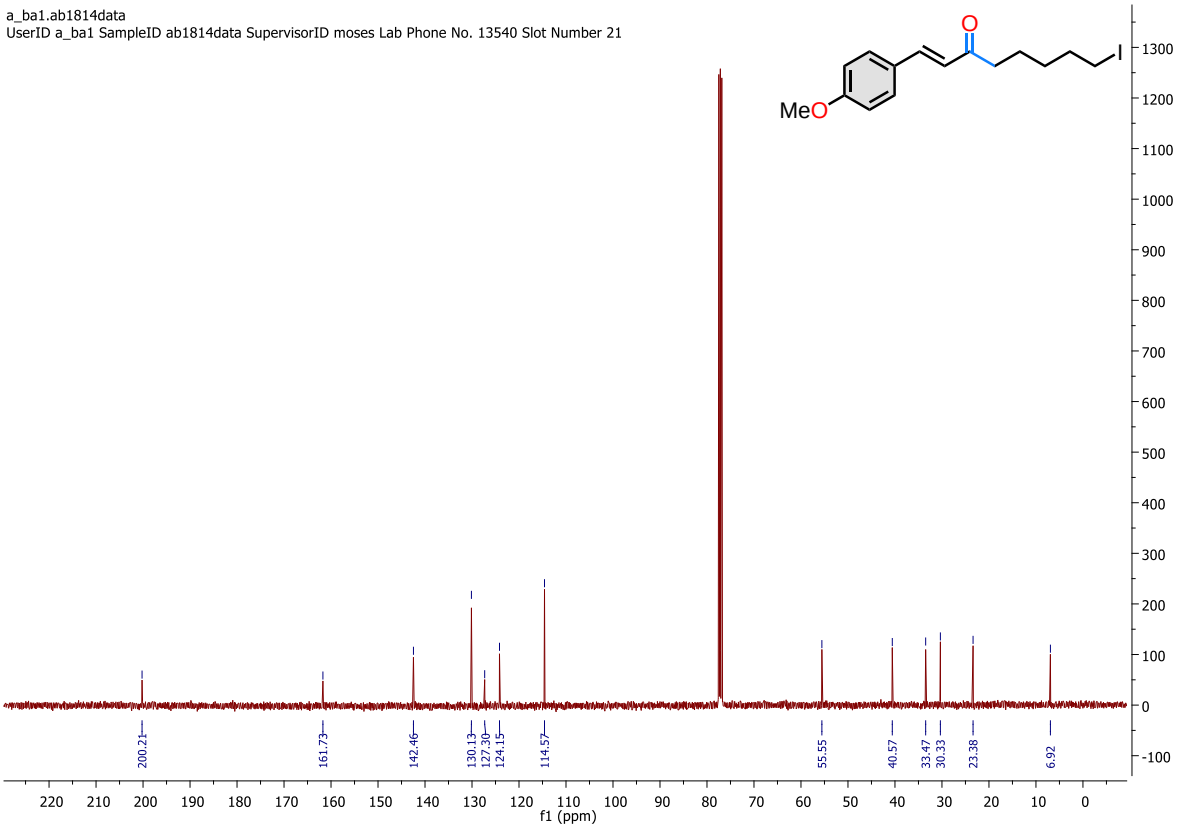

mcg489dat
EtO
EtO
O
f1 (ppm)
1.00
1.00
0.98
1.03
1.00
4.03
1.99
6.24
8.63

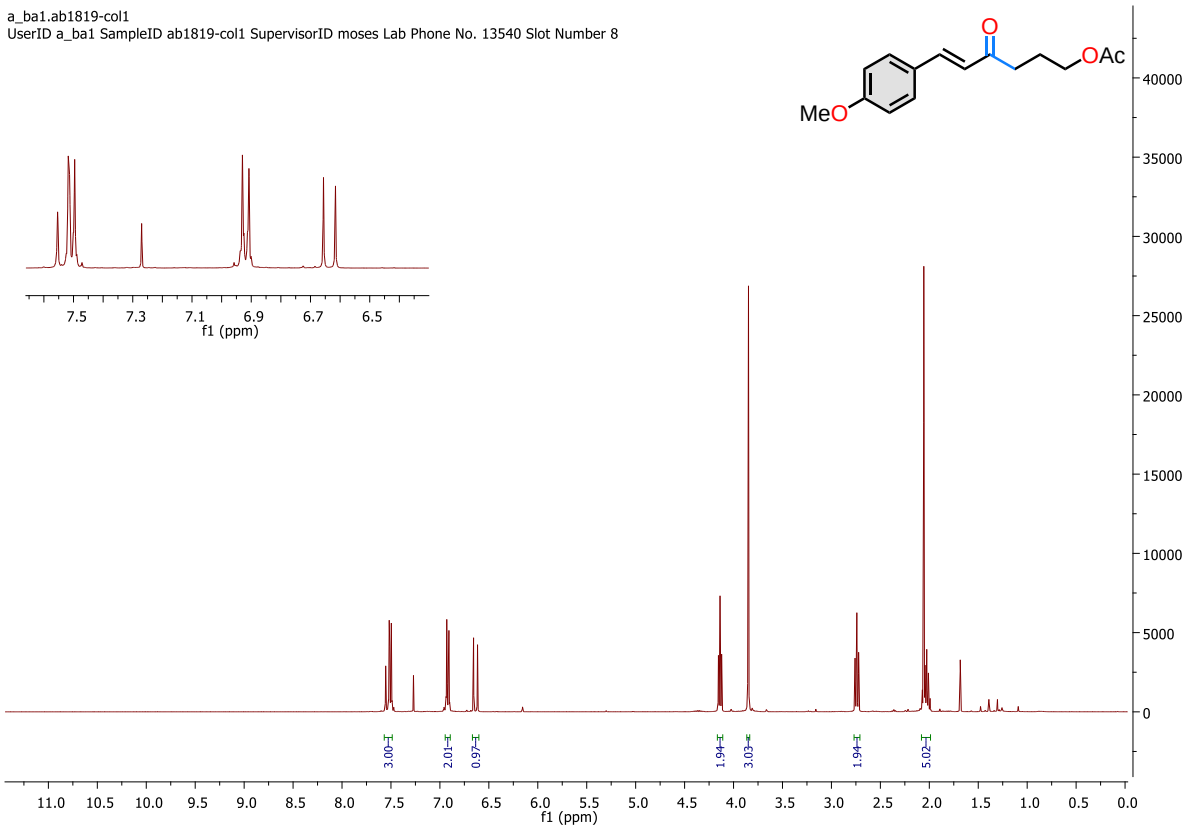

mcg489dat
EtO
EtO
O
f1 (ppm)
200.33
151.25
148.98
142.50
127.60
125.86
123.05
112.92
112.33
64.81
64.64
53.61
31.73
30.21
14.91
14.83

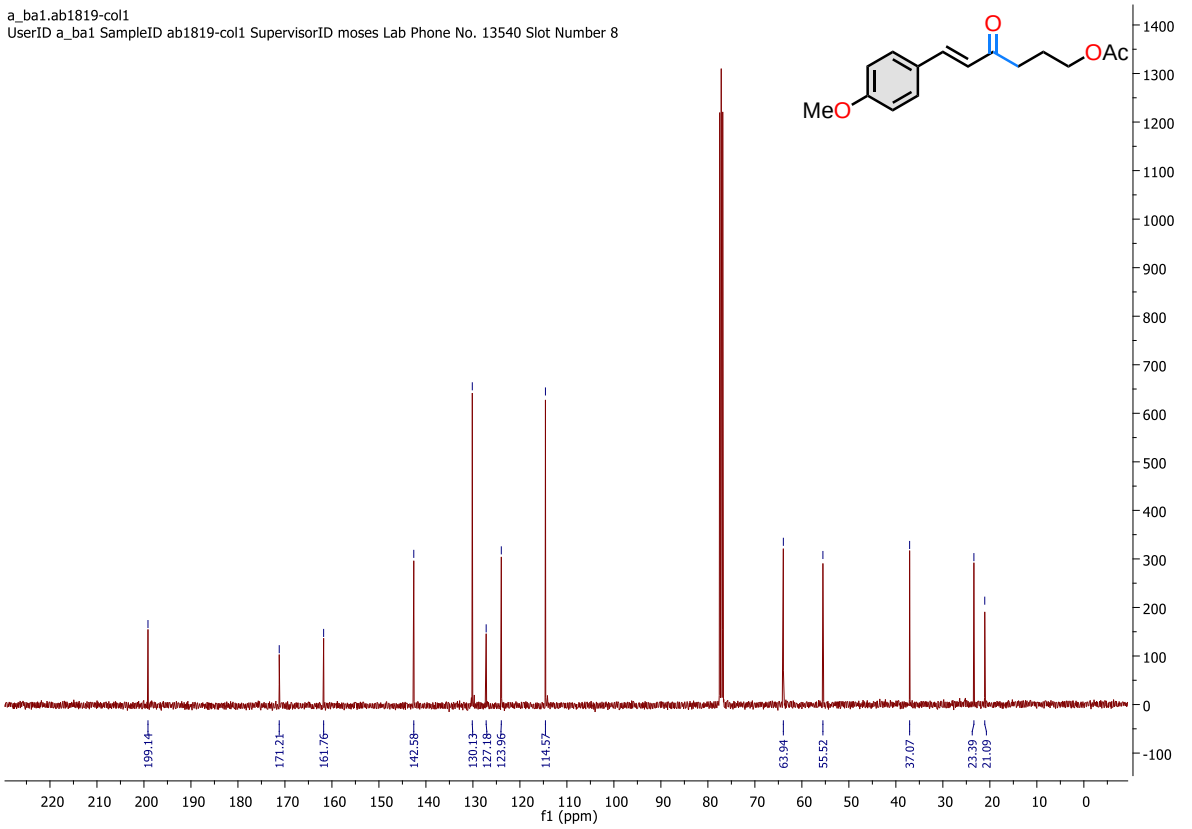

ab1407
O
Cl
MeO
7.6
7.4
7.2
7.0
6.8
6.6
f1 (ppm)
2.95
2.00
1.00
3.12
2.11
2.01
2.12
2.31
2.38
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

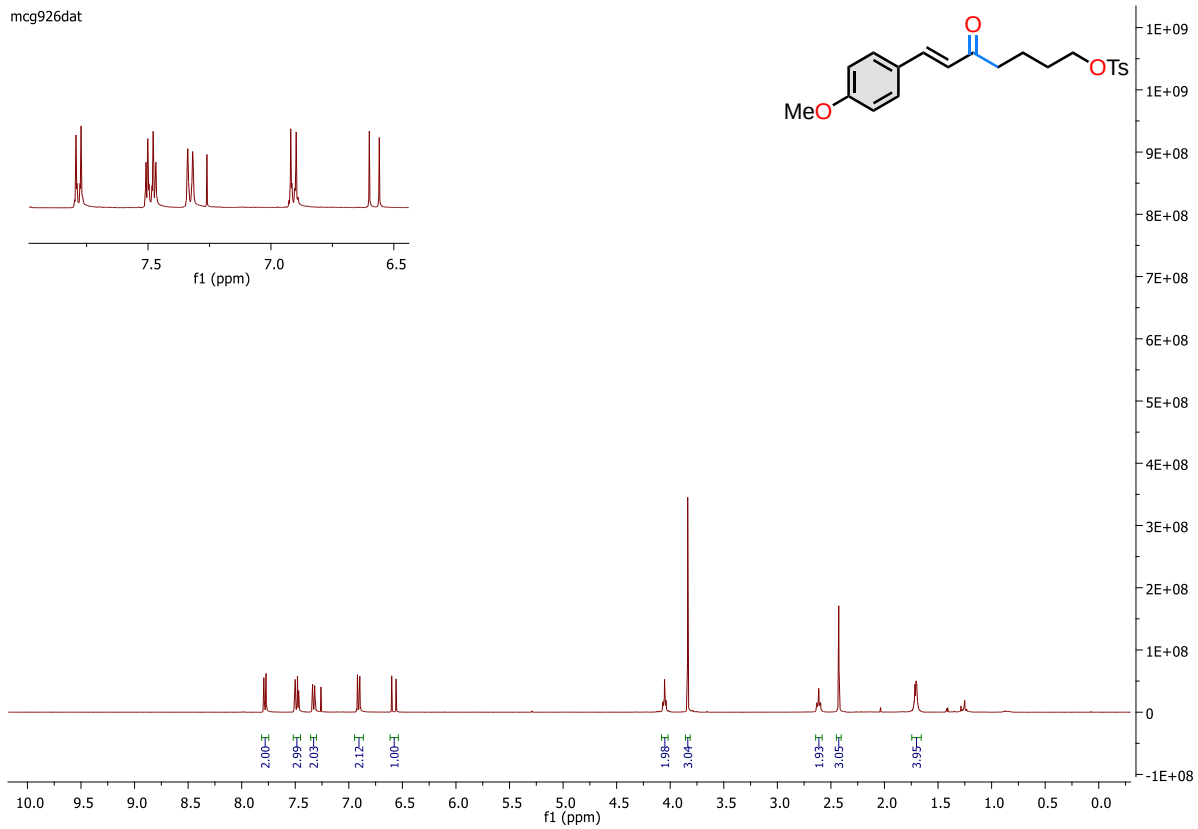

ab1407
O
Cl
MeO
200.24
161.74
142.46
130.13
127.32
124.17
114.58
55.55
45.02
40.63
32.60
26.75
23.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

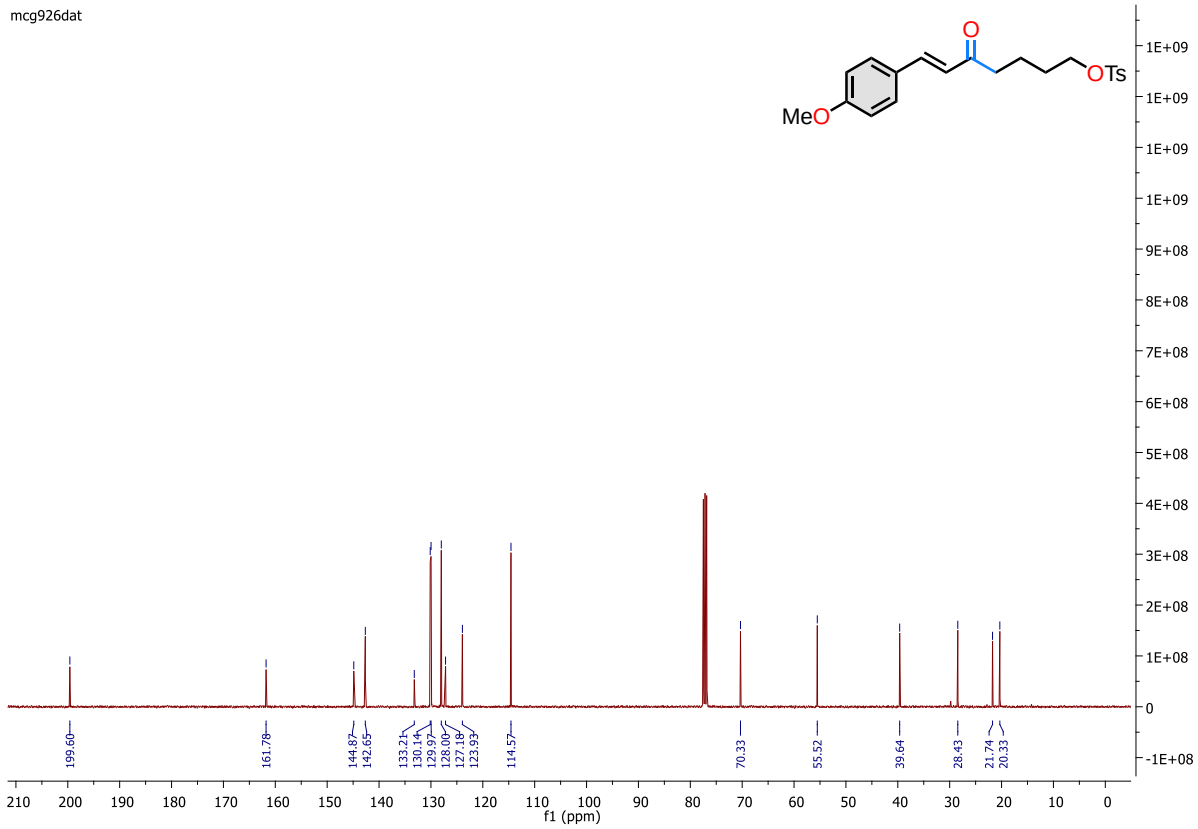

a_ba1.ab1814data
UserID a_ba1 SampleID ab1814data SupervisorID moses Lab Phone No. 13540 Slot Number 21
MeO
O
I
f1 (ppm)
3.00
1.98
1.00
3.05
2.04
2.05
2.03
2.09
2.02

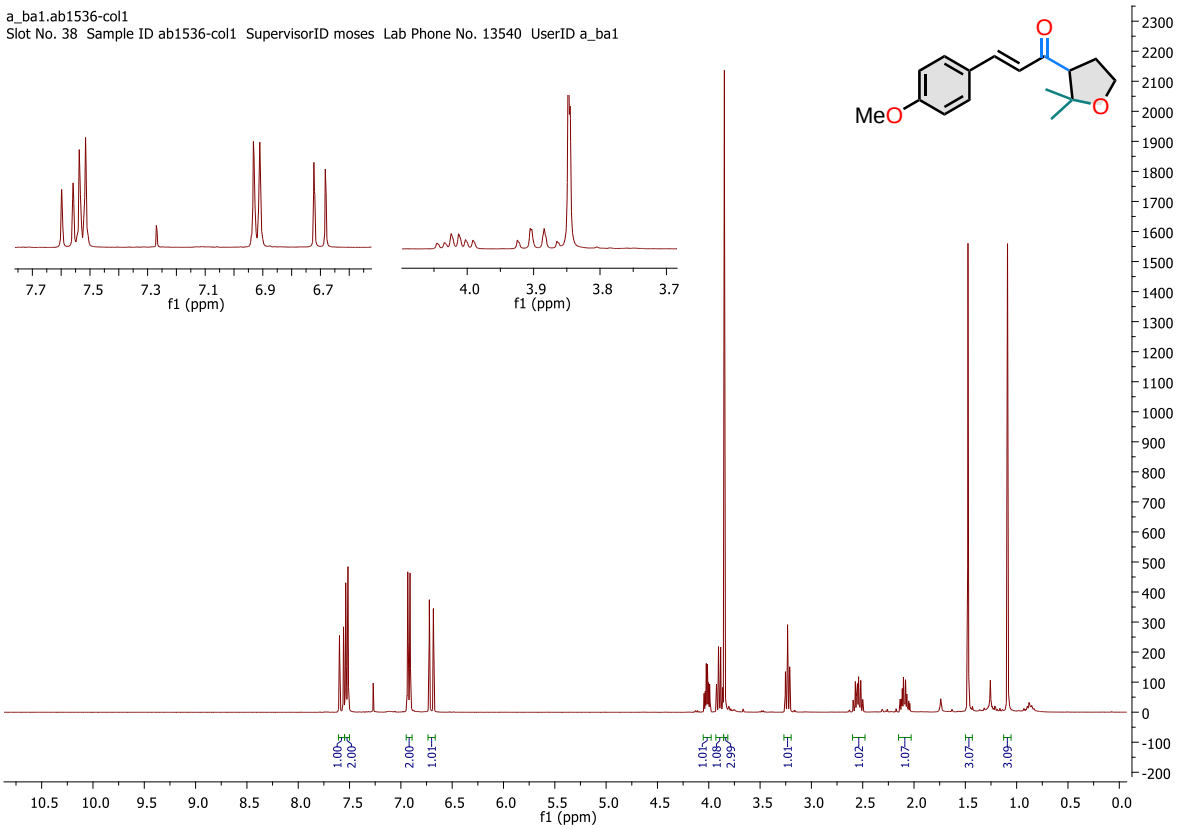

a_ba1.ab1814data
UserID a_ba1 SampleID ab1814data SupervisorID moses Lab Phone No. 13540 Slot Number 21
MeO
O
I
f1 (ppm)
200.21
161.73
142.46
130.13
127.39
124.15
114.57
55.55
40.57
33.47
30.33
23.38
6.92

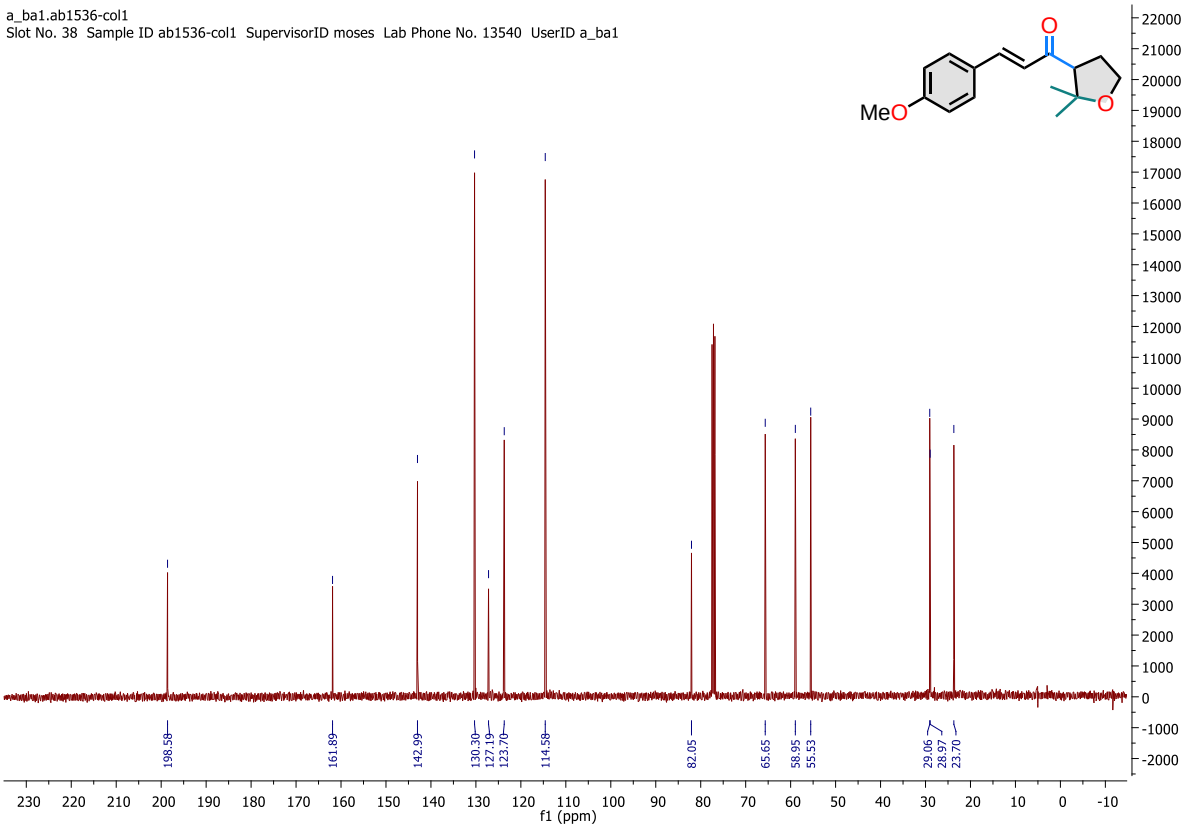

a_ba1.ab1819-col1
UserID a_ba1 SampleID ab1819-col1 SupervisorID moses Lab Phone No. 13540 Slot Number 8
O
OAc
MeO
7.5
7.3
7.1
6.9
6.7
6.5
f1 (ppm)
40000
35000
30000
25000
20000
15000
10000
5000
0
3.00
2.01
0.97
1.94
3.03
1.94
5.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

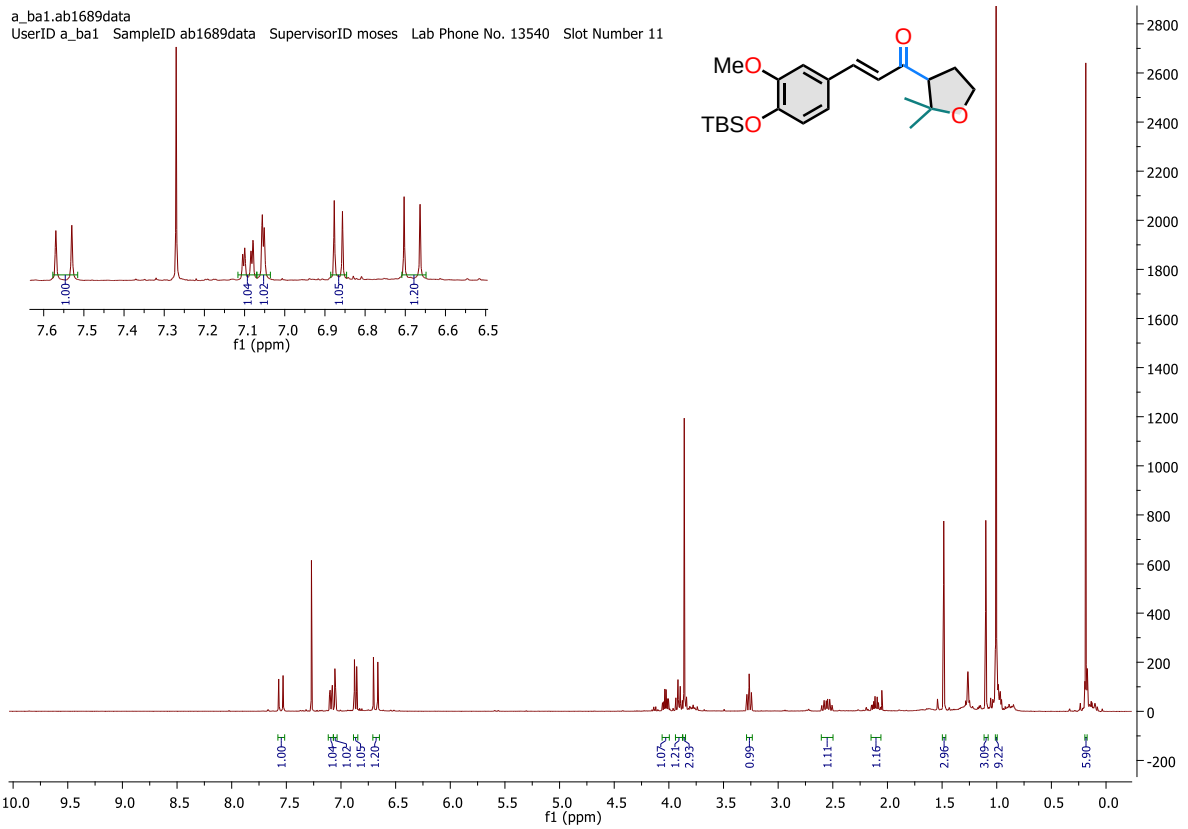

a_ba1.ab1819-col1
UserID a_ba1 SampleID ab1819-col1 SupervisorID moses Lab Phone No. 13540 Slot Number 8
O
OAc
MeO
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
199.14
171.21
161.76
142.58
130.13
127.18
123.96
114.57
63.94
55.52
37.07
23.39
21.09
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

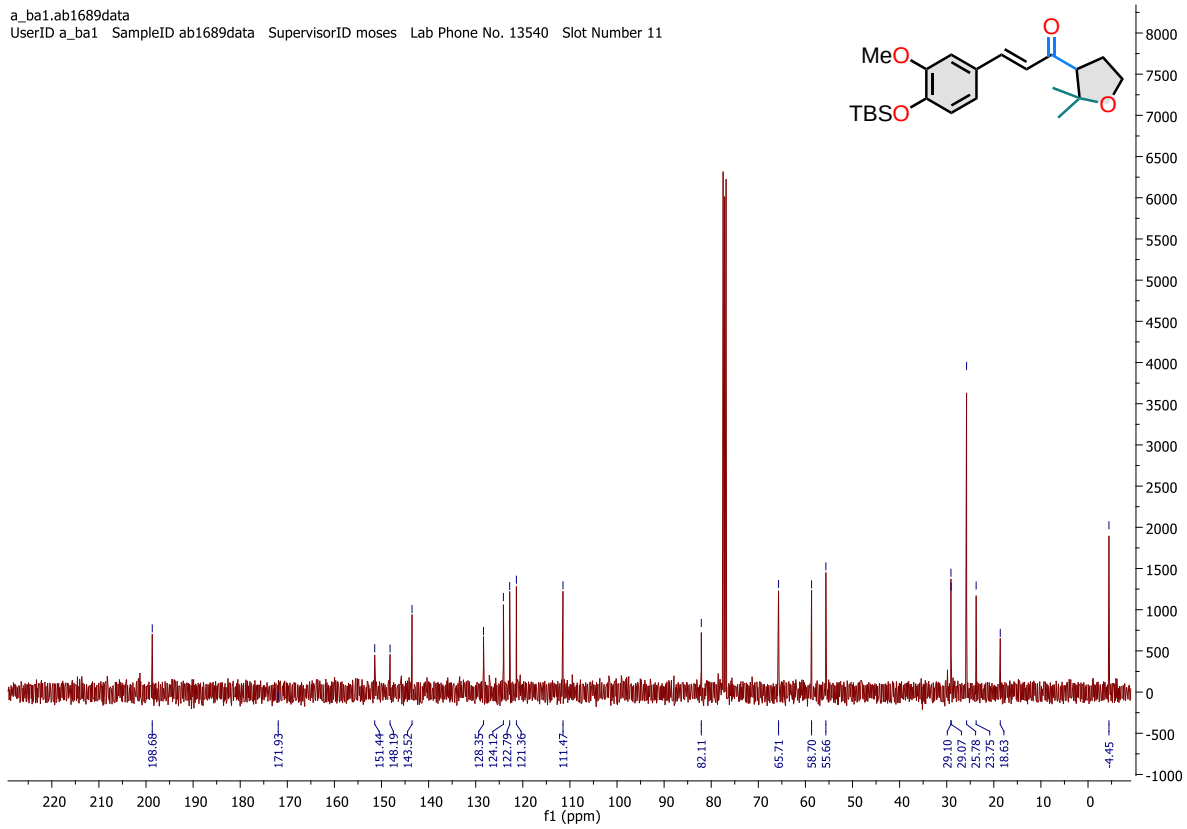

mcg926dat
MeO
O
OTs
f1 (ppm)
2.00
2.99
2.03
2.12
1.00
1.98
3.04
1.93
3.05
3.95

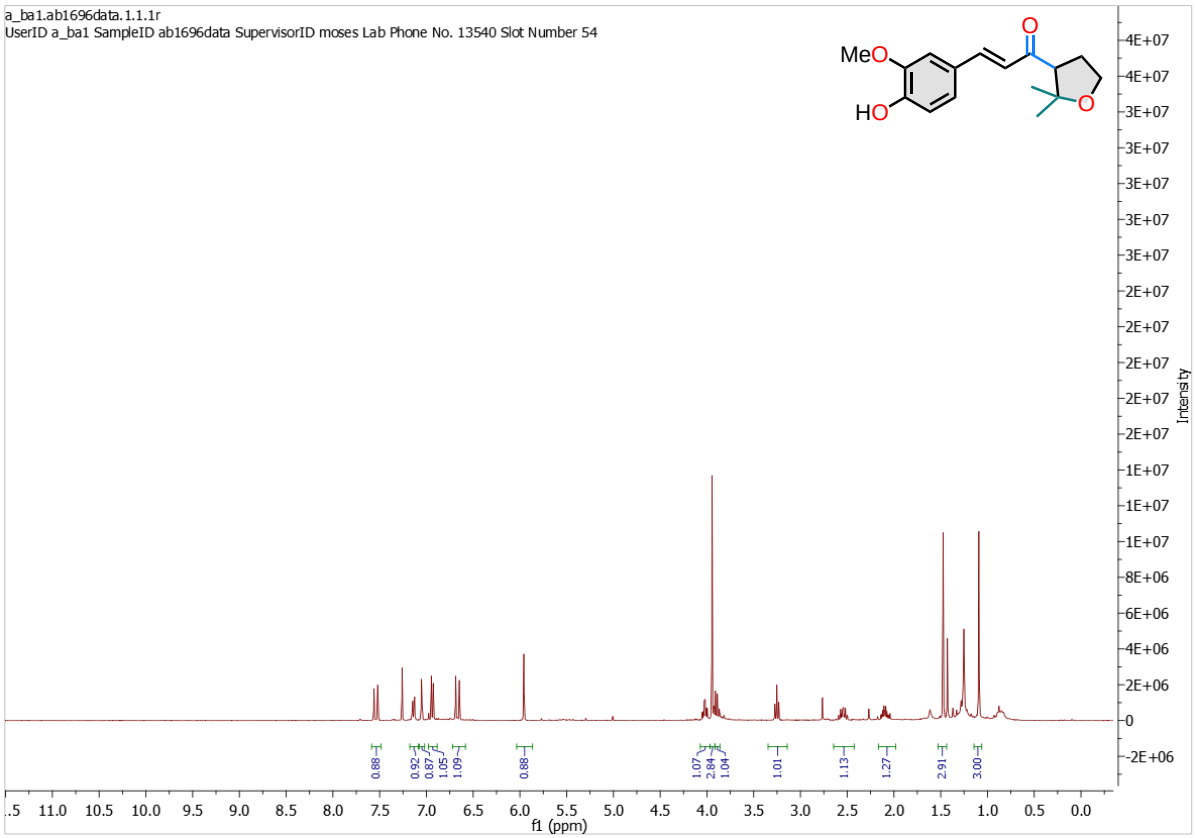

mcg926dat
MeO
O
OTs
f1 (ppm)
199.60
161.78
144.87
142.65
133.21
130.14
129.97
128.00
127.18
123.93
114.57
70.33
55.52
39.64
28.43
21.74
20.33

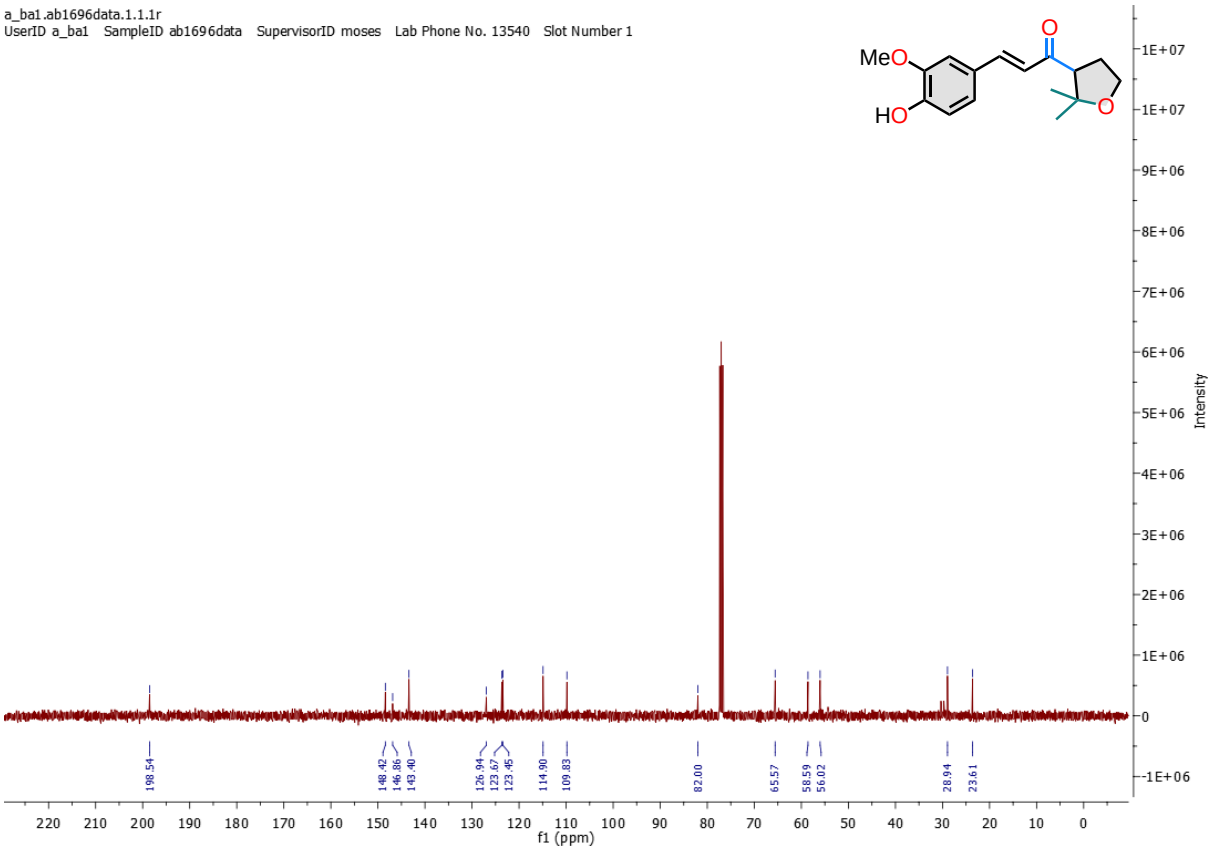

a_ba1.ab1536-col1
Slot No. 38 Sample ID ab1536-col1 SupervisorID moses Lab Phone No. 13540 UserID a_ba1
MeO
O
O
f1 (ppm)
1.00
2.00
2.00
1.01
1.01
1.08
2.99
1.01
1.02
1.07
3.07
3.09

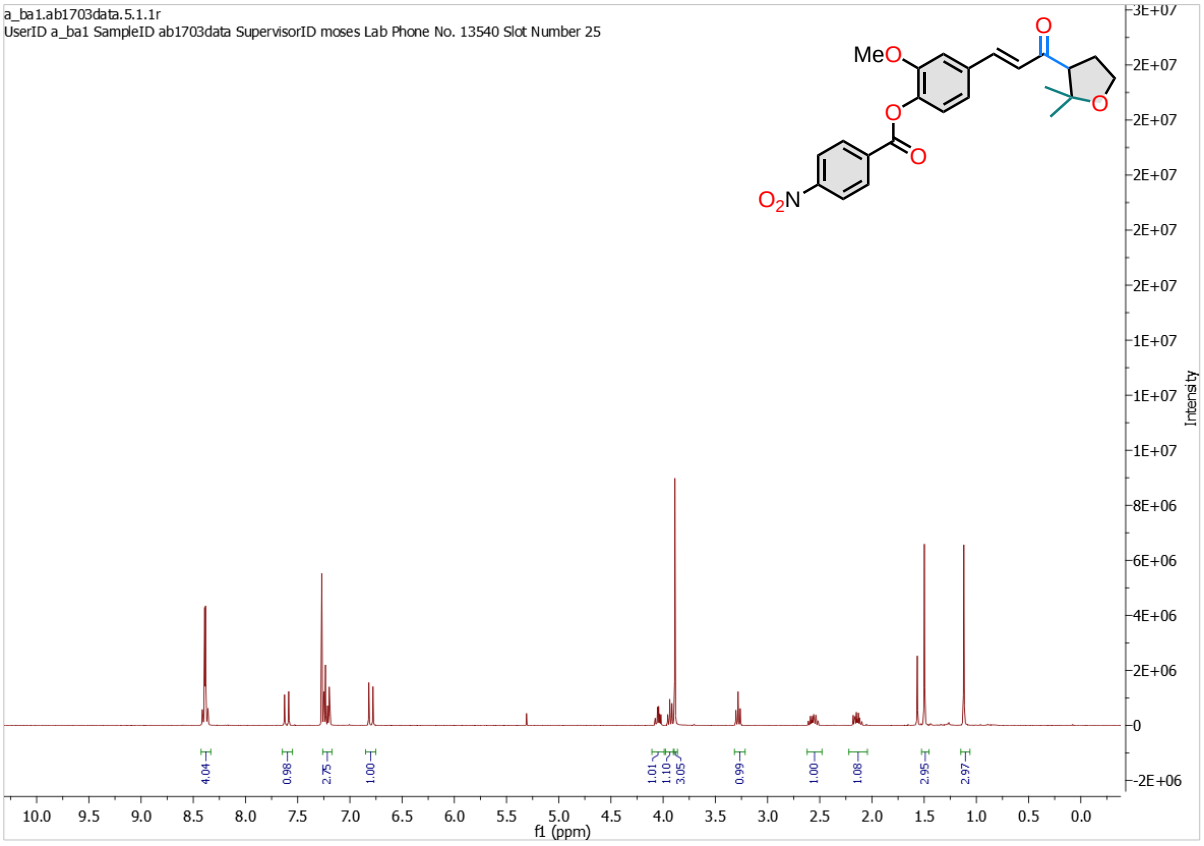

a_ba1.ab1536-col1
Slot No. 38 Sample ID ab1536-col1 SupervisorID moses Lab Phone No. 13540 UserID a_ba1
MeO
O
O
f1 (ppm)
198.58
161.89
142.99
130.30
127.19
123.70
114.58
82.05
65.65
58.95
55.53
29.06
28.97
23.70

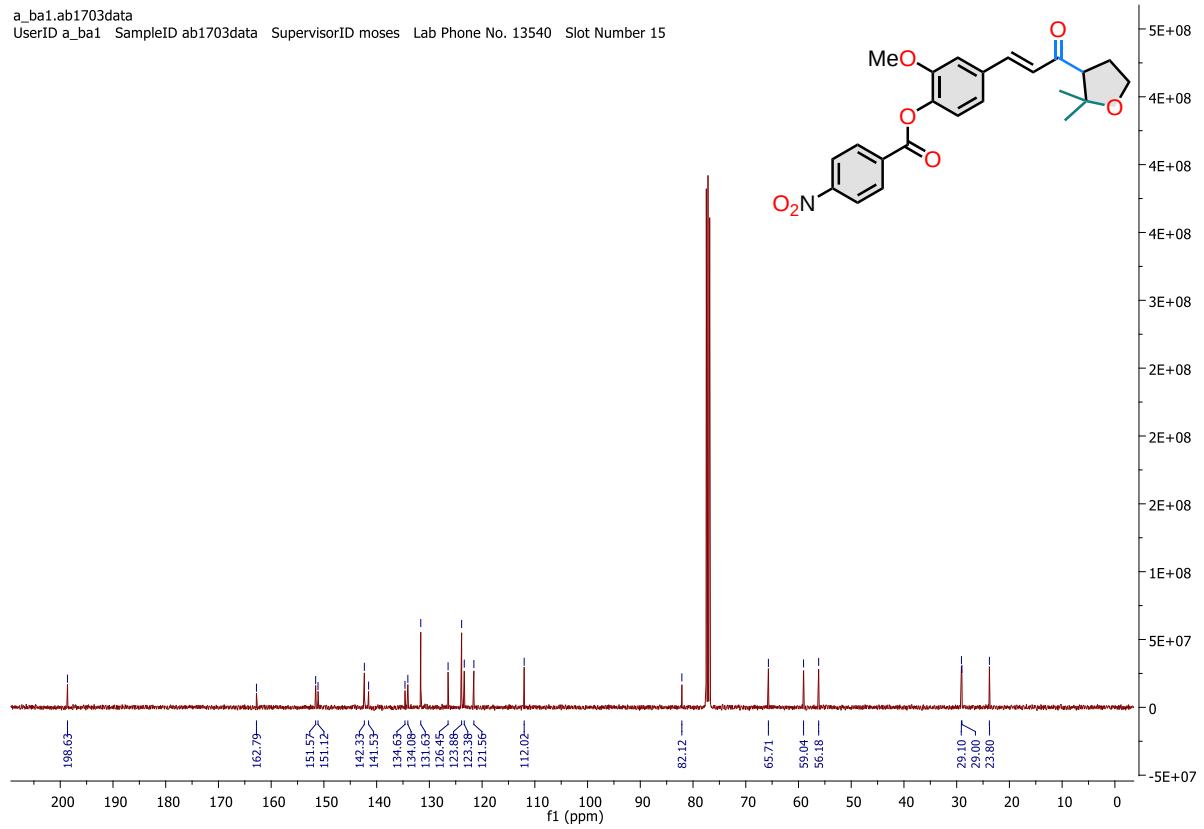

a_ba1.ab1689data
UserID a_ba1 SampleID ab1689data SupervisorID moses Lab Phone No. 13540 Slot Number 11
MeO
TBSO
O
O
f1 (ppm)

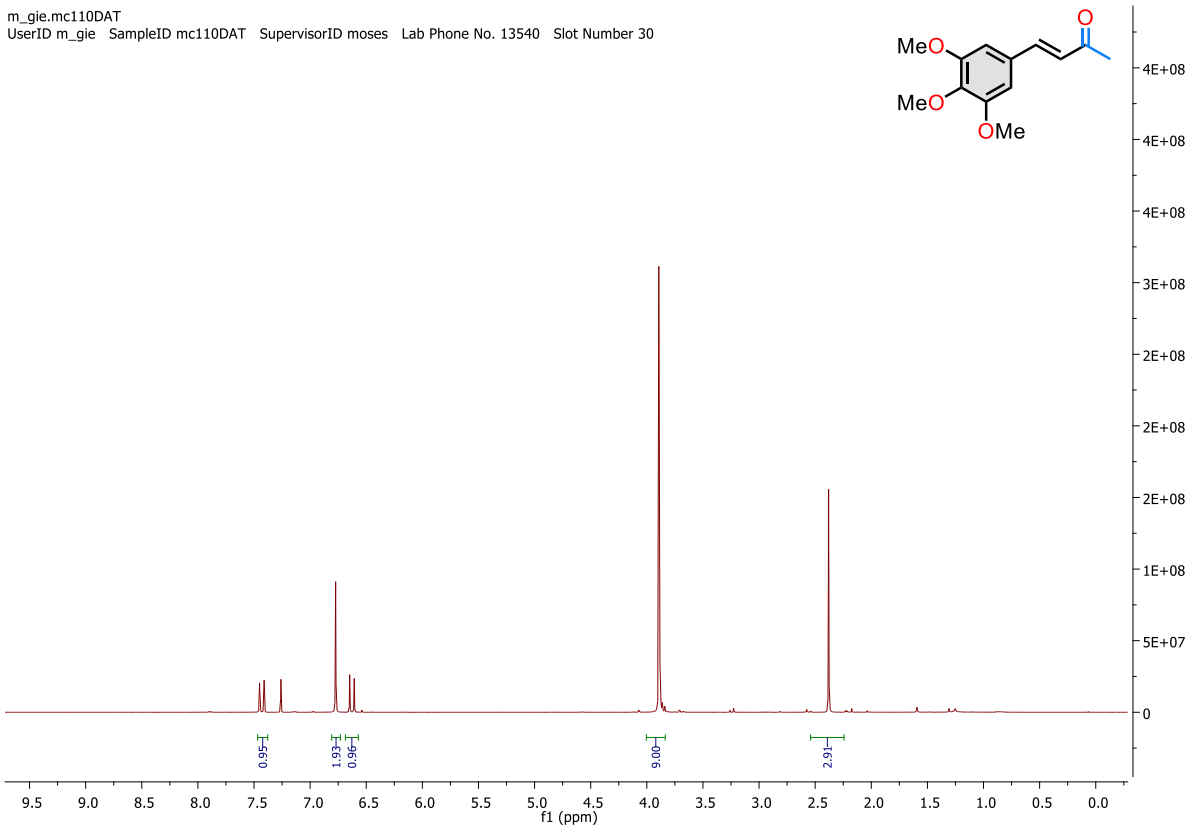

a_ba1.ab1689data
UserID a_ba1 SampleID ab1689data SupervisorID moses Lab Phone No. 13540 Slot Number 11
MeO
TBSO
O
O
f1 (ppm)

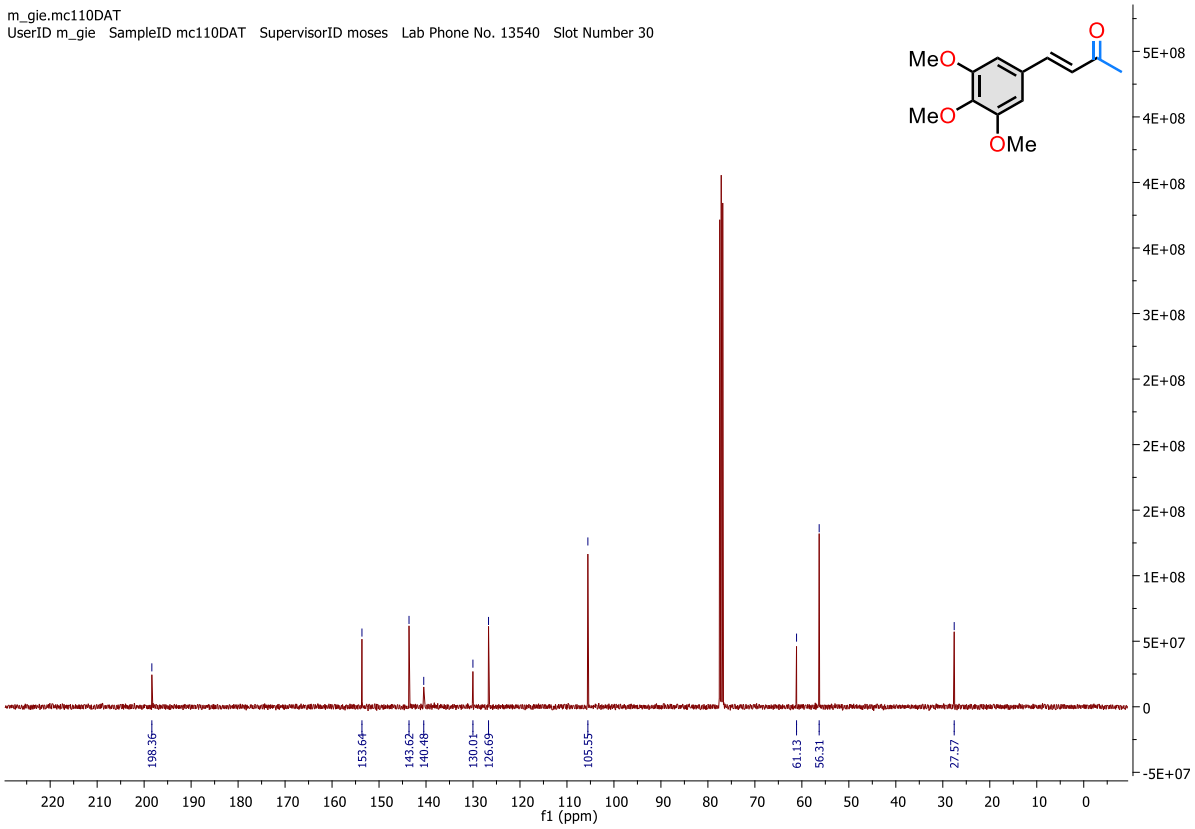

a_ba1.ab1696data.1.1.1r
UserID a_ba1 SampleID ab1696data SupervisorID moses Lab Phone No. 13540 Slot Number 54
MeO
HO
O
O
Intensity
f1 (ppm)

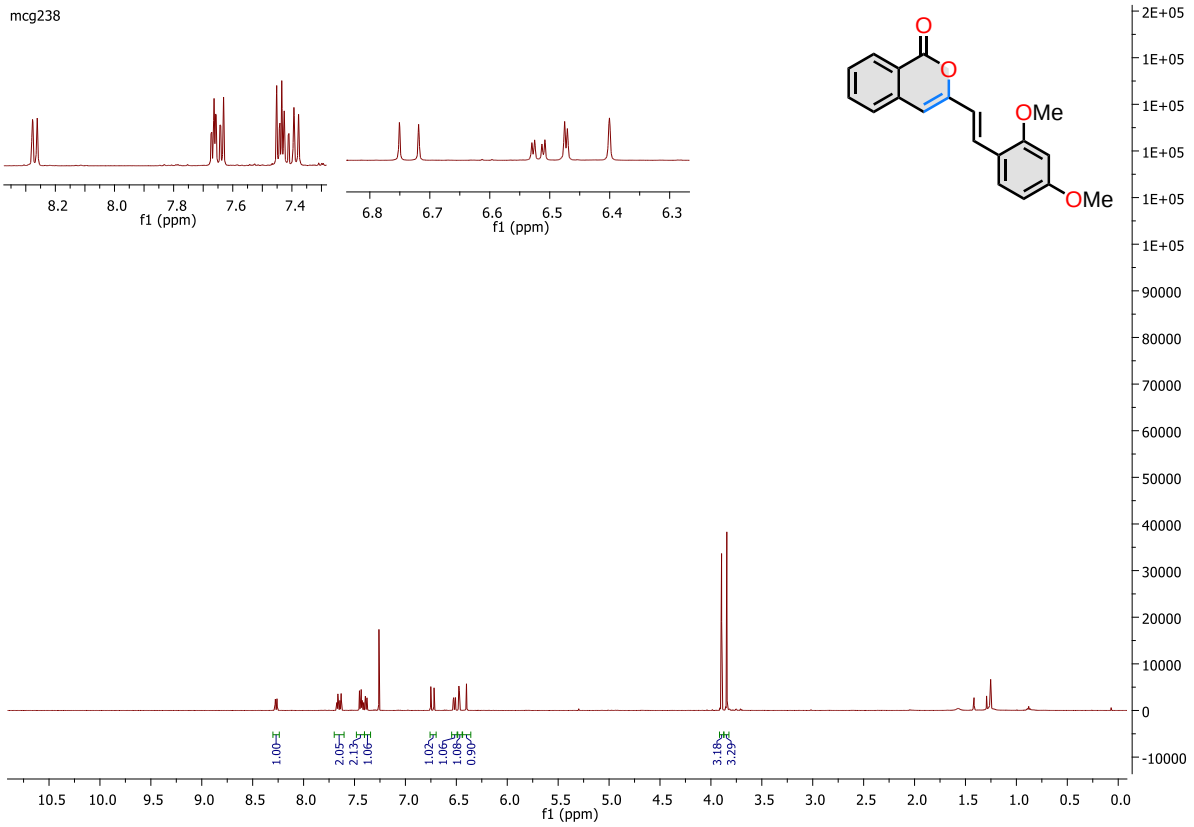

a_ba1.ab1696data.1.1.1r
UserID a_ba1 SampleID ab1696data SupervisorID moses Lab Phone No. 13540 Slot Number 1
MeO
HO
O
O
Intensity
f1 (ppm)

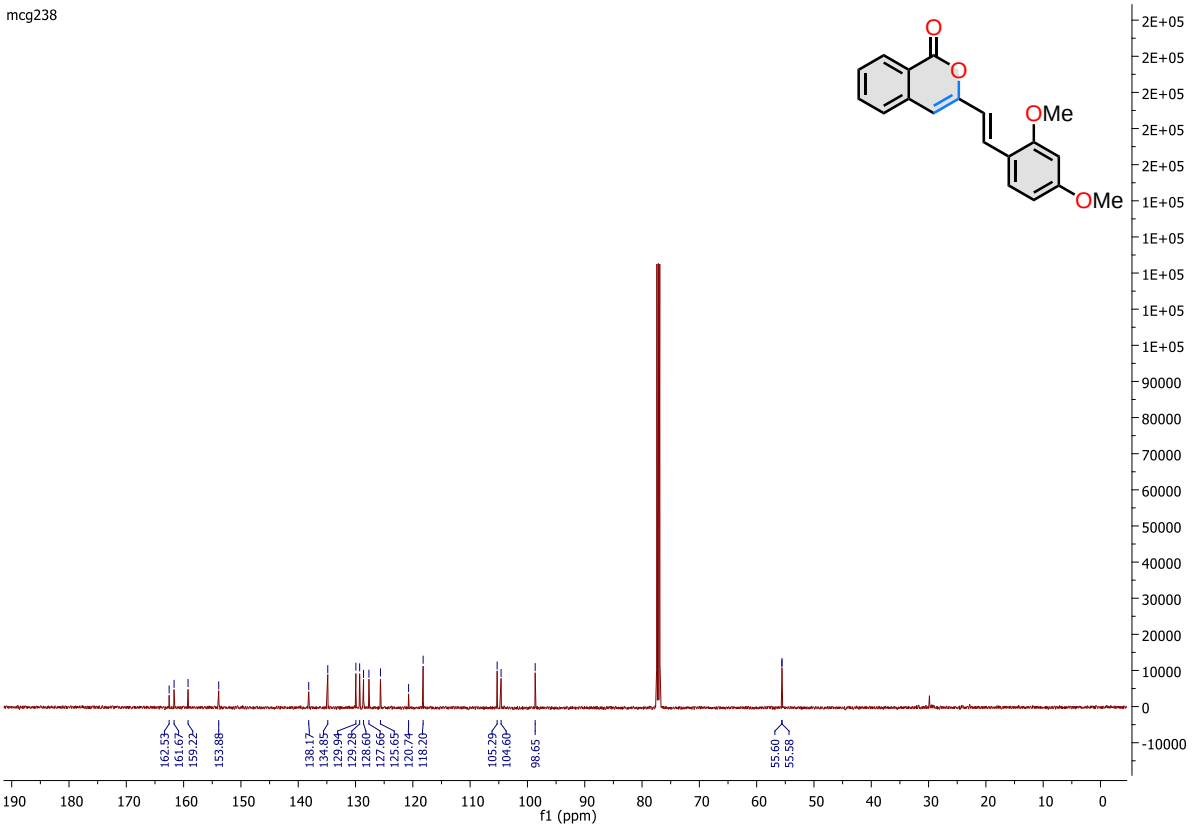

a_ba1.ab1703data.5.1.1r
UserID a_ba1 SampleID ab1703data SupervisorID moses Lab Phone No. 13540 Slot Number 25
MeO
O
O
O
O2N
Intensity
f1 (ppm)

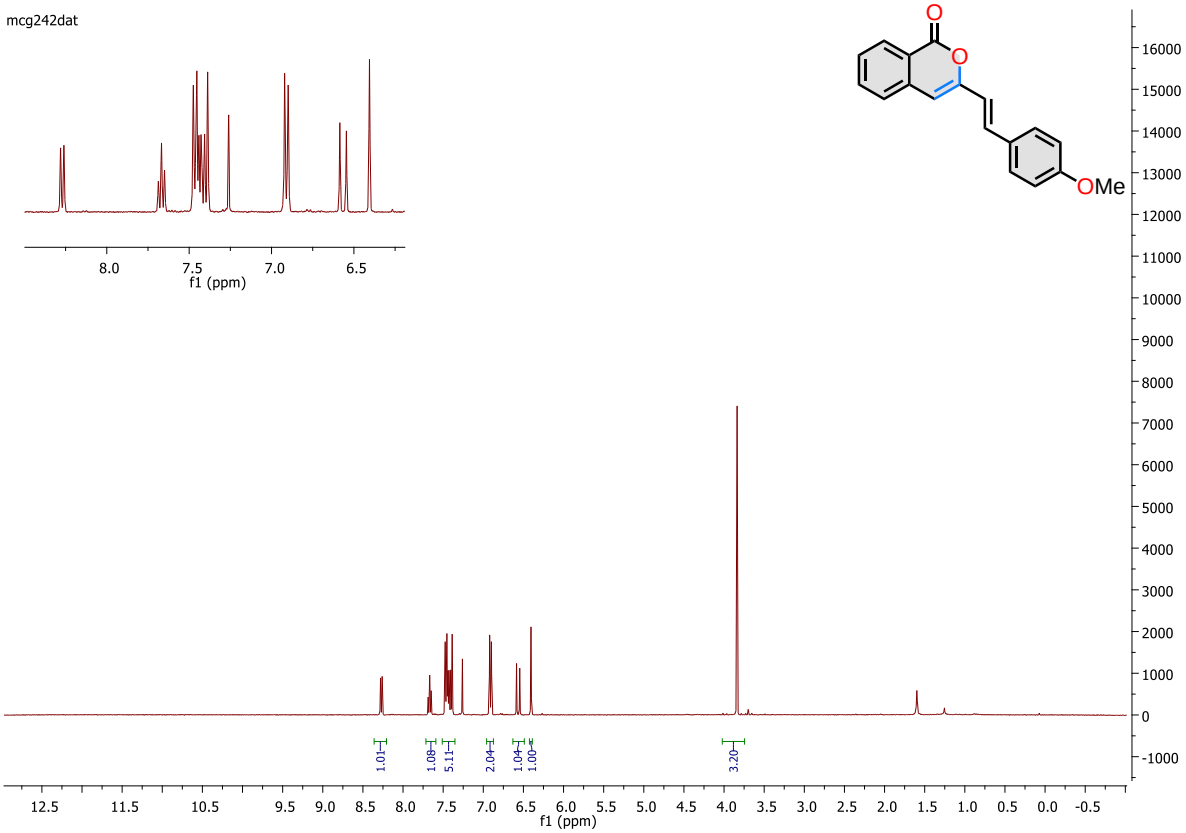

a_ba1.ab1703data
UserID a_ba1 SampleID ab1703data SupervisorID moses Lab Phone No. 13540 Slot Number 15
MeO
O
O
O
O2N
f1 (ppm)

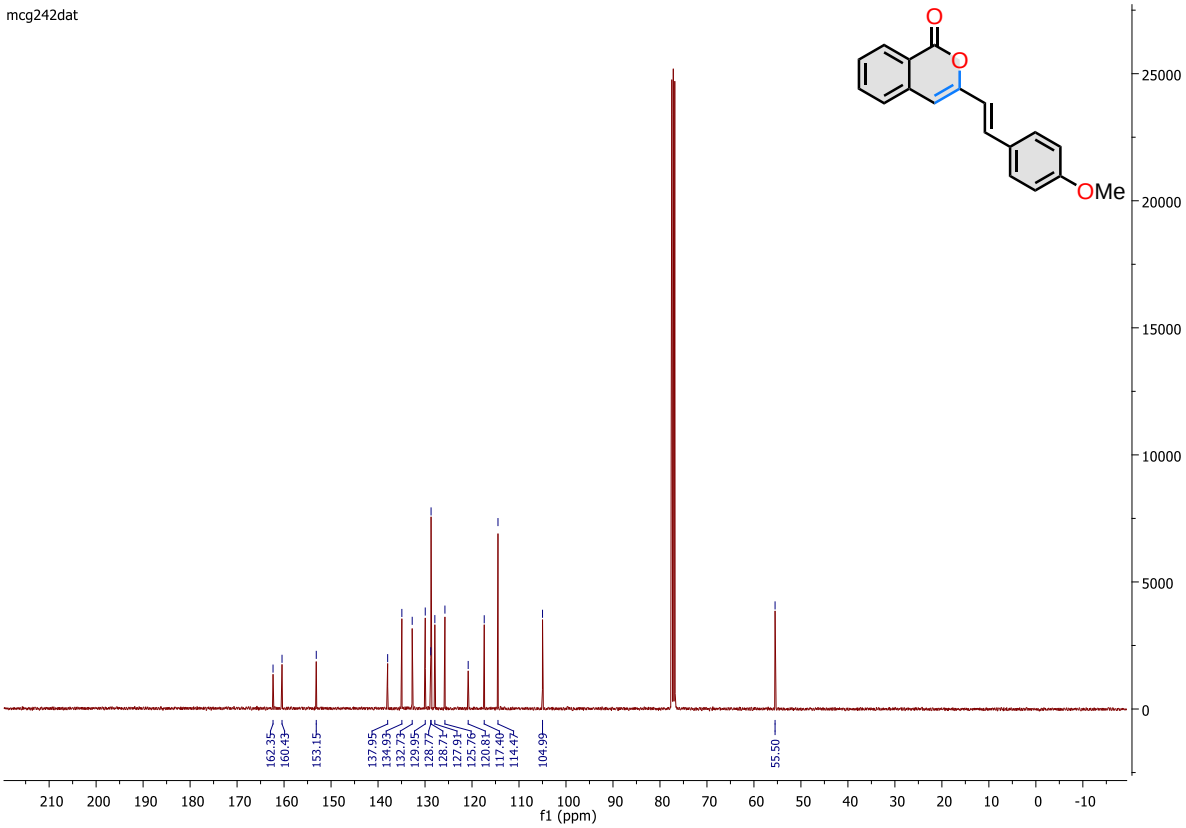

m_gie.mc110DAT
UserID m_gie SampleID mc110DAT SupervisorID moses Lab Phone No. 13540 Slot Number 30
MeO
MeO
OMe
O
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
0.95
1.93
0.96
9.00
2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

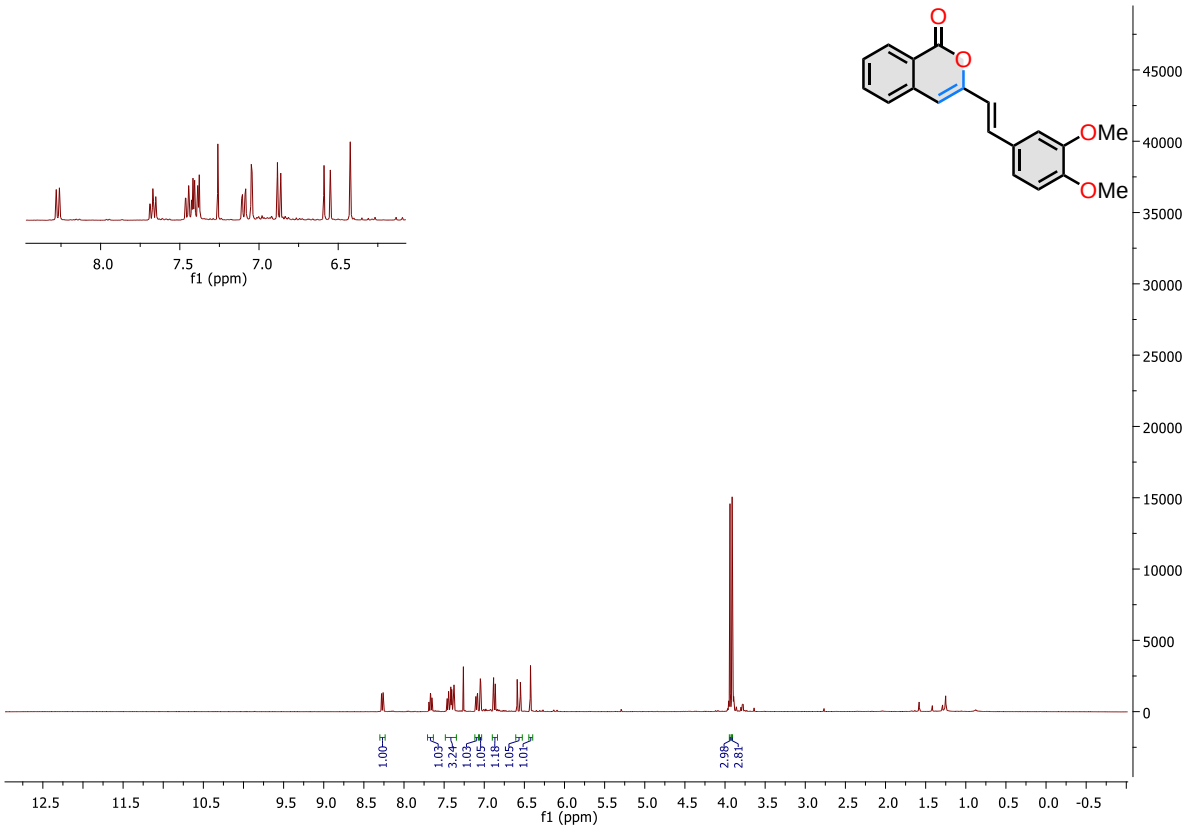

m_gie.mc110DAT
UserID m_gie SampleID mc110DAT SupervisorID moses Lab Phone No. 13540 Slot Number 30
MeO
MeO
OMe
O
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
198.36
153.64
143.62
140.48
130.01
126.69
105.55
61.13
56.31
27.57
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

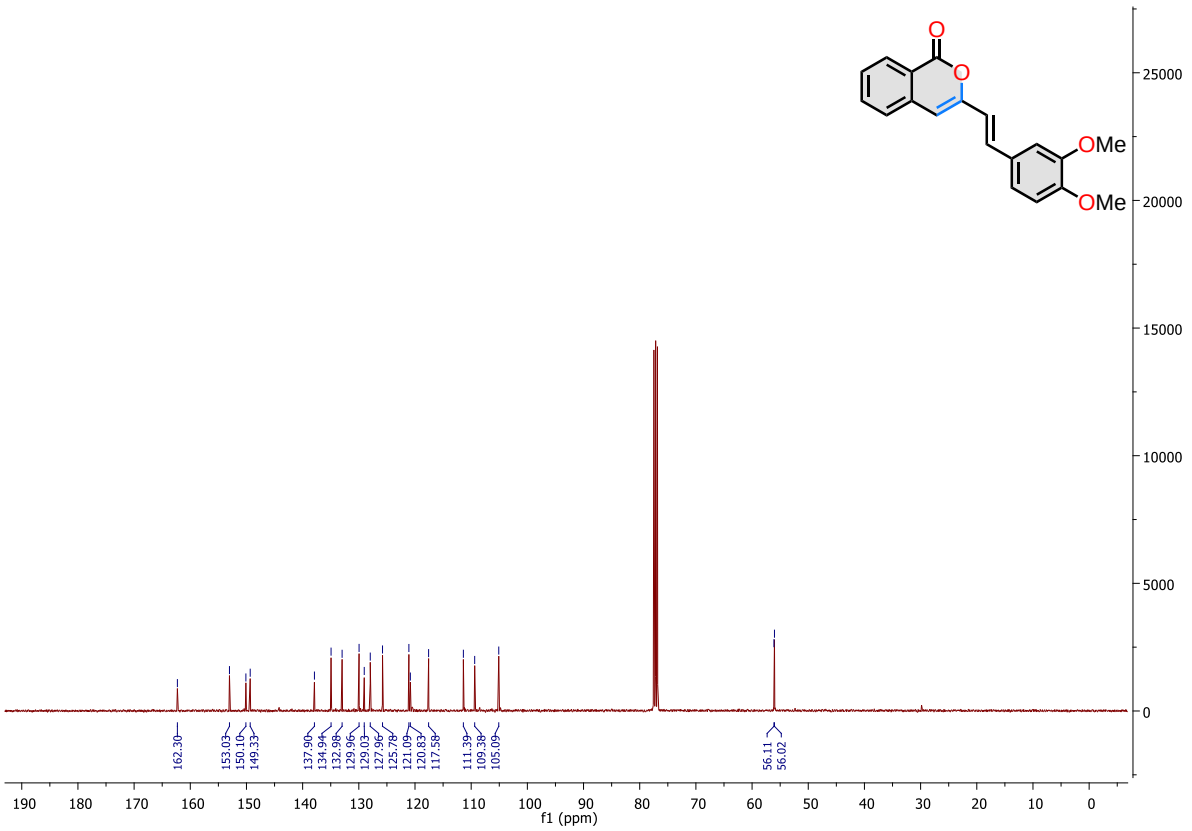

mcg238
8.2
8.0
7.8
7.6
7.4
f1 (ppm)
6.8
6.7
6.6
6.5
6.4
6.3
f1 (ppm)
O
O
OMe
OMe
1.00
2.05
2.13
1.06
1.02
1.06
1.08
0.90
3.18
3.29
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000

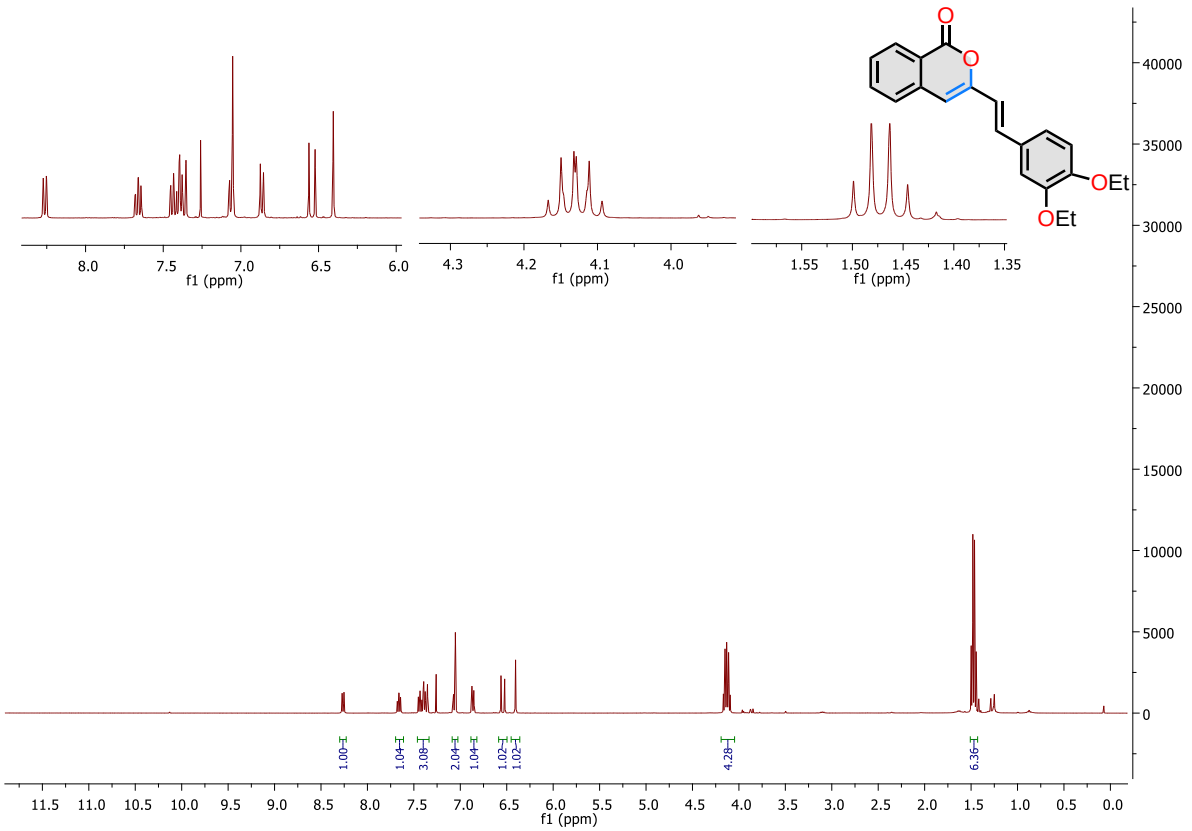

mcg238
O
O
OMe
OMe
162.53
161.67
159.22
153.88
138.17
134.85
129.94
129.28
128.60
127.66
125.65
120.74
118.20
105.29
104.60
98.65
55.60
55.58
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000

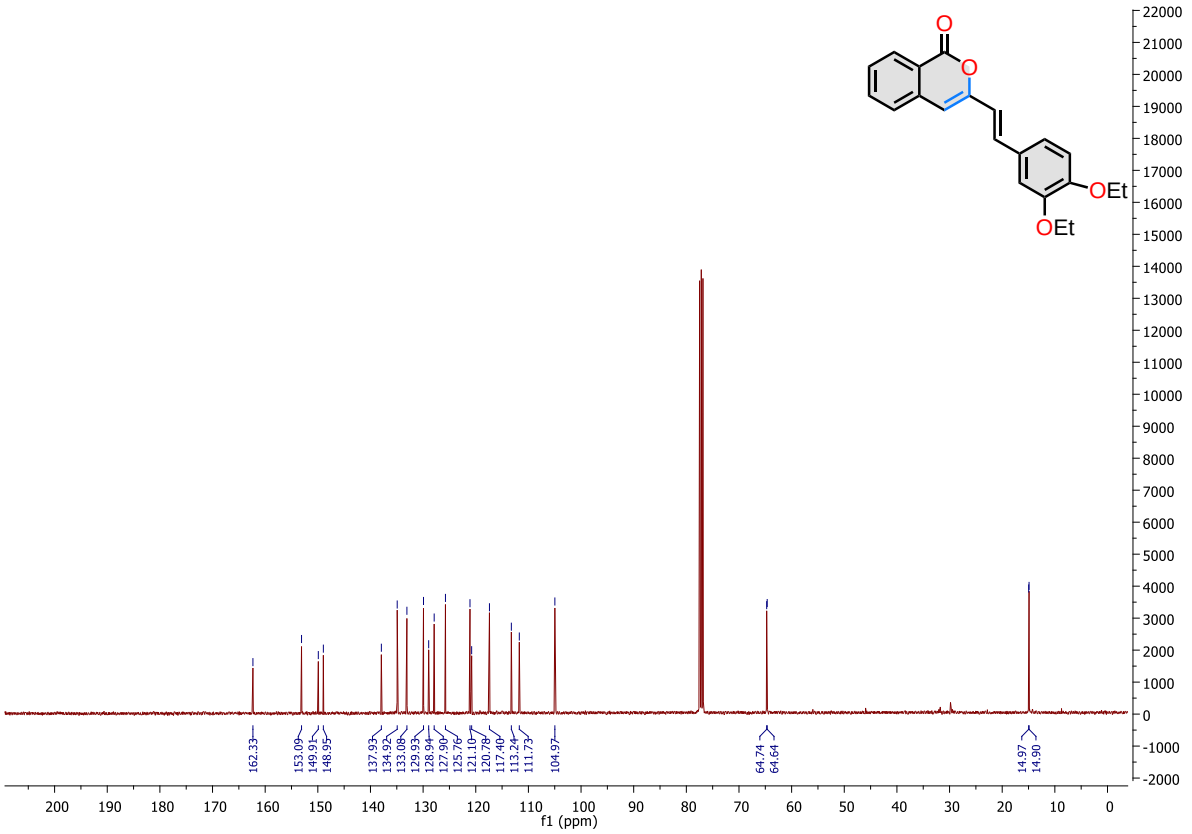

mcg242dat
O
O
OMe
8.0
7.5
7.0
6.5
f1 (ppm)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.01
1.08
5.11
2.04
1.04
1.00
3.20
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

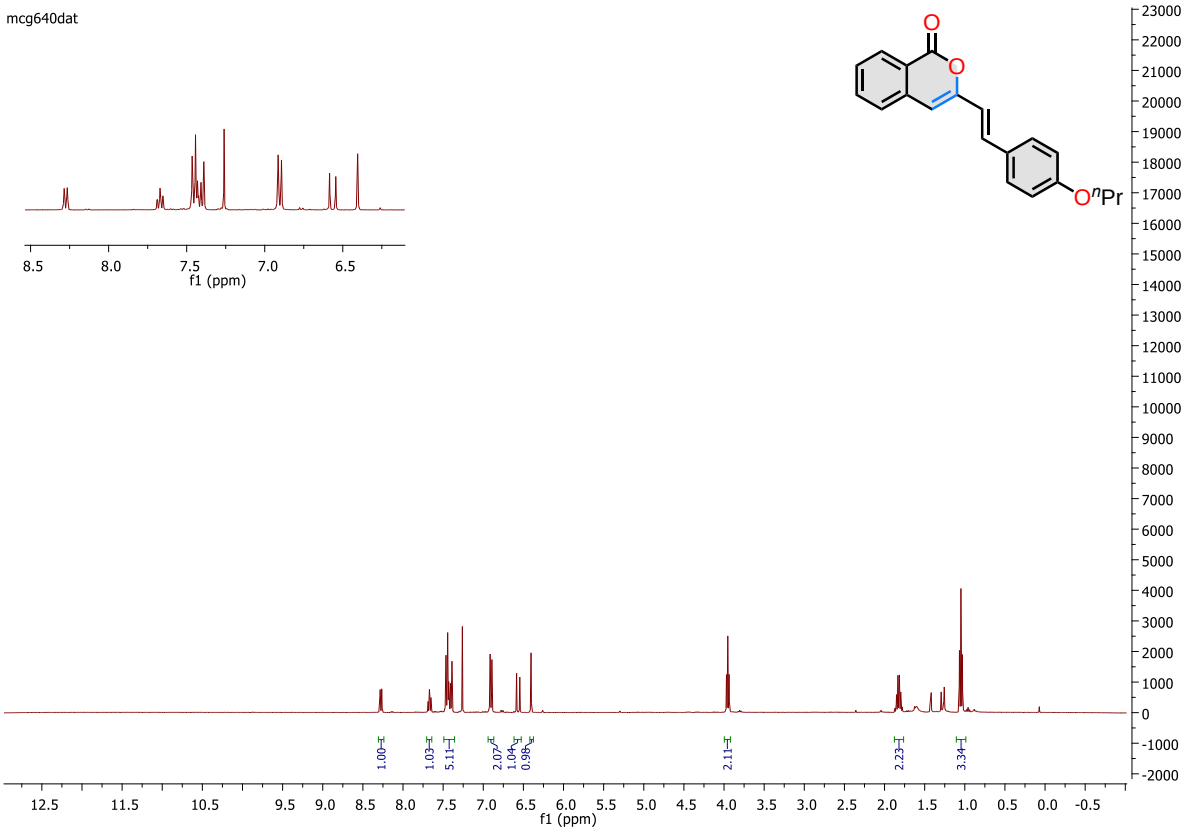

mcg242dat
O
O
OMe
25000
20000
15000
10000
5000
0
162.35
160.43
153.15
137.95
134.93
132.73
129.95
128.77
128.71
127.91
125.76
120.81
117.40
114.47
104.99
55.50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

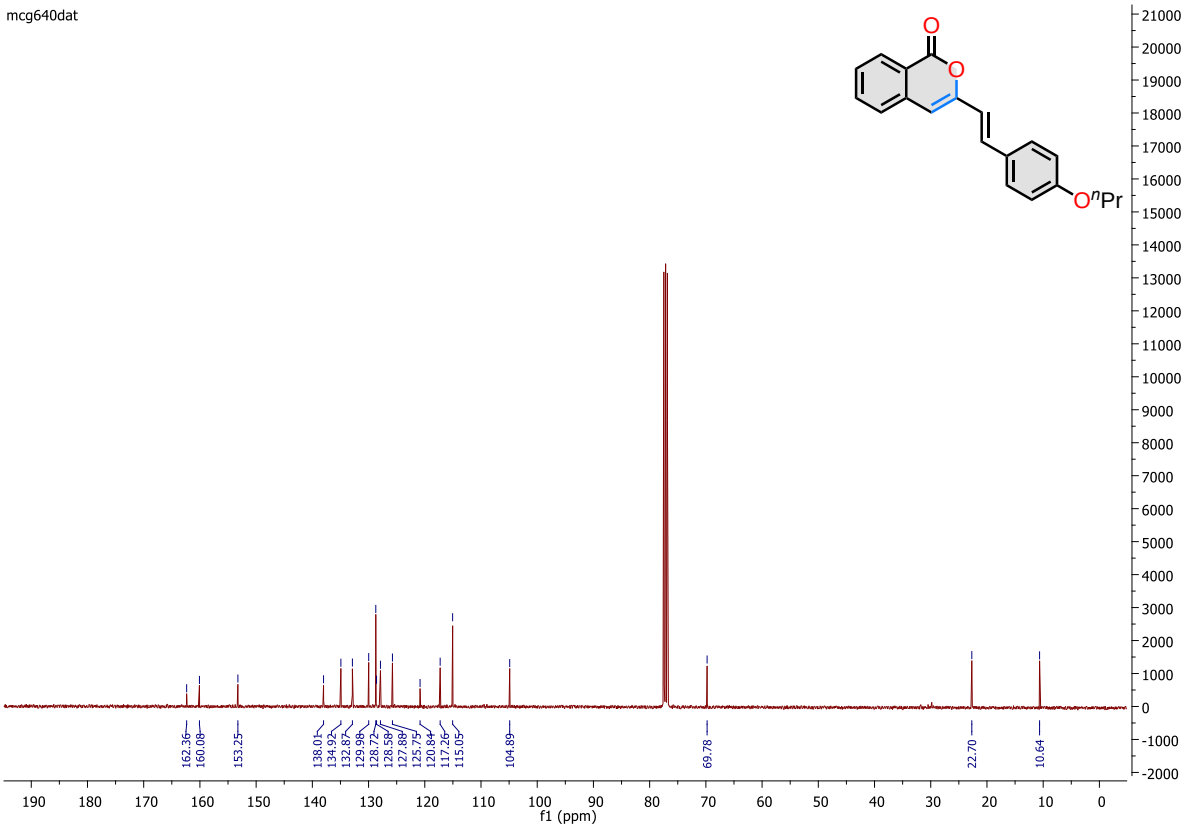

O
O
OMe
OMe
8.0
7.5
7.0
6.5
f1 (ppm)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
1.03
3.24
1.03
1.05
1.18
1.05
1.01
2.98
2.81
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

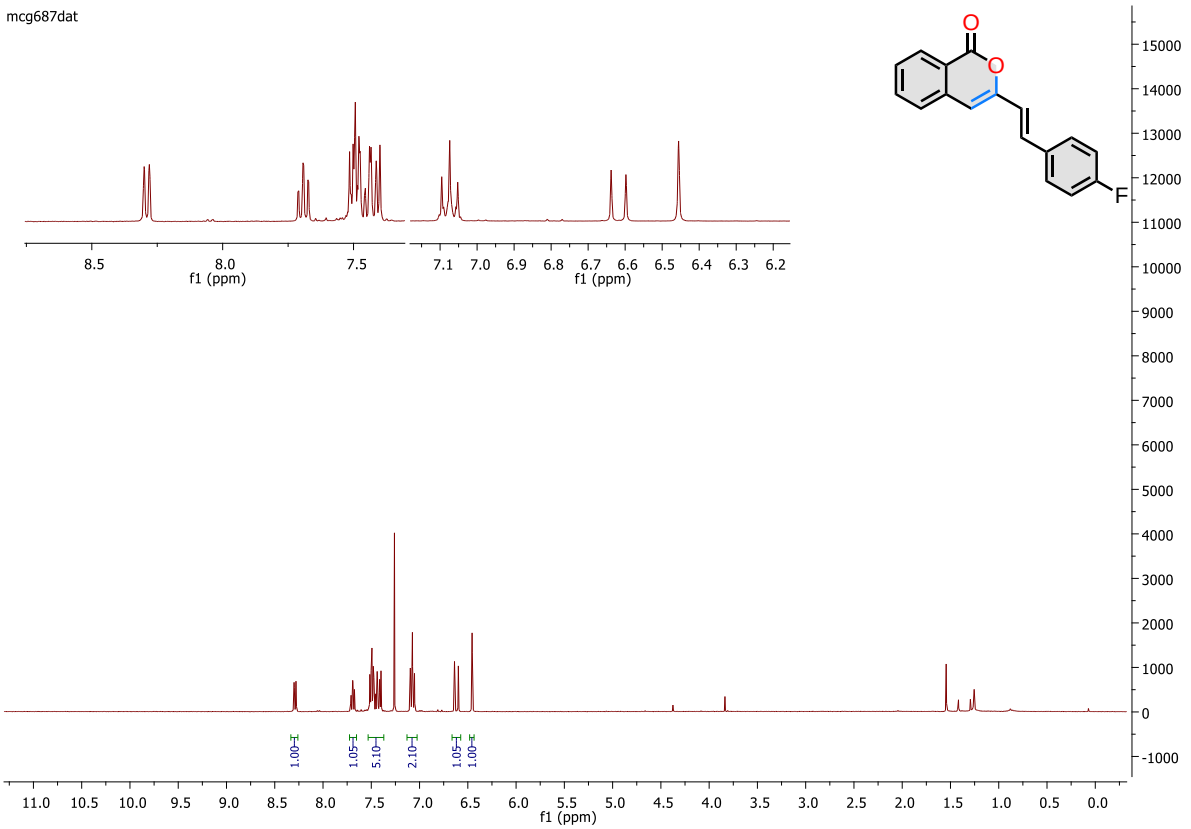

O
O
OMe
OMe
25000
20000
15000
10000
5000
0
162.30
153.03
150.10
149.33
137.90
134.94
132.98
129.96
129.03
127.96
125.78
121.09
120.83
117.58
111.39
109.38
105.09
56.11
56.02
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

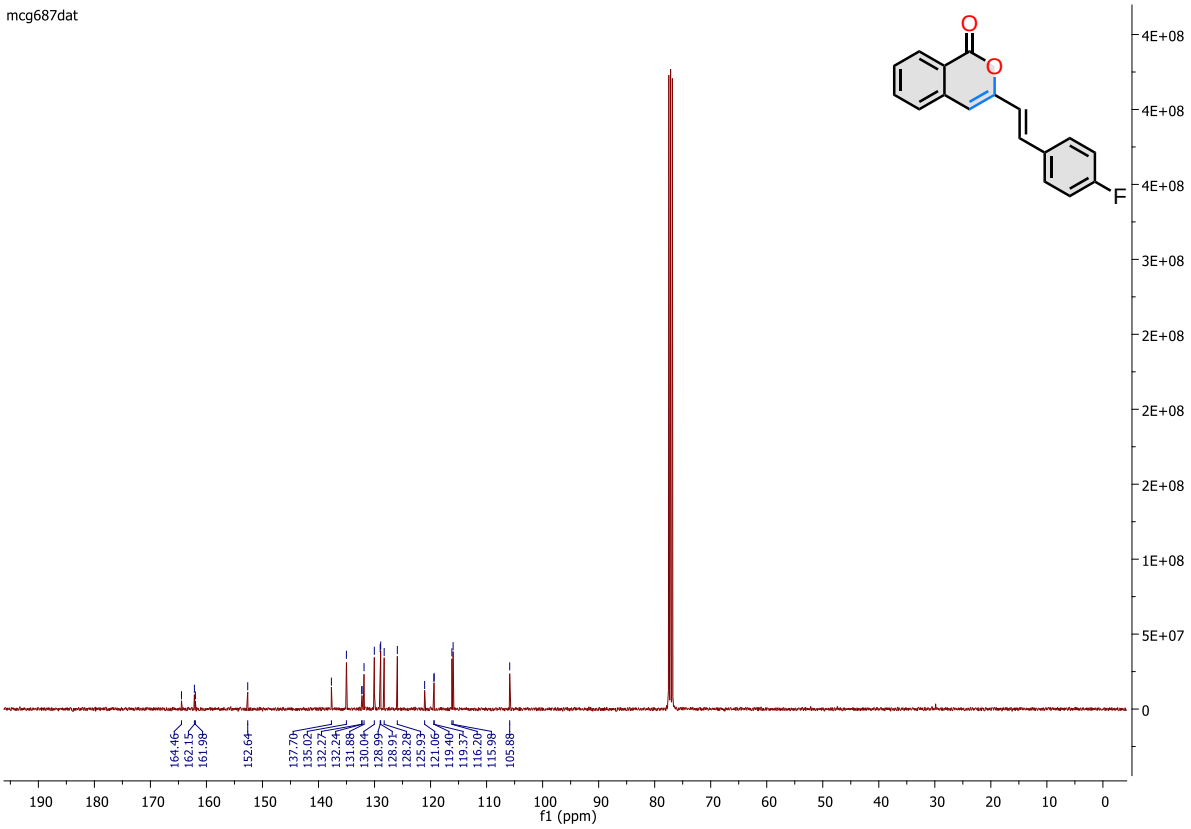

O
O
OEt
OEt
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
4.3
4.2
4.1
4.0
f1 (ppm)
1.55
1.50
1.45
1.40
1.35
f1 (ppm)
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
1.04
3.08
2.04
1.04
1.02
1.02
4.28
6.36
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

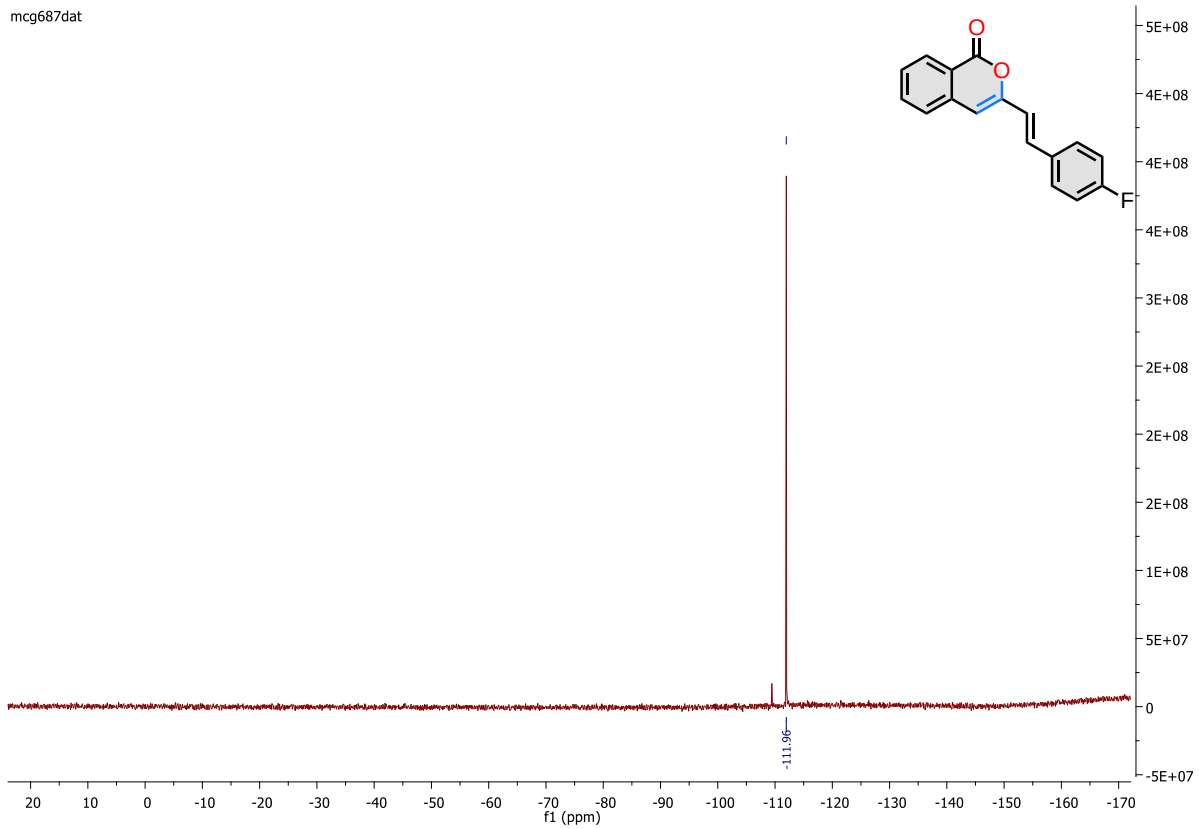

O
O
OEt
OEt
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
162.33
153.09
149.91
148.95
137.93
134.92
133.08
129.93
128.94
127.90
125.76
121.10
120.78
117.40
113.24
111.73
104.97
64.74
64.64
14.97
14.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

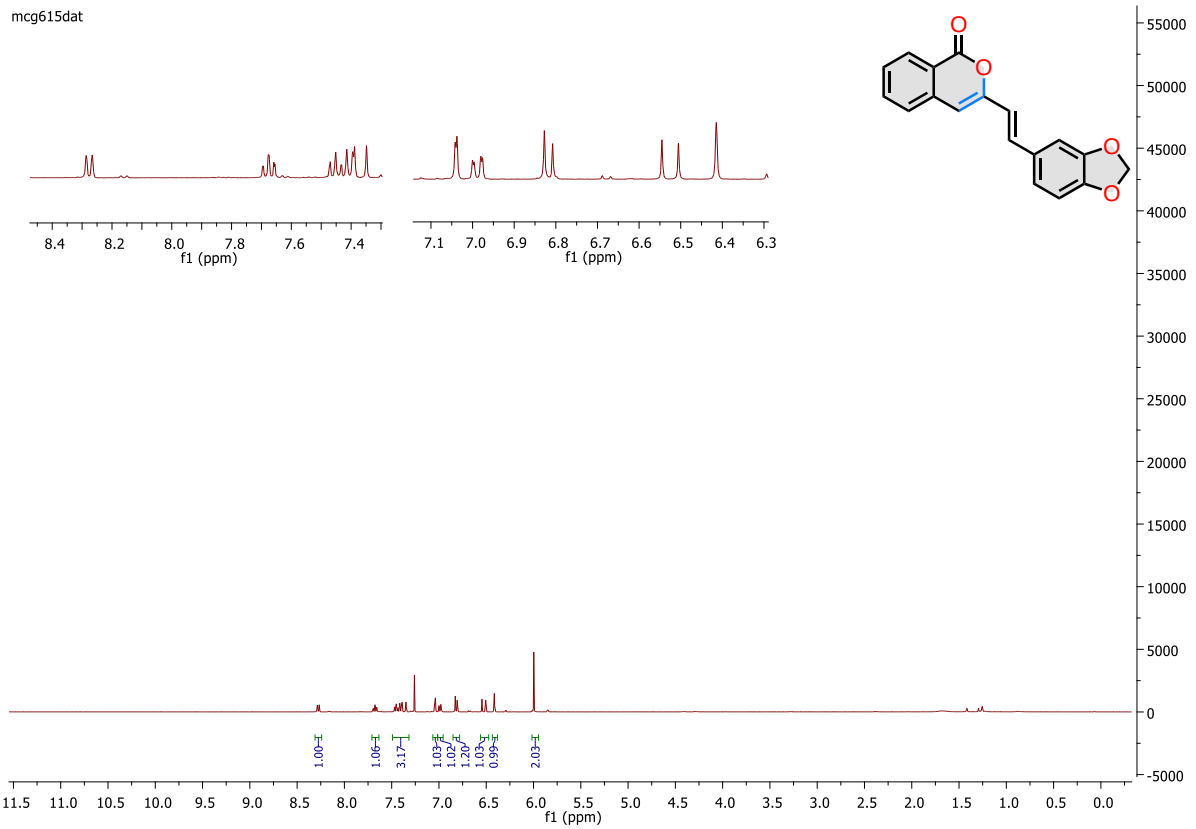

mcg640dat
O
O
O^{n}Pr
8.5
8.0
7.5
7.0
6.5
f1 (ppm)
1.00
1.03
5.11
2.07
1.04
0.98
2.11
2.23
3.34
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

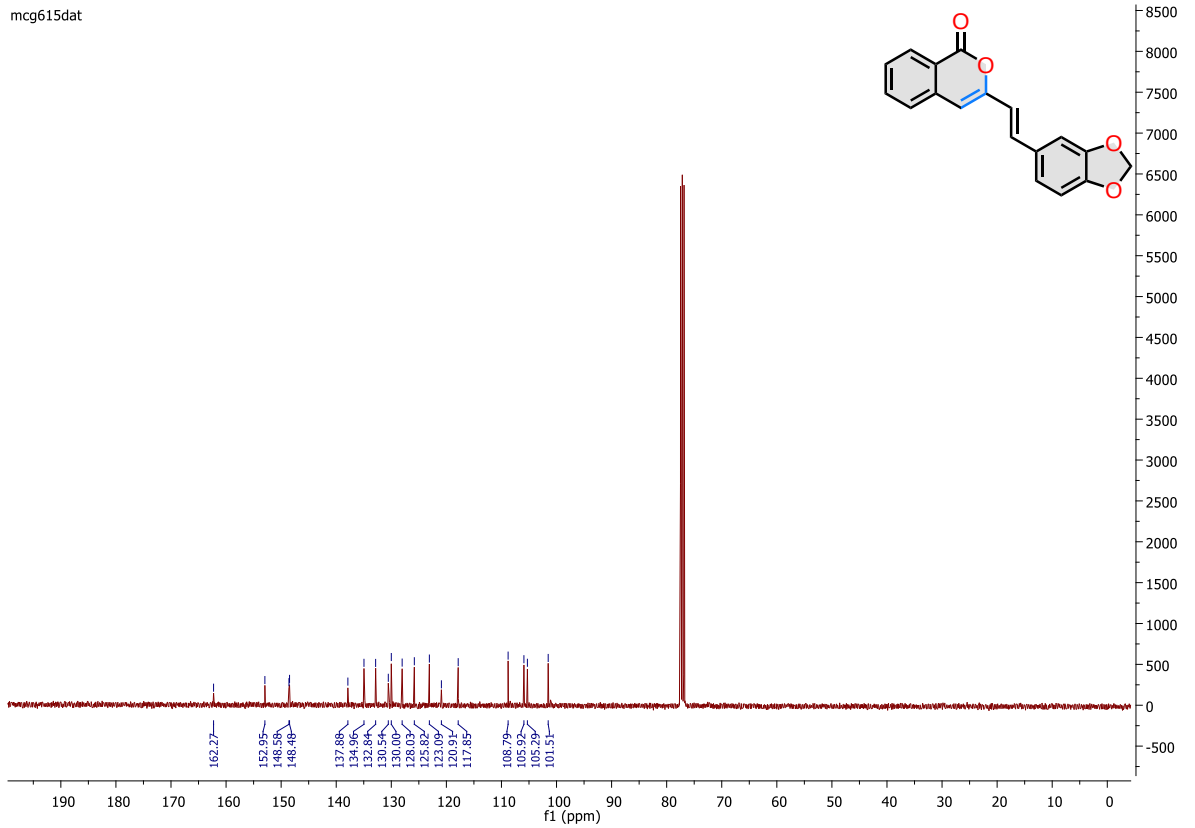

mcg640dat
O
O
O^{n}Pr
162.36
160.08
153.25
138.01
134.93
132.87
129.98
128.72
128.59
127.89
125.79
120.94
117.26
115.05
104.89
69.78
22.70
10.64
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

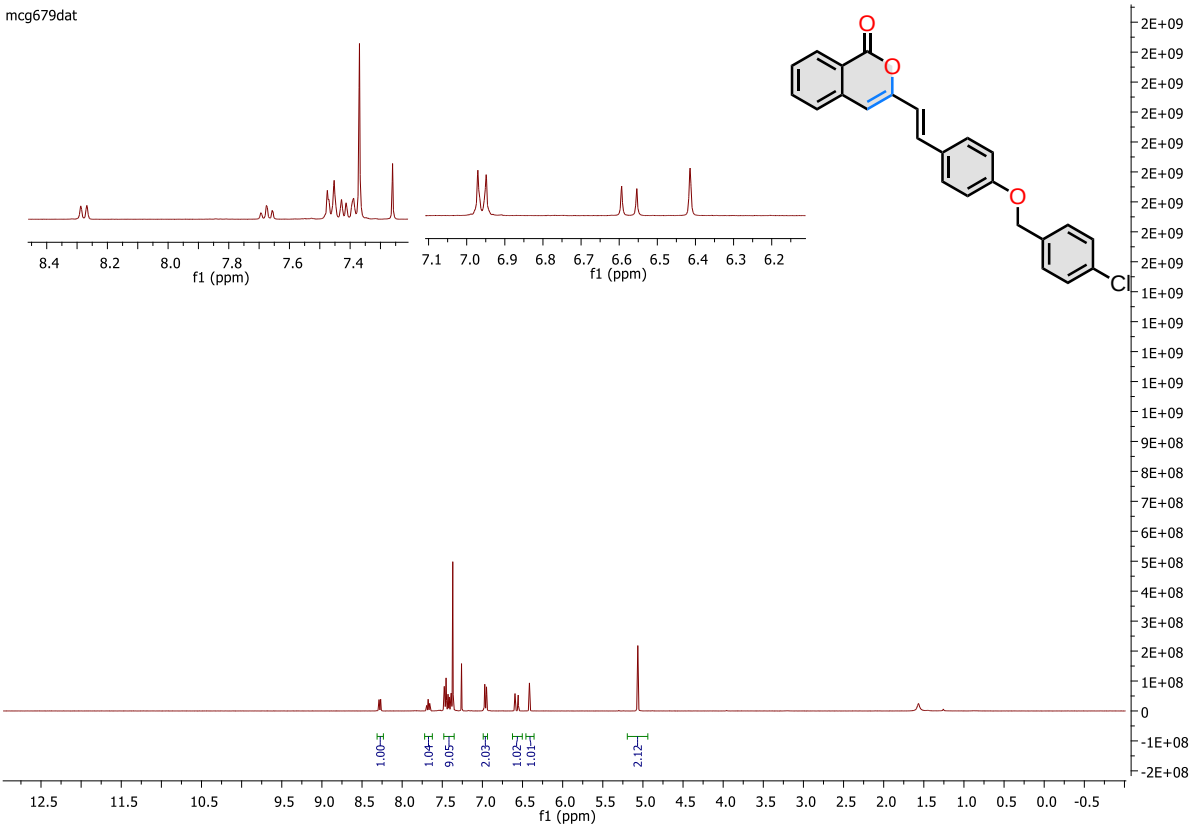

mcg687dat
O
O
F
8.5
8.0
7.5
f1 (ppm)
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
f1 (ppm)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.05
5.10
2.10
1.05
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

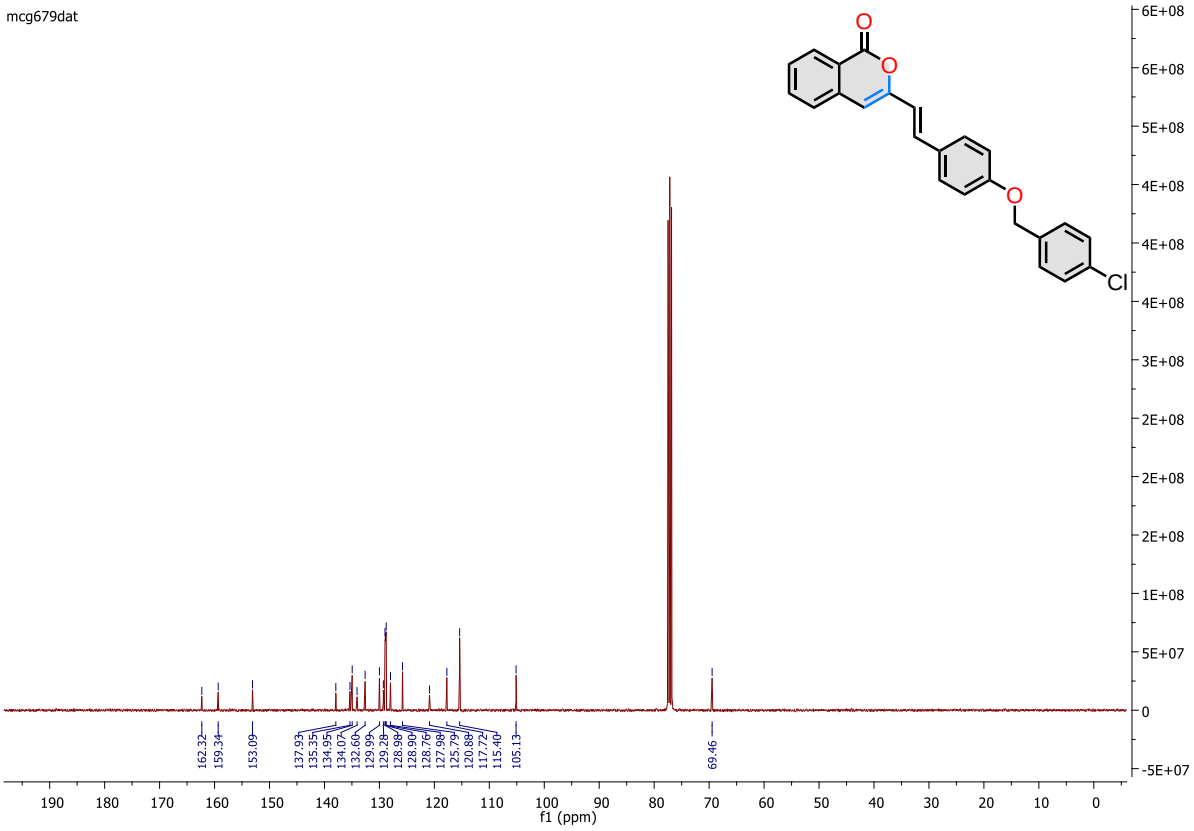

mcg687dat
O
O
F
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
164.46
162.15
161.98
152.64
137.70
135.02
132.27
132.24
131.88
130.04
128.99
128.91
128.28
125.93
121.06
119.40
119.37
116.20
115.98
105.88
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

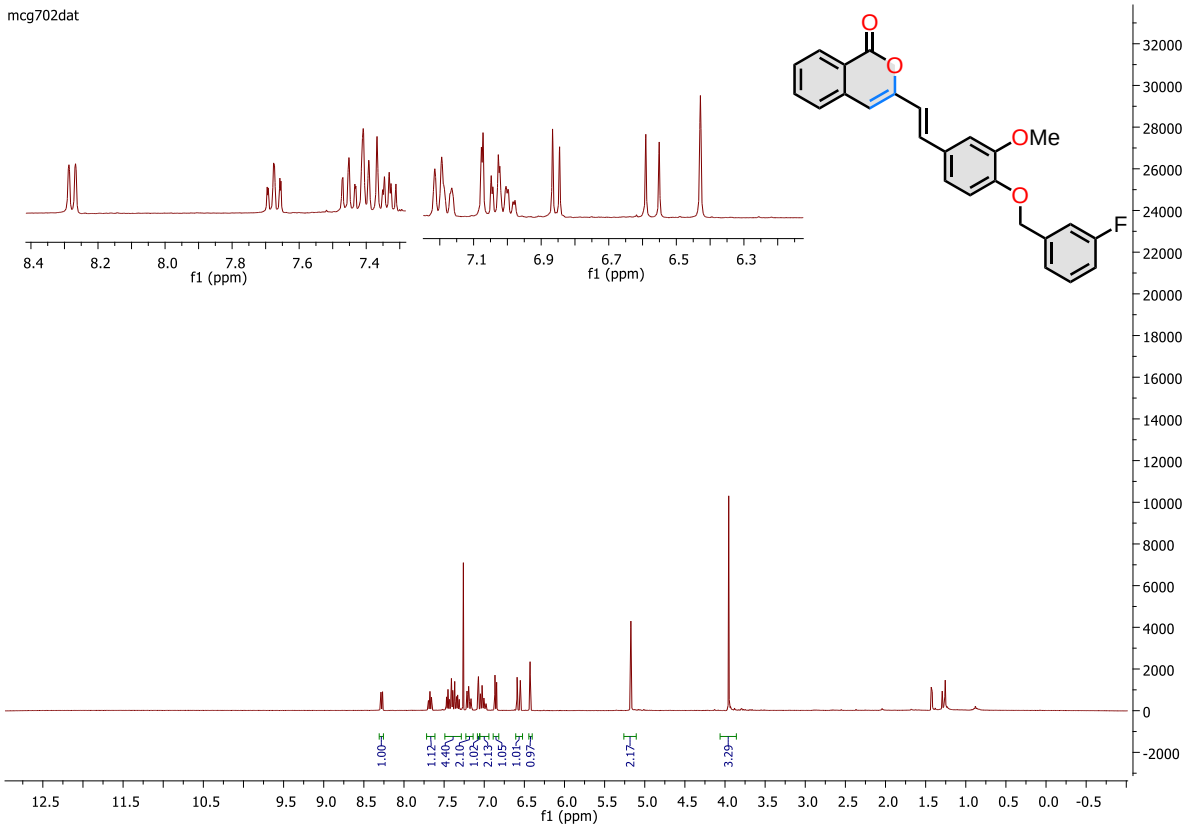

mcg687dat
O
O
F
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-111.96
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

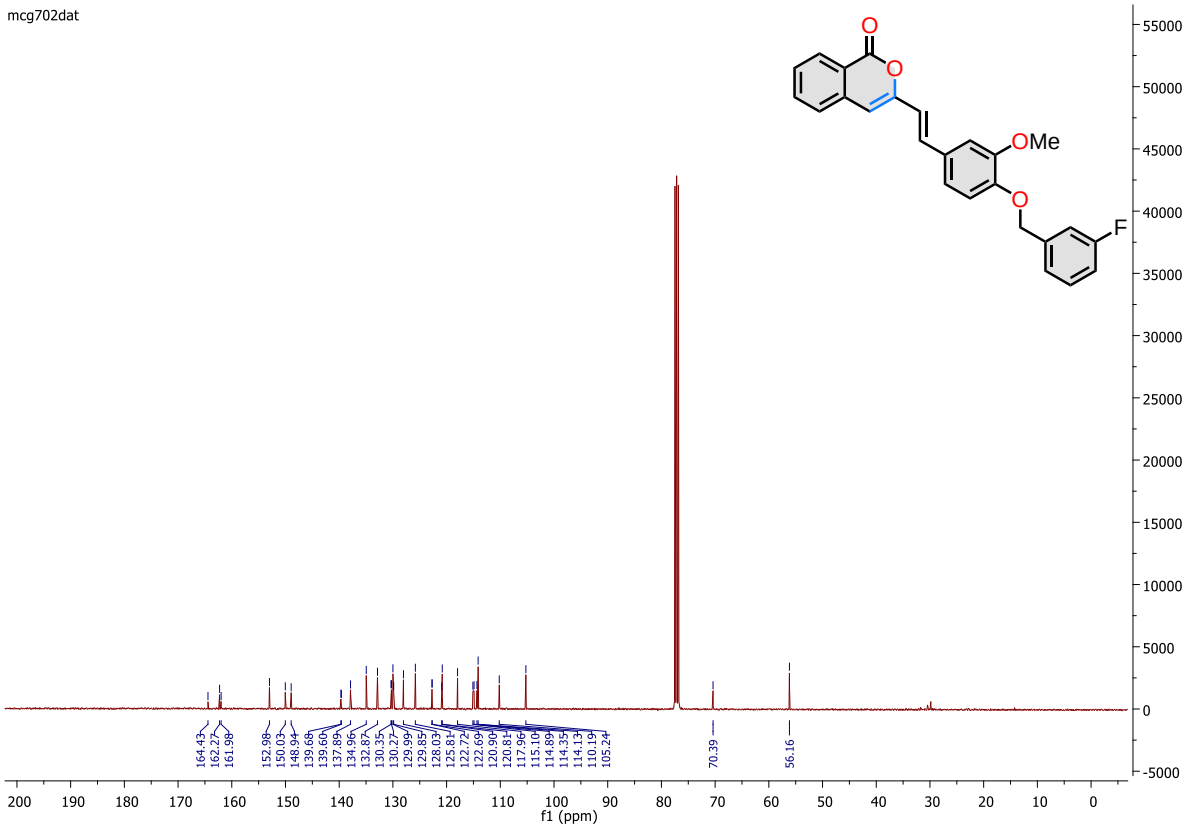

mcg615dat
f1 (ppm)
1.00
1.06
3.17
1.03
1.02
1.20
1.03
0.99
2.03

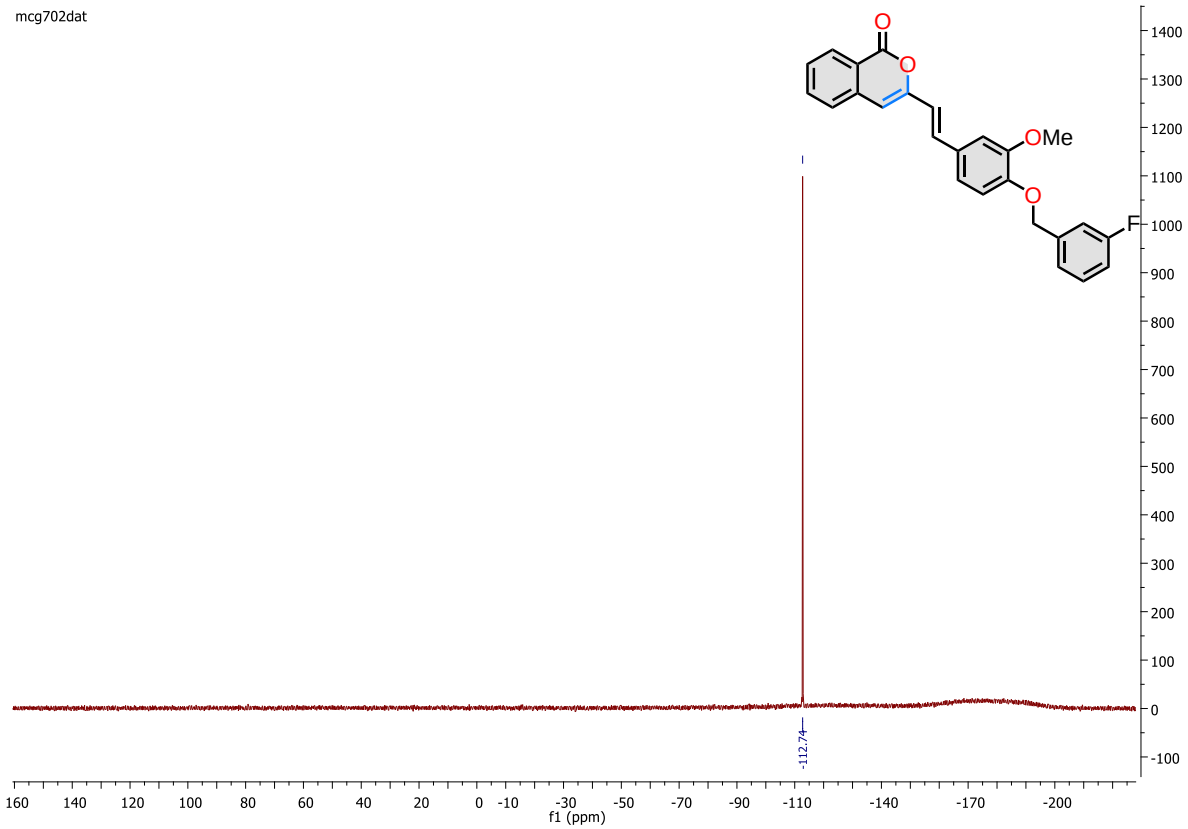

mcg615dat
f1 (ppm)
162.27
152.95
148.58
148.48
137.88
134.96
132.84
130.54
130.00
128.03
125.82
123.09
120.91
117.85
108.79
105.92
105.29
101.51

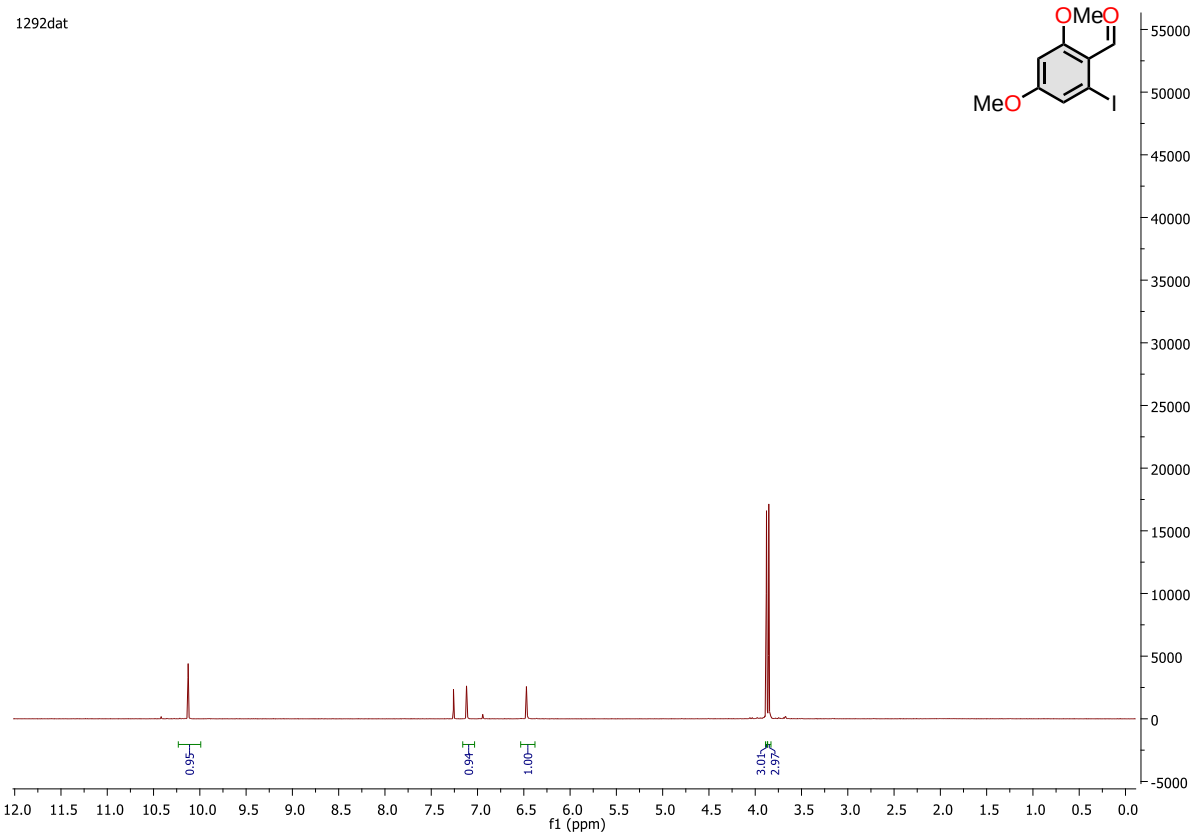

mcg679dat
f1 (ppm)
1.00
1.04
9.05
2.03
1.02
1.01
2.12
O
O
O
Cl

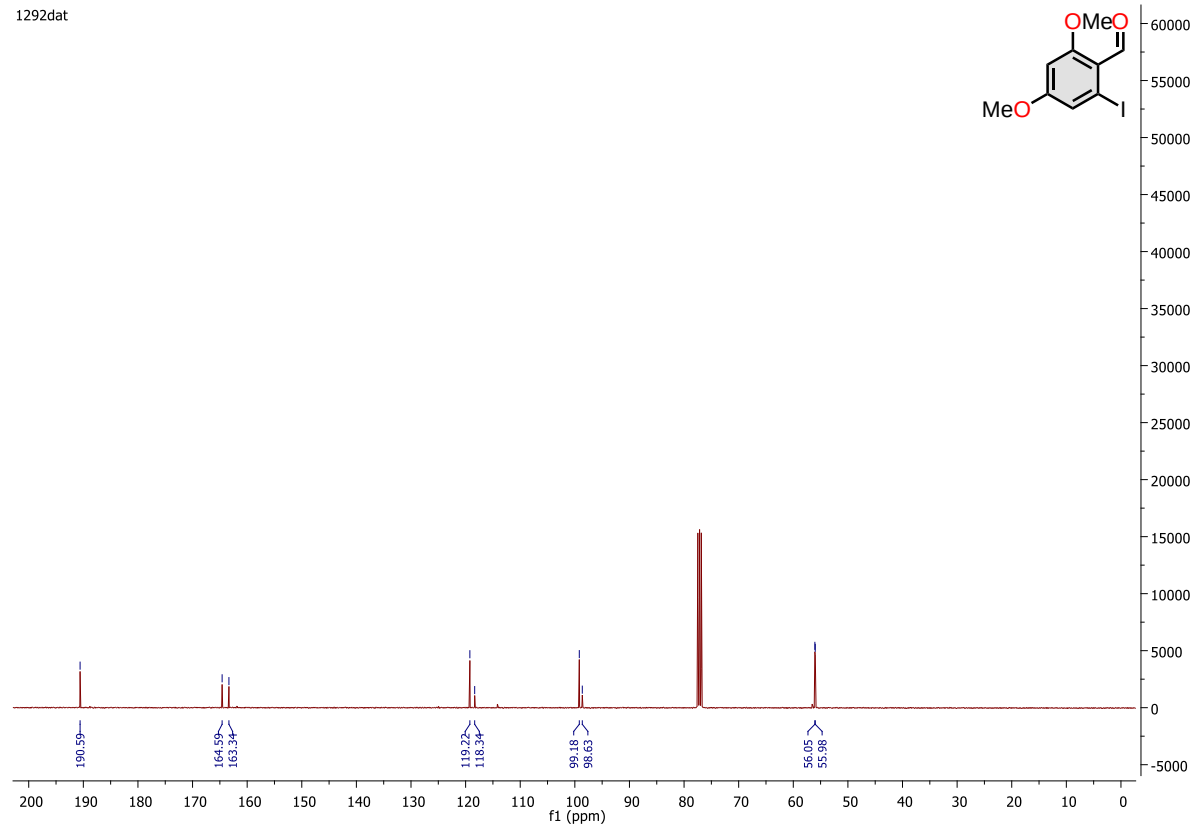

mcg679dat
f1 (ppm)
162.32
159.34
153.09
137.93
135.35
134.95
134.07
132.60
129.99
129.28
128.98
128.90
128.76
127.98
125.79
120.88
117.72
115.40
105.13
69.46
O
O
O
Cl

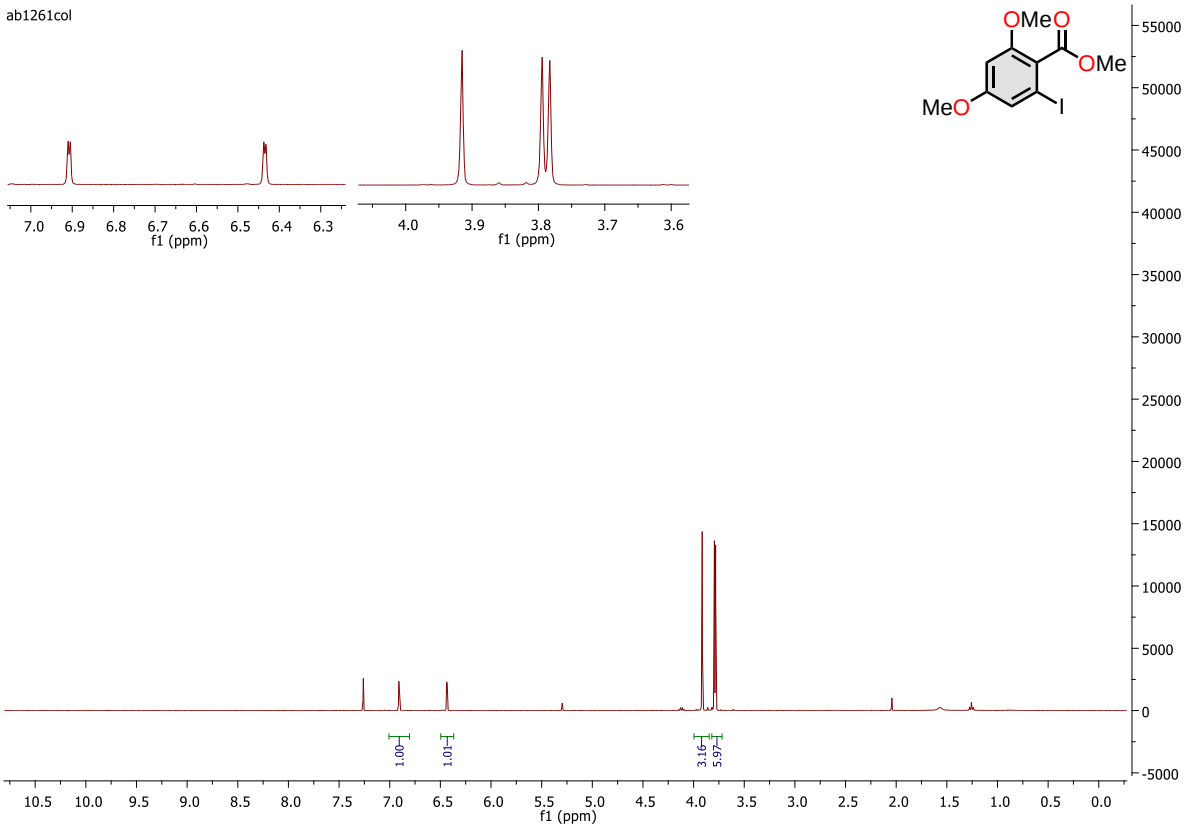

mcg702dat
OMe
F
f1 (ppm)

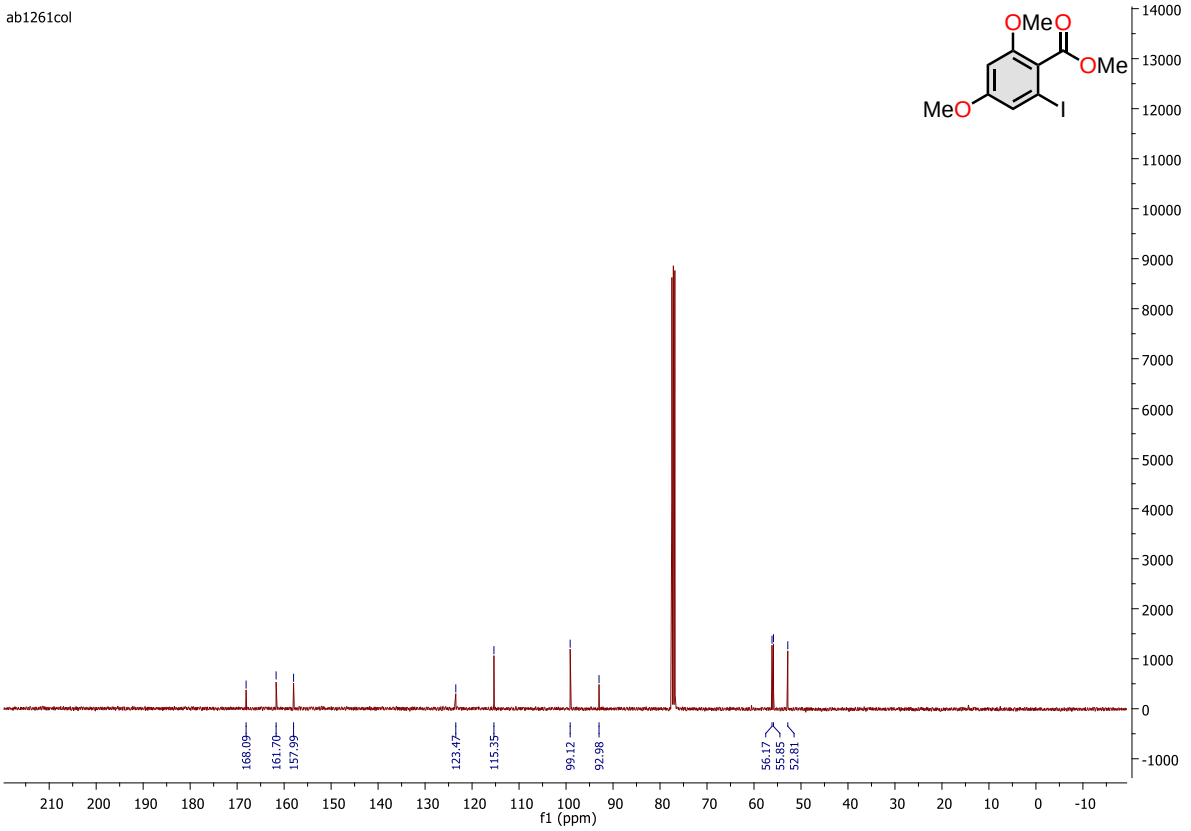

mcg702dat
OMe
F
f1 (ppm)

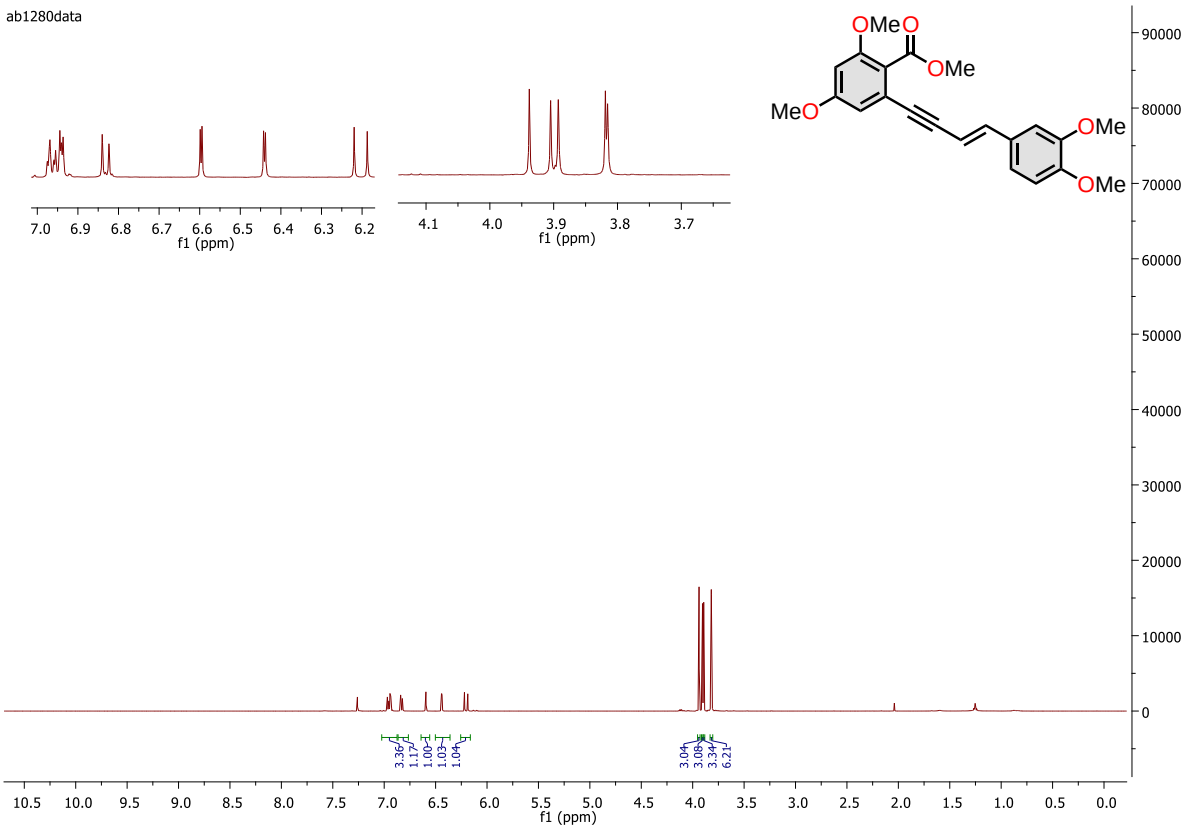

mcg702dat
O
O
OMe
O
F
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-112.74
160
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-140
-170
-200
f1 (ppm)

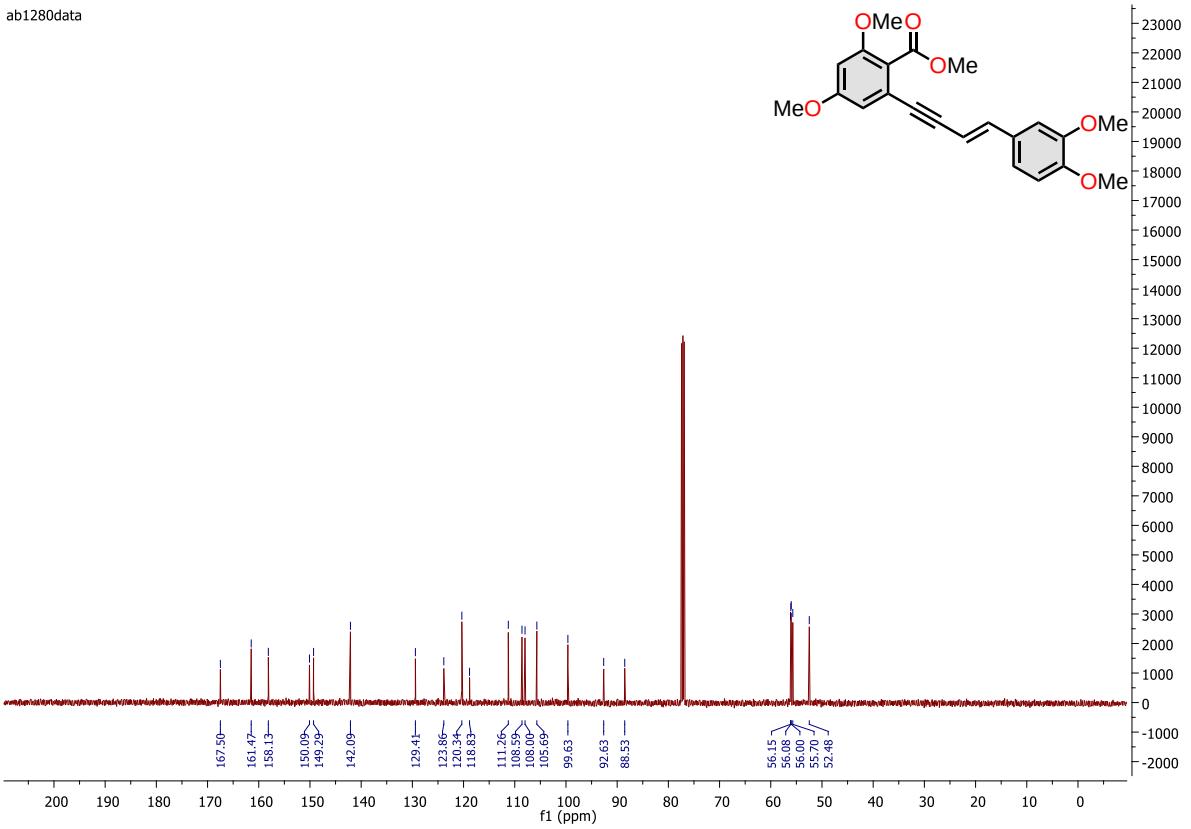

1292dat
OMeO
MeO
I
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0.95
0.94
1.00
3.01
2.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

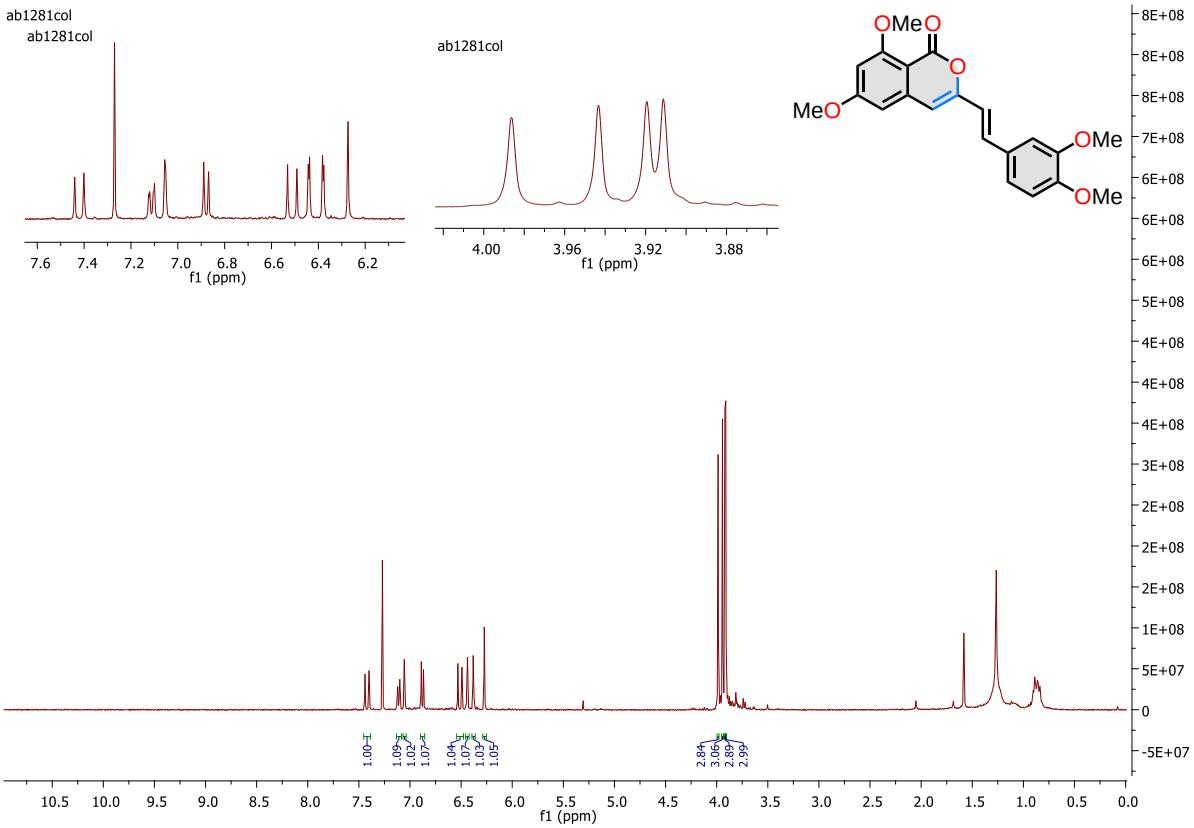

1292dat
OMeO
MeO
I
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190.59
164.59
163.34
119.22
118.34
99.18
98.63
56.05
55.98
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

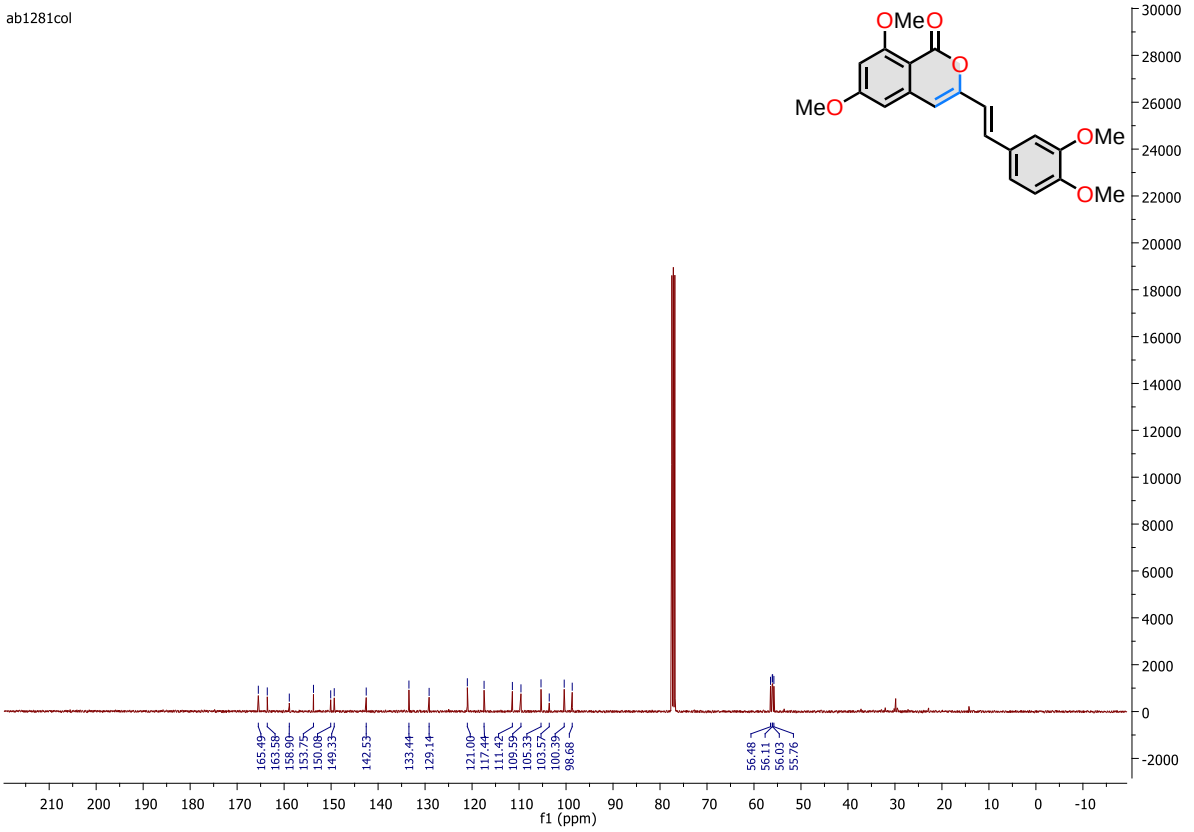

ab1261col
OMe
O
OMe
MeO
I
7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f1 (ppm)
4.0 3.9 3.8 3.7 3.6
f1 (ppm)
1.00
1.01
3.16
5.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


ab1261col
OMe
O
OMe
MeO
I
168.09
161.70
157.99
123.47
115.35
99.12
92.98
56.17
55.85
52.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ab1280data
OMe
O
OMe
MeO
OMe
OMe
f1 (ppm)
f1 (ppm)
3.36
1.17
1.00
1.03
1.04
3.04
3.08
3.34
6.21
f1 (ppm)


ab1280data
OMe
O
OMe
MeO
OMe
OMe
167.50
161.47
158.13
150.09
149.29
142.09
129.41
123.86
120.34
118.83
111.26
108.59
108.00
105.69
99.63
92.63
88.53
56.15
56.08
56.00
55.70
52.48
f1 (ppm)


ab1281col
ab1281col
ab1281col
OMe
O
O
MeO
OMe
OMe
f1 (ppm)
f1 (ppm)
f1 (ppm)


ab1281col
OMe
O
O
MeO
OMe
OMe
165.49
163.59
158.90
153.75
150.08
149.33
142.53
133.44
129.14
121.00
117.44
111.42
109.59
105.33
103.57
100.39
98.68
56.48
56.11
56.03
55.76
f1 (ppm)